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**Gas Sorption and Binding Site Studies in Metal
Organic Frameworks**

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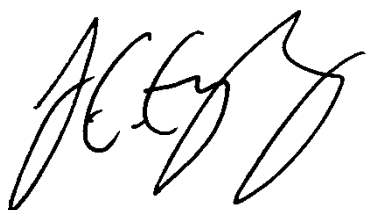
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Doctor of Philosophy

January 2017

Declaration

Except where specific reference is made to other sources, the work presented in this thesis is the original work of the author. It has not been submitted, in whole or in part, for any other degree.

Signed:

A handwritten signature in black ink, appearing to read 'J. Eyley', written in a cursive style.

Jennifer Eyley

Date: 28th January 2017

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Abstract

This thesis describes the design and synthesis of a series of Cu(II)-paddlewheel based metal organic frameworks (MOFs) for the adsorption of gaseous fuels and pollutants. The frameworks comprise V-shaped pyridyl carboxylate ligands, which are progressively modified to increase gas adsorption capacity and selectivity of the resultant materials.

Chapter 1 introduces the history and structure of MOFs, including an exploration of their varied applications. Particular attention is paid to gas adsorption within these materials, considering the best performing materials for each gas discussed.

Chapter 2 explores the ability of uncoordinated pyridyl groups to form strong interactions with adsorbed CO₂. A new self-interpenetrated Cu(II) MOF (MFM-170) is synthesised from a V-shaped pyridyl carboxylate ligand, in which the pyridyl nitrogen coordinates to the axial site of the interpenetrating net. The porosity and gas adsorption properties of this material are discussed in detail.

Chapter 3 describes how functional groups can introduce binding sites into MOFs, strengthening framework-adsorbate interactions and improving gas adsorption capacities. Three isostructural analogues of MFM-170 are synthesised (MFM-171, MFM-172, MFM-173), each with a different functional group directed into the pore. Differences in the gas adsorption properties of these materials are rationalised by identification of CO₂ binding sites by IR microspectroscopy and Single Crystal X-ray Diffraction experiments.

Chapter 4 draws on knowledge of CO₂ binding sites identified in Chapter 3 to selectively target areas of the framework where strongly coordinating functional groups would have the greatest effect of CO₂ adsorption and selectivity. A new Cu(II) framework (MFM-175) is reported, incorporating triazole groups directed into the void. The structure, stability and gas adsorption properties of MFM-175 are studied in detail and compared to MFM-170.

Chapter 5 investigates the synthesis of a non-interpenetrated analogue of MFM-170 with the aim of liberating the pyridyl nitrogen group to improve framework-adsorbate interactions. A new Cu(II) MOF (MFM-176) is synthesised, featuring a two-fold interpenetrated structure. Nevertheless MFM-176 demonstrates improved selectivity parameters and additionally a promising strategy for the successful synthesis of a non-interpenetrated framework.

Summary of Ligands and MOFs Discussed in this Thesis

Ligand Structure	Long Name	Short Name	MOF
	5,5'-(pyridine-3,5-diyl) diisophthalic acid	H ₄ pdia	[Cu ₆ (pdia) ₃ (H ₂ O) ₆] ¹
	3,5-bis(3,5-dicarboxylphenylethynyl)- pyridine	H ₄ EPYD	[Cu ₂ EPYD] ²
	1,3-bis(3,5-dicarboxylphenylethynyl)- benzene	H ₄ EBNZ	[Cu ₂ EBNZ] ³
	5,5'-((Pyridine-3,5-dicarbonyl)bis(azanediy l)) diisophthalate	H ₄ APYD	PCN-124 ⁴ NJU-Bai21 ⁵
	4',4'''-(pyridine-3,5-diyl)bis((1,1'-biphenyl)-3,5-dicarboxylic acid))	H ₄ PPYD	MFM-170 ⁶
	4',4'''-(pyrazine-3,5-diyl)bis((1,1'-biphenyl)-3,5-dicarboxylic acid))	H ₄ PPYZ	MFM-171 ⁶
	4',4'''-(4- methylpyridine-3,5-diyl)bis((1,1'-biphenyl)-3,5-dicarboxylic acid))	H ₄ PPME	MFM-172 ⁶

	4',4'''-(4-carboxypyridine-3,5-diyl)bis([1,1'-biphenyl]-3,5-dicarboxylic acid))	H ₄ <u>P</u> PCA	MFM-173 ⁶
	4',4'''-(4-aminopyridine-3,5-diyl)bis([1,1'-biphenyl]-3,5-dicarboxylic acid))	H ₄ <u>P</u> PAN	
	4',4'''-(4-carbamoylpyridine-3,5-diyl)bis([1,1'-biphenyl]-3,5-dicarboxylic acid))	H ₄ <u>P</u> PAD	
	5,5'-(pyridine-3,5-diyl)bis(1H-1,2,3-triazole-4,1-diyl))diisophthalic acid	H ₄ <u>T</u> PYD	MFM-175 ⁶
	3,5-bis(3',5'-dicarboxy-[1,1'-biphenyl]-4-yl)pyridine N-oxide	H ₄ <u>P</u> PNO	
	3,5-bis(3,5-dicarboxy-[1,1'-biphenyl]-4-yl) toluene	H ₄ <u>P</u> TOL	MFM-176 ⁶

1. Z. Lu, L. Du, K. Tang and J. Bai, *Cryst. Growth Des.*, 2013, **13**, 2252–2255.
2. P. Zhang, B. Li, Y. Zhao, X. Meng and T. Zhang, *Chem. Commun.*, 2011, **47**, 7722–7724.
3. X. Liu, M. Park, S. Hong, M. Oh, J. W. Yoon, J.-S. Chang and M. S. Lah, *Inorg. Chem.*, 2009, **48**, 11507–11509.
4. J. Park, J.-R. Li, Y.-P. Chen, J. Yu, A. A. Yakovenko, Z. U. Wang, L.-B. Sun, P. B. Balbuenaba and H.-C. Zhou, *Chem. Commun.*, 2012, **48**, 9995–9997.
5. Z. Lu, J. Bai, C. Hang, F. Meng, W. Liu and Y. Pan, *Chem. Eur. J.*, 2016, **22**, 6277–6285.
6. This Work

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Chapter 1: Introduction

1.1 Evolution of Porous Materials

Porous materials are ubiquitous in the natural world and have been manipulated for the storage and separation of different substances for millennia. Materials range from those with visible pores, such as honeycomb, pumice and sponges; to those with pores that are undetectable by the naked eye, such as activated charcoal or porous rocks used for water filtration.

Zeolites, the first known crystalline nanoporous structures were discovered over 250 years ago;¹ however determination of their structure was not realised until 1930.² Purely inorganic in nature, zeolites are aluminosilicate frameworks constructed from SiO_4 and AlO_4 tetrahedra (Figure 1.1). They can be used as molecular sieves, separating molecules *via* size-exclusion; allowing them to be used ion exchange materials for water purification,³⁻⁶ and catalysts for petrochemical refinement.⁷ Notably zeolites were recently used to adsorb radioactive Cs(I) ions from seawater after the 2011 Fukushima disaster.⁸ Applications of zeolites are limited due to narrow pores, low surface areas and a lack of control over the pore surface.⁹

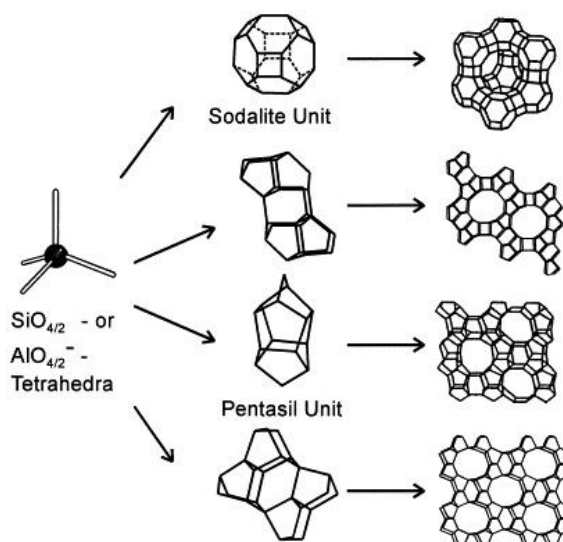


Figure 1.1: Structure of some common zeolite cages constructed from SiO_4 and AlO_4 tetrahedra.

In 1897 Hofmann synthesised the first porous coordination network containing transition metal ions.¹⁰ The Hofmann clathrates comprise two-dimensional layers of nickel cyanide square grids in which alternate Ni(II) ions adopt an octahedral structure with two additional ammonia ligands projecting above and below the plane.¹¹ The ammonia ligands prevent the close approach of two adjacent layers, giving cavities in which benzene molecules are encapsulated (Figure 1.2). This concept was then expanded upon in 1968 by Iwamoto who synthesised a three-dimensional hybrid inorganic-organic framework, using ethylenediamine as a bidentate pillaring ligand between $[\text{Cd}(\text{CN})_2]$ layers;¹² while Zhdanov reported in 1941 that $\text{Zn}(\text{CN})_2$ and $\text{Cd}(\text{CN})_2$ crystallise in interpenetrated three-dimensional diamond frameworks with tetrahedral M(II) nodes.^{13–15}

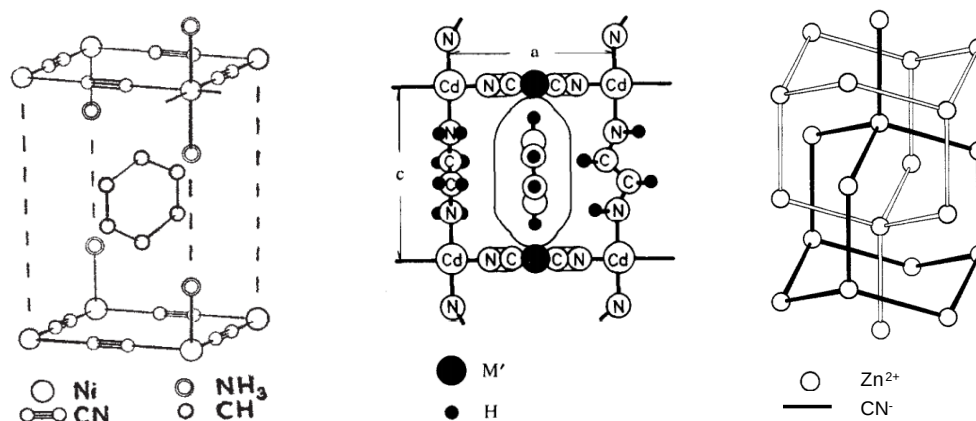


Figure 1.2: Progression of Hofman clathrate complexes from two-dimensional layers to three dimensional frameworks with layers bridged by ethylenediamine ligands. Structure of the three-dimensional diamond net of $\text{Zn}(\text{CN})_2$, the inspiration behind the first metal-organic framework.

In 1990 Hoskins and Robson predicted that infinite frameworks could spontaneously form from geometrically compatible rods and nodes, giving porous solids through which molecular species can diffuse.¹⁵ Working on $\text{Zn}(\text{CN})_2$ related frameworks, they first synthesised $[\text{N}(\text{CH}_3)_4][\text{CuZn}(\text{CN})_4]$, a charged framework in which half the tetrahedral Zn(II) centres in the diamond net were substituted for Cu(I). A non-interpenetrated isostructural diamond framework was formed with $[\text{N}(\text{CH}_3)_4]^+$ counterions preventing interpenetration. Subsequently the remaining $\text{Zn}(\text{CN})_4$ nodes were replaced with the tetrahedral ligand 4,4',4'',4'''-tetracyanotetraphenylmethane (tctpm), to give

$[\text{Cu}^{\text{I}}(\text{tctpm})]\text{BF}_4 \cdot x\text{C}_6\text{H}_5\text{NO}_2$, an isostructural three-dimensional metal organic framework (Figure 1.3).¹⁶

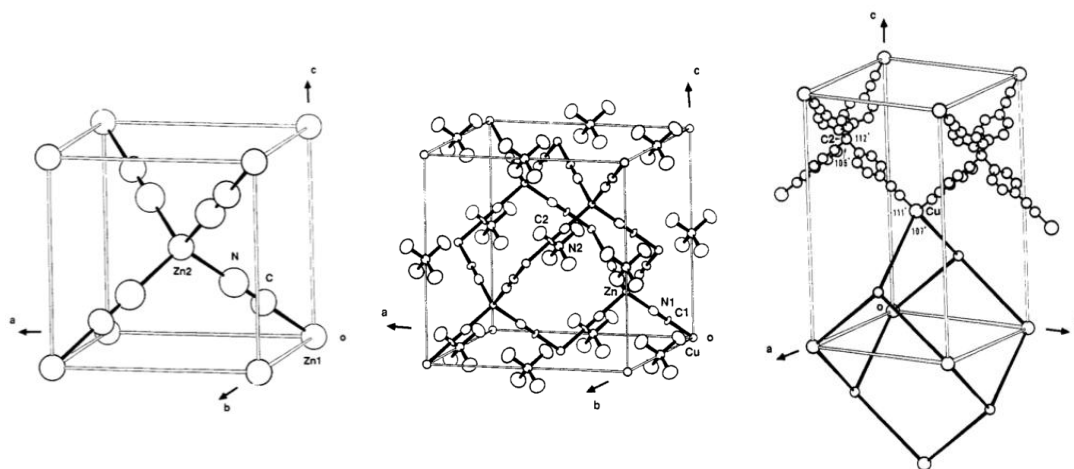


Figure 1.3: Evolution of the extended $\text{Zn}(\text{CN})_2$ adamantane framework to incorporate $\text{Cu}(\text{I})$ tetrahedral metal centres in $[\text{N}(\text{CH}_3)_4][\text{CuZn}(\text{CN})_4]$ and further to include tetrahedral organic ligands in $[\text{Cu}^{\text{I}}(\text{tctpm})]\text{BF}_4 \cdot x\text{C}_6\text{H}_5\text{NO}_2$ ($\text{tctpm} = 4,4',4'',4'''$ -tetracyanotetraphenylmethane).

Robson and co-workers noted the possibility to use longer, ever more complex and chemically functionalised ligands in order to deliberately design porous materials with cavities of a determined size and shape. This observation laid the foundation for the study Metal Organic Frameworks (MOFs); porous supramolecular solids comprising metal ion nodes connected by organic ligands to form infinite networks in two or three dimensions.^{17,18} MOFs are often considered superior to zeolites due greater ability to tune pore sizes and surface functionality for specific applications and thus have increased exponentially in popularity over recent years.¹⁹

1.1.1 Applications of Metal-Organic Frameworks

The high stability and tuneable properties of MOFs has lead to their use in a wide range of fields, most commonly in the storage and separation of gaseous fuels and pollutants, discussed later in this chapter. More varied applications involve the development of heterogeneous catalysts;^{20–27} including those that demonstrate enantioselectivity;^{28–31} and luminescent sensors for biological assays^{33–35} or detection of chemical warfare agents and explosives.^{35–37} Chelating groups within the pores allow for metal extraction from

solution,^{38–40} whilst proton relay pathways can lead to conductive MOFs for applications in hydrogen fuel cells.^{41,42} Other novel applications include controlled drug delivery or contrast agents for MRI.^{43,44} A small selection of MOFs have been industrially synthesised in large quantities,^{45–48} although most MOFs remain at the laboratory scale.

1.2 Synthesis and Structure of Metal Organic Frameworks

MOFs are commonly synthesised through solvothermal or hydrothermal methods, although greener techniques such as microwave^{49,50} or mechanochemical synthesis⁵¹ have also been reported. MOFs form through a self-correcting self-assembly mechanism, requiring a perfect balance of reaction conditions, usually determined through iterative trials.

1.2.1 Topological Analysis

As the structure of most MOFs are highly intricate, due to complicated ligand shape, functionality and coordinated solvent molecules, it is easier to first consider the underlying net, or topology, of a framework by simplifying the structure down to the smallest number of connected nodes, known as SBUs (Figure 1.4).⁵² These topological nets are identified by three letter codes in a bold typeface and are either based on the natural material which shares the same underlying net, such as **dia** (diamond) and **sod** (sodalite) or randomly assigned e.g. **rhr**. Frameworks that share the same topological nets, with differing metal nodes and linker molecules are termed isorecticular, an expression coined by Yaghi in 2003.⁵³

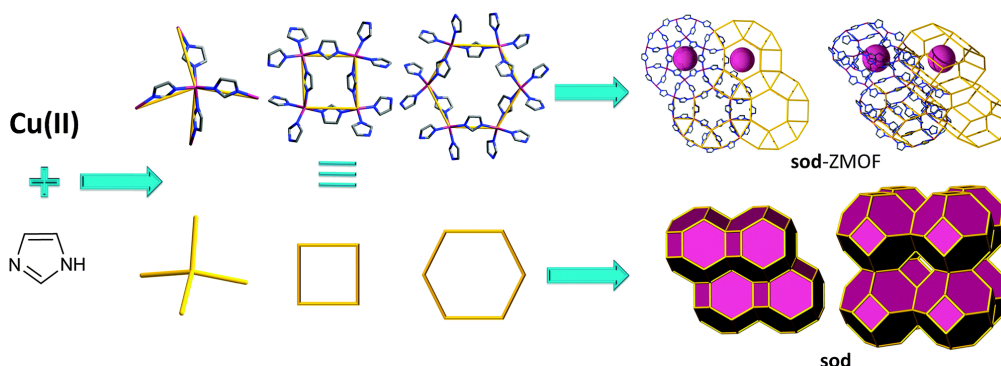


Figure 1.4: Topological analysis of $[\text{Cu}(\text{im})_2]$ (*im* = imidazole) showing the combination of tetrahedral Cu(II) nodes with linear linkers to give a sodalite (*sod*) framework.⁵⁴

1.2.2 Secondary Building Units

Topological nodes are characterised by their points of extension and geometry. A 6-connected octahedral node can either be constructed from a single metal ion bonded to six linker molecules (e.g. MOF-74),⁵⁵ or an octahedral metal cluster, such as the “zinc acetate” cluster seen in MOF-5 (Figure 1.5).⁵⁶ Common examples of metal cluster SBUs are the 4-connected square copper acetate paddlewheel (HKUST-1),⁵⁷ and the 6-connected trigonal prism chromium acetate cluster (MIL-101) (Figure 1.5).⁵⁸ Although commonly formed with transition metals, MOFs have been synthesised from alkali,^{59,60} alkali earth,^{61,62} main group,^{63–65} lanthanide⁶⁶ and actinide^{67,68} metal centres. The metal ion can have a profound effect on the structure of the framework; controlling the coordination geometry, the number of charge balancing ligands or counterions, and the preferred coordination due to hard/soft, acid/base compatibility.⁶⁹ Additionally, coordinating solvent molecules can be removed upon activation, revealing strong Lewis acidic binding sites for interactions with guest molecules.

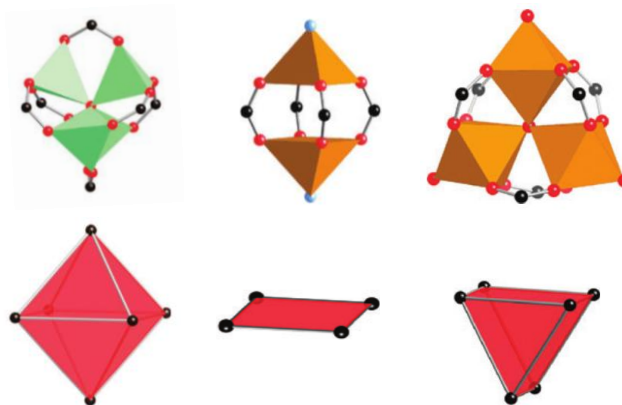


Figure 1.5: Three common metal organic clusters and their respective topological representations: 6-connected octahedral zinc acetate, 4-connected square copper acetate paddlewheel and 6-connected trigonal prism chromium acetate.

As demonstrated by Robson, topological nodes can also be constructed from organic SBUs, for example two-connected linear, 3-connected trigonal or 4-connected tetrahedral linkers (Figure 1.6). Ligand flexibility and rotation means that it can be difficult to predict the geometry of ligands within the framework structure; for example the 4-connected ligand

TCCPPDA (N,N,N',N'-tetrakis(4-carboxyphenyl)-1,4-phenylenediamine) has been shown to adopt both square planar and tetrahedral conformations, giving Cu(II) frameworks with **nbo** and **pts** topologies respectively.⁷⁰ Carboxylic acids are most commonly used as coordinating nodes; however other binding groups include phosphonates,⁷¹ cyanides,⁷² and heterocyclic groups such as pyridine,⁷³ pyrimidine⁷⁴ and imidazoles.⁷⁵

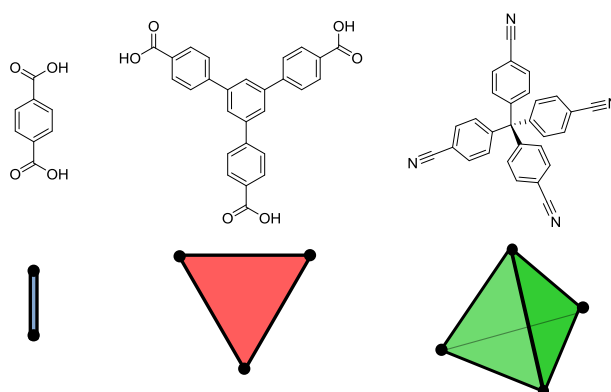


Figure 1.6: SBUs constructed from ligand molecules; linear two-connected terephthalic acid, trigonal 1,3,5-phenyltrisbenzoic acid, tetrahedral 4,4',4'',4'''-tetracyanotetraphenylmethane.

1.2.3 Ligand Design

Highly conjugated, rigid, symmetrical ligands are favoured for the growth of robust crystals with limited disorder.⁷⁶ Many commercially available molecules such as terephthalic acid have been used in MOF synthesis;⁷⁷ however a desire for larger pores and surface areas, has led to the use of longer, specially designed ligands.⁵³ A classic example of ligand extension is the NOTT-100 series,⁷⁸ where biphenyltetracarboxylate ligands are extended in length to give an isorecticular series of frameworks with progressively larger pores (Figure 1.7).⁷⁹

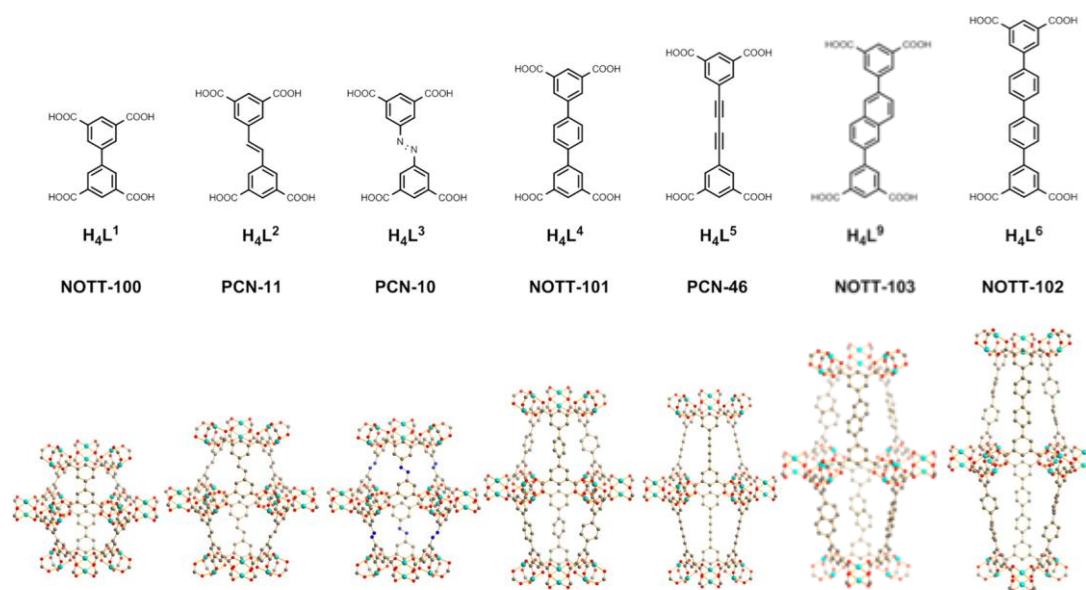


Figure 1.7: Isophthalate tetracarboxylate linkers and their corresponding Cu(II)-based framework materials, showing elongation of the $[Cu_{24}(L)_6]$ pore upon ligand extension.

In addition to controlling pore size and shape, ligands can enhance the properties of MOFs by introducing additional functionality to the pore surface. Ligands can be rationally designed to incorporate functional groups which protrude into the pores and interact with guest species. Highly polar groups such as amines or amides can lead to the selective adsorption of CO_2 over other gases;^{80,81} chromophores such as N-aryl-benzimidazole pyridine-2-carboxylic acids can increase luminescence from metal centres;⁸² chelating groups such as 2,2'-bipyridine can offer a platform for the encapsulation of guest species;⁸³ whilst amino acid based linkers have been shown to act as catalytic binding sites.⁸⁴

1.2.4 Interpenetration and Guest Species in the Pores

MOFs assemble with solvent molecules, counterions or templating agents within the pores. Framework voids and open metal sites can be accessed by solvent exchange with a more volatile solvent, followed by activation under a vacuum at elevated temperatures.^{85,86}

Interpenetration occurs when the pores within a MOF are sufficiently large to allow another copy of the same framework net to form within the void, giving two individual nets that

cannot be separated without the breaking of chemical bonds. Two-fold interpenetrated structures are well documented, whilst those with higher levels (up to four-fold) and fractional amounts of interpenetration are less common (Figure 1.8).^{87,88} Although interpenetration decreases the porosity of the material, it can greatly enhance stability as interactions between the two nets prevent framework collapse. Further advantages and disadvantages of interpenetration, along with methods of preventing the formation of catenated nets are discussed further in chapter 5.

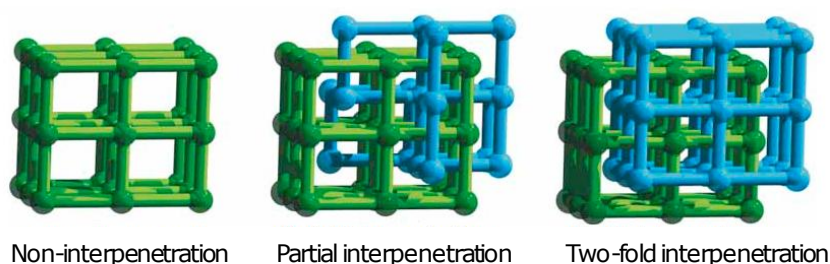


Figure 1.8: Partial interpenetration seen in NOTT-202⁸⁸

1.2.5 Postsynthetic Modification

Functionality is usually introduced into MOFs by decoration of ligands prior to solvothermal synthesis; however, this approach does not always afford the desired framework as functional groups can coordinate to metal centres rather than pointing into the pores. In these situations functional groups can be introduced into the framework *via* post-synthetic modification (Figure 1.9);⁸⁹ for example the condensation of an amine group to give an amide functionality,⁹⁰ or removal of a Boc (*tert*-butoxycarbonyl) protecting group to reveal an amine group.⁹¹

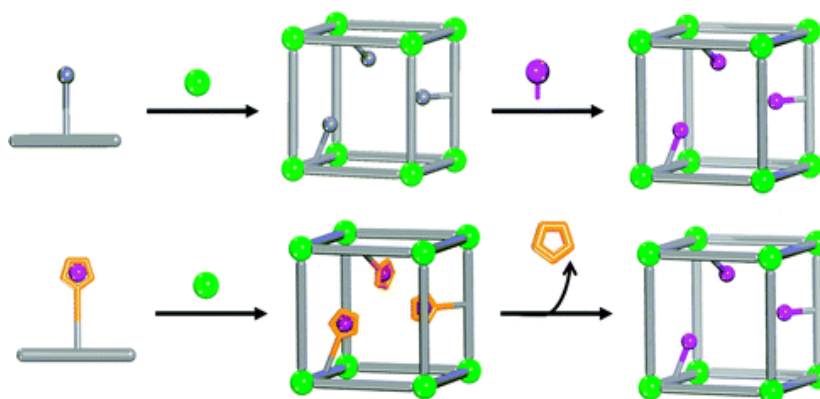


Figure 1.9: Two methods of postsynthetic modification; covalent postsynthetic modification and postsynthetic deprotection.

1.3 Gas adsorption in Metal-Organic Frameworks

In order for global warming to be limited to 2 °C, as agreed at the 2015 Paris Climate Change Conference, global CO₂ emissions must be limited to 1,100 Gt over the next 40 years.⁹² The UK alone emits around 500 Mt of CO₂ a year, of which 40% is spent on meeting our energy demands and 25% on transport emissions.⁹³ Not only does the burning of fossil fuels contribute to CO₂ emissions, but crude oil reserves are predicted to be exhausted by 2060, raising an urgent demand for alternative fuel solutions.⁹⁴

MOFs offer a solution for both of these issues; showing promise as a storage medium for alternative gaseous fuels, or by selectively capturing and storing CO₂ from waste streams. The ability to fine tune properties such as surface functionality and porosity allows for development of materials with high adsorption capacities for gases such as H₂, N₂, CO₂ and CH₄; with the ultimate aim of producing materials capable of storing or selectively adsorbing these gases at ambient temperatures and pressures.

MOFs are characterised by their Brauner-Emmet-Teller (BET) surface areas, accessible pore volumes and pore size distributions, all of which can be determined theoretically from the crystal structure or experimentally from measurement of an N₂ isotherm at 77 K. The majority of MOFs are microporous materials and therefore display classic type I isotherms.

Exceptions occur in MOFs with extra large pores or those which show hysteresis due to framework breathing effects,⁸⁷ or the blocking of pore apertures (Figure 1.10).⁶⁵

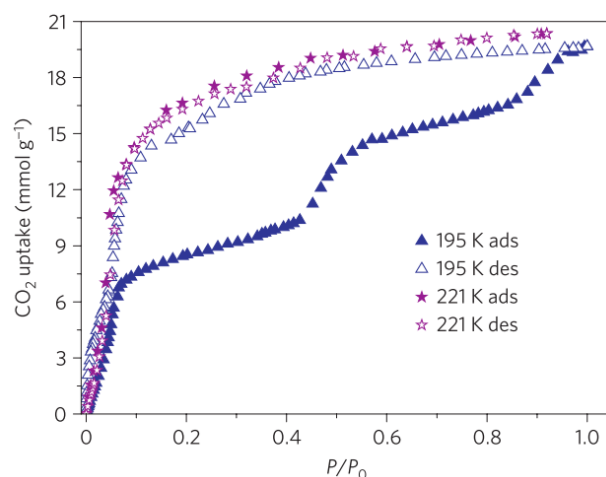


Figure 1.10: *CO₂ adsorption of NOTT-202, demonstrating a reversible type-I isotherm at 221 K and hysteresis at 195 K, attributed to temperature dependent framework breathing effects.*

Whilst high pressure adsorption capacities are improved by designing MOFs with large internal porosities,⁹⁵ small pores and large internal surface areas are beneficial for low pressure applications, where adsorbate-framework interactions are stronger than adsorbate-adsorbate interactions. Selective addition of functional groups and open metal sites can introduce strong binding sites for adsorbed gases, particularly relevant for separation applications. Methods of confirming the presence of such binding sites are discussed further in Chapter 3.

1.3.1 Storage of Alternative Fuels

The main issue inhibiting the development of natural-gas powered cars is finding safe, economic and efficient methods of storage that do not require large cylindrical pressurised containers or expensive cooling systems.⁹⁶ Interaction between gaseous molecules are generally weak at ambient pressure;⁹⁷ however the storage density can be increased upon physisorption into a porous materials, where strong gas-host interactions cause the gas molecules pack closer (Figure 1.11).⁹⁸ The use of porous materials means that fuel tanks can operate at lower, safer pressures and can be designed to fit the shape of a vehicle.

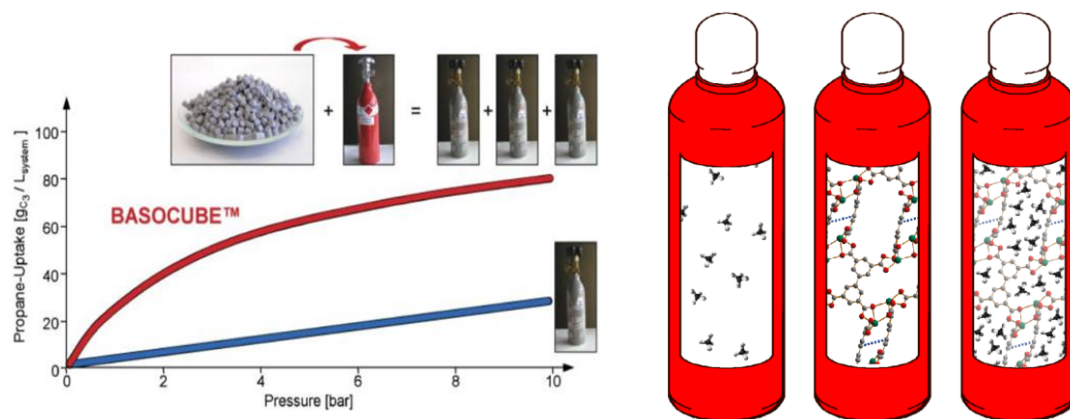


Figure 1.11: Demonstration of the improved gas sorption capabilities of gas canisters containing MOFs: MOF-5 triples the volumetric storage capabilities of propane⁹⁹ due to an increase packing density, as depicted for CH_4 adsorption in NOTT-220.

1.3.1.1 Hydrogen Storage

Hydrogen is an ideal clean fuel source, producing water as the only waste product upon combustion. The potential for practical H_2 storage gripped the interest of early researchers within the field of MOFs and materials were specifically designed to target H_2 adsorption. Despite considerable improvements in total H_2 uptake capacities, record adsorption of 9.9 wt% has only been achieved at cryogenic temperatures (77 K) and high pressures (70 bar),¹⁰⁰ which is unsuitable for fast and easy refuelling of vehicles. Although H_2 adsorption is still measured routinely in gas sorption analysis, its popularity has waned in recent years.

1.3.1.2 Natural Gas Storage

Methane is a viable alternative to gasoline as it demonstrates a low C:H ratio, producing less CO_2 upon combustion. Although CH_4 is still a non-renewable fuel, it is relatively abundant and benefits from an established production and transportation infrastructure. Challenges include the low volumetric energy density at ambient temperature, which is usually increased by a expensive liquefaction processes, and can be improved by adsorption into a porous host. Recently BASF showcased a fleet of natural-gas powered vehicles, featuring fuel tanks packed with MOF materials;⁴⁵ however, in order for MOFs to offer a commercially feasible on-board storage solution, materials must meet the ARPA-E

(Advanced Research Projects Agency-Energy) target of delivering a volumetric capacity of $350 \text{ cm}^3 \text{ cm}^{-3}$ at 298 K across a deliverable working range of 65 bar (maximum pressure generated by inexpensive two-stage compressors) to 5 bar (minimum delivery pressure to the internal combustion engine).¹⁰¹

HKUST-1 and UTSA-76 demonstrate two of the highest CH_4 adsorption capacities to date, adsorbing a total of 266 v/v and 257 v/v at 65 bar and 298 K, respectively.^{102,103} The high adsorption capacity in UTSA-76 is attributed to “dynamic” pyrimidine functional groups, which rotate to maximise the packing of CH_4 at high pressures.

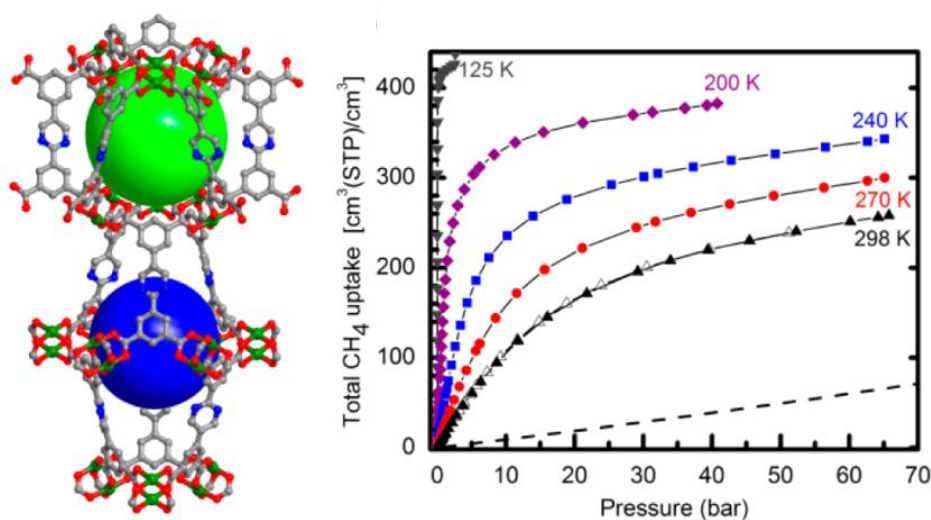


Figure 1.12: Structure and CH_4 adsorption isotherms for UTSA-76, which demonstrates one of the highest deliverable CH_4 capacities at 298 K to date.

1.3.2 Selective Capture and Separation of Pollutants

1.3.2.1 Carbon Dioxide Capture and Storage

Current carbon capture and storage technologies for the extraction of CO_2 from flue gas streams rely on the use of strongly binding amine-based scrubbers.¹⁰⁴ The cost of electricity produced from power stations fitted with these post-combustion capture technologies can rise by 42-81%;¹⁰⁵ a large proportion of the cost is due to the high energy penalty required to regenerate the amine-based solvent. MOFs have shown high adsorption capacities for CO_2 at ambient temperatures,¹⁰⁶ which can be easily reversed upon application of a light vacuum.

The highest gravimetric CO₂ adsorption capacity to date is demonstrated by Cu-TDPAT (Figure 1.13), a Cu(II)-paddlewheel based **rht** framework comprising a triazine based ligand.¹⁰⁷ Cu-TDPAT adsorbs 44.5 wt% of CO₂ at 273 K and 1 bar; an industrially relevant pressure for extraction of CO₂ from waste streams.

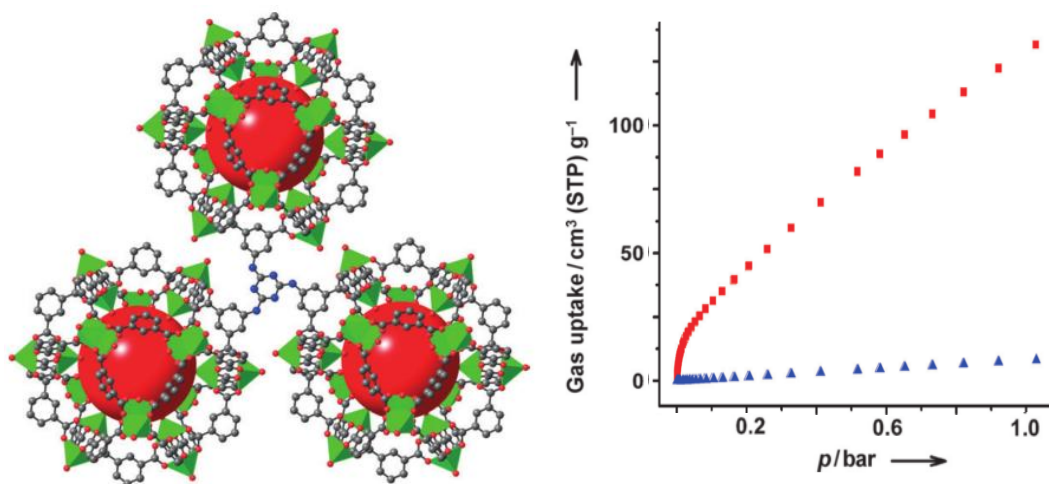


Figure 1.13: Structure of Cu-TDPAT; Cu(II) MOF which demonstrates the highest gravimetric adsorption capacity for CO₂ at 1 bar and 273 K to date. Gas adsorption isotherm demonstrating high selectivity for CO₂ over N₂ at 298 K.

In order for MOFs to selectively adsorb CO₂ over N₂, the main component of flue gas, the framework must contain strong CO₂-philic binding sites.¹⁰⁸ The quadrupolar moment of CO₂ favours highly polar functional groups, such as amides^{80,81} and amines;^{109,110} interactions with Lewis acidic open metal sites^{111,112} or Lewis basic groups such as nitrogen-containing heterocycles.^{111,113} For a MOF to be industrially applicable for post-combustion capture it must be stable to humid acidic conditions as flue gas streams often contain large volumes of water vapour and small amounts of SO₂.^{64,114} [Mn₂(Hcptz)₂(Cl)(H₂O)] demonstrates one of the highest selectivities for CO₂ over N₂ to date, adsorbing 78 times more CO₂ than N₂ at 298 K and 1 atm (Figure 1.14).¹¹⁵ The pore surface is lined with open metal sites, uncoordinated N atoms and aromatic rings, which form multiple interactions with the adsorbed CO₂ molecules. The use of uncoordinated pyridine and triazole nitrogen groups to increase CO₂ adsorption is discussed further in Chapters 2 and 4 respectively.

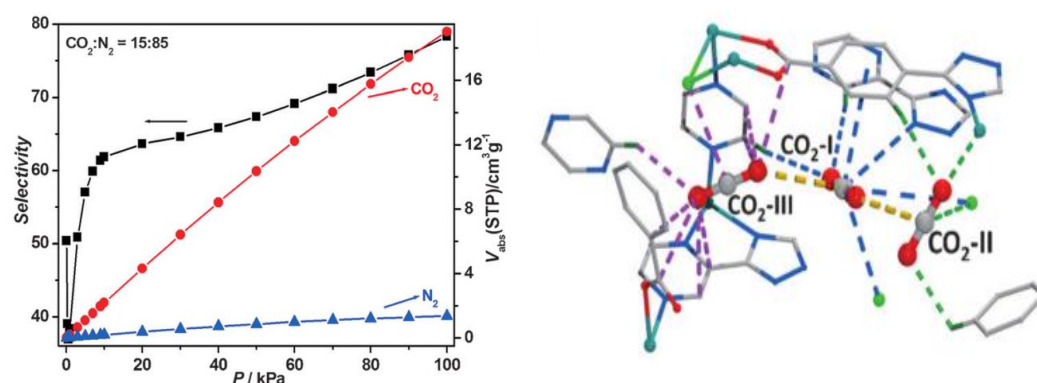


Figure 1.14: CO_2 adsorption properties of $[\text{Mn}_2(\text{Hcptz})_2(\text{Cl})(\text{H}_2\text{O})]$ at 298 K, showing CO_2 and N_2 adsorption isotherms to 1 bar in red and blue respectively. The CO_2/N_2 selectivity is depicted in black, calculated for a flue gas mixture of 15% CO_2 in N_2 .

1.3.2.2 Purification of Natural Gas

Biogas is an important source of renewable natural gas; however some sources comprise up to 45% non-combustible CO_2 , which must be removed before injection into a pipeline.¹¹⁶ MOFs can selectively adsorb CO_2 over CH_4 and can be used in place of traditional amine scrubbers to remove CO_2 contaminants. Mg-MOF-74 displays exception selectivity values of 108:1 at 313 K and 1 bar.¹¹⁷ The framework features open Mg(II) sites which are directed into the centre of honeycomb-shaped channels and provide a strong binding site for CO_2 molecules, a key feature in highly selective MOFs (Figure 1.15).

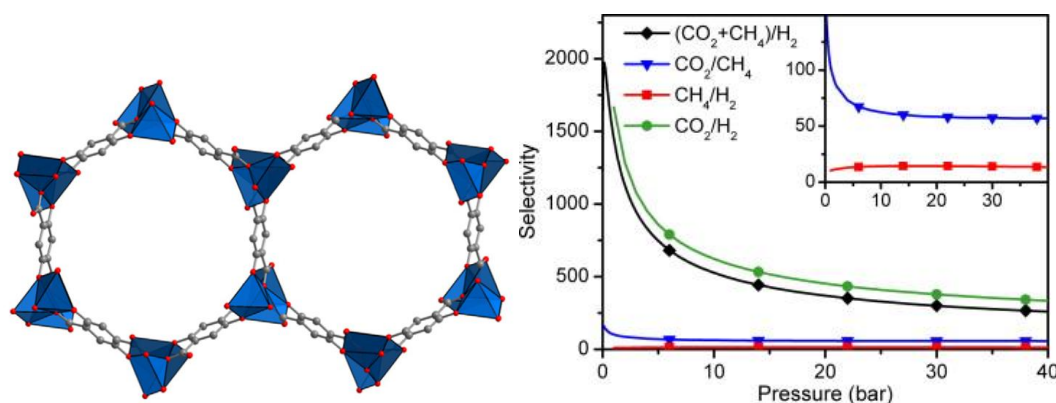


Figure 1.15: Structure of Mg-MOF-74 and high pressure selectivity parameters for an equimolar mixture of CO_2/CH_4 (shown in blue).

1.3.2.3 Separation of Light Hydrocarbons

Short chain unsaturated hydrocarbons such as ethylene and propylene are valuable petrochemical products, used to make plastics. 75-85% of the costs associated with ethylene production arise from its cryogenic distillation from ethane, with a typical mixture comprising 1:1 v/v.¹¹⁸ The state-of-the-art cryogenic distillation processes currently in use are highly energy-intensive and expensive; adsorption into porous solids is potentially a more energy efficient and cheaper alternative for this process. MOFs have shown a high adsorption capacity and selectivity for light hydrocarbons. One of the best performing MOFs to date is Fe(dobdc) (also known as Fe-MOF-74),¹¹⁹ which features a honeycomb arrangement of channels surrounded by unsaturated Fe(II) cations (Figure 1.16). Fe(dobdc) demonstrates good C₂H₄/C₂H₆ selectivity, adsorbing 13 times more ethylene than ethane at 1 bar and 318 K. Neutron powder diffraction studies concluded that the high selectivity for unsaturated hydrocarbons can be attributed to the side-on binding modes with the open metal site, resulting in shorter contacts (2.42 Å *c.f.* 2.59 Å) and stronger heats of adsorption (-45 kJ mol⁻¹ *c.f.* -25 kJ mol⁻¹).

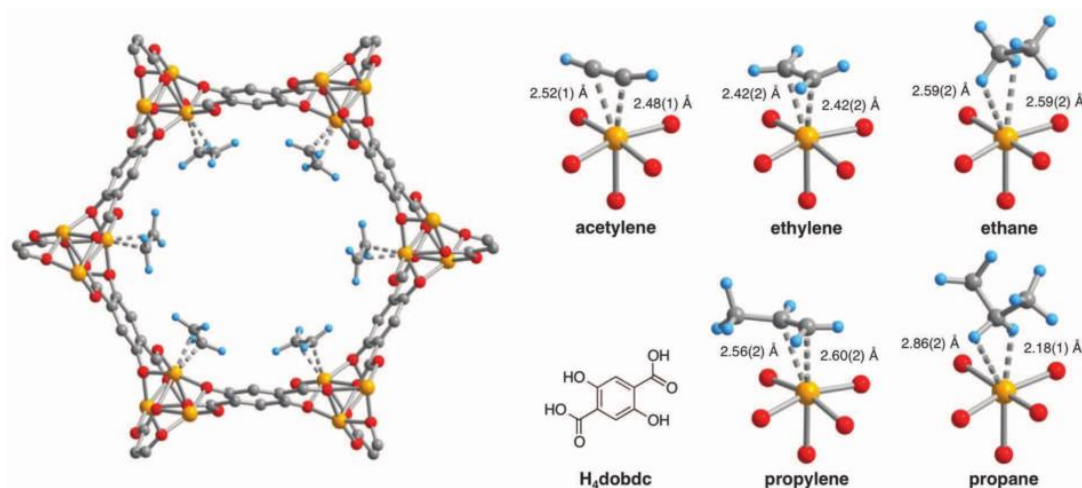


Figure 1.16: Structure of Fe(dobdc) (Fe-MOF-74) depicting interactions between unsaturated Fe(II) sites and adsorbed ethylene. The high selectivity for ethylene over ethane is attributed to shorter bond distances, identified by neutron diffraction studies.

1.4 Aim of this Thesis

The aim of this thesis is to investigate the structure and gas adsorption properties of metal organic frameworks constructed from pyridyl carboxylate ligands, particularly targeting the selective adsorption and storage of CO₂. The existence of two coordinating groups within such ligands can lead to the formation of unusual topologies; whilst uncoordinated pyridyl groups can offer strong binding sites for adsorbed gases. We intend to develop a detailed understanding of the binding interactions between guest molecules and the framework surfaces in order to systematically increase the gas adsorption capacity and selectivity of the materials synthesised.

1.5 References

- 1 E. M. Flanigen, *Stud. Surf. Sci. Catal.*, 2001, **137**, 11–35.
- 2 L. Pauling, *Zeitschrift für Krist. - Cryst. Mater.*, 1930, **74**, 213–225.
- 3 S. Wang and Y. Peng, *Chemical Engineering Journal*, 2010, **156**, 11–24.
- 4 A. Dyer, *Stud. Surf. Sci. Catal.*, 2007, **168**, 525–553.
- 5 K. Margeta, B. Vojnovic and N. Zabukovec Logar, *Recent Pat. Nanotechnol.*, 2011, **5**, 89–99.
- 6 D. Kalló, *Rev. Mineral. Geochemistry*, 2001, **45**, 519–550.
- 7 T. F. Degnan, *Top. Catal.*, 2000, **13**, 349–356.
- 8 T. Kobayashi, M. Ohshiro, K. Nakamoto and S. Uchida, *Industrial Eng. Chem. Res.*, 2016, **55**, 6996–7002.
- 9 A. Corma and M. E. Davis, *ChemPhysChem*, 2004, **5**, 304–313.
- 10 K. A. Hofmann and F. Küspert, *Zeitschrift für Anorg. Chemie*, 1897, **15**, 204–207.
- 11 H. M. Powell and J. H. Rayner, *Nature*, 1949, **163**, 566–567.
- 12 T. Iwamoto, *Inorganica Chim. Acta*, 1968, **2**, 269–272.
- 13 H. Zhdanov, *Comptes Rendus l'Académie des Sci.*, 1941, 350.
- 14 E. Shugam and H. Zhdanov, *Acta Physiochimica*, 1945, **20**, 247.
- 15 B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546–1554.
- 16 B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1989, **111**, 5962–5964.
- 17 S. R. Batten, N. R. Champness, X.-M. Chen, J. Garcia-Martinez, S. Kitagawa, L. Öhrström, M. O’Keeffe, M. P. Suh and J. Reedijk, *CrystEngComm*, 2012, **14**, 3001–3004.
- 18 S. R. Batten, N. R. Champness, X. Chen, J. Garcia-Martinez, S. Kitagawa, L. Öhrström, M. O. Keffe, M. P. Suh and J. Reedijk, *Pure Appl. Chem*, 2013, **85**, 1715–1724.
- 19 J. R. Long and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1213–1214.
- 20 J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450–1459.
- 21 S. H. Doan, K. D. Nguyen, P. T. Huynh, T. T. Nguyen and N. T. S. Phan, *J. Mol. Catal. A*, 2016, **423**, 433–440.
- 22 N. Devarajan and P. Suresh, *ChemCatChem*, 2016, **8**, 2953–2960.
- 23 Z. Miao, Y. Luan, C. Qi and D. Ramella, *Dalton Trans.*, 2016, **45**, 13917–13924.
- 24 H. Liu, F. Xi, W. Sun, N. Yang and E. Gao, *Inorg. Chem.*, 2016, **55**, 5753–5755.
- 25 D. Saha, D. K. Hazra, T. Maity and S. Koner, *Inorg. Chem.*, 2016, **55**, 5729–5731.

- 26 S. Bhattacharjee, Y. Lee, P. Puthiaraj, S. Cho and W.-S. Ahn, *Catal. Surv. from Asia*, 2015, **19**, 203–222.
- 27 J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang and C.-Y. Su, *Chem. Soc. Rev.*, 2014, **43**, 6011–6061.
- 28 K. Tanaka, K. Kubo, K. Iida, K. Otani, T. Murase, D. Yanamoto and M. Shiro, *Asian J. Org. Chem.*, 2013, **2**, 1055–1060.
- 29 S. Regati, Y. He, M. Thimmaiah, P. Li, S. Xiang, B. Chen and J. C.-G. Zhao, *Chem. Commun.*, 2013, **49**, 9836–9838.
- 30 Z. Xu, Y. Tan, H. Fu, J. Liu and J. Zhang, *Inorg. Chem.*, 2014, **53**, 12199–12204.
- 31 G. Nickerl, A. Henschel, R. Grünker, K. Gedrich and S. Kaskel, *Chemie Ing. Tech.*, 2011, **83**, 90–103.
- 32 Z. J. Sun, J. Z. Jiang and Y. F. Li, *Analyst*, 2015, **140**, 8201–8208.
- 33 F. Liu, J. He, M. Zeng, J. Hao, Q. Guo, Y. Song and L. Wang, *J. Nanoparticle Res.*, 2016, **18**, 106–115.
- 34 P. Chandrasekhar, A. Mukhopadhyay, G. Savitha and J. N. Moorthy, *Chem. Sci.*, 2016, **7**, 3085–3091.
- 35 I. Stassen, B. Bueken, H. Reinsch, J. F. M. Oudenhoven, D. Wouters, J. Hajek, V. Van Speybroeck, N. Stock, P. M. Vereecken, R. Van Schaijk, D. De Vos and R. Ameloot, *Chem. Sci.*, 2016, **7**, 5827–5832.
- 36 X. Li, L. Yang, L. Zhao, X. Wang, K. Shao and Z. Su, *Cryst. Growth Des.*, 2016, **16**, 4374–4382.
- 37 Q. Li, Z. Ma, W. Zhang, J. Xu, W. Wei, H. Lu, X. Zhao and X. Wang, *Chem. Commun.*, 2016, **52**, 11284–11287.
- 38 M. Mon, T. Grancha, F. R. Fortea-Pérez, J. Gascon, A. Leyva-Pérez, D. Armentano and E. Pardo, *J. Am. Chem. Soc.*, 2016, **138**, 7864–7867.
- 39 L. L. Wang, F. Luo, L. L. Dang, J. Q. Li, X. L. Wu, S. J. Liu and M. B. Luo, *J. Mater. Chem. A*, 2015, **3**, 13724–13730.
- 40 M. Zha, J. Liu, Y. Wong and Z. Xu, *J. Mater. Chem. A*, 2015, **3**, 3928–3934.
- 41 S. Pili, S. P. Argent, C. G. Morris, P. Rought, V. Garc, I. P. Silverwood, T. L. Easun, M. Li, M. R. Warren, C. A. Murray, C. C. Tang, S. Yang and M. Schröder, *J. Am. Chem. Soc.*, 2016, **138**, 6352–6355.
- 42 S. Tominaka and A. K. Cheetham, *RSC Adv.*, 2014, **4**, 54382–54387.
- 43 P. Horcajada, C. Serre, G. Maurin, N. a Ramsahye, F. Balas, M. Vallet-Regí, M. Sebban, F. Taulelle and G. Férey, *J. Am. Chem. Soc.*, 2008, **130**, 6774–6780.
- 44 W. J. Rieter, K. M. L. Taylor, H. An, W. Lin and W. Lin, *J. Am. Chem. Soc.*, 2006, **128**, 9024–9025.
- 45 Front/Back Matter, *Chem. Soc. Rev.*, 2014, **43**, 6173–6174.
- 46 M. Taddei, D. A. Steitz, J. A. Van Bokhoven and M. Ranocchiari, *Chem. Eur. J.*, 2016, **22**, 3245–3249.
- 47 M. Rubio-Martinez, T. D. Hadley, M. P. Batten, K. Constanti-Carey, T. Barton, D. Marley, A. Mönch, K. Lim and M. R. Hill, *ChemSusChem*, 2016, **9**, 938–941.
- 48 A. S. Munn, P. W. Dunne, S. V. Y. Tang and E. H. Lester, *Chem. Commun.*, 2015, **51**, 12811–12814.
- 49 R. Sabouni, H. Kazemian and S. Rohani, *Microporous Mesoporous Mater.*, 2013, **175**, 85–91.
- 50 W. Liang and D. M. D'Alessandro, *Chem. Commun.*, 2013, **49**, 3706–3708.
- 51 A. Pichon, A. Lazuen-Garay and S. L. James, *CrystEngComm*, 2006, **8**, 211.
- 52 D. J. Tranchemontagne, J. L. Mendoza-Cortés, M. O'Keeffe and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1257–1283.
- 53 O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705–14.
- 54 M. Eddaoudi, D. F. Sava, J. F. Eubank, K. Adil and V. Guillerme, *Chem. Soc. Rev.*, 2015, **44**, 228–249.
- 55 N. L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O. Keffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 1504–1518.

- 56 H. Li, M. Eddaoudi, M. O’Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276–279.
- 57 S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148–1151.
- 58 G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040–2042.
- 59 T. K. Kim, J. H. Lee, D. Moon and H. R. Moon, *Inorg. Chem.*, 2013, **52**, 589–595.
- 60 C.-H. Jiang, L.-F. Song, C.-L. Jiao, J. Zhang, L.-X. Sun, F. Xu, Y. Du and Z. Cao, *J. Therm. Anal. Calorim.*, 2010, **103**, 373–380.
- 61 M. Kang, D. Luo, X. Luo, Z. Chen and Z. Lin, *CrystEngComm*, 2012, **14**, 95–97.
- 62 Q. Zhai, Q. Lin, T. Wu, S.-T. Zheng, X. Bu and P. Feng, *Dalton Trans.*, 2012, **41**, 2866–2868.
- 63 S. Yang, X. Lin, A. J. Blake, K. M. Thomas, P. Hubberstey, N. R. Champness and M. Schröder, *Chem. Commun.*, 2008, 6108–6110.
- 64 S. Yang, J. Sun, A. J. Ramirez-Cuesta, S. K. Callear, W. I. F. David, D. P. Anderson, R. Newby, A. J. Blake, J. E. Parker, C. C. Tang and M. Schröder, *Nat. Chem.*, 2012, **4**, 887–894.
- 65 S. Yang, S. K. Callear, A. J. Ramirez-Cuesta, W. I. F. David, J. Sun, A. J. Blake, N. R. Champness and M. Schröder, *Faraday Discuss.*, 2011, **151**, 19–36.
- 66 P. R. Matthes, C. J. Höller, M. Mai, J. Heck, S. J. Sedlmaier, S. Schmiechen, C. Feldmann, W. Schnick and K. Müller-Buschbaum, *J. Mater. Chem.*, 2012, **22**, 10179–10187.
- 67 P. Thuéry, *Inorg. Chem.*, 2011, **50**, 1898–1904.
- 68 C. Volkringer, I. Mihalcea, J.-F. Vigier, A. Beaurain, M. Visseaux and T. Loiseau, *Inorg. Chem.*, 2011, **50**, 11865–11867.
- 69 D. T. de Lill, A. de Bettencourt-Dias and C. L. Cahill, *Inorg. Chem.*, 2007, **46**, 3960–3965.
- 70 D. Sun, Y. Ke, T. M. Mattox, B. A. Ooro and H. Zhou, *Chem. Commun.*, 2005, 5447–5449.
- 71 G. K. H. Shimizu, R. Vaidhyanathan and J. M. Taylor, *Chem. Soc. Rev.*, 2009, **38**, 1430–1449.
- 72 J. Yoshida, S. Nishikiori and R. Kuroda, *Chemistry*, 2008, **14**, 10570–10578.
- 73 J. Jia, X. Lin, C. Wilson, A. J. Blake, N. R. Champness, P. Hubberstey, G. Walker, E. J. Cussen and M. Schröder, *Chem. Commun.*, 2007, **3**, 840–842.
- 74 P. Pachfule, R. Das, P. Poddar and R. Banerjee, *Cryst. Growth Des.*, 2010, **10**, 2475–2478.
- 75 K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O’Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 10186–10191.
- 76 F. A. Almeida Paz, J. Klinowski, S. M. F. Vilela, J. P. C. Tomé, J. A. S. Cavaleiro and J. Rocha, *Chem. Soc. Rev.*, 2012, **41**, 1088–1110.
- 77 Z. Amghouz, S. García-Granda, J. R. García, R. A. S. Ferreira, L. Mafra, L. D. Carlos and J. Rocha, *Inorg. Chem.*, 2012, **51**, 1703–1716.
- 78 X. Lin, I. Telepeni, A. J. Blake, A. Dailly, C. M. Brown, J. M. Simmons, M. Zoppi, G. S. Walker, K. M. Thomas, T. J. Mays, P. Hubberstey, N. R. Champness and M. Schröder, *J. Am. Chem. Soc.*, 2009, **131**, 2159–2171.
- 79 Y. Yan, S. Yang, A. J. Blake and M. S. Oder, *Acc. Chem. Res.*, 2014, **47**, 296–307.
- 80 N. H. Alsmail, M. Suyetin, Y. Yan, R. Cabot, C. P. Krap, J. Lü, T. L. Easun, E. Bichoutskaia, W. Lewis, A. J. Blake and M. Schröder, *Chemistry*, 2014, **20**, 7317–7324.
- 81 Z. Lu, J. Bai, C. Hang, F. Meng, W. Liu and Y. Pan, *Chem. Eur. J.*, 2016, **22**, 6277–6285.
- 82 N. M. Shavaleev, S. V. Eliseeva, R. Scopelliti and J.-C. G. Bünzli, *Inorg. Chem.*, 2010, **49**, 3927–3936.
- 83 W. A. Maza, R. Padilla and A. J. Morris, *J. Am. Chem. Soc.*, 2015, **137**, 8161–8168.
- 84 M. Sartor, T. Stein, F. Hoffmann and M. Fröba, *Chem. Mater.*, 2016, **28**, 519–528.
- 85 A. Uzun and S. Keskin, *Prog. Surf. Sci.*, 2014, **89**, 56–79.

- 86 X. Hou, P. He, H. Li and X. Wang, *J. Phys. Chem. C*, 2013, **117**, 2824–2834.
- 87 S. Yang, X. Lin, W. Lewis, M. Suyetin, E. Bichoutskaia, J. E. Parker, C. C. Tang, D. R. Allan, P. J. Rizkallah, P. Hubberstey, N. R. Champness, K. M. Thomas, A. J. Blake and M. Schröder, *Nat. Mater.*, 2012, **11**, 710–716.
- 88 N. R. Champness, *Chem. Commun.*, 2013, **49**, 331–333.
- 89 S. M. Cohen, *Chem. Rev.*, 2012, **112**, 970–1000.
- 90 J. E. Halls, A. Hernán-Gómez, A. D. Burrows and F. Marken, *Dalton Trans.*, 2012, **41**, 1475–1480.
- 91 K. K. Tanabe and S. M. Cohen, *Chem. Soc. Rev.*, 2011, **40**, 498–519.
- 92 C. McGlade and P. Ekins, *Nature*, 2015, **517**, 187–190.
- 93 L. Bates, *UK Greenhouse Gas Emissions – 4th Quarter 2013 Provisional Figures Statistical Release: Experimental statistics*, Department of Energy and Climate Change, London, 2014.
- 94 R. Priddle and F. Birol, *IEA World Energy Outlook*, International Energy Agency, Paris, 2014.
- 95 O. K. Farha, I. Eryazici, N. C. Jeong, B. G. Hauser, C. E. Wilmer, A. Sarjeant, R. Q. Snurr, S. T. Nguyen, A. Ö. Yazaydin and J. T. Hupp, *J. Am. Chem. Soc.*, 2012, **134**, 15016–15021.
- 96 M. Beckner and A. Dailly, *Int. J. Energy Res.*, 2016, **40**, 91–99.
- 97 R. C. Weast, *CRC Handbook of Chemistry and Physics*, CRC Press Inc. West Palm Beach, FL, 1994.
- 98 J. L. Belof, A. C. Stern, M. Eddaoudi and B. Space, *J. Am. Chem. Soc.*, 2007, **129**, 15202–15210.
- 99 U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt and J. Pastré, *J. Mater. Chem.*, 2006, **16**, 626–636.
- 100 O. K. Farha, A. Ö. Yazaydin, I. Eryazici, C. D. Malliakas, B. G. Hauser, M. G. Kanatzidis, S. T. Nguyen, R. Q. Snurr and J. T. Hupp, *Nat. Chem.*, 2010, **2**, 944–948.
- 101 J. A. Mason and M. Veenstra, *Chem. Sci.*, 2014, **5**, 32–51.
- 102 Y. Peng, V. Krungleviciute, I. Eryazici, J. T. Hupp, O. K. Farha and T. Yildirim, *J. Am. Chem. Soc.*, 2013, **135**, 11887–11894.
- 103 B. Li, H. Wen, H. Wang, H. Wu, M. Tyagi, T. Yildirim, W. Zhou and B. Chen, *J. Am. Chem. Soc.*, 2014, **136**, 6207–6210.
- 104 R. J. Perry and J. L. Davis, *Energy Fuels*, 2012, **26**, 2512–2517.
- 105 B. Metz, O. Davidson, H. de Coninck, M. Loos and L. Meyer, *IPCC, 2005: IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change*, Cambridge University Press, Cambridge, 2005.
- 106 K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724–781.
- 107 B. Li, Z. Zhang, Y. Li, K. Yao, Y. Zhu, Z. Deng, F. Yang, X. Zhou, G. Li, H. Wu, N. Nijem, Y. J. Chabal, Z. Lai, Y. Han, Z. Shi, S. Feng and J. Li, *Angew. Chem. Int. Ed.*, 2012, **51**, 1412–1415.
- 108 B. Li, H. Wang and B. Chen, *Chem. Asian J.*, 2014, **9**, 1474–1498.
- 109 R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, P. G. Boyd, S. Alavi and T. K. Woo, *Science*, 2010, **330**, 650–653.
- 110 I. Erucar and S. Keskin, *Ind. Eng. Chem. Res.*, 2013, **52**, 3462–3472.
- 111 B. Liu, S. Yao, C. Shi, G. Li, Q. Huo and Y. Liu, *Chem. Commun.*, 2016, **52**, 3223–3226.
- 112 E. Groppo, S. Chavan and R. Blom, *Chem. Commun.*, 2008, **2**, 5125–5127.
- 113 C. Song, Y. Ling, L. Jin, M. Zhang, D. Chen and Y. He, *Dalton Trans.*, 2016, **45**, 190–197.
- 114 H. Liu, Y. Zhao, Z. Zhang, N. Nijem, Y. J. Chabal, X. Peng, H. Zeng and J. Li, *Chem. Asian J.*, 2013, **8**, 778–785.
- 115 H.-H. Wang, W.-J. Shi, L. Hou, G.-P. Li, Z. Zhu and Y.-Y. Wang, *Chem. Eur. J.*, 2015, **21**, 16525–16531.

- 116 Z. Bao, L. Yu, Q. Ren, X. Lu and S. Deng, *J. Colloid Interface Sci.*, 2011, **353**, 549–556.
- 117 Z. R. Herm, R. Krishna and J. R. Long, *Microporous Mesoporous Mater.*, 2012, **151**, 481–487.
- 118 L. Pinto and V. K. Saini, *Appl. Mater. Interfaces*, 2014, **6**, 12093–12099.
- 119 E. D. Bloch, W. L. Queen, R. Krishna, J. M. Zadrozny, C. M. Brown and J. R. Long, *Science*, 2012, **335**, 1606–1610.

Chapter 2: Synthesis and Characterisation of a New Pyridyl Isophthalate MOF

2.1 Pyridyl Carboxylate Containing Metal-Organic Frameworks

Pyridyl-containing ligands are often used in mixed ligand MOFs as pillaring agents to provide separation between two-dimensional layers.¹⁻⁸ In recent years, however, there has been a growing trend for the pyridyl functionality to be used in conjunction with other groups. Pyridyl carboxylate ligands are often chosen as the hard carboxylate group has a variety of well understood binding modes; whereas the soft pyridyl site can selectively bind to some metal centres, leading to MOFs with unusual connectivities.⁸⁻¹¹ Pyridyl groups do not always coordinate directly to a metal centre and can provide a free Lewis basic site with which guest species can interact.¹² Computational investigations have indicated that pyridine has the ability to form stronger interactions with CO₂ than benzene and pyrrole via Lewis acid-base interactions.¹³

Chelating pyridyl based moieties such as bipyridine or terpyridine are often used for post-synthetic capture or encapsulation of active species. UiO-67 is a highly robust zirconium framework comprising tetrahedral and octahedral cages constructed from a twelve connected Zr₆O₄(OH)₄(CO₂)₁₂ clusters and a 4,4'-biphenyldicarboxylic acid linker.¹⁴ Substituting the two phenyl rings within the ligand with 2,2'-bipyridine gives [2,2'-bipyridine]-5,5'-dicarboxylic acid, an isostructural framework is afforded.¹⁵ This modified UiO-67 framework has been used to encapsulate a range of active species,¹⁶ for example *fac*-Mn(bpy)(CO)₃Br, a CO₂ reduction catalyst;¹⁷ the photoactive ruthenium(II) bis(2,2'-bipyridine), RuDCBPY;¹⁸ and palladium nanoparticles for the conversion of nitrobenzene to aniline (Figure 2.1).¹⁹

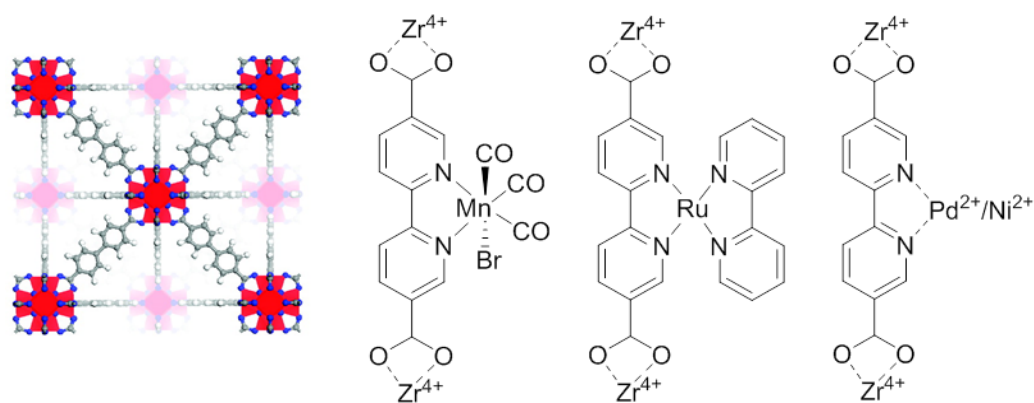


Figure 2.1: Structure of UiO-67¹⁴; and post synthetically modified linkers incorporated into the UiO-67 structure; *fac*-Mn(bpy)(CO)₃Br,¹⁷ RuDCBPY,¹⁸ and palladium nanoparticles.¹⁹

The use of one-ring pyridyl carboxylate ligands, such as pyridine-3,5-dicarboxylic acid and isonicotinic acid (Figure 2.2), to synthesise MOFs has been well studied. Structures often form two-dimensional sheets, which may be bridged by the pyridyl group to reveal small pores.^{9,12,20–22} The resulting properties, including open metal and Lewis basic sites, photochemical responses and regulated release of guest species, have been targeted for applications in epoxidation catalysts,²³ selective adsorption²⁴ and photoactive materials.²⁵

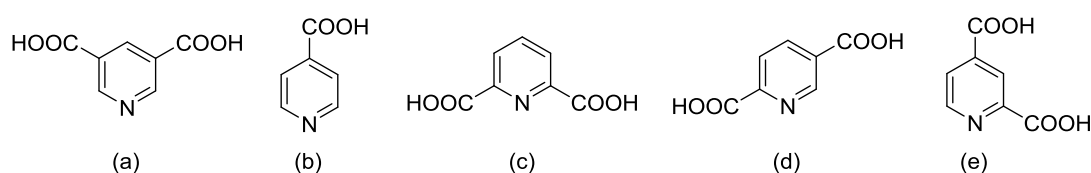


Figure 2.2: A selection of simple one-ring pyridyl carboxylate ligands used in the formation of metal-organic frameworks.

2.1.1 Linear Extension of Pyridine-3,5-dicarboxylic Acid

MOFs with small pores often demonstrate low adsorption capacities for gas species; thus ligand extension is often used as a strategy to increase porosity and gas uptake in MOFs. Previous work carried out in the Schröder group concerned the extension of pyridine-3,5-dicarboxylic acid in a linear direction (Figure 2.3) and the formation of Cu(II)-based frameworks for hydrogen storage.²⁶ Analogous to the NOTT-100 series, extension of the

ligand beyond three phenyl rings (Figure 2.3e) led to a two-fold interpenetrated structure with no porosity; whilst inclusion of a bulky naphthalene spacing group gave a MOF which collapsed upon desolvation.

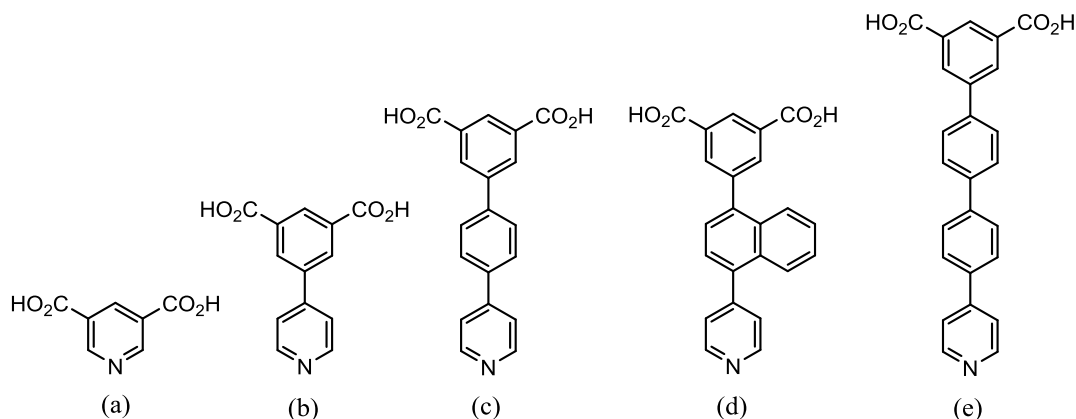


Figure 2.3: Extended series of pyridyl carboxylate ligands studied previously in the Schröder group.²⁶

5-(Pyrin-4-yl)isophthalic acid (Figure 2.3b) has been widely used to produce frameworks with metals ions as varied as Cu(II),²⁷ Co(II),^{28–31} Tb(III)^{32,33}, Eu(III),³² Gd(III)^{34,35} and Mn(II)²⁸ In each framework the pyridyl nitrogen binds directly to the metal clusters, leaving it unavailable for interactions with guest species within the pore.

2.1.2 Trigonal Extension of Pyridine-3,5-dicarboxylic Acid

In addition to elongation, the spacing between the carboxylic acid groups can be extended to give V-shaped ligands. Pyridine-3,5-dicarboxylic acid has been extended by inserting phenyl rings between the pyridyl ring and carboxylic acid groups to give 4,4'-(pyridine-3,5-diyl)dibenzoic acid (Figure 2.4). This ligand has been reported to form a series of isostructural **xmz** frameworks with Fe(II/III),^{36,37} Ni(II),^{36,37} Co(II),³⁷ In(III)^{38,39} and Mg(II).^{37,40} The frameworks are formed from the well-studied⁴¹ $[M_3(\mu_3\text{-OH})(\text{CO}_2)_6]$ SBU shown in Figure 2.4. Three metal centres are connected by one central bridging oxygen ligand and six bridging carboxylate groups, with three ligands lying above and three below the plane of the metal nodes. Pyridyl ligands are particularly suited for use in these clusters as they bind to the metal in the apical position, removing the need for a terminal solvent

molecule and thus stabilising the structure to desolvation. A total of nine ligands coordinate to each metal cluster, giving a (3,9) or 12-connected framework. Additional non-isostructural frameworks have been reported with other metals.^{42–45}

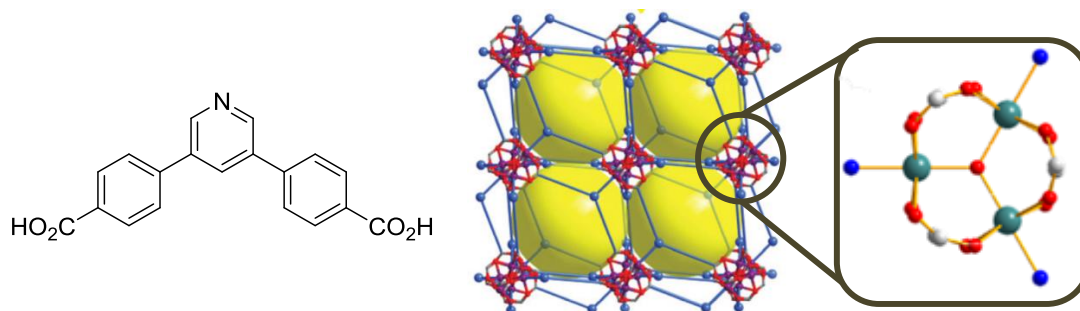


Figure 2.4: Structure of 4-[5-(4-carboxyphenyl)pyridin-3-yl]benzoic acid and the 12-connected framework formed upon reaction with Fe(III), Ni(II), Co(II), Mg(II) and In(III) metal salts, highlighting the trinuclear $[M_3(\mu_3\text{-OH})(\text{CO}_2)_6]$ metal cluster formed.

The only example of these 12-connected **xmz** frameworks to report CO₂ adsorption properties to date is JLU-Liu18,³⁹ an In(III)-based cationic framework featuring NO₃[−] counterions in the pores. The total CO₂ uptake at 1 bar is 129 cm³ g^{−1} and 63 cm³ g^{−1} at 273 K and 298 K, respectively.

2.1.3 Substitution of Benzoic Acid Groups with Isophthalate Rings

Framework conformation can not only be modified by ligand extension but also by altering the relative angles between the coordinating groups on the ligand. Replacing the benzoic acid groups with isophthalic acid moieties in the previous example gives the ligand 5,5'-(pyridine-3,5-diyl)diisophthalic acid, denoted H₄pdia (Figure 2.5). H₄pdia has been reported to form a Cu(II)-containing framework, [Cu₆(pdia)₃(H₂O)₆] in which the pyridyl groups are uncoordinated and point into the framework voids.^{46,47} [Cu₆(pdia)₃(H₂O)₆] displays high H₂ adsorption (9.5 wt% at 77 K, 100 bar) and CH₄ storage capacity (198.6 cm³ cm^{−3}, ambient temperature, 35 bar), which surpassed the DOE target for CH₄ storage at time of publication.⁴⁶ Additionally, [Cu₆(pdia)₃(H₂O)₆] exhibits a reasonable CO₂ uptake of 23.2 wt% (273 K, 1 bar) and shows selectivity for CO₂ over CH₄ and N₂.⁴⁷

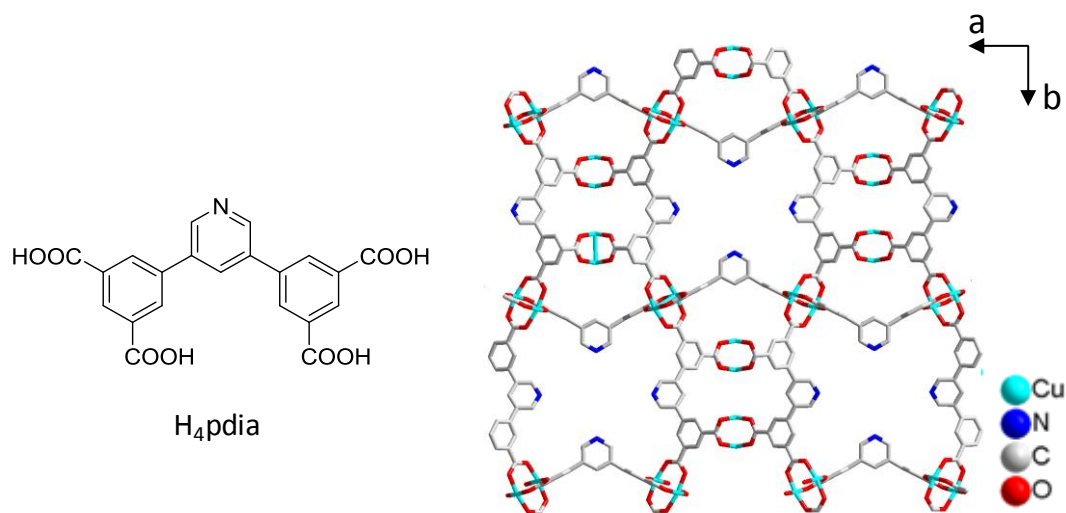


Figure 2.5: Structure of H_4pdia and view of $[Cu_6(pdia)_3(H_2O)_6]$ along the c axis, showing pyridyl groups pointing into the pores.

2.1.4 Further Extension of H_4pdia and Resulting Frameworks Formed

$[Cu_6(pdia)_3(H_2O)_6]$, described above, contains both open metal sites and pyridyl donors for interactions with gas molecules; however the capacity for gas storage is restricted by the proximity of these donor groups which mainly face directly across the windows of the pores. When van der Waals radii of the framework atoms are taken into account, they are only 3.6 Å apart, which only allows for only one site to be occupied by CO_2 (kinetic diameter of $CO_2 \sim 3.3$ Å).⁴⁸

Zhang *et al.* reported the extension of H_4pdia by inclusion of an ethyne group to form 3,5-bis(3,5-dicarboxylphenylethynyl)-pyridine, denoted H_4EPYD in this thesis (Figure 2.6).⁴⁹ Rather than a framework isostructural to $[Cu_6(pdia)_3(H_2O)_6]$ being formed, the pyridyl nitrogen binds to the axial site of the $Cu(II)$ -paddlewheels, creating a three dimensional network of **txt** topology. It can be considered self-interpenetrated – a phenomenon in which two interpenetrated networks are chemically connected, in this instance by the pyridyl- $Cu(II)$ bridge.

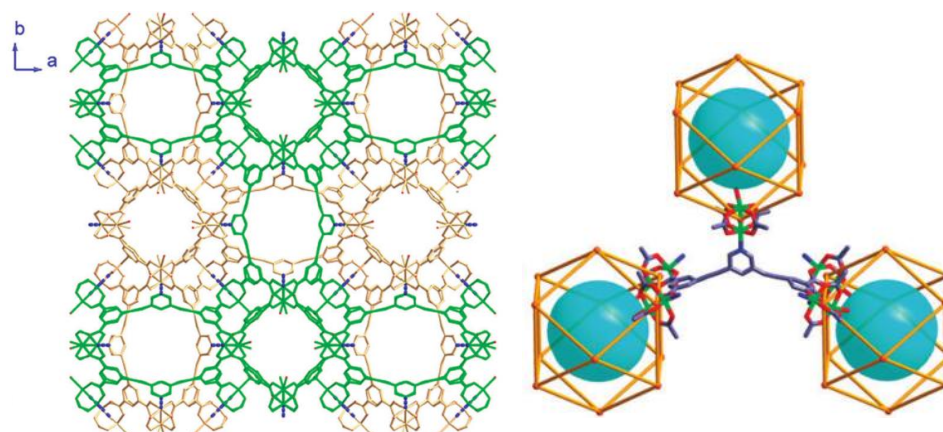


Figure 2.6: Structure of $[\text{Cu}_{24}(\text{EPYD})_{12}(\text{H}_2\text{O})_{12}] \cdot 12\text{DMF} \cdot 180\text{H}_2\text{O}$ ($\text{H}_4\text{EPYD} = 3,5\text{-bis}(3,5\text{-dicarboxylphenylethynyl})\text{-pyridine}$); showing the twofold self-interpenetrated nets with the $\text{Cu(II)}\text{-N}$ bonds represented in blue; view of the coordination of the $\text{C}_2\text{-symmetric}$ ligand EPYD^{4-} to three metal-organic cuboctahedra.

Although interpenetration and the associated reduced porosity initially appear detrimental, $[\text{Cu}_2\text{EPYD}(\text{H}_2\text{O})]$ shows enhanced stability in comparison to a similar two-fold interpenetrated framework $[\text{Cu}_2\text{EBNZ}(\text{DMF})_2]$ ($\text{H}_4\text{EBNZ} = 1,3\text{-bis}(3,5\text{-dicarboxylphenylethynyl})\text{ benzene}$), in which no $\text{Cu(II)}\text{-N}$ bond is present.⁵⁰ The CO_2 adsorption capacity of $[\text{Cu}_2\text{EPYD}]$ is reported to be 12.5 wt% at 1 bar and 298 K; unfortunately no data is available for comparison to $[\text{Cu}_2\text{EBNZ}]$.

H_4pdia has also been extended by an amide group, giving rise to 5,5'-((**P**yridine-3,5-dicarbonyl)bis(**a**zanediyl))diisophthalate, denoted H_4APYD in this thesis. Reaction with Cu(II) metal ions also results in the formation of a **txt** framework, referred to as both PCN-124 and NJU-Bai21 (Figure 2.7).^{51,52} The introduction of amide groups greatly improves CO_2 adsorption, with PCN-124 adsorbing $114 \text{ cm}^3 \text{ g}^{-1}$ (18.3 wt%) at 295 K and $204 \text{ cm}^3 \text{ g}^{-1}$ (28.6 wt%) at 273 K.

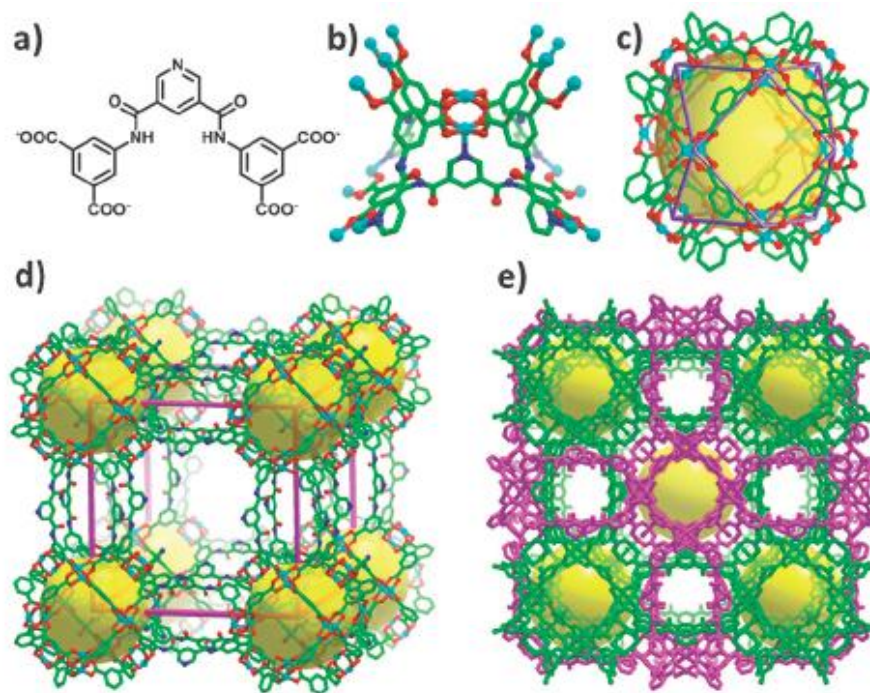


Figure 2.7: (a) 5,5'-((Pyridine-3,5-dicarbonyl)bis(azanediyl))diisophthalate (*H*₄APYD). (b) Coordination environment of the dinuclear Cu(II) paddlewheel motifs and ligands in PCN-124. (c) A cuboctahedral cage in PCN-124. (d) A single cubic framework of PCN-124 constructed by ligand skeletons bridging cage molecular building blocks (Cu atoms are shown in cyan, O atoms in red, N atoms in blue, C atoms in green). (e) The self-interpenetrated structure of PCN-124.⁵¹

2.2 Aims and Objectives

The objective of the work in this Chapter was to increase the gas uptake capacity of [Cu₆(pdia)₃(H₂O)₆] by separation of the Lewis basic pyridyl sites. Previous work carried out by the Zhang and Bai groups showed that the extension of H₄pdia to give H₄EPYD and H₄APYD, respectively, led to the formation of self-interpenetrating frameworks of **txt** topology in which the pyridyl nitrogens coordinate to the Cu(II) ions. The angles between the disubstituted ligand arms in [Cu₂(EPYD)(H₂O)] are strained to 140°, far beyond the ideal angle of 120°. It was proposed that a single constituent net of the self-interpenetrated framework could be isolated by increasing the length and rigidity of the ligand. Incorporating a phenyl ring in place of the ethyne group should constrain the angle between the ligand arms to 120°, geometrically preventing the self interpenetrated framework from forming. On this basis, 4',4'''-(pyridine-3,5-diyl)bis((1,1'-biphenyl)-3,5-dicarboxylic acid))

– referred to in this work as H₄PPYD for **Phenyl** extended **PYriDyl** core (Figure 2.8) – was designed as the target ligand for avoiding self-interpenetration.

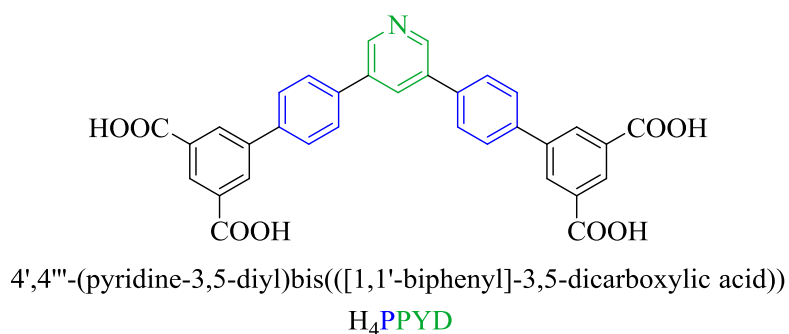
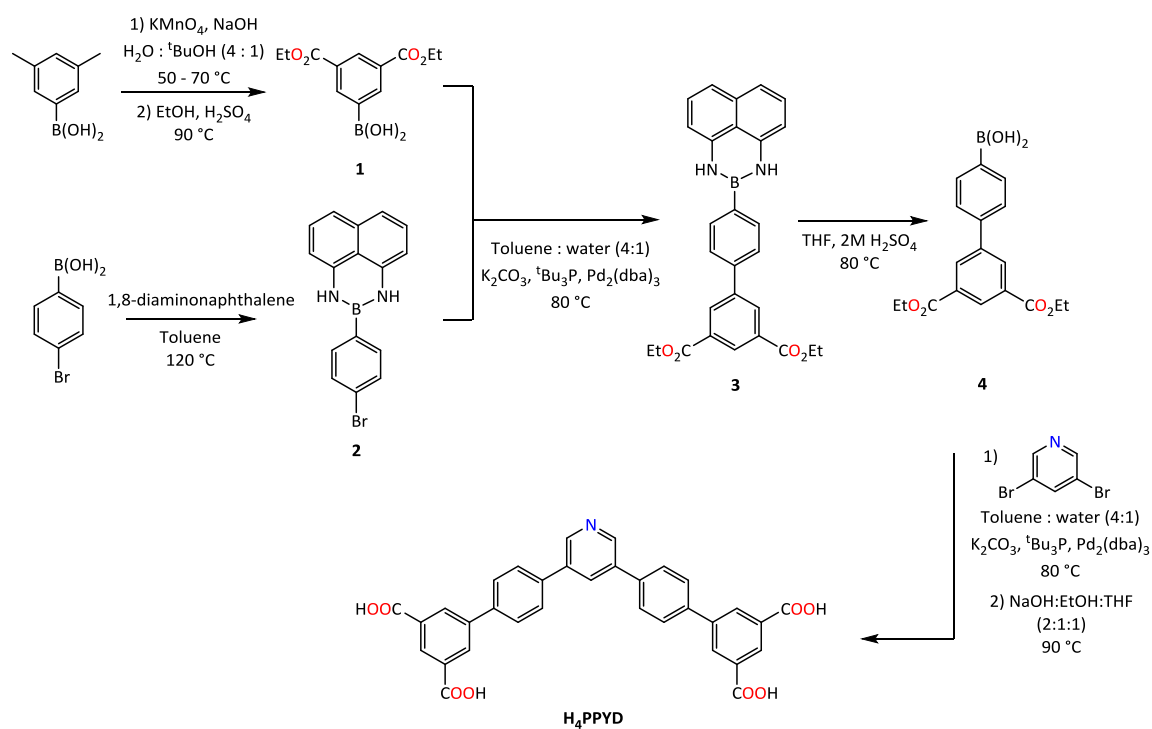


Figure 2.8: Structure and systematic name of the ligand H₄PPYD

2.3 Results and Discussion

2.3.1 Ligand Synthesis

The synthetic route to H₄PPYD involved the preparation of an “extended boronic acid isophthalate” unit, followed by Suzuki coupling to 3,5-dibromopyridine (Scheme 2.9).



Scheme 2.9: Synthetic route to H₄PPYD

3,5-Dimethylphenyl boronic acid was oxidised by addition of potassium permanganate in a basic solution, followed by esterification in acidic ethanol to give 3,5-diethoxy phenylboronic acid (**1**). Concurrently, 4-bromophenylboronic acid was protected via a condensation reaction with 1,8-diaminonaphthalene in toluene at 120 °C (**2**). **1** and **2** were coupled together via a Suzuki cross-coupling reaction (**3**), which was deprotected by hydrolysis to give the “extended boronic acid isophthalate” unit (**4**). H₄PPYD was synthesised via Suzuki coupling between dibromopyridine and **4**, followed by hydrolysis in aqueous NaOH.

2.3.2 Synthesis of [Cu₂PPYD(H₂O)]·(DMF)₄(H₂O)₂ (MFM-170)

Solvothermal reaction of H₄PPYD with Cu(NO₃)₂·5/2(H₂O) in DMF/water (5:1 v/v) under acidic (HNO₃) conditions afforded blue octahedral crystals of [Cu₂PPYD(H₂O)]·(DMF)₄(H₂O)₂ denoted **MFM-170**.

2.3.3 Structure Determination of MFM-170

MFM-170 crystallises in the cubic space group *Im-3m* with unit cell parameter *a* = 33.4733(3). MFM-170 comprises a pair of self-interpenetrating cubic nets constructed from Cu(II)-paddlewheel based metal-organic cuboctahedra. Although we predicted that extension of H₄pdia with a rigid phenyl ring would geometrically prevent the formation of a self-interpenetrated framework, the two cubic nets are linked by the pyridyl-N of one net to the axial Cu(II) site of the other (Figure 2.10). MFM-170 is isostructural to [Cu₂EPYD(H₂O)] and PCN-124 but features expanded crystal axes ([Cu₂EPYD(H₂O)] = 31.105(2), PCN-124 = 30.585(12)) due to the use of a longer, more rigid ligand. The relative stability, gas adsorption capacities and selectivity of MFM-170 compared to [Cu₂EPYD(H₂O)] and PCN-124 remain of interest.

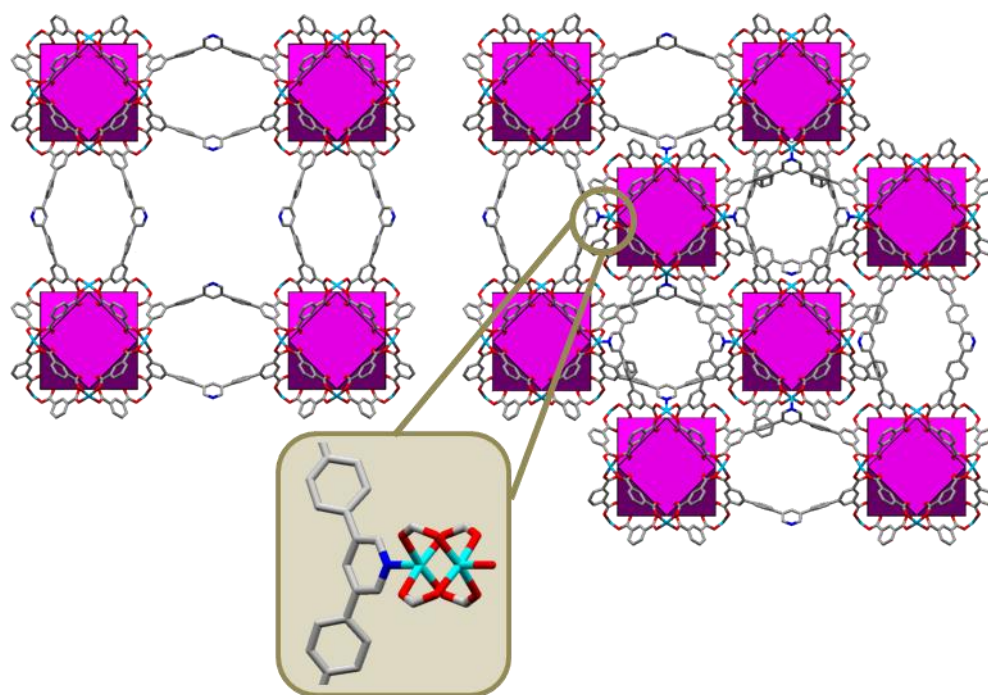


Figure 2.10: View of the interpenetration of cubic nets in MFM-170, with metal organic cuboctahedra shown in purple; on the left, the structure of one cubic net demonstrates the large void space formed in the centre of the cube; on the right, a second metal organic cuboctahedron fills this gap, forming a self-interpenetrated structure in which the Cu(II)-N linkage has been highlighted.

The topology of the framework was analysed using the TOPOS⁵⁵ software and confirmed as a (3,3,5)-connected net of **txt** topology, a rare class of frameworks; to the best of our knowledge found only in [Cu₂EPYD(H₂O)] and PCN-124 related materials.^{49,51,52} Figure 2.11 shows the two topological nodes that are present within the ligand: one 3-connected node centred on the pyridyl ring and one 3-connected node on each isophthalate ring. Each Cu(II)-paddlewheel is coordinated to five independent ligand molecules: four through carboxylate groups and one through the Cu(II)-N linkage.

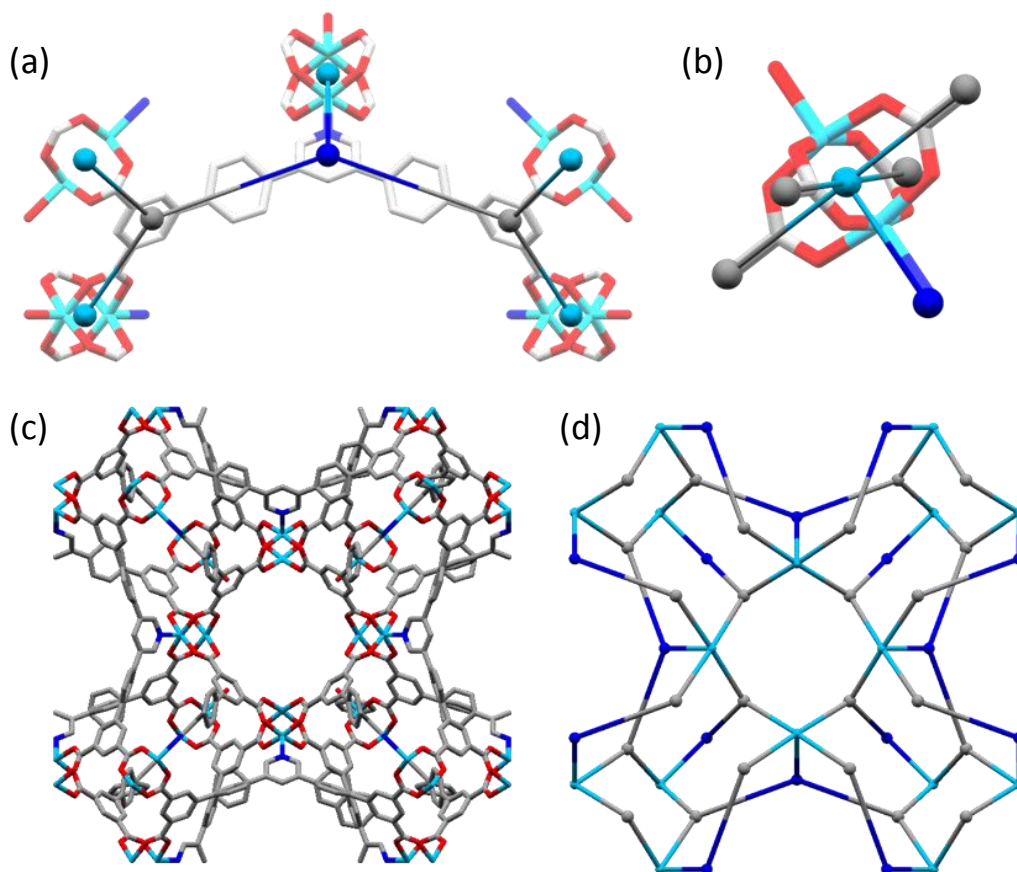


Figure 2.11: Topological analysis of MFM-170; (a) assignment of two 3-connected ligand topological nodes; (b) 5-connected Cu(II)-paddlewheel node; (c) unit cell of MFM-170; (d) topological representation of MFM-170.

The overall structure of MFM-170 and its isostructural analogues ($[\text{Cu}_2\text{EPYD}(\text{H}_2\text{O})]$ and PCN-124) can be viewed as the packing of three interconnected cages, A, B and C, shown in Figure 2.12.

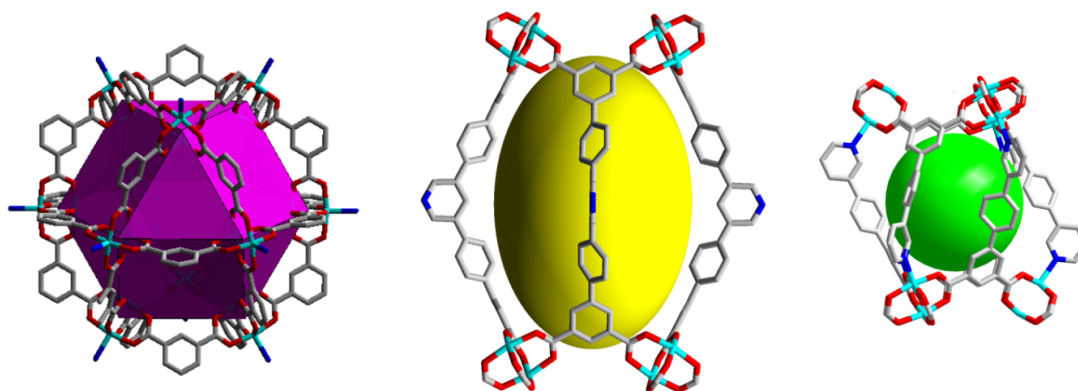


Figure 2.12: View of the three cages found in MFM-170; from left to right: Cage A (purple), cage B (yellow), cage C (green).

Cage A is a frequently observed $\{\text{Cu}_{24}(\text{RC}_6\text{H}_3(\text{CO}_2)_2)_{24}\}$ metal-organic-cuboctahedron,^{23–26} composed of twelve Cu(II)-paddlewheel vertices bridged by 24 isophthalate groups. These cuboctahedral cages, formed from alternating square and triangular faces, are commonly found in Cu(II) MOFs constructed from isophthalate based ligands.^{55–57} The cage measures 15.9 Å across, measured from opposite Cu(II) atoms and is identical in size across all three isostructural frameworks. Cage A packs in a body centred cubic (bcc) array, with six copies of cage B linking the square faces of cuboctahedra within each individual cubic net and eight copies of cage C joining the triangular faces of adjacent cuboctahedra, linking the two interpenetrated nets (Figure 2.13).

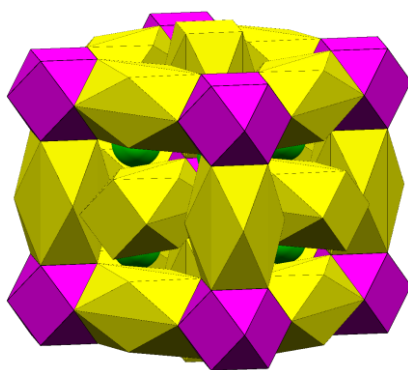


Figure 2.13: *MFM-170 is constructed from the packing of cage A (purple) in a bcc array with cage B (yellow) linking the square faces of the cuboctahedra within one net and cage C (green) linking the triangular faces of the two unique nets.*

Cage B is defined by the full length of four V-shaped ligands, which bow outwards to define a prolate pore, with length 22.2 Å and width 16.3 Å (measured between the centre of the square faces and opposite C atoms, respectively). The central pyridyl ring of the ligand is perpendicular to the pore surface, meaning that the C-H group opposite the pyridyl nitrogen points directly into the centre of the pore. The increased length and rigidity of H₄PPYD is reflected in the dimensions of cage B. MFM-170 exhibits the largest pore dimensions of the isostructural series; PCN-124 (17.5 Å × 12.4 Å) and [Cu₂EPYD(H₂O)] (18.0 Å × 13.0 Å). The angle described by the ligand arms in MFM-170 is 128°, compared to 140° in [Cu₂EPYD(H₂O)] and 124° in PCN-124. The decrease in angle is expected to decrease the

framework strain and thus increase the stability of MFM-170 in comparison to $[\text{Cu}_2\text{EPYD}(\text{H}_2\text{O})]$.

Cage C connects the triangular faces of two cuboctahedral A cages. The two triangular faces capping the top and bottom of cage C are staggered, rotated by 60° with respect to each other. The walls of cage C consist of six halves of the PPYD^{4-} ligand moieties, bound *via* isophthalate carboxylate groups at one end and *via* their pyridyl nitrogen donor at the other. The six heterotopic ligands alternate in direction around the cage. As with cage B, MFM-170 has the greatest pore dimensions: cage C measures $12.8 \text{ \AA}$ (between triangular faces) $\times$ $14.2 \text{ \AA}$ (between diagonally opposite C atoms) compared with $11.8 \text{ \AA} \times 14.1 \text{ \AA}$ in $[\text{Cu}_2\text{EPYD}(\text{H}_2\text{O})]$ and $11.3 \text{ \AA} \times 14.0 \text{ \AA}$ for PCN-124.

2.3.3.1 Porosity

The total solvent accessible volume of MFM-170 after removal of the guest and coordinated water molecules was estimated to be 61% using the PLATON/VOID routine.⁵⁸ The accessible porosity of MFM-170 is higher than that of PCN-124 (56%) due to the increased pore dimensions but slightly lower than the 67% calculated for $[\text{Cu}_2\text{EPYD}(\text{H}_2\text{O})]$ due to extra ligand volume from the symmetrically disordered phenyl rings.

As MFM-170 contains large pores, the limiting factor for adsorption is the size of the pore windows. The smallest, triangular pore window has a solvent accessible diameter of $5.2 \text{ \AA}$, calculated by considering the van der Waals radii of the framework. This window is more than sufficient to accommodate CO_2 (kinetic diameter $\sim 3.3 \text{ \AA}$), CH_4 ($\sim 3.8 \text{ \AA}$) and the light hydrocarbons acetylene ($\sim 3.3 \text{ \AA}$), ethylene ($\sim 4.2 \text{ \AA}$) and ethane ($\sim 4.4 \text{ \AA}$).⁵⁹

2.3.3.2 Powder X-Ray diffraction

The purity of the bulk material was analysed by PXRD and matched closely to the simulated values, proving that the single crystal structure is representative of the whole sample. A

Pawley refinement indexed the pattern to $a = 33.5811 \text{ \AA}$ with a goodness of fit of 2.18 (Figure 2.14).

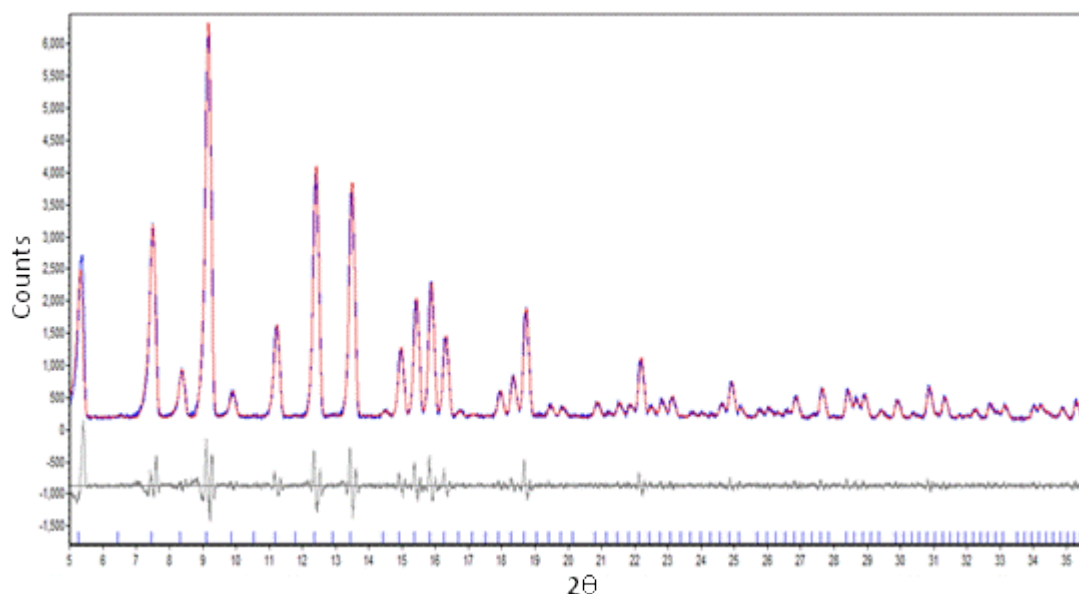


Figure 2.14: PXRD pattern of an as-synthesised sample of MFM-170 and Pawley Refinement giving unit cell parameters of $a = 33.5811 \text{ \AA}$, $GOF = 2.18$.

2.3.4 Stability

2.3.4.1 Solvent stability

The as-synthesised sample of MFM-170 was solvent exchanged by soaking in a regularly refreshed acetone solution for five days. Activation was carried out by heating the acetone-exchanged sample under dynamic vacuum at $100 \text{ }^{\circ}\text{C}$ overnight. Upon activation the light blue sample turned a deep purple owing to the loss of coordinated solvent molecules on the axial Cu(II) sites. A green-blue colour returned upon exposure to moist air. All samples were analysed by PXRD and are shown in Figure 2.15. The activated sample was prepared under inert conditions and protected from air with Kapton film.

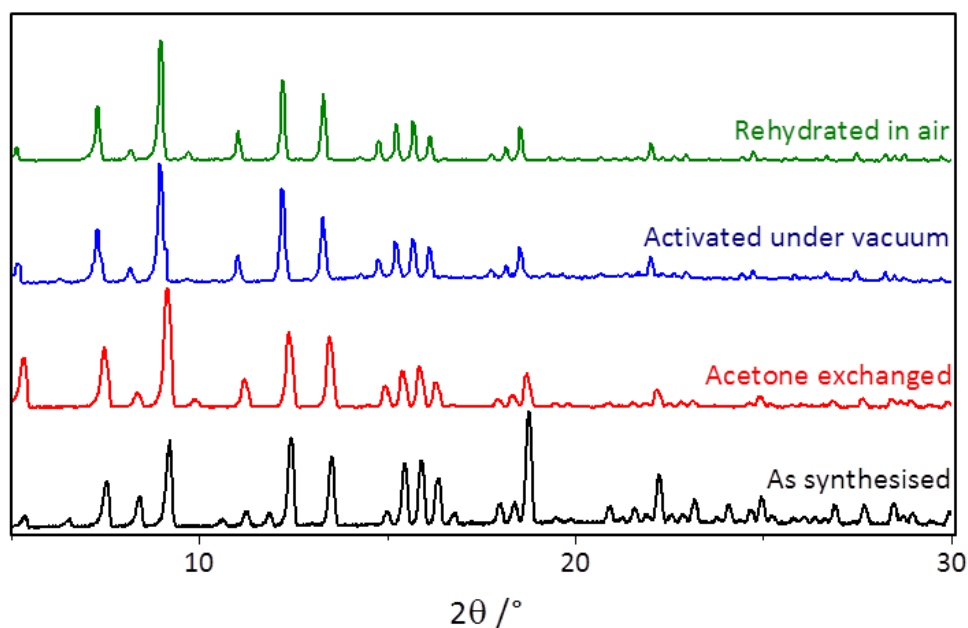


Figure 2.15: PXRD analysis of MFM-170 throughout the activation procedure. From bottom to top: as-synthesised sample (black), acetone exchanged sample (red), sample activated by heating to 100 °C under a vacuum overnight (blue), activated sample re-exposed to air (green).

In order to ascertain the stability of MFM-170 to water, samples were stirred in water at room temperature and 100 °C for 8 hours. A further sample was exposed to high levels of humidity by vapour diffusion at 100 °C. All three samples retained crystallinity, as observed by PXRD (Figure 2.16), thus proving the stability of MFM-170 to water, which is unusual in coordinatively unsaturated Cu(II) MOFs.⁶⁰⁻⁶¹

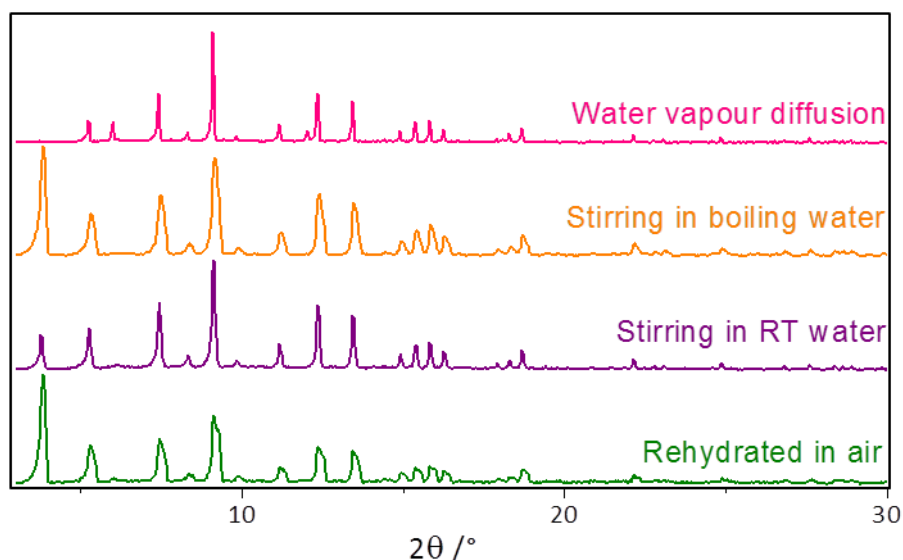


Figure 2.16: PXRD analysis of the stability of MFM-170 to water. From bottom to top: sample rehydrated in air after activation (green), sample that was stirred in water at room temperature for 8 hours (purple), sample stirred in boiling water for 8 hours (orange) and sample subjected to vapour diffusion by being suspended in a sealed flask of boiling water for 8 hours.

The PXRD patterns fit well to the crystallographic unit cell parameters upon Pawley refinement (Table 2.1). The goodness of fit values varied throughout the solvation process for two main reasons; the first being the variance in peak intensity for the (011) reflection at 3.85° 2θ , the second due to the emergence of an extra peak at 6° 2θ in the water vapour diffusion sample.

Table 2.1: Pawley fitting parameters of samples of MFM-170 upon activation and subsequent solvation.

	<i>a</i> parameter (Å)	Volume (Å ³)	GOF
As synthesised	33.60	37900	1.37
Acetone exchanged	33.54	37728	1.15
Activated	33.60	37930	2.05
Rehydrated in air	33.73	38379	3.38
Stirring in water at RT	33.58	37872	1.29
Stirring in water at 100 °C	33.71	38322	4.35
Vapour diffusion	33.55	37764	2.32

Analysis of the crystal structure reveals that the (011) plane cuts directly through the Cu(II)-paddlewheels and thus the changes in intensity can be attributed to unevenly solvated Cu(II)-axial sites. It can be seen that the highest relative peak intensities are present in the

sample that is rehydrated in air, which experiences the poorest vapour transport into the centre of the crystal; followed by the sample that was stirred in boiling water, which features the greatest evaporation from the pores. The (011) reflection was completely absent in the water vapour sample, where high levels of diffusion lead to even hydration of all the open metal sites within the framework. The second source of inconsistency between the experimental and simulated PXRDs is the emergence of a new peak at $6^\circ 2\theta$ upon exposure of the sample to water vapour diffusion (Figure 2.17). Upon drying in air this new peak disappears, indicating that is likely to be due to highly ordered water within the pores.

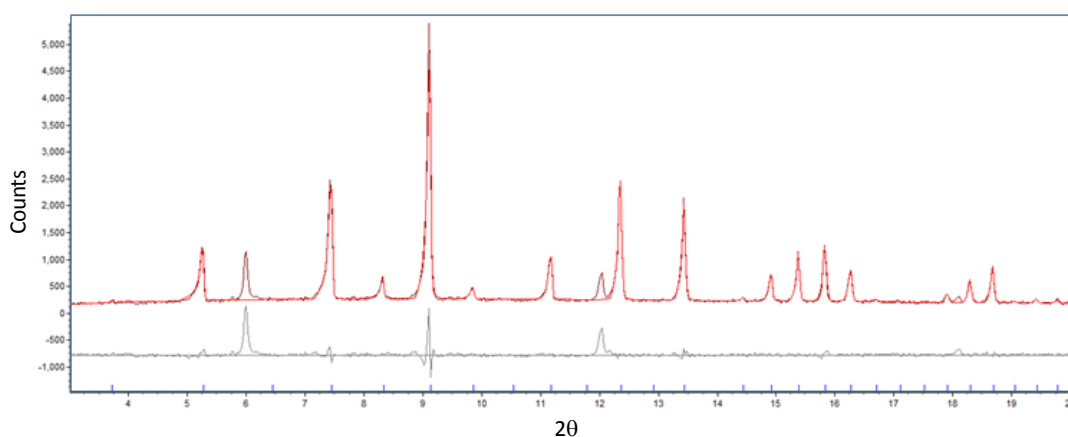


Figure 2.17: Pawley refinement of MFM-170 after water vapour diffusion showing the emergence of an additional peak at $6^\circ 2\theta$.

2.3.4.2 Thermal Stability

Thermogravimetric analysis (TGA) of MFM-170 (Figure 2.18) shows thermal stability to 370°C . The high thermal stability of **txt** frameworks can be attributed to the ligand bracing effect of the self interpenetrating framework.⁶³ As predicted from analysis of ligand angles in cage B, MFM-170 decomposes at a higher temperature than both PCN-124 (300°C) and $[\text{Cu}_2\text{EPYD}(\text{H}_2\text{O})]$ (350°C); attributed to less internal strain in MFM-170 compared to the isostructural frameworks.

Considering the “as synthesised” sample of MFM-170, an initial mass loss of 10% ($25^\circ\text{C} - 60^\circ\text{C}$) and 27% ($60^\circ\text{C} - 130^\circ\text{C}$) corresponds to the loss of two H_2O and four DMF molecules per formula unit from the pores. A third mass loss of 9% ($130^\circ\text{C} - 250^\circ\text{C}$)

relates to the removal of one DMF molecule per Cu(II) paddlewheel, giving a plateau for activated MFM-170. A decomposition mass loss of 39 wt% matches well to the loss of one molecule of PPYD⁴⁺ per formula unit, leaving a final mass of 14.4 wt% relating to 2CuO. The acetone exchanged framework demonstrated an initial mass loss of 8% (25 °C – 80 °C) for acetone within the pores, followed by a 4% loss between 65 °C and 130 °C corresponding to the removal of one H₂O molecule per Cu(II) paddlewheel and finally a mass loss of 64% upon decomposition.

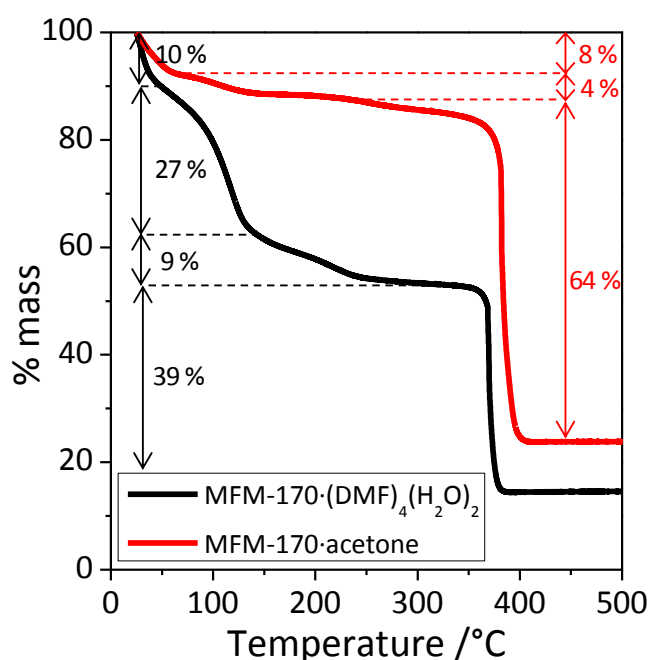


Figure 2.18: TGA of as synthesised and acetone exchanged samples of MFM-170.

Variable temperature PXRD analysis of an acetone exchanged sample of MFM-170 (Figure 2.19) shows retention of crystallinity to high temperatures. The sample was heated between 25 and 400 °C at a rate of 5 °C/min, with half an hour of dwell time at each temperature step. The diffraction patterns show a high level of crystallinity up to 300 °C, with complete decomposition taking place by 350 °C.

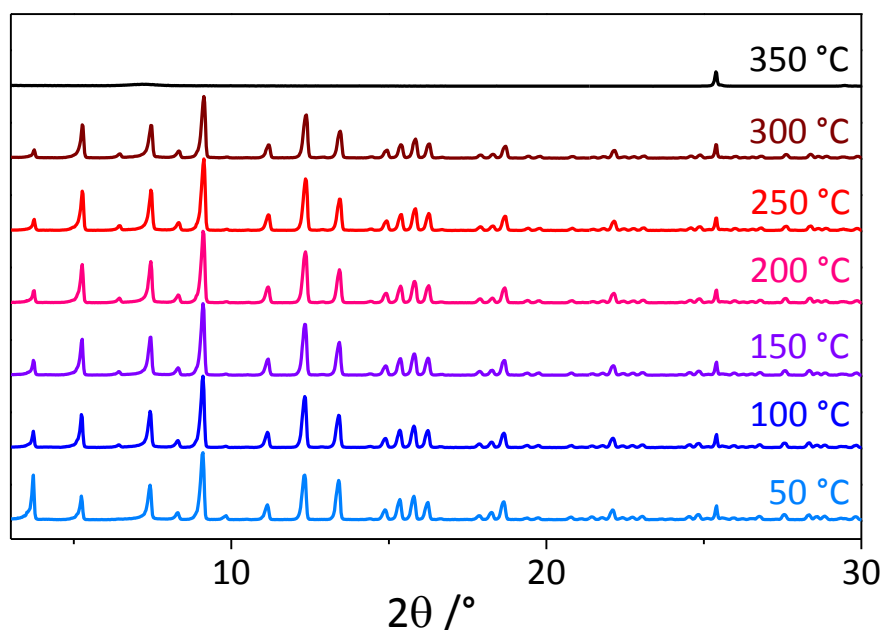


Figure 2.19: Selected diffraction patterns from the variable temperature PXRD analysis of acetone exchanged MFM-170 between 50 °C and 350 °C. The sample was heated at a rate of 5 °C min⁻¹ with a 30 minute dwell time before each measurement.

Pawley refinement of the PXRD patterns collected during variable temperature analysis (Table 2.2) revealed low levels of unit cell contraction with $\Delta V/V$ of only 0.5%. This is attributed to the strong interlocking self-interpenetrated nature of the structure. Goodness of fit values are high across all temperatures (4.62 – 5.07) as diffraction from the stationary sample stage within the oven led to uneven peak profiles and poor peak shape fitting.

Table 2.2: Pawley fitting parameters for the variable temperature PXRD analysis of MFM-170.

	<i>a</i> parameter	Volume	GOF
25 °C	33.65	38100	4.73
50 °C	33.64	38061	4.82
75 °C	33.66	38130	5.07
100 °C	33.63	38022	4.62
125 °C	33.62	38002	4.70
150 °C	33.62	37994	4.72
175 °C	33.62	37998	4.88
200 °C	33.61	37970	4.84
225 °C	33.60	37948	4.88
250 °C	33.59	37914	4.84
275 °C	33.59	37903	4.78
300 °C	33.58	37883	4.45

2.3.5 Gas Adsorption

2.3.5.1 BET Surface Area and Pore Size Distribution

The porosity of MFM-170 was confirmed by N₂ adsorption at 77 K, showing a fully reversible Type-I isotherm, (Figure 2.20), indicative of a microporous material. The BET surface area was calculated via the Rouquerol method (see Appendix A) to be 2408 m² g⁻¹. The measured surface area of MFM-170 is significantly higher than that of [Cu₂EPYD] and PCN-124 (1879 m² g⁻¹ and 1372 m² g⁻¹, respectively), which can be ascribed to the increased dimensions of cages B and C and larger surface area of the phenyl rings. The BET surface area of MFM-170 is greater than the commonly studied, highly stable MOFs; HKUST-1: 692-1944 m² g⁻¹,⁶⁴ MIL-53: 1140 m² g⁻¹,⁶⁵ UiO-66: 1187 m² g⁻¹,¹⁴ and MFM-300: 1370 m² g⁻¹,⁶⁶ giving great promise for high capacity gas adsorption applications.

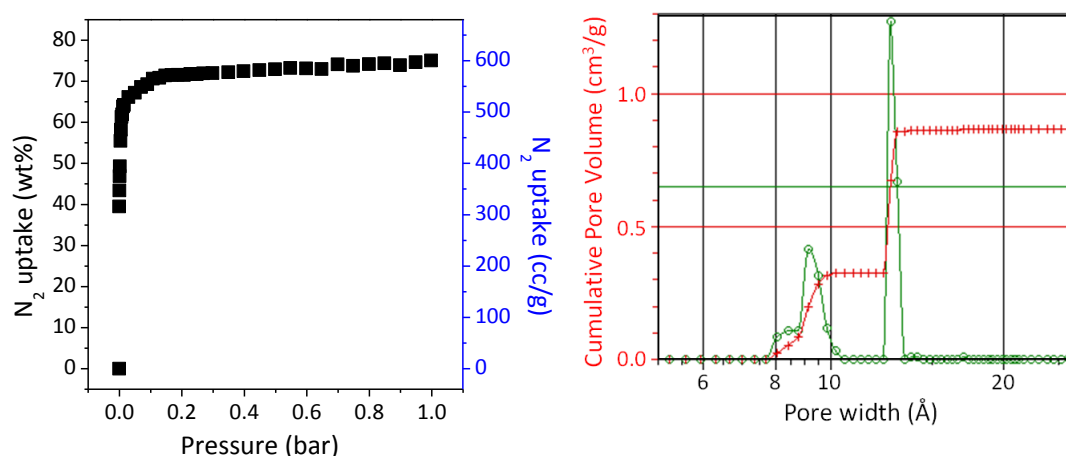


Figure 2.20: N₂ isotherm of MFM-170 at 77 K and pore size distribution calculated via DFT modelling of cylindrical pores on an oxide surface using data from the N₂ isotherm.

The total micropore volume and pore size distribution was calculated from the N₂ isotherm via DFT modelling of cylindrical pores on an oxide surface (Figure 2.20). The pore size distribution showed good agreement with the crystal structure; values of 8 Å, 9 Å and 13 Å compare well with 9 Å, 12 Å and 12 Å measured from the crystal structure. The calculated MFM-170 micropore volume is 0.87 cm³ g⁻¹, consistent with the crystallographic value of 0.82 cm³ g⁻¹ calculated by PLATON. The lower crystallographic pore volume can be

attributed to the modelling of two phenyl rings in the crystal structure due to rotational disorder across a mirror plane.

2.3.5.2 Nitrogen Adsorption in MFM-170

Measuring of N₂ isotherms to 20 bar at room temperature allows for the calculation of selectivity values for gas mixtures. MFM-170 adsorbs 19.67 wt% (157 cm³ g⁻¹) of N₂ at 273 K and 15.17 wt% (121 cm³ g⁻¹) at 298 K, a relatively high volume compared to highly selective MOFs: NOTT-300 < 10 cm³ g⁻¹,⁶⁶ bio-MOF-11 = 0.4 mmol g⁻¹ (9 cm³ g⁻¹)⁶⁷ and [Cu₃(CPT)₄(μ₃-OH)] < 5 cm³ g⁻¹.⁶⁸ The high uptake capacity of N₂ at ambient temperature foretells low selectivity values for CO₂/N₂.

2.3.5.3 Carbon Dioxide Adsorption in MFM-170

The CO₂ uptake capacity of MFM-170 at 1 bar is 27.34 wt% (6.21 mmol g⁻¹, 139 cm³ g⁻¹ STP) at 273 K and 13.25 wt% (3.01 mmol g⁻¹, 67 cm³ g⁻¹ STP) at 298 K, (Figure 2.21). MFM-170 adsorbs more CO₂ at 1 bar than [Cu₂EPYD] (12.47 wt% at 298 K, 1 bar),⁶⁹ but slightly less than PCN-124 (204 cm³ g⁻¹ at 273 K, 1 bar),⁵¹ indicating that the strongest interactions are between CO₂ and the amide functional group. The 1 bar CO₂ uptake capacities of the **txt** isostructural series are respectable but mid-range for Cu(II)-paddlewheel based MOFs; the highest uptakes at 273 K are reported as 42.6 wt% ([Cu₃(TPBTM)])⁷⁰ and 44.5 wt% ([Cu₃(TDPAT)])⁷¹. The low uptakes at atmospheric pressure can be attributed to fewer guest-framework interactions due to the large voids within the frameworks. At low pressures the adsorption of CO₂ increases linearly, indicating saturation has not been reached.

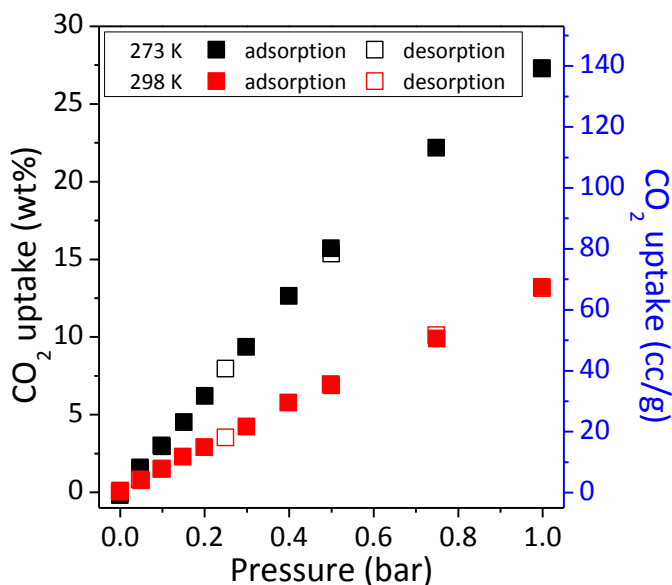


Figure 2.21: Gravimetric isotherms of CO₂ adsorption in MFM-170 up to 1 bar at 273 K and 298 K.

The 20 bar CO₂ adsorption isotherm (Figure 2.22) shows a linear increase in adsorption to approximately 4 bar, followed by the gradual onset of a plateau which almost saturates by 20 bar. The maximum CO₂ uptake at 20 bar was measured to be 94.95 wt% (21.57 mmol g⁻¹, 483 cm³ g⁻¹) at 273 K and 82.50 wt% (18.75 mmol g⁻¹, 420 cm³ g⁻¹) at 298 K.

No high pressure adsorption isotherms were measured for [Cu₂EPYD]; however, NJU-Bai22 (PCN-124) is reported to adsorb ~650 cm³ g⁻¹ of CO₂ at 20 bar, 298 K. NJU-Bai21 far exceeds the uptake capacity of MFM-170, thus proving that polar amide groups are an excellent method for enhancing the binding of CO₂ to the framework.^{70,72-75}

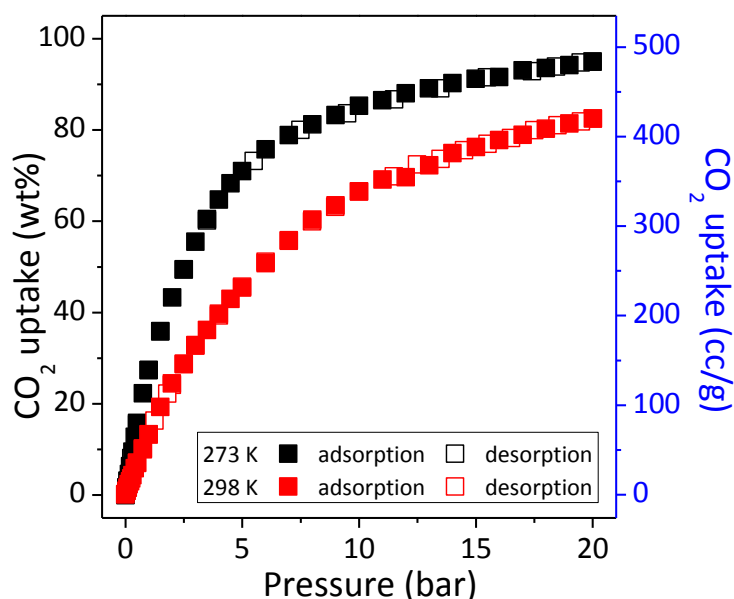


Figure 2.22: Gravimetric isotherms of CO₂ adsorption in MFM-170 up to 20 bar at 273 K and 298 K.

The isosteric heat of adsorption (Q_{st}) for CO₂ was calculated by fitting a virial-type equation to the 273 K and 298 K isotherms (see appendix A) and was found to be -18 kJ mol^{-1} at zero loading. The Q_{st} for MFM-170 is low in comparison to PCN-124 (-26 kJ mol^{-1}), confirming that the higher uptake capacity of PCN-124 at 1 bar is due to stronger interactions between CO₂ and the framework. No Q_{st} values were reported for [Cu₂EPYD]. Higher enthalpies of adsorption have been reported, mainly for amine containing frameworks MIL-53-NH₂(Al): $-38.4 \text{ kJ mol}^{-1}$, Cu₃(TDPAT): $-42.2 \text{ kJ mol}^{-1}$,⁷¹ bio-MOF-11: -45 kJ mol^{-1} ,⁶⁷ and MOF-74-Mg: -47 kJ mol^{-1} ,⁷⁶ indicating that the inclusion of amine groups is the best strategy to improve the strength of interactions between a MOF and CO₂.

Table 2.3: Summary of CO₂ adsorption data for MFM-170

	273 K	298 K
Maximum uptake (1 bar)	27.34 wt% 139 cm ³ g ⁻¹	13.25 wt% 67 cm ³ g ⁻¹
Maximum uptake (20 bar)	94.95 wt% 484 cm ³ g ⁻¹	82.50 wt% 420 cm ³ g ⁻¹
Isosteric heat of adsorption	-18 kJ mol^{-1}	

In order to understand the theoretical binary mixture separation properties of MFM-170, the Ideal Adsorbed Solution Theory (IAST) was used to model the separation ratio using the single component isotherms. (The IAST model is described in Appendix A).

The binary mixture ratio for CO₂:N₂ was determined from the composition of a typical waste gas stream containing 85% N₂:15% CO₂. The CO₂/N₂ selectivity of MFM-170 was calculated using the IAST model giving 11.5 at 273 K and 7.4 at 298 K (Figure 2.23). Although MFM-170 demonstrates relatively high CO₂ adsorption, the selectivity for CO₂ is low in comparison to other MOF materials due to the high adsorption capacity of N₂.

NJU-Bai21 (PCN-124) demonstrates a CO₂/N₂ selectivity of 93,⁵² higher than many well known MOFs to date. The CO₂/N₂ selectivity of MFM-170 could be improved by including amine groups to increase CO₂ uptake, such as in the bifunctionalised UiO-66-NO₂-NH₂ (selectivity = 64);⁸⁸ whilst a combination of exposed metal sites, uncoordinated N atoms, narrow channels and Cl⁻ basic sites lead to a selectivity of 78 in [Mn₂(Hcbptz)₂(Cl)]Cl.⁸⁹

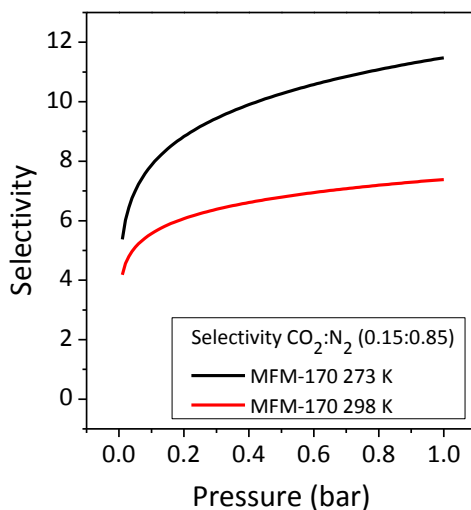


Figure 2.23: Selectivity values for the post-combustion capture of CO₂ from N₂ in MFM-170 at 273 K and 298 K, with a 0.15:0.85 mixture of CO₂:N₂.

2.3.5.4 Methane Adsorption in MFM-170

The 1 bar CH₄ adsorption properties of MFM-170 were determined to be 3.18 wt% (44 cm³ g⁻¹) at 273 K and 2.10 wt% (29 cm³ g⁻¹) at 298 K. No methane adsorption was reported for [Cu₂EPYD] to allow for comparison. PCN-124 exhibits lower CH₄ adsorption values than MFM-170; 33.4 cm³ g⁻¹ (2.33 wt%) at 273 K, despite showing a far superior CO₂ uptake capacity. This behaviour is ascribed to the lower pore volume in PCN-124 (0.63 cm³ g⁻¹ *cf.* 0.82 cm³ g⁻¹) and confirms that amide groups do not enhance the binding affinity of CH₄.⁷² The CH₄ uptake capacity at 20 bar was measured to be 21.10 wt% (295 cm³ g⁻¹) at 273 K and 16.78 wt% (234 cm³ g⁻¹) at 298 K, matching well to high performing MOFs, comfortably beating NOTT-220 (165 cm³ g⁻¹, 8.2 wt % at 20 bar and 293 K),⁷⁷ and NOTT-125 (142 cm³ g⁻¹ at 20 bar and 298 K).⁷² Thus MFM-170 is predicted to be a good platform upon which methane adsorption could be explored in the future.

Unlike with CO₂ adsorption, MFM-170 does not reach CH₄ saturation by 20 bar (Figure 2.24). At the time of measurement, equipment in the group was limited to 20 bar in pressure; however most high-pressure measurements in the literature are carried out to 35 bar: the limit of a natural gas pipeline, or 65 bar: the limit of inexpensive two-stage compressors.⁷⁸ The shallow adsorption gradient of CH₄ means that MFM-170 demonstrates the high deliverable capacity required for a natural gas powered vehicle (deliverable capacity = the difference between the total uptake and typical working capacity of an internal combustion engine at ~5 bar).⁷⁹ Unfortunately MFM-170 falls short of the ARPA-E (Advanced Research Projects Agency-Energy) target of delivering 350 v/v at 298 K;⁸⁰ the total 20 bar uptake at 298 K is 174 v/v, giving a deliverable capacity of 103 v/v; however MFM-170 is expected to approach this target if loaded at 65 bar.

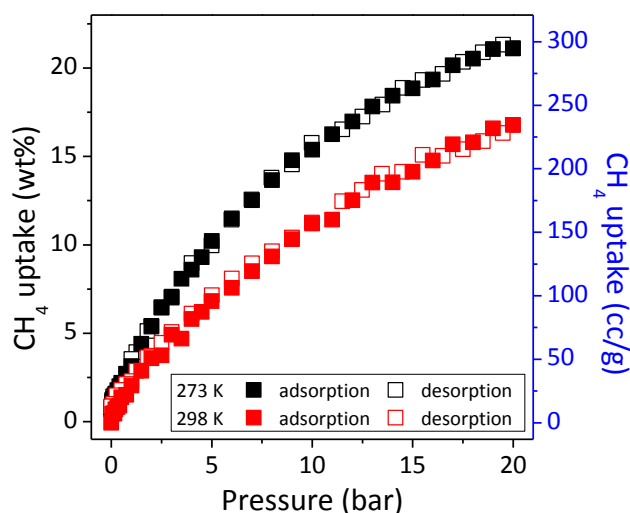


Figure 2.24: Gravimetric isotherms of CH_4 adsorption in MFM-170 up to 20 bar at 273 K and 298 K.

The Q_{st} for CH_4 in MFM-170 was calculated to be -11 kJ mol^{-1} at zero loading, indicating a lack of strong binding sites between adsorbed CH_4 and the framework surface. Comparison of MFM-170 to PCN-124 reveals that the amide functionalised framework demonstrate a higher initial Q_{st} (PCN-124 = $-15.7 \text{ kJ mol}^{-1}$) indicating that the superior CH_4 uptake in MFM-170 is due to higher porosity. The highest Q_{st} reported for CH_4 adsorption to date is PCN-14 at -30 kJ mol^{-1} ,⁸¹ whilst other leading MOFs demonstrate similar binding energies to MFM-170; NOTT-125 = $-14.5 \text{ kJ mol}^{-1}$,⁷² HKUST-1 = $-17.0 \text{ kJ mol}^{-1}$,⁷⁸ and Ni-MOF-74 = -21.4 .⁷⁸

Table 2.4: Summary of CH_4 adsorption data for MFM-170

	273 K	298 K
Maximum uptake (1 bar)	3.18 wt% 44 $\text{cm}^3 \text{ g}^{-1}$	2.10 wt% 29 $\text{cm}^3 \text{ g}^{-1}$
Maximum uptake (20 bar)	21.10 wt% 295 $\text{cm}^3 \text{ g}^{-1}$	16.78 wt% 234 $\text{cm}^3 \text{ g}^{-1}$
Isoteric heat of adsorption	-11 kJ mol^{-1}	

CO_2/CH_4 separation is a necessary industrial process for natural gas sweetening. As varying amounts of CO_2 contaminants can be found in natural gas, an equimolar ratio is used as standard for the purpose of selectivity calculations.

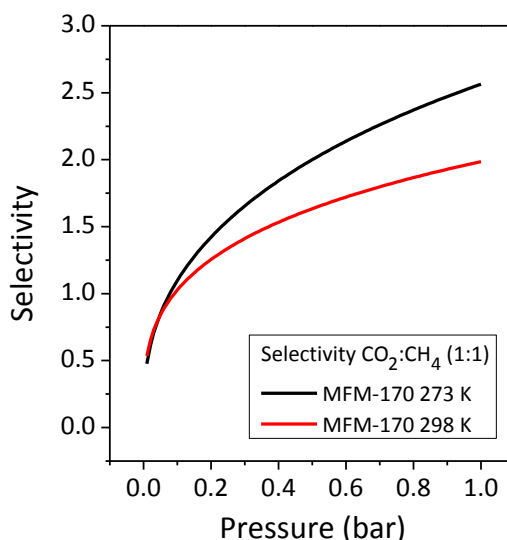


Figure 2.25: IAST selectivity values of an equimolar mixture of CO_2 and CH_4 in MFM-170 at 273 K and 298 K based on single component isotherms.

At 273 K, MFM-170 adsorbs only 2.6 times more CO_2 than CH_4 , dropping to a ratio of 2.0:1 at 298 K (Figure 2.25). Due to the high uptake capacities of both gases and the similar adsorption isotherm profiles of CO_2 and CH_4 , the CO_2/CH_4 selectivity of MFM-170 at 1 bar is low in comparison to other frameworks; selectivity values for $\text{CO}_2:\text{CH}_4$ generally fall in the range 4-5.⁹⁰ Selectivity for CO_2 can be increased by introducing CO_2 -philic sites into a MOF; the oxamide functionality in NOTT-125 leads to strong interactions with CO_2 and thus a high selectivity value of 9.2 at 273 K.⁷² Likewise ZJU-8,⁹¹ an amine functionalised MOF has an equally high selectivity value of 8.2 at 273 K, whilst the cationic $[\text{Mn}_2(\text{Hcbptz})_2(\text{Cl})]\text{Cl}$ demonstrates a selectivity of 10.3 at 298 K.⁸⁹

2.3.5.5 Hydrocarbon Adsorption in MFM-170

At 1 bar and 273 K, MFM-170 adsorbs 23.50 wt% ($175 \text{ cm}^3 \text{ g}^{-1}$, 7.81 mmol g^{-1}) of C_2H_4 and 27.84 wt% ($207 \text{ cm}^3 \text{ g}^{-1}$, 9.26 mmol g^{-1}) of C_2H_6 (Figure 2.26); 298 K adsorption values are listed in Table 2.6. MFM-170 shows one of the highest ambient adsorption capacities for both ethylene and ethane; comparable to leading MOFs such as Cu-TDPAT,⁸² and Fe(dobdc) (Table 2.5).⁸³ High C_2 hydrocarbon adsorption capacities are relatively uncommon and are accredited to the large pore volumes in addition to the strong $\text{CH}-\pi$

interactions between the hydrocarbon CH and the multiple phenyl rings lining each cage in MFM-170.⁸⁴

Table 2.5: Comparison of the C_2H_4 and C_2H_6 uptake capacities of MFM-170 to high performing MOFs in the field of hydrocarbon adsorption.

MOF	C_2H_4 adsorption ($cm^3 g^{-1}$)		C_2H_6 adsorption ($cm^3 g^{-1}$)		ref
	273 K	298 K	273 K	298 K	
MFM-170	175	117	207	134	This Work
Cu-TDPAT	218	-	218	-	82
Fe(dobdc)	-	135	-	112	83
ZJU-30	-	44.3	-	47.7	12
SBMOF-1	-	30.0	-	29.5	85
SBMOF-2	-	59.8	-	62.2	85

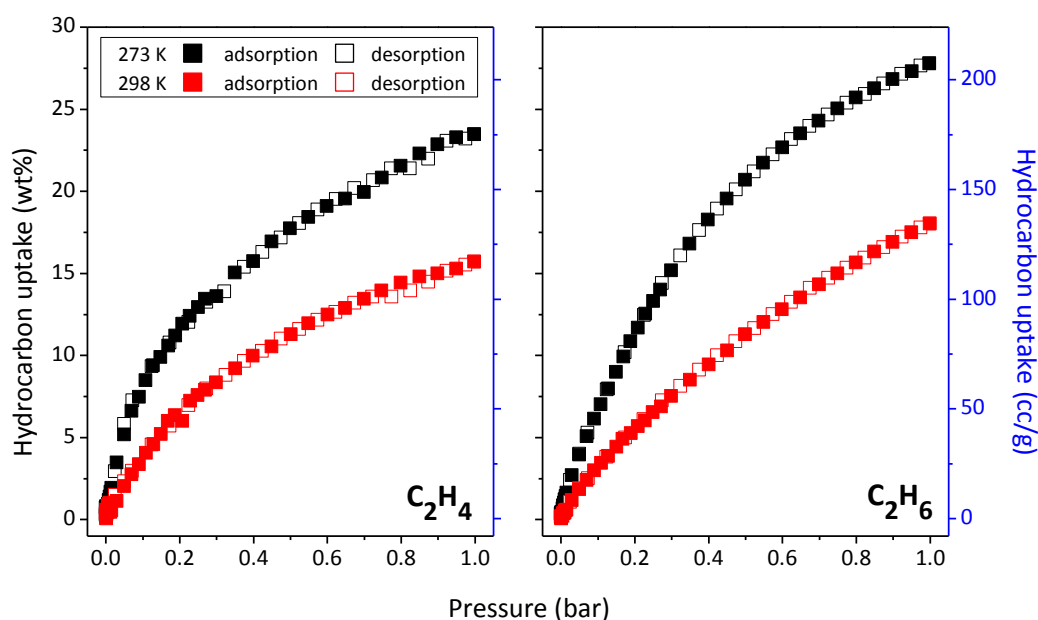


Figure 2.26: Gravimetric isotherms of C_2H_4 and C_2H_6 adsorption in MFM-170 up to 20 bar at 273 K and 298 K.

In line with the excellent gravimetric adsorption capacities, MFM-170 exhibits unusually high enthalpies of adsorption for the C_2 hydrocarbons; -28 kJ mol^{-1} for C_2H_4 and -36 kJ mol^{-1} for C_2H_6 . These values compare favourably to frameworks such as MFM-202,⁸⁶ which exhibits an enthalpy of adsorption of -18 kJ mol^{-1} for both gases.

When compared to MFM-170, Cu-TDPAT reports a stronger enthalpy of adsorption with C_2H_4 ($-49.5 \text{ kJ mol}^{-1}$). DFT analysis of Cu-TDPAT predicts that the strongest binding

energy between Cu-TDPAT and the C_2 hydrocarbons is the electrostatic interaction with the axial Cu(II) site.⁸² Both MFM-170 and Cu-TDPAT are constructed from metal organic cuboctahedra comprising Cu(II)-paddlewheels. The close proximity of Cu(II) sites on the inside surface of the cuboctahedron (7.8 Å) combined with the length of C_2H_4 (4.84 Å)⁵⁹ leads us to assume that the majority of interactions between Cu-TDPAT and C_2H_4 take place on the outside of the cuboctahedron; sites which are blocked in MFM-170 by the self-interpenetrating framework.

Table 2.6: Summary of the C_2 hydrocarbon adsorption data for MFM-170 at 1 bar.

	273 K	298 K	Q_{st} (kJ mol ⁻¹)
C_2H_4 (1 bar)	23.5 wt% 175 cm ³ g ⁻¹	15.7 wt% 117 cm ³ g ⁻¹	-29
C_2H_6 (1 bar)	27.8 wt% 208 cm ³ g ⁻¹	18 wt% 134 cm ³ g ⁻¹	-36

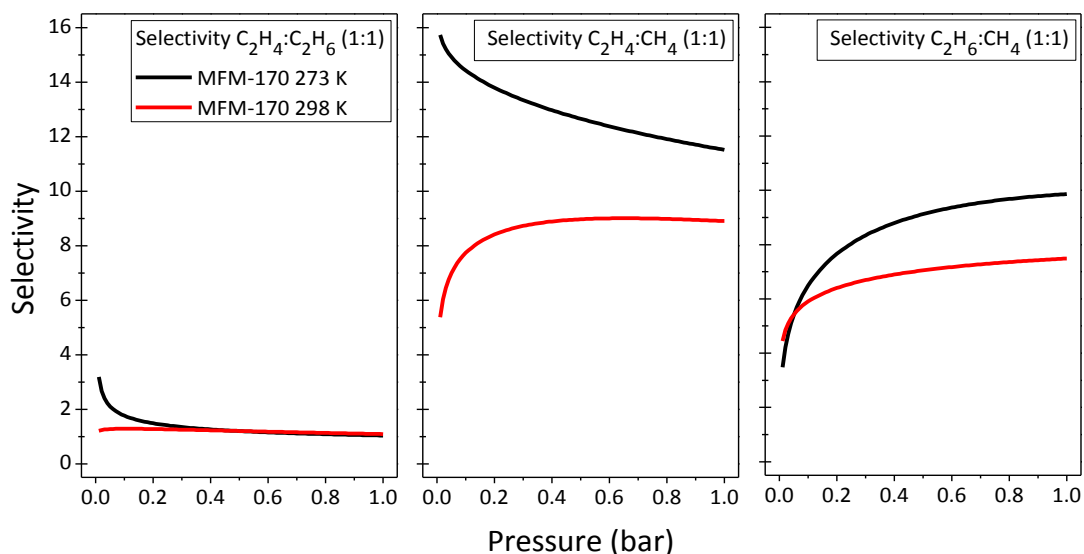


Figure 2.27: IAST selectivity values of 1:1 mixtures of hydrocarbon gases to ambient pressures at 273 K and 298 K based on single component isotherms of each gas. From left to right: $C_2H_4:C_2H_6$, $C_2H_4:CH_4$ and $C_2H_6:CH_4$.

As suggested by the similar isotherm profiles of C_2H_4 and C_2H_6 , MFM-170 demonstrates negligible selectivity between the two light hydrocarbons (Figure 2.27), making MFM-170 a poor candidate for separation applications. Despite demonstrating a high CH_4 adsorption capacity, MFM-170 reveals good C_2/C_1 hydrocarbon selectivity, attributed to the high heats

of adsorption for the C₂ hydrocarbons. At 1 bar and 298 K, MFM-170 adsorbs 8.9 times more C₂H₄ than CH₄, whilst the C₂H₆/CH₄ selectivity value is 7.5. The IAST parameters are similar to NOTT-202 (C₂H₄/CH₄ = 6.4, C₂H₆/CH₄ = 9.4),⁸⁶ and Fe₂(dobdc) (C₂H₄/CH₄ = 7.8, C₂H₆/CH₄ = 6.5) although far from the parameters demonstrated by highly selective materials FJU-12 (C₂H₄/CH₄ = 26.4, C₂H₆/CH₄ = 30.3)⁹³ and Cu-TDPAT (C₂H₄/CH₄ = 47.2, C₂H₆/CH₄ = 14.6).⁸² Both FJU-12 and Cu-TDPAT contain heterocyclic uncoordinated nitrogen rings and open metal sites; therefore the inclusion of a triazole ring and liberation of the second Cu(II)-paddlewheel site may be the key to improving C₂ hydrocarbon selectivity in MFM-170.

2.4 Conclusions

MFM-170, constructed from Cu(II)-paddlewheel based metal-organic cuboctahedra linked by PPYD⁴⁻ ligands, forms a self-interpenetrated net with two cubic frameworks linked by an pyridyl N-Cu(II) bond. Despite hopes that the increased length and stability of H₄PPYD would prevent interpenetration, the framework is isostructural to the ethyne functionalised [Cu₂EPYD(H₂O)]⁴⁹ and the amide functionalised PCN-124⁵¹/NJU-Bai21.⁵² MFM-170 displays a high stability to activation and hydration, suggested by the retention of crystallinity by PXRD. The longer length of H₄PPYD in comparison to H₄EPYD and H₄APYD leads to increased dimensions of cage B and cage C, increasing the total pore volume compared to PCN-124 and increasing the BET surface area in both cases.

The larger BET surface area and pore dimensions result in an increase in the CO₂ adsorption capacity of MFM-170 compared to [Cu₂EPYD]; however PCN-124 shows superior CO₂ adsorption, attributed to strong interactions between the CO₂ and amide group. The amide groups do not effect CH₄ adsorption capacity and MFM-170 adsorbs more CH₄, and is expected to be a promising candidate for fuel delivery in natural gas vehicles due to its shallow adsorption profile. MFM-170 demonstrates some of the highest adsorption capacities for the light hydrocarbons C₂H₄ and C₂H₆, although the lack of easily-accessible

non sterically-hindered Cu(II) sites reduces the potential for exceptional C₂H₄ adsorption, as seen in Cu-TDPAT.

The large pore volume and high gas adsorption capacities in conjunction with high thermal and chemical stability make MFM-170 a promising framework to use as a base for selective gas sorption applications, which could be improved by the introduction of strong binding sites. Whilst cage A is functionalised by the unsaturated Cu(II)-paddlewheel axial sites, cages B and C remain relatively unfunctionalised and are a suitable target for including guest-specific binding sites.

2.5 Outlook

Cage B, with the largest accessible volume is the obvious first choice for pore functionalisation. There are two potential sites for functionalisation (Figure 2.28); the first site points directly into the centre of cage B and is located *para*- to the pyridyl nitrogen on the central pyridyl ring. With a pore diameter of 16.3 Å there is more than sufficient space to include a range of functional groups, including the CO₂-philic amine group, without detracting on the available space for guest molecules.

The second strategy involves functionalising the “spacer” phenyl ring by either attaching a number of functional groups or substituting the phenyl ring for a heterocyclic ring such as triazine. This approach would simultaneously functionalise cages B and C, due to phenyl ring rotation.

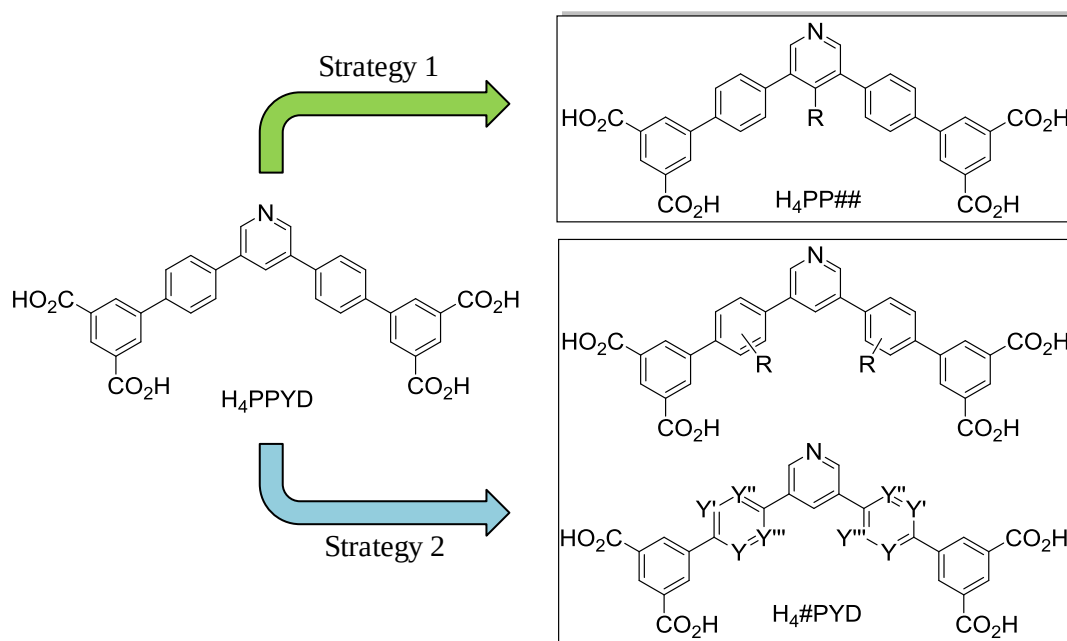
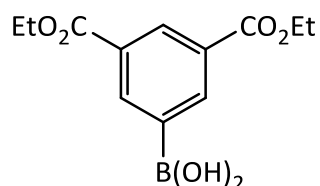


Figure 2.28: The two proposed strategies to functionalise MFM-170 in order to improve specific gas binding interactions and selectivity.

The third and final strategy proposed is to increase the density of both open metal sites and uncoordinated nitrogen atoms by disrupting the formation of the Cu(II)-N bond to synthesise a single net, non-interpenetrated framework. These three approaches to improve the gas uptake and selectivity of MFM-170 will be covered in turn in the next three chapters of this thesis.

2.6 Experimental

Synthesis of 1,3-diethoxy phenyl-5-boronic acid ester (1)

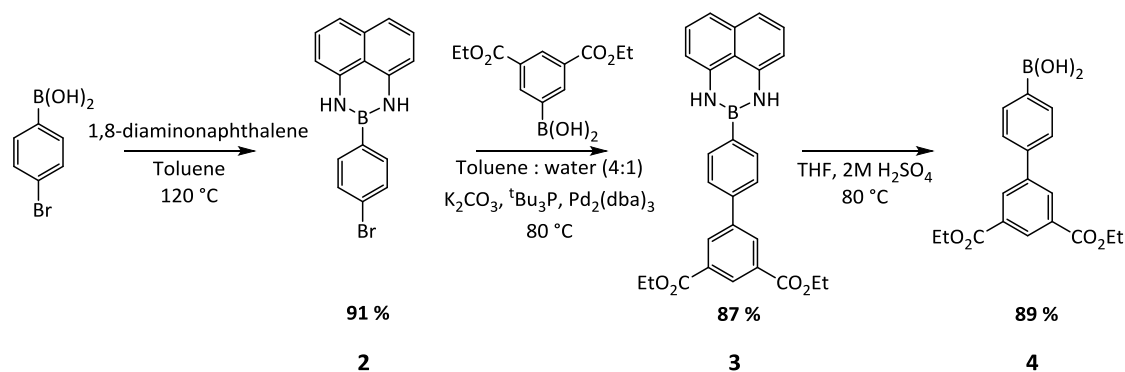


3,5-Dimethylboronic acid (25 g, 0.17 mol) and NaOH (24 g, 0.6 mol) were dissolved in H₂O:BuOH (1L, 4:1 v/v). The mixture was heated to 50 °C and potassium permanganate (165 g, 1 mol) was added portion-wise over a period of five days. The temperature was increased to 70 °C after two thirds had been added. Excess KMnO₄ was reduced by refluxing with isopropyl alcohol (150 ml). Precipitated MnO₂ was removed by filtration and

washed with boiling water. The solvent was reduced *in vacuo*. before addition of HCl resulted in the precipitation of a white solid, isolated by filtration. (29 g, 83%). ^1H NMR (300 MHz, DMSO- d_6) δ ppm: 8.10 (2 H, d, $J = 1.8$ Hz), 8.29 (1 H, t, $J = 1.8$ Hz), 8.87 (2 H, br s). ^{13}C NMR (75 MHz, CDCl_3) δ ppm: 165.9, 139.6, 131.6, 130.2, 61.7, 31.2, 14.7. MS (ESI) m/z : 209.0255 (M-H) $^-$. IR (ATR) cm^{-1} : 3243 (O-H), 1772 (C=O). Elemental analysis (%): crude: C 46.16, H 4.49, calculated for $\text{C}_8\text{H}_7\text{BO}_6$: C 45.77, H 3.36.

The product was suspended in a solution of EtOH (500 ml) and H_2SO_4 (10.5 ml) and refluxed at 80 °C overnight. The solvent was reduced *in vacuo*. and product precipitated by the addition of water. The solid was isolated by filtration, washed with water and dried. (29 g, 78%). ^1H NMR (300 MHz, DMSO- d_6) δ ppm: 1.35 (6 H, t, $J = 7.06$ Hz), 4.36 (4 H, q, $J = 7.06$ Hz), 8.51 (1 H, t, $J = 1.79$ Hz), 8.64 (2 H, d, $J = 1.79$ Hz). ^{13}C NMR (67.5 MHz, DMSO- d_6) δ ppm: 165.1, 138.9, 130.9, 129.5, 60.9, 14.0. MS (ESI) m/z : 267.1033 (M+H) $^+$. IR (ATR) cm^{-1} : 1721 (C=O). Elemental analysis (%): crude: C 54.22, H 5.68, calculated for $\text{C}_{12}\text{H}_{15}\text{BO}_6$: C 54.17, H 5.68.

Synthesis of the “extended isophthalate boronic acid” unit



Diaminonaphthalene protection of (4-bromophenyl)boronic acid (2)

4-Bromophenylboronic acid (3.11 g, 15.5 mmol) and 1,8-diaminonaphthalene (2.69 g, 17 mmol) were dissolved in toluene (250 ml) and heated to 120 °C in an open flask for 2 hours. The solvent was removed *in vacuo*. and the product recrystallised from DCM with petroleum ether. (4.55 g, 91%). ^1H NMR (400 MHz, CDCl_3) δ ppm 6.00 (2 H, br s), 6.45 (2 H, dd, $J = 7.22, 0.94$ Hz), 7.10 (2 H, m), 7.18 (2 H, m), 7.54 (2 H, m), 7.61 (2 H, m). ^{13}C

NMR (67.5 MHz, $CDCl_3$) δ ppm: 140.7, 136.3, 133.0, 131.4, 127.6, 124.9, 119.8, 118.0, 106.1. MS (ESI) m/z : 369.0215 ($M+COOH$)⁻. IR (ATR) cm^{-1} : 3413 (N-H). Elemental analysis (%): crude: C 59.33, H 3.65, N 8.70, calculated for $C_{16}H_{12}BN_2Br$: C 59.50, H 3.74, N 8.67.

Suzuki coupling reaction to give 1,3-diethyl 5-(4-{2,4-diaza-3-boratricyclo[7.3.1.0^{5,13}]trideca-1(12),5,7,9(13),10-pentaen-3-yl}phenyl)benzene-1,3-dicarboxylate (3)

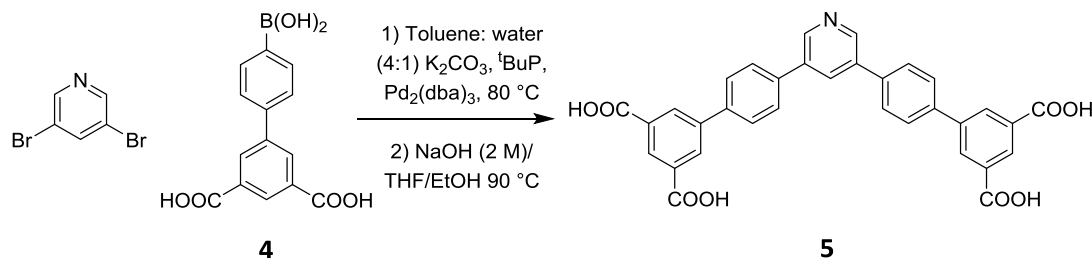
1 (4.65 g, 17.5 mmol), **2** (3.77 g, 11.7 mmol) and K_2CO_3 (5 g, 36 mmol) were dissolved in a solution of toluene:water (500 ml, 4:1 v/v) and degassed at 60 °C. Tris(tertbutyl)phosphine (1 M solution in toluene, 0.3 ml, 0.3 mmol) and $Pd_2(dba)_3$ (250 mg, 0.3 mmol) were added and the reaction heated to 80 °C until deemed complete by TLC. The product was extracted into DCM and the solvent removed *in vacuo*. before being recrystallised from DCM with petroleum ether to give a yellow solid. (4.5 g, 87%). ^1H NMR (300 MHz, $CDCl_3$) δ ppm: 1.46 (6 H, t, $J = 7.2$ Hz), 4.47 (4 H, q, $J = 7.2$ Hz), 6.11 (2 H, s), 6.46 (2 H, dd $J = 7.3$ Hz, 1 Hz), 7.12 (4 H, m), 7.76 (4 H, d, $J = 2.7$ Hz), 8.50 (2 H, d, $J = 1.6$ Hz), 8.68 (2 H, $J = 1.6$ Hz). ^{13}C NMR (67.5 MHz, $DMSO-d_6$) δ ppm: 165.4, 142.0, 140.0, 135.6, 132.0, 131.8, 128.9, 126.5, 62.0, 14.7. MS (ESI) m/z : 465.1550 ($M+H$)⁺. IR (ATR) cm^{-1} : 3414 (N-H), 1704 (C=O). Elemental analysis (%): crude: C 72.14, H 5.40, N 5.88, calculated for $C_{28}H_{25}BN_2O_4$ C 72.43, H 5.43, N 6.03.

Deprotection of (3) to give {4-[3,5-bis(ethoxycarbonyl)phenyl]phenyl}boronic acid (4)

3 (4.5 g, 9.7 mmol) was dissolved in a mixture of THF (300 ml) and H_2SO_4 (2 M, 50 ml). The solution was refluxed at 80 °C. Precipitated diaminonaphthalene was removed by filtration. Solvent was reduced *in vacuo*. and the product precipitated from solution by addition of water to give a light brown powder. (2.95 g, 89%). ^1H NMR (400 MHz, $DMSO-d_6$) δ ppm: 1.37 (6 H, t, $J = 7.1$ Hz), 4.40 (4 H, q, $J = 7.1$ Hz), 7.72 (2 H, d, $J = 8.2$ Hz), 7.94 (2 H, d, $J = 8.2$ Hz), 8.15 (2 H, br s), 8.42 (2 H, d, $J = 1.6$ Hz), 8.46, (1 H, t, $J = 1.6$ Hz). ^{13}C NMR (67.5 MHz, $DMSO-d_6$) δ ppm: 165.4, 142.0, 140.0, 135.6, 132.0, 131.8, 128.9,

126.5, 62.0, 14.7. MS (ESI) m/z : 343.1337 ($M+H$)⁺. IR (ATR) cm^{-1} : 3379 (O-H), 3414 (N-H), 1697 (C=O). Elemental analysis (%): crude: C 62.69, H 5.58, calculated for $\text{C}_{18}\text{H}_{19}\text{BO}_6$: C 63.19, H 5.60.

Synthesis of H_4PPYD (5)



4 (1.5 g, 4.4 mmol), 3,5-dibromopyridine (0.41 g, 1.8 mmol) and K_2CO_3 (0.73 g, 5.4 mmol) were dissolved in a solution of toluene:water (125 ml, 4:1 v/v) and degassed at 60 °C. Tritertbutylphosphine (1 M solution in toluene, 0.1 ml, 0.1 mmol) and $\text{Pd}_2(\text{dba})_3$ (82 mg, 0.1 mmol) were added and the reaction heated to 80 °C until deemed complete by TLC. The product was extracted into DCM and the solvent removed *in vacuo*, before being recrystallised from DCM with MeOH. (1.1 g, 93%). ^1H NMR (300 MHz, CDCl_3) δ ppm: 1.47 (12 H, t, $J = 7.1$ Hz), 4.48 (8 H, q, $J = 7.1$ Hz), 7.83 (8 H, m), 8.19 (1 H, t, $J = 2.2$ Hz), 8.53 (2 H, d, $J = 1.6$ Hz), 8.70 (2 H, t, $J = 1.6$ Hz), 8.93 (2 H, d, $J = 2.2$ Hz). ^{13}C NMR (100 MHz, CDCl_3): 165.56, 141.54, 140.27, 140.07, 139.95, 137.34, 133.06, 132.13, 131.84, 130.10, 128.75, 127.93, 61.65, 14.36. MS (ESI) m/z : 673.2547 ($M+H$)⁺. IR (ATR) cm^{-1} : 2976 (C-H), 1726 (C=O). Elemental analysis (%): crude: C 73.28, H 5.34, N 1.95, calculated for $\text{C}_{41}\text{H}_{17}\text{NO}_8$: C 73.31, H 5.55, N 2.09.

The product was suspended in a solution of NaOH (2 M, 50 ml), THF (25 ml) and EtOH (25 ml) and stirred at 90 °C overnight. (0.84 g, 89 %). ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ ppm: 7.88 (4 H, d, $J = 8.45$ Hz), 8.04 (4 H, d, $J = 8.45$ Hz), 8.35 (4 H, d, 1.5 Hz), 8.48 (1 H, t, 2.1 Hz), 8.49 (2 H, t, $J = 1.5$ Hz), 8.99 (2 H, d, 2.1 Hz). ^{13}C NMR (400 MHz, $\text{DMSO}-d_6$) δ ppm: 166.46, 142.25, 140.26, 139.07, 136.86, 136.60, 135.08, 132.24, 131.35, 129.16, 128.40, 127.77. MS: (ESI) m/z 560.1348 ($M+H$)⁺. IR (ATR) cm^{-1} : 3349 (O-H), 1698 (C=O).

Elemental analysis (%): crude: C 69.12, H 4.12, N 2.88, calculated for $C_{33}H_{21}NO_8$: C 70.84, H 3.78, N 2.50.

Synthesis of MFM-170

5 (192 mg, 0.36 mmol) and $Cu(NO_3)_2 \cdot 5/2(H_2O)$ (298 mg, 1.28 mmol) were dissolved in a solution of DMF:H₂O (48 ml, 5:1) and acidified with concentrated HNO₃ (0.3 ml). The solution was heated in a Schott bottle at 80 °C overnight until blue octahedral crystals precipitated. The product was filtered, washed with hot DMF and dried in air. (320 mg, 86 %). IR (ATR) cm^{-1} : 3349 (O-H), 1698 (C=O). Elemental analysis (%): crude: C 52.93, H 4.61, N 7.18, calculated for $[Cu_2PPYD(H_2O)] \cdot (H_2O)_3(DMF)_5$: C 51.47, H 5.40, N 7.50.

2.7 References

- 1 V. Zelenák, Z. Vargová, M. Almáši, A. Zelenáková and J. Kuchár, *Microporous Mesoporous Mater.*, 2010, **129**, 354–359.
- 2 H. Wang and S. Liu, *Synth. React. Inorganic, Met. Nano-Metal Chem.*, 2016, **46**, 1422–1425.
- 3 Y. Wu, G. Yang, X. Zhou, J. Li, Y. Ning and Y. Wang, *Dalton Trans.*, 2015, **44**, 10385–10391.
- 4 X. Zhao, F. Liu, L. Zhang, D. Sun and R. Wang, *Chem. Eur. J.*, 2014, **20**, 649–652.
- 5 F. Wang, X. Jing, B. Zheng, G. Li, G. Zeng, Q. Huo and Y. Liu, *Cryst. Growth Des.*, 2013, **13**, 3522–3527.
- 6 P. Smart, C. A. Mason, J. R. Loader, A. J. H. M. Meijer, A. J. Florence, K. Shankland, A. J. Fletcher, S. P. Thompson, M. Brunelli, A. H. Hill and L. Brammer, *Chem. Eur. J.*, 2013, **19**, 3552–3557.
- 7 X.-Y. Cao, Z.-J. Li, J. Zhang, Y.-Y. Qin, J.-K. Cheng and Y.-G. Yao, *CrystEngComm*, 2008, **10**, 1345.
- 8 M. Xue, G. Zhu, H. Ding, L. Wu, X. Zhao and Z. Jin, *Cryst. Growth Des.*, 2009, **9**, 1481–1488.
- 9 J. Qian, F. Jiang, K. Su, J. Pan, L. Liang, F. Mao and M. Hong, *Cryst. Growth Des.*, 2015, **15**, 1440–1445.
- 10 X. Yan, L. Qin, L. Yu and L. Han, *J. Mol. Struct.*, 2013, **1051**, 164–168.
- 11 D. Deng, A. G. Kang, C. B. Ji, D. H. Li, G. Qu, B. X. Fan, B. C. Ruan and C. T. Li, *Aust. J. Chem.*, 2013, **66**, 1342–1351.
- 12 X. Rao, J. Cai, J. Yu, Y. He, C. Wu, W. Zhou, T. Yildirim, B. Chen and G. Qian, *Chem. Commun.*, 2013, **2**, 4–6.
- 13 A. Maiti, *Int. J. Quantum Chem.*, 2014, **114**, 163–175.
- 14 J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 13850–13851.
- 15 C. Wang, Z. Xie, K. E. deKrafft and W. Lin, *J. Am. Chem. Soc.*, 2011, **133**, 13445–13454.
- 16 J. M. Chem, S. M. Barrett, C. Wang and W. Lin, *J. Mater. Chem.*, 2012, **2**, 10329–10334.
- 17 H. Fei, M. D. Sampson, Y. Lee, C. P. Kubiak and S. M. Cohen, *Inorg. Chem.*, 2015, **54**, 6821–6828.
- 18 W. A. Maza, R. Padilla and A. J. Morris, *J. Am. Chem. Soc.*, 2015, **137**, 8161–8168.

- 19 L. Chen, X. Chen, H. Liu and Y. Li, *Small*, 2015, **11**, 2642–2648.
- 20 V. I. Isaeva, O. P. Tkachenko, T. R. Brueva, V. D. Nissenbaum, I. V. Mishin, W. Gruenert and L. M. Kustov, *Russ. J. Phys. Chem. A*, 2011, **85**, 462–465.
- 21 KR 2013026183, 2013.
- 22 S. M. Humphrey, T. J. P. Angliss, M. Aransay, D. Cave, E. A. Gerrard, G. F. Weldon and P. T. Wood, *Zeitschrift für Anorg. und Allg. Chemie*, 2007, **633**, 2342–2353.
- 23 S. Sha, H. Yang, J. Li, C. Zhuang, S. Gao and S. Liu, *Catal. Commun.*, 2014, **43**, 146–150.
- 24 G. Chen, Z. Zhang, S. Xiang, B. Chen, H. Xu, Y. He, Z. Zhang, S. Xiang, J. Cai, Y. Cui, Y. Yang, G. Qian and B. Chen, *J. Mater. Chem. A*, 2013, **1**, 77–81.
- 25 Y. Liu, Y. Zhang, G. H. Hu, S. Zhou, R. Fan, Y. Yang and Y. Xu, *Chem. Eur J.*, 2015, **21**, 10391–10399.
- 26 H. S. Athwal, *Thesis*, 2012.
- 27 S. Xiang, J. Huang, L. Li, J. Zhang, L. Jiang, X. Kuang and C.-Y. Su, *Inorg. Chem.*, 2011, **50**, 1743–1748.
- 28 Y. Liu, H. Li, Y. Han, X. Lv, H. Hou and Y. Fan, *Cryst. Growth Des.*, 2012, **12**, 3505–3513.
- 29 J. Jia, H. S. Athwal, A. J. Blake, N. R. Champness, P. Hubberstey and M. Schröder, *Dalton Trans.*, 2011, **40**, 12342–12349.
- 30 S.-J. Liu, L. Xue, T.-L. Hu and X.-H. Bu, *Dalton Trans.*, 2012, **41**, 6813–6819.
- 31 H. Li, W. Shi, K. Zhao, Z. Niu, X. Chen and P. Cheng, *Chemistry*, 2012, **18**, 5715–5723.
- 32 Q. Zhang, F. Hu, S. Wang, D. Sun, D. Wang and J. Dou, *Aust. J. Chem.*, 2012, **65**, 524–530.
- 33 J. Huang, H. Li, J. Zhang, L. Jiang and C.-Y. Su, *Inorganica Chim. Acta*, 2012, **388**, 16–21.
- 34 Q. Li and S. Du, *RSC Adv.*, 2015, **5**, 9898–9903.
- 35 Y. Sun, G. Xiong, V. Dragutan, I. Dragutan, F. Ding and Y. Sun, *Inorg. Chem. Commun.*, 2015, **62**, 103–106.
- 36 J. Jia, X. Lin, C. Wilson, A. J. Blake, N. R. Champness, P. Hubberstey, G. Walker, E. J. Cussen and M. Schröder, *Chem. Commun.*, 2007, **3**, 840–842.
- 37 Y.-S. Wei, K.-J. Chen, P.-Q. Liao, B.-Y. Zhu, R.-B. Lin, H.-L. Zhou, B.-Y. Wang, W. Xue, J.-P. Zhang and X.-M. Chen, *Chem. Sci.*, 2013, **4**, 1539–1546.
- 38 X. Zhao, C. Mao, K. T. Luong, Q. Lin, Q. Zhai and P. Feng, *Angew. Chem. Int. Ed.*, 2016, **55**, 2768–2772.
- 39 S. Yao, D. Wang, Y. Cao, G. Li, Q. Huo and Y. Liu, *J. Mater. Chem. A*, 2015, **3**, 16627–16632.
- 40 Q. Zhai, Q. Lin, T. Wu, S.-T. Zheng, X. Bu and P. Feng, *Dalton Trans.*, 2012, **41**, 2866–2868.
- 41 D. J. Tranchemontagne, J. L. Mendoza-Cortés, M. O’Keeffe and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1257–1283.
- 42 R. Yun, Y. Jiang, S. Luo and C. Chen, *RSC Adv.*, 2014, **4**, 36845–36848.
- 43 P. Cui, X. Zhang, Y. Zhao, A. Fu and W. Sun, *Dalton Trans.*, 2016, **45**, 2591–2597.
- 44 P.-P. Cui, X.-D. Zhang, Y. Zhao, K. Chen, P. Wang and W.-Y. Sun, *Microporous Mesoporous Mater.*, 2015, **208**, 188–195.
- 45 T. Ding, L. Ren, X. Du, L. Quan, Z. Gao, W. Zhang and C. Zheng, *CrystEngComm*, 2014, **16**, 7790–7801.
- 46 Z. Lu, L. Du, K. Tang and J. Bai, *Cryst. Growth Des.*, 2013, **13**, 2252–2255.
- 47 Y. Liu, J.-R. Li, W. M. Verdegaal, T.-F. Liu and H.-C. Zhou, *Chemistry*, 2013, **19**, 5637–5643.
- 48 S. Ma, X. Wang, C. D. Collier, E. S. Manis and H.-C. Zhou, *Inorg. Chem.*, 2007, **46**, 8499–8501.
- 49 P. Zhang, B. Li, Y. Zhao, X. Meng and T. Zhang, *Chem. Commun.*, 2011, **47**, 7722–7724.

- 50 X. Liu, M. Park, S. Hong, M. Oh, J. W. Yoon, J.-S. Chang and M. S. Lah, *Inorg. Chem.*, 2009, **48**, 11507–11509.
- 51 J. Park, J.-R. Li, Y.-P. Chen, J. Yu, A. A. Yakovenko, Z. U. Wang, L.-B. Sun, P. B. Balbuenaba and H.-C. Zhou, *Chem. Commun.*, 2012, **48**, 9995–9997.
- 52 Z. Lu, J. Bai, C. Hang, F. Meng, W. Liu and Y. Pan, *Chem. Eur. J.*, 2016, **22**, 6277–6285.
- 53 V. A. Blatov, *IUCr CompComm Newsl.*, 2006, **7**, 38–143.
- 54 Y. Yan, S. Yang, A. J. Blake, W. Lewis, E. Poirier, S. A. Barnett, N. R. Champness and M. Schröder, *Chem. Commun.*, 2011, **47**, 9995–9997.
- 55 C. Tan, S. Yang, N. R. Champness, X. Lin, A. J. Blake, W. Lewis and M. Schröder, *Chem. Commun.*, 2011, **47**, 4487–4489.
- 56 Z.-J. Lin, Y.-B. Huang, T.-F. Liu, X.-Y. Li and R. Cao, *Inorg. Chem.*, 2013, **52**, 3127–3132.
- 57 Y. Inokuma, T. Arai and M. Fujita, *Nat. Chem.*, 2010, **2**, 780–783.
- 58 A. L. Spek, *Acta. Crystallogr. Sect. D*, 2009, **65**, 148.
- 59 X. Duan, Y. He, Y. Cui, Y. Yang, R. Krishna, B. Chen and G. Qian, *RSC Adv.*, 2014, **4**, 23058–23063.
- 60 W. Gao, R. Cai, T. Pham, K. A. Forrest, A. Hogan, P. Nugent, K. Williams, L. Wojtas, R. Luebke, Ł. J. Weselin, M. J. Zaworotko, B. Space, Y. Chen, M. Eddaoudi, X. Shi and S. Ma, *Chem. Mater.*, 2015, **27**, 2144–2151.
- 61 P. M. Schoenecker, C. G. Carson, H. Jasuja, C. J. J. Flemming and K. S. Walton, *Ind. Eng. Chem. Res.*, 2012, **51**, 6513–6519.
- 62 D. Ma, Y. Li and Z. Li, *Chem. Commun.*, 2011, **47**, 7377–7379.
- 63 X. Wang, W. Gao, J. Luan, L. Wojtas and S. Ma, *Chem. Commun.*, 2016, **52**, 1971–1974.
- 64 M. Klimakow, P. Klobes, A. F. Thünemann, K. Rademann and F. Emmerling, *Chem. Mater.*, 2010, **22**, 5216–5221.
- 65 T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille and G. Férey, *Chemistry*, 2004, **10**, 1373–1382.
- 66 S. Yang, J. Sun, A. J. Ramirez-Cuesta, S. K. Callear, W. I. F. David, D. P. Anderson, R. Newby, A. J. Blake, J. E. Parker, C. C. Tang and M. Schröder, *Nat. Chem.*, 2012, **4**, 887–894.
- 67 J. An, S. J. Geib and N. L. Rosi, *J. Am. Chem. Soc.*, 2010, **132**, 38–39.
- 68 D.-M. Chen, X.-P. Zhang, W. Shi and P. Cheng, *Inorg. Chem.*, 2015, **54**, 5512–5518.
- 69 P. Zhang, B. Li, Y. Zhao, X. Meng and T. Zhang, *Chem. Commun.*, 2011, **47**, 7722–7724.
- 70 B. Zheng, J. Bai, J. Duan, L. Wojtas and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2011, **133**, 748–751.
- 71 B. Li, Z. Zhang, Y. Li, K. Yao, Y. Zhu, Z. Deng, F. Yang, X. Zhou, G. Li, H. Wu, N. Nijem, Y. J. Chabal, Z. Lai, Y. Han, Z. Shi, S. Feng and J. Li, *Angew. Chem. Int. Ed.*, 2012, **51**, 1412–1415.
- 72 N. H. Alsmail, M. Suyetin, Y. Yan, R. Cabot, C. P. Krap, J. Lü, T. L. Easun, E. Bichoutskaia, W. Lewis, A. J. Blake and M. Schröder, *Chemistry*, 2014, **20**, 7317–7324.
- 73 S. Xiong, Y. He, R. Krishna, B. Chen and Z. Wang, *Cryst. Growth Des.*, 2013, **13**, 2670–2674.
- 74 Z.-H. Xuan, D.-S. Zhang, Z. Chang, T.-L. Hu and X.-H. Bu, *Inorg. Chem.*, 2014, **53**, 8985–8990.
- 75 B. Zheng, X. Lin, Z. Wang, R. Yun, Y. Fan, M. Ding, X. Hua and P. Yi, *CrystEngComm*, 2014, **16**, 9586–9589.
- 76 S. R. Caskey, A. G. Wong-Foy and A. J. Matzger, *J. Am. Chem. Soc.*, 2008, **130**, 10870–10871.
- 77 M. Savage, S. Yang, M. Suyetin, E. Bichoutskaia, W. Lewis, A. J. Blake, S. A. Barnett and M. Schröder, *Chem. Eur. J.*, 2014, **20**, 8024–8029.

- 78 Y. Peng, V. Krungleviciute, I. Eryazici, J. T. Hupp, O. K. Farha and T. Yildirim, *J. Am. Chem. Soc.*, 2013, **135**, 11887–11894.
- 79 C. E. Wilmer, O. K. Farha, T. Yildirim, I. Eryazici, V. Krungleviciute and A. A. Sarjeant, *Energy Environ. Sci.*, 2013, **6**, 1158–1163.
- 80 J. A. Mason and M. Veenstra, *Chem. Sci.*, 2014, **5**, 32–51.
- 81 K. Konstantas, T. Osl, Y. Yang, M. Batten, N. Burke, J. Hill and M. R. Hill, *J. Mater. Chem.*, 2012, **22**, 16698–16708.
- 82 K. Liu, D. Ma, B. Li, Y. Li, K. Yao and Z. Zhang, *J. Mater. Chem. A*, 2014, **2**, 15823–15828.
- 83 E. D. Bloch, W. L. Queen, R. Krishna, J. M. Zadrozny, C. M. Brown and J. R. Long, *Science*, 2012, **335**, 1606–1610.
- 84 J. Ran and M. W. Wong, *J. Phys. Chem. A*, 2006, **110**, 9702–9709.
- 85 A. M. Plonka, X. Chen, H. Wang, R. Krishna, X. Dong, D. Banerjee, W. R. Woerner, Y. Han, J. Li and J. B. Parise, *Chem. Mater.*, 2016, **28**, 1636–1646.
- 86 S. Gao, C. G. Morris, Z. Lu, Y. Yan, H. G. W. Godfrey, C. Murray, C. C. Tang, K. M. Thomas, S. Yang and M. Schröder, *Chem. Mater.*, 2016, **28**, 2331–2340.
- 87 B. Li, H. Wang and B. Chen, *Chem. Asian J.*, 2014, **9**, 1474–1498.
- 88 Z. H. Rada, H. R. Abid, H. Sun and S. Wang, *J. Chem. Eng. Data*, 2015, **60**, 2152–2161.
- 89 H.-H. Wang, W.-J. Shi, L. Hou, G.-P. Li, Z. Zhu and Y.-Y. Wang, *Chem. Eur. J.*, 2015, **21**, 16525–16531.
- 90 C. Song, Y. He, B. Li, Y. Ling, H. Wang, Y. Feng, R. Krishna and B. Chen, *Chem. Commun.*, 2014, **50**, 12105–12108.
- 91 J. Cai, H. Wang, H. Wang, X. Duan, Z. Wang, Y. Cui, Y. Yang, B. Chen and G. Qian, *RSC Adv.*, 2015, **5**, 77417–77422.
- 92 L. Pinto and V. K. Saini, *Appl. Mater. Interfaces*, 2014, **6**, 12093–12099.
- 93 Y. Chen, Z. Li, Q. Liu, Y. Shen, X. Wu, D. Xu, X. Ma, L. Wang, Q. Chen, Z. Zhang and S. Xiang, *Cryst. Growth Des.*, 2015, **15**, 3847–3852.

Chapter 3: Investigating the Effect of Functionalisation of Cage B on the Gas Adsorption Properties of MFM-17X

3.1 Introduction

MFM-170, described in Chapter 2, is a highly promising base for selective gas sorption applications due to its high thermal and chemical stability. Large BET surface area and pore volumes lead MFM-170 to demonstrate good gas adsorption capacities at high pressure, whereas a lack of strong binding sites on the framework surface limit low pressure uptake. Modification of MOFs to introduce additional organic functional group binding sites into the framework has been shown to be an effective method to target and enhance the adsorption of specific gases. Highly polar functionalities such as amino,¹ hydroxyl, trifluoromethyl and carboxylic acid groups have been shown to exhibit strong interactions with the quadrupole moment of CO₂. The effects of modifying a material with an additional functional group can also be more indirect; electron donating substituents such as methyl groups strengthen the interactions between CO₂ and the aromatic π -electron clouds of their adjoining framework phenyl rings;^{2,3} whilst electron withdrawing aromatic substituents, such as halogens, can enhance the acidity of aromatic protons, allowing for the formation of weak hydrogen-bond interactions with guest species.² For the next generation of high performing MOFs, it is essential to generate materials with optimal pore geometries and functionalities for gas adsorption.

Computational methods such as Density Functional Theory (DFT) and Grand Canonical Monte Carlo (GCMC) simulations have been used widely to determine the location of strong binding sites within MOFs. An emerging alternative to computational simulations is to study the structure and dynamics of MOFs under usage conditions (*in situ*). The highly crystalline nature of these materials makes visualisation of binding sites possible by X-ray and neutron diffraction techniques, while strong interactions between gas molecules and the framework surface allow for the dynamics to be investigated by spectroscopic means. While these experiments can provide a unique insight into the materials under investigation, they

can also be extremely challenging as the low concentrations of localised guest species often make only a small contribution to commonly weak diffraction patterns or the overall spectra. Each technique has its own advantages and disadvantages, which are explored further below.

By far the most common method used to visualise guest molecules within a framework is PXRD⁴ which is capable of analysing large amounts of sample, increasing the strength of diffraction peaks. The analysis of microcrystalline samples avoids the often laborious process of growing single crystals; however PXRD data can be difficult to manipulate. Data is projected onto one axis, resulting in overlapping diffraction peaks; therefore refinement requires complex computational models with large unit cells and numbers of constituent atoms.

SCXRD offers a large data/parameter ratio, with data collected in three dimensions, allowing unambiguous determination of the position of adsorbed guest species.^{1,5-8,9} Recently, Fujita *et al.* notably used a MOF as a crystalline porous support, performing guest-loaded SCXRD to determine the molecular structure and chiral configuration of a scarce marine natural product, miyakosyne A.¹⁰ This exciting development allows for analysis of liquid or volatile compounds and is highly sensitive; materials can be analysed in nano- to microgram quantities. Disadvantages of SCXRD include weak diffraction from a single crystals and awkward guest loading procedures, requiring the use of custom-made gas panels and goniometers.

Neutron diffraction is particularly suited to locating species which contain a large proportion of hydrogen atoms (such as H₂ or CH₄); as H has one of the highest neutron scattering cross sections but is almost X-ray transparent.¹¹ Samples can be exposed to harsher activation temperatures as the vanadium sample holder used for neutron diffraction can be subjected to larger extremes of temperature and pressure than the glass capillary required for PXRD; however prohibitively large quantities (>1g) of deuterated sample are required for routine analysis.

IR and Raman spectroscopy are limited to analysis of functional groups;¹²⁻¹³ but allows for studies on the dynamics of adsorption. The magnitude of shift in the peak position of an IR band attributed to a functional group can indicate the strength of binding interaction, whilst time dependent experiments allow for kinetic studies.¹³

This chapter concerns the synthesis of functionalised analogues of MFM-170 and a comparison of their gas adsorption properties. In order to rationalise the relative gas adsorption capacities, CO₂ binding sites are identified by *in situ* IR spectroscopic and SCXRD experiments, leading to a deeper understanding of the properties of the MFM-17X series.

3.1.1 *In Situ* Studies in MIL-53

The earliest *in situ* PXRD experiments on MOFs concerned guest induced structural changes in flexible materials such as NOTT-202,¹⁴ MIL-47¹⁵ and MIL-53.^{8,15-18} MIL-53 is constructed from inorganic chains of corner sharing octahedra joined by terephthalate ligands in a two-dimensional diamond net (Figure 3.1). The framework has been synthesised from a wide range of different metal centres,¹⁹⁻²⁴ and is frequently studied due to its unusual reversible breathing effect. MIL-53 has three main conformations; a non porous, as-synthesised structure gives way to a porous framework upon guest loading at low pressure, with narrow pores measuring 2.6 Å × 13.6 Å; whilst adsorption of CO₂ at high pressures leads to a large pore structure with channel diameters of 8.5 Å × 8.5 Å. Both transitions are reversible upon desorption.

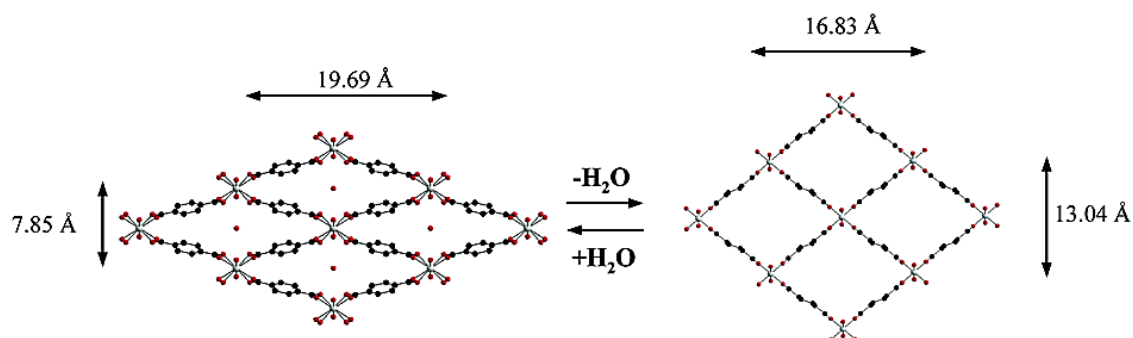


Figure 3.1: Demonstration of the breathing effect in MIL-53(Cr) showing the hydrated narrow pore conformation and dehydrated large pore conformation. (Cr(II), white; C, black; O, red).

Serre *et al.* reported the location of two adsorbed CO₂ molecules in the low pressure (narrow pore) structure of MIL-53(Cr) by PXRD.⁸ The location of the binding sites allowed for the determination of a key quadrupolar interaction between adsorbed CO₂ and the hydroxyl group on the MO₆ backbone (Figure 3.2). The interaction with the hydroxyl group was backed up by IR spectroscopic measurements; significant perturbation of the $\nu(\text{OH})$ ($\Delta\nu = 22 \text{ cm}^{-1}$) and $\delta(\text{OH})$ ($\Delta\nu = 30 \text{ cm}^{-1}$) bands can be seen upon CO₂ adsorption. A second interaction was observed between the two parallel adsorbed CO₂ molecules [$\text{C}\cdots\text{O} = 3.15 \text{ \AA}$] and was discovered to play an important part in the transition from the high pressure to low pressure structure upon desorption.

In order to explain the breathing effect on desorption, a computational model of the large pore structure was loaded with the same number of CO₂ molecules found in the narrow pore structure at lower pressures. Geometry optimisation calculations were performed using DFT and showed that adsorbed CO₂ molecules attempt to interact with both hydroxyl groups on opposite sides of the pore, whilst maintaining the parallel arrangement, which pulls the two walls towards each other.

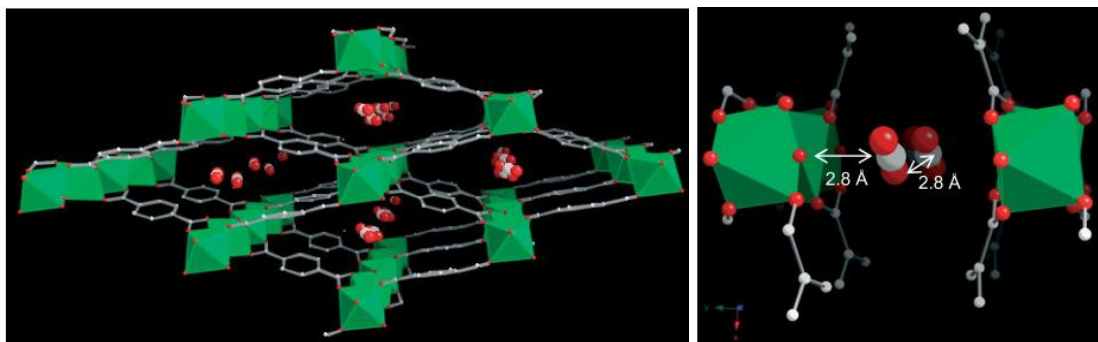


Figure 3.2: *In situ* PXRD of CO₂ adsorption in MIL-53(Fe); location of two CO₂ binding sites in the low pressure (narrow pore) conformation of MIL-53, demonstrating a quadrupolar interaction between CO₂ and the framework hydroxyl group and a parallel CO₂-CO₂ interaction. (Cr(II), green; C, grey; O, red).

In a second study Devic *et al.*²⁵ attempted to increase the CO₂ adsorption capacity of MIL-53(Fe) by introducing strongly interacting amine groups; however MIL-53(Fe)-NH₂ demonstrated no CO₂ adsorption. PXRD analysis revealed strong intra-framework hydrogen bonds between the amine and hydroxyl groups which prevent the non-porous framework from expanding. Conversely MIL-53(Al)-NH₂ demonstrates good adsorption and high selectivity for CO₂. PXRD analysis showed that the intermolecular OH $\cdots$ CO₂ interactions are strong enough to overcome the intramolecular OH $\cdots$ NH₂, whilst the non-porous framework is maintained for other gases.²⁶

3.1.2 *In Situ* Studies in NOTT-300

Schröder *et al.* have used *in situ* CO₂ loaded PXRD to determine host-guest interactions of CO₂ with the family of materials designated MFM-300 (previously NOTT-300).²⁵ The structure of MFM-300 consists of chains of corner sharing [MO₄(O)₂]_n (M=Al, In, Ga, Fe) octahedra linked by biphenyl tetracarboxylate ligands to give one-dimensional square channels, lined with μ_2 -(OH) groups. *In situ* PXRD and inelastic neutron scattering studies on MFM-300(Al) revealed a hydrogen bonding interaction O=C=O(δ^-) $\cdots$ H(δ^+) between adsorbed CO₂ and the hydroxyl groups, reinforced by weak supramolecular interactions with C-H groups on the aromatic rings. These observations were strongly corroborated by SCXRD studies of CO₂ adsorption within MFM-300(In) (Figure 3.3).²⁸ Due to large

amounts of thermal disorder, SCXRD was carried out at 195 K to reduce the thermal motion and disorder of the adsorbed CO_2 molecules. Two independent CO_2 adsorption sites were located; the first, CO_2^{I} , adsorbs in an end-on configuration to the bridging hydroxyl group disordered over a mirror plane, whilst CO_2^{II} was located perpendicular to CO_2^{I} , lying parallel to the pore channel. The binding distances of the adsorbed CO_2 molecules (3.44 Å) are similar to those observed in the pure component crystal structure of dry ice (3.10 Å), indicating the high packing efficiency of CO_2 at 195 K. Recently *in situ* IR microspectroscopy on $\text{MFM-300(Ga)} \cdot (\text{CO}_2)$ at 298 K revealed a shift of the $\nu(\text{OH})$ hydroxyl band by 7 cm^{-1} , consistent with the formation of a hydrogen bond. The $\nu(\text{OH})$ shift in MFM-300(Ga) is much smaller than that seen in MIL-53(Cr) (22 cm^{-1}), indicating a weaker bond between the hydroxyl group and adsorbed CO_2 in MFM-300(Ga) . Analysis of polarised spectra alluded to the presence of a secondary binding site, consistent with SCXRD observations.⁶

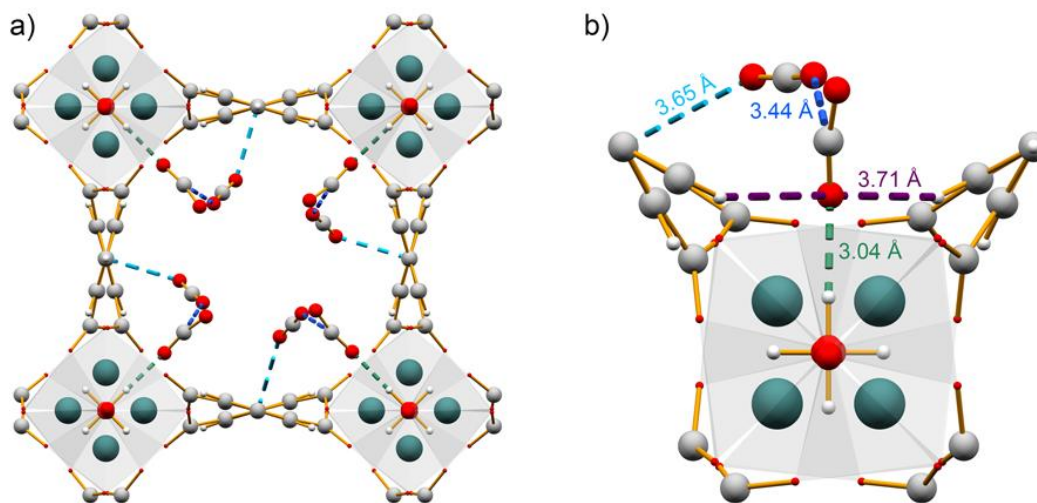


Figure 3.3: View of the positions of adsorbed CO_2 molecules and interactions with MFM-300(In) as determined by single crystal X-ray diffraction. $\text{O}=\text{C}=\text{O}^{\text{I}} \cdots \text{O}-\text{H}$ bonds (green); $\text{O}=\text{C}=\text{O}^{\text{I}} \cdots \text{H}-\text{phenyl}$ bonds (purple); $\text{O}=\text{C}=\text{O}^{\text{II}} \cdots \text{X}=\text{O}^{\text{I}}$ bonds (blue); $\text{O}=\text{C}=\text{O}^{\text{II}} \cdots \text{pore wall}$ bonds (cyan).

3.1.3 In Situ Studies in MOF-74

Open metal sites are regularly reported as important binding sites for adsorbent gases. The MOF CPO-27-Ni (also known as Ni-MOF-74) comprises honeycomb channels with vertices constructed from octahedral Ni(II) metal nodes which feature an open face upon desolvation (Figure 3.4). Adsorbed CO₂ molecules were located by analysis of the PXRD Fourier difference maps of the CO₂ dosed material and were found to coordinate to the Lewis acidic open Ni(II) site in an end-on fashion [Ni...O: 2.29(2) Å]. This distance is shorter than the sum of the van der Waals radii, indicating a strongly physisorption interaction, corroborating the experimentally calculated heat of adsorption of -40 kJ mol⁻¹.⁹ Complementary IR spectroscopic studies reveal a splitting of the doubly degenerate bending mode (ν_2) of CO₂, giving a doublet at 659 and 651 cm⁻¹; attributable to the coordination of bent CO₂ via $\eta^1(\text{O})$ to the Ni(II) ion.

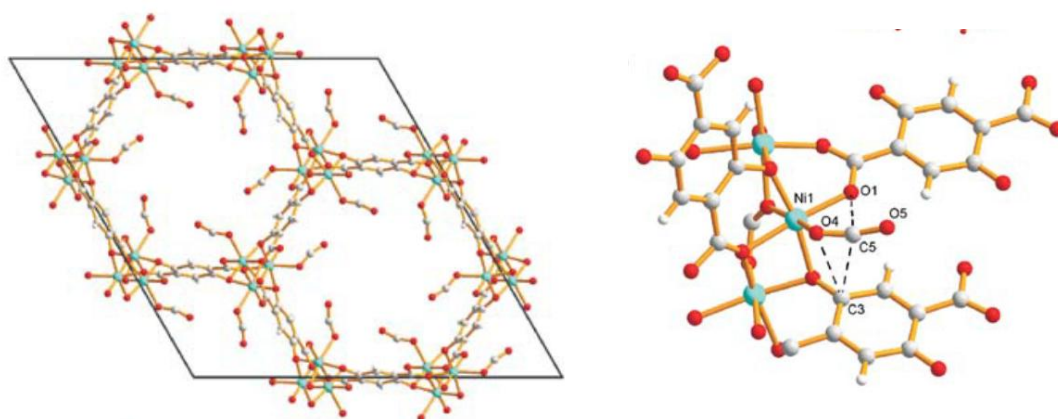


Figure 3.4: The structure of CO₂ loaded CPO-27-Ni, determined by in situ PXRD analysis. The presence of and Ni(II)···O=C=O end-on binding interaction was additionally confirmed by IR spectroscopy.

Wu *et al.* located the adsorbed CO₂ molecules in Mg-MOF-74 (isostructural to CPO-27-Ni) by neutron diffraction; confirming the population of a single binding site located at the unsaturated metal centre.²⁹ Upon increasing the CO₂ pressure, Queen *et al.* observed via neutron diffraction a decrease in the Mg···O=C=O distance (2.39 Å to 2.24 Å) and the formation of a second adsorption site.³⁰ The second CO₂ molecule in Mg-MOF-74 was found canted between two molecules in site I allowing full surface coverage of the pore

(Figure 3.5). Van der Waals density functional (vdW-DF) modelling of IR spectra above 12 Torr (the pressure at which all Mg(II) coordination sites are occupied) corroborate the formation of a secondary adsorption site.³¹

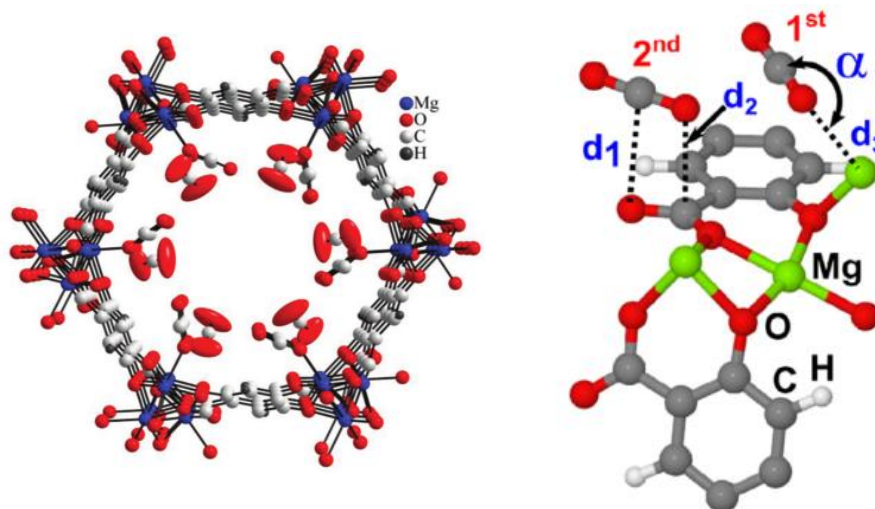


Figure 3.5: Location of the primary and secondary CO₂ adsorption sites in Mg-MOF-74 via neutron diffraction (l) and vdW-DF modelling of IR spectroscopic data (r). The CO₂ molecules in site-II retain anisotropic atomic displacement parameters in the diffraction refinement model due to a difficulty in modelling disorder.

3.1.4 In Situ Studies in ScBDC

ScBDC (BDC = benzenedicarboxylate) is a Sc(III) containing MOF which adopts an orthorhombic *Fddd* symmetry.³² The structure comprises chains of ScO₆ octahedra which are joined by terephthalate ligands to reveal small (3 Å) one-dimensional triangular channels, linked by small windows (ca. 2 Å).

Miller *et al.* studied the adsorption sites of a number of fuel and exhaust gases (CO₂, H₂, CH₄ and C₂H₆) in ScBDC by gas loaded SCXRD.⁷ Upon adsorption of CO₂ at 235 K and 1 bar the terephthalate rings bordering the channels rotate to accommodate more guest species and the space group of the crystal changes from orthorhombic *Fddd* to monoclinic *C2/c*. The phenyl ring rotation gives rise to two different types of triangular channels (A and B) which alternate in rows perpendicular to the *b* axis (Figure 3.6). In the orthorhombic structure the phenyl rings are rotated by 8° away from the *a* axis, whereas in the monoclinic structure

rotation of ring 2b increases to 14° to allow two adsorption sites within channel B, whereas the angle of rotation of ring 2a decreases to 5.8° , allowing only one adsorption site within channel A. The occupancies of the located CO_2 molecules gives a total loading of 3.4 mmol g^{-1} identical to the adsorption isotherm value (250 K and 1 bar), despite a 15 K difference in temperature.

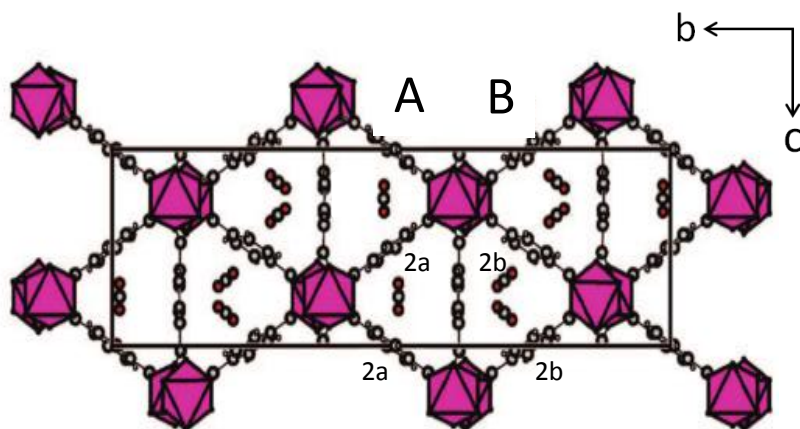


Figure 3.6: View of adsorbed CO_2 within ScBDC, located by SCXRD. A tilting of the aromatic rings by upon CO_2 adsorption leads to the formation of two types of channel, A and B; distorting the crystallographic space group from orthorhombic $Fddd$ to monoclinic $C2/c$. The aromatic rings surrounding channel A rotate by 5.8° , allowing only one CO_2 molecule to be adsorbed in the channel; whereas the aromatic rings surrounding channel B rotate by 14° , giving sufficient space for two CO_2 binding sites.

Greenaway *et al.* studied CO_2 adsorption in the isostructural amine functionalised ScBDC- NH_2 (BDC = 2-amino-1,4-benzenedicarboxylate) by IR microspectroscopy.¹³ Analysis of polarised spectra determined that the adsorbed CO_2 molecules are oriented closer than 20° to the channel axis in ScBDC- NH_2 .

3.2 Aims and Objectives

The aim of the work carried out in this chapter was to increase the gas adsorption capacity of MFM-170 by introducing additional binding sites into cage B. The central pyridyl ring of each H_4PPYD ligand lies perpendicular to the pore surface and the C-H groups *para*- to the pyridyl N point directly into the centre of the pore. Substituting the C-H group for functional groups was predicted to introduce four additional binding sites into the centre of cage B. The effectiveness of three different strategies are assessed; the first featuring uncoordinated

nitrogen atoms, the second including polar carboxylic acid, amine and amide groups and finally incorporating electron donating methyl groups.

The target ligands (Figure 3.7) comprise cores of **pyrazine** (**H₄PPYZ**), **pyridine-4-carboxylic acid** (**H₄PPCA**), **4-aminopyridine** (**H₄PPAN**), **isonicotinamide** (**H₄PPAD**) and **4-methylpyridine** (**H₄PPME**) rings and were synthesised in the same manner as **H₄PPYD** (Chapter 2), substituting the 3,5-dibromopyridine starting material for a functionalised analogue.

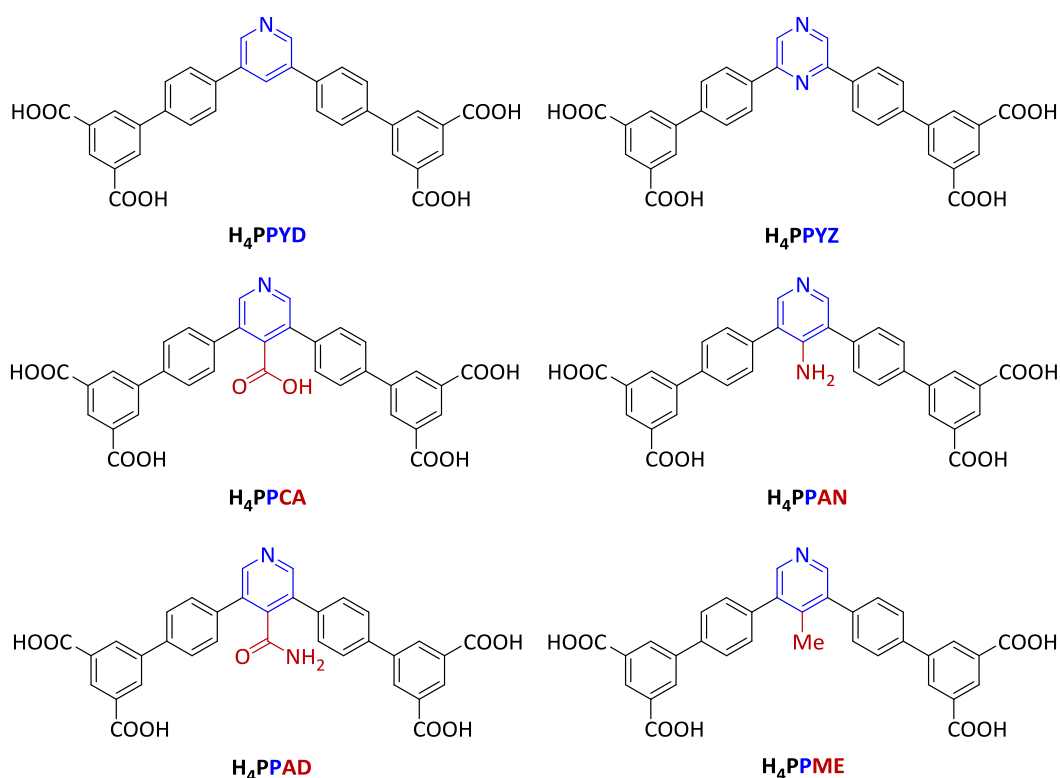


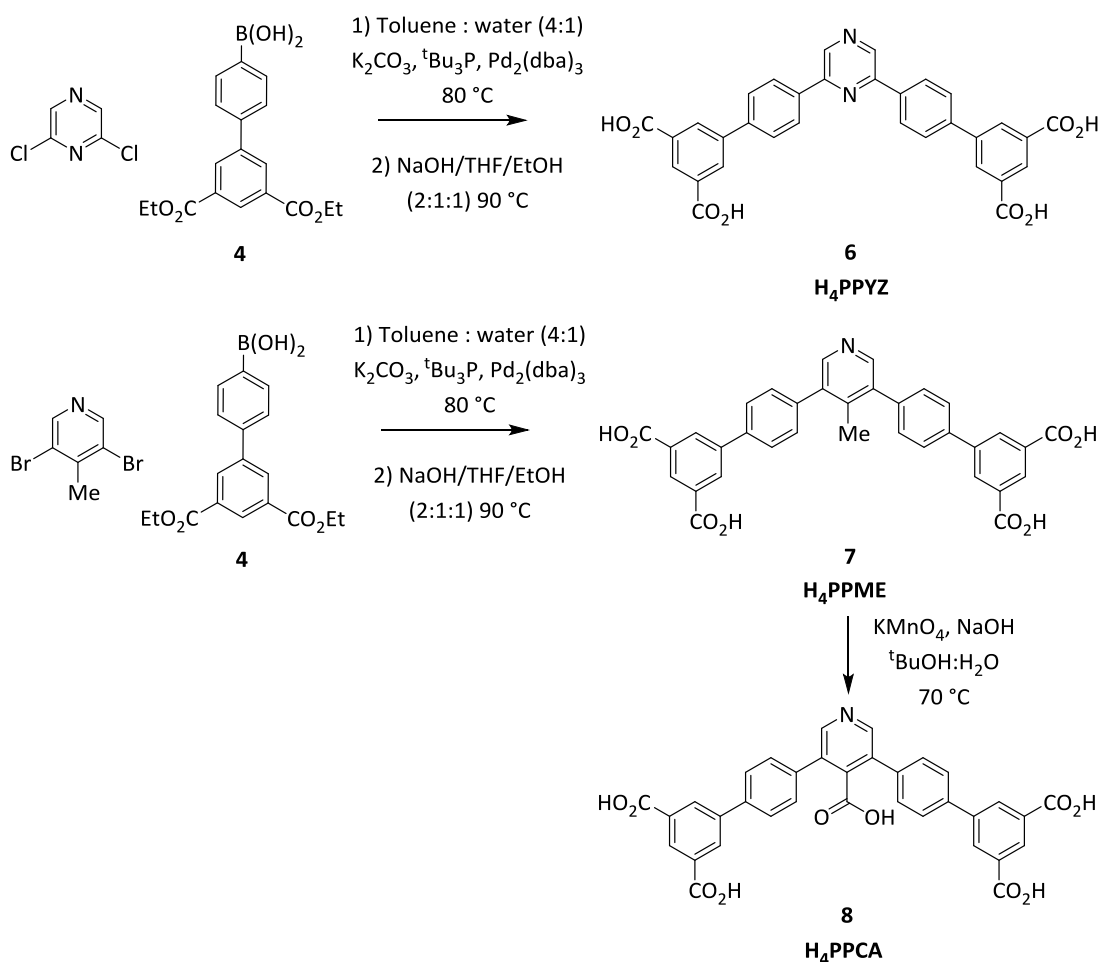
Figure 3.7: Structure and naming strategy of the ligands described in this chapter.

3.3 Results and Discussion

3.3.1 Ligand Synthesis

The “extended boronic acid isophthalate” unit (**4**) described in chapter 2 was Suzuki coupled to 2,6-dichloropyrazine and 3,5-dibromo-4-methyl-pyridine to give **H₄PPYZ** (**6**) and **H₄PPME** (**7**), respectively (Scheme 3.1). Both reactions were successful, with total yields of 74% (**H₄PPYZ**) and 81% (**H₄PPME**) after hydrolysis. **H₄PPME** was oxidised to **H₄PPCA** (**8**)

using KMnO_4 ; with poor oxidation returns leading to an overall yield of 48%. Attempts to synthesise H_4PPAN and H_4PPAD from 3,5-dibromo-4-amino pyridine and 3,5-dibromoisonicotinamide were unsuccessful and are discussed further below.

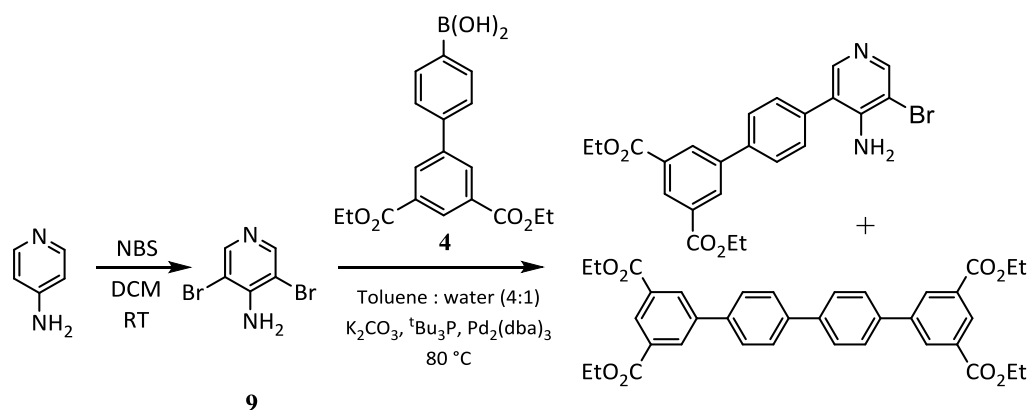


Scheme 3.1: Synthetic routes to the ligands H_4PPYZ , H_4PPME and H_4PPCA from a commercially available core and the “extended boronic acid isophthalate” unit synthesised and described in chapter 2.

3.3.1.1 Attempted Synthesis of the Amine Functionalised Ligand H_4PPAN

Following the route outlined in Scheme 3.2, 4-aminopyridine was brominated with N-bromosuccinimide (NBS) to yield 3,5-dibromo-4-aminopyridine.³³ Attempts at Suzuki coupling reactions were unsuccessful, resulting in a mixture of the monocoupled and homocoupled product in low yields (ca. 10%). In order to improve yields for the Suzuki coupling reaction, variations were made to the reaction conditions; resulting in many iterations of solvents, bases and catalysts (Table 3.1). All efforts were unsuccessful at

producing a di-coupled species, although use of dry toluene resulted in smaller quantities of homocoupled product. The failure of the Suzuki coupling to 3,5-dibromo-4-aminopyridine was attributed to the electron donating amine group preventing oxidative addition of the halide core.³⁴



Scheme 3.2: Synthetic route to synthesise H_4PPAN from the commercially available 4-amino pyridine and the “extended boronic acid isophthalate” unit described in Chapter 2. The two major products isolated from the reaction mixture, purified by column chromatography and identified by NMR spectroscopic analysis are the monocoupled ligand and homocoupled boronic acid.

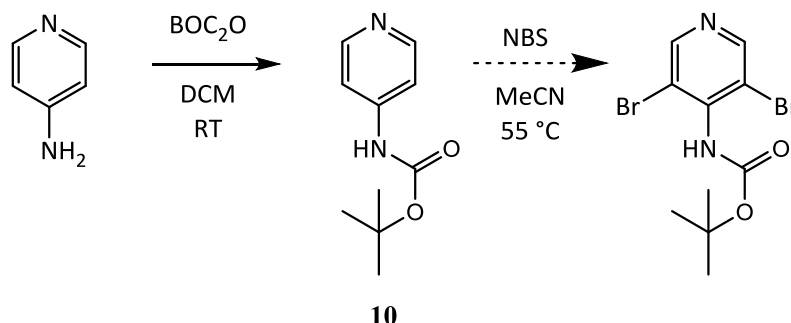
Table 3.1: Variables changed in Suzuki coupling reaction to synthesise Et_4PPAN . A large number of iterations were tested, with dry toluene reducing the fraction of homocoupled product in the mixture.

Solvents	Bases	Catalysts
Dioxane	K_2CO_3	$Pd_2Cl_2(dppf)$
DMA	KOAc	$Pd(PPh_3)_4$
H_2O	CS_2CO_3	$Pd_2(dba)_3 \cdot tBu_3P$
Toluene	K_3PO_4	
Dry Toluene	$NaCO_3$	

3.3.1.1.1 BOC Protection of 4-Aminopyridine for the Synthesis of H_4PPAN

In order to overcome the electron donating problem, the amine group was protected with an electron-withdrawing di-*tert*-butyl dicarbonate (BOC) group.³⁵ BOC protection of 4-amino-3,5-dibromopyridine was unsuccessful, returning only starting materials. Following published procedures,³⁶ 4-aminopyridine was first protected with a *tert*-butoxycarbonyl (BOC) group, followed by bromination (Scheme 3.3). BOC protection was carried out successfully but attempted bromination resulted only in the recovery of starting material,

identified by NMR and MS analysis. The failure of both routes was attributed to steric hindrance between the bulky BOC group and two large bromo- substituents; therefore this approach was not pursued further.

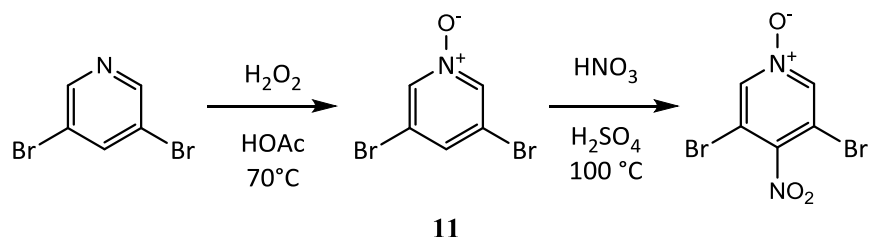


Scheme 3.3: Synthetic route to BOC-protected 4-amino-3,5-dibromopyridine; failure was attributed to steric hindrance between the bulky BOC group and two large bromo-substituents.

3.3.1.1.2 Nitration of the Pyridyl Core for the Synthesis of H₄PPAN

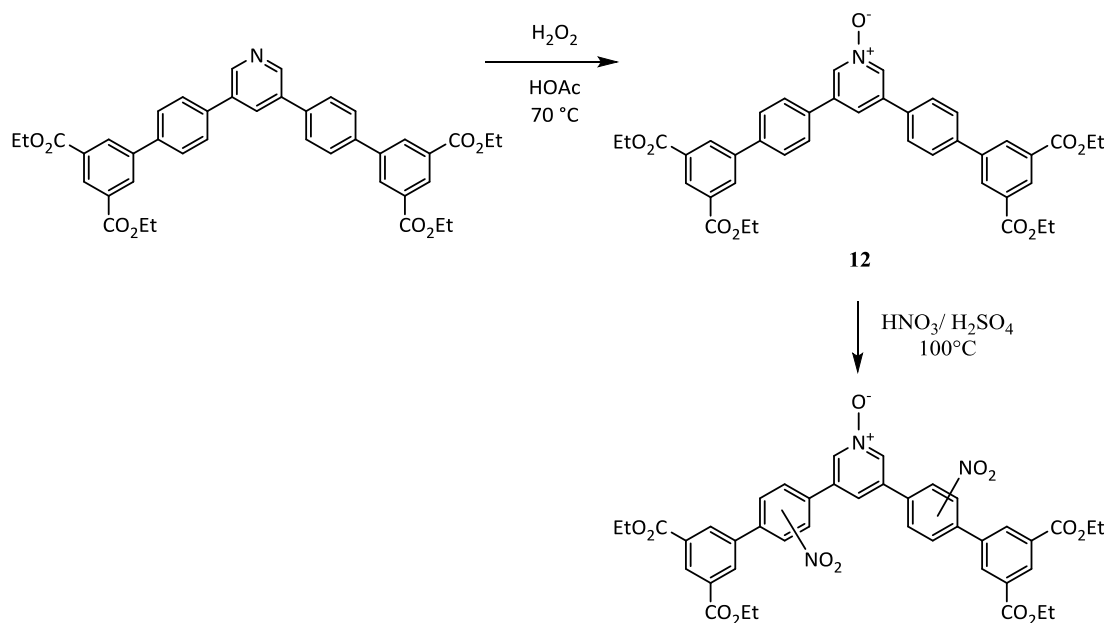
The next approach used a highly electron-withdrawing nitro group, which could subsequently be reduced to the amine group after coupling. Direct nitration of 3,5-dibromopyridine was unsuccessful, as the inclusion of a pyridyl N in a ring activates the ring to meta-directed electrophilic aromatic substitution, relative to the pyridyl group. Literature investigation revealed that oxidation of the pyridyl group to the corresponding pyridine-N-oxide activates the ring, resulting in *para* substitution.³⁷ The pyridyl nitrogen was successfully oxidised using H₂O₂ in acetic acid to give 3,5-dibromopyridine-N-oxide (**11**) (Scheme 3.4),^{38,39} however nitration of **11** proceeded with mixed results. The highly polar nature of the N⁺-O⁻ bond hindered attempts to follow the reaction by TLC; subsequently parallel reactions were stopped after periods of 6, 12 and 24 hours and the products analysed. The substrates and products were found to decompose in the harsh acidic reaction conditions; after 6 hours a crude yield of 50% by mass was isolated, whilst after 24 hour no product was obtained. Analysis of the crude product isolated after six hours indicated that the reaction had not gone to completion; integration of the pyridyl proton peaks in the ¹H

NMR spectrum revealed 2:1 mixture of starting material: product. As increasing reaction times were already shown to be highly detrimental, this approach was not taken any further.



Scheme 3.4: Synthetic route to a nitrated 3,5-dibromopyridine core for the synthesis of H_4PPAN . Although oxidation of the pyridyl N was successful, nitration resulted in an inseparable mixture of starting material and nitrated product.

A second strategy involved direct nitration of the pre-coupled ligand Et_4PPYD (Figure 3.5). Oxidation of the pyridyl N was successful; however nitration resulted in multiple substitutions on the phenyl spacer rings and thus was not investigated further.

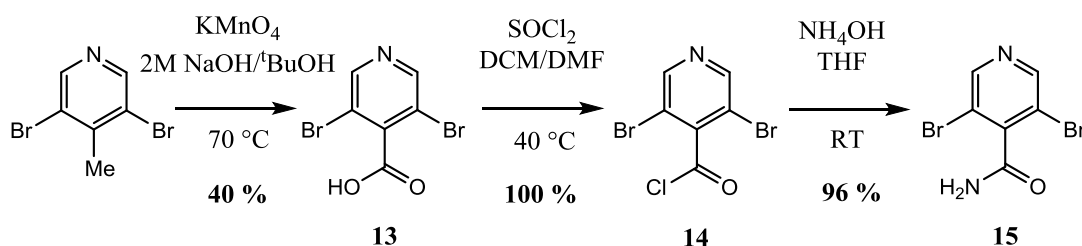


Scheme 3.5: Synthetic route to selectively nitrate Et_4PPYD para- to the pyridyl N. Nitration resulted in multiple substitutions on the phenyl rings.

3.3.1.2 Attempted Synthesis of the Amide Functionalised Ligand H_4PPAD

Addition of a weakly electron withdrawing amide group *para*- to the pyridyl N was expected to promote the Suzuki coupling reaction between a functionalised pyridyl core and

the extended boronic acid unit, whilst still introducing a highly polar amine group into the ligand for host-guest interactions between CO₂ and the MOF. 3,5-Dibromoisonicotinamide was synthesised from 4-methyl-3,5-dibromopyridine in good yields (Scheme 3.6). The commercially available starting material was oxidised with potassium permanganate to give 3,5-dibromoisonicotinic acid (**13**), which was acylated with thionyl chloride (**14**)^{40,41} and reacted with ammonium hydroxide to afford 3,5-dibromoisonicotinamide (**15**). Suzuki coupling reactions between 3,5-dibromoisonicotinamide and the “extended boronic acid isophthalate” unit were attempted with the wide range of reaction conditions outlined previously in Table 3.1. Reactions were unsuccessful, with starting materials retrieved in 15-30% yields.



Scheme 3.6: Reaction scheme for the synthesis of 3,5-dibromoisonicotinamide from 4-methyl-3,5-dibromopyridine.

As the synthesis of H₄PPAN and H₄PPAD were found to be highly challenging, ligand synthesis was halted in order to concentrate on analysing the materials properties of MOFs synthesised from existing ligands. H₄PPYZ, H₄PPME and H₄PPCA include a range of functional groups, sufficient to investigate the effect that functionalisation of cage B has on the gas adsorption properties of the framework.

3.3.2 Preparation of MOF Series MFM-17X

Solvothermal reaction between H₄PPYZ and H₄PPCA with Cu(NO₃)₂·5/2(H₂O) in a mixture of DMF and water (5:1 v/v) under acidic (HNO₃) conditions afforded blue octahedral crystals of **MFM-171** and **MFM-173**, respectively. **MFM-172** was synthesised from

H₄PPME under the same conditions without the addition of water. Table 3.2 outlines the overall formulae and name designation for the ligands discussed in this Chapter.

Table 3.2: Formulae and MFM-17X name designation for the ligands discussed in this chapter.

Ligand	MOF formula	MOF name
H ₄ PPYD	[Cu ₂ PPYD(H ₂ O)]·(DMF) ₄ (H ₂ O) ₂	MFM-170
H ₄ PPYZ	[Cu ₂ PPYZ(DMF)]·(DMF) ₅ (H ₂ O) ₃	MFM-171
H ₄ PPME	[Cu ₂ PPME(H ₂ O)]·(DMF) ₆	MFM-172
H ₄ PPCA	[Cu ₂ PPCA(H ₂ O)]·(DMF) ₆ (H ₂ O) ₃	MFM-173

3.3.3 Crystal Structures and Topologies of the MOF Series MFM-17X

MFM-171, -172 and -173 form self-interpenetrated cubic frameworks, isostructural to MFM-170, with functional groups pointing directly into the centre of cage B. The introduction of pendant functional groups was found to decrease the porosity of the frameworks; however none of the additional functional groups completely fill cage B; there is still a 9 Å accessible pore diameter between the carboxylic acid groups in MFM-173. Compared to MFM-170, which had a porosity of 61%, MFM-171, MFM-172 and MFM-173 decrease in line with the increase in size of the functional group, with porosities of 61%, 60% and 58%, respectively (Table 3.3).

Table 3.3: Unit cell and refinement parameters obtained from single crystal analysis of the MFM-17X series.

MOF	Space Group	a parameter /Å	Volume / Å ³	Fractional Porosity	Total micropore volume/ cm ³ g ⁻¹
MFM-170	<i>Im-3m</i>	33.4733(3)	37505.4(9)	61%	0.82
MFM-171	<i>Im-3m</i>	33.3732(1)	37169.9(3)	61%	0.81
MFM-172	<i>Im-3m</i>	33.4016(2)	37265.1(5)	60%	0.79
MFM-173	<i>Im-3m</i>	33.2925(3)	36901.1(6)	58%	0.78

3.3.4 Synthesis and Purity of Bulk Samples of the MFM-17X Series.

3.3.4.1 Analysis of Bulk Purity of MFM-17X Series

The alignment of peak positions in PXRD diffraction patterns of MFM-170 to MFM-173 is consistent with the presence of an isostructural series (Figure 3.8). Slight differences in relative peak intensities are attributed to preferred orientation effects arising from the flat plate sample holder and a greater signal:noise ratio due to smaller quantities of sample in the case of MFM-173. Pawley refinements of these data (Figure 3.9) were found to match the unit cell dimensions determined from single crystal X-ray diffraction, confirming that the single crystal structure is representative of the bulk sample (Table 3.4).

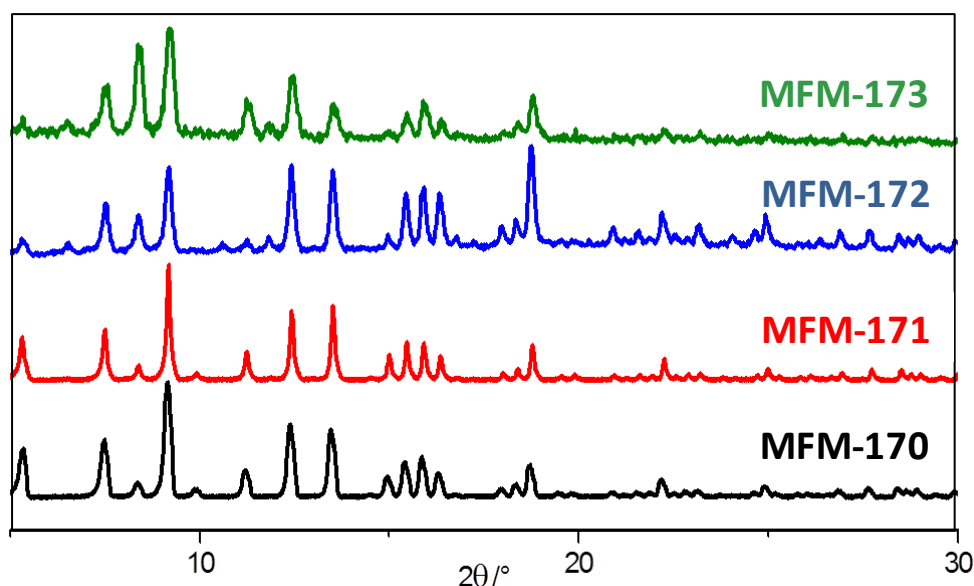


Figure 3.8: PXRD patterns of as-synthesised samples of MFM-170 (pyridine), MFM-171 (pyrazine), MFM-172 (methyl pyridine) and MFM-173 (isonicotinic acid), consistent with the formation of an isostructural series.

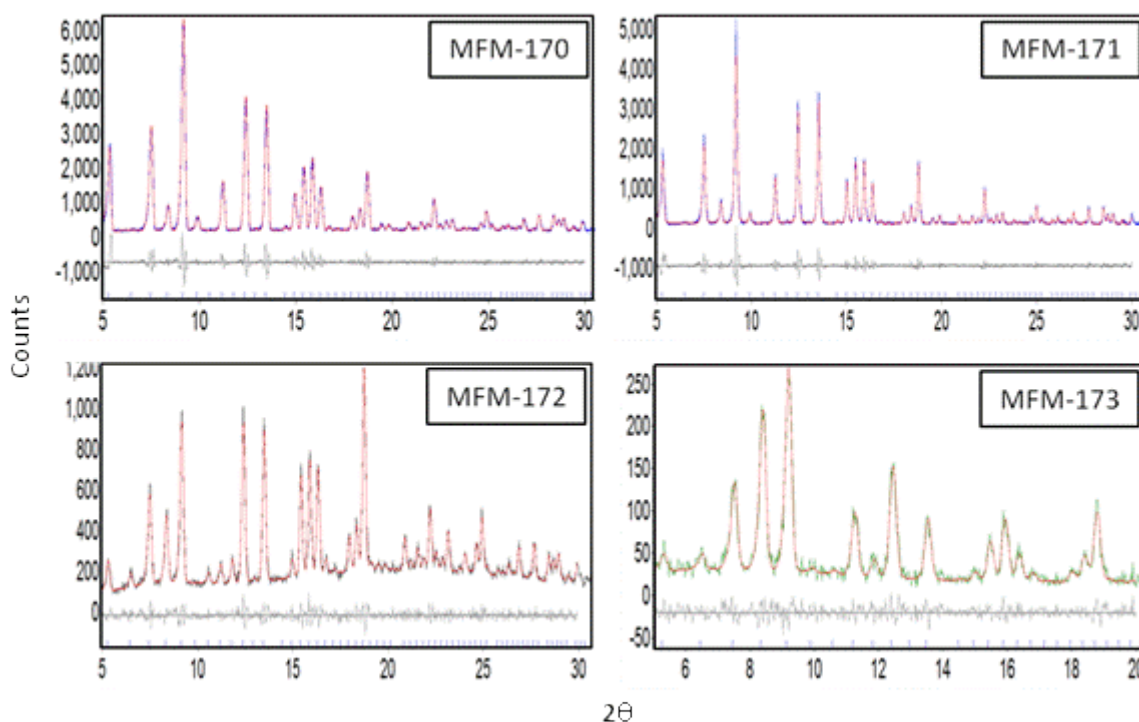


Figure 3.9: Pawley refinements of the as synthesised samples of MFM-170 – MFM-173, demonstrating that PXRD diffraction patterns taken from the bulk material closely match closely to the structure obtained from SCXRD analysis.

Table 3.4: Pawley refinement indexing parameters of the MFM-17X series and comparison to unit cell parameters obtained from SCXRD.

MOF	SCXRD		Pawley Refinement	
	<i>a</i> parameter (Å)	<i>a</i> parameter (Å)	Volume (Å ³)	GOF
MFM-170	33.4733(3)	33.54	37728	1.15
MFM-171	33.3732(1)	33.46	37467	2.22
MFM-172	33.4016(2)	33.58	37852	1.28
MFM-173	33.2925(3)	33.50	37592	1.08

3.3.4.2 Challenges Regarding the Synthesis of MFM-173

The preparation of H₄PPCA (carboxylic acid functionalised ligand) was not reliably reproducible and insufficient quantities were isolated to prepare enough bulk sample of MFM-173 for further studies. Oxidation of H₄PPME afforded low yields (<30%) of impure H₄PPCA; attributed to steric hindrance around the methyl group. Furthermore, the preparation of MFM-173 was also problematic, with reactions across a wide range of synthetic conditions yielding large quantities of amorphous product or copper oxide impurities, identified by PXRD.

3.3.5 Thermal Stability Measurements

The thermal stability of the remaining as-synthesised and acetone exchanged samples were assessed by TGA (Figure 3.10). Thermal analysis of MFM-171 and MFM-172 demonstrate identical decomposition temperatures of 350 °C, the point at which MFM-170 was found to collapse by variable temperature PXRD (Chapter 2).

TGA analysis of MFM-171 shows an initial mass loss of 8%, followed by a plateau at 100 °C corresponding to the loss of five unbound water molecules per formula unit within the pores; the second mass loss (26%) between 100 °C – 160 °C represents the decomposition and loss of four unbound DMF from within the pores of the material; finally a third small (8%) mass loss (160 °C – 260 °C) can be attributed to loss of one coordinated DMF per Cu(II)-paddlewheel. A final plateau corresponds to the fully desolvated material, which is followed by a significant mass loss (43%) at *ca.* 350 °C, corresponding to the loss of one PPYZ⁴⁺ molecule per formula unit, leaving 2CuO.

MFM-172 was synthesised in the absence of water and thus the initial mass loss of 23% (25 °C – 160 °C) corresponds to six solvent DMF molecules per formula unit in the pore. A small mass loss (3%) between 160 °C and 250 °C corresponds to the loss of coordinated DMF, which is followed by a plateau for the bare framework material and decomposition at *ca.* 350 °C. A final mass loss of 47% represents the loss of one PPME⁴⁺ molecule per formula unit.

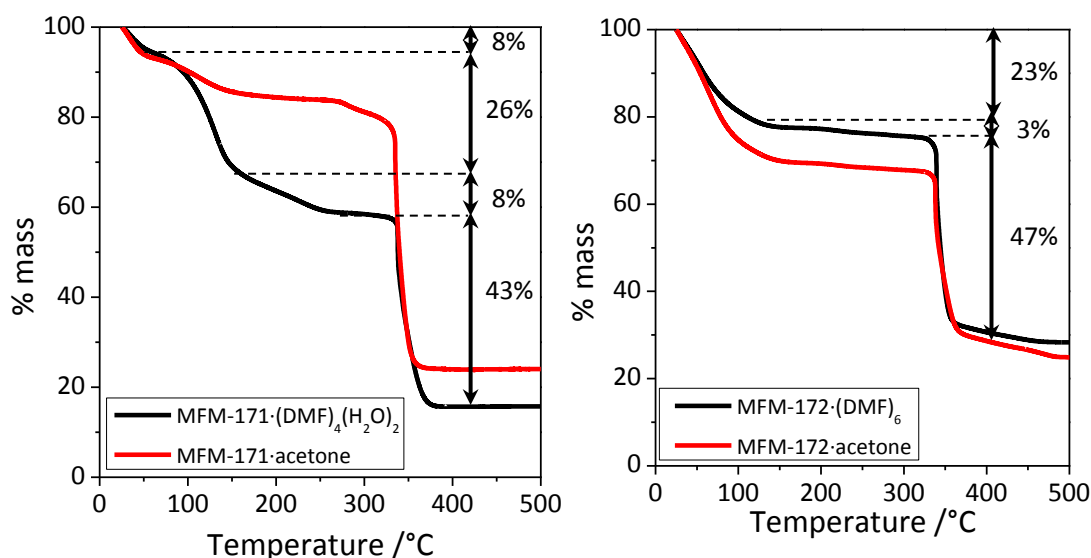


Figure 3.10: Thermogravimetric analysis of MFM-171 and MFM-172, demonstrating the high thermal stability of the MFM-17X series (decomposition at 350 °C). Analysis of the mass losses for the as-synthesised samples allows for determination of the void solvent content.

In the acetone-exchanged frameworks, initial mass losses between room temperature and 50 °C can be attributed to the loss of solvated acetone, whilst the second mass loss up to 120 °C corresponds to the loss of water as hydrated acetone was used for solvent exchange. Importantly no mass loss can be seen at 160 °C which indicates that all coordinated DMF molecules have been successfully exchanged with either water or acetone.

3.3.6 Gas Sorption Measurements in the MFM-17X Series

3.3.6.1 Nitrogen Adsorption in the MFM-17X Series

MFM-17X demonstrate similar reversible type-I N₂ adsorption isotherm profiles at 77 K (Figure 3.11) with decreasing N₂ adsorption in line with increasing functional group size and decreasing porosity. The BET surface areas of the materials follow the same trend; MFM-170: 2408 m² g⁻¹, MFM-171: 2196 m² g⁻¹ and MFM-172: 1787 m² g⁻¹ (Table 3.5). The decrease in surface area from MFM-170 to MFM-172 is expected as the bulky methyl groups intrude into cage B, truncating the triangular void space between the two ligand arms. Both frameworks display a greater surface area than the isostructural PCN-124 (1372 m² g⁻¹)

whilst MFM-172 falls slightly short of isostructural [Cu₂EPYD] (1879 m² g⁻¹),⁴² which benefits from the high surface area:mass ratio of ethyne groups.⁴³

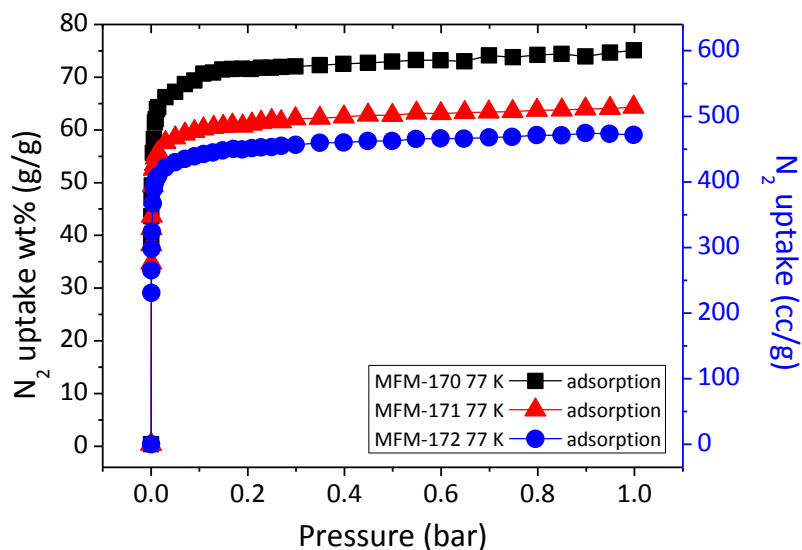


Figure 3.11: Gravimetric N₂ isotherms of the MFM-17X series carried out at 77 K.

The pore size distribution plots of the MFM-17X series (Figure 3.12) clearly show that the introduction of four methyl groups into cage B of MFM-170 leads to a sharp decrease in the intensity of the 9 – 10 Å peak due to the truncation of cage B. The measured pore volumes decrease in agreement with the calculated pore volumes from SCXRD (Table 3.5), with slight discrepancies attributed to modelled disorder and a lack of flexibility in the crystal structure.

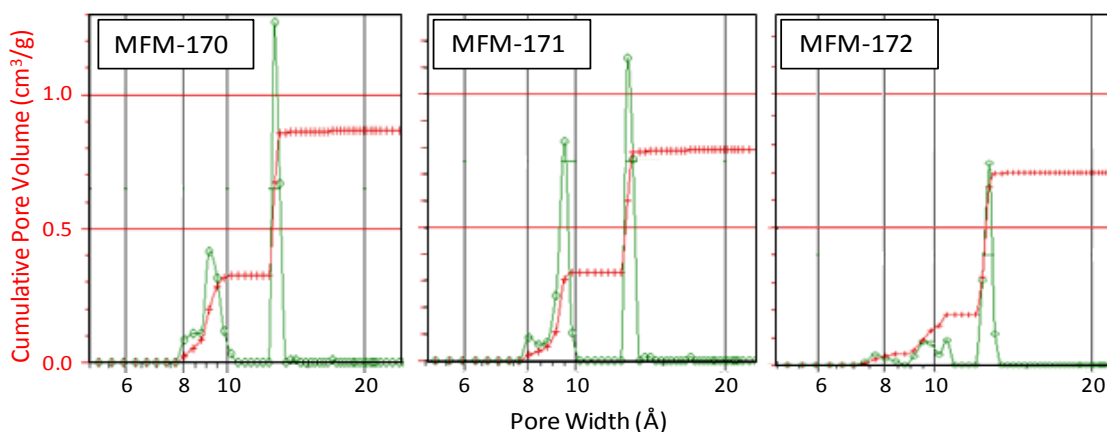


Figure 3.12: Pore size distributions of the MFM-17X series calculated by DFT modelling of cylindrical pores on an oxide surface using data from the N₂ isotherm at 77 K.

Table 3.5: Summary of the surface area and porosities of the MFM-17X series calculated from SCXRD crystal structures and N_2 isotherms.

MOF	Surface Area /m ² g ⁻¹	Calculated Porosity	Calculated pore volume /cm ³ g ⁻¹	Measured pore volume /cm ³ g ⁻¹
MFM-170	2408	61%	0.82	0.87
MFM-171	2196	61%	0.81	0.79
MFM-172	1787	60%	0.79	0.70

The room temperature N_2 adsorption capacities for MFM-170 – 172 to a pressure of 20 bar are effectively equal (Table 3.6), demonstrating that functionalisation has very limited effect on the N_2 adsorption capacity at high pressure, although none of the frameworks have reached saturation. The MFM-17X MOFs are expected to show only modest selectivity for CO_2/N_2 as low N_2 adsorption is preferred for the production of highly selective MOFs such as NOTT-300 < 10 cm³ g⁻¹,²⁷ bio-MOF-11 = 9 cm³ g⁻¹,⁴⁴ and [Cu₃(CPT)₄(μ₃-OH)] < 5 cm³ g⁻¹.⁴⁵

Table 3.6: Summary of N_2 adsorption capacities of the MFM-17X series to 20 bar at 273 K and 298 K.

	N_2 adsorption, 273 K			N_2 adsorption, 298 K		
	wt%	cm ³ g ⁻¹	cm ³ cm ⁻³	wt%	cm ³ g ⁻¹	cm ³ cm ⁻³
MFM-170	19.67	157	117	15.17	121	90
MFM-171	18.53	148	111	14.47	116	87
MFM-172	19.52	156	119	15.22	121	93

3.3.6.2 Carbon Dioxide Adsorption in the MFM-17X Series

The functionalised analogues of MFM-170 were expected to demonstrate superior CO_2 uptake capacities due to predicted Lewis acid/base interactions between adsorbed CO_2 and the uncoordinated pyrazine N in MFM-171 or electrostatic interactions between CO_2 and the electron-rich pyridyl ring in MFM-172. CO_2 adsorption isotherms measured to 20 bar at 273 K and 298 K show similar profiles for all three MFM-17X frameworks (Figure 3.13). MFM-170 demonstrates the highest gravimetric CO_2 adsorption at 20 bar (94.95 wt%) followed by MFM-172 (90.20 wt%) and then MFM-171 (85.29 wt%). Once the reduction in pore volume is taken into account, MFM-170 and MFM-172 demonstrate very similar uptake capacities (359 cm³ cm⁻³ and 351 cm³ cm⁻³ respectively). The lack of improvement in CO_2

uptake from MFM-170 to MFM-171 suggests that no interactions are formed between CO₂ and the Lewis basic sites.

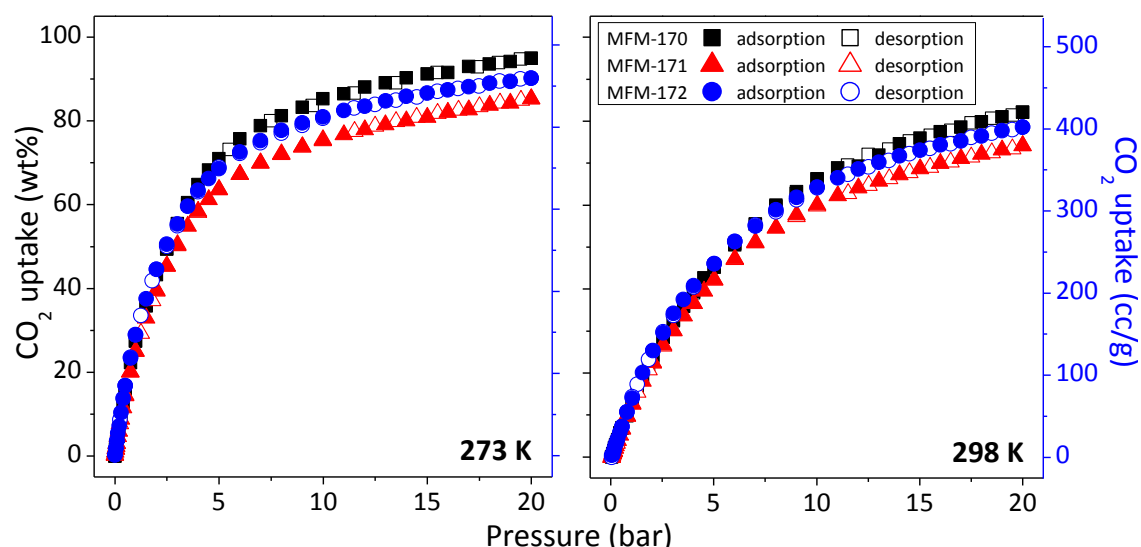


Figure 3.13: Gravimetric CO₂ adsorption isotherms for the MFM-17X series, measured to 20 bar at 273 K and 298 K.

At 1 bar the effect of additional functionalisation is apparent; MFM-172 demonstrates the highest gravimetric and volumetric CO₂ adsorption capacity at ambient pressure, followed by MFM-170 and finally MFM-171 (Table 3.7). The poor performance of MFM-171 implies that no interactions are present between CO₂ and the Lewis basic pyrazine N at all pressures. The increase in CO₂ adsorption in the methyl functionalised MFM-172 suggests the existence of a key binding interaction between the pyridyl π -electron cloud and adsorbed CO₂ as the electron donating methyl substituent is known to increase CO₂ adsorption by increasing the electron density in the adjoining ring as opposed to directly interacting with guest species. The existence of a binding site with the π -electron cloud surrounding the central pyridyl ring is further supported by the reduction in adsorption in MFM-171, where inductive effects from the second nitrogen withdraw electron density from the pyrazine ring, weakening the interaction between the π -electrons and adsorbed CO₂. All three frameworks adsorb more CO₂ than [Cu₂EPYD] under similar conditions,⁴² despite similar pore volumes. In [Cu₂EPYD] the electron density of the central pyridyl ring is reduced due to conjugation across two ethyne triple bonds.⁴⁶ Conjugation is avoided in the MFM-17X series as the

phenyl and pyridyl rings are not coplanar within the framework. Although the electron donating methyl group in MFM-172 increases the volumetric CO₂ adsorption capacity, the total adsorption at 1 bar does not reach the uptake capacity seen in PCN-124 (Table 3.7), signifying that the interactions between CO₂ and the π -electrons are weaker than those with between CO₂ and the amide group.⁴⁷

Table 3.7: Summary of CO₂ adsorption capacities for the MFM-17X series at 1 bar.

	CO ₂ adsorption, 273 K			CO ₂ adsorption, 298 K		
	wt%	cm ³ g ⁻¹	cm ³ cm ⁻³	wt%	cm ³ g ⁻¹	cm ³ cm ⁻³
MFM-170	27.34	139	103	13.25	67	50
MFM-171	24.95	127	95	12.87	66	49
MFM-172	28.87	147	112	14.18	72	55
[Cu ₂ EPYD]	-	-	-	12.47	-	-
PCN-124	-	204	-	-	-	-

The isosteric heats of adsorption (Q_{st}) for CO₂ at zero loading were calculated by the virial method (Table 3.8). MFM-172 demonstrates the highest Q_{st} of the MFM-17X series, in line with the stronger proposed interaction between the π - electron cloud of the pyridyl ring and adsorbed CO₂. Surprisingly MFM-171 has a slightly higher binding energy at zero loading than MFM-170, attributed to an increase in aromatic proton acidity due to inductive effects of the pyrazine ring.

Table 3.8: Summary of CO₂ adsorption capacities for the MFM-17X series at 20 bar and calculated enthalpies of adsorption.

	CO ₂ adsorption, 273 K			CO ₂ adsorption, 298 K			Q_{st} kJ mol ⁻¹
	wt%	cm ³ g ⁻¹	cm ³ cm ⁻³	wt%	cm ³ g ⁻¹	cm ³ cm ⁻³	
MFM-170	94.95	484	359	82.50	420	312	-18
MFM-171	85.29	434	326	74.48	379	285	-20
MFM-172	90.20	459	351	78.95	402	308	-23

In a flue gas mixture containing 15% CO₂ in N₂ at 1 bar and 273 K, MFM-172 shows the highest separation ability, with an IAST selectivity parameter of 13.0 compared to 11.9 for MFM-171 and 11.5 for MFM-170 (Figure 3.14). The increase in selectivity for MFM-172 can be accounted for by the high adsorption capacity for CO₂ at 1 bar, whilst the increase in selectivity from MFM-170 to MFM-171 can be attributed to the higher initial enthalpy of

adsorption. Although functionalisation has been shown to be an effective method of improving CO₂/N₂ selectivity, the difference in the IAST parameters between the three frameworks are marginal; there is only a 13% improvement in selectivity from MFM-170 to MFM-172. Other functional groups may have more impact as functionalisation of UiO-66-NO₂ with an amine group demonstrated a 23% increase in selectivity from 45.3 to 56.0;⁵⁰ whilst functionalisation of NOTT-101 with methyl and methoxyl groups almost doubled the selectivity from 12.4 to 20.9.⁵¹

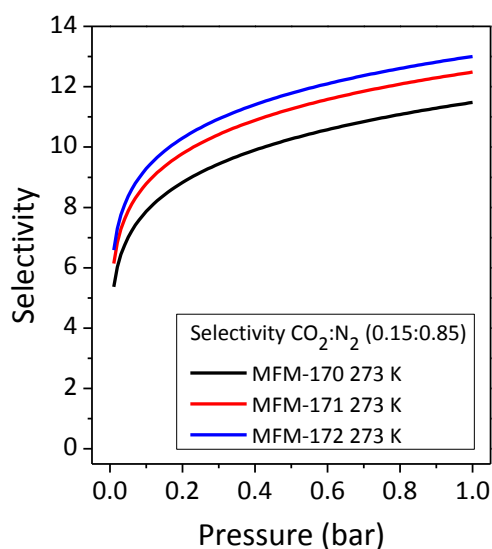


Figure 3.14: IAST selectivity parameters calculated for CO₂/N₂ in the MFM-17X series to 1 bar at 273 K.

3.3.6.3 Methane Adsorption in the MFM-17X Series

The CH₄ adsorption isotherms of the MFM-17X series (Figure 3.15) show only small differences between the MFM-17X materials, indicating that functionalisation of cage B has little effect on CH₄ uptake capacity. The inclusion of functional groups is not commonly used to enhance CH₄ adsorption as CH₄ molecules usually bind to open metal sites or phenyl rings. The addition of Lewis basic nitrogen sites has previously been shown to enhance CH₄ uptake at high pressures;^{48,49} however in this instance MFM-171 was found to adsorb the least CH₄ (Table 3.9), confirming the inaccessibility of the pyrazine nitrogen sites. Whilst MFM-170 exhibits the highest gravimetric CH₄ uptake, the volumetric uptakes of MFM-170

and MFM-172 are equal ($219 \text{ cm}^3 \text{ STP cm}^{-3}$ and $218 \text{ cm}^3 \text{ STP cm}^{-3}$ respectively at 20 bar and 273 K) once the difference in porosity is taken into account.

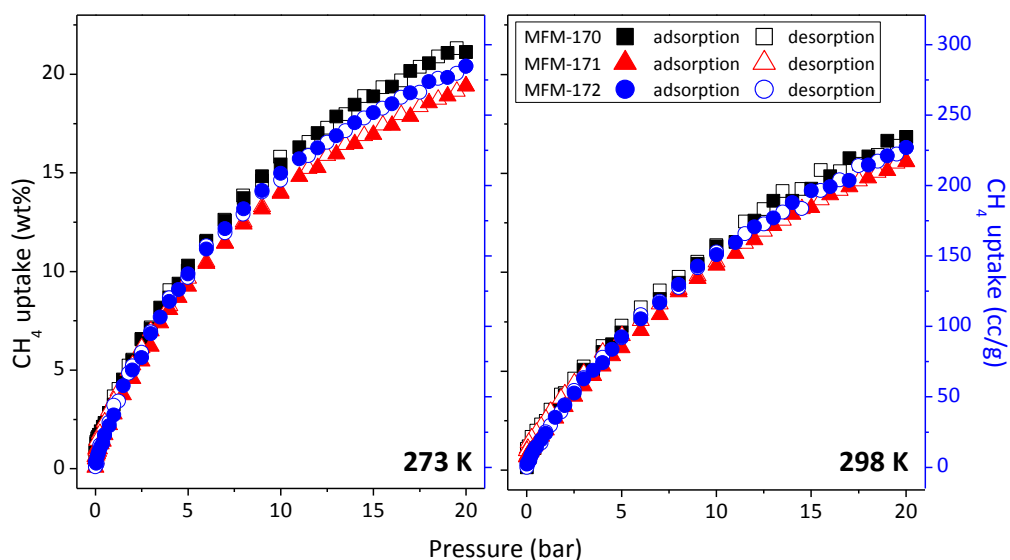


Figure 3.15: Gravimetric CH_4 adsorption isotherms for the MFM-17X series to 20 bar at 273 K and 298 K

Unlike CO_2 adsorption, at 1 bar the CH_4 adsorption capacities follow the trend seen at higher pressures, decreasing in line with decreasing porosity. All three frameworks demonstrate similar volumetric uptake capacities (MFM-170: $33 \text{ cm}^3 \text{ cm}^{-3}$, MFM-171: $28 \text{ cm}^3 \text{ cm}^{-3}$ and MFM-172: $28 \text{ cm}^3 \text{ cm}^{-3}$), confirming that functionalisation has no effect on CH_4 uptake across the pressure range. The Q_{st} values for CH_4 adsorption at zero loading are low (Table 3.9), indicating weak interactions between the framework surface and adsorbed CH_4 . This is advantageous for fuel delivery systems as it decreases the energy penalty required for desorption of gas molecules. As the addition of functional groups to MFM-170 does not have much effect on CH_4 adsorption, yet can improve CO_2 uptake at 1 bar, the functionalised analogues MFM-171 and MFM-172 are expected to demonstrate increased the CO_2/CH_4 selectivity.

Table 3.9: Summary of CH₄ adsorption capacities in the MFM-17X MOF series at 20 bar and calculated enthalpies of adsorption.

	CH ₄ adsorption, 273 K			CH ₄ adsorption, 298 K			Q _{st} kJ mol ⁻¹
	wt%	cm ³ g ⁻¹	cm ³ cm ⁻³	wt%	cm ³ g ⁻¹	cm ³ cm ⁻³	
MFM-170	21.10	295	219	16.78	234	174	-11
MFM-171	19.37	271	203	15.52	217	163	-11
MFM-172	20.38	285	218	16.24	227	174	-8

In the separation of CO₂ from a natural gas stream (1:1 CO₂:CH₄) at 1 bar and 273 K, MFM-172 demonstrates the highest IAST selectivity parameter of 4.5, with values of 3.6 and 2.6 for MFM-171 and MFM-170, respectively (Figure 3.16). The trend can be attributed to the relative difference in Q_{st} values at zero loading; MFM-172 displays the highest Q_{st} for CO₂, whilst showing the lowest Q_{st} for CH₄. The increase of 31% between the IAST selectivity parameters of MFM-170 and MFM-172 matches a number of different techniques used in to improve selectivity for natural gas sweetening. Doubling the number of open metal sites in JLU-Liu20 increased the CO₂/CH₄ selectivity from 5.9 to 6.9 (+17%);⁵² adding a benzothiadiazole ring to the centre of NOTT-101 increases the IAST selectivity parameter from 4.6 to 6.0 (+30%);⁵³ whilst the inclusion of methyl/methoxy groups to NOTT-101 shows a similar increase from 4.6 to 6.1 (+33%).⁵¹ As with CO₂/N₂ selectivity, however, other functional groups are reported to be more successful; the addition of a hydroxyl group to Zn(BDC)(DABCO)_{0.5} to give UTSA-25a leads to an increase in the IAST CO₂/CH₄ selectivity parameter from 4.4 to 17.2.⁵⁴

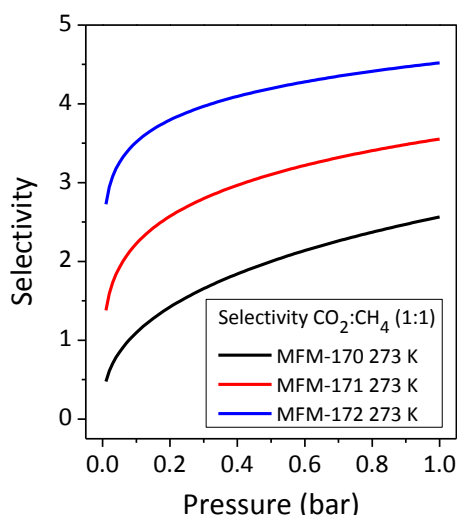


Figure 3.16: IAST selectivity parameters calculated for CO_2/CH_4 in the MFM-17X series to 1 bar at 273 K.

3.3.6.4 Hydrocarbon Adsorption in the MFM-17X Series

The adsorption of ethane and ethene were measured to 1 bar at 273 K and 298 K (Figure 3.17). MFM-172 shows the greatest gravimetric and volumetric uptake for both C_2 hydrocarbons, followed by MFM-170 and MFM-171 in that order (Tables 3.10 and 3.11). The main interactions between C_2 hydrocarbons and the MOF surface are dipole-dipole interactions between the hydrocarbon C-H and the π -electron cloud surrounding the pyridyl rings. The difference in uptake capacities can be attributed to the higher electron density on the central pyridyl ring in MFM-172 due to the electron donating nature of the methyl group.

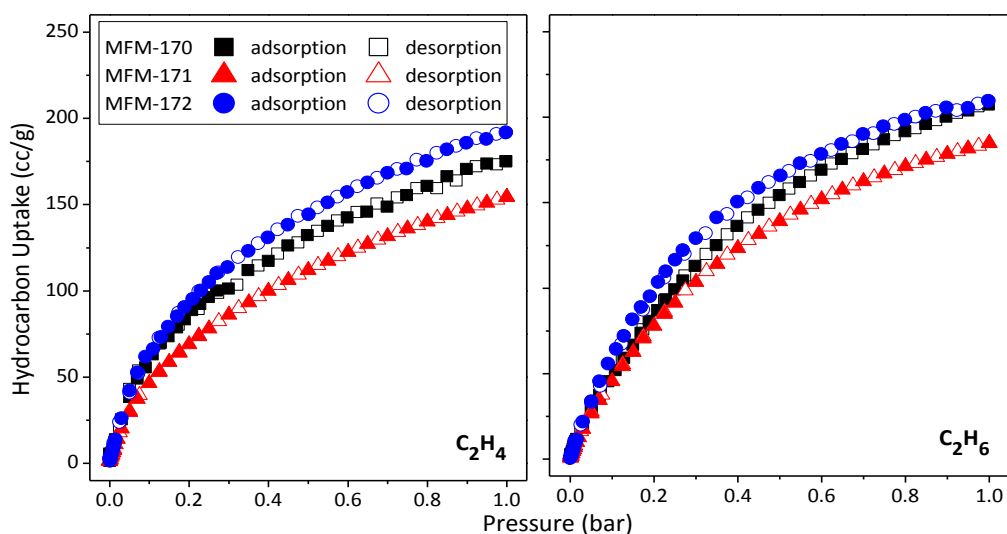


Figure 3.17: Gravimetric C_2H_4 and C_2H_6 isotherms for the MFM-17X series to 1 bar at 273 K.

Table 3.10: Summary of C_2H_4 adsorption capacities for the MFM-17X series to 1 bar.

	C_2H_4 adsorption, 273 K			C_2H_4 adsorption, 298 K		
	wt%	$cm^3 g^{-1}$	$cm^3 cm^{-3}$	wt%	$cm^3 g^{-1}$	$cm^3 cm^{-3}$
MFM-170	23.50	175	130	15.71	117	87
MFM-171	20.72	154	116	13.73	102	77
MFM-172	24.01	192	147	16.30	130	100

Table 3.11: Summary of C_2H_6 adsorption capacities for the MFM-17X series to 1 bar.

	C_2H_6 adsorption, 273 K			C_2H_6 adsorption, 298 K		
	wt%	$cm^3 g^{-1}$	$cm^3 cm^{-3}$	wt%,	$cm^3 g^{-1}$	$cm^3 cm^{-3}$
MFM-170	27.84	154	154	18.04	134	100
MFM-171	24.78	185	139	16.34	122	91
MFM-172	28.12	210	160	19.15	143	109

The MFM-17X series shows no significant selectivity for the adsorption of C_2H_4 over C_2H_6 , with selectivity values at 1 bar close to 1 (Figure 3.18). All three frameworks show high selectivity for the C_2 hydrocarbons over methane, due to strong electrostatic interactions between the C-H groups on the hydrocarbon molecules and the π -electron cloud surrounding the aromatic rings of the framework. The C_2H_4/CH_4 selectivity parameters are 16.0 for MFM-172, 11.2 for MFM-171 and 11.5 for MFM-170 at 1 bar, whilst the C_2H_6/CH_4 selectivity parameters are very similar at 15.7, 11.8 and 9.9, respectively. MFM-172 demonstrates the highest selectivity due to stronger interactions between the hydrocarbon C-H and the π -electron cloud surrounding the aromatic ligand rings.

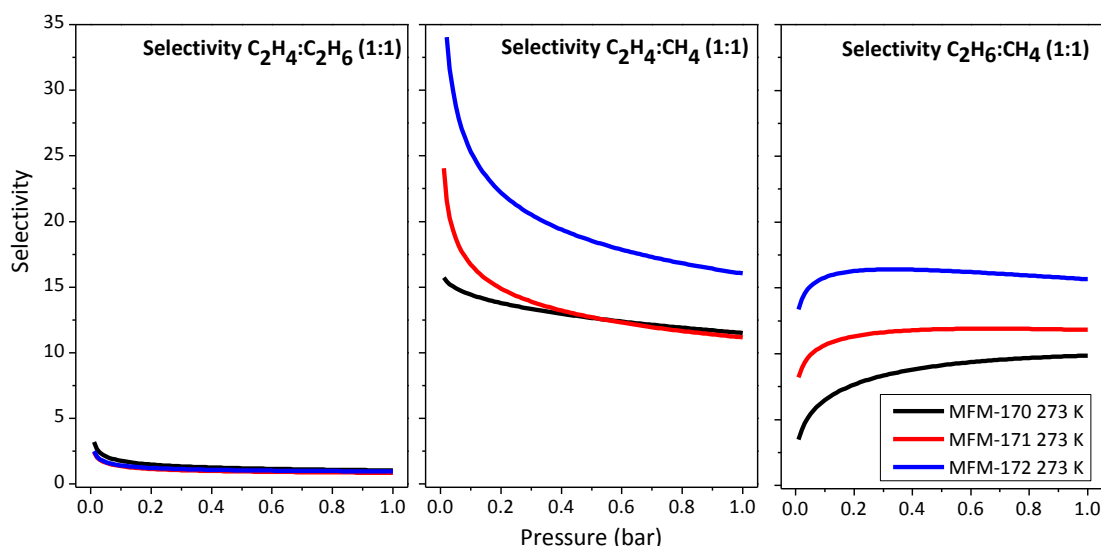


Figure 3.18: IAST selectivity parameters calculated for C_2H_4/C_2H_6 , C_2H_4/CH_4 and C_2H_6/CH_4 in the MFM-17X series to 1 bar

3.3.7 Location of CO_2 Binding Sites within MFM-17X

Analysis of the CO_2 isotherms of the MFM-17X MOF series indicated the likely presence of a key binding site between adsorbed CO_2 and the π -electron cloud surrounding the central pyridyl ring in the ligand. Confirmation of this binding site would improve understanding of the interactions of CO_2 within **txt** frameworks and could lead to a more targeted approach to enhancing CO_2 adsorption by future functionalisation of similar frameworks. *In situ* gas loaded SCXRD and IR microspectroscopy studies were carried out on CO_2 loaded crystals of MFM-170 and MFM-171 in order to confirm the presence of the proposed binding site and rationalise the relative adsorption behaviour of the three frameworks.

3.3.7.1 *In situ* Infrared Microspectroscopy Studies

3.3.7.1.1 Sample Preparation and Treatment

A single crystal of MFM-170 was studied by *in situ* IR spectroscopy using a synchrotron IR source coupled to an IR microscope. The sample of MFM-170 was activated by heating to 100 °C under a flow of dry helium. Activation was monitored by the removal of an intense broad peak centred at 3500 cm^{-1} (Figure 3.19) attributed to both coordinated and unbound water and acetone. Once cooled to 25 °C, the partial pressure of CO_2 in the helium stream

was increased incrementally from 0-1 bar and IR spectra collected at each step. The contribution from gaseous CO₂ in the cell was subtracted from the final spectrum at each partial pressure, leaving only the bands relating to the framework and adsorbed CO₂.

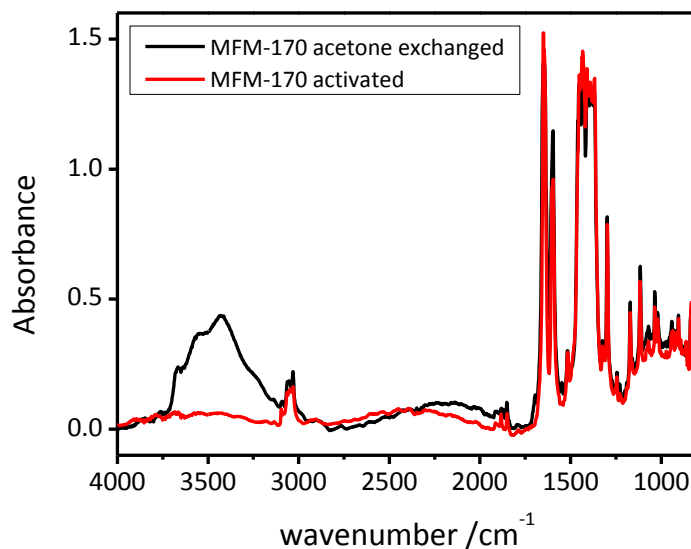


Figure 3.19: IR spectra of MFM-170 before and after activation, showing the removal of the water -OH band upon heating to 100 °C under a flow of dry helium.

3.3.7.1.2 IR Bands Relating to Adsorbed CO₂ Molecules in MFM-170

CO₂ has three fundamental vibrational modes;⁵⁵ the symmetric stretching ν_1 mode (1388 cm⁻¹), a doubly degenerate ν_2 bending mode (667 cm⁻¹) and ν_3 asymmetric stretch (2349 cm⁻¹) (Figure 3.20). Both the bending mode and asymmetric stretch are IR active, whilst the symmetric stretch is Raman active. At high wavenumbers weaker $\nu_1+\nu_3$ and $2\nu_2+\nu_3$ combination bands can be seen at 3714 and 3612 cm⁻¹ respectively in the IR spectrum.

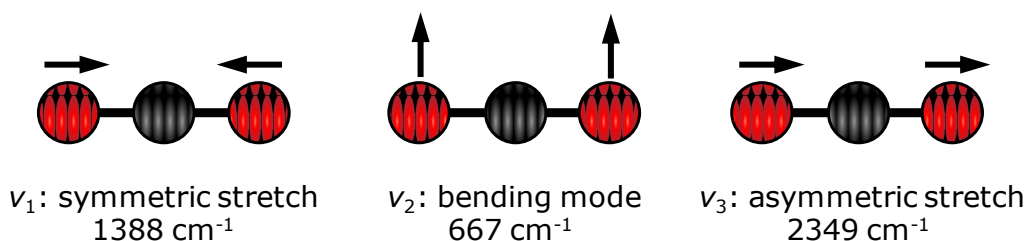


Figure 3.20: View of the vibrational modes of gaseous CO₂. The ν_2 and ν_3 modes involve a change in dipole moment and are IR active.

The fundamental ν_1 asymmetric stretch of gaseous CO_2 , seen at 2349 cm^{-1} , is very intense and saturates in this experiment at partial pressures above 0.2 bar,^{13,56} obscuring the adsorbed ν_1 band at 2339 cm^{-1} . The presence of adsorbed CO_2 was monitored by the growth of the ν_2 bending mode and the $\nu_1+\nu_3$ and $2\nu_2+\nu_3$ combination bands (Figure 3.21).

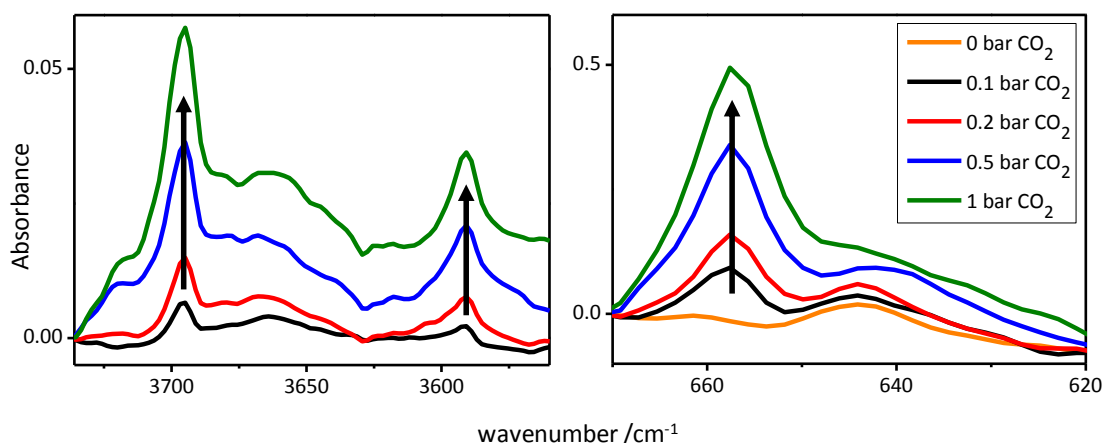


Figure 3.21: IR spectra showing the adsorption of CO_2 into MFM-170, demonstrating the growth in $\nu_1+\nu_3$ and $2\nu_2+\nu_3$ CO_2 combination bands at 3696 cm^{-1} and 3590 cm^{-1} and the ν_2 bending mode at 658 cm^{-1} .

For each partial pressure of CO_2 , the ν_2 bending mode was fitted to a Lorentzian peak shape centred at 658 cm^{-1} , with a second Lorentzian fitted at $\sim 640\text{ cm}^{-1}$ to model the neighbouring framework peak (see appendix A). The peak positions, FWHMs and areas were allowed to refine freely and the peak integrals plotted against pressure, revealing a linear trend that matches the CO_2 isotherm measured by gas adsorption to 1 bar (Figure 3.22). Unfortunately the combination bands were badly affected by the superposition of interference fringes due to scattering of infrared light from the sample particles and suitable Lorentzian peaks could not be reliably fitted to the combination bands for the same procedure to be followed.

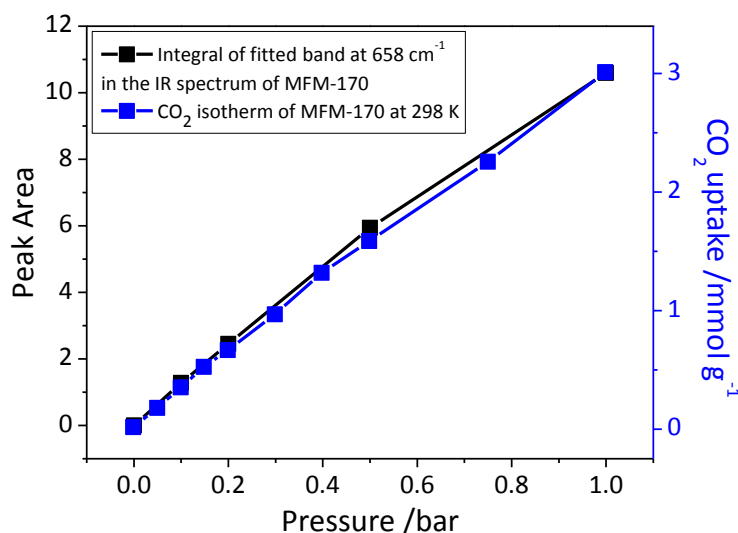


Figure 3.22: Increase in the peak integral of the ν_2 bending mode (658 cm^{-1}) in the spectra of CO_2 loaded MFM-170 at 298 K. Scaled 298 K CO_2 isotherm for comparison

Upon adsorption of CO_2 into MFM-170, a combination of electrostatic and dispersion forces between CO_2 and the pore surface leads to a weakening of the C=O bonds. As a result, the IR bands of adsorbed CO_2 shift to lower frequencies than those observed in the gas phase (Table 3.12).

Table 3.12: Frequency of IR active vibrational modes in gaseous and adsorbed CO_2 and the shifted frequency exhibited by adsorbed CO_2 in MFM-170.

CO ₂ Vibrational mode	Observed frequency in gaseous CO ₂ (cm ⁻¹)	Observed frequency in adsorbed CO ₂ in MFM-170 (cm ⁻¹)
ν_2	667	658
ν_3	2349	2339
$\nu_1+\nu_3$	3714	3696
$2\nu_2+\nu_3$	3612	3590

If CO_2 coordinates to an open metal site the molecular symmetry is lowered, causing the ν_1 mode to become IR active⁵⁷ and the degeneracy of the ν_2 bending mode to be removed, splitting the band into two peaks.^{9,58} Comparison of the IR spectra of activated and CO_2 loaded MFM-170 (Figure 3.23) reveals neither a growth in the ν_1 symmetric stretch or a splitting of the ν_2 bending mode (Figure 3.23), indicating that there are limited interactions between the Cu(II) paddlewheel sites in this sample of MFM-170 and adsorbed CO_2 . As the adsorption of CO_2 on open metal sites is well known, having previously been shown by

neutron diffraction experiments,²⁹ the lack of interaction between CO₂ and the Cu(II)-paddlewheels in MFM-170 suggests that heating the sample to 100 °C under a flow of dry helium is not sufficient to desolvate the Cu(II)-paddlewheels. Application of a vacuum would be a better method of displacing axial solvent molecules; however was not possible in this experimental setup due to the fragility of the ZnSe cell windows in the sample stage.

Whilst initially disappointing, this provides the opportunity to probe key interactions between adsorbed CO₂ and the functionalised pore surface, allowing conclusions to be drawn on the role that the ligand plays in CO₂ adsorption. Culp *et al.* concluded that the shifting of the ν_3 antisymmetric CO₂ stretching mode to lower frequencies in combination with a broadening rather than splitting of the ν_2 bending mode indicates that the dominant interactions are electrostatic in nature between CO₂ and aromatic framework rings with no accessible Lewis basic sites.⁵⁸ This further confirms the hypothesis from gas isotherm analysis that the pyrazine N is not available for interactions with adsorbed CO₂.

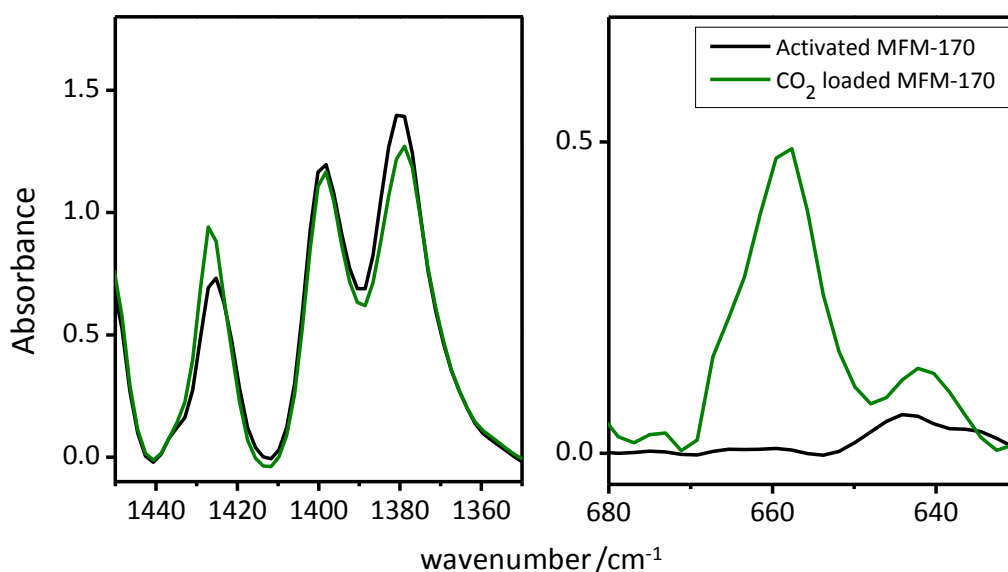


Figure 3.23: Comparison of the IR spectra of activated and CO₂ loaded MFM-170 shows no appearance of the IR inactive ν_1 symmetric stretch, expected at 1388 cm⁻¹, and the formation of one broad band at 658 cm⁻¹, indicating that mainly electrostatic interactions exist between CO₂ and the framework aromatic rings, rather than adsorption onto Lewis basic or acidic sites.

3.3.7.1.3 IR Bands of the Framework Structure of MFM-170

Interactions between adsorbed CO₂ and the framework can be proposed from observation of changes in the IR bands pertaining to MFM-170 (Figure 3.24). The carboxylate C=O stretch at 1648 cm⁻¹ shifts by ~2 cm⁻¹ to lower energy upon CO₂ loading to 1 bar, consistent with an interaction between adsorbed CO₂ and the carboxylate group on the ligand. As CO₂ does not appear to coordinate to the Cu(II)-paddlewheel, this likely arises from a CO₂ molecule binding close to the Cu(II) paddlewheels in the cage windows. More notably, the band at 1068 cm⁻¹, describing the in-plane pyridyl ring deformation and C-H bend,⁶¹ shifts to 1098 cm⁻¹. The large change in the IR vibrational modes corresponding to the pyridyl ring confirms the presence of an important interaction between the π -electron cloud surrounding the pyridyl ring and adsorbed CO₂. Additionally the shifting of the C-H bend implies a secondary interaction between CO₂ and the aromatic C-H groups. Due to the close proximity and overlapping nature of the bands in the fingerprint region, it was impossible to perform quantitative analysis on band formation, as has been reported for interactions with functional groups located at >1700 cm⁻¹ such as -NH₂ and -OH.^{6,13,28,57}

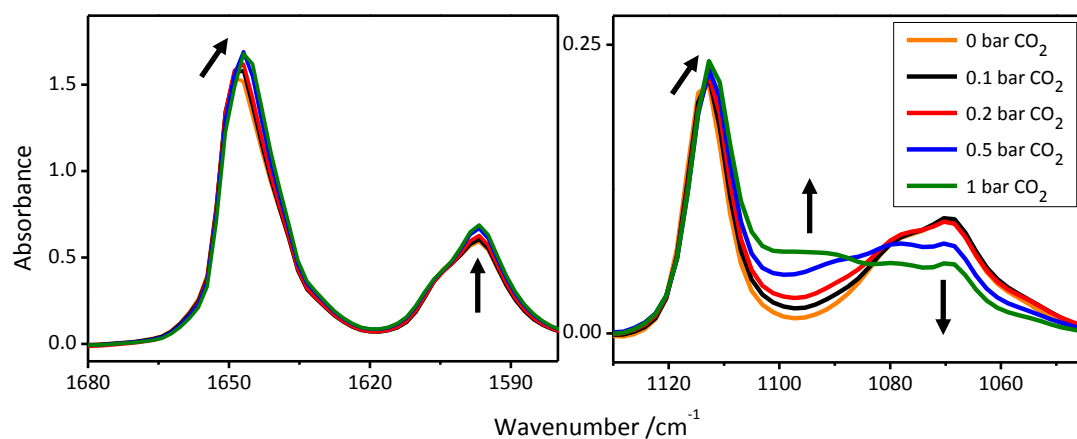


Figure 3.24: Observed changes to the framework IR bands of MFM-170 upon increasing the partial pressure of CO₂ in the sample. The carboxylate C=O stretch at 1648 cm⁻¹ red shifts by 2 cm⁻¹, whilst the band at 1068, describing the in-plane pyridyl ring deformation and C-H bend blue shifts by 30 cm⁻¹ to 1098 cm⁻¹.

3.3.7.1.4 IR Microspectroscopy of CO₂ Loaded MFM-171

The same procedure was followed for a sample of MFM-171; however a thicker crystal caused some of the framework IR absorption bands to saturate. Attempts were made to grind the sample; however this resulted in an increase in the number of interference fringes and was not pursued further. Despite some saturation in the fingerprint region, changes in the framework IR spectrum can still be seen upon CO₂ loading. (Figure 3.25). The C-H deformation band⁶⁰ at 1352 cm⁻¹ shifts by 10 cm⁻¹ to lower energy and the pyrazine C-H bend (1086 cm⁻¹)⁶¹ decreases in intensity, confirming the same type of interaction between CO₂ and the aromatic protons as proposed for MFM-170. Notably, the band at 1016 cm⁻¹, a pyrazine ring bending mode,⁶⁰ shifts by 8 cm⁻¹ to lower energy in the sample loaded to 0.5 bar, before saturating at 1 bar, corroborating the presence of an interaction between adsorbed CO₂ and the π -electron cloud. Finally a broadening rather than splitting of the CO₂ band at 657 cm⁻¹ and shift of the ν_3 antisymmetric stretch to lower energy confirms that the pyrazine N is also inaccessible for Lewis basic interactions with adsorbed CO₂.⁵⁸

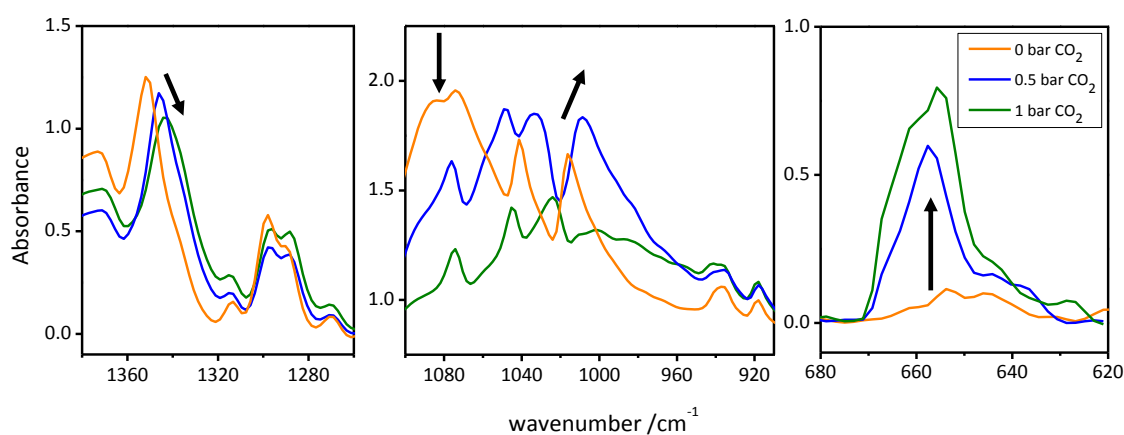


Figure 3.25: Observed changes in the framework IR bands of MFM-171 and growth of the ν_2 bending mode of CO₂ (658 cm⁻¹) upon increasing CO₂ loading. The C-H deformation band at 1352 cm⁻¹ shifts by 10 cm⁻¹ to lower energy whilst the pyrazine bending mode at 1016 shifts by 8 cm⁻¹ to lower energy before saturating in the 1 bar loaded sample.

3.3.7.2 Gas Loaded Single Crystal X-Ray Diffraction

3.3.7.2.1 CO₂ Loaded Single Crystal X-Ray Diffraction in MFM-170

In order to corroborate the CO₂ binding sites proposed from isotherms and IR spectroscopic studies, the locations of adsorbed CO₂ within MFM-170 and MFM-171 were investigated by *in situ* SCXRD. A single crystal of acetone-exchanged MFM-170 was mounted into a flow gas cell and activated *in situ* by heating to 423 K under a dynamic vacuum using a heated stream of N₂ gas directed on the outside of the capillary. SCXRD analysis of the evacuated crystal revealed a small contraction in cell volume of 2% $\Delta V/V$ and decrease in void electron count of 80%, indicating successful removal of solvent molecules from within the pores on the whole (Table 3.13).

The as-synthesised crystal structure of MFM-170 features a coordinated solvent molecule on the axial site of the Cu(II)-paddlewheel; attributed to a highly disordered mixture of DMF and H₂O and is modelled by an anisotropic oxygen atom. In the acetone exchanged crystal used in this study, the coordinated O is likely to be a mixture of H₂O and acetone. Upon evacuation, the crystallographic occupancy of the Cu(II)-bound O (O1W) was reduced to 19%, with incomplete activation attributed to poor heat transfer in the vacuum; the crystal is suspended in the middle of the capillary rather than resting on a heated surface. The incomplete activation even with application of a vacuum supports the difficulty of activating the sample in the IR experiment.

The activated crystals were cooled to 273 K and 1 bar of CO₂ was flowed through the cell. SCXRD analysis revealed a doubling of the void electron count upon CO₂ loading compared to the activated crystal (Table 3.13), confirming the presence of CO₂ within the void. The occupancy of the Cu(II)-bound oxygen atom (O1W) increased to 94% and is considered a mixture of coordinated H₂O/acetone and bound CO₂. The remaining atoms pertaining to the Cu(II)-bound CO₂ could not be modelled due to a high degree of rotation of adsorbed CO₂ across two mirror planes.

Table 3.13: Summary of the key parameters used to track the degree of desolvation and CO₂ loading from the SCXRD analysis of MFM-170.

	Temp.	Unit cell volume	Squeezed e ⁻ density	Highest q peak before squeeze	Occupancy of O1W
Solvated	120 K	37505	22914	2.63	1.0
Evacuated	473 K	37143	1214	0.26	0.19
CO ₂ Loaded	273 K	37213	2239	1.15	0.94

Fourier electron density maps generated for the three cages (Figure 3.26) demonstrates the successful removal of solvent molecules from the pores of the activated crystal and allows location of adsorbed CO₂ within the gas loaded crystal. Areas of positive electron density are shown in green, whilst areas where too much electron density has been assigned are highlighted in red. The level of the Fourier difference map is set at 3σ : three times the background noise in the electron density map. The solvated structure contains large regions of positive electron density, reflecting the four DMF and two H₂O molecules present per Cu(II)-paddlewheel in the void. This electron density is physically removed in the activated structure, reflecting the decrease in SQUEEZE electron count (electron density removed *in silica*).

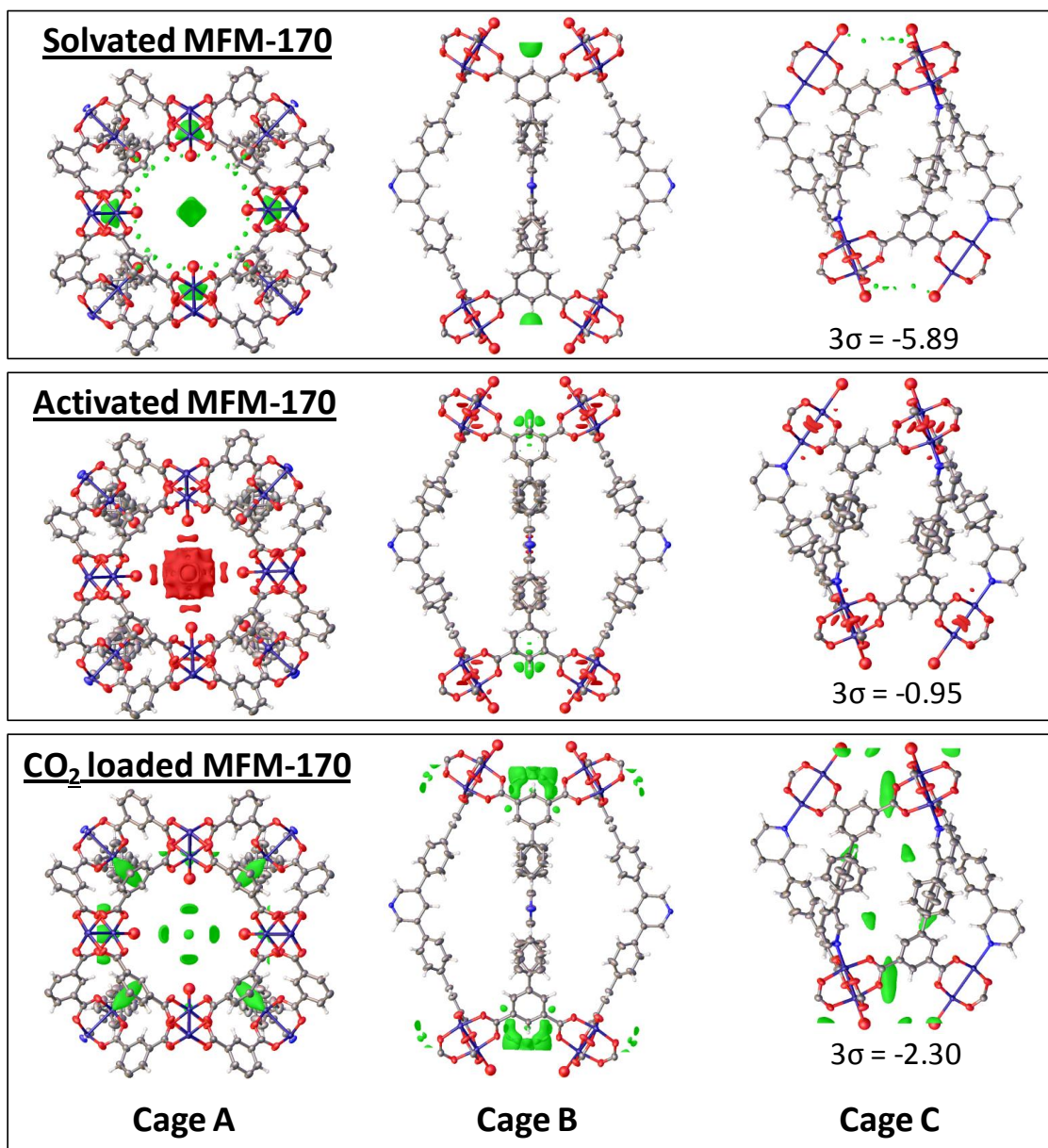


Figure 3.26: Electron density maps showing removal of electron density upon activation and the increase in electron density upon CO₂ loading of the crystal. Areas of unmodelled electron density are shown in green, whilst red surface indicate areas where too much electron has been modelled. The level of the electron density map is set at 3σ – three times the background noise in the electron density map.

Difference Fourier map analysis of the CO₂ loaded crystal revealed a large amount of highly dispersed electron density in cage A. The electron density in this cage could not be modelled with individual CO₂ molecules, indicating that the CO₂ adsorbed within the cage is highly disordered. Consideration of the smaller pores reveals four areas of localised electron density towards the ends of cage B and C.

The electron density in the triangular window of cage C can be modelled as two independent CO_2 molecules (Figure 3.27), populating at site I (CO_2^{I} $\text{O}_{1\text{A}}=\text{C}_{2\text{A}}=\text{O}_{3\text{A}}$) and site II (CO_2^{II} $\text{O}_{1\text{B}}=\text{C}_{2\text{B}}=\text{O}_{3\text{B}}$). Site I is confined to the centre of the triangular face, situated on the threefold rotation axis, with a refined occupancy of 0.19. Meanwhile site II (occupancy 0.14) is located just beneath, tucked into the shoulder of the Cu(II)-paddlewheels that define the triangular window and interacting with a pyridyl C-H group ($\text{O}_{1\text{B}}=\text{C}_{2\text{B}}=\text{O}_{3\text{B}}\cdots(\text{H})-\text{C} = 3.93$ Å). The location of these two binding sites validates two of the shifts seen earlier in the IR spectroscopic studies; the first, the 2 cm^{-1} red shift of the carboxylate C=O band, we partially assign to the proximity of both CO_2^{I} and CO_2^{II} to the Cu(II)-paddlewheels ($\text{O}_{1\text{A}}=\text{C}_{2\text{A}}=\text{O}_{3\text{A}}\cdots\text{O}-\text{C} = 3.83$ Å, $\text{O}_{1\text{B}}=\text{C}_{2\text{B}}=\text{O}_{3\text{B}}\cdots\text{O}-\text{C} = 3.89$ Å); whilst the position of CO_2^{II} near to the pyridyl C-H is likely to cause the shifting of the IR band relating to the pyridyl C-H bend.

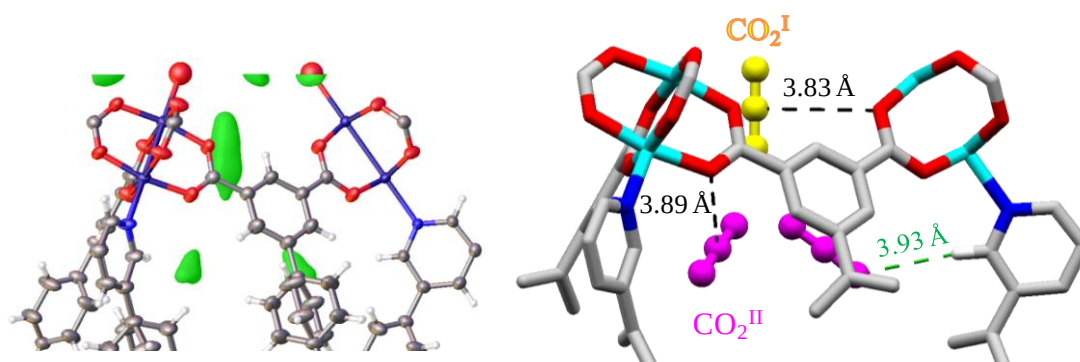


Figure 3.27: View of the Fourier electron density difference map of the triangular window capping cage C in MFM-170. The electron density was modelled to two binding sites; site I (yellow) sits on the threefold rotation axis in the centre of the window, whilst site II (pink) lies beneath with two symmetry generated equivalents. Interactions between CO_2 molecules and carboxylate C-O groups and their distances are shown in black, whilst interactions between adsorbed CO_2 molecules and acidic aromatic protons are shown in green.

At the end of cage B, the electron density can be modelled as two CO_2 molecules (Figure 3.28), located at site III (CO_2^{III} $\text{O}_{1\text{C}}=\text{C}_{2\text{C}}=\text{O}_{3\text{C}}$) and site IV (CO_2^{IV} $\text{O}_{1\text{D}}=\text{C}_{2\text{D}}=\text{O}_{3\text{D}}$). Site III (occupancy 0.13) is located in the corner of the square window, in close proximity to the Cu(II)-paddlewheels. Site IV (occupancy 0.08) is positioned below CO_2^{III} . Both CO_2^{III} and CO_2^{IV} are closer to the carboxylate groups than the CO_2 molecules in sites I and II

($O_{1C}=\underline{C}_{2C}=O_{3C}\cdots\underline{O}-C = 3.34 \text{ \AA}$, $O_{1D}=\underline{C}_{2D}=O_{3D}\cdots\underline{O}-C = 3.35 \text{ \AA}$), causing the C=O stretch in the IR spectrum to shift upon CO₂ adsorption.

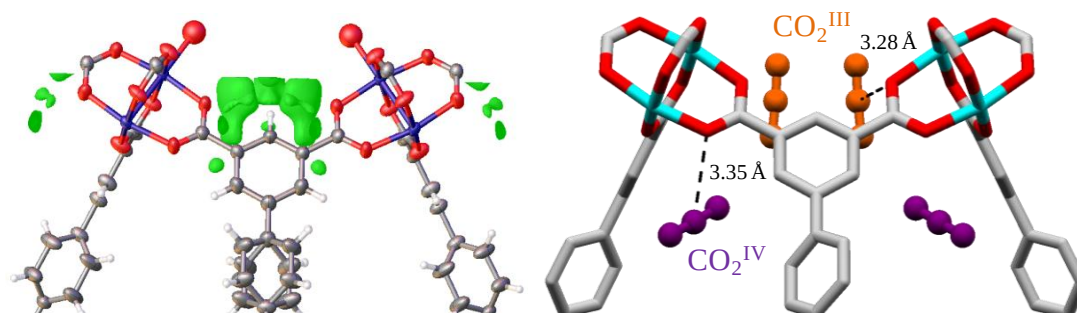


Figure 3.28: View of the Fourier electron density difference map of the square window at of cage B in MFM-170. The electron density was modelled as two CO₂ binding sites, site III (orange) is located within the square window; whilst site IV (purple) is located further into cage B. Interactions between adsorbed CO₂ and the framework C-O carboxylate groups are shown with distances in black.

CO₂^{IV} is situated low in the square window of cage B, protruding out of the side of the cage between two ligand molecules. Consequently, the lone pair on CO₂^{IV} points directly towards the ligand lining the neighbouring orthogonal cage (Figure 3.29); directed at the centre of the π -electron cloud situated around the pyridyl ring ($O_{1D}=\underline{C}_{2D}=O_{3D}\cdots\underline{\text{centroid}} = 3.43 \text{ \AA}$). This interaction accounts for the shifting of the pyridine bending mode in the IR spectra from 1068 cm⁻¹ in the activated MFM-170 to 1098 cm⁻¹ in the CO₂ loaded sample. Confirmation of the interaction between adsorbed CO₂ and the pyridyl ring validates the theory drawn from CO₂ isotherm analysis; CO₂ adsorption capacities in the MFM-17X series at 1 bar are heavily influenced by the electronic properties of the pyridyl ring and therefore the electron withdrawing or donating characteristics of the substituent group.

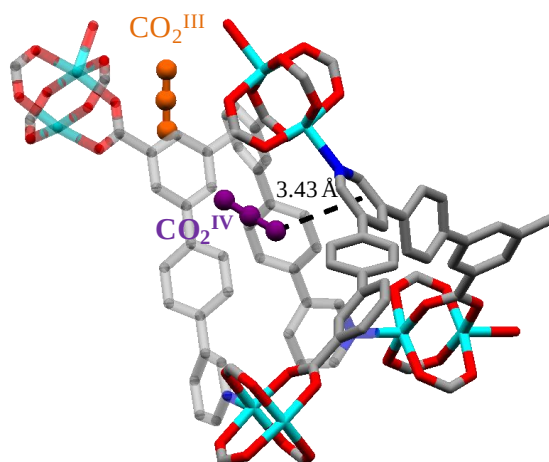


Figure 3.29: Rotated view of CO₂ molecules located in sites III and IV at the end of cage B. CO₂^{IV} protrudes out the side of cage B and points towards the pyridyl ring of the ligand bounding the edge of the perpendicular cage. The O=C=O...centroid interaction is shown in black

The combined occupancies of the four sites located by SCXRD (Table 3.14) yields an overall formula of [Cu₂PPYD]·0.55CO₂, far below the [Cu₂PPYD]·3CO₂ calculated from the CO₂ isotherm at 273 K and 1 bar. The lack of confinement in the large cage voids of MFM-170 means that a large amount of the remaining CO₂ is non-localised and can be accounted for by the remaining electron density within cage A.

Table 3.14: Crystallographic occupancies of the CO₂ binding sites located in the CO₂ loaded crystal of MFM-170 at 273 K

	Occupancy of located CO ₂				Total
	Site I	Site II	Site III	Site IV	
MFM-170	0.19	0.13	0.14	0.09	0.55

3.3.7.2.2 CO₂ Loaded Single Crystal X-Ray Diffraction in MFM-171

A single crystal of MFM-171 was loaded into a quartz capillary and activated by heating to 423 K in a metal heating block under a dynamic vacuum. The cell was cooled to room temperature, sealed, and mounted on the diffractometer, where a dataset was collected at 243 K. Activation of MFM-171 lead to a reduction in cell volume of <1% ΔV/V and a decrease in the void electron count to 2054 electrons per unit cell (Table 3.15). The total electron count in the activated sample of MFM-171 is higher than that seen in MFM-170

(1214 electrons), indicating that use of a metal heating block is a less successful method of activation than heating the capillary with a stream of N₂. This is confirmed by the higher occupancy of Cu(II)-bound solvent (O1W); only half of the Cu(II)-paddlewheels were desolvated in MFM-171 compared to over 80% in MFM-170. Inferior activation is attributed to poor contact between the glass walls of the capillary and the metal heating block.

The cell was attached to a custom-made gas panel and loaded with CO₂ to *ca.* 3 bar at room temperature. The cell was sealed and cooled to 95 K using a N₂ cryostream, where the capillary was removed to allow for low temperature studies without interference from CO₂ condensing inside the glass. The void electron count of the CO₂-loaded crystal of MFM-171 is higher than that seen in MFM-170 (5172 vs. 2239), reflecting the greater quantity of CO₂ within the pore from loading at higher pressures

Table 3.15: Summary of the key parameters used to track the degree of desolvation and CO₂ loading from the SCXRD analysis of MFM-171.

MFM-171	Temp	Unit cell volume	Squeezed e ⁻ density	Highest q peak before squeeze	Occupancy of O1W
Solvated	120 K	37170	22675	2.09	1.0
Evacuated	243 K	36966	2054	0.96	0.46
CO ₂ Loaded	95 K	37081	5172	3.80	1.0

Difference Fourier map analysis of CO₂ loaded MFM-171 reveals the presence of the same four binding sites seen in MFM-170. Due to the higher loading pressure, the areas of positive electron density in the Fourier difference map are more distinct, and all four sites demonstrate higher occupancies (Table 3.16). There are subtle differences in the located CO₂ molecules between the two frameworks; attributable to both lower experimental temperatures and weaker interactions between adsorbed CO₂ and the framework surface of MFM-171, suggested by gas adsorption isotherms.

The CO₂ molecule in site I aligns with the Cu(II)-paddlewheels surrounding the triangular window of cage C, displaying threefold disorder instead of the central averaged position

seen at higher temperatures (Figure 3.30). With a crystallographic occupancy of 3×0.29 , site I is almost fully occupied as the three positions are mutually exclusive. Site II, lying slightly below, is at maximum occupancy at 65% as the short distances between CO_2^{I} and CO_2^{II} ($\text{O}_{1\text{A}}=\text{C}_{2\text{A}}=\text{O}_{3\text{A}}\cdots\text{O}_{1\text{B}}=\text{C}_{2\text{B}}=\text{O}_{3\text{B}} = 1.1 \text{ \AA}$) exclude the position situated directly below site I. CO_2^{II} in MFM-171 is located slightly closer to the aromatic ring than in MFM-170 ($\text{O}_{1\text{B}}=\text{C}_{2\text{B}}=\text{O}_{3\text{B}}\cdots(\text{H})-\text{C} = 3.67 \text{ \AA}$ cf. $3.93 \text{ \AA}$). The stronger interaction between adsorbed CO_2 and the aromatic C-H group is attributed to an increase in the acidity of the aromatic protons; the electron density surrounding the pyrazine ring is reduced due to the inductive effects of the pyrazine N. This strong interaction explains the larger shift in the IR C-H deformation band by 10 cm^{-1} to lower energy upon CO_2 loading. The CO_2 molecules in sites I and II in MFM-171 are located slightly closer to the carboxylate groups than in MFM-170. Unfortunately saturation of the IR spectrum between 1360 and 1660 cm^{-1} means that no comparison can be drawn between the relative shifts of the C=O stretch in MFM-170 and MFM-171 but are expected to show greater shifts due to stronger interactions.

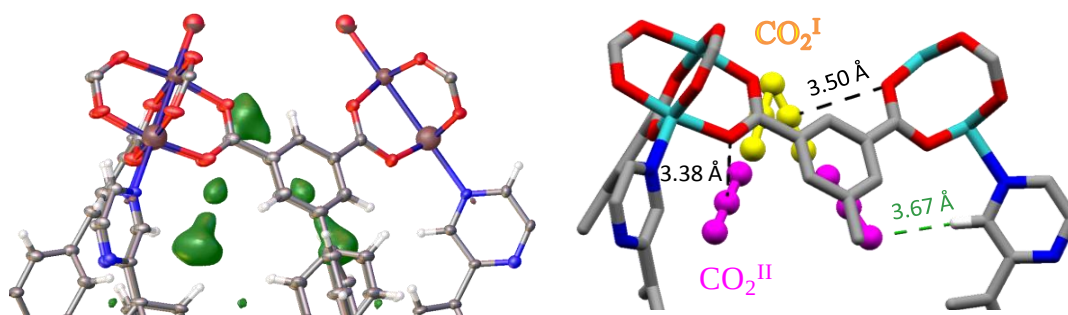


Figure 3.30: View of the Fourier electron density difference map of the triangular window capping cage C in MFM-171. The electron density was modelled to two binding sites; site I (yellow) is tilted away from the threefold rotation axis in the centre of the window, displaying threefold disorder with a maximum site occupancy of 0.33; whilst site II (pink) lies beneath with two symmetry generated equivalents. Interactions between CO_2 molecules and carboxylate C-O groups and their distances are shown in black, whilst interactions between adsorbed CO_2 molecules and acidic aromatic protons are shown in green.

In cage B, Site III (occupancy 0.25) and site IV (occupancy 0.39) are positioned lower in the square cage window than in MFM-170 (Figure 3.31). As a result, CO_2^{III} and CO_2^{IV} are situated slightly further away from the carboxylate groups on the Cu(II)-paddlewheels

($O_{1C}=C_{2C}=O_{3C}\cdots O-C = 3.69 \text{ \AA}$ cf. $3.34 \text{ \AA}$; $O_{1D}=C_{2D}=O_{3D}\cdots O-C = 3.41 \text{ \AA}$ cf. $3.35 \text{ \AA}$), indicating weaker interactions within the carboxylate groups in this cage. CO_2^{IV} is marginally further away from the π -electron cloud surrounding the neighbouring pyridyl ring in MFM-171 compared to MFM-170 ($O_{1D}=C_{2D}=O_{3D}\cdots \text{centroid} = 3.45 \text{ \AA}$ cf. $3.43 \text{ \AA}$), reflecting the weaker electrostatic interactions with the π -electron cloud above the pyrazine ring, which leads to a reduction in the CO_2 uptake capacity at 1 bar.

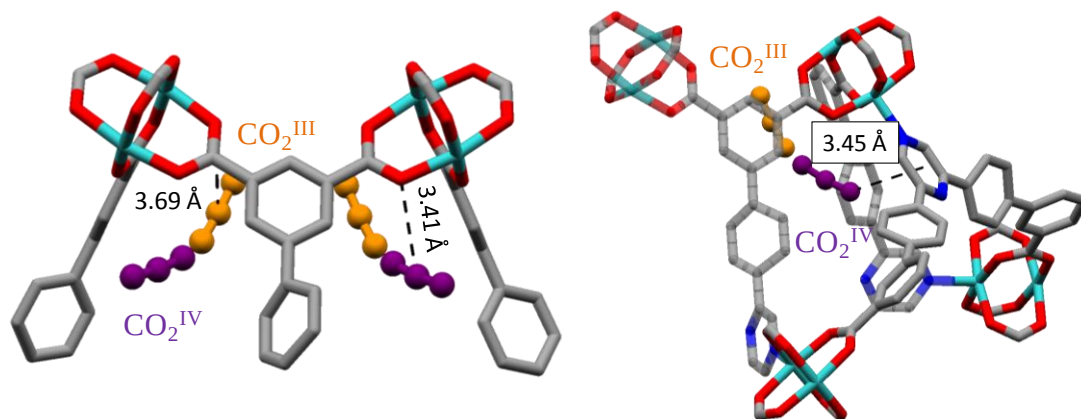


Figure 3.31: Location of the two CO_2 binding sites modelled in the square window of cage B in MFM-171. Site III (orange) is positioned within the square window; whilst site IV (purple) is located further into cage B. Site IV protrudes out of the side of cage B, towards the pyrazine ring of another ligand molecule oriented perpendicular to the pore. Interactions between adsorbed CO_2 and the framework C-O carboxylate groups and $CO_2\cdots\text{centroid}$ interactions are shown in black.

The use of lower temperatures to study MFM-171 reduces rotational disorder within the ligand and allows two further binding sites to be visualised (Figure 3.32). Sites V and VI are situated between two phenyl rings oriented in a face-to-face fashion along the outside edge of cage C ($O_{1E}=C_{2E}=O_{3E}\cdots \text{centroid} = 3.38 \text{ \AA}$ and $O_{1F}=C_{2F}=O_{3F}\cdots \text{centroid} = 3.40 \text{ \AA}$). Occupancy of site V/VI is mutually exclusive and requires two neighbouring phenyl rings to be aligned; giving a maximum combined occupancy of 50%. The presence of electrostatic interactions between CO_2^V/CO_2^{VI} and the π -electron clouds surrounding the phenyl rings is thought to increase the broadening of the ν_2 bending mode in the IR spectra.

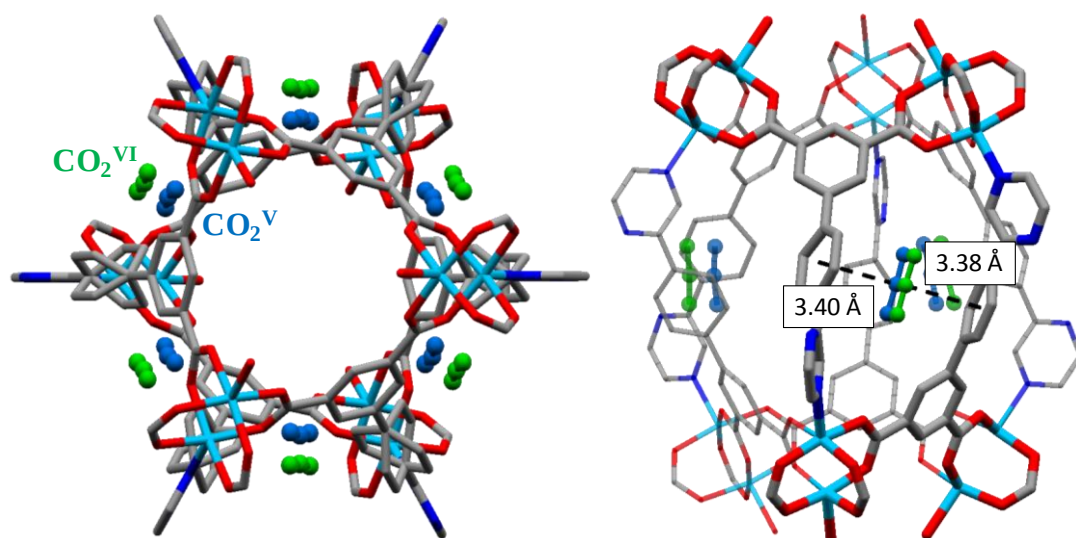


Figure 3.32: Positions of sites V (blue) and VI (green) modelled between the phenyl rings surrounding cage C in MFM-171. Occupancy of sites V/VI requires two neighbouring phenyl rings to be aligned; thus only half of the sites can be occupied in the crystal structure at any one time. Interactions between the modelled CO₂ molecules and centroids of the sandwiching phenyl rings are represented in black.

The higher CO₂ loadings used to study MFM-171 increases the localised electron density (Table 3.16). As CO₂ can leach out of the crystal upon removal of the glass capillary and it is impossible to determine the final CO₂ pressure in the sealed cell upon cooling, it is inappropriate to compare the total amount of located CO₂ to that expected from the CO₂ isotherm.

Table 3.16: Crystallographic occupancies of the CO₂ binding sites located in the CO₂ loaded crystal of MFM-171 at 95 K and comparison to the occupancies in MFM-170 at 273 K.

Temp		Occupancy of located CO ₂ (%)						Total
		Site I	Site II	Site III	Site IV	Site V	Site VI	
MFM-170	273 K	0.19	0.13	0.14	0.09	-	-	0.55
MFM-171	95 K	0.29	0.65	0.25	0.39	0.22	0.29	2.09

Fourier difference map analysis after modelling of the located CO₂ binding sites in MFM-171 reveals limited green peaks of positive electron density (Figure 3.33), indicating that the remaining CO₂ is distributed between the large void spaces in the centre of cages A and B. The lack of electron density in the middle of cage B confirms that the pyrazine N does not

act as a binding site for adsorbed CO₂, which we attribute to steric hindrance between the two arms of the ligand.

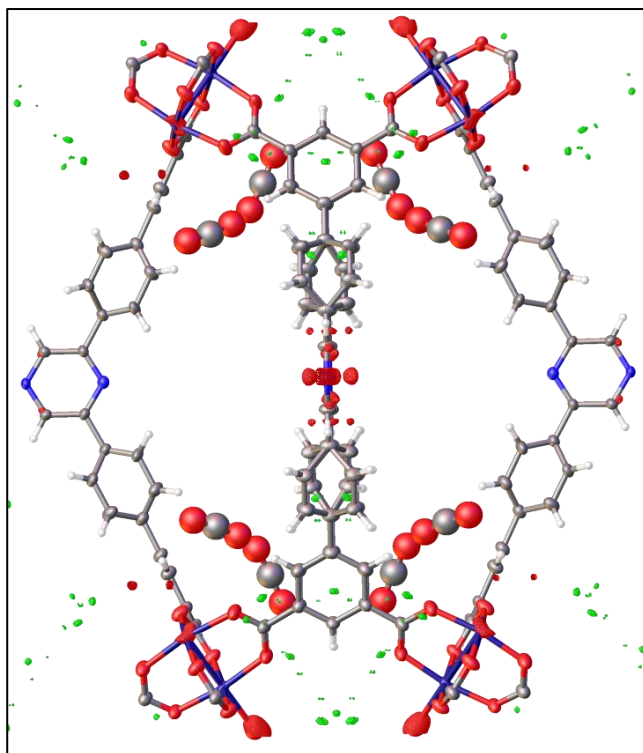


Figure 3.33: *Electron density map of cage B in MFM-171 after modelling of all located CO₂ molecules, showing no residual electron density in the centre of the functionalised cage.*

It may be prudent to note that all six CO₂ molecules located by SCXRD experience multiple interactions with the framework surface. Situated in the corners of Cu(II)-paddlewheels, sites I-IV interact with two carboxylate groups, whilst sites V and VI are sandwiched between two phenyl rings. In order for binding sites to be visualised by SCXRD within a framework, it is advantageous for CO₂ molecules to experience multiple synergic interactions with the framework surface, which result in more constricted sites for CO₂ to occupy.

3.3.7.3 GCMC simulations of CO₂ binding sites within MFM-170

GCMC simulations were carried out by Dr Matt Lennox. The CO₂ binding sites observed *via* SCXRD were verified *via* snapshots of the GCMC simulation of CO₂ adsorption in MFM-170 at 1 bar and 273 K. All six binding sites are observed (Figure 3.34), although the

CO₂ molecules were allowed to rotate freely and adopt different orientations to those seen in SCXRD studies in order to minimise steric inhibition. Site IV aligns parallel with, rather than end-on to the pyridyl ring in order to maximise the electrostatic interaction with the donut of positive electrostatic potential around the central carbon atom.⁵⁷ In contrast to the SCXRD data, binding site V/VI was observed in MFM-170 at 273 K, and found to be indistinguishable in GCMC simulations.

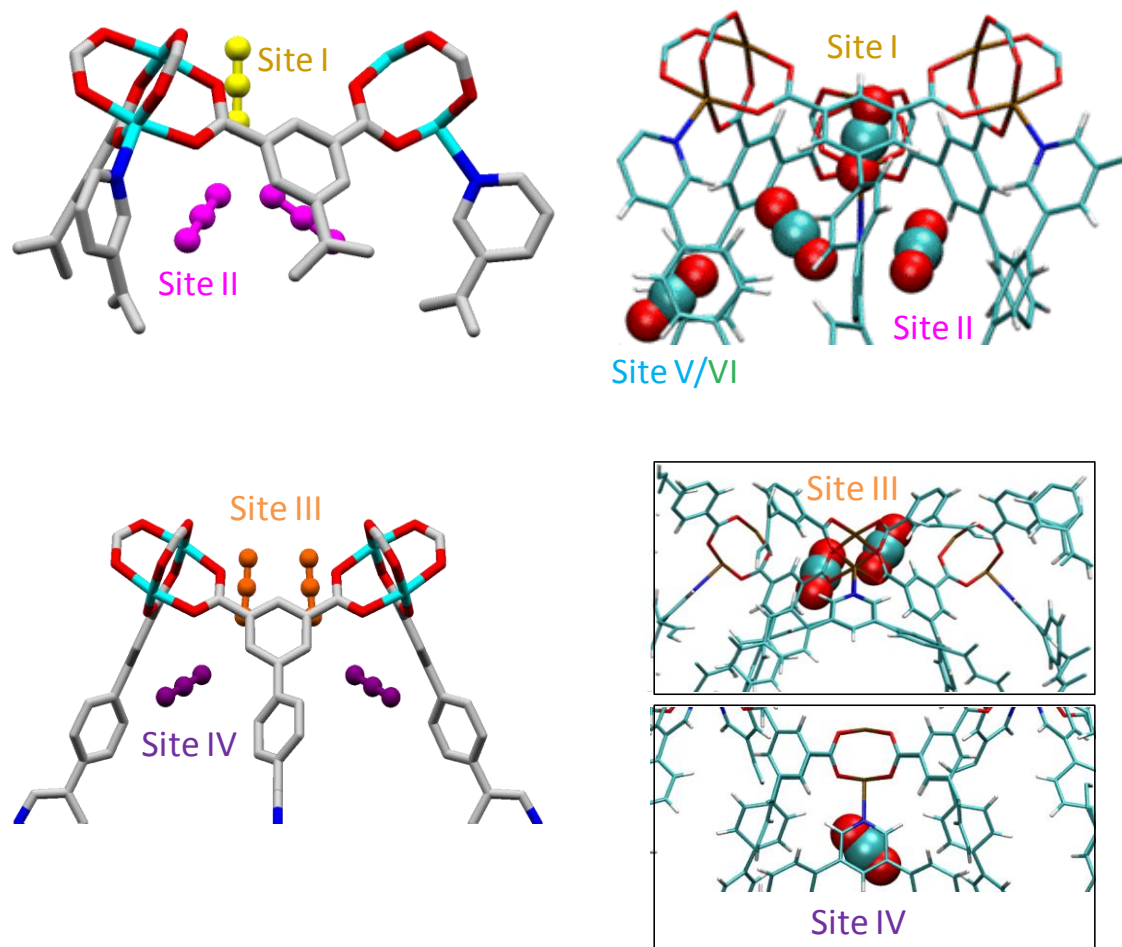


Figure 3.34: Comparison of the positions of modelled CO₂ molecules in the single crystal structure of MFM-170 to the CO₂ molecules located by snapshots of GCMC simulations. All six sites are located by GCMC simulations, albeit the CO₂ molecules are oriented in different directions.

Interaction energies were found to lie in the range of -25 kJ mol⁻¹ to -17.5 kJ mol⁻¹, in agreement with the calculated isosteric heats of adsorption for MFM-170 and MFM-171 (-18 kJ mol⁻¹ and -20 kJ mol⁻¹ respectively). Dot colour coding was used to display the interaction energies of each CO₂ molecule simulated in both frameworks (Figure 3.35).

MFM-171 demonstrates a greater number of strong interactions around the carboxylate groups (marked in yellow: $-22.5 \text{ kJ mol}^{-1}$ to -25 kJ mol^{-1}). Not only does this support the closer contacts observed in the SCXRD studies of MFM-171, but also explains the higher initial heat of adsorption for MFM-171 if site II is the first to be occupied (Table 3.17).

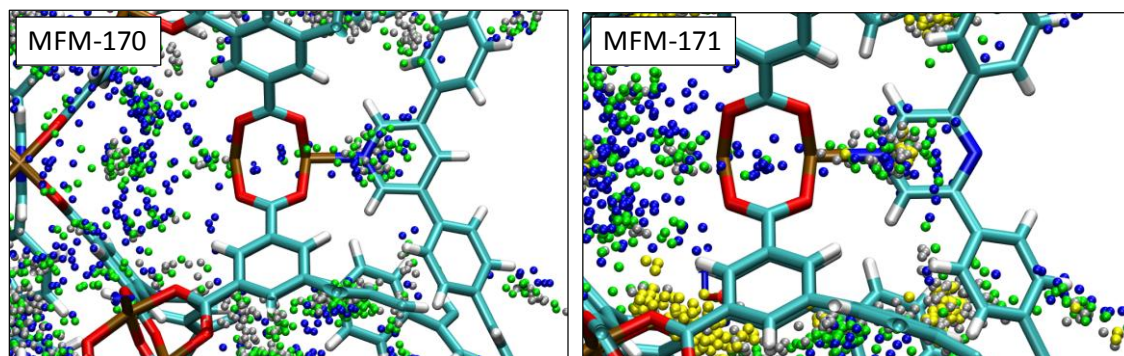


Figure 3.35: Dot colour coding to show difference in interactions between the two frameworks on the edge of cage B, 195 K, averaged over $P = 0$ to 0.2 . Dot colour coding: Yellow: -22.5 to -25.0 kJ/mol ; White: -20 to -22.5 kJ/mol ; Green: -17.5 to -20.5 kJ/mol .

Table 3.17: Comparison of SCXRD located CO_2 adsorption sites within MFM-170 and MFM-171 with the GCMC calculated interaction energies.

Binding Site	SCXRD occupancy		GCMC interaction energy / kJ mol^{-1}
	MFM-170, 273 K	MFM-171, 95 K	
I	0.19	0.29	-27.5 to -31.5
II	0.13	0.65	-22.5 to -27.5
III	0.14	0.25	-17.5 to -22.5
IV	0.09	0.39	-17.5 to -20.5
V	-	0.22	-17.5 to -25.0
VI	-	0.29	-17.5 to -25.0

3.4 Conclusions

The functionalisation of H_4PPYD , used to synthesise MFM-170 gave rise to an isostructural series of frameworks incorporating pyrazine (MFM-171), methyl (MFM-172) and carboxylic acid (MFM-173) functional groups pointing into the centre of cage B. Attempts to synthesise and amine or amide functionalised ligand were unsuccessful due to the strong electronic properties of the substituent groups and unfortunately a bulk sample of MFM-173 could not be synthesised for further investigations.

MFM-171 showed no improvement in the total uptake capacity of N₂, CO₂, or CH₄ compared to MFM-170, indicating that the Lewis basic pyrazine group is too sterically hindered to interact with gas molecules. MFM-172 demonstrated an improvement in the adsorption capacity of CO₂ at 1 bar, indicating the presence of a strong interaction between the framework and adsorbed CO₂, which is outweighed at high pressure by the reduction in pore volume. This increase in CO₂ adsorption at atmospheric pressure leads to improved selectivities at lower pressure and the proposition of a key binding interaction between adsorbed CO₂ and the π -electron cloud above the central pyridyl ring.

In order to rationalise the adsorption behaviour of the MFM-17X series and validate the CO₂ binding site predicted from the adsorption isotherms, *in situ* IR experiments were performed on single crystals of MFM-170 and MFM-171. Analysis of the IR active bands of CO₂ indicates that the interactions between adsorbed CO₂ and the ligand are primarily electrostatic and do not include strong Lewis acid/base interactions with uncoordinated Cu(II) or N sites. Changes in the framework IR bands signify the presence of three different binding sites within the framework. A red shift in the carboxylate C=O stretch indicates that CO₂ molecules bind in close proximity to the Cu(II)-paddlewheels, presumably within the cage windows. Changes to the aromatic C-H bending modes hints towards interactions with acidic aromatic protons; whilst in-plane pyridyl/pyrazine ring deformations confirm the proposed interaction with the π -electron cloud surrounding the central aromatic ring.

To confirm the proposed binding sites, CO₂ loaded X-ray diffraction was performed on single crystals of MFM-170 and MFM-171. Four individual CO₂ molecules were located in MFM-170 and modelled within the cage windows of cages B and C. All four molecules are situated close to the carboxylate groups of the Cu(II)-paddlewheels, validating the red shifted C=O stretch in the IR spectra. Site II and site IV are positioned slightly lower in the cage window, where CO₂^{II} interacts with an aromatic C-H group and CO₂^{IV} interacts with a pyridyl ring of a neighbouring cage, accounting for the changes in the C-H bending modes and pyridyl/pyrazine deformation bands and confirming that the electronic properties of the

central pyridyl ring dictates the binding strength with CO₂^{IV}. The use of lower temperatures for the analysis of MFM-171 revealed two further binding sites, situated between the faces of two neighbouring phenyl rings, corroborating the mainly electrostatic interactions between CO₂ and the framework surface.

GCMC simulations confirmed the presence of all six located CO₂ sites. Analysis of the interaction energies of each binding site revealed that the higher Q_{st} in MFM-171 compared to MFM-170 appears to be due to stronger interactions with the carboxylate groups; the first sites to be filled within the framework.

The work in this chapter suggests that pore functionalisation in MFM-170 has potential to increase the selectivity for the adsorption of CO₂ over N₂ and CH₄; however the choice and positioning of such functional groups should be judicious. Whilst the addition of functional groups *para*- to the pyridyl N can influence adsorption behaviour by changing the electronics of the ligand molecule, the position is highly sterically hindered and heterocyclic functional groups are likely to be unavailable for interactions with guest species. The location of adsorbed CO₂ molecules within the framework reveals that the strongest binding sites are situated within cage C; therefore careful placement of functional groups within this cage has the greatest potential to improve CO₂ adsorption and selectivity.

3.5 Outlook

The diameter of cage C measures only 14 Å across its widest cross-section and is lined by sections of six ligand molecules. With a guest-accessible diameter of 8 Å, determined from experimental pore size distribution calculations, the inclusion of six bulky functional groups will undoubtedly block space within the pore, reducing the total porosity and gas adsorption capacity.

We propose a strategy to include additional Lewis basic nitrogen sites into the phenyl spacer rings of the ligand H₄PPYD (Figure 3.36), which can rotate to functionalise either cage C or cage B. Location of these binding sites on the outside edge of the phenyl rings should avoid

previous problems involving steric hindrance, leaving them available for strong Lewis base interactions with adsorbed CO₂.

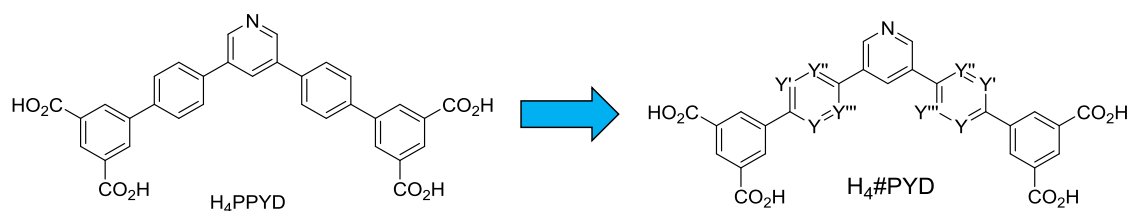
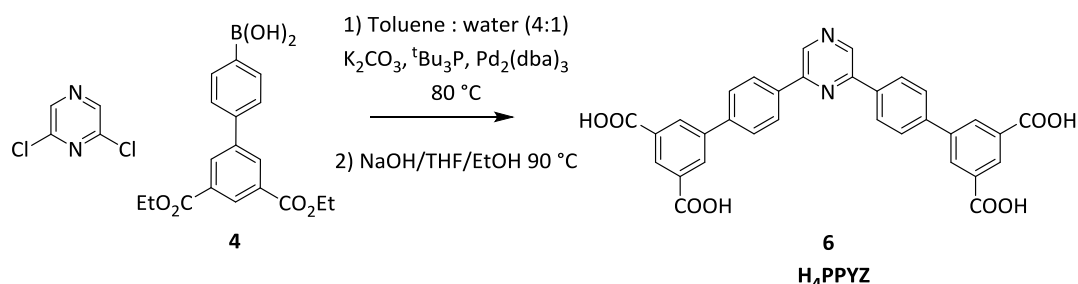


Figure 3.36: Proposed strategy to functionalise MFM-170 in order to improve specific gas binding interactions and selectivity.

3.6 Experimental

Synthesis of H₄PPYZ (6)

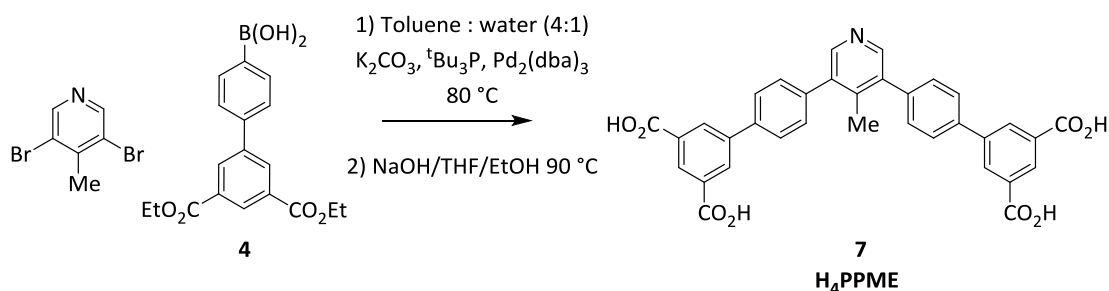


4 (0.57 g, 1.7 mmol), 2,6-dichloropyrazine (0.1 g, 0.67 mmol) and K₂CO₃ (0.1 g, 1.3 mmol) were dissolved in a solution of toluene:water (50 ml, 4:1 v/v) and degassed with argon at 60 °C for 30 minutes. Tritertbutylphosphine (1 M solution in toluene, 0.05 ml, 0.05 mmol) and Pd₂(dba)₃ (40 mg, 0.05 mmol) were added and the reaction heated to 80 °C. The product was extracted into DCM and the solvent removed *in vacuo* before being purified by column chromatography (EtOAc:PE. 1:1 v/v on silica) (0.26 g, 58%). ¹H NMR (300 MHz, CDCl₃) δ ppm: 9.07 (2 H, s), 8.71 (2 H, t, *J* = 1.6 Hz), 8.56 (2 H, d, *J* = 1.6 Hz), 8.33 (4 H, d, *J* = 8.5 Hz), 7.88 (4 H, d, *J* = 8.5 Hz), 4.48 (8 H, q, *J* = 7.1 Hz), 1.47 (12 H, t, *J* = 7.1 Hz). ¹³C NMR (100 MHz) δ ppm: 142.67, 132.13, 131.68, 130.50, 129.80, 128.96, 128.38, 128.00, 127.92, 127.76, 61.57, 14.35. MS (ESI) *m/z*: 673.2547 [M+H]⁺. IR (ATR) cm⁻¹: 2982 (C-H), 1718

(C=O). Elemental analysis (%): crude: C 66.91, H 5.11, N 5.06, calculated for $C_{40}H_{36}N_2O_8$: C 71.42, H 5.39, N 4.16

The product was suspended in a solution of aqueous NaOH (2 M, 50 ml), THF (25 ml) and EtOH (25 ml) and stirred at 90 °C overnight. The product was precipitated by addition of HBF_4 to the aqueous layer and isolated by filtration. (0.21 g, 98%) ^1H NMR (300 MHz, $DMSO-d_6$) δ ppm: 13.45 (4H, br s), 9.34 (2 H, s), 8.50 (6 H, m), 8.45 (4 H, d, $J = 8.45$ Hz), 8.00 (4 H, d, $J = 8.45$ Hz). ^{13}C NMR (100 MHz, $DMSO-d_6$) δ ppm: 166.48, 149.89, 140.56, 140.32, 139.82, 135.72, 132.19, 131.35, 129.19, 127.69, 127.62. MS (ESI) m/z : 559.1319 $[M-H]^-$. IR (ATR) cm^{-1} : 3071 (O-H) 1694 (C=O). Elemental analysis (%): crude: C 70.53, H 4.09, N 5.26, calculated for $C_{32}H_{20}N_2O_8$: C 68.57, H 3.60, N 5.00.

Synthesis of H_4PPME (7)

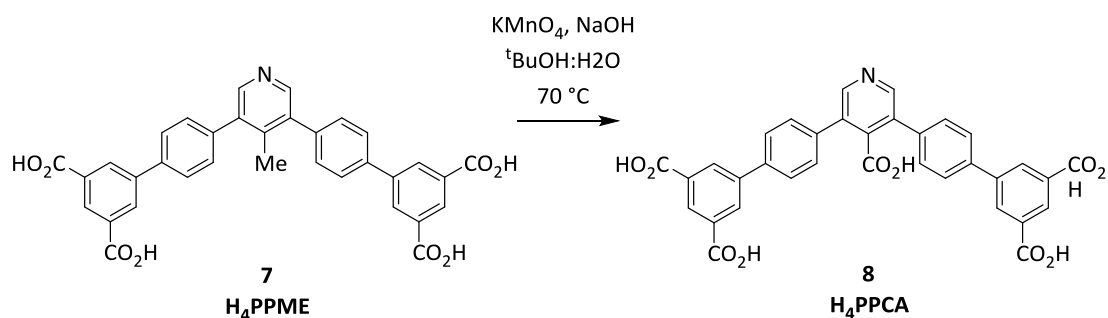


4 (500 mg, 1.5 mmol), 4-methyl-3,5-dibromopyridine (145 mg, 0.6 mmol) and K_2CO_3 (420 mg, 3 mmol) were dissolved in a solution of toluene:water (50 ml, 4:1 v/v) and degassed at 60 °C for 30 minutes. Triterbutylphosphine (1 M solution in toluene, 0.2 ml, 0.2 mmol) and $Pd_2(dba)_3$ (30 mg, 0.03 mmol) were added and the reaction heated to 80°C. The product was extracted into DCM and the solvent removed *in vacuo*. before being recrystallised from DCM with petroleum ether. (358 mg, 90%). ^1H NMR (300 MHz, $CDCl_3$) δ ppm: 8.70 (2 H, t, $J = 1.6$ Hz), 8.54 (2 H, d, $J = 4.6$ Hz), 8.52 (2 H, s), 7.80 (4 H, m), 7.53 (4 H, m), 4.47 (4 H, q, $J = 7.1$ Hz), 1.46 (6 H, t, $J = 7.1$ Hz). ^{13}C NMR (100.6 MHz, $DMSO-d_6$) δ ppm: 166.44, 150.96, 141.84, 140.31, 139.17, 138.69, 135.38, 132.26, 131.39, 130.49, 129.14, 127.31, 19.36. MS (ESI) m/z : 686.2749 $[M]^+$. IR (ATR) cm^{-1} : 2992 (C-H), 2903, 1707

(C=O). Elemental analysis (%): crude: C 72.19, H 5.84, N 2.14, calculated for $C_{42}H_{39}NO_8$: C 73.56, H 5.73, N 2.04.

The product was suspended in a solution of NaOH (2 M, 50 ml), THF (25 ml) and EtOH (25 ml) and stirred at 90 °C overnight. The product was precipitated by addition of HBF_4 and isolated by filtration. (0.21 g, 98%) ^1H NMR (400 MHz, $DMSO-d_6$) δ ppm: 8.49 (2 H, s), 8.48 (2 H, s), 8.46 (4 H, s), 7.9 (4 H, d, J = 8.2 Hz), 7.65 (4 H, d, J = 8.2 Hz). ^{13}C NMR (100 MHz, $DMSO-d_6$): 166.44, 151.07, 141.84, 140.31, 139.17, 138.69, 135.38, 132.26, 131.39, 130.49, 129.14, 127.31, 19.36. MS (ESI) m/z : 574.1 $[M+H]^+$. IR (ATR): 2981 (C-H), 1698 (C=O). Elemental analysis (%): crude: C 64.17, H 4.05, N 2.24, calculated for $C_{34}H_{23}NO_8$: 71.20, 4.04, 2.44.

Synthesis of H_4PPCA (8)



7 (250 mg, 0.44 mmol) was dissolved in $^t\text{BuOH}:\text{H}_2\text{O}$ (100 cm^3 , 3:1 v/v) with NaOH (200 mg, 5 mmol) and heated to 50 °C. KMnO_4 (500 mg, 3 mmol) was added portion-wise over one day. The reaction temperature was increased to 70 °C and the solution stirred overnight. Excess KMnO_4 was reduced by refluxing with isopropanol and precipitated MnO_2 was removed by filtration. The solvent was reduced *in vacuo* and the product precipitated by addition of formic acid (211 mg, 80%). ^1H NMR (300 MHz, $DMSO-d_6$) δ ppm: 8.53 (2 H, s), 8.47 (2 H, s), 8.43 (4 H, s), 7.82 (8 H, m). ^{13}C NMR (100.6 MHz, $DMSO-d_6$) δ ppm: 166.65, 166.46, 134.43, 132.24, 131.48, 131.32, 130.43, 130.39, 130.19, 129.54, 129.44, 129.83, 127.25, 127.15. MS (ESI) m/z : 602.1 $[M-H]^-$. IR (ATR) cm^{-1} : 2821 (C-H), 1680 (C=O).

Synthesis of MFM-171

6 (200 mg, 0.36 mmol) and $\text{Cu}(\text{NO}_3)_2 \cdot 5/2(\text{H}_2\text{O})$ (330 mg, 1.42 mmol) were dissolved in a solution of DMF:H₂O (48 ml, 5:1) and acidified with conc. HNO_3 (0.3 ml). The solution was heated in a Schott bottle at 80 °C overnight until blue octahedral crystals precipitated. The product was filtered, washed with hot DMF and dried. (310 mg, 84 %). IR (ATR) cm^{-1} : 3063 (O-H), 1711 (C=O). Elemental analysis (%): crude: C 49.45, H 4.66, N 9.25, calculated for $[\text{Cu}_2\text{PPYZ}(\text{DMF})] \cdot (\text{DMF})_5(\text{H}_2\text{O})_3$: C 51.06, H 5.48, N 9.53.

Synthesis of MFM-172

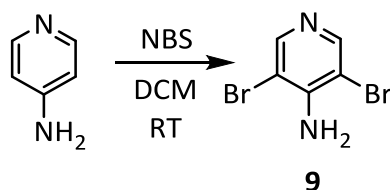
7 (550 mg, 0.96 mmol) and $\text{Cu}(\text{NO}_3)_2 \cdot 5/2(\text{H}_2\text{O})$ (950 mg, 4.1 mmol) were dissolved in DMF (100 ml) and acidified with conc. HNO_3 (1.5 ml). The solution was heated in a Schott bottle at 80 °C for two days until a blue powder precipitated. The product was filtered, washed with hot DMF followed by acetone and dried. (644 mg, 95%). IR (ATR) cm^{-1} : 3060 (O-H), 1713 (C=O) 1643. Elemental analysis (%): crude: C 49.04 H 3.36 N 1.79, calculated for $[\text{Cu}_2\text{PPME}(\text{H}_2\text{O})] \cdot (\text{H}_2\text{O})_4$: C 51.91 H 3.72 N 1.78.

Synthesis of MFM-173

(8) (10 mg, 0.17 mmol) and $\text{Cu}(\text{NO}_3)_2 \cdot 5/2(\text{H}_2\text{O})$ (18.6 mg, 0.08 mmol) were dissolved in DMF (3 ml) and acidified with three drops of HNO_3 . The solution was heated to 80 °C in a sealed Wheaton vial for two days until blue crystals precipitated. IR (ATR) cm^{-1} : 3324 (O-H), 1645 (C=O). Elemental analysis (%): crude: C 49.04, H 3.36, N 1.79, calculated for $[\text{Cu}_2\text{PPCA}(\text{H}_2\text{O})] \cdot (\text{H}_2\text{O})_4$: C 50.00 H 3.33 N 1.72.

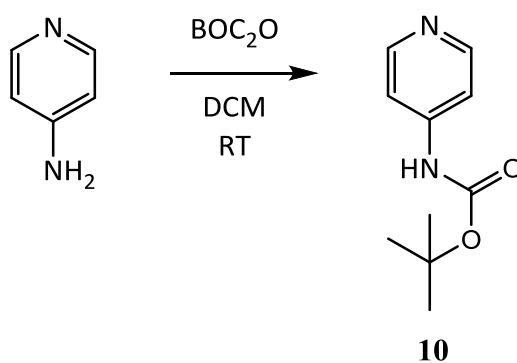
Synthesis of precursors for H₄PPAN

Synthesis of 3,5-dibromo-4-aminopyridine (**9**)

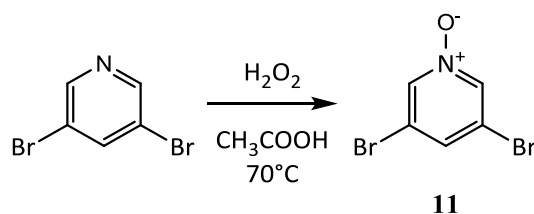


4-Aminopyridine (3.76 g, 40 mmol) was dissolved in chloroform (160 ml). N-bromosuccinimide (14.2 g, 80 mmol) was added and the reaction flask covered in foil to prevent photodegradation. The reaction was stirred at room temperature until complete by TLC and filtered to remove an orange precipitate. The filtrate was washed with water, dried with MgSO_4 , and the solvent removed to give a yellow/orange powder (5 g, 50%). ^1H NMR (300 MHz, CDCl_3) δ ppm: 8.33 (2 H, s), 5.09 (2 H, s). ^{13}C NMR (100 MHz, CDCl_3) δ ppm: 149.81, 147.64, 106.01. MS (ESI) m/z : 252.879 $[\text{MH}]^+$. IR (ATR) cm^{-1} : 3426 (N-H), 3264 (N-H), 3085 (C-H). Elemental analysis (%): crude: C 24.03 H 4.56 N 10.95, calculated for $\text{C}_5\text{N}_2\text{H}_4\text{Br}_2$: C 23.84 H 4.60 N 11.12.

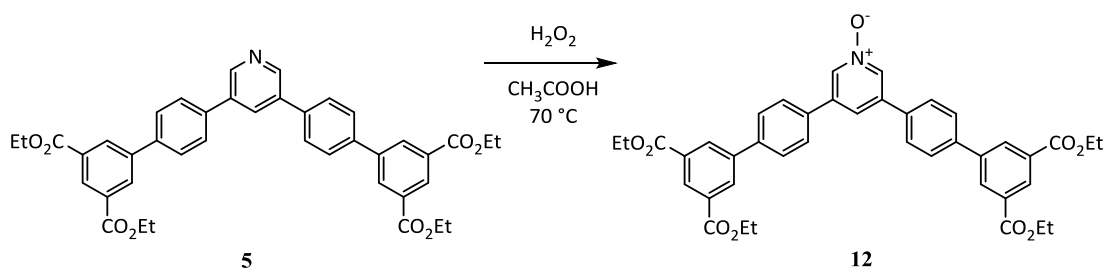
Synthesis of BOC-protected 4-aminopyridine (10)



4-Aminopyridine (0.5 g, 5.3 mmol) and di-tert-butyl dicarbonate (1.2 g, 5.5 mmol) were dissolved in DCM (50 ml) and stirred at room temperature overnight. The product was extracted into EtOAc and isolated as a white powder (0.95 g, 92 %). ^1H NMR (400 MHz, CDCl_3) δ ppm: 8.45 (2 H, m), 7.31 (2 H, m), 6.77 (1 H, s), 1.54 (9 H, s). ^{13}C NMR (125.76 MHz, $\text{DMSO}-d_6$) δ ppm: 152.34, 150.06, 146.35, 112.19, 80.03, 27.93. MS (ESI) m/z : 195.115 $[\text{M}+\text{H}]^+$. IR (ATR) cm^{-1} : 3230 (N-H), 2978 (C-H), 1674 (C=O), 1249 (C-N). Elemental analysis (%): crude: C 62.14 H 7.30 N 12.86, calculated for $\text{C}_9\text{H}_{14}\text{N}_2\text{O}_2$: C 61.84 H 7.27 N 14.42.

Synthesis of 3,5-dibromopyridine-N-oxide (11)

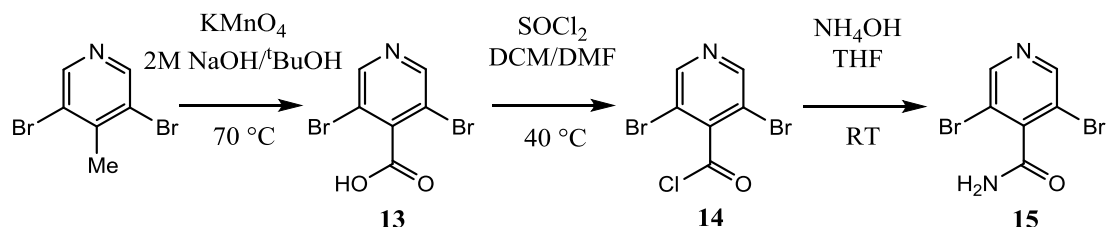
3,5-Dibromopyridine (100 mg, 0.4 mmol) was dissolved in glacial acetic acid (2 ml). H_2O_2 (0.3 ml, 30% in H_2O , 3 mmol) was added dropwise and the solution stirred at 70 °C until the reaction was deemed complete by TLC. Excess peroxide was quenched by addition of activated charcoal (0.05 g) and the solution filtered through Celite. The pure product was obtained by silica column chromatography in neat EtOAc (100 mg, 99%). ^1H NMR (400 MHz, CDCl_3) δ ppm: 8.30 (2 H, s), 7.58 (1 H, s). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 140.0, 131.7, 120.6; IR (ATR) cm^{-1} : 1248 (N^+-O^-); MS: (ESI) m/z 251.866 $[\text{MH}]^+$. Elemental analysis (%): crude: C 23.67 H 1.07 N 4.99, calculated for $\text{C}_5\text{H}_3\text{NOBr}_2$: C 23.75, H 1.20, N 5.54.

Synthesis of 3,5-bis(3',5'-bis(ethoxycarbonyl)-[1,1'-biphenyl]-4-yl)pyridine-N-oxide (12)

5 (100 mg, 0.15 mmol) was dissolved in glacial acetic acid (2 ml). H_2O_2 (0.3 ml, 30%, 3 mmol) was added dropwise and the solution stirred at 70 °C until the reaction was determined to be complete by TLC. Excess peroxide was quenched by addition of activated charcoal (0.05 g) and the solution filtered through Celite. The pure product was obtained by silica chromatography in EtOAc (70 mg, 70%). ^1H NMR (300 MHz, CDCl_3) δ ppm: 8.98 (2 H, s), 8.73 (2 H, t, $J = 1.6$ Hz), 8.52 (4 H, d, $J = 1.6$ Hz), 8.29 (1 H, s), 7.86 (8 H, m). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 165.7, 140.6, 140.4, 139.6 136.1, 135.0, 132.2, 131.8, 129.8,

128.3, 127.7, 123.4, 61.6, 14.4. MS (ESI) m/z : 574.115 $[M-H]^-$. IR (ATR) cm^{-1} : 1708 (C=O), 1237 (N^+-O^-). Elemental analysis (%): crude: C 67.56 H 4.25 N 2.14, calculated for $C_{33}H_{21}NO_9$: C 68.87 H 3.68 N 2.43.

Synthesis of precursors for H₄PPAD



Synthesis of 3,5-dibromoisonicotinic acid (13)

3,5-Dibromo-4-methyl-pyridine (500 mg, 2 mmol) was dissolved with NaOH (1.6 g, 40 mmol) in a solution of t BuOH:H₂O (4:5 v/v, 180 ml) and heated to 55 °C. $KMnO_4$ (4 g, 25 mmol) was added in aliquots, with subsequent additions after the purple colour had faded. The temperature was increased to 70 °C and the solution reacted overnight. IPA (50 ml) was added to quench any remaining permanganate and the solution refluxed for 1 hour. MnO_2 was removed by filtration and washed with boiling water. The solvent was removed *in vacuo*, and the product recrystallised from 2 M HCl to give colourless crystals (400 mg, 40%). ^1H NMR (300 MHz, DMSO- d_6): 8.82 (2 H, s). ^{13}C NMR (75 MHz, DMSO- d_6): 165.13, 150.25, 145.24, 116.05. MS (ESI) m/z : 277.7 $[M-H]^-$.

Synthesis of 3,4-dibromoisonicotinoyl chloride (14)

13 (340 mg, 1.2 mmol) was dissolved in DCM (10 ml). Thionyl chloride (0.13 ml, 1.8 mmol) and DMF (1 drop) was added and the solution heated to 40 °C overnight. The solvent was removed *in vacuo* to give orange crystals (360 mg, 100 %) ^1H NMR (300 MHz, $CDCl_3$): 8.80 (2 H, s). MS (ESI) m/z : 295.8729 $[M+OMe]^+$.

Synthesis of 3,5-dibromoisonicotinamide (15)

14 (360 mg, 1.2 mmol) was dissolved in THF (10 ml) and NH_4OH (0.32 ml 35%) was added. The reaction was stirred at room temperature until complete by TLC. The product was extracted into DCM and the solvent removed to give an orange/brown solid (268 mg, 80%). ^1H NMR (300 MHz, CDCl_3): 8.69 (2 H, s), 5.95 (1 H, br s), 5.78 (1 H, br s). MS (ESI) m/z : 278.8759 $[\text{M}+\text{H}]^+$.

3.7 References

- 1 R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, P. G. Boyd, S. Alavi and T. K. Woo, *Science*, 2010, **330**, 650–653.
- 2 A. Torrisi, C. Mellot-Draznieks and R. G. Bell, *J. Chem. Phys.*, 2009, **130**, 194703–194713.
- 3 H. Liu, Y. Zhao, Z. Zhang, N. Nijem, Y. J. Chabal, X. Peng, H. Zeng and J. Li, *Chem. Asian J.*, 2013, **8**, 778–785.
- 4 E. J. Carrington, I. J. Vitórica-Yrezábal and L. Brammer, *Acta. Crystallogr. Sect. B*, 2014, **B70**, 404–422.
- 5 J. L. C. Rowsell, E. C. Spencer, J. Eckert, J. A. K. Howard and O. M. Yaghi, *Science*, 2005, **309**, 1350–1354.
- 6 C. P. Krap, R. Newby, A. Dhakshinamoorthy, H. García, I. Cebula, T. L. Easun, M. Savage, J. E. Eyley, S. Gao, A. J. Blake, W. Lewis, P. H. Beton, M. R. Warren, D. R. Allan, M. D. Frogley, C. C. Tang, G. Cinque, S. Yang and M. Schröder, *Inorg. Chem.*, 2016, **55**, 1076–1088.
- 7 S. R. Miller, P. A. Wright, T. Devic, C. Serre, P. L. Llewellyn, R. Denoyel, L. Gaberova and Y. Filinchuk, *Langmuir*, 2009, **25**, 3618–3626.
- 8 B. C. Serre, S. Bourrelly, A. Vimont, N. A. Ramsahye, G. Maurin, P. L. Llewellyn, M. Daturi, Y. Filinchuk, O. Leynaud, P. Barnes and G. Férey, *Adv. Mater.*, 2007, **19**, 2246–2251.
- 9 P. D. C. Dietzel, R. E. Johnsen, H. Fjellvåg, S. Bordiga, E. Groppo, S. Chavan and R. Blom, *Chem. Commun.*, 2008, 5125–5127.
- 10 Y. Inokuma, S. Yoshioka, J. Ariyoshi, T. Arai, Y. Hitora, K. Takada, S. Matsunaga, K. Rissanen and M. Fujita, *Nature*, 2013, **495**, 461–466.
- 11 V. F. Sears, *Neutron News*, 1992, **3**, 29–37.
- 12 W. Yang, A. J. Davies, X. Lin, M. Suyetin, R. Matsuda, A. J. Blake, C. Wilson, W. Lewis, J. E. Parker, C. C. Tang, M. W. George, P. Hubberstey, S. Kitagawa, H. Sakamoto, E. Bichoutskaia, N. R. Champness, S. Yang and M. Schröder, *Chem. Sci.*, 2012, **3**, 2993–2999.
- 13 A. Greenaway, B. Gonzalez-Santiago, P. M. Donaldson, M. D. Frogley, G. Cinque, J. Sotelo, S. Moggach, E. Shiko, S. Brandani, R. F. Howe and P. A. Wright, *Angew. Chem. Int. Ed.*, 2014, 13483–13487.
- 14 S. Yang, X. Lin, W. Lewis, M. Suyetin, E. Bichoutskaia, J. E. Parker, C. C. Tang, D. R. Allan, P. J. Rizkallah, P. Hubberstey, N. R. Champness, K. M. Thomas, A. J. Blake and M. Schröder, *Nat. Mater.*, 2012, **11**, 710–716.
- 15 S. Biswas, T. Rémy, S. Couck, D. Denysenko, G. Rampelberg, J. F. M. Denayer, D. Volkmer, C. Detavernier and P. Van der Voort, *Phys. Chem. Chem. Phys.*, 2013, **15**, 3552–3561.
- 16 L. Chen, J. P. S. Mowat, D. Fairen-Jimenez, C. A. Morrison, S. P. Thompson, P. A. Wright and T. Düren, *J. Am. Chem. Soc.*, 2013, **135**, 15763–15773.

- 17 P. Serra-Crespo, E. Gobechiya, E. V. Ramos-Fernandez, J. Juan-Alcañiz, A. Martinez-Joaristi, E. Stavitski, C. E. A. Kirschhock, J. A. Martens, F. Kapteijn and J. Gascon, *Langmuir*, 2012, **28**, 12916–12922.
- 18 P. L. Llewellyn, P. Horcajada, G. Maurin, T. Devic, N. Rosenbach, S. Bourrelly, C. Serre, D. Vincent, S. Loera-Serna, Y. Filinchuk and G. Férey, *J. Am. Chem. Soc.*, 2009, **131**, 13002–13008.
- 19 J. P. S. Mowat, V. R. Seymour, J. M. Griffin, S. P. Thompson, A. M. Z. Slawin, D. Fairen-Jimenez, T. Düren, S. E. Ashbrooka and P. A. Wright, *Dalton Trans.*, 2012, **41**, 3937–3941.
- 20 M. Anbia and S. Sheykhi, *J. Nat. Gas Chem.*, 2012, **21**, 680–684.
- 21 F. Millange, N. Guillou, R. I. Walton, J.-M. Grenèche, I. Margiolaki and G. Férey, *Chem. Commun.*, 2008, 4732–4734.
- 22 T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille and G. Férey, *Chem. Eur. J.*, 2004, **10**, 1373–1382.
- 23 C. Serre, F. Millange, C. Thouvenot, M. Noguès, G. Marsolier, D. Louër and G. Férey, *J. Am. Chem. Soc.*, 2002, **124**, 13519–15326.
- 24 F.-X. Coudert, A. U. Ortiz, V. Haigis, D. Bousquet, A. H. Fuchs, A. Ballandras, G. Weber, I. Bezverkhy, N. Geoffroy, J.-P. Bellat, G. Ortiz, G. Chaplais, J. Patarin and A. Boutin, *J. Phys. Chem. C*, 2014, **118**, 5397–5404.
- 25 T. Devic, F. Salles, S. Bourrelly, B. Moulin, G. Maurin, P. Horcajada, C. Serre, A. Vimont, J.-C. Lavalley, H. Leclerc, G. Clet, M. Daturi, P. L. Llewellyn, Y. Filinchuk and G. Férey, *J. Mater. Chem.*, 2012, **22**, 10266.
- 26 S. Couck, E. Gobechiya, C. E. A. Kirschhock, P. Serra-Crespo, J. Juan-Alcañiz, M. Joaristi, E. Stavitski, J. Gascon, F. Kapteijn, G. V Baron and J. F. M. Denayer, *ChemSusChem*, 2012, **5**, 740–750.
- 27 S. Yang, J. Sun, A. J. Ramirez-Cuesta, S. K. Callear, W. I. F. David, D. P. Anderson, R. Newby, A. J. Blake, J. E. Parker, C. C. Tang and M. Schröder, *Nat. Chem.*, 2012, **4**, 887–894.
- 28 M. Savage, J. E. Eyley, T. L. Easun, S. Yang and M. S. Schröder, *Adv. Mater.*, 2016, **28**, 8705–8711.
- 29 H. Wu, J. M. Simmons, G. Srinivas, W. Zhou and T. Yildirim, *J. Phys. Chem. Lett.*, 2010, **1**, 1946–1951.
- 30 W. L. Queen, C. M. Brown, D. K. Britt, P. Zajdel, M. R. Hudson and O. M. Yaghi, *J. Phys. Chem. C*, 2011, **115**, 24915–24919.
- 31 N. Nijem, P. Canepa, L. Kong and H. Wu, *J. Phys. Condes. Matter*, 2012, **24**, 424203–424211.
- 32 S. R. Miller, P. A. Wright, C. Serre, T. Loiseau, J. Marrot and G. Férey, *Chem. Commun.*, 2005, **2**, 3850–3852.
- 33 V. Cañibano, J. F. Rodríguez, M. Santos, M. A. Sanz-Tejedor, M. C. Carreño, G. González and J. L. García-Ruano, *Synthesis*, 2001, **14**, 2175–2179.
- 34 N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457–2483.
- 35 U. Ragnarsson and L. Grehn, *RSC Adv.*, 2013, **3**, 18691.
- 36 US 2003207920.
- 37 G. Panke, T. Schwalbe, W. Stirner, S. Taghavi-Moghadam and G. Wille, *Synthesis*, 2003, **18**, 2827–2830.
- 38 D. P. Khrustalev, G. T. Khamzina, S. D. Fazylov and Z. M. Muldakhmetov, *Russ. J. Gen. Chem.*, 2008, **78**, 1577–1578.
- 39 D. H. Bremner, K. R. Sturrock, G. Wishart, S. R. Mitchell, S. M. Nicoll and G. Jones, *Synth. Commun.*, 1997, **27**, 1535–1542.
- 40 Y. Dai, K. Hartandi, N. B. Soni, L. J. Pease, D. R. Reuter, A. M. Olson, D. J. Osterling, S. Z. Doktor, D. H. Albert, J. J. Bouska, K. B. Glaser, P. A. Marcotte, K. D. Stewart, S. K. Davidsen, M. R. Michaelides, *Bioorganic Med. Chem. Lett.*, 2008, **18**, 386–390.

- 41 J. R. Porter, S. C. Archibald, J. A. Brown, K. Childs, D. Chritchley, J. C. Head, B. Hutchinson, T. A. H. Parton, M. K. Robinson, A. Shock, G. J. Warreallow, A. Zomaya, *Bioorganic Med. Chem. Lett.*, 2002, **12**, 1591–1594.
- 42 P. Zhang, B. Li, Y. Zhao, X. Meng and T. Zhang, *Chem. Commun.*, 2011, **47**, 7722–7724.
- 43 O. K. Farha, C. E. Wilmer, I. Eryazici, B. G. Hauser, P. Parilla, K. O'Neill, A. Sarjeant, S. T. Nguyen, R. Q. Snurr and J. T. Hupp, *J. Am. Chem. Soc.*, 2012, **134**, 9860–9863.
- 44 J. An, S. J. Geib and N. L. Rosi, *J. Am. Chem. Soc.*, 2010, **132**, 38–39.
- 45 D.-M. Chen, X.-P. Zhang, W. Shi and P. Cheng, *Inorg. Chem.*, 2015, **54**, 5512–5518.
- 46 K. M. Gaab, A. L. Thompson, J. Xu, T. J. Martínez and C. J. Bardeen, *J. Am. Chem. Soc.*, 2003, **125**, 9288–9289.
- 47 J. Park, J.-R. Li, Y.-P. Chen, J. Yu, A. A. Yakovenko, Z. U. Wang, L.-B. Sun, P. B. Balbuenaba and H.-C. Zhou, *Chem. Commun.*, 2012, **48**, 9995–9997.
- 48 B. Li, H. Wen, H. Wang, H. Wu, M. Tyagi, T. Yildirim, W. Zhou and B. Chen, *J. Am. Chem. Soc.*, 2014, **136**, 6207–6210.
- 49 B. Li, H. Wen, H. Wang, H. Wu, T. Yildirim, W. Zhou and B. Chen, *Energy Environ. Sci.*, 2015, **8**, 2504–2511.
- 50 Z. H. Rada, H. R. Abid, H. Sun and S. Wang, *J. Chem. Eng. Data*, 2015, **60**, 2152–2161.
- 51 C. Wang, L. Li, S. Tang and X. Zhao, *ACS Appl. Mater. Interfaces*, 2014, **6**, 16932–16940.
- 52 B. Liu, S. Yao, C. Shi, G. Li, Q. Huo and Y. Liu, *Chem. Commun.*, 2016, **52**, 3223–3226.
- 53 C. Song, Y. He, B. Li, Y. Ling, H. Wang, Y. Feng, R. Krishna and B. Chen, *Chem. Commun.*, 2014, **50**, 12105–12108.
- 54 Z. Chen, S. Xiang, H. D. Arman, P. Li, D. Zhao and B. Chen, *Eur. J. Inorg. Chem.*, 2011, 2227–2231.
- 55 G. Herzberg, *Molecular Spectra and Molecular Structure*, van Nostrand Reinhold, New York, 1950.
- 56 B. Bonelli, B. Civalleri, B. Fubini, P. Ugliengo, C. O. Area, V. P. Giuria, I.- Torino, D. De Quimica, V. Uni and D. Islas, *J. Phys. Chem. B.*, 2000, **104**, 10978–10988.
- 57 J. G. Vitillo, M. Savonnet, G. Ricchiardi and S. Bordiga, *ChemSusChem*, 2011, **4**, 1281–1290.
- 58 J. T. Culp, A. L. Goodman, D. Chirdon, S. G. Sankar and C. Matranga, *J. Phys. Chem. C*, 2010, **114**, 2184–2191.
- 59 F. Partal Ureña, M. F. Gómez, J. J. López González and E. Martínez Torres, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.*, 2003, **59**, 2815–2839.
- 60 S. Breda, I. D. Reva, L. Lapinski, M. J. Nowak and R. Fausto, *J. Mol. Struct.*, 2006, **786**, 193–206.
- 61 K. L. Kauffman, J. T. Culp, A. Goodman and C. Matranga, *J. Phys. Chem. C*, 2011, **115**, 1857–1866.

Chapter 4: Investigating the effect of functionalisation of cage C on the gas adsorption properties of MFM-17X

4.1 Introduction

In order to further improve the CO₂ uptake capacity and selectivity of the MFM-17X series (Chapter 3), additional CO₂ binding sites were introduced on to the framework surface; however the pyrazine group in MFM-171 was too sterically hindered to have a positive impact on CO₂ uptake capacities. The work in this chapter aims to incorporate a Lewis basic functionality into the MFM-17X series by introducing heterocyclic nitrogen-containing rings in less sterically demanding environments in order to increase the CO₂ adsorption and selectivity of this family of materials.

Triazole groups have strong Lewis basic characteristics and have been incorporated into a number of different metal organic frameworks via post-synthetic “click” reactions.¹ The effect of this modification on CO₂ uptake capacity has been studied in MIL-101,² a highly stable chromium based framework, with high accessible porosity and a large internal surface area. The framework, constructed from terephthalic acid ligands, was postsynthetically nitrated, the nitro group reduced and converted to an azide group, followed by a “click” reaction with ethynamine (Figure 4.1) to give MIL-101-triazo-NH₂. Despite a reduction in porosity and BET surface area upon post synthetic modification (1950 vs 3850 m² g⁻¹), the CO₂ adsorption capacity increases from 87.1 cm³ g⁻¹ to 128.3 cm³ g⁻¹ for MIL-101 to MIL-101-triazo-NH₂ at 1 atm and 273 K (Figure 4.1), indicating a favourable interaction between CO₂ and the pendant functional groups (Figure 4.1).

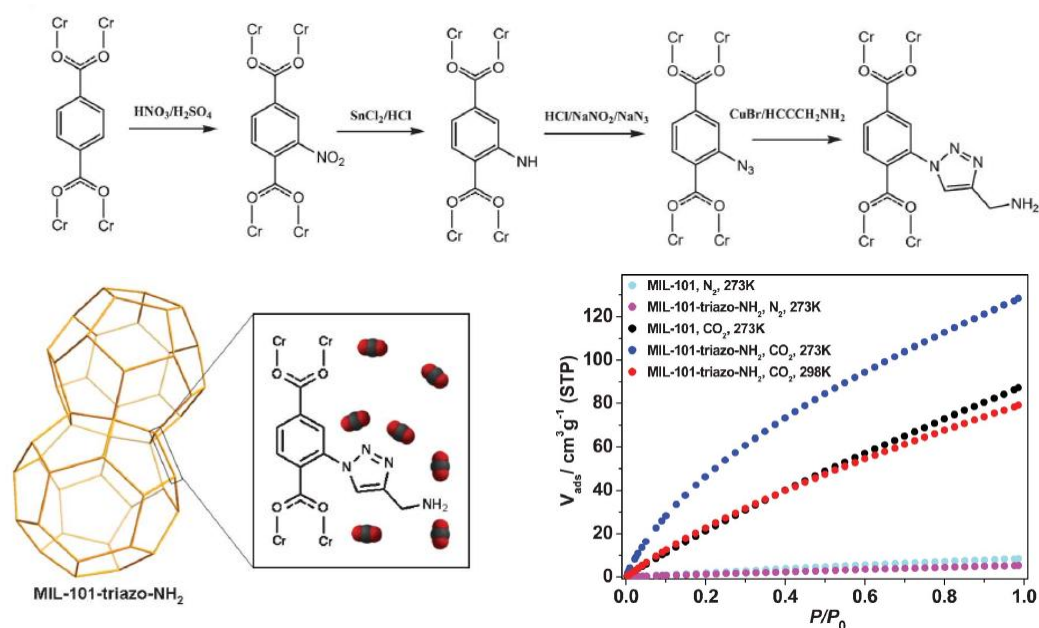


Figure 4.1: Post-synthetic modification of MIL-101 to incorporate a pendant triazole ring and amine group; scheme showing the four stage reaction involving nitration, reduction and azotization of terphthalic acid, followed by “click” addition of ethynamine. View of the proposed interaction of CO₂ with the framework and demonstration of the increase in CO₂ adsorption capacity of MIL1-101-triazo-NH₂ (blue) compared to bare MIL-101 (black) at 273 K.

Construction of MOFs from triazole containing ligands can result in the formation of unusual SBUs, in which nitrogen groups coordinate to the metal ions. These coordination mode occur either when the triazole group is pendant on a ligand, such as 5-(2H-1,2,3-triazol-4-yl)isophthalic acid (Figure 4.2a),^{3,4} or when other coordinating moieties are in close proximity to the triazole nitrogens and provide a chelating effect, such as 1,2,3-triazole-4,5-dicarboxylate (Figure 4.2b),⁵⁻⁷ or H₂cbptz (Figure 4.2c).⁸ Although interesting on a structural level the addition of these triazole groups do not always increase CO₂ capacity as the Lewis basic sites are inaccessible to guest species.

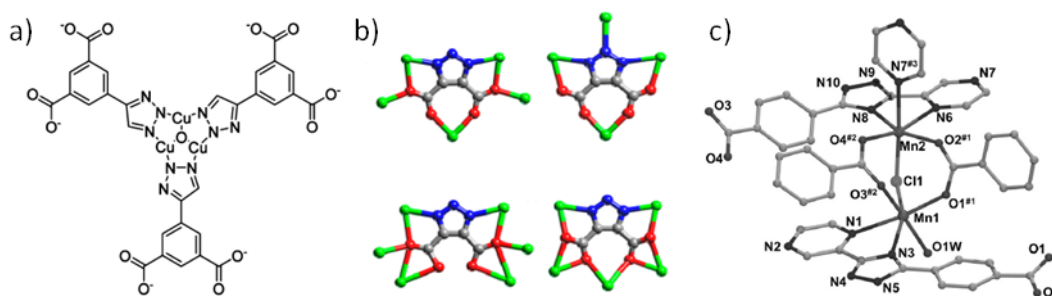


Figure 4.2: Interesting SBUs and coordination modes seen in triazole-containing ligands
a) 5-(2H-1,2,3-triazol-4-yl)isophthalic acid,^{3,4} b) a selection of the coordination modes seen with 1,2,3-triazole-4,5-dicarboxylate,⁵⁻⁷ c) chelating mode seen in $\text{Mn}_2(\text{Hcptz})_2(\text{Cl})(\text{H}_2\text{O})]$ ⁸

$[\text{Mn}_2(\text{Hcptz})_2(\text{Cl})(\text{H}_2\text{O})]$ is constructed from a nitrogen-rich pyrazine triazolyl carboxyl ligand H_2cptz (3-(4-carboxylbenzene)-5-(2-pyrazinyl)-1H-1,2,4-triazole).⁸ H_2cptz was specifically designed to contain multiple nitrogen atoms in order that some of the Lewis basic sites would remain unsaturated upon coordination to metal centres. $[\text{Mn}_2(\text{Hcptz})_2(\text{Cl})(\text{H}_2\text{O})]$ forms a three-dimensional framework with narrow one-dimensional channels constructed from interconnected cavities of 7 Å in diameter. The pore surface is lined with open metal sites, uncoordinated N atoms and aromatic rings. The CO_2 isotherm at 1 bar and 298 K shows high uptake capacity of $70.1 \text{ cm}^3 \text{ g}^{-1}$ (13.8 wt%), superior to MFM-170 (13.25 wt%) under the same conditions, despite only a 35% fractional void volume (*c.f.* 60% in MFM-170). The high uptake capacity leads to exceptional selectivity for CO_2 over N_2 and CH_4 ; IAST selectivity parameters of 78:1 and 10.3:1, respectively. GCMC simulations identified four favourable CO_2 binding sites in $[\text{Mn}_2(\text{Hcptz})_2(\text{Cl})(\text{H}_2\text{O})]$ (Figure 4.3) which demonstrate a number of synergistic interactions with acidic aromatic protons, electronegative uncoordinated N atoms, the π -electron cloud surrounding aromatic rings and exposed Mn(II) ions. The exceptional uptake capacity and selectivity parameters are attributed to small confined pores, which allow for multiple interactions to form with a single CO_2 molecule, and the high framework polarity, which results in strong electrostatic interactions with the pore surface.

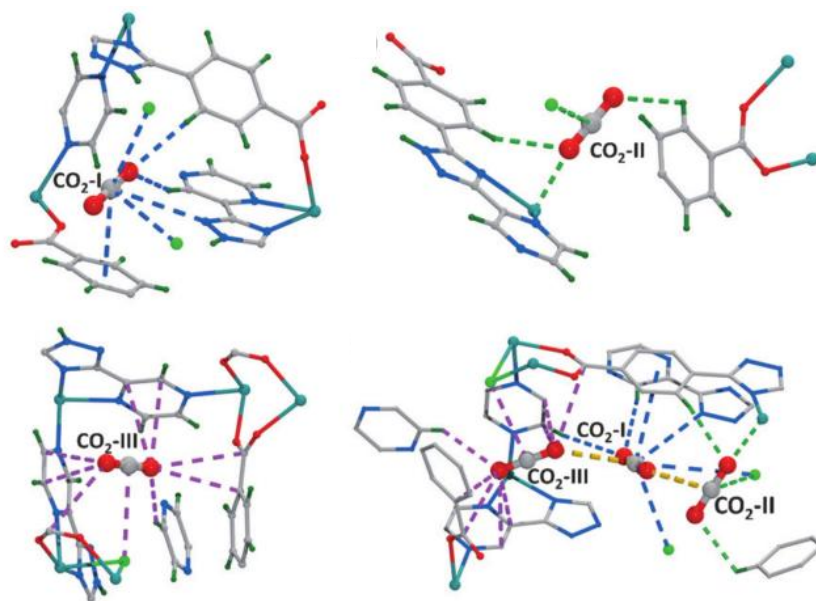


Figure 4.3: Visualisation of three CO_2 binding sites in $[\text{Mn}_2(\text{Hcptz})_2(\text{Cl})(\text{H}_2\text{O})]$ identified by GCMC calculations. The small cavities (7 Å) allow for the formation of multiple synergistic binding interactions, leading to high affinity for CO_2 , with exceptional IAST selectivity parameters over N_2 and CH_4 .

Incorporating a triazole ring between two bulky coordinating groups can prevent coordination of the triazole nitrogen atoms, leaving these donor sites free to interact with guest molecules. H_4TADIP (5,5'-(1H-1,2,3-triazole-1,4-diyl)-diisophthalic acid) is such a ligand, with a triazole ring situated between two isophthalate rings. H_4TADIP has been included in zinc and copper (NTU-101, Figure 4.4);⁹ lanthanide;¹⁰ manganese and cobalt¹¹ frameworks, adopting either a square or tetrahedral conformation, resulting in a wide variety of network topologies. The CO_2 uptake of NTU-101-Cu was measured to be $101 \text{ cm}^3 \text{ g}^{-1}$ (16.6 wt%) at 1 bar and 273 K, a little lower than NOTT-101, which contains a similar ligand with a phenyl rather than triazole group ($150 \text{ cm}^3 \text{ g}^{-1}$ under the same conditions).¹² It is inappropriate to directly compare the uptake capacities of these two materials as they have different framework structures (**pts** and **nbo** topologies) and therefore different accessible void volumes and surface areas.

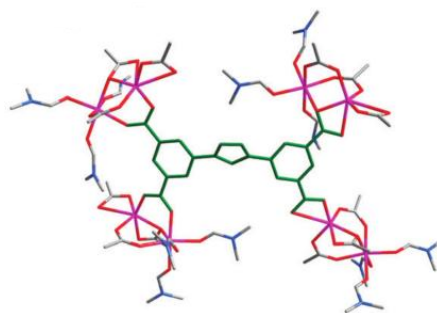


Figure 4.4: Structure of NTU-101-Cu, synthesised by post-synthetic metal ion exchange from NTU-101-Zn, featuring the triazole containing linker TADIP⁴⁻ in which the triazole nitrogens are available to interact with guest species.

A similar ligand, H₄TADIPA (5,5'-(1H-1,2,4-triazole-3,5-diyl) diisophthalic acid), containing a 1,2,4-triazole core, has been reported in JLU-Liu21, a MOF comprising truncated tetrahedral and large octahedral cages, constructed from copper paddlewheels (Figure 4.5).¹³ With a high porosity of 68.6% and a BET surface area of 2080 m² g⁻¹, JLU-Liu21 exhibits an exceptional CO₂ adsorption capacity of 41.2 wt% (210 cm³ g⁻¹) at 273 K, 1 bar. This value is amongst the highest for metal organic frameworks, which suggests that 1,2,4-triazole rings may be beneficial for CO₂ adsorption. The highest reported CO₂ adsorption at 1 bar is 44.5 wt% (227 cm³ g⁻¹) at 273 K in Cu-TDPAT, an **rht** framework comprising a 1,3,5-triazine core.¹⁴

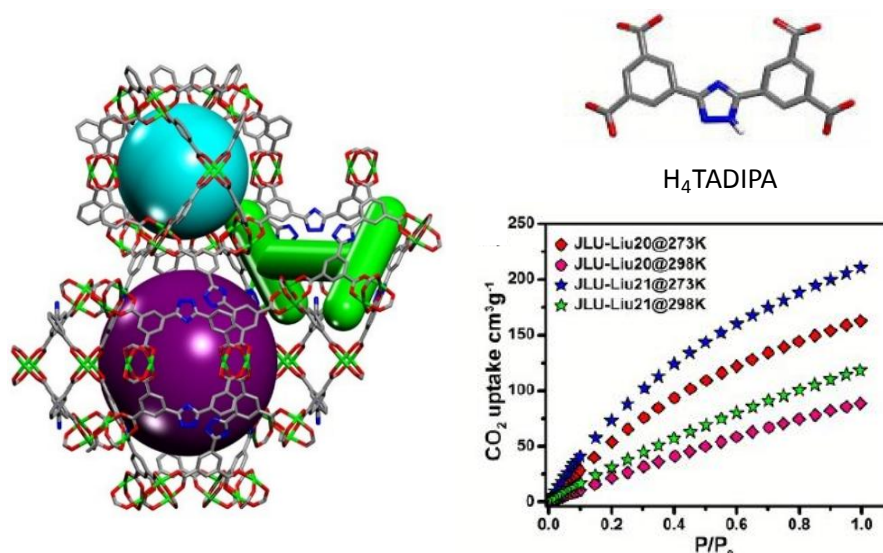


Figure 4.5: Structure of JLU-Liu21 constructed from Cu(II) paddlewheels and H₄TADIPA to give three cages: a metal-organic cuboctahedron (blue), an octahedral cage (purple) and a tetrahedral cage (green). CO₂ isotherms of JLU-Liu 21 and JLU-Liu20, demonstrate the high CO₂ uptake capacity at ambient temperature and pressure.

NOTT-122, reported by Schröder,¹⁵ and others^{16,17} is a **rht**-network constructed from a Cu(II) paddlewheel based metal-organic cuboctahedra connected by C_3 -symmetric hexacarboxylate linkers (Figure 4.6). Incorporation of an angular 1,2,3-triazole group, in position of phenyl or acetyl spacer units, results in a more densely packed structure with smaller pores, in addition to providing further binding sites for the gas molecules. NOTT-122 displays one of the highest ambient pressure CO_2 adsorption values in a MOF reported to date, adsorbing 39.7 wt% ($202 \text{ cm}^3 \text{ g}^{-1}$ STP) at 273 K and 20.4 wt% ($104 \text{ cm}^3 \text{ g}^{-1}$ STP) at 298 K, (Figure 4.6).

GCMC simulations of NOTT-122 reveal three preferential binding sites for CO_2 (Figure 4.6); the first, identified as (I), is located on the open metal site of CuA on the Cu(II) paddlewheel, the second (II) is situated in the centre of the triangular window of the metal-organic cuboctahedron, identical to the position of CO_2^{I} located MFM-17X (Chapter 3) and the third interacts with the triazole groups lining the cage. Binding site (III) is located in a similar position to CO_2^{II} in MFM-17X, indicating that the addition of triazole groups to the structure of MFM-17X could strengthen the binding interaction of CO_2^{II} , thus increasing the selective uptake of CO_2 over N_2 and CH_4 .

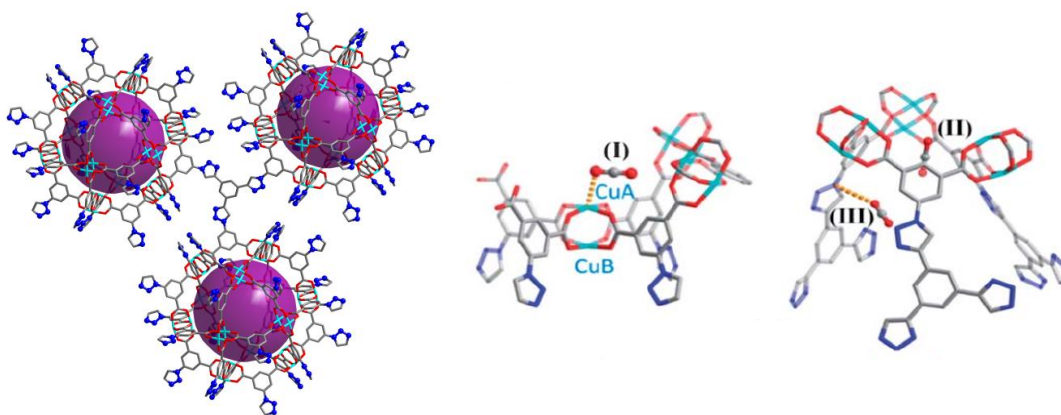


Figure 4.6: View of the structure of NOTT-122, depicting Cu(II) paddlewheel based metal-organic cuboctahedra (purple) connected by a C_3 symmetrical ligand to give an **rht** net. CO_2 adsorption sites located in NOTT-122 by GCMC calculations: (I) adsorption onto the open metal site of a Cu(II) paddlewheel, (II) confinement in the triangular window of the metal-organic cuboctahedron, (III) interaction with the triazole nitrogen.

To further investigate the impact that triazole groups have on CO₂ adsorption in NOTT-122, we can consider the work of Li *et al.* who report the synthesis of an isostructural **rht** framework, Cu-ABTA in which one triazole group has been switched for an amide group (Figure 4.7) to give an inostructural framework.¹⁸ Amide groups have been shown to be highly beneficial to CO₂ adsorption,¹⁹ and in Chapter 2 we showed that the amide-containing PCN-124 has a greater capacity for CO₂ than MFM-170, its isostructural phenyl-containing analogue.²⁰

Cu-ABTA demonstrates a reduced CO₂ adsorption capacity in comparison to NOTT-122, adsorbing 30.1 wt% (153 cm³ g⁻¹ STP) at 273 K, compared to 39.7 wt% (202 cm³ g⁻¹ STP) in NOTT-122. This indicates that the substitution of phenyl rings in MFM-170 for triazole groups could result in CO₂ adsorption capacity superior to PCN-124.

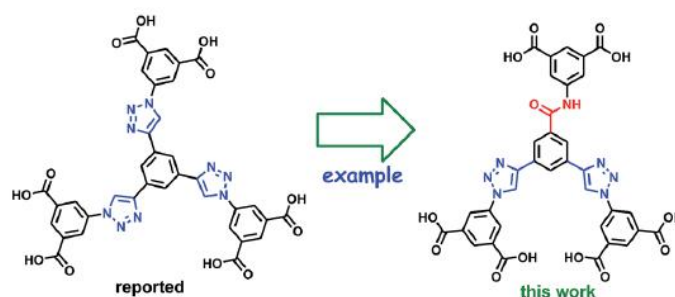


Figure 4.7: Substitution of a triazole ring in NOTT-122 for an amide group in Cu-ABTA, resulting in an isostructural **rht** framework with reduced CO₂ adsorption at ambient conditions.

4.1.1 Aims and Objectives

Chapter 3 studied the effect of additional functional groups in cage B on the gas adsorption properties of MFM-17X. Substitution of the central pyridyl ring in H₄PPYD with pyrazine and methyl-pyridine lead to the formation of two new isostructural frameworks; MFM-171 and MFM-172, respectively. Although additional functionalisation improved the CO₂/N₂ and CO₂/CH₄ selectivity values compared to MFM-170, these IAST selectivity parameters could be further improved by including strong CO₂-philic sites. In this chapter we aim to

strengthen the interactions between the framework and adsorbed CO₂ within the MFM-17X series by introducing strong Lewis basic triazole groups into the structure.

Spectroscopic and X-ray diffraction analyses carried out in Chapter 3 demonstrated that the CO₂ binding sites in MFM-17X are mainly situated in cage C, located towards the triangular cage window. We proposed that addition of pendant functional groups to the phenyl ring in H₄PPYD (MFM-170) may block access to cage C, which is lined by six ligand molecules and has a guest accessible diameter of only 8 Å. With this in mind we aim to functionalise the pore walls of cage C by substitution of the phenyl ring in MFM-170 for a triazole group, giving 5,5'-(pyridine-3,5-diylbis(1*H*-1,2,3-triazole-4,1-diyl))diisophthalic acid (Figure 4.8), referred to in this chapter as H₄TPYD (for **T**riazole extended **P**yr**D**yl core).

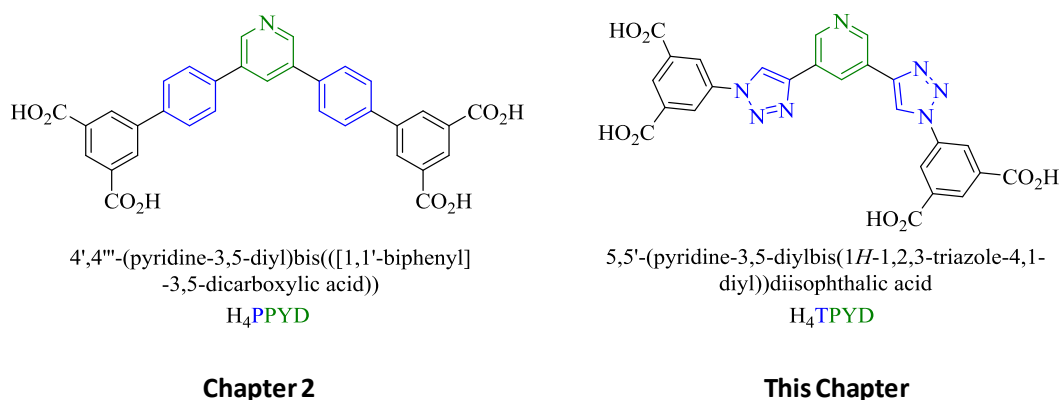


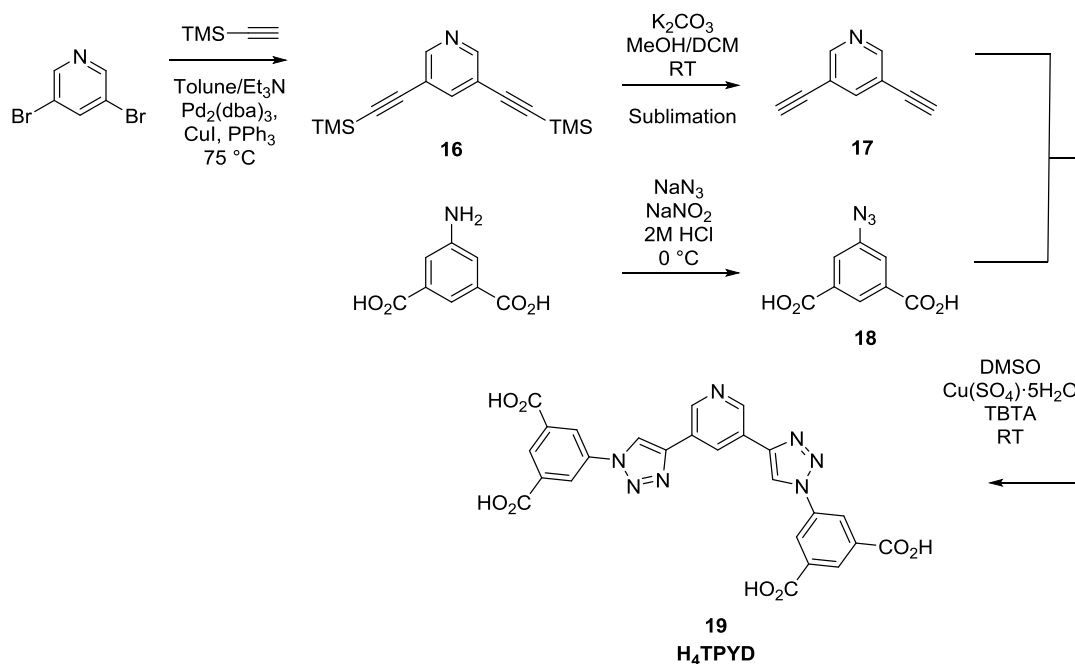
Figure 4.8: Structure and naming strategy of the ligand H₄TPYD, with reference to H₄PPYD from MFM-170 (Chapter 2).

4.2 Results and Discussion

4.2.1 Ligand Synthesis

3,5-Diethynylpyridine (**17**) was synthesised from 3,5-dibromopyridine via a Sonogashira coupling at 75 °C (**16**), followed by deprotection under basic conditions and purification by vacuum sublimation (Scheme 4.1). Concurrently, 5-azidoisophthalic acid (**18**) was synthesised from 5-aminoisophthalic acid in a one-pot procedure with sodium azide.

H₄TPYD (**19**) was synthesised via a “click” reaction between 3,5-diethynylpyridine (**17**) and 5-azidoisophthalic acid (**18**) at room temperature. The reaction was catalysed by Cu(I) species and stabilised by tris(benzyltriazolylmethyl)amine (TBTA). The product precipitated from solution upon the addition of water and was washed with an EDTA⁴⁺ solution to remove traces of remaining Cu(I) and Cu(II) species.



Scheme 4.1: Synthetic route to the formation of H₄TPYD

4.2.2 Synthesis of [Cu₂TPYD(H₂O)]·(DMF)₄(H₂O)₄ (MFM-175)

[Cu₂TPYD(H₂O)]·(DMF)₄(H₂O)₄ (**MFM-175**) was synthesised by solvothermal reaction of H₄TPYD with Cu(NO₂)₃·5/2(H₂O) in acidified DMF, affording a blue crystalline product.

4.2.3 Crystal Structure Analysis of MFM-175

MFM-175 was found to crystallise in the monoclinic *I2/m* space group with unit cell parameters: *a* 32.1695(2) Å, *b* 32.0968(2) Å and β : 90°. MFM-175 is constructed from a bcc-packing array of metal-organic cuboctahedra and retains the **txt** topology displayed in MFM-170; however upon closer inspection there are large differences in ligand orientation, most distinguishable down the *b* axis (Figure 4.9).

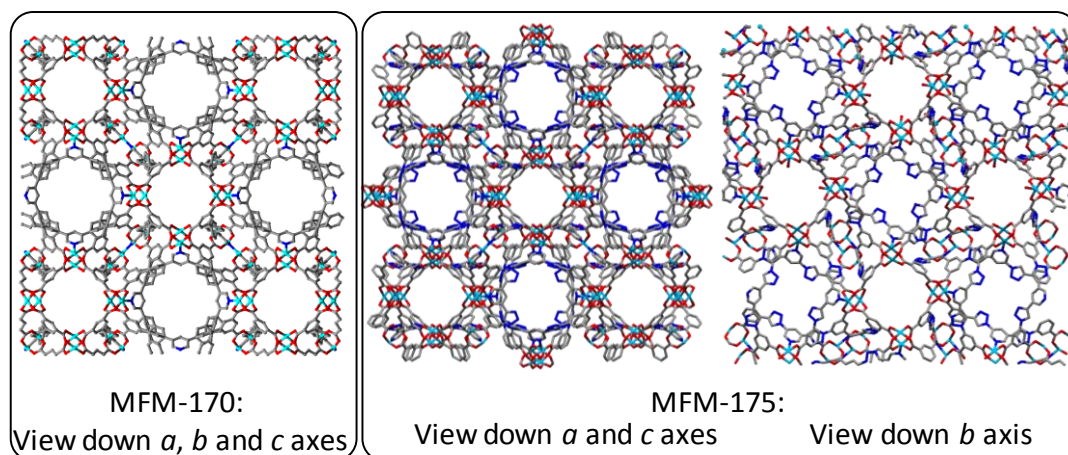


Figure 4.9: Structural comparison of MFM-175 with MFM-170 showing one unit cell viewed down each of the crystallographic axes. The *bcc* packing of metal-organic cuboctahedra (cage A) is retained in both crystals, with minor differences in ligand orientation visible.

In MFM-170 both arms of the PPYD⁴⁻ ligand are fixed in position giving rise to a rigid V-shaped conformation; whereas in MFM-175, the five-membered triazole ring can rotate, introducing a degree of rotation and flexibility. In order to investigate the effect of rotation on the conformational stability of H₄TPYD, a dihedral driver calculation was performed on energy minimised structures using the MM2 forcefield in ChemDraw3D. Two energy minimised conformations of each ligand arm were observed (Figure 4.10); the “up” conformation with a dihedral angle of $\pm 180^\circ$ and the “down” conformation with a dihedral angle of 0° . When both ligand arms are permitted to rotate, three different energy minimised ligand orientations are possible; down-down (76.91 kcal mol⁻¹), up-down (77.0 kcal mol⁻¹) and up-up (77.41 kcal mol⁻¹). The up-down and up-up conformations of TPYD⁴⁻ are both present in MFM-175, giving rise to two types of tetragonal cage B, distinguished as cage B1 and cage B2.

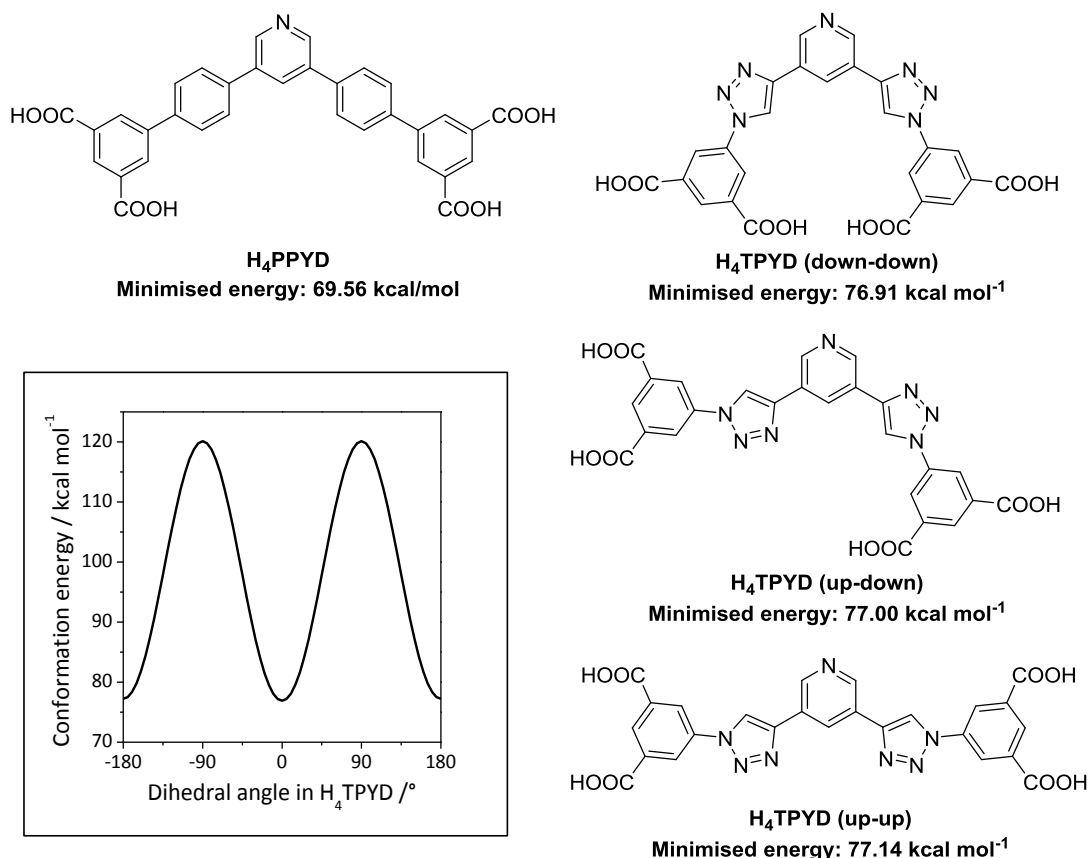


Figure 4.10: H_4TPYD displays three possible energy-minimised conformations due to rotation around the pyridyl-triazole bond. The dihedral driver calculation shows the change in conformation energy upon rotation of one ligand arm, demonstrating two energy minima in the up (-180°/180°) and down (0°) conformations.

Cage B1 most closely resembles the tetragonal cage from MFM-170 (Figure 4.11) and can be found running along the b axis, making up a third of all B-type cages in MFM-175. The tetragonal cage is capped at both ends by square windows constructed from Cu(II) paddlewheels and is defined by four V-shaped ligands which bow outwards, lining the inside of the pore with the edge of the ligand. All four ligands adopt the up-up conformation with the heterocyclic triazole nitrogens pointing into cage B. This 19.1 Å × 15.0 Å cage is slightly smaller than cage B in MFM-170 (22.2 Å × 16.3 Å) due to the shorter ligand length.

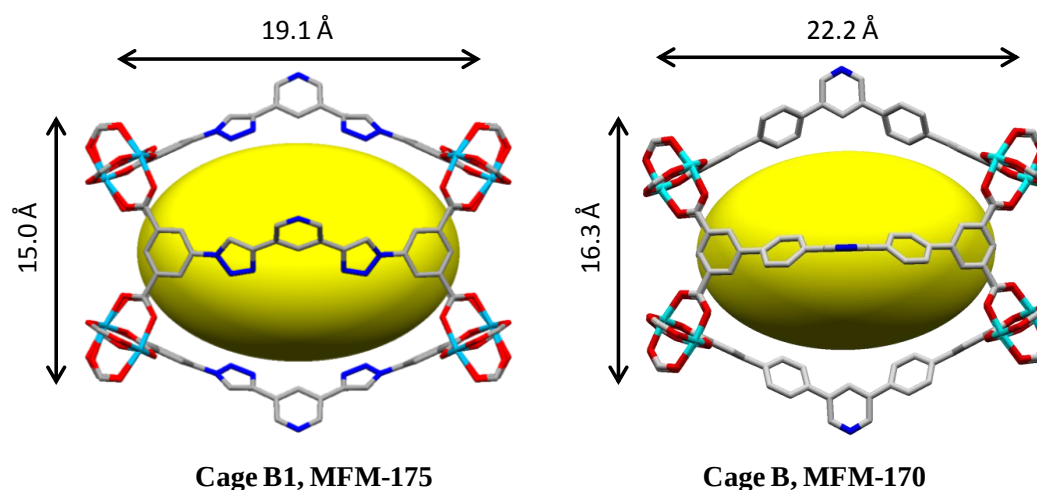


Figure 4.11: Comparison of the structures of Cage B1 in MFM-175 and cage B in MFM-170. The cages have similar dimensions and are bounded by four symmetrical ligand molecules in a V-shaped formation.

The up-up conformation of TPYD^{4-} results in a distortion of the interplanar angle between the isophthalate and pyridyl rings compared to MFM-170. Whereas the angle between the pyridyl and isophthalate planes in MFM-170 is near orthogonal, at 91° , the twist induced in TPYD^{4-} results in a dihedral angle of 51° in MFM-175 (Figure 4.12). The misalignment of this pyridyl binding group will impact the coordination to the interpenetrating net and is expected to introduce strain and instability into the framework.

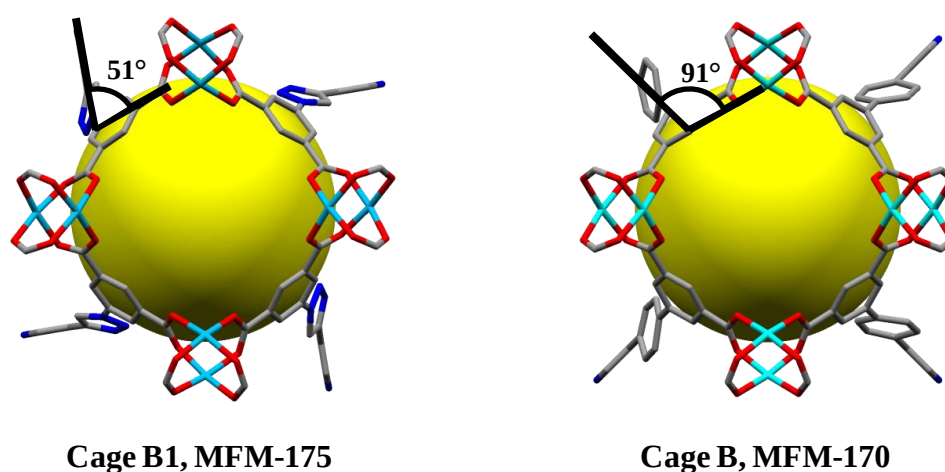


Figure 4.12: Adoption of the up-up conformation of TPYD^{4-} in cage B1 of MFM-175 results in a dihedral angle of 51° between the pyridyl and isophthalate rings in comparison to the near-perpendicular ring planes in MFM-170.

Some of the strain from the misaligned pyridyl rings (N(B1)) is absorbed into the coordinating Cu(II) paddlewheels; the Cu-O-C angles comprising the Cu(II)-paddlewheel are distorted from the ideal angle of 123° seen in MFM-170 (Figure 4.13) and the O-Cu-N(B1) angle is bent by 8° to 104° .

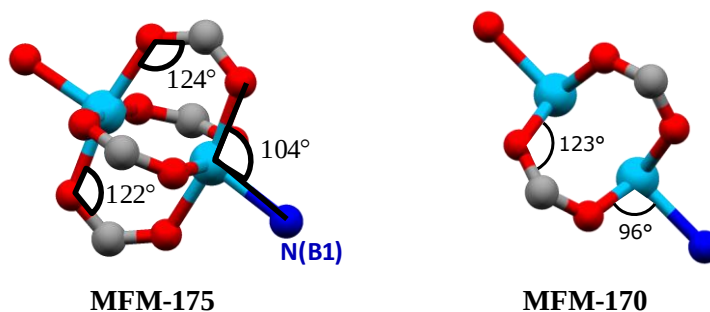


Figure 4.13: Comparison of Cu(II) paddlewheels in MFM-175 and MFM-170 showing distortion resulting from the misalignment of the coordinating pyridyl rings.

Cage B2 is capped at both ends by the square windows belonging to two metal-organic cuboctahedra and is defined by four TPYD⁴⁻ ligands which adopt an up-down conformation. The ligands alternate in direction around the edge of the pore, leading to a cage with monoclinic symmetry (Figure 4.14). As a result, half of the triazole nitrogen groups point into cage B2, while the other half point outwards into the neighbouring cage C. Cage B2 measures $19.0 \text{ \AA} \times 14.8 \text{ \AA}$ in dimension, almost identical to cage B1, and can be found running along the *a* and *c* axes.

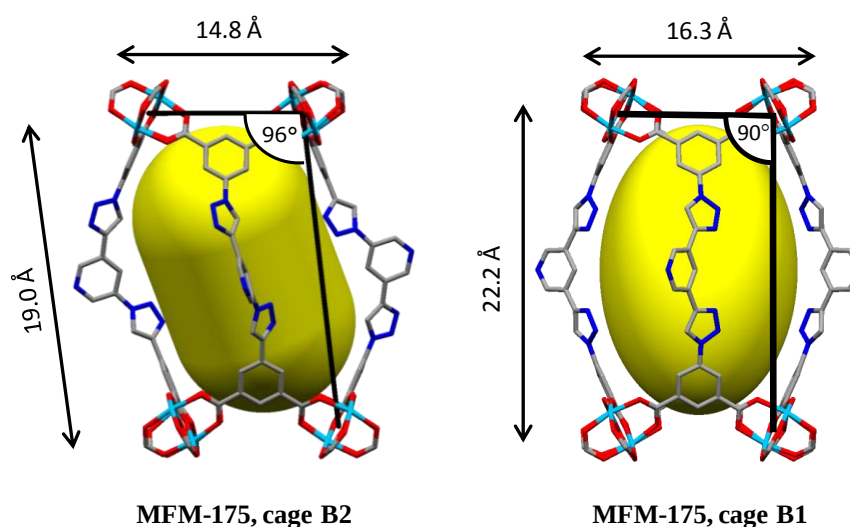


Figure 4.14: Monoclinic cage B2, showing the up-down conformation of TPYD⁴⁻ ligands and comparison to tetragonal cage B1.

The up-down conformation of TPYD^{4-} leads to an interplanar angle of 83° between the isophthalate and pyridyl rings (Figure 4.15). This angle is closer to the ideal angle from MFM-170, leading to a smaller Cu-N(B2) angle of 102° . The overall monoclinic symmetry of cage B2 leads to a greater distortion of the Cu-O-C bond angles, varying up to 5° away from the ideal value of 123° in MFM-170.

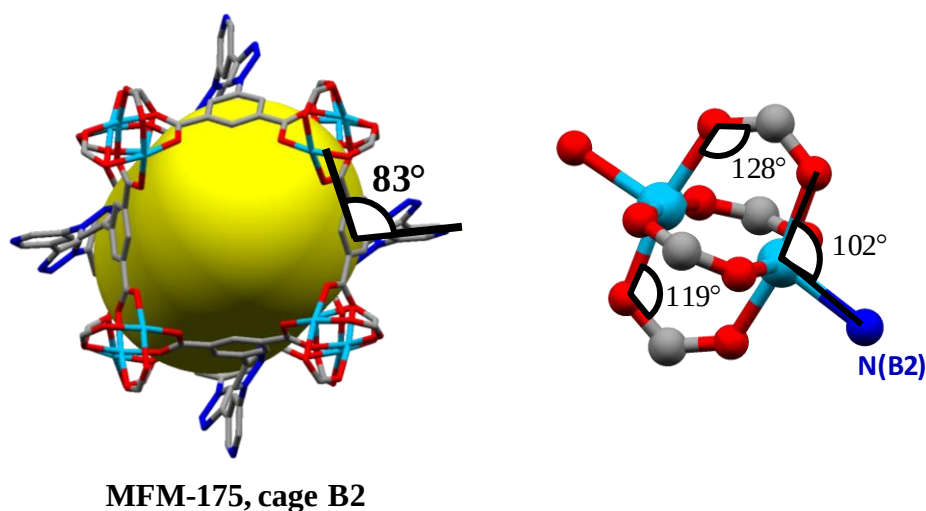


Figure 4.15: The up-down conformation of the TPYD^{4-} ligands surrounding cage B2 results in a dihedral angle of 83° , reducing the O-Cu-N(B2) coordination angle to 102° . The induced strain in the framework can be seen in the distortion of the Cu-O-C angles away from the ideal angle of 123° .

Cage C displays distortion in line with the overall framework, with dimensions $12.8 \text{ \AA} \times 14.2 \text{ \AA}$, slightly smaller than the corresponding cage in MFM-170 ($13.8 \text{ \AA} \times 14.7 \text{ \AA}$). Half of the heterocyclic rings lining cage C are orientated so that the triazole Ns point towards the centre of the pore. The location of these Lewis basic functional groups is expected to result in strong interactions with the CO_2 molecules in binding site II, identified in Chapter 3 (pink, Figure 4.16). Unfortunately, the triazole groups are fixed in position and are unable to rotate to form the parallel arrangement required for occupancy of binding site V/VI (blue/green, Figure 4.16), which may lead to a reduction in the overall CO_2 adsorption capacity.

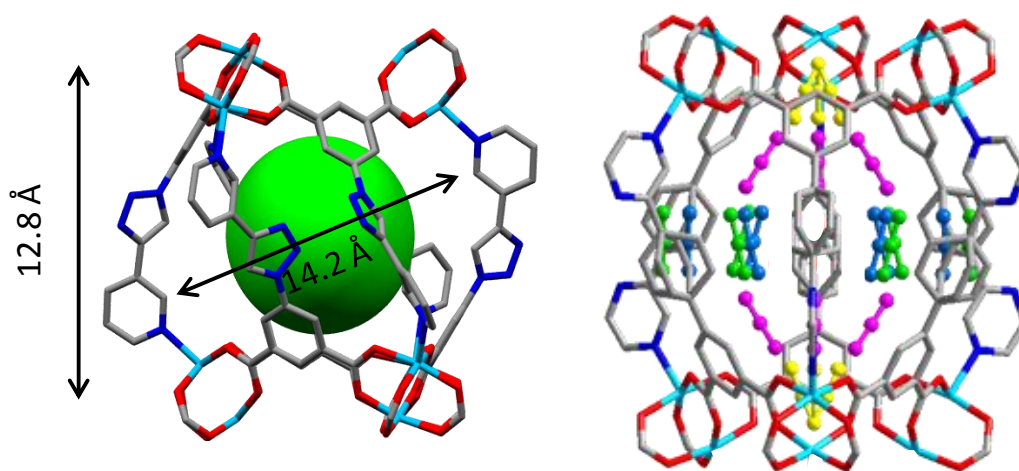


Figure 4.16: Structure and dimensions of cage C in MFM-175. Half of the triazole groups surrounding the cage point directly into the centre of the cage, ideal for interactions with the located CO_2 molecules in MFM-171 in Chapter 3: Site I (yellow), site II (pink), site V (green) and site VI (blue).

Analysis of the crystal structure of MFM-175 confirms the successful synthesis of a **txt** framework with Lewis basic heterocyclic groups pointing into cage C. MFM-175 is expected to show stronger interactions with CO_2 than MFM-170 due to the existence of strong Lewis basic binding sites on the pore surfaces. However MFM-175 is likely to be less stable than MFM-170 due to the high amounts of strain upon the framework visible through the distorted Cu(II) paddlewheel angles.

4.2.3.1 Porosity of MFM-175

The total solvent accessible volume of MFM-175 after removal of the guest solvent was estimated to be 64% using the PLATON/VOID routine.²¹ MFM-175 displays slightly higher porosity than MFM-170 (60%), partially attributed to the absence of rotational disorder in the structure of MFM-175, which is not accounted for in the PLATON model. MFM-175 also features closer packing of ligand molecules than MFM-170 (as a result of the twisting of the triazole rings (3.49 Å between the ligands lining orthogonal cages *c.f.* 4.05 Å in MFM-170)).

4.2.4 Stability of MFM-175

The stability of MFM-175 to desolvation was investigated by PXRD. The as synthesised sample was suspended in acetone over five days, giving the acetone-exchanged sample, followed by heating to 100 °C under a dynamic vacuum overnight. Upon activation the sample changed from a bright blue-green material to a dull navy colour, as opposed to the bright purple observed in the MFM-17X series. The majority of PXRD peaks are still present after activation and Pawley refinement (Figure 4.17) confirm that all three materials match well to the single crystal structure; however there is a distinct loss of crystallinity upon activation, indicating a partial framework collapse.

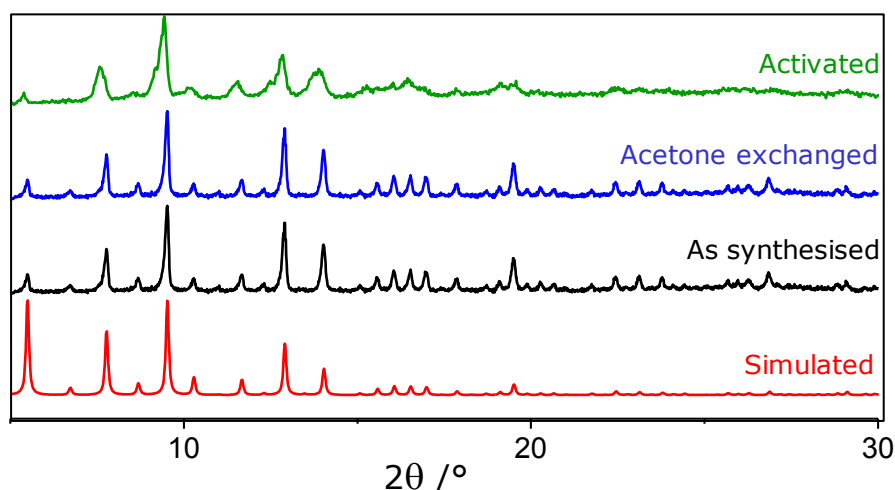


Figure 4.17: PXRD analysis of MFM-175 throughout the activation procedure. From bottom to top: simulated PXRD pattern from single crystal structure (red); as-synthesised sample (black); acetone-exchanged sample (blue); activated sample (green) consistent with loss of crystallinity upon activation.

Table 4.1: Pawley fitting parameters of PXRD patterns of MFM-175; as-synthesised sample, acetone exchanged sample and activated sample.

MOF	a (Å)	b (Å)	c (Å)	β (°)	Volume (Å ³)	GOF
Solvated	32.0746	32.2280	32.0747	89.48	33154	1.87
Acetone	32.0131	32.1860	32.0130	90.65	32983	1.77
Activated	32.0906	31.6389	31.8679	88.26	32341	1.34

Poor stability to activation typically occurs in highly porous MOFs, where the ligand is too long to support the framework in a vacuum and buckles upon evacuation of the pores.²² The self-interpenetrating nature of the **txt** topology introduces a ligand bracing effect;²³ thus the instability of MFM-175 is more likely to be due to strongly binding guest molecules, which

tear the framework apart under the forcing conditions required for activation. The TPYD⁴⁻ ligands surrounding cage B1 in the up-up formation feature two triazole groups pointing into the centre of the pore, which could act as a chelating binding site for solvent molecules. Removal of guest solvent molecules with supercritical CO₂ has previously been used within the Schröder group to circumvent the collapse of NOTT-125;¹⁹ however supercritical drying of MFM-175 resulted in the formation of a dull blue powder, which showed no crystallinity by PXRD.

4.2.5 Thermal Stability of MFM-175

Thermogravimetric analysis shows a reduction in the thermal stability of MFM-175 in comparison to MFM-170 (Figure 4.18); with decomposition occurring at 290 °C as opposed to 350 °C. The reduction in thermal stability can be attributed to the increase strain on the framework originating from the twisting of the triazole rings. For the as-synthesised sample of MFM-175, initial mass losses of 7% (up to 50 °C) and 28% (50 °C – 185 °C), correspond to the loss of four molecules of H₂O and four molecules of DMF per formula unit from the pores. A subsequent mass loss of 9% (185 °C – 260 °C) refers to the removal of one coordinated DMF molecules from each Cu(II) paddlewheel, which is swiftly followed by framework decomposition, leaving a mass corresponding to 2CuO. The acetone exchanged sample demonstrates similar behaviour; an initial mass loss of 34% (25 °C – 160 °C) corresponds to five acetone and four water molecules per formula unit from within the pores of MFM-175 and coordinating to the Cu(II)-paddlewheels, whilst a second mass loss of 51% relates to the decomposition of the framework and the loss of one TPYD⁴⁻ ligand, leaving 2CuO.

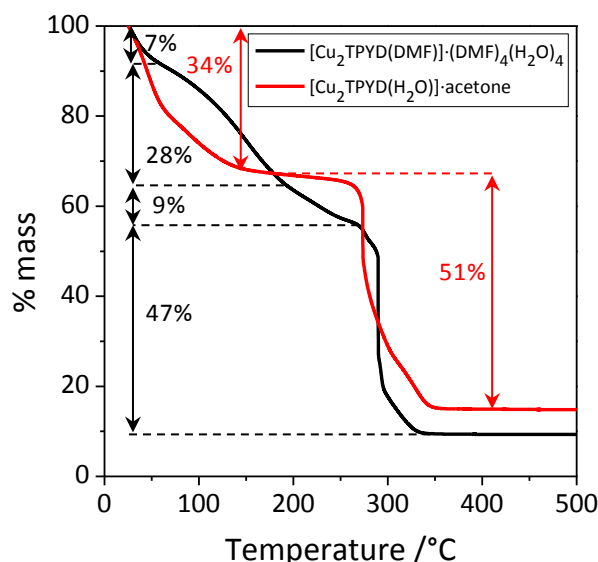


Figure 4.18: Thermogravimetric analysis of as-synthesised (black) and acetone exchanged (red) samples of MFM-175.

4.2.6 Gas Adsorption Isotherms of MFM-175

4.2.6.1 N₂ Adsorption Isotherms and BET Surface Area of MFM-175

MFM-175 demonstrates a reversible type-I N₂ isotherm at 77 K, adsorbing a total of 162 cm³ g⁻¹ at 1 bar and reveals a BET surface area of only 498 m² g⁻¹ (Figure 4.19). Both the total adsorption capacity and BET surface area are around a quarter of those measured for MFM-170 (600 cm³ g⁻¹, 2048 m² g⁻¹), confirming collapse of MFM-175 upon activation. As it is likely that the framework collapses upon activation, it is inappropriate to quantitatively compare the gas uptake capacities of MFM-175 with other frameworks; however assuming no additional framework collapse upon removal of adsorbed gases, it is still possible to calculate isosteric heats of adsorption and selectivity values for MFM-175.

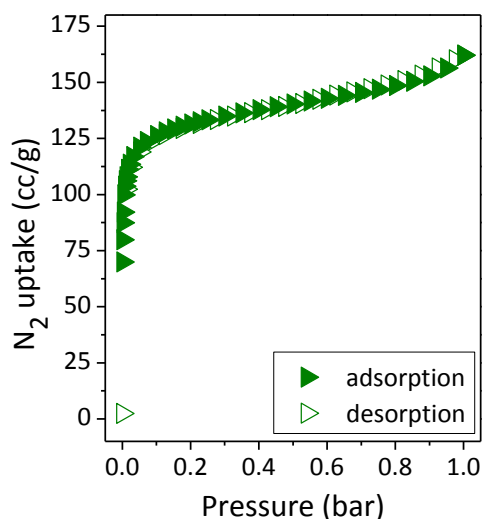


Figure 4.19: Reversible gravimetric N_2 isotherm of MFM-175 at 77 K and 1 bar.

4.2.6.2 Carbon Dioxide Adsorption and Selectivity in MFM-175

MFM-175 adsorbs 45.16 wt% ($230 \text{ cm}^3 \text{ g}^{-1}$) of CO_2 at 273 K and 20 bar, dropping to 39.66 wt% ($202 \text{ cm}^3 \text{ g}^{-1}$) at 298 K. The CO_2 uptake capacities for MFM-175 are around half of those exhibited by MFM-170 (Figure 4.20), in line with the overall framework collapse.

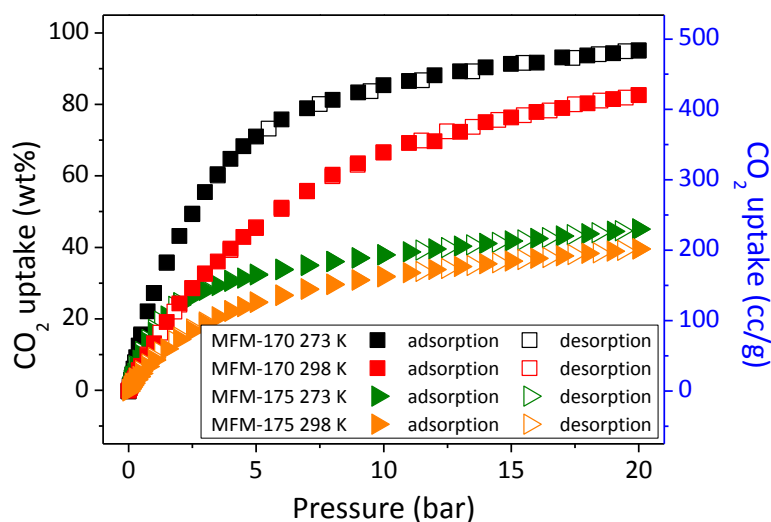


Figure 4.20: Gravimetric isotherms of CO_2 adsorption in MFM-170 and MFM-175 up to 20 bar at 273 K and 298 K.

The heat of adsorption for CO_2 in MFM-175 was calculated to be -35 kJ mol^{-1} , around double the value for MFM-170 (Table 4.2). The high Q_{st} indicates strong interactions between adsorbed CO_2 and the framework surface; suggesting that the triazole functionality is a promising method to enhance CO_2 -framework interactions. MFM-175 displays the

highest CO₂ Q_{st} value of all the previously discussed triazole-containing MOFs: NOTT-122 = -24.5 kJ mol⁻¹,¹⁵ NTU-101 = -25-20 kJ mol⁻¹,⁹ and MIL-101-triazo-NH₂ = -30 kJ mol⁻¹.² It is unclear whether the high Q_{st} value is attributable to interactions between CO₂ and the triazole groups or whether it is a feature of the collapsed framework as smaller pore sizes increase CO₂···CO₂ interactions;⁵ however the Q_{st} value is not unreasonably high, with a number of MOFs achieving CO₂ heats of adsorption greater than 30 kJ mol⁻¹.²⁴⁻²⁹

Table 4.2: Comparison of 20 bar CO₂ adsorption parameters of MFM-170 and MFM-175.

MOF	CO ₂ adsorption, 273 K	CO ₂ adsorption, 298 K	Q _{st} (kJ mol ⁻¹)
MFM-170	94.95 wt% (484 cm ³ g ⁻¹)	82.50 wt% (420 cm ³ g ⁻¹)	-18
MFM-175	45.16 wt% (230 cm ³ g ⁻¹)	39.66 wt% (202 cm ³ g ⁻¹)	-35

Strong interactions between MFM-175 and adsorbed CO₂ in conjunction with low N₂ uptake lead to high IAST selectivity parameters for a simulated flue-gas stream containing 15% CO₂ in N₂. The CO₂/N₂ selectivity values of MFM-175 were calculated from single-component isotherms to be 27.4 at 273 K and 13.4 at 298 K (Figure 4.21). Although MFM-175 shows superior CO₂/N₂ selectivity compared to MFM-170 (11.5 at 273 K), the IAST selectivity parameters are still only moderate in comparison to other reported triazole-containing frameworks; MIL-101-triazo-NH₂: 40.1,² [Zn₄(bpydb)₃(datz)₂(H₂O)]: 54.4,³⁰ and [Mn₂(Hcbptz)₂(Cl)]Cl: 78.8.⁸ Future strategies to increase CO₂ selectivity could include the introduction of amine functional groups (MIL-101-triazo-NH₂ and [Zn₄(bpydb)₃(datz)₂(H₂O)])^{2,29} or formation of a cationic framework ([Mn₂(Hcbptz)₂(Cl)]Cl).⁸

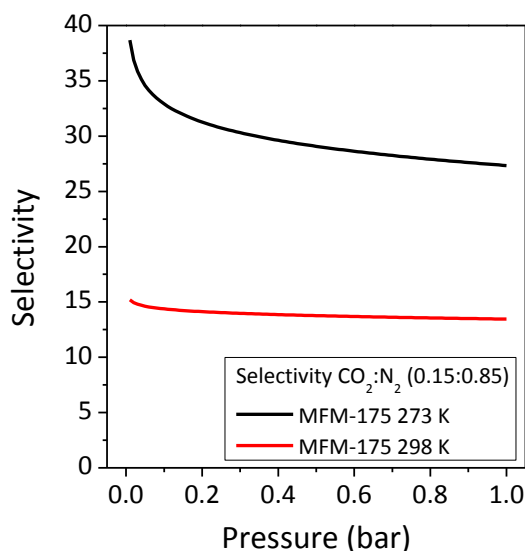


Figure 4.21: Selectivity values for the post-combustion capture of CO_2 from N_2 in MFM-175 at 273 and 298 K in a 0.15:0.85 mixture of $\text{CO}_2:\text{N}_2$.

4.2.6.3 Methane adsorption and selectivity in MFM-175

The methane uptake capacity of MFM-175 was measured to be 9.21 wt% ($129 \text{ cm}^3 \text{ g}^{-1}$) at 273 K and 20 bar, dropping to 7.8 wt% ($109 \text{ cm}^3 \text{ g}^{-1}$) at 298 K. As seen in Figure 4.22, these values are roughly half the uptake capacities exhibited by MFM-170, consistent with the difference in CO_2 uptake capacity between the two frameworks.

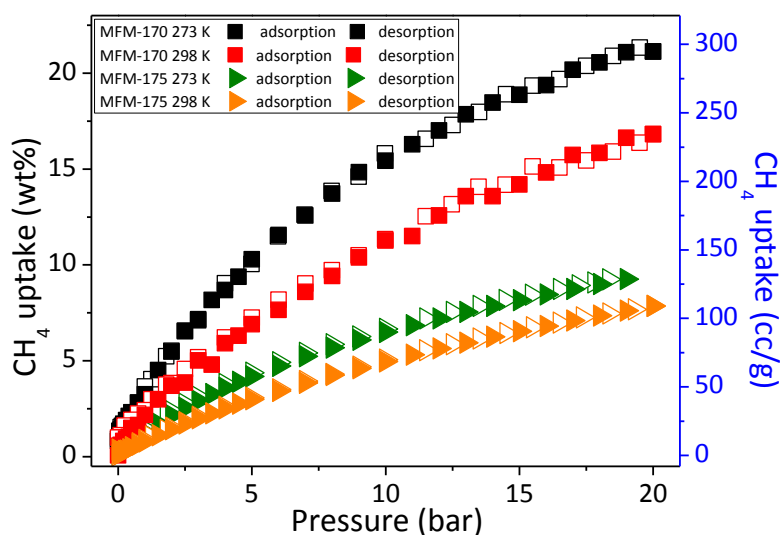


Figure 4.22: Gravimetric isotherms of methane adsorption in MFM-170 and MFM-175 up to 20 bar at 273 K and 298 K. The calculated volumetric uptake is shown for reference.

The isosteric heat of adsorption was calculated to be -20 kJ mol^{-1} , much higher than that measured in MFM-170 (Table 4.3). As triazole groups do not traditionally have an impact

on raising CH₄ adsorption,¹³ this is attributed to the formation of smaller pores and increased adsorbate-adsorbate interactions upon framework collapse.

Table 4.3: Comparison of 20 bar CH₄ adsorption parameters in MFM-170 and MFM-175.

MOF	CH ₄ adsorption, 273 K	CH ₄ adsorption, 298 K	Q _{st} (kJ mol ⁻¹)
MFM-170	21.10 wt% (295 cm ³ g ⁻¹)	16.78 wt% (234 cm ³ g ⁻¹)	-20
MFM-175	9.21 wt% (129 cm ³ g ⁻¹)	7.81 wt% (109 cm ³ g ⁻¹)	-11

Nevertheless, MFM-175 demonstrates a high selectivity for CO₂ in an equimolar mixture of CO₂:CH₄, with IAST selectivity parameters of 9.8 at 273 K and 5.6 at 298 K (Figure 4.23), a trend which is seen across triazole containing MOFs.^{8,13,19,30,31} Whilst MFM-175 does not give any reliable selectivity parameters due to framework collapse, it demonstrates that incorporation of triazole containing groups is a promising strategy for CO₂/CH₄ separation.

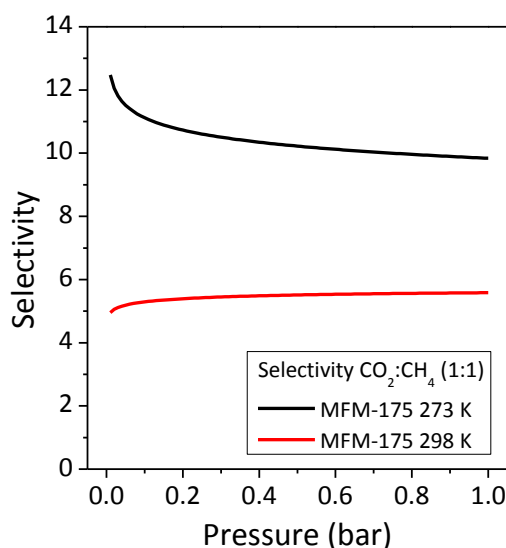


Figure 4.23: Selectivity values for the pre-combustion capture of CO₂ from CH₄ in MFM-175 at 273 and 298 K in an equimolar mixture of CO₂:CH₄.

4.3 Conclusions

Reaction of H₄TPYD with Cu(II) yielded single crystals of MFM-175 which were found to have the same **txt** topology as MFM-170, but with a monoclinic structure. The monoclinic structure arises from the twisted conformations of TPYD⁴⁻ ligands within the framework, due to non-symmetrical rotation around the triazole-pyridine bond. The structure of MFM-175 is thought to be highly strained as the twisting of the ligand arms leads to a high degree

of distortion in the bond angles of the Cu(II) paddlewheels. The reduction in stability is confirmed by a loss of crystallinity upon activation and a reduction of 60 °C in the decomposition temperature compared to MFM-170. Attempts to activate the framework using supercritical CO₂ were unsuccessful.

Gas adsorption isotherms were measured for N₂, CO₂ and CH₄. Analysis of the BET surface area and total pore volume of MFM-175 indicated a loss in porosity in line with framework collapse. The reduction in porosity lead to a halving of the gas uptake capacities in comparison to MFM-170, making it impossible to quantitatively compare the adsorption values with other frameworks. Assuming no further loss in porosity between isotherm measurements, the relative enthalpies of adsorption and selectivity parameters could be compared to MFM-170.

Although not all the triazole groups point into cage C as planned, they are sufficiently well placed to increase the enthalpy of adsorption between CO₂ and the framework to -35 kJ mol⁻¹ compared to only -18 kJ mol⁻¹ in MFM-170. This in turn leads to an improved CO₂/N₂ and CO₂/CH₄ selectivity for post- and pre-combustion capture applications. Although gas adsorption data from MFM-175 cannot be reliably compared to any standard, it demonstrates that the introduction of triazole groups is a promising method to improve selective adsorption of CO₂ and potentially increase the CO₂ uptake capacity of the MFM-17X series.

4.4 Outlook

In order for the high CO₂ selectivity of MFM-175 to be applicable for future applications, the gas uptake capacity must be maximised by preventing framework collapse upon activation. The strain in the framework is thought to be induced by the non-perpendicular dihedral angle between the isophthalate and pyridyl rings in cage B1. Addition of a more flexible aliphatic unit between the isophthalate and triazole rings (Figure 4.24) should introduce a point of rotation and absorb some of the strain in the ligand. A similar approach

has been used by Seth *et al.* to facilitate the self-assembly reaction using a triazole functionalised linker with a sterically-hindered rigid core (Figure 4.24).³⁵

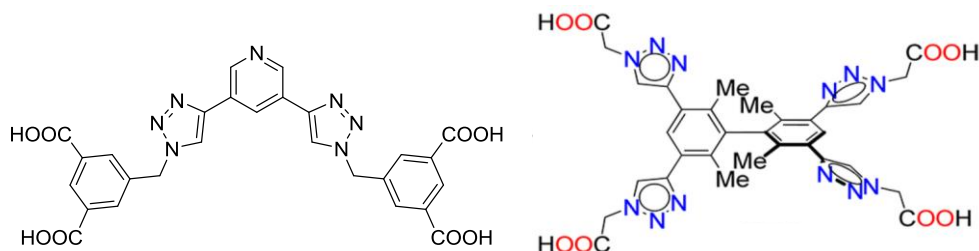
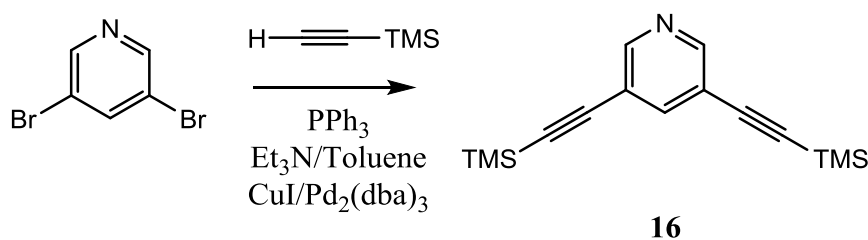


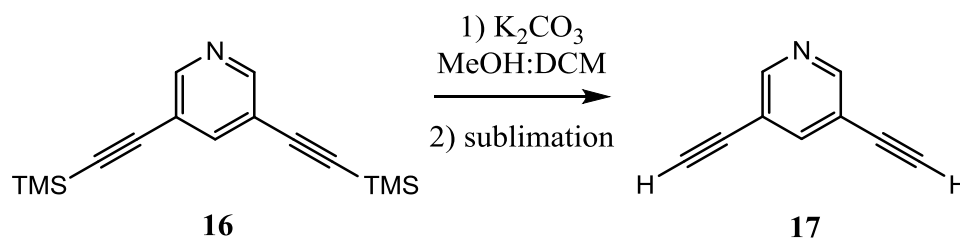
Figure 4.24: Proposed improvement to the structure of H_4 TPYD in order to reduce framework strain in MFM-175; structure of ligand used by Seth *et al.* using flexible aliphatic groups to promote framework formation.

4.5 Experimental

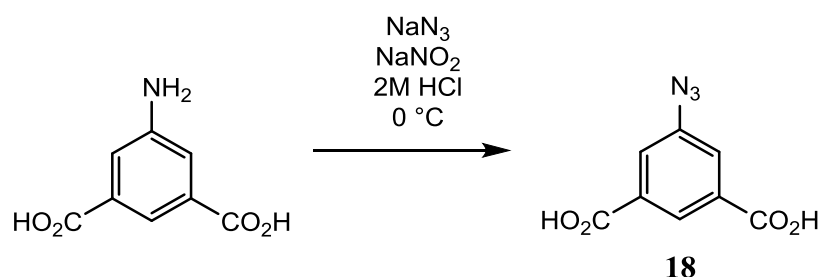
Synthesis of 3,5-bis((trimethylsilyl)ethynyl)pyridine (**16**)



3,5-dibromopyridine (2 g, 8.4 mmol) and triphenylphosphine (0.4 g, 1.5 mmol) were dissolved in toluene:Et₃N (100 ml, 4:1 v/v) and degassed under argon for 30 minutes. CuI (100 mg, 0.5 mmol) and Pd₂(dba)₃ (320 mg, 0.3 mmol) were added and the solution stirred under inert atmosphere for 5 minutes before addition of TMS-acetylene (2.7 ml, 19.5 mmol). The temperature was increased to 75 °C and reacted overnight. The solvent was removed *in vacuo* and the product extracted into DCM. (1.85 g, 81 %). ¹H NMR (300 MHz, CDCl₃) δ ppm 0.26 (18 H, s), 7.82 (1 H, t, *J* = 2 Hz), 8.58 (2 H, d, *J* = 2 Hz), 0.28 (18 H, s). ¹³C NMR (100 MHz, CDCl₃) δ ppm: 133.97, 133.52, 129.55, 128.55. MS: (ESI) *m/z*: 272.1281. IR (ATR) cm⁻¹: 3045 (C-H). Elemental Analysis (%): crude: C 64.10, H 7.15, N 4.85, calculated for C₁₅H₂₁NSi₂: C 66.36, H 7.80, N 5.16.

Synthesis of 3,5-diethynylpyridine (17)

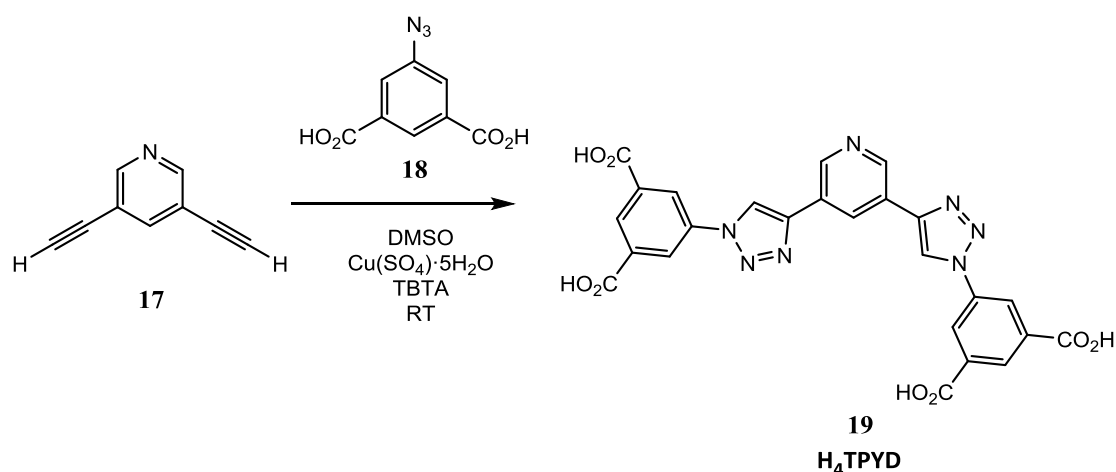
16 (1.35 g, 5 mmol) and K_2CO_3 were dissolved in a solution of $\text{MeOH}:\text{DCM}$ (50 ml, 1:1 v/v) and stirred at RT for two hours. The reaction mixture was washed with water and the solvent removed *in vacuo* to give a black solid. The product was purified by cold finger sublimation to give white crystals. (0.33 g, 52%). ^1H NMR (300 MHz, CDCl_3) δ ppm 7.88 (1 H, s), 8.66 (2 H, s), 3.25 (2 H, s). ^{13}C NMR (100 MHz, CDCl_3) δ ppm: 151.90, 141.87, 118.94, 81.43, 79.32. MS: (ESI) m/z : 127.9. IR: 3208 (C-H), 2104 ($\text{C}\equiv\text{C}$). Elemental Analysis (%): crude: C 84.52, H 4.02, N 10.85, calculated for $\text{C}_9\text{H}_5\text{N}$ C 85.02, H 3.96, N 11.02.

Synthesis of 5-azidoisophthalic acid (18)

5-aminoisophthalic acid (1g, 5.5 mmol) was dissolved in HCl (2 M, 100 ml) and cooled to 0°C . Concurrently NaNO_2 (0.4 g, 5.8 mmol) was dissolved in water (10 ml) in a second flask and also cooled to 0°C . $\text{NaNO}_{2(\text{aq})}$ was added dropwise to the 5-aminoisophthalic acid, ensuring the temperature was maintained, and the solution was stirred for a further 15 minutes at 0°C . NaN_3 (0.38 g, 5.8 mmol) was dissolved in water (10 ml) and cooled to 0°C before being added dropwise over a period of 20 minutes. The solution was stirred for a 30 minutes at 0°C before being allowed to warm to room temperature and stirred overnight. The solid product was filtered from the reaction mixture, washed with water and dried in air.

(1.14 g, 100%). ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ ppm: 8.23 (1 H, t, $J = 1.5$ Hz), 7.76 (2 H, d, $J = 1.5$ Hz). ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ ppm: 165.87, 140.76, 133.06, 126.23, 123.52. MS: (ESI) m/z 205.9 $[\text{M}-\text{H}]^-$. IR: 3547 (O-H), 3099 (C-H), 2118 (C-N), 1714 (C=O). Elemental Analysis (%): crude: C 45.13, H 2.34, N 19.68, calculated for $\text{C}_8\text{H}_5\text{N}_3\text{O}_4$ C 46.39, H 2.43, N 20.29.

Synthesis of H_4TPYD (19)



18 (710 mg, 2.7 mmol), sodium-L-ascorbate (62 mg, 3.1 mmol) and TBTA (84 mg, 1.6 mmol) were dissolved in $\text{DMSO}:\text{H}_2\text{O}$ (60 ml, 2:1 v/v) and degassed for 30 minutes. **17** (200 mg, 1.6 mmol) and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (40 mg, 0.16 mmol) were added and the solution stirred overnight. The product was isolated by filtration and washed with a weak solution of Na_4EDTA (0.1 M) to remove remaining Cu(I) and Cu(II) ions. The product was dried in air (0.83 mg, 99%). ^1H NMR (300 MHz, $\text{DMSO}-d_6$): 9.82 (2 H, s), 8.20 (2 H, s), 8.94 (1 H, s), 8.69 (4 H, s), 8.56 (2 H, s). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): 166.07, 144.91, 137.34, 133.62, 129.92, 124.17, 121.44. MS: (ESI) m/z : 540.0924 $[\text{M}-\text{H}]^-$. IR: 3086 (O-H), 2932 (C-H), 1724 (C=O). Elemental Analysis (%): crude: C 50.74, H 3.62, N 16.66. Calculated for $\text{C}_{25}\text{H}_{15}\text{NO}_8 \cdot 3\text{H}_2\text{O}$: C 50.42, H 3.55, N 16.47.

Synthesis of MFM-175 (crystals)

19 (10 mg, 0.018 mmol), $\text{Cu}(\text{NO}_3)_2 \cdot 5/2(\text{H}_2\text{O})$ (18.6 mg, 0.08 mmol) were dissolved in DMF (2.8 ml) and water (0.2 ml) and acidified with HNO_3 (2 drops). The solution was heated at 80 °C for 16 hours, affording blue crystals.

Synthesis of MFM-175 (bulk)

19 (162 mg, 0.3 mmol) and $\text{Cu}(\text{NO}_3)_2 \cdot 5/2(\text{H}_2\text{O})$ (279 mg, 1.2 mmol) were dissolved in DMF (45 ml) which was acidified with HNO_3 (45 drops). The solution was heated to 80 °C overnight to give a blue precipitate. IR: 3097 (O-H), 1705 (C=O). Elemental Analysis (%): crude: C 44.61, H 3.93, N 9.96. Calculated for $\text{Cu}_2\text{TPYD}(\text{H}_2\text{O}) \cdot (\text{H}_2\text{O})_3 \cdot (\text{C}_3\text{H}_6\text{O})_2$ C 45.13 H 3.79 N 9.87.

4.6 References

- 1 M. Savonnet, E. Kockrick, N. Bats, V. Lecocq, C. Pinel and D. Farrusseng, *New J. Chem.*, 2011, **35**, 1892–1897.
- 2 P.-Z. Li, X.-J. Wang, R. H. D. Tan, Q. Zhang, R. Zou and Y. Zhao, *RSC Adv.*, 2013, **3**, 15566–15570.
- 3 W. Gao, R. Cai, T. Pham, K. A. Forrest, A. Hogan, P. Nugent, K. Williams, L. Wojtas, R. Luebke, L. J. Weselin, M. J. Zaworotko, B. Space, Y. Chen, M. Eddaoudi, X. Shi and S. Ma, *Chem. Mater.*, 2015, **27**, 2144–2151.
- 4 D.-M. Chen, X.-P. Zhang, W. Shi and P. Cheng, *Inorg. Chem.*, 2015, **54**, 5512–5518.
- 5 T. Zhao, X. Jing, J. Wang, D. Wang, G. Li, Q. Huo and Y. Liu, *Cryst. Growth Des.*, 2012, **12**, 5456–5461.
- 6 J.-Y. Zou, W. Shi, N. Xu, H.-L. Gao, J.-Z. Cui and P. Cheng, *Eur. J. Inorg. Chem.*, 2014, **2014**, 407–412.
- 7 W. Zhang, W. Xue, J. Lin, Y. Zheng and X. Chen, *CrystEngComm*, 2008, **10**, 1770–1776.
- 8 H.-H. Wang, W.-J. Shi, L. Hou, G.-P. Li, Z. Zhu and Y.-Y. Wang, *Chem. Eur. J.*, 2015, **21**, 16525–16531.
- 9 X.-J. Wang, P.-Z. Li, L. Liu, Q. Zhang, P. Borah, J. D. Wong, X. X. Chan, G. Rakesh, Y. Li and Y. Zhao, *Chem. Commun.*, 2012, **48**, 10286–10288.
- 10 L. Sun, Y. Li, Z. Liang, J. Yu and R. Xu, *Dalton Trans.*, 2012, **41**, 12790.
- 11 L. Sun, Q. Pan, Z. Liang and J. Yu, *Inorg. Chem. Front.*, 2014, **1**, 478–486.
- 12 C. Wang, L. Li, S. Tang and X. Zhao, *ACS Appl. Mater. Interfaces*, 2014, **6**, 16932–16940.
- 13 B. Liu, S. Yao, C. Shi, G. Li, Q. Huo and Y. Liu, *Chem. Commun.*, 2016, **52**, 3223–3226.
- 14 B. Li, Z. Zhang, Y. Li, K. Yao, Y. Zhu, Z. Deng, F. Yang, X. Zhou, G. Li, H. Wu, N. Nijem, Y. J. Chabal, Z. Lai, Y. Han, Z. Shi, S. Feng and J. Li, *Angew. Chem. Int. Ed.*, 2012, **51**, 1412–1415.
- 15 Y. Yan, M. Suyetin, E. Bichoutskaia, A. J. Blake, D. R. Allan, S. A. Barnett and M. Schröder, *Chem. Sci.*, 2013, **4**, 1731–1736.
- 16 X.-J. Wang, P.-Z. Li, Y. Chen, Q. Zhang, H. Zhang, X. X. Chan, R. Ganguly, Y. Li, J. Jiang and Y. Zhao, *Sci. Rep.*, 2013, **3**, 1149–1154.

- 17 C. E. Wilmer, O. K. Farha, T. Yildirim, I. Eryazici, V. Krungleviciute, A. A. Sarjeant, R. Q. Snurr and J. T. Hupp, *Energy Environ. Sci.*, 2013, **6**, 1158–1163.
- 18 J. Li, P.-Z. Li, Q.-Y. Li, Y. Cao, H. Lu, H. Wu, F. Li, Y. Shi, X.-J. Wang, Y. Zhao, *RSC Adv.* 2014, **4** 53975–53980.
- 19 N. H. Alsmail, M. Suyetin, Y. Yan, R. Cabot, C. P. Krap, J. Lü, T. L. Easun, E. Bichoutskaia, W. Lewis, A. J. Blake and M. Schröder, *Chemistry*, 2014, **20**, 7317–7324.
- 20 Z. Lu, J. Bai, C. Hang, F. Meng, W. Liu and Y. Pan, *Chem. Eur. J.*, 2016, **22**, 6277–6285.
- 21 A. L. Spek, *Acta. Crystallogr. Sect. D*, 2009, **65**, 148.
- 22 Y.-X. Tan, Y.-P. He and J. Zhang, *Inorg. Chem.*, 2012, **51**, 9649–9654.
- 23 X. Wang, W. Gao, J. Luan, L. Wojtas and S. Ma, *Chem. Commun.*, 2016, **52**, 1971–1974.
- 24 S. Mukherjee, A. V Desai, Y. D. More and A. I. Inamdar, *ChemPlusChem*, 2016, **81**, 702–707.
- 25 M. Savage, S. Yang, M. Suyetin, E. Bichoutskaia, W. Lewis, A. J. Blake, S. A. Barnett and M. Schröder, *Chem. Eur. J.*, 2014, **20**, 8024–8029.
- 26 S. R. Caskey, A. G. Wong-foy and A. J. Matzger, *J. Am. Chem. Soc.*, 2008, **130**, 10870–10871.
- 27 S. Xiong, Y. He, R. Krishna, B. Chen and Z. Wang, *Cryst. Growth Des.*, 2013, **13**, 2670–2674.
- 28 R. Yun, R. Cui, F. Qian, X. Cao, S. Luo and B. Zheng, *RSC Adv.*, 2014, **5**, 2374–2377.
- 29 D. Chen, N. Xu, X. Qiu and P. Cheng, *Cryst. Growth Des.*, 2015, **15**, 961–965.
- 30 D.-M. Chen, N. Xu, X.-H. Qiu and P. Cheng, *Cryst. Growth Des.*, 2015, **15**, 961–965.
- 31 Q. Gao, X. Zhao, Z. Chang, J. Xu and X. Bu, *Dalton trans.*, 2016, **45**, 6830–6833.
- 32 K. Chen, R. Lin, P. Liao, C. He, J. Lin, W. Xue, Y. Zhang, J. Zhang and X. Chen, *Cryst. Growth Des.*, 2013, **13**, 2118–2123.
- 33 P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, L. Wojtas, M. Eddaoudi and M. J. Zaworotko, *Nature*, 2013, **495**, 80–84.
- 34 B. Li, H. Wang and B. Chen, *Chem. Asian J.*, 2014, **9**, 1474–1498.
- 35 S. Seth, G. Savitha and J. N. Moorthy, *Inorg. Chem.*, 2015, **54**, 6829–6835.
- 36 P. M. Krishna, D. B. Ramachary and S. Peesapati, *RSC Adv.*, 2015, **5**, 62062–62066.

Chapter 5: Preventing the Formation of the Self-interpenetrated Net in MFM-17X.

5.1 Introduction

Interpenetration is a common phenomenon in MOFs, involving the entanglement of two or more frameworks which cannot be separated without the breaking of covalent bonds. A disadvantage of interpenetration is the corresponding decrease in porosity, producing smaller pores, lower surface areas and higher density – traditionally seen as detrimental for gas sorption. Recently smaller pores have been recognised as beneficial for low pressure adsorption, although a decrease in porosity still reduces the high pressure uptake capacity. For MOFs targeting size separation or catalytic applications, small pores and channels limit the size of the guest species which can pass through the framework, especially important for catalytic substrates and products.¹

Conversely, interpenetration can be advantageous, improving stability by minimising the systematic energy through filling the void space and producing repulsive forces between the constituent nets. The repulsive forces prevent the frameworks from collapsing in upon themselves, especially important for those with long, highly strained ligands. Manipulating the positive and negative aspects of interpenetration is a key consideration in MOF design and synthesis.² The self-interpenetrating nature of MFM-170 means that the pyridyl groups are not available for interactions with adsorbed CO₂ within the pores. If a single framework net could be isolated, the higher pore volume and free pyridyl groups could greatly increase the CO₂ adsorption capacity.

The most common method of preventing interpenetration is variation of synthetic conditions such as reaction temperature, concentration or acidity.^{3–6} Introduction of templating agents can prevent interpenetration by occupying the space usually held by the second net;^{3,7} whilst the solvent can also play a large role as a templating agent or modulator.⁸

5.1.1 Manipulation of Steric Effects to Prevent Interpenetration

To investigate whether solvent steric effects would prevent interpenetration in MUF-9, Ferguson *et al.* substituted the DMF used in solvothermal synthesis with bulky amine solvents (*N,N*-diethyl formamide (DEF), *N,N*-dibutylformamide (DBF), *N,N*-isopropylformamide and *N*-formylpiperidine) (Figure 5.1).⁹ Synthesis of MUF-9 from the smaller solvent molecules from (DMF and DEF) resulted in the formation of a doubly interpenetrated framework (β -MUF-9), whilst use of a bulkier solvent (DBF) produced a non-interpenetrated phase (α -MUF-9). Doping a DBF solution with only 5% of DMF resulted in the formation of a partially interpenetrated framework with occupancy of the second framework ranging from 33-65%, only the second reported partially interpenetrated framework reported to date.¹⁰

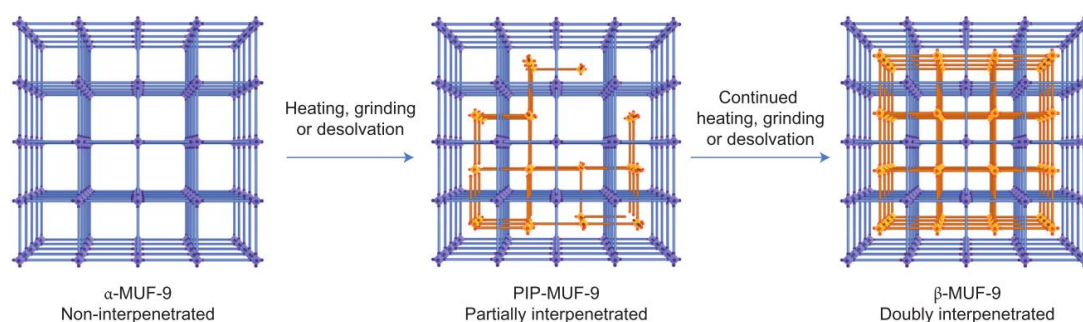


Figure 5.1: Structures of three MUF-9 frameworks; α -MUF-9, the non-interpenetrated framework synthesised in pure DBF; PIP-MUF-9, the partially-interpenetrated framework synthesised from a 0.05:0.95 DMF:DBF mixture with occupancy of the second framework ranging from 33-65% depending on heating time; β -MUF-9, the doubly interpenetrated framework synthesised in DMF.

Interpenetration can be prevented by using sterically encumbered ligands; rational ligand design involves the incorporation of large bulky functional groups^{11,12} which decrease the pore volume and restrict the formation of a second framework. Roberts *et al.* reported the synthesis of two azolium containing frameworks for organocatalytic applications (Figure 5.2).¹³ NU-503 is synthesised from a 4,4'-biphenyl dicarboxylic acid based ligand featuring an imidazolium “side arm” protruding from one ring. Reaction with Zn(II) affords a two-fold interpenetrated cubic framework featuring small pores that are unsuitable for the

diffusion of products and substrates. NU-504 is isostructural to NU-503; however the addition of a second imidazolium “side arm” results in a single non-catenated net in which the additional “side arm” protrudes into the pore.

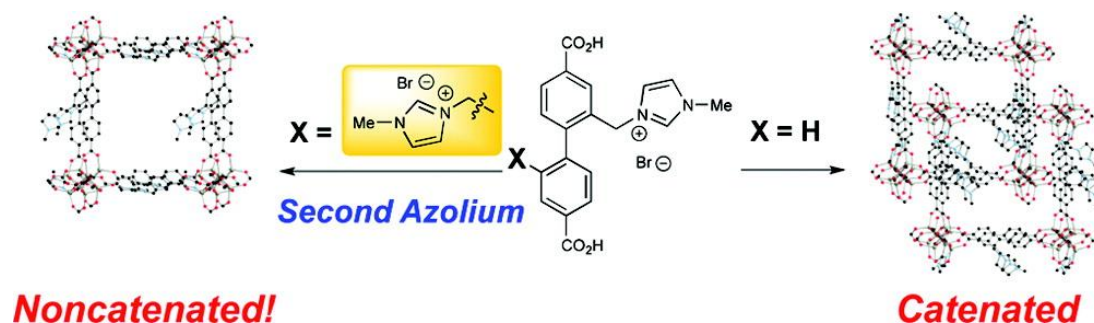


Figure 5.2: Non-interpenetrated cubic structure of NU-504 synthesised from a di-substituted imidazolium ligand. Isostructural interpenetrated structure of NU-503, featuring a 4,4'-biphenyl dicarboxylate ligand with a single imidazolium group.

5.1.2 Manipulation of electronic effects to prevent interpenetration

Ligand functionalisation does not only have steric implications; electronic effects can be manipulated in order to prevent interpenetration. $(\text{NH}_4)\text{UO}_2(\text{BDC})_{1.5} \cdot 2.5\text{H}_2\text{O}$ (BDC = 1,4-benzene dicarboxylate) is an unusual uranium based MOF, featuring two-dimensional honeycomb nets which stack in two-fold interpenetrated pairs (Figure 5.3). Substitution of the benzene ring for a naphthalene group in $\text{C}(\text{NH}_2)_3\text{UO}_2(\text{NDC})_{1.5} \cdot 2.5\text{H}_2\text{O}$ (NDC = 1,4-naphthalene dicarboxylic acid) forms identical honeycomb nets which preferentially adopt a π - π stacking arrangement to stabilize the framework and form a non-interpenetrated net.

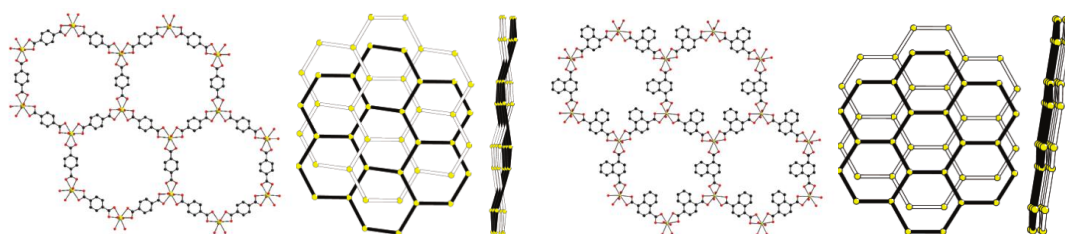


Figure 5.3: Isostructural 2D-honeycomb nets formed in two-fold interpenetrated $(\text{NH}_4)\text{UO}_2(\text{BDC})_{1.5} \cdot 2.5\text{H}_2\text{O}$ and non-interpenetrated $\text{C}(\text{NH}_2)_3\text{UO}_2(\text{NDC})_{1.5} \cdot 2.5\text{H}_2\text{O}$.

Further non-covalent interactions investigated by Liu *et al.*¹⁴ relate to electron-deficient aromatic (π -acidic) systems and lone-pair-bearing electronegative atoms (Figure 5.4). The porous cuboid *ab2* architecture is constructed from 2-dimensional square nets of bipyridyl organic ligands and Zn(II) nodes, pillared by infinite ZnSiF_6 chains. Ligand elongation typically leads to interpenetration; however the incorporation of electron deficient N,N'-di(4-pyridyl)-1,4,5,8-naphthalene diimide (DPNDI), whose length would normally predict interpenetration, produces only a single, non interpenetrated net.

Interpenetration is prevented in this instance by the non-covalent interaction between DPNDI units and *N*-methylpyrrolidin-2-one (NMP) solvent molecules. Although the solvent molecules cannot be identified within the crystal structure due to disorder, the lone pair- π interaction has been identified in a parallel study of the cocrystal structure of DPNDI and NMP.¹⁵ Addition of I_2 during synthesis reveals an isostructural tetragonal framework, where intercalated I_2 molecules replace NMP as I_2 forms stronger lone pair- π interactions.

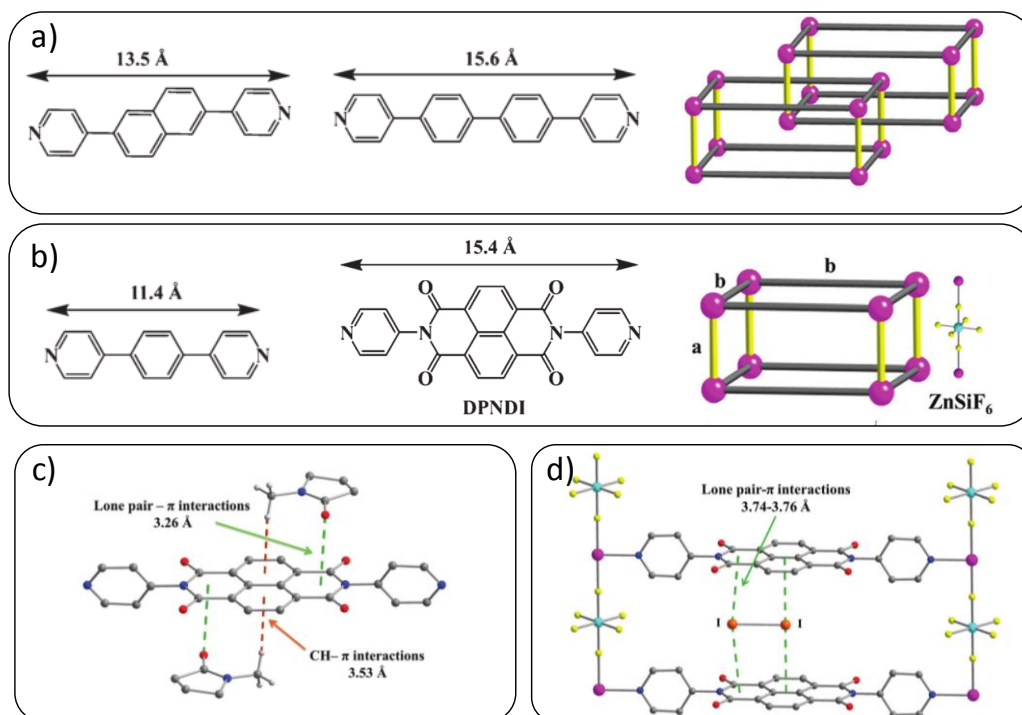


Figure 5.4: Formation of a non-interpenetrated structure from a DPNDI ligand due to lone pair- π interactions. (a) length of ligands that form interpenetrated structures; (b) ligands that for non-interpenetrated structures; (c) Single crystal structure of NMP/DPNDI cocrystal, highlighting the lone pair- π and CH- π interactions; (d). Cuboid framework of I₂@ZnDPNDI(SiF₆) showing lone pair- π interactions.

5.1.3 Use of Protecting Groups to Prevent Secondary Binding Sites

In this thesis the term self-interpenetrated framework is defined as a framework in which when one single bond is broken, two identical interpenetrating nets are formed. Self-interpenetrated frameworks usually require coordination of secondary binding sites, such as nitrogen atoms, to metal ions. Additional coordinating sites can also hinder the formation of crystalline MOFs by coordinating to the metal centre in a disordered manner. Protecting groups can be applied to secondary binding sites to prevent coordination and give an ordered structure. Lun *et al.* attempted to synthesise IRMOF-Pro, a cubic Zn(II) MOF with proline pointing into the pores (Figure 5.5).¹⁶ Whilst no framework formed from the proline functionalised ligand reaction, protection with a bulky *tert*-butoxycarbonyl (Boc) group afforded cubic crystals of IRMOF-Pro-Boc, which undergo single-crystal-to-single-crystal

transformation to IRMOF-Pro upon heating. Thus the use of protecting groups is a promising method for introducing otherwise-coordinating groups into the framework.

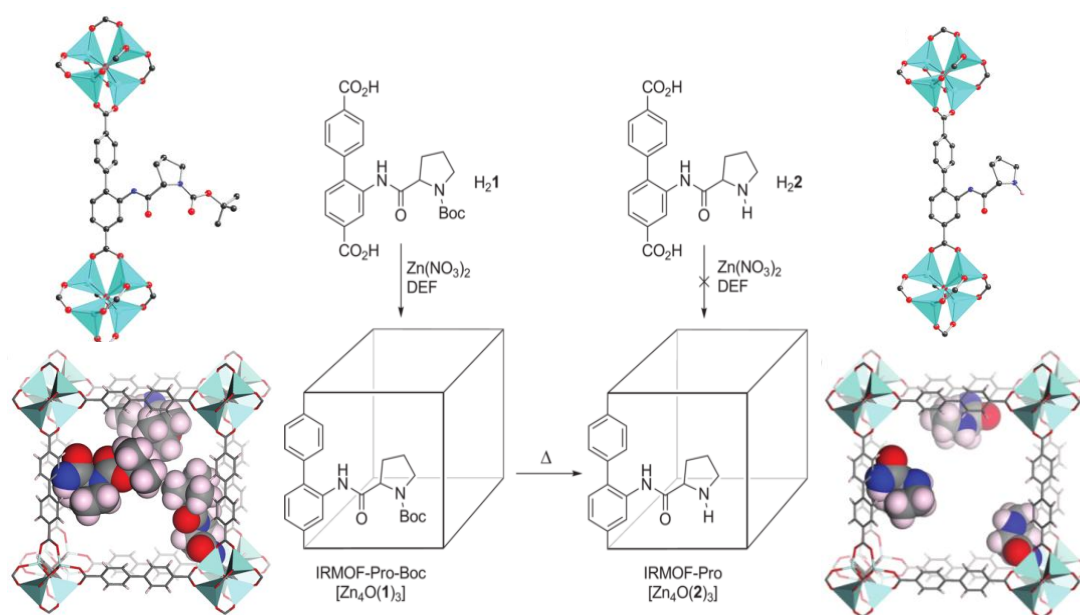


Figure 5.5: Formation of IRMOF-Pro via a thermally induced single-crystal-to-single-crystal transformation from IRMOF-Pro-Boc. Ligand coordination and space filling representations of IRMOF-Pro and IRMOF-Pro-Boc.

5.2 Aims and Objectives

The self-interpenetrating nature of the MFM-17X series reduces the framework porosity and consequently the gas uptake capacity at high pressure. In this chapter we aim to synthesise a single-net framework of MFM-170 by preventing the formation of a self-interpenetrated framework. Removal of the second framework should theoretically increase the porosity from 61% to nearly 80%; 39% of the cell volume corresponds to the framework structure, of which half would be removed. Additionally, breaking the Cu(II)-N bond would double the number of open metal sites per net and reveal four pyridyl sites pointing directly into a large (25 Å) pore; a prime location for interaction with guest species. Immobilised pyridyl sites could also have applications as a nucleophilic catalyst for acylation.¹⁷

5.3 Results and Discussion

5.3.1 Preventing Interpenetration in MFM-170 by using Pyridine-N-oxide as a Protection Group

The creation of a self-interpenetrated framework in the MFM-17X series is driven by the formation of an axial Cu(II)-N bond between the Cu(II)-paddlewheel and the pyridyl group; thus the addition of a protecting group to the pyridyl nitrogen should prevent the binding of an interpenetrated framework to the metal SBU. Upon removal of the Cu(II)-N bond both axial sites on the Cu(II)-paddlewheels would coordinate solvent molecules, resulting in steric collision with the secondary framework and the formation of a single, non-interpenetrated net of MFM-170.

The proposed strategy involved protecting H_4PPYD by oxidation of the pyridyl group to give a pyridine-N-oxide functionalised ligand, named H_4PPNO (3,5-bis(3',5'-dicarboxy-[1,1'-biPhenyl]-4-yl)Pyridine N-Oxide) (Figure 5.6). This approach allows for post-synthetic regeneration of the pyridine functionality by reduction with PCl_3 . Although the pyridine-N-oxide functionality could additionally coordinate to the Cu(II) centres, this would lead to a framework with interesting connectivity and polarity.^{18–22}

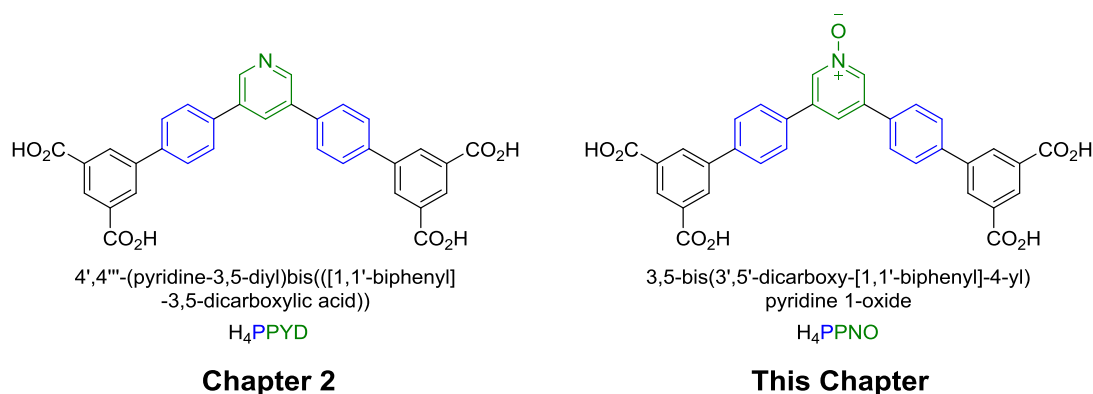
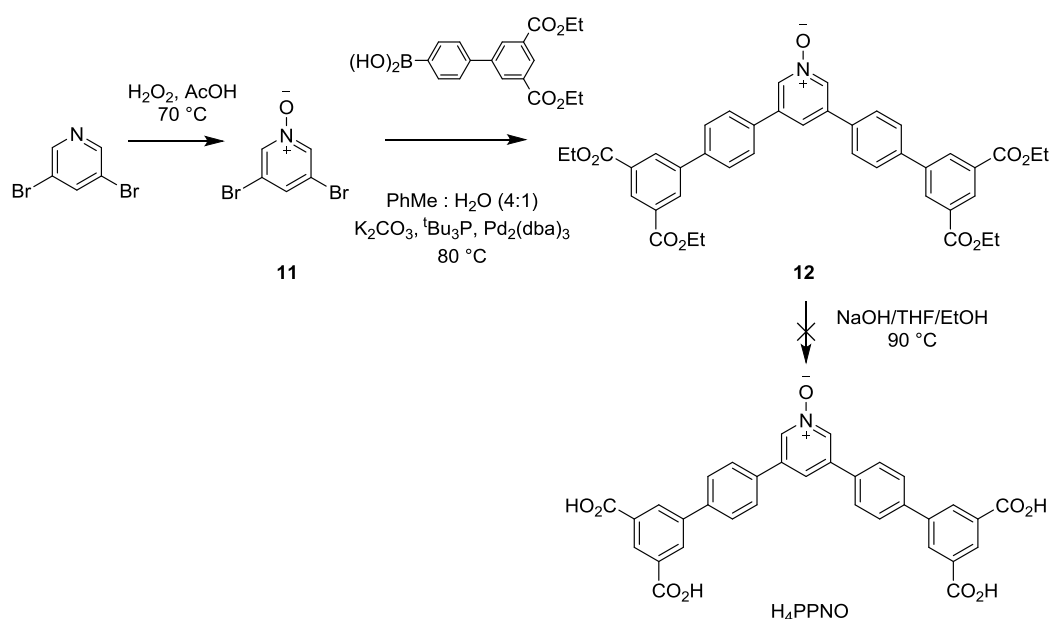


Figure 5.6: Structures and systematic names of H_4PPYD and H_4PPNO .

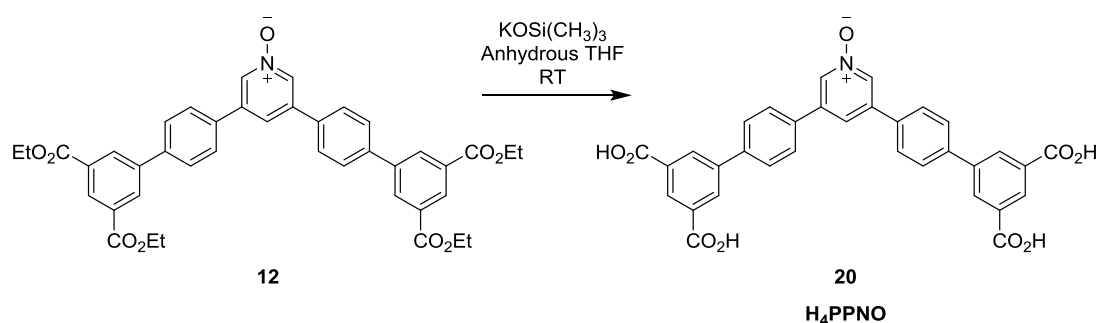
5.3.1.1 Synthesis of Pyridine-N-oxide Protected Ligand, H_4PPNO

Synthesis of H_4PPNO proceeded via Suzuki coupling to an oxidised 3,5-dibromopyridine core, previously described in Chapter 3. Normal hydrolysis conditions using NaOH stripped

away the N-oxide functionality; therefore milder conditions using potassium trimethylsilanolate in dry THF were used (Scheme 5.2).²⁴



Scheme 5.1: Proposed route to H₄PPNO via initial oxidation of the 3,5-bromopyridine core.



Scheme 5.2: Modified hydrolysis method to give H₄PPNO.

5.3.1.2 Attempts to Synthesise a Cu(II) Containing MOF from H₄PPNO

A systematic investigation into the most favourable conditions for crystal growth involved many permutations of different copper salts, solvent conditions and acidic modulators, as shown in Table 5.1. Unfortunately, despite repeated attempts, no crystalline MOF was formed from H₄PPNO; PXRD analyses of some of the most successful conditions are seen in Figure 5.7.

Table 5.1: Conditions used to attempt to synthesise a Cu(II) containing MOF with H₄PPNO.

Metal salts	Solvent	Modulator	Reaction conditions
Cu(NO ₃) ₂ ,	DMF	HNO ₃	Wheaton vials
CuCl ₂	DEF	HBF ₄	Glass pressure tubes
CuCl ₂	H ₂ O	HCl	Teflon lined autoclaves
CuSO ₄	DMF:H ₂ O (29:1 – 2:1 v/v)	0.1 M HCl	70 – 170 °C
Cu(OAc) ₂	DEF:H ₂ O:EtOH	0.1 M NaOH	
	DMF:H ₂ O:EtOH	0.1 M HNO ₃	
	DMF:DMSO (29:1 – 2:1 v/v)	0.1 M H ₂ SO ₄	
		0.1 M HBF ₄	
		0.1 M AcOH	

Following previously successful conditions used for the MFM-17X series, initial attempts varied the volume of water and acid in DMF. All precipitates displayed very little crystallinity by PXRD. Alternative conditions used DEF as a bulkier solvent, with ethanol introduced as an antisolvent and the solution acidified using HCl. PXRD analysis of the resultant materials showed vestiges of crystallinity, an improvement on previous conditions.

As poor solubility of H₄PPNO was thought to be responsible for the lack of success at MOF formation; high temperature hydrothermal synthesis was attempted, heating CuCl₂ and H₄PPNO in water at 170 °C, with addition of an acidic modulator (0.1 M HCl). Hydrothermal conditions resulted in the formation of a green powder, which showed diminished crystallinity in comparison to the solvothermal syntheses. Upon the addition of small volumes of DMSO to aid the solubility of the ligand, no precipitate was formed, even after extending the reaction periods to weeks rather than days.

Since acidic conditions could lead to further protonation of the negative N-oxide oxygen atom,²⁵ basic (0.1 M NaOH) hydrothermal conditions were also attempted with near-identical results obtained to the acidic hydrothermal conditions.

Finally a series of conditions were tested using a vast range of different metal salts in DMF/H₂O: CuCl₂, CuSO₄, Cu(NO₃)₂ and Cu(OAc)₂. The solutions were acidified with varying volumes of 0.1 M stock solutions of HNO₃, HCl, AcOH, H₂SO₄ and HBF₄ in DMF.

PXRD analyses of the resulting precipitates were mainly amorphous in character, with some broad humps visible, assigned to an extended framework, in addition to sharp peaks assigned, due to the high 2θ angle, to the recrystallised ligand rather than framework structure.

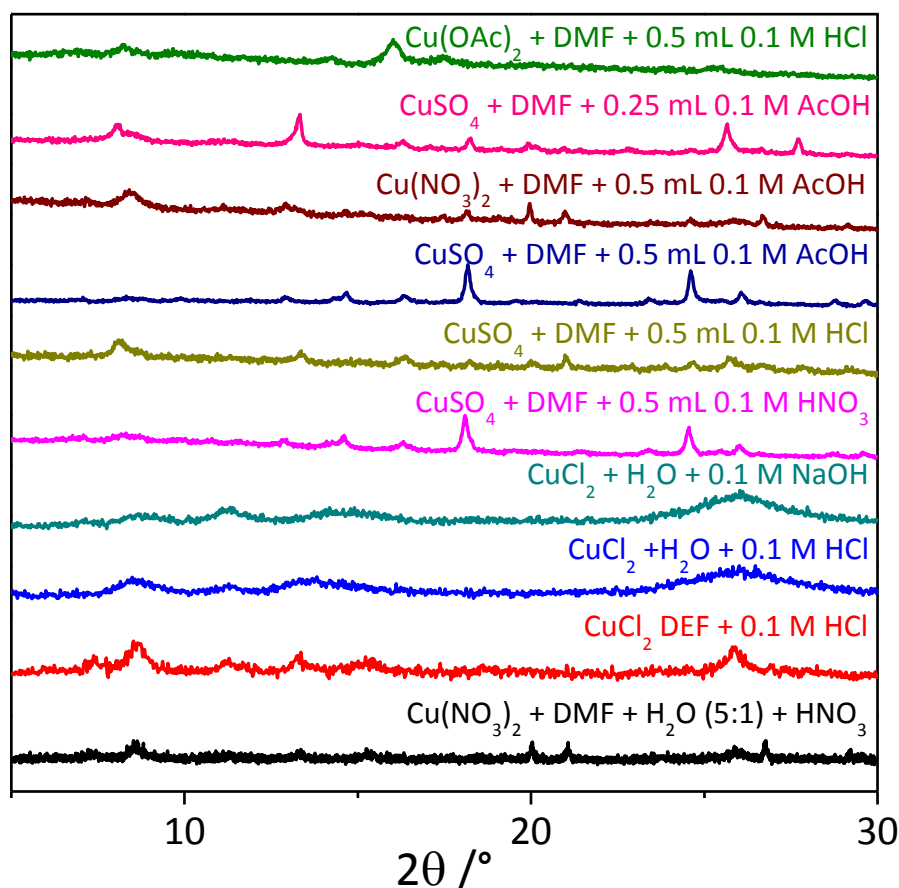


Figure 5.7: A selection of PXRD analyses of the precipitates formed from the reaction of Cu(II) salts and H_4PPNO . Although a degree of long range order is present, evident by the broad humps in the diffractogram, no crystalline MOF sample was synthesised.

5.3.1.3 H_4PPNO Summary and Conclusions

H_4PPNO was successfully synthesised; however despite persistent attempts to synthesise a MOF from this ligand, solvothermal reaction products showed no signs of long range crystalline order by PXRD. The N-oxide O^- is thought to coordinate to the metal centre, in this instance resulting in a disordered, amorphous product. Whilst investigations into solvothermal conditions were ongoing, alternative strategies were investigated.

5.3.2 Preventing Interpenetration in MFM-170 by Increasing the Steric Bulk of the Framework.

It was previously postulated that removal of the pyridyl binding site would prevent interpenetration in **txt** frameworks due to steric hinderance between the ligand and axial solvent molecules. In order to see whether the pyridine-N-oxide group in H₄PPNO is large enough to prevent interpenetration, a second ligand H₄PTOL (3,5-bis(3',5'-dicarboxy-[1,1'-biPhenyl]-4-yl) **TOL**uene) was designed (Figure 5.8). Although a tolyl core does not allow synthetic regeneration of the pyridyl N, the similarity in size between a methyl and N-oxide functional group can be used as a proof of concept, removing the challenges resulting from coordination of the pyridine-N-oxide to the metal centres. At the very least, the inclusion of an electron donating methyl substituent will increase the electron density around the central phenyl ring, strengthening the binding interaction between adsorbed CO₂ and the π -electron cloud, identified in Chapter 3 by IR spectroscopy and SCXRD.^{26,27}

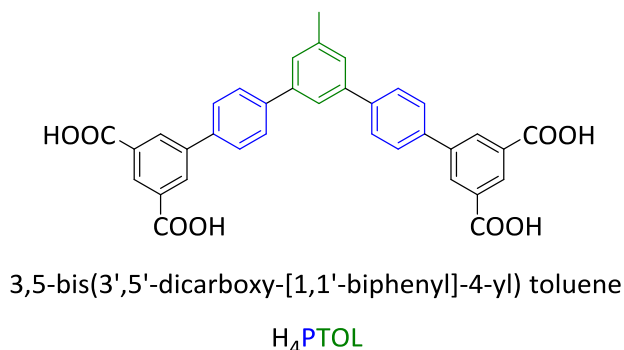


Figure 5.8: Structure and systematic name of the ligand H₄PTOL

[Cu₂EPYD], previously discussed in Chapter 2,²⁸ forms a self-interpenetrated **txt** framework, isostructural to MFM-170, with ethyne rather than phenyl spacing groups between the isophthalate and pyridyl rings. A similar ligand, reported by Liu *et al.*,²⁹ features a central non-coordinating phenyl ring, designated H₄EBNZ, (Figure 5.9). Reaction of H₄EBNZ with Cu(II) affords a two-fold interpenetrated **zmj** framework, [Cu₂EBNZ]. Although removal of the Cu(II)-N dative bond results in steric clash between the ligand and coordinated solvent on the Cu(II)-paddlewheel, the energy penalty required for formation of a non-

interpenetrated structure is too great and the framework rearranges, the cuboctahedra rotate by 45°, in order to accommodate the additional steric bulk.

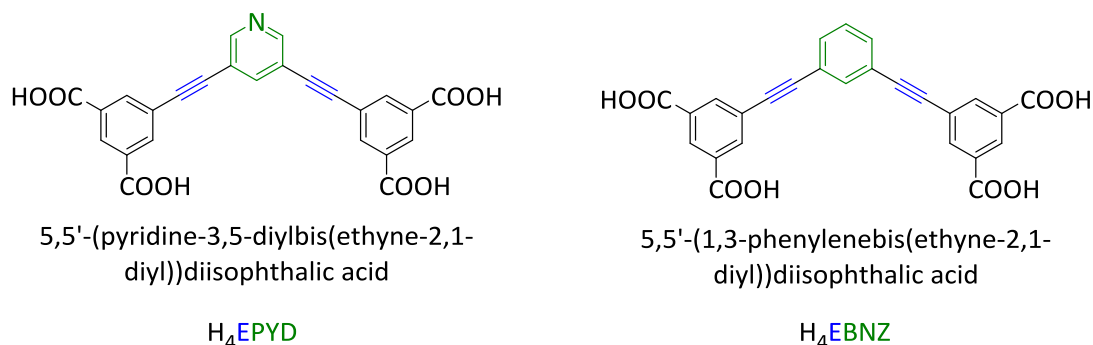
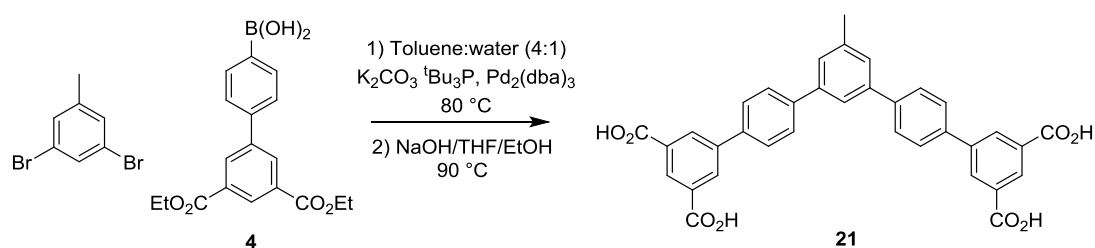


Figure 5.9: Structures and systematic names of H₄EPYD and H₄EBNZ

H₄PTOL was synthesised by Suzuki coupling of the “extended boronic acid” unit described in Chapter 2 to 3,5-dibromotoluene, followed by hydrolysis with NaOH (Scheme 5.3).



Scheme 5.3: Synthetic route to H₄PTOL

5.3.2.1 Synthesis and Structure of [Cu₂PTOL(DEF)₂](DEF)(H₂O) (MFM-176)

Solvothermal reaction of H₄PTOL in acidified (HCl) DEF and ethanol yielded blue crystals of [Cu₂PTOL(DEF)₂](DEF)(H₂O), henceforth referred to as MFM-176. MFM-176 crystallises in the tetragonal space group *P4/nmm*, *a* = 33.1245(2) Å, *c* = 31.6860(5). Analysis with the TOPOS software³⁰ reveals a two-fold interpenetrated structure with **zmj** topology, identical to [Cu₂EBNZ].²⁹ From this structure we conclude that the methyl substituent does not introduce enough steric bulk into the framework to prevent interpenetration and thus we can infer that H₄PPNO would act in a similar manner.

5.3.2.2 Structure of MFM-176 and Comparison to MFM-170

Initial comparison of MFM-176 and MFM-170 (**txt** topology) reveals two similar structures comprising Cu(II)-based metal organic cuboctahedra (cage A) linked together by tetragonal cages (cage B). Side-by-side comparison of one single net reveals a subtle change in the *ab* plane. In order to avoid a steric clash between the axial solvent molecules and interpenetrated framework, cage A rotates 45° about the *c* axis in relation to the square net, shown in Figure 5.10.

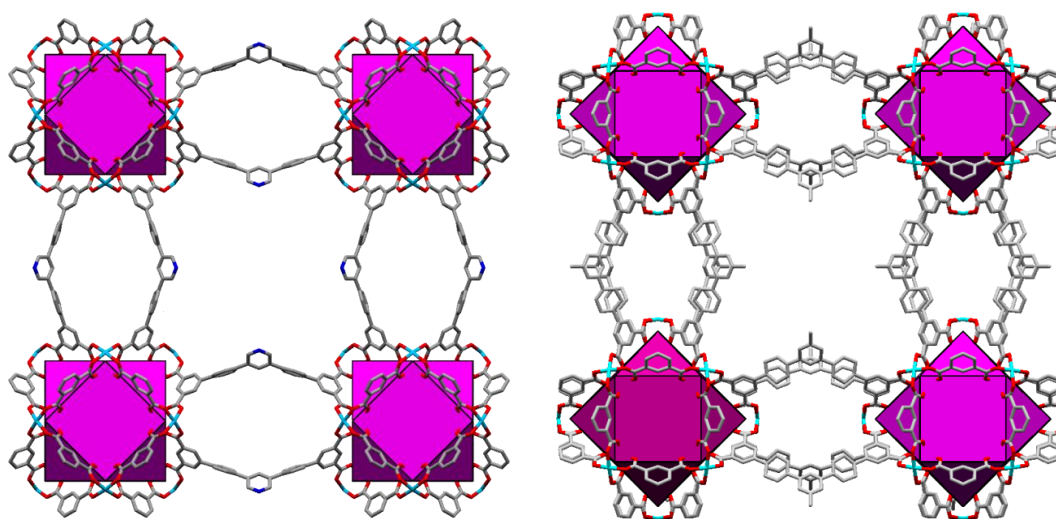


Figure 5.10: Single net of MFM-170 and MFM-176 viewed down the *c* axis; cage A depicted in purple.

The rotation of cage A around the *c* axis results in the formation of truncated tetragonal cages in the *ab* plane (Figure 5.11). These truncated tetragonal cages, denoted cage B3, connect the cuboctahedra between vertices rather than between the square faces. Along the *c* axis, the tetragonal cages, denoted cage B1, connect square faces, equivalent to the tetragonal cages found in MFM-170.

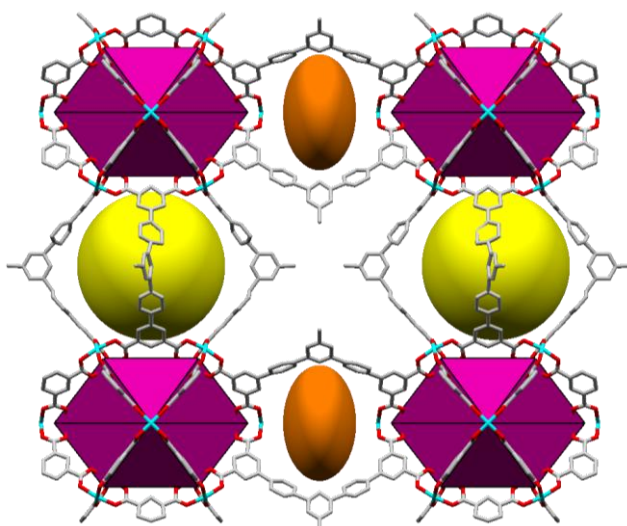


Figure 5.11: Structure of single net of MFM-176 viewed down the *a* axis, showing the two different types of tetragonal cages; cage B3 depicted in orange and cage B3 depicted in yellow.

Cage B3, unique in the MFM-17X series to MFM-176, is capped at both ends by the vertex of a metal-organic cuboctahedron and constructed from four PTOL⁴ ligands which bow outwards to define an oblate spheroid pore with dimensions $8 \times 13 \text{ \AA}$ (Figure 5.12). The ligands are only slightly compressed below the ideal angle of 120° , with the angle between the ligand arms measured to be 115° . The vertices of the capping cuboctahedra intrude into the cage, reducing the available void space and blocking access to cage B3 from cage A, which would usually be accessible through square windows constructed from Cu(II)-paddlewheels.

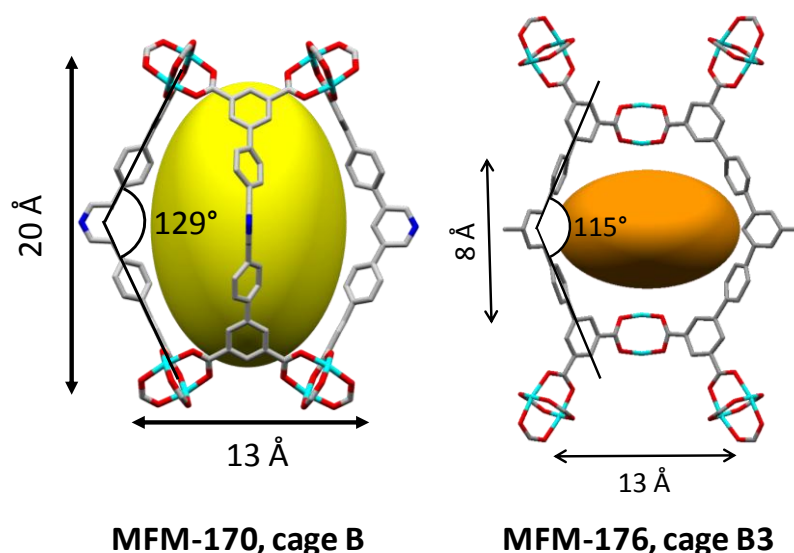


Figure 5.12: Comparison of cage B in MFM-170 to cage B3 in MFM-176.

Cage B1 is isostructural to cage B in MFM-170; capped at both ends by square windows of the metal-organic cuboctahedra and defined by four V-shaped ligands. Cage B1 is slightly shorter and squatter than cage B in MFM-170, with a spherical rather than oblate shaped void space (Figure 5.13). The height of the cage decreases from 20 Å to 17.5 Å (measured between the centres of the square faces) whilst the width increases from 13 Å to 17 Å. The compression of cage B1 leads to a vast reduction in the angle between the two arms of the ligand; with a ligand angle of 107° as opposed to 129° in MFM-170, which is expected to decrease stability.

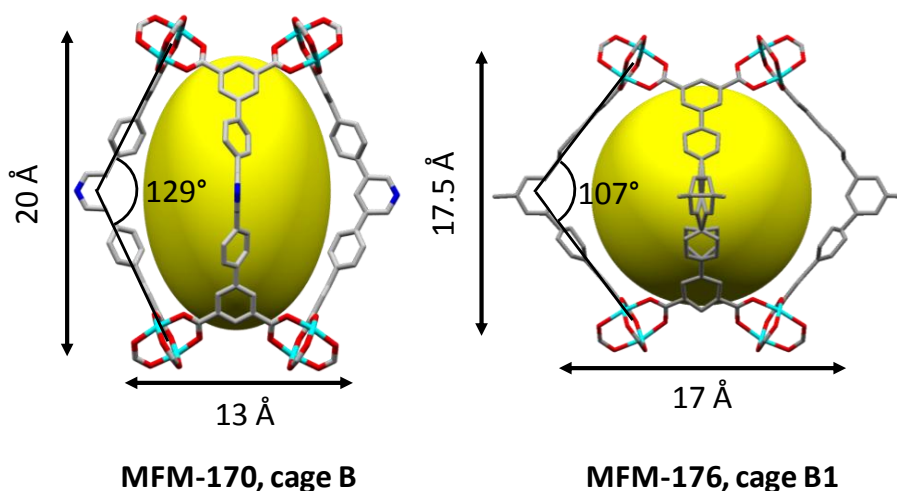


Figure 5.13: Structural comparison of cage B in MFM-170 to cage B1 in MFM-176.

A key difference between MFM-170 and MFM-176 is the orientation of the interpenetrated net within the large square channel. When viewing down the c axis, the ligands defining the edges of cage B in MFM-170 are situated in the corners of the encapsulating square channel, whilst in MFM-176, the edges of cage B1 run up the sides, as highlighted in Figure 5.14.

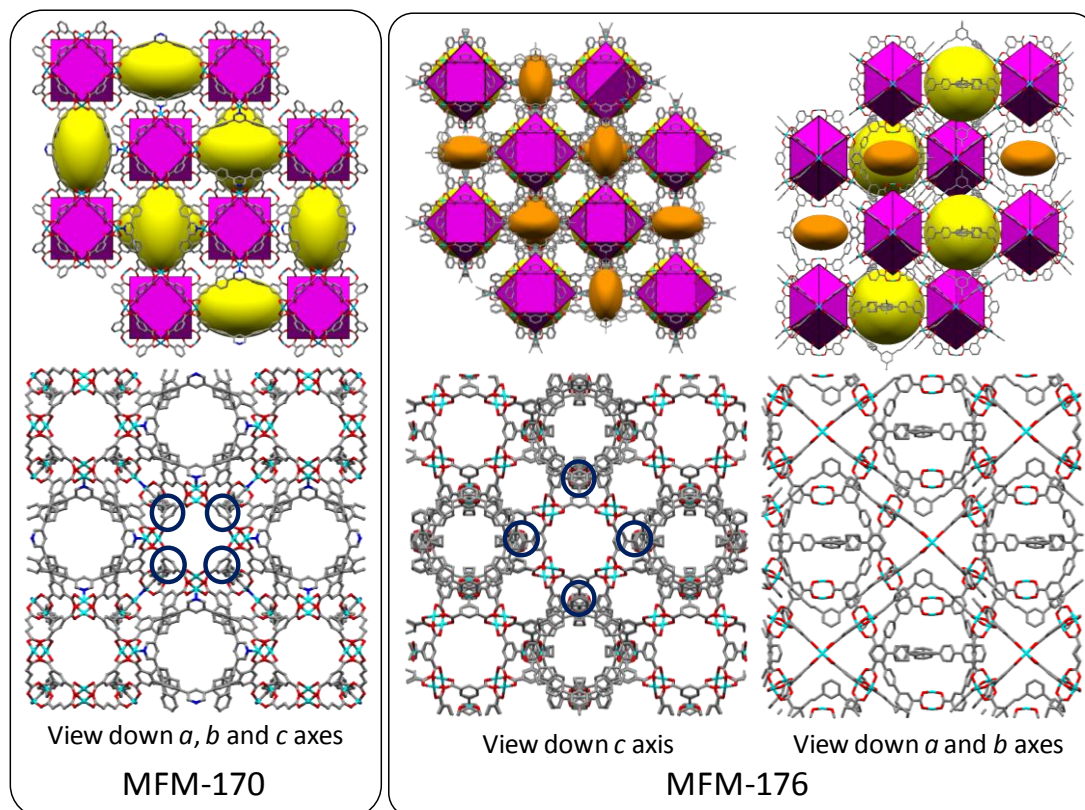


Figure 5.14: Depiction of the channel structures within MFM-170 and MFM-176. In MFM-170, channels are present down all three dimensions. In MFM-176 they are located only along the c axis. This is due to the orientation of the interpenetrating net within the central square channel of the framework; in MFM-170 the pore walls of the interpenetrating cage are located in the corners of the square channel, whereas in MFM-176 the pore walls are located pointing towards the edges of the square channels; pore walls of the interpenetrating net are highlighted with navy circles.

The orientation of the interpenetrating net along the sides of the central square channel in MFM-176 means that the edge of the interpenetrating cage B1 block the pore windows of cage B3 in the ab plane. As access to cage B3 is already restricted at both ends of the cage MFM-176 demonstrates one-dimensional channels down the c axis, as opposed to the three-dimensional porous structure in MFM-170 (Figure 5.15).

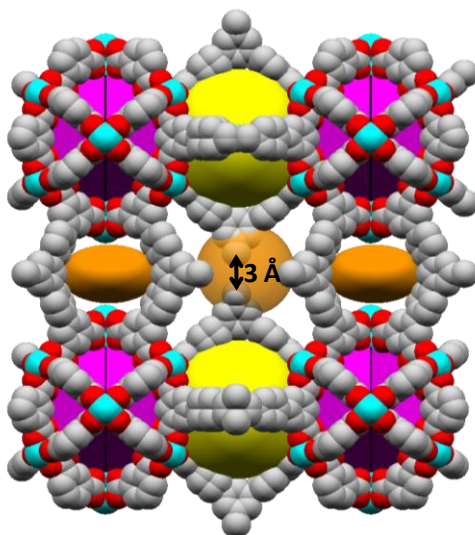


Figure 5.15: Space-filling representation of a single net of MFM-176. The interpenetrating cage B3 is included, defined as a $8 \times 3 \text{ \AA}$ transparent spheroid. It is clear to see how the edges of the yellow cage B1 intrude into the central pore, reducing the accessible void space in the centre to only $3 \text{ \AA}$.

Considering the van der Waals radii of the framework atoms, the distance between two opposite methyl groups is only $3 \text{ \AA}$, suggesting that substitution of the methyl group for a larger functional group would result in sufficient steric encumbrance to prevent interpenetration. During the course of this work this theory was confirmed. Sartor *et al.*³¹ reported the synthesis of UHM-25 (Figure 5.16); a series of non-interpenetrated **ucp** cubic frameworks (topological code for a single **txt** net) comprising V-shaped linkers with bulky amino acid cores. Further extension of H₄PTOL, by inclusion of a larger substituent group should be sufficient to achieve a non-interpenetrated framework.

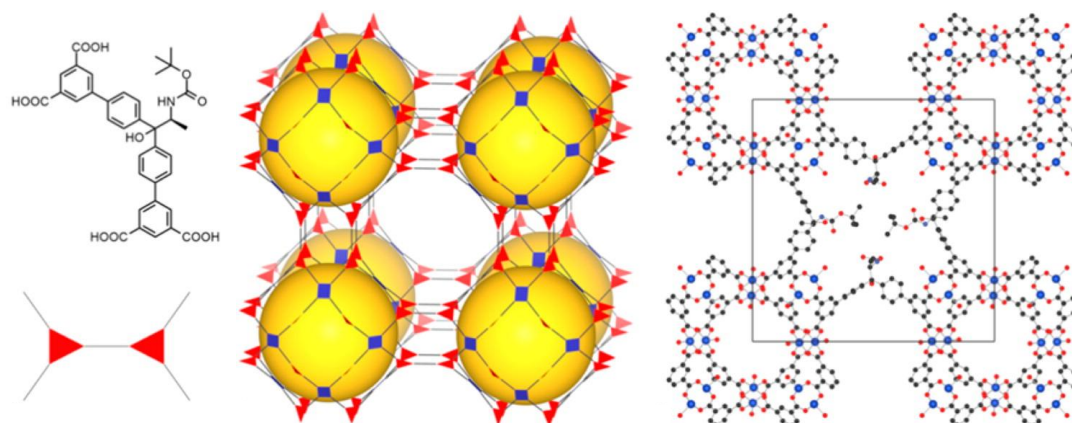


Figure 5.16: Formation of a non-interpenetrated ucp net in UHM-25, synthesised from Cu(II) paddlewheels and bulky V-shaped amino acid containing ligands.

The confinement of CO₂ binding sites within the smallest cage in Chapter 3 suggest that the reduction in the volume of cage B3 and formation of more defined pores rather than channels in MFM-176 is likely to be beneficial for low pressure gas adsorption. The overall porosity of MFM-176, calculated by PLATON,³² is only 51%, compared to 61% for MFM-170 and 56% for [Cu₂EBNZ]²⁸ which is expected to reduce gas uptake capacity at high pressures.

5.3.2.2.1 Bulk Sample Properties of MFM-176

Bulk purity of MFM-176 was confirmed by PXRD, with a Pawley Refinement (Figure 5.17). confirming unit cell of $a = 33.345851 \text{ \AA}$, $c = 31.864058 \text{ \AA}$.

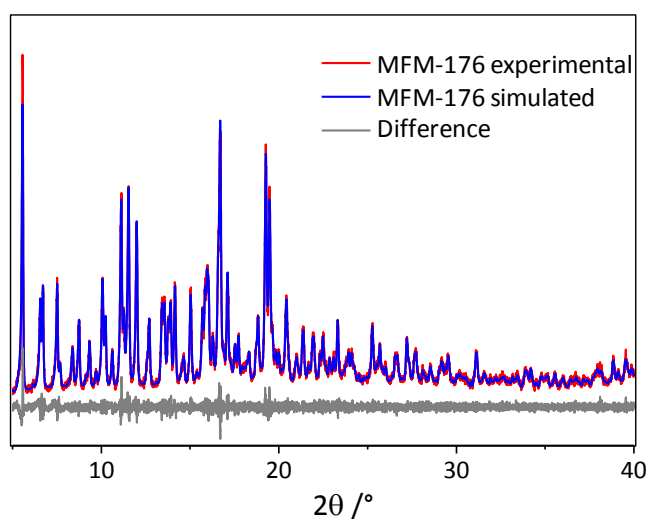


Figure 5.17: PXRD pattern of an as-synthesised sample of MFM-176 and Pawley Refinement to single crystal values. $a = 33.345851 \text{ \AA}$ $c = 31.864058 \text{ \AA}$ $GOF = 1.33$.

5.3.2.3 Stability of MFM-176

The as synthesised sample of MFM-176 was solvent exchanged by soaking in a regularly refreshed acetone solution for five days. Activation was carried out by heating the acetone-exchanged sample under a dynamic vacuum at 100 °C overnight, resulting in the formation of a dark blue powder. PXRD analysis demonstrates that MFM-176 retains stability to the activation process and that the framework does not collapse, as seen in MFM-175 (Figure 5.18).

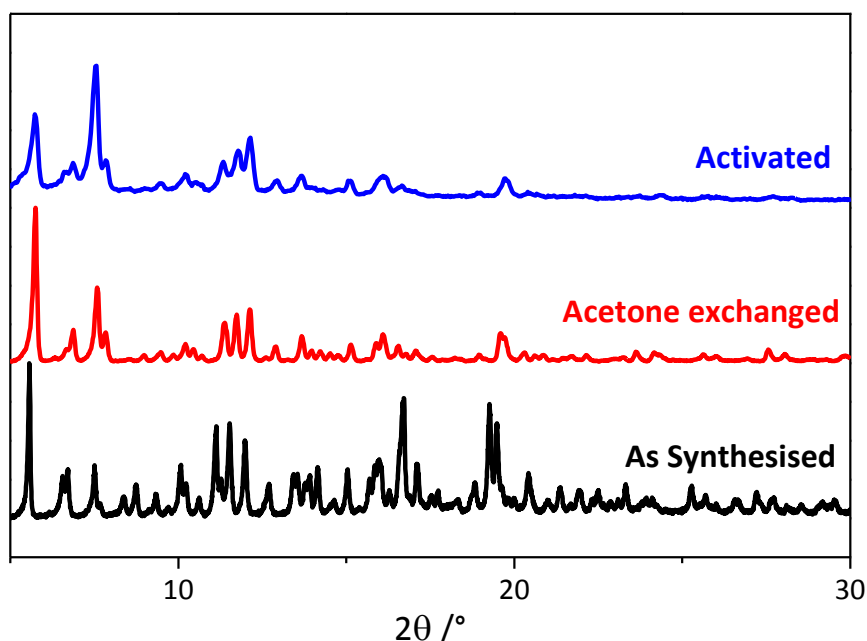


Figure 5.18: PXRD analysis of MFM-176 throughout the activation procedure. From bottom to top: as-synthesised sample (black), acetone exchanged sample (red), sample activated by heating to 100 °C under a dynamic vacuum (blue).

Thermogravimetric analysis of MFM-170 demonstrates high thermal stability, with decomposition taking place at 320 °C, compared to 350 °C in MFM-170 (Figure 5.19). Although the structure does not contain a Cu(II)-N bonded self-interpenetrated motif, the presence of an interpenetrated framework still provides stability to MFM-176.

In the as-synthesised framework an initial mass loss of 32% (25 °C – 300°C) corresponds to the loss of one DEF molecule and one H₂O molecule per formula unit within the pores, followed by the removal of two coordinating DEF molecules from either end of the Cu(II) paddlewheel. A decomposition mass loss of 46 wt% matches the loss of one molecule of

PPYD⁴, leaving a final mass relating to 2CuO. The acetone exchanged framework demonstrated an initial mass loss of 10% for acetone within the pores (25 °C – 100 °C), followed by a 9% loss corresponding to bound acetone and water (100 °C – 220 °C), and finally a mass loss of 62% upon decomposition, corresponding to the loss of one ligand molecule.

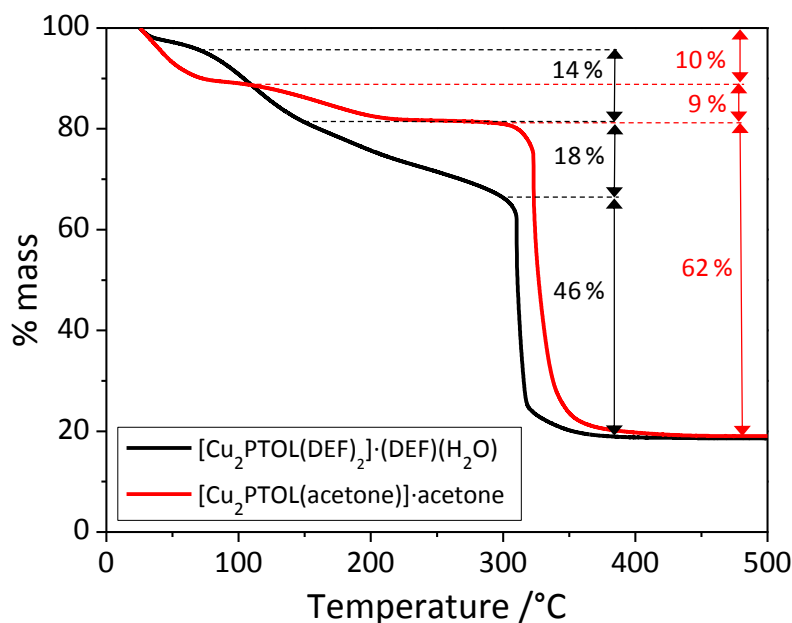


Figure 5.19: TGA analysis of as-synthesised and acetone exchanged samples of MFM-176

5.3.3 Gas Adsorption in MFM-176

5.3.3.1 BET Surface Area and Pore Size Distribution

The porosity of MFM-176 was confirmed by N₂ adsorption at 77 K, showing a fully reversible type I isotherm (Figure 5.20). The BET surface area was calculated to be 1486 m² g⁻¹. As expected, MFM-176 demonstrates a lower surface area than MFM-170 (2408 m² g⁻¹) due to the formation of a two-fold rather than self-interpenetrated framework. The surface area of MFM-176 is also lower than that of the isostructural counterpart [Cu₂EBNZ] (1840 m² g⁻¹) as ethyne groups have a greater surface area per unit mass than phenyl rings and is expected to result in lower adsorption uptake capacities for all gases.

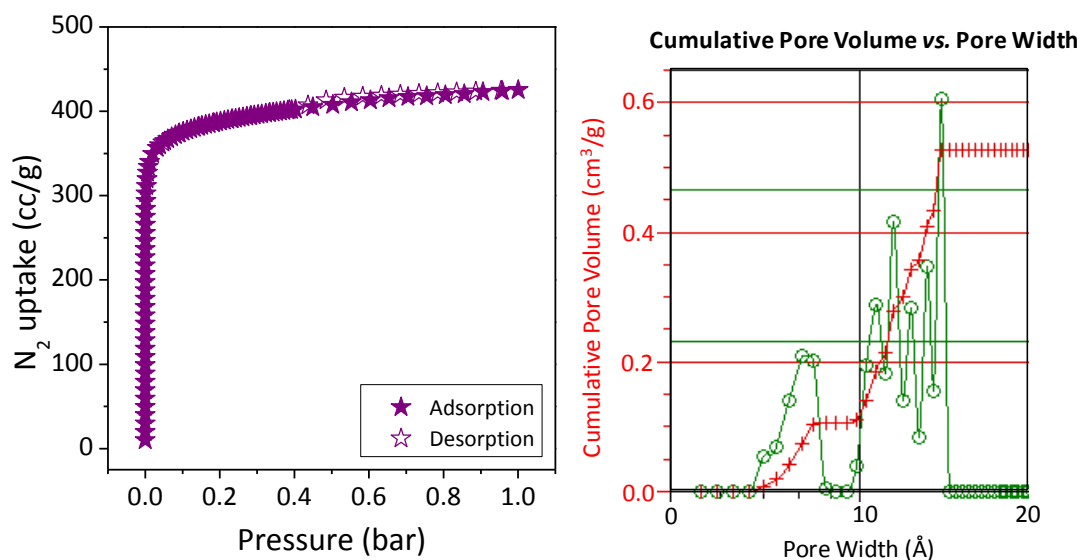


Figure 5.20: N_2 iostherm of MFM-176 at 77 K and pore size distribution calculated via DFT modelling of cylindrical pores on an oxide surface using the N_2 isotherm.

The pore size distribution of MFM-176 (Figure 5.20) reflects the large variation void spaces within the framework and the measured pore volume of $0.54 \text{ cm}^3 \text{ g}^{-1}$ is comparable to the calculated value of $0.52 \text{ cm}^3 \text{ g}^{-1}$, determined via PLATON. The pore volume of MFM-176 is lower than MFM-170 ($0.87 \text{ cm}^3 \text{ g}^{-1}$), which is expected to lead to lower uptake capacities at higher pressures.

5.3.3.2 CO_2 Adsorption in MFM-176

As predicted, the effect of low porosity on CO_2 adsorption in MFM-176 becomes apparent at higher pressures (Figure 5.21). At 20 bar, MFM-176 adsorbs only 78.75 wt% ($401 \text{ cm}^3 \text{ g}^{-1}$) of CO_2 at 273 K compared to 94.95 wt% in MFM-170. The 20 bar uptake capacity of CO_2 in MFM-176 corresponds to 83% of the total CO_2 adsorbed in MFM-170, consistent with the reduction in porosity from $0.87 \text{ cm}^3 \text{ g}^{-1} - 0.52 \text{ cm}^3 \text{ g}^{-1}$ (83%).

At 1 bar, MFM-176 adsorbs 26.56 wt% ($135 \text{ cm}^3 \text{ g}^{-1}$) of CO_2 at 273 K and 14.86 wt% ($76 \text{ cm}^3 \text{ g}^{-1}$) at 298 K. The adsorption capacity of MFM-176 at 1 bar and 298 K is higher than that measured for MFM-170 under the same conditions (Table 5.2) indicating stronger

interactions with the framework surface. This is likely to be due to the existence of twice as many open metal sites within the unit cell owing to the lack of Cu(II)-N bond.

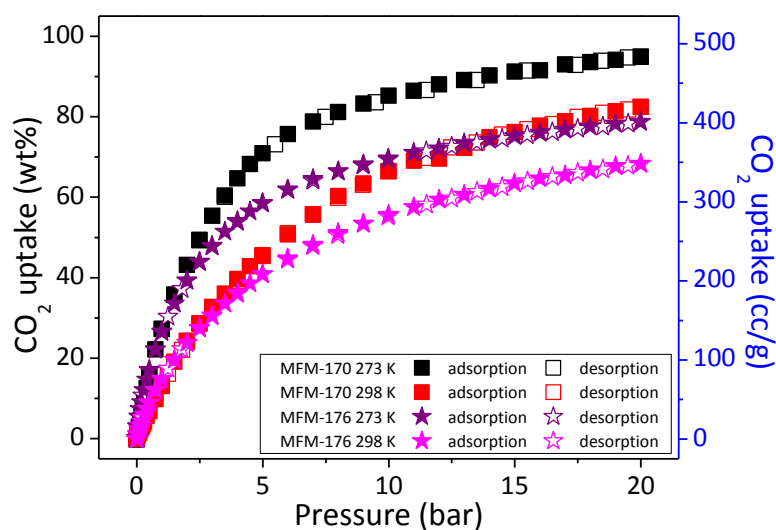


Figure 5.21: Gravimetric isotherms of carbon dioxide adsorption in MFM-176 up to 20 bar at 273 K and 298 K, with comparison to MFM-170. The calculated volumetric uptake is shown for reference.

Comparing MFM-176 to the isostructural framework [Cu₂EBNZ], Liu *et al.* report a saturation capacity for CO₂ of 725 g/L ($\sim 420 \text{ cm}^3 \text{ g}^{-1}$) at 1 bar, 195 K. Extrapolation of the Langmuir fitting curves indicates a CO₂ saturation capacity in MFM-176 of $21.11 \text{ mmol g}^{-1}$, corresponding to $470 \text{ cm}^3 \text{ g}^{-1}$. This slight increase in saturation capacity is surprising considering the decrease in fractional void volume (51% for MFM-176 *c.f.* 56% for [Cu₂EBNZ]) and is indicative of stronger framework-adsorbate interactions. At 298 K and 40 bar, Liu *et al.* report a CO₂ adsorption capacity of 148 v/v ($\sim 295 \text{ cm}^3 \text{ g}^{-1}$), in [Cu₂EBNZ], distinctly less than the $348 \text{ cm}^3 \text{ g}^{-1}$ measured in MFM-176 at the same temperature and half the pressure (20 bar). The improved uptake of MFM-176 compared to [Cu₂EBNZ] at 298 K can be attributed to the electron donating properties of the tolyl group, which strengthens the interaction between CO₂ and the π -electron cloud (binding site IV in Chapter 3).

The heat of adsorption in MFM-176 (-28 kJ mol^{-1}) is higher than that calculated for MFM-170 (-18 kJ mol^{-1}), indicative of stronger interactions between CO₂ and the framework, attributed to a doubling of open metal sites. Unfortunately no Q_{st} value is reported for

[Cu₂EBNZ] to compare the effect of the additional methyl substituent. The higher Q_{st} value at low loading is expected to lead to an improved selectivity for CO₂/N₂ and CO₂/CH₄.

Table 5.2: Summary of CO₂ adsorption data for MFM-176 and comparison to MFM-170.

	MOF	CO ₂ Adsorption, 273 K	CO ₂ Adsorption, 298 K	Q_{st} (kJ mol ⁻¹)
20	MFM-170	94.95 wt% (483.58 cm ³ g ⁻¹)	82.50 wt% (420.17 cm ³ g ⁻¹)	-18
bar	MFM-176	78.75 wt% (401.08 cm ³ g ⁻¹)	68.32 wt% (347.96 cm ³ g ⁻¹)	-28
1	MFM-170	27.34 wt%, (139 cm ³ g ⁻¹)	13.25 wt% (67 cm ³ g ⁻¹)	
bar	MFM-176	26.56 wt% (135 cm ³ g ⁻¹)	14.86 wt% (76 cm ³ g ⁻¹)	

The IAST selectivity value for a 0.15:0.85 mixture of CO₂/N₂ in MFM-176 at ambient pressure was calculated from single component isotherms to be 21.2 at 273 K and 14.1 at 298 K (Figure 5.22). Although demonstrating lower total uptake, MFM-176 displays the highest selectivity for CO₂ over N₂ from all the frameworks in the MFM-17X series. (MFM-170: 11.5, MFM-171: 11.9, MFM-172: 13.0) The high selectivity is attributable to an increased density of accessible open metal sites from breaking the axial Cu(II)-N bond, in addition to effects of the electron donating tolyl group increasing the electron density surrounding the central phenyl ring.

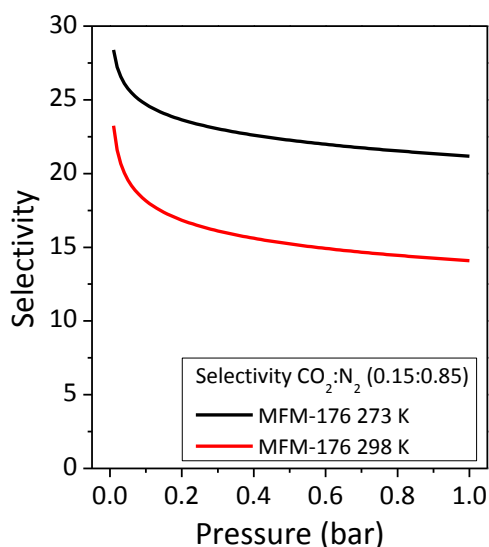


Figure 5.22: Selectivity values for the post-combustion capture of CO₂ from N₂ at 273 and 298 K in a 0.15:0.85 mixture of CO₂:N₂.

5.3.3.3 Methane Adsorption in MFM-176

The CH₄ adsorption capacity of MFM-176 at 20 bar (Figure 5.23) was measured to be 16.79 wt% (235 cm³ g⁻¹) at 273 K and 13.66 wt% (191 cm³ g⁻¹) at 298 K. MFM-176 demonstrates superior high pressure, room-temperature adsorption of CH₄ compared to [Cu₂EBNZ]: Liu *et al.* report a CH₄ uptake capacity of 148 v/v (~165 cm³ g⁻¹) at 298 K and 50 bar, whereas MFM-176 adsorbs 191 cm³ g⁻¹ at the lower pressure of 20 bar. The CH₄ uptake capacities of MFM-176 are lower than MFM-170 across the entire pressure range (Table 5.3), in line with the decrease in porosity of the framework.

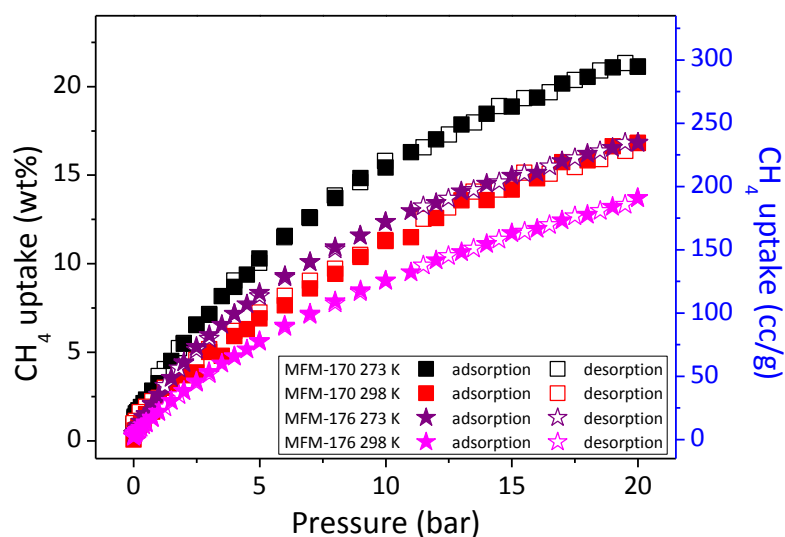


Figure 5.23: Gravimetric isotherms of carbon dioxide adsorption in MFM-176 up to 20 bar at 273 K and 298 K. The calculated volumetric uptake is shown for reference.

The isosteric heat of adsorption of CH₄ in MFM-176 was calculated to be -17 kJ mol⁻¹. Not only is this higher than MFM-170 (Table 5.3), attributed to increased interactions in smaller pores, this matches some of the highest performing MOFs for CH₄ adsorption; -14.5 kJ mol⁻¹ for NOTT-125,³³ -17.0 for HKUST-1,³⁴ and -21.4 for Ni-MOF-74.³⁴

Table 5.3: Summary of CH₄ adsorption data for MFM-176 and comparison to MFM-170.

MOF	CH ₄ Adsorption, 273 K	CH ₄ Adsorption, 298 K	Q _{st} (kJ mol ⁻¹)
MFM-170	21.10 wt% (294.79 cm ³ g ⁻¹)	16.78 wt% (234.47 cm ³ g ⁻¹)	-11 kJ mol ⁻¹
MFM-176	16.79 wt% (234.63 cm ³ g ⁻¹)	13.66 wt% (190.84 cm ³ g ⁻¹)	-17 kJ mol ⁻¹

The high CO₂ uptake in MFM-176 results in high selectivity for CO₂ over CH₄ (Figure 5.24), with ambient pressure IAST selectivity values of 6.4 at 273 K and 4.6 at 298 K. Again, MFM-176 outperforms MFM-170, 171 and 172 in this area, achieving above-average values for CO₂:CH₄ selectivity (values usually lie in the range of 4-5).³⁵

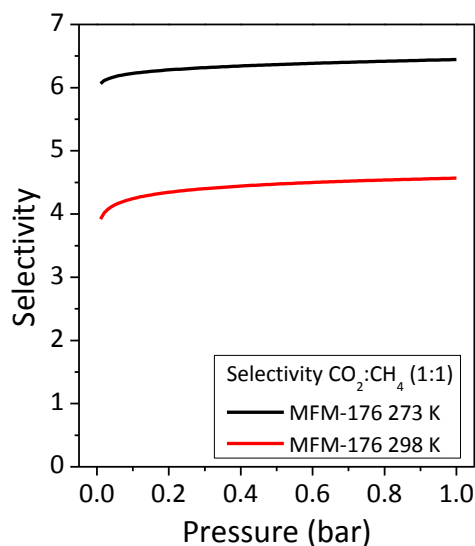


Figure 5.24: Selectivity values for the post-combustion capture of CO₂ from CH₄ at 273 and 298 K in a 1:1 mixture of CO₂:CH₄.

5.3.3.4 Hydrocarbon adsorption in MFM-176

The adsorption capacities of C₂H₄ and C₂H₆ in MFM-176 were measured at ambient pressure (Figure 5.25). At 298 K MFM-176 adsorbs equimolar volumes of ethylene and ethane (92 cm³ g⁻¹, 4.1 mmol g⁻¹), indicating that there are no strong preferential interactions between the C₂ hydrocarbons and the surface of MFM-176. The total uptake capacities for the C₂ hydrocarbons in MFM-176 are lower than those measured in MFM-170 (Table 5.4 and Table 5.5), reflecting the reduction in accessible void space and smaller cage windows which can hinder diffusion of these bulkier gases.

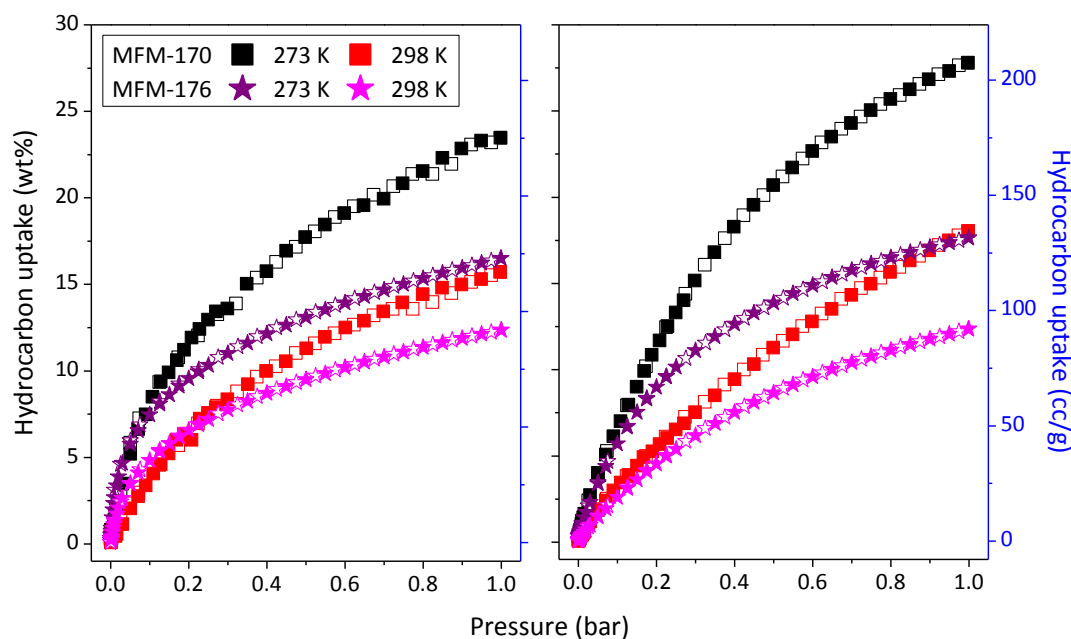


Figure 5.25: Gravimetric isotherms of ethylene and ethane adsorption in MFM-176 up to 20 bar at 273 K and 298 K. The calculated volumetric uptake is shown for reference.

The Isothermic heats of adsorption for the C_2 hydrocarbons are slightly lower in MFM-176 than in MFM-170 (Table 5.4 and Table 5.5), attributed to restricted access to cage B3 in MFM-176 as the bulkier ethylene and ethane gases can only migrate along channels in one dimension.

Table 5.4: Summary of C_2H_4 adsorption data for MFM-176 and comparison to MFM-170.

MOF	C_2H_4 273 K	C_2H_4 298 K	Q_{st}
MFM-170	23.50 wt% (175.16 cc/g)	15.71 wt% (117.07 cc/g)	-29 kJ mol ⁻¹
MFM-176	15.39 wt% (122.96 cc/g)	11.51 wt% (91.94 cc/g)	-27 kJ mol ⁻¹

Table 5.5: Summary of C_2H_6 adsorption data for MFM-176 and comparison to MFM-170.

MOF	C_2H_6 273 K	C_2H_6 298 K	Q_{st}
MFM-170	27.84 wt% (154.17 cc/g)	18.04 wt% (134.47 cc/g)	-36 kJ mol ⁻¹
MFM-176	17.64 wt% (131.48 cc/g)	12.34 wt% (91.97 cc/g)	-34 kJ mol ⁻¹

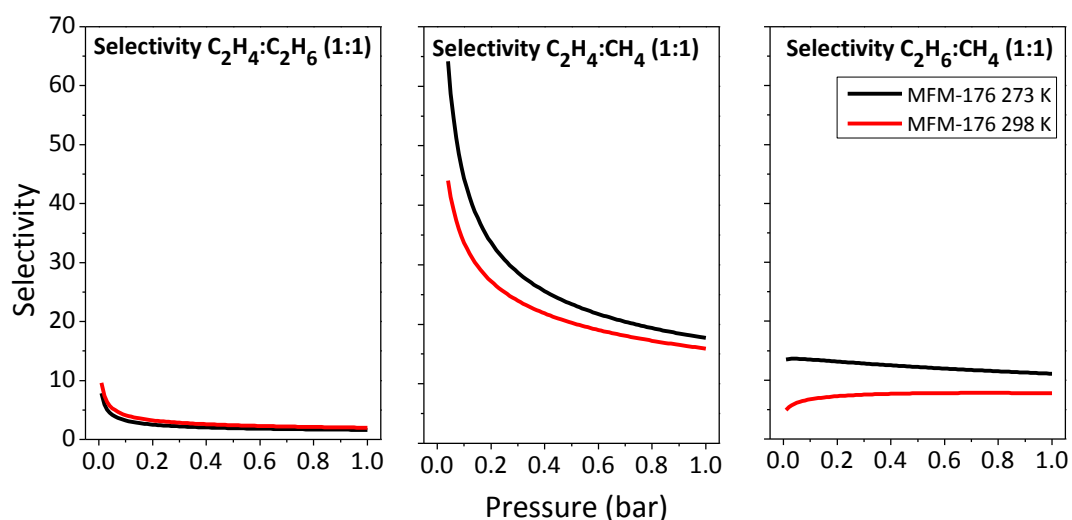


Figure 5.26: Selectivity values for the separation of equimolar mixtures of hydrocarbon gases in MFM-176 at 273 and 298 K; ethene from ethane, ethene from methane and ethane from methane.

MFM-176 shows a slight selectivity for ethene over ethane at 1 bar, with IAST selectivity parameters calculated as 1.6 at 273 K and 2.0 at 298 K for a 1:1 mixture (Figure 5.26). This is surprising considering the identical adsorption capacities for both gases at 298 K (4.1 mmol g⁻¹); however can be attributed to the differing adsorption profiles for both gases. Adsorption of ethene in MFM-176 at 298 K follows a steeper adsorption curve at low pressures, indicating that the adsorption of ethene is more kinetically favoured due to its smaller size, whilst the adsorption of ethane is more thermodynamically favoured, as evidenced by the higher heat of adsorption.

MFM-176 selectively adsorbs both C₂ hydrocarbons over methane; with C₂H₄ showing a superior selectivity value of 17.7 in comparison to 11.1 for C₂H₆ at 273 K. These selectivity values fall within the range calculated for the MFM-17X series (Table 5.6). The high selectivities for MFM-172 and MFM-176, both of which contain electron donating methyl substituents, indicates that the primary interaction between adsorbed C₂ hydrocarbons and the framework surface is between the hydrocarbon C-H groups and the π -electron cloud surrounding the framework aromatic rings.

Table 5.6: Selectivity values for adsorption of the C₂ hydrocarbons in the MFM-17X series at 273 K.

	MFM-170	MFM-171	MFM-172	MFM-175	MFM-176
C ₂ H ₄ :C ₂ H ₆	1.0	0.9	1.0	1.2	1.6
C ₂ H ₄ :CH ₄	11.5	11.2	16.0	16.9	17.7
C ₂ H ₆ :CH ₄	9.9	11.8	15.7	14.8	11.1

5.4 Conclusions

This chapter outlines the different strategies taken with the aim of synthesising a non-interpenetrated framework of MFM-170. The first involved protection of the pyridyl nitrogen in H₄PPYD to give a pyridine-N-oxide functionalised ligand, H₄PPNO. Despite many attempts, synthesis of a MOF from Cu(II) salts and H₄PPNO was unsuccessful. This was attributed to the coordination of the O⁻ to the metal ions, resulting in a highly disordered, non-crystalline structure. To remove this coordinating feature and investigate the effect that the additional steric bulk of H₄PPNO would have on the framework structure, a second ligand with a tolyl rather than pyridyl core, H₄PTOL, was synthesised. Reaction of H₄PTOL with Cu(II) resulted in the successful formation of a metal organic framework, designated MFM-176.

MFM-176 forms a two-fold interpenetrated framework of **zmj** topology, isostructural to [Cu₂EBNZ] reported by Liu *et al.* The framework is similar to MFM-170, comprising metal-organic cuboctahedra connected by tetragonal cages constructed from four V-shaped ligand molecules. Rotation of the cuboctahedral cage A by 45° around the *c* axis results in the formation of two types of tetragonal cages; the smaller of which is located in the *ab* plane, whilst the second runs along the *c* axis. Access to the smaller of the two cages is restricted in two dimensions by the interpenetrating framework, which encroaches through the windows on both sides of cage B3, leaving only a 3 Å space in the centre of the cage for guest molecules. The close proximity of these two ligands suggests that a further increase in steric bulk in this position would be successful in generating a single-net structure, a tactic that was proven successful by Sartor *et al.*³⁶

Analysis of the 20 bar isotherms of MFM-176 shows a reduction the uptake capacities of all gases compared to MFM-170, attributed to a reduction in the pore volume and restricted access to cage B3. An increase in the CO₂ and CH₄ Q_{st} values is attributed to the liberation of Cu(II) open metal sites and an increase in the electron density surrounding the central phenyl ring, due to the electron donating methyl group, which in turn increases the selectivity for CO₂/N₂ and CO₂/CH₄. If the high enthalpy of adsorption was combined with a greater pore volume, MFM-176 would have the potential to reach and exceed the CO₂ selectivities of common high-performing MOFs.

5.5 Outlook

Sartor *et al.* proved that adding bulky aliphatic groups to the apical position of a V-shaped ligand can be sufficient to prevent formation of the doubly-interpenetrated **zmj** framework, giving a non-catenated cubic net with **ucp** topology. With this in mind, MFM-170 could be extended with a bulky alkyl chain to prevent interpenetration, whilst incorporation of a boc-protected amine group or heterocyclic rings would retain the number of CO₂ binding sites within the void upon deprotection. (Figure 5.27).

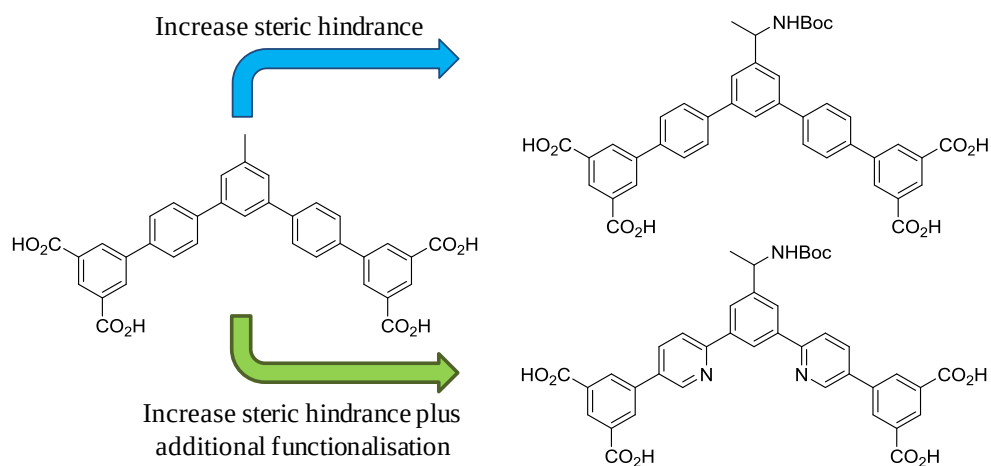
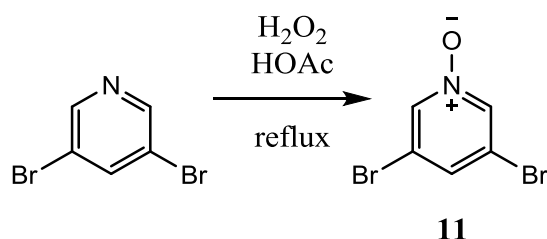


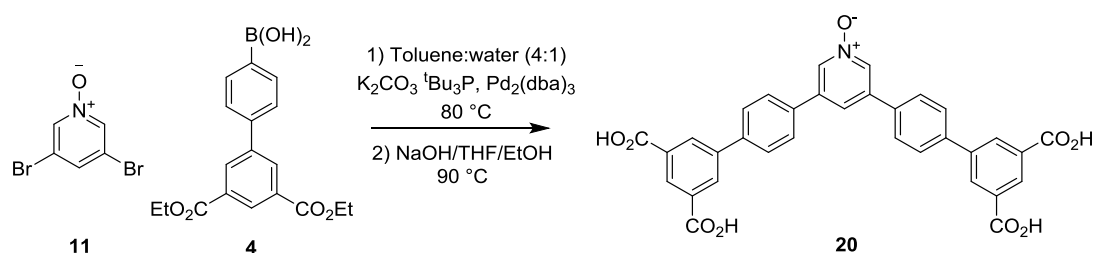
Figure 5.27: Strategies proposed to remove the two-fold interpenetrated net from MFM-176 in order to utilise the high heats of adsorption generated from the liberation of the Cu(II)-paddlewheel axial sites.

5.6 Experimental

Synthesis of H₄PPNO



3,5-Dibromopyridine (0.84 g, 3.56 mmol) was dissolved in glacial acetic acid (16.8 ml). H₂O₂ (2.5 ml, 30 % in H₂O, 24 mmol) was added drop wise and the solution heated to reflux overnight. Excess H₂O₂ was quenched with activated carbon (0.5 g) and the solution was filtered through Celite. The solvent was removed *in vacuo* and the product recrystallized from hot DCM with MeOH to give a white solid. (0.79 g, 88 %). ¹H NMR (270 MHz, CDCl₃) δ ppm 7.58 (1 H, t, *J* = 1.5 Hz), 8.28 (2 H, d, *J* = 1.5 Hz); ¹³C NMR (100 MHz, CDCl₃) δ ppm 140.0, 131.7, 120.6; IR (ATR) cm⁻¹: 3042 (C-H), 1248 (N⁺-O⁻). MS (ESI) *m/z*: 251.866 [M+H]⁺. Elemental analysis (%): crude: C 23.67, H 1.07, N, 4.99, calculated for C₅H₃NOBr₂: C 23.75, H 1.20, N 5.54.

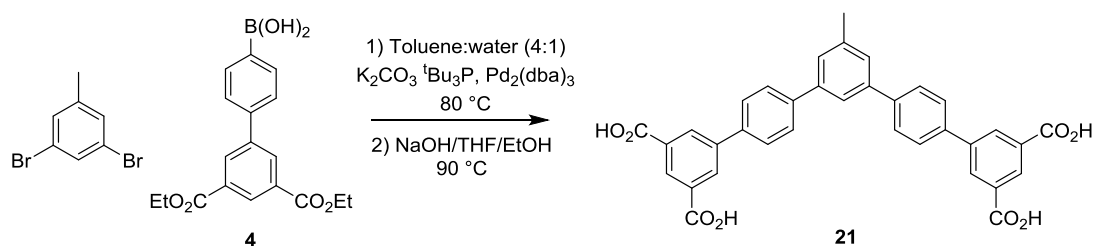


4 (2.00 g, 5.85 mmol), **11** (0.59 g, 2.34 mmol) and K₂CO₃ (1.94 g, 14.04 mmol) were dissolved in a mixture of toluene/water (90 ml 4:1 v/v) and degassed under argon at 60 °C for 1 hour. Tritertbutylphosphine (1 M solution in toluene, 0.70 ml, 0.70 mmol) and [Pd₂(dba)₃] (0.21 g, 0.23 mmol) were added, the reaction heated to 80 °C and followed by TLC. The product was extracted into DCM, was removed *in vacuo* before being recrystallised from DCM with MeOH to give a white product (1.16 g, 72 % yield). ¹H NMR (270 MHz, CDCl₃) δ ppm 1.43 (12 H, q, *J* = 7.2 Hz), 4.44 (8 H, q, *J* = 7.2 Hz), 7.73 (5 H,

m), 7.83 (4 H, m), 8.49 (4 H, m), 8.51 (2 H, m), 8.68 (2 H, t, $J = 1.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 165.7, 140.6, 140.4, 139.6, 136.1, 135.0, 132.2, 131.8, 129.8, 128.3, 127.7, 123.4, 61.6, 14.4; IR (ATR) cm^{-1} : 1720 (C=O), 1238 (N⁺-O⁻); MS (ESI) m/z : 688.253 $[\text{M}+\text{H}]^+$. Elemental analysis (%): crude: C 66.63, H 5.51, N 1.80, calculated for $\text{C}_{41}\text{H}_{37}\text{NO}_9$: C 71.60, H 5.42, N 2.04.

The product (0.30 g, 0.44 mmol) and potassium trimethylsilanolate (0.27 g, 2.09 mmol) were suspended in dry THF (50 ml) and stirred at room temperature until completion, determined by TLC. The solvent was removed *in vacuo* before water (150 ml) was added. The brown product was precipitated with HCl, isolated by filtration and washed with copious amounts of water (0.21 g, 85 % yield). ^1H NMR (270 MHz, CDCl_3) δ ppm 7.90 (4 H, m), 8.03 (4 H, m), 8.46 (4 H, d, $J = 1.4$ Hz), 8.51 (2 H, t, $J = 1.4$ Hz), 8.64 (2 H, m); ^{13}C NMR: 166.4, 140.2, 139.1, 138.5, 135.3, 134.7, 133.3, 132.2, 131.3, 129.1, 128.1, 127.6. IR (ATR) cm^{-1} : 1708 (C=O), 1237 (N⁺-O⁻); MS: (ESI) m/z 574.115 $[\text{M}-\text{H}]^-$. Elemental analysis (%): crude: C 67.56, H 4.25, N 2.14, calculated for $\text{C}_{33}\text{H}_{21}\text{NO}_9$: C 68.87, H 3.68, N 2.43.

Synthesis of H₄PTOL



4 (0.75 g, 2.19 mmol), 3,5-dibromotoluene (0.22 g, 0.88 mmol) and K_2CO_3 (0.61 g, 4.39 mmol) were dissolved in a mixture of toluene/water (35 ml 4:1 v/v) and degassed under argon at 60 °C for 1 hour. Triterbutylphosphine (1 M solution in toluene, 0.13 ml, 0.13 mmol) and $[\text{Pd}_2(\text{dba})_3]$ (0.04 g, 0.04 mmol) were added and the reaction heated to 80 °C. The product was extracted into DCM, the solvent removed *in vacuo* before being recrystallised from DCM with MeOH to give a white product (0.58 g, 97 % yield). ^1H NMR (270 MHz, CDCl_3) δ ppm 1.43 (12 H, t, $J = 7.2$ Hz), 2.52 (3 H, s), 4.45 (8 H, q, $J = 7.2$ Hz),

7.47 (2 H, d, $J = 0.8$ Hz), 7.70 (1 H, s), 7.77 (8 H, s), 8.51 (4 H, d, $J = 1.6$ Hz), 8.66 (2 H, t, $J = 1.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 165.9, 141.4, 141.2, 141.1, 139.2, 138.2, 132.1, 131.6, 129.3, 127.9, 127.6, 127.2, 123.3, 61.5, 14.4; IR (ATR) cm^{-1} : 1714 (C=O); MS: (ESI) m/z : 699.293 $[\text{M}+\text{H}]^+$ Elemental analysis (%): crude: C 75.20, H 5.84, calculated for $\text{C}_{43}\text{H}_{40}\text{O}_8$: C 75.42, H 5.89.

The product (0.70 g, 1.02 mmol) was suspended in NaOH (2M, 60 ml), THF (30 ml) and EtOH (30 ml) and refluxed at 90 °C overnight. The product was precipitated from the aqueous layer with HCl (5 ml), isolated by filtration and allowed to dry in air (0.51 g, 87 % yield). ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ ppm 2.08 (3 H, s), 7.81-7.90 (5 H, m), 7.91-7.98 (4 H, m), 8.45 (4 H, d, $J = 1.5$ Hz), 8.48 (2 H, t, $J = 1.5$ Hz) ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ ppm 167.1, 141.1, 140.7, 140.6, 139.6, 138.0, 132.8, 131.7, 128.3, 128.0, 127.4, 122.9, 21.8; IR (ATR) cm^{-1} : 1693 (C=O), 3029, (O-H); MS (ESI) m/z : 571.130 $[\text{M}-\text{H}]^-$. Elemental analysis (%): crude: C 72.92, H 4.17, calculated for $\text{C}_{35}\text{H}_{24}\text{O}_8$: C 73.42, H 4.22.

Synthesis of MFM-176

CuCl_2 (14.1 mg, 0.105 mmol) and **21** (10 mg, 0.018 mmol) were added to DEF (1.5 ml), EtOH (0.5 ml) and HCl (0.1 M, 1 ml) and heated to 80 °C in Wheaton vials over 22 hours. IR (ATR) cm^{-1} : 3365 (O-H), 1698 (C=O). Elemental analysis (%): crude: C 49.60, H 3.53, calculated for $[\text{Cu}_2\text{PTOL}(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})_7$: C 49.01 H 4.47.

5.7 References

- 1 F. Song, C. Wang, J. M. Falkowski, L. Ma and W. Lin, *J. Am. Chem. Soc.*, 2010, **132**, 15390–15391.
- 2 H. Jiang, T. A. Makal and H. Zhou, *Coord. Chem. Rev.*, 2013, **257**, 2232–2249.
- 3 J. Duan, J. Bai, B. Zheng, Y. Li and W. Ren, *Chem. Commun.*, 2011, **47**, 2556–2558.
- 4 J. Zhang, L. Wojtas, R. W. Larsen, M. Eddaoudi and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2009, **131**, 17040–17041.
- 5 H.-L. Jiang, Y. Tatsu, Z.-H. Lu and Q. Xu, *J. Am. Chem. Soc.*, 2010, **132**, 5586–5587.
- 6 G. Chang, B. Li, H. Wang, T. Hu, Z. Bao and B. Chen, *Chem. Commun.*, 2016, **52**, 3494–3496.
- 7 S. Ma, D. Sun, M. Ambrogio, J. A. Fillinger and S. Parkin, *J. Am. Chem. Soc.*, 2007, **129**, 1858–1859.
- 8 O. Shekhah, H. Wang, M. Paradinas, C. Ocal, B. Schüpbach, A. Terfort, D. Zacher, R. A. Fischer and C. Wöll, *Nat. Mater.*, 2009, **8**, 481–484.

- 9 A. Ferguson, L. Liu, S. J. Tapperwijn, D. Perl, F. Coudert, S. Van Cleuvenbergen, T. Verbiest, M. A. Van Der Veen and S. G. Telfer, *Nat. Chem.*, 2016, **8**, 250–257.
- 10 S. Yang, X. Lin, W. Lewis, M. Suyetin, E. Bichoutskaia, J. E. Parker, C. C. Tang, D. R. Allan, P. J. Rizkallah, P. Hubberstey, N. R. Champness, K. M. Thomas, A. J. Blake and M. Schröder, *Nat. Mater.*, 2012, **11**, 710–16.
- 11 S. Freye, R. Michel, D. Stalke, M. Pawliczek, H. Frauendorf and G. H. Clever, *J. Am. Chem. Soc.*, 2013, **135**, 8476–8479.
- 12 C. Hua, B. F. Abrahams and D. M. D. Alessandro, *Cryst. Growth Des.*, 2016, **16**, 1149–1155.
- 13 J. M. Roberts, O. K. Farha, A. A. Sarjeant, J. T. Hupp and K. A. Scheidt, *Cryst. Growth Des.*, 2011, **11**, 4747–4750.
- 14 J. Liu, Y. Hong, Y. Guan, M. Lin, C. Huang and W. Dai, *Dalton Trans.*, 2015, **44**, 653–658.
- 15 X. Fang, X. Yuan, Y. B. Song, J. D. Wang and M. J. Lin, *CrystEngComm*, 2014, **16**, 9090–9095.
- 16 D. J. Lun, I. N. Waterhouse and S. G. Telfer, *J. Am. Chem. Soc.*, 2011, **133**, 5806–5809.
- 17 T. G. Bonner and P. McNamara, *J. Chem. Soc. B*, 1968, 795–797.
- 18 L. Zhang, D. Xu, Y. Zhou and F. Jiang, *New J. Chem.*, 2010, **34**, 2470–2478.
- 19 A. S. Munn, G. J. Clarkson, F. Millange, Y. Dumont and R. I. Walton, *CrystEngComm*, 2013, **15**, 9679–9687.
- 20 L. Wen, D. Dang, C. Duan, Y. Li, Z. Tian and Q. Meng, *Inorg. Chem.*, 2005, **44**, 7161–7170.
- 21 L. Wen, Z. Tian, J. Lin, H. Zhu and Q. Meng, *Zeitschrift für Anorg. und Allg. Chemie*, 2006, **632**, 689–694.
- 22 W. Wu, Y. Wang, C. Wang, Y. Wu, P. Liu and Q. Shi, *Inorg. Chem. Commun.*, 2006, **9**, 645–648.
- 23 M. Kumar, M. Srivastava and R. A. Yadav, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, 2013, **111**, 242–251.
- 24 M. Lovrić, I. Cepanec, M. Litvić, A. Bartolinčić and V. Vinković, *Croat. Chem. Acta*, 2007, **80**, 109–115.
- 25 C. Klotfutar, Š. Paljk and D. Kremser, *Spectrochim. Acta Part A*, 1973, **29**, 139–145.
- 26 A. Torrisi, C. Mellot-Draznieks and R. G. Bell, *J. Chem. Phys.*, 2016, **130**, 194703–194713.
- 27 H. Liu, Y. Zhao, Z. Zhang, N. Nijem, Y. J. Chabal, X. Peng, H. Zeng and J. Li, *Chem. Asian J.*, 2013, **8**, 778–785.
- 28 P. Zhang, B. Li, Y. Zhao, X. Meng and T. Zhang, *Chem. Commun.*, 2011, **47**, 7722–7724.
- 29 X. Liu, M. Park, S. Hong, M. Oh, J. W. Yoon, J.-S. Chang and M. S. Lah, *Inorg. Chem.*, 2009, **48**, 11507–11509.
- 30 V. A. Blatov, *IUCr CompComm Newsl.*, 2006, **7**, 38–143.
- 31 M. Sartor, T. Stein, F. Hoffmann, M. Fröba, M. Sartor, T. Stein, F. Hoffmann and M. Fröba, *Chem. Mater.*, 2016, **28**, 519–528.
- 32 A. L. Spek, *Acta. Crystallogr. Sect. D*, 2009, **65**, 148.
- 33 N. H. Alsmail, M. Suyetin, Y. Yan, R. Cabot, C. P. Krap, J. Lü, T. L. Easun, E. Bichoutskaia, W. Lewis, A. J. Blake and M. Schröder, *Chemistry*, 2014, **20**, 7317–7324.
- 34 Y. Peng, V. Krungleviciute, I. Eryazici, J. T. Hupp, O. K. Farha and T. Yildirim, *J. Am. Chem. Soc.*, 2013, **135**, 11887–11894.
- 35 C. Song, Y. He, B. Li, Y. Ling, H. Wang, Y. Feng, R. Krishna and B. Chen, *Chem. Commun.*, 2014, **50**, 12105–12108.
- 36 M. Sartor, T. Stein, F. Hoffmann and M. Fröba, *Chem. Mater.*, 2016, **28**, 519–528.

6. Summary

The work in this thesis concerns the synthesis and gas adsorption properties of a series of MOFs constructed from Cu(II)-paddlewheel based metal-organic cuboctahedra and V-shaped pyridyl carboxylate ligands. The inclusion of pyridyl groups was designed to target Lewis basic interactions with guest species, in particular CO₂, leading to high adsorption capacities and selectivities.

Reaction of H₄PPYD with Cu(II) resulted in the formation of a self-interpenetrated **txt** framework, in which the pyridyl nitrogen coordinates to the axial Cu(II)-paddlewheel sites (MFM-170). The framework consists of three cages; cage A, a metal-organic cuboctahedron; cage B, an oval cage lined by the inside edges of four ligand molecules; and cage C, occupying the remaining space and constructed from the outside edges of six ligand molecules. MFM-170 was found to show a high adsorption capacity for all gases; however the inclusion of additional binding sites was expected to further improve the gas uptake and selectivity.

MFM-171 and MFM-172 were constructed from ligands containing pyrazine and methyl pyridyl cores. Both frameworks are isostructural to MFM-170 and feature four functional groups pointing directly into the centre of cage B. Neither MOF was found to demonstrate enhanced gas adsorption capacities at high pressure; however MFM-172, showed an increase in CO₂ uptake at 1 bar. In order to gain an understanding of these gas adsorption properties, *in situ* IR microspectrometry and SCXRD experiments were performed on CO₂ loaded crystals of MFM-170 and MFM-171 and allowed for the determination of two key binding sites within the framework. CO₂^{II} was found to interact with aromatic protons on the pyridyl ring, while CO₂^{IV} demonstrates an end-on interaction between a lone pair on the CO₂ and the π -electron cloud surrounding the central pyridyl ring. These observations suggest that the low pressure adsorption capacity of CO₂ in **txt** frameworks is dependent on the electronic properties of the aromatic substituents. The electron donating methyl group

increases the electron density of the pyridyl ring, strengthening interactions with CO₂; whilst inductive effects of the pyrazine nitrogen reduces the electron density, leading to a lower CO₂ uptake capacity. No interactions could be seen between adsorbed CO₂ and the Lewis basic pyrazine site, leading to the conclusion that this functional group is too sterically hindered to interact with guest molecules directly.

Lewis basic heterocyclic groups were introduced into the framework by means of triazole groups, giving rise to an isostructural **txt** framework MFM-175, which is highly strained and collapses upon activation. Although total uptake capacities could not be compared to the MFM-17X series, MFM-175 showed increased selectivity for CO₂, demonstrating that the inclusion of triazole groups is a promising strategy to increase the CO₂ adsorption and selectivity in MOFs.

Finally, attempts were made to increase the CO₂ adsorption capacity of MFM-170 by liberating pyridyl nitrogens for interaction with guest species. Attempts to prevent interpenetration by protecting the coordinating pyridyl group with a pyridine-N-oxide group gave no crystalline product. Steric effects were investigated by substituting the central pyridyl core for a tolyl group, resulting in the formation of a two-fold interpenetrated **zmj** framework, proving that larger functional groups are required to prevent interpenetration. The reduced porosity of this two-fold interpenetrated framework results in lower uptake capacities than MFM-170, but MFM-176 shows greater selectivity for CO₂ over N₂ and CH₄, attributed to the electron donating properties of the tolyl group.

Appendices

7.1 Experimental Procedures

Chemicals, solvents and gases were used as received without further purification unless otherwise stated.

^1H and ^{13}C NMR spectra were recorded on Bruker DPX-300, Bruker DPX-400 and Bruker DPX-500 spectrometers. Residual protonated species in the deuterated solvents were used as internal references; all shifts are reported in ppm, with J values in Hz.

Mass spectrometry was performed on a Bruker Esquire electrospray (ESI) ion-trap spectrometer with samples dissolved in the appropriate solvent and data are reported as m/z.

FTIR spectra were measured with a Thermo Scientific Nicolet iS5 IR spectrometer in ATR sampling mode.

Elemental analyses (C, H, and N) were performed on a CE-440 elemental analyser at the University of Nottingham and a Flash 2000 elemental analyser at the University of Manchester. Elemental analyses of organic molecules were performed on the crude samples whereas elemental analyses of MOF samples deviate from the predicted values due to varying solvent content and drying of the “as synthesised” samples.

Thermal gravimetric analyses (TGA) were performed under a flow of air (20 mL min⁻¹) with a heating rate of 5 °C min⁻¹ using a TA SDT-600 thermogravimetric analyser.

Powder X-ray diffraction (PXRD) measurements were performed on a PANalytical X'Pert PRO flat plate diffractometer using Cu-K α radiation (λ = 1.5418 Å) at 40 kV, 40 mA, at a scan-speed of 0.034 s⁻¹ and a step size of 0.0065 in 2 θ .

Single crystal X-ray diffraction (SCXRD): Single crystals of MFM-170, MFM-171 and MFM-172 were analysed on an Agilent GV1000 CuK α 1 X-Ray Diffractometer at 120 K during data collection. A single crystal of MFM-173 was analysed using high-intensity

synchrotron radiation on Beamline I19 at Diamond Light Source. Structures were solved by direct methods and developed by difference Fourier techniques using the SHELXTL¹ software package. The hydrogen atoms on the ligands were placed geometrically and refined using a riding model. The coordinated solvent molecules could not be fully refined due to being a mixture of water and DMF, and are assumed to be water in the final formula. The diffraction from disordered solvent within the unit cell was analysed using PLATON/SQUEEZE² and removed to produce a set of solvent-free diffraction intensities. The final formula was calculated from a combination of SQUEEZE electron count, elemental and TGA analysis: the contents of the solvent region are therefore included in the unit cell contents but not in the refinement model. Crystal structure pictures were generated using Diamond 3.2.

Gas Adsorption isotherms: Low pressure nitrogen isotherms were measured to 1 bar using a Micromeritics 3Flex analyser at 77 K, cooled using a liquid nitrogen bath. High pressure (20 bar) isotherms of N₂, CO₂ and CH₄, along with 1 bar isotherms for C₂H₄ and C₂H₆ were measured using a Hiden Isochema Intelligent Gravimetric Analyser (IGA) system at 273 K and 298 K, using a temperature controlled water bath. In all cases the desolvated sample was generated in situ within the reactor of the instrument by heating the acetone-exchanged sample to 100 °C under vacuum (1×10^{-6} mbar).

In situ IR microspectroscopy studies were carried out on beamline B22 at Diamond Light Source. The instrument comprises a Bruker Hyperion 3000 microscope in transmission mode, with a 15x objective and liquid nitrogen cooled MCT detector, coupled to a Bruker Vertex 80 V Fourier Transform IR interferometer using radiation generated from a bending magnet source. Spectra were collected (256 scans) in the range 650-4000 cm⁻¹ with 4 cm⁻¹ resolution and an infrared spot size at the sample of approximately 25 × 25 μm. Solvent exchanged single crystals of MFM-170 and MFM-171 were loaded into a Linkam FTIR 600 temperature-controlled stage fitted with ZnSe windows. He and CO₂ were dosed into the cell as a function of partial pressure using mass flow controllers and maintaining a constant

flow rate of $100 \text{ cm}^3 \text{ min}^{-1}$. Dry He was used as provided, whereas the CO_2 was pre-dried using a zeolite filter. The sample was activated by heating to $100 \text{ }^\circ\text{C}$ under a flow of dry helium. After cooling to $25 \text{ }^\circ\text{C}$, a baseline spectrum was collected before loading the sample with varying amounts of CO_2 . Further spectra were collected, with the background gaseous CO_2 in the cell subtracted each time. The sample deemed to have reached equilibrium when no change could be seen between three spectra measured at one minute intervals.

***In situ* SCXRD:** Gas loaded single crystal X-ray diffraction experiments of MFM-170 were carried out at beamline 11.3.1 of the Advanced Light Source, Berkeley. Single crystals of MFM-170 ($100 \times 100 \times 100 \text{ }\mu\text{m}$) were attached to a MiTeGen MicroGripper *via* a minimum amount of epoxy glue. The crystal pin was then glued into a quartz capillary gas handling cell. The cell containing MFM-170 was mounted onto the goniometer and outgassed *in situ* on the diffractometer by heating to a temperature of 423 K using a stream of N_2 centred on the crystal in the capillary. Diffraction data were collected for the crystal at 423 K . The crystal was then cooled to 298 K , dosed with 1 bar of CO_2 and cooled further to 273 K before another dataset was collected. The high humidity combined with cooling *via* a N_2 cryostat led to problems at temperatures below 273 K , with icing on the outside of the glass capillary obscuring diffraction from the crystal.

Studies of MFM-171 were carried out at Nottingham University's X-ray diffraction suite using a Dual Source Agilent SuperNova CCD area detector diffractometer and Mo K_α radiation source. Temperature control was achieved using Oxford Cryostreams open-flow nitrogen gas cryostat. Single crystals of MFM-171 ($100 \times 100 \times 100 \text{ }\mu\text{m}$) were attached to a MiTeGen MicroGripper *via* a minimum amount of epoxy glue. The crystal pin was then glued into a quartz capillary gas handling cell. The cell containing MFM-171 was attached to a custom gas-interface panel and was outgassed using a turbomolecular pump (10^{-6} mbar) whilst the outside of the cell was heated to 423 K in a metal heating block for 48 hours. The cell was cooled to room temperature, sealed and mounted onto a goniometer where an evacuated dataset was collected at 243 K . After data collection, the cell was reattached to

the gas interface panel and dosed with CO₂ (1 bar), sealed and re-mounted on the diffractometer and cooled to 95 K using the cryostream. Once cooled and any CO₂ inside the cell had frozen, the quartz capillary was broken and removed, allowing for low-temperature crystallographic studies without problems with icing or diffraction from solid CO₂.

Structure solution was achieved by direct methods and least squares refinements. The desolvated structures were refined anisotropically and hydrogen atoms modelled using a riding model. Neither structure showed a complete removal of copper-bound water due to poor heat transfer in a vacuum, with MFM-170 having an occupancy of 19% at 423 K and MFM-171 having an occupancy of 46% at 243 K.

In the CO₂ loaded structures, analysis of the Fourier difference maps reveals the location of the adsorbed CO₂ molecules which were refined isotropically. Rigid body constraints were applied to define the C=O bond lengths and geometry, with C-O bond lengths of 1.16 Å and O···O distances of 2.32 Å (DFIX) and the isotropic displacement parameters were fixed to 0.1. The occupancies for each CO₂ molecule were refined globally using free variables.

Grand Canonical Monte Carlo (GCMC) simulations CO₂ adsorption in MFM-170 and MFM-171 at 195, 273 and 298 K was simulated via grand canonical Monte Carlo simulations implemented in the MuSiC software package³ and using translation, rotation and energy-biased insertion and deletion moves. All simulations were allowed at least 8×10^6 equilibration steps, followed by 12×10^6 production steps for each pressure point. The frameworks were treated as rigid, with atoms kept fixed at their crystallographic positions from the solvated crystal structures at 120 K. Lennard-Jones parameters for the framework atoms were taken from the OPLS force field⁴ with the exception of copper, for which UFF⁵ parameters were used. Framework partial charges were calculated using the extended charge equilibration method.⁶ CO₂ was simulated as a rigid molecule using the TraPPE model,⁷ incorporating both Lennard-Jones parameters and partial charges.

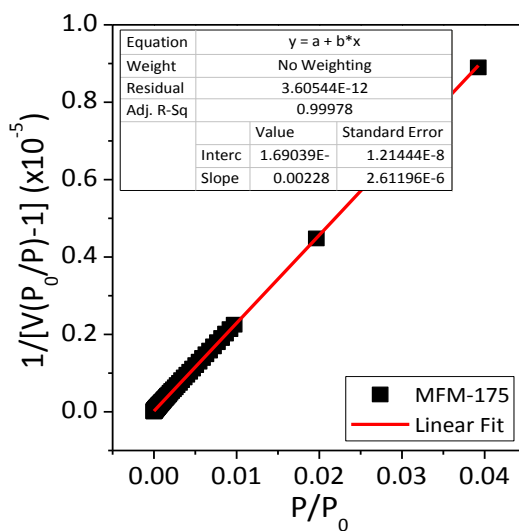
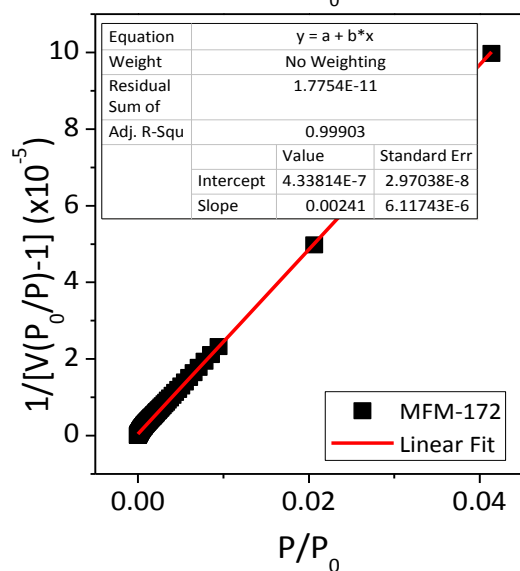
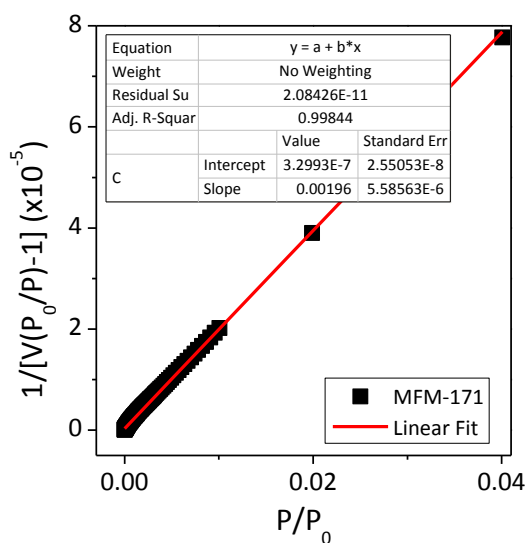
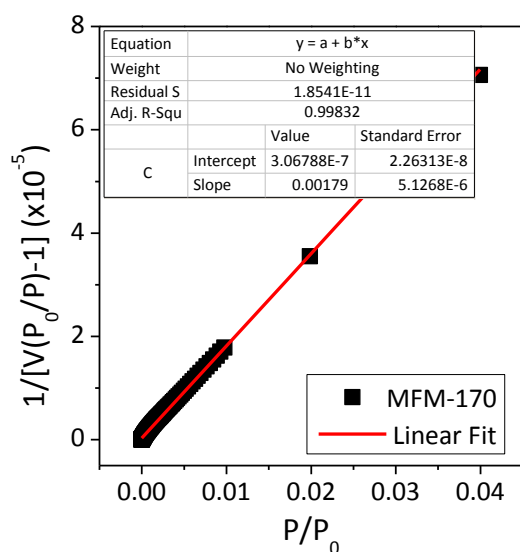
7.2 Calculations from gas adsorption isotherms

7.2.1 BET surface areas

Appropriate data points were identified from the 77 K N₂ isotherms by a Roquerol transform and subsequently plotted to a BET transform. A linear fit obtained, from which the BET surface area was calculated using the following equation.

$$n_{ads}(1 - \frac{p}{p_0})$$

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c - 1}{v_m c} \frac{p}{p_0}$$



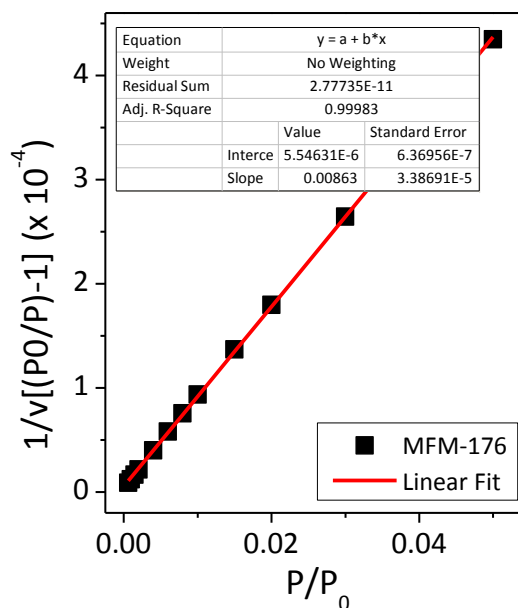


Figure 7.1: BET transform plots and linear fit parameters for MFM-170, MFM-171, MFM-172, MFM-175, MFM-176.

Table 7.1: BET surface areas calculated via the Rouquerol method.

BET surface area (m ² g ⁻¹)	
MFM-170	2408
MFM-171	2196
MFM-172	1787
MFM-175	1890
MFM-176	1486

7.2.2 Heats of Adsorption

The heats of adsorption were calculated using the Clausius-Clapeyron equation using isotherms measured at 273 K and 298 K and fitted to a Virial-type equation.

$$\ln\left(\frac{n}{p}\right) = A_0 + A_1n + A_2n^2 + A_3n^3 + A_4n^4 \quad (1)$$

Where P is the pressure, n is the total amount adsorbed and A₀, A₁ etc. are Virial coefficients.

The enthalpy of adsorption at zero coverage is determined from the relationship:

$$\delta A_0 = RQ_{st}^{n=0} \delta(T^{-1}) \quad (2)$$

7.2.2.1 CO₂ heats of adsorption

The Virial fitting for each curve has an R^2 greater than 0.99, indicating the consistency of the isotherm data and the quality of the fit.

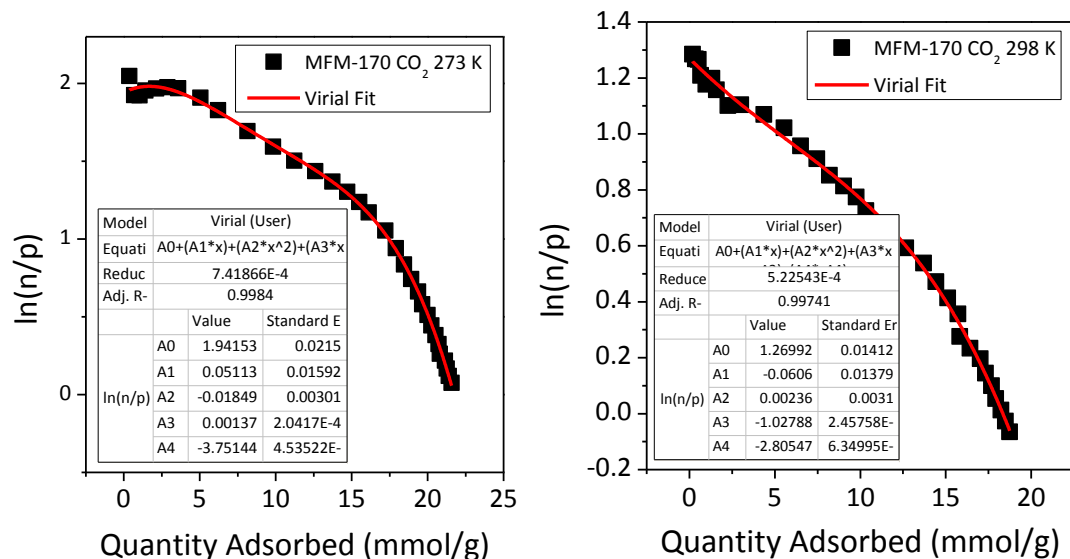


Figure 7.2: Virial fittings of CO₂ isotherms of MFM-170 at 273 K and 298 K.

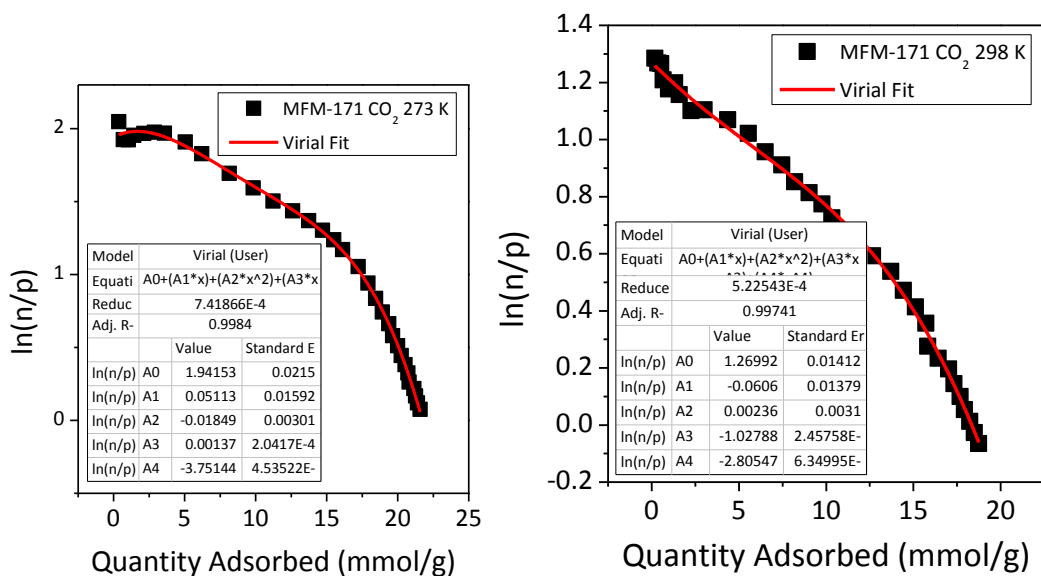


Figure 7.3: Virial fittings of CO₂ isotherms of MFM-171 at 273 K and 298 K.

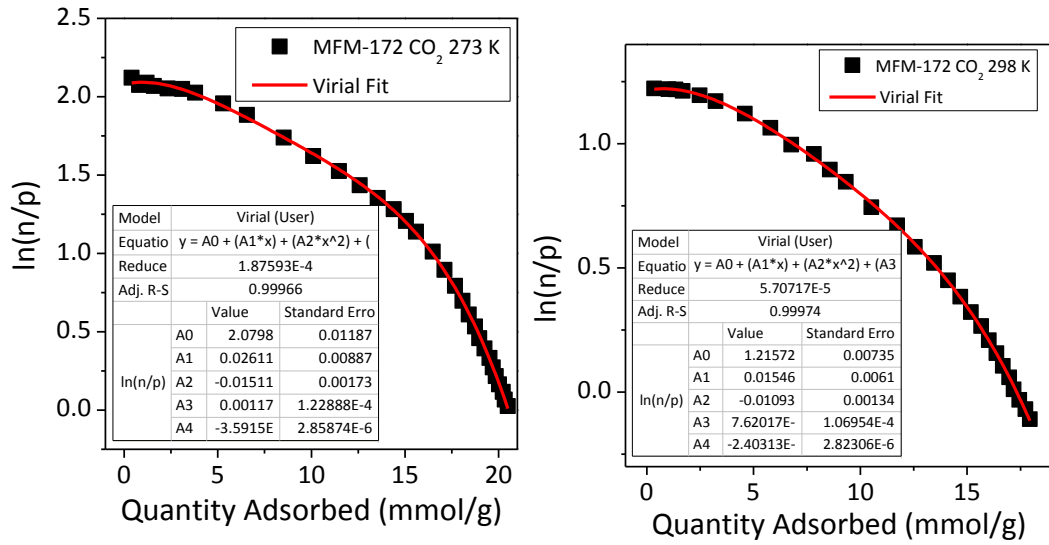


Figure 7.4: Virial fittings of CO₂ isotherms of MFM-172 at 273 K and 298 K.

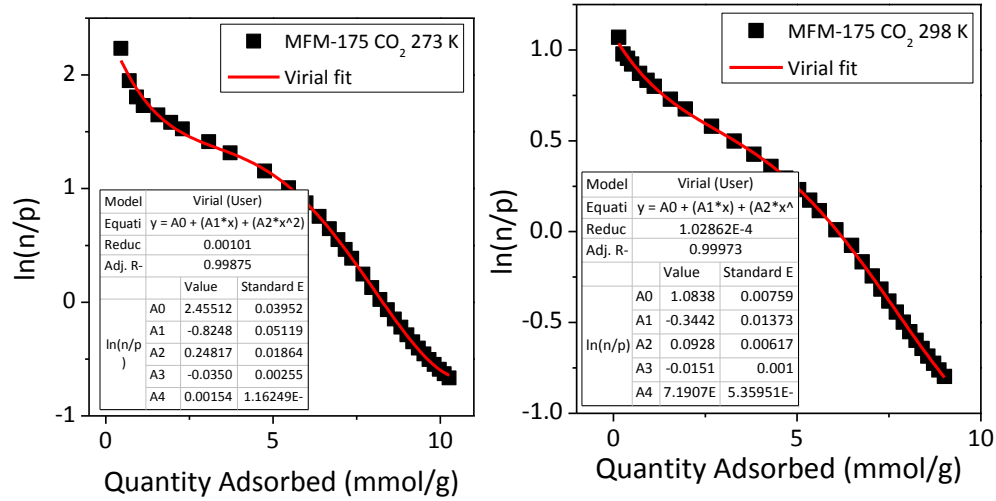


Figure 7.5: Virial fittings of CO₂ isotherms of MFM-175 at 273 K and 298 K.

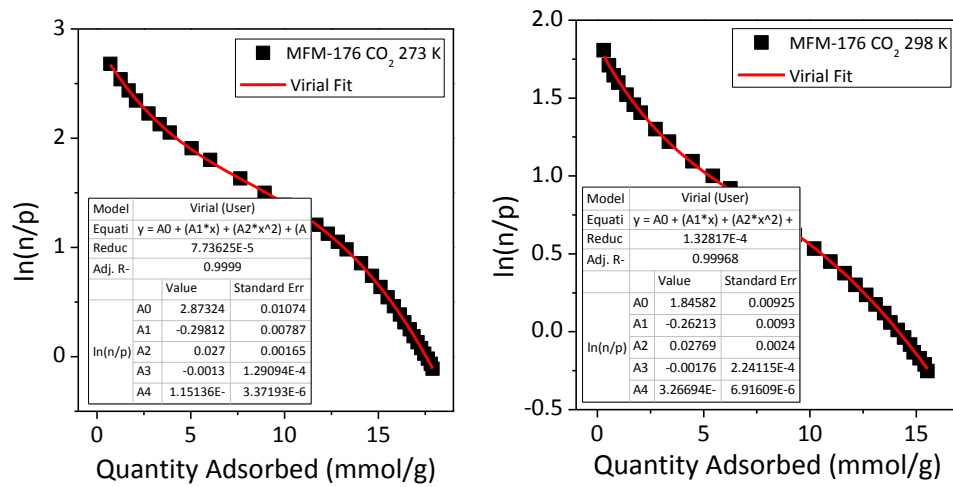
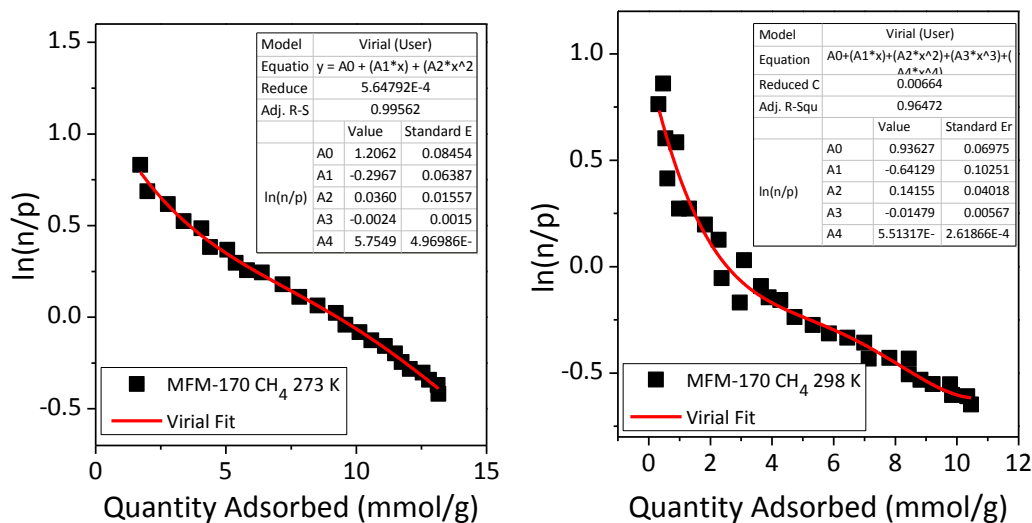
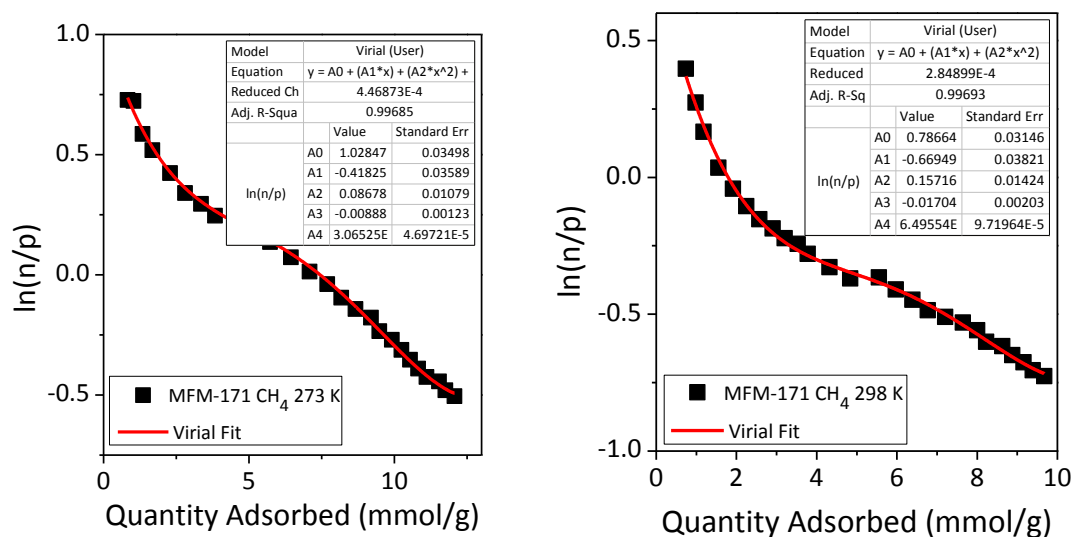


Figure 7.6: Virial fittings of CO₂ isotherms of MFM-176 at 273 K and 298 K.

7.2.2.2 CH₄ heats of adsorptionFigure 7.7: Virial fittings of CH₄ isotherms of MFM-170 at 273 K and 298 K.Figure 7.8: Virial fittings of CH₄ isotherms of MFM-171 at 273 K and 298 K.

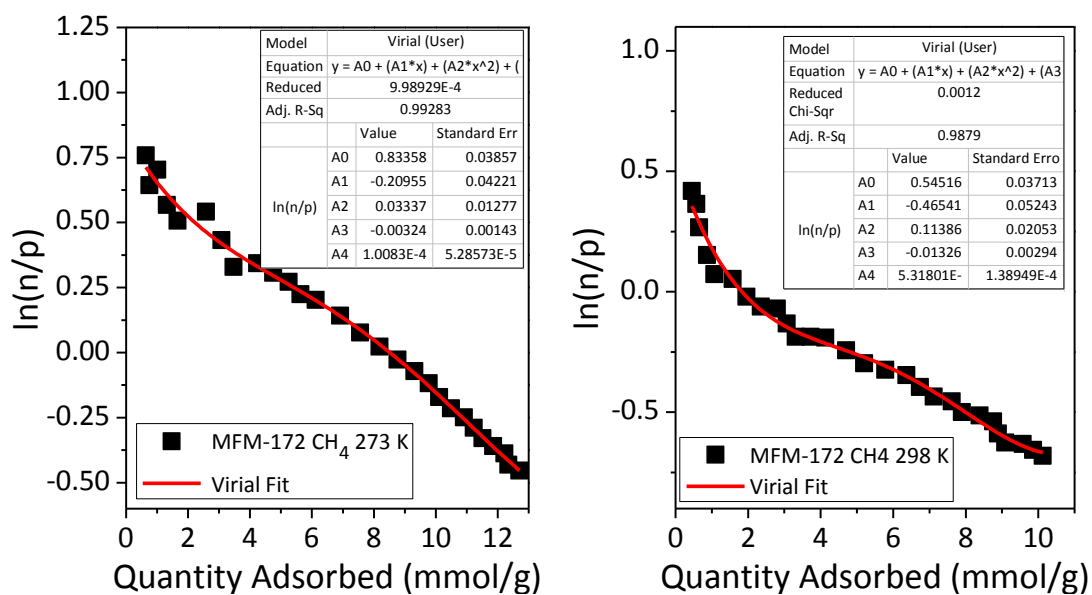


Figure 7.9: Virial fittings of CH_4 isotherms of MFM-172 at 273 K and 298 K.

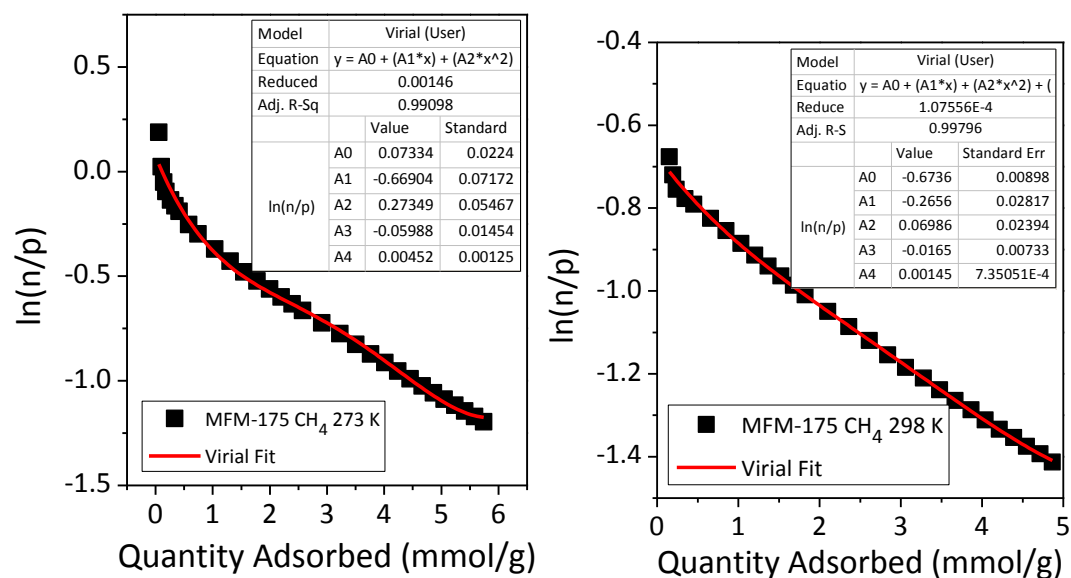
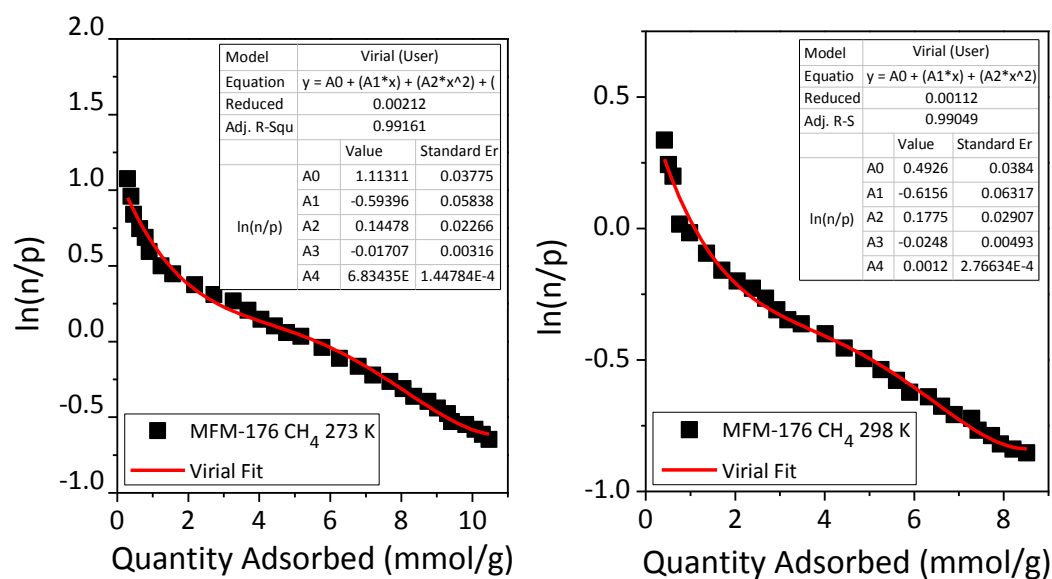
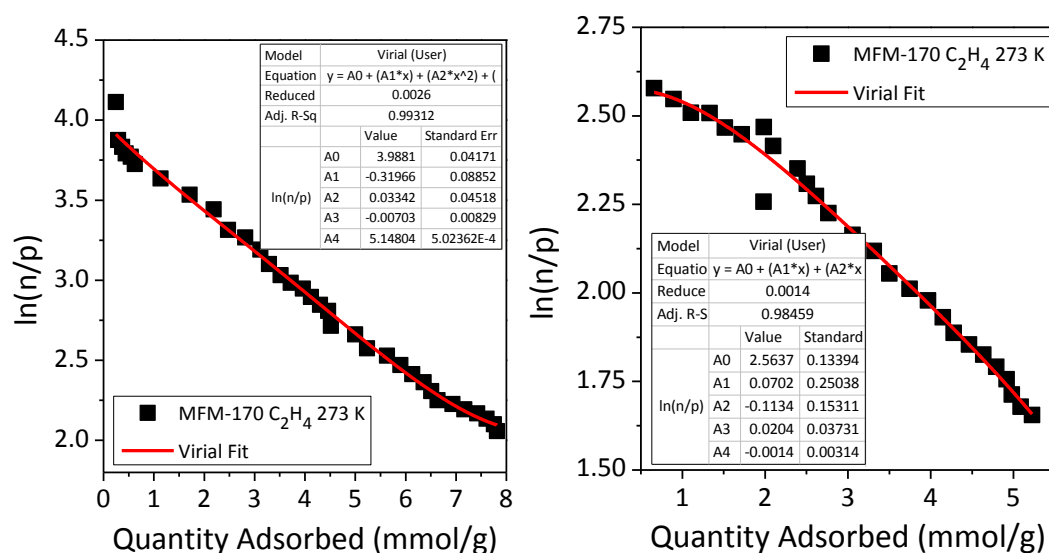


Figure 7.10: Virial fittings of CH_4 isotherms of MFM-175 at 273 K and 298 K.

Figure 7.11: Virial fitting of CH₄ isotherms of MFM-176 at 273 K and 298 K.7.2.2.3 C₂H₄ heats of adsorptionFigure 7.12: Virial fittings of C₂H₄ isotherms of MFM-170 at 273 K and 298 K.

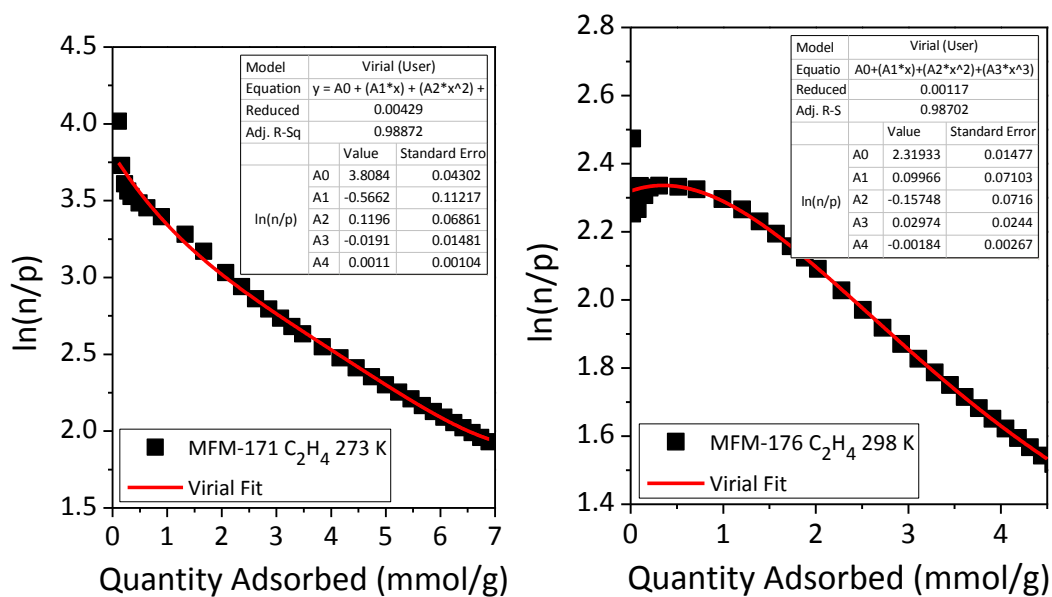


Figure 7.13: Virial fittings of C_2H_4 isotherms of MFM-171 at 273 K and 298 K.

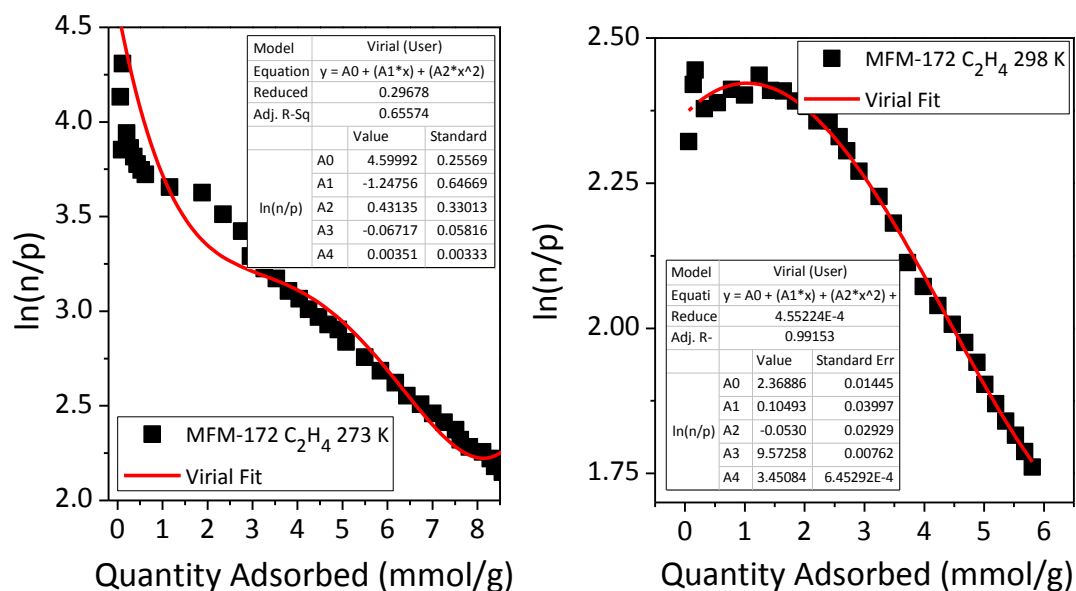
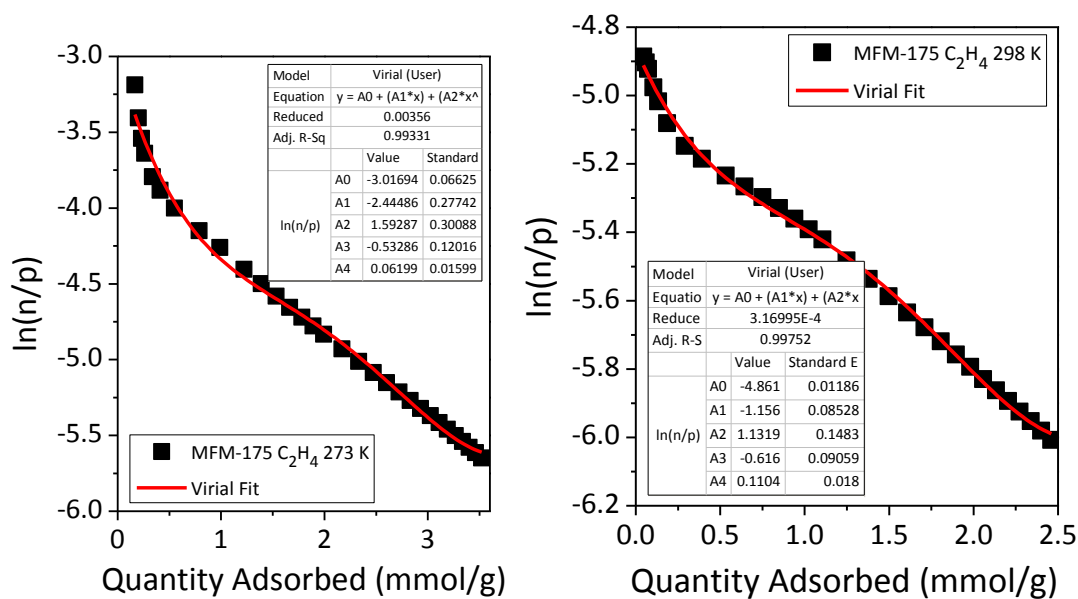
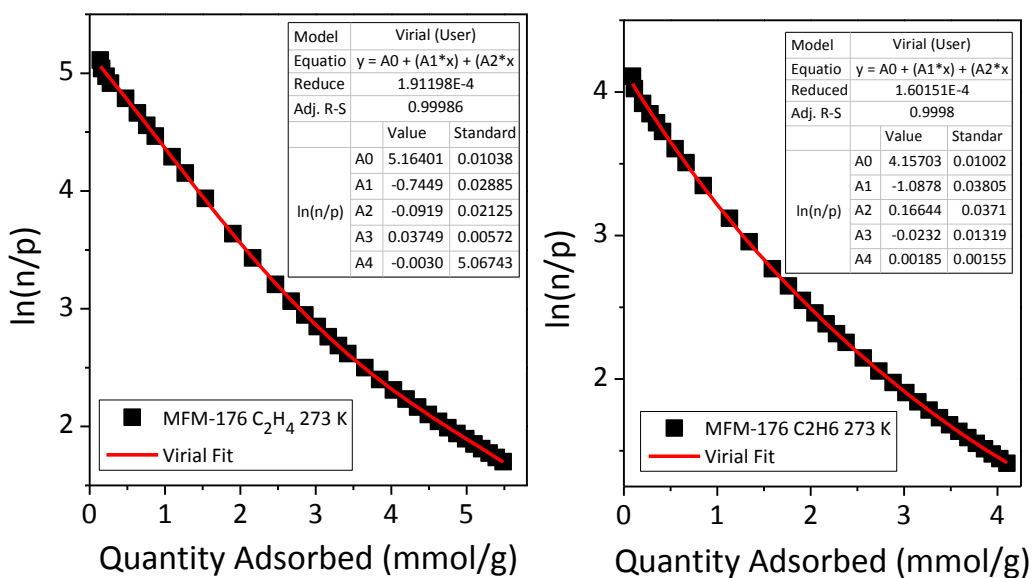
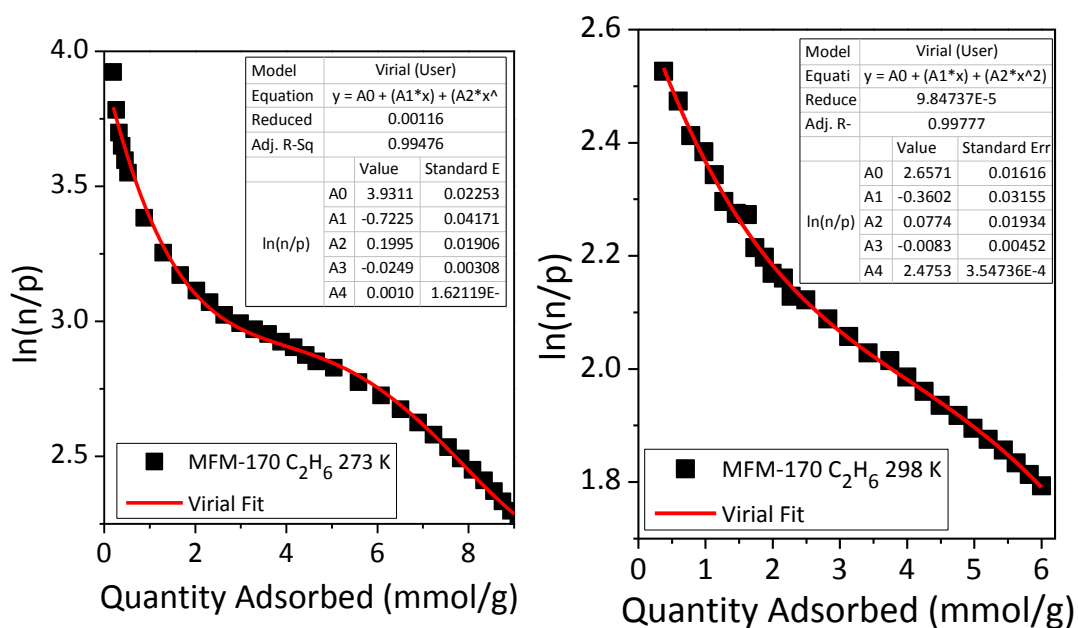
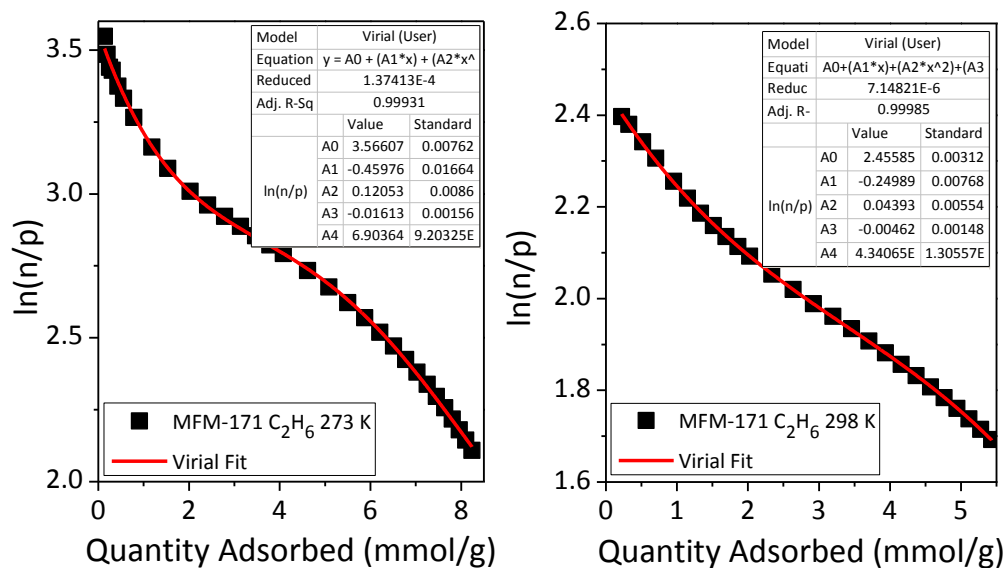


Figure 7.14: Virial fittings of C_2H_4 isotherms of MFM-172 at 273 K and 298 K.

Figure 7.15: Virial fittings of C_2H_4 isotherms of MFM-175 at 273 K and 298 KFigure 7.16: Virial fittings of C_2H_4 isotherms of MFM-176 at 273 K and 298 K

7.2.2.4 C₂H₆ heats of adsorptionFigure 7.17: Virial fitting of C₂H₆ isotherms of MFM-170 at 273 K and 298 K.Figure 7.18: Virial fittings of C₂H₆ isotherms of MFM-171 at 273 K and 298 K.

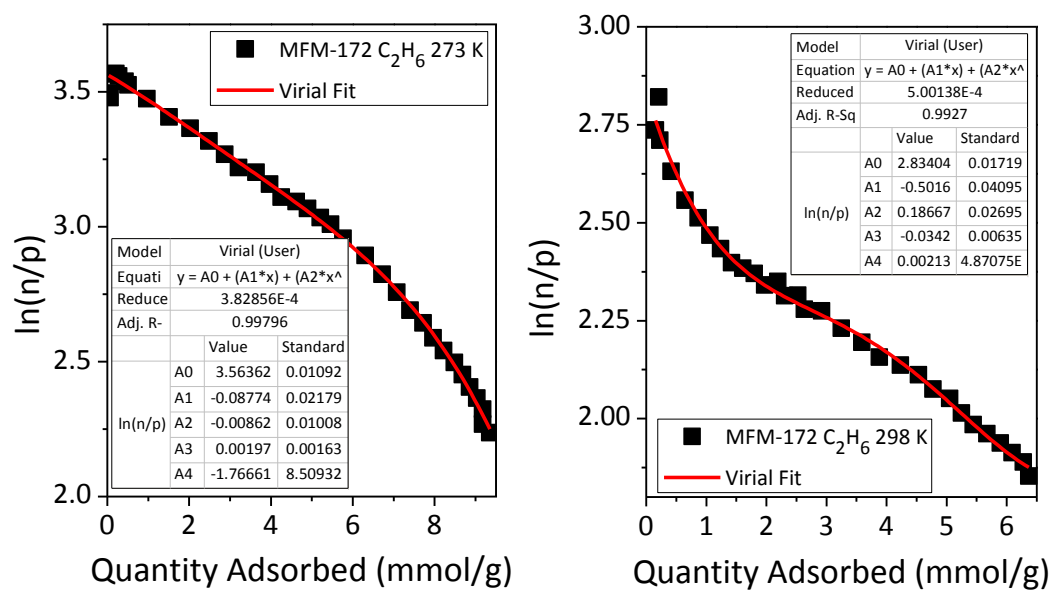


Figure 7.19: Virial fitting of C_2H_6 isotherms of MFM-172 at 273 K and 298 K.

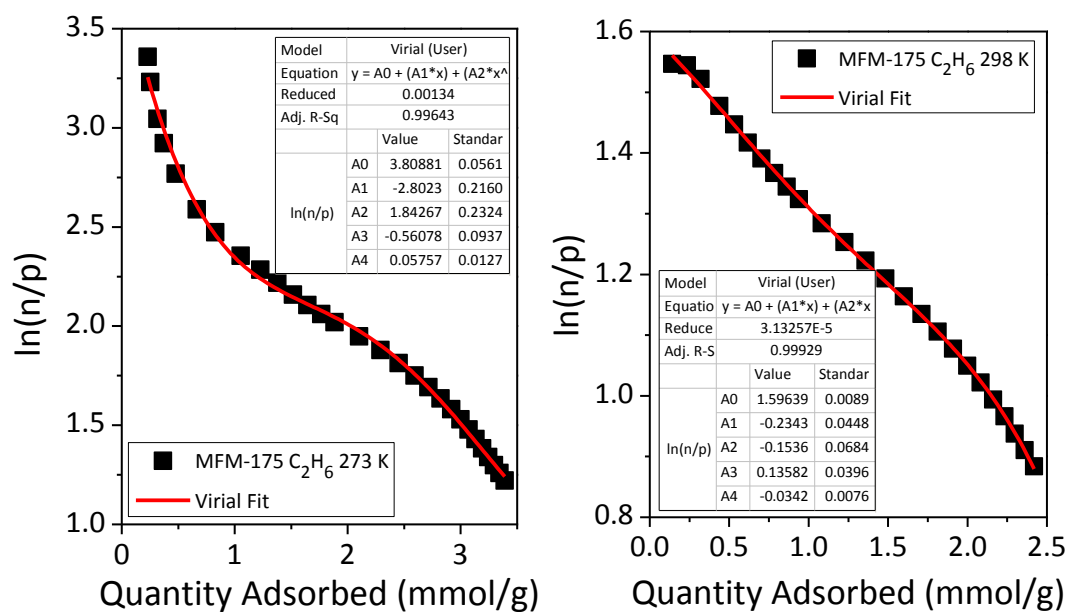


Figure 7.20: Virial fitting of C_2H_6 isotherms of MFM-175 at 273 K and 298 K.

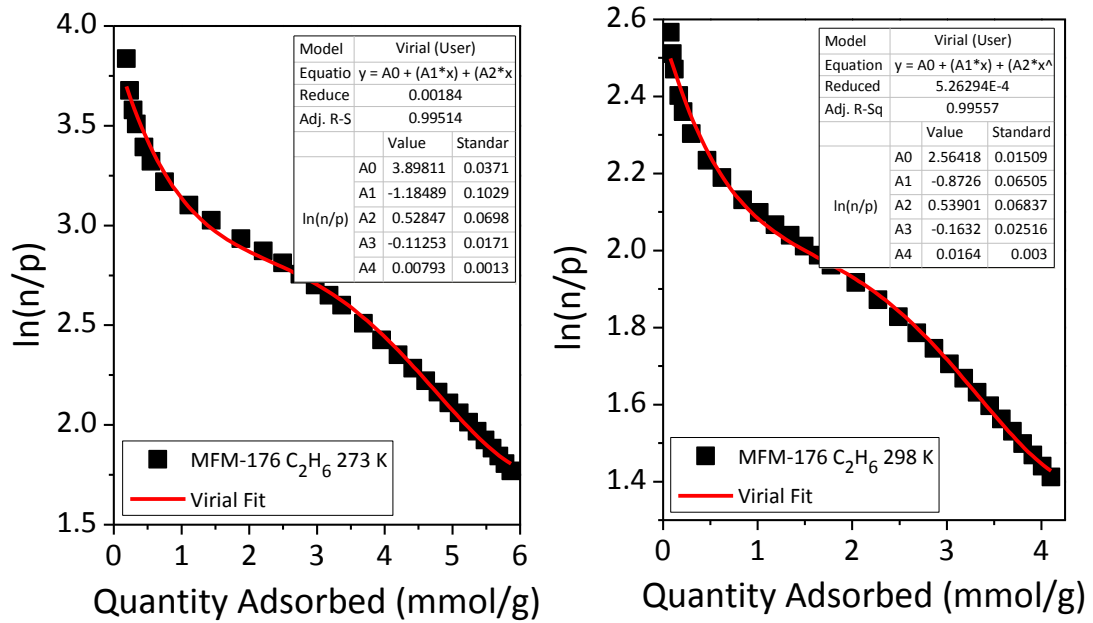


Figure 7.21: Virial fitting of C_2H_6 isotherms of MFM-176 at 273 K and 298 K.

7.2.3 IAST selectivity Fittings

Selectivity calculations were performed using the IAST method calculated from single component isotherms. The adsorption isotherms of N_2 and CO_2 were fitted using the single site Langmuir model;

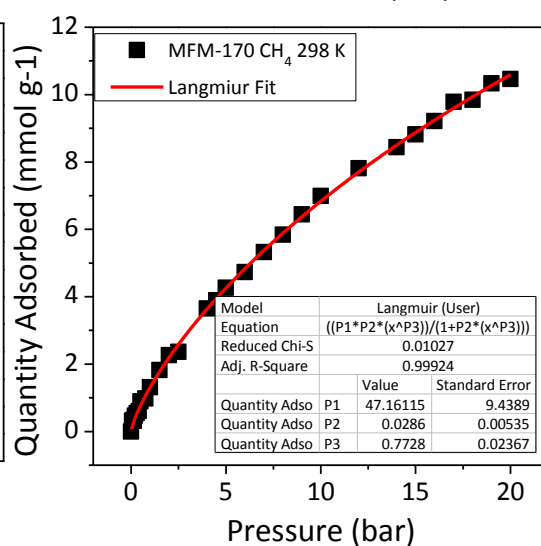
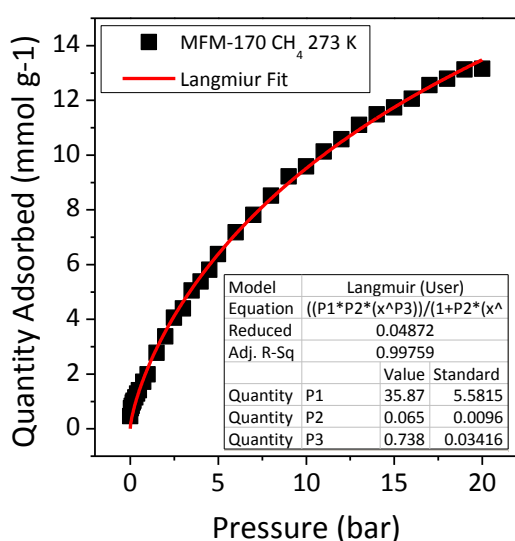
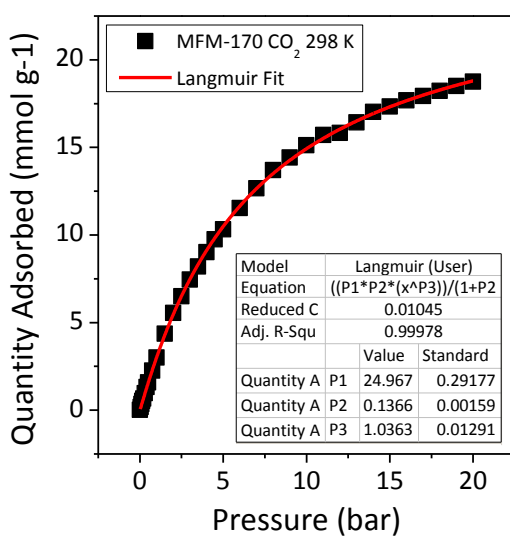
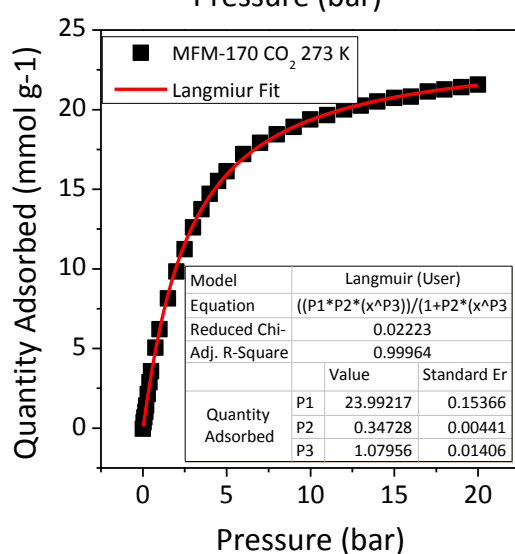
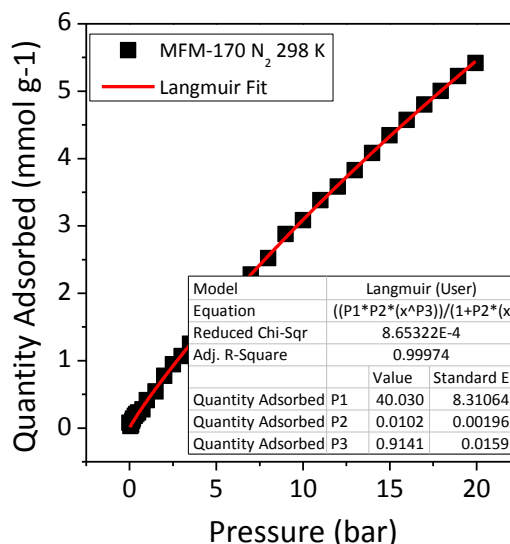
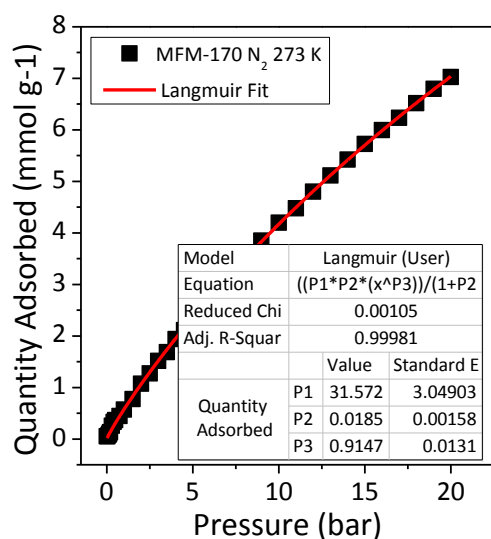
$$n = \frac{q_{sat} b_1 P^{v_1}}{1 + b_1 P^{v_1}} \quad (3)$$

where n is the total amount adsorbed in mmol/g, P is the pressure in bar, q_{sat} is the saturation capacity in mmol/g and b_1 is the Langmuir parameter in bar^{-1} for the adsorption site. The regression parameters for all of the fits are above 0.99, confirming the reliability of the modelling.

Ideal Adsorbed Solution Theory (IAST) was used to determine the selectivity factor, S , for binary mixtures using pure component isotherm data. S is defined according the equation;

$$S = \frac{x_1/y_1}{x_2/y_2} \quad (1)$$

where x_i is the amount of each component adsorbed, as determined by IAST and y_i is the mole fraction of each component in the gas phase at equilibrium.



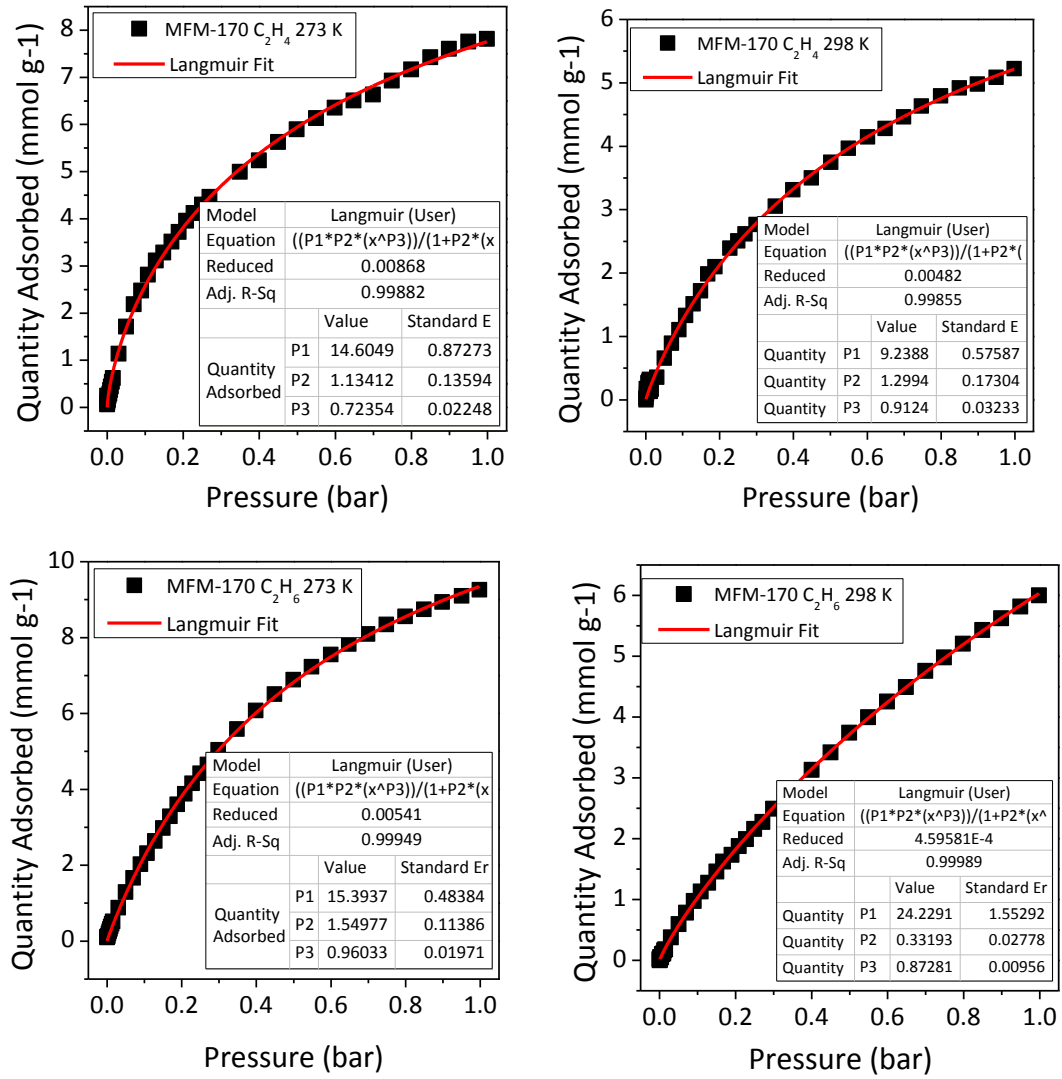
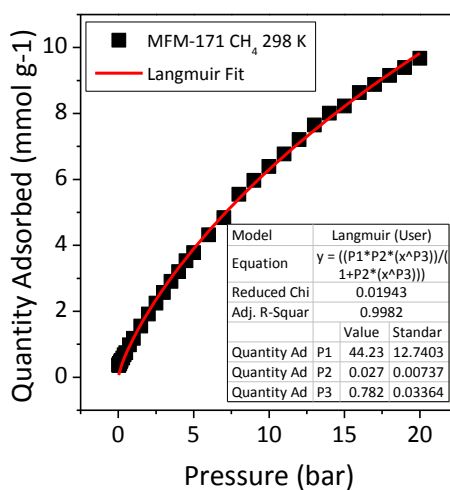
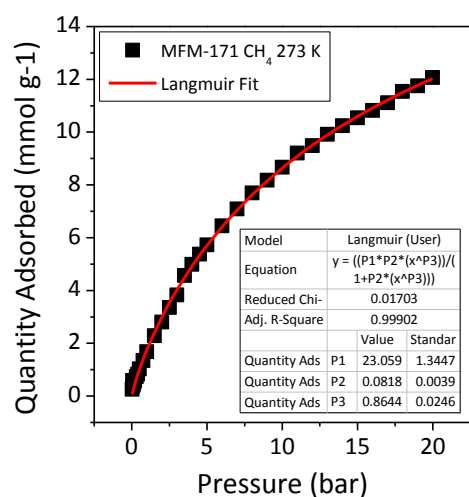
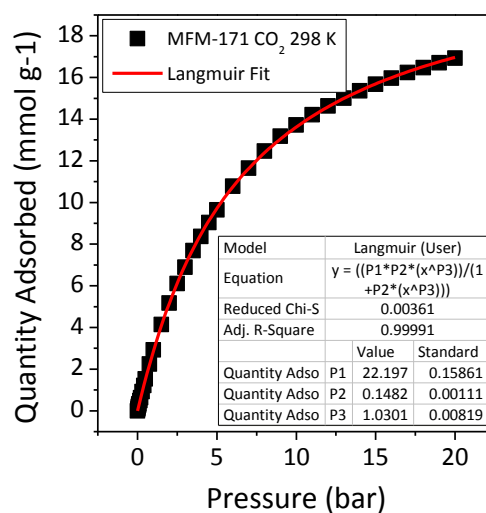
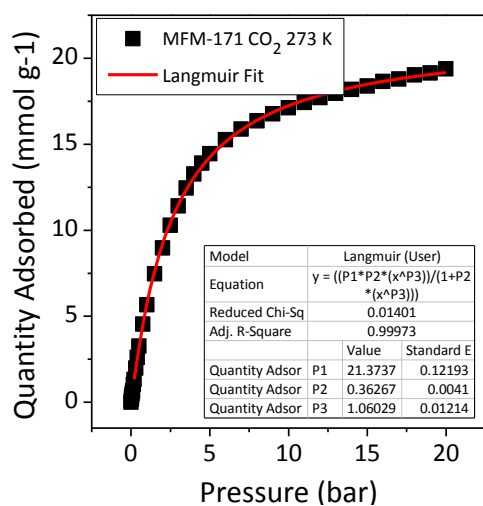
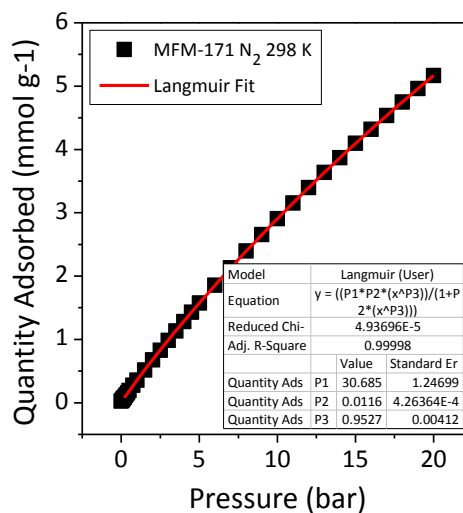
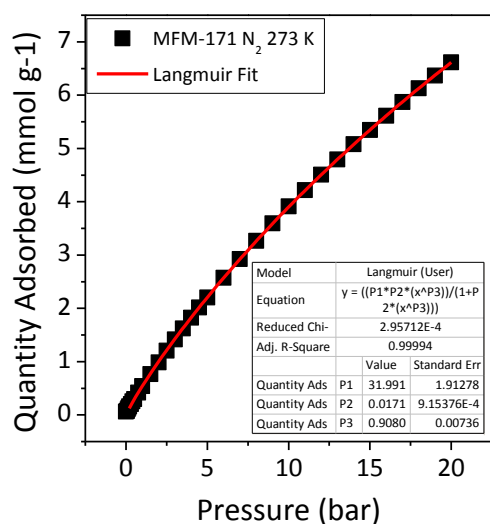


Figure 7.22: Langmuir fitting of N₂, CO₂, CH₄, C₂H₄ and C₂H₆ adsorption isotherms of MFM-170 at 273 K and 298 K.



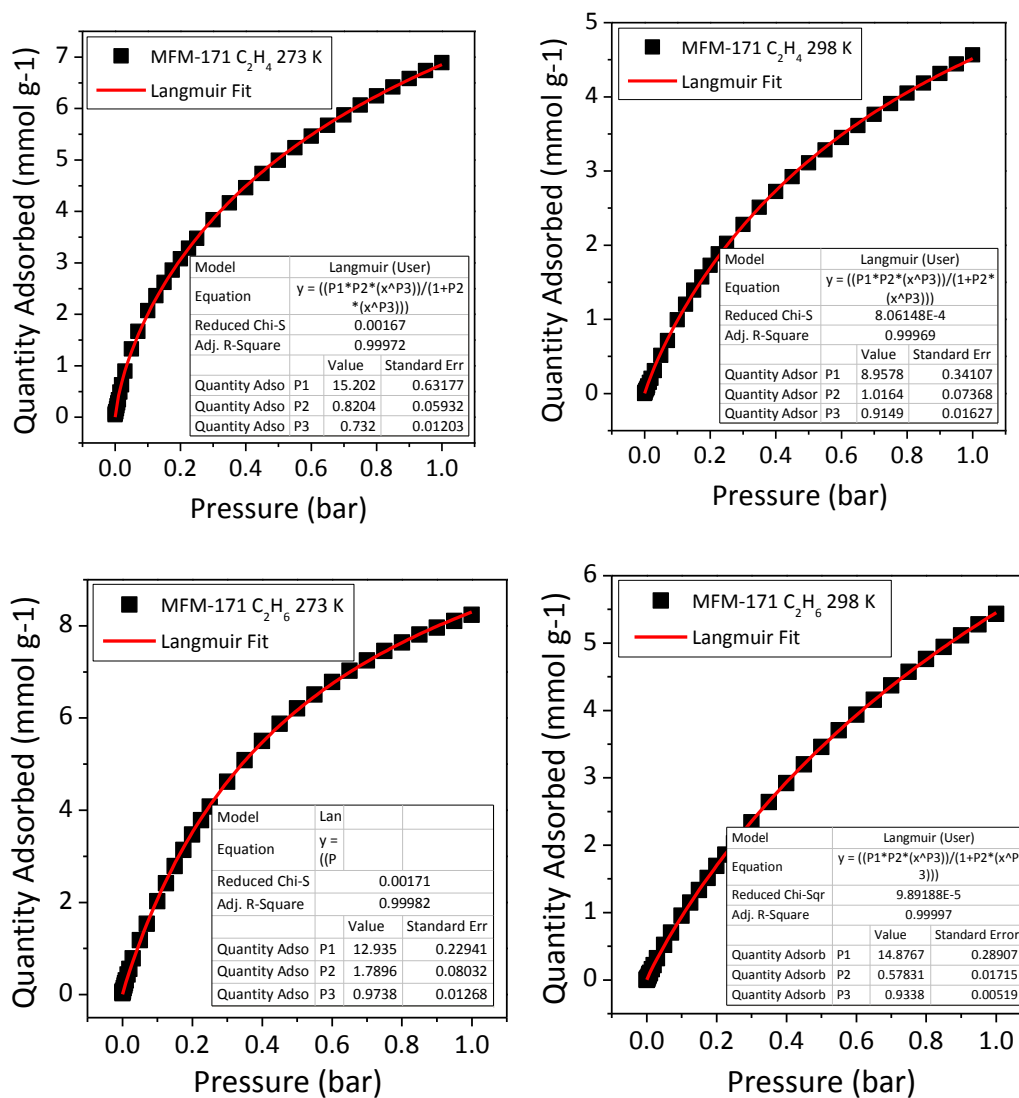
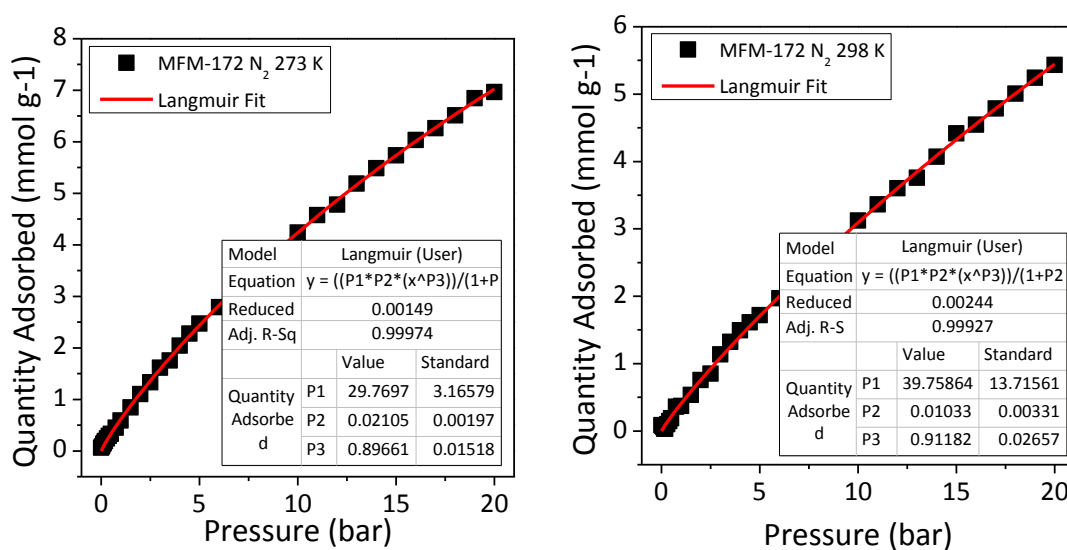
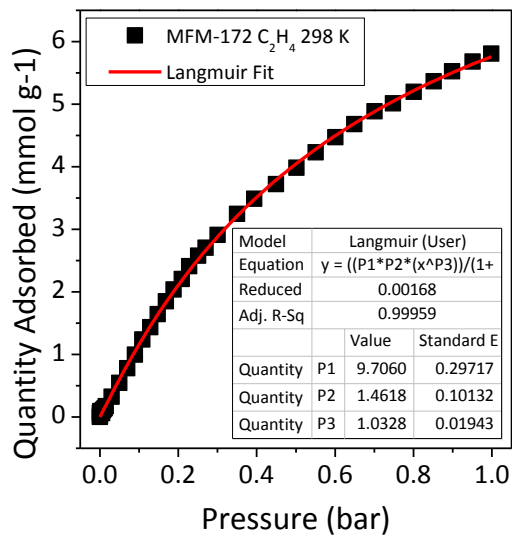
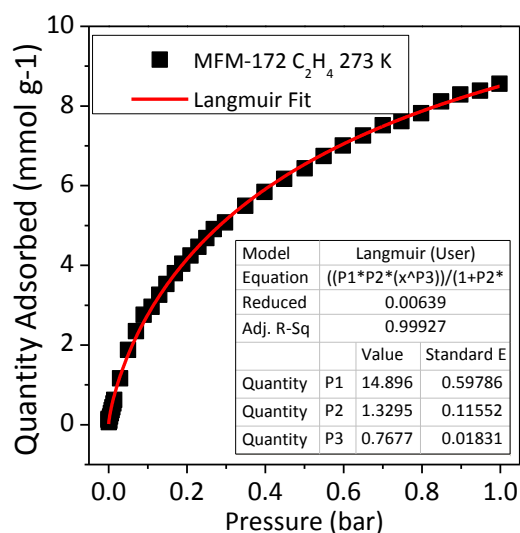
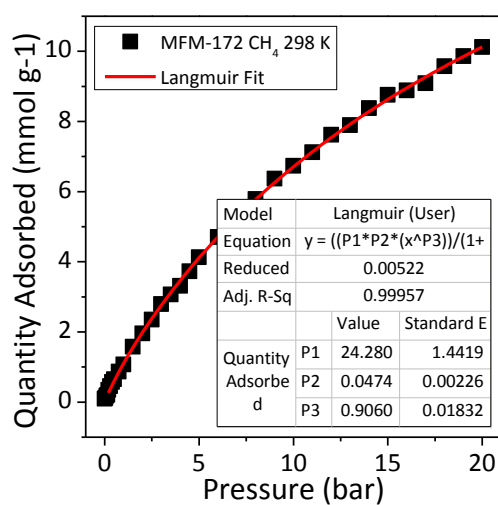
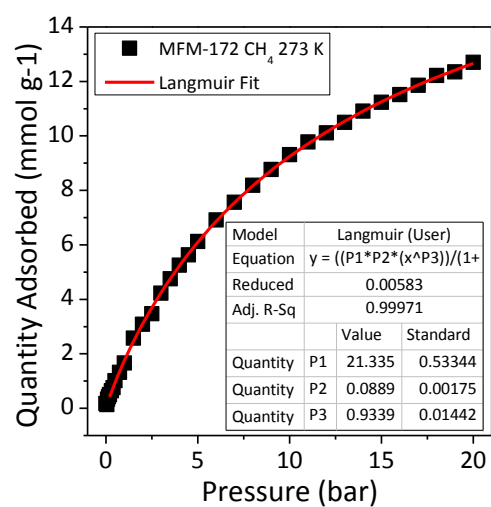
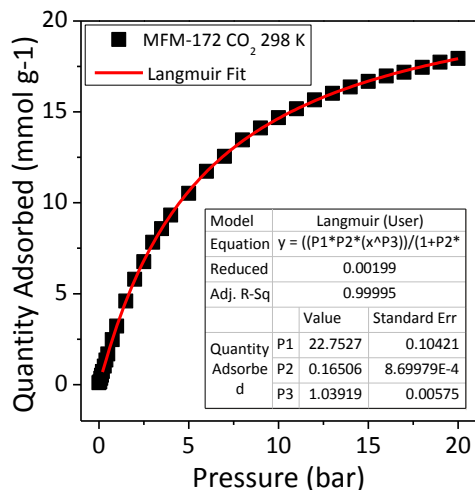
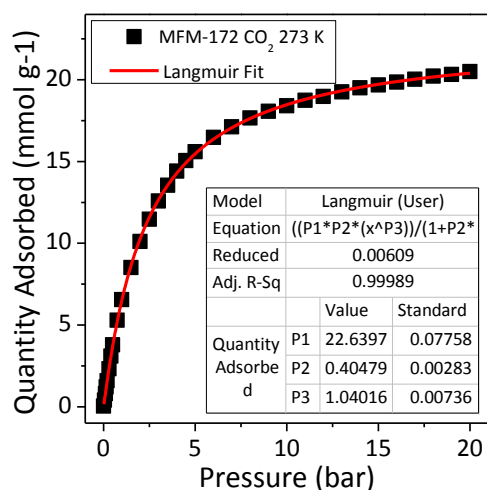


Figure 7.23: Langmuir fitting of N₂, CO₂, CH₄, C₂H₄ and C₂H₆ adsorption isotherms of MFM-171 at 273 K and 298 K.





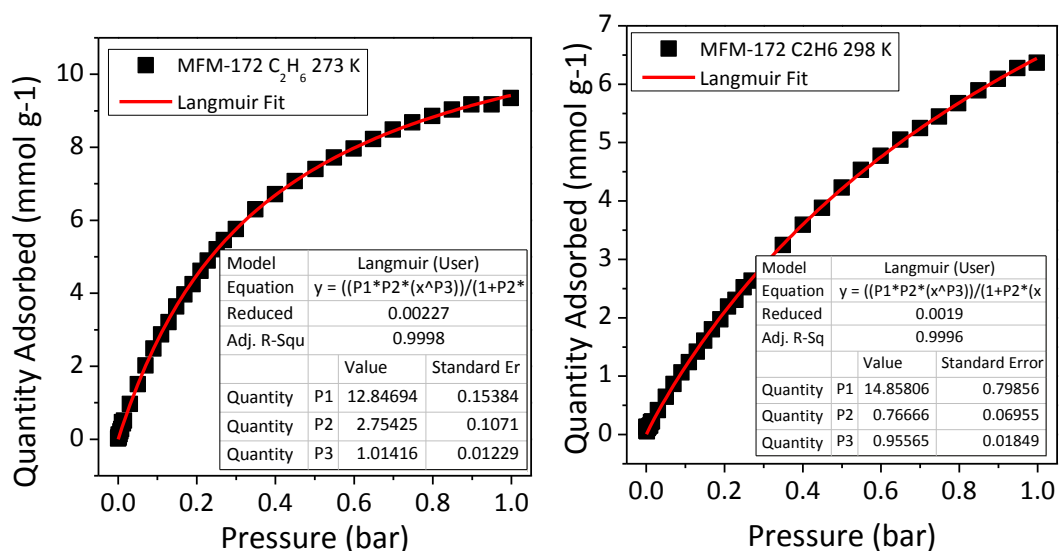
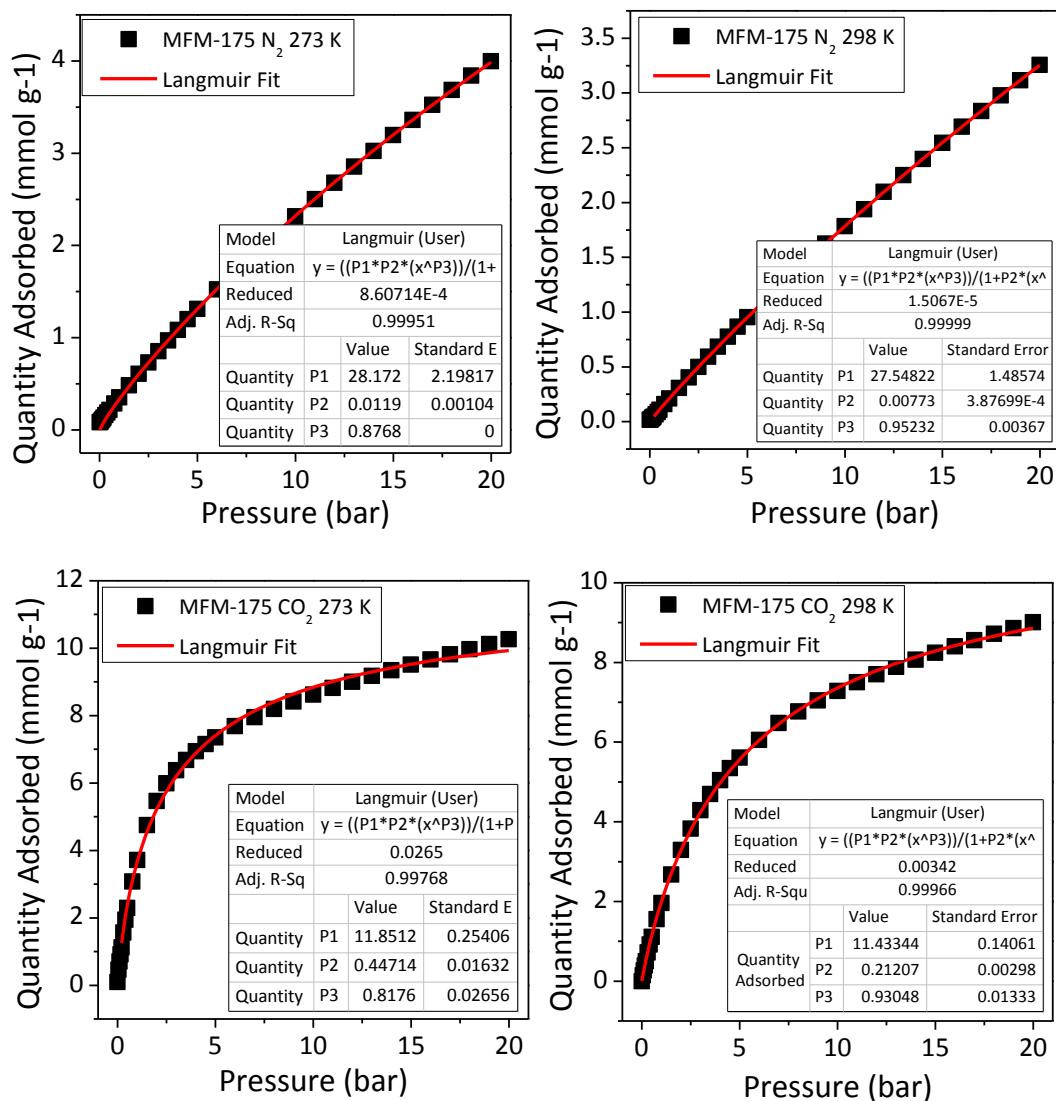


Figure 7.24: Langmuir fitting of N₂, CO₂, CH₄, C₂H₄ and C₂H₆ adsorption isotherms of MFM-172 at 273 K and 298 K.



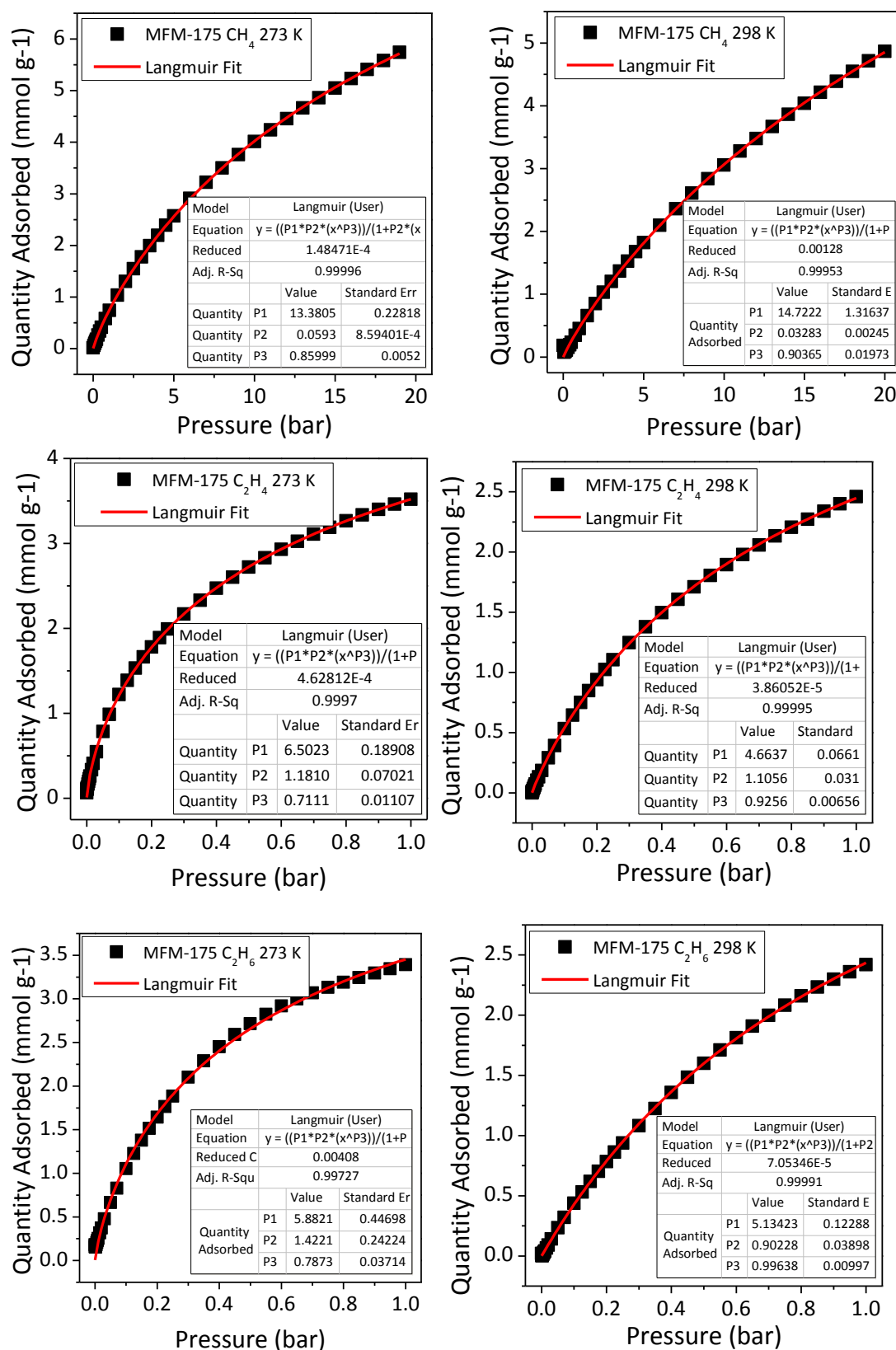
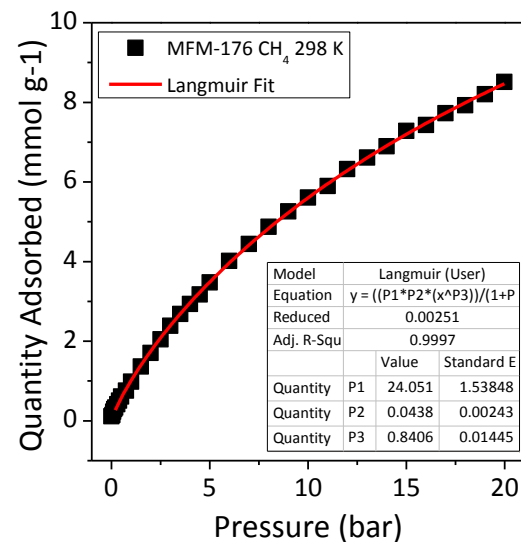
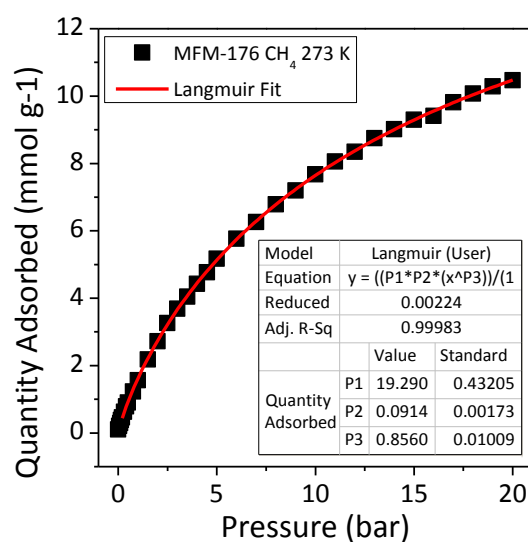
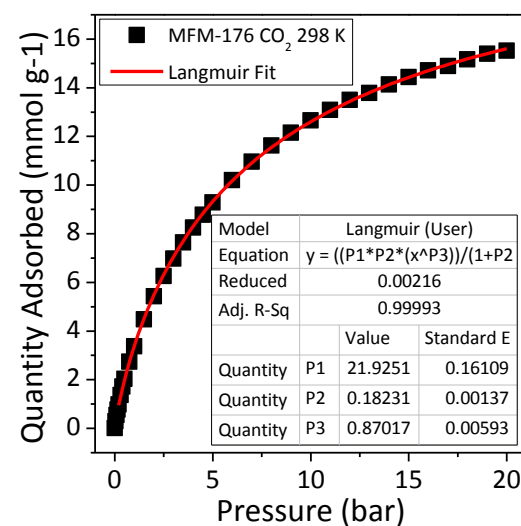
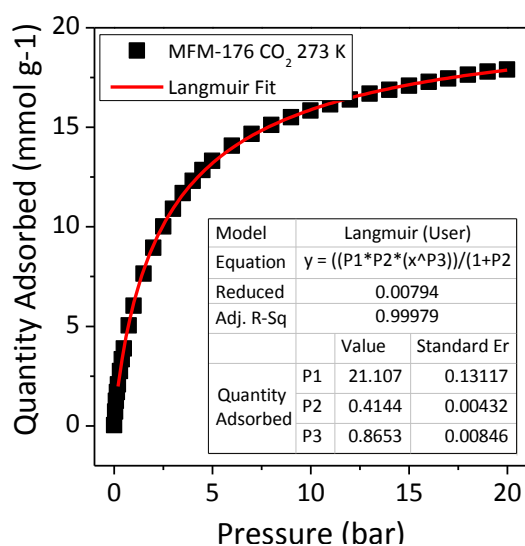
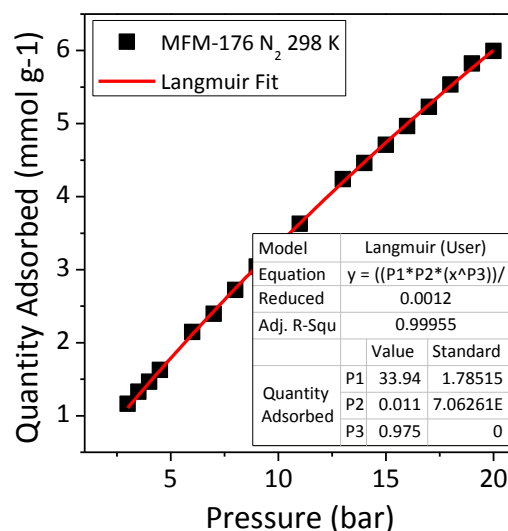
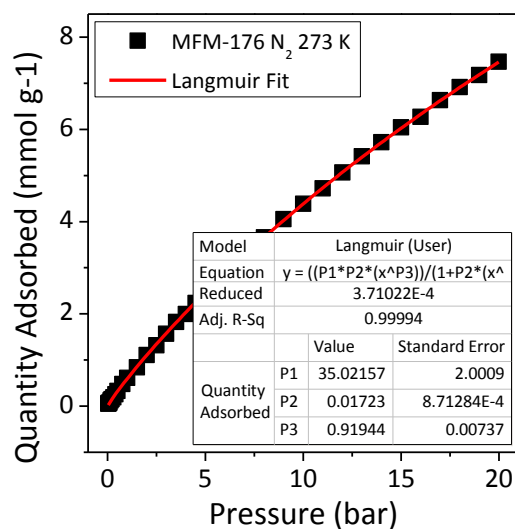


Figure 7.25: Langmuir fitting of N₂, CO₂, CH₄, C₂H₄ and C₂H₆ adsorption isotherms of MFM-175 at 273 K and 298 K.



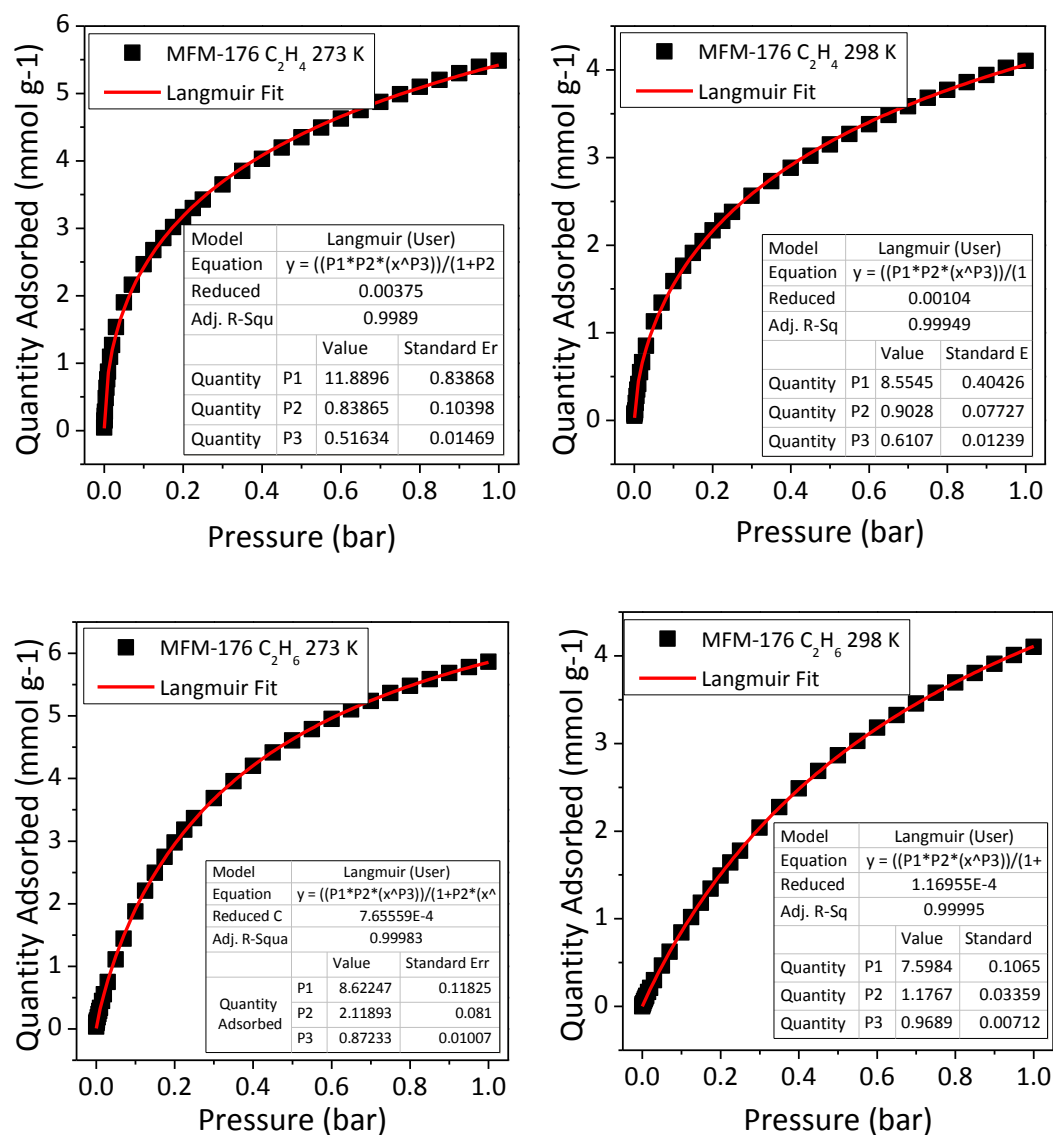


Figure 7.26: Langmuir fitting of N₂, CO₂, CH₄, C₂H₄ and C₂H₆ adsorption isotherms of MFM-176 at 273 K and 298 K.

7.2.4 Fitting of CO₂ ν_2 bending mode in IR spectra of MFM-170

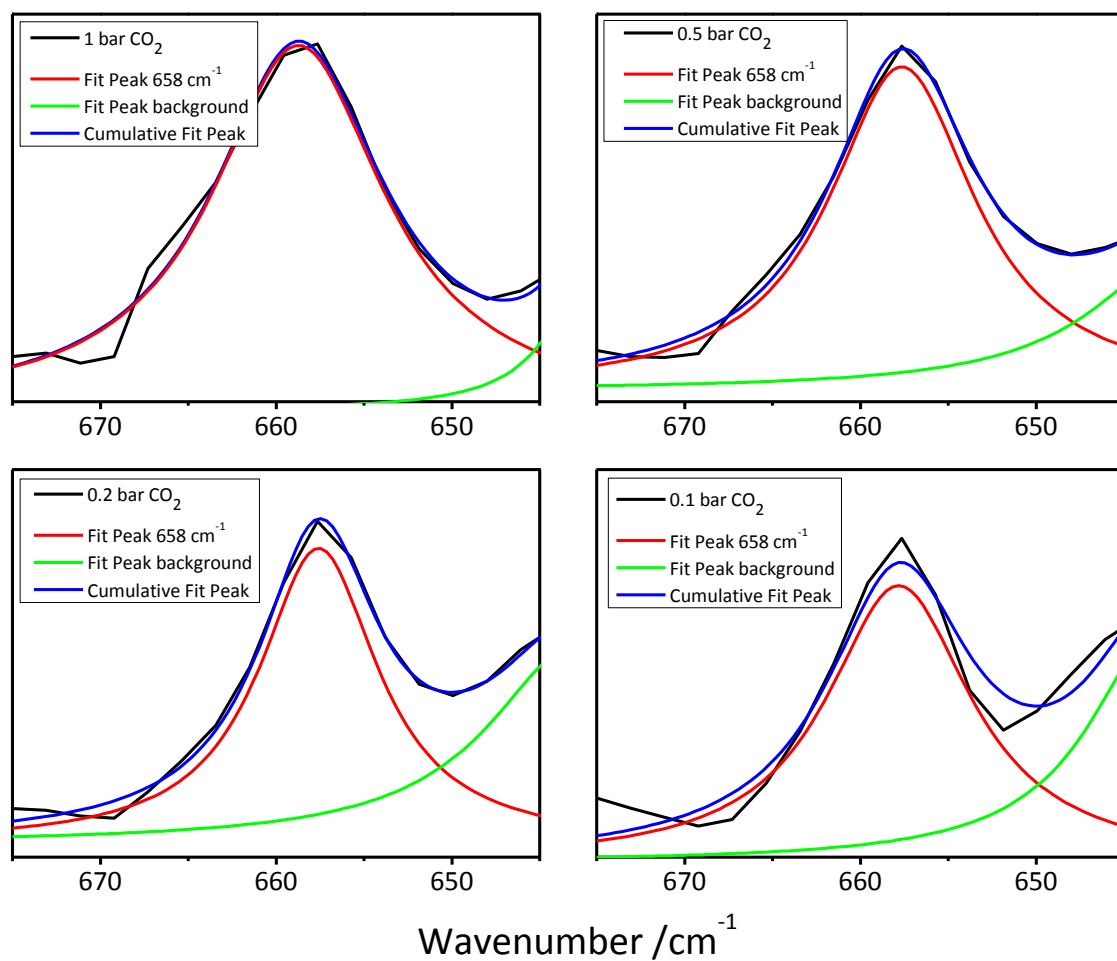


Figure 7.27: Fitting of the IR band at 658 cm⁻¹ pertaining to the ν_2 bending mode of adsorbed CO₂ within MFM-170.

Table 7.2: Fitting parameters for the ν_2 bending mode of adsorbed CO₂ in MFM-170 at increasing partial pressures of CO₂.

	0.1 bar CO ₂	0.2 bar CO ₂	0.5 bar CO ₂	1 bar CO ₂
Peak Position /cm ⁻¹	657.8	657.6	657.6	658.7
FWHM	10	8.2	10.0	11.9
Peak Area	1.8	2.5	5.9	10.6

7.2.5 Crystallography Tables

	MFM-170·solv	MFM-171·solv	MFM-172·solv	MFM-173·solv
Chemical formula	0.04(C ₇₉₂ H ₄₀₈ Cu ₄₈ N ₂₄ O ₂₁₆)	0.04(C ₇₆₈ H ₃₈₄ Cu ₄₈ N ₄₈ O ₂₁₆)	0.04(C ₈₁₆ H ₅₂₈ Cu ₄₈ N ₂₄ O ₂₁₆)	0.04(C ₈₁₆ H ₃₈₄ Cu ₄₈ N ₂₄ O ₂₆₄)
M_r	698.55	1121.09	1154.18	741.56
Crystal system, space group	Cubic, <i>Im3m</i>	Cubic, <i>Im3m</i>	Cubic, <i>Im3m</i>	Cubic, <i>Im3m</i>
Temperature (K)	120	120	120	120
a (Å)	33.4733 (3)	33.37315 (13)	33.4016 (2)	33.2925 (3)
V (Å ³)	37505.4 (9)	37169.9 (3)	37265.1 (4)	36901.1 (10)
Z	24	24	24	24
Radiation type	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$	Synchrotron
μ (mm ⁻¹)	1.08	1.39	1.38	0.668
Crystal size (mm)	0.18 × 0.13 × 0.13	0.16 × 0.14 × 0.11	0.10 × 0.08 × 0.04	0.08 × 0.08 × 0.08
Data collection				
Diffractometer	GV1000, Atlas	GV1000, Atlas	GV1000, Atlas	Rigaku Saturn724+
Absorption correction	Gaussian	Gaussian	Gaussian	None
$T_{\min}$, $T_{\max}$	0.994, 0.996	0.995, 0.997	0.997, 0.998	n/a
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	41322, 3598, 3442	45900, 3536, 3207	39869, 3497, 2750	240402, 6293, 1893
R_{int}	0.023	0.030	0.051	0.621
$(\sin \theta/\lambda)_{\max}$ (Å ⁻¹)	0.625	0.625	0.623	0.765
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.060, 0.168, 1.09	0.062, 0.184, 1.04	0.070, 0.239, 1.10	0.1596, 0.3610, 1.022
No. of reflections	3598	3536	3497	6293
No. of parameters	135	135	146	146
No. of restraints	138	138	159	144
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	1.40, -0.75	1.24, -0.87	1.40, -0.63	1.460, -0.469

	MFM-175·solv
Chemical formula	0.04(C ₆₀ 0 H ₂₆₄ Cu ₄₈ N ₁₆₈ O ₂₁₆)
M_r	680.49
Crystal system, space group	<i>I</i> 2/ <i>m</i>
Temperature (K)	120
a (Å), b (Å), c (Å)	32.16954(16), 32.0968(2), 32.16954(16)
V (Å ³)	33216.4(3)
Z	24
Radiation type	Synchrotron
μ (mm ⁻¹)	0.738
Crystal size (mm)	0.06 × 0.08 × 0.04
Data collection	
Diffractometer	Rigaku Saturn724+
Absorption correction	None
$T_{\min}$, $T_{\max}$	n/a
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	214801, 53861, 41471
R_{int}	0.0883
$(\sin \theta/\lambda)_{\max}$ (Å ⁻¹)	0.765
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0517, 0.1751, 1.113
No. of reflections	53819
No. of parameters	1166
No. of restraints	0
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	3.333, -1.226

	MFM-176·solv
Chemical formula	0.05(C ₄₂₀ H ₂₄₀ Cu ₂₄ O ₁₂₀)
M_r	695.91
Crystal system, space group	Tetragonal, <i>P</i> 4/ <i>nmm</i>
Temperature (K)	120
a (Å) b (Å)	33.1245 (2), 31.6860 (5)
V (Å ³)	34766.9 (7)
Z	44
Radiation type	Cu $K\alpha$
μ (mm ⁻¹)	2.09
Crystal size (mm)	0.18 × 0.15 × 0.12
Data collection	
Diffractometer	GV1000, Atlas
Absorption correction	Gaussian
$T_{\min}$, $T_{\max}$	75964, 18427, 14203
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	0.043
R_{int}	0.624
$(\sin \theta/\lambda)_{\max}$ (Å ⁻¹)	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.160, 0.486, 2.08
No. of reflections	18427
No. of parameters	820
No. of restraints	869
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	1.23, -1.46

Chapter 7: Appendices

	MFM-170•(vac)	MFM-170•CO₂	MFM-171•vac	MFM-171•CO₂
Chemical formula	0.04(C ₇₉₂ H ₄₀₈ Cu ₄₈ N ₂₄ O _{196.68})	0.04(C ₇₉₂ H ₄₀₈ Cu ₄₈ N ₂₄ O _{214.07})·0.88(CO ₂)	0.04(C ₇₆₈ H ₃₈₄ Cu ₄₈ N ₄₈ O ₂₁₆)	0.04(C ₇₆₈ H ₃₈₄ Cu ₄₈ N ₄₈ O ₂₁₆)·3.58(CO ₂)
<i>M_r</i>	685.67	735.92	699.55	877.51
Crystal system, space group	Cubic, <i>Im3m</i>	Cubic, <i>Im3m</i>	Cubic, <i>Im3m</i>	Cubic, <i>Im3m</i>
Temperature (K)	423	273	243	95
<i>a</i> (Å)	33.365 (4)	33.386 (4)	33.3121 (10)	33.3466 (7)
<i>V</i> (Å ³)	37142 (13)	37212 (13)	36966 (3)	37081 (1)
<i>Z</i>	24	24	24	24
Radiation type	Mo <i>Kα</i>	Mo <i>Kα</i>	Mo <i>Kα</i>	Mo <i>Kα</i>
μ (mm ⁻¹)	0.71	0.72	0.72	0.72
Crystal size (mm)	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.1	0.10 × 0.08 × 0.07
Data collection				
Diffractometer	Bruker D8 diffractometer	Bruker D8 diffractometer	SuperNova-Duo, Atlas	SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Gaussian	Gaussian	Multi-scan	Gaussian
<i>T_{min}</i> , <i>T_{max}</i>	0.535, 0.745	0.542, 0.745	0.825, 1.000	0.908, 0.925
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	91446, 1910, 1602	91576, 1910, 1643	28849, 3094, 1822	64154, 4235, 2656
<i>R_{int}</i>	0.147	0.107	0.223	0.156
(sin θ/λ) _{max} (Å ⁻¹)	0.502	0.501	0.595	0.672
Refinement				
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.044, 0.100, 1.14	0.053, 0.156, 1.14	0.084, 0.237, 1.04	0.100, 0.340, 1.07
No. of reflections	1910	1910	3094	4235
No. of parameters	136	161	135	172
No. of restraints	138	151	138	156
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.26, -0.42	0.47, -0.57	1.71, -2.13	1.57, -2.92

7.2.6 References

- 1 G. M. Sheldrick, *Acta. Crystallogr. Sect. A.*, 2008, **64**, 112.
- 2 A. L. Spek, *Acta. Crystallogr. Sect. D*, 2009, **65**, 148.
- 3 A. Gupta, S. Chempath, M. J. Sanborn, L. A. Clark and R. Q. Snurr, *Mol. Simulations*, 2003, **29**, 29–46.
- 4 W. L. Jorgensen, D. S. Maxwell and J. Tirado-Rives, *J. Am. Chem. Soc.*, 1996, **118**, 11225–11236.
- 5 A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard and W. M. Skiff, *J. Am. Chem. Soc.*, 1992, **114**, 10024–10035.
- 6 J. J. Potoff, J. R. Errington and A. Z. Panagiotopoulos, *Mol. Phys.*, 1999, **97**, 1073–1083.
- 7 C. E. Wilmer, K. C. Kim and R. Q. Snurr, *J. Phys. Chem. Lett.*, 2012, **3**, 2506–2511.