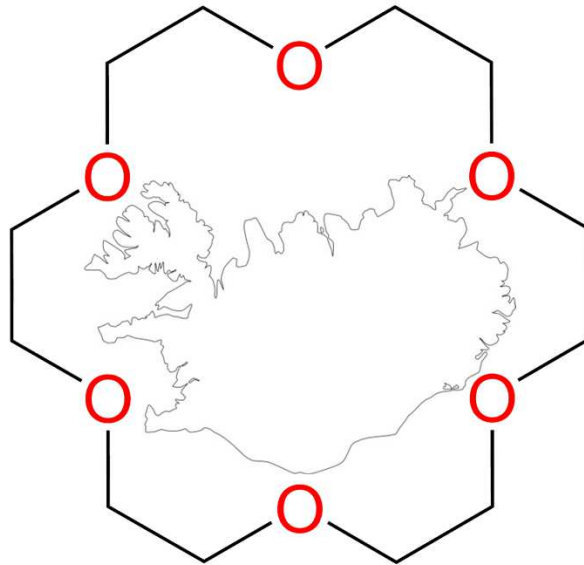


Abstracts: Poster Presentation



ISMSC 2023 Reykjavík - Iceland

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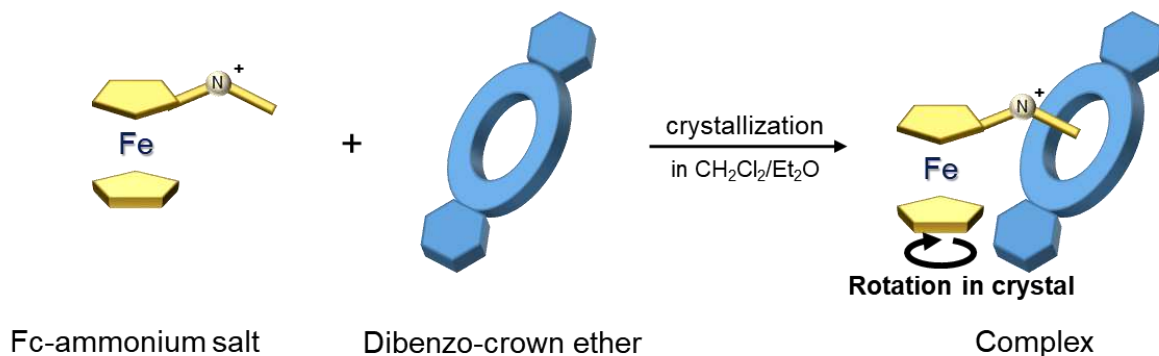
Abstract No: M1

M1 The Rotation of Ferrocene Complexes in Crystals

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² , ,



Caption: Figure1. Schematic illustration of ferrocene complexes.

Motions of ferrocene and its derivatives have been studied, because they have a unique sandwich structure and characters. Compared to their studies in solutions, films, aggregates, or computational calculations, studies in crystals have been limited because their restricted motions resulted in tight molecular packing structures. We have reported the exciting finding of the complexes of ferrocene-tethered ammonium (Fc-ammonium) salts and dibenzo-crown ether rings. The internal rotation of ferrocenyl moiety in interlocked molecules in the crystalline state was discovered by single-crystal X-ray diffraction (SCXRD) for the first time.^{1,2} Thus, it is essential to further investigate the relationship between molecular motions and macroscopic crystal motions. In this work, we synthesize and crystallize a series of ferrocene complexes. Crystal structures of the complexes were gathered by SCXRD at various temperatures. We found that the rotation of one of the cyclopentadienyl (Cp) rings of ferrocene is affected by a neighboring complex in the packing structure. We proposed a new perspective and profound comprehension of the design of stimuli-responsive ferrocene complexes.

Abstract No: M2

M2 Open Supramolecular Problems in Condensed Matter Physics

Ryan Evenson Daniel Nocera

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Correlated matter, in which the behavior of single quantum constituents cannot be understood isolated from the bulk, poses great challenges for much of established physics. Quantum spin liquids (QSLs) are a variety of correlated matter of high theoretical and practical interest for their potential to illuminate theories of superconductivity and provide a means of noise-resistant quantum computation.

Over the past 20 years, significant interest has accrued in $S = \frac{1}{2}$ triangular lattice materials composed of organic charge-transfer salts. These “organics” reproduce the rich phase diagrams of conventional magnetic materials, complete with superconducting, insulating, metallic, and possible QSL states depending upon the specific geometry of a layer of open-shell molecular dimers common to the structural family.

Advancement of the broader project of exercising synthetic control over organic QSL ground states requires advances in the molecular and supramolecular chemistry that directs their construction. State of the art structural modeling and open synthetic problems will be discussed.

Abstract No: M3

M3 Crystal Engineering with Molecular Triangles for Gas Adsorption

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Functional nanoporous materials have the potential to find broad industrial application and to surpass traditional methods in fields such as gas storage and separation, water purification, and energy storage.^[1] The metal-organic-frameworks (MOFs) and covalent-organic-frameworks (COFs) are highly porous as reflected in the high surface areas.^[2] However, the polymeric nature of MOFs and COFs limits their solubility and complicates to apply post-synthetic modifications without disrupting their crystallinity.

Shape-persistent macrocycles can be viewed as basic units of the layers in 2D COFs. However, macrocycles are discrete molecules that allow for a chemical modification in homogenous solution prior to the crystallization process.^[3] As a result, the formation of both intrinsic and extrinsic voids can be precisely tailored. Consequently, applications such as gas storage and challenging separations of organic molecules can be achieved.^[4]

Here, we will present the synthesis of functionalized macrocyclic equilateral triangles based on pyromellitic diimide substituted with halogen atoms.^[5] They direct the intermolecular interactions between individual macrocycles in successive layers in the solid-state varying the packing density. Such manipulation of the crystal structure allows to engineer crystal morphologies with either small intrinsic channels, large extrinsic pores, or columnar superstructures. The nature of the intermolecular interactions is investigated computationally based on structures obtained from single crystal diffraction. The specific surface area and the capability of the obtained materials to separate small molecules from gas mixtures will be discussed. Finally, attempts to construct tubular supramolecular co-polymers using halogen-bonding will be disclosed.

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M4 Structure:Function Relationships for Spin-Crossover Phase Transitions under Thermodynamic and Kinetic Control

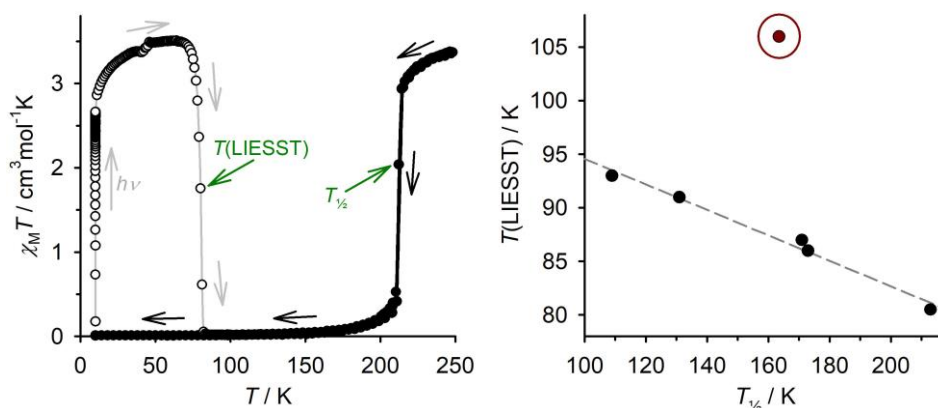
Malcolm Halcrow ¹ Rafal Kulmaczewski ¹, Elzbieta Trzop ², Laurence Kershaw Cook ¹, Sergi Vela ³, Eric Collet ², Guillaume Chastanet ⁴

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⁴ University of Bordeaux, Bordeaux, France



Caption: Left: thermal SCO (black) and LIESST relaxation (white) in an SCO material. Right: $T_{1/2}$ vs $T(\text{LIESST})$ correlation for six isomorphous solvate crystals.

Spin-crossover (SCO) compounds undergo a spin state transition under a physical or chemical stimulus. Materials showing switchable thermochromism, conductivity, fluorescence, dielectric, mesogenic and mechanical properties mediated by SCO have been designed. Optimisation of SCO materials as switching centres in nano- or macro-scale devices, as reporters for sensor applications, or as solid state coolants will benefit from the design of new materials with bespoke switching properties. More generally, SCO crystals are also useful testbeds for mechanistic studies of crystallographic phase changes and other solid state dynamics.

Triggering SCO photochemically at low temperatures can trap materials in their excited high-spin state – the ‘LIESST effect’. The sample cannot relax to its low-spin ground state until it is warmed sufficiently, for its lattice dynamics to accommodate the structural changes associated with the spin state change. The temperature of this kinetic relaxation, $T(\text{LIESST})$, is inversely proportional to the thermodynamic SCO temperature $T_{1/2}$ when similar materials are compared. Since the LIESST effect is a form of bistability, structure: function relationships governing $T(\text{LIESST})$ can help extend the effect to higher temperatures.

The compounds $[\text{FeL}_2][\text{BF}_4]_2 \cdot \text{solv}$ and $[\text{FeL}_2][\text{ClO}_4]_2 \cdot \text{solv}$ ($L = 4\text{-}\{isopropylsulfanyl\}\text{-}2,6\text{-di}\{pyrazol\text{-}1\text{-}yl\}pyridine$; solv = MeOH, MeNO₂, MeCN, EtCN, acetone or H₂O) are all isomorphous, but exhibit a range of spin-state behaviours. Some compounds are high-spin, while others exhibit thermal SCO with varying degrees of cooperativity and completeness [1]. LIESST measurements on the SCO-active materials demonstrate an excellent linear $T_{1/2}$ vs $T(\text{LIESST})$ relationship for five of the compounds. However $T(\text{LIESST})$ for a sixth example ($[\text{FeL}_2][\text{BF}_4]_2 \cdot \text{MeCN}$) is 20 K higher than expected from the other data [2]. Photocrystallography demonstrates unexpectedly complicated phase behaviour in one sample during the LIESST experiment [2, 3], while solid state DFT calculations imply the anomalous $T(\text{LIESST})$ for $[\text{FeL}_2][\text{BF}_4]_2 \cdot \text{MeCN}$ reflects reorientation of the MeCN molecule during the LIESST relaxation [3]. This is the first structure: function study of spin-state trapping in isomorphous crystalline materials.

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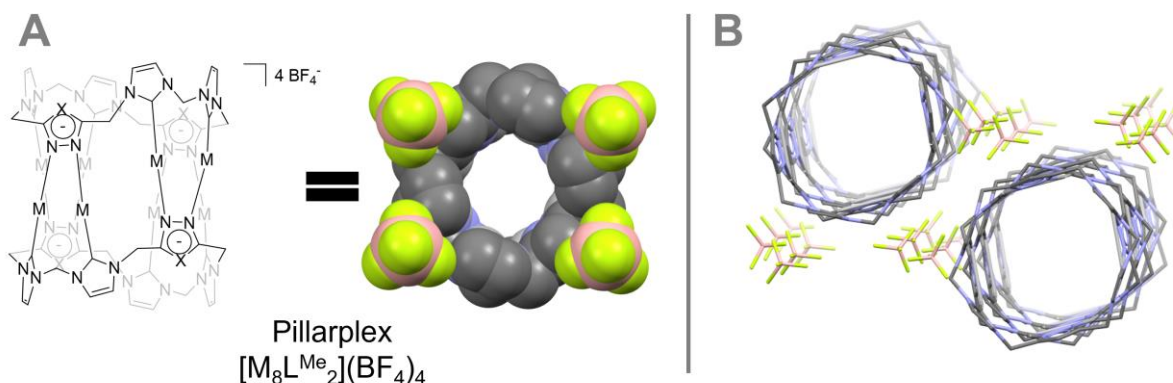
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Abstract No: M5

M5 Pore-Aligned $[M_8L^{Me_2}](BF_4)_4$ Pillarplex

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Caption: (A) Schematic drawing of pillarplex with space-filled top view; (B) Crystal arrangement of $[Ag_8L^{Me_2}](BF_4)_4$.

To achieve a specific arrangement of materials in the crystal packing, the intermolecular interactions (e.g. hydrogen bonding, halogen bonding, π -interactions) of the molecular building units need to be utilized to design new molecular crystals. The chemical and adsorption properties of the obtained solid materials can then be predicted and hence tuned by smart synthetic design.¹

The supramolecular organometallic pillarplexes $[M_8L^{Me_2}](X)_4$ ($M = Au, Ag$; $X = PF_6, OAc, \text{etc.}$)² show tuneable solubility dependent on the counter-anion, intrinsic luminescence and possibilities for rim-functionalization. Their tubular shape enables selective encapsulation of linear guest alkanes. By investigating several pillarplex salts, it was found, that the counter-anion X is crucial for the structural arrangement in solid-state due to (non-)covalent interactions and hence significantly influences the gas adsorption and separation properties of the materials. Previously reported pillarplex salts $[M_8L_2](PF_6)_4$ and $[M_8L^{Me_2}](OAc)_4$ ($M = Au, Ag$) were already investigated towards their crystal arrangement, the gas adsorption, gas separation and especially the correlation of the before-mentioned properties. As a free cavity with pillarplex cation in a pore-aligned fashion leads to maximal access of the cavity, the relatively small, tetrahedral anion BF_4^- was found to perfectly achieve these goals.

After successful synthesis, the pillarplex salt $[Ag_8L^{Me_2}](BF_4)_4$ was validated by NMR, IR spectroscopy, elemental analysis and mass spectrometry. The solid-state structure was investigated by TGA, PXRD and micro-ED measurements. As highly symmetric pore-alignment of the pillarplex cations was found, the adsorption properties of $[Ag_8L^{Me_2}](BF_4)_4$ were analysed.

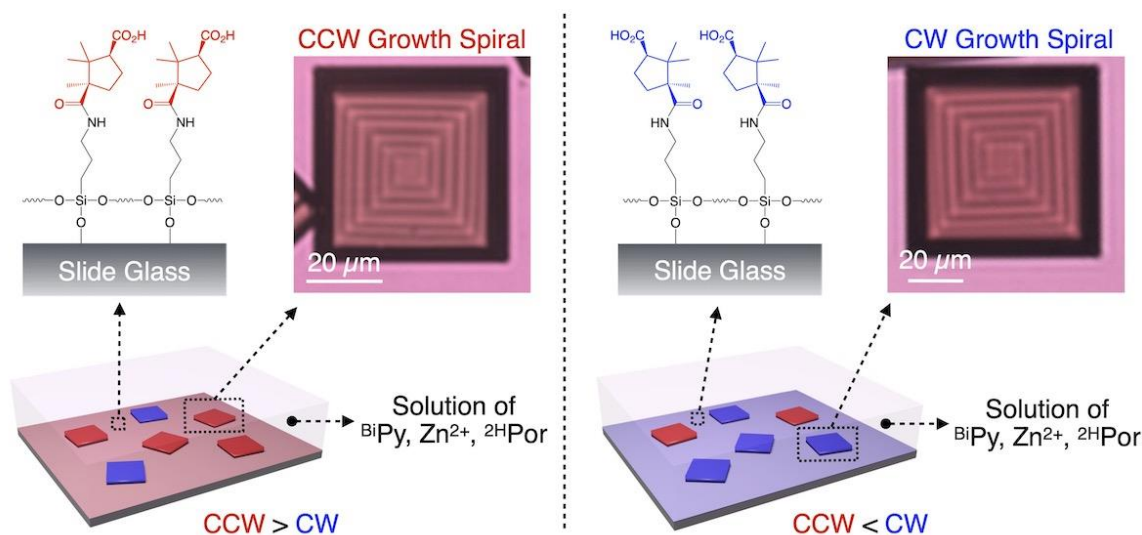
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M6 Noncentrosymmetric Crystallization Modulated by Surface-Mounted Chiral Monolayers

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Caption: Figure 1. Noncentrosymmetric crystallization modulated by surface-mounted chiral monolayers.

Screw dislocation and the associated helical structures have recently gained prominence in modern materials science, and crystal science and engineering. Despite the nearly 100 years since the first discovery of screw dislocation-induced spiral markings on silicon carbide crystals, it remains a challenge to tailor the handedness of helical twists or spirals induced by screw dislocation. Here we demonstrate the translation of molecular chirality from surface-mounted chiral monolayers to heterogeneously nucleated metal-organic framework crystals by regulating the displacement vector of screw dislocation. By covalently tethering a surface with enantiomeric carboxylic acid-based modulators (CAM), we observed the dominance of *P*-helix spirals in crystals, nucleating and growing from surfaces covered by *D*-CAM, and *M*-helix for *L*-CAM, as determined by statistical analysis. The enantiomeric excess (*ee*) of helical crystals exhibited a close correlation with the extent of coverage of chiral molecular monolayers, reaching 0.4 when the crystals heterogeneously nucleate and grow on a surface with densely packed enantiomeric CAM. Interestingly, such a translation of the surface monolayer chirality to screw dislocation also holds true when enantiomeric camphoric acids or their derivatives are introduced into the reaction mixture for crystallization. The physically adsorbed CAM monolayer confirmed by quartz crystal microbalance is also capable of modulating the chirality of screw dislocation the heterogeneous nucleation stage. This work represents the first example of how to modulate the chirality of screw dislocation from the molecular level.

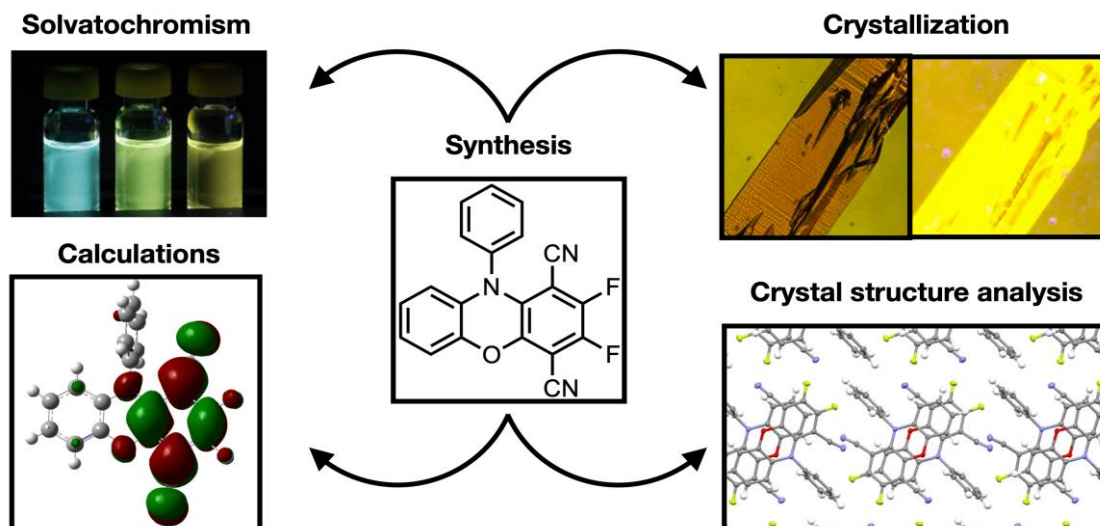
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M7 Phenoxazine-based solution and solid-state emitters - a novel approach to engineering terephthalonitrile luminophores

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Caption: Figure 1: Concept of novel phenoxazine SSSEs.

For a long time, luminescence phenomena were strictly distinguished between isolated emissive species and luminescent close-packed structures such as powders or aggregates. This changed with the breakthrough observation of dual-state efficient materials that can achieve balanced emissions with disregarded molecular surroundings.¹ Hence, they are believed to bridge the gap of hitherto known aggregation-sensitive compound classes and offer various applications. The molecular design of SSSEs can be simplified into two subgroups: spatially separated stator and rotor moieties (classic SSSEs) or indistinguishably fused non-classic SSSEs.²

Our group previously reported terephthalonitrile-based non-classic SSSEs with dibenzo chalcogen motifs.³ However, absorption maxima were still in the ultraviolet/blue region; hence, wavelength tuning ensued. Therefore, we developed novel SSSEs based on a phenoxazine scaffold, as similar phenoxazine dyes such as Nile Red are known for their bathochromically shifted emissive properties and solvatochromism. Furthermore, a phenyl linkage allows another way of packing modulation and substituent introduction to investigate their influence on the electronic perturbation of the core chromophore. Hence, derivatives with carefully chosen donor-acceptor substituents were synthesized and analyzed regarding their photophysical properties. We performed an in-depth X-ray diffractometric analysis to understand the molecular packing comprehensively. The experimental results were then correlated with quantum chemical calculations to provide further insights into the absorption and emission processes.

With the optimization of this novel luminescent system, application in biomedical imaging is envisioned, such as organelle-specific colouration.

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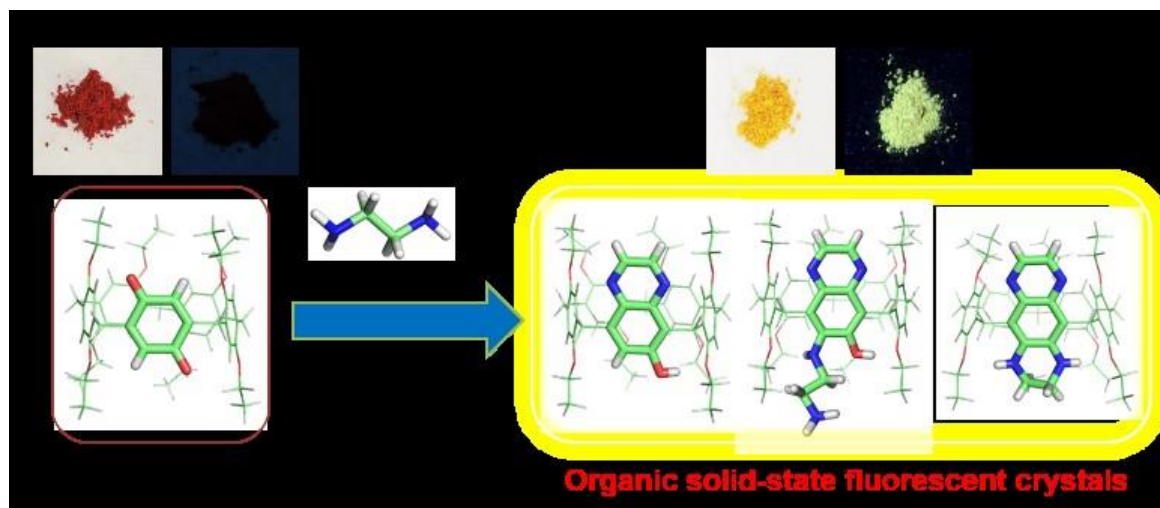
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Abstract No: M8

M8 Postsynthetic modification of nonporous adaptive crystals

Li Errui

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Porous crystalline materials have attracted lots of attention due to their potential applications in catalysis, adsorption, separation, sensing, detection, biomaterials and so on.¹ To achieve, improve and alter a certain property of porous materials, chemists or materials scientists use a strategy called postsynthetic modification to change their pore size, shape and chemical environment. However, because of the difficulty in mass transfer as well as the exposure of reactive sites, such a strategy can hardly be applied to modify the properties of nonporous materials or porous materials whose pore structures are not stable enough during postsynthetic modification.

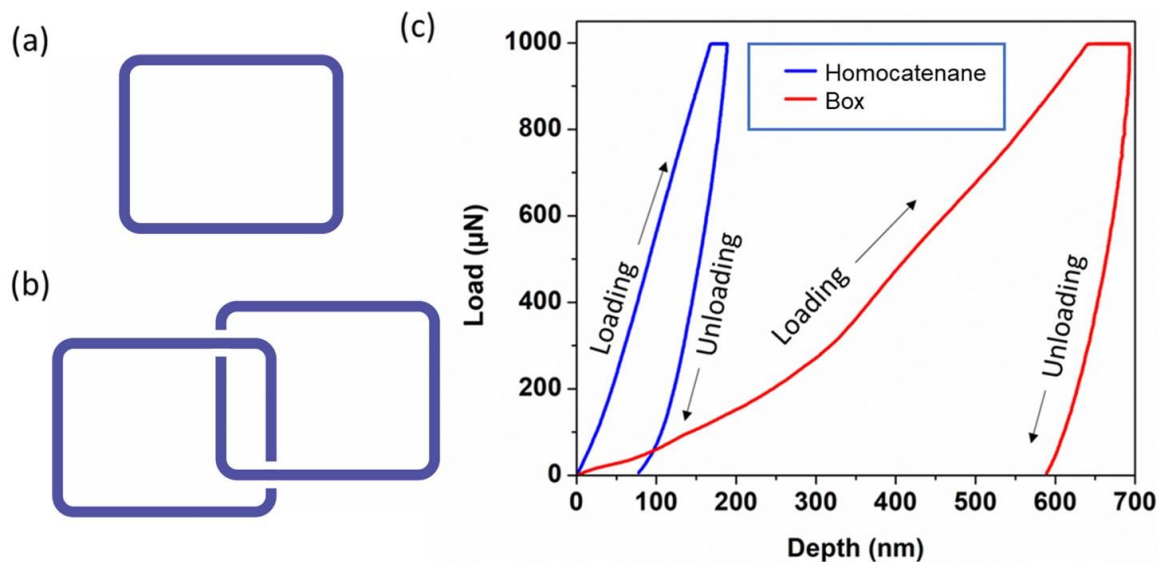
We previously reported a kind of nonporous adaptive crystals (NACs) based on pillararenes that can be used for adsorptive separation of hydrocarbons and removal of micropollutants. To alter the properties of NACs, we also achieved postsynthetic modification of NACs of pillar[4]arene[1]quinone (EtP4Q1).² Aliphatic amine vapors that can be physically adsorbed by NACs react with the EtP4Q1 backbone via Michael addition with in situ formation of new crystal structures. What is more interesting is that when EtP4Q1 NACs were exposed to ethylenediamine (EDA) vapor, fluorescent organic crystals can be generated from non-emissive EtP4Q1 NACs.³ Solution-phase reaction of EtP4Q1 with EDA affords three distinct compounds with different fluorescent properties, which are demonstrated to be the main components of the fluorescent organic crystals that are generated by the solid-vapor postsynthetic modification. Furthermore, this interesting phenomenon is applied for facile fluorescence turn-on sensing of EDA vapor to distinguish EDA from other aliphatic amines. At last, the adsorption properties of NACs of EtP4Q1 can be readily and precisely tuned via a facile substituent-size-dependent solid-vapor PSM method.⁴ Before PSM, NACs of pillar[4]arene[1]quinone EtP4Q1 show negligible selectivity for C5 hydrocarbons. PSM with a larger substituent, cyclopentylamine, onto EtP4Q1 NACs does not improve the selectivity, while EtP4Q1 NACs after PSM with a slightly smaller substituent, cyclobutylamine, is endowed with very high preference of n-pentane over cyclopentane.

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Flash Talks / 26-06-2023 16:40 - 17:00 Harpa - Silfurberg A/B 2nd floor

M9 Designing Mechanically Robust Organic Crystals: Role of Mechanical Bond

Pramita Kundu ¹ Surojit Bhunia ¹, Chun Tang ², James S. W. Seale ¹, Long Zhang ¹, J. Fraser Stoddart ¹¹ Northwestern University, Evanston, United States² Northwestern University, Evanston, United States

Caption: Figure 1. (a) Pictorial representation of Box and (b) corresponding homocatenane. (c) Comparison of nano-mechanical response between box and catenane

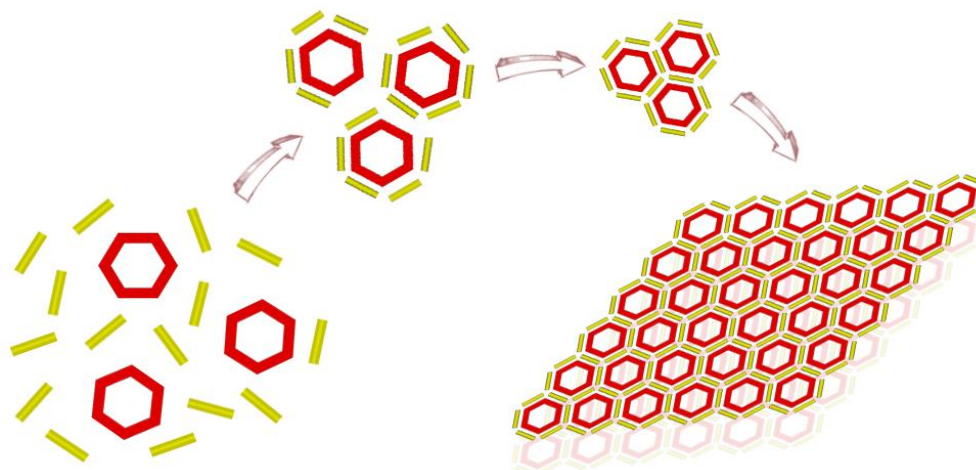
Mechanically robust materials are in present demand for their load-bearing applications such as in aircrafts, automobiles, building materials, etc. The robustness is the trade-off between higher strength/toughness and flexibility (includes elastic stretching-compression, multi-dimensional bending-unbending etc.). The enhancement of mechanical strength by covalent cross-linking of polymer chains often makes them less-flexible, which eventually leads to sudden fracture in the material. Recently, it has been shown that the inclusion of these polyrotaxane networks in functional polymer composites can alter substantially the elasticity and robustness of the resulting material, in which the threaded rings on neighboring chains are covalently crosslinked which rendering in them remarkable elasticity and stress-dissipation compared to traditional crosslinked polymers.^[1] The domain of organic crystalline material, however, with mechanical interlocking is still under-explored, although they have huge implications in various eco-friendly technological applications. With this motivation, in this current work we have compared systematically the nano-mechanical response of the box and homocatenanes with the help of state-of-the-art nanoindentation technique. Our initial results show many-fold increase of mechanical strength upon mechanical interlocking in catenanes owing to their robust interlocked structure and local-movements to dissipate the external stress. Although further investigation is going on, we believe this investigation will open-up lots of possibilities towards real-life application of mechanically interlocked molecules (MIMs).

Abstract No: M10

M10 Supramolecular Tessellations via Pillar[n]arenes-Based Exo-Wall Interactions

Ming Li, Feihe Huang

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Caption: Fantastic hexagonal tessellations based on regular hexagonal EtP6 were well prepared in an in-plane 2D framework through co-crystallization.

Structural aesthetics have received considerable attention from all aspects of life since antiquity.¹ Tessellation, known as a process of creating repeating patterns using one or more regular polygons to cover a plane entirely without overlaps or gaps, has been used to tile kinds of regular polygons for decoration in art since ancient times.² In modern chemistry, the design of tessellations at the atomic and molecular level is highly interesting because these highly-ordered structures showed potential material properties in optics and magnetics.³ It should be noted that in most tessellation systems, the design of vertices is of utmost importance because the symmetry elements of vertices determine the geometry architecture of molecular tessellation. Scientists always change different vertices to fabricate various tessellations, which have been widely reported.⁴ In contrast, constructing tessellations with shape persistent polygonal macrocycles is an alternative method but less investigated.⁵ The difficulties include the synthesis of perfect polygonal macrocycles and how to achieve large-scale controllable self-assembly by using these macrocycles as building blocks.

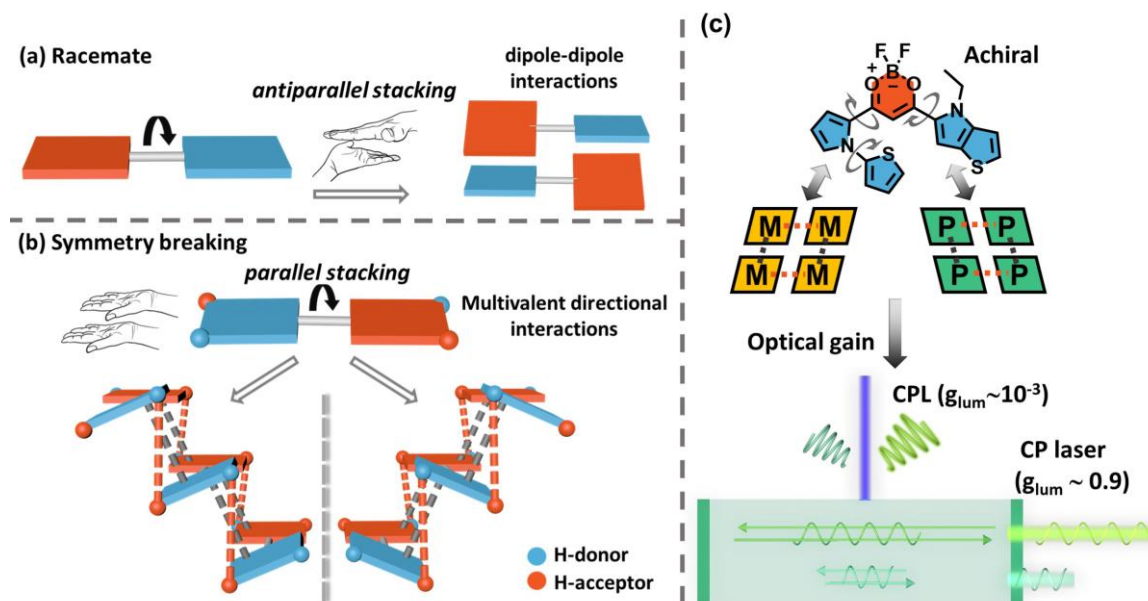
In this work, a series of outside binding behavior of perethylated pillar[5]arenes (**EtP5**) and pillar[6]arenes (**EtP6**) with electron-deficient compounds tetrafluoro-1,4-benzoquinone (**TFB**) and 1,5-difluoro-2,4-dinitrobenzene (**DFN**) were investigated. By using **TFB** and **DFN** as linkers, the fantastic hexagonal tessellations based on regular hexagonal **EtP6** were well prepared in an in-plane 2D framework through co-crystallization. Additionally, it turned out that solvent modulation and guest selection played a critical role in the resulting self-assembled molecular arrangement and the construction of supramolecular tessellation.

In brief, the novelty of this research included as follows: i) pillararenes as a new member of polygonal building blocks were used for the first time to construct supramolecular tessellations, ii) rarely investigated pillar[n]arene-based exo-wall interactions were used here for supramolecular tessellation, and iii) pillar[n]arene-based tunable self-assembled superstructures in the solid state were confirmed.

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M11 Achiral Molecules with Conformal Flexibility form Homochiral Superstructure with Circularly Polarized Laser Emission

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Caption: Figure 1. The schematic illustration of symmetry breaking of conformationally flexible achiral molecules and amplification for CP laser.

Homochirality is a characteristic feature of life. Understanding the function and origin of homochirality in biological and synthetic systems has been a fascinating yet challenging endeavor.¹ As a pair of enantiomers tend to pack more closely to form a centrosymmetric structure,² it is well perceived that intermolecular interactions of sufficient specificity and strength are required for a homochiral species to collectively expel. On the other hand, more puzzling is the emergence of homochiral domains from achiral molecules, as they often exhibit complex interplay among molecular symmetry, conformational flexibility, and noncovalent interactions,³ which therefore imposes formidable challenge on the rational design as compared to the resolution from molecules with intrinsic chirality.

In order to elucidate a possible design principle of achiral molecules that incline to symmetry breaking, herein we report on a series of conformationally flexible molecules composed of electron-donor (D) and acceptor (A) moieties. By virtue of the dipole-dipole interactions between D and A moieties, such conformationally interconvertible molecules often adopt antiparallel stacking, which therefore are prone to form centrosymmetric superstructures (Figure 1a). However, we demonstrate that this symmetry can be broken by multivalent noncovalent interactions, which overcome the dipole-dipole interactions and thus facilitate the parallel stacking of the achiral molecules (Figure 1b) during crystallization.⁴ These D-A molecules also exhibit excellent optical gain characteristics, when coupled with the emergent homochirality, they are exploited as supramolecular materials of circularly polarized (CP) lasing with an amplified g_{lum} value up to 0.9 (Figure 1c).

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Abstract No: M12

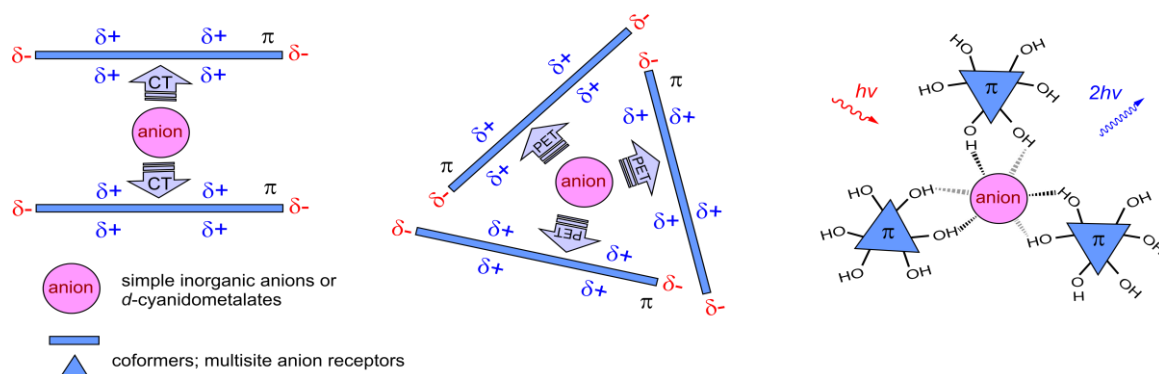
M12 New co-crystal salt architectures: structural hierarchy, charge transfer (CT), photoinduced electron transfer (PET), second harmonic generation (SHG)

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Caption: Schemes of non-covalent synthons and functional properties in new co-crystal salts involving d-metal ion complexes and multisite anion receptors

Molecular co-crystalline architectures are important in the context of design and preparation of not only easy-to-absorb drugs, but also advanced optical systems, charge transfer and energy transfer systems, or magnetic and conductive materials. From a fundamental point of view, such studies also provide useful information on various supramolecular synthons and molecular ordering including molecular matching, host-guest systems, structural hierarchy, and combinatorial potential that might contribute to the rational design of functional materials through structure-properties-application schemes. For example, double salts involving coordination complexes have been widely represented by family of organic-inorganic perovskites revealing order/disorder thermal phase transitions contributing to switchable dielectric properties, non-centrosymmetry and chirality related properties, symmetry-independent third-harmonic generation (THG), and photoluminescent performance [1].

In this contribution, we present our approach to the field, exploiting specific *anion- π* synthons and *hydrogen-bond* synthons formed by the selected multisite anion receptors and polycyanidometalates or simple inorganic anions, assisted by *multiple aryl embraces* (MAE) of organic cations or *o*-phenanthroline complexes, respectively. The presented advanced co-crystal architectures shows new interesting supramolecular topologies and structural hierarchy that contribute to controlled optical charge transfer (CT) or photoinduced electron transfer (PET) properties, photoluminescence, or second harmonic generation (SHG) (Figure) [2].

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Acknowledgements

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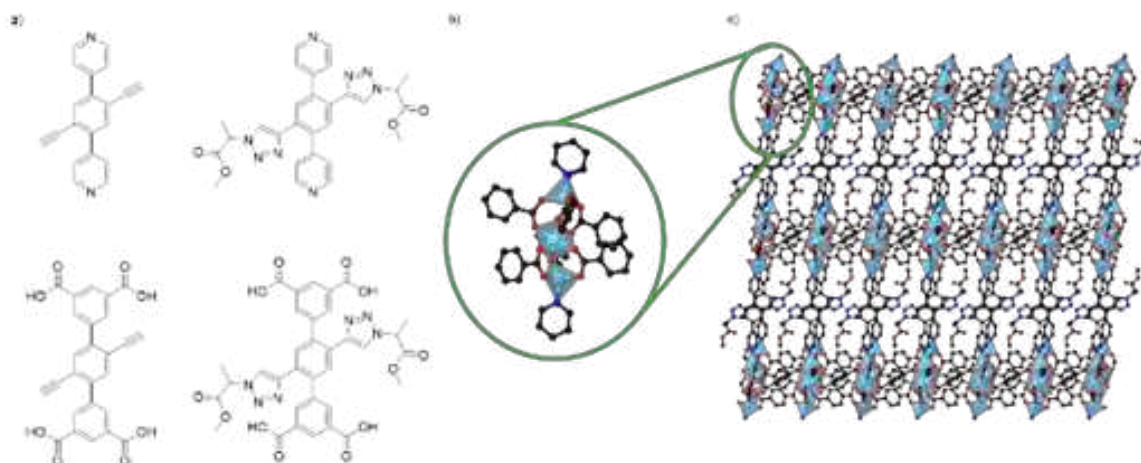
Abstract No: M13

M13 Zinc(II) MOFs synthesised from bulky ligands to investigate the impact on MOF assembly and gas adsorption

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Caption: Ligands for synthesis of MOFs, b) Zn(II) trimer and c) MOF [Zn₃(bdc)₃(L)] illustrating a pillar and sheet structure.

Metal-Organic Frameworks (MOFs) have gained increased attention as synthetic approaches for target applications, such as gas capture, have been uncovered. The use of pillar ligands as well as carboxylic acid ligands to construct these materials are an interesting aspect of MOF design as they can vary the level of interpenetration and provide a scaffold for interactions with guest molecules such as gases. Additionally, ligand functional groups can not only interact with adsorbents but also alter the growth of the MOFs.

Our work has focused on the formation and characterisation, via single crystal X-ray diffraction and powder diffraction, of a series of MOFs synthesised using both pillar and carboxylic acid ligands in combination with zinc(II). The ligands are functionalised with either triazole esters or alkynes and have different modes of coordination either through nitrogen donors or carboxylic acids (Figure 1a). The functionality promotes both ligand bulkiness to affect MOF assembly as well as providing sites for interaction of adsorbing molecules. An extension pillaring ligands in literature, these material utilise the bulkiness of the pillar ligand to synthesise non-interpenetrated 3D MOFs, two with a rare zinc(II) trimer (Figure 1b), acting as the MOFs node.

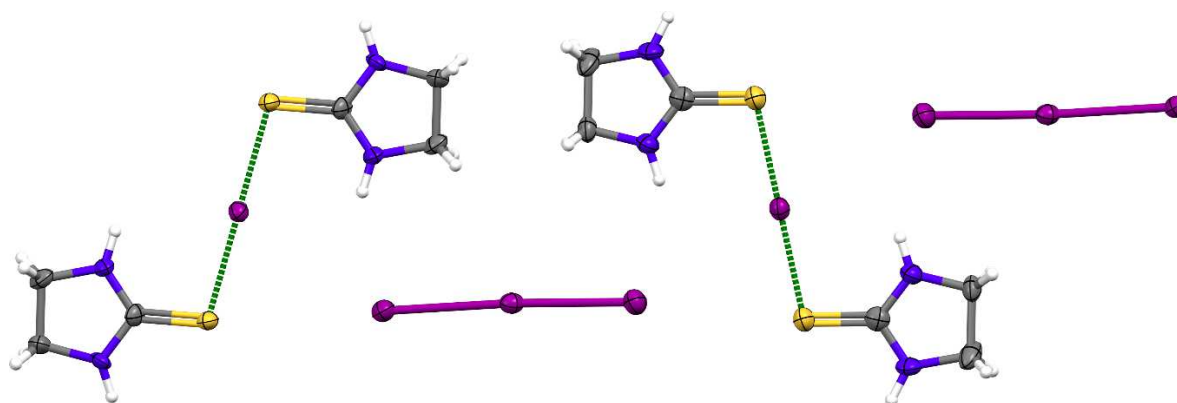
One of the synthesised MOFs, [Zn₃(bdc)₃(L)], is composed of 2D sheets stacked together by pillar ligands forming a 3D framework, (Figure 1c). These sheets are made up of zinc(II) nodes coordinated via the carboxylate groups of 1,4-dicarboxylic acid. The 3D framework is then formed via the nitrogen donor ligands, acting as pillars between the sheets. Gas adsorption techniques were used to uncover the surface area and potential for selective CO₂ adsorption.

Abstract No: M14

M14 [S–I–S]⁺ Interactions — Any Future?

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Caption: A crystal structure showing two [S–I–S]⁺ cations and I₃[−] anions.

Sulfur is a versatile acceptor in halogen bonding (XB) point of view. It is very well known acceptor with dihalogens and interhalogens¹ as well as with variety of organoiodines.^{1–4} Sulfur has also been shown to form strong three-center-four-electron (3c4e) [S–I–S]⁺ halogen bonds with iodine.⁵ However, the number of reported 3c4e XB interactions involving sulfur acceptors is very limited. There are only 10 different [S–I–S]⁺ cations found from Cambridge Structural Database (CSD) in 16 reported single crystal structures. And mostly these [S–I–S]⁺ systems (Figure) have been accidentally obtained.

In this presentation the known crystal structures of [S–I–S]⁺ systems are reviewed and our systematic efforts to obtain single crystals of such thiocarbonyl-based systems are discussed. General difficulties in their preparations are outlined. It seems that the behavior of thiocarbonyls with iodine is not so well predictable, the mixture of products is usually formed and a lot of luck is often needed to obtain single crystals of [S–I–S]⁺ systems. Thus, the problems in their preparation and analysis must be solved

before these 3c4e interactions can be utilized in any applications, e.g., crystal engineering. However, when these systems have been obtained they seem to be quite stable in the solid-state.

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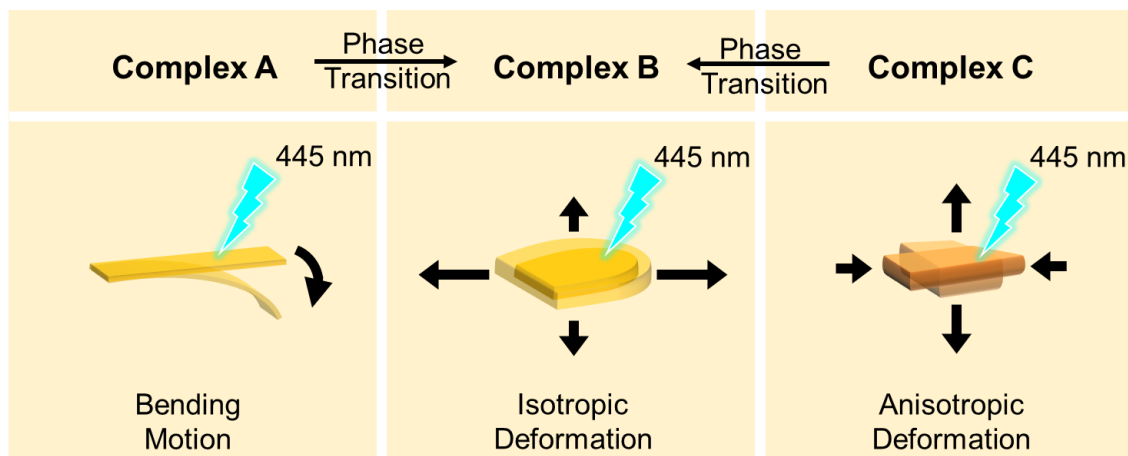
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Abstract No: M15

M15 Multifunctional azobenzene-based polymorphs achieved by non-covalent constraints

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Caption: Figure 1. Optical images and schematic illustration of polymorphs depicting photoinduced deformations.

Mechanically flexible organic crystals have been designed and generated considerably over the past few decades owing to their potential applications in smart materials such as photonics, sensors, actuators, energy storage, and medical treatment.¹ However, general deformation mechanisms and structure–property relationship of these crystals have not been well established which limits the development of design strategies and precise control of flexible molecular crystals. Polymorphic crystals, identical in chemical composition but with different structural alignments in the lattice, provide an ideal platform to explore the correlation between structures and properties.² In this work, we report three azobenzene-based polymorphic complexes exhibiting multifunctional photomechanical properties and distinct thermal-induced phase transitions by introducing non-covalent bonding in the crystalline state. Firstly, the molecular structures and interactions of polymorphs were determined by single-crystal X-ray diffraction. Upon heating to certain temperatures, both Forms I and III underwent single-crystal-to-single-crystal phase transitions to Form II, the thermally stable state. Additionally, each of the polymorphs presented unique photoresponses, including bending motion, isotropic and anisotropic deformations. These photo-mechanical outputs were further quantified by force measurement and nanoindentation. UV-vis spectroscopy, variable temperature, and laser-induced single crystal X-ray diffraction were conducted to understand the mechanism of stimuli-responsive properties. We expect this simple design to provide an effective strategy for preparing flexible molecular crystals that can be precisely operated.

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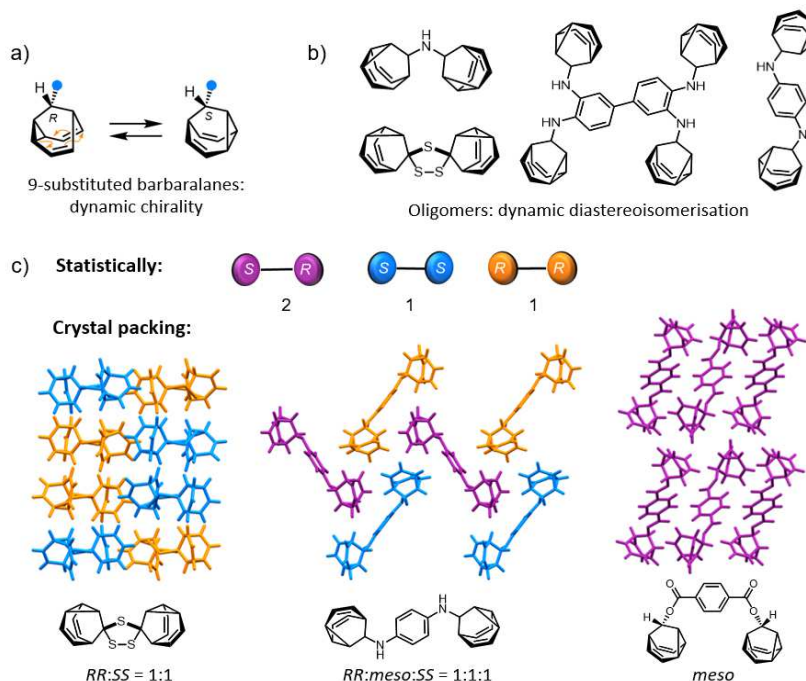
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Abstract No: M16

M16 The Influence of Noncovalent Bonding Interactions on the Dynamic Preferential Crystallisation of Fluxional Diastereoisomers

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Caption: a) Fluxional chirality of a 9-substituted barbaralane; b) barbaralane oligomers; c) theoretical and experimental results of barbaralane dimer crystals

Kinetic resolution is an important concept in asymmetric synthesis whereby enantiomers are separated or selectively reacted to provide stereochemically enriched materials. In one form of resolution – preferential crystallisation of enantiomers (conglomerates) – the outcome is dictated by noncovalent interactions in the crystal packing structure. We have recently reported 9-substituted barbaralanes that enantiomerise spontaneously, fluctuating between their (*R*)- and (*S*)-isomers without the addition of external reagents. Consequently, their dynamic sp^3 -C stereochemistry (Figure 1a) is responsive to covalent and noncovalent control.¹ Separately, we have also shown that regioisomeric barbaralanes can be crystallised preferentially. The innate energetic preference of the fluxional equilibrium can be overcome and reversed by crystal packing interactions.²

Here, we report barbaralane oligomers that fluctuate between diastereoisomeric structures (Figure 1b). We investigate their crystallisation phenomena, illustrating dynamic preferential crystallisation. Four dimers and one tetramer of 9-substituted barbaralanes were synthesised. In solution, the dimers form *meso*, and (*S,S*)-isomers in ratios close to their statistical 1:2:1 mixtures, however, in the crystal state (Figure 1c) all three dimers deviate from this isomer distribution. We use Hirshfeld analysis to analyse the noncovalent interactions between molecules, giving insights into how the crystal packing behaviour directs the fluxional stereochemical equilibrium.

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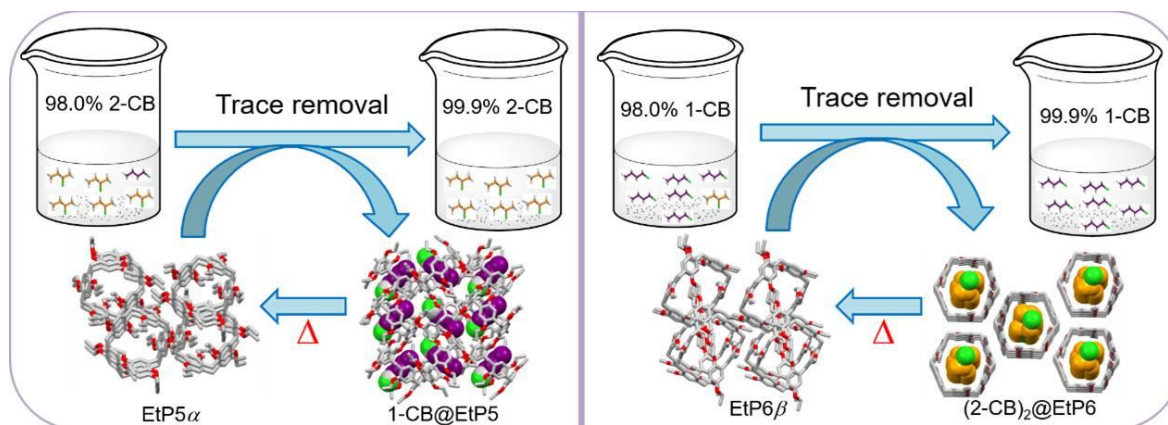
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Abstract No: M17

M17 Highly Selective Removal of Trace Isomers by Nonporous Adaptive Pillararene Crystals for Chlorobutane Purification

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Caption: Trace 1-Chlorobutane from a Chlorobutane Mixture Using EtP5 α (left) and Trace 2-Chlorobutane from a Chlorobutane Mixture Using EtP6 β (right).

Removal of trace chlorobutane (CB) isomers is highly desired to produce high grade 1-chlorobutane (1-CB) and 2-chlorobutane (2-CB). Here, we report that nonporous adaptive crystals (NACs) of perethylated pillar[5]arene (EtP5) and pillar[6]arene (EtP6) effectively remove trace CB isomers.^[1] EtP5 NACs can remove trace 1-CB (2%) from 2-CB to improve its purity from 98.0% to 99.9%, while EtP6 NACs can remove trace 2-CB from 1-CB to improve its purity from 98.0% to 99.9%. The adsorption of trace CB isomers results in the formation of new CB-loaded crystal structures, whose thermostability is higher than their corresponding isomer-loaded structures. This determines the selectivity of NACs toward the trace CB isomers. Reversible transformations between nonporous guest-free and guest-loaded structures make EtP5 and EtP6 highly recyclable.^[2]

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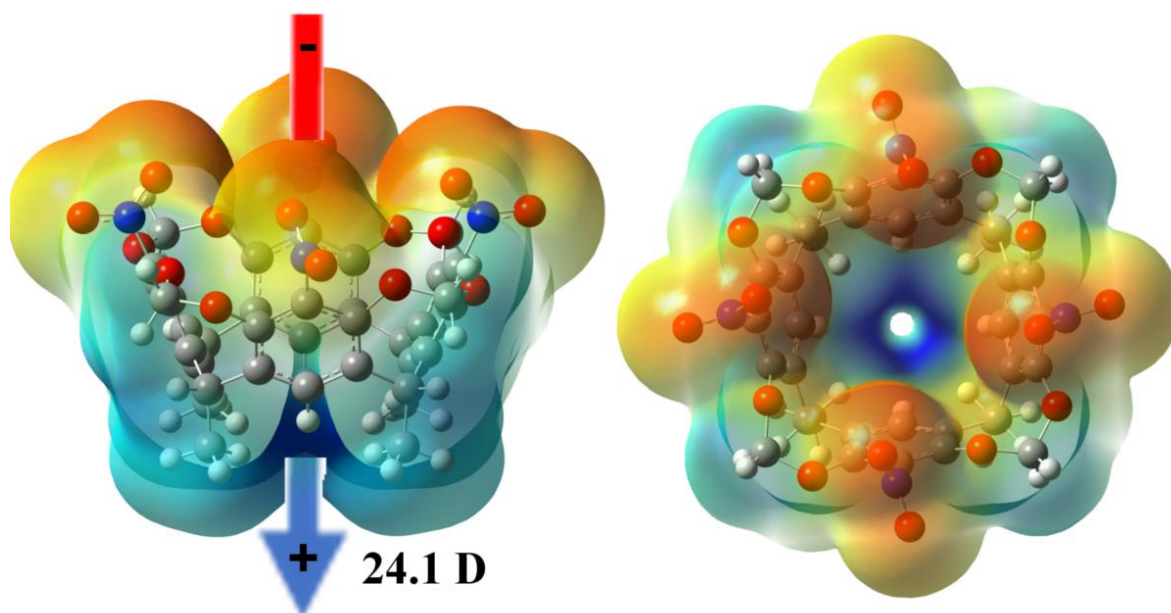
Abstract No: M18

M18 New resorcinol[4]arenes with high dipole moments: synthesis and molecular recognition

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² Institute of Organic Chemistry of the Polish Academy of Sciences, Warsaw, Poland



Caption: Fig. 1 New resorcinol[4]arenes with high dipole moments

The dipole moment (DM) is a quantity that characterizes many key properties related to their relative position in the condensed phase and to phenomena related to electron transport and interaction with light. Non-ionic organic molecules with high DM find applications as ferroelectrics, in non-linear optics (NLO), and as elements of solar cells promoting charge separation at the interface. Inducing a high DM usually involves placing electron-donating and electron-withdrawing groups (the negative and positive poles of the dipole, respectively) at opposite ends of an aromatic backbone or another conjugated multiple-bond system. Aminobenzonitriles, used in NLO, have DM in the range of 5.0–5.6 D, and the highest DM obtained so far for substituted benzene is 14.5 D.

Resorcinarenes are macrocyclic polyphenolic compounds, which, due to the shape of the vase and the gap, are used in the construction of receptors and as building blocks of molecular capsules. Due to unique geometry, the vertical components of the dipole moments add up, while the horizontal ones are canceled. We have recently synthesized tetranitroresorcinarene **1**, which, shows unique binding properties. The results of DFT calculations suggest that this molecule has a very large dipole moment in the range of 20-24 D. Macroyclic compounds with such large dipole moments are not known. These theoretical findings, together with unusual recognition properties detected experimentally open new directions in the construction of supramolecular receptors.

Abstract No: M19

M19 Supramolecular Porous Organic Nanocomposites for Heterogeneous Photocatalysis of a Sulfur Mustard Simulant

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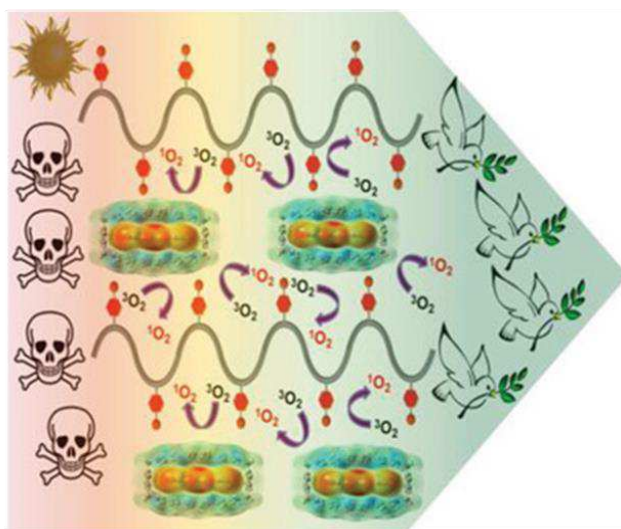


Figure 1. Schematic representation of the sulfur mustard simulant heterogeneous photocatalysis by the supramolecular photosensitizer **TBP-ExBox⁴⁺-PSS** nanocomposite

Developing efficient and sustainable organic heterogeneous photocatalysts¹ that can find application in eliminating chemical warfare agents are highly desirable. Efficient heterogeneous photosensitizing materials require both large accessible surface areas and excitons of suitable energies and well-defined spin structures. Our approach to generating² porous nanocomposites consists of blending cationic cyclophanes (e.g., **ExBox⁴⁺**) with commercially available anionic polymers such as polystyrene sulfonate (**PSS**) to form microporous composites (**ExBox⁴⁺-PSS**). Manipulating the excited-state evolution in donor-acceptor host-guest (H-G) complexes has been proved² to be crucial in enhancing the efficient production of triplet-excited states in organic compounds upon light photoexcitation. Although the lowest triplet state (T_1) in the guest molecule 1,3,5,8-tetrabromopyrene (**TBP**) is low in energy, it is inaccessible on account of the significant energy barrier separating the T_1 state from the upper singlet (S_1) and triplet (T_2) states. In the case of the **ExBox⁴⁺**, the S_1 state is long-lived in the solid state. The heterogeneous photocatalytic activities of both the H and G components are inefficient, showing a ~50% conversion of the sulfur mustard simulant after 60 minutes of photo-irradiation. The **TBP-ExBox⁴⁺** complex displays a charge transfer (CT) band at 450 nm and an exciplex emission at 520 nm, indicating the formation of new mixed-electronic states in the H-G complex. The lowest triplet state (T_1 , 1.89 eV) is localized on the **TBP** and is close in energy to the charge-separated state (CT, 2.14 eV). Experimental spectroscopic techniques combined with theoretical calculations have been conducted to decipher the excited state evolution in the H-G supramolecular complex. The homogeneous and heterogeneous photocatalytic activities of the **TBP-ExBox⁴⁺**, for eliminating sulfur mustard simulant, has proved significantly more efficient than **TBP** and **ExBox⁴⁺**, confirming the importance of the newly formed excited-state manifold in **TBP-ExBox⁴⁺** for the population of the low-lying T_1 state. Incorporating these supramolecular cationic photosensitizers¹ within anionic polymeric matrices offers (Fig. 1) porous composites with efficient photocatalytic performances against sulfur mustard simulant.

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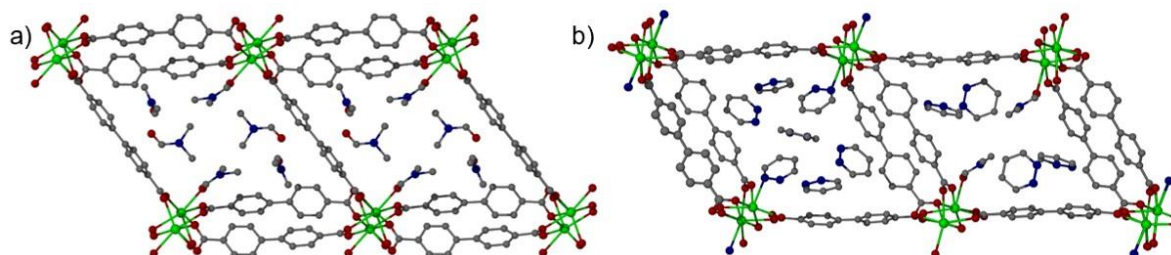
Abstract No: M20

M20 MOFs as Confinement Matrices for Trapping Nuclei

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Caption: Figure 1: Single crystal structures of 1) DU-1 and b) PYZ@DU-1. Grey: C. Red: O. Green: La. Blue: N. H atoms omitted for clarity

Crystallization under nanoscale confinement can lead to substrates exhibiting different physicochemical properties compared to their bulk.¹ This phenomenon has implications toward applications in the fields of catalysis, gas capture, water harvesting and the pharmaceutical industry.^{2,3} Furthermore, understanding nanoscale aggregation pathways can subsequently lead to gaining control over polymorphic selectivity, which will aid in producing crystalline materials with consistent properties and efficacies. In this context, metal-organic frameworks (MOFs) are promising confining matrices due to their crystallinity, versatile topologies and pore sizes. Herein, we aim to study molecular clusters inside a novel mesoporous lanthanum metal-organic framework (MOF) by means of single crystal X-Ray diffraction (SXRD).

A solvothermal reaction of La³⁺ with 4,4'-biphenyldicarboxylic acid leads to the formation of a mesoporous lanthanum MOF (DU-1). Initially, DU-1 is comprised of coordinated and non-coordinated dimethylformamide guest molecules that can be exchanged with pyridazine to yield PYZ@DU-1. Crucially, this exchange can be visualized via SXRD (Figures 1 a-b), making DU-1 an appealing framework for not only observing newly formed molecular clusters, but also to study their evolution. Current work is focused on exchanging the pore-occupying solvent molecules with different types of guests such as small explosive substrates, phosphates and sulfoxides.

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Abstract No: M21

M21 Novel Macrocycle-Polymer Networks for Efficient Iodine Capture

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Since the nuclear disasters of Chernobyl in 1986 and Fukushima in 2011, the treatment of radioactive pollutants has become a crucial environmental issue. In Fukushima's case, many pollutants were released, contaminating the air, freshwater, and seawater. One of the most harmful elements released by these disasters is the isotopes of iodine, ^{131}I with a half-life of 8 days and ^{129}I with a half-life of 15.7 million years.[1]

Currently, there is a strong interest to find effective means to capture iodine isotopes. An effective iodine sorbent should be stable during the treatment processes and capable of capturing large amounts of iodine. More recently, adsorption has been considered to be an effective method to capture iodine from liquids or gases.

In this regard, several solid adsorbent materials have been investigated, including zeolites, carbon materials, mesoporous silica, Metal-organic framework (MOFs), Covalent organic framework (COFs), Porous organic polymers (POPs), and molecular sieves. However, the major problem of these porous materials for industrial applications is that they are in form of powder that makes their handling and transportation difficult.[2] In addition, they are sensitive to pressure, dust, clogging, mass loss and moisture. Moreover, the regeneration of powders after adsorption relies on energy and time-consuming techniques such as centrifugation and filtration, which hamper their industrial development.

In this work, we prepared a crosslinked polymer network (CPN) containing macrocycle and polymer for efficient iodine removal from vapor phase, water and seawater. In vapor phase, the CPN could capture 6 g g^{-1} of iodine, ranking among the most performant materials for iodine vapor capture. In liquid phase, the synthesized CPN is also capable of capturing iodine at high rates from aqueous media (water and seawater). The CPN also displayed fast adsorption kinetics and they are fully recyclable. The synthesized CPN are extremely interesting since they are inexpensive and the synthesis could easily be scaled up to be used as the material of choice in response to accidents in nuclear industry.

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Abstract No: M22

M22 3,5-Diaminobenzoic Acid-Based Supramolecular Barrel-Rosette Ion Channel for Cation-Anion Symport

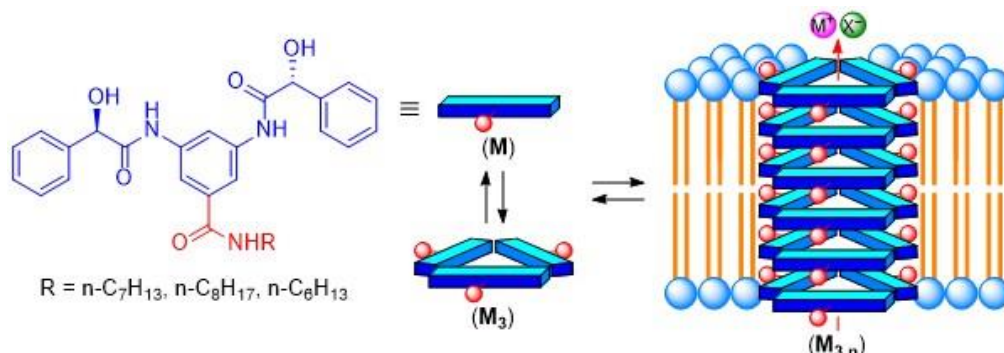
Sandip Chattopadhyay ¹ Anupam Ghosh ², Titas Kumar Mukhopadhyay ², Rashmi Sharma ¹, Ayan Datta* ², Pinaki Talukdar* ¹¹ IISER Pune, Pune, India² IACS Kolkata, Kolkata, India

Figure: Structure of channel forming molecules and the construction of barrel-rosette ion channel.

Transmembrane ion channels operate selective ion homeostasis to perform various pivotal biological processes.¹ Recently, abundant mutations of ion channels have been found to cause channel malfunctions, eventually leading to therapeutically targeted ion channelopathies.² Numerous synthetic molecules have been developed to transport cations³ or anions⁴ and imitate both the structure and function of natural ion transport systems in order to address the structural and functional complexity of natural ion channels. However, synthetic cation-anion symporter channels have received limited attention due to difficulties in decorating the channel selectivity filter to transport both cation and anion selectively. Hence, despite efforts to create a channel with single ion selectivity in a lipid bilayer by artificial channels, a general synthetic strategy for realizing more complex dual ion selectivity is challenging to be proposed.

Here, we have developed bis-(*R*)-(*S*)-mandelic acid substituted 3,5-diaminobenzoic acid-based self-assembled barrel-rosette ion channels. Concentration-dependent transport activity studies provided a Hill coefficient of 3 for each derivative indicating the participation of three monomers in forming the active structure during the construction of the ion channel. Therefore, a self-assembled trimeric rosette model was proposed for ion channel formation. Transport studies with liposomes revealed cation-anion cotransport with preferential selectivity towards K⁺ and ClO₄⁻ ions. The formation of ion channels was confirmed by planar bilayer conductance studies that verified the selectivity towards K⁺ and ClO₄⁻ ions as compared to Na⁺ and Cl⁻. Finally, molecular dynamics simulations of (M_{3,6}) channel were carried out in the pre-equilibrated DPPC lipid bilayer with water molecules with different salts to understand the supramolecular channel formation and its ion selectivity pattern.

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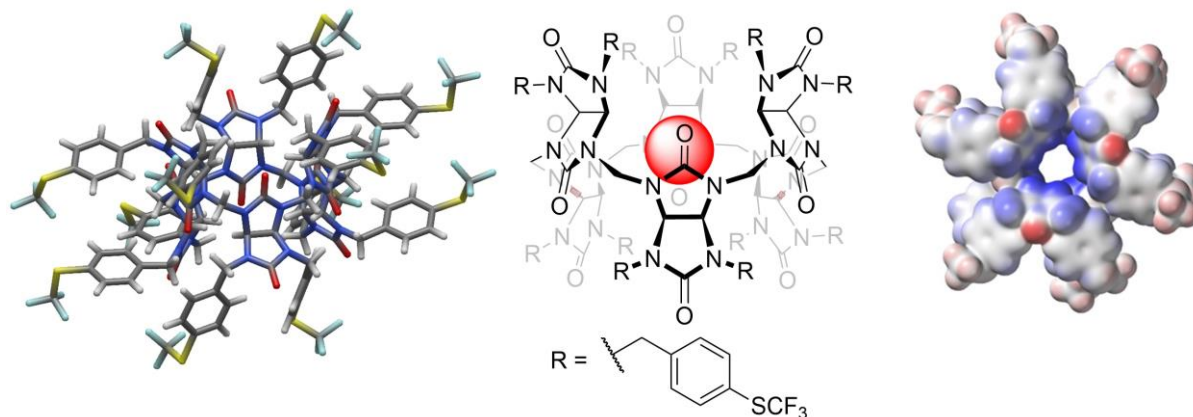
Abstract No: M23

M23 Novel fluorinated bambusurils and their anion binding and transport properties

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Caption: An example of a fluorinated BU derivative, its crystal structure, graphical representation of complex with anion and electrostatic potential map.

Bambusurils are macrocyclic substances made of six glycoluril building units connected via methylene linkers.¹ Bambusurils are appreciated for their strong anion binding in solution, which is mediated by twelve C-H...anion hydrogen bond interactions. Their anion affinity was improved even further by introduction of fluorinated substituents, leading to exceptionally high association constants ranging between 10^7 - 10^{11} M⁻¹ for Cl⁻, NO₃⁻, and HCO₃⁻ in acetonitrile.² These fluorinated substituents appended to the bambusurils did also increase their lipophilicity and, in combination with their high anion binding strength, very efficient anion transporters were obtained.

Here, new fluorinated bambusuril derivatives will be presented. Appending more strongly electron-withdrawing substituents further decreased the electron density inside the cavity of the bambusuril macrocycle. This resulted in stronger anion binding, which was studied by a ¹H and ¹⁹F NMR spectroscopy. The effect of increased anion binding strength on anion transport properties was evaluated using liposomes, using the lucigenin assay for chloride/bicarbonate antiport studies.

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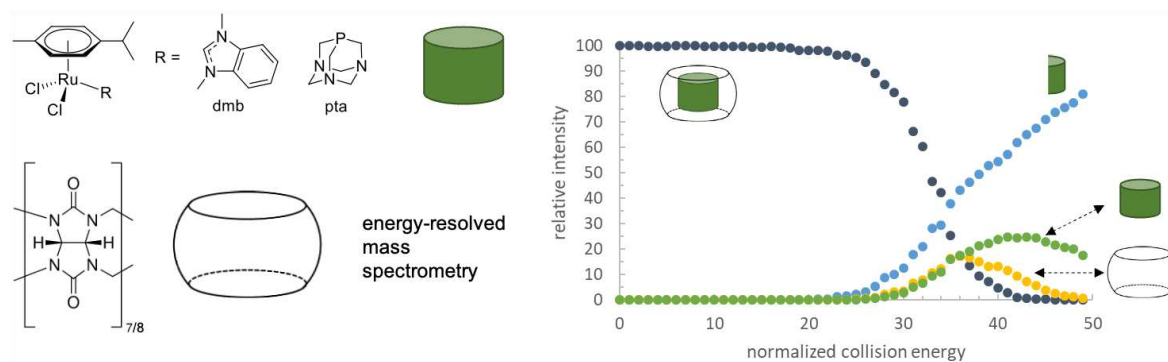
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Abstract No: M24

M24 Host-Guest Interactions of Ruthenium(II) Arene Complexes with Cucurbit[7/8]uril

Monika Cziferszky Elisa Roth

University of Innsbruck, Innsbruck, Austria



Caption: The host-guest chemistry of selected ruthenium (II) complexes with CB[7] and CB[8] was investigated by NMR and (ER-)MS.

Cucurbit[n]urils (CBs) hold promise as host molecules for drug delivery applications on account of their biocompatibility and ability to form high-affinity inclusion complexes with a variety of guest compounds. An increasing number of reports on CB-binding of biologically active compounds including benzimidazole derivatives, alkaloids, steroids, amino acids and metallodrugs, showcase the versatility of CB-based drug delivery.¹ Among others, the encapsulation in CBs can enhance the solubility of poorly soluble drugs as well as protect the drug against degradation by biological nucleophiles. The latter point is especially relevant for metallodrugs.

Despite the fact, that the three worldwide approved platinum(II)-based chemotherapeutics cisplatin, oxaliplatin and carboplatin exhibit a variety of severe and dose-limiting side effects, they are the drugs of choice for many types of cancer, often in combination with other drugs.² Encapsulation of these metallodrugs in macrocyclic hosts improved drug stability and dramatically reduced the dose required to inhibit tumour growth compared to the free drug.^{3,4}

In this study, we investigated the interactions of three ruthenium(II) complexes with CB[7] and CB[8] by NMR and MS. Ruthenium (II) arene complexes belong to a promising new class of metal-based anticancer agents, for which modes-of-action different from the platinum(II) based drugs are assumed. However, all metallodrugs containing labile ligands such as chlorido are facing stability issues in the sense that they can be inactivated by biological nucleophiles. This reactivity of metallodrugs is both blessing and curse, and controlling it by encapsulation in macrocyclic hosts might be a way forward to reduce side effects and increase efficacy of metal-based agents.

In a series of NMR and MS experiments, we found that CB binding of the ruthenium(II) complexes $\text{Ru}(\text{cym})(\text{dmb})\text{Cl}_2$, RAPTAC and $[\text{Ru}(\text{cym})\text{Cl}_2]_2$ (see Figure) directly correlates with the aquation of the compounds, that is how fast and to what extent the chlorido ligands exchange for aqua ligands, a process that can be controlled through addition of additives such as NaCl or AgNO_3 . The aqua ligands impose a positive charge on the ruthenium(II) center, which distinctly enhances the affinity of the compounds to CBs due to ion-dipole interactions in the portal regions.

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M25 Development of Novel Anion Receptors for Reactive Sulfur, Nitrogen, & Oxygen Containing Species

Amanda Davis, Michael Pluth

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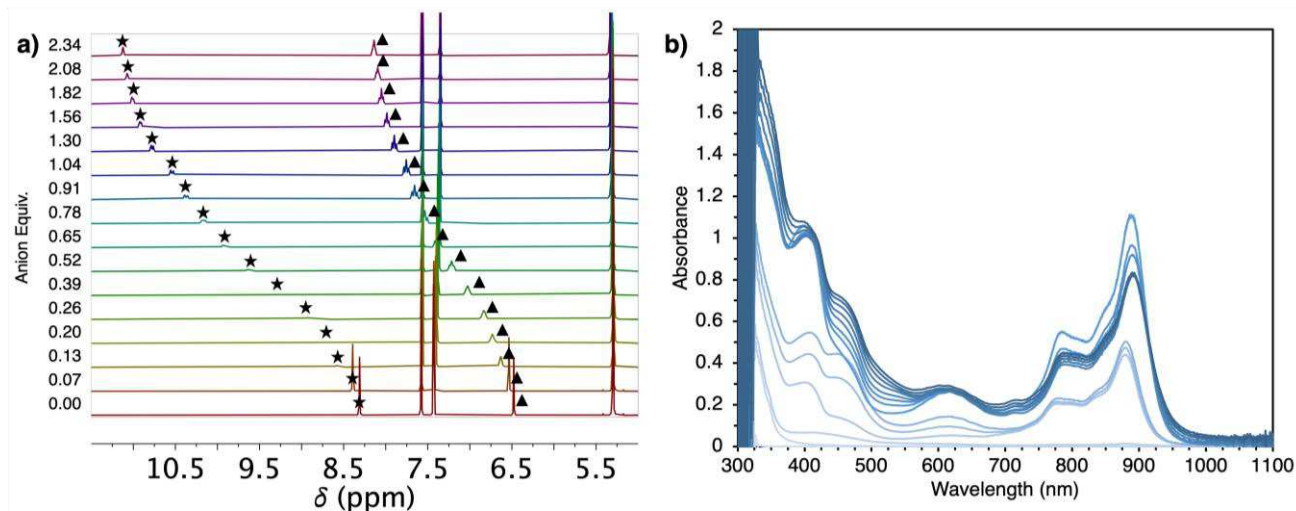


Figure 1. Supramolecular titrations with a) anion binding of RSS via ^1H NMR spectroscopy, and b) charge transfer induced reactivity of RSS via UV-Vis

Gasotransmitters, such as H_2S and NO , are small molecule bioregulators that are responsible for regulating different aspects of physiological functions and cellular signaling.^[1] The crosstalk between these and related biologically active species can lead to the formation of reactive sulfur species (RSS), reactive nitrogen species (RNS), and reactive oxygen species (ROS), which have their own roles in physiological mechanisms.^[2] Although often written as a neutral species, H_2S and other reactive sulfur, nitrogen and oxygen species are typically anionic under physiological conditions. The complexity and reactivity of these small reactive species in biological environments make understanding their interconnectivity and specific involvement in signaling pathways incredibly difficult. Molecular recognition offers the opportunity to elucidate the reactivities and properties of these understudied class of anionic targets.

This presentation highlights current efforts of developing methods of molecular recognition to target RSS and RNS with the more long-term goal of understanding specific molecular environments that stabilize these reactive species. Specifically, we have demonstrated that simple host molecules containing C–H hydrogen bonding motifs exhibit selectivity toward forming strong C–H \cdots S interactions. Additionally, we have uncovered unique charge transfer reactivity of RSS with electron deficient π -systems. As a whole, this work highlights the development of new tools to investigate biologically relevant, reactive anions.

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Abstract No: M26

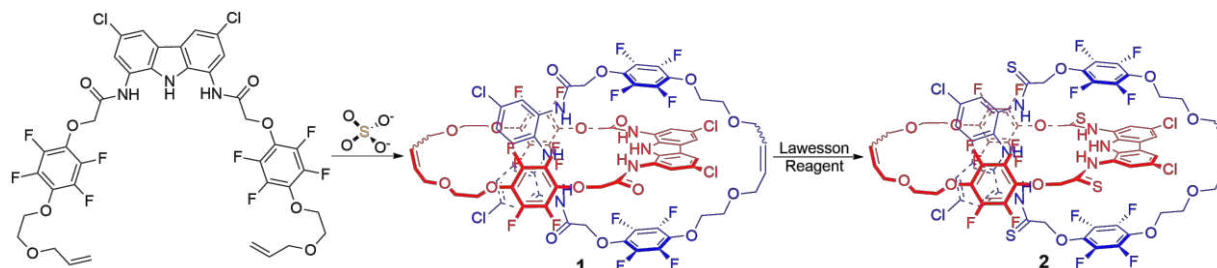
M26 Catenanes as a new class of transmembrane anion carriers

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Caption: figure 1.

The development of artificial transmembrane carriers for extremely hydrophilic anions, such as sulfate or phosphate, is one of the major challenges in supramolecular chemistry. Catenanes seem to be particularly promising transporters for these tetrahedral anions owing to their unique 3D cavities with orthogonal arrangement of binding units. Furthermore, the high degree of flexibility provided by mechanical bonding should enable rapid exchange kinetics and hence facilitate fast transport across lipid bilayers. Despite that, so far there are no precedents in the literature of catenanes acting as transmembrane anion carriers.[1]

In this presentation, we disclose a multi-step, anion-templated synthesis of two carbazole-based catenanes **1** and **2** (Fig. 1) and the results of our studies on their anion transport properties in liposomal models.

Figure 1. Sulfate-templated synthesis of carbazole-based catenanes **1** and **2**.

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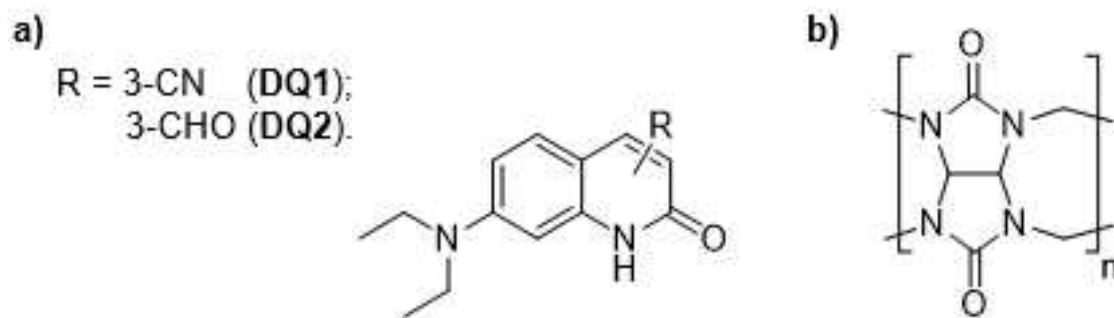
1) For an example of interlocked anion channel, see: August, D. P.; Borsley, S.; Cockroft, S. L.; della Sala, F.; Leigh, D. A.; Webb, S. J.; *J. Am. Chem. Soc.*, **2020**, *142*, 18859–18865.

Abstract No: M27

M27 STUDY OF THE STABILIZATION OF HOST-GUEST COMPLEXES BETWEEN QUINOLINONES AND CUCURBITURILS. FROM AN EXPERIMENTAL AN IN-SILICO POINT OF VIEW

Kevin Droguett Edwin Perez, Denis Fuentealba, Margarita Aliaga, Angélica Fierro

Pontificia Universidad Católica de Chile, Santiago, Chile



Caption: Figure 1: a) Quinolinone derivatives studied in this work (DQ1-2) b) Cucurbit[n]uril, n=7 and 8.

Studying the host-guest interaction between a macrocycle and a dye is highly attractive. The above is due to the potential applications of those systems, such as drug delivery, catalytic process, sensing, and functional materials, among others¹. There are a variety of host-guest systems being studied in the literature. On the side of the host, there are several examples of macromolecules with attractive properties, and one example is the cucurbituril family. Those macrocycles are water-soluble, have two identical portals, and have a cavity size capable of harboring various guests with different molecular structures. On the other hand, several guests can be suitable for a supramolecular study. One example is the family of quinolinones, molecules with good chemical and thermal stability and interesting optical properties². Interestingly, thermodynamics studies on supramolecular systems could be helpful for the understanding of the affinity between the host and guest, their interactions, and the main stabilization energy of the complex³.

In this work, the inclusion of two 7-(diethylamino)quinolin-2(1H)-one derivatives (**DQ1-2**) and its interaction with cucurbit[n]uril (CB[n], n= 7, 8) (see Fig.1) were studied from an experimental and in-silico point of view. For the experimental section, the complexes showed a 1:1 stoichiometry by HRMS-ESI. The inclusion of the derivative on the macrocycles leads to an upward shift in the fluorescence intensity, and the pK_a value of **DQ1-2** exhibits almost no variation after the formation of the complex. The thermodynamics of the inclusion complexes was investigated using isothermal titration calorimetry; the results demonstrate a non-classical hydrophobic effect³ with entropy as the driving force for the inclusion. The molecular dynamic study was carried out during 300 ns in explicit solvent at NTP conditions. Our finding shows that the complexes remain stable during the simulation (RMSD \sim 1 Å), and hydrogen bonds contribute to the system stabilization. Finally, thermodynamic parameters from MM-PBSA calculations were obtained to generate new computational insights to compare with experimental results.

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Abstract No: M28

M28 Taming the Chlorine Radocal: Observation and Control of Chlorine Radical-Mediated C–H Activation

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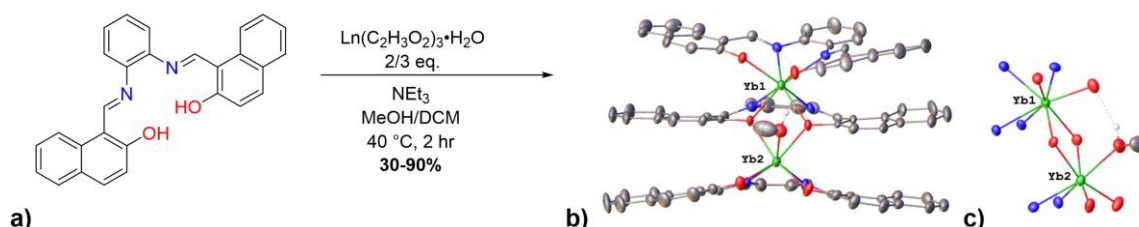
The activation of C–H bonds requires the generation and control of high-energy intermediates. In particular, chlorine radicals readily cleave strong C(sp³)–H bonds, but their inherently high reactivity leads to nearly indiscriminate activation of molecules with different C–H bonds. We demonstrate that photochemical generation of chlorine radicals within the secondary coordination sphere of an iron(iii) pyridinediimine complex enables the spectroscopic and photocrystallographic observation of the preferential activation of a C–H bond in the solid state. Furthermore, we designed a series of iron(iii) pyridinediimine complexes that confine photoeliminated chlorine radicals within the secondary coordination sphere through arene–Cl• interactions, thereby enforcing steric control over chlorine radical reactivity. As a result, these complexes exhibit selectivity for the activation of more accessible primary and secondary C–H bonds, overriding thermodynamic selectivity for weaker tertiary C–H bonds.

Abstract No: M29

M29 Structural Coordination in Lanthanide Naphthylsalopen and Naphthylpyrasal L3:M2 Multidecker Sandwich Coordination Complexes

Anne Gorden

Texas Tech University, Lubbock, United States



Caption: Figure 1. Reaction scheme for preparation of the lanthanide (III) naphthylsalopen complex and X-ray structure of Yb₂L₃ complex.

We developed a series of ligands combining an imine with hydroxy naphthylaldehyde to make tetradentate ligands, the naphthylsalophens with a benzene linker and pyrasals with a pyrazine linker. These unique supramolecular coordination architectures are assembled combining different components including the spacer ligand, central metal ion, coordination bite angle, binding domain, sterics, solvents, and geometry. The naphthylsalophen complexes were characterized with actinides^{1,2} and lanthanides³ and used these to compare the effects of ligand coordination and the differences in the nature of and degree of covalency in binding with the 4f and 5f elements.⁴ The lanthanide naphthylsalophen complexes were found to form as 3:2 ligand:metal sandwich complexes as shown in figure 1. The small changes in ionic radii between the lanthanides were found to affect the emissions properties with somewhat tunable emissions both in solution and the solid state.³ Due to the favorable arrangement and proximity of the two metal ions, the 3:2 Ln(III) naphthylsalophen sandwich complexes were found to display two-photon absorption and up-conversion luminescence using 980 nm excitation and emission spectra.⁵ Here, changes to the ligand modifying the outer coordination sphere or introducing the more electron withdrawing pyrazine backbone allowed us to observe the effects these components on self-assembly of structures and emissions.

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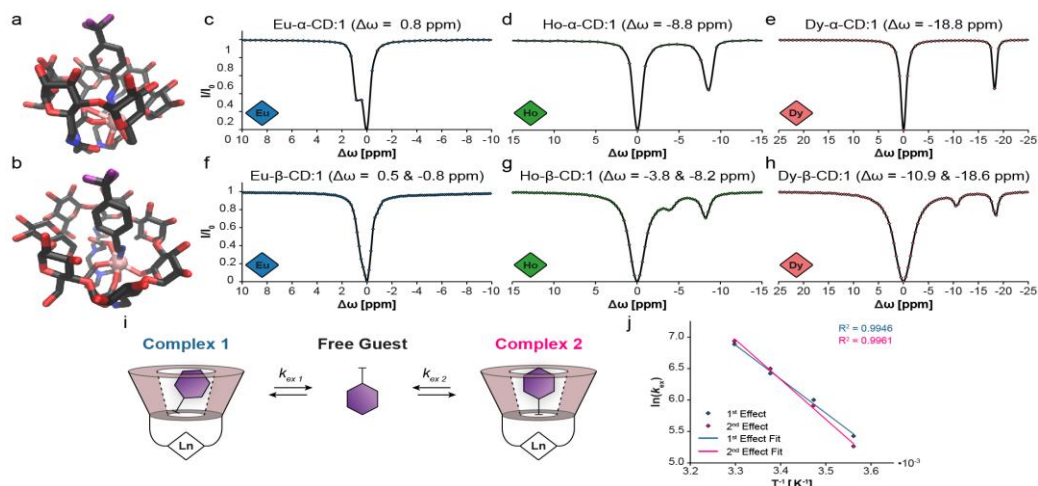
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Flash Talks / 26-06-2023 16:40 - 17:00 Harpa - Silfurberg A/B 2nd floor

M30 ^{19}F -Paramagnetic Guest Exchange Saturation Transfer (^{19}F -ParaGEST) Revealing Hidden Interactions in Supramolecular Host-Guest Systems

Elad Goren, Liat Avram, Amnon Bar-Shir

Weizmann Institute of Science, Rehovot, Israel



Caption: Figure 1. ^{19}F -paraGEST of Lanthanide-Alpha-Cyclodextrins (Ln- α -CDs) and Lanthanide-Beta-cyclodextrins (Ln- β -CDs).

The implementation of supramolecular architectures in a desired field is driven by the dynamic processes those systems possess, providing them with unique properties. However, studies of such dynamic processes, particularly in host-guest systems, are limited for specific (and slow) dynamic regimes, primarily due to the inaccessibility of proper analytical tools. Therefore, robust approaches, which can be easily and extensively used for the quantitative evaluations of kinetic characteristics of such molecular systems, are greatly needed.

Previously, we have established and exploited the fluorine-19 guest exchange saturation transfer (^{19}F -GEST) technique to study slow-to-intermediate exchanging host-guest systems¹ and expanded it into ^{19}F -paraGEST by introducing paramagnetic lanthanides to host-guest systems of α -cyclodextrins (α -CDs)², adopting the principles of the paraCEST MRI approach³.

Here, we use ^{19}F -paraGEST to investigate guest exchange in systems of **Ln- α -CDs** (Fig. 1a) and **Ln- β -CDs** (Fig. 1b), exhibiting intermediate-to-fast exchange rates in the NMR time scale (well-above the currently applicable limit). Specifically, we adapted the same lanthanide modification for two types of CD macrocycles, characterized by different cavity sizes, and studied their ^{19}F -paraGEST features utilizing the same ^{19}F -guest (4-Trifluoromethylbenzylamine, structure is shown in Fig. 1a and Fig. 1b). Benefitting from the increasing pseudo-contact shift (PCS) effects of specific lanthanides (Eu, Ho and Dy, Fig. 1c-h), we were able to increase the spectral resolution of ^{19}F -GEST (Fig. 1c-e and Fig 1f-h for **Ln- α -CDs** and **Ln- β -CDs** respectively), which, consequently, revealed two distinct populations of bound ^{19}F -guests in **Ln- β -CDs**. This observation, not obtainable for **Ln- α -CDs**, could not be detected with other analytical tools such as mass spectrometry (MS), 1D-NMR, diffusion measurements, and UV-vis spectroscopy, emphasizing the uniqueness of ^{19}F -paraGEST as an analytical tool for studying binding kinetics in supramolecular assemblies.

The observations summarized here imply different CDs-binding geometries for a given guest in **Ln- β -CDs** (Fig. 1i), characterized by similar activation energies (Fig. 1j), and highlight the importance of ^{19}F -paraGEST not only as a tool for future development of non-fluorescent-CD-based-sensing but also for studying “NMR-invisible” host-guest systems.

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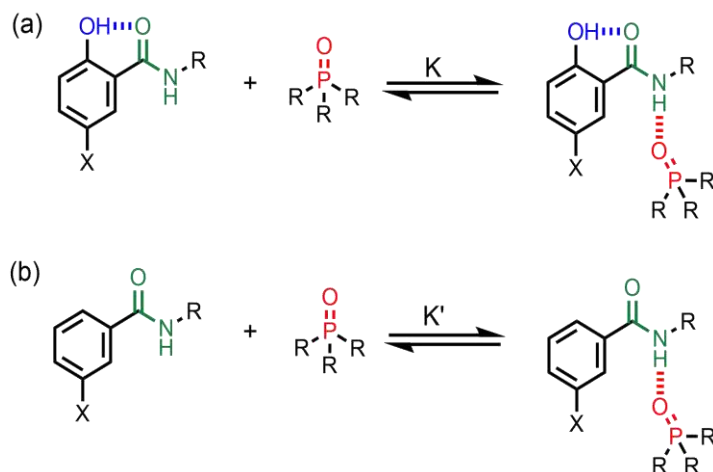
Abstract No: M31

M31 H-bond cooperativity: Polarisation Effects on Secondary Amides

Fergal Hanna ¹, Christopher A. Hunter ² Cristina Misuraca , Daniil O. Soloviev

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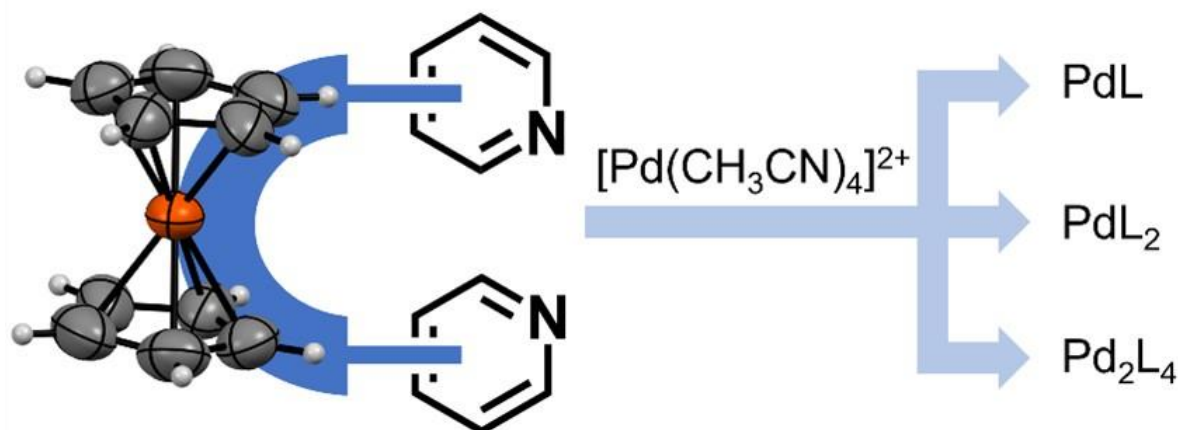
Caption: (a) Interaction of a H-bonded amide with a phosphine oxide. (b) Reference interaction of a non-H-bonded amide with a phosphine oxide. X is a substituent

Non-covalent interactions are present in systems across chemistry, materials science, and biology. H-bonding to an amide leads to polarization of the amide, which in turn makes the second H-bond the amide forms stronger, thus making H-bonding in chains of amides cooperative. The work presented in this poster quantifies the magnitude of the polarization effect by measuring the association constant between tri-*n*-butyl phosphine oxide and a series of benzamides.¹ Comparison of the association constant for benzamides with and without a 2-hydroxyl group allows for quantification of the effect of an intramolecular H-bond to the amide carbonyl on the ability of the amide NH to act as a H-bond donor for intermolecular H-bonds. By varying the substituent X, it is possible to develop a quantitative structure-activity relationship that describes the effect of the strength of the intramolecular interaction on the strength of the intermolecular interaction.

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M32 Heterometallic Supramolecular Architectures: From the Design of Building Blocks to Stimulus-responsive Guest Binding

Christian Hartinger¹, William Tremlett¹, Hayden Gearing¹, James Crowley², James Wright¹¹ University of Auckland, Auckland, New Zealand² University of Otago, Dunedin, New Zealand

Caption: Figure 1. Preparation of Fe-Pd supramolecular architectures.

Metallosupramolecular architectures are investigated for application in a wide range of research areas. We are particularly interested in their use in host-guest chemistry with applications in biology, especially drug delivery.¹ A key difference between healthy and cancerous tissues is the presence of hypoxic areas in the latter which results in more acidic and more reductive tumor microenvironments.² These distinct differences can be exploited by the design of stimulus-responsive structures that open upon change in pH or reduction.

In this project, we designed and prepared heterometallic structures for selective release of guest molecules which can reversibly open and close and bind guest molecules. We followed two approaches: we built ferrocene-based ditopic ligands based on pyridyl substituents to prepare structures of the general formula PdL , PdL_2 and Pd_2L_4 after reaction with $[\text{Pd}(\text{CH}_3\text{CN})_4]^{2+}$ (Figure 1).³ Furthermore, our work on the development of novel PdPtL_4 compounds will be presented, expanding on the structural diversity of recently introduced low symmetry cages.^{4,5} The preparation and characterization data will be complemented by experiments demonstrating the stimulus-responsive assembly and disassembly of such structures and in particular the reversible binding and release of guest molecules.

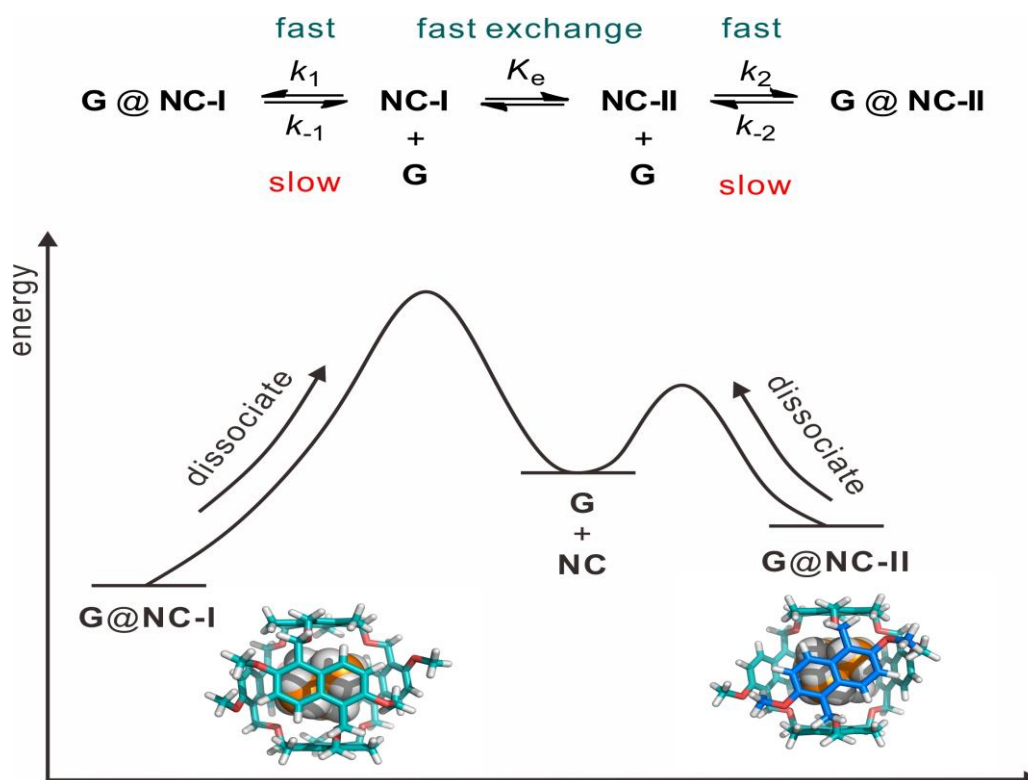
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Abstract No: M33

M33 Kinetics and Thermodynamic Correlation of Conformational Changes of a Flexible Naphthocage
Shan HE

The University of Hong Kong, Hong Kong, China



While conformational changes are critical to protein-ligand binding, kinetic understanding of conformational changes and its relationship with the binding thermodynamics is rather limited. In this work, a flexible naphthocage (**NC**) is discovered to be a suitable synthetic receptor for studying the kinetics and the thermodynamic correlation of conformational changes between two slowly interconverting conformations upon the binding of a series of ammonium guests. Variable temperature NMR studies showed that the free **NC** exists as several conformations due to the rapid flipping of the naphthyl groups, and that two conformations are formed upon binding to a suitable guest and slowly interconvert at room temperature. The self-adaptation of the flexible host to give the most stable conformation is proposed to involve a “dissociation-conformational change-binding” mechanism. Rate constants of the dissociation kinetics were determined and found to be linearly correlated to the binding constants of the most stable conformer, suggesting that the activation barrier of the conformational change can be governed by controlling the thermodynamics of the binding, and hence allowing the prediction of kinetic parameters using thermodynamic information which are generally more easily available. Results from this work that bridges the kinetics and thermodynamics of molecular recognition are hence valuable for studying and understanding the kinetic aspect of guest binding and selectivity.

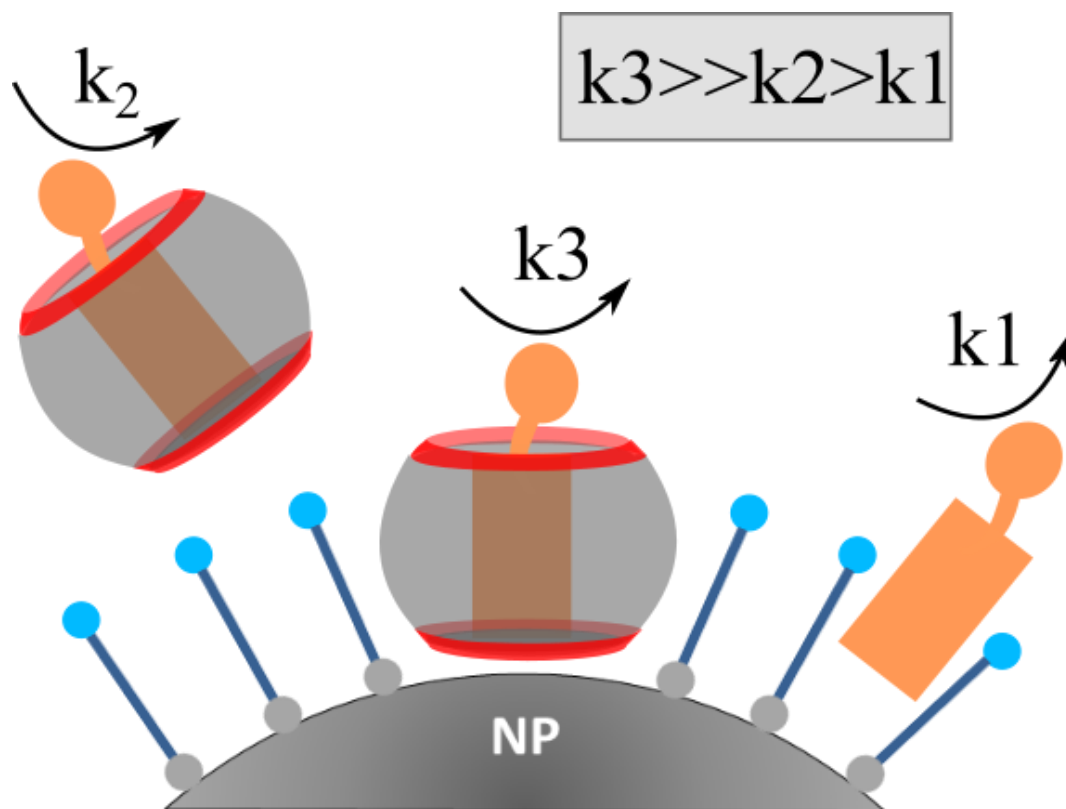
Abstract No: M34

M34 Enhanced catalysis by cucurbit[7]uril-gold nanoparticles ensembles

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² Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland



Caption: Supramolecular ensemble

The simultaneous use of macrocycles and metal nanoparticles is well-established, but their catalytic potential has remained largely untapped.¹ Here, we introduce a supramolecular system that leverages the catalytic properties of cucurbit[7]uril (CB[7]) attached to gold nanoparticles (AuNPs). We show that the adsorption of CB[7] onto the AuNP surface occurs via non-covalent attachment, and an additional organic layer between the two components improves stability and enhances interactions. The resulting supramolecular ensemble exhibits remarkable catalytic efficiency, accelerating condensation reaction far beyond what either component alone can achieve. Our work highlights the synergistic catalytic effect of the supramolecular system, which represents a significant step forward in the development of novel catalytic materials.

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Abstract No: M35

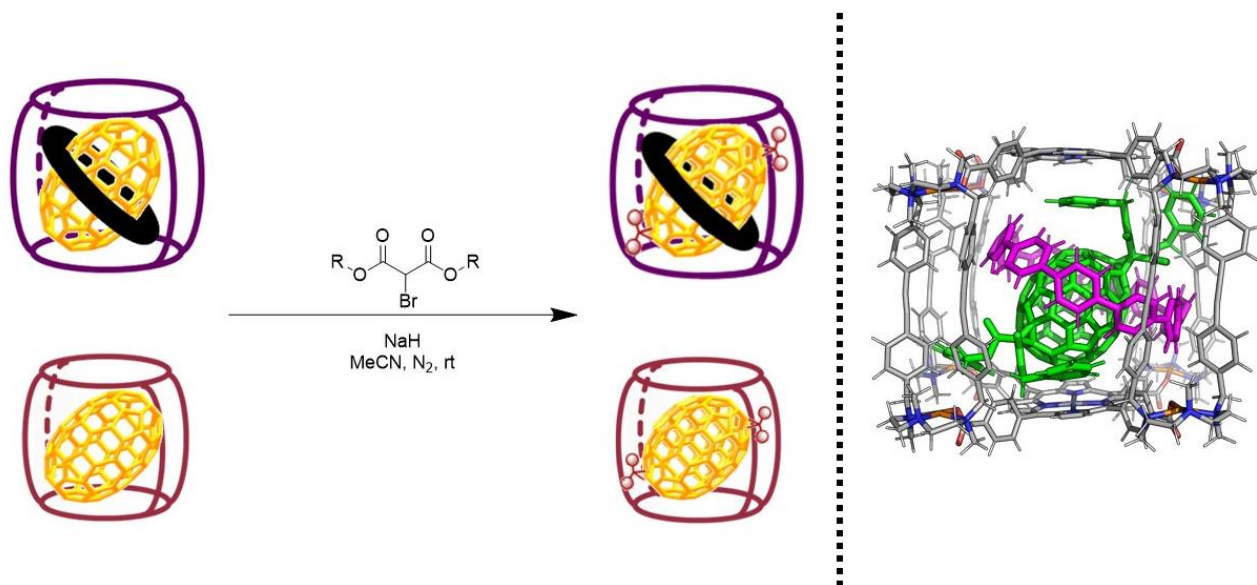
M35 Divergent regioselective Bingel bis-functionalization of fullerene C70 via supramolecular masks

Valentina Iannace ¹ Ernest Ubasart ², Clara Sabrià ², Max Von Delius ³, Ferran Feixas ², Xavi Ribas ²

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³ Ulm University, Ulm, Germany



Caption: Bingel cyclopropanation of C70 using supramolecular nanocapsules and Matryoshkas as masks. MD Simulation of the (2 o'clock) bis-adduct Matryoshka.

Isomer-pure poly-functionalized fullerenes are required to boost the development of fullerene chemistry in any field, specifically in solar cell design [1]. Developing new synthetic strategies capable to restrict the regioisomer formation is a challenge, especially for C₇₀, less abundant than C₆₀, and with 8 distinct bonds at which mono-functionalization may occur, leading to a complicate mixture of multiple adducts when functionalized.

In this work we show the regioselective synthesis of bis-C₇₀-adducts upon Bingel cyclopropanation using supramolecular nanocapsules as masks [2]. In order to deep into the subtle mask-mediated regiofunctionalization, a tetragonal prismatic nanocapsule (C₇₀@(Pd-pp)Cage) and a three shell Matryoshka complex [2] (C₇₀@[10]cycloparaphenylene@(Pd-pTp)Cage) have been explored; additionally a series of malonates differing in bulkiness have been tested.

Strikingly, a single pure regio-isomer (2 o'clock) of the Bingel bis-adduct of C₇₀ is obtained by using the dibenzyl bromomalonate and the three shell Matryoshka complex, preventing the poly-functionalization and achieving a 100% regioselectivity.

Molecular Dynamics simulation have help in rationalizing the experimental results showing that the high regioselectivity is due to the conformation of the 2 o'clock regio-isomer inside the Matryoshka complex.

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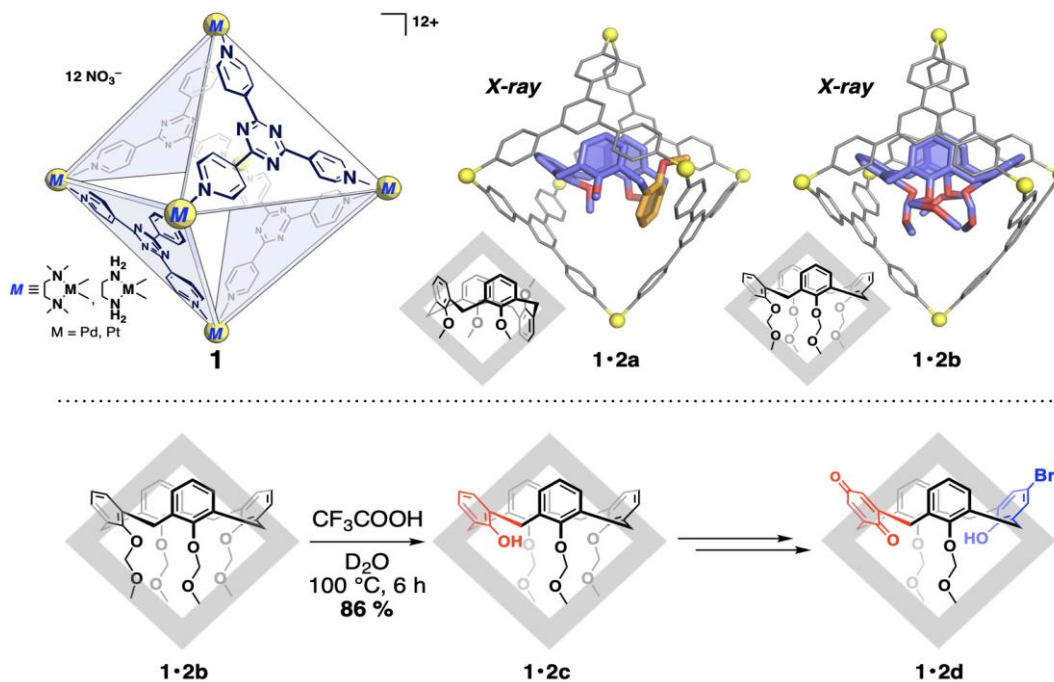
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Abstract No: M36

M36 Selective, Partial, and Asymmetric Functionalization of Calix[4]arenes through Conformational Fixation in a Self-Assembled Hollow Cage

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Caption: Figure. Structure of inclusion complexes and reaction products.

Abstract

Calixarenes are versatile molecules with a tunable host property by functionalization¹. However, it is still challenging to functionalize the hosts partially and selectively because of their isolated, multiple active sites. In this work, we succeeded in the selective functionalization of calix[4]arenes through conformational fixation in a self-assembled hollow cage^{2,3}.

Calix[4]arene variants **2a**, **b** were encapsulated in cage **1** by stirring in an aqueous solution of cage **1** and heating for hours. ¹H NMR and SC-XRD analysis revealed that the conformation of **2** was fixed in the cage cavity. When inclusion complex **1•2a** was subjected to a reaction with *N*-bromosuccinimide (NBS), selective bromination at one active site that is sticking out of the portal of the cage, out of the four active sites on the aromatic rings of **2a**, was proceeded as revealed by ¹H NMR, ESI-MS and SC-XRD analysis. Heating an aqueous solution of **1•2b** with trifluoroacetic acid gave mono-hydrolyzed **1•2c** in 86 % yield. We also opened asymmetric functionalization of calix[4]arenes by a combination of multiple reactions in the cage. ¹H NMR and ESI-MS analysis showed oxidation of **1•2c** by iodine and following bromination by NBS resulted in selective production of asymmetric calix[4]arene **2d**.

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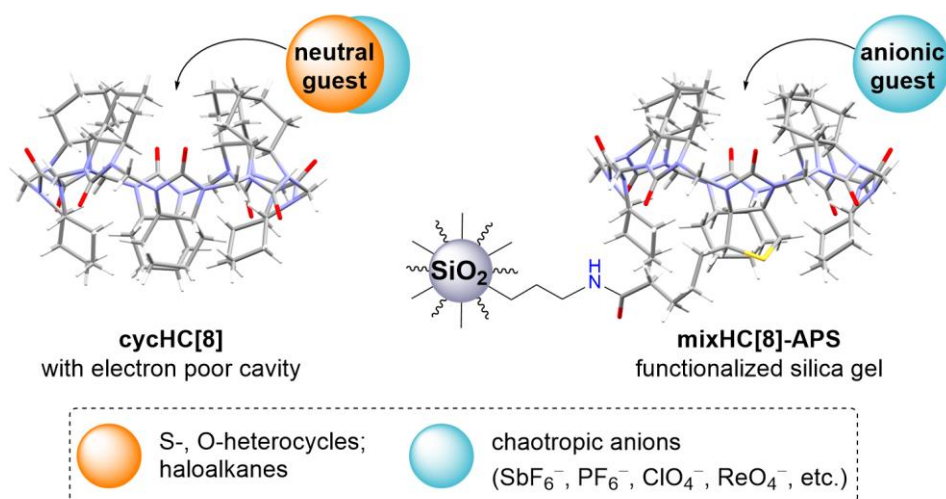
Abstract No: M37

M37 Cyclohexanohemicucurbit[8]urils as Receptors for Electron-Rich Guests

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Caption: Figure 1. Cyclohexanohemicucurbit[8]urils suitable for encapsulation of electron-rich guests

Cyclohexanohemicucurbit[*n*]urils are chiral macrocyclic molecular containers with a well-defined electron-deficient cavity suitable for accommodation of different electron-rich guests.^{1–3} Both the homomeric cyclohexanohemicucurbit[8]uril (cycHC[8])⁴ and the new mono-biotinylated cyclohexanohemicucurbit[8]uril (mixHC[8]) are formed via templated mechanochemically-assisted self-assembly and can be applied in various host-guest interactions. The current work describes: a) the use of cycHC[8] as a cavitand for encapsulation of small neutral organic molecules, including environmental pollutants; b) anion binding properties of mixHC[8] (Figure 1). Complexation studies in solution by ¹H NMR and ITC proved that cycHC[8] forms inclusion complexes with hydrophobic S- and O-containing neutral heterocycles, as well as small haloalkanes, in methanol and methanol-water media, showing stronger binding in more polar system. Since the macrocycle is not soluble in water, it was further utilized for solid-state extraction of the neutral guests from aqueous solutions.³ The anion binding properties of the new mixHC[8] were investigated by mass spectrometry in gas phase and ITC in solution, revealing high affinity towards chaotropic anions. Covalent immobilization of mixHC[8] on the aminated silica affords a functional material that can be employed in selective removal of anionic guests.

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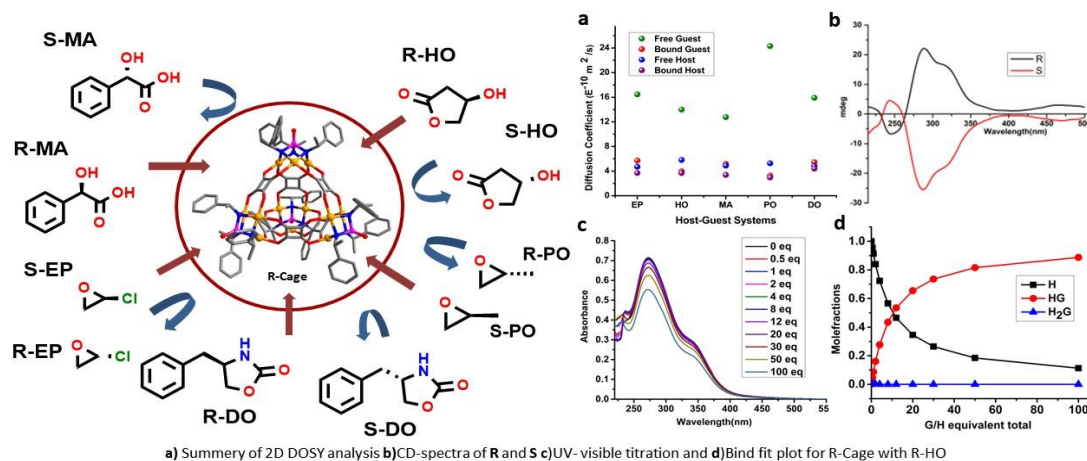
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Flash Talks / 26-06-2023 16:40 - 17:00 Harpa - Silfurberg A/B 2nd floor

M38 Unusual Squarate-Tethered Neutral Imido-Pd(II) Cages Exhibiting Efficient Enantiomeric Recognition and Separation

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a) Summary of 2D DOSY analysis b) CD-spectra of R and S c) UV- visible titration and d) Bind fit plot for R-Cage with R-HO

Caption: Summary

The metal-organic cages (MOCs) have gained much recognition due to their application in catalyzing reactions, stabilizing molecules by providing a chemically unique and favorable environment inside its pore, chemoselective recognition of various molecules and gas storage, etc.^[1-2]. By introducing chirality into the cage molecules, a more comprehensive range of possibilities was unlocked, as chirality is a fundamental property of molecular systems that plays a central role in various fields ranging from chemical, pharmacological, biological, and materials science^[3-4]. Here, we report an unusual enantiomeric pair of tetrahedral cages of formula $[(Pd_3X^*)_4(C_4O_4)_6]([X^*]^{3-}=RRR\text{or}SSS-[PO(N^*CH(CH_3)Ph)_3]^{3-})$ that are constructed from Pd₃-building units supported by tris(imido)phosphate trianions and squarate-acid linkers. These cages were crystallized in chiral cubic-spacegroup F432, with an intrinsic void volume of 289Å³ and a window size of 5.09Å, which is the highest intrinsic cavity volume and portal size amongst all known tetrahedral cages of this family. This results from unusual non-geminal coordination from the squarate linkers to two different Pd atoms, giving rise to a slightly different isomeric structure with respect to the previously reported oxalate and anilate-based tetrahedral cages. These cages exhibit considerable enantioselective recognition capabilities towards a series of small organic guest molecules such as 4-Hydroxydihydrofuran-2(3h)-one, Epichlorohydrin, 4-Benzyl-2-oxazolidinone, Propyleneoxide, and Mandelic acid which was quantitatively determined by UV-Visible titrations. The binding constant values were obtained by Bindfit-tool. The guest bindings were confirmed by ¹H NMR, MALDI-TOF spectroscopy, and ¹H DOSY NMR studies. The highest binding selectivity value of 67 is obtained for the (R)-4-Hydroxydihydrofuran-2(3h)-one. The separation studies suggest a 93% enantiomeric excess is achieved for the (S)-Epichlorohydrin. These results put forward the need to explore the potential of such supra-molecular self-assemblies toward the effective enantiomeric separation of sensitive organic racemates.

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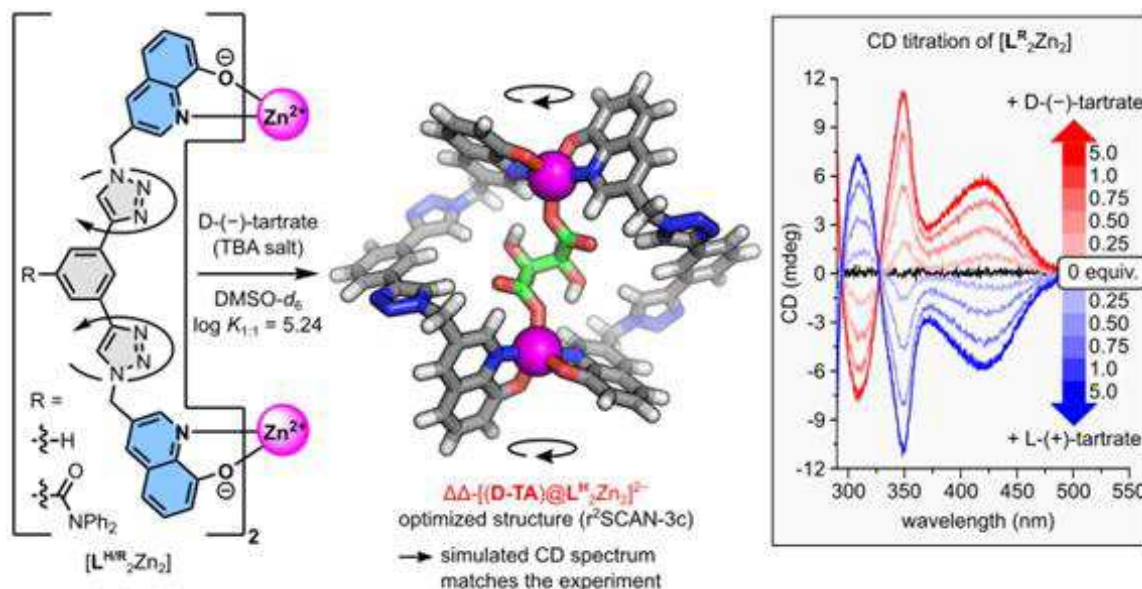
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Abstract No: M39

M39 Chiroptical recognition of anions with neutral L2Zn2 helicates

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Caption: Figure 1: Enrichment of the $\Delta\Delta$ -form upon binding D-(-)-tartrate with the charge-neutral $[L_2Zn_2]$ helicate and chiroptical recognition of D-(-)- and L-(+)-tartrate.

Chirality analysis of small molecules is crucial for determination of their enantiopurity. Current methods utilize streamlined chromatographic techniques with chiral stationary phases. However, chiroptical probes based on host-guest interactions offer an alternative approach, using common spectroscopic techniques like CD spectroscopy to distinguish enantiomers and quantify their ratio.^[1]

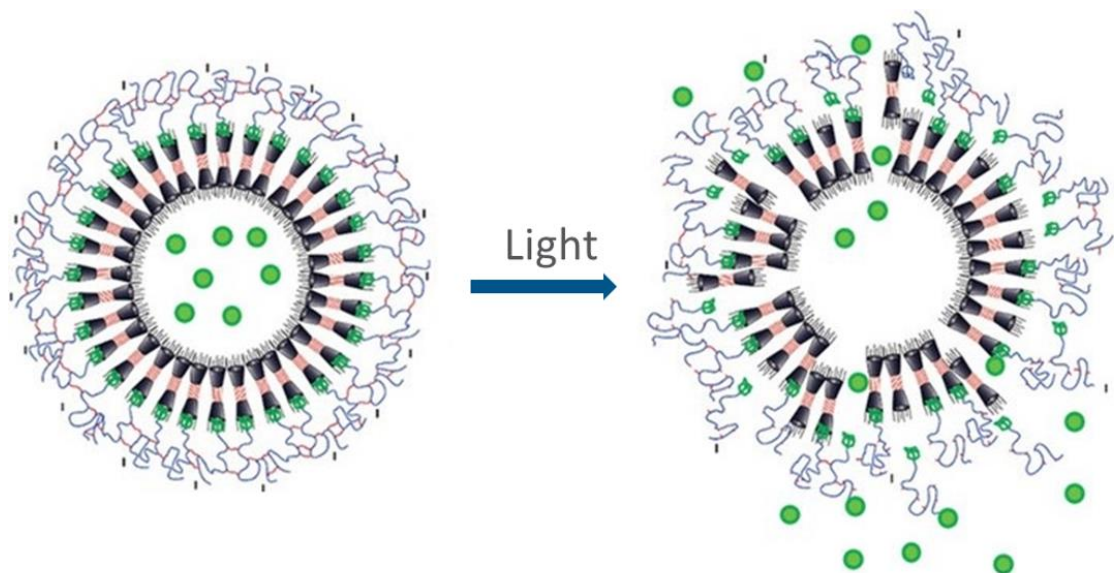
Aiming at this, we explored the potential of charge-neutral double-stranded zinc(II) helicate-based anion receptors, incorporating triazole units that can rotate and give rise to a meso structure or a racemic mixture of the right- and left-handed complex. This receptor was proved to have high binding affinities towards dicarboxylates with association constants ranging up to $10^8 M^{-1}$ in DMSO as shown in previous study.^[2] By utilizing chiroptical responses upon recognition of chiral mono- or dicarboxylates, we conduct chirality analysis of tartrate using CD spectroscopy. Enrichment of one of the enantiomers of the racemic helicate occurs upon chiral guest binding which results in cotton effects.^[3] This receptor-based approach offers high-throughput screening capabilities with minimal waste production and provides an alternative to current methods in chiral analysis.

Abstract No: M40

M40 Self-Assembled Bio-functional Photo-responsive Nanoparticles

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Caption: Figure 1. Schematic representation of payload release upon light irradiation in self-assembled stimuli responsive vesicles

Stimuli responsive systems have emerged as an important strategy to deliver drug in a spatial, temporal and dosage-controlled manner. These systems respond to a specific type of stimuli such as redox, enzyme, pH, heat, light and other exogenous and endogenous stimuli as well. These stimuli have been studied in various systems such as micelles, dendrimers, liposomes and vesicles. [1]

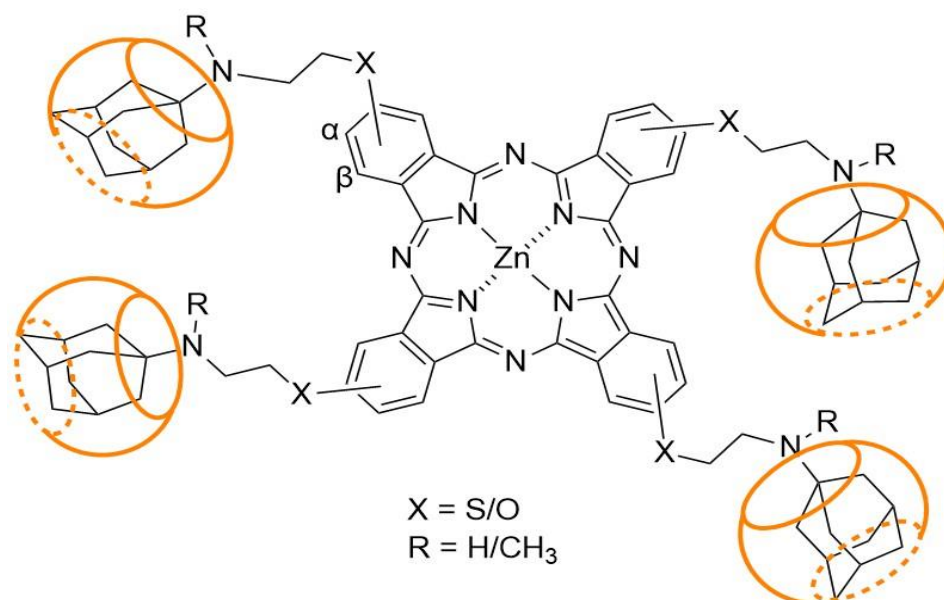
In this work, the focus lies on self-assembling system of vesicles that have cyclodextrin-adamantane host guest chemistry at the core. It has linker motif that is responsive to light and it also provides a robust, more controllable and targeted delivery. This modified cyclodextrin assembly has been designed with the vision to meet the challenges that have been faced by drug delivery systems such as biocompatibility, controllable payload release, minimal toxicity and is also compatible for effortless diffusion into cellular systems. [2]

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Abstract No: M41

M41 Improving Monomerization of Phthalocyanines via Their Supramolecular Interactions with Cucurbiturils

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Phthalocyanines (Pc) are macrocyclic compounds structurally related to porphyrins, which are used e.g. as dyes, pigments, quenchers, fluorophores or photosensitizers in photodynamic therapy. Pc have planar structure and because of π - π interactions they form aggregates in water environment and therefore lose their desired photodynamic activity. Based on formation of a supramolecular complex with cucurbiturils (CB), we can potentially improve solubility and decrease aggregation of Pcs in water. CB macromolecules composed of methylene bridged glycoluril oligomers.¹ They have hydrophobic cavity and hydrophilic portals where they can bind appropriate guest molecules. In this project, we used one of the strongest reported supramolecular interactions between CB[7] and 1-aminoadamantane² as peripheral or non-peripheral substituent on the Pc ring.

Five zinc Pcs, α peripherally or β non-peripherally substituted with aminoadamantane, with oxygen or sulphur as connecting heteroatom were prepared. Their absorption and fluorescence spectra were studied and they showed substantially improved (but not complete) monomerization in water after addition of four equivalents of CB[7].³ This ratio confirms previously obtained crystallographic structure and computer model of phthalonitrile precursor, where one molecule of aminoadamantane is complexed by one molecule of CB[7]. Biological tests on HeLa cells did not show higher photodynamic activity of Pc-CB[7] complex even though higher monomerization should also result in higher activity. It was probably due to low cell uptake because of highly hydrophilic Pc-CB[7] complex.

This work was supported by SVV 260 547 and Czech Science Foundation (20-09212S).

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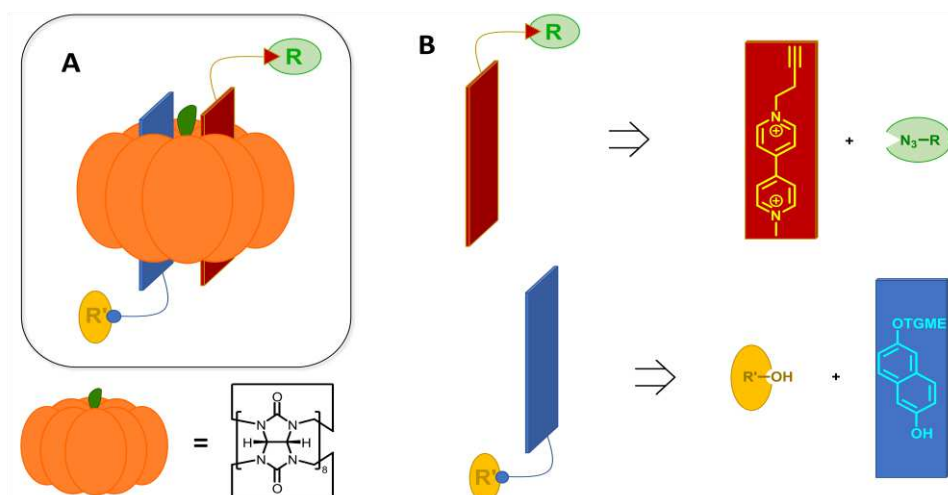
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Abstract No: M42

M42 Synthesis of Versatile Building Blocks for CB[8] Facilitated Heteroternary Complexes

Jana Lapesova Petr Zimcik

Charles University, Faculty Of Pharmacy in Hradec Kralove, Hradec Kralove, Czech Republic



Caption: Figure 1. Schematic representation of a heteroternary complex (A), and general structures of the presented guest derivatives (B).

Cucurbit[*n*]urils, CB[*n*], are widely used water soluble macrocyclic hosts. They can bind various types of guests (metallocene derivatives, adamantane derivatives, pyridinium derivatives); however, their prototypical guests are endowed with amino or ammonium substituents.^{1,2} Interestingly, the size of CB[8] cavity allows binding of two same or different guests at the same time. Therefore, ternary complexes with CB[8] can be formed by encapsulating homodimers or heterodimers of guests with corresponding electronic and/or steric properties. For a successful formation of a heteroternary complex (Figure 1A), an electron deficient and electron rich structure motives are required.³ As the first-mentioned, a diammonium cation can be used. A very common moiety used for this purpose is a viologen cation. In our case, we decided to alkylate bipyridyl with methyl on one nitrogen atom and homopropargyl on the other (Figure 1B), so it can later be used for a click reaction with azide. Subsequently, derivatives of 2,6-naphthalenediol can be used as electron rich guest. One of the 2,6-naphthalenediol hydroxyls was alkylated with triethylglycolmonomethylether (TGME) to improve water-solubility (Figure 1B). Another one can be used for modifications *via* Mitsunobu reaction. The synthesis of versatile precursors for both the described CB[8] guests will be presented, as well as the first supramolecular studies testing their ability to form ternary complexes.

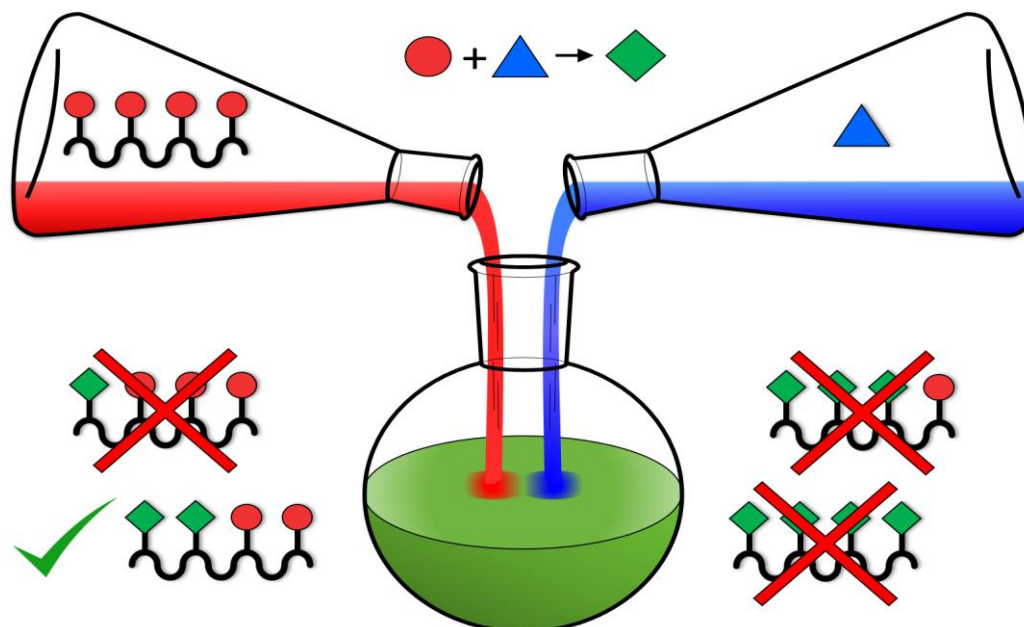
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M43 Iteroselectivity: how to control the number of repeated reactions

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Caption: Figure 1. Illustration of an iterative reaction where a single iteromer is formed iteroselectively.

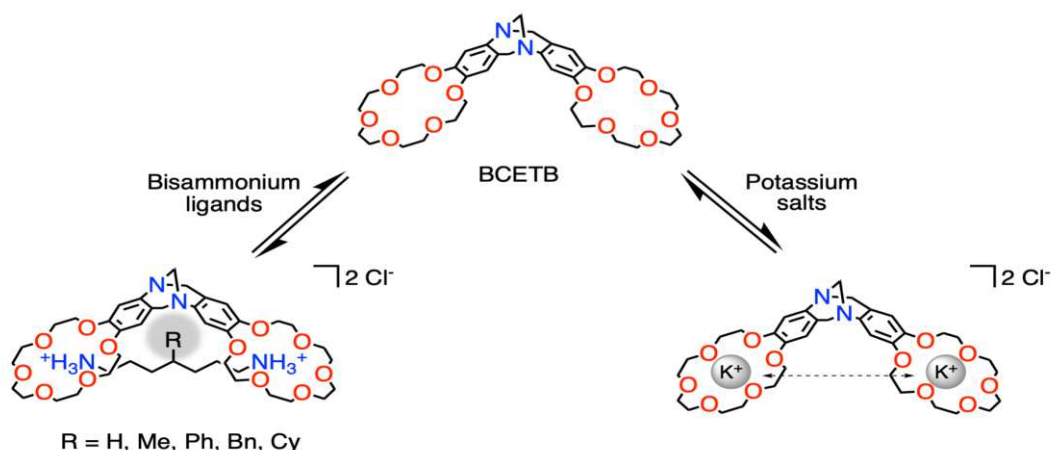
Our ability to synthesize organic molecules efficiently often revolves around selective reactions. The most commonly studied selectivities are the chemo-, stereo-, and regioselectivities. These selectivities are, however, not sufficient to describe all selective chemical transformations. For instance, when a substrate can undergo the same reaction repeatedly (Figure 1), a new kind of selectivity is needed to obtain one product preferentially. In this context, we conceptualized the “iteroselectivity” that governs the number of repeating chemical transformations that occur on substrates that can undergo at least twice the same reaction.¹ Such an iterative process applies to polyfunctional substrates bearing the same type of functional group (e.g. ethylene glycol, sugars, oligomeric macrocycles), and to reactions where the reactive functional group is regenerated (e.g. polymerizations). The different products after each iteration are named iteromers. To achieve high iteroselectivity, it may be necessary to tune the reactivity of the functional groups in a controllable manner. Supramolecular chemistry is a toolbox offering numerous options to modify the reactivity of functional groups by changing their local environment without direct modification of the functional groups in contrast to classical covalent protecting groups. In this communication, we explore examples from the literature of iteroselective reactions based on supramolecular protection, supramolecular activation, and templating effects.

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Abstract No: M44

M44 Studying non-covalent interactions using a small synthetic receptor

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Caption: Binding of bisammonium ligands (left) and potassium ions (right) to a bis(18-crown-6) Tröger's base receptor (BCETB).

Receptors capable of receiving and transducing chemical signals are crucial for a number of essential biochemical processes. These receptors, located inside or on the surface of cells, work by binding external ligands, which in turn activates different physiological functions. The interactions between the receptor and the ligand are governed by intermolecular forces such as hydrogen bonding, hydrophobic and ion-ion interactions, and van der Waals forces. In order to study and better understand the fundamental thermodynamic factors governing these interactions, the development of synthetic receptors and model systems are of high interest.

We have developed a synthetic receptor consisting of a Tröger's base motif with 18-crown-6 moieties fused to each end of the aromatic cavity (BCETB). Crown-ethers are known to complex efficiently with cations such as primary ammonium ions and potassium ions, and the V-shaped Tröger's base affords a well-defined hydrophobic cavity. We have used this synthetic receptor to study different intermolecular interactions, including interactions between different non-polar substituents and the aromatic cavity,¹ and the interaction between cations bound to the crown-ether moieties.² By combining experimental and computational methods, we have been able to estimate binding energies, study conformational changes and rationalize observed trends.

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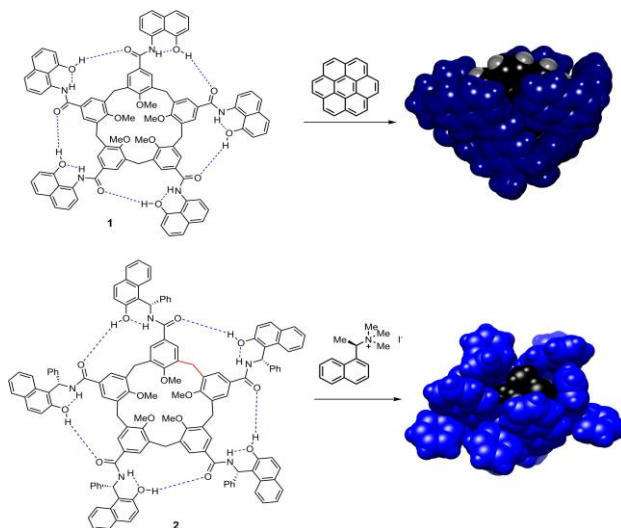
Abstract No: M45

M45 Self-folding cavitands of increased dimensions and flexibility. Applications in selective molecular recognition.

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Self-folding cavitands are synthetic receptors that fold into hydrophobic concavities with the assistance of bio-inspired hydrogen bond networks. They are promising systems for the isolation of reactive intermediates and for the development of supramolecular catalysis, among other applications.^[1] These hosts have traditionally been built-up from resorcin[4]arenes, resulting in highly symmetrical cylindrical cavities of reduced dimensions. Their binding spaces are relatively rigid, limiting the emergence of genuine induced fit behavior as observed in proteinogenic receptors. Altogether, these features limit the development of truly bio-inspired molecular recognition phenomena.

We present a new family of self-folding cavitand receptors based on calix[5]arene that display heightened dimensions and flexibility (**1** and **2**).^{[2][3]} These receptors are stabilized in cone-like conformers by cooperative hydrogen bond networks akin to those operating in resorcin[4]arene congeners, but benefit from the increased flexibility of the calix[5]arene scaffold thanks to a lower degree of covalent restriction. Despite this higher flexibility, the calix[5]arene-derived cavitands display bowl inversion barriers comparable to those of the more rigid resorcin[4]arene derivatives. Molecular dynamics simulations corroborate the higher flexibility of the new hosts and the emergence of superior induced fit behavior. The cavitands' structures fluctuate among different irregular conformers, adapting to the shape of the bound guests without disruption of the stabilizing hydrogen bond seams.

Different shapes can be accessed by varying the structure of the upper panels of the receptor. Cavitand **1**, featuring 1,8-amidonaphthol panels, favors flattened conformations that are ideal for the molecular recognition of large Polycyclic Aromatic Hydrocarbons (PAH).^[2] In particular, **1** is a selective host for the binding of coronene over smaller PAHs. Cavitand **2** features 1-(amidomethyl)-2-naphthol panels and adopts more spherical shapes.^[3] The central chirality of the panels favors the unidirectional arrangement of the hydrogen bond seam, relaying the chiral information onto the macrocyclic structure of the host. As a result, a chiral and highly adaptable binding space is obtained, which provides unprecedented levels of enantioselective molecular recognition with a series of chiral quaternary ammonium salts (K_R/K_S ratios up to 18.7:1).

Overall, a new promising and versatile platform for self-folding cavitands has been developed, offering good prospects for applications in sensing and catalysis thanks to superior induced fit properties.

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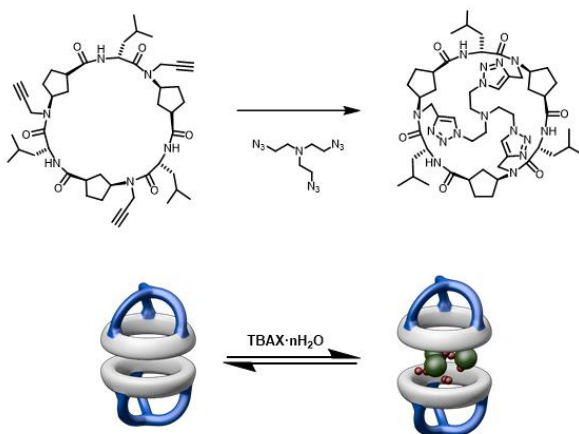
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Abstract No: M46

M46 ANION-SENSITIVE SUPRAMOLECULAR PEPTIDIC CAPSULES

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Since the anion complexation processes started to be studied in the late nineties,¹ this topic has been receiving the attention of researchers due to the huge amount of recognition pathways and applications. In fact, a multitude of biological issues are directly affected by the lack or excess of specific anions, such as the cystic fibrosis.²

Even though the anion recognition has been addressed from different areas in chemistry,³ here we propose a supramolecular approach that has allow us to create a proper environment for the detection of several anions.

Regarding this supramolecular view, the group of the professor Granja is focused in the study of cyclic peptides, their properties and applications.⁴ In this work, a cyclic hexapeptide has been the elementary building block on wich we have create a capsule that responds to the presence of anions. More specifically, our capsule hosts clusters formed between some anions and water molecules. In the presence of halides and some others, the dimeric structure of the host is disrupted and completely distorted in order to accommodate, as far as we know, three anion units, surrounded by water molecules.

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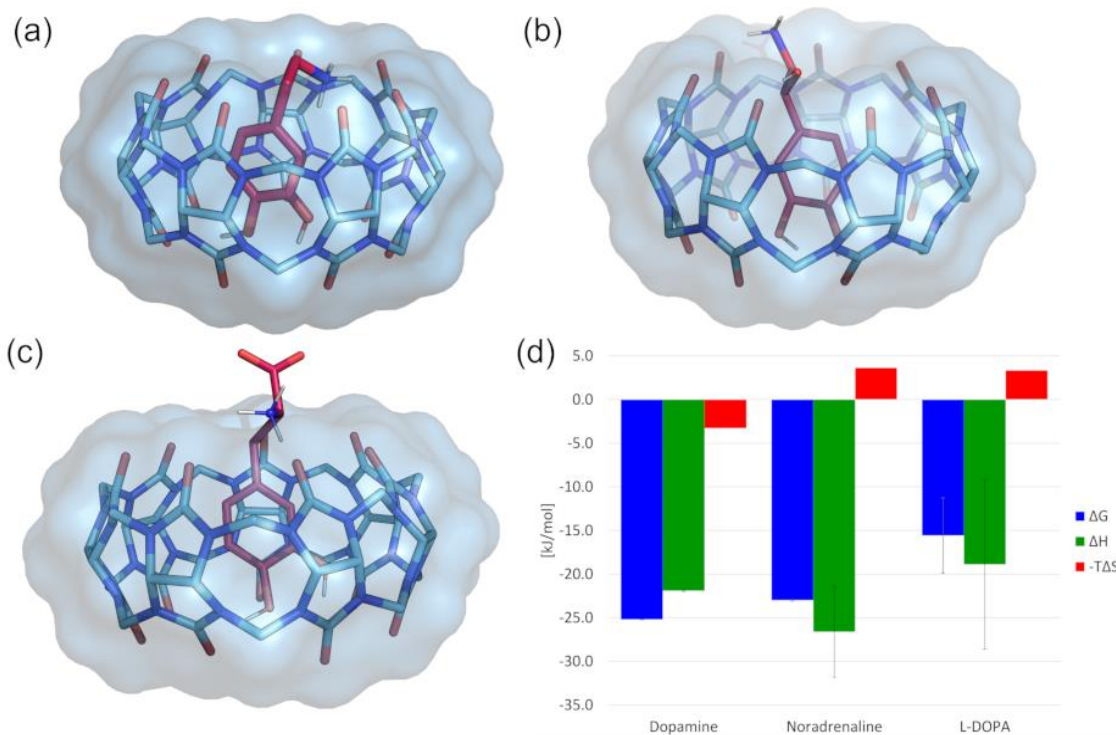
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Abstract No: M47

M47 Unlocking the Secrets of Molecular Recognition in Aqueous Solutions: A Study on the Properties of Cucurbit[7]uril and Neurotransmitters/Amino Acids Complexes

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Caption: CB[7] complexes with dopamine (a), L-noradrenaline (b), and L-DOPA (c). Thermodynamic parameters of CB[7] binding (d).

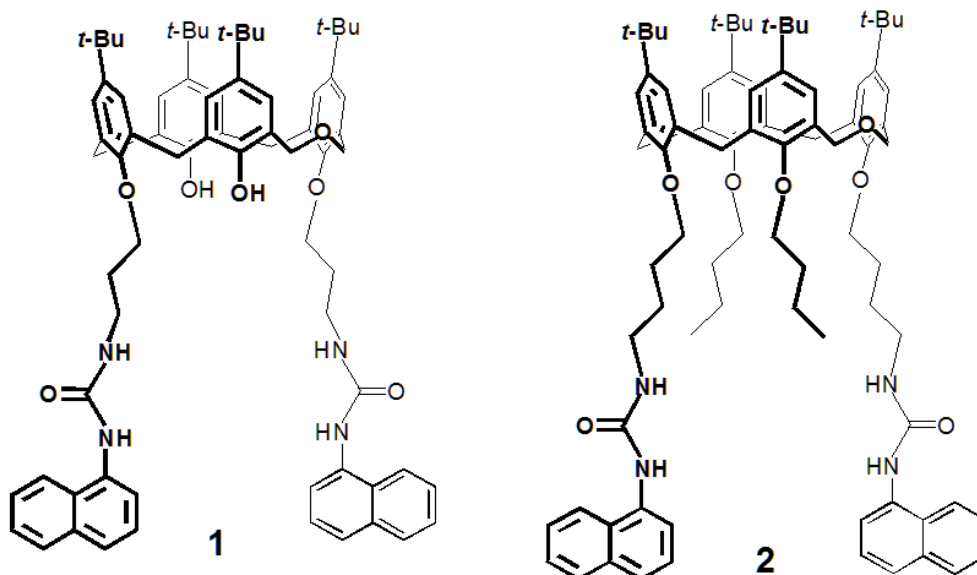
Studies of molecular recognition in water using model macrocyclic systems derived key findings on the remarkable properties exhibited by proteins: high binding affinity, superior binding selectivity, and extreme catalytic performance. A better understanding of the governing factors of molecular recognition will lead to more accurate predictions of protein-ligand binding affinity, which can reduce the cost of drug discovery in structure-based drug design. The study examines the intermolecular forces involved in the reversible binding of ligands, as well as the hydrophobic and Hofmeister effects in aqueous solution between the macrocyclic host molecule cucurbit[7]uril (CB[7]) and amino acids (AAs) or neurotransmitters (NRs) to understand the source of CB[7]'s high selectivity. NRs are generally synthesized in neurons and are made up of, or derived from, precursor molecules that are found abundantly in the cell e.g. amino acids, monoamines, and peptides. The formation of nine complexes between CB[7] and each neurotransmitter or amino acid was examined in solution by isothermal titration calorimetry, and the results were further combined with computational investigations and X-ray diffraction studies. Generally, the NRs show higher binding affinities than the precursor AAs in buffer solutions with various pH values. However, the gas-phase interaction energies between host and guest show a negative correlation to binding affinities, suggesting that the role of non-covalent interactions between the polar side chains is diminished in the presence of water. In contrast, the transfer of the hydrophobic groups from the bulk into the hydrophobic CB[7] cavity suffers less from the desolvation penalty, resulting in higher binding affinities in water. Therefore, initial guest solvation is another key factor that should be prioritized over the optimization of strong electrostatic interaction e.g. hydrogen bonds during ligand and drug design.

Abstract No: M48

M48 Fluorescent Dihomooxalix[4]arene-based Receptors for the Recognition of Relevant Anions and Organic Ion Pairs

Alexandre Miranda, José Ascenso, Mário Berberan-Santos

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Anion recognition by receptors based on calixarenes continues to attract much attention. Anions play essential roles in biological systems, as well as in environmental and industrial processes.¹ The incorporation of urea units has been intensively studied since those receptors use NH groups as H-bond donors to interact with the anions. Calixarenes having optical sensing ability for different types of analytes have been developed, and fluorescence spectroscopy has been increasingly used for ion detection, owing to its simplicity and high sensitivity.² Heteroditopic receptors, molecules capable of simultaneously bind both ions of a given pair, have been obtained and are an emerging area in supramolecular chemistry.

Following our previous studies on anion binding and organic ion pair recognition by (thio)ureido-homooxalixarene receptors,³⁻⁵ we have extended our research to fluorescent dihomooxalix[4]arenes.

This work reports the anion and organic ion pair recognition by two dihomooxalix[4]arene di-substituted receptors bearing naphthyl urea groups on the lower rim via a propyl (**1**) or a butyl (**2**) spacer. The binding properties of these compounds were evaluated by proton NMR, UV-Vis absorption and steady-state fluorescence studies.

Authors thank Fundação para a Ciência e a Tecnologia, Project UIDB/00100/2020 and A. S. Miranda thanks a PhD Grant, ref. SFRH/BD/129323/2017.

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Abstract No: M49

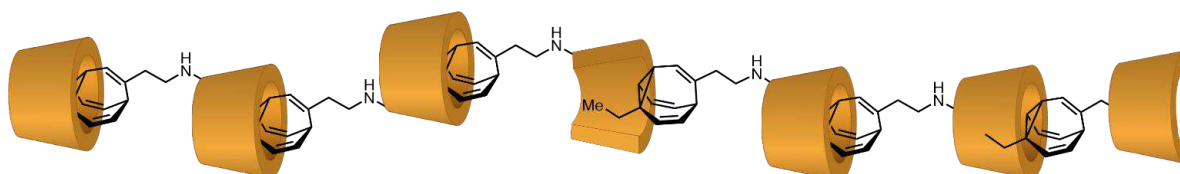
M49 Noncovalent Control of Bullvalene Isomerism

Will Maturi ¹ Yulong Son ², Paul McGonigal ³

¹ University of Durham, University of York, York, United Kingdom

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Caption: Bullvalene-Cyclodextrin Self Assembled Structure

Bullvalene is a fluxional molecule which can undergo cope rearrangements to occupy any one of up to 1,209,600 isomers degenerate isomers.¹ When substituents are present some isomers become non-degenerate and may occupy different volumes and have unique shapes which gives rise to different isomer populations. Bullvalene has previously exhibited the ability to alter its isomer distribution in the presence of certain guests, acting as part of a supramolecular host with its substituents.^{2,3} This poster will describe attempts at using a substituted bullvalene as a supramolecular guest to exhibit control over its isomer distribution. Firstly, synthesis of a heterodisubstituted bullvalene is detailed, which imparts the molecule with more enantiomer pairs than a homodisubstituted bullvalene. Next, the bullvalene is attached to the β -cyclodextrin. Attempts at crystallisation of a self-assembled structure are described. Heterodisubstituted bullvalenes can occupy any one of eighteen enantiomeric isomers or twelve achiral isomers. When in the chiral binding environment of a cyclodextrin host, we expect that the bullvalene will show a preference for one of these isomers, i.e., not just through a bias towards one regioisomer, but also towards a single fluxional stereoisomer.⁴

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Poster Session I, Venue: Harpa - Flóí 1st floor, 26-06-2023 17:00 - 19:00

Abstract No: M50

POSTER
WITHDRAWN

Abstract No: M51

M51 Building Supramolecular Architectures from Sequence-Specific Peptides

Charlie McTernan

The Francis Crick Institute and King's College London, London, United Kingdom

Herein, we discuss recent breakthroughs in our lab, looking at how peptides can be used to build metal-organic assemblies; and how the sequence of the peptide can determine the identity of the structure formed. We discuss the advantages of the approach, in terms of tailoring the self-assembled structures to specific purposes, and also the challenges of working with metal-peptide architectures. We will discuss our initial, unpublished results in the area, and highlight areas of future focus.

Abstract No: M52

M52 Calorimetric Analysis of the Interaction of Endocrine Disrupting Chemicals (EDCs) with Cyclodextrins

Margaret (Maggie) Meadows ¹ Alexa Richardson ², Oneeka Kohli ²

¹ Mercer University, Macon GA, United States

² , ,

Endocrine disrupting chemicals (EDCs) are persistent in the environment, food, and consumer products; these chemicals have been implicated in hormone function interference, abnormal reproduction, and an increased risk of cancer. The binding and subsequent removal of EDCs from aqueous media is therefore of interest to both the chemistry and medical communities. Although the mode of action for each individual EDC has not been fully elucidated, many EDCs are believed to act as xenoestrogens, or estrogen mimics, and bind to steroid hormone receptors. Cyclodextrins (CDs) have been reported to bind steroids including estrogen and to bind one of the most common EDCs, bisphenol A (BPA). We investigated the host-guest interaction of β - and γ -CDs with a range of suspected xenoestrogens via isothermal titration calorimetry (ITC) in aqueous solution. We found the binding of EDCs varied widely among the suspected xenoestrogens, with the largest binding constant that of BPA with β -CD. Several EDCs exhibited much lower binding ($K_a < 1 \times 10^3$) which suggests that these EDCs are less likely to adopt an estrogen-like conformation in aqueous solution. Currently we are investigating the use of dissociative titrations to examine these weaker binding interactions.

Abstract No: M53

M53 Benzene triimide hemicryptophanes for synergistic anion- π and cation- π interactions.

Louise Miton Yoann Cotelte, Alexandre Martinez

ISM2, Marseille, France

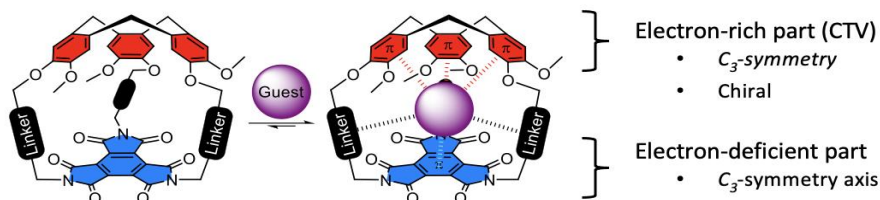


Figure 1: Host guest equilibrium and the possible interactions between the host and the guest.

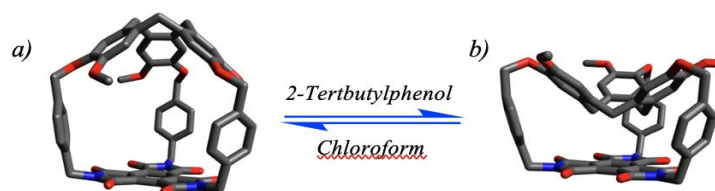


Figure 2: Molecular modeling in gas phase (PBE0-D3/def2-TZVP) of the two conformations of the para-cage: a) usual crown conformation, b) fully imploded crown conformation. ($\Delta E_{a-b} = 53,4$ KJ/mol in gaz phase)

Caption: Figure 1: Host guest equilibrium and the possible interactions between the host and the guest. Figure 2: Conformational Exchange.

Noncovalent interactions involving aromatic rings play a key role in many processes of molecular recognition. Among them, pi-pi and cation-pi interactions are known to be important bonding forces in biological systems. Furthermore, these interactions are also observed in many supramolecular assemblies with artificial hosts. On the contrary, anion-pi interactions, which can be broadly defined as the attraction of anions to electron deficient pi-systems, have been recognized theoretically only since the beginning of this century.¹ The vital role of anions in many key chemical and biological processes, and the involvement of pi-rings in molecular anion recognition and transport, indicate that anion-pi contacts could be prominent players in medicinal and environmental applications.²

Molecular cages are attracting considerable attention in modern supramolecular chemistry due to their possible applications in molecular recognition, catalysis, drug delivery, biosensing, separation and storage. Hemicryptophanes are heteroditopic host compounds built from a cyclotrimeratrylene (CTV) unit with another C₃-symmetrical moiety. They are able to recognize various charged or neutral guests, such as ion pairs, zwitterions, ammoniums, carbohydrates and fullerenes.³

We have developed a series of chiral molecular cages based on electron-deficient units in order to encapsulate anionic species. A drastic modulation of the recognition properties was achieved demonstrating the selectivity of our systems.

The synthesis of hemicryptophanes, their special conformational isomerism with a switch of chirality and the study of their molecular recognition properties will be highlighted.

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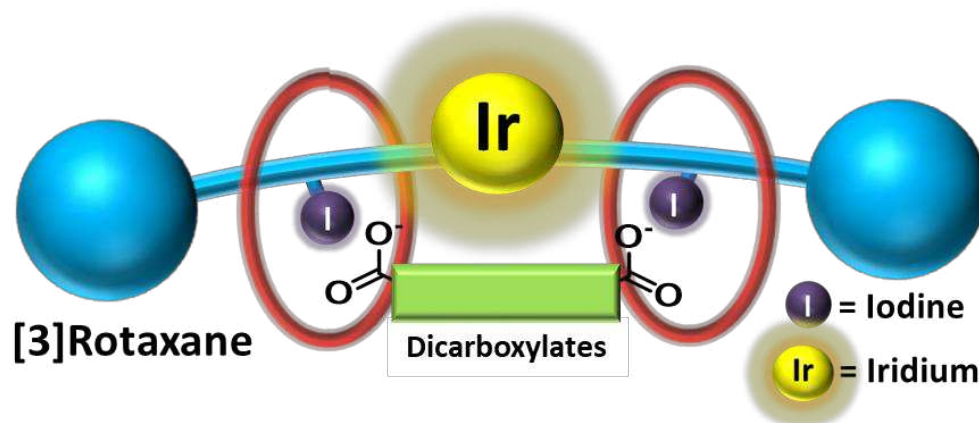
Abstract No: M54

M54 A transition metal-based halogen bonding [3]rotaxane for strong and selective dicarboxylate anion recognition and sensing

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² University of Oxford, Oxford, United Kingdom



Caption: Schematic representation of the dicarboxylate bound Ir(III) XB [3]rotaxane

Halogen bonding (XB) interactions have gained increased attention in the field of anion recognition which has been stimulated by XB host systems displaying unique anion selectivity trends and superior binding affinities over analogous hydrogen bonding (HB) hosts.¹ Complexing luminescent transition metals proximal to XB donors enables optical sensing of anions while further augmenting anion recognition by preorganising and polarising XB donors. Despite these advantages, transition metal-based XB receptors are rare, especially mechanically interlocked transition metal-based XB receptors with only a handful reported to date.²

Utilising the potential ditopic host architecture of a higher order [3]rotaxane structural framework,³ herein we report the first example of a transition metal based XB [3]rotaxane which is capable of recognising and sensing dicarboxylate anions of biological and environmental importance. The novel iridium(III) complexed XB [3]rotaxane exhibited higher luminescence quantum yields and superior dicarboxylate anion recognition and sensing properties compared to an analogous XB [2]rotaxane and simple acyclic host systems, emphasising the importance of the higher order mechanical bond effect in strategic XB receptor design for larger anion guest species.

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Abstract No: M55

Flash Talks / 26-06-2023 16:40 - 17:00 Harpa - Silfurberg A/B 2nd floor

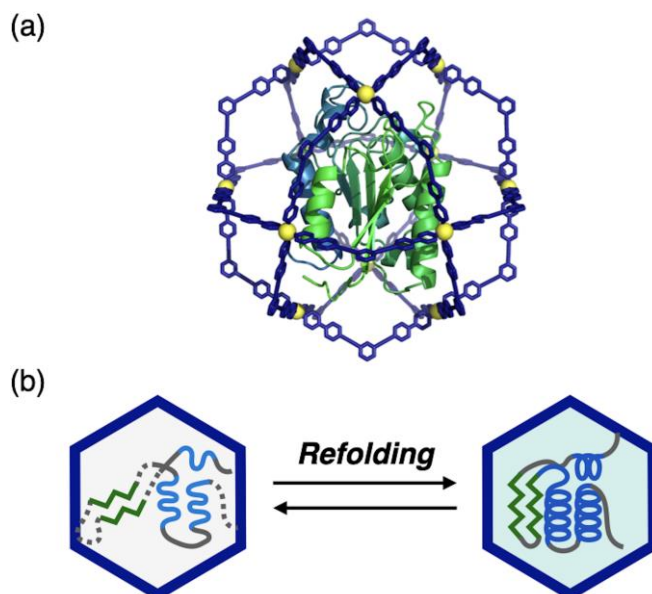
M55 Protein refolding by isolation in a gigantic coordination cage

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² Kyoto University, Kyoto, Japan

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Caption: Figure (a) Protein encapsulated in M12L24 coordination cage. (b) Protein refolding by isolation in the M12L24 cage.

Molecular chaperones, such as chaperonin proteins, assist in the refolding of proteins to their native structure. Encapsulating an unfolded protein in the isolated cavity of a chaperone allows it to regain the original folded structure.

We report here that isolation in a gigantic coordination cage can induce refolding of a denatured protein (Figure).^[1,2] A self-assembled M₁₂L₂₄ cage was used as a synthetic host to confine a protein of interest in its 5 nm cavity. We developed a one-pot encapsulation scheme by the N-terminus selective conjugation with a protein and subsequent coordination with Pd^{II} ions.^[1] It enables us to encapsulate a native protein in an M₁₂L₂₄ cage without changing its tertiary structure. A caged protein, CLE (cutinase-like enzyme) was significantly stabilized against denaturants including organic solvents. In 90% acetonitrile, caged CLE retained enzymatic activity for over 1,000 h, whereas uncaged CLE lost the activity within a few hours (>10³ stability enhancement). NMR analysis of this remarkable stabilization revealed that a denatured protein was refolded in the cavity of the M₁₂L₂₄ cage: caged CLE lost its native tertiary structure by acetonitrile, but the structure was recovered upon exposure to an aqueous solvent in which the enzymatic activity was assayed. In contrast, uncaged CLE rapidly unfolded and irreversibly aggregated to lose its activity. Thus, the spatial isolation in the metallo-cage serves as a molecular chaperone, helping an unstable denatured protein refold back to its native structure.

A more detailed NMR analysis revealed the unfolding and refolding processes of the protein.^[2] By stepwise varying the acetonitrile ratio, the structural changes of CLE in the transition points were clearly visualized. Moreover, we found the hysteresis behavior that implies different pathways in the unfolding and refolding processes. Accordingly, our M₁₂L₂₄ coordination cage can be applied not only to stabilize proteins under denaturing conditions but also to analyze unstable protein structures in bulk solutions by isolation in its cavity.

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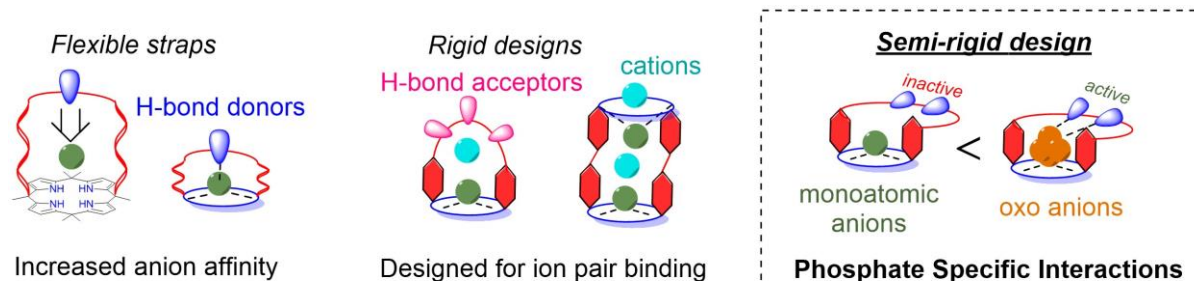
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Abstract No: M56

M56 Design and Synthesis of Phosphate Specific Transmembrane Transporters

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Caption: Calix[4]pyrrole strap designs for anion binding, showcasing the previously reported strategies alongside a novel, volume-specific design for phosphate

To date, no efficient carriers have been reported that can capture the size and geometry of phosphates and transport them through the lipid bilayer. Achieving selectivity for oxyanions over more simple spherical anions (e.g. chloride, fluoride) is yet a challenging task. Because of the strong hydration energies (which makes extraction from the aqueous phase into the apolar interior of the lipid bilayer more difficult), the speciation of organic phosphates (RHPO_4^- and RPO_4^{2-}), and multiple negative charges of organic polyphosphates (e.g. triphosphate $\text{RH}_2\text{P}_3\text{O}_{10}^{2-}$, $\text{RHP}_3\text{O}_{10}^{3-}$) extraction and transport of phosphorylated compounds are particularly difficult.

The key to transporting and extracting such highly hydrated anions is the formation of multiple H-bonds to the anion.¹ With the rapid expansion of the synthetic transmembrane transporters field over the past few decades,² "strapped" calix[4]pyrroles developed by the Sessler and Gale laboratories have emerged as carrier systems with excellent transmembrane transport properties.³ The presence of additional cooperative binding sites on the straps enhances preorganization and substrate affinity, resulting in what may be termed a "strap effect".⁴

We envisage that by controlling the rigidity of the multiple H-bond donor strap component, we will be able to construct phosphate-specific supramolecular structures based on calix[4]pyrroles. Thus, here we introduce a "semi-rigid" design that consists of two separate ion binding sites fixed at the desirable distance for more favourable binding of oxoanions (such as phosphate) over the monoatomic anions (like chloride). We have synthesized a semi-rigid strap system showing the cooperative binding of phosphate. Volume-specific sites with multivalent interactions facilitate the extraction of strongly hydrated H_2PO_4^- into the lipid bilayer enabling the cohesive transfer of the anion through the membrane by shielding its charges from the lipophilic bilayer interior.

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Abstract No: M57

M57 Flexibility drives oxalate recognition with neutral L₂Zn₂ helicates

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Dicarboxylic acids and their corresponding anions are involved in several industry processes and are omnipresent in nature. Many dicarboxylic acids are, for example, intermediates in the biosynthesis of proteins and environmental metabolites.^[1,2] Oxalic acid, the simplest dicarboxylic acid, may cause a multitude of health problems including kidney stones, nephropathy and liver damage.^[3] Thus, research tackling new receptors/sensors for especially oxalate is of great importance.^[4] Recently, our group published the first version of a charge-neutral metal-based self-assembled L₂Zn₂ helicate with the capability of binding dicarboxylates with astonishing binding affinities in competitive media.^[5] Inspired by its size selectivity regarding the dicarboxylate length with naphthalene-2,6-dicarboxylate (log K_{1:1} = 8.16) as aromatic and pimelate (log K_{1:1} = 7.42) as aliphatic analyte being ideal matches for the receptor, the goal of this project is to bind now very short dicarboxylates. By modulation of the planar backbone with rather rigid bond angles to a more flexible backbone based on dipropargylamine, the host-system increases its degree of freedom. In this way the system is capable of binding oxalate. Recently, it has also been found that the host system is able to recognize tetrabutylammonium salts of ibuprofen and naproxen, both of which have carboxylic acid functionality. Overall, the synthesis of the more flexible ligand is easier to handle, as the dipropargylamine is commercially available and it only takes one classic Schotten-Baumann-Reaction for its derivatization and a copper(I) catalyzed alkyne-azide cycloaddition (CuAAC) to connect the backbone with the coordination units based on 8-hydroxyquinolines.

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Abstract No: M58

M58 Size-selective capture and extraordinary storage of halogenated organic compounds by molecular-scale cavities of crystalline pillar[n]quinones

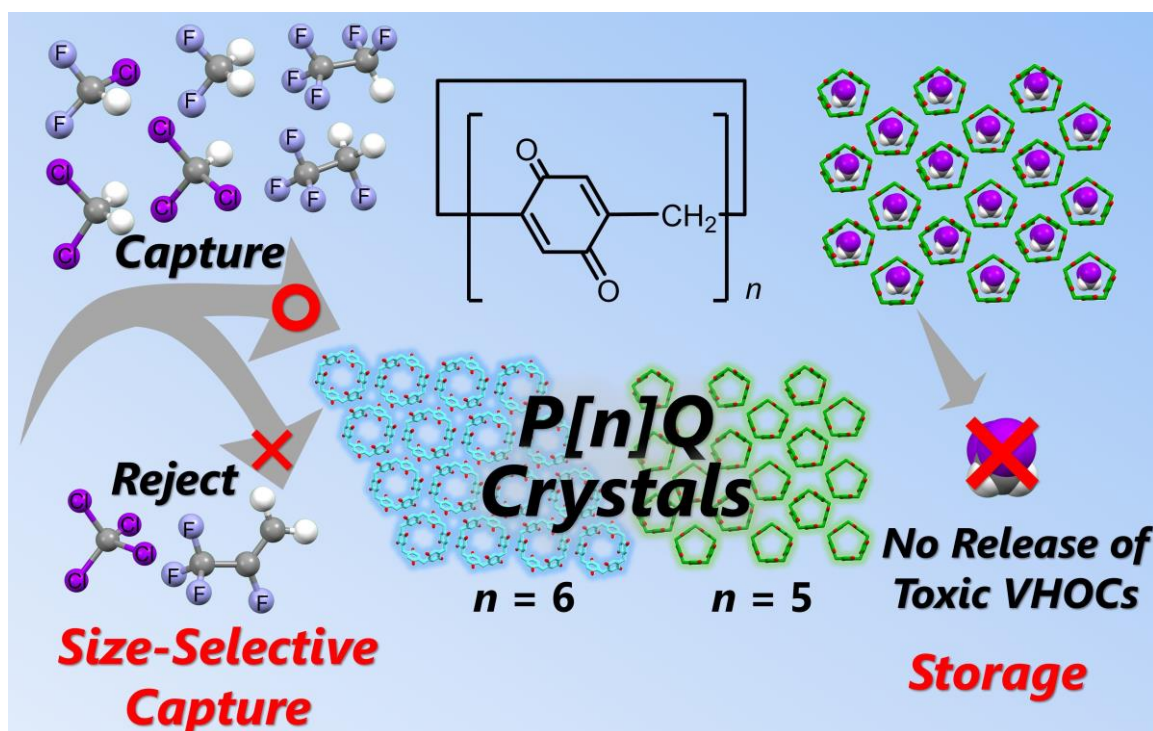
Shunsuke Ohtani ¹ Katsuto Onishi ¹, Keisuke Wada ¹, Tomoki Hirohata ², Shinsuke Inagi ², Jenny Pirillo ³, Yuh Hijikata ³, Motohiro Mizuno ⁴, Kenichi Kato ¹, Tomoki Ogoshi ¹

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⁴ NanoMaRi, Kanazawa University, Kanazawa, Japan



Caption: Figure 1. Schematic representation of the size-selective capture of halogenated compounds in the atmosphere by crystalline P[n]Q.

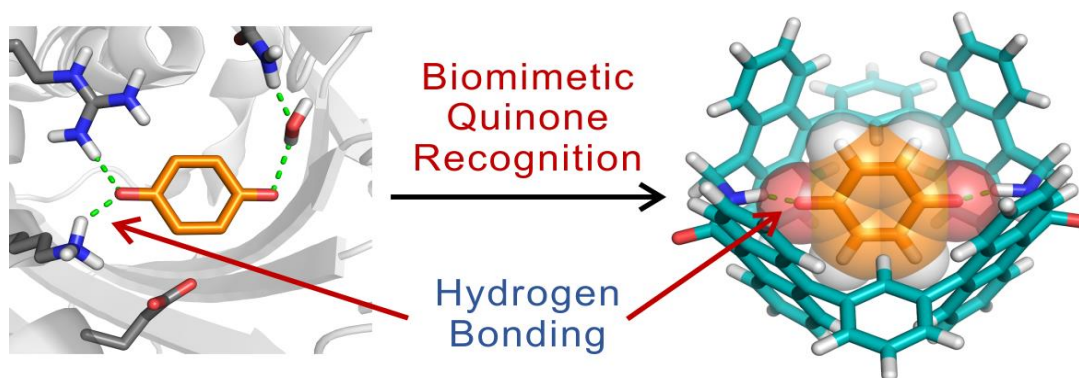
Halogenated organic compounds in the atmosphere are highly toxic and hazardous owing to their damaging effects on the environment and human health.^{1,2} Accordingly, the development of materials that can sequester them from the environment and store them is in great demand. Herein, we report that crystalline pillar[n]quinones (P[n]Q) can selectively capture fluorocarbon gases as well as volatile halogenated organic compound (VHOC) vapors owing to their molecular-scale cavities (Figure 1). Interestingly, the volatilities of VHOCs within the one-dimensional (1D) channels of P[5]Q are drastically reduced compared with those of the bulk VHOC solvents due to the formation of 1:1 host-guest complexation inside the cavities. Further investigation using FTIR, solid-state NMR and computational analyses revealed that the excellent storage abilities of the crystalline P[n]Q are a synergic result of their electron-deficient macrocyclic scaffolds and the basic carbonyl oxygen atoms on their rims.

Abstract No: M59

M59 Amide Anthryltube: A Biomimetic Receptor of Quinones in Water

Xin-Yu Pang

Southern University of Science and Technology, Shenzhen, China



Caption: biomimetic recognition of p-benzoquinone in water.

Selective recognition of organic molecules in water by bioreceptors is the foundation of numerous biological functions.¹ In contrast, this remains a challenge for most of synthetic hosts.² Recently, several biomimetic hosts brought hope by employing hydrogen bonding shielded in a relatively hydrophobic microenvironment.³ However, such biomimetic hosts are rare and general guidance for their design is needed. Herein, we employ the general strategy of “simultaneous construction” for efficient synthesis of biomimetic hosts.⁴ The concept and the strategy were demonstrated in the construction of a biomimetic host with anthracene sidewalls for selective recognition of quinones in water. The host was synthesized by joining two bent anthracene dimers through amide bond formation, affording a deep hydrophobic cavity and inward-directing hydrogen bonding sites simultaneously. The host can selectively recognize quinones over their close analogues in water, and the association constant for *p*-benzoquinone is $3.1 \times 10^4 \text{ M}^{-1}$, which is much better than other synthetic hosts and is comparable to that of the bioreceptor. The binding with anthraquinone even reaches nanomolar affinity ($K_a = 1.5 \times 10^9 \text{ M}^{-1}$). Hydrogen bonding, C-H \cdots π , charge transfer interactions, and the hydrophobic effect were revealed to be responsible for the high binding affinity and selectivity. The concept and the synthetic strategy demonstrated here may be used as one of general guides for biomimetic molecular recognition in water.

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Abstract No: M60

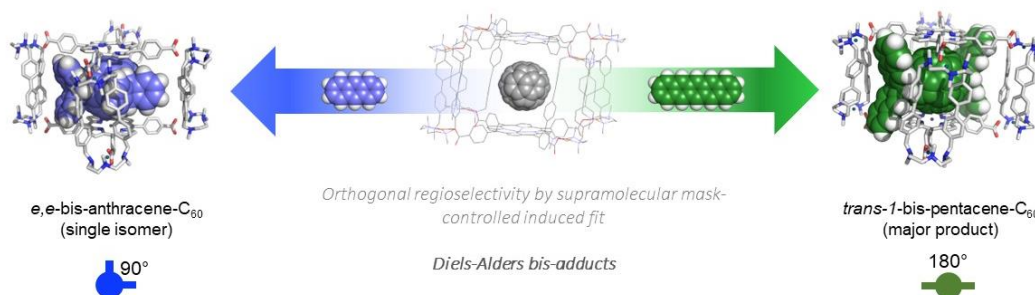
M60 Regioselective access to orthogonal Diels-Alder C₆₀ bis-adducts via supramolecular mask strategy

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Fullerenes are carbon molecules with a spherical-like shape. Their functionalization is not region-controlled and renders mixtures of regioisomers, not amenable for applications.¹ In this regard, only easily accessible mono-functionalized fullerenes are used as electron transport layers in solar cell (SC) devices. Pure regioisomers of poly-adducts are envisioned as an excellent alternative to achieve boosting the efficiency of SC. For this reason, there is a great interest in developing new strategies for synthesizing C₆₀ derivatives with multiple addends in a pure regioisomeric way.

Here, we present a strategy using a tetragonal prismatic supramolecular nanocapsule as a supramolecular mask,^{2,3} that directs the Diels-Alder 4+2 cycloaddition reaction on fullerene C₆₀ towards pure bis-adduct isomers in a tunable fashion. The unprecedented *trans-1* bis-adduct has been obtained in excellent relative yields by using pentacene as the diene of the reaction. In contrast, *equatorial* bis-adduct has been achieved in a regioisomerically pure way using anthracene as the diene.⁴ These differences in regioselectivity have been studied using computational tools, such as Molecular Dynamics simulations and Frontier Molecular Orbitals analysis, to fully understand the behaviour of these host-guest complexes. To gain more insights into the impact of the diene size on the regioselectivity control on the reaction, to promote the formation of the *trans-1* regioisomer over the *equatorial*, a new Diels-Alder mono-adduct has been computationally modelled, using the 2,3,6,7-tetramethylantracene as the acene moiety, which presents an intermediate size between the anthracene and pentacene moieties.

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Abstract No: M61

M61 Towards biocompatible organic cages: water solubility and stability by post-assembly modification

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Abstract

Molecular recognition is ubiquitous in biological processes, and a key factor in plenty technological applications. Molecular cages are a type of discrete synthetic recognition units that possess well-defined inner void spaces where guest molecules can be accommodated.[1] A large variety of these cages have been prepared in recent years by applying molecular self-assembly. Imine condensation has been the most fruitful strategy for the preparation of these types of structures.[2] However, two important disadvantages have difficult the use of these fascinating cages into biological applications, their poor water solubility, and the instability of imine bonds in the presence of water or other nucleophiles, e.g., amine-containing molecules.[3]

In this work, molecular self-assembly and covalent chemistry were combined to overcome the former limitations. Stable covalent containers were obtained after a first step of imine-based self-assembly followed by their reduction. We found that the presence of secondary amino groups generated in the reduction are not sufficient to provide a significant solubility in aqueous solution at neutral pH. Importantly, we found that a second post-assembly modification is an ideal strategy to overcome the former solubility limitations. This strategy is based on taking advantage of the amino groups to bind solubilizing moieties through amide formation. Using this synthetic approach, we found that it is also possible to tune the host-guest properties of the containers.

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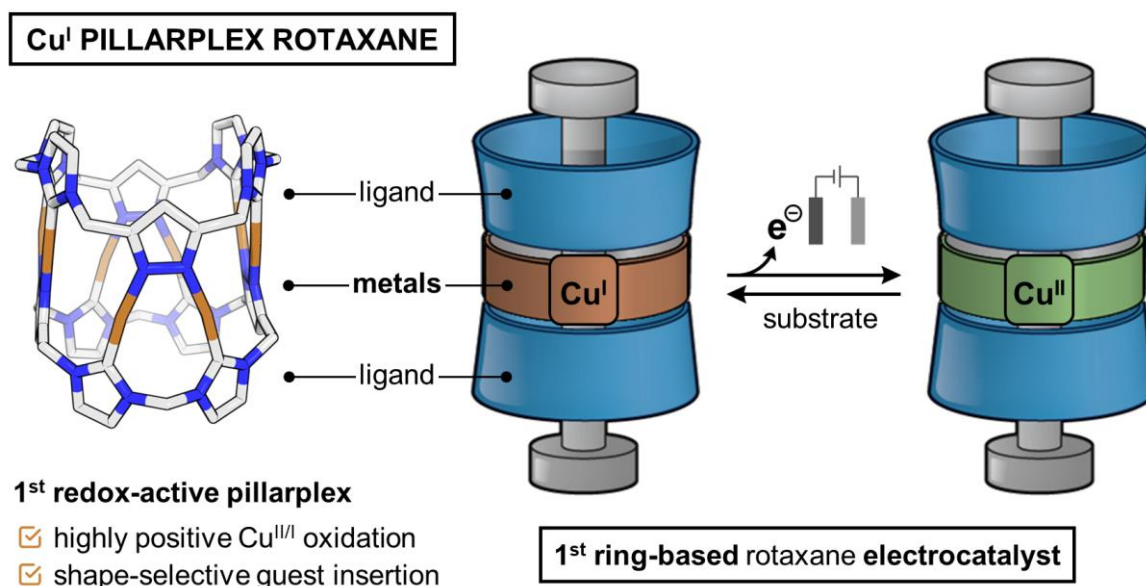
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M62 Copper(I) Pillarplexes as Redox-Active Building Blocks for Rotaxane Electrocatalysts

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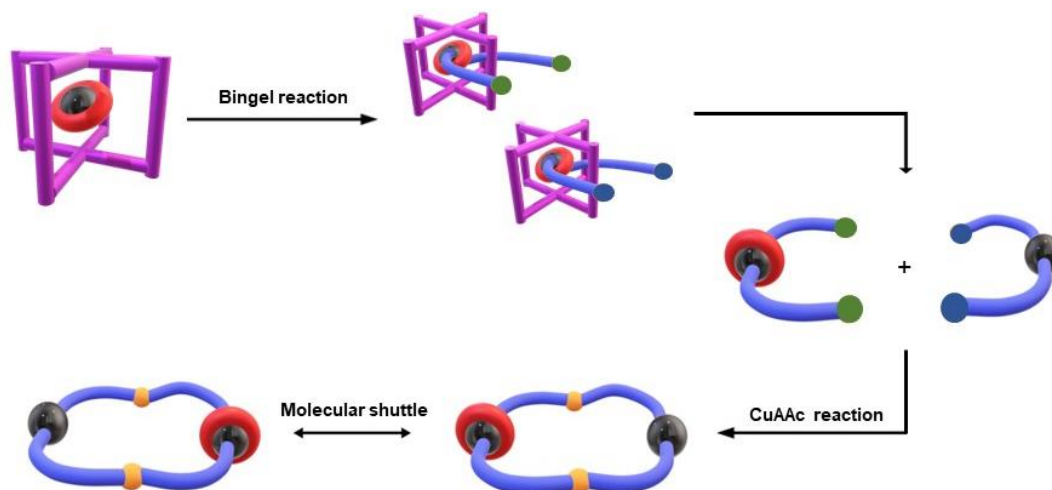
Rotaxanes are functional building blocks for complex molecular machines. Functionality may be introduced in such platforms by redox processes that enable molecular motion, electrochemical sensing, or catalysis. We herein introduce a copper(I)-based metallocavitand as an electrocatalytically active ring component in rotaxanes. This new member of our pillarplex family shows metal-based redox activity while preserving the platform-characteristic affinity for the shape-specific insertion of linear molecules which is essential for rotaxane formation. The redox properties of such a rotaxane were studied by EPR spectro-electrochemistry, revealing an unusually high Cu^{III} oxidation potential (+1.05 V vs. Fc⁺/Fc), caused by the supramolecular arrangement of the macrocyclic ligands coordinating to the Cu^I ions. We exploited this extreme oxidation power for the electrocatalytic oxidation of 3-bromophenol, conceptually demonstrating electrocatalytic activity of the Cu^I rotaxane. Thus, we show that metal ions incorporated in a rotaxane ring component can be strategically used for electrocatalysis, paving the way for complex nanoscale architectures using such redox functionality.

Abstract No: M63

M63 Towards the synthesis of a fullerene-based molecular shuttle using supramolecular nanocapsules

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There is a huge interest to develop new approaches to synthesize fullerene derivatives with multiple addends in a pure regioisomeric way, as poly-functionalization of fullerenes presents a significant lack of regioselectivity. Here, we present the use of a three-shell supramolecular complex which enables the *trans*-3 Bingel bis-cyclopropanation of fullerene C_{60} confined in a 10-cycloparaphenylene ring (10[CPP]) and, at the same time, in a prismatic tetragonal nanocapsule as a single regioisomer.¹ In this work, we have taken advantage of the Bingel type bis-regioselectivity by envisioning the construction of a macrocyclic molecular shuttle featuring two C_{60} units and a 10[CPP]. We have thus designed two different C_{60} bis-adducts – one featuring two terminal alkyne groups and another presenting two terminal azide moieties, which will be macrocyclised by means of Click chemistry, i.e. copper(I)-catalyzed Azide-Alkyne cycloaddition (CuAAC).² The 10[CPP] ring will be left in one counterpart to give rise to an interlocked molecular system of two macrocyclic rings. The excellent affinity between 10[CPP] ring and fullerenes converts this system in a perfect molecular shuttle, in which the aromatic ring can oscillate between both recognition sites (fullerenes) along the thread. The development of new synthetic molecular machines opens a new door towards the transmission of information in a highly controlled manner at the molecular level.

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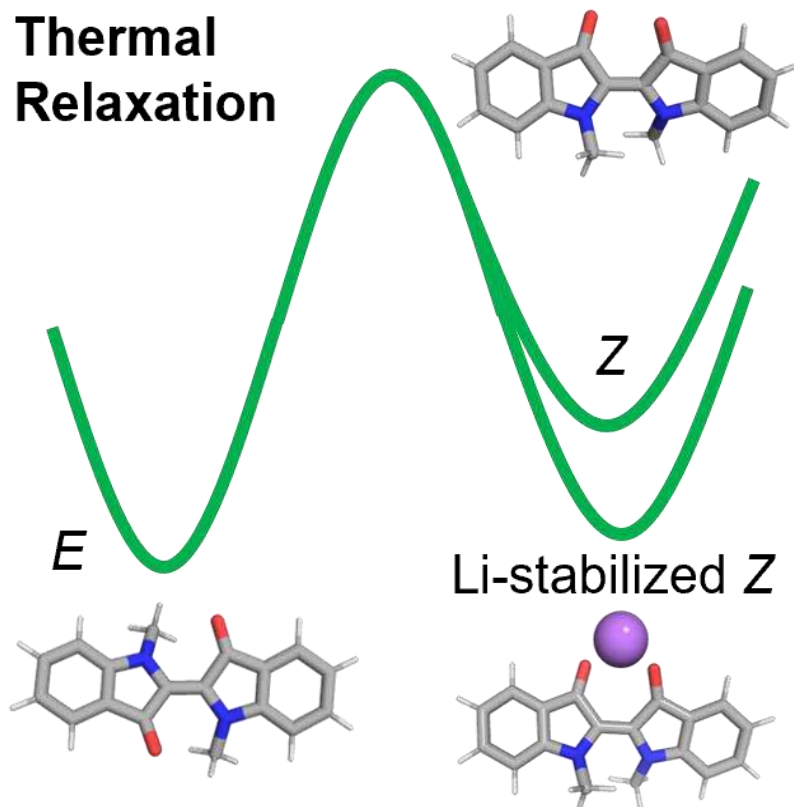
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Abstract No: M64

M64 Non-covalent Interactions Between Metal Cations and Indigoid Photoswitches Impact Their Thermal Relaxation Properties

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Photoswitches have wide applications including molecular machines, information storage, and light-responsive materials. There have been many examples of incorporating non-covalent interaction sites in photoswitches that enable the resulting molecules to respond to other external stimuli such as concentration, temperature, guest molecules, and solvent polarity. These responsive properties allow the photoswitches to have complex functions for potentially more advanced applications. However, to the best of our knowledge, there are very few works demonstrating the use of non-covalent interactions to regulate the properties of the un-modified parent structures of photoswitches. Thus, in this work, we study the non-covalent interactions between metal cations and indigoid photoswitches. We found that certain cations could selectively bind to one of the two photo-isomers of indigoid switches and extend their thermal relaxation half-lives. More interestingly, several transition metal cations were found to significantly accelerate the thermal relaxation process of indigoid photoswitches. These findings allowed us to utilize metal cations to control the mechanical properties of cross-linked polymer networks bearing indigoid photoswitches.

Abstract No: M65

M65 A prismatic cage for encapsulation of aromatic guest molecules

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Coordination-driven self-assembly has been well recognised as an efficient strategy for the construction of a vast range of metallo-supramolecular architectures.¹ Palladium(II) driven self-assembled coordination cages are constructed by combination of a suitable mono/polydentate pyridine appended ligand, **L** with either *cis*-protected palladium(II) component *i.e.* [PdL'] (where L' stands for *cis*-protecting group) or simple palladium(II) component. The resulting assemblies can be formulated as [Pd_xL'_x(L)_y] and [Pd_mL_n] respectively. Metallo supramolecular cages have been explored in various fields such as catalysis, drug delivery, molecular recognition, and reactive species stabilization.² Among various solvents used for complexation, water is an inexpensive green solvent and eco-friendly, thus can be preferred over other solvents. Here we have synthesized a new template free water-soluble Pd₆L'₆L₃ cage by co-ordination driven self-assembly, where a tetradentate ligand **L** reacts with *cis*-protected Pd(tmeda)(NO₃)₂ in 1:2 molar ratio in H₂O:CH₃CN (4:1) mixture. The ¹H NMR, ESI-MS, and single crystal XRD data analysis revealed formation of a discrete cage with prismatic shape. The cage was found to encapsulate neutral aromatic guest molecules. Radical initiators also found to be encapsulated and stabilised inside the cage.

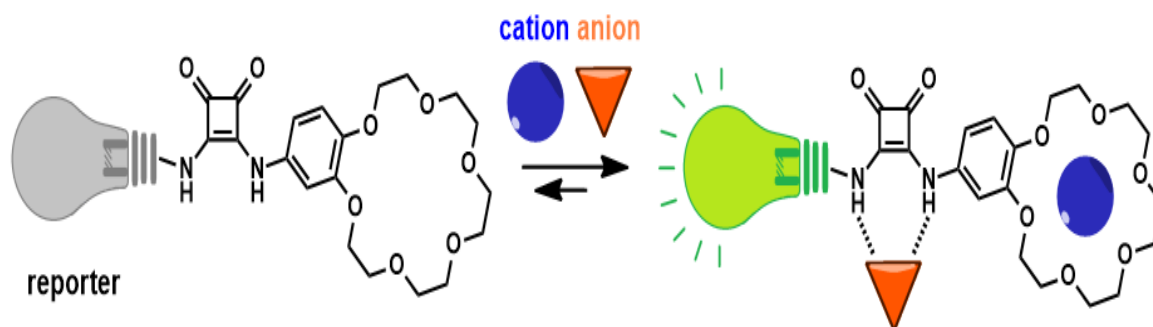
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Abstract No: M66

M66 Squaramide-based modular ion pair receptors and sensors

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Ion recognition, extraction, and transport are among the particular and still challenging tasks of modern supramolecular chemistry. They are extremely important because they are closely related to real problems including the regulation of ion transport in organisms, their detection, water treatment, and waste disposal. Research has shown that one solution to these problems may involve the use of monotopic anion receptors possessing binding domains capable of interacting with negatively charged species. This group of compounds comprises squaramides, which are a special class of monotopic anion receptors able to interact with anions more effectively than their urea or thiourea analogues. However, monotopic receptors are capable of interacting with one type of ion (anions), which in the presence of strongly coordinating counterions (cations) may lose their effectivity in ion binding due to the formation of ion pairs out of the receptor's binding site. To eliminate this dysfunction, ion pair receptors, compounds capable of simultaneously binding anions and cations, have been proposed and recently intensively investigated. Cooperative binding by heteroditopic receptors can be achieved by properly oriented binding domains within a receptor platform. Squaramides are readily accessible from the reaction of amines with diesters of squaric acid and both symmetrical and unsymmetrical compounds are easy to obtain. This opens up an opportunity to synthesize squaramide based receptors in a modular fashion and to combine two functional parts whose properties can be tailored to specific purposes. Based on this protocol, and utilizing sequential amidation of dimethyl squarate with a cation binding site functionalized with amine function, squaramide based ion pair receptors or sensors capable of binding or recognizing cations and anions simultaneously can be synthesized. The enhancement in anion binding was achieved by complexation of cation into the crown ether cavity and the change in the nature of the substituents on the phenyl ring directly linked to the squaramide unit, from electron-donating to more withdrawing. The basis for distinguishing specific salts is the formation of complexes of various stoichiometry depending on the type of receptor and the properties of the anions tested.

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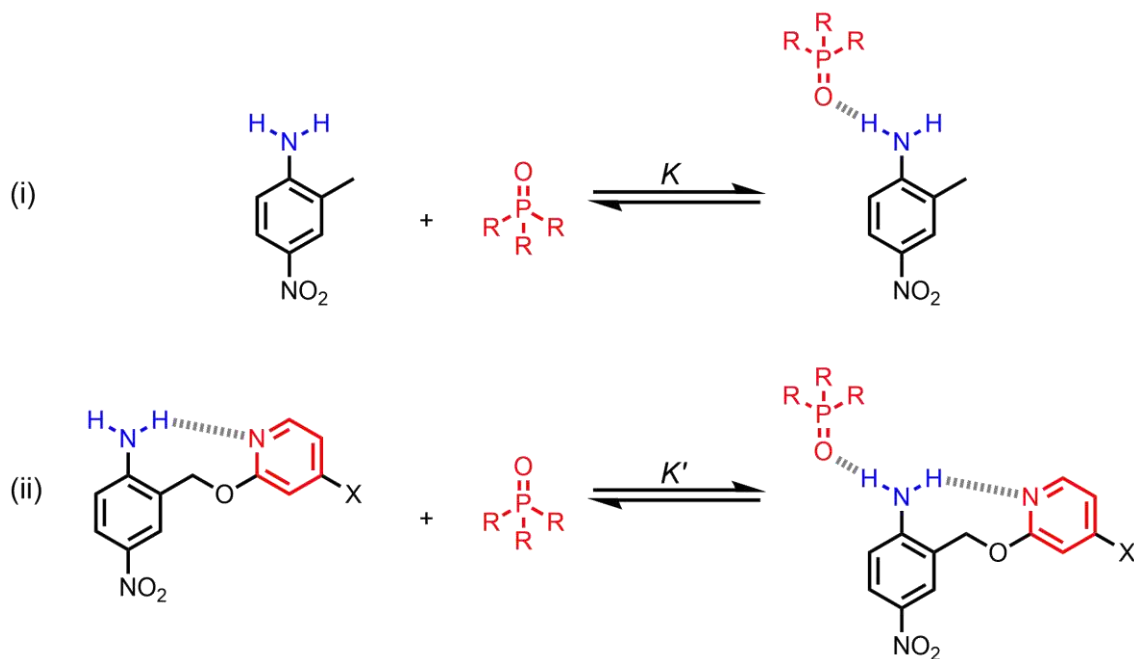
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Abstract No: M67

M67 H-bond cooperativity: Polarisation Effects on Anilines

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Caption: Binding of a phosphine oxide to (i) an aniline and (ii) an aniline involved in an intramolecular H-bond.

Non-covalent interactions are ubiquitous in systems and processes in chemistry, biology, and materials science. H-bonding can lead to polarization of a functional group, which in turn changes the strength of subsequent H-bonding interactions, thus leading to cooperativity in H-bonded networks^{1,2}. The work presented in this poster quantifies the magnitude of cooperative effects in a series of nitroanilines. Comparison of the association constant for binding of tri-*n*-butyl phosphine oxide to an aniline (K) with the association constant for binding to an aniline that is involved in an intramolecular H-bond with a pyridine (K') can be used to quantify the magnitude of cooperative effects on the H-bond donor properties of the H-bonded aniline group. By varying the pyridine substituent X, it is possible to develop a quantitative structure-activity relationship that describes the effect of the strength of the intramolecular interaction on the strength of the intermolecular interaction.

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Abstract No: M68

M68 Rylene Bisimide Cyclophanes with Versatile Cavities and Their Host-Guest Interactions

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Among different types of macrocycles, cyclophanes have reached special interest in the last years due to their rigid structures and aromatic moieties which enable a large variety of applications in supramolecular chemistry. A rather new class are the rylene bisimide cyclophanes. The first presentation of a perylene bisimide cyclophane with an open cavity in 2015 opened up this new field of research with the advantage that these chromophoric systems can easily be studied by optical spectroscopy.¹ The open cavity is ideally suited for the encapsulation of guest molecules between the two π -surfaces, which can be studied by UV/Vis absorption and emission spectroscopy. Additionally, the rigidified structure allowed to study the dependence of the linker length on the interaction of the chromophores of empty PBI cyclophanes could be studied.² In a new hetero-cyclophane a chirality- and energy transfer across the cavity could be observed.³ Recent results including newly synthesized cyclophanes will be presented, including their interaction with a large variety of guest molecules.

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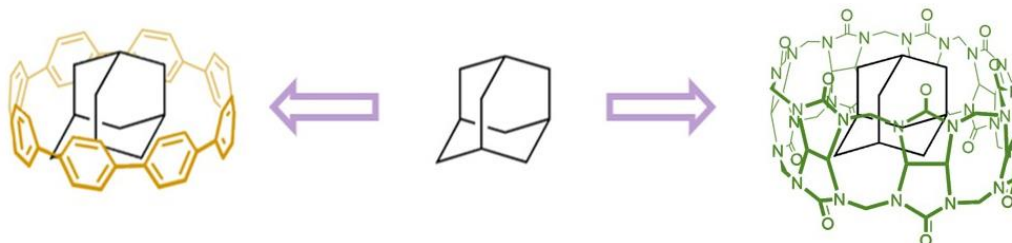
Abstract No: M69

M69 Host-guest chemistry of diamondoids with carbon rings

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Diamondoids are hydrogen-terminated hydrocarbons with a diamond-like structure and a sp^3 hybridation. The smallest one is the adamantane, which has a single cage-shaped subunit, and it is followed by the diamantane, which has two face-fused cages. Due to their unique properties, derivatives of these molecules have been used in a wide range of applications. The adamantane scaffold is present in some pharmaceutical drugs or in many catalysts. Also, it is used as monomer in the synthesis of polymers.

Here, the host-guest chemistry of diamondoids is explored. It has been reported the encapsulation of adamantane molecules inside carbon nanotubs¹ but the analogy with much simpler nanorings as hosts is missing. In this work, the encapsulation of adamantane and adamantane monoderivatives in nanorings, such as cycloparaphenylenes (CPP)² and cucurbiturils (CB),^{3,4} is tested and analysed by spectroscopic and spectrometric techniques. To study further this host-guest chemistry, molecular dynamic simulations (MD) is a powerful predictable tool to explain, at molecular level, how the encapsulation process takes place and how the molecules are placed inside the cavity of the hosts. Future experiments will be devoted to construct ternary assemblies with supramolecular nanocapsules.⁵

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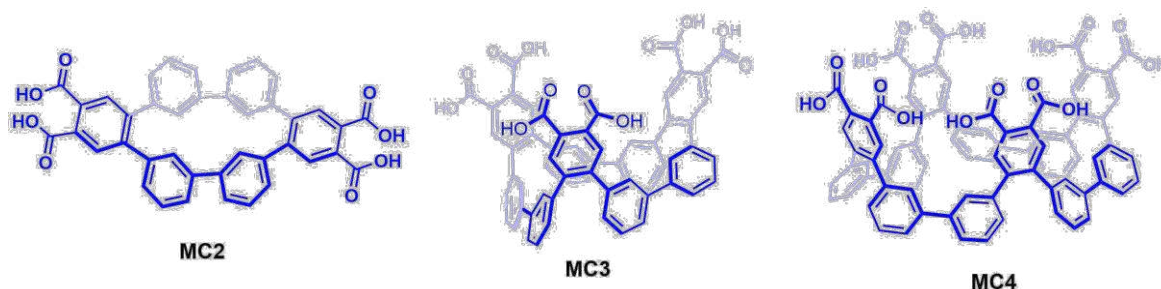
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Abstract No: M70

M70 Synthesis and Supramolecular Recognition Properties of Conjugated Oligomeric Macrocylic Hosts in Water

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Caption: Figure 1. Chemical diagrams of synthesized polyacid containing conjugated macrocycles

Conjugated macrocyclic architectures have unprecedented impact in modern research for their cyclic conjugation, preorganised π -system, rigid structure, size-dependent photophysical properties, and host-guest chemistry.¹ These characteristics eventually make them attractive for organic chemists, theoreticians, materials engineers, and physicists.² However, the synthesis of these interesting molecules are really challenging, requires proper methodologies involving C-C coupling reaction as the key step. Also, there are very few examples of these conjugated macrocycles which are soluble in water;³ this limits these molecules for utilizing them in extensive biological applications.⁴ In this direction, we have synthesized a new class of water soluble oligomeric conjugated macrocycles (dimeric, trimeric and tetrameric macrocycles **MC2**, **MC3** and **MC4** respectively) (Figure 1) containing multiple carboxylic acid functionalities via Ni⁰ catalyzed one-pot C-C coupling oligomerization reaction. These macrocycles are systematically characterized by various 1D-2D NMR spectroscopy and mass spectrometry. The well-organized structures as well as the recognisable photophysical properties has directed the supramolecular recognition properties of these macrocycles with various amino acids in water. Particularly, for the trimeric macrocycle (**MC3**), L-tyrosine has shown binding behaviour with nearly micromolar affinity in water via fluorescence titration method, which is also confirmed via UV-Vis and NMR titration experiments. Suitable L-tyr based dipeptides and polypeptides are also recognised in water by the **MC3** and **MC4** via fluorescence titration experiments.

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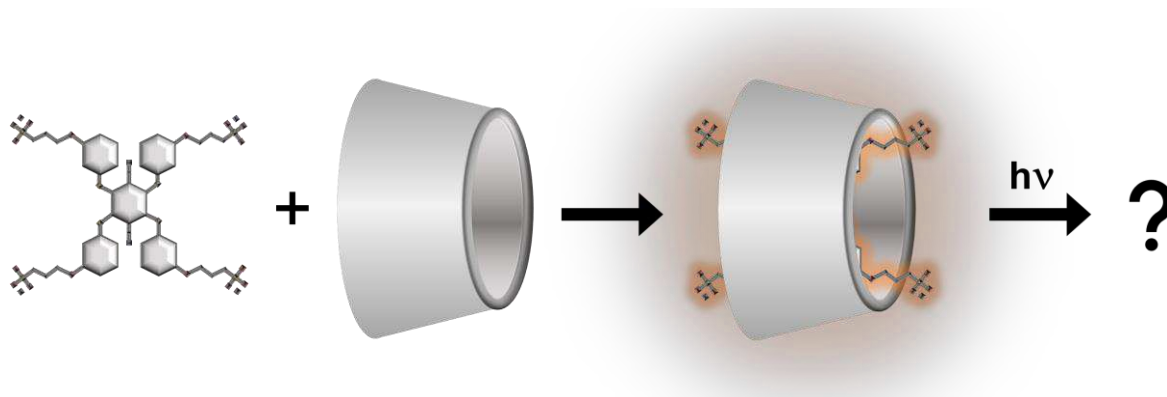
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Abstract No: M71

M71 Inducing Organic Room Temperature Phosphorescence in Water by Host-Guest Complexation with Cyclodextrins

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University of Duisburg-Essen, Essen, Germany



Caption: Complexation-induced phosphorescence of a water soluble thioether in a cyclodextrin cavity.

Among room temperature phosphorescence (RTP) materials, purely organic compounds are of great interest thanks to their chemical versatility.^{1,2} However, these dyes are usually only investigated in organic solvents, vastly limiting their potential applications. Achieving RTP in aqueous solution remains a challenge due to quenching effects of the solvent and dissolved molecular oxygen.³

Firstly, we present water soluble thioether-based dyes that form stable host-guest complexes with γ -cyclodextrins (CD) capable of inducing RTP in water.⁴ As determined by isothermal titration calorimetry (ITC), very strong 1:1 inclusion complexes (K_a up to $5.13 \times 10^5 \text{ M}^{-1}$) are formed with γ -CD. Although all of the investigated compounds formed host-guest complexes, only the regioisomers with *meta*-substitution pattern in the peripheral rings exhibit RTP. Interestingly, the *para*-substituted derivatives showed the highest association constants. Thus, the restriction of motion leading to emission not only requires strong binding to the cyclodextrin cavity, but also a specific conformation of the guest. This is supported by an extensive NMR study and molecular dynamics simulations.

Secondly, we aim to transfer a photochemical cyclization of related dyes from organic into aqueous medium as well. So far, the reaction that yields phosphorescent dibenzothiophenes has only been performed in organic solvents. By employing cyclodextrins, we hope to expand the scope of the reaction and generate efficient RTP in water at the same time.

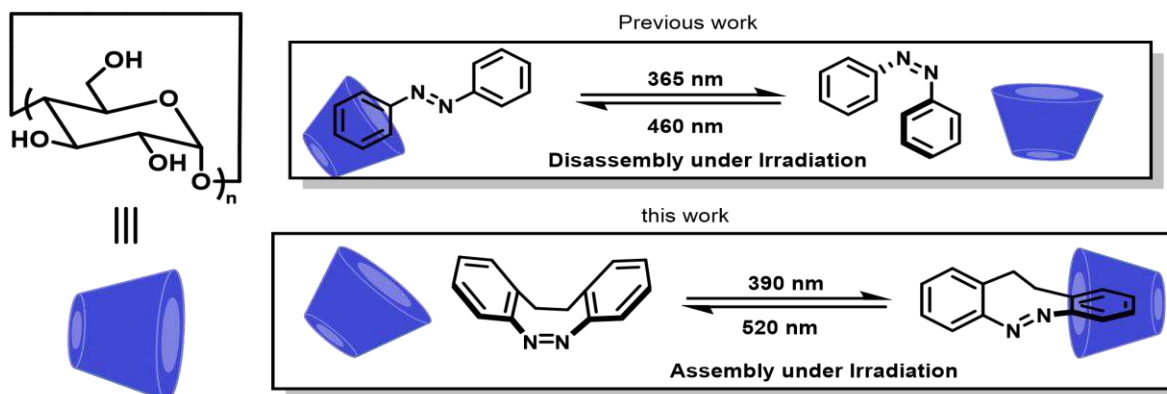
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M72 Diazocines as building blocks for novel light responsive host-guest systems

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Caption: schematic representation of the host-guest interactions and comparison between azobenzene and diazocine.

Stimuli responsive host-guest complexes are known for a long time and have been incorporated in many different kinds of self-assembled systems and stimuli responsive materials^[1,2]. One of the most famous systems, is the Inclusion-complex formed from azobenzene and cyclodextrin, which can be broken up *via* irradiation with UV light^[3]. To turn this concept on its head, we substituted azobenzene with its ethylene-bridged derivative, the diazocine. This modification leads to a reversal in the thermodynamic stability of the isomers, so that in contrast to azobenzene, the weaker or non-binding *cis*-isomer is the default configuration^[4]. Therefore, there is only very little binding without external stimuli and the formation of the complexes can be triggered by irradiation with blue light. The disassembly happens either over time, as the stronger binding *trans*-isomer slowly reverts back to the more stable isomer, or very quickly *via* irradiation with green light.

In this work a simple water soluble diazocine derivative was designed, synthesized, and characterized. In order to assess the suitability of this building block for applications in host-guest chemistry and supramolecular chemistry the interaction with different cyclodextrins was investigated. Therefore, the formation of inclusion complexes, binding behavior of the isomers and the photoresponsive assembly and disassembly of the newly formed complexes was analyzed. With this proof-of-principle, the further use of this reversed behavior upon irradiation in more complex systems has been investigated.

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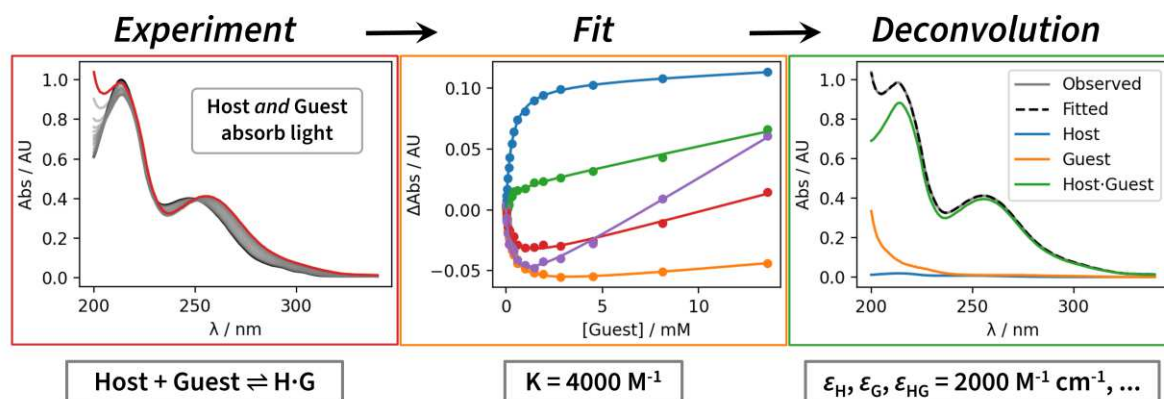
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Flash Talks / 26-06-2023 16:40 - 17:00 Harpa - Silfurberg A/B 2nd floor

M73 Musketeer: a Software Tool for the Analysis of Titration Data

Daniil Soloviev Christopher Hunter

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We present Musketeer: a powerful open-source software tool for the analysis of titration data. A simple graphical interface imports data directly from UV-Vis, fluorescence and NMR spectrometers or from spreadsheets. The fast data analysis algorithm determines equilibrium constants for simple binding isotherms or for more complex systems with multiple competing equilibria. This presentation will demonstrate applications of Musketeer for the analysis of a range of different supramolecular and biomolecular systems, including UV-Visible titrations with multiple absorbing species, competitive binding assays, cooperative polymerisation, and denaturation experiments on H-bonded duplexes.

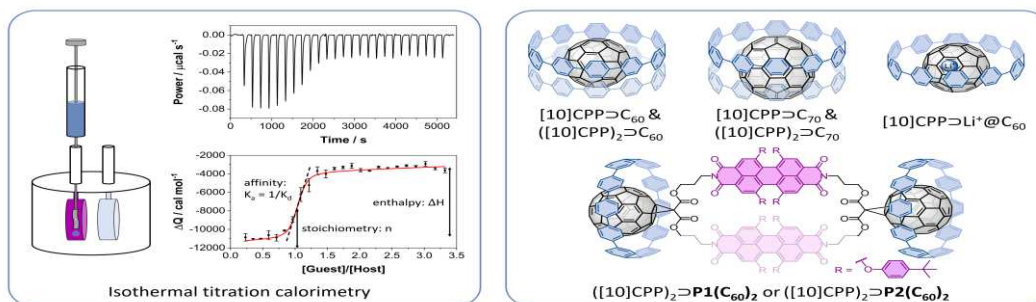
Abstract No: M74

M74 New Insights into the Complexation of Fullerene Derivatives and [10]Cycloparaphenylene using Isothermal Titration Calorimetry

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Caption: Fig. 1 Illustration of the ITC instrument with an exemplary thermogram and corresponding analysis. Molecular structures of the investigated complexes.

The interplay of molecular sizes, complementary shapes, charge distribution and binding sites is of great importance for host-guest recognition.¹ Therefore, cycloparaphenylenes (CPPs) with concave cavities are particularly well suited hosts for the complexation of guest molecules with convex surfaces such as fullerenes. For these host-guest systems absorption and fluorescence titrations have been the most commonly used methods to quantify binding affinities. However, band overlap can occur, making it impossible to determine binding constants.² Thus, we present herein the study of various complexes consisting of fullerene derivatives and [10]CPP by isothermal titration calorimetry (ITC) in *o*-DCB. In addition to the binding constants, this technique allows us to obtain the stoichiometry and thermodynamic parameters (see Fig. 1, left) as well as to follow the species distribution of the titrations. By studying C₆₀ and C₇₀ with [10]CPP, not only the already known 1:1 complexes but also the 2:1 complexes [10]CPP₂⊃C₆₀ and [10]CPP₂⊃C₇₀ were detected.³ Furthermore, the bis-pseudorotaxane formation of various dumbbell molecules with C₆₀ substituents and [10]CPP was successfully investigated.⁴ Most recently, the high binding constant of about 10⁷ M⁻¹ for the complex [10]CPP⊃[Li⁺@C₆₀](PF₆)⁻ was determined.⁵

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Abstract No: M75

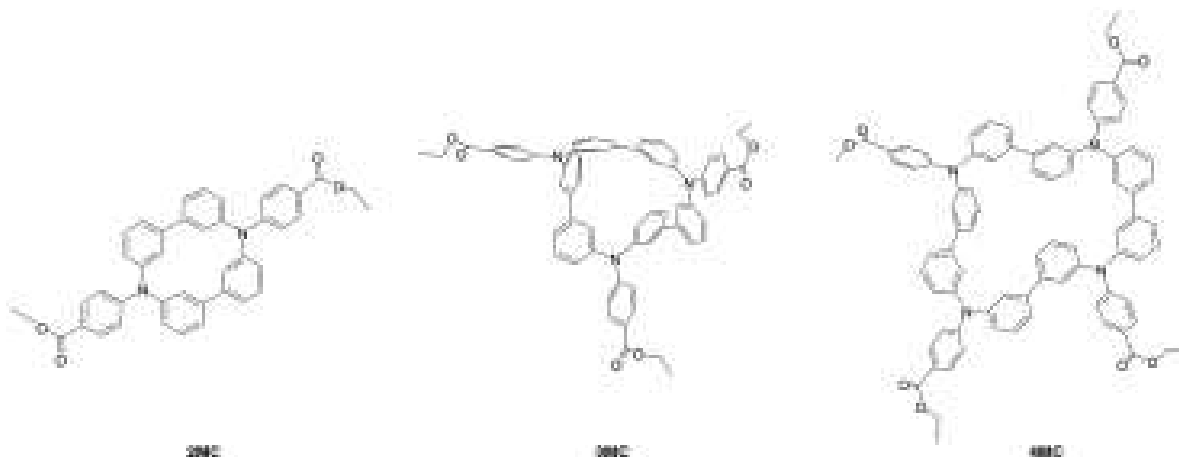
M75 Macrocylic hosts based on triphenylamine

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Caption: Figure 1. Chemical structures of Triphenylamine containing macrocycles.

Supramolecular chemistry plays an important role in understanding and controlling the behavior of complex systems, including host-guest interactions.^[1] In recent years, the recognition and binding of fullerene molecules by conjugated macrocycles has received significant attention due to their potential applications in areas such as drug delivery, sensors, and organic electronics.^{[2] [3]} Recently, we have developed the synthesis of a new family of oligomeric macrocyclic compounds based on triphenylamine. They were synthesized via Yamamoto oligomerization by using Ni(0)-containing reagents. The macrocyclic compounds are soluble in organic solvents. The ester groups can be hydrolyzed to form macrocyclic acids, which give rise to the solubility in an aqueous solution. We have investigated the host-guest chemistry of the obtained molecules in both organic and aqueous solutions. Since the macrocycles have a vase-shape conformation they can recognize C₆₀ and C₇₀ in chloroform solution. Recognition of amino acids by new hosts have been studied in aqueous buffered solution.

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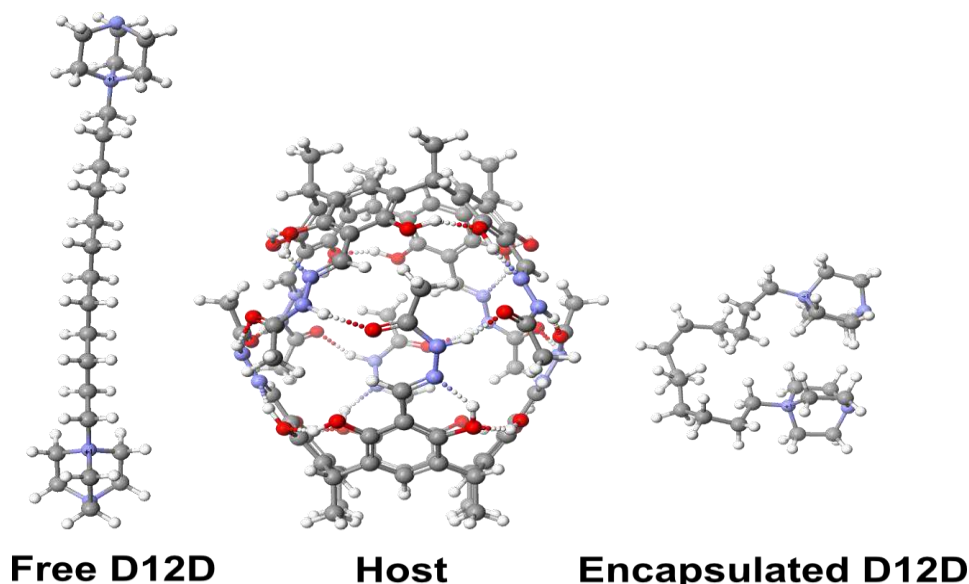
Abstract No: M76

M76 Guest Distortion in a Hydrogen Bonded Resorcinarene Capsule Shown by Mass Spectrometry

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Resorcinarenes are widely utilised in host-guest chemistry due to their electron rich cavity making them useful in binding cationic guests with potential modifications at both the upper and lower rim making them highly versatile hosts. Here, Resorcinarene scaffolds are functionalised at the upper rim via acylhydrazone chemistry with peptide like strands which can intertwine to allow the self-assembly into hydrogen bonded dimers. Different strands result in the formation of capsules with differing cavity sizes and BisDABCONium with various spacer lengths (DnD) were employed to study the effect of guest size of on binding into the cavity of the hosts. Cation- π interactions with the resorcinarene cavity should favour guest encapsulation, but some guests would be expected to be too large to bind inside the cavity. Somewhat surprisingly when measuring with electrospray ionisation (ESI) mass spectrometry (MS), ions corresponding to the dimer plus guest ($[M_2 + D_nD]^{2+}$) were observed for all guests, even those that were expected to be too large to be encapsulated. MS was then used to uncover the motif of this unexpected binding.

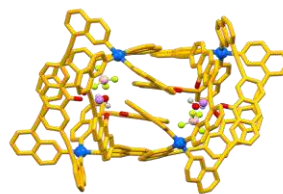
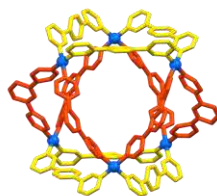
MS is ideally suited to the study of the supramolecular systems as it can easily provide information related to composition from the mass to charge ratio (m/z). Beyond m/z , structural information can be gained by using more advanced techniques such as collision induced dissociation (CID), ion mobility mass spectrometry (IMS), and hydrogen deuterium exchange experiments (HDX) providing information related to stability, size and h-bonding networks, respectively. Even with such possibilities, MS is sadly underutilised in the supramolecular field. Herein, CID, IMS and HDX and complementary computational modelling were used to study the unusual binding results. It was determined that the DnDs which were too large to be encapsulated fully extended were distorting into a horseshoe like arrangement in an effort to maximise cation- π interactions between host and guests at the expense of steric clash and hydrogen bond disruption. This provides insight into the interplay between the different forces responsible for guest binding and shows the potential applications of MS in the study of supramolecular chemistry

Abstract No: M77

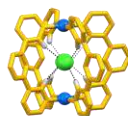
M77 PALLADIUM-BASED METALLOSUPRAMOLECULAR ASSEMBLIES: FROM COMPLEX STRUCTURES TO SIMPLE WATER-SOLUBLE ANION-RECEPTORS

Sylvain Sudan Kay Severin

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a) Hexanuclear heteroleptic species b) Reduced-symmetry LiBF₄ receptor

c) Water-soluble chloride receptors



Caption: Figure 1

The combination of palladium salts and bipyridyl ligand can lead to the formation of a variety of coordination complexes with different shapes and sizes displaying a very versatile host-guest chemistry. Increasing their structural complexity remains a central challenge in the field. One way it can be achieved is by combining two or more different ligands to obtain the corresponding heteroleptic species and design strategies have been developed to favor their formation over the range of possible outcomes that can result from the self-assembly process. This approach however reaches its limit when aiming for species comprising more than two palladium centers. The development of a screening method based on the formation of a virtual combinatorial library of [Pd_nL_{2n}](BF₄)_{2n} complexes allowed us to identify a new hexanuclear species with formula [Pd₆L₆L']¹²⁺ as the most stable product (**Figure 1a**).¹

On the other hand, homoleptic assemblies can also display a significant structural complexity. We recently investigated the Li⁺-binding properties of Pd-based structures. One of the complexes underwent a significant structural rearrangement when LiBF₄ was added. Namely, the initial Pd₂L₄ species was converted to a low-symmetry Pd₄L₈ assembly enclosing two solvated LiBF₄ ion pairs (**Figure 1b**).² The flexibility of the ligand, its extended π system and the presence of Lewis-basic sites confer a good adaptability to the related Pd-complexes and allow the formation of stabilizing intramolecular interactions.

Nevertheless, complexity is not a necessity to achieve strong host-guest interactions and the positively charged environment of the Pd₂L₄ lantern-shaped structures makes them ideal candidates for the encapsulation of anions. Complexation in aqueous solutions yet remains highly challenging. Our latest work showed that functionalizing a simple bipyridyl ligand with water-solubilizing groups allowed to access water-soluble assemblies that could bind chloride anions with an apparent association constant as high as $K_a = 1.8(\pm 0.1) \times 10^5 \text{ M}^{-1}$ (**Figure 1c**).³

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Abstract No: M78

M78 Modulation of selectivity in catalytic systems through molecular recognition.

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Catalysis is fundamental in making the modern world, mediating the selective transformations required for bulk and fine chemical manufacture (drugs, pesticides, etc) and advanced materials. Selectivity is paramount: to provide the desired product only and ensure resource efficiency. Design of well-defined complexes of precious metals for use as catalysts has driven fantastic advances in our control of organic chemistry. Unfortunately, they are expensive, and – being composed of precious metals, ‘endangered elements’ – it is becoming clear that they are not sustainable. While the mainstream of supramolecular catalysis has tended to address this by designing ever-more elaborate catalytic species, over many years[1] some supramolecular chemists have controlled reactions by using molecular recognition away from the catalyst, to control the access of reagents or catalysts to substrate molecules.[2, 3] In this poster I will set out our recent results building on these ideas, and present data showing the ability to impart selectivity to reactions which would otherwise be unselective.

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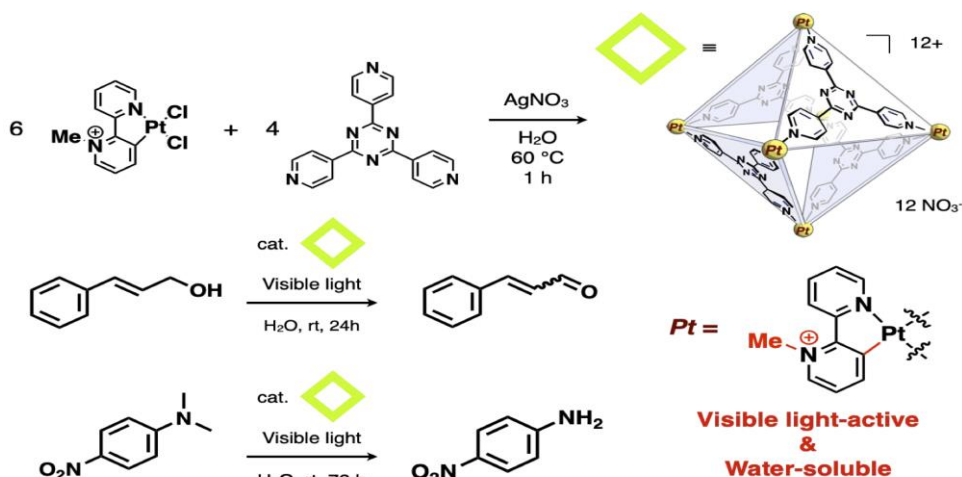
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Abstract No: M79

M79 Photocatalytic reaction within a visible light-active M6L4 hollow cage

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Caption: Figure 1 The visible light-active M₆L₄ hollow cage and photocatalytic reaction with the cage

Many visible light-active supramolecular hosts assembled from platinum group complexes such as Ir(III) and Ru(II) have been reported to apply to photocatalytic reactions¹. These hosts sometimes suffer from weak encapsulating abilities that limit a substrate scope and selectivity, although they show excellent photocatalytic abilities. In this study, we achieved the construction of a visible light-active M₆L₄ hollow cage assembled from a cyclometalated platinum(II) complex, which shows excellent molecular recognition and conformational control ability². We demonstrate visible light-induced catalytic reactions within the internal space. Visible light irradiation to the host-guest complex produced the corresponding photoproduct via an oxidative mechanism. Control experiments confirmed that the guest confinement within the cavity facilitates photo-induced electron transfer to enhance the conversion of the reaction.

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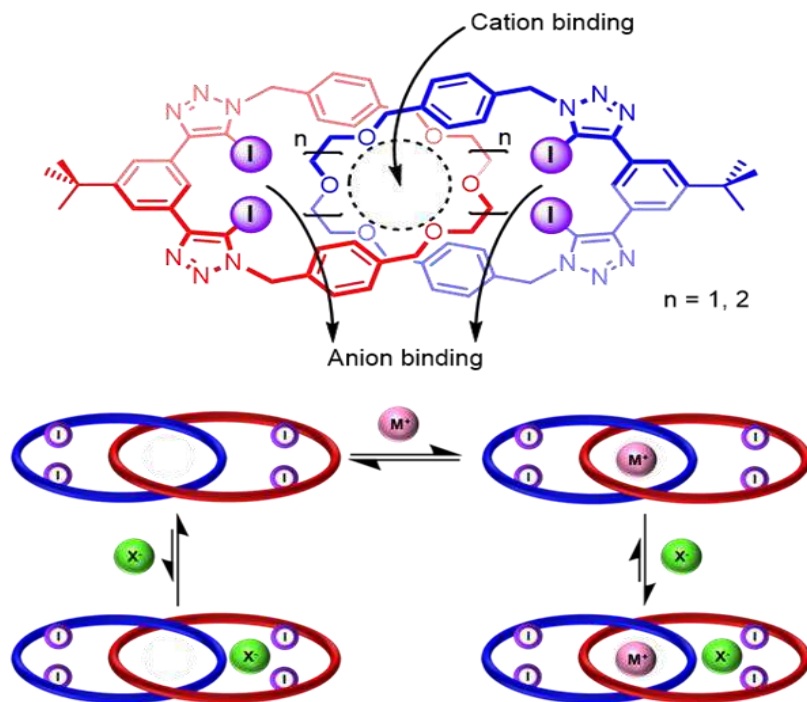
Abstract No: M80

M80 Halogen bonding heteroditopic [2]catenanes for alkali metal halide ion pair recognition

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The first examples of neutral all-halogen bonding (XB) heteroditopic homo[2]catenanes were prepared by an alkali metal cation template-directed approach and their ion-pair recognition properties investigated. Extensive ¹H NMR spectroscopic anion, cation and ion-pair recognition studies show that the [2]catenane hosts exhibit positive cooperative ion-pair recognition behaviour, wherein XB-mediated anion recognition is dramatically enhanced by alkali metal cation pre-complexation. Notably, subtle changes in the respective XB catenane's oligo(ethylene glycol) chain length dramatically influences ion binding affinity, stoichiometry, complexation mode and conformational dynamics. Solution phase and single crystal XRD studies provide evidence for competing host-separated and direct contact ion-pair binding modes, which is governed by a mechanical bond effect. Furthermore, exploiting these cooperative ion-pair binding properties we demonstrate the [2]catenanes are capable of extraction of solid sodium or potassium halide salts into organic media.

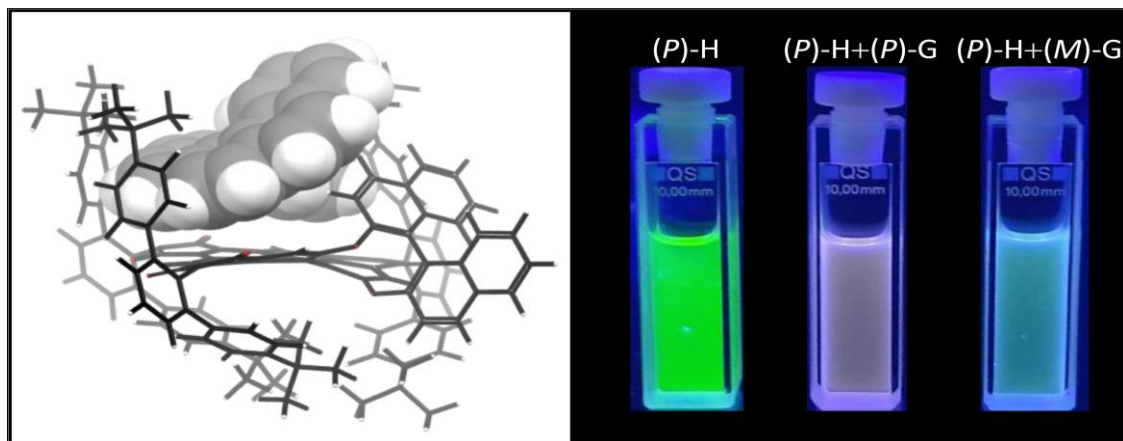
Abstract No: M81

M81 Enantioselective Recognition of Helicenes by a Tailored Chiral Benzo[ghi]perylene Trisimide π -Scaffold

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Caption: Helicenes are bound by a newly designed chiral π -scaffold dye with superb enantiodifferentiation.

Enantioselective molecular recognition of chiral molecules that lack specific interaction sites for hydrogen bonding or Lewis acid-base interactions remains challenging. Recently, we introduced the concept of tailored chiral π -surfaces toward the maximization of shape complementarity.^[1] As we demonstrated for helicenes it is indeed possible by pure van-der-Waals interactions (π - π -interactions and CH- π -interactions) to accomplish enantioselective binding. This is demonstrated for a novel benzo[ghi]perylene trisimide (BPTI) receptor whose π -scaffold is contorted into a chiral plane by functionalization with 1,1'-bi-2-naphthol (BINOL). Complexation experiments of enantiopure (*P*)-BPTI with (*P*)- and (*M*)-[6]helicene afforded binding constants of 10700 M⁻¹ and 550 M⁻¹, respectively, thereby demonstrating the pronounced enantiodifferentiation by the homochiral π -scaffold of the BPTI host. The enantioselective recognition is even observable by the bare eye due to a specific exciplex-type emission originating from the interacting homochiral π -scaffolds of electron-rich [6]helicene and electron-poor BPTI.

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M82 Supramolecular.org / bindfit / Opendatafit - past, present and future

Varvara Efremova James Wilmot, Pall Thordarson

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Opendatafit

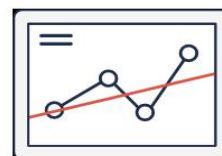
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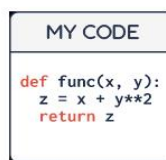
Perform analysis on the web



Visualise data



Select from library of analysis algorithms



Write and contribute custom algorithms

Caption: Opendatafit workflow - final outcome would then be published with a link to a single URL (or DOI)

Following our work towards a more robust methodological framework for determining binding constants in supramolecular chemistry,^{1,2} we launched in 2015 a web-portal supramolecular.org³ that allows end-users to freely use verifiable binding models and save all their results with a permanent identifier (url) in a F.A.I.R.⁴ (fair, accessible, interoperable and re-usable) manner. The website itself has two key tools; binding which allows for analysis binding constants for NMR and UV-Vis (and fluorescence) titration data and bindsim which allows you simulate NMR and UV-Vis binding isotherms at different concentrations with 1:1, 1:2 and 2:1 binding models.

This website has been very popular in the supramolecular community with over 60,000 visit to dates from nearly 150 countries. The Scopus citation data base shows over 300 citations with “supramolecular.org” in the citation list but many others have probably used the website in their published work without citing this website.

Here, we will summarise the work we have been doing the last 3 years on expanding the capabilities of our platform technology within what we call Opendatafit, which builds on the concept introduced with supramolecular.org. The Opendatafit platform is a more holistic data analysis and publication platform (see Figure). The development work was funded by the Australian Research Data Commons (ARDC) through the Australian Characterisation Commons at Scale (ACCS) platform and in close collaboration with the Australian Nuclear Science and Technology Organisation (ANSTO) – focusing initially on data analysis requirements for high-end small angle X-ray and neutron scattering equipment (SAXS and SANS) at ANSTO. To that end we have adopted the popular “SasView” package for SAXS/SANS data analysis into our platform.

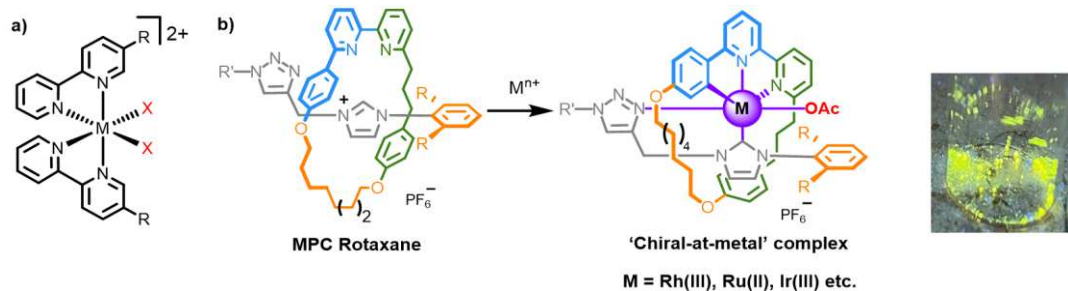
With the SAXS/SANS data analysis part of our project now nearly completed, we moved on to porting our NMR and UV-Vis analysis capabilities from supramolecular.org to this new platform. This should both improve user-experience but also allow people to start to contribute their own binding models etc via our write and contribute custom algorithm. We are also working on modules for ITC data analysis and some basic kinetic data analysis.

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Abstract No: M83

M83 Synthesis of 'Chiral-at-Metal' Complexes Using Mechanically Planar Chiral Rotaxane-Based Ligands

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Caption: Figure 1 - a. An example of a CAM complex based on a bidentate ligand; b. Schematic approach to a CAM complex based on an MPC rotaxane ligand.

Octahedral metal complexes can exhibit chirality owing solely to the different arrangement of ligands around the metal center. Such complexes have been termed "chiral-at-metal" (CAM) and were first demonstrated experimentally by Alfred Werner in 1911.¹ Later, Fontecave introduced the **CAM catalysis** concept in which the at-metal stereochemistry dictates the reaction stereoselectivity.² The most common approach to CAM complexes is to use bidentate ligands, as this simplifies the coordination chemistry by reducing the range of possible isomers, with enantiomer resolution achieved by either using a temporary chiral ligand or chiral stationary phase HPLC (Figure 1a).³ The ability of the mechanical bond to alter the coordination chemistry of endotopic donor atoms was established by Sauvage in the 1980s.⁴ We report that confined nature of mechanical bond can control the stereochemistry at a metal centre by using an enantiopure mechanically planar chiral (MPC) rotaxane as a ligand (Figure 1b).⁵ This study presents the first efficient synthesis of luminescent cyclometalated CAM-MPC rotaxanes in which all ligand donor atoms are chemically distinct. We are now exploring their luminescent and catalytic properties.

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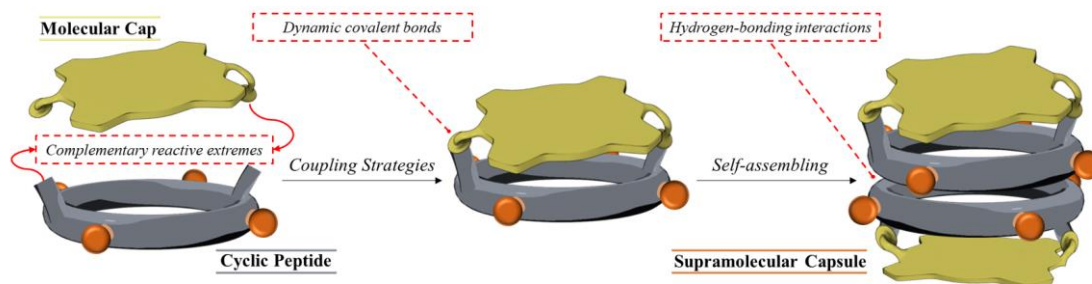
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Abstract No: M84

M84 Supramolecular Catalysis based on Cyclic Peptide Nanoreactors

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Caption: Figure 1: General design of a cyclic peptide capsule

Over the past years, the development of new catalytic supramolecular systems has experienced considerable growth with essential contributions in academia and industry.[1] However, despite all the improvements achieved, the construction of new catalysts with high selectivity control and with the ability to imitate enzymatic properties is highly needed.

In addition, nature can achieve high levels of selectivity by using enzymes with a perfectly engineered binding pocket, capable of selectively binding a specific substrate. Inspired by this, several research groups have designed self-assembled nanoreactors that are able to select from a range of different molecules or intermediates, a single molecule able to fit into the cavity, resulting in a new tool to gain selectivity control.[2]

In our group, we have designed a new class of self-assembled capsules based on cyclic peptides that are able to encapsulate transition metal complexes,[3] anions,[4] and organic molecules.[5] Herein, we present the synthesis of new molecular containers in which a certain molecular cap is anchored to the cyclic peptide through different strategies in order to cap the upper cavity of the dimers and, thus, completing the architecture of the cages. We envisioned that these kinds of peptide-based capsules could be attracting tools to gain control over selectivity in different reactions by trapping the substrate inside the cavity.

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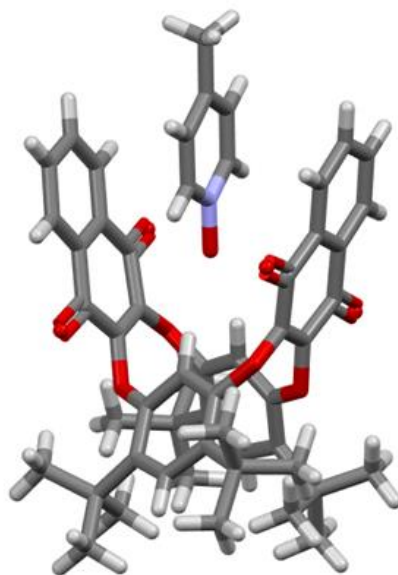
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Abstract No: M85

M85 Synthesis, Structure, and Host-Guest Binding of Cambiarene Macrocycles

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Caption: Cambiarene:Pyridine-N-Oxide Host-Guest Complex

This poster will feature the research from our lab on the synthesis of a new class of redox active oxacyclophanes containing *p*-benzoquinones that we have named “cambiarenes” (1). These macrocycles can be accessed in one-pot, base catalyzed reactions from the corresponding dihaloquinones and diphenols in good yields. We have begun structurally investigating our first cambiarene in both its oxidized and reduced forms and its ability to act as a supramolecular host for the binding of electron rich guests in the oxidized state.

Reference

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Abstract No: M86

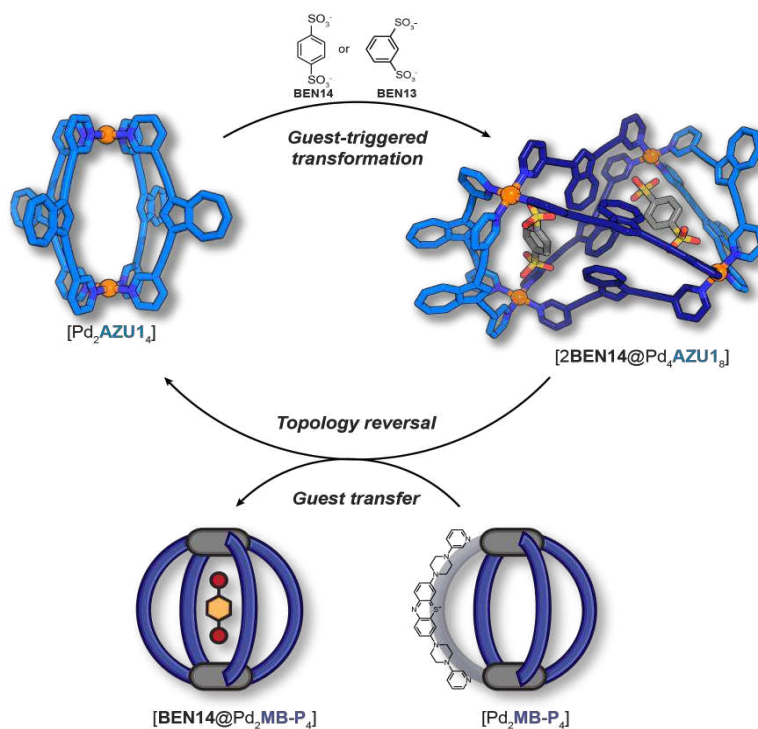
M86 Guest-induced transformations in coordination cages

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The topology of coordination cages depends on several factors, notably the coordination geometry of the metal centres and the shape of the organic ligands constituting the walls of the cages. Based on these parameters, it is possible to predict the final structure of the final assembly. However, introducing guest species to the coordination assemblies' cavities can trigger unpredictable transformations to different shapes and topologies, a feat enabled by the labile nature of the coordination bond.

From the first example shown by the lab of Ken Raymond [1] to the recent work of our group, this talk will explore the different structures and transformation pathways that were uncovered, turning seemingly simple systems into more complex ones as they react to guest binding. In particular, we will explore the halide-triggered dimerization of lantern-shaped Pd_2L_4 cages,[2][3] or a more recent example of the reversible transformation from a Pd_2L_4 cage to a Pd_4L_8 tetrahedron by the recapture of the guest by a second lantern-shaped cage.[4]

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Abstract No: M87

Flash Talks / 26-06-2023 16:40 - 17:00 Harpa - Silfurberg A/B 2nd floor

M87 Sulfo-pillar[6]arenes: efficient synthesis and novel derivatives for biological applications

Chelsea Wilson Austia Puckett, Evan Chen, Fraser Hof

University of Victoria, Victoria, Canada

Sulfo-pillar[6]arene is an ultra-high affinity ($K_d < 1 \mu\text{M}$) supramolecular host that has promising biological applications. This molecule has shown potential as a supramolecular reversal agent for neuromuscular blocking agents, opioids and fentanyl.^{1,2} However, the applications of sulfo-pillar[6]arene are underexplored due to limited access to the key synthetic starting material, ethoxypillar[6]arene. Isolating large quantities of ethoxypillar[6]arene is challenging due to the disfavored cyclization reaction leading to the predominant formation of ethoxypillar[5]arene, a less desired analog. To address this challenge, we developed a large 40-gram scale chromatography-free synthesis to exclusively isolate ethoxypillar[6]arene.³ This method yields ~ 20 grams of product in a day's work. With easy access to large quantities of this key intermediate we have developed methods to functionalize the parent sulfo-pillar[6]arene scaffold. We have generated novel functionalized sulfo-pillar[6]arene analogs with improved binding and recognition properties. These analogs maintain the parent sulfo-pillar[6]arenes ultra-high affinity and display improved binding strength of targeted guests. Our new derivatives bind active pharmaceutical ingredients (APIs) with sub- μM binding affinity in salty media.

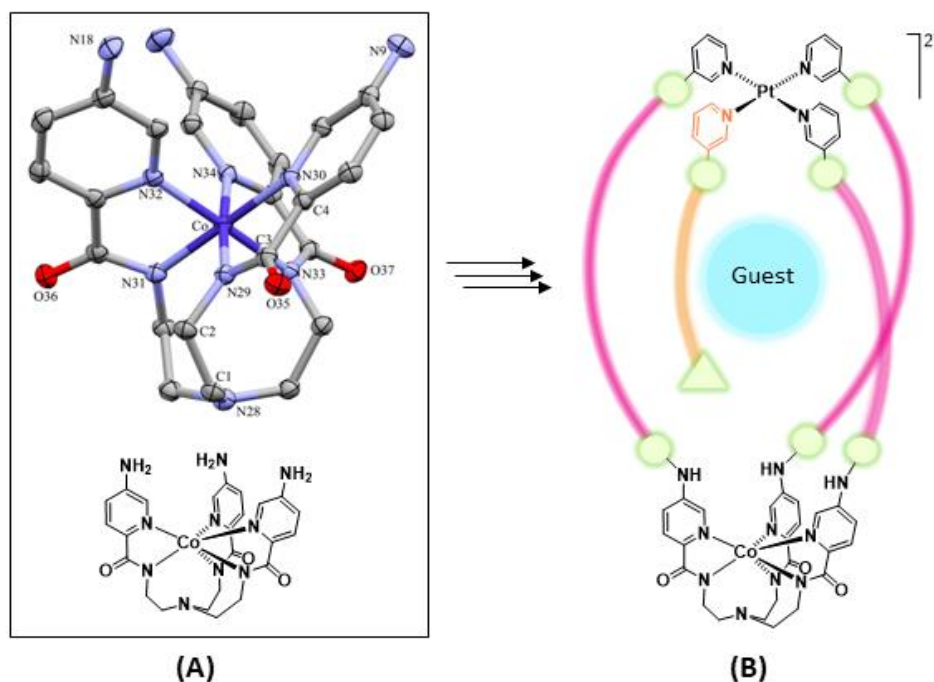
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Abstract No: M88

M88 A Heterodimetallic Supramolecular Cage that Incorporates a Trapdoor

Leonard Wright ¹ Dylan Giffard ¹, James Crowley ², Christian Hartinger ¹¹ University of Auckland, Auckland, New Zealand² University of Otago, Dunedin, New Zealand

Caption: Figure 1. Heterodimetallic Supramolecular Cage.

There is considerable interest currently in developing lower symmetry self-assembled metallo-supramolecular cage systems, and this is driven primarily by efforts to enhance the applications of these assemblies. These include utilizing them as reaction flasks and catalysts, molecular traps and containers and biomedical therapeutics.^{1,2} The potential to use cages of this type for stimulus-responsive reversible guest binding is especially relevant in the area of drug delivery.³

We have designed and synthesized in a stepwise procedure a heterodimetallic cage system (Figure 1) by first attaching three arms (pink arcs) to a robust metallotripodal base unit (Figure 1, A) and then capping the termini of the three arms using three of the four 3-picolinaldehyde (pcla) ligands in the complex $[\text{Pt}(\text{pcla})_4]^{2+}$. The fourth picolinaldehyde ligand was then used to form a “trapdoor” (orange arc) for the cage (Figure 1, B). Guest binding studies of the heterodimetallic cage will be reported, as well as the reversible opening and closing of the palladium analogue of B through sequential addition of 4-dimethylaminopyridine (DMAP) and p-toluenesulfonic acid.

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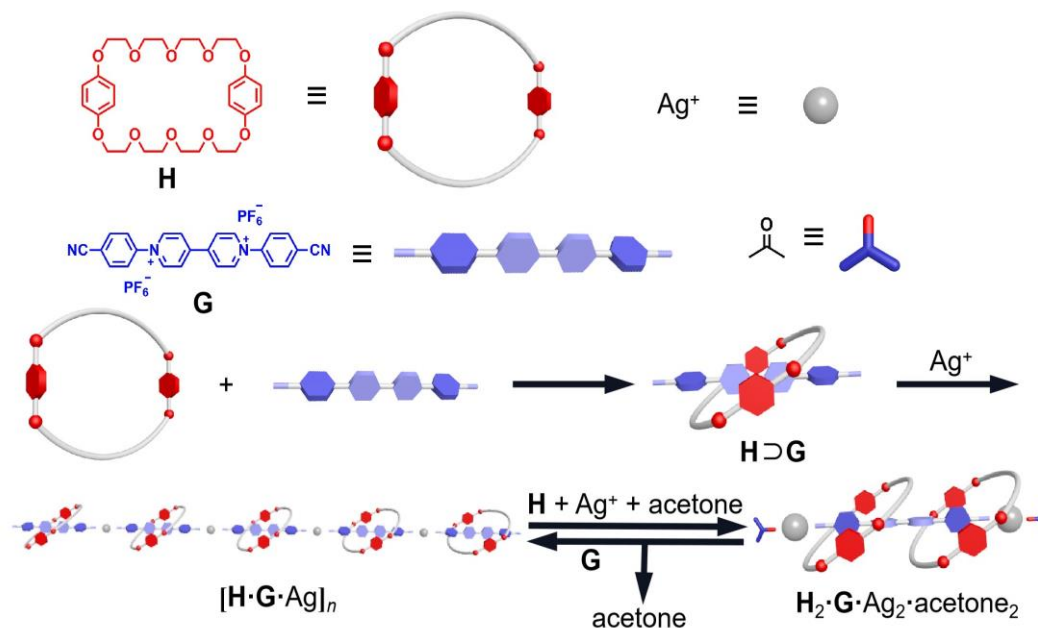
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Abstract No: M89

M89 Chemoresponsive Supramolecular Polypseudorotaxanes with Infinite Switching Capability

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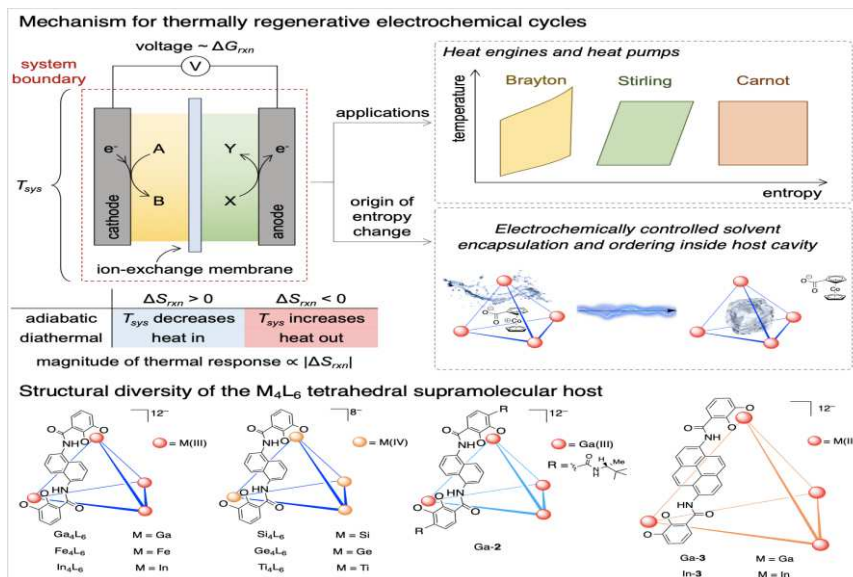


Caption: Chemical structures and cartoon representations of H, G, Ag⁺ and acetone, and cartoon representations of the transformations

Chemoresponsive supramolecular systems with infinite switching capability are important for applications in recycled materials and intelligent devices. To attain this objective, here a chemoresponsive polypseudorotaxane is reported on the basis of a bis(*p*-phenylene)-34-crown-10 macrocycle (**H**) and a cyano-substituted viologen guest (**G**). **H** and **G** form a [2]pseudorotaxane (**H⊃G**) both in solution and in the solid state. Upon addition of AgSF₆, a polypseudorotaxane (denoted as **[H·G·Ag]_n**) forms as synergistically driven by host-guest complexation and metal-coordination interactions. **[H·G·Ag]_n** depolymerizes into a [3]pseudorotaxane (denoted as **H₂·G·Ag₂·acetone₂**) upon addition of **H** and AgSF₆, while it reforms with successive addition of **G**. The transformations between **[H·G·Ag]_n** and **H₂·G·Ag₂·acetone₂** can be switched for infinite cycles, superior to the conventional chemoresponsive supramolecular polymeric systems with limited switching capability. Therefore, by taking advantage of the adaptive macrocycle/guest complexation characters, the current study opens up new avenues toward precision engineering of chemoresponsive supramolecular polymers.

Abstract No: M90

M90 High entropy supramolecular electrolytes for thermogalvanic devices

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Caption: Scheme depicting the mechanism for thermally regenerative electrochemical cycles (TRECs) and structures of M4L6 supramolecular hosts

An aqueous electrochemically controlled host-guest encapsulation system addresses the need for electrolyte design in thermally regenerative electrochemical cycles (TRECs) through a solvent phase-change strategy. TRECs utilize reversible electrochemical processes with large molar entropy change for thermogalvanic waste-heat harvesting and electrochemical cooling.¹⁻³ A supramolecular host-guest system demonstrates a molar entropy change of up to $98.8 \text{ cal mol}^{-1} \text{ K}^{-1}$, exceeding that of the state-of-the-art aqueous TREC electrolyte, potassium ferricyanide.⁴ Upon encapsulation of a guest in an M_4L_6 supramolecular host, water molecules that structurally resemble amorphous ice are displaced from the host cavity,⁵ exploiting a phase transition to increase entropy. Protein-like redox inhibition of encapsulated guests at the electrode is overcome using a small molecule mediator. This host-guest system represents the first to undergo a solvent phase change rather than an electrolyte phase change. Furthermore, the M_4L_6 host has proven amenable to structural modifications at the metal vertices and of the ligand at both its linker and its end groups. This synthetic diversification allows for an unprecedented mechanistic exploration of encapsulation entropy, showing a range of $48.4 \text{ cal mol}^{-1} \text{ K}^{-1}$ depending on ligand and metal vertex modifications. The host-guest electrolyte system demonstrates the potential for rational design of TREC electrolytes and a new strategy to overcome theoretical limits^{6,7} on solvent reorganization entropy.

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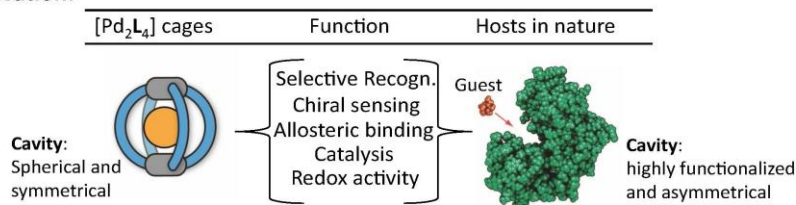
Abstract No: M91

M91 Towards Coordination Cages with Catalytically Functional Ligands

Ertugrul Yalcin

Technical University of Dortmund, Dortmund, Germany

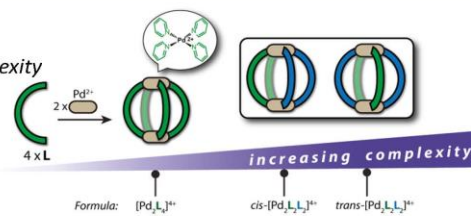
Motivation:



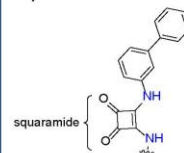
Aim:

➤ Increase of:

- Structural complexity
- Functionality



Hydrogen-Bonding functionality by squaramide based ligands



Caption: Schematic comparison of a [Pd₂L₄] cage and an enzyme. Illustration of a squaramide based bis-monodentate ligand.

Inspired by the high selectivity and reaction rate of enzymatic catalyst in nature we study the incorporation of catalytic functionality in the ligand backbones of coordination cages, aimed at the realization of discrete nanoscale molecular flasks to perform reactions under nano-confinement.

To achieve greater structural complexity and functionality in metallocsupramolecular cages, the use of [Pd₂L₂L'₂] heteroleptic cages composed of two different ligands is envisioned as a promising milestone towards mimicking enzymatic activity. Introducing hydrogen-bonding functions in coordination cages enables various catalytic reactions. The first aim of this study was to form a coordination cage with squaramide-based ligands and square-planar Pd(II) cations. Formation of homo- and heteroleptic cages were analyzed by NMR spectroscopy in solution, mass spectrometry in the gas phase and by single crystal X-ray in the solid state.

Solvents have a crucial effect on hydrogen bonding properties in solution and DMSO is a competitive hydrogen acceptor, therefore increasing Squaramide's solubility is fundamental for the host-guest and catalysis studies.

Squaraine dyes are also derivatives from squaric acid and have a zwitterion property. Squaraine-based ligands have been studied with respect to cage formation and then host-guest chemistry.

Formation of Squaraine-based coordination cage were analyzed by NMR spectroscopy in solution, mass spectrometry in the gas phase and by single crystal X-ray in the solid state.

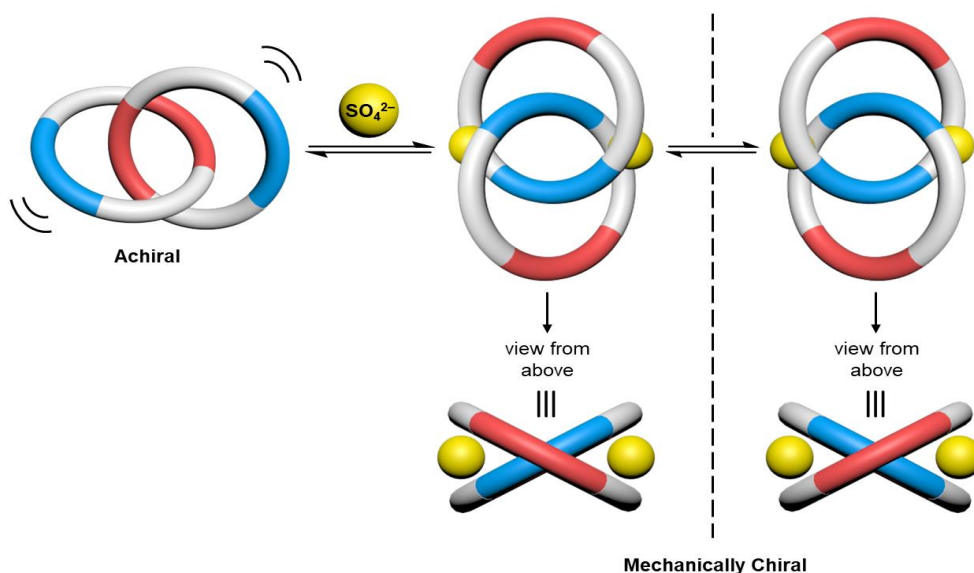
Host-guest interaction of Allura Red AC with a Squaraine-based coordination cage was studied by NMR and UV-Vis spectroscopy.

Abstract No: M92

M92 Mechanical Achiral-Chiral Switching of a Sulfate-Binding Tetra-Urea [2]Catenane Host

Yueliang Yao Ho Yu Au-Yeung

The University of Hong Kong, Hong Kong, Hong Kong



Caption: Mechanical achiral-chiral switching of the tetra-urea [2]catenane upon sulfate binding

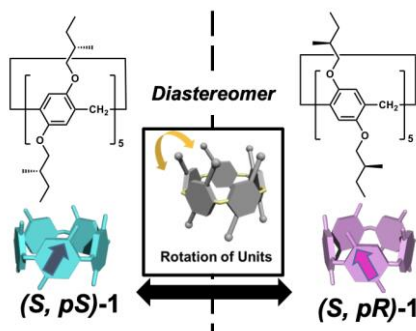
Utilizing mechanically interlocked molecules (MIMs) as receptors for recognizing ionic guests not only could enhance the ion binding selectivity and affinities, but also provide large-amplitude, guest-induced co-conformational changes for developing sensors, transporters, ion-controlled molecular switches and machines.^{1,2} In this work, a heterotopic [2]catenane host containing both cation and anion binding moieties is assembled from dynamic urea bond formation. The catenane host displays a strong and selective binding towards sulfate ion over other anions in competitive aqueous-organic environment. Notably, the sulfate binding leads to a co-conformational rearrangement of the interlocked macrocycles and stabilizes a mechanically chiral co-conformation of the [2]catenane, representing a rare example of guest-induced achiral-chiral mechano-stereochemical switching in Hopf link topology.

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Abstract No: M93

M93 Highly Diastereoselective Rotaxane Synthesis with Pillar[5]arenes via Crystallization Amplification Process

Kiichi Yasuzawa ¹ Keisuke Wada ¹, Shixin Fa ¹, Yuya Nagata ², Kenichi Kato ¹, Shunsuke Ohtani ¹, Tomoki Ogoshi ¹¹ Grad. Sch. Eng., Kyoto Univ., Kyoto, Japan² WPI- ICRoDD, Hokkaido Univ., Sapporo, Japan

Caption: Figure 1. Chemical structure of pillar[5]arene 1 and dynamic planar chirality.



Caption: Figure 2. Rotaxane synthesis via crystallization process for highly diastereomeric enriched rotaxane formation.

Synthesis of chiral compounds is one of the central topics in chemistry. Among them, chiral interlocking structures such as rotaxanes and catenanes are attracted attention and actively studied in recent years for not only their intrinsic structures but also the potential possibilities working as catalysts, chemosensing and chiroptical materials.

In synthesis of the chiral interlocking molecules, equivalent amounts of racemates are produced. Thus, selective synthesis based on differences in diastereomeric stability is useful for chiral interlocked molecules. However, to achieve diastereoselective synthesis of the chiral interlocked molecules, a large energy difference between diastereomers is required. In other words, from diastereomers with small energy differences, interlocked molecules with high diastereomeric excess cannot access in normal pathway, resulting in losing the chance to develop a wide variety of chiral rotaxanes.

Pillar[5]arenes (P[5]As) are pillar-shaped macrocycles that exhibit planar chirality (*i.e.*, *pR* and *pS*) due to the positions of the alkoxy substituents on the rims. These two stereoisomers can interconvert in solution via rotation of benzene units, resulting in a 1:1 racemic mixture. Thus, 1:1 racemic mixture of rotaxanes are yielded from enantiomeric P[5]A.¹ P[5]A-1 with 2-(*S*)-methylbutoxy groups in the side chains (**Figure 1**) provides diastereomeric relationship referred to as (*S*, *pR*)-1 and (*S*, *pS*)-1.² As a result, an energy difference is generated between *pR* and *pS* forms and the *pR/pS* ratio can be changed. However, in previous our work, the high *pR/pS* ratios of the P[5]A-1 complex could not be generated even in various solvents due to their low energy difference.³

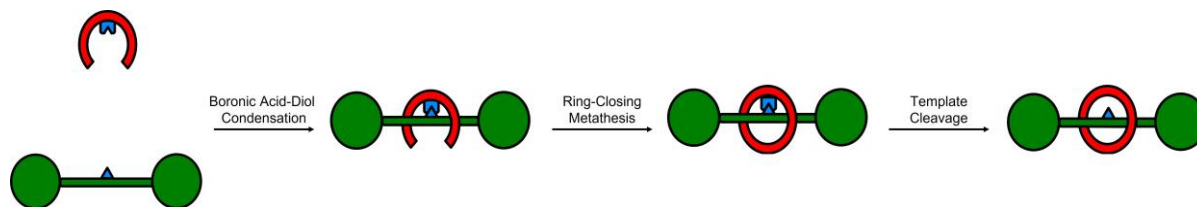
In this study, planar chirality of P[5]A-1 was amplified by co-crystallization with an axle molecule, which could not be achieved in a solution system. This chirality induction depends on the end groups and length of the guest molecules. Subsequent solid-phase end capping reaction in solvent-free condition memorized the planar chirality during rotaxane formation. Overall, we have demonstrated that the use of the co-crystallization process and mechanically solid-phase reactions allow highly diastereoselective rotaxane synthesis with P[5]A-1, which could not be achieved in a solution system (**Figure 2**).

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Abstract No: M94

M94 [2]Rotaxane Synthesis Based on Dynamic Boron Chemistry

Jingjing Yu ¹, Fredrik Schaufelberger ²¹ KTH Royal Institute of Technology, Stockholm, Sweden² KTH Royal Institute of Technology, Stockholm, Sweden

Caption: Scheme 1. Synthetic strategy of [2]rotaxane by a dynamic boronic ester template.

Over last few decades, many different types of rotaxanes have been developed¹, and the early-stage applications of MIMs have been explored with great success in sensing², catalysis³, and materials science⁴. The traditional synthetic methods for rotaxanes are all based on non-covalent templates such as hydrogen bonding. However, this means that the resulting rotaxanes can be only operated in organic solvents, since weak noncovalent interaction are easily outcompeted in water. This is a huge obstacle for further applications of MIMs in for example biomedical contexts. Synthesizing rotaxanes via covalent templating is an attractive idea, as the robust and strong covalent bond can resist harsher environments and conditions, but the final bond cleavage to remove the covalent template is a challenge⁵. Therefore, dynamic covalent bonds (DCBs) could be ideal template for synthesizing rotaxanes due to their reversible nature – strong and robust under some conditions (“assembly”) and labile and weak under others (“template removal”).

Here, we choose the dynamic covalent boronic ester bond as the template for rotaxane synthesis. This bond type has already been extensively used for selective carbohydrate recognition⁶, and we have developed a boron receptor for the diol-templated clipping-type creation of [2]rotaxanes. To verify this synthetic methodology, a new type of [2]rotaxane has been synthesized and analysed with, among other techniques, 1D/2D ¹H NMR and ¹¹B NMR spectroscopy as well as advanced mass spectrometry.

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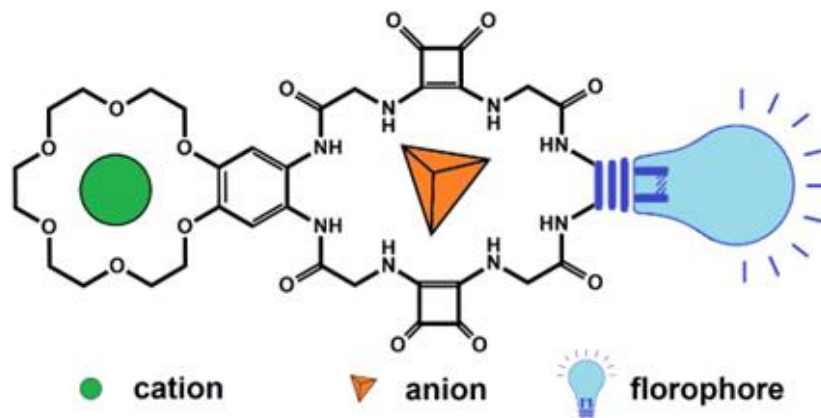
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Abstract No: M95

M95 Selective Recognition of Sulfates Using Squaramide Based Ion Pair Sensors

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Caption: Macrocyclic ion pair sensor

Fluorescent methods are among the most desirable due to their low cost, high sensitivity and good selectivity. So far, several effective single-function fluorescent sensors have been proposed, i.e. capable of interacting with one type of ion: cations or anions. Unfortunately, such receptors have some disadvantages. Namely, the energy cost of separating a single ion from its counterion or solvation sphere is too high, therefore effective recognition of them usually requires the use of a lipophilic anion or cation. In nature, anions occur mainly with strongly interacting counterions, e.g. alkali metal cations. For this reason, an effective solution to the problem could be the use of receptors capable of binding anions and cations simultaneously and informing about the complexation process through optical changes in the system.¹

The aim of my research was to develop the synthesis of macrocyclic ion pair receptors, through appropriate combinations of individual elements of simple libraries consisting of synthesized diamines and esters of square acid derivatives. The incorporation of a fluorescent signaling unit near the amide function made it possible to obtain a sulfate-selective optical sensor. Three new macrocyclic ion pair receptors and their homotopic counterpart were characterized by proton nuclear magnetic resonance, UV-Vis absorption and fluorescence spectroscopy.²

The synthesis of acyclic ion pair sensors with an anthracene unit was also developed. The anthracene unit located near the anion-binding domain of the receptors provided optical salt detection capability. The system capable of visual detection of salts was developed. By adjusting the water content in the system, varying with the type of salts added to the solution and recognizing the electron transfer process in the excited state (eT) a different response was observed. The ability to recognize sulfates by increasing or quenching the fluorescence intensity using the same molecule has been demonstrated.³

References:

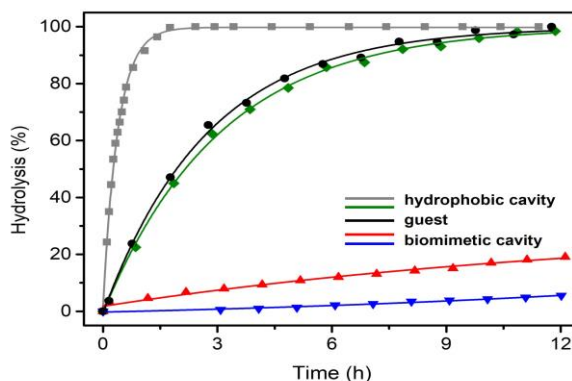
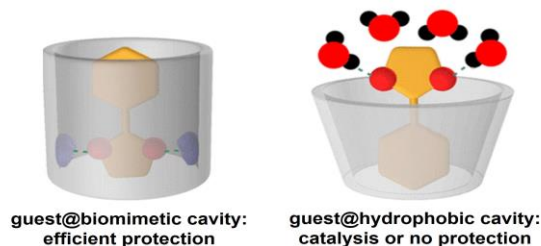
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Abstract No: M96

M96 Supramolecular Protection of Functional Organic Molecules in Water Using Biomimetic Receptors

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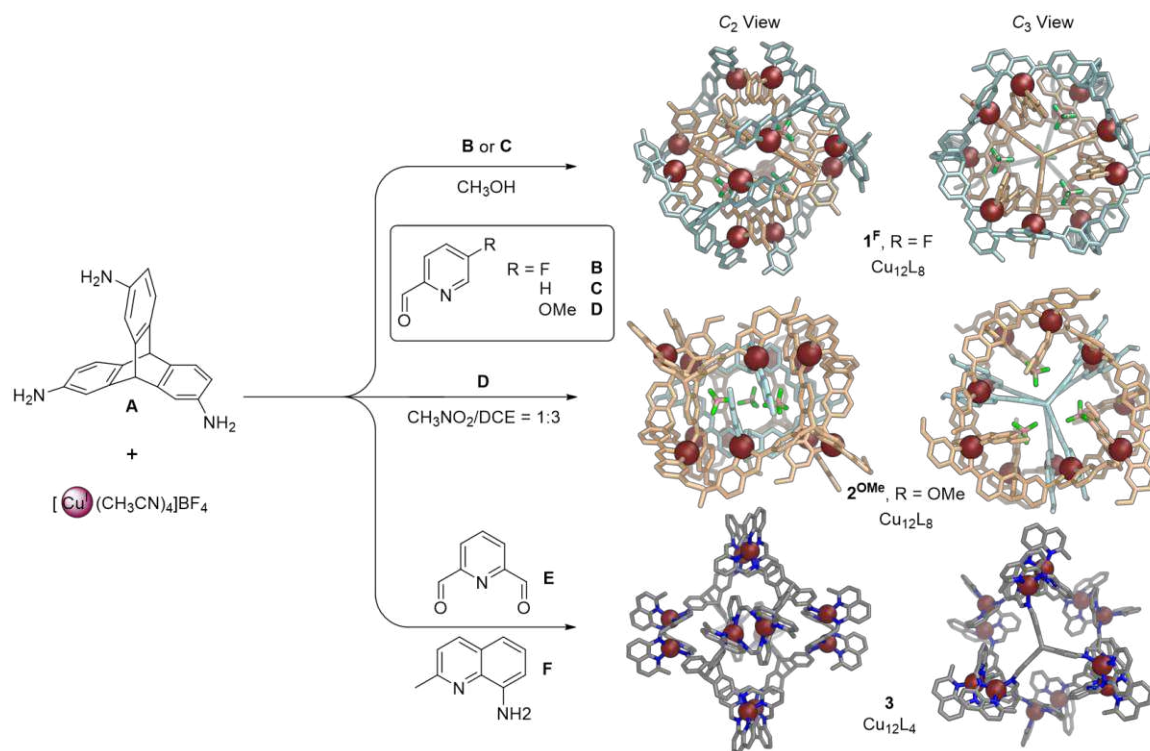


Efficient protection of reactive substrates is crucial for chemical synthesis, pharmaceuticals, and material sciences.¹ While molecular receptors can act as protecting groups to stabilize reactive guests, protecting polar functional organic molecules in water remains challenging due to inefficient recognition of polar functional groups of reactive guests. In this study, we report the biomimetic recognition and protection of various functional organic molecules in water using receptors with endo-functionalized cavities. Bioreceptors can effectively bind polar groups of guests by decorating their hydrophobic binding pockets with polar binding sites, which can anchor the polar groups of substrates into the binding pockets. Inspired by bioreceptors, we developed a series of biomimetic macrocyclic receptors with polar binding sites inside their cavities, such as naphthotubes and anthryltubes.² Among them, amide naphthotube and amide anthryltube can selectively encapsulate polar reactive functional groups into their well-shielded cavities with the combination of hydrogen bonding and the hydrophobic effect. These receptors can serve as efficient supramolecular protecting groups for a wide range of reactive substrates. Amide naphthotubes show unique protection to acetals, which could not be well protected by classical macrocyclic receptors without polar binding sites in their hydrophobic cavities (e.g., β -cyclodextrin and cucurbit[7]uril). Amide naphthotubes can prolong the half-life of acetals by over 1000 times, which is the most effective protection for acetals so far. Furthermore, selective protection of acetals is observed and used for kinetic resolutions of constitutionally isomeric acetals. Additionally, the universality of supramolecular protection with biomimetic receptors in water is confirmed by the successful protection of organic molecules containing different functional groups, such as esters, α , β -unsaturated carbonyls, disulfide bonds, and donor-acceptor Stenhouse adducts. This work demonstrates the potential applications of biomimetic receptors in supramolecular protection.

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Abstract No: M97

M97 Steric and Geometrical Frustration of Ligand Generate Complex Cu₁₂L₈ and Cu₁₂L₄ AssembliesHuangtianzhi Zhu ¹, Jonathan R Nitschke ¹, Tanya K. Ronson ², Kai Wu ²¹ University of Cambridge, Cambridge, United Kingdom² , ,

Caption: Figure 1. Chemical structures of subcomponents and self-assemblies of three novel copper(I)-based structures.

Copper(I) complexes have useful properties, but the flexibility of tetrahedral Cu^{I} adds challenge to the design of supramolecular structures that incorporate this metal ion.^{1,2} This flexibility results in a tendency to form lower-nuclearity structures, such as helicates and grids. Here we introduce a strategy to incorporate steric and geometric frustration of triptycene, which enabled the preparation of two Cu_{12}L_8 assemblies and a helicate-containing Cu_{12}L_4 cage with pyridylimine ligands. The syntheses and structural transformation of these two structurally distinct Cu_{12}L_8 frameworks, a T -symmetric double octahedron and a D_3 -symmetric hexagonal prism, clarify the interplay between ligand curvature, steric hindrance, electronic and solvent effects. The helicate-containing Cu_{12}L_4 cage exhibit chiroptical properties by stereoselective synthesis in the presence of BINOL. These assemblies have implications in the construction of large and functional coordination capsules based on tetrahedral metal ions *via* subcomponent self-assembly, with properties and potential applications distinct from those of cages built from octahedral metals.

Abstract No: M98

M98 Application of Novel Coordination and Supramolecular Chemistries to Respond to Chemical Warfare Agent Challenges.

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Military first responders encounter complex, time-constrained and challenging conditions when responding to scenarios involving chemical warfare agents (CWAs). As such, there is a requirement to develop and evaluate a suite of reliable, fast and efficient scientific and technological solutions to facilitate a customisable response to the management of chemical incidents in order to protect lives and return personnel and equipment to service faster.

DSTG has a specific interest in technologies that can be applied to the response of chemical incidents including:

Detection: sensing chemistries and devices for the detection of vapours and deposited hazards.

Decontamination: catalysts to accelerate the destruction of CWAs.

Disclosure and Decontamination Assurance: visual indicators of contamination location and decontamination success.

Forensics: sample preservation and presumptive identification.

Protection: new materials for PPE and assessment of PPE.

DSTG collaborates with Academia to conduct innovative foundational and applied research to address these requirements and facilitate the transition of prototypes to Industry for development into operationally useful technologies and products. In recent years, DSTG has applied numerous coordination and supramolecular chemistry-based strategies to combat the challenges posed in responding to a chemical incident including the development of:

Colorimetric and luminescent chemosensors,¹

Novel, low toxicity simulants for R&D activities,²

Non-corrosive decontamination and decontamination assurance solutions,³

Multifunctional and target and trigger systems,⁴

Disclosure sprays,⁵

Sample preservation techniques.⁶

This poster will demonstrate some of these research programs and their application to CBRN Defence.

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⁵ Unpublished work **2022 – 2023**.

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Abstract No: M99

M99 PTFE (“TEFLON”) Sealing Ring for hermetic greaseless Glass Joints

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Fig.1. Left: PTFE-sealing ring fixed elastic (no groove necessary). Middle: Sealing ring intransparent without pressure. Right: Sealing ring transparent under sealing pressure. Far right: A similar PTFE ring and a piston groove make an all-glass-syringe gastight.

There is a prejudice that PTFE (often called “Teflon”) is too inelastic to be a hermetic sealant for greaseless conical joints. Therefore, teaching books [1,2] recommend threaded or flanged “O-ring joints” for hermetic manipulation of air- and moisture sensitive chemicals if joint grease is no option.

Here we show [3] (Figure 1) that the common ground conical glass joint can be sealed relatively hermetic and at low cost with a narrow flat PTFE sealing ring (less than 1 mm wide and 0.1 mm thick, weight only 5 mg PTFE).

The sealing ring is high-vacuum tight (air leakage rate $10^{-8} \dots 10^{-6}$ mBar*Liter/sec), solvent tight (loss of ethyl acetate out of containers < 0.1 mg/day) and resistant to fluctuation of temperature (freezing-thawing-heating cycles). The reusable PTFE sealing ring prevents stuck joints, is thin enough to be used with all joint clamps and is fixed elastically (without groove) on the glass joint. We demonstrate also a new all-glass-syringe ((Figure 1, 1 - 100 mL) that is gastight at fluctuating temperatures (freezing-thawing-cycles) by a similar exchangeable sealing ring (PTFE) in a groove of the glass piston [4].

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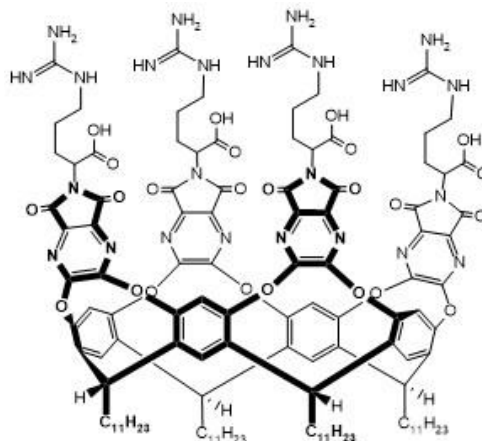
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Abstract No: M100

M100 Resorcinarene with Arginine Functional Groups Used to Separate Perfluoroalkyl Acids

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Caption: Figure 1. Resorcinarene with arginine arms.

Perfluoroalkyl substances pose a worldwide environmental health risk. It is important to develop new quantification methods for perfluoroalkyl substances. Currently, liquid chromatography-tandem mass spectrometry is the proposed method to analyze perfluoroalkyl substances. Ion chromatography, with its ability to use water samples as they are collected, could be a promising technique to detect anionic perfluoroalkyl acids in water.^{1,2} A new cationic stationary phase, composed of a resorcinarene bound to arginine (Figure 1), was synthesized and used to separate perfluoroalkyl substances by ion chromatography. The new packing material under the right gradient conditions separates perfluoroalkyl substances such as perfluorobutanoic acid, perfluorobutanesulfonic acid, perfluoropentanoic acid, perfluorohexanoic acid, perfluorohexanesulfonic acid, and perfluorooctanoic acid.³ It was found that decreasing the NaOH concentration in the eluent resulted in better perfluoroalkyl substances separation which is different from common IC. The detection limits of the perfluoroalkyl substances were 0.44 to 4.0 mg/L and the limits of quantification were 1.5 to 13 mg/L. The number of CF₂ units correlated to retention times of the perfluoroalkyl substances. Also, the detection of perfluoroalkyl substances in tap and lake water was performed.

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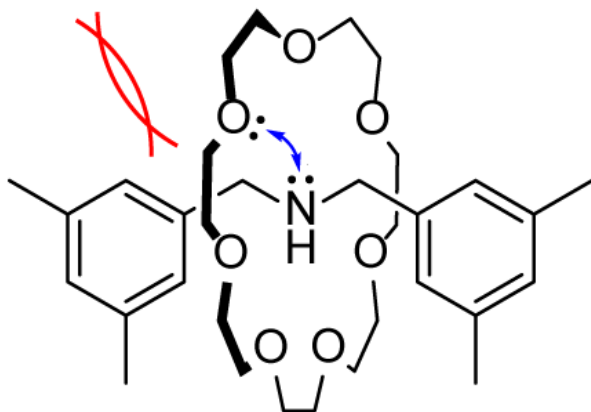
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Abstract No: M101

M101 Compact Rotaxane Superbases

Martin Power, Morris David, David Leigh Vitorica-Yrezabal Inigo

University of Manchester, Manchester, United Kingdom



- $pK_a H^+$ up to 32.2 in MeCN
- Low amine nucleophilicity
- Fast substrate deprotonation
- Hydrolytically stable

Caption: Compact Rotaxane Superbases

Organic superbases are routinely used to promote a range of chemical transformations.¹ Challenges for the development of novel superbases include their ease of synthesis, chemical stability and high basicity, while minimizing nucleophilicity that can result in unwanted side reactions. Here we introduce a new family of organic superbases, compact amine-crown ether rotaxanes that show desirable characteristics in all these regards.^{2,3}

Metal-free active template synthesis provided access to a range of rotaxanes with as few as three atoms between the stoppering groups, locking the location of a small crown ether (21C7 and 24C8 derivatives) over the amine group of the axle. The forced proximity of the interlocked protophilic components results in $pK_a H^+$ values as high as 32.2 in acetonitrile, which is comparable to that of phosphazene superbases. The rotaxane superbases are generally chemically stable and, in a model reaction for superbases, eliminated HBr from a primary alkyl bromide with complete selectivity for deprotonation over alkylation. Their modest size, ease of synthesis, hydrolytic stability, high basicity, low nucleophilicity and, in the best cases, rapid deprotonation kinetics, make compact amine-crown ether rotaxane superbases intriguing candidates for potential applications in synthesis and supramolecular chemistry.

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Abstract No: M102

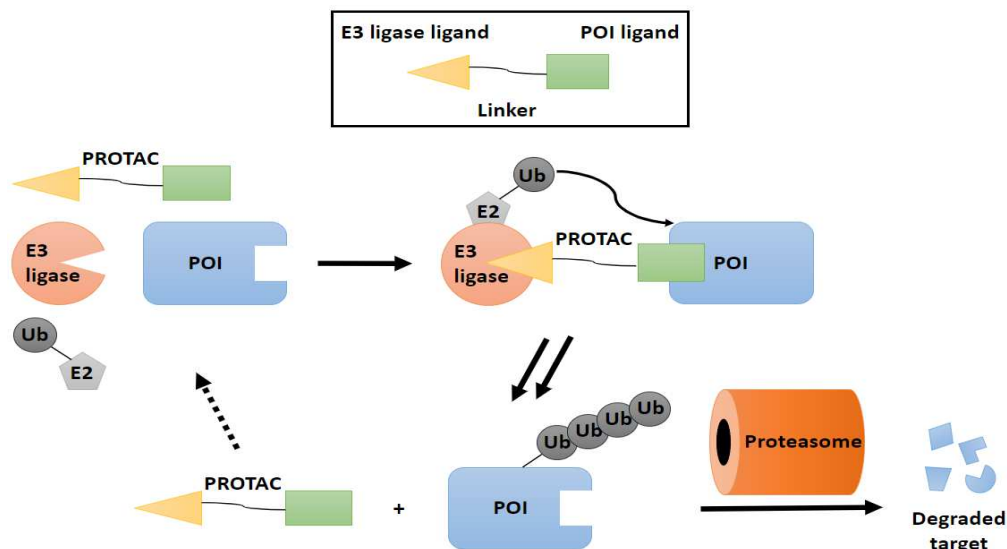
M102 Understanding Proteolysis Targeting Chimeras

Martin Screen ¹ James McCabe ², Mark Wilson ¹, Clare Mahon ¹, Jonathan Steed ¹, Sean Askin ³

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Caption: PROTACs bind simultaneously to the protein of interest and an E3 ligase to form a ternary complex, ubiquitylating the protein before its degradation.

Targeted protein degradation (TPD) is an emerging therapeutic modality with the potential to tackle disease-causing proteins previously deemed "undruggable" with conventional small molecules. In the 20 years since the conception of a proteolysis targeting chimera (PROTAC), a molecule capable of harnessing the ubiquitin-proteasome system to degrade a target protein, TPD has moved from academia to industry and is attracting substantial interest, with more than 10 PROTACs now in clinical trials.¹ However, PROTACs are very poorly water-soluble and face challenges regarding their development into drug products with sufficient bioavailability. Formulation strategies successfully employed for other poorly water-soluble small-molecule pharmaceuticals, such as amorphous solid dispersions, may help to improve their bioavailability by increasing their solubility and/or dissolution rate.²

Pre-formulation studies are required first to understand the physicochemical properties of PROTACs before any such strategies can be implemented, since there is very little literature in the nascent field of PROTACs formulation.² Understanding the role non-covalent interactions have on both crystal packing and aggregation in solution is an important step for implementing various formulation strategies. We are currently investigating the crystallisability, stabilisation of amorphous solid forms, formation of coamorphous systems and inclusion compounds of an estrogen-degrading cereblon PROTAC, as well as studying its aggregation behavior in aqueous and other polar media.

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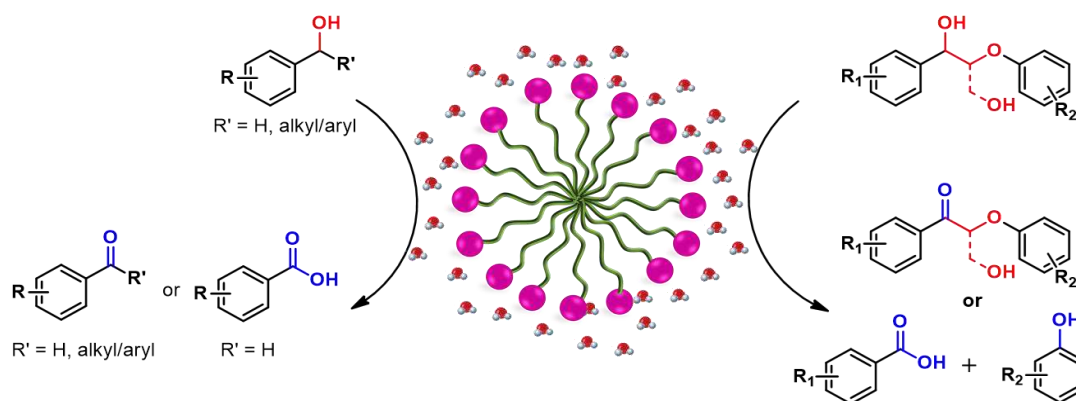
Abstract No: M103

M103 A Molybdenum Based Metallomicellar Catalyst for Controlled and Selective Oxidation/Oxidative cleavage of Feedstock Materials in Water under Open Air

PRAGYANSMRUTI SUNANI ¹ Prabaharan Thiruvengadam ², Dillip Chand ²

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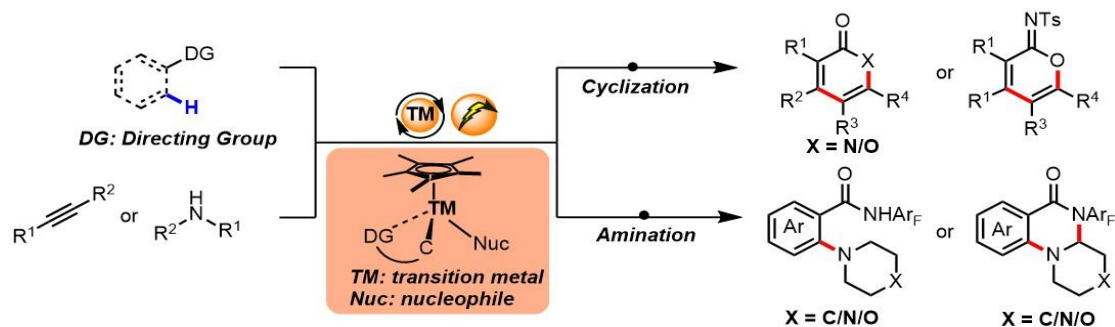
Micellar systems are known as efficient catalysts for various organic transformations that are performed under aqueous conditions.¹ A suitable micellar medium accommodates the organic substrates in its hydrophobic core which helps to solubilize the relevant substrates in water medium and increases the rate of the reactions. Commercially available or designer surfactants are well explored for such transformations in the absence or presence of suitable transition metal components. However, micelle forming metal complexes termed as metallomicellar systems are relatively less explored in this area of research. Hence, we developed molybdenum based metallomicellar catalysts for selective oxidation of sulfides,² activated alcohols,³ and activated/unactivated C(sp³)-H bonds⁴ to corresponding oxidized products in water, where the anionic coordination entity is the reactive catalyst component and the cationic long chain form the micellar aggregation. Although, above-mentioned metallomicellar systems are efficient, the disadvantage is their unstable nature under atmospheric condition and the position of metal units in micellar aggregation of reaction medium need to be addressed further. Herein, we present a new surfactant-based molybdenum complex (**Mo1**) where the coordination entity and long chain are attached with covalent bond. The complex **Mo1** is explored for controlled and selective oxidation of feedstock materials like alcohols to corresponding aldehydes/ketones and acids in water under open air, for the first time. Also, the developed methodology has been extended for the oxidative cleavage of β -O-4 linkages and real lignin to their corresponding carbonyl compounds. The asset of this strategy has been highlighted by its functional group tolerance, recyclability experiments, and upscale multi-gram synthesis. Further, a plausible mechanism has been proposed on the basis of few controlled experiments, kinetic, and computational studies.

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Abstract No: M104

M104 Transition Metal Catalyzed Electrochemical C-H Functionalization

YiKang Xing ¹ Qiliang Yang ², Fraser Stoddart ¹, Tiansheng Mei ²¹ Northwestern university, Evanston, United States² Shanghai Institute of Organic Chemistry, Shanghai, China

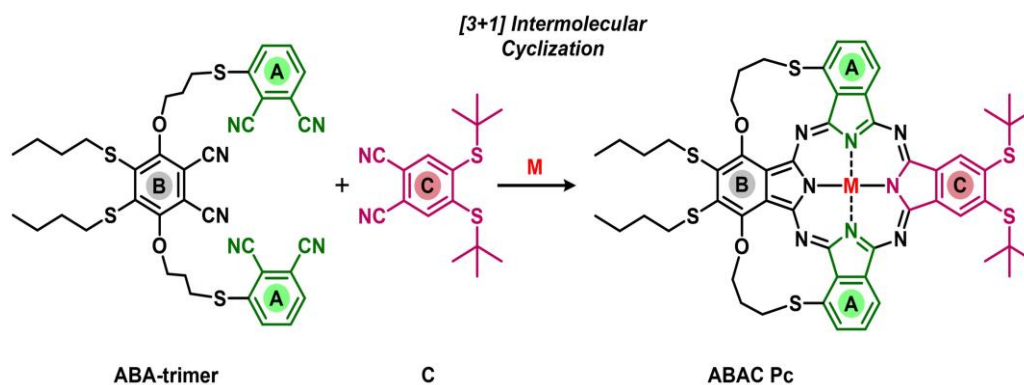
Caption: Transition Metal Catalyzed Electrochemical C-H Functionalization

Electrochemical organic synthesis has received tremendous attention in recent years.¹ The synergistic use of electrochemistry and transition metal catalysis has shown advantages in site-selective, bond-forming steps as well as functional group tolerance.² Moreover, dangerous and toxic redox reagents can be avoided, thus decreasing the chemical waste and undesired by-product reductive elimination from the metal center. Electrochemical C-H functionalization represents one of the most promising reaction types among many transformations since this process avoids prefunctionalization of substrates and provides novel retrosynthetic disconnections. Through synergistic use of electrochemistry and transition metal catalysis, we successfully achieved several different C-H functionalization reactions including cyclization of acrylic acids with alkynes, cyclization of acrylic amides with alkynes and C-H amination. These reactions also provided powerful methods to access useful chemical compounds such as α -pyrone, α -pyridone, arylamine and dihydroquinazolinone. By isolating possible intermediates in the reaction, DFT calculation and other mechanistic experiment, the mechanism of reaction was carefully studied. Looking forward, it is our belief that the merger of electrochemical methods and transition metal catalysis will continue to develop as a dynamic and promising field of research for modern synthetic methodology, and such reactions will be embraced by more and more chemists³.

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M105 Synthesis of Low-Symmetry Phthalocyanines via [3+1] Intermolecular Cyclization Reaction

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Caption: Synthetic scheme for the synthesis of low-symmetric phthalocyanine

Phthalocyanines (Pc) are a class of π -conjugated heteroaromatic macrocycles, consisting of four isoindole rings linked by nitrogen bridges. Upon introducing asymmetry, the molecular structure gets perturbed electronically allowing a fine-tuning of the physical properties. However, the chemistry of structurally modified low-symmetric phthalocyanine has received mediocre attention than that of Pc^{2-} or Pc metal complexes with D_{4h} symmetry. In general, Pc's are synthesised via the cyclotetramerization of phthalonitriles or from other precursors such as phthalic anhydrides, phthalimides, 1,3 diiminoisoindolines, and phthalamides.¹ The mixed condensation reactions using multiple precursors limit the feasibility of the formation of low-symmetric Pc's by troublesome chromatographic separation owing to the identical molecular weight and properties of the product formed.

Controlled formation of target Pc with a minimal amount of side products could be achieved by a [3 + 1] approach i.e., a base-promoted condensation of pre-linked trisphthalonitrile (ABA-trimer) and a free phthalonitrile (C) in the presence of a metal template (M).^{2,3} We have successfully synthesised the subunit B of ABA-trimer with *n*-butylthio linkers at the β -position and propoxy linkers at the α -position. Correspondingly, the propoxy linkers at the α -position of subunit B are connected to the α -position of phthalonitrile A, via a sulphur atom constituting the targeted trimer. Eventually, the phthalocyanine derivative is obtained via the cyclization reaction of ABA trimer with 4,5-bis(tert-butylsulfanyl) phthalonitrile (C).

With improved selectivity and yield, this approach could be pursued for the preparation of low-symmetrical phthalocyanines having hydrophilic and/or lipophilic moieties attached covalently. Also, the thio-linker attached to the α -position could induce pronounced effects on their structural properties. Moreover, the pre-connected ABA-trimer and free phthalonitrile C can be appropriately chosen to generate exotic phthalocyanine derivatives for varied applications.

This work was supported by EFSA-CDN project (reg. No. CZ.02.1.01/0.0/0.0/16_019/0000841) co-funded by the European Union.

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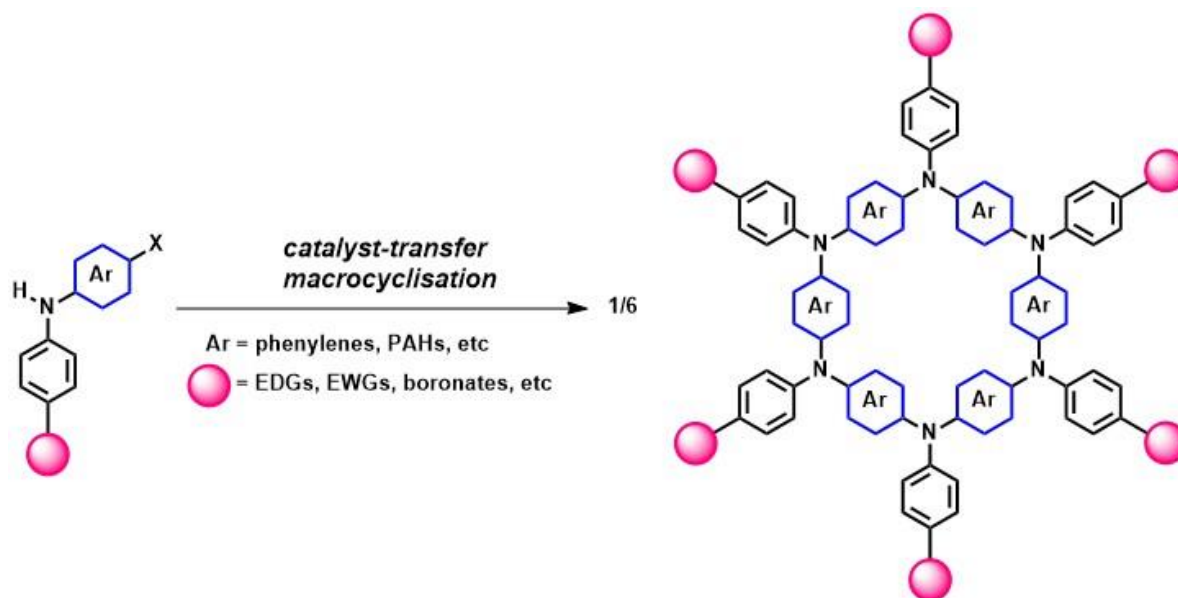
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Abstract No: M106

M106 A cornucopia of ouroboroi: A general catalyst-transfer C-N macrocyclisation for aza-paracyclophanes

Josue Ayuso-Carrillo Davide Bonifazi, Federica Fina

University of Vienna, Vienna, Austria



Caption: Catalyst-transfer macrocyclisation for aza-paracyclophanes

Aza[1_n]paracyclophanes display interesting multi-redox activity and optoelectronic properties due to their cyclic nature and the presence of nitrogen atoms.¹ Their incorporation into desired functional materials² is limited mainly due to their challenging synthesis that require multi-step procedures and difficult purifications.

A catalyst-transfer macrocyclisation (CTM) process to form aza-paracyclophanes based on the Buchwald-Hartwig cross-coupling is described. The discovery, development, and scope of CTM, as well as mechanistic insights via combined experimental and computational approaches are discussed. A range of rationally designed simple heterobifunctional monomers efficiently undergo CTM in one-step to form exclusively macrocycles, with predominantly 6-membered rings obtained. Structural and steric/electronic diversity of these macrocycles are exemplified by the introduction of oligo-phenylenyl and annulated arylens (naphthalenyl) in the inner macrocyclic framework, as well as electron withdrawing/donating groups or boronate esters in the macrocyclic periphery. The methodology features mild reaction temperature, short reaction times and excellent isolated yields. Photophysical and electrochemical characteristics of select examples are illustrated.

Thus, the generality of CTM as a powerful method to make a plethora of aza-paracyclophanes with multiple functionalities is demonstrated. Further extension to multiply decorated hexaaza[1₆]paracyclophanes and their congeners is currently underway in our laboratories.

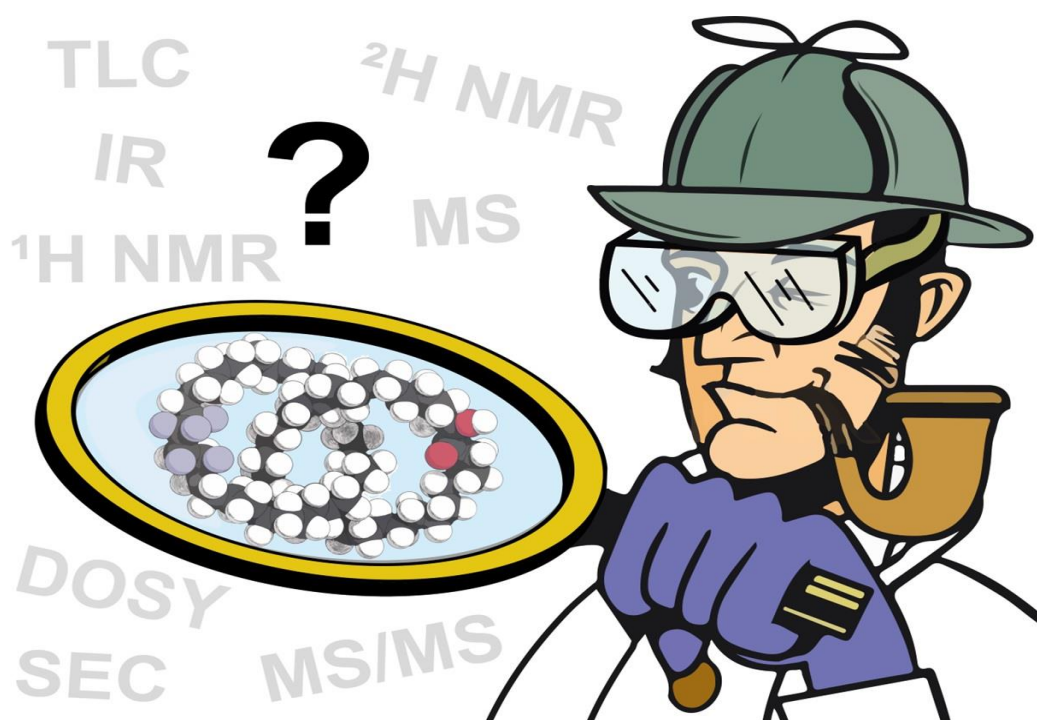
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M107 In Search of the First Catenane

Andrei S. Baluna¹, Albano Galan¹, David A. Leigh^{*1,2}, Gareth D. Smith¹, Justin T. J. Spence¹, Daniel J. Tetlow¹, Iñigo J. Vitorica-Yrezabal¹ and Min Zhang^{1,2}

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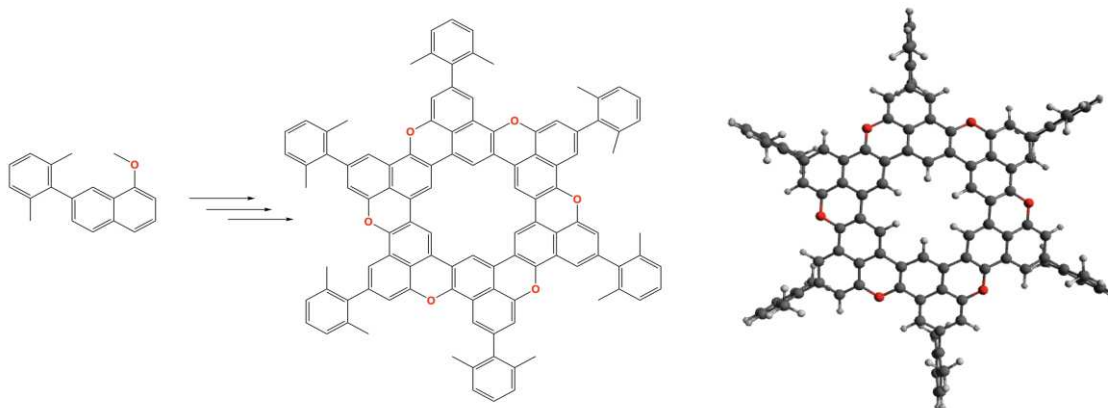
We repeat the first claimed [2]catenane synthesis, reported by Wasserman over 60 years ago, in order to confirm whether or not a non-template, statistical, synthesis by acyloin macrocyclization does, indeed, form mechanically interlocked rings. The lack of direct experimental evidence for Wasserman's catenane has led to it being described as a "prophetic compound", a technical term used in patents for claimed molecules that have not yet been synthesized. Contemporary synthetic methods were used to reconstruct Wasserman's deuterium-labeled macrocycle and other building blocks on the 10-100 gram reaction scale necessary to generate, in principle, ~1 mg of catenane. Modern spectrometric and spectroscopic tools and chemical techniques (including tandem mass spectrometry, deuterium nuclear magnetic resonance (NMR) spectroscopy and fluorescent tag labeling) were brought to bear in an effort to detect, isolate and prove the structure of a putative [2]catenane consisting of a 34-membered cyclic hydrocarbon mechanically linked with a 34-membered cyclic α -hydroxyketone.

Abstract No: M108

M108 O-Doped Kekulene: Synthesis, Electronic Structure and Aromaticity

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Cycloarenes are polycyclic aromatic hydrocarbons (PAHs) with an enclosed cavity consisting of circularly fused π -conjugated rings, widely studied as repeating unit of periodic “graphene meshes”.¹ The incorporation of heteroatoms such as N, O, and S into cycloarenes leads to heterocycloarenes, which display enhanced stability, different geometries and electronic properties when compared to the all-carbon analogues.² Despite their great potential application in host-guest assemblies and organic optoelectronics,³ the significant synthetic challenge has led to only a handful examples.

Herein we report the design and synthesis of an O-embedded Kekulene derivative as a model unit of nanoporous graphene oxide. The methoxynaphthalene unit was chosen as building block, modified with a xylyl moiety to provide solubility. Such a unit was used to prepare the macrocycle precursor, followed by periphery fusion strategy via Pummerer oxidative cycloetherification.⁴

Both the symmetry and the charge distribution of the frontier electronic levels in various electronic states have been addressed computationally. Further experimental studies to evaluate its aromaticity, as well as the p-type semiconductor behaviour are currently underway in our laboratories.

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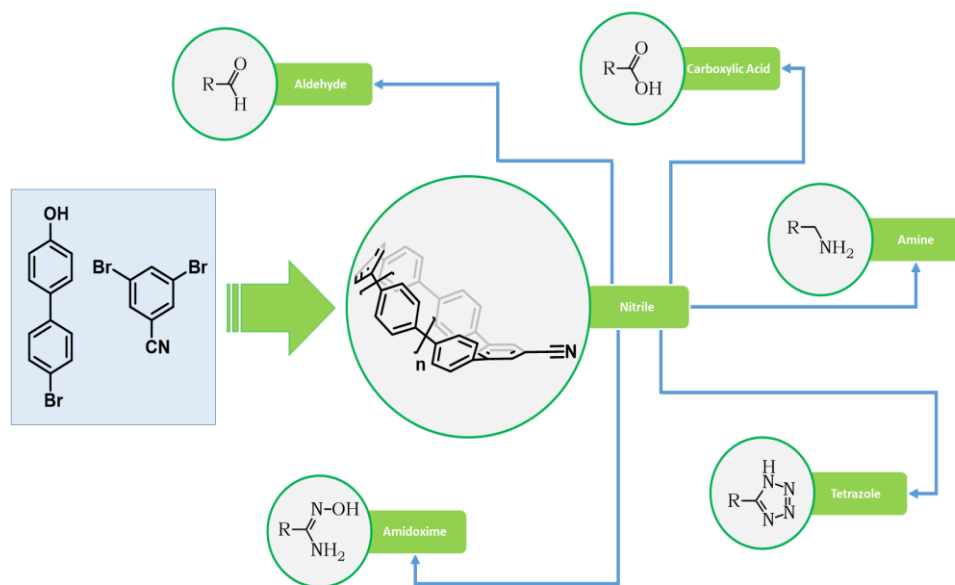
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Abstract No: M109

M109 Synthesis and Properties of Substituted meta[n]Cycloparaphenylenes

Felix Bernt Hermann Wegner

Institute of Organic Chemistry, Justus-Liebig-University, Giessen, Germany

Caption: Synthesis of CN-*m*[*n*]CPPs and conversion of the vast synthetic potential of the nitrile scaffold.

Since its first synthesis in 2008 by Jasti and Bertozzi, [*n*]cycloparaphenylenes (*[n]*CPPs) have been intensively studied in organic synthesis, as well as material sciences.^[1,2] Two exceptional properties of [*n*]CPPs beside the highly strained macrocyclic structure are the size independent absorption band (around 340 nm), and the red-shifting fluorescence maximum with decreasing ring size.^[3,4] The quantum yield decreases with smaller ring size, for which reason [5]- and [6]CPP show no fluorescence.^[5] In 2019, Jasti and coworkers presented a synthesis for *meta*[*n*]CPPs, where one phenyl unit is connected in *meta* position. Interestingly, for these two derivatives the fluorescence is turned again by breaking the orbital symmetry.^[6]

Based on this fundamental work, we present three different sized cyano-substituted *meta*[*n*]CPPs. Bearing such versatile functional group at the *meta*-unit opens a vast synthetic potential for various chemical transformations. Because [10]CPP acts as an excellent host for fullerenes,^[7] cyano-*meta*[10]CPP was explored in host-guest studies with fullerene (C₆₀).

The convenient handle of cyano-substituted *meta*[*n*]CPPs with its intriguing photophysical properties and potential in supramolecular chemistry will attract increasing attention in organic synthesis, as well as material sciences in the future.

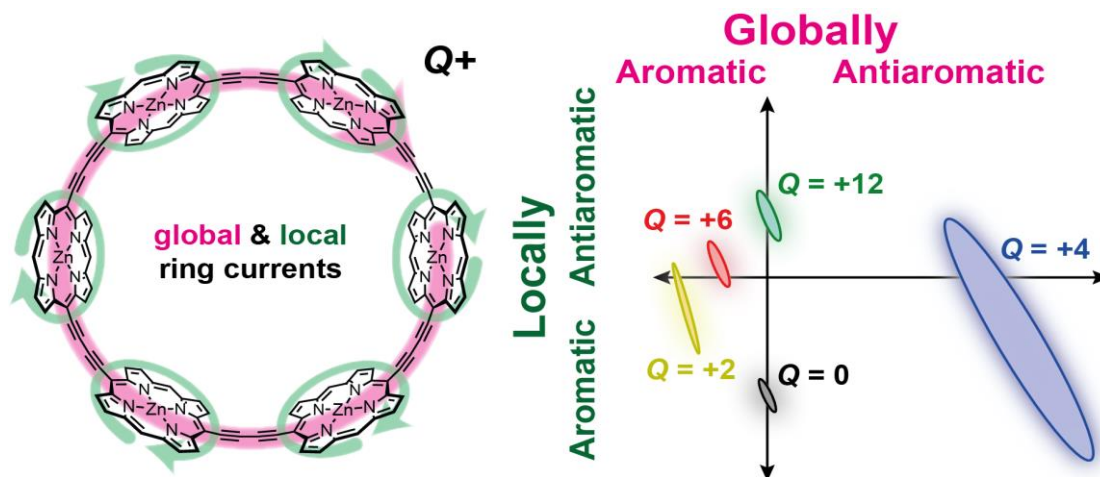
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M110 Disentangling global and local ring currents

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Caption: Global and local ring currents in porphyrin nanorings

It is surprisingly difficult to assign the aromaticity of organic molecules. The most common way is by observing chemical shifts in NMR spectroscopy: in aromatic compounds, such as benzene, nuclei outside of the aromatic ring are deshielded. This effect is usually sufficiently diagnostic for simple molecules, but when multiple aromatic compounds are conjugated in series, emergent properties, such as “global” aromaticity, can arise. Such properties have been observed in porphyrin nanorings, in which global ring currents can be observed in some oxidation states.¹ It then becomes difficult to interpret the NMR spectra of these compounds: do the (de)shielding effects we observe in the spectrum come from local porphyrin ring currents or global nanoring ring currents? We have developed a method to disentangle these individual contributions, allowing us to quantify global AND local ring currents in complex molecules.²

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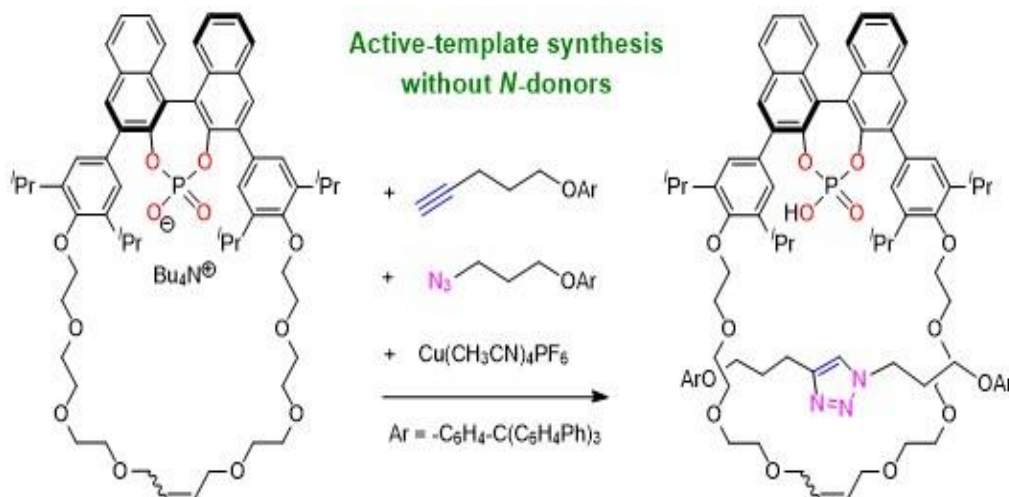
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Abstract No: M111

M111 Novel active-template strategies for the synthesis of interlocked molecules

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Caption: Rotaxane formation via a phosphate-based active template method.

Active template methods are well known for their reliability towards the synthesis of mechanically interlocked molecules.¹ The starting macrocycles often contain a pyridine or bipyridine unit in which a metal ion can be coordinated. This allows for the bond-formation to occur through the macrocycle, thus establishing the mechanical bond. For rotaxane-synthesis via the active-template methods, most commonly an alkyne and an azide half-thread are used, which upon Cu-catalyzed click-reaction through the macrocycle yields rotaxanes with a triazole-functionalized thread.

We have previously reported the synthesis of BINOL-phosphate rotaxanes via a passive-template strategy by making use of a phosphate-ammonium interaction.² Herein, the synthesis of chiral BINOL-based rotaxanes via an active metal template strategy is reported. This kind of active template relies on a nitrogen free phosphate-donor which is used to coordinate copper(I) in the cavity of the BINOL-macrocycle. Click-reaction of alkyne and azide half-threads yields the chiral rotaxanes, which might find application as catalysts in Brønsted acid catalysis (in their POOH form) or Lewis acid catalysis (when used as phosphate metal complexes).

This represents a key extension of previously known active-template methods, for the first time allowing for the use of nitrogen-free macrocycles that do not contain a pyridine or bipyridine unit.

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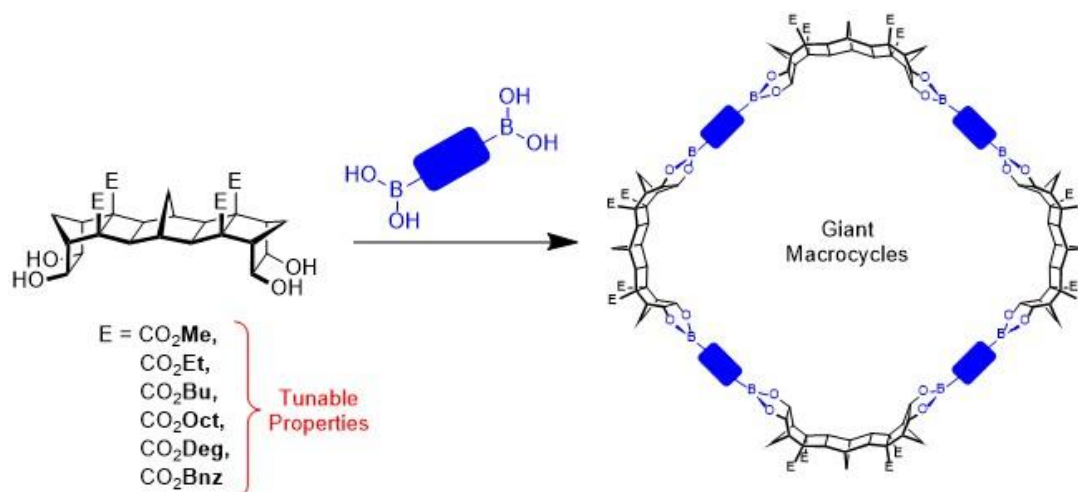
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Abstract No: M112

M112 Giant macrocycles with tuneable properties from fused polynorbornane frameworks

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Caption: Self-assembly of [4+4] macrocycles from fused polynorbornane tetraols and diboronic acids.

The self-assembly of carefully designed molecular building blocks into complex, functional architectures represents a key focus of supramolecular and macrocyclic chemistry. Fused polynorbornanes are a class of rigid hydrocarbons with well-defined molecular geometries, and through a series of stereospecific cycloaddition protocols these frameworks can be tailored to specific geometries and functionalities. As such they are noteworthy building blocks for supramolecular assemblies.

Self-assembly protocols that use boronic acids and catechols have been successful in accessing a wide range of supramolecular assemblies (1), however the use of fused polynorbornane diols in the self-assembly of supramolecular structures has not yet been reported, despite evidence that norbornane diols react far more effectively than catechols with boronic acids (2).

This research is focused on the development of a new series of covalent organic structures based on fused polynorbornane frameworks. The reaction of fused polynorbornane tetraols with diboronic acids to form macrocycles with tuneable properties will be presented, as well as strategies for the functionalisation of the surfaces and cavities of the macrocycles.

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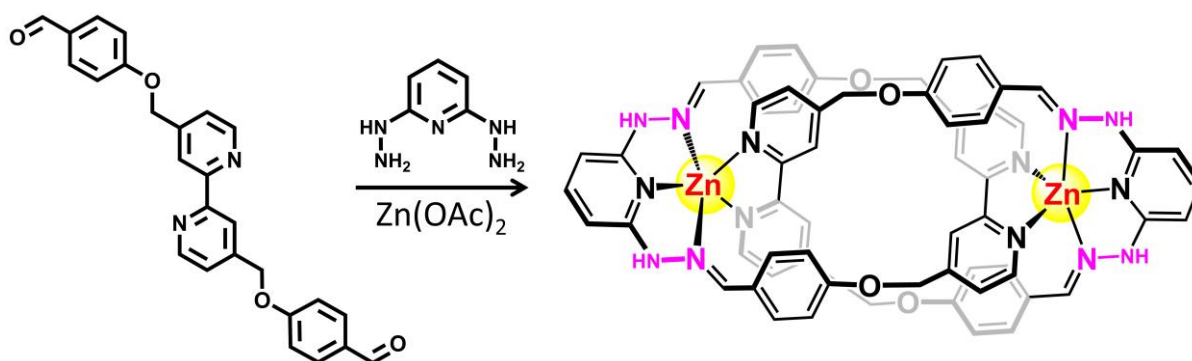
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Flash Talks / 26-06-2023 16:40 - 17:00 Harpa - Silfurberg A/B 2nd floor

M113 Synthesis of dihydrazonepyridine-bipyridine based [2]catenane via hydrazone condensation

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Caption: Scheme 1: bFPB and PDH are reacted in the presence of zinc acetate to synthesize hydrazone [2]catenane

Mechanically interlocked molecules (MIMs) and topologically unique molecules had been an interest to scientists since the 1960s due to its pharmaceutical and industrial applicability as molecular machines, catalysts, and molecular cargo carriers. While imine bond condensation had been a widely used method of MIM synthesis due to its advantage of participating in dynamic covalent chemistry (DCC) for self-correction, it has low thermal and acidic stability, vastly limiting its applications. We report a novel [2]catenane synthesized via hydrazone condensation between bFPB (4,4'-bis(((4-formylphenyl)oxy)methyl)-2,2'-bipyridine) and PDH (2,6-pyridine dihydrazine) in the presence of zinc salt. (Scheme 1) The synthesized [2]catenane is made of two dihydrazonepyridine-bipyridine macrocycles interlocked with two zinc ions coordinating 5 nitrogens (2 of bipyridine and 3 of bishydrazone pyridine). The resulting [2]catenane was characterized by NMR spectroscopy, mass spectrometry, and X-ray crystallography, demonstrating the formation of stable and well-defined structures. Our results show that hydrazone functionalized catenane exhibits higher thermal and acidic stability as compared to imine-based catenanes introduced before in literature¹. Thus, the reported hydrazone [2]catenane is anticipated to be applicable to a wider pharmaceutical and industrial settings with harsher chemical environments. We believe that in the future hydrazone functionalization will open new grounds for all other imine-based MIMs in widening their applications as well.

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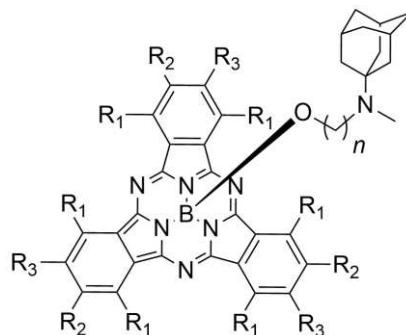
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Abstract No: M114

M114 Subphthalocyanines Bearing an Amino Adamantyl Substituent as Candidates for Supramolecular Assembly with Cucurbiturils

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- 1 $R_1 = \text{—S—}$; $R_2 = R_3 = \text{H}$; $n = 2$
- 2 $R_1 = \text{H}$; $R_2 = R_3 = \text{—S—}$; $n = 2$
- 3 $R_1 = R_2 = R_3 = \text{—S—}$; $n = 2$
- 4 $R_1 = R_3 = \text{H}$; $R_2 = \text{I}$; $n = 2$
- 5 $R_1 = R_3 = \text{H}$; $R_2 = \text{I}$; $n = 6$

Caption: Scheme 1

Photodynamic therapy is a promising approach to cancer treatment that relies on the administration of a photosensitizer and subsequent illumination of the tumor. The generated oxidative stress leads to the activation of several mechanisms of cell death.¹ Subphthalocyanines (SubPcs), chemically versatile molecules whose properties can be tuned through axial as well as peripheral substitution, belong among the novel groups of photosensitizers. Due to their macrocyclic core, they suffer from low solubility and high aggregation in water, even though they are less prone to the latter thanks to their conical π surface.²

This project aimed to overcome these drawbacks limiting the biological application of SubPcs by the formation of supramolecular host-guest complexes with highly hydrophilic cucurbiturils (CBs). CB[7] forms one of the most stable supramolecular interactions in water with 1-amino adamantane,³ which was therefore proposed as the axial substituent on the SubPc core.

Synthesis of the originally intended compounds **1**, **2**, and **3** with ethylsulfanyl moieties at the periphery was unsuccessful. Therefore, alternative structures **4** and **5**, bearing iodine atoms as peripheral substituents, were designed. They were successfully prepared *via* cyclotrimerization of the respective phthalonitriles with boron trichloride, and subsequent nucleophilic substitution of chlorine by amino adamantane derivatives. Their photophysical properties (including the quantum yields of singlet oxygen and fluorescence), and host-guest interactions with CB[7] were investigated.

This work was supported by Charles University (GA ĀR 21-14919J).

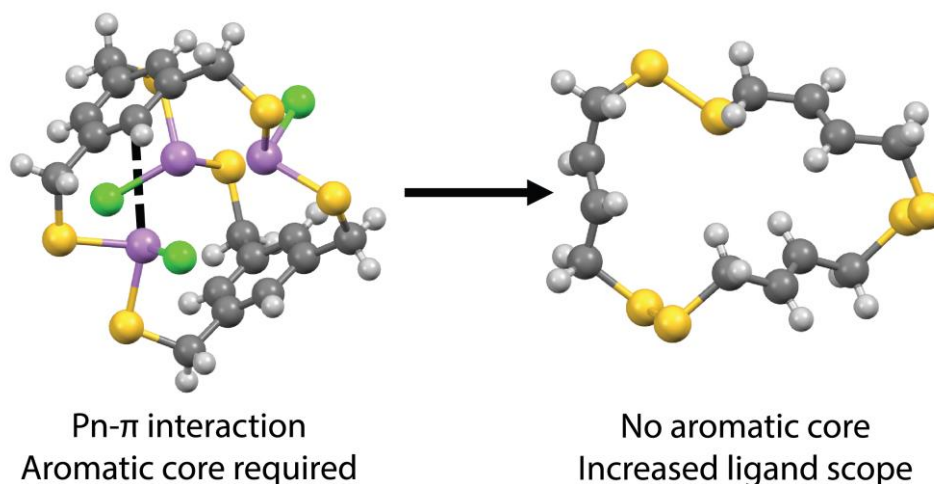
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M115 Expanding the library of pnictogen-assisted self-assembly reactivity

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Caption: Figure 1. Crystal structures of pnictogen-thiolate cryptand, with Pn- π interaction shown, and butene-1,4-dithiol disulfide trimer macrocycle.

Previous work in the Darren W. Johnson lab has shown that pnictogen-assisted self-assembly, where a pnictogen (Pn) is used as a directing agent to bring together multiple thiolated ligands into discrete disulfide macrocyclic species, is effective with benzylic thiol motifs¹. This was initially thought to work because of a favorable interaction between the Pn and the π -system of the ligand's aromatic core, an interaction which was observed in crystal structures of the Pn-thiolate cryptands². More recently, this idea has been investigated and these methods have proven effective for the self-assembly of thiolated ligands with a wide range of motifs, including longer core to thiol linkages, like ethanethiols, and non-aromatic cores^{3,4}. Further efforts, described in this poster, are being made to continue expanding the scope of available ligand reactivity for these methods, moving towards the self-assembly of more complex and targeted macrocycles. Current work involves the use of various core to thiol-linkage lengths, and assembly in diverse solvents.

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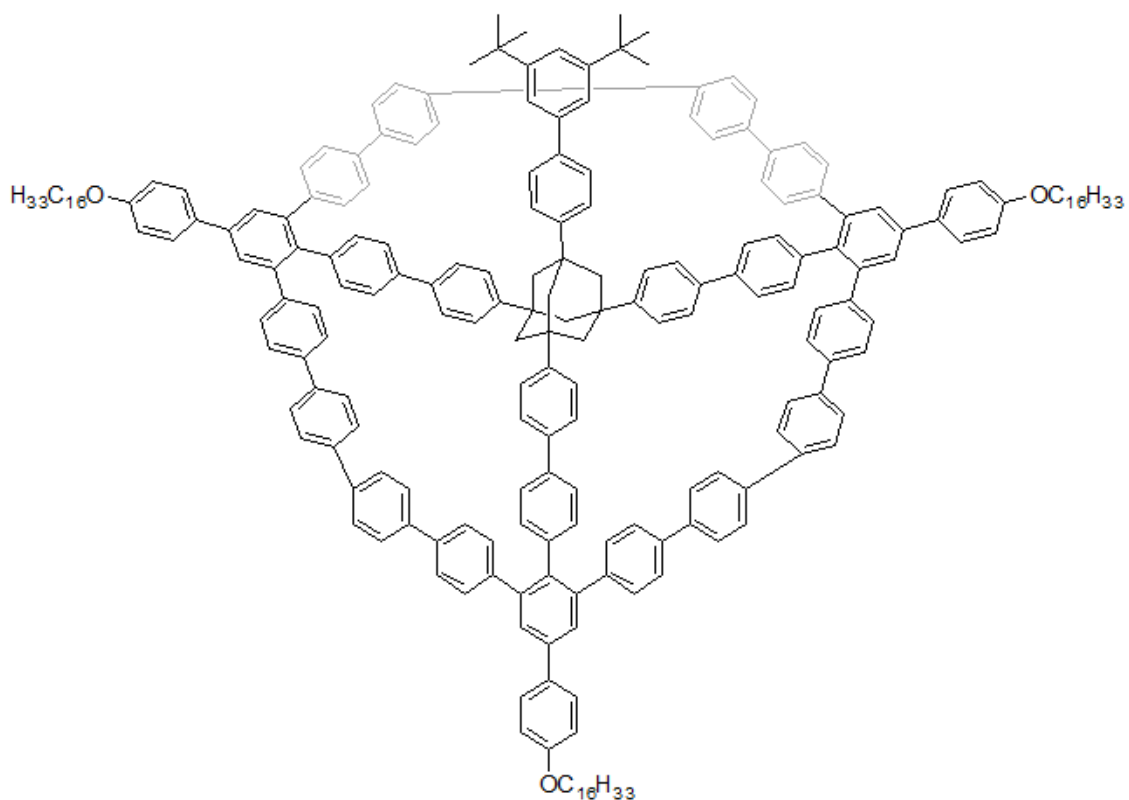
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Abstract No: M116

M116 Phenylene-based molecular spoked wheel with orthogonal pillar

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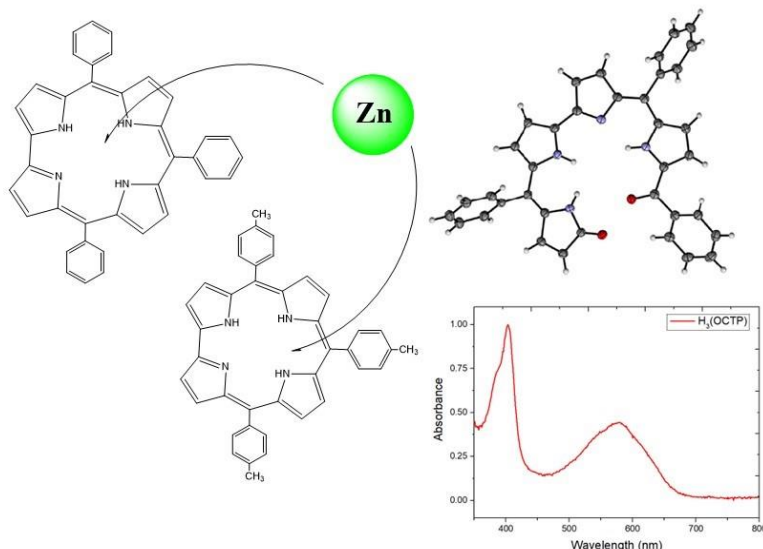


Molecular spoked wheels (MSWs) are established as broadly applicable compounds with regards to two-dimensional (2D) surface patterning, as they can function as a platform for functionalization in 3D.[1] Other attractive molecular platforms are - despite their strain - cyclophanes as they have shown highly crystalline surface decoration as well while carrying moieties which protrude from the surface at the intraannular bridges.[2] Combining the two molecular platform approaches may lead to new insights into how the volume phase above a surface can be addressed. Here we report on the synthesis of a phenylene-based MSW with an orthogonal pillar while the STM investigations are in progress.

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M117 Zinc aryl-corroles: synthesis and characterization

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From the discovery of corrole in 1965, this macrocycle assumed a leading role in the porphyrinoids family due to the development of simple and highly efficient synthetic strategies from commercially available precursors, able to simplify the synthesis process.^{1,2} The simple and direct synthesis of arylcorroles and their specific properties prompted to investigate their coordination chemistry.³ Corroles highlight a notable coordinative versatility with the possibility to introduce different metals allowing the expansion of so-called Periodic Table of Metallocorroles.⁴ Indeed, their trianionic character and their high electron density make the corrole a strong σ -donor able to stabilize metals in high oxidation state with the formation of corrole π -radical can act as a non-innocent ligand.⁵ These features make corrole complexes of interest in a huge range of applications. However, in the overview of elements of the periodic table, zinc ion widely used in the porphyrin field has been scarcely studied in the case of corroles. One of the reasons is surely to be ascribed to the oxidation number of the metal, which is not optimally combined with the trianionic character of macrocycle. The first Zn metalation example is reported by the group of Bröring⁶ that, exploiting the oxidation of the macrocycle and the formation of corrole radical, was able to isolate the corresponding zinc complex, even though a full characterization of the product and explanation of the mechanism is still missing. Therefore, this work aims to study the complexation of aryl corrole with zinc salts leading to its spectroscopic and electrochemical characterization.

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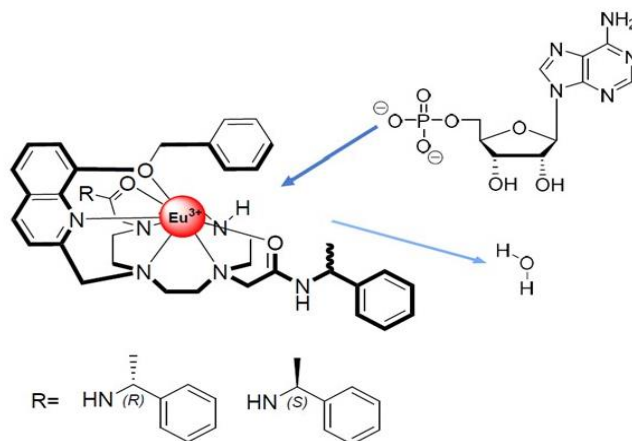
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Abstract No: M118

M118 Selective sensing of AMP through total emission and circularly polarised luminescence by sterically demanding chiral Eu(III) complexes

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Caption: Binding of adenosine monophosphate to tricationic europium (III) complexes

The design of molecular receptors that bind and sense anions in biologically relevant aqueous solution is a key challenge in supramolecular chemistry.¹ A variety of receptors have been designed that signal anion binding by emission spectroscopy, whereas receptors that provide a change in circularly polarised luminescence (the emission equivalent of circular dichroism) are comparatively rare. Adenosine monophosphate (AMP) represents a valuable but elusive target for supramolecular detection because of its structural similarity to the more negatively charged anions, ATP and ADP. We report a pair of new tricationic macrocyclic Eu(III) complexes, bearing chiral phenylethyl amide arms, capable of selectively sensing AMP in aqueous solution, with minimal interference from ATP or ADP. The receptor contains a sterically demanding 8-(benzyloxy)-quinoline pendant arm that coordinates to the metal centre, creating a binding pocket suitable for AMP, whilst excluding potentially interfering chelating anions (e.g. ATP, bicarbonate and lactate).

The sensing selectivity of our Eu(III) receptor follows the order AMP > ADP > ATP, which represents a reversal of the order of selectivity observed for most reported nucleoside phosphate receptors.^{2,3} The presence of two chiral phenylethylamide pendant arms leads to preferential stabilisation of one stereoisomeric Eu(III) complex, producing a weak circularly polarised luminescence (CPL) signal in water. Pleasingly, we observed a much stronger induced CPL signal upon binding of AMP, thereby offering vast potential for the development of emissive probes that can signal the presence of chiral biological phosphates by enhancement of their CPL spectral fingerprint.^{4,5}

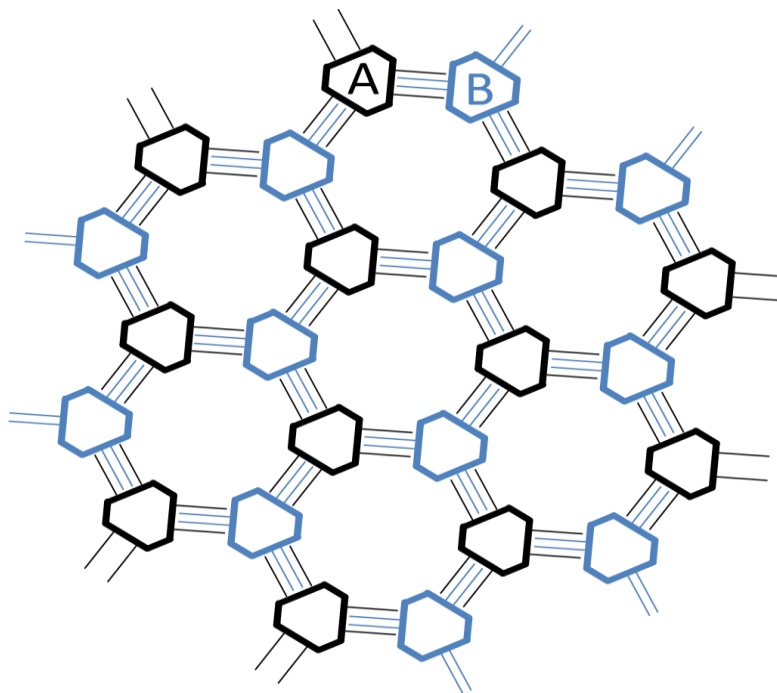
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M119 Achiral Honeycomb Nanopatterns

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Caption: Figure 1: Proposed achiral honeycomb nanopattern of the alkoxy-substituted macrocycles A and B (schematically).

The adsorption of arylene-alkynyls on solid surfaces is an effective way to produce long-range ordered two-dimensional (2D) nanoscale functional arrays. Alkyl side chains enhance the solubility of the respective compound in organic solvents and mediate the adsorption of the macrocycles on highly oriented pyrolytic graphite (HOPG). E.g., predictable achiral honeycomb nanopatterns can be obtained by means of macrocyclic oligomers with D_{3h} symmetry, carrying pairs of side chains on each of its three sides.^{[1][2]} Here we report on the synthesis of two macrocyclic target structures, having short and wide distances of the pairs of the side chains, respectively. A binary mixture of the two macrocycles on the surface will be utilized to produce an achiral honeycomb surface structure (see Figure 1) due to complementary interdigitation of the alkoxy chains. Scanning tunneling microscopy (STM) is used to obtain submolecularly resolved insights into the nanopatterns formed.

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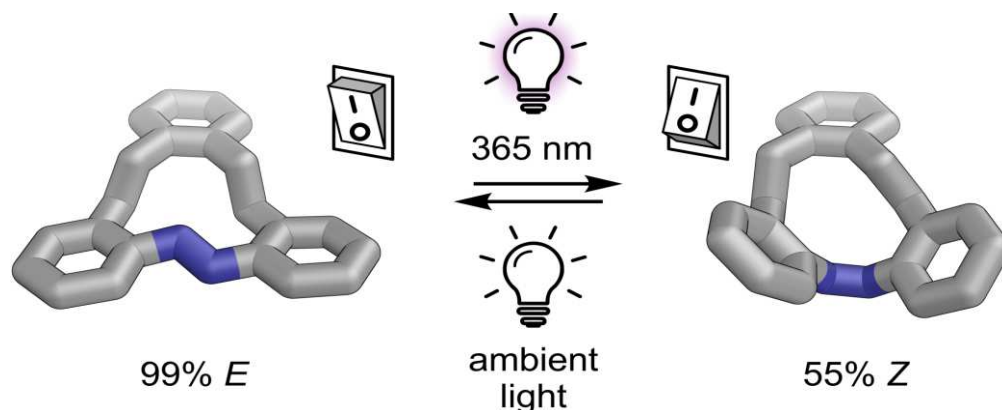
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M120 A 12-membered ring photoswitch with excellent band separation

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Caption: DFT-optimized structures (ω B97X-v def2-QZVPP) of an azobenzene photoswitch embedded in a 12-membered ring.

Photoswitchable molecules can reversibly interconvert between two different isomers. Due to the distinct, different properties of these two isomeric states of a photoswitch, they are applied in non-linear optics, data storage, biomolecules, and phase changing materials. With new applications constantly emerging, the necessity arises to continue to develop photoswitches with different properties than the already established ones. Azobenzenes are amongst the most reliably operating photoswitches. Their photoswitching can be modified by *ortho*- and *para*-substituents, respectively, as well as incorporating them into macrocycles.^[1,2]

We have synthesized a new azobenzene based photoswitch, in which the switchable azo moiety is embedded in an all-carbon 12-membered ring (Figure 1), in three facile steps with 58% overall yield. Furthermore, we modified the photoswitch by different *ortho*- and *para*-substituents (with respect to the azo group). The incorporation of the azo moiety into the 12-membered ring results in excellent separation of the λ_{\max} for $E(\pi \rightarrow \pi^*)$ and $Z(n \rightarrow \pi^*)$ by approx. 120 nm, which is important to be able to selectively address the two constitutional isomers by irradiation with different wavelengths. The ring also increases the thermal half-life $T_{1/2}$ to 16 d at 25 °C, whereas azobenzene has a $T_{1/2}$ of 1 d at the same temperature. The ability of macrocyclic photoswitch to undergo photoinduced $E \rightarrow Z$ isomerisation is moderate with a photostationary state (PSS) of 55% after irradiating with 365 nm light. $Z \rightarrow E$ isomerisation is almost quantitative even under ambient light. Intriguingly, most azo-based photoswitches occur as a mixture of their *E*- and *Z*-isomers under ambient light, with the *E*-isomer being the prominent species. Macrocyclic photoswitch, however, is 99% in its *E*-isomeric form under ambient light, potentially rendering it useful for materials applications under ambient conditions.^[3]

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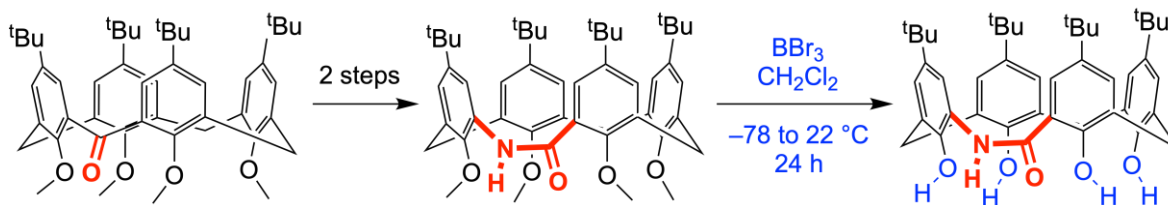
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Abstract No: M121

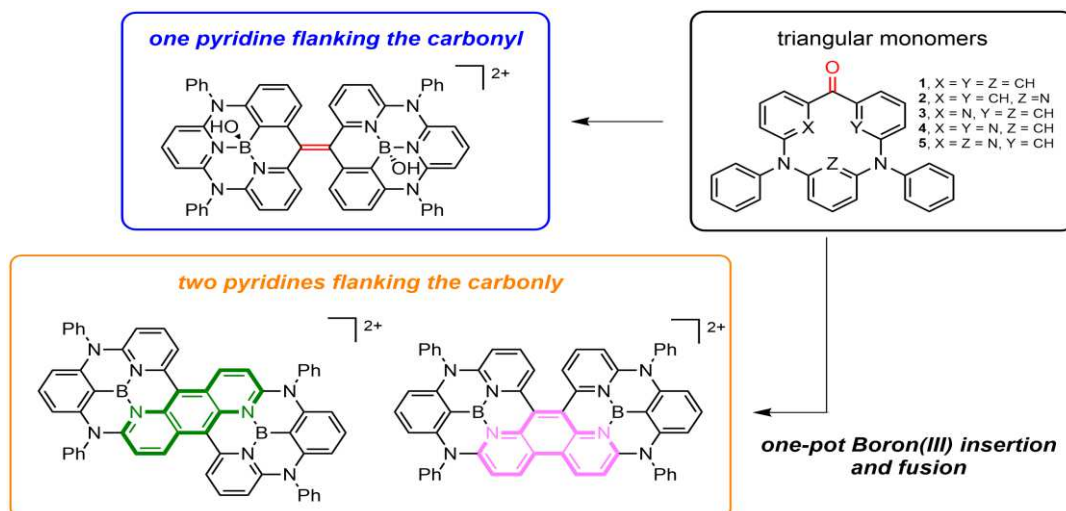
M121 An amide group incorporated in the calixarene macrocycle: synthesis, structure, and reactivity

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Calixarenes are synthetic macrocycles with well defined shapes and distinct regions of reactivity. The upper and lower rims are frequent targets for elaboration while modifications to the methylene position is considerably less explored. Transformation of a single methylene group of a tetramethoxycalix[4]arene to an amide linkage was achieved in a multistep synthesis via a ketone. Following installation of the amide, demethylation (BBr_3) gave a tetrahydroxy cis-amide in the cone conformation. Preliminary ^1H - ^1H NOESY data (75 °C, $\text{C}_2\text{D}_2\text{Cl}_4$) show that the macrocycle ring of the tetrahydroxy species is considerably more rigid than the parent calixarene. The isomerization of this species to the trans diastereomer and other reactivity will be described.

M122 Tridentate macrocyclic frames for the bottom-up synthesis of B,N-doped π -extended systemsMarco Farinone ¹, Miłosz Pawlicki ¹ Monika Kijewska ², Joanna Cybińska ², Miłosz Siczek ²¹ Jagiellonian University, Kraków, Poland² University of Wrocław, Wrocław, Poland

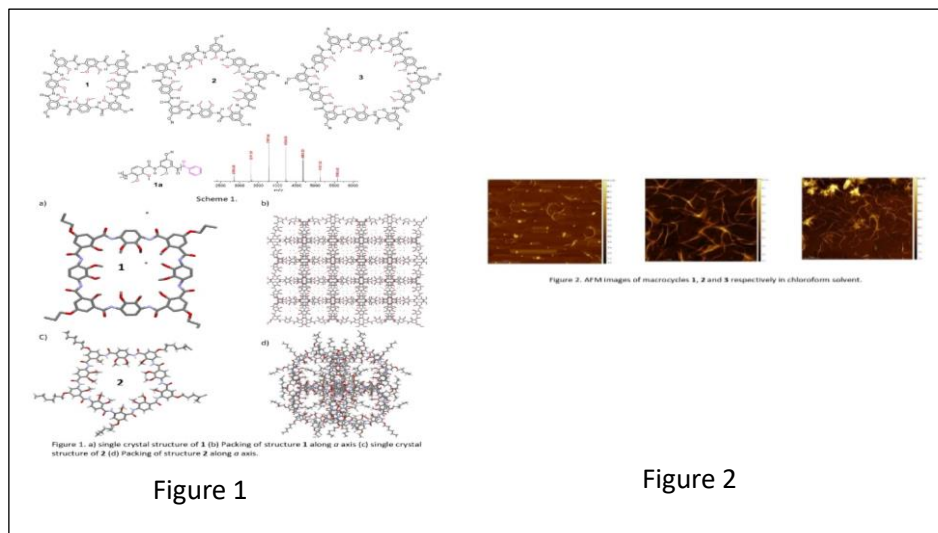
Caption: Figure 1. Triangular monomers obtained in this work and the fused boron(III) complexes.

The doping of graphene and other polycyclic aromatic hydrocarbons leads to substantial modification of their photophysical properties opening many possibilities for specific applications.[1] On the other hand, preparing defected systems requires a lot of effort. The top-down approach has shown substantial limitations leading to a stronger interest in the development of the bottom-up approach which, additionally, has the great advantage of precisely localize the point defects such as carbon-heteroatom exchange or shape alteration.[2] Interestingly, the incorporation of Boron and Nitrogen as dopants in a graphene sheet has been reported to strongly influence its structure and properties, leading to the development of sensors, electrochemical catalysts, and supercapacitors.[3] In this work, we efficiently prepared a set of triangularly shaped macrocyclic monomers that were used for the preparation of B,N-doped π -extended systems following a post-synthetic modulation of macrocycle-like tridentate space.[4] The library of monomers was prepared through Buchwald-Hartwig cross coupling reaction (Figure 1; **1-5**). All the derivatives were armed with a carbonyl moiety which was previously reported to effectively modulate the peripheral reactivity of pyridine-containing macrocycles.[5] We focused our attention on the correlation between the specific design of the monomers and the quality of the formed π -extended system. We observed that, when one or no pyridines were present, only carbonyl activation was taking place. On the other hand, when two pyridines are flanking the carbonyl subunit, B,N-doped π -extended systems were efficiently obtained. This work shows the application of a convergent approach for the formation of defected/doped systems and the precise design of macrocyclic derivatives with a carbonyl unit.

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M123 Synthesis of hollow square macrocycle as nanochannels and hollow square helices

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Macrocycles and foldamers with substantial tubular cavities are intriguing and have captured significant attention. Foldamers and macrocycles with non-collapsible hydrophilic cavities have demonstrated exceptional properties in areas such as cation recognition and highly conducting membranes.¹ Conversely, helical foldamers and macrocycles that are rich in hydrophobic interior surfaces have shown exceptional performance in the field of water permeation.² Recent work by Takuzo Aida's group³ has highlighted how these hydrophobic interior surfaces in macrocycles act as artificial water channels responsible for water permeation, using a densely fluorinated interior surface system. However, the yield of these macrocycles is low, 0.0055-0.16%, which limits their potential for use in membrane technology for water purification. Furthermore, the diacid and diamine monomers used in this system restrict the ability to synthesize helices of a specific length with narrow dispersity.

We have developed a novel category of hollow square macrocycles (**1**) with an internal diameter of 0.9 nm, as well as helices (**1a**) (Scheme 1) that feature a non-collapsible cavity of roughly 0.9 nm, and possess hydrophobic interior surfaces. Additionally, we obtained macrocycles with a diameter of 1.5 nm (**2**) and 2 nm (**3**) (Scheme 1). The square shape of the macrocycle was confirmed by the solid-state structure of (**1**). Dynamic light scattering (DLS) of these macrocycles and helices revealed significant aggregation in chloroform solution, which increased with increasing concentration. Evidence of nanochannels was found in these macrocycles, based on the crystal structure packing of **1** and **2** (Figure 1). Furthermore, the linear stacking of macrocycles **1**, **2**, and **3** was confirmed by atomic force microscopy (AFM) analysis (Figure 2)

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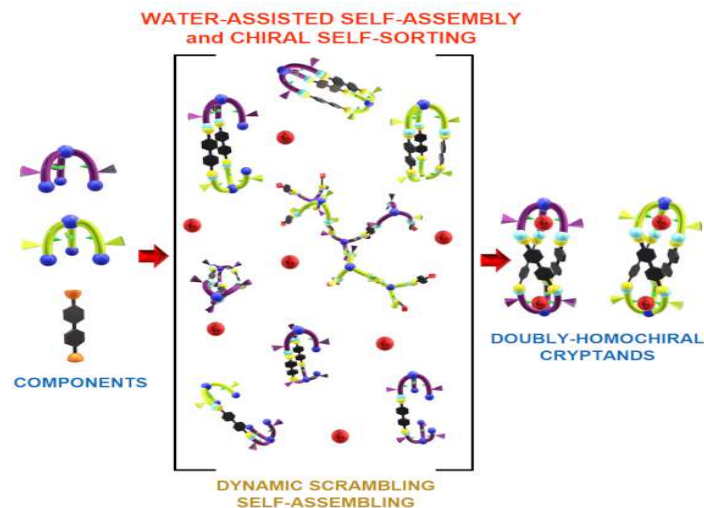
Abstract No: M124

M124 Synthesis of Dynamic Pseudopeptidic Macrobicycles: Water-assisted Self-assembly and Homochiral Self-sorting

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Caption: The supramolecular encapsulation of two water molecules stabilizes the macrobicycles and leads to homochiral self-sorting

The synthesis of preorganized three-dimensional species is generally challenging as the macrocyclization steps must always overcome competing oligomerization/polymerization processes [1]. Dynamic Covalent Chemistry (DCC) serves as a thermodynamically driven approach that minimizes the generation of such by-products as a result of the occurrence of component exchange, structural rearrangement, and error checking [2]. Albeit several inspiring self-sorting examples have been reported based on cation coordination preferences, the study of systems that contain solely organic components and are able to self-assemble into a defined outcome are still scarce.[3] Among the diverse self-sorted examples described to date, the ones experiencing chiral self-sorting (*i.e.*, the selection for a supramolecular assembly of an interaction partner with a specific chirality from a complex mixture of possible partners) are of paramount relevance as chirality is an omnipresent property in nature. In fact, an appropriate design of chiral self-sorting systems may shed light on the formation of complex molecular architectures and could contribute to an understanding of the biological homochirality.[4]

Taking advantage of the DCC approach, four different cages were synthesized by condensation of tripodal pseudopeptides with 4,4'-biphenyldicarboxyaldehyde. Whereas undesired products of polymeric nature were obtained in polar solvents, the [3+2] cryptand-type macrobicyclic architectures were obtained in excellent yields using chloroform as solvent, even at relatively high concentrations. This outcome was assigned to the encapsulation of two water molecules in the cage-like structures (favoured in apolar media) that acted as thermodynamic supramolecular templates in the self-assembling process. The final macrobicycles display a combination of two types of chirality: D,L chirality due to the asymmetric α -C centers and P,M helical chirality. The homochiral helicity found for all the enantiomerically pure molecular cages indicates strong chirality induction by the asymmetric α -C. Besides, the self-sorting properties of the different chiral pseudopeptides have been studied, resulting in high-fidelity homo-self-sorting. DFT calculations point out that the self-sorting outcome may also be a result of the water encapsulation within the hydrophilic pockets [5].

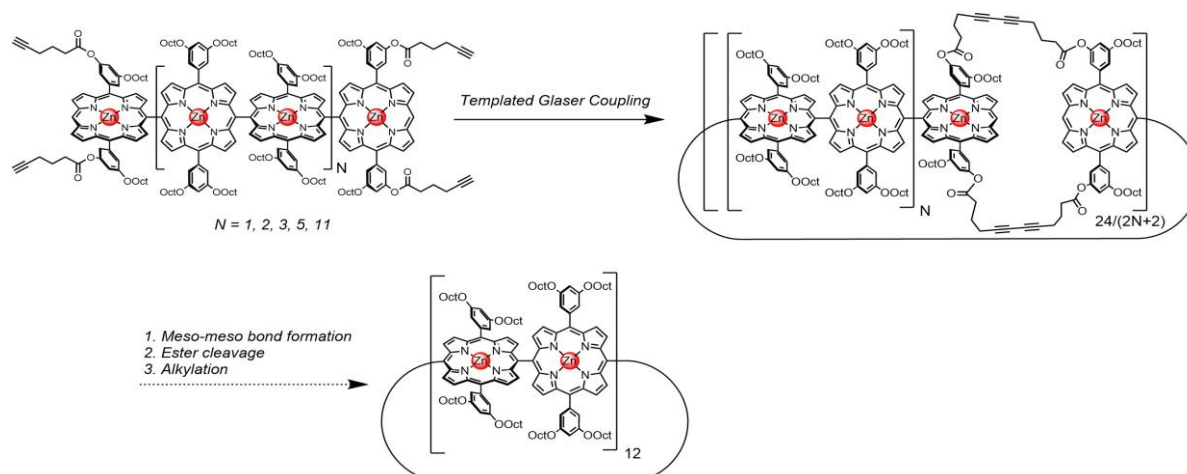
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M125 Temporary Tethers in the Synthesis of Porphyrin Arrays

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Caption: Proposed synthesis of an all meso-meso linked cyclic porphyrin array using templated alkyne Glaser coupling of shorter oligomers.

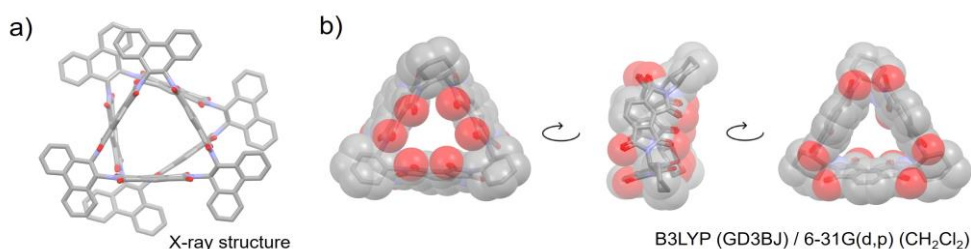
Synthesis of cyclic porphyrin arrays enables investigation of their photophysical and charge-delocalization properties, as models for natural photosynthetic light-harvesting systems, and for testing the limits of aromaticity in nanoscale rings.^{1,2} Template-directed synthesis³ is an effective method for preparing such macrocycles, including those with butadiyne or ethyne units between adjacent porphyrins,² but it has not yet been applied to create nanorings with direct *meso-meso* bonds between all adjacent porphyrin units. Such nanorings should allow access to fully-fused porphyrin nanobelts, which are predicted to have very low HOMO-LUMO gaps.⁴ A macrocyclic Glaser coupling reaction between cleavable alkyne tethers present at either end of a linear porphyrin oligomer, held in close spatial proximity through use of an appropriate template, gives a porphyrin oligomer held in a cyclic conformation even after template removal. Final *meso-meso* bond formation, cleavage of the ester bonds, and subsequent alkylation should give the desired all *meso-meso* linked macrocycle. Work towards this proposed synthesis will be presented.

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Abstract No: M126

M126 Are all molecular triangles created equilaterally?

William Glover-Humphreys¹, Alyssa-Jennifer Avestro*¹ Fraser Arnold², Ruhee Dawood², Mariia Kuznetsova², Adrian Whitwood²¹ University of York, York, United Kingdom² , ,

Caption: (a) The solid-state superstructure of strained 3PMDIΔ with alternative vertices and (b) DFT models of MDIΔ

Shape persistent molecular triangles composed of chiral trans-1,2-cyclohexane vertices and three aromatic diimide (ADI) units have emerged over the last decade with promising applications in light-emitting devices, host-guest molecular recognition¹ and lithium-ion battery technology.² These unique properties are in part attributed to the ADI units participating in through-space π -orbital overlap to form a globally conjugated macrocycle with a highly electron-deficient cavity.² Despite advances over the years yielding access to both equilateral and isosceles products³, fundamental design approaches for molecular triangles have notably remained the same, never venturing beyond the use of relatively low-strain (60° torsion) trans-1,2-cyclohexanediamine and 180° linear ADI building blocks. Here, we present two structurally novel variations to molecular triangle design that play with i) vertex torsion or ii) diimide geometry to access new functional and supramolecular properties. For instance, by swapping the trans-1,2-cyclohexane vertices for a more strained (51°) chiral 9,10-dihydrophenanthrene-9,10-diamine⁴ vertices (Figure 1a), the electronegativity of the ADI core is reduced resulting the six individual redox states to be accessible at a significantly less demanding reduction potential. Meanwhile, subjecting bent ($<180^\circ$) ADIs known as mellophanic diimide⁵ to traditional molecular triangle synthetic conditions affords a new class of redox-active molecular polygons or molecular "frustrums" (Figure 1b) with distinct head and tail polarities reminiscent of calixarenes and cyclodextrins. Our group is currently working to establish the fundamental structural dynamics, electronic and supramolecular properties of these new classes of molecular hosts. Future research aims to explore core halogenated MDI for core functionalization with the intention to achieve extended molecular nanotubes.

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Abstract No: M127

M127 Synthesis, Photophysical Characterization, and HER Activity of Metalloporphyrins

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Porphyrin macrocycles have diverse functionalities including energy-relevant catalysis reactions such as carbon dioxide reduction, oxygen reduction, and hydrogen evolution (HER). The electronic properties and catalytic activity of porphyrins can be tuned via the modification of the ligand scaffold and substitution of varying metal centers. Herein, we present the synthesis of Zn(II), Cu(II), and Ni(II) 5,10,15,20-tetrakis(4-fluoro-2,6-dimethylphenyl)porphyrins (TFPs) and explorations of their photophysical properties (Zn(II)-TFP) and HER activity (Cu(II)-TFP).¹ Consistent with previous reports, our Zn(II)-TFP closed shell metalloporphyrin displays a long excited state lifetime (2.3 ns).² Our Cu(II)-TFP displays catalytic HER activity, and by using foot of the wave analysis, we determined the reaction between Cu(II)-TFP and benzoic acid to be first order with respect to proton concentration, as well as quantified the turnover frequency and average apparent rate constant ($k_{app} = 5.79 \pm 0.47 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$)³.

This project was undertaken as part of an undergraduate advanced inorganic chemistry class at Harvard University, where students learned the skills necessary to synthesize and characterize these novel porphyrins. In addition to our results, we will discuss how the synthesis and characterization of these macrocycles was utilized as a tool for undergraduate chemistry education.

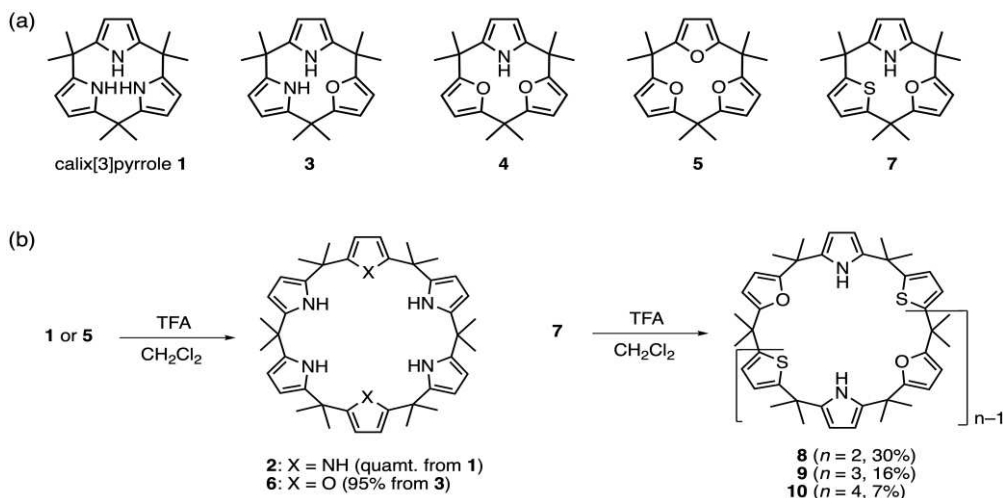
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M128 Strain-Induced Ring Expansion Reactions of Calix[3]pyrrole Analogs

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Caption: Figure 1. (a) Structure of calix[3]pyrrole and analogs. (b) Strain-induced ring expansion reaction of 1, 5, and 7.

Macrocyclic strain exerts a unique impact on properties and reactivities of the macrocycle, and strain-induced reaction of macrocycles often enables reactions that were not observed in non-strained molecules. Recently, we synthesized calix[3]pyrrole **1**, the smallest analog of calixpyrroles. Calix[3]pyrrole **1** has a highly strained structure which causes rapid ring expansion reaction under acidic conditions to give calix[6]pyrrole **2** in a few seconds.¹ Such a twofold expansion of ring size is quite rare but promising for the synthesis of larger macrocycles. In this research, we synthesized calix[3]pyrrole analogs bearing furan or thiophene with different strain energies to investigate the mechanism and scope of this ring-expansion reaction.^{2,3}

Furan embedded analogs, calix[n]furan[3- n]pyrroles **3–5** ($n = 1\sim 3$, Figure 1a), were synthesized from the cyclic oligoketone precursor via Paal-Knorr type pyrrole formation reaction. Single crystal X-ray diffraction analysis and computational calculations revealed that the macrocyclic strain decreases as the number of pyrrole units decreases among these macrocycles, including **1**. When these analogs were subjected to acidic conditions, **3** underwent regioselective ring expansion reaction to give **6** in just 5 minutes (Figure 1b, left). In contrast, the less strained analogs **4** and **5** showed almost no reactivity under the same conditions. The mechanism analysis revealed that the ring expansion reaction consists of two steps: ring cleavage to release macrocyclic strain and subsequent cyclodimerization.

Furthermore, calix[1]furan[1]pyrrole[1]thiophene **7** was prepared in a manner similar to **3–5**. The crystal structure of **7** revealed significant macrocyclic strain, which caused ring expansion reaction under acidic conditions. Unlike **1** or **3**, ring expansion reaction of **7** gave calix[n]furan[n]pyrrole[n]thiophenes **8–10** ($n = 2, 3, 4$) in 30, 16, and 7% yield, respectively (Figure 1b, right). Spectroscopic and X-ray crystallographic analyses revealed that furan, pyrrole and thiophene in ring expanded products, including calix[4]furan[4]pyrrole[4]thiophene, are periodically arranged, attributed to site-selective ring cleavage and cyclo-oligomerization. These findings support that calix[3]pyrrole analogs can serve as unique precursor for structurally defined large macrocycle syntheses.

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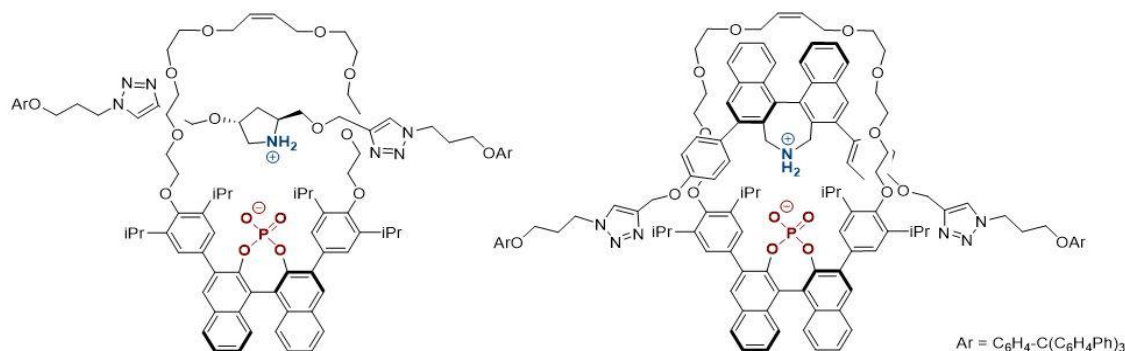
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Abstract No: M129

M129 Heterobifunctional rotaxanes for cooperative organocatalysis

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Caption: Heterobifunctional rotaxanes for cooperative organocatalysis

Mechanically linked molecules are suitable for acting as artificial receptors or sophisticated chemical catalysts due to their unique nature.^[1] We recently reported the application of a homobifunctional [2]catenane featuring two 1,1'-binaphthyl phosphoric acids for the stereoselective transfer hydrogenation of quinolines.^[2] Moreover, we could show that heterobifunctional rotaxanes featuring a chiral phosphate-based macrocycle and an achiral ammonium-thread can be applied as catalysts for stereoselective Michael-additions.^[3] In both cases, we could prove that the mechanical bond leads to a cooperative behaviour of both functional groups, resulting in significantly increased stereoselectivities in comparison to the non-interlocked control catalysts.

Here, we present the preliminary steps for extending this project toward the study of heterobifunctional rotaxanes that feature two chiral subunits (see Fig. 1). We have established a viable synthetic route to the novel interlocked structures and have investigated their application as bifunctional organocatalysts. Here, we have compared different rotaxane types (binaphthyl-amine thread or prolinol thread) and stereochemical combinations of chiral subunits (matched/mismatched cases) to see which gives the best stereoselectivities.

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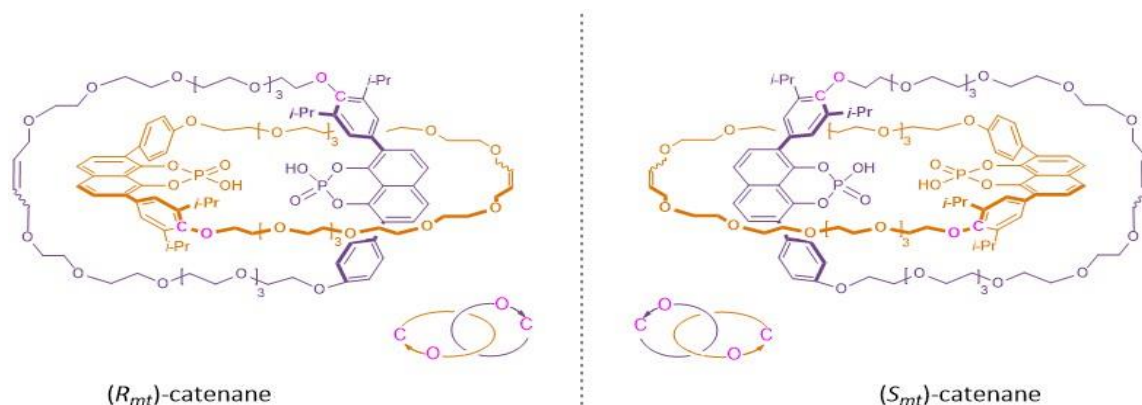
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Abstract No: M130

M130 Topologically Chiral [2]Catenanes

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Caption: Overview of the topologically chiral [2]catenanes and their schematic representation

Interlocked molecules such as catenanes offer conceptually new possibilities through their unique structure and the potential to introduce different types of chirality. ^[1]

Recently our group has developed an axially chiral [2]catenane which consists of two 1,1'-binaphthyl-phosphoric acids. It has been used as bifunctional catalysts for the transfer hydrogenation of 2-substituted quinolines. We could prove that the cooperative behavior of the functional groups results in a significantly increased stereoselectivity in comparison to the non-interlocked catalysts. ^[2]

Here, we present the preliminary steps for the extension of this project towards the synthesis of chiral [2]catenanes that feature a non-classical topological chirality. Such topological chirality can be generated by interlocking two achiral, but directional, macrocycles.

Although the potential of topological chirality in catenanes was identified in 1961, little is known about their potential application. With our approach of naphthalene-based catenanes, we aim to develop the first application of a topologically chiral catenane in Brønsted-acid organocatalysis (Figure 1). ^[1]

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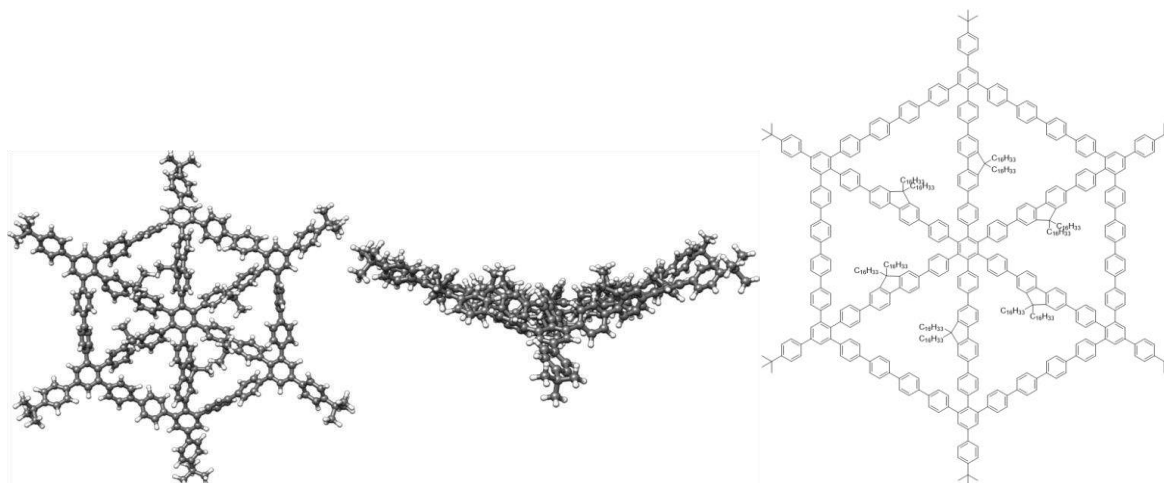
Abstract No: M131

M131 Bowl-shaped Molecular Spoked Wheels of larger diameters

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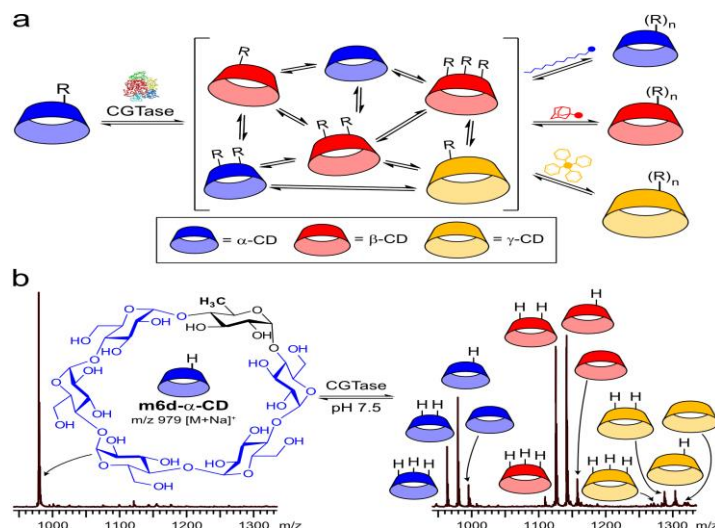


Caption: Scheme 1: Model of a fluorene-based MSW (alkyl chains replaced by methyl groups for simplicity) (left, middle); fluorene-based all-phenylene MSW with alkyl chain groups (right).

Molecular Spoked Wheels were synthesized in the Höger group for several years featuring various functionalization and substitution patterns. Limiting the used structural units to only phenylene also limited the size of the synthetically accessible target molecules unintentionally. For all-phenylene based Molecular Spoked Wheels, it was not possible to extend the molecules' core diameter beyond seven units, since the open-framed precursors aggregated promoting intermolecular over intramolecular coupling reactions when attempting to close the rim. The implementation of fluorene as spoke unit enabled the synthesis of larger Molecular Spoked Wheels suppressing the aggregation by alkylation of the respective spokes. Aside from the bowl-shaped geometry, the new functionalized spoke also frees the rim from previously inevitable alkyl chains while keeping large structures soluble.

This grants access to a broad scope of old and new functional groups and combinations testing if it is possible to implement specific chemical and physical properties into macromolecules deliberately.

M132 Enzyme-mediated Dynamic Combinatorial Chemistry of Modified Cyclodextrins

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Caption: Dynamic libraries of CDs with modifications (R = I, N3, OTos, SH) on C-6 can be produced by treating CDs containing a single modified glucopyranose.

Background

Enzyme-mediated dynamic combinatorial chemistry allows the formation of dynamic systems of interconverting oligomers of biomolecules. We have demonstrated this principle using cyclodextrin glucanotransferase (CGTase) to produce a dynamic system of cyclodextrins (CDs). The system operates as an out-of-equilibrium dynamic system of CDs, and enables template-directed synthesis of α, β or γ-CD with 6, 7 or 8 glucopyranose units.¹ It also allows formation of larger CDs, e.g. δ and ε-CD with 9 or 10 glucopyranose units. With proper choice of templates, the system can also be controlled by light² or pH,³ and the distribution of CDs can be fine-tuned by varying the temperature or co-solvents,⁴ or by addition of chaotropic or kosmotropic salts.⁵

Dynamic systems of modified CDs

In this project we demonstrate that dynamic systems of CDs enabled by native CGTase can incorporate unnatural glucopyranose-derived building blocks, expanding the applicability of enzyme-mediated dynamic combinatorial chemistry by using synthetically modified substrates (figure panel a).⁶ Starting dynamic combinatorial libraries from CDs with a single 6-modified glucopyranose results in a dynamic mixture of CDs containing several modified glucopyranoses. We demonstrate this principle in detail with 6-deoxy-glucopyranose-containing CDs (figure panel b). We also show that commercial CGTase accepts replacing the 6-OH-group with either an iodo, azido, O-Tosyl or thiol group, the latter giving access to doubly-dynamic systems where CDs also dynamically form intermolecular disulfide bonds. The relative concentrations of modified α, β or γ-CDs can be controlled by the addition of templates, providing a novel way to access modified CDs.

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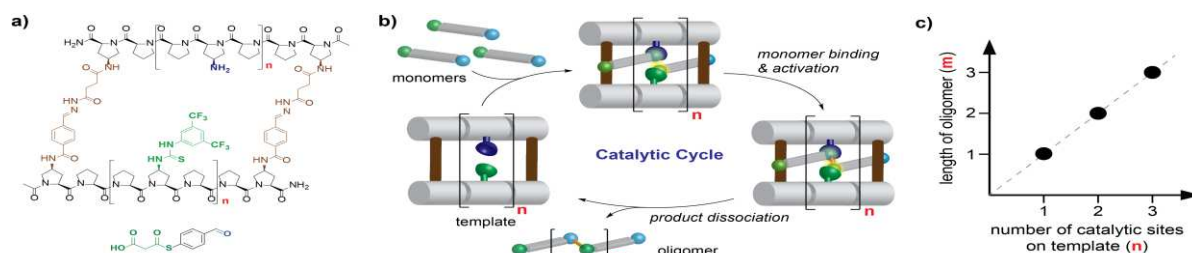
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M133 Catalytic Length-Controlled Oligomerization with Synthetic Programmable Templates

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Caption: Fig.1 a) Structures of the templates and the monomer; b) Catalytic oligomerization; c) Correlation between the template size and oligomer length.

Nature uses templated synthesis to produce oligomers from monomer building blocks.¹ For example, genetic information is processed by transcription of DNA into RNA and subsequent translation into peptides and proteins. DNA- and RNA-based,² as well as fully synthetic,³ templates have also been developed for the preparation of non-natural linear oligomers^{2b,2c,4} as well as macrocycles,⁵ cages,⁶ and knots.⁷ A common limitation of templated oligomerization is the tight binding between the template and the oligomer. The newly formed oligomer is therefore only accessible in stoichiometric amounts relative to the template and the complex between the template and the oligomer needs to be disassembled in a subsequent release step.⁸

Herein, we present catalytic macrocyclic templates that promote the formation of oligomers of a small molecule substrate with a remarkable degree of length-control.⁹ The templates consist of rigid oligoproline moieties decorated with thiourea and amine catalytic sites at defined distances on both sides of the macrocyclic cavity (Fig.1a). Oligomer formation is achieved through multiple recognition and activation events which facilitate the catalytic process (Fig.1b). The dimensions of the macrocycles and the number of catalytic moieties thereon determine the number of monomers that are incorporated into the growing oligomer, thus allowing access to specific products with lengths pre-programmed by the template (Fig.1c).

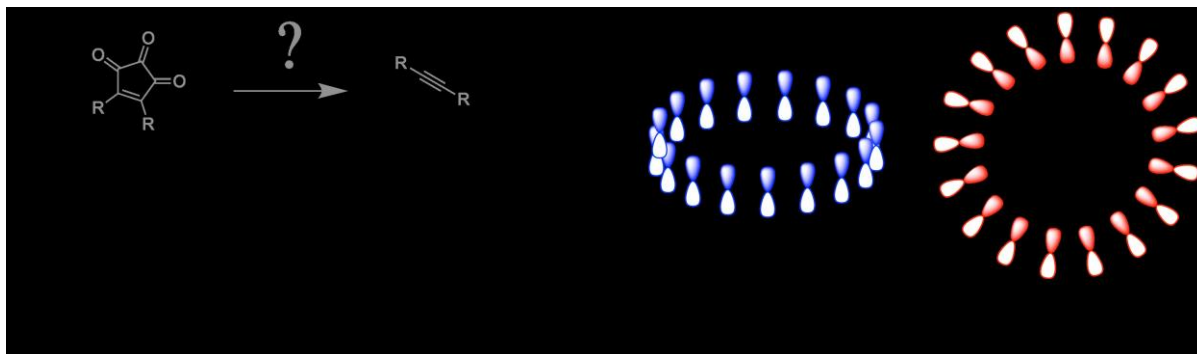
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M134 Cyclopentenodehydroannulenes.

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Abstract:

Novel carbon allotropes represent an exciting opportunity to push the limit of different chemical concepts such as (anti)aromaticity, bond angle or bond length alteration. Until Gross, Anderson *et al.* presented the AFM/STM picture of cyclo(18)carbon using squaric acid as a masked alkyne equivalent (MAE), these carbon allotropes were only detected in the gas phase.¹

DFT calculations show that a balance between the aromatic or anti-aromatic character exists in odd-numbered cyclocarbons depending on their number of carbons ($4k+1$ or $4k+3$).² This property is due to the unique double (anti)aromaticity of cyclocarbons provided by their *in-plane* and *perpendicular* set of overlapping π orbitals. The synthesis of such cyclocarbons may thus provide experimental answers to these computed properties.

Croconic acid, a lesser-known member of the oxocarbon family, was chosen as another potential MAE. The smaller *bite-angle* of this five-membered ring (72° versus 90° for squaric acid) also offers a new perspective for macrocyclization. Unreported croconate derivatives were successfully prepared to test the potential of this oxocarbon as an MAE. Initial results indicate a successful decarbonylation in the gas phase, while photoreactions of these compounds led to rearrangements akin to squaric acid. Attempts are currently underway to perform flash vacuum pyrolysis on these molecules to produce an isolable amount of the corresponding alkynes.

Two routes towards odd-numbered cyclo($4k+3$)carbon were then explored: (1) using the Sonogashira reaction as a platform reaction for the alkyne coupling of a new diiodo croconate derivative and (2) employing Rubin's squaric acid strategy for the first time on dimethyl croconate leading to asymmetrical alkyne products.³ Both strategies successfully led to the first alkyne derivatives of croconic acid. First results of the macrocyclization step and formation of odd-numbered cyclo($4k+3$)carbon will be presented.

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Abstract No: M135

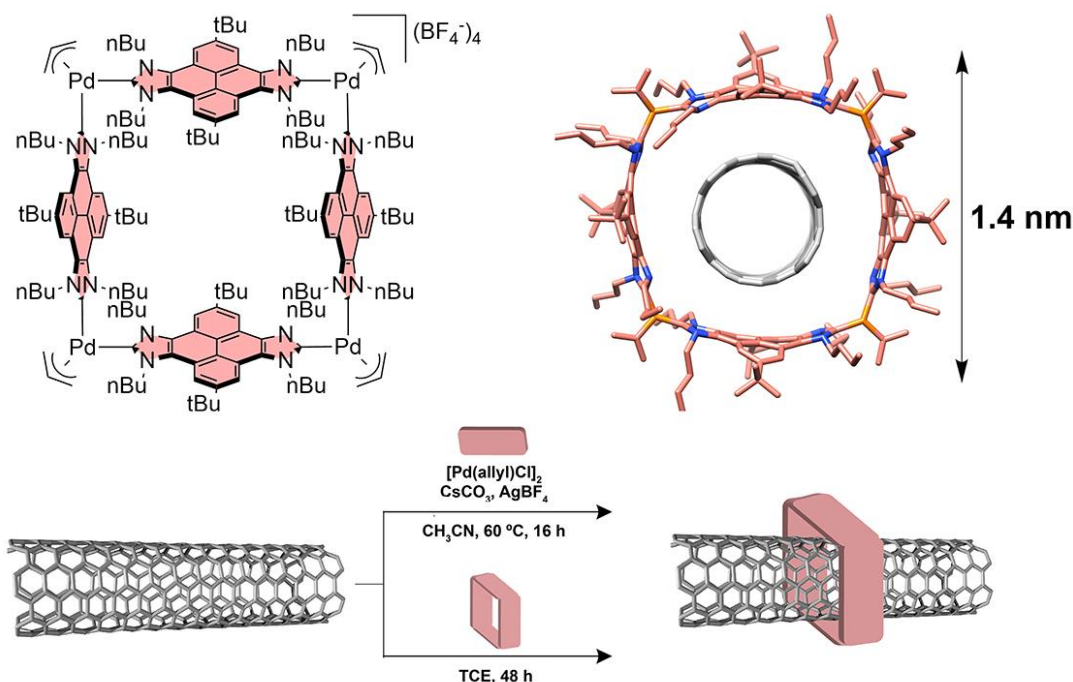
M135 Single-Walled Carbon Nanotubes Encapsulated within Metallacycles

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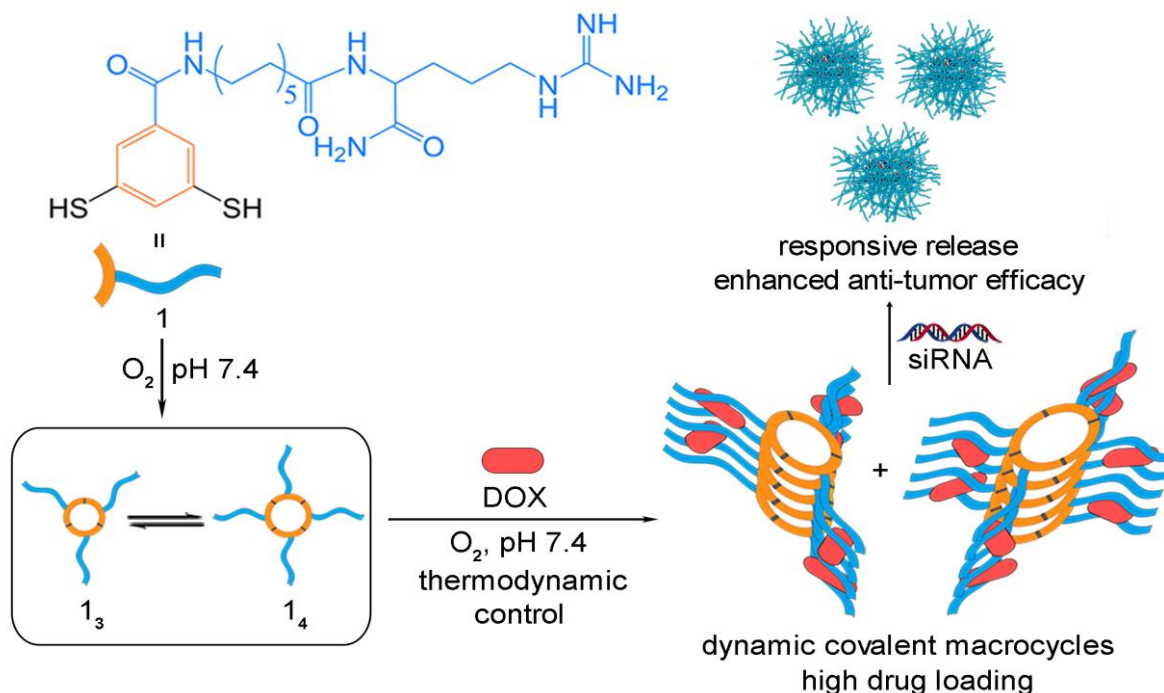
Caption: Top: Chemical structure of metallosquare and Energy-minimized (UFF) model of MINT; Bottom: Schematic representation of MINT preparation

We report the synthesis of mechanically interlocked derivatives of carbon nanotubes (MINTs) using palladium-based metallosquares. MINTs are interesting nanotube products that show high stability without altering the carbon nanotube structure and have been synthesized using a variety of techniques including ring-closing metathesis,^[1] disulfide exchange reaction,^[2] H-bonding,^[3] and direct threading with macrocycles.^[4] Our approach involves the encapsulation of single-walled carbon nanotubes within a palladium-based metallosquare, which was found to be remarkably sensitive to structural variations of the metallo-assemblies.^[5] When a metallosquare with a cavity of appropriate shape and size is used, the formation of the MINT proceeds successfully by both templated clipping and direct threading. Our studies also provide insights into how supramolecular coordination complexes can help expand the potential applications of MINTs, including in areas such as reinforcing polymers, and designing metal-free catalysts, and qubits. This work represents a new direction in the synthesis of MINTs and demonstrates the potential of palladium-based metallosquares as hosts for the mechanical interlocking of carbon nanotubes.

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M136 Dynamic covalent macrocycles for co-delivering genes and drugs in cancer cell lines

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Caption: Scheme 1. Schematic illustration of dynamic covalent macrocycle for the co-delivery system showing strong drug-loading capacity

The clinical outcome of chemotherapy for cancer treatment is often unsatisfactory due to multiple drug resistance (MDR). A promising approach to addressing this issue is to disrupt MDR at the genetic level using a small interfering RNA (siRNA) while the anti-cancer drug is administered. Many efforts have been made for this objective by developing functional nanosystems that can co-deliver chemotherapeutic drug molecules and genes.¹ In general, polymers are the main carrier molecules for the co-delivery system due to their excellent stability. However, the inefficient drug and gene release in cancer cells and the low loading capacity are the main problems of the polymeric delivery system. Thus, exploring biocompatible and stable but responsive co-delivery systems with a strong loading capacity is the most urgent.

Here, we report the first example of using dynamic covalent macrocycles to explore a gene and drug co-delivery system against MDR.² The macrocycles were oxidized by a dithiol building block **1** while non-covalently associating with an anti-cancer drug doxorubicin (DOX) to form nanofibers (Scheme 1). The thermodynamically based macrocycle achieved a drug-loading content of 30.2%, whereas a disulfide polymer prepared from **1** under kinetic control could not load DOX. In combination with siRNA, the macrocycles exhibited excellent delivery efficiency and enhanced anti-tumor efficacy *in vitro* without systemic toxicity. Our findings suggest that dynamic covalent chemistry offers a powerful strategy for exploring macrocyclic carriers that could replace conventional polymers for co-delivery systems, paving the way to more efficient clinic therapies.

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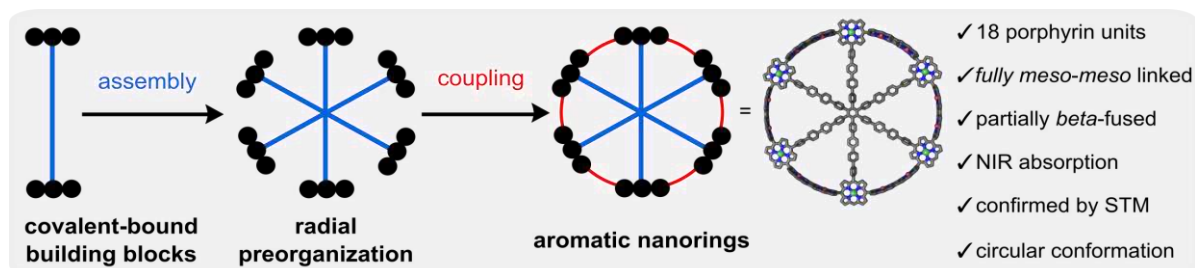
M137 Getting Into Shape: Covalent Template-Directed Synthesis of Aromatic Macrocycle(s)

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Caption: Schematic representation of template-assisted assembly (left-center) and the target nanoring (right).

The structural diversity and unique repertoire of methods used to synthesize aromatic macrocycles has made them one of the fastest developing fields of modern organic chemistry. This is often accompanied by extraordinary reactivity patterns and unusual electronic features, stemming from their geometry and extended π -conjugation, making them an interesting target for exploration of fundamental properties of aromatics and promising candidates for functional organic materials. A general synthetic challenge in constructing nanoscale, shape-persistent structures lies in harnessing the macrocyclization step in order to drive the reaction toward a specific ring size and minimize linear polymerization, and one of the possible solutions is the use of templates. Template assisted self-assembly has been known as an efficient tool for creating many novel macrocycles, rotaxanes and catenanes.^{1,2} A great example of such structural diversity can be seen in acetylene-porphyrin systems. Over the years, the Anderson group has perfected the use of coordinating templates for directing self-assembly to create a series of unique nanorings and similar three-dimensional architectures.^{3,4} This work will showcase an alternative synthetic strategy, where a novel macrocycle, made of partially fused porphyrin subunits, is assembled by the use of a covalently-bound polyphenylene template. Construction of the key, radial, hexameric precursor is possible by cyclotrimerizing porphyrin tolans, similar to smaller examples reported in the past.^{5,6} These nano-molecules were then characterized in solution and on surface. Further studies on carbazole-based systems will also be shown.

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Abstract No: M138

M138 The Development of Mechanically Interlocked Molecules Using the 2,6-Bis(1,2,3-triazol-4-yl)pyridine Motif

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The field of mechanically interlocked molecules (**MIMs**) is an ever-growing area of research and has garnered much interest as of late due to Sauvage, Stoddart, and Feringa receiving the Nobel Prize in Chemistry in 2016,¹ furthermore **MIMs** have become ubiquitous in the field molecular switches and shuttles. **MIMs** can be used as chemosensors as their intrinsic cavity can be utilised as a host site for molecular recognition. The chemical environment of these cavities are tuneable through the functionalisation of the systems component parts. These systems are, by their nature, dynamic and thus there is the possibility of guest induced conformational switching, ergo they have been implemented as stimuli responsive chemosensors.² The incorporation of **MIMs** into materials such as polymers and gels hold much potential for the development of novel materials with unique physical and sensing properties.³

Previous work within the Gunnlaugsson group demonstrated that the 2,6-bis(1,2,3-triazolyl)pyridine (**btp**) based [2]catenanes are a selective anion hosts for phosphate due to triazolyl hydrogen-bonding interactions within the cavity of the interlocked system.⁴ Going forward from these findings, this work details the further development of novel [2]catenanes derived from the **btp** structural motif. An improved synthetic approach to these systems was developed, accompanied with the introduction of several new functional groups at the 4-pyridyl position in order to control the self-assembly and material properties of the resulting catenane, and furthermore; to serve as a synthetic handle for incorporation of **btp** catenanes in materials such as polymers and gels. Selective quaternisation of the **MIMs** four triazolyl N-1 positions was also carried out, leading to a change in cavity shape, opening the door for the uptake of new guest anions.

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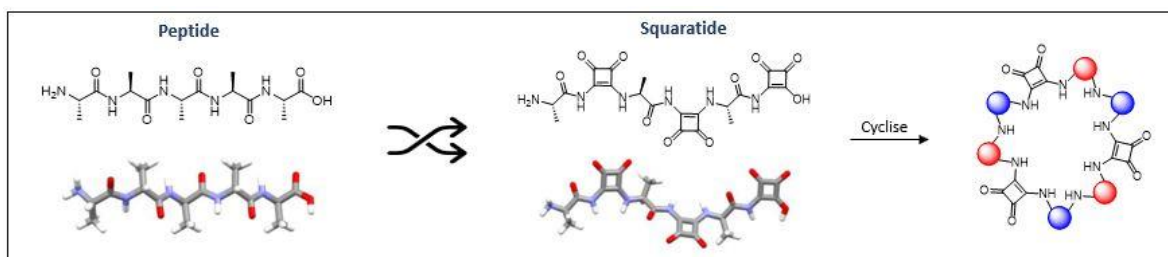
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Abstract No: M139

M139 Towards the Design and Synthesis of a new class of biomimetic receptors: Squaratides

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Caption: Schematic structural comparison of peptides vs. squaratides

Nature uses a large variety of molecular architectures to carry out a stunning array of complex tasks, from cell signaling to the catalysis of biochemical transformations ^[1]. However, the ability of chemists to reproduce these functions using synthetic systems remains an elusive challenge. The modular construction and structural diversity that nature displays in the biosynthesis of proteins provide ample inspiration for the design of new receptors with controlled conformations and defined structures ^[2]. It is the 3-D arrangement of the protein that dictates its biological activity and control over structure is particularly important given the rise of peptide and protein-based biologic drugs in recent years.

Taking inspiration from nature and through judicious molecular design, we propose to design and synthesize a completely new class of peptidomimetic receptors – a hybrid mix of squaramides and peptides that we call squaratides (Figure 1). We have set out to create a library of modified amino acid building blocks from which we will construct a new class of biopolymer; one that can be synthesized in an automated stepwise manner to create a diversity of receptors subtypes- varying cavity size, lipophilicity and charge, to name just a few key parameters.

This poster will demonstrate our initial results where we have taken advantage of both solution phase and solid phase syntheses to assemble a series of acyclic squaratides of varying lengths. We will also outline our approach toward the cyclic derivatives where we have already demonstrated the successful synthesis of several macrocyclic derivatives of varying ring sizes that show high binding affinity for a range of anionic species.

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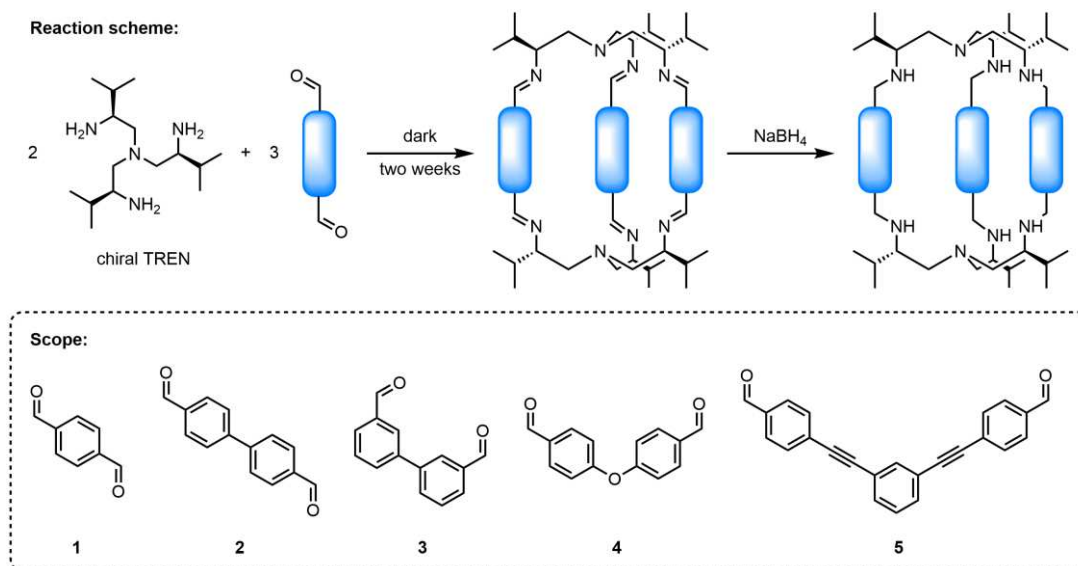
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Abstract No: M140

M140 Synthesis and Chiroptical Spectroscopy of Chiral Azacryptands

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Caption: Synthesis of Chiral Azacryptands.

Azacryptands are macrocyclic cage compounds first synthesized by Lehn and co-workers.^[1] Chiral versions of these systems are not known in literature so far. In this work, we present the synthesis of novel chiral azacryptands obtained by condensation of chiral TREN (tris(2-aminoethyl)amine)^[2] units, derived from valine, with different dialdehydes. Our synthetic procedure is suitable to access a large scope of linker groups: Starting with a simple phenyl linker (**1**), different aryl linker groups (**2-5**) with diverse substitution patterns have been examined.

Vibrational circular dichroism (VCD) spectroscopy was employed to characterize the structural preferences of the cage compounds. VCD spectroscopy is the IR version of CD spectroscopy and the difference between left and right circularly polarized light is measured. It is highly sensitive to, for instance, solvent-induced conformational changes.^[3] Literature precedence for VCD spectra of cage compounds is rare.^[4] The VCD spectra of the novel azacryptand cages have been recorded and compared with spectra obtained by DFT-based methods. Short linker groups as the phenyl linker group show a rigid conformation. By increasing the length of the linker groups, the cryptands become more twisted and adopt a helical conformation.

Azacryptands are known to bind metal ions and anions as guest molecules and thus are used for sensing and recognition.^[5] In our study, transition metal ions have been introduced into the cavity and the IR and VCD spectra of these complexes were measured and compared to computed spectra. Several anions were encapsulated in these cationic complexes and their conformational preferences were elucidated.

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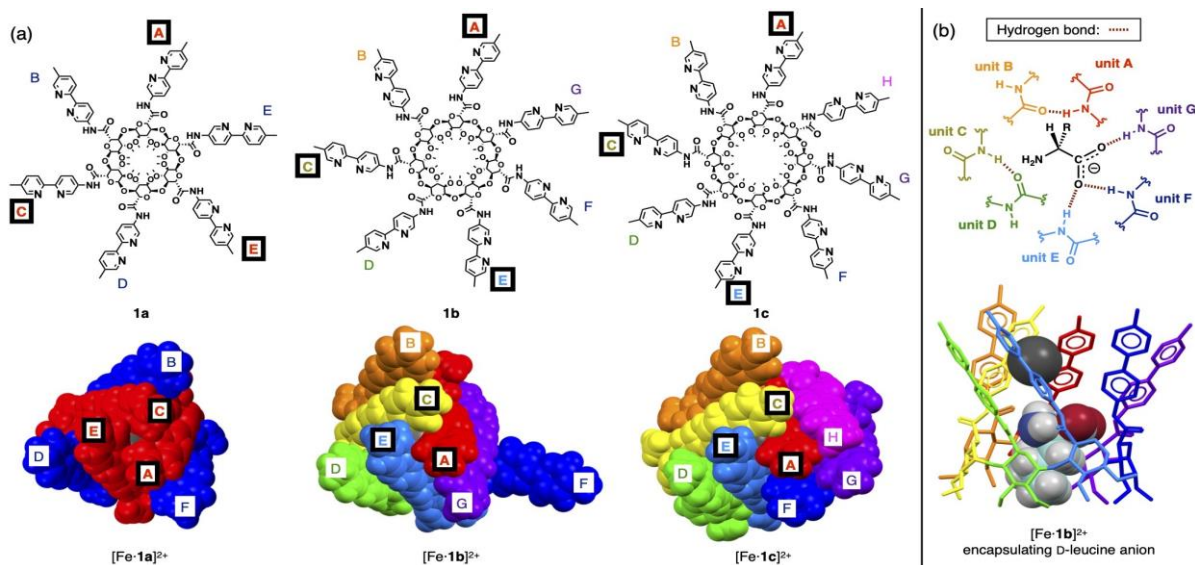
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Abstract No: M141

M141 Amide Cyclodextrins that Form Single Isomeric Complexes with Dissymmetric Structures for Precise Anion Recognition

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Caption: Figure (a) Structures amide cyclodextrins bearing 6, 7, and 8 bpy, and their single-isomeric iron complexes. (b) Recognition of D-amino acid anions.

Macrocycles with dissymmetric structures can realize precise molecular recognition utilizing their unsymmetrically arranged functional groups.^[1] We have previously reported cyclodextrin derivatives whose amide groups are directly attached to the 5 position of each pyranose ring.^[2,3] They have unsymmetrical shapes due to the intramolecular hydrogen bonds between some of the amides as well as the steric hindrance between aromatic rings.

As a next step to create functional desymmetrized macrocyclic hosts based on homooligomers, selective metal complexation of coordination units was investigated. We have synthesized a series of amide-cyclodextrins **1a**, **1b**, and **1c** possessing 6, 7, and 8 bpy (2,2'-bipyridyl) groups, respectively (Fig. a).^[4] Many isomers can be considered as possible products in the complexation of **1a–1c** and metal ions. Nevertheless, the formation of single isomeric mononuclear complexes whose three specific bpy groups (units A,C,E in Fig. a) are linked in the *fac*- Λ configuration was demonstrated. Furthermore, the iron complex of β -cyclodextrin derivative $[\text{Fe}\cdot\mathbf{1b}]^{2+}$ achieved chiral recognition of amino acid anions utilizing the distinctive amide groups arranged on the unsymmetrically fixed scaffold. For example, the binding constant of D-leucine anion was 5.2 times larger than that of L-leucine anion. Benefitting from the fixation and desymmetrization by metal complexation, the ¹H NMR signals of $[\text{Fe}\cdot\mathbf{1b}]^{2+}$ were sharp and well split. Detailed 2D NMR analysis revealed that the recognition of the carboxylate group by multipoint hydrogen bonds with specific amides set the orientation of the included D-amino acid anion, and high chiral selectivity was realized (Fig. b). In the presentation, the successful formation of a giant dissymmetric trimer of β -cyclodextrin derivative $[\text{Fe}\cdot\mathbf{1b}]^{2+}$ as a single isomer by the intermolecular complexation of its tilted bpy group (unit F in Fig. a) will also be presented.

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Abstract No: M142

M142 Cyclic Bis(triarylamines) and their Molecular Conductance Properties

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Caption: Cyclic (left) and acyclic (right) bis(triarylamines) shown between two gold electrodes.

Charge transport on the nanoscale has its own intricacies and offers unique opportunities when compared to the macroscopic scale. This applies in particular for electrical circuits.^[1,2,3] At odds with macroscopic electrical circuits, the transmission over a nanoscopic circuit scales with the square of the number n of identical connectors, *i. e.* $T(E_F) = n^2 T_0(E_F)$, where $T(E_F)$ is the overall transmission of the molecular circuit and $T_0(E_F)$ the transmission over each individual channel.^[2] First forays to experimentally probe and verify the computationally derived superposition law for molecular conductance were provided in 2012 by Vazquez *et al.*^[1] Only very few additional studies on this phenomenon have appeared since in the literature.^[4]

We have devised and synthesized different pairs of cyclic and acyclic bis(triarylamines), as exemplarily shown in Figure 1, with different spacer topologies and compare their molecular conductances. The latter were measured by means of a custom-built scanning tunneling microscope, according to an established design.^[5] We present indications for a non-additive increase in molecular conductance for the cyclic compounds with regard to their acyclic congeners, which we attribute to constructive interference between the individual conduction paths.

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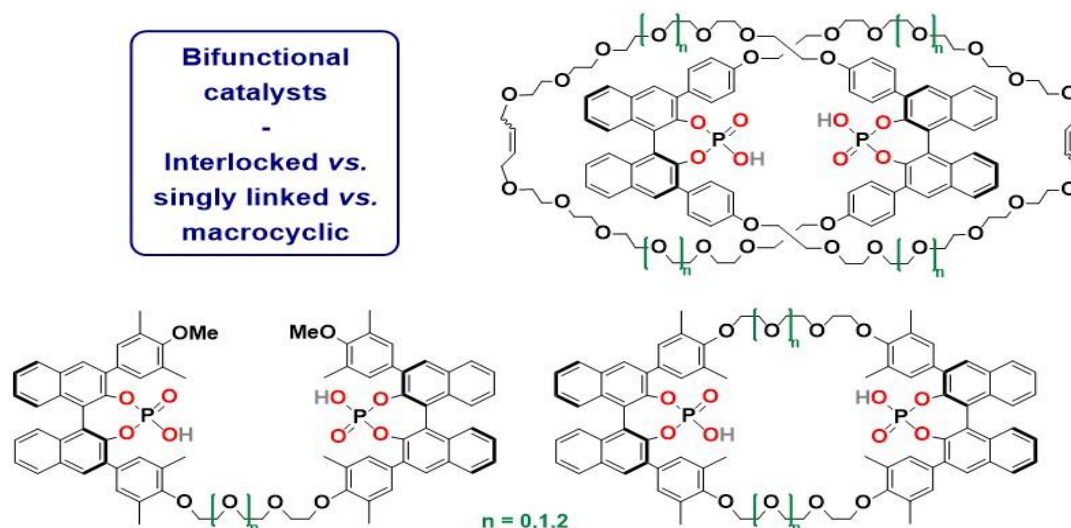
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Abstract No: M143

M143 Bifunctional organocatalysts – How do interlocked, singly linked and macrocyclic catalysts compare?

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The development of highly efficient organocatalysts has revolutionized chemical catalysis in the last decade. Especially the use of chiral Brønsted-acids, such as 1,1'-binaphthyl-phosphoric acids, has found considerable attention. These systems are robust, easy to synthesize and easily modified by variation of the substituents. However, the supramolecular chemistry of these catalysts (e.g. catalyst dimerization) still offers surprising new insights and developments. Our group has recently developed chiral bifunctional [2]catenanes based on 1,1'-binaphthyl-phosphoric acids which were successfully applied for the enantioselective transfer-hydrogenation of 2-substituted quinolines. Mechanistic investigations clearly pinpointed at the cooperative action of two phosphoric acids to be responsible for the high stereoselectivities.¹

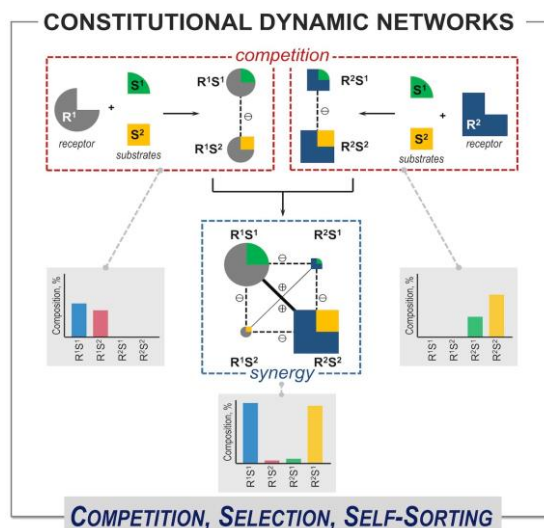
We have now investigated whether the interlocked nature of the bifunctional catalyst is crucial for a successful cooperative catalysis. To this end, we generated a series of singly linked and doubly linked (i.e. macrocyclic) bifunctional catalysts (see figure) and investigated their application in organocatalysis. Indeed, we could find that covalent linking can also lead to highly selective cooperative catalysts. However, the number, the nature and the length of the linkers has a profound influence on the stereoselectivity, as shown in enantioselective transfer hydrogenations and electrophilic fluorination reactions.²

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M144 Competition, Selection, and Self-Sorting Processes in Constitutional Dynamic Networks of Cryptates

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Caption: Figure 1. Generalized illustration of the outputs of the system in terms of reaction networks.

Understanding dynamic systems is a crucial step toward the design of complex matter.^{1,2} Unraveling the operation of complex systems greatly benefits from studying chemical models such as sets of dynamic molecular constituents capable of exchanging their building blocks within an adaptive molecular network responding to perturbation by external agents.³ Thus, dynamic networks of metal cation complexes may serve to set up complex systems and provide proof of principle for their behavior.⁴

Here, we aim to study the behavior of Constitutional Dynamic Networks (CDNs) in conditions of dynamic competition, taking cryptands and metal cations as a test bed. The CDNs of cryptates were analyzed by NMR spectroscopy, and the experimental results were complemented by extensive numerical simulations,⁵ based on a large amount of thermodynamic and kinetic data available in the literature for cryptates.⁶ The combination of theoretical simulations and experiments enables building models to design more complex systems. Introducing hierarchical sequences of effectors and/or kinetic features provides access to adaptive networks of higher complexity.

Although the CDN's output results from the interplay between the individual stability constants of the complexes in a mixture, the overall effect may be governed by only one—the most thermodynamically stable member of a network. Significantly, these findings indicate that increasing network complexity (in terms of multiplicity and connectivity) may lead to a simpler output, i.e., result in "simplicity" as the population of constituents is reduced in number by dynamic competition, enforcing self-sorting of the network.

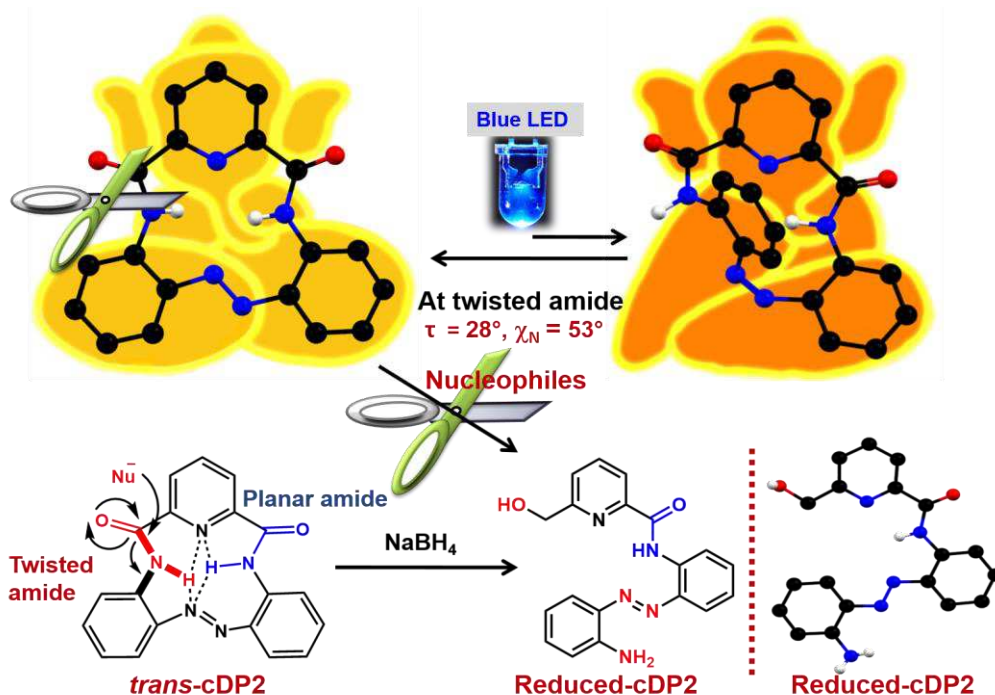
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M145 Macrocyclic Enforcement of Twist in a Secondary Amide: Reactivity and Influence on Photoisomerisation

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Caption: Secondary Twisted Amide its reactivity and photoisomerization

Nature has selected amide residues as one of the key building blocks for proteins due to their remarkable inertness under physiological conditions that arise from the delocalization of nitrogen lone pair (N_{lp}) onto $\pi^*_{C=O}$ imparting partial double bond character to the N-C(O) bond (1). Deviation from the planarity of these atoms produces the “twisted amides” with reduced double bond character and susceptibility to nucleophilic attack. Much research has been conducted to establish the structure-to-reactivity relationship of twisted tertiary amide (2,3,4,5,6). However, twisted secondary amide remains to be investigated in detail (7). Herein, we report a penta-azamacrocycle (cDP2) containing a twisted secondary amide residue with a twist angle (τ) of 28° and pyramidalization parameter (χ_N) of 53° . Consequently, cDP2 undergoes hydrolysis, transamidation, reduction, and thio-esterification reactions at the twisted secondary amide center. Moreover, upon photo-irradiation, the *trans*-to-*cis* photoisomerization of the diazobenzene residue in cDP2 leads to it adopting an open book-like structure with the twisted amide facilitating the molecule's folding around the diazo unit (8).

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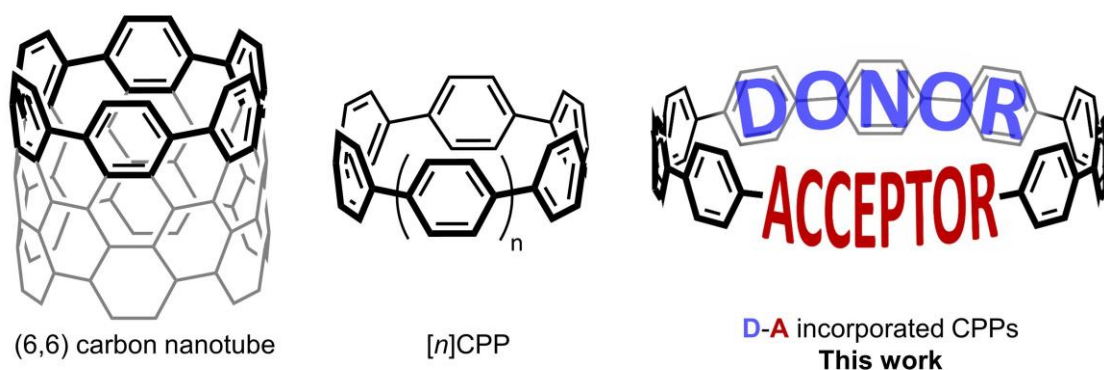
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M146 Carbon Nano hoops: Donor-Acceptor Systems and Late-Stage Functionalization

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Caption: Fig. 1: Left: Schematic of (6,6) armchair carbon nanotube, highlight: [6]CPP. Middle: [n]Cycloparaphenylene ([n]CPPs). Right: D-A incorporated CPP.

Exploring the emerging field of electronic materials based on organic compounds is an ongoing interest for organic and material chemists alike. Unique features are provided by carbon allotropes, from two-dimensional graphene to three-dimensional C_{60} or carbon nanotubes (CNT). In 2008 Jasti and coworkers reported the first example of a cyclo[n]paraphenylene (CPP)[1], corresponding to a bottom-up synthesis of the smallest segment of an (n,n) armchair carbon nanotube. Functionalization of CPPs can lead to a range of new properties from sensors to fluorescent probes, for active-template reactions and fluorescent polymer materials.[2]

Electronically the CPP backbone can be regarded as an electron donor, and we reckoned that by functionalizing it with electron acceptor units, new donor-acceptor systems would evolve with interesting optical and electrochemical properties. Here we disclose the synthesis of a series of CPPs with the incorporation of acceptor units and a handle for late-stage functionalization. We investigated the photophysical properties of these D-A carbon nano hoops by UV-vis absorption spectroscopy and fluorescence and their solvent dependency, along with electrochemical analysis in attempts to elucidate the structure-property relationships between different acceptors and the size of the nano hoops.

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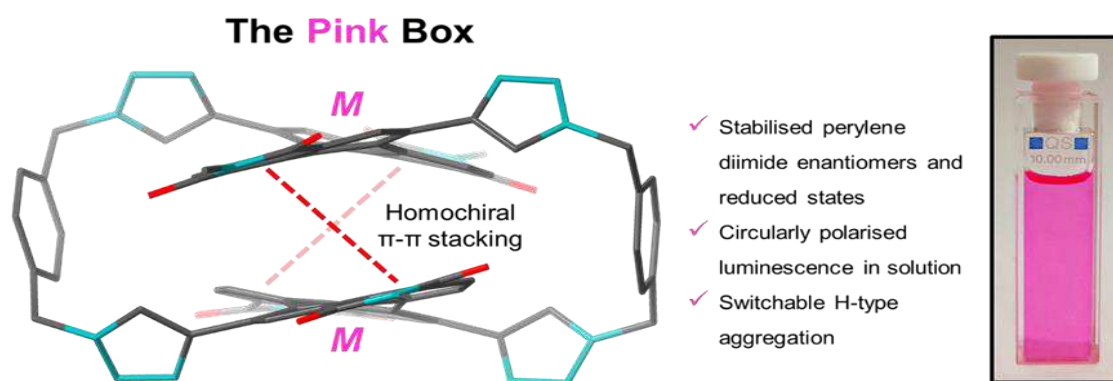
M147 The Pink Box: Exclusive Homochiral Aromatic Stacking in a Bis-Perylene Diimide Macrocycle

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Caption: Figure 1: Exclusive homochiral π - π stacking in a bis-PDI macrocycle, the “Pink Box”.

Perylene diimides (PDIs) are a class of organic dye molecules that are promising building blocks for semiconducting and optoelectronic materials.¹⁻³ PDIs can be engineered to exhibit axial chirality by functionalisation of the perylene core,¹ ideal for chiroptical applications including optical communication,⁴ advanced security inks⁵ and biological imaging.⁶

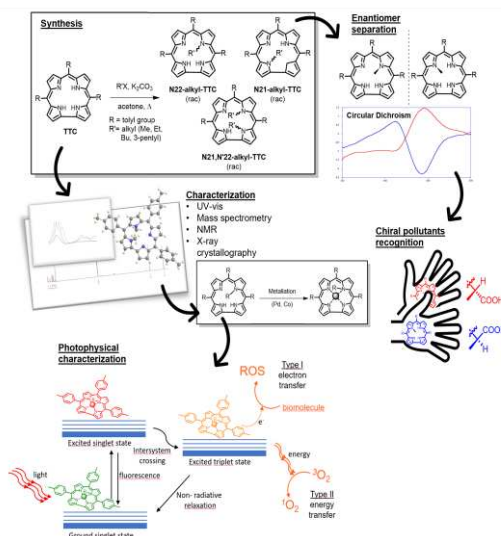
In this presentation, we showcase our recent work that exploits bay connectivity of chiral PDIs to produce a dynamic bis-PDI macrocycle (the “Pink Box”), in which homochiral PDI–PDI π - π stacking interactions are switched on exclusively (Figure 1).⁷ This anchors the twisted PDI cores, yielding stabilised enantiomers that can be resolved and investigated. Excitingly, this chiral complementarity affords the macrocycle red-shifted circularly polarised luminescence and one of the highest dissymmetry factors of any small organic molecule in solution ($g_{lum} = 10^{-2}$ at 675 nm). Our latest developments towards next generation configurationally locked macrocycles will also be presented.

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Abstract No: M148

M148 Chiral N-alkyl corroles : development, synthesis and application.

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Caption: synthetic pathways and application of N-alkyl corroles

In the large family of porphyrinoid, corrole represent a category that has aroused great synthetic and applicative interest in various fields, ranging from sensors to pharmaceuticals.

Among the numerous derivatives developed in recent years, one class in particular has been somehow neglected: N-substituted corroles. These compounds, having chirality induced by the alkylation of the inner core nitrogens, were first synthesized in 1965 by Johnson and Kay [1], but a small number of studies have been published since then, possibly due to low yields and the difficulties in isomers separation [2][3]. For this reason, we have developed an effective alkylation synthetic strategy starting with the simplest N-methyl derivate, obtaining an increase of two N-methylated isomers as racemate of 5,10,15-tri-p-tolylcorrole (TTC), reducing the di-methylated product. The products were separated into their respective enantiomers by chiral chromatography and then characterized by UV, NMR, X-ray diffractometry analysis and Circular Dichroism.

At this point, numerous alkylation tests were carried out changing the chain length, and their complexation reaction has been studied using different metals : interesting results have been obtained with Cobalt and Palladium. With a view to a possible use in photodynamic therapy, the Pd-corrole complexes were subjected to photophysical analysis in collaboration with the group of Professor Prodi of the University of Bologna, producing interesting data proving to be potentially useful for medical applications [4].

Being able to obtain different chiral derivatives would also allow application as sensors for the recognition of chiral pollutants and in the catalysis field for enantioselective reactions [5][6].

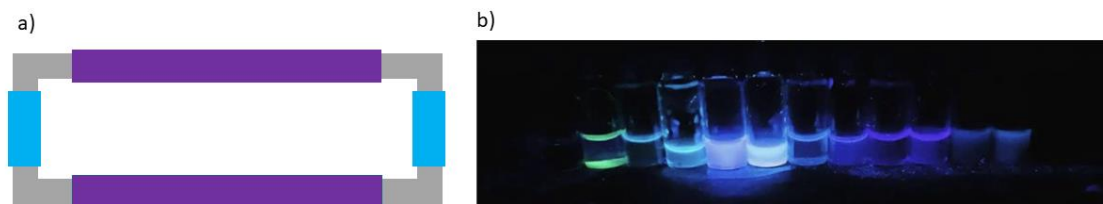
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M149 Host-Guest Chemistry of Naphthalene Diimide based Macrocyces

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Caption: Figure 1. a) Schematic of novel cyclophane b) fluorescence capabilities of host upon ingress of guest

Macrocyclic structures act as hosts, providing complementarity to guest molecules through various means, including matched size, shape, and the chemical nature of binding sites. These structures have various applications, such as chemosensing¹, catalysis², and facilitated transport³. This work presents macrocycles synthesised using templated self-assembly and probes their host-guest interactions. A novel tetracationic cyclophane was successfully synthesised and characterised. Investigations into the host-guest chemistry of the compound were carried out, using a variety of polycyclic aromatic compounds. Data obtained through single X-ray crystallography, ¹H NMR spectroscopy and photophysical measurements infers the successful ingress of these guest molecules. The host-guest binding suggests that the motif may be incorporated in larger supramolecular structures.

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Abstract No: M150

M150 Investigating the excited state dynamics of open shell Mn(III) metalloporphyrin via femtosecond transient absorption spectroscopy

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Closed shell metalloporphyrins are generally known to have long excited state lifetimes¹⁻³. In contrast, many open shell metalloporphyrins display much shorter excited state lifetimes due to accessible ligand field excited states and spin-orbit coupling with the unpaired electrons of the metal center. Herein we perform femtosecond transient absorption spectroscopy of the Mn(III)TFP(Cl) open shell, high spin metalloporphyrin. We show that the initially prepared 5S_1 excited state rapidly decays to the ground state through a trip-multiplet manifold ($^5T_1, ^7T_1$) of states which are heavily mixed with the porphyrinic excited states⁴ giving rise to sub-picosecond singlet, and sub-nanosecond triplet excited state lifetimes as compared with closed shell Pd(II)TFP. These results highlight the importance of low-lying triplet excited states and metal induced spin-orbit coupling in the deexcitation pathways of open shell metalloporphyrins and add before unseen sub-picosecond decay dynamics to the photo-physics of Mn(III)TFP(Cl).

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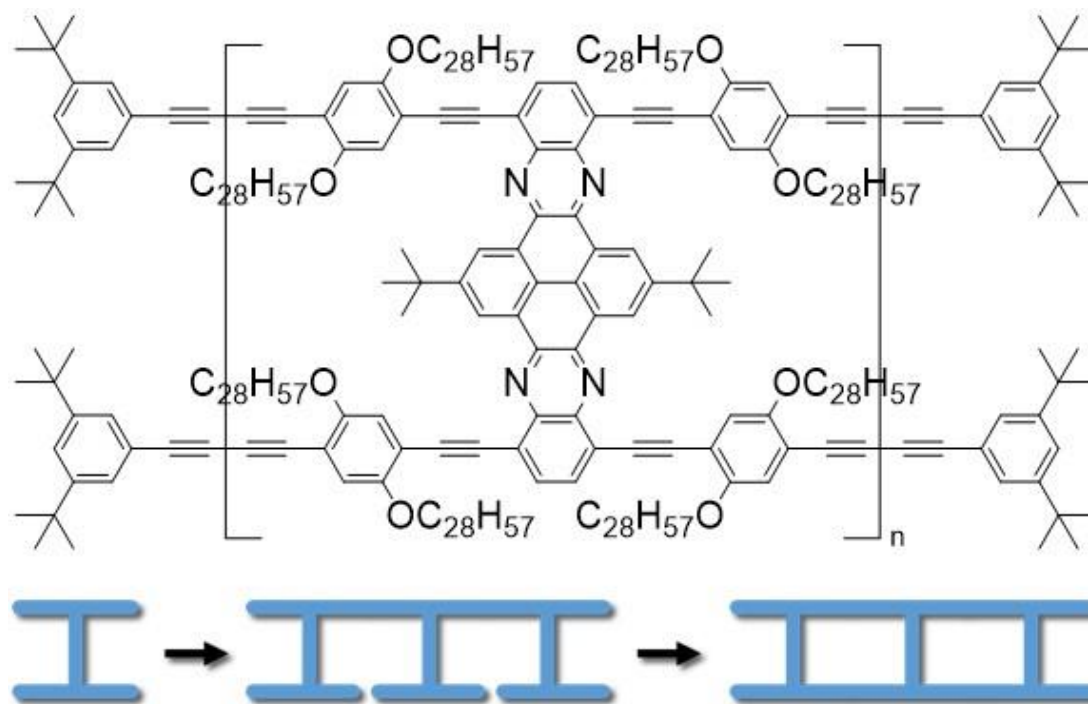
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Abstract No: M151

M151 New π -conjugated nanoscale ladder polymers

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A fascinating class of polymers deals with ladder polymers (LPs), which consist of an uninterrupted sequence of adjacent rings sharing at least two atoms. Therefore, the polymer does not break apart if one of the two strands breaks and LPs are thus expected to possess a high resistance to thermal, mechanical and chemical degradation.^[1] Furthermore, most LPs own an exceptionally rigid structure in which the two strands are held at a discrete distance defined by the spacer. This allows investigation of the influence of interchain interactions (H-type coupling) between the two π -conjugated strands as well as intrachain interactions (J-type coupling) within the strands and HJ-type aggregate formation by means of single molecule fluorescence spectroscopy.^[2]

A fully π -conjugated, pyrene-based monomer was synthesized. The monomer was oligomerized according to the "zipping strategy" in a sequence of an acetylene-deprotection followed by an oligomerization under *Glaser-Eglinton* conditions and separation of the oligomers performed by gel permeation chromatography. The dimer and tetramer LP were obtained after deprotection using TBAF and closure of the second strand under *Glaser-Eglinton* conditions.

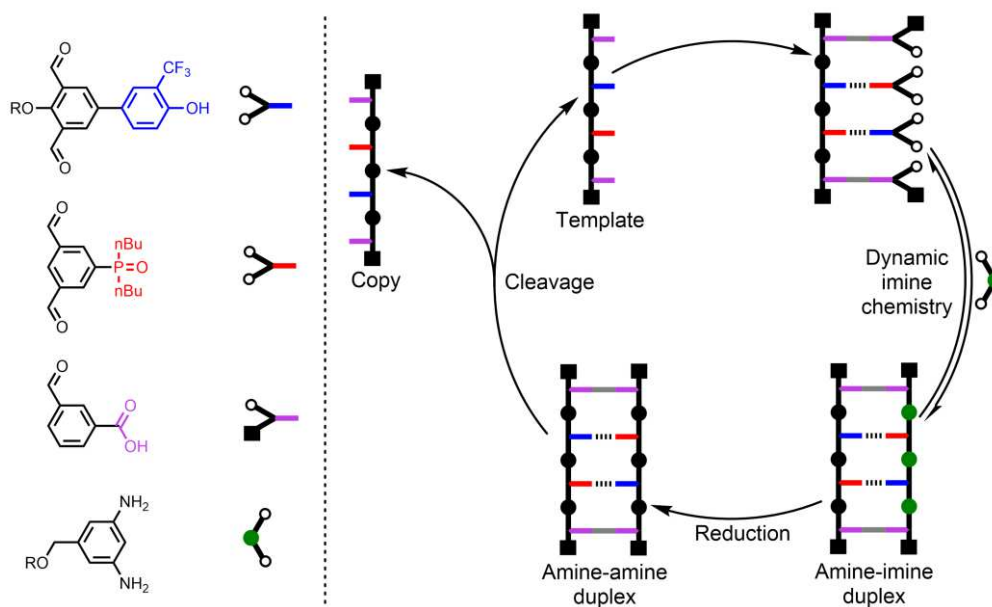
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M152 Template-directed synthesis of information oligomers using dynamic imine chemistry

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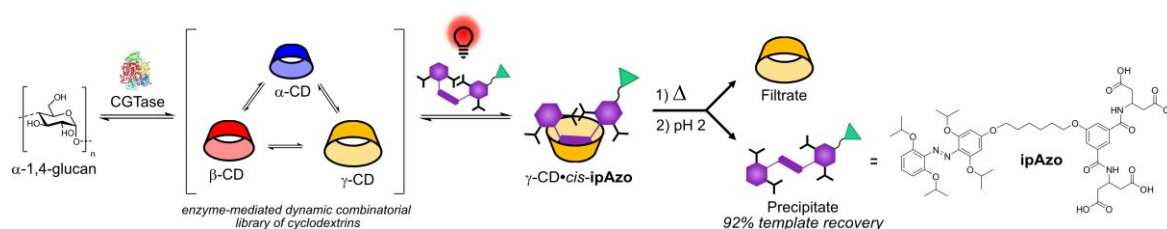
Caption: The replication cycle of the information oligomers. The building blocks for the oligomers are shown on the left.

Information-bearing oligonucleotides are essential in nature, with complex structures and functions. Enzymatic templating of these oligonucleotides has enabled evolution as information is passed between generations of oligonucleotides. The Hunter group is developing synthetic oligomers that function in organic solvents and are capable of non-enzymatic replication. One such oligomer design is based on the reductive amination of dialdehyde monomers with dianiline linkers.¹⁻³ In this poster, progress towards the template-directed synthesis of these oligomers is presented. The scheme below shows the building blocks and the key steps required for a replication cycle, which relies upon dynamic imine chemistry to form the backbone of the copy strand, which can be trapped by reduction to form the templated product.

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Abstract No: M153

M153 Light-controlled dynamic enzymatic synthesis of γ -CD using a recyclable azobenzene templateJuliane Sørensen ¹, Sophie Rachel Beeren ¹, Emilie Ljungberg Hansen ², Dennis Larsen ², Mathias Albert Elmquist ², Andreas Buchleithner ², Luca Florean ²¹ Technical University of Denmark, Kongens Lyngby, Denmark² , ,Caption: Synthesis of γ -CD from a DCL of CDs using a recyclable isopropoxy-substituted azobenzene template and red light

Cyclodextrins (CDs) are cyclic α -1,4-linked oligosaccharides commonly made up of 6, 7, or 8 glucopyranose units named α -, β -, and γ -CD, respectively. They have a truncated cone-like shape, a hydrophobic interior and hydrophilic exterior, which makes them ideal hosts for many different hydrophobic guests in water.¹

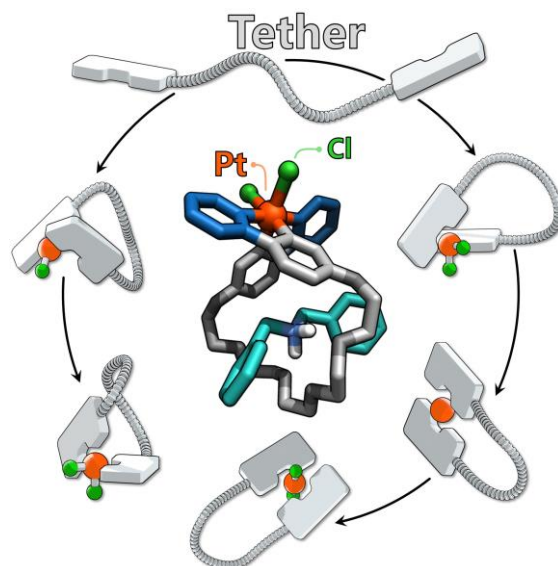
We have shown that when CGTase acts on an α -1,4-glucan source an interconverting mixture of CDs and linear α -1,4-glucans is formed. The CDs exist in an out-of-equilibrium kinetically trapped subsystem, which operates under *pseudo*-thermodynamic control, and wherein the product distribution reflects the relative stabilities of the CDs.² This system can be considered a dynamic combinatorial library (DCL). The distribution of CDs can be altered by external stimuli such as pH, salinity, or a template molecule that selectively binds to, stabilises, and amplifies a specific CD.³ We have previously reported the use of a photoswitchable azobenzene template to enable light-control of the outcome of the enzymatic reaction, where the distribution could be changed towards the selective formation of either α - or β -CD just by irradiating with different wavelengths of light in the UV-vis range.⁴

In this study the scope of this light-responsive dynamic system has been broadened to also include light-controlled synthesis of γ -CD. We present the synthesis of a set of water-soluble tetra-*ortho*-substituted azobenzene templates; a non-substituted, a methoxy-substituted, and an isopropoxy-substituted azobenzene.⁵ Depending on the *ortho*-substituents, and the wavelength of light used to irradiate the DCL, we can favour the synthesis of α -, β -, or γ -CDs. Using the isopropoxy-substituted template, we can obtain γ -CD in vastly improved yield, compared with an untemplated library. Moreover, this template can be readily recovered, enabling its recycling and re-use in subsequent enzymatic syntheses.

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M154 Cycling Tethers into Multiple Metallomacrocycles

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Caption: Figure 1. A cartoon representation of rings assembled with phenylpyridine-containing tethers and platinum ions.

Making rings has been a continuing research topic in the field of Supramolecular Chemistry.¹ The beauty of synthetic rings lays on their fascinating structures that keep wowing us, and the unique functions they perform — from sensing and molecular recognition to cargo delivery and nanomachinery.² When synthesizing a ring, one can obtain a mishmash of macrocycles (kinetic approach) with different sizes, or a single ring if a template is accessible (thermodynamic approach). We envisioned that uniting these approaches with postsynthetic modifications would allow us to controllably transform a single linear molecule —the tether— into multiple rings.

Recently, our group developed a synthetic platform that relies on phenylpyridine proligands and platinum centers to produce cyclometalated complexes with intriguing properties, including selective chromic behavior, rich reactivity, and rare intermetallic bonding.^{3–5} Using these advances, we have wrapped a phenylpyridine-containing tether around a platinum ion to render up to five different rings with pseudocrown ether cavities (Figure 1). These metallomacrocycles differ in shape, size, and host activity. The Pt ion in the rings is redox-responsive and stays active even if the host is occupied by a guest, which facilitates fast pseudorotaxane-to-pseudorotaxane transformations, guest-directed ring reactivity, and release of guests upon redox stimulation.⁶

In this presentation, I will discuss the rationale behind our approach and the design of the tethers, as well as relevant synthetic information. Spectroscopic characterization of the isolated rings (10 obtained from 2 tethers) will be detailed and accompanied by a discussion on their host activity. Finally, I will discuss some of the exciting avenues that this research is opening in our group.

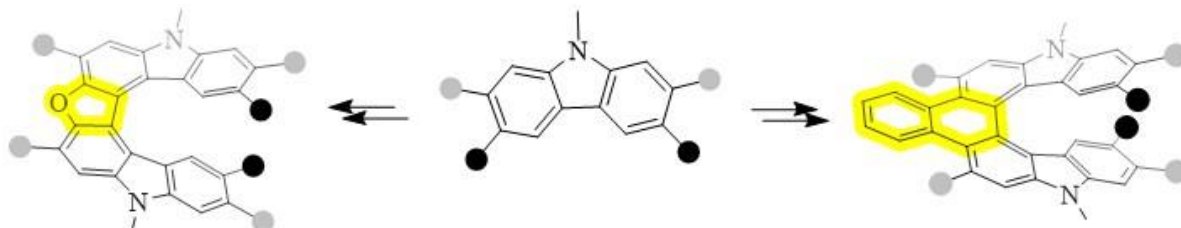
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M155 DESIGN AND SYNTHESIS OF MULTI-TURN HELICENES FOR ENHANCED FUNCTIONALITY

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Caption: Scheme 1. Schematic representation of the synthetic goals of our previous research (left) and our current synthetic strategy (right)

Helicenes are aromatic compounds consisting of angularly annulated aromatic rings ultimately forming a stereogenic axis. The preparation of long fully conjugated helicenes with two or more helical turns represents a significant challenge.¹ These types of π -conjugated molecules exhibit an extraordinarily large response in circular dichroism (CD) and circularly polarized luminescence (CPL) which has led to their increased popularity in the last years in the construction of state-of-the-art optical devices.²

Previously, we described the synthesis of a series of azaoxa[n]helicenes, which is based on iterative oxidative furan formation between 3,6-dihydroxycarbazoles and/or 2-naphthols.³ The flexibility of this method allows the convenient and scalable synthesis of symmetric and asymmetric chiral structures.

In this contribution we present our attempts to further elongate carbazole-based helicenes by using C-C coupling reactions. This way we can explore new ways of accessing longer helicenes starting from simple building blocks. We hope that by increasing the length of our helicenes we can also achieve enhancing of the dissymmetry factors in the CPL output.

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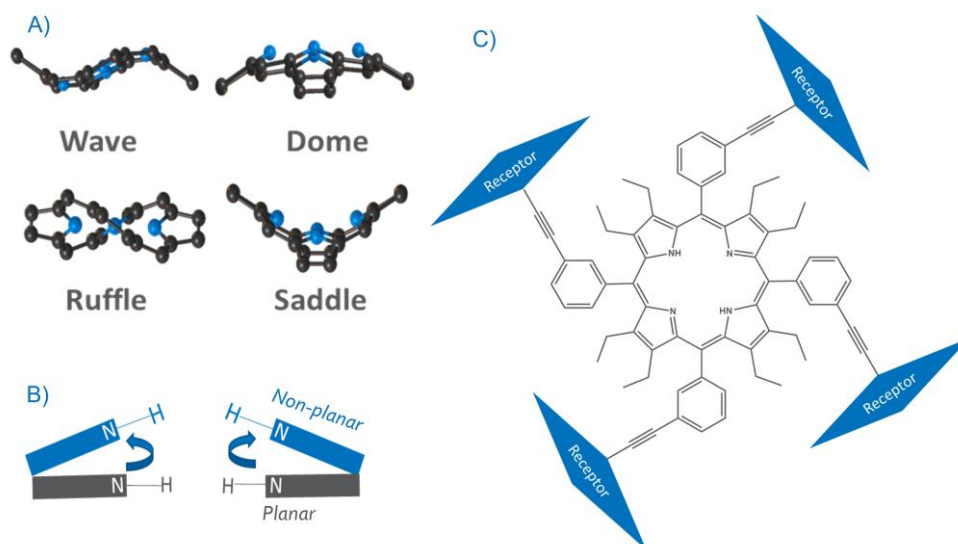
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M156 Tailoring substrate binding to influence catalytic behaviour in non-planar porphyrins

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Caption: Figure 1: A) The non-planar distortions of porphyrins. B) Sketch of the distortion of the inner core. C) General structure of the target porphyrins.

The exquisitely precise molecular structures found in nature, such as the active sites of enzymes and the photosynthetic reaction centre highlight the unique properties of porphyrin-based materials. As such, the design of structurally complex synthetic porphyrins has attracted attention for a myriad of applications, from energy generation, to catalysis, and in medicine.¹ While many porphyrin structures are planar, the introduction of sterically demanding peripheral substituents can introduce non-planar distortions of the macrocycle (Fig. A). As such structural distortions expose the inner core nitrogen atoms and NH groups, (Fig. B), these materials can act as organocatalysts and as receptors for small molecules.^{2,3}

Here, we aim to further investigate the potential of these systems by designing new materials with tailored binding pockets. This is achieved by incorporating a variety of peripheral 'receptor units' capable of forming non-covalent interactions with different substrates. (Fig. C). The influence of the structure of these units is investigated by changing their size and orientation, as well as comparing the effects that different binding groups, such as ester and amide functionalities, have on their interactions with specific target substrates.

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Abstract No: M157

M157 Nanoscale π -conjugated ladder oligomers and polymers

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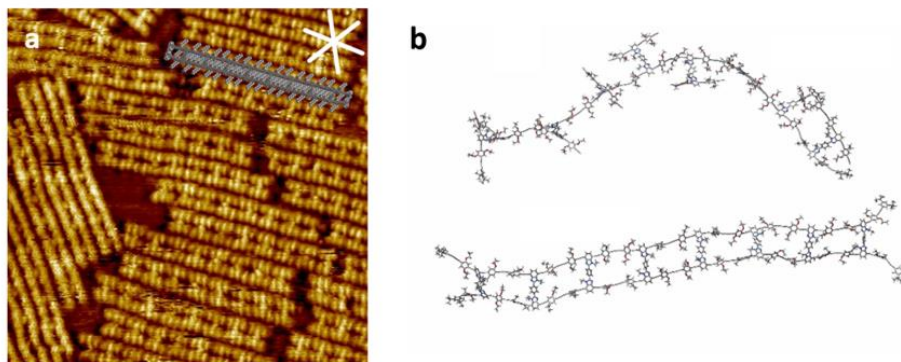


Figure 1: (a) STM-image of the ladder octamer at the solid/liquid interface (HOPG/TCB); b) Representative structures computed from room temperature molecular-dynamics simulations.

We introduce a versatile synthetic strategy towards π -conjugated ladder polymers. Two rigid-rod polymer chains are repeatedly covalently connected by stiff molecular rungs, which prevent the polymer from collapsing. The synthesis is based on the zipping strategy: “H”-shaped monomers are polymerized along one strand and afterwards an intramolecular zipping reaction yields almost perfect ladder oligomers and polymers. The ladder molecules can be visualized by scanning tunneling microscopy (STM). The two π -conjugated strands and discretely spaced rungs are clearly resolved for the oligomers (e.g. the octamer, Fig. 1).

The enhancement of molecular rigidity is confirmed by fluorescence depolarization dynamics and complemented by molecular-dynamics simulations. The ladder polymer strands retain their native environment, implying that they can be employed in optoelectronic applications.

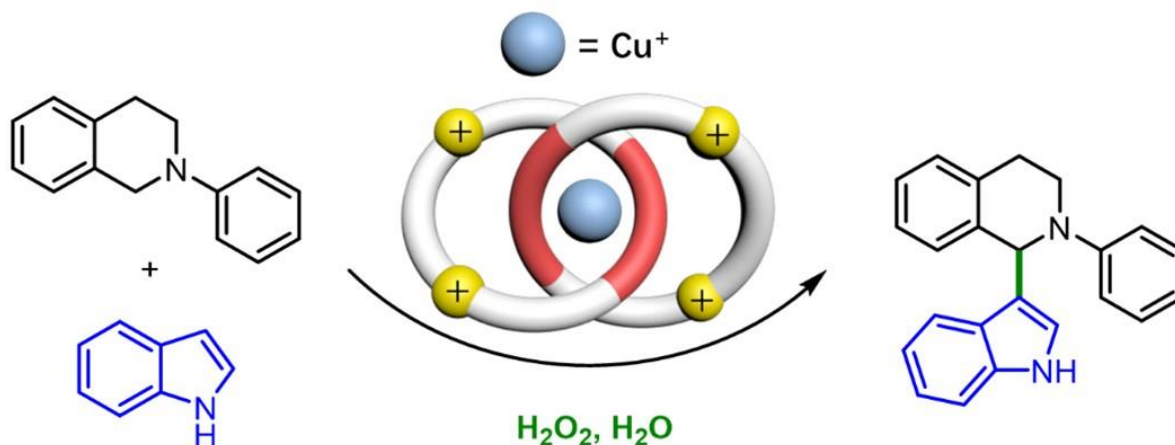
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M158 Stable Copper(I) Catalysts Supported by Catenane-based Ligands for Cross Dehydrogenative C–C Coupling in Water

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Transition metal catalysts derived from Earth abundant metals for organic transformation under aqueous conditions are of central importance to the sustainable development of our society. While copper complexes are known for their rich catalytic potential, the facile ligand exchange and ease to disproportionate/oxidize of Cu^{I} pose challenges in developing stable copper catalysts with sustained activity and lifetime in aqueous systems. In this work, the use of the mechanically interlocked catenane as a ligand for developing aqueous stable Cu^{I} catalysts for $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^2)$ coupling is described. The tetracationic catenane ligand not only provides a kinetically stabilized Cu^{I} due to the catenand effect, but also a good aqueous solubility that enables the Cu^{I} complexes to be effective catalysts for the oxidative coupling of indoles and tetrahydroisoquinolines (THIQ) using H_2O_2 as the oxidant with a high atom economy.

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Abstract No: M159

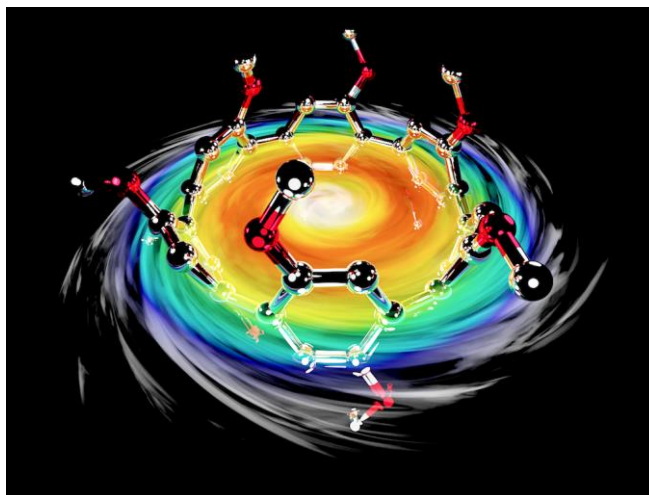
M159 Supramolecular Chemistry of Dodecamethoxy[6]cycloparaphenylene

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[*n*]Cycloparaphenylenes ([*n*]CPPs, where *n* is the number of phenylene groups), consisting of 1,4-linked phenylene unit, are macrocyclic organic molecule, which has attracted much attention due to their unique π -conjugated structures and physical properties.^{[1][2][3]} [*n*]CPPs have a curved π -conjugated system extends throughout the cyclic molecule and the ring size can be precisely tuned by the number of benzene rings, making them a promising new host molecule. However, [*n*]CPPs have been reported to show inclusion ability only for guest molecules with curved π -conjugated systems, such as fullerenes,^[4] and [*n*]CPPs with small ring size.^[5]

In this study, we have successfully synthesized a new [6]cycloparaphenylene derivative (**1**) with twelve methoxy groups at the 2,5-positions of all benzene rings. The synthesis of the compound **1** was achieved by utilizing our developed CPP synthesis method via a macrocyclic gold complex.^[6] The compound **1** adopts a cylindrical molecular structure with a planar chirality due to multiple introductions of methoxy groups. The compound **1** functions as a supramolecular host, and successfully included electron-deficient guest molecules with a flexible alkyl chain unit. In addition, the compound **1** has an extremely high HOMO level compared to the unsubstituted [6]CPP by the electron-donating ability of the methoxy groups, allowing facile oxidation to give dicationic species with an in-plane aromaticity.^[7]

Furthermore, we succeeded in synthesizing a [2]rotaxane by end-capping using the urea-forming reaction of the inclusion complex composed of the compound **1** and a hexamethylene diisocyanate with adamantylmethylamines. Surprisingly, upon two-electron oxidation of [2]rotaxane, the ¹H NMR signals of the methylene protons of the axial molecule shifted significantly to -14.5 ppm, which is due to the shielding effect by a diatropic ring current on the CPP macroring by the appearance of in-plane aromaticity.^[8]

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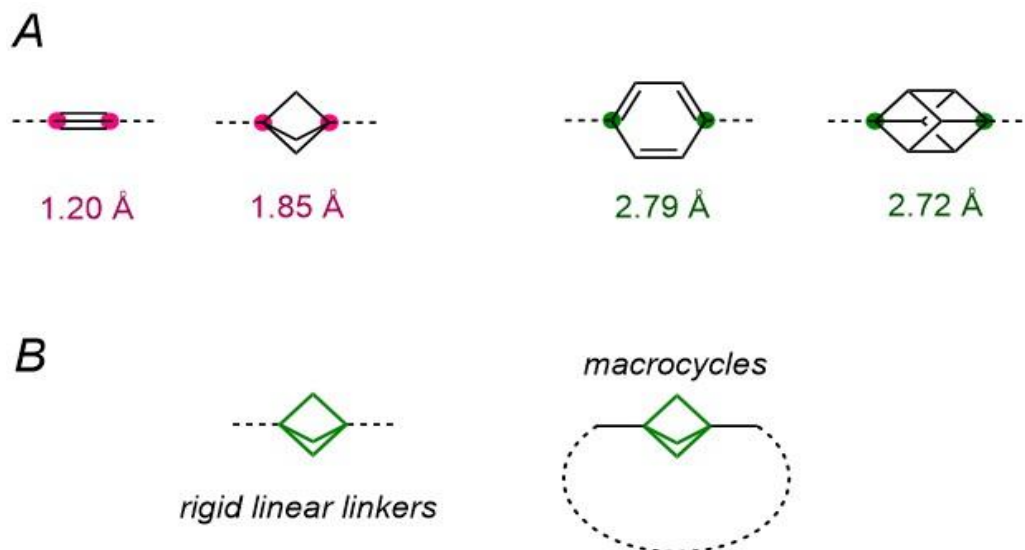
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Abstract No: M160

M160 Rigid aliphatic hydrocarbons as key structural motifs in material precursors

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Bicyclo[1.1.1]pentane (BCP) and cubane are representants of rigid non-conjugating hydrocarbons, a group of compounds characterized by highly strained three dimensional skeletons. Due to their molecular size and shape, these rigid aliphatic compounds serve as isosteres to internal alkyne and 1,4-disubstituted benzene structural motifs (Figure 1A).^[i] Taking advantage of this structural trait, numerous new biomedical and material applications of those rigid hydrocarbons are being reported currently. However, the poor tolerance of the BCP and cubane towards functional group interconversion and certain transition metal-catalyzed processes^[ii] make it difficult to introduce this polycyclic motif into functional molecular architectures.

This contribution presents our recent synthetic advances towards the functionalization of rigid aliphatic hydrocarbons,^[iii] and their application as key structural motifs in molecular electronics and new responsive systems. The latter including macrocycles, donor-acceptor molecules, and bis-porphyrin tweezers (Figure 1B).^[iv]

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Abstract No: M161

M161 Assess the role of proximal Lewis-bases in directing NH₃ oxidation through hangman porphyrins

Samuel Veroneau, Daniel Nocera

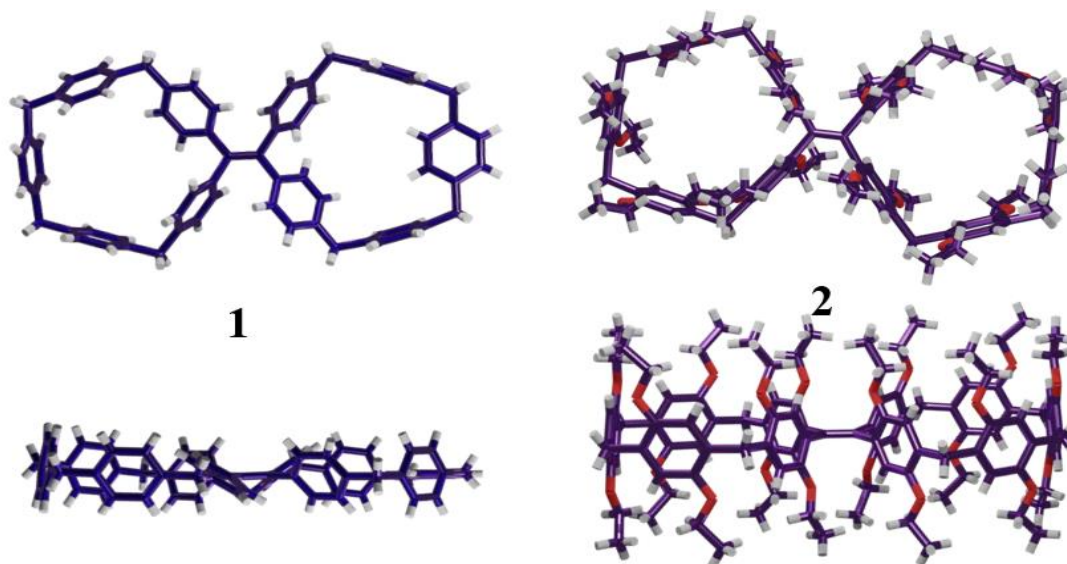
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The oxidation of NH₃ to NO₃⁻ is highly exergonic when coupled to the production of water ($\Delta G^\circ \approx -230$ kJ per mol). Nature, however, relies upon the *endergonic* formation of a single N–O bond to begin this process, with the conversion of NH₃ into NH₂OH (Fig. 1a). It is through the subsequent oxidation of NH₂OH that energy is liberated, though the mechanism of this reaction remains elusive. The hydroxylamine oxidoreductase enzyme has historically been believed to generate nitrite; however, recent work suggests nitric oxide (NO) to instead be the requisite initial product. This ambiguous reactivity is directed by a conserved iron-based P460 cofactor with a tyrosine cross-link to position a glutamate residue within its secondary coordination sphere. The appendage of this Lewis-basic site above the iron center has been shown necessary for activity, despite the underlying reaction being ambiguous. Hangman porphyrins are employed now to investigate this reactivity. Hangman porphyrins and related architectures (e.g., hangman corroles, pacman scaffolds) are a group of heterocyclic macrocycles where a pendant functionality is “hanging” above an active metal site. Lewis-acidic groups (e.g., carboxylic acids) are commonly employed to enhance the CO₂ reduction reaction, positioning protons and proton relays directly over the active site. Lewis-*basic* groups (e.g., carboxylates) could be similarly incorporated, and the implication of the secondary coordination sphere in *hao* posits hangman porphyrins as ideal model systems to study its unique functionality and reactivity.

M162 Dual macrocycles exhibiting interesting photophysical and host-guest properties

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Caption: Top and front view of the crystal structures of dual macrocycles 1 and 2

The design of new macrocycles, which offer well-defined cavities with different sizes, is at the heart of supramolecular chemistry. $[1_n]$ paracyclophanes ($[1_n]$ PCP) and pillararenes, are macrocyclic oligomers of aromatic rings, which are bridged by methylene groups at the *para* positions. Their highly symmetrical and relatively rigid structures have attracted much attention of chemists due to the easy accessibility to functionalization and their versatile host-guest chemistry.¹⁻² These features make them good candidates as host molecules for the fabrication of sophisticated (supra)molecular, advanced materials, or molecular machines. The construction of novel PCP- and pillararene-based hosts with luminescent properties has also garnered great attention. Herein, we have fabricated two novel macrocyclic dimer **1**³ and **2**⁴, in which a tetraphenylethylene (TPE) moiety was embedded as a linker in the center of the molecules, thus making them aggregation-induced emission luminogens (AIEgen). Our novel molecular design orthogonally incorporates supramolecular cavities with AIE properties. Meanwhile, the macrocycles partially restrict the rotation of the propeller-like TPE aromatic rings, stimulating an obvious fluorescence colour change both in solution and in the solid state. In addition, it was found that both macrocycles could act as hosts for various guests.

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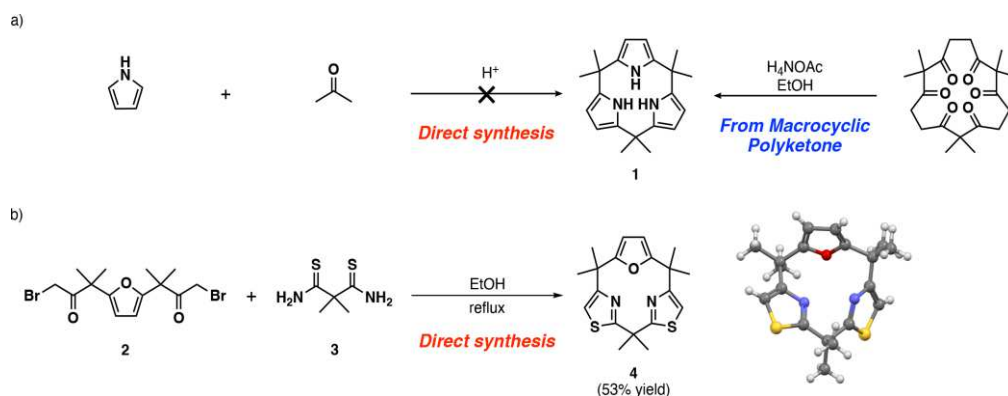
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Abstract No: M163

M163 Direct Macrocyclization of Calix[3]pyrrole analogs via Thiazole Formation

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Caption: Scheme1. (a) Indirect synthesis of calix[3]pyrrole 1 (b) Direct synthesis of calix[1]furan[2]thiazole 4

The acid-catalyzed condensation reaction between pyrrole and carbonyl compound leads to tetrapyrrolic macrocycles such as calix[4]pyrrole and porphyrin, whereas tripyrrolic macrocycle, calix[3]pyrrole (**1**), has not been observed. Instead, calix[3]pyrrole (**1**) has been synthesized from a macrocyclic hexaketone precursor (**Scheme 1a**) because the macrocyclic ring strain in **1** triggers strain-induced ring expansion reactions to give calix[6]pyrrole under acidic conditions.¹ The limited and circuitous routes for calix[3]pyrrole analogs have hindered fundamental understandings and applications of this chemistry. In this research, we aimed to enable direct macrocyclization of calix[3]pyrrole analogs by reducing their macrocyclic ring strain by an appropriate molecular design. Here, we report achieving this via Hantzsch thiazole formation reaction from α -bromoketone and bis(thioamide).

In our previous research, we have disclosed that the macrocyclic ring strain of calix[3]pyrrole-related macrocycles increases as the number of inner NH sites increases.^{2,3} However, replacing a pyrrole with a furan or a thiazole ring, would result in decreasing of ring strain. Furthermore, Hantzsch thiazole synthesis between α -haloketone and thioamide can proceed under neutral conditions, thus avoiding strain-induced ring expansion. To realize this strategy, we synthesized α -bromoketone **2** from linear tetraketone to be coupled with bis(thioamide) **3**. When **2** and **3** were reacted in refluxing ethanol under neutral conditions, calix[1]furan[2]thiazole (**4**) was obtained in 53% yield (**Scheme 1b**). Single crystal X-ray diffraction analysis revealed that the macrocycle **4** has a partial cone conformation. As expected, the less-strained **4** did not undergo strain-induced ring expansion reaction even under acidic conditions. Instead, we achieved hydrolysis of the furan subunit in **4** to give a 1,4-diketone-embedded macrocycle, which can be derivatized to pyrrole or thiophene-embedded calix[2]thiazole[1]heteroarene analogs. This direct macrocyclization approach also offers novel synthetic routes for calix[3]pyrrole analogs with diverse substituents at the *meso*-positions, as well as potential applications as π -conjugated chromophores.

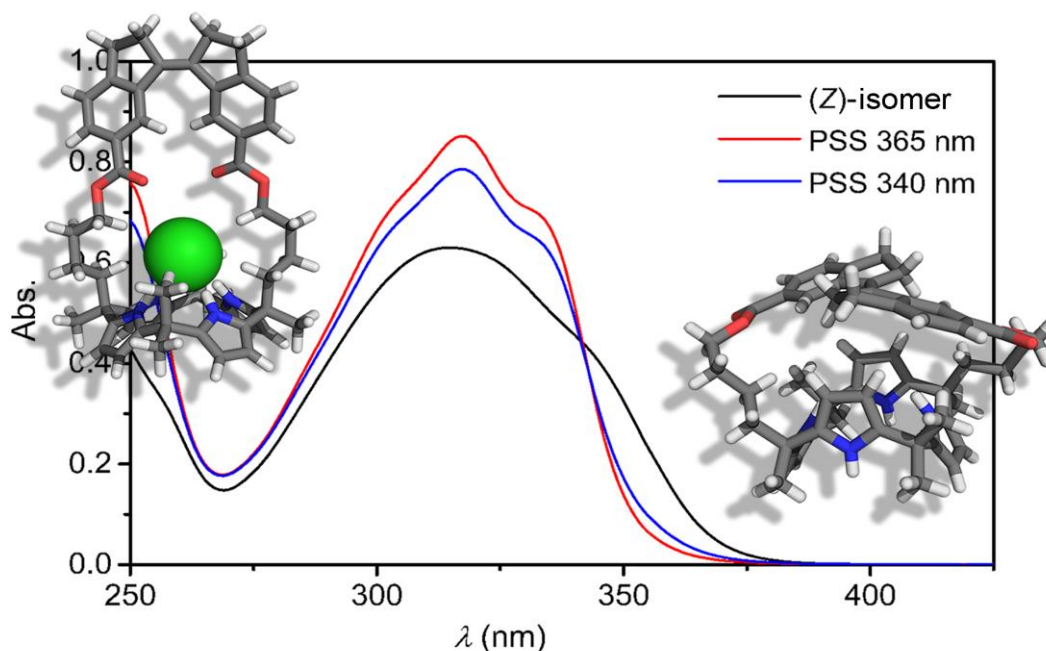
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M164 Photoswitch-strapped calix[4]pyrroles: Exceptional control of binding affinity and selectivity

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Caption: Control of chloride binding to photoswitch-strapped calix[4]pyrrole

Synthetic anion receptors have found practical use in a variety of applications such as analyte sensing, waste water extraction, and transmembrane transport.¹ Dynamic control of their binding properties will provide many advantages, for example, recovery in extractions as well as local (de)activation of transmembrane transport processes. Several strategies to modulate anion binding properties by external stimuli have therefore been developed over the past decade, most notably using light. Nevertheless, to achieve substantial differences in affinity between switchable states remains challenging and often the lowest affinity form is still significantly capable of binding.

We have incorporated molecular photoswitches as linker in strapped calix[4]pyrrole receptors² to control binding affinity and selectivity by light. The use of stiff-stilbene gave rise to a record 8000-fold difference in chloride binding strength between the photoaddressable *E* and *Z* isomers, surpassing by two orders of magnitude the best affinity differences achieved earlier in photoswitchable anion receptors.^{3,4} Recently, we expanded this work to the use of a dithienylethene photoswitch, which beside successful control of affinity, allowed – for the first time – to switch selectivity for halide ions. Further, recent work in our lab towards imprinting chiral information, in addition to application of these type of systems as recyclable extractants and light-gated transporters, will be presented.

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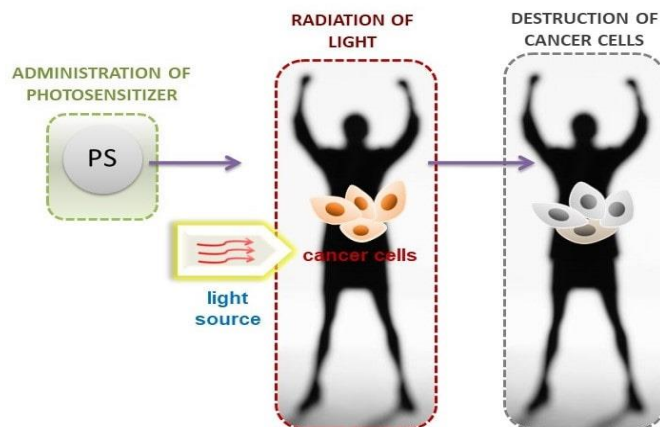
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Abstract No: M165

M165 Magnesium porphyrazines as potential photosensitizers in PDT

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For the last 20 years, macrocyclization reactions of dicyanitrile derivatives have led to a plethora of various porphyrazines. Porphyrazines have been evaluated for their electronic properties, for the tendency for aggregation and photodegradation, singlet oxygen generation efficiency and *in vitro* photodynamic activity. PDT is based on the irradiation of photosensitizer localized at the affected site of the tissue. This process causes generation of the singlet oxygen. It is known that conversion of light energy into chemical energy leads to chemical destruction of tissues or pathogens [1].

Herein, an overview of the synthetic, physicochemical and biological activity of the family of macrocyclic systems will be described. Four new compounds from the porphyrazine family were obtained. Porphyrazines were subjected to physicochemical and biological tests. Moreover, the absorption and emission properties, the tendency to form aggregates, photochemical stability, as well as the quantum yield of singlet oxygen generation were determined for all macrocycles. *In vitro* photodynamic activity of porphyrazines was determined against the LNCaP tumor cell line. The studies included incubation of tumor cells with porphyrazines both in their free form and after their incorporation into liposomes. Next, the tumor cells containing studied molecules were treated with the red light using LEDs, allowing to determine photocytotoxicity [2-4].

This approach is a very promising research path to design unique photosensitizers based on dipyrromethen and aza-dipyrromethen ligands. These will function as singlet oxygen generator anchored on gold nanoparticles, which is currently being pursued in our laboratory.

Financial support from the National Science Centre, Poland (SONATINA grant UMO-2022/44/C/ST4/00017) is gratefully acknowledged.

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Abstract No: M166

M166 Self-Sorting in Constitutional Dynamic Networks of Covalent Organic Macrocycles and Cages

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Self-sorting involves a screening process on the permutations and combinations of components and selects the optimal ones for generating specific organized structures presenting thermodynamically optimal constitutions, involving in particular molecular recognition processes. Our preceding studies focus on the concurrent generation of self-assembled structures of different nature via dynamic covalent connections under kinetic control.

Herein, we study the self-assembly and self-sorting processes of covalent organic macrocycles and macrobicyclic cages via multiple [2+2] and [3+2] polyimine condensations. The progressive assembly of the dynamic covalent architectures involves component selection and self-correction processes to generate self-sorted outputs. Many efforts have been devoted to studying how the process of a self-sorting system can be influenced by reaction kinetics. By operating through both kinetic and thermodynamic properties, self-sorting systems are allowed to reveal the occurrence of kinetic switching via component exchange in the course of the formation of macrocycles and macrobicyclic cages. The results showed that with an appropriate choice of precursor components, dynamic covalent libraries (DCLs) could undergo fast selection and amplification of the kinetic product which then adapts with time towards the thermodynamic product via component exchange. This approach was further exploited for the orthogonal amplification and switching from a kinetically trapped out-of-equilibrium distribution of constituents to the thermodynamically self-sorted one in the diagonal of their associated [2 × 2] constitutional dynamic networks (CDNs). In addition, constitutional dynamic networks of higher complexity, i.e., [3 × 2] and [4 × 2], have been constructed from five and six-component DCLs, respectively.

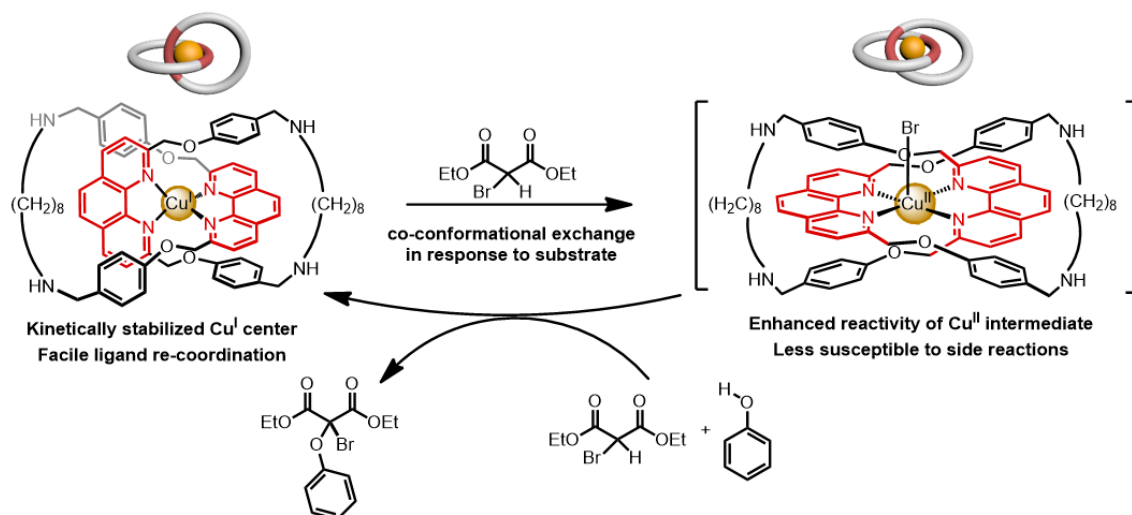
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M167 Catenane-Coordinated Copper Complexes in Catalytic C-O Cross Coupling Reactions

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In this presentation, catalytic activity of copper(I) complexes supported by phenanthroline-derived [2]catenane ligands towards a new C(sp³)-O dehydrogenative cross-coupling of phenols and bromodicyclopentadienes is reported. By interlocking the phenanthroline ligands as a catenane, ligand re-coordination and pre-catalyst regeneration are facilitated by the mechanical bond and result in an active catalyst with a longer lifetime. The catenane supported Cu(I) is highly efficient with a broad substrate scope and can be applied in gram-scale transformations without a significant loss of the catalytic activity. This work demonstrates the advantages of using a catenane structure to provide a dynamic and responsive coordination sphere, highlighting the potential of mechanical bond as a design element in transition metal catalyst development.

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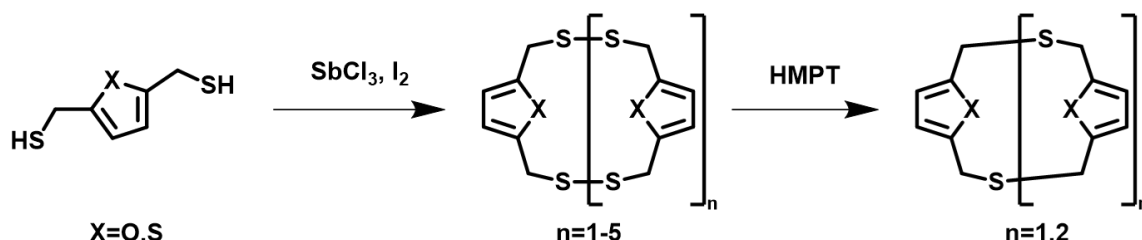
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Abstract No: M168

M168 Heteroarene incorporation into pnicogen directed self-assembly

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Caption: Synthetic overview for the formation of heteroarene macrocycles via pnicogen directed self-assembly

The formation of macrocyclic molecules is of great importance to the scientific community due to their range of uses and functional tunability^{1,2}. Established synthetic methods while producing a range of useful molecules are often challenging and low yielding³. Previous work in the DWJ lab has established a method for the synthesis of disulfide macrocycles utilizing pnicogen directed self-assembly^{4,5}. This approach has produced a range of interesting systems, however most of the previous established body of work with this technique has focused on benzylic systems. This poster will describe work on the formation and crystallization of novel furan- and thiophene-based disulfide dimer and trimer macrocycles⁶. This showcases the viability of incorporating systems with endohedral heteroatoms into the scope of accessible systems available through this assembly method as well as providing a platform for future studies on the host guest interactions of these systems.

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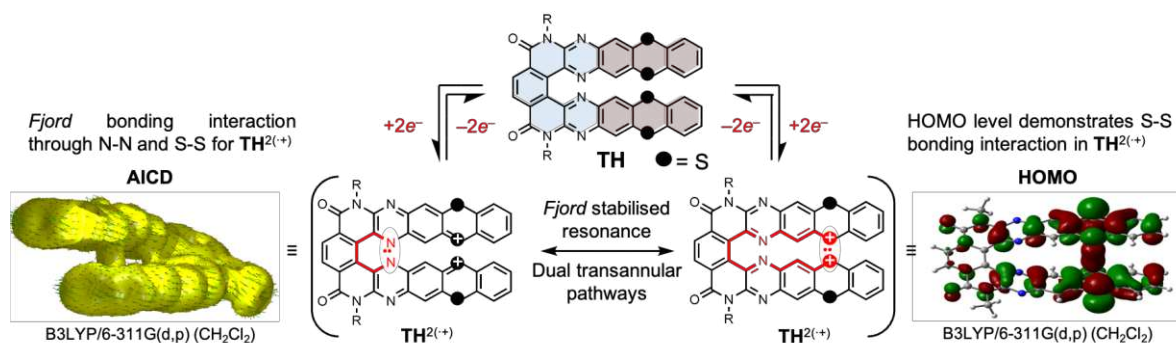
Abstract No: M169

M169 Redox-controlled Zimmerman–Möbius aromaticity

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² , ,



Electroactive helicenes have a wide range of applications in redox and/or photoinduced chiroptical molecular switches, charge-transfer materials in organic electronics, organic/metal-organic conducting polymers, and so on.¹ Recently, our group developed a concise three-step synthesis to generate electroactive helicenes derived from aromatic diimides that, upon reduction, showed unexpected through-space *fjord* bonding interactions. The through-space electronic stabilisation achieved in this case is one of few examples of ground-state Zimmerman–Möbius aromaticity.² Now, we present the next stage of this research to introduce new electroactive motifs to our helicene designs and explore the nature of redox-controlled Zimmerman–Möbius aromaticity further. Notably, preliminary DFT models of thianthrene-extended helicene (**TH**) suggest that two-electron oxidation to form the diradical dication $\text{TH}^{2(++)}$ leads to the formation of new *fjord* spin-pairing interactions reminiscent of Zimmerman–Möbius aromatic ground states obtained previously by reduction. Moreover, **TH** displays bright orange solid-state luminescence, which we attribute to a combination of internal push–pull donor–acceptor effects. These observations together offer exciting opportunities to study the emergence of *fjord*-stabilised spin–spin and electronic properties using dual stimuli as well as potentially probe the nature of exotic Zimmerman–Möbius aromaticity in the excited state.

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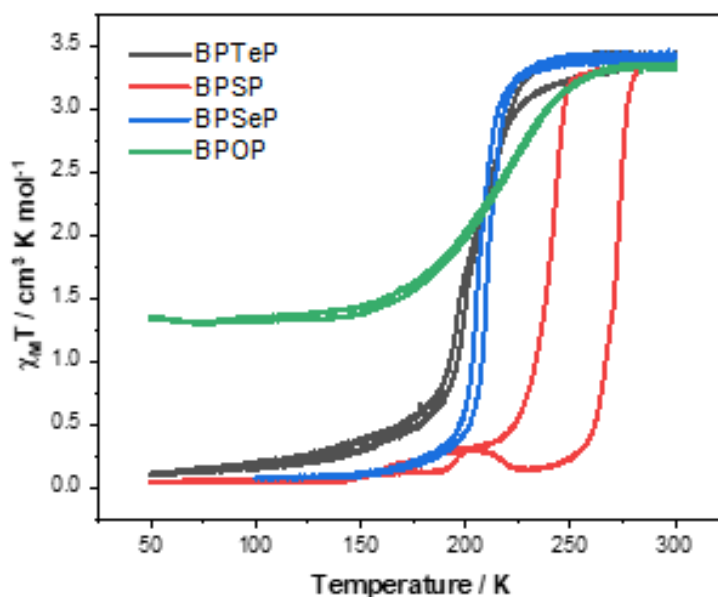
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Abstract No: M170

M170 Spin crossover in chalcogen-containing heterocyclic metal–organic frameworks

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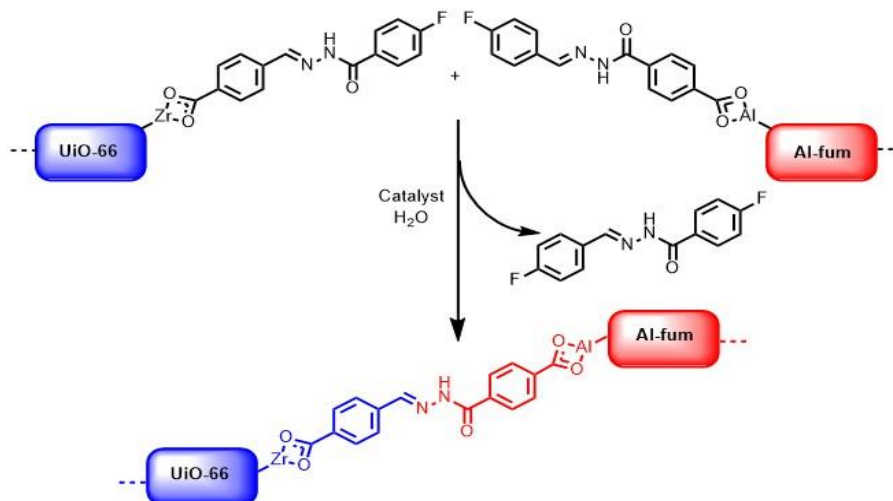


Caption: Magnetic susceptibility of each Hofmann-like framework with varying ligand heteroatoms.

Metal–Organic Frameworks (MOFs) are an exciting class of materials that are capable of a multitude of properties owing to their synthetic flexibility. One such property is spin crossover (SCO), whereby the spin state of a metal centre can be switched from a paramagnetic high spin (HS, $S = 2$) state to a diamagnetic low spin (LS, $S = 0$) state through external stimuli such as temperature, light, pressure, or even guest inclusion. To date, a great array of spin crossover complexes and MOFs has been synthesised largely incorporating linear bidentate bipyridyl ligands and cyanidometallate coligands. Here, we present a family of iso-structural SCO MOFs containing non-linear bipyridyl chalcogen-containing heterocycles $[\text{Fe}(\text{BPXP})(\text{Au}(\text{CN})_2)_2] \cdot x\text{Guest}$ (where $X = \text{O}, \text{S}, \text{Se}, \text{or Te}$), which exhibit a variety of SCO dependent on the central heteroatom. The abrupt, single-step transition was shown to differ quite considerably, with both the temperature and hysteresis width varying with each heteroatom replacement. Furthermore, inclusion of several different guest species was observed to induce multi-step transitions in several of the frameworks when compared to the as-synthesised materials. This broad range of behaviours highlights the sensitivity of the electronic switching behaviour to small changes in structure and host-guest interactions, presenting an avenue towards further tuning of SCO materials as a whole.

Abstract No: M171

M171 Dynamic Covalent Exchange on Metal–Organic Framework Nanoparticles

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The field of highly porous metal-organic frameworks (MOFs), which are highly porous, complex 3D structures which allow flexibility in their chemical nature, has grown steadily over the past few decades.^{1,2} On reducing the MOF particle size to the nanoscale, even the inherent benefits of nanomaterials, such as their controllable outer surface properties and high external surface-area-to-volume ratio, can be incorporated.¹ This affords the opportunity to tune the architecture of MOF nanoparticles, e.g., their outer surface, by selectively utilising properties from both the MOF- and nano-fields. Consequently, different chemical entities with many functional groups can be incorporated into their structure either directly through the diverse chemical building units, or post-synthetically by covalent modification of the linker and/or coordination to the metal.²

Herein, we focus on the ability to reversibly ‘switch’ between two different chemical entities on the surface of the MOF, whilst maintaining its inherent porosity and stability. In our work, we aim to incorporate the concept of dynamic covalent chemistry onto the surface of MOF nanoparticles, as in monolayer stabilized gold nanoparticles,³ with the goal of controlling both the chemical and physical properties of the MOF surface. So far, this approach has been very limited in the MOF field.⁴ UiO-66(Zr) and Aluminum Fumarate (Al-fum) nanoparticles with complementary hydrazone units attached were first synthesized, and subsequently interacted with reactive groups, to demonstrate their adaptable external surfaces. These particles could then allow us a route to reversibly link MOF nanoparticles together into extended assemblies (scheme 1).

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Abstract No: M172

M172 Chiral Crystals-on-Crystals: Predictable Morphologies with Local Functionalization

Ofir Eisenberg Qiang Wen, Maria Chiara Di Gregorio, Linda J. W. Shimon, Lothar Houben, Ifat Kaplan-Ashiri, Tali Dadosh, Yoseph Addadi, Michal Lahav, Milko E. Van der Boom

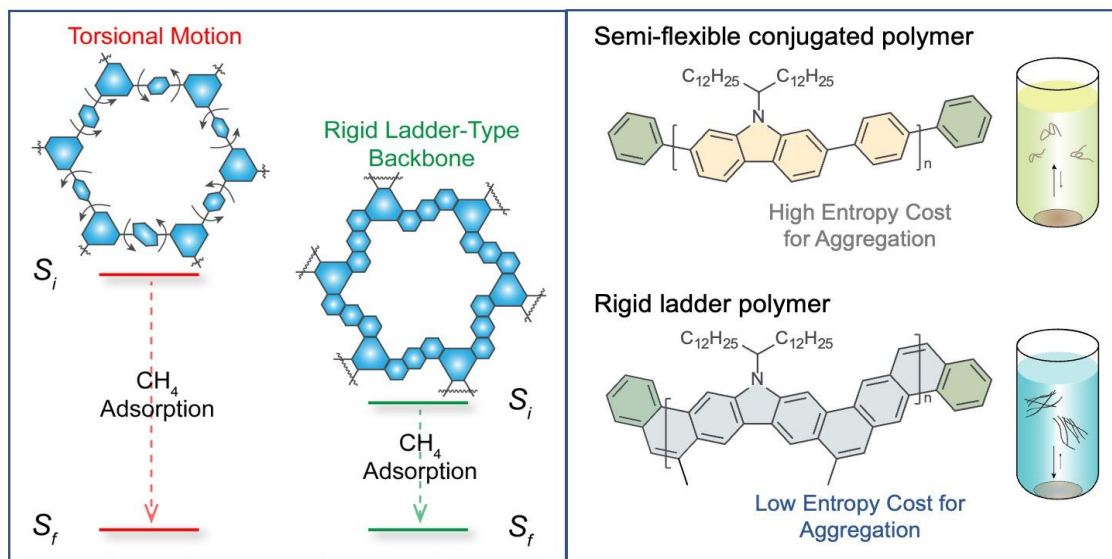
Weizmann Institute of Science , Rehovot, Israel

Metal-organic frameworks (MOFs) are a promising class of porous, crystalline materials with diverse potential applications. Their properties depend on their structures, including both their compositions and architectures. The intensive research of MOFs has led to an emerging family of hybrid crystals constructed by the conjugation of two or more different MOF units. Such hybrid crystals mainly consist of a core-shell structure, in which a guest MOFs is grown on a pre-synthesized host MOF, isotropically. We designed a unique co-MOF by combining two known crystal structures resulting in a dumbbell-shaped morphology. The dumbbell "weights" have been formed by epitaxial growth on the bases of the dumbbell's "bar", due to a common (001) facet. These unique crystals maintain their original morphologies and crystal structures in the co-MOF and their chiral nanosized channels are perfectly aligned along their long axis. Moreover, single crystal X-Ray analysis and modelling confirmed that there is chirality transfer from the "bar" to the "weights". The two crystal structures have channel walls with different chemical properties. We were able to utilize this difference and selectively confine different chromophores to the "bar" and "weight" regions resulting in selective optical functionalization of these micro-scale objects.

M173 Rigidity induced supramolecular functions of low-entropy organic materials

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Caption: (left) Significantly reduced entropy penalty during the methane adsorption process of a rigid ladder-type porous polymer network compared to t

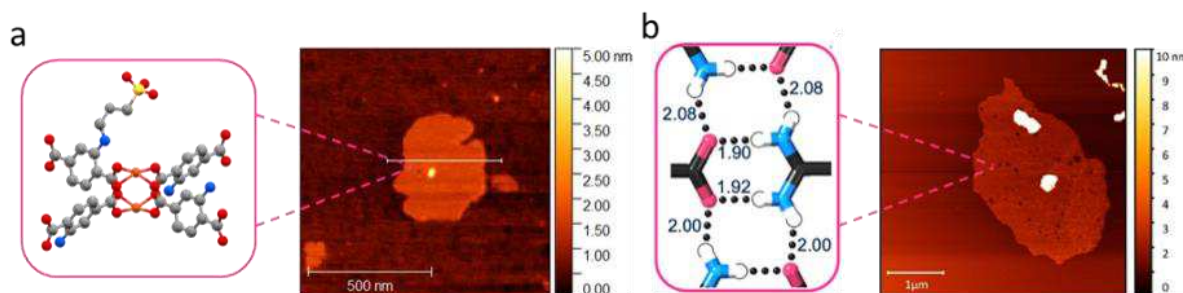
Conformational rigidity leads to intriguing supramolecular properties and functions in fused aromatic molecules. Thermodynamically, rigid molecules or materials backbones possess lower degree of freedom compared to their non-rigid counterparts, incurring lower entropy penalty when they self-aggregate or to bind with other species. Here I present several case studies of host-guest interaction and self-aggregation with rigid molecules and materials building blocks. Unconventional functions, such as turned-on thermofluorescence, high performance gas adsorption (Figure Box Left), and robust solution-phase aggregation (Figure Box Right), have been achieved in a series of low-entropy rigid organic materials.

Abstract No: M174

M174 Liquid exfoliation of framework materials to form nanosheets

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Caption: Figure 1: AFM topographical image and graphical representation of a) post-synthetically functionalised MONs used for tandem in catalysis in [5] b) HON

Liquid exfoliation is a simple and scalable approach for converting layered materials into free-standing single- and few-layer nanosheets with high aspect ratios. Early studies focussed on inorganic two-dimensional materials such as graphene but more recent examples have shown this approach can be adapted to exfoliate supramolecular structures. The high surface area, aspect ratios, and nanoscopic dimensions of these supramolecular nanosheets combined with their diverse and tunable chemistry make them ideal for a wide range of applications. However, despite intensive research into these materials, the formation of monolayer nanosheets with high aspect ratios in good yields remains a challenge.¹

In our work, we have developed a library of metal-organic framework nanosheets (MONs) based on the metal-paddlewheel secondary building unit (Figure 1a). By synthesising isorecticular series of layered frameworks incorporating dicarboxylate linkers with different functional groups we have sought to understand the design principles behind nanosheet formation.²⁻⁴ We have also post-synthetically functionalised the frameworks with different functional groups to enhance exfoliation and add new properties. We are working with academic and industrial collaborators to develop MONs for a wide range of sensing, catalytic, electronic and separation applications.⁴⁻⁷

We also recently utilised liquid exfoliation to access monolayer hydrogen-bonded organic nanosheets (HONs) with micron-sized lateral dimensions (Figure 1b).⁸ These HONs show remarkable stability and maintain their extended crystallinity and monolayer structures even after being boiled in water.

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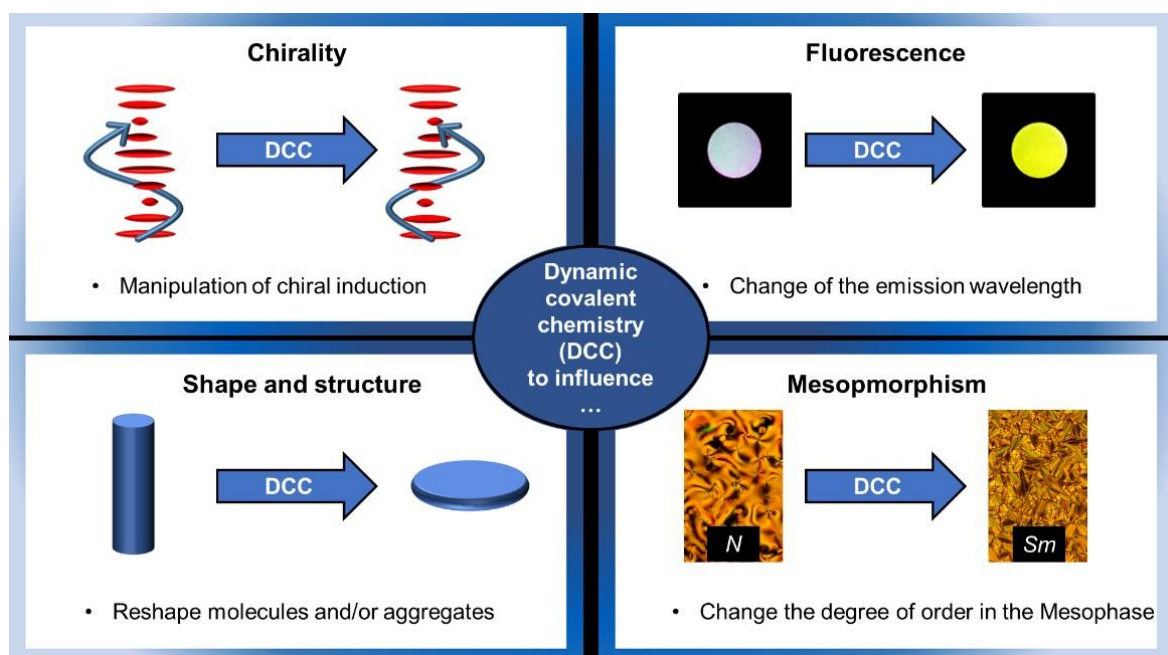
M175 Dynamic Covalent Chemistry – A Way towards Adaptive and Reusable Materials

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Caption: Figure 1: Schematic representation of the different properties which can be influenced by dynamic covalent chemistry.

The relevance of the development of sustainable functional materials is continually increasing. In this context the combination of functionality with adaptivity and reusability is a challenge and focus of research activities. Dynamic covalent chemistry plays a significant role in the field of functional, adaptive and reusable materials e.g. in polymeric networks or molecular cages.[1] But it is rarely used in liquid crystalline materials with adaptive properties.

In this project we want to use dynamic covalent imine bonds to allow the development of new adaptive and reusable materials in the field of liquid crystals (LC). Since the formation of imines occurs in a dynamic fashion covalent bonds are continually formed and broken. This leads to an adaptive manipulation of the properties and reuse of imine-based materials.[1,2] With the design of LCs based on a library of tailored imines we want to develop materials which can be manipulated by transamination reactions to tune properties such as chirality, fluorescence and the molecular shape of the mesogens.[3,4]

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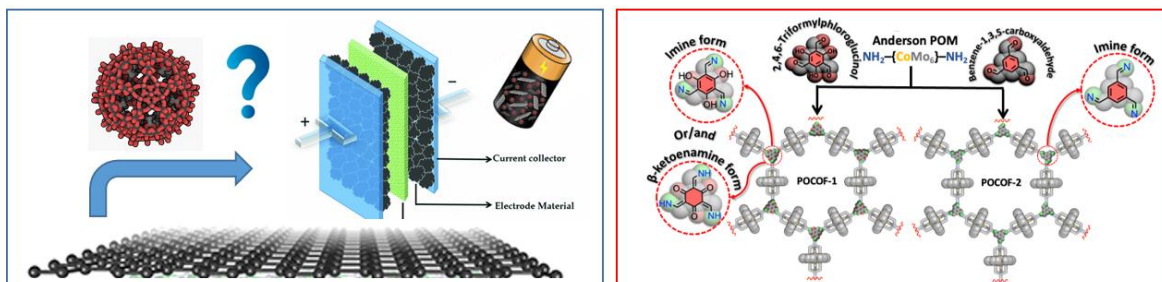
M176 Utilization of polyoxometalate (POM)-based hybrid materials for high-performance supercapacitors

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Polyoxometalates (POMs) represent a well-defined family of anionic metal oxide clusters, exhibiting rich redox characteristics, thus appearing as ideal candidates to achieve enhanced pseudocapacitive behaviour in supercapacitors (SC). Nonetheless, high solubility of POMs in water and organic solvents, followed by stability and processability issues can make them unsuitable for practical applications.[1] Fortunately, this problem can be overcome via the hybridization of POM counterparts with other materials. Here, we would like to show two approaches, which follow this rationale to observe enhanced SC properties.

First one shows the production of a novel hybrid architecture based on Keplerate type POM (Mo_{132}) functionalized with organic surfactant (DTAB), which upon mixing with electrochemically exfoliated graphene (EEG) nanosheets results in the formation of porous 3D superstructures. Mo_{132} -DTAB-EEG combines the redox activity of POMs and high electrical conductivity of graphene, all synergically mediated by the surfactant-assisted porosity enhancement, to form new electrode materials for SCs (**Figure 1 blue frame**).[2] This system exhibits high specific capacitance combined with excellent stability at different current densities, overall displaying significantly improved performance compared to pristine EEG material and other hybrid POM/carbon-based systems.

Second one takes advantage of the diamino-functionalized Anderson POM, which can be integrated into the robust three-dimensional architecture to form unique polyoxometalate-covalent organic frameworks (POCOF) hybrids (**Figure 1 red frame**). The electrochemical performance of the POCOF electrodes is studied in a symmetric system and shows outstanding values compared to other POM-based electrodes in terms of specific, areal and volumetric capacitance and high cyclability. Studies on the POMOF related monomeric counterparts prove that fine-tuning of the aldehyde structure is responsible for the observed differences in performance *i.e.* the POCOF that contains the β -ketoenamine form exhibits not only a superior electrochemical performance, but also a higher chemical stability when compared with the pure imine-type linkage. Presented results prove that integration of POM inorganic building block into the organic COF structural framework is a viable and promising alternative towards the generation of advanced electrochemical materials with superior properties.

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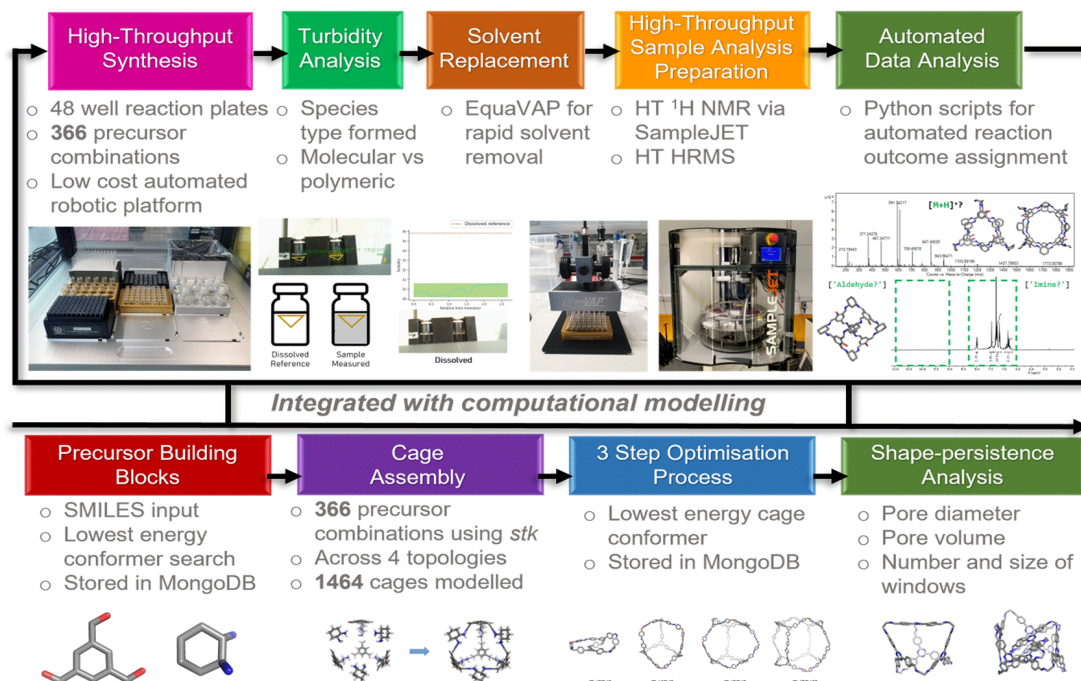
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Abstract No: M177

M177 Streamlining the Automated Discovery of Organic Cages as Supramolecular Building Blocks

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Caption: Figure 1: Automated high-throughput workflow for the synthesis, characterisation, and analysis of organic cages.

Dynamic covalent chemistry (DCvC) is a powerful tool for assembling complex organic molecules, such as macrocycles, cages, catenanes, and molecular knots. However, the targeted design of such molecules can be challenging, especially as the systems become more elaborate, because the reversibility and dynamic nature of DCvC has the potential to form a wide range of different species, making the prediction of the reaction outcome particularly difficult. Traditional experimental approaches, such as making small iterative changes to precursors, trial and error screening of reaction parameters, and relying on serendipitous discovery, are both labour intensive and time consuming. The combination of building blocks possessing varying functionality and topicity, across a range of reaction conditions, creates a chemical space too vast to explore manually on a reasonable timescale. High-throughput automation can be used to rapidly screen a broad synthetic space, and we have previously shown it is particularly effective for organic cages.¹ However, even with the aid of high-throughput automation, bottlenecks remained in data acquisition and characterisation on an equally high-throughput timescale. In addition, the majority of commercially available automated platforms are prohibitively expensive making adoption in other labs difficult. Here, we will present a streamlined high-throughput workflow for the synthesis and characterisation of organic cages formed via imine condensations, that makes use of a low-cost, open-source automated platform, computer vision, and automated data analysis in combination with computational modelling, to streamline the automated discovery of organic cages in the first instance (Figure 1). Finally, we will introduce how we are starting to use these organic cages as building blocks to access larger, more complex supramolecular assemblies.

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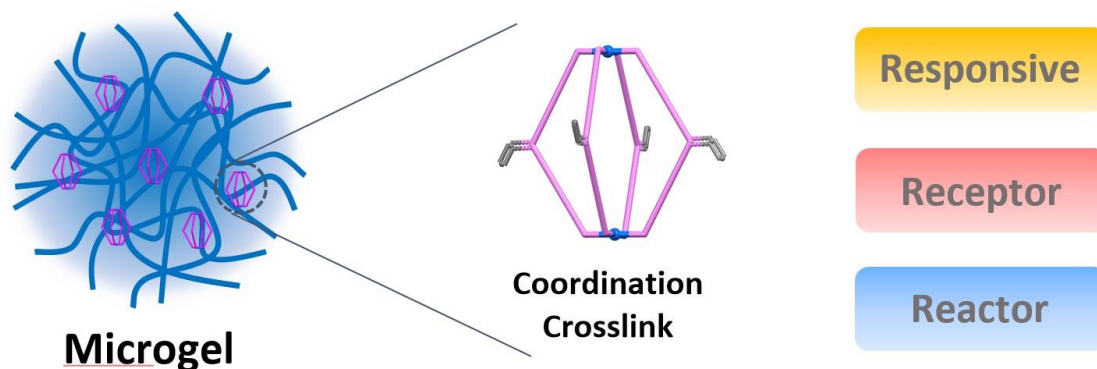
¹ R. L. Greenaway *et al.*, *Nature Communications*, 2018, 9, 2849

Abstract No: M178

M178 Microgels with Metal-Organic Coordination Cages as Responsive Crosslinks

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Microgels are crosslinked, colloidal hydrogels with swelling behavior. Owing to their tunable size, colloidal stability, and high surface area, as well as diverse shapes and compositions, microgels have received considerable interest. Microgels have found applications in bio-sensing, separation techniques, catalysis, and drug delivery. Generally, the networks of microgels are crosslinked chemically with covalent crosslinks or physically by hydrogen bonding. Herein, we describe the synthesis of microgels with metal-organic coordination cages (MOCs) as responsive crosslinks. The microgels were obtained via free radical polymerization using pre-formed MOCs as crosslinkers. They exhibit high stability and a narrow size distribution in aqueous media. Thermal responsiveness of the microgels was observed by dynamic light scattering. The dynamic nature of coordination bonds allows to alter or to disrupt the network structure of MOC microgels with chemical stimuli. Furthermore, MOC microgels can be used as specific sorbents because the metal-organic crosslinks can act as highly selective hosts.

Abstract No: M179

M179 Anion-templated synthesis of catalytically active metal-organic frameworks (MOFs) with amide functionalities

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Metal-organic frameworks (MOFs)¹ are an excellent class of catalytic materials for CO₂ capture and conversion² due to their versatility in tuning the pore size, topology, and ligand functionality. The templated synthesis of MOFs³ helped us to develop MOFs with intriguing topologies, which are not achieved by traditional synthetic routes. Anion-templated synthesis of MOFs³ is an excellent approach because anions play a crucial role in directing the assembly process of the building blocks in coordination networks and MOFs (Scheme 1), resulting in a wide range of functional materials with intriguing topologies. We have reported the anion-templated synthesis of catalytically active metal-organic frameworks (MOFs) with urea functionalities derived from a copper(II) paddle-wheel cluster and urea-carboxylate linker achieved at room temperature (Figure 1).² In this work, we are exploring the anion-binding properties of amide functionalities to generate catalytically active MOFs because of the formation of cooperative and unidirectional hydrogen bonding involving amide units and amide moieties are known to interact with the anions and the solvent molecules. A series of dicarboxylate ligands based on amide functionalities have been synthesized and these ligands were reacted with metal centers with different anions at room temperature. We have isolated MOFs with copper(II) paddle-wheel cluster and amide-carboxylate linker at room temperature and the catalytic activity of these MOFs in CO₂ conversion reaction is ongoing.

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Abstract No: M180

M180 Towards Engineering the Pore Environment of a Crystalline Sponge for Precise Structural Determination of Viologens

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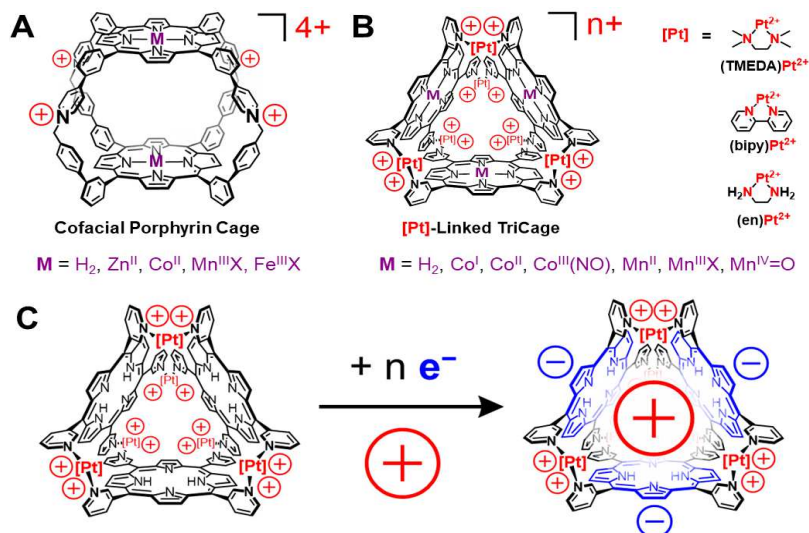
Throughout the years chemists have been appreciating the beautiful and precise structures of atoms and molecules using single-crystal X-ray diffraction (SCXRD)¹. On account of the challenging single crystal growth process required, however, the crystalline sponge (CS) technique — a method that aligns target guest molecules in the CS hosts for their SCXRD structural analysis without target molecule crystallization — is often used as an alternative approach². Whereas all reported CS hosts feature electron-poor pore environments, we hereby present our effort in search of the first electron-rich CS based on a metal-organic framework (MOF)—which could selectively capture and align electron-poor or cationic guest molecules through strong Coulombic host-guest interactions in its pores. We have successfully synthesized ultrahigh-quality single crystals of the selected MOF, which has a tailored anionic environment in its pores that can recognize the cations selectively. The facile capture and incorporation of several viologen cations — bipyridinium dication derivatives that have long been utilized to construct host-guest complexes³— are observed and confirmed to occur within a matter of seconds. We are endeavouring to characterize the host-guest complexes formed between the MOF host and the viologen cationic guests, obtain facilely the precise structures of selected viologens through SCXRD, and potentially expand our methodology to other electron-poor or cationic small molecules other than viologens in the near future.

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Abstract No: M181

M181 Cation-coupled redox processes in porphyrin-walled nanocages

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Caption: (A) Covalently linked and (B) Platinum-linked nanocages that will be discussed. (C) Reduction-induced cation uptake.

Nanoporous materials, such as MOFs,¹ COFs,² and discrete nanocages,³ are increasingly targeted as tunable supports for molecular electrocatalysts. In these materials, the reactivity of the confined catalytic sites is influenced by the local pore environment, creating a complex mechanistic picture since the pores must dynamically rearrange to accommodate the movement of protons and electrons during electrochemical changes. This presentation will describe the development of robust redox-active porphyrin nanocages^{4,5} as soluble model structures for examining how nanoconfined environments influence and respond to proton-coupled and other cation-coupled redox processes. Notably, these cages can reversibly exchange up to 18 e⁻, providing ideal platforms for studying how redox changes affect the enclosed chemical environment in these structures. Reduction was found to induce the uptake of organometallic cations, illustrating one way that a porous structure can respond to redox changes.⁶ This cation-coupled redox behavior was extended to studying proton-coupled electron transfer (PCET) in these cages since PCET processes are critical to electrocatalytic reactivity. The pK_a of confined carboxylic acid groups was increased dramatically by the reduction of Co^{II} sites hosted in the porphyrin walls of the cages, providing lessons for how the redox state of a pore might influence the chemistry of proton relays and key intermediates (e.g., M-CO₂⁻ species) involved in electrocatalytic transformations. Conversely, a manganese-functionalized derivative was observed to undergo proton-coupled oxidation to a tris-Mn^{IV}=O state, representing the first time that high-valent oxo complexes have been generated electrochemically in nanocages. The implications of these findings for catalytic reduction and oxidation processes will be discussed.

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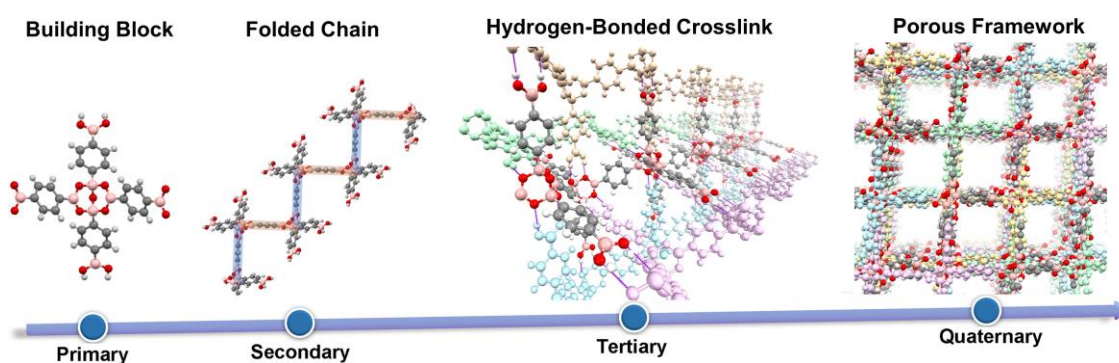
M182 A Single-Crystal Porous Polymer Based Hydrogen-Bonded Organic Framework

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Caption: Figure 1. Hierarchical structures of porous polymer-based hydrogen-bonded organic framework.

The direct synthesis of single-crystal porous polymers is a great challenge in polymer science and crystal engineering¹. Inspired by the hierarchical structures of protein crystals², we proposed and implemented successfully a strategy to achieve single crystals of a porous polymer by designing a 1D chain with dynamic covalent bonds and tunable supramolecular interactions. 1,4-Phenylenebisboronic acid monomers polymerize into a tetramer to afford a nine-membered $B_4O_5^{2-}$ cluster (primary structure), which further extends into 1D covalent chains (secondary structure) that are non-covalently cross-linked by hydrogen bonds and electrostatic interactions (tertiary structure), ultimately evolving to afford a hydrogen-bonded organic framework³ (quaternary structure). Compared to insoluble 2D or 3D crosslinked porous polymers, the 1D polymer chains show excellent solubility and solution processability. The dissolved chains can regenerate reversibly in single-crystal or amorphous states depending on the solvent evaporation rate. Further taking advantage of the solution processability, we continuously coated it onto a non-woven fabric to afford a functional composite textile capable of capturing NH_3 . The design strategy may open a new avenue for the exploration of single-crystal porous polymer materials with precise structural information, confined pore spaces, and straightforward solution processability.

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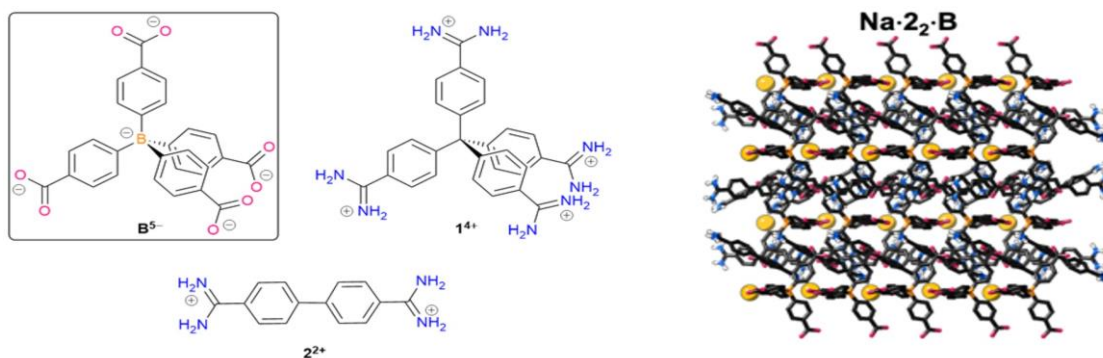
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Abstract No: M183

M183 Cation Exchange of an Anionic Hydrogen Bonded Framework

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Although porous materials with neutral charge are common, frameworks containing an overall negative charge are underexplored. This is particularly the case for hydrogen bonded materials.^{1,2} In this work, we explored the synthesis of anionic charge-assisted hydrogen bonded frameworks, consisting of a borate-centred tetracarboxylate B^{5-} and poly-amidinium tectons, including tetraamidinium 1^{4+} and biphenyl bisamidinium 2^{2+} . With only four accessible H-bond accepting sites on the carboxylate component, the remaining negative charge can electrostatically attract cations in solution, which allows an initially-present organic cation to be exchanged for group 1 and group 2 metal ions. The framework also shows selective uptake of the organic dye methylene blue.

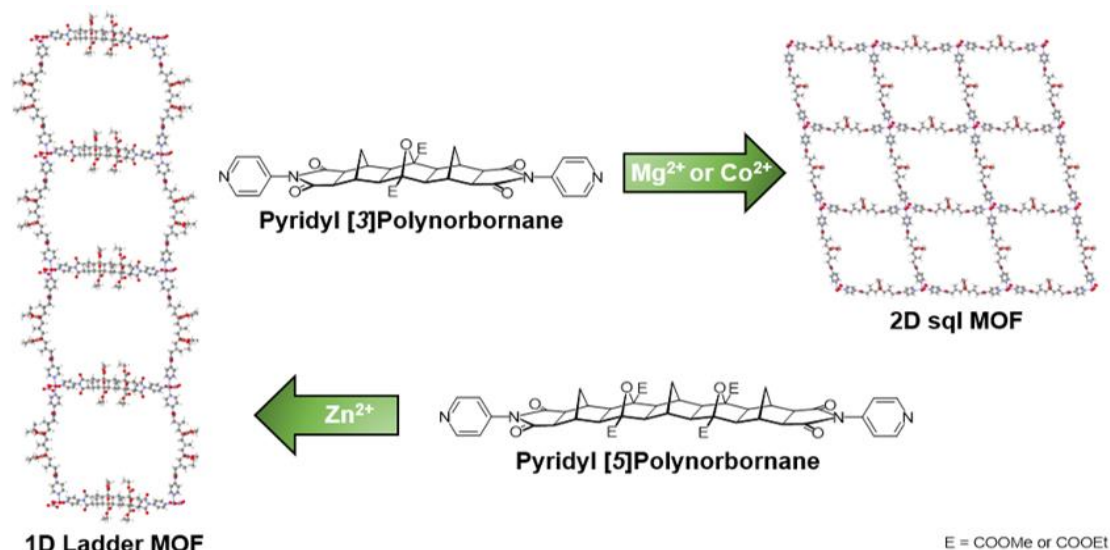
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Abstract No: M184

M184 Fused [n]Polynorbornanes for Metallosupramolecular Assemblies

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Caption: Figure 1. Examples of [n]polynorbornane ligands and their assemblies.

One key weakness of Metal-Organic Frameworks (MOFs) is the potential for the network architecture to collapse due to the presence of internal voids.¹ Structural collapse causes the network to drastically lose both pore volume² and surface area.¹ Two methods used to improve the stability of MOFs are increased hydrophobicity² and heightened ligand rigidity.^{1,2}

Fused [n]polynorbornanes are rigid, aliphatic molecules that have been used previously for supramolecular applications, including the formation of discrete coordination cages.³ While fused [n]polynorbornanes appear ideally suited as ligands for MOF formation, no instance of [n]polynorbornane being used in this way has been reported to date.

In this project, a collection of fused [n]polynorbornane ligands have been synthesised. Using these ligands, a collection of MOFs have been synthesised to including a 1D square ladder 2D sqI nets. These MOFs display voids of remarkable diameters (~2-3 nm) and an absence of interpenetration.

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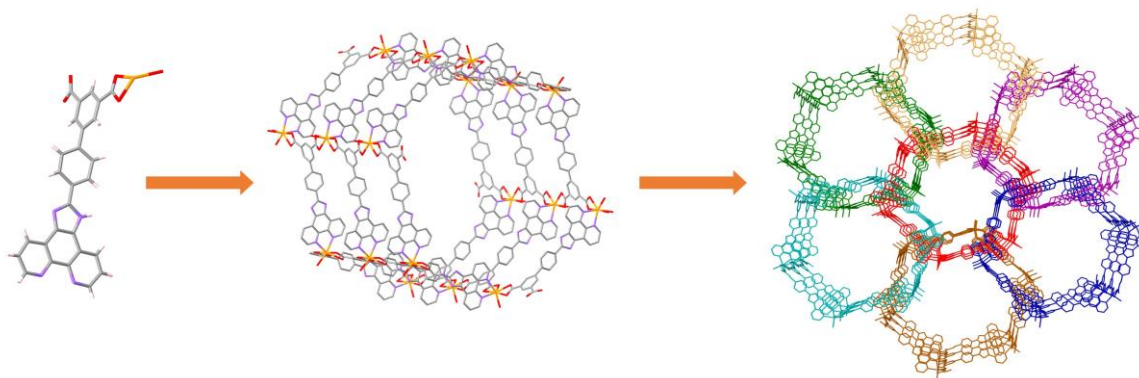
Abstract No: M185

M185 The Versatility of 6-fold interpenetrated 1D to 3D Metal Organic Nanotubes

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Caption: Scheme showing details of 6-fold interpenetrated MONT

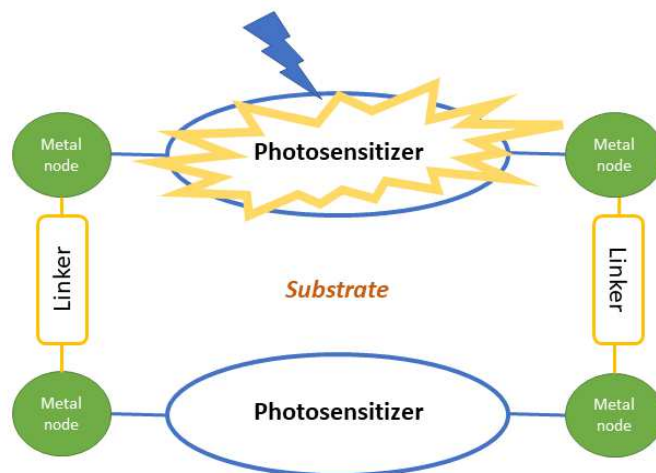
Metal-Organic Nanotubes (MONTs) are a relatively new and rare subclass of inorganic material stemming from the rise in popularity of Metal-Organic Frameworks. In theory, a MONT can have the same functionality as a MOF however this is commonly let down by the lack of thermal stability that is present in most structures. With only a hand full of examples present in the literature, the majority have do not work well as functional materials.

Using a mixed donor, T-shaped ligand, and a self-assemble approach, we have synthesized two isomorphous, multifunctional MONTs. These show a complex 1D to 3D, 6-fold interpenetration while being held back from space filling channels in the material through a large amount of pi-bonding. This provides thermal stability to the material as well as keeping the one-dimensional channels, allowing for the functionality of the structures. We will present gas sorption data showing the uptake of N₂, CO₂ and H₂ at values that rival some of the top MOFs. As well as results from high pressure crystallography performed in a diamond anvil cell, showing the strength and flexibility of the material, along with variable temperature IR studies to show the interactions of the material with ethane and CO₂ gas.

M186 Photoredox Catalysis in Confined Spaces

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- Close proximity of the photosensitizer and the substrate because of binding in the cavity
- Stabilization of the photosensitizer
- Use of a chiral photosensitizer creates a chiral surrounding, enabling enantioselective catalysis

Caption: Substrate and photocatalyst pre-organization by binding

With the large demand of energy worldwide, the use of fossil fuels will reach its limit as a non-renewable energy source. Therefore, a sustainable approach is required where the energy can be collected and used from more abundant and renewable sources. Light, which is non-toxic and inexpensive as it is available from our sun, has been investigated a lot over the past decades in chemical applications. Mainly the field of photoredox chemistry has displayed the ability to perform chemical reactions at milder conditions by the use of a photosensitizer, a molecule which is excited by light and can participate in the chemical reaction by either single electron transfer or energy transfer.^[1]

Unfortunately, photoredox chemistry comes with three big challenges, namely i) photodegradation of the photosensitizer ii) electron-hole recombination and iii) achieving enantioselectivity.^[1] A potential solution for these challenges could be incorporating the photosensitizers as ligands in metal-organic cages (MOC). MOCs have proven in literature to stabilize ligands^[2], pre-organize substrates in the cavity by various interactions^[3] and transfer chirality from the host to the product by performing reactions in a chiral confined space.^[4] This project focuses on using such photoactive MOCs for (enantioselective) light-driven catalysis to explore various reactions that could be beneficial for further applications.

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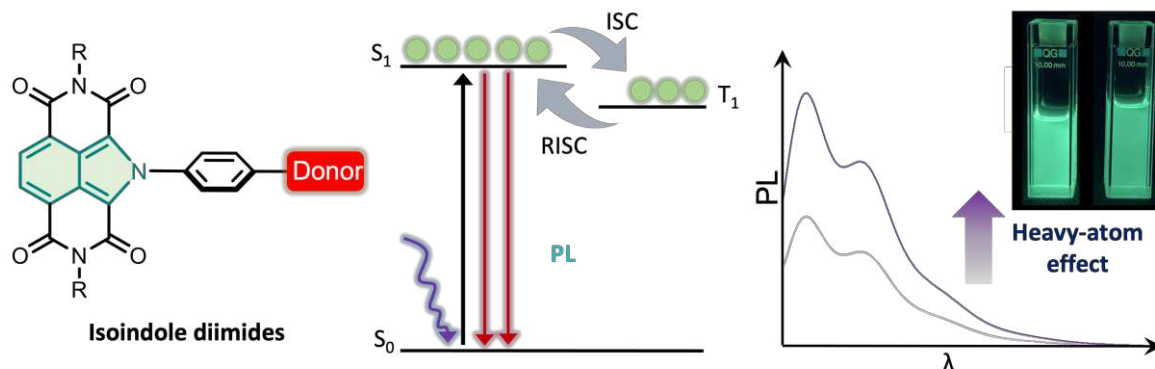
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M187 Twist and shine: Isoindole diimide-based organic light emitters

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² , ,



Isoindole diimides (IDIs) are a new class of redox-active aromatic diimide consisting of an *N*-annulated isoindole core.¹ Unlike unsubstituted naphthalene diimides² (NDIs), which possess rather unremarkable light-emitting properties ($\Phi_{PL} < 0.001$), core-heteroannulated IDI molecules display bright and tunable green emission (Φ_{PL} up to 0.85 in CH_2Cl_2), thereby raising their attractiveness as electroactive materials for future organic electronics and display applications. Notably, our group has shown through library synthesis of core-*N*-substituted IDI derivatives that their redox and optoelectronic properties are tuneable by even weak intramolecular H-bonding and lone pair- π interactions in addition to more conventional covalent conjugated bond approaches. In this work, we modified twisted phenyl-substituted IDIs to develop donor-acceptor dyads bearing heavy atoms (such as F, Br) and photoactive π -donors to explore their utility in organic light-emitting devices. The intramolecular charge transfer processes resulting from the twisted topology of these IDI-based dyads facilitate narrower singlet-triplet energy gaps (ΔE_{ST}), giving access to different excited transitions. Enhanced photoluminescence (Φ_{PL} up to 0.30) is achieved, thanks to internal heavy-atom effects³, overcoming the fluorescence quenching otherwise caused by unsubstituted phenyl groups. Encouraging experimental spectroscopic observations, combined with appropriate ΔE_{ST} values obtained from DFT models demonstrate the potential of IDI-based dyads to achieve energy-efficient red emission with a potential to display thermally-activated delayed fluorescence (TADF) for, ultimately, future 1st and 3rd generation OLEDs.

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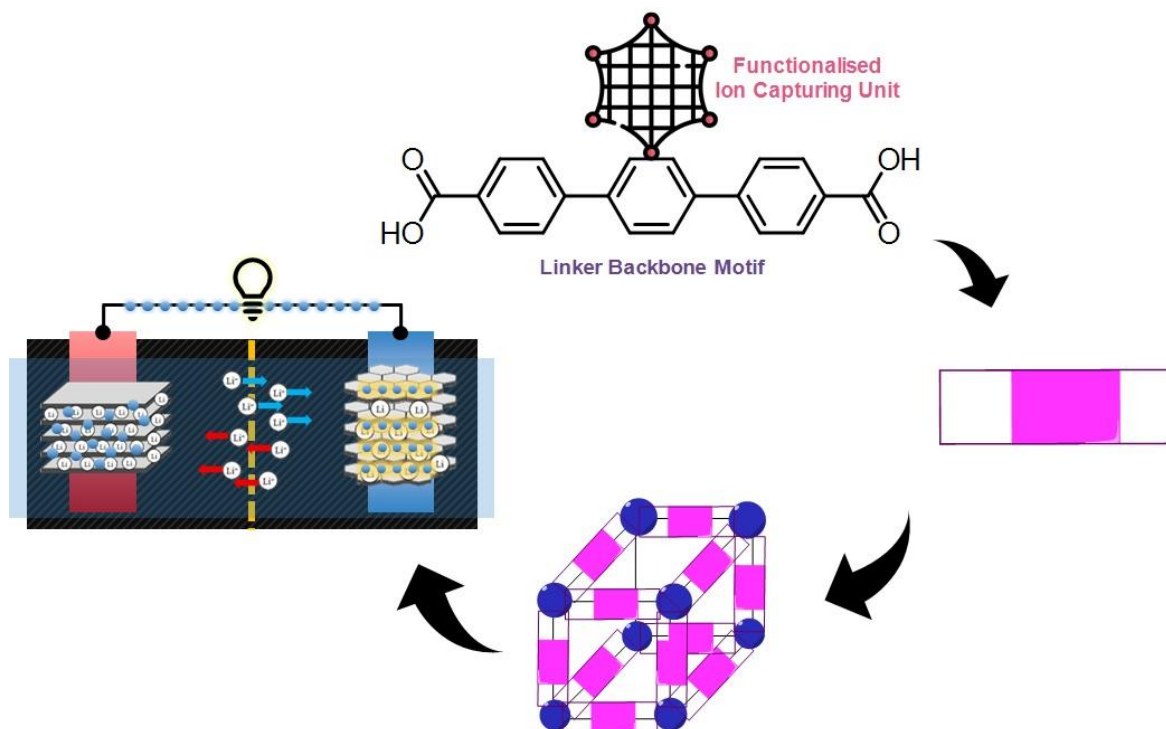
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Abstract No: M188

M188 The Use of MOFs as Alternative Electrochemical Materials in Li-ion Batteries

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Caption: An Illustration of the use of a linker candidate for the formation of a battery compatible MOF.

In this work, MOFs will be explored as promising candidates for their implementation into battery cells. A novel approach to this would be the utilisation of reticular chemistry. Reticular chemistry has steadily been researched and improved, leading to porous, versatile, and tuneable crystalline frameworks that have demonstrated their advantages in many areas. MOFs, in particular, have exhibited ionic and electronic conduction potentials leading to the design of a few materials for electrodes in lithium-ion batteries. Most of these, however, do not perform optimally due to their poor redox activity and instability in the aqueous environment of the electrolyte. This work aims to explore the implementation of MOFs into modern day battery cells, as well as investigate methods of improving their overall stability in the battery environment with selected ligands.^{1,2}

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Abstract No: M189

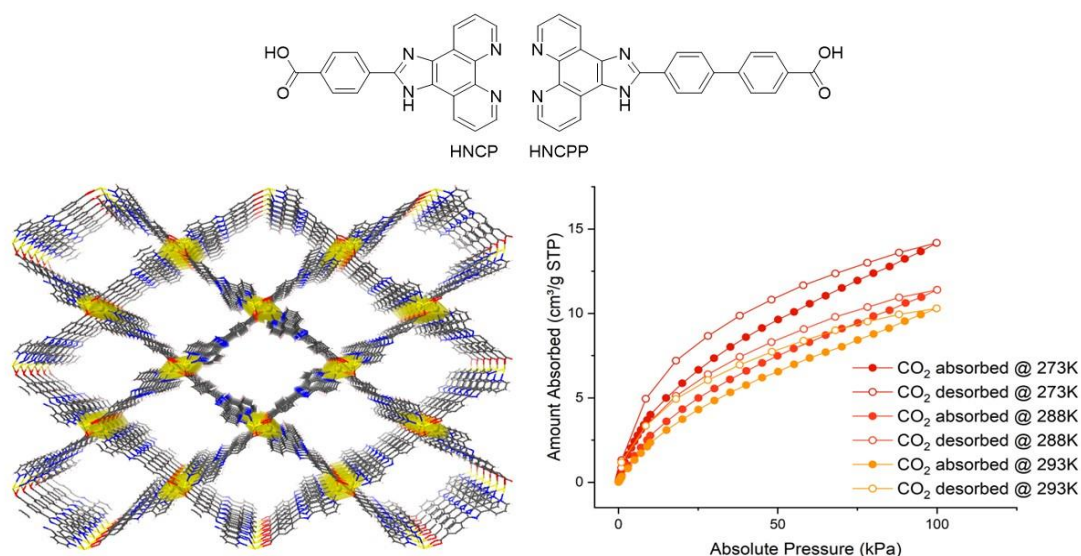
M189 Lightweight Metal Organic Frameworks with Mixed Donor Ligands

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Caption: Phenanthroline-carboxylate ligands (top), Na-HNCP MOF (left), Na-HNCP MOF CO₂ adsorption/desorption isotherms (right).

Metal organic frameworks (MOFs) have become well known for their gas adsorption properties due to their ordered porous structures. One approach to further increase the by weight gas absorption of MOFs is to decrease the density of the framework. The vast majority of metals used in MOFs are heavy transition metals. The s-block metals are significantly lighter allowing for the creation of lower density frameworks. These metals come other advantages including a high abundance and low toxicity when compared to their transition metal counterparts. The use of S-block metals in MOFs while only making up a minor fraction of published MOF structures have been growing in popularity the most notable of which is Mg-MOF-74 due having the highest known CO₂ uptake of 23.6 wt. %.

Mg-MOF-74 as with the majority of other MOFs primarily use carboxylate as their donor group to bridge together the metal nodes. As MOF chemistry has matured there is a shift away from these simpler bridging ligands. This work details the use of the mixed-donor phenanthroline-carboxylate ligand HNCP and the linearly extended HNCPP with the lightweight metals lithium, sodium, magnesium, and calcium. The resulting MOFs are ordered, rational and low-density frameworks. Subsequent gas adsorption analysis has shown promising selectivity for the uptake of carbon dioxide.

Abstract No: M190

M190 Electrically Conductive Metallacages and Metal–Organic Frameworks Featuring Alternating π -Donor/Acceptor Stacks

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Alternating π -donor/acceptor (π -D/A) arrays are excellent through-space charge transport conduits that can give rise to electrical conductivity. However, limited stability of supramolecular π -D/A complexes means that meticulous design and synthetic strategies are essential to assemble stable extended π -D/A arrays that can facilitate long-range charge transport in resulting materials. The most common way to construct stable extended π -D/A stacks is to covalently tether π -donor and acceptor units into alternating π -D/A foldamers and co-polymers having π -donor and acceptor pendants. Although such covalently tethered π -D/A arrays often exhibit tunable optical properties stemming from π -D/A charge-transfer (CT) interactions, their electronic properties, especially electrical conductivity are underwhelming and largely overlooked because of the lack of long-range order and periodicity. To overcome these limitations of covalently linked π -D/A arrays and to exploit their charge transport capability to create electrical conductivity, we have developed bottom-up strategies to form stable non-covalently linked extended π -D/A arrays by using metallacages having π -donor faces and metal–organic frameworks (MOFs) having parallel π -donor ligands located at certain distances that allow intercalation of complementary planar π -acceptor guests leading to formation of guest-mediated extended π -D/A stacks. I will present our recent work, which shows that a tetragonal metallacage having two parallel Zn-porphyrin faces located ca. 7 Å apart allows selective intercalation of planar π -acceptor guests, such as hexacyano-hexaazatriphenylene (HATCN, LUMO: -4.8 eV), hexacyano-triphenylene (HCTP, LUMO: -3.7 eV), and naphthalene-diiimide (NDI, LUMO: -3.3 eV) compounds inside its cavity. The host–guest binding affinities of resulting inclusion complexes determined by NMR, UV-Vis, and fluorescence spectroscopies as well as the electrical conductivity measured by electrochemical impedance spectroscopy were dictated by the π -acidity of intercalated π -acceptors, with the strongest π -acidic HATCN guest forming the inclusion complex having the highest binding affinity ($K_a = 5 \times 10^6 \text{ M}^{-1}$ in 2:1 $\text{CH}_2\text{Cl}_2/\text{MeCN}$) and highest electrical conductivity ($2 \times 10^{-6} \text{ S/m}$ at 22 °C) due to the strongest π -D/A interaction with the Zn-porphyrin faces of the metallacycle host. In addition, I will also demonstrate that a novel 2D π -intercalated graphitic MOF (iGMOF-1) containing hexagonal $\text{Cu}_3(\text{HATP})_2$ scaffold (HATP = hexaamino-triphenylene) located in xy-plane and built-in π -donor acceptor stacks of Cu(II)-coordinated HATP ligands and non-coordinatively intercalated π -acidic HCTP molecules along the z-axis simultaneously allow in-plane (through-bond) and out-of-plane (through-space) charge transport, which leads to remarkable bulk electrical conductivity (30 S/m). These studies exemplify the abilities of alternating π -D/A stacks to promote long-range through-space charge transport and generate electrical conductivity.

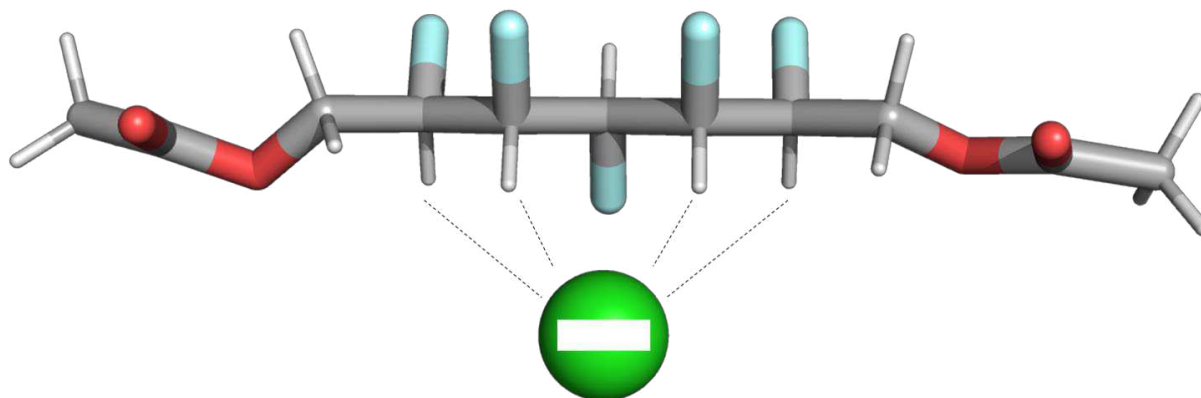
Abstract No: M191

M191 Novel Electrolytes Based on Anion Recognition

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² , ,



Caption: The binding model between CHF and anion

Solid polymer electrolytes are expected to have wide applications in high-performance lithium-ion batteries (LIBs) for their superior safety and processability features.^[1] However, their low lithium ion conductivity (typically lower than 10^{-4} S cm^{-1} at room temperature) severely limits such applications.^[2] Among the reported polymer electrolytes so far, most of them rely on cation recognition (polymer bearing cation interaction sites) to dissociate and solvate lithium salts. There have been studies showing that the strong interactions between polymer electrolytes and Li^+ could hinder the segmental motion of the polymer chains and create energy barriers for lithium diffusion,^[3] resulting in low lithium conductivity.^[4] To solve this problem, in this work, we incorporate fluorine-polarized C-H hydrogen bond donors (CHF) in a flexible molecular backbone to develop a new type of electrolyte materials that is expected to dissolve and conduct lithium salts primarily through anion recognition. We expect our electrolyte material to have higher Li^+ conductivity than the conventional polymer electrolytes and have good chemical/electrochemical stability.

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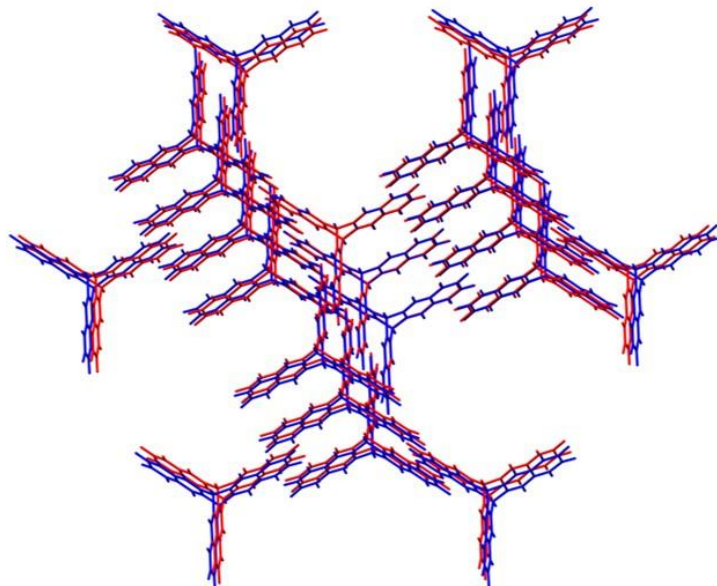
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Abstract No: M192

M192 Experimental Confirmation of a Predicted Porous Hydrogen-bonded Organic Framework

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blue = prediction
red = experimental

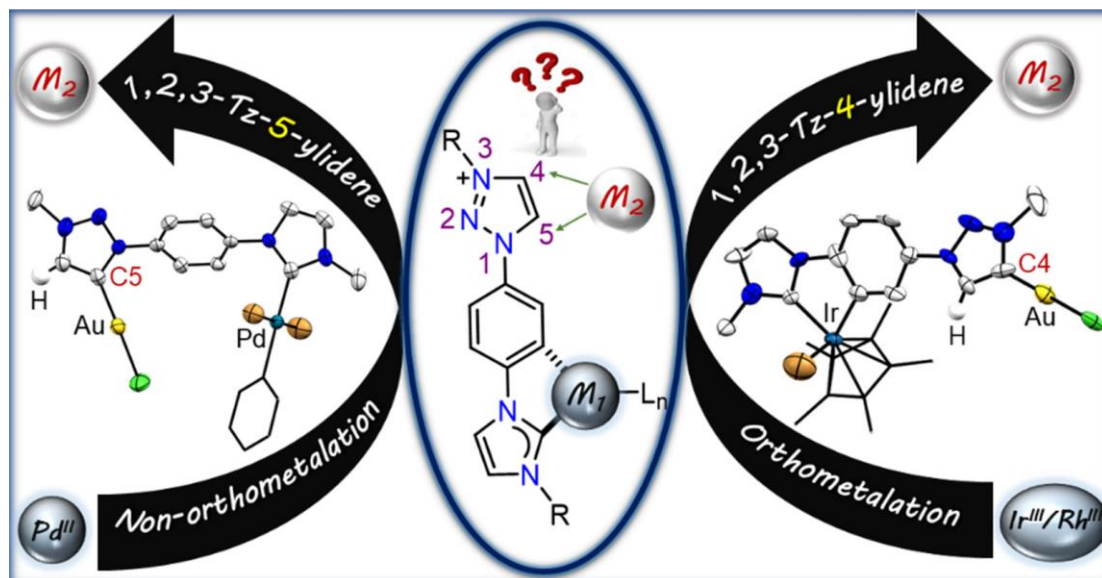
Caption: Comparison of predicted (blue) and experimental (red) crystal structures for TH5-A.

Despite a surge of reports regarding hydrogen-bonded organic frameworks (HOFs),¹ molecular crystals with low densities and high porosity levels are still rare and challenging to design. This is because most molecules have a strong energetic preference for close packing to maximise intermolecular interactions.² Crystal structure prediction (CSP) methods can rank the crystal packings available to an organic molecule based on their relative lattice energies, and this is a powerful tool for the a priori design of porous molecular crystals.³ Previously, we demonstrated how CSP could be combined with structure-property predictions to generate energy–structure–function (ESF) maps for a series of triptycene-based molecules with quinoxaline hydrogen-bonding functionality.⁴ From these ESF maps, **TH5** was predicted to form a metastable porous HOF with a remarkably low density of 0.37 g cm⁻³ and a three-dimensional (3-D) pore structure (**TH5-A**). Here, we demonstrate the reliability of those ESF maps by discovering this **TH5-A** polymorph experimentally. This material has a very high accessible surface area of 3,284 m² g⁻¹, as measured by nitrogen adsorption, making it one of the most porous HOFs discovered to date.

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M193 Towards New Coordination Modes of 1,2,3-Triazolylidene: Controlled by the Nature of 1st Metalation in a Heteroditopic Bis-NHC Ligand

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Caption: Towards New Coordination Modes of 1,2,3-Triazolylidene: Controlled by the Nature of 1st Metalation in a Heteroditopic Bis-NHC Ligand

In 2008, the group of Albrecht introduced the 1,2,3-triazolylidenes into the NHC family as an abnormal congener (mesoionic carbenes, MICs) of normal NHCs.¹ They exhibit superior donor properties, due to less heteroatom stabilization, which influences the reactivity of their transition metal complexes. Further, easy accessibility of the precursor triazolium salts *via* simple [3+2] cycloaddition reaction of azides and alkynes ('click reaction') has made the 1,2,3-triazolylidenes attractive in organometallic and supramolecular chemistry.² Among them, the 1,2,3-triazol-5-ylidenes derived from the corresponding C4-protected triazolium salts are well explored, whereas the related MICs, generated from the analogous C4- and C5-unsubstituted triazolium salts, are rarely studied.³ This might be due to the availability of two backbone carbons (C4 and C5), which could, in principle, be deprotonated to yield either the C4- or C5-ylidenes restricting the selective metalation. An unusual effect of the nature of first metal coordination of a heteroditopic N-heterocyclic carbene ligand towards the coordination behaviour of 1,2,3-tzNHC is explored in the present work. The first metal coordination at the ImNHC site was noted to substantially influence the electronics of the 1,2,3-triazolium moiety leading to an unprecedented chemistry of this MIC donor. Along this line, the Rh^{III}/Ir^{III}-orthometalation in complexes makes the triazolium C4-H more downfield shifted than C5-H, whereas a reverse trend, although to a lesser extent, is observed in the case of the non-chelated Pd^{II}-coordination. This difference in behaviour assisted us to achieve the selective activation of triazole C4/C5 positions, not observed before, as supported by the isolation of the homo- and hetero-bimetallic complexes *via* C5- and C4-metalation, respectively.⁴ Further, the %*V*_{bur} calculations suggest that the observed selectivity is primarily controlled by the electronic nature of the first metal coordination. Moreover, the DFT studies of selected complexes strongly support the exclusive formation of a particular regioisomer, as observed experimentally.

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Abstract No: M194

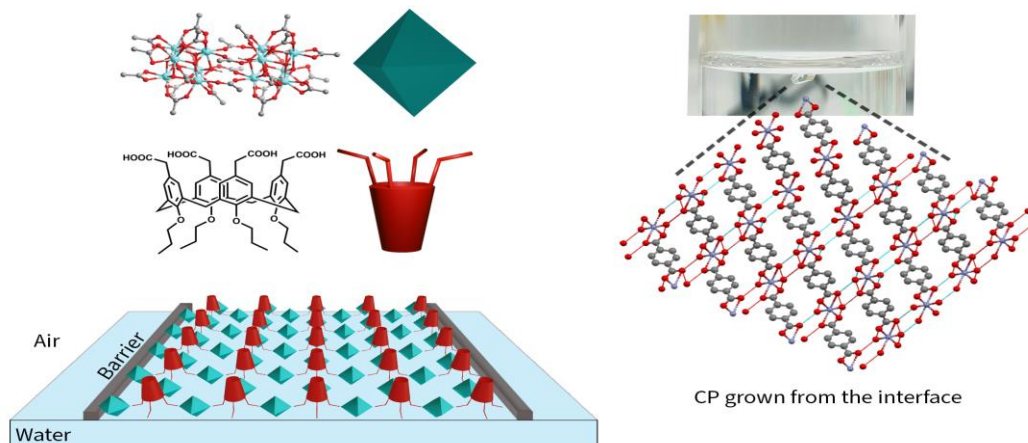
M194 Self-assembled monolayers: designer nanocrystals for the fabrication of 2D and 3D metal-organic frameworks

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Caption: Schematic representation of the self-assembly of amphiphiles and SBUs (left), interface-assisted crystal growth of a coordination polymer (right).

Metal-organic frameworks (MOFs) consist of a regular array of metal ions or clusters with polytopic organic linkers. They are an interesting class of materials with several applications owing to their porous structure (e.g., catalysis, gas storage, and separation).¹ Similarly, coordination polymers (CPs) are supramolecular compounds with one-dimensional infinite chains of metal ions and ligands, crosslinked through non-covalent interactions. The choice of secondary building units (SBUs), organic linkers, modulators, temperature, reaction time, and the method of synthesis collectively control the shape, size, and morphology of the MOF and CP crystals. Despite their excellent physicochemical properties, implementing such desirable materials in practical applications is limited because of their relatively small size, typically in the micrometer range. We aim to address the challenge of producing large MOF and CP crystals through interface-assisted methods and template effects.

Langmuir monolayers of amphiphilic calix[4]arenes have been used to favor the nucleation and surface-templated crystal growth of small organic molecules.² Here, we chose different transition metal ions and oxo clusters as SBUs, and a series of amphiphilic organic linkers. The newly produced SBUs and amphiphiles were combined at the air-water interface to create monomolecular thin films in the form of 2D MOFs. Amphiphilic terephthalates couldn't form a monolayer on water, but stable Langmuir monolayers were formed in the presence of dissolved metal oxo clusters. Calix[4]arenes chosen can form self-assembled layers on water.³ However, combining them with metal ions or oxo clusters also formed monolayer islands with high surface pressure. The self-assembly properties and interfacial behavior were studied using the Langmuir balance method and Brewster-angle microscopy. Later, the layers were transferred and imaged with atomic force microscopy and cryo-transmission electron microscopy. Finally, the produced layers were assessed to template the growth of large MOF and CP single crystals.

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Abstract No: M195

M195 Luminescent metal–organic frameworks constructed from dipyrindyl benzochalcogenadiazole ligands

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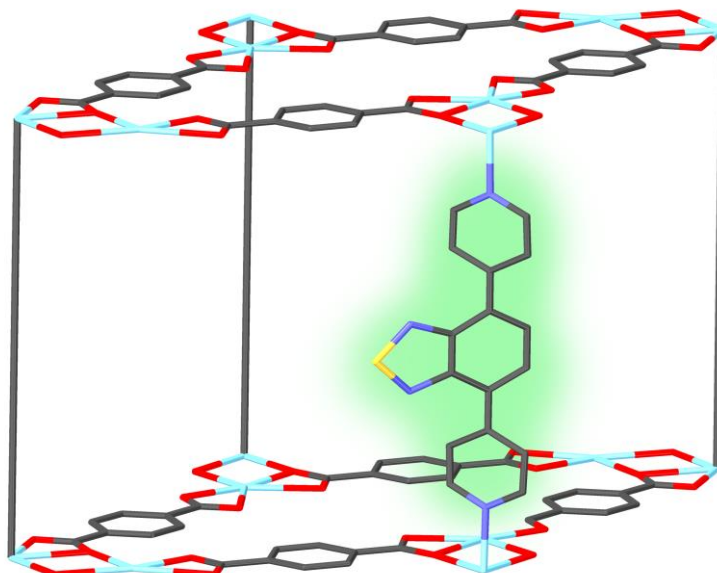


Fig 1. General structure of the new MOF series based on the fluorescent 4,7-di(4-pyridyl)-2,1,3-benzochalcogenadiazole ligands (**L₁-O** = oxadiazole, **L₂-S** = thiadiazole, and **L₃-Se** = selenadiazole). Atom colours: C (grey), N (blue), O (red), S (yellow), and Cd (light blue); long grey lines represent pillaring L_x ligands.

Luminescent metal–organic frameworks (MOFs) have been investigated for their potential applications within non-linear optics, bio-imaging, photovoltaics, and molecular sensing. [1] [2] Introducing tailored organic luminophores into MOF structures remains an appealing prospect in modulating their photophysical response. However, this can produce undesirable effects of solid-state fluorescence quenching which reduces the emissive yields and limits their potential applications.[3]

Benzochalcogenadiazoles are fused heterocyclic ring systems that have experienced renewed interest as functional components in organic light-emitting diodes and electroluminescent devices due to their large fluorescence quantum yields and tuneable electronic band and resonance structures. Herein, an isostructural series of three new multi-component MOFs containing different 2,1,3-benzochalcogenadiazole ligands was synthesised and characterised by an array of different crystallographic and physical techniques including X-ray diffraction and luminescent sensing experiments. These MOFs adopt the form [Cd(1,4-bdc)(L_x)] (1,4-bdc = benzene-1,4-dicarboxylate; L_x = **L₁-O** (oxadiazole), **L₂-S** (thiadiazole), or **L₃-Se** (selenadiazole)). This study investigates the effect of chalcogen swapping of the L_x ligand on the emissive properties of this MOF series and investigates their potential applications as host–guest sensors of small molecule solvents, nitroaromatic compounds, and heavy metal ions.

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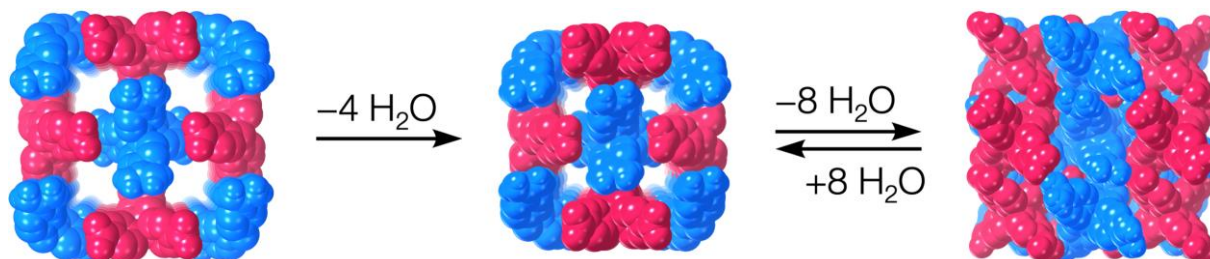
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Abstract No: M196

M196 Massive structural arrangements in hydrogen bonded frameworks

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We have investigated the self-assembly of frameworks assembled through charge-assisted hydrogen bonding between amidinium and carboxylate groups.¹ These crystalline materials are prepared in water by simply mixing the two components and waiting for crystallisation to occur.² As prepared, the channels of the materials are filled with water molecules, which can be removed under vacuum or with modest heating. Unlike most porous materials, solvent removal causes huge structural changes with the whole framework rearranging on dehydration, and then again in response to water vapour. Remarkably, crystallinity is retained throughout this process allowing us to follow the changes using X-ray crystallography.³ This process appears to be general to a large number of frameworks including those relevant to water harvesting applications.^{4,5}

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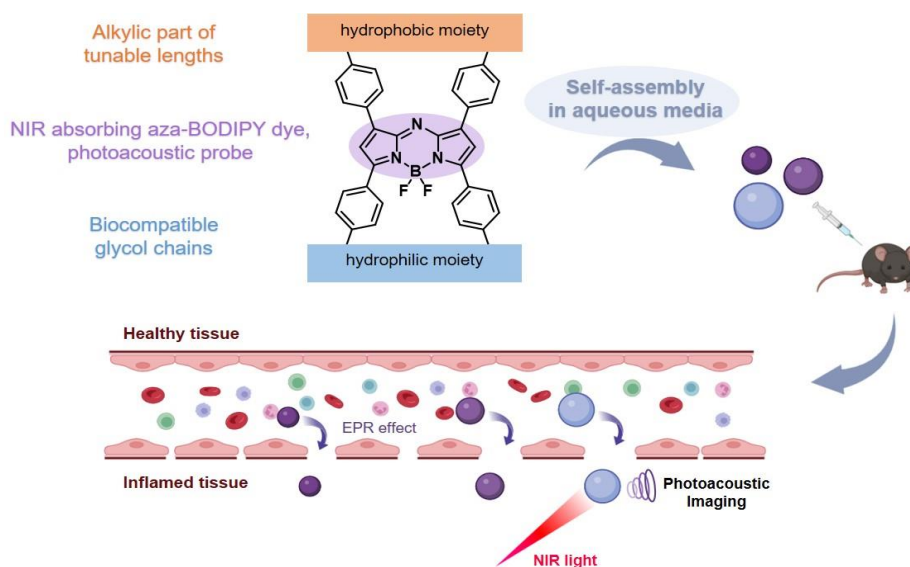
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Abstract No: T1

T1 Quantitative Assessment of Endothelial Permeability by Scalable Self-Assembled aza-BODIPY Nanostructures Serving as Contrast Agents for Multispectral Optoacoustic Tomography

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Caption: Self-assembly of amphiphilic aza-BODIPY derivatives and their application as contrast agents for assessing endothelial permeability in inflamed tissue

Endothelial cells, connected by adherens and tight junctions, form a semi-permeable barrier that plays a central role in regulating the transmigration of biomolecules between blood circulation and tissue in a size-selective manner. In response to inflammatory pathologies, for example caused by ischemia, cell damage or infection, endothelial permeability is distinctly altered.^{1,2} Therefore, endothelial barrier function is essential for understanding the change of affected tissues within inflammatory events and resulting tissue injury. However, current contrast agents for non-invasive imaging of these dynamic processes are limited by their fixed size and properties. Herein, we evaluate newly designed amphiphilic aza-BODIPY dyes, that can self-assemble in aqueous media into well-defined nanostructures of systematically variable size and shape controlled by the relation between hydrophobic and hydrophilic fragments within the molecular design. Aza-BODIPY dyes are ideal candidates in this regard due to their high chemical stability, biocompatibility and their remarkable photophysical properties.³ Furthermore, the synthesized aza-BODIPY derivatives exhibit an electronic push-pull character enabling near-infrared (NIR) absorption which provides excellent conditions for deep tissue penetration and multispectral optoacoustic tomography (MSOT).⁴ The tunable size and shape of the formed nanostructures allows assessment of endothelial barrier function in order to study local and systemic mechanisms of inflammation-associated permeability and consecutive tissue damage within different vascular beds *in vivo* in a quantitative manner.

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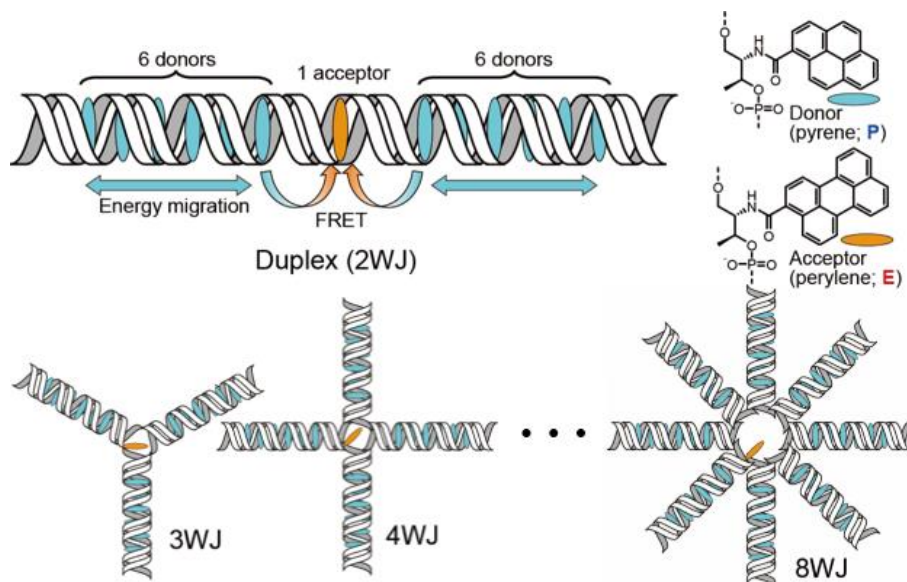
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Abstract No: T2

T2 Development of efficient light harvesting antenna using DNA junction with multiple fluorophores

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Caption: DNA duplex and junctions prepared in this study, and chemical structures of the pyrene donor and perylene acceptor.

In natural photosynthesis, highly efficient harvesting is achieved by accumulating multiple fluorophores with strictly controlled distance and orientation. Artificial light harvesting systems, which utilize covalent bonding and/or metal coordination have been developed^[1, 2]. On the other hand, DNA has unique characters as a supramolecule: it can form a duplex spontaneously with a complementary strand. We introduced various fluorophores into DNA through D-threoninol, and found that the distance and orientation between fluorophores can be strictly controlled^[3]. Therefore, fluorophores can be aligned with pre-determined distance, size, orientation and sequence by using this linker. In this study, we developed highly efficient light harvesting DNA antennae by accumulating fluorophores into DNA junction structures. Multiple donors were introduced into arms of DNA junctions and an acceptor was introduced at the center. As a result, excitation energy is efficiently transported to the acceptor through homo and hetero fluorescence resonance energy transfer (FRET). 3- to 8- way junctions were prepared and their light harvesting efficiencies were systematically evaluated.

Light harvesting efficiencies of these DNA junctions were evaluated by effective absorption coefficients (ϵ_{eff}), which is the product of absorption coefficients of donors (ϵ_{D}) and energy transfer efficiencies from donor to acceptor (Φ_{T}). Energy transfer efficiency was calculated by decrease of fluorescence intensity of donors. ϵ_{D} increased in proportion to the number of arms. In contrast, Φ_{T} decreased as the number of arms increased. This result indicates that the increase of number of arms inhibit the formation of DNA junctions. Interestingly, Φ_{T} s of 6- and 8-ways were higher than those of 5- and 7-ways, respectively. As a result, ϵ_{eff} s of 6- and 8-way junctions were higher than other junctions. Therefore, 6- and 8-way junctions exhibit the highest light harvesting efficiency. The effective absorption coefficient of acceptor in 8-way junction increased by 8.5 times compared with the absorption coefficient of acceptor alone.

In conclusion, we successfully prepared highly efficient light harvesting antenna by using DNA junction^[4].

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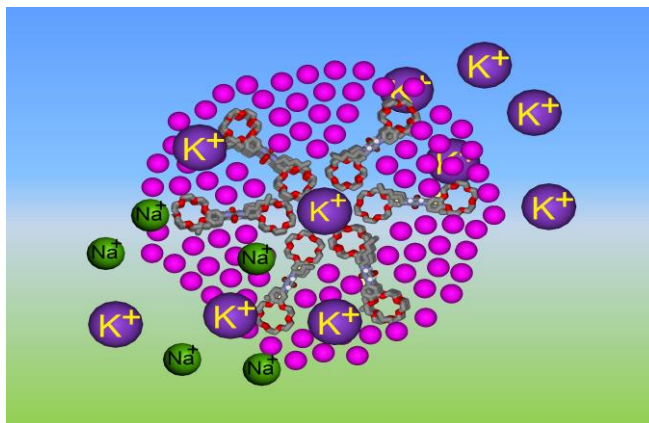
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Abstract No: T3

T3 Highly Selective Biomimetic Artificial K⁺ Channels

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Caption: Top view of self-assembled crown ether stacks acting as a molecular bricks to stabilize a toroidal pore

Natural KcsA channel conduct K⁺ cations at high rates excluding Na⁺ cations. Biomimetic artificial channels have been designed in order to mimick the ionic activity of KcsA channels, but simple artificial systems presenting high K⁺/Na⁺ selectivity are rare. Here we report an artificial ion-channel of H-bonded hexyl-benzoureido-15-crown-5-ether, where K⁺ cations are highly preferred to Na⁺ cations. The K⁺-channel conductance are interpreted as arising in the formation of oligomeric highly cooperative channels, resulting in the cation-induced membrane polarization and enhanced transport rates without or under pH-active gradient. The macrocycles aligned along the central pore surround the K⁺ cations in a similar manner to the water around the hydrated cation, compensating the energetic cost of their dehydration. Differently the Na⁺ cation is fitting the macrocyclic binding sites, so its dehydration is not completely compensated. These channels are selectively responsive to the presence of K⁺ cations, even in the presence of a large excess of Na⁺. From the conceptual point of view these channels express a synergistic adaptive behaviour: the addition of the K⁺ cation drives the selection and the construction of constitutional polarized ionchannels toward the selective conduction of the K⁺ cation that promoted their generation in the first place.

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Abstract No: T4

T4 Synthesis of Urea-Based Transporters and Their Anion Transport Activity

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Control of chloride transport across the membrane is a challenging subject due to the intrinsic properties of the cellular membrane. An unbalanced transport of those anions can lead to a variety of diseases, such as cystic fibrosis. In most cases, insertion of synthetic transporters in the membrane can restore chloride transport by various mechanisms. Our main goal is to synthesize anion transporters, with high specificity towards chloride, whose self-assembly in the membrane bilayer is driven by supramolecular interactions. Amphiphilic urea derivatives have been used as small molecules to transport chloride for over a decade.¹⁻⁴ Our goal is to develop new urea derivatives bearing different ligands to further improve chloride's transport efficiency. Addition of a metal source will promote formation of new supramolecular structures in the membrane using organometallic chemistry as a driving force. Those metallic complexes are opening new avenues in the possible geometry of active synthetic transporters.

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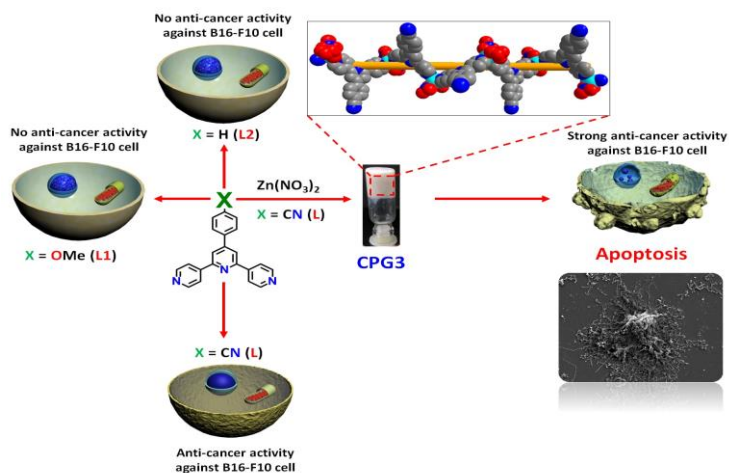
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Flash talks 27-06-2023 16:40 - 17:00 Harpa - Silfurberg A/B 2nd floor

T5 Supramolecular metallogels as self-drug-delivery system in melanoma therapy

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Indian Association for the Cultivation of Science, Kolkata, India



Caption: Schematic representation of the overall work

Supramolecular chemistry mainly deals with the noncovalent interactions.¹ By exploiting these types of interaction one can develop metallogels. If the metallogel is prepared with drug or active pharmaceutical ingredients (API) then the drug molecule become a part of the gel network- it is termed as self-drug-delivery (SDD) system.² A SDD system has several advantages over conventional drug delivery systems as one can easily avoid delivery vehicle related disadvantages.

Herein an attempt has been made to develop metallogel based self-drug-delivery system against melanoma by utilizing supramolecular chemistry concept. For that reason, a series of coordination polymer based metallogelators (CP1-CP6) have been synthesized by reacting a nitrile-containing terpyridyl ligand (L) and transition metal salts (Cu(I)/Zn(II)). Nitrile functional group, due to its low metabolic property and bio isostere of carbonyl, halogen etc. often found in anticancer drugs. The synthesized coordination polymers have been thoroughly characterized by a number of physicochemical techniques (single crystal X-ray diffraction, IR etc.). Reactions between the coordination polymers ingredients guided by their SXR structures produced four metallogels (CPG2-CPG5) which were also characterized by dynamic rheology and TEM. After that the nitrile linker containing xerogels were employed to determine the anticancer activity against melanoma cells B16-F10. The MTT assay on both murine melanoma (B16-F10) and macrophage (Raw 264.7) cells suggested CPG3 was the best among other metallogelators. Anticancer activity of some other linkers which were devoid of nitrile functionality clearly suggested the role of nitrile. Various biological experiments (scratch, cell cycle, nuclear condensation, annexin V-FITC/PI, mitochondrial membrane potential, Ho-efflux assays) not only supported the “druglike” action against melanoma cells but also suggested that the mechanism of cancer cell death was via mitochondrial membrane potential depolarization-driven apoptosis. Thus, a concept of supramolecular chemistry was employed in designing of coordination polymer based metallogels as self-drug-delivery system to deliver a nitrile containing active molecule to highly aggressive murine melanoma cell B16-F10-a human skin cancer model.³

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Abstract No: T6

T6 A Supramolecular Approach to Anti-Microbial Resistance: Anionophores that Induce Disruption of Bacterial Chloride Homeostasis

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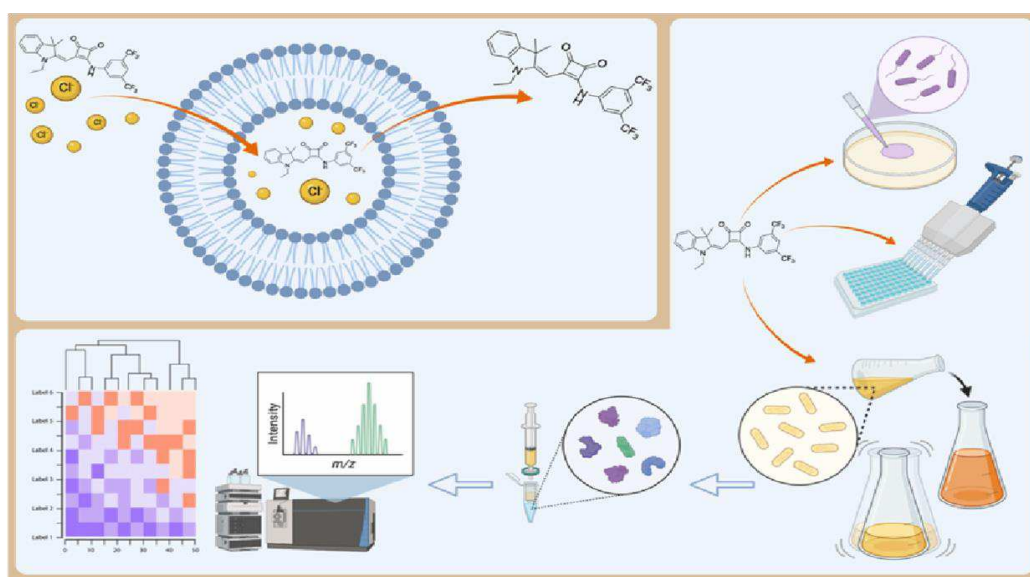
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Anion transport has in recent years become an increasingly important aspect of supramolecular chemistry.^[1] Indeed, the cross-applicability of anion transport in the field of medicinal chemistry has stimulated a wealth of research.^[2]

For example, a number of synthetic anion transporters have already been proposed as possible treatments for Cystic Fibrosis (CF) or as potential anti-cancer therapeutics.^[3] However there is a lack of anion transporters being exploited as antimicrobial agents. This work describes the design, synthesis and biological evaluation of four novel semi-squaramide indolium conjugates which possess strong chloride binding affinity and potent chloride transport capabilities (Figure 1). Moreover, using several cell based assays and label-free quantitative (LFQ) proteomics we investigate, for the first time, the underlying mechanism of the observed antimicrobial effect induced by these anionophores.

We have also verified all compounds exhibit low toxicity toward mammalian cell lines *in-vitro* and *Galleria melonella in-vivo*. We expect the results from this study may inform the design of a new class of antimicrobials that act through disruption of bacterial chloride homeostasis.

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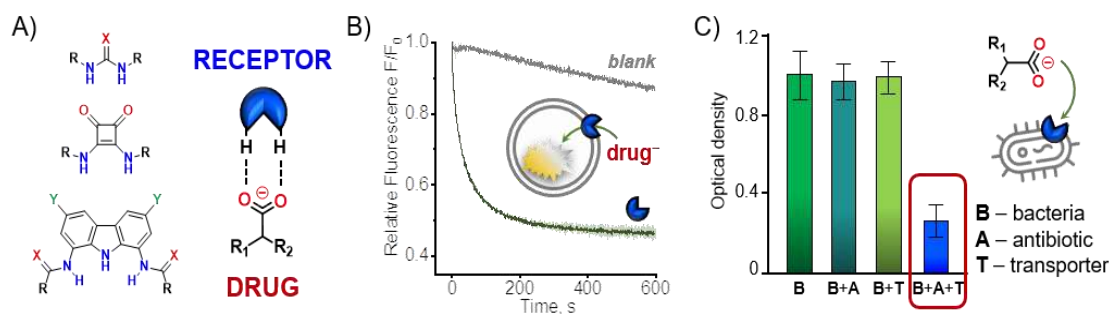
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T7 Synthetic anionophores as drug transporters: studies in liposomes and bacteria

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Caption: Figure 1. A) Synthetic transporters investigated herein. B) The transport of anionic drugs into LUVs. C) Synergy between an antibiotic and a drug

Many drugs are anionic at physiological pH and hence cannot easily pass through hydrophobic biological membranes. Synthetic anion transporters could help to solve this problem by accelerating the migration of anionic drugs across lipid bilayers. In 2020, we demonstrated the first example of anionic drug transport by a synthetic transporter.¹ The following year, Busschaert and co-workers showed that even simple diphenyl ureas can accelerate the transport of some anionic drugs through the lipid bilayers of synthetic liposomes.² In this presentation, we summarize our investigations on the transport of antibiotics and anticancer drugs by a range of highly active small molecule anion carriers. Using large unilamellar vesicles (LUVs) as model lipophilic membranes, we showed that anionophores can accelerate the transport of anionic drugs up to several hundred times, while their concentration in the biological membrane remains as low as 0.1 mol%. Moreover, our *in vivo* studies in bacteria provided the first examples of synergy between an antibiotic and a transporter. Based on these promising results, we propose that synthetic transporters may be useful in the fight against antibiotic-resistant bacteria and cancer, some of the most serious contemporary health threats.

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Abstract No: T8

T8 NMR analysis of transient structures in protein unfolding/refolding by encapsulation within spherical metallo-cages

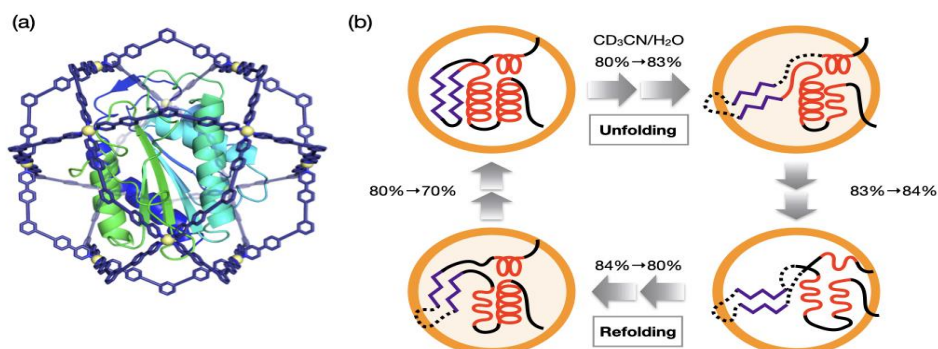
Risa Ebihara ¹ Takahiro Nakama ², Anouk Rossen ², Maho Utsumi-Yagi ³, Daishi Fujita ⁴, Koichi Kato ³, Makoto Fujita ²

¹ School of the Engineering, The university of Tokyo, Tokyo, Japan

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Caption: (a) Protein within M₁₂L₂₄ spherical metallo-cage. (b) Cartoon representation of CLE hysteresis unfolding/refolding in acetonitrile-water mixtures.

The transient protein structures in unfolding/refolding are a critical target for understanding how proteins gain and lose their function in dynamic biological processes. However, the structures are often elusive because of the immediate and irreversible aggregation of unfolding proteins.

We have previously reported protein encapsulation in an M₁₂L₂₄ spherical complex that forms through the self-assembly of Pd(II) ions (M) and bis(pyridine) ligands (L) (Fig. a).^[1] A protein was isolated in the metallo-cage, where the protein aggregation was prevented in denaturing organic solvents. In this study, we analyzed transient structures in protein unfolding and refolding by encapsulation within the M₁₂L₂₄ cages.^[2] The confinement in the metallo-cages allows us to isolate an unfolding protein that is otherwise aggregated and irreversibly precipitated. The caged protein was subjected to different ratios of acetonitrile-water mixtures, and its structural changes during unfolding/refolding were investigated by ¹H-¹⁵N HSQC NMR.

A cutinase-like enzyme, CLE was encapsulated in an M₁₂L₂₄ cage, and its HSQC spectra were acquired with stepwise increasing acetonitrile content (Fig. b). Caged CLE retained its native structure up to 82% acetonitrile (v/v), whereas uncaged free CLE was heavily precipitated due to its aggregation. At 83% acetonitrile, however, many HSQC crosspeaks became faint, indicating that the CLE structure was sharply changed. The transient structure was elucidated by analyzing the peak attenuation of each residue, showing that CLE unfolding initiates at the flexible domains close to its active site. When the acetonitrile ratio was decreased back, we found that the transition points in unfolding and refolding are different: the denatured CLE begins refolding at 80% and restores its native structure at 70% (Fig. b). The hysteresis behavior can be attributed to different pathways of the unfolding and refolding, which are suggested by the transient structures.

The unfolding and refolding were also analyzed by confining CLE in an expanded M₁₂L₂₄ cage. Although CLE can freely fluctuate in the expanded cavity, the protein showed the same unfolding/refolding behavior in the larger cage. This indicates that the protein refolding was not due to the tight packing in the cavity but due to the isolation in their inner space. Thus, the spatial isolation in the metallo-cages enables structure analysis of proteins that are transiently present in bulk solutions.

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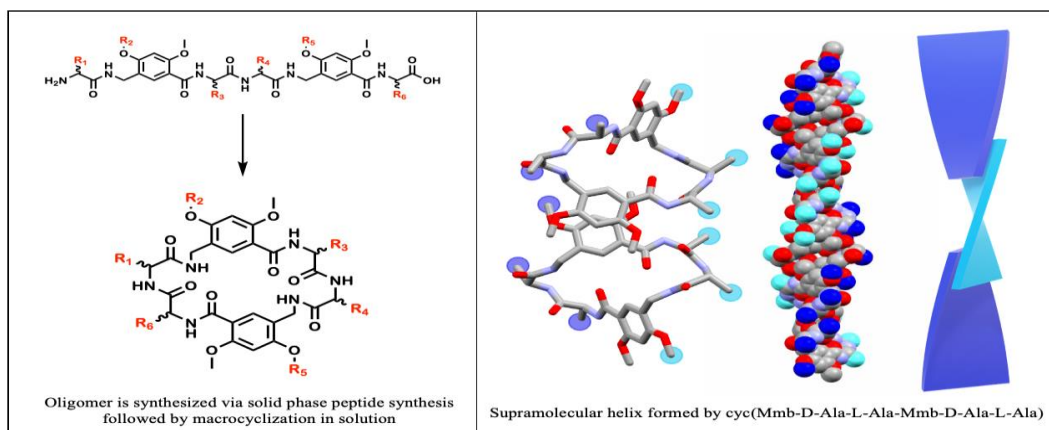
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Abstract No: T9

T9 Macrocycles with a Twist: Endocyclic Stereosequence Controls Cyclic Oligoamide Topography

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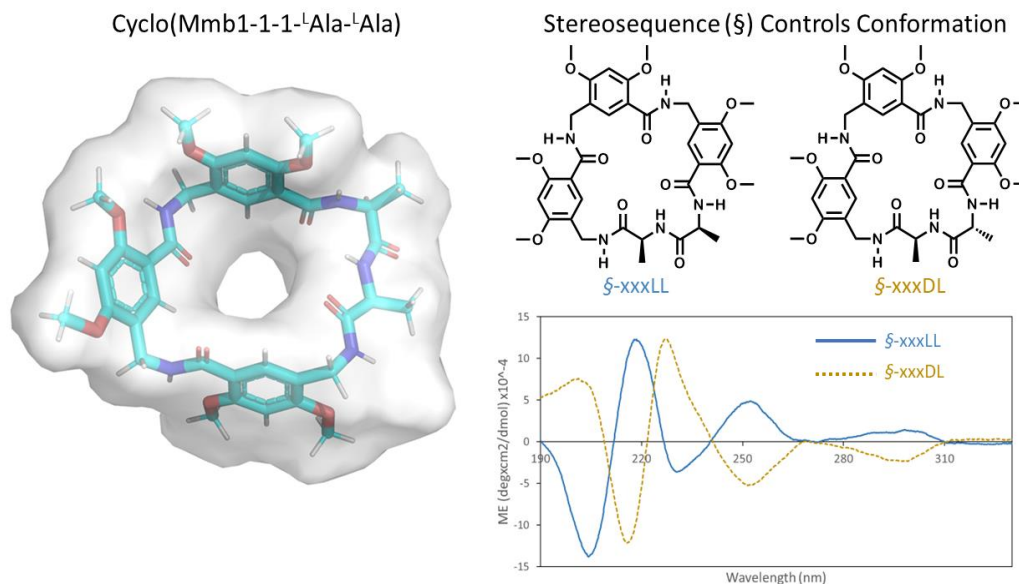
Foldamers, oligomers that achieve specific conformations in solution, are an increasingly important tool in molecular recognition. Cyclic oligoamide foldamers allow for the introduction of endocyclic chirality due to the use of L and D α -amino acids in the macrocycle backbone thus creating an opportunity for the control of conformation and supramolecular interactions. We present a series of macrocycles that fold in solution with the general structure cyc(Mmb-Xaa-Xaa-Mmb-Xaa-Xaa), where Xaa is any α -amino acid and Mmb, 2,4-dialkoxy-*meta*-aminomethylbenzoic acid, is a dipeptide mimetic.¹ Linear oligoamides were synthesized using solid-phase peptide synthesis and macrocyclization was achieved in solution. Six stereoisomers of cyc(Mmb-Ala-Ala-Mmb-Ala-Ala) were prepared and each showed dramatic changes in conformation as a function of endocyclic stereocenter sequences, as observed using Nuclear Magnetic Resonance (NMR) and Circular Dichroism. The conformation of these macrocycles remained unperturbed when other α -amino acids were introduced to the backbone and when the Mmb residue was functionalized at the exocyclic 4-position. The presence of charged residues in the cyclic scaffold also conferred water solubility. X-ray crystallography and variable temperature NMR shows that intramolecular transannular hydrogen bonds are formed in one stereoisomer, and the macrocycle adopts a twisted β -sheet motif. In the solid state, this stereoisomer also showed the formation of a supramolecular helix resulting from the twisted topography and from π stacking interactions between adjacent macrocycles. The determination of the effects of endocyclic stereosequence and macrocycle functionalization on scaffold folding and packing is a necessary step towards the rational design of shape-persistent scaffolds for molecular recognition.

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Meisel, J. W., Hu, C. H., Hamilton, A. D. Heterofunctionalized Cavitands by Macrocyclization of Sequence-Defined Foldamers. *Org. Lett.* **2019**, 21 (19), 7763–7767.

Abstract No: T10

T10 Stereosequence Determines Cavitand Conformation through Arylamide-Peptide Hydrogen Bond

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Caption: Left: Electron Diffraction crystal structure of MAMBA-Alanine macrocycle. Right: Circular dichroism shows how stereosequence controls conformation.

Macrocyclic peptides are promising candidates for molecular recognition of protein surfaces due to their ease of functionality and synthesis. Arylamide cavitands possess the synthetic advantages of peptides, reduce the number of rotatable bonds, and provide a binding site for convex protein surfaces.¹ However, these macrocyclic compounds still suffer from structural complexities that make preorganization for binding difficult. Ring strain, steric strain, and transannular noncovalent interactions propagate along macrocyclic backbones such that small alterations in chemical structure can have significant effects on conformation. Thus, controlling for conformational heterogeneity remains a challenge in the design for optimal binding interactions. In our work we investigate the role of *stereosequence* – the sequence of chiral monomers in an oligomer – in controlling the global conformation of arylamide cavitands. We synthesized a library of oligomers comprised of alpha amino acids and *meta*-aminomethylbenzoic acid (MAMBA) dipeptide mimetics using solid phase peptide synthesis methods. The oligomers were then cyclized into arylamide cavitands. Using variable temperature and two-dimensional nuclear magnetic resonance techniques combined with circular dichroism spectroscopy, we studied conformational changes that arise from the stereosequence of endocyclic alpha amino acids. We found specific intramolecular hydrogen bonds are critical for transmitting stereochemical information throughout the oligoamide backbone. This information is conveyed through the secondary structure of linear and macrocyclic oligomers and highlights the role that stereosequence plays in controlling the conformation of our macrocycles.

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Abstract No: T11

T11 Amphiphilic Iminoguanidines as Potent Anionophores for the Treatment of Pancreatic Cancer

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In the field of cancer treatment, amphiphilic anionophores have recently proven to be efficient both in cellular membrane crossing, and apoptosis induction. Particularly, amphiphilic chloride transporters have the ability to induce a chloride concentration imbalance inside the cell, which activates an enzymatic cascade responsible for the programmed cell death^{1,2}. Given the pi-stacking allowed by their aromatic side chains, and their H-bond donor properties, those molecules have been able to both supramolecularly assemble in the cell membrane, and to transport chloride inside the cell inducing apoptosis.

In our group, we decided to consider those previous supramolecular properties, and to focus on a particular core of interest, namely iminoguanidine. Indeed, amphiphilic iminoguanidines with side chains of interest can be easily synthesized, and their H-bond donor properties can allow them to complex chloride anions. Thus, we have synthesized a library of aromatic and heteroaromatic symmetric diiminoguanidines that have anticancer properties on pancreatic cancer cell lines. Moreover, their chloride transport properties were evaluated using synthetic cellular membrane models. Our amphiphilic diiminoguanidines have the ability to cross the cellular membrane and to act as mobile chloride transporter, inducing cancer cell death. Thus, our new amphiphilic diiminoguanidines represent interesting and potent anionophores for the treatment of pancreatic cancer.

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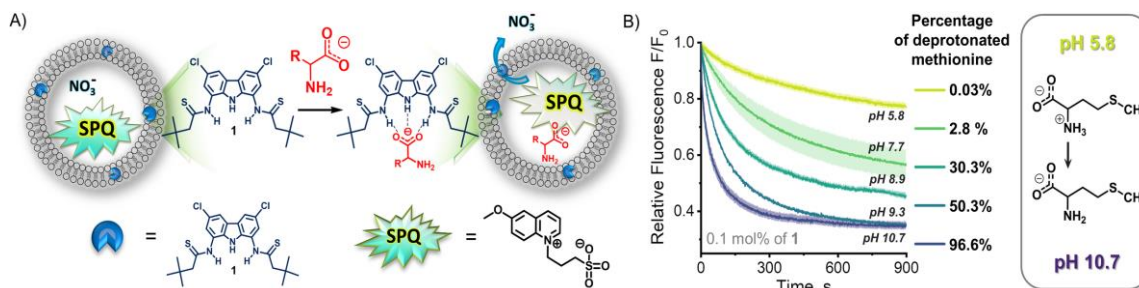
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Abstract No: T12

T12 pH-Dependent transport of amino acids across lipid bilayers by simple monotopic anion carriers

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University of Warsaw, Warsaw, Poland



Caption: Figure 1.A) Schematic representation of a new assay for studying the transport of deprotonated amino acids. B) pH-dependent kinetics of Met⁻ transport.

The transport of amino acids across lipid membranes is vital for the proper functioning of every living cell. In spite of that, examples of synthetic transporters that can facilitate amino acid transport are rare.¹ This is mainly because at physiological conditions amino acids predominantly exist as highly polar zwitterions and proper shielding of their charged termini, which is necessary for fast diffusion across lipophilic membranes, requires complex and synthetically challenging heteroditopic receptors.

Herein, we present the first simple, monotopic anion receptor **1** that efficiently transports a variety of natural amino acids across lipid bilayers at physiological pH.² Mechanistic studies revealed that **1** works by rapidly transporting deprotonated amino acids, even though at pH 7.4 these forms account for less than 3% of the total amino acid concentration. Apparently, the unfavorable speciation of amino acids at physiological pH is compensated by the exceptionally high activity of **1**. The above-described insights were possible owing to the new assay (Fig. 1A), which enables selective measurement of transmembrane transport of deprotonated amino acids. This assay, based on fluorescence quenching of SPQ, allowed us to study the pH dependence of amino acid transport and thus shed light on its mechanism (Fig. 1B). Using the same assay, we have also screened five other monotopic anion transporters, three of which showed promising activity in amino acid transport.

The results presented here imply that heteroditopic receptors are not necessary for achieving high amino acid transport activities and that many of the previously reported anionophores might be active amino acid transporters. This reveals a new strategy for the development of artificial amino acid transporters with improved properties. Since numerous biologically active substances, including neurotransmitters or drugs, are also amino acids, our discovery opens up new research perspectives and potential applications for synthetic amino acid transporters.

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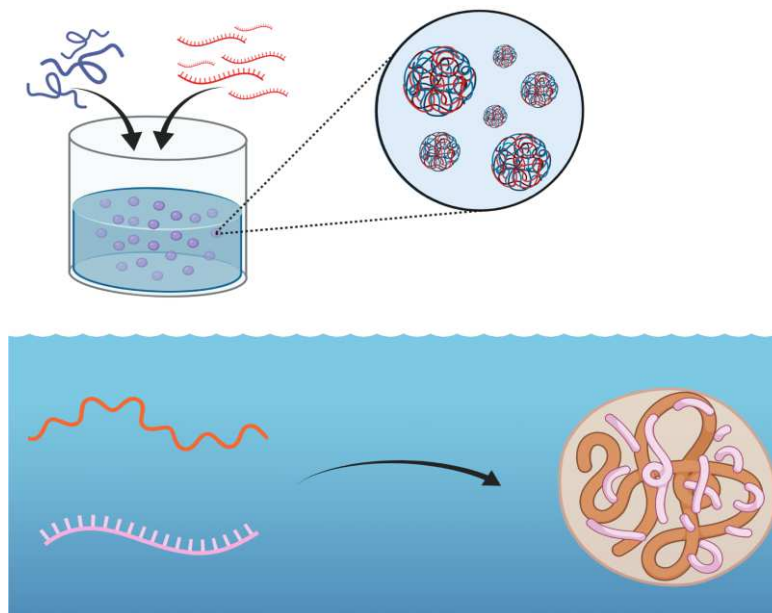
Abstract No: T13

T13 Control of Simple Peptide and RNA Driven Liquid-Liquid Phase Separation

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² University of New South Wales, Kensington, Australia



Caption: Active Liquid-Liquid Phase Separation driven by small peptides and RNA. Can the lab translate to our understanding of the origins of life.

Liquid-liquid phase separation is a spontaneously occurring process where groups of molecules separate into distinct chemical environments – a dilute phase and a concentrated. Concentrated phase environments, commonly referred to as coacervates or condensates, retain solute from the dilute phase – most commonly water. The process is often divided into two types: passive coacervation and active coacervation. Simple coacervation occurs when changes to the dilute phase chemical environment (such as pH, salt, and temperature) induce coacervation; whereas complex coacervation is triggered by active associative phase separation with another type of molecule and is driven by electrostatics, pi-pi interactions, pi-cation interactions and more (Figure 1).¹ Liquid-liquid phase separation has recently been uncovered as a method of organisation for biochemical reactions in living cells. This discovery inspired the investigation of coacervates as a method to chemical reactions for non-enzymatic membraneless biological catalysis.²

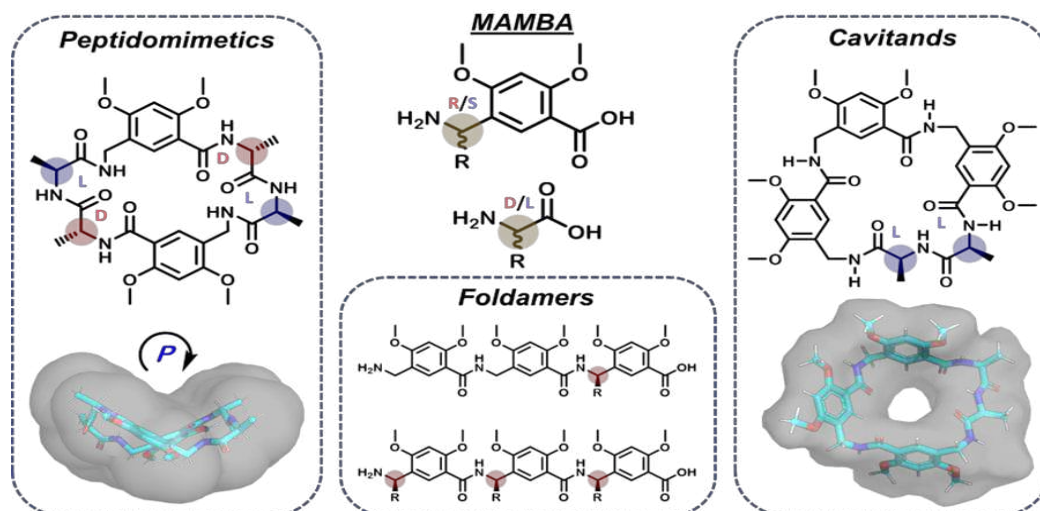
Building on methods of cellular organisation, my research is investigating the use of micro RNA and small peptides as a simple model for driving prebiotic catalysis; and sequence dependency on coacervate formation and catalysis. This investigation has systematically studied the factors that lead to prebiotically plausible coacervation by utilizing the simplest available biopolymers to form a range of coacervates. These coacervates are also capable of responding to environmental changes such as pH and concentration.

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Abstract No: T14

T14 Stereosequence-Defined Arylamide Foldamers and CavitanDs

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Nature uses homochiral monomers to form larger biopolymers, while shorter oligomeric and macrocyclic natural products often comprise heterochiral subunits that can induce conformations that are inaccessible or unfavorable with homochiral building blocks. The macrocyclic antibiotics vancomycin and valinomycin each fold into an active conformation that is dependent on the sequence and stereochemistry of its constituent monomers. Inspired by such stereosequence-defined natural products, we have developed synthetic scaffolds based on a *meta*-aminomethylbenzoic acid (MAMBA) backbone that can be prepared with a defined configuration pattern.¹ Chiral MAMBA monomers were prepared by enantioselective functionalization at the benzylic position. Stereosequence-defined cyclic and acyclic oligomers were synthesized using both solution- and solid-phase synthesis methods.² Spectroscopic techniques, including circular dichroism and NMR spectroscopy, demonstrated that the stereosequence had a profound effect on the conformation of these scaffolds in solution and the effect was enhanced by macrocyclization to form MAMBA cavitanDs and twisted β -sheet peptidomimetics. Our results show that stereosequence-defined foldamers and cavitanDs can be useful tools for investigating the structural bases of supramolecular phenomena.

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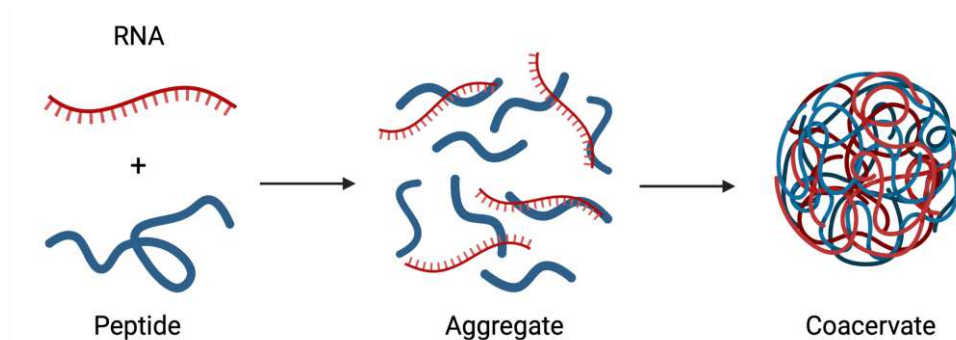
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Abstract No: T15

T15 A Supramolecular Perspective on RNA-peptide interactions

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Caption: How relatively weak RNA-peptide interactions contribute to larger aggregated systems.

RNA's role in the body is largely dictated by its ability to interact with a variety of other biomolecules, namely proteins, lipids, and sugars. These four classes of molecules constitute the four major macromolecules responsible for life.¹ It has been well established that non-covalent interactions between RNA molecules and proteins are responsible for a variety of cellular functions by biologists, such as the regulation of protein synthesis and formation of liquid-liquid phase separated structures (membraneless organelles)². Chemists have investigated the supramolecular behaviour of individual nucleobases and modified nucleobase structures. Nucleobases interact primarily by hydrogen bonding and pi stacking with other species³. However, these studies fail to investigate how entire nucleotides or oligonucleotides behave. The sugar-phosphate backbone of oligonucleotides is ignored in these studies, where the potential electrostatic and dipole interactions are not investigated. Furthermore, single nucleotides rarely exist in biology, so the exploration of how oligonucleotides interact on the supramolecular level would provide a link between the two disciplines.

This investigation designed and synthesised a library of heptamer peptides based on the -RGG motif and triglycine repeats commonly found in intrinsically disordered proteins such as Fused in Sarcoma (FUS). Three RNA sequences have been investigated so far, which are the homopentameric sequences **AAAAA** (penta-adenosine), **CCCCC** (penta-cytidine) and **UUUUU** (penta-uridine). The peptide and RNA libraries were designed with the intent to investigate the sequence selectivity of these molecules and better understand the mechanisms which determine RNA-peptide binding.

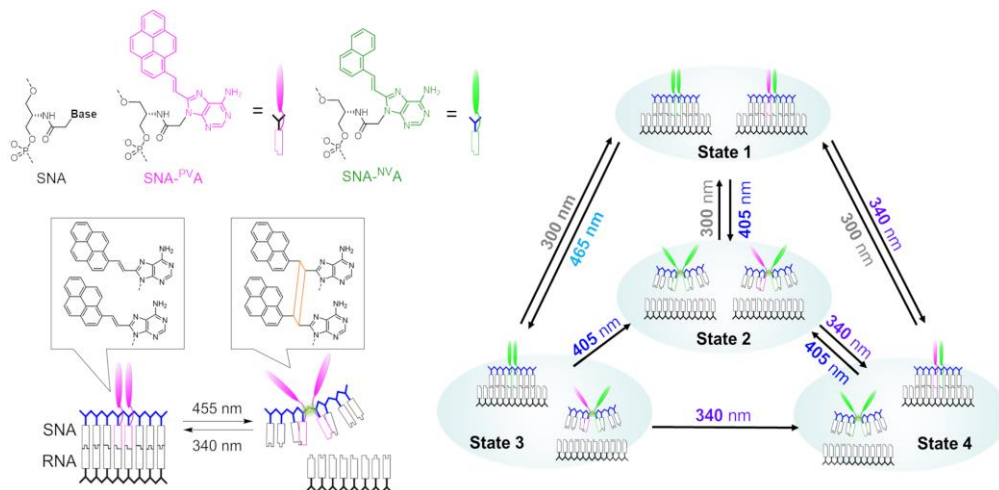
Preliminary data from Isothermal Titration Calorimetry has shown that the more aromatic **AAAAA** and **CCCCC** bind with aromatic phenylalanine containing peptides more strongly than **UUUUU**. The opposite trend is seen with non-aromatic, positively charged arginine containing peptides. This suggests that the hydrogen bonding and electrostatic interactions play a more important role in binding. Overall, a stronger interaction is observed with arginine containing peptides than phenylalanine. This suggests the electrostatic interactions contribute more to binding with RNA than aromatic ones.

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Abstract No: T16

T16 Photo-controllable Acyclic Xeno Nucleic Acid with Adenine Analogues

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Caption: Illustration of photo-regulation system by modified SNA

Xeno nucleic acids (XNAs) are artificial nucleic acids composed of unnatural scaffolds and natural nucleobases.¹ Herein, we newly designed photo-control system for XNA. Photocontrol of duplex formation between the serinol nucleic acid (SNA),² which is an acyclic XNA, and complementary RNA was made possible by incorporation of a photo-responsive nucleobase 8-pyrenylvinyl adenine (^{PVA}) into SNA.³ We synthesized ^{PVA}-SNA that has two ^{PVA} residues in the middle of an SNA strand. When the ^{PVA}-SNA/RNA duplex was irradiated with 455 nm light, ^{PVA} residues in SNA caused intrastrand [2+2] photocycloaddition by 455 nm light, resulting in dissociation of the duplex. Effective cycloreversion of the ^{PVA} photo-dimer results from irradiation with 340 nm light, which regenerate the duplex of ^{PVA}-SNA/RNA. These reactions occurred in high yield, rapidly, selectively, and reversibly. This is first example of use of photocycloaddition and cycloreversion to photo-regulate canonical duplex formation and dissociation reversibly at constant temperature. We also synthesized a new photo-reactive nucleobase 8-naphthylvinyladenine (^{NVA}) that can be photo-regulated by shorter wavelength compared to ^{PVA}.⁴ Two ^{NVA} residues in an SNA strand caused crosslinking by 340-405 nm light, and cycloreversion by ≤ 300 nm light. In an SNA strand with adjacent ^{NVA} and ^{PVA} residues, an intrastrand crosslink resulted from irradiation with 405-465 nm light that was reversed by irradiation with ≤ 340 nm light. Combinational use of ^{PVA}/^{NVA} and ^{NVA}/^{NVA} photo-switches enabled orthogonally photo-control of four hybridization states of two SNA/RNA duplexes by irradiation with a suitable wavelength of light, which can expand the variation of photo-manipulating system. Overall, SNA photo-control system using ^{PVA} and ^{NVA} has potential for use in photo-controllable biological tools targeting endogenous RNAs in cell as well as photo-driven SNA machine.

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Abstract No: T17

T17 Design, synthesis and biological evaluation of new peptides containing pyrrole derivatives.

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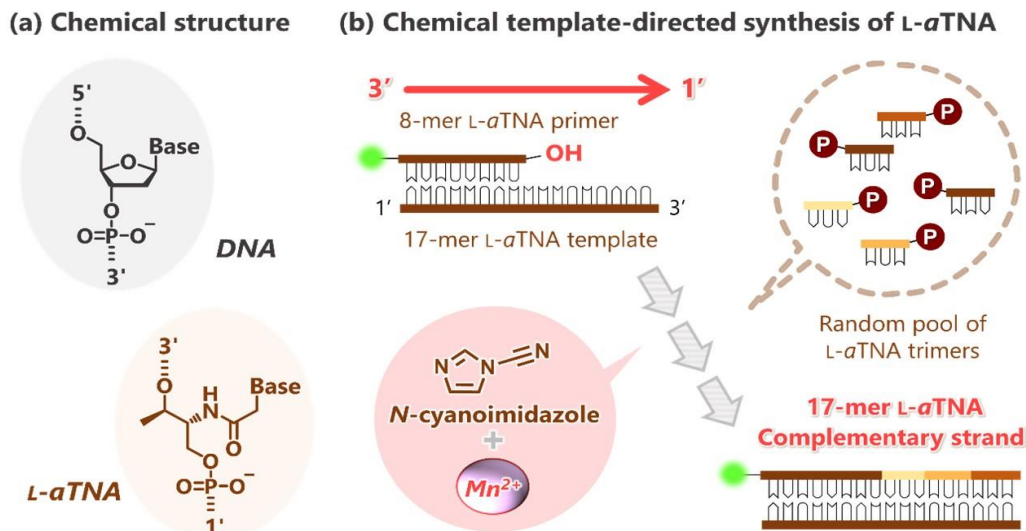
University of Chemical Technology and Metallurgy, Sofia, Bulgaria

Tumor diseases are abnormal cell growth. Targeted drugs recognize and attack cancer cells without destroying normal cells. The pyrrole ring is one of the most studied heterocycles and a major pharmacophore unit in a number of biologically active compounds. A large number of pyrrole-containing drugs, such as potent anticancer, antimicrobial, antiviral, antipsychotic, anxiolytic, antibacterial, antifungal, and antimalarial drugs, have established themselves in the medical practice. The change in the structure of some peptides and their combination in hybrid structures with different heterocyclic compounds are being studied as a promising alternative to existing commercial drugs, such as non-steroidal anti-inflammatory, analgesic, antiviral and antitumor agents. Objective: This work includes synthesis of new pyrrole-containing compounds with biological activity to influence the development of Chronic Myeloid Leukemia. The new peptides containing a pyrrole ring in their molecule were obtained by solid phase peptide synthesis Fmoc - strategy. The peptides Pyr-Lys-Lys-Lys-NH₂, Pyr-His-Lys-Lys-NH₂, contain at the N-position a pyrrole structural unit with different substituents. The compounds were tested for antineoplastic activity against two leukemia-derived cell lines, namely BV-173 (B-cell precursor leukemia) and AR-230 (Chronic myeloid leukemia) using the MTT-dye reduction assay for cell viability. The MTT-bioassay data were fitted to sigmoidal dose-response curves and the corresponding equieffective IC₅₀ values were calculated using non-linear regression analysis. The tested compounds exerted concentration dependent cytotoxic effects in micromolar concentration range against the malignant cell. Acknowledgements: This research is realized in a frame of National Program "EUROPEAN SCIENTIFIC NETWORKS" of Ministry of Science and Education of Bulgaria, project D01-278/05.10.2020, "Drug Molecule".

T18 Chemical Template-Directed Synthesis for Replication of Acyclic L-Threoninol Nucleic Acids

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Caption: (a) Chemical structures of DNA and L- α TNA. (b) Schematic illustration of nonenzymatic template-directed synthesis of 17-mer L- α TNA.

DNA is a significant biopolymer as a genetic carrier and used for fundamental nanostructured materials. Although DNA has been applied to nucleic acid medicine, DNA can be readily degraded by *in vivo* enzymes such as DNA nuclease. Our group has designed *acyclic* artificial nucleic acids consisted of amino acid derivatives, which gained the high durability against enzymatic digestion for solution of the above problem. In particular, *acyclic* L-threoninol nucleic acid (L- α TNA) can form more stable homo-duplex than DNA duplex (Fig a).¹ L- α TNA strand can also hybridize to the complementary strands of DNA and RNA. However, enzymatic reaction using L- α TNA remained difficult because enzymes cannot recognize the acyclic scaffold of L- α TNA. Herein, we developed nonenzymatic template-directed synthesis of L- α TNA for pseudo-primer extension reaction by chemical ligation with a condensing agent, *N*-cyanoimidazole and divalent metal cation, Mn^{2+} ion as an alternative to enzymes.² Based on the ligation system, 8-mer L- α TNA primer was sequentially elongated on 17-mer template in the presence of a pool of random trimer fragments as substrates, selectively generating 17-mer full-length L- α TNA strand complementary to the template (Fig b).³ The yield was 90% after 24h incubation. Consequently, we succeeded in establishment of the chemical replication system of L- α TNA. In the future, we will provide L- α TNA-based *in vitro* selection / SELEX method to obtain a unique L- α TNA aptamer.

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Abstract No: T19

T19 Antimicrobial Activity and Mechanism of Action of Bis-Benzimidazolium Salts to Combat Antibiotic Resistance and Biofilms

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The appearance of resistant strains to antibiotics has become an alarming threat to the global health care system. This project aims at establishing the first steps towards the development of new antibiotics in order to combat the increase in antimicrobial resistance and bacterial persistence associated with biofilms. Our approach consists in mimicking the structural properties of natural compounds, cationic antimicrobial peptides (AMPs), in order to reproduce their biological activity while overcoming their disadvantages.

To limit the development of resistance, we designed a library of bis-benzimidazolium salts that target the bacterial membrane in a selective but non-specific manner through supramolecular interactions. The cationic amphiphilic nature of the compounds enables selective targeting of the bacterial membrane by electrostatic interactions, followed by the disruption of the lipid bilayer by hydrophobic interactions.

A study of the structure-activity relationship has been carried out by testing the compounds on a range of pathogens presenting resistance to conventional antibiotics. Then we thought to elucidate the relevant physicochemical properties of the structure for enhanced antimicrobial activity, selectivity and anti-biofilm activity. In this study we also examine the mechanism of action of the compounds by following the chloride efflux through membrane models of bacterial and mammalian cell membranes.

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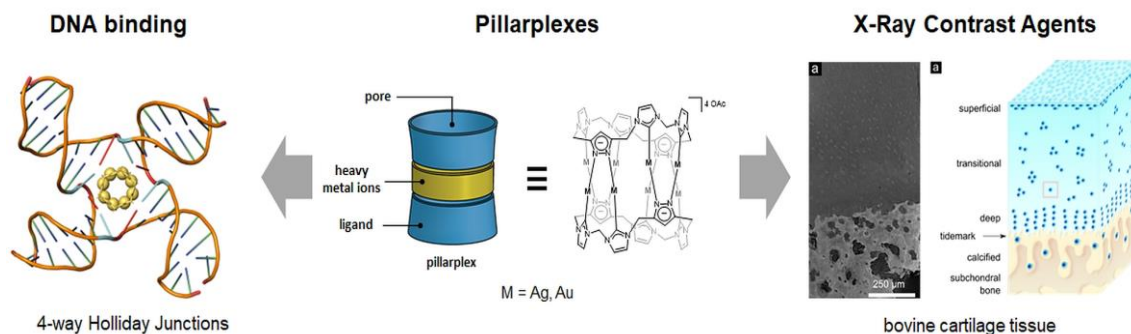
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Abstract No: T20

T20 Towards Biomedical Application of Pillarplexes

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Caption: Potential application of pillarplexes in the biomedical context: DNA binding (left) and X-Ray contrast agent for tissue staining (right).

Pillarplexes are supramolecular organometallic complexes¹ which exhibit defined tubular cavities and additionally possess intrinsic functionality, e.g. photoluminescence, selective guest recognition, easily adjustable polarity/solubility.²⁻⁴ Furthermore, the complexes can be employed as building blocks in mechanically-interlocked molecules, namely rotaxanes, forming a pH-responsive molecular switch.⁵ Depending on the metal employed, they also show different toxicity which renders them interesting candidates for applications in the biological context.⁶ The structural features of the pillarplexes, in particular their tetra-cationic charge as well as the tubular shape including a significant amount of pi-surface, renders these compounds ideal for interaction with negatively charged biomacromolecules.

Herein we present, that the pillarplex is able to interact with DNA, in particular so-called 4-way Holliday Junctions.⁷ The Au pillarplexes can also bind designed 3-way junctions but their size leads them to open up and expand that junction, disrupting the base pairing which manifests in an increase in hydrodynamic size and a lower junction thermal stability. This pillarplex binding contrasts with (but complements) that of the metallo-supramolecular cylinders, which prefer 3-way junctions and we show can rearrange 4-way junctions into 3-way junction structures. Additionally, we present an X-ray staining method based on pillarplex salts as contrast agents,⁸ which enables for the first time 3D visualization of articular cartilage at high resolution using laboratory based computed tomography. This method will allow for future studies at the to gain deeper understanding of diseases derived from this special soft tissue. The developed staining procedure is fully compatible with conventional histology.

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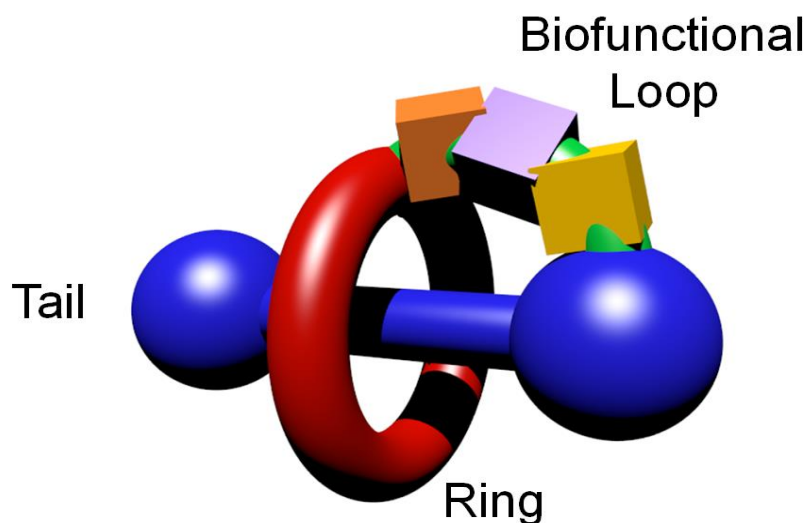
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Abstract No: T21

T21 Taking Inspiration from Nature: Displaying Biological Functionality in the Loop Region of [1]Rotaxanes as Synthetic Analogues of Lasso Peptides

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Caption: Figure 1: Schematic of the components of a [1]rotaxane.

In the search for new therapeutic agents, lasso peptides have emerged as promising candidates.¹ These naturally occurring peptides have [1]rotaxane-like motifs, where the mechanically interlocked macrocyclic 'ring' and axle are covalently attached to one another (Figure 1). Their self-tangled structures are believed to be imperative for their bioactivity; not only does the peptide chain show increased stability (in contrast to linear counterparts), but the interlocked nature also enforces specific conformational display of the amino acids within the 'loop' region.

While the first chemical synthesis of a lasso peptide was reported in 2019,² this approach can be synthetically arduous. However, by using non-covalent template synthesis, both Coutrot,³ and subsequently Bode,⁴ have generated more accessible [1]rotaxane analogues.

Here, we present our work on preparing families of [1]rotaxanes incorporating biological functionality (initially through amino acids) in the critical loop region. We have explored two approaches: (a) the cyclisation of a peptide attached to a [2]rotaxane scaffold⁵ and (b) the expansion of the loop of a [1]rotaxane.⁶

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Abstract No: T22

T22 Neuropharmacology study of new bioconjugates opioid peptides

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Hemorphins are endogenous bioactive signaling oligopeptides with an opioid-like activity that are a product of hemoglobin degradation. The VV-hemorphin-7 demonstrated a rank order of receptor potency $\mu > \kappa > \delta$. Hemorphins are considered potential drug candidates and biomarkers of breast cancer, pediatric brain tumors, neurodegenerative disease and aging. The neuropharmacology of a series of new bioconjugated hemorphin peptides was studied in three seizure tests in mice. The rotarod test was used to determine acute neurological toxicity. From the eight hemorphin peptides, the **H7-1** peptide analogue showed the highest activity in the 6-Hz psychomotor seizure test. The **H7-6** and **H7-7** peptides showed anticonvulsant activity against the generalized seizures in the maximal electroshock test, which was comparable to the positive hemorphin peptide **H7**. A dose-dependent elevation of the threshold for ivPTZ-induced clonic seizures was indicated for the **H7-5** to **H7-8** peptide analogues. A lack of neurotoxic side activity was shown for the tested peptides. Our results suggest that manipulating the N- and C-ends is a background for designing new LVV- and VV-hemorphin-7 analogues with potential biological activity with preclinical and clinical implications.

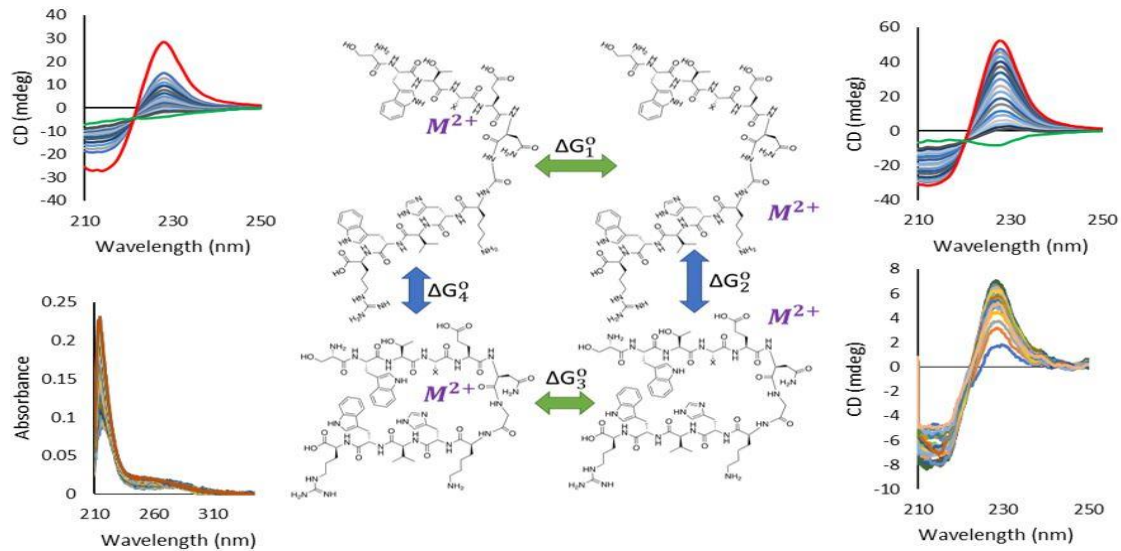
Acknowledgment: This study is funded by the European Union-NextGenerationEU, through the National Recovery and Resilience Plan of the Republic of Bulgaria, project № BG-RRP-2.004-0002, "BiOrgaMCT".

Abstract No: T23

T23 Tailored Tryptophan Zippers reversibly fold and bind metal cations in solution

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Caption: A tryptophan zipper in aqueous solution can exist in four possible states that constitute a square scheme.

Tryptophan Zippers, short β -hairpin peptides, can be tailored to promote folding by the addition of a metal binding factor. Four distinct zippers, differing only in the fourth amino acid (SWTXENGKHWVR, X = N, C, H, or Y) have been thermodynamically characterized via CD and UVvis spectroscopy. Thermal denaturation experiments, both in the presence of metal and without, were monitored with CD spectroscopy, which differentiates the folded and unfolded states. Titrations with $\text{Cu}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_3$ were monitored with CD and UVvis, which differentiates the cation bound and unbound states. By simultaneously modeling all four datasets for a chemical system, the free energy, enthalpy, and entropy values relating all four possible states (un/bound, un/folded) were quantified with 95% confidence intervals. The results indicate that folding can be invoked to great effect when residues 4 and 9 of the zipper are both histidine (H) residues, as expected. Weak folding is observed for zippers with asparagine (N), cysteine (C), or tyrosine (Y) at the fourth position.

Abstract No: T24

T24 Design and Synthesis of Biguanides Conjugates Targeting Energy Metabolism of Cancer Cells

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Recent studies on metformin's anti-cancerous properties led to a growing interest in the use of biguanides derivatives for cancer treatment and prevention. The mechanism of action of metformin on cancerous cells is still not fully understood and different hypotheses have been proposed in the literature. However, it is a well-known fact that one of its effects is to disturb energy metabolism of cancer cells by acting on the respiratory chain of mitochondria. Since its activity has only been observed for high doses of this drug, our recent interest is to design and develop biguanide derivatives that will be more efficient than metformin when used in small amounts for the inhibition of the proliferation of cancer cells. Our strategy is to design bifunctional molecule containing a biguanide moiety and a second ligand that will enhance the drugs activity.

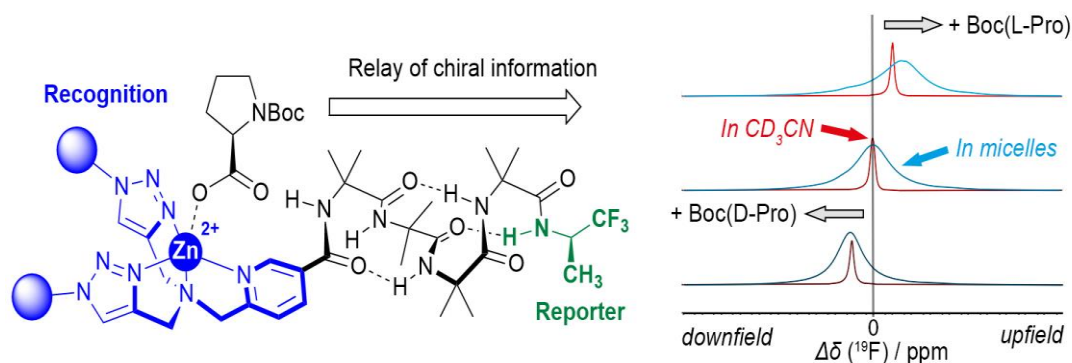
Our approach consists in synthesizing a library of Biguanides conjugates, that would induce the degradation of biguanides target. Proteolysis Targeting Chimeras (PROTACs) and Autophagy Targeting Chimeras (AUTACs) are bifunctional molecules containing 2 ligands. The first one recruits preexisting biological systems to enhance the degradation of a protein of interest bound by the second ligand. This system will be used to study biguanides effects on mitochondria and develop new anticancer agents targeting the energy metabolism of cancer cells.

Abstract No: T25

T25 Using ^{19}F NMR Spectroscopy to Study Foldamer Conformation in Bilayers and Micelles

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Understanding and controlling peptide foldamer conformation in phospholipid bilayers is a key step toward their use as molecular information relays in membranes.¹ To this end, a new ^{19}F "reporter" tag, (*R*)-TFEA, has been developed and attached to the C-terminus of dynamic α -amino-*iso*-butyric acid (Aib) foldamers. In organic solvents, the ^{19}F NMR chemical shift of the CF₃ resonance reported on the ability of different N-terminal groups to induce either an *M* or a *P* helix in solution.

This ^{19}F NMR reporter permitted solution NMR spectroscopy to also be used to understand the conformational behaviour of the same family of (*R*)-TFEA-labelled foldamers in small unilamellar vesicles (SUVs). Broadened but resolvable ^{19}F resonances were observed, with the relative positions of the CF₃ resonances from each family member mirroring their positions in organic solvents. These studies showed that foldamer conformational preferences are the same in phospholipid bilayers as in organic solvents and revealed that phospholipid chirality has little influence on conformation.²

Access to this chemically robust (*R*)-TFEA reporter then permitted a new recognition motif to be developed at the N-terminus. A Zn(II) bis(triazole)(2-pyridyl) recognition pocket could be synthesised with relative ease through "click" chemistry, installing triazole arms that both chelate the metal ion and give access a breadth of functionalities around the pocket rim. The Zn(II) centre bound carboxylate ligands tightly. If the carboxylate is chiral, the resulting chiral complexes exert a local conformational preference that is relayed along the length of the Aib foldamer to the (*R*)-TFEA reporter at the other end. Not only was this binding and relay of chiral information observable in organic solvents, but the (*R*)-TFEA reporter allowed both to be observed in lipid micelles by solution ^{19}F NMR spectroscopy.

It is hoped that by developing NMR analysis methods in micelles and SUVs, a new pathway towards synthetic signal transduction can be developed; membrane-spanning foldamers dynamically interacting with encapsulated soluble reagents to produce outcomes that can be studied by the full suite of multinuclear NMR techniques.

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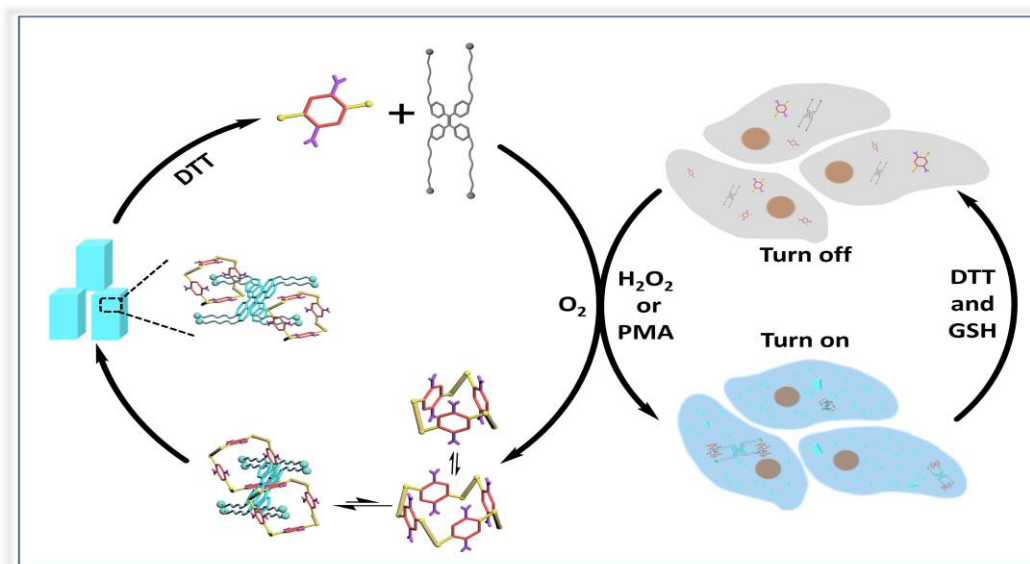
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Abstract No: T26

T26 Regulating Synthetic Molecular Networks in Cellular Environments

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Caption: Scheme Schematic illustration of the construction and regulation of a synthetic dynamic molecular network (SDMN) in cellular environments

Systems chemistry is a rapidly growing field that investigates how interacting molecules in synthetic molecular networks contribute to the emergent properties and overall function of the system.¹ In recent decades, systems chemistry has made significant progress in developing new experimental and theoretical tools for investigating complex chemical systems. This progress, in particular, has been made possible by advances in supramolecular chemistry.² However, nearly all of these studies, have been carried out in synthetic chemical systems, leaving us with a limited understanding of how complex chemical systems interact with far more intricate biological systems.

In this study, we demonstrate the regulation of a synthetic dynamic molecular network (SDMN) in cellular environments. The SDMN was constructed using a dithiol building block X that spontaneously formed disulfide macrocycles when exposed to air. By incorporating a non-emissive tetraphenylethylene (TPE) derivative as a template, the entire system became emissive upon full oxidation of the thiols. The TPE template selectively amplified a network member through molecular recognition, leading to the formation of self-assembled supramolecular nanomaterials with aggregation-induced emission (AIE) properties. The change in fluorescence allowed us to monitor the network's reversibility in living cells *in situ*. When we introduced the SDMN into cells under oxidative stress, the cells' fluorescence was activated. Conversely, the fluorescence could be switched off when the cellular environment became reductive. Our findings open a door to manipulating the dynamic process of SDMN in biological systems, encouraging us to engineer the function of life using complex chemical systems in the near future.

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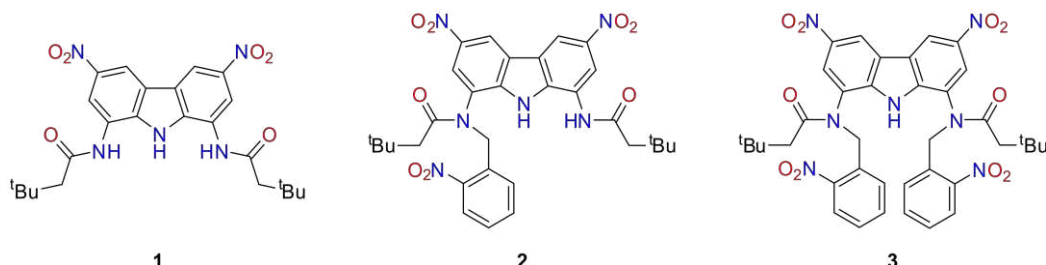
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Abstract No: T27

T27 Dual stimuli-responsive transmembrane anion carriers

Bartłomiej Zawada Michał Chmielewski

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Caption: Fig. 1. Structures of the pH-switchable transporter **1** and its caged congeners **2** and **3**.

Synthetic anion transporters show promise as potential anticancer agents owing to their ability to effectively perturb ion gradients across cell membranes, what leads to apoptosis.¹ Unfortunately however, such transporters may also be toxic to healthy cells, what limits their practical utility in anticancer therapy. A solution to this problem might be the development of stimuli-responsive carriers, which could be selectively activated in cancer cells. Several strategies towards this goal have been proposed. For example, pH-switchable transporters exploit differences in pH between healthy and cancer cells,² while light-switchable transporters may be remotely controlled by irradiation with light of an appropriate wavelength. Since none of these strategies affords perfect selectivity, we propose to combine two of them in the same transporter in order to apply two selectivity filters at the same time. As a case in point, we describe herein the synthesis and anion transport properties of the first dual stimuli-responsive anion carriers.

In our laboratory, we have recently developed a pH-switchable transporter **1** that is extremely active in chloride transport under slightly acidic conditions, but rapidly loses its activity at pH above ca. 6.5.³ In the present contribution, we use the photocageing strategy developed by Talukdar and co-workers⁴ to inactivate (cage) **1** with a photolabile o-nitrobenzyl protecting group(s). Thus, mono- and doubly caged transporters **2** and **3** have been synthesised and found to be inactive in anion transport across the lipid bilayers of Large Unilamellar Vesicles (LUVs). We show here that simultaneous application of both light and protons as stimuli is necessary to regain the activity of **2** and **3**.

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Abstract No: T28

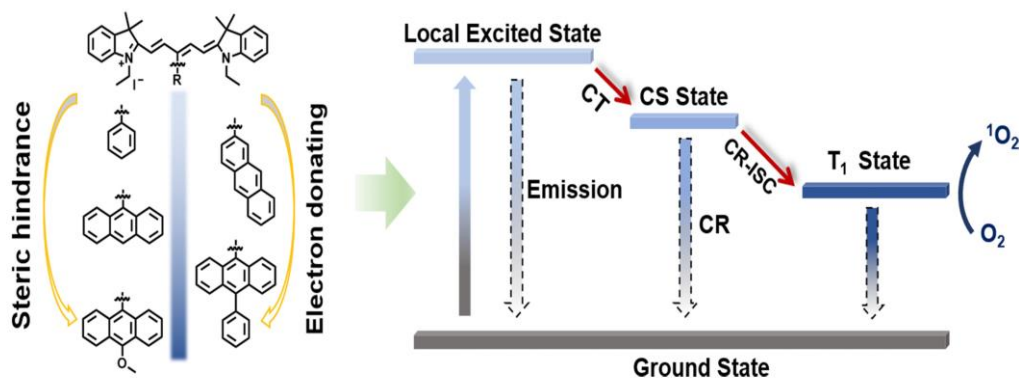
T28 Cyanines Based on Photoinduced Electron Transfer (PET) with Simultaneous Intersystem Crossing Enhancement and Excited-State Lifetime Elongation

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Caption: Chemical structures and excited-state mechanism of PET-based cyanine photosensitizer

Heavy-atom-based photosensitizers usually exhibit high cost, large toxicity and shortened triplet-state lifetimes, which are not ideal for hypoxic tumor photodynamic therapy^[1] (PDT). Herein, we developed a novel near-infrared (NIR) heavy-atom-free photosensitizer design strategy by introducing sterically bulky and electron-rich moieties at the *meso* position of the pentamethine cyanine (Cy5) skeleton, which simultaneously enhances intersystem crossing (ISC) and prolongs excited-state lifetimes. We found that the ¹O₂ generation ability is directly correlated to the electron-donating ability of the *meso* substituent, and the excited-state lifetime is simultaneously much elongated when the substituents are 9-anthracene derivatives. Among the newly designed compounds, ANOMe-Cy5 exhibits intense NIR absorption, the highest ¹O₂ quantum yield (4.5-fold higher than Cy5) and the longest triplet-state lifetime (9.8-fold longer than Cy5). Such excellent photophysical properties coupled with its inherently cationic and hydrophilic nature enable the photosensitizer to realize photoablation of solid tumor and antitumor lung metastasis. We also believe that such molecular reconstruction tactic provides a reference for the design and development of photosensitizers in other fields, such as photocatalysis^[2] and triplet-triplet annihilation (TTA) upconversion.

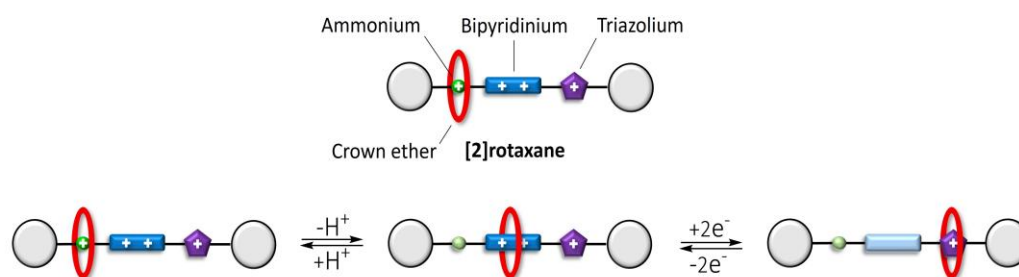
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Abstract No: T29

T29 A novel prototype of acid-base and redox switchable [2]rotaxane

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Caption: Schematic representation of the [2]rotaxane and of its operation.

Rotaxanes are the most explored class of mechanically interlocked molecules (MIM), and rotaxanes with two interaction sites for the ring, i.e. two stations, are versatile platforms for the development of artificial molecular machines.¹ Rotaxanes with higher number of stations are more sophisticated systems, in which complex operations can be performed.² However, relatively few examples of these systems are present in literature, due to their higher complexity.

Here, we report the investigation of a novel three-station [2]rotaxane (Figure 1), performed by voltammetric methods, NMR spectroscopy and UV-Vis spectroscopy. The rotaxane is composed by a crown ether macrocycle and an axle comprising an ammonium primary station, a bipyridinium secondary station and a triazolium tertiary station.

The primary and the secondary stations can be de-activated by means of orthogonal stimuli: the ammonium site can be switched-off by deprotonation (*chemical stimulus*), while the bipyridinium site by reduction (*electrochemical stimulus*). Both processes are reversible and, therefore, a combination of chemical and electrochemical stimuli can be used to control the motion of the ring from one station to the others.

The [2]rotaxane can be switched between three stable states (Figure 1), in which the ring is sequentially moved on the axle from one extremity to the other, i.e. a processive linear motion is obtained. In each state, the ring is not distributed between multiple stations and surrounds only one of them, resulting in a precise operation of the rotaxane. An important property of this system is the modularity: indeed, the investigation of model molecules indicates that each station of the [2]rotaxane behaves almost independently from the others. This feature enables the design of novel MIMs based on the same molecular components, capable of exploiting the high degree of control over the ring motion to perform work.

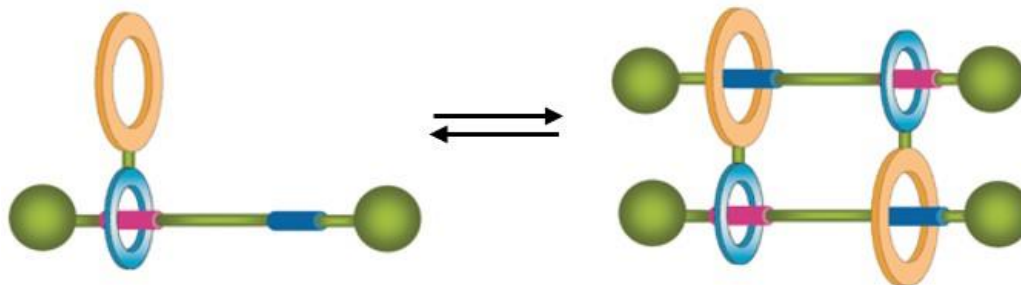
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Abstract No: T30

T30 Studies on the hydrogen-bonding-driven assembly of a cyclic pseudorotaxane

JOSE BERNA CANOVAS ² Adrian Saura-Sanmartin ¹, Tomas Nicolas-Garcia ¹, Aurelia Pastor ¹, David Quiñonero ¹, Mateo Alajarin ¹, Alberto Martinez-Cuezva ¹² Universidad de Murcia, ALBATERA, Spain

Caption: Figure 1. Assembly of a multi-stimuli responsive [4]pseudorotaxane

The design of artificial molecular machines that mimic those controlling key biological processes attracts nowadays the attention of the scientific community.^[1] Molecular scaffolds incorporating two or more components linked by a mechanical bond (mechanically interlocked molecules, MIMs) are considered ideal candidates to this goal.^[2] Stimuli responsive MIMs, whose dynamic properties can be controlled at will, are being incorporated into advanced materials.^[3] Hence, the preparation of MIMs with advanced structural complexity is still highly appreciated.^[4]

In this regard, heterorotaxanes can be considered as suitable molecular architecture for programming unconventional functions. These structures contain more than one type of interlocked macrocycles, providing appealing species for studies on sequence isomerism and stereochemical complexity.^[5] Herein we communicate our experimental and computational studies on the hydrogen-bonding-driven assembly of a cyclic hetero[4]pseudorotaxane from a self-complementary [2]rotaxane. Remarkably, the controlled disassembly of this supramolecular interlocked structure can be achieved by applying different stimuli is enabled to reduce the level association of the systems into the interlocked building-blocks.^[6] This set of approaches can be effectively employed for switching different working states.

[Insert Figure 1 here]

Acknowledgements.

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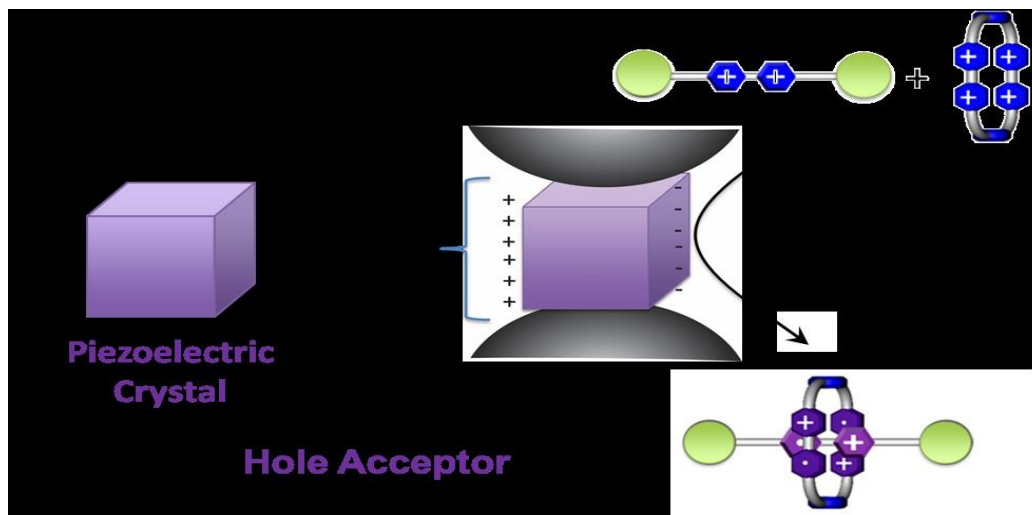
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Abstract No: T31

T31 Piezoelectricity-Induced Mechanical Bond Formation

Surojit Bhunia Pramita Kundu, James S. W. Seale, Long Zhang, Chun Tang, Partha Jyoti Das, Guangcheng Wu, Ruihua Zhang, Yuanning Feng, J. Fraser Stoddart

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Caption: Figure 1. Schematic depiction of piezoelectricity based mechano-redox solid-state chemistry for the synthesis of MIMs

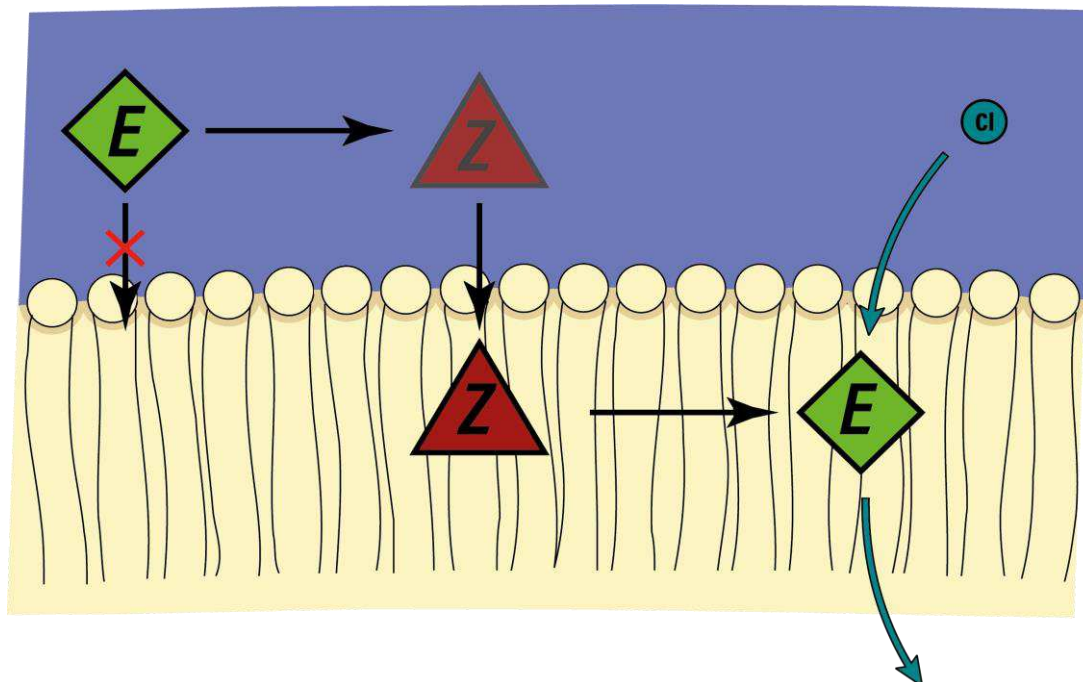
Mechanochemistry has been emerging as a powerful tool to execute a variety of chemical reactions aimed towards the formation of cage compounds and mechanically interlocked molecules (MIMs). The immense potential of mechanochemistry to initiate electron/hole catalysis has not been explored until lately. Such a catalytic system could be realized for the piezoelectric nanoparticles which, being exposed to mechanical stress and deformation can lead to temporary polarization, resulting in electron hole charge separation. This methodology could be further deployed as either a reductant or oxidant with certain redox potentials so as to initiate a redox mediated molecular recognition for the successful synthesis of MIMs and molecular pumps in the solid state.

To accomplish the aforementioned idea, we have chosen BaTiO_3 as a potential piezoelectric material for the desired mechanoredox transformations. Using the ball-milling instrument we were able to perform a two electron reduction of cyclobis(paraquat-*p*-phenylene) (CBPQT^{4+}) rings purely in solid-state in presence of BaTiO_3 , which opens up the unlimited possibilities of solid-state mechanoredox chemistry in the supramolecular regime. Further, employing similar methodology the reduction of 1,1'-dialkyl-4,4'-bipyridinium (BIPY^{2+}) and CBPQT^{4+} lead to the synthesis of pseudorotaxane *via* triradical formation (radical pairing) without use of any reducing agent, completely in solid state. Propelled by this exciting outcome we deployed this methodology for the successful demonstration of redox-based molecular pumping in solid state set-up. Therefore, this methodology can be useful to perform molecular pumping utilizing insoluble polymers. Although further investigations are going on, this piezoelectricity-based solid-state methodology can be a game changer in field of molecular pumping^[1].

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T32 Photocontrol over Transmembrane Anion Transport through Modulation of Membrane Incorporation and Mobility

Jasper Bos¹ Maxime Siegler², Sander Wezenberg³¹ Leiden university, Leiden, Netherlands² Johns Hopkins University, Baltimore, United States³ Leiden University, Leiden, Netherlands

Caption: Photocontrol over membrane incorporation and mobility leads to anion transport

The transport of anions across the cell membrane underlies many important regulatory functions in biology, and is controlled by proteins that respond to external stimuli. A number of synthetic receptors have been developed that are capable of facilitating transmembrane transport, yet their precise control by stimuli remains a major challenge.¹ Particularly interesting is the design of transporters of which the activity can be regulated by light, as its use as a stimulus gives both spatial and temporal control and does not produce waste.²

In recent years, several photoswitchable transporters have been developed whose activity can be controlled by modulating their binding affinity.³⁻⁵ However, differences in transport activity between photoaddressable states were found to be much larger than what can be explained based on the difference in binding affinity alone, indicating that additional factors related to the photoswitching process played an important role. We show here that the activity of an anion transporter can be controlled by changing both membrane solubility and mobility using light, while the anion binding site remains virtually unaltered. This study will be of great importance to the future design and improvement of anion transport systems and is an important step towards their application in biological systems.

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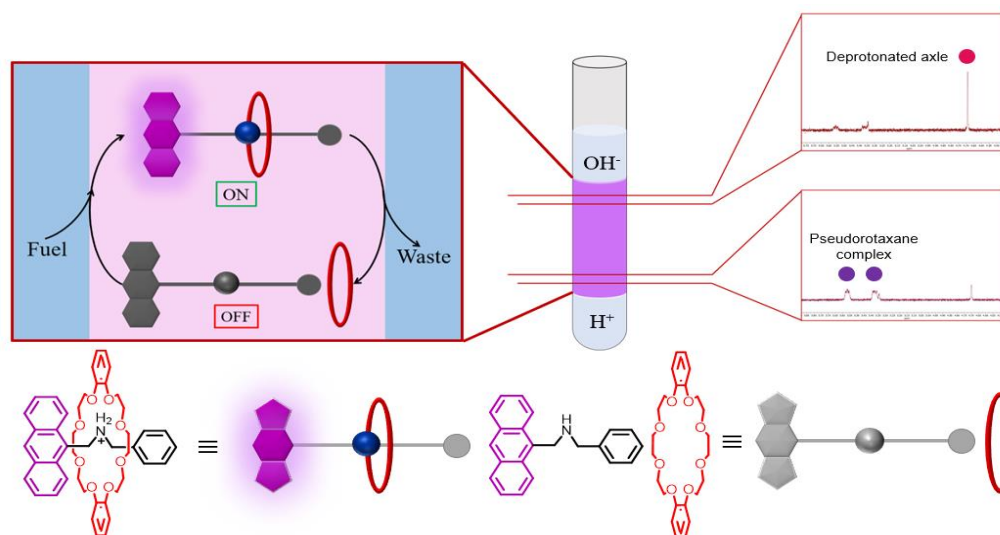
Abstract No: T33

Flash talks 16:40 - 17:00

T33 Operation of molecular machines in a compartmentalized environment

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One of the key characteristics that distinguish molecular motors and molecular switches is the way they utilize the fuel. The working cycle of thermodynamically controlled molecular switches can be described as “operator-dependent” since they require successive addition of reactants (fuels) to complete each equilibrium step of switching. Such systems cannot autonomously repeat their operating cycle, unlike molecular motors which exploit chemical energy input autonomously to do work.¹

In this project, we employed an anthracene-based axle endowed with a secondary amine that, upon protonation, can form a supramolecular complex with a crown ether ring, while in the deprotonated state, the axle does not thread through the crown ether ring. The designed structure represents a molecular switch which would require alternating additions of the acid and base. Our goal is to operate this molecular switch in a compartmentalized system, in which the acid and the base are separated by a liquid membrane containing the molecular switch components. The switch effectively acts as a phase-transfer catalyst for the reaction between acid and base. On the flip side, taking advantage of the catalytic strategy, the acid-base reaction fuels the continuous operation of the switch operating a simple molecular switch as a molecular machine.² We investigated the kinetics of the molecular machine operation and performed the steady-state characterization of the system by the NMR techniques.

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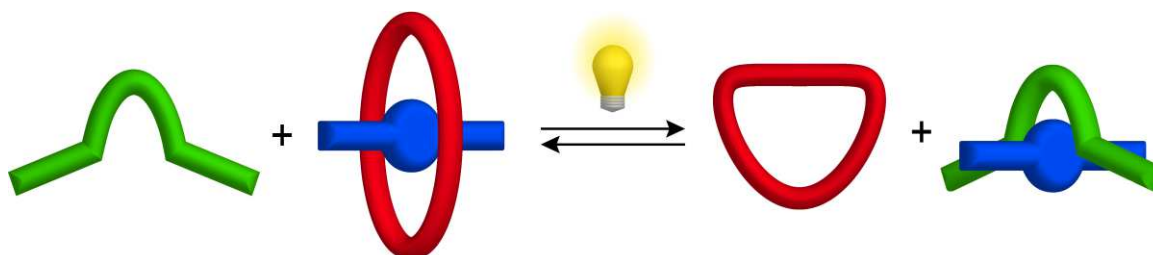
Abstract No: T34

T34 Photocontrolled Threading of Anion-Templated Pseudorotaxanes

Jorn De Jong ¹ Maxime Siegler ², Sander Wezenberg ¹

¹ Leiden University, Leiden, Netherlands

² Johns Hopkins University, Baltimore, United States



Caption: Photocontrolled threading of anion-templated pseudorotaxanes resulting in reversible axle translocation to a secondary host.

In recent years, the use of molecular machines to control motion on the nanoscale has gained significant interest.¹ Several approaches have been taken to create new types of molecular machines able to perform specific functions. Herein, pseudorotaxanes have played an important role, e.g. in the development of supramolecular pumps and ratchets, where an external stimulus can be used to regulate threading.² While reported examples are still limited, notable current strategies have made use of light as a stimulus to control binding affinity and kinetics of crown ether-ammonium complexes.³ To extend the versatility and modularity of such systems, we have developed photoresponsive pseudorotaxanes making use of the anion-templated approach reported by Beer.⁴ Our design is based on stiff-stilbene light-switchable macrocycles of which the *Z*-isomer is able to form a pseudorotaxane structure upon addition of a pyridinium halide axle, *via* anion binding between the three components.⁵ Photoisomerization to the *E*-isomer leads to contraction of the macrocycle and concomitant dethreading. Interestingly, addition of a secondary host to the pseudorotaxane system allowed for light-triggered translocation of the axle between the macrocycle and this secondary host. The presented approach opens up new opportunities towards the development of molecular machines and stimuli-responsive mechanically-interlocked anion receptors.

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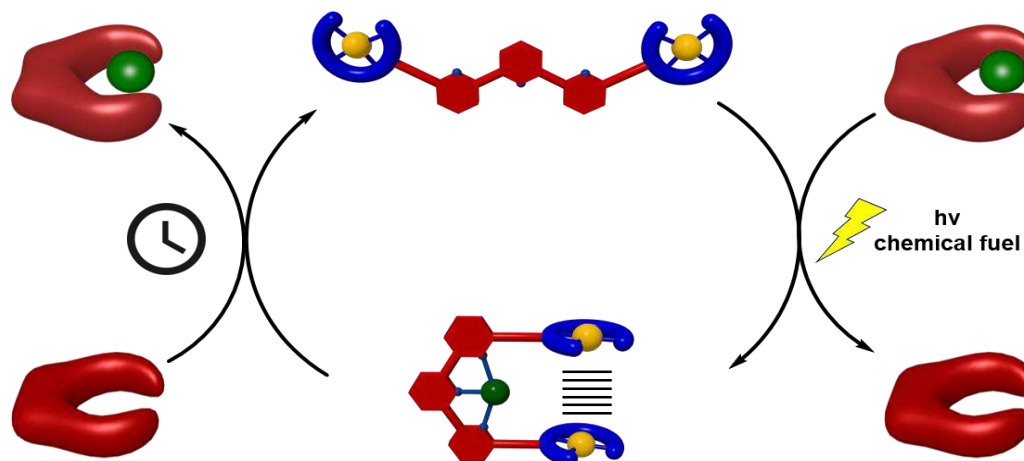
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Abstract No: T35

T35 Molecular Tweezers for Multifunctional Communicating Systems

Maksym Dekhtiarenko, Guillaume Vives

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During the past thirty years chemists have designed, constructed and investigated a large variety of molecular devices and machines by exploiting chemical, photochemical and electrochemical stimuli to transform appropriately designed supramolecular systems. This research has led to the design of diverse molecular machines inspired by nature or their macroscopic counterparts such as molecular motors, switches, cages and tweezers.¹ A significant, yet challenging goal is the development of systems whose actuation is triggered by cooperative or coordinated actions.

We have recently developed switchable molecular tweezers that can be controlled by metal coordination. Our system is based on a terpyridine ligand functionalized by metal salphen complexes. The open tweezers adopt a "W" shaped conformation that can be switched to a closed "U" conformation, bridging the two functional salphen complexes into proximity.^{2,3} We aim to combine such versatile mechanical machines with other orthogonal switches to achieve dynamic smart systems.⁴⁻⁶

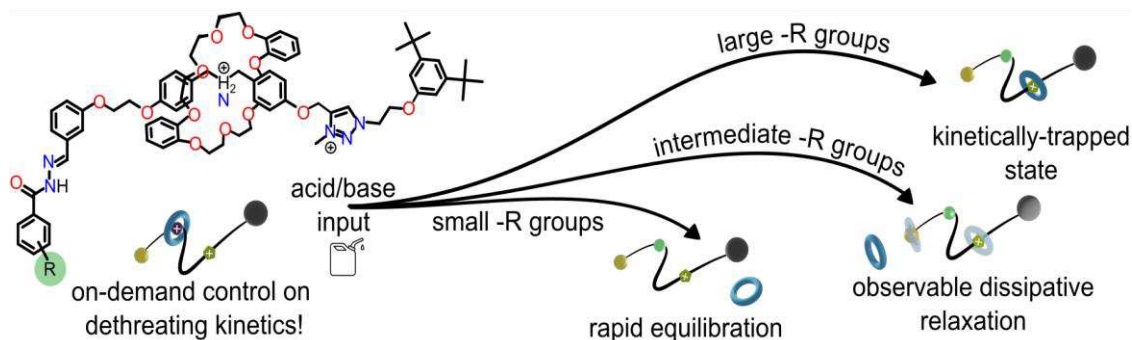
We report herein the multicomponent switching cascades based on terpyridine molecular tweezers and stimuli-responsive organic acids designed to switch the tweezers with photochemical or temporal control. This multicomponent system allows in situ remote control over the conformation and thus the interaction between the tweezer functional units. Such a concept can be beneficial for molecular recognition leading to applications in catalysis or controlled delivery.

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Flash talks 27-06-2023 16:40 - 17:00

T36 Control over Dethreading Kinetics Allows Evaluating the Entropy Stored in an Interlocked Molecular Machine Out-of-Equilibrium

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One of the outcomes of unidirectional movement in molecular machines can be the formation of high-energy states, resulting in an overall endergonic reaction.^[1] What is the energy content of such non-equilibrium states?

To address this question, we studied a minimal model of an acid/base-powered molecular machine^[2] capable of operating the energetically demanding transport of a macrocycle, according to an energy ratchet mechanism.^[1,3] The machine is composed of a recognition site for a crown ether macrocycle, allowing the formation of pseudorotaxane structures, and an aldehyde terminal unit that can be dynamically stoppered with a functionalized benzohydrazide, giving control of the rotaxane formation. Supplying proper acid/base inputs allows the threading of the macrocycle, which remains trapped in a high-energy state as a result of an operating ratchet mechanism.

Employed benzohydrazides, acting as kinetic stoppers, display a sharp *all-or-nothing* effect in terms of dethreading kinetics, spanning from stable kinetically-trapped state to rapid equilibration. Calculation of wSterimol parameters^[4] offers deeper rationalization over the different dethreading behavior, which strongly depends on the substituent groups attached to the stopper.

Careful selection of the operation solvent allows fine-tuning the dethreading kinetics, making it possible to follow dethreading by ¹H-NMR spectroscopy, gaining direct evidence on machine operation, which can be repeated multiple times in situ.

By operating the machine under dissipative conditions, it can be measured the heat exchanged during the dethreading process, confirming experimentally by calorimetry measurements that such molecular machines have a remarkable entropy content stored in their high-energy state.^[5]

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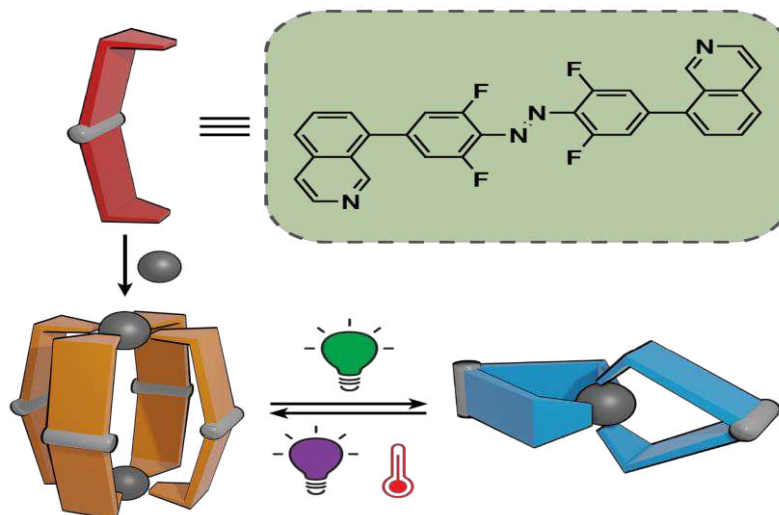
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Abstract No: T37

T37 Visible-light-responsive Self-Assembled Complexes: Improved Photoswitching Properties by Metal Ion Coordination

Ray DiNardi

UNSW, Sydney, Australia



Assembling a quinoline-appended azobenzene with Pd(II) affords a Pd₂L₄ coordination cage that can be reversibly photoswitched to a PdL₂ mononuclear species. Assembly enhances the photoswitching selectivity towards the photoswitch's metastable isomer and extends its thermal half-life from 40 to 850 days.

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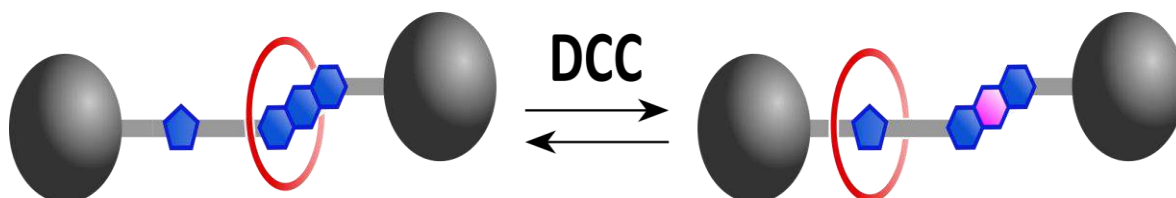
Abstract No: T38

T38 Operating a Molecular [2]Rotaxane Shuttle in Water with Dynamic Covalent Chemistry

Marius Gaedke ¹, Fredrik Schaufelberger ¹ Anja Ramström ²

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The noncovalent interaction between preorganized components in mechanically interlocked molecules such as rotaxanes can be tuned by addition of external stimuli.^[1] Addressing selective co-conformational changes such as controlled shuttling in complex (aqueous) media remains a challenging goal. So far, there are only few examples employing dynamic covalent chemistry (DCC) to operate rotaxane switches described.^[2] Though cycloaddition reactions have been known for almost a century now and constitute highly selective and efficient chemical transformations, they have not been widely used for operating rotaxanes.^[3] Here, we present a reversible Diels-Alder reaction to operate rotaxanes at ambient temperatures in water. The switching process is evaluated by means of NMR, MS and fluorescence spectroscopy.

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T39 The Evolution of Light Effected Autonomous Molecular Pumps

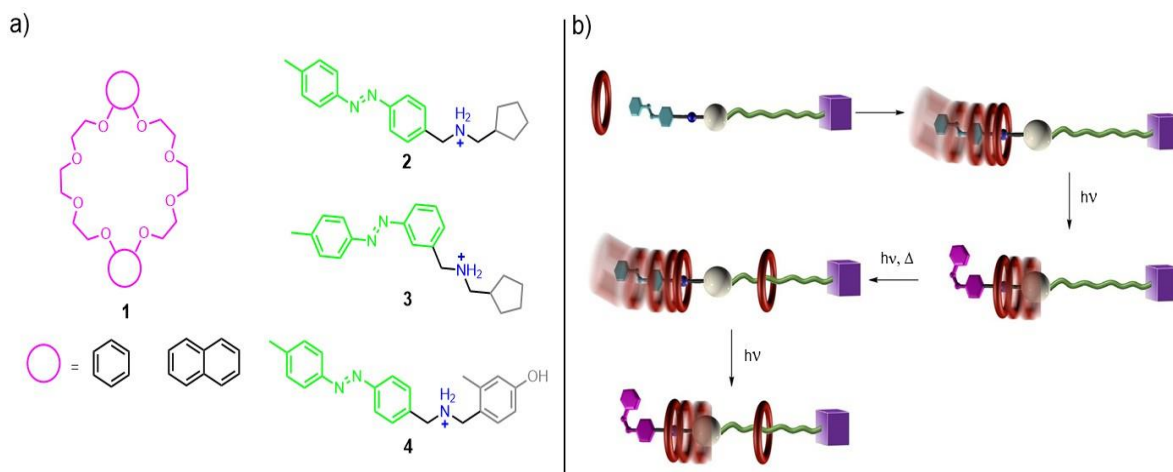
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Caption: Figure 1: a) Structures of the components of the pumping module. b) Schematic representation of the reservoir modified pump operation mode

The development of molecular devices able to operate autonomously away from equilibrium and perform tasks when an external source of energy is applied, still represents one of the major challenges in supramolecular chemistry, with very few examples available.¹ We reported a pseudorotaxane system which, upon light irradiation, acts as a molecular pump allowing the unidirectional transit of the thread through the macrocycle in a dissipative way, operating cyclically according to energy and information ratchet mechanisms (Fig 1a).² We recently demonstrated that slight variations in the structure of the axle component can enhance the performance of the motor and ¹H NMR spectroscopy allowed to observe the dissipative out-of-equilibrium state of the system under light irradiation.³ Moreover, we proved the dependence of the pump dissipative states on the intensity of the energy input provided and determined, through a combination of experimental data and thermodynamical modelling, the parameters describing the operation of the device.⁴ Finally, the pump module was modified in order to be introduced in more complex architectures. Following focused design and modelling, a suitable phenylene derivative was identified to be used as an alternative pseudostopper.⁵ The structure was therefore expanded to include a reservoir, which would allow to pump, and potentially trap, the macrocycles in a higher energy state once light of the appropriate wavelength is shined upon the system (Fig. 1b).

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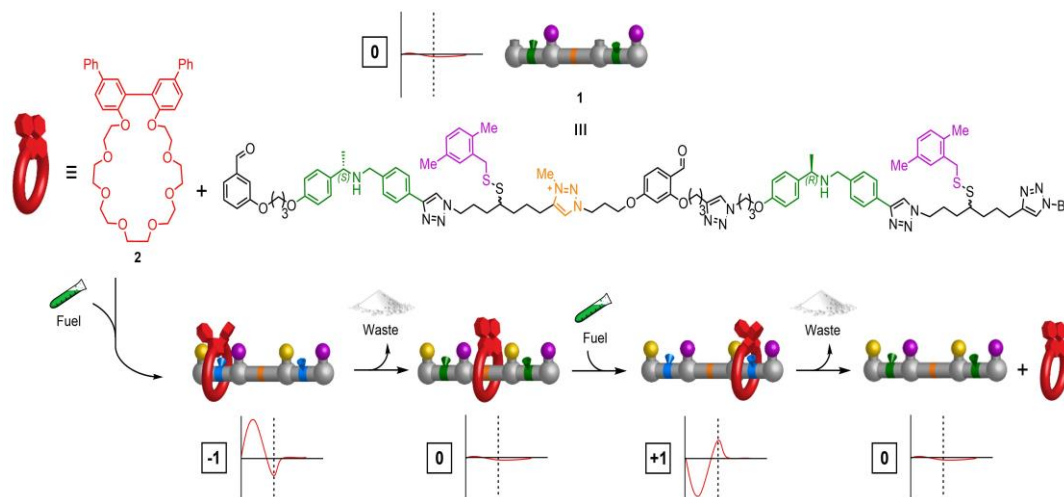
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Abstract No: T40

T40 A Tape-Reading Molecular Ratchet

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Caption: Graphic abstract of tape-reading molecular ratchet

Cells process information in a manner reminiscent of a Turing machine¹, autonomously reading data from molecular tapes and translating it into outputs². Randomly processive macrocyclic catalysts that can derive threaded polymers have been described³, as have rotaxanes that transfer building blocks from a molecular strand to a growing oligomer⁴. However, synthetic small-molecule machines that can read and/or write information stored on artificial molecular tapes remain elusive. Here⁵, we report on a molecular ratchet in which a crown ether (the 'reading head') is pumped from solution onto an encoded molecular strand (the 'tape') by a pulse of chemical fuel⁶. Further fuel pulses transport the macrocycle through a series of compartments of the tape via an energy ratchet⁷ mechanism, before releasing it back to bulk off the other end of the strand. During its directional transport, the crown ether changes conformation according to the stereochemistry of binding sites along the way. This allows the sequence of stereochemical information programmed into the tape to be read out as a string of digits in a non-destructive manner through a changing circular dichroism response. The concept is exemplified by the reading of molecular tapes with strings of balanced ternary digits ('trits'), $-1, 0, +1$ and $-1, 0, -1$. The small-molecule ratchet is a finite-state automaton: a special case of a Turing machine that moves in one direction through a string-encoded state sequence, giving outputs dependent on the occupied machine state⁸. It opens the way for the reading—and ultimately writing—of information using the powered directional movement of artificial nanomachines along molecular tapes.

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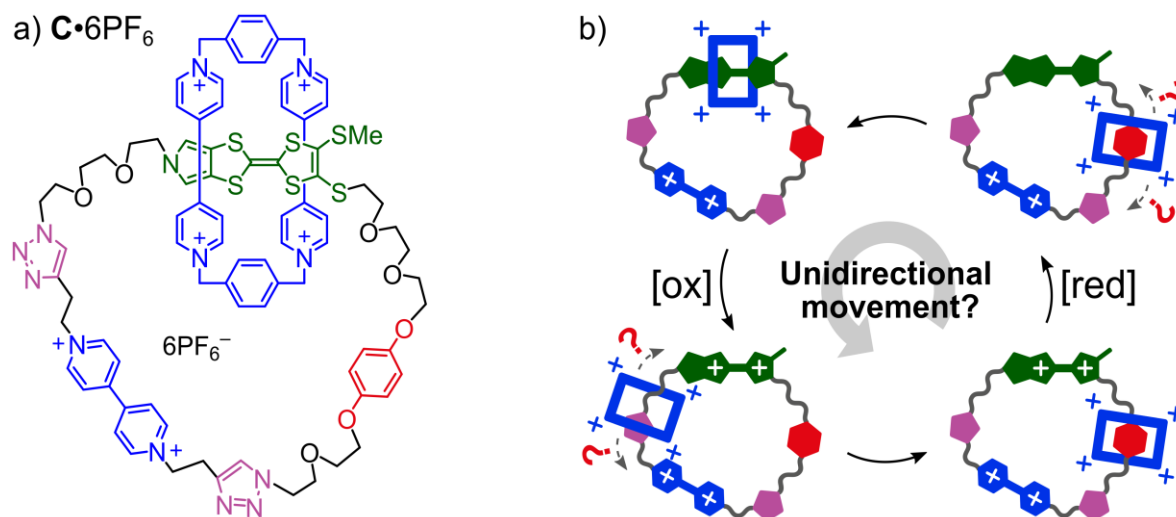
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Abstract No: T41

T41 Towards Unidirectional Rotational Movement in a Redox-Active [2]Catenane

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Caption: Figure 1. a) Structure of the [2]catenane. b) Proposed movement in the [2]catenane upon oxidation and subsequent reduction of the MPTTF unit.

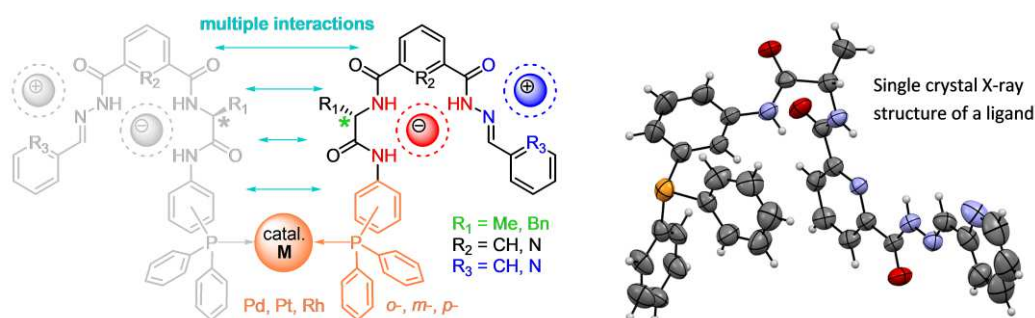
Only recently, the first example of a redox-active [3]catenane molecular motor was reported.¹ Here, we present a possible candidate for a redox-active [2]catenane molecular motor. The [2]catenane C^{6+} (Figure 1a) contains a non-symmetric monopyrrolotetrathiafulvalene (MPTTF, green) unit as the primary station for the cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺, blue macrocycle) ring, a hydroquinone (HQ, red) unit as a secondary station, and a viologen (V^{2+} , blue) electrostatic barrier.² Upon oxidation of the non-symmetric MPTTF station to the MPTTF²⁺ dication (Figure 1b), the tetracationic CBPQT⁴⁺ ring will move away from the oxidized MPTTF station because of Coulombic repulsion. The CBPQT⁴⁺ ring is expected to move over the pyrrole-end (<15 kcal mol⁻¹)³ of the MPTTF²⁺ dication in the counterclockwise direction to encounter the V^{2+} electrostatic barrier rather than directly over the combined thiotriethyleneglycol and thiomethyl (SMe) barrier (>22 kcal mol⁻¹).⁴ To obtain unidirectional movement in the counterclockwise direction, the CBPQT⁴⁺ ring must continue in the counterclockwise direction and move across the V^{2+} dication² to reach the secondary HQ station rather than moving back across the MPTTF²⁺ dication.⁴ Reducing the MPTTF²⁺ dication back to the neutral MPTTF station while CBPQT⁴⁺ encircles the HQ station (Figure 1b), will prompt the CBPQT⁴⁺ ring to return to the primary MPTTF station. This requires CBPQT⁴⁺ to move across either an SMe steric barrier or a V^{2+} electrostatic barrier, where the movement across the SMe steric barrier will result in the desired counterclockwise movement. Preliminary studies on the [2]catenane C^{6+} and model systems have been carried out to elucidate the direction of movement in the [2]catenane.

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Abstract No: T42

T42 Enantioselective Catalysis with Photo-switchable Phosphine Ligand Receptors for Ion-pairs

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Caption: Catalyst design and a ligand X-ray structure.

Artificial supramolecular catalytic systems which permit fine tuning of their catalytic function through various stimuli are of special interest in the field of catalysis,¹ where minute changes in catalyst conformation may significantly impact the e.g. enantioselectivity of a reaction. In this respect, catalysts incorporating molecular machines and switches are investigated,² enabled to facilitate ON/OFF switching of selectivity or activity. One of the more desirable approaches in conducting switching is the use of light irradiation facilitating high spatio-temporal resolution.³ Phosphines are privileged ligands that promote various transition metal catalysed transformations, but their use as photo-switchable ligands is still very limited.⁴ Many asymmetric catalytic transformations incorporate charged intermediates, where ionic interactions can be harvested to induce selectivity. However, incorporating photo-switches into such catalytic systems is scarce up to date, especially with respect to host-guest anion recognition.⁵ A majority of these systems are organo-catalysts, whereas enantioselective transition-metal catalysis facilitating photo-switching and ion-pair recognition has been elusive up to now.

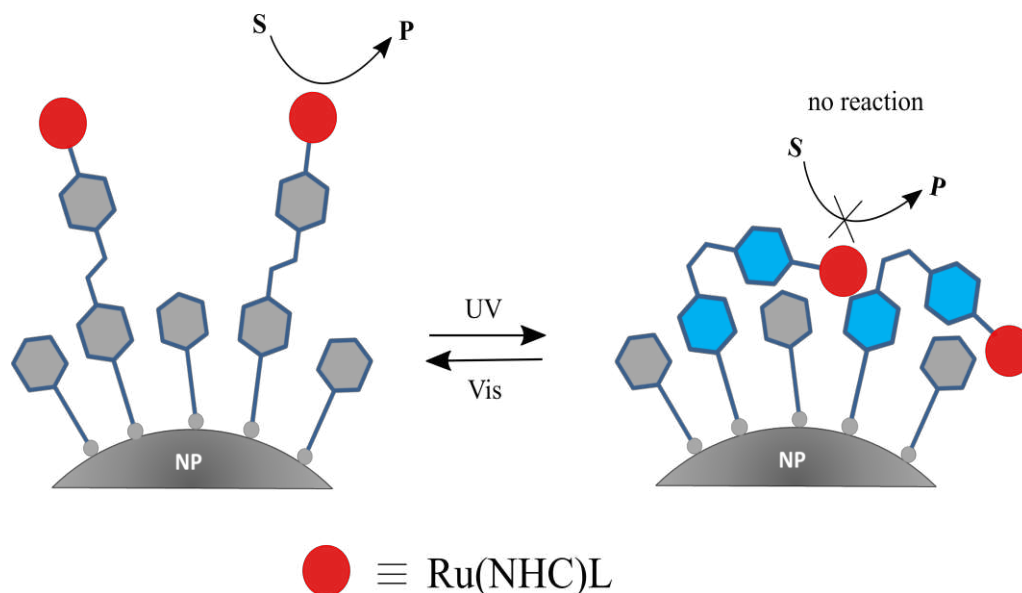
Herein, we report novel supramolecular transition metal catalysts based on acyl-hydrazone photo-switch⁶ and monodentate phosphine ligands. The ligands act as receptors for anions, cations, and ion-pairs, and to form complexes with Pd, Pt, and Rh through the triphenylphosphine moiety. The complexation to transition metals as well the binding of anions, cations, and ion pairs was confirmed by NMR, CD, and UV spectroscopic measurements in different solvents. Deshielding of amide and shielding of aromatic protons peaks in ¹H NMR spectra upon complexation indicated the formation of hydrogen bonding and aromatic stacking interactions. Irradiation by near UV light resulted in the photoswitching between the E- and Z- isomers of both the ligands and the complexes. The ability of complexes to catalyze enantioselective hydrogenation and allylic substitution was tested and the influence of photoswitching and ion binding on the enantioselectivity of the reaction will be reported.

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Abstract No: T43

T43 Improving the OFF State of Photoswitchable Nanocatalysts through Monolayer Design

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Caption: Figure 1. Cartoon representation of the system.

Complete turning off catalytic activity has remained a significant challenge in the field of photoswitchable catalysis.¹ In our recent work, we proposed a new approach that involves burying catalytic centers within an organic monolayer on the surface of gold nanoparticles.² However, the first prototype we developed exhibited residual catalytic activity in the OFF state. To address this issue, we refined our approach by introducing a more bulky organic monolayer.

We synthesized a ruthenium-NHC complex that was attached to the gold surface through an azobenzene linker. The obtained nanocatalyst was employed in ring-closing olefin metathesis. By converting the azobenzene to its *cis*-form, we were able to completely stop the reaction in the presence of bulky coligands. However, with less bulky coligands, the nanoparticles exhibited a slow but sustained catalytic activity.

Interestingly, we observed that for the more constrained monolayer, the switching process was irreversible, while for the less bulky monolayer, the nanoparticles were able to restore their catalytic activity. Our approach represents a significant step towards achieving precise control over catalytic activity in photoswitchable catalysis.

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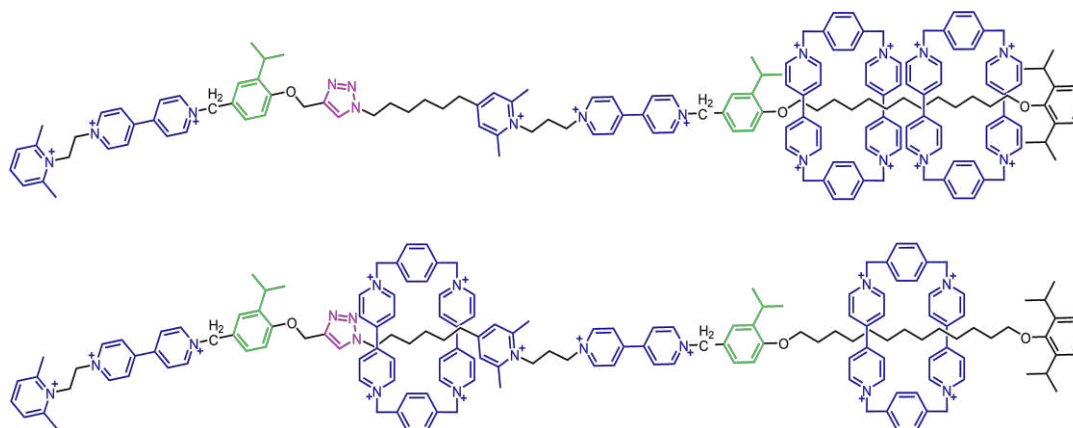
Abstract No: T44

T44 Synthesis of Rotaxane Translational Isomers with Molecular Dual Pump

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Caption: Structural formulae for the possible [3]rotaxane isomers

Recently, a dual artificial molecular pump has been reported¹ for the controlled capture and release of cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺) rings from solution. The presence of an accumulation region between two pumping cassettes provides the opportunity to integrate a terminal collecting chain after the second cassette. A pump with two regions for ring accumulation gives rise to the possibility of translational isomerism in [3]rotaxanes (Figure. 1). This dual pump would then provide a platform for the efficient synthesis and investigation of such [3]rotaxane co-conformational isomers.

The dual pump has been synthesised in good yield and investigations on the synthesis and analysis of the [3]rotaxanes translational will be presented.

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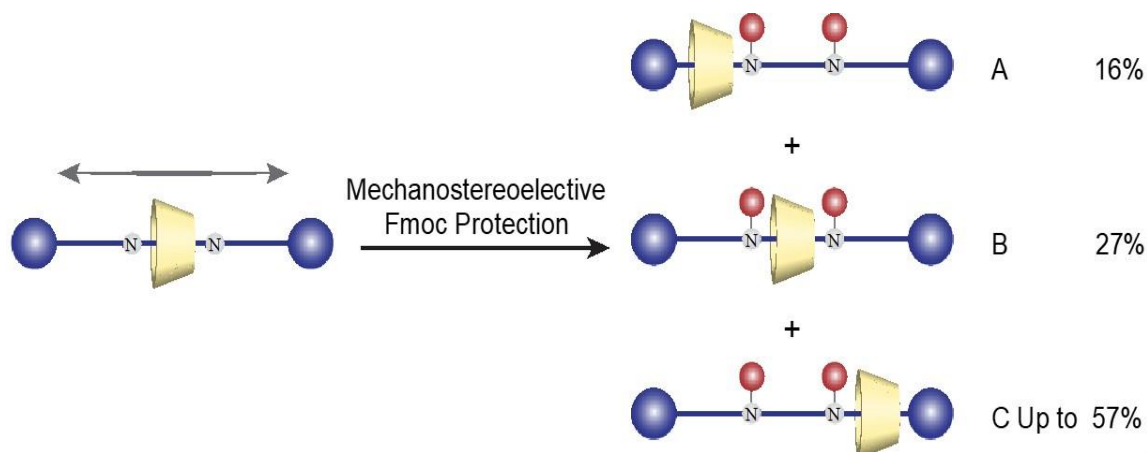
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Abstract No: T45

T45 A molecular information ratchet using a cone shaped macrocycle

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Molecular machines¹, defined as an assembly of a discrete number of molecular components designed to perform mechanical-like movements as a consequence of external stimuli², have drawn attention of the scientific community. Although various examples of small molecular machines have been described³, the regulation of the unidirectional movement remains a challenge.

Information ratchets⁴ are a general class of mechanism in which an energy barrier is regulated on a potential energy surface in order to directionally drive the Brownian particle distribution away from equilibrium. Therefore, creating molecular information ratchet is crucial to reach unidirectional movement of molecular machines. Cyclodextrins⁵ could be good candidates for this system because of their asymmetric cone-like shape and chiral cavity.

Herein, we describe a permethylated cyclodextrin [2] rotaxane which can perform ratcheting motion. The rotaxane is composed of three alkyl spacers separated by two secondary amines as reactive sites that can react with Fmoc derivatives. During the Fmoc-protection a kinetic bias resulting in a non-statistical distribution between the three possible mechano-isomers was observed. This bias can be rationalized by the asymmetry of the CD that favors the reaction when the amine is facing the secondary rim rather than the primary rim. Different factors controlling the ratcheting mechanism, such as solvent and reactivity of the Fmoc derivatives were investigated and the determination of such kinetic bias by Macro simulation and Curtin-Hammett principle will be presented.

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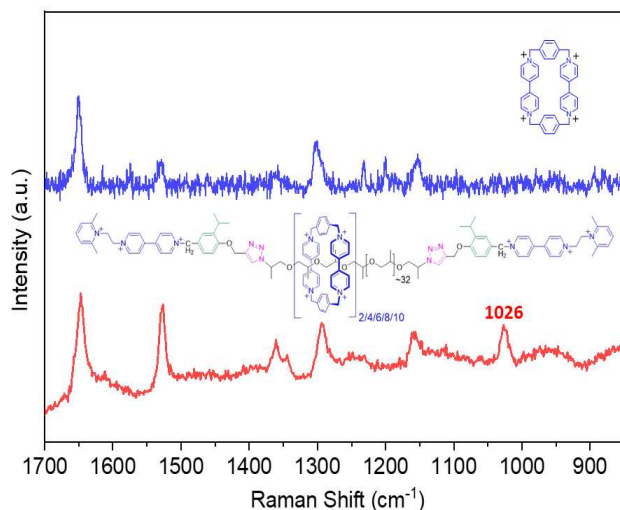
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Abstract No: T46

T46 Chemical and Structural Insights of Non-Equilibrium Poly(propylene glycol) Polyrotaxanes Molecular Pumps

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Caption: Raman spectra of CBPQT⁴⁺ ring (blue) and PPG-CBPQT⁴⁺ polyrotaxanes (red). Counterions are not shown.

Recently, our group addressed¹ the use of molecular pumps to recruit up to 10 cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺) rings from solution and store them threaded on a poly(propylene glycol) (PPG) chain (molecular weight ~2800g/mol). In an effort to determine and analyze the detailed structural and chemical properties of such complex polyrotaxane (PR) structures, we have investigated the system using solid-state Raman spectroscopy and other surface analyzing techniques, such as atomic force microscopy (AFM) and scanning tunneling microscopy (STM). The inclusion of CBPQT⁴⁺ rings into the PPG PRs was found to be responsible for geometric distortion in the CBPQT⁴⁺ rings. The structural properties of CBPQT⁴⁺ rings were investigated by carrying out micro-Raman measurements (Figure)

The geometry of the CBPQT⁴⁺ ring is found to change as the inclusion happens during the pumping process. Raman spectra of PPG-CBPQT⁴⁺ PRs (specifically for 8 and 10 CBPQT⁴⁺ rings) and the individual CBPQT⁴⁺ component all show many peaks in 1700 to 850 cm⁻¹ range. Most of the observed vibrational modes in the PPG-CBPQT⁴⁺ PRs are also found in the Raman spectra of the CBPQT⁴⁺ ring component. A certain shift of 8-10 cm⁻¹ in some of the peaks is also observed which hints toward certain structural adjustments. Furthermore, one notable new peak at 1026 cm⁻¹ is observed only in PPG-CBPQT⁴⁺ PRs. This mode is most likely a motion that becomes more allowed because of symmetry breaking in the CBPQT⁴⁺ ring structure. Additionally, surface characterization techniques such as AFM and STM characterization are ongoing. They could provide an opportunity for direct visualization of these molecular pumps in real space, possibly at the single-molecule level.

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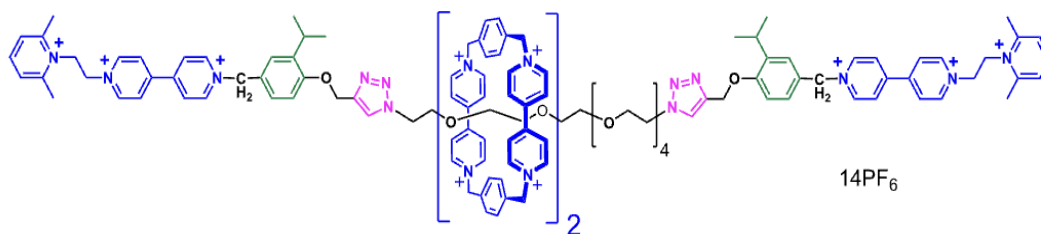
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Abstract No: T47

T47 Crystalline Polyrotaxanes

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Northwestern University, Chicago, United States



Caption: The structural formula of the synthesized oligorotaxane (oligomer chain bearing threaded rings).

A polyrotaxane (PR) is a mechanically interlocked molecule in the shape of a dumbbell with rings encircling the central rod of the dumbbell. The application of artificial molecular pumps (AMPs) for the construction of PRs has allowed precise control over the number of rings threaded onto polymer chains.^{1,2} PRs with cyclobis(paraquat-p-phenylene) (CBPQT⁴⁺) rings threaded on polyethylene glycol¹ (PEG) and polypropylene glycol (PPG) polymer chains, formed using molecular pumps, have been reported.^{1,2} The upper limit of ring threading, however, has still not been verified for these systems. Furthermore, attempts at the crystallization of the molecules have not been mentioned.^{1,2} The aims of this research project are to discover the upper limit of the number of CBPQT⁴⁺ rings that can be pumped onto polymer chains of known number average molecular weight and to investigate whether the resulting highly charge dense PRs can be crystallized.

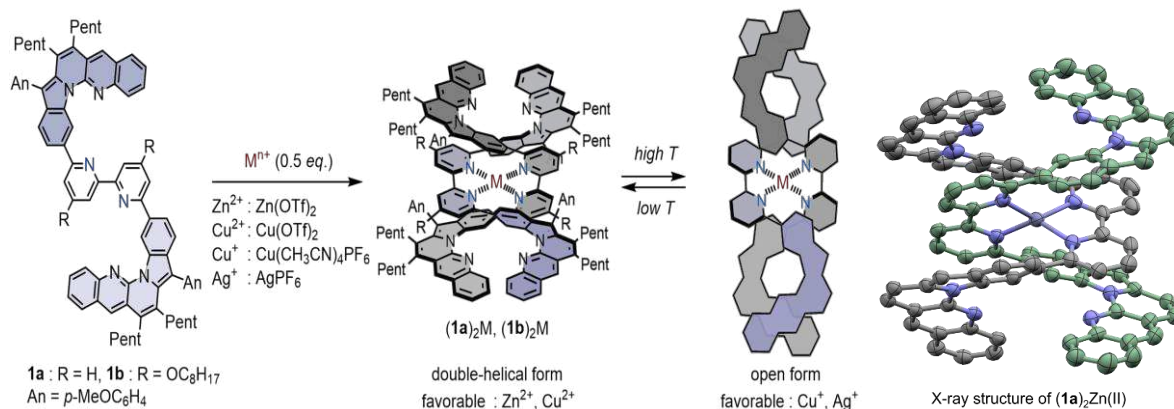
An oligomeric analog of the polyrotaxane system has been synthesized, in which a central oligoethylene glycol chain (6 repeating units) is flanked by two terminally located pumping cassettes. An oligorotaxane bearing two rings has been synthesized by the use of bis(cyclopentadienyl)cobalt(II) as a reducing agent and nitrosonium hexafluorophosphate as an oxidizing agent within an inert N₂ environment. This oligorotaxane already demonstrates the highest ring density on repeating units of ethylene glycol—one ring per three repeat units. The next steps of this project are to attempt ring pumping beyond two rings. With the most ring-dense oligorotaxane, crystallization will be attempted through vapour diffusion with acetonitrile as solvent and di-isopropyl ether as a supersaturating agent. Following these crystallization attempts, maximal ring pumping and subsequent crystallization will be investigated with polymer chains. Examples of crystals of polyether chains are few and far between in the literature. If successful, molecular pumping may allow crystallization of a wide range of polymer chains that have never been captured in crystals before. Long-term, crystallization could introduce unusual electronic properties from such high-order crystals of PRs.

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Abstract No: T48

T48 Temperature and Solvent-Dependent Open-Closed Conformational Switching of Double-helical Monometallofoldamers

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Helical foldamers, which adopt helical conformations through supramolecular interactions, have attracted attention as cooperative supramolecular systems, guest-selective receptors and tunable chiroptical materials due to their chiral and conformational properties. Double-helical structures can also exhibit more complex function through their structural changes. Double-helix complexes have been extensively reported,¹⁻³ however most of them derived from multinuclear complexes and structural switchability is limited in exchange for the stability. In this study, the double-helical mononuclear complexes **(1)₂M** were designed and synthesized, by bridging two L-shaped dibenzopyrrolo[1,2-*a*][1,8]naphthyridine-type^{4,5} foldamers^{6,7} with a metal cation to utilize the structural changes at both ends of the double helix.

The foldamers **1a** and **1b** consisting of two L-shaped skeletons linked by a bipyridine yielded double-helical mononuclear complexes **(1a)₂M** and **(1b)₂M** upon addition of a metal cation. The double-helical structure of **(1a)₂Zn(II)** was confirmed by X-ray analysis, and the bipyridine spacer was stacked between the two L-shaped skeletons. Interestingly, the helix terminals of the “double-helical form” folded by π - π interactions can open into the “open form” in solution. The equilibrium bias could be modulated by the charge of the cations; the “double-helical form” was favored for **(1b)₂Zn(II)**, whereas the “open form” was favored for **(1b)₂Cu(I)** and **(1b)₂Ag(I)**. The structural switching of the double-helical foldamer was demonstrated to be controlled by temperature and solvents. The VT-NMR study revealed an equilibrium between the two forms, the open form was favored at high temperatures, and the double-helical form was favored at low temperatures.

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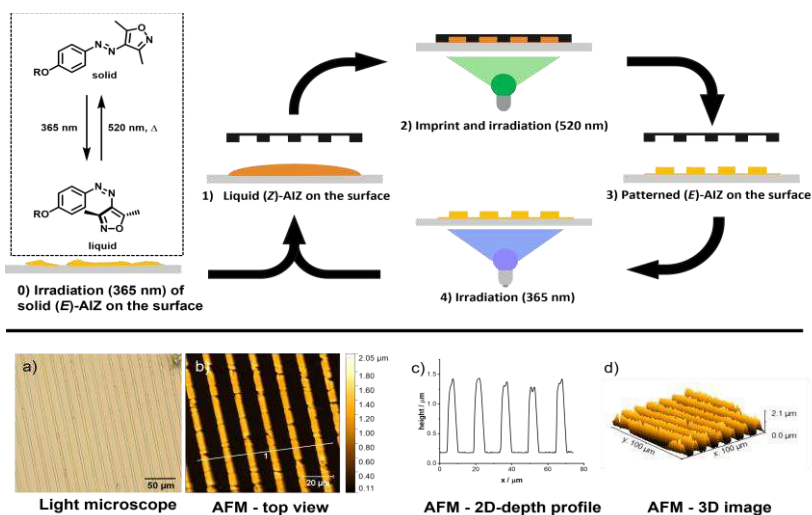
Abstract No: T49

T49 Versatile Surface Patterning with Low Molecular Weight Photoswitches

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Surface patterning of functional materials is a key technology in various fields such as microelectronics, optics and photonics. In micro- and nanofabrication, polymers are frequently employed either as photoreactive or thermoresponsive resists that enable further fabrication steps, or as functional adlayers in electronic and optical devices. However, these patterning techniques usually lack reversibility and do not allow for fine-tuning or reconfiguring the components to be fabricated. Taking advantage of easy-to-synthesize and low molecular weight arylazoisoxazoles, that show robust and highly efficient photoswitching upon irradiation with UV (365 nm) and green light (520 nm), we developed a facile method for imprint lithography (Figure 1). These photoswitches switch more efficiently than azobenzenes with comparable substitution patterns and exhibit rapid and reversible solid-to-liquid phase transition at room temperature upon photo-isomerization. Thus, these photoswitches are highly suitable for surface patterning and functionalization at ambient conditions. We imprinted different patterns with motif sizes of 3 µm over the whole stamp area in a matter of minutes, which could be obtained on glass, but also on non-transparent surfaces such as silicon or gold. UV-light induced liquefaction of the patterned AIZ allowed for multiple write-and-erase cycles with virtually no loss in pattern quality. Beyond the general concept we present two prospective applications: 1) The use as a patterned matrix for different nanoparticles, adding another level of complexity to the material. These composites could be repatterned and stored for several weeks with only minor particle aggregation occurring. 2) The AIZ as an etch resist on gold, enabling to permanently modify surfaces without the risk of being erased.

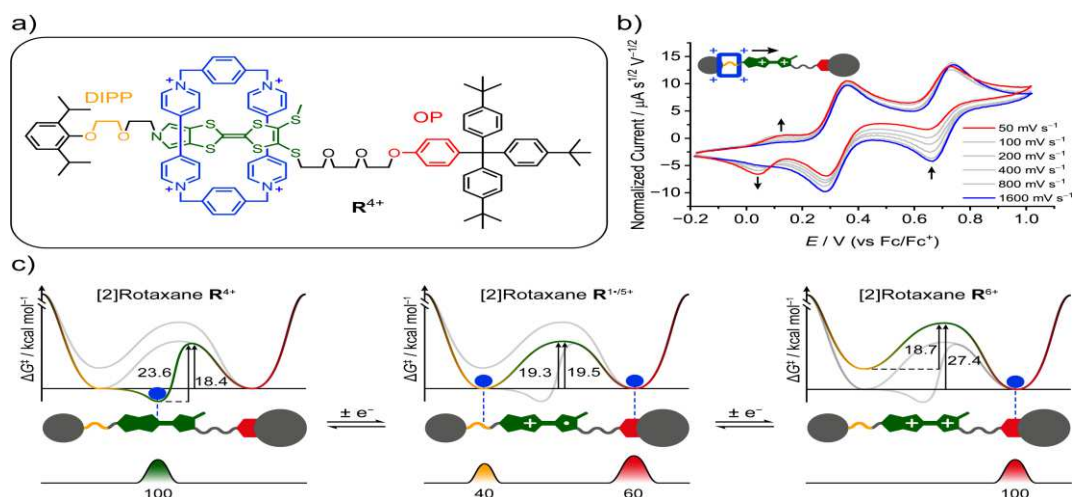
The idea was developed by Prof. Bart Jan Ravoo and the work was carried out under his supervision at the University of Muenster, Germany

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Abstract No: T50

T50 Kinetic Studies of a [2]Rotaxane in Three Different Redox-States using Time-Resolved Electrochemistry

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Caption: Figure 1. a) Structure of the [2]rotaxane. b) Variable scan rate experiment using cyclic voltammetry. c) Energy landscapes of the three redox states.

Mechanically interlocked molecules are multi-component architectures held together by mechanical bonds. Their ability to undergo large amplitude movement of one component along the other as a consequence of external stimuli has inspired scientists to design artificial molecular machines, such as switches and motors. The attractive interaction that exists between the tetracationic macrocycle cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺, blue) and tetrathiafulvalene (TTF) derivatives combined with the unique redox properties of TTF has been used to prepare numerous redox-switchable rotaxanes and catenanes. Recently, we have discovered that the non-symmetric monopyrrolotetrathiafulvalene (MPTTF, green) can be used to induce directional movement of the CBPQT⁴⁺ ring in mechanically interlocked molecules, and simultaneously act as a redox-switchable kinetic barrier,¹ suggesting that the MPTTF unit could be used to control the movement of CBPQT⁴⁺ through a flashing energy ratchet mechanism.

In this study, we investigate the movement of CBPQT⁴⁺ from a high-energy metastable state (i.e., **R**•DIPP^{n+/n+4+}) across all accessible redox states of MPTTF to form the ground state isomer (i.e., **R**•OP^{n+/n+4+}) of the [2]rotaxane **R**⁴⁺ (Figure 1a), to elucidate the hitherto unexplored switching in the radical cation state of MPTTF in **R**^{1•/5+}. To study the movement of CBPQT⁴⁺, the frequently used ¹H NMR kinetic analysis was insufficient, but the difference in the redox profiles of the meta-stable isomer and the ground state isomer enabled time-resolved cyclic voltammetry to be used (Figure 1b). Analysis of the change in isomer distribution as a function of scan rate provided us with quantitative energy landscapes of the three redox states (**R**⁴⁺, **R**^{1•/5+}, and **R**⁶⁺) of the [2]rotaxane (Figure 1c).

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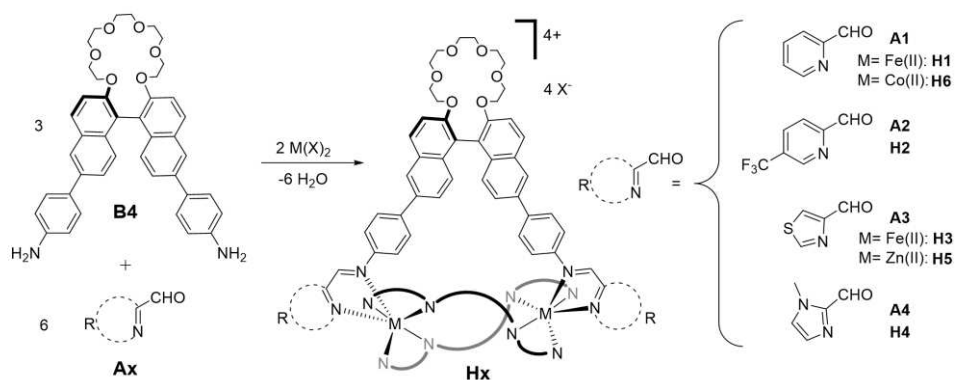
Abstract No: T51

T51 Allosterically controlled metallo-supramolecular spin crossover complexes

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Caption: Overview of the complexes synthesized in this work.

Bistable materials are an exciting area of research as they can be used as molecular switches and in molecular machines. One example can be found in supramolecular spin-crossover (SCO) complexes, which contain metal ions which can exist in two spin states.^[1] The ligands for these SCO capable complexes must hit a sweet spot where both spin states are accessible, resulting in an easily disturbed balance. Small covalent changes can result in a complex which can only exist in one spin state. Minute changes in electronic and geometric structure can have drastic effects, hence, coupling SCO molecules with a secondary switchable unit, such as an allosterically controlled switch, opens the potential for a double action switch in which four discrete states are accessible in just one (supra-)molecule.^[2]

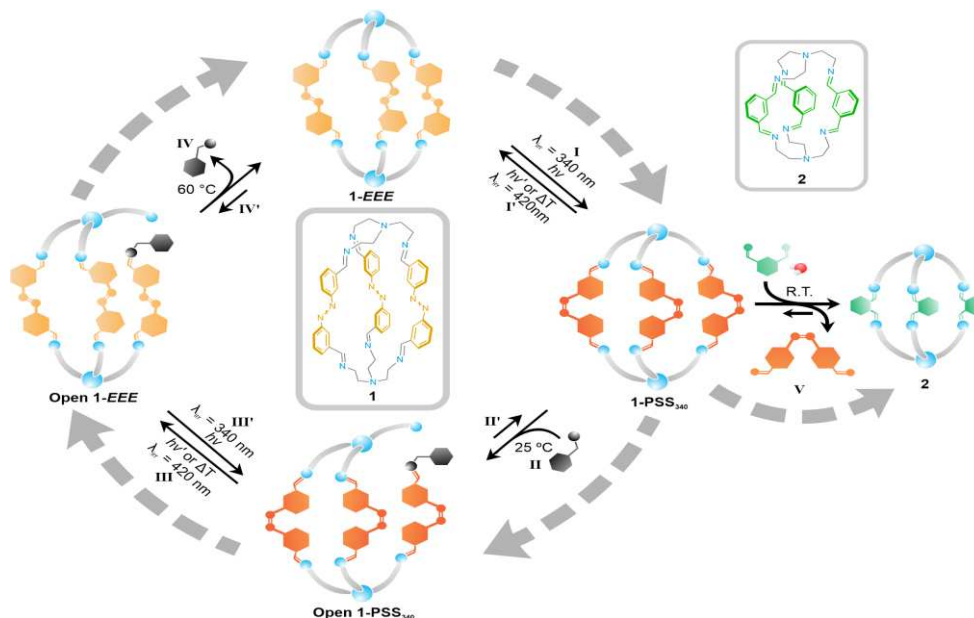
Inspired by a previously published^[3] homochiral binaphthyl scaffold, a series of $Fe^{II}L_3$ helicates **H1–H4** with crown-ethers embedded in their ligand scaffolds was synthesized and their spin-crossover and host-guest properties were investigated.

The ligand was designed in such a way that conformational changes of the binaphthyl units caused by a binding event to the crown ether change their torsion angle directly disturbs the coordination geometry of the iron cations. Indeed, addition of alkali metal cations to complex **H3** resulted in an 18 °C change in the SCO temperature.

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T52 Light-Fueled Transformations of a Dynamic Cage-Based Molecular System

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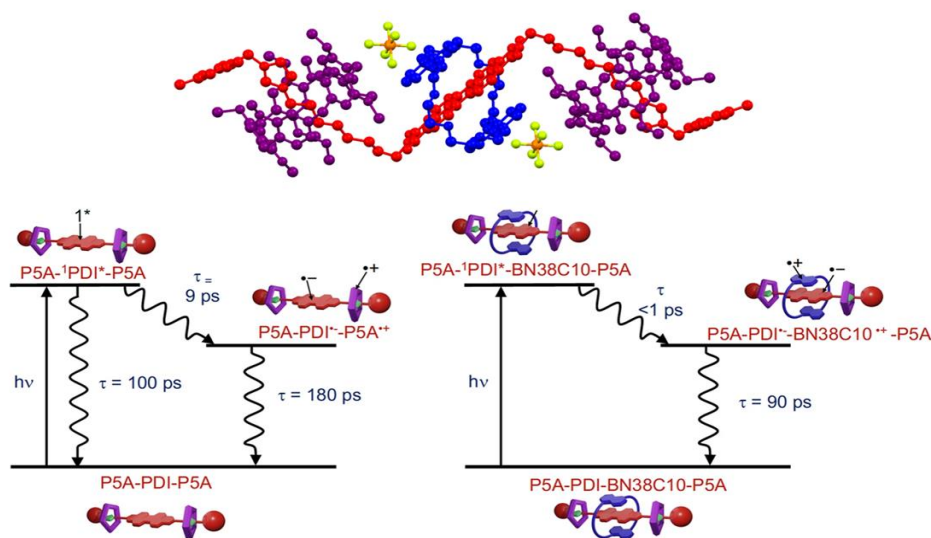
Caption: Figure 1. Light-induced transformations of 1

In a chemical equilibrium, the formation of high-energy species – in a closed system – is inefficient due to microscopic reversibility.^{1,2} Here, we demonstrate how this restriction can be circumvented by coupling a dynamic imine equilibrium to a light-induced *E/Z* isomerization of a tris-azobenzene imine macrobicyclic cage **1**.³ The self-assembled all-*E*-cage (**1-EEE**) is highly stable and resists intermolecular nucleophile-imine exchange reactions that would break the macrocycles, thus “opening” the constrained structure. Upon photoswitching (Step I, figure 1), a mixture (**1-PSS₃₄₀**) containing 95% of the switched isomers (**1-ZZZ**, **1-ZZE**, and **1-ZEE**) is generated. The isomerization process in the constrained molecular architecture results in induced strain in the macrocycles that conform the cage, turning them into highly unstable species compared with the self-assembled and not switched **1-EEE** isomer. These strained isomers react with a nucleophile (step II, figure 1), thus allowing the breaking of the macrocycle or “opening” of the cage (**Open 1**). Subsequent (photo)isomerization (Step III, figure 1) of the azobenzenes present in the different species in the mixture. This results in an out-of-equilibrium state that favors the regeneration of **1-EEE** (step IV, figure 1). We then used this principle to perform a light-induced cage-to-cage transformation adding a competing ditopic aldehyde instead of a competing nucleophile.

We envision that this operational principle for caged-based molecular machines will be a valuable tool for sophisticated manipulations of self-assembled molecular architectures based on dynamic chemistry. These dynamic and responsive materials can be used to promote energetically demanding transformation of constrained dynamic compounds in a controlled and reversible manner. For example, the cage opening/closing cycle explored here might be a valuable tool to avoid product inhibition in cage catalysis, control uptake and release of nucleophiles with light, drug release and modulate transient dissipative self-assemblies with high spatiotemporal control.

Abstract No: T53

T53 Macrocycle Selective Charge Transfer in Rotaxanes

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Caption: Top: Electron diffraction crystal structure of a hetero[4]rotaxane. Bottom: experimental charge separation pathways in related [3] and [4]rotaxanes

Mechanically interlocked dyad molecules consisting of electron rich macrocycles and electron deficient axles offer an exciting avenue to examine photoinduced charge transfer processes across the mechanical bond. We have studied two related rotaxanes: a homo[3]rotaxane, **PDI-(P5A)₂** consisting of a perylene diimide (PDI) axle whose ends are threaded through two pillar[5]arene (P5A) macrocycles and a hetero[4]rotaxane, **PDI-BN38C10-(P5A)₂** that contains an additional bis(naphtho) crown ether (BN38C10) that encircles the PDI core.

The structure of this heterorotaxane was elucidated using electron diffraction crystallography and represents one of the only solid state structures of such a complex molecule. This structure was also the first to be published from a commercial electron diffractometer, demonstrating the value of this technique.

Electrochemical characterization including cyclic voltammetry, spectroelectrochemistry and electron paramagnetic resonance spectroscopy established the redox behavior of these rotaxanes which was used to support photophysical studies into their excited state properties. Time-resolved infra-red and transient absorption spectroscopies reveal that photoinduced host-to-guest charge separation occurs for both molecules, but invokes a different macrocyclic donor in each case. Electron transfer in the homorotaxane occurs between one of the P5A components and the PDI, breaking the molecular symmetry. A kinetically distinct electron transfer pathway involves only the BN38C10 host in the case of the heterorotaxane, showing that photoinduced charge transfer processes within rotaxanes can be controlled by the organization of components within the structure.

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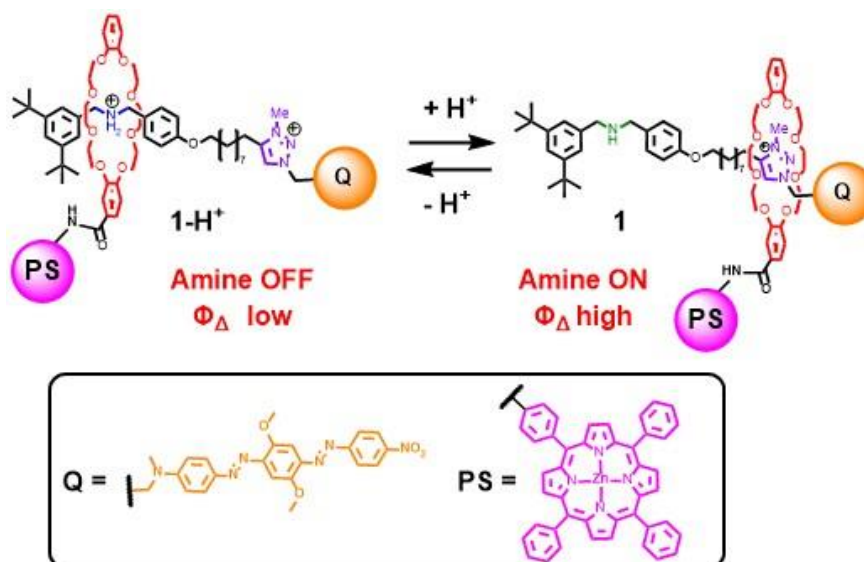
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Abstract No: T54

T54 Switchable [2]rotaxanes for pH-responsive generation of singlet oxygen

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Caption: Structure of a pH-switchable [2]rotaxane with dual catalytic switchability.

The photochemical generation of singlet oxygen offers applications in synthetic chemistry and in therapy (for example photodynamic therapy, PDT). Controlling the generation of singlet oxygen is important for selectivity in both of these fields, to avoid unwanted side reactions like overoxidation in synthesis or sensitivity towards sunlight during PDT.¹

Exploiting the special features of the mechanical bond, for example for the construction of switchable systems, is a novel strategy for improving and tuning the action of medically active compounds² and catalysts.³ Utilizing this approach, we propose the incorporation of a Photosensitizer (PS) and a Quencher (Q) into the structure of a bistable [2]rotaxane (see Figure).⁴ This enables the stimuli responsive control by controlling the distance between PS and Q. Unexpectedly, we found that singlet oxygen production in rotaxane **1-H⁺** was turned off (singlet oxygen quantum yield $\Phi_{\Delta} < 1\%$), while it could be turned back on by deprotonation of the ammonium-station to give **1** ($\Phi_{\Delta} = 6\%$). Control systems showed that this behavior is truly an effect of the location of the macrocycle on the different binding stations on the axle. Time-resolved spectroscopy showed significant shortening of singlet lifetimes in **1**, suggesting energy transfer from the S₁ state of the porphyrin to the quencher.

Furthermore, the controlled position of the macrocycle can reveal or block the availability of the secondary amine for taking part in enamine-catalyzed processes.⁵ Applications of switchable rotaxanes with parallel (shown here) or orthogonal switchability of amine and singlet oxygen production for catalysis are currently under investigation.

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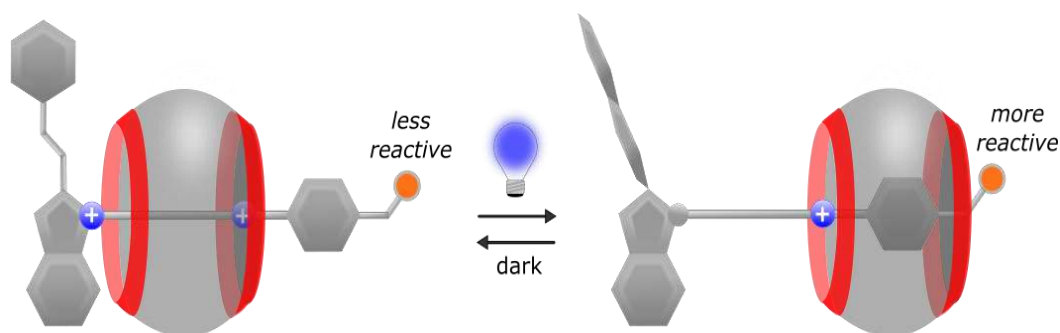
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Abstract No: T55

T55 Photoswitchable Pseudorotaxane for Controlling Reaction Rate and Selectivity

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Caption: General representation of the system

Competitive inhibition is a widely used mechanism for regulating catalytic reactions that requires an excess of either substrate or catalyst to be overcome.¹ Herein we present a system that operates outside of this paradigm.² We demonstrate that a single molecule, comprising a photoswitch linked to a substrate, can impede an increase in the reaction rate despite an increase in the amount of catalyst. After the deactivation of the inhibitor by light, the reaction accelerates until the reaction site becomes saturated with the catalyst. The resulting pseudorotaxane can control not only self-reaction but also the outcome of external reactions. When exposed to light, the pseudorotaxane shifts the chemical equilibrium, leading to a change in the final product ratio. Our results pave the way for the development of more advanced systems with remote control.

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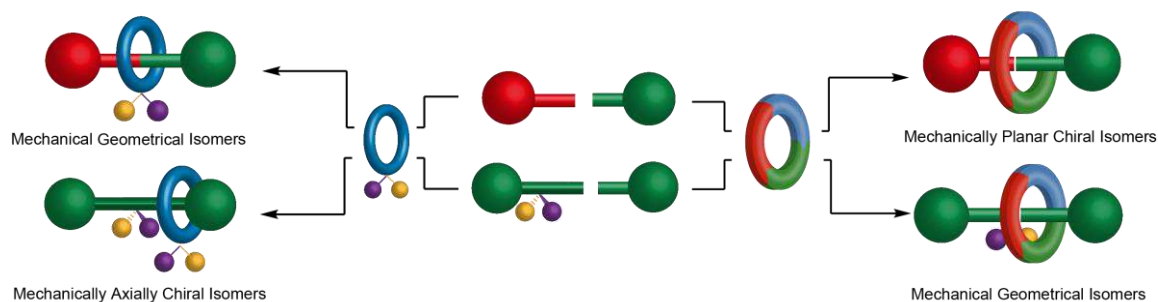
Abstract No: T56

T56 Controlling Mechanical Geometrical Isomerism in Rotaxanes

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The orientation of a macrocycle with distinct faces on the axle of a rotaxane can give rise to previously recognized mechanical geometrical and mechanically axial chiral stereoisomers¹, while “oriented” macrocycles can give rise to mechanically planar chiral² and “non-canonical” geometric stereoisomers. Of all these, only mechanically planar chiral systems have been studied significantly.³ Recently, our group reported the first stereoselective synthesis of a mechanically axially chiral catenane and the rotaxane analogue.⁴ Here we reported a study of the factors that controls the selectivity of mechanical geometric isomers and the first direct enantioselective synthesis of a mechanically axially chiral rotaxane.⁵

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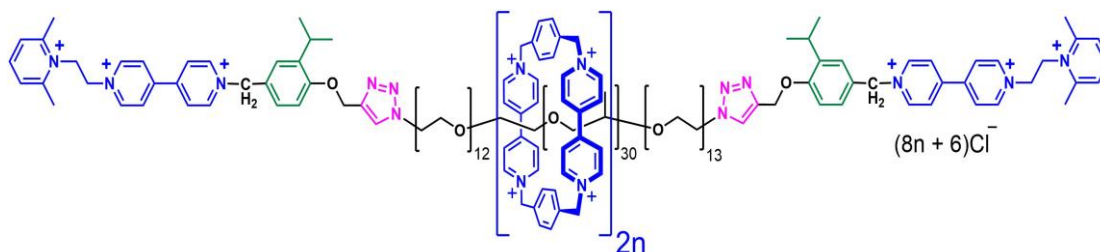
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Abstract No: T57

T57 Molecular Pumps Operating on Block Copolymers

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Caption: Structural formula of the synthesized triblock copolymer polyrotaxanes

Recently, we reported^{1,2} the use of molecular pumps to recruit up to 10 cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺) rings from solution and store them threaded on PEG or PPG chains. The ability to pump rings onto both hydrophilic (PEG) and hydrophobic (PPG) chains now provides an opportunity to operate rotaxane-forming molecular pumps in soft matter systems. The ability of triblock copolymers of polyethylene glycol (PEG) and polypropylene glycol (PPG) to form polymeric micelles is well-known in the literature³. In the present project, we aim to combine these well-studied collecting chains by pumping CBPQT⁴⁺ rings onto triblock copolymers in order to: (1) investigate the localization of rings on the chain of segmented constitution and (2) attempt to pump rings from solution into polymeric micelles.

Triblock copolymers (PEG-PPG-PEG) bearing terminal molecular pumps have been synthesized. The pumping of pairs of rings onto the polymer backbones by electrosynthesis has been achieved. Variable temperature NMR spectroscopic studies in D₂O indicate that there may be a temperature-dependent localization of CBPQT⁴⁺ rings on certain segments of the chain. The formulation of aqueous polymeric micelles bearing the molecular pumps on their surfaces is ongoing.

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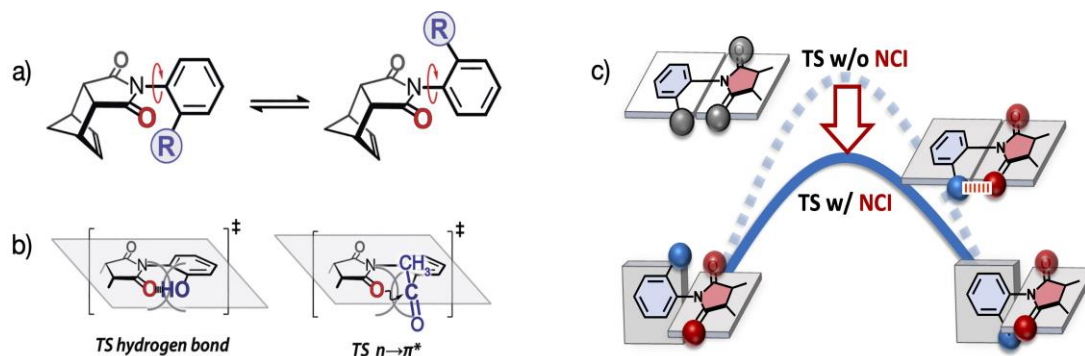
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Abstract No: T58

T58 Molecular Rotors: A new platform to measure and study non-covalent interactions

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Caption: Schematic representation of the a) molecular rotors, b) intramolecular TS interactions, and c) kinetic effects on the rotational barriers

Non-covalent interactions have been identified as a key factor in the catalytic abilities of enzymes and synthetic catalysts by stabilizing transition states. However, most studies of non-covalent interactions have focused on their thermodynamic effects such as in self-assembly and folding. Few methods have been developed to study the kinetic effects of non-covalent interactions. Therefore, we have developed a versatile molecular rotor platform to measure the ability of non-covalent interactions to stabilize transition states. The rotors form the non-covalent interactions of interest in the bond rotation transition states. Therefore, the stabilizing effects can be assessed by the changes in rotational barrier. A wide range of non-covalent interactions have been types of non-covalent interactions, including hydrogen bonding, $n \rightarrow \pi^*$, chalcogen bonding, lone pair-lone pair, and electrostatic interactions. The rotational barriers were measured using dynamic NMR methods such as EXSY and line shape analyses. The results showed that moderate strength non-covalent interactions, such as neutral hydrogen bonds and $n \rightarrow \pi^*$ interactions, could stabilize transition states by 4-10 kcal/mol. Molecular modeling was used to study the structures and geometries of the non-covalent interactions and energy decomposition analysis provided insight into their effects on the transition states.

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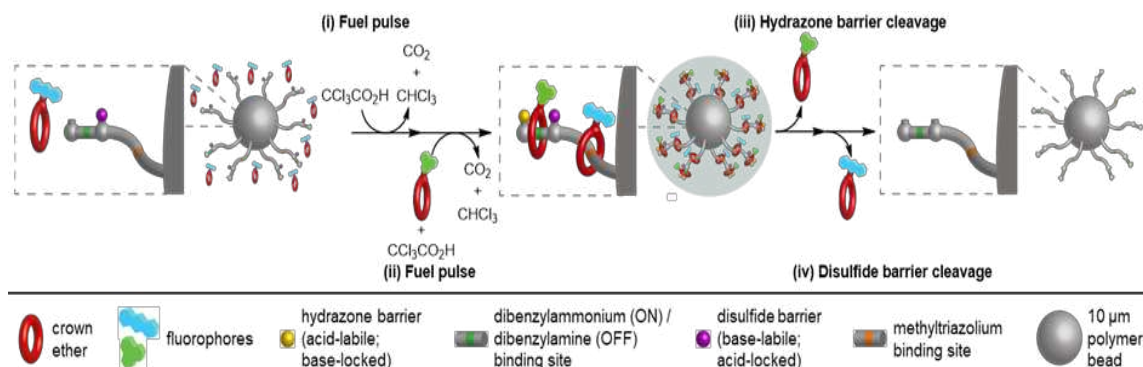
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Abstract No: T59

T59 Pumping Between Phases Using a Pulsed-Fuel Molecular Ratchet

David Leigh Dean Thomas, Daniel Tetlow, Yansong Ren, Salma Kassem, Ulvi Karaca

University of Manchester, Manchester, United Kingdom



Caption: Pumping from solution to the solvent-accessible sites of polymer beads with a pulsed chemical fuel.

We report on molecular pumps immobilised on polymer beads that use an energy ratchet mechanism to directionally transport substrates from solution onto the beads.

Upon addition of trichloroacetic acid ($\text{CCl}_3\text{CO}_2\text{H}$) fuel, micrometre-diameter polystyrene beads functionalised with solvent-accessible molecular pumps sequester from solution crown ethers appended with fluorescent tags. Following fuel consumption, the rings are mechanically trapped in a higher energy, out-of-equilibrium, state on the beads and cannot be removed by dilution or exhaustive washing. This differs from dissipative assembled materials, which require a continuous supply of energy to persist, and conventional host-guest complexes.

Addition of a second fuel pulse causes the uptake of more macrocycles, driving the system further away from equilibrium. The second macrocycle can be labelled with a different fluorescent tag, conferring sequence information on the absorbed structure. The polymer-bound substrates can be released back to the bulk either one compartment at a time or all at once.

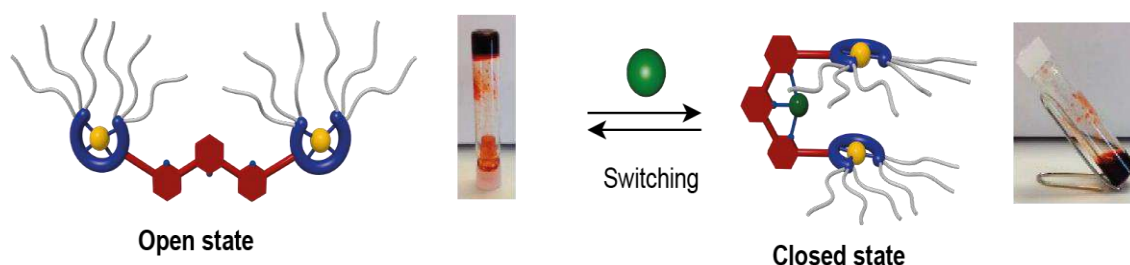
Non-equilibrium sorption by immobilised artificial molecular machines enables the transduction of energy from chemical fuels for the storage and release of energy and information.

Abstract No: T60

T60 Switchable molecular tweezers for stimuli-responsive organogels

Guillaume Vives Pablo Msellem, Geoffrey Gros Lambert, Clément Guibert

Sorbonne Université, Paris, France



In recent years, molecular machines^[1] have attracted increasing interest for their ability to control motion at the molecular level. However, artificial systems are far from approaching the complexity of natural systems and exploiting their inherent properties to perform useful functions remains a major challenge. We are interested in harnessing the mechanical motion of molecular switches as an innovative approach to control physical or chemical properties at the molecular level.

We have developed a versatile family of switchable molecular tweezers based on a terpyridine ligand functionalized by metal-salen complexes. By switching the conformation of the terpyridine moiety using a coordination stimulus, the distance between the two functional salen complexes can be controlled. Drastic modulation of luminescence,^[2] magnetic^[3] or even catalytic^[4] properties has been achieved using Pt(II), Cu(II) and Zn(II) salen moieties, respectively. A remarkable six-level system was also achieved by combining the ion-triggered mechanical motion with the redox activity of Ni(II)-salen complexes.^[5] Our current work focuses on utilizing the mechanical motion of tweezers functionalized with alkyl chains as gelling groups for the development of multi-functional switchable organogels. The large structural reorganization driven by the mechanical motion results in reversible sol-gel transitions.^[6] The synthesis and characterization of the reversible gelation of such systems will be highlighted.

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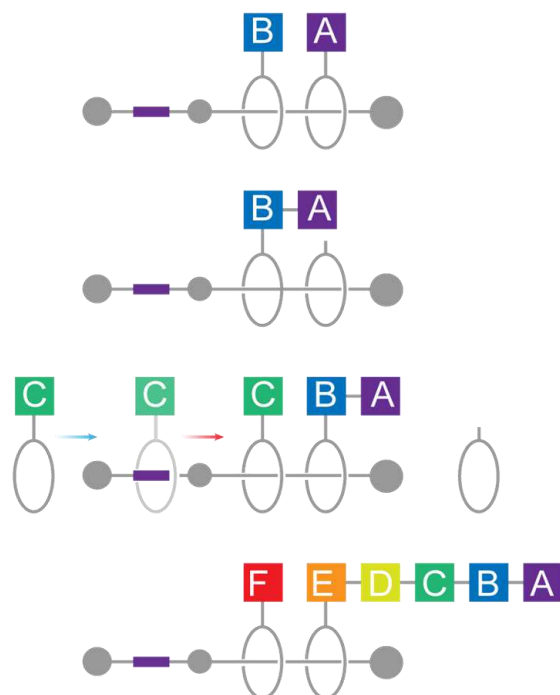
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Abstract No: T61

T61 Artificial Molecular Machines: A Path to Sequence-Defined Polymer Synthesis

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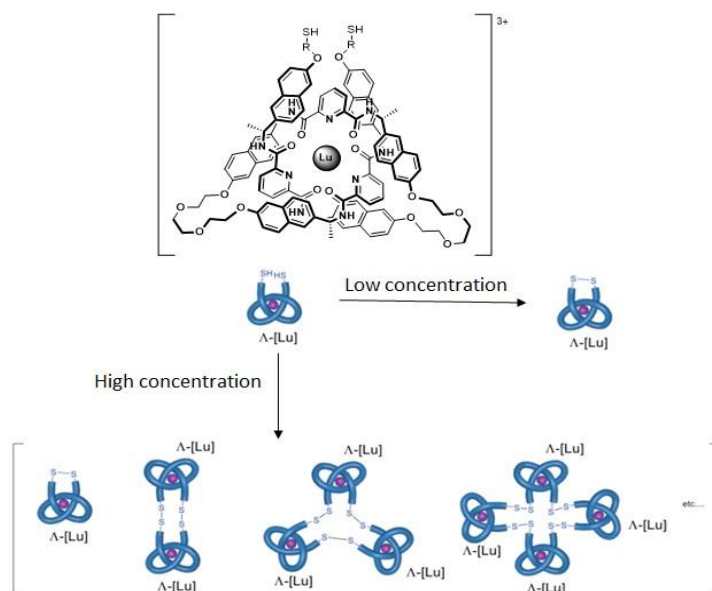


Caption: Artificial molecular pump enabled sequence-defined polymer synthesis

Learning from nature about how to design and use molecular machines to perform specific synthesis has the potential to revolutionize the whole approach to functional-molecule and materials design.¹ Among the most complex of all biomolecular machines, the ribosomes² lie at the heart of protein synthesis. The ribosomes use the sequence information contained in messenger RNA (mRNA) to assemble a functional protein. Taking inspiration from these powerful biomachines, our aim is to develop synthetic machines that can mimic their behavior and functionality. One approach to realizing this goal is through the use of artificial molecular pumps³. Here, we report the design, synthesis, and operation of an artificial molecular pump based on a rotaxane, in which a dumbbell is designed to hold a maximum of two positively charged rings. Sustainable unidirectional pumping process has been demonstrated. The small rings can be designed as cargos to assist intramolecular reactions that happen inside the rotaxanes. Further, implementation of this strategy will be able to achieve sequence-defined polymer synthesis.

Abstract No: T62

T62 Forming a dynamic library of molecular composite knots

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The use of dynamic combinatorial chemistry (DCC) has allowed to gain chemists access to large dynamic libraries of compounds, resulting from the different combinations of the individual components.¹ In dynamic covalent chemistry, reversible bonds such as imine, hydrazone and disulfide bonds, form and break until reaching thermodynamic product. The reversible character of these reactions promotes exchange between the components and can be used to produce complex architectures. Indeed, topologically complex structures are hardly accessible using the traditional static covalent method. Nevertheless, DCC has been exploited by numerous groups to access such complex molecules, such as, Hopf and Solomon links as well as trefoil and figure of eight knots.²

The synthesis of composite knots, which are defined as ring opened prime knots that are covalently joined together, is still a challenge due to their inherent complexity. An overhand trefoil knot has previously been synthesised by our group through lanthanide metal template strategy and has been used so far to prepare composite square, granny and triskelion knots.² A ligand consisting of three pyridine dicarboxylate units wraps around a lanthanide ion to form a pseudo trefoil knot which can be closed by either ring close metathesis or click chemistry (or both) to form a purely organic knot after removal of the templating metal ion.

Here, we aim to use a pseudo trefoil knot building block and adapt it for use with DCC to hopefully again gain access to various higher order composite knots (Figure 1). Instead of alkenes pendant chains, thiol appendages have been utilised. The ligand was synthesised and various thiol connectors have been investigated. Differences in rigidity and bond angles in the chains bearing the thiol might lead to different architectures. Various conditions (temperature, concentration, oxidising agent) were tested. The size (ie. number of trefoil knots) of the resulting structures produced by DCC were analysed by mass spectrometry and DOSY NMR.

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Abstract No: T63

T63 Exploring functionalization of silicon oxide microchips for photodynamic therapy applications

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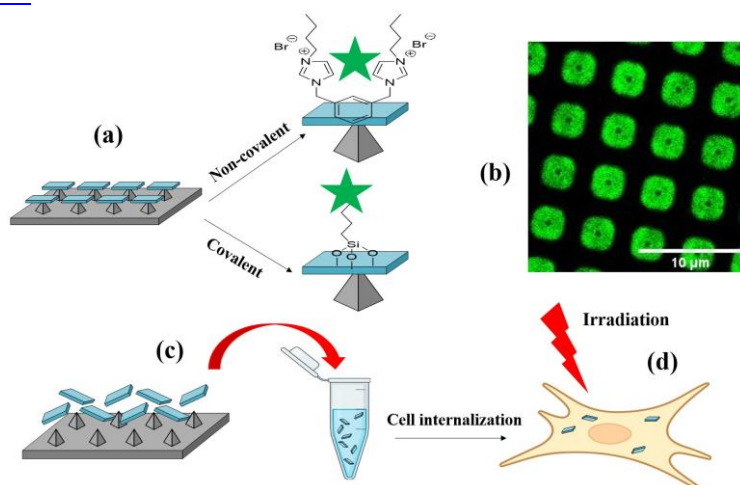
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Caption: Fig a) Scheme and b) fluorescence microscope image of functionalized SiO₂ microchips. (c) Releasing microchips and (d) photodynamic experiment

Photodynamic therapy, which uses photosensitizers (PS) to trigger the production of reactive oxygen species upon irradiation, is an advantageous cancer treatment strategy.¹ Conjugation of PS to suspended chips can overcome the low drugability of some PS. In this context, one of our aims is to explore the non-covalent and covalent functionalization of silicon oxide microchips^{2,3} for photo-induced cell death. Fluorescent PS -such as porphyrins or BODIPY derivatives- were either conjugated or supramolecularly encapsulated using an imidazolium-gemini amphiphile.

PS- functionalized microchips were finally released in suspension from the wafer by using a mounting medium and characterized by confocal microscopy. The cell-internalization of functionalized microchips and photodynamic experiments were also investigated in HeLa and Raw 264.7 cell lines.

Acknowledgment: Project PID2020-115663GB-C3 was funded by MCIN/AEI/10.13039/501100011033. We also thank AGAUR (Generalitat de Catalunya) for a grant to consolidated research groups 2021 SGR 01085. S. B. thanks Generalitat de Catalunya for a predoctoral FIDUR scholarship.

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Abstract No: T64

T64 STM Investigations of Bicyclopentane Monolayers Entering the Third Dimension

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Different bicyclopentanes of varying architectures with regard to the aromatic backbone have been synthesized. Within these architectures, different central units are present. Attached trihexadecyloxybenzyloxy groups and other alkyl groups on each species enhance not only solubility but result in the capability to form highly crystalline self-assembled monolayers (SAMs) on the surface of highly-oriented pyrolytic graphite (HOPG). These SAMs are investigated via in-situ scanning tunneling microscopy (STM) at the solid/liquid interface of HOPG and a solution of the respective compound in 1-phenyloctane. Insights from sub-molecularly resolved STM images reveal the impact of the footprint of the different molecular backbones on the overall surface pattern. The central units are observable as three-dimensional pillars perpendicular to the surface and are the starting point for a variety of potential functionalizations in a modular approach.

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Abstract No: T65

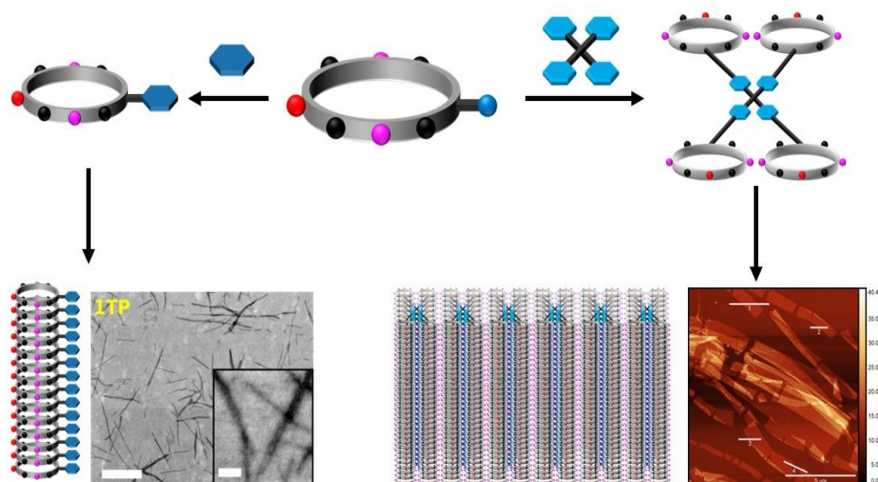
T65 Modulating Cyclic Peptide assemblies by side-chain functionalization.

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Caption: Scheme 1. Peptide side chain modification that rises two different structures.

Cyclic peptides (CPs) formed by an even number of alternating D-,L-amino acids (aa) have programmed propensity to self-assemble into nanotubes (1). The control of their internal and external properties by modification of the aa side chains have paved the way to a gamut of different structures and applications (2). Recently, their hierarchical assembly into soft materials such as hydrogels (3,4) and nanosheets (5) has been explored.

Herein we will show that D,L-CPs scaffolds can be efficiently tuned by anchoring a range of aromatic aldehydes. Those key modifications impact the nanotube assembly and organization, and in those cases where hydrogels are formed they influence the viscoelastic behavior.

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T66 Self-assembly of phthalocyanines into J-dimers

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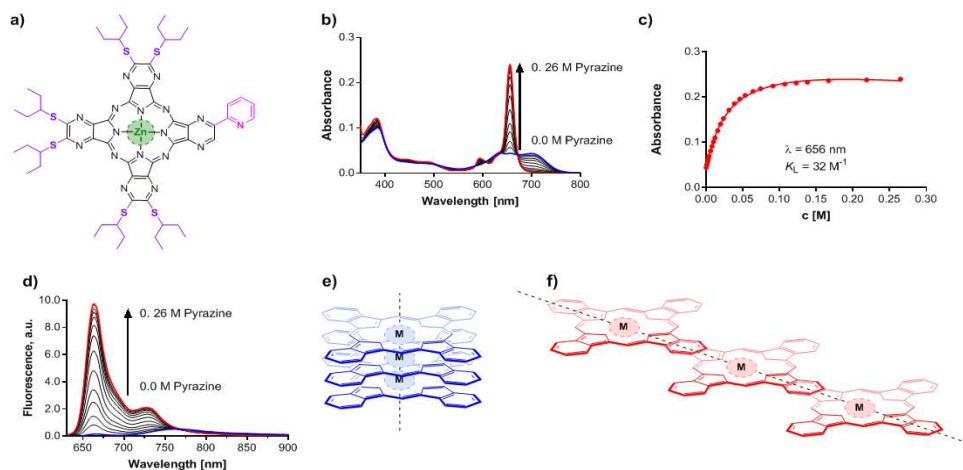


Fig. 1 Synthesized unsymmetrical zinc(II) Pc (a) containing pentan-3-ylthio substituents and pyridine as coordinating moiety - (b) absorption spectrum during titration with pyrazine (dimer and monomer), (c) plot of the spectral changes of monomer absorbance against ligand concentration, (d) changes of emission spectrum during titrations (dimer and monomer), (e) H-aggregate, (f) J-aggregate

Phthalocyanines (Pcs) are synthetic macrocyclic dyes formed by four isoindoline units connected by azomethine bridges, structurally close to porphyrins. Due to their extended 18 π -conjugated system, they show unique photophysical properties and they have been largely investigated in various fields such as fluorescence sensors or photosensitizers in photodynamic therapy (PDT).¹

However, these properties are related mostly to monomeric form of the Pcs only. Aggregation of the Pcs is usually unfavorable phenomenon which plays major role in final photophysical properties. The planar Pc core tends to aggregate due to π - π stacking interactions leading to formation of supramolecular structures. The most common, H-type aggregates (Figure 1e) align molecules into sandwich-like arrangement that results in increased absorption at blue-shifted wavelengths and strongly decreased fluorescence emission and singlet oxygen production. However, J-aggregates (Figure 1f) give rise to red-shifted absorption bands, and they retain fluorescent properties as well as singlet oxygen production.²

In this work, we synthesized unsymmetrical Pc derivatives containing one ligand (coordinating moiety, e.g., pyridyl) that formed slipped J-dimers upon coordination to the central cation of the second Pc molecule in non-coordinating solvents. Absorption, emission and NMR spectra unequivocally confirmed formation of J-dimers. Dissociation into monomers was studied using the previous methods after titration with competing ligand, e.g., pyrazine, and association constants were determined.

This study was supported by Czech Science Foundation (project No.23-06177S).

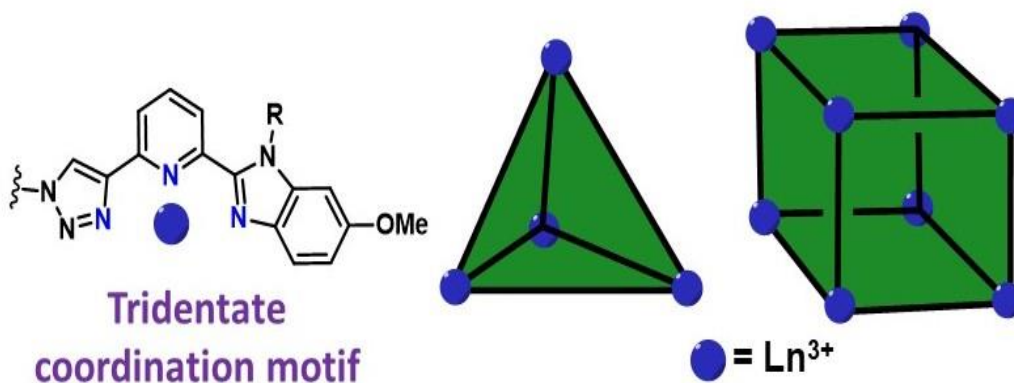
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Abstract No: T67

T67 Geometric adventures with self-assembled LnIII-coordination architectures

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Designing supramolecular architectures with unusual geometries embedded with useful functional motifs is of immense importance. Self-assembly is one of the most sophisticated techniques of combining simple molecular units together into hierarchically more complex architectures. Among all synthetic self-assembly approaches, metal coordination-driven self-assembly has emerged as a potent tool for developing a suite of 2D and 3D coordination architectures.¹ This approach is graced with many synthetic advantages including the reversible nature of bond formation, the ability for one-pot synthesis, and the high yields typically obtained. The geometries of several supramolecular assemblies are inherently divergent due to the versatility of available organic linkers and orientation of the coordination vectors.²

These metal-organic self-assemblies (MOS) are typically constructed from transition metal ions, where the sole function of the metal ions is to serve as the connection node holding the structure together.³ Due to the challenges associated with high and unpredictable coordination numbers, high lability of metal-ligand bonds, and the lower degree of covalent bonding making coordination geometries far more flexible, research on lanthanide-based MOSs still lags far behind that of transition metals. However, the wealth of unique photophysical and magnetic properties of lanthanide ions make this area worthy of study.⁴

In this poster, I will present a new tridentate coordination motif incorporating a 1,2,3-triazole. The motif has the advantage of facile construction through the 'click' Huisgen azide-alkyne cycloaddition reaction, in addition to a modular synthesis that can be readily modified to incorporate substituent groups at various positions on the ligand. This poster will discuss the coordination complexes constructed from this motif, from mononuclear complexes to complex and unusual helical and tetrahedral architectures.

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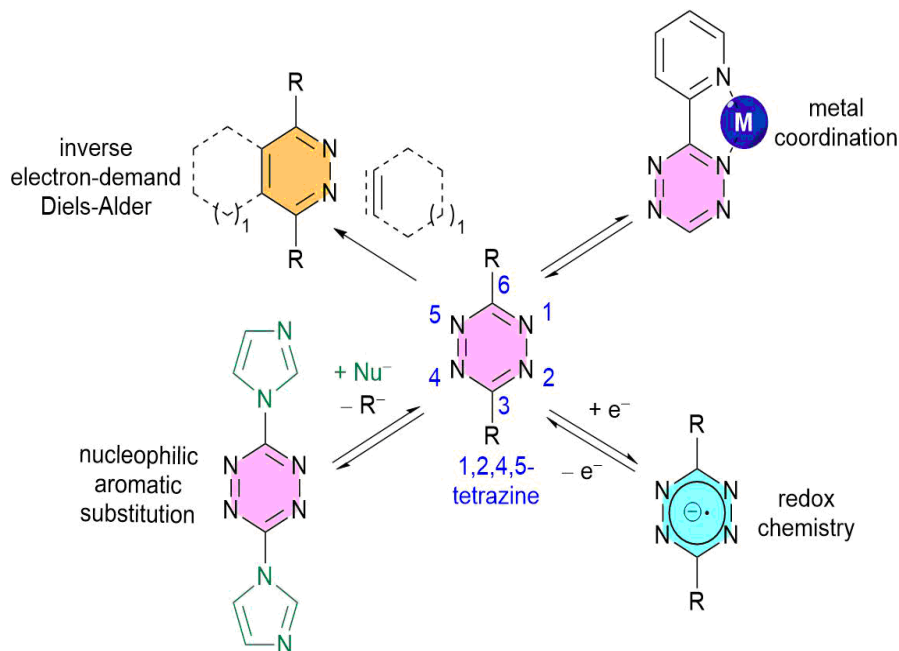
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Abstract No: T68

T68 Towards Tetrazine Incorporated Supramolecular Architectures

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Caption: The functionality of 1,2,4,5-tetrazines

Tetrazines are a fascinating functional group which can act as the 4π diene component in inverse electron-demand Diels-Alder (IEDDA) reactions.^[i] This reaction, which is often placed under the “click” umbrella, occurs without the need of a catalyst and under mild conditions. They also possess several other interesting modes of reactivity such as nucleophilic aromatic substitution under basic conditions,^[ii] reduction to the radical anion and metal coordination.^{[iii], [iv]} The use of tetrazine is ubiquitous in biological applications due to their biorthogonal nature however their use in supramolecular chemistry is less thoroughly investigated.

The past few decades have seen a soaring growth in the development of self-assembled supramolecular complexes. Among all the approaches, metal-ligand coordination driven self-assembly has been the standout strategy for constructing complex architectures (2D/3D) from simple building blocks with predesigned shapes and sizes. By building tetrazine based architectures it may be possible to influence the ability for IEDDA to occur and develop post-assembly modifications. Such a strategy enables us to play around with different geometries of self-assembled metal-organic cages.

Herein I shall demonstrate work towards incorporating the tetrazine moiety into a variety of metal-organic cages. Demonstrating progress towards understanding how post-assembly modification of the complexes with a variety of alkene and alkyne dienophiles affects the steric and binding angle environments of the ligands leading to the formation of different cage topologies.^[v]

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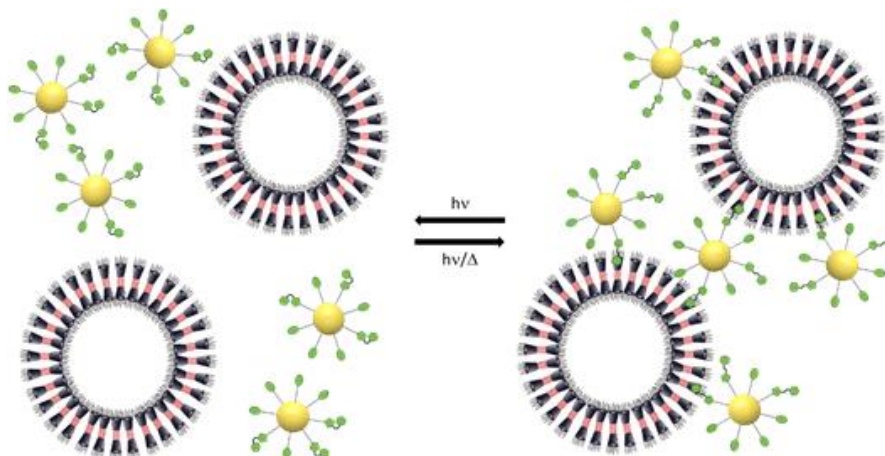
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Abstract No: T69

T69 Arylazopyrazole Functionalized Gold Nanoparticles as Supramolecular Building-Blocks

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Caption: Schematic assembly and disassembly of cyclodextrin vesicles using arylazopyrazole functionalized gold nanoparticles.

In the development of intelligent matter, photoresponsive nanoparticles can act as important building blocks. Due to the possibility of ligand-based supramolecular assembly, they can be employed to realize the four key functional elements: sensor, actuator, network and long-term memory.[1] Therefore, we present gold nanoparticles functionalized with a mixed ligand shell containing arylazopyrazoles (AAPs) as photoresponsive unit. In doing so, the advantages of AAPs as excellent photoswitches and the plasmonic properties of the particles can be combined in a single material.

In this project, thiolated AAP was employed as a responsive ligand in combination with a dummy ligand, in order to sustain responsiveness and tune solubility.[2,3] To the best of our knowledge, this excellent class of photoswitches has not been used in such a way yet. Subsequently, the photophysical properties of the obtained particles as well as their response to changes in pH were analyzed. Finally, the particles were deployed as linker for cyclodextrin-based structures like vesicles and nanoparticles, utilizing the well-known host-guest interaction between AAPs and β -cyclodextrin.

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Abstract No: T70

T70 Diversity of multinuclear structures of imine-based supramolecular complexes and their electrochemical properties

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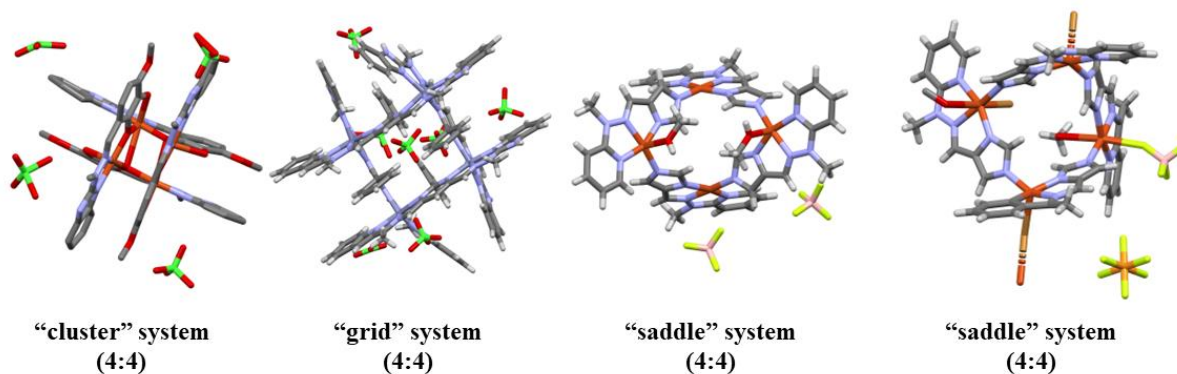


Figure. Representative structures of copper supramolecular complexes with various types of structures.

Design principles for preparation of multimetallic supramolecular materials are rather well established, but their shape and size can significantly affect their properties and eventually functionality¹. Some of their interesting applications include biology and biomimetics², catalysis³ or electrochemistry^{4,5}. The latter are particularly interesting, since they can help to solve some of the global challenges related to electrochemical transformations of small molecules⁴ and/or faster detection of neurodegenerative diseases (Parkinson's disease, Alzheimer's disease, Tourette syndrome, schizophrenia)⁵.

Herein, a set of tetrametallic copper(II) discrete [4x4] coordination compounds will be presented, which exhibit varying molecular architectures (e.g. cluster-, grid- and saddle-type systems – see Figure) based on the choice of the imine-type ligand.

The ability to function as selective dopamine sensors, especially in aqueous environments, will be evaluated for selected architectures.

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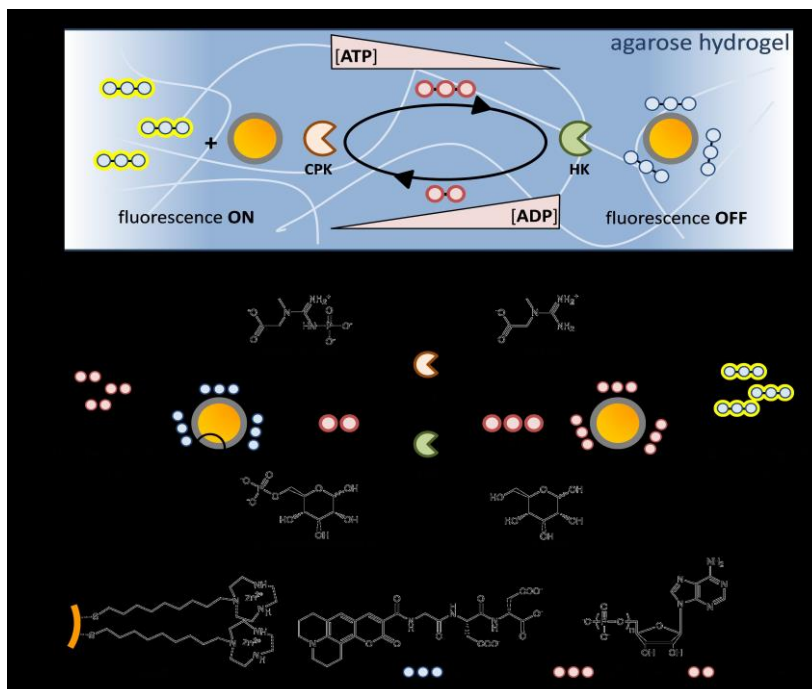
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Abstract No: T71

T71 Persistent ATP-concentration gradients in a hydrogel sustained by chemical fuel consumption

Yingjuan CAO

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Caption: Local enzyme activity in a hydrogel result in the formation of ATP- and ADP-concentration gradients.

Local enzyme activity in the cell installs macroscopic concentration gradients which play an important role in regulating biological processes such as cell division and microtubule dynamics^{1,2}. The development of "active" synthetic matters with life-like properties requires methodology to maintain a macroscopic synthetic system in a non-equilibrium state. Here, we show the formation of macroscopic ATP-concentrations in an agarose gel and demonstrate how these gradients can be sustained in time at the expense of the consumption of a chemical fuels³. The approach relies on the spatially controlled activation of ATP-producing and ATP-consuming reactions through the local injection of enzymes in the matrix. The reaction-diffusion system is maintained in a stationary non-equilibrium state if chemical fuel, phosphocreatine, is present. The reaction-diffusion system is coupled to a supramolecular system composed of monolayer protected gold nanoparticles and a fluorescent probe. As a result of this coupling, fluorescence signals emerge spontaneously in response to the ATP-concentration gradients. We show that the approach permits the rational formation of complex fluorescence patterns that change over time as a function of the evolution of the ATP-concentrations present in the system^{4,5}.

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Abstract No: T72

T72 Towards a Greener Aerobic Oxidative Cleavage of Vicinal Diols in Water

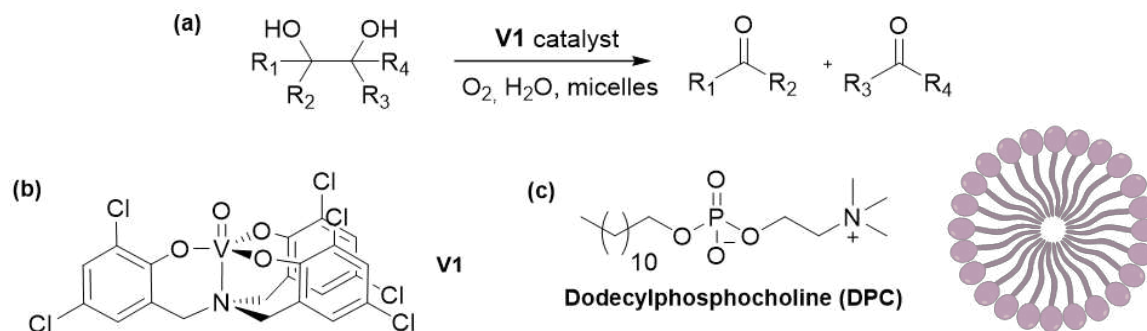
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Figure 1. (a) Reaction scheme (b) Catalyst V1 (c) DPC surfactant and micellar representation

Water is a sustainable, eco-friendly and safe (non-toxic, non-flammable, non-volatile) solvent and interest in using it as a solvent in chemical processes has been growing steadily over the last years. Many catalysts and substrates are however not soluble or stable in water and the use of aqueous micellar systems is a simple and yet very effective strategy to transfer organic reactions into water.^[1] Confinement and high local concentrations are reported to be key factors favoring the rate of reaction in micelles.^[2] This work focuses on the aerobic oxidative cleavage of vicinal diols in micellar media, a reaction which is known to be efficiently catalyzed by vanadium aminotriphenolate complexes in organic solvents (Figure 1a).^[3]

The catalyst **V1** (Figure 1b) was successfully incorporated in dodecylphosphocholine micelles (DPC, Figure 1c) and was tested with a wide scope of vicinal diol substrates. Reaction times varied considerably and DOSY NMR experiments were undertaken to determine the local concentration of the different substrates in the micellar phase. These results were put in perspective with the reactivity in toluene. Results suggest that the ease with which the substrate can access the catalyst, and therefore the precise location of the substrate molecules and the catalyst in the micellar phase, must also be considered when trying to rationalize reactivity in micelles.^[4]

References

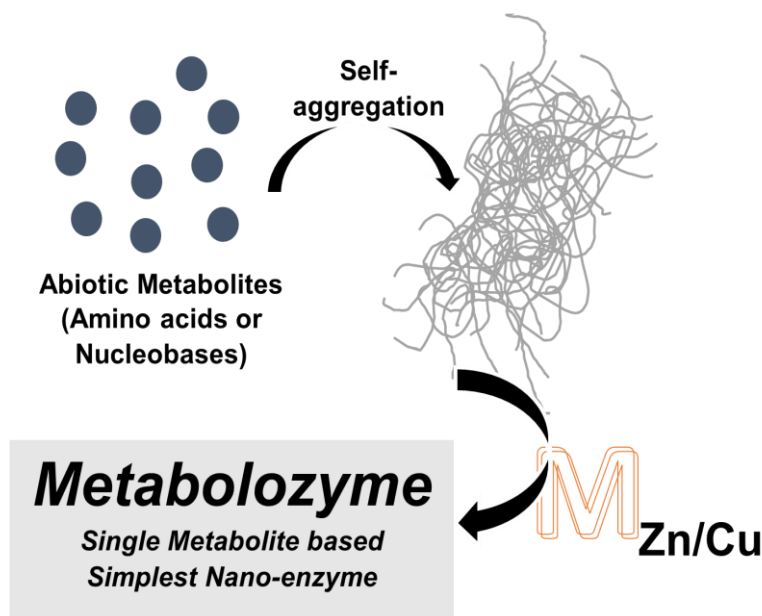
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Flash talks 27-06-2023 16:40 - 17:00

T73 Abiotic "Metabolites" – A Potential Key to the Missing Link in the Origin of Life

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Caption: Abiotic metabolite based simplest nanoenzyme_Metabolozyme

The origin of life is a complex event and no theory can fully explain its origin. Although the RNA-world and later the amyloid-world hypotheses gained momentum in the origin of life discussion, it is difficult to explain the existence of such entities (small functional RNA molecules or the amyloidogenic peptides) in abiotic samples. Therefore, there is still a missing link between these theories and the origin of life. The ability of simple metabolites found on meteorites and early-earth mimicking conditions,^{1,2} to self-assemble into ordered and functional amyloid-like structures^{3,4} may provide the connection between the theories. The catalytic activity of such metabolites is an added advantage as it enforces the probability of such a system as the initiator of today's extant enzymes. A single amino acid, proline, having pronounced catalytic activity⁵ hints towards their prebiotic relevant operational significance. Recently, the catalytic activity of metal-coordinated single amino acids has also been demonstrated to complement the concept.⁶ Therefore, metabolite-based nano-enzymes may have the potential to be the left piece in the puzzle of the origin of life. In our attempt, a metal complex library of the origin of life-relevant amino acids is being developed. In the current work, the Zn-complexes of glycine and valine – two amino acids that are the most abundant in the prebiotic soup and meteorites^{1,2} were synthesized. The structural elucidation by single crystal X-ray diffraction (SXRD) analysis of the complexes obtained was made possible after their crystallization in the biogenic water medium. Both formed a two-dimensional array of supramolecular networks which was also assessed through scanning electron microscopy (SEM). The complexes showed significant esterase-like activity as assessed by p-nitrophenyl acetate (pNPA) reaction assay. Between them, the Zn-Glycine exhibited better catalytic activity as assessed by time-dependent UV kinetics. Initial results of relevant prebiotic reactions including phospho-ester bond hydrolysis and amide bond formation were also obtained with the catalysts based on chromatography and mass spectrometry analysis.

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T74 Self-Assembly of Bile Acid Derivatives into Metallosupramoleculer Architectures

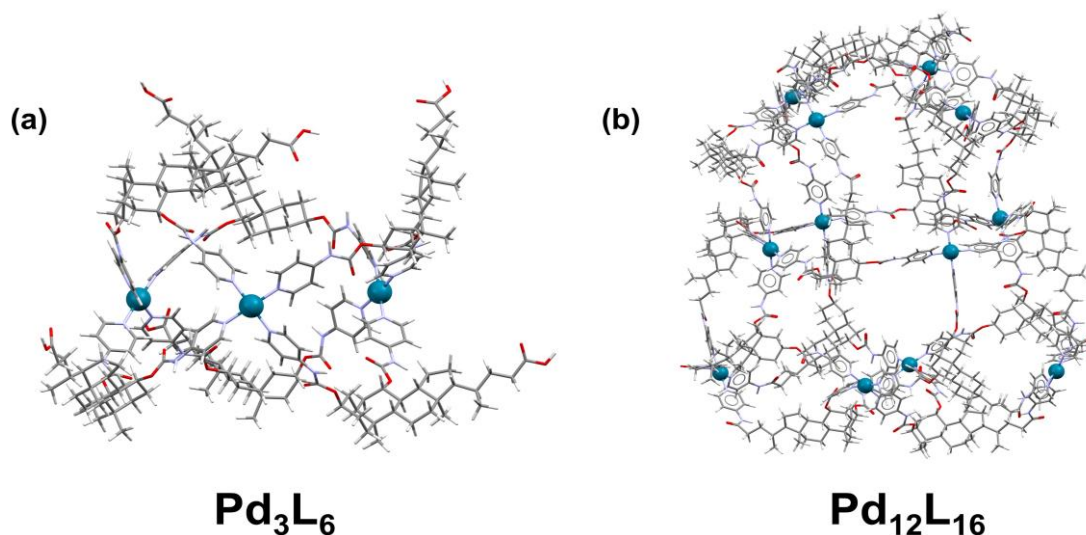
Subhasis Chattopadhyay ¹, Ondřej Jurček ¹, Anniina Kiesilä ², Elina Kalenius ², Juha Matti Linnanto ³, Radek Marek ¹¹ Masaryk University, Brno, Czech Republic² University of Jyväskylä, Jyväskylä, Finland³ University of Tartu, Tartu, Estonia

Figure 1. Bile acid-based metallosupramolecular (a) macrocycle and (b) cage.

Natural chiral hydrophobic cavity/pocket containing structures (e.g., metalloenzymes, proteins) are important for many biological functions (e.g., transport, recognition, catalysis). To mimic these natural systems and mechanisms, development of such supramolecular systems (e.g., cages, macrocycles) from chiral natural molecules is required.

Coordination-driven self-assembly is a well-established method to build hollow metallosupramolecular (MSM) structures. However, majority of self-assemblies are made of symmetric, achiral ligands (L) and Pd²⁺. Recently in our group, first bile acid (BA)-based (ursodeoxycholic acid, UDCA) MSM macrocycles Pd₃L₆ (Figure 1a) were introduced¹ and studied.² Beside this, there is only one report about BA-based Pd₂L₄ MSM cages.³ We further expanded on the family of BAs by synthesizing chenodeoxycholic acid-based ditopic pyridyl ligand, forms a mixture of Pd_nL_{2n} species ranging from Pd₂L₄ to a large Pd₆L₁₂.

Thus far, only BA-based ditopic pyridyl ligands were used to prepare MSM systems. Therefore, our latest study presents UDCA-based tritopic pyridyl ligand and its self-assembly with Pd²⁺, which results in Pd₆L₈ (Figure 1b) or **first-ever giant Pd₁₂L₁₆** MSM cage depending on solvent and metal-ligand ratio.

These studies provide better understanding of unsymmetric natural molecule-based ligands self-assembly, effect of their flexibility, topology, and bend angle in design and construction of chiral cavity containing MSM architectures.

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T75 Nanoscale probing of the supramolecular assembly in a two-component gel by near-field infrared spectroscopy

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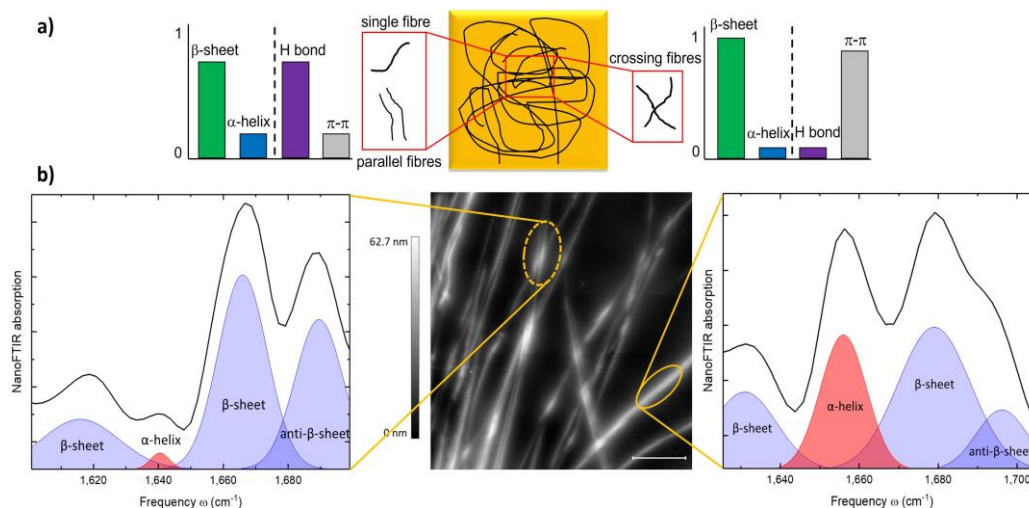


Figure 1. a) Schematic depiction of the system's heterogeneity showing the contribution of π - π stacking, hydrogen bonding, β -sheet and α -helix depending on the network geometry; b) nanoFTIR spectra of the amide I region of fibres in perpendicular (left) and parallel (right) arrangement.

The transient gel materials resembling many features of dynamic natural assemblies have been extensively studied during the past decade. These materials have many potential applications, such as drug delivery platforms. Therefore, a deep understanding of the self-assembly of the molecular building blocks is required. Scattering scanning near-field optical microscope (sSNOM) is an emerging tool that has gained momentum over the past decade for the nanoscale study of cells, viruses, organic films and protein fibrils.^{1,2,3,4}

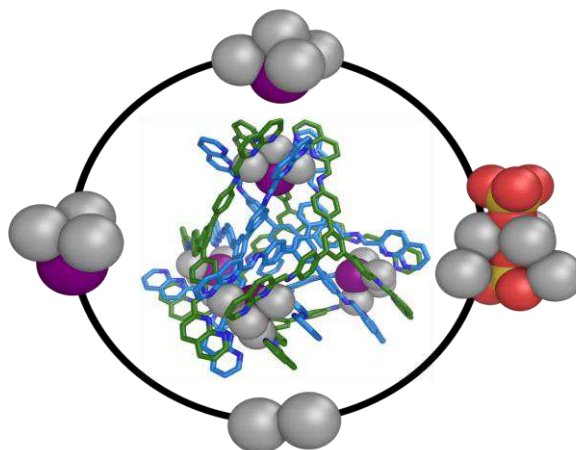
In this work, we focused on designing and studying novel out-of-equilibrium, transient supramolecular gel systems triggered by complex chemical equilibria in a chemically active solvent, which dictates both the assembly event and the collapse of the gel network with a definite lifetime.⁵ Using IR spectroscopy, we highlight the heterogeneity of the system, non-covalent interactions responsible for gelation and the resulting secondary structures present in the fibrous network of our dual-component gel system. We show that structural features of the network, such as fibre orientation and geometry-dependant proximity, directly affect the self-organisation of the gelator molecules, resulting in the alteration of the secondary structure at specific nano-locations. Indeed, the parallel orientation of fibres is prone to hydrogen bonding with both β -sheet and α -helix secondary structures, while π - π stacking interactions prevail at the crossing of two fibres with a dominant β -sheet motif. Near-field nanospectroscopy has proven to be a powerful tool for the nanoscale distinction of non-covalent interactions.

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Abstract No: T76

T76 Self-Assembly Directed Synthesis of Atomically Precise Silver(I) Nanoclusters

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Metal-organic cages possess a rich variety of potential applications, from sensing and separations,^[1] to stabilisation of reactive species and catalysis.^[2-3] These applications can be readily accessed *via* subcomponent self-assembly; a route to complex metal-organic architectures, whereby simple organic subcomponents and metals are combined, triggering the formation of metal coordination bonds. In these assemblies, metals typically occupy the vertices of a Platonic^[4] or Archimedean^[5] solid with organic ligands occupying the faces or edges of the polyhedron.

Diverse vertices, containing atomically-precise silver nanoclusters, have been demonstrated by our group with clusters containing three,^[6] four,^[7] and six^[8] silver atoms supported at the vertices of metal-organic tetrahedra, or hexameric helicates. These nanoclusters were demonstrated to bind halides, with the exchange of harder halides for softer halides observed. Furthermore, the binding of other anions, such as sulphate, at the cluster has been observed. In the case of the tetrahedra, we have observed host-guest behaviour in the interior or exterior of the cage – with host-guest complexes subsequently dissociated by halide substitution and guest expulsion.

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Abstract No: T77

T77 Metal-Mediated Length Control of Supramolecular Assemblies

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Benzene-1,3,5-tricarboxamide (BTA) is a versatile supramolecular building block in which the three amide bonds can give rise to three-fold intermolecular hydrogen bonding interactions. These molecules have applications as liquid crystals, MRI contrast reagents, and microcapsules for drug delivery.^[1] On functionalizing the BTA core with metal complexes, we observed that BTA-nickel complexes rapidly self-assemble into uniform fibers of low polydispersity. We have been able to precisely tune the length of these nanofibers by manipulating the self-assembly conditions.^[2] Intrigued by these results, we synthesized similar BTA molecules functionalized with other metal complexes. The self-assembly and co-assembly of these molecules was investigated by transmission electron microscopy (TEM), energy dispersive X-ray (EDX) spectroscopy, and UV-visible spectroscopy. The co-assembly of the metal complexes maintained the low polydispersities. In this poster presentation, I'll describe how we were able to tune nanofiber lengths through controlled assembly of the metal complexes and the possible mechanism for tunable supramolecular assemblies with low polydispersities.

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Abstract No: T78

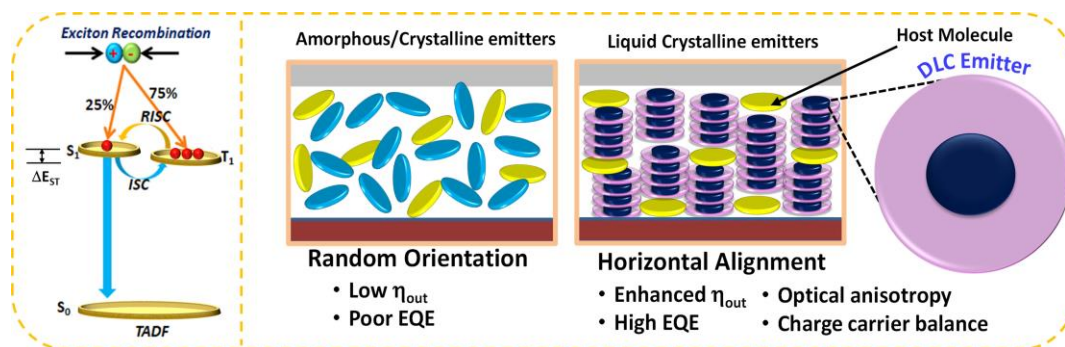
T78 MR-TADF active self-assembled columnar discogens as efficient emitters in solution-processed blue OLEDs

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$$\eta_{EQE} = \eta_{int} \times \eta_{out}$$

$$\eta_{int} = \eta_{rec} \times \eta_{ns} \times \eta_{PL}$$

η_{int} denotes IQE: η_{rec} is the recombination efficiency of the injected holes and electrons, η is the EUE of the device, η_{PL} is the PLQY of the emitter. η_{out} represents the light outcoupling efficiency of the emitter.

Vacuum-deposited organic light-emitting diodes (OLEDs) are now commercialized and used in displays for portable devices, flat-panel televisions, and solid-state lighting sources for the automotive industry. The emitters in these devices consist of a combination of fluorescent and phosphorescent materials, each of which has weaknesses in terms of either performance or sustainability. Thermally activated delayed fluorescent (TADF) emitters offer the potential to overcome these weaknesses. Vacuum-deposition fabrication processes are, however, both costly and materials-wasteful and the cost becomes prohibitive for the fabrication of large-area pixels given the size of the evaporator. Solution-processed OLEDs address these detracting features of the fabrication process. State-of-the-art solution-processed OLEDs, and in particular blue OLEDs typically show poor device performance both in terms of stability and external quantum efficiency (EQE), especially compared to vacuum-deposited devices.

Herein, we address these specific issues using an innovative approach. We developed solution-processable blue multi-resonance TADF (MR-TADF) emitters based on promising self-assembled dynamic soft materials, discotic liquid crystalline (DLC) molecules, which we contend will show horizontal alignment of the transition dipole moment in solution-processed films, in order to improve the light-outcoupling efficiency and hence the EQE (Figure 1).

Abstract No: T79

T79 Orientational self-sorting in octahedral palladium cages: scope and limitations of the cis-rule

Jean Charles Edouard De Montmollin Farzaneh Fadaei Tirani, Kay Severin

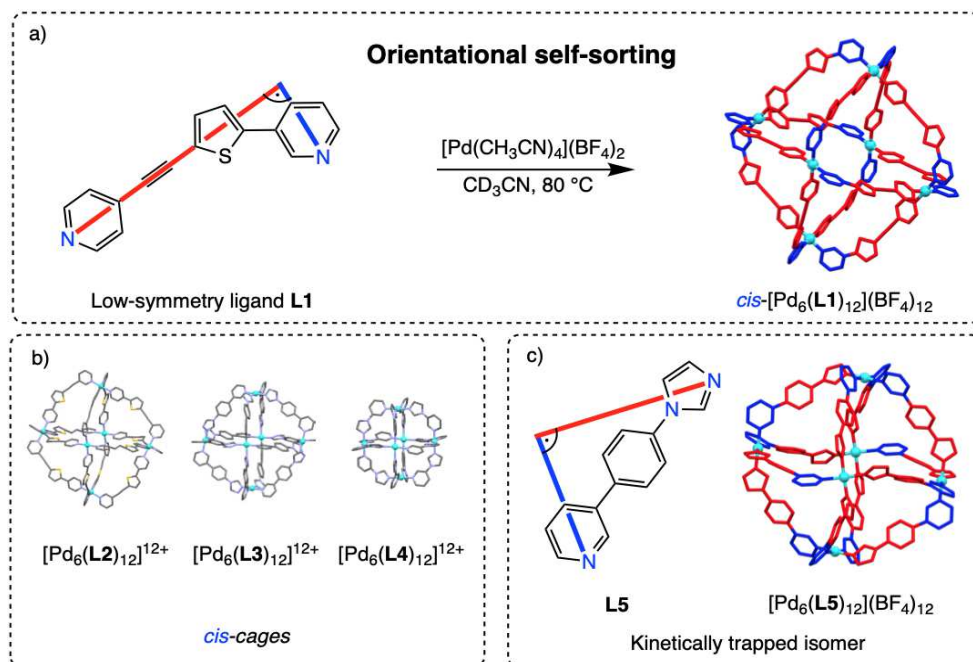
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Fig. 1 Orientational self-sorting in $[\text{Pd}_6\text{L}_{12}]^{12+}$ cages using low-symmetry ligands. a+b) The thermodynamic isomers with *cis*-configuration at every Pd-center are obtained exclusively. c) A kinetically trapped isomer with *cis*-configuration at only 2 Pd-centers.

Palladium-based metal-organic cages (MOCs) have been widely studied and have applications in medicinal chemistry as well as in catalysis. The understanding of their self-assembly is therefore of great importance. Ditopic N-donor ligands L and Pd(II) precursors form a variety of MOCs of the general formula $[\text{Pd}_n\text{L}_{2n}]^{2n+}$ in which the bend angle of L, for the most part, dictates the geometry of the cage. Using various low-symmetry heteroditopic ligands L with a bend angle of 90° , hexanuclear $[\text{Pd}_6\text{L}_{12}]^{12+}$ metal-organic cages (MOCs) were synthesized with $[\text{Pd}(\text{CH}_3\text{CN})_4(\text{BF}_4)_{12}]$ in acetonitrile. Due to the low symmetry of the ligands many isomers can potentially be formed. The obtained structures provide additional evidence for orientational self-sorting^{1,2}: Out of 112 possible isomers for $[\text{Pd}_6\text{L}_{12}]^{12+}$, we show the one isomer with *cis*-configuration at all Pd-centers is thermodynamically favored (Fig. 1a and 1b). Various characterization methods including ^1H NMR, ^{13}C NMR, COSY, NOESY, DOSY and single crystal XRD structure determination confirm the formation of a single isomer. Using ligands with different coordination vector ratios and donor groups (pyridyl-, triazolyl- and imidazolyl-donor) we discuss the scope and limitations of the aforementioned selectivity. A kinetically trapped product was obtained from imidazolyl-ligand **L5** (Fig. 1c). Furthermore, we provide a geometrical explanation using a coordination vector model for the experimentally observed *cis*-isomers.

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Abstract No: T80

T80 Hexaazatrinaphthylene based supramolecular polymer for electronic applications

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The use of supramolecular materials holds great potential in the design of systems for energy applications. The employment of supramolecular motifs creates the opportunity to integrate multiple different functionalities into one system. As a result, molecules with drastically different properties can be combined, charge transport can be maximized, and exciton recombination can be avoided [1]. The vast majority of self-assembly studies in the field has been devoted to p-type organic molecules, while the development of electron transporting materials has lagged behind. Therefore, we focused our research on utilizing hexaazatrinaphthylene (HATNA), an n-type organic molecule, as a building block to form supramolecular polymers. The HATNA motif consists of 3 fused nitrogen-rich pyrazine moieties, which make it a relatively rare electron-deficient aromatic discotic molecule with a high charge carrier mobility [2]. In order to make a supramolecular building block, the HATNA core was equipped with amide based citronellol tails to introduce hydrogen-bonding and chirality. Purification yielded two constitutional isomers, which could be isolated by utilizing preparative thin layer chromatography. Subsequently, the properties and self-assembly mechanism of the two isomers were investigated by means of ultraviolet-visible, circular dichroism and fluorescence spectroscopy, atomic force microscopy, and cyclic voltammetry. Bulk properties were investigated by polarized light microscopy, differential scanning calorimetry, and small-angle X-ray scattering. We found that supramolecular polymers are formed via a cooperative mechanism, which form sub- μm sized branched fibers for the symmetric isomer and μm sized coiled fibers for the asymmetric isomer.

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Abstract No: T81

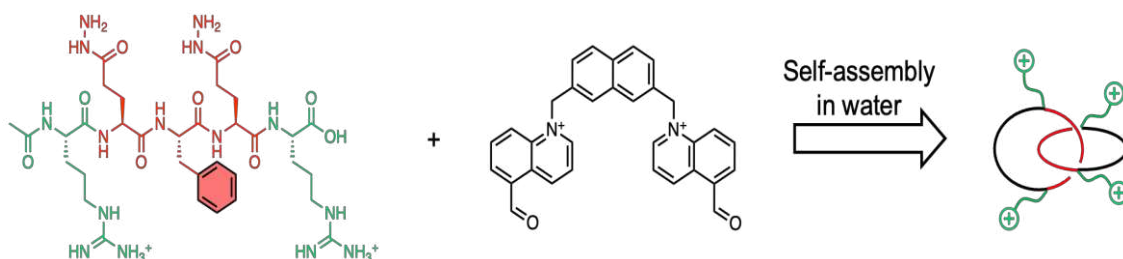
T81 Entangled molecules for nucleic acid recognition and gene delivery

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Caption: Self-assembly in water of hybrid catenane from the combination of L-Arginine based pseudo-peptide dihydrazide and synthetic aromatic dialdehyde

Cationic peptides promote DNA condensation via electrostatic interactions, increasing its resistance towards mutagens or oxidizing species. Peptides containing L-Arginine as cationic source are known to promote efficient DNA condensation. [1] Many synthetic molecules have been tested for DNA condensation, but entangled molecules [2] have never been utilized. Yet it has been established that it is possible to have access to new physical and chemical properties by introducing entanglement. We have previously developed a method to synthesize interlocked molecules, resulting to the dynamic combination of dihydrazides with dialdehydes in water. [3] Now, we demonstrate that it is possible to use the hydrophobic effect to drive the synthesis of hybrid catenanes, composed of synthetic aromatic components and L-Arginine based pseudo-peptides (Figure 1). The efficiency of these new L-Arginine based catenanes will be tested in DNA condensation. If successful, this work is an overture to the development of new applications regarding interlocked molecules.

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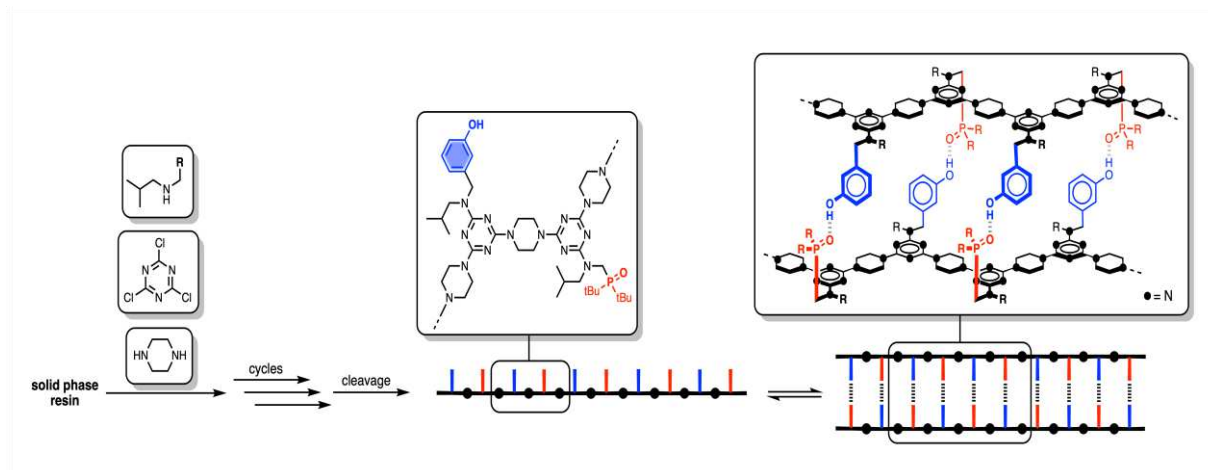
Keywords: Catenane, DNA condensation, Hydrophobic effect, L-Arginine based peptide.

Abstract No: T82

T82 Solid-phase synthesis of synthetic information oligomers

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Caption: Solid-phase synthesis of triazine-based oligomers

The elaborate functional properties of biological polymers found in nature are encoded by the sequence of monomer building blocks. Solid-phase methods to synthesise sequence-defined peptides and oligonucleotides allow exploitation of this relationship between sequence and folded three-dimensional structure to make biopolymers with interesting non-natural catalytic or binding properties.

Synthetic oligomeric systems might allow exploration of the vast chemical space for new structures with functional properties in non-aqueous media. It has been shown that triazine-based oligomers equipped with hydrogen-bonding base-pairing groups form sequence- and length-selective duplexes and are a promising candidate for such a system.

Here will be presented an automated solid-phase synthesis approach to rapidly make sequence-defined triazine-based oligomers in high yield. The development of methods for solid phase synthesis will be described, and studies of the relationship between sequence and self-assembly properties will be shown.

Abstract No: T83

T83 Rational design for hierarchical 2D self-assembly of cyclic peptides nanotubes

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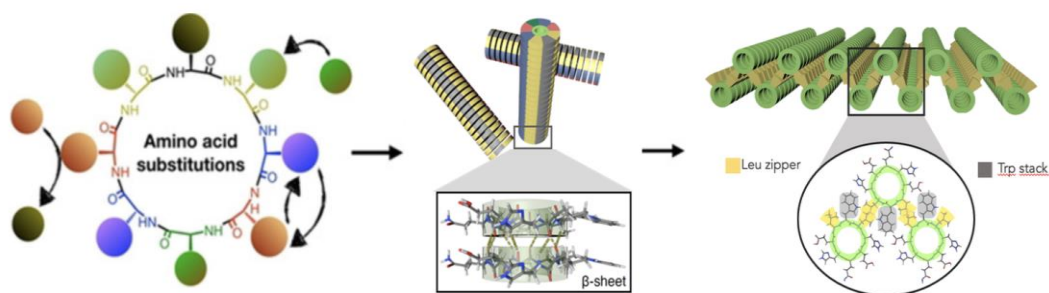


Figure 1. Scheme of the proposed model for the sequential self-assembly of amphiphilic cyclic peptides (left) in 1D forming nanotubes (middle) and in 2D forming nanosheets (right).

The unique physical-chemical properties and high surface-to-volume ratios of 2D nanomaterials have made them highly attractive as components of complex functional devices in a wide range of biomedical and technological applications. However, many of these materials are non-dynamic and have undefined dimensions due to the complex methodologies used in their preparation. To address this issue, the fabrication of supramolecular 2D nanomaterials with hierarchical control offers a bottom-up approach to assembling responsive 2D materials with precise structural control.

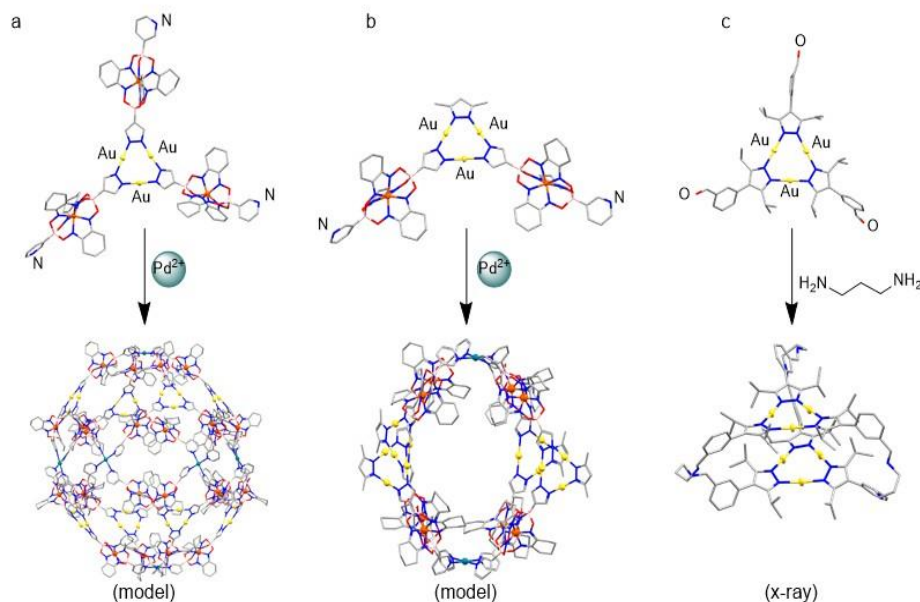
Here, we describe an innovative strategy using a single cyclic peptide as building block to create large supramolecular nanosheets through sequential self-assembly from 1D to 2D¹. This new concept is based on the ability of D/L-alternating cyclic peptides to form nanotubes through 1D self-assembly, which then arrange laterally to form 2D nanosheets in an aqueous environment (see Figure) The resulting supramolecular material exhibits reversible structural changes in response to external stimuli, such as changes in attractive and repulsive forces, making it a promising material for biomedical and technological applications. Furthermore, the study examines the relationship between structure and assembly of this modular 2D assembly, in which specific amino acid mutations provide insight into the key features of the primary sequence responsible for self-assembly².

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Abstract No: T84

T84 [Au(pyrazolate)]₃ complexes as building blocks for the construction of molecular cagesNoga Eren¹ Kay Severin²¹ EPFL, Lausanne, Switzerland² EPFL, 1015 Lausanne, SwitzerlandCaption: Figure 1. Molecular cages containing [Au(pyrazolate)]₃ complexes.

Cyclic trinuclear complexes (CTCs) are known for their tunable p basicity and interesting optical properties. However, there are limited examples of incorporating these motifs into molecular cages.¹ In order to construct cages with CTC building blocks, we synthesized pyrazole ligands with substituents suitable for further reaction, such as complexation with metal ions or imine condensation.

Heterometallic coordination cages were obtained by combining Au^I CTC containing pyridyl donor groups with Pd²⁺ (Figure 1a and 1b). In the first case, a homoleptic CTC was used as a metalloligand, while a heteroleptic CTC with two pyridyl ligands was used in the latter. The cages were characterized by NMR and HR-ESIMS. Molecular modeling indicates that the cages have a diameter of approximately 5 and 3.5 nm.

A prismatic cage with imine linkages was obtained by condensation of a Au^I CTC bearing formylphenyl substituents with 1,3-diaminopropane (Figure 1c). A crystallographic analysis of the cage revealed a roughly co-planar arrangement of the p-basic CTCs, with a distance between the planes of approximately 7 Å. NMR studies revealed that the cage is able to bind octafluoronaphthalene in CD₂Cl₂ with moderate affinity.

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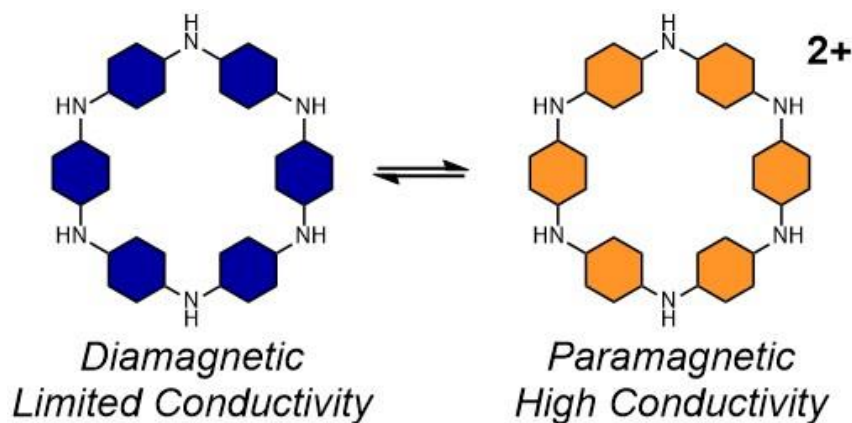
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Abstract No: T85

T85 Coaxially Conductive Organic Wires by Macrocyclic Self-Assembly

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Coaxially Conductive Organic Wires by Macrocyclic Self-Assembly

Austin M. Evans, *George & Josephine Butler Polymer Research Laboratory, Center for Macromolecular Science & Engineering, Department of Chemistry, University of Florida, Gainesville, FL, USA.*

Constructing one-dimensional nanostructures by the bottom-up assembly of molecular macrocycles is an appealing materials science goal.¹ Here, we leverage that design paradigm to create mixed ionic-electronic conductors.² We cooptimize the electronic and ionic conductivities of these species by molecular design. Specifically, we construct *N*-aryl containing macrocycles that are spontaneously oxidized and assemble in acidic environments. The nanotubes produced through this approach host impressive electronic conductivities. The electronic conductivity of these assemblies is measured by a series of direct contact measurements performed on single-crystals and thin-films of these nanowires. We explore the nature of this conductivity using a combination of ultraviolet-visible spectroscopy and electron paramagnetic resonance spectroscopy. Using these techniques and by directly probing the electronic conductivity, we show that these macrocycles have switchable conductivities, that can be modified as a function of electronic bias or acid/base addition. This report lays the groundwork for highly electronically and ionically conductive nanowires to be produced through macrocyclic assembly.

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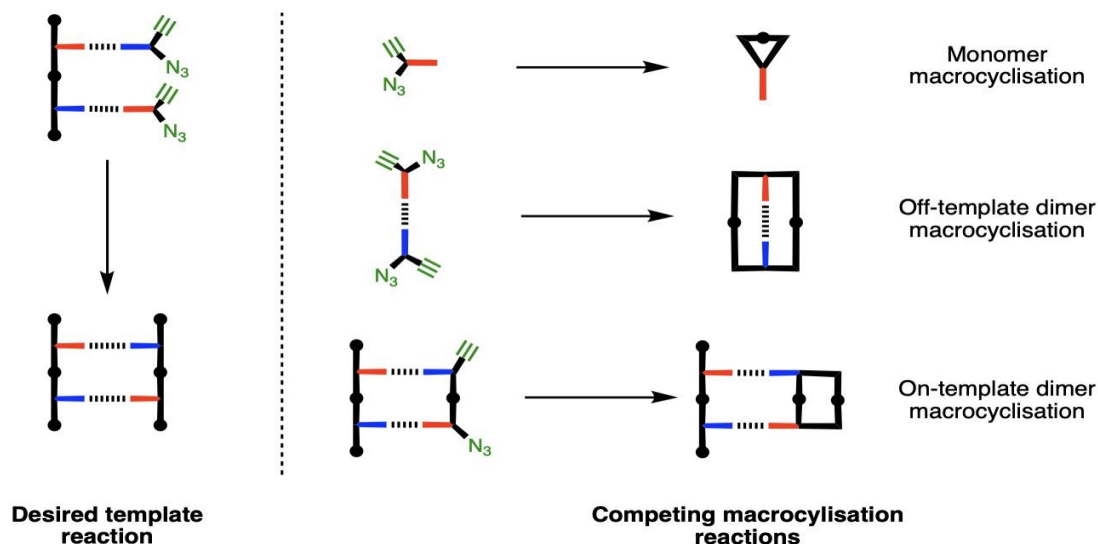
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Abstract No: T86

T86 Template-directed synthesis of information oligomers through non-covalent interactions

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Caption: Schematic representation showing the desired reaction, that zips up the backbone of the copy strand (left), and the competing processes (right)

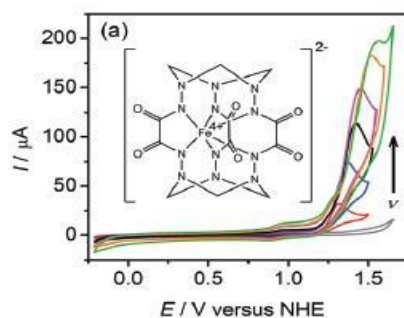
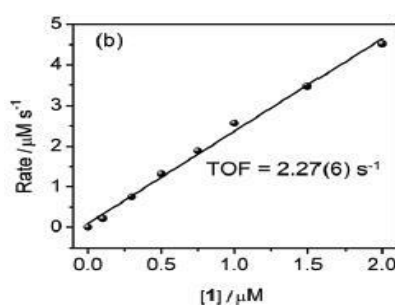
Directed evolution of biopolymers is based on the ability of DNA to mutagenically replicate. However, reliance on DNA limits the application of directed evolution to DNA-compatible molecules. The development of a synthetic oligomer which can mutagenically replicate could unlock the power of directed evolution to explore different areas of chemical space constituted by synthetic polymers. The Hunter group have shown that sequence-selective replication of oligotriazoles can be achieved using covalent ester base-pairing chemistry.¹ This method requires a cycle of six reaction steps, involving base protection and deprotection and base-pair coupling and cleavage, as well as the key reaction that zips up the backbone of the copy strand. The use of non-covalent base-pairing chemistry in template-directed synthesis could allow coupling of adjacent monomers bound to a template in a single chemical reaction. Unfortunately, such templated reactions are susceptible to a wide variety of competing processes (see below). By studying these reactions, this work aims to inform the design of a system in which non-covalent interactions can be used for reliable, high-fidelity template-directed synthesis of information oligomers.

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Abstract No: T87

T87 HIGHLY EFFICIENT PHOTOCATALYTIC WATER OXIDATION USING IRON(IV) AND MANGANESE(IV) CLATHROCHELATES

Igor Fritsky ¹ Sergii Shylin ², Mariia Pavliuk ², Luca D'Amario ², Fikret Mamedov ², Jacinto Sá ², Gustav Berggren ², Iryna Golenia ¹¹ Taras Shevchenko National University of Kyiv, Kyiv, Ukraine² Uppsala University, Uppsala, SwedenCaption: Cyclic voltammograms and molecular structure of **1** (0.25 mM) at pH 8.0 recorded at scan rates v from 10 to 1000 mV s⁻¹, and background (grey line).Caption: Initial rate of O₂ formation versus concentration of **1**.

Water oxidation (WO) powered by visible light at ambient temperature and neutral pH is a major challenge in the direct conversion of solar energy into dihydrogen fuel through photochemical water splitting. As the most efficient homogeneous WO catalysts rely on Ru and Ir complexes, there is significant interest in developing inexpensive 3d-metal complexes for WO. In this study, we present water-stable clathrochelate complexes Na₂[M^{IV}(L-6H)]·nH₂O (M = Fe, Mn) obtained through template synthesis using oxalodihydrazide (**oxh**) and formaldehyde. The ligand **L** is constructed by linking three **oxh** residues with six methylene bridges (Fig. 1a).^[1] Cyclic voltammograms carried out in borate buffer at pH 8.0 exhibit quasi-reversible features at E_{1/2} = +1.05 and +0.92 V vs. NHE, for Mn and Fe, respectively, and corresponding to the M^V/M^{IV} couples. These are followed by oxidative processes starting at +1.25 (Mn) and +1.15 V (Fe) vs. NHE assigned to WO (Fig. 1).

The activity of the complex with M = Fe (**1**) in photochemical WO was studied using [Ru(bpy)₃](ClO₄)₂ as photosensitizer and excess amount of Na₂S₂O₈ in a buffered aqueous solution.^[2] At [**1**] = 0.5 μM, oxygen evolution was observed with a TON = 365, the highest value observed for mononuclear iron complexes in photochemical WO. A TOF = 2.27(6) s⁻¹ reflects considerably higher reaction rates with respect to other iron-based molecular WO catalysts (Fig. 2). An Fe(V) intermediate generated under catalytic conditions is trapped and characterized using EPR and Mössbauer spectroscopy. Various spectroscopic and DLS experiments show that the molecular catalyst remains intact during WO and no low-valent iron species are formed.

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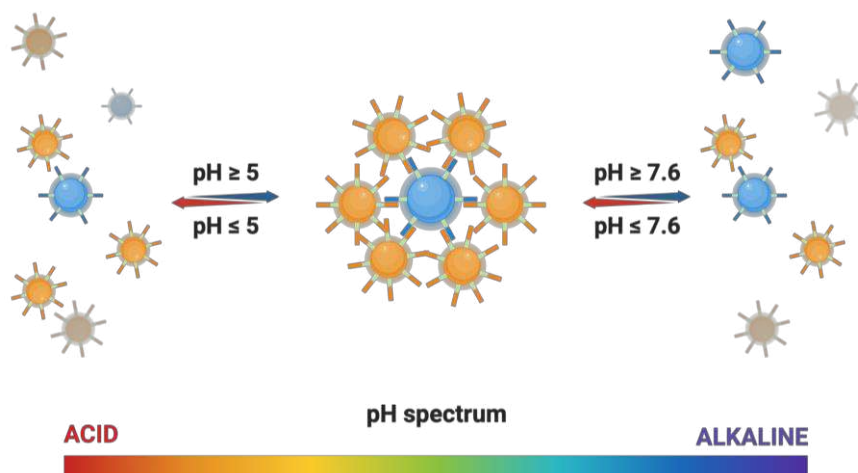
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T88 Dynamic quorum behavior in enzyme-powered stomatocyte nanomotors

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Chemically powered Micro-/Nano-Motors are synthetic structures able to transduce chemical energy to mechanical motion. They are essential in understanding fundamental motility processes on the nano- and micron-length scales. Generally speaking, at the nanoscale, Brownian motion and rotational diffusion negatively affect the motion of motors and hamper precise control of their motion.¹ To reduce hydrodynamic issues, we present a reversible system based on clustering stomatocyte nanomotor populations functionalized with complementary pH-responsive ligands. By clustering to larger sizes, the rotational drag forces on the particles will increase, and stomatocyte aggregates undergo minimal rotation compared to their individual counterparts.

The intended reversible behavior is transient and is based on the widely known complex-forming behavior of nitrilotriacetic acid (NTA) and histidine (His) moieties, in the presence of nickel ions and high pH. The attachment of such functional groups to the surfaces of stomatocytes would induce their grouping in the presence of nickel ions and, ultimately, allow the control of cluster and individual motors' motion regimes by pH.

The clustering behaviors of stomatocyte nanomotor populations at different ratios were analyzed in ultrapure water and buffered systems by dynamic light scattering and microscopy. In both continuous phases, the stomatocytes display a maximum clustering interaction at pH between 6 and 7.5 and interparticle repulsive behaviors outside the range. Within the detectable region of the dynamic light scattering, individual stomatocytes can aggregate to agglomerates 20x their volumes.

Ongoing work involves incorporating the motor function in stomatocyte populations to enable directed motion (chemotaxis) and analyzing population behavior as a response to pH. Understanding population behavior in chemotactic colloids can facilitate the achievement and execution of remote navigation and cooperative tasks not feasible for individual MNMs.¹

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Abstract No: T89

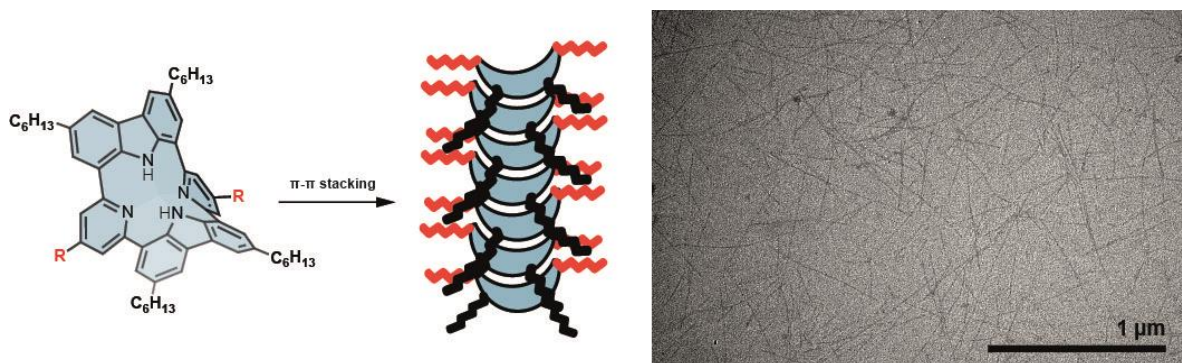
T89 Restricting the Shape-Assisted Self-Assembly of Carpyridines to One Dimension

Lucía Gallego ¹ Joseph Wods ², Piotr Szwedziak ², Andreas Vargas Jentzsch ³, Michel Rickhaus ²

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² University of Zurich, Zurich, Switzerland

³ University of Strasbourg, Institut Charles Sadron, Strasbourg, France



Caption: Schematic representation of a carpyridine molecule with six substituents on the periphery that self-assembles into fibers, as seen in the TEM image.

Shape-Assisted Self-Assembly (SASA) is a process in which the shape of a monomeric unit enforces the order between monomeric units needed for supramolecular assemblies in the absence of strong non-covalent interactions such as H-bonding.^{1,2} Saddle-shaped molecules stand out for these processes due to the translational and rotational rigidity of the monomers within the stacks. Carpyridines (CPs) are porphyrin-related metal-containing macrocycles bearing two carbazole and two pyridine units alternately connected through ortho aryl-aryl bonds.^{1,3} This arrangement results in a saddle-shaped structure, where prefunctionalized building blocks allow the synthesis and tuning of properties of these macrocycles. These units have shown to be effective towards supramolecular assembly purely based on p-p interactions and assisted by the shape of the monomers, demonstrating the significance of shape in self-assembly processes. Alkyl substitution onto the carbazoles has allowed us to study 2D sheet formation,¹ which combined with substitution onto the pyridines with different side chains allows us to study the mechanism of assembly of the monomers into oligomers, and ultimately, into micrometer-long fibers.

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Abstract No: T90

T90 Spectral and electrochemical investigation of metal-induced peptide self-assembly

Stela Georgieva Spas Nikolov, Petar Todorov, Petia Peneva

University of chemical technology and metallurgy, Sofia, Bulgaria

Naturally occurring peptides interact with various metal ions, which control the structures and functions of many biological processes in organisms. Numerous studies have been conducted in metallopeptide chemistry, with the primary goal of developing synthetic peptide analogs that coordinate with metal ions via their functional groups to introduce special reactivity or construct nanostructures. Here, we present strategies for hemorphin peptide analog self-assembly induced by metal coordination to various natural and non-natural peptide binding sites. Hemorphins are naturally occurring endogenous opioid peptides that belong to the hemorphin family. Metal binding of basic functional groups of amino acid residues in hemorphin molecule causes structural changes in the peptide molecule and is responsible for peptide self-assembly. Spectral (circular dichroism, IR spectrometry, fluorescence analysis) and electrochemical techniques were used to show that peptide derivatives undergo structural changes when exposed to Cu(II) ions, resulting in the formation of metallocyclopeptides or partial changes to the larger α -helix (or β -sheet) structure. The structures and functions of obtained aggregates have been described as well. We also highlight some examples of metal-induced peptide self-assembly relevant to the potential biological applications.

Acknowledgment: This study is funded by the European Union-NextGenerationEU, through the National Recovery and Resilience Plan of the Republic of Bulgaria, project № BG-RRP-2.004-0002, "BiOrgaMCT".

Abstract No: T91

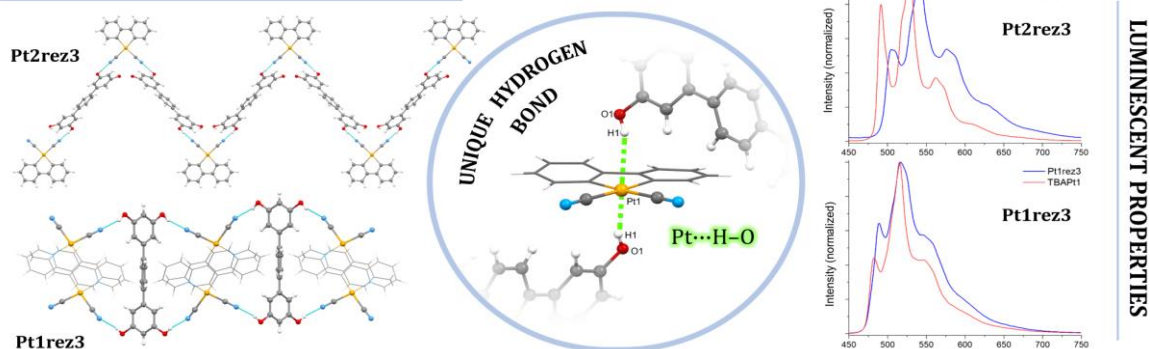
T91 Diversity of hydrogen bond synthons in supramolecular architectures involving luminescent Pt(II) complex anions and polyresorcinol cofomer

Doroła Głosz ¹ Katarzyna Jedrzejowska ¹, Marlena Gryl ¹, Jakub J. Zakrzewski ¹, Igor Koshevoy ², Robert Podgajny ¹

¹ Jagiellonian University, Krakow, Poland

² University of Eastern Finland, Joensuu, Finland

HYDROGEN BONDS - RIBBON MOTIFS



Caption: Hydrogen bonds in crystal structures of Pt2rez3 and Pt1rez3 and their emission spectra compared with TEAPt2 and TBAPt1 precursors.

The photoluminescence of square planar Pt(II) complexes might be tuned by modification of ligands, or through shaping the second coordination sphere, to achieve diverse non-covalent synthons.^[1] Here, we present two new co-crystal salts, **Pt2rez3** and **Pt1rez3**, involving $[\text{Pt}^{\text{II}}(\text{bph})(\text{CN})_2]^{2-}$ (**Pt2**)^[2] or $[\text{Pt}^{\text{II}}(\text{CN})_2(\text{ptpy})]^-$ (**Pt1**)^[3] complexes and oligophenylene polyresorcinol cofomer **rez3**^[4]. Both architectures are stabilized by classical hydrogen bonds $\text{Pt}-\text{CN}\cdots\text{H}-\text{O}_{\text{rez3}}$ within 1D ribbons, whereas **Pt2rez3** shows additionally a unique $\text{Pt}\cdots\text{H}-\text{O}_{\text{rez3}}$ synthons involving directly the Pt(II) center. **Pt2rez3** and **Pt1rez3** exhibit yellow luminescence in the solid state. The shape and vibronic structure of the emission bands observed both at $T = 298$ K and at $T = 77$ K suggest the phosphorescence originating from the anionic luminophores. For both cocrystal salts some bathochromic shift in emission patterns can be notified compared with the precursors. A relatively large shift of 13 nm for **Pt2rez3** may be due to a unique $\text{rez3O}-\text{H}\cdots\text{Pt}\cdots\text{H}-\text{O}_{\text{rez3}}$ arrangement, $d(\text{Pt}\cdots\text{H}) = 2.581$ Å, where the valence electronic density of Pt complex is interfered by the positive electrostatic potential of proton. Combination of the organic cofomer with the presented luminophores did not quench their phosphorescence, and high-intensity emission might be still observed and tuned.

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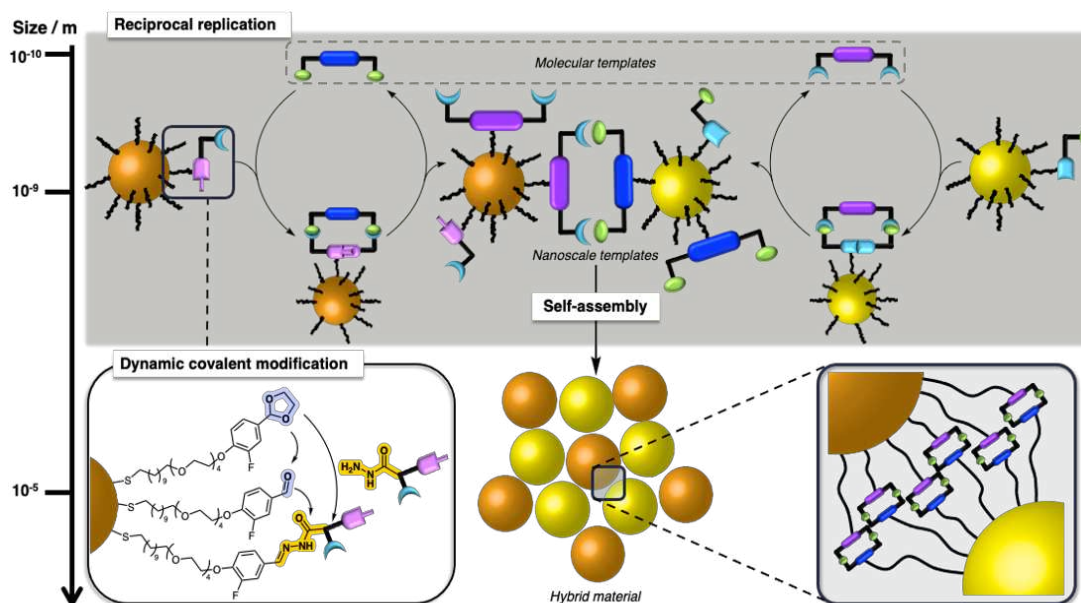
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Abstract No: T92

T92 Hierarchical reaction networks: replication induced formation of hybrid materials

Laura Gravener Euan Kay, Douglas Philp

University of St Andrews, St Andrews, United Kingdom



Caption: Schematic showing the instructed formation of nanoscale templates through reciprocal replication, and their self-assembly to form a hybrid material.

De novo life requires systems capable of replication, compartmentalisation, and metabolism.¹ Artificial replicating systems that are based on molecular templates² and on micelles³ and fibres⁴ have been developed to mimic the replication processes observed in nature.

Through dynamic covalent modification of nanoparticle-bound molecular monolayers,⁵ we aim to incorporate an artificial molecular replicator onto the surface of colloidal nanoparticles (NPs) to create replication-enabled NPs (RENPs). These RENPs serve as platforms to transmit information from the level of a molecular template to the formation of hybrid materials that incorporate both metal nanoparticles and organic materials in a controlled manner. A molecular replicating template (Figure) initiates a hierarchical reaction network where this molecular instruction is amplified through reciprocal template effects to create nanoparticle surfaces that are decorated with recognition sites. These recognition active NPs can then undergo assembly with complementary NPs to create a hybrid material. The use of reciprocal replicating templates enables the selective incorporation of more than one type of nanoparticle building block in the same hybrid self-assembling nanomaterial.

This poster will show the development of a reciprocal replicating system, as well as the attachment strategy of one of these reciprocal recognition units on to the surface of a NP using dynamic covalent modification.

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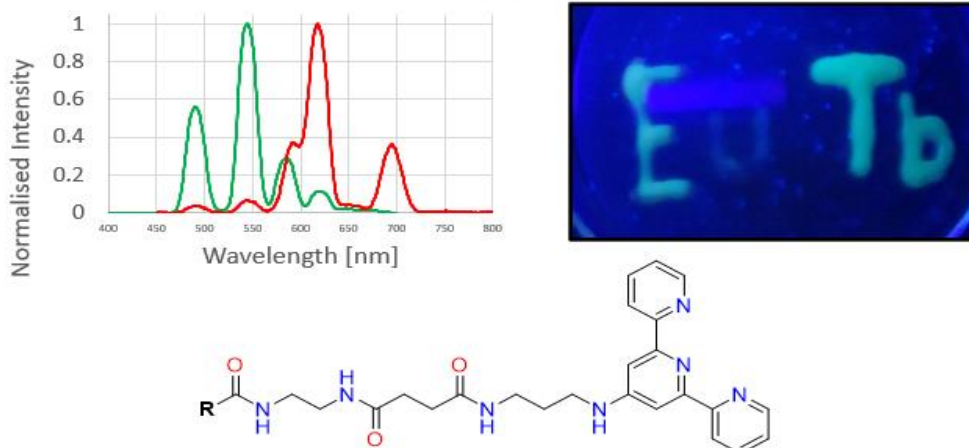
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T93 Engineered Supramolecular Gels as 3D-Printable Functional Materials

Tomas Gudmundsson, Thorfinnur Gunnlaugsson Sebastian A. Barwich, Matthias Moebius

Trinity College Dublin, Dublin, Ireland

Metal detection: Tb(III) and Eu(III)



Caption: The figure displays the gelator structures, R represents the different functional groups on each gelator. Luminescent gels were made and 3D-printed.

The development of functional supramolecular gels for 3D-printing is an emerging field with impressive potential. Supramolecular gels are viscoelastic soft materials which have seen significant success in biomedical applications, as electronic devices, and in luminescence-based technologies.¹ Additionally, 3D-printing facilitates the generation of complex shapes and structures which can be easily adapted for the desired purpose, such as polymer gels that have been 3D-printed for specific tissue engineering.² Supramolecular gels, unlike polymer-based gels, form by reversible non-covalent interactions which endow the gel with inherent self-healing properties that can be manipulated for extrusion-based printing. Under strain, the gels will turn into viscous liquids and regain their gel state once the extrusion is complete, making them ideal for facile extrusion-based printing.³ Introducing supramolecular gels to 3D-printing opens up new avenues in the generation of novel functional materials.

Using rational design rules, various gelators were generated from small terpyridine-based gelators to large tripodal molecules based on a previous motif from the group.⁴ Gels formed successfully in many cases, and their self-assembly properties were characterised using a variety of techniques to correlate the gelator structure to the macro-properties. We found that doping the gels with lanthanide ions resulted in 3D-printable, luminescent soft materials. Additionally, the metal-free gels responded to metal ions and could be used as lanthanide metal detectors. Analysis of the materials to understand the 3D printing properties will be presented along with a demonstration of their functionalities.

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Abstract No: T94

T94 Structurally Equivalent Packing Motifs of Acid-Terminated Arylene-Alkynylenes and Monodisperse Oligomers on Graphite

David Ari Hofmeister, Sigurd Höger, Stefan-Sven Jester Lucas Rothe, Tristan Johannes Keller, Dirk Laux

University of Bonn, Bonn, Germany

Arylene-alkynylenes with different lengths form supramolecular nanopatterns at the solid/liquid interface of graphite (HOPG) and a solution, that are imaged by scanning tunneling microscopy (STM) with submolecular resolution. In general, the structure of supramolecular nanopatterns depends on (i) the exact geometry of shape persistent backbones, (ii) the substitution with functional groups, and (iii) (intermolecularly interdigitating) alkoxy side chains. Acid-terminated rigid rod molecules for example are known to form a pattern consisting of dimers which propagates on a large scale on a surface like graphite.^[1,2] This predictability of interactions on the surface can be used to design nanopatterns with specific characteristics. Here, we report on the surface patterning of arylene-alkynylene rods that carry hexadecyloxy side chains and carboxylic acid end groups, and monodisperse oligomers of alike systems. Both species form structurally equivalent packing motifs on a surface, which is drawn back to similar spatial requirements of carboxylic acid dimers that form after adsorption and butadiynylene units.

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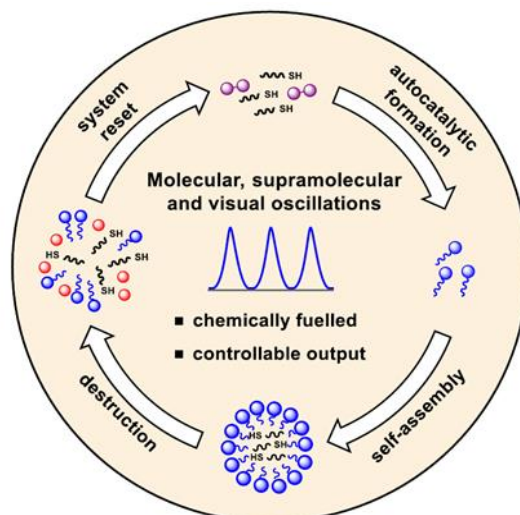
Abstract No: T95

T95 Encoding information and transporting cargo with a supramolecular oscillator

Michael G. Howlett, Anthonius H. J. Engwerda and Stephen P. Fletcher

Chemistry Research Laboratory, University of Oxford, Oxford, UK

Keywords: autocatalysis, out-of-equilibrium, lipids, origins of life, replicators



Caption: Chemical fuelling of an autocatalytic reaction network enables the periodic, and controllable, growth and decay of micelle structures.

A key goal of chemistry is to develop synthetic systems that mimic biology, such as self-assembling, self-replicating models of minimal life forms. Oscillations are often observed in complex biological networks, and are fascinating non-equilibrium phenomena. Yet, life-like oscillators using self-replicating chemical species are unknown, and how to control autonomous supramolecular level oscillations is also not established.

We have developed a chemically-fuelled supramolecular system where a population of self-reproducing lipids autonomously oscillates, causing micellar species to repeatedly appear and disappear in time [1]. The reaction swings back and forth like a pendulum, oscillating between enhanced micelle formation and enhanced micelle destruction. The interplay of molecular and supramolecular events is key to observing oscillations and by understanding the feedback in this dynamic system, we have been able to freely tune the amplitude and frequency of the waveforms produced.

If harnessed, chemical oscillators such as this may unlock new directions for (supra)molecular technology across different length scales. To this end, our recent studies also show that these oscillations can transport material in an oscillation-driven pump and can encode information in the form of chemical waves.

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T96 Functional Supramolecular Materials Based on Orthogonal Self-assembly

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Supramolecular self-assembly is an important means of creating novel structures and generating new functionality. With the rapid development of supramolecular chemistry, researchers are no longer satisfied with just constructing novel supramolecular structures, but are thinking about how to use the synergistic assembly process to realize the construction of complicated but highly ordered supramolecular systems with specific functions at the molecular level and above, thus providing new material basis and theoretical guidance for the research fields such as material science, life science, and information science.

Focusing on the two important challenges in supramolecular chemistry, including how to achieve successful control of the collaborative self-assembly processes and how to realize the in-depth applications of the fabricated assemblies, we have been engaged in the construction of functional supramolecular systems and proposed an efficient “cooperative orthogonal self-assembly” strategy to investigate the controllable supramolecular assembly process and achieve its functionalization through the incorporation of different types of non-interfering non-covalent interactions,¹ and has accomplished the following achievements: (1) Based on the orthogonal self-assembly of different supramolecular interactions, smart drug delivery systems have been successfully constructed to achieve accurate delivery and controlled release of anticancer drugs.² (2) Based on the orthogonal integration strategy of different properties, controllable construction of the stimuli-responsive supramolecular assemblies and their functional regulation such as in fabricating switchable materials for smart windows and artificial light harvesting systems have been realized.³ The above research results provide new insights for the construction and functional application of novel supramolecular materials with specific architectures and functionalities.

In future work, we aim to develop an innovative strategy of “orthogonal integration of non-covalent interactions and performance”⁴ to clarify the structure-activity relationship of molecular design, structural assembly, and functional regulation from molecular, mesoscopic, and macroscopic levels, which is expected to realize the controllable construction and functional integration of complicated assembly systems and functional materials.

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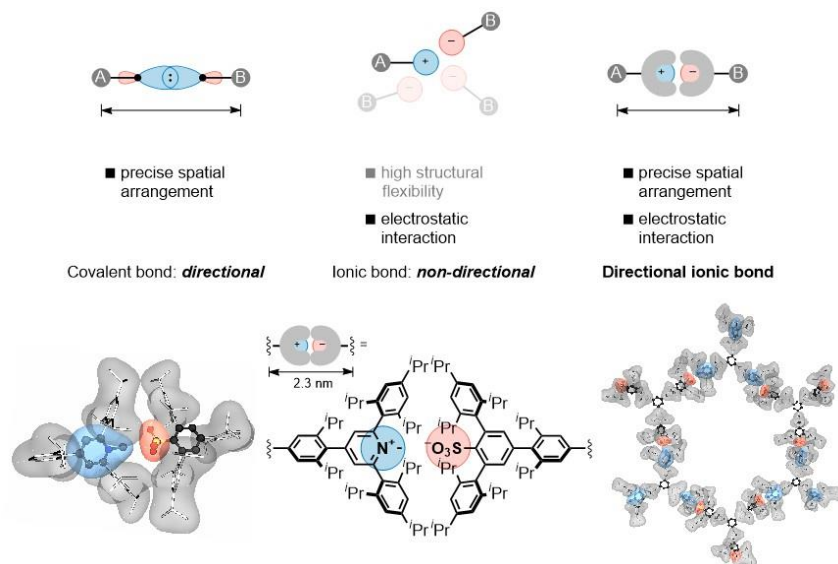
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Abstract No: T97

T97 Directional Ionic Bonds

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Non-covalent interactions (NCIs) are ubiquitous element in biomolecules and play a critical role in the three-dimensional structuring of the matter.^{1,2} Ionic bonds are the strongest type of NCIs and might reach energies comparable to covalent bonds.^{3–5} High directionality is a hallmark of the bonds with major covalent character, however, the ionic bonds inherently lack such property due to the spherically-symmetrical nature of the electric field around simple ions.⁶ We describe a strategy to impart the directionality to ionic bonds allowing them to acquire a predictable directional orientation.⁷

Our design of directional ionic bonds includes the installation of a sterically demanding shielding nonpolar hydrocarbon environment around the ions that leaves the charged group exposed in one direction only. In this way, a directional approach of two oppositely charged ions is possible, which minimizes the charge separation and maximizes the Coulomb attractive forces, while other relative orientations result in larger charge separations due to the steric repulsion between the shielding backbones.

The generality of our concept is showcased with a series of N-methylpyridinium···arylsulfonate ion pairs that possess different shielding groups around the charged moieties. The X-ray diffraction analysis revealed the presence of geometrically predictable directional ionic bonds. Furthermore, multiple directional ionic bonds were utilized to build supramolecular systems at the scale of several nanometers by the formation of a two-dimensional hexagonal lattice with a 5.2 nm diagonal, composed of six directional ionic bonds. Such ionically bonded framework is an example of a complementary strategy for the directional construction of organic materials at the nanoscale by exploiting the otherwise non-directional Coulomb interaction between two ions.

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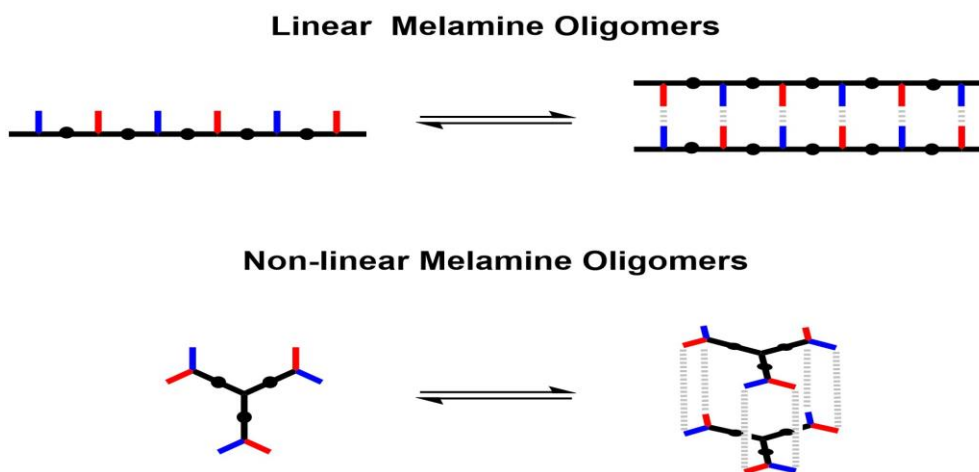
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Abstract No: T98

T98 Self-Assembly of Recognition-Encoded Melamine Dendrimers

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Caption: Schematic representation of the self-assembly of a non-linear recognition-encoded melamine oligomer

A promising synthetic system capable of storing and replicating chemical information consists of a melamine-based backbone encoded with phenol and phosphine oxide recognition units. Hydrogen bonding between these recognition units leads to sequence-selective duplex formation between complementary oligomers¹.

The trifunctional melamine unit also provides scope for the design of non-linear recognition-encoded oligomers. The work presented in this poster investigates the self-assembly of low-generation melamine dendrimers encoded with hydrogen bonding recognition units in chloroform and toluene by ITC and NMR experiments. Comparison of the measured association constants with those of the corresponding linear oligomers provided evidence that the dendritic structures self-assemble into discrete bimolecular complexes with all hydrogen bonding interactions formed. The formation of higher order complexes was also observed and structures for these complexes were proposed.

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Abstract No: T99

T99 From New Hydrogen-Bond cis-Chelate $\{M(CN)_6\}^{3-};(\text{polyresorcinol})_x$ Synthons Towards Non-Centrosymmetric Space Groups and Second Harmonic Generation

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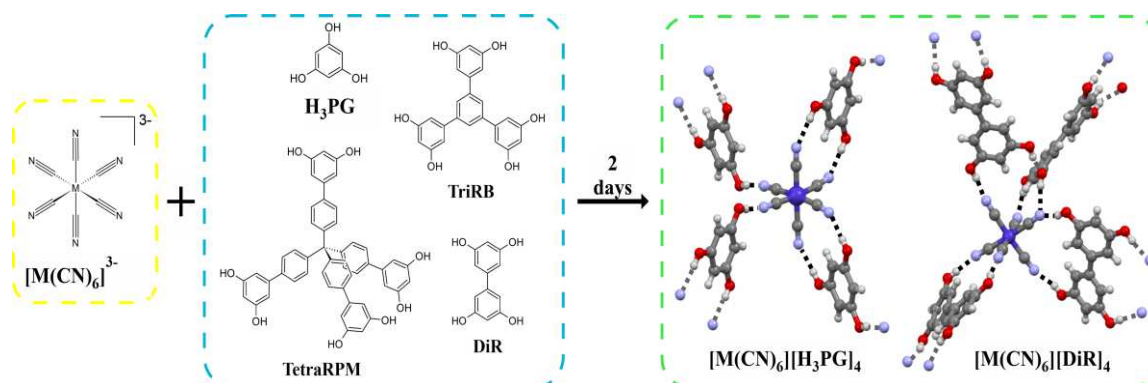
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Caption: Towards new $\{[M(CN)_6]^{3-};(\text{polyresorcinol})\}$ synthons and the related co-crystalline salts

Co-crystals are multicomponent systems composed of two or more different molecular or ionic compounds that are present in the stoichiometric ratio and assembled together by non-covalent interactions in the crystal lattice. The non-covalent interactions affect co-crystal lattice energy what results in generally more stable structures compared to the crystal structures of the individual components.^[1] The intermolecular interactions and resulting crystal structures can generate physical and chemical properties that differ from the properties of the individual components, i.e., solubility, chemical stability, or optical second harmonic generation (SHG) properties.^[2]

In this work we present new co-crystalline salts involving co-formers dedicated to the binding of anionic complexes. We present the new series of isomorphous co-crystalline salts $(PPh_4)_3\{[M(CN)_6](H_3PG)_2\} \cdot 2MeCN$ (H_3PG - 1,3,5-trihydroxybenzene) exhibiting unique supramolecular “cis-chelate” topological synthons modifying physicochemical properties of $[M(CN)_6]^{3-}$. Further, we develop this family in a modular manner using DiR, TriRB or TetraRPM polyresorcinol oligophenylene molecules^[3] acting as multisite $[M(CN)_6]^{3-}$ receptors. The resulting new co-crystalline salts $(PPh_4)_3\{[M(CN)_6](L)_x\} \cdot nMeCN \cdot nMeOH$ ($L = DiR, TriRB, TetraRPM; x = 1, 2; n = 0, 0.5, 1, 2$) were crystallized in centrosymmetric, non-centrosymmetric or chiral space groups. We discuss crystalline phases stability and pseudo-polymorphism, modification of spectroscopic properties, and notable photoluminescent or SHG performance and THz spectroscopic properties, according to the individual properties of tectons, and due to the obtained space groups.^[4]

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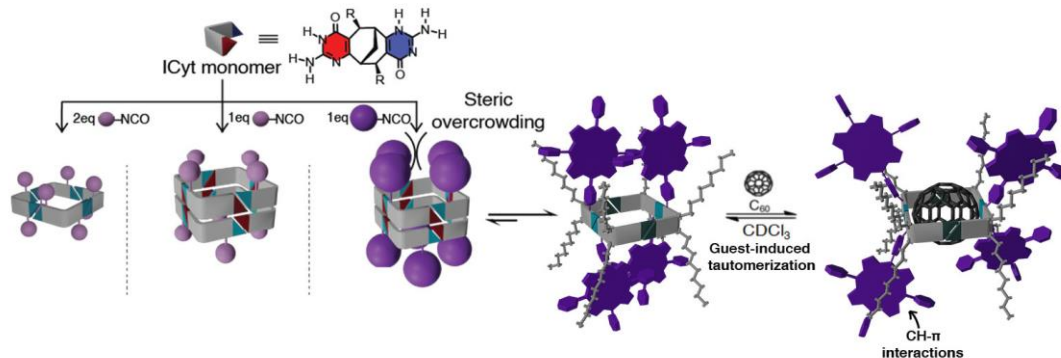
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T100 CONCAVE SUPRAMOLECULAR ARCHITECTURES EXHIBITING DYNAMIC PROPERTIES

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Caption: Dynamic hydrogen-bonded tubular supramolecular assemblies.

Despite being widely abundant in nature, synthetic self-assembling systems are still underdeveloped, and there are several challenges that must be overcome before fully functional molecular devices can be achieved. The individual components utilized in the bottom-up construction have to be equipped with appropriate shape and symmetry to be able to aggregate in a well-defined, controlled manner and to overcome the entropic penalty arising from the loss of disorder. The current discoveries in the field emphasize on more dynamic models of molecular recognition, such as induced-fit and conformational selection in pursuit of synthetic receptors, catalysts or cross-membrane transporters. These advances stress the necessity to go beyond conventional rigid supramolecular architectures, challenging us to develop reversible biomimetic supramolecular systems encompassing conformationally flexible frameworks.^{1,2}

To contribute to these efforts, we became interested in development of hollow supramolecular architectures with adaptable cavity utilizing enantiopure bicyclo[3.3.1]nonane monomers. The ability to control self-complementary scaffold via tautomerization reinforced by secondary interactions¹, different number of hydrogen bonds or recognition behavior of rival components provide facile access to different binding models². Subsequently, as a means to probe the dynamic host properties of supramolecular capsules, fullerene C₆₀ was complexed within its well-defined inner space.

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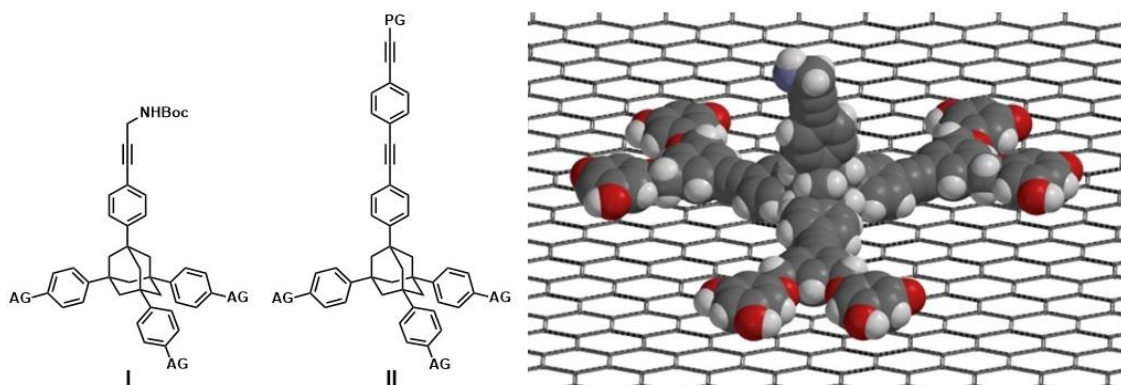
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Abstract No: T101

T101 Tripod-Shaped Molecules – Towards Surface Functionalization

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Caption: Structural formula of platform molecule I (left) and II (middle), as well as a simplified supramolecular model of I (right) on graphene.

In recent years the research concerning supramolecular self-assembly on various surfaces has mostly focused on the understanding of self-assembly processes, as well as characterizing the structures and properties of the resulting nanopatterns. Mono- as well as multi-component self-assembly processes have been studied. Due to the intense research, a deep understanding has developed, and the next step is to go beyond “decorative” self-assembly.^[1]

This work focuses on the synthesis and templated self-assembly of tripodal platform molecules^[2] I and II (Figure 1) with functionalized head-groups. After applying an organic solution thereof to highly oriented pyrolytic graphite (HOPG), its anchoring groups (AG) orient in parallel to the surface and mediate the formation of robust self-assembled monolayers. These are in-depth investigated by submolecularly resolved scanning tunnelling microscopy. Hence, functionalities are generated, that are decoupled from the surface and thus have potential applications for instance as molecular rotors, sensing materials or molecular switches.^[3]

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Abstract No: T102

T102 Heterogeneous water oxidation catalysis in porous materials

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Mimicking the oxygen evolving Photosystem II (OEC-PSII) has been a successful strategy for the design of supramolecular architectures for homogenous water oxidation catalysis.^[1-3] The implementation of well-defined molecular water oxidation catalysts (WOCs) into crystalline framework materials would lead to heterogeneous catalysts with improved stability, recyclability and structural integrity. As one of the very few examples available in the literature so far, we recently reported on Ru(bda)-containing (bda = 2,2'-Bipyridine-6,6'-dicarboxylate) COF nanoparticles with excellent performance in heterogeneous water oxidation.^[4] Here, we expand on this concept and report on the incorporation of Ru(bda) units as linear building blocks in MOFs or the encapsulation of molecular WOCs in crystalline organic cages. The immobilization of Ru(bda) WOCs within the porous matrices significantly improved the stability of the catalysts and resulted in heterogeneous WOCs with excellent durability and performance.

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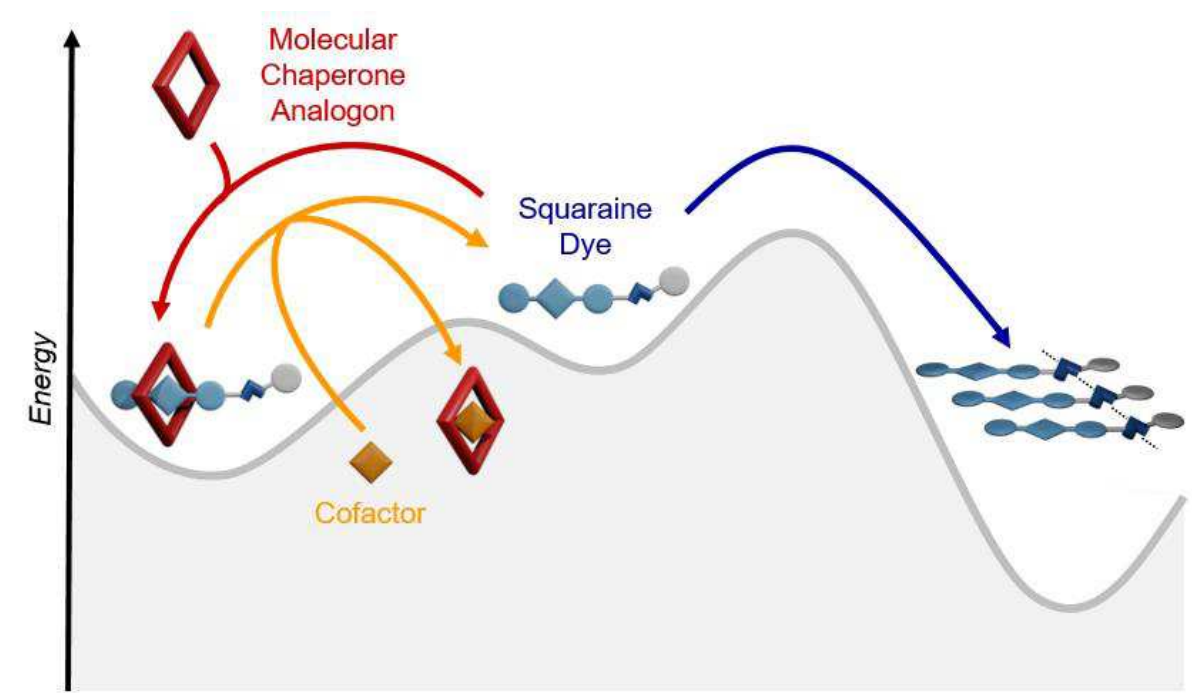
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Abstract No: T103

T103 Controlling the Supramolecular Polymerization of Squaraine Dyes by Molecular Chaperone Analoga

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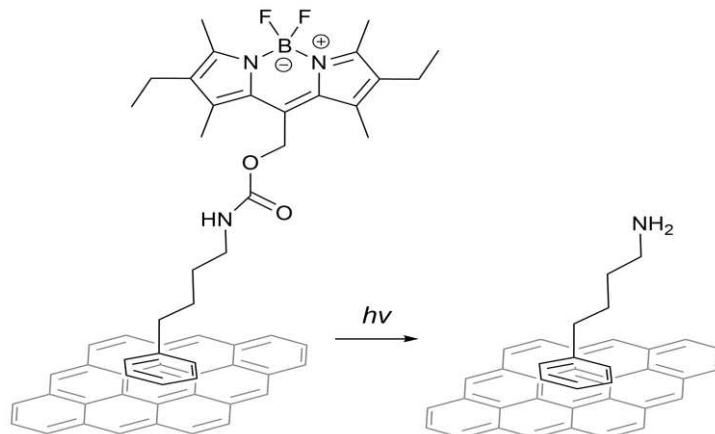
Molecular chaperones are proteins that assist the (un)folding and (dis)assembly of other macromolecular structures towards their biologically functional state in a non-covalent manner. Transferring this concept from nature to artificial self-assembly processes, here we show a new strategy to control supramolecular polymerization via a chaperone-like two-component system. A new kinetic trapping method was developed which enables efficient retardation of the spontaneous self-assembly of a squaraine dye monomer. The suppression of supramolecular polymerization could be regulated with a cofactor which precisely initiates self-assembly. In this way, we demonstrate a new possibility for effective control over supramolecular polymerization processes.

Abstract No: T104

T104 Photocleavable BODIPY-based compounds for selective graphene functionalization

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Caption: Figure 1. Schematic presentation of green light (520 – 540 nm) induced photocleavage of the BODIPY compound while bound to graphene via π -interactions.

Using photocleavable protecting groups (PPGs) allows selective light-induced bond breaking *in situ*, which is beneficial for materials chemistry applications and chemical surface modification. Boron-dipyrromethene (BODIPY) compounds can be used as PPGs, which can be removed with visible light in green to red light regions.^{1,2} BODIPY-based PPGs are especially useful for biological and medical applications because visible light is less harmful than UV light required to deprotect many other PPGs.³

Our project aims at guiding neuron growth on graphene-based surfaces using BODIPY-protected amines. When amines are deprotected *via* photoexposure, they can enhance neuron growth⁴. For this purpose, we designed and synthesized BODIPY-protected amines with an aromatic end groups to enable π -interaction-based attachment to the graphene surface (Figure 1). After attaching the molecule on the graphene, amines can be deprotected selectively by directing light to specific regions. Green light-induced photocleavage of the compounds was proved in solution with UV-vis and NMR spectroscopies. Results from Raman spectroscopy supported attachment of the compound (Figure 1) to graphene and its photodegradation on graphene.

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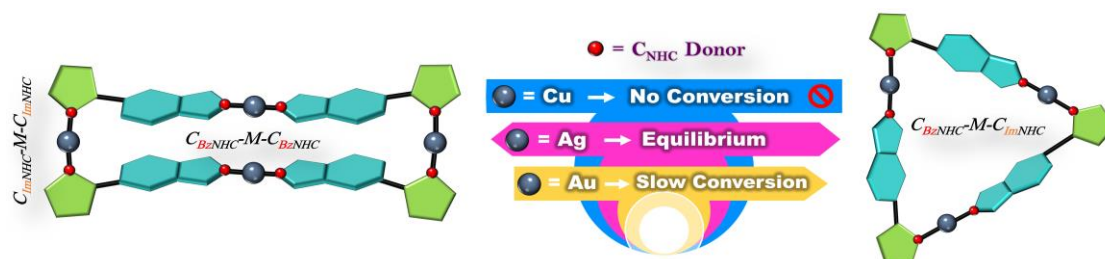
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Abstract No: T105

T105 Unprecedented Metal Driven Chemistry between the Self-Assembled Tri- and Tetranuclear Species of a Heteroditopic Bis-N-Heterocyclic Carbene Ligand and Coinage Metal Ions

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Metallo-supramolecular chemistry has evolved into a mature and highly interdisciplinary domain of research by transcending the conventional boundaries of science partly due to the captivating physical/chemical properties and fascinating structures possessed by the supramolecules.¹ Coordination-driven self-assembly is the most commonly adopted strategy for accessing such discrete architectures, which utilizes the directional advantages of metal-ligand coordination to provide a better control over the design of various supramolecules. Further, 'self-correction' is an important feature of self-assembly process, which allows the system to thermodynamically control the formation of a specific architecture over other possible forms. However, absence of a clear thermodynamic preference often leads to the existence of several species, occasionally also in equilibrium, in solution. After the first report of such equilibrium by Fujita *et al.* in 1996,² varieties of such self-assemblies have been reported however, they are based on only the Werner type ligands (N and/or O donor). Whereas, such type of systems with C-donor (NHC) ligands are unknown. This could possibly be attributed to the relatively strong M-C_{NHC} bond, which makes it difficult for the system to self-sort by breaking and making of bonds. Nevertheless, the labile nature of Ag-C_{NHC} bond provides the unique opportunity to attain such equilibrium if combined with the suitable NHC based ligands. Along this line, we have used a bis-NHC ligand,³ possessing a free to rotate imidazolylidene (ImNHC) donor installed on a benzimidazolylidene (BzNHC) platform. We are delighted to report here that the corresponding Ag^I-NHC complexes exist in equilibrium between the tri- and tetranuclear forms in solution, observed first time for C_{NHC}-donor to the best of our knowledge, which is supported by various studies like NMR (¹H, VT, 2D-DOSY), ESI-MS, and the concentration studies. It is important to note that this process is exclusive for the Ag^I-ion in combination with our heteroditopic bis-NHC ligand as with other coinage metals (Au^I and Cu^I), no such equilibrium was noticed in the solution. Interestingly, a slow conversion from tetra- to trinuclear form in solution, increases with temp., was observed for the analogous Au^I-complexes, whereas the Cu^I-complexes exist exclusively in tetranuclear form both in solution and solid state.

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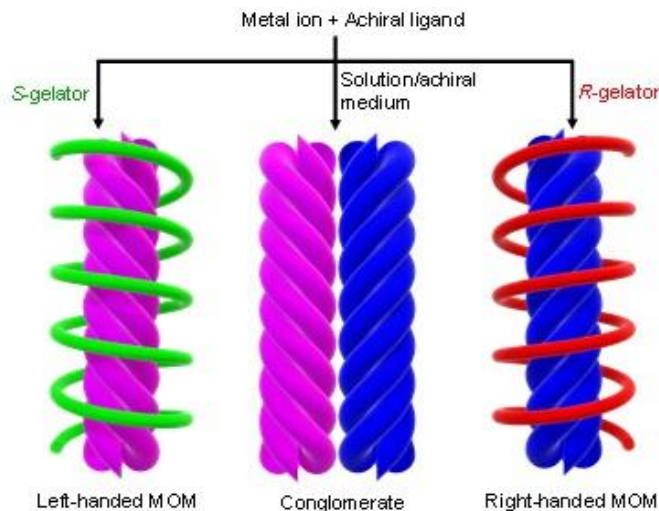
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Abstract No: T106

T106 Chiral LMWGs based on amino acid derivatives for inorganic synthesis

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Caption: Figure 1. Formation of MOMs in chiral gel and solution/achiral medium

Supramolecular gels based on chiral low molecular weight gelators (LMWGs) have been an exciting class of soft materials due to their emerging applications¹ in catalysis and templates for crystallizing inorganic materials and as confined media for organic/synthesis. We have shown that the chirality of the gelator bias towards a specific enantiomer that will help to isolate a particular enantiomer² and have reported the gel phase synthesis of enantiopure metal-organic materials (MOMs) from achiral components (Figure 1). The chiral LMWGs used were C2-/C3-amides based on amino acid derivatives and C3-symmetric trimesic amides showed better enantioselectivity in MOM synthesis compared to C2-symmetric terephthalic amides.² The role of amide moiety of LMWGs in gel phase synthesis was analysed by replacing the amide groups with urea moieties. Urea moieties have been extensively used in supramolecular gelators because urea motifs self-assemble via complementary hydrogen bonding ($N-H \cdots O=C$) involving N-H donor and C=O acceptor³⁻⁴ into one-dimensional arrays of hydrogen-bonded chain to form \square -tapes (fibrils). The formation of the 1-D hydrogen-bonded chains can be considered as the key parameter for gel network formation and the aggregation of these fibrils results in an entangled three-dimensional framework.

In this work, we will synthesise C2-/C3-urea based on amino acid derivatives for the gel phase synthesis of enantiopure metal-organic materials (MOMs). To achieve this task, we have synthesised C3-symmetric 1,3,5-tris-(aminomethyl)-benzene urea of enantiopure alanine, valine and phenylalanine. We have tested the gelation properties of these compounds and the gel strength was analysed by sol-to-gel transition temperature and rheology, and the morphologies were analysed by scanning electron microscopy. The gel phase synthesis of MOMs using these gels is ongoing, which will enable us to study the role of urea moieties in the enantioselective synthesis of MOMs.

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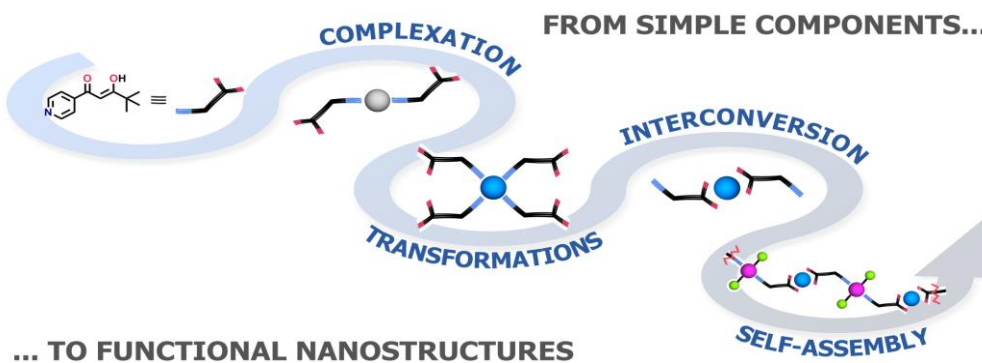
Abstract No: T107

T107 Coordination-driven structural switching from simple Ag(I), Pd(II) and Pt(II) complexes to functional heterometallic nanomaterials

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Caption: Supramolecular transformations within coordination-driven assemblies based on HL.

Metal-ligand interactions are the primary driving force in the generation of simple coordination compounds, as well as of metallosupramolecular architectures with a high degree of complexity and a precisely defined structure.¹ Taking into account the character of a coordinate bond, *i.e.* its high strength but commonly dynamic nature, coordination-driven self-assembly processes are characterized by high controllability at the molecular level with respect to directionality, reversibility and post-synthetic switchability.² In the presented research, a bifunctional ligand 4,4-dimethyl-1-(pyridin-4-yl)pentane-1,3-dione (HL) able to provide two distinct coordination sites, *i.e.* anionic β -diketonate (after deprotonation) and neutral pyridine, has been used in the synthesis of Ag(I), Pd(II) and Pt(II) complexes that then have been applied as metalloligands for the construction of new heterometallic polymeric materials. The ambidentate nature of L^- enables switching between different modes of coordination within mononuclear complexes or their conversion into polymeric species in a fully controllable way. The coordination-driven processes can be triggered by various stimuli, *i.e.* a metal salt addition or acid-base equilibria, and presents an efficient strategy for the generation of metallosupramolecular materials. As a consequence of self-assembly, new multimetallic coordination aggregates have been synthesized and characterized in depth in solution as well as in the solid state. Furthermore, the Pd-based assemblies have been found to be efficient catalyst precursors in the Heck cross-coupling reaction, demonstrating a direct impact of compositional and morphological differences on their catalytic activity.

Acknowledgements: The financial support was provided by the National Science Centre (GK, grant PRELUDIUM 2022/45/N/ST4/00518; ARS, grant SONATA BIS 2018/30/E/ST5/00032).

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Abstract No: T108

T108 Drop-cast superhydrophobic coating from side-chain fluorinated low molecular weight gelators

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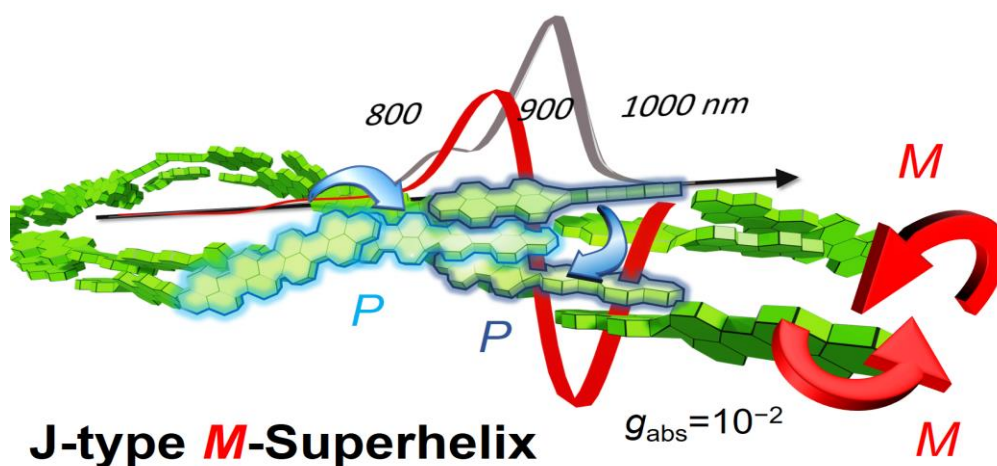
Superhydrophobic surfaces can be quickly formed with supramolecular materials. Incorporating low molecular weight gelators (LMWGs) with perfluorinated side chains generates xerogel coatings with low surface energies and high roughness. These LMWGs all have a cyclohexyl-1,2-diamide core and two perfluorinated ponytails, whose lengths varies from three to ten carbon atoms (CF₃ to CF₁₀). The self-assembled aggregates of the LMWGs were examined with scanning electron microscopy, showing particular structures and morphologies. Superhydrophobicity and oleophobicity are observed on the xerogel coatings. To test their stabilities, the xerogel coatings were multiply flushed with a standardized water flush test. The removal of material from the surface in these flushes was monitored by a combination of water contact angle, contact angle hysteresis and coating thickness measurements. A new method based on image processing techniques was developed to reliably determine the change of coating thickness. In addition, pull-off force measurements with atomic force microscopy are adopted to provide quantitative results about how the presence of the fluorinated chains, and the length of these chains, affects the adhesion force measured on the bulk material. To broaden the applicability, acrylate monomers are added to the coating mixture. After irradiation, the polymer-supramolecular co-assembly provides coating that is hydrophobic and highly scratch-resistant.

Abstract No: T109

T109 An Enantiopure J-Aggregate of Quaterrylene Bisimides for Strong Chiroptical NIR-Response

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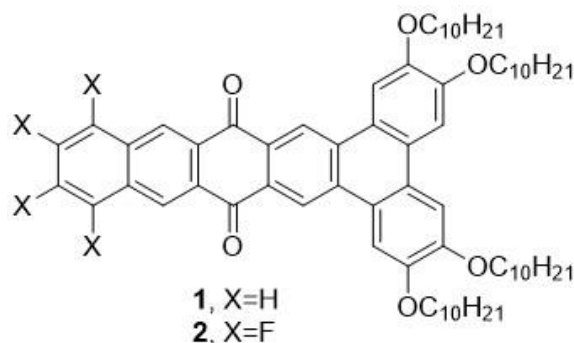
Chiral polycyclic aromatic hydrocarbons (PAH) can be tailored for next-generation photonic materials by carefully designing their molecular as well as supramolecular architecture. Hence, excitonic coupling can boost the chiroptical response in extended aggregates but is still challenging to achieve by pure self-assembly. Whereas most reports on these potential materials cover the UV and visible spectral range, systems in the near infrared are underdeveloped. We report a new quaterrylene bisimide (QBI) derivative with a conformationally stable twisted π -backbone enabled by the sterical congestion of a fourfold bay-arylation. Rendering the π -subplanes accessible by small imide substituents allows for a slip-stacked chiral arrangement by kinetic self-assembly in apolar *n*-hexane. The well dispersed solid-state aggregate reveals a sharp optical signature of strong J-type excitonic coupling in both, absorption (897 nm) as well as emission (913 nm) far in the NIR region and reaches absorption dissymmetry factors up to 1.1×10^{-2} . The structural elucidation was achieved by AFM and single-crystal X-ray analysis which we combined to derive a structural model of a fourfold stranded enantiopure superhelix. We could deduce the role of phenyl substituents not only granting stable axial chirality but also guiding the chromophore into a chiral supramolecular conformation needed for strong excitonic chirality.

Abstract No: T110

T110 Self-Assembly of Polycyclic Hydrocarbons: the Design of New Liquid Crystalline Materials

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Columnar liquid crystalline materials are ordered phases that feature extended π -stacked arrays, making them potentially useful as organic semiconductors.¹ The formation of columnar liquid crystals is influenced by π -stacking interactions,² so the successful design of stable columnar liquid crystals incorporates strategies to control these interactions. Here we will describe strategies for promoting π -stacking for the design of stable columnar liquid crystals. In particular, we will focus on using arene-perfluoroarene interactions, which have been used effectively in crystal engineering to promote effective stacking between neighbouring molecules.³ These interactions have not been widely used in the design of columnar liquid crystals.⁴ For example, we report the synthesis and mesophase characterization of a dibenzopentacenequinone derivative and a homolog with a partially fluorinated terminal ring. While both compounds display columnar hexagonal mesophases, compound the fluorinated compound exhibits its mesophase over a dramatically broader temperature range.⁵ These results suggest that arene-perfluoroarene interaction effectively promote π -stacking, leading to a stabilization of the columnar mesophase.

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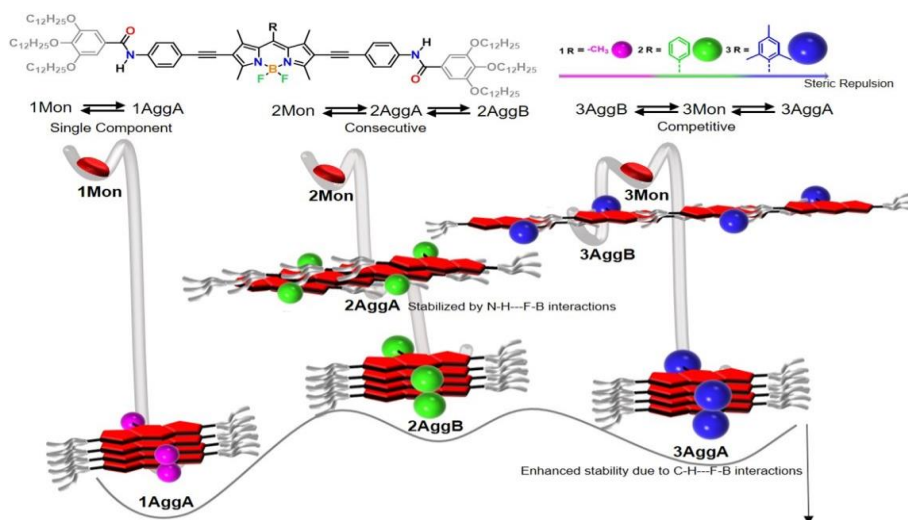
Abstract No: T111

T111 Sterically favoured H-type Supramolecular Polymerizations

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Caption: Molecular structures of 1, 2 & 3 and corresponding energy profiles illustrating their aggregation pathways.

Balancing attractive and repulsive interactions is a powerful design strategy for achieving precise supramolecular interaction patterns and target-associated (photophysical) properties ^[1, 2]. However, systematic investigations on these effects are still lacking, which represents a bottleneck in supramolecular polymer design. Herein we demonstrate that a sequential increase in steric demand on a chromophore can result in an unusual rise in supramolecular stability, owing to unconventional intermolecular recognition patterns. In our approach, we have investigated two new 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) dyes that differ in the substituents at the meso position (phenyl (**2**) & mesitylene (**3**)). Based on a combination of experimental studies and theoretical calculations we have discovered that the on-pathway kinetic aggregate **2AggA** is stabilized by an unusual N-H...F-B hydrogen bonding interaction in solution, while all other aggregates are stabilized by classical amide hydrogen bonding interactions. In addition, unexpected C-H...F-B hydrogen bonds lead to enhanced stability of the mesitylene H aggregates (**3AggA**), resulting in an unconventional increase in supramolecular stability upon increasing steric demand. As a consequence of the more favorable placement of the hydrogen atoms in **3** due to the added C-spacer when compared to **2**, an overall decrease in dye-dye distance can be observed. In turn, this arrangement also leads to a tighter hydrogen bonding pattern between the amides and an overall stabilization of the ensemble. By using this approach, we anticipate that the emerging balancing between attractive forces and steric effects along with decreased interchromophoric interaction between the BODIPY dyes will enrich the area of controlled supramolecular polymerization in non-polar media and open new research avenues.

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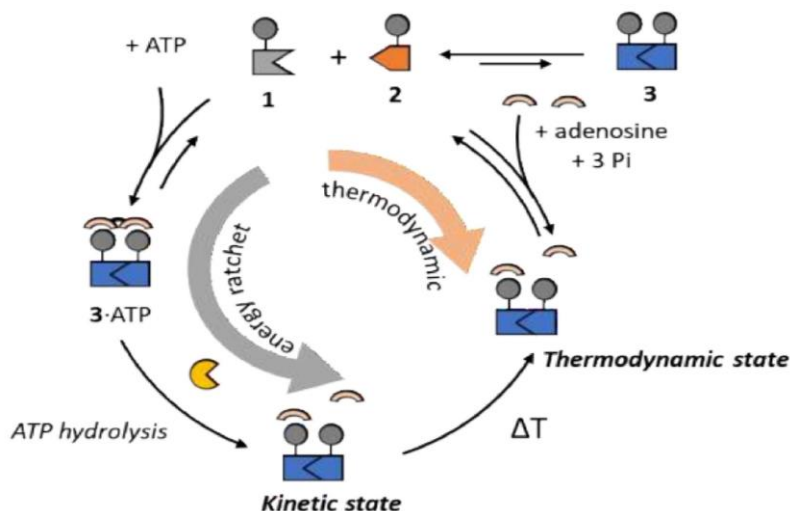
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Abstract No: T112

T112 ATP drives a dynamic covalent reaction to a non-equilibrium composition using an energy ratchet mechanism

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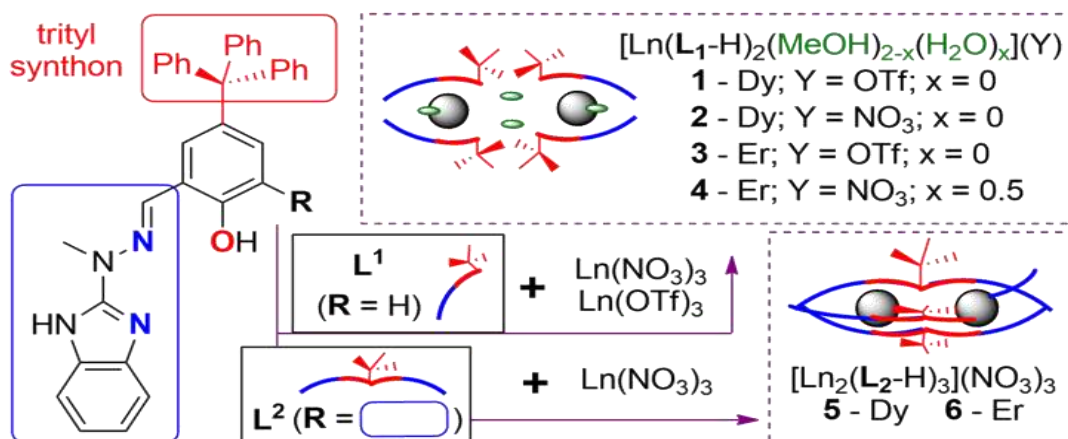
The development of synthetic matter endowed with life-like properties requires the ability to rationally design systems that operate away from thermodynamic equilibrium at the expense of energy¹. Great strides have been made in the development of synthetic molecular machinery able to convert energy in the form of light, electricity, or chemicals into work². Dissipative materials have been developed that rely on energy input to maintain structural integrity and display emerging properties³. At the macroscopic level it has been shown that systems can reside in a macroscopic non-equilibrium steady state as a result of energy consumption⁴. Here, we show that an energy consumption process can also be coupled to a single chemical reaction. The coupling results in a non-equilibrium composition that is shifted in favour of the product. We have studied hydrazone-bond formation between aldehyde **1** and hydrazide **2**. This equilibrium reaction falls into the class of imine-type dynamic covalent bond formation, which is one of the most applied reactions for the development of supramolecular systems⁵. An energy ratchet mechanism is exploited in which in the first step a chemical trigger, ATP, is used to accelerate the reaction and stabilize the hydrazone **3**. In the second step, ATP hydrolysis installs a kinetically stable state in which the hydrazone concentration is higher than the one at equilibrium, which is restored by heating the sample (ΔT). We show that the system in the non-equilibrium state has a higher catalytic activity in the hydrolysis of an RNA-model compound compared to the equilibrium state.

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Abstract No: T113

T113 Supramolecular architectures based on lanthanide metal ions as a single-ion magnets

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Caption: Figure 1. Structural representation of trityl-appended ligands used in this study and their Ln(III) coordination assemblies.

The rational design and appropriate modification of molecular architectures is a primary step for generation of tailor-made advanced multifunctional materials. Materials based on supramolecular approach are readily tunable at the molecular level, and in principle, information programmed into the molecular-scale building blocks can be translated through the nano- and micro-scales up to the macroscopic level. Various future applications like molecular spintronics quantum information processing and high-density information storage has rendered Single Molecule Magnets (SMMs) a thoroughly studied domain of a priority importance. Along this line, numerous studies were performed to understand and predict unique properties of these systems, magnetic hysteresis below their blocking temperature (T_B) and magnetic bi-stability that rely on the effective energy barrier to spin reversal (U_{eff}). [1]

Triphenylmethane (trityl) group has been recognized as a supramolecular synthon in crystal engineering, molecular machine rotors and stereochemical chirality inductors in materials science. [2]

Herein we demonstrate for the first time how it can be utilized in the domain of molecular magnetic materials through tuning of the slow magnetic relaxation processes within the lanthanide single molecule magnets in tandem with other non-covalent interactions. Trityl-appended mono- (L^1) and bis-compartmental (L^2) hydrazone ligands were synthesized (Figure 1) and complexed with Dy(III) and Er(III) triflate and nitrate salts to generate six, effectively dinuclear complexes. While high level of isostructurality was observed in all coordination compounds within the given ligand class, the fourfold phenyl embraces and hydrogen bonding are responsible for transformation of monometallic complexes (1 - 4) into the pseudo-dimeric assemblies with the N^2O L^1 ligand. [3]

This work was supported by: PRELUDIUM grant UMO-2022/45/N/ST4/00344 from National Science Centre, Poland and IDUB-UAM "Scientific conferences - support for the participation of scientists and doctoral students in prestigious scientific conferences"

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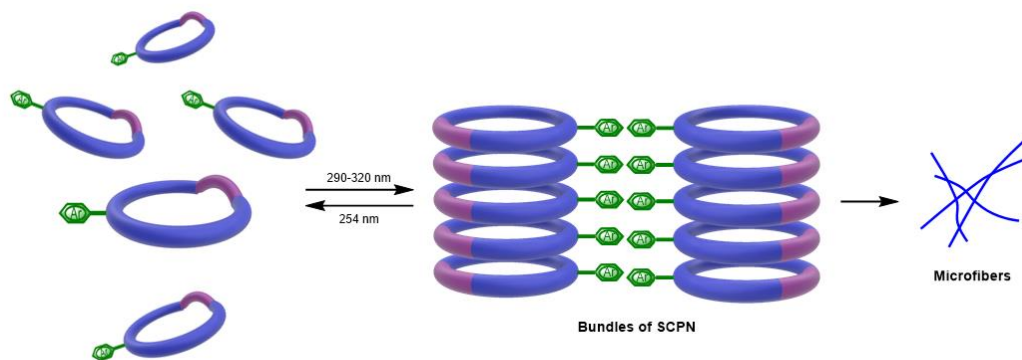
T114 PHOTO-MODULATED ASSEMBLY OF CYCLIC PEPTIDE NANOTUBES

Vilela-Picos Marcos ¹, Granja Juan R. ³ Novelli Federica ¹, Pazó Antía ¹, Méndez-Ardoy Alejandro ¹, Marafon Giulia ², Amorín Manuel ¹, Moretto Alessandro ²

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Caption: Figure 1. Illustration of the photo-modulated assembly process of peptide nanotubes.

Self-assembling cyclic peptide nanotubes (SCPNs) are tubular supramolecular polymers formed by the orderly stacking of peptide macrocycles through hydrogen bonding interactions.^[1] These hollow assemblies are ideal tools for the construction of functional materials due to the easy modulation of their internal and external properties for different applications.^[1,2] However, it remains a challenge to precisely control the nanotube dynamics. In this regard, recently our group has been focused on the study of changes in the SCPN self-assembling properties by light irradiation. For example, we have reported the photo-induced bending of the peptide architecture.^[3]

Herein, we present the design, synthesis and application of novel SCPNs in which the assembly/disassembly process can be induced by appropriate light irradiation. These cyclic peptides were obtained by solid-phase synthesis and their stimuli-responsive self-assembly properties were investigated through various techniques. Our outcomes also show the spatially controlled polymerization of cyclic peptides in confined spaces. We envisage that these photo-responsive properties can enable new functions for these peptide assemblies.

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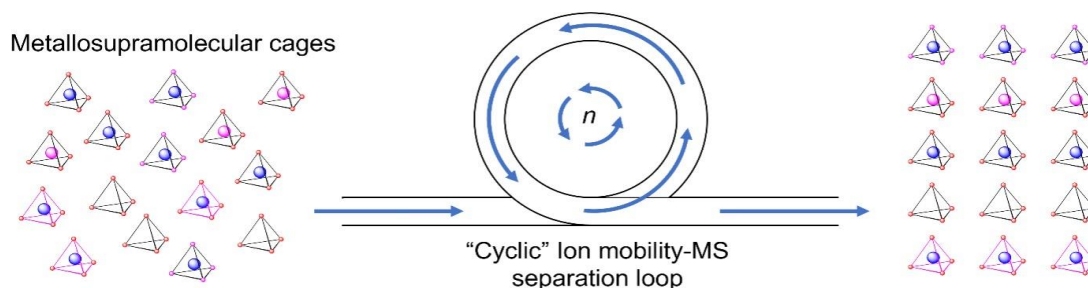
Abstract No: T115

T115 Separation and identification of diastereomers of metallocupramolecular cages from dynamic mixtures of interconverting species

John McMurtrie ¹ Michael Pfrunder ², Therese Fulloon ², Jason Hong ², David Marshall ², Berwyck Poad ², Stephen Blanksby ², Jack Clegg ², Kathleen Mullen ²

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² , ,



Caption: Separation and identification of components in complex mixtures of metallocupramolecular cages.

Metallocupramolecular cages with internal cavities have myriad applications including enantio- and regioselective catalysis, molecular sensing, stabilisation of reactive species and drug delivery.^[1] Characterisation of pure high symmetry species is relatively straight forward but heteroleptic, mixed metal and/or low symmetry species are often present in confounding mixtures. These species can be difficult to characterise, not just due to their structural complexity, but because their dynamic behaviour in solution leads to isomer interconversion, reversible guest binding and other structural rearrangements. Traditional techniques including nuclear magnetic resonance, single crystal X-ray diffraction and electrospray ionisation mass spectrometry (MS) are typically employed to achieve this end with variable success. Another technique, ion-mobility MS, is growing in popularity^[2] as it can provide information about the shape and size of many co-existing species simultaneously without requiring purification or growth of single crystals.

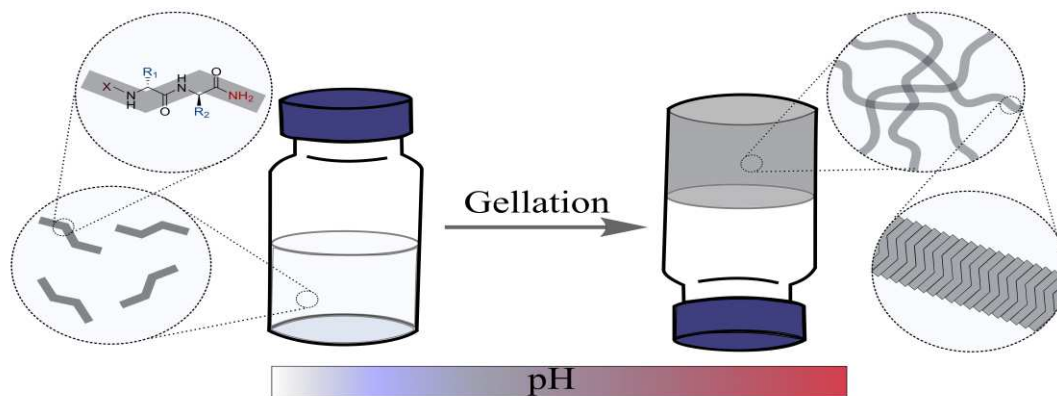
Using the separating power of cyclic ion-mobility, we have extracted and resolved diastereomers of a series of M_4L_6 cages from a complex mixture of kinetically labile interconverting molecules. We have extended this methodology to investigate cages containing mixtures of different metals, including paramagnetic ions such as octahedral Co^{2+} and Ni^{2+} revealing information regarding the equilibrium ratio of isomers that is not possible to discern using traditional techniques. The potential applications for this technique as both a specialist tool and a standard characterisation technique for the analysis of metallocupramolecular cages will be explored and our progress to date on this will be discussed.

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Abstract No: T116

T116 pH sensitive dipeptides for hydrogelation in physiological conditions

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Caption: Fig. 1: pH-triggered hydrogelation of our novel self-assembled dipeptide family. X: pH-responsive group; R1 and R2: CH₃ or CH₂Ph. Adapted from (1).

Peptide hydrogels are systems composed of small peptides that are arranged to form a network of fibers capable of trapping water inside (**Fig.1**) (1). These supramolecular materials hold great potential as drug-releasing reservoirs, wound healing and cell culture among others due to their liquid-semisolid transition in response to pH changes, in addition to their biocompatibility and biodegradability (2). On account of the pH response of the 20 natural amino acids, which is restricted to acidic media (pH < 7), it has not been possible to expand their applicability across the whole range of physiological pH thus far. Consequently, the development of peptide hydrogels with liquid-gel transitions at pH values close to neutrality (e.g., physiological pH = 7.4) will be a powerful tool in the field of pharmaceutical technology and biological and materials chemistry.

With this aim, we designed, synthesized and characterized a library of 16 structural derivatives of the Fmoc-FF-OH, one of the most widely used dipeptides in gelation, by modifying its three key positions: the hydrophobic peptide chain, and the C- and N-terminal ends. In this sense, the acid-base role traditionally played by the carboxy-terminal group is replaced by a pH sensitive group at the N-terminal end (X), using a neutral amide instead. Furthermore, the influence of the hydrophobicity of the peptide chain on the gelation tendency was studied through the permutation of the side chain phenylalanine group for an alanine side chain in the two different possible positions.

This work not only breaks with the traditional structure of gelling dipeptides, but also presents a novel family of dipeptide hydrogels with sol-gel transition in the desired pH range, thus extending their applicability as biomaterials in the physiological pH range.

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Abstract No: T117

T117 Templated Out-of-Equilibrium Self-Assembly of Branched Au Nanoshells

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Out-of-equilibrium self-assembly of metal nanoparticles (NPs) has been devised using different types of strategies and fuels, but achieving finite 3D structures with a controlled morphology through this assembly mode is still rare. Here, a spherical peptide-gold superstructure (PAuSS) is used as a template to control the out-of-equilibrium self-assembly of Au NPs, obtaining a transient 3D-branched Au-nanoshell (BAuNS) stabilized by sodium dodecyl sulphate (SDS). The BAuNS dismantles upon SDS concentration gradient equilibration over time in the sample solution, leading to NPs disassembly and regression to PAuSS. Notably, BAuNS assembly and disassembly promotes temporary interparticle plasmonic coupling, leading to reversible and tunable changes of their plasmonic properties, a highly desirable behavior in the development of optoelectronic nanodevices.

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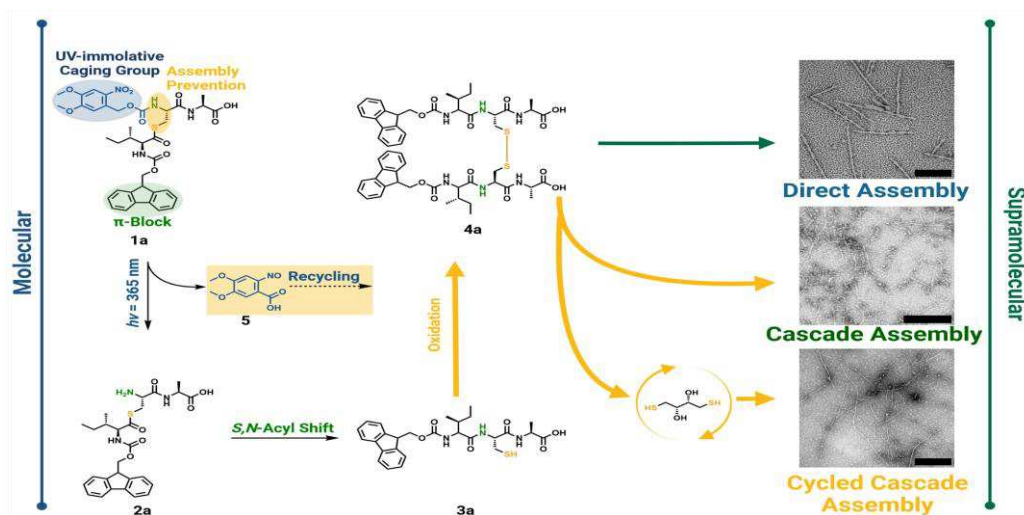
Marchetti, A.; Gori, A.; Ferretti, A. M.; Arenas Esteban, D.; Bals, S.; Pigliacelli, C.; Metrangolo, P. *Small* 2023, <https://doi.org/10.1002/smll.202206712>.

Abstract No: T118

T118 Supramolecular Assembly Guided by Photolytic Redox Cycling

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Caption: Photolytic cascade production of different supramolecular assemblies.

The ability to control the assembly of peptide nanostructures and their morphology is not only crucial in nature but also allows for tailor-made synthetic materials with various applications in biomedical or material science. Precise nanostructures require a facile and accessible synthetic platform that offer a dynamic control over assembly and morphology.

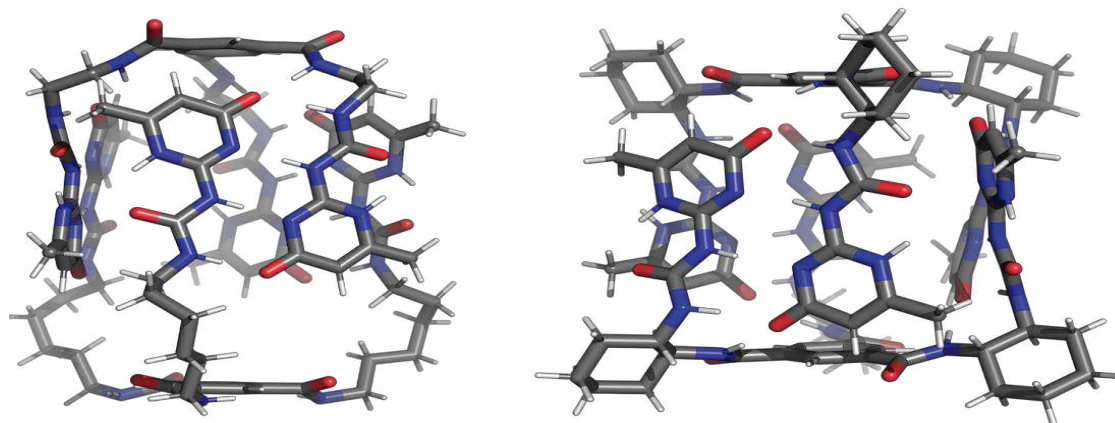
To achieve this, we designed a pro-assembling peptide that can perform a photolytic reaction cascade with different redox pathways, which determine the molecular, as well as the supramolecular structure. The redox state of the peptide can be modulated by introducing different thiols to either stop the cascade at the thiol level or delay its oxidation to the disulfide. Furthermore, this reaction cascade generates hierarchical assemblies different of those produced by direct dissolving of compounds.

Abstract No: T119

T119 H-bonded Supramolecular Capsules

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Vilnius University, Vilnius,



Caption: Supramolecular H-bonded trigonal prisms

Supramolecular capsules are a class of self-assembled molecular containers that have garnered significant attention in various fields of chemistry due to their potential for a wide range of applications including unique modes of catalysis in a confined inner space. They are formed through non-covalent interactions between molecular building blocks, which allows for their reversible assembly and disassembly, making them highly dynamic and responsive to external stimuli.

Supramolecular capsules assembled from several subunits enable precise sculpting of molecular surface for selective guest recognition. As a rule, more structurally elaborated monomers give more predictable outcomes of the self-assembly, but unfortunately at the expense of synthetic efforts involved in their preparation. Herein we present our approach toward well-defined capsular H-bonded aggregates using non-preorganized monomers. The strategy relies on the utilization of H-bonding between multitopic ureidopyrimidinone containing monomers further shaping the overall structure with secondary H-bonding within the linker. The proposed concept greatly simplifies the monomer design and allows an introduction of curvature starting from acyclic and flexible units.

Abstract No: T120

T120 Structural influences on the self-assembly of BTA derivatives

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Building blocks based on benzene-1,3,5-tricarboxamide (BTA) have been widely investigated, due to their simple synthesis and countless possibilities of modification. Very well-studied and extremely important group of BTAs is amino ester decorated molecules.¹ The amino acid moiety as a structural motif has major impact on the supramolecular structure, due to encoded H-bonding pattern, which generally leads to helical structures.²

But not only columnar structures can form as a result of self-assembly of BTA molecules, as we have shown in the example of the non-covalent aggregation of four benzene-1,3,5-tricarboxamide derivatives formed from glycine or L-valine esters (-Me, -iPr), in the solid-state and in chloroform solution.³ Two types of self-assembled structures were characterized: a dimeric capsule and a columnar assembly. In-depth solid-state studies revealed the significant role of the steric bulk of the C-terminus protecting group in supramolecular aggregation in the solid-state. On the other hand, in chloroform solution, the amino acid sidechain determines the self-assembly outcome.³

However, we already shown that such a molecules are also able to form octameric nanocapsule⁴ when decorated with three s-trityl-L-cysteine molecules and having free carboxyl group. This component in solid state and as a solution in chlorinated solvents forms a large hydrogen bonded octameric nanocapsule held together by 48 hydrogen bonds having the ability to selectively bind fullerene C₇₀ as guest molecules.⁴

The presentation will show how structural changes in the BTA amino acids decorated building blocks affect their self-assembly products in solution and solid state.

We thank National Science Centre (SONATA BIS 2018/30/E/ST5/00032) for financial support.

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Abstract No: T121

T121 New Dimension in Supramolecular Chemistry: 3D- Cages to 2D- Nanosheets

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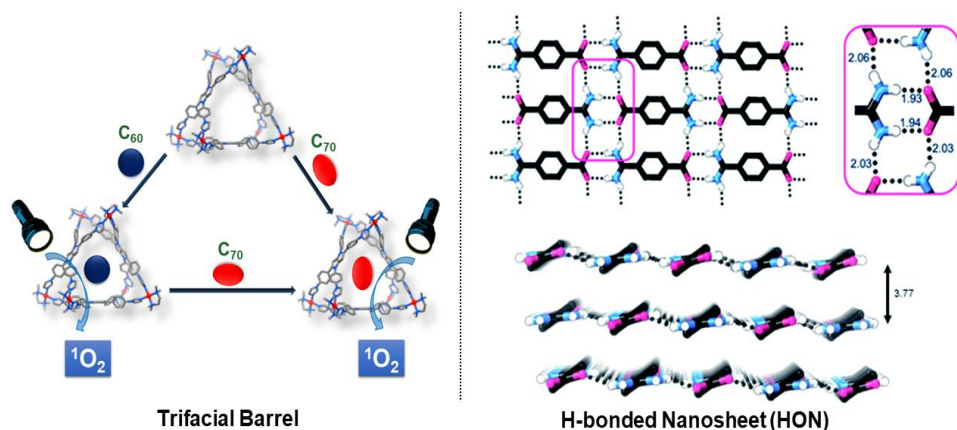


Figure: (left) Trifacial barrel showing preferential binding towards C₇₀ over C₆₀ and (right) two-dimensional hydrogen bonded nanosheet.

Supramolecular Chemistry offers limitless possibilities for designing well-defined architectures with interesting properties and applications. Through my research, I am interested in development of structurally diverse supramolecular systems, ranging from three-dimensional cages to two-dimensional nanosheets and investigating their applications.

During this presentation, I will show highlights from my recent work where metal-ligand coordination driven self-assembly approach has been employed to develop cages. A new Pd₆ trifacial barrel will be presented, which is composed of three 1,4-dihydropyrrolo[3,2-b]pyrrole panels, clipped through six *cis*-Pd(II) acceptors.¹ Large open windows and cavity make it an efficient host for large guest. Thorough investigation reveals that, barrel has stronger binding affinity towards C₇₀ over C₆₀ which leads to the predominant extraction of C₇₀ from their mixture. Another NHC based cage shows rigidity induced enhancement of emission and selectivity towards nitroaromatics sensing².

I will also discuss my current research which is focused on the liquid exfoliation of layered supramolecular materials to convert them into two-dimensional nanosheets. The high surface area, aspect ratios, and nanoscopic dimensions of these nanosheets make them potential candidate for a wide range of applications like sensing, catalysis, separation. I will show the first example of generation of free standing monolayered hydrogen bonded nanosheets (HONs)³ that are connected in two-dimensions.

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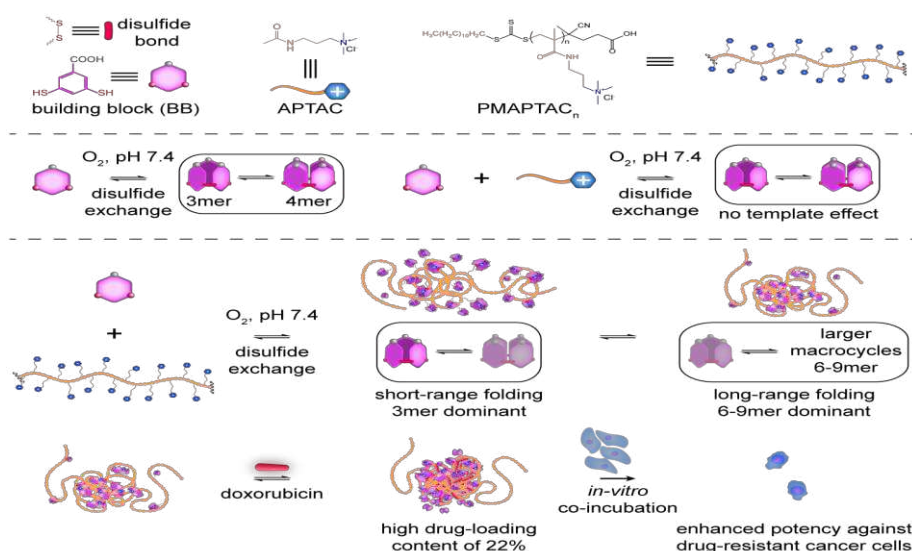
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Abstract No: T122

T122 Dynamic Combinatorial Chemistry: A Synchronising Strategy to Explore Single-Chain Folded Nanoparticle

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Caption: The synchronization between dynamic network of macrocycles and polymer's folding, which was further applied as nanocarrier for anti-cancer drug.

In terms of biomimetic synthesis of single-chain folded nanoparticles (SCNPs) with dynamic, adaptive and biocompatible properties as proteins, many efforts have been made to explore supramolecular SCNPs of polymer folded by non-covalent crosslinkers.¹ However, it remains challenging to catch up the natural paradigm. Previous works has primarily used crosslinkers with immutable chemical structures, which limited the possibility to unravel, fit and exploit the dynamic arrangements of the polymer's chain segments during folding.

Here, rather than optimizing the fixed chemical structures of non-covalent crosslinkers, we used dynamic combinatorial chemistry (DCC) to fabricate libraries of interconvertible anionic macrocycles with various sizes as potential non-covalent crosslinkers (Fig.1),² from which the macrocycles' distribution was spontaneously adjusted to accommodate the dynamic folding process. The parent linear cationic homo-polymer was in a more extended conformation before being added to the library in excessive positive charge. As polymer's cationic pendants and the macrocycles were complexed through electrostatic interactions, the complexed pendants became hydrophobic, and triggered folding. Trimeric macrocycles facilitated the first-stage short-range folding, which gradually rendered more up-coming long-range folding to amplify the entropically unfavorable larger macrocycles.

Moreover, these SCNPs were less cytotoxic than the parent polymer and functioned as stimuli-responsive nanocarrier for the anti-cancer drug doxorubicin, enhancing its potency against the multi-drug resistant ovarian cancer cells *in vitro*. Our findings demonstrated that DCC is a powerful tool to explore adaptive molecular systems synchronizing the dynamic process of folding in SCNPs, opening new possibilities in reducing functional nano-devices' size for specific applications. i.e. delivering drug molecules against brain diseases.

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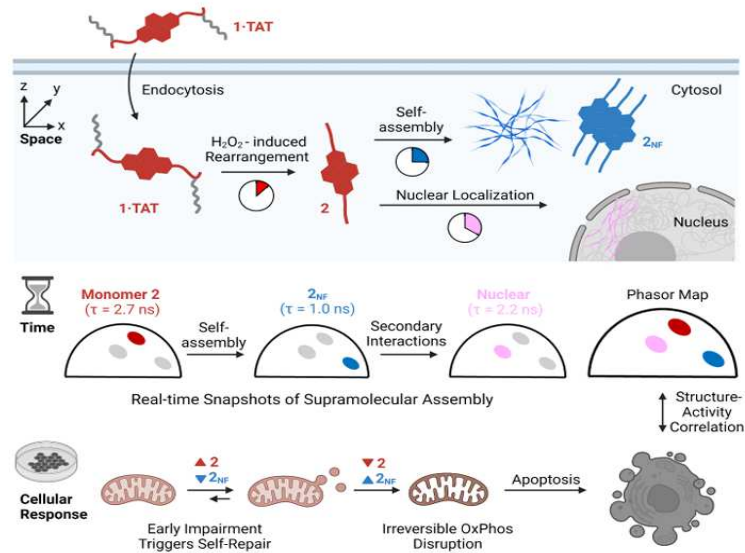
Abstract No: T123

T123 Resolving Bioactive Supramolecular Structure Formation in Live Cells by Phasor-Fluorescence Lifetime Imaging

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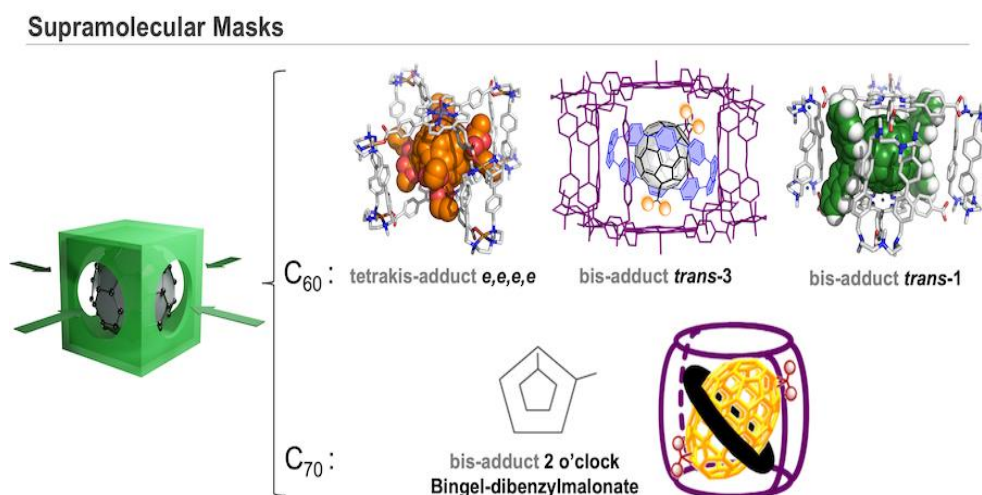
Supramolecular polymerization creates transient and life-defining functions in complex cellular systems but synthetically driven analogues has been held back by the lack of real-time correlation. Most synthetically assembled nanostructures in cells are studied when structure formation has reached equilibrium, creating a knowledge divide to the events initiated during the dynamic polymerization phase. Fourier transformed fluorescence lifetime fluctuations allow us to observe these molecular events on the fly, enabling the visualization of the monomers, intermediates, nanostructures and secondary cellular interactions on a 2-D phasor plot. We study the time-lapsed polymerization of amyloid-like naphthalene diimide peptides in MDA-MB 231 cells and show that the growth phase shuts ATP production. The cells then react to overcome the initial stress by mounting an increased respiratory capacity as structure formation nears equilibrium. By coupling simple and fit-free fluorescence lifetime responses to supramolecular chemistry, we reliably detail assembly dynamics and their biological effects with spatiotemporal resolution.

T124 REGIOFUNCTIONALIZATION OF FULLERENES BY THE SUPRAMOLECULAR MASK STRATEGY

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² , ,



The regioselective functionalization of fullerenes and the control of the number of adducts is highly important to unbar the development of fullerene chemistry. Nowadays, easy-accessible C₆₀ and C₇₀ fullerene mono-adducts are mainly used in any application¹ due to the hampered accessibility to pure alternative fullerene poly-adduct derivatives. In a general basis, multi-adduct mixtures with uncontrolled regioselectivity (multi-isomers) are obtained, and chromatographic purification is too costly and time consuming to be used in the synthesis of multi-adduct fullerene species. Herein, supramolecular tetragonal prismatic nanocapsules^{2,3} are used as supramolecular masks to tame the over-reactivity of Bingel-Hirsch-type cyclopropanation reactions and, more importantly, to have full control on the equatorial regioselectivity and on the number of additions. Thus, exclusively equatorial bis-, tris- and tetrakis-C₆₀ adducts using ethyl-bromomalonate are stepwise obtained and fully characterized (NMR, UV-vis and XRD). Furthermore, the regioselectivity control is finely tuned using a three-shell Matryoshka-like assembly towards the synthesis of a single *trans*-3 bis-Bingel-C₆₀ for the first time. Also, the mask strategy is extended to Diels Alder reactions with full control of the regioselectivity in the synthesis of *trans*-1 bis-pentacene-C₆₀.⁵ Results in the bis-regiofunctionalization of C₇₀ with dibenzyl-bromomalonate to obtain exclusively the 2 o'clock Bingel regioisomer will be presented. These results, fully attributed to the confinement control imposed by the capsule's cavity, represent a novel and unique strategy to infer regio-control to the synthesis of fullerene multi-adducts, which might find use in multiple applications.

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Abstract No: T125

T125 Design and Synthesis of Acid Terminated Rods and Monodisperse Oligomers for Surface Decoration

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Due to their intriguing properties rigid rods consisting of phenylene–ethynylene (PE) or phenylene–ethynylene–butadiynylene (PEB) units have gained large interest as building blocks for optoelectronic devices, such as OLEDs.^[1,2] Oligomeric rods (e.g. OPEs and OPEBs) are prepared from their respective monomeric structures by a stepwise synthesis *via* sonogashira and glaser coupling reactions. OPEs and OPEBs are known to form two-dimensionally (2D) crystalline packings on highly oriented pyrolytic graphite (HOPG).^[3] The structure of two-dimensional crystals depends on the exact geometry of the shape-persistent backbones, the substitution with functional groups that mediate the interaction of such species, and (intermolecularly interdigitating) alkoxy side chains. Here we report on the synthesis of three rigid rod systems containing different numbers of monomer units. For investigations on their surface patterning, acid-terminated monomer rods are synthesized for comparison with oligomeric rods, which are connected by butadiynylene units.

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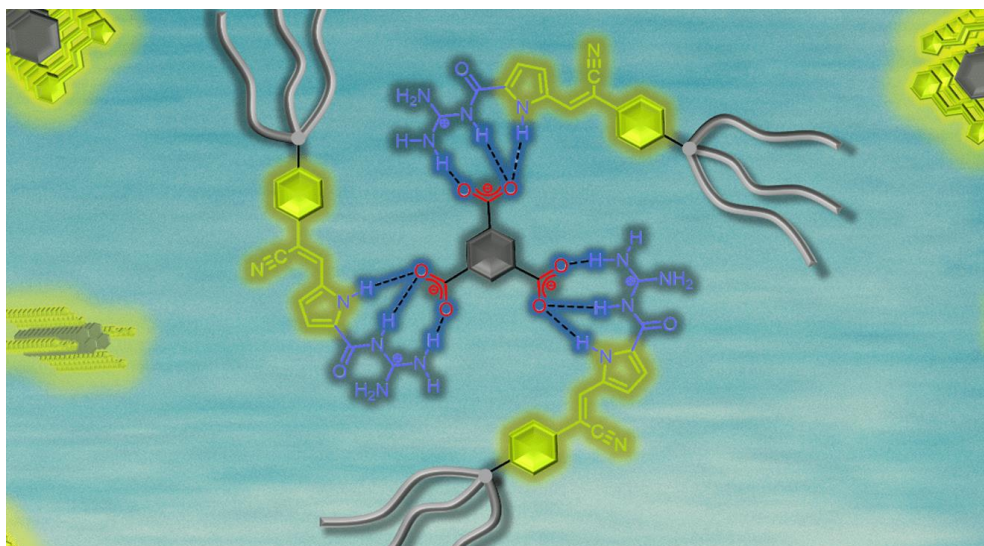
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Abstract No: T126

T126 Oxo-Anion Binding Amphiphiles – Supramolecular Assembly and Photophysical Properties

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Caption: Schematic presentation of expected amphiphile-complexes.

Amphiphiles are part of our daily lives. From mass-produced surfactants in cleaning processes to special synthesized micelles for gene-transfection, there are many applications for spontaneously self-assembling molecules.^[1-3] Combining such materials with other intrinsic properties, like luminescence or sensor-like binding moieties, can widen this span even further. One of these is the Guanidinio-Carbonyl-Pyrrol (GCP) motif, established by Carsten Schmuck in 2000.^[4] By forming several hydrogen bonds in a certain spatial arrangement, this group exclusively binds to oxo-anions like carboxylates or phosphates. GCP is known for over a decade and was recently functionalized into a planar-shaped emitter featuring aggregation-induced emission properties by our group.

In the presented work all three fields, self-assembly, oxo-anion-binding- and AIE-behaviour, are combined into single molecules: Phenylacetonitrile-GCP-amphiphiles. Two of these are tested towards their binding behaviour to aromatic oligo-carboxylates and their resulting self-assembly. Because of the overall planar shape of both components forming the supra-amphiphile, we expect defined structures from stacked complexes, which will be examined by electron-microscopy. Moreover the emission properties are enhanced in the formed complexes due to the restricted molecular motion. The photophysical properties are screened for the monomers and the formed complexes.

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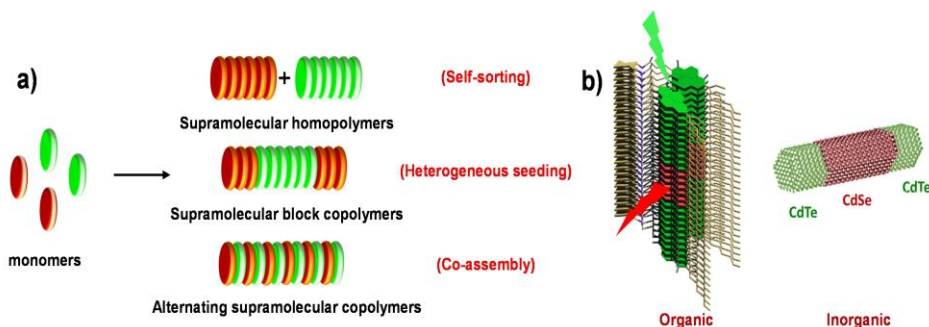
Abstract No: T127

T127 Axial Organic Heterostructures via Sequence Controlled Supramolecular Block CoPolymerization

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Sequence control is a vital and ubiquitous phenomenon observed in nature. The genetic information encrypted in sequence controlled biological polymers like DNA and RNA gets translated into polypeptide synthesis which determines protein and many biological functions. Taking nature as an inspiration, recent challenges in synthetic polymer chemistry is more directed towards control over the monomer sequences.¹ However such label of control in supramolecular polymers is more challenging considering the dynamic nature of non-covalent bonds and interactions.² Mastery of such label of control would bring new macroscopic and microscopic properties in supramolecular polymers.

However, supramolecular polymerization with even two components is challenging and the sequence outcome could be either self-sorted supramolecular homopolymers (AAA and BBB), a random or alternate supramolecular co-polymer (ABABAB) or complex supramolecular block co-polymer (AABBAA) whose sequence is determined by the free energy of intermolecular (homo AA, BB vs. hetero AB) inter-actions, monomer structure and monomer exchange dynamics. Particularly synthesis of supramolecular block copolymer is a grand challenge in this field which has been achieved in very limited number of examples.²

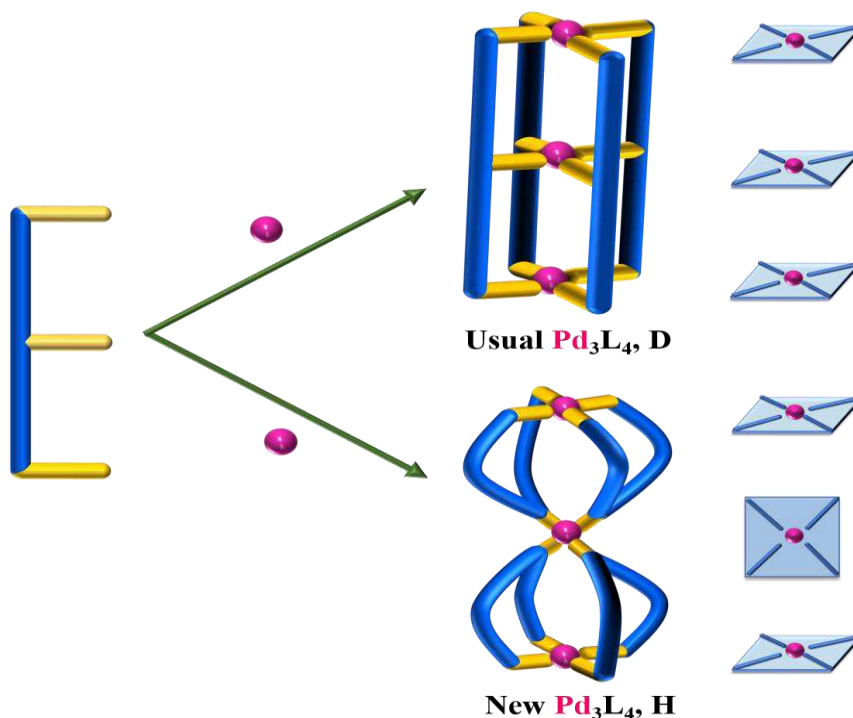
In my talk, I will showcase our recent efforts in controlling multicomponent supramolecular polymerization of fluorescent core-substituted naphthalene diimides via manipulation of various kinetic and thermodynamic routes. I will introduce structured illumination microscopy (SIM) as a unique tool to study these fluorescent multicomponent structures. Considering the diverse electronic and optical properties of the core-substituted naphthalene diimides, sequence controlled polymers were further shown to act as a directional light harvesting axial organic heterostructures. Finally, I will show our efforts in controlling more complex tri-component sequences and the future programs to strengthen our hold over sequence controlled multicomponent supramolecular polymerization.

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Abstract No: T128

T128 Usual double-decker and unusual hour-glass type Pd₃L₄ cagesMOUMITA SARKAR ¹ Hareesha Dasary ², Dillip Chand ²¹ IIT Madras, Chennai, India² IIT Madras, CHENNAI, India

A vast variety of single cavity Pd_nL_{2n} type self-assembled discrete cationic cages, constructed by tailor-made C-shaped bidentate non-chelating ligands and Pd(II) ions have been well explored.¹ However, the use of E-shaped/W-shaped tridentate non-chelating ligands obtained via the linear extension of bidentate is only sporadically explored. When four of such ligands (flexible/ rigid) are bound unidirectionally to all three metal centers it affords Pd₃L₄ type double-decker shaped² (**D**) molecules having two cavities that are conjoined through a common metal center (along with its immediate coordination environment). In **D**-type cage, now a familiar design, all three PdN₄ planes are vertical and parallel to each other. We have observed a new hour-glass (**H**) type Pd₃L₄ complex where ligand strands adopt a distorted V-shape giving the middle Pd(II) center coordinated with all four ligands and two terminal Pd(II) centers coordinated with a pair of ligands in *cis*-fashion. As a result, two terminal PdN₄ planes are disposed parallel to each other keeping the central PdN₄ plane perpendicular to them. In the present work, three regioisomeric tridentate ligands (**L1**, **L2**, and **L3**) are employed to prepare a set of Pd₃L₄ type, known double-decker shaped conjoined-cages ([Pd₃(**L1**)₄]⁶⁺, [Pd₃(**L2**)₄]⁶⁺, and [Pd₃(**L3**)₄]⁶⁺). Interestingly, a mixture of **D** and **H**-type Pd₃L₄ cages was observed in the case of **L1** and **L2** whereas only **D**-type cage was obtained with **L3**. Single crystal X-ray diffraction analysis of cage, [Pd₃(**L1**)₄]⁶⁺ supports the unprecedented hour-glass shape. The trinuclear complexes are well characterized by NMR spectroscopy, ESI mass spectrometry, and single crystal XRD.³ The introduction of flexibility in the backbone of E-shaped ligands could favour hour-glass shaped trinuclear conjoined cages. These complexes represent an interesting category of ligand isomerism.

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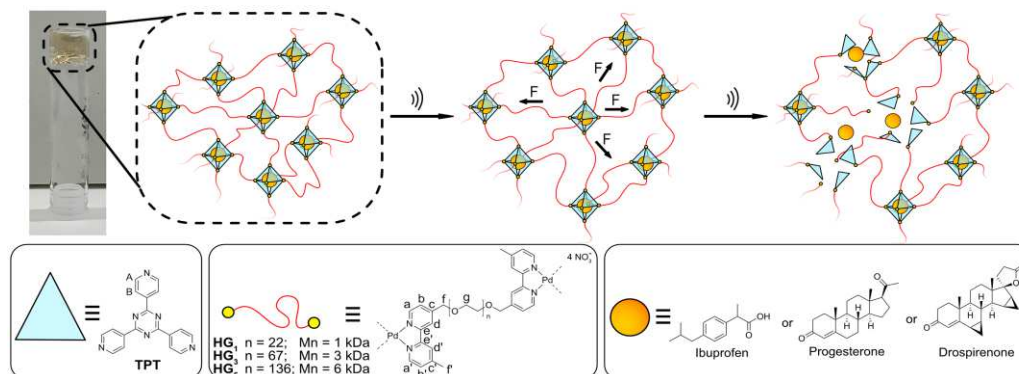
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Abstract No: T129

T129 Mechanoresponsive Metal-Organic Cages and Cage-Crosslinked Polymer Hydrogels

Bernd M. Schmidt

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Caption: Formation of metal-organic cage-crosslinked polymer hydrogels by terminal functionalization of PEG with bipyridine ligands, with hydrogels formed from

The mechanochemical release of cargo molecules from their respective latent carrier polymers is challenging.^[1] To overcome this problem, we present a versatile system based on a supramolecular coordination cage. By combining metal-mediated self-assembly of organic ligands into a discrete nanoscopic structure with polymer chains on each vertex, we realised the first ultrasound-induced disassembly of a cargo-loaded, self-assembled supramolecular Pd^{II}₆(TPT)₄ cage, entailing the release of its nanoconfined guests. This was exemplarily demonstrated for several non-covalently bound, completely unmodified, but pharmaceutically active compounds.^[2]

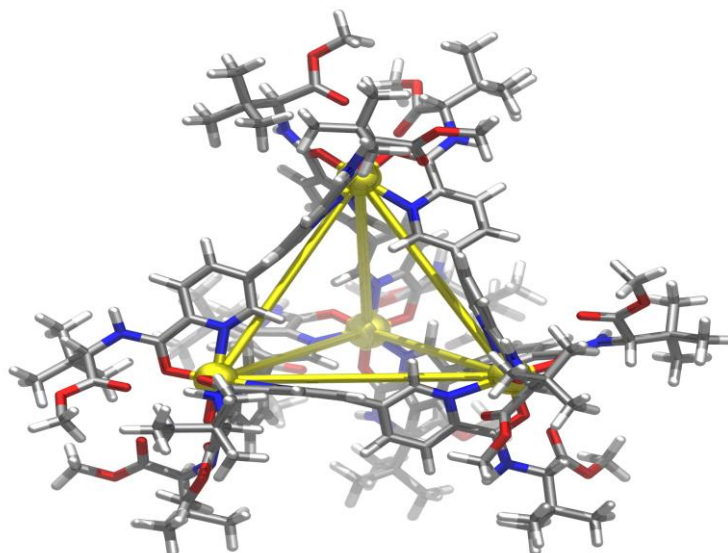
The water-soluble nanocage is decorated with poly(ethylene glycol) polymer chains on the outside, making it susceptible to ultrasonic activation in solution. These systems can be expanded into cage-crosslinked hydrogels by using homodifunctionalized poly(ethylene glycol) chains terminally substituted with bipyridines as ligands for the Pd₆L₄-type cages (Figure 1).^[3] The gels HG₁₋₆ were characterised by nuclear magnetic resonance (NMR) techniques, rheology, and comprehensive small-angle X-ray scattering (SAXS) experiments. The constrained geometries simulating external force (CoGEF) method and barriers using a force-modified potential energy surface (FMPES) suggest that the cage-opening mechanism starts with the dissociation of one pyridine ligand at around 0.5 nN.

Abstract No: T130

T130 Synthesis of M₄L₆ Metal Organic Cages via a Chiral Auxiliary Strategy

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The University of Queensland, Brisbane, Australia



Caption: Figure 1: [ZnII₄L₆]⁸⁺ cage modelled on Spartan '14. L = 3,3'-bipyridine with L-tert-leucine auxiliaries.

Metal organic cages are a promising class of discrete molecular containers that exhibit highly selective guest encapsulation for applications in molecular separations,¹ catalysis,² and the stabilisation of reactive species.³ The rational design of organic ligand binding modes and corresponding metal coordination geometries leads to the predictable self-assembly of complex architectures such as M₄L₆ tetrahedra. Here, we have designed M₄L₆ edge-linked tetrahedral cages with planar, C₂-symmetric bis(bidentate) 3,3'-bipyridine ligand backbones to provide the rigidity necessary for structure predictability. Together with octahedral transition metal nodes that define the vertices of the tetrahedron, these components self-assemble to enclose a central cavity that defines a distinct microenvironment. Metal organic cages possess extremely specific binding pockets with well-defined size, shape and chemical environments that promote selective guest uptake. Their high modularity enables metal organic cages to act as an excellent system for the separation of racemic mixtures.

Enantiopure coordination cages have presented a long-standing challenge to the field, as a mixture of diastereomers generally form upon self-assembly of achiral components around chiral metal centres, due to the lability of metal-ligand interactions. The aim of this study is to synthesise a series of chiral metal organic cages for the enantioselective discrimination of guest molecules. Here, we employ chiral amino acid motifs on the capping positions of 3,3'-bipyridine based ligands to impart permanent chirality throughout the M₄L₆ tetrahedral cage (Figure 1). This synthetic route establishes predetermined chirality in the cage structure, which would successfully define a chiral cavity for the enantioselective encapsulation of guest molecules.

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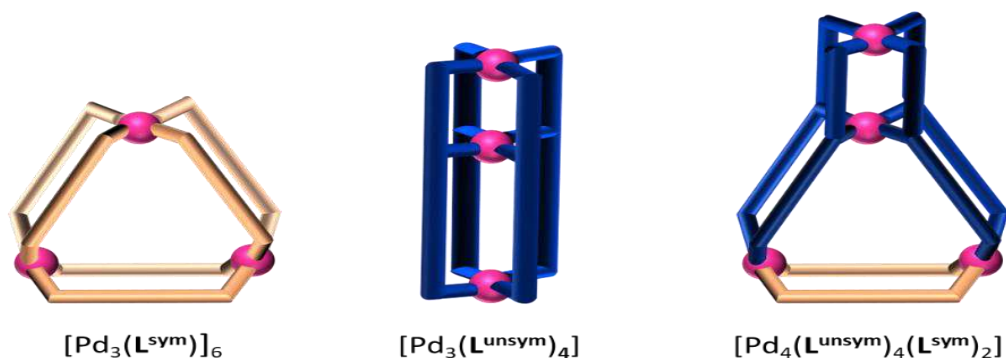
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Abstract No: T131

T131 Towards a Pd(II)-based Self-sorted Multi-cavity Coordination Cage

Shruti Sharma Soumyakanta Prusty, Dillip Chand

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Construction of self-assembled coordination cages utilizing palladium(II) and suitable non-chelating organic ligand has been an efficient approach and it has received immense attention in the field of supramolecular chemistry.¹ The labile/self-correcting nature of Pd-N bond assists in the construction of thermodynamically stable discrete high symmetry and low symmetry metallosupramolecular architectures comprising of well-defined cavities.¹ Formation of high and low symmetry complexes of Pd_nL_m variety are well explored^{1,2} whereas related multi-cavity systems^{1,3} are not well explored and is a new research interest of chemists. Reduced symmetry complexes can be prepared by inducing dissymmetry in ligand backbone or mixing of different organic ligand. Herein, building on our previous work,⁴ we have prepared a symmetrical bidentate ligand, L^{sym} and an unsymmetrical tridentate ligand, L^{unsym} . Complexation of palladium(II) with L^{sym} and L^{unsym} in separate reactions in 1:2 ratio produced $[\text{Pd}_3\text{L}^{\text{sym}}_6]$ and $[\text{Pd}_3\text{L}^{\text{unsym}}_4]$ type complexes, respectively. One pot combination of palladium(II), L^{sym} and L^{unsym} in a 4:2:4 ratio in DMSO resulted in integrative self-sorted mixed-ligated complex of $[\text{Pd}_4(\text{L}^{\text{unsym}})_4(\text{L}^{\text{sym}})_2]$ type. It was noticed that the $[\text{Pd}_4(\text{L}^{\text{unsym}})_4(\text{L}^{\text{sym}})_2]$ type complex encapsulates a nitrate anion in smaller cavity and DMSO molecules in bigger cavity as observed from crystal structure of the complex. The encapsulated nitrate could be easily replaced by halides like fluoride, chloride or bromide. The set of complexes shown here along with set of complexes prepared earlier,⁴ illustrates ligand isomerism in these special cages.

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Abstract No: T132

T132 Design and Synthesis of Cyclic Nucleobase as a New Scaffold for Molecular Recognition and Ion Separation

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Guanosine with 2-amino and 6-carbonyl groups as a hydrogen bond donor and receptor can assemble into a unique G₄-quartet building block through ion-dipole interactions between the central oxygens and cations. With the modification on guanine (8-aryl) and ribose (sterically hindered 2', 3' position), a well-defined metal templated G₈-octamer was formed. K⁺ complexes showed an excellent binding affinity over Ba²⁺, even over the potassium 18-crown-6, indicating the potential potassium receptor. Furthermore, the covalently tethered 8-aryl G₈-octamer remains intact in protic solvent, which demonstrates the significantly enhanced stability of G-quadruplexes. This is one of the few stable G-quadruplex systems from small molecule self-assembly to survive in a H bond competitive environment. Isoguanosine is a structural isomer of guanosine. The self-assembled pentaplexes are excellent Cs⁺ ionophores. To avoid the dynamic equilibrium of isoG subunits in solution, the post-assembly modification of a templated isoG complex through the olefin metathesis is applied to cross-link subunits within isoG pentaplexes constructing cyclic pentamer. The covalently tethered isoG oligomer can be used more effective than the corresponding free monomer to extract Cs⁺ from an aqueous source into an organic receiving phase. The results clearly demonstrate the power of covalent tethered molecular self-assembly for the construction of highly selective and stable ionophores. The successful synthesis and study of these covalent tethered cyclic complexes based on the supramolecular template are very promising building blocks in chemical, material, and medicinal research.

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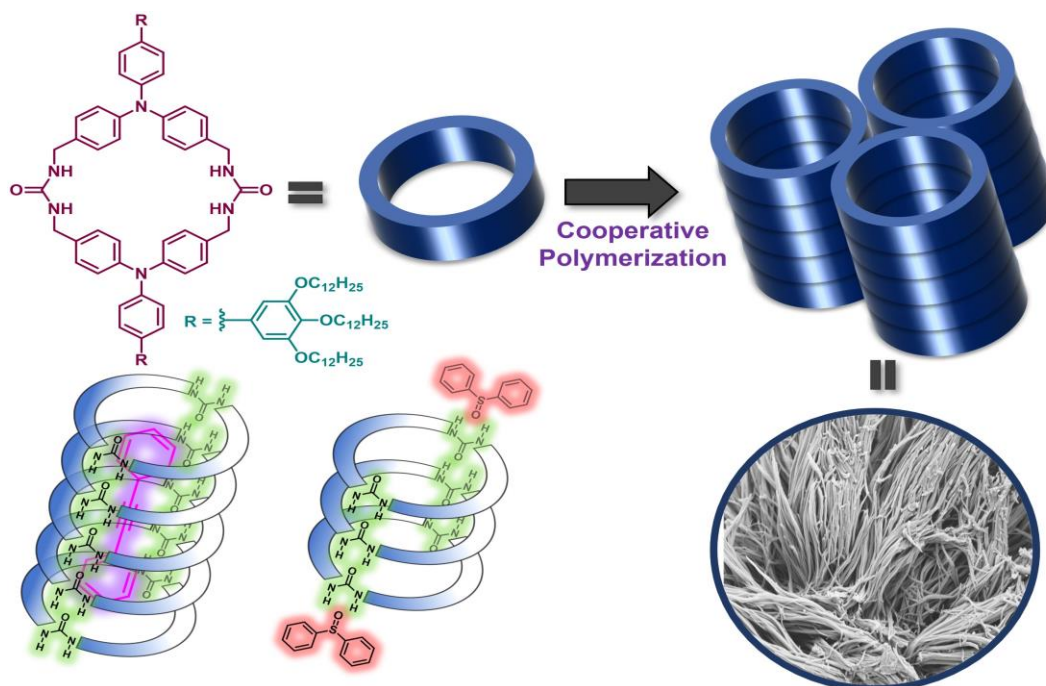
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Abstract No: T133

T133 Cooperative Supramolecular Polymerization of bis-Urea Macrocycles

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Caption: Probing the mechanism of assembly of bis-urea macrocycles in the presence of guests and chain stoppers

Herein, we probe the hydrogen bond-driven self-assembly of triphenylamine (TPA) *bis*-urea macrocycles in the presence and absence of guests demonstrated to fit within its cavity. *Bis*-urea macrocycles consisting of two urea groups and two rigid C-shaped spacers typically assemble from DMSO into columnar structures to form porous crystals.^{1,2} Appending exterior tridecyloxy benzene groups enhance the solubility of these macrocycles and enable one to probe the mechanism of *bis*-urea macrocycle assembly in a broader range of solvents. Macrocycle **1** exhibits concentration-dependent aggregate formation in THF and THF/H₂O mixtures as characterized by ¹H NMR and DOSY experiments. Its assembly and disassembly processes were further probed by temperature-dependent UV/vis and fluorescence spectroscopy. Thermodynamic analysis of the emission spectra indicates a cooperative self-assembly pathway with distinct nucleation and elongation regimes. Fluorescence measurements were used to study the impact of guests, such as diphenylacetylene (DPA), and chain stoppers. The similarity of the emission spectra suggested that **1** undergoes a similar assembly & disassembly process in the presence of guests. The cooperative assembly of **1** was most favorable in the presence of DPA, which may be encapsulated within the assembled structures. Strategies for selecting (co) monomers that may modulate the function and size of these supramolecular systems will be discussed.

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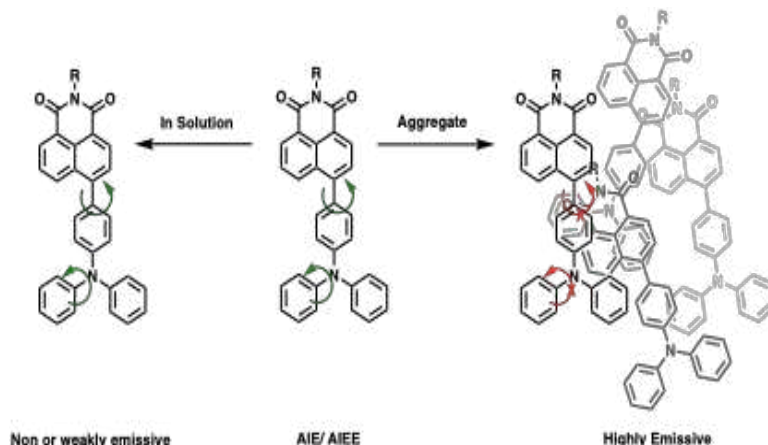
Abstract No: T134

T134 Naphthalimides Exhibiting Aggregation Induced Emission for Bioimaging Applications

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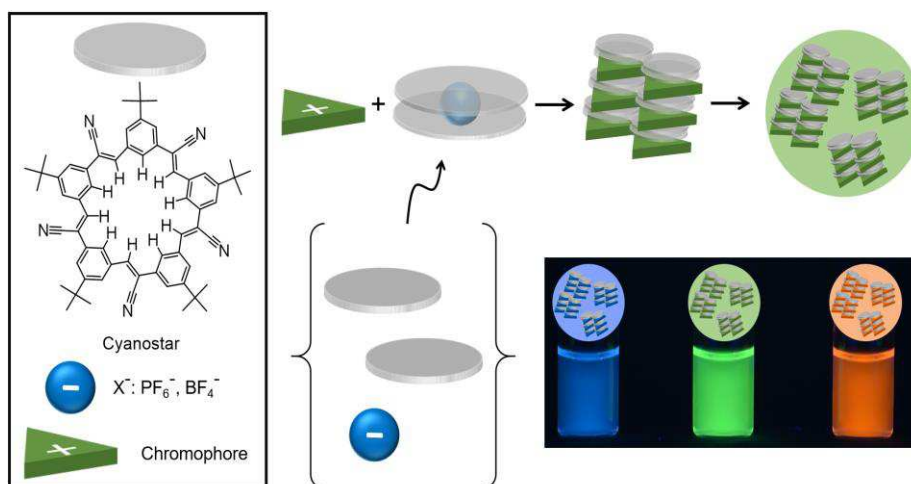


Caption: Aggregation induced emission/enhancement of Nap.

In this report, a 1,8-naphthalimide (Nap) is functionalised with two triphenylamino (TPA) moieties which, by virtue of having multiple freely rotating aromatic rings, are capable of exhibiting aggregation induced emission (AIE) in aqueous environments. The synthesis of this Nap is undertaken via a double Suzuki-Miyaura coupling procedure and the compound is fully characterised using ¹H and ¹³C NMR, IR, mass spectrometry, elemental analysis, and the structure determined unequivocally by single crystal X-ray diffraction. Photophysical studies reveal that the emission of this TPA Nap is bluer and more emissive in more apolar solvents, emitting from a planarized charge transfer (CT) state, while the emission redshifts and becomes quenched in polar media as it adopts a twisted intramolecular charge transfer state (TICT). Accordingly, in pure THF the molecule is emissive but upon addition of a small amount of water, the fluorescence is immediately quenched. However, at a critical water content (>70% water in THF), the TPA Nap once again becomes luminescent due to an AIE phenomenon becoming the dominant process. The self-assembly into emissive aggregates was studied further using scanning electron microscopy (SEM) and, with a view to using this molecule as an imaging agent, its self-assembly into a nanoparticle loaded with the TPA Nap (poloxamer P188) was demonstrated using dynamic light scattering (DLS). These successfully synthesised Nap loaded nanoparticles were then tested as bioimaging agents and the compound was found to undergo localisation within the lipid droplets of the MDA-MB-231 human breast cancer cell line following release from the poloxamer within the cell.

Abstract No: T135

T135 SMILES Nanoparticles – reinstating fluorescence in solid-state

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Caption: SMILES principle in nanoparticles.

Organic chromophores have long been known to quench in solid-state due to close packing generating strong coupling. Many approaches to reinstate luminescence in solids have been reported, most by increasing the distance between the chromophores. By introducing the macrocycle Cyanostar¹ as an anionic receptor, it is possible to create well-ordered lattice using cationic chromophores. Cyanostar has a high 2:1 binding affinity for large anions like PF_6^- and BF_4^- and creates a large anionic disk-like complex. This allows highly efficient directed packing of the cationic chromophores in *small-molecule isolation lattices*² (SMILES), which separates the chromophores and reinstates the photophysical properties as in solution.

Using the SMILES concept to create fluorescent nanoparticles in water we show the plug and play transfer of very specific optical properties of the chromophores to solid-state in water.^{3,4}

Acknowledgments: This work was supported by the Danish Council of Independent Research (DFF-0136-00122B)

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Abstract No: T136

T136 An insight into the Self-Assembly modes in Multi-Component Supramolecular Gels using enantiomers tagged with donor-acceptor pairs

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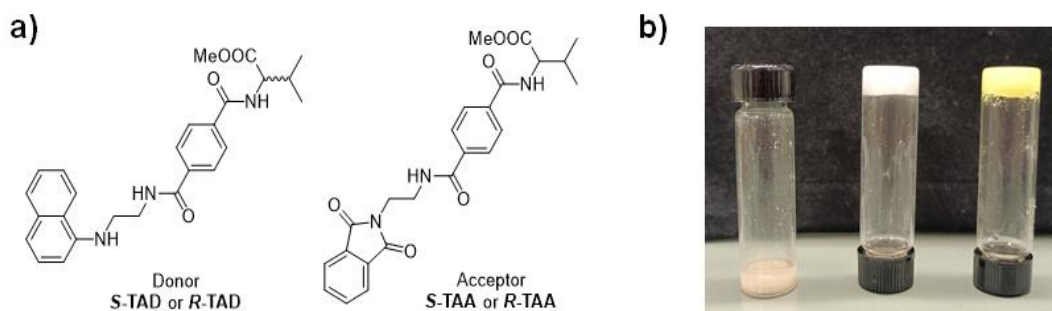


Figure 1. Structure of (a) enantiomeric donor and acceptor-based molecules, (b) from the left- 2.0 wt% of donor, acceptor and equimolar (donor+acceptor) in mesitylene.

Multi-component gels^[1] based on mixing enantiomeric compounds tagged with electron-rich (donor) or electron-deficient (acceptor) moieties will result in the formation of fascinating material with potential application in optoelectronic devices. The enantiomeric gelator molecules interact either constructively or destructively to undergo self-sorting or co-assembled network, which mainly depends on various parameters (gelator structure, the spatial orientation of the functional groups and solvent system, etc.).^[2] We have shown that mixing enantiomeric gels based on amide functionality favors co-assembled fibers rather than self-sorting,^[2] which will enhance the thermal and mechanical stabilities compared to the individual enantiomeric gels.^[2-3] In this work, we have designed enantiomers based on donor-acceptor system to analyze the effect of enantiomeric donor and acceptor in the self-assembly process in multi-component gels^[4] and to study the charge-transfer (CT) interaction mediated alternate stacking of donor-acceptor molecules. The enantiomeric donor-acceptor multi-component system was designed by tagging the donor (naphthalene-based) or the acceptor (phthalimide-based) to one end of the enantiomeric mono-amide of 1,4-benzenedicarboxylic acid and valine methyl ester (Figure 1a). We have synthesized the enantiomeric (*R*- and *S*-) donor and acceptor-based molecules and the gelation properties of the individual/equimolar mixed enantiomeric compounds were studied in *p*-xylene and mesitylene.

The gelation experiments revealed that the enantiomeric acceptor molecules are supergelators, and the enantiomeric donor molecules are non-gelators (Figure 1b). However, equimolar mixing of the enantiomeric donor-acceptor molecules resulted in a yellow-colored gel suggesting the possibility of self-assembled network between the donor and acceptor molecules (Figure 1b). This result shows that the gelation properties of the mixed gels can be tuned by introducing donor and acceptor moieties in the enantiomeric compounds. Further photophysical studies with these molecules are ongoing.

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Abstract No: T137

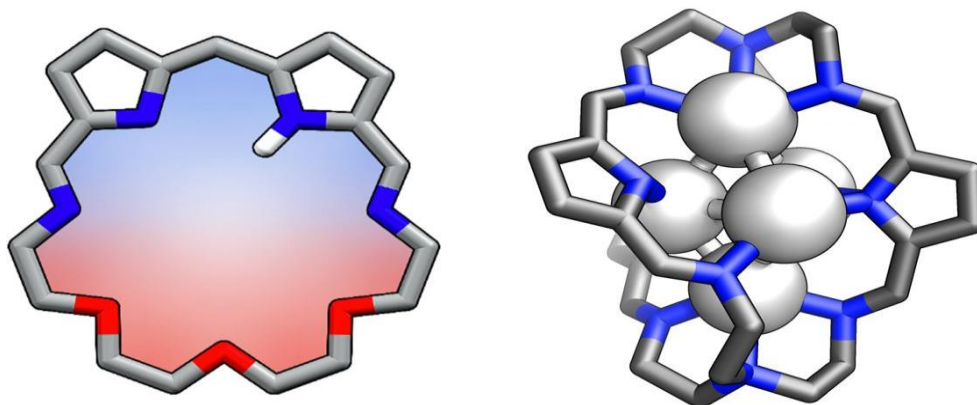
T137 Iminopyrroles – versatile building blocks for macrocyclic and supramolecular chemistry

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² , ,

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Caption: Figure 1. Iminopyrrole-based macrocycle – crownphyrin (left) and silver(I)-filled cage – plenate (right).

The flourishing of modern macrocyclic and supramolecular chemistry largely relies on ligand molecules capable of forming transition metal complexes. Using imine synthons as building blocks allows for constructing molecular architectures of incredible complexity. The popularity of these compounds originates from their facile syntheses allowing for significant accessibility, the possibility of tuning their properties through a simple modification of the aldehyde and amine components, and the reactivity towards transition metal cations resulting in the formation of coordination compounds with well-defined geometries. The synthons incorporating heterocyclic nuclei, e.g., pyridine or pyrrole, and imine sidearm(s), are essential for constructing macrocyclic and supramolecular architectures with the use of self-assembly. Their ability to act as di- or tridentate ligands in reactions with a variety of transition metal cations made this class of molecules an essential toolbox for the construction of numerous architectures spanning from the simple coordination compounds, helicates, macrocycles, and cages to topologically complex molecular links and knots. In the communication, the exploitation of the iminopyrrole motif for the construction of macrocyclic and capsular architectures will be demonstrated. In particular, the discussion of hybrid macrocycles merging structural facets of porphyrins and crown ethers, namely crownphyrins, will be provided.¹ Irrespectively, the exploitation of iminopyrrole building blocks for constructing cryptates incorporating silver(I) clusters, i.e., plenates, will be discussed.²

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Abstract No: T138

T138 Intercalation of dicarboxylic acids into porous supramolecular nanopatterns on graphite (HOPG)

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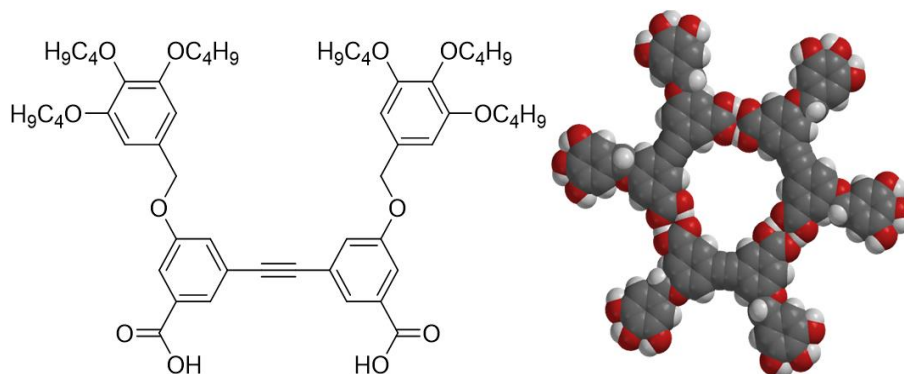


Figure 1: Dicarboxylic acid (*left*) and space-filling model of a supramolecular cyclotrimer thereof (*right*; alkoxy chains omitted for clarity).

Caption: Figure 1

Rigid entities consisting of ethynylene and phenylene units are of great interest due to their wide range of applications, including metal chelate ligands^[1], enzyme transporters^[2], molecular electronics^[3], or surface studies.^[4] One aspect of the latter deals with supramolecular nanopatterns, that form at the solid/liquid interface of a solution of an organic species and a solid material, such as highly oriented pyrolytic graphite (HOPG). Here, we report on the synthesis and self-assembly of an arylene alkynylene carrying two carboxylic acid units and 3,4,5-trialkoxybenzyloxy units (Figure 1). The former are prone to interact non-covalently, while the latter mediate sufficient compound solubility. When a solution of dicarboxylic acid (Figure 1, *left*), is applied to a porous supramolecular template layer of arylene-alkynylene macrocycles, cyclotrimers are found (Figure 1, *right*) in its nanopores, that act as a host. In all cases, the supramolecular adsorbate structures formed are visualized by scanning tunneling microscopy (STM) with submolecular resolution.

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Abstract No: T139

T139 Synthesis and characterization of new self-assembling bioconjugates of N-modified hemorphins

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Hemorphins are endogenous opioid peptides found in nature that are members of the hemorphin family. These peptides have a wide range of biological activities, including anticancer, antidiabetic, antihypertension, antiepilepsy, and so on. Small peptides that self-assemble are appealing building blocks because they are relatively easy to synthesize and allow for systematic study using experimental and computational analyses to associate peptide sequences with properties and functionality, making them promising candidates for producing functional nanomaterials. A new series of self-assembling N-modified hemorphin analogs with cinnamoyl moiety has been synthesized and characterized. Solid-phase peptide synthesis—Fmoc-strategy—was used to create the novel peptide analogs. The crude neuropeptides were purified using an RP-HPLC, and the molecular weights and specific angles of optical rotation were determined using ES-MS. We used also Fourier transform infrared and circular dichroism to understand peptides' secondary structures.

Acknowledgment: This study is funded by the European Union-NextGenerationEU, through the National Recovery and Resilience Plan of the Republic of Bulgaria, project № BG-RRP-2.004-0002, "BiOrgaMCT".

T140 De Novo Construction of Peptide Steric Zipper Structures by Metal-induced Folding and Assembly

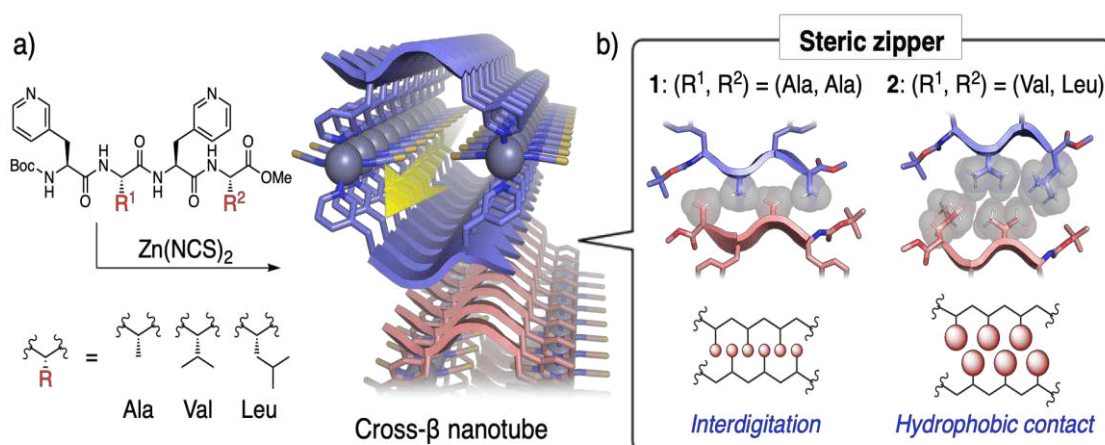
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Figure 1. (a) Synthetic scheme of cross-β nanotubes and (b) the observed steric zippers.

The molecular mechanism of the robustness of amyloid fibrils derives from the cross-β structure, in which two-layers of parallel β-sheets are aggregated in the same direction. The layers are stabilized by a hydrophobic packing of peptide side chains called as a steric zipper.¹ In this work, to achieve the de novo construction of such cross-β nanostructures, we examined metal-induced folding and assembly² of tetrapeptide fragments, having various alternating sequences of coordinating/hydrophobic residues (Fig. 1a). From peptide **1**, with a pair of two Ala side chains, a crystalline nanotube was obtained in a high yield through the complexation with Zn(NCS)₂. Crystallographic study revealed Zn₂(**1**)₂ macrocyclic units were orderly aligned by intermolecular hydrogen bonding, forming the cross-β structure. At the same time, among the nanotubes, a steric zipper of an “interdigitation” type³ was clearly observed (Fig. 1b, left). In contrast, when a sequence of a pair of Val and Leu side chains (**2**) was examined, an analogous nanotube was successfully formed, but the steric zipper changed to a “hydrophobic contact” type³ due to their large steric bulk (Fig. 1b, right). This synthetic strategy could also be applied to various tetrapeptides with aromatic or hydrophilic sidechains, resulting in observation of not only known types but also a novel type steric zipper that has never been observed in the previous crystallographic studies.⁴

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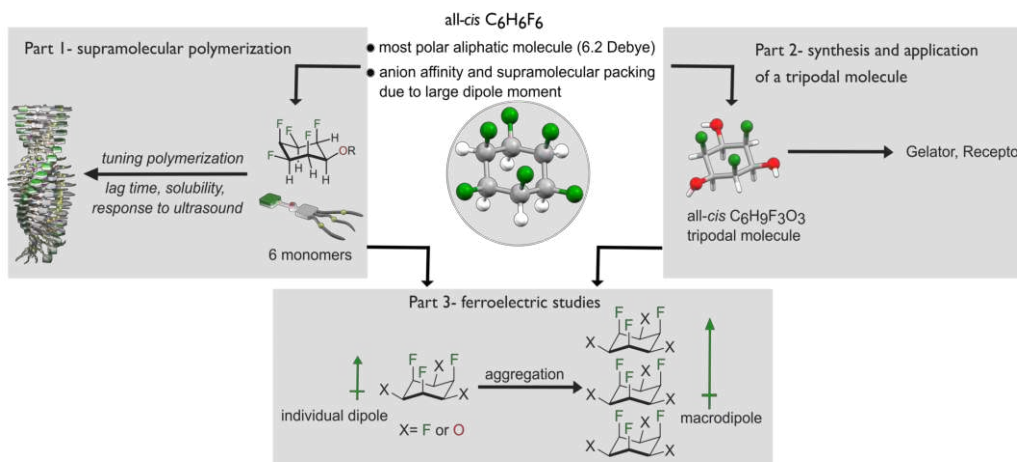
Abstract No: T141

T141 Supramolecular systems and organic materials based on all-*cis* fluorinated cyclohexanes.

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All-*cis* hexafluoro cyclohexane is the most polar aliphatic molecule synthesized so far¹- having a dipole moment of 6.2 Debye. Because of its large dipole moment and one step synthesis from hexafluoro benzene which became possible in 2017², the interest towards this molecule is growing fast. Recently our group has shown the binding of all-*cis* hexafluoro cyclohexane to the chloride ion³ and living supramolecular polymerization of fluorinated cyclohexanes,⁴ indicating its supramolecular potential.

The first part of the project is about the synthesis and supramolecular polymerization of various monomers based on all-*cis* fluorinated cyclohexane which bear different side chains. Indeed, we observed changes in polymerization properties such as lag time, solubility and response to ultrasound and seeds. By carefully tuning the conditions of polymerization, it was possible to make kinetically controlled supramolecular polymers.

The second part of the project is about synthesizing a tripodal molecule. We replaced three fluorines in the all-*cis* hexafluorocyclohexane by oxygen to do this. Crystal structures of several derivatives are obtained. A gelator and an anion receptor were made using this tripodal molecule.

Because of the large dipole moment and ability to stack, we hypothesized that all-*cis* fluorinated cyclohexanes could be an interesting molecule for organic polarized materials. Several crystal structures we obtained and theoretical calculations⁵ were in support for this hypothesis. We observed ferroelectricity in some of our molecules and further studies are ongoing.

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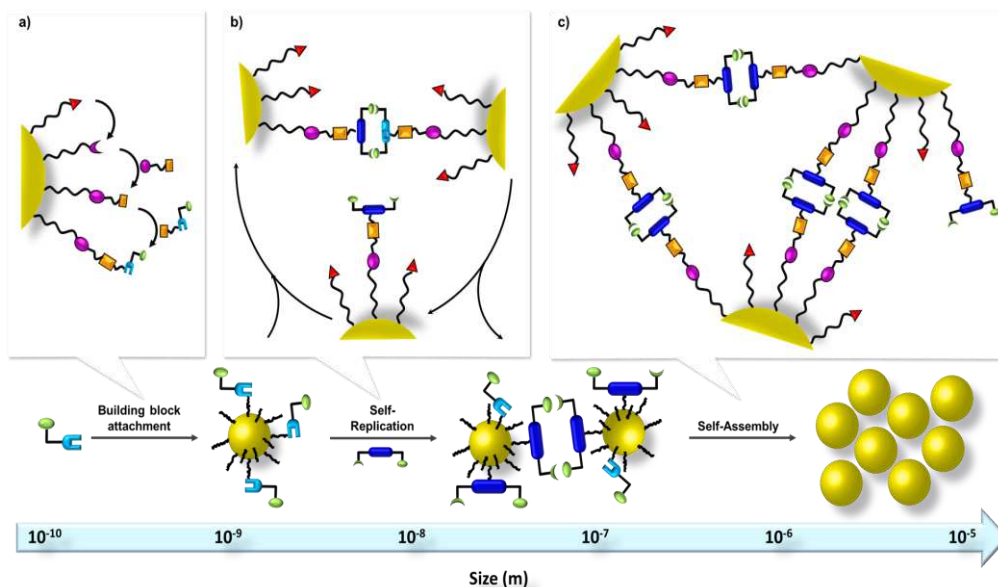
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Abstract No: T142

T142 Dynamic Nanomaterials: Self-Replication-Enabled Nanoparticles

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Caption: Design and elaboration of self-replication-enabled nanoparticles

Self-replication corresponds to the ability of a system to amplify and transmit structural information through a specific autocatalytic process.¹ Years of evolution have led to a complex network of chemical processes, where molecular information is amplified and translated to produce an effect on biological structures spanning sizes from the molecular to macroscopic.²

Artificial replicating systems have recently been developed in an attempt to mimic – and understand – such biological networks from the bottom up. Combining self-replicating molecular systems³ with monolayer-stabilized nanoparticles,⁴ replication-enabled nanoparticles would provide an artificial platform whereby replication processes can translate and amplify specific molecular instructions into programmable macroscale structures. Control of the molecular input allows control over the composition of the assembly, leading to new types of dynamic material with controlled composition and structure on several length-scales.

In this work, we created monolayer stabilised gold nanoparticles presenting a versatile terminal function. Post-synthetic modification allowed possible attachment of more sophisticated molecules (figure a) as well as obtention of mixed monolayer nanoparticles in a control manner. In parallel, a efficient self-replicating system was designed and synthesised. Presenting an attachment site complementary to the nanoparticles, this system will allow replication to take place on the nanoscale level (figure b), leading to controlled nanoparticle assembly (figure c).

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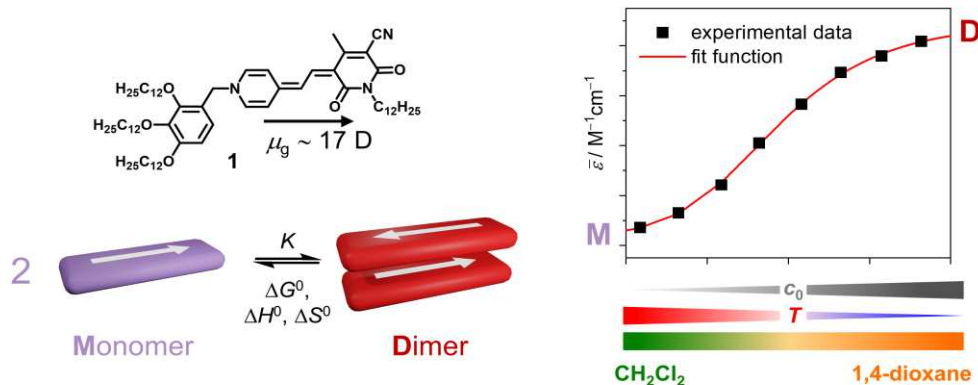
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Abstract No: T143

T143 Concentration-, Temperature- and Solvent-Dependent Self-Assembly: Merocyanine Dimerization as a Showcase Example for Obtaining Reliable Thermodynamic Data

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Caption: Figure 1. Schematic representation of the dimerization of dipolar merocyanine 1.

Association constants K and the thermodynamic parameters ΔG^0 (Gibbs free binding enthalpy), ΔH^0 (binding enthalpy) and ΔS^0 (binding entropy) are of fundamental importance for the characterization of self-assembly processes. They are the basis to compare and evaluate supramolecular systems. To study self-assembly processes in solution, concentration-, temperature- as well as solvent-dependent experiments have been used in literature. Each of these methods has advantages, but to choose the best approach and to obtain reliable results it is important to understand and mind the underlying assumptions behind these data evaluation models.

This is illustrated here by comprehensive UV/Vis absorption studies for the dimerization of a dipolar merocyanine dye **1** in 1,4-dioxane. Due to the large molecular ground state dipole moment ($\mu_g \sim 17$ D) of the chromophore defined anti-parallel dimers are formed by strong dipole-dipole interactions (Figure 1).¹ Additionally, the pronounced changes in the absorption properties of the π -stacked dimer compared to the monomer due to H-type exciton coupling allow easy monitoring of the self-assembly process by UV/Vis spectroscopy. This provides us with an easy showcase example to compare the different approaches and to point out advantages and disadvantages. Additionally, isothermal titration calorimetry (ITC) dilution experiments were performed as an independent reference technique. While the concentration-dependent analysis is according to our studies the most reliable method, also the less time-consuming temperature-dependent evaluation can give accurate results in the present example, despite small thermochromic effects. In contrast, the strong negative solvatochromism of the merocyanine tampers with the results from the solvent-dependent evaluation. Even though the studies presented in this work are limited to the monomer-dimer equilibrium of a dipolar dye, the basic principles can be transferred to other chromophores and different self-assembly models, including those for supramolecular polymerization.

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Abstract No: T144

T144 Supramolecular self-associating amphiphiles: a novel class of broad-spectrum antimicrobial agent

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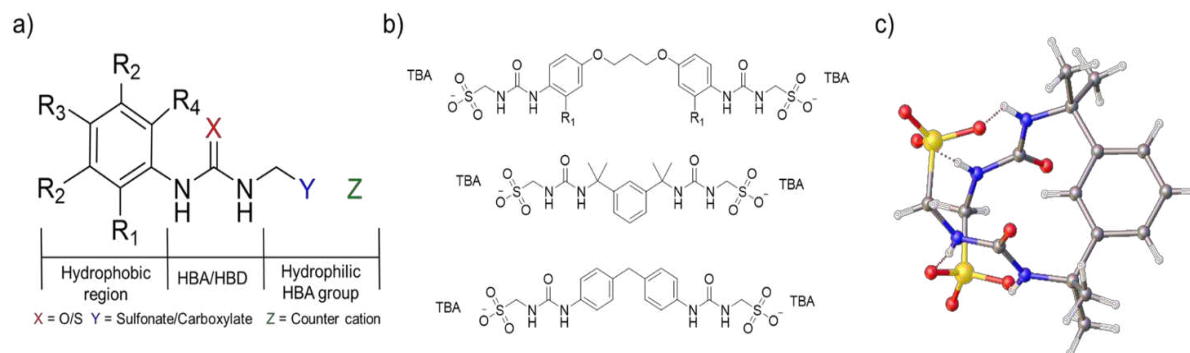


Fig. 1 (a) General structure of SSAs (b) Di-anionic SSAs (TBA = tetrabutylammonium) and (c) single-crystal x-ray structure showing the formation of an anionic, helical macrocycle, stabilised through four hydrogen bonds.

As a result of the looming antimicrobial resistance (AMR) crisis (3.57 million deaths associated with AMR in 2019),¹ there is an urgent need for new antimicrobial agents. We report a novel class of supramolecular self-associating amphiphiles (SSAs - Fig. 1a), which have shown to act as antimicrobial agents against clinically relevant Gram +ve methicillin-resistant *Staphylococcus aureus* (MRSA) and Gram -ve *E. coli*.² Additionally, we have shown a small subset, selected from our extensive library of SSAs to exhibit 'druggable' profiles through the completion of a variety of *in vivo* and *in vitro* drug metabolism and pharmacokinetic studies.³ SSAs are a class of amphiphilic salt, the anionic component of which is able to undergo hydrogen bonded self-association events. These events result in the controllable formation of environment-dependent anionic dimers (polar organic),⁴ spherical aggregates $d_H \approx 100\text{-}550$ nm (aqueous),⁴ and hydrogel fibers (in the presence of extra salt).⁵ The antimicrobial activity of SSAs has been linked to their inherent ability to self-assemble. To build SSA antimicrobial efficacy–molecular structure relationships, a series of stepwise modifications have been made to the original construct, resulting in a library of > 100 compounds, enabling the informed design of next-generation antimicrobial SSAs. These modifications have also included the production of a series of di-anionic antimicrobial SSAs (1b), which have also produced a number of bespoke anionic, hydrogen bonded macrocycles (1c).⁶

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Abstract No: T145

T145 Self-assembly and structural elucidation of molecularly thin nanosheets from saddle-shaped macrocycles

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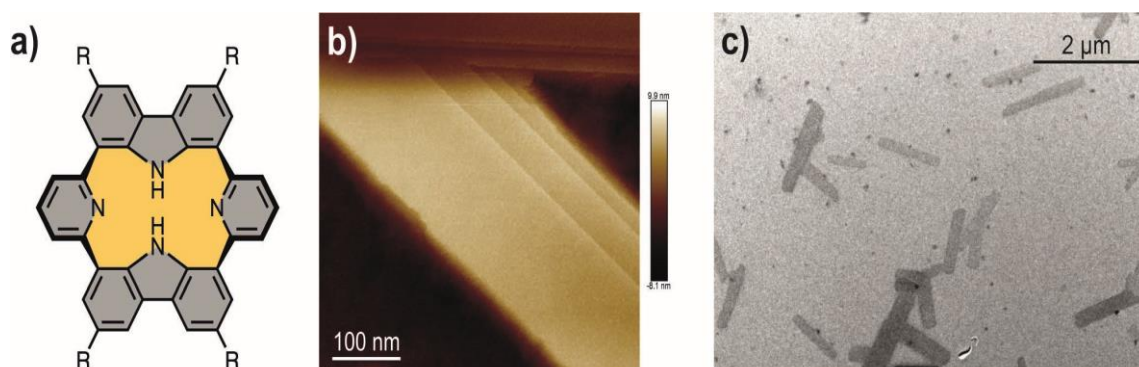


Figure. (a) Structure of Carpyridine (2H-Car-R) functionalised with R groups, and when R = n-hexyl, assemblies were seen under b) AFM and c) TEM

Questioning how molecular topography can govern supramolecular ordering is a relatively unexplored avenue of thought and one which poses great synthetic challenge that could lead towards new functional materials. “Carpyridines” (Figure, a) — macrocycles fused from carbazoles and pyridines — are an underdeveloped example of a simple system bearing negative Gaussian curvature that could hold such promise (1). Derivatisation of these non-planar systems through peripheral functionalisation of the aromatic core has yielded supramolecular assemblies (Figure, b, c) in the form of 2D sheets on surface with the thickness of a single molecule and fantastic edge definition (2). Varying the length of alkyl chain in the macrocycle has then resulted in different types of nanosheet, which hints at the subtle interplay between weak forces alongside the assisting role of shape. Using a combination of diffraction techniques, including micro-electron diffraction, the composition of these nanosheets can be elucidated to examine what effect shape has upon supramolecular ordering within the assembly.

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Abstract No: T146

T146 Modulation of triplet excited state by supramolecular assembly

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Triplet excited states of the molecules play crucial roles in many fields. However, the generation of triplet excited state from organic chromophores are very inefficient due to its spin-forbidden transition character. The presence of multiple relaxation processes also tremendously restricts the applications of triplet excited states. My research work aims to modulate triplet excited state by supramolecular assembly. We achieved a series of assemblies with visible and near infrared light excited pure organic room temperature phosphorescence (RTP) in aqueous solution and disclosed the underlying mechanism for the phosphorescence.^[1-2] Through molecular design and assembly strategy, we suppressed Kasha's rule to give fluorescence and phosphorescence from upper excited states.^[3] Room temperature fluorescence and phosphorescence from monochromophore-based assembly in aqueous solution have been constructed to realize highly sensitive ratiometric hypoxia detection.^[4-6]

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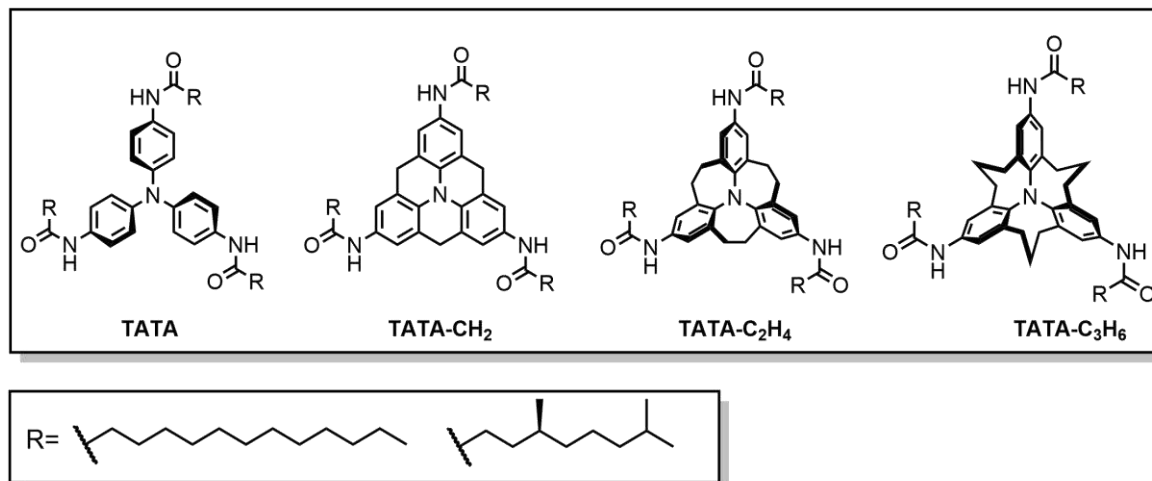
Abstract No: T147

T147 At the Core of Dynamic Polymers: The Self-Assembly of Twisted Aryl Amines

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Family A: Distorted Cores



Triphenylamines (TPAs) and its derivatives have received considerable attention over the past years thanks to their attractive properties that enable their electroactive and photoactive applications. Their molecular configurations and electronic properties greatly influence their aggregation states as well as their charge carrier-transporting properties. Previous studies reported that substituting the TPA with at least one amide group could induce supramolecular polymerization that can form helical structures via intermolecular H-bonds. To date, there is no reliable method to predict how exactly a given building block will organize itself in solution or the solid state, consequently allowing us to formulate the following questions:

What rules govern supramolecular order? And how do we encode these rules into molecular building blocks?

Can we predict new properties that emerge as a result of an assembly of subunits?

To address these seminal goals, we aim to study the influence of systematic variations of the core of a triarylamine trisamide (TATA) core unit, while keeping the outer layer (i.e. sidechains) constant. This ensures that the main driving force for the assembly (the hydrogen bonds) located at the periphery remain in place, leading to columnar stacking. For this purpose, we have devised Family A (Figure 1), which aims at highlighting different parameters such as geometry, steric hindrance, size, and flexibility. The length of the bridge is anticipated to induce different degrees of twist to the core, distorting the available π -surface. The main objective in this family is thus to investigate if it is possible to find a direct relationship between the distortion of the flat surface and the observed degrees of supramolecular order.

Abstract No: T148

T148 Pathway Complexity in Nanotubular Supramolecular Polymerization: Metal–Organic Nanotubes with a Planar-Chiral Monomer

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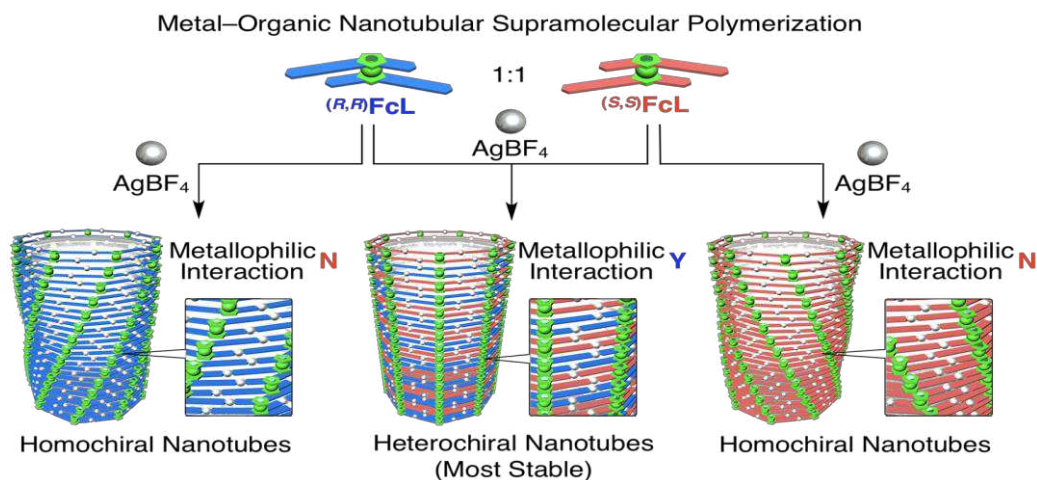


Figure 1. Schematic illustration of stereochemical supramolecular copolymerization of (R,R)Fcl and (S,S)Fcl with AgBF₄.

Stereochemistry is one of the most essential topics in supramolecular polymerization, because it may help us understand mechanistic details about the nucleation and elongation involved in the polymerization process. Particular attention has been given to the issue of how the stereochemical sequence of a supramolecular polymer is affected by the enantiomeric excess (%*ee*) of the constituent chiral monomer. In general, depending on the mutual affinity of two enantiomers, the following three different polymer sequences emerge. If two enantiomers are exclusive to each other, chiral self-sorting would occur to give a mixture of two homochiral sequences. In contrast, if they are highly affinitive to each other, a heterochiral alternating sequence would result. Meanwhile, if their affinity is moderate, two enantiomers copolymerize randomly. Among them, examples of heterochiral supramolecular polymerization are still very limited^{1,2} since the enantiomers share the same molecular structure and differ only in the optical properties, which is difficult to give a structural difference to the resultant polymer.

Here we report a one-handed helical (homochiral) metal–organic nanotube (**FcNT**) with an unprecedentedly large diameter of 9.1 nm by Ag⁺-mediated supramolecular polymerization of **FcL**, a planar-chiral ferrocene-cored tetrapodal pyridyl monomer (**Figure 1**). When its enantiomers ^(R,R)**FcL** and ^(S,S)**FcL** were allowed to copolymerize, we found an occurrence of heterochiral elongation to give **FcNT** with a non-helical geometry (**Figure 1**). Furthermore, the as obtained non-helical **FcNT** showed an enhanced thermodynamical stability than homochiral **FcNT**. How does this emerge? Here, we must consider the stereochemical requisite that the metallamacrocycles **FcNRs** must always be homochiral because the heterochiral connection between ^(R,R)**FcL** and ^(S,S)**FcL** suffers from a geometrical mismatch for cyclization. Namely, if **FcL** is enantiopure, the acyclic precursor is homochiral and advantageous for cyclization to produce **FcNR**, leading to homochiral **FcNT**. However, this mechanism cannot explain why **FcNR** efficiently forms with racemic **FcL** and AgBF₄. We propose another assembly pathway, *i.e.*, template-assisted chain elongation via a Ag⁺/Ag⁺ metallophilic interaction. Even though when chiral **FcL** is racemic, ^(R,R)**FcNR** and ^(S,S)**FcNR** could form, although with a low probability and serve as a template to arrange **FcL** and Ag⁺ at their cross-sectional edges. Eventually, thermally stable heterochiral **FcNT** forms with a heterochiral stereochemical preference.

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Abstract No: T149

T149 AXIAL AZA-CROWN MACROCYCLES AS FLUORESCENT CATION SENSING AGENTS

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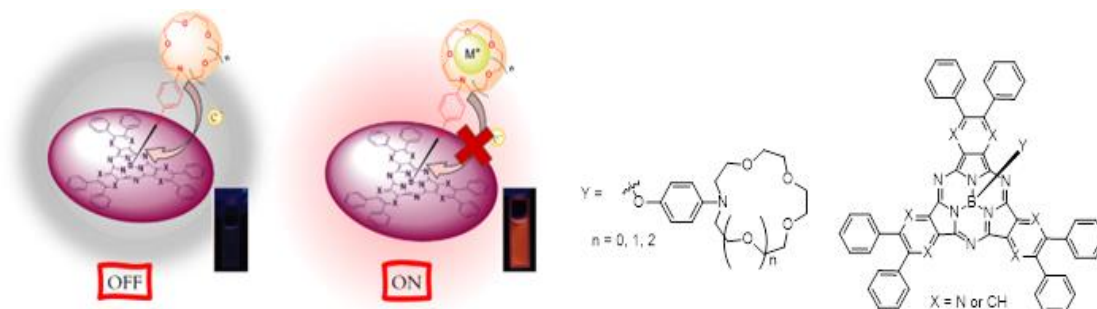


Fig. 1: a) Schematic representation of PET quenching the sensor. b) Subphthalocyanines and Subazaphthalocyanine, prepared and studied in the project.

Phthalocyanines and their analogues have interesting and highly applicative photophysical properties, whose switching is controlled by photo-induced electron transfer (PET)¹ (Fig. 1.a) and are investigated to be used in photodynamic therapy, fluorescence sensing, and as logic gates.²

This work aimed to prepare fluorescence sensors for alkali and alkaline earth metal cations by designing subphthalocyanines and their pyrazine analogues bearing axial aza-crown ligands as recognition moiety (Fig. 1.b). Microemulsions of the sensors were prepared to achieve water solubility.

The synthetic pathway included the multi-step synthesis of the axial ligands, and synthesis of macrocycles coordinating BCl, after which the metal ion-sensitive ligands were attached to the axial positions. The switching properties were studied by titration with various metal cations and their binding constants were determined. The selectivity and sensitivity towards metal cations, the influence of counter anion towards sensitivity, photostability, stoichiometry of interaction and pH dependence in aqueous medium of the prepared macrocyclic sensors (in microemulsions), were studied. A study on the unconventional behaviour of Ba²⁺ with the sensors was also carried out.

The study was supported by Czech Science Foundation (project No. 21-14919J) and Charles University (SVV 260 547).

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T150 AXIAL AZA-CROWN MACROCYCLES AS FLUORESCENT CATION SENSING AGENTS

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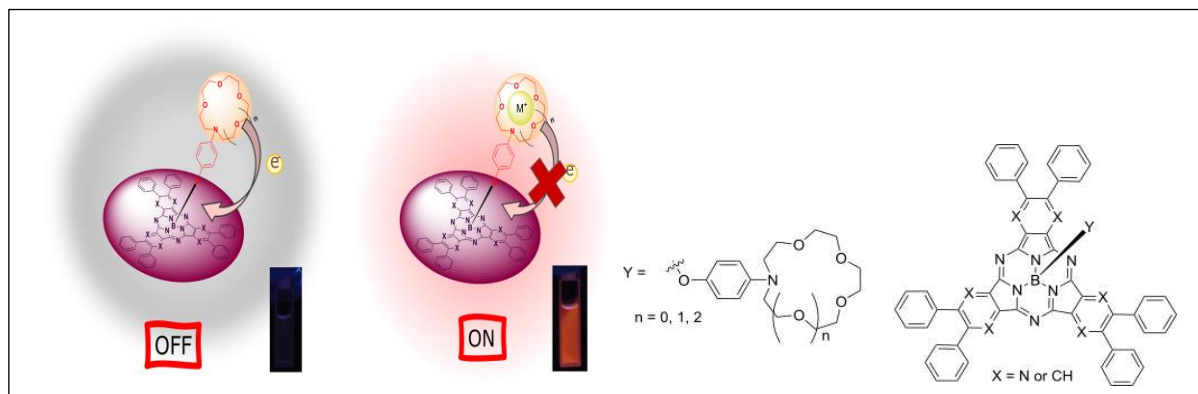


Fig. 1. a) Schematic representation of PET quenching the sensor (right) and Fig. 1. b) Subphthalocyanines and Subzaphthalocyanine, prepared and studied in the project (left).

Phthalocyanines and their analogues have interesting and highly applicative photophysical properties, whose switching is controlled by photo-induced electron transfer (PET)¹ (Fig. 1.a) and are investigated to be used in photodynamic therapy, fluorescence sensing, and as logic gates.²

This work aimed to prepare fluorescence sensors for alkali and alkaline earth metal cations by designing subphthalocyanines and their pyrazine analogues bearing axial aza-crown ligands as recognition moiety (Fig. 1.b). Microemulsions of the sensors were prepared to achieve water solubility.

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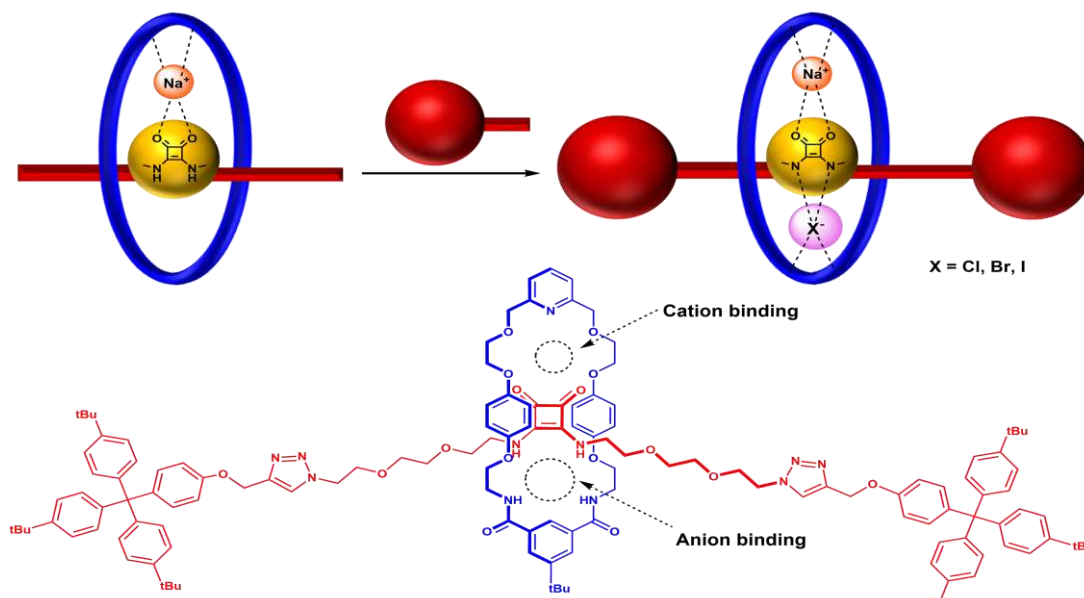
Abstract No: T151

T151 Squaramide-based heteroditopic [2]rotaxanes for sodium halide (NaX) ion-pair recognition

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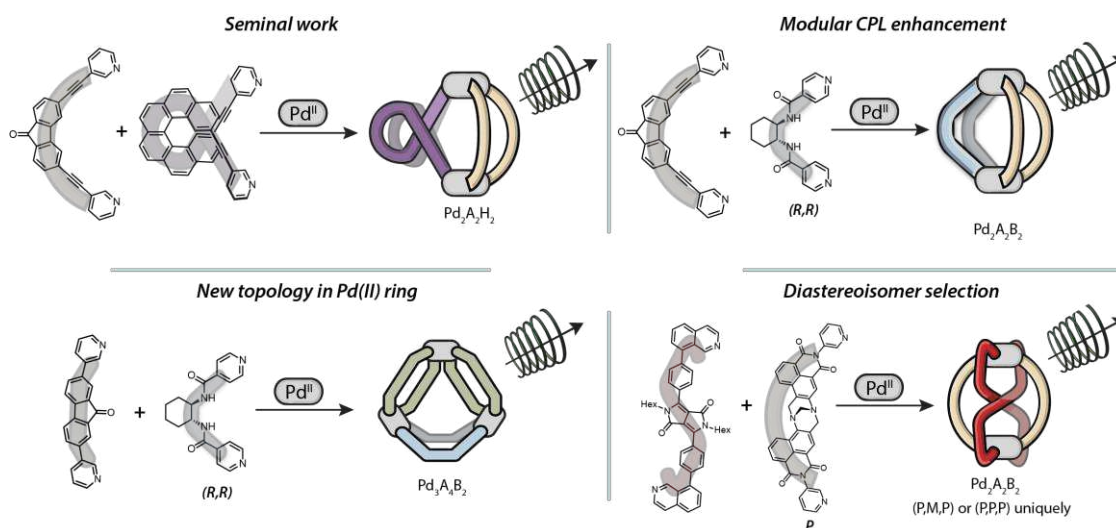


Caption: a) Schematic showing synthesis and ion-pair recognition of the squaramide-based [2]rotaxane systems; b) Chemical structure of one the [2]rotaxanes

A series of squaramide-based heteroditopic [2]rotaxanes were synthesised using an alkali metal cation template-directed approach and their ion-pair recognition properties investigated. ¹H NMR spectroscopic anion and cooperative ion-pair recognition studies show that the [2]rotaxane hosts exhibit positive cooperative ion-pair recognition behaviour, wherein the HB-mediated anion recognition is significantly enhanced in the presence of alkali metal sodium cation. Notably, changes in the cation binding unit of the macrocycles dramatically influences the ion-pair binding affinities of the [2]rotaxanes, overcoming direct contact ion-pair binding modes in polar organic solvents. Furthermore, by exploiting these cooperative ion-pair binding properties we show that the [2]rotaxanes are able to successfully extract solid sodium halide salts into organic media.

Abstract No: T152

T152 Chirality transfer and (chiro)-optical properties in coordination cages

Elie Benchimol ¹ Guido Clever ²¹ TU Dortmund, Dortmund, Germany² , ,

The recent development of heteroleptic cages has proven to be an interesting tool to bring multiple functionalities in discrete assemblies.¹ While the focus was first set on increasing the complexity of assemblies, the past years have witnessed the emergence of functional structures with singular properties. Among them, the combination of chiral ligands with chromophore counterparts has attracted our attention. We have recently reported the first example of ligand to ligand chirality transfer for circularly polarized luminescence application, combining helicene and fluorenone backbone in a discrete architecture.² While this example paves the way to the use of chiro-optical properties of coordination assemblies based on Pd(II) it also presents several limitations. With this in mind, we are developing further systems for the modular enhancement of CPL properties. Modification of the chiral ligand from helicene to *trans*-cyclohexane³ has allowed us to create an assembly with higher g_{lum} values using the same fluorenone chromophore.⁴ This chiral moiety also enabled us to unveil a new topology for supramolecular rings, presenting once more reasonable CPL properties. Finally, taking advantage of a diketopyrrolopyrrole based ligand, we have shown that it is possible to selectively form one single diastereoisomer of a *figure of eight* cage showing an impressive quantum yield of luminescence for Pd(II) based cage, as well as CPL properties.

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Abstract No: T153

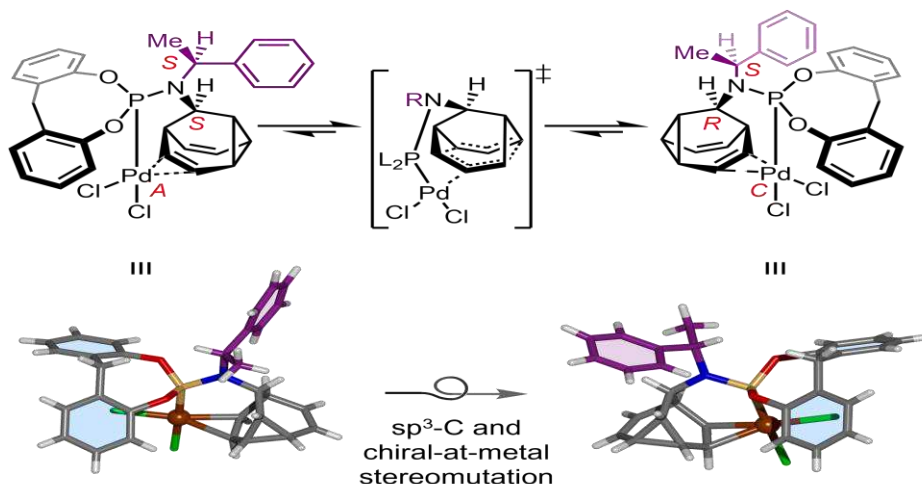
T153 Control of Dynamic sp³-C StereochemistryAisha Bismillah ¹ Toby Johnson ², Paul McGonigal ¹¹ University of York, York, United Kingdom² University of Durham, County Durham, United Kingdom

Figure 1. Transfer of dynamic sp³-carbon stereochemistry: Pd(II) ions ‘walks’ along a side of the barbaralane cage as the Cope rearrangement proceeds.

Stereogenic sp³-hybridised carbon centres are fundamental building blocks of chiral molecules. Unlike dynamic stereogenic motifs such as sp³-nitrogen centres or atropisomeric biaryls, sp³-carbon centres are usually fixed, requiring intermolecular reactions to undergo configurational change. Here, we report a series of chiral fluxional carbon cages^{1,2} that exhibit responsive sp³-carbon-centered stereochemistry, adapting to and transmitting surrounding stereochemical information.³ By analysing NMR spectra of solution, solid and powdered samples, X-ray crystal structures and DFT models, we observe that the sp³-carbon stereochemistry of the rigid tricyclic cages is inverted through strain-assisted Cope rearrangements, emulating the low-barrier configurational dynamics typical for sp³-nitrogen inversion or conformational isomerism. This dynamic enantiomerisation can be stopped, restarted, or slowed by external reagents, while the configuration of the cage is controlled by neighbouring, fixed stereogenic centres. As part of a phosphoramidite–olefin ligand, the fluxional cage acts as a conduit to transmit stereochemical information from the ligand while also transferring its dynamic properties to chiral-at-metal coordination environments (Figure 1), influencing catalysis, ion pairing and ligand exchange energetics.

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Abstract No: T154

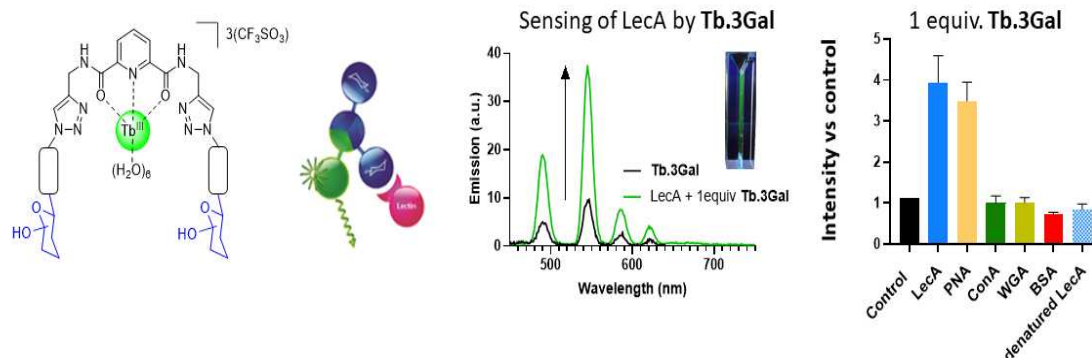
T154 Carbohydrate-functionalised lanthanide self-assemblies: inhibition and supramolecular sensing of bacterial carbohydrate-binding proteins

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Caption: Schematic of lanthanide-based glycocluster lectin sensing, enhancing Tb(II) emission; selectivity of galactoside sensor for various lectins

Supramolecular carbohydrate–protein interactions are key to vital biological processes including adhesion, infection and biofilm formation by bacteria.[1] These interactions are targets for therapeutic or diagnostic exploitation, through careful design of glycoconjugates or glycomimetics, which optimise weak interactions with carbohydrate-binding proteins to achieve micromolar to nanomolar affinities. Targeting carbohydrate-binding proteins (lectins) of *P. aeruginosa* (PA) has recently become an area of increasing interest in glycoconjugate chemistry, including for inhibition of biofilms and sensing.[2] While various multivalent glycoconjugate approaches are reported, including using calixarene and rotaxane scaffolds, use of metal coordination-chemistry and metal-directed self-assembly in design of lectin-targeting compounds is underexploited.[3]

Carbohydrate-functionalised coordination-complexes allow properties of both carbohydrates and metals to be employed to address the issue of antimicrobial resistance. We used Ru(II) coordination geometry to assemble lower valency ligands into tetravalent glycoclusters.[3a] Their ability to inhibit PA biofilm formation was found to depend on the identity and presentation of the carbohydrate motif, which could bridge adjacent lectin binding-sites. Related self-assemblies with Eu(III) have antiadhesive activity against fungal pathogens also.

Building on this work, we designed novel luminescent glycoclusters, assembled in solution with lanthanide ions, including Tb(III), to act as sensors for these biomolecules. The coordination sphere of these luminescent systems contains several quenching water molecules, and show clear 'switch-on' sensing behaviour upon interaction with various lectins in buffer solution, including PA's galactophilic lectin. The selectivity of the lectin for different carbohydrate structures determines the sensors' luminescence response.[3b] Studies are ongoing with further lectins of different selectivities to establish the full scope of this sensing paradigm, towards creating visually-readable diagnostic platforms for critical priority pathogens.

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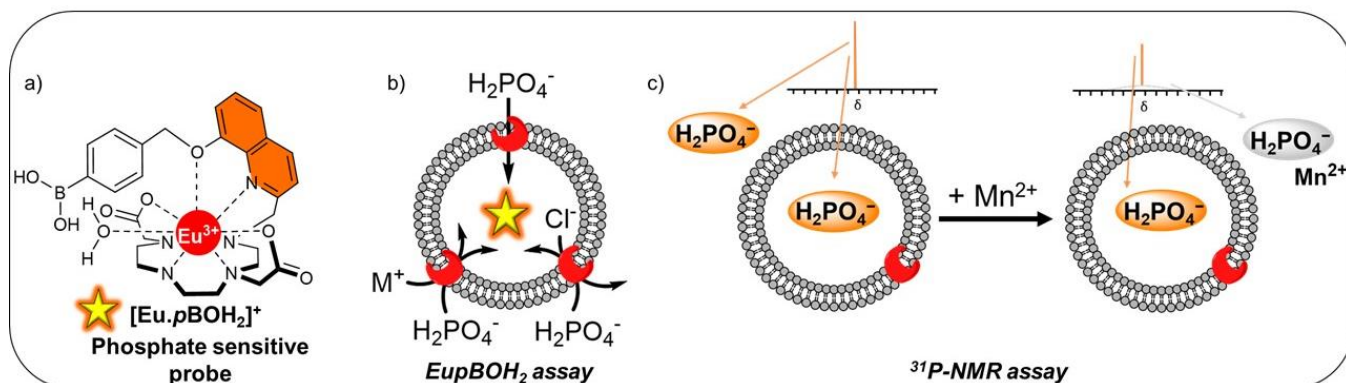
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T155 Transmembrane transport of phosphate: opening a new door.

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Caption: Figure 1. a) Schematic representation of the EupBOH₂ assay and structure of the probe. b) Schematic representation of the ³¹P-NMR assay.

Inorganic phosphate is essential for the functioning of organisms. Its homeostasis is regulated by the concerted work of different phosphate transport proteins,¹ whose malfunction can lead to a variety of diseases.² A potential treatment for diseases caused by malfunctioning anion transport proteins could be the use of small synthetic molecules that mimic the behaviour of such proteins, and thus work as anion transporters.^{3,4}

However, there are no reported examples of transmembrane transport of phosphate mediated by synthetic carriers. The reasons must be sought in the intrinsic properties of phosphate such as its high hydration energy, its pH dependence speciation (e.g. at neutral pH H₂PO₄⁻ and HPO₄²⁻), and its tetrahedral geometry.

Driven by this challenge, we have developed the first phosphate transporter and two methods to monitor its ability to transport inorganic phosphate into liposomes. Phosphate transport was monitored by emission spectroscopy using the EupBOH₂ assay, based on the use of an encapsulated phosphate sensitive europium(III) probe.⁵ Furthermore, the ³¹P-NMR spectroscopy assay was used, not only to obtain further proof, but also to study the pH dependence of phosphate transport.

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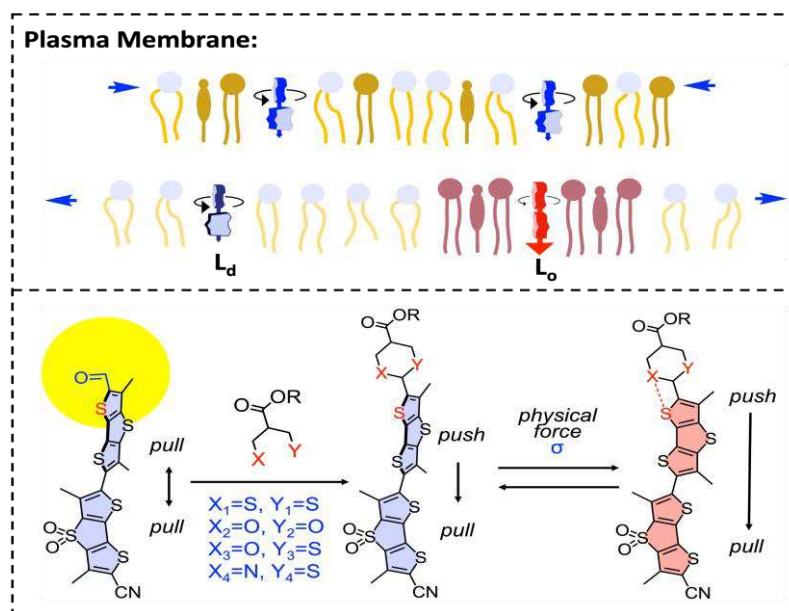
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Abstract No: T156

T156 Saturated 1,3-Heterocycles as Clickable Dual-Purpose Donor Junctions: A New Paradigm for Fluorescent Flipper Probes

Xiaoxiao Chen ¹, Xiao-Xiao Chen ¹, Nerea Gonzalez Sanchis ², Maxime Vonesch ², Aurelien Roux ², Naomi Sakai ²

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Caption: The concept of chalcogen-bond switching donor

In 1665, when the apple fell in Newton's garden, it already revealed that visualizing the physical force directly is very difficult in nature. This is also true for imaging the physical force in living systems. In the plasma membrane, membrane tension plays an important role in different biological processes, such as endocytosis, exocytosis and etc. However, conventional methods, including micropipette aspiration, optical tweezer, and atomic force microscopy exhibit many drawbacks for membrane tension imaging, such as poor time resolution, low efficiency, and technical challenge. To overcome these problems, our group developed a push-pull mechanophore, called "fluorescent flipper", that responds to membrane tension by planarization in the ground state. This planarizable push-pull probe is composed of two dithienothiophenes that are twisted by chalcogen-bond repulsion between methyls and endocyclic sulfurs around the twistable bond in the liquid-disordered phase (L_d). Their mechanical planarization turns on a push-pull system, which is red-shifted to a longer excitation wavelength and fluorescence lifetime in the liquid-ordered phase (L_o). In this paper, we continue to develop a new generation flipper by turning on the donor junction. Through this donor junction, saturated 1,3-heterocycles will be generated and different donor atoms can be introduced into the same fluorescent flipper backbone simultaneously. In addition, we can continue to introduce different targeting groups based on the 1,3-heterocycles, which is beneficial to open a wide chemical space for membrane tension imaging in living systems.

Reference:

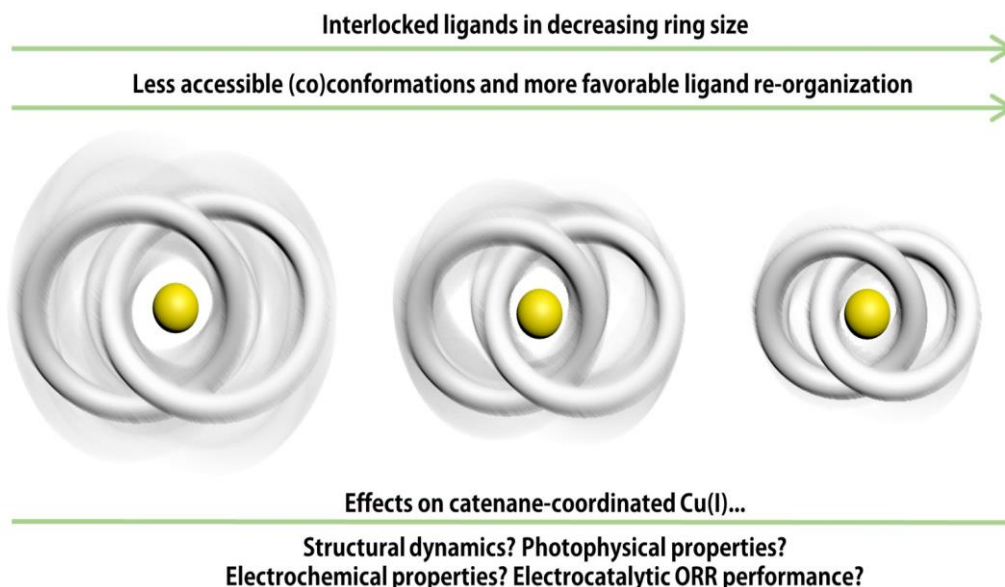
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Abstract No: T157

T157 Effects of Mechanical Interlocking on Copper Coordination Features: Structures, Photophysical, Electrochemical and Electrocatalytic Properties

Yulin Deng Ho Yu Au-Yeung

The University of Hong Kong, HONG KONG, Hong Kong



While transition metal-templated synthesis has been very successful in obtaining catenanes and other mechanically interlocked molecules, the effects of catenane ligands on the coordinated transition metals are not fully understood yet except for the kinetic stabilization known as the “catenand effect”.¹ In this work, a systematic investigation of how the size of the interlocked rings in catenanes affects the coordination properties of Cu(I) is presented. A range of structural, photophysical and electrochemical characterization by NMR, X-ray crystallography, steady-state and transient absorption spectroscopy, and cyclic voltammetry studies will be discussed. Moreover, by tuning the mechanical bond tightness, enhanced electrocatalytic oxygen reduction performance with improved activity and selectivity using the catenane-coordinated Cu(I) will be described.²

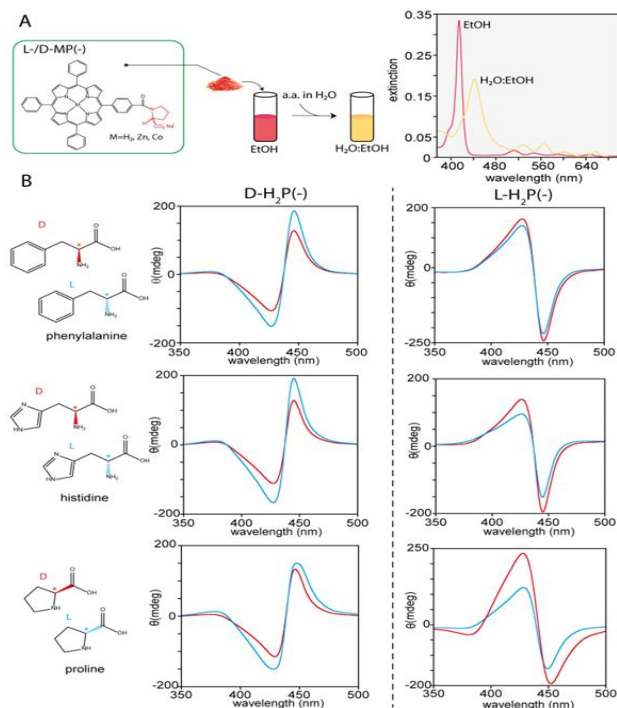
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Mo, X.;# Deng, Y.;# Lai, S. K.-M.; Gao, X.; Yu, H.-L.; Low, K.-H.; Guo, Z.; Wu, H.-L.; Au-Yeung, H. Y.;* Tse, E. C. M.* Mechanical Interlocking Enhances the Electrocatalytic Oxygen Reduction Activity and Selectivity of Molecular Copper Complexes. *J. Am. Chem. Soc.* **2023**, just accepted.

Abstract No: T158

T158 Chiral recognition of amino acid enantiomers by chiral porphyrins aggregates

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Caption: A) schematic representation of the porphyrin aggregations in hydroalcoholic solution; B) CD spectra of different porphyrins-a.a. co-solutions.

Porphyrins are among the most versatile and tunable molecular elements used to assemble organized materials expressing elements of chirality at the supramolecular level. A protocol to obtain these suprastructures consists in driving the self-assembly of chiral porphyrins in controlled conditions of solvent composition, pH, ionic strength or temperature. Over the years, we have exploited this approach by conjugating the porphyrin ring with a proline residue in order to confer both amphiphilicity and chirality to the macrocycle and by adopting the “good-bad solvent” strategy (i.e. ethanol/water medium) to induce the aggregation [1].

Herein we report the self-assembly in aqueous ethanol solutions of these porphyrin derivatives in the presence of amino acids as co-solute (panel A). Specifically, the studies were carried out using different enantiomeric pairs of amino acids (e.g., histidine, proline and phenylalanine) and choosing different porphyrin-amino acid ratios. The aggregation process has been investigated by UV-Visible (UV-Vis) and Circular Dichroism (CD) spectroscopies to study both its kinetic and thermodynamic behaviour. The results show that the two porphyrin enantiomers interact in a different and specific way with the (L)- and (D)-amino acids dissolved in water: aggregation of a given porphyrin enantiomer (L- or D-) in the presence of amino acids with opposite chirality leads to an increase in CD signal intensity (panel B) and UV-Vis spectral changes typical of J-type aggregates (panel A). This finding demonstrates the effective occurrence of molecular recognition phenomena of amino acids by supramolecular porphyrin aggregates.

The present contribution will illustrate in depth the recent results with these systems that represent a proof of concept for the preparation of sensitive materials with tunable stereoselectivity for the potential discrimination of amino acid enantiomers.

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Abstract No: T159

T159 Double-dynamic molecular cage as fluorescent stimuli-responsive material for metal ion detection.

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Adam Mickiewicz University, Poznan, Poland

Dynamic materials, both molecular and supramolecular, are becoming more and more popular among scientists from various fields of science, mainly chemistry, biology and medical sciences. Due to the lability of connections, the obtained architectures are able to reversibly create/decompose and exchange components. In addition, such materials are capable of structural and qualitative transformation under the influence of thermodynamic changes in the system. Precisely planned synthesis and selection of appropriate components allow self-assembled molecular dynamic structures like cages to be obtained.¹

Cage represents a very interesting group of architectures with a wide range of applications ranging from (bio)molecular recognition, drug transport to supramolecular catalysis.² These compounds, due to their internal void space, have become an attractive product with potential use as "nanocontainers." Supramolecular chemistry has been particularly effective in the synthesis of such structures using coordination chemistry and hydrogen interactions. However, Dynamic Covalent Chemistry (DCC) has become increasingly important in creating covalent architectures.³ The advantage of this method is the ability to generate an extensive yet diverse dynamic combinatorial library (DCL) in which the number of its individual components can be intensified both spontaneously and using the templating effect. The use of reversible covalent interactions makes it possible to create dynamic systems that exhibit self-repair properties in order to transform kinetic intermediates into stable thermodynamic products.

Considering the advantages of DCC, it was possible to selectively generate a doubly dynamic organic cage with stimuli-responsive properties. Appropriate selection of conditions allowed the simultaneous formation of two orthogonal bonds - a disulfide bond and an acylhydrazone bond. On the other hand, the presence of a chromophore unit - triphenylamine, as well as an empty cavity made it possible to use the obtained architecture in host-guest chemistry, for the detection of metal ions with the aid of fluorescence. Addition of a competitive agent (chemical stimuli), results in an exchange of the cage's components and consequently the release of the guest.

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Acknowledgment:

SONATINA UMO-2019/32/C/ST4/00565

SONATA BIS 2018/30/E/ST5/00032

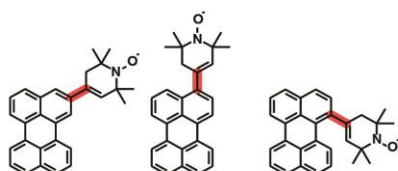
Abstract No: T160

T160 Strain-Controlled Systems: Understanding the Role of Chirality in Spin Coupling and Supramolecular Self-Assembly

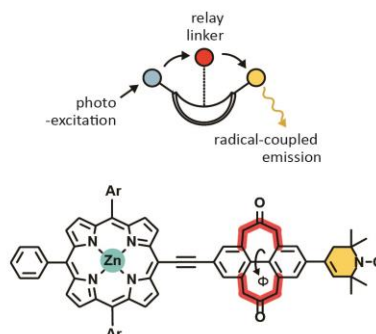
Mélissa El Bitar Nehme

Universität Zürich, Zürich, Switzerland

Regio-selective Spin Interactions



Design, Synthesis, and Study of Tunable Spin Information Relays in Metalated Porphyrin Systems



The interdisciplinary field of molecular spintronics has attracted much attention over the years as it allows the development of nanoscale devices and comprises several branches such as molecular quantum technologies, organic spintronics, and molecular magnetism.¹ One of the greatest challenges in this field is to find new materials that exhibit the desired magnetic properties to allow efficient generation, transport, and storage of spin information. Based on these requirements, photogenerated molecular three-spin systems which are composed of an organic chromophore that is covalently linked to a stable free radical are ideal candidates to explore the factors governing spin communication on a molecular level.² While the radical acts as a sensitizer that improves the intersystem crossing rate, the delicate covalent linkage between chromophore-radical systems serves as a means of controlling the excited state dynamics of the chromophore.³ The aim of this project is to develop covalent multi-spin systems to study spin-information transfer and storage. This is performed by engineering systems that consist of at least two organic spin centers that we connect by a conjugated framework. The bridge between the two spin centers is then systematically modified to trace the changes in the resulting spin communication. By choosing a bridged biphenyl⁴ as the linker between the chromophore and the radical, the electronic communication throughout the synthon is expected to vary with the torsion angle Φ between the planes of the two phenyl rings, which in turn modulates the spin-spin interaction.

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Abstract No: T161

T161 Benzothiadiazole Cage as a Selective Endoplasmic Reticulum Staining Dye for long-term Live Cell Imaging and Stress Detection

Aliyah Fakim Batoul Maatouk, Bappa Maiti, Basem Moosa, Niveen Khashab

King Abdullah University of Science and Technology, Thuwal, Saudi Arabia

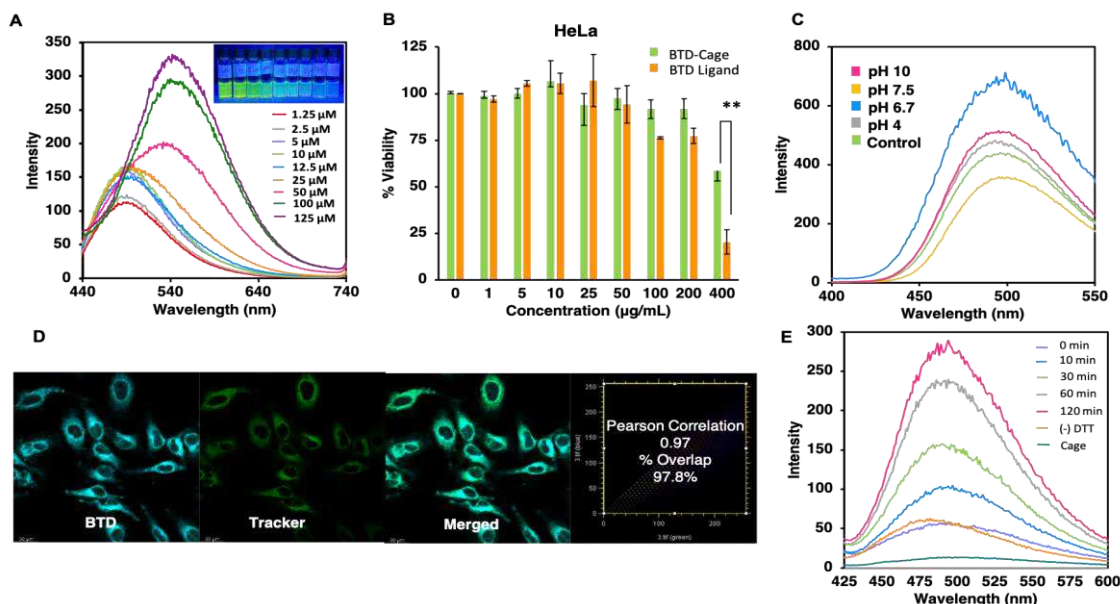


Figure 1. A) Fluorescence emission spectrum of cage in PBS with increasing concentration B) Cytotoxicity assay on HeLa cells at different concentrations C) Fluorescence emission spectrum of cage in DMSO (8 μ M) at different pH (λ_{exc} = 390 nm) D) Confocal images of cellular localization of cage in HeLa Cells after 12h of incubation E) Fluorescence response of BTD-cage to protein (BSA) aggregation with time in HEPES buffer (λ_{exc} = 390 nm).

Organic fluorophores are powerful tools for interrogating biological processes owing to their noninvasive labelling of cellular organelles. Fluorescent 2,1,3-benzothiadiazole (BTD) derivatives piqued interest as a live cell fluorescence imaging scaffold for their interesting features such as high quantum yield, large stoke shifts, high chemical and photostability. To date, all the reported BTD probes are small molecules which selectively stain specific organelles with some exceptions (the endoplasmic reticulum (ER)).¹ The chemical space around BTDs has yet to be fully explored but aims to succeed where classical fluorophores, e.g., BODIPYs have shown their limitations such as unreliable photostability.² As such, the BTD moiety has not been investigated in the supramolecular form which offers the possibility of interfering with biological systems. We have, therefore, designed and synthesized a BTD-containing cage through dynamic covalent chemistry.

The BTD-cage has emission maxima in the blue-green region in both DMSO and buffer and upon increasing cage concentration in PBS, a red shift is observed due to the formation of aggregates (Figure 1A). The cage has excellent cell viability (Figure 1B), and stability at different pH (Figure 1C) while co-localization experiments in HeLa cells showed translocation into the ER (Figure 1D). Herein, is the first report of a BTD-fluorophore which selectively stains the ER. Furthermore, we observed a fluorescence response of the cage to protein aggregation (Figure 1E). We postulate that this can be utilized as an ER-targeting protein aggregate fluorescent sensor during accumulation of unfolded protein under ER stress.³

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Abstract No: T162

T162 Towards Dicarboxylates Detection in Water: Development of Zn(II)-Salophen Based Plasmonic Nanosensors

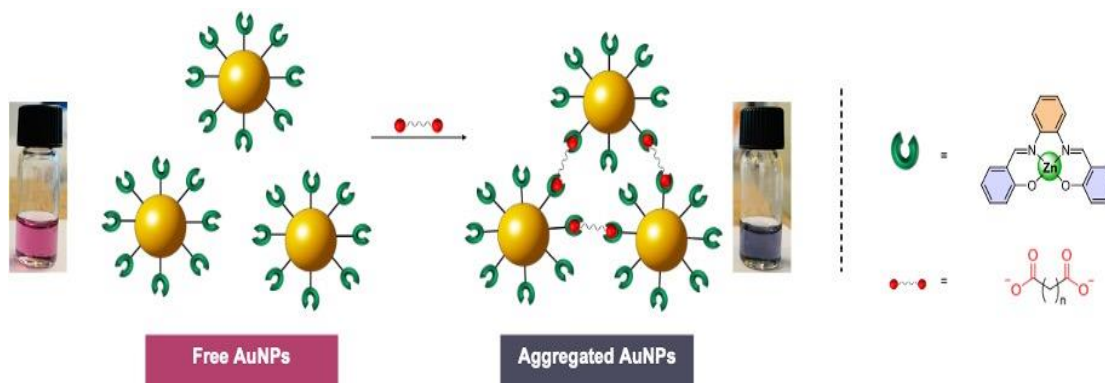
Alessia Fantoni ¹ Gilles Bruylants ², Antonella Dalla Cort ³¹ Sapienza Università di Roma, Université libre de Bruxelles, Roma, Belgium² Université libre de Bruxelles, Bruxelles, Belgium³ Sapienza Università di Roma, Roma, Italy

Fig 1. Schematic diagram for the aggregation of functionalized AuNPs upon a supramolecular interaction with the target analyte.

The development of molecular sensors that can selectively bind analytes in an aqueous environment is an important and topical field of research constantly fuelled by applications ranging from environmental monitoring to biology and medicine.

In this regard, dicarboxylic acids are important targets for molecular recognition and sensing due to the role they play in biological and industrial processes,¹ as well as their potential effect on the environment and health.² Although considerable progress has been made in the development of receptors and sensors for carboxylic acids in organic solvents,² the synthesis of receptors capable of performing such function in an aqueous environment remains a challenge since potential receptors are often large hydrophobic organic molecules that are poorly soluble in water. Moreover, at biological pH most dicarboxylic acids exist in their anionic deprotonated form, characterized by high solvation energy, that further complicates the molecular recognition process.

It is known that Lewis acid-base interactions may survive in the competitive aqueous medium since, in most cases, they are less affected by the competition with water molecules than other non-covalent interactions such as hydrogen bonds or dipole-dipole interactions.³

In this context, we are developing new plasmonic nanosensors for dicarboxylate species in water capable of producing an easily readable response. Those are based on Zn(II)-Salophen complexes, known to present a good affinity towards carboxylic groups in organic solvents,⁴ grafted on gold nanoparticles. The advantage of using gold nanoparticles is that they can (i) transfer lipophilic receptors into water and (ii) be used as colorimetric sensors thanks to their remarkable plasmonic properties, enabling an easy detection of the supramolecular interaction between the grafted receptor and the target analyte (Fig 1).

Different strategies for the functionalization of gold nanoparticles with Zn(II)-Salophen complexes will be reported as well as the evaluation of these hybrid nanostructures for the sensing of aliphatic dicarboxylates in water.

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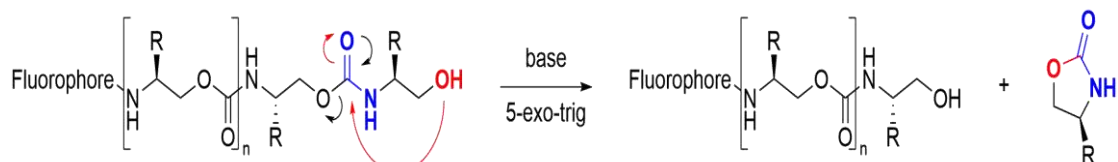
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Abstract No: T163

T163 Information Storage and Retrieval in Sequence-Defined Oligourethanes

Hazel Fargher Julia Shuluk, Christopher Wight, Hyun Park, Fathima Pary, Le Zhang, Eric Anslyn

University of Texas at Austin, Austin, United States



Caption: Controlled self-sequencing of sd-OU through base catalyzed 5-exo-trig cyclization.

Sequence-defined polymers, such as DNA, have gained attention for their potential in biomimetics, catalysis, and information storage. Our group has developed the solid phase synthesis of sequence-defined oligourethanes (sd-OU) using commercially available amino alcohols.¹ We have shown that sd-OU self-sequence in a controlled manner through 5-exo-trig cyclization of the urethane backbone, which can be monitored by LC-MS.¹ This has inspired us to study functional group effect on both the chemical and enzymatic degradation of polyurethane plastics. We also applied this self-sequencing ability to information storage. As a proof of concept, a passage from Jane Austen's *Mansfield Park* was encoded into hexadecimal in sd-OU and then decoded by a third party with full accuracy.² To further expand upon this work in information storage, we have increased information density and speed of information retrieval by sequencing up to eight sd-OU at a time³ and we are currently developing methods to selectively isolate and sequence information stored in "hash-tag" functionalized sd-OU. To demonstrate the versatility of sd-OU for information storage in languages other than English, we are encoding phrases in pictographic languages, such as Mandarin, and code written in scripting languages, such as Python. Finally, our goal is to automate every process of information storage and retrieval, from sd-OU synthesis, sequencing, and decoding, even working towards developing a natural language processor to "spell-check" retrieved information.

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Abstract No: T164

Flash talks 27-06-2023 16:40 - 17:00 Harpa - Silfurberg A/B 2nd floor

T164 Synthesis of new ratiometric fluorescent probes for late endosome pH tracking

Patricia Fúlias-Guzman Alicia Rioboo, Jose Juan Reina, Irene Lostale-Seijo, Javier Montenegro

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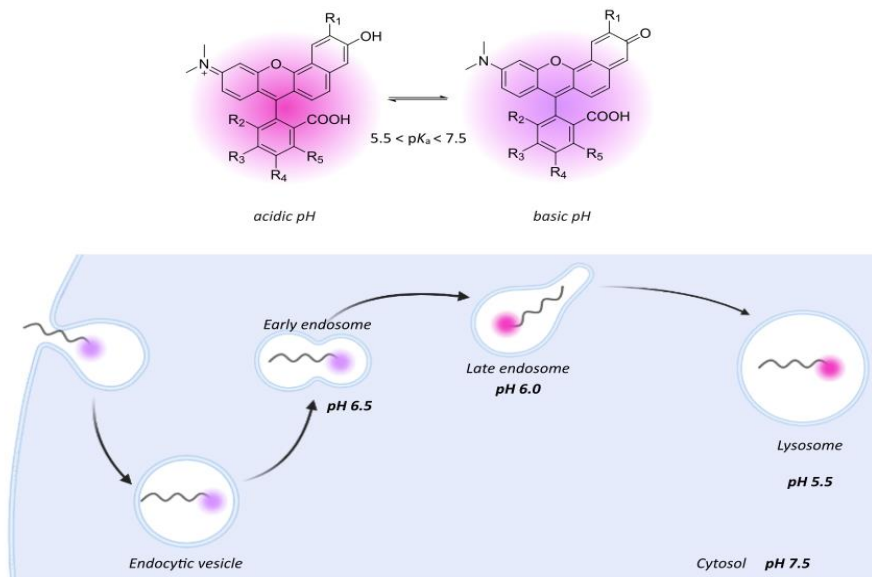


Figure 1. Endosomal internalisation of the probe coupled to a peptide

The control of fluorescent molecular properties, such as the emission wavelength or quantum yield, enables the development of new supramolecular sensors capable of responding to external stimuli, such as pH [1]. pH-sensitive ratiometric fluorophores are widely used in chemical biology for studying internalisation mechanisms, as well as for designing smart materials that respond to changes in pH. By having two or more wavelengths of fluorescence emission that depend on pH, a more precise characterisation of the pH value of the medium can be achieved. This ratiometric quantification avoids intensity artefacts due to instrumental errors or dilution factors. Supramolecular systems based on peptides or hydrogels attached to these probes can be used to directly measure the local pH by fluorescence microscopy using white light with harmless effects in cells assays [2]. Therefore, these molecules are excellent tools to obtain valuable information about cellular internalisation pathways and target areas for new therapeutic agents [3]. However, the difficult synthetic routes of these ratiometric probes hinder their promising applications in cell studies.

To overcome this challenge, we designed and synthesised a variety of derivatives of C. SNARF-1 with varied functionalisation, where the incorporation of electron-withdrawing groups to the xanthene core optimizes the pH response of the molecule (Figure 1) [4]. The new fluorine-functionalised derivatives allow tailoring the pKa to expand the working range of the probe without losing its ratiometric character. The new derivatives were incorporated to the supramolecular vectors and used to track the endosomal internalisation route in cells.

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Abstract No: T165

T165 Detection of Lanthanides Utilizing ^{19}F -Paramagnetic Guest Exchange Saturation Transfer Magnetic Resonance Fingerprinting (^{19}F -ParaGEST MRF)

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¹ Weizmann Institute of Science, Rehovot, Israel

² Tel Aviv University, Tel Aviv, Israel

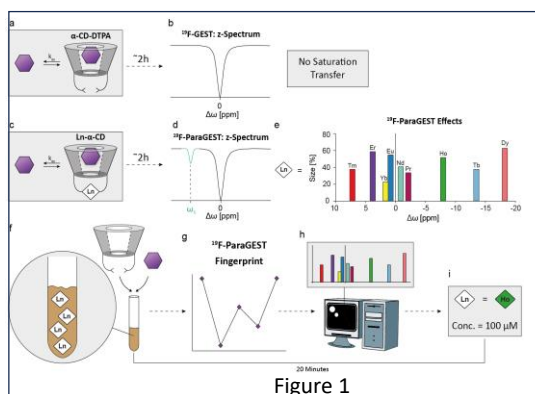


Figure 1

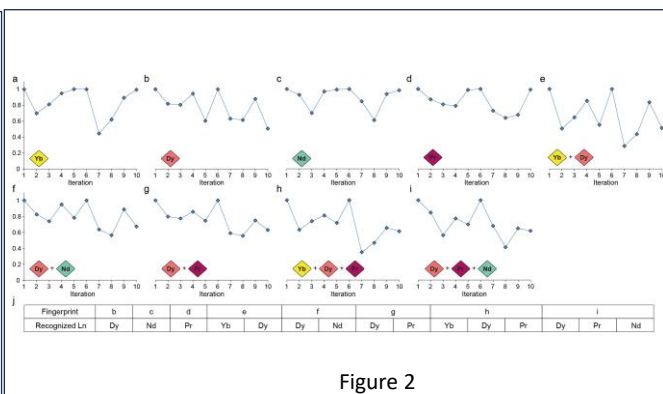


Figure 2

Figure 1. ^{19}F -Paramagnetic Guest Exchange Saturation Transfer Magnetic Resonance Fingerprinting (^{19}F -ParaGEST MRF) Principles and Figure 2. ^{19}F -ParaGEST Fingerprints and Their Analysis Results for solutions containing Yb, Dy, Nd, Pr and Their Combinations.

Lanthanides possess unique electronic, luminescent, magnetic, and catalytic properties making them extremely important for modern technologies. However, lanthanide disposal impacts the environment and human health and calls for analytical tools for monitoring the trace levels of lanthanides in complex media. The emerging field of lanthanides sensors, based on fluorescence materials, does not apply to murky samples and suffers from a limited selectivity due to the highly similar chemical properties of lanthanides.

Here, we aim to enhance our ^{19}F paramagnetic guest exchange saturation transfer (^{19}F -paraGEST) approach¹ (Fig. 1a-e), based on different lanthanide-induced NMR readouts (Fig. 1e), with magnetic resonance fingerprinting (MRF)²⁻⁴ capabilities to create a **^{19}F -ParaGEST MRF lanthanide sensing platform** (Fig. 1f-i).

To this end, a Bloch-McConnell-equations-based database ('dictionary') of simulated ^{19}F -paraGEST effects will be generated for more than 5.25m combinations of **paramagnetic lanthanide-modified α -cyclodextrin hosts ($\text{Ln-}\alpha\text{-CDs}$)**: fluorinated guest (Fig. 1h). Next, this 'dictionary' will be used for suggesting an optimized MRF acquisition protocol that generates a unique ^{19}F -paraGEST pattern (i.e., ^{19}F -paraGEST **fingerprint**, Fig. 1g) for a solution of unknown lanthanide content (Fig. 1f). Last, the 'dictionary' will be used for training an AI-based system to analyze ^{19}F -paraGEST fingerprints to reveal lanthanides' identity and concentration in their corresponding solutions (Fig. 1i).

This new suggested platform was examined for 4 lanthanides (Yb, Dy, Nd and Pr) through 'dictionary' generation and ^{19}F -paraGEST fingerprints analyses for different **$\text{Ln-}\alpha\text{-CDs}$:guest** combinations (Fig. 2, the selected lanthanides are represented as diamonds), utilizing an optimized MRF acquisition protocol. The accurate compositions for mixtures of up to three lanthanides were successfully identified by the AI-MRF system (Fig. 2j). Importantly, this tool can also quantify the concentrations of the identified lanthanides in each sample (data not shown here).

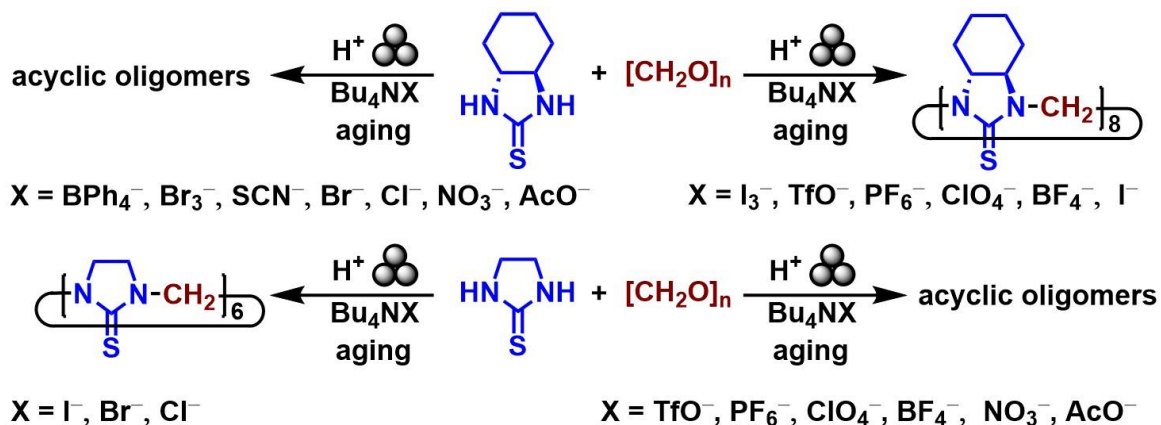
Recently, the **^{19}F -paraGEST MRF** approach was extended for studies of up to nine lanthanides and their combinations and experimental data is currently examined to determine the ability to study mixtures with further enhanced complexity. We envision this new approach will allow fast sensing and selective recognition of lanthanides in waste samples for future green chemistry applications.

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Abstract No: T166

T166 Substrate-controlled and Template-assisted Mechanochemical Synthesis of thio-Hemicucurbiturils

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Caption: Synthesis of thio-hemiCucurbiturils

Hemicucurbiturils (hemiCB[n]s) consist single hoop of methylene linkers interconnecting 2-imidazolidone (ethylene urea) subunits. In contrast to the rigid pumpkin shape of cucurbiturils and their affinity toward cationic species, the structure of hemiCB[n] adopts an alternating conformation and encapsulates anions. To date, fewer 2-imidazolidone derivatives were successfully cyclooligomerized, and the resulting macrocycles were anion template-controlled.

Here we present novel sulfur-containing hemiCB[n]s by following the heteroatom replacement approach, which is the replacement of oxygen atoms in hemiCB[n]s by sulfur affording new homologs of *thio*-hemiCB[n] ($n = 6, 8$).

Because the sulfur-analog of 2-imidazolidone is acid-sensitive, the classic synthetic methodology used for hemiCB[n]s is not applicable in synthesizing *thio*-hemiCB[n]s. Therefore, we applied a mechanochemical approach that involves solid-phase reactants in a nearly solvent-free environment. Optimization reactions included the effect of the templating agent, the nature of the acid catalyst, and aging duration and temperature. Following the optimized reaction conditions, we successfully prepared 6- and 8-membered *thio*-hemiCB[n]s in high selectivity. Ring-size selectivity was attributed to the nature of the building block. Acyclic oligomers vs. macrocycles were determined by choice of anion template. X-ray studies and isothermal titration calorimetry (ITC) confirmed the selective anion-binding affinities of each *thio*-hemiCB[n] homolog.

Abstract No: T167

T167 Ion pair recognition and sensing by squaramide-based receptor possessing pyrene reporter.

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Over the recent years molecular recognition has become a frequent topic in the area of supramolecular chemistry¹. Special examples of this type of compounds are electrically neutral ion pair receptors, which are able to simultaneously bind anions and cations. Significant increase of interest in this type of structures is due to the fact that anions and cations playing a important role in many areas such as medicine, biology, or environmental protection². Three things are crucial in the design of these compounds: choice of molecular platform, selection of suitable binding domains and their appropriate arrangement in the receptor molecule³. The latter is of particular importance in squaramide-based molecular receptors, because linking suitable groups directly to anion binding domains may affect its effectiveness. Especially, proper incorporation of the cation binding domain to the squaramide function can lead to ion pair receptors capable of interacting with ion pairs in a cooperative manner.

We have designed and synthesized a family of squaramide-based ion pair receptors consisting of a crown ether as a cation binding domain and squaramide unit allowing for interaction with anions. The cation binding domain was installed on the phenyl ring directly linked with squaramide in this way to act as an electron withdrawing group, thus enhancing anion binding. Further enhancement was achieved by increasing the binding strength of the receptor to anions due to simultaneous binding with cations. This opened the opportunity to use electron rich fluorescent reporter as an signalling unit and maintain the ability of this sensor to strongly interact with ion pairs. Based on fluorometric measurements we showed that the strongest fluorescent response was obtained upon the interaction of sensor with monobasic phosphates. The presence of a pyrene group enabled the docking of this sensor on graphene quantum dots, which made it possible to obtain a conjugate capable of sensing ion pairs more effectively.

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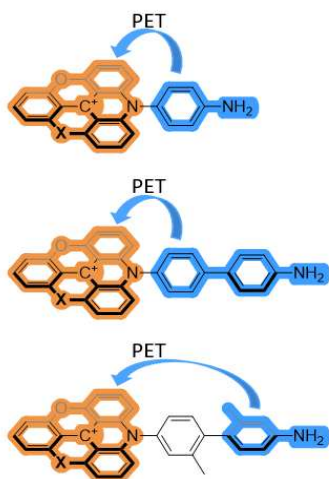
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Chen, L.; Berry, S. N.; Wu, X.; Howe, E. N. W.; Gale, P. A. *Chem* **2020**, *6*, 61-141.
McConnel, A. J.; Docker, A.; Beer, P. D. *ChemPlusChem* **2020**, *85*, 1824-1841.

Abstract No: T168

T168 Exploring the Fundamentals of PET Quenching in Triangulenium ADOTA and DAOTA Systems

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Caption: Visual presentation of PET-quenching in 1-3.

In a series of triangulenium PET-systems, we have exploited the efficient electron-donating ability of an aniline towards both ADOTA and DAOTA.^{1,2} We have investigated three different quenchers, a short (**1**), a long (**2**) and a twisted (**3**), 1,4-diaminobenzene, benzidine and 2,2'-dimethylbenzidine, respectively. The rate of PET-quenching is expected to be faster for ADOTA than DAOTA due to a lower lying HOMO, which results in a larger driving force. When increasing the donor-triangulenium-quencher distance **1** to **2**, the small blue-shift introduced upon protonation of the amine (ON-state) disappears, showing a complete decoupling of the triangulenium fluorophore and PET-quencher.

In order to measure the rate constant of PET (k_{PET}) in the OFF-state, the emission spectra were obtained using a ps time scale in a streak camera since our TCSPC was found to be insufficient. Surprisingly, k_{PET} is identical for **1** and **2**, even with the additional phenyl group which increases the distance between the donor and the acceptor in **2**. However, upon introduction of methyl groups in **3**, a 20-fold decrease in quenching is found. This clearly shows that the orbital overlap is involved in the quenching by **1** and **2**. The main difference between **2** and **3** is the dihedral angle which is 32° and 88° , respectively.^{3,4} Even with the decrease in k_{PET} the quenching in **3** for ADOTA and DAOTA is still highly efficient, with nearly 99 % quenching, nevertheless the high quality data allows us to resolve the effect of molecular structure on the PET-quenching process in triangulenium systems.

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Abstract No: T169

T169 Crown ether-appended cyclometalated Pt(II) complex for organic guests complexation

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Platinum(II) complexes are appealing candidates for photoluminescent applications due to their high spin-orbit coupling, which facilitates fast intersystem crossing and formally spin forbidden singlet to triplet excited state transitions, leading to large Stokes shift, longer emission lifetimes and high luminescence quantum yields.¹ Additionally, their square planar geometry with open axial coordination sites allows intermolecular Pt...Pt or π -stacking interactions. Different stimuli such as heat, mechanical force, pH and solvents have been shown to modify such interactions producing optical and luminescent chromic behavior in both solid and solution states.²

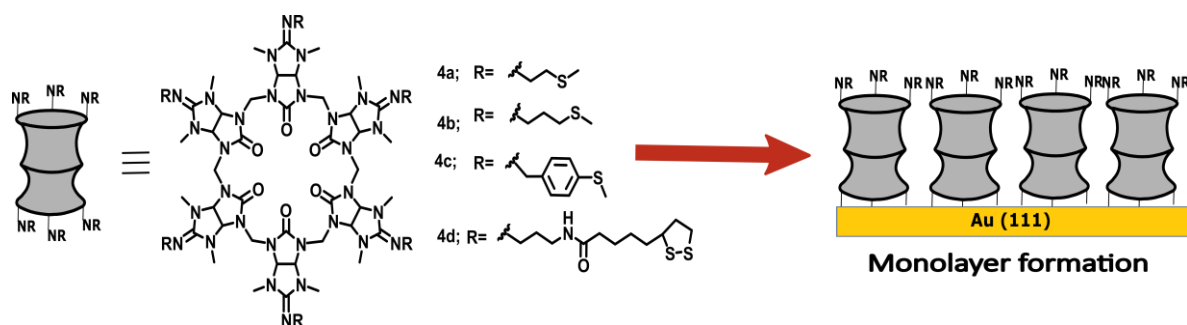
Recently, our group used an oxo-bridged bis(phenylpyridine) ligand to synthesize a Pt(II) complex that showed solvatochromism in the solid state and aggregation-induced emission in polar solvents.³ Furthermore, the metal center exhibited diverse and easily accessible oxidation states that imparted different photoluminescent properties to the complex. When the methoxy groups in this cyclometalated complex were replaced with an 18C6-crown ether cavity, the resulting compound demonstrated cation sensing with accompanying color and luminescence changes.⁴ The complex could additionally detect vapor in the solid state and undergo controlled supramolecular polymerization modulated by the receptor property of the monomer. The multi-responsiveness of this compound motivated us to expand the cavity to introduce new functions and properties. In this work, I present the synthesis and characterization of a 24C8-crown ether cavity appended to the same cyclometalated Pt(II) complex and discuss the fascinating features afforded by guest-complexation of organic cations.

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Abstract No: T170

T170 Selective Electrochemical Impedance Sensing of Perchlorate through Self-Assembled Monolayers of semiaza-Bambusuril Derivatives

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Caption: Schematic representation of structure of semiaza-BU[6] derivatives and the formation of SAM as a selective anion recognition layer.

Salts containing perchlorate anions are persistent pollutants threatening human health by impairing the thyroid gland's function over long-term exposure. Consequently, many analytical methods were developed for detecting perchlorates in water sources, soil, and food products. High-throughput electrochemical techniques are also attractive for developing and easily operating sensory devices.

Here we report the synthesis of new semiaza-bambusurils (BUs) equipped with surface anchoring groups, such as thioether or disulfide groups and their implementation into SAM-based electrochemical anion sensing layers. We characterized the interactions at the interface between the anchoring groups of semiaza-BUs and the metal substrate via Cyclic voltammetry (CV) with $\text{Fe}(\text{CN})_6^{3-/4-}$ as a redox probe together with X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and ellipsometry techniques. Data showed that the anion receptors' packing patterns on the gold strongly depend on the anchoring group. Electrochemical impedance spectroscopy (EIS) supported by CV measurements, was used for detecting perchlorate anion in aqueous solutions.

With short thioether alkyl chains, no interfacial solid-liquid electrochemical activities were detected. In contrast, SAMs based on semiaza-BUs equipped with either aryl thioether or lipoic chains followed a significant change in their CV and impedance plots upon titration of perchlorate. Both SAMs showed high selectivity compared to other inorganic anions.

Interestingly, the impedance behaviour of the lipoic SAM were depend upon the concentration of incubating solution and was significantly more sensitive at 1 mM concentration of lipoic semiaza-BUs incubating solution to detect the perchlorate concentration (down to 2-4 mM), which was explained by the highly compact, dense monolayer film due to cross-linking between disulfide moieties. This crosslinking phenomenon could be an elegant solution for pinholes and defects commonly associated with SAMs. The SAMs of the disulfide-substituted semiaza-BU provided a way to tune the dynamic range and sensitivity of anion detection by variation of their thickness. Remarkably, strong binding of perchlorate anion over other anions was detected with SAMs of the semiaza-BU.

Abstract No: T171

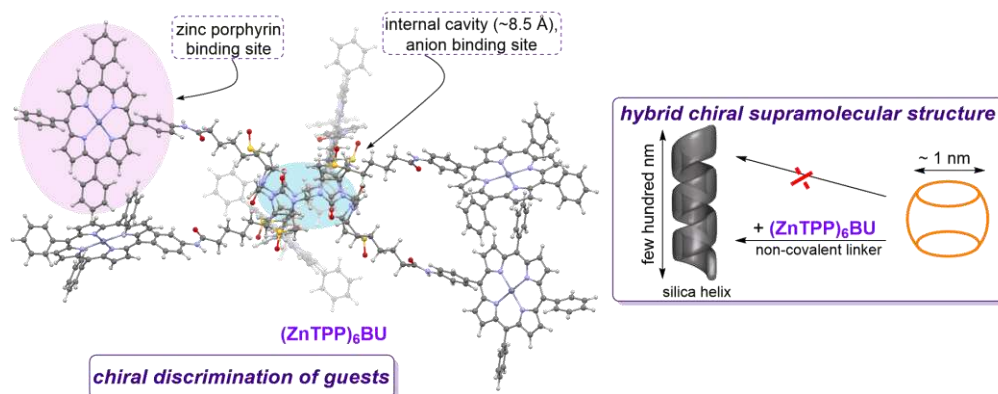
T171 Hexakis(Zn-tetraphenylporphyrin)-biotin-L-sulfoxide[6]juril: a hexapod cavitand which enables chiral recognition of nanosized objects

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Caption: Figure. Computational model (PM6 theory) of (ZnTPP)₆BU and its supramolecular characteristics.

Biotin-L-sulfoxide[6]juril is a chiral cucurbituril-type macrocycle which contains an electron deficient central cavity capable of capturing anions (1). Its amide coupling with corresponding tetraphenylporphyrin derivative affords a novel bulky and chiral hexakis(Zn-tetraphenylporphyrin)-biotin-L-sulfoxide[6]juril ((ZnTPP)₆BU), in which six achiral porphyrin moieties are linked to the chiral macrocycle via flexible side chains. Metalloporphyrins possess unique spectral and coordination properties which make them excellent chemosensors (2). Therefore, combination of the chiral structure of biotin-L-sulfoxide[6]juril reinforced by the specific features of porphyrins enables extraordinary binding and chiroptical properties to (ZnTPP)₆BU. In addition to the internal biotinuril cavity, the conformational flexibility of (ZnTPP)₆BU side chains allow assembling of “super-structures”, in which the host-guest interactions are led by the zinc porphyrin units. Due to its size-adaptable properties, (ZnTPP)₆BU is able to form different complexes with objects of various size, ranging from few angstroms-size molecules to hundred-nanometers nano objects (e.g., silica nano helices (3)). Such complexes create new hybrid supramolecular structures which act as hosts themselves. Moreover, (ZnTPP)₆BU can be sensitive to its guests' chirality.

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Abstract No: T172

T172 Synthesis and anion recognition properties of a new family of 1,8-diaminocarbazole-based receptors

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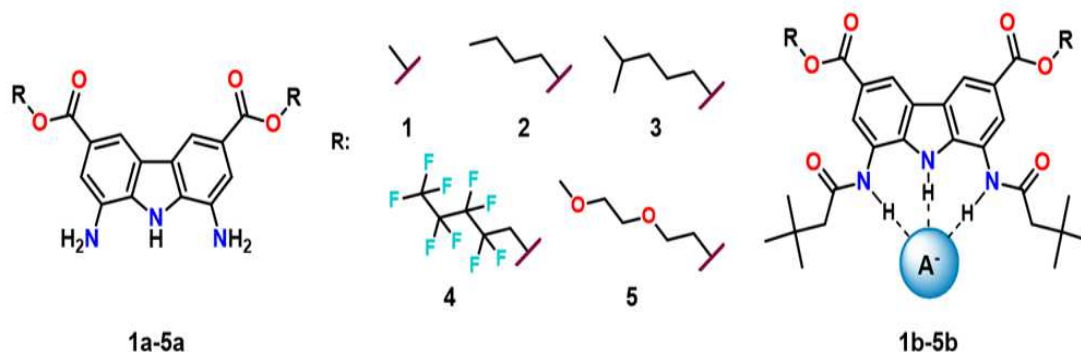


Figure 1. Structures of the new 1,8-diaminocarbazole building blocks (1a-5a) with ester substituents and the simple model receptors (1b-5b).

1,8-Diaminocarbazole is one of the privileged building blocks for the synthesis of anion receptors, sensors and transporters owing to its synthetic versatility, fluorescence, and the presence of strong, preorganized hydrogen bond donors. Unfortunately, however, amides and ureas derived from 1,8-diaminocarbazoles suffer from low solubility, what severely limits their practical utility.¹ Furthermore, tuning the properties of 1,8-diaminocarbazole-derived receptors by changing substituents in the carbazole core is rather difficult, although alkyl chains, chlorine,² nitrile³ and nitro³ groups have been already introduced in positions 3 and 6.

Here we present the synthesis of a new generation of 1,8-diaminocarbazole building blocks with ester substituents in positions 3 and 6. The ester groups offer easily tunable solubility, lipophilicity, as well as other properties, while their mildly electron-withdrawing character enhances the anion binding affinity of the respective receptors. Furthermore, in contrast to some other electron-withdrawing substituents, such as -Cl or -NO₂, the ester groups do not quench the fluorescence of the carbazole fluorophore significantly.

The development of the new generation of building blocks disclosed herein made it possible to obtain anion receptors which combine strong binding with high fluorescent response. In addition, better solubility of both the starting diamines and the receptors derived thereof enables the synthesis of more complex carbazole-based structures, such as macrocycles, cryptands, or catenanes, which may result in enhanced binding strength, selectivity, and fluorescent response.

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Abstract No: T173

T173 Multibranch Metal-complexes as a Two-Photon Initiating Platform for Direct Laser Writing Applications.

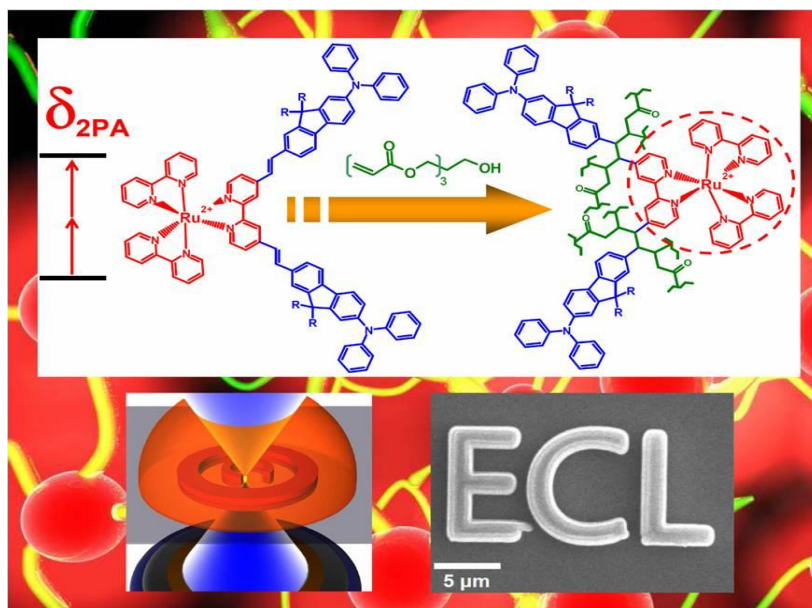
Jean-Pierre Malval¹, Rana Mhanna², Nicolas Durand³, Stephania Abdallah², Huriye Akdas-Kiliç³, Neso Sojic⁴, Jean-Luc Fillaut³

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Caption: Micropatterning of electrochemiluminescent polymers based on multipolar Ru-complex two-photon initiators

Multiphoton stereolithography is an advanced additive manufacturing technology which is being disseminated in diverse applied domains¹. Its main driving force relies on the intrinsic spatial containment promoted by non linear absorption processes which allow the fabrication of 3D photo patterned structures of arbitrary geometries and with feature sizes as small as 100 nm. Two-photon induced polymerization constitutes the spearhead of this technology². In this context, important research efforts have been devoted to design new photoinitiators that both exhibit efficient two-photon absorption ability and high initiating reactivity. With this respect, metal complexes constitute a powerful assembling platform which offers an easy way to build up 2D or 3D octupolar architectures with extremely high two-photon absorption cross-sections that can be judiciously oriented for additive manufacturing applications³. In the present lecture, we will present some relevant supramolecular building strategies of two-photon activable initiators⁴ whose photoreactivity is directly correlated to the fine control of their respective dimensionality.

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Abstract No: T174

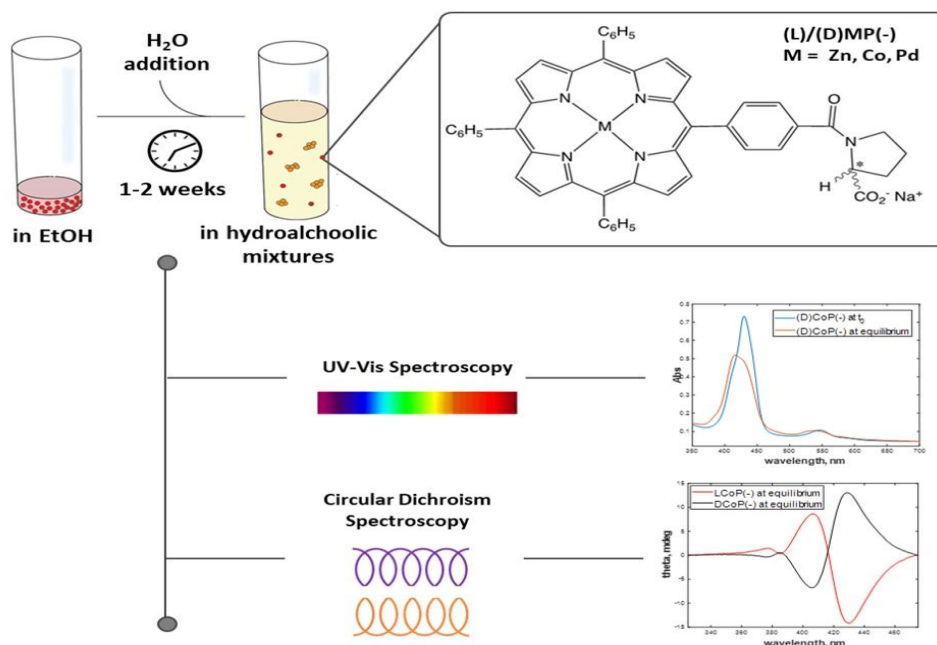
T174 Metal-Ligand-Mediated Self-Assembly of (L)/(D) Prolinated Porphyrins in Hydroalcoholic Mixtures

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Porphyrin derivatives covalently linked to L- or D-proline enantiomers self-organize in hydroalcoholic solution into chiral, specular suprastructures thanks to the amplification of chiral information stored in the single proline residue [1]. The complex interplaying of molecular interactions among the macrocycles determines the chiroptical properties and the morphology of the final assemblies. We found that free-base and Zn complex in EtOH/H₂O 25:75 (v:v) formed chiral assemblies, where both the aggregation mechanism and the resulting chiroptical features were strictly dependent on the inner core properties [1]. Indeed, the coordination of the proline carboxyl group by Zn ion was found crucial for the evolution of aggregates displaying remarkable supramolecular chirality.

In this work, we extended these studies on the two enantiomers of Co(II) and Pd(II) porphyrin complexes. Indeed, we surmised that the different coordination abilities of the two metal ions, forming preferentially hexacoordinated and square planar complexes, respectively, could be reflected on the aggregation process.

In detail, while in the case of the free base porphyrin, the interaction between the macrocycles is mediated by hydrogen bonds which are established between the NH groups of the core and the proline carboxylate group, the metalloderivatives generally display a slower (about 1-2 weeks), multi-step and distinctive reorganization of the individual monomers into highly specific aggregates, having highly recognizable patterns both as regards the UV-Vis and the Circular Dichroism (CD) spectra. The obtained results reported in this contribution opens up interesting possibilities regarding the exploitation of the metal-ligand mediated self-assembly to tune the chiral arrangement and properties of the assembled systems.

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Abstract No: T175

T175 Bio-inspired luminescent peptide foldamers integrating lanthanide emitters

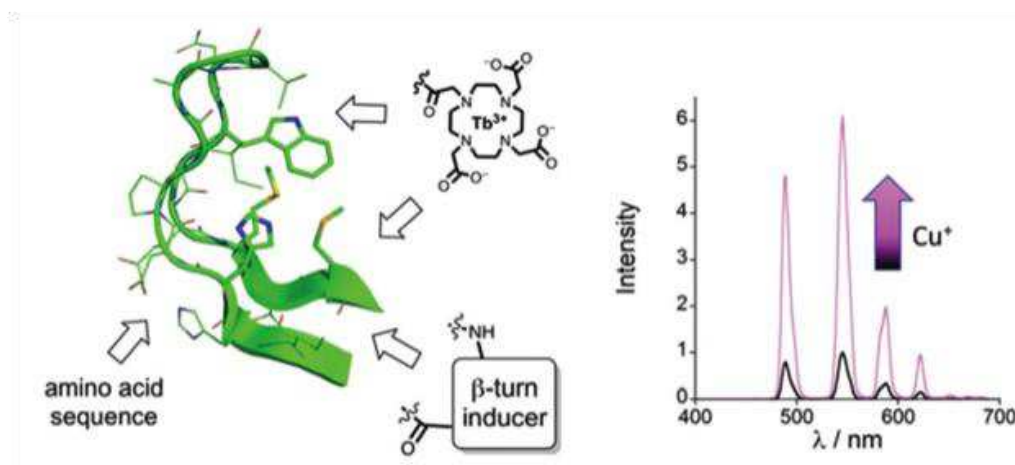
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Caption: Figure 1. A bio-inspired Cu⁺-responsive luminescent probe.[1], [2]

Herein, we describe a series of luminescent foldamer complexes comprising bio-inspired cyclic peptide ligands which, being structurally related to the naturally-occurring copper chaperone CusF, adopt a folded 3D geometry conferring high ion selectivity and sensitivity. Indeed, highly sensitive probes are required to detect minute quantities (down to sub-picomolar) of Cu⁺ ions in physiological conditions and understand its homeostasis, as well as the diseases associated with its misregulation. The current peptide probes comprise the 16-amino acid loop of CusF cyclized by a β-turn inducer dipeptide and functionalized by a Tb³⁺ complex for its luminescence properties. The mechanism of ion-induced luminescence enhancement relies on the modulation of the antenna effect between a tryptophan residue and the Tb³⁺ ion within the probe when Cu⁺ forms a cation-π interaction with tryptophan, as revealed by steady-state and time-resolved spectroscopies.^{[1], [2]}

We thank the French *Agence Nationale de la Recherche* (project ANR RECODNA) for funding.

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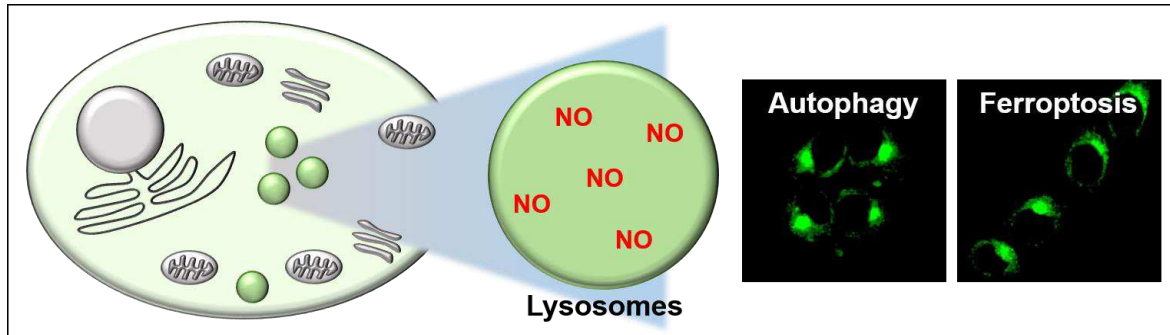
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Abstract No: T176

T176 Lysosomal NO-selective bioorthogonal fluorescent probe and its applications in autophagy and ferroptosis

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Organelle-selective bioorthogonal fluorescent chemosensors are indispensable chemical tools for investigating live cell processes involving the sensors' target metabolites. In this study, we developed a lysosomal NO-selective chemosensor (**Lyso-NO**), composed of a 4-(4-nitrophenyl)thiosemicarbazide-linked naphthalimide and a morpholine moiety as an NO-mediated fluorogenic reporter and a lysosome-targeting unit, respectively. Upon selective reaction with NO in solution and within live cells, **Lyso-NO** showed a strong fluorescence intensity at 550 nm, and its predominant lysosomal location was revealed by confocal microscopy. Further, lysosomal NO increase was demonstrated to be deeply involved in autolysosome formation during autophagy, and in ferroptosis. **Lyso-NO** was considered to act as a lysosomal NO-selective sensor, allowing for the bioorthogonal analysis of lysosome-related biological processes.

Abstract No: T177

T177 ADP-responsive europium probes bearing conjugated alkynyl quinoline antennae.

Hannah Kathleen Pyle Samantha Bodman, Luke Russell, Felix Plasser, Stephen Butler

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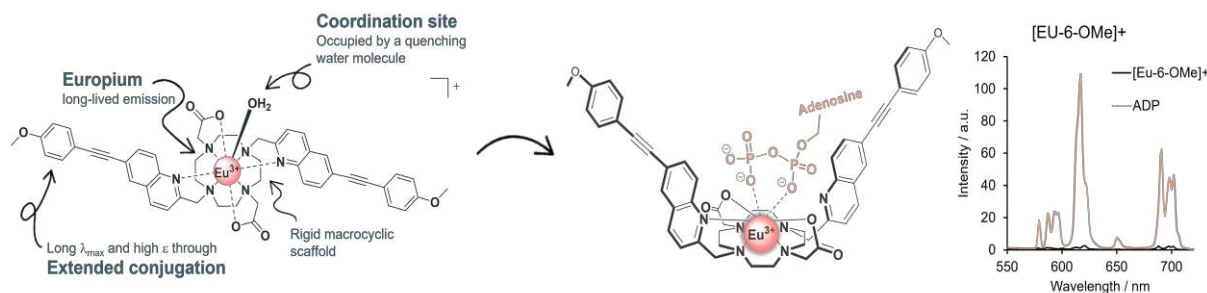


Figure 1. (left) Design features of Eu(III) complex [Eu-6-OMe]⁺, (right) proposed ADP binding mode and increase in emission seen upon adding ADP.

The enzymatic conversion of ATP to ADP releases energy that powers most cellular chemistry. In order to monitor these cellular processes, molecular receptors are needed that can distinguish between ATP and ADP; however, this is challenging because of their similar structures and charge.¹ Recently we developed a luminescent europium complex that can selectively recognise ADP over ATP and other nucleoside monophosphates, enabling us to monitor enzymatic reactions in real time.^{2,3} In this study we describe progress in our ambitious goal to translate the europium complex into an imaging probe for monitoring ADP levels in living cells.

Four novel europium complexes were designed and synthesised, each bearing conjugated alkynyl quinoline antennae, and their photophysical properties were studied. We have pinpointed the structural elements that affect how well nucleoside phosphate anions can be distinguished in buffered aqueous solution. Of the four novel compounds, complex [Eu-6-OMe]⁺ containing methoxy-functionalized phenylacetylene antennae (Figure 1) demonstrated preferential binding to ADP over ATP and other biologically significant anions. We discovered how to tune the excitation wavelength to a lower energy, thereby better-matching microscope lasers. Complex [Eu-4-Ph]⁺ has the highest effective energy transfer ascribed to an intra-ligand charge transfer (ILCT) state. A combination of NMR spectral analysis, emission band shape changes and extended X-ray absorption fine structure (EXAFS) revealed additional information about the host binding mode towards ADP. With the addition of water-solubilizing groups, future research will build on the desirable features of [Eu-6-OMe]⁺ in order to monitor ADP levels in living cells.

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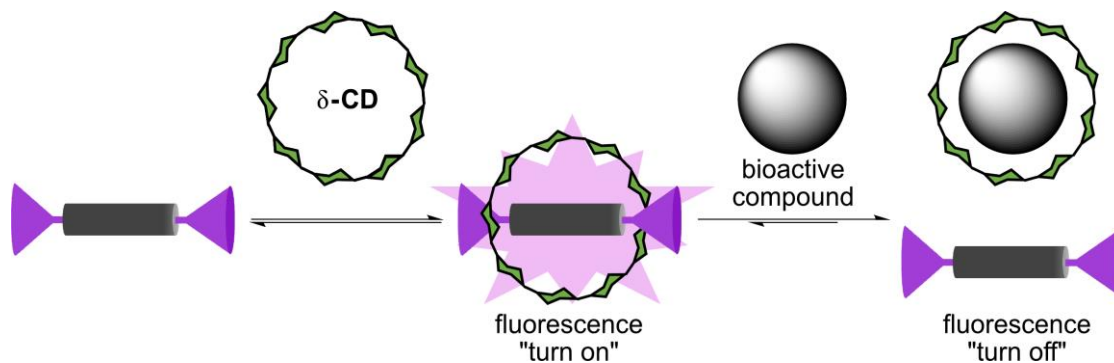
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Abstract No: T178

T178 δ -Cyclodextrin – The fellowship of the ring

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Caption: Fluorescent "turn-off" displacement assay for detection of host-guest interactions between δ -CD and bioactive compounds.

The use of supramolecular host-guest interactions with α -, β - and γ -cyclodextrins (CDs) to stabilize bioactive molecules have shown great use within the pharmaceutical, food and cosmetic industries.^[1] Recently we have discovered a feasible method for the preparation of the previously synthetically unavailable δ -CD on gram-scale by templated enzymatic synthesis^[2], allowing us to elaborate on its vastly unexplored supramolecular properties. Here we present a fluorescent "turn-off" displacement assay for detection of host-guest interactions between δ -CD and bioactive compounds.

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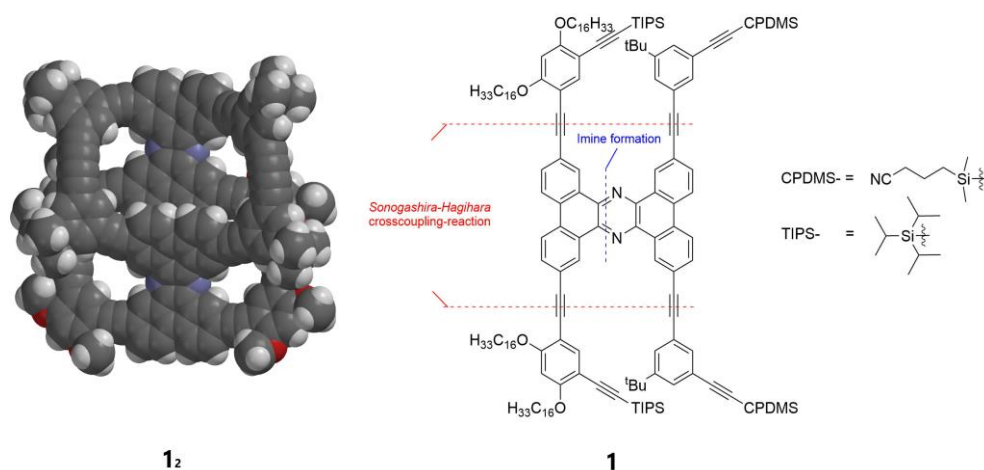
Abstract No: T179

T179 Phenanthracene Nanotubes for Explosive Detection

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Caption: Optimized structure of a nanotubular heterocycle on the GFN2-xTB level of theory (left); retrosynthetic approach to the H-shaped precursor (right).

The template-assisted self-assembly of organic molecules can optimize the performance of organic electronic devices, contributing to mitigate the worldwide increasing energy consumption and the undesirable effects resulting thereof. Here we present insights on template-assisted self-assembly of organic molecules by the synthesis of nanotubular heterocycles, which can be perceived as an expansion to the third-dimension of molecular polygons investigated before.^[1]

The research focus was set on the formation of self-assembled monolayers of these molecules, that were investigated via scanning tunnelling microscopy at the solid/liquid-interface using highly oriented pyrolytic graphite as template. Moreover, the host-guest chemistry was studied enabling the manufacturing of chemiresistive sensors based on single-walled carbon nanotubes. This way, novel sensors for *TNT*-detection were made. Regarding the synthesis, a modular approach inspired by preliminary work on the oligomerization of H-shaped molecules via a *Glaser*-coupling, was used.^[2]

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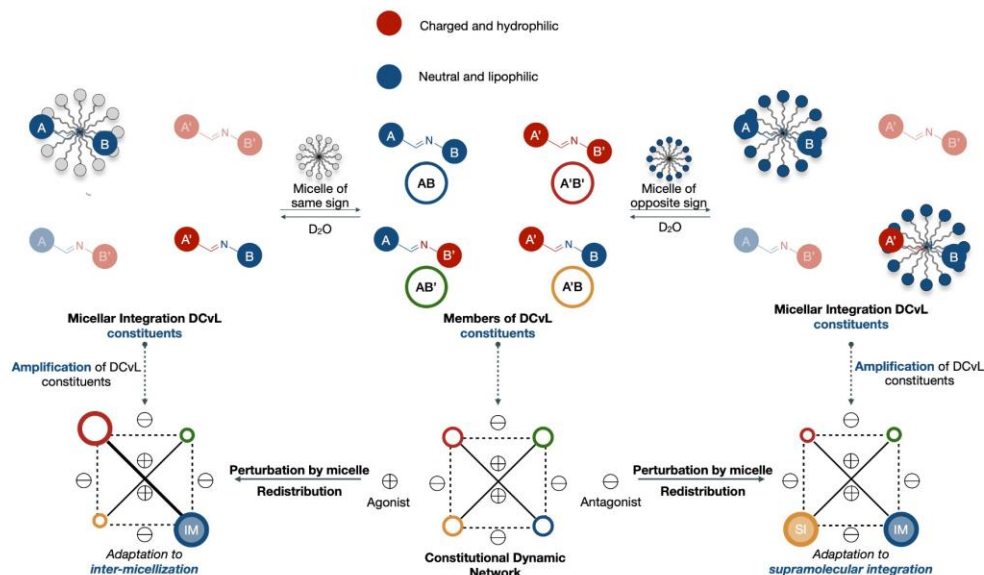
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Abstract No: T180

T180 Adaptation in Constitutional Dynamic Networks of Imines in Response to Micellar Integration: Dynamic Sensing for Information Processing and Pattern Generation

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The transition from simple molecular building blocks to complex systems is gradual, with self-organization driving the progression towards greater complexity and the emergence of new functions.¹ For instance, *micro-compartmentalization* plays a crucial role to regulate the expression of *adaptive* chemical reaction networks.² However, it is still rather unclear how chemical systems adapt and evolve, with direction, in response to interactions between molecular components and their compartmental environment. The design of systems able to evolve under changing environmental conditions is a central area in systems chemistry. Constitutional Dynamic Chemistry (CDC) has been extensively used to develop functional systems *responsive* to various effectors.³ Here, we demonstrate that imine formation yields can be increased in highly competitive media using *micro-compartmentalization* strategies (micelle formation) that preclude the hydrolysis of such dynamic covalent bonds. DOSY NMR experiments reveal two different mechanisms of micellar integration, depending on the charge state of the imine and of the surfactant. Non-charged constituents can be integrated by *inter-micellization* relying on hydrophobic forces, while charged ones exhibit *supramolecular integration* by means of electrostatic forces. Thus, two stabilization pathways can be used to selectively modulate the expression of molecular constituents. These interactions allow for the self-organization of Constitutional Dynamic Networks (CDNs) of imines through *adaptation* in response to varying environmental conditions by the *micro-compartments*. Two different [2×2] networks, based on anionic and cationic imines, show similar *adaptation to micellar micro-compartments*, displaying surfactant-specific *compositional distribution patterns*. Hence, the emergence of self-organized networks and compositional complexity is dictated by the change in the environment in response to *micellar dynamic sensing* of the constituents. In addition, this *information transfer* from the environment to the molecular system -leading to altered *distribution patterns*- showcases to a certain extent biological network regulation behaviors. We anticipate this work might pave the way for implementing chemical evolution to reaction networks within micro-compartments.

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T181 Nitrile detection with a dually crosslinked supramolecular gel sensor based on pillar[5]arene

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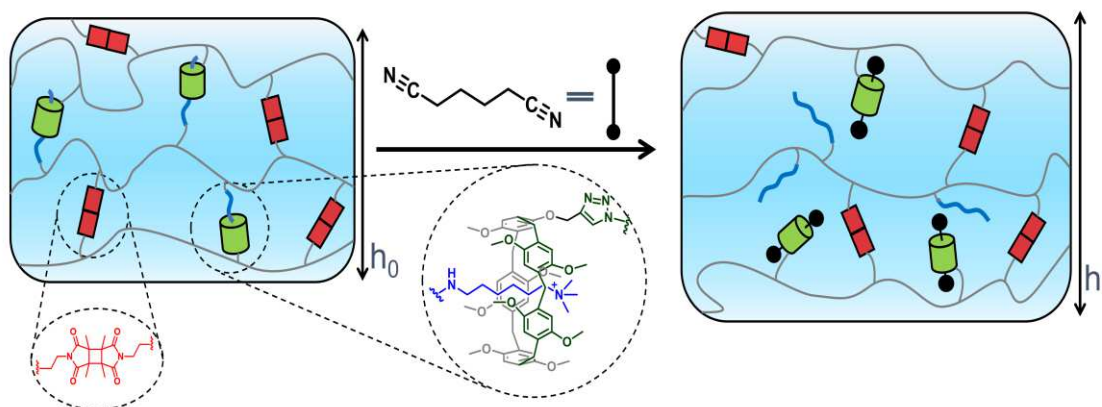


Figure 1. The concept of the dually crosslinked gel sensor.

Being important precursors in industrial production of various synthetic polymers, nitriles (such as adiponitrile, AN) present a highly toxic class of substances, which makes an accidental spillage of them into water dangerous for the environment and human beings, therefore, it is crucial to monitor the nitriles levels in industrial wastewater [1]. Pillar[5]arenes (P5As) is a novel class of macrocyclic compounds with a distinguished ability to form inclusion complexes with neutral as well as positively charged molecules, which can be tuned by rim group modification. Due to their dynamicity, host-guest complexes with P5As attached to polymer chains were reported in a fabrication of smart materials such as actuators and sensors [2]. Recently in our group a supramolecular gel sensor for ovarian cancer biomarker was developed based on cyclodextrin [3, 4]. The aim of this work is a fabrication of a gel sensor containing P5A-based supramolecular crosslinks for the detection of nitriles (Figure 1).

Mono-functionalized P5A (HM) and trimethylhexylammonium-containing guest species (GM) were synthesized. The complexation between P5A and GM as well as AN was proved by NMR, MS and quantified by NMR-titration in CDCl_3 . Copolymer poly(dimethyl acrylamide-co-4,4-dimethyl-2-vinylazlactone) was modified with HM and GM as well as with photo-crosslinker moieties to obtain host (HP) or guest (GP) polymers, respectively, with ca. 5 mol. % of supramolecular crosslinkers. A dually crosslinked sensor chip was obtained on a quartz wafer from HP/GP solution by spin-coating and subsequent UV-irradiation. In a flow cell, the chip was swollen in CHCl_3 and subsequently in solutions of AN of different concentrations. Using surface plasmon resonance spectroscopy the dependence of the gel layer thickness (h_1 vs. h_0) from the analyte concentration was established.

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Abstract No: T182

T182 Porphyrin-cyclohexanohemicucurbit[n]uril complexes for chiral sensing

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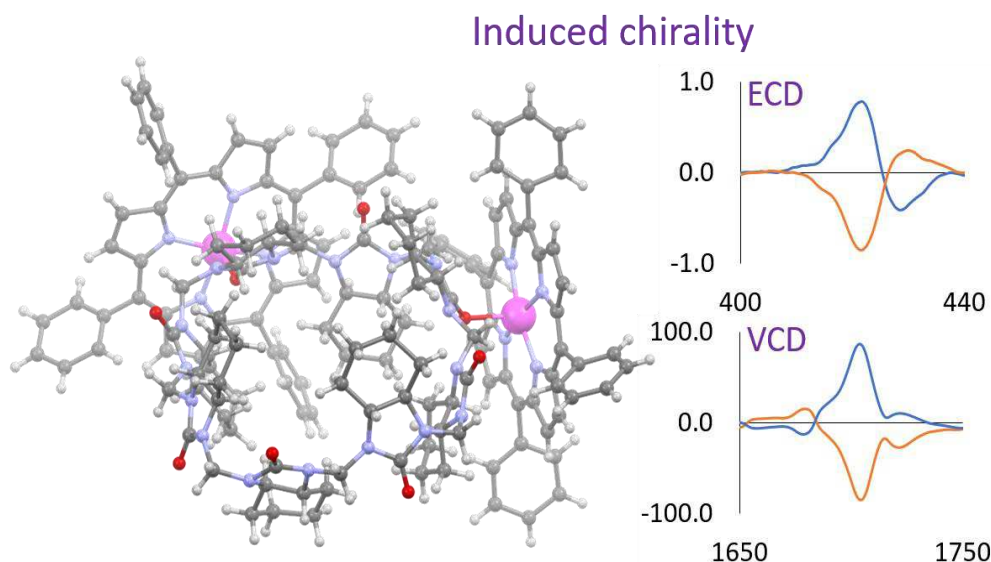


Figure 1. Crystal structure of (R,R)-cycHC[8] and ZnTPP complex (left), and electronic and vibrational circular dichroism (ECD and VCD) (right).

Enantiomerically pure chiral cyclohexanohemicucurbit[n]urils (cycHC[n], $n = 6, 8$) form stable complexes with zinc porphyrins and simultaneously induce chirality in planar porphyrins in solution.¹ Sensing capabilities of porphyrinoids have widely been studied but their enantioselective recognition is hampered by laborious synthesis of their chiral derivatives.² We explored an idea of using variety of commercially available metalloporphyrins in corresponding complexes with cycHC[n] to form solid material for an array of chiral sensors. The solid-state complexes were characterized as monocrystals in a mixture with KBr and in thin layer films. Electronic- and vibrational circular dichroism measurements of KBr pellets and thin layer films showed that the chirogenesis in porphyrins takes place. Moreover, analysis of the SC-XRD data for monocrystals of porphyrin-cycHC[n] complexes indicated general trends of crystal formation for different sizes of cycHC[n] and derivatives of porphyrin.

Changes in the sensing system (porphyrin-chiral host) properties upon interaction with various analytes were followed by infrared spectroscopy, UV-Vis spectroscopy, circular dichroism spectroscopy, and quartz crystal microbalances. Examples of chiral recognition will be presented.

This research was funded by the Estonian Research Council Grant (PRG399, MOBJD592) and European Union's H2020-FETOPEN Program 828779 INITIO project.

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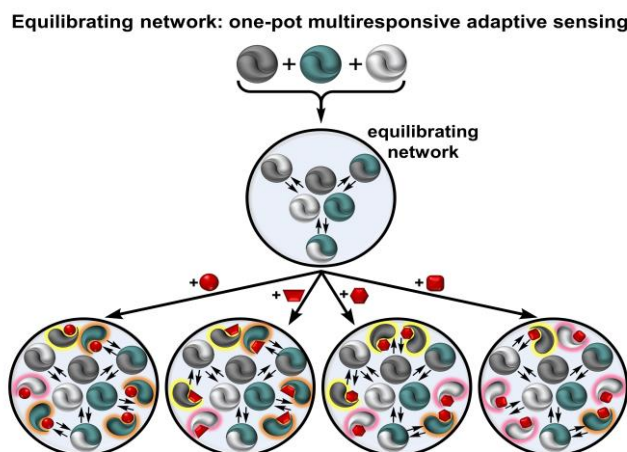
Abstract No: T183

T183 One-pot adaptive supramolecular systems and multi-responsive sensor arrays for analyte discrimination in biological solutions

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¹ University of Victoria, Victoria, Canada

² Karlsruhe Institute of Technology, Karlsruhe, Germany



We have recently developed a new adaptive systems approach, combining multiple sensors in solution to form a one-pot network of cross-reactive sensor elements. Here we report new self-assembling dimeric calix[4]arene and calix[5]arene chemosensor analogs (DimerDyes),¹ that respond by both color change and turn-on fluorescence upon analyte binding. We show that a mixture of interacting sensors ranging in structural and photophysical properties has emergent supramolecular and photophysical responses, providing data-rich outputs. As a proof of concept, we show this adaptive network of sensors can discriminate between highly conserved proteins through non-site-specific interactions in aqueous solution. We also report new supramolecular sensing systems that incorporate both calix[4]arene and cucurbit[*n*]uril hosts, broadening the scope of sensing capabilities to cationic and neutral analytes. Using an array of these sensor systems we achieve identification and discrimination of illicit drugs and common adulterants. We also report on the discrimination of real-world samples of mixed drugs (polysubstances) obtained from a harm-reduction oriented drug checking site.

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Abstract No: T184

T184 Photochromic Nanostructured Films Assembled Through Supramolecular Interactions for Multiple Applications in Photo Encryption and Sensing

Yihan Shi Miguel Soto, Mark MacLachlan

University of British Columbia, Vancouver, Canada

Photochromic materials are a class of materials that exhibit light-induced coloration due to reversible intermolecular, or intramolecular electron transfer.¹ Viologen derivatives are commonly used in this area because they can easily be reduced to colorful radicals by ultraviolet (UV) light and oxidized to their original state by the oxidant.²

However, methyl viologen, or paraquat, doesn't show photochromism in the solid state without extra metal ion coordination or embedding in a reactive matrix.¹⁻³ In a previous study, cellulose was shown to aid the photoreduction process, but low light sensitivity and bad editability of cellulose-paraquat films limit the application of this material.^{3, 4}

In this work, we used cellulose nanocrystals (CNCs) to enhance the sensitivity of photochromic properties in paraquat/CNC films. These films also show good stability over multiple irradiation/oxidation cycles. In this presentation, I will discuss 1) the fabrication and characterization of paraquat/CNC film by supramolecular interactions, 2) the photochromic property of this material which relates to their paraquat concentration and substrates, and 3) the applications in photo-patterning, encryption, and UV light sensing.

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Abstract No: T185

T185 Subnanomolar Peptide Binding with Cucurbit[8]uril

Paolo Suating Lauren Kimberly, Sarah Chang, John Fontenot, Adam Urbach

Trinity University, San Antonio, United States

The selective recognition of peptides and proteins in aqueous solution at submicromolar concentrations is an ongoing challenge in biomolecular and supramolecular chemistry. The cucurbit[n]urils are particularly promising in this area. Although the work of our group and others has shown high-affinity binding is possible when targeting the *N*-terminus, much less is known about sites that do not include the *N*-terminal residue. By characterizing leads identified from a library screen using isothermal titration calorimetry, NMR spectroscopy, mass spectrometry, and CD spectroscopy, we have discovered a short peptide sequence that binds cucurbit[8]uril with submicromolar affinity at a non-terminal site and with subnanomolar affinity when placed at the *N*-terminus. To the best of our knowledge, these are the highest affinity complexes for a synthetic receptor in either of these contexts. This peptide sequence therefore has exceptional promise as a protein affinity tag that can operate at low concentration and with minimal impact on protein structure and function.

Abstract No: T186

Flash talks 27-06-2023 16:40 - 17:00 Harpa - Silfurberg A/B 2nd floor

T186 Fingerprinting of Graphenes: Rapid low-cost characterisation of graphene-based materials to address the challenges of inhomogeneity and irreproducibility.

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The 'wonder material' potential of atomically-thin graphene materials (graphene, graphene oxide, etc) is real, but despite considerable international investment it remains unrealised. Irreproducibility is a notorious barrier to developing applications: every batch can be different, and anecdote suggests that it frequently is. A recent landmark study[1] demonstrated massive variation in 60 commercial samples: few were predominantly graphene (see recent "War on Fake Graphene"[2,3] headlines). Addressing this irreproducibility problem should remove the barrier to exploiting these promising materials, but requires that materials users and producers alike have access to fast, cheap, characterisation, allowing them to ask "*Is this batch like the last one?*".

Here I will present results from an ongoing project in our lab to develop a 'supramolecular fingerprinting' approach to rapidly and cheaply characterising graphene oxide (GO). We show that this kind of approach can complement the slow expensive 'gold standard' characterisation (weeks, \$thousands) with a 'quick and dirty' QC-level characterisation (minutes, \$few), removing another barrier to realising the potential of GO and of the graphene-based materials.[4]

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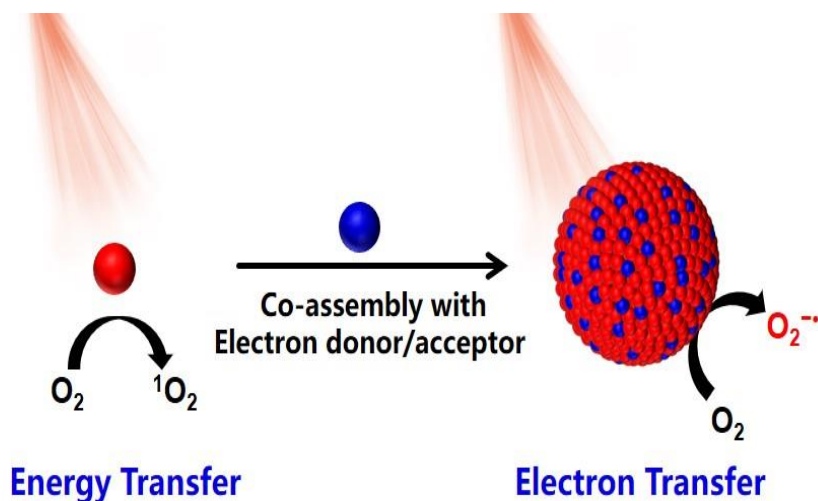
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T187 Supramolecular Engineering for Converting the Photodynamic Agents from Type-II to Type-I

Kun-Xu Teng, Qing-Zheng Yang

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Caption: Convert the photodynamic agents from Type-II to Type-I by supramolecular strategy

Photodynamic therapy (PDT) is a promising approach for the treatment of cancer due to its noninvasive nature, spatiotemporal controllability, and minimal systemic toxicity. It involves exposing a photosensitizer (PS) to a light source to generate cytotoxic reactive oxygen species (ROS) by interacting with molecular oxygen.¹ So far, most PSs produce singlet oxygen ($^1\text{O}_2$) through the Type-II process by direct excitation energy transfer (EET) between the excited triplet state of PS ($^3\text{PS}^*$) and O_2 . Unfortunately, PDT based on Type-II PSs are highly O_2 -dependent, thus the hypoxia of solid tumors would severely reduce the therapeutic efficacy in clinic. In contrast, Type-I PSs generate cytotoxic radicals through a cascade electron transfer (ET) reaction among $^3\text{PS}^*$, adjacent substrates and molecular oxygen. Type-I PSs can lower O_2 dependence and overcome the tumor hypoxia, thereby attracting increasing attention in recent years.² However, the available Type-I PSs are rarely reported and the design of Type-I PS remains a challenge. The main reason for this is that the inefficient cascade ET reaction is always tough to compete with EET of the $^3\text{PS}^*$ with oxygen. Recently, our group has proposed a supramolecular strategy for converting the PDT mechanism from Type-II to Type-I. Various electron donors/acceptors were designed and co-assembled with classical Type-II PSs by host-guest complexation or quadruple hydrogen-bonded interaction to produce supramolecular photodynamic agents.³⁻⁵ Proximity of the PS to electron donors/acceptors with matched redox potential promotes the photo-induced electron transfer between the PS and adjacent electron donors/acceptors, leading to efficient generation of ROS through the Type-I mechanism.

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Abstract No: T188

T188 Self-assembling depsipeptides on aggregation-induced emission luminogens as a new way to create programmable nanovesicles, soft nanocarriers and Trojan horses of drug-peptide conjugates

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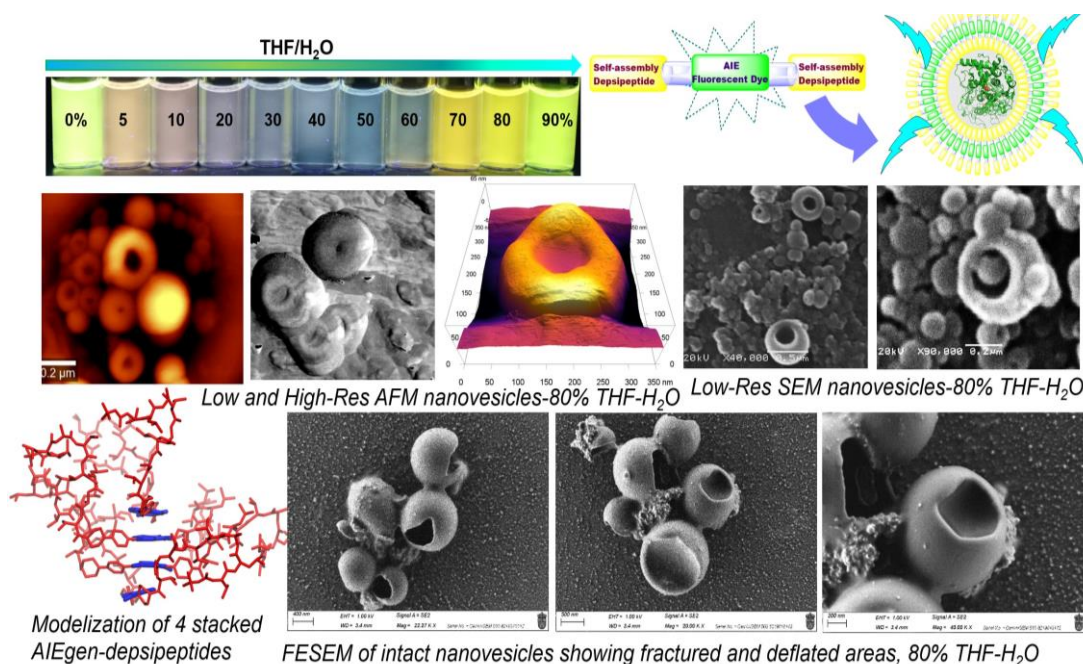


Figure 1

We describe a new methodology to produce robust hollow nanovesicles stable in water or water/solvent mixtures. The bottom-up produced nanovesicles are formed by self-assembly of depsipeptide chains of natural origin¹ combined to new aggregation-induced emission luminogens (AIEgens), that function as constitutional vesicle-forming moieties and fluorescent indicators of the structure of the nanovesicle. The newly formed nanovesicles are robust enough to be used to carry large molecules such as physiological peptides without losing their structural characteristics, therefore acting as programmable nanocarrier systems within living cells, enzymatic systems for environmental microplastic degradation² or stable nanocontainers. Optimization of structures was performed by using natural depsipeptides¹ bonded to naphthalimide structures developed for TATP sensing in the gas phase.³ The hybrid depsipeptide-AIEgen structures promote the supramolecular self-assembly into fluorescent hollow nanovesicles (Figure 1), that can be used to transport active peptides to cellular compartments, acting as both biomarkers and nano-transporters. As a first achievement, a physiologically active peptide has been successfully delivered via nanovesicles into human lung cancer cell line A549 cells, behaving as a Trojan horse for subsequent cell apoptosis.

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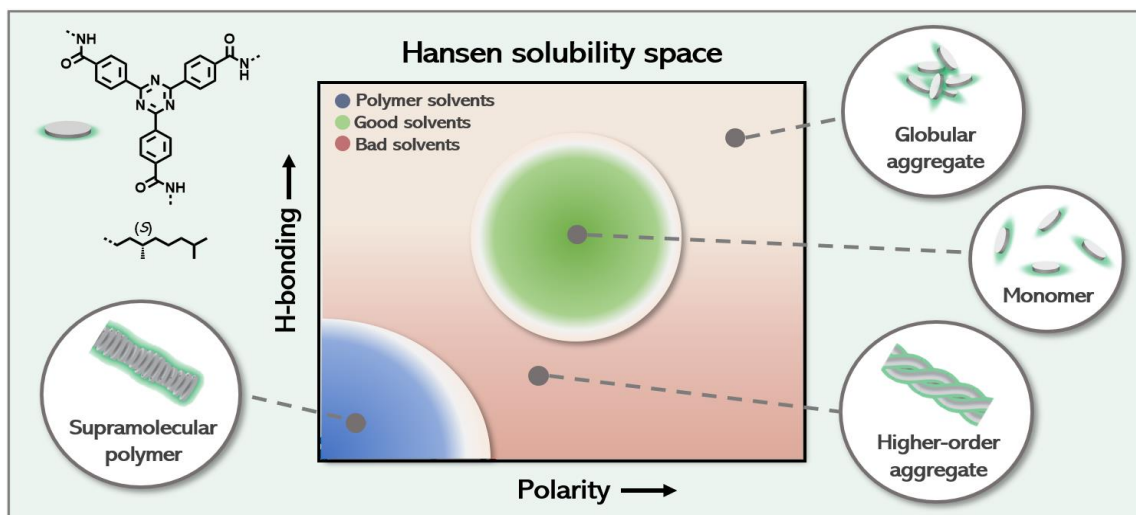
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Abstract No: T189

T189 Solvent-Induced Pathway Complexity of Supramolecular Polymers Unveiled Using the Hansen Solubility Parameters

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Caption: Schematic 2D representation of the Hansen solubility space of chiral supramolecular monomer S-T based on 58 different solvents. The solvents are divided

Supramolecular building blocks assembling into helical aggregates are ubiquitous in current literature. More recently, functional supramolecular building blocks have been developed comprising exciting new properties such as conductivity, exciton migration and aggregation induced emission.¹ However, these supramolecular systems are often restricted to dilute conditions and apolar solvents due to their high sensitivity to impurities and susceptibility for kinetic traps and complex assembly pathways. Therefore, fundamental knowledge on the manifold of interactions within such a system, i.e. solvent-solute, solute-solute and solvent-solvent,² is crucial for the development of multicomponent functional materials and understanding the pathway complexity that comes along with this problem.

Here, we present a systematic study that quantifies the interactions between solvent and supramolecular building block – 4,4',4''-(1,3,5-triazine-2,4,6-triyl)tribenzamide (**S-T**) – using the Hansen solubility parameters (δ_D , δ_H and δ_P). Due to the amphiphilic nature of **S-T**, a dual sphere model based on 58 solvents was applied describing the solubility space of the monomeric (green sphere) and supramolecular polymer state (blue sphere). Further in-depth spectroscopical and morphological studies unveiled a distinct solubility region in-between the two spheres giving rise to the formation of higher-order coiled structures. This phenomenon occurs due to subtle differences in polarity between the solvent and the side chains and highlights the solvent-induced pathway complexity of **S-T**. Subsequent variations in concentration and temperature led to expansion and contraction of both solubility spheres providing two additional features to tune the monomer and supramolecular polymer solubility. Finally, we applied our solubility model on structurally disparate monomers, such as Zn-porphyrin (**S-P**) and triphenylamine (**S-A**), demonstrating the generality of the model and the importance of supramolecular monomer design. This work unravels the solvent-induced pathway complexity of discotic supramolecular building blocks using a parametrized approach in which interactions between solvent and solute play a crucial role.

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Abstract No: T190

T190 More than just labelling – Fusion of a supramolecular ligand with switchable luminophores

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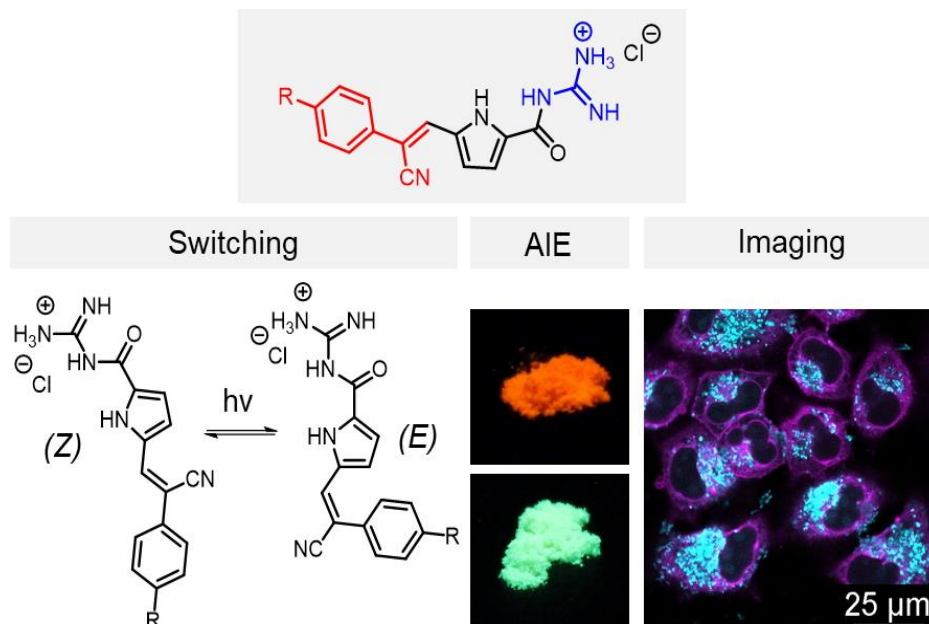


Fig. 1: Molecular structure of the novel hybrid molecules, its switching ability, the AIE properties and its application in bioimaging.

The guanidiniocarbonyl-Pyrrole (GCP) binding motif, which has been designed and applied by Carsten Schmuck more than 20 years ago, is known to be a versatile supramolecular ligand, known to efficiently bind oxo-anions. This can be used in numerous scientific fields, such as biomedicine and materials science.^[1] Ever since its discovery, it was applied as ligand for protein inhibition^[2], transfection^[3] as well as the formation of supramolecular gels^[4] and polymers.^[5] One major drawback of the system was a lack of potential tracking via e.g. microscopy. Standard labelling techniques with commercial fluorophores changed the overall performance drastically due to its size and chemical composition, compared to the small GCP binding motif.

Here we describe a novel approach to overcome this drawback. We designed a hybrid probe by merging the GCP unit and cyanostilbenes, which are known to feature the well-known aggregation-induced emission (AIE) phenomenon (Fig. 1). This phenomenon, known since around 20 years, describes the emission enhancement upon binding and aggregation.^[6] A library of differently substituted compounds was synthesized and its photophysical performance was evaluated. Moreover toxicity and cellular uptake was investigated. It was found that the designed luminophores are superb imaging agents, able to enter the cytosol or even the nucleus in dependence to the substitution and functional groups attached. The (Z) to (E) conversion of the central double bond via UV-light irradiation was investigated. Both isomers were successfully isolated and X-ray structures were obtained. We believe that this approach will be the next step for the design of multifunctional, highly active and trackable supramolecular ligands.

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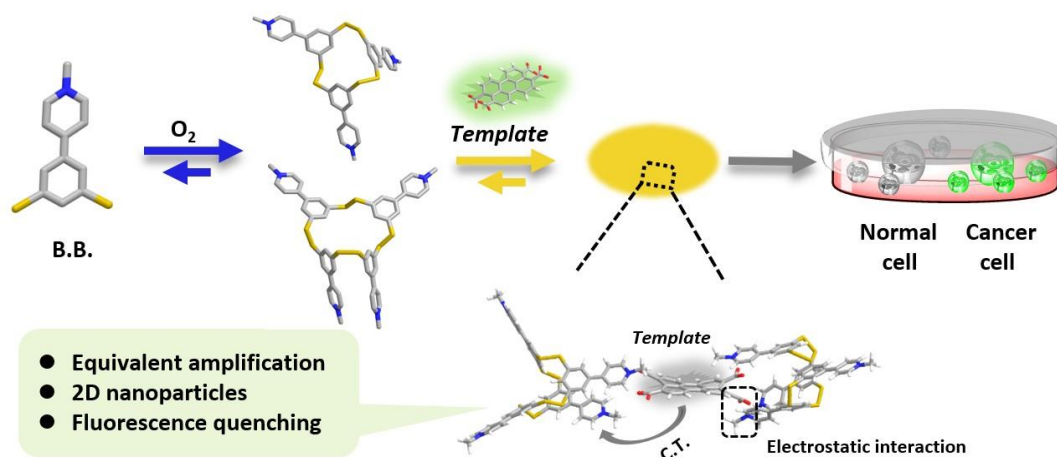
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Abstract No: T191

T191 A Dynamic Combinatorial Library for Cancer Cell Recognition

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Caption: Scheme . Schematic illustration of the oxidation of thiol building block, selectively distinguish of cancer cell.

Dynamic combinatorial library (DCL)¹ was generated through reversible covalent chemical reactions between building blocks. Introducing a stimulus into the library induces the compositional responsiveness of the complex chemical system. Such a responsive working feature has been thought to resemble that of immune systems and inspired a new strategy for sensing at the systems level. The sensing function of almost all DCL sensors has been studied in vials so far.² This simple working environment has limited the broad and advanced applications in much more complex biological systems. Herein, we update the DCL-based sensing to living cells by showing a DCL that can distinguish cancer cells from normal cells. A simple dithiol building block and a fluorescent template were chosen for the DCL. When the library was fully oxidized, a size-specific positively charged tetramer linked by disulfide bonds was selected and amplified by the template and the fluorescence of the library was quenched. The library could be transferred into living cells due to the facilitated uptake by cells arising from the formation of co-self-assembled nanoparticles from the disulfide macrocycle and the template. Interestingly, the nucleus of a cancer cell incubated with the oxidized library became fluorescent while a whole normal cell remained dark, which allowed us to distinguish cancer cells from normal cells. This work initiates the sensing of DCLs in living cells and opens a new door to cancer discovery and diagnosis, providing a green and convenient strategy for synthesizing positively charged macrocycles.

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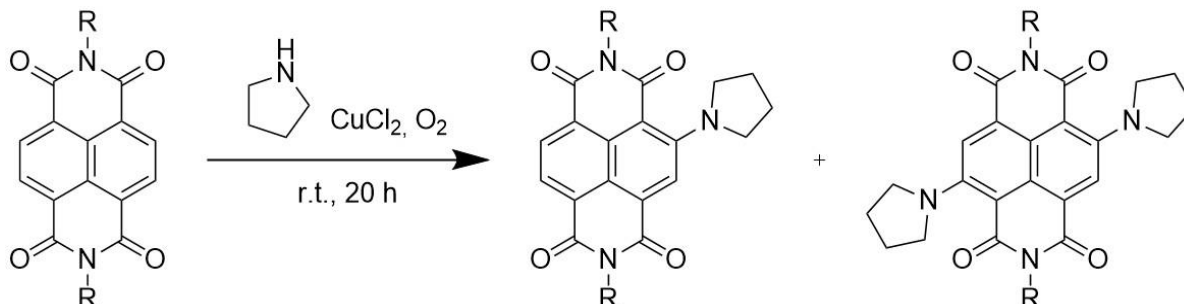
Abstract No: T192

T192 Cu(II) catalyzed direct amination of naphthalene diimides

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² , ,



Caption: Figure 1: Reaction mechanism for direct amination of NDI.

Naphthalene diimides (NDI) and perylene diimides (PDI) are interesting chromophores in the dye chemistry, but also show some interesting optoelectronic properties that could be useful for organic light emitting diodes (OLEDs) or organic field-effect transistors (OFETs). Furthermore, these compounds are interesting building blocks for complex supramolecular architectures.^[1] Substituents on the core of the NDI can alter these properties.^[2] This research focuses on the introduction of pyrrolidine to the core of different NDI.

Usually substituted NDIs or PDIs can be obtained by first brominating the NDIs or PDIs core and then substituting the bromine by the wanted substituent.^[3] But some studies^[2] has shown that it is possible to skip this step and get a direct amination of the NDI using CuCl₂ and oxygen. The mechanism for this direct amination is only postulated but not fully cleared.^[2] To get more insight into this mechanism different amines were used for the synthesis of the NDIs to examine how they influence the reaction.

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Abstract No: T193

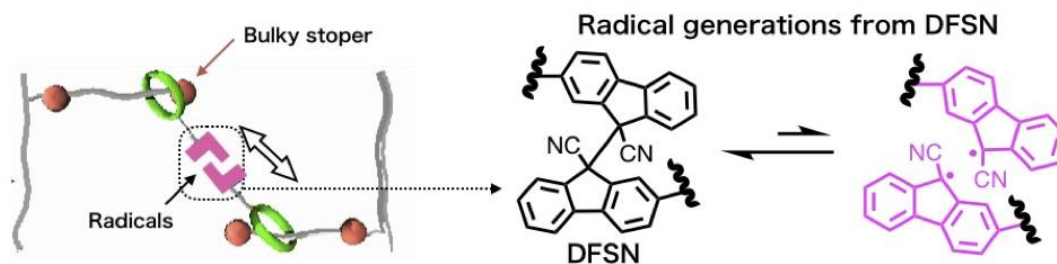
T193 Elucidation of Toughening Mechanism of Rotaxane Cross-Linked Polymers by Using Mechanoresponsive Unit

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Caption: Conceptual diagram of mechanochromic rotaxane-linked polymers (MRPs).

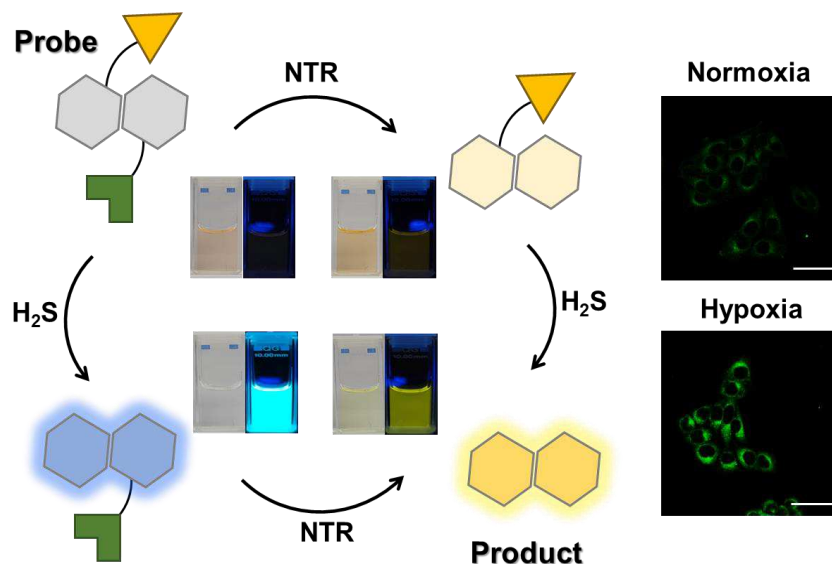
Rotaxane-cross-linked polymers (RCPs) with rotaxane structures at the crosslinking points are known to exhibit superior mechanical properties than covalently crosslinked polymers (CCPs) due to their movable linkage. The main mechanism for the high toughness of RCP is the pulley effect, but there are phenomena that cannot be explained by this alone. In this study, to reveal the true mechanism of RCPs, deformation and stress relaxation processes derived from rotaxane structures at the cross-linked points were visualized through the activation of mechanoresponsive unit. Namely, mechanochromic rotaxane-linked polymers (MRPs) were developed by introducing difluorenylsuccinonitrile (DFSN) mechanophore which is homolytically cleaved into pink-colored stable radicals upon mechanical stress, into the rotaxane cross-linked points. The physical and mechanochromic properties of the obtained MRPs were compared with several RCPs and CCPs to explore the secret of their toughness.

Abstract No: T194

T194 A rationally designed dual-sensitive fluorescent probe for nitroreductases and H₂S enables precise detection of hypoxic cancer

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Hydrogen sulfide (H₂S) is a crucial redox molecule and endogenous gas transmitter, physiological and cellular protective functions in biological systems. Nitroreductases (NTR) are flavoenzymes that catalyze the NAD(P)H-dependent reduction of the nitro group on nitroaromatic compounds and play a key role in the detoxification of carcinogens. Recently, some literatures have reported that the NTR activity and H₂S increase under hypoxia in cancer cells.

In this study, we developed a dual-sensitive probe (**1**) capable of providing a fluorescence response to H₂S and NTR in living cells. Probe **1** is equipped with the naphthalimide as a signal unit and two different recognition moieties, H₂S-sensitive 7-nitro-2,1,3-benzoxadiazole (NBD) and NTR-sensitive 4-nitrobenzyl ester groups. Probe **1** showed emission at 547 nm in the presence of both H₂S and NTR respectively. Moreover, probe **1** showed selective and sensitive detection ability for H₂S and NTR in solution and it was applicable to various cell lines such as breast, prostate, liver, and gastrointestinal origin cancer. In addition, through CoCl₂-induced hypoxia and 3D spheroid experiments, it was found that probe **1** could image H₂S and NTR under hypoxia.

Abstract No: T195

T195 Towards Operando Modelling in Supramolecular Catalysis: Assessing the Reaction Dynamics of Cu-calix[8]arene for C-X coupling by QM/MM MD

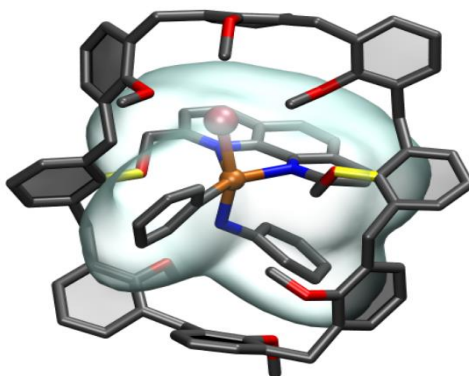
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C-N Coupling with Cu calix[8]arene



Caption: Computational model of the Cu phenanthrolyl calix[8]arene catalyst with coordinated aryl halide and aniline before the final C-N coupling step.

Development of C-X coupling methods with efficient catalysts, utilizing earth abundant metals such as Cu, is a promising strategy for environmentally more benign processes. However, such Cu-based catalysts often suffer from fast deactivation and/or low catalytic activity. A successful strategy to prevent this is the encapsulation of the catalytic center by a macrocyclic ligand. Recently, a complex consisting of Cu(I), anchored to a bidentate phenanthrolyl moiety enclosed by calix[8]arene, was reported to exhibit remarkable yields in C-N and C-S coupling reactions at low catalyst loadings.^{1,2}

However, the rational development of such systems has been hampered by the lack of an adequate computational protocol to provide a comprehensive atomistic picture of the reaction. In particular, the inherent flexibility of the calixarene cage needs to be taken into account, as it can have a significant influence on the way the reaction proceeds.

We developed a multistep and multiscale protocol based on density functional theory (DFT), molecular mechanics (MM), and molecular dynamics (MD) to determine the dynamics of the calixarene cage and the mechanism of catalytic C-X bond formation in solution.^{2,3} Our QM/MM MD approach makes use of semi-empirical tight binding methods, such as GFN2-xTB, reducing the computational costs by orders of magnitude with little loss of accuracy. Our protocol facilitates extensive sampling of the reaction pathway at experimental conditions, i.e., at ambient temperature and pressure and in explicit solvent. Statistical analyses of these data revealed the dynamic response of the macrocycle upon changes in the Cu coordination sphere and allowed us to assess free energies and transition state ensembles of the elementary steps⁴

Our computational protocol provides an operando model thereby opening up new avenues for the investigation and design of biomimetic supramolecular catalysts.

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Abstract No: T196

T196 Rupturing Aromaticity by Periphery Overcrowding

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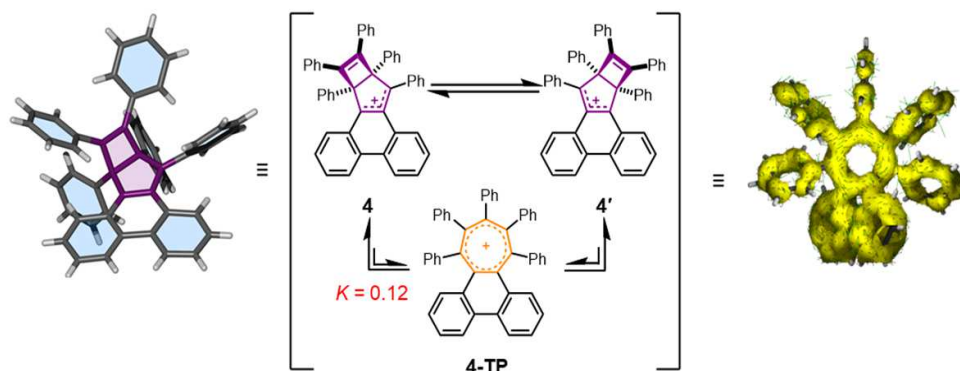


Fig. 1. Rupture of aromaticity in the solid state, and dynamic aromatic–nonaromatic equilibrium in solution due to strain

The balance between strain relief and aromatic stabilization dictates the form and function of nonplanar π -aromatics.^{1,2} Overcrowded systems undergo geometric deformations, but the energetically favourable π -electron delocalization of their aromatic ring(s) is typically preserved.^{3,4} This presentation will describe the use peripheral overcrowding to increment the strain energy of an aromatic system beyond its aromatic stabilization energy, causing the ring system to rearrange and aromaticity to be ruptured. Firstly, increasing steric bulk around the periphery of π -extended tropylium ring systems leads them to deviate from planarity. We observe contorted conformations with end-to-end twists of up to 45.2°. Aromatic stabilization and strain energies are closely matched at this critical point. Upon further increasing the strain, the aromatic π -electron delocalization of the system is broken—the aromatic tropylium ring rearranges to a nonaromatic, bicyclic analogue, ‘Dewar tropylium’. Remarkably, by counterbalancing strain against aromatic stabilization energy, we observe that these aromatic and nonaromatic isomers can exist in equilibrium with one another. Dynamic NMR measurements reveal that the isomers interconvert rapidly. This investigation of the antagonistic relationship between aromaticity and strain provides direct experimental insights into the fundamental nature of aromaticity and demarcates the extent of steric deformation tolerated by an aromatic carbocycle.

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