4th Annual UK Porous Materials Conference

UKPorMat 2019

Cardiff University
1st – 2nd July

UKPorMat 2019 Programme

Day 1 – Monday, 1st July 2019

Time	**Event**
09:00 - 09:50	Conference Registration in the Viriamu Jones Gallery, Main Building, Cardiff University
09:50 - 10:00	***Timothy Easun**, Cardiff University* *Welcome and opening remarks*
Session 1	Chair: Timothy Easun
10:00 - 10:40	**Caroline Mellot-Draznieks**, Collège de France *Functionalizing Metal-Organic Frameworks towards photocatalysis and molecular recognition*
10:40 - 11:00	**Miguel Jorge**, University of Strathclyde *Understanding the mechanism of formation of porous silica materials through multi scale modelling*
11:00 - 11:30	*Coffee – VJ Gallery*
Session 2	Chair: Thomas Bennett
11:30 - 11:50	**Dominic Bara**, University of Glasgow *Investigating the Synthesis and Flexibility of Trivalent MOFs*
11:50 - 12:10	**Pu Zhao**, University of Oxford *Structural dynamics of a metal-organic framework induced by CO_2 migration in its non-uniform porous structure*
12:10 - 12:30	**Lauren Macreadie**, Massey University *Hydrocarbon Adsorption within MOFs Containing a Contoured, Aliphatic Pore Environment*
12:30 - 12:50	**Sven Rogge**, Ghent University *Unravelling the Thermodynamic Criteria for Size-Dependent Spontaneous Phase Separation in Soft Porous Crystals*
12:50 - 13:00	***Thomas Bennett**, University of Cambridge* *Message from RSC Porous Materials Interest Group Chair*
13:00 - 14:00	*Lunch and RSC Porous Materials Interest Group Annual Meeting*
Session 3	Chair: Andrea Laybourn
14:00 - 14:40	**Xiaodong Zou**, Stockholm University *Ab Initio Structure Determination and Phase Analysis of Porous Materials by 3D Electron Diffraction*
14:40 - 15:00	**Ronny Pini**, Imperial College London *Digital adsorption: 3D imaging of adsorption equilibria and dynamics in technical microporous solids*
15:00 - 15:20	**Francesca Firth**, University of Cambridge *Using Defect Engineering in Synthesis to create New Phases of UiO Family MOFs*
15:20 - 15:30	**Sheena Hindocha**, Knowledge Transfer Network *Introduction to KTN and the UK innovation support landscape*
15:30 - 16:00	*Coffee*
Session 4	Chair: Tina Düren
16:00 - 16:20	**Qilei Song**, Imperial College London *Microporous Polymer Membranes for Energy Conversion and Storage*
16:20 - 16:40	**Alex James**, University of Sheffield *Synthesis of solvent dispersible porous polymeric particles via RAFT-mediated PISA*
16:40 - 17:20	**Neil McKeown**, University of Edinburgh *Porous Materials without a Framework*
17:30 - 19:00	*Poster Session – VJ Gallery*
19:30 -	**Conference Dinner** ZERODEGREES, 27 Westgate Street Cardiff, CF10 1DD (close to Principality stadium and Central train station)

Day 2 – Tuesday, 2nd July 2018

Time	**Event**
Session 5	Chair: Darren Bradshaw
09:00 - 09:40	****Sponsored by *Chemical Science***** **Paolo Falcaro**, Graz University of Technology *Porous Biocomposites Prepared via Biomimetic Mineralization of MOFs*
09:40 - 10:00	**Ifty Ahmed**, University of Nottingham *Manufacturing Highly Porous Phosphate Glass Microspheres for Bone Regenerative Orthobiologic Applications*
10:00 - 10:20	**Shichun Li**, University of Cambridge *Chemical Stability and Thermo-Mechanical Property of Bulk Metal-Organic Framework Glasses and Crystal-Glass Composites*
10:20 - 10:50	*Coffee – VJ Gallery*
Session 6	Chair: Ross Forgan
10:50 - 11:30	****Sponsored by *Communications Chemistry***** **Camille Petit**, Imperial College London *Approaches to Materials Development to Address Separation Challenges*
11:30 - 11:50	**Shane Telfer**, Massey University *Gas Separations using Sustainable and Robust Metal-Organic Frameworks*
11:50 - 12:10	**Lydia Briggs**, University of Manchester *A bimetallic Metal organic framework balancing the requirements between enhanced gas uptake and maintaining selectivity*
12:10 - 12:30	**Hamish Yeung**, University of Oxford *Control of Metal–Organic Framework Crystallization by Metastable Intermediate Pre-equilibrium Species*
12:30 - 13:30	*Lunch – VJ Gallery*
Session 7	Chair: Thomas Bennett
13:30 - 13:50	**Rachel Kearsey**, University of Liverpool *Accelerating the discovery of Type II porous liquids using high-throughput automation*
13:50 - 14:10	**Jonathan Foster**, University of Sheffield *Programmable Two-dimensional Materials for Sensing, Catalysis and Solar Cells*
14:10 - 14:30	**Shaojun Xu**, University of Manchester *Sustaining metal-organic frameworks for water-gas shift catalysis by non-thermal plasma*
14:30 - 14:50	**Alex Forse**, U. C. Berkeley *NMR Studies of Adsorption and Diffusion in New Materials for CO2 Capture*
14:50 - 15:20	*Coffee – VJ Gallery*
Session 8	Chair: Andrea Laybourn
15:20 - 15:40	**Jenny Vitillo**, University of Insubria *Single Fe(II) sites in MIL-type metal organic frameworks for the oxidation of light alkanes to alcohols*
15:40 - 16:00	**Alex Katsoulidis**, University of Liverpool *Chemical control of structure and guest uptake by a conformationally mobile porous material*
16:00 - 16:40	**Lee Brammer**, University of Sheffield *MOF Flexibility and Guest Response*
16:40 - 16:50	*Poster Prizes and Close*

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Invited Talks

Functionalizing Metal-Organic Frameworks towards photocatalysis and molecular recognition

Caroline Mellot-Draznieks

Laboratoire de Chimie des Processus Biologiques, UMR 8229 CNRS, Sorbonne Université, Collège de France, 11 Place Marceline Berthelot, 75231 Paris Cedex 05, France

Metal-Organic Frameworks (MOFs) are attracting intense research efforts in the scientific community with the demonstration of high value-added applications in heterogeneous catalysis or sensing. Their hierarchical porous structures and confined pockets allow protection of catalytic centres and enhanced substrate specificity whilst maintaining efficient diffusion. In the very active context of artificial photosynthesis, I will illustrate through specific examples how the close tandem of computational approaches and synthesis has allowed us to explore the functionalization of MOFs towards photocatalysis and molecular recognition: i) The practical reduction of CO_2 requires mediating the multi-electron and multi-proton processes while achieving desired product selectivity in a cost effective manner. The incorporation of molecular catalysts into MOFs offers the possibility to maintain the advantageous properties of homogeneous catalysis while moving towards practical system designs afforded by heterogeneous catalysis. Moving towards photocatalysis, I will present recent research efforts towards the control of the optical response of MOFs through the choice of its organic linkers and of its catalytic activity through its functionalization with active molecular catalysts. Alternatively, the immobilization of a molecular catalyst into a photosensitizing MOF allows another strategy for turning a MOF into a photocatalytic composite, illustrated here for the photo-assisted reduction of water in a POM@MOF noble-metal free photosystem. ii) Tremendous efforts have been made to introduce chirality into porous solids to allow chiral recognition thanks to the conformational adjustment between the substrate and the designed chiral adsorption/catalytic site. In this context, I will illustrate our strategy for studying MOFs functionalized with peptides, highlighting their potential for chiral recognition and asymmetric catalysis through in-depth atomic level investigations.

Ab Initio Structure Determination and Phase Analysis of Porous Materials by 3D Electron Diffraction

Xiaodong Zou
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Porous materials are often synthesised in polycrystalline and multiphasic forms, which are too small or too complicated for X-ray diffraction. Electron crystallography has a unique advantage for studying such materials[1-5]. Here I will present the latest development of 3D electron diffraction techniques for fast and high-throughput data collection by continuous rotation electron diffraction (cRED).[4] Today a complete cRED data can be collected in less than 5 min, and the crystal structures can be solved on a routine base within a few hours. I will show the quality of structure determination from cRED data using several examples of novel zeolites and MOFs.[4-5]

To further speed up and automate data collection, we have developed serial electron diffraction (SerialED), which can automatically screen > 3500 particles/hour and collect the ED patterns on a standard TEM![6] This provides new possibilities for studying very beam sensitive crystals. We also combined data collection by SerialED with cRED and developed SerialRED to perform fully automated data collection and data analysis for 3D electron diffraction.[7] The large number of particles makes it possible for phase analysis, and for detection of minor impurity phases that may not be detectable even by X-ray diffraction (Fig. 1). I will show their impacts in structure determination and phase analysis on novel zeolites and MOFs.

The rapid development of new electron diffraction techniques offers fast and accurate structure determination of zeolites and MOFs. We expect that the SerialRED in combination with hierarchical cluster analysis will make 3D ED a promising technique for high throughput phase analysis and *ab initio* structure determination.

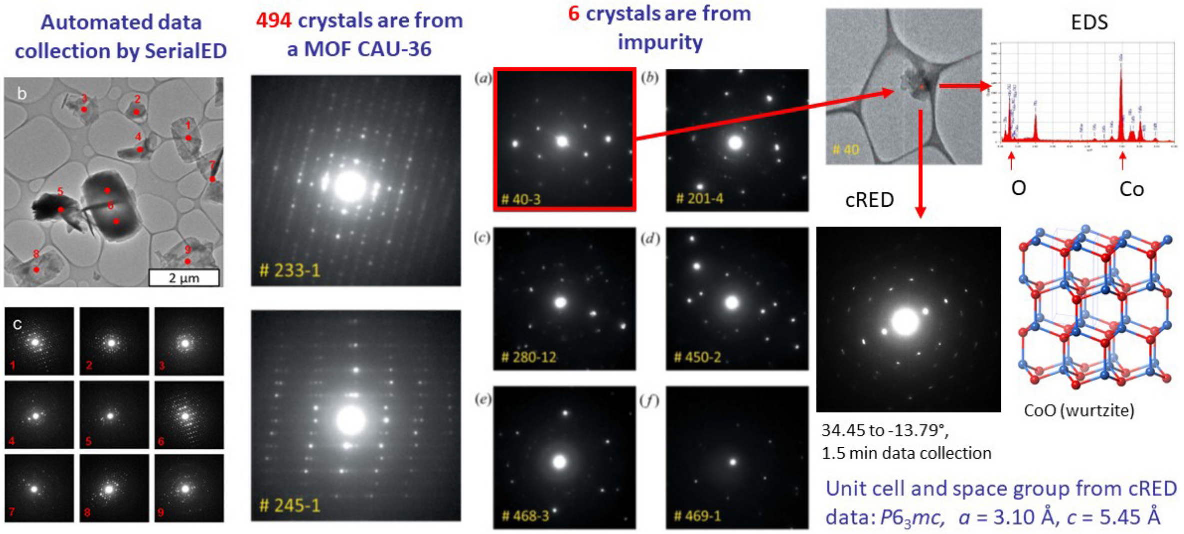

Fig. 1 High throughput 3D electron diffraction and its application on *ab initio* structure determination and phase analysis. The method can screen hundreds of crystals/hour, and perform cRED data collection and analysis. Minor phases can be detected and the structure can be determined. An example on a Co-CAU-36 sample is shown.[5,7]

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Porous materials without a framework

N. B. McKeown

School of Chemistry, University of Edinburgh, UK, neil.mckeown@ed.ac.uk

Conventional nanoporous materials are stabilized by a framework of covalent bonds and so are not soluble or solution processable. Instead, we aim to make nanoporous materials from discrete molecules or macromolecules. For example, Polymers of Intrinsic Microporosity (PIMs) are non-network materials that generate porosity from their rigid and contorted macromolecular chains. The combination of microporosity, chain rigidity and solution processability facilitates applications of PIMs in sensors, for which a commercial device now exists, and as membranes for separations. The emerging structure-property relationships for PIMs will be discussed including the design concept of using 2D chains to enhance intrinsic microporosity to achieve ultrapermeable polymers for selective gas separations.[1]

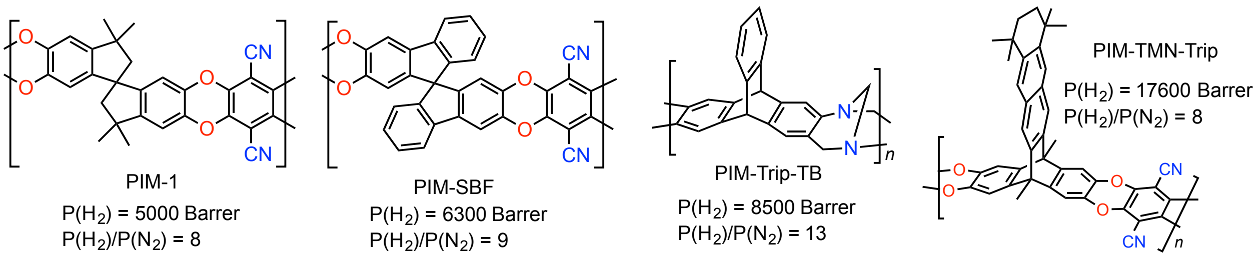

Figure 1. The evolution of gas permeability in PIMs.

In addition, we are interested in porous molecular crystals composed of discrete molecules, between which there are only non-covalent interactions. We have demonstrated that the macrocycle 2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propyl-phenoxy)-phthalocyanine, even with a large diversity of central metal cations and attached ligands, dependably forms molecular crystals containing massive solvent-filled interconnected voids of >10 nm^3 volume. Strategies to stabilize these porous molecular crystals using molecular wall-ties, including fullerenes,[2] will be discussed together with their potential applications as magnetic materials and catalysts.

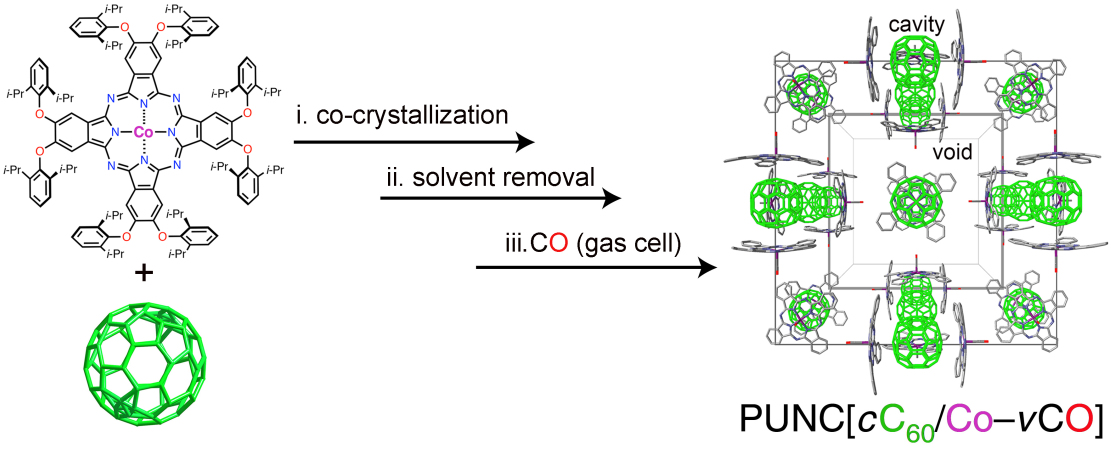

Figure 2. The crystallisation and reactivity of a fullerene-stabilised Phthalocyanine Nanoporous Unsolvated Crystal (PUNC).

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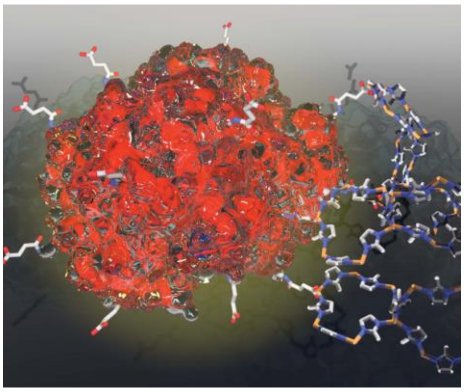
Porous Biocomposites Prepared via Biomimetic Mineralization of MOFs

Paolo Falcaro[1,2], Christian Doonan[2]

[1]Graz University of Technology, Austria, paolo.falcaro@tugraz.at, [2]The University of Adelaide, Australia.



A recent development in Metal-organic Framework (MOF) research is the preparation of porous biocomposites.[1,2] Biomolecules can be integrated with MOFs through infiltration, grafting and encapsulation.[2] Our group is working on novel encapsulation protocols. In this presentation, we detail progress which has been made in encapsulation technologies.[3,4,5,6,7] Then, we will discuss our recent progress using the biomimetic mineralization protocol for the preparation of biocomposites based on biomacromolecules (e.g. proteins, enzymes, carbohydrates) using Zeolitic Imidazolate Framework-8 (ZIF-8) and its related polymorphs.[6,8,9,10]
The protective and bioactive properties of such porous biocomposites will be illustrated and the synergy between biotherapeutics, biocatalysts and MOFs will be explored.[11,12] Then, opportunities towards the extension of MOF biomineralization in complex biological systems (e.g. yeast cells) will be highlighted.[13,14]
Finally, we will focus on the current limitations of these systems as possible challenges for the future progress of MOFs for biotechnology and biomedicine.

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Approaches to materials development to address separation challenges

Camille Petit

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Using examples from our recent work, I will present two approaches used by our group to develop porous materials to be applied in a variety of separation applications. The first one is a curiosity-driven approach, which we employ either for new separation challenges for which benchmark and/or performance targets are ill-defined or in the context of emerging adsorbent materials. I will illustrate this aspect through our recent findings on porous boron nitride. Our second approach, based on molecular engineering, accelerates materials development for well-defined applications. Such approach links molecular modelling, experiments and process modelling to quickly identify the best adsorbent(s) for a given separation. In this context, I will present our work on the use of metal organic frameworks for industrially relevant gas separations.

Title: MOF Flexibility and Guest Response

L. Brammer[1]

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Dynamic behaviour in MOFs is one of the attributes that sets them apart from other crystalline porous materials.[1,2] This can arise through various means including flexibility of the linker ligands,[3,4] bond-breaking or formation,[5-7] reorganisation of interpenetrated networks,[8] and deformations in metal-ligand coordination as found in so-called "breathing" MOFs.[9] These dynamic behaviours can affect adsorption properties, which are at the heart of most applications of MOFs.

Recently we have reported breathing behaviour in a diamondoid MOF, $(Me_2NH_2)[In(BDC\text{-}NH_2)_2]$ (SHF-61),[10] which is unusual in a number of respects: (i) activation from different solvents leads to different activated forms; (ii) these different activated forms exhibit different gas adsorption behaviour; (iii) pore-solvent content can be used to switch the MOF from non-gated to gated adsorption of CO_2 gas; (iv) dynamic behaviour can be monitored by PXRD or by single-crystal X-ray diffraction.

We have also begun to explore post-synthetic modification as a means of further tuning the dynamic response of the MOF.

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Oral presentations

Day 1

Understanding the Mechanism of Formation of Porous Silica Materials through Multi-scale Modelling

Miguel Jorge[1], **Germán Pérez-Sánchez**[2], **Szu-Chia Chien**[3], **Alessia Centi**[1], **Joseph. R. H. Manning**[4], **Vibha Srivastava**[4], **Sandra van Meurs**[4], **Siddharth V. Patwardhan**[4], **José R. B. Gomes**[2], **Scott M. Auerbach**[3], **Peter A. Monson**[3]

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Porous silica materials play a crucial role in a myriad of adsorption applications, but despite their success, relatively little is known about how they self-assemble from aqueous solution[1]. Yet understanding the synthesis mechanisms of porous materials is crucial to enhance our ability to control and design their properties for adsorption processes. The synthesis process relies on a delicate interplay of chemical reactions, self-assembly and phase equilibrium, taking place over a wide range of time and length scales, which makes it highly challenging to probe experimentally. This talk will report recent advances by our group in the development of a new multi-scale modelling approach to describe the synthesis of nanoporous silica materials, that bridges time and length scales from the quantum to the coarse-grained levels.

Our simulations of the synthesis of MCM-41 have revealed unprecedented details of the molecular-level interactions that control the process. The addition of silica to an aqueous alkylammonium surfactant solution initially gives rise to micelle size increase and micelle fusion, promoting a shape transition from spherical to rod-like aggregates. The strong adsorption of silicates at the micelle surface facilitates silica polymerisation. Once silica oligomers are present in the system, they act as multi-dentate binders inducing the formation of a hexagonally-ordered mesophase[2]. It is this mesophase that ultimately determines the pore network structure of MCM-41, upon further condensation and template removal. Our multi-scale model correctly describes experimental observations on this system, and makes useful predictions for future design of these materials.

We have extended our model to describe the synthesis of bioinspired silica. Inspired by the natural process of biosilicification, this strategy makes use of polyamine templates to produce porous silica materials under much more environmentally friendly conditions (ambient temperature and pressure, near-neutral pH) than currently employed in industry[3]. When applied to this class of materials, our results conclusively demonstrate that the tacitly accepted "neutral templating route" is not viable under the experimental synthesis conditions. Instead, the mechanism hinges on charge-matching interactions between precursor molecules[4,5]. Recent experimental data supports our interpretation of the synthesis mechanism, paving the way for computational design of this exciting new class of materials.

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Investigating the Synthesis and Flexibility of Trivalent MOFs

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Flexible metal-organic frameworks (MOFs) are materials that exhibit structural changes upon external stimuli and have potential applications in separation processes and biomedical applications, among others.[1] MOFs containing trivalent metals (such as Fe^{3+}, Cr^{3+}, Sc^{3+}, etc.) and linear dicarboxylates tend to adopt structures with MIL-88 (MIL stands for Materiaux Institut Lavoisier) topology, whereby six connected $[M^{3+}{}_3O(RCO_2)_6(H_2O)_2X]$ (X = monoanion) SBUs are linked to form hexagonal networks.[2] These structures can be highly flexible and undergo transformations upon the adsorption of solvent molecules, leading to large changes in their unit cell parameters.[3] Fe-MOFs have attracted interest due to the endogenous nature iron and low relative cost, making them especially suited for biomedical applications. Most of these structures have been solved by a combination of powder X-ray diffraction (PXRD) refinements and computation modelling, which is a time-consuming process requiring high quality PXRD data and assumptions about the metal-containing clusters. Therefore, the growth of large single crystals is preferable in order to enable structure solution by single-crystal X-ray diffraction. The chromium analogues have also been identified as highly desirable for industrial applications due to their chemical stability, a consequence of their slow linker exchange rates,[4] however this in turn makes synthesis more challenging and thus relatively few Cr-MOFs have been reported to date.

Herein we present enhanced synthetic protocols for synthesising both Fe- and Cr-MOFs using coordination modulation, the addition of monotopic ligands which compete with the ditopic linkers, and by varying the metal precursor. A range of novel Cr-MOFs have been obtained as highly crystalline powders with uniform crystal size, enabling their stability, gas uptake, and flexibility to be studied. These synthetic protocols, which most importantly avoid the use of HF, are a significant step in the development of chromium frameworks. Additionally, we present a study of the swelling properties of a novel Fe-MOF using single-crystal diffraction, whereby the unit cell increases by up to 150% depending on the nature of the guest solvent in the structure and this can be correlated to the aspect ratios of the crystals when observed by optical microscopy.

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Structural dynamics of a metal-organic framework induced by CO_2 migration in its non-uniform porous structure

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Stimuli-responsive behaviors of flexible metal-organic frameworks (MOFs) make these materials promising in a wide variety of applications such as gas separation[1], drug delivery[2], and molecular sensing[3]. Considerable efforts have been made over the last decade to understand the structural changes of flexible MOFs in response to external stimuli. Uniform pore deformation has been used as the general description. However, recent advances in synthesizing MOFs with non-uniform porous structures, i.e. with multiple types of pores which vary in size, shape, and environment, challenge the adequacy of this description[4]. Here, we demonstrate that the CO_2-adsorption-stimulated structural change of a flexible MOF, ZIF-7, is induced by CO_2 migration in its non-uniform porous structure rather than by the proactive opening of one type of its guest-hosting pores. Structural dynamics induced by guest migration in non-uniform porous structures is rare among the enormous number of MOFs discovered and detailed characterization is very limited in the literature. The concept presented in this work[5] provides new insights into MOF flexibility.

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Hydrocarbon Adsorption within MOFs Containing a Contoured, Aliphatic Pore Environment

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Aromatic ligands, with polycarboxylate or multitopic functionalities, govern the synthetic chemists' toolbox when forming metal-organic frameworks (MOFs) due to their rigid nature, commercial availability and the numerous variable coordination modes exhibited by these functionalities. Conversely, despite their extensive success in creating a rich foundation for the development of new and archetypal MOFs, restriction to solely phenyl interactions within adsorbates represents a possible limitation and reduced variation in the pore chemical environment of the materials.[1] Separation of hydrocarbons using low energy processes is a key area from an industrial standpoint where the strategic design of the MOF pore chemical environment can avoid energy expensive separations based on changes of phase.[2]

Cubane-1,4-dicarboxylic acid (1,4-H_2cdc) is a rigid, aliphatic dicarboxylate linker that contains eight carbon atoms arranged in a near-perfect cubic arrangement. Of notable interest is the structural similarity between 1,4-H_2cdc and benzene-1,4-dicarboxylic acid (1,4-H_2bdc) – providing significant scope for the employment of the cubane molecule in MOF synthesis.[3] Through the incorporation of 1,4-H_2cdc into prominent MOF architectures, we demonstrate the striking effects a contoured, aliphatic pore environment has on gas and hydrocarbon adsorption, compared with its aromatic counterpart, and explore the potential separation capacities these frameworks may pose.[1] Here we present a single-component ($[Zn_4O(1,4\text{-cdc})_3]_n$, CUB-5) and a multi-component ($Zn_4O(\text{hmtt})_{4/3}(\text{bpdc})_{1/2}(\text{cdc})_{1/2}]_n$, CUB-30) MOF material which contain 1,4-H_2cdc as an aliphatic linker. The stark difference in vapour adsorption between the topologically analogous frameworks highlights the importance of pore shape during the adsorption process.[1] Interestingly, both MOFs show promise for tuneable, selective hydrocarbon adsorption at low pressures, where CUB-5 shows a propensity for benzene adsorption at low partial pressures, providing a promising landscape for future investigations into benzene separations from an industrial standpoint.

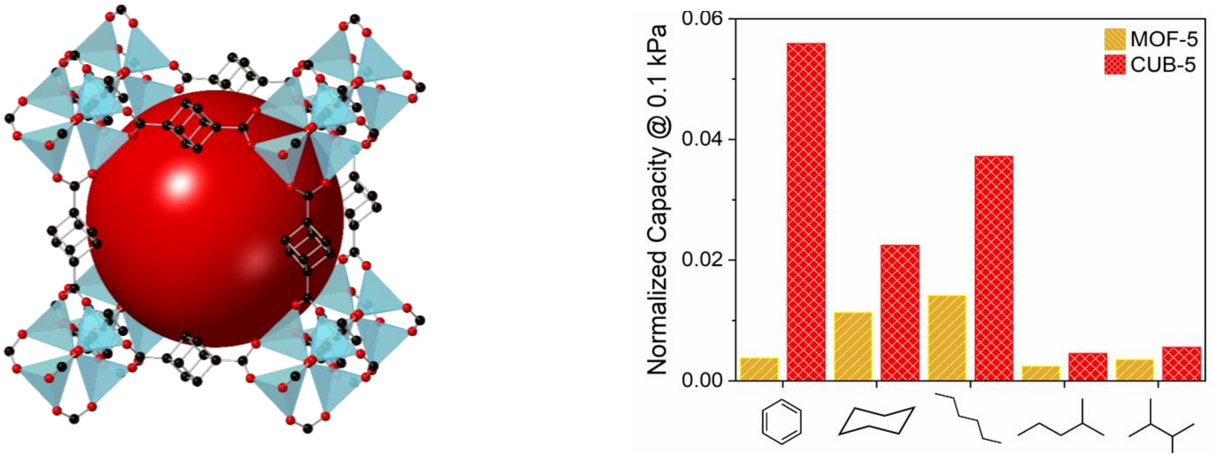

Figure 1. (Left) Cubic cavity of CUB-5; (right) normalized hydrocarbon capacity uptake of CUB-5 and MOF-5.[1]

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Unravelling the Thermodynamic Criteria for Size-Dependent Spontaneous Phase Separation in Soft Porous Crystals

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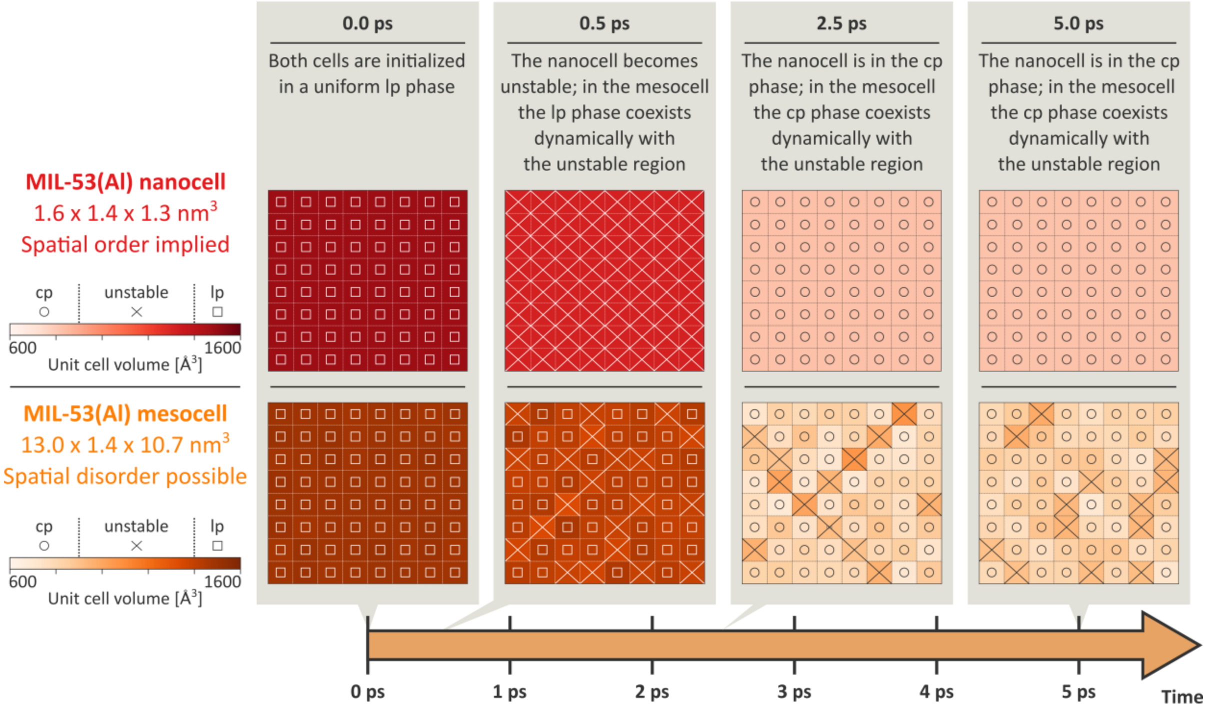
Soft porous crystals (SPCs) or flexible metal-organic frameworks (MOFs) harbour an unparalleled potential as functional nanoporous materials owing to their tuneable morphing between different crystalline phases in response to external stimuli.[1,2] These large-amplitude phase transitions are generally assumed to occur cooperatively throughout the whole crystal, thereby retaining the material's perfect crystalline order. However, this traditional picture of a 'perfect MOF crystal' for flexible MOFs sharply contrasts with the intrinsic spatial disorder recently discovered in rigid MOFs, varying from point-like defects to completely amorphous or glass-like phases lacking any long-range structural order. While one might assume that also flexible MOFs are much more disordered than originally thought, it is still generally accepted that a flexible MOF crystal can only exhibit a single phase at any given time. Here, we disprove this preconception through mesoscale first-principles based molecular dynamics simulations, demonstrating that phase transitions in SPCs induce spatial disorder in the material that propagates along preferential directions determined by the SPC's topology. Interestingly, this instantaneous coexistence of multiple metastable phases within a given sample can be stabilized by carefully tuning the experimental control variables such as pressure, temperature, and chemical potential. The observed phase coexistence forms a key ingredient to rationalize yet elusive phenomena in SPCs, such as the impact of crystal downsizing on their flexible behaviour, adding the crystal size as an easily controllable but crucial design parameter for future SPC-based stimuli-responsive devices.



Both cells are initialized in a uniform lp phase

The nanocell becomes unstable; in the mesocell the lp phase coexists dynamically with the unstable region

The nanocell is in the cp phase; in the mesocell the cp phase coexists dynamically with the unstable region

The nanocell is in the cp phase; in the mesocell the cp phase coexists dynamically with the unstable region

Figure. Spontaneous phase coexistence of large-pore (lp), unstable, and closed-pore (cp) states in MIL-53(Al) when accounting for spatial disorder in a mesocell simulation at 300 K and 40 MPa.

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Preferred presentation type: oral

Digital adsorption: 3D imaging of adsorption equilibria and dynamics in technical microporous solids

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Gas adsorption is one of the key physical processes that underlie the numerous industrial uses of porous solids. Typical applications include separation processes, catalytic reactions, energy storage, and gas recovery from unconventional plays. Key to maximise the efficiency of these processes is our ability to understand the microsctructure of the material at the pores scale (1–10 Å) and its interaction with the operating fluids. Yet, to be useful for industrial implementation, the powders obtained in the laboratory need to be shaped into so-called technical solids, i.e. millimetre-sized bodies with sufficient porosity, with improved chemical and mechanical stability. However, these densified solids also reveal variations in terms of the structure and composition over length-scales much larger than the pore size, from a single pellet (µm–mm) up to the packed-bed (cm – dm)[1]. Understanding the scale and extent of heterogeneity in technical adsorbents by means of advanced experimentation is a precursor to the rational scale-up of tailor-made materials, from powders to the sub-kilogram scale, and to the robust design of separation processes. Multi-dimensional imaging techniques represent an essential tool to characterise these systems over the range of relevant length scales. However, the application of these methods to systems whose function is based on the presence of nanometre sized pores remains a challenge due to the trade-off between sample size and image resolution.

We show here how X-ray transmission Computed Tomography (XCT) can be applied to obtain a three-dimensional spatial characterisation of an adsorbent bed (50 cm^3) in terms of its microstructural properties, non-invasively. We report the results of two case studies with commercially available samples of activated carbon and zeolite 13X, demonstrating the deployment of digital adsorption workflow[2,3] to produce for the first time an integrated and quantitative three-dimensional visualisation of a packed-bed adsorber *operando*. Results are presented that include both static and dynamic (breakthrough) experiments using Helium and CO_2 as inert and adsorbing gas, respectively. From the static experiments, spatially distributed adsorption isotherms are measured at mm resolution and pressures 0.1–3 MPa; when combined with conventional analyses of physisorption data, we determine three-dimensional maps of the specific surface area, pore volume and other process performance metrics. We further use a machine learning approach to identify and locate different materials within the packed bed. The breakthrough experiments have been carried out at a total pressure of 0.1 MPa and at room temperature, while varying inlet composition, flow rates and tracking the adsorption fronts by XCT. All measured outputs (outlet *and* internal profiles) are described by a detailed model of the column that solves the partial differential equations consisting of mass, energy and momentum balances coupled with the appropriate initial and boundary conditions. Notably, while 1D and average properties are well captured by the model, significant variability is observed in the local adsorbed amount. The latter is associated with packing variability at the mm-scale and, possibly, inter-pellet heterogeneity

This novel ability to measure the adsorbed amount in-situ with both spatial and temporal resolution paves the way towards the characterisation of adsorption processes over the continuum of relevant length scales. This is key towards reconciling fundamental studies on the scale of a single crystal or pellet with those performed at the column scale. The gained insight is expected to contribute in bridging the gap between materials research and process design.

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Using Defect Engineering in Synthesis to create New Phases of UiO Family MOFs

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Metal-organic frameworks (MOFs) consist of metal nodes or clusters linked by multidentate organic ligands to encompass void space; altering the identity of these components allows the exploration of a wide range of properties, including porosity, reactivity and electronic properties.[1] There is also increasing interest in making nano-structures derived from MOFs, with a wide range of prospective functionalities for real-world applications; the UiO family of MOFs is especially promising due to its stability.[2]

UiO MOFs exhibit the potential for a wide range of defect chemistry, *e.g.* linker or cluster vacancies.[3,4] Deliberate introduction of defects into a MOF, or "defect engineering", is a particularly significant method of modifying its properties. Although most defect structures are random, we have previously shown that controlling the synthesis conditions of UiO-66 and UiO-67 allows control over the spatial distribution of defects, creating not only correlated defect nano-regions (nano-**reo** UiO-66),[4] but also an entire defect-ordered phase, **hcp** UiO-67.[5] Moreover, postsynthetic transformation of **hcp** UiO-67 allows topotactically-selective delamination into nanosheets.[5] Thus by harnessing correlated defects, it is possible to obtain previously inaccessible MOF topologies with new and distinct properties.

Inspired by the discovery that defect engineering can be used to control the phase and dimensionality of UiO-67, we extended investigation to other UiO family MOFs. We demonstrate that the synthetic conditions are critical in the creation and control of defects, and are instrumental to the phase selection [Fig. 1]; we use this understanding of defect engineering to synthesise new UiO MOFs with the **hcp** topology.[6] This discovery raises the possibility of harnessing defects to produce new phases of other MOFs, potentially leading to novel nano-materials for applications such as sensors for battery materials.

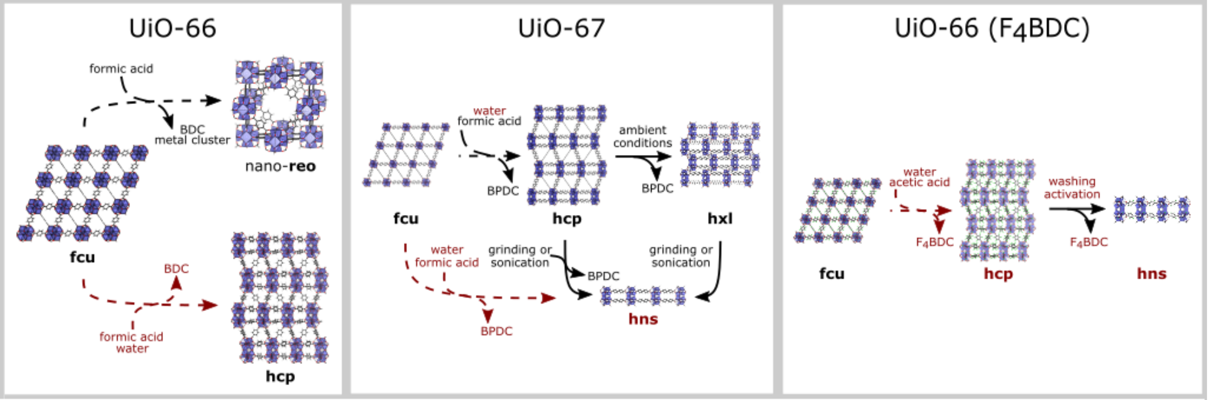

Figure 1. Phases of UiO family MOFs, showing the key synthetic conditions (dashed arrows) and postsynthetic treatments (solid arrows) used to obtain different phases; black text indicates previously-known phases or syntheses, while red text indicates those discovered or assigned in this report.[8]

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Microporous Polymer Membranes for Energy Conversion and Storage

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Membrane separators with fast ion transport and selective molecular transport properties play important roles in fuel cells and advanced batteries for electrochemical energy conversion and storage. Redox flow batteries (RFBs) have great potential for grid scale energy storage owing to their large-scale energy storage capacity, decoupled power and energy, long-term cycle performance, and quick response time. In redox flow batteries, membranes should not only allow fast ionic transport, but also limit the crossover of electrochemically active materials to extend cycling stability. Commercial ion-exchange membranes such as Nafion are being widely used in electrochemical devices, however, their high costs limit the large-scale applications of flow battery technology for grid scale energy storage. Next-generation ion-selective polymer membranes with low cost production, high ionic conductivity and selectivity, and durability are required for large scale applications of electrochemical energy conversion and storage devices.

We will present interdisciplinary research on developing low-cost, high-performance, ion-conductive membranes for advanced batteries such as organic redox flow batteries, involving collaborations with several universities in the UK. A new generation of ion-conductive membranes were developed from polymers of intrinsic microporosity (PIMs). Owing to their microporosity and ion-conducting functionality, PIM membranes present fast ion transport and high selectivity towards electrochemical active materials. The versatile chemistry of polymer membranes can be tailored on the molecular level to precisely tune the pore size and ion-conducting functionality to match the batteries with different redox chemistries. The new design approach of ion-selective membranes has broad implications on advancing large scale electrochemical energy conversion and storage.

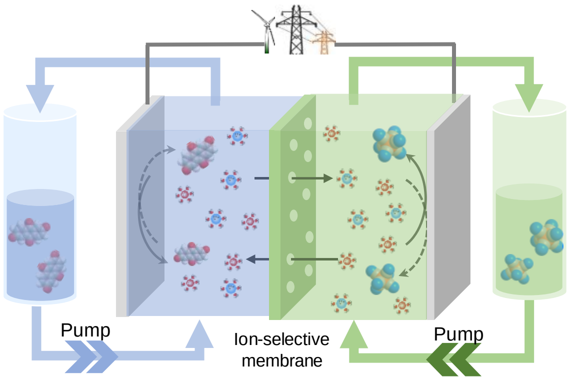

Figure 1. Microporous ion-selective membranes enable efficient and stable operation of organic redox flow batteries.

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Synthesis of solvent dispersible porous polymeric particles via RAFT-mediated PISA

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Abstract for oral presentation

Microporous polymers (MOPs) are a class of porous material synthesised from organic building blocks which possess very high surface areas (up to 5000 m^2/g).[1] They are chemically and thermally stable (they can be boiled in acid without the loss of porosity), are readily functionalisable and can be synthesised *via* cheap and facile chemistries. As such they find use in a variety of different areas from gas separation to waste water treatment and even catalysis. One major drawback of MOPs (and porous materials in general) is their lack of solubility in all organic solvents - limiting both applications and processability.

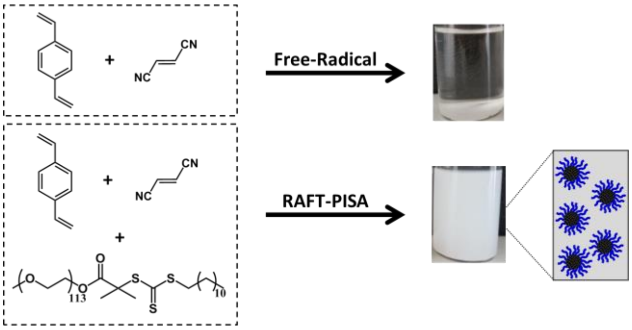

Figure 1. Synthesis procedure towards PPDs compared to conventional radical polymerisation.

In this work porous polymeric dispersions (PPDs) were synthesised through the successful union of free radical and RAFT-mediated PISA. Nanoassembly formation was induced through the application of a PEG-based macro-chain transfer agent (CTA) which both mediates the copolymerisation as well as disperses the particles. Porosity was induced through the co-polymerisation of divinylbenzene (DVB) and fumaronitrile (FN), and were found to have BET surface areas exceeding 400 m^2/g.[2]

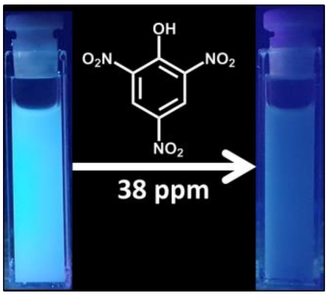

Figure 2. PPD sample applied to solution phase chemosensing

Unlike most porous polymers, due to the RAFT-mediated PISA synthesis, these materials were able to be dispersed in a wide variety of common organic solvents allowing them to be applied in solution phase applications. Current work in our group has seen these materials be applied to solution-phase chemosensing (Figure 2) as well as white light emission and even as catalysts. This work highlights the great potential and ability to create porous materials from a generic, facile and versatile synthetic procedure before applying the materials to solution phase applications.

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Oral presentations

Day 2

Manufacturing Highly Porous Phosphate Glass Microspheres for Bone Regenerative Orthobiologic Applications

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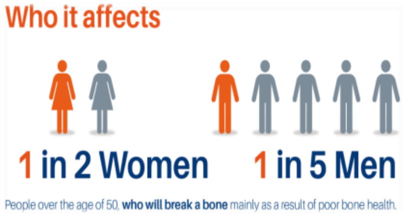
1 in 2 women and 1 in 5 men over 50 will suffer a fracture as a result of osteoporosis and with the over 50 population expected to reach 25 million by 2020, this represents a major healthcare concern[1]. Osteoporosis related fragility fractures constitute a 'silent epidemic' since there are no associated warning signs prior to fracture. Occurrence of a first fracture creates a significant risk factor for subsequent fractures. Therefore, new materials and technologies are required for fracture prevention strategies which represent a significant clinical need, especially for an ageing population. There has recently been an on-going shift towards 'orthobiologic' products (which incorporate biology and/or biochemistry to repair, replace or regenerate musculoskeletal structures).



Fully resorbable calcium phosphate-based glasses (PBGs) have been heavily investigated for hard and soft tissue repair applications[2,3]. These glasses are totally unique amorphous biomaterials due to their fully controllable resorbable characteristics, with formulations possessing chemical compositions similar to the mineral phase of natural bone. They can be made to completely dissolve in aqueous environments with controllable degradation rates and have excellent cytocompatibility properties (unlike materials such as HA and TCP, which are non-resorbable and have been shown to not effect bone repair of critical sized defects[4].

Recently, PBGs have been developed into highly porous microspheres (see Figure 1) which can be manufactured via a single-stage production process, in the size range of 60-350 µm, with fully interconnected porosity features (ranging in size from microporous to mesoporous[5]). The yield of porous microspheres produced is greater than 95% at a lab-scale quantity of 1-2 kg/h.

The aim of these microspheres is to deliver mesenchymal stem cells (MSCs) and through the release of biotherapeutic ions will influence MSCs down osteogenic pathways, leading to new bone formation. Thus, developing a prophylactic stem cell therapy that could potentially prevent fractures by strengthening bone in key areas where fractures normally occur such as the vertebra and hip in the ageing osteoporotic population.

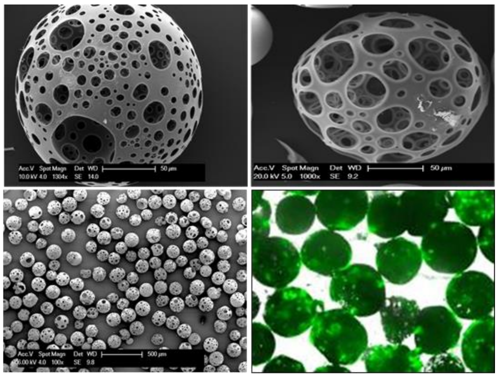


Fig 1: Porous calcium phosphate microspheres

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Chemical Stability and Thermo-Mechanical Property of Bulk Metal-Organic Framework Glasses and Crystal-Glass Composites

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Large-scale applications of metal–organic frameworks (MOFs) in catalysis, energy, gas storage, and molecular separation have been proposed for decades, but not fully realised. One of the primary problems for real-world applications of MOFs is the considerable difficulty in processing crystalline MOF powders into bulk monolithic forms. Compared with crystalline MOFs, the recently discovered melt-quenched MOF glasses, e.g. a_gZIF-62, possess better processability. However, current processing methodologies used to produce MOF glasses are restricted to the preparation of small glass pieces, alternative procedures for production of bulk, bubble-free samples are required.

Herein, we present a new processing route for the fabrication of bulk MOF glasses, centered on remelting. A transparent, bubble-free bulk a_gZIF-62 specimen with diameter of 13 mm and thickness of 1mm was obtained. The chemical stability of a_gZIF-62 was studied by soaking a bulk specimen in HCl or NaOH aqueous solution at 30^{o}C for 7 days. The a_gZIF-62 exhibits excellent stability in the pH range of 5 to 12. Moreover, the thermo-mechanical property of a_gZIF-62 was measured for the first time. The a_gZIF-62 has a thermal expansion coefficient of 35×10^{-6} K^{-1}, which is higher than silica based inorganic glass, while lower than most polymers except for Kapton.

The remelting strategy was then used to fabricate MOF crystal-glass composites (CGCs). The a_gZIF-62 was used as the matrix which not only provides a 'glue' to stick MOF crystallites together, but also enhances the chemical stability of the crystallites. Crystalline components selected are ZIF-67 and UiO-66. Loadings of the crystalline components of up to 80 wt.% led to bulk MOF CGC 'disks' with diameters of 13 mm and thicknesses of 1 mm. Crystallinity, and porosity are preserved in these samples. The chemical stabilities and thermo-mechanical properties of the CGCs were measured, and found to be a significant improvement upon pelletized samples of the pure crystalline components.

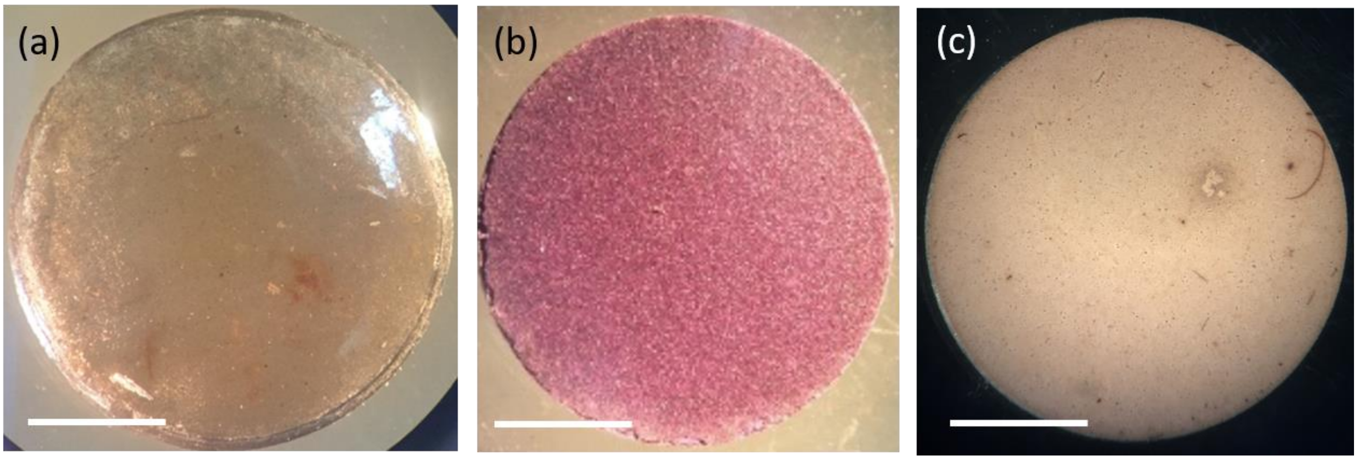

Figure 1 Photographs of bulk samples of (a) agZIF-62, (b) CGC with ZIF-67, and (c) CGC with UiO-66, scale bar of 5 mm.

Gas Separations using Sustainable and Robust Metal-Organic Frameworks

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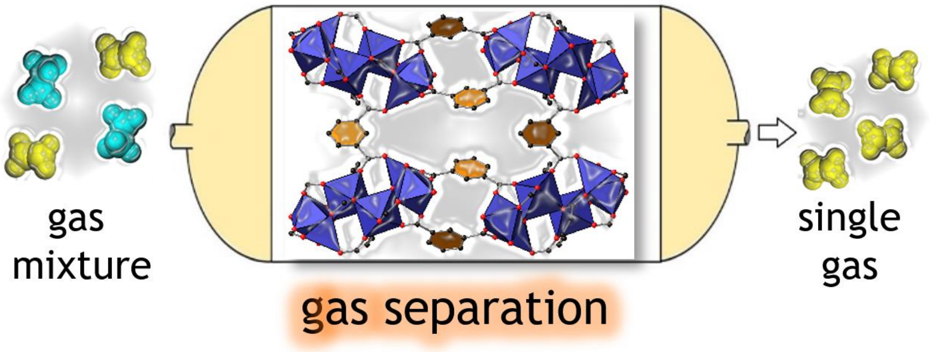
Metal-organic frameworks (MOFs) are porous crystalline materials that can sequester molecular guests. MOFs are distinguished from other porous materials by their diversity and structural regularity. Bottom-up self-assembly of these frameworks allows for control over the shape, size and chemical characteristics of their pore spaces. While many MOFs are too expensive or sensitive to consider for bulk separations, robust high-performance materials can be inexpensively. Advances in this area are likely to underpin sustainable applications to real-world separations with low capital overheads.

I will relay our recent research in the realm of molecular separations using some structurally straightforward materials. We have built up a series of robust MOFs using inexpensive precursors. The spatial environment in these materials can be precisely tailored to the selective capture of various guest molecules. Owing to these characteristics, these materials can effect the separation of very similar gases and remove low-level impurities. I will highlight our recent work on the capture of carbon dioxide and the separation of ethane, ethylene, and acetylene.[1]



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A Bimetallic Metal-Organic Framework Balancing the Requirements Between Enhanced Gas Uptake and Maintaining Selectivity

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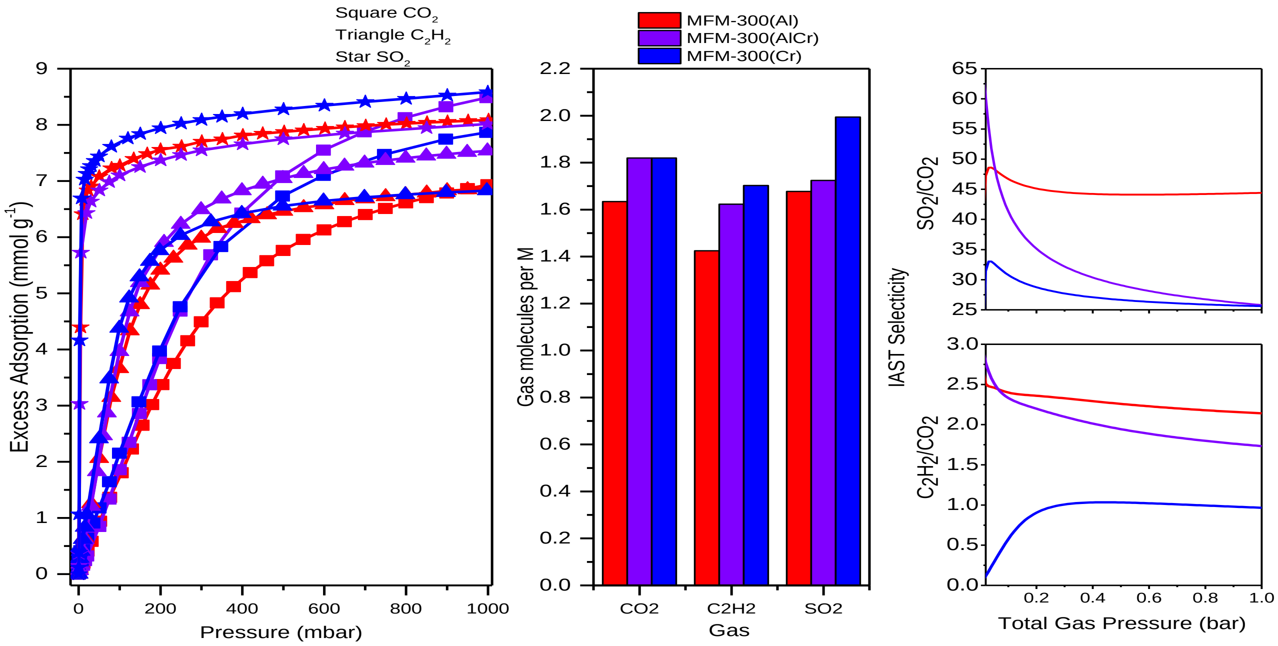
The incorporation of functional groups to form additional supramolecular guest-host interactions is an effective methodology for enhancing gas sorption in metal-organic framework (MOF) chemistry. However, this can impede the available surface area for guest-host interactions, therefore reducing the total uptake of gas by the material. Alternatively, employing MOFs with open metal sites (OMSs) is an approach also used yet often leads to instability upon desolvation and materials with limited chemical stability and recyclability. Herein, we report the CO_2, C_2H_2 and SO_2 gas sorption capabilities (CO_2 = 8.1 mmol g^{-1}, C_2H_2 = 8.0 mmol g^{-1} and SO_2 = 8.6 mmol g^{-1} at 273 K, 1 bar) of a new, ultrastable Cr based MOF, MFM-300(Cr), {$[Cr^{III}_2(OH)_2(L)]$, LH_4 = biphenyl-3,3',5,5'-tetracarboxylic acid} accompanied by respective direct gas visualizations via in situ synchrotron high resolution PXRD. We explore the role of changing metal center and the effects on gas interactions and uptake capacity and compare to a previously reported isostructural MOF, MFM-300(Al).[1,2] A hybrid material, MFM-300(AlCr) (2:1 ratio of metal ion content), MFM-300(AlCr), $[Al_{1.33}{}^{III}Cr_{0.66}{}^{III}(OH)_2L]$, was synthesized and optimized to incorporate the high gas sorption and chemical stability of MFM-300(Cr), along with the stable gas selectivity of MFM-300(Al). *In situ* synchrotron micro-FTIR spectroscopy found distinct Al-OH-Al, Cr-OH-Cr and Al-OH-Cr CO_2 binding environments in the mixed metal analogue which not only confirmed the homogenous dispersion of trivalent ions in the structure but also the presence of additional hybrid μ_2-OH peaks. The optimized material, MFM-300(AlCr), was found to have a higher concentration of CO_2, C_2H_2 and SO_2 molecules per metal than MFM-300(Al) and improved C_2H_2/CO_2 selectivity compared to MFM-300(Cr) (*Figure 1*). The incorporation of Al and Cr within the same framework allows for the synergistic property exploitation of each respective parent homometallic material for applications in gas sorption.



a) b) c)

Figure 1: a) CO_2, C_2H_2 and SO_2 adsorption isotherms at 293 K, 1 bar (optimised CO_2 positions for MFM-300(Cr) shown in inset along c axis); b) Calculated number of gas molecules per metal calculated from gas loaded CIFs and c) C2H2/CO2 and SO2/CO2 gas selectivities for MFM-300(Al) (red), MFM-300(AlCr) (purple) and MFM-300(Cr) (blue).

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Control of Metal–Organic Framework Crystallization by Metastable Intermediate Pre-equilibrium Species

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We present new insight into MOF formation, gained using *in situ* X-ray diffraction and *p*H measurements to uncover for the first time the evolution of metastable intermediate species in the canonical zeolitic imidazolate framework system, ZIF-8.[1] We reveal that the intermediate species exist in a dynamic pre-equilibrium prior to network assembly and, depending on the reactant concentrations and the progress of reaction, the pre-equilibrium can be made to favour under- or over-coordination species, thus accelerating or inhibiting crystallization, respectively (Figure 1). We thereby find that concentration can be effectively used as a synthetic handle to control particle size and space-time-yield, with implications for industrial scale-up and gas sorption applications. These findings enable us to rationalise the apparent contradictions between previous studies and, importantly, they open up opportunities for the control of crystallization of network solids more generally, from the design of local structure to assembly on mesoscopic length scales.

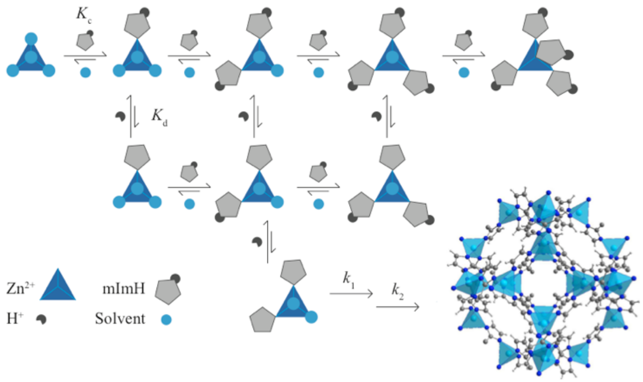

Figure 1. Kinetic model for pre-equilibrium in ZIF-8 crystallization (structure shown bottom right).

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Accelerating the discovery of Type II porous liquids using high-throughput automation

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In 2007, James *et al.* proposed a new class of material referred to as 'porous liquids'. In contrast to other types of porous material, these are liquids with permanent 'intrinsic' porosity. They remain vacant to occupy with small guests; either as a neat liquid or in combination with size excluded solvent. [1,2] We have recently found that porous organic cages (POCs) can be used as the soluble pores in different types of porous liquids,[4,5] because they are discrete covalent molecules that have an internal cavity. [3] The combination of fluidity and porosity are unique to porous liquids and could be implemented, for example, in the flow of gas containing solutions around continuous systems, something that cannot be achieved with conventional porous solids. However, there are only a few examples of POC based porous liquids reported in the literature and these materials are highly viscous, difficult to synthesise, or prepared with the highly toxic solvent, perchloropropene. [4,5]

In this study, we aimed to advance the field of porous liquids by utilising state-of-the-art robot platforms to discover new Type II porous liquids; from POC synthesis and purification through to their solubility testing in size-excluded solvents. Through this high-throughput methodology, we have generated a library of 100 new porous liquids comprised of various POC and size-excluded solvents, and we have studied the effects of changing these components on the overall properties of porous liquids. For example, one system had a 150% improvement in cavity concentration and a 79% increase in xenon uptake, compared to the first POC based porous liquid. [4,5] We have also studied methods to make porous liquids more commercially viable, by exploring gas capture and temperature release swings.Our work has significantly advanced the current understanding about porous liquid design and enabled us to demonstrate some of the unique properties possessed by these new materials. It is an important step for an emerging area of research as it opens up exciting possibilities for future applications.

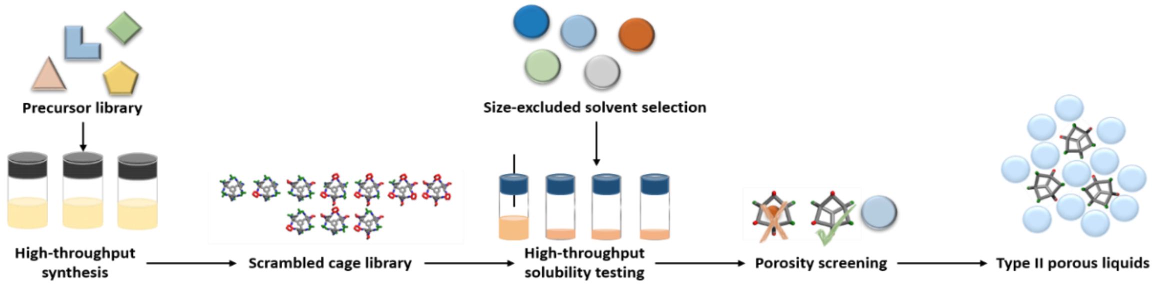

Figure 1: Graphical representation of high-throughput methodology developed to discover new Type II porous liquids

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Programmable Two-dimensional Materials for Sensing, Catalysis and Solar Cells

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Metal-organic framework nanosheets (MONs) are an emerging class of two-dimensional materials. MONs are free-standing, sheet-like materials approaching monolayer thickness composed of organic linkers co-coordinated to metal-ions or clusters. They display the high surface area and aspect ratios of 2D materials but have a modular structure which readily allows for systematic tuning of their electronic, optical and mechanical properties and introduction of new chemical functionalities. This has led to their use in a wide range of separation, sensing, catalysis and electronics applications.[1]

We have developed a series of MONs formed by the liquid exfoliation of layered metal-organic frameworks based around the popular metal paddlewheel secondary building unit (Figure 1). Isoreticular series of compounds have been synthesised in order to elucidate the effect of different functional groups on the exfoliation process and the stability of the resulting suspensions in different solvents.[2,3]

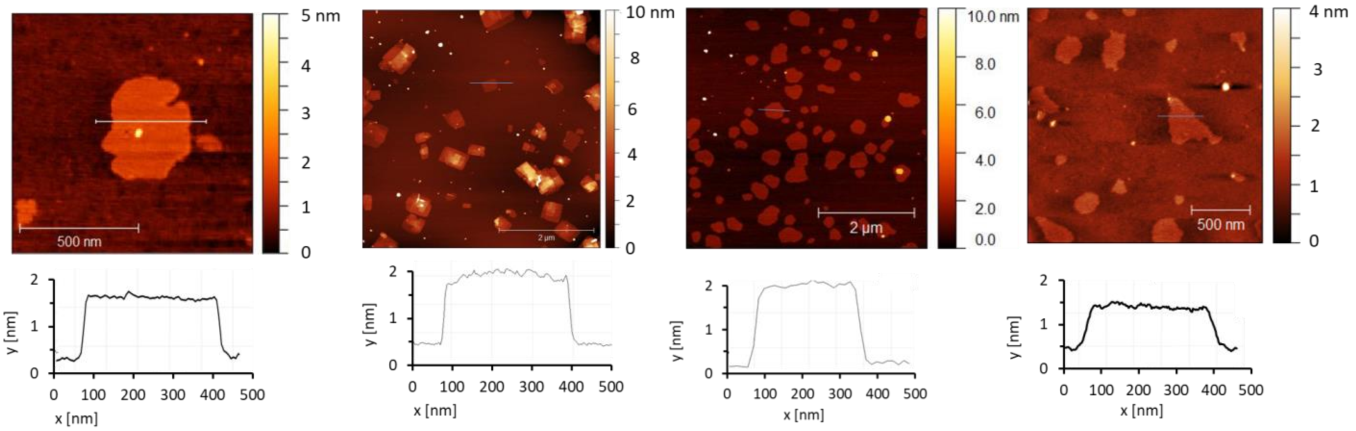

Figure 1: AFM images and height profiles showing single and bilayer MONs formed by ultrasonic liquid liquid exfoliation of different metal-paddlewheel based layered metal organic frameworks.

Recently, we demonstrated how covalent post-synthetic functionalisation (PSF) can be used as a novel method to enhance the exfoliation of layered MOFs in order to form predominantly single layer MONs. PSF was also used to introduce catalytically active functional groups enabling the MONs to facilitate tandem acid-base catalysis with 82% yield compared to 3% for the bulk functionalised MOF.[4]

We have also shown for the first time how MONs can be added to the active layer of bulk heterojunction solar cells. Addition of the zinc-porphyrin based MONs lead to devices with power conversion efficiency up to 5.2%, almost double that of the reference devices without MONs at 2.67%. Detailed analysis indicates that the complimentary electronic, optical and surface properties of the MONs allows them act as a surface to template the crystallisation of the donor polymer and as a barrier to inhibit overgrowth of fullerene acceptors without creating traps that would induce charge recombination.[5]

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Sustaining metal-organic frameworks for water-gas shift catalysis by non-thermal plasma

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The limited thermal and water stability of metal-organic frameworks (MOFs) often restricts their applications in conventional catalysis involving thermal treatment and/or use of water[1]. Non-thermal plasma (NTP) is a promising technique that can overcome barriers in conventional catalysis[2]. Here we report an example of NTP-activated water-gas shift reaction (WGSR) over a MOF (HKUST-1). Significantly, the exceptional stability of HKUST-1 has been sustained under NTP activation and in the presence of water, leading to a high specific rate of 8.8 h^{-1}. We found that NTP-induced water dissociation has a two-fold promotion effect in WGSR, facilitating WGSR by supplying OH, and sustaining the stability and hence activity of HKUST-1 despite the presence of water. *In situ* characterisation of HKUST-1 revealed the critical role of open Cu sites in the binding of substrate molecules[3]. This study paves the way for utilising MOFs for a wider range of catalysis.

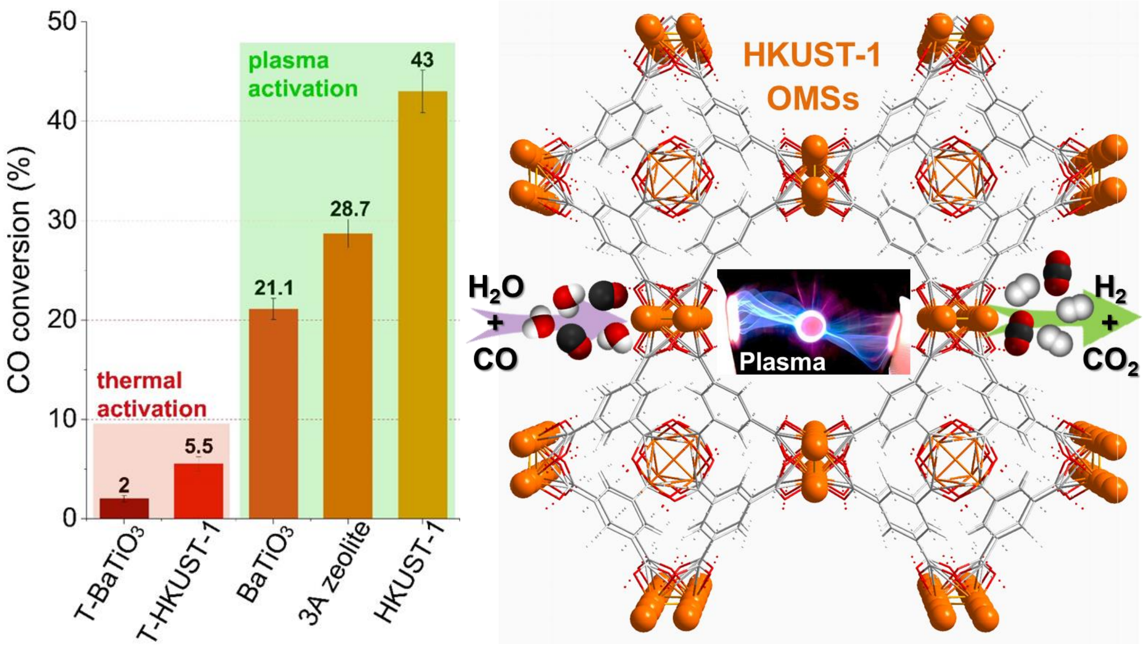

Fig. 1. Catalytic water-gas shift reaction (WGSR) by thermal and NTP activation

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NMR Studies of Adsorption and Diffusion in New Materials for CO_2 Capture

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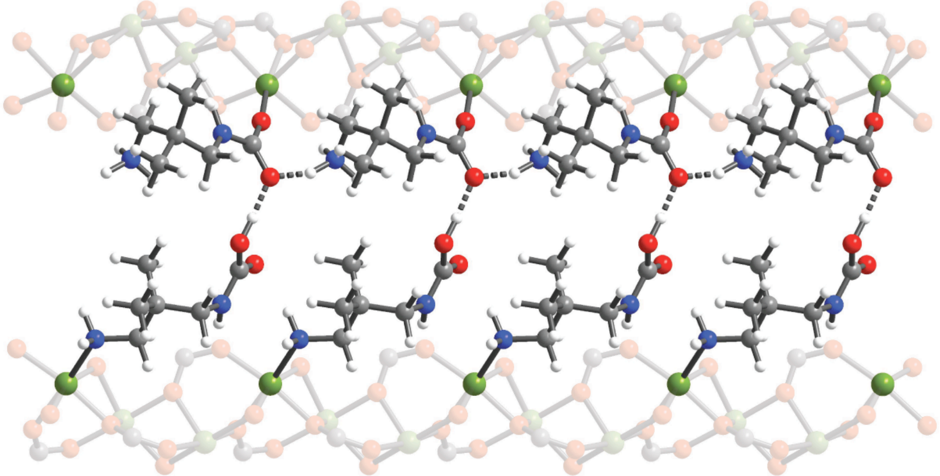
Carbon capture and storage is one of several technologies that must be rapidly deployed to reduce greenhouse gas emissions. Recent research has shown that amine-appended metal-organic framework (MOF) materials can capture CO_2 from target gas mixtures in a more energy efficient manner than traditional amine solvents. The commercialisation (ongoing at a start-up company) and deployment of these materials could be facilitated if the molecular mechanisms of CO_2 uptake and transport could be understood and optimised.

We have developed *in situ* nuclear magnetic resonance (NMR) spectroscopy to study CO_2 adsorption in amine-appended MOF materials. In particular we use solid-state NMR experiments of gas-dosed samples combined with density functional theory calculations to probe different states of adsorption in what is termed "NMR isotherms." The measurements reveal a rich chemistry with the chemisorption mechanism dependent on the MOF composition.[1,2] Crucially, we link our results to the CO_2 capture performance of MOF materials, and discover a new mechanism for capturing CO_2 from power station flue gases (Figure).

We further present a method for measuring the extremely anisotropic diffusion of CO_2 in MOF materials featuring 1-dimensional pores.[3] By combining our pulsed field gradient NMR experiments with spectral simulations we obtain accurate diffusion anisotropy values.[4] Our measurements are complemented by single-crystal diffraction experiments and molecular dynamics simulations to unravel the structural basis of the observed diffusion behaviour. Finally we show how the MOF structure can be systematically tuned to optimise gas transport in MOF materials, something that is vital for their practical implementation.



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Single Fe(II) sites in MIL-type metal organic frameworks for the oxidation of light alkanes to alcohols

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Site-isolated Fe(II) centers have been recently linked to the activity of synthetic catalysts for methane oxidation to alcohols.[1-2] Isolation of the iron species requires metal loading lower than few mass%, thus limiting the number of active sites in the materials studied so far. We report the results of a computational study[3] assessing single non-heme Fe(II) ions present as structural metals in several metal organic frameworks (e.g. MIL-100) as promising catalysts for C-H bond activation. The barriers associated with the homolytic C-H bond scission are as low as 40 kJ mol^{-1} for ethane and 60 kJ mol^{-1} for methane that is lower than those reported previously for other iron-based MOFs.[4] Through consideration of the full reaction profile leading to the corresponding alcohols ethanol and methanol, we have identified key changes in the chemical composition of the node that would modulate catalytic activity. The thermal and chemical stability of these MOFs together with the scalability of their syntheses make them attractive catalysts for the selective low temperature conversion of light alkanes to higher-value oxygenates.

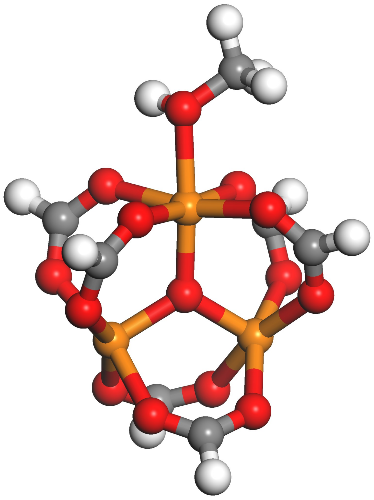

Figure: Single non-heme Fe(II) sites in MIL-100 coordinating a methanol molecule. Color code: orange (Fe), red (O), grey (C) and white (H).

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Chemical control of structure and guest uptake by a conformationally mobile porous material

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The selection of the optimum porous material for sorption and catalysis on industrial applications is based on properties such as pore dimensions and available chemical functionalities, which are fixed for rigid structures of zeolites and MOFs. This contrasts with biological manufacturing of living systems that operates using the structural adaptability of multifunctional soft materials such as proteins. Design and synthesis of porous materials that dynamically select the appropriate structure to carry out the desired chemical function in response to their environment will enable the manufacturing of chemicals in a way that resembles the selectivity and efficiency of biological systems. Here we show a new metal organic framework, ZnGGH, based on a conformational flexible tripeptide linker, glycine-glycine-L-histidine (GGH)[1]. The rotation about the covalent bonds of the peptide linker allows ZnGGH to adopt nine distinct structures responding sensitively to the presence, shape and chemistry of the species in the pores. The extensive changes on torsion angles, up to 150°, result on different conformations of GGH linker, which are clustered in three types straight, twisted and folded. Computational optimization of the experimental structures by DFT produces three theoretical structures that have one of the above linker conformation. These three structures correspond to the local minima of the conformational energy landscape that describes the extent of the structural transformability of ZnGGH porous framework. Adsorption experiments by the ZnGGH materials revealed the effect of structure and in particular of linker conformation on the uptake of small molecules guests. ZnGGH-2•(DMSO) which adopt twisted linker conformation, shows no uptake of guests such as dioxane and cyclopentanol in contrast to structures with straight linker conformation, ZnGGH-1•(DMF-H_2O) and ZnGGH-3•(DMF), that adsorb significant of these molecules. Addition of DMF in the presence of dioxane or cyclopentanol to ZnGGH-2•(DMSO) removes DMSO and selects the straight linker conformation. This transforms ZnGGH from the twisted linker minimum of the conformational energy landscape that is inactive for adsorption to the active straight linker minimum and enables the uptake of the dioxane and cyclopentanol guests. This chemically triggered conformational selection of the peptide modifies the structure and thus controls the functional behaviour of the porous ZnGGH framework in a similar manner that proteins select their optimum structure to perform their function.

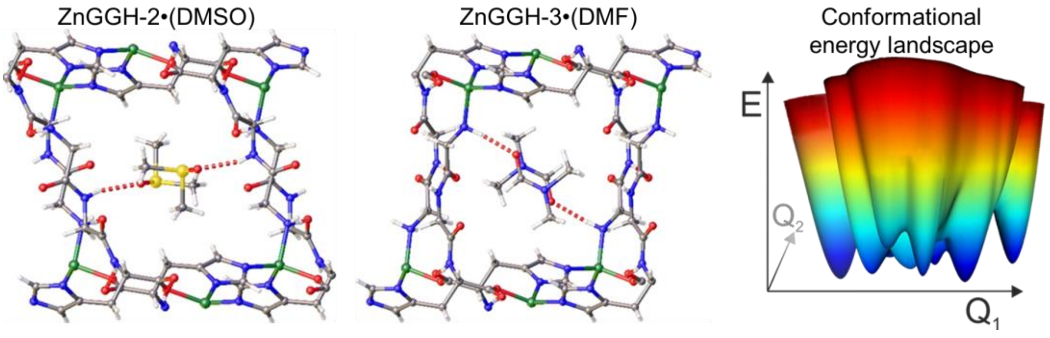

Figure 1 The view down the one-dimensional pores of ZnGGH-2•(DMSO) and ZnGGH-3•(DMF) shows the different pore shapes and the orientation of functional groups. The conformational energy landscape of ZnGGH framework presents multiple minima that correspond to the nine distinct experimentally observed crystal structures.

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Poster Abstracts

Filling MOFs: Where do complicated molecules stick?

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From MOF-Ionic Liquid hybrid materials, to advanced sensors, to structure-determining residual solvent, a variety of applications require modelling complex molecules in equally complex pores of molecular framework materials.

We share our first attempt at combining our framework structure generator, AuToGraFS[1] with a stochastic structure generator, Kick[3],[2] and show results for two polymer@MOF hybrid systems.

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Measuring and Modelling Supercritical Adsorption of CO_2 and CH_4 in Mesoporous Materials

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Mesoporous adsorbents are of considerable interest due to their widespread applications such as catalysis and electrochemical energy storage. They possess a tunable porosity, high specific surface area and a large total pore volume[1]. The use of a mesoporous material also overcomes the diffusional limitations typically associated with microporous materials. This is particularly true for zeolites, which has led to the development of novel hierarchical zeolites, which incorporate both micro- and meso- porosity[2]. Carbonaceous mesoporous adsorbents have also received a substantial amount of attention due to their unique chemical and physical properties[3]. Although there is significant progress in understanding the effect of mesoporosity on adsorption at subcritical conditions in these materials, adsorption data at high pressures and temperatures is required to ascertain the role of mesoporosity at supercritical conditions and to qualify the materials for their intended applications.

In this work, we perform a systematic adsorption study on two mesoporous materials: (i) mesoporous carbon and (ii) mesoporous zeolite. A comprehensive set of supercritical CO_2 and CH_4 adsorption isotherms have been measured using a Rubotherm Magnetic Suspension Balance over a wide range of conditions, i.e. temperatures in the range 300-360 K and in the pressure range of 0-300 bar. We report excess and net adsorption isotherms, and quantify all experimental uncertainties. The materials have also been characterised using a combination of cryogenic low-pressure (<1 bar) physisorption methods including N_2 at 77K, CO_2 at 273K and 298K and Ar at 87K. The Non-Local Density Functional Theory (NLDFT) model has been applied to the data to extract textural properties such as pore size distributions, total pore volume and specific surface area. The mesoporosity of these materials is clearly evident in both subcritical and supercritical isotherms, particularly at near-critical conditions at elevated pressures. The microporosity within the hierarchical zeolites also plays a role; the shape of the adsorption isotherms of the zeolites are noticeably distinguishable from the adsorption isotherms of the purely mesoporous carbon. We also observe a substantial adsorption selectivity of both materials towards CO_2 as compared to CH_4. The adsorption isotherms enable the extraction of key adsorption parameters such as Henry constants and the heat of adsorption as well.

To support the experimental results, the supercritical adsorption results have been successfully described using a Lattice Density Functional Theory (LDFT) model[4], which is extended to the cylindrical pore geometry in this work. The model uses the pore size distribution obtained from the subcritical adsorption data as an input parameter. The LDFT model is capable of capturing the unique adsorption behaviour of mesoporous materials and the adsorption energetics. Using this model, pore-specific adsorption behavior can be extracted and insights into the interaction between the adsorbate and adsorbent can be ascertained. The model also has predictive capability, which is a significant deviation from empirical approaches such as the Langmuir or BET models.

Through this novel and extensive workflow, we have been able to characterize the supercritical adsorption behavior of two relevant fluids (CO_2 and CH_4) in mesoporous materials, and parameterise the adsorption isotherms using the LDFT model.

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Exploring the World of 2D Paddlewheel-Based Metal-Organic Nanosheets (MONs)

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Metal-organic nanosheets (MONs) are an emerging class of two-dimensional (2D) nanomaterial which already show promise for use in a wide range of applications including gas separation, water purification, catalysis, batteries and optoelectronics.[1] MONs share advantages of other MO materials (e.g. MOFs–MO frameworks): the ease with which their structure can be varied and new properties introduced. They also benefit from vast external surface area and nanoscopic dimensions, shared with other 2D materials.

The design of these materials remains in its infancy. Current MONs utilise well-known building blocks, however properties could be easily varied by using different metals, and the breadth of organic chemistry could be used to tune ligands to influence both macroscopic and chemical properties. Systematic variation of functional groups (**R**) on ligands used provided insights into the crystal engineering rules governing the design of layered MOFs, and their exfoliation to produce MONs with controllable properties.

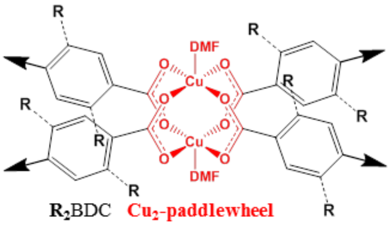

Fig. 1. *MON layer structure.*

We synthesised isoreticular series of layered MOFs, based on copper “paddlewheel” nodes, linked in 2D with 2,5-di**R**-1,4-benzenedicarboxylates (**R**$_2$BDC) (**Fig. 1**).[2,3] Incorporating different functional moieties (**R**) influenced the exfoliation to MONs, imparted a degree of control over MONs formed, and altered their surface chemistry and chemical properties.

Functionalisation with hydrophilic or hydrophobic moieties influenced the concentration, morphology and size of MONs when exfoliated in a wide range of solvents (**Fig. 2a,b**). Altering the surface chemistry allowed tuning of binding properties of small aromatic molecules to the labile axial copper coordination sites.[2] Functionalisation with a series of alkoxy chains of increasing length increases the interlayer distance within the MOFs from 8.37 – 9.91 Å (**R** = propoxy – pentoxy) (**Fig. 2c**), and CO_2 adsorption increases nearly 50 % from 27.2 to 40.2 cm^3 g^{-1}. Increasing the chain length produced MONs with larger lateral dimensions and decreased height – observed down to five nm, just 5 layers of material.[3] Multiple ligands can be incorporated within the same 2D layer, which enabled fine-tuning of the binding properties of molecules to the axial copper sites, and produced monolayer MONs (**Fig. 2d**) with non-uniform surface chemistry.[4] Potentially limitless **R** groups will enable further tuning and property introduction.

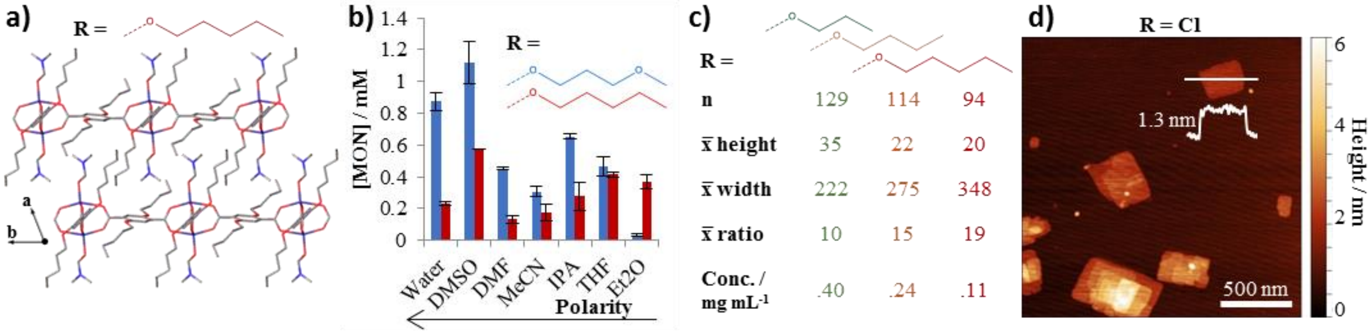

Fig. 2. a) *Crystal structure of [Cu(**R**$_2$BDC)(DMF)]$_n$;*[3] ***b)*** *[MON] after exfoliation in indicated solvents;*[2] ***c)*** *mean sizes (nm) of MONs after exfoliation in MeCN;*[3] ***d)*** *AFM image of MONs.*[4]

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Significant changes in CO_2 uptake in ultra-microporous metal-organic frameworks elicited by framework flexibility

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Escalation of the atmospheric CO_2 level, resulting from the industrial effluents (Flue gas) is a significant contributor to the global greenhouse effect.[1] However, the substantial low concentration of CO_2 as compared to N_2 in the flue gas streams has made the selective CO_2 capture from these sources a challenging task.[1] Another critical factor to be accounted is the presence of water vapour in the flue gas stream, which competes with CO_2 for the adsorbing sites, thus reducing the effective CO_2 adsorbing capacity of the adsorbent and also degrades its quality.[1] Typically alcohol amines are used as CO_2 scrubbers from the flue gas streams. However, the chemical bond formation between the alcohol amine and CO_2, makes the regenerative process energy exhaustive and costly, limiting its reusability.[1] To overcome this issue, adsorbents showing physisorption, which could be easily regenerated, are investigated for CO_2 capture and storage. Adsorbents with optimal interaction and pore dimensions which could facilitate both thermodynamic and kinetic separation will be a suitable candidate for selective CO_2 capture from flue gas sources.[1,2] Ultra-microporous metal-organic frameworks (UMMOFs), with optimal pore dimension (less than 7 Å) favour kinetic separation of CO_2 from N_2, and have emerged as appropriate candidates for selective adsorption and separation of CO_2 from flue gas or post-combustion conditions.[1,2] In addition to this, polar functional groups tethered in the pores of the UMMOFs will facilitate thermodynamic separation of gases.[2] Furthermore, one of the attractive properties shown by few MOFs is the reversible framework dynamicity in response to some external stimuli. These dynamic frameworks are referred to as *3rd generation MOFs*.[3] Framework flexibility can be beneficial for gas adsorption since it opens up extra space to accommodate more gas molecules, but for the large pore MOFs this could be not as advantageous for selective CO_2 capture from post-combustive sources, as the larger pores will compromise on the kinetic separation of CO_2 and N_2. On the other hand, UMMOFs built up of short and rigid linkers tends to be more robust. Hence it will be fascinating if flexibility could be incorporated in these UMMOFs, since framework dynamicity could increase the gas uptake capacity, without compromising on the selectivity.[4] Here, I will be presenting such ultra-microporous MOFs, built up of short and rigid linkers which show structural dynamism.[4] It will be discussed how variation in different synthetic parameters like solvent, temperature and metal cations assists in bringing up and tuning the flexibility in the otherwise rigid UMMOFs.[4] Further, a detailed crystallographic analysis will be provided to show the effect of framework flexibility on the overall gas uptake property of these UMMOFs.

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Computational Discovery of Molecular and Extended Porous Materials

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We have been developing software towards assisting in the discovery of molecular materials with targeted structures and properties.[1,2] The supramolecular toolkit (*stk*) provides robust and general methods for the construction and analysis of many classes of functional materials including porous cages, polymers, and covalent organic frameworks. As part of our software, we have implemented an evolutionary algorithm, which applies the premise of the "survival of the fittest", to efficiently screen thousands of possible candidate structures for a target application. Our evolutionary algorithm automates the assembly of promising, hypothetical molecules from a library of precursors based on a given target property. Initially, we have focused on porous molecular materials, specifically porous organic cages formed through dynamic covalent chemistry (DCC), where we are addressing questions such as which topologies or DCC reactions maximise void size or whether specific chemical functionalities promote targeted applications.[3,4] Furthermore, we are developing approaches to design stable asymmetric cage structures with specific functionalities.[5] Finally, we will discuss the extension of our approach to network materials, where the consideration of local and bulk properties is required to predict material properties but complicates the construction and analysis of the corresponding molecular models.

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Stability Study of Surface-Functionalised Metal-Organic Framework UiO-66 for Drug Delivery

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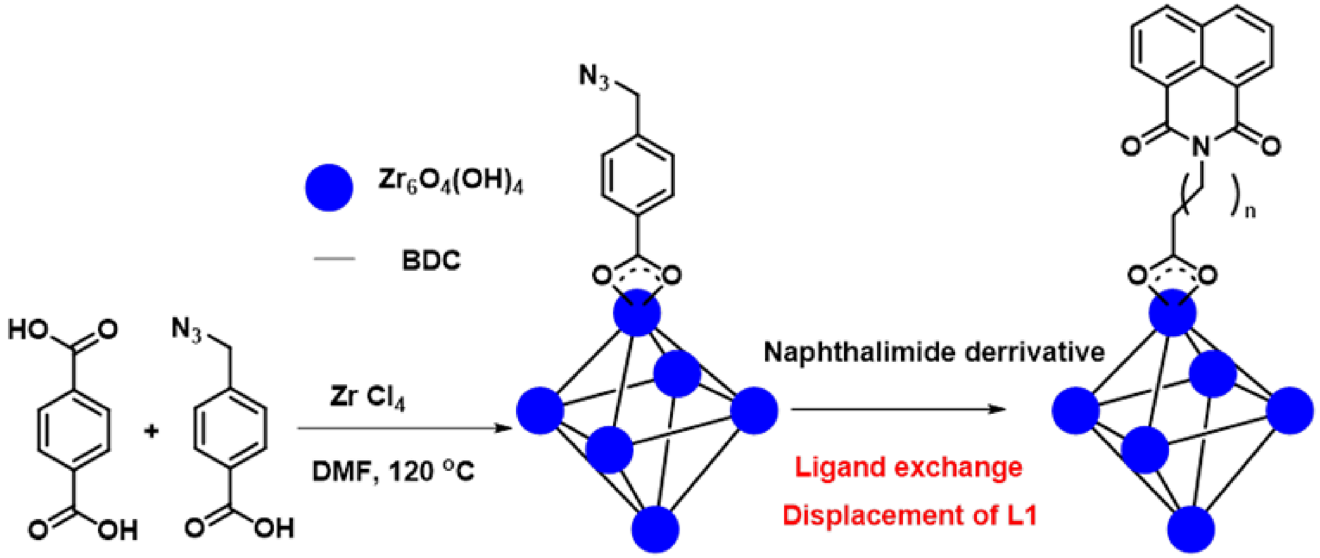
In recent years the interest in Metal-Organic Frameworks (MOFs) has increased exponentially due to their porosity, robustness and ease of functionalisation.[1] The possibility to tailor the framework makes MOFs very attractive for various applications, one of them being drug delivery, where drugs are loaded into nanoparticulate MOFs for delivery in the body.[2] This ability to tune frameworks gives the opportunity to control cytotoxicity, release kinetics, and size of the drug carriers.

Surface stability of nanoparticles is of great importance when used in drug delivery. That is because the surface can be used to attach targeting groups, solubilising polymers, stimuli-responsive release mechanisms, or drugs. We will report a comprehensive study of the surface functionalisation of the modulated Zr MOF UiO-66 to assess surface stability. A number of naphthalimides have been synthesised and incorporated on the surface of the MOF, in order to compare and contrast the effect of the different anchoring groups of the surface reagents. Initial results show that a small variability in the length of the surface reagents leads to significant differences in the surface stability in simulated biological conditions. Scanning Electron Microscopy (SEM) and Dynamic Light Scattering (DLS) show that MOFs are of the desired size for drug delivery. Initial cytotoxicity studies show that surface-functionalised UiO-66 nanoparticles are biocompatible. These results will have important implications for the design and applicability of MOF-based drug delivery devices.



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Hybrid metal-polymer materials for adsorption and catalytic applications

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MOF-mixed membranes are an attractive area of research for CO_2 separation as they can combine in one material the adsorption properties and the synthetic flexibility of metal organic frameworks (MOF) with the easy processability, the selectivity and the flexibility of organic polymers.[1] However, the research on these mixed systems is still in embryonic stage and there is still a lot of space for improvements in terms of performance, stability as well as for the discovery of new hybrid metal-polymer materials to explore new applications for this type of membranes. In this work we have developed two approximations for the synthesis of new hybrid materials.

From one side, and in the mark of GENESIS project, a European funded project with the objective to develop and upscale MOF-mixed matrix membranes systems for CO_2 capture in post-combustion process, we have explored and developed the optimal integration of MOFs on porous polymer membranes for CO_2 capture. We will present strategies for an optimized preparation of these new membranes as well as the scale-up of synthesis of nanozised MOFs, such as ZIF-8 and ZIF-67.

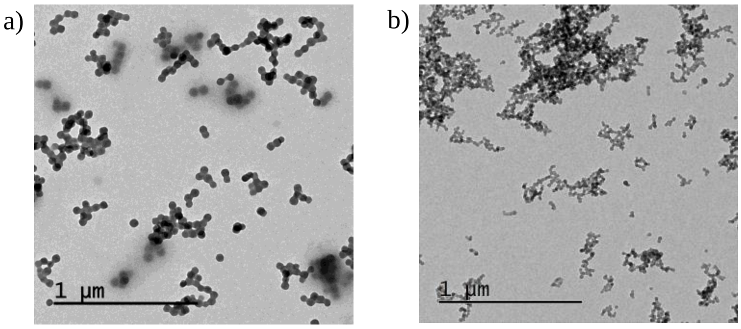

Figure 1: ZIF-8 nanooparticles. a) 56 nm ZIF-8 nanoparticles. b) 33 nm ZIF-8 nanoparticles.

On the other side, we have developed a new approach in which MOFs Secondary Building Units or clusters are connected through polymeric monomers to obtain new hybrid porous metal-polymer materials. In particular we focused in monomers used in the synthesis of polymers of intrinsic microporosity (PIMs).[2] As discovered by McKewon *et al.* these monomers present structural properties that favor the formation of porous polymers. In this communication we will present the synthesis of polymeric chains by the assembly of paddle-wheel rhodium clusters connected through rigid spiro molecules that can present catalytic and adsorption properties (these polymers have been characterized by ^{1}H NMR and UV-vis for the moment).

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Structures of Polymorphic Zeolitic Imidazolate Framework Systems and Their Associated Melting Behaviour

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Research in the field of metal organic frameworks (MOFs) has, until recent years, focussed on the development of ordered crystalline materials. However, greater focus is now moving towards disordered materials and amorphous structures.[1] Recent work has shown that several structures melt on heating.[2] These MOF liquids can then be quenched to form amorphous glasses with interesting properties compared to their crystalline counterparts.[3,4] Of these MOFs, very few have been reported to melt: ZIF-4 (via ZIF-zni), ZIF-62, TIF-4, $Zn(Im)_2$ (GIS) and ZIF-76.[2,3] Both computational and experimental studies have highlighted that MOF structure strongly influences melting behaviour.[4,5] Although much work has gone into finding novel MOFs that melt, the discovery of these has been limited to date.

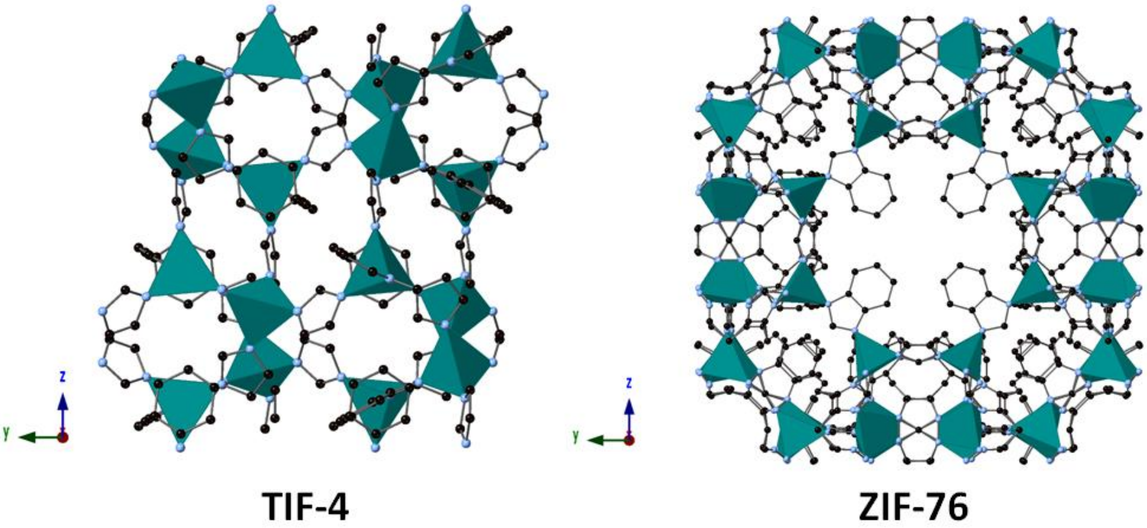

Figure 1: Crystal structures of TIF-4 and ZIF-76. Hydrogen and chlorine atoms omitted for clarity.

In order to discover novel melting MOFs, it is first desirable to have a greater understanding of the factors which influence melting of the known systems – for example the interplay between network topology and chemical composition. The melting behaviour of two ZIF polymorphs, ZIF-76-mbIm and TIF-4, has therefore been studied. Both structures are composed of Zn^{2+} cations, and imidazolate and 5-methylbenzimidazolate organic linkers.[2,3,6,7] However, ZIF-76-mbIm has an open cubic crystal structure with the P-43m space group and the lta topology whilst TIF-4 has an orthorhombic crystal structure with the Pbca space group and the cag topology. [2,3,6,7] Furthermore, the structure of TIF-4 is extremely similar to that of other melting MOFs such as ZIF-62, whilst no other MOFs with a crystal structure similar to that of ZIF-76 have been reported to melt.[1] The synthesis of both of these materials has been investigated along with their thermal response and the results compared. The thermal response of mixtures of these ZIF polymorphs has also been probed to investigate which factors govern melting behaviour.

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Metal-organic Nanosheets for Water Purification Applications

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Clean, safe drinking water is essential for all life on earth and it is becoming a dwindling resource due to growing populations, industrialisation and climate change.[1,2] The utilization of unconventional water sources (wastewater, seawater etc.) must be explored to meet the growing water demand, however without treatment these water sources are not fit for use.[3,4]
The ideal membrane has high flux, good selectivity and rejection rates, resistance to fouling and good stability. Metal-organic materials have attracted considerable attention for separation due to their high chemical stability, controllable porosity and good permeability.[5] These can be integrated into membranes to give an improved separating layer that selectively allows species to pass through.[6]

It is from here that the inspiration for this project originates, using two-dimensional (2D) metal-organic materials in conjunction with polymer membranes to improve the performance of water purification membranes. The atomic thickness, high aspect ratio, robustness and tunable nature of these materials lends them to separation applications.

In 2017 Ang and Hong first reported the use of iron centred porphyrin complexes interconnected with divalent metal ions (M-TCP(Fe)) in membranes for water purification.[7] These nanosheets were then deposited onto membranes to form and ultrathin selective layer, exhibiting very high water permeance of 4243 LMH bar-1 and 90% rejection of organic dyes.

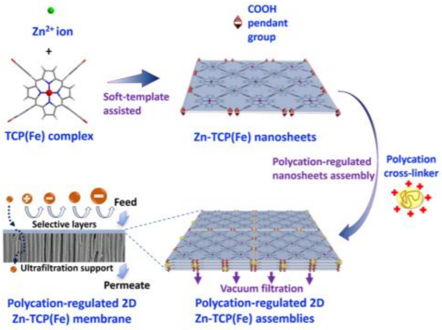

Figure 1. Schematic depicting the fabrication of M-TCP(Fe) membranes, where M = Zn. Image reproduced from reference 59.

Z. Wang et al. reported the use of CuBDC MONs in thin-film nanocomposite membranes for forward osmosis in 2018.[8] The incorporation of CuBDC MONs gave a ~50% increase in flux and an improvement in selectivity of the CuBDC containing membrane. The final example of the use of metal-organic nanosheets in membranes for water purification uses the layered system from the group of MOFs known as ZIFs.[9] This showed an enhanced rejection rate of organic dye molecules (from 17% to 99.4%), however this came at a cost of a water flux reduction (from 421 to 67 LMH bar-1).

This research aims to find suitable MON systems for use in membranes for water purification applications. Starting with current literature examples, then progressing onto other systems in order to create successful MON-polymer membrane water purification technology. The new membrane system should aim to have improved water flux, rejection rates and anti-fouling properties when compared to the commercial alternative.

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Role of metal, metal-coordination and pore size in honeycomb metal-organic frameworks for CO/N_2 separation

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Technologies to separate carbon monoxide (CO) from N_2 currently involve expensive cryogenic distillation or toxic solutions[1]. MOFs with a high density of accessible metal sites, such as MOF-74, however have shown potential in replacing these approaches yet the development of a suitable MOF for CO/N_2 separation is hampered by the lack of information for designing a competitive material.

Here, we study four MOFs: MOF-74[2], M_2mDOBDC[3], M_2Cl_2BBTA[4] and M_2Cl_2BTDD[5] (M= Co, Ni) which all share a similar 1-dimensional pore structure enabling direct comparisons. Using a combination of static and dynamic gas adsorption experiments alongside *in-situ* diffuse infrared Fourier transform spectroscopy, a series of interesting trends form within the series that are dependent on the metal element within the MOF, its coordination environment and the pore size of the framework. A decrease in CO adsorption is seen for all Co analogues though the resulting decrease in N_2 has minimal impact on the selectivity. The highly polarizing ligands found in MOF-74 and MmDOBDC increase the CO heat of adsorption and adsorption at lower pressures but have minimal effect on the CO binding to the metal center. Increasing the pore aperture however decreases the equilibrium adsorption of both CO and N_2. Careful consideration of these reported trends should enable the design of new MOFs for specialist applications.

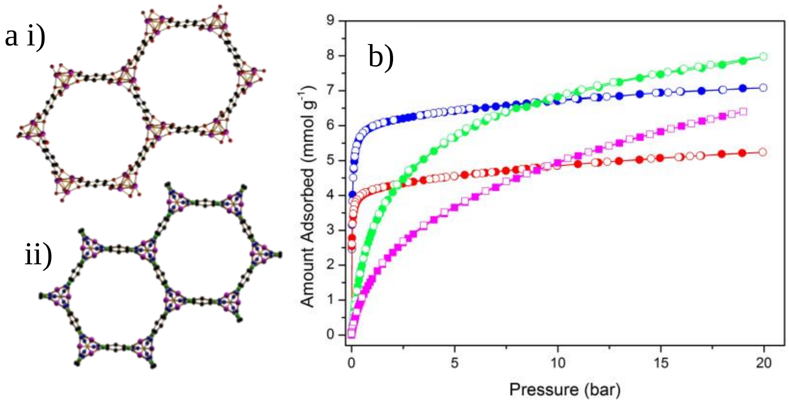

Figure 1a) Representation of i) MOF-74 and ii) M_2Cl_2BBTA looking down the c-axis b) 298 K CO isotherms of Co analogues of MOF-74 (blue), MmDOBDC (red), M_2Cl_2BBTA (green) and M_2Cl_2BTDD (pink).

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Guiding adsorbent development for post-combustion capture using an adsorbent screening tool

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Significant research efforts have been directed towards adsorbent development over the past 10 – 15 years, mostly driven by the discovery of metal-organic frameworks (MOFs) and the recognition that carbon capture is one of the necessary technologies required to abate greenhouse gas emissions. The predominant volume of this research is focussed on adsorbent discovery and basic evaluation of separation performance, with less emphasis being placed on process and economic evaluation. The latter aspects are important to drive adsorbent deployment.

In this work, a reduced order pressure/vacuum swing adsorption (PVSA) model[1] was used as the basis on which we have added a process design and economics tool to screen several MOFs. The PVSA model accounts for the non-isothermal nature of the adsorption process to more accurately evaluate the adsorbent performance, and the process design and economics tool enables adsorbent comparison on an overall cost basis (£ per tonne of CO_2 captured) for a given application. This allows the association of adsorbent properties to relevant large-scale performance metrics (e.g. purity and recovery) as well as the cost of capture. *This model can then be used to guide adsorbent development*.

For a feed of 4 $\%_{mol}$ CO_2 at 150 kPa_a, reducing the desorption pressure from 15 kPa_a to 1 kPa_a for ZIF-8 caused a 44 % and 57 % increase in CO_2 purity and recovery, however the cost of capture increased by 3.8 times. Taking Mg-MOF-74 as a candidate to investigate the influence of adsorbent properties at the same conditions, doubling the CO_2 adsorption capacity resulted in a 6 % reduction in cost, however, halving the N_2 adsorption resulted in a 46 % decrease in capture cost relative to the 'unmodified' material. It was also found that at the large scales investigated (> 1000 tons per day) reductions in adsorbent cost from the lab scale price to ~100 $£\cdot kg^{-1}$ do reflect noticeably in the cost of capture due to the significant amount of adsorbent required, validating efforts in scale-up and cost reduction. Below that value, significant capture cost reductions were not seen due to capital and utilities costs becoming the governing factor.

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Using Aerosol Assisted Chemical Vapour Deposition for the Synthesis of MOF Thin Films

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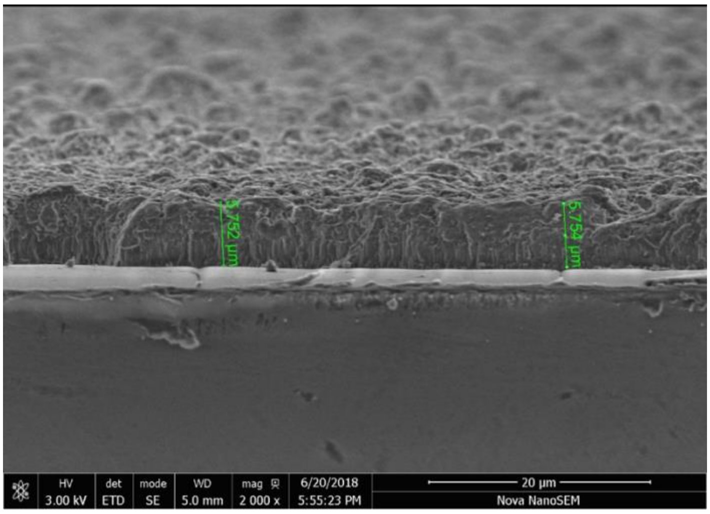
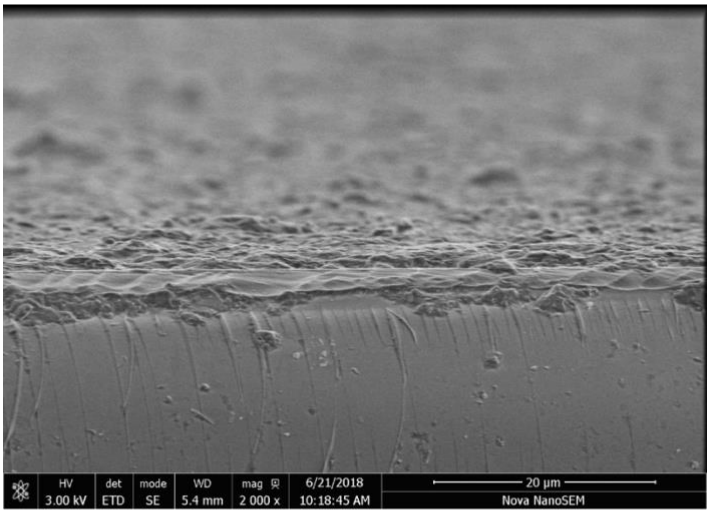
As MOF applications are becoming more diverse, the need for an industry suited synthetic method for MOF thin films is ever more pressing. Currently many methods used for the synthesis of MOF thin films are modifications of the solvothermal synthesis, and as such are not well suited for large scale synthesis. This project focuses on the use of aerosol assisted chemical vapour deposition (AACVD), a technique already implemented in industry for thin film synthesis.

AACVD is a variant of CVD, in which the precursors are transported via aerosol droplets. The precursors are dissolved in a suitable solvent, one that has a low vapor pressure, low viscosity and a suitably high surface tension to endure the formation of an aerosol. This therefore means solvents commonly used to synthesise MOFs, such as water and DMF are unsuitable for the AACVD process, as they are unable to form suitable aerosols.[1] Despite this, one major advantage of AACVD over CVD is that the precursors used do not have to be volatile, they are only required to be soluble in the suitable solvents.[2]

In this project it has been demonstrated that AACVD can offer a simple and scalable synthetic route to adherent and crystalline MOF thin films. The quality of the film was judged by its crystallinity, purity, adherence and coverage of the 15 x 5 cm substrate. Four MOFs, ZIF-8, ZIF-67, Zn-CPO-27 and Co-CPO-27 have been successfully synthesised using AACVD on two different substrates. The two-step process involved the dissolution of the precursors into the solution, and the ultrasonication of the solution into an aerosol, which was carried into the reactor using a carrier gas. Through optimisation it was found that similar conditions were needed for the synthesis of all 4 films. The conditions were designed to limit MOF formation before entering the reactor. Thin film thickness can be controlled by altering the quantity of precursors. Zinc oxide was deposited onto substrate prior to the MOF deposition to investigate the effect on the MOFs adherence. The adherence and coverage of these films make these films promising for applications such as separation and catalysis.





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Soluble Macroporous Polymer Particles Towards OLED technology

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OLEDs (Organic Light-Emitting Diode) are a class of material with high luminescence, low power consumption, fast response rates and ultra-thin & ultra-light. They work across a wide temperature range, and have high resolution properties, compared with traditional LCDs. [1] These properties have seen them applied as materials in mobile phone screens, TV screens, car lights, luminous wallpaper, and many other areas (Figure 1). When designing OLEDs the most important characteristics that need to be tuned are bright fluorescence emission, high quench yields, good conduction characteristics, solution processability, and high thermal & light stability.

Fig 1. The diverse applications of OLED

Microporous organic polymers (MOPs) are a class of highly researched materials with interesting properties such as high specific surface area, low skeleton density, chemical & thermal stability and ease of functionality. [2] Moreover, some MOPs can be designed to be highly conjugated which imparts electric conductivity and fluorescence characteristics into the final material useful properties for OLED. However, a key disadvantage to most MOPs is the lack of solubility in common organic solvents.

Based on the structure of MOPs, we report a solvent-dispersible porous polymer which is synthesized by reversible addition-fragmentation chain transfer mediated polymerisation-induced self-assembly to form a core-shell structure with good film coating properties and fluorescence properties. The polyacrylic acid block imparts dispersibility where the divinylbenzene (DVB)/fumaronitrile (FN) block creates porosity and functionality, has good processability can be used as fluorescence matter (Figure 2).

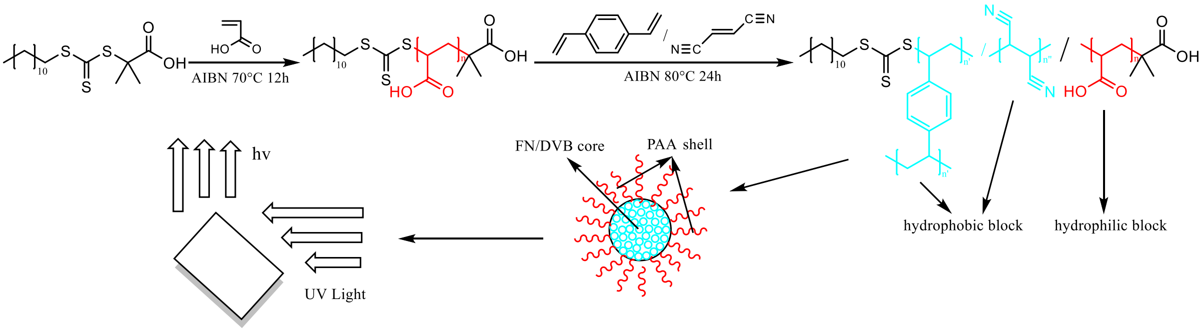

Fig 2. The diblock structure of fluorescence matter

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Temperature-dependent interchromophoric interaction and excimer formation in a pyrene-based metal–organic framework

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Compounds exhibiting tuneable fluorescence emission are considered smart materials as their optical properties can be exquisitely controlled by external stimuli.[1,2] A novel porous pyrene-based metal–organic framework synthesised from Mg^{II} and H$_4$TBAPy,[3] named **SION-7** (Figure 1a), is found to be such a material. The intensity and position of the fluorescence emission band of **SION-7** is temperature-dependent, with a structured emission spectrum characteristic for pyrene-derivative monomers at low temperature of 80 K, which gradually transforms to a structureless red-shifted emission spectrum when the temperature is increased to 450 K (Figure 1b), indicating the presence of excimers due to interchromophoric interaction.[4] Consequently, the fluorescence emission colours gradually change from blue at low to yellow-green at high temperature (Figure 1c). Ex-situ variable-temperature single-crystal X-ray diffraction studies were performed to provide insights into the relationship between the structure and the temperature-dependent interchromophoric interaction between the pyrene moieties.

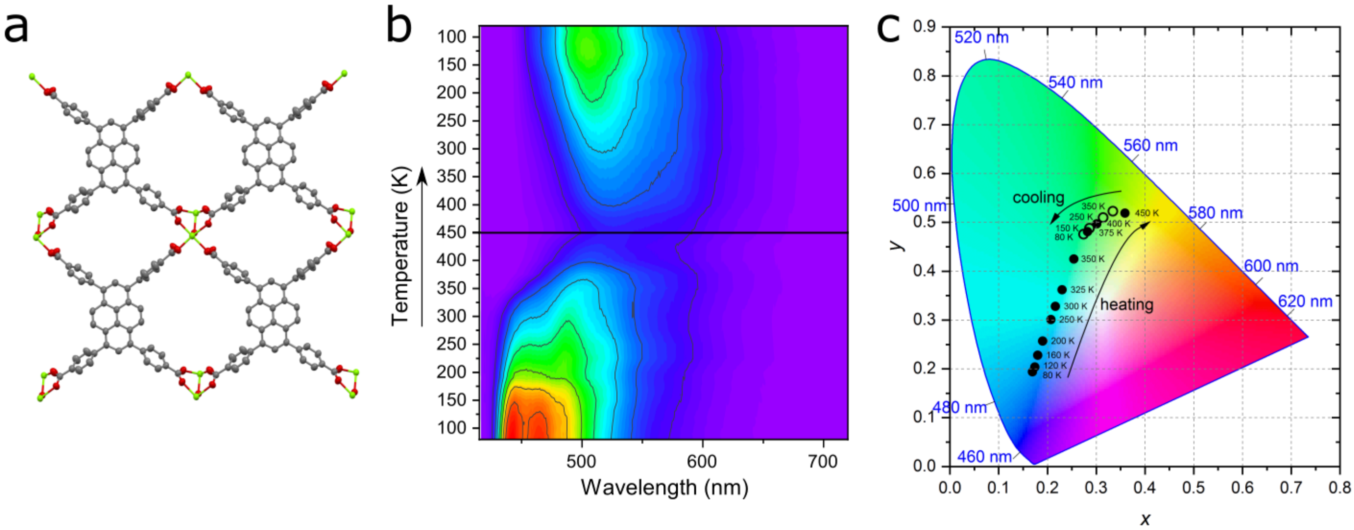

Figure 1. (a) A 2-dimensional layer constructed from HTBAPy^{3-} ligands joined together by Mg^{II}-clusters, constituting the structure of **SION-7**. (b) Fluorescence spectra of **SION-7** measured in the 80–450 K temperature range on heating and cooling. (c) CIE-1931 chromaticity diagram displaying the colour coordinates (x,y) of the fluorescence from **SION-7** during heating (filled circles) and cooling (empty circles) in the 80–450 K temperature range.

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A computational screening of porous materials for biogas upgrading

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Biogas is a renewable energy source that is mainly formed from the anaerobic digestion of organic matter.[1] Mainly composed of CH_4 (50-70%) it also contains large quantities of CO_2 (35-50%) and small amounts of various trace gases such as H_2S, N_2, H_2 and NH_3. In addition, the mixture can contain siloxanes and is generally saturated in water vapour. Across the UK, there are more than 600 biogas purification plants used for generating heat and electricity.[2] Moreover, biogas can be used as a source for transport applications but requires the raw gas to be purified; increasing the CH_4 content while decreasing the CO_2 and trace gas content. Biogas purification (upgrading) generally employs chemical processes such as absorption (water, amine and organic scrubbing), adsorption (pressure and temperature swing) or cryogenic separation to create high purity biomethane streams with a CH_4 content greater than 95%.[3] However, these methods suffer from high investment and operational costs making smaller purification plants less economically viable. To overcome these issues, a great deal of research has focussed on using membranes as promising alternatives for gas separation.

Membranes are commonly made from organic polymers or inorganic materials such as zeolites, metal-organic frameworks (MOFs) or carbon molecular sieves. While each of these materials possess desirable properties, it can be advantageous to combine the organic and inorganic materials into a mixed matrix membrane (MMM). Such membranes possess better mechanical properties than pure organic membranes and high selectivity, permeability and tuneability provided from the inorganic dispersed phase.[4] One of the main challenges of designing new MMMs is choosing an inorganic phase which is both compatible with the organic polymer and provides high permselectivity. For example, MOFs can hypothetically be made from an infinite number of different metal-ligand combinations, giving rise to varying structural and chemical properties. As such, it is difficult to determine which polymer-MOF combination will lead to an MMM with good performance for biogas upgrading. Furthermore, it is not feasible or cheap to synthesise different membranes based on a "trial and error" approach. In these situations, the use of high-throughput computational modelling can be an effective and rational means of discovering real and hypothetical candidates for separation and storage applications. [5-8]

Herein, we use a combination of computational tools to screen the Cambridge structural database (CSD) and the CoRE COF database for biogas upgrading. Using a multi-level screening protocol, we identify the best candidates for these separations and use the large datasets to make structure-performance relationships which may ultimately aid the design of future materials with exceptional biogas upgrading capabilities.

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Fabrication of Metal-Organic Framework Thin Films for Energy Applications

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Metal organic frameworks (MOFs) are hybrid materials composed of inorganic and organic building blocks, in which metal centres are coordinated to organic linkers. Applications such as chemical sensing, gas storage and catalysis have been proposed due to the large surface area, high porosity and tuneable functionality of these materials in the bulk form.[1] One of the most recent advances in the MOF research field is the development of structures that exhibit electrical conductivity.[2] This subclass of MOFs comprises metal nodes coordinated to highly conjugated ligands, which facilitate overlap between the metal and ligand orbitals enhancing the electronic properties of the material. To implement their practical use the synthesis and study of ultrathin MOFs nanosheets[3] have recently been reported; however, the processing at large scale of these materials is still a challenge.

In this work we present different approaches to the growth of conducting thin films of the 2D MOF $Cu_3(HHTP)_2$ (where HHTP = 2,3,6,7,10,11-hexahydroxytriphenylene). The electrical conductivity of this MOF has been reported to be 0.2 S cm-1, which is among the best conducting MOFs. Bulk $Cu_3(HHTP)_2$ was synthesized solvothermally according to the literature[4] and we have subsequently fabricated thin films of this important framework by dip coating, spray coating and electrochemical techniques. The characterization of the powders and thin films were conducted by X-ray diffraction, Scanning Electron Microscopy, UV-Vis Spectroscopy and Thermal Gravimetric Analysis.

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

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Nanoporous molecular crystals are materials constructed from discrete molecular components held together by weak non-covalent interactions which display permanent porosity upon guest removal.[1] These materials can be split into two classes defined by the nature of their porosity. Intrinsic porous materials derived from shape-persistent organic cages,[2,3] or extrinsic porous materials, where non-porous precursors self-assemble to form a porous structure due to inefficient crystal packing.[4,5]

Herein we present a series of nanoporous molecular crystals based on trityl-protected pyrazolecarboxylic acid ligands coordinated to copper acetate paddlewheel dimers. These molecular clusters assemble further *via* weak non-covalent interactions to form extrinsically porous crystals with up to 42% solvent accessible volume. These materials are found to display guest-responsive behaviour, resulting in the expansion and contraction of pores to fit the encapsulated guests as determined by powder diffraction. Introduction of methyl groups into the molecular precursor is found to modulate the degree porosity and guest response, affording the potential to tailor porosity selectivity and substrate sensing. Furthermore, these materials rapidly crystallise at room temperature (<10 s) with high efficiency (>80 %).

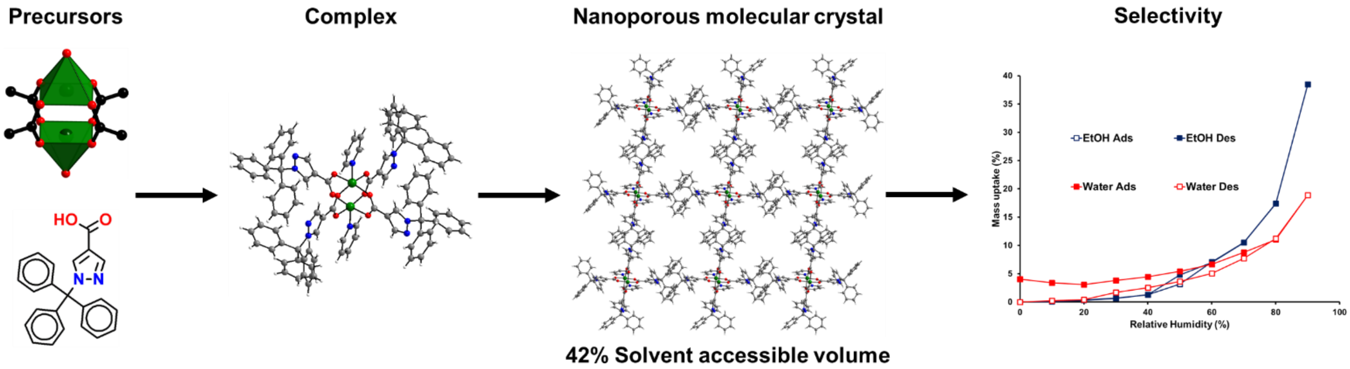

Figure 1. Hierarchical assembly and selectivity of the [$Cu_2(Trt\text{-}PzCO_2)_4$] materials.

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Surface Modification of Metal-Organic Frameworks with Substituted Azobenzenes for Controlled Hydrogen Trapping and Release

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In recent years, there has been a surge in research activities aimed at mitigating climate change. In this context, hydrogen is regarded as a clean alternative which can potentially replace fossil fuels. A key challenge in the development of the hydrogen economy is hydrogen storage. Current technology relies on high pressure tanks and cryogenic temperatures,[1] which can lead to safety concerns and energy inefficiency. Metal-organic frameworks (MOFs) are a relatively new class of porous materials which has been widely studied for hydrogen storage applications due to their excellent properties such as high surface area, high porosity and tunable pore surface.[2] However, oftentimes these materials can only store hydrogen at very low temperatures (*e.g.* 77 K). A new approach is to develop MOFs that can adsorb hydrogen at low temperatures and have the ability to trap and retain this gas at higher temperatures (*e.g.* 298 K). One possible way of achieving this is by decorating MOF surfaces with photo-responsive substituted azobenzenes. Although azobenzene-containing MOFs have been studied before, these systems were only used for the controlled release of CO_2 and organic compounds.[3,4] Our work aims to extend the application of azobenzene MOF systems to hydrogen trapping by incorporating substituted azobenzenes on the MOF surfaces. The grafting of these photoactive compounds on the MOF surfaces can be accomplished *via* post-synthetic modification (PSM), a process in which a pre-formed MOF is transformed into a new MOF *via* crystal-to-crystal transformation.[5] PSM is of interest as it can allow for the formation of functionalised MOFs which cannot be formed using direct synthesis. PSM can also be used to introduce specific functionalities in the MOF pores thus altering their physical and chemical properties such as gas storage capacities.

We will present an overview of the development of the substituted azobenzene MOF systems, along with insights into their gas uptake capacities. The photoactive moieties on the MOF surfaces are anticipated to undergo a reversible change in structure to induce controlled and reversible pore blocking of molecular hydrogen (H_2). This behaviour would either allow or obstruct the movement of H_2 to or from the MOF pores. This new approach can potentially increase the hydrogen storage capacity in MOFs at room temperature, making economical storage of hydrogen possible in the near future.

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Fused-ring pyrazoles and pyrazolates: new linkers for “strong and stable” MOFs

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The chemical stability of Metal-Organic Frameworks is still an area where improvement is needed before these promising materials can achieve broader uptake in industrial processes. For MOFs based on late first row *d*-block metals, hydrolysis at the coordination sphere is usually the prime cause of framework collapse under normal operating conditions.[1] Ligands capable of forming stronger metal-ligand bonds, or those capable of stabilising the coordination sphere through outer-sphere hydrogen bonding, are therefore attractive alternatives to the classic carboxylate-rich coordination spheres prevalent in most conventional MOFs. Among a wealth of possible donor groups, pyrazole is an attractive ligand species as it can fulfil both of these roles; the pyrazolate anion forms extremely robust coordination bonds,[2] while the neutral *1H*-pyrazole moiety frequently engages in rigidifying hydrogen bonding interactions.[3]

To expand the scope of pyrazole-based MOFs beyond symmetric polypyrazoles and carboxypyrazoles, we have explored a variety of fused-ring pyrazole species. The additional scope for substitution offered by fused-ring pyrazoles gives new opportunities for ligand-centred functionality (Figure 1). Access to such systems can be achieved in simple high-yielding synthesis from either *ortho*-methylanilines or saturated cyclic ketones. In particular, our aim has been to install additional coordinating groups using pyrazolopyridines or carboxyindazoles,[4] increasing hydrophobicity by fusion of cyclic alkanes, and appending photophysical antennae in pyrazolonaphthalenes and pyrazoloquinolines.[5] In each case, the impact of outer-sphere hydrogen bonding on both the framework topologies and chemical stabilities is evident, and balanced against the competing drive for strong metal-pyrazolate bonds from the deprotonated species.

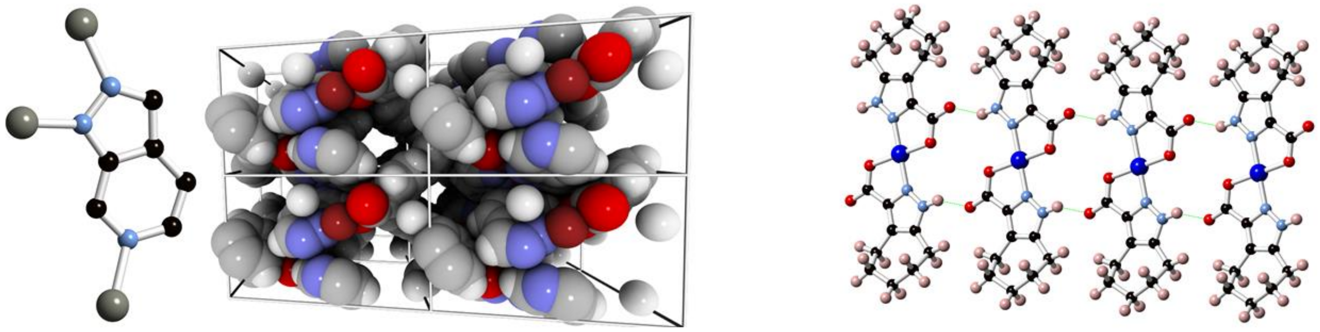

Figure 1 Examples of coordination from fused-ring pyrazoles into extended coordination architectures, showing pyrazolo[3,4-c]pyridine (left) and a cyclohepta[c]pyrazole carboxylate (right).

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Inherent Ethyl Acetate Selectivity in A Trianglimine Molecular Solid

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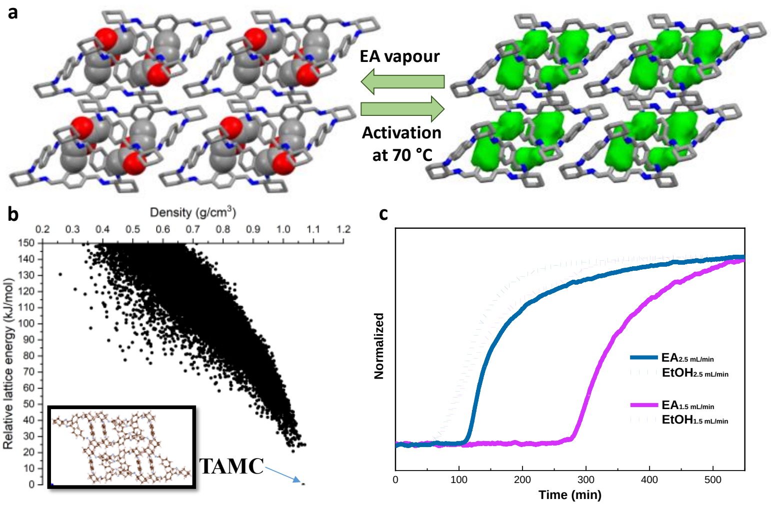

Figure 1. (a) Single-crystal structures: EA@TAMC (left); α-TAMC (right); (b) CSP energy-density plot generated using α-TAMC; (c) Breakthrough profiles for ethanol/ethyl acetate mixture at 25 °C. Colors indicate sorbate rate of flow: (blue) 2.5 mL/min; (purple) 1.5 mL/min. Total rates of flow: both 5 mL/min with carrier gas of N_2.

Ethyl acetate (EA) is an important chemical raw material and solvent. It is also a key VOC (volatile organic compound) in brewing industry as well as for the early detection of cancer.[1-3] Material that has pre-dominate selectivity over ethyl acetate is highly desirable for its separation and detection. Here we reported a well-studied trianglimine macrocycle (TAMC) can selectively adsorb ethyl acetate by forming a global minimum energy structure in solid state, as confirmed by crystal structure prediction. Moreover, the guest-free TAMC molecules pack in their minimum energy fashion containing perfect voids for ethyl acetate, which further contribute to the high selectivity for ethyl acetate over ethanol (EtOH). With this "inherent" high selectivity, breakthrough experiments have suggested that TAMC can be used to separate ethyl acetate from its azeotropic mixture with ethanol, a very challenging industrial separation[4]. This material can be readily synthesised from cheaper starting materials and has shown good reliability after multiply adsorption cycles, holds high promise for actual separation or detection application in the future.

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Metal-Free activated boron nitride as an effective adsorbent for carbon capture

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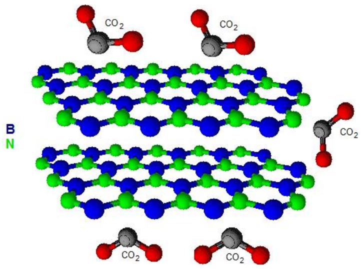

Limiting CO_2 emissions into the atmosphere is one of the major climate change targets. Carbon capture and storage plays an important role in industry for achieving significant reduction in atmospheric CO_2 emissions[1]. Among the wide range of technologies, solid sorbents by post-combustion processes are regarded as being green and economic technologies. This study aims to develop high-performance and low-cost adsorbents for post-combustion carbon capture[2,3]. More recently, literature has emerged that porous boron nitride is an ideal candidate for carbon capture and separation. However, the majority of these publications have led to a low CO_2 sorption capacity[4,5,6]. To fill this gap, we produced activated metal-free boron nitride (BN) adsorbent by adding a surfactant into precursors during the synthesis strategy. By tuning the variety of surfactants (such as F127, P123) and using different nitrogen sources (e.g. melamine and urea), the adsorptive performance of activated BN was optimized. The CO_2 uptake of optimized BN-P123 is 2.83 mmol g^{-1}. This value significantly higher than pristine porous BN. Moreover, the excellent reusability of the material has also been confirmed by performing several cycles of operation. The current synthetic approach opens up the route to modify porous boron nitride structures to be applied as effective solid sorbent for CO_2 capture.

Keywords: porous materials, activated boron nitride, adsorption, carbon capture

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Predicting Adsorption of Polar and Non-polar Adsorbates in Metal Organic Frameworks with Open Metal Sites

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Metal-Organic Frameworks (MOFs) are porous materials of great potential for adsorption applications due to their many desirable characteristics such as large surface areas, high porosity and high degree of tailorability. Recent years have seen an exponential increase in the number of computational studies aiming to predict adsorption in MOFs, including efforts devoted to large-scale computational screening. By identifying the most promising candidates for particular applications from amongst thousands of candidate structures, these approaches can potentially reduce the time and money currently spent on experimental testing of MOFs, fast-tracking their translation into commercial applications. However, a crucial but often overlooked fact is that conventional molecular models for adsorption in MOFs neglect important physics of the process, and thus can lead to spectacularly inaccurate predictions. This is particularly the case for MOFs that possess coordinatively unsaturated sites (CUS), or open metal sites – the specific nature of the coordination bonds formed by these sites with particular adsorbate molecules is not captured by standard force fields. The impact of neglecting these interactions can be huge, particularly considering that MOFs that contain CUS are among the most promising materials for gas storage and separation applications, precisely due to these strong and selective binding sites[1].

This work reports the outcome of a systematic effort in our research group to develop a generally applicable and transferable approach for incorporating specific coordination-type interactions between CUS and adsorbate molecules into standard molecular models, based on a combination of quantum mechanical calculations with classical Monte Carlo simulations. Crucially, our approach makes use of only a small number of QM calculations in the vicinity of the CUS, thus keeping computational expense low, while making use of conventional classical approaches to describe interactions away from the CUS[1,2]. We demonstrate generality by applying our model to describe adsorption of both polar and non-polar adsorbates (paraffins, olefins, nitrogen and carbon monoxide)[3], and demonstrate transferability by predicting adsorption in different MOFs with the same type of metal unit (copper paddlewheel)[4]. In all cases, excellent agreement with experimental adsorption isotherms is obtained. This means that the procedure is amenable for incorporation into large-scale screening efforts, and has the potential to greatly improve the accuracy of computational screening of MOFs for adsorption applications. Overall, our new model provides detailed insight into the molecular level adsorption mechanisms on MOFs with CUS, and constitutes a useful tool to design new materials for challenging separations.

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Oxygen-doped nanoporous carbon materials toward CO_2 capture

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Porous materials that can be generally made of inorganic, organic, and inorganic–organic composite materials play a key role in many new technologies. For example, pore walls are usually able to interact with atoms, ions, and molecules or to load and hold solid particles and liquid and gas molecules making porous structures highly interesting for frontier research. Porous carbon materials have been vastly utilized as gas adsorbents for their advantages such as high surface area and pore diversity, cheapness, high mechanochemical stability against high temperature and humidity, sustainability, and good biocompatibility.[1]

The extensive and continuing use of fossil fuels throughout the world has led to the fast and large accumulation of carbon dioxide (CO_2) in the atmosphere. Both CO_2 and methane are well-known as greenhouse gases and the further increase of CO_2 emission causes global climate changes and serious greenhouse effects. Therefore, CO_2 capture is a major issue to protect environment and it must be significantly addressed. Among various strategies developed for the CO_2 capture, physisorption via porous materials possessing a high surface area and pore volume is one of the most important techniques, because the porous materials represent high adsorption capacity at ambient temperature.[2-4]

Here, we fundamentally investigate the production of a series of porous carbon materials differing in oxygen content morphology obtained by the thermal treatment of benzoic acid and benzoate derivatives for CO_2 capture application. The prepared porous materials have been characterized by SEM, STEM, TEM, Raman, TGA, FT-IR, elemental analysis, XPS. As a representative sample, the porous carbon obtained from potassium trimesate with a surface area of 1530 m^2 g^{-1} showed CO_2 uptake of 4.4 mmol/g at 25 ^{o}C and 1 bar.

We believe that our study provides new infornmation for better understanding of the relationship between morphology and oxygen content of porous carbons for CO_2 capture at different pressures ranging from 1 to 10 bar.

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Controlling the Geometry and Surface Chemistry of Nanoclusters Embedded in Metal-Organic Frameworks with Linker Functionalisation

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I would like to apply to present a poster at the 2019 UK Porous Materials Conference about the embedding of Pd nanoclusters (NCs) into the pores of metal-organic frameworks (MOFs) and the impact of the functionalisation of the organic linkers used in building the frameworks.

MOFs are known for their high porosity, with an abundance of relevant inorganic and organic building blocks that give way to numerous different pore geometries[1]. These pores offer suitable environments for the confinement of metal NCs, producing materials capable of acting as catalysts for a wide variety of reactions[2]. The anchoring of the NCs in the pores increases the cyclability of the catalyst with the added benefit of increased activity due to strong host-guest interactions between the NCs in the pores and the framework[3].

We have been working on embedding Pd NCs into a series of MOFs of the UiO topology with variations in the functional group on the organic linker. These MOFs consist of zirconia-like nodes connected by benezenedicarboxylic acid linkers, with the capability to functionalise the benzene ring[4]. The MOFs that we have synthesised are referred to as X-UiO-66 (X= -H, $-NH_2$, Br, Cl_2 and $(-OH)_2$) and each have undergone loading with Pd.

We have set out to demonstrate the presence of strong host-guest interactions between these Pd NCs and the functional groups on the linkers in the MOFs. DFT calculations have been used to calculate the enthalpy of adsorption of Pd atoms and predict the effect of the presence of the functional groups on the formation of the NCs. According to the results Pd would embed in the pores of the $–NH_2$ and –Br UiO-66 of those that were being investigated. A series of characterisation methods were used to confirm whether or not this was the case with the prepared samples, including TEM to verify particle sizes. Well dispersed Pd NCs were observed in NH_2-UiO-66, however none were immediately observable in Br-UiO-66. EDX showed the presence of Pd in the –Br MOF. FTIR spectroscopy has been used to probe changes in molecular vibration that would indicate presence of host-guest interactions. For NH_2-UiO-66, the peak corresponding to the N-H bend at 1430 cm^{-1} has a much lower intensity in the Pd-laden MOF, implying that a Pd-N bond formation has occurred to restrict this vibrational mode. The extent of the interactions has been probed using XPS, looking at shifts in the oxidation states of the Pd NCs and the functional groups.

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Surface functionalisation of porous boron nitride to increase hydrolytic stability for use in molecular separations

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Industrial separation processes account for 10-15% of the global energy consumption[1]. The energy cost of large-scale gas and liquid separation processes (e.g. distillation) could be significantly reduced by moving towards adsorption processes, *i.e.* using porous materials to separate molecules based on size and/or chemistry. An example of an adsorbent is porous boron nitride (BN): this material exhibits high surface area, high porosity and benefits from greater oxidative and thermal stability than common carbonaceous adsorbents[2]. In this project, we are exploring the potential of porous BN as an efficient and recyclable adsorbent for molecular separations at industrial scale.

Recently, our group developed a new method to produce porous BN with enhanced surface area, tuneable porosity[3] and promising liquid and gas separations performance. To further advance the use of porous BN, we must investigate its chemical stability. In this regard, the effect of moisture is particularly important, given the prevalence of water in several chemical separations and the fact that preliminary tests in our group point to the instability of the material in presence of water[4].

Considering this aspect, we have initiated studies to functionalise the surface of porous BN to enhance hydrophobicity and resistance to moisture. Specifically, the surface chemistry of porous BN was modified either *via* silylation or *via* coating followed by fluorination. The samples were characterised before and after functionalisation using FTIR, XRD, XPS and SEM-EDX. The changes in hydrophobicity/hydrophilicity were monitored using water vapour sorption. In addition, the porosity and crystallinity of the material was probed before and after exposure to moisture and liquid water with nitrogen sorption. The results of this work will be discussed during the presentation.

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MOF biomineralisation: a synthesis inspired by nature

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Metal-Organic Frameworks (MOFs) tend to be one of the most appealing family of porous materials. Their unique structures and properties, as well as their versatile porosity, make MOFs the best candidates for a variety of different applications, such as gas storage, separations, catalysis, drug delivery and molecular recognition.[1]

Lately, more and more studies have focused on the addition of biological molecules in MOFs' syntheses in order to control their final morphology and topology. A variety of biomolecules including amino acids, peptides, proteins and nucleotides have been used either as building blocks, templates or guest molecules to guide the growth or the well-organized design of inorganic nanomaterials.[2,3] Although these biomolecules can improve the features of the resulting materials following bio-inspired synthetic routes, the interactions between the two interfaces remain unknown.[4]

In this study, we report the use of short oligopeptides, identified by the combinatorial phage display method, on syntheses of different MOFs in order to control the crystallinity, crystal morphology and framework topology of the final materials. Briefly, we focused on using different defined peptide sequences, holding the role of crystal-directing agents, to influence MOF synthesis in a wide range of crystallization times and varying crystal nanoshapes under mild, environmentally benign conditions.

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Understanding the impact of template function on pore-wall chemistry in templated amorphous silicas

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Templating of porous materials is a key route towards otherwise hard to access pore types. For siliceous materials, templating is found naturally as well as used artificially to produce structures with features on a range of length scales from 1-1000nm. This largely depends on the type of template used to produce the feature. Simple small organic molecules such as ammonium salts imprint porosity only through negative space, providing templating in the 0-2nm range. Self-assembling molecules such as surfactants enable templating at larger length scales, creating materials with ordered pores ranging between 2 and 25nm. Biological templates with multiple functionality enable even more complex structures on a variety of hierarchical length scales, creating incredibly ornate nanostructures with biologically active pores.

Although the relationship between template structure and silica material structure has been well studied, the relationship between template functionality and eventual silica chemistry is a relatively unexplored field. The majority of work in these fields has focused on classical surfactant templates, showing for example how varying functional group chemistry can control the degree of pore order, or tuning the reagent interactions can control eventual surface acidity. Here we present recent work on amorphous porous 'bioinspired' silicas - materials made using artificial analogues of biological templates.[1] Using mild solvent extraction techniques to control template concentration at the as-made interface, we probed template-silica surface chemistry of these materials, both to assess specific template-silica interactions and silica surface acidity.[2]

When comparing against prior analyses of surfactant-silica interactions, a discrepancy appears - bonding between bioinspired templates and silica occurs at less favourable Si-O-Si surface sites instead of the expected Si-OH sites. Furthermore, binding to this less favourable site also disagrees with simulations of the bioinspired templates on silica surfaces. We reconcile these findings as a further function of the template chemistry: unlike surfactant molecules, bioinspired templates are catalytically active towards silica polymerisation, leading to unexpected further polymerisation even after they are encapsulated within the silica framework. Use of catalytically active templates in this way could potentially be an important additional tool in templated materials design, directly producing passivated pore surfaces to improve stability.

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Biocompatibility Screening of Metal Organic Frameworks

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The robustness of MOFs, along with the ability to tune their properties, makes them promising candidates for utilisation in a variety of applications including biomedicine[1]. The plethora of available metal ion precursors and linkers gives the opportunity to tune the cytotoxicity of MOFs so that they combine the advantages of each of their components (low cytotoxic metal precursors and biocompatible organic linkers). One of the most commonly suggested biomedical application of MOFs is their use as drug delivery systems (DDS). Drugs or therapeutic molecules can be accommodated in their pores and protecting or targeting groups can be attached to their surface. Even though MOFs exhibit many advantageous properties for use as DDS, their potential cytotoxicity may limit their use in these types of applications.

Testing the biocompatibility of a compound is a very common practice during drug delivery research however, when it comes to applying the same techniques for nanomaterials it can prove challenging. Herein, we present an in vitro biocompatibility screening of some of the most commonly used MOFs proposed for such applications. We decided to test many different MOFs consisting of various metals and linkers to cover a wide chemical space and investigate how different properties (size, surface chemistry, building components) affect the biocompatibility of MOFs. For this goal to be achieved we tested a variety of techniques. Firstly, we employed metabolic assays which are the most common techniques used in literature when it comes to testing the biocompatibility of MOFs. In order to further validate our results, we monitored the proliferation of cells utilising an innovative method that allows real-time observation of cell growth/death. Finally, we further studied the cytotoxicity of MOFs along with their cellular internalisation with Flow Cytometry. This way we managed to establish that different MOFs exhibit different cytotoxicity profiles and levels of toxicity, with the new technique providing overtime information on cell and Flow Cytometry giving an insight to the uptake of MOFs from different cell lines.

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Modulating Proton Diffusion and Conductivity in Metal-Organic Frameworks

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Proton-exchange membrane fuel cells (PEM-FC) show great potential for generating clean electrical power from hydrogen gas for use in applications such as transport. A key constraint on the operating efficiency of PEM-FCs is the performance of the membrane material, which must allow selective permeation of protons across the cell. Metal-Organic Frameworks (MOFs) present a viable alternative to existing PEM materials, due to their high stability, tunability and crystallinity. The functionalisation of the ligand with acidic groups (such as -COOH, $-PO_3H_2$ and $-SO_3H$) is one method to provide MOF materials that support efficient proton transfer pathways. Herein, we report the progressive design and synthesis of three organic linkers containing multi-carboxylic acid functionality which were used to prepare barium MOFs.[1] The measured proton conductivity was found to directly correlate with the number of accessible carboxylic acid groups, with a two-fold increase in conductivity from MFM-511 to MFM-512. Performance of the MOFs were also highly dependent on the humidity of the environment, with a direct link found between water uptake capacity and proton conductivity at 99% RH. To probe the nature of proton dynamics, quasi-elastic neutron scattering was undertaken at various temperatures on MFM-512. It was found that proton transport within the MOF is mediated by “free diffusion inside a sphere”,[2] with a sphere radius of 1.90 Å corroborating the hydrogen bonding distances observed crystallographically. This confirms that the inclusion of free carboxylic acid groups within the pores of MOFs is an efficient albeit synthetically challenging strategy to improve proton conductivity.

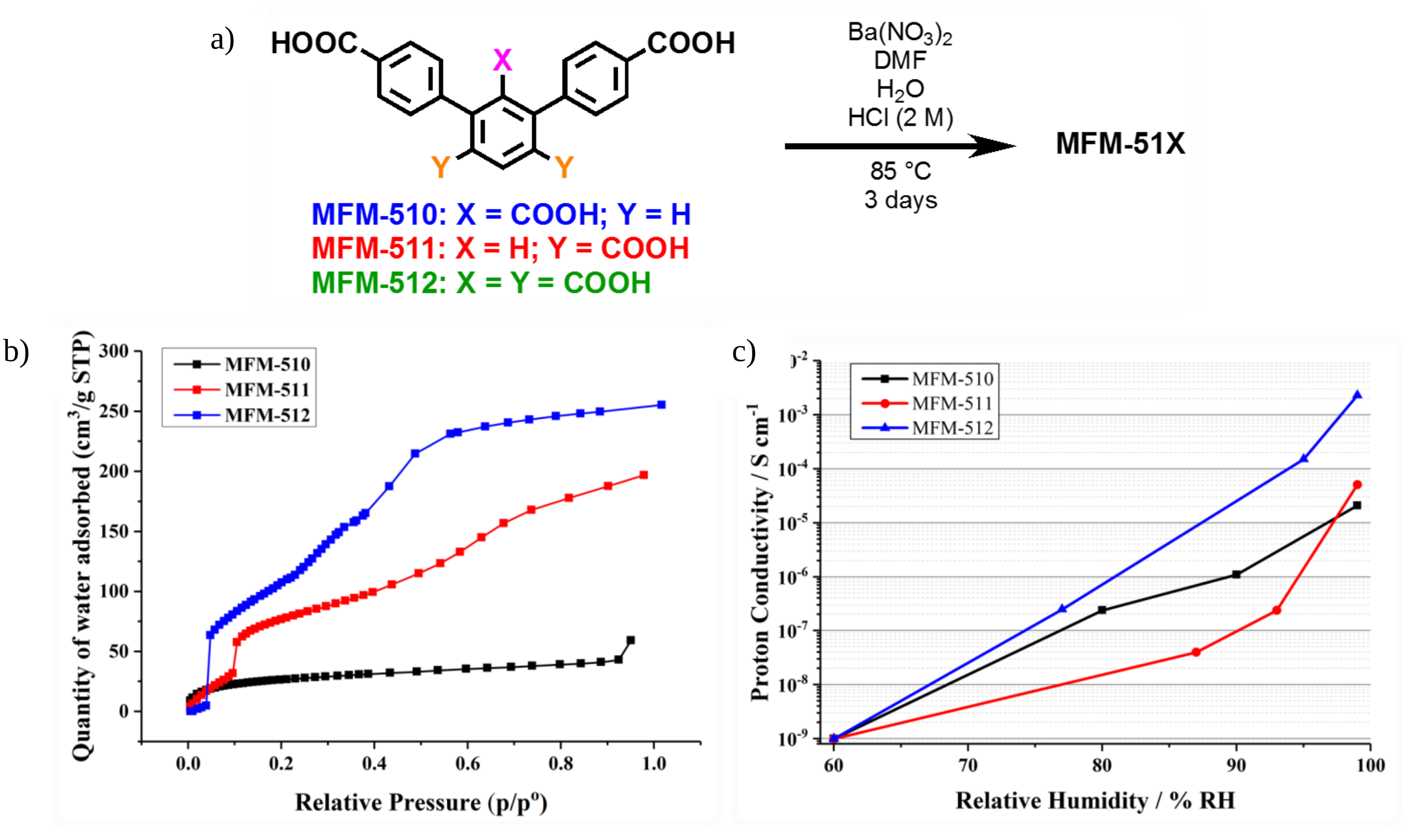

Figure 1: a) Synthetic route to barium MOFs; b) Water sorption isotherms for MFM-51X; c) Proton conductivity as a function of relative humidity.

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Defect Engineered Metal-Organic Frameworks for Carbon Capture: Amino Acids as Functional Groups for improving CO_2 uptake in Zr-MOFs.

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Zirconium-based metal-organic frameworks (Zr-MOFs) have been widely reported as displaying excellent stability at varied temperatures and in the presence of water. The latter particularly makes them a potential candidate for industrial carbon capture, where water is omnipresent and difficult to exclude without adding significant cost or effort to a process. An ongoing obstacle to their adoption to replace liquid amine solutions is their moderate CO_2 capacity which is only a fraction of some of the top-performing MOFs reported.[1] Conversely, the frameworks with the highest reported CO_2 capacity often display limited stability in "real-world" conditions. While there have been widely reported efforts to use ligands with pendant amine groups[2] or direct grafting of ethanolamines to metal-clusters,[3] which show an improvement in the CO_2 capacity, we aim to first engineer defects in the structure of Zr-MOFs and fill those defects with amine functionalities.

Defective structures are common in the reported Zr-MOFs and the ability to generate them in a controlled manner by the addition of monocarboxylate species to the reaction mixture is well documented.[4] By generating large numbers of these defects, sites suitable for the post-synthetic grafting of molecules with amino-functionalities that can act to increase the CO_2 capacity of the materials are created. Use of amino-functionalised mono-carboxylates of aromatic, heterocyclic and aliphatic nature in defective UiO-66 leads to a reduction of surface area and pore volume yet the uptake of CO_2 and selectivity for CO_2 over N_2 are improved. [5] Current work is aimed at expanding the scope of the method to other frameworks such as MOF-801 and MOF-808.

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

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

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

Crystal Growth and Form of Lattice-Mismatched Core-Shell Metal-Organic Framework Revealed by In Situ Atomic Force Microscopy

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Porous metal-organic frameworks (MOFs) form the largest family of crystalline porous material that is commanding great interest due to their diverse array of form and function.[1] One class of these material that is still somewhat rare, but has considerable potential structural and functional diversity, are core-shell lattice-mismatched MOFs in which the shell MOF has a different framework composition and unit cell from the underlying core MOF to which it is directly connected. Currently, information is known concerning the bulk crystal morphology of these core-shell MOFs and the diffraction details of the shell MOF.[2] However, little is known concerning the actual nanoscale growth mechanism of the lattice-mismatched shell MOF over the core MOF, and the influence on the crystal form of the shell MOF resulting from such mismatch. Herein, two isoreticular pillared Kagome net MOFs, $[Zn_2(bdc)_2(bpy)]$ (a = 21.619(8) Å, c = 14.104(5) Å)[3] (bdc = 1,4-benzenedicarboxylate, bpy = 4,4'-bipyridine) and $[Zn_2(bdc)_2(dabco)]$ (a = 21.620(1) Å, c = 9.6282(8) Å)[4] (dabco = diazabicyclo[2,2,2]octane) that have similar a-lattice parameters but a ~32% mismatch in c-lattice parameters were selected as the core and shell MOF respectively (see figure 1b). Atomic force microscopy was able to captured 2D nuclei and/or growth islands of the shell MOF on all faces of the core MOF to reveal the growth mechanism. The work shows the mechanism through which the shell MOF overgrows core terrace height mismatches is via a process of growing a shell layer terminated by a core terrace edge before allowing overgrowth of subsequent continuous shell layers as illustrated in figure 1c. The crystal form of the shell MOF is heavily influenced by the lattice mismatch which hinders continuous spreading of the interfacial and subsequent shell layers on some facets. The results from in situ AFM described the crystal growth versatility of MOFs to accommodate lattice mismatch and to give possible many more defects in the core-shell MOF than either of the component MOFs.

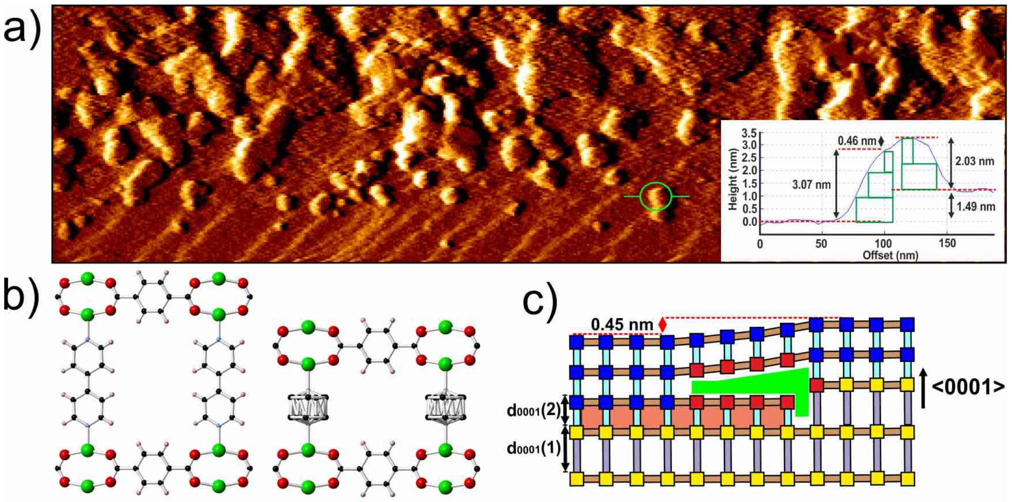

Figure 1. AFM deflection image and its cross-section analysis (a) with the crystal structure (b) of core (left) and shell (right) MOFs. Schematic illustration of shell growth mechanism on the surface of core crystal MOF.

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Fluorescent surface functionalisation of metal-organic framework nanoparticles to target hard-to-treat cancers

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The survival rate of cancer patients has significantly increased over the past four decades, owing to advances in pharmacological and surgical interventions, as well as improved patient care. Nevertheless, there exists a number of hard-to-treat cancers, such as those of pancreatic, brain, lung and oesophageal origin, that are still defined by low survivability and whose survival rates have remained largely unaffected over the same period of time. These cancers are difficult to remove surgically, they are highly invasive and drugs cannot efficiently reach them. Hence, other approaches have been investigated for their treatment through the targeted delivery of drugs with the use of nanoparticles. Metal-organic framework nanoparticles (NMOFs) have currently been established as the ideal biocompatible candidates to fulfil this role as they offer high drug loading capacity, targeting efficiency through surface functionalisation and increased bioavailability of drugs through controlled drug release in the delivery site. Thus, NMOFs have been proposed as a new delivery tool to transport drugs to tumours in large concentrations and with high specificity, minimising unwanted off-target toxicity. Here, we propose the use of a fluorescent functionalised NMOFs to readily assess drug loading capacity, targeting specificity and cellular internalisation for hard-to-treat cancers. Specifically, we employed a photochemical approach to surface functionalise the biocompatible NMOF UiO-66 with a fluorescent linker. This photoreaction was established as a self-reporting system, where the fluorescent product could be readily used to evaluate both the functionalisation process and drug loading capacity of the NMOF. Furthermore, the resulting fluorescent NMOF allowed for the study of cellular internalisation of the functionalised UiO-66, targeting specificity and subsequent assessment of the drug release profile. Our results suggest that this self-reporting system could be employed for the assessment of NMOF surface functionalisation and cancer drug loading processes, as well as for the study of cellular internalisation, targeted drug release and organismal biodistribution.

Nanoporous polymers and composites for energy applications

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This poster aims at demonstrating the versatility of nanoporous organic materials for a broad range of energy-related applications.

In particular, solid-state hydrogen storage promises to significantly improve upon the conventional forms of storage technologies such as liquid or compressed gas. In recent years a remarkable research effort has been devoted to the development of adsorbents with very high surface areas, such as metal-organic frameworks (MOFs), covalent organic frameworks (COFs) and amorphous organic polymers. A frequent drawback of these materials is that they exist in powder or particulate forms, which limits their processability and mechanical properties. In this context, materials combining solution-based processability, good mechanical strength and flexibility, and high hydrogen uptake capacity are highly desirable.

This poster will underline recent work on the use of polymers of intrinsic microporosity (PIMs) as supporting matrices for high surface area adsorbents (fillers), and the resulting composites combining the processability of PIMs with the high hydrogen uptake capacity of the fillers.[1,2] The long-term stability of PIMs for hydrogen storage purposes was also investigated, shedding light on potential for realistic applications.[3]

Other applications of nanoporous materials in the field of energy will be discussed, with focus on energy harvesting and catalysis. The importance of their porous and electronic structures will be emphasized in this context.

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Poster presentation

Title: **How Fermi level shifts impacts photocatalytic enhancement in 2D-2D MOF-based heterojunctions**

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Solar fuels have a role to play in the long-term vision for clean energy. To realise their potential, researchers must identify a relevant routes to producing them. Photocatalysis has been identified as promising option. Yet, to reach acceptable solar-to-fuel efficiencies, one must overcome challenges, such as high charge recombination and limited light adsorption.

In this regard, the formation of heterojunctions effectively separates charges spatially. For instance, MOF-based heterojunctions perform better toward gas phase CO_2 photoconversion than their individual components.[1-3] A recent proof-of-concept study highlights the importance of the interface geometry in MOF-based heterojunctions to reduce charge recombination.[3]

Building on this finding, we have launched an optimization study on MOF-based heterojunctions. To promote charge transfer across the heterojunction, we have focused our attention on 2D-2D heterojunctions as they offer high contact area. In addition, the use of 2D MOFs positively impacts CO_2 fixation and activation. In this study the 2D visible light photocatalyst graphitic carbon nitride acts as one heterojunction component. The 2D MOF ZIF-67 acts as the other. We have tested the heterojunction for CO_2 photoconversion under UV-Vis light irradiation. To enable efficient charge transfer across the heterojunction, a thermodynamic favorable band energy alignment between both components is necessary. In this study, we demonstrate the impact of Fermi level shifts on photocatalytic efficiency during heterojunction formation. We show the importance of considering those effects while developing new MOF-based heterojunctions. We studied these effects through a combination of spectroscopic analyses (i.e. XPS, DRS UV-vis) along with CO_2 photoreduction testing the gas phase.

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Synthesis of non-linear phosphonic linkers for producing porous metal-organic frameworks

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Phosphonic acids are of particular interest for use as linkers in MOFs due to their increased chemical and thermal stability when compared with carboxylic acids. Another interesting point on phosphonic acids is the increased number of bonding modes, which is due to the divalent and tridentate nature of the structure. Early work on these phosphonates tended to result in densely packed, layered structures, in part due to the linear or non-dimensional nature of the linkers.[1,2] One method of getting around this issue is mixed-ligand synthesis, but this often requires much greater control of the parameters of the reaction.

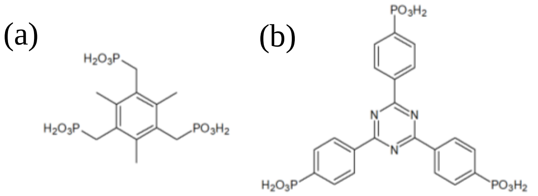

Figure 1. The structures of non-linear linkers (**a**) 2,4,6-trimethylbenzene-1,3,5-triyl) tris(methylene)triphosphonic acid), and (**b**) 2,4,6-tri-(phenylene-4-phosphonic acid)-s-triazine.

Since these early structures, there have been a number of notable examples of permanently porous metal phosphonate structures which incorporate non-linear linkers. Notable examples of these non-linear linkers take the form of tritopic molecules, two of which can be seen in figure 2. The first of these was used by Tang et al. to produce the porous MOF $Al(H_3L)(H_2O)$, where L=2,4,6-trimethylbenzene-1,3,5-triyl) tris(methylene)triphosphonic acid), see figure 2a.[3] This MOF has large hexagonal channels which have a diameter of 1.24 nm and have shown reasonably high uptake of N_2, H_2, and CO_2. The second of these linkers comes from Hermer and Stock, who used it to produce the MOF $[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$ (CAU-14).

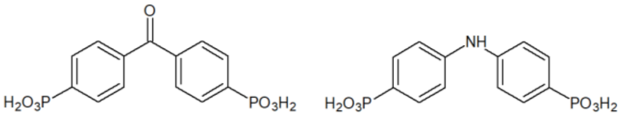

Figure 2. The first two V-shaped linkers that are currently being explored as part of this research.

There is also scope to take inspiration from the structure of MOFs based on carboxylic acids. Sticking with the non-linear theme, a series of linkers termed ‘V-shape linkers’ (Figure 2) are of particular interest in this research. While they aren’t directly inspired by carboxylate analogues,[4,5] comparison with these analogues suggests the geometry could produce porous materials with the potential for isoreticular structures, since the carboxylate MOFs both show high CO_2 adsorption properties and large surface areas (>1000 m^2/g).[6] The approach of this research will be to explore these linkers, as well as those with similar structures, in an effort to obtain porous metal-organic frameworks for use as CO_2 capture materials.

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Reversible Coordinative Binding and Separation of SO_2 in a Stable Porous Material

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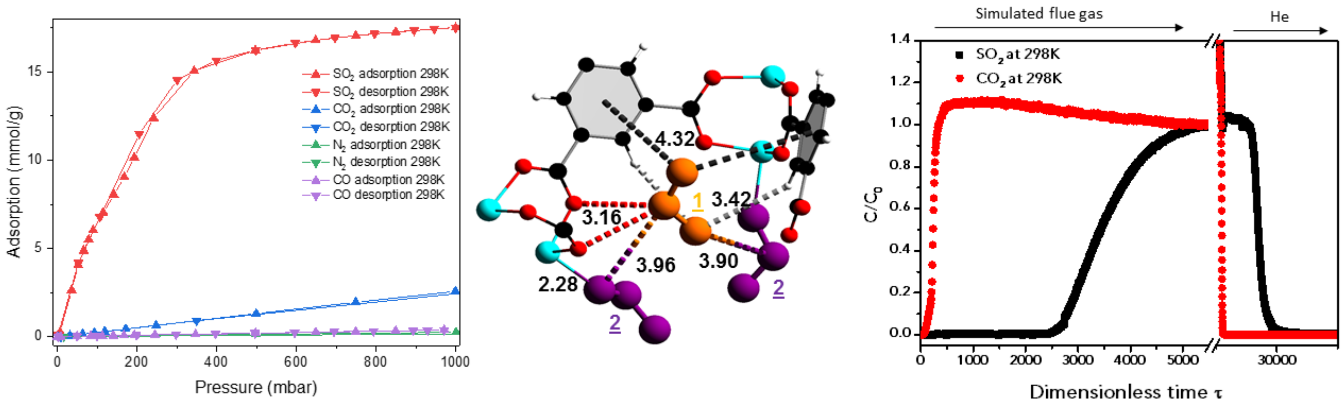
Sulphur dioxide (SO_2) from anthropogenic sources (namely fossil fuels) account for over 87% of global emissions and is greatly damaging to both the environment and human health. However, SO_2 is also an incredibly valuable feedstock for sulphuric acid production, and so utilisation of waste SO_2 for this purpose would be both environmentally and economically beneficial. Established SO_2 scrubbers are generally based on a once-through lime or limestone processes and are not suitable for thorough SO_2 removal (>95%). Thus, the development of dry, regenerable and selective solid sorbents of SO_2 is of increasing importance.

Here we report the exceptional adsorption capacity of SO_2 in a new stable copper metal-organic framework (MOF) MFM-170.[1] MFM-170 exhibits a reversible SO_2 uptake capacity of 17.5 mmol g^{-1} at 1 bar and 298 K, markedly higher than leading porous materials.[2-3] Full adsorption capacity is maintained over 50 adsorption-desorption cycles and the high stability of the material to basic and acidic aqueous conditions have been investigated. MFM-170 also exhibits selective uptake of SO_2 over other gases such as CO_2, N_2, CO and CH_4. Dynamic breakthrough experiments have confirmed that MFM-170 is able to separate SO_2 from simulated flue gas mixtures with excellent efficiency, which is crucial for practical applications. Furthermore, MFM-170@SO_2 has been studied in detail using *in situ* crystallographic and spectroscopic techniques, revealing six key binding sites within the MOF. Significantly, we found the first example of reversible co-ordination of SO_2 to open Cu(II) sites in a porous material. The soft host-guest interactions identified explain the selective and fully reversible SO_2 adsorption which is unusual amongst porous materials.



a **b** **c**

Figure 1. (a) 1 bar adsorption isotherms for SO_2, CO_2, N_2 and CO at 298 K; (b) Two key binding sites of SO_2 within MFM-170 solved from scXRD data; (c) dynamic breakthrough separation of SO_2 and CO_2 mixtures.

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Controlling the nanostructure of mesoporous silica films for the fabrication of semiconductors nanodevices

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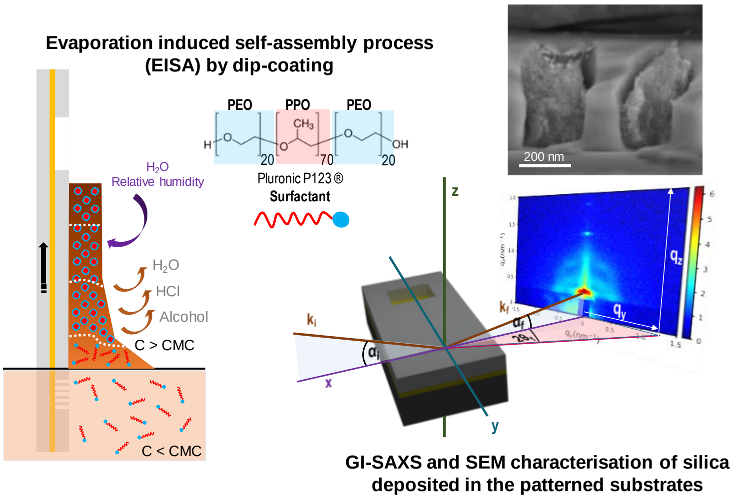
Surface nanostructuring has attracted growing interest in nanotechnology since miniaturising objects down to the nanoscale can lead to a considerable increase in device efficiency. Pushing feature size and spatial resolution down to sub-100 nm length scales has thus become a challenge.

Under the Advanced Devices by ElectroPlating project (EPSRC EP/N035437/1), we are interested in combining top-down lithographical processes and bottom-up chemistry to produce industrially relevant devices. Particularly, our aim is to develop ordered mesoporous silica films (sub-10 nm pores) that can be integrated with the lithographical methods and be used as host for the electrodeposition of semiconductor nanowires.

The templating sol-gel process is a promising approach for the fabrication of hierarchically structured inorganic materials allowing the facile preparation of large surfaces, patterned with sub 100 nm periodical assemblies, and overcoming the resolution limits of most lithographic methods.[1]

In this work, mesostructured silica films were prepared via the sol-gel method using the evaporation induced self-assembly (EISA) process.[2] However, using this method, the pores are often preferentially oriented parallel to the surface preventing their use as template for electrodeposition. Among the different strategies to induce normal orientation, confining the growth of mesoporous silica in porous nanochannels has been developed in this study to drive the mesopore orientation perpendicularly to the substrate.

The EISA process was first optimised with anodic alumina membrane (as confined spaces) by drop casting and we have been able to produce mesoporous silica characterised by a hexagonal arrangement of pores oriented perpendicularly to the substrate.


Evaporation induced self-assembly process (EISA) by dip-coating

GI-SAXS and SEM characterisation of silica deposited in the patterned substrates

Figure 1: Mesostructured thin-film formation by dip-coating (EISA) and characterisation by GI-SAXS and SEM

Towards the development of devices, patterned substrates were fabricated by e-beam lithography considering the fabrication limitations as well as the effect of the patterns aspect ratio on the mesopores orientation.

Dip-coating was used as a deposition method to prepare the mesoporous silica films and by playing with the processing conditions (relative humidity, withdrawal speed) and chemistry (concentration, pH, dilution), we have been able to drive the micelles packing and curvature resulting in various mesostructures as shown by GI-SAXS and SEM.

Whereas the nature of the alcohol influences significantly the mesostructuration of the pores, the surface chemistry of the patterns help to orient the pores perpendicular to the substrate.

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Highly Sensitive Membranes with Metal Organic Frameworks for sub-ppm Ammonia Detection: Luminescence and Absorption Turn-On by Ligand Exchange and Fluorophore Release

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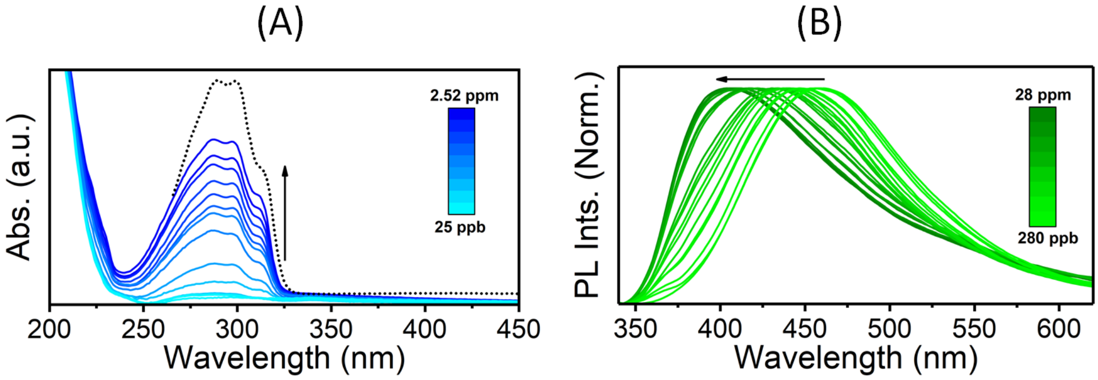
The ever-increasing adoption of environmental policies by world-wide organizations demands for new ways to detect and reduce polluting by-products released in air, soil and water.[1] This fact has triggered a vast activity in search for responsive materials for detection and management of hazardous compounds.[2,3] In the last two decades, metal-organic frameworks (MOFs) composed of a combination of organic (ligand) and inorganic (metal ions or cluster) parts arranged in one, two or three-dimensions have attracted much attention. Luminescent metal-organic frameworks (LMOFs) are promising materials for lighting and sensing applications which nevertheless need strategies for their immobilization on substrates. Herein, we report a simple solvent-free method to prepare mixed matrix membranes (MMMs) by mixing a highly luminescent $Zn_2(bpdc)_2(bpee)$ LMOF (H_2bpdc = 4,4'-biphenyldicarboxylic acid and bpee = 1,2-bipyridylethene), with dimethylvinyl-terminated dimethylsiloxane (base) and dimethylhydrogen siloxane (curing agent). This method enables for free-standing and permeable MMMs containing $Zn_2(bpdc)_2(bpee)$ of high transparency. Exposure of MMMs to sub-ppm ammonia contents turns-on new absorption and luminescence bands unambiguously ascribed to free bpee molecules. These findings combined with IR and PXRD spectra of exposed LMOF confirm that bpee ligands are exchanged by ammonia and released inside the MMMs, triggering absorption and luminescence features which can be exploited for highly sensitive chemical recognition.[4]



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Phase-transition and Dielectric Relaxation in New Metal-Formate Frameworks

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Organic−inorganic hybrid perovskites, ABX_3, exhibit many interesting properties ranging from photovoltaics, (multi)ferroics and light-emitting applications.[1] In such hybrid perovskites the small molecular organic cations occupy the cubic cavities of the anionic framework. Ferroelectricity, particularly, in such hybrid perovskites results from the polar ordering of the small A-site organic cations and its interaction with the framework via weak but directional hydrogen bonds.[2] $AB(HCOO)_3$ (A = an monovalent amine cation and B is a divalent transition metal or Mg) frameworks often adopt perovskite structures and have generated significant attention for their multiferroic and ferroelectric properties.[1] Generally, the ordering of the organic A-site cations in the $AB(HCOO)_3$ family is governed by relatively weak hydrogen bonding and exhibits multiple phase transitions and interesting dielectric properties like ferroelectricity. It has been found that increasing the electronegativity difference in the anionic framework can lead to attain (anti)ferroelectric ordering at much higher temperatures, as this indirectly strengthens the hydrogen-bonding responsible for polar order. One such way of increasing the electronegativity difference is by using less electronegative B-site cation. For example, the metal-formate framework, having the dimethylammonium cation at the A-site, orders at 160-185 K for the transition metals as B-site cation compared to a ferroelectric transition at 270 K when the less electronegative Mg is used as the B-site cation.[3] Thus we strategically choose other polar A-site cations in the $AMg(HCOO)_3$ series. Herein, the synthesis, structure and initial characterization of $AMg(HCOO)_3$ frameworks will be discussed, with emphasis on their lattice dynamics, cation ordering, phase transitions and dielectric relaxation.

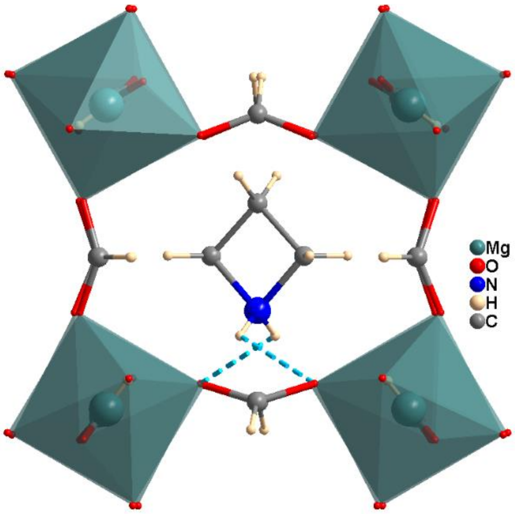

Figure: Crystal structure of (Azetidinium)$Mg(HCOO)_3$ framework showing the hydrogen bonding (dashed bond) between the organic cation and the anionic framework.

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Nucleobase pairing and photodimerization in a biologically derived metal–organic framework nanoreactor

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Biologically derived metal-organic frameworks (bio-MOFs), a subclass of MOFs made of biologically derived ligands and metal ions, are of great importance as they can be used as models for bio-mimicking and in catalysis, allowing us to gain insights into how large biological molecules function. Through rational design, here we report the synthesis of a novel bio-MOF featuring unobstructed Watson-Crick faces of adenine (Ade) pointing towards the MOF cavities. We show, through a combined experimental and computational approach, that thymine (Thy) molecules diffuse through the pores of the MOF and become base-paired with Ade. The Ade-Thy pair binding at 40-45% loading reveals that Thy molecules are packed within the channels in a way that fulfill both the Woodward-Hoffmann and Schmidt rules, and upon UV irradiation, Thy molecules dimerize into Thy<>Thy. This study highlights the utility of accessible functional groups within the pores of MOFs, and their ability to 'lock' molecules in specific positions that can be subsequently dimerized upon light irradiation, extending the use of MOFs as nanoreactors for the synthesis of molecules that are otherwise challenging to isolate.[1]

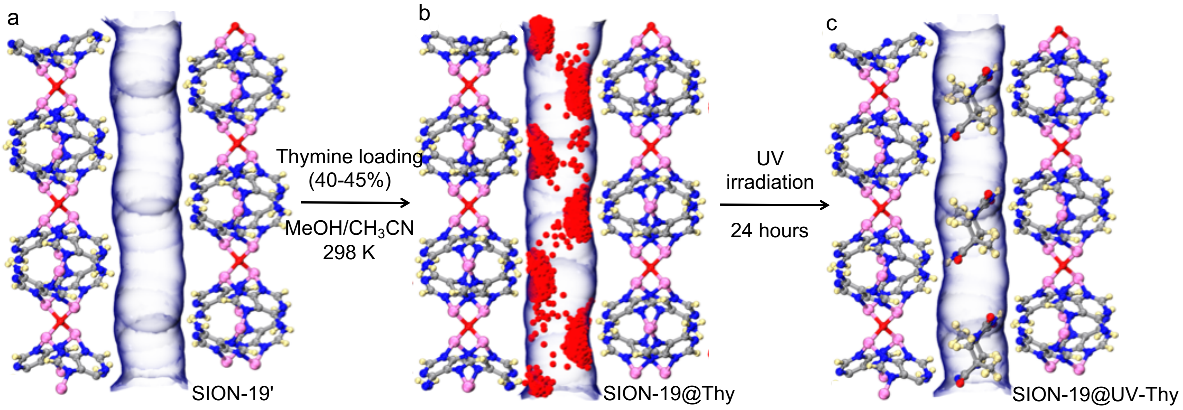

Figure 1. Schematic representation of thymine loading, location and dimerization within SION-19'. **a)** 1-dimensional base-pore surface for SION-19' prepared using HOLE2, **b)** Thy snapshots (red dots) from an MD trajectory of 44% thymine loading in the base pore of SION-19. Here, Ade acts as a structure directing agent that 'locks' Thy molecules into positions close enough to another Thy molecule for photodimerization to occur. **c)** DFT optimized positions of Thy<>Thy dimers arising from a 44% loading of Thy. Atom color code: pink, Zn; red, O; blue, N; grey, C; light yellow, H.

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The shape of Zr-MOFs to come: optimisation of the compaction process for Zr-fumarate (MOF-801)

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Ever since their discovery, MOFs have been considered promising materials for application in gas separation and storage, owing to their large porosity and ease of functionalisation. Deployment of MOFs as solid sorbents for application in industrial scale gas separation or storage processes requires that powders be compacted into industrially acceptable forms, such as tablets, pellets or extrudates.[1] Use of free-flowing, fine powders in industrial scale gas separation processes is indeed not desirable, mainly due to the large pressure drop along the sorbent bed.[2] In storage applications, high volumetric adsorption capacity is a key requirement to minimize the size of the gas container, calling for densification of the sorbent.[3] Compaction of MOF powders under pressure often leads to partial collapse of their porous framework, thus reducing surface area and pore volume, with an impact on the gas sorption performance. The challenge is therefore to identify the right conditions to ensure mechanical stability of the shaped bodies while preserving the performance of the original powder.

We have undertaken a systematic approach aimed at identifying the optimal conditions for compaction of MOF-801, a small-pore, zirconium-based MOF, containing fumaric acid as the linker, that can be easily synthesized in aqueous medium.[4] Pellets of the MOF were prepared by compressing the powder either in neat form or dry-mixed with binders (sucrose, polyvinylalcohol, polyvinylbutyral) under a range of pressures and for different times. The mechanical stability of the pellets was tested by simple drop tests and shake tests, finding that addition of 5% of polyvinylbutyral is enough to produce highly resistant pellets that do not release significant amounts of powder upon cracking. The crystallinity, textural properties and CO_2 adsorption performance of the MOF were successively assessed, observing the best preservation of the original properties in pellets compressed at 132 MPa for just 15 seconds. Compaction at higher pressures compromises the performance more heavily, with no evident benefit from the mechanical point of view, whereas compression time does not have a relevant effect.

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MOF Electrolyte Membranes for Solid-State Batteries

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Batteries are essential for a wide range of applications including electronic devices, electric vehicles, stationary energy storage system and so on. Conventional membrane separators in Li-ion batteries with liquid electrolytes have high conductivity, however they usually suffer from insufficient electrochemically and thermal stability and poor safety. These drawbacks can be significantly improved by replacing liquid electrolytes with solid electrolytes, leading to development of new solid-state batteries that provide higher energy density and improved safety at wider operating temperature. New emerging solid-state Li-ion batteries have been proposed recently, including all-solid-state Li-ion batteries, Li-S and Li-air batteries with solid-state electrolytes. Existing polymer electrolyte membranes show narrow electrochemical stability and low ionic conductivity at room temperature. Inorganic ceramic electrolyte membranes offer high ionic conductivity but the manufacturing process is complex and the interfaces between membrane and electrodes limit the ion transport.

We will report novel ion-conducting solid electrolyte membranes derived from metal-organic frameworks (MOFs) with high conductivity and good electrochemical stability and applications in solid-state lithium-ion batteries. Functional MOF nanocrystals are processed into solid electrolyte membranes, and characterised by a range of physicochemical techniques. The ion transport properties in MOF composites and electrochemical performances are also investigated by assembling solid state Li-ion batteries. Key parameters including MOFs with different pore structures and functional groups, mass loadings of MOFs in the membranes, and particle size were considered to improve the ion transport performance. The membrane design strategy will generate new types of electrolyte membranes and high-performance batteries for a wide range of energy storage applications.

Conjugated Microporous Polymers for Heterogeneous Catalysis

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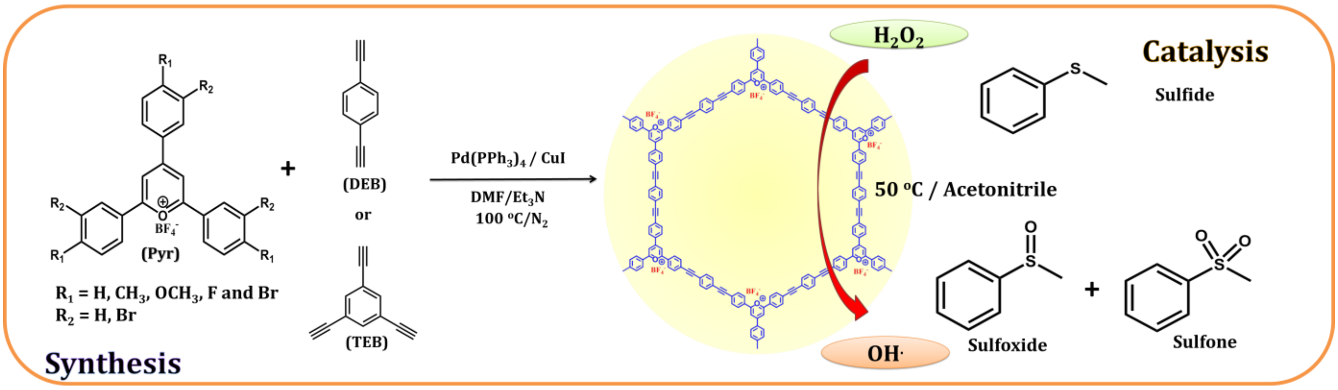
Conjugated microporous polymers (CMPs), a subclass of microporous organic polymers (MOPs) contain pore sizes smaller than 2 nm and extended π conjugation system giving them a high surface area and excellent electronic properties. Moreover, due to highly crosslinked structure, they have very high chemical and thermal stabilities. In this work, pyrylium based conjugated microporous polymers (Pyr-CMPs) with different substituted groups e.g., $-CH_3$, $-OCH_3$ and -F have been synthesised via Sonogashira-Hagihara reaction. The obtained polymers were characterised by surface area analysis, solid state nuclear magnetic resonance (ss-NMR), solid state UV visible spectrophotometry, fourier-transform infrared spectroscopy (FTIR) and elemental analysis (EA). The ss-NMR, FTIR and EA confirmed that pyrylium monomers have been incorporated into the polymer networks. The prepared materials showed a high surface area up to 554 m^2/g. The synthesised Pyr-CMPs have been utilised as a catalyst for thioanisole oxidation using hydrogen peroxide (H_2O_2) as an oxidant. The effect of reaction parameters on thioanisole oxidation were studied including polymer structures, H_2O_2 concentration, and reaction time. The optimum conditions for this reaction were 50 °C after 4 hours using 3.0 mmol of H_2O_2 and 30 mg of F-Pyr+DEB catalyst giving a high conversion at 99% with a high selectivity of sulfoxide product at 97%.



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Synthesis and Characterisation of Novel Scandium Metal Organic Frameworks

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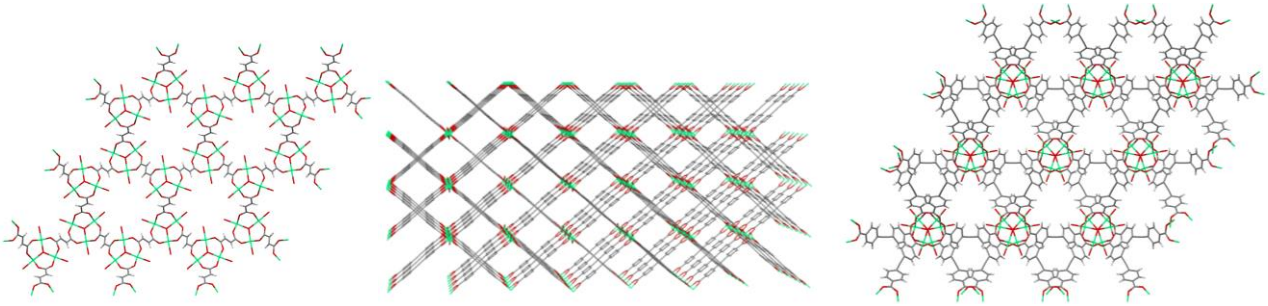
Scandium metal-organic frameworks (MOFs) have received limited attention since the first reported Sc MOF in 2005.[1] Since then there has been notable work carried out looking at the synthesis, structure and potential as gas storage materials, however, there has not been a comprehensive study carried out to elucidate the vast array of other possible structures by coordination modulation. Modulation has been used successfully in the past to enhance crystallinity, increase phase purity and has also been used to dictate the formation of different MOFs from the same starting materials.[2] The principles of isoreticular chemistry allow us to use a range of linkers that increase in size when moving through the isoreticular MOF series, and as such we should see similar properties across the materials. The aim of this work was to assess the suitability of modulation as a technique in the synthesis of novel Sc MOFs. A series of Sc MOFs have been synthesized, using rational linker design and modulation techniques, yielding several new structures. These materials have been characterized using single crystal and powder XRD, BET analysis and SEM imaging, TGA and IR spectroscopy. A number of linkers, including fumaric acid, 1,4-naphthelene dicarboxylic acid, 2,6-naphthalene dicarboxylic acid and 4,4'-(Ethyne-1,2-diyl)dibenzoic acid have been used to synthesize novel Sc MOFs. Using the modulation technique, we have been able to dictate which structure is formed in the Sc 4,4'-(Ethyne-1,2-diyl)dibenzoic acid system and enhance phase purity and crystallinity in all the other samples. This study further demonstrates the importance of modulation as a technique and highlights its ability to be used in multiple MOF systems.



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Title: Engineering of hematite band gap

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There is a broad agreement among scientists on the necessity to replace fossil fuels by renewable energy sources, and carriers. Hydrogen is a promising energy carrier as it has a high energy density (142 MJ/kg) and its combustion does not result in the emission of greenhouse gases[1]. However, its sustainable production and storage still hinder its large-scale application. Photocatalytic water splitting (light-driven conversion of water into hydrogen and oxygen) is a promising approach to generate hydrogen without negatively impacting the environment. Semiconductor photocatalysts have the potential to use solar power for hydrogen production, when their band energies and band gap are of appropriate size to i) absorb in the visible light and ii) catalyse the relevant electrode reactions[2]. Hematite (α-Fe_2O_3) is a promising water-splitting photocatalyst, which however suffers from poor charge separation and carrier dynamics, and low conduction band energy[3]. The first challenge might be overcome by reducing its particle dimensions, as nanomaterials have high surface-to-volume ratios, limiting charge carrier path lengths. However, quantum confinement also affects the band energies of the semiconductor[4].

We aim on this project to find how to open the band gap of hematite (and adjust the band energies), thus to align them with the potentials required to split water without using an external bias voltage. To this end, we synthesise hematite nanoclusters inside the pores of metal-organic frameworks, taking advantage of their uniform size and shape distribution, which in turn acts as a template for the growth of nanoclusters. Thereby we envision to control the optoelectronic properties of hematite, which we have modelled and would then further be refined through DFT calculations with the goal of computationally optimising the α-Fe_2O_3@MOF system for enhanced photocatalytic water splitting.

In this poster, I will discuss our preliminary results on the computational simulation of the α-Fe_2O_3-MOF interactions for UiO(Zr) systems, and our first results on embedding α-Fe_2O_3 inside the pores of UiO-67 and UiO-66.

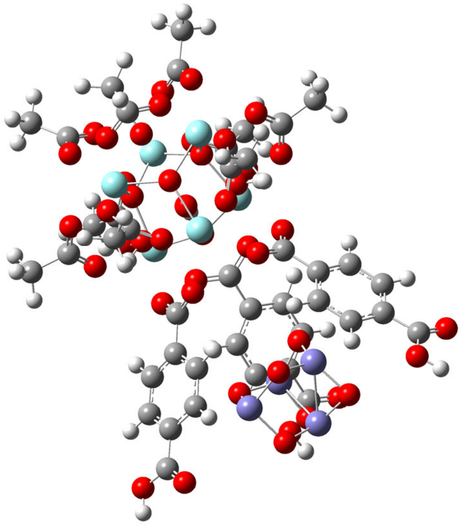

Figure 1:Visual representation of hematite nanocluster (Fe=purple and O=red) embedded into MOF UiO-66 (H= white; C=grey; Zr=green) and modelled from B3LYP/def2-TZVP.

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Hydrophilic Microporous Membranes for Ultrafast Ion Transport and Precise Molecular Sieving

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Fast and selective ion transport has broad significance from biological processes to industrial membrane separation processes, such as desalination and water purification[1], and to emerging technologies, such as redox flow batteries[2], fuel cells and electrochemical reactors. However, it remains challenging to design and fabricate ion-conductive membranes with well-defined ion transport channels that have suitable and narrowly distributed pore size and affinity with guest molecules (e.g., water) and preferred ions.

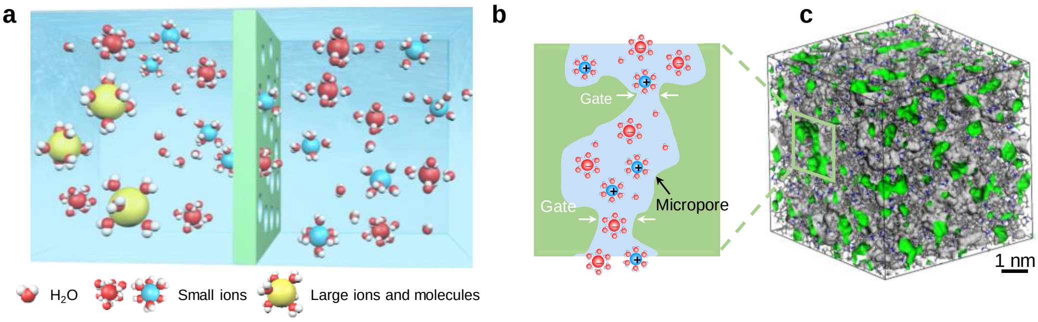

Figure 1. **a** Working principle of hydrophilic microporous membranes for fast ion transport and precise molecular sieving. **b** Schematic diagram of interconnected micropores in microporous membranes for rapid and selective ion transport. c, Three-dimensional view of an amorphous cell of PIM polymer.

Recent advances in microporous materials enable the design of ion-transport membranes with well-defined ion channels that could achieve precise ion transport.[3,4] Polymers of intrinsic microporosity (PIMs) are particularly attractive for membrane applications owing to the combination of intrinsic microporosity and solution processability.[5,6] Much efforts have been made to the development of PIM synthetic chemistry and the understanding of fundamental relationship between polymer chain structure and gas transport properties, mainly targeting at improved gas separation performance.[7-9] Here, we report a new approach to designing intrinsically microporous polymeric membranes with narrow molecular-sized ionic channels and hydrophilic functionality that enable fast transport of charge-carrying ions and high size-exclusion. Microporous hydrophilic ion-sieving membranes enable efficient and stable operation of aqueous organic flow batteries with high energy efficiency and high capacity retention. Our membrane design strategy sheds light on the design of next-generation of ion-selective polymeric membranes for a variety of energy processes and water purification applications.

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Screening and testing Metal-Organic Frameworks for challenging CO/N_2 separation through a multi-scale approach

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The most challenging step to obtain industrial reagent pure CO (> 99 mol %) is to separate CO from N_2[1]. Current technologies such as cryogenic distillation suffer from low efficiency and/or high cost[2]. Adsorbents such as Metal-Organic Frameworks (MOFs), that can selectively adsorb CO over N_2, are promising candidates to address this issue[3]. In this study, we performed a screening procedure using flux-response technology (FRT) as well as equilibrium testing to examine the CO uptake and CO/N_2 selectivities of various MOF structures. We then conducted an in-depth investigation of the dynamic adsorption behaviour of the best performing MOFs. In particular, we studied: the effect of the CO/N_2 feed composition, the effect of CO_2 impurity (ppm level) and the recyclability. We identified Co-MOF-74 and Ni-MOF-74 as the most promising candidates, due to their microporosity and high density of strongly CO binding Co^{2+} and Ni^{2+} sites. We observed selectivities up to 223 and a decrease in dynamic performance of 13 % upon 20 cycles. These findings point to the potential of M-MOF-74 structures for the challenging CO/N_2 separation.

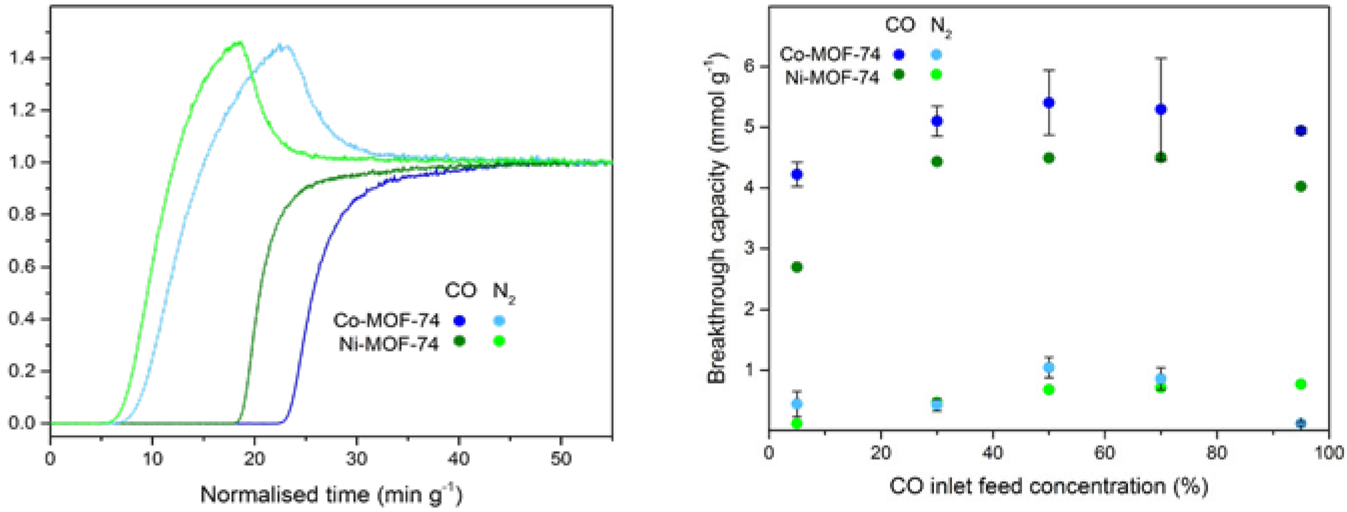

Figure 1. The CO/N_2 breakthrough curves for Co-MOF-74 and Ni-MOF-74 (50:50 *v:v* CO:N_2) (left), and the breakthrough capacities at varying inlet feed concentrations (CO:N_2=5:95, 30:70, 50:50, 70:30, 95:5) (right) at 298 K and 1 bar.

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MOF-808 as a Delivery Vehicle for Anticancer Drugs

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From the discovery of Cisplatin until today, a lot of anti-cancer drugs have been used as chemotherapy agents to save millions of lives.[1] Regardless of the millions of lives that they have saved, they come with a lot of side effects, such as bone marrow suppression and high cardiotoxicity among others, which can add to the lethality of the disease.[2] In order to bypass these side effects scientists have suggested many versatile materials as vehicles, but their applicability is hindered by their relatively big size, their loading capacity, poor targeting, etc. The ideal drug carrier must be small enough in order to effectively permeate and deliver the drug within the cell (ideally below 200 nm) and have a large enough pore in order to facilitate the drug molecule.[3] At the same time it must be relatively non-toxic by itself towards the cells that it targets. For this we employed MOF-808 as a drug delivery vehicle.[4] This Zr^{4+} MOF has a median pore diameter of approximately 18 Å with 10 Å hexagonal windows leading into them and could possibly facilitate loading of antineoplastic agents. In order to grow small crystallites of MOF-808 we used acetic acid as a modulator under solvothermal conditions that yielded a powder material with a particle size of approximately 60 nm. Subsequently the MOF was loaded with three potent anticancer drugs, Doxorubicin (DOX), Chlorambucil (CHLOR) and Paclitaxel (TAX) at 23%, 26.6%, and 10.9%, respectively. Experiments on one healthy cell line (HEK-293) and three cancer cell lines (MCF-7, HEPG2 and A2780ADR) indicate that the loaded materials exhibit comparable or better cytotoxicity towards the cancer cell lines. More specifically, although DOX is more cytotoxic by itself, DOX@MOF kills the cancer cells in a more controlled manner compared to the free drug. On the other hand, CHLOR@MOF and TAX@MOF display a slightly increased cytotoxicity towards the cancer cells compared to the free drugs. These results indicate that MOF-808 can be considered as a candidate MOF carrier for several anticancer drugs.

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[3] L. Wang, M. Zheng and Z. Xie, *Journal of Materials Chemistry B*, 2018, **6**, 707-717.
[4] H. Furukawa, F. Gándara, Y.-B. Zhang, J. Jiang, W. L. Queen, M. R. Hudson and O. M. Yaghi, *Journal of the American Chemical Society*, 2014, **136**, 4369-4381.

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UK Porous Materials Conference 2019

Cardiff University, School of Chemistry, 1st – 2nd July 2019

Information for delegates

Conference Location

The event is being held in and around Cardiff School of Chemistry, Main Building, Park Place, Cardiff CF10 3AT.

Access to the site is via Park Place or Museum Avenue. The postcode location is a few hundred yards further north along Park Place than Main Building itself. The Park Place entrance is in the car-park, in the centre of the building.

Walking

If you're walking, Main Building is approx. 15 mins from Cardiff Queen Street train station, approx. 25 mins from Cardiff Central train station and approx. 8 mins from Senghennydd Hall.

By bus

The nearest bus stop is on Park Place, outside Main Building. A useful nearby stop is College Road, approx. 6 min walk to Main Building, where a lot of the buses stop. Service information is available at www.cardiffbus.com. Many other services stop in the city centre, approx. 15-30 mins walk.

By train

Cardiff Cathays train station is over the road from Main Building and is on a direct line from Cardiff Central train station. Cardiff Central is served by many local and national services and is approx. 25 mins walk.

By coach

National Express services stop in Sophia Gardens approx. 20 mins walk from the School of Chemistry. Mega Bus also runs to Cardiff, both drop off on Kingsway, approx. 10 mins walk away.

By air

Cardiff Airport is approx. 15 miles from the School of Chemistry; please see https://www.cardiff-airport.com/to-and-from/ for transport options to the city. Bristol Airport is approx. 47 miles away, details at https://www.bristolairport.co.uk/to-and-from-the-airport.

Parking

Pay and display parking is available on Museum Avenue (behind Main Building) and in Greyfriars Road NCP Car Park (approx. 10 mins walk). Disabled parking is available on site, please let us know if you require a space.

Park and Ride information is available via the Cardiff Council website www.cardiff.gov.uk.

Presentations, Posters and Refreshments

Presentations are 15 mins +5 mins questions and session chairs will be keeping speakers to time. If you are speaking, please ensure your talk is loaded onto the available PC in good time, or that you have tested your laptop with the system.

Presentations will be in the Large Lecture Theatre.

Posters, coffee and lunch will be in the Viriamu Jones Gallery in the centre of Main Building. Please ensure all posters are put up in advance of the poster session on Monday evening and removed by the end of the conference or they will be disposed of.

Wifi and Twitter

Eduroam is available; if you don't have access wifi information will be on the registration desk. The Twitter hashtag is #UKPorMat2019. Conference tweets will be from the @UKPorMat account. The interest group Twitter can be found @RSC_PorMat

Welcome reception Sunday 30th July

Early arrivals can join us for drinks on Sunday from 8 pm.

The informal welcome drinks will be in the upstairs room of the Head of Steam, feel free to join when available.
(https://www.theheadofsteam.co.uk/bars/cardiff)

Questions before the event

If you have any queries please email UKPorMat@gmail.com.

Large Lecture Theatre
(all talks)

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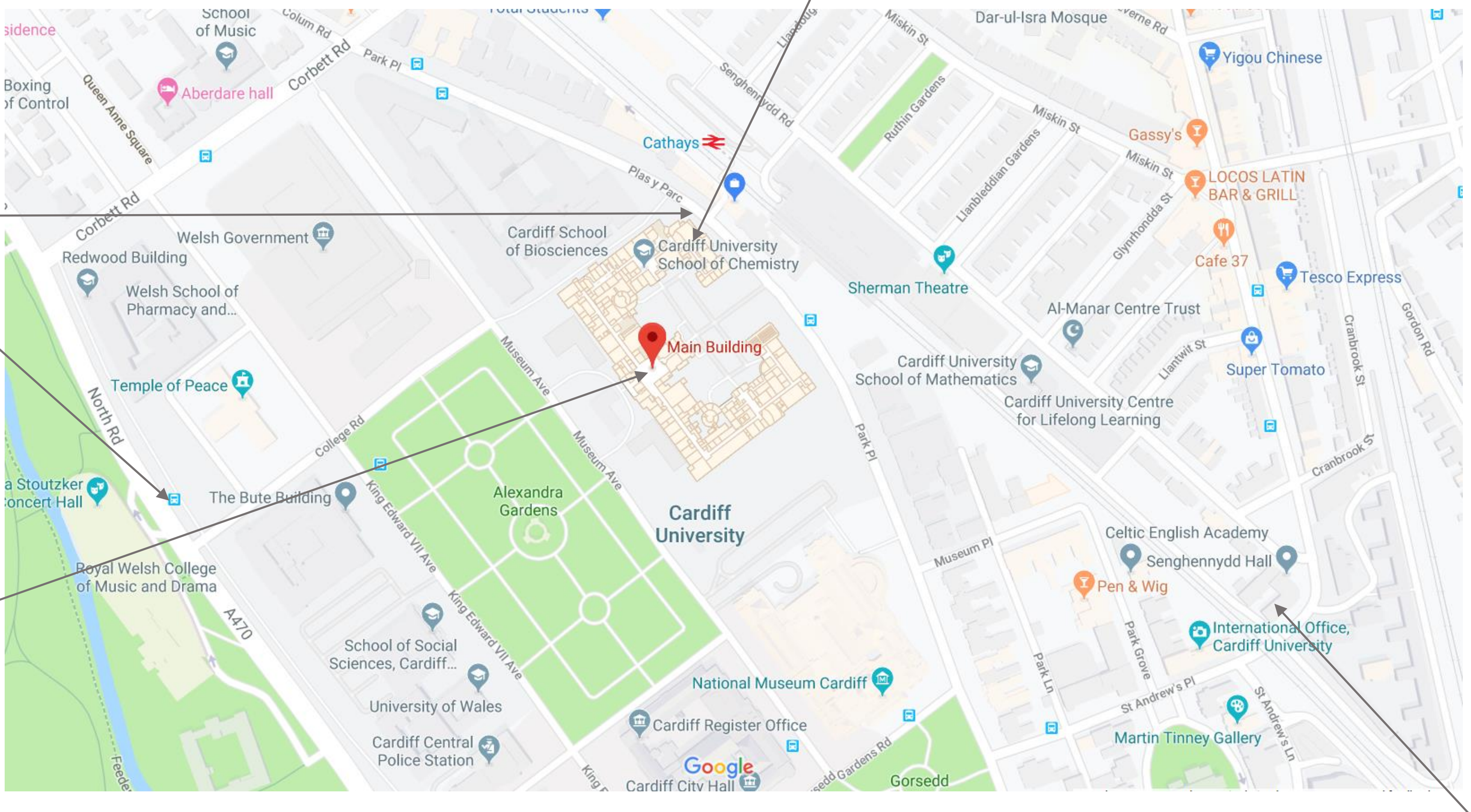
(posters, coffee,
lunch)



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City Centre & conference dinner (ZeroDegrees)

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