Host-guest dynamics in copper-based Metal-Organic Frameworks

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Declaration

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December 2017
This work is dedicated to my grandparents who raised me.

Sarah Bezuidenhout and Johannes Jacobus Bezuidenhout
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Abstract

A vast number of metal-organic framework materials (MOFs) and structures have been reported in the literature. These materials are of interest as they exhibit a wide range of remarkable properties such as porosity, magnetism, chromism, thermal expansion and dynamic phase-change behaviour. However, many of the reports do not include investigations of all these possible properties, which provides an opportunity to revisit such materials. This study reports three sets of related MOFs that were studied in order to gain insight into their properties and dynamic host-guest interactions.

In the first section three isoreticular copper(II)glutarate based 3D MOFs, whose pore dimensions vary according to the length of the 4,4'-bipyridyl linkers, allows exploration of the effect of increasing pore dimensions on the sorption behaviour of the frameworks. These MOFs capture CO$_2$ under supercritical conditions and retain the gas under ambient conditions. The retention of the CO$_2$ makes it possible to model the positions of the molecules within the channels of the frameworks using single-crystal X-ray diffraction analysis (SCXRD). Comparison of the CO$_2$ gas sorption isotherms with the trend in thermal evolution of the CO$_2$ adducts provided insight into the dynamics of the host-guest interactions within the MOFs. Theoretical models constructed from crystallographic data were used to calculate framework electrostatic potential maps through DFT and semi-empirical methods. The maps yielded a detailed picture of the electrostatic interactions prevailing at the sorption sites, which shows an electrostatic complementarity between the sorption sites and the CO$_2$ molecules for two of the MOFs. The $\delta^+$ carbon of the CO$_2$ molecules interacts with the $\delta^-$ carboxylate moieties of the framework. Furthermore, both $\delta^-$ oxygen atoms of each of the CO$_2$ molecules interact with several $\delta^+$ hydrogen atoms of the framework. This electrostatic complementarity between CO$_2$ and the sorption site results in a strong interaction, which stabilises the gas within these MOFs.

The second set of MOFs studied comprises two 3D Cu(II)-glutarate-based MOFs with flexible linkers, [Cu$_2$(glu)$_2$(bpa)] and [Cu$_2$(glu)$_2$(bpp)], that undergo spontaneous phase changes upon solvent loss at room temperature. These MOFs are an extension of the isoreticular series of the previous section. Using SCXRD, we show that the phase changes result in new narrow-channel phases, with a large reduction in solvent accessible volume as compared with the original wide-channel phases. Moreover, the [Cu$_2$(glu)$_2$(bpa)] MOF displays a stepped sorption isotherm upon CO$_2$ sorption at RT. This is indicative of the framework reverting to the wide-channel phase. The positions of the CO$_2$ molecules in the channels of the frameworks were determined using SCXRD analysis of crystals exposed to supercritical CO$_2$. Finally, a scan of the potential energy surface using molecular mechanics was conducted to elucidate the mechanism by which the phase change occurs. This appears to be a direct enantiomeric conversion of the glutarate ligands as a result of structural constraints.

The third section describes a one-dimensional porous coordination polymer (PCP) [Cu$_2$(acetate)$_2$(dptz)].n.2CHCl$_3$, that possesses pleochroic properties, i.e. the crystals appear to have different colours depending on their orientation. Solvent exchange with acetonitrile and nitromethane reveals that crystals of this PCP are also solvatochromic. This allows the solvent exchange process to be monitored using optical microscopy with polarised light. The experiment revealed an unexpected double V-shaped pattern in the crystals, which could be explained using an overlay of the measured crystal facets with the crystal structure, along with...
modelling of crystal surface adsorption at the different crystal facets. Furthermore, we identified that the crystals must be growth twins subject to the double re-entrant corner effect.
Opsomming

Daar is 'n groot aantal metaal-organiese raamwerk materiale (MOFs) en strukture in die literatuur gerapporteer. Hierdie materiale is van belang aangesien dit 'n wye verskeidenheid van merkwaardige eienskappe soos porositeit, magnetisme, optiese, termiese uitsetting en dinamiese fase-verandering gedrag openbaar. Daar is egter baie publikasies wat nie die ondersoek van al hierdie moontlike eienskappe behels nie, en bied dus 'n geleentheid aan om sulke materiaal te heroorweeg vir studie. Hierdie studie omhels drie stelle verwante MOFs wat gebestudeer word ten insig van hul materiaal eienskappe en dinamiese gasheer-gas interaksies.

Die eerste artikel omhels drie iso-retikulêre Cu(II)-glutaraat-gebaseerde MOFs, waarvan die porie dimensies wissel na gelang van die 4,4-bipyridyl koppelingsligand lengte, om die effek van verhoging in porie dimensies op die sorpsie gedrag van die raamwerke te bestudeer. Hierdie MOFs neem CO\(_2\) op onder superkritiese kondisies en behou die gas onder omringende omstandighede. Die behoud van CO\(_2\) maak dit moontlik om die posisies van die molekules te modelleer binne die kanale van die raamwerke duer gebruik te maak van enkel-kristal X-straal diffraksie analyse (SCXRD). Vergelyking van die CO\(_2\) gas sorpsie isoterme met die tendens in die termiese evolusie van die CO\(_2\) gevulde MOFs bied insig in die dinamika van die gasheer-gas interaksies binne die materiaale. Teoretiese modelle opgebou uit kristallografiese data word gebruik om raamwerk elektrostatiese potensiaal afbeelding te bereken deur gebruik te maak van DFT en semi-empiriese metodes. Die afbeelding lever 'n gedetailleerde prent van die elektrostatiese interaksie wat heersend is by die sorpsie lokasies. Hierdie interaksies is elektrostatiese ooreenstemmend tussen die sorpsie lokasies en die CO\(_2\) molekules vir twee van die MOFs. Die δ\(^+\) koolstof atoom van die CO\(_2\) molecule form 'n interaksie met die δ\(^-\) karboksilaatgroep van die raamwerk. Boonop dit is daar 'n interaksie tussen beide δ\(^-\) suurstof atome van die CO\(_2\) molecule en verskeie δ\(^+\) waterstof atome van die raamwerk. Dit elektrostatiese komplementariteit tussen CO\(_2\) en die sorpsie lokasie lei tot 'n sterk interaksie wat die gas binne hierdie MOFs stabiliseer.

Die tweede stel MOFs gebestudeer bestaan uit twee 3D Cu(II)-glutaraat-gebaseerde MOFs met buigsame koppelingsligande, [Cu\(_2\)(glu)\(_2\)(bpa)] en [Cu\(_2\)(glu)\(_2\)(bpp)], wat spontaan faseveranderinge ondergaan tydens verlies van die ingeslote oplosmiddel by kamer temperatuur. Hierdie MOFs is 'n uitbreiding van die iso-retikulêre reeks in die vorige afdeling. Die gebruik van enkel-kristal X-straal diffraksie wys dat die faseveranderinge lei tot nuwe smal-kanaal fases met 'n groot afname in gas toeganklik volume in vergelyking met die oorspronklike wyse-kanaal fases. Verder vertoon die [Cu\(_2\)(glu)\(_2\)(bpa)] MOF 'n staps gewyse sorpsie isoterms vir CO\(_2\) by kamer temperatuur. Dit is 'n aanduiding dat die raamwerk terugkeer na die wye-kanaal fase. Die posisies van die CO\(_2\) molekules in die kanale van die raamwerke is bepaal met behulp van SCXRD analyse van kristalle blootgestel aan superkritiese CO\(_2\). Ten slotte, 'n skandering van die potensiële energie oppervlak met behulp van molekulêre mekanika is gedoen om die mekanisme waardeer die faseverandering plaasvind uit te lig. As gevolg van structurele beperkinge skyn dit na 'n direkte enantiomeriese omskakeling van die glutaraat ligande.

In die derde deel bestudeer ons 1D poreuse koördinasie polymer (PCP) [Cu\(_2\)(asetaat)\(_2\)(dptz)]\(_n\)•2ChCl\(_3\), wat besit veelvoudig kleur eienskappe, die kristalle het aansienlik
verskillende kleure afhangend van die crystal se ruimtelike oriëntasie. Oplosmiddel verwisseling met acetonitril en nitro metaan onthul dat die kristalle van hierdie PCP ook oplosmiddel-verkleuring vertoon. Dit beslaan die moonlikheid om die oplosmiddel uitruilings proses te monitor deur gebruik te maak van optiese mikroskopie met gepolariseerde lig. Die eksperiment onthul 'n onverwagse tweeledige V-patroon in die kristalle. Hierdie waarneming kan verklaar word deur 'n samestelling van die afgemete crystal facet bo-op die kristalstruktuur en die modellering van kristal-opervlak-adsorpsie op die verskillende Kristal facette. Verder moet die kristalle onderhewig wees aan meervoudige deurgroeiing soos die dubbel-intrede hoek effek.

Stellenbosch University  https://scholar.sun.ac.za
Publications


Conferences

1. **ICCOSS XXIII**: 23rd International Conference on the Chemistry of the Organic Solid State in Stellenbosch, South Africa on 2 - 7 April 2017
   Poster: *Solvent and Pressure-Induced Phase Changes in Two 3D Copper Glutarate-Based MOFs via Glutarate (+gauche ⇔ -gauche) Con-formational Isomerism.*

2. **Indaba 8**: Serendipity vs Prediction, organised by the South African Crystallographic Society, 16-21 August 2015, held in Skukuza, Kruger National Park, South Africa.
   Poster: Pleochroism as a probe to monitor the solvent exchange process in a 1-D metal-organic framework with 1-D solvent accessible channels.

   Oral presentation: *Host and guest dynamics Copper Glutarate based metal-organic frameworks (MOFs).*
   Poster: *Pleochroism as a probe to monitor the solvent exchange process in a 1-D metal-organic framework with 1-D solvent accessible channels.*

4. **Indaba 7**: Insights from Structure, organised by the South African Crystallographic Society, September 2012, held in Skukuza, Kruger National Park, South Africa.
   Poster: *Extreme stability of CO₂ in open channel MOF: [Cu₂(glutarate)₂(trans-bis(4-pyridyl)ethylene)]ₙ.*
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<th>Definition</th>
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<tr>
<td>1D</td>
<td>1-dimensional</td>
</tr>
<tr>
<td>2D</td>
<td>2-dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>3-dimensional</td>
</tr>
<tr>
<td>MOF</td>
<td>Metal-organic framework</td>
</tr>
<tr>
<td>PCP</td>
<td>Porous coordination polymer</td>
</tr>
<tr>
<td>SBU</td>
<td>Secondary building unit</td>
</tr>
<tr>
<td>np</td>
<td>Narrow-pore</td>
</tr>
<tr>
<td>lp</td>
<td>Large-pore</td>
</tr>
<tr>
<td>nc</td>
<td>Narrow-channel</td>
</tr>
<tr>
<td>wc</td>
<td>Wide-channel</td>
</tr>
<tr>
<td>E-ray</td>
<td>Extraordinary ray</td>
</tr>
<tr>
<td>O-ray</td>
<td>Ordinary ray</td>
</tr>
<tr>
<td>CSD</td>
<td>Cambridge Structural Database</td>
</tr>
<tr>
<td>QM</td>
<td>Quantum Mechanics</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular Dynamics</td>
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<tr>
<td>MEP</td>
<td>Molecular Electrostatic Potential</td>
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<tr>
<td>MM</td>
<td>Molecular Mechanics</td>
</tr>
<tr>
<td>PQeq</td>
<td>Periodic charge equilibration</td>
</tr>
<tr>
<td>Qeq</td>
<td>Molecular charge equilibration method</td>
</tr>
<tr>
<td>SCXRD</td>
<td>Single-crystal X-ray diffraction</td>
</tr>
<tr>
<td>PXRD</td>
<td>Powder X-ray diffraction</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>H₂glu</td>
<td>Glutaric acid</td>
</tr>
<tr>
<td>glu</td>
<td>Glutarate anion</td>
</tr>
<tr>
<td>scCO₂</td>
<td>Supercritical carbon dioxide</td>
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**Atomic colour key**

- **Copper**
- **Carbon**
- **Oxygen**
- **Hydrogen**
- **Nitrogen**
- **Chlorine**
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CHAPTER 1

INTRODUCTION

Porous materials have attracted much attention owing to growing interest in their applications in heterogeneous catalysis, storage and separation. In the 1990s, carbon-based and inorganic materials were the two types of porous materials of general interest, with the most well-known inorganic 3-dimensional crystalline materials being zeolites. Their frameworks contain typically interconnected guest-accessible voids occupied by water molecules and metal ions. Removal of the water molecules from the framework results in a robust and highly porous material. Activated carbons, on the other hand, have a disordered structure with high porosity and high specific surface areas.

These compounds have since been surpassed by a class of materials known as porous coordination polymers (PCPs), which are compounds formed by self-assembly through coordination bonds of metal cations and inorganic or organic ligands to form extended networks with potential guest-accessible space. The first example had, in fact, been discovered in 1897 when Hofmann et al. identified a coordination network based on ammonia-nickel cyanide (Hofmann complex). However their study of this and related materials was inhibited by the shortcomings of structural characterisation techniques at the time. In 1949, with the aid of X-ray studies, Powell and Rayner revealed the crystal structure of this Hofmann complex to be an extended 2D framework with benzene solvent molecules trapped within the structure (Ni(CN)₂(NH₃)·C₆H₆). In 1990, Hoskins and Robson reported the first 3D extended coordination assembly with Cu(I) and 4,4ʹ,4ʺ,4ʺʺ-tetracyanotetraphenylmethane as an organic linker. These framework materials are the earliest forms of PCPs.

PCP research increased greatly in the 1990s due to interest in their regular topologies, high porosity and designable frameworks, yielding early examples of functional microporous materials. A desired extended network assembly can be constructed by reacting certain combinations of metallic nodes or inorganic clusters with multidentate ligands under relatively mild conditions. For instance, Robson et al. reported anion exchange using a PCP in 1990, while in 1994 Fujita et al. reported the catalytic properties of [Cd(4,4ʹ-bpy)₂] (bpy=bipyridine). In 1995, Yaghi et al. and Moore et al. independently studied the adsorption of aromatic solvent molecules in PCPs, followed by a report by Kitagawa et al.’s of gas sorption at ambient temperatures, in 1997. Kitagawa et al. summarised the possible framework architectures that could be constructed by combining different connectors (a metal node or metal clusters) and linkers (Figure 1 – left). As illustrated in Figure 1, this strategy allows for the formation of one-, two- and three-dimesional (1D, 2D and 3D) framework architectures.

In 1995 Yaghi et al. introduced the term “Metal-Organic Framework” (MOF) to describe a material that consists of organic ligands coordinated to metal-cations yielding a stable
permanently porous framework.\textsuperscript{8, 19} It has to be noted that there is little distinction in the definitions of PCPs and MOFs. According to IUPAC guidelines a MOF is an extended coordination network, thus confining it to 2D and 3D frameworks, whereas PCP can be used to describe all three framework dimensionalities.\textsuperscript{12} However, in the IUPAC guideline communication, it is noted that PCPs could be based on only inorganic components whereas MOFs must contain organic components as well. In light of this, since the framework materials discussed in this dissertation contain organic components, the term "MOF" will be used to describe 2D and 3D frameworks, whereas PCP will be used to describe 1D coordination polymers.

![Figure 1](image_url)

**Figure 1.** Components of coordination polymers. Possible frameworks that can be assembled using different combinations of connectors and linkers. Figure recreated from Kitagawa et al.\textsuperscript{11}

1.1. 1D PCPs

1D coordination polymers have attracted considerable interest owing to their electrical, chromic, and gas sorption properties, as well as structural flexibility.\textsuperscript{13} The 1D polymeric coordination chains form extended assemblies through directional electrostatic interactions, \(\pi\cdots\pi\) interactions and close packing van der Waals interactions.\textsuperscript{14-15} The simplicity of PCP topologies allows for easy modification of their structures through the choice of metal centers and organic linkers. This enables 1D coordination polymers to adopt various types of architectures such as linear chains, zigzag chains, ladders, ribbons, etc. (Figure 1 - right).\textsuperscript{11} 1D coordination polymers often form close-packed structures. However, porous structures can be formed as a result of appropriate structure-directing interactions.\textsuperscript{16} In 2002 Takamizawa et al. prepared an empty single-crystal host, \([\text{Rh}^{\text{II}}]^2(\text{O}_2\text{CPh})_4(\text{pyz})]_n\) (Figure 2 (a) and (b)), and established its porosity through nitrogen adsorption,\textsuperscript{17} and later its carbon dioxide (CO\textsubscript{2}) adsorption capabilities.\textsuperscript{18} The later result was accompanied by the structural visualization of the CO\textsubscript{2} host-guest adduct obtained by single crystal X-ray diffraction (SCXRD) under CO\textsubscript{2} atmosphere at 93 K (Figure 2 (c)). The empty host was shown to have insufficient void space to accommodate the CO\textsubscript{2} molecules, and had thus undergone a phase change upon CO\textsubscript{2} adsorption in order to accommodate the guest molecules.
1.2. METAL-ORGANIC FRAMEWORKS (MOFS)

Although MOF research did not attract much initial interest, the discovery of the remarkably stable and highly porous tetra nuclear zinc-carboxylate MOF by Li et al. in 1999 highlighted the potential of MOFs for applications such as gas storage.\textsuperscript{19} This sparked a rapid increase in MOF-related research, leading to a highly active area of study.\textsuperscript{11, 20-24} In 2000, based on their work on MOF-5, Eddaoudi et al. synthesised three MOFs using zinc(II) cations combined with terephthalate and trimesate linkers (Figure 3).\textsuperscript{25} The porosity of the MOFs was demonstrated by ethanol vapour sorption, and it was suggested that the unsaturated zinc metal site in the Zn\textsubscript{2}(BTC)(NO\textsubscript{3}) framework (MOF-4) could be useful for catalysis.

Figure 2. (a) Schematic of \([\text{Rh(II)}_2(\text{O}_2\text{CPh})_4(\text{pyz})]_n\) (b) The close packed structure of the empty host. (c) The CO\textsubscript{2} host-guest adduct. Figures taken from Takamizawa et al.\textsuperscript{18}

Figure 3. Schematic representation for the basic concept behind MOF framework assemblies using the MOF-5 crystal structure as an example. (a) The components of a MOF framework. (b) A typical framework that can be formed using these components.
1.2.1. Synthesis of MOFs

Part of the appeal of MOFs is the diversity of synthetic methods that can be employed, which hold the possibility of obtaining a large variety of interesting structures and structural phases (even with the same metals and ligands). Furthermore, the characteristics of the material, such as crystal size or shape, thin films, membranes, etc., are greatly affected by the employed method of synthesis. Conventional methods for synthesising MOFs include room temperature mixing, conventional electric heating and solvothermal methods. In recent years alternative synthetic routes have been explored such as microwave heating, electrochemical, mechanochemical, and sonochemical methods. Figure 4 provides an overview of the synthetic methods used for MOFs, as well as the temperature regime of each. The two most used methods are hydrothermal- or solvothermal- and microwave-assisted synthesis:

- Hydrothermal or solvothermal: *Synthesis using solvents such as water (hydrothermal) or dimethylformamide (solvothermal). These solvent also act as a reagent at elevated temperature to deprotonate the carboxylic acid groups of the ligands used. According to the definition given by Rabenau, solvatothermal reactions “take place in closed vessels under autogenous pressure above the boiling point of the solvent”.*

- Microwave-assisted synthesis: *This method utilises the interaction of electromagnetic waves with polar species in a solution or electrons/ions in a solid as a very energy efficient homogeneous method of heating.*

Figure 4. An overview of synthesis methods in the preparation of MOFs. Figure taken from Stock et al.
1.2.2. Secondary building units (SBUs)

Research has progressed towards a modular approach in the synthesis and design of new MOFs. The realisation of reoccurring metal cluster motifs and framework architecture in MOFs led to the term “secondary building units” (SBUs) as a way of describing these motifs (Figure 5). The underlying topology of MOF structures can also be classified based on the SBUs employed. Most SBUs are built from metal-carboxylate clusters owing to the predominant use of rigid aromatic multidentate carboxylic acids as linkers in the exploration for new MOFs. Figure 5 shows some of the most common metal-carboxylate SBUs, which may be combined with different linker geometries to afford a wide range 3D architectures. A more comprehensive catalogue of these MOF SBUs was reported by Tranchemontagne et al. in a review in 2009.

It should be noted that the term “linker” describes a ligand that participates in the coordination assembly of a MOF and should not be confused with uncoordinated ligands located within the MOF structure. Thus, all linkers are ligands, but all ligands need not be linkers.

Figure 5. Schematic illustration of the construction of MOFs from SBUs and rigid linkers.
1.2.3. Ligand design for isoreticular synthesis of MOFs

Using the concept of SBUs researchers were able to reproduce certain MOF architectures and topologies by replacing the organic ligands with those containing a modified spacer. The spacer in a ligand is generally a synthetically inert part of the ligand with respect to MOF synthesis, but can alter the functional properties of the material. MOFs produced using this method that possess the same network topology are referred to as “isoreticular”.\textsuperscript{33} The isoreticular series based on MOF-5, reported by Eddaoudi \textit{et al.},\textsuperscript{28} are prime examples of such MOFs and are referred to as IRMOFs (isoreticular MOFs, \textbf{Figure 6}). This series shows a systematic increase in pore volume through lengthening of the spacer in the organic dicarboxylate linker, as well as functionalisation of the pores by adding side groups (–Br, –NH₂, etc.) to the spacer. This approach allows tuning of properties such as sorption capacity and selectivity.\textsuperscript{32} In addition, such isoreticular series are useful platforms for the systematic study of the properties of MOFs.\textsuperscript{34-37}

\textbf{Figure 6.} The isoreticular doubly-interpenetrated IRMOFs. The change in the MOF cavity size is indicated by the large yellow spheres. Figure taken from Eddaoudi \textit{et al.}\textsuperscript{28}
1.2.4. Porosity

A material is considered porous if it contains voids within its structure that could be occupied by guest molecules. To prove that a material is porous, permeability specific to a host phase should be demonstrated.\textsuperscript{38} The degree of porosity can be established experimentally by determining the surface area of a material, generally applying BET (Brunauer-Emmett-Teller) theory to nitrogen sorption data measured at 77 K.\textsuperscript{39} However, this only demonstrates the permeability of the material with respect to nitrogen and does not guarantee the adsorption of other guests. From this perspective, a material could have voids within its structure without being porous, or it could be only be porous towards selected guests. Kitagawa \textit{et al.} categorised porosity based on the spatial dimensions of the voids (\textbf{Figure 7}).\textsuperscript{11} Zero-dimensional pores are isolated within the host framework. One-dimensional porosity refers to non-intersecting channels, while two-dimensional porosity exists in assemblies of separate layers. Three-dimensional porosity constitutes a system of intersecting channels.

![Four categories of porosity in MOFs/PCPs: 0D, 1D, 2D, and 3D](image)

\textbf{Figure 7.} The four categories for the dimensionality of porosity in MOFs/PCPs: 0D, 1D, 2D, and 3D porosity. Figure recreated from Kitagawa \textit{et al.}\textsuperscript{11}

1.2.5. Gas sorption

Sorption capacity is influenced by three factors: (i) the molecular sieving effect, which is based on a size/shape exclusion principle, (ii) the thermodynamic effect, which results from preferential packing of gas molecules in the pores of the host, the channel topology and the surface interactions between gas molecules and the channel walls, and (iii) the kinetic effect, resulting from different gases having different kinetic diameters and energies, which in turn leads to variation in diffusion rates. Together, these factors contribute to the characteristic isotherms associated with sorption; in this regard the IUPAC has classified six typical sorption isotherms (\textbf{Figure 8 (a)}).\textsuperscript{40-41} The Type I isotherm is usually associated with microporous
frameworks, Types II, III and VI with non-, meso- or macroporous materials, and Types IV and V exclusively with mesoporosity. According to Fletcher et al.\textsuperscript{42} the shapes of the isotherms are influenced by pore size, host-guest and guest-guest interactions. Moreover, the shapes of the isotherms for rigid frameworks are greatly influenced by electrostatic interactions, which can produce artifacts (e.g. adsorption hysteresis and stepped isotherms) similar to those induced by framework flexibility.\textsuperscript{43}

Figure 8. (a) Types of physisorption isotherms. (b) The four typical hysteretic isotherms.\textsuperscript{40-41, 44}

Adsorption hysteresis occurs when the sorption and desorption isotherms do not overlap, and may result from intrinsic framework flexibility, a phase transition, capillary condensation or gas trapping within the pore apertures.\textsuperscript{45} Sorption isotherms that display hysteresis can be classified into several categories, as shown in Figure 8 (b): extreme (H1 and H4) and intermediate (H2 and H3). In H1 the hysteretic sorption and desorption isotherms are close to vertical and almost parallel to each other (Figure 9 (a)) while in H4 they are close to horizontal and almost parallel. Types H2 (Figure 9 (b)) and H3 have shapes that fall between those of H1 and H4.\textsuperscript{44} Sorption hysteresis can be exploited in various applications such as storage where the materials are filled at a high gas pressure and then stored at a lower pressure while still maintaining a high gas loading.\textsuperscript{45} This is a result of the difference in loadings involved in the adsorption and desorption processes at particular pressures, as determined by sorption analysis (Figure 9 (b)).

Figure 9. Examples of experimental hysteretic CO\textsubscript{2} sorption. (a) Zn(terephthalate)(1,2,3-triazolate) at 25 °C,\textsuperscript{46} and (b) [Ni(1,2-bis(4-pyridyl)ethylene)][Ni(CN)\textsubscript{4}] at different temperatures.\textsuperscript{45}
1.2.6. Flexible MOFs

Flexible MOFs or 'soft porous crystals' are materials that respond dynamically to stimuli such as pressure, atmospheric vapour or gas pressure, changes in temperature, and electromagnetic radiation. In 2005, Kitagawa et al. classified these materials under three categories: first, second and third generation based on the framework response to guest removal (Figure 10). The first generation compounds collapse and lose all structural integrity when the guest is removed. The second generation materials are permanently porous, usually rigid frameworks. The third generation compounds are soft porous crystals that undergo reversible transformations upon guest removal, uptake or exchange. In 2009, Kitagawa et al. updated their definition to state that "at least one crystal phase possesses space that can be occupied by guest molecules, so that the framework exhibits reproducible guest adsorption".

Figure 10. Schematic representation of first, second and third generation porous coordination polymers as described by Kitagawa et al.

Schneemann et al. summarised the different modes of flexibility in MOF structures (Figure 11). These include breathing, swelling, linker rotation and subnetwork displacement. Often such changes lead to distinct phases, a narrow-pore (np) and a large-pore (lp) phase. The sorption properties of the materials is greatly affected by this kind of flexibility and can produce steps (gate-opening) in the sorption isotherm at particular pressures for certain gases. This gate-opening step occurs upon transformation of the MOF from the np to the lp phase. The MIL-53(M) ([M(1,4-benzenedicarboxylate)(OH)]ₙ where M = Al, Fe, Cr, Sc, Ga, In) series are typical examples of breathing flexibility (Figure 12 (a) and (b)). Lama et al. reported linker rotation of both ligands in the MOF [Zn(terephthalate)(1,2,3-triazolate)]ₙ upon sorption of CO₂ at high pressures (Figure 12 (c) and (d)). Other types of np/lp transformations include conformational isomerism of the organic ligands by irradiation with light or temperature and breaking/reformation of metal-ligand coordination bonds. The terms narrow-pore and large-pore are generic terms pertaining to all dimensionalities of porosity. However, in work presented in this dissertation, we use the terms narrow-channel (nc) and wide-channel (wc), which are more specific to 1D porosity (i.e. channels).
1.2.7. Solvatochromism in MOFs and PCPs

Solvatochromism is the propensity of a compound or material to change colour when exposed to a different solvent. This property was first studied for organic dye molecules in solution using UV-vis absorption spectroscopy. The first systematic study of solvatochromism was
carried out by Kosower in 1958 as a means to probe solvent polarity.\textsuperscript{57} Recognizing MOFs and PCPs as versatile platforms for hybrid-organic materials, researchers have sought to incorporate the properties of organic dyes and chromophores into porous materials.\textsuperscript{58} In MOFs, solvatochromism generally originates from d-d transitions of metal centres undergoing a change in their coordination sphere.\textsuperscript{59-60} This is usually accompanied by large structural changes in the framework that can lead to deterioration of the material.\textsuperscript{61-63} A shift in the d-d absorption of the metal can also be induced through interaction of guest molecules with the organic ligands, which in turn affects the electronic structure of the metal.\textsuperscript{64} As a result, effort has gone into generating MOFs with stable pores upon guest exchange and with chromophores as organic linkers forming the walls of the pores. Building this property into a MOF can turn the material into a functioning small-molecule sensor. A prime example of a MOF-based small-molecule sensor, shown in Figure 13, contains stable pores with the channel walls comprising hydrogen-bonded solvatochromic tetrazine-based bipyridyl ligands (Figure 13 (a)). Figure 13 (b) shows the large visible colour difference for each solvate.\textsuperscript{65}

\[ \text{Figure 13. (a) Structure of a nanotubular MOF. (b) Photograph of different inclusion compounds showing considerable changes in colour. Figure taken from Zhen-Zhong Lu et al.}\]

### 1.3. PLEOCHROISM

Double refraction (birefringence)\textsuperscript{66} is the division of a beam of light into two rays (two principal vibrations) when it passes through an anisotropic material (Figure 14 (a)): an ordinary ray (O-ray) and an extraordinary ray (E-ray). These mutually perpendicular principal vibrations are oriented perpendicular to the direction in which the waves propagate. The paths of the two rays diverge as they travel through the crystal, thus resulting in different path lengths. Since the rays follow different path lengths through the anisotropic material the extent of their absorption by the material may be different (seen as different intensities, Figure 14. (b)). By using a polariser and a calcite crystal, the mutually perpendicular nature of the split ray can be observed visually (Figure 14 (b)).\textsuperscript{67} When the crystal is coloured, the O- and E-rays have specific frequencies. Owing to the different rates of absorption of the two rays, the crystal then appears to have different colours when viewed from different angles (the pathways of the two rays change giving rise to pleochroism). Rotating the crystal relative to a polariser has the effect of selecting which ray may pass through, thus changing the colour of the crystal upon
rotation (Figure 14. (c)). Polarised light also enhances the saturation of the observed colours. This makes polarised light microscopy ideal for observing pleochroism.  

Figure 14. (a) Schematic principles of birefringence. (b) Electric vector orientations of a birefringent calcite crystal. The P denotes the polarising plane, E denotes the extraordinary ray and O the ordinary ray.  

1.4. COMPUTATIONAL METHODOLOGIES AND APPROACHES IN MATERIAL SCIENCE.

In the field of materials science, important fundamental insight can be obtained regarding the properties of materials by applying quantum-mechanical (QM) methods. In this regard density functional theory (DFT) is the most cost effective method as compared to wave function-based coupled-cluster and perturbation methods. The latter are computationally very demanding for large systems, which cannot always be avoided when studying materials such as MOFs. Furthermore, the development of efficient periodic DFT methods has greatly reduced the computational cost for calculating large unit cells with heavy metal atoms such as MOF systems. Simulation of these systems at an atomistic or molecular level provides sub-microscopic insight that is experimentally inaccessible, and reveals the underlying physics. In addition, it can be used to validate the interpretation of experimental observations as well as to establish the structure-property relationship. When it comes to simulating properties that requires multi-unit-cell models, molecular dynamics (MD) and molecular mechanics (MM) simulation are the only option. These methods, parameterised using experimental and QM methods, have been successfully utilised for the prediction of possible structures and determination of properties (such as sorption) for MOFs. When used in conjunction with high resolution powder diffraction measurements, it is possible to determine the actual crystal structure of the MOF.
1.4.1. DFT for periodic systems

DFT approximates a solution for the many-electron Schrödinger equation for calculating the ground state energy of a system. DFT uses electron density \( \rho(\vec{r}) \), which is the central quantity in the method, to determine the energy of a system. A key assumption in DFT that the ground state of the system \( E_0 \) is connected to the electron density for which the energy is minimised under the constraint that the total number of electrons represented by \( \rho(\vec{r}) \) remains constant. This means that it is possible to have numerous \( \rho(\vec{r}) \) configurations for a certain system. Thus, DFT uses an iterative process, also known as the self-consistent field (SCF) procedure, to search for a \( \rho(\vec{r}) \) configuration that yields \( E_0 \).\(^{80}\)

When attempting to apply DFT to periodic systems some difficulties must be overcome. Electronic wavefunctions extend over the entire solid and consequently require an infinite basis set to expand each wavefunction. This can be overcome by applying Bloch's theorem to the cell-periodic part of the electronic wavefunctions when conducting calculations involving periodic systems. The Bloch theorem allows for the expansion of the electronic wavefunctions in terms of a distinct set of plane waves with wave vectors that are reciprocal lattice vectors of the crystal.\(^{81}\) Plane-wave basis sets can be truncated by introducing a cut-off for the kinetic energy that only includes plane waves with kinetic energies less than a particular value. Plane waves with small kinetic energies are generally more significant than those with large kinetic energies. This results in the construction of a finite basis set that significantly reduces the computational load. The plane-wave method is efficient for \textit{ab initio} MD and uses the same basis set for molecules and solids (unlike Gaussian basis sets).\(^{82}\) Calculating stresses and forces are computationally cheap in this approach, leading to efficient geometry optimisation and molecular dynamics schemes. The main computational task in plane-wave electronic calculations is fast calculation of Fourier transforms. It is an efficient way of transforming various entities such as wavefunctions, potentials and search directions from real to reciprocal space and back, which reduces the overall computational cost.\(^{83-84}\)

Pseudopotentials are required for the plane-wave method to be efficient. The basis sets for these pseudo wavefunctions are reasonably small owing to the absence of nodes inside the core regions (not \textit{“all-electron”, i.e. frozen core}). The core region is approximated by using a weaker pseudopotential that acts on a set of pseudo wavefunctions. The application of these concepts is particularly useful for describing chemical bonding.\(^{85-86}\)

The quantum mechanical (QM) DFT-based code CASTEP in the Materials Studio software\(^{87}\) suite utilises a plane wave basis-set approach and several methods to handle pseudopotentials. All calculations in CASTEP must be performed on a periodic system since the code is based on a supercell method. This code has local (LDA) and gradient-corrected (GGA) exchange-correlation functionals available. Materials Studio also incorporates the semi-empirical dispersion-correction schemes put forth by Grimme (2006, DFT-D2),\(^{88}\) Jurecka \textit{et al.} (2007),\(^{89}\) Ortmann, Bechstedt and Schmidt (2006, OBS) and by Tkatchenko and Scheffler (2009, TS).\(^{90}\) CASTEP has been successfully applied to MOFs for the study of various properties such as chemical bonding,\(^{91}\) guest-binding,\(^{92}\) gate-opening,\(^{93}\) adsorption,\(^{94-96}\) to name a few.
1.4.2. Molecular electrostatic potential (MEP) mapping

The molecular electrostatic potential \( V(\mathbf{r}) \) is a well-established and highly useful tool for the study of molecular properties and noncovalent interactions between molecules.\(^97\) The electrostatic potential is derived, as a classical Coulombic interaction using atomic monopoles, from the electron density and nuclear charges as described by Eq. 1:

\[
V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \quad \text{Eq. 1}
\]

where \( Z_A \) is the charge on nucleus \( A \), located at \( \mathbf{R}_A \), and \( \rho(\mathbf{r}) \) is the molecule’s electron density. \( V(\mathbf{r}) \) is the interaction energy between the system and a unit positive point charge at \( \mathbf{r} \) and it is typically expressed in units of energy. \( V(\mathbf{r}) \) is a three-dimensional function that can be evaluated at any point \( \mathbf{r} \) within the system, with the exception of at the nuclei \( (\mathbf{R}_A \neq \mathbf{r}, \text{Eq. 1}) \).\(^98\) These results can be mapped onto 2D planes (slices though the system under investigation) or 3D surfaces of molecules at a particular electron density contour, depending on the relevance and aspect of interest.\(^99\) The contour utilised for the 3D surface can be defined arbitrarily, which may lead to ambiguity in the analysis of the results. In this work we use the 0.0015 e/Bohr\(^3\) (0.01 e/\(\text{Å}\)^3) outer contour of the molecule’s electron density \( \rho(\mathbf{r}) \) as suggested by Bader et al.\(^100-101\) This contour contains 95-98\% of a molecule’s electron density and 97\% of a molecule’s electronic charge.\(^102\) Of the various representations of MEPs, the most common are 2D and 3D contour maps.\(^71\) The VAMP module\(^103\) of the Materials Studio software package provides high quality molecular electrostatic potentials (MEPs) a great deal faster than comparable methods.\(^104\) This code utilises a choice of standard semi-empirical Hamiltonian methods, four NDDO Hamiltonians and four ZINDO Hamiltonians. Amongst these Hamiltonians NDDO-AM1\(^*\) is parameterised for systems containing transition metals thus making it suitable for the study of MOFs.\(^105-107\)

1.4.3. Molecular mechanics (MM).

QM theory is generally employed for accurate simulation of atomic and molecular systems. However, owing to their computational expense, QM techniques are typically only applied to small systems comprising fewer than 100 atoms. Alternative more practical methodologies are required for modelling large systems such as condensed polymers and crystal structures with large unit cells.\(^108\) The goal in simulating large systems is predominantly to extract bulk (statistical) properties such as adsorption isotherms, which mainly depend on the position or average configurations of the atomic nuclei.\(^73, 109\) MM makes use of forcefields (potentials), an empirical fit to the potential energy surface, to perform such calculations. Classical simulation methods provide a number of forcefields and distribution generating techniques which generate configurations by integrating the Newtonian (classical) equations of motion. The solution of these equations is called molecular dynamics (MD).\(^110\) Since using QM to perform MD simulations is computationally very expensive, forcefield methods are more frequently employed for the treatment of large systems. MM focuses on finding static time-independent properties such as equilibrium structures, relative energies, harmonic vibrational frequencies and transition states, and essentially provides a snapshot of the system. MM allows for cheap exploration of large configurational spaces of a system in order to accomplish tasks such as
conformational searches (quench dynamics) and potential energy surface scans for very large systems.

1.4.4. Forcefields

A crucial part of any MD or MM simulation is the choice of forcefield. The forcefield is an approximate description of the potential energy hypersurface on which the atomic nuclei move. The utility of a forcefield is its description of the potential energy surface for very large systems with reasonable accuracy. Forcefields are parameterised using empirical data of a small set of models and extrapolates to larger sets of related models. Forcefields are usually tuned (parameterised) for particular groups of systems and therefore the choice of forcefield depends on the type of structure being investigated. The most common forcefields in use include pcff, COMPASS (a new version of pcff), cvff, Dreiding and Universal. Forcefields can reproduce experimental parameters such as crystal structures, sublimation energies and vibrational frequencies depending on their “fitness” (quality of the forcefield parameterisation) and therefore has quantum effects empirically included. Recently, for hybrid materials such as MOFs, there has been successful forcefield development derived from electronic structure calculations for application in gas adsorption and transport studies. However, there are chemical reactions and physical processes that are not well defined for a mechanical approach and they should always be considered.

The areas where forcefield methods cannot be used successfully are:

- Proton transfer (acid/base reactions)
- Electronic transitions (photon absorption)
- Electron transport phenomena etc.

The advantages of forcefield methods are:

- The simulation costs of forcefield-based simulations are exceedingly lower (and faster) than QM-based calculations, which allows them to handle large systems for utilisation in the study of condensed-phase molecules, macromolecules, crystal structures, etc.
- The energy can be decomposed into the contributions of the bond stretching, angle deformations, non-bonding energies, etc. The non-bonding energies can be further partitioned into its coulombic and van der Waals components.

1.4.5. Atomic partial charge calculation

The contributions of long-range electrostatic intermolecular interactions are often dominant in systems such as MOFs and have to be considered in the application of computational methods. Since Coulombic interactions decrease at a slow rate with respect to distance ($1/r$), their contribution to the interaction energy is not negligible, even at substantial distances. It is therefore important to assign the proper atomic charges, as electrostatic interactions are crucial in determining the packing and structures of organic and inorganic systems. However, the precise nature of the variation in electrostatic interaction energy with distance depends on
the structure of the material. The electrostatic potentials of MOFs are often represented by assigning partial charges on the framework atoms, which provides both computational accuracy and efficiency. Some of the typical methods for determining partial charges used in MOF studies are summarised below.

- **Mulliken Population Analysis.**
  
  This is a means of estimating partial atomic charges from calculations that use methods based on the linear combination of atomic orbitals (LCAO) molecular orbital approach.\(^{118}\) DFT calculations performed on periodic structures of MOFs utilise a plane-wave basis set, which provides no information regarding the localisation of the electrons in the system. The technique described by Sanchez-Portal *et al.* is used to project the plane-wave states onto a localized basis in order to implement population analysis. This method is used in the plane wave calculations employed by the CASTEP code running in the Materials Studio software package for periodic models.\(^{119-120}\)

- **ESP charges**
  
  Cluster-Based Quantum Mechanics are used to obtained electrostatic potential (ESP) derived charges from single-point energy DFT calculations implemented on representative clusters of a MOF. The unsaturated atoms and bonds within the models that exist due to “abbreviating” the framework are corrected using moieties such as methyl groups or hydrogen atoms.\(^{121-122}\)

- **Molecular Charge Equilibration Method (QEq).**
  
  The basic idea of charge equilibration (QEq) is the prediction of the charges and their distribution based on experimental atomic properties and the geometry of the system.\(^{123}\) This method is mainly used in the application of fast and reasonable high-throughput MOF screening.\(^{124-125}\)

- **Periodic Charge Equilibration Method (PQEq).**
  
  PQEq is an extension of QEq that includes the effect of a lattice on the charge distribution. This method only requires the unit cell content and dimensions.\(^{126}\)

### 1.5. AIMS

Owing to the versatility of MOF synthesis and applications, there has been a large increase in the number of MOF structures that have been deposited in the Cambridge Structural Database (CSD).\(^{127}\) In general, the focus in MOF research has been to produce very high porosity for applications such as sorption. However, this has led to a large number of unexplored materials in the literature and the CSD. Using the CSD we aimed to obtain MOFs with structural similarities (such as isoreticular frameworks) that could be used as platforms for the systematic study of host-guest dynamics. Using a range of complementary experimental and computational methods we sought to systematically target some fundamental aspects of the host-guest dynamics in MOFs, as well as the structure-property relationships of these materials. We opted for five copper-glutarate-based MOFs that form an isoreticular series in which only the bipyridyl ligands are substituted. These MOFs were separated in two groups for study: three containing rigid bipyridyl ligands and two with flexible bipyridyl ligands. We also studied host-guest dynamics and the related optical properties of a copper-acetate-based
PCP constructed using an optically active ligand. We investigated the link between the properties of these selected MOFs and the organic ligands used to construct them. Such a study can provide some insight into the fundamental nature of ligand-derived properties in multi-component systems such as MOFs and PCPs.

1.6. THESIS OUTLINE

The systems reported in this study were analysed using various techniques such as single-crystal X-ray diffraction, powder X-ray diffraction, thermal analysis, gas sorption, solid-state UV-vis spectroscopy, optical microscopy, and computational methods. The methodologies, experimental conditions and instrumentation used during the course of this work are described in Chapter 2 of this dissertation.

Chapter 3 describes a systematic study of three closely related microporous 3D copper(II)-glutarate-based MOFs whose pore dimensions vary according to the choice of rigid 4,4'-bipyridyl linker. The tuneable linker allows exploration of the effect of increasing pore dimensions on the sorption behaviour of the frameworks. The MOFs described here capture CO$_2$ under supercritical conditions and continue to sequester the gas under ambient conditions. The trend in the gas sorption isotherms for CO$_2$ is compared with the thermal stability of the CO$_2$ adducts formed by the three MOFs. Computational models constructed using crystallographic data were used to calculate framework electrostatic potential maps in order to elucidate the nature of the framework—CO$_2$ interactions.

In Chapter 4 the isoreticular series of rigid MOFs in Chapter 3 is extended to two MOFs containing flexible, rather than rigid, 4,4'-bipyridyl linkers. These two materials undergo spontaneous phase changes upon solvent loss at room temperature. The crystal structures of these phases, along with the CO$_2$ adducts, were analysed for insight into the phase change behaviour. Gas sorption studies were conducted using various gases to determine if the phase change can be induced using gas pressure at room temperature. Potential energy surface scans employing density functional theory and molecular mechanics were used to elucidate the phase change behaviour of these flexible 3D MOFs.

Chapter 5 describes the solvent exchange process and related structural change in a 1D PCP comprising 1D channels occupied by solvent guest molecules. This coordination polymer uses the same copper carboxylate paddle-wheel SBU as the MOFs described in Chapters 3 and 4. The bipyridyl tetrazine-based ligand used to construct this PCP afforded crystals with solvatochromic properties. These properties were exploited in order to observe the solvent exchange process involving two polar organic solvents using polarised light optical microscopy. This yielded unusual solvent exchange behaviour, which we rationalised using a computational approach.

Finally, Chapter 6 summarises this work and presents some concluding remarks.
REFERENCES


Chapter 1 - Introduction

Chapter 1 - Introduction


2.1. MATERIALS

All materials were purchased from Sigma Aldrich and used without further processing or purification except for the N,N’-bis-pyridine-4-ylmethylene-hydrazine (bpymh) and 3,6-di(pyridin-4-yl)-1,2,4,5-tetrazine (dptz) ligands, which were synthesised according to literature procedures.¹²

2.2. SYNTHESIS OF MOFS

2.2.1. Chapter 3

[Cu₂(glu)₂(bpy)]ₙ·2.9H₂O: Cu(NO₃)₂ (1 mmol), glutaric acid (H₂glu, 1 mmol) and 4,4’-bipyridine (bpy, 0.5 mmol) and 100 ml H₂O were mixed in a 100 ml reagent glass bottle and placed in a pre-heated oven at 100 °C. Green block-shaped crystals forms at 100 °C after 24 – 48 hours.

[Cu₂(glu)₂(bpe)]ₙ·3H₂O: Cu(NO₃)₂ (1 mmol), glutaric acid (H₂glu, 1 mmol) and trans-bis(4-pyridyl)ethylene (bpe, 0.5 mmol) and 100 ml H₂O were mixed in a 100 ml reagent bottle and placed in a pre-heated oven at 100 °C. Green block-shaped crystals forms at 100 °C after 24 – 48 hours.

[Cu₂(glu)₂(bpymh)]ₙ·7.5H₂O: Cu(NO₃)₂ (1 mmol), glutaric acid (H₂glu, 1 mmol) and N,N’-bis-pyridine-4-ylmethylene-hydrazine (bpymh, 0.5 mmol) and 100 ml H₂O were mixed in a 100 ml reagent glass bottle and placed in a pre-heated oven at 100 °C. Green block-shaped crystals forms at 100 °C after 24 – 48 hours.

2.2.2. Chapter 4

[Cu₂(glu)₂(bpa)]ₙ·2.4H₂O: Cu(NO₃)₂ (1 mmol), glutaric acid (1 mmol) and 1,2-bis(4-pyridyl)ethane (bpa, 0.5 mmol) and 100 ml H₂O were mixed in a 100 ml glass bottle with a plastic screw cap. One molar eqv. of NaOH was added dropwise with swirling to prevent precipitation. The blue solution was placed in an oven pre-heated to 80 °C. Green block-shaped crystals were obtained after 24 – 48 hours.

[Cu₂(glu)₂(bpp)]ₙ·2acetone: 50 ml of a H₂O/acetone (1:1) buffer solution was layered on a solution of glutaric acid (1 mmol), 1 eqv NaOH (1M) and 1,3-bis(4-pyridyl)propane (bpp, 0.5 mmol) in 50 ml H₂O/acetone (2:1). A solution of Cu(NO₃)₂ (1 mmol) in 50 ml acetone (ace) was
then layered on the buffer solution. Slow solvent diffusion was allowed to occur in an oven heated to 50-55° C. Green block and plate-like crystals form at 50-55° C and were isolated after 48 hours.

2.2.3. Chapter 5

$[\text{Cu}_2(\text{acetate})_2(\text{dptz})]_n \cdot 2\text{CHCl}_3$: 50 ml methanol:chloroform buffer (1:1) was layered on a chloroform solution of 3,6-di(pyridin-4-yl)-1,2,4,5-tetrazine (dptz). A methanolic solution of Cu(acetate)$_2$ (0.5 mmol in 50 ml) was then layered on top of the buffer solution. The layered mixture was kept in a 200 ml reagent bottle at 50 °C to afford dark-purple block-shaped crystals.

2.3. SINGLE-CRYSTAL X-RAY DIFFRACTION (SCD)

Suitable single-crystals were selected and loaded onto a diffractometer using a MiTeGen MicroCrystal mount. Single-crystal X-ray diffraction data were collected using a Bruker SMART or an APEX-II DUO diffractometer. Both diffractometers are equipped with APEX-II CCD area-detectors and Oxford Cryosystems 700Plus cryostats. For the SMART X-rays were generated from a sealed tube (MoK$\alpha$ radiation $\lambda = 0.71073 \text{ Å}$) fitted with a multilayer monochromator, while the APEX-II DUO uses an Incoatec $\text{I}_\mu$S microfocus source fitted with a multilayer monochromator. All data were collected at 100 K.

Data reduction was carried out by means of a standard procedure using the Bruker software package SAINT$^3$ and absorption corrections and the correction of other systematic errors were performed using SADABS$^4$. Using Xseed$^5$-$^6$ and Olex2$^7$, each structure was solved with the ShelXS$^7$ structure solution program using Direct Methods and refined with the ShelXL$^8$ refinement package using least squares minimisation. Hydrogen atoms were placed in calculated positions using riding models. PLATON SQUEEZE$^9$ was used to determine the total electron count per unit cell (e/\text{unit cell}) of guest molecules within the MOFs. These values were used to determine the total occupancy of the guest molecules within the MOFs.

2.4. POWDER X-RAY DIFFRACTION (PXRD)

A benchtop Bruker D2 PHASER equipped with a Lynxeye 1D detector and Ni-filtered Cu K$\alpha$ radiation ($\lambda = 1.5418 \text{ Å}$, generator power is set at 30 kV and 10 mA, and the X-ray beam is restricted by a 1.0 mm divergence slit and a 2.5 mm Soller collimator) was used for routine powder X-ray diffraction (PXRD) data collections. Samples were ground into a powder (with a mortar and pestle) if needed and then loaded onto zero-background sample holders. Samples that lose solvent spontaneously at RT were wrapped with clingfilm to prevent solvent loss during the experiment. A PXRD trace was first measured for the clingfilm on its own in order to ensure that it does not interfere with the PXRD trace of the material of interest.

2.5. THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermogravimetric analysis was conducted using a TA Instruments Q500 analyser. Samples were weighed into a standard TA Instruments aluminium pan and heated from room
temperature at 10 °C/min under a N\textsubscript{2} flow of 50 mL/min up to 600°C. A typical sample size of 1–10 mg was used. Data were exported using the Universal Analysis 2000 v 4.5A (TA Instruments) software while the analyses and figures were prepared using OriginPro.\textsuperscript{10}

2.6. DIFFERENTIAL SCANNING CALORIMETRY (DSC)

DSC provides information regarding the physical and chemical changes of a material as a function of temperature. Thermal events are observed as either endothermic or exothermic peaks. A TA Instruments Q100 with Liquid Nitrogen Cooling Accessory (LNCS) was used for differential scanning calorimetry. DSC measures the heat flow into or out of the sample, relative to a reference (empty pan identical to the sample pan), as a function of time and temperature in a controlled atmosphere (Typically N\textsubscript{2} with a flow rate of 50 ml/min). A sample of 1–10 mg was placed in a standard TA Instruments aluminium pan and either analysed as an open pan or covered with an aluminium lid, crimped and pricked to form a pin hole in the lid. The reference pan is subjected to the same protocol as the sample pan. The sample was then heated and cooled at a rate of 10 °C/min. Data were exported using the Universal Analysis 2000 v 4.5A (TA Instruments) software while the analyses and figures were prepared using OriginPro.\textsuperscript{10}

2.7. SUPERCRITICAL CO\textsubscript{2} EXPERIMENTS

Newly synthesised MOF crystals were exposed to supercritical CO\textsubscript{2} (scCO\textsubscript{2}) for 24 h to obtain the apohost or activated phase. Supercritical CO\textsubscript{2}, having properties of both liquid and gas, exerts little or no surface tension on the walls of the channels in the crystal. Depending on the solvent present in the channels and the exact conditions of temperature and pressure (31.1 < T\textsubscript{c} < 44 °C; 73 < P\textsubscript{c} < 110 bar – beyond the critical temperature and pressure) scCO\textsubscript{2} is able to dissolve the solvent molecules and leave behind the activated phase. Typically, after the experiment the vial containing the crystals is placed directly onto dry-ice in a Dewar flask for transport to the analytical instruments.

2.8. VOLUMETRIC SORPTION MEASUREMENTS

A Setaram PCTPro-E&E gas sorption analyser with MicroDoser attachment was utilised to conduct high pressure gas sorption experiments with test gases such as N\textsubscript{2}, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8} and CO\textsubscript{2}. The instrument is a volumetric gas analyser which utilises Sievert’s volumetric method. The sample temperature was maintained to an accuracy of ± 0.05 °C using a Grant refrigerated recirculation bath filled with antifreeze and water. A sample at known pressure and volume was connected to a reservoir of known volume and pressure through an isolation valve. The valve was opened and the system allowed to equilibrate. The difference between the measured pressure and calculated pressure was used to determine the amount of gas adsorbed. NIST software was used to calculate the thermodynamic corrections in order to account for the non-ideal behaviour of the gases at relatively high pressures. The PCTPro-E&E with the MicroDoser attachment is used for small sample sizes and has a range of vacuum to 60 bar. Sample sizes of 100-250 mg were used and activated in-situ using vacuum and heat, if necessary. Blank runs for each gas were recorded to further correct for any other residual
systematic errors in the experiment. Figure preparation and data analyses were performed using Microsoft Excel and OriginPro.\textsuperscript{10}

2.9. **FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)**

A Thermo Nicolet iS10 spectrometer with ATR attachment was used to measure IR spectra. A background scan was collected immediately before each sample scan.

2.10. **SOLID-STATE UV-VISIBLE SPECTROSCOPY**

Solid-state UV-visible absorption spectra were measured using a SPECORD 210 PLUS spectrophotometer with an integrating sphere supplied by Analytik Jena. The data were analysed and exported using the native software package WinAspect PLUS 3.9.14. and then plotted using Origin Pro.

2.11. **TIME-LAPSED POLARISED-LIGHT OPTICAL MICROSCOPY**

Single crystals of the relevant compounds were immersed in acetonitrile and nitromethane and sealed within a chamber with windows at the top and bottom. Adjustment (lighting, crystal position, polariser, etc.) were made rapidly and photographs were taken using an appropriate time interval (10 s – 5 min).

![Observer diagram](image)

**Figure 15.** The Leica optical microscope setup used to conduct solvent-exchange experiments.

2.12. **CAMBRIDGE STRUCTURAL DATABASE (CSD)\textsuperscript{11}**

The CSD (version 5.37 + February 2016 data base update) is a structural database that contains published single-crystal and powder diffraction data. The user can conduct searches with specific constraints to obtain a refined set of structural data consistent with the imposed constraints. This makes it possible to study systems with similar traits, synthons and so on to
further understand the nature of intermolecular interactions, molecular conformations, and their roles in the formation of crystals. In this work a search was carried out for glutarate conformations within the database and the frequency of occurrence of these conformations was evaluated.

2.13. GAUSSIAN09

DFT calculations were carried out using the Gaussian09 software package. This was used to compute a gauche torsional scan of a single glutaric acid molecule. All optimisations were carried out at the mPW1PW91/6-311+G(d,p) (hybrid Hartree–Fock density functional) level of theory. The SCF=QC option was used to manage conversion difficulties and consequently a larger DFT integration grid (Int=UltraFine) was chosen.

2.14. BIOVIA MATERIALS STUDIO

Materials Studio is a modelling and simulation platform for materials science and chemistry-related fields that enables the user to predict and understand the structure-property relationships of a material.

2.14.1. Materials Visualiser

BIOVIA Materials Studio Visualiser is the core interface of all the materials studio computational modules combined with modelling, analysis, and visualisation tools. The interactive sketching, building and editing tools allow for the construction of molecules as well as periodic models (crystal structures). Results from calculations can be visualised and animated (potentials scans, dynamics trajectories, etc.). Volumetric and surface data (from calculations) of charge density, potentials, and orbitals can be visualised and overlaid. Morphology calculations combined with crystal facets (from SCXRD face indexing) are used to display crystal habits, which can be overlaid with the crystal structures from which they were generated. The Visualiser module also provides a scripting tool which allows for receptive, iterative and linked tasks (between Materials Studio modules). The "MaterialsScript" Application Programming Interface (API) also supports scripts written in Perl and allows for debugging with the Visualiser. The scripting capabilities allow one to perform tasks well beyond the capability of the user interface. In this study scripting was mostly used to perform potential energy scans on both molecular and periodic systems.

2.14.2. CASTEP (Cambridge Serial Total Energy Package)

CASTEP is a contemporary quantum mechanics-based program specifically designed for solid-state materials science. CASTEP utilises the DFT plane-wave pseudopotential method which allows for first-principles quantum mechanics calculations that explore the properties of crystals in materials such as semiconductors, ceramics, metals, minerals, zeolites and metal-organic frameworks (MOFs). CASTEP was used to optimise the hydrogen atoms of all the MOF crystal structures as periodic systems. Optimisations was performed using the GGA PBE functional with Grimme’s DFT-D dispersion correction. The thresholds for the geometry optimisation and SCF convergence were chosen as $1 \times 10^{-6}$ eV. Mulliken charges were
calculated at the end of the optimisation process (this is given as an option in the properties tab of the calculation setup). These atomic charges were used in all the molecular mechanics and molecular dynamics calculations.\textsuperscript{14}

2.14.3. DMOL\textsuperscript{3}

DMol\textsuperscript{3} is an all-electron numerical method for solving density functional theory (DFT) to model the electronic structures and energetics of molecules, solids, and surfaces. In this work, DMol\textsuperscript{3} was used to perform single-point energy calculations (using CASTEP geometries) in order to extract the electron density grid. In this study the 0.01 $e^{-}/\AA^{3}$ outer contour of the molecule or framework’s electron density ($\rho(r)$) was used to generate a 3D surface on which to map the electrostatic potential of the molecule or framework.\textsuperscript{15-16}

2.14.4. Forcite Plus

Forcite is a collection of molecular mechanics tools for the investigation of a wide range of systems. The potential energy surface, on which the atomic nuclei move, is represented by a classical forcefield. High level quantum mechanical calculations and experiment data were used to parameterise the forcefields. Forcite employs several forcefields, namely COMPASS\textsuperscript{17}, Dreiding\textsuperscript{18}, Universal\textsuperscript{19} and pcff\textsuperscript{20}. Forcite can perform the following tasks: single-point energy calculation, geometry optimisation, molecular dynamics (MD), quench dynamics (QD), anneal dynamics, shear, confined shear, cohesive energy density calculation, mechanical properties calculation, solvation free energy calculation. Forcite can perform calculations on single molecules and periodic systems (crystal structures). In this work geometry optimisations, MD and MaterialsScript API (see 2.14.1) were using in conjunction with one another to perform various complex simulations.

2.14.5. VAMP

VAMP is a semi-empirical molecular orbital package optimised to be highly numerically stable and fast. VAMP also implements the natural atomic orbital/point charge (NAO-PC) model for molecular electrostatic properties. It gives accurate dipole and quadrupole data, and high quality molecular electrostatic potential (MEP) data. In this work VAMP was used to calculate MEPs that were mapped on the outer electron density contour of a molecule or MOF. The electrostatic potentials were calculated as part of single-point energy calculations using the NDDO - AM1* method. An SCF convergence threshold of $5 \times 10^{-7}$ kcal mol$^{-1}$ was used and the grid size for the imported electrostatic potential was set to 0.1 Å. The electron density data obtained from CASTEP (periodic systems) and DMol\textsuperscript{3} (molecular models) calculations were used to construct the 3D 0.01 e$^{-}/\AA^{3}$ electron density contours of the molecules or frameworks.

2.14.6. Adsorption Locator

The Adsorption Locator module was used to simulate a substrate loaded with an adsorbate. Adsorption Locator can determine low energy adsorption sites on both periodic and non-periodic substrates to investigate preferential adsorption. Adsorption Locator uses an MD simulated annealing approach to identify possible adsorption configurations by carrying out
Monte Carlo searches of the configurational space of the substrate-adsorbate system as the temperature is slowly decreased stepwise. In this work it was used to study the interactions between two solvents (nitromethane and acetonitrile) and two experimentally identified crystal faces.
REFERENCES

[10] Origin (OriginLab, Northampton, MA)
CHAPTER 3

EXTREME CO$_2$ SORPTION HYSTERESIS IN OPEN-CHANNEL RIGID METAL-ORGANIC FRAMEWORKS

3.1. COMMUNICATION IN ANGEWANDTE CHEMIE INTERNATIONAL EDITION (PUBLISHED)

Contributions of the author:

- Design of project with Dr Vincent J. Smith
- Preparation of MOFs
- Supercritical CO$_2$ experiments
- Collection of single-crystal X-ray data
- Solution and refinement of single-crystal X-ray structures
- Recording of PXRD patterns
- Recording of TGA and DSC thermograms
- Sorption analysis with Dr. Prashant M. Bhatt
- Computational modelling and electrostatics calculations
- Interpretation of results with Dr Vincent J. Smith
- Writing the first draft of the article
Extreme CO₂ Sorption Hysteresis in Open-Channel Rigid Metal-Organo Frameworks

Charl X. Bezuidenhout, Vincent J. Smith, Prashant M. Bhatt, Catharine Esterhuysen and Leonard J. Barbour

Abstract: We report a systematic study of three closely related microporous metal-organic frameworks whose pore dimensions vary according to the choice of 4,4’-bipyridyl linker. The tunable linker allows exploration of the effect of increasing pore dimensions on the sorption behaviour of the frameworks. The MOFs described here capture CO₂ under supercritical conditions and continue to sequester the gas under ambient conditions. Gas sorption isotherms for CO₂ are compared with thermogravimetric data and the CO₂ molecules in the channels of the frameworks could be modeled using single-crystal X-ray diffraction analysis. Crystallographic data were used to construct a theoretical model based on DFT methods in order to calculate framework electrostatic potential maps with a view to understanding the nature of the sorbate-sorbent interactions.

The potential advantages of metal-organic frameworks (MOFs) for CO₂ capture and storage are derived from a number of their inherent properties. These include chemical versatility, robustness, high thermal and chemical stability, large surface areas, and large void volumes. High guest-accessible volumes and surface areas result in low densities, which in turn may yield high CO₂ sorption capacities by weight. This is evidenced by superior active surface areas per unit weight (up to 7100 m² g⁻¹ for MOFs) when compared to other sorbents such as activated carbon and zeolites (400 to 1500 m² g⁻¹). However, for some applications (e.g. separation), sorption capacity is less important than selectivity. The latter is influenced by three factors: (i) the molecular sieving effect, which is based on a size/shape exclusion principle, (ii) the thermodynamic effect, which results from preferential packing of gas molecules in the pores of the host, the channel topology and the surface interactions between gas molecules and the channel walls and (iii) the kinetic effect, resulting from different gases having different kinetic diameters and energies, which in turn leads to variation in diffusion rates. Together these factors contribute to the characteristic isotherms associated with sorption; in this regard the IUPAC have classified six typical sorption isotherms (Figure S1, ESI), five of which are based on the work by Brunauer et al. (BDPT system).[13] The Type I isotherm is usually associated with microporous frameworks, Types II, III and VI with non-, meso- or macroporous materials and Types IV and V exclusively with mesoporosity. According to Fletcher et al.[40] the shapes of the isotherms are influenced by pore size, host-guest and guest-guest interactions. Moreover, the shapes of the isotherms for rigid frameworks are greatly influenced by electrostatic interactions, which can produce artifacts (e.g. adsorption hysteresis and stepped isotherms) similar to those induced by framework flexibility.[43,46]

Adsorption hysteresis occurs when the sorption and desorption isotherms do not overlap and it may result from intrinsic framework flexibility, a phase transition, capillary condensation or gas trapping within the pore apertures.[45] Sorption isotherms that display hysteresis can be classified into several categories as shown in Scheme 1: extreme (H1 and H4) and intermediate (H2 and H3). In H1 the hysteretic sorption and desorption isotherms are close to vertical and almost parallel to each other while in H4 they are close to horizontal and almost parallel. Types H2 and H3 have shapes that fall between those of H1 and H4.[43]

The positions of guest molecules in a channel or cavity are determined by steric forces resulting from Pauli repulsion (host-guest fit) and attractive interactions with the walls of the channel or cavity. The latter are primarily due to electrostatic attraction, although dispersion may also play a role. In a largely uniform channel, steric repulsion and attractive dispersion interactions remain relatively constant along the channel length. Hence the electrostatic interactions between the guest and the walls of the channel play a dominant role in determining the guest sorption site.[45] Therefore molecular electrostatic potential (MEP) maps can provide significant insight into the nature of the electrostatic interactions between guest molecules and the host framework.

The MEP (V(r)) is a well-established and highly useful tool for the study of molecular properties and noncovalent interactions between molecules. Of the various representations of MEPs, the most common are two-dimensional (2D) and three-dimensional (3D) contour maps.[46,47] The application of MEPs is mainly associated with the study of electrostatic (Coulombic) interactions,[51] e.g. in the study of protonation processes,[52] molecular recognition,[52] differentiation between agonists and antagonists,[53] enzyme-ligand interactions,[54] excited electronic...
states,\textsuperscript{10} molecular reactivity,\textsuperscript{11} and autoamination.\textsuperscript{12}

The hydrothermal reaction of Cu(NO\textsubscript{3})\textsubscript{2}–2.5H\textsubscript{2}O, glutaric acid (gluH\textsubscript{2}) and L\textsubscript{4} where L\textsubscript{1} = 4,4′-bipyridine (bpy), L\textsubscript{2} = trans-bis(4-pyridyl)ethylene (bpe) and L\textsubscript{3} = $N,N'$-bis-pyridine–4-$N'$-methylene-hydrazine (bpymh) in H\textsubscript{2}O yielded three 3D MOFs: [Cu(glu)(bpy)2(H2O)]·3H\textsubscript{2}O = 1a, [Cu(glu)(bpymh)·3H\textsubscript{2}O] = 2a and [Cu(bpe)(bpy)mH\textsubscript{2}O]·7.5H\textsubscript{2}O = 3a.\textsuperscript{13} Green block-shaped crystals of the as-synthesized frameworks were dehydrated by placing them under dynamic vacuum at 150 °C for 24 h, affording crystals of the apohosts 1, 2 and 3 (Figure 1). Single-crystal X-ray diffraction analysis (SCD) reveals the homeotypic\textsuperscript{14} nature of frameworks 1a, 2a, 3a, 1, 2 and 3. All of the frameworks crystallize in the monoclinic space group C2/c with their a axes, b angles, unit cell volumes and channel dimensions responding to changes in the length of the bipyridyl linker. The three rigid microporous frameworks are related to the α-polonium net and contain open 1D corrugated channels with constriction and dilation dimensions of 2.8 × 5.5 Å and 5.6 × 7.6 Å for 1, 4.7 × 6.5 Å and 7.3 × 10.9 Å for 2, and 6.2 × 7.2 Å and 9.2 × 10.6 Å for 3. The framework structures can be described as 2D corrugated layers comprising glutarate anions that are equatorially coordinated to two pentacoordinate Cu cations, thus forming paddlewheel secondary building units (SBUs). Adjacent corrugated layers are joined by the various axially coordinated linkers that form crisscrossed pillars (Figure S2).

In order to distinguish between the idealized arrangements of CO\textsubscript{2} molecules in dry ice and those observed in frameworks 1b, 2b and 3b, we prefix the term describing the arrangement with "pseudo". The CO\textsubscript{2} molecules in 1b are pseudo-crossed along the channel while those in 2b are both pseudo-crossed along the channel and pseudo-slipped-parallel diagonally across the channel (Figure S3). The CO\textsubscript{2} molecules of 3b only adopt the pseudo-slipped-parallel arrangement diagonally across the channel.

Owing to the remarkable stability of 1b, 2b and 3b to guest-loss under ambient conditions it was possible to analyse each sample using thermogravimetric analysis (TGA) (Figure 3), differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR). Comparative FTIR analysis of the as-synthesized, activated and scCO\textsubscript{2} exposed materials confirmed the presence of CO\textsubscript{2} in 1b, 2b and 3b (Figure S4). The evolution ranges for the guest CO\textsubscript{2} in the three frameworks are 40 – 250 °C for 1b, 30 – 90 °C for 2b and 30 – 80 °C for 3b (Figure S5). Stechiometric data obtained from TGA and SQUEEZE\textsuperscript{10} (calculations are tabulated in Table S1). Thermal stability, defined here as the temperature corresponding the maximum rate of expulsion of CO\textsubscript{2} from the framework, is inversely related to the size of the channel, with 1b >> 2b ≈ 3b (164, 66 and 64 °C, respectively), implying that CO\textsubscript{2} evolution follows a trend of decreasing steric stabilization.

We also investigated whether the as-synthesized frameworks could be desolvated under supercritical CO\textsubscript{2} (scCO\textsubscript{2}) conditions according to a procedure similar to that first reported by Hupp et al.\textsuperscript{15} After separately exposing 1a, 2a and 3a to scCO\textsubscript{2} for 24 h, crystals of suitable quality were selected under ambient conditions and then subjected to SCD analysis at 100 K. The crystal structures reveal that the original H\textsubscript{2}O molecules had been replaced by CO\textsubscript{2} molecules, which are then retained in the channels after removal of the crystals from scCO\textsubscript{2}. The new phases 1b, 2b and 3b are also homeotypic with respect to the as-synthesized and apohost phases. In all three cases it was possible to model the CO\textsubscript{2} molecules in the dilated regions of the channels using SCD analysis (Figure 2); guest arrangements in the channels of 1b, 2b and 3b resemble two of those observed in dry ice i.e. slipped-parallel and crossed (Figure S3). However, the T-shaped motif is not observed. The intermolecular distances between neighboring CO\textsubscript{2} molecules are much larger than those observed in dry ice, and this is most likely due to corrugation of the channel.
Figure 3. TGA thermograms for 1b, 2b and 3b.

Figure 4. Type-I CO₂ sorption and desorption isotherms, measured at 25 °C, for frameworks 1, 2 and 3.

The isotherms shown in Figure 4 are characteristically Type-I, as expected for microporous frameworks. Furthermore, all three isotherms exhibit hysteresis, with 1 and 2 displaying a combination of H1 and H4 extreme hysteresis, while 3 displays type H3 intermediate hysteresis. For each isotherm, we have calculated the extent of hysteresis (as defined in the ESI, and specifically for use in this work), which is expressed as a percentage. The isotherm for 2 exhibits the most extreme hysteresis (21.1%), followed by 1 (13.1%) and 3 (3.3%). It is interesting to note that framework 2, with intermediate channel dimensions, experiences the most extreme hysteresis while the order of hysteresis experienced by 1 and 3 corresponds inversely to their relative channel dimensions. The results for 2 are also at odds with the thermal stability data determined from TGA and a computational investigation was therefore undertaken in order to explain this apparent anomaly.

Figure 5. FEP surfaces of 1, 2 and 3 mapped onto their respective 0.01 e Å⁻³ electron density contours. Bottom left: The molecular electrostatic potential (MEP) of an isolated CO₂ molecule mapped onto the 0.01 e Å⁻³ electron density contour (upper) and a 2D slice of the CO₂ electrostatic potential (lower).

The unusual hysteretic behaviour of 2 cannot be explained by steric interactions (i.e., channel topology) alone. We therefore investigated the host-guest electrostatic interactions in order to quantify the stability of CO₂ in frameworks 1, 2 and 3. For each framework, the electrostatic potential (FEP) was calculated based on a channel with three unit cells in length along [001] (Figure 5). Using electron density data obtained from DFT calculations (see ESI for details), three-dimensional electron density contours at 0.01 e Å⁻³ intervals were calculated for both the CO₂ molecules and the framework channels. The electrostatic potential calculated for each framework was then mapped onto the two electron density contours for each host-guest system (Figure 5). From the channel electron density contours it appears that the three frameworks have similar electrostatic topologies. In order to elucidate how this influences the CO₂ molecules, the FEPs were mapped onto the CO₂ electron density contours in their crystallographically determined positions. For comparison, the molecular electrostatic potential of an isolated CO₂ molecule is shown at the bottom left of Figure 5; negative potentials are present on the oxygen atoms and, consequently, a highly positive potential is centred on the carbon atom. This suggests that a CO₂ carbon atom can form stronger electrostatic interactions as compared to the oxygen atoms.

The significance of the electrostatic potential becomes apparent when we consider the Coulombic interactions between CO₂ molecules and the three frameworks. The FEPs of 1, 2 and 3 mapped onto the CO₂ molecules provide a detailed representation of their electrostatic interactions with the frameworks. Attractive interactions between the CO₂ molecules and the surrounding framework occur where the MEPs and FEPs display opposite colouring (in the extreme, blue on red). The bottom right-hand side of Figure 5 shows that 1 possesses moderate positive and negative potentials near the oxygen atoms of the CO₂ molecules, as well as a weak positive potential around the carbon atom. Since there is little overall electrostatic stabilization between the CO₂ molecules and the host framework, the CO₂ is mostly stabilized by dispersion interactions (London forces). Frameworks 2 and 3 have strong negative potentials (almost double the magnitude of those of their positive potentials, see Table S2) near the carbon atom of the CO₂ molecule (Figure 5, blue regions). These strong electrostatic interactions therefore determine the positions of the CO₂ molecules within the frameworks of 2 and 3. Further fine-tuning of the CO₂ position and orientation is achieved through weaker electrostatic interactions between the framework and the oxygen atoms of the CO₂ molecules. The only destabilizing electrostatic interactions in 2 and 3 are due to negative potentials on the oxygen atoms of the CO₂ molecules that are repelled by the negative potentials β and γ for their respective frameworks (Table S2). Framework 3 has a slightly larger value for the negative potential γ, thus forming a more stabilizing interaction with the positive potential on the CO₂ as compared to 2, while β and γ for 2 are far lower in magnitude than those for 3 (indicating lower electrostatic repulsion and hence less destabilization). Moreover, 2b shows the largest positive potentials around the oxygen atoms of the CO₂, confirming that framework 2 possesses the most electrostatically stabilized site for CO₂ binding. All of the positive FEP maxima are due to framework hydrogen atoms, while the FEP minima are due to the carboxylate oxygen.
atoms (Figure S7). The guest docking sites in 2 and 3 thus appear to be electrostatically complementary to CO$_2$ molecules. In 1 the CO$_2$ molecules are bound sterically, whereas those in 2 and 3 are able to adjust their positions in accordance with the electrostatics of the framework, thereby maximising host-guest interactions.

We have shown that open-channelled MOFs are capable of trapping CO$_2$ under sCO$_2$ conditions while also being able to sequester CO$_2$ at room temperature (RT). These MOFs display extreme hysteresis at high pressures and RT and we have shown that framework electrostatic maps (FEPs) provide a powerful means of understanding trends in host-guest binding stability. We have shown that MOFs 1, 2 and 3 meet two of the three principles of selectivity mentioned earlier: (i) the size/shape exclusion principle and (ii) the thermodynamic effect due to preferential packing, surface interactions and suitable topology. The third principle (i.e. the kinetic effect) is a property of the gas and not of the framework. From our test-case study of three analogous frameworks, we can conclude that the steric and electrostatic/topologies of framework 2 provide the most favourable combination of factors for binding CO$_2$ guest molecules, thus explaining the observed extreme sorption-desorption hysteresis.

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**Keywords:** carbon dioxide sorption • extreme hysteresis • framework electrostatic potential • molecular electrostatic potential • high pressure sorption

3.2. SUPPORTING INFORMATION

Materials. All materials were purchased from Sigma Aldrich and used without further processing or purification except for \(N,N'\text{-bis}-\text{pyridine}-4\text{-ylmethylene-hydrazine, which was synthesized according to the literature procedure.}\)[2]

Synthesis of 1, 2 and 3. The hydrothermal reaction of \(\text{Cu(NO}_3\text{)}_2\cdot2.5\text{H}_2\text{O, glutaric acid (H}_2\text{glu) and L (where L = 4,4'\text{-bipyridine [bpy], trans-bis(4-pyridyl)ethylene [bpe] or N,N'\text{-bis-pyridine}-4\text{-ylmethylene-hydrazine [bpymh]) in H}_2\text{O at 100 °C and 60 °C for bpymh yielded three 3D metal-organic frameworks: [Cu}_2\text{(glu)}_2\text{(bpy)}\cdot2.9\text{H}_2\text{O} = 1a, [Cu}_2\text{(glu)}_2\text{(bpe)}\cdot3\text{H}_2\text{O} = 2a and [Cu}_2\text{(glu)}_2\text{(bpymh)}\cdot7.5\text{H}_2\text{O} = 3a. Green block-shaped crystals of the as-synthesized frameworks were dehydrated by placing them under vacuum at 150 °C for 24 h to afford crystals of the apohosts 1, 2 and 3.}

Supercritical \(\text{CO}_2\) Experiments. Newly synthesized MOF crystals were exposed to supercritical \(\text{CO}_2\) (scCO\(_2\)) for 24 h to obtain the apohost or activated phase. Supercritical \(\text{CO}_2\), having properties of both liquid and gas, exerts little or no surface tension on the walls of the channels in the crystal. Depending on the solvent present in the channels and the exact conditions of temperature and pressure (31.1 < \(T_c\) < 44 °C; 73 < \(P_c\) < 110 bar) (beyond the critical temperature and pressure) scCO\(_2\) is able to dissolve the solvent molecules and leave behind the activated phase. Typically, a vial containing the crystals is placed directly onto dry-ice while being moved to the instruments for analysis.
Figure S1. Types of isotherms as described by Brunauer, Deming, Deming and Teller.[1]

Figure S2. Framework 1 viewed along [0 0 1] to illustrate the crisscrossed arrangement of the bipyridyl linkers.
**Figure S3.** The different CO$_2$ arrangements found in dry ice.
Figure S4. Fourier transform infrared spectroscopy (FTIR) spectra of the as-synthesized, activated and supercritical CO₂ exposed materials.
Figure S5. Thermogravimetric analysis (TGA) and 1st derivatives of the (a) as-synthesized (1a, 2a and 3a) and (b) supercritical CO₂ exposed material (1b, 2b and 3b). The temperatures of maximum guest evolution are indicated on the 1st derivative curves. (c) Differential scanning calorimetry (DSC) thermograms of the materials exposed to supercritical CO₂: 1b, 2b, 3b.
Table S1. Quantification of CO$_2$ in the three frameworks after supercritical CO$_2$ exposure (expressed as number of CO$_2$ molecules per asymmetric unit).

<table>
<thead>
<tr>
<th></th>
<th>1b</th>
<th>2b</th>
<th>3b</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGA</td>
<td>0.512</td>
<td>0.765</td>
<td>1.39</td>
</tr>
<tr>
<td>SQUEEZE</td>
<td>0.505</td>
<td>0.92</td>
<td>1.38</td>
</tr>
</tbody>
</table>

SQUEEZE results are based on an electron count of 22 electrons per CO$_2$.

\[
\text{Extent of Hysteresis} = \frac{\text{AREA}_{\text{Desorption isotherm}} - \text{AREA}_{\text{Sorption isotherm}}}{\text{AREA}_{\text{Sorption isotherm}}} \times 100\%
\]

Equation E1. The formula used for determining the percentage hysteresis of the sorption experiment (OriginPro was used to integrate the isotherm across the same pressure range to yield the areas).

Computational Modeling. The electrostatic potential is derived from the electron density and nuclear charge as described by Eq. 1:

\[
V(r) = \sum_A \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r') dr'}{|r' - r|} \quad (1)
\]

Since \(V(r)\) is the interaction energy between the system and a unit positive point charge at \(r\) it is typically expressed in units of energy. In the case of Eq. 1, \(V(r)\) is given in atomic units (a.u., Hartree), which can easily be converted to any convenient unit (kcal/mol, kJ/mol etc.). \(V(r)\) is a 3-dimensional function which can be evaluated at any point \(r\) within the system with the exception of the nuclei \((R_A \neq r, \text{Eq. 1})[3]\) These results can be mapped onto 2D planes (slices though the system under investigation) or 3D surfaces of molecules at a particular electron density contour, depending on the relevance and aspect of interest.[4] The contour utilized for the 3D surface can be defined arbitrarily, which may lead to ambiguity in the analysis of the results. In this work we use the 0.0015 au (e$^-$/Bohr$^3$, 0.01 e$^-$/Å$^3$) outer contour of the molecule's electron density \(\rho(r)\) as suggested by Bader et al.[5]

The CO$_2$ positions determined from the SCD structures of the crystals exposed to supercritical CO$_2$ were used as initial geometries to construct all the computational models. The hydrogen atoms in the framework and CO$_2$ molecules were first optimized as part of a periodic system using the CASTEP module of the Materials Studio software suite.[6] The optimization was performed using the GGA PBE functional with Grimme's DFT-D dispersion correction; thresholds for geometry optimization and SCF convergence were chosen as $1 \times 10^{-6}$ eV. The electrostatic potentials were calculated using the VAMP module of the Materials
Studio Software suite as a single point energy calculation using the NDDO Hamiltonian type and the AM1* Hamiltonian. An SCF convergence threshold of $5 \times 10^{-7}$ kcal/mol was used and the grid size for the imported electrostatic potential was set to 0.1 Å. A single point energy calculation using CASTEP (with the same parameters) on only the CO₂ molecules was also performed. The electron density data obtained from these calculations were used to construct the three-dimensional 0.01 e⁻/Å³ electron density contours of the CO₂ molecules. CASTEP electron density data of the three frameworks were used to construct the surface of their channels as 0.01 e⁻/Å³ electron density contours. The electrostatic potential calculated for each framework (FEP) was then mapped onto the electron density contours of both a CO₂ molecule for each framework and their respective channel contours. The maximum and minimum values of $V(r)$ on the surfaces, $V_{S,\text{max}}$ and $V_{S,\text{min}}$, are given in Table S2.

**Figure S6.** The computational models used for the VAMP electrostatic potential calculations viewed along the crystallographic c axis (TOP) and the crystallographic a axis (BOTTOM) for all three frameworks.
Figure S7. Portions of the frameworks of 1, 2 and 3 in stick representation showing the origin of the FEPs mapped onto the 0.01 e⁻/Å³ electron density contours of CO₂ molecules.

Table S2. Highest values of the electrostatic potentials of the three frameworks as mapped onto the 0.01 e⁻/Å³ electron density contours of the included CO₂ guest molecules (in kcal/mol).

<table>
<thead>
<tr>
<th>FEPs (kcal/mol)</th>
<th>V₅,max</th>
<th>V₅,min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>α⁺</td>
<td>β⁺</td>
</tr>
<tr>
<td>1</td>
<td>20.65</td>
<td>9.73</td>
</tr>
<tr>
<td>2</td>
<td>29.70</td>
<td>19.90</td>
</tr>
<tr>
<td>3</td>
<td>17.10</td>
<td>14.08</td>
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</table>

<table>
<thead>
<tr>
<th>MEP (kcal/mol)</th>
<th>V₅,max</th>
<th>V₅,min</th>
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<tbody>
<tr>
<td></td>
<td>α⁺</td>
<td>α⁻</td>
</tr>
<tr>
<td>CO₂ MEP</td>
<td>35.70</td>
<td>-10.84</td>
</tr>
</tbody>
</table>
Figure S9. Powder diffraction data of as-synthesized and activated materials of all three frameworks.
Figure S10. 2-Dimensional electron difference density map of 1b showing the electron density of the CO$_2$ molecules within the framework (F$_0$-F$_c$). (a) Along the crystallographic a-axis. (b) Along the crystallographic c axis. (c) 2-Dimensional electron difference density map of 1b showing the electron density of the CO$_2$ molecules within the framework. The scale bar on the right is in e/Å$^3$. Images (a) and (b) were obtained with Materials Studio using difference density data generated with WinGX V2013.3, whereas (c) was generated using WinGX V2013.3.
### Table S4. Crystal data and structure refinement of [Cu₂gluL]·XCO₂ frameworks

<table>
<thead>
<tr>
<th></th>
<th>[Cu₂(gluc)(apbc)·0.51CO₂]</th>
<th>[Cu₂(gluc)(apbc)·0.77CO₂]</th>
<th>[Cu₂(gluc)chppno·0.29CO₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C₄₀H₄₅CaNO₇₃</td>
<td>C₄₀H₄₅CaNO₇₃</td>
<td>C₄₀H₄₅CaNO₇₃</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>392.93</td>
<td>318.78</td>
<td>311.00</td>
</tr>
<tr>
<td><strong>Temperature (K)</strong></td>
<td>100(2)</td>
<td>100(2)</td>
<td>290(2)</td>
</tr>
<tr>
<td><strong>Wavelength (Å)</strong></td>
<td>0.7073</td>
<td>0.7073</td>
<td>0.7073</td>
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<tr>
<td><strong>Crystal system</strong></td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>C2/c</td>
<td>C2/c</td>
<td>C2/c</td>
</tr>
<tr>
<td><strong>Unit cell dimensions (Å,°)</strong></td>
<td>a = 20.990(7)</td>
<td>a = 24.241(2)</td>
<td>a = 27.680(6)</td>
</tr>
<tr>
<td></td>
<td>b = 13.152(5)</td>
<td>b = 13.2483(1)</td>
<td>b = 13.170(3)</td>
</tr>
<tr>
<td></td>
<td>c = 8.579(3)</td>
<td>c = 8.5771(7)</td>
<td>c = 8.5800(19)</td>
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<tr>
<td></td>
<td>β = 100.343(4)</td>
<td>β = 99.880(1)</td>
<td>β = 95.783(3)</td>
</tr>
<tr>
<td><strong>Volume (Å³)</strong></td>
<td>2134.3(14)</td>
<td>2754.6(4)</td>
<td>3114.3(12)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td><strong>Calculated density (g cm⁻³)</strong></td>
<td>1.667</td>
<td>1.537</td>
<td>1.329</td>
</tr>
<tr>
<td><strong>Absorption coefficient (mm⁻¹)</strong></td>
<td>1.881</td>
<td>1.604</td>
<td>1.414</td>
</tr>
<tr>
<td><strong>Fmax</strong></td>
<td>1189</td>
<td>1296</td>
<td>1267</td>
</tr>
<tr>
<td><strong>Crystal size (mm³)</strong></td>
<td>0.27 × 0.16 × 0.11</td>
<td>0.35 × 0.27 × 0.25</td>
<td>0.15 × 0.14 × 0.10</td>
</tr>
<tr>
<td><strong>θ range for data collection (°)</strong></td>
<td>1.57 to 28.39</td>
<td>1.68 to 28.72</td>
<td>1.71 to 28.68</td>
</tr>
<tr>
<td><strong>Miller index ranges</strong></td>
<td>-27 ≤ h ≤ 28, -15 ≤ k ≤ 17, -11 ≤ l ≤ 6</td>
<td>-19 ≤ h ≤ 32, -35 ≤ k ≤ 17, -41 ≤ l ≤ 11</td>
<td>-36 ≤ h ≤ 37, -12 ≤ k ≤ 17, -9 ≤ l ≤ 11</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>6800</td>
<td>8740</td>
<td>9075</td>
</tr>
<tr>
<td><strong>Independent reflections</strong></td>
<td>2688 [Rint = 0.0175]</td>
<td>3296 [Rint = 0.0314]</td>
<td>3090 [Rint = 0.0521]</td>
</tr>
<tr>
<td><strong>Completeness to θmax (%)</strong></td>
<td>91.5</td>
<td>92.6</td>
<td>91.8</td>
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<tr>
<td><strong>Max. and min. transmission</strong></td>
<td>0.7055 and 0.5110</td>
<td>0.6019 and 0.6050</td>
<td>0.8762 and 0.8127</td>
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<tr>
<td><strong>Refinement method</strong></td>
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<td>Full-matrix least-squares on F³</td>
<td>Full-matrix least-squares on F³</td>
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<tr>
<td><strong>Data / restraints / parameters</strong></td>
<td>2688 / 23 / 155</td>
<td>3296 / 0 / 182</td>
<td>3090 / 0 / 191</td>
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<tr>
<td><strong>Goodness-of-fit on F²</strong></td>
<td>1.135</td>
<td>1.077</td>
<td>1.183</td>
</tr>
<tr>
<td><strong>Final R indices (I &gt; 2σ(I))</strong></td>
<td>R1 = 0.0357, wR2 = 0.1069</td>
<td>R1 = 0.0320, wR2 = 0.0810</td>
<td>R1 = 0.0386, wR2 = 0.1024</td>
</tr>
<tr>
<td><strong>R indices (all data)</strong></td>
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<td>R1 = 0.0357, wR2 = 0.0912</td>
<td>R1 = 0.0409, wR2 = 0.1072</td>
</tr>
<tr>
<td><strong>Extinction coefficient</strong></td>
<td>none</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td><strong>Largest diff. peak and hole (e Å⁻³)</strong></td>
<td>1.451 and -0.431</td>
<td>0.7811 and -0.3800</td>
<td>1.124 and -0.551</td>
</tr>
</tbody>
</table>
Chapter 4

SOLVENT AND PRESSURE-INDUCED PHASE CHANGES IN TWO 3D COPPER GLUTARATE BASED MOFS VIA GLUTARATE (+GAUCHE ⇔ -GAUCHE) CONFORMATIONAL ISOMERISM.

4.1. FULL ARTICLE IN JOURNAL OF THE AMERICAN CHEMICAL SOCIETY (ACCEPTED AND REVISED)

Contributions of the author:

- Design of project with Dr Vincent J. Smith
- Preparation of MOFs
- Supercritical CO₂ experiments
- Collection of single-crystal X-ray data and refinement of single-crystal X-ray structures
- Recording of PXRD patterns, TGA thermograms and FRIR spectra
- Sorption analysis
- Computational modelling
- Interpretation of results with Dr Vincent J. Smith
- Writing the first draft of the article

Stellenbosch University  https://scholar.sun.ac.za
Solvent and Pressure-Induced Phase Changes in Two 3D Copper Glutarate-Based MOFs via Glutarate (+gauche ⇄ –gauche) Conformational Isomerism.

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Department of Chemistry and Polymer Science, University of Stellenbosch, Matieland, 7602, South Africa

KEYWORDS: gauche rotamers, phase-change, high pressure sorption, carbon dioxide, potential energy scan.

ABSTRACT: Two isoreticular 3D Cu(II)-glutarate based pillared-layered MOFs with flexible pillars, [Cu(glu),(bpa)] and [Cu(glu),(bpp)] (bpa = 1,2-bis(4-pyridyl)ethane, bpp = 1,3-bis(4-pyridyl)propane), undergo spontaneous phase changes upon solvent loss at room temperature. Using single-crystal X-ray diffraction analysis (SCXRD), we show that the phase changes result in new narrow-channel forms that experience a large reduction in solvent-accessible volume. Moreover, the [Cu(glu),(bpa)] MOF displays a stepped sorption isotherm for the uptake of CO$_2$ at RT. This is indicative of the framework reverting to the wide-channel form under CO$_2$ pressure. Supercritical CO$_2$ was used to isolate the gas-included structures and, by means of single-crystal X-ray diffraction analysis we were able to determine the positions of the CO$_2$ molecules in the channels of the frameworks. Finally, we report the use of molecular modelling simulations to elucidate the phase-change mechanism, including the energetic changes involved. Structural limitations in both MOFs allow for only direct gauche-gauche enantiomer interconversion of the glutarate moieties.

INTRODUCTION

The vast structural versatility of metal-organic frameworks (MOFs) is due to the myriad potential combinations of metal ions and coordinating organic ligands.$^{8-11}$ A variety of metal ions form recurring secondary building unit (SBUs) motifs that allow for rational design of new materials from new and existing organic building blocks (i.e. reticular synthesis).$^{6-9}$ These recurring SBUs are essential in the design of isoreticular MOFs and are crucial to the systematic study of the physical properties of MOFs,$^{8, 10-12}$ particularly the preparation of stable (rigid), porous MOFs with wide-ranging topologies.$^{5, 9-10}$ Rigid exo-polydentate aromatic carboxylic acids and pyridyl-based ligands are the most widely employed linkers in the exploration of new MOFs.$^{5, 6, 8, 12-15}$

In recent years there has been a shift towards soft porous materials that can distort or even change phase upon gas uptake.$^{16-20}$ These types of materials have demonstrated high uptake capacity and selectivity for gases that induce the structural change.$^{16-20}$ Bousquet et al.$^{21}$ and Coudert et al.$^{22}$ have described different modes of flexibility in MOFs: breathing, swelling, linker rotation, subnetwork displacement (in catenated MOFs) and slippage of interdigitated and stacked layers.$^{16, 17, 21-22}$ These modes of flexibility greatly affect the sorption behavior of the materials and generally give rise to stepped sorption profiles.$^{23-25}$ An inflection is usually associated with a structural transformation from a narrow-pore to a wide-pore phase and the sudden increase in guest-accessible space results in increased gas uptake.$^{26-28}$ For a given material, these gate-opening events tend to depend on three factors: the nature of the gas, the temperature and the pressure.$^{29-32}$ The relationship between these factors, as well as the mechanisms that govern gate opening, are still active topics of study.$^{33-35}$

Figure 1. Newman projections (top) of glutaric-acid (H$_2$glu) rotamers generated around the C$_2$-C$_3$ bond and the frequency plot (bottom) of the glu C$_2$-C$_3$ gauche torsion angles from 318 structures in the CSD.$^{36}$

Conformational isomerism of bridging ligands is also possible and is associated with either breathing or linker rotation. Most attempts to produce flexible MOFs using aliphatic dicarboxylic acids generally lead to polymorphs or structural isomers containing different conformations of the organic ligands.$^{37}$ Once crystallized, the conformation
of the flexible aliphatic backbone is locked in by close contacts and M-L coordination. Recently, Reinsch et al. synthesized a MIL-53-type MOF using adipic acid, where the change in pore volume was attributed to conformational isomerism of the adipate linkers. However, in that case the length of the linker in the large-pore structure is shorter than that in the narrow-pore structure, but the authors did not comment on the relationship between conformational isomerism and pore volume.

Glutaric acid is another example of a flexible dicarboxylic acid that could be used as a linker in MOFs. In 2003 Zaworotko et al. surveyed the Cambridge Structural Database (CSD) for the conformations of glutarate (glu) anions in coordination compounds. They identified 30 structures and noted that the glutarate moiety exhibits three conformations (or rotomers): trans-trans (tt), gauche-trans (gt) and gauche-gauche (gg), where the gauche conformation can either be -gauche or –gauche, depending on the C1-C2-C3-C4 torsion angle (Figure 1, top).

We repeated the survey using version 5.37 of the CSD (November 2015 with February and May 2016 updates) and identified 348 relevant structures. A plot of the torsion angle frequency distribution (Figure 1, bottom) shows a broad peak with two maxima for both +g and –g. Variation of approximately 30° is evident and serves to highlight the most common angles that the gauche rotamers adopt for the reported coordination compounds. The observed behavior of the glu ligand may lead to structural flexibility in MOFs, provided there are no inhibiting constraints. Here we present an investigation of the solvent and pressure-induced phase changes of two previously reported 3D Cu-glu based MOFs that are pillared by flexible bipyridyl ligands.

RESULTS AND DISCUSSION

Synthesis and structural description. The linker 1,2-bis(4-pyridyl)ethane (bpa) was reacted with Cu(NO3)2.5H2O and glutaric acid (H2glu) under hydrothermal conditions to yield [Cu(glu)2l(bpa)]-2.4H2O (1a) while 1,3-bis(4-pyridyl)propane (bpp) was reacted with Cu(NO3)2.5H2O and glutaric acid using the layering method in acetone (ace) to produce [Cu(glu)2l(bpp)]-2ace (2a) (Scheme S1). Both methods yielded green prismatic crystals from which suitable specimens were selected for single-crystal X-ray diffraction analysis (SCXRD) at 100 K. 1a crystallizes in the monoclinic space group C2/c and 2a crystallizes in the orthorhombic space group Pccn (Table S1). In each case the framework structure consists of 2D corrugated layers with Cu-glu paddlewheel SBUs as nodes. The bipyridyl ligands coordinate to the axial sites of the paddlewheel SBUs, crisscrossing one another, and joining adjacent 2D corrugated layers to form a 3D MOF (Figure 2a top). Both frameworks contain 1D corrugated channels and the networks are related to the e-polyonnet. Phase change behavior. Crystals of 1a were allowed to desolvate at ca. 5°C. A single crystal of sufficient quality was selected for SCXRD analysis, which revealed that the structure had undergone a phase change to 1a', [Cu(glu)2l(bpa)]-0.93H2O (Figure 2a). The same procedure for 2a yielded a polycrystalline material, 2a'. However, it was possible to isolate a new phase as single crystals using supercritical CO2 (SC-CO2) activation (see ESI for details) and the corresponding crystal structure 2b, [Cu(glu)2l(bpp)]-8.2CO2 (Figure 2a) was determined by SCXRD analysis. We refer to the guest-free (virtual) framework structures of 1a and 2b as 1' and 2', respectively. They are the narrow-channel (nc) forms while 1 and 2
2 (the host frameworks of 1a and 2a, respectively) are the wide-channel (wc) forms (Figure 2a and Table S2). The dimensions of the wide channels are 8.202 × 5.853 Å (1) and 9.077 × 7.385 Å (2), while those of the narrow channels are 7.296 × 4.714 Å (1') and 7.830 × 6.393 Å (2'). There is a relatively large decrease by 44% in the solvent-accessible volume during the conversion of 1 (520 Å³) to 1' (281 Å³), as compared to the 22% change during the conversion from 2 (749 Å³) to 2' (490 Å³) (see Figure 2a and Table S1). The most significant changes in the unit cell dimensions for both 1→1' and 2→2' are evident in the b and c axes; the b axis shrinks while the c axis expands in concert with the changes in channel dimensions (Table S1). During the phase change the signs of the torsion angles of the glu trans (t) and gauche (g) moieties become inverted — i.e. all the negative torsion angles become positive and vice versa (Figure 2b and Figure S1). The inversion of the signs of the glu gauche torsion angles indicate an enantiomeric conformational change (+g and −g are mirror images, Figure 2b).

The glu trans torsion angles (±57.5 (1), ±75.7 (1'), ±59.2 (2) and ±77.1 (2')) compare well with the peak frequencies observed for the glu ±g torsion angles reported here and in the CSD survey of Zaworotko et al. (Figure 1 and Table S3).[^1] Related changes occur in the orientation of the Cu-glu paddlewheel SBUs (Figure 2c, S2 and Table S3). MOFs isoreticular to 1 and 2 that contain rigid bipyrindyl linkers do not appear to undergo phase changes[^16].[^15] It is therefore plausible that the flexibility of the bpa and bpp linkers, compared to rigid analogues, is crucial in accommodating these structural changes. In the case of bpa (1→1'), an increase in the scissor-angle and ligand inclination (relative to the a-plane) results in shortening of the a axis (Figure 3a, b and Table S4). Similarly, during the transformation 2→2', bpa experiences a decrease in the ligand bend angle and an increase in the scissor angle (Figure 3c, d and Table S4).

**Figure 3.** (a) Inclination of the bpa linker relative to (100). (b) Scissor angle formed by the bpa linkers. (c) Bend angle of the bpp linker. (d) Scissor angle formed by the bpp linkers.

**Figure 4.** Gas sorption isotherms, recorded at 298 K, for (a) 1' and (b) 2'.

**Gas sorption studies.** Thermogravimetric analysis of 1a and 2a showed that complete solvent loss occurs before 100 °C (Figure S3); activation was carried out under dynamic vacuum at 150 °C. Powder X-ray diffraction (PXRD) analysis shows that the activated phases match those simulated for guest-free 1a and 2a (Figures S4 and S5), confirming that they comprise the nc frameworks 1' and 2' (the PXRD traces were indexed using the TOPAS 4.2[^9] software package; see Tables S5 and S6). Gas sorption experiments were carried out at 25 °C using 1' and 2' (Figure 4). Sorption/desorption hysteresis was observed for all of the investigated gases in the case of 1' (Figure 4a), and also for CH₄ and C₂H₆ in the case of 2' (Figure 4b). The isotherms for CO₂ and CH₄ sorption by 2' are characteristic of microporous materials (Figure 4b). For both materials, the maximum molar CO₂ sorption capacity is twice that measured for the other gases. Moreover, 1' appears to exhibit a gate-opening event between 4 – 5 bar during CO₂ adsorption but, unusually, a corresponding inflection for a gate closing event is not apparent in the desorption isotherm (Figure 4a). The CO₂ loading for 1' tends towards 4 molecules per unit cell before the gate-opening event, and thereafter towards 8 molecules per unit cell. A gate-opening event is usually associated with a phase change and could be a transformation from 1' to 1.3a;[^10] the solvent accessible space for 1 is almost double that of 1', which is consistent with the observed doubling in CO₂ occupancy after the gate-opening event.

The CO₂ loaded crystal structures, 1b and 2b (Figure 5), were obtained via solvent exchange using SC-CO₂ (see ESI for details), where the presence of CO₂ was confirmed using FTIR spectroscopy[^20].[^19] (Figure 5b). The simulated powder pattern for virtual guest-free 1b matched that recorded for guest-free 1a, implying that SC-CO₂ exposure does not change the host structure. This observation is consistent with the lack of a gate-closing event in the CO₂.
desorption isotherm for \( r' \), i.e. \( \mathbf{1b} \) remains in the wc form. According to SCD data recorded for \( \mathbf{1b} \) approximately 5 minutes after removal from SC-CO, the CO\(_2\) occupancy, determined using SQUEEZE,\(^{96-99}\) is ca.1 molecule per unit cell. However, when another crystal was selected and data collected more rapidly, the CO\(_2\) occupancy was determined to be approximately 9 molecules per unit cell. These observations imply that CO\(_2\) is lost rapidly under ambient conditions. The total guest-accessible volume per unit cell of \( r' \) is 903 Å\(^3\). The nc form (\( \mathbf{x} \)) has significantly less guest-accessible space (28 Å\(^3\) per unit cell), as compared to \( \mathbf{1b} \).

The simulated PXRD pattern of virtual guest-free \( \mathbf{2b} \) matches the pattern recorded for \( \mathbf{x} \) (Figure S5). The absence of a gate-opening event for CO\(_2\) adsorption is consistent with the crystal structure \( \mathbf{2b} \) (Figure 5b). The SQUEEZE electron count for \( \mathbf{2b} \) indicates 8.2 CO\(_2\) molecules in the unit cell, which could be modelled over 10 positions with partial occupancies and without any structural constraints. The CO\(_2\) molecules in both \( \mathbf{1b} \) and \( \mathbf{2b} \) utilize sorption sites and guest-host orientations similar to those identified in our previous work.\(^{97}\) Additional slipped-parallel CO\(_2\)-CO\(_2\) interactions are also present in the case of \( \mathbf{2b} \) (Figure 5b and Figure S8). The phase changes occurring in \( r' \) and \( \mathbf{x} \) were further investigated using a computational approach, first by studying the result of rotation around the C1-C2-C3-C4 torsion angle (Figure 1) on an individual glutarate linker, and then by extending this procedure to determine the effect on the crystal structure of the MOF. The gate-opening event in \( r' \) and absence thereof in \( \mathbf{x} \) was confirmed using pressure-ramped differential scanning calorimetry P-DSC (Figure S7).

**Figure 5.** Crystal structures of \( \mathbf{1b} \), (a), and \( \mathbf{2b} \), (b), viewed along the crystallographic c axis. Hydrogen atoms have been omitted for clarity and the CO\(_2\) molecules are shown in space-filling representation.

**Computational Study.** The largest structural changes during the phase transitions involve the glu linkers, particularly the gauche torsion angle (Table S3). In order to investigate this further we focused on a single glutaric acid molecule (H\(_{\text{glu}}\)). A conformational scan of the H\(_{\text{glu}}\) gauche torsion angle was carried out using DFT methods (see Figure 6a and ESI for details). The scan consisted of a 250° sweep with a 5° step size (Figure 6b). The relative energy plot generated from the scan shows minima at 60° (\( B+g \)) and -90° (\( D-g \)) with an expected cis-barrier at 0° (X, when atoms C1 and C4 involved in the torsion angle are eclipsed).\(^{60-69}\) The torsion angles of the \( \pm g \) rotomers for the H\(_{\text{glu}}\) molecule compare well with those determined from the crystal structures (Table S3). The cis-barriers for moving between the two rotamers are 4.4 kcal mol\(^{-1}\) (B\( \rightarrow D \)) and 5.4 kcal mol\(^{-1}\) (D\( \rightarrow B \)). These energy values are similar to those determined for other molecules with aliphatic backbones (4 - 8 kcal mol\(^{-1}\)).\(^{60-64}\) The asymmetry in the relative potential energy plot is due to the asymmetry in the carboxylic acid functional group (\(-\text{COOH}\) (Figure 6a). This indicates that the phase transition could simply be an enantiomeric conversion between the two gauche glutarate rotamers.

**Figure 6.** (a) Computational model used in the DFT level calculations for glutaric acid. The C1-C2-C3-C4 gauche torsion angle is the scan parameter in these calculations. (b) The relative potential energy plot of a DFT-based torsional scan using a single H\(_{\text{glu}}\) model.

To confirm this, we investigated the effect of the conformational change of the glu moieties on the Cu-gluc 2D grid (Figure 2c and Figure S2) using a larger computational model that consists of 4 paddlewheel units connected by 4 glu ions to form a parallelogram (Figure 7). A conformational scan of the glu torsion angles was carried out (similarly to the previous scan) using molecular mechanics (MM, see ESI for details). The scan was only performed through the cis-barrier (0°, Figure 7). With reference to Figure 7, the vertical diagonal of the parallelogram is equivalent to the crystallographic c axis, whereas the horizontal diagonal corresponds to the b axis. The simulation yielded
changes in the vertical (increase) and horizontal (decrease) diagonals that correspond to the changes in the $b$ and $c$ axes for wc→nc (Figure 5a). The molecular models at the minima A ($\pm g, wc$) and E ($\pm g, nc$) (Figure 7) were overlaid, revealing significant differences in the orientations of the paddlewheel SBUs (Figure Si6, Video Si1). This is consistent with the structural observations from SCXRD (Table Si1) and also highlights the requirement for some flexibility within the bridging pyridyl ligands and/or the ability of the metal–ligand coordination bond to deform.

![Figure 7](image-url) Figure 7. The glutamate $\pm g \rightarrow \mp g$ ($\pm gauche \rightarrow gauche$ and $\mp gauche \rightarrow gauche$) torsional potential energy scan using a larger model and calculated using DMol3. The gauche torsion angle, scan sweep and step size used in the computational simulations are indicated. A plot of the relative energies is shown, along with a few key structures (indicated by the red spheres). The green and yellow parallelograms represent the wide (59°) and narrow (76°) channel forms, respectively.

<table>
<thead>
<tr>
<th>Experimental</th>
<th>Simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1'</td>
</tr>
<tr>
<td>C2/c</td>
<td>C2/c</td>
</tr>
<tr>
<td>a/Å</td>
<td>24.777(6)</td>
</tr>
<tr>
<td>b/Å</td>
<td>13.233(8)</td>
</tr>
<tr>
<td>c/Å</td>
<td>8.623(6)</td>
</tr>
<tr>
<td>β°</td>
<td>91.377(8)</td>
</tr>
<tr>
<td>2</td>
<td>2'</td>
</tr>
<tr>
<td>Pccn</td>
<td>Pccn</td>
</tr>
<tr>
<td>a/Å</td>
<td>27.65(2)</td>
</tr>
<tr>
<td>b/Å</td>
<td>12.90(3)</td>
</tr>
<tr>
<td>c/Å</td>
<td>8.57(3)</td>
</tr>
</tbody>
</table>

Table 1. Experimental and simulated unit cell parameters of 1, 1', 2 and 2', including the relative differences (rel. diff.) between the unit cell parameters of the wc and nc forms.

The $\pm gauche$ torsion angle can change from $\pm g \rightarrow \mp g$ via two routes: direct interconversion ($\pm g \leftrightarrow \mp g$, Route 1) or via the trans route ($\pm g \leftrightarrow t \leftrightarrow \mp g$, Route 2). Both of these routes were simulated using a complete unit cell as the computational model (Figure 5a). The MM calculations were carried out in the space group P31 by scanning the $\pm gauche$ torsion angles and optimizing the entire unit cell. The unit cell contains eight glu moieties that were scanned simultaneously with a step size of 0.5° for both routes. The unit cell parameters of the experimental and simulated wc (initial minima) and nc (final minima) structures are different but still comparable (Table 1). The relative differences between 1 and 1' compare very well for the experimental and simulated structures along the $b$ and $c$ axes. The simulated $a$ and $b$ angle have relative differences that are smaller in magnitude than those of the experimental structures, but still with the correct trend. In the case of 2 there is good agreement between the experimental and simulated unit cells. The relative differences are similar in both magnitude and direction of change (Table 1). This demonstrates that the phase change is adequately simulated by merely scanning the $\pm gauche$ torsion angles.

The energy barrier for Route 2 (trans route) is significantly higher than for Route 1 (direct route) for both 1 and 2 (Figure 8a). MOF 1 has energy barriers of 2.99 and 4.99 kcal mol$^{-1}$ for Route 1 and 14.77 and 16.77 kcal mol$^{-1}$ for Route 2, while MOF 2 has energy barriers of 4.32 and 6.47 kcal mol$^{-1}$ for Route 1 and 14.9 and 17.04 kcal mol$^{-1}$ for Route 2 (Figures 8b, Table 5). This indicates that the phase change in each MOF occurs via a direct $\pm gauche$ interconversion ($\pm g \leftrightarrow \mp g$). The $\pm gc \leftrightarrow \mp gc$ energy barriers for 2 are 1.33 kcal mol$^{-1}$ (A→B1: wc→nc) and 1.48 kcal mol$^{-1}$ (A→B2: wc→nc).
CONCLUSIONS
We have obtained newly identified nc phases for the two previously reported frameworks 1 and 2. The phase changes occur spontaneously upon solvent loss at room temperature. The crystal structures for both phases reveal an enantiomeric conformational change in the glu moieties through inversion of the gauche torsion angles. The distance between the carboxylate functional groups can be different depending on the conformation of the aliphatic chain: for instance, the trans-trans conformer of glu is more extended than the gauche-gauche conformer. However, even though the $\phi$ and $\gamma$ conformers have the same effective length, the change from $\phi$ to $\gamma$ gives rise to the observed phase change in each MOF. The changes in orientation, bend angles and coordination angle of the 4,4'-bipyridyl linkers suggest that these moieties play a crucial role in accommodating the glu conformational change. The activated MOF 1 shows a gate-opening event at 4 bar CO$_2$ gas pressure, opening up from the nc form to the wc form.

Computational simulation revealed that the phase change is due to a direct gauche-gauche enantiomeric conversion. The flexible bipyridyl ligands are crucial in accommodating the variations in the Cu-glu paddlewheel orientation and thus allowing the conversion to occur. Furthermore, the energy barrier for Route 1 is ca 10 kcal mol$^{-1}$ (per glu moiety) more stable than for Route 2. Additionally, the energy barriers for Route 1 for MOFs 1 and 2 are in the same range as that of a free H$_2$ glu molecule (3 – 7 kcal mol$^{-1}$). These energies are comparable to those of reported conformational barriers for molecules such butane and its derivatives, which spontaneously interconvert under ambient conditions.

ASSOCIATED CONTENT
Supporting Information. Experimental details, Computational details, additional analysis, and figures (PDF).
Crystallographic details for 1a (CIF)
Crystallographic details for 1b (CIF)
Crystallographic details for 1a (CIF)
Crystallographic details for 2a (CIF)
Crystallographic details for 2b (CIF)
Periodic optimized geometries for 1 and 2 (CIF)

This material is available free of charge via the Internet at http://pubs.acs.org.


4.2. SUPPORTING INFORMATION

Solvent and Pressure-Induced Phase Changes in Two 3D Copper Glutarate-Based MOFs via Glutarate (+gauche ⇄ −gauche) Conformational Isomerism.

Charl X. Bezuidenhout, Vincent J. Smith, Catharine Esterhuysen* and Leonard J. Barbour*

Department of Chemistry and Polymer Science, University of Stellenbosch, Matieland, 7602, South Africa

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1. Synthesis and characterization

Materials

All materials were purchased from a commercial source and used without further purification.

Synthesis

$[\text{Cu}_2(\text{glu})_2(bpa)]_{n\cdot2}\text{H}_2\text{O} \ (1a)$ $\text{Cu(NO}_3)_2 \ (1 \text{ mmol})$, glutaric acid (1 mmol) and 1,2-bis(4-pyridyl)ethane (bpa, 0.5 mmol) were mixed in 100 ml H$_2$O. 1 molar eqv. of NaOH was added dropwise with swirling to prevent precipitation. The blue solution was placed in an oven preheated to 80 °C. Green block shaped crystals were obtained after 24 – 48 hours.

$[\text{Cu}_2(\text{glu})_2(\text{bpp})]_{n\cdot2}\text{acetone} \ (2a)$ 50 ml of a H$_2$O/acetone (1:1) buffer solution was layered on a solution of glutaric acid (1 mmol), 1 eqv NaOH (1M) and 1,3-bis(4-pyridyl)propane (bpp, 0.5 mmol) in 50 ml H$_2$O/acetone (2:1). A solution of Cu(NO$_3$)$_2$ (1 mmol) in 50 ml acetone (ace) was then layered on the buffer solution. The vessel was carefully placed and allowed to diffuse in an oven heated to 50-55 °C. Green block and plate like crystals were collected after 48 hours.

Scheme S1. Synthesis of $[\text{Cu}_2(\text{glu})_2(bpa)]_{n\cdot2}\text{H}_2\text{O} \ (1a)$ and $[\text{Cu}_2(\text{glu})_2(\text{bpp})]_{n\cdot2}\text{ace} \ (2a)$. 
2. Methods

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out using a TA Instruments Q500 analyzer. The sample was loaded in an aluminum pan and heated at 10 °C/min from room temperature up 600 °C.

Supercritical CO₂ Experiments

Newly synthesized MOF crystals were exposed to supercritical CO₂ (scCO₂) for 24 h to obtain the apohost or activated phase. Supercritical CO₂, having properties of both liquid and gas, exerts little or no surface tension on the walls of the channels in the crystal. Depending on the solvent present in the channels and the exact conditions of temperature and pressure (31.1 < Tc < 44 °C; 73 < Pc < 110 bar) scCO₂ is able to dissolve the solvent molecules and leave behind the activated phase. Typically, a vial containing the crystals was placed directly onto dry-ice while being transported for analysis.

Single-crystal X-ray Diffraction

Suitable single crystals were selected and mounted onto a diffractometer using a MiTeGen MicroCrystal mount. Single-crystal X-ray diffraction data were collected using a Bruker SMART diffractometer equipped with an APEX-II CCD area-detector, and an Oxford Cryosystems 700Plus cryostat for temperature control. X-rays were generated from a sealed tube (MoKα radiation λ = 0.71073 Å) fitted with a multilayer monochromator. All data were collected at 100 K.

Data reduction was carried out by means of the standard procedure using the Bruker software package SAINT2 and the absorption corrections and the correction of other systematic errors were performed using SADABS.3. Using X-Seed [S1] and Olex2 [S2], the structure was solved with the SHELXS [S3] structure solution program using Direct Methods and refined with the SHELXL [S4] refinement package using least squares minimization. Hydrogen atoms were placed in calculated positions using riding models.
3. Computational Methods

**Density functional theory (DFT)**
DFT calculations were carried out using the Guassian09 software package.[55] This software was used to compute the gauche torsional scan of a single glutaric acid. All optimizations were carried out at mPW1PW91/6-311+G(d,p) (hybrid Hartree–Fock density functional) level of theory. The SCF=QC option was used to manage conversion difficulties and consequently a larger DFT integration grid (Int=UltraFine) was chosen.

**Atomic charges**
Only the hydrogen atoms of the frameworks were optimized as part of a periodic system using the CASTEP module of the Materials Studio software suite.[56] The optimization was performed using the GGA PBE functional with Grimme's DFT-D dispersion correction; thresholds for geometry optimization and SCF convergence were chosen as $1 \times 10^{-6}$ eV. The Mulliken charges were calculated at the end of the optimization process (this is given as an option in the properties tab of the calculation setup). These atomic charges were used in all the molecular mechanics calculations.

**Molecular Mechanics (MM)**
All MM calculations were performed using the Forcite-Plus module within the Biovia Materials Studio software suite.[56]

**Forcite energy parameters (Materials Studio)**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
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<td>Quality</td>
<td>Ultra-fine</td>
</tr>
<tr>
<td>Force field</td>
<td>COMPASS</td>
</tr>
<tr>
<td>Charges</td>
<td>Current (obtained from CASTEP)</td>
</tr>
<tr>
<td>Summation method</td>
<td>Ewald</td>
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<tr>
<td>Electrostatic</td>
<td>Ewald</td>
</tr>
<tr>
<td>van der Waals</td>
<td>Ewald</td>
</tr>
<tr>
<td>Ewald accuracy</td>
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</tr>
</tbody>
</table>

**Forcite Geometry optimization parameters (Materials Studio)**

<table>
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<tr>
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<th>Value</th>
</tr>
</thead>
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<tr>
<td>Algorithm</td>
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<td>Energy tolerance</td>
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<tr>
<td>Force</td>
<td>0.001 kcal/mol/Å</td>
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<td>Max iterations</td>
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<td>Keep motion groups rigid</td>
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4. Crystallographic tables and structural analysis

Table S1. Crystallographic table of 1a, 1'a, 2a and 2'b. PXRD indexed unit cells for 1' and 2'.

<table>
<thead>
<tr>
<th></th>
<th>1b</th>
<th>1a</th>
<th>1'a</th>
<th>1'</th>
<th>2a</th>
<th>2'b</th>
<th>2'</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method</td>
<td>SCXRD</td>
<td>SCXRD</td>
<td>SCXRD</td>
<td>PXRD</td>
<td>SCXRD</td>
<td>SCXRD</td>
<td>PXRD</td>
</tr>
<tr>
<td>Temp</td>
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<td>RT</td>
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<td>100.15</td>
<td>RT</td>
</tr>
<tr>
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<td>monoclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>orthorhombic</td>
<td>orthorhombic</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space</td>
<td>C2/c</td>
<td>C2/c</td>
<td>C2/c</td>
<td>C2/c</td>
<td>Pccn</td>
<td>Pccn</td>
<td>Pccn</td>
</tr>
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<td>a Å</td>
<td>24.55(2)</td>
<td>24.42(11)</td>
<td>23.72(9)</td>
<td>23.970</td>
<td>12.90(11)</td>
<td>27.25(9)</td>
<td>27.378</td>
</tr>
<tr>
<td>b Å</td>
<td>12.97(12)</td>
<td>13.10(6)</td>
<td>11.80(4)</td>
<td>11.888</td>
<td>27.61(2)</td>
<td>11.81(4)</td>
<td>12.065</td>
</tr>
<tr>
<td>c Å</td>
<td>8.60(8)</td>
<td>8.62(4)</td>
<td>9.23(4)</td>
<td>9.121</td>
<td>8.57(7)</td>
<td>9.14(3)</td>
<td>9.151</td>
</tr>
<tr>
<td>β°</td>
<td>91.79(2)</td>
<td>91.62(2)</td>
<td>90.47(4)</td>
<td>91.845</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume</td>
<td>2759.1(4)</td>
<td>2760.5(2)</td>
<td>2585.7(17)</td>
<td>2597.7</td>
<td>3054.6(4)</td>
<td>2946.6(17)</td>
<td>3022.6</td>
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<tr>
<td>Void volume per cellÅ³</td>
<td>466.89*</td>
<td>520.43*</td>
<td>281.27*</td>
<td>645.25*</td>
<td>490.65*</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The void volumes were calculated using the Materials Studio Visualizer with a probe radius of 1.4 Å.

5. Structural phase classification

We refer to the guest-free (i.e. virtual)[7] framework structures of 1a and 2a as 1 and 2, respectively. These structures are the wide-channel (wc) forms. We refer to the guest-free (virtual) framework structures of 1'a and 2'b as 1' and 2', respectively. These structures with the "prime" notation are the narrow-channel (nc) forms.

Table S2. Classification of the different structural phases of 1 and 2.

<table>
<thead>
<tr>
<th></th>
<th>Wide-channel</th>
<th>Narrow-channel</th>
<th>Wide-channel</th>
<th>Narrow-channel</th>
</tr>
</thead>
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<tr>
<td>Crystal structures</td>
<td>1a and 1b</td>
<td>1'a</td>
<td>2a</td>
<td>2'b</td>
</tr>
<tr>
<td>Host framework structures</td>
<td>1</td>
<td>1'</td>
<td>2</td>
<td>2'</td>
</tr>
<tr>
<td>Guest-free (virtual)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activated forms</td>
<td>1'</td>
<td>2'</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure S1. The Cu-glutarate 2-D grids for 1, 1', 2 and 2' viewed along the crystallographic c-axis. The blue and red bands indicate the sign of the glu gauche torsion angles. Hydrogen atoms have been omitted for clarity.
Table S3  The glutarate *anti* and *gauche* torsion angles (in degrees) of 1, 1', 2 and 2'. The copper paddle-wheel axial orientations relative the *bc*, *ab* and *ac* planes.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>1'</th>
<th>Relative Difference</th>
<th>2</th>
<th>2'</th>
<th>Relative Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glu <strong>Gauche</strong> torsion angle (°)</td>
<td>±57.5</td>
<td>±75.7</td>
<td>133.2</td>
<td>±59.2</td>
<td>±77.1</td>
<td>136.3</td>
</tr>
<tr>
<td>Glu <strong>Anti</strong> torsion angle (°)</td>
<td>±176.0</td>
<td>±161.9</td>
<td>22.1</td>
<td>±172.0</td>
<td>±162.3</td>
<td>25.7</td>
</tr>
</tbody>
</table>

**Cu-paddlewheel axial orientation (°)**

<table>
<thead>
<tr>
<th></th>
<th>Relative to <em>bc</em> plane</th>
<th>Relative to <em>ab</em> plane</th>
<th>Relative to <em>ac</em> plane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>56.91</td>
<td>53.79</td>
<td>3.12</td>
</tr>
<tr>
<td></td>
<td>23.93</td>
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<td></td>
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</tr>
<tr>
<td></td>
<td>0.35</td>
<td>12.88</td>
<td>15.61</td>
</tr>
</tbody>
</table>

The *gauche* and *anti*-torsion angles exist with both + and - signs within the crystal structures in an ABAB fashion. The positive angle changes to negative while the negative angle changes to positive. Thus we use ± and ± to denote the inversion.
Figure S2. The Cu-glutarate 2-D grids for 1, 1', 2 and 2' viewed along the crystallographic c axis. The yellow lines connect centroids of each paddle-wheel SBU in order to show the grid topology. Hydrogen atoms have been omitted for clarity.
Table S4. The \(ab\) plane inclination, bend angles and scissor angles formed by both linkers.

<table>
<thead>
<tr>
<th></th>
<th>1a (Bpa)</th>
<th>1'a (Bpa)</th>
<th>Relative Difference</th>
<th>2a (Bpp)</th>
<th>2'b (Bpp)</th>
<th>Relative Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(ab) plane inclination (°)</td>
<td>35.73</td>
<td>38.05</td>
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</tr>
<tr>
<td>Scissor angle (°)</td>
<td>58.75</td>
<td>61.85</td>
<td>3.10</td>
<td>47.37</td>
<td>51.48</td>
<td>4.11</td>
</tr>
<tr>
<td>Bend angle (°)</td>
<td></td>
<td></td>
<td>94.12</td>
<td>84.03</td>
<td>-10.09</td>
<td></td>
</tr>
</tbody>
</table>

All the angles were measured using the Mercury CSD 5.3.1. software.

6. TGA thermograms

![TGA thermogram](image1)

**Figure S3.** Thermogravimetric analysis of various solvates and the activated materials of 1 and 2. The weight % and its derivative are shown. The large mass loss for as-synthesised 1 (1a) is not reliable owing to the presence surface solvent, which could not be avoided. Our interest lies in the temperature at which the guest/solvent evolution is complete.
7. Powder X-ray diffraction

**Figure S4.** PXRD traces for MOF 1. (a) Full scale PXRD trace. (b) Zoomed in at 10° to 30° for better comparison of the PXRD traces. Crystal structures determined at 100 K were used to generate the simulated PXRD traces.

**Figure S5.** PXRD traces for MOF 2. (a) Full scale PXRD trace. (b) Zoomed in at 10° to 30° for better comparison of the PXRD traces. Crystal structures determined at 100 K were used to generate the simulated PXRD traces.
### Table S5. Crystallographic tables for 1a and 1'a. PXRD indexed unit cells for 1a, 1' and 1'a.

<table>
<thead>
<tr>
<th></th>
<th>1a</th>
<th>1a</th>
<th>1'a</th>
<th>1'a</th>
<th>1'a</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental Method</strong></td>
<td>SCD</td>
<td>PXRD</td>
<td>PXRD</td>
<td>PXRD</td>
<td>SCD</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
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<td>RT</td>
<td>RT</td>
<td>RT</td>
<td>100.15</td>
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<tr>
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<td>monoclinic</td>
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<td>monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
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<td>$C2/c$</td>
<td>$C2/c$</td>
<td>$C2$</td>
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<tr>
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<td>24.4258(11)</td>
<td>25.318</td>
<td>23.970</td>
<td>23.989</td>
<td>23.720(9)</td>
</tr>
<tr>
<td>$b$/Å</td>
<td>13.1097(6)</td>
<td>13.284</td>
<td>11.888</td>
<td>11.923</td>
<td>11.800(4)</td>
</tr>
<tr>
<td>$c$/Å</td>
<td>8.6242(4)</td>
<td>8.731</td>
<td>9.121</td>
<td>9.203</td>
<td>9.239(4)</td>
</tr>
<tr>
<td>$\beta'$</td>
<td>91.627(2)</td>
<td>94.62</td>
<td>91.84</td>
<td>91.81</td>
<td>90.476(4)</td>
</tr>
<tr>
<td><strong>Volume/Å³</strong></td>
<td>2760.5(2)</td>
<td>2926.9</td>
<td>2597.7</td>
<td>2630.5</td>
<td>2585.7(17)</td>
</tr>
</tbody>
</table>

### Table S6. Crystallographic tables for 2a and 2'b. PXRD indexed unit cells for 2a, 2' and 2'a.

<table>
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<th></th>
<th>2a</th>
<th>2a</th>
<th>2'a</th>
<th>2'a</th>
<th>2'b</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental Method</strong></td>
<td>SCD</td>
<td>PXRD</td>
<td>PXRD</td>
<td>PXRD</td>
<td>SCD</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>100.15</td>
<td>RT</td>
<td>RT</td>
<td>RT</td>
<td>100.15</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
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<td>orthorhombic</td>
<td>orthorhombic</td>
<td>orthorhombic</td>
<td>orthorhombic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>$Pccn$</td>
<td>$Pccn$</td>
<td>$Pccn$</td>
<td>$Pccn$</td>
<td>$Pccn$</td>
</tr>
<tr>
<td>$a$/Å</td>
<td>12.9025(11)</td>
<td>28.220</td>
<td>27.3778</td>
<td>27.270</td>
<td>27.255(9)</td>
</tr>
<tr>
<td>$b$/Å</td>
<td>27.615(2)</td>
<td>13.012</td>
<td>12.065</td>
<td>11.836</td>
<td>11.819(4)</td>
</tr>
<tr>
<td><strong>Volume/Å³</strong></td>
<td>3054.6(4)</td>
<td>3203.6</td>
<td>3022.6</td>
<td>2969.4</td>
<td>2946.6(17)</td>
</tr>
</tbody>
</table>
8. FTIR

**Figure S6.** FTIR spectra, recorded at RT, of 1 and 2 with different guests. The band associated with the CO$_2$ anti-symmetric stretch is indicated.
9. Pressure-ramped differential scanning calorimetry (P-DSC)

![Graph showing heat flow vs. pressure for different P-DSC scans.](image)

**Figure S7.** P-DSC scans for $1'$ and $2'$ with CO$_2$ at 25 °C.

10. CO$_2$—CO$_2$ interactions in MOF 2.

![Diagram showing the arrangement of CO$_2$ molecules in the crystal structure of MOF 2.](image)

**Figure S8.** The arrangement of CO$_2$ molecules in the crystal structure of MOF 2. The central molecule forms slipped-parallel electrostatic interaction with the surrounding CO$_2$ molecules.
11. Computational models and data

**Figure S9.** Data obtained from the four paddle-wheel computational simulation. A parallelogram is drawn by connecting centroids generated for each paddlewheel unit. (a) The horizontal (acute) and vertical (obtuse) diagonals of the parallelogram. (b) The acute and obtuse angles of the parallelogram.

**Figure S10.** Overlay of the initial (red, wc) and final (blue, nc) structures of the glutarate $\theta g \leftrightarrow \bar{\theta}g$ torsional potential energy scan.
Figure S11. Full unit cell computational models for 1 and 2 used in the molecular mechanics simulations for the potential energy scans.
Table S7. The energy barriers (kcal/mol) for all the computational models and potential energy scan.

<table>
<thead>
<tr>
<th>Energy Barrier</th>
<th>Free Glu model</th>
<th>4 Paddle-wheel model</th>
<th>Full unit cell model - MOF 1</th>
<th>Full unit cell model - MOF 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔE(C–B)</td>
<td>4.4</td>
<td>ΔE(A–B)</td>
<td>4.76</td>
<td>2.99</td>
</tr>
<tr>
<td>ΔE(A–B)</td>
<td>3.03</td>
<td>ΔE(C–B)</td>
<td>2.9</td>
<td>4.57</td>
</tr>
<tr>
<td>ΔE(C–D)</td>
<td>5.41</td>
<td>ΔE(E–B)</td>
<td>3.89</td>
<td>4.99</td>
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<tr>
<td>ΔE(E–D)</td>
<td>3.85</td>
<td>ΔE(D–C)</td>
<td>0.22</td>
<td>0.76</td>
</tr>
<tr>
<td>ΔE(B–D)</td>
<td>1.01</td>
<td>ΔE(D–E)</td>
<td>1.22</td>
<td>1.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ΔE(A–B2)</td>
<td>14.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ΔE(B2–C2)</td>
<td>16.77</td>
</tr>
</tbody>
</table>
## 12. Full crystallographic table

### Table S8. Crystal data and structure refinement.

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<thead>
<tr>
<th></th>
<th>1b</th>
<th>1a</th>
<th>1’a</th>
<th>2a</th>
<th>2’b</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C_{115}H_{12}CuNO_{54} &amp; C_{114}H_{12}CuNO_{4} &amp; C_{114}H_{12}CuNO_{6} &amp; C_{114}H_{12}NO_{5}Cu &amp; C_{114}H_{12}NO_{5}Cu</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>314.80 &amp; 285.76 &amp; 285.76 &amp; 350.85 &amp; 328.31</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Temperature/K</strong></td>
<td>100.15 &amp; 100.15 &amp; 100.15 &amp; 100.15 &amp; 100.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>C2/c &amp; C2/c &amp; C2/c &amp; Pccn &amp; Pccn</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>a/Å</strong></td>
<td>24.566(2) &amp; 24.4258(11) &amp; 23.7209(9) &amp; 12.9055(11) &amp; 27.255(9)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>b/Å</strong></td>
<td>12.9794(12) &amp; 13.1097(6) &amp; 11.800(4) &amp; 27.615(2) &amp; 11.819(4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>c/Å</strong></td>
<td>8.6609(8) &amp; 8.6242(4) &amp; 9.239(4) &amp; 8.5728(7) &amp; 9.148(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>α°</strong></td>
<td>90 &amp; 90 &amp; 90 &amp; 90 &amp; 90</td>
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<td></td>
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<tr>
<td><strong>β°</strong></td>
<td>91.796(2) &amp; 91.627(2) &amp; 90.476(4) &amp; 90 &amp; 90</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td><strong>γ°</strong></td>
<td>90 &amp; 90 &amp; 90 &amp; 90 &amp; 90</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Volume/Å³</strong></td>
<td>2759.1(4) &amp; 2760.5(2) &amp; 2585.7(17) &amp; 3054.6(4) &amp; 2946.6(17)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>8 &amp; 4 &amp; 2 &amp; 8 &amp; 8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>ρ_{calc}g/cm³</strong></td>
<td>1.516 &amp; 1.375 &amp; 1.468 &amp; 1.526 &amp; 1.480</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>μ/mm⁻¹</strong></td>
<td>1.599 &amp; 1.583 &amp; 1.690 &amp; 1.451 &amp; 1.502</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>1284.0 &amp; 1168.0 &amp; 1168.0 &amp; 1456.0 &amp; 1342.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Crystal size/mm³</strong></td>
<td>0.625 × 0.177 × 0.088 &amp; 0.542 × 0.081 × 0.056 &amp; 0.173 × 0.096 × 0.067 &amp; 0.652 × 0.228 × 0.098 &amp; 0.21 × 0.155 × 0.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Radiation</strong></td>
<td>MoKα (λ = 0.71073) &amp; MoKα (λ = 0.71073) &amp; MoKα (λ = 0.71073) &amp; MoKα (λ = 0.71073) &amp; MoKα (λ = 0.71073)</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td><strong>2θ range for data collection”</strong></td>
<td>3.318 to 56.58</td>
<td>3.336 to 49.426 &amp; 3.434 to 53.978 &amp; 2.94 to 56.88 &amp; 2.98 to 55.12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Index ranges</strong></td>
<td>-32 ≤ h ≤ 32, -17 ≤ k ≤ 17, -11 ≤ l ≤ 11 &amp; -28 ≤ h ≤ 28, -13 ≤ k ≤ 15, -10 ≤ l ≤ 7 &amp; -30 ≤ h ≤ 22, -15 ≤ k ≤ 13, -11 ≤ l ≤ 11 &amp; -12 ≤ h ≤ 17, -36 ≤ k ≤ 36, -11 ≤ l ≤ 7 &amp; -35 ≤ h ≤ 34, -15 ≤ k ≤ 13, -11 ≤ l ≤ 7</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td><strong>Reflections collected</strong></td>
<td>24894 &amp; 10270 &amp; 7007 &amp; 18023 &amp; 16238</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Independent reflections</strong></td>
<td>3422 (R_{int} = 0.0392, R_{sigma} = 0.0236) &amp; 2341 (R_{int} = 0.0366, R_{sigma} = 0.0275) &amp; 2793 (R_{int} = 0.0726, R_{sigma} = 0.0977) &amp; 3676 (R_{int} = 0.0209, R_{sigma} = 0.0172) &amp; 3372 (R_{int} = 0.0556, R_{sigma} = 0.0448)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Data/restraints/parameters</strong></td>
<td>3422/0/187 &amp; 2341/0/152 &amp; 2793/0/154 &amp; 3676/0/197 &amp; 3372/0/200</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Goodness-of-fit on F²</strong></td>
<td>1.118 &amp; 1.075 &amp; 0.949 &amp; 1.050 &amp; 1.044</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Final R indices [I&gt;2σ(I)]</strong></td>
<td>R₁ = 0.0371, wR₂ = 0.1078 &amp; R₁ = 0.0265, wR₂ = 0.0669 &amp; R₁ = 0.0482, wR₂ = 0.0808 &amp; R₁ = 0.0228, wR₂ = 0.0570 &amp; R₁ = 0.0385, wR₂ = 0.0895</td>
<td></td>
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<td></td>
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<tr>
<td><strong>Final R indices [all data]</strong></td>
<td>R₁ = 0.0437, wR₂ = 0.1114 &amp; R₁ = 0.0280, wR₂ = 0.0678 &amp; R₁ = 0.0875, wR₂ = 0.0910 &amp; R₁ = 0.0254, wR₂ = 0.0583 &amp; R₁ = 0.0609, wR₂ = 0.0995</td>
<td></td>
<td></td>
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</tr>
<tr>
<td><strong>Largest diff. peak/hole / e Å⁻³</strong></td>
<td>0.99/-0.37 &amp; 0.51/-0.34 &amp; 0.50/-0.64 &amp; 0.38/-0.46 &amp; 0.48/-0.45</td>
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<td></td>
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<td></td>
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</table>
13. Absolute energies for single H$_2$glu torsional scan.

<table>
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<tr>
<th>C1-C2-C3-C4 dihedral angle (°)</th>
<th>E (Hartree)</th>
<th>Relative E (kcal mol$^{-1}$)</th>
<th>C1-C2-C3-C4 dihedral angle (°)</th>
<th>E (Hartree)</th>
<th>Relative E (kcal mol$^{-1}$)</th>
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<td>-496.30773</td>
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</table>
14. References

Chapter 5

SOLVATOCHROMISM AS A PROBE TO OBSERVE THE SOLVENT EXCHANGE PROCESS IN A 1-D POROUS COORDINATION POLYMER WITH 1-D SOLVENT ACCESSIBLE CHANNELS.

5.1. COMMUNICATION IN CHEMICAL COMMUNICATIONS

Contributions of the author:
- Design of project
- Synthesis of Ligand and PCP
- Collection of single-crystal X-ray data solution and refinement of single-crystal X-ray structures
- TGA thermograms
- Optical microscopy experiments
- Computational modelling
- Interpretation of results
- Writing the first draft of the article
Solvatochromism as a probe to observe the solvent exchange process in a 1-D porous coordination polymer with 1-D solvent accessible channels.

Charl X. Bezuidenhout, Catharine Esterhuysen* and Leonard J. Barbour*

A one-dimensional porous coordination polymer (PCP) ([Cu(acetate)2](3,6-dipyrindin-4-yl)-1,2,4,5-tetrazine)•2CH3OH, possesses pleochroic properties. Solvent exchange with acetonitrile and nitromethane reveals that single crystals of the PCP are also solvatochromic, with the solvent exchange process occurring in an unexpected double V-shaped pattern. Crystal surface adsorption modeling shows that the origin of this effect is preferential sorption at two faces of the crystal.

The development of new porous coordination polymers (PCPs) is a rapidly growing area, primarily owing to the remarkable diversity of potential building blocks and preparative procedures.1 PCPs comprise 1D, 2D and 3D porous polymeric networks and frameworks consisting of metal ions/clusters tethered by organic linkers.1,2 The potential to incorporate the functionalities and properties of the separate components into a functional material provides a very attractive platform for studying gas and small molecule storage, separation or sensing.2a-c,3 Systematic modification of the individual components (metal ion, organic linker, solvent, etc.) or synthetic conditions allows for tuning of these properties.1a,4

Chromophoric organic linkers are often used to obtain PCPs that exhibit solvatochromism or other optical properties.4a-c It is well known that most chromophores exhibit colour changes when dissolved in different polar solvents.4c Hence, building this property into a PCP can turn the material into a functional sensor for small-molecules.5 Optical properties can also arise from the presence of metal clusters that may become distorted through guest-induced structural changes, or from the interaction of guest molecules with the organic ligands, in turn affecting the electronic structure of the metal.6c

Tetrazine-based chromophores have recently been used for the synthesis of PCPs,7b,c,d their optical properties are derived from the transitions between the HOMO and LUMO centered on the tetrazine ring. If the linker is conjugated then interactions with the tetrazine rings could influence the optical properties of the metal centres to which they are coordinated.7e The potential to utilise the solvatochromism of a PCP for sensing small molecules, shifts in the \( \lambda_{\text{max}} \) values in the solid-state UV-vis spectra of different solvates of the PCP would potentially differentiate between the solvents (small molecules). Generally a \( \lambda_{\text{max}} \) shift of 10 nm or more is considered suitable.5

A visible colour change of solvatochromic crystals can facilitate the observation of the solvent exchange process (the colours and contrast of the observed crystals can be enhanced by using a polariser). Polarisated-light optical microscopy of thin rock slices, i.e. optical mineralogy within petrology, is commonly employed by geologists to study the growth morphology and features of rocks.10 Time-lapse polarised-light optical microscopy experiments, using single crystals of a solvatochromic material, can visually reveal how a newly introduced solvent permeates the crystals, in addition to showing the preferred crystal face (facet) of entry.11 The study of crystal features such as morphology, structure, surface electrostatic potential, and dimensionality of porosity (1D, 2D or 3D) can provide insight into the solvent exchange process.

Here we report a 1D Cu(II)(acetate)2 paddlewheel based PCP which undergoes twisting of the organic linkers upon exchange of solvent. The organic chromophoric ligand 3,6-dipyrindin-4-yl)-1,2,4,5-tetrazine (dptz) was used to link the Cu(II)(acetate)2 paddlewheel units into a 1D chain. The solvatochromic and pleochroic properties of this material enable the observation of the solvent exchange process and elucidation of a possible mechanism for the observed solvent-exchange pattern.

Layering Cu(acetate)2 in methanol and dptz in chloroform, with a 1:1 methanol-chloroform buffer, at 50°C afforded dark purple crystals of ([Cu2(acetate)2](dptz))•2CH3OH, (1a). Single-crystal X-ray diffraction (SCD) shows that the PCP crystallises in...
the space group P1. The Cu(acetate), paddlewheel secondary building units are linked by dptz to form a 1D coordination polymer (Fig. 1, top). These 1D chains form weak C–H–N contacts between the tetrazine nitrogen atoms of dptz and the pyridyl C–H moieties of each neighbouring dptz linker to form 2D sheets similar to those observed by Lu et al.75 (Fig. 1, bottom left). These 2D sheets stack together to form 1D open channels with chloroform as included solvent (Fig. 1, top left).

![Image](https://scholar.sun.ac.za)

Fig. 1: Top: perspective views along the channels of 1a, 1b and 1c running parallel to [100]. The guest-accessible space is represented by the yellow “capsules” and hydrogen atoms have been omitted for clarity. Bottom: A projection along [010] with the yellow parallelograms indicating the dptz linkers rotated out of the hydrogen-bonded (101) plane. The copper acetate paddlewheel motifs are shown as coordination polyhedra.

Thermogravimetric analysis of 1a showed complete solvent loss by 120 °C (Fig. S1). The apophth crystal structure could not be obtained owing to insufficient quality of desolvated single crystals. On the other hand, solvent exchange with pure acetonitrile (ACN) and nitromethane (NM) yielded solvates 1b (ACN) and 1c (NM) as intact single crystals (Fig. 1, top). SCD analysis reveals that 1b and 1c also pack in space group P1 with host structures similar to that of 1a. However, the exchanged guest molecules induce distinctive changes in the dptz linker orientations with respect to the channel walls parallel to [101]. In 1a all of the dptz linkers are only slightly tilted towards the channel. However, one in three linkers is tilted significantly further in towards the channel while for 1c two out of three linkers are tilted towards the channel (Fig. 1, bottom).

The solvent accessible volumes decrease from 1a to 1c, with increasing number of tilted dptz linkers as opposed to the size of the included guest (i.e. the trend is not due to host-guest fit, Table 1). Tilting of the dptz linkers consequently reduces the D–H–A interactions between the adjacent dptz linkers (Fig. S2, Table S1). The D–A distances increase and the D–H–A angles decrease from 1a to 1c, resulting in weakening of these interactions (Table S1).

Table 1. Framework and guest molecular volumes.

<table>
<thead>
<tr>
<th>guest</th>
<th>CF</th>
<th>ACN</th>
<th>NM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guest-accessible space</td>
<td>246 Å³</td>
<td>181 Å³</td>
<td>177 Å³</td>
</tr>
<tr>
<td>Guest volume</td>
<td>73.5 Å³</td>
<td>46.4 Å³</td>
<td>53.9 Å³</td>
</tr>
</tbody>
</table>

All volumes were determined with a probe radius of 1.5 Å using the Materials Studio software suite.

In 1a the chloroform (CF) guest molecules interact with the π-system of the tetrazine moiety through all three chlorine atoms. The partially positive hydrogen atom of CF is directed towards the pyridyl nitrogen atom of a second dptz linker across the channel (Fig. S3). In the cases of 1b and 1c, the ACN and NM guest molecules form dimers (through anti-parallel dipole–dipole interactions) and then interact with neighbouring dimers via head-to-tail dipole–dipole interactions along the channel axis (Fig. S4). The ACN and NM molecules interact with both the tetrazine and pyridyl moieties of dptz in a side-on fashion. ACN adopts a head-on alignment to the tetrazine moieties in every third dptz linker (Fig. S5). This interaction could be the reason for the dptz linker rotating out of the plane of each 2D layer of 1b. Furthermore, ACN forms weak C–H–O interactions with the pyridyl and acetate moieties, whereas the nitro groups of the NM molecules in 1c form weak C–H–O interactions with the acetate moieties (Fig. S6). 1a is the only solvate that remains stable when removed from the mother liquor, while 1b and 1c desolvate rapidly upon drying, losing their single-crystal nature.

The crystals of 1a grow as rectangular slabs, with only one set of large crystal faces, (01-1) and (0-11). One of these faces was observed using an optical microscope with a polariser (but not an analyser) to enhance the observation of pleochroism. Upon rotating the stage the crystal appears blue when the long side of the crystal (Fig. S7) is perpendicular to the direction of polarisation and yellow when aligned with it. Additional colours are observed when different crystal faces are viewed, i.e. depending on the orientation of the crystal (see Fig. S8). Videos illustrating the pleochroism of 1a upon rotation of the crystals are available in the ESI (1b and 1c desolvate rapidly in air, thus only 1a could be studied).

Solid-state UV-Vis analysis of the three solvates reveals two dominant reflectance peaks at ca 450 (blue) and 600 nm (yellow) (Fig. S9); these colours correspond to those observed by optical microscopy (Fig. S7). The blue peak can be ascribed to the presence of Cu(II) ions in the PCP. Uncoordinated dptz is red, owing to the transition between the HOMO and LUMO orbitals situated on the tetrazine ring.15 Therefore, coordination of the linker to the metal, along with the D–H–A interaction between dptz linkers and the host-guest interactions could combine to yield the yellow colour. The difference in colour from 1a to 1c is due to blue-shifting of the peaks in the spectra. The colour change was initially thought to be due to tilting of the pyridyl and tetrazine rings, but the measured tilt angles (Fig. S10) do not correlate with the blue-shift trend. However, the simulated UV-Vis spectra of the dptz linkers show that the systematic weakening of the C–H–N interactions from 1a to 1c results in changes in the energies of the LUMO, HOMO and HOMO-1 molecular orbitals, leading to a lowering of the HOMO-1→LUMO transition and a consequent blue-shift in the UV-Vis spectra (Fig. S11). Additionally, the simulated UV-vis spectra of a paddlewheel moiety with two coordinated bptz linkers in the presence of CF, ACN and NM also produce a blue-shift trend from 1a > 1b > 1c (Fig. S12, see ESI for computational details). Therefore, the overall observed blue shift upon guest exchange results from a combination of weakening of the C–H–N interactions due to ligand rotation, and changes in host-guest interactions.

Owing to the blue-shift and the solvatochromism of 1a, the solvent exchange process from 1a to 1b or to 1c could be
studied visually. The change in colour was not easily discernible when viewed with normal light, and polarised light was therefore used to enhance the observations. Each crystal was oriented with its large (01-1) facet facing the camera and, because blue provides a better contrast than yellow, its long axes normal to the direction of polarisation. The crystals were doused with ACN or NM and time-lapse photography was used to record the solvent exchange process in each case. The initial colour darkens when CF is exchanged with ACN and NM, and is suitable for visually tracking the progress of the solvent through the crystal (Fig. 2). For both ACN and NM the solvent enters via facets (212) and (-2-1-2), forming a hourglass-shaped pattern reminiscent of the arrangement of polar molecules diffused into organic crystals containing 1D channels.\(^{13}\) The latter is not due to a difference in rate of diffusion (or exchange), but is rather a result of a systematically decreasing probability of the alignment of the polar molecules away from the centre of the crystal. Similarly, the hourglass patterns observed for sectional zoning, which results from the facet-selective inclusion of organic dyes into calcite crystals during their growth,\(^{16}\) as well as a reported case of a thermally induced structural transition\(^{15}\) arise from variations in the process of crystallisation. That is, they are due to different physical properties and not the diffusion of solvent molecules into the crystal.

For similarly sized crystals complete darkening requires about 5.5 hours for ACN and 14 hours for NM. We can gain further insight into the solvent exchange process by overlaying the crystal habit with the crystal structure and mapped channels of 1a (Fig. S13; facets used to determine the habit were identified by face-indexing several crystals using Bruker’s APEX II software, see ESI). The channels are angled relative to both the (212) and (10-2) facets, thereby opening onto both surfaces, but they do not protrude through the (01-1) facet (Fig. 2 and Fig. S13). Although this implies that guest molecules can enter the crystal at both the (212) and (10-2) facets, Fig. 2 shows that the solvent only enters from (212) facet.

The Adsorption Locator module of the Biovia Materials Studio 7.0 Software Suite uses simulated annealing (molecular dynamics simulating heating and cooling) and Monte Carlo searches of the configurational space of the substrate-adsorbate system during the cooling process to simulate the adsorption of molecules onto a specified surface of a crystal (see ESI for details). This has the effect of allowing the guest molecules to be released from and reattached to the crystal surface; the process is repeated a number of times to ensure that statistically meaningful results are obtained (parameters given in the ESI, Fig. S14). The \(\Delta H_{\text{adsorption}}\) values (Fig. S15) are in the range of moderate to weak metal—ligand bond dissociation energies,\(^{16}\) suggesting that the values are slightly high, nevertheless, the relative differences and trends are still relevant. ACN and NM both have a significantly higher \(\Delta H_{\text{adsorption}}\) for (212) compared to (10-2) (relative \(\Delta H_{\text{adsorption}}\) of 6.07 and 3.75 kcal mol\(^{-1}\) for ACN and NM, respectively). Moreover the \(\Delta H_{\text{adsorption}}\) for ACN is always higher than that for NM (relative \(\Delta H_{\text{adsorption}}\) of 0.65 and 2.97 kcal mol\(^{-1}\) for (10-2) and (212), respectively) (Fig. S15). This could be attributed to ACN having a higher dipole moment (4.5 D)\(^{17}\) as compared to NM (3.56 D),\(^{18}\) thus increasing the electrostatic interaction of ACN with the crystal surfaces. Furthermore, the (212) facet comprises open metal sites and free pyridyl moieties, resulting in strong positive and negative electrostatic potential sites not present on (10-2). This yields stronger solvent interactions with (212) compared to (10-2) and subsequently a higher \(\Delta H_{\text{adsorption}}\) for (212) relative to (10-2) (Fig. S15). This difference in calculated \(\Delta H_{\text{adsorption}}\) values explains the slower solvent-exchange rate observed in the optical microscopy experiments for NM (taking 5 hours to produce the hourglass pattern, while ACN requires only 30 minutes, Fig. 2), although differences in diffusion rates within the channels are also expected to play a role. The large difference in adsorption enthalpies between (212) and (10-2) for both ACN and NM is responsible for the surface recognition effect and supports the optical microscopy observations that solvent entry occurs first via (212), and then via (10-2) over a longer period of time. Similarly, surface recognition is a key factor in the elucidation of the sectional zoning phenomenon of dye-included calcite crystals\(^{13}\) and the formation of polarity in crystals by polar molecules diffusing into 1D channels.\(^{15}\) Nevertheless, it is not obvious why the solvent-exchange process yields the observed hourglass-shaped pattern in this case. Overlaying the crystal structure of 1a with its crystal habit (Fig 3a) reveals a solvent exchange pattern with only the two opposite corners involved in the exchange process. This solvent exchange pattern is angled relative to both the (212) and (10-2) facets (Fig 3a). The pattern produced is thus inconsistent with the observation of the hourglass shape (Fig. 3a), indicating that a single crystal of 1a cannot produce the observed solvent exchange pattern.

A closer examination of single crystals of 1a revealed that only the larger crystals have an elongated double ribbon shape (Fig. 3b). This growth morphology is indicative of twinning although no evidence of twinning was observed in the SCD data. The observed crystal morphology and twinning features are consistent with the “two re-entrant corner effect” (Fig. 3b), which results in a crystal with four domains where the corner-opposite domains are identical (Fig. 3c). Combining this with the knowledge that the solvent enters (212) first, we can construct
the proposed model shown in Fig. 3d. This model is similar to intergrowth structures reported for zeolite crystals. With the channels angled in towards the centre of the crystal, the solvent can enter via facet (212), thus producing the hourglass-shaped pattern observed using optical microscopy.

In conclusion, a 1D PCP (1a) with channels occupied by chloroform molecules has been prepared using the chromophore dpz as a linker. 1a was shown to undergo a phase change and solvatochromism upon solvent exchange with acetonitrile and nitromethane. The solvatochromism allowed tracking of the solvent progress through a single crystal using time-lapse polarised light optical microscopy. Observation of the solvent-exchange process revealed a hourglass-shaped pattern with solvent entering through facet (212) first, and after considerably more time, through (10-2). MM adsorption simulations showed that the difference in exchange rate between the two crystal-faces is due to (212) having a larger \( \Delta H_{\text{adsorption}} \) compared to (10-2). The observed solvent-exchange pattern is inconsistent with a pattern that would result from a single crystal. We have proposed a twinned crystal with a two re-entrant corner effect, which results in a growth morphology consistent with 1a single crystals and reproduces the observed solvent-exchange pattern. The unique combination of surface selectivity and solvatochromism exhibited by 1a has therefore provided us with a means of explaining the mechanism by which it undergoes solvent exchange, and has allowed us to identify the presence of an unusual mode of crystal growth (yielding twinning) that would otherwise have gone unnoticed.

We thank the National Research Foundation (NRF) of South Africa and Stellenbosch University for financial support, as well as the Centre for High Performance Computing (CHPC) in Cape Town, South Africa for computational resources.

Notes and references


5.2. SUPPORTING INFORMATION

Materials and synthesis

All chemicals were obtained from commercial sources (mainly Sigma Aldrich) and used without further purification. The 3,6-di(pyridin-4-yl)-1,2,4,5-tetrazine (dptz) linker was synthesised according to reported procedures[S1].

Single-crystal X-ray Diffraction

Suitable single-crystals were selected and loaded onto the diffractometer using a MiTeGen MicroCrystal mounts. Single-crystal X-ray diffraction data were collected using a SMART diffractometer with an APEX-II CCD area-detector using an Oxford Cryosystems 700Plus cryostat for temperature control. X-rays were generated from a sealed tube (MoKα radiation λ = 0.71073 Å) fitted with a multilayer monochromator. All data were collected at 100 K.

Data reduction was carried out by means of the standard procedure using the Bruker software package SAINT2 and the absorption corrections and the correction of other systematic errors were performed using SADABS3. Using Xseed [S2] and Olex2 [S3], the structure was solved with the ShelXS [S4] structure solution program using Direct Methods and refined with the ShelXL [S5] refinement package using least squares minimisation. Hydrogen atoms were placed in calculated positions using riding models.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was conducted using a TA Instrument Q500. The sample is loaded in an aluminium pan and heated from room temperature at 10 °C/min up to 600°C.

Time-Lapsed Polarized-light Optical Microscopy

Single crystals of the chloroform solvate (1a) were immersed in acetonitrile and nitromethane and sealed within a chamber with windows at the top and bottom. Adjustment (lighting, crystal position, polarizer, etc.) were made very quickly and pictures were taken every 10 seconds.

![Scheme 1. The Leica optical microscope setup used in the solvent-exchange experiments.](image)

Computational Methods
Geometry Optimizations and Atomic charges

Only the hydrogen atoms of the frameworks are optimized as part of a periodic system using the CASTEP module of the Materials Studio software suite.\cite{56} The optimization was performed using the GGA PBE functional with Grimme’s DFT-D dispersion correction; thresholds for geometry optimization and SCF convergence were chosen as $1 \times 10^{-6}$ eV. The Mulliken charges were calculated at the end of the optimisation process (this is given as an option in the properties tab of the calculation setup). These atomic charges are used in all the subsequent molecular mechanics calculations.

DMol³ UV-vis calculations

UV-vis data was calculated at the end of the optimization step using the DMol³ module within the Biovia Materials Studio software suite.\cite{56-58} The optimization was performed using the The Perdew et al.\cite{59} generalized gradient approximation (GGA/PBE) for the exchange–correlation functional \cite{510} and the dispersion corrected with Grimme’s DFT-D. The thresholds for the geometry optimizations and SCF convergence were chosen as $1 \times 10^{-6}$ eV. An all-electron core treatment with the TNP basis (Triple Numerical plus polarization) was chosen to describe the electronic structure for the organic models and the Effective Core Potentials with a DNP (Double Numerical plus polarization) basis was chosen for the models containing copper cations.\cite{511} The UV-vis spectra were calculated at the GGA/PBE level using TD-DFT with the ALDA (adiabatic local exchange functional approximation) approach that is recommended by the DMol³ author as a cost-efficient implementation of TD-DFT.\cite{512} The TD-DFT excitations were calculated using the ALDA kernel with exchange-correlation terms included, other options include: ALDAX - calculates TD-DFT excitations using a modified ALDA kernel with the exchange term only; RPA - no exchange-correlation response, only electrostatic response included) for calculating the 50 lowest singlet states.\cite{513, 514} Only the grid data for 10 orbitals above and below the Fermi level were calculated for visualization.

Adsorption calculations

All adsorption calculations were performed using the Adsorption Locator module within the Biovia Materials Studio software suite.\cite{56} This module allows for the simulation of pure and mixed adsorbates, with fixed composition, onto a substrate. The Adsorption Locator module identifies possible adsorption sites by carrying out Monte Carlo searches of the configurational space of the substrate-adsorbate system as the temperature is slowly decreased within the simulated annealing process of a molecular dynamics run. \cite{515-518} In this work we simulated the adsorption of a solvent molecules onto particular crystal facets in order to acquire relative interaction strengths of the different solvents with the different crystal facets. This can provide insight into the facet preferences of solvent exchange processes. The adsorption locator is essentially a simulated annealing simulation with geometry optimizations in-between successive heat-cool cycles. A model several unit cells in size were constructed and cleaved along a plane ((10-2) and (2 1 2)) to create the appropriate crystal face onto which a vacuum slab is added. One hundred adsorbate molecules were introduced into the vacuum as part of the simulated annealing calculation. The isosteric heat, or enthalpy of adsorption, can be extracted from the adsorption calculation and is an average over all the lowest energy configurations (obtained using Monte Carlo simulations) returned after each annealing cycle of the MD run. 30 cycles containing 1 000 000 steps per cycle with annealing temperatures of 298 to 500 K were used for reproducible results. The Monte Carlo parameters were set to a probability of 0.29 (ratio = 1) for ‘conformer’, ‘rotate’ and ‘translate’ while ‘regrow’ was set to 0.14 (ratio = 0.5). The
COMPASS force field (COMPASS II 1.0)[S19] was used in conjunction with atomic charges calculated using CASTEP single point energy calculations. Ewald and group based summation methods were chosen for the electrostatic and van der Waals energy components respectively with the cut-off’s set at 25 Å. The parameterisation and validation of COMPASS for metal oxides was performed by Zhao and co-workers. [S20] The list of models covered by the COMPASS II 1.0 force field is given below:

**Table S1.** All the models covered by the COMPASS II 1.0 force field.

<table>
<thead>
<tr>
<th>COMPASS II 1.0</th>
<th>Group A - Covalent Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkanes</td>
<td>C\text{H}_{2n+2}</td>
</tr>
<tr>
<td>Alkenes</td>
<td>C\text{H}_{2n}</td>
</tr>
<tr>
<td>Alkynes</td>
<td>C\text{H}_n</td>
</tr>
<tr>
<td>Benzenes/Aromatics</td>
<td>C\text{H}_n, -C\text{H}_n, C\text{H}_10</td>
</tr>
<tr>
<td>Cycloalkanes</td>
<td>C\text{H}_{2n}</td>
</tr>
<tr>
<td>Ethers</td>
<td>-R-O-R-</td>
</tr>
<tr>
<td>Acetals</td>
<td>-C(OR)\text{2-}</td>
</tr>
<tr>
<td>Alcohols</td>
<td>-R-OH</td>
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<tr>
<td>Phenols</td>
<td>Ar-OH</td>
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<tr>
<td>Amines</td>
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<tr>
<td>Ammonia</td>
<td>NH\text{3}</td>
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<tr>
<td>Aldehyde/ketone</td>
<td>-CO-</td>
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<td>Acids</td>
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<tr>
<td>Esters</td>
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<tr>
<td>Carbonates</td>
<td>-OCO-</td>
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<tr>
<td>Amides</td>
<td>-CONH-</td>
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<table>
<thead>
<tr>
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</thead>
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<tr>
<td>Metals</td>
<td>Al, Na, Pt, Pd, Au, Ag, Sn, K, Li, Mo, Fe, W, Ni, Cr, Cu, Pb, Mg</td>
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<td>Metal halides</td>
<td>Li\text{+}, Na\text{+}, K\text{+}, Rb\text{+}, Cs\text{+}, Mg\text{2+}, Ca\text{2+}, Fe\text{2+}, Cu\text{2+}, Zn\text{2+}, F\text{-}, Cl\text{-}, Br\text{-}, I\text{-}</td>
</tr>
<tr>
<td>Silica/Aluminosilicates</td>
<td>SiO\text{2}, AlO\text{2}</td>
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<tr>
<td>Metal oxides</td>
<td>Li\text{2+}, Na\text{2+}, K\text{2+}, Mg\text{2+}, CaO, SrO, BaO, TiO\text{2}, FeO\text{2}, Al\text{2}O\text{3}, MnO\text{2}, SiO\text{2}, CuO</td>
</tr>
</tbody>
</table>
Fig. S1  TGA of 1a from RT to 600 °C.

Fig. S2. The C—H⋅⋅⋅N contacts for the dptz ligands of 1a, 1b and 1c.
### Table S2. C—H···N contacts for the dptz ligands of 1a, 1b and 1c.

<table>
<thead>
<tr>
<th></th>
<th>D—H···A</th>
<th>Distance (D—A)</th>
<th>Angle (D—H···A)</th>
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<tr>
<td>1a</td>
<td>C(11)—H(11)···N(21)*</td>
<td>3.469(2)</td>
<td>142.52</td>
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<td></td>
<td>C(21)—H(21)···N(31)*</td>
<td>3.440(2)</td>
<td>134.87</td>
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<tr>
<td>1b</td>
<td>C(11)—H(11)···N(21)*</td>
<td>3.494(4)</td>
<td>126.14</td>
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<tr>
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<td>C(12)<em>—H(12)</em>···N(23)</td>
<td>3.573(4)</td>
<td>139.76</td>
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<td></td>
<td>C(13)<em>—H(13)</em>···N(22)*</td>
<td>3.518(4)</td>
<td>128.97</td>
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<tr>
<td></td>
<td>C(21)—H(21)···N(31)*</td>
<td>3.481(4)</td>
<td>117.14</td>
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<td>C(22)<em>—H(22)</em>···N(33)</td>
<td>3.547(4)</td>
<td>130.97</td>
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<td>C(23)<em>—H(23)</em>···N(32)*</td>
<td>3.475(4)</td>
<td>122.26</td>
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<tr>
<td>1c</td>
<td>C(11A)—H(11A)···N(21A)*</td>
<td>3.595(6)</td>
<td>124.50</td>
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<td></td>
<td>C(11A)—H(11A)···N(21B)*</td>
<td>3.382(6)</td>
<td>127.54</td>
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<td>C(11B)—H(11B)···N(21A)*</td>
<td>3.677(6)</td>
<td>112.06</td>
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<td>C(11B)—H(11B)···N(21B)*</td>
<td>3.437(6)</td>
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<td>C(21A)—H(21A)···N(31A)*</td>
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<td>124.84</td>
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<td></td>
<td>C(21B)—H(21B)···N(31B)*</td>
<td>3.429(6)</td>
<td>131.00</td>
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</table>
**Fig. S3**  The interactions of chloroform with the dptz linkers in 1a.

**Fig. S4**  Left – the acetonitrile guest molecule arrangement within the 1D channel with the channel direction along [0 1 1]. Right – disordered nitromethane which can also form head-to-tail and anti-parallel dipole-dipole interactions (channel direction along [1 0 0]).
Fig. S5  Head-on interaction of acetonitrile molecules with every 3rd out-of-plane twisted dptz linker.

Fig. S6  The hydrogen bonding (electrostatic interaction) of acetonitrile and nitromethane with the methyl-group of the acetate moiety.
Fig. S7  The colour of a 1a single crystal parallel and normal to the plane of polarization as viewed through an optical microscope.

Fig. S8  Left - Crystals of 1a viewed without a polarizer (the mirror at the bottom of the microscope could slightly polarize the light). Right – Crystals of 1a viewed with polarized light showing the colour enhancement. The colour of the crystals vary depending on the orientation of the crystals thus illustrating the pleochroism of 1a.
Fig. S9  Normalized reflectance UV-vis spectra of the activated PCP and the three solvates. The peaks of interest are indicated with the green lines.

Fig. S10  The tilt angles between the tetrazine and pyridyl rings measured using the Mercury 3.7 software.[S21]
Fig. S11. UV-vis calculations using a single dptz molecule surrounded by 2 pyridine molecules forming C–H...N electrostatic interactions. The dptz molecule was tilted by 45° with respect to its original orientation. The UV-vis spectra and frontier orbitals was calculated for both scenarios. Bottom-Left: the energy diagram for the frontier orbitals. Left: visualization of the frontier orbitals of interest. These calculation were performed using the DMol³ module in the Materials Studio software package.[S6]
Fig. S12. UV-vis calculations using a paddlewheel moiety with two coordinated dptz linkers and the three solvents. (a) The computational models used for the UV-vis calculations. The solvent molecules is shown in space filling representation. (b) The UV-vis absorption spectra generated using these models. These calculation were performed using the DMol³ module in the Materials Studio software package.[S6]
Fig. S13. Left: Overlay of the crystal structure and crystal habit with the channels and facets indicated. Right: The resulting solvent exchange pattern of a single crystal with channels as shown in the overlay. The size and direction of the purple arrows indicate the growth rate of the facets.

Fig. S14. The models used for the Adsorption Locator simulations with the copper atoms shown in space-filling representation and the rest of the model shown in stick representation. (a) (212) and (b) (10-2).
Fig. S15. Left – Molecular Mechanics models used to perform adsorption simulations of ACN and NM onto the (10-2) and (212) surfaces of a crystal of 1a. Middle – ACN adsorption. Right – NM adsorption. Several snapshots were combined to produce the solvent-containing figures. Solvent molecules are represented in space-fill format and the coordination polymer in grey stick representation.
Chapter 5

References

Chapter 6

CONCLUDING REMARKS

The three sets of related MOFs described in this thesis have provided some insight into the subtleties of MOF properties and their dynamic host-guest interactions. The combination of experimental studies and molecular modelling is pivotal to a detailed understanding of the behaviour of such materials.

Three open-channel robust 3D MOFs, with varying pore dimensions constructed using 4,4'-bipyridyl linkers of different lengths, facilitates exploration of the effect of increasing pore dimensions on the sorption properties and dynamic host-guest interactions of the frameworks. These MOFs were synthesised hydrothermally to yield \([\text{Cu}_2(\text{glu})_2(\text{bpy})\cdot2.9\text{H}_2\text{O}]_n\) (1a), \([\text{Cu}_2(\text{glu})_2(\text{bpe})\cdot3\text{H}_2\text{O}]_n\) (2a) and \([\text{Cu}_2(\text{glu})_2(\text{bpymh})\cdot7.5\text{H}_2\text{O}]_n\) (3a) as green block-shaped crystals. Since these MOFs have the same coordination topology and a varying ligand, they can be considered isoreticular. The crystals of these frameworks are extremely robust and survived dehydration under dynamic vacuum at 150 °C for 24 h to afford crystals of the apohosts 1, 2 and 3. There was no discernible deterioration in the crystals, thus demonstrating the stability of these MOFs. No significant change in the structures and unit cell parameters were observed. The channel dimensions of the MOFs increase from 1 to 3 as a result of the length of the varied linkers. Closer inspection of the guest-accessible space of the three MOFs revealed prominent corrugation of the channels. It was noted that the degree of corrugation of the channel could influence how guest molecules diffuse through the channels.

CO\(_2\) adducts of the MOFs were obtained by solvent exchange of the as-synthesised crystals with CO\(_2\) under supercritical conditions (1b, 2b, 3b). The samples were transported in a Dewar flask onto dry ice in order to maintain the guest occupancy during SCXRD and TGA analysis. From the crystal structures obtained, a well-defined sorption site could be discerned for 2b and 3b, while 1b forms a sterically driven adduct. The sorption sites for 2b and 3b are centred on two carboxylate oxygen atoms directed into the channel. 1b contains four CO\(_2\) per unit cell, while 2b and 3b enclose eight molecules each.

The host-guest dynamics resulting from the combination of channel size and corrugation were explored using CO\(_2\) gas sorption and thermal analysis of CO\(_2\) adducts of all three MOFs. The sorption capacities for the three MOFs are in agreement with the CO\(_2\) loaded structures with only 3 absorbing slightly more than eight molecules per unit cell. This is not surprising since MOF 3 still contains some accessible space in between the CO\(_2\) molecules occupying the MOF sorption sites. However, the sorption isotherm for MOF 3 displays the least hysteresis, which we attribute to its large channel diameter. The sorption isotherm for 2 shows the highest degree of sorption hysteresis and CO\(_2\) retention under vacuum. Numerous static-vacuum exposure (volumetric sorption apparatus) over a three day period were still insufficient...
for complete desorption of the MOF, thus indicating the high retention stability of CO\textsubscript{2} within the framework. TGA was carried out for the same material used for the SCXRD analysis. There was a clear trend in the temperature of complete thermal evolution of the CO\textsubscript{2} guest molecules: 1 > 2 > 3, corresponding to increasing channel size. For 1, in particular, thermal evolution only completes upon decomposition of the host framework (164 °C), which is contrary to the observations from the gas sorption analysis at RT. However, owing to the narrow constrictions of the channels in 1 (as a result of the channel corrugation), the CO\textsubscript{2} molecules follow an extremely hindered path through the channels and egress is further exacerbated by the increase in kinetic diameter of the CO\textsubscript{2} with increasing temperature. Conversely, for 2 and 3, the guest molecule can move more freely through the channel, thus lowering the temperature of complete thermal evolution of the guest (66 and 64 °C, respectively).

Theoretical models constructed from crystallographic data were used to calculate framework electrostatic potential maps through DFT and semi-empirical methods. The maps yielded a detailed picture of the electrostatic interactions at the sorption sites. Both the CO\textsubscript{2} (MEP) and framework (FEP) electrostatic potentials where mapped onto an electron density contour of a CO\textsubscript{2} molecule. The MEP and FEPs shows overlapping of opposite electrostatic potentials, thus indicating the presence of stabilising coulombic interactions. The highest potentials are centred on the $\delta^+$ carbon atom of the CO\textsubscript{2} molecule and the $\delta^-$ carboxylate oxygen atoms of the glutarate moieties. Furthermore, multiple weaker interactions exist between the $\delta^-$ CO\textsubscript{2} oxygen atoms and various $\delta^+$ methylene hydrogens of the glutarate moieties. This demonstrates complete electrostatic complementarity between the sorption sites and the CO\textsubscript{2} molecules, resulting in a strong interaction responsible for stabilising the gas within these MOFs. Finally, from this study we can conclude that MOF 2 possesses the most favourable combination of steric and electrostatic topologies for binding CO\textsubscript{2} guest molecules, thus explaining the observed extreme sorption hysteresis and guest retention.

The second set of 3D Cu(II)-glutarate-based MOFs, [Cu\textsubscript{2}(glu)\textsubscript{2}(bpa)]\textsubscript{n} (1) and [Cu\textsubscript{2}(glu)\textsubscript{2}(bpp)]\textsubscript{n} (2), utilise flexible 4,4’-bipyridyl linkers as pillars. These MOFs can be grouped with the previous set as an isoreticular series. These two MOFs undergo spontaneous phase changes upon solvent loss at RT. The structures of the new phases reveal a reduction in the guest-accessible volumes, denoted as the narrow-channel (nc) forms (1’ and 2’), although crystals of 2 large enough for SCXRD analysis could only be obtained by means of CO\textsubscript{2} guest exchange under supercritical conditions. Visual inspection of the crystal structures for both phases revealed an enantiomeric conformational change in the glu moieties through inversion of the gauche torsion angles. Although the $+$gauche and $-$gauche conformations have the same molecular size and shape, they are spatially distinct, which results in the observed phase change. The changes in orientation, bend angles and coordination angles of the 4,4´-bipyridyl linkers suggest that these moieties play a crucial role in accommodating the glu conformational change.

CO\textsubscript{2} sorption analysis at RT reveals a stepped sorption profile for 1’, with the loading doubling from ca 4 to 8 molecules per unit cell. The step in the sorption isotherm is attributed to the phase change of 1’ to 1, thus approximately doubling the guest-accessible volume. Sorption of other gases such as methane, ethane and propane did not yield any steps in the sorption isotherms. MOF 2’ produced Type I isotherms for all the gases (no step) with significant hysteresis for ethane and propane sorption. The gas loading remains at its
maximum until vacuum is reached, thus indicating a high stability for sorbed ethane and propane within MOF 2. The CO\textsubscript{2} content within 2 is double that of the other gases, further highlighting the affinity of these MOFs towards CO\textsubscript{2}.

Using supercritical CO\textsubscript{2}, it was possible to obtain CO\textsubscript{2} loaded crystal structures for both MOFs 1\textsuperscript{b} and 2\textsuperscript{b}. The CO\textsubscript{2} molecules could be modelled and were found to utilise the same electrostatically stabilised sorption sites as the two rigid MOFs described in Chapter 3. More significantly, 1\textsuperscript{b} is in the wide-channel (wc) form, yielding eight CO\textsubscript{2} sorption sites. This is in agreement with the assertion that 1\textsuperscript{'} (nc) must convert to 1 (wc) in order to accommodate eight CO\textsubscript{2} molecules. Conversely, 2\textsuperscript{'} can accommodate eight CO\textsubscript{2} molecules per unit cell in the nc form. Although the crystal structure of 2\textsuperscript{b} shows ten CO\textsubscript{2} positions per unit cell, a SQUEEZE electron-count of the guest-attributed density confirmed only eight CO\textsubscript{2} molecules. This is in good agreement with the sorption data.

The glu gauche-gauche enantiomeric conversion can follow paths: direct gauche-gauche (±g ↔ ±g, Route 1) or via the trans conformation (±g ↔ t ↔ ±g, Route 2). The conformational barriers for a single uncoordinated H\textsubscript{2}glu molecule were first determined by performing a scan of the potential energy surface. The cis-barrier (±g ↔ ±g) is 1.4 kcal mol\textsuperscript{-1} higher than the ±g ↔ t barrier, thus indicating a higher probability for Route 2, although not exclusively (91% according the Boltzmann distribution at 298 K). The computational model was then scaled up to include four glu and four paddlewheel moieties, the smallest representation of the Cu-glu 2D grid. In this scan large changes in the orientation of the copper paddlewheel moieties were observed. Such changes have to be accommodated by the 4,4\textsuperscript{-}bipyridyl linkers coordinated to the paddlewheel. This also explains the absence of a conformational change for the MOFs with rigid 4,4\textsuperscript{-}bipyridyl linkers in the first set. In order to obtain a complete description of the enantiomeric conversion, we proceeded with a potential energy surface scan using a full unit cell as the computational model. The scan was performed in the space group P1, from wc to nc for both Routes 1 and 2, and allowing for optimisation of the entire unit cell except for the scan parameter (gauche torsion angles). Firstly, the simulations yielded the appropriate nc phase with relative differences in cell parameters (between wc and nc) very close to the experimental data. Furthermore, the energy barrier for Route 1 is ca 10 kcal mol\textsuperscript{-1} (per glu moiety) more stable than for Route 2. Additionally, the energy barriers for Route 1, for MOFs 1 and 2, are in the same range as that of a free H\textsubscript{2}glu molecule (3 – 7 kcal mol\textsuperscript{-1}). These energies are comparable with reported conformational barriers of molecules such as butane and its derivatives, which spontaneously interconvert under ambient conditions. Thus the only option for spontaneous enantiomeric conversion is via a direct gauche-gauche interconversion: ±g ↔ ±g. Analysis of the scan trajectories shows a large degree of distortion within the 4,4\textsuperscript{-}bipyridyl linkers, therefore highlighting their role in accommodating these phase changes.

Our investigation of the solvent exchange process of the 1D PCP, [Cu\textsubscript{2}(acetate)\textsubscript{2}(dptz)]\textsubscript{n} demonstrated that guest exchange in porous materials is not always straightforward. This material displays pleochroic properties that are evident when observing the crystals from different angles. 1D chains, formed by copper acetate paddlewheel moieties and the bptz linkers, form 2D layers through C–H⋯N interactions between adjacent linkers. These layers combine to form 1D guest-accessible channels occupied by chloroform guest molecules (1\textsubscript{a}). Solvent exchange with acetonitrile (1\textsubscript{b}) and nitromethane (1\textsubscript{c}) yielded structures where the linkers are rotated inwards towards the open channel. This adjustment maximises host-guest interactions and ensures optimal host-guest fit. Additionally, the solvent exchange revealed
the solvatochromic properties of the PCP, with a blue shift in the solid-state UV-vis spectra. This can be attributed to the rotation of the bptz linkers, which results in the loss or weakening of the C—H⋯N interaction between adjacent linkers. Calculated UV-vis spectra, for a dptz ligand with and without C—H⋯N interactions show blue-shifts in the absorption bands, consistent with our experiment. The solvatochromic properties could then be used as a probe to further our understanding of the solvent exchange process for this PCP. Optical microscopy with polarised light proved to be an invaluable tool for monitoring the solvent exchange. The crystals show an initial double V-shaped exchange pattern prior to complete solvent exchange for both acetonitrile and nitromethane.

The crystal facets, determined from face indexing single crystals using SCXRD, were overlaid with the crystal structure of 1a to show that the mapped channels run diagonally, connecting two of the facets, (212) and (10-2). This implies that the solvent molecules must have a preference for (212) since solvent exchange is initiated through this facet first. Adsorption simulation using MM showed a higher adsorption enthalpy for (212) compared to (10-2), thus confirming the facet selectivity of the solvents. Furthermore, the adsorption enthalpy for acetonitrile was found to be higher than that for nitromethane, thus explaining the faster exchange kinetics for acetonitrile. All of the evidence suggested that a single crystal could not form this double V-shaped profile for the solvent exchange. We therefore proposed that the crystals must be growth twins subject to the double re-entrant corner effect. This effect results in the growth morphology observed for 1a crystals and yields four mirrored domains which can produce a double V-shaped solvent exchange pattern.

This study highlights the subtleties of the underlying physics that influence the properties exhibited by MOFs. In particular, it has been shown that complementary weak electrostatic interactions can be more stabilising than a single strong interaction. This is a concept that also applies to the binding of biological molecules where more complex weak electrostatic interactions facilitate the functions and activities of these molecules. In the case of gas sorption, strong interactions can lead to higher gas uptake, but are often indiscriminate compared to weaker interactions. Electrostatic complementarity can also lead to greater selectivity for gas separation applications, and needs to be studied further for both the weak and strong electrostatic interaction regimes. A better understanding of this electrostatic-interaction landscape can improve the design of new functional materials for intended applications.

Relatively weak electrostatic interactions can also greatly influence the optical properties of a MOF and additionally could extent to other properties of these materials. Investigation of the correlation between these interactions and the associated properties of these materials can significantly improve our understanding of the host-guest dynamics in MOFs and should not be overlooked. Optically active organic ligands combined with an electrostatic complementarity is one approach towards targeted sensing of small molecules. Furthermore, in order to produce reusable and robust sensors, reversible host-guest binding would be preferred. The perfect sensor would have the optimum combination of substrate binding strength (for a measurable effect) and binding reversibility. Electrostatic interactions play a crucial role in the interplay between these properties and can lead to improved ligand design for optical applications.
Finally, conformational changes of the linkers in MOFs are greatly affected by the rest of the framework structure and have to be facilitated by other moieties within the MOF. This non-locality of framework flexibility indicates that the phase change behaviour of a MOF can be tuned by modifying both the ligands undergoing the conformational change and the ligands that are distorted to accommodate the change. This concept lies at the heart of classical engineering where construction facilitates function and both aspects are always considered in conjunction with one another. The study of all the afore-mentioned concepts are part of a larger scope driving the area of MOF research towards true “CRYSTAL ENGINEERING”.

Future work on the systems presented here include extending these MOF to the use of different metal cations. There are several published structures (see discussion in Chapter 3) isoreticular to the copper-glutarate MOFs that contain zinc and cadmium cations instead of copper. Such systems provide the means for investigating the phase-change energy barriers as a function of metal-ligand coordination strength. This adds another dimension to the possibility of tuning the properties of these and other MOFs. It is also possible to pillar MOFs using cationic organic ligands with large non-coordinating anions. The anions would likely include into the MOF structure to charge balance the system and can therefore be systematically exchanged with smaller anions, such as the halide series. This has the effect of tuning both the electrostatics and pore size, which in turn leads to modulated sorption behaviour. The solvent exchange studies can be expanded to include 2D and 3D porous MOFs. In most MOF crystals, especially those of multi-ligand MOFs, the surface functionalities are distinct and can lead to different rates of adsorption of small molecules. Furthermore, surface modification of the MOFs with appropriate organic reagents can be used to vary the surface adsorption of solvent molecules and therefore tune the surface selectivity. The overlay of the crystal habit and structure allows for the identification of the crystal surface functionality and can therefore facilitate suitable selections of organic reagent for surface modification. These experiments are all plausible and do not require instrumentation beyond those presented in this dissertation.
APPENDIX

A CD containing all the supporting files and videos provides the following:

Chapter 3:
- CIF files and CheckCIF reports

Chapter 4:
- CIF files and CheckCIF reports
- Video S1 shows the potential energy surface scan for the square model.
- Videos S2 and S3 show the potential energy surface scan for the full unit cell model of MOFs 1 and 2.

Chapter 5:
- CIF files and CheckCIF reports
- Videos showing the solvent exchange of acetonitrile and nitromethane
- Videos showing the pleochroic properties of the chloroform solvate (1a).