



Program and Book of Abstracts

14th International Seminar on Inclusion
Compounds



Institute of Chemical Sciences, Heriot-Watt
University, Riccarton, Edinburgh, UK

August 18-23, 2013

www.isic14.eps.hw.ac.uk

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Message from the Chairman of the Organising Committee



On behalf of the Organising Committee I would like to welcome all our delegates to Heriot-Watt University. Thank you for agreeing to participate in the 14th International Seminar on Inclusion Compounds. We have put together a stimulating scientific program and have also attempted to include generous amounts of free time to encourage delegates to socialise and discuss science in many different ways. We have also arranged a whisky tour and private tasting to either enhance the knowledge of those already familiar with it, or to offer a perfect introduction to our national drink. We encourage you to explore and enjoy the famous Edinburgh Festival that takes place at hundreds of venues across the city. Should you require assistance at any point feel free to call on us without hesitation. Finally, we hope you will have a successful week of conferencing, and also that you have an enjoyable time exploring the many features that Edinburgh has to offer.

Scott Dalgarno
ISIC14 Chairman

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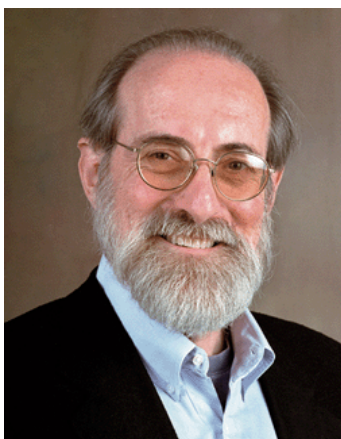
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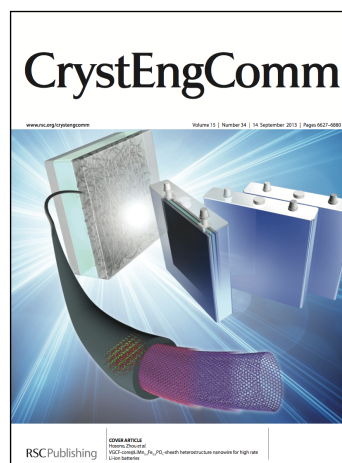
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Prof. Jerry L. Atwood

Gifts

Poster and flash poster prizes have been generously provided by:



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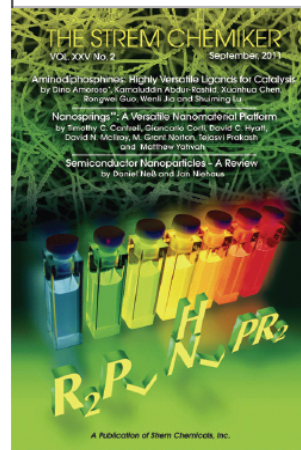
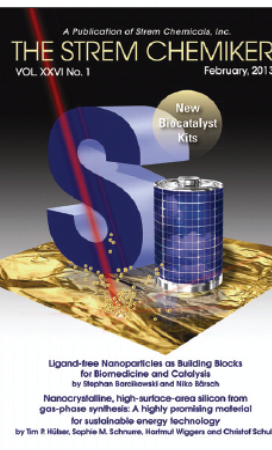
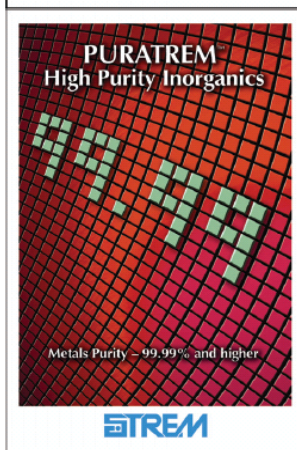
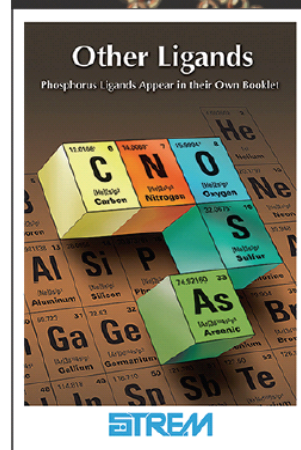
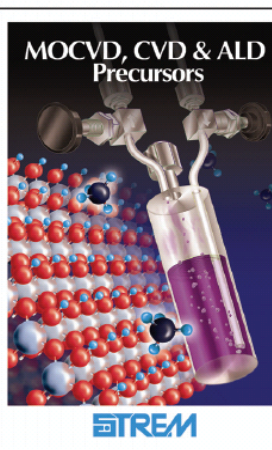
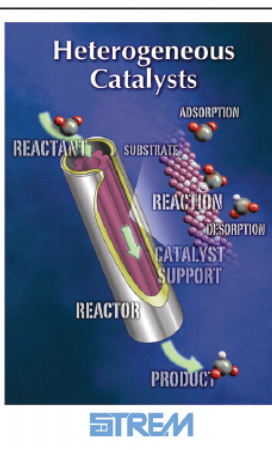
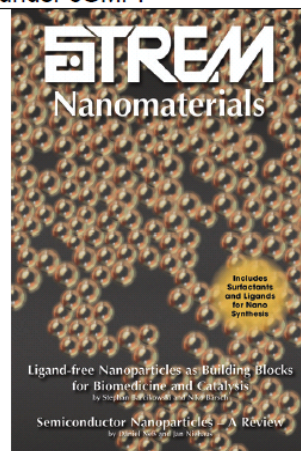
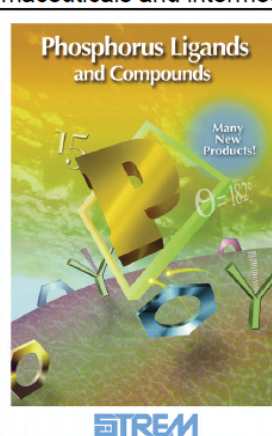
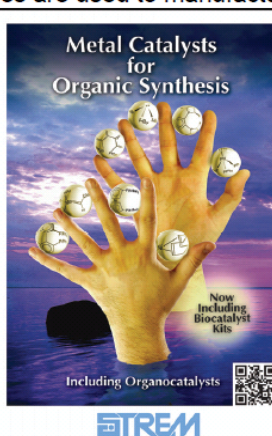
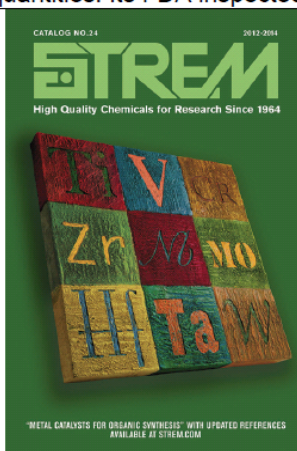


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GPE Scientific Ltd will be exhibiting in atrium on the 18th July 2013 from 10am.

GPE will be showcasing a range of products from the following brands:

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Local Organising Committee

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International Advisory Board

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Travis Holman (USA)	Mike Zaworotko (USA)

General Information

Arrival to Heriot-Watt University / Accommodation

Please proceed to main reception of the University to check-in for your accommodation (3pm onwards) and to obtain your room key. If you are driving into HWU you can leave your car at the main reception for a few minutes before moving to a nearby car park (see maps).

Arrival to Edinburgh by Air

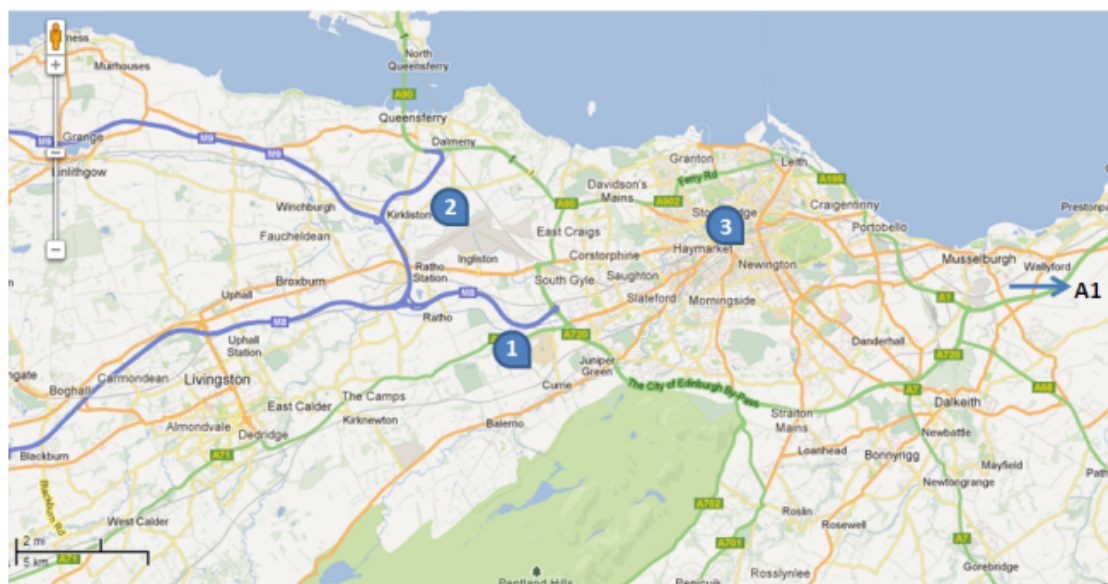
Heriot-Watt University (1) is located on the periphery of the city (around 5 miles from Edinburgh International Airport, airport code EDI, 2) both of which have excellent transport links to the centre (3, around 6 miles). HWU can be reached by a short taxi ride from EDI if you are staying on campus, or frequent Airlink buses run to the city centre. A combination of buses (35 or Airlink followed by a 25 or 34) offers a cheaper alternative by changing at the appropriate route point (if in doubt ask the driver). **Note:** no change will be given on buses (Lothian Buses and Airlink charge 1.40 and 3.50 GBP single fare respectively). Hire cars can be sourced through Edinburgh International Airport.

Arrival to Edinburgh by Rail

Visitors are advised to travel to Edinburgh Haymarket and take either a taxi or a 25 bus to HWU. Those arriving into Waverley can take a 25 or 34 from Princes Street.

Arrival to Edinburgh / HWU by Car

HWU is accessible via the M8 from Glasgow or the A1 via the A720 ring road (see map below). Parking for visitors is located in car parks A, B and C on the detailed HWU campus map. The postcode is EH14 4AS for use with satellite navigation.



1: Heriot-Watt University

2: Edinburgh International Airport

3: Edinburgh City Centre

Travelling to and from HWU During the Conference

Bus tickets will be provided to delegates and depending on where you stay (if not on campus) a variety of routes can be taken to and from the city centre. Bus routes 25, 34 and 45 run frequently and night buses also run after normal routes terminate in the late evening. Bus timetables will also be provided to each delegate upon registration.

Taxis (black cabs) to HWU from the city centre will cost around 15 - 20 GBP each way and can accommodate up to five people at a time. These may be difficult to find at times during the Festival but can just be flagged down.

Registration and Information Desk

Registration will be open from 15:00 – 18:00 on Sunday afternoon in the Postgraduate Centre located at Gait 2 (see map on next page). If you arrive later on Sunday or from Monday morning onwards please see one of the HWU organisers to obtain your conference bag and complete registration. If you require a certificate of attendance please inform us during registration. A welcome function will take place from 19:00 – 22:00 on Sunday, details of which can be found below.

The PG Centre is most easily located via an external route in the following way:

1. Walk down from reception across the bridge link to Hugh Nisbet Building.
2. Go down the stairs and go along the Hugh Nisbet Building until you reach Lecture Theatres 1 - 3.
3. Turn right and exit the Hugh Nisbet Building onto the tarmac path.
4. Turn left and proceed down the steps.
5. Turn right and then left under the bridge linking the two buildings nearby in Gait 2.
6. Head down Gait 2 until you reach the Postgraduate Centre at the bottom.



Language

The official language of the congress is English and no translation will be provided.

Internet Access

Internet access will be available in the accommodation and details will be provided by the reception staff. There will be wireless internet access in the conference venue, details of which will follow.

Safety: Edinburgh is generally a very safe city but there will be many visitors for the Fringe and the town will be extremely busy. We would advise caution with valuables (e.g. to avoid pickpockets) when visiting the city centre during the conference. In the unlikely event of an emergency the police / ambulance / fire services can be contacted by dialing 999. The non-emergency police contact number is 101.

Contact Information

If you encounter problems during your stay in Edinburgh, you may contact Scott Dalgarno at +44(0)782 583 5140.

Campus Map

Postgraduate Centre – Building 18, bottom of Gait 2



Venues and Facilities

Oral Presentations

All ***oral presentations*** will convene in the Cairn Auditorium within the Postgraduate Centre (located at the bottom of Gait 2, see Campus Map). The auditorium is fully equipped with all necessary conference facilities. Student technicians will be available to assist speakers in loading their presentations. In order to facilitate smooth operation we encourage all speakers to submit their files well in advance of their designated sessions, and to ensure that their presentations display correctly.



Tea / Coffee Breaks

Refreshments will be served in the foyer of the Postgraduate Centre. Drinks can be purchased at any time from Da Vinci's café located in the PG Centre.

Posters

The poster boards will be placed in the Earl Mountbatten Building in an open area adjacent to the lunch venue (EM 1.82 see below). Please have your posters up by the end of Monday the 19th August at the latest. The posters must be taken down by the end of Wednesday the 21st. Presenters are requested to be present at their posters during the official poster session on Tuesday the 20th August.

Lunch

Lunch will be provided from Monday – Thursday in the same location, room EM 1.82 of the Earl Mountbatten building. The Earl Mountbatten building is located directly across from the PG Centre. To reach the lunch venue please:

1. Exit the PG centre via the rotating door.
2. Cross the road and head through the quad to the door underneath the red metal-roofed entrance.
3. Go through the doors, up the stairs and then through the doors to reach the Earl Mountbatten crush area (poster venue).
4. Turn right and enter room EM 1.82.

Social Program

Welcome Function

The welcome reception will take place from 19:00 – 22:00 in room EM 1.82 of the Earl Mountbatten Building (Building 21 on Campus Map). As it is a Sunday evening we have arranged for buildings to be left open to provide access via an **internal route only**. To reach the EM building please:

7. Walk down from reception across the bridge link to Hugh Nisbet Building.
8. Go down the stairs and all the way along the Hugh Nisbet Building, passing Lecture Theatres 1, 2 and 3 before reaching a crossroad point. This crossroad links the Hugh Nisbet, Scott Russell, James Naysmith and David Brewster Buildings.
9. Turn right and proceed through the David Brewster Building.
10. Continue along this corridor and pass into the William Perkin Building.
11. Go along to the end of the William Perkin spine and turn left into the William Perkin spur.
12. Continue all the way along past the laboratories, go down one half-flight of stairs and enter the Earl Mountbatten building.
13. Go along until you reach the open area with poster boards.

Signs will be placed along the route but we would encourage you to have a walk around following registration to familiarise yourselves with the campus.

Tuesday 20th August

Poster Session – to take place in the Earl Mountbatten crush area (adjacent to EM 1.82 [lunch / welcome function venue]) from 14:00 – 16:00. Poster presenters are requested to be at their posters during this time. *Chemical Communications* and *CrystEngComm* have generously donated poster and flash poster prizes respectively.

Wednesday 21st August

The conference excursion is a trip to the Scotch Whisky Experience located close to Edinburgh Castle. The event will last approximately three hours and will involve a tour and private tasting experience with an expert to explain the many interesting features of our national drink. More information can be found at the following web address:

www.scotchwhiskyexperience.co.uk

A bus will be departing after lunch, and more information will be provided on location of departure during the conference.

Thursday 22nd August

The conference dinner will be held at Pollock Halls located reasonably near the city centre. Reception drinks will begin at 19:00 and a bus (for those staying on campus) will be departing at approximately 18:15, but more information will be provided on location of departure during the conference.

Sunday 18 th August	
15:00 – 18:00	Registration at HWU Postgraduate Centre
19:00 – 22:00	Welcome function at Earl Mountbatten Building
Monday 19 th August (FULL DAY)	
08:50 – 09:00	Opening Remarks
Session 1	Chair: Len Barbour
09:00 – 09:45	Jerry Atwood <i>CrystEngComm</i> Lecture, Title: TBC
09:45 – 10:15	Tomislav Friščić Title: Focusing on self-assembly: minimising the input of energy and solvent in the synthesis of metal-organic architectures
10:15 – 10:35	Jonathan Foster Title: Electroluminescence and heat-set gelation in a series of dynamic-covalent metallo-polymers
10:35 – 11:05	Coffee Break
Session 2	Chair: Tomislav Friščić
11:05 – 11:50	Paul Raithby Title: Assembling and manipulating molecules to generate materials with targeted properties
11:50 – 12:20	Graeme Day Title: Global lattice energy exploration for predicting porosity and inclusion behavior in organic molecular crystals
12:20 – 12:40	Therese Bergendahl Title: A computational study of macrocycles and their excited states
12:40 – 13:30	Lunch
Session 3	Chair: Paul Raithby
13:30 – 14:15	Bruno Therrien Title: Transporting and shielding photosensitizers using organometallic cages: A new strategy in drug delivery and photodynamic therapy
14:15 – 14:45	Leigh Jones Title: The Super Bowl: <i>Pseudo</i> metallocalix[6]arene heptanuclear solid state host-guest materials
14:45 – 15:05	Ross McLellan Title: TBC[4] bound Mn ^{III} : A versatile building block in the construction of polynuclear 3d and 3d-4f cluster systems
15:05 – 15:35	Coffee Break
Session 4	Chair: Travis Holman
15:35 – 16:20	Alan Rowan Title: Catalysis and motion. Threading of nanocages onto polymer threads
16:20 – 16:50	Gareth Cave Title: Encapsulating nano-rust: From therapeutic vectors to potatoes...
16:50 – 17:10	Marcus Winter Title: Advances in X-ray crystallography
Free time	

Tuesday 20 th August (HALF DAY)	
Session 1	Chair: Enrico Dalcanale
09:00 – 09:45	Javier de Mendoza Title: Hydrogen-bonded and metal-induced self-assembled capsules from calixarenes
09:45 – 10:15	Vladislav Komarov Title: Polymorphism of ionic clathrate hydrates
10:15 – 10:35	Paul Raithby (DAESTP) Title: Assembling and manipulating molecules to generate materials with targeted properties
10:35 – 11:00	Flash Poster Presentations Paul Symmers Title: Spin-crossover ‘click’ coordination capsules Krishna Damodaran Title: Supramolecular gels: Versatile growth media for pharmaceutical polymorphs Robyn Fairbairn Title: Oxacalix[4]arenes as metal cluster supports Tiia-Riika Tero Title: Unusual benzofuran resorcinarene - Structural and spectroscopic properties
11:00 – 11:35	Coffee Break
Session 2	Chair: Guido Clever
11:35 – 12:20	David Leigh Title: Making the tiniest machines
12:20 – 12:50	Willem Verboom Title: Design and evaluation of novel ligands for nuclear waste treatment
12:50 – 13:15	Flash Poster Presentations James Henkelis Title: Supramolecular architectures with CTVs: Cryptophanes, catenanes and coordination cages Rachael Lee Title: Structure of supramolecular solids under high pressure Himanshu Aggarwal Title: Role of single crystal to single crystal transformations in crystal engineering Christopher Wood Title: A tridentate ligand for the synthesis of diverse metal-organic structures Muxin Han Title: Functional coordination cages: Shape control and light-switchable guest binding
13:15 – 14:00	Buffet Lunch
14:00 – 16:00	Poster Session
Free time	

Wednesday 21st August (HALF DAY)	
Session 1	Chair: Mike Ward
09:00 – 09:45	Guido Clever Title: Control over cavity size and shape in self-assembled coordination cages
09:45 – 10:15	Travis Holman Title: Highly selective capture and extreme confinement of gases
10:15 – 10:35	Magdalena Ceborska Title: Native and modified cyclodextrins as molecular receptors for folic acid
10:35 – 11:05	Coffee Break
Session 2	Chair: Bruno Therrien
11:05 – 11:50	Enrico Dalcanale Title: Solid state molecular recognition for supramolecular sensing
11:50 – 12:35	Wais Hosseini Title: Molecular turnstiles
12:35 – 13:30	Lunch
13:30	Bus to Excursion Venue
14:00 – 17:00	Excursion (Whisky Experience Tour & Tasting)

Thursday 22nd August (FULL DAY)	
Session 1	Chair: Wais Hosseini
09:00 – 09:45	Andrew Cooper Title: Functional organic solids – design or discovery?
09:45 – 10:05	Clement Schouwey Title: Large imine-based cages: synthesis via orthogonal self-assembly and use as receptors for alkali metal ions
10:05 – 10:25	Piotr Cholewa Title: Metal-directed assembly of coordination polymers and molecular capsules
10:25 – 11:00	Coffee Break
Session 2	Chair: Graeme Day
11:00 – 11:45	Anthony Davis Title: Synthetic lectins: Progress in biomimetic carbohydrate recognition
11:45 – 12:05	Oleg Chepelin Title: Photoactive iridium-based supramolecular capsules
12:05 – 12:25	Oksana Danylyuk Title: Supramolecular host-guest assemblies of cucurbituril: Kinetic trapping and phase transformations
12:25 – 13:30	Lunch

Session 3	Chair: Javier de Mendoza
13:30 – 14:15	Jonathan Steed Title: Supramolecular gels: Orthogonal self-assembly far from equilibrium
14:15 – 14:45	Maija Nissinen Title: Resorcinarene crowns: double functionalized supramolecular receptors
14:45 – 15:05	Aleksander Shkurenko Title: Self-assembly of selected (pseudo-)amphiphilic calix[4]arenes in solid state – X-ray diffraction studies
15:05 – 15:35	Coffee Break

Session 4	Chair: Anthony Davis
15:35 – 16:20	Len Barbour Title: Porosity in flexible metal-organic systems
16:20 – 16:45	Janusz Lipkowski Title: Pseudopolymorphism in cyclodextrin solvates
16:45 – 17:05	Barbara Leśniewska Title: Structural characterization of inclusion complexes of <i>para</i> -sulfonatocalixarenes
18:00 – 18:15	Bus Departure to Conference Dinner
19:00 – 23:00	Conference Dinner

Friday 23 rd August (HALF DAY)	
Session 1	Chair: Leigh Jones
09:00 – 09:45	Mike Ward Title: Host-guest chemistry in a coordination cage: dissection of hydrogen-bonding, van der Waals' and solvophobic contributions to guest binding
09:45 – 10:15	Kinga Suwinska Title: Self assemblies in calixarene inclusion compounds
10:15 – 10:35	Harshita Kumari Title: Investigating solution properties of supramolecular nanoassemblies
10:35 – 11:05	Coffee Break
Session 2	Chair: Jonathan Steed
11:05 – 11:50	Michaele Hardie Title: Metallo-cages and metallo-supramolecular assemblies for guest binding
11:50 – 12:20	Gareth Lloyd Title: Inclusion and structure: Property characteristics of small molecule supramolecular gels
12:20 – 13:05	Mohamed Eddaoudi Title: TBC
13:05 – 13:20	Closing Remarks

How Solid is the Organic Solid State?

Jerry L. Atwood

University of Missouri-Columbia USAatwoodj@missouri.edu

More than 900 papers have been published on p-tert-butylcalix[4]arene. More than a decade ago, we discovered that this well-known macrocycle undergoes single-crystal-to-single crystal phase transitions upon guest uptake and release. The calixarene does not possess pores or channels in the solid state. However, despite a lack of porosity of the material, guest transport through the solid occurs readily until a thermodynamically stable structure is achieved. In order to actively facilitate this dynamic process, the host molecules undergo significant positional and/or orientational rearrangement. This transformation of the host lattice is triggered by weak van der Waals interaction between the molecular components. In order for the material to maintain its macroscopic integrity, extensive cooperativity must exist between molecules throughout the crystal, such that rearrangement can occur in a well-orchestrated fashion. Implications of this discovery for gas separation and gas storage have been developed. Several new, non-porous organic solids have also been found to exhibit remarkable sorption behavior. This has led us to the so-called 'frustrated organic solids'. Now, we have discovered solid-state transformations that surmount seemingly enormous energy barriers, moving away from thermodynamic structures. In related work, gas-induced solid-state transformations of the well-known pharmaceuticals clarithromycin and lansoprazole have been discovered. For clarithromycin, gas pressure stimulus is capable of converting the kinetic solvate and guest-free crystal forms to the commercial thermodynamically stable polymorph with a huge saving in energy cost relative to industrially employed methods. The synthesis of the marketing form of lansoprazole involves a solvate that readily decomposes and that is stirred in water, filtered, and dried intensively. Our method readily circumvents such synthetic problems and transforms the sensitive solvate to the marketed drug substance with ease. Such expedient transformations hold great implications for the pharmaceutical industry in general when considering the ease of transformation and mild conditions employed. The discussion began with the question "How solid is the organic solidstate?" and will end with the question "How solid is the organic solid state?"

Assembling and Manipulating Molecules to generate Materials with Targeted Properties

Paul R. Raithby, Mathew Bryant, Lauren E. Hatcher, Thomas P. Robinson

University of Bath, Department of Chemistry, Bath BA2 7AY, UK; e-mail p.r.raithby@bath.ac.uk

Material properties change and evolve with increasing length scales, and the solid-state offers a unique environment to control these properties as molecules are assembled into nanoscale, meso- and macroscopic particles [1]. An obvious target property is that of colour, and this can be modified at the molecular or supramolecular level within a crystalline solid by introducing a second component, such as a solvent or gas molecule, to the crystalline form, where the colour change is the result of a structural rearrangement within the ordered crystal. A second property that can be modified within a crystalline environment is refractive index, where the photoactivation of a moiety within the crystal leads to a geometric change that alters refractive index of the material.

As exemplars of the use of a crystalline environment to generate materials that undergo dynamic structural and property changes we will:

- i. discuss recent studies on platinum pincer complexes that show dramatic colour changes upon the introduction of solvent molecules into crystal lattice
- ii. describe photocrystallographic studies on a series of nickel(II) complexes that contain nitro ligands that undergo reversible linkage isomerism, in the crystalline state, upon photoactivation [2]. The results will be discussed in terms of the “reaction cavity” within the crystal lattice.

These examples can be considered of crystalline systems that contain only two components. A question to pose for the future is what properties and functions could be generated by the controlled assembly of three or more molecular components and how powerful this technique might become?

[1] M. D. Ward and P. R. Raithby, *Chem. Soc. Rev.*, 2013, **42**, 1619.

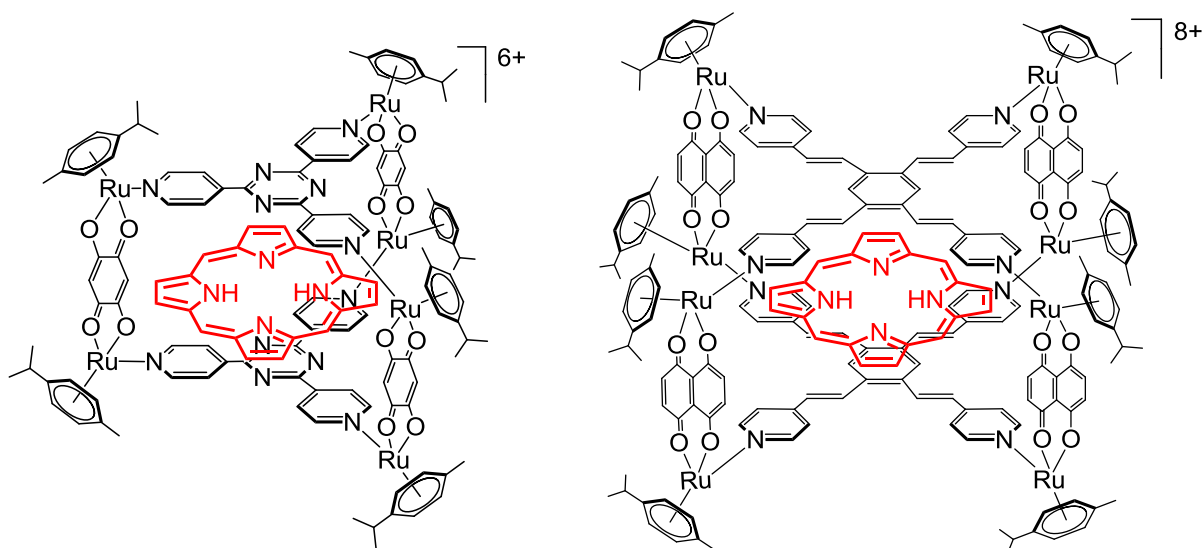
[2] L. E. Hatcher, M. R. Warren, D. R. Allan, S. K. Brayshaw, A. L. Johnson, S. Fuertes, S. Schiffers, A. J. Stevenson, S. J. Teat, C. H. Woodall and P. R. Raithby, *Angew. Chem.-Int. Edit.*, 2011, **50**, 8371.

Transporting and shielding photosensitizers using organometallic cages: A new strategy in drug delivery and photodynamic therapy

Bruno Therrien

University of Neuchâtel, Institute of Chemistry, Ave. de Bellevaux 51, CH-2000 Neuchâtel, Switzerland, email: bruno.therrien@unine.ch

The last decade has seen the field of metalla-assemblies moving towards applications [1]. Not only are we still seeing beautiful new two and three-dimensional assemblies appearing in the literature at regular pace, but nowadays, we are observing as well metalla-assemblies with functions. Indeed, they have been used as micro-reactors, sensors or as molecular flasks [2]. In recent years, another application for metalla-assemblies capable of encapsulating guest molecules has emerged: The ability of water-soluble metalla-cages to act as containers to solubilize and protect guest molecules in biological media [3,4]. This application offers new opportunities in the fascinating field of coordination-driven self-assembly. Our most recent metalla-assemblies incorporating photosensitizers in their cavities will be presented and their biological potential as photodynamic agents will be discussed.



[1] R. Chakrabarty, P.S. Mukherjee, P.J. Stang, *Chem. Rev.*, 2011, **111**, 6810.

[2] H. Amouri, C. Desmarets, J. Moussa, *Chem. Rev.*, 2012, **112**, 2015.

[3] B. Therrien, *Top. Curr. Chem.*, 2012, **319**, 35.

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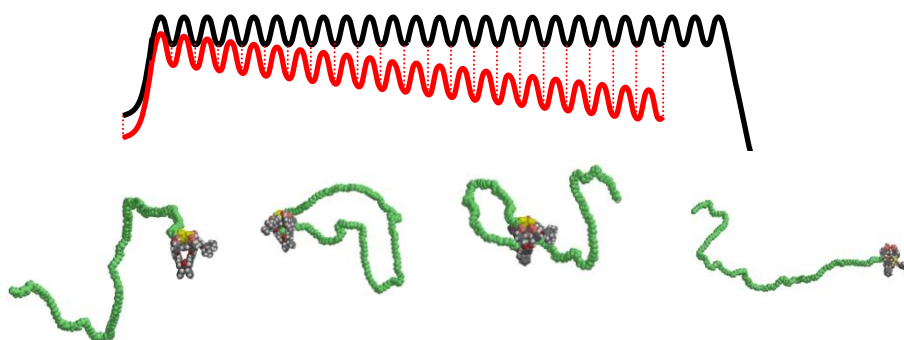
Catalysis and Motion. Threading of Nanocages onto Polymer Threads

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Nature has developed a myriad of approaches for the efficient catalysis of biopolymers, multistep catalysis using capsules and macrocycles. The natural processive enzymes, such as λ -exonuclease or DNA polymerase III, operate by threading a DNA strand in a pseudo-rotaxane topology and subsequently slide along the chain performing several rounds of catalysis before they dissociate.¹ These highly efficient biocatalysts have inspired us to develop the first example of a synthetic processive rotaxane catalyst:² in which a manganese porphyrin-containing macrocycle was threaded onto a polybutadiene strand and catalyzed the epoxidation of the double bonds of the polymer while sliding along its chain.



In order to investigate this threading in more detail a series of mono functionalized polymers were synthesized which contain a blocking N,N'-dialkyl-4,4'-bipyridinium trap at one side of the polymer chain and an open end at the other side.³ Fluorescence emission studies revealed that the kinetics of threading followed a second order process and that the rate of threading was found to be entropically driven⁴ and dependent on the polymer length with a length-dependent barrier of 61 J/nm which increases to 93 J/nm when a larger more flexible macrocycle was used. Intriguingly it was observed that if the polymer has even a slight affinity for the outside of the macrocycle an alternative looping mechanism occurs resulting in enhanced threading rates and a unidirectional motion (see above).⁵ This pseudo rotaxane geometry leads to an increased effective molarity between substrate and catalyst, which allows reactions to take place faster and in some cases leads to new reactions.⁶

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Hydrogen-bonded and Metal-induced Self-assembled Capsules from Calixarenes

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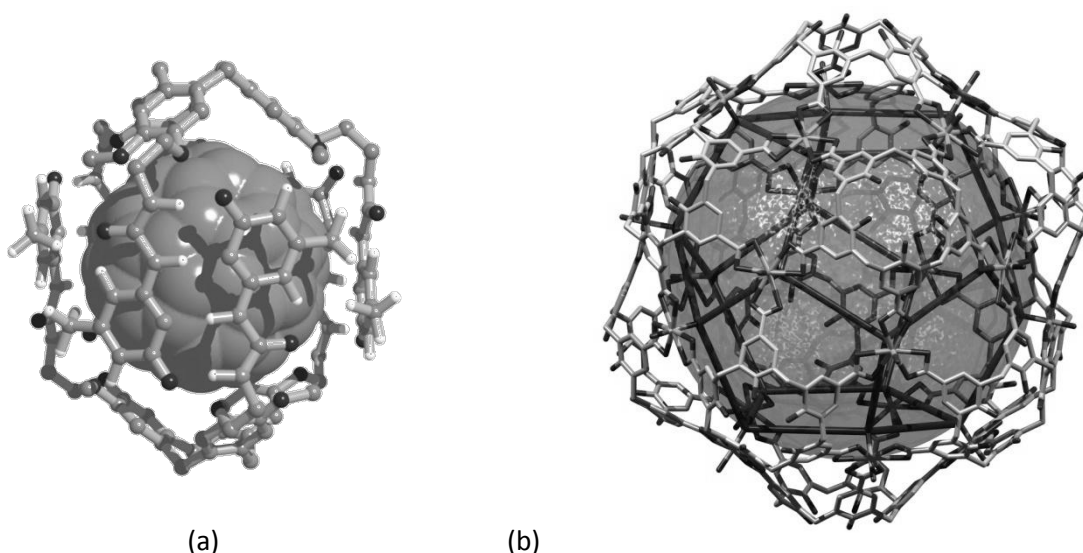


Figure 1. (a) A hydrogen-bonded capsule based on ureidopyrimidinones and cyclotrimeratrylene for fullerenes' separation. (b) A giant capsule from uranyl and calix[5]arene pentacarboxylate.

The bowl shapes of calixarenes and resorcinarenes has been often employed as a building block for self-assembly into capsules and deep cavities. A current strategy is to use multiple hydrogen bond arrays, such as ureidopyrimidinones, to provide directionality and bonding strength. Since addition of an acid or a polar solvent provokes disassembly, these capsules can be applied in separation processes. We will describe examples of fullerene recognition and separation without chromatography (Figure 1a). [1,2]

On the other hand, metals are ideal gluing elements in the design of large capsules, due to the robustness of the assembly and their precise and often unique coordination modes, which combine with suitable ligands in a predictable way. We have recently demonstrated that unique octahedral and icosahedral anionic giant metallocages can be easily assembled from uranyl and calixarene carboxylates with an unusually small number of components. Unlike most metallocages reported to date, the metals in these nanoscopic assemblies are not located at the corners or the edges of the resulting polyhedra but on the faces instead, acting both as a gluing element for the assembly of the components and a functional key substructure (Figure 1b). [3]

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Making the Tiniest Machines

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Over the past few years some of the first examples of synthetic molecular level machines and motors—all be they primitive by biological standards—have been developed [1]. These molecules respond to light, chemical and electrical stimuli, inducing motion of interlocked components held together by hydrogen bonding or other weak molecular interactions.

Perhaps the best way to appreciate the technological potential of controlled molecular-level motion is to recognise that nanomotors and molecular-level machines lie at the heart of every significant biological process. Over billions of years of evolution Nature has not repeatedly chosen this solution for achieving complex task performance without good reason. In stark contrast to biology, none of mankind's fantastic myriad of present day technologies exploit controlled molecular-level motion in any way at all: every catalyst, every material, every polymer, every pharmaceutical, every chemical reagent, all function exclusively through their static or equilibrium dynamic properties. When we learn how to build artificial structures that can control and exploit molecular level motion, and interface their effects directly with other molecular-level substructures and the outside world, it will potentially impact on every aspect of functional molecule and materials design. An improved understanding of physics and biology will surely follow.

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Control over Cavity Size and Shape in Self-Assembled Coordination Cages

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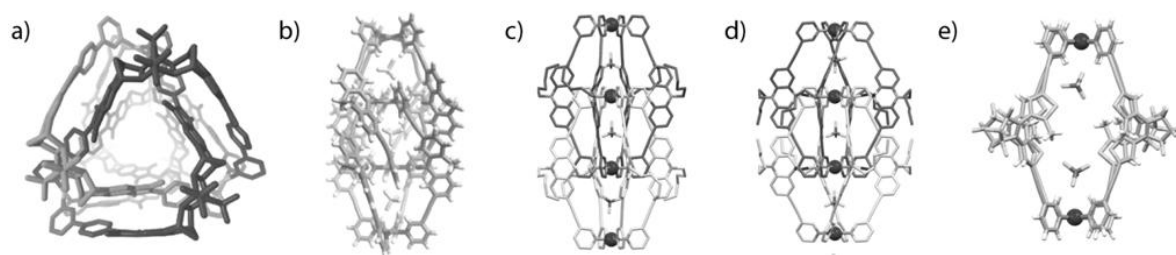
Supramolecular coordination cages are used for the recognition, transport and stabilization of small molecules.^[1] Switchable host-guest systems promise to find application in fields such as uptake & release of molecular cargo, sensing and separation as well as catalysis inside confined molecular environments. Our current research efforts include the realization of non-trivial cage topologies (Figure a)^[2] and the implementation of static and dynamic control over the size and shape of their cavities.

Previously, we have reported a dibenzosuberone-based interpenetrated double-cage [Pd₄Ligand₈] which is capable of allosteric anion binding with a tremendous affinity for the inclusion of two chloride anions in its outer pockets (Figure b).^[3-5]

Based on this work, we could show now, that the interpenetration principle can be extended onto other functional backbones such as the redox active compounds phenothiazine and anthraquinone when certain design requirements are fulfilled. It was found, that both the backbone structure as well as the size of the templating anion inside the central pocket of the interpenetrated double-cages have an effect on the size and hence anion binding capabilities of the outer pockets (Figure c and d).

The solution and solid state structures, the reversible electrochemistry and the electrochemical transformation of these new systems will be reported.

In contrast, we show that a photochromic coordination cage based on dithienylethene (DTE) ligands gives us full dynamic and reversible control over uptake and release of the guest [B₁₂F₁₂]²⁻ by irradiation with UV and white light, respectively (Figure e).^[6]



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Solid state molecular recognition for supramolecular sensing

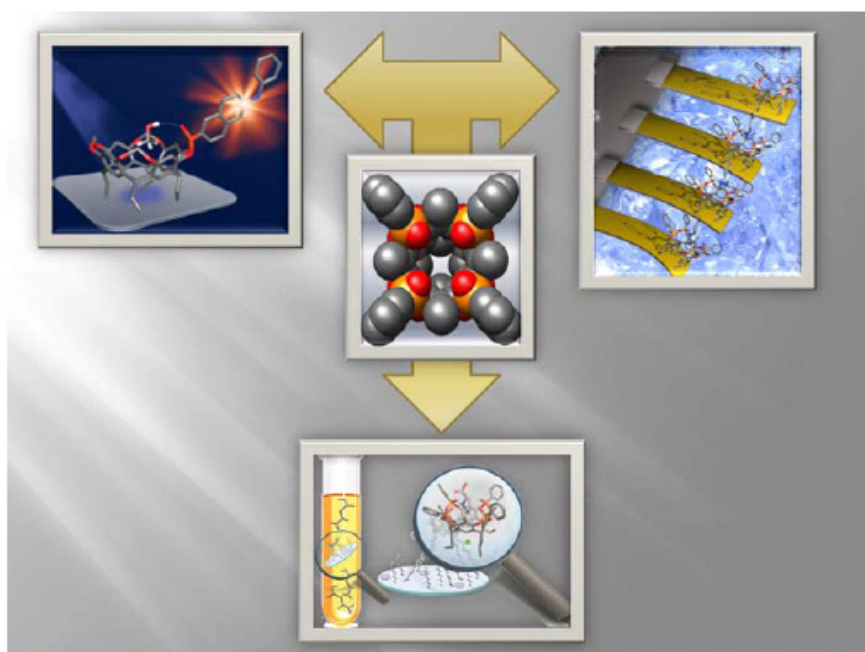
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A chemical sensor is a device that transforms chemical information into an analytical useful signal. Optimal sensors for environmental, security and biomedical applications must be sufficiently responsive to allow detection of the target analyte at low concentrations, and selective enough to respond primarily to a single chemical species in presence of interferents. In this respect, cavitands, synthetic organic compounds with enforced cavities of molecular dimensions,[1] represent a very important class of molecular receptors for chemical and biochemical sensing. When designing a cavitand, the mastering of weak interactions at the molecular level is an essential feature, as well as the choice of the bridging groups which determine shape, dimensions and complexation properties of the resulting cavity. The study of the host-guest complexes at the solid state through X-ray diffractions on single crystals is hence fundamental for understanding and tailoring the weak interactions operating on functional surfaces, which are responsible for the desired functions. Effective strategies for the precise transfer of the intrinsic molecular recognition properties of cavitands from the solid state to solid-gas and solid-liquid interfaces will be presented through the following examples:

- Solid-gas interface: Fluorescent cavitands as selective layers for the specific detection of C₁-C₄ alcohols in the gas phase.[2]
- Solid-liquid interface: Exclusive detection of sarcosine in water and urine with cavitand-functionalized SWCNTs[3] and cavitand-functionalized silicon wafers.[4]
- Solid-liquid interface: Nanomechanical recognition of *N*-methylated derivatives.[5]



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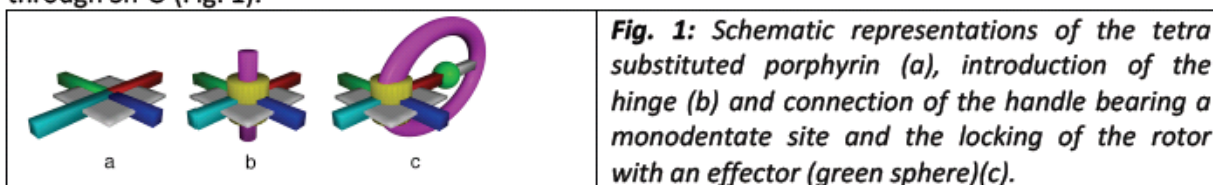
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Molecular Turnstiles

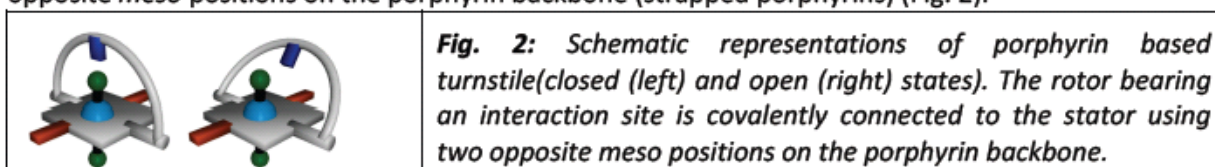
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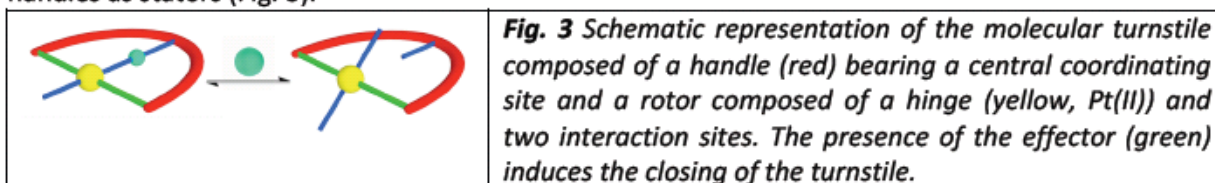
Molecular translational or rotational motors are molecular architecture for which movements between a fixed and a mobile portion may be induced by external stimuli.¹ As a first step towards molecular motors, a series of molecular turnstiles have been designed and synthesized. The first category is based on Sn(IV)porphyrins as stators bearing at the *meso* positions interactions sites and equipped with different handles as rotors. The connection between stators and rotors is achieved through Sn-O (Fig. 1).²⁻⁷



The second design principle is based on the covalent attachment of the rotor to the stator using two opposite *meso* positions on the porphyrin backbone (strapped porphyrins) (Fig. 2).^{8,9}



Finally, the third approach is based on organometallic Pt complexes as rotors and coordinating handles as stators (Fig. 3).^{10,11}



The design, synthesis and structural characterisations, both in solution by multidimensional ¹H-NMR techniques and in the solid state by X-ray diffraction on single crystals, of a series of molecular gates and turnstiles of both categories is presented and discussed.

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Functional organic solids – design or discovery?

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Porous molecular crystals are an alternative to porous extended frameworks such as zeolites, metal-organic frameworks (MOFs), and polymer networks. Interest in such systems dates back to the first 'organic zeolites',¹ but only recently have these materials started to show properties of potential practical interest.² Unlike extended frameworks, molecular crystals can be processed in solution into a variety of formats.³ They can also show unique physical properties, such as reversible on/off porosity switching⁴ and perfect shape selectivity for organic isomers.⁵

However, molecular crystals also pose problems in terms of the purposeful design of solid-state function.⁶ In large part, this is because the energy landscape for molecular crystals is frequently not dominated by a single intermolecular interaction, unlike bonded crystalline frameworks such as MOFs and covalent organic frameworks. Hence, molecular crystal engineering has so far failed to become the "new organic synthesis" that has been envisaged,⁷ even though that vision is still highly attractive when one considers the importance of crystalline organic solids, which extends well beyond the area of porous materials.

This lecture will discuss strategies for the design and synthesis of new functional organic crystals by using underpinning computational approaches.⁸ We will exemplify this with recent examples of function in real porous molecular solids, such as molecular selectivity, that was targeted using computation. We will also discuss the potential for high-throughput synthesis and characterization methods to work in tandem with computation, and to generate workflows that might lead us more effectively to new materials with specific properties. Our central aim will be to cast light on the question: can *in silico* 'design' compete with iterative synthesis and measurement for crystalline organic materials?

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We thank EPSRC (EP/H000925/1 & EP/K018396/1) and the European Research Council (project RobOT) for funding.

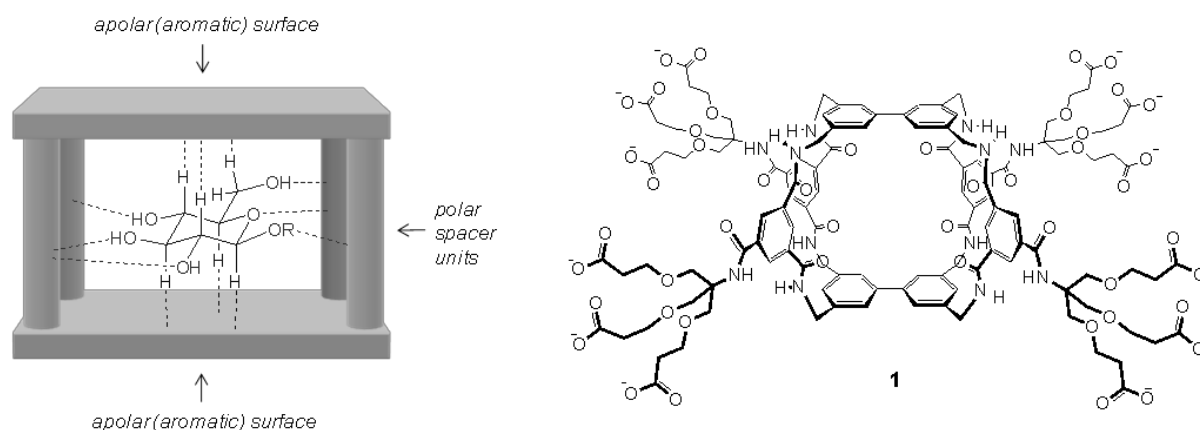
Synthetic Lectins: Progress in Biomimetic Carbohydrate Recognition

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Carbohydrate recognition is a difficult task, even for natural receptors such as lectins. The problems are two-fold. Firstly, saccharides are coated with hydroxyl groups and are therefore hydromimetic, being difficult to distinguish from a background of water molecules. Secondly they are structurally complex, and often differ only subtly from each other. It is not surprising, therefore, that lectins show notoriously weak affinities and often quite modest selectivities. If proteins perform moderately, one might expect that synthetic receptors would fail completely. However surprisingly good results have been achieved for one family of carbohydrate substrates, those with all-equatorial arrays of functionality (β -glucosyl, β -GlcNAc etc.). The key to success is the provision of cavities which complement both apolar and polar moieties. For all-equatorial saccharides, this implies parallel apolar surfaces separated by polar spacers, as illustrated in the cartoon below and exemplified by prototype **1**.^[1] This lecture will discuss the chemistry and binding properties of **1** and, especially, more recent systems based on similar principles.^[2] At their best, these “synthetic lectins” come close to matching the affinities of some lectin-carbohydrate interactions, while showing selectivities which are arguably superior. Given such performance, the prospects for applications may soon be realistic. For example, further development could lead to tools for studying the *O*-GlcNAc protein modification, and to molecular components for glucose sensors.



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SUPRAMOLECULAR GELS: ORTHOGONAL SELF-ASSEMBLY FAR FROM EQUILIBRIUM

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A vast and diverse array of organic compounds and coordination complexes form gels by hierarchical self-assembly either because of hydrophobic effects in water or by more directional interactions such as hydrogen bonding in less polar solvents. Of recent interest is the emergence of metal-, anion and salt-containing gelators based on small-molecule 'low molecular weight gelators (LMWG).¹ Particular attractions of LMWGs to the scientific community are the reversible nature of the interactions between the gelator molecules, the wide (essentially unlimited) range of solvents that can be gelled and the possibility of tuning the gels' behaviour by introducing responsive or switching functionality either as part of the gelator itself or by an external chemical stimulus such as a change in pH, or addition of molecules or ions that interact with the dynamic gel. Gels derived from LMWGs have been proposed in a range of applications and include templation of nanoparticles and nanostructures, drug delivery and wound healing and as crystal growth media.

This presentation focuses on a particular niche of tuneable LMWG chemistry, namely the use of concepts borrowed from anion host-guest chemistry to control and trigger the materials properties of small molecule (supramolecular) gels. We show how concepts firmly rooted in supramolecular host-guest chemistry and supramolecular self-assembly can be married with the materials science of soft matter in order to utilise a molecular-level understanding of supramolecular chemistry to control and manipulate bulk materials properties. This 'evolution' has been described in a recent review,² and the application of these kinds of switchable gels as novel media for pharmaceutical crystal growth has also recently been published.³ A picture of carbamazepine crystals growing in a LMWG organogel is shown right.



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Porosity in flexible metal-organic systems

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Over the past decade the study of porous crystalline solids has become highly topical, especially with regard to potentially important applications such as gas storage, separation and sensing. Well-known systems include zeolites and metal-organic frameworks and, to a lesser extent, organic molecular crystals. However, discrete metal complexes have received little attention as components of porous materials. One of the basic tenets of the solid state is that molecules tend to pack closely, thus affording minimal free space at the molecular scale. We are attempting to overcome this tendency by designing simple complexes that cannot pack efficiently without including solvent molecules. Indeed, we are specifically interested in forming solvent-templated complexes that do not collapse upon subsequent solvent removal [1-7]. We have recently discovered several systems that behave in this manner; some of these structures can be considered to be porous in the conventional sense, but we have also noted that conventional porosity is not a prerequisite for mass transport in the solid state. These systems have now been studied using a variety of complementary techniques, including X-ray diffraction, isothermal gas sorption, calorimetry and molecular modeling. Non-conventional use of these techniques has enabled us to gain a deep understanding of the relationship between structure and gas sorption dynamics.

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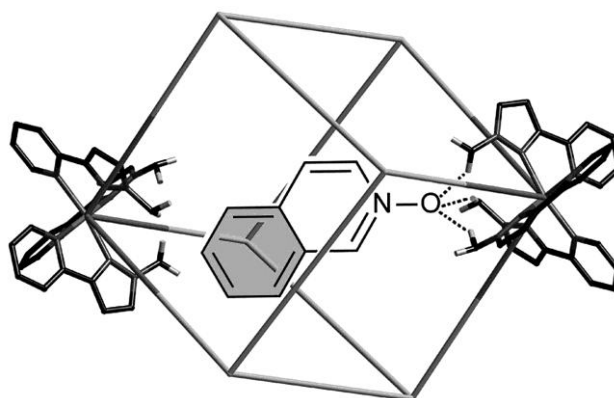
Host-guest chemistry in a coordination cage: dissection of hydrogen-bonding, van der Waals' and solvophobic contributions to guest binding

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An M_8L_{12} coordination cage with an approximately cubic structure, having a metal ion at each vertex of the cube and a bridging ligand spanning each edge, acts as a remarkably size- and shape-selective host for a family of small organic molecules such as cyclic esters, amides and pyridine *N*-oxides that contain an H-bond accepting O atom and no more than two aromatic rings. In MeCN the strength of guest bonding correlates linearly with the β (H-bond accepting) parameter of the guest's O atom because of an electrostatic interaction with a set of convergent C–H protons on the interior surface of the cage at a region of high positive electrostatic potential which acts as an H-bond donor site comparable in strength to phenol (see figure) [1,2].

In addition to the H-bonding component, addition of a second fused aromatic ring adds a consistent 10 kJ/mol to the binding free energy associated with interactions of this unit with the internal walls of the cavity [2]. Further, comparing binding strengths of guests in MeCN to binding strengths in an isostructural host that is water-soluble allows us to quantify the solvophobic contribution to guest bonding of specific substituents on the guests [3]. Thus the H-bonding contribution to binding associated with the O atom of the monocyclic H-bond acceptor, the additional van der Waals' contributions from the secondary aromatic ring, and the solvophobic contribution from the secondary aromatic ring, can all be quantified separately.



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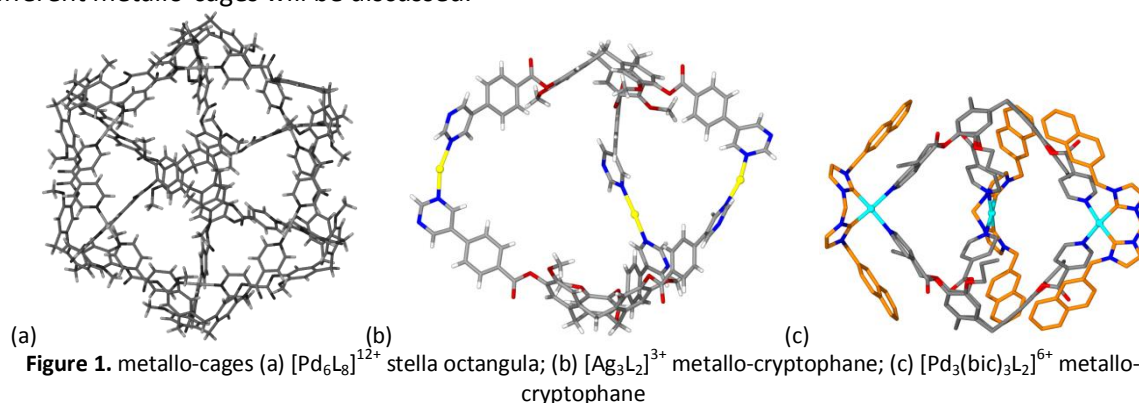
Metallo-cages and metallo-supramolecular assemblies for guest binding

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A series of pyramidal-shaped ligands based on the cyclotrimeratrylene (=CTV) molecular host can be synthesised with N-donor or O-donor functionality suitable for binding to transition metal or lanthanide cations. Complexes thus formed include crystalline coordination networks and discrete metallo-supramolecular assemblies such as metallo-cages. The pyramidal shape of the ligands gives cages with distinctive “star-burst” shapes or stellated polyhedra, while their host functionality imparts specific molecular recognition sites. For example, a family of “stella octangula” $[\text{Pd}_6\text{L}_8]^{12+}$ metallo-cages (Figure 1a) can be formed, the smallest of is around 3 nm in diameter.^[1] These contain significant internal cavities and solution studies show that large neutral or anionic guests, including *o*-carborane or surfactants, can be contained within the cage. Smaller $[\text{M}_3\text{L}_2]^{n+}$ metallo-cryptophanes have been shown to form as the anticipated single cages with large windows (Figure 1b), or as triply interlocked [2]catenane cages.^[2] The formation of topologically complicated metallo-assemblies has also been observed with a $[\text{Pd}_4\text{L}_4]$ “Solomon’s cube”, a type of self-interlocked cube.^[3] We have recently synthesised a series of $[\text{Pd}_3(\text{bic})_3\text{L}_2]^{6+}$ metallo-cryptophanes where bic = bisimidazoylcarbene, Figure 1c. The self-assembly behaviour and host-guest chemistries of these different metallo-cages will be discussed.



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Focusing on self-assembly: minimising the input of energy and solvent in the synthesis of metal-organic architectures

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Low-solvent or solvent-free reactivity, including reactions induced or sustained by mechanical force (mechanochemistry), has attracted considerable interest of synthetic chemists as a means of achieving cleaner and "greener" routes to molecules and materials.[1] Such reactions also provide an opportunity to explore molecular recognition and self-assembly without the interfering effects of bulk solvents, such as solubility, complexation with solvent, or solvolysis.[2] For our research group, solvent-free chemistry provides an opportunity to investigate the formation of metal-organic architectures directly from metal oxides, without the influence of counterions (nitrates, sulfates etc.) found in conventional solution-based syntheses.

This presentation will highlight our recent explorations of solvent-free chemistry as a means of understanding the assembly and collapse of porous metal-organic frameworks. First, the recently developed methodology for real time and *in situ* monitoring of mechanochemical reactions will be presented. This methodology uses highly penetrating synchrotron X-ray radiation ($\lambda \approx 0.14 \text{ \AA}$) for the direct observation of transformations of crystalline substances in a mechanical milling assembly, with resolution in seconds.[3] With the aid of this methodology, it was possible to illuminate for the first time the mechanisms of milling reactions as they take place, and observe new intermediate metal-organic phases lasting only seconds or minutes. The second part of the presentation will focus on 'accelerated aging', a simple, diffusion-controlled and catalytically accelerated methodology for the transformation of metal oxides into metal-organic architectures under the conditions mimicking those of normally slow natural mineral "weathering".[4] This solvent-free and low-energy technique provides reactant generality not yet demonstrated in mechanochemical processes, and allows the transformations of diverse transition and main group metal oxides, as well as lanthanide oxides, into metal-organic products whose structures can be templated towards two- and three-dimensional open architectures. The applications of accelerated aging in the clean synthesis of metal-organic frameworks and low-energy, solvent-free metallurgy will be discussed.

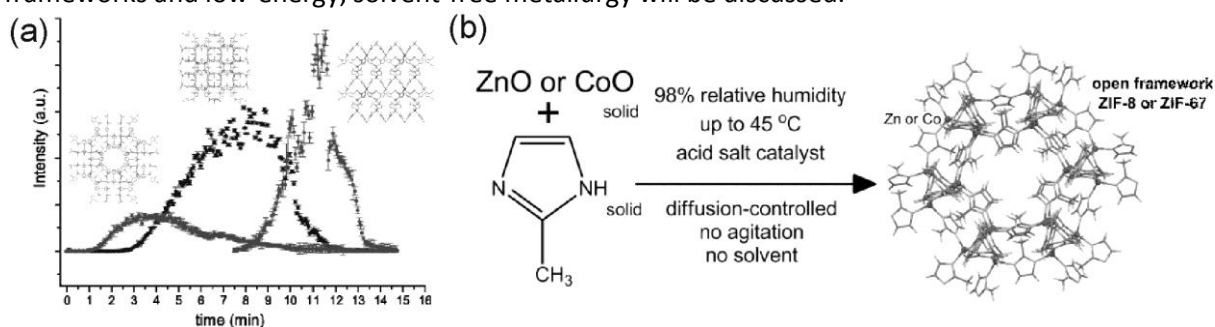


Figure 1. (a) Mechanistic study[3] of mechanochemical formation of a metal organic framework; (b) conversion of metal oxides into porous architectures by accelerated aging.[4]

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Global lattice energy exploration for predicting porosity and inclusion behavior in organic molecular crystals

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The prediction of crystal structure from a chemical diagram alone has been a long-term goal in the field of computational chemistry. The past few years has seen significant progress in the reliability and scope of methods based on a global exploration of the lattice energy surface; trial crystal structures are generated to sample all packing possibilities and these are ranked by their calculated lattice energies. The main target application of these methods has been as a tool to guide solid form selection for pharmaceutical materials, although these methods are finding applications in a range of areas of crystal engineering.

Our interest in the area of porosity and inclusion behaviour began with the observation that the trigonal form II of the anticonvulsant drug carbamazepine is located by global lattice energy exploration of the pure drug [1], despite the importance of solvent inclusion in the formation of this structure [1,2]. We have since then shown that the same is true for several well-known inclusion hosts: observed host frameworks can be located amongst the structures generated when considering the host molecule alone [3]. Recent developments of these methods and their applications will be presented [4], where we are investigating the role of guest molecules in stabilizing host frameworks. Prospects for the computational screening of molecules for the formation of microporous crystals that are stable to desolvation will also be discussed.

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The Super Bowl: *Pseudo* Metallocalix[6]arene Heptanuclear Solid State Host-Guest Materials

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Interest in solid-state host materials lie in their potential as (for example) gas storage and separation vessels [1] and as containers for magnetic nanoparticles towards imaging [2]. Indeed both organic and metal-organic molecular flasks / containers are well known in the literature. Examples of both classes are the bowl-like calix[n]arene cyclophanes ($n = 3, 4, 5, 8$ etc) [3] and their metallocalix[n]arene structural relations [4].

With these thoughts in mind we present a large family of heptanuclear $[M_7]$ ($M = \text{Ni(II)}, \text{Zn(II)}, \text{Co(II/III)}$) complexes, each member comprising *pseudo* metallocalix[6]arene topologies derived from the Schiff base ligands used in their construction (L_1H to L_4H in Fig. 1). These complexes possess metallic planar hexagonal disc cores and their organic exteriors form double bowl shaped topologies which (due to their crystal packing), result in the formation of molecular cavities in the solid state. These spaces behave as solid state hosts for guests including charge balancing counter anions and small organic molecules [5].

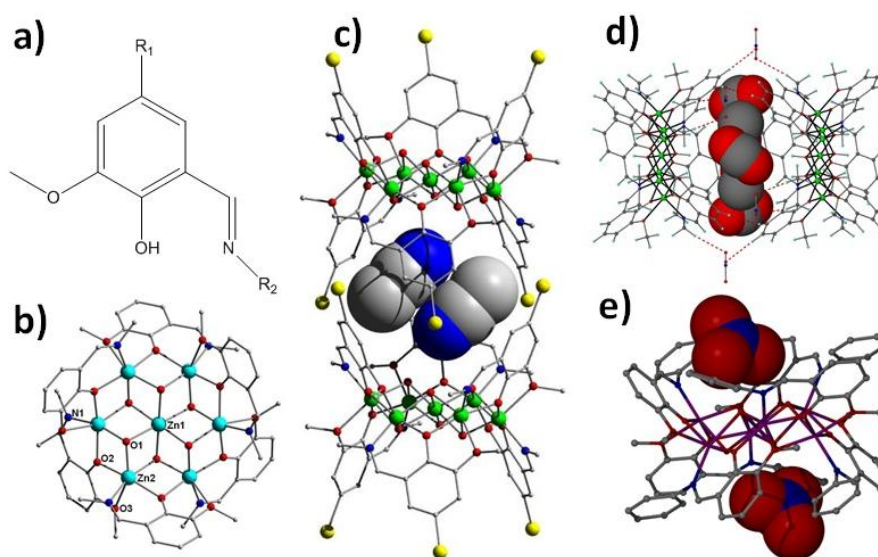


Figure 1 (a) Structure of the Schiff base ligands L_xH ($x = 1-4$) utilised in this work ($R_1 = H, R_2 = \text{Me}$ (L_1H); $R_1 = \text{Br}, R_2 = \text{Me}$ (L_2H); $R_1 = H, R_2 = \text{Ph}$ (L_3H); $R_1 = \text{Ph}, R_2 = \text{Me}$ (L_4H)). (b-e) Examples of Metallocalix[6]arene double bowl complexes to be presented.

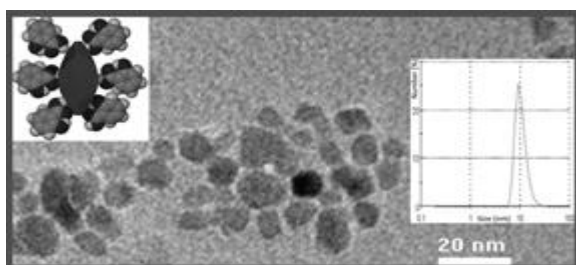
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Encapsulating nano-rust: From therapeutic vectors to potatoes...

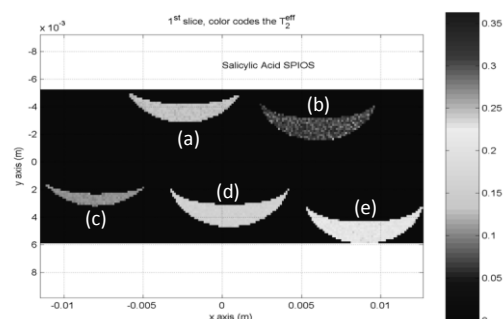
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Well it's not quite rust but it nearly is... Iron oxide comes in a variety of different forms but the one we have been experimenting around with for the last few years is Magnetite, Fe_3O_4 . It is naturally occurring and is in fact the most magnetic of all the naturally occurring minerals on Earth; the other nice thing is that it is FDA (Food and Drug Administration) approved. So how so how can we take a material as old as the earth and do something new and exciting? In three words, "make it nano". By controlling the size the Magnetite particles we can control its magnetic behaviour and switch it on and off *i.e.* make it paramagnetic or even better, super paramagnetic.



TEM image and DLS graph of SPIO nano-particles encapsulated in a monolayer of the drug salicylic acid, showing the uniform size distribution and morphology.



MRI T_2^* relaxation for salicylic acid coated SPIO at different concentrations: (a) 0.187, (b) 0.467, (c) 0.093, (d) 0.280, (e) 0.374 mg/mL.

Our first adventures with super paramagnetic iron oxide, SPIO, started with utilising them as magnetic resonance imaging (MRI) contrast agents to non-invasively monitor therapeutic delivery systems in real time. But we soon realised that this was only the tip of the iceberg. The problem with SPIO is that, like rust, it does not dissolve up in water, so the first thing we had to do is come up with a method for coating or capping the SPIO with something that would help solubilise it in water and other solvents. The answer was to grind, grid and then grind some more. Once we nailed that (and patented it)^[1] we started to explore the properties of these new materials including their applications in MRI, micro arrays, therapeutic vectors, magnetic hyperthermia, transdermal delivery, food and drink supplements, cosmetics, magnetic yarn and potatoes...

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Polymorphism of Ionic Clathrate Hydrates

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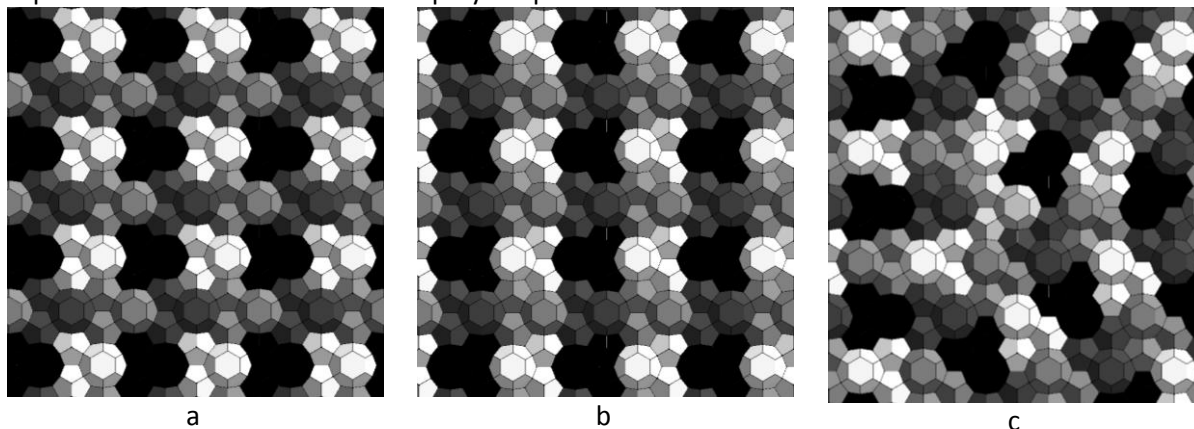
Ionic clathrate hydrates (*ICH*) are classical objects of inclusion chemistry. The most widely investigated are hydrates of tetrabutyl- and tetraisoamylammonium (*TBA*, *TiAA*) salts with singly charged anions (halides, carboxylates, etc.). Nevertheless, there is no consensus about *ICH* structures and phase diversity, despite the long history of their investigation and large amount of data, obtained by wide variety of methods.

There is a hierarchy of structural sources of *ICH* phase diversity considered previously [1,2]:

1. Variation of host framework type;
2. Possibility of different guest arrangement for the same framework type;
3. Existence of conformation alternatives for guest species for the same arrangement.

Typically only the first reason was taken into account. Only special features observed for some *TBA* and *TiAA* carboxylate hydrates were explained by the other reasons.

Data on these compounds that we have accumulated in recent years allow us to assert the importance of the second source of polymorphism.



Possible periodic (a,b) and aperiodic (c) arrangement of 4-compartment cavities in a host framework of the *hexagonal type I*, typical for *ICH* of *TiAA* salts

A number of physical reasons can be proposed for this type of polymorphism. It may be caused by contradictions of electrostatic and “mechanical” interactions (due to van der Waals interaction). Another possible reason is “incommensurability” of host framework and compartment cavities for guest species allocation. Both reasons may be tangled by complex ways of guest species inclusion, some arbitrariness of anion species incorporation, local water framework rearrangements, and disorder of proton positions in host frameworks.

The above features are illustrated by X-ray diffraction, NMR spectroscopy and *in silico* experiments. Further perspectives of comprehension of *ICH* structures by contemporary investigation methods are discussed.

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Design and Evaluation of Novel Ligands for Nuclear Waste Treatment

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Partitioning of actinide (An(III)) / lanthanide (Ln(III)) cations is an important step in nuclear waste treatment, which utilizes different types of ligands in different processes.

Novel ligands, a sort of hybrids, were prepared by combining essential parts of different well-known classes of ligands, viz. malonamides and glycolamides. However, their extraction behavior turned out to be not as good as that of the original parent ligands [ⁱ].

N,N,N',N'-Tetraoctyl-3-oxapentanediamide (TODGA) is currently one of the innovative-SANEX reference compounds due to its high distribution ratios for An(III) and Ln(III) from highly acidic media. TODGA was pre-organized on tripodal [ⁱⁱ] and calix[4]arene platforms [ⁱⁱⁱ] and the resulting ligands were evaluated for the extraction of various An(III) cations. The extraction results clearly showed the positive effect of bringing together ligating sites on a molecular platform. Water-soluble TODGA derivatives and tripodal ligands [^{iv}] showed interesting back-extraction properties.

Diglycolamide-based ionic liquids were prepared. They were capable of exceptionally high extraction of trivalent actinide ions, such as Am³⁺, and even higher extraction of Eu³⁺ (about 5-10 fold) [^v].

Many nitrogen-donor extractants are known to lose their complexation ability due to protonation of nitrogen under the highly acidic nuclear waste conditions. To possibly overcome this drawback a series of novel pyrazine-based *O,N,O*-donor ligands was designed and synthesized, employing a newly developed methodology for palladium-catalyzed phosphorus-carbon coupling of chloropyrazines with various phosphorus pronucleophiles [^{vi}]. Several appropriately functionalized pyrazines were grouped together on a calix[4]arene and their extraction behavior compared with that of the individual pyrazines [^{vii}].

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Highly Selective Capture and Extreme Confinement of Gases

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There is much contemporary interest in the development of new molecule-based materials for gas capture/sequestration, separation, sensing, *etc.*, and efforts in this regard have mainly been directed toward materials that exhibit permanent microporosity (*e.g.* inorganic zeolites, metal-organic frameworks, covalent organic frameworks, polymers of intrinsic microporosity, and intrinsically porous molecules). Much less is known, however, about the properties of what we refer to as “microcavity materials”—that is, molecule-derived materials that possess molecule-sized microcavities, but do not formally exhibit micropores. Such materials may exhibit advantages with respect to selective gas capture. Moreover, the kinetics of gas uptake and/or release are slower than in microporous materials and are largely dependent upon molecular and crystalline structure, factors which may be tunable. This presentation will focus upon efforts in our laboratory aimed at engineering crystalline microcavity materials for the highly selective inclusion, and in some cases extreme kinetic confinement, of various gases, with emphasis on a diverse family of container compounds [1]. Some simple molecular compounds exhibit highly selective (*e.g.*, $C_2 > C_3$ or $C_3 > C_4$ hydrocarbons, $Xe > Kr$, *etc.*), and tunable, gas enclathration properties. Others are capable of confining gases in the solid state at temperatures more than 300°C above their normal boiling points (Figure 1).

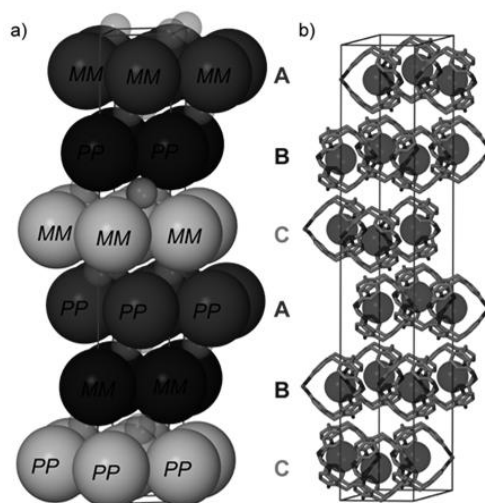


Figure 1. Crystal packing of a highly stable noble gas-container molecule inclusion compound.

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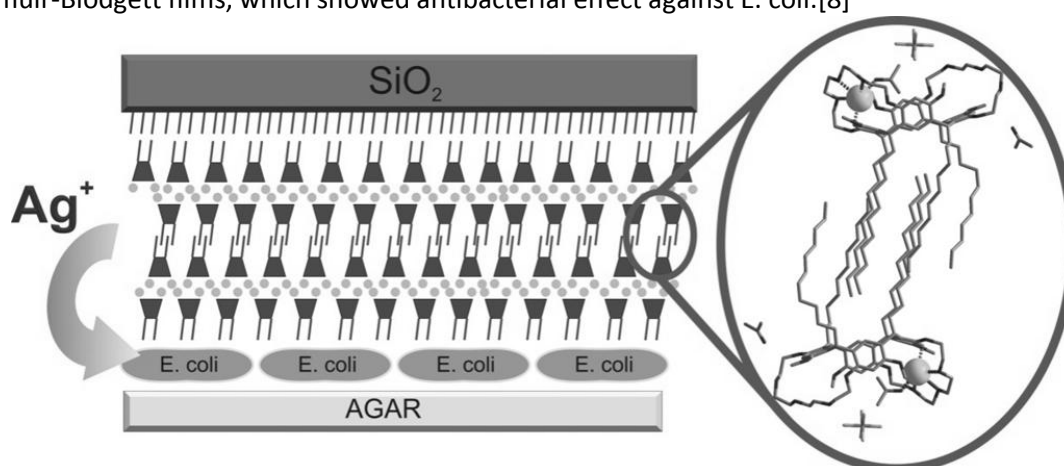
Resorcinarene Crowns: Double Functionalized Supramolecular Receptors

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Resorcinarenes with the structural features of aromatic cavity and hydrogen bonding hydroxyl groups at the upper rim have been successfully used as supramolecular receptors for cations, anions and small organic molecules for the past few decades.[1] The possibilities to functionalize their upper and lower rims have further provided means to control their binding properties, as well as, brought new insights into their self-assembling properties.

During the recent years we have synthesized a series of crown ether functionalized resorcinarene derivatives, resorcinarene crowns, and explored their self-assembling properties and properties as cation hosts. The structural variation of our series includes, for example, mono- and bis-crown derivatives [2], thiocrowns [3] and varying lower rim alkyl chain lengths [4], as well as previously unknown benzofuran fused resorcinarene derivative [5]. The resorcinarene crowns have proven to be effective hosts for binding of alkali metal [6] and silver cations [7]. The capacity to bind silver combined with the ability to self-assemble into layers has been utilized in the preparation of Langmuir-Blodgett films, which showed antibacterial effect against *E. coli*. [8]



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Pseudopolymorphism in Cyclodextrin Solvates

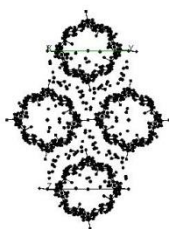
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Cyclodextrins are commonly known as materials having intra-molecular cavity able to accommodate guest species. This property, when combined with sorption in the inter-molecular space in the solid state structures of CDs leads to very interesting structures and properties. In general, such behavior may be observed only when CD moieties are at equilibrium with a solution of the respective guest and solvent species. The equilibria are quite sensitive to minor changes of solution chemical composition what may be observed microscopically as morphology changes of the crystalline phases. This phenomenon will be illustrated with short movies demonstrating crystal behavior on change of its environment. Novel x-ray structures will also be demonstrated.

The examples will include cyclodextrin inclusion complexes with organic guest species as well as some brand new structures of cyclodextrin coordination complexes of zinc(II) and cobalt (II) as well as some mixed coordination complexes.

In the picture below a projection of a tubular structure of gamma-cyclodextrin coordination complex is shown. The structure was obtained by partial desorption of the guest (solvent) species which is accompanied by minor lattice contraction and significant change of the unit cell, as listed in the table.



Lattice constants:

The structure shown in the picture: $a = 15.461$;

$b = 19.591$; $c = 33.426 \text{ \AA}$, orthorhombic

The structure before desorption: $a = 62.419$;

$b = 33.740$; $c = 19.549 \text{ \AA}$, orthorhombic

Temperature of data collection – 100 K.

The phenomenon of lattice dilation/contraction is characteristic for an 'organic zeolite' type structure which is one of the cyclodextrin structural type recently found in our studies.

This work was supported by grant POIG.01.01.02-14-102/09.

Self assemblies in calixarene inclusion compounds

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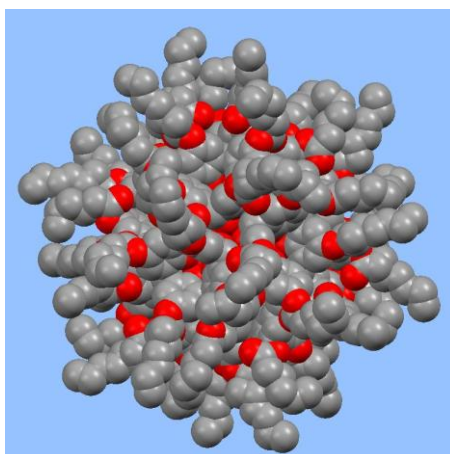
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Calix[n]arenes are aromatic macromolecules that can generate a wide range of derivatives thanks to their easy and selective chemical modifications. They are well known to self-assemble in layers (mono- and bilayers), capsules and tubes, spheres and other geometrical forms. Many of these are dependent on the chemical character of substituents, other are common for different substituents independent of their chemical character. An extremely wide range of solid-state studies have been undertaken on different types of derivatives. E.g. for *para*-sulphonatocalix[4]arene classical organic clay bilayer systems, zig-zag bilayers, stepped bilayers, capsules and tubes, spheres and other geometrical solids have been observed. Concerning calix[4]arene dihydroxyphosphonic acid, there is an apparent constant in self-organization, the same interpenetrating motif.

The aim of this paper is to present the most frequent molecular assemblies of calixarenes in solid state as well as these which are rare and spectacular.



Inclusion and Structure: Property Characteristics of Small Molecule Supramolecular Gels

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Supramolecular gelators or low molecular weight gelators (LMWGs) are a class of small molecules that are capable of gelling a large variety of solvents at low concentrations. These colloidal materials consist of a solid continuous matrix within a dispersed liquid phase. They are interesting as they consist by weight and volume of mostly liquid, yet behave like a solid. The majority of their behaviours relate to the structural properties of the solid matrix [1].

In this presentation we describe the characterisation and tuning of gel material behaviours; namely stability, rheology, fluorescence and molecular packing. Phenylalanine is a simple chiral model compound that can be used to describe the characteristics of this class of materials. We shall describe the gelation phenomenon of phenylalanine and the structural properties of its water (hydrogel) and DMSO gel forms in terms of morphology, rheology and molecular packing. We especially determined the relationship between the crystal [2] and gel forms where water inclusion is important. The gelation by a series of benzene-1,3,5-triamide (BTA) based aromatic carboxylic acid compounds is also presented [3]. Fluorescence variation of the hydrogel materials and the characterisation of the nucleation phenomena of the gelation process utilising rheology is presented. In addition, we will highlight the use of solid solution concepts to form co-gelator materials. We will also show the unique modulation of the swelling/shrinking of the BTA-based metallogel materials utilising coordination inclusion chemistry.

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[2] P. A. Williams, C. E. Hughes, A. B. M. Buanz, S. Gaisford, K. D. M. Harris, *J. Phys. Chem.*, 2013, **117**, 12136.

[3] R. C. T. Howe, A. P. Smalley, A. P. M. Guttenplan, M. W. R. Doggett, M. D. Eddleston, J. C. Tan & G. O. Lloyd, *Chem. Commun.*, 2013, **49**, 4268.

Electroluminescence and heat-set gelation in a series of dynamic-covalent metallo-polymers

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Unlike conventional polymers which are irreversibly formed, supramolecular polymers can reform and reconfigure their structure and properties in response to stimuli. We report a series of dynamic-covalent metallo-polymers that are readily synthesised by the condensation of linear diamine and dialdehyde subcomponents around copper(I) templates in the presence of bidentate phosphine ligands. When fabricated into light-emitting electrochemical cells (LECs) the polymers show electroluminescence, making them part of an increasingly important class of LEC device not dependent on expensive, earth-scarce elements such as platinum(II), iridium(III) and osmium(II).[1]

The devices emit red light when a low bias is applied but undergo a hypsochromic shift in emission as the voltage is increased, eventually emitting yellow light. In solution, the red polymers undergo a sol-gel transition upon heating to form a yellow gel which shows rapid self-healing behavior. The mechanism underlying these apparently disparate responses is deduced to be due to a rearrangement of ligands at the copper centres.[2] The distinct changes in photophysical and rheological properties observed as a result of rearrangement of the polymer system holds potential for use in a variety of sensing, imaging and information storage applications.

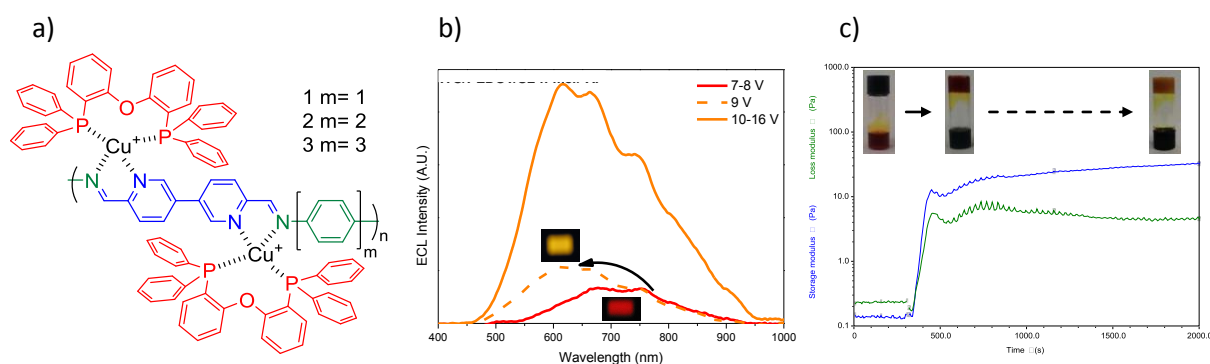


Figure 1. A series of dynamic-covalent metallo-polymers (a) show a hypsochromic shift in electroluminescent emission with increasing voltage (b) and the formation of self-healing gels at high temperatures (c).

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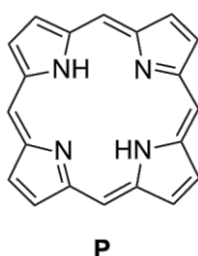
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A Computational Study of Macrocycles and their Excited States

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The most common supramolecular units present in nature are without a doubt the Porphyrin family of macrocycles. Free base porphyrins, as well as complexed to guest metals, are building blocks that have been known and manipulated for nearly a century[1]. This is especially true when it comes to the investigations of compounds with accessible photochemical pathways. The porphyrinic macrocycle has an intriguing structure that can be tuned in photochemical activity with relative synthetic ease. From dye-sensitized solar cells to biological imaging agents and Photodynamic Therapy (PDT); Porphyrins are the go-to photochemical starting point [2,3].



As the field of computational chemistry has developed, so has the ability to model the ground state potential energy surfaces and reaction profiles for compounds of the size of porphyrins. When it comes to the excited states of porphyrins, the development of new functionals for use in Time-Dependent (TD) Density Functional Theory (DFT) has made it possible to investigate both linear and non-linear absorption processes in compounds as large as porphyrins [4]. This is true even for porphyrins with large substituents, as well as complexed to a guest metal [5,6].

This talk will present the use of TD-DFT to replicate absorption spectra in porphyrinic macrocycles, both for linear and non-linear absorption, and show examples of how computation can be used to investigate, and predict, absorption characteristics. This will be done from the viewpoint of PDT applications, in biological environment.

Further, this talk will go on to describe the methods available for characterisation of excited states of these compounds, as well as investigations into the relaxation pathways available.

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[2] K. Szacilowski et al., *Chem. Rev.* 2005, **105**, 2647-2694

[3] A. Hagfeldt, *Chem Rev*, 2010, **110**, 6595-6663

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[5] L. T. Bergendahl, M. J. Paterson, *J. Phys Chem B*, 2012, **116**, 11818-11828

[6] I. Lopez-Duarte, J. E. Reeve et al. *Chem Sci*, 2013, **4**, 2024-2027

TBC[4] bound Mn^{III} : A versatile building block in the construction of polynuclear $3d$ and $3d-4f$ cluster systems

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In recent years we have investigated the role of *p*-*tert*-Butylcalix[4]arene (TBC[4]) as a suitable organic supporting ligand in polynuclear cluster formation [1]. The combination of Mn^{III} ions situated within the TBC[4] tetraphenolic cavity has emerged as a particularly common motif (figure 1a). This presentation discusses the versatility of the aforementioned Mn^{III} -TBC[4] building block in the construction of polynuclear clusters. Systematic studies of reaction conditions and solvents of crystallisation determine the composition and topology of a variety of $3d$ and $3d-4f$ clusters. Furthermore, the presence of additional co-ligands (e.g. salicylaldoxime based ligands) in cluster forming reactions has led to markedly different clusters while maintaining the Mn^{III} -TBC[4] motif. Finally, functionalisation at one methylene bridge of TBC[4] yields a biscalixarene [2] which is an intriguing new addition to our coordination chemistry library (figure 1b) and has been used to prepare a new Mn8 cluster.

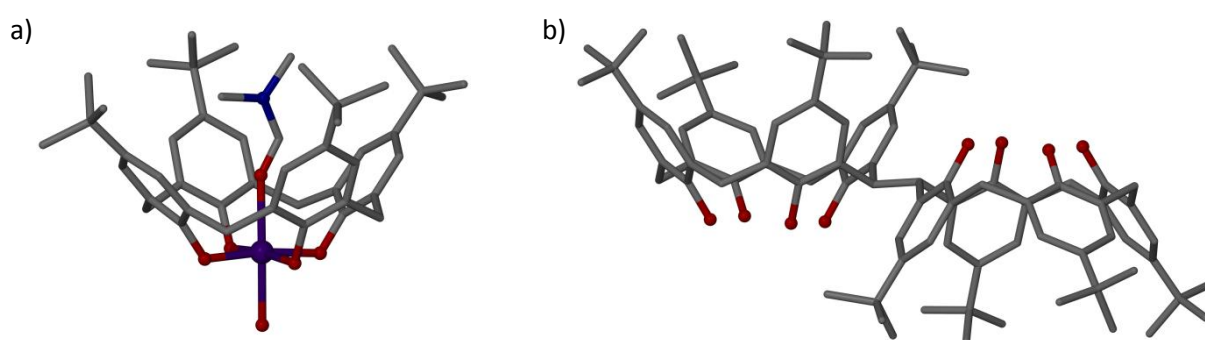


Figure 1: a) Common Mn^{III} -TBC[4] motif. b) Bis-TBC[4] molecule linked at CH_2 moiety.

[1] G. Karotsis, S. J. Teat, W. Wernsdorfer, S. Piligkos, S. J. Dalgarno and E. K. Brechin, *Angew. Chem. Int. Ed.*, 2009, **48**, 8285.

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Advances in X-ray Crystallography

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Agilent Technologies (XRD) – formerly Oxford Diffraction, has made some of the most notable advances in X-ray crystallography over recent years. These include the adaption of graded monochromating / focussing X-ray mirrors to ‘conventional’ fine focus X-ray sources - to achieve the high brilliance Enhance Ultra (Cu) X-ray source. Further advances in X-ray source design are marked by the Mova (Mo) and Nova (Cu) microfocus X-ray sources: whilst operating at low powers (typically 40 – 50 W), these sources achieve X-ray brightnesses considerably higher than is possible using 2 – 3 kW fine focus X-ray tubes, and comparable with rotating anode – type sources.

In parallel with X-ray source breakthroughs, CCD area detector technology has been considerably improved: for instance with the Eos and Atlas CCD detectors. The Eos is the highest sensitivity CCD detector which is commercially available – with a gain of 330 electrons per Mo photon, rapid read-out and 18-bit dynamic range. The much superior dark current (background) and read-out noise characteristics of CCD detectors mean that they considerably outperform the integrating CMOS detector technology.

The benefits of these developments in X-ray source and detector technologies and in the CrysAlis^{Pro} data-collection and data-analysis software suite will be illustrated through examples from a number of applications.

As a further valuable assistance to the crystallographer, the PX Scanner has been established: this is for the evaluation of the X-ray diffraction properties of crystals directly in situ in crystallisation plates: whilst the (putative) crystals are still growing in their mother liquor. Some applications of the PX Scanner system will be summarised.

Assembling and Manipulating Molecules to generate Materials with Targeted Properties

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Material properties change and evolve with increasing length scales, and the solid-state offers a unique environment to control these properties as molecules are assembled into nanoscale, meso- and macroscopic particles [1]. An obvious target property is that of colour, and this can be modified at the molecular or supramolecular level within a crystalline solid by introducing a second component, such as a solvent or gas molecule, to the crystalline form, where the colour change is the result of a structural rearrangement within the ordered crystal. A second property that can be modified within a crystalline environment is refractive index, where the photoactivation of a moiety within the crystal leads to a geometric change that alters refractive index of the material.

As exemplars of the use of a crystalline environment to generate materials that undergo dynamic structural and property changes we will:

- i. discuss recent studies on platinum pincer complexes that show dramatic colour changes upon the introduction of solvent molecules into crystal lattice
- ii. describe photocrystallographic studies on a series of nickel(II) complexes that contain nitro ligands that undergo reversible linkage isomerism, in the crystalline state, upon photoactivation [2]. The results will be discussed in terms of the “reaction cavity” within the crystal lattice.

These examples can be considered of crystalline systems that contain only two components. A question to pose for the future is what properties and functions could be generated by the controlled assembly of three or more molecular components and how powerful this technique might become?

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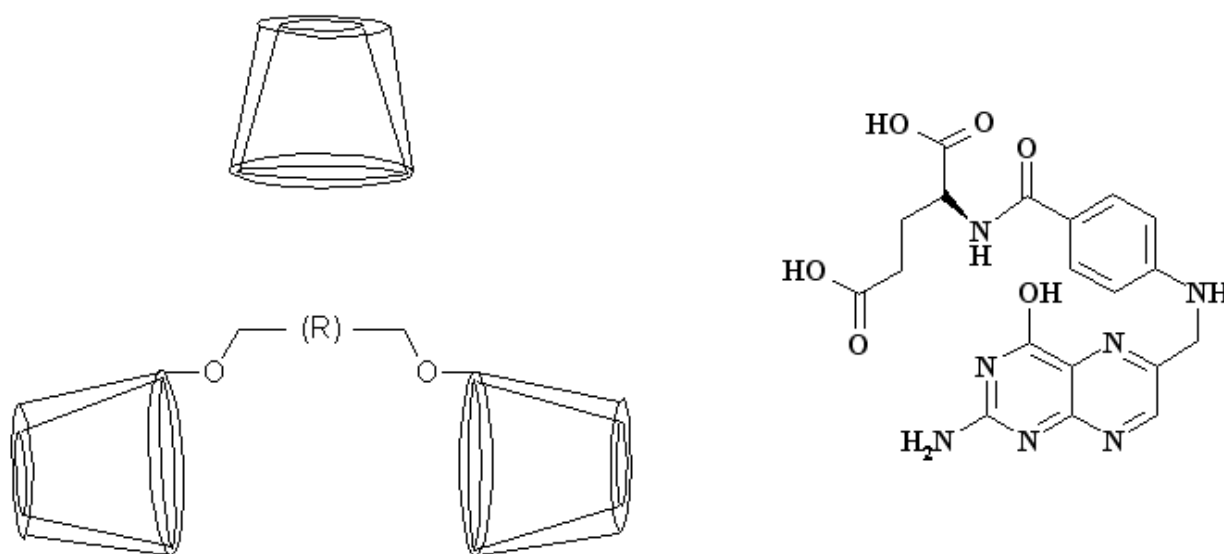
Native and modified cyclodextrins as molecular receptors for folic acid

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Folic acid (FA) belongs to the group of vitamin B₉ and is essential for human biological processes. Deficiency of FA is a major cause of the neural tube effects (NTDs) in newborns; it is also responsible (among others) for disorders such as megaloblastic anemia. Due to its limited bioavailability the search for “carrier” molecules designed for delivery of folic acid into the human body still remains the hot topic progress. The usage of cyclodextrins as nontoxic encapsulating materials is based on their ability to form inclusion complexes with a wide variety of organic and inorganic compounds.

The aim of our work was to study a formation of native and modified cyclodextrins complexes with folic acid.



¹H NMR and 2D ROESY measurements of various folic acid/cyclodextrin complexes gave comprehensive information about the obtained compounds. These results were supported by data obtained by Electrospray Ion Mass Spectrometry and Ion Mobility Mass Spectrometry.

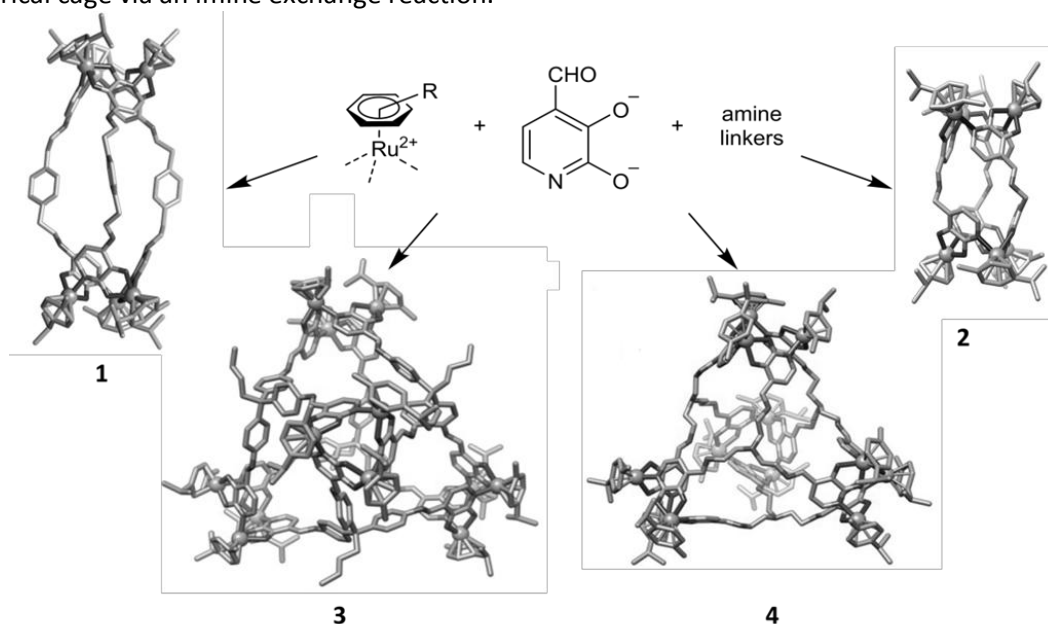
This research was partly financed by the European Union within the European Regional Development Fund (POIG.01.01.02-14-102/09)

Large imine-based cages: synthesis via orthogonal self-assembly and use as receptors for alkali metal ions

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Large cage structures were obtained by combination of metallasupramolecular chemistry with dynamic covalent chemistry.^[1,2] Our approach is based on three types of building blocks: (arene)Ru^{II} complexes, formyl-substituted hydroxypyridone ligands, and amine linkers. By variation of the building blocks, we were able to change the size and the topology of the cages substantially. It was thus possible to obtain hexanuclear cages with a cylindrical shape (e.g. **1** and **2**) and dodecanuclear cages with huge cavities (e.g. **3** and **4**). Notably, all dodecanuclear and most hexanuclear cages were formed in a highly diastereoselective fashion. A unique feature of our approach is the fact that the dynamic covalent bonds are formed in an orthogonal fashion, i.e. the imine bonds are not formed in the first coordination sphere of the metals. Reactivity studies have shown that it is possible to address the imine bonds selectively as demonstrated by the conversion of a tetrahedral cage into a cylindrical cage via an imine exchange reaction.^[2]



Some of these cages were found to display interesting host-guest chemistry. Cage **2**, for example, is able to accommodate large alkali metal cations such as Rb⁺ and Cs⁺ in the inside, and small alkali metal cations such as Li⁺ and Na⁺ on the outside.^[3] The presence of two distinct binding sites results in a surprising selectivity pattern: cage **2** binds preferentially the small Li⁺ and the large Cs⁺. The coordination of Cs⁺ is associated with a colour change, which can be used for the naked-eye detection of Cs⁺.^[3]

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Metal-directed assembly of coordination polymers and molecular capsules

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The controlled formation of multi-component nanostructures is a persistent challenge of both supramolecular chemistry and crystal engineering, primarily because of the need to simultaneously control numerous different intermolecular interactions. Calix[4]arenes have been widely used in these fields of research due to their synthetic accessibility, cavity that can be used in host-guest chemistry and possibility of introducing functionality to the general molecular framework.¹ However, surprisingly the p-carboxylatocalix[n]arenes (pCO₂[4]s) have not yet been exploited in the formation of coordination polymers (CPs) and metal-organic frameworks (MOFs), especially considering that the resulting structures may potentially be tailored so as to present unique host cavities for use in gas sorption and separation (amongst other things).

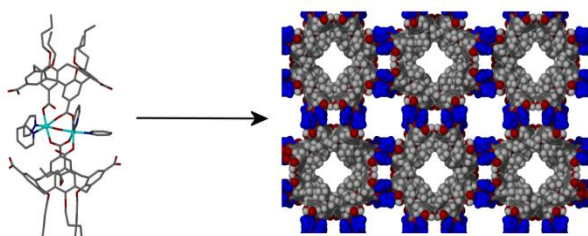


Fig. (1): Bi-nuclear TM pCO₂[4] cluster that assembles into metal-organic nanotubes due to tilt in the constituent building block.

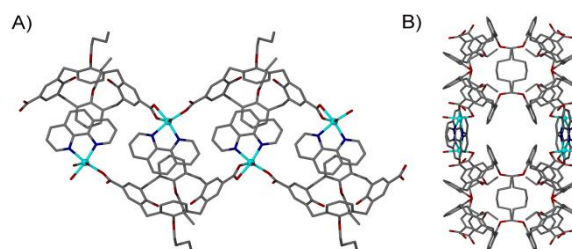


Fig. (2): A) Neighbouring interweaving CP chains B) Extended structure showing tilt between CPs - formation of nanotubes.

Our group have already demonstrated, that by using pyridine, a high degree of control over self- and metal-directed assembly of pCO₂[4]s can be achieved.² With the use of pyridine, through complementary non-covalent interactions, a sufficient tilt angle to the metal cluster is invoked, forcing nanotube assembly in the solid state. In the presentation we will present a rational approach towards the construction of versatile CPs / MOFs from nanoscale panels comprising transition metals such as Mn²⁺, Co²⁺ and Cd²⁺, pCO₂[4]s and various bipyridyl linkers.³ We will also demonstrate a new method of accessing novel metal-organic porous materials with the use of TM, chelating ligands and pCO₂[4]s.⁴

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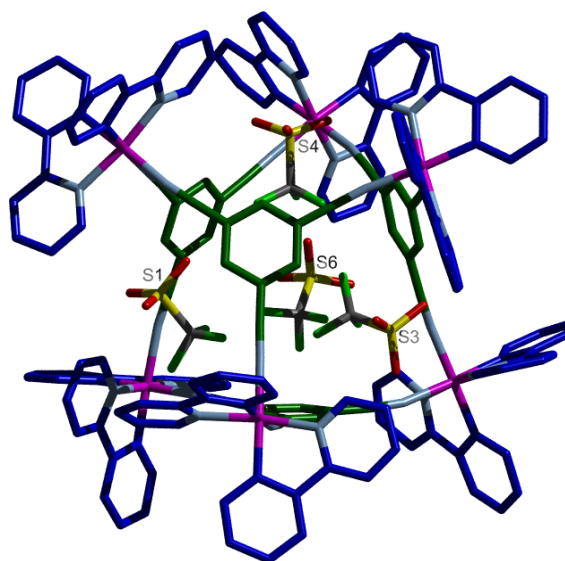
Photoactive Iridium-Based Supramolecular Capsules

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The combination of transition metal ions and geometrically complementary, multitopic bridging organic ligands has led to the preparation of numerous molecular capsules and cages.[1] These assemblies possess well-defined internal cavities that promote the ingress of *guest* molecules so that interesting functions, such as catalysis or the stabilisation of reactive species may be observed. By and large, the transition metal ions within these systems have played solely a structural role, offering advantages such as predictable, well-defined coordination preferences and bond strength. However, transition metals and their complexes often possess many other notable features, such as interesting photophysical properties. Although several examples of metallocycles, dendrimers and helicates exist in literature, the use of Ru poly(pyridyl) or cyclometalated Ir complexes as structural components in metallosupramolecular assemblies, in particular polyhedral architectures, remains rare.[2]

Here we present the first molecular capsule based on an $[\text{Ir}(\text{ppy})_2]^+$ unit (ppy = 2-phenylatopyridine).[3] Following the development of a method to resolve rac- $[(\text{Ir}(\text{ppy})_2\text{Cl})_2]$ into its enantiopure forms, homochiral Ir_6L_4 octahedra were assembled with the tritopic 1,3,5-tricyanobenzene ligand. The self-assembly process has been demonstrated to be guest template driven with a number of different anions (OTf , BF_4 , ClO_4 , PF_6) facilitating the formation of the same octahedral scaffold. Subsequent experiments have also shown that the self-assembly and stability of these scaffolds are highly dependent on the counterions located within the capsules' cavity and that an ensemble of cooperative, weakly coordinating ligands can lead to luminescence not present in comparative, mononuclear analogues.



- [1] For a comprehensive review on molecular capsules, see a) R. Chakrabarty, P. S. Mukherjee, P. J. Stang, *Chem. Rev.*, 2011, **111**, 6810-6918. For examples of molecular capsules which use cyclometalated corner groups, see b) P. J. Lusby, P. Müller, S. J. Pike, A. M. Z. Slawin, *J. Am. Chem. Soc.*, 2009, **131**, 16398-16400; c) O. Chepelin, J. Ujma, P. E. Barran, P. J. Lusby, *Angew. Chem. Int. Ed.*, 2012, **51**, 4194-4197.
- [2] For examples of multinuclear metallosupramolecular assemblies based on an $[\text{Ir}(\text{ppy})_2]^+$ motif, see a) E. Baranoff, E. Orselli, L. Allouche, D. Di Censo, R. Scopelliti, M. Grätzel, M. K. Nazeeruddin, *Chem. Commun.*, 2011, **47**, 2799-2801; b) V. Chandrasekhar, T. Hajra, J. K. Bera, S. M. W. Rahaman, N. Satumtira, O. Elbjerrami, M. A. Omary, *Inorg. Chem.*, 2012, **51**, 1319-1329.
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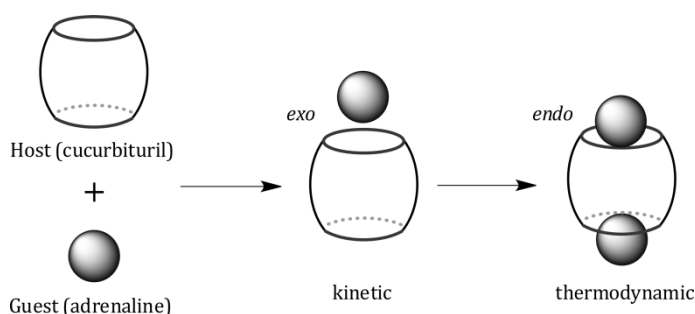
Supramolecular Host-Guest Assemblies of Cucurbituril: Kinetic Trapping and Phase Transformations

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Slow kinetics of supramolecular self-assembly allows unique insight into host-guest complexation mechanism and enables observation and characterization of individual supramolecular transformation steps. The molecular recognition and self-assembly between host cucurbit[6]uril and cationic adrenaline as guest lead to kinetic trapping and crystallization of intermediate exclusion complex, which was characterized by X-ray diffraction. [1] The crystalline kinetic complex undergoes slow spontaneous dissolution and subsequently recrystallizes as thermodynamic inclusion complex. The isolation and structural characterization of both complexes enabled to reproduce the each step of the inclusion process, thus, to ultimately confirm the predicted two-step complexation model for cucurbit[6]uril host-guest systems with organic cations. [2] In the case of neutral adrenaline the direct crystallization of inclusion complex with cucurbit[6]uril was observed. In strongly acidic conditions the inclusion complexes with oligomerized adrenaline were obtained due to condensation reaction between adrenaline molecules. The high degree of structural diversity in quite simple host-guest system is interpreted in terms of different non-covalent interactions involved in the assembly process as well as the influence of supramolecular reaction conditions.



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Self-assembly of selected (pseudo-)amphiphilic calix[4]arenes in solid state – X-ray diffraction studies

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Crystal engineering is based on the controlled use of intermolecular interactions which can vary from weak, such as van der Waals interactions or induced dipoles, through medium aromatic stacking or hydrogen bonds to strong metal coordination bonds or electrostatic interactions. Obviously it might be expected that the stronger interactions should dominate and control the solid state assembly. But if an approximate balance between different types of intermolecular forces exist in solid, non-predictable packing might occur, multiple types of crystal may be present or the system simply becomes reluctant to crystallize.

Self-assembly of amphiphilic calix[n]arenes is much better investigated in liquids than in the solid state. Nevertheless, such complex super-structures as bilayers [1], nanocapsules [2], helical tubes [3], micelles [4], reversed micelles [5] etc., were observed in the solid state. In this study, changes in self-assembling mode of non-substituted at the upper rim, *para-tert-butyl*- and *para-nitro-O*-alkylated calix[4]arenes will be discussed. It will be shown, that a 'balance' between the head group-to-head group interaction forces and the tail-to-tail van der Waals forces depends not only on the length and number of alkyl chains at the lower rim, but also on the type of substituent at the upper rim and the conformation of calix[n]arene macrocyclic ring.

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Structural characterization of inclusion complexes of *para*-sulfonatocalixarenes

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Water-soluble *para*-sulfonatocalixarenes have a high ability to form complexes with molecules containing nitrogen atoms: 1,2-bis(4-pyridyl)-ethane and 1,3-bis(4-pyridyl)-propane, 1,10-phenanthroline. The host-guest complexes formed by these compounds are stabilized mainly by π - π interactions between aromatic rings of guest molecules and aromatic rings of calixarene molecules. The contribution of C-H $\cdots$ π interactions in the inclusion complexes formation is of minor importance. Additionally, in the complex of *para*-sulfonatocalix[8]arene with 1,3-bis(4-pyridyl)-propane the inclusion is stabilized by one N-H $\cdots$ O hydrogen bond.

Large molecule of *para*-sulfonatocalix[8]arene may form molecular complex with two or more guest molecules. A flexible molecule of this calixarene easily adapts its conformation to the shape of guest molecules. Additionally, guest molecules with some degrees of freedom like 1,2-bis(4-pyridyl)-ethane and 1,3-bis(4-pyridyl)-propane also adapt their conformation to the shape of calixarenes. In this paper we report new conformations of *para*-sulfonatocalix[8]arene which are not described yet in the literature.

para-Sulfonatocalix[6]arene forms 1:2 complex with phenanthroline. Additional four guest molecules which are not included within macrocyclic cavities form tetrameric stacks which are intercalated between two calixarene molecules. Such packing show similarities to intercalating phenanthroline in DNA and confirm the possibility of using calixarenes as models of enzymes and biomimetics.

In the presented crystal structures structural motifs such as layers, columns and capsules are observed. Three-dimensional network of channels which appear in the crystal structures are partially filled with water molecules. The resulting supramolecular structures may have potential applications as stabilizers and carriers of biomolecules, and also as nanoporous materials.

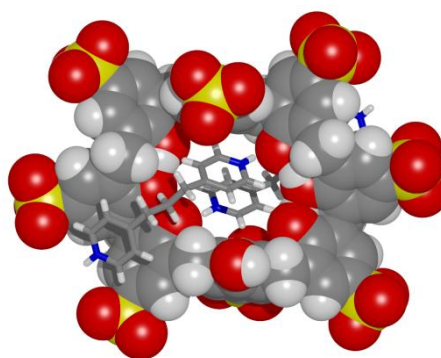


Fig. Host-guest complex of *para*-sulfonatocalix[8]arene with 1, 3-bis (4-pyridyl)-propane (1:2 stoichiometry).

Investigating solution properties of supramolecular nanoassemblies

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The use of solid-state structural knowledge to aid in the understanding of solution structure and behaviour has served the scientific community well for the past many years. However, with the advent of the application of complex supramolecular architectures in solution, solution structure must be evaluated by newer techniques in addition to solid-state models.^[1] More recently, we have used solution structures to guide the solid state studies by employing quasi-elastic light scattering, elastic scattering (small-angle neutron scattering) and diffusion NMR studies.^[2] Solutions structure of fragile supramolecular aggregates, such as ellipsoidal geometry of copper-seamed C-heptadecylpyrogallol[4]arene hexameric nanocapsule and the tubular architecture of iron-seamed C-methylpyrogallol[4]arene, are excellent examples of species that are difficult to crystallize.^[3] The results obtained have served as a guide to deduce the relation between solid-state structure and solution geometries. The guiding principle in determining the stability of solution structures has been the solvent, temperature, concentration or pH conditions.^[3a, 4] Future studies entail the use of solution conditions and geometries to isolate the supramolecular aggregates in solid state.

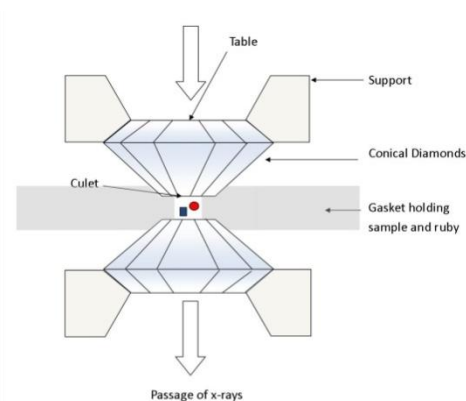
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Structure of Supramolecular Solids under High Pressure

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High pressure structural studies have seen an increase in interest in recent decades due in large part to improvements in the accessibility of such extreme conditions thanks to advancements in both equipment and methodology. Diamond Anvil Cells (DACs), a descendant of Bridgman's original opposed anvil cell [1], provide an efficient and ostensibly simple method for taking single crystal samples to high pressures, although this construct comes with its own set of drawbacks, in data collection and treatment [2]. Facilities at Durham University have been developed with extreme conditions in mind, one machine, XIPHOS II, having a Ag-K α generator specifically for samples to be studied at high pressure [3]. DACs and XIPHOS II have been used to investigate a range of supramolecular solids, ureas in particular, as examples of extensively hydrogen bonded structures which are susceptible to structural distortion upon a change in environment. In addition to this, single crystals of some common Active Pharmaceutical Ingredients (APIs) have been screened for changes in crystal structure at elevated pressures.



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Supramolecular Gels: Versatile Growth Media for Pharmaceutical Polymorphs

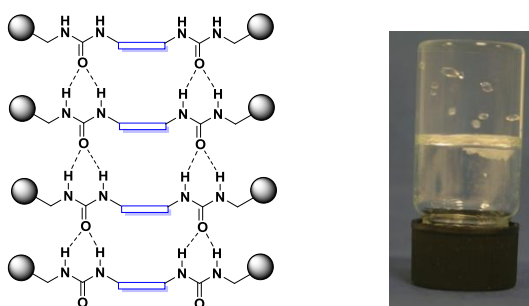
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The control of the solid state properties of drug substances is of tremendous importance to the pharmaceutical industry. The first preparation of hard-to-nucleate polymorphs is an ever present issue and even after the discovery of a range of possible forms it can remain challenging to selectively crystallise the most desirable form chosen for further development. Hydrogels,[1] particularly based on polymers have been used to crystallise a range of substances however the crystallization of molecular organic compounds such as pharmaceuticals from low molecular weight organogels is highly underexplored although Coquerel and coworkers have obtained two polymorphs of the drug ($\pm$)-modafinil from a hydrogel medium [2]. Recently, our group has reported a novel polymorph discovery technique involving drug crystal growth in supramolecular organogels [3].

In this work, we are exploring the structural correlation between the drug fibrils and pharmaceutical compounds. We have designed gelators based on bis-urea backbone and introduce complementary functional group similar to the target drug with a view to providing a template for epitaxial crystallization.



Crystal habit modification was observed in metronidazole upon crystallising from gels designed to mimic the drug substance chemical structure. These results indicate that tailored Supramolecular gels can act as templates, and interact with the drug solute potentially to initiate the nucleation of novel polymorphs and bring about new morphologies.

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Functional coordination cages: Shape control and light-switchable guest binding

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Self-assembled coordination cages have found applications in fields such as specific selective guest recognition and transportation, stabilization of active substances and intermediates, catalysis and material science. Our current research interests include the rational design and construction of new coordination cages with shapes beyond the Platonic or Archimedean solids, unusual topologies [1], and switchable functions such as structural conversion upon guest inclusion [2] or light-triggered guest binding and release [3].

Two systems of our ongoing studies will be presented:

(I) By manipulating the coordination denticity and direction of pyridyl ligands based on a dibenzosuberone backbone and Pd^{2+} ions, we can successfully reduce the symmetry from one cubic cage Pd_6L_{12} into another face-centered square cuboid Pd_6L_8 , which comprises two topologically different and non-interfering sets of $\text{Pd}(\text{pyridine})_4$ coordination environments.

(II) Based on photoswitchable dithienylethene (DTE) units and *square-planar*-coordinated Pd^{2+} ions, we were able to obtain a light-triggered photochromic coordination cage system $[\text{M}_2\text{L}_4]$, in which all four ligands exhibit reversible interconversion between a conformationally flexible “open-ring” form and a rigid “closed-ring” form under alternating irradiation wavelengths (Figure 1a). This light-driven interconversion of the cages provides us full dynamic and reversible control over the uptake and release of suitable guests, such as the spherical anion dodecafluorododecaborate $[\text{B}_{12}\text{F}_{12}]^{2-}$ (Figure 1b).

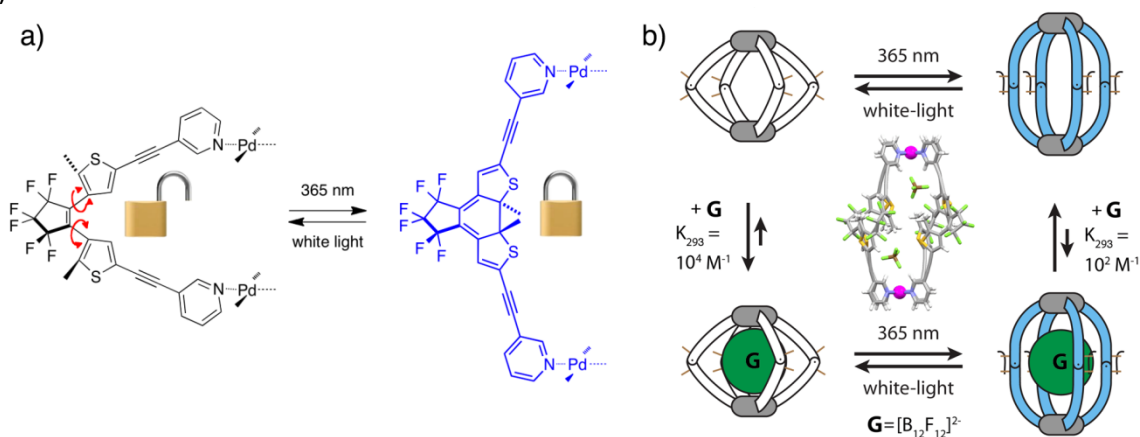


Figure 1. a) Chemical structure of the switching process and b) light-triggered uptake and release of anionic guests of a photochromic coordination cage (inset: X-ray structure of the “open-ring” cage).

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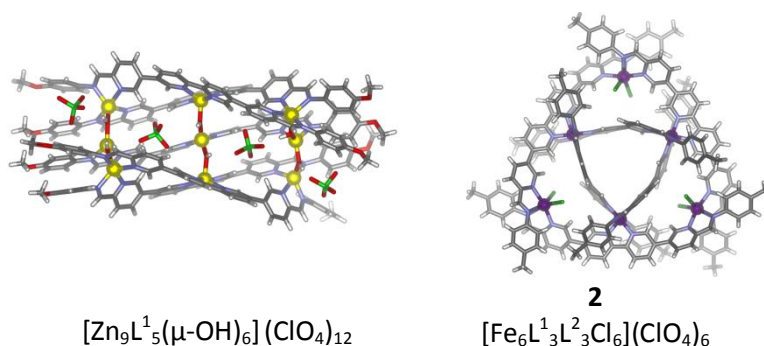
A tridentate ligand for the synthesis of diverse metal-organic structures

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The dynamic covalent pyridyl imine motif combined with metal coordination, termed “subcomponent self-assembly”, is a powerful tool that has been used in the synthesis of varied metal-organic polyhedra [1]. These structures display a diverse range of host-guest chemistry that has been applied to produce systems capable of molecular recognition [2], reactivity modulation [3], and catalysis [4]. The aim is now to increase the range of shapes, sizes and chemical functionalities available in order to increase the functions that can be performed by these systems.



To this end an extended rigid ligand containing a bipyridine binding site was designed and synthesised envisioning the formation of more complex metal-organic architectures. The reaction of this ligand, $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 4-methoxyaniline produced **1** a twisted helical assembly containing three $(\text{Zn}_3(\mu\text{-OH})_2)$ units bridged by five ligands. The structure contains a hydroxide lined groove with four bound perchlorate anions. Further investigations into mixed ligand systems using previously reported [2,2'-bipyridine]-5,5'-dicarbaldehyde [5] produced **2** which comprises of two circular helicates linked by coordination to the three central bipyridine sites of the larger helicate. These structures exhibit complex topology and provide potential binding sites whose shape hints at the possibility of binding DNA or RNA bases.

In conclusion we have demonstrated that this long ligand which incorporates multiple geometrically frustrated metal binding sites produces a range of unexpected but highly complex metal-organic structures. Studies are underway to investigate the factors involved in their formation and potential functions derived from their structure.

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Unusual Benzofuran Resorcinarene - Structural and Spectroscopic Properties

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Resorcinarene bis- and mono-crown ether derivatives with varying alkyl chain lengths ($R = C_nH_{(n+1)}$, $n = 1-5$ and $9-11$) have previously been shown to form complexes with alkaline and transition metals, as well as, with biologically active acetyl choline.[1]-[3] In addition, silver complexes of the long alkyl chain derivatives have also been proven to be applicable to form antibacterial coatings.[4]

Crown ether bridging of ethyl tetramethoxy resorcinarene in the presence of a base in DMF produces both resorcinarene mono-crown and bis-crown derivatives but also an intriguing and previously unknown third product, namely resorcinarene mono-crown benzofuran (**MC5Bf**), having benzofuran ring fused into the resorcinarene core (Figure 1).[5] Herein, we report the synthesis and unique structural properties of **MC5Bf**, which were studied using NMR spectroscopy and X-ray diffraction. The formed benzofuran ring in the resorcinarene core caused the resorcinarene skeleton to adapt a severely twisted boat conformation, and the modified resorcinarene core was also observed to show improved fluorescent properties at certain excitation wavelengths compared to the mono-crown derivative indicating a possible use, for example, as a fluorescent marker. 1D and 3D steady-state excitation and emission fluorescence spectra were measured in different solvents showing three fluorophores with characteristic fluorescence properties.

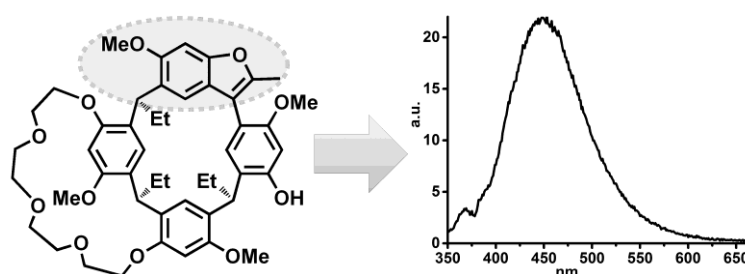


Figure 1. Structure and fluorescence spectrum (solvent: THF) of **MC5Bf**.

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Supramolecular Architectures with CTVs: Cryptophanes, Catenanes and Coordination Cages

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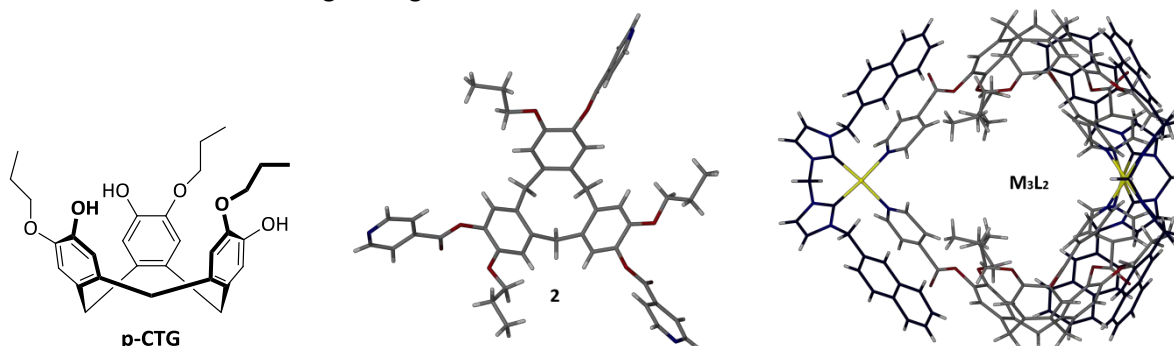
Cyclotrimeratrylene (CTV) is a rigid, bowl-shaped cavitand with intriguing host-guest capabilities.^[1] Rational design and functionalisation of the chiral, *tris*-hydroxy analogue, cyclotriguaiacylene (CTG) affords ligands that are capable of self-assembling with suitable metal tectons into a wide range of metallo-supramolecular architectures, often with a high degree of control. Complexes include capsules and cages,^[2] various 1, 2 and 3-dimensional coordination polymers,^[3] and topologically non-trivial constructs, such as knots^[4] and catenanes.^[5] Such species highlight interesting properties and applications, including gas storage and sequestration, anion recognition, and catalysis.^[6]

We report herein the preparation and crystallographic elucidation of a number of architectures, of increasing complexity, based on dual-functionalised ligands bearing secondary, solubilising moieties, where the constructs described are not accessible with the parent, methylated ligands. Ligands **1-3** were synthesised from a novel, propylated cyclononatriene core, **p-CTG**, which allows for the use of less coordinating solvents, thus facilitating the formation of discrete assemblies.

The self-assembly of **1** (*tris*(nicotinoyl)**p**-CTG) with silver (I) cations results in the formation of a M_2L_2 dimer, $[Ag_2\mathbf{1}_2] \cdot 2PF_6$, where formation of the M_3L_2 head-to-head capsule is unfavoured due to sterics. The metallocryptophane, however, was identified when using a heteroleptic mixture of **1** and its methylated congener.

Formation of the M_3L_2 metallocryptophane, $[Pd_3(aux)_3\mathbf{2}_2] \cdot 6BF_4$, was achieved through self-assembly of **2** (*tris*(isonicotinoyl)**p**-CTG) and *cis*-protected palladium (II) salts. Nitrogen based auxiliary ligands were unsuitable and thus synthesis of stable metallo-cryptophanes was effected using *cis*-chelating *bis*(NHCs) as the kinetically inert auxiliary ligands. The metallo-cryptophanes formed were highly stable and displayed simple host-guest chemistry in solution. Degradation of the M_3L_2 metallocryptophanes, when using nitrogen-based auxiliaries, resulted in the formation of a stellated, octahedral coordination cage, $[Pd_6\mathbf{2}_8] \cdot 12BF_4$. Homo- and heteroleptic cage studies were undertaken which highlighted an inherently stable cage, that did not self-sort once formed. The larger cage was also seen to interact with guests, such as *o*-carborane and sodium dodecyl sulfate.

Quinolyl-derived ligand **3** (*tris*(2-quinolylmethyl)**p**-CTG) was seen to form a tetrameric complex with palladium (II) centres, $[Pd_6\mathbf{3}_4] \cdot 12CF_3CO_2$. In contrast to the previous species, the assembly is flat and formed through clathrate-type behavior and π - π interactions. Crystal packing results in large, uni-directional channels running through the extended lattice.



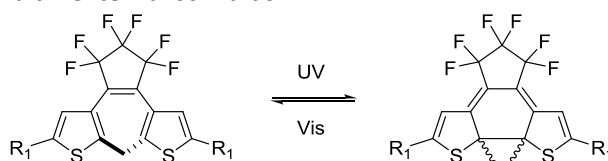
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Towards Photoswitchable Thiophene Metal-Organic Frameworks

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The establishment of porous materials for the storage and separation of gasses represents an important undertaking, with widespread academic and industrial research into their properties and production. A popular approach has been the use of metal organic coordination complexes, due to the reliability and directionality of known metal organic interactions.[1] While many porous systems have been successfully engineered, the development of increasingly sophisticated materials capable of selective gaseous uptake or possessing tunable functionality remains high,[2] specifically where porosity can be altered via an external stimulus.



The ring-opening ring-closing photochemically induced isomerisation of thiophene substituted diarylethene systems display both remarkable photochemical conversion as well as durability in the reversibility of the reaction (Scheme).[3] This isomerisation has also been shown to produce rapid shape changes in the solid state.[4] We present our efforts towards the synthesis of diarylethene metal-organic frameworks, and the study of their porosity and photochemically induced transformations.

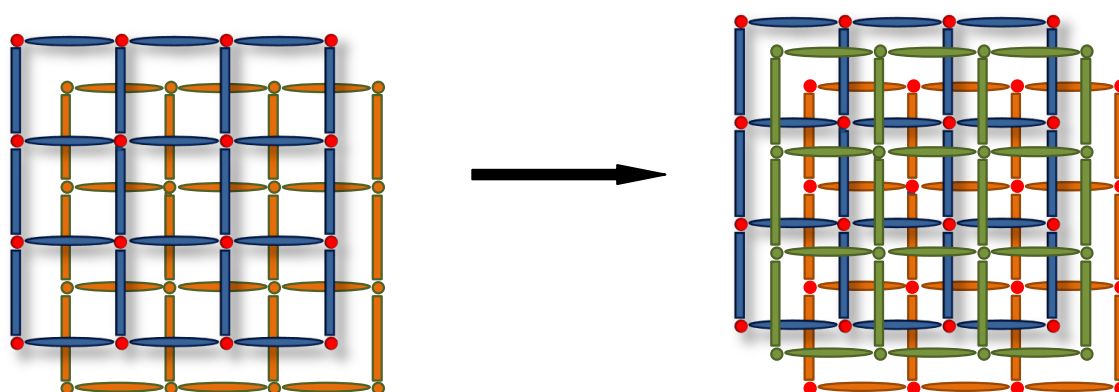
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Role of Single Crystal to Single Crystal Transformations in Crystal Engineering

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Single-crystal to single-crystal transformations have recently received much attention in the field of crystal engineering. Such transformations not only provide insight into the changes taking place within the crystal at the molecular level, but they also aid our understanding of the structure-property relationships. Most of the reports thus far have involved dimerization or polymerisation of molecules or guest exchange in porous frameworks. However, there are rare examples of the structural transformations on the host framework initiated by removal of guest or change in physical conditions such as temperature or pressure. This contribution will highlight recent work involving single-crystal transformations that occur via labile and transient changes in coordination geometry of transition metal based coordination polymers.



Oxacalix[4]arenes as Metal Cluster Supports

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Methylene-bridged calix[4]arenes have recently emerged as versatile bowl-shaped ligands for the formation of novel polynuclear metal clusters. We have utilised *p*-^tBu-calix[4]arene (TBC4) and other related calix[4]arenes for the construction of such clusters that possess interesting magnetic properties [1]. Their recent studies have generated, among others a family of enneanuclear Cu^{II} tri-capped trigonal prismatic clusters, supported by three TBC4s, that act as versatile anion binding materials depending on the copper salt employed during synthesis [2]. More recently we have reported the formation of a series of calix[4]arene-supported Ln^{III}₆ clusters, which is the first polynuclear lanthanide cluster to be synthesised with TBC4 [3].

In contrast, the homooxacalix[4]arenes have received limited attention as candidates for complexation studies which is surprising as they possess a more flexible framework than their methylene bridged analogues and contain two different types of binding site with the propensity to incorporate metal ions. Two ligands from this family of molecules were synthesised in anticipation of preparing new polynuclear clusters; Mono-homooxa-*p*-^tBu-calix[4]arene (H4L1) (figure 1A) and tetra-homodioxo-*p*-^tBu-calix[4]arene (H4L2) (figure 1B) were reacted with copper nitrate and a series of lanthanide salts. This resulted in the formation of three copper and three lanthanide clusters [4]. These structures have been characterised by X-ray crystallography as well as other methods. In all cases the oxacalix[4]arene adopts the cone conformation, and the resulting complexes display interesting binding properties depending on the metal salt employed during synthesis.

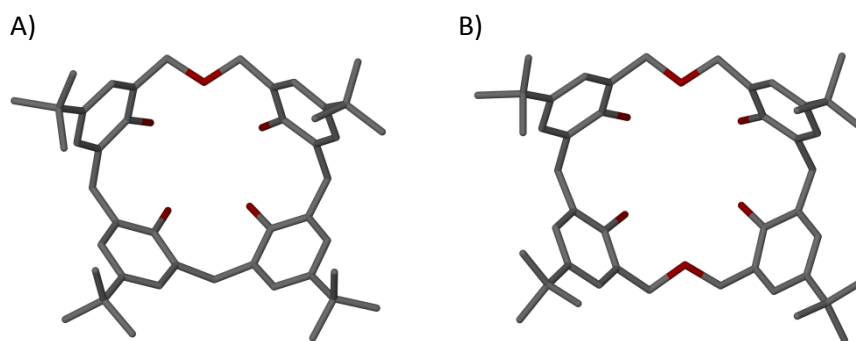


Figure 1. A) Homooxacalix[4]arene, H4L1. B) Homodioxacalix[4]arene, H4L2.

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Spin-Crossover 'Click' Coordination Capsules

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Over recent years, there has been significant interest in coordination-driven supramolecular cages and capsules, particularly in relation to the functions or properties that they possess, as a result of their well-defined cavities.[1–3]

Here we will discuss the design, synthesis and properties of a series of M_4L_6 -type tetrahedral cages based on bis-(pyridyl-triazole) ligands. As well as providing a coordination site, the kinetically-robust triazole linkage also permits easy access to a range of capsules with different external groups, and therefore ensembles with modifiable properties (e.g. solubility or bio-targeting features). In the case of the iron (II) compound (Figure 1), both NMR spectroscopy and SQUID measurements have shown that spin-crossover phenomena is exhibited in both solution and the solid state. Routes to similar metallocupramolecular assemblies with substitutionally-inert transition metal ions are also discussed.

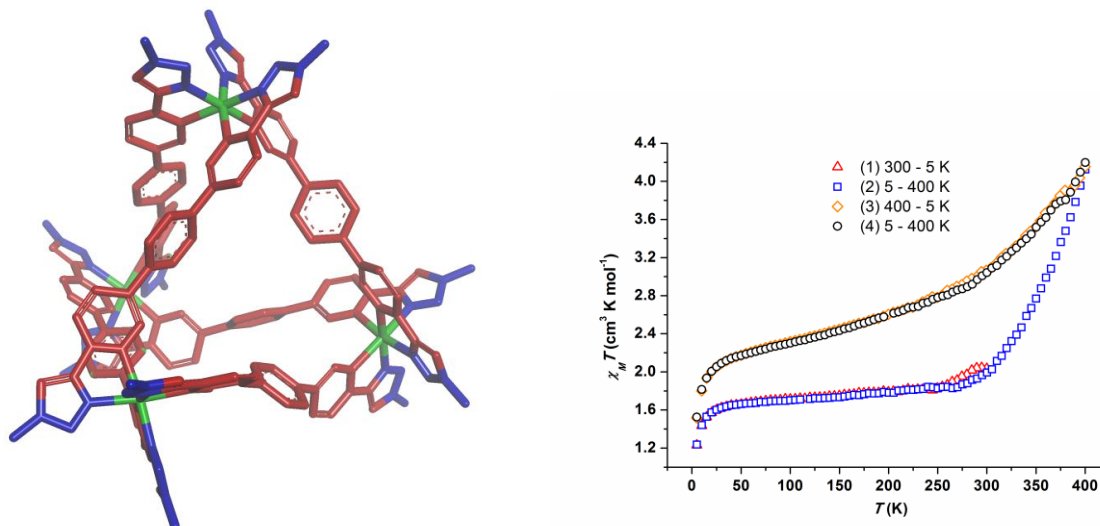


Figure 1: Molecular model of Fe_4L_6 pyridyl-triazole tetrahedron and a plot of $\chi_m T$ vs. T .

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- [2] P. Mal, B. Breiner, K. Rissanen, J. R. Nitschke, *Science* 2009, **324**, 1697.
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Metal-directed assembly of coordination polymers and molecular capsules

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The controlled formation of multi-component nanostructures is a persistent challenge of both supramolecular chemistry and crystal engineering, primarily because of the need to simultaneously control numerous different intermolecular interactions. Calix[4]arenes have been widely used in these fields of research due to their synthetic accessibility, cavity that can be used in host-guest chemistry and possibility of introducing functionality to the general molecular framework.¹ However, surprisingly the p-carboxylatocalix[n]arenes (pCO₂[4]s) have not yet been exploited in the formation of coordination polymers (CPs) and metal-organic frameworks (MOFs), especially considering that the resulting structures may potentially be tailored so as to present unique host cavities for use in gas sorption and separation (amongst other things).

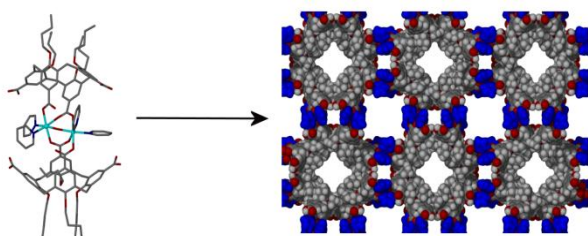


Fig. (1): Bi-nuclear TM pCO₂[4] cluster that assembles into metal-organic nanotubes due to tilt in the constituent building block.

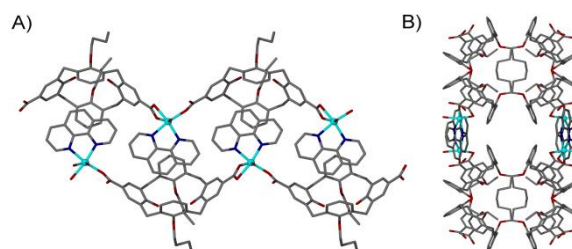


Fig. (2): A) Neighbouring interweaving CP chains B) Extended structure showing tilt between CPs - formation of nanotubes.

Our group have already demonstrated, that by using pyridine, a high degree of control over self- and metal-directed assembly of pCO₂[4]s can be achieved.² With the use of pyridine, through complementary non-covalent interactions, a sufficient tilt angle to the metal cluster is invoked, forcing nanotube assembly in the solid state. In the presentation we will present a rational approach towards the construction of versatile CPs / MOFs from nanoscale panels comprising transition metals such as Mn²⁺, Co²⁺ and Cd²⁺, pCO₂[4]s and various bipyridyl linkers.³ We will also demonstrate a new method of accessing novel metal-organic porous materials with the use of TM, chelating ligands and pCO₂[4]s.⁴

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[3]. P. P. Cholewa, C. M. Beavers, S. J. Teat and S. J. Dalgarno, *Cryst. Growth Des.*, 2013, **13** (7), 2703.

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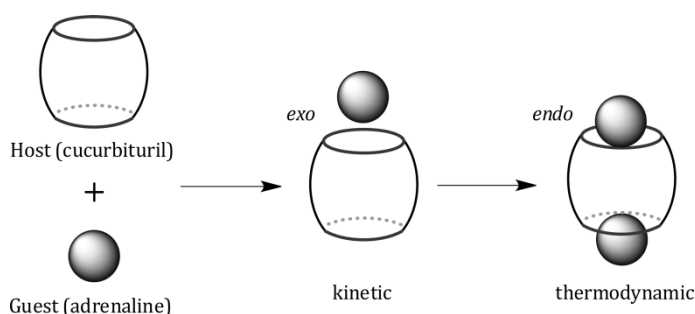
Supramolecular Host-Guest Assemblies of Cucurbituril: Kinetic Trapping and Phase Transformations

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Slow kinetics of supramolecular self-assembly allows unique insight into host-guest complexation mechanism and enables observation and characterization of individual supramolecular transformation steps. The molecular recognition and self-assembly between host cucurbit[6]uril and cationic adrenaline as guest lead to kinetic trapping and crystallization of intermediate exclusion complex, which was characterized by X-ray diffraction. [1] The crystalline kinetic complex undergoes slow spontaneous dissolution and subsequently recrystallizes as thermodynamic inclusion complex. The isolation and structural characterization of both complexes enabled to reproduce the each step of the inclusion process, thus, to ultimately confirm the predicted two-step complexation model for cucurbit[6]uril host-guest systems with organic cations. [2] In the case of neutral adrenaline the direct crystallization of inclusion complex with cucurbit[6]uril was observed. In strongly acidic conditions the inclusion complexes with oligomerized adrenaline were obtained due to condensation reaction between adrenaline molecules. The high degree of structural diversity in quite simple host-guest system is interpreted in terms of different non-covalent interactions involved in the assembly process as well as the influence of supramolecular reaction conditions.



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Electroluminescence and heat-set gelation in a series of dynamic-covalent metallo-polymers

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Unlike conventional polymers which are irreversibly formed, supramolecular polymers can reform and reconfigure their structure and properties in response to stimuli. We report a series of dynamic-covalent metallo-polymers that are readily synthesised by the condensation of linear diamine and dialdehyde subcomponents around copper(I) templates in the presence of bidentate phosphine ligands. When fabricated into light-emitting electrochemical cells (LECs) the polymers show electroluminescence, making them part of an increasingly important class of LEC device not dependent on expensive, earth-scarce elements such as platinum(II), iridium(III) and osmium(II).[1]

The devices emit red light when a low bias is applied but undergo a hypsochromic shift in emission as the voltage is increased, eventually emitting yellow light. In solution, the red polymers undergo a sol-gel transition upon heating to form a yellow gel which shows rapid self-healing behavior. The mechanism underlying these apparently disparate responses is deduced to be due to a rearrangement of ligands at the copper centres.[2] The distinct changes in photophysical and rheological properties observed as a result of rearrangement of the polymer system holds potential for use in a variety of sensing, imaging and information storage applications.

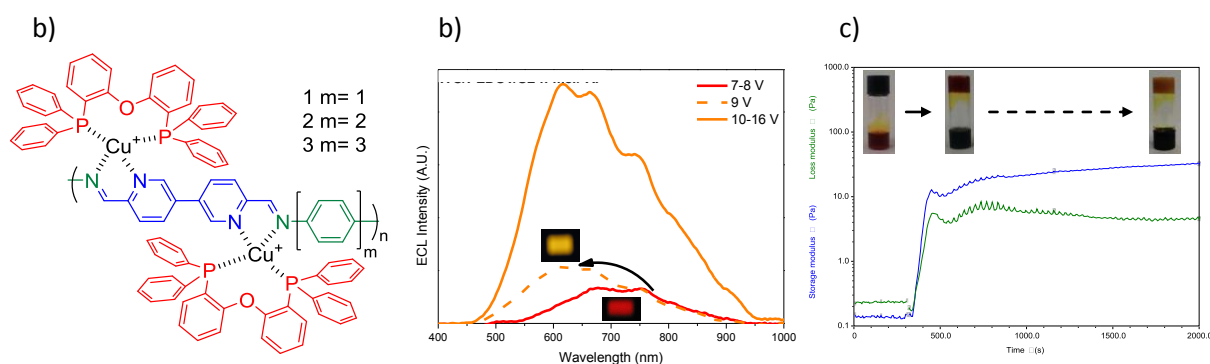


Figure 1. A series of dynamic-covalent metallo-polymers (a) show a hypsochromic shift in electroluminescent emission with increasing voltage (b) and the formation of self-healing gels at high temperatures (c).

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[2] X. de Hatten, N. Bell, N. Yuffa, G. Christman, J. R. Nitschke, *J. Am. Chem. Soc.*, 2011, **133** (9), 3158

Microporous crystals of Trianglimine

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Porous solids such as zeolites, metal–organic frameworks and organic polymer frameworks have excited much interest for many years due to their great potential in gas storage/separation and catalysis applications.[1] Purely molecular porous systems remain more scarce than in the metal–organic area because such discrete molecules tend to pack in the most efficient manner and hence their design is more challenging and unpredictable.

Here we report on the cyclic organic host trianglimine [2], which assembles into a microporous pillared structure with isolated 1D channels passing through the inner cavity. The investigated macrocycle was obtained in a [3+3]-cyclocondensation reaction between *trans*-1,2-diaminocyclohexane and terephthalic aldehyde with creation of a relatively rigid skeleton. The utilization of the fixed geometry of the building blocks in its construction allows full control over its shape and size of its inner cavity. These features make trianglimine a promising compound for the inclusion of small and medium sized organic molecules and for gases sorption. The structural features of trianglimine have been studied using a variety of analytical methods.

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Self-assembled Metal-Organic Capsules: Structure and Host-Guest Properties

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The study of hollow self-assembled polyhedral metal-organic cages within the wider context of container molecules has been a topic of great interest in recent years. These structures' selective guest encapsulation properties have led to their application in trapping and stabilising unstable species, separation of gases and fullerenes, the discrimination of chiral guest species and as catalysts and photoreactors. We have reported the formation of a variety of different three-dimensional metal-organic container molecules using *subcomponent self-assembly*, which relies upon metal template effects to generate complex structures from simple molecular precursors through the formation of both dynamic-covalent (C=N) and coordinative (N→M) linkages in a single reaction step.^[1] We will show how the properties of M_4L_6 tetrahedra^[2-3] can be altered through variation of the subcomponents employed and larger more complex and less symmetric architectures^[4] can be prepared that offer new and useful functionality.

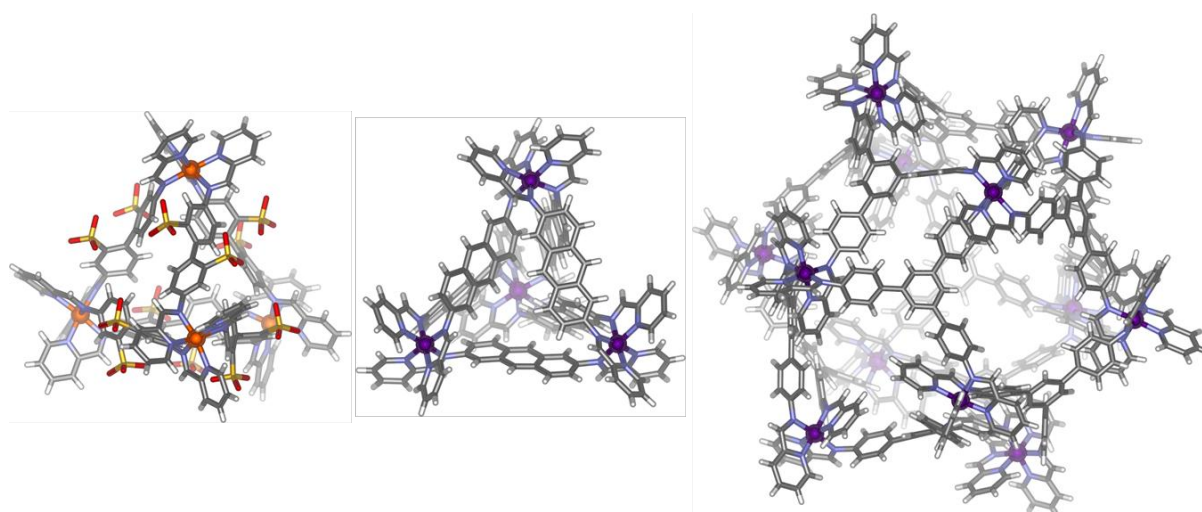


Figure 1: Examples of self-assembled architectures prepared through *subcomponent self-assembly*.

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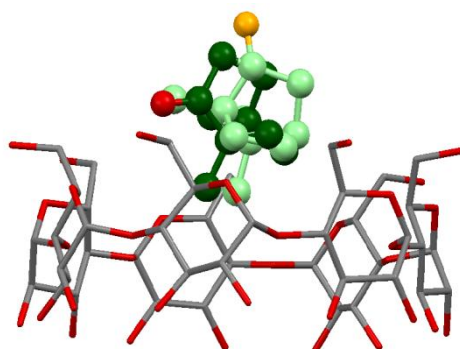
β -cyclodextrin as a Suitable Molecular Container for Camphor Enantiomers

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Camphor belongs to the family of terpenoids and exists in two enantiomeric forms. As it undergoes rapid sublimation, its usage is limited. One of the possibilities to decrease the volatility of the compound is the formation of complexes with macrocyclic receptors. Cyclodextrins are macrocyclic carbohydrate compounds, torus-like shaped consisting of glucopyranose units combined by 1,4-o-glycosidic bonds. They are widely known for their complexing properties towards large number of inorganic and organic compounds.

In the present study, the formation of the molecular complexes of β -cyclodextrin with (-)-camphor and (+)-camphor is reported. The desired compounds were obtained by addition of methanol solution of (-)- or (+)-camphor to the water solution of β -cyclodextrin (1:1 molar ratio). Stoichiometry of both diastereomeric complexes is 1:1. Both of the crystal structures reveal that one guest molecule is accommodated inside the cavity of β -cyclodextrin molecule.



This research was partly financed by the European Union within the European Regional Development Fund (POIG.01.01.02-14-102/09)

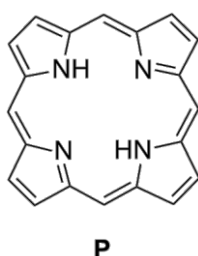
A Computational Study of Macrocycles and their Excited States

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The most common supramolecular units present in nature are without a doubt the Porphyrin family of macrocycles. Free base porphyrins, as well as complexed to guest metals, are building blocks that have been known and manipulated for nearly a century[1]. This is especially true when it comes to the investigations of compounds with accessible photochemical pathways. The porphyrinic macrocycle has an intriguing structure that can be tuned in photochemical activity with relative synthetic ease. From dye-sensitized solar cells to biological imaging agents and Photodynamic Therapy (PDT); Porphyrins are the go-to photochemical starting point [2,3].



As the field of computational chemistry has developed, so has the ability to model the ground state potential energy surfaces and reaction profiles for compounds of the size of porphyrins. When it comes to the excited states of porphyrins, the development of new functionals for use in Time-Dependent (TD) Density Functional Theory (DFT) has made it possible to investigate both linear and non-linear absorption processes in compounds as large as porphyrins [4]. This is true even for porphyrins with large substituents, as well as complexed to a guest metal [5,6].

This talk will present the use of TD-DFT to replicate absorption spectra in porphyrinic macrocycles, both for linear and non-linear absorption, and show examples of how computation can be used to investigate, and predict, absorption characteristics. This will be done from the viewpoint of PDT applications, in biological environment.

Further, this talk will go on to describe the methods available for characterisation of excited states of these compounds, as well as investigations into the relaxation pathways available.

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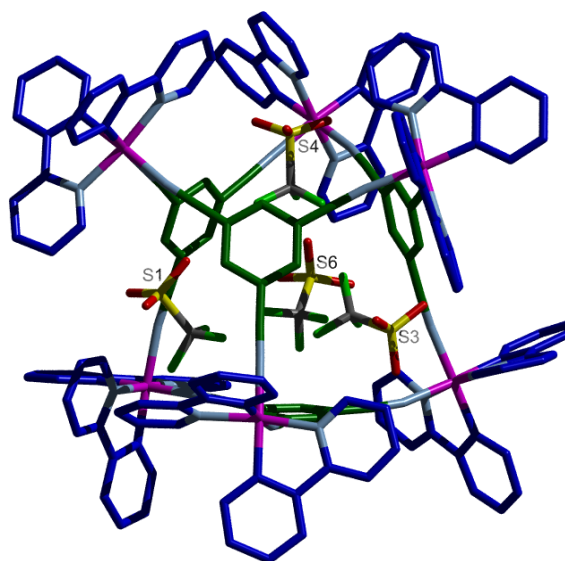
Photoactive Iridium-Based Supramolecular Capsules

Oleg Chepelin, Paul J. Lusby*

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The combination of transition metal ions and geometrically complementary, multitopic bridging organic ligands has led to the preparation of numerous molecular capsules and cages.[1] These assemblies possess well-defined internal cavities that promote the ingress of *guest* molecules so that interesting functions, such as catalysis or the stabilisation of reactive species may be observed. By and large, the transition metal ions within these systems have played solely a structural role, offering advantages such as predictable, well-defined coordination preferences and bond strength. However, transition metals and their complexes often possess many other notable features, such as interesting photophysical properties. Although several examples of metallocycles, dendrimers and helicates exist in literature, the use of Ru poly(pyridyl) or cyclometalated Ir complexes as structural components in metallosupramolecular assemblies, in particular polyhedral architectures, remains rare.[2]

Here we present the first molecular capsule based on an $[\text{Ir}(\text{ppy})_2]^+$ unit (ppy = 2-phenylatopyridine).[3] Following the development of a method to resolve rac- $[(\text{Ir}(\text{ppy})_2\text{Cl})_2]$ into its enantiopure forms, homochiral Ir_6L_4 octahedra where assembled with the tritopic 1,3,5-tricyanobenzene ligand. The self-assembly process has been demonstrated to be guest template driven with a number of different anions (OTf , BF_4 , ClO_4 , PF_6) facilitating the formation of the same octahedral scaffold. Subsequent experiments have also shown that the self-assembly and stability of these scaffolds are highly dependent on the counterions located within the capsules' cavity and that an ensemble of cooperative, weakly coordinating ligands can lead to luminescence not present in comparative, mononuclear analogues.



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- [1] For a comprehensive review on molecular capsules, see a) R. Chakrabarty, P. S. Mukherjee, P. J. Stang, *Chem. Rev.*, 2011, **111**, 6810-6918. For examples of molecular capsules which use cyclometalated corner groups, see b) P. J. Lusby, P. Müller, S. J. Pike, A. M. Z. Slawin, *J. Am. Chem. Soc.*, 2009, **131**, 16398-16400; c) O. Chepelin, J. Ujma, P. E. Barran, P. J. Lusby, *Angew. Chem. Int. Ed.*, 2012, **51**, 4194-4197.
- [2] For examples of multinuclear metallosupramolecular assemblies based on an $[\text{Ir}(\text{ppy})_2]^+$ motif, see a) E. Baranoff, E. Orselli, L. Allouche, D. Di Censo, R. Scopelliti, M. Grätzel, M. K. Nazeeruddin, *Chem. Commun.*, 2011, **47**, 2799-2801; b) V. Chandrasekhar, T. Hajra, J. K. Bera, S. M. W. Rahaman, N. Satumtira, O. Elbjeirami, M. A. Omary, *Inorg. Chem.*, 2012, **51**, 1319-1329.
- [3] O. Chepelin, J. Ujma, X. Wu, A. M. Z. Slawin, M. B. Pitak, S. J. Coles, J. Michel, A. C. Jones, P. E. Barran, P. J. Lusby, *J. Am. Chem. Soc.*, 2012, **134**, 19334-19337.

Structural characterization of inclusion complexes of *para*-sulfonatocalixarenes

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Water-soluble *para*-sulfonatocalixarenes have a high ability to form complexes with molecules containing nitrogen atoms: 1,2-bis(4-pyridyl)-ethane and 1,3-bis(4-pyridyl)-propane, 1,10-phenanthroline. The host-guest complexes formed by these compounds are stabilized mainly by π - π interactions between aromatic rings of guest molecules and aromatic rings of calixarene molecules. The contribution of C-H $\cdots$ π interactions in the inclusion complexes formation is of minor importance. Additionally, in the complex of *para*-sulfonatocalix[8]arene with 1,3-bis(4-pyridyl)-propane the inclusion is stabilized by one N-H $\cdots$ O hydrogen bond.

Large molecule of *para*-sulfonatocalix[8]arene may form molecular complex with two or more guest molecules. A flexible molecule of this calixarene easily adapts its conformation to the shape of guest molecules. Additionally, guest molecules with some degrees of freedom like 1,2-bis(4-pyridyl)-ethane and 1,3-bis(4-pyridyl)-propane also adapt their conformation to the shape of calixarenes. In this paper we report new conformations of *para*-sulfonatocalix[8]arene which are not described yet in the literature.

para-Sulfonatocalix[6]arene forms 1:2 complex with phenanthroline. Additional four guest molecules which are not included within macrocyclic cavities form tetrameric stacks which are intercalated between two calixarene molecules. Such packing show similarities to intercalating phenanthroline in DNA and confirm the possibility of using calixarenes as models of enzymes and biomimetics.

In the presented crystal structures structural motifs such as layers, columns and capsules are observed. Three-dimensional network of channels which appear in the crystal structures are partially filled with water molecules. The resulting supramolecular structures may have potential applications as stabilizers and carriers of biomolecules, and also as nanoporous materials.

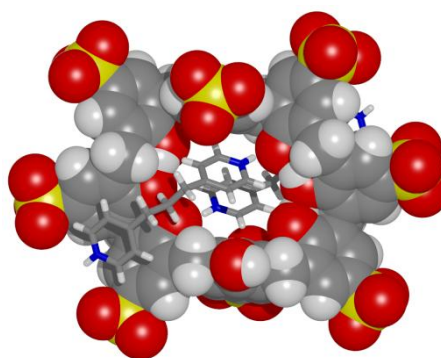


Fig. Host-guest complex of *para*-sulfonatocalix[8]arene with 1, 3-bis (4-pyridyl)-propane (1:2 stoichiometry).

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