

# Welcome

The scientific and organizing committees are glad to welcome all participants to the 2nd Meeting on Porous Molecular Solids.

Following the successful 1<sup>st</sup> POMOS meeting in April 2015 in Stellenbosch, the conference is a friendly gathering of students, post-docs and principal investigators to share the latest advances and boost the progress in the field of porous molecular materials.

Invited lectures, selected oral contributions and a poster session will give the opportunity to discuss the state of the art in this fruitful and promising field of research.

The topics to be discussed will focus on the design and synthesis of porous molecular solids, their structural characterization, the analysis of the chemical and physical properties. To allow a proper comparison specific sessions will be dedicated also to porous polymers and MOF based materials.

A lot of people contributed to the success of this meeting.

First of all we thank all the scientists, coming from all over the world, who accepted to give keynote lectures or submitted oral or poster presentations. We are sure that all the contributors will provide interesting and stimulating ideas for future research and projects.

Then, we would like to thank all the institutions and companies, who financially supported the meeting. To all participants, we warmly wish a fruitful and pleasant stay in Vietri sul Mare.

For the Scientific and Organizing Committees,

Leonard J. Barbour  
Stellenbosch University  
South Africa

Consiglia Tedesco  
University of Salerno  
Italy

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# Meeting policy

## EQUALITY, DIVERSITY AND INCLUSION

The organizing and the scientific committees of the 2nd Meeting on Porous Molecular Solids adopt the fundamental principles of nondiscrimination and equality and will make every effort to apply them through inclusion policies.

# International Union of Crystallography

## IUCr Scientific Freedom Policy Statement

The Organizing Committee of the 2nd Meeting on Porous Molecular Solids shall observe the basic policy of non-discrimination and affirms the right and freedom of scientists to associate in international scientific activity without regard to such factors as ethnic origin, religion, citizenship, language, political stance, gender, sex or age, in accordance with the Statutes of the International Council for Science. At this meeting no barriers will exist which would prevent the participation of bona fide scientists.

June 6th 2018, Vietri sul Mare

The Organizing Committee

# Programme

## Wednesday June 6th 2018

14:00-15:15

Registration

Opening  
ceremony

chair **C. Tedesco & L. J. Barbour**

15:15-15:30

**Prof. P. Neri**  
University  
Salerno

of Head of the Dept of Chemistry and Biology "A. Zambelli"

Session I

chair **G. Guerra**

15:30-16:00

**L. J. Barbour**  
Stellenbosch  
University

Structural flexibility in the solid state

16:00-16:30

**K. T. Holman**  
Georgetown  
University

Closed to open pore behaviour in 0D porous molecular solids

16:30-17:00

Coffee-break

Session II

chair **L. J. Barbour**

17:00-17:30

**M. Mastalerz**  
University of  
Heidelberg

Intrinsically porous molecules for selective gas sorption

17:30-18:00

**A. I. Cooper**  
University  
Liverpool

of Porous molecular crystals: designing properties 'from scratch' using energy-structure-function maps

*IUCr & ECA Prizes Session*

chair **C. Tedesco**

18:00-18:15

**C. Beuzidenhout**  
University  
Milano-Bicocca

**X.** CO<sub>2</sub> stabilisation and phase transitions in open-channel MOFs

18:15-18:30

**I. Brekalo**  
Georgetown  
University

of Are bisguanidinium organodisulfonates formally microporous?

18:30-18:35

**I. Claassens**  
Stellenbosch  
University

Stepped sorption behaviour in a highly porous MOF

18:35-18:40 **S.-Q. Wang** High performance separation of C8 aromatics  
**Stellenbosch**  
**University**

19:30-20:30 *Welcome party*

## Thursday June 7th 2018

### *Session III*

chair **I. Izzo**

09:00-09:30 **N. B. Mckeown** Structural diversity within a reliable nanoporous molecular  
University of Milano- crystal  
Bicocca

09:30-10:00 **C. Tedesco** Dynamic architecture of macrocycles  
University of Salerno

10:00-10:15 **R. Schettini** Structural investigation of cyclic octapeptoids  
University of Salerno

10:15-10:30 **S. Quaresma** BioMOFs based on azelaic and dipyridamole as potential  
University of Lisbon systems for biomedical applications

10:30-11:00 *Coffee-break*

### *Session IV*

chair **F. De Riccardis**

11:00-11:30 **M. W. Hosseini** Chirality in molecular tectonics  
University of Strasbourg

11:30-12:00 **C. H. Görbitz** DNA-inspired porous materials  
University of Oslo

12:00-12:30 **C. Esterhuysen** Mechanisms of guest uptake in copper-based MOFs  
Stellenbosch University

12:30-13:00 **L. R. Nassimbeni** Characterisation of porous inclusion compounds  
University of Cape Town

13:00-15:00 *Buffet Lunch*

### *Session V*

chair **S. A. Bourne**

15:00-15:30 **A. Comotti** Porous supramolecular architectures: ultra-fast molecular rotors  
University of Milano- and dynamics control by chemical stimuli  
Bicocca

15:30-15:45 **N. Burtch** Negative thermal expansion design strategies in MOFs  
Sandia National  
Laboratories

15:45-16:00	<b>J. Gertenbach</b> Malvern-Panalytical	Probing porous materials using a powder diffractometer <i>Sponsored contribution</i>
16:00-16:30		<i>Poster session</i>
16:30-17:00		<i>Coffee-break</i>
17:00-17:30		<i>Poster session</i>
	<i>Session VI</i>	chair <b>P. Neri</b>
17:30-17:45	<b>V. Colombo</b> University of Milan	<i>In situ</i> crystallography over a interpenetrated MOF for CO <sub>2</sub> adsorption in humid conditions
17:45-18:00	<b>S. M. F. Vilela</b> IMDEA Energy	A novel bismuth-tetracarboxylate MOF as a proton conductor
18:00-18:30	<b>J. L. Atwood</b> University of Missouri-Columbia	Porosity of seemingly non-porous organic solids
18:30-18:40		<i>IUCr Journals Best Poster Prize</i>
19:30-22:00		<i>Banquet Dinner</i>

## Friday June 8<sup>th</sup> 2018

	<i>Session VII</i>	chair <b>N. B. McKeown</b>
09:00-09:30	<b>G. Guerra</b> University of Salerno	Nanoporous-crystalline polymers and industrial innovations
09:30-10:00	<b>P. Sozzani</b> University of Milano-Bicocca	Porous materials: the interplay with linear polymers
10:00-10:15	<b>P. Rizzo</b> University of Salerno	Nanoporous-crystalline polymer films with unexpected high optical activity and circularly polarized luminescence

10:15-10:30	<b>L. Baldino</b> University of Salerno	From microporous to nanoporous: the role of supercritical CO <sub>2</sub> in the formation process
10:30-11:00		<i>Coffee-break</i>
	<i>Session VIII</i>	chair <b>L. R. Nassimbeni</b>
11:00-11:30	<b>M. Eddaoudi</b> KAUST	MOF design to applications: impact of pore system control on gas separations and storage
11:30-12:00	<b>S. A. Bourne</b> University of Cape Town	Guest exchange in dynamic frameworks
12:00-12:30	<b>D. A. Haynes</b> Stellenbosch University	Framework materials from ionic organic components
12:30-13:00	<b>M. Zaworotko</b> University of Limerick	Taxonomy of porous solids: a crystal engineering perspective
13:00-13:05	<i>Conclusive remarks</i>	chair <b>C. Tedesco &amp; L. J. Barbour</b>
13:05-15:00		<i>Lunch</i>
15:00-23:00		<i>Excursion</i>



## KEYNOTE LECTURES

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## Structural flexibility in the solid state

L. J. Barbour

Department of Chemistry and Polymer Science, Stellenbosch University, Stellenbosch 7600, South Africa

In order to understand solid-gas inclusion processes at the molecular level it is important to correlate physico-chemical data (e.g. sorption isotherms and calorimetric analysis) with structural data. It is therefore desirable to carry out structural elucidation and calorimetric analysis under conditions that closely mimic those of the sorption/desorption experiments. However, the crystallographic analysis of samples under controlled gas environments poses significant technical challenges, particularly given the limited space associated with the sample compartment of standard commercial diffractometer. In this regard, an environmental gas cell has been developed in parallel with a pressure-programmed differential scanning calorimeter. Use of these complementary techniques has provided new insight into features such as pressure-induced phase transformations that give rise to inflections and hysteresis in sorption isotherms. The influence of guest molecules on aspects such as structural flexibility and changes in network interpenetration will be discussed.

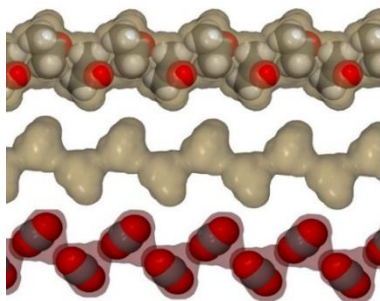


Figure 1. Perspective view showing the change in guest-accessible space upon activation, followed by CO<sub>2</sub> uptake.

## Closed to open pore behaviour in 0D porous molecular solids

K. T. Holman

Department of Chemistry, Georgetown University, Washington, DC, USA 20057

There is much contemporary interest in the development of new micro/nanoporous materials for gas capture/sequestration, separation, sensing, *etc.* Efforts have mainly been directed toward molecule-derived materials that exhibit permanent “open” pores (*e.g.*, metal-organic frameworks (MOFs), covalent organic frameworks (COFs), polymers of intrinsic microporosity (PIMs), and even intrinsically porous molecular solids (PoMoSs). Much less is understood about the properties of zero dimensional (0D) porous solids, which, in a static view of their structures, do formally possess interconnected pores, but nonetheless exhibit accessible voids/cavities of useful volume. As will be discussed, members of this growingly ubiquitous family of PoMoSs can offer several advantages: i) solution processability; ii) many are intrinsically incollapsible; iii) they are amenable to organic alloying; iv) many are low-cost materials. Moreover, by offering pores that completely encapsulate putative sorbates, they have the potential to optimize thermodynamic selectivity with respect to gas/guest capture. Additionally, the kinetics of substrate uptake and/or release can vary enormously, are largely dependent upon molecular and crystalline structure, and can therefore be engineered. The presentation will highlight studies in our laboratory concerning the design and widely varying properties of 0D PoMoSs derived from shape persistent macrocycles,<sup>[1-2]</sup> container molecules,<sup>[3]</sup> hydrogen bonded frameworks, and even some metal-organic frameworks (MOFs). It will be argued that such materials are ubiquitous, but have gone relatively unrecognized because of experimental biases.<sup>[1]</sup> The intrinsic 0D pores of these materials have been exploited for the capture, sorption, kinetic separations, and/or extreme kinetic confinement of commodity gases and other small molecules.<sup>[2,3]</sup>

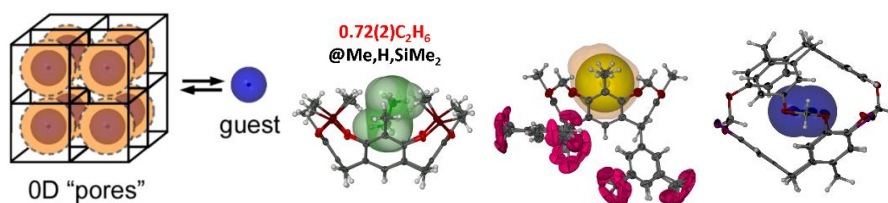


Figure 1. Various 0D PoMoSs and their gas-occupied ( $C_2H_6$ ,  $Xe$   $N_2$ , respectively) structures.

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# Intrinsically porous molecules for selective gas sorption

M. Mastalerz

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In recent years, the interest in porous materials based on discrete molecules has risen tremendously, because their solubility allows the processing of the materials into thin-films or membranes or even the construction of porous liquids.<sup>[1]</sup> Shape-persistent organic cages have been synthesized in different sizes and geometries by applying dynamic covalent chemistry (DCC). In the talk, the synthesis of cages with new geometries are presented, the influence of the precursors degree of flexibility as well as their gas-sorption properties are discussed.<sup>[2,3]</sup> Furthermore, metal-containing OMIMs (organic molecules of intrinsic microporosity) are compared to their porous polymeric counterparts.<sup>[4]</sup>

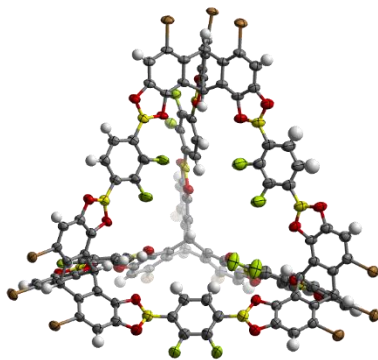


Figure 1. A tetrahedral [4+6] boronic ester cage

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# Porous molecular crystals: designing properties ‘from scratch’ using energy–structure–function maps

A. I. Cooper,<sup>1,2</sup> G. M. Day<sup>2,3</sup>

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Porous molecular crystals are an alternative to porous extended frameworks such as zeolites, metal-organic frameworks (MOFs), covalent organic frameworks (COFs), and polymer networks.<sup>[1]</sup> Interest in such systems dates to the first ‘organic zeolites’,<sup>[2]</sup> but only recently have these materials started to show properties that are competitive with extended, bonded frameworks.<sup>[3]</sup>

However, molecular crystals—porous or otherwise—also pose problems in terms of the purposeful design of function.<sup>[4]</sup> This is because the energy landscape for molecular crystals is often not dominated by a single intermolecular interaction, unlike bonded crystalline frameworks. As a result, despite elegant strategies for molecular crystal engineering,<sup>[5]</sup> extended, bonded frameworks have tended to dominate the functional materials scene.

This lecture will discuss the design and synthesis of new functional organic crystals—and related amorphous materials, such as “porous liquids”<sup>[6]</sup>—using computationally-led approaches.<sup>[6]</sup> In particular, we will discuss a new approach for designing function in molecular crystals, based on knowledge of the building blocks alone, by constructing “energy–structure–function maps”.<sup>[7]</sup> We will show that this design strategy can work for known molecules<sup>[8]</sup>, for ‘old’ molecules, and for hypothetical molecules that have not yet been made in the laboratory.

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## Structural diversity within a reliable nanoporous molecular crystal

N. B. McKeown, C. G. Bezzu, L. A. Burt, A. Stamos, S. Moggach

EastChem, School of Chemistry, University of Edinburgh, Edinburgh, EH9 3JF, UK

Crystal Engineering remains a problematic concept due to the unpredictability of molecular crystallisation. One of its pioneers, Braga, in a recent review states that, “*the full realisation of the crystal engineering paradigm – namely the exact, fully predictable, surprise-free engineering of a new crystal starting from the assembly of molecules, ions, and complexes – remains an elusive objective.*”<sup>[1]</sup> Despite great strides being made to improve crystal structure predictability, particularly for porous crystals such as MOFs and those prepared from molecular cages, it remains a challenge to design functional porous molecular crystals. Our approach to this problem is to use the extraordinary reliability of the crystal formed by 2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)-phthalocyanine,<sup>[2]</sup> which contain solvent-filled interconnected voids of 10 nm<sup>3</sup> volume, to produce a family of structurally related crystals with a vast diversity of metal cations and ligands. By using bidentate ligands that can bind two metal cations together it is possible to stabilise the crystal towards solvent removal to produce a material with permanent porosity.<sup>[3]</sup> More recently, we have found that it is possible to form co-crystals of the structure-directing phthalocyanine derivative with either fullerenes or porphyrins (Fig. 1). The structure of these porous molecular crystals will be discussed together with their potential applications as magnetic materials and catalysts

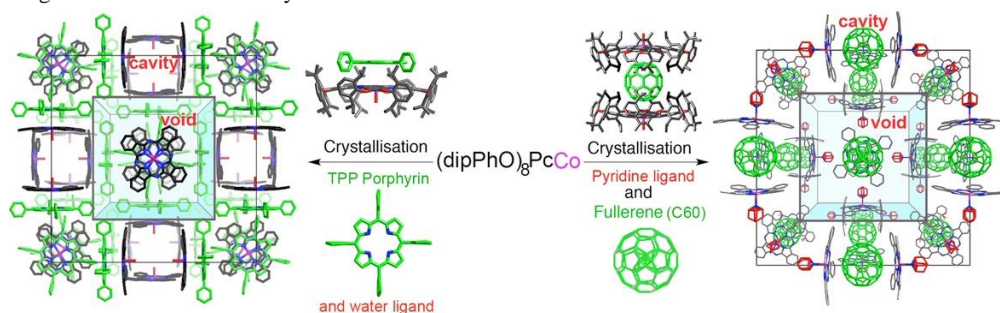


Figure. 1. Molecular co-crystals from the structure directing (dipPhO)<sub>8</sub>PcCo with a porphyrin (TPP) and fullerene (C<sub>60</sub>) incorporated within the void and cavity, respectively. Due to blocking by supramolecular interactions, the ligand (pyridine or H<sub>2</sub>O) attached to the Co<sup>2+</sup> cation is placed in the void for the C<sub>60</sub>/PNC and in the cavity for the TPP/PNC.

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## Dynamic architecture of macrocycles

C. Tedesco,<sup>1</sup> G. Pierri,<sup>1</sup> E. Macedi,<sup>1</sup> A. N. Fitch,<sup>2</sup> L. J. Barbour,<sup>3</sup> F. De Riccardis,<sup>1</sup> I. Izzo<sup>1</sup>

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- 3 Dept. of Chemistry and Polymer Science, Stellenbosch University, South Africa

The design and synthesis of artificial systems able to mimic biological functions has been the aim of extensive research activity in the field of molecular nanotechnology. Cyclic peptoids for their biostability and potential diversity are ideal candidates to evoke biological activities and novel chemical properties.<sup>[1,2]</sup>

Peptoids differ from peptides in the backbone position of the side chains, which are attached to the nitrogen atoms. Our recent studies on the solid state assembly of cyclic peptoids evidenced the solvatomorphic behaviour of cyclic peptoids. The exceptional structural diversity of the solid state assembly is accompanied by peculiar host-guest chemistry and sorption properties.<sup>[3,4]</sup>

The role of the solvent molecules and the peculiar conformational flexibility of the peptoid macrocycles will be discussed to understand how molecular recognition drives the aggregation in the solid state to give the final crystal form.

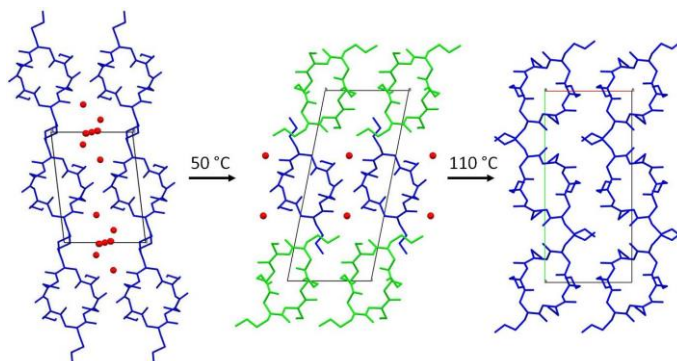


Figure 1. Solvatomorphic behaviour of cyclo-(Npa-Nme<sub>2</sub>)<sub>2</sub>, Npa=N-(propargyl)glycine, Nme= N-(methoxyethyl)glycine.

### References

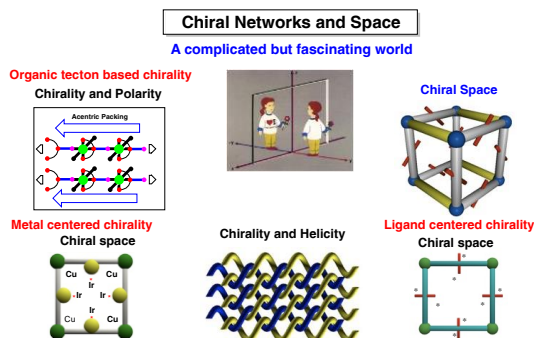
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## Chirality in molecular tectonics

M. W. Hosseini

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Chirality is a complicated yet fascinating area. It plays a fundamental role in biology. In synthetic chemistry, considerable efforts have been devoted to control the chirality. The design and construction of chiral extended architectures is of prime importance for chiral separation and chiral catalysis. More specifically, the formation of enantiomerically pure crystals is rather challenging. Applying the concepts developed in molecular tectonics<sup>[1]</sup> based on combinations of informed construction units (tectons) and connecting units, the design of enantiomerically pure extended architectures may be achieved using either enantiomerically pure organic tectons (ligand centred chirality) or enantiomerically pure metal complexes as nodes of the network (metal centred chirality). A variety of chiral crystals will be presented and discussed.<sup>[2-10]</sup>



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## DNA-inspired porous materials

C. H. Görbitz, L. Qi, L.-L. Gundersen

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All life forms on Earth use DNA/RNA for storage of genetic information. Given the wealth of other options, this pivotal choice highlights the unique hydrogen bonds and molecular recognition between the two strands of the double helix. Chemists dealing with crystal engineering also use hydrogen bonds as design tools, but such supramolecular synthesis is hampered by low predictability compared to base pairing in DNA. We aim to develop a series of nucleobase-functionalized molecules for construction of a new class of porous organic materials with a wide range of potential applications.<sup>[1]</sup>

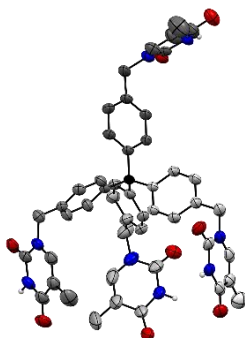


Figure 1. Molecular structure of the **T<sub>4</sub>** node molecule.<sup>[1]</sup>

Using tetraphenylmethane as a scaffold, we have till now synthesized one potential node with four thymine groups, called **T<sub>4</sub>**.<sup>[1]</sup> Attempts were made to co-crystallize it with ethylene-9,9'-diadenine, **A<sub>2</sub>**, in a MOF-like node-and-linker model held together by DNA-type **A≡T** hydrogen bonds, but the individual building units crystallized separately.<sup>[2]</sup> Future plans to be discussed focus on formation of porous frameworks with interactions between two complimentary nodes such as **T<sub>4</sub>** and **A<sub>4</sub>**. Research efforts into DNA-inspired porous materials have been scarce in the past,<sup>[3]</sup> in part due to the low solubility of molecules with multiple nucleobase moieties, but the impressive progress in the development of functional materials derived from DNA<sup>[4]</sup> indeed suggests interesting possibilities.

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## Mechanisms of guest uptake in copper-based metal-organic frameworks

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Intermolecular interactions play a fundamentally important role in the properties of solid materials. For instance, guests are taken up into the host framework of porous materials as a result of the interactions between these species, while the manner in which they interact has an influence on the sorption ability of the porous material. In this work calculations on a series of copper-based porous metal-organic frameworks allow us to explain the role that intermolecular interactions play in the unusual sorption properties of these compounds. Firstly, the origin of anomalous sorption isotherms are shown to be the result of interactions between carbon dioxide and the host framework.<sup>[1]</sup> Similarly, intermolecular interactions are responsible for the change in colour along an hourglass pattern of a crystalline porous compound during sorption of particular solvents. Calculations show that the origin of this effect is that the channels in the porous framework are anisotropic, allowing sorption only from particular faces.<sup>[2]</sup> Finally, we show that the large structural changes that occur during sorption and desorption of CO<sub>2</sub> by two copper-paddlewheel-based MOFs while still maintaining the integrity of the crystalline nature of the compounds occur as a result of the flexibility of the glutarate linker (Figure 1).<sup>[3]</sup>

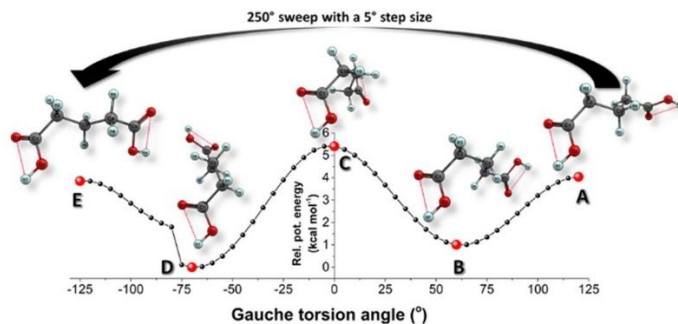


Figure 1. Change in potential energy with conformations of glutarate linkers.

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## Formation and characterisation of porous inclusion compounds

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Inclusion compounds are of two types:

- a) Both Host (H) and Guest (G) components are made of single molecules
  - b) The Host (H) is a framework structure and the Guest (G) is derived from a gas or a liquid.
- The results of syntheses of MOF's are generally more predictable than those with single molecule hosts. In type b), the frameworks are usually stable to relatively high temperatures upon guest desorption, while type a) structures often collapse upon guest removal.

An important application of both types of Inclusion compounds is the separation of individual components in a mixture when these have similar physico-chemico properties, as occurs in isomers.

The techniques which are employed to understand the mechanism of separation include

- 1) Competition experiments
- 2) Structure elucidation
- 3) Thermal Analysis
- 4) Packing efficiency
- 5) Hirshfeld surface analysis
- 6) Lattice energy

Various publications dealing with these topics will be outlined and recent experimental results will be presented.

## Porous supramolecular architectures: ultra-fast molecular rotors and dynamics control by chemical stimuli

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A challenging issue is the dynamics of nanoporous solids after the insertion of molecular rotors in their building blocks and promises access to the control of rotary motion by chemical and physical stimuli.<sup>[1]</sup> The combination of porosity with ultra-fast rotor dynamics was discovered in molecular crystals, covalent organic frameworks and MOFs by <sup>2</sup>H spin-echo NMR spectroscopy and T<sub>1</sub> relaxation times.<sup>[2-5]</sup> The rotors, as fast as 10<sup>11</sup> Hz at 150 K, are exposed to the crystalline channels, which absorb CO<sub>2</sub> and I<sub>2</sub> from the gas phase, even at low pressures. Interestingly, the rotor dynamics can be switched on and off by vapor absorption/desorption, showing a remarkable change of material dynamics, which, in turn, produces a modulated physical response. Novel mesoporous organosiloxane frameworks allowed us to realize periodic architectures of fast molecular rotors on which C-F dipoles are mounted.<sup>[6]</sup> These dipolar rotors showed not only rapid dynamics (10<sup>9</sup> Hz at 325 K) in solid-state NMR experiments, but also a dielectric response typical of a fast dipole reorientation. Moreover, crystals with permanent porosity were exploited in an unusual way to decorate crystal surfaces with regular arrays of dipolar rotors. The inserted molecules carry alkyl chains which are included as guests into the channel-ends.<sup>[7]</sup> The rotors stay at the surface due to a bulky molecular stopper which prevents the rotors from entering the channels. In a final example, flexible molecular crystals were fabricated by a series of shape-persistent azobenzene tetramers that form porous molecular crystals in their *trans* configuration. The efficient *trans*→*cis* photoisomerization of the azobenzene units converts the crystals into a non-porous phase but crystallinity and porosity are restored upon *Z*→*E* isomerization promoted by visible light irradiation or heating. We demonstrated that the photoisomerization enables reversible on/off switching of optical properties as well as the capture of CO<sub>2</sub> from the gas phase.<sup>[8]</sup>

We would like to thank Cariplo Foundation/Lombardy Region/INSTM Consortium.

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## Porosity of seemingly non-porous organic solids

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Our group first discovered the porosity of seemingly non-porous organic solids more than 15 years ago. The useful properties of porous organic and inorganic solids were well known at that time. Indeed, the field of crystal engineering had emerged as an important area of scientific endeavour. However, organic solids that change structure under the external stimulus of modest pressure of a gas is still rare. Rarer yet are organic solids that change structure in response to pressure from a specific gas. This presentation will focus on the 'porosity of seemingly non-porous organic solids' in which the organic solid is one of pharmaceutical utility.

## Nanoporous-crystalline polymers and industrial innovations

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For two commercial thermoplastic polymers, syndiotactic polystyrene (s-PS)<sup>[1-3]</sup> and poly(2,6-dimethyl-1,4-phenylene)oxide (PPO),<sup>[4,5]</sup> crystalline phases including empty cavities of molecular size in their unit cell have been obtained and named *nanoporous-crystalline* phases. These nanoporous-crystalline phases unprecedentedly exhibit density lower than the corresponding amorphous phases and are obtained by guest removal (e.g., by carbon dioxide in supercritical conditions) from co-crystalline host-guest phases, between a polymer host and low-molecular-mass guest.

These nanoporous-crystalline phases are able to absorb guest molecules also from very dilute solutions. Most studies have been devoted to s-PS, which exhibits two different nanoporous-crystalline phases,  $\delta$ <sup>[1]</sup> and  $\epsilon$ ,<sup>[2]</sup> whose nanoporosity is organized as isolated cavities and channels, respectively.

Physically crosslinked monolithic aerogels, whose physical knots are crystallites exhibiting a nanoporous crystalline form, will be also discussed.<sup>[6-8]</sup> These *aerogels* present beside disordered amorphous micropores (typical of all aerogels) also all identical nanopores of the crystalline phases. Their outstanding guest transport properties combined with low material cost, robustness, durability and easy of handling and recycle make these aerogels suitable for applications in chemical separations, purification and molecular storage.<sup>[6-8]</sup>

The final part of the presentation will be devoted to possible industrial innovations of materials based on co-crystalline and nanoporous crystalline s-PS phases. In particular, applications of nanoporous films for active packaging of fruit and vegetable (by removal of ethylene and carbon dioxide),<sup>[9,10]</sup> of nanoporous staple for removal of pollutants from water and air<sup>[11]</sup> and of nanoporous aerogels as support for nanostructured catalysts,<sup>[12]</sup> will be presented.

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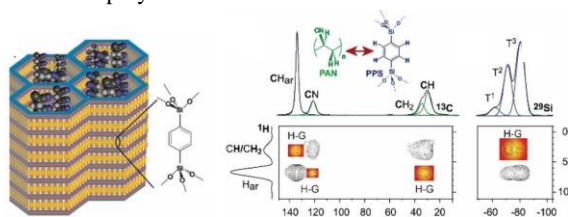
## Porous materials: the interplay with linear polymers

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Porous materials provide great opportunities for the construction of architectures with linear polymers. The chains can be generated *in situ* starting from the absorbed monomers, co-assembled or diffused from a fluid phase. The influence of the porous framework surrounding the included polymers allows for the control on the conformational arrangement, which, in turn, determines extended chain morphology and conductive properties. On higher hierarchical scales it was feasible to build integrated constructions among single-chains or nanobundles and the 3D networks. Thermal transformation of the polymer chains into graphitic fibers, semiconductive and conductive polyaromatic chains was performed starting from polyacrylonitrile generated in the nanopores. In some cases we could achieve the participation of the chains in the network by copolymerization reactions with the formation of covalent bonds between the framework and the polymer.

The porous materials were chosen among crystalline molecular materials (PMCs), metal organic (MOFs), porous organic frameworks (POFs) and hybrid organosiloxane mesoporous matrices (PMOs). If desired, the host can be removed from the polymer in distinct ways depending on the easiness of subliming and dissolving as in PMCs, digesting the metal-organic bonds in MOFs, or dissociating carbon-silicon bonds in PMOs. On the contrary, reactive elements were inserted into the porous material in such a way to connect adjacent chains. Distinct cross-section pores (from 0.5 - 4 nm) allow for an individual or a limited number of polymer chains to be collected.



Therefore, it was demonstrated that a variety of solutions may be designed to optimize the couple framework/linear-polymer, with the goal in mind to orient the nanocomposite structure and properties. The generation of multiple heterogeneous interactions in the sophisticated architectures was an ideal playground for solid state multinuclear NMR, which could recognize specific interactions and nanometric intimacy among the constituents.

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## MOF design to applications: impact of pore system control on gas separations and storage

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Demand for functional materials targeted for specific applications is ever increasing as societal needs and demands mount with advancing technology. The building-block approach, whereby at the design stage the desired properties and functionality can be introduced in preselected molecular building blocks (MBBs) prior to the assembly process, has emerged as a prominent pathway for the rational construction of functional solid-state materials.

One class of inorganic-organic hybrid materials, metal-organic frameworks (MOFs), has burgeoned in recent partly years due to effective design strategies (i.e. reticular chemistry) for their synthesis and their inherent [and readily interchangeable] hybrid, functional character.

Various key gas/vapors separations are accomplished using energy intensive processes as exemplified by the olefin/paraffin separation, an essential separation in chemical industry.

Here we present our progress in the development of functional metal-organic frameworks (MOFs) to address some energy-intensive separations. Successful practice of reticular chemistry had afforded the fabrication of chemically stable fluorinated MOF adsorbent materials (**NbOFFIVE**-1-Ni, also referred to as **KAUST-7** and **AlFFIVE**-1-Ni, also referred to as **KAUST-8**). The restricted MOF window resulted in the selective molecular exclusion of propane from propylene at atmospheric pressure, as evidenced by multiple cyclic mixed-gas adsorption and calorimetric studies. Remarkably, **KAUST-7** maintains its distinctive separation properties in the presence of water as a result of its high chemical and hydrolytic stability.<sup>[1]</sup>

The development of suitable storage and refining processes makes natural gas an excellent alternative fuel, but before its transport and use, natural gas must first be dehydrated. Conventional dehydration agents are energy intensive. **KAUST-8** selectively removes water and requires just 105°C for regeneration of the dehydrating agent.<sup>[2]</sup>

The deliberate control of the pore aperture-size of various selected MOFs and its impact on various separations will be discussed.

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## Guest exchange in dynamic frameworks

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Dynamic materials, capable of responding to their environment, require flexibility which may be achieved using weak interactions such as hydrogen bonding or through the use of suitable metals and ligands in coordination compounds. Thermochromic and mechanochromic coordination networks have recently received a great deal of attention. Materials of this type are particularly of interest if they are able to revert to their original state on application of another external perturbation signal.

The process of guest exchange within porous solids is of interest in a range of applications, such as selective absorption or separation of gases and heterogeneous catalysis. Frameworks may be made up of relatively strongly bound entities such as those that make up metal-organic frameworks (MOFs) or may be more loosely bound such as host-guest systems where the host molecules crystallise as independent entities but leave spaces which can accommodate guest molecules. In all cases the topology and dynamism of the framework, as well as its capacity to include and to exchange guests, is determined by the nonbonded interactions occurring in the system under defined conditions of temperature and pressure.<sup>[1-4]</sup> Nonbonding interactions include hydrogen and halogen bonding as well as other disperse interactions. All play an important role in the properties of porous crystalline solid materials. Rational design of such systems remains a challenge however, and is thus an exciting area for application of crystal engineering principles.

In this presentation, examples from recent work in our laboratory will be presented, including MOFs and 3D hydrogen bonded frameworks constructed from the same flexible ditopic ligands, 4-(4-pyridyl)benzoate and 3-(4-pyridyl)benzoate. The influence of halogen versus hydrogen bonding on a molecular host-guest system will also be described. Their ability to exchange guest molecules selectively as well as their chromic behaviour on application of external stimuli such as heat, grinding or exposure to solvent vapours will be described.

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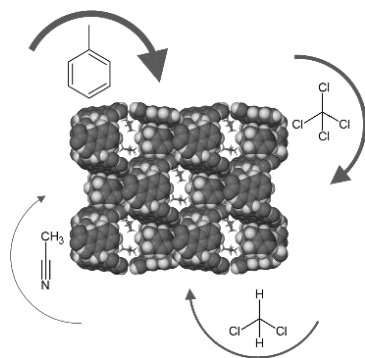
## Framework materials from ionic organic components

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During a systematic investigation of organic carboxylate salts in the solid state, our group identified a particularly interesting salt of pamoic acid. This material, 3,4-lutidinium pamoate hemihydrate (**1**), crystallises as a remarkably robust framework with stoichiometric amounts of various solvents included in channels.<sup>[1]</sup> When **1** is synthesised from THF, it crystallises as **1**·THF. The solvent in **1**·THF can be exchanged for a variety of other organic solvents, including in a stepwise fashion. The THF can also be exchanged for volatile solids such as iodine or pyrazine. If **1** is crystallised from a mixture of solvents, framework **1** shows a clear preference for inclusion of some solvents over others.<sup>[2]</sup> This porous organic salt has been extensively investigated in terms of its selectivity for particular solvents, as well as the kinetics of the exchange process.

The robust nature of framework **1** led us to expand our investigations on porous materials constructed using charge-assisted hydrogen bonds. Recently, our group reported the serendipitous synthesis of a series of organic zwitterions from acetylenedicarboxylic acid (ADC) and various pyridine derivatives.<sup>[3]</sup> Due to their awkward shape and varied hydrogen bonding capabilities, we have investigated the potential of these zwitterions as porous hosts. One zwitterion, the 4-benzylpyridine derivative, has four polymorphs and three solvates. Interconversion between the various forms has been studied in detail, and one of the polymorphs has been shown to be porous to dioxane.<sup>[4]</sup>



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# Taxonomy of porous solids: a crystal engineering perspective

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That composition and structure can profoundly impact the properties of crystalline materials has provided impetus for continued growth in the field of crystal engineering over the past three decades.<sup>[1]</sup> Crystal engineering has thereby evolved from its initial focus upon structure design to address control over bulk properties. Today, crystal engineering when coupled with molecular modelling, represents a paradigm shift from the more random, high-throughput methods that have traditionally been utilised in materials discovery and development. Custom-design of the right materials for the right application is therefore at hand. Porous crystalline materials exemplify this situation. Whereas purely inorganic materials (*e.g.* zeolites) and those based upon coordination chemistry (*e.g.* MOFs, and Porous Coordination Polymers) are well studied and offer great promise for separations and catalysis, they are handicapped by cost or performance (*e.g.* poor chemical stability, interference from water vapour, low selectivity) limitations. They are also handicapped by design issues since, with the notable exceptions of networks with **pcu** (primitive cubic) or **dia** (diamondoid) topology, there are few topologies that are inherently modular across a range of metals and ligand types. This in turn makes it difficult to systematically determine structure-property relationships across a family of related materials. *Hybrid Ultramicroporous Materials*, HUMs, represent an exception to this situation and offer a case study for the power of crystal engineering in terms of understanding pore size and pore chemistry. Families of HUMs can be built from metal or metal cluster “nodes” (molecular building blocks, MBBs) and combinations of organic and inorganic “linkers” can be exploited to fine-tune their pore chemistry and pore size (< 0.7 nm). The benchmark performance of **pcu** topology HUMs with respect to important gas separation (*e.g.* CO<sub>2</sub><sup>[2]</sup> capture, C<sub>2</sub>H<sub>2</sub> capture<sup>[2]</sup> and natural gas upgrading) applications will be discussed. Unfortunately, applying the same crystal engineering approach to less common topologies still represents a design challenge because topology is inherently qualitative and, by definition, pays no attention to bending or stretching of the shape or scale of a geometric form. We have therefore developed a taxonomic approach to classify porous materials. This approach will be presented with emphasis on how to most effectively exploit topology from a crystal engineering perspective. For example, how to decipher less common topologies such as **bnn** (*e.g.* Mg-MOF-74, aka Mg/bodc and CPO-27-Mg) and how to exploit networks based upon rod building blocks (RBBs) will be addressed.

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## **SELECTED ORAL CONTRIBUTIONS**

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## CO<sub>2</sub> stabilisation and phase transitions in open-channel metal-organic frameworks (MOFs).

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MOFs are very versatile materials and are sought after for various properties such as gas sorption and gas selectivity. Through the study of a previously reported microporous metal-organic framework whose pore dimensions can be varied systematically through the judicious choice of suitable rigid 4,4'-bipyridine-type linkers, CO<sub>2</sub> host-guest and guest-guest interactions can be studied. Using single-crystal X-ray diffraction data and framework electrostatic potential maps we elucidated the nature of the CO<sub>2</sub>-MOF interactions that uses several electrostatic interactions to stabilize the CO<sub>2</sub> within the framework channels.<sup>[1]</sup> Similar to the previous study suitable flexible 4,4'-bipyridine-type linkers were used to synthesise MOFs analogous to the rigid linkers. The flexibility of the pyridyl linkers allowed for the MOFs to undergo a phase transition and subsequent reduction in guest accessible space. Understanding these properties and the role they play in various metal-organics is pivotal to the understanding of not only CO<sub>2</sub> sorption, but also the ligand-MOFs property relationships.<sup>[2]</sup>

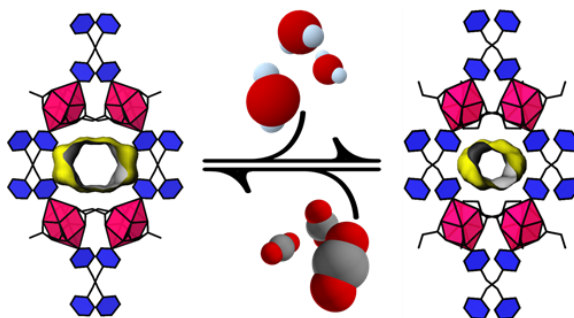


Figure 1. Crystal structure of a copper-glutarate MOF containing modelled CO<sub>2</sub> shown in space-filling representation.

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# Are bisguanidinium organodisulfonates formally microporous?

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With the recent emphasis on the importance of porous materials, so called porous hydrogen bonded organic frameworks (HOFs)<sup>[1]</sup> have started gaining attention. A well-known class of HOFs are bisguanidinium organodisulfonates (GS). GS have been extensively explored for the last 20 years due to their diverse host-guest chemistry, as well as their inclination towards architectural isomerism, a phenomenon in which a material can have the same composition and the same supramolecular bonding motive, but still differ in the overall crystal structure due to topological differences.<sup>[2]</sup>

Especially interesting is the persistence of the 2D hydrogen bonded sheet motif, which is so reliable that it can allow for targeted synthesis of a multitude of different pillared architectures, such as the bilayer or brick structure, where the type of architecture depends on the size of the guest and the pillar type. Most importantly, these materials have been shown to exchange guest molecules in a single crystal-to-single crystal fashion.<sup>[3]</sup>

Surprisingly, despite the stability of these frameworks, the desolvation of GS has not been extensively studied, and the structures of their empty forms-either 'collapsed' or 'open/porous'-have gone unreported. As a result, despite 20 years of prominence in the crystal engineering community, the formal existence of microporosity in the GS class of compounds has not yet been established.

In this work we study the desolvation of guanidinium organodisulfonate materials and demonstrate that they are formally microporous. Furthermore, we study the absorption of gases into these materials via Single Crystal-to-Single Crystal transformations.

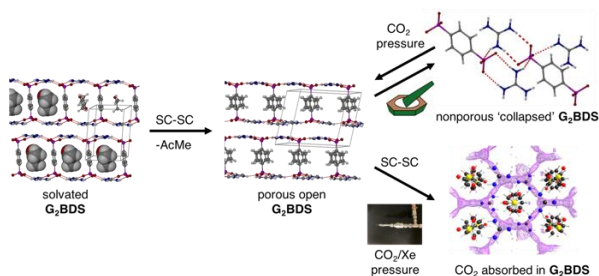


Figure 1. The structural transformations between different forms of guanidinium 1,4-benzenedisulfonate.

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## Structural investigation of cyclic octapeptoids

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The fascinating world of cyclopeptoids, cyclic oligomers of *N*-alkyl glycines, in recent years is showing unique and intriguing structural features on solid state.<sup>[1]</sup> Recently, we have established that the macrocycle's size and side chains strongly affect the solid state assembly. For instance, the cyclic hexapeptoid containing propargylic side chains shows a layered architecture while the cyclic octapeptoid **1** possesses a tubular structure.<sup>[2]</sup> The incorporation of two methoxyethyl side chains in a cyclic hexapeptoid with four propargylic side chains furnished a tubular solid state assembly, that features a reversible single-crystal-to-single-crystal transformation upon guest release/uptake.<sup>[3]</sup> With the aim to explore novel supramolecular architectures the first purpose was to synthesize the macrocycle **2** in order to achieve a more robust structure. The synthesis of a small library of cyclic octapeptoids, decorated with an increasing number of methoxyethyl side chains, was performed (Figure 1). In this communication, their synthesis, conformational order in solution and crystal packing in solid state will be discussed.

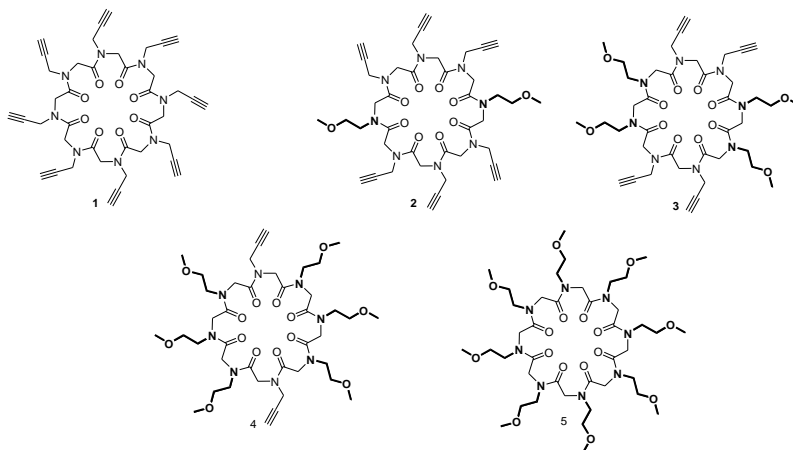


Figure 1. Novel cyclic octapeptoids.

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## BioMOFs based on Azelaic and Dipyridamole as potential systems for biomedical applications

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In the last decade, Metal Organic Frameworks (MOFs) emerged as potential systems for biomedical applications, in particular for the controlled delivery of active pharmaceutical ingredients (APIs). We are particularly interested in obtaining BioMOFs using APIs and safe metals as building blocks. When compared to MOFs, BioMOFs present additional benefits. Porosity is no longer required as the release of the API is achieved through the degradation of the solid. The API is part of the matrix, avoiding multistep procedures to prepare the loaded material. The metal can also be bioactive promoting a synergetic effect. The use of porous BioMOFs presents enhanced applications, as it can lead to the co-delivery of other APIs adsorbed in the pores. <sup>[1-3]</sup>

Here we present BioMOFs synthesized using Na, K, Mg, Ag, Zn, Ca and azelaic acid, an API commonly used to treat skin disorders, and dipyridamole, a phosphodiesterase inhibitor that blocks uptake and metabolism of adenosine. These novel compounds were structurally characterized, and their temperature, time and humidity stability are being explored.

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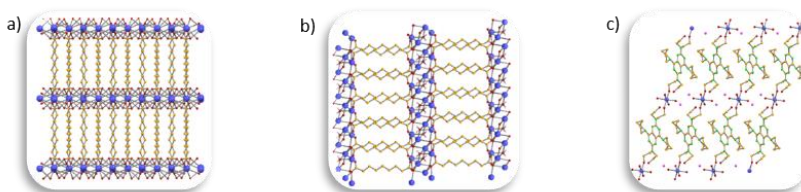


Figure 1. Molecular diagrams for azelaic acid with a) Na and b) K and c) dipyridamole with Mg

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## Negative thermal expansion design strategies in metal-organic frameworks

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Positive thermal expansion can cause significant stress or even catastrophic device failure in applications where materials are placed in confined environments. A mismatch in the coefficient of thermal expansion between a MOF thin film and its substrate can also produce residual stresses that cause material fatigue or even compromise the connection between the MOF and its electrical contact. Consequently, it is important to understand this behaviour so that device reliability issues can be avoided.<sup>[1]</sup> The ability to precisely tailor thermal expansion properties in metal-organic frameworks (MOFs) would mitigate such problems and be of significant value for a wide array of material design and engineering challenges.<sup>[2]</sup> This presentation will discuss the fundamental understanding and development of MOFs as pre-designed negative, positive, and zero-thermal expansion materials. Through complimentary synchrotron-radiation and molecular modeling efforts, various MOF structural design strategies will be discussed. The implications of these design strategies for the use of MOFs as a novel class of negative thermal expansion materials will also be discussed.

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## *In situ* crystallography over a interpenetrated metal-organic framework for CO<sub>2</sub> adsorption in humid conditions

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An important goal in devising technologically relevant metal-organic frameworks (MOFs) lies in the synthesis of robust networks capable of withstanding sustained use under wet conditions. The research of materials able to work in such condition is still underway and very challenging, particularly regarding CO<sub>2</sub> adsorption (for instance as scrubbers in postcombustion carbon capture). Water is, in effect, the strongest competitor to CO<sub>2</sub> in the adsorption on microporous materials and the first depolymerizing agent, thus affecting their performances and turnover. In this scenario, the synthesis of stable MOFs, the comprehension of their functional properties and the knowledge of their crystallographic features, is indispensable for the design and development of well performing materials.<sup>[1]</sup> In this field, non-ambient crystallography is becoming an attractive technique to rationalize and understand the structure/properties relationships in porous materials. *In situ* gas adsorption on single crystals and also polycrystalline powders are nowadays techniques that are getting more and more attention. This is particularly true when gate-opening effects have to be rationalized to well describe adsorption processes.<sup>[2]</sup>

In this contribute we will present our results obtained in the rationalization of the crystallographic features observed during *in situ* CO<sub>2</sub> adsorption in humid conditions on a water-stable metal-organic frameworks Cu(FMA)(4,4'-Bpe), Figure 1.<sup>[3]</sup> Moreover, the relationship between the crystallographic features observed during CO<sub>2</sub> adsorptions and the material performances, determined either by classical methods (isotherm collection) and advanced characterization techniques (breakthrough curves) will be also highlighted.

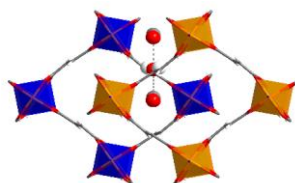


Figure 1. CO<sub>2</sub> adsorption in humid conditions over Cu(FMA)(4,4'-Bpe); FMA = fumaric acid, 4,4'-Bpe = 4,4'-pyridylethene.

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## A novel bismuth-tetracarboxylate MOF as a proton conductor

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Metal–Organic Frameworks (MOFs), also known as Porous Coordination Polymers (PCP), are a new class of hybrid materials built from inorganic units and organic polycomplexant ligands,<sup>[1]</sup> combining a very high regular porosity (up to  $S_{\text{BET}} = 6000 \text{ m}^2/\text{g}$ ; pore diameter = 3–60 Å)<sup>[2]</sup> with an easily tunable hybrid composition. Additionally, some of these porous hybrid solids are flexible with a reversible modulation of their pore size upon adsorption of guest molecules. Known for their large porosity with diverse pore sizes, shapes and functionalities, MOFs are promising candidates for many strategic societal and industrial applications such as fluid storage and separation, catalysis, sensing, biomedicine, magnetism and, more recently, energy, among others.<sup>[3]</sup>

Here, we describe the successful preparation of a novel 3D porous MOF (termed as IEF-2; where IEF stands for IMDEA Energy Framework) based on an azobenzene-tetracarboxylate organic linker and bismuth cations. IEF-2 was easily isolated and scaled-up to the gram-scale by using a simple green hydrothermal method. While its crystal structure was unveiled by single-crystal X-ray diffraction, its physicochemical properties (optical, texture, chemical/thermal/mechanical stability, etc.) were fully characterized by several standard solid-state techniques [spectroscopy, thermogravimetric, elemental analysis, electron microscopy, gas sorption, etc]. Some structural changes associated with solvent release were evidenced by using *in situ* advanced techniques (variable-temperature techniques powder X-ray diffraction and infrared spectroscopy) in order to further understand the relationship between those structural modifications and their intrinsic properties. The proton conductivity of IEF-2 was exhaustively measured and the results suggest that this material is an efficient and robust proton conductor, being not observed any structural change after the studies. Additionally, proton conductivity is directly related with both temperature and relative humidity parameters.

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# Nanoporous-crystalline polymer films with unexpected high optical activity and circularly polarized luminescence

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Syndiotactic polystyrene (s-PS) is a commercial thermoplastic polymer which crystallizes with many low-molecular-mass guest molecules leading to co-crystalline host-guest phases. When amorphous s-PS films crystallize by temporary sorption of non-racemic guest molecules (like carvone or limonene) they not only exhibit high optical activity, both in the UV-Visible and Infrared ranges,<sup>[1-5]</sup> but also present circularly polarized luminescence (CPL).<sup>[6]</sup>

The intense chiral optical response of s-PS films remains unaltered by removing the non-racemic guest molecules leading to *nanoporous-crystalline* phases as well as by replacement of non racemic guest molecules with achiral chromophores like for instance azulene and 4-nitro-aniline.<sup>[4]</sup>

In this communication, the degree of circular polarization ( $G$ ) of Infrared and UV-Visible bands of achiral molecules being guests of s-PS films with different thickness, will be presented.<sup>[2-3]</sup>

Surprisingly, for all examined thicknesses and spectral ranges, the chiral response of the considered achiral guests (azulene and 4-nitro-aniline) is definitely higher than for the chirality-inducing non-racemic guest (carvone). This clearly indicates that the origin of the chiral-optical response is extrinsic to the site of photon absorption and is associated with a non-racemic helical morphology of crystallites, as induced by the non-racemic guest.<sup>[4-5]</sup>

Finally, the occurrence of circularly polarized luminescence (CPL) of s-PS films, whose crystallization has been induced by the temporary sorption of non-racemic guest molecules, will be also presented.<sup>[6]</sup>

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## From microporous to nanoporous: the role of supercritical carbon dioxide in the formation process

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Polymeric porous devices formation processes, such as freeze drying, air drying, phase separation, show several limitations: reduced flexibility in controlling sample morphology, long processing time and samples have to be accurately cleaned after processing in order to eliminate organic solvents used during the preparation step. Supercritical CO<sub>2</sub> (SC-CO<sub>2</sub>) assisted drying and phase separation have been proposed to improve porous devices production of several polymers, that in some cases were loaded with pharmaceuticals and active agents for biomedical and food applications.<sup>[1-4]</sup> Using this green techniques, in a fast process and directly eliminating the organic solvent, polymer sample characterized by a regular and homogeneous microporous or nanoporous morphology were produced. These results are due to the peculiar characteristics of SC-CO<sub>2</sub>: high solvent power and high diffusivities, that allow an efficient control of the polymeric matrix morphology and low surface tension, that avoids the collapse of the polymeric structure during the formation process.

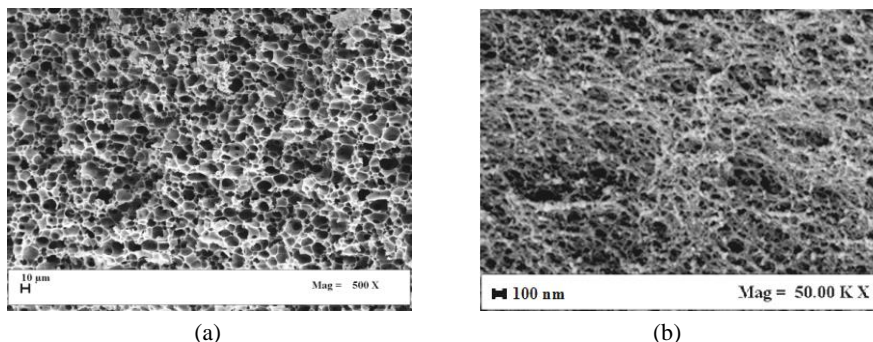


Figure 1. Examples of polymer devices morphology at micro and nanoscale, obtained by: (a) SC-CO<sub>2</sub> phase separation; (b) SC-CO<sub>2</sub> drying.

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## Probing porous materials using a powder diffractometer

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X-ray powder diffraction is ideally suited to studying structural modifications of porous materials, particularly since the bulk material is analysed, allowing the averaged structural features of the material to be correlated with its bulk physical properties, in this case the porosity. In addition, rapid X-ray diffraction data collection allows the determination of intermediate phases, onset points of reactions and information about the reversibility of structural conversions. X-ray diffractograms are easily modelled by Rietveld refinement using the HighScore Plus software<sup>[1]</sup> to study structural transformations.

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**POSTERS**



## Stepped sorption behaviour in a highly porous four-fold interpenetrated zinc-based MOF

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The study of flexible or soft porous crystals is an exciting and fast expanding area of metal-organic framework (MOF) research. Understanding the solid-state crystal dynamics and flexibility in MOFs exhibiting multiple structural changes is highly necessary for the design of materials with potential applications in gas sorption, sensing and recognition.<sup>[1]</sup>

This contribution describes a new zinc-based MOF exhibiting flexible behaviour coupled with multi-stepped sorption of ethane and carbon dioxide with large hysteresis. The sorption isotherm and pressure-ramped DSC results suggested that the framework undergoes structural transformation upon the uptake of guest molecules at increased pressure. In-situ single-crystal XRD studies were carried out using an environmental gas cell. The framework is highly flexible and exhibits ‘breathing’ behaviour through subnetwork displacement when incorporating guest molecules. The framework is four-fold interpenetrated and the four different nets form the channels in the structure. The ability of these nets to slide through one another is the basis of the flexibility of the framework towards guest molecules.

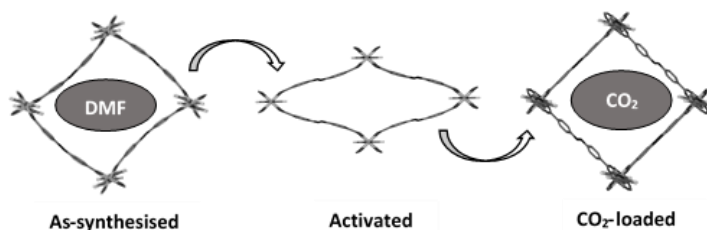


Figure 1. Guest-induced structural changes in the framework.

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## High performance separation of C<sub>8</sub> aromatics by a switching adsorbent layered material

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The separation and purification of chemical feedstocks currently accounts for 10–15 % of the world's energy consumption; traditional separation processes (distillation, drying, evaporation, etc.) surprisingly account for more than 80 % of this energy.<sup>[1]</sup> Increasing demand for pure commodities over the coming decades requires more energy-efficient purification technologies. One of the most challenging separations in this context involves xylenes and ethylbenzene, i.e. C<sub>8</sub> aromatics, which are widely used for the industrial production of fibers, plastics, solvents and fuel additives. Their similar sizes and boiling points make their separation difficult by conventional methods. One promising method is adsorptive separation utilizing porous materials such as zeolites, the current industrial adsorbents. However, they just offer relatively low capacity (~10–20 wt%) and selectivity (~5),<sup>[2]</sup> overshadowing their advantages of low cost and ready availability.

Here, we describe a new approach to C<sub>8</sub> aromatics separation that counterintuitively involves a non-porous material that switches to open phases when exposed to C<sub>8</sub> aromatics. More importantly, the switching pressures and/or the adsorption rates of this material are quite different (Figure 1), enabling high performance separation of C<sub>8</sub> aromatics. Our further studies reveal that this material combines benchmark ortho-xylene selectivity and high saturation capacity, holding great promise for the related applications.

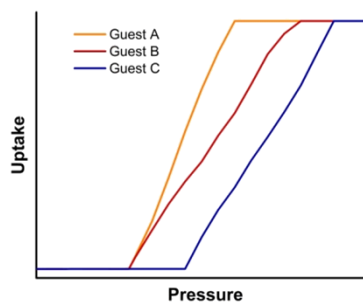


Figure 1. Schematic of the adsorption behaviour of the switching adsorbent layered material triggered by different guests.

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# Single-crystal to single-crystal uptake of volatile solids and associated chromatic response in a porous metallocycle

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Metallocycles<sup>[1-3]</sup> are an ideal class of porous materials for the study of structure-property relationships by single-crystal X-ray diffraction methods. They have simple zero-dimensional structures and the guest accessible space is small enough to allow included guests to be located in the channels easily. It is well known that guest removal or exchange processes in metallocycles can occur in a single-crystal to single-crystal manner.

Reports of the sorption and separation of solvents (in liquid or vapour form) and gases are abundant. In contrast only a few studies that involve sorption of vapours of solids have been reported. Moreover, studies that involve structural evidence of the adsorbed guest molecules are still rare.

Apart from being used as chemical intermediates, many of these volatile solids are used in our everyday lives as moth repellents, tanning agents, in odour applications and as flavouring agents. It is therefore useful to study the interactions, capture and sensing of these molecules.

Volatile solids were included into a metallocycle by means of sublimation at room temperature. The guest exchanges are accompanied by colour changes. Due to the conservation of the single crystal nature, structural evidence of the included guest could be obtained using single-crystal X-ray diffraction. The results are supported by thermogravimetric analysis, powder X-ray diffraction, Fourier transform infrared spectroscopy and UV-Vis spectroscopy.

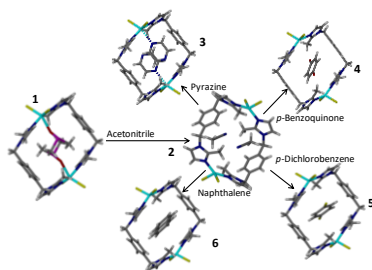


Figure 1. Formation of inclusion compounds 2-6 by exposing 1 to acetonitrile and 2 to pyrazine, *p*-benzoquinone, *p*-dichlorobenzene and naphthalene, respectively.

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## A view of the crystal form landscape of a peptidomimetic compound

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Our studies on cyclic alpha-peptoids<sup>[1]</sup> evidenced that NH...OC hydrogen bonds in peptides are substituted by CH<sub>2</sub>...OC hydrogen bonds in peptoids. In particular, backbone to backbone CH<sub>2</sub>...OC hydrogen bonds can provide face to face or side by side arrangement of macrocycles, mimicking β-sheet secondary structures in proteins.<sup>[2]</sup> Moreover backbone-to-side chain interactions may promote the formation of a columnar arrangement, where the side chains act as pillars, extending vertically with respect to the macrocycle planes.<sup>[3]</sup> In particular, methoxyethyl and propargyl side chains extend vertically with respect to the macrocycle plane and interact by means of CH...OC hydrogen bonds with the backbone atoms belonging to the macrocycles below and above.<sup>[4]</sup> Moreover, conformational flexibility of cyclic peptoids can lead to unexpected solid state dynamic properties. Variable temperature single crystal and powder XRD and hot stage microscopy helped in exploring the landscape of crystal forms for a cyclic hexapeptoid decorated with four methoxyethyl and two propargyl side chains (compound **1**).

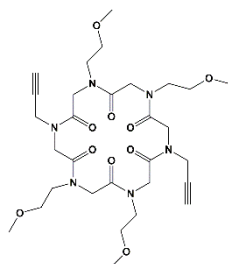


Figure 1. Cyclo-(Npa-Nme)<sub>2</sub>, Npa=N-(propargyl)glycine, Nme= N-(methoxyethyl)glycine.

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## Solvatomorphic behavior of a cyclic peptoid

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Cyclic alpha-peptoids emerged recently as interesting building blocks for their biostability and potential diversity, but also for their elegant and intriguing architectures.<sup>[1,2]</sup> Unlike peptides, in peptoids the side chains are connected to the nitrogen atom of the peptide backbone to give *N*-substituted oligoglycine. The lack of the amide proton prevents the formation of NH...OC hydrogen bonds and weaker interactions, as CH...OC hydrogen bonds and CH- $\pi$  interactions, play a key role.

In particular, the side chains have a key role in the solid state assembly of peptoid macrocycles promoting the formation of peptoid nanotubes by acting as pillars, extending vertically with respect to the macrocycle planes.<sup>[3-5]</sup>

The hexameric cyclopeptoid **1** with four methoxyethyl and two propargyl side chains (Figure 1) crystallizes from chloroform and isopropanol forming a hydrate form. The macrocycle shows a *cctcct* configuration of the peptide bonds and assemble into columns bridged by water molecules.<sup>[5]</sup>

A polymorph screening showed the capability of the columnar assembly of **1** to host different guest molecules, as toluene, acetonitrile, aniline and hydroquinone. Laboratory single crystal X-ray diffraction and thermal analysis were used to identify and characterize the different crystal forms.

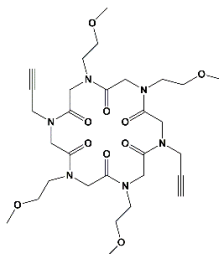


Figure 1. Hexameric cyclopeptoid C<sub>30</sub>H<sub>46</sub>N<sub>6</sub>O<sub>10</sub> with four methoxyethyl and two propargyl side chains.

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## Striking effects of chiral side-chains on the conformation of cyclic oligopeptoids

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Peptoids, oligomers of *N*-substituted glycines, show many synthetic advantages over their natural peptide counterparts, however they lack conformational stability, which influences their design and application.<sup>[1]</sup> In order to tackle this disadvantage, the introduction of bulky chiral side-chains such as 1-phenylethyl or 1-naphthylethyl in linear peptoids has proven to be fundamental to induce the formation of stable stereocontrolled *cis*-amide helical structures.<sup>[1, 2]</sup> Moreover, it has been recently shown by our research group how the introduction of a single stereogenic center on the oligopeptoid's backbone (for tri-, tetra- and hexapeptoids) can induce the formation of an unique stereoisomer as result of the cyclization.<sup>[3]</sup> In this communication, we report the synthesis and characterization of a library of cyclic tri-, tetra-, hexa- and octapeptoids, whose side-chains have been functionalized with a bulky chiral residue, to investigate the possible effect on conformational chirality. Once again, we exemplified the possibility to achieve central to conformational chirality induction, proving the potential to construct unique chiral molecular platforms, with variable size and substitution.

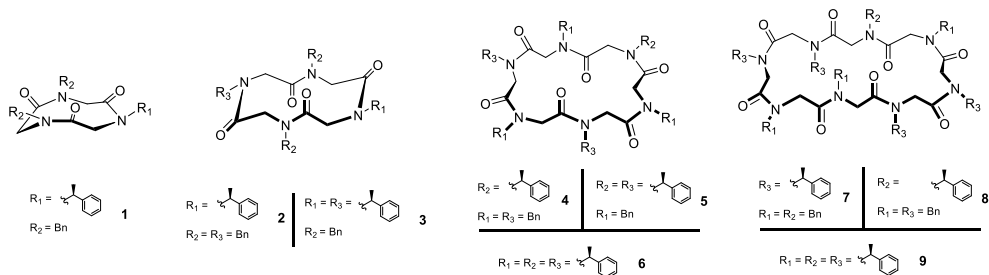


Figure 1. Schematic structures of cyclic peptoids **1-9**

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# Solvatochromic properties and solid-state inclusion of a *p*-pyridinium-calix[4]arene

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Calix[*n*]arenes are a popular class of easily derivatizable macrocycles with strong ability to form host-guest complexes exploiting the possible functions present at their lower and/or upper rim.<sup>[1,2]</sup> Recently, our attention has been focused on the preparation of a new type of bifunctional calixarenes, containing two different binding sites, such as H-bond-donating and electron-withdrawing groups. In this communication, we report the synthesis, structural characterization, and solvatochromic properties<sup>[3]</sup> of bifunctional *p*-pyridinium-calix[4]arene **1**. The X-ray structure of **1** shows an interesting dimeric capsule based on van der Waals interactions.<sup>[4]</sup> Several solvent CH<sub>3</sub>CN molecules were accommodated inside this nanocontainer. A visible band with a different  $\lambda_{\max}$  was observed in the UV spectrum of **1** in different media indicating a solvatochromic behavior. In addition, distinct colors were visually observed according to the polarity of organic solvents.

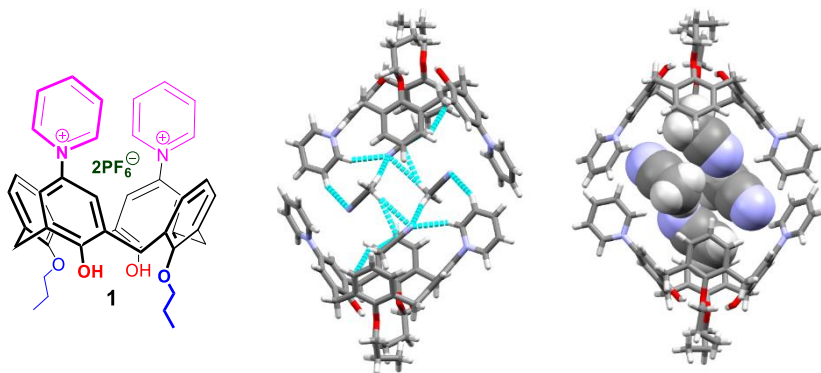


Figure 1. X-Ray structure of *p*-pyridinium-calixarenes **1**.

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## Solid state self-assembly of resorcin[6]arene macrocycles in a twin molecular capsule

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In the last two decades, the study of self-assembled molecular capsules<sup>[1]</sup> have received considerable attention. The nanoconfined environment in molecular capsules has been exploited for the stabilization of reactive species as well as in catalysis for the acceleration and the stereo and regiochemical control of chemical reactions.<sup>[1,2]</sup> In addition, the encapsulation of guests inside self-assembled capsules has led to novel forms of isomerism and peculiar conformational aspects.<sup>[2]</sup> The recent publication<sup>[3]</sup> of an improved procedure for the synthesis of the larger resorcin[6]arene macrocycle **1** now obtainable in 30-35% yield,<sup>[3]</sup> has induced us to investigate the its solid state assembling properties.<sup>[4]</sup> In the solid state, the resorcin[6]arene **1** adopts a pinched cone conformation stabilized by intramolecular H-bonds between OH groups, which is very similar to that reported for *p*-*tert*-butylcalix[6]arene macrocycle. Our studies reveal that in the solid state the resorcin[6]arene **1** assembles in a twin molecular capsule sealed by two square arrays of intra- and intermolecular H-bonds between OH groups (Figure). The molecular capsule **1**<sub>2</sub> is able to host toluene and ethyl acetate solvent molecules, by  $\pi\cdots\pi$  and C-H $\cdots\pi$  interactions.

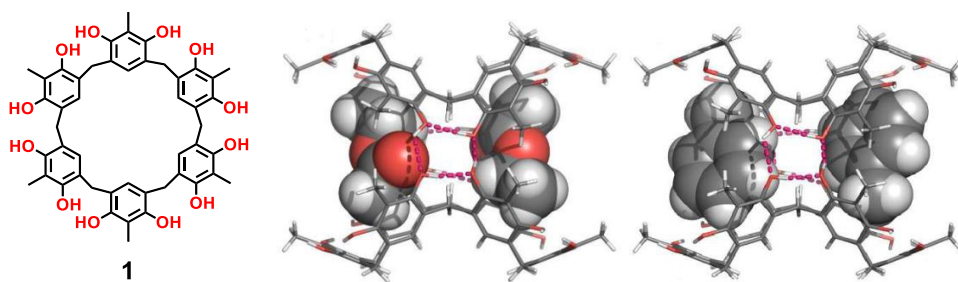


Figure 1. Resorcin[6]arene **1** (left). Encapsulation of ethyl acetate (middle) and toluene (right) guest molecules in the molecular capsule **1**<sub>2</sub>.

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# The hexameric resorcinarene capsule as nanoreactor for the catalysis of Friedel-Crafts reactions

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Recently, the self-assembled resorcinarene **1** hexameric capsules **C** [1,2] have been intensively investigated as nanoreactors for the catalysis of organic reactions.<sup>[3-8]</sup> The nanoreactor **C** shows some catalytically relevant features, which the stabilization of cationic intermediates and transition states, and a remarkable Brønsted acidity. In this communication, we show that the bridged water molecules of the resorcinarene capsule are able to activate the C–Cl bond of benzyl chloride by H-bonding (Figure 1), and, as a consequence, to promote a mild Friedel-Crafts benzylation of several arenes and heteroarenes. Interestingly, the self-assembled capsule exerts a supramolecular control on the reaction outcome. The nanoconfined environment allows the benzylation of *N*-methylpyrrole in the unusual  $\beta$ -position and has a strong influence on the reactivity of the nucleophiles mediated by their affinity for the inner cavity of the capsule rather than by their nucleophilicity.<sup>[9]</sup>

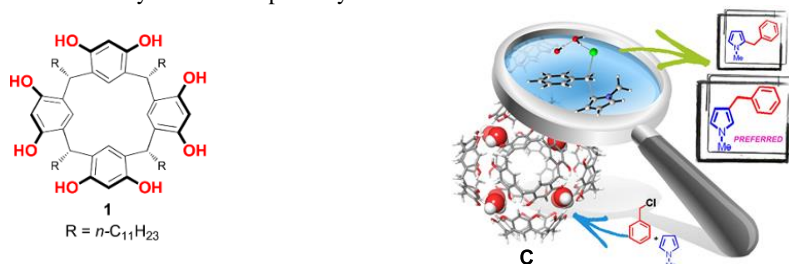


Figure 1. Water molecules of the resorcinarene capsule (**C**) are able to activate C–Cl bond and promote benzylation of *N*-methylpyrrole in  $\beta$ -position.

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## Michael addition reactions inside a self-assembled resorcin[4]arene hexameric capsule

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In the last few years there has been a significant growth of interest in performing different types of reactions in confined nanometer-scale spaces taking inspiration from the biological reactions catalysed by natural enzyme in their hydrophobic pocket.<sup>[1]</sup> In fact, the confinement of the substrates within a molecular container can lead to new reactivities and selectivities different from those normally observed in the bulk medium. Resorcin[4]arene hexameric capsules<sup>[2, 3]</sup> have been already exploited as nanoreactors thanks to their ease of preparation, their large cavity, and their ability to encapsulate different substrates and stabilize cationic intermediate.<sup>[4]</sup>

Our group recently highlighted that the hydrogen-bond-donor capabilities of the bridging water molecules of the capsule are able to promote the Friedel-Crafts benzylation reaction with high efficiency and regioselectivity.<sup>[5]</sup>

On this basis, we envisioned that this capability of the hexameric resorcinarene capsule could play a role in the catalysis of Michael addition of pyrrole to electron-deficient nitroolefins through the hydrogen-bonding activation of the nitroolefin and we herein report our recent results.

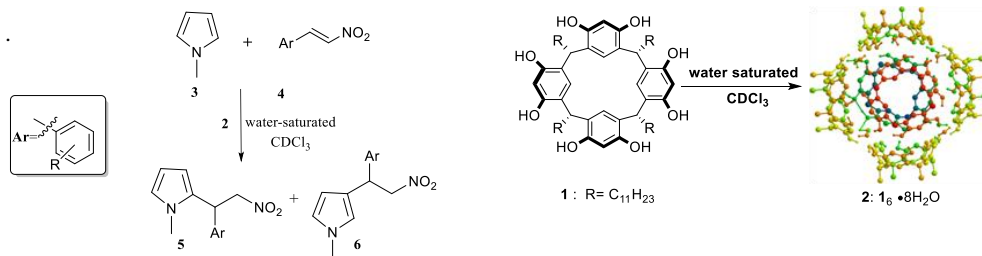


Figure 1. Conjugate addition between pyrrole 3 and nitroolefins 4 inside the hexameric resorcin[4]arene capsule 2.

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# Hydroamination reaction of alkynes catalysed by gold nanoparticles supported onto a porous host polymer matrix

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Metal nanoparticles have recently played an increasing important role in catalysis and green chemistry. Generally, their application requires the use of supports as metal oxides, carbon-based materials or organic polymers; when compared to the inorganic supports the latter offer some advantages such as easy synthesis, solvent swelling and reactant selectivity. Gold nanoparticles (AuNPs) supported onto a crystalline porous polymer scaffold consisting of syndiotactic polystyrene-polybutadiene block copolymer (AuNPs-sPSB) were found particularly effective in aerobic alcohol oxidation<sup>[1]</sup> and cross coupling esterification of cinnamyl alcohol with aliphatic alcohols;<sup>[2]</sup> moreover nitroarenes were readily reduced to anilines using sodium borohydride as reductant.<sup>[3]</sup> Recently we were interested in hydroamination reaction of alkynes with anilines.

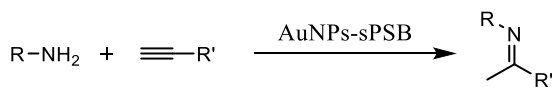


Figure 1. Hydroamination of alkynes catalyzed by AuNPs/sPSB

This reaction is an atom-economical efficient process which leads to a wide range of products of practical application. The challenge to overcome is the high activation barrier due to the repulsion between the nitrogen lone pair and alkyne  $\pi$ -system; moreover the reaction pathway is also intricate to control the regioselectivity toward the Markovnikov and anti-Markovnikov products. We investigated hydroamination reaction of alkynes catalysed by AuNPs-sPSB aiming to explore the role of the support porosity on reactant selectivity and stereocontrol of the addition reaction. The coupling of phenylacetylene with aniline was preliminary screened under solventless condition; the scope of the reaction was thus extended to different substrates such as arylanilines, arylacetylenes and alkylic alkynes. Regioselective Markovnikov addition producing the *E* isomers as the main reaction product was always observed with all of the investigated reagents. The AuNPs-sPSB catalyst is effective and recyclable, with performances that well compare with those of the best commercially available catalyst Au-TiO<sub>2</sub>.

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