



# 17<sup>th</sup> International Seminar on Inclusion Compounds and Porous Materials

Poznań, Poland, 2-6 September 2024



## 17 ISIC

# BOOK OF ABSTRACTS

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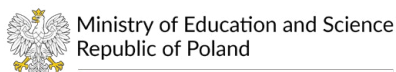
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## Conference Timetable

Sunday, September 1st	
16:30 – 17:30	Registration: Conference Venue
17:30 – 20:00	Welcome reception: Conference Venue
Monday, September 2nd	
8:30 – 9:00	Registration
9:00 – 9:30	Opening Remarks  <i>Chair: Maciej Kubicki</i>
9:30 – 10:30	<b>Jean-Marie Lehn (PL-1)</b> <i>'From Supramolecular Chemistry Towards Adaptive Chemistry'</i>
10:30 – 11:00	Coffee/Tea Break
11:00 – 11:40	<b>Reiko Kuroda (IL-1)</b> <i>'Guest Molecules in Inclusion Crystals Play Key Roles in Chirality Recognition'</i>
11:40 – 12:20	<b>Consiglia Tedesco (IL-2)</b> <i>'Molecular Conformation, Self-Assembly And Host-Guest Chemistry Of Cyclic Peptoids'</i>
12:20 – 12:40	<b>Maura Malińska (O-1)</b> <i>'Untangling Amino Acid-Cucurbit[7]uril Binding in Water: Hydrophobic Effect versus Ion-Dipole Interactions'</i>
12:40 – 13:00	<b>Zarik Yusaf (O-2)</b> <i>'Organic Cage Rotaxanes'</i>
13:00 – 13:10	Photo Group
13:00 – 14:30	Lunch <i>Faculty of Chemistry, the first floor</i>  <i>Chair: Consiglia Tedesco</i>
14:30 – 15:10	<b>Harshita Kumari (IL-3)</b> <i>'Engineering Supramolecular Assemblies in Solution and Soft Materials'</i>
15:10 – 15:30	<b>Priya Paul (O-3)</b> <i>'Exploration of Supramolecular Organogelators: Effect of Gelation and Degelation on Specific End Group and Chain Length of Alcohols'</i>
15:30 – 16:00	Coffee/Tea Break
16:00 – 16:40	<b>Kathi Edkins (IL-4)</b> <i>'Supramolecular Recognition in Pharmaceutical Drug Materials – from Fundamental Prediction to Application'</i>
16:40 – 17:00	<b>Carsten Lenczyk (O-4)</b> <i>'Uncovering the Details: Get the Most out of Your MOF/COF Samples'</i> <b>Gold Sponsor – BRUKER</b>
17:00 – 17:20	<b>Andrew J. Davies (O-5)</b> <i>'Vapour Adsorption Studies of Porous Materials'</i> <b>Surface Measurement Systems</b>
19:30 – 20:45	Event 1 <i>Poznań Sighseeing by old-fashion Tram</i>



Tuesday, September 3rd

8:30 – 9:00	<b>Registration</b>
	<i>Chair: Kari Rissanen</i>
9:00 – 9:40	<b>Len Barbour (IL-5)</b> <i>'Perspectives from More Than a Decade of In Situ Structural Analysis of Porous Materials'</i>
9:40 – 10:20	<b>Michaele Hardie (IL-6)</b> <i>'Metal-Directed Cage and Network Assemblies from Pyramidal Host-Type Ligands'</i>
10:20 – 10:40	<b>Anna Pietrzak (O-6)</b> <i>'Ambiguous Faces Of Water-Based Inclusion Compounds: Case Study of Intercalato-Clathrate Of Pt(II) Complex'</i>
10:40 – 11:10	<b>Coffee/Tea Break</b>
11:10 – 11:50	<b>Valentina Colombo (IL-7)</b> <i>'In situ insights into adsorption and catalysis in Metal-Organic Framework'</i>
11:50 – 12:30	<b>Scott Dalgarno (IL-8)</b> <i>'CaliX[4]arenes as Highly Versatile Platforms for Self- and Metal-Directed Assembly'</i>
12:30 – 12:50	<b>David Gonzalez Rodriguez (O-7)</b> <i>'Host-Guest Chemistry within Novel Adaptable Porphyrin Nanocages'</i>
12:50 – 13:00	<b>Sebastian Machowski</b> <i>TESTCHEM Sponsor presentation</i> Bronze Sponsor
13:00 – 13:10	<b>Photo Group</b>
13:00 – 14:30	<b>Lunch</b> <i>Faculty of Chemistry, the first floor</i>
	<i>Chair: Kathi Edkins</i>
14:30 – 15:30	<b>Niveen Khashab (PL-2)</b> <i>'Porous Supramolecular Hosts: From Energy Intensive Separations to Sensors and Soft Robotics'</i>
15:30 – 16:00	<b>Coffee/Tea Break</b>
16:00 – 16:40	<b>Daniel Maspoch (IL-9)</b> <i>'Clip-off Chemistry: Synthesis by Bond Cleavage'</i>
16:40 – 17:00	<b>Agnieszka Czapik (O-8)</b> <i>'From Triangles to Squares – Highly Solvated Overcrowded Chiral Macrocycles'</i>
17:00 – 18:30	<b>Poster Session</b> <i>Faculty of Chemistry, the first floor</i>
17:30 – 20:30	<b>Barbecue</b> <i>Faculty of Chemistry, the first floor</i>



**Wednesday, September 4th**

*Chair: Len Barbour*

<b>9:00 – 9:40</b>	<b>Stefan Kaskel (IL-10)</b> <i>'Stimuli Responsive Metal-organic Frameworks'</i>
<b>9:40 – 10:00</b>	<b>Alan Eaby (O-9)</b> <i>'An ultramicroporous physisorbent sustained by a trifecta of directional supramolecular interactions'</i>
<b>10:00 – 10:20</b>	<b>Kyriaki Koupepidou (O-10)</b> <i>'Structural Transformations in a Transiently Porous Coordination Network'</i>
<b>10:20 – 10:40</b>	<b>Sebastian Ehrling (O-11)</b> <i>'The Limits of Surface and Pore Volume Characterization'</i>
<b>10:40 – 11:10</b>	<b>Coffee/Tea Break</b>
<b>11:10 – 11:50</b>	<b>Silvia Bracco (IL-11)</b> <i>'Rotor dynamics, luminescent properties and gas reorientation in crystalline nanoporous architectures'</i>
<b>11:50 – 12:10</b>	<b>Volodymyr Bon (O-12)</b> <i>'Boosting the Negative Gas Adsorption Transitions Using Multivariate Framework Approach'</i>
<b>12:10 – 12:30</b>	<b>Mihails Arhangel'skis (O-13)</b> <i>'Computational Crystal Structure Prediction for the Design of Functional Metal-Organic Frameworks'</i>
<b>12:30 – 12:50</b>	<b>Damian Jędrzejowski (O-14)</b> <i>'Click and Collect: Versatile Covalent Functionalization of Novel Tetrazine-Based MOFs'</i>
<b>12:50 – 13:00</b>	<b>Adam Fordon</b> <i>3P and UNI-EXPORT Sponsor presentation</i> Bronze Sponsor
<b>13:00 – 14:30</b>	<b>Lunch</b> <i>Faculty of Chemistry, the first floor</i>
<b>Chair: Michael Zaworotko</b>	
<b>14:30 – 15:30</b>	<b>Omar M. Yaghi (PL-3)</b> <i>'Organic Chemistry and Molecular Weaving in All Dimension' - online lecture</i>
<b>15:30 – 16:00</b>	<b>Coffee/Tea Break</b>
<b>16:00 – 16:40</b>	<b>Jan J. Weigand (IL-12)</b> <i>'Well-defined Polyhedral Coinage-Metal Phosphinidenides as Isolable Building Blocks for Polydimensional Metal-Organic Frameworks'</i>
<b>16:40 – 17:00</b>	<b>Michał Chmielewski (O-15)</b> <i>'The Inner Life of a MOF: Templated Self-Organization of Linkers in a Pillared-Layer MOF'</i>
<b>17:00 – 17:20</b>	<b>Wojciech Bury (O-16)</b> <i>'Pre- and Postsynthetic Strategies Applied To Zr-Based MOFs –S'lected Catalytic Applications'</i>
<b>20:00 – 0:00</b>	<b>Banquet</b>



Thursday, September 5th

*Chair: Michael Hardie*

9:00 – 9:40	<b>Michael Zaworotko</b> (IL-13) <i>'Crystal Engineering: Then, Now and Next'</i>
9:40 – 10:20	<b>Takafumi Kitazawa</b> (IL-14) <i>'Supramolecular Soma-Iwamoto type Spin Crossover Coordination polymer Compounds'</i>
10:20 – 10:40	<b>Yizhi Xu</b> (O-17) <i>'Ab initio Crystal Structure Prediction of Metal-Organic Frameworks with Machine-Learned Potentials'</i>
10:40 – 11:10	<b>Coffee/Tea Break</b>
11:10 – 11:50	<b>Kari Rissanen</b> (IL-15) <i>'Supramolecular Halogen(I) Chemistry'</i>
11:50 – 12:20	<b>Clive Oliver</b> (O-18) <i>'Structurally-Dynamic, 2-Periodic MOFs as Hosts for Included Solvents, Gases and Water Vapour'</i>
12:20 – 12:40	<b>Szymon Sobczak</b> (O-19) <i>'Solvent-Solute Interactions Probed by Piezosolvatochromism'</i>
12:40 – 13:00	<b>Ivana Brekalo</b> (O-20) <i>'The Use of Computationally Informed Mechanochemistry in the Synthesis of New Zinc Imidazolate Forms'</i>
13:00 – 14:30	<b>Lunch</b> <i>Faculty of Chemistry, the first floor</i>
<i>Chair: Scott Dalgarno</i>	
14:30 – 15:30	<b>Tomislav Frisic</b> (PL-4) <i>Mechanochemistry: Unlocking Rapid, Scalable and Green Synthesis of Covalent, Supramolecular and Framework Targets</i>
15:30 – 16:00	<b>Coffee/Tea Break</b>
16:00 – 16:40	<b>K. Travis Hollman</b> (IL-16) <i>'Sorbent Properties of Dimethoxypillar[5]arene (DMP5)'</i>
16:40 – 17:20	<b>Mohamed Eddaoudi</b> (IL-17) <i>to be announced</i>



Friday, September 6th

*Chair: Kinga Suwińska, Kornel Roztocki*

9:00 – 10:00	<b>Jerry Atwood (PL-5)</b> <i>to be announced</i>
10:00 – 10:40	<b>Janusz Lipkowski (IL-18)</b> <i>'Inclusion Compounds Chemistry – Historical Remarks and Introduction to Conference Series'</i>
10:40 – 11:10	<b>Coffee/Tea Break</b>
11:10 – 11:30	<b>Shaheen Sultana (O-21)</b> <i>'Exploration [2+2] Reactions for Dimerizations and Polymerizations in the Metal-Organic Gels and Single Crystals of Coordination Polymers'</i>
11:30 – 11:45	<b>Yassin H. Andaloussi (O-22)</b> <i>'Dinuclear copper sulfate-based switching adsorbent layered materials for water harvesting and hydrocarbon selectivity'</i>
11:45 – 12:05	<b>Krzysztof Oliwa (O-23)</b> <i>'Development of a Characterisation Toolbox for Porous Liquid Solutions to Understand Their Gas Inclusion and Selectivity Capabilities'</i>
12:05 – 12:25	<b>Shumaial Razzaque (O-24)</b> <i>'Hypercrosslinked Polymers for the electrocatalytic Oxygen Reduction Reaction'</i>
12:25 – 12:45	<b>Seyed Soroush Mousavi Khadem (O-25)</b> <i>'Photocatalytic conversion of CO<sub>2</sub> into Valuable Products by Porphyrin based Metal-Organic Frameworks'</i>
12:45 – 13:00	<b>Closing Remarks</b> <i>Granting Diplomas and Prizes for the best Poster Presentations</i>
13:00 – 14:30	<b>Lunch</b> <i>Faculty of Chemistry, the first floor</i>









# PLENARY LECTURES



# From Supramolecular Chemistry Towards Adaptive Chemistry

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Supramolecular chemistry is intrinsically a *dynamic chemistry* in view of the lability of the interactions connecting the molecular components of a supramolecular species and the resulting ability to exchange components. The same holds for molecular chemistry when the molecular entity contains covalent bonds that may form and break reversibly. These features allow for a continuous change in constitution by reorganization and exchange of building blocks and define a *Constitutional Dynamic Chemistry* (CDC) covering both the molecular and supramolecular levels.

CDC takes advantage of dynamic diversity to allow variation and selection and operates on dynamic constitutional diversity in response to either internal or external factors to achieve *adaptation*.

It generates networks of dynamically interconverting constituents, *constitutional dynamic networks*, that may respond to perturbations by physical stimuli or to chemical effectors. Of special interest is the case where the driving force is an *increase in organization/order*.

The implementation of these concepts points to the emergence of adaptive and *evolutive chemistry*, towards *systems of increasing complexity*.

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# Porous Supramolecular Hosts: From Energy Intensive Separations to Sensors and Soft Robotics

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Host-guest based mechanisms have been heavily exploited for molecular recognition and eventual separation/ entrapment of a guest molecule. Choosing the right porous host has in most of the cases depended on complimentary size and charge thus, focusing mainly on the intrinsic interactions of the guest in the cavity of a macrocycle or a cage. Interestingly, expanding host-guest interactions to the extrinsic environment of the host afforded an intriguing set of molecular descriptors that ultimately led to unexplored host-guest interactions. In this talk, a set of supramolecular hosts ranging from 2D macrocycles to 3D cages are presented with intriguing intrinsic and extrinsic host-guest interactions that enabled them to be used for hydrocarbon and isomers separation from crude oil as well as smart recognition units in polymer composites for sensors and soft robotics. Understanding the full range of supramolecular interactions will ultimately promote a better integration of molecular building blocks to design and fabricate the “next -generation” sustainable and smart materials.



# Organic Chemistry and Molecular Weaving in All Dimensions

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PLENARY  
LECTURES

PL 3

This presentation is about extending organic chemistry in infinite 2D and 3D through the discovery of covalent organic frameworks (COFs): 2005 for 2D COFs and 2007 for 3D COFs. The applications of this chemistry in climate and to the discovery of molecular weaving will be presented.



# Mechanochemistry: Unlocking Rapid, Scalable and Green Synthesis of Covalent, Supramolecular and Framework Targets

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- Mechanochemical techniques,[1] such as grinding, milling or other types of mechanical impact and shear permit the exploration of chemical reactivity in a non-conventional environment, conducted either neat or in the presence of a small amount of a liquid additive.[2] Mechanochemistry permits access to chemical reactions and products that are difficult to achieve under more conventional solution-based approaches, and this presentation will outline the applications of mechanochemistry for the simple, environmentally-friendly generation of targets based on supramolecular chemistry and self-assembly, including cocrystals, metal-organic frameworks (MOFs), as well as complex covalent structures, such as covalent-organic frameworks (COFs). We will outline methods for the synthesis of MOFs from the simplest precursors, as well as the application of methods for real-time *in situ* reaction monitoring to elucidate mechanochemical reaction mechanisms, including the discovery of new materials.[3] It will be shown how such methods can support advances in materials science, such as improved understanding of MOF thermodynamics, wtheir applications as energetic materials, and the development of methods for the discovery of functional MOFs *via ab initio* Crystal Structure Prediction (CSP).[4] Finally, we will describe the recent emergence of Resonant Acoustic Mixing (RAM) as a technology that enables a uniquely scalable approach to MOFs, COFs and molecular targets[5]

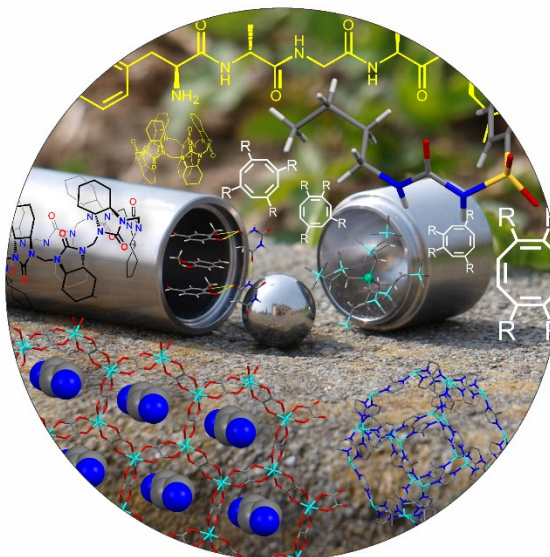


Figure 1: Mechanochemistry for the synthesis of a wide range of covalent, supramolecular and materials targets.[1]

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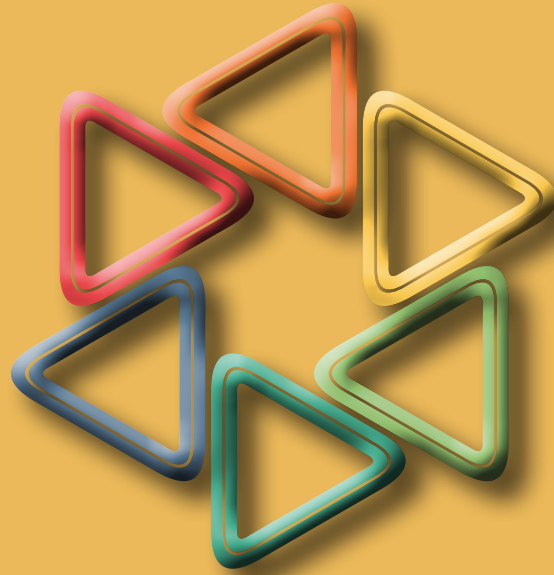


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Jerry Atwood









# INVITED LECTURES



# Guest Molecules In Inclusion Crystals Play Key Roles In Chirality Recognition

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Chirality is fundamental and ubiquitous in nature. This presentation will focus on the key roles played by guest molecules in inclusion/adduct crystals, in chirality recognition/transfer and in the rearrangement of molecules. Several examples will be discussed.

- Optical resolution of secondary alkyl alcohols is difficult but it has been efficiently achieved by simple crystallization of a non-chiral dicarboxylic acid and (1*R*,2*R*)-diphenylethylenediamine using the racemic alcohol as a solvent [1]. The alcohol molecules are trapped in the inclusion crystals with high ee (enantiomeric efficiency). It should be noted that the water molecules present in the alcohol are essential for the chiral discrimination. Similarly, in the case of chiral sodium ammonium tartrate crystal (Pasteur crystal) and its racemic crystal (Scacchi crystal), water of crystallization plays an important role in chiral discriminations [2].

- The compound 7-bromo-1,4,8-triphenyl-2,3-benzo[3.3.0]octa-2,4,7-trien-6-one (**1**) forms 1:1 inclusion crystals with various organic solvent molecules. Exposure of these crystals to solvent vapour leads to polymorphic transformation with or without guest exchange. In one case, polymorphic transformation from non-chiral to chiral crystals occurred accompanied by guest exchange, the first case of spontaneous optical resolution that occurred in the crystalline state [3].

- 2-thioaryloxy-3-methylcyclohexen-1-ones (**2**) are prochiral. The *para*-Cl derivative (*p*-Cl) crystallizes in the non-chiral space group *P* $\bar{1}$ , whereas its methyl analogue (*p*-Me) crystallizes in the chiral space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>. We successfully deracemized the *p*-Cl crystals by using a solid solution between the two compounds, followed by Temperature Cycling Induced Deracemization [4]. When the *o*-Br compound was trapped in a 1:1 adduct crystal with the chiral host compound, (–)-(R,R)–(–)-trans-2,3-bis(hydroxydiphenylmethyl)-1,4-dioxaspiro-[4,4]nonane (**3**), it exhibited substantial CD (circular dichroism) in a KBr matrix. Irradiation of the crystal afforded a chiral photocyclization product with an optical purity of 82% ee [5]. This result contrasts with the corresponding solution reaction, which resulted in a racemic product. The reaction process was followed by solid-state CD spectroscopy [6]. As exemplified by this study, chiral spectroscopy in crystals, films, and gels provides rich information necessary to understand the unique solid-state chemistry, but it suffers from substantial intrinsic macroscopic anisotropies. We have devised the KBr disc measurement method (now used worldwide) [6,7], and developed versatile chiroptical spectrophotometers, UCS-1, 2, and 3 (UCS = Universal Chiroptical Spectrophotometer) for real-time transmittance as well as diffuse reflectance CD measurements [8].

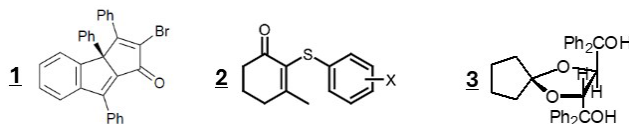


Figure: Structures of **1**, **2** and **3**.

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# Molecular Conformation, Self-Assembly And Host-Guest Chemistry Of Cyclic Peptoids

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Peptoids are N-substituted polyglycines with useful biological activities and interesting chemical properties both in solution and in the solid state [1]. Our group reported on how inter-annular  $\text{CH}\cdots\text{OC}$  hydrogen bonds allow for face-to-face or side-by-side arrangement of the macrocycles mimicking secondary structure in proteins and forming porous crystalline frameworks [2]. By combining in-situ powder and single crystal X-ray diffraction, thermal analyses, hot-stage optical microscopy we showed how environmental changes (such as temperature, humidity, gas pressure) may trigger the dynamic behaviour of cyclic peptoids in the solid state [3,4]. By conformational and lattice energy calculations we demonstrated the role of intermolecular host-guest interactions in closing and reopening a peptoid porous framework upon reversible guest release and uptake.

More recently, we crystallized and structurally characterized for the first time cyclic dodecapeptoid compounds, with five consecutive *cis* residues in a typical right-handed PPI helical conformation bridged by two *trans* residues to other five consecutive *cis* residues in a left-handed PPI helical conformation. We were able to highlight the role of intramolecular backbone-to-backbone  $\text{CO}\cdots\text{CO}$  interactions and C5  $\text{CH}\cdots\text{OC}$  hydrogen bonds in the stabilization of the molecular conformation (Figure 1).

In this contribution we will review how the lack of the amide proton prevents the formation of  $\text{NH}\cdots\text{CO}$  bonds and makes peptoids the ideal platform for evidencing the influence of  $\text{CH}\cdots\text{OC}$  and  $\text{CO}\cdots\text{OC}$  interactions in stabilizing molecular conformations, triggering conformation polymorphism and phase transitions.

The authors wish to acknowledge FARB funding (University of Salerno) and PRIN 2022 PNRR P2022ZBNC2 (Ministero dell'Università e della Ricerca).

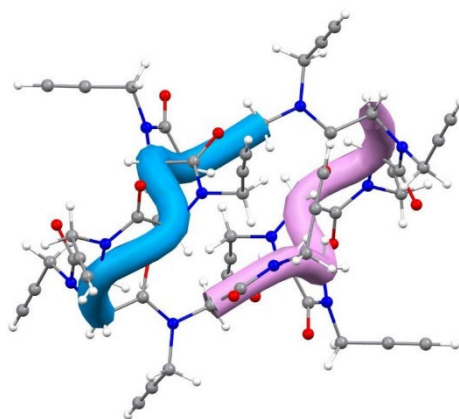


Figure 1: Enantiomorphous right- and left-handed PPI helices in a cyclic dodecapeptoid with propargyl side chains.

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# Engineering Supramolecular Assemblies In Solution And Soft Materials

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Supramolecular gelation is a captivating self-assembly process that mirrors significant natural and biological phenomena. The supramolecular characteristics of these materials confer reversibility and adaptability to the system. The structural evolution during the assembly process is primarily driven by the individual or collective contributions of various non-covalent interactions, such as hydrogen bonding,  $\pi$ - $\pi$  stacking, metal-ligand coordination, host-guest interactions, and van der Waals interactions. Over the past few decades, supramolecular gels have been extensively studied, primarily focusing on their functional outputs for technological and medicinal applications. However, purely structural investigations of these materials are relatively limited. The scarcity of convincing structural data has several implications, with the two most critical factors being the experimental time scale and the sensitivity of measurements to structural evolution. In this study, we will explore the self-assembly processes of supramolecular nanoassemblies under ambient and non-ambient conditions. Specifically, we will examine how real-time measurements provide valuable insights into the nucleation and self-assembly of materials. The information obtained will offer valuable insights into the structure-function correlation of materials, potentially benefiting fields such as pharmaceuticals and personal care.



# Supramolecular Recognition in Pharmaceutical Drug Materials – from Fundamental Prediction to Application

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Pharmaceutical materials have to be safe for the patient while also delivering the drug payload with tight control. This starts with the crystalline drug material itself, which has a significant influence on the dissolution behaviour and hence the bioavailability of the final formulation. It is currently impossible to predict the outcome of a crystallisation experiment before performing it. In this presentation, I will cover how supramolecular recognition in solution can be used to understand the crystallisation process, how solvent can influence this process and how we can start to tailor materials to suit their pharmaceutical application.

In the first part, I will present the model compound cimetidine, a H<sub>2</sub>-receptor antagonist in the treatment of stomach ulcers, which is known to form a range of hydrated crystal forms. By using solution spectroscopy and neutron total scattering experiments, the interactions between cimetidine and water in solution can be observed and quantified, which in turn sheds light on why these hydrates form in the first place.

The second part will focus on pharmaceutical co-crystallisation and how supramolecular recognition in solution can be used to find the best solvent to obtain the co-crystal. The model system of caffeine – benzoic acid is reported to nucleate only in the presence of hetero-nuclei.[1] By using solution-state spectroscopy verified against ternary phase diagrams, we can show that the co-crystal can form directly from solution. Solution aggregation also allows us to choose which solvents to use to obtain this crystal form.[2] Changing benzoic acid to sodium benzoate increases the caffeine solubility in water up to 20-fold by forming a hydrotrope. While multiple supramolecular interaction types have been suggested to lead to hydrotropism, none of these have been observed experimentally. I will show how neutron total scattering can help elucidating the supramolecular interactions between caffeine and sodium benzoate to enhance caffeine solubility, which can feed forward into developing new hydrotropic systems.[3]

In the last part of the presentation, I will show how co-crystallisation and supramolecular recognition in solution may be used in pharmaceutical application towards taste masking, which is particularly important in paediatric medication. For the model system of nevirapine, an anti-retroviral drug compound used in the treatment of HIV infection, we have screened five co-crystal systems towards taste improvement using the electronic taste testing setup of the e-tongue. [4] We could further correlate the improvement in bitterness of the drug to a combination of the strength of molecular aggregation in solution and the taste of the co-former, opening a novel route to tailor materials with improved taste.

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# Perspectives from more than a decade of in situ structural analysis of porous materials

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The inclusion of small guest molecules into porous crystalline materials promises several exciting innovations in a wide range of areas, including separation and storage of gases or vapors, chemical sensing, and catalysis. Using now well-established principles of crystal engineering we can aspire to design porous materials with tailored structural and physical properties. However, there is still a need to develop new approaches to understanding the sometimes-complicated relationships between molecular-level structure and physico-chemical properties. In this regard, devising a range of complementary experiments to characterize materials under controlled environments such as gas pressure can be particularly challenging. This presentation will describe the development and application of a suite of approaches to structural analysis by means of in situ X-ray diffraction, complemented by physico-chemical characterization using a combination of sorption analysis and thermoanalytical techniques.<sup>[1-4]</sup>

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# Metal-directed Cage and Network Assemblies from Pyramidal Host-type Ligands

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Cyclotrimeratrylene (= CTV) is a pyramidal host molecule. We have developed a range of chiral tripodal CTV-analogues (L-type ligands) where the CTV scaffold has been functionalized with metal-binding ligand groups. These form discrete metallated cavitands, coordination cages, [1] coordination polymers [2] and other networked assemblies. These include unusual topologically complicated assemblies including a unique chain-mail of Borromean rings.[3] Examples of coordination cages include trigonal bipyramidal  $M_3L_2$  cages,  $M_6L_8$  stella octangula cages and  $M_{12}L_8$  cubes. For example,  $[Pd_3(bis-NHC)_3L_2]$  cages where *bis*-NHC is a chelating *N*-heterocyclic carbene ligand forms crystalline materials that bind  $I_2$ , Fig. 1 [4] and  $[Ir(C^{\wedge}N)_2\}_3L_2]^{3+}$  metallocryptophanes, where  $C^{\wedge}N$  is a 2-phenylpyridine ligand, which are luminescent, and where variants include cages that show whole-body photoswitching through embedded azo-aromatic groups (Fig. 1) [5]. A large (and unpredictable) variety of coordination polymers can be accessed using these L-type ligands including those composed of networked  $M_nL_2$  cages, which have shown guest-uptake [6] or photocatalytic activity. A recent example is a  $[Cu_6L_4Cl_{12}]$  material with a highly unusual structure that is composed of networked cage-catenane assemblies linked through different types of Cu-Cl-Cu bridges (Fig. 1), and where a mixed anion  $Cl/NO_3$  analogue forms dimers of cage-catenanes that transform into coordination polymer on solvent-exposure.[7]

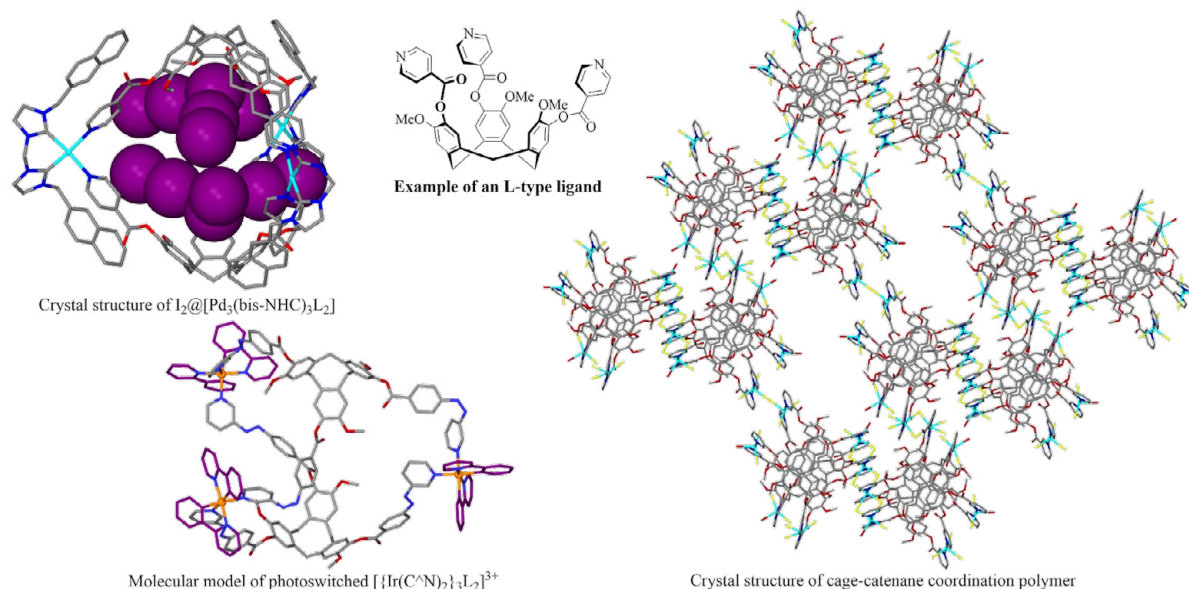


Figure 1: Examples of discrete and polymeric cage-assemblies using L-type ligands

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# In situ insights into adsorption and catalysis in Metal-Organic Frameworks

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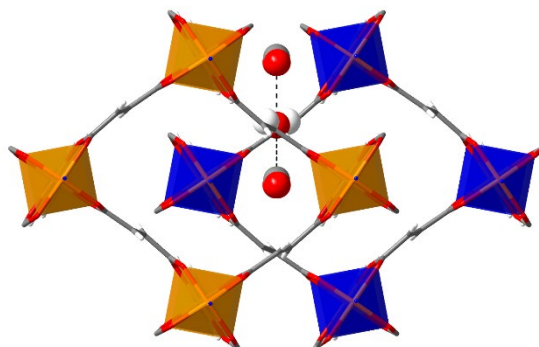
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To develop and optimize novel adsorbents that exhibit selective metal-adsorbate interactions or specific guest adsorption, and to thoroughly characterize their crystal structure, electronic, and oxidation/charge states, it is essential to elucidate the role of coordinatively unsaturated metal centers, specific adsorption sites, and key physical changes upon guest binding. To this aim, the combination of in situ and operando crystallographic and spectroscopic techniques is becoming essential for understanding the structure-function relationships of metal-organic frameworks (MOFs) demonstrating that a multi technique approach can uncover unprecedented details about the underlying processes.

My research group focuses on understanding the structural changes in long-range order and local environments during adsorption processes and catalysis. We utilize in situ X-ray diffraction and operando X-ray absorption experiments, or a combination of both. Our work includes synthesizing novel adsorbent MOF materials, rationalizing gate-opening effects and cooperative gas adsorption phenomena, and identifying key active sites during adsorption and catalysis.

In this lecture, I will present our recent findings, achieved through a combination of advanced techniques, including custom-made setups. Key studies to be discussed include: i) in situ detection of specific adsorption sites for CO<sub>2</sub> adsorption under humid conditions; ii) Combined XAS/PXRD experiments to describe the evolution of long-range and local structures during adsorption experiments; iii) in-depth analysis of 'PXRD CO<sub>2</sub> adsorption isotherms', encompassing the retrieval of heat of adsorption and host-guest interactions through ab-initio structure solution and Rietveld methods.



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# Calix[4]arenes As Highly Versatile Platforms For Self- And Metal-Directed Assembly

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The calix[4]arene (C[4]) framework presents three distinct regions of the macrocycle that can be synthetically modified with relative ease: the upper- and lower-rims, as well as the methylene bridge positions, though this is more challenging in nature (Figure 1). The talk will present a broad overview of functionalization in these areas, discussing self- and metal-directed assembly via each region through variation of functionalities introduced to C[4].

Discussion of the lower-rim will focus on the use of the tetra-phenolic pocket to programme the assembly of series of C[4] and bis-C[4]-supported polymetallic clusters,[1] highlighting the persistence of structural trends before moving on to new approaches in constructing hybrid C[4]-supported clusters; these being clusters constructed using both methylene and heteroatom-bridged C[4]s in tandem.

Upper-rim carboxylate groups provide a convenient entry point to the metal-directed assembly of C[4]s (akin to MOP / MOF methodology), and examples of both discrete and polymeric systems will be presented. Calix[4]arene conformation is also found to be critical in driving metal-directed assembly,[2] with pinched cone conformers facilitating the formation of fascinating new polymetallic clusters. Finally, synthesis of C[4]s exhaustively functionalized at the methylene bridge positions will be presented along with initial efforts in metal-directed assembly.[3] This synthesis is challenging for various reasons, but holds potential for the assembly of a range of MOPs with tailored properties, some of which relate to the topics outlined above.

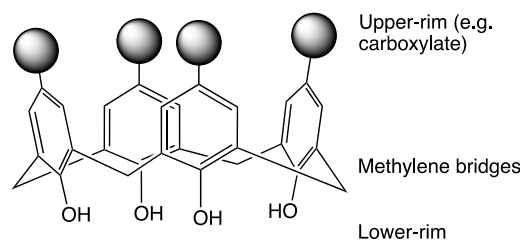


Figure 1: Schematic of the calix[4]arene framework indicating points for synthetic alteration (and subsequent application in both self- and metal-directed assembly).

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# Clip-off Chemistry: Synthesis by Bond Cleavage

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Historically, innovations in synthetic methods and reactions have changed the way scientists think about designing and synthesizing materials and molecules. Indeed, novel synthetic methods not only unlock access to previously unattainable structures, but also inspire new concepts as to how we design and build materials to address global social, economic and industrial needs. In this talk, I will present the concept of bond breaking as a new synthetic methodology that we have named Clip-off Chemistry. Unlike most state-of-the-art synthetic approaches, which use bottom-up strategies to link atoms and molecules through the formation of new bonds, Clip-off Chemistry is based instead on the selective cleavage of existing bonds in molecules and materials, providing precise spatial control over bond cleavage. Therefore, Clip-off Chemistry represents a new synthetic methodology, whereby the programmed selective disassembly affords new molecules and materials. This disassembly occurs at the molecular level through a chemical reaction; in a first approach, through ozonolysis, a gas/solid reaction that enables cutting of constituent organic molecular building blocks or linkers via direct cleavage of their alkene bonds. In this talk, I will show the principles of Clip-off Chemistry, and the first examples of structures and molecules synthesized through controlled bond fission in porous reticular materials (*i.e.* MOFs, macrocycles and cages).



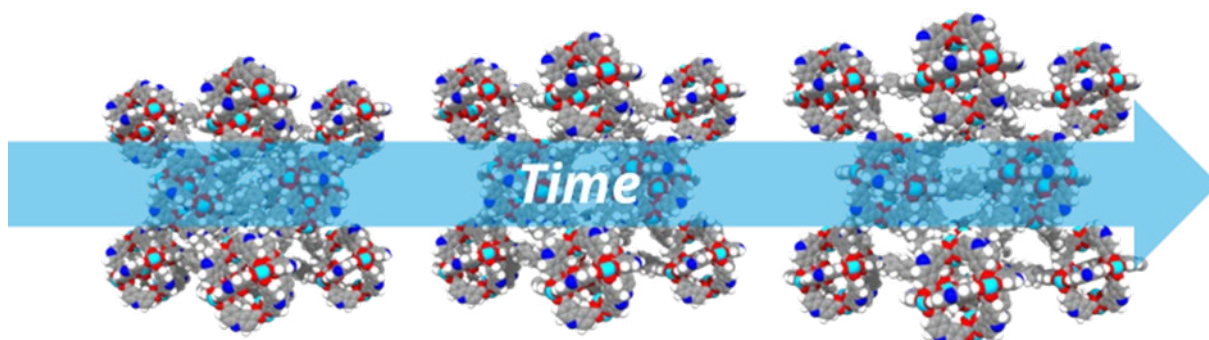
# Stimuli Responsive Metal-Organic Frameworks

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Responsivity of MOFs towards gas and liquid phase stimuli presents tremendous chances for applications in gas storage, separation, sensing and actuation. Despite emerging applications, the rationalization of flexibility phenomena is still at an early stage. In recent years *in silico* methodologies have made great progress to model the entire energetic landscape of complex host-guest interactions and framework dynamics. However, experimental observations such as finite size effects, activation barriers and sample history require an interplay of experimental and analytical techniques combined with simulation [1-11]. We emphasize the importance of MOF model materials to shine light on the complex interplay of materials descriptors (structure, disorder, finite size, morphology, history etc.) and their analyses using dedicated *in situ* characterization tools (XRD, NMR, EPR, XAS etc.) for advancing the understanding of stimuli-responsive porous framework materials in future.



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# Rotor dynamics, luminescent properties and gas reorientation in crystalline nanoporous architectures

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Nanoporous architectures offer stimulating opportunities for the development of smart materials endowed with fast dynamics and stimuli-responsive properties. Molecular rotors, motors and switches in the solid state find a favorable playground in porous materials, such as Metal Organic Frameworks, thanks to their large free volume.

We have realized a fast molecular rotor in a Zn-MOF whose rotation speed approaches that of unhindered rotations in organic moieties even at very low temperatures (2 K) [1]. Pillared-MOFs built from two distinct ultrafast and interacting molecular rotors form a multidynamical architecture wherein the rotors experience sequential motional behavior activated at distinct temperatures. The manipulation by chemical stimuli, such as CO<sub>2</sub>, which diffused from the gas phase into the porous matrix, resulted in the selective control over rotary dynamics [2]. Attractive functional properties, such as dielectric, optical and ferroelectric switchable properties, can be activated by incorporating fast-reorientable dipoles onto molecular rotors to produce materials responsive to static or oscillating electric fields. Fluorinated Al-MOFs, comprising a wheel-shaped ligand with geminal rotating fluorine atoms, produced a benchmark dynamics of correlated dipolar rotors at 2 K with practically null activation energy (17 cal mol<sup>-1</sup>). Gas accessibility, shown by hyperpolarized-Xe NMR, allowed for chemical stimuli intervention: CO<sub>2</sub> triggered dipole reorientation, reducing their collective dynamics and stimulating a dipole configuration change in the crystal [3]. Multiple molecular rotating elements, such as bicyclopentane, pyridyl, and trans azogroups, were integrated successfully into a flexible pillared MOF. As result of the open porosity, both structure and rotary motion were fine-tuned and even enhanced, in response to stimuli, as diffused CO<sub>2</sub> or I<sub>2</sub> vapors. Indeed, the dynamic MOF undergoes a piston-like displacement of the framework, propelled by the guest absorption [4].

The modular approach to MOF materials allowed the precise assembly of inorganic and organic building blocks at nanometric distances promoting the formation of mixed ligand innovative photonic materials which display fast scintillation and large Stokes shift emission [5, 6]. Moreover, scintillating MOFs were simultaneously capable of concentrating radioactive gases and efficiently producing visible light revealed with high sensitivity. We demonstrated the capability of a hafnium-based MOF incorporating dicarboxy-9,10-diphenylanthracene as a scintillating conjugated ligand to detect gas radionuclides [7].

CO<sub>2</sub> diffusion in a porous crystalline material, in which the channels are decorated by double helices of electrostatic charges, has been described by solid state NMR. The remarkable CO<sub>2</sub>-matrix association allowed direct observation of the gas exploring the nanochannels and the identification of the specific interaction sites, providing peculiar details about the role of electrostatic interactions in gas transport phenomena [8].

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# Well-defined Polyhedral Coinage-Metal Phosphinidenides as Isolable Building Blocks for Polydimensional Metal-Organic Frameworks

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The supramolecular building block (SBB) approach facilitates the formation of metal-organic frameworks (MOFs) via the linkage of pre-organized metal-organic polyhedra (MOPs).[1] While the judicious design of both the MOP and the organic linkers has been used to address unprecedented architectures of highly connected MOFs with topologic control,[2] the approach can also be used to organize nanoclusters with exceptional features into a rigid framework to fine-tune their properties.[3]

In this regard, coinage-metal based nanoclusters are highly attractive materials owing to their structural diversity and tunable properties, that have enabled their use in several applications, including optoelectronics, medicine and catalysis.[4,5] Albeit great potential can be envisioned for these materials, their synthetic strategies are often plagued by low selectivities and yields limiting their incorporation into larger frameworks.

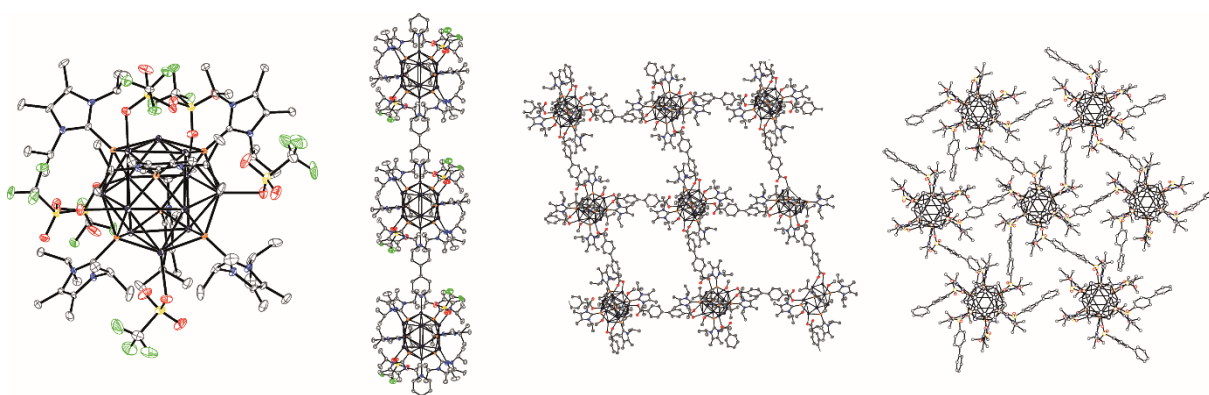


Figure 1: Molecular structures of silver-phosphinidenides and its 1D, 2D, and 3D frameworks.

Herein, we introduce a new family of isolable and highly stable polyhedral silver complexes, namely silver-phosphinidenides, that feature well-defined anion-dependent architectures. Their facile and modular synthesis can be conveniently scaled-up to afford multigram yields. Furthermore, they can be used as SBBs for the construction of one-, two- and three-dimensional frameworks upon accessing the vacant Ag coordination sites or by facile anion exchange with polytopic linkers. We will disclose the synthesis, characterization, and inclusion properties of these novel materials in detail.

Acknowledgment: We thank the Deutsche Forschungsgemeinschaft (DFG grant numbers WE4621/6-2) and the Fonds der Chemischen Industrie (Kekulé Fellowship for P.R.) for financial support.

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# Crystal Engineering: Then, Now and Next

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That composition and structure can so profoundly impact the properties of crystalline solids has provided impetus for exponential growth in the field of *crystal engineering*<sup>1</sup> over the past 30 years. This contribution will address how crystal engineering has evolved from its initial focus upon design (form) to its current emphasis on properties (function). Three classes of sorbent materials will be presented:

- **Ultramicroporous materials** offer exceptional control over pore chemistry, pore size and pore shape. New benchmarks for CO<sub>2</sub> (see Figure), C<sub>2</sub>H<sub>2</sub> and C<sub>6</sub>H<sub>6</sub> have been observed<sup>2</sup> thanks to tight binding sites and strong electrostatics associated with these coordination networks, which remain underexplored when compared to materials such as large pore MOFs. Studies that address water harvesting will be presented.
- **Flexible metal-organic materials**, FMOMs, were once seen as a curiosity but it is now recognized that they can offer solutions to important gas storage and separation applications, especially when they reversibly switch from closed (non-porous) to open (porous) phases.<sup>3</sup> New examples of switching FMOMs will be discussed.
- **Sorption in non-porous solids**. Non-porous solids that undergo pressure-induced switching between closed and open phases are of interest for storage and separations applications.<sup>4</sup> New examples of such “switching adsorbent materials” covering 0D, 1D and 2D materials will be covered.<sup>5</sup>

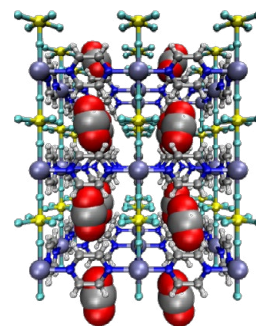


Figure. CO<sub>2</sub> capture by an ultramicroporous material<sup>2a</sup>

The overall goal of this presentation is to convey how and why crystal engineering can teach us how to custom design the right crystalline material for the right application, including what this means for global challenges such as carbon capture and water purification.

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# Soma-Iwamoto-type Spin Crossover Supramolecular Coordination Polymers

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On supramolecular spin crossover compound kingdoms, guest-triggered spin crossover “Soma–Iwamoto-type” penetration coordination polymer compounds  $\{\text{Fe}(\text{4-methoxypyrimidine})_2[\text{M}(\text{CN})_2]_2\} \cdot \text{Guest}$  ( $\text{M} = \text{Ag}, \text{Au}$ ) have been in progress [1]. Materials based on iron(II) ion coordination polymer compounds with bistable systems between the low spin and the high spin states, usually triggered by external stimuli, such as temperature, light, pressure, and guest molecules, are opening a class of potential candidates for valuable smart materials [2].

Due to the important SCO behavior of the original-Hofmann type reported in 1996, linking to Soma-Iwamoto type,  $\text{Fe}(\text{pyridine})_2\text{Ni}(\text{CN})_4$  was demonstrated using mainly  $^{57}\text{Fe}$  Mössbauer spectroscopy [3], SCO Hofmann-like frameworks associated with Soma-Iwamoto type have been developed to get potential applications in smart materials [4,5].

In the hot atom chemistry connected with radio chemistry and nuclear chemistry, the nuclear-decay-induced excited spin state trapping (NIESST) for  $^{57}\text{Co}$ -labelled Hofmann analogous compound  $^{57}\text{Co}(\text{pyridine})_2\text{Ni}(\text{CN})_4$  was found using the emission Mössbauer spectroscopic research in nuclear probes for obtaining the local daughter site information [6]. Recently a soft X-ray-induced excited spin state trapping (SOXEISST) effect in SCO coordination polymers of  $\text{Fe}^{\text{II}}(\text{4-methylpyrimidine})_2[\text{Au}(\text{CN})_2]_2$  associated with Soma–Iwamoto-type has been found. A soft X-ray absorption spectroscopy (XAS) study on these SCO Coordination polymer compounds has demonstrated that the high spin configuration (HS;  $S = 2$ ) was prevalent in  $\text{Fe}^{2+}$  ions during the measurement even at temperatures much lower than the critical temperatures ( $>170$  K), manifesting HS trapping due to the X-ray irradiation [7]. In a sense, NIESST effects has a relationship with SOXEISST effects as to the hot atom chemistry in nuclear chemical sciences.

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# Supramolecular Halogen(I) Chemistry

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An exciting research challenge in supramolecular chemistry is to design, synthesize, and characterize novel architectures with applications in biology, chemistry, and materials science.[1] Predicting and designing non-covalently bound supramolecular complexes and assemblies is difficult because of the weakness of the interactions involved, thus the resulting superstructure is often a compromise between the geometrical constraints of the building blocks and the competing weak intermolecular interactions.[2]

Our research interest has been focused on the studies of weak non-covalent intermolecular, *viz.* supramolecular interactions as the driving force in complex formation, self-assembly and molecular recognition, especially in the solid state by single crystal X-ray diffraction. The lecture will highlight some of our recent studies on supramolecular complexes based on halogen-bonded systems, especially focusing on those based on halogen(I) cations.[3]

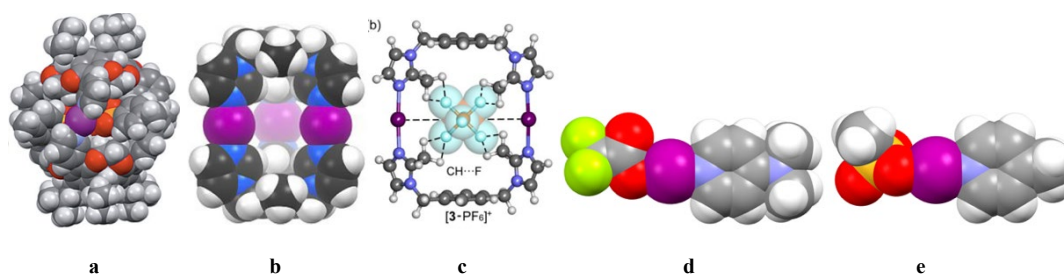


Figure 1. The X-ray or modelled structures of iodine(I) cation containing dimeric cages ( $a^{3a}$  and  $b^{3b}$ ), a macrocycle ( $c^{3h}$ ), DMAP iodine(I) trifluoroacetate ( $d^{3s}$ ) and 4-methylpyridine iodine(I) methylsulfonate ( $e^{3k}$ )

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## Sorbent Properties of Dimethoxypillar[5]arene (DMP5)

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A variety of shape-persistent organic macrocyclic compounds are prized for their easy synthesis and exceptional solution-phase host-guest binding properties. This talk will focus on the small molecule complexation properties of Ogoshi's dimethoxypillar[5]arene (**DMP5**)—the cheapest and most readily available of the pillar[n]arenes—in organic solvents and in the solid state. It will be shown that, due to neglect of solvent competition in binding studies, the intrinsic affinity of **DMP5** for apolar small molecules (*e.g.*, normal hydrocarbons and non-polar gases) has probably been underestimated by at least an order of magnitude. This observation has ramifications in the context of small molecule gas complexation and the potential for the various solid forms of guest-free **DMP5** to function as porous and pseudo-porous sorbents. The ability of **DMP5** to selectively scavenge complementary gases from solution and the gas phase will be discussed. For example, guest-free forms of **DMP5** are shown to transform to a  $\beta$ - $x(\text{CO}_2)@$ DMP5 gas clathrate in the solid-state when pressurized with  $\text{CO}_2$ . A metastable, partially  $\text{CO}_2$ -occupied b-phase,  $\beta$ - $x(\text{CO}_2)@$ DMP5 ( $x \approx 0.16$ ) has been isolated and demonstrated to be formally porous, exhibiting a  $\text{CO}_2$  uptake capacity similar to the related (dihydroxy)pillar[5]arene compound. The scavenging of complementary organic molecules from the vapor phase of complex liquid mixtures, such as gasoline, will also be discussed.

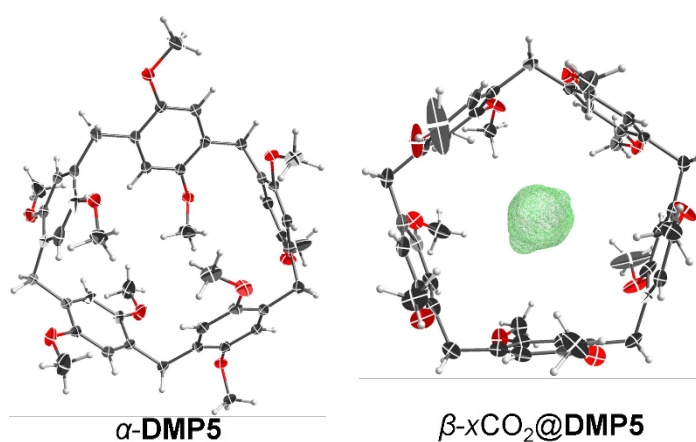


Figure 1: Single crystal structures of (left) guest-free  $\alpha$ -DMP5, and (right) the  $\beta$ - $x(\text{CO}_2)@$ DMP5 ( $x \approx 1$ ) inclusion compound.



•  
Mohamed Eddaoudi



# Inclusion Compounds Chemistry – Historical Remarks and Introduction to Conference Series

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When chemistry began to be considered a ‘science’, one of the fundamental problems to solve was the ‘daltonide versus berthollide’ controversy - quite vigorous and firmly based upon experimental evidence. The battle has been won by daltonide, and since then we have the chemistry teaching scheme based on the concept of stoichiometry and its consequences. The exceptions, well known at the time, were put on margins.

Nowadays the situation is different, although not at the school level. If we use lithium batteries, non-stoichiometry of bonding lithium is clearly evident (inclusion, or intercalation). Single crystals of silicon, the basis of modern electronics, receive their desired characteristics after successful doping by respective additives, again in non-stoichiometric proportions. Zeolites are the next example but the whole chemical world now is dominated by the ‘berthollide’ forms of matter.

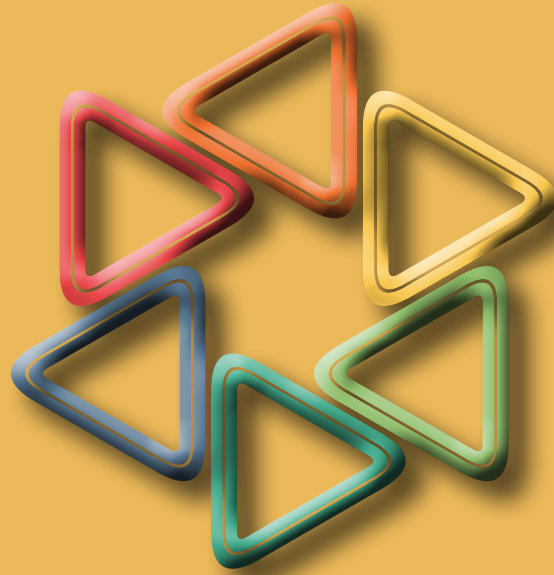
## *History of the conferences*

The story of the conferences starts with the symposium entitled ‘Clathrate Compounds and Molecular Inclusion Phenomena’ was organized in Jachranka. The very first one from the present series was held in a resort area in the South of Poland (Jaszowiec, 1987). In order to make it even more attractive for young researchers from the communist block the meeting was bilingual, English and Russian were spoken there. The idea was excellent, regular meetings, named International Seminars, from the series were organized biennially (odd years, to avoid conflicts with the Symposia). The second Seminar was held in Novosibirsk (Russia), then we had ones in Slovakia, Czech Republic, Ukraine, Turkey and South Africa, in some places even more than once. Numbering the Seminars was ‘corrupted’ since in Novosibirsk the Organizers decided that the No. 1 was not ours in Poland but in 1981 in Slovakia where Anna Sopkova organized a microsposium with some participation of Czech and Polish guests. The list is given below.

1981 Stara Lesna, Czechoslovakia (A. Sopkova); 1987 Jaszowiec, Poland (J. Lipkowski); 1989 Novosibirsk, Russia (Yu. A. Dyadin); 1991 Stara Lesna, Czechoslovakia (A. Sopkova); 1994 Odessa, Ukraine (S. Andronati); 1995 Istanbul, Turkey (S. Akyuz, C. Erk); 1997 Pardubice-Sec, Czech Republic (K. J. Kolousova); 2001, Popowo Poland (K. Suwinska); 2003 Novosibirsk, Russia (V. P. Fedin); 2005 Kazan, Russia (A. I. Kononov); 2007 Kyiv, Ukraine (V. Kalchenko); 2009 Stellenbosh, South Africa (L. Barbour); 2013 Edinburgh, Scotland (S. Dalgarno); 2011; Gierloz, Poland (K. Suwinska); 2015 Warsaw, Poland (K. Suwinska); 2017 Kazan, Russia (S. Antipin); 2019 Chisinau, Moldova (Yu. Simonov).

More data on the history as well as new notation of the clathrates will be presented.





# **ORAL COMMUNICATIONS**



# Untangling Amino Acid-Cucurbit[7]uril Binding in Water: Hydrophobic Effect versus Ion-Dipole Interactions

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Molecular recognition plays a crucial role in a wide range of chemical and biological processes, encompassing phenomena such as crystallization, molecular assembly, enzyme catalysis, cellular signaling, and protein-protein interactions. Molecular recognition typically occurs within a solvent environment. This complexity makes understanding the process challenging. CB7, cucurbit[7]uril, a model hydrophobic pocket, offers insight into the interplay between non-covalent interactions and solvation, influencing the change in free energy ( $\Delta G$ ) of binding. Notably, CB7 exhibits a preference for binding molecules with positively charged amine groups, often accompanied by the release of water molecules from its binding pocket. Molecular dynamics simulations estimate that water release contributes significantly to the enthalpy of binding ( $\Delta H$ ), reaching  $-102$  kJ/mol for CB7 [1]. Given water release's pivotal role, binding affinity likely depends on volume. We explore whether ion-dipole interactions at the negatively charged portal of CB7 remain constant across amino-containing ligands and how solvation affects these weak interactions. Our study involves measuring binding affinities (ITC), crystallizing CB7 complexes with amino acids (XRD), and examining ion-dipole interactions (fSAPT), and solvation changes (COSMO-RS). While certain amino acids, like Phenylalanine (Phe), exhibit strong affinities due to minimal solvation penalties in water, crystallization studies of Phe, Tyrosine (Tyr), Tryptophan (Trp), Leucine (Leu), Methionine (Met), L-DOPA, and Histidine (His)[2] reveal the complex nature of ligand-CB7 interactions. CB7's shielding effect alters ligand pKa values, leading to diverse protonation states and the presence of water molecules within the CB7 cavity, impacting the positioning of amino groups and, consequently, the strength of ion-dipole interactions. While ion-dipole interactions play a role, interactions involving the hydrophobic portions of amino acids are also significant. On average, ion-dipole interactions for zwitterionic amino acids contribute approximately  $-266$  kJ/mol, while for positively charged amino acids, it reaches around  $-314$  kJ/mol. However, the most substantial variability is observed in the interaction energies of the side chains with CB7. Predicting  $\Delta G$  remains an ambitious goal with profound implications for ligand design. However, our study highlights the challenges and the progress required to achieve this goal, even for the relatively small, rigid cavity of CB7.

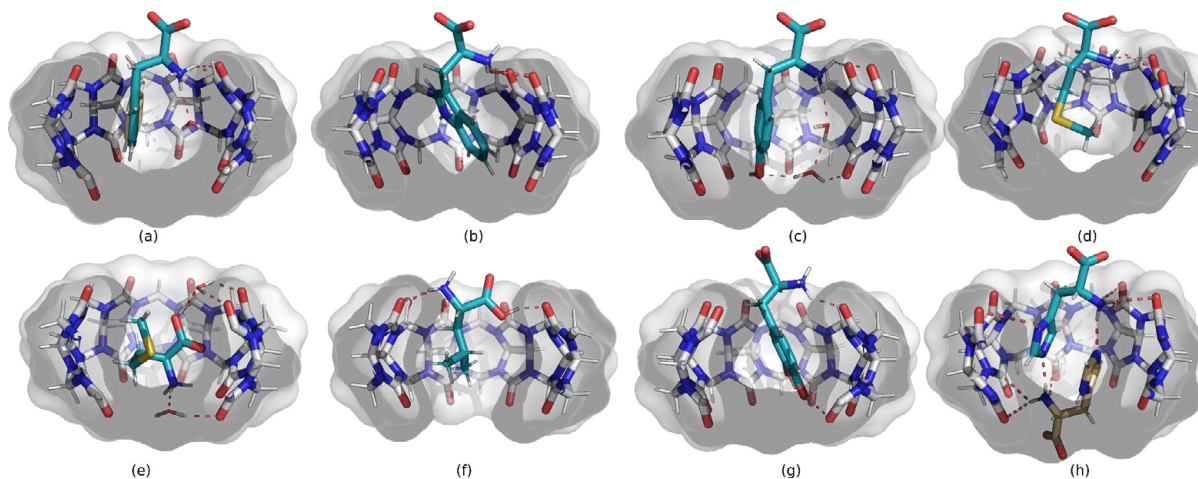


Figure 1: Complexes of CB7 with Phe (a), Trp (b), Tyr (c), Met (d), Met (+1) (e), Leu (+1) (f), L-DOPA (g), and 2 His (h) in the asymmetric part of the unit cell of the crystal structures. CB7 molecules are depicted partially to better show the ligand position.

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# Organic Cage Rotaxanes

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Organic cages are materials constructed from covalent bonds with internal cavities that enable them to accept guests. These cages can be post-synthetically modified (PSM) by incorporation of handles, which can be derivatised further to introduce additional functionality.<sup>1</sup> Whilst there are numerous methods to synthesise these materials, they are commonly formed by exploiting the dynamic nature of reversible bonds, which has provided access to a range of cage structures with varying degrees of complexity, from small, capsular cages to mechanically interlocked molecules (MIMs).<sup>2</sup> The popularity of MIMs, such as rotaxanes, in the field has led to the design and synthesis of functional materials with varied complexity, such as multiply interlocked rotaxanes, dendrimers, and recently, cage-based rotaxanes.<sup>3,4</sup> Although organic cages have been incorporated into rotaxane structures, the axle component tends to occupy the cavity, limiting function as a host.<sup>3</sup> In contrast, there are a handful of metal-organic and metalloid-organic rotaxanes that incorporate unoccupied cage-like structures.<sup>5,6</sup> In this work, we sought to use organic cages as part of the axle to maintain cavity vacancy, expanding upon our previous work on organic cage dumbbells,<sup>7</sup> and thus yield materials that could exhibit complex host-guest chemistry and molecular motions. Mono-, di- and tri-terminal alkyne functionalised cages were formed by separating statistical mixtures of cages containing different numbers of alkyne handles formed via a ‘scrambling’ approach,<sup>8</sup> which were then used to develop a synthetic strategy and selectively prepare organic cage[*n*]rotaxanes (where *n* = 2, 3, or 4, Figure 1), by exploiting the copper(I)-catalysed azide-alkyne cycloaddition active-template approach with a small bipyridine macrocycle, chosen for their efficacy in yielding stable rotaxane structures.<sup>9</sup> Using this approach, we obtained rotaxanes incorporating organic cages where the cavity was unoccupied by the axle, offering a potential strategy to access cage-based rotaxanes that could exhibit interesting host behaviour.

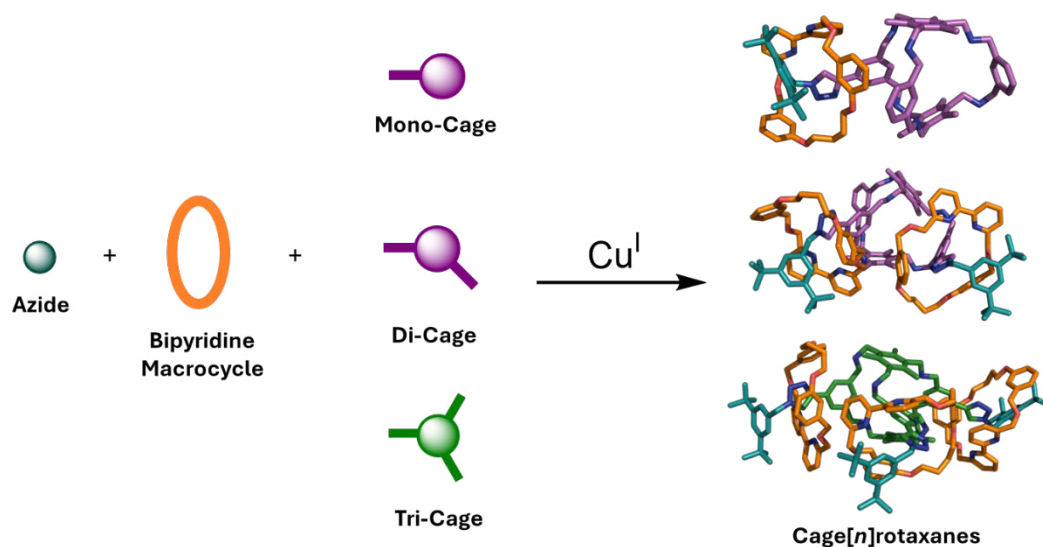


Figure 1: Synthesis of targeted cage[*n*]rotaxane structures.

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# Exploration of Supramolecular Organogelators: Effect of Gelation and Degelation on Specific End Group and Chain Length of Alcohols

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Supramolecular gels have an extensive range of potential applications, including drug delivery, actuators, stimuli-responsive materials, and fabricating optical devices, out of which stimuli-responsive materials serve as a backbone of contemporary research.[1] Gels, being kinetically entrapped materials, can be easily tuned to different forms using external chemical stimuli.[2] In this context, three different triazine gelators, each containing a unique end group, were examined for gelation in various solvent systems. Nevertheless, the gelation was limited to only alcoholic solvents, suggesting that the hydrogen bonds between the gelating solvent and gelator play a crucial role in gelation. Interestingly, it was found that these gelators could gelate only with aliphatic alcohols, which could be degelled easily using aromatic alcohols. Based on their end groups, the three gelators exhibited distinct gelation behaviour with different aliphatic alcohols. The gelator with the polar-aromatic end group (C<sub>5</sub>H<sub>4</sub>N) was found to gelate with lighter alcohols, whereas that with the nonpolar aromatic end group (C<sub>6</sub>H<sub>5</sub>) was found to prefer higher alcohols, and the cyclic aliphatic end group (C<sub>6</sub>H<sub>11</sub>) shows an in-between behaviour. The MGC and T<sub>gel</sub> values also depended on the alkyl chain length/branching of the alcoholic solvents. The crystal structure of one of the gelators provides insights into the model structure of the gelation. Among all the studied gelation solvents, cyclohexanol was the only solvent to produce gels with all three of the as-synthesised gelators. The process of degelation by aromatic alcohols was monitored at different points of the disassembly process by rheological and morphological measurements to understand the extent of controlled degelation.[3] These gels have great potential for use in controlled drug delivery and chemical sensing, among other areas. In summary, recent works carried out regarding the above-mentioned supramolecular organogelators in our laboratory will be portrayed in this presentation.

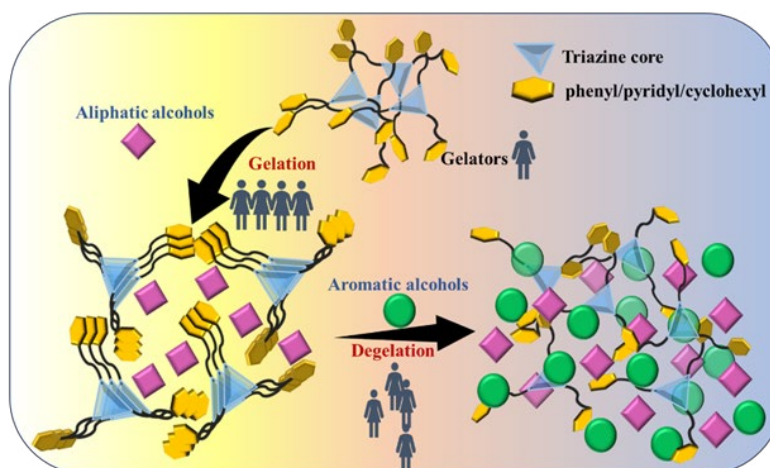


Figure 1: Schematic representation of gelation and degelation behaviour of triazine based organogelators.

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## Uncovering the Details: Get the Most out of Your MOF/COF Samples

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Being among the most porous materials known<sup>[1]</sup> Metal-Organic Frameworks (MOFs) and Covalent-Organic Frameworks (COFs) have transformed into a fully qualified field of modern research.<sup>[2]</sup> A detailed understanding of their pore volume, flexibility, and binding behavior is crucial for the success in that field. Single-Crystal X-ray diffraction (SC-XRD) analysis is the key method for uncovering vital insights such as gas adsorption mechanisms and chemical transformations.<sup>[3][4]</sup>

These complex frameworks often present crystallographic challenges, such as crystal sizes in the 10-micrometer range, poor crystallinity, or disorder within the host and/or the guest components.<sup>[5]</sup>

From the instrumentation point of view, MOFs and COFs exhibit distinct features, such as a strong and weak reflections in proximity and a rapid intensity decay at low resolutions. These specific characteristics require bright and well-focused sources alongside with high dynamic range detectors.

Equipped with a blend of charge integrating and photon counting mechanisms, the Photon III detector proves to be a versatile solution to effectively detect more reflections per frame resulting in complete data sets, with high redundancy in an overall shorter measurement time.

The use of high-performance microfocus sealed tubes ensures optimal photon intensity that is precisely directed towards the sample, thereby minimizing photon loss, and reducing background noise. In addition, the minimal power consumption of our I $\mu$ S microfocus sources underscores their effectiveness and sustainability in crystallographic research.

High quality data must be accompanied by high-quality, easy-to-use software. The graphical user interface, the level of automation, and the reliability of the underlying engines allow researchers to find the answers quickly and efficiently to even their most challenging questions.

Using a few carefully selected samples we will demonstrate how the integration of advanced hardware and software results in a solution that enables scientists to address all structural challenges associated with this exciting field of research.

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# Vapour Adsorption Studies of Porous Materials

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The presence of pollutants in the air is becoming an area of significant interest and there has been an increasing concern about air quality and its impact on health due to the presence of volatile organic compounds (VOC) in the air. VOC molecules include toluene, formaldehyde, methylene chloride, tetrachloroethylene, xylene, acetone, and benzene which may appear in different forms as in solvents, paints, or packaging materials. It is important to find a solution for the removal of volatile organic pollutants from the air. Porous materials are considered a cost-effective route to capture VOC pollutants and the reason for their success is the high fraction of pore volume and adsorption sites for trapping volatile species. Zeolites and activated carbons are widely used due to their low cost and ease of availability.

VOC concentrations can vary in different environments but are significantly lower than the moisture concentration. Therefore, water molecules would be competing for the same adsorption sites as VOCs and it would be important to assess the impact of humidity on the choice of porous materials for removing certain VOC molecules. This study will look at the impact of humidity on a series of common industrial porous materials which are potentially usable for capturing VOCs, as shown in Figure 1.

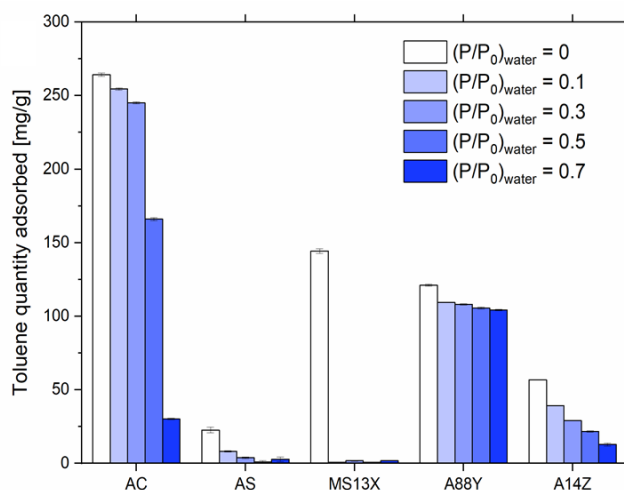


Figure 1: Adsorption capacities of toluene under different relative humidity conditions for: activated charcoal (AC); amorphous silica (AS); molecular sieve 13X (MS13X); zeolite Y (A88Y) & ZSM-5 zeolite (A14Z).

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# Ambiguous Faces Of Water-Based Inclusion Compounds: Case Study of Intercalato-Clathrate Of Pt(II) Complex

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Clathrate hydrates are among the most intensively studied H-bond inclusion compounds. Despite the broad definition for this class of compounds, their meaning commonly refers to closed polyhedral nanocages that encapsulate small guest molecules. On the other hand, larger solutes enforce another type of encapsulation because of the solute size effect. Herein, we report a series of structures containing various molecules encapsulated by intercalated water layers constructed of polycyclic moieties of L4(4)8(8) topology. We parametrized the corrugation of individual layers and characterized interactions governing their formation which is mostly driven by hydrophobic hydration. On the basis of intralayer interactions and other factors promoting clathrate formation we discussed applicability of intercalato-clathrate definition for particular systems.

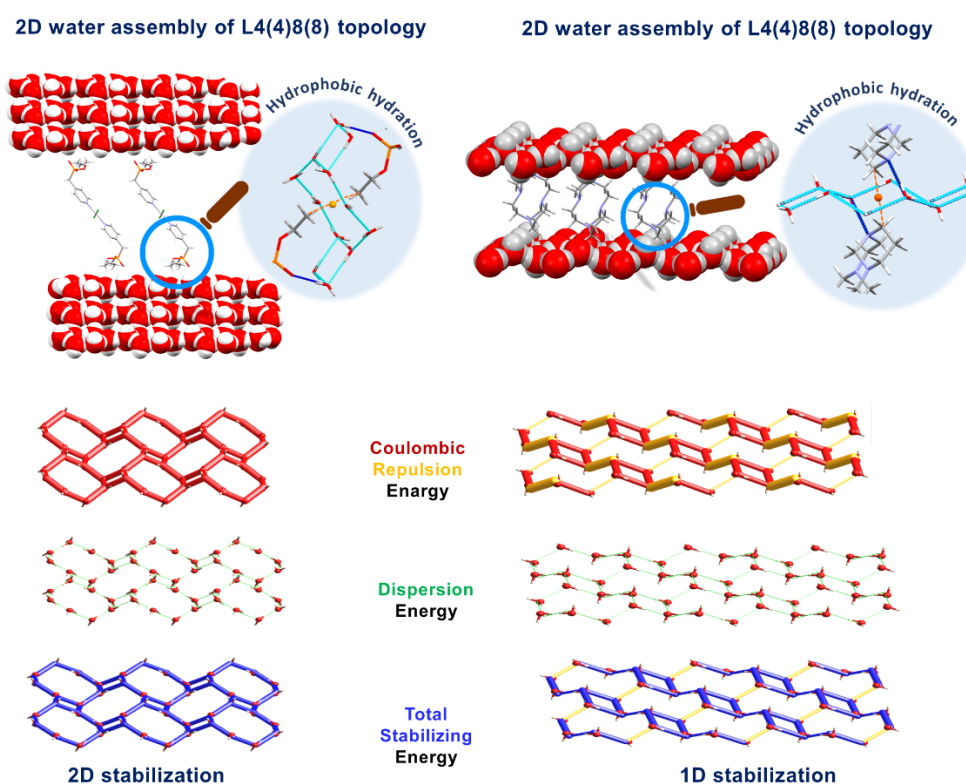


Figure 1: Topologies of intermolecular interactions stabilizing water layers in within selected intercalato-clathrates.

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# Host-Guest Chemistry within Novel Adaptable Porphyrin Nanocages

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Nature represents a shining model of inspiration on how to deal with energy, waste and raw material source issues. In Nature, optimally organized molecules and enzymes transform solar energy into chemical energy, consuming and regenerating O<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub>, H<sub>2</sub>... in a perfect-functioning closed cycle.[1] Within this biological cycle, there is an omnipresent family of molecules that work at the core of these (photo)chemical events and transformations: the porphyrinoids.[2] They are responsible for executing many of the essential life processes, such as oxygen transport/storage (*hemoglobin* and *myoglobin*), electron transfer (*cytochrome b5*), CO and NO gas sensing (*guanylyl cyclase*), enzymatic oxidation/oxygenation (*cytochromes P450*, *peroxidases*), and convert sunlight in photosynthetic systems (*chlorophylls*).

Part of the recent research in our group aims to exploit the confined nanopspaces purposely tailored in self-assembled nanostructures to selectively host specific molecules and ultimately promote their chemical transformations.[3] One of these supramolecular systems comprise a novel kind of bisporphyrin nanocages[4] constructed by imine linkages under thermodynamic control. The cage has two main conformations -*extended* and *compact* -, depending on the arrangement of the imine bonds, and can host a wide diversity of ditopic nitrogen ligands that fit into its relatively rigid nanocavity. Remarkably, the mutual conformational adaptation of host and guest results in strong chelate cooperativities the ultimately derive in record association constants. Interestingly, these systems are also excellent hosts for  $\pi$ -conjugated molecules, and actually act as kinetic jails for fullerenes.

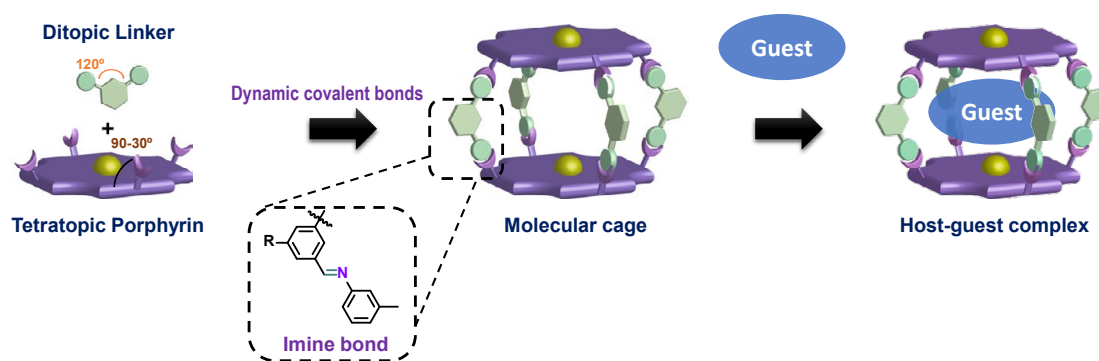


Figure 1: Schematic representation of molecular cage self-assembly and host-guest complex formation.

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# From Triangles To Squares – Highly Solvated Overcrowded Chiral Macrocycles

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Chiral but symmetrical cyclic polyazamacrocycles represent an unique class of compounds of shapes resembling geometric figures. Since the first report, there has been a constant increase in interest in these compounds. On the one hand, this is due to the relative ease of their synthesis from structurally predisposed substrates. On the second hand, these macrocycles are characterized by multitude of applications at both molecular and supramolecular levels.[1,2] At the single molecule level the macrocycles can be used as effective ligands and catalysts in asymmetric transformations. However, in the condensed matter macrocyclic molecules interact non-covalently, creating higher-order porous structures, from discrete molecular cages through amorphous molecular aggregates to crystalline materials. Moreover, these materials exhibit the ability to specifically “absorb” guest molecules.[3] The advantage of crystalline materials based on macrocycles is high thermal and chemical stability and resistance to moisture, hence the spectrum of their applications is wider than in the case of coordination materials or dynamic covalent systems like MOF’s or COF’s.

Recently, it has been shown that the nature of the  $\pi$ -electronic system and functional groups in the aromatic linkers control the stoichiometry of the forming products and are crucial for further applications of these macrocycles as tectons [4]. Feeling that the chemistry of chiral and shape-persistent macrocyclic polyimines containing bulky substituents is still at an early stage of research, we have decided to expand our interest on highly crowded macrocycles as molecules of great potential in crystal engineering. Having chosen known sterically crowded macrocycle having trimethylsilyl groups as a model system (Figure 1)[4], we have shown how increasing the sterical demands of the substituents affects the structure of the compounds under study. The mode of packing of these compounds in the crystal lattice and above all the possibility of forming the inclusion systems will be discussed.

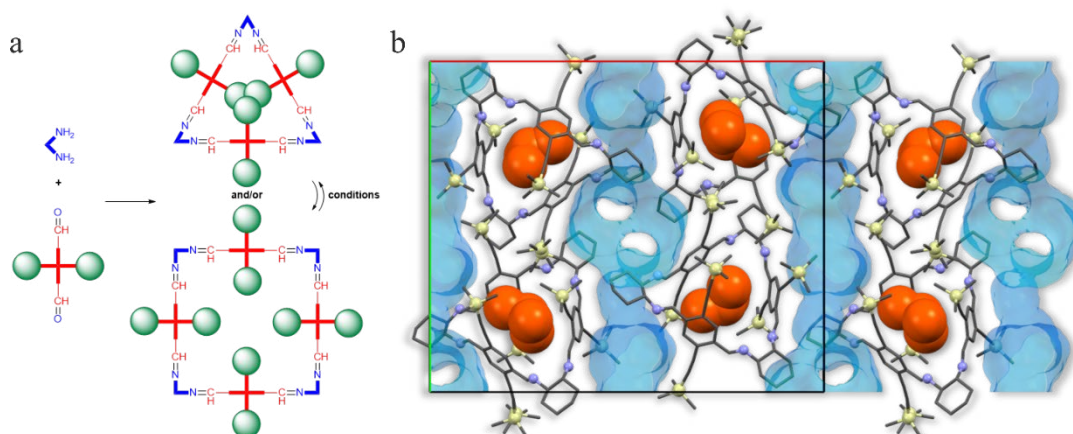


Figure 1: a) Synthesis of macrocyclic compounds and b) molecular packing in crystal structure of exemplary macrocycle.

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# An ultramicroporous physisorbent sustained by a trifecta of directional supramolecular interactions

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Two-dimensional (2D) and three-dimensional (3D) porous coordination networks (PCNs) have garnered interest for their potential utility as sorbents for molecular separations, capture and storage.<sup>[1]</sup> The inherent modularity of such PCNs has enabled the development of design (crystal engineering) strategies for systematic fine-tuning of pore size and chemistry in families of related PCNs.<sup>[2]</sup> The same cannot be said about one-dimensional (1D) coordination polymers (CPs) which are understudied with respect to porosity.<sup>[3]</sup> Here, we report on a permanently porous family of linear 1D porous CPs (PCPs, **1**) whose pore structure comprises 1D channels sustained by three types of directional interaction: coordination bonds; hydrogen bonds; offset  $\pi$ - $\pi$  interactions. That **1** exhibits permanent porosity was supported by CO<sub>2</sub> and water sorption measurements, which resulted in reversible Type I and stepped (S-shaped, Figure 1a) isotherm profiles, respectively. The water sorption properties are relevant to atmospheric water harvesting applications as the onset of the step occurred at *ca.* 12% relative humidity, activation required only mild heat or vacuum, adsorption/desorption kinetics were rapid and performance was retained for >100 ad/desorption cycles (Figure 1). Water harvesting productivity of **1** is projected to be 3.3 L kg<sup>-1</sup> d<sup>-1</sup>, which is on par with leading desiccants.<sup>[4]</sup> DFT and Monte Carlo simulations were conducted to provide insight into the structure of water molecules in the channels, their influence on the host framework and provide a plausible argument for the water vapor isotherms. This work demonstrates that easily scalable 1D PCPs can form robust porous structures sustained by directional supramolecular synthons and that they can exhibit desirable water sorption properties.

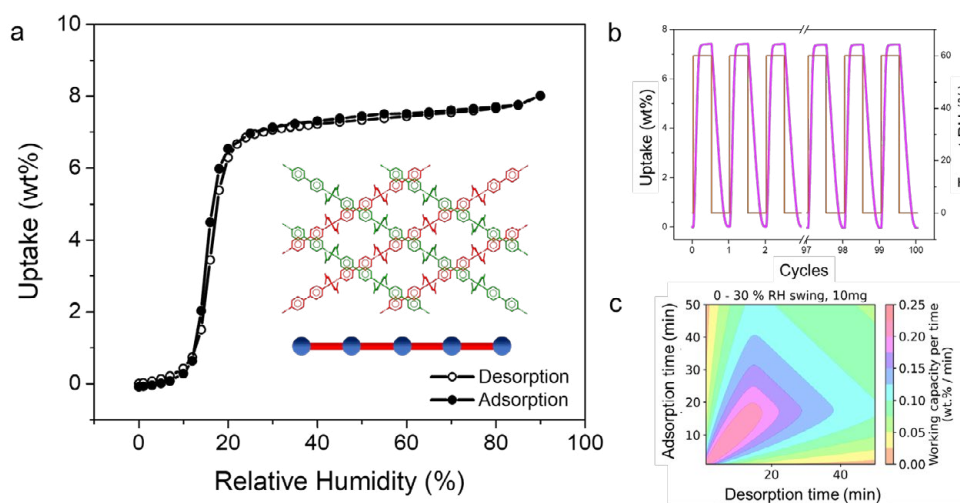


Figure 1: Evaluation of the water sorption properties of **1** using dynamic vapor sorption (DVS) analysis at 25 °C: (a) Water vapor sorption isotherms. Inset: schematic of 1D chains forming ABAB stacking arrangement; (b) Water vapor sorption cycling experiments carried out over 100 consecutive 0–60% RH swing experiments; (c) Water vapor sorption productivity ‘heatmaps’ calculated from the water vapor adsorption isotherm of **1**.

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# Structural Transformations in a Transiently Porous Coordination Network

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Transient porosity is a concept that only a few coordination networks fulfill.[1] In such cases, guest transport is possible even in the absence of connecting channels and is enabled through independent voids.[2,3] The quest for transiently porous materials extends beyond scientific curiosity, especially since it has implications in gas sorption. In this context, materials able to undergo phase transformations between two (or more) nonporous phases often exhibit S-shaped gas sorption isotherms, as a result of ‘gate-opening’ or ‘breathing’.[4] This is particularly useful in gas storage, as sorbents with S-shaped isotherms can overcome the limitations of traditional sorbents with type I isotherms in terms of working capacity and heat management.[5] However, a detailed strategy to develop transiently porous coordination networks remains elusive and can only be derived through systematic structure–function relationships. Herein, we describe the deliberate design of a square lattice (sql) topology coordination network, **sql-bib-Co-Cl**, that exhibits transient porosity. Specifically, **sql-bib-Co-Cl** can undergo structural transformations between the as-synthesised **sql-bib-Co-Cl- $\alpha$**  phase, the activated **sql-bib-Co-Cl- $\beta$**  phase, and a water-loaded **sql-bib-Co-Cl- $\beta'$**  phase (Figure 1). This contribution will detail how single-crystal and powder X-ray diffraction were used to provide insight into the mechanism of guest transport through discrete voids, and how these observations can be exploited to guide the design and control of transiently porous materials.

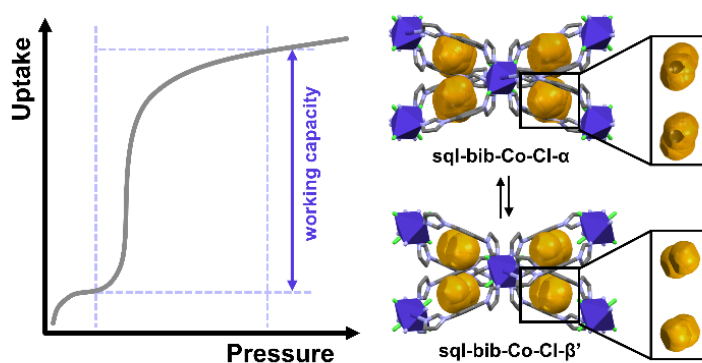


Figure 1: Working capacity for an S-shaped isotherm (left) and structural transformation from **sql-bib-Co-Cl- $\alpha$**  (top right) to **sql-bib-Co-Cl- $\beta'$**  (bottom right).

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# The limits of surface and pore volume characterization

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Not only the IUPAC recommends the use of argon at 87 K instead of nitrogen at 77 K for the characterization of porous materials [1], also the ISO 9277 [2] describes problems when using the BET method for the determination by the use of N<sub>2</sub>. Therefore, regardless of the fact that N<sub>2</sub> interaction problems with a material surface can influence specific area and pore size distribution results, N<sub>2</sub> near 77 K is still the most common technique due e.g. for comparison reasons. However, when it comes to samples with narrow ultramicropores or a very small surface area, such as thin films or non-porous samples, N<sub>2</sub> and Ar reach their limits.

A common approach to characterize small surface areas is the reduction of the saturation pressure  $p_0$  to minimize the amount of free gas molecules. Therefore, IUPAC recommends the use of Kr with a fixed  $p_0$  value of 0.35kPa at 77.35 K, but this does not take into account the dependence of the coolant on ambient pressure. Since the  $p_0$  value of the supercooled liquid krypton adsorbate (see Fig. 1) cannot be measured directly, it has to be calculated either from a temperature measurement of the coolant or an exact temperature control. For accurate measurements, we used a new temperature control (cryoTune 77), which allows the use of the correct  $p_0$  for the undercooled liquid adsorbates of Kr and Ar near 77 K.

For the characterization of macropores we recommend the use of *n*-butane. This new developed method is based on the reduction of the measuring temperature. At  $p/p_0=0.995$ , N<sub>2</sub> at 77 K fills pore diameters of about 400 nm, *n*-butane at 273 K of 500 nm, but *n*-butane at 190 K of 1000 nm. Our results will demonstrate that method by use of a cryoTune 195 regarding the limits of both pore filling and sample amount available.

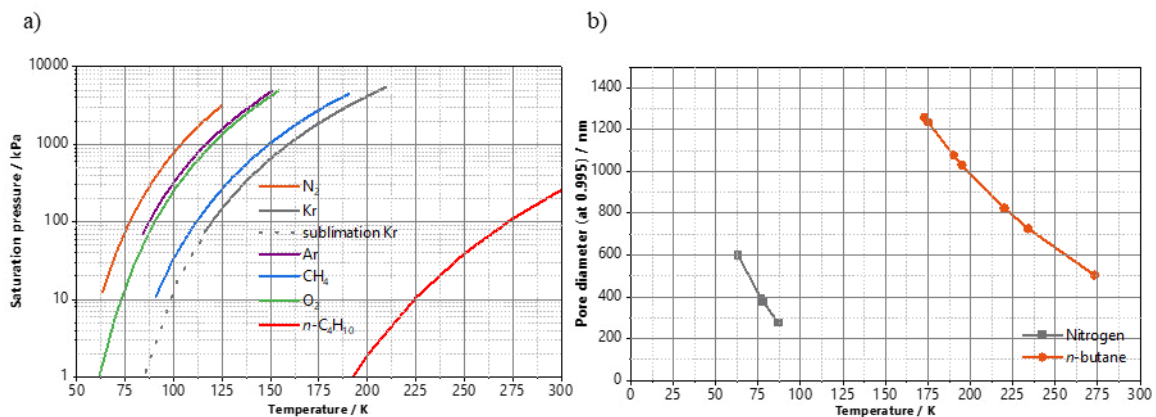


Figure 1: a) Saturation pressure vs T for typical adsorbates and b) Potential pore filling vs T at  $p/p_0 = 0.995$

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# Boosting the Negative Gas Adsorption Transitions using multivariate framework approach

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Bistable Metal-Organic Frameworks shows reversible guest-induced phase transitions upon physisorption of gases and vapours.<sup>[1]</sup> These solids show remarkable performance in gas storage and separation,<sup>[2]</sup> but also discussed as sensors<sup>[3]</sup> and actuators.<sup>[4]</sup> A while ago we discovered a new phenomenon in a mesoporous DUT-49 framework with hierarchical pore structure, coined as a “Negative Gas Adsorption”.<sup>[5]</sup> The solid expels the gas upon adsorption of subcritical gases at the temperatures close to the standard boiling point, accompanied by the structural contraction from gas-loaded metastable open pore phase to contracted pore phase with reduced porosity.<sup>[6]</sup> Further loading of the structure leads to reopening to open pore phase and can be described as a breathing, previously reported in MIL-53 structures.<sup>[7]</sup> One of the most important characteristics of pressure amplification materials is  $\Delta n_{NGA}$ , describing the amount of the gas, expelled from the framework at the defined temperature. This value can be manipulated by variation of experimental conditions such as guest molecule and adsorption temperature<sup>[8]</sup> or vary the mechanical the properties of the host structure such as the length of the strut connecting carbazole units.<sup>[9]</sup>

A more sophisticated approach is to enhance the  $\Delta n_{NGA}$  by keeping above mentioned conditions constant and engineer the micromechanics of the host structure, more specifically to design the ligand molecules with the desired stress/strain properties, namely the buckling of the ligand should happen at maximum possible loading or in another words to stabilize the overloaded metastable open pore phase until highest possible loading before buckling. This strategy was applied in DUT-147, DUT-148 and DUT-160 framework series, containing the struts with different mechanical stiffness and the highest  $\Delta n_{NGA}$  of -12 mmol $g^{-1}$  was reached for DUT-160 upon nitrogen physisorption at 77 K.<sup>[10]</sup> Nevertheless, the targeted design of the frameworks showing NGA at desired guest/gas pressure/temperature condition is still challenging because of lacking of organic struts with desired stiffness. Therefore, the design of multivariate NGA frameworks, containing the ligands with different stiffness may allow to tune  $\Delta n_{NGA}$  value at desired experimental conditions.

Herein we applied mixed-ligand approach to synthesize the serie of multivariate MTV-DUT-49 frameworks showing gradual expansion of the unit cell and resulting in different guest-responsive properties. Methane physisorption, conducted at 111 K indicate that at certain ratios of the ligands  $\Delta n_{NGA}$  could be boosted from 6.34 mmol $g^{-1}$  in pure DUT-49 framework to 11.26 mmol $g^{-1}$  in MTV-MOF due to the implementation of more rigid linker, which stabilizes the metastable state of the op phase at higher loadings.

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# Computational Crystal Structure Prediction For The Design Of Functional Metal-Organic Frameworks

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Computational design of metal-organic frameworks (MOFs) entails computational prediction of structures and their associated properties, with an ultimate aim of proposing structures that meet desired search criteria, as targets for experimental synthesis.

The presentation will outline the progress made in the development of crystal structure (CSP) method for the design of MOFs. The key feature of this CSP methodology is that structures are generated without assuming any particular network topology, thereby ensuring complete generality of structure search for a given combination of metal nodes and organic linkers. Initial tests aimed at reproducing the existing MOF structures and exploring the hypothetical polymorph energy landscape of the diverse types of MOFs, including hexafluorosilicate, carboxylate and zeolitic imidazolate frameworks (ZIFs), will be presented.[1,2] These energy landscapes will highlight the effect of porosity and void volume within the MOF structures on the relative lattice stability of the predicted MOF polymorphs. In the context of prediction of MOF polymorph stability under experimental stability, the energetic effect of solvent inclusion within MOF pores has to be considered, which can be done with the help of molecular dynamics (MD) simulations. These simulations allow us to explain, while highly porous structures can readily form in preference to their non-porous polymorphic analogues.

The presentation will continue with the demonstration of the first example of CSP to design MOFs that rapidly ignite upon contact with an oxidizing agent, displaying hypergolic performance.[3] A family of copper (II) ZIF structures were predicted using the CSP method, and their energy output upon combustion was calculated. When the materials were synthesized, the experimentally determined structures matched the lowest energy structures found with CSP, demonstrating how this method enables the computational design of new functional MOFs.

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## Click and collect: versatile covalent functionalization of novel tetrazine-based MOFs

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Metal-organic frameworks (MOFs) have gained recognition as advanced materials of the future, attributed to their distinctive properties that enable the exploitation of their intrinsic porosity and chemical environment for diverse applications. These include gas storage and separation, selective adsorption of various molecules from different phases, catalysis of challenging chemical reactions, serving as carriers for biomolecules, among others. However, these capabilities are often constrained or entirely negated by limitations in stability and synthetic feasibility. A promising strategy to address these limitations is through post-synthetic modifications (PSMs). An ideal PSM is selective, efficient, irreversible, versatile, operates under mild conditions, and preserves the integrity of the MOF's framework. The inverse electron-demand Diels-Alder (iEDDA) reaction, widely utilized in bioorthogonal chemistry and honored with the Nobel Prize in 2022, exemplifies such a nearly ideal modification.<sup>1</sup>

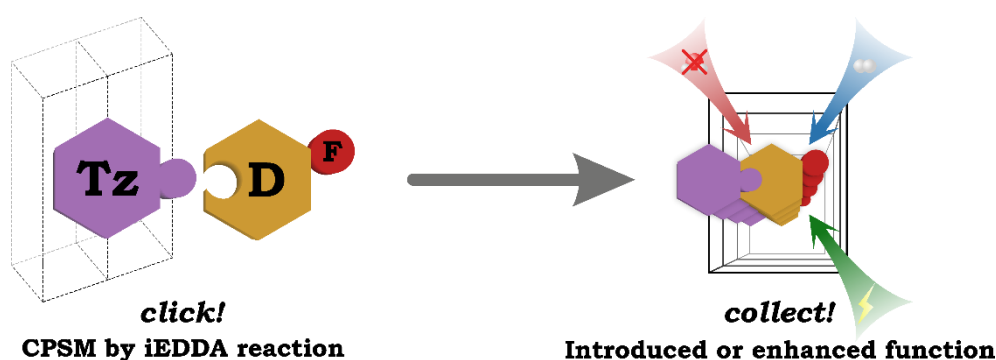


Figure 1: Schematic representation of post-functionalization of metal organic-framework using iEDDA reaction on tetrazine ligand. Tz = s-Tetrazine, D = Dienophile, F = Functional group.

Despite its significant synthetic and application potential, the use of iEDDA reactions for the post-functionalization of MOFs is scarcely reported in the literature. The work presented highlights the modification of JUK-20(Cd), where a series of modifications with dienophiles of increasing size were performed, resulting in the progressive rigidification of the flexible MOF framework.<sup>2</sup> Another example is the JUK-20(Zn) material, wherein the introduction of pendant OH groups via dienophiles of varying lengths led to the development of a flexible luminescent humidity sensor.<sup>3</sup> Additionally, our recent advances in new tetrazine-based platforms, including UiO-68-TZDC,<sup>4</sup> JUK-21,<sup>5</sup> and JUK-74,<sup>6</sup> will be discussed. Ongoing research is focused on integrating new functionalities such as proton conductivity, hydrophobicity, enhanced sorption capacity for hydrogen, and improved photocatalytic performance.

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### Acknowledgments

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# The inner life of a MOF: templated self-organization of linkers in a pillared-layer MOF

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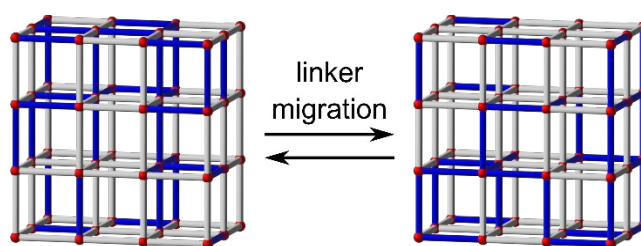
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Metal-organic frameworks (MOFs) are well-known to undergo post-synthetic linker exchange and reorganization. [1] Surprisingly, however, structural reorganizations in which linkers simply reshuffle their positions in a metal-organic framework, without changing the overall composition and topology of the MOF (Scheme 1), have not been investigated thus far.

Here we show that linker migration in MOFs may indeed take place, and that the kinetics of this process may be easily controlled by changing temperature, solvent, and catalysts. More importantly, we show also that linker reshuffling allows templated self-organization of the MOF structure, giving unprecedented control over spatial distribution of linkers in the crystalline lattice.



Scheme 1: Schematic representation of random linker place exchange in a MOF.

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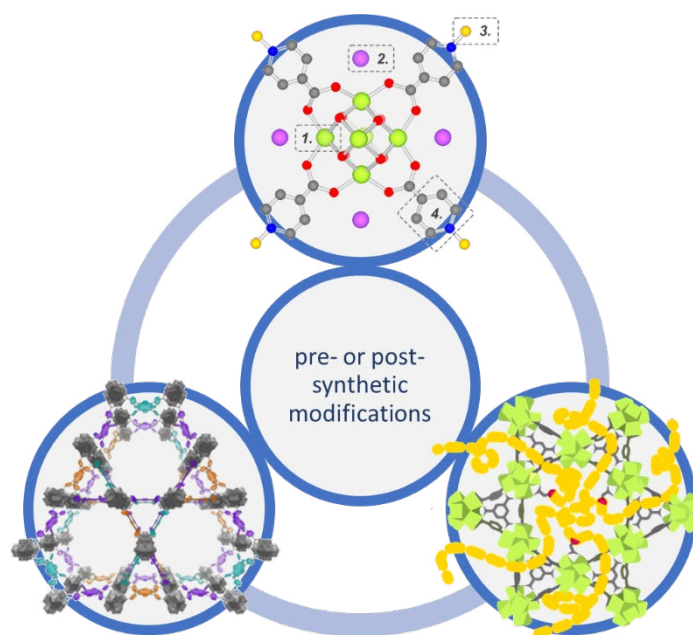
# Pre- and Postsynthetic Strategies Applied To Zr-Based MOFs – Selected Catalytic Applications

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The observed rapid growth of interests in metal-organic frameworks (MOFs) has been the result of their numerous intriguing properties, which lead to many potential applications of MOFs, including gas storage, separations, heterogeneous catalysis, biomedical applications, and others. Proper selection of building blocks allows to design MOF structure and often its desired physicochemical properties [1]. Post-synthetic modifications of MOFs allow for their further functionalization, expanding their possible applications [2]. Nevertheless, presynthetic design of MOFs is of great importance for the construction of multivariate systems. In this presentation our approach to the application of MOFs as platforms and precursors for further transformations into functional systems will be presented.



The aim of our studies was to evaluate pre- and postsynthetic functionalization strategies in model zirconium-based MOFs to test the possibility of incorporating new functions into MOFs with special focus on three research topics: (1) catalytic synthesis of cyclic carbonates under mild reaction conditions [3], (2) synthesis of polymer@MOF hybrids based on radical polymerization of acrylic monomers [4], and (3) imprinting desired compositions into MTV-MOFs to obtain heterogeneous catalysts for decomposition of liquid hydrogen sources [5].

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# Ab initio crystal structure prediction of metal-organic frameworks with machine-learned potentials

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Metal-organic frameworks (MOFs) are class of highly versatile materials with many exciting applications, such as gas separation and storage, water harvesting, platforms for drug delivery and many more [1]. The exact functionality and properties of MOFs are directly linked to the choice of metal nodes and organic linkers. In theory, there is an unlimited number of node-and-linker combinations one can choose, but how can we find the best MOF composition for desired purposes? The current main MOF design is based on isorecticular or node-and-linker approaches, which can often lead to rigid and expected framework geometries and topologies. Herein, I will be presenting our *ab initio* crystal structure prediction (CSP) method, with the aid of machine learnt (ML) potentials to provide a more general and efficient way to predict MOF structures as well as their functional properties.

The *ab initio* CSP method [2], which utilises the *ab initio* random structure search (AIRSS) algorithm and Wyckoff Alignment of Molecules (WAM) has been shown to accurately predict structures of diverse classes of MOFs, reliably finding structures matching with experiment. Later, this CSP method has been showcased in the first example of predicting three novel hypergolic ZIFs, [3] where the low energy predicted structures were all validated by experimental screenings. However, the main challenge for MOF CSP has been the use of expensive periodic density-functional theory (DFT) calculations for energy ranking of the predicted structures. Given that MOFs are with unit cells exceeding 10000 Å<sup>3</sup> are known, the high computational cost of the calculations restricted the size of the systems that could be targeted by the structure search. This presentation will demonstrate the use of machine learned (ML) potentials to achieve a major reduction in the computational cost of CSP. The new method will be applied to the highly polymorphic Zn(II)-imidazolate zeolitic imidazolate frameworks (ZIFs) system. So far, the ML predicted structures have showed excellent agreement with periodic DFT-optimised structures. More importantly, experimentally matching ZIF structures with SOD and GIS topologies were also predicted by the ML potentials. Overall, with the aid of well-trained ML potentials, rapid screening of MOFs can be achieved, where simultaneous MOF structures and properties can be predicted prior to direct experimental synthesis.

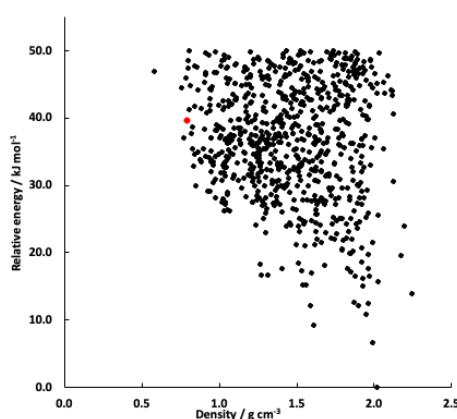


Figure 1: CSP energy landscape of Cu(VIm)<sub>2</sub>, the experimental matching global minimum structure is shown.

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# Structurally-dynamic, 2-periodic MOFs as hosts for included solvents, gases and water vapour

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Metal-organic frameworks (MOFs), which may consist of 1-periodic, 2-periodic- or 3-periodic coordination networks comprised of a metal coordinated to organic linkers, have attracted widespread attention for their porosity and potential applications in separation chemistry, catalysis, molecular sensing and gas storage.[1] In most cases MOFs contain solvent of crystallization either as included guest molecules or ligated to the metal ions (or both) and have been classed according to the effect on their structures when these guest molecules are evacuated.[2] Upon desolvation, first-generation MOF structures collapse irreversibly, whilst second-generation MOFs structures are robust to the exit and entry of guest molecules. The frameworks of third-generation MOFs, due to their inherent flexibility, adapt to the presence or absence of guest molecules (or to other external stimuli such as heat and light) and have been classed as 'breathing' MOFs.[3] In studying the breathing behaviour of MOFs, single-crystal-to-single-crystal (SCSC) transformation phenomena have proven to be invaluable, since these provide insight into the mechanisms of breathing by elucidation of the 'before' and 'after' structures.[4]

In this talk a series of 2-periodic MOFs, synthesised and structurally analysed in our laboratory, will be presented. These MOFs were constructed from transition metals and commonly available ligands, are single and mixed-ligand MOFs, entangled and non-entangled and include different solvent molecules.[5] These MOFs have been assessed for their thermal, gas and water vapour sorption properties. In selected cases, desolvation and solvent exchange processes occur via SCSC transformations, allowing structural analyses that indicate that the MOFs undergo dynamic structural changes in response to their environments.

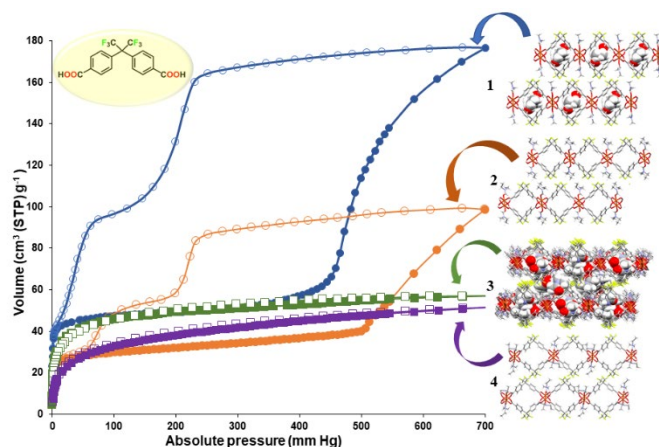


Figure 1: A series of 2-periodic MOFs with different ligated solvent molecules.

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# Solvent-solute interactions probed by piezosolvatochromism

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Molecular interactions formed between solute and solvent can profoundly affect the optical spectra of solutions, altering the position, intensity, and shape of absorption and emission bands. Solvatochromic dyes, which are particularly sensitive to the physicochemical nature of the surrounding medium, manifest a strong, visible changes in their solution colour.<sup>1</sup> This phenomenon, known as solvatochromism, not only provides a visual representation of dye-solvent interactions, including hydrogen bonds, dipole-dipole, and van der Waals interactions but also offers deep insights into the electronic structure of the dye.

In this study, we employ high-pressure in-situ crystallization and high-pressure UV-vis spectroscopy to investigate the structure-property relationships of solvatochromic effects in the simplest pyridinium N-betaine dye (Figure 1), 4-(2,4,6-triphenyl-1-pyridinio)phenolate, thereafter referred to as ET(1).<sup>2</sup> Our comprehensive examination of ET(1) in various solvent environments—methanol, ethanol, and acetone—under high pressure, reveals a close correlation between solvatochromism and solvatomorphism. We demonstrate that ET(1) preferentially crystallizes in the form of solvates, with the crystal colour reflecting that of the solutions. The observed piezosolvatochromic effects may be associated to the intricate interplay between solvent polarity, hydrogen bonding, molecular conformation, and crystal packing.

Our findings pave the way for the development of pressure-sensitive photonic materials and molecular sensors, leveraging solvatochromic shifts to design devices capable of optical modulation under varied environmental conditions. This work not only advances our understanding of the solvatochromism process but also highlights the correlation between crystal structure and solute-solvent interactions, marking a significant step towards the practical application of solvatochromic compounds in materials science and nonlinear optoelectronics.

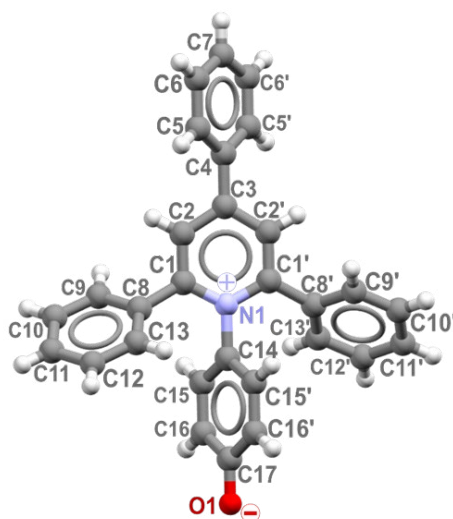


Figure 1: Zwitterion of 4-(2,4,6-triphenylpyridinium-1-yl)-phenolate, ET(1), investigated at high-pressure.

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# The Use of Computationally Informed Mechanochemistry in the Synthesis of New Zinc Imidazolate Forms

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Zeolitic Imidazolate Frameworks (ZIFs), a class of MOFs built from tetrahedral metal centers and imidazolate linkers, can adopt many of the 251 different zeolitic topologies, only some of which have potential for applications such as separations, gas capture, and catalysis.<sup>1</sup> Their solvothermal synthesis is energy intensive, low-yielding and often gives mixtures of different ZIF frameworks. Many of these drawbacks can be addressed by using mechanochemistry – inducing chemical reactions by application of mechanical force. Mechanochemical ZIF synthetic procedures are fast, conducted at room temperature, quantitative in yield, independent of solubility, and create little to no waste.<sup>2</sup> However, the mechanochemical syntheses of ZIFs are also governed by many factors, so the use of liquid or ionic additives and even different reaction times can change the topological outcome. Computational methods have recently been used to start shedding light on these effects. For example, calorimetry-validated periodic Density Functional Theory was used to model the different topological products of mechanochemical Zn(EtIm)<sub>2</sub> synthesis.<sup>3</sup> The milling synthesis was shown to follow the Ostwald rule of stages, where the thermodynamically least stable (and most porous) phases are formed first and convert into more stable ones upon further milling. The less stable phases can, however, be stabilized and isolated by incorporation of liquid additives or simple salts<sup>4</sup>, presumably by a templation effect that hasn't yet been extensively studied neither experimentally nor computationally. We now explore the use of such simple templates – small molecule liquid additives – in the mechanochemical synthesis of the simplest ZIFs, unsubstituted zinc imidazolates. An experimental mechanochemical screening was performed and powder X-Ray diffraction (PXRD) used to assess the yield and topological outcome of all experiments. Computational modelling using periodic DFT was performed on the crystal structures of the observed products, with and without incorporated templates, to explain the observed synthetic results and inform further experiments..

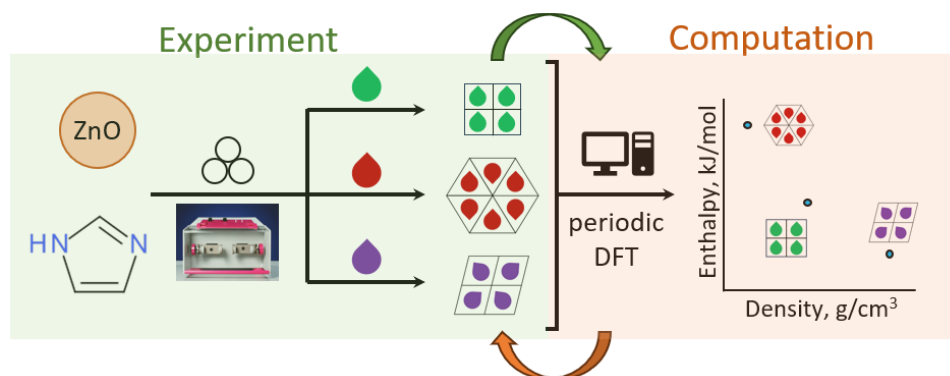


Figure 1: Schematic representation of the dependence of topological outcome of the mechanochemical synthesis on the liquid additive used, and the interplay of computation and experiment..

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# Exploration [2+2] Reactions for Dimerizations and Polymerizations in the Metal-Organic Gels and Single Crystals of Coordination Polymers

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Since the pioneering work of Schmidt et al. in 1960s, which led to postulation of topochemical criteria for [2+2] photocycloaddition reaction; design strategies have significantly exploited crystal engineering rationale to parallelly align alkene pair within reactive distance ( $< 4.2 \text{ \AA}$ ). Supramolecular interaction such as hydrogen and halogen bonds,  $\pi$ - $\pi$ , metallophilic interactions provide insights into structure- property relationship, furthering the scope of solid-state materials for facile [2+2] reactions.[1] Being inherently soft material, Metal-Organic Gels (MOGs) provide an affluent platform for synthesizing highly stereo-selective cyclobutane based polymers, which are inaccessible in constrained crystalline solids. [2+2] cycloaddition reactions can also be a clean route to improve gel property (rigidity, color etc.) through gel-to-gel transformation of photoresponsive MOGs. We have shown for the first time, [2+2] photopolymerization substantially increases mechanical strength of MOGs of a rigid and angular diene **3PMA**. [2, 3] On the other hand, due to limited movement of reactive units in the crystals, such reactions often proceed through single-crystal-to-single-crystal fashion, giving the opportunity to synthesize higher dimensional Coordination Polymers (CPs) or Metal-Organic Frameworks (MOFs). Recently, we have successfully dimerized otherwise photo stable rigid and linear diene **4PMA** in its Co(II) CPs with different dicarboxylates. Structural artefact such as bimetallic SBU played major role in aligning **4PMA** in favorable position and hence forming a 3D CP with **fsc** topology from 2D layered CP.[4] Overall following work summarizes recent advances of [2+2] photocycloaddition reactions in MOGs and CPs and its effect on those materials from our lab.

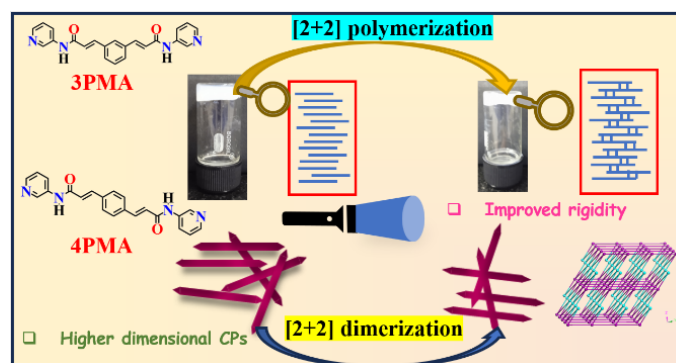


Figure 1: Illustration of [2+2] di-/polymerization in MOGs and CPs.

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# Dinuclear copper sulfate-based switching adsorbent layered materials for water harvesting and hydrocarbon selectivity

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Porous coordination materials (PCNs) offer a vast selection of metal, organic, and inorganic components to form porous frameworks allowing for tuning of uptake and selectivity. In an effort to increase selectivity, the use of highly electronegative anions has been popularised such as in SIFSIX (hexafluorosilicate) linked materials, while the use of flexible or switching materials [1] can boost the working capacity of porous materials. The use of SIFSIX however is undesirable [2] due to cost and safety issues (the use of HF in production) while the synthesis of flexible porous materials is generally unpredictable and rarely found in anion-based PCNs. Herein, [3] we present a series of imidazole-based PCNs formed from a rare dinuclear copper sulfate molecular building block [4] (MBB) that enables the formation of 2D layered materials. A combination of conformational flexibility around the imidazole ligand, shifting in the 2D layers, and conformational flexibility within the copper sulfate MBB allows for these materials to offer water vapor uptake under conditions of water-harvesting/dehumidification applications and selectivity towards  $C_2H_2$  over  $CO_2/C_2H_4/C_2H_6$ , an important industrial separation. This expansion of PCNs towards the use of environmentally sustainable yet effective materials is hoped to lead to greater viability for such materials in industrial applications.

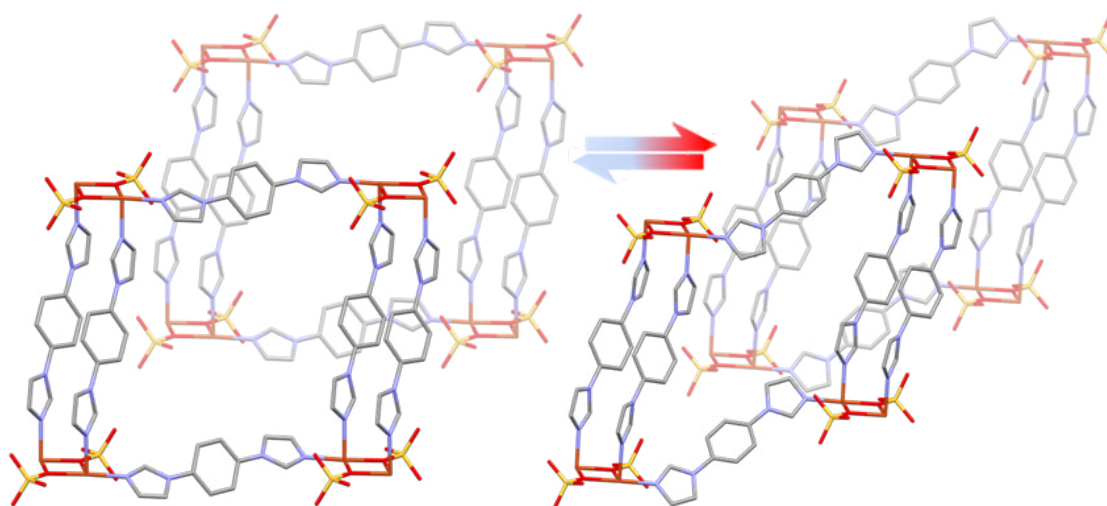


Figure 1. Example of copper sulphate-based 2D net showing switching behaviour

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# Development of a Characterisation Toolbox for Porous Liquid Solutions to understand their Gas Inclusion and Selectivity Capabilities

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Porous liquids (PLs) are a new class of porous materials that combine microporosity, traditionally associated with solid substances, with the flowability and processability of liquids [1]. One type of PL, PL dispersions, have recently been shown to demonstrate carbon dioxide selectivity from  $\text{CO}_2/\text{CH}_4$  mixtures comparable to industrially used sorbents, with potential applications as selective sorbents in sweetening of natural gas and carbon capture from flue gas [2]. PL solutions (Figure 1, left), another type of PL, consist of intrinsically porous molecules - such as porous organic cages (POCs) - dissolved in a pore-excluded solvent. POCs are an ideal pore carrier; their modularity allows the pore guest inclusion to be controlled to suit the needs. Solvent selection must also be cautiously made to ensure good pore loading - thus warranting high gas uptake (Figure 1, right) - and flowability (low viscosity), pore exclusion, as well as suitability for the methods used to measure the properties. While previous studies on PLs measure the neat gas adsorption of the materials, studies often do not explore the interactions between the pore carrier and the gas molecules sufficiently. To do this, we now have a toolkit for understanding the behavior of new PL solutions, specifically, a toolkit of accessible techniques that can be easily applied to these materials. We use dual quantitative  $^1\text{H}$ - $^{13}\text{C}$  and diffusion NMR spectroscopy to determine selectivity for gas uptake and inclusion from  $\text{CO}_2/\text{CH}_4$  mixtures, combined with nuclear Overhauser effect experiments to suggest mechanistic insight into selectivity by providing evidence of selective gas inclusion in the pores. Other methods employed in this work include an instrument adapted for measurements of PL uptakes, providing information on the kinetics of gas uptake into PLs, scarcely available in literature, and NMR gas titrations in PLs. Overall, the insights provided by this toolbox of techniques can be translated to other PL solution systems, providing an understanding of the guest selectivity observed in these systems, with an outlook towards the development of selective materials for molecular separations.

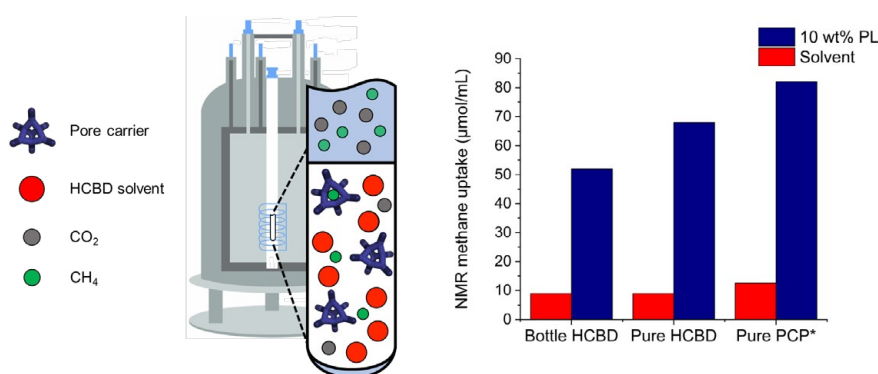


Figure 1: Left: A diagram of a PL solution capturing gas molecules in an NMR tube [4]. PCP – perchloropropene, HCBD – second generation solvent. Right: A graph of methane uptakes in HCBD PL solutions compared to previous high-capacity PL solutions in PCP [3].

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# Hypercrosslinked Polymers for the electrocatalytic Oxygen Reduction Reaction

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Hypercrosslinked polymers (HCPs) are the promising materials for the storage and utilization of small gas molecules. As, these materials are well exploited in gas capture due to their high surface area, intrinsic microporosity, tunable chemistry and high stability. The synthesis of HCPs is very simple that involves the polymerization of the aromatic units in the presence of Lewis acid. Various factors are participating in controlling the morphology, textural properties and functionality.<sup>1</sup> For instance, the wise selection of monomers, crosslinking strategy, and porogen template affects the final properties of the HCPs.<sup>2</sup> Therefore, the design of the robust porous framework is the necessity for the storage and conversion of the O<sub>2</sub> molecules.

Current research work focused on the fabrication of series of the functional HCPs with the heteroatoms (N, O, S, etc.) following the Scholl coupling strategy. The unique structural features of heteroatom rich HCPs, including high surface area and tailored functional groups, is suitable to facilitate efficient O<sub>2</sub> adsorption through physisorption mechanism. Additionally, the presence of functional groups enables the activation of O<sub>2</sub> molecules for further conversion into value-added products. The physicochemical properties are the key factor to achieve the maximum adsorption efficiency of synthesized porous material to realize its application for the gas storage and catalysis. Thus, the textural characterization of the HCPs suggested their high surface area up to 1000 m<sup>2</sup>/g. Therefore, the HCPs synthesized has the hierarchical pore size distribution that is useful for their utilization in the adsorption and catalysis of small gas molecules. We have also identified the HCPs synthesized by Scholl coupling can achieve high surface area and more retention of the heteroatoms that are useful to achieve the adsorption of O<sub>2</sub>. Additionally, the utilization of Scholl process induces the long-range  $\pi$ - $\pi$  conjugation that is beneficial for the photo-electrocatalytic conversion of O<sub>2</sub> molecules. The extended conjugation not only support the high surface area, hierarchical porosity but also improves the conductivity. The high conductivity ensures the better development of porous electrode material that can efficiently catalyze the substrate such as O<sub>2</sub>.

In summary, this presentation showcases the versatility of HCPs as multifunctional materials for integrated O<sub>2</sub> capture and conversion, offering a sustainable pathway towards mitigating climate change and transitioning to a carbon-neutral future.

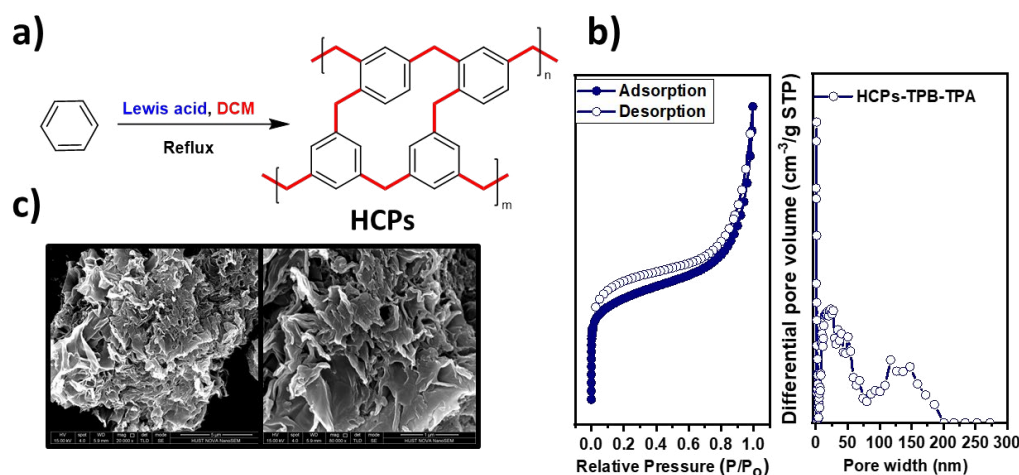


Figure 1: a) Synthesis methodology illustration of HCPs. b) N<sub>2</sub> ads-des isotherm and pore size distribution of HCPs. c) SEM micrographs of HCPs.

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# Photocatalytic conversion of CO<sub>2</sub> into Valuable Products by Porphyrin based Metal-Organic Frameworks

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This study investigates the photoconversion of carbon dioxide (CO<sub>2</sub>) to formic acid using porphyrin-based MOF, known as Al-TCPP, as a promising photocatalyst. Porphyrin-based metal-organic frameworks (MOFs) like Al-TCPP offer superior light absorption and tunable structures, making them highly effective for catalytic applications such as the photoconversion of CO<sub>2</sub> [1] This study aims to enhance the efficiency of CO<sub>2</sub> photoconversion by modifying Al-TCPP with various metals, such as Co, Zn, Ni, and Cu. [2] In addition, this study addresses the gap of the need for more effective and sustainable photocatalysts for CO<sub>2</sub> conversion.

A comprehensive characterization approach encompassing X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area analysis, scanning electron microscopy (SEM), UV-Vis spectroscopy, and Thermogravimetric analysis (TGA) is employed to unravel the intrinsic properties of Al-TCPP that contribute to its efficacy in formic acid production.

Comprehensive characterization methods were employed, including X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area analysis, scanning electron microscopy (SEM), UV-Vis spectroscopy, and CO<sub>2</sub> sorption measurements. XRD analysis confirmed the crystalline nature of Al-TCPP. BET analysis revealed a substantial surface area of 785 m<sup>2</sup>/g for pristine Al-TCPP, with slight reductions for Ni, Cu, Co, and Zn modifications. SEM imaging showcased elongated nano-plate-like structures and UV-Vis spectroscopy indicated a band gap of 1.68 eV, suitable for visible light absorption. Thermal stability tests validated Al-TCPP's stability up to 400 °C. HCOOH generation was measured under UV-Vis light to assess the photocatalytic performance. Pristine Al-TCPP produced 42 μmol.g<sup>-1</sup> of HCOOH after 4 hours of irradiation. Metal modifications significantly enhanced HCOOH production, where Co/Al-TCPP yielded 65 μmol.g<sup>-1</sup> showed the highest improvement, and different variants indicated that cobalt modification significantly boosts the photocatalytic activity.

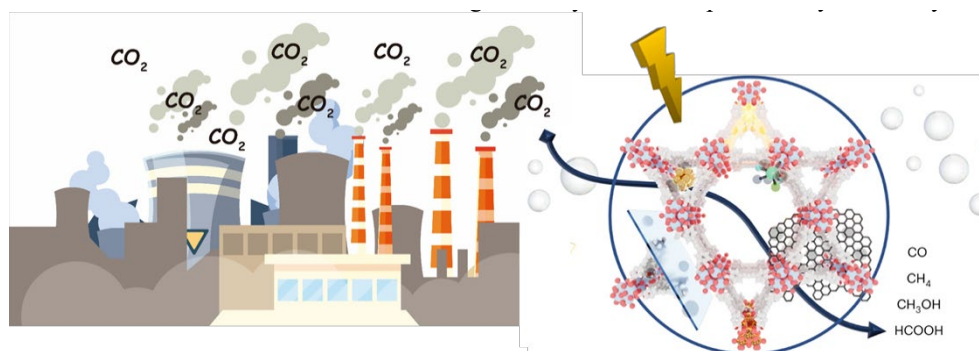


Figure 1: Scheme of CO<sub>2</sub> emissions from industrial sources being converted into valuable chemicals through a photocatalytic process.

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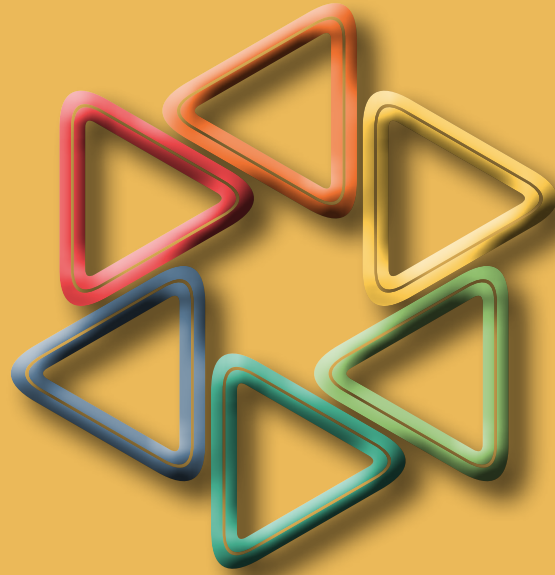
## Acknowledgment

The Polish National Science Center supported this research under the grant 2021/41/B/ST4/00849.









# POSTER SESSION



# Anhydrous proton conduction in imidazole-filled ordered mesoporous materials

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Energy conversion is one of the most popular research topics today. PEMFCs (Proton Exchange Membrane Fuel Cells) are part of this trend, enabling the conversion of chemical energy into electrical energy without the production of environmentally harmful substances. Nafion is a widely used electrolyte with a water-mediated proton conduction mechanism. Unfortunately, the importance of water molecules in Nafion contributes to limiting the operating temperatures of Nafion-based PEMFCs to around 80°C, which is unfavourable for PEMFC operation. What's more, water molecules in Nafion need to be replenished, which can be problematic. These difficulties are one of the motivations for research into anhydrous proton conductors. [1].

In recent years, much attention in the field of proton conduction has been paid to nanoporous materials, including MOFs, COFs, zeolites and silicas. Due to their porosity, these materials can host molecules that could act as proton carriers. For example, the pores of porous materials can be filled with inorganic acids, counterions or azoles [2-4]. In addition, proton-donating acidic groups (e.g. sulfonic, phosphonic and carboxylic acid groups) can be attached to the building blocks of porous materials to further increase their conductivity [5,6]. Interestingly, sometimes several strategies are successfully combined in one process to obtain the final proton-conducting material [7].

The present study concerns anhydrous proton-conducting composites obtained by introducing imidazole into ordered mesoporous materials with KIT-6 structure. The aim of the research was to investigate the effect of chemical properties of KIT-6 materials on the conductivity of the obtained composites. Aluminosilicate KIT-6 materials with different aluminium contents (Si/Al from 25 to 200) and mesoporous silica as a reference material were obtained. The selected materials were then subjected to additional modifications. These included the introduction of sulfonic and amine groups by grafting with different amounts of organosilanes. In the next stage of the research, imidazole was introduced into the porous materials, resulting in the formation of azole composites. The studies showed that the obtained composites exhibit high proton conductivity over a wide temperature range (27-120°C), with the highest conductivity in the range of 10<sup>-3</sup> S/cm measured in anhydrous conditions. The conductivity of the composites increases with increasing temperature and imidazole loading and also depends, for example, on the type and amount of organosilanes used in the modification of the porous material.

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# Development of a Characterisation Toolbox for Porous Liquid Solutions to understand their Gas Inclusion and Selectivity Capabilities

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Porous liquids (PLs) are a new class of porous materials that combine microporosity, traditionally associated with solid substances, with the flowability and processability of liquids [1]. One type of PL, PL dispersions, have recently been shown to demonstrate carbon dioxide selectivity from  $\text{CO}_2/\text{CH}_4$  mixtures comparable to industrially used sorbents, with potential applications as selective sorbents in sweetening of natural gas and carbon capture from flue gas [2]. PL solutions (Figure 1, left), another type of PL, consist of intrinsically porous molecules - such as porous organic cages (POCs) – dissolved in a pore-excluded solvent. POCs are an ideal pore carrier; their modularity allows the pore guest inclusion to be controlled to suit the needs. Solvent selection must also be cautiously made to ensure good pore loading - thus warranting high gas uptake (Figure 1, right) - and flowability (low viscosity), pore exclusion, as well as suitability for the methods used to measure the properties. While previous studies on PLs measure the neat gas adsorption of the materials, studies often do not explore the interactions between the pore carrier and the gas molecules sufficiently. To do this, we now have a toolkit for understanding the behavior of new PL solutions, specifically, a toolkit of accessible techniques that can be easily applied to these materials. We use dual quantitative  $^1\text{H}$ - $^{13}\text{C}$  and diffusion NMR spectroscopy to determine selectivity for gas uptake and inclusion from  $\text{CO}_2/\text{CH}_4$  mixtures, combined with nuclear Overhauser effect experiments to suggest mechanistic insight into selectivity by providing evidence of selective gas inclusion in the pores. Other methods employed in this work include an instrument adapted for measurements of PL uptakes, providing information on the kinetics of gas uptake into PLs, scarcely available in literature, and NMR gas titrations in PLs. Overall, the insights provided by this toolbox of techniques can be translated to other PL solution systems, providing an understanding of the guest selectivity observed in these systems, with an outlook towards the development of selective materials for molecular separations.

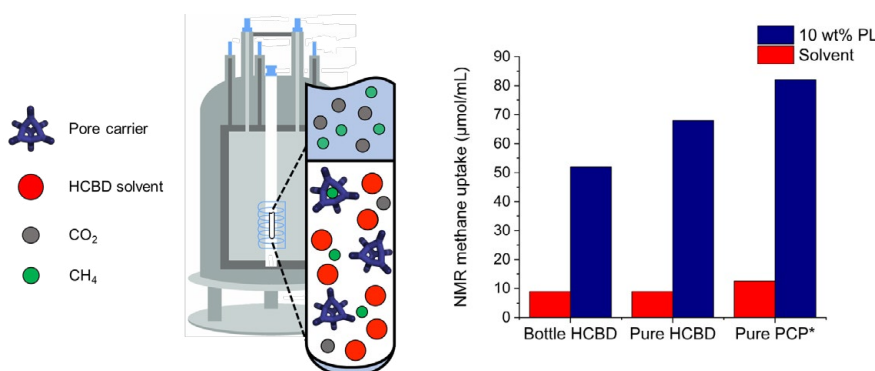


Figure 1: Left: A diagram of a PL solution capturing gas molecules in an NMR tube [4]. PCP – perchloropropene, HCBD – second generation solvent. Right: A graph of methane uptakes in HCBD PL solutions compared to previous high-capacity PL solutions in PCP [3].

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# Enhanced Electrochemical Sensing of Aldehydes Using Zeolitic Imidazolate Frameworks

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Zeolitic Imidazolate Frameworks (ZIFs) consist of tetrahedrally coordinated metal ions (commonly zinc or cobalt) and imidazolate building blocks, forming cage-like three-dimensional structures similar to zeolites. [1] Thanks to their similarity to both metal organic framework and zeolites, they possess unique properties such as thermal and chemical stability, high crystallinity, ultrahigh surface area, abundant functionalities and unimodal pores. These attributes make them attractive candidates for application in gas adsorption/storage, sensing, separation, catalysis, drug delivery, etc. [2] However, the electrochemical performance of ZIFs remains behind, particularly in terms of sensitivity and selectivity, when compared to conventional analytical methods. The challenge in enhancing the sensitivity and selectivity of ZIFs for sensing applications lies in the need for systematic studies tailored to each target analyte. [3]

The project involved the synthesis of distinct ZIFs and the optimization of their electrochemical sensing capabilities for detecting three aldehydes. Aldehydes, specifically formaldehyde, acetaldehyde, and benzaldehyde, are chosen as model analytes in the present case due to their biological significance. Aldehydes in water are formed during its chlorination and ozonation involving the oxidation of organic matter and also can be leaked from damaged pipes which though water is supplied to the households. Due to their reactivity, aldehydes can form DNA-protein cross-links, potentially leading to carcinogenesis and mutagenesis. [4, 5]

The structure of obtained ZIFs and changes in their structures upon exposure to aldehydes were investigated using FT-IR, XPS and PXRD. Their morphology was observed with SEM. The obtained compounds were mixed with Nafion to improve stability of ZIFs and deposited on the Glassy Carbon Electrode. Electrochemical analysis was conducted in the three-electrode system (ZIF@GCE as a working electrode, Ag/AgCl reference electrode and platinum wire as a counter electrode). All ZIFs were tested for sensitivity to acetaldehyde, benzaldehyde and formaldehyde.

Acknowledgments: This research was supported by a french government scholarship France Excellence.

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# Mechanistic Insights into Flexible MOFs for Gas Storage, Separation, Logic Construction, and Sensing Applications

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The spatiotemporal adaptivity of flexible metal-organic frameworks gives rise to novel phenomena that are not observed in their rigid counterparts [1]. This not only broadens our knowledge of the universe of porous materials but is also important for technological advances. Herein, we will present a mechanistic understanding of the flexible platforms [2,3,4] JUK-8 and UAM-1, along with chemical methods of their adjustment [5,6]. The gained nanounderstanding of observed phenomena through in situ techniques, along with theoretical considerations, forms the basis for the applicability of these materials in logic construction [7], gas storage, and separation[3,4].

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# New MOFs Formed By Azamacrocyclic Ni(II), Zinc(II) And Copper(II) Cations and [3,2-*b*]thiophene-2,5-dicarboxylate As Linker

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First-row transition-metal cationic complexes of tetradentate 14-membered cyclam-like tetraaza macrocycles (cyclam = 1,4,8,11-tetraazacyclotetradecane; L1, Fig. 1) are characterized by high thermodynamic stability and kinetic inertness [1] and are, in combination with oligocarboxylates as bridging ligands, popular metal-containing building blocks for the construction of MOFs – crystalline porous materials displaying many promising properties [2-5]. Chemical structures of both the cationic and anionic constituents of MOFs are very important factors determining their crystal structures, in particular, the dimensionality of polymeric networks and the porosity of the materials. They are characterized by rich structural variability (the dimensionality of polymeric networks, packing peculiarities, the porosity *etc*) that is connected with the chemical structures the cationic and anionic constituents of MOFs.

The aim of the present work was the study of the influence of the chemical features of macrocyclic cationic component (the nature of the metal ion and the number of the non-coordinated distal nitrogen atoms in the ligand) on the structures of the complexes formed by the Ni(II), Zn(II) and Cu(II) macrocyclic cations (Fig. 1) with the bidentate bridging ligand – the anion of thieno[3,2-*b*]thiophene-2,5-dicarboxylic acid ( $H_2A$ ) which was never used formerly for construction of MOFs based on macrocyclic metalocomplex nodes.

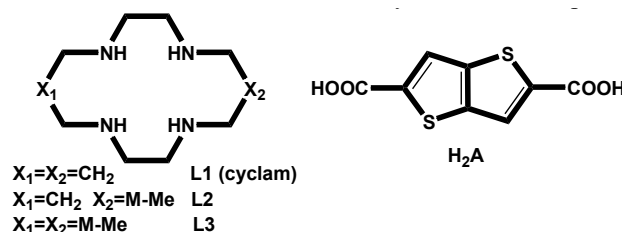


Figure 1: The structures of the ligands studied in this work.

Five new compounds crystallizing in different space groups have been obtained *via* the reactions of the acid with perchlorate salts of corresponding macrocyclic cations in the presence of pyridine. *i.e.*,  $\{[Ni(L1)(A)] 2DMF\}_n$  (P(-)1) (**1**),  $\{[Ni(L2)(A)] solvent\}_n$  (P4<sub>3</sub>2<sub>1</sub>2) (**2**),  $\{[Ni(L3)(A)] 0.77H_2O\}_n$  (R(-)3) (**3**),  $\{[Zn(L1)(A)]\}_n$  (P2<sub>1</sub>/c) (**4**) and  $[Cu(H_2O)_2]$  (P2<sub>1</sub>/c) (**5**). The compounds **5** is an ionic complex with the axial positions in the coordination sphere of the Cu(II) occupied by water molecules, while the other are 1D coordination polymers. The distances between ions of metal ions in **1**, **3** and **4** characterizing with linear polymeric chains are close (13.072-13.306 Å). The non-linearity of polymeric chain in **2** (the angle Ni...Ni...Ni 172.0°) results in slightly shorter Ni...Ni distance (12.592 Å). Due to the different symmetry operations inherent in each space group, mutual orientation of the chains is specific. So, in **1** the chains are parallel, while in **4**, **3** and **2** they are, respectively, doubly, triply and fourfold crossed. Such diversity of packing features results in essential differences of porosity of compounds and according to PLATON calculations solvent accessible voids equals 18.1, 19.0 and 39.5% in **2**, **3** and **1**, correspondingly. The crystals **4** are non porous. Spectral characteristic of the complexes are also discussed.

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# Synthesis and Characterization of d10 Metal-Organic Frameworks Utilizing 2,5-Bis(4-(pyridin-4-yl)phenyl)thiazolo[5,4-d]thiazole and V-Shaped Dicarboxylate

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Metal-organic frameworks (MOFs) are porous coordination polymers consisting of metal cation or clusters bound together by organic linkers. Due to their porous structure and high internal surface is expected that they will play crucial role in gas storage, separation and sensing. Moreover, their unique properties can be easily modified by changing the metal ion or/and linker [1].

Herein, we present four novel luminescent MOFs. They were synthesized in reactions between zinc(II) nitrate or cadmium(II) nitrate, 4,4'-oxybis(benzoic acid) ( $H_2oba$ ) or 4,4'-thiodibenzoic acid ( $H_2sba$ ), and 2,5-bis(4-(pyridin-4-yl)phenyl)thiazolo[5,4-d]thiazole (BPPTzTz) in N,N-dimethylformamide.

The Cd(*oba*), Zn(*oba*), and Zn(*sba*), are three-dimensional, while the dimensionality of Cd(*sba*) is reduced to two. All materials show distinguish arrangements of thiazolo[5,4-d]thiazole units in space, which result in different luminescence properties when materials were excited. Furthermore, the Zn(*oba*) material was used as a chemical sensor for the selective detection of ions in aqueous solutions.

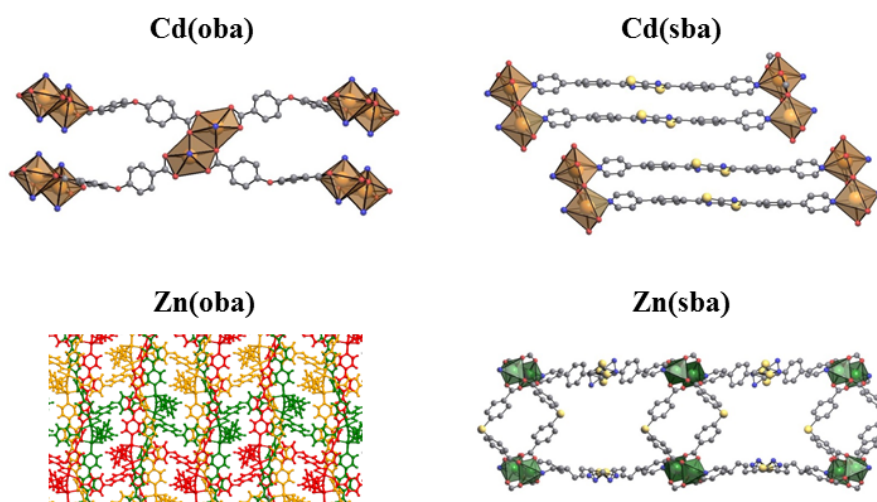


Figure 1: Fragments of the structures of the obtained materials: Cd(*oba*)=Cd(*oba*)(BPPTzTz)\*DMF, Cd(*sba*)=Cd(*sba*)(BPPTzTz), Zn(*oba*)=Zn<sub>2</sub>(*oba*)<sub>2</sub>(BPPTzTz)\*0.5DMF, Zn(*sba*)=Zn<sub>2</sub>(*sba*)<sub>2</sub>(BPPTzTz)\*DMF.

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# Computational design of magnetic metal-organic frameworks (MOFs)

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Magnetic materials are widely used in modern technology, their applications ranging from electric engines to data storage systems. There are several well-established magnetic materials, such as inorganic magnets (rare-earth metals based), however, they face limitations in tuneability [1]. Improving the tunability of magnetic properties can be done by altering the alignment of magnetic ions within its structures [2].

Transition metal-based metal-organic frameworks (MOFs) present a promising opportunity for the development of novel magnetic materials. The design of MOFs focuses on their topological diversity, which can be enhanced by the interplay between metal nodes and organic linkers. By creating MOFs with specific topologies, the relative orientation of magnetic metal centers can be strategically adjusted [3], providing a systematic approach to achieve desired magnetic properties.

As exploring the vast combinations of nodes (metal ions) and linkers becomes important in the study of magnetic MOFs, the demand for effective techniques to undertake this task is also rising. Traditionally, experimental screening has been the primary approach. However, because of the vast array of available potential metals and linkers, this approach becoming increasingly challenging. Therefore, a theoretical approach supported by robust computing performance emerges as a suitable technique to fulfill this task. This approach will not only explain observed magnetic phenomena but also predict new possibilities for experimental verification, fostering a synergistic relationship between theory and experiment.

Our approach to the theoretical investigation of magnetic MOFs involves crystal structure prediction (CSP) based on ab initio random structure searching (AIRSS) [4] combined with Wyckoff Alignment of Molecules (WAM) [5]. This method excels at generating entirely new crystal structures from the molecular blueprints of individual nodes and linkers. This process is also fast because it involves reducing the dimensionality of the search space through symmetry imposition on trial structures. The validity of this approach has been confirmed through the successful reproduction of existing MOF structures [5] and the subsequent design of novel functional MOFs with applications as rocket fuels [6].

To identify the likelihood of the generated structures existing under experimental conditions, it is essential to evaluate their energy ranking. For this purpose, periodic density functional theory (DFT) is employed. However, due to the need to consider the magnetic ordering of metal ions within the MOF lattice, a more advanced periodic DFT approach is required. This involves testing potential enhancements like the Hubbard U correction [7]. This comprehensive strategy allows for extensive structure searches of magnetic MOFs while maintaining high computational accuracy, ultimately leading to the identification of promising candidates for experimental validation.

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## New MOF-based composites for photocatalysis

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The need for sustainable energy and fuel production methods with minimal environmental impact is crucial due to the global pollution crisis and the depletion of fossil fuel resources. In this regard, technologies like photocatalytic CO<sub>2</sub> reduction, pollutant photodegradation, and water-splitting using solar radiation have emerged as promising solutions for converting CO<sub>2</sub> into valuable fuels such as methane, methanol, formic acid, and formaldehyde. Metal-organic frameworks (MOFs), known for their unique cage-like structures, large surface areas, and selective reactions, have gained attention as photocatalysts in CO<sub>2</sub> conversion. Modifying these frameworks with metals like copper enhances their photocatalytic activity under visible light and improves charge separation.

This research involved creating two series of MOF-based photocatalysts. The first series consisted of composites containing PCN-222 (Cu) with varying amounts of Cu<sub>2</sub>O and CuO, which boosted photocatalytic performance in photoconversion CO<sub>2</sub> under visible light. The second series featured thin layers of titanium dioxide nanotubes decorated with NH<sub>2</sub>-MIL-125 (Ti/Co). These materials showed significant potential in hydrogen photogeneration and the photo-degradation of a model organic pollutant. Characterization of these materials, including UV-Vis spectroscopy, FTIR, XRD, as well as BET surface analysis and CO<sub>2</sub> sorption analysis, allowed for the correlation of the properties of the obtained materials with their activity and the explanation of the photocatalytic mechanism.

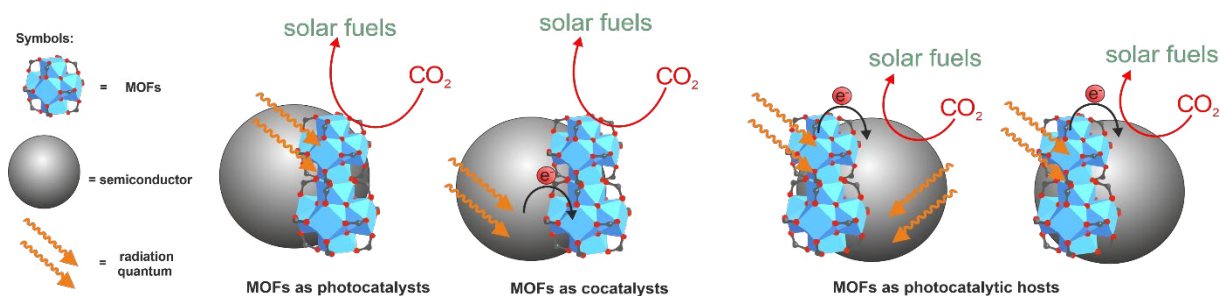


Figure 1: Possible functions of MOFs in semiconductor composites.

These studies highlight the pivotal role of MOFs in advancing sustainable energy and chemical technologies. They offer new opportunities for utilizing visible irradiation to convert CO<sub>2</sub> into valuable chemicals, thereby reducing pollution and supporting clean energy production.

### Acknowledgments:

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# Multi-directional ferroelastic strain coupled to the conformation of linkers and the metal cation coordination

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Three-dimensional (3D) materials are a class of compounds attracting significant interest due to their versatile applications, such as adsorption and separation agents, chemical and physical sensors, and material storage [1]. Designing a framework with specific and highly desired properties depends on many factors, including the physical and chemical characteristics of both the metal cluster and ligands, the anion type, and the synthesis method. Given the key role of ligands in the self-assembly of porous 3D frameworks, we have considered a non-rigid, aliphatic diamine (1,6-hexanediamine, HDA) to be an excellent candidate as a building element for multidimensional networks [2]. HDA has been widely used in organic polymers (like Nylon-66), plastics, detergents, textile additives, flotation agents, and antistatic agents, among others [3-4]. Combined with its stereochemical flexibility, HDA-based supramolecular materials are now the subject of extensive study by many groups.

In this work, we carried out a simple one-pot diffusion synthesis to obtain three distinct supramolecular frameworks with different structures. In these materials (1)  $\text{Cd}(\text{HDA})_2(\text{NO}_3)_2$ , (2)  $\text{Cd}(\text{HDA})_{1.5}(\text{NO}_3)_2$ , and (3)  $\text{Cu}(\text{HDA})_2(\text{MeCN})_2 \cdot 2\text{BF}_4^-$ , the flexible linker HDA adopts different bent or straight conformations depending on the metal center and the strength of the interaction in its immediate environment. We investigated how changes in the strength of the intramolecular interactions influenced the structure and properties of these materials by introducing compression strain at high pressure.

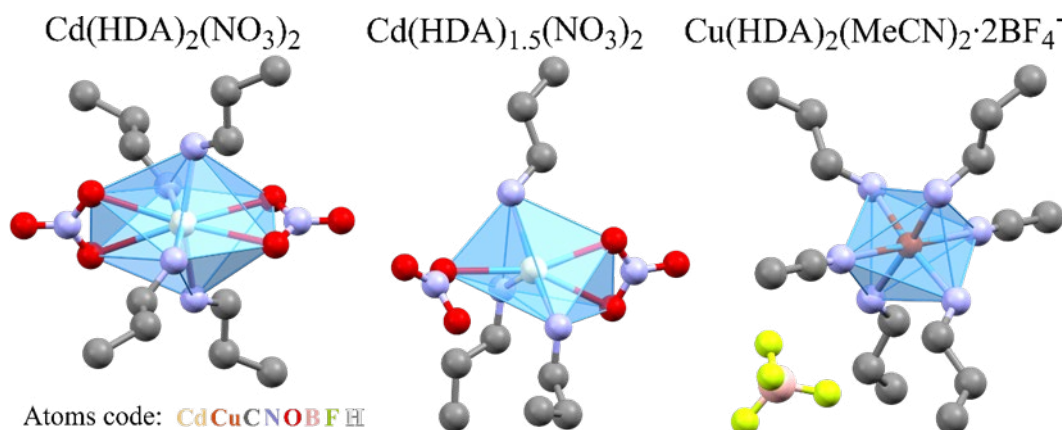


Figure 1: Three polymeric frameworks synthesized with 1,6-hexanediamine linkers (showed as a half molecule).

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# Spatial Distribution of Microstrains in the Crystal Lattice of MOFs Differing in the Degree of Structure Opening

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MOFs have been widely studied due to their unique features. [1,2] The characteristics and quality of MOFs depend on the framework structure and various synthesis techniques. MIL-88B(V) can „breathe” and immersion of the material in various solvents causes its structure to expand. The lattice parameters take on different values depending on the synthesis method, and the product synthesis diagrams for vanadium MOFs contain both single- and multiphase regions. [3]

The broadening of the diffraction peak of MOFs may be caused by microstrain of the lattice, which means that the lattice parameters obtained from the powder X-ray diffraction change and do not exactly correspond to the lattice parameters of the highly crystalline structure. These defects can also affect the microporosity of the structure.

To gain insight into the microstructure of the multiphase sample, we used profile intensity partitioning, specifically the Le Bail technique, which works particularly well in the case of overlapping intensities because in this method the intensity is assigned based on the multiple intensities contributing to a specific peak (Figure 1). We modeled the anisotropic strain broadening of the reflections using the method reported by Stephens. [3]

The anisotropy of microstrain broadening can reveal anisotropy of the internal properties of the solid that may otherwise be difficult to determine. Our results open the way to the discovery of new, responsive MOFs exhibiting more complex phase change behavior.

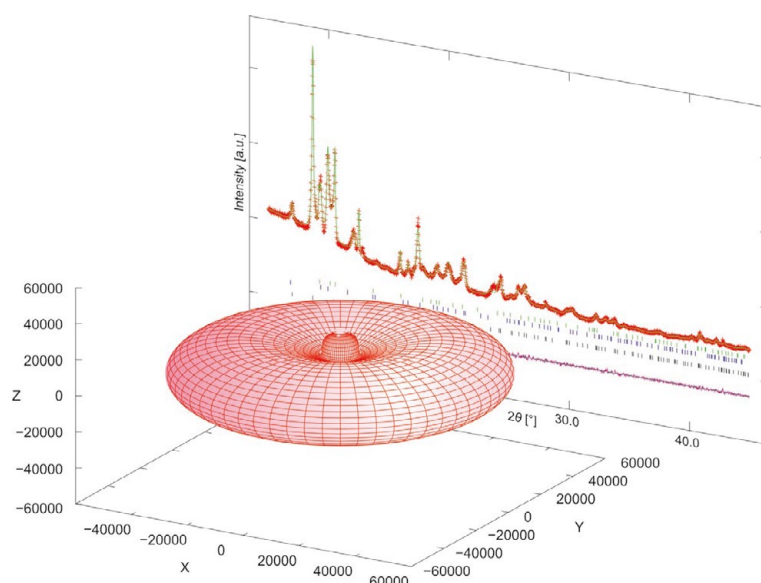


Figure 1: 3D representation of experimentally determined  $hkl$ -dependent microstrain and Le Bail refinement for the as-obtained MIL-88B(V) powder.

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# Tuning Porphyrin based Metal–Organic Frameworks Topology by Selection of Auxiliary Ligands and Lanthanide Nodes – Syntheses, Structures and Electrochemical Properties

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Metal-organic framework (MOF) materials have quickly matured from a structural curiosity to materials with wide potential in various fields including gas separation and storage as well as catalysis. Importantly, MOFs are promising materials in applications aimed to tackle the urgent societal needs to solve issues regarding clean energy production and storage<sup>1</sup>. For example, MOFs that act as water splitting and CO<sub>2</sub> reduction catalyst as well as energy storage materials, such as batteries, are under active investigation<sup>2</sup>. However, one of the main challenges of applying MOFs for energy storage applications is the often poor (electronic) conductivity of MOFs, which can be improved by the use of redox-active ligands and metal nodes. While this strategy typically enhances the local (short range) electron mobility, conductive guest molecules or polymers introduced within the MOF pores can act as charge carriers over longer distances within or at the surface of the material.

Here, we present three different MOF materials, all synthesized using the same 5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin-FeCl as the redox active linker, but by using different lanthanide nodes and two different co-ligands. The presented results focus in the electrochemical properties. In particular, we show that conductive polymers can be synthesized inside MOF pores starting from the respective monomeric units, which provides significant increase in the MOF conductivity and supercapacitance.

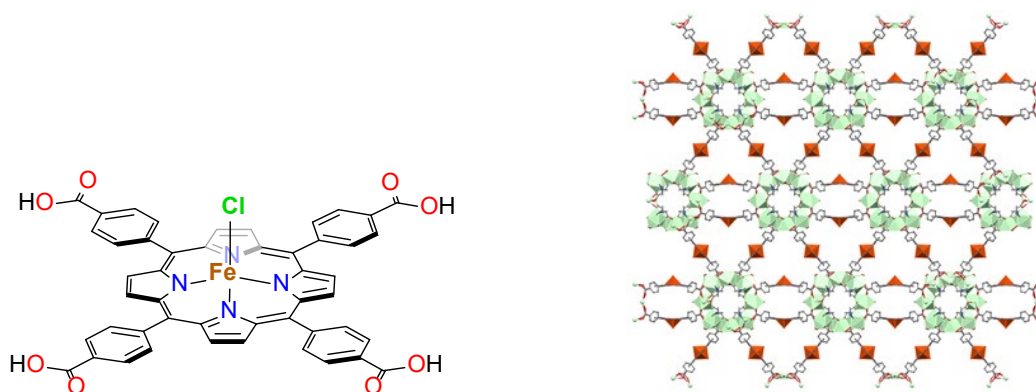


Figure 1. Left: 5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin-FeCl ligand. Right: Illustration of crystal structure of lanthanide-based porphyrin-MOF with lanthanide nodes shown with crimson polyhedra and Fe-centers shown with red polyhedra.

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# Theoretical and Experimental Insights into Stimuli Responses of Two Isostructural MOFs Differing by a Single Atom

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Flexible metal-organic frameworks change their structure in response to external stimuli, e.g. due to changes in temperature, exposure to light or interaction with an electric field.<sup>[1,2]</sup> UAM-1O and UAM-1S are isostructural MOFs composed of zinc cation, thiazolo[5,4-d]thiazole, and dicarboxylate ligands (4,4'-oxydibenzoate (UAM-1O) and 4,4'-thiodibenzoate (UAM-1S)) that exhibit different CO<sub>2</sub> adsorption mechanism<sup>[3]</sup>. We attribute their different behaviours to variations in their closed-phase structures. To obtain closed phases, it is necessary to remove guest molecules by activation. The activation process, involving the exchange of DMF with DCM followed by DCM removal at 80°C under vacuum, leads to crystal fragmentation, resulting in crystals that are too small and generally of poor quality for Single Crystal X-ray Diffraction (SC-XRD) measurements.

Nevertheless, the crystal structure of the closed phases was determined using Microcrystal Electron Diffraction (microED). During the activation of UAM-1O, a reorganization of the metal cluster occurs, accompanied by a reduction in the coordination number of the zinc cation from 5 to 4. In contrast, the cluster structure of UAM-1S remains intact. Interestingly, when UAM-1O is activated under mild conditions, such as exchanging DMF with DCM, followed by repeated DCM exchanges and leaving crystals in air, some crystals remain stable despite the solvent escape, leading to the formation of an "empty open phase".

Data obtained using microED combined with computational methods have allowed for a precise explanation of the MOFs closure mechanism during activation. The Density Functional Theory method enabled the identification of energy minima, dependent on the unit cell volume, for both open and closed forms. Calculations indicated that in UAM-1O (cp), breaking Zn-O bonds in the metal cluster is much more energetically favourable than maintaining these bonds in the closed form. In the case of UAM-1S, the situation is reversed and the hypothetical closed form UAM-1S, in which one Zn-O bond in the cluster, similar to UAM-1O, has been broken, is characterized by higher energy than the structure in which the bonds in the cluster have been preserved. The bond-breaking process in the UAM-1O cluster during activation was investigated using the solid-state nudged elastic band (ssNEB) methodology. This method enabled the determination of the transition path from a coordination number of 5 to 4, described as a "bond shift".

Furthermore, we utilized time-dependent X-ray diffraction during CO<sub>2</sub> adsorption to determine the response time of these materials, as well as to gain experimental insights into the energetic barriers between the open and closed phases of both materials.

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# A Theoretical And Experimental Study On CO<sub>2</sub> Binding Sites And Transformability Of CALF-20 Metal-Organic Framework

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Calgary Framework 20 (CALF-20) is a readily obtained and reproducible zinc-based metal-organic framework that exhibits excellent durability in the CO<sub>2</sub> sorption process [1]. In our study, we monitored this process at atomic resolution using *in situ* single-crystal X-ray diffraction under controlled gas pressure. The experiment revealed slight structural changes in the framework upon gas sorption and allowed us to determine the real positions of carbon dioxide in the pores (Fig. 1).

Recent reports on CALF-20 suggest its susceptibility to humidity [2] and pressure-induced phase transformations [3]. We studied changes in CALF-20 triggered by temperature, including a single-crystal-to-single-crystal transition of the initial phase  $\alpha$ -CALF-20 into  $\gamma$ -CALF-20, assisted by solvent included in the pores (Fig. 1). We were also able to capture a transient phase of CALF-20 called  $\tau$ -CALF-20 (Fig. 1). Interestingly, its calculated powder pattern correlates perfectly with that of the previously reported  $\beta$ -CALF-20 [2] (Fig. 1). However, the crystal structure determined by SC-XRD experiment differs significantly from the structure based on the powder data described in the literature.

Theoretical analysis of CALF-20 has proven that the presence of water molecules is crucial in stabilizing the structure, leading to its exceptional stability. Nevertheless, under anhydrous conditions, the energetically favourable phase is  $\alpha$ -CALF-20, as supported by experimental data. Furthermore, a contracted phase is predicted to exist only at extremely low temperatures.

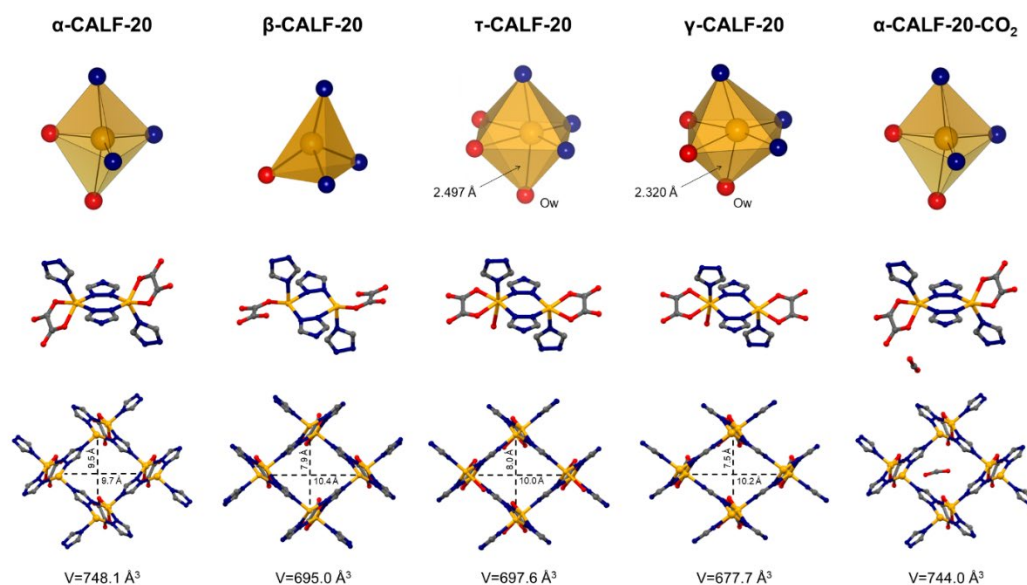


Figure 1: A structural comparison of all known CALF-20 phases.

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# The Inclusion Phenomena In Chiral Macrocylic Compounds

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X-ray investigations were carried out on inclusion crystals of two types of macrocyclic compounds: a bridged isotrianglamine [1] and an ester-substituted calixsalen [2]. Both compounds were obtained in a [3+3] cyclocondensation reaction between *trans*-1,2-diaminecyclohexane and a suitable aromatic 1,3-dialdehyde. The utilisation of molecular building blocks with fixed and defined geometry during synthesis led to creation of vase-shaped macrocycles with relatively rigid skeletons and well-defined cavities, capable of inclusion of small and medium-sized guest molecules.

The average cavity size equals 7.2 Å for the isotrianglamine and 6.1 Å for the calixsalen. Regardless of the type of guest molecule, the isotrianglamine forms stacks with one-dimensional channels passing through the cavities of stacked macrocyclic molecules (Fig. 1a). In turn, the calixsalen self-associates into two types of supramolecular dimers: a capsule (Fig. 1b) with the host molecules arranged in a head-to-head motif and the hour-glass (Fig. 1c) where the macrocycles are assembled in a tail-to-tail manner. Both dimers are stabilized by a variety of interactions, ranging from C-H $\cdots$ O to  $\pi\cdots\pi$  stacking interactions. In the crystals investigated, both intra- and intermolecular inclusion is observed.

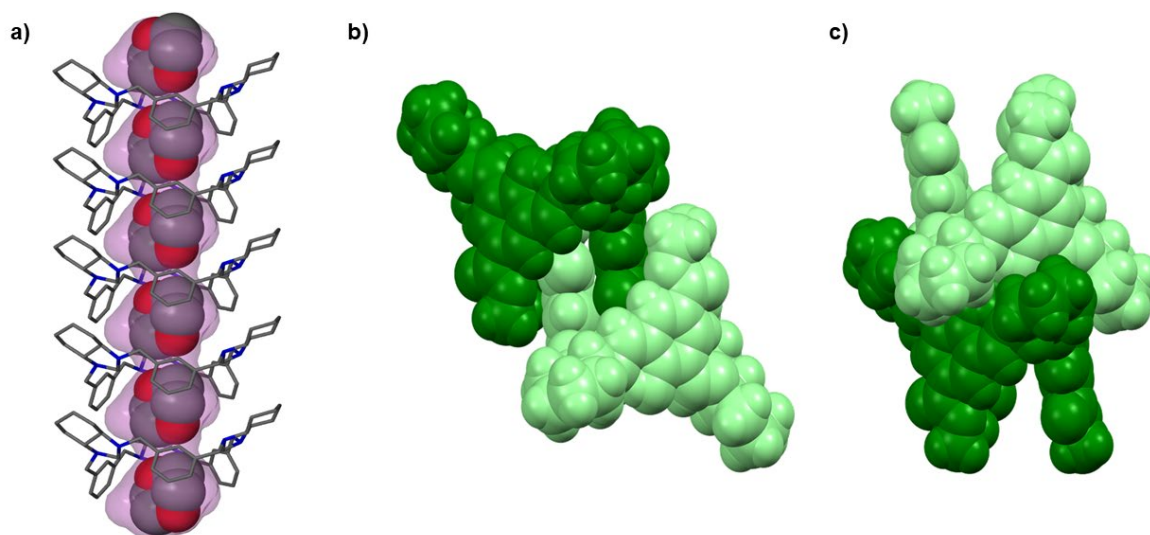


Figure 1: Supramolecular motifs observed in crystals: a) stack formed by the bridged isotrianglamine,

The compounds investigated were synthesised in the Department of Organic Stereochemistry at the Faculty of Chemistry, AMU.

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# *In Situ* Crystallographic Visualisation Of Gas Uptake By A Trianglimine Molecular Crystal

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A trianglimine molecular crystal was recently reported to reversibly absorb atmospheric water, with water release occurring at temperatures even as low as -70 C. The crystal consists of a hexagonal arrangement of macrocycles that stack to form 1 nm wide channels. The apertures of the molecules also form hybrid intrinsic-extrinsic voids with no obvious connection to the channels (Figure 1). Water molecules only access the hydrophilic channels and do not become lodged in the isolated hydrophobic voids. Inspired by previous work,[1-3] we undertook experiments to investigate whether the isolated voids can be accessed by suitable guests. Indeed, exposure of the crystals to gases such as CO<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> results in gradual filling of the voids, as revealed by *in situ* single-crystal X-ray diffraction analysis employing an environmental gas cell. Details of the structural analyses will be presented, as well as a possible mechanism for the diffusion of gas into spaces with no permanent link to the surroundings.

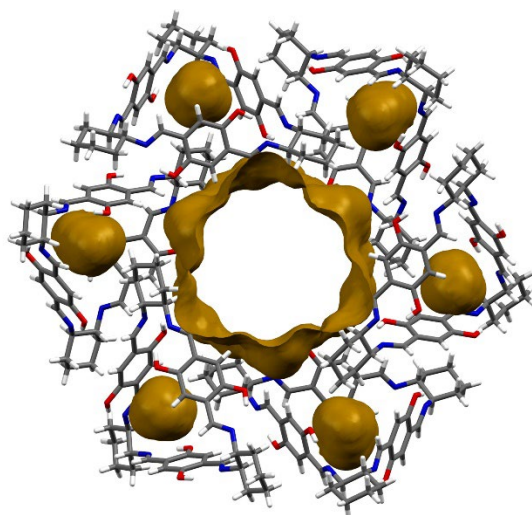


Figure 1: Trigonal arrangement of six molecules of trianglimine to form 1 nm wide 1D extrinsic channels propagating along [001], and six hybrid intrinsic/extrinsic 0D voids.

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# Mechanochemical Synthesis of Carcerands

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Carcerands are supramolecular containers which are capable of harboring molecular guests, and which do not permit these guests to exit without breaking covalent bonds [1]. Hemicarcerands, carcerands with a built-in window, allow guests to exchange with heating [2], and have been used to stabilize otherwise fleeting molecular species within their cavities, including *o*-benzyne [3], anti-Bredt bridgehead olefins [4], and cyclobutadiene [5]. While these supramolecular hosts can offer access to fascinating host-guest chemistry, their syntheses are often low-yielding and demand large amounts of organic solvent as a medium for both reactivity and purification.

Mechanochemistry, chemical reactions conducted under the influence of mechanical force, has emerged as a green method for the synthesis of complex organic molecules [6], pharmaceuticals [7], inorganic materials [8], MOFs [9], and more [10]. Here, we present our efforts to improve the efficiency of carcerand synthesis by applying mechanochemical techniques which involve the mechanical grinding or mixing of reagents with either small amounts of or no organic solvent. Such methods have led to improvements in yields and the simplification of purifications, improving the overall efficiency of the preparation of carcerand host materials and their constituent supramolecular building blocks.

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# Exploring Halogen Bonding in Water: Cucurbit[7]uril Interactions with Halogenated 1-Phenylpiperazine Molecules

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Cucurbit[7]uril (CB7) stands as an important molecular host extensively employed in molecular recognition, surpassing even the renowned avidin-biotin pair in binding affinity [1]. With applications ranging from protein crystallization to sensor development and supramolecular assemblies [2], CB7 versatility underscores its significance in diverse fields [3]. Understanding the energetics [4] of these interactions is crucial for elucidating the design of new molecular partners for CB7. In this study, we investigate the interaction between CB7 and a series of halogen derivatives of 1-phenylpiperazine and 1-(2-Pyrimidyl)piperazine molecules to explore the influence of halogen atoms on molecular recognition. Utilizing isothermal titration calorimetry, we measured the free energy of binding, encompassing enthalpy and entropy contributions. Computational methodologies [5], including density functional theory (DFT) calculations, Symmetry-Adapted Perturbation Theory [6], and Attachment-Pull-Release molecular dynamics simulations [7], were validated against our experimental observations. As predicting the proper binding pose of these flexible ligands is a challenging task, the crystal structures of five derivatives were determined by X-ray diffraction experiments. By decomposing the binding free energy into its constituent components, including two-body dispersion energy, solvation free energy, entropy variation, and deformation energy, we analyze the contributions of each term to comprehend the binding affinity of each ligand. Our findings shed light on the molecular factors governing the CB7-1-phenylpiperazine interactions, showing that the addition of a fluorine or chlorine atom in *ortho* or *para* positions of the phenyl ring enhances the affinity the most.

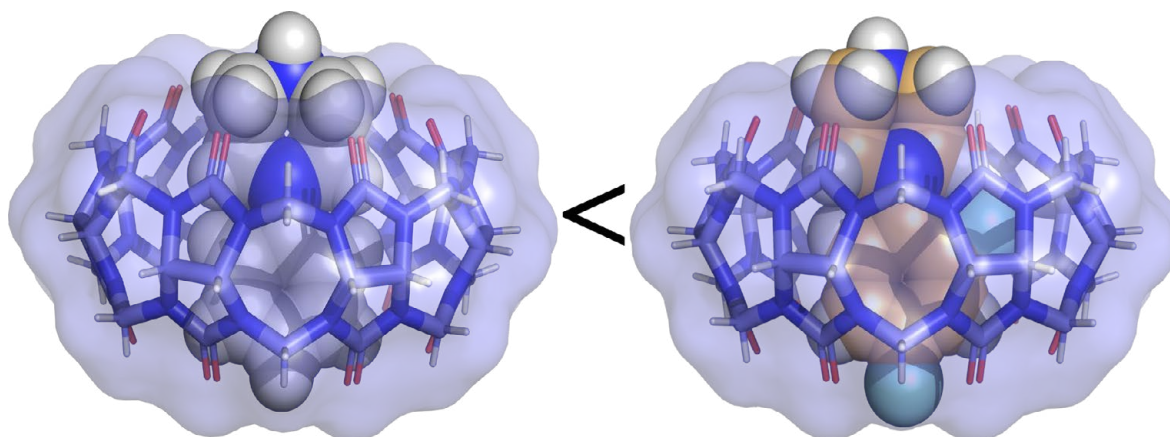


Figure 1: Binding affinities predicted from theoretical calculations, which correlate with experimental results, for NNH@CB7 and NNF2@CB7 are  $-84.2 \text{ kJ mol}^{-1}$  and  $-87.8 \text{ kJ mol}^{-1}$ , respectively.

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# Pentamidine and Alexidine Fold in the Bowl-Shaped Cavity of a Macrocyclic Host

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The inner space of the water-soluble macrocyclic hosts enables the recognition and confinement of various guest molecules due to the non-covalent interactions and hydrophobic effect in aqueous media. Such host-guest ensemble formed *via* induced fit or mutual induced fit mechanism is usually more prompt to crystallize, paving the way to the structural characterization benefitting from single crystal X-ray diffraction analysis. The mode and degree of the compression of flexible guest molecule would be defined by the geometry and chemical identity of the host molecule serving as a confinement vessel. In the current work we target guest molecules of high conformational freedom that are otherwise difficult to crystallize. Pentamidine and alexidine are FDA-approved drug compounds currently rediscovered as membrane-targeting antibiotic sensitizers/potentiators helping restore antibiotic activity against multidrug resistant bacteria pathogens. [1] The objective of this work was to study host-guest conformational and structural behavior of these highly flexible drug molecules in the confined space of a well-known macrocyclic host, *p*-sulfonato-calix[4]arene. The insight into host-guest chemistry of these compounds would be beneficial in terms of new potential supramolecular formulations and/or crystal forms with a view to controlled pharmacological kinetics and improving their toxicology profiles.

The simple bowl-shaped cavity of *p*-sulfonato-calix[4]arene effectively mediates U-shaped folding of ditopic drug molecules alexidine and pentamidine. The combination of  $C_4$  symmetric bowl of calix[4]arene and  $C_{2h}$ -symmetric flexible guest molecules results in the clamping down the central linker (hexyl or pentyl) of the guest by its inclusion and coiling inside the macrocyclic cavity. The binding site in both crystal structures is the central aliphatic chain enabling guest folding through adopting *gauche* conformation upon entering the confined space of the host, Fig. 1A. The biguanidinium and amidinium cationic groups support complexation and assembly in terms of multiple charge-assisted hydrogen bonding with sulfonate groups. The synergy of hydrophobic effect and multiple charge-assisted hydrogen bonds sustains conformational fixation of these highly flexible guest molecules in the crystal state. Additionally, the host-guest complexation has been studied in the solution/gas phase by means of ion mobility mass spectrometry (IM-MS) complemented by theoretical calculations, Fig. 1B,C.

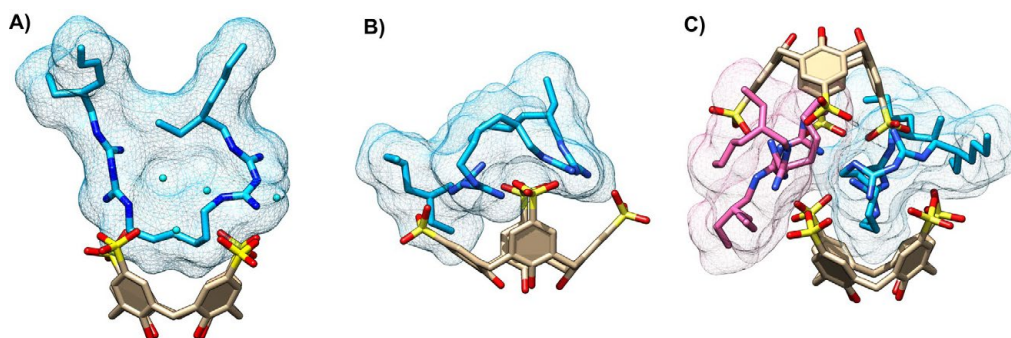


Figure 1: Crystal structure of the alexidine inclusion complex with *p*-sulfonato-calix[4]arene (A); the lowest energy conformations of 1:1 (B) and 2:2 (C) host-guest complexes obtained by IM-MS studies and theoretical calculations.

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# Unclosed cryptands as matrices stabilizing water clusters in the solid state

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Unclosed cryptands, (UCs, Fig. 1a), macrocyclic polyamides with flexible lariat arm, are structurally related to cryptands, but they are more labile than their rigid analogues [1]. They have been, up to date, utilized in various applications, including selective anion recognition [2], and as catalysts in PTC [3]. During our studies we found out that 26-membered UC utilizes its amide groups and polarized aromatic substituents connected by butylene linkers to self-assemble stable octameric water cluster built from a cyclic tetramer and four water molecules attached to each corner of the tetramer [4]. This phenomenon inspired us to look more closely at the impact of changes in the structure of various UCs on their ability to stabilize water associates in the solid state. We have shown that for UCs with a phenyl group in the lariat arm substituted by an electron withdrawing group (-NO<sub>2</sub>), as well as an electron donating group (-OMe), the water octamer is stabilized (Fig. 1b); however UC with unsubstituted phenyl group in the lariat arm stabilizes two water chains of different length [5,6].

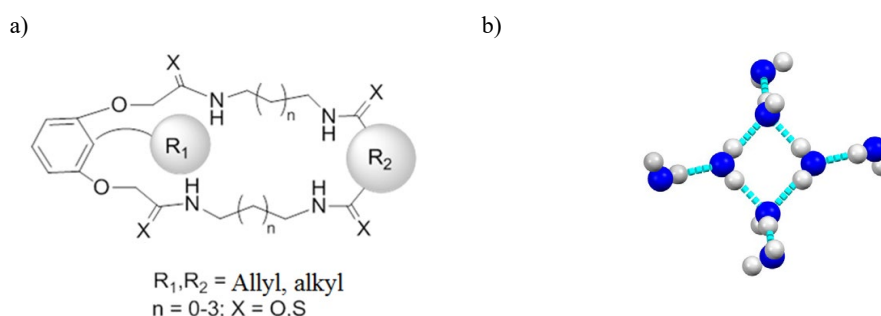


Figure 1: a) General structure of UCs b) octameric water cluster.

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# Improving solubility and separation efficiency of antidepressant drugs through cucurbituril complexation

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Tricyclic antidepressants (TCAs) like Imipramine and Amitriptyline treat depression by inhibiting serotonin and noradrenaline reuptake. However, their poor aqueous solubility limits their effectiveness, prompting research into methods to enhance their bioavailability. Strategies include buccal film formulations, micronization techniques, and oil-miscible ionic liquids.[1-3] This study explores using cucurbit[n]urils (CBs) to form complexes with Imipramine and Amitriptyline, significantly improving their solubility in water. Cucurbiturils are known for their ability to self-assemble and bind with various compounds,[4] making them excellent candidates for enhancing drug solubility and delivery. Their structure, with carbonyl groups outside and a hydrophobic cavity, allows them to form complexes with positively charged organic compounds like TCAs. CB6 encapsulates alkyl chains, while CB8 can also bind aromatic rings. Host-guest complexes with CBs can form in water solutions with high binding affinity, reducing organic solvent contamination, crucial for pharmaceutical use. Notably, studies suggest no toxicity of CB complexes within therapeutic dosages. CBs also have applications in materials design and sensors. We initially crystallized Imipramine and Amitriptyline hydrochlorides, elucidating their structures using X-ray diffraction, which informed solvation energy calculations. Surprisingly, Imipramine formed cocrystals exclusively with CB8, while Amitriptyline formed cocrystals solely with CB6. Imipramine created two distinct cocrystals with CB8: one with a 1:2 host-guest ratio in the  $Pca2_1$  space group, and another with a 1:3 ratio in the  $P2_1/c$  space group. Amitriptyline cocrystals with CB6 were found in a 1:1 ratio in the  $C2/c$  space group and a 2:2 ratio in the  $R-3$  space group. The presence of 5-10% KI or  $ZnCl_2$  was essential for successful crystallization of these forms.

Isothermal titration calorimetry (ITC) revealed high selectivity in binding affinities: Imipramine showed a measurable binding constant with CB6 ( $K_d = 10^{-4}$  M), while Amitriptyline exhibited a  $K_d$  value of  $0.2 \times 10^{-4}$  M with CB8. Binding constants for Imipramine with CB8 and Amitriptyline with CB6 exceeded the measurable range ( $K_d > 10^{-2}$  M). Theoretical analyses indicate that this selectivity arises from a 20 kJ/mol higher solvation penalty for Imipramine and its structural inflexibility to coil within the CB8 cavity. This study highlights the potential of cucurbit[n]urils to enhance the solubility and separation efficiency of TCAs, paving the way for improved bioavailability and therapeutic efficacy of these antidepressants.

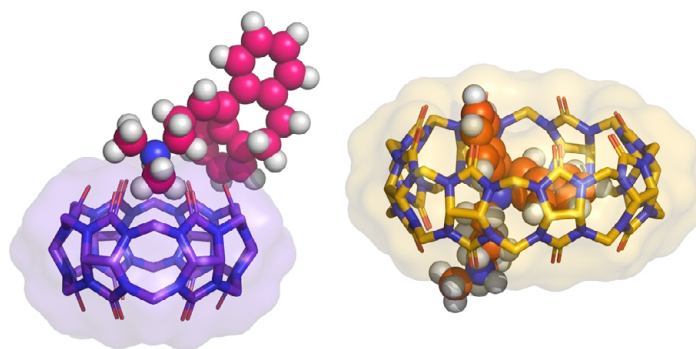


Figure 1: Binding pose of Amitriptyline with CB6 (left) and Imipramine with CB8 (right)

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# Organic Cage Rotaxanes

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Organic cages are materials constructed from covalent bonds with internal cavities that enable them to accept guests. These cages can be post-synthetically modified (PSM) by incorporation of handles, which can be derivatised further to introduce additional functionality.<sup>1</sup> Whilst there are numerous methods to synthesise these materials, they are commonly formed by exploiting the dynamic nature of reversible bonds, which has provided access to a range of cage structures with varying degrees of complexity, from small, capsular cages to mechanically interlocked molecules (MIMs).<sup>2</sup> The popularity of MIMs, such as rotaxanes, in the field has led to the design and synthesis of functional materials with varied complexity, such as multiply interlocked rotaxanes, dendrimers, and recently, cage-based rotaxanes.<sup>3,4</sup> Although organic cages have been incorporated into rotaxane structures, the axle component tends to occupy the cavity, limiting function as a host.<sup>3</sup> In contrast, there are a handful of metal-organic and metalloid-organic rotaxanes that incorporate unoccupied cage-like structures.<sup>5,6</sup> In this work, we sought to use organic cages as part of the axle to maintain cavity vacancy, expanding upon our previous work on organic cage dumbbells,<sup>7</sup> and thus yield materials that could exhibit complex host-guest chemistry and molecular motions. Mono-, di- and tri-terminal alkyne functionalised cages were formed by separating statistical mixtures of cages containing different numbers of alkyne handles formed via a ‘scrambling’ approach,<sup>8</sup> which were then used to develop a synthetic strategy and selectively prepare organic cage[*n*]rotaxanes (where *n* = 2, 3, or 4, Figure 1), by exploiting the copper(I)-catalysed azide-alkyne cycloaddition active-template approach with a small bipyridine macrocycle, chosen for their efficacy in yielding stable rotaxane structures.<sup>9</sup> Using this approach, we obtained rotaxanes incorporating organic cages where the cavity was unoccupied by the axle, offering a potential strategy to access cage-based rotaxanes that could exhibit interesting host behaviour.

Figure 1: Synthesis of targeted cage[*n*]rotaxane structures.

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## Diversity of *p*-sulfonatocalix[4]arene-benzamidine complexes caused by counterion and crystal “aging” in the mother liquor

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Of the available abiotic macrocyclic hosts operating in water, the family of anionic *p*-sulfonatocalix[*n*]arenes is particularly attractive due to the rich palette of molecular recognition properties and biocompatibility making them potentially useful for diverse life sciences and pharmaceutical applications.[1] In terms of providing confinement for biomolecules, the smallest *p*-sulfonatocalix[4]arene (**C4S**) of rigid bowl-shaped cavity have been well explored both in the solution and solid state. The early structural work of Coleman and Raston showed the inclusion of folded amino acid molecules into the **C4S** macrocyclic cavity either in the presence or absence of sodium cations.[2] Crowley and team took the anionic *p*-sulfonatocalix[*n*]arenes to a higher level of molecular recognition, namely using macrocycles as scaffolds that mold to cationic surfaces of various proteins promoting assembly and crystallization.[3]

Although a lot is known on the structure of **C4S** supramolecular assemblies, many aspects involving **C4S** cocrystallization with small guest molecules as well as biological macromolecules are still enigmatic and deserve more attention. One of such aspect is the role of **C4S** counterion, as this macrocyclic host is commercially available in two forms – either sodium salt or tetrasulfonic acid form. We and others have observed the occasional incorporation of sodium cations into **C4S** crystal complexes. However, systematic studies on the role of **C4S** counterions in the host-guest crystallization and assembly are lacking. In this work, we explore two commercially available forms of **C4S** in the cocrystallization with benzamidine ligand. We have found, that indeed two different host-guest crystal forms can be obtained under the same conditions depending on the **C4S** counterion. In the case of **C4S** sulfonic acid, the 1:4 host-guest complex crystallizes, while in the case of **C4S** sodium salt, the mixed host-guest coordination complex is obtained with 3 benzamidines and two sodium cations coordinated to **C4S**. In the presence of sodium cations, one of the **C4S** phenolic groups is deprotonated and **C4S** is a penta-anion. Additionally, we have studied the effect of “aging” of both crystal complexes kept in contact with the mother solution in the vial open to air and allowing slow evaporation in the room conditions. Such crystal aging in contact with mother liquor results in the appearance of new crystal forms differing in chemical composition as well as crystal structure from the initial complexes.

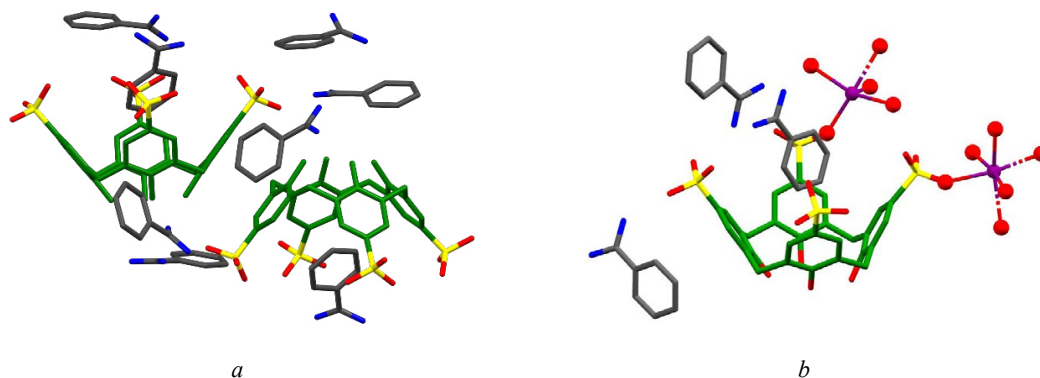


Figure 1: Host-guest complexes of *p*-sulfonatocalix[4]arene with benzamidine: (a) **C4S** in the acidic form, (b) **C4S** in the form of sodium salt (sodium is violet).

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# Intermolecular Interactions in Design of Self-Organizing Macrocylic Compounds

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Due to their versatile applications macrocyclic compounds have received unflagging interest from the scientific community, since the first reports [1-3]. A well-recognized feature of materials built on the basis of chiral polyaromatic macrocyclic imines is their ability to self-organize. As a result of non-covalent interactions, these compounds often form porous higher-order structures ranging from discrete molecular cages through amorphous aggregates of molecules to crystalline materials. A major advantage of these compounds relies on their availability. The macrocycle can be conveniently synthesized from structurally predisposed substrates and also “post-synthetically” modified in a relatively simple manner. By appropriately selecting the functional groups, which are attached to “the arms” of the macrocycle, one can modify the types and strengths of interactions between molecules. Consequently, the mutual alignment of these molecules and, equally importantly, the host-guest interactions may be controlled.

In the present study, the effects of thiol substitution of aromatic fragments present in trianglimine on the formation of macrocyclic compounds, both symmetric and asymmetric, have been examined. In these compounds conformationally labile arms were attached to the conformationally rigid backbone of the macrocycle. This design was intended to allow the molecules of the macrocycle to conformationally match each other, while matching the shape of the molecule to that of the potential guest. In order to demonstrate the mode of intermolecular interactions in which macrocycles might be involved, diimines, which constitute the equivalent of the “side” of a given macrocycle, have been also studied. The experimental, solid state studies were complemented by quantum mechanical calculations. By combining empirical data with computational models, studies aimed to understand the factors influencing the self-assembly and functional properties of these macrocyclic systems.

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# Enhanced Catalytic Performance of Cucurbit[7]uril-Gold Nanoparticle Assemblies

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The catalytic potential of combining macrocycles and metal nanoparticles remains largely unexplored despite their well-established use[1]. In this study, we introduce a supramolecular system that merges cucurbit[7]uril (CB[7]) with gold nanoparticles (AuNPs). We demonstrate that CB[7] non-covalently adsorbs within an organic monolayer on the AuNP surface, even though the former possesses highly electronegative rims and the latter is polyanion. This supramolecular ensemble exhibits exceptional catalytic efficiency, markedly accelerating a model condensation reaction beyond the capabilities of individual CB[7] and AuNPs. Our findings highlight the synergistic effects of this new system, representing a significant advancement in the development of enzyme-like catalysts.

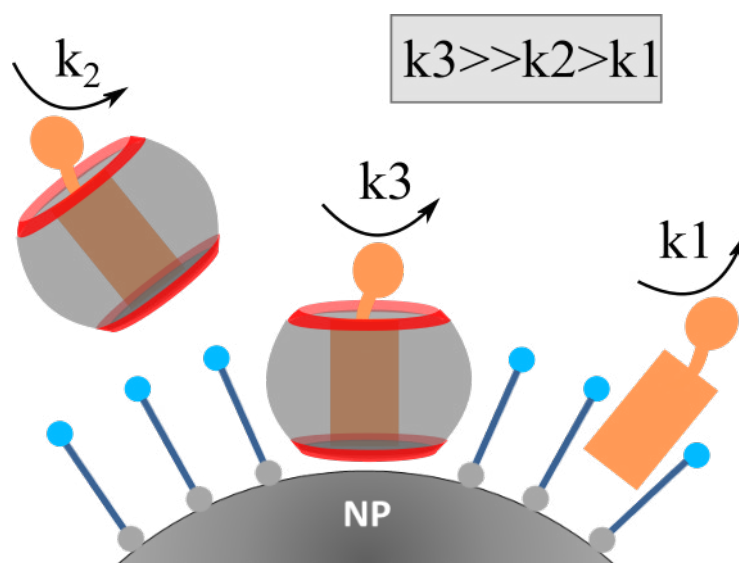


Figure 1: Supramolecular ensemble

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# Chirality Of Flexible Triphenylamine Propellers Ruled By Chiral Substituent In Solution And In Solid Phase

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The triphenylamine molecule exists as an equimolar mixture of two interconverting enantiomeric propellers. In this behavior, it resembles the previously studied trityl group [1,2]. Both groups are sensitive to their surroundings and can adopt their chirality in response to near-in-space chiral substituents. Chirality transfer can be observed in both the crystal phase and in solution. In the latter case, it can be examined by measuring circular dichroism spectra. The mechanism of this action is based on steric interaction between a chiral, optically active inductor molecule and a conformationally flexible reporter molecule.

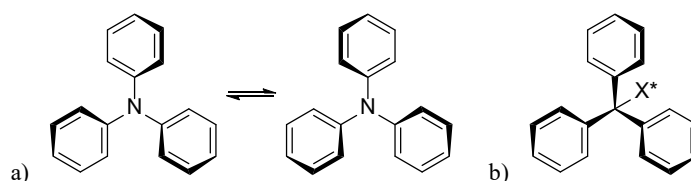


Figure 1: (a) Enantiomerization of  $C_3$ -symmetry triphenylamine propeller (b) triphenylmethyl propeller.

In this study, we demonstrate the transfer of chirality from a chiral amine to two triphenylamine moieties. A convenient platform for linking these two elements is the terephthalaldehyde molecule [3,4]. The properties of the terephthalaldehyde-based imines have been investigated in both solution (CD) and the solid state (X-ray). In the case of the presented molecules, the transfer of chirality from the chiral secondary amine to the triphenylamine group (linked in the *ortho*, *para* and *meta* positions) resulted in the generation of induced Cotton exciton-type effects in the ultraviolet-visible absorption region. The observed magnitude of Cotton effects depends on the magnitude of steric interactions. However, in solution, the molecules under study exist as a mixture of several conformers with a small energy difference, whereas in the crystal only one of them is observed.

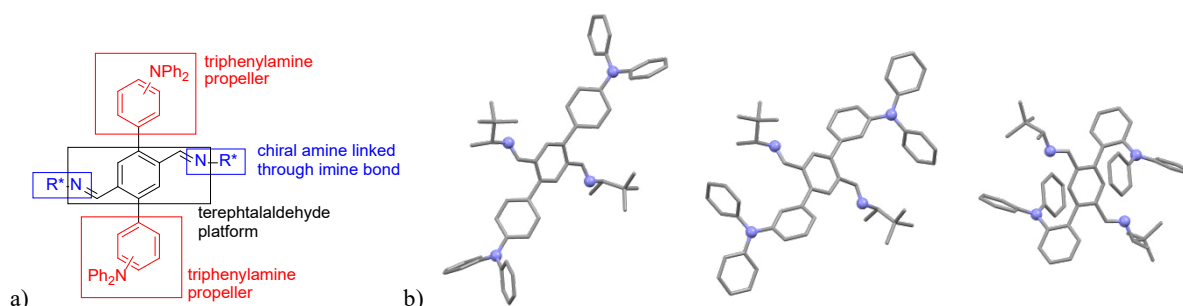


Figure 2: (a) Design of triphenylamine derivatives (b) Molecular structures of *p*-, *m*- and *o*-triphenylamine derivatives.

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# Supramolecularly Assembled Metal-Free Negative Linear Compressibility Material

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Negative linear compressibility (NLC) is a rare behavior of crystals, that is associated with expansion of the crystal along one principal axis in response to compression [1]. NLC materials can find application as optical sensors or telecommunication systems that are required to function under high pressure [2]. So far, the most significant NLC effects were reported for framework materials [1]. Unfortunately, these cases pose several disadvantages: (i) expensive and/or environmentally unfriendly synthesis [3,4]; (ii) compressibility restricted by metal hinges [5], (iii) sensitivity to small molecules that can be adsorbed in pores [4]). Herein we introduce an alternative to metal-containing NLC materials: the cocrystal of 1,2-bis(4-pyridyl)ethane and fumaric acid (ETYFUM) [6].

In crystal of ETYFUM, molecules of 1,2-bis(4-pyridyl)ethane (ETY) and fumaric acid (FUM) are supramolecularly assembled via  $\text{OH}\cdots\text{N}$  hydrogen bonds into, conformationally rigid chains. The chains are then aggregated by  $\text{CH}\cdots\text{O}$  interactions to form a wine rack (Figure 1), a motif widely associated with NLC.

We investigated crystals of ETYFUM up to 3.6 GPa using X-ray diffraction techniques. It has been revealed it exhibits NLC of significant median compressibility and compressibility capacity [1], which is exceptional for a purely organic material. Additionally, ETYFUM can be synthesized in environmentally-friendly manner using solvent-assisted ball milling.

ETYFUM exemplifies how combining conformationally rigid cofomers and supramolecular approach metal-free NLC materials can be synthesized.

The funding from National Science Centre, Poland (grant No. UMO-2020/39/D/ST4/00260) is kindly acknowledged.

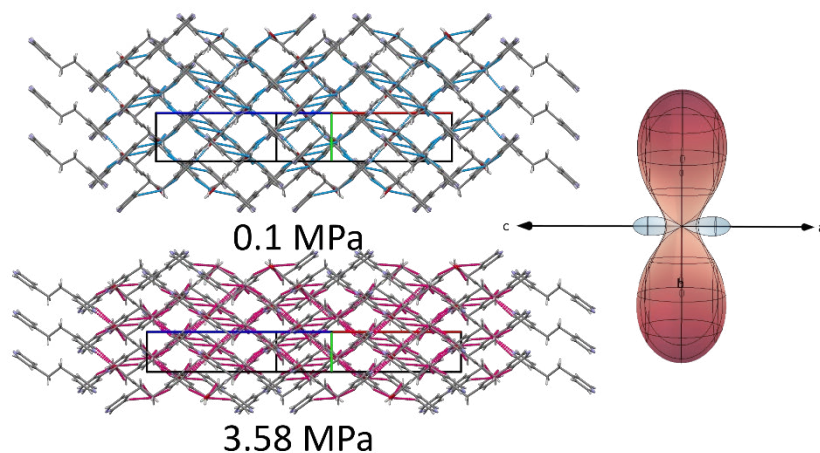


Figure 1: Fragment of a crystal structure of ETYFUM at 0.1 MPa (blue) and 3.58 GPa (pink), as well as indicatrix plot representing compressibility tensors (NLC marked in blue, PLC in red).

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# Dipyromethene and azadipyromethene complexes as a new approach in photodynamic therapies

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In the present era, the objective of researchers and oncologists alike is the establishment of a comprehensive framework for the eradication of cancer, with a concomitant reduction in the toxicity of the treatment and an improvement in the quality of life of patients. The most promising and non-invasive method for treating cancer is photodynamic therapy (PDT). PDT induces tumour cell necrosis and/or apoptosis by producing reactive oxygen species (ROS) through the activation of a photosensitizer (PS), which accumulates specifically in the tumour (Fig. 1) [1-3].

This work presents an overview of our recent findings regarding the synthesis of potential photosensitizers, such as dipyromethene and azadipyromethene complexes with d-block metal ions that possess bromine substituents in their structure. The designed compounds, because of their structure, exhibit the desired spectroscopic, electrochemical, and photochemical properties, which make them suitable for application in PDT as new photosensitizers.

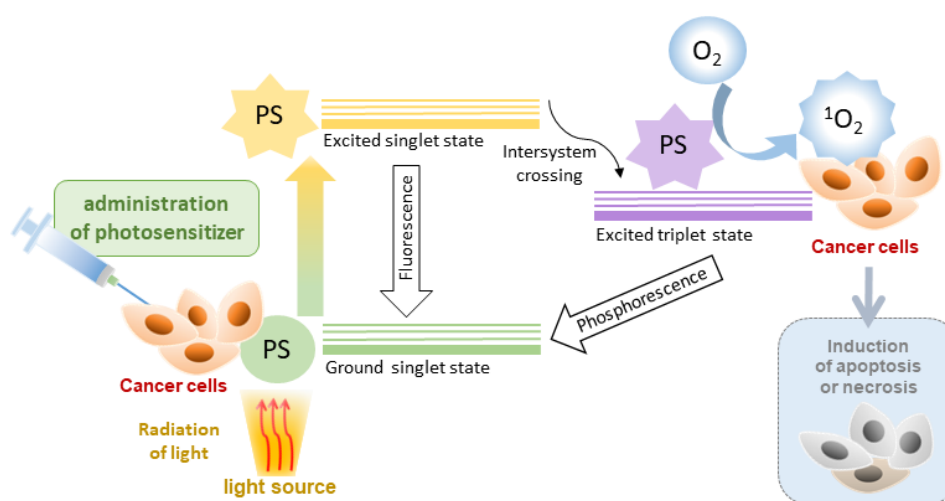


Figure 1: Simplified mechanism of PDT

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# Crystal Engineering of Lanthanide(III) Supramolecular Systems

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The coordination chemistry of lanthanide ions is constantly focusing attention due to their ability to form a variety of supramolecular compounds. The formation of structurally different lanthanide ion-based assemblies can be triggered by ligand molecules, donor atoms, lanthanide contraction phenomena, preference for a specific coordination number to form stable metal complexes, influence of the reaction conditions used, or solvent/anion- dependent coordination environment. [1-4] The number of important factors influencing the diversity of coordination modes around Ln(III) center in these supramolecular systems make it difficult to predict the arrangement of the final supramolecular architectures, therefore the synthesis of new lanthanide-based molecular complexes remains important, especially in the search for factors influencing self-organization processes and the determination of structure-dependent properties.

In the present study, we have investigated the complexation reactions of the N<sub>3</sub>-tridentate Schiff-base ligand L with a series of lanthanide(III) salts with the aim to characterize the structural dependencies and examine the influence of counterions, reaction conditions, metal ions and solvent molecules on the formed lanthanide(III) complexes (Figure 1).

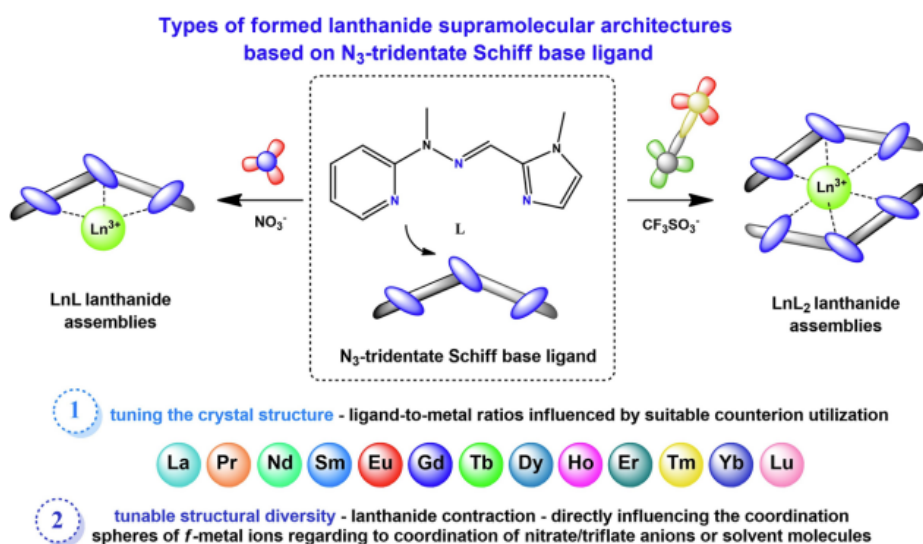


Figure 1: The coordination behavior of the N<sub>3</sub>-tridentate Schiff-base ligand L with various lanthanide(III) salts influences the formation of supramolecular architectures. [5]

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# Mechanochemistry as an effective method for the synthesis of multicomponent systems containing praziquantel

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Praziquantel (PZQ, Fig. 1), developed by Bayer AG and Merck KgaA, is used as a potent antiparasitic agent for parasitic diseases caused by most flukes and tapeworms. It has been included in the WHO Model List of Essential Drugs. [1] Praziquantel is classified as a Biopharmaceutics Classification System (BCS) class II drug [2], due to its low solubility in aqueous media ( $0.31 \pm 0.01$  mg/mL in water at 25°C) [3] and high permeability (logP value of 2.3) [4]. Several strategies to enhance the solubility and dissolution profile of PZQ, are employed, including the screening of polymorphs [1,5–7], solvates [8], and cocrystals with appropriate coformers [1,9–11]. Cocrystals are defined as single-phase solid materials composed of two or more different molecular components in a stoichiometric ratio, which are also solids under neutral conditions [12]. Due to the absence of ionizable groups in the PZQ molecule, salt formation is not considered. Coformers previously utilized for PZQ cocrystallization include benzoic acid derivatives [10,13], aliphatic dicarboxylic acids [1,14] and flavonols [9].

A few novel praziquantel multicomponent systems with chosen carboxylic acids as coformers were synthesized by liquid-assisted grinding using a Retsch MM400-mixer mill. The obtained solids (cocrystals and cocrystal solvates) were analyzed by X-ray diffraction. Coformers such as 3-hydroxybenzoic acid (PZQ·3HBA 1:1), pyromellitic acid (PZQ·BTC 2:1), trimesic acid (PZQ·TRI·H<sub>2</sub>O 1:2:2, PZQ·TRI·MeOH 1:1:1), or 5-hydroxyisophthalic acid (PZQ·5HIP·MeCN 1:4:2, PZQ·5HIP·MeOH 1:4:1) were used [15].

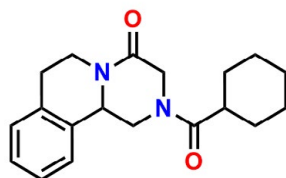


Figure 1: Structure of praziquantel.

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# Unlocking The Potential Of Pyridyl- $\beta$ -diketonate Ligands For Constructing Functional Coordination Nanostructures With Applications In Catalysis

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Ambidentate pyridyl- $\beta$ -diketonate ligands are a fascinating class of organic species commonly employed as building block in coordination and metallocupramolecular chemistry. Such units possess the unique ability to bind metal-ion centers in multiple ways through various combinations of donor atoms. The distinct coordination sites, namely anionic  $\beta$ -diketonate and neutral pyridine, render them versatile donors for a wide range of metal cations, encompassing both hard and soft acids according to the HSAB theory. Primarily, they act as  $O,O'$ -chelates or simple  $N$ -donors through the pyridine ring, although alternative coordination modes are achievable. Their structural diversity has led to numerous applications in the construction of intricate coordination assemblies, including complex compounds, macrocycles, metallocages, multimetallic polymers, and metal-organic frameworks (MOFs), showcasing significant potential across various fields. Here, their utilization as key constituents in the generation of efficient catalytic systems will be demonstrated across a wide range of reactions, including cross-couplings, reductions, substitutions, and hydroadditions.[1-4]

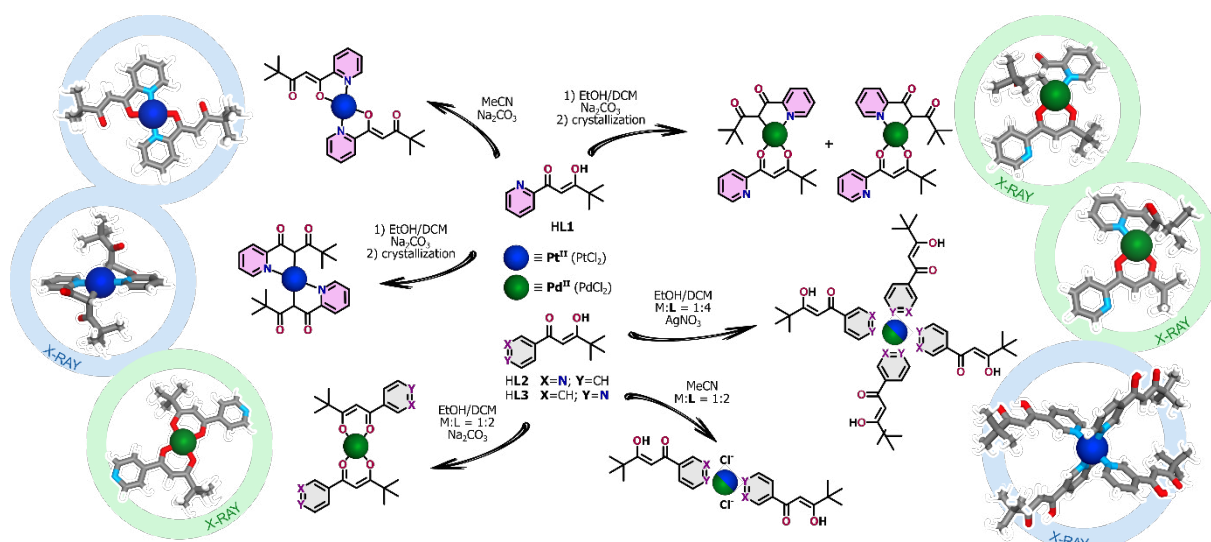


Figure 1: Different coordination variants within Pd<sup>II</sup> and Pt<sup>II</sup> complexes depending on  $N$ -atom position and reaction conditions.

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# Supramolecular Polymers Based on Biphenyldiimides – Side-chain Influence on the Thermodynamics of the Self-assembly Process

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One kind of dynamic supramolecular aggregates are hydrogen-bonded polymers, whose self-assembly may be readily manipulated by minor internal or external stimuli. However, rationally creating chiral supramolecules is exceedingly difficult, particularly when flexible components are included [1]. Unrestricted molecule movements and the intrinsic weakness and dynamic nature of the intermolecular connections in these assemblies add complexity that can affect the self-assembly process [2]. In this work the self-assembly process of four chiral biphenyldiimides was studied both in solution and in the solid state. The results show that those compounds spontaneously form non-covalent chain-type supramolecular polymers, as a result of formation of COOH $\cdots$ HOOC hydrogen bridges in non-polar solvents [Fig. 1]. While the aggregates obtained are of similar topology, significant differences in their stability were observed, because of the influence of the amino acid side chains. The aromatic side chains were shown to increase the overall stability of the assembly, by restricting the molecular motions and shielding the COOH $\cdots$ HOOC bridges. On the other hand, the presence of secondary hydrogen bonding sites destabilizes the assembly and disturbs the polymerization process due to preferential formation of intramolecular interactions in diluted solutions. However, in the solid state, the above features seem to have a positive role and an increase in the size of the aggregates is observed. We believe, that the use of conformationally labile building blocks based on biphenyl cores opens up new pathways for the formation of chiral supramolecular polymers, which we will explore in the future.

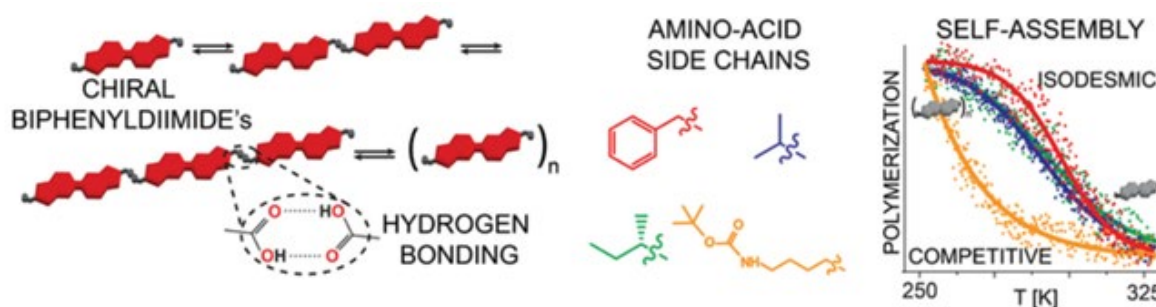


Figure 1: Self-assembly mechanism of amino-acid substituted biphenyldiimides.

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## Guest-Induced Transformation of TMEDA-Based Water-Soluble Coordination Cage

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Metallo-supramolecular cages are a class of structures that self-assemble from metal ions and organic ligands through coordination-driven bonds.[1] The interest in these architectures stems not only from the synthetic challenge of their design, but also from their host-guest chemistry and the potential to bind guest molecules with high affinity and selectivity.[2] Moreover, coordination cages with empty cavities can significantly alter their architecture due to encapsulated guests, temperature or solvents.[3]

In our research we focused on the synthesis and design of tmEDA-based cage. The architecture was acquired using a palladium acceptor and a specially designed tetradentate ligand, enabling the formation of a barrel-type cage. Unlike closed architectures, this type of cage allows for the encapsulation of guests from the open parts at the top and bottom.

Research on the encapsulation properties of the cage revealed that small polycyclic aromatic hydrocarbons, such as phenanthrene, anthracene or pyrene, cause significant changes in the cage structure. Similar to enzymes, the cage adjusts its shape to encapsulate the guests inside. Furthermore, not only do the guests influence the cage structure, but temperature also plays a role. After heating, a mixture of structures was obtained. Additionally, when structures of cages 1 and 2 were heated, they both transformed into the same mixture of structures (Figure 1).

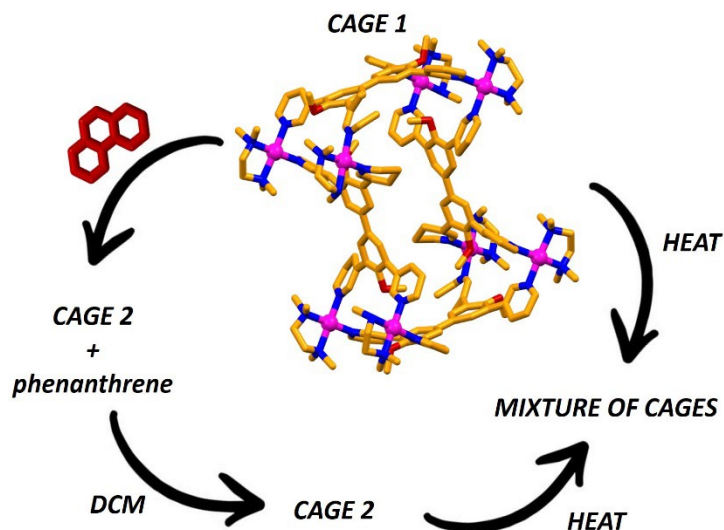


Figure 1: Diagram illustrating the evolution of cage structures

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# Developing Novel Heterometallic Dynamic Cages: Synthesis, Structural Design, and Applications

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Metallo-supramolecular cages are highly promising structures known for their intricate geometries, distinctive physicochemical properties, and versatile functionalities.[1] These cages have been applied across various branches of chemistry, serving as stabilizers for highly reactive compounds [2] and as nanoreactors in catalytic processes.[3]

In this study, we successfully synthesized heterometallic cages (Fig. 1) using ambidentate pyridyl- $\beta$ -diketonate ligands in combination with Al(III), Fe(III), and Pd(II) ions through a hierarchical synthetic approach. The resulting metallo-supramolecular assemblies were thoroughly characterized both in the solid state (XRD) and in solution (NMR, ESI-MS). While cubic and trigonal bipyramidal cages based on ambidentate pyridyl- $\beta$ -diketonates have been previously reported, this work presents the first example of heterometallic cages with a tetrahedral geometry. Notably, these systems exhibit a dynamic equilibrium in solution, shifting between a tetrahedral cage structure and a trigonal bipyramidal form. The large capacity of these cages, coupled with the presence of Pd(II) ions, suggests significant potential for applications in catalysis, gas sorption, and molecular encapsulation. The structural design of these heterometallic cages is intricately influenced by the choice of different building blocks. The use of ambidentate pyridyl- $\beta$ -diketonate ligands in combination with various metal ions—Al(III), Fe(III), and Pd(II)—allows for precise control over the geometry and functionality of the resulting assemblies. Each metal ion contributes distinct coordination preferences and electronic characteristics, enabling the construction of cages with tailored shapes and properties. This strategic selection of building blocks not only facilitates the formation of unique tetrahedral structures but also enables the modulation of the cages' dynamic behavior in solution, where they can toggle between different geometries. Consequently, the diversity in building blocks opens up avenues for designing cages with specific functionalities suited for targeted applications in catalysis, gas sorption, and encapsulation.

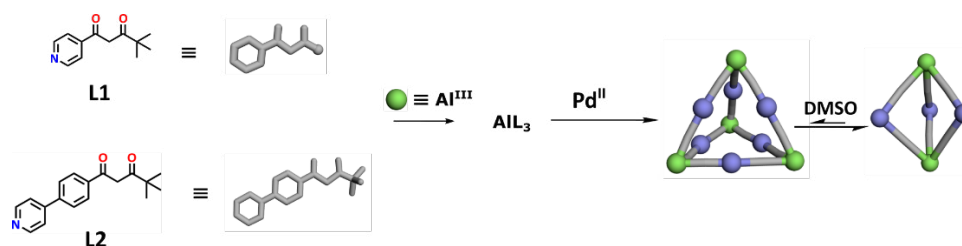


Figure 1: Synthesis of metallo-supramolecular cages.

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# Design and Functionalization of Hydrogen-Bonded Octameric Capsules for Targeted Guest Encapsulation and Separation

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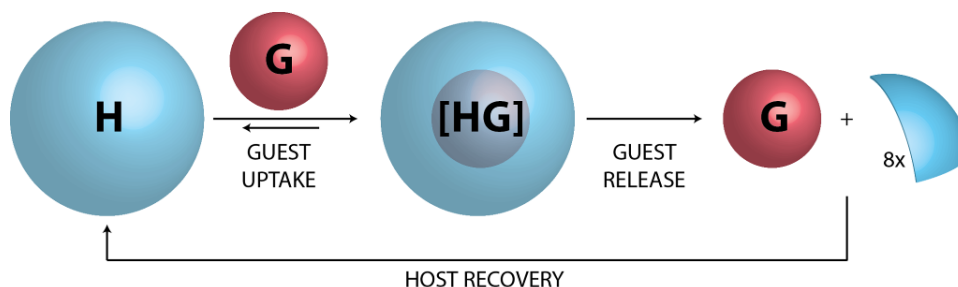
Wiktoria Adamska,<sup>1</sup> Grzegorz Markiewicz,<sup>2</sup> Artur R. Stefankiewicz<sup>1,2</sup>

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Supramolecular chemistry leverages non-covalent interactions, such as hydrogen bonds,  $\pi$ - $\pi$  interactions, and van der Waals forces, to guide molecular self-assembly and recognition processes. Through the strategic application of these weak forces, it is possible to construct complex supramolecular structures from synthetically simple molecules, resulting in systems with tunable functions and properties.<sup>1</sup> Among these structures, self-assembled capsules have garnered significant attention due to their unique ability to encapsulate guest molecules within well-defined internal spaces.

Our research team previously reported the first hydrogen-bonded octameric capsule based on a benzene-1,3,5-tricarboxylic acid (BTA) core, stabilized by 48 cooperative hydrogen bonds.<sup>2</sup> This capsule, featuring a large internal cavity of 1719 Å<sup>3</sup>, demonstrates strong affinity for C<sub>70</sub> and C<sub>60</sub> fullerenes, with a preference for C<sub>70</sub>. In our recent work, we present a synthetic strategy aimed at optimizing the solubility of these octameric capsules, facilitating their use in preparative guest separation and the encapsulation of catalytically active species.



## ACKNOWLEDGEMENTS

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# A Green Approach to Synthesis of 2-Amino Thiophene Derivatives by Using PEG-400: Antioxidant and Anti-cancer Studies

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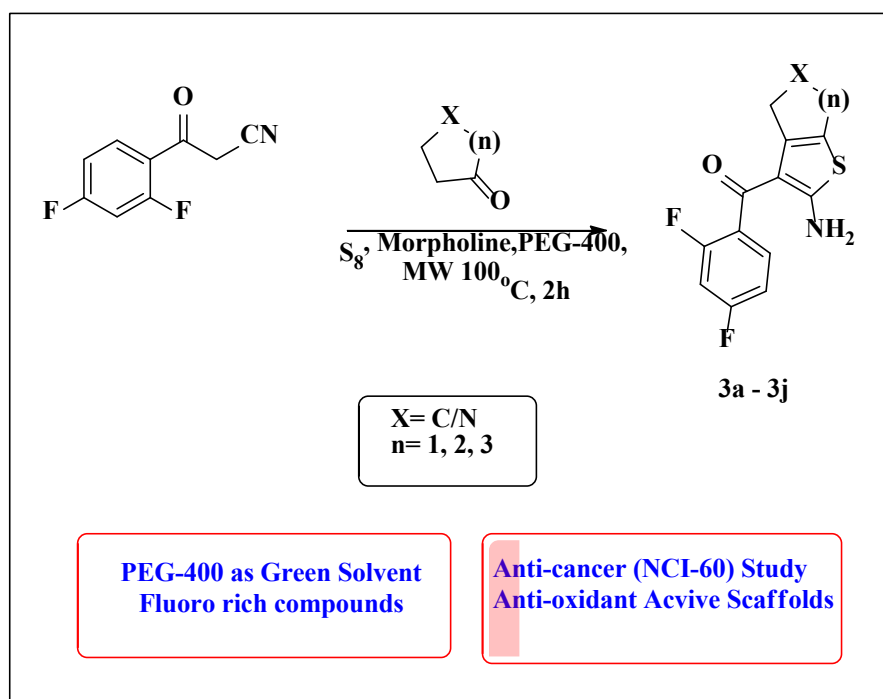
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A green approach, efficient and microwave assisted one pot synthetic procedure has been developed, Series of 2-amino Thiophene derivatives were synthesised by using multicomponent reaction in PEG-400. The reaction was optimized through various conditions and their 2-amino thiophene derivatives are discussed. The synthesized compounds (3a-3j) were characterized by spectroscopic data ( $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, LC-MS) and were evaluated for antioxidant activity by DPPH method against their pharmaceutical market opted standards and anti-cancer activity against NCI-60 cell lines in nine different cancer panels. It was found that the Boc containing N-containing ring substituents (3h & 3i) were found to be most active with negative values (lethality).



Scheme 1: Green approach for the synthesis of 2-amino thiophene framework.

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## Hybrid Coordination Network Family with Metal-dependent Dynamic Behavior

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Hybrid Coordination Networks (HCNs)[1] constitute a subset of metal-organic materials comprised of two types of linker ligand, typically organic linkers and inorganic pillars. HCNs have emerged as modular platforms of porous materials with highly modifiable structures with properties dictated by host-guest binding sites originating from inorganic pillars.[2-4] Herein, we introduce a new family of HCNs based on an N-donor organic linker ligand and the inorganic pillar  $\text{NbOF}_5^{2-}$  (**NbOFFIVE-14-M**, M = Cu, Zn, Ni, Co).

The **NbOFFIVE-14-M** family was synthesized at room temperature in a green solvent mixture of methanol and water, resulting in a primitive cubic (**pcu**) topology network. This family demonstrated isostructural as-synthesized phases with ca. 25 % void space and 1D channels along the *c*-axis. These techniques facilitated the observation of phase transformations from the water-loaded (open) phases of **NbOFFIVE-14-Cu- $\alpha$**  and **NbOFFIVE-14-Zn- $\alpha$**  into narrow-pore phases **NbOFFIVE-14-Cu- $\beta$**  and **NbOFFIVE-14-Zn- $\beta$**  with discrete cavities (closed pores). XRD provided structural insights into the dynamic behavior of the networks in response to changes in temperature and pressure for the **Cu** and **Zn** variants whereas no phase transformations were observed by dehydration of the as-synthesized **Ni** and **Co** variants.  $\text{CO}_2$  sorption revealed different sorption isotherm types: Type-I for rigid **NbOFFIVE-14-Ni** and **NbOFFIVE-14-Co**; stepped isotherms for **NbOFFIVE-14-Cu** and **NbOFFIVE-14-Zn**. *In situ* PXRD measurements conducted at 1 bar  $\text{CO}_2$  revealed the expected phase transformations for the **Cu** and **Zn** variants and validated the rigidity of the **Ni** and **Co** analogs. Additionally, this family demonstrated stepped water sorption isotherms, where flexible **Cu** and **Zn** exhibited a structural transformation, while **Co** and **Ni** displayed a rare induce-fit phenomenon induced by water molecules (Figure 1).

In summary, our results represent the first report of metal-dependent dynamic behavior in hybrid coordination networks. We will present our experimental results, including the sorption studies conducted with hydrocarbon gases and discuss them in the broader context of flexible HUMs.

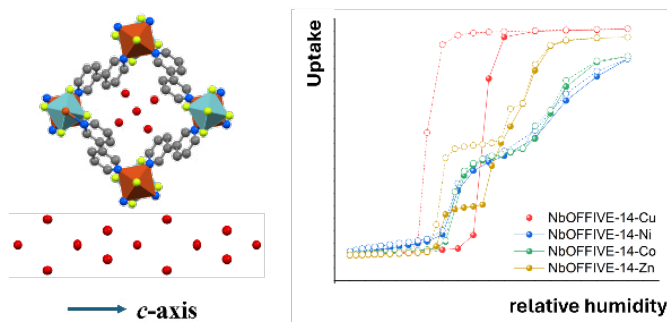


Figure 1: Water-loaded structure with water molecules along *c*-axis (left) and water vapor sorption isotherms of **NbOFFIVE-14-M** family (right).

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