

Toward the Development of Oligonucleotide Rotaxanes

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We present a simple strategy for the synthesis of main chain oligonucleotide rotaxanes with precise control over the position of the macrocycle. By combining Goldup's small macrocycle variation of the AT-CuAAC approach, with the DNA click ligation approach developed by Tavassoli et al., it is possible to "click" azide and alkyne modified oligonucleotides together inside the cavity of a macrocycle, facilitating the formation of the triazole backbone and the mechanical bond simultaneously. The resulting mechanical bond was found to suppress duplex formation, effectively acting as a cage to suppress oligonucleotide activity.

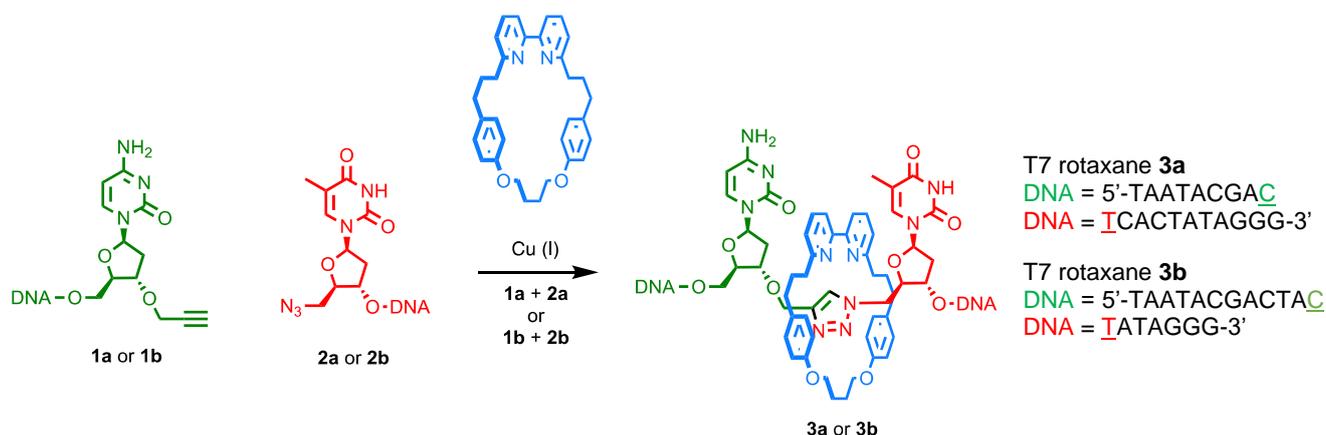


Figure 1. Synthesis of oligonucleotide rotaxanes **3a** and **3b** using Goldup's small macrocycle modification of the CuAAC approach with modified oligonucleotide alkyne **1a** (DNA = 5'-TAATACGAC) or **1b** (DNA = 5'-TAATACGACTAC) with azide **2a** (DNA = ICACTATAGGG-3') or **2b** (DNA = IATAGGG-3') respectively.

References (please use RSC format style)

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Ferrocene-Based Sensors and Wires

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Sensors - Traditional molecular sensors employ passive receptor molecules, designed to investigate analytes in only one state. The static nature of the resultant receptor/analyte interaction contributes to challenges in selectivity faced by the sensor field. To attack this challenge, we introduce the concept of 'Thumb and Forefinger' sensors, featuring receptors that can adjust their grip and investigate analytes as we do when picking up and feeling an unknown object. Through the electrochemical manifold of ferrocene, receptor states can be reversibly accessed that feature compressed and expanded structures in addition to very different electrostatic properties.

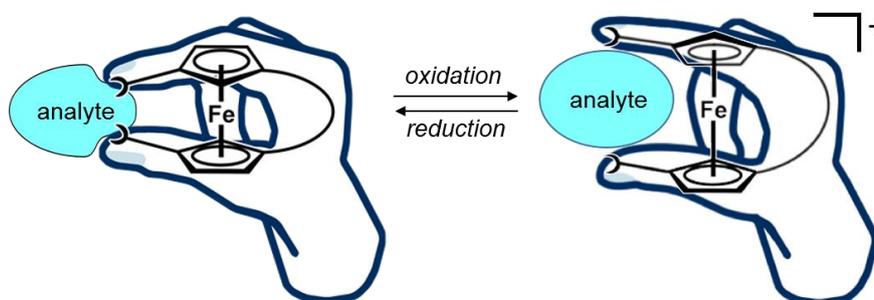


Figure 1. Receptors with an adjustable grip investigate analytes in the same way we do using our thumb and forefinger. This move away from 'static' receptors aims towards unprecedented sensor selectivity.

Wires - A key research focus of our group is the self-assembly of organometallic building blocks to create new types of electronically-active materials. Recently, we identified conditions to assemble a unique supramolecular wire from a simple ferrocene analogue. The topology is evocative of an insulated metal wire featuring a stacked ferrocene core sheathed with a helical seam of H-bonded benzamide arms. Investigations of the wire's electronic behaviour is underway.

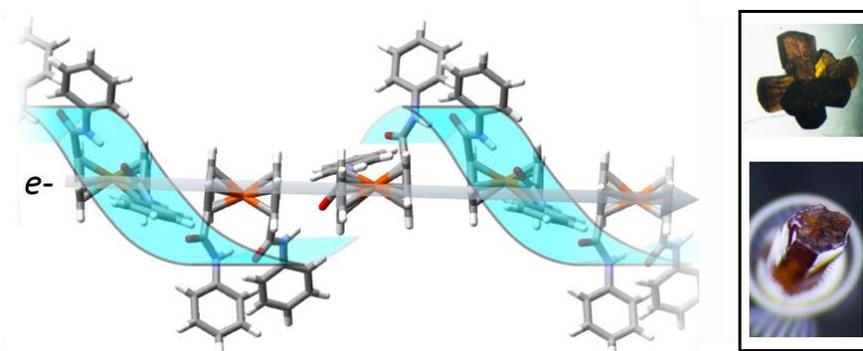


Figure 2. X-ray crystal structure of the ferrocene-based supramolecular wire discovered by our group. Helical arrangement of amide-amide hydrogen bonds highlighted by blue ribbon. Inset shows photos of two examples of wire crystals clearly displaying the hexagonal shape induced by the P6₁ space group.

Polyurethane Analogues and their Nanocarbon Composites

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Our group has developed routes to three new classes of polyurethane analogues (PUAs, Figure 1). Each novel material takes advantage of ambiphilic comonomer building blocks that can be chosen from large pools of commercially available examples. Issues of selectivity were overcome with a study of polymerisation kinetics revealing conditions that furnish polymeric materials with high purity for a single type of linkage structure.

The three basic classes of material introduced here present different electrostatic surfaces defined by their thiocarbamate, carbamate or allophanate linkages and the R groups present on the corresponding comonomers. In collaboration with the Raston Group (Flinders University, Adelaide) we have harnessed vortex fluidics to marry these surfaces with those of nanocarbon materials and prepare polymer/nanocarbon composite materials. Pleasingly, the surface functionalisation can be modified through the application of the different polyurethane analogues.

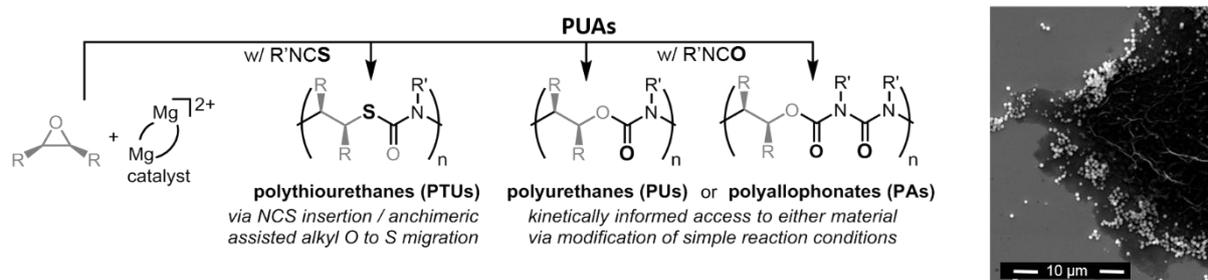


Figure 1. Our group has developed highly divergent routes to three new classes of polyurethane analogues. These novel materials present electrostatically tuneable surfaces perfect for application in site-specific coating of nanocomposites (see inset).

THE SYNTHESIS AND ANALYSIS OF NANODIAMOND-PERYLENE NANOCOMPOSITES

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Nanodiamonds (**NDs**) are known for their interesting mechanical and optical properties making them promising candidates for a wide range of applications. Covalently linking NDs with dye molecules should lead to composite materials which combine the properties of both components and potentially introduce novel hybrid properties that arise from the interplay between the linked constituents.

This study details the synthesis of novel ND-erylene diimide composites, in which the perylene diimide acts as the dye component. Nanodiamonds were functionalised with perylene diimides via ester bonds using a two-step process. This included synthesis and characterisation of disubstituted perylene diimides (N,N'-di(5-hydroxypentyl)-1,7-dimorpholino-3,4:9,10-perylene-tetracarboxylic diimide (**PDI-1**) and N,N'-di(5-hydroxypentyl)-1,6-dimorpholino-3,4:9,10-perylene-tetracarboxylic diimide (**PDI-2**). Pristine nanodiamond was oxidized using a known procedure¹, and the resulting carboxylated nanodiamonds (**ND-COOH**) were functionalized with the perylene alcohol using a Steglich esterification. The novel nanocomposite material (**ND1** and **ND2**) was characterised using a variety of different techniques including UV-vis spectroscopy, IR spectroscopy, photoluminescence (PL), dynamic light scattering (DLS), thermogravimetric analysis (TGA) and transmission electron microscopy (TEM).

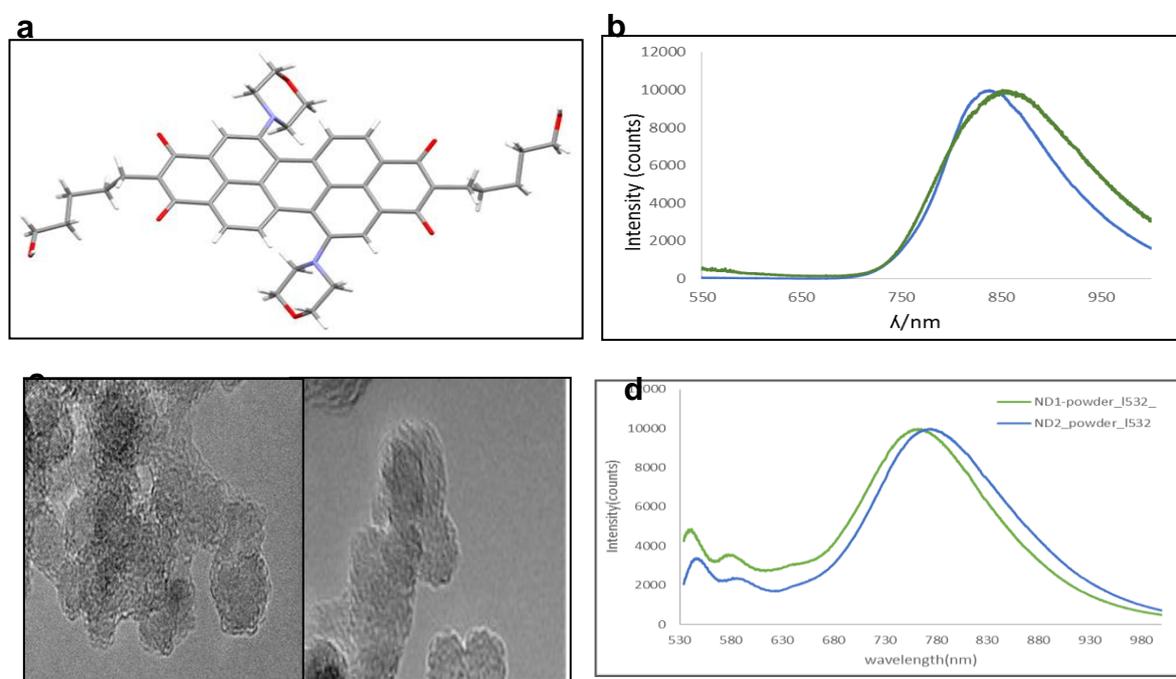


Figure. (a) Crystal structure of **PDI-1**, (b) Normalized PL spectra of **PDI-1** (green) and **PDI-2** (blue), (c) TEM Photograph left **ND1** and right **ND2**, (d) Normalized PL data of **ND1** (green) and **ND2** (blue).

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Singlet Fission of Supramolecular Structures

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Singlet fission is a spin-allowed process where a singlet exciton undergoes fission into two, lower energy, triplet states, yielding two excitons from one photon (see Fig. 1). This presents a remarkable opportunity to surpass the Shockley-Queisser photo-conversion efficiency limit of ca. 33%, and reach a new theoretical limit of ca. 50%. Singlet fission has thus received significant attention in literature, mostly with the search for clean, reliable energies in mind. However, progress in the development of suitable materials to exploit Singlet Fission has been hindered by the elusive mechanism underpinning the process, and the difficulty of modelling these mechanisms in the solid-state, due to complications arising in covalent dimer moieties.^[1]

One molecule of particular attention in this field is pentacene, a well-known chromophore which exhibits exoergic SF. Previous work by the Champness group, in the synthesis of rotaxane based molecular handcuffs, has led to the conceptualisation of a pentacene-pentacene handcuff architecture, which would orient two pentacene motifs into a dimer arrangement, without the necessity for any covalent or rigid structures.^[2] In principle, this would allow for investigation into solid state pentacene dimers previously inaccessible through other conventional means. The progress towards realising this structure will be discussed, including attempted synthetic routes and current strategies.

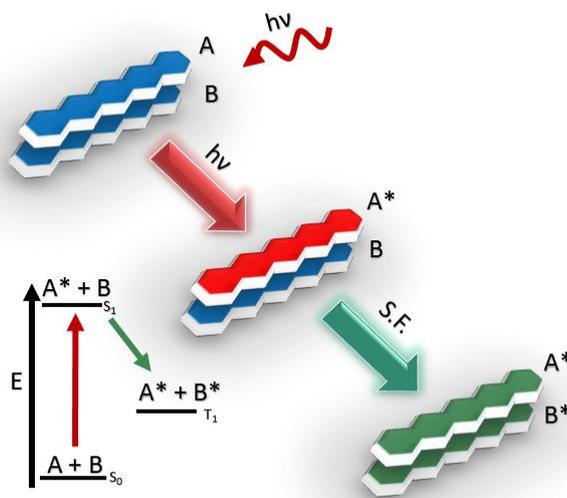


Figure 1. Schematic of Singlet Fission in a pentacene dimer. Dimer A+B (top – blue + blue) is irradiated with light, exciting A to A* (middle – red + blue), Singlet Fission occurs effectively sharing the charge of A* (red) with B (blue), resulting in two triplets A*+B* (bottom - green + green) of a lower energy.

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Hydroxamate-Based Coordination Cages in Catalysis

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Scientists have constantly taken inspiration from nature when developing new processes, materials and chemical transformations. The built-in cavity found in most supramolecular cages is analogous to the binding pocket of an enzyme, and thus, if engineered properly, can be used for substrate recognition. As a result, it can then act as an active site for catalytic transformations. Moreover, the ability of such systems to be equipped with various chiral groups can enable the creation of an asymmetric microenvironment within the cluster's cavity that enables the promotion of various enantioselective transformations.¹ Hydroxamic acids (HA) are a class of molecules which are known to exhibit interesting and important medicinal properties due to their ability to form stable complexes with various metal ions, particularly gallium and iron.² Being such good chelators, hydroxamate ligands are an excellent choice for binding units in supramolecular complexes, due to the high stability of these chelates with 3+ ions affording octahedral coordination environments. As such, they tend to form neutral $M(\text{hydroxamate})_3$ units. For those reasons, the Lloyd lab has used hydroxamic acids in the past to form small organic cages.³ Recently, we have developed a library of chiral 2,6-naphthalene dihydroxamic acids, as well as fluorescent tetraaryl-1,4-dihydropyrrolo[3,2-b]pyrrole dihydroxamic acids, in order to use them as scaffolds for the synthesis of catalytically useful coordination cages (Figure 1).

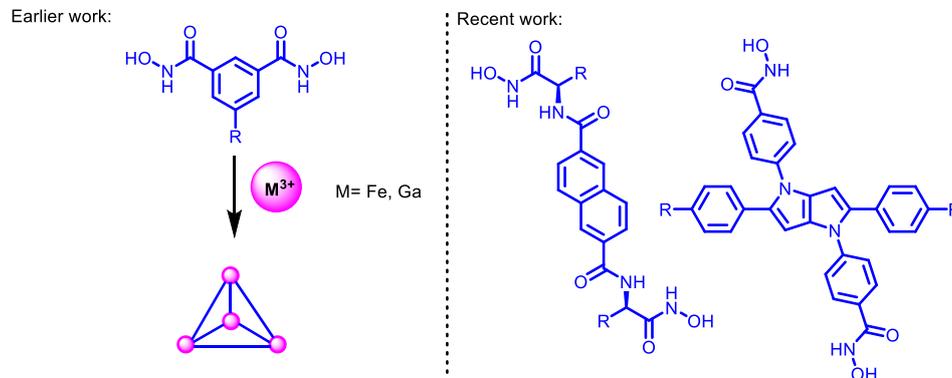


Figure 1 Dihydroxamic acids as ligands for cage formation

Acknowledgements

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Highly soluble fullerene derivatives as charge carriers for redox flow batteries

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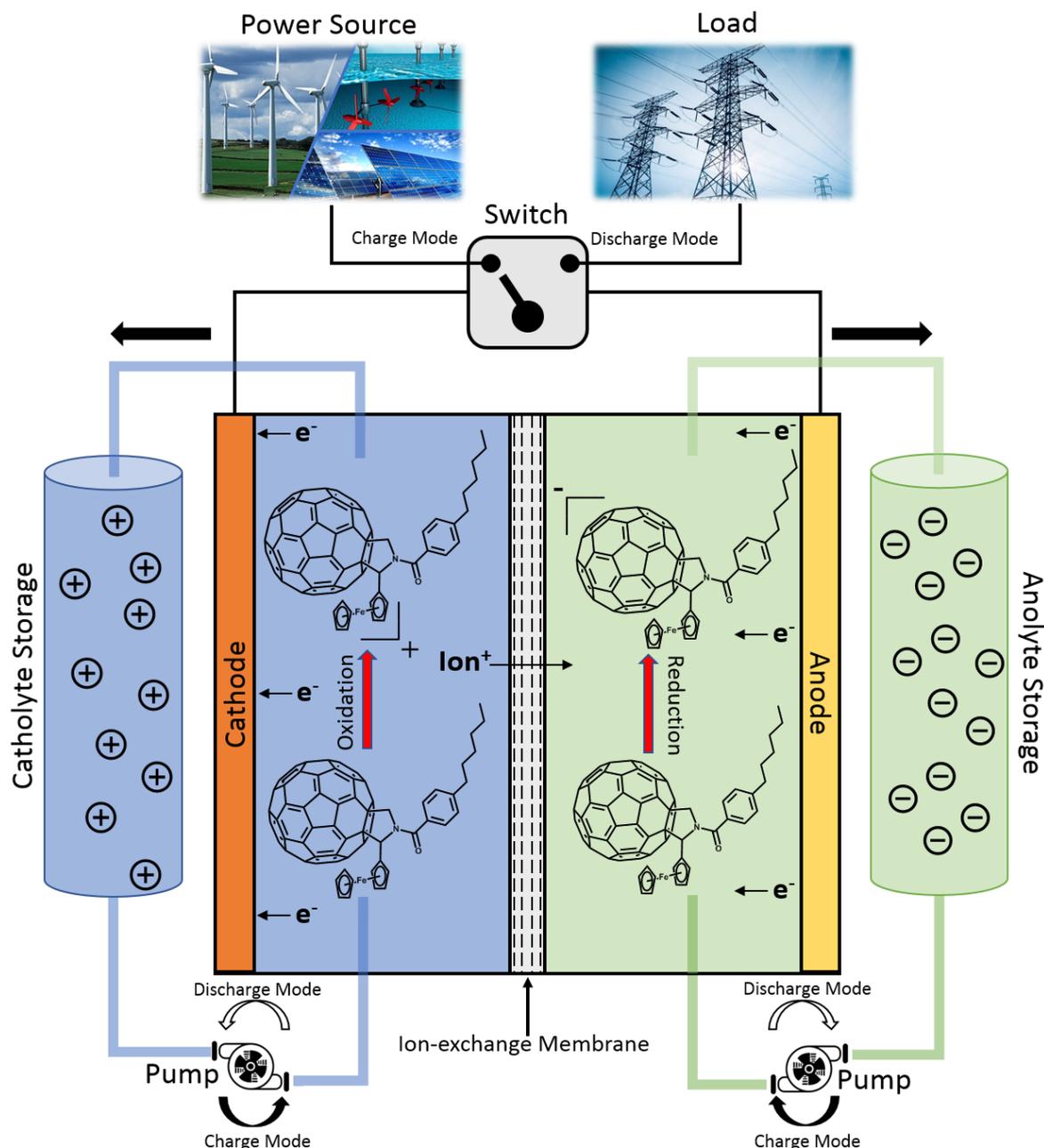


Figure 1. Schematic of a fullerene based RFB.

Due to the rapid depletion of the fossil fuels and increasing problem of carbon dioxide emission, sources of renewable energy such as wind, tidal and solar cell are going to prove more and more important. However, these sources are intermittent and unpredictable, which makes improving large scale energy storage essential if sustainable energy sources are to be

harnessed successfully. Redox flow batteries (RFBs) have the potential to solve this problem, providing a large scale, affordable and safe storage mechanism.¹ RFBs use reversible redox couples to convert electrical energy into electrochemical potential energy. In charging mode, solutions of a catholyte species, which are oxidised at the cathode, and anolyte species, which are reduced at the anode, are pumped through a cell and then stored separately in large tanks. The charged solutions are then pumped back into the cell and the reaction reversed to discharge the energy when required.¹

Due to the scale at which RFB systems operate (1000s of litres) it is essential that the redox couples are based on inexpensive starting materials. To date, through a wide variety of cheap, organic based redox couple systems have been investigated in both aqueous and organic solvents,²⁻⁴ no systems have been found to match the performance of the commercially available but unsustainable vanadium based system.⁴

Fullerene is well-known for its inherent multi-electron accepting properties and chemistry has been established to enable different moieties to be added onto the cage, to create a range of fullerene derivatives with multiple functionality. In this work, we utilise fullerene based bifunctional molecules as RFB redox couples (Figure 1). Ferrocene groups, appended to the cage, act as the catholyte active moiety, whilst the fullerene cage itself accepts electron as the anolyte active moiety. Using the same species for both sides of the cell negates the problems associated with membrane crossover and alkyl chains act as solubilising group to expand the solubility, resulting in a higher total energy density.⁵ A series of molecules have been synthesised, achieving solubility of 250 mM in ODCB, which is almost 2.5 times that of the reported record for fullerene based RFB system (107 mM).⁵ In the future, different solubilising groups will be explored to obtain better solubility, followed by cell performance and stability tests. This work paves the way for RFBs to be utilised for large scale energy storage and thus will enable renewable energy sources to become a pivotal part of global power provision in the future.

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Electrochemical Gels for Biological Applications

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Electrochemically grown low molecular weight gels (EGLMWG) have great potential to help improve performance for a variety of existing biological technologies such as membrane technology, tissue culture and drug delivery systems. EGLMWGs are grown in the presence of hydroquinone.^{1,2} The oxidation of hydroquinone produces protons which forms a pH gradient at the electrode surface which acts as the gelation trigger.^{1,2}

Due to hydroquinone being toxic, EGLMWG are non-cell viable, which limits the use of these materials for biological application. Currently EGLMWG are used only as moulds where the gel and hydroquinone is removed before cells are added.^{3,4} Here, we show an alternative to hydroquinone that forms EGLMWG that are cell viable for use in biological applications, for example as a synthetic alternative for tissue culture to commonly used biological gels such as matrigel and collagen.

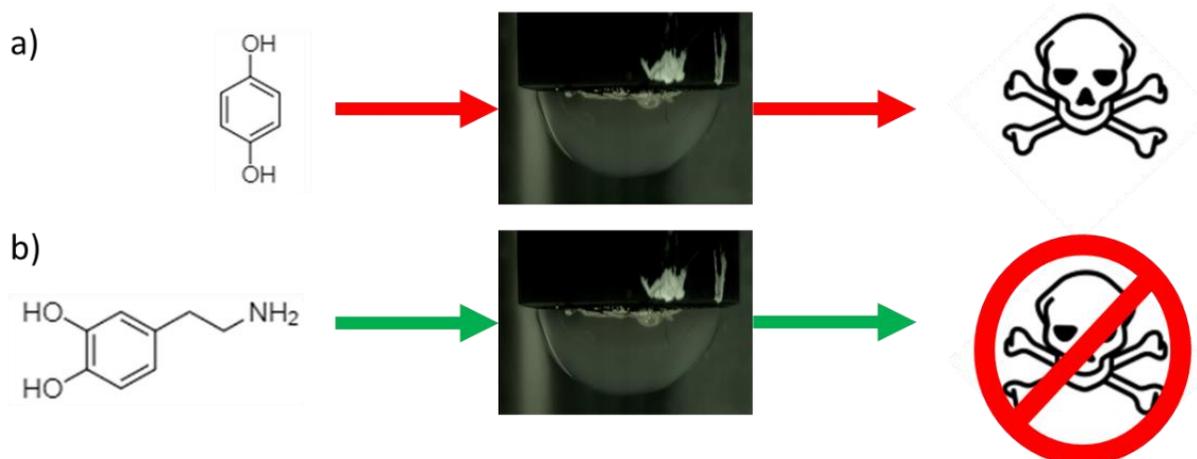


Figure 1. a) Hydroquinone used to form EGLMWG causing cell death b) Hydroquinone substitute used to form EGLMWG that are cell viable.

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Supramolecular Gelation of Sustainable Low Molecular Weight Gelators

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Low molecular weight gelators (LMWGs) are organic compounds with molecular weights of less than 2000 Da that show gelation behaviour in a solvent.[1] In recent years, LMWGs have been the subject of intensive research as they are an important class of functional materials, finding applications in various industries such as cosmetics, food processing, healthcare and many more.[2] In this work, novel 'green' LMWGs, containing acetal groups, were synthesised from naturally occurring sugar alcohols. These compounds were characterised and tested for their gelation ability in organic solvents and aqueous solutions. Rheological data were studied on certain lead gelators, 1,3:2,4-di(4-*isopropylbenzylidene*-D-sorbitol) (DBS-*i*Pr) and 2,4(4-*isopropylbenzylidene*)-D-sorbitol (MBS-*i*Pr) (Figure 1), to determine and compare the strength of their networks.

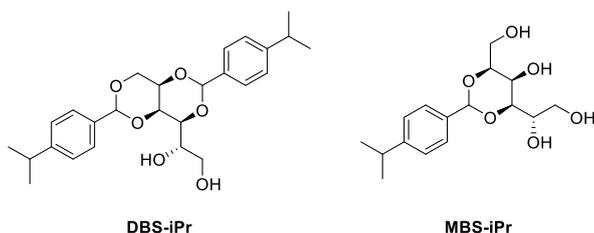


Figure 1 | Structure of DBS-*i*Pr and MBS-*i*Pr

The effect of solvent on the self-assembly morphology of these gelators were investigated *via* scanning electron microscope (SEM) (Figure 2). By virtue of π - π interaction, DBS-*i*Pr undergoes gelation in polar solvents to form smooth non-helical fibres, whereas gelation in non-polar solvents such as cyclohexane, aided by hydrogen bonding interactions, results in helical fibres.

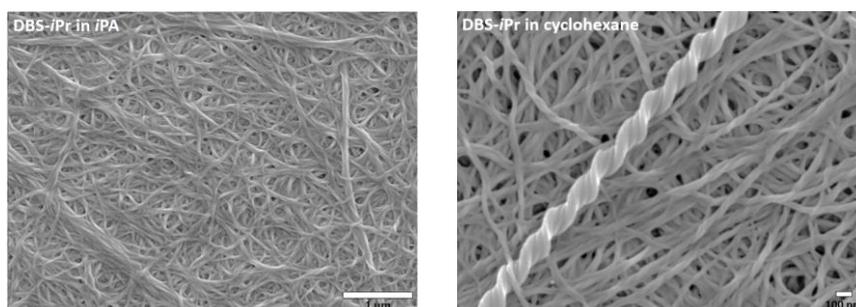


Figure 2 | SEM images of 10 mg/mL DBS-*i*Pr in *i*PA and cyclohexane showing the differences of the fibres.

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Switching the enantioselectivity of a reaction with a [2]rotaxane organocatalyst

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Artificial switchable catalysts have proved to be effective tools to control the chemo-, regio- and enantioselectivity of chemical transformations.¹ We present the synthesis of a light/pH switchable [2]rotaxane organocatalyst *E/Z*-1 bearing a *pseudo*-meso 2,5-disubstituted pyrrolidine as the catalytic unit. The macrocycle of the rotaxane can shuttle between two binding stations depending on the state of the switch, thus blocking either side of the pyrrolidine catalyst at will. This control of the blocking side of the pyrrolidine core dictates the facial bias in the enamine catalyzed conjugative addition of aldehydes to vinyl sulfones².

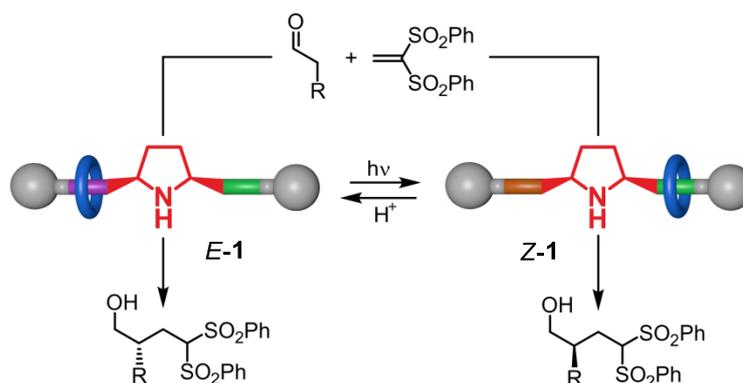


Figure 1. Switching between the *E* and *Z* states, the organocatalyst **1** can selectively produce either enantiomer in the conjugative addition of aldehydes to vinyl sulfones.

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Aromatic Interactions in Solution

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Interactions involving aromatic rings are frequently implicated in supramolecular phenomena ranging from asymmetric catalysis¹ to biomolecule recognition.² Such interactions have been extensively studied in the gas phase by computational chemists, but the practical limitations of modelling solvation *in silico* have hindered investigations into solution-phase behaviour. As the vast majority of chemical phenomena occur in solution, an understanding of the underlying factors is required for informed application of these interactions.

Here we have used synthetic molecular torsion balances to systematically vary the nature of competing CH- π and π - π interactions to assess the physicochemical basis of these interactions in the solution state.

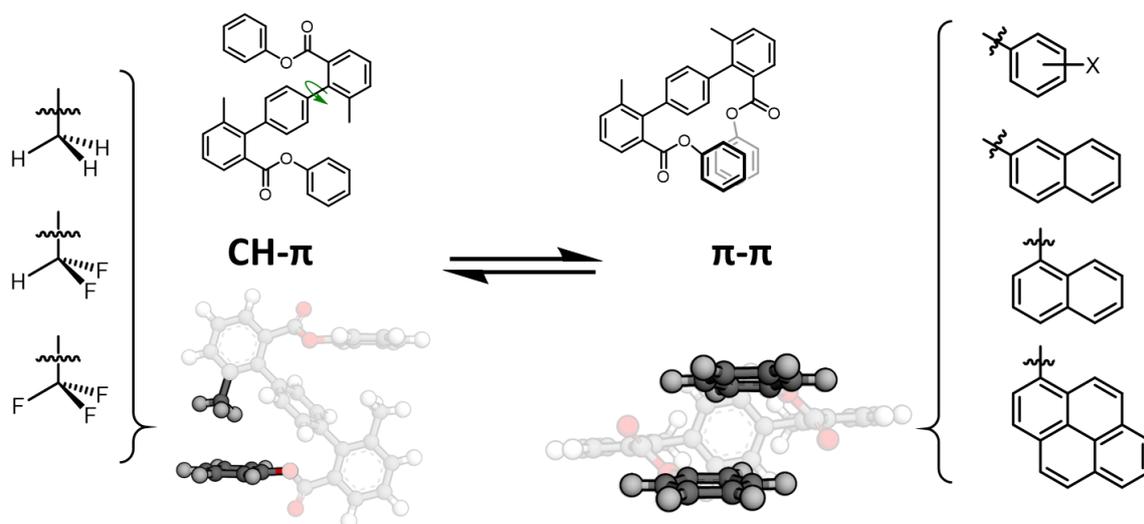


Figure 1. Molecular balances used to probe the physicochemical nature of CH- π and π - π interactions

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Oligonucleotide Rotaxanes

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We present a simple strategy for the synthesis of main chain oligonucleotide rotaxanes with precise control over the position of the macrocycle. By combining Goldup's small macrocycle variation¹ of the AT-CuAAC reaction,² with the DNA click ligation approach,³ it is possible to "click" azide and alkyne modified oligonucleotides together inside the cavity of a macrocycle, facilitating the formation of the triazole backbone and the mechanical bond simultaneously. The resulting mechanical bond was found to suppress duplex formation, effectively acting as a cage to silence oligonucleotide activity.

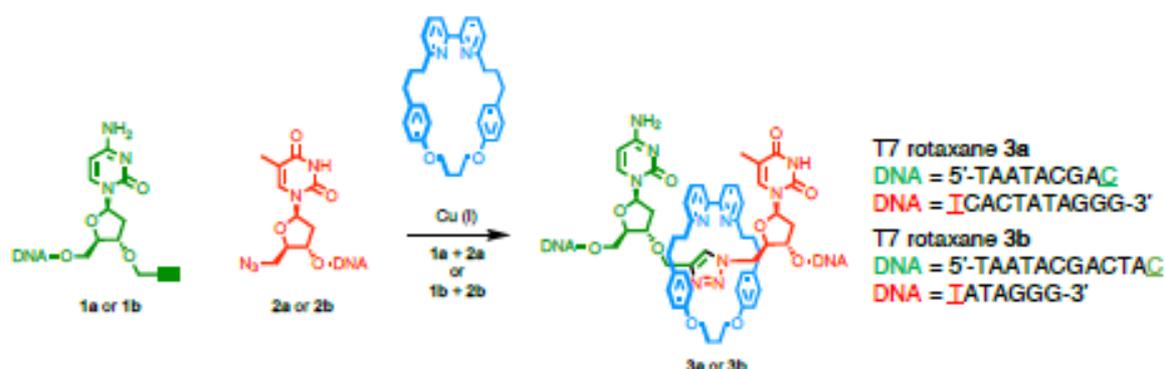


Figure 1. Synthesis of oligonucleotide rotaxanes **3a** and **3b** using Goldup et al's., small macrocycle modification of the CuAAC approach with modified oligonucleotide alkyne **1a** (DNA = 5'-TAATACGAC) or **1b** (DNA = 5'-TAATACGACTAC) with azide **2a** (DNA = ICACTATAGGG-3') or **2b** (DNA = IATAGGG-3') respectively.

- 1 H. Lahlali, K. Jobe, M. Watkinson and S. M. Goldup, *Angew. Chemie - Int. Ed.*, 2011, **50**, 4151–4155.
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Using Cavitation Rheology to Understand Dipeptide-Based Low Molecular Weight Gels

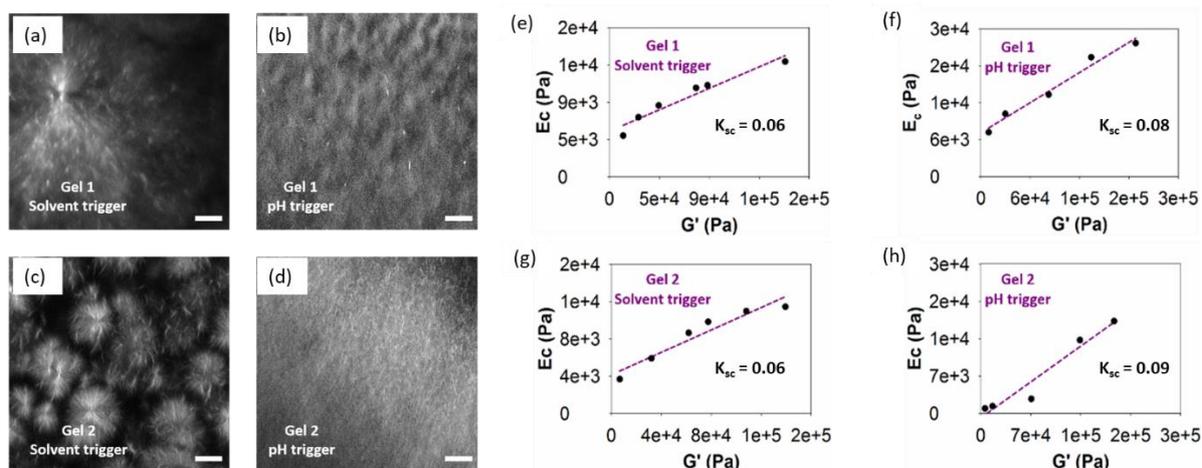
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The study of dipeptide-based hydrogels has been the focus of significant effort recently due to their potential for use in a variety of biomedical and biotechnological applications. It is essential to study the mechanical properties in order to fully characterise and understand this type of soft materials. In terms of mechanical properties, the linear elastic modulus is normally measured using traditional shear rheometry. This technique requires millilitre sample volumes, which can be difficult when only small amounts of gel are available and can present difficulties when loading the sample into the machine.

Here, we describe the use of cavitation rheology, an easy and efficient technique, to characterise the linear elastic modulus of a range of hydrogels. Unlike traditional shear rheometry, this technique can be used on hydrogels in their native environment, and small sample volumes are required. We describe our set-up and show how it can be used to probe and understand different types of gels. Gels can be formed by different triggers from the same gelator and this leads to different microstructures. We show that the data from the cavitation rheometer correlates with the underlying microstructure in the gels, which allows a greater degree of understanding of the gels than can be obtained from the bulk measurements.



Further Exploring the Structural Diversity of Yttrium Metal-Organic Frameworks Through Linker Alteration

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Research revolving around metal-organic frameworks (MOFs) has rapidly increased in recent years following their discovery in 1995, with there being approximately 70,000 MOF structures reported in the Cambridge Structural database as of 2018.¹ The reason for this interest can be attributed to the permanent porosity and vast range of structural and chemical properties that can be imparted on MOFs, leading to an array of applications, from gas storage to drug delivery.

Coordination modulation – addition of monotopic linkers as capping agents or crystallisation promoters – is a technique routinely implemented in the synthesis of MOFs not only to enhance crystallinity, but also often to control particle size and physical properties whilst maintaining the same overall structure. It has been established that the role of modulators varies when used in the synthesis of yttrium based frameworks; a series of six different Y-MOFs connected by the same 2,6-naphthalenedicarboxylic acid linker (NDC) were produced under different modulation conditions.² The transferability of the modulated syntheses have thus been examined through the synthesis of frameworks containing the 1,4-benzenedicarboxylic acid linker. Commonly, alteration of the organic linker results in frameworks of the same topology. Several of the modulated syntheses successfully produce phase pure Y-BDC material of the same topology as the corresponding Y-NDC framework. However, alteration of the linker in some instances leads to the synthesis of topologically different materials, with a change of heating source, from conventional oven heating to microwave-assisted, also allowing phase selection. This study demonstrates the complexity in crystallising new Y-MOFs.

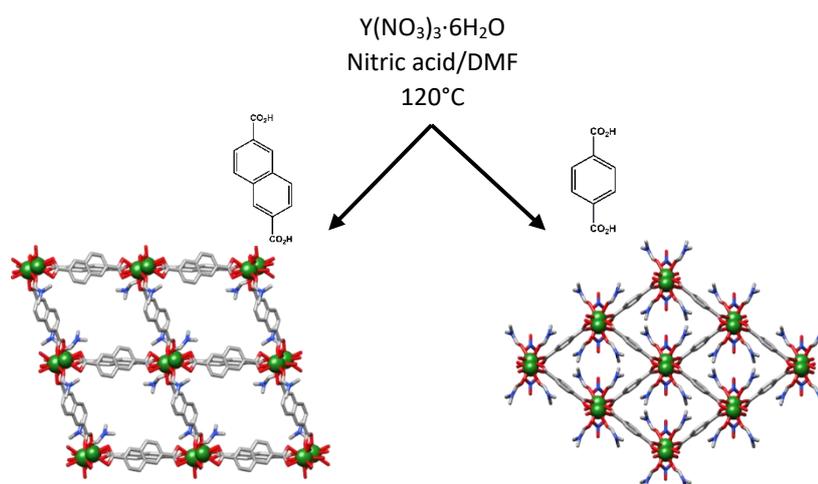


Figure 1. Crystal structures of Y-NDC and Y-BDC produced from nitric acid modulated syntheses.

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Tuneably Nanosized Crystalline 2D Organic Membranes for Versatile Molecular Separations

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We have developed two novel methods to prepare 2D crystalline macrocycle membranes, using interfacial crystallisation and layer-by-layer deposition. Interestingly, these porous organic cages have guest selective microporous structures if they can be processed into specific polymorphic forms.^[1] Therefore, we are interested in templating the packing arrangements of porous organic cages in the porous membranes to modulate selective guest permeation. Their surface morphology has been characterised by SEM and AFM, showing the formation of continuous films with the embedded triangle or hexagon crystals, and their thickness has been determined in the range of 20–200 nm. These resulted porous organic cage membranes are continuous, defect-free, and they have exhibited excellent dye rejection with good permeability of solvents. It has been observed that there was a shift on the cut-off curve for these membranes of different polymorphs, which indicates we have successfully modulated the pore structures of these membrane materials. It is anticipated that the synthesis technique and templating method reported herein for the fabrication of defect-free, free-standing porous organic cage membranes would broaden the realm of practical application of these macrocycle materials.

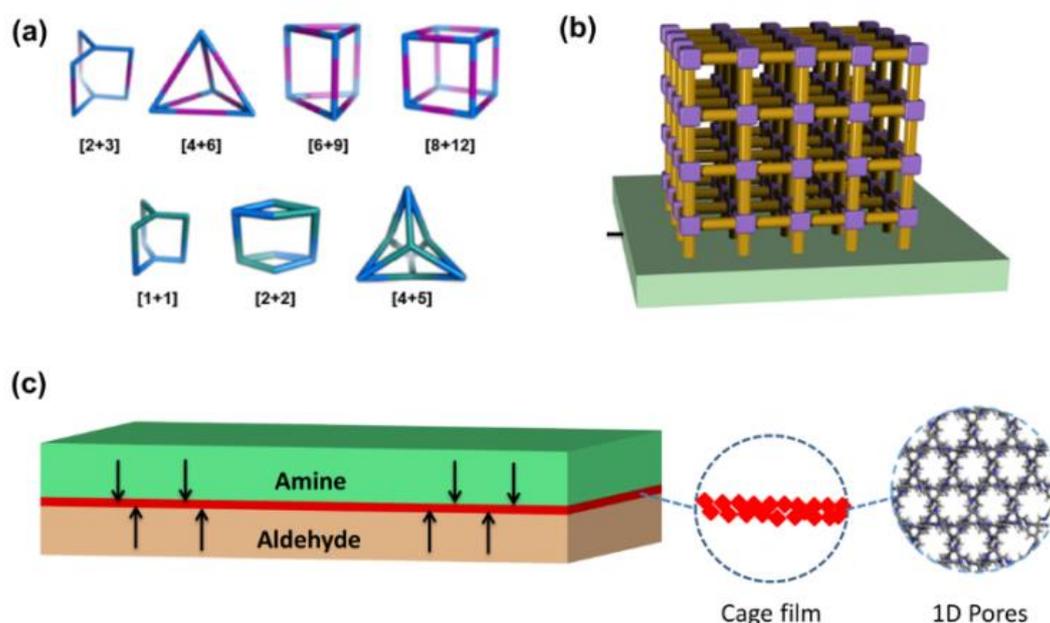


Figure 1. Scheme showing (a) a series of shape-persistent covalent organic cage topologies.^[2] (b) Illustration of films grown via a layer-by-layer method on a substrate^[3] and (c) interfacial synthesis method to fabricate organic cage film and its connected pore structure.

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Inherent Ethyl Acetate Selective Adsorption in a Macrocycle based Molecular Solid

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Ethyl acetate (EA) is an important raw material and solvent for the chemical industry. Detection of EA is also important for the brewing industry and as a chemical marker for some cancers.¹⁻³ Therefore, materials that selectively adsorb EA are highly desirable for molecular separations and EA detection. Here, we report that a well-studied macrocycle (TAMC) selectively adsorbs EA over ethanol (EtOH). Selective adsorption of EA is an inherent feature of the guest free crystalline α -TAMC material, as this porous structure contains voids which perfectly match the size and shape of EA. Interestingly, crystal structure prediction calculations shown that the α -TAMC structure is energetically preferred (Figure 1b), highlighting that the perfect voids for EA adsorption in α -TAMC can be predicted and that this structure is energetically stable. With this “inherent” selectivity for EA, breakthrough experiments were performed using α -TAMC. These measurements revealed that α -TAMC can effectively separate EA from EtOH, which is a very challenging industrial separation.⁴ Importantly, α -TAMC can be readily synthesised from cheap starting materials and the separation performance is reproducible over multiple adsorption cycles, indicating that α -TAMC could be useful for actual separations or detection applications in the future.

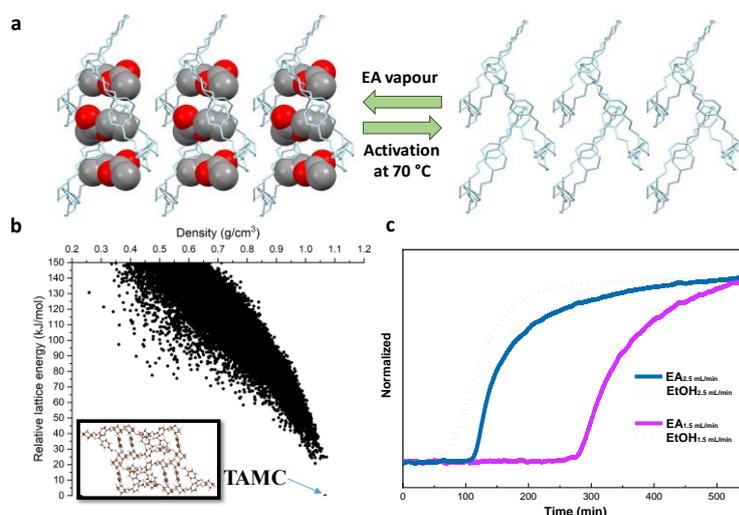


Figure 1. (a) Single-crystal structures: EA@TAMC (left); α -TAMC (right); (b) CSP energy-density plot generated for TAMC; (c) Breakthrough profiles for EA/EtOH mixture recorded at 25 °C. Colours indicate sorbate flow rate: (blue) 2.5 mL/min; (purple) 1.5 mL/min.

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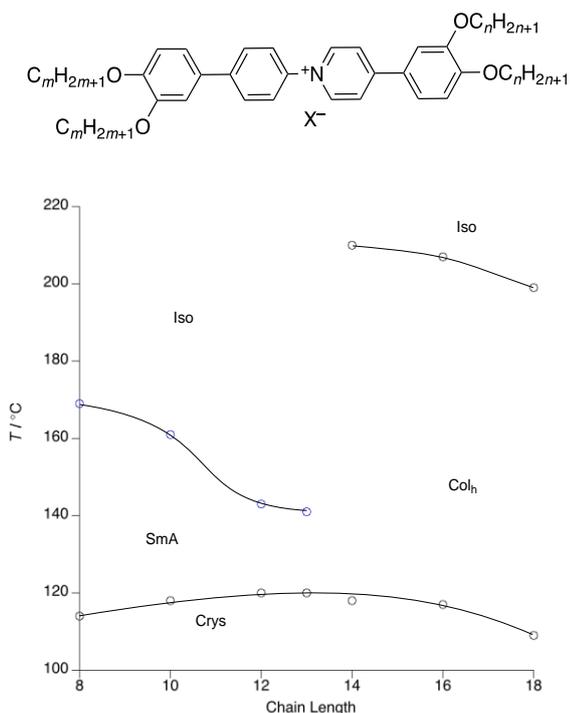
Polycatenar Ionic Liquid Crystals based on the *N*-Phenylpyridinium Cation: a Remarkable Example of Phase Stabilisation

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Polycatenar liquid crystals, rod-like liquid crystals (LCs) with between three and six terminal chains, typically show a rather rich liquid crystal phase behaviour.^[1] In particular, certain tetracatenar (four-chained) examples are of special interest as at short terminal chain lengths they can show phase behaviour associated with rod-like LCs, whereas phases akin to disc-like LCs are formed at longer chain lengths.^[2] On the other hand, the LC behaviour of ionic materials has often been quite limited.^[3] While previously we have reported on formally ionic polycatenar LCs based on salts of silver(I),^[4] in reality these exist as tight-bound ion pairs. Therefore, we now report what we believe to be unique examples of truly ionic, polycatenar LCs.



The compounds (opposite) are based on an *N*-phenylpyridinium core, accessed through Zincke chemistry^[5] and, as the figure shows, they may be prepared as unsymmetric materials.^[6] The behaviour of different series of materials with different anions will be discussed. In particular for the four-chain materials opposite, while at longer chain lengths a Col_h phase is found, uniquely for polycatenar materials, we find a SmA phase at shorter chain lengths. However, perhaps the most remarkable observation is the massive difference in phase stability between the salt where $n = m = 13$ and $n = m = 14$ ($X = \text{OTf}$). We argue that the presence of the anion destabilises the SmA phase and we will back this claim up with detailed literature comparisons and experimental data.

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A Macromonomer Route to Redox-Active Synthetic Amyloids with NDI Cores

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Hydrogen bonding and other weak reversible interactions have been successfully¹ exploited in driving together small molecular building blocks into impressive supramolecular architectures, whilst achieving an equal level of control over the assembly of synthetic high-molecular weight *macromolecules* still remains a grand challenge for both supramolecular chemistry and synthetic biology. Macromolecular assemblies bear the potential to achieve higher levels of structural hierarchy, which are inherently inaccessible² by the multicomponent small molecular approach, thus enabling new opportunities to discover unprecedented material properties. Amyloid fibres, such as those comprising collagen and spider silks, serve as our initial inspiration for preparing mechanically robust nanostructures with one-dimensional order. Towards this end, we have prepared an (Ala-Gly)_x-based peptide macromonomer containing a redox-active naphthalene diimide (NDI) π -electron acceptor within the primary chain, reactive termini, and a solubilising amide protecting group. “Click” polymerisation of these macromonomers using Cu(I)-assisted azide–alkyne cycloaddition (CuAAC) affords artificial β -hairpin-like structures³ (via the 1,4-triazole unit) that is intended to facilitate polymer folding into β -sheet rich structures upon removal of the protecting group (Figure 1). Peptide-driven assembly of the embedded NDI units into cofacial aggregates within the core of 1D nanostructures is expected to yield low-energy pathways for electrons to delocalise as well as enable optoelectronic phenomena, e.g., through the formation of photo-emissive excimers. NDI–NDI intramolecular interactions, as well as one-dimensional fibre formation, will be probed using a combination of solution- and solid-state spectroscopic and electrochemical analyses in both the assembled and non-assembled states.

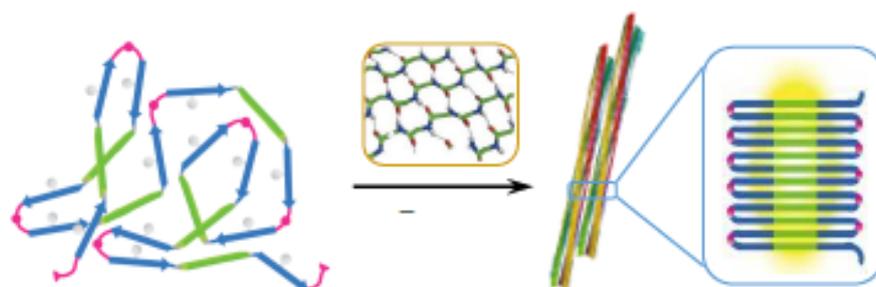


Figure 1: Stimuli-responsive macromolecular assembly will result in novel optoelectronic fibres

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Waving and Ruffling in 3-D Hypervalent Siloxane Porphyrins

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This work explores an underutilised method to enhance the properties of porphyrin dyes by introducing (Figure 1) hypervalent siloxane cores and axially oriented capping groups. Previously, investigations into hypervalent silane porphyrins have shown correlations between Si–N bond lengths and the formation of unusually distorted conformations.¹ Herein, we report a series of hydrophobic silane porphyrin siloxanes that are not only highly soluble, but exhibit distorted conformations as a result of intramolecular noncovalent bonding interactions. We have performed an in-depth structure property relationship study by varying the silyl caps in the axial positions of silyl tetraphenylporphyrins. This study includes physicochemical characterisation in solution and the solid state using NMR spectroscopy, X-ray crystallography, cyclic voltammetry, fluorescence measurements and DFT analysis, revealing the origins of the unusual conformational dynamics of these compounds.

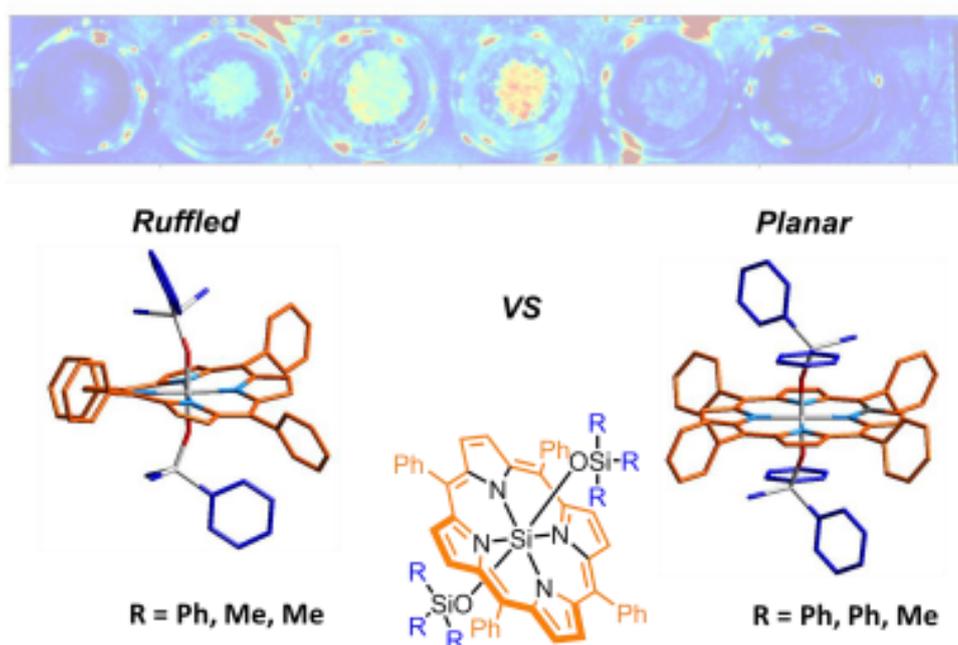


Figure 1. Structure of 3-D hypervalent silane porphyrin with siloxane caps and the shape-selectivity of a select set of porphyrin derivatives

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Supramolecular Gel Materials Enabled by and Enabling Photochemical Transformations.

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Supramolecular gel materials, formed *via* the assembly of low molecular weight gelators (LMWGs), have been a developing field of research within recent years. Dissimilar to their macromolecular polymeric counterparts, LMWG molecules form directional and reversible non-covalent interactions, which drive the self-assembly process. Fibres are formed which intertwine and entangle, resulting in a large network matrix which can entrap the solvent of the system by surface tension effects, inhibiting its ability to flow and thus, resulting in a non-Newtonian fluid with solid-like behaviour. The reversibility of such interactions results in adaptive materials, capable of reacting to external stimuli and changes in their environment.¹

However, this adaptability is minor in comparison to naturally occurring supramolecular structures. This is a result of the underlying thermodynamics; most biological systems exist in states far from equilibrium, with constant formation and destruction of transiently stable species. Such species are produced to serve a specific function and change according to energetic inputs from their environment, giving rise to unique properties such as self-healing. Taking cues from nature, research into synthetic out-of-equilibrium systems is generating momentum, largely due to the wide range of possible applications including, but not limited to, drug delivery and regenerative medicine.²

The pioneering examples of such systems require toxic chemicals such as methyl iodide and dibenzoyl-(L)-cystine that will prove problematic when considering biomedical applications.^{3,4} In order to build upon this work, our current research involves the incorporation of photochemistry, namely singlet oxygen (¹O₂) mediated reactions. This chemistry is inherently 'green' requiring only light, a photosensitiser and air, allowing reactions to occur under mild conditions, circumventing the requirement of toxic materials.⁵ For this reason, amongst others, we believe that photochemistry and ¹O₂ can make a significant contribution to the chemistry surrounding out of equilibrium systems.

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Hierarchical Assembly and Guest-Responsive Behaviour in Extrinsicly Nanoporous Copper Paddlewheel Complexes

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Crystalline porous materials that display guest-responsive behaviour are of high interest as substrate-specific structural transformations can be lead to applications in sensing and separation.¹ Nanoporous molecular crystals (NMCs) are materials constructed from discrete molecular components held together by weak non-covalent interactions which display permanent porosity upon guest removal.^{2,3} Due to the non-covalent nature of material formation, these materials are typically soluble in most solvents, which gives them the advantage of high-processability, but makes their application with liquids problematic. In addition, dynamic 'breathability' (guest adaptability) within these materials has not yet been realised.

Here, we present a new class of NMCs based on trityl-protected pyrazole carboxylic acid ligands (e.g., **1**, Figure 1) that hierarchically assemble into extrinsicly porous structures *via* the formation of copper acetate paddlewheel dimers and higher-order aromatic interactions. Our NMCs possess up to 42% solvent accessible volume and display dynamic responsive behaviour, resulting in the expansion and contraction of pores, to accommodate encapsulated guest molecules. Notably, powder X-ray diffraction measurements reveal that these transformations take place without any loss of NMC crystallinity. We show that ligand substitution effects can modulate the degree of crystal porosity and guest sensitivity, thereby affording the potential to tailor the selectivity of NMCs for applications in advanced substrate sensing within complex mixtures, such as the detection of alcohol or effluents from water.

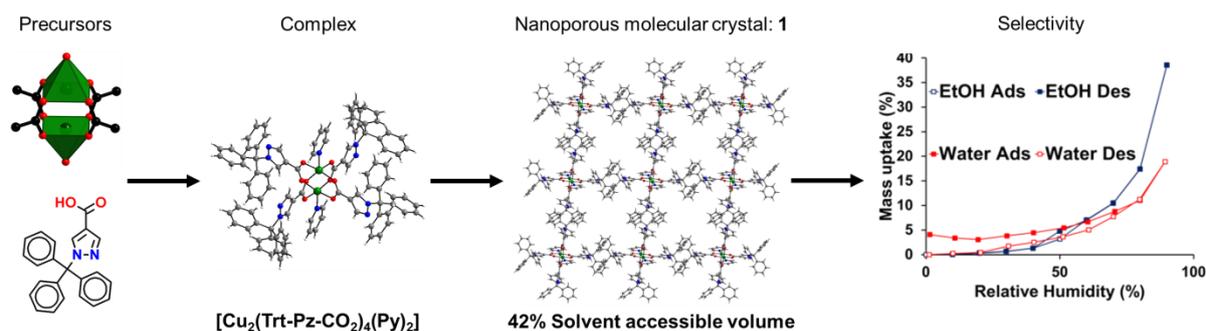


Figure 1. Hierarchical assembly and selectivity of the [Cu₂(Trt-PzCO₂)₄(Py)₂] materials.

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Redox-Controlled Assembly of Rigid Oligoproline Scaffolds

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Redox-responsive moieties can be exploited to introduce new means of guiding 1D assembly and molecular actuation in well-defined secondary structures of polypeptides such as oligoprolines,¹ which even at short lengths, are able to undergo interconversion between a tight, right-handed helical structure in hydrophobic solvents and an expanded left-handed helical structure in aqueous or polar organic solvents. As a consequence of its turn periodicity, functional groups installed at every third proline residue reside on the same face of oligoproline helices, leading to enhanced conformational stability in solution² and a reliable platform for studying 1D through-space processes, such as photo-induced electron transfer between photo-excited donors and electron acceptors in a 1D array.³ To-date, only solvent-induced changes in oligoproline conformation and assembly have been explored. However, in this research, we have exploited simple and robust chemistries such as the Zincke reaction and Cu(I)-assisted azide–alkyne cycloaddition, to introduce redox-active viologen dications to the backbone of oligoproline scaffolds. Solution-state spectroscopy and electrochemistry are used to probe the conformational stability and reversible assembly (both intramolecularly and intermolecularly) of these functionalised oligoprolines in response to chemical and electrochemical stimuli. Meanwhile, solid-state analysis of single crystals provide us with deeper insight towards the through-space interactions adopted within these materials. The reversible pimerisation of viologen radical cations⁴ is anticipated to afford 1D actuation (expansion/contraction) of the rigid scaffold (Figure 1) and may also lead to the formation of hierarchically assembled nanostructures that exhibit high energy capacities and long-range electron delocalisation that would be relevant to the development of advanced organic electronic devices.

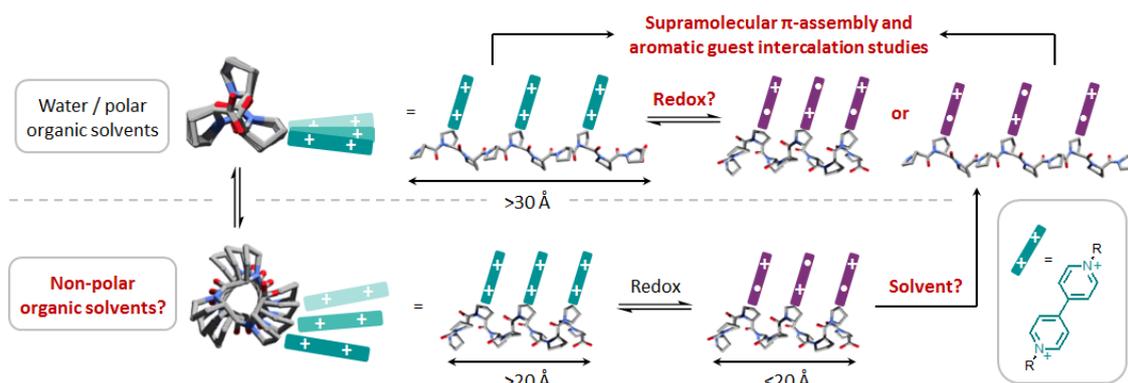


Figure 1: Potential conformations adopted by viologen functionalised oligoprolines.

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Metal and Organic Templates Together Control the Size of Covalent Macrocycles and Cages

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Most supramolecular assemblies involving palladium(II) revolve around the use of two to four pyridyl-based ligands coordinated to the palladium center.¹ As one of the rare exceptions, we previously described the self-assembly of anilines, 2,6-diformylpyridine and Pd(II) to form covalent macrocycles, (pseudo)rotaxanes and catenanes.² The 2,6-bis(imino)pyridyl tridentate motif present in these assemblies binds Pd(II) while leaving one free coordination site which can accommodate a mono-dentate ligand. We have now used the 2,6-bis(imino)pyridyl-Pd(II) motif as a building block in the self-assembly of covalent macrocycles and cages (Figure 1). The binding of multi-topic ligands to the free coordination sites in these assemblies could be used to control product size. Multi-topic ligands also bridged metallomacrocycles to form higher-order supramolecular assemblies. Furthermore, we developed an efficient method to reduce the imine bonds to secondary amines, leading to fully organic covalent macrocycles and cages, which were inaccessible through other means.

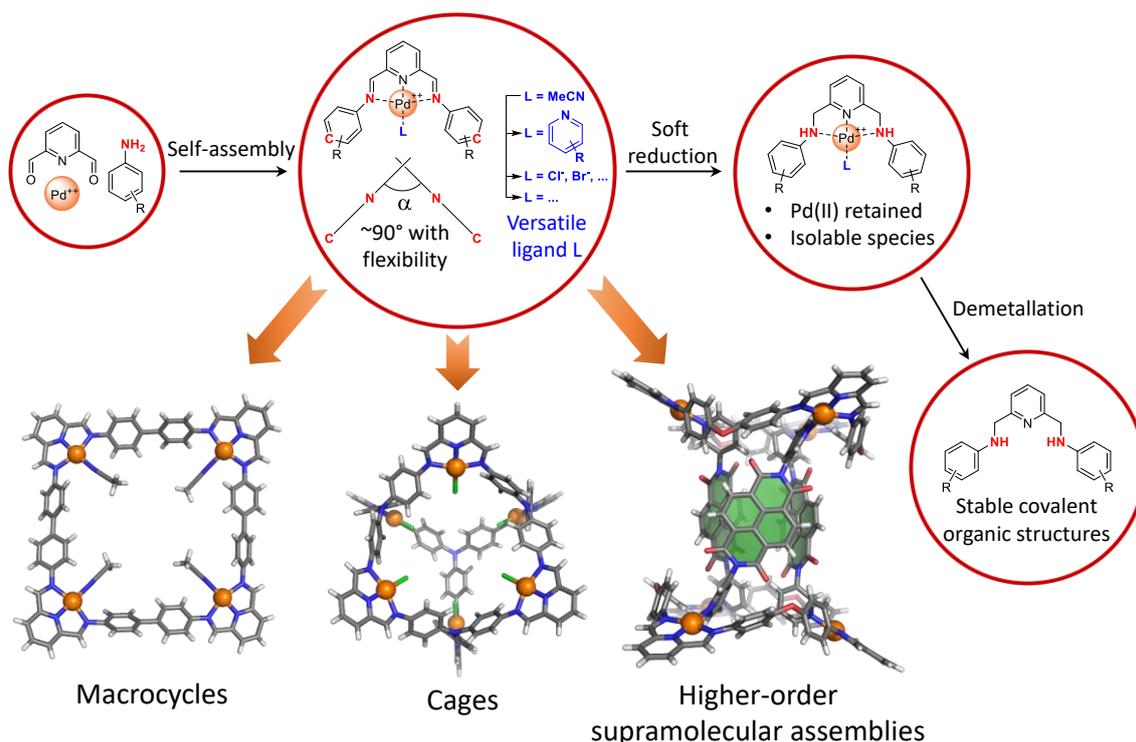


Figure 1. Features of the 2,6-bis(imino)pyridyl-Pd(II) building block.

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A Size-Flexible Palladium Cage Encapsulates Fullerenes

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In the last decades, coordination self-assembly has evolved into the most effective strategy for the rational construction of discrete supramolecular coordination complexes (SSCs).^[1] The presence of cavities with well-defined sizes and shapes that are able to encapsulate selected substrates is the most important property of a self-assembled structure due to most of the properties that can result in applications are directly related to the host-guest chemistry of a supramolecular assembly.^[2] We recently became interested in preparing organometallic hosts based on N-heterocyclic carbene (NHC) ligands for the selective recognition of organic substrates.^{[3][4]} In this work, a palladium-cornered molecular square with four pyrene-bis(imidazolylidene) bridging ligands is reported. This metallo-polygon was able to encapsulate C₆₀ and C₇₀. The X-ray diffraction structures of the empty cage as well as the cages complexed with both fullerenes are described. The fullerene encapsulation produces perturbations in the structural parameters of the metallo-square, showing that it can adjust the shape of its cavity to the size of each fullerene (Figure 1).

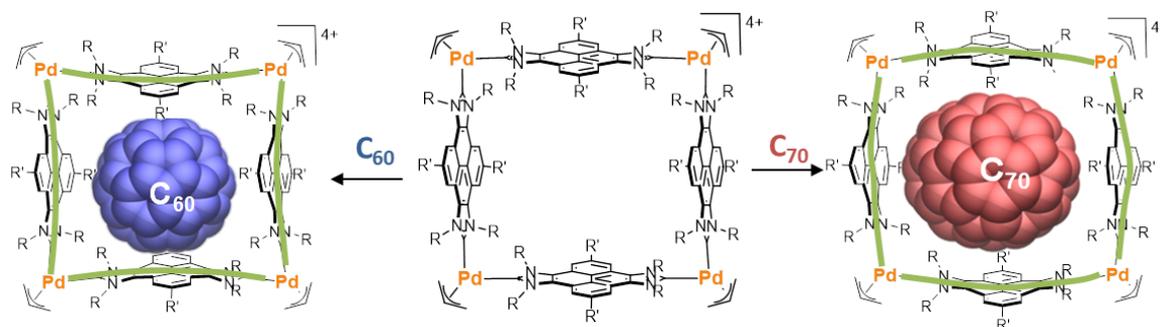


Figure 1. C₆₀@PdCage Host-Guest adduct (left), empty PdCage (middle) and C₇₀@PdCage Host-Guest adduct (right).

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MULTIFUNCTIONAL LAYERED MAGNETIC MATERIALS: 2-D MAGNETIC COORDINATION POLYMERS

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The field of coordination polymers (CPs) and metal–organic frameworks (MOFs) has evolved over two decades to a stage where it is one of the most widely investigated areas of materials chemistry. The field has impacted many areas of science including commercial applications from gas storage agents to new investigations as drug-delivery vehicles.¹ CPs and MOFs are prepared from the combination of metal cations, commonly d- or f-block metals, and ligands capable of bridging metal centres to create polymeric structures which extend in one, two or three dimensions. Careful consideration of the properties of these components permits rational and systematic synthesis of compounds with known and expected properties.²

This project focuses on the synthesis, structural and magnetic characterisation of three different groups of 2-D CPs; a ferromagnetic copper compound prepared *via* a modified Solvay process,³ a series of multifunctional lanthanide CPs illustrating the effect of solvent, and a series of hexagonal oxalate layers where very subtle changes to the structure result in marked changes to the magnetic properties. Each of these groups of compounds illustrates the combination of structural design of two-dimensional coordination polymers and molecular magnetic properties.

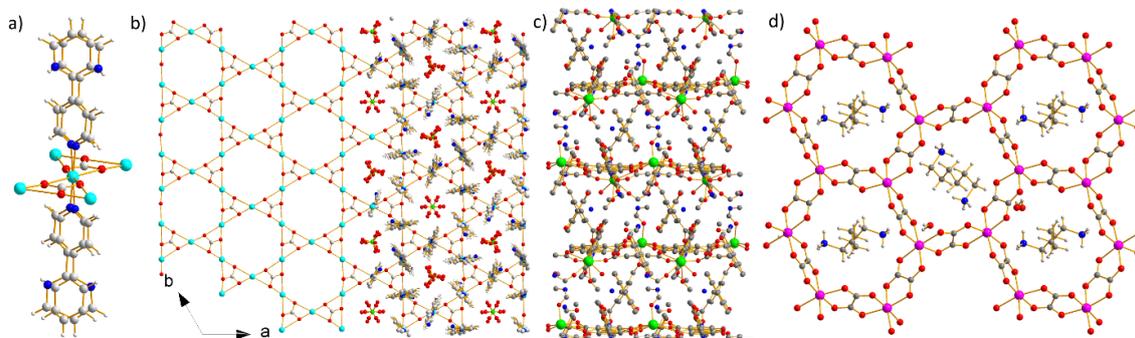


Figure 1. Various layered compounds left-right – (a/b) copper kagome CP, (c) layered europium compound, (d) hexagonal oxalate compound.

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Rotaxanes for Metal-Organic Rotaxane Framework Synthesis

Mark Newman^a

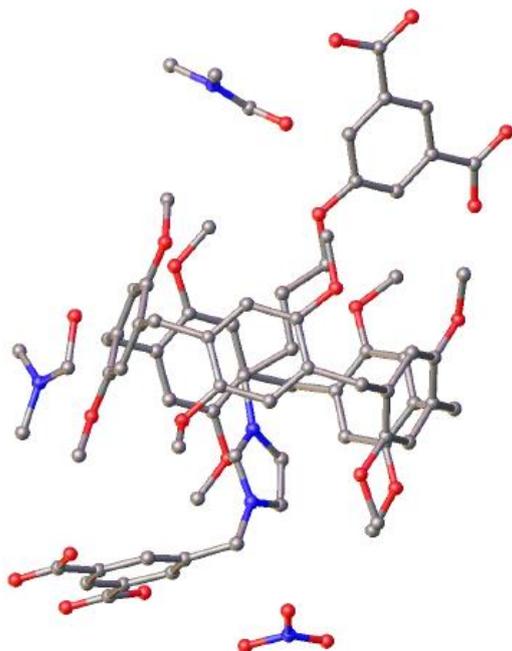
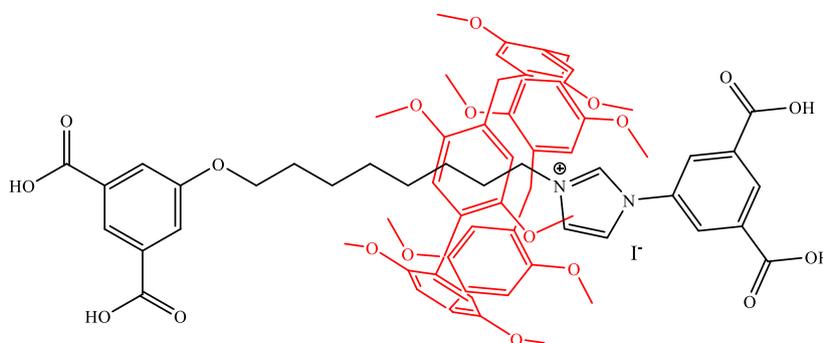
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Metal-organic rotaxane frameworks (MORFs) are porous three-dimensional architectures that contain rotaxane molecules joined together by metal centres, sometimes with the addition of another spacing ligand. These structures are relatively unexplored with only a handful of examples of these structures existing in literature. The first MORF structure was reported in 2005 by Loeb.[1]

Herein, two rotaxanes are synthesised with structures suitable for potential MORF assembly, the synthesis of which will be detailed. Both of these structures utilise an ‘active templating’[2] approach of rotaxane formation, based on a imidazolium/pillararene interaction[3], to form two different tetra-acid rotaxanes.

The identities of these rotaxanes species have been ascertained by NMR studies and the shielding effects of the pillararene analysed.



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Chemical heat engine drives transport of a $\text{Fe}^{\text{II}}_4\text{L}_4$ cage and cargo

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Transport of chemical species against a potential gradient is a fundamental feature of living systems, underpinning processes that range from ATP synthesis to neurotransmission. The development of artificial active cargo transport could enable new modes of chemical purification and pumping. Here we describe a heat engine composed of a functionalised $\text{Fe}^{\text{II}}_4\text{L}_4$ coordination cage, grafted with oligoethylene glycol chains. These chains undergo a conformational change upon heating, causing the cage and its cargo to reversibly transfer between aqueous and organic phases. Furthermore, sectional heating and cooling allow for the cage to traverse multiple phase boundaries, allowing for longer-distance transport than would be possible using a simple pair of phases.

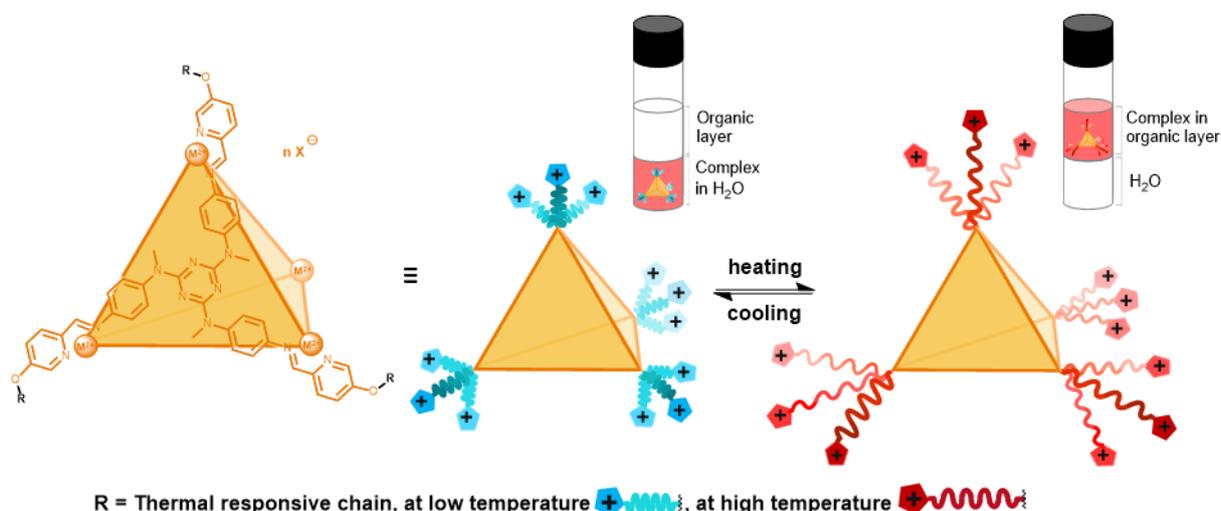


Figure 1. Illustration of the cage undergoing structural transformation with temperature change. At low temperature, the cage is soluble water. At high temperature, the cage transfers from the aqueous to the organic layer.

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Post-synthetically functionalised metal-organic nanosheets: programmable 2D catalysts.

Metal-organic nanosheets (MONs) are an emerging class of 2D materials with expansive surface areas and tunable structures that have already led to their use in a plethora of applications: from catalysis and sensing, to functional devices and composite materials. Work within our group has focused on demonstrating the versatility of MONs as molecular scaffolds upon which different functional groups can be placed to tune their surface properties.¹

In the work to be presented, covalent post-synthetic functionalisation of a layered MOF is demonstrated as a new approach to forming ultrathin MON. An aminoterephthalate framework, partially functionalised with sulfonate chains, was exfoliated to form predominantly monolayer nanosheets. These were demonstrated to be efficient, recyclable catalysts for a two-step, acid-base reaction performed in one-pot. This work demonstrates the potential of MONs to act as molecular scaffolds, upon which multiple catalytically active groups can be deposited, forming greener and more efficient catalytic systems.²

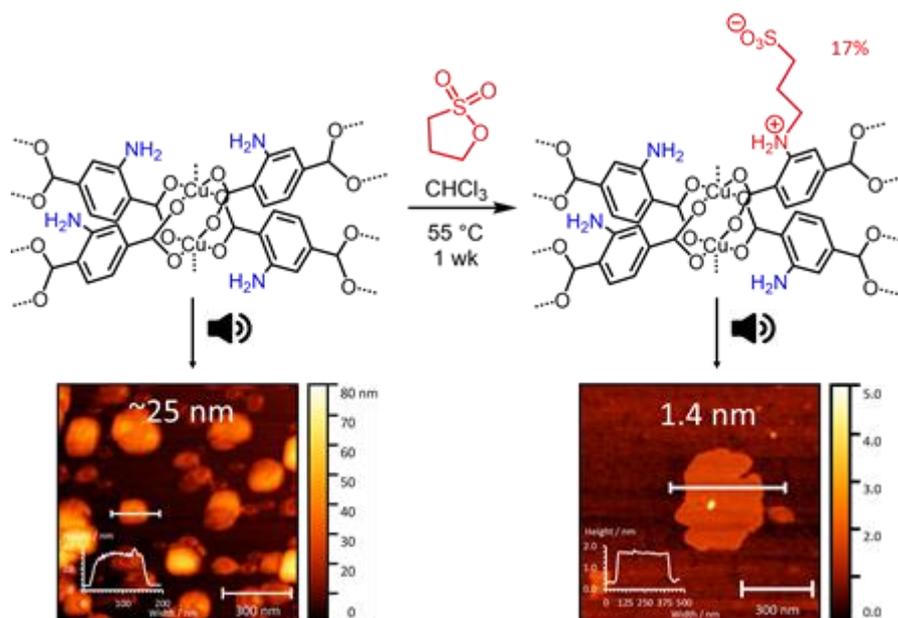


Figure 1. Scheme showing the post-synthetic functionalisation of the aminoterephthalate paddlewheel MOF into the PS-MOF, and subsequent exfoliation of both MOFs into two different MON systems, with differing average thicknesses.

References

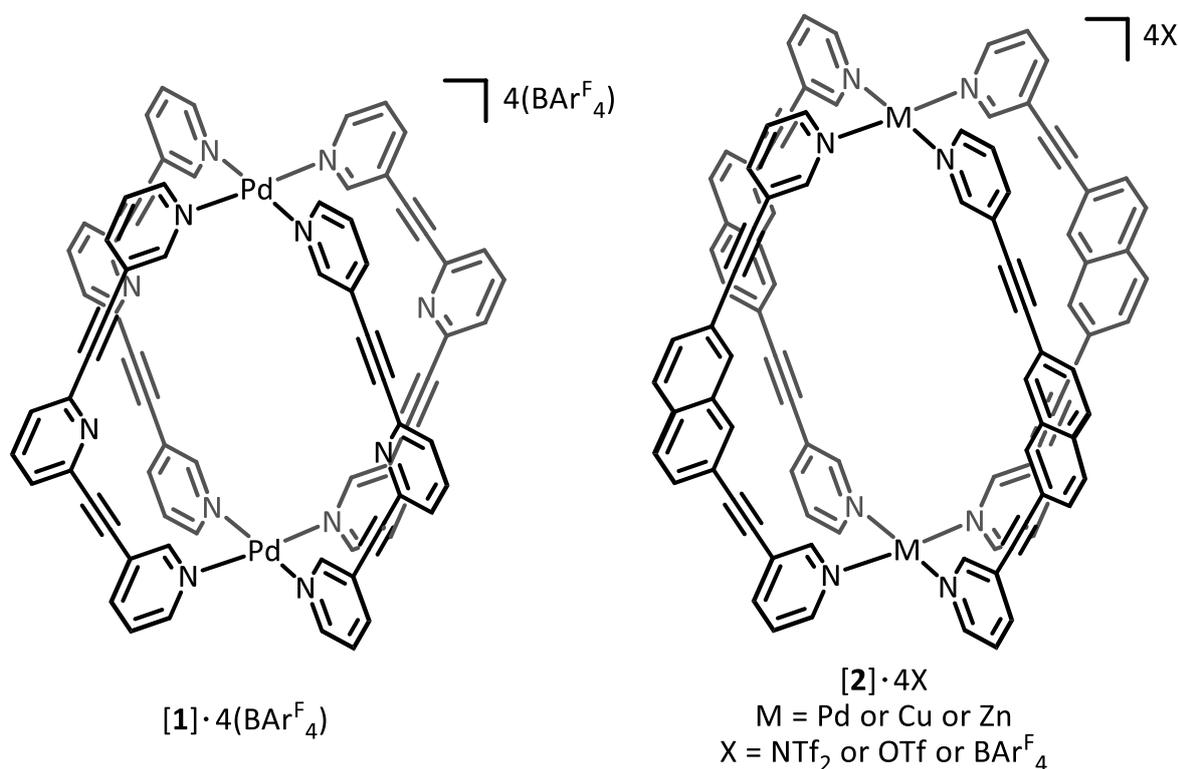
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Naphthalene-based M₂L₄ Coordination Capsules

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The ability of self-assembled capsules to host small molecules has led to their effective use in a variety of areas, including photochemistry, stabilisation of reactive molecules, and catalysis.¹⁻³ Fundamental to this phenomenon is the ability of these capsules to proffer strong enthalpic interactions within the internal cavity, often leading to a profound influence on the electronic properties of guest molecules. We have previously used the Pd₂L₄ capsule **1** in our work to encapsulate *p*-quinone-type guests in apolar solvents, altering their reactivity, and allowing them to undergo [4+2] cycloadditions with no significant problems in product inhibition.³ Herein, we present a new series of M₂L₄ capsules, **2**, which can play host to larger guests than that of **1**. The inclusion of these larger guests should not only allow us to explore different catalytic reactions, but it will also allow us to further probe guest encapsulation in the solid-state, and examine the modulation of magnetic interactions through host-guest interactions.



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RYLENE DIIMIDE-CONTAINING PILLARED PADDLE - WHEEL METAL ORGANIC FRAMEWORKS

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Herein the synthesis and characterisation of two rylene diimides – N,N'-bis(2,6-diisopropyl-4-(pyridine-4-yl)phenyl)-1,4,5,8-naphthalenetetracarboxydiimide (DPPNDI) and N,N'-bis(2,6-diisopropyl-4-(pyridine-4-yl)phenyl)-3,4:9,10-perylenetetracarboxydiimide (DPPPDI) are reported alongside four paddle-wheel open framework materials. Each of the materials contains a redox-active functionalised naphthalenediimide (NDI) or perylenediimide (PDI) – which acts as a pillar – in combination with a carboxylate linker; all of which are coordinated to either a Co²⁺ or Ni²⁺ centre. The MOFs were all made by a straight-forward solvothermal method and characterised using SCXRD, PXRD, and TGA. The frameworks containing DPPNDI are all doubly interpenetrated whereas the one obtained from DPPPDI exhibits four-fold interpenetration. In terms of dimensionality, all the materials are 3-dimensional (3D) and possess the conventional M₂(μ₂-O₂CR)₄ paddle-wheel secondary building unit (SBU). These materials, due to the presence of the redox-active ligands, hold great potential for the entrapment of electron-rich species which can in turn lead to new and exciting chemical properties.

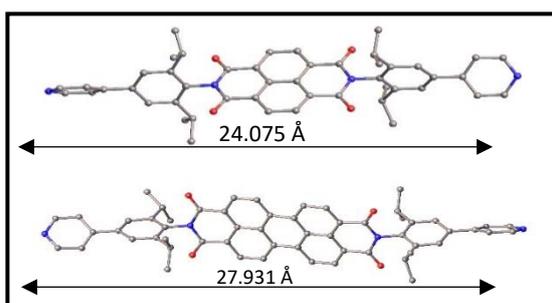


Fig. 1 Crystal structure of the ligands

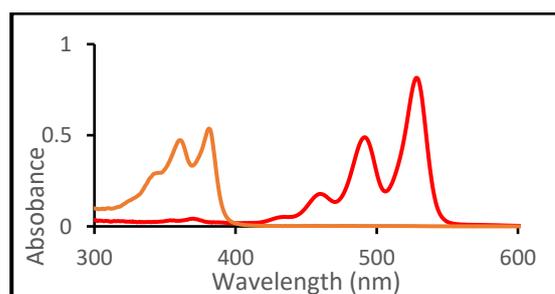


Fig. 2 UV-Vis spectrum of DPPNDI (orange) and DPPPDI (red) in DCM

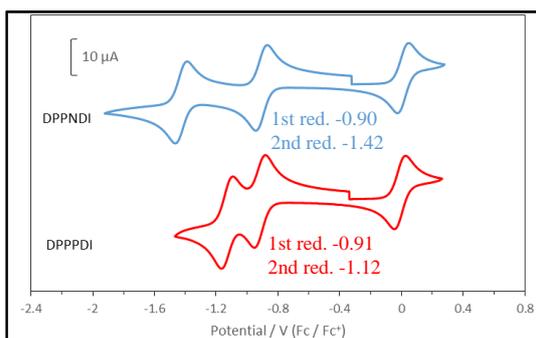


Fig. 3 Electrochemistry – Cyclic Voltammetry

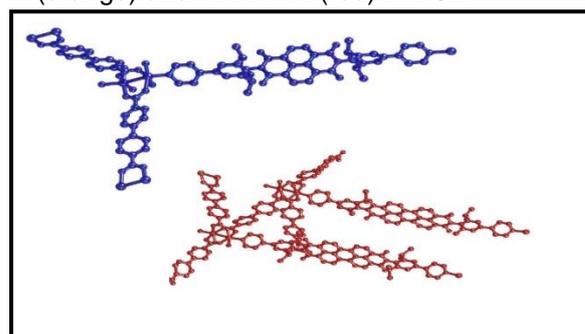


Fig. 4 Crystal structures of the MOFs

Synthesis and Crystallographic Characterisation of Lanthanide Diacylamide Tetracid Metal – Organic Frameworks

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Lanthanide metal – organic frameworks (MOFs) are a rather new class of materials that have emerged in recent decades. Highly connective lanthanides (coordination number up to 9) can generate a wide range of topologies that are not observed in transition metal-based MOFs. With the topological variety and interesting luminescence properties afforded by lanthanides, they have potential for applications in luminescent sensors. The synthesis of Ln-based MOFs is rather complicated, as small changes in reaction conditions can lead towards different phases of desired product. Therefore, a number of architectures can be prepared by varying the synthetic conditions.

Herein, we present a collection of eight different topologies of lanthanide MOFs from one diacylamide tetracid ligand, with 28 architectures in total. A range of lanthanides (La to Lu) has been investigated and modulated solvothermal synthetic methods have been developed to yield a series of topologically similar architectures using different lanthanides. We have investigated various parameters such as temperature, time, solvent systems and modulating agents for the preparation of different Ln-MOF phases. Comprehensive crystallographic analysis showed that synthesised architectures fall in two types of crystal systems – monoclinic and triclinic. Early lanthanides (Ln – Nd) exhibited capabilities of forming porous 2D MOFs. Furthermore, later series of lanthanides (Sm – Lu) yielded 3D porous nets. Additionally, we performed a topological analysis to understand connectivity and tiling in obtained architectures. Overall, the obtained results exhibit the diversity of lanthanides through their preparation of MOFs, as well topologies that can be of interest for research of further applications.

Pillar[5]arene based Molecular Shuttles

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Rotaxanes have been widely employed in the construction of molecular machines, utilising the possibility of relative motion between their axle and macrocyclic components.¹ Pillarenes are a relatively new class of macrocycle and are a highly symmetrical, tubular macrocycle consisting of [n]1,4-dialkoxybenzene (or hydroquinone) units bridged in the para-position by methylene units in the 2 and 5 positions. The electron rich cavity of a pillar[5]arene makes it a compelling candidate for host-guest interactions with electron deficient rod like molecules such as bis(imidazole) alkanes for use in the construction of rotaxanes.²

In this work, two rotaxanes, a [2]rotaxane and a [3]rotaxane have been synthesised, along with its corresponding dumbbell molecule, using pillar[5]arene macrocycles as hosts for the interaction. Under analysis of ¹H NMR, the [2]rotaxane has shown the macrocycle to be barricaded onto one side of the 1,4-dioxybenzene ring along the dumbbell molecule in CDCl₃. Proton NMR in DMSO-d₆ has shown that the macrocycle can bypass the barricade and shuttle freely between both alkyl chain stations. Additionally, the [3]rotaxane pushes the macrocycles close together in DMSO-d₆.

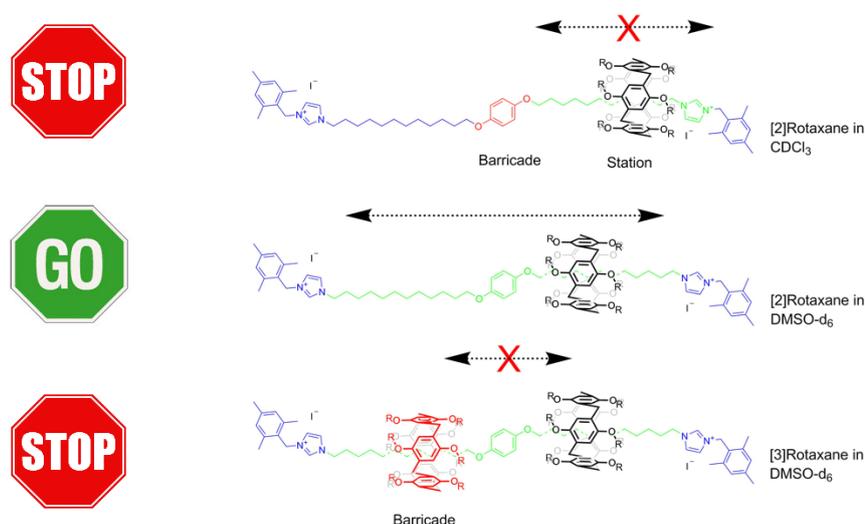


Figure 1. Top, a [2]rotaxane in chloroform, confined to one side of the dumbbell molecule; middle, [2]rotaxane with shuttling ability over the 1,4-dioxybenzene component in DMSO; and bottom, the [3]rotaxane in DMSO where the macrocycles are pushed together.

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Donuts and Holes

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We have developed a robust synthetic approach for the formation of mechanically interlocked molecules that centres around the pillararene:imidazole interaction. Pillararene, a five membered macrocycle (our donut) has an especially strong binding interaction with imidazole,¹ which has been exploited to thread various molecular components through the pillararene cavity.

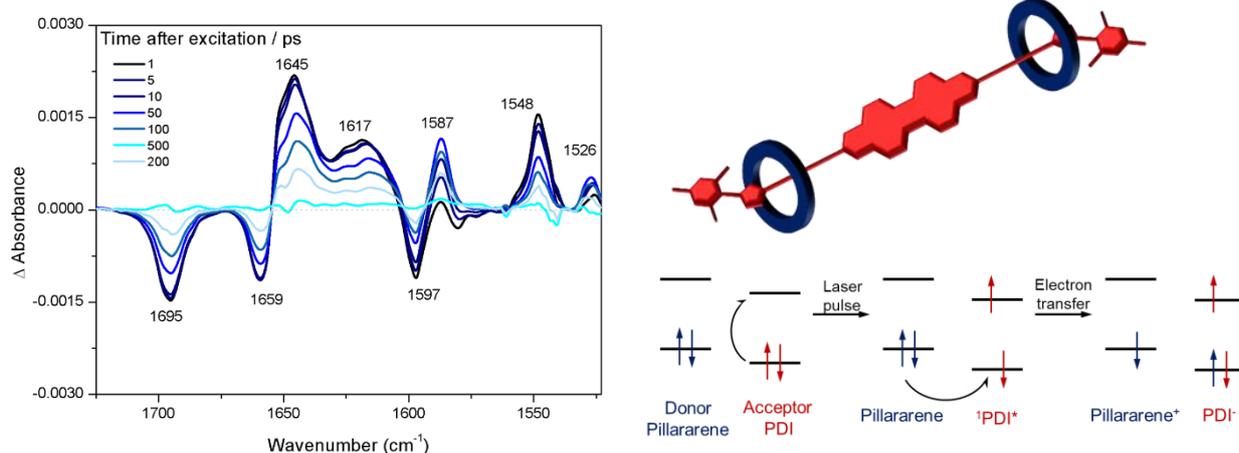


Figure left: Time resolved infra-red spectra of a PDI-(bis)pillar[5]arene [3]-rotaxane following photoexcitation at 532 nm; top right: Schematic representation of a PDI-(bis)pillar[5]arene [3]-rotaxane; bottom right: Proposed mechanism for charge-transfer from the pillar[5]arene 'donut' to the perylene diimide 'hole' in a rotaxane structure.

This research focusses on the synthesis of mechanically interlocked systems in which either the imidazole-component or pillararene-component contains a redox active chromophore. By combining molecular entities in this manner, nonstandard interactions can occur,² with unusual effects on the properties of the system. Electron-acceptors (i.e. the holes) have been utilised in these structures and we have determined through time resolved photoexcitation experiments that the electrons can be passed through space from the pillararene to a perylene diimide electron acceptor, without the need to covalently link these components.

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1,3,4,2-dioxazaboroles in Dynamic Covalent Chemistry: A Novel Boron Heterocycle For Dynamic Assembly.

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Abstract: The reversible condensation reaction between hydroxamic acids (the diol-like conformer of hydroxamic acids) and boronic acids is presented for the first time and results in the formation of a novel boron-containing heterocycle – 1,3,4,2-dioxazaborole. Exploitation of the dynamic character of this new species could lead to potential applications in dynamic self-assembly of macrocycle/cages, covalent organic frameworks, sensors, or even in catalysis, to name just a few potential applications.¹⁻⁶

⁶ The dynamic covalent chemistry of the 1,3,4,2-dioxazaborole group with both boronic acids and hydroxamic acids occurs through both a dissociative (hydration) and concerted mechanism (involving Lewis Acid-Base adduct formation).

Dynamic exchange chemistry associated with Lewis Acid character of the boron to coordinating Lewis Bases, such as 4-(dimethylamino)pyridine and with solvents such as methanol and water, were determined when analysed by mass spectrometry (MS), computational calculations, magnetic resonance spectroscopy (NMR), and single crystal x-ray diffraction. When compared to other boron-containing species which also contain this Lewis Acid character, we've found that the Lewis Acidity of the 1,3,4,2-dioxazaboroles is greatly reduced but also tuneable utilising substitutional groups and would have great potential within sensing applications. Most interesting though, was the isolation of several hydroxamate complexes of 1,3,4,2-dioxazaboroles, giving us a plausible dynamic exchange mechanism between the hydroxamic acid and boronic acid complex, which were confirmed through computational results. Furthermore, we have observed the exchange between different hydroxamic acid groups, in both solution and solid-state reactions (mechanochemistry), monitored by NMR and MS.

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Turning Capsule Catalysis Inside Out

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Self-assembled metallocapsules offer an alternative method to synthesise complex catalysts.¹ Almost all current catalytic approaches utilise substrate encapsulation, wherein the microenvironment influences various factors such as enantio-² and regioselectivity.³ The drawbacks of this approach include narrow substrate scope and the frequent occurrence of product inhibition, which limits genuine catalysis to quite specific reaction types. We have recently shown that a simple Pd₂L₄ system can bind *p*-quinone guests via favourable polar interactions,⁴ and that the bound dienophile is activated for cycloaddition with a range of dienes.⁵

Here we will show how encapsulation chemistry can be used to mimic the way enzymes utilise cofactors to generate active catalysts. Whilst the independent host and guest components are catalytically inactive, we will demonstrate how the combined host-guest complex acts as the catalyst. By altering the properties of the bound guest, we are able to use this modular approach to access different catalyst types.

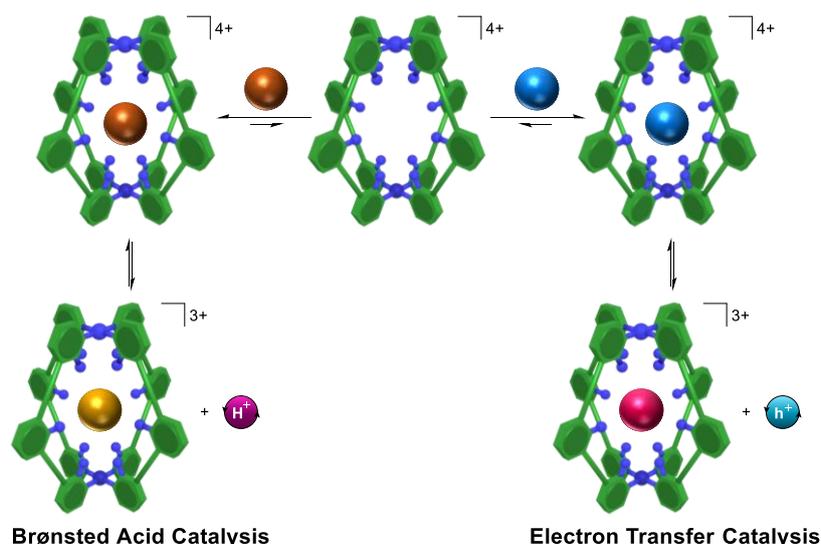


Figure 1. The capsule can be used modularly with varied guests to access different catalytic processes.

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Site-Specific Iron Binding Within a Mixed Oxidation and Spin-State Trigonal Bipyramidal Complex

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Self-assembly is a coordination-driven design strategy used to form three-dimensional metal-organic architectures. Traditionally, symmetric multitopic ligands have been employed to form highly symmetric metal-organic products that can be readily characterised spectroscopically.¹ In contrast, the synthesis and self-assembly of heterotopic ligands with metal salts has been sparsely explored. These synthetically more challenging ligands could however lead to the construction of more elaborate architectures with a wider range of applications.²

Pyridyl benzoimidazole and pyridyl aldehyde motifs are commonly incorporated in symmetric homotopic ligands employed in self-assembly reactions. Here we report the design and synthesis of an asymmetric heteroditopic ligand (**L**) incorporating both motifs. In combination with tritopic linker TREN and $\text{Fe}(\text{BF}_4)_2$, ligand **L** forms the trigonal bipyramidal complex $[\text{Fe}_6\text{L}_6\text{F}_6\text{T}_2](\text{BF}_4)_7$. This architecture displays unprecedented site-specific binding of iron in three distinctly different electronic configurations and incorporates a unique $[\text{Fe}^{\text{III}}(\mu\text{-F})_6(\text{Fe}^{\text{II}})_3]^{3+}$ star motif at its core.

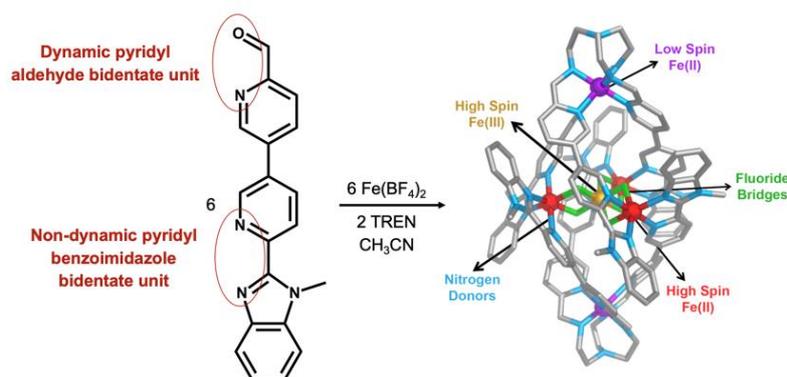


Figure 1. Heteroditopic ligand **L** undergoes self-assembly in the presence of $\text{Fe}(\text{BF}_4)_2$ and TREN to give a C_3 -symmetric trigonal bipyramidal architecture.

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Probing Through-Space Effects in the Aggregation-Induced Emission of Molecular Rotors

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The photoluminescence of phenyl-ring molecular rotors bearing seven phenyl groups are reported to originate, not from the localised excited state as one might expect, but from unanticipated through-space aromatic-dimer states.¹ These relaxed dimer states can form as a result of intra- or intermolecular interactions in both solution and solid samples. Here, we report a series of minimal configurational changes to heptaphenyl molecular rotors in order to enhance and suppress the observed through-space emission. The selective formation of a single C-C bond between neighbouring phenyl groups gives two new molecular rotors (a symmetric and asymmetric isomer) with enhanced emissive states. Alternatively, a simple one-step epoxidation suppresses the through-space emission, vastly altering the observed fluorescence. We demonstrate the power of epoxidation in dictating the photoluminescent properties through the addition of a single atom. Herein we report the sensitivity of conformational modification in the tuning of photoluminescence.

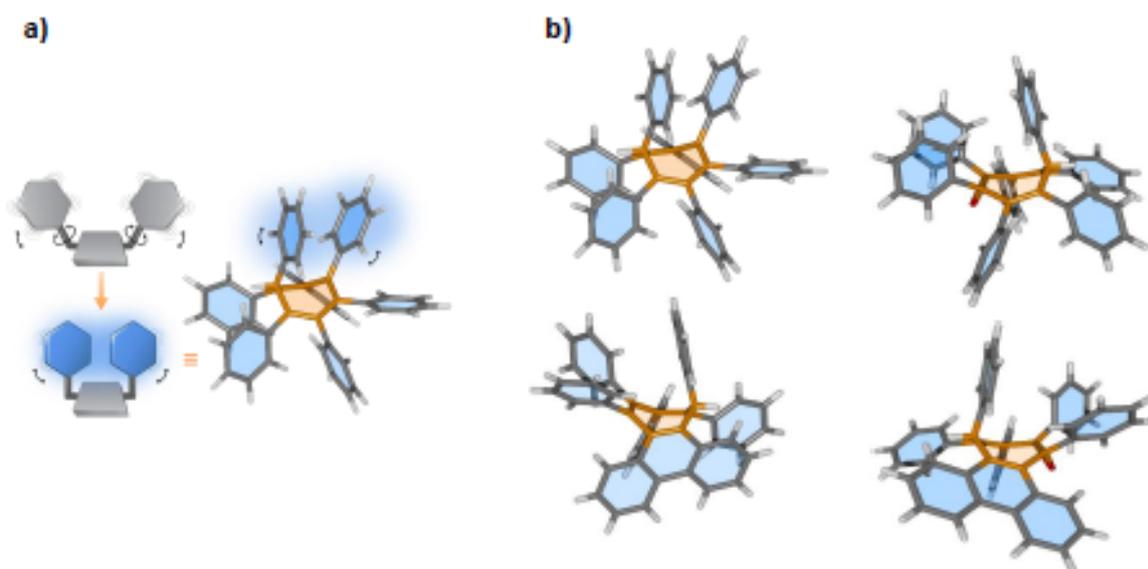


Figure 1. (a) Through-space aromatic interactions in the excited state alter the conformation and fluorescence properties of cycloheptatriene rotors. (b) X-ray structures show that small structural changes alter the relative orientations of the aromatic groups and the degree of conjugation.

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From molecular self-association to a novel class of antimicrobial

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Abstract: Since the 1980's the development of novel antibiotics has dramatically reduced. This, combined with the ever-increasing prevalence of antibiotic resistance in bacteria, means that some bacterial strains have now been identified that are resistant to treatment with all known classes of antibiotic currently available. Therefore, the development of novel antibacterial agents represents one of the most significant challenge facing human-health and well-being today in both developed and developing worlds.

Supramolecular Self-associating Amphiphiles (SSAs)¹⁻⁵ (Fig. 1) are a novel class of amphiphilic salts that contain an uneven number of covalently linked hydrogen bond donating and accepting groups, meaning that they are 'frustrated' in nature. The hydrogen-bonded, self-associative properties for members of this class of over 70 compounds synthesised to date have been extensively studied in the gas phase, solution state, solid state and *in silico*. Through these studies we have shown correlations between certain physicochemical properties that maybe predicted by simple, low-level, high-throughput, easily accessible computational modelling. In addition, members from this class of compound have been shown to kill a variety of different bacteria, including those with known antibiotic resistance (e.g. Methicillin Resistant *Staphylococcus aureus* (MRSA)),⁶ and are competitive in activity with commonly prescribed antibiotics.

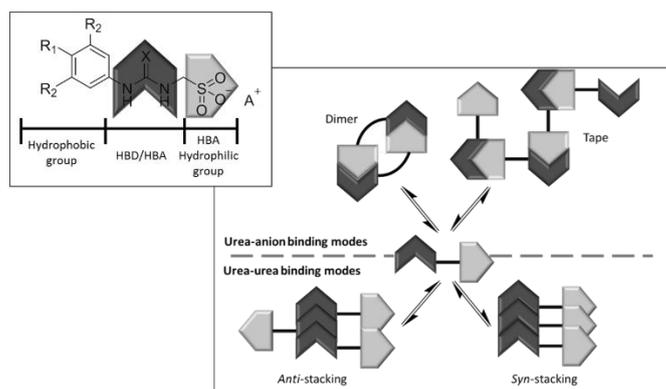


Fig. 1 The possible self-associative binding modes of SSAs.

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Isoindole Diimides: A Tunable Class of Fluorescent Heteroannulated Diimides

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Core-functionalised naphthalene diimides¹ (cNDIs) are one of the most widely investigated classes of π -conjugated organic molecules, finding broad applicability in supramolecular chemistry, chemical sensors, synthetic ion channels, biomedical theranostics, organic semiconductors and electronic/energy devices. The diversity of cNDI molecules is traditionally accessed via 2,7- and 2,3,6,7-halogenated derivatives that can be substituted further by S_NAr chemistry to afford tunable π -electronic-dependent properties (i.e., absorption, emission, and two-electron redox).² Recently, it was shown³ that π -electron deficient NDIs are susceptible to RuO_4 -catalysed oxidation chemistry to furnish a diketone diimide (DKDI) intermediate. This new diketone reactive site has proven useful for generating new aromatic diimides, such as core-heteroannulated isoindole diimides (IDIs; Figure 1). In this work, we set out to establish the scope of RuO_4 -catalysed oxidation to produce DKDIs bearing a range of R-solubilising groups before investigating the X-substituent effect on IDI optical, redox, and self-assembly properties. Notably, DKDIs and IDIs display reversible solution-state redox as three- and two-electron acceptors, respectively. In addition, IDIs are inherently fluorescent, giving off bright emission ($\Phi > 0.85$) under UV light irradiation that can be influenced not only by traditional through-bond effects, but intramolecular (i.e., through-space) π -interactions as well. Similar yet unlike their predecessor cNDIs, the higher functionality offered by more redox-dense DKDIs and fluorescent IDIs presents new opportunities to develop self-assembled molecular, gel and crystalline materials⁴ derived from strong intermolecular π -stacking interactions.

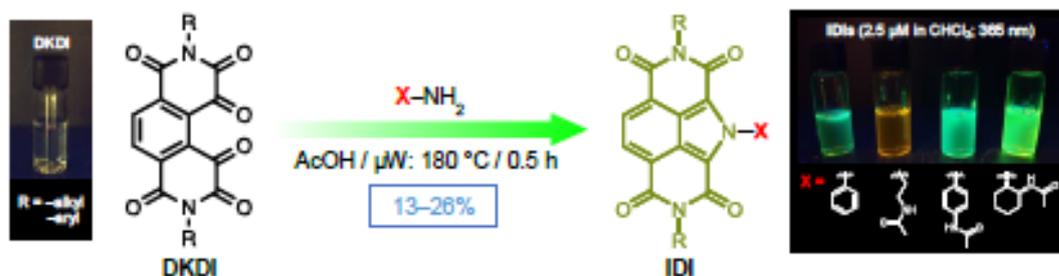


Figure 1. Synthesis of fluorescent IDIs

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Synthesis and Post-Synthetic Modification of Novel Scandium MOFs

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Metal-organic frameworks (MOFs) represent a relatively novel class of crystalline materials, on which a lot of research has focussed on syntheses of systems linked by trivalent metal centres, e.g. Cr(III), Fe(III), Al(III), to create chemically stable structures. However, significantly less work has focussed on the use of Sc(III) in MOFs. Chemical stability allows properties to be tailored using a post-synthetic modification (PSM) method. Since 2009, minimal work has focused on post-synthetic bromination of integral, non-terminal unsaturated carbons and as such scandium systems with extended linkers are investigated for their stability to PSM.^{1,2}

Using 4,4'-ethynylendibenzoate (edb) as a linker, two phases, a triply interpenetrated MIL-88-edb(Sc) topology phase and a doubly interpenetrated MIL-53-edb(Sc) topology phase, have been successfully synthesised under various solvothermal conditions using a coordination modulation approach. Mixed-phase samples of these MOFs have been brominated, using neat bromine and a crystal structure has been obtained for MIL-88-edb-Br₂(Sc). Results have indicated that the MIL-53-edb(Sc) phase is resistant to bromination due to its densely-packed structure.

Another scandium MOF was also produced using the methyl-substituted 4,4'-(1,2-ethynediyl)bis[3-methylbenzoate] as the linker, creating a MOF that structurally flexes depending on the solvent environment in which it resides. Work is being done to fully understand this system and produce single-crystals of this MOF. Using various techniques, results have shown that this MOF has been successfully brominated, however, single-crystal X-Ray diffraction would be a useful technique to view this change. This method of PSM gives rise to additional functional groups on the MOF and could improve the gas uptake properties of modified MOFs.

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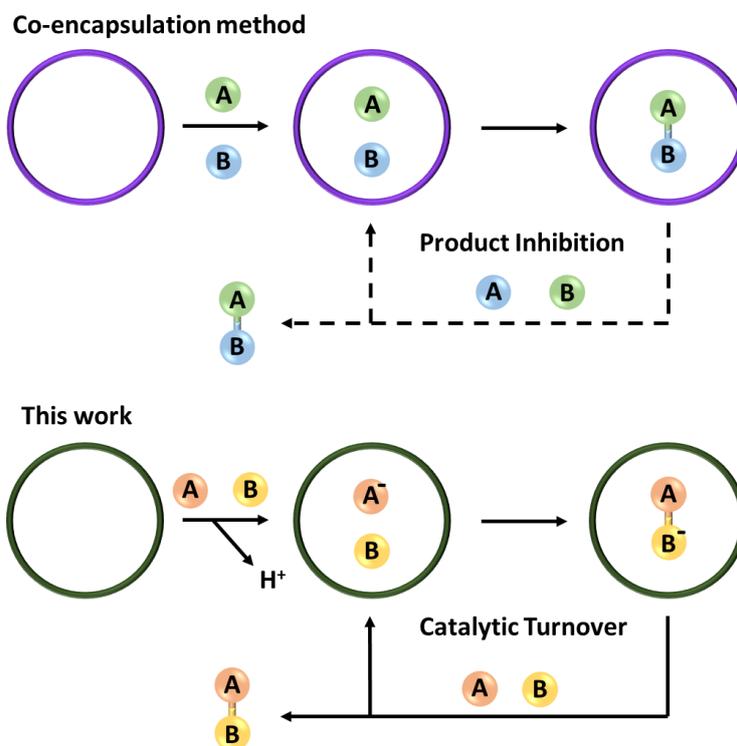
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Using Enthalpy to Avoid Product Inhibition

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Supramolecular capsules have demonstrated the potential to catalyse a wide range of unimolecular reactions^{1,2,3}. Pre-organisation of substrates was also shown to enhance bimolecular fusion reactions. However, this co-encapsulation paradigm often leads to product inhibition^{4,5,6}. This is largely because replacing one strongly binding product molecule with two weakly binding substrates is entropically disfavoured. Here we present a novel method that achieves turnover of a Michaelis complex. This catalytic model utilises enthalpic pathways to overcome previous deficiencies associated with entropic mechanisms.



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The Synthesis, Assembly and Material Properties of Aromatic Cation Liquid Crystals

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Discotic liquid crystals, made of disc-shaped molecules that are able to self-assemble into column structures, are of interest as directional charge transporting functional materials in electronics.¹ These charge transfer properties can be introduced by the addition of ionic species into the liquid crystal molecules, or aromatic regions in the molecular core.² These properties can be combined together by the use of a stable aromatic carbocation as the molecular core of a discotic liquid crystal. By the use of a Friedel–Crafts synthesis with aromatic ether molecules, we are synthesising (Figure 1) cyclopropenium cations bearing pendant oligomethylene chains with the charge distributed across an expanded aromatic core. We synthesised a family of ionic compounds of different lengths and with the positive charges balanced by a range of different counter anions. We are investigating the effect that these changes in the molecular structure have upon the phase behaviour (Figure 2) and electronic properties of these different materials.

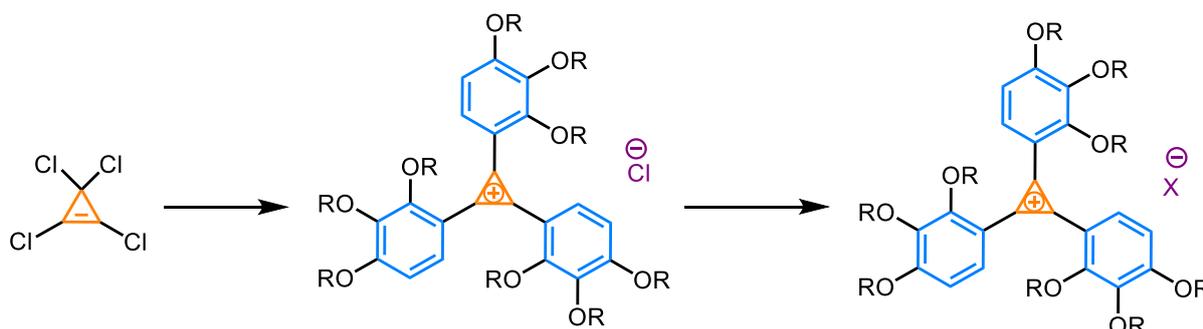


Figure 1: Synthetic overview for liquid crystal cation formation.



Figure 2: Visual microscopy image of synthesised cationic liquid crystal phase.

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