

Design, Synthesis and Analysis of Isoreticular, 2-Periodic, Co(II)/(Mn(II) Mixed- and Zn(II) Single-Ligand Metal-Organic Frameworks For Sorption of Energy- and Environmentally- Relevant Molecules

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Thesis presented for the degree of

DOCTOR OF PHILOSOPHY

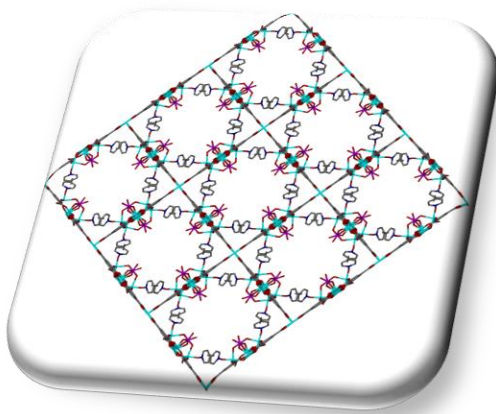
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Abbreviations

Experimental techniques

DSC – differential scanning calorimetry

HSM – hot stage microscopy

TGA – thermogravimetric analysis

Chemical compounds

bppdo – 1,3-bis(4-pyridyl)propane-*N,N'*-dioxide

H₂ia – isophthalic acid

H₂hfipbb – 4,4'-(hexafluoroisopropylidene)bis(benzoic acid)

Solvents

DMA – *N,N'*-dimethylacetamide

DMF – *N,N'*-dimethylformamide

EtOH – ethanol

MeOH - methanol

Crystallographic terms

ASU – asymmetric unit

BET – Brunauer-Emmett-Teller

CSD – Cambridge structural database

MOF – metal-organic framework

Q_{st} – isosteric heat of adsorption

RMS – root-mean-square

SBU – secondary building unit

SCSC – single-crystal-to-single-crystal

SCXRD – single crystal X-ray diffraction

sof – site occupancy factor

VT-SCXRD – variable-single crystal X-ray diffraction

PXRD – powder X-ray diffraction

VT-PXRD – variable-temperature powder X-ray diffraction

Compound codes

The synthesised metal-organic compounds are designated as MOF **1 – 6**, with these designations being unrelated to the numbering or naming conventions of MOFs published in the literature.

MOF **1** - $[\text{Co}_3(\text{ia})_3(\text{bppdo})(\text{MeOH})]_n \cdot n(\text{DMF})$

MOF **2** - $[\text{Mn}_3(\text{ia})_3(\text{bppdo})(\text{MeOH})]_n \cdot n(\text{DMF})$

MOF **3** - $[\text{Zn}(\text{hfipbb})(\text{MeOH})]_n \cdot n(\text{MeOH})_{0.5}$

MOF **4** - $[\text{Zn}(\text{hfipbb})(\text{EtOH})]_n \cdot n(\text{EtOH})_{0.5}$

MOF **5** - $[\text{Zn}_2(\text{hfipbb})_2(\text{DMF})_2]_n \cdot n(\text{DMF})_4$

MOF **6** - $[\text{Zn}_4(\text{hfipbb})_4(\text{DMA})_4]_n \cdot n(\text{DMA})_8 \cdot n(\text{H}_2\text{O})$

MOF **1'** - $[\text{Co}_3(\text{ia})_3(\text{bppdo})(\text{MeOH})]_n \cdot n(\text{DMF})$ desolvated - $[\text{Co}_3(\text{ia})_3(\text{bppdo})]_n$

MOF **2'** - $[\text{Mn}_3(\text{ia})_3(\text{bppdo})(\text{MeOH})]_n \cdot n(\text{DMF})$ desolvated - $[\text{Mn}_3(\text{ia})_3(\text{bppdo})]_n$

MOF **3'** - $[\text{Zn}(\text{hfipbb})(\text{MeOH})]_n \cdot n(\text{MeOH})_{0.5}$ desolvated - $[\text{Zn}(\text{hfipbb})]_n$

MOF **4'** - $[\text{Zn}(\text{hfipbb})(\text{EtOH})]_n \cdot n(\text{EtOH})_{0.5}$ desolvated - $[\text{Zn}(\text{hfipbb})]_n$

MOF **5'** - $[\text{Zn}_2(\text{hfipbb})_2(\text{DMF})_2]_n \cdot n(\text{DMF})_4$ desolvated - $[\text{Zn}_2(\text{hfipbb})_2]_n$

MOF **6'** - $[\text{Zn}_4(\text{hfipbb})_4(\text{DMA})_4]_n \cdot n(\text{DMA})_8 \cdot n(\text{H}_2\text{O})$ desolvated - $[\text{Zn}_4(\text{hfipbb})_4]_n$

MOF **1W** - $[\text{Co}_3(\text{ia})_3(\text{bppdo})(\text{MeOH})]_n \cdot n(\text{DMF})$ desolvated and air exposed - $[\text{Co}_3(\text{ia})_3(\text{bppdo})(\text{H}_2\text{O})_2]_n \cdot n(\text{H}_2\text{O})$

MOF **2W** - $[\text{Mn}_3(\text{ia})_3(\text{bppdo})(\text{MeOH})]_n \cdot n(\text{DMF})$ desolvated and air exposed - $[\text{Mn}_3(\text{ia})_3(\text{bppdo})(\text{H}_2\text{O})_2]_n$

MOF **3W** - $[\text{Zn}(\text{hfipbb})(\text{MeOH})]_n \cdot n(\text{MeOH})_{0.5}$ water exchanged - $[\text{Zn}(\text{hfipbb})(\text{H}_2\text{O})]_n$

Abstract

The study of porous materials, particularly Metal-Organic Frameworks (MOFs), has garnered significant attention due to their tunable structures and potential for diverse applications. MOFs, constructed from metal ions or clusters and organic ligands, offer structural versatility where the choice of ligand influences pore size, geometry, flexibility, and adsorption properties. Mixed-ligand MOFs, incorporating two or more distinct ligands, enhance structural complexity and enable tuning of pore features in multiple dimensions, making them highly suitable for gas sorption applications. This study reports the design, synthesis, and characterisation of novel 2-periodic, isorecticular Co(II)/Mn(II) mixed-ligand and Zn(II) single-ligand MOFs. The mixed-ligand systems, synthesised using isophthalic acid (H₂ia) and 1,3-bis(4-pyridyl)propane-*N,N'*-dioxide (bppdo), yielded isorecticular frameworks with formulae $[\text{Co}_3(\text{ia})_3(\text{bppdo})(\text{MeOH})]_n \cdot n(\text{DMF})$ (**1**) and $[\text{Mn}_3(\text{ia})_3(\text{bppdo})(\text{MeOH})]_n \cdot n(\text{DMF})$ (**2**). The single-ligand systems, constructed using 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (H₂hfipbb), produced two pairs of MOFs: doubly interpenetrated frameworks $[\text{Zn}(\text{hfipbb})(\text{MeOH})]_n \cdot n(\text{MeOH})_{0.5}$ (**3**) and $[\text{Zn}(\text{hfipbb})(\text{EtOH})]_n \cdot n(\text{EtOH})_{0.5}$ (**4**) and non-interpenetrated frameworks $[\text{Zn}_2(\text{hfipbb})_2(\text{DMF})_2]_n \cdot n(\text{DMF})_4$ (**5**) and $[\text{Zn}_4(\text{hfipbb})_4(\text{DMA})_4]_n \cdot n(\text{DMA})_8 \cdot n(\text{H}_2\text{O})$ (**6**). The ligands' unique rigidity and functionality yielded MOFs with varying porosity and structural flexibilities. Desolvated studies of the mixed-ligand MOFs revealed drastic void space reductions (to 3.7 and 5.7% for **1'** and **2'**, respectively, at 298 K) compared to the as-synthesised structures (potential void spaces of 21.6 and 22.3% for **1** and **2**, respectively, at 298 K). Despite inaccessible void spaces at 195 K, significant CO₂ sorption at this temperature indicated structural transformations enabling adsorption. Water vapour sorption at 298 K induced similar transformations, as confirmed by single-crystal X-ray diffraction, showcasing the dynamic adaptability of these frameworks.

For the single-ligand MOFs, void space ranged from 12 to 25% of the unit cell volume, with notable differences between interpenetrated and non-interpenetrated structures. Comparison with Cu-based counterparts from the literature highlighted that the Zn-based MOFs exhibited superior N₂ and H₂ adsorption due to higher crystallinity and stability upon desolvation. However, Cu-based MOFs displayed stronger CO₂

adsorption interactions, with two-step adsorption isotherms and higher Q_{st} values (up to 31.8 kJ mol^{-1}), reflecting greater framework flexibility. Water vapor sorption studies emphasised the stronger interaction of Cu-based MOFs with unsaturated Cu(II) metal sites. These findings underscore the potential of Zn-based MOFs for gas storage and the dynamic structural responses of the mixed-ligand frameworks.

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Chapter 1:

Introduction

This chapter provides a comprehensive foundation for understanding metal-organic frameworks (MOFs) by exploring key concepts such as supramolecular chemistry, crystal engineering, reticular synthesis, interpenetration, and single-crystal-to-single-crystal transformations. It compares MOFs to other solid adsorbents like zeolites and activated carbon, emphasising the advantages of MOFs, such as their tunable porous structures, high surface area, and functionalisation potential. Additionally, the chapter discusses the importance of porosity in relation to MOF applications, such as gas and water vapour sorption, and rationalises the use of mixed ligands in the synthesis of the studied compounds. It concludes with the motivation and objectives of the research project.

1.1. Supramolecular Chemistry and Crystal Engineering

The term "supramolecular chemistry" was introduced by the Nobel Prize-winning chemist Jean-Marie Lehn to describe the study of molecular interactions and assemblies, thus the study of structures beyond the level of individual molecules.^{1,2,3} Unlike traditional covalent bonding, where atoms share electrons to form stable bonds, supramolecular interactions involve non-covalent, intermolecular forces such as van der Waals forces, hydrogen bonding, π - π stacking, and electrostatic interactions.⁴ In supramolecular chemistry, molecules act as building blocks that can self-assemble into more complex and functional chemical systems, often resembling natural processes seen in biological systems.^{3,5,6} Supramolecular chemistry has far-reaching applications across various scientific disciplines, including host-guest chemistry, materials science, biology, nanotechnology, and drug development.^{4,7,8,9}

Crystal engineering is closely associated with the principles derived from supramolecular chemistry.¹⁰ The term "crystal engineering" was first coined by R. Pepinsky in 1955 but is more commonly associated with G. M. J. Schmidt, who, in 1964, carried out the first modern application of this concept.^{11,12,13} Schmidt investigated the solid-state photochemical reactivity of *trans*-cinnamic acids and other alkenes, demonstrating how molecular arrangement within a crystal lattice influences chemical reactivity. Desiraju defines crystal engineering as "the understanding of intermolecular interactions in the context of crystal packing and in the utilisation of such understanding in the design of new solids with desired physical and chemical properties".¹⁴ Crystal engineering is characterized by three aspects, comprising (i) the study of intermolecular interactions, (ii) the study of packing modes with which these interactions are associated to design a strategy for crystal construction and (iii) the

study of crystal properties. These aspects represent the essence of crystal engineering, addressing its purpose, methodology, and motivation.

1.1.1. Porous Materials

Porous materials have garnered significant attention from physicists, chemists, and materials scientists due to their ability to create nanometer-sized spaces and their broad applications in separation, storage, and heterogeneous catalysis.¹⁵ Before the mid-1990s, porous materials were predominantly classified into two main categories: inorganic and carbon-based materials.

Among inorganic porous solids, zeolites and aluminophosphates are the most prominent subclasses, each with distinct structural and functional properties. Zeolites are crystalline aluminosilicates with well-defined microporous structures, formed by a 3D framework of SiO_4 and AlO_2 tetrahedra linked through shared oxygen atoms (Figure 1.1).¹⁶ The removal of water molecules from their hydrated structure reveals robust frameworks, with pore sizes and arrangements determined by the surrounding polyhedral geometry.¹⁵ These properties make zeolites highly effective in ion exchange, gas separation and catalytic processes.^{15,17}

Aluminophosphates (AlPO_4s) are composed of tetrahedra formed by Al^{3+} and P^{+5} ions linked through oxygen atoms, forming a 3D neutral framework with molecular-sized channels.^{15,18} Unlike zeolites, aluminophosphates often exhibit unique crystal structures and have inspired the development of related crystalline oxides, including silicoaluminophosphates, metallophosphates, and porous chalcogenides.^{15,19,20,21}

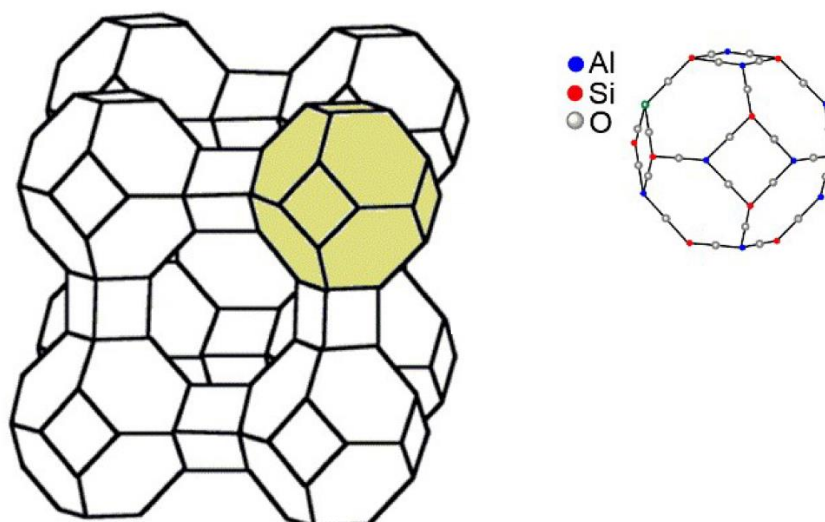


Figure 1.1. Illustration of the structural framework of a specific zeolite.²²

Activated carbons, another important class of porous materials, are characterised by high porosity and specific surface areas but lack structural regularity.^{15,23} They consist of disordered networks of defective hexagonal carbon layers, cross-linked by aliphatic bridging groups.¹⁵ Functional groups and heteroelements incorporated into these structures enhance their utility in gas storage, filtration, and adsorptive separation. Activated carbons are typically derived from pyrolysis of precursors such as coal, pitch, biomass, or synthetic polymers, with the latter offering better control over structure and composition.²⁴ However, their structural non-uniformity and limited tunability restrict their applicability compared to advanced porous materials.

1.1.2. Metal-Organic Frameworks (MOFs)

Building on the success of zeolites and activated carbons, porous coordination polymers (PCPs) emerged as a new class of porous materials with highly regular structures, exceptional porosity, and customisable frameworks.^{15,25} PCPs are

synthesised through the coordination of metal ions with organic linkers under mild conditions.¹⁵

Early examples of PCPs include transition metal cyanide compounds such as Hofmann clathrates, Prussian blue structures, and Werner complexes.^{15,26} These frameworks, built from cyanide linkages between tetrahedral or octahedral metal units, were recognised for their reversible adsorption of small molecules.¹⁵

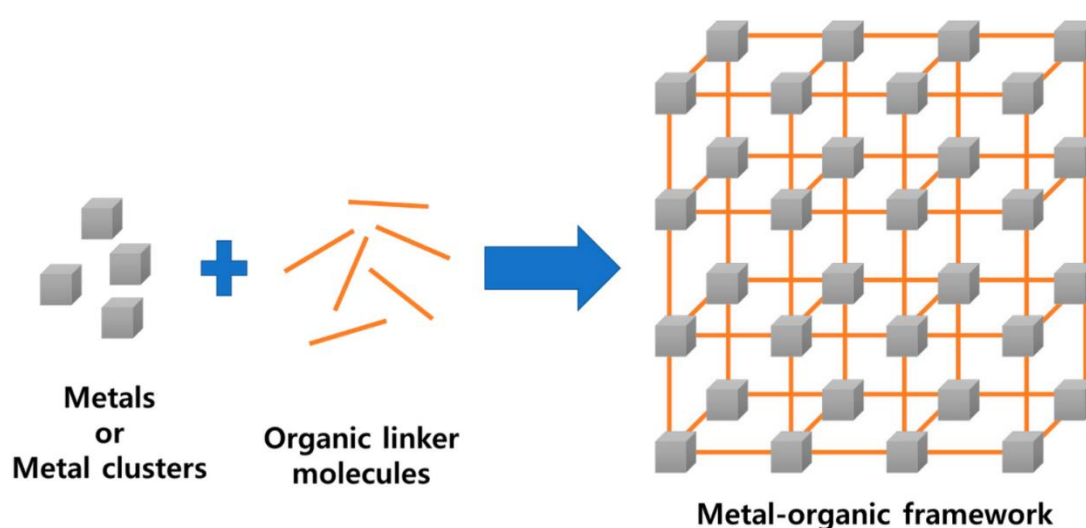


Figure 1.2. The assembly of a metal-organic framework from its constituents. Reprinted (adapted) with permission from Felix Sahayaraj, A.; Joy Prabu, H.; Maniraj, J.; Kannan, M.; Bharathi, M.; Diwahar, P.; Salamon, J. *Metal-organic frameworks (MOFs): the next generation of materials for catalysis, gas storage, and separation. J. Inorg. Organomet. Polym. Mater.* **2023**, 33, 1757–1781. Copyright (2023) Macmillan Magazines.²⁷

Although PCPs incorporating metal-organic units gained renewed attention in the 1990s, a major limitation of these early materials was their inability to maintain permanent porosity.²⁶ Structural rearrangements, or even complete collapse of the framework, often occurred upon the removal or exchange of guest molecules.

To overcome these challenges, research in the 1990s focused on designing more robust and permanently porous materials. This led to the development of what are now commonly referred to as metal-organic frameworks (MOFs) – a term introduced by Omar Yaghi in 1995.^{28,29} According to the IUPAC definitions, “MOFs are a coordination network with organic ligands containing potential voids” (Figure 1.2).³⁰ MOFs enable precise control over geometry, connectivity, and spatial arrangement.²⁸ A major milestone in the development of MOFs occurred in 1999 with the publication of two notable structures: HKUST-1 ($[\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3]_n$, BTC = 1,3,5-benzenetricarboxylate) and MOF-5 ($[\text{Zn}_4\text{O}(\text{BDC})_3]_n \cdot n(\text{DMF})_8 \cdot n(\text{C}_6\text{H}_5\text{Cl})$, BDC = 1,4-benzenedicarboxylate, DMF = *N,N'*-dimethylformamide) (Figure 1.3).^{31,32,33} These MOFs, in their as-synthesised forms, include coordinated solvent molecules in

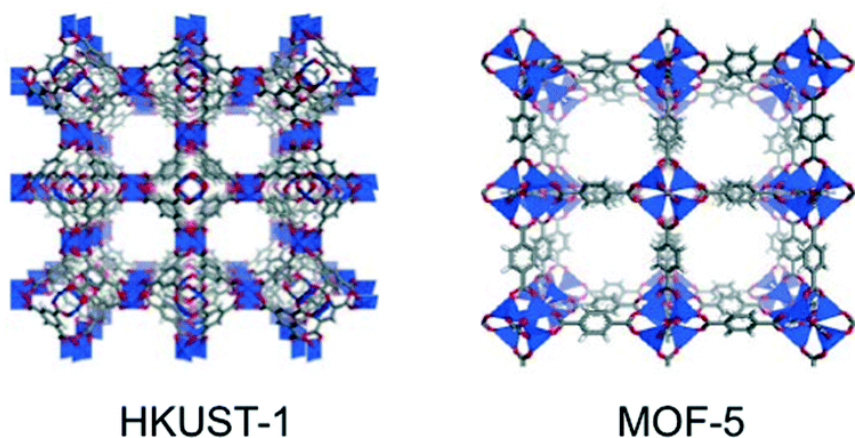


Figure 1.3. Crystal structures of HKUST-1 and MOF-5. *Figure reprinted (adapted) with permission from Allendorf, M. D.; Stavila, V. Crystal engineering, structure-function relationships, and the future of metal–organic frameworks. CrystEngComm* **2015**, 17, 229-246. Copyright (2015) Royal Society of Chemistry.³¹

HKUST-1 and uncoordinated solvents in MOF-5, which can be removed without compromising the structural integrity of the frameworks. Both materials exhibit

nanoscale porosity, high thermal stability, and the potential for chemical functionalisation of their pores. MOF-5 set a record at the time with a Langmuir surface area of approximately $2\,900\text{ m}^2\text{ g}^{-1}$ based on nitrogen adsorption, surpassing other porous materials such as zeolites.^{31,33} The exceptional properties of HKUST-1 and MOF-5 sparked widespread enthusiasm for MOFs, especially in applications such as hydrogen storage, where there was significant demand for advanced materials.³¹ Since the discovery of HKUST-1 and MOF-5, thousands of MOFs with diverse structures, compositions, and properties have been synthesised.^{34,35,36}

1.1.2.1. Properties and Applications

Scientists in academia and industry find MOFs attractive due to their tunable properties, which they can finely adjust by altering the metal ions, ligands, and synthesis conditions.²⁷ MOFs are highly crystalline materials with ultrahigh porosities (up to 90%) and exceptionally high surface areas (up to $10\,000\text{ m}^2\text{ g}^{-1}$).^{37,27} They feature tunable pore sizes and surface chemistry, allowing customisation based on specific applications.³⁸ MOFs are generally stable under various conditions, such as high temperatures (up to $500\text{ }^{\circ}\text{C}$) and exposure to diverse chemicals.^{27,39} Certain MOFs display distinctive optical and electronic properties, such as luminescence and conductivity, while others can exhibit structural flexibility, responding to external stimuli like temperature or pressure.²⁷

MOFs promise a wide range of applications due to their unique properties.³⁴ They effectively store and separate gases, especially in relation to carbon dioxide and hydrogen.⁴⁰ MOFs efficiently act as heterogeneous catalysts in various reactions, such as photocatalysis for dye degradation and electrocatalysis for hydrogen production.^{41,42} Biomedical applications of MOFs are also significant, including drug

delivery, MRI contrast agents, and radiotherapy.^{34,43,44,45} Additionally, MOFs can eliminate and separate harmful chemicals, enhancing environmental safety.⁴⁶ Furthermore, MOFs excel in water harvesting technologies, outperforming other alternative materials in arid climates due to their exceptional adsorption properties.^{34,47}

1.1.2.2. Nomenclature

MOFs are named using various conventions. The abbreviation MOF generally refers to the class of compounds, but when followed by a numerical identifier, it identifies a specific MOF, such as MOF-74 ($[\text{Zn}_2(\text{DOT})(\text{DMF})_2(\text{H}_2\text{O})_2]_n$), (DOT = 2,5-dihydroxy-1,4-benzenedicarboxylate) (DMF = *N,N'*-dimethylformamide), MOF-101 ($[\text{Cu}_2(\text{BDC-Br})_2(\text{H}_2\text{O})_2]_n$) (BDC-Br = 2-bromo-1,4-benzenedicarboxylate), and MOF-253 ($[\text{Al}(\text{OH})(\text{BPYDC})]_n$) (BPYDC = 2,2'-bipyridine-5,5'-dicarboxylate).^{48,49} MOFs sharing the same connectivities are isorecticular and may therefore be named according to the IRMOF (isorecticular metal-organic framework) naming convention, such as IRMOF-1 ($[\text{Zn}_4\text{O}(\text{BDC})_3\cdot 7(\text{DEF})\cdot 3\text{H}_2\text{O}]_n$) (BDC = 1,4-benzenedicarboxylate) (DEF = *N,N'*-diethylformamide) and IRMOF-16 ($[\text{Zn}_4\text{O}(\text{TPDC})_3\cdot 17(\text{DEF})\cdot 2\text{H}_2\text{O}]_n$) (TPDC = *p*-terphenyl-4,4'-dicarboxylate).⁴⁹ Some MOFs are named based on where they were first synthesised, e.g., UiO-66 ($[\text{Zr}_5\text{O}_5(\text{BDC})_5]_n$), UiO-67 ($[\text{Zr}_5\text{O}_5(\text{BPDC})_5]_n$) (BPDC = biphenyl-4,4'-dicarboxylic acid), UiO-68 ($[\text{Zr}_5\text{O}_5(\text{TPDC})_5]_n$) (first synthesised at Universitetet i Oslo), MIL-53 ($[\text{Al}(\text{OH})(\text{BDC})]_n$) (from the Materials of Institut Lavoisier), HKUST-1 (MOF-199) ($[\text{Cu}_3(\text{BTC})_2]_n$) (BTC = 1,3,5-benzenetricarboxylate) (from Hong Kong University of Science and Technology), and LIC-1 ($[\text{Gd}_2(\text{BDC-NH}_2)_3(\text{DMF})_4]_n$) (Leiden Institute of Chemistry).^{48,49} Another subset of MOFs, with a topology similar to zeolites, consists of nitrogen-containing tetrahedrons

linked by imidazole rings, and are known as ZIFs (zeolitic imidazole frameworks), each distinguished by a numerical suffix.^{49,50}

1.1.2.3. Synthesis

The synthesis of MOFs involves using a variety of metals, including transition metals, alkaline earth metals, *p*-block elements, actinides, and even combinations of different metals.⁵¹ These metals (in ionic form) are connected by organic ligands, which commonly include nitrogen-containing aromatics or multitopic aromatic carboxylate anions. The metal ions in MOFs can be selected according to their abilities to adopt various oxidation states and coordination geometries, whilst organic ligands can be customised with specific functional groups.²⁷ This customisation enables the incorporation of additional chemical functionalities into the materials. The synthesis process generally involves combining metal ions with organic linkers in a suitable solvent, carried out under carefully regulated conditions of temperature, pressure, and duration. Various synthesis methods include sonochemical, conventional solution, diffusion, microwave, electrochemical, and solvothermal synthesis, as well as the iono-thermal process method (Figure 1.4).⁵² Among these, the solvothermal and microwave-assisted synthesis methods are more commonly used.²⁷

Choosing an appropriate synthesis method and adjusting reaction conditions are critical factors in controlling the morphology, structure, surface area, and physicochemical properties of the product obtained.^{27,52} For example, Jung *et al.*, compared sonochemical, conventional solvothermal, and microwave synthesis methods for the formation of MOF-177, which is formulated as $\text{Zn}_4\text{O}(\text{BTB})_2$ (BTB = 4,4',4''-benzene-1,3,5-triyl-tribenzoate).⁵³ The sonochemical method was the most efficient, completing synthesis in 40 minutes with a 95.6% yield and producing 5 – 20 μm crystals with the highest BET surface area ($4898 \text{ m}^2 \text{ g}^{-1}$) and

CO₂ adsorption capacity (1315 mg g⁻¹ at 30 bar). The solvothermal method required 48 hours, yielding 0.5 – 1.5 mm crystals with a BET surface area of 4833 m² g⁻¹ and a CO₂ adsorption capacity of 1286 mg g⁻¹ at 30 bar. The microwave method took 35 minutes, producing 5–50 µm crystals with a lower BET surface area (4197 m² g⁻¹) and CO₂ adsorption capacity (1218 mg g⁻¹ at 30 bar), with inferior crystallinity.

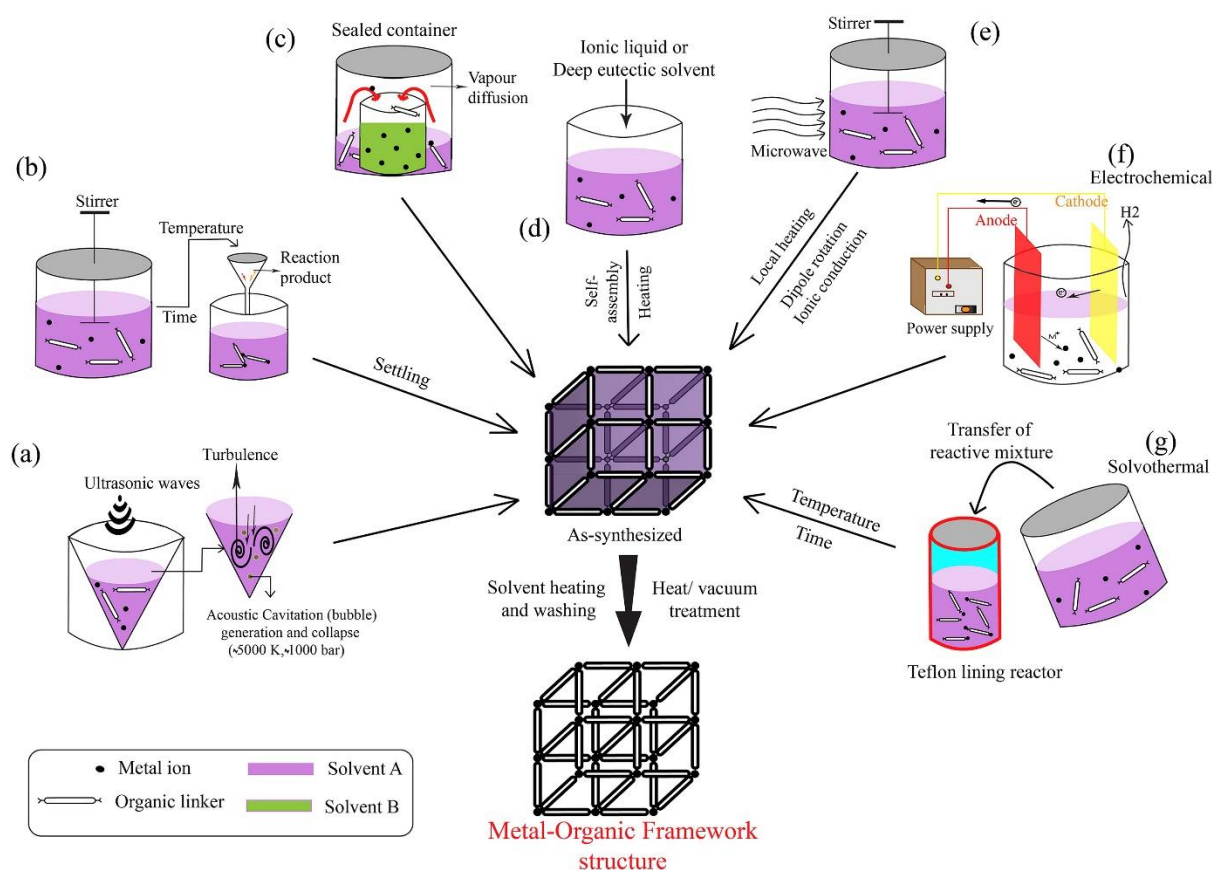
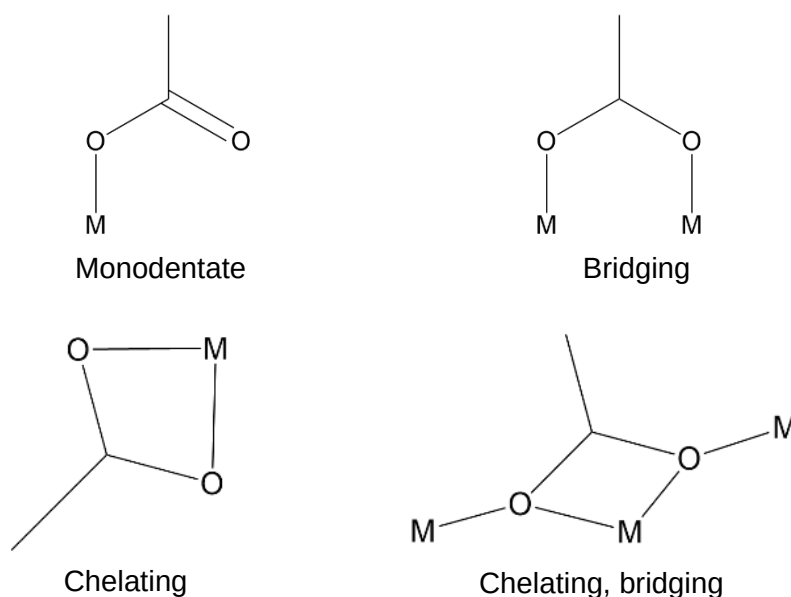


Figure 1.4. Various methods for MOF synthesis, (a) Sonochemical synthesis method, (b) Conventional solution method, (c) Diffusion synthesis method, (d) Iono-thermal process method, (e) Microwave synthesis method, (f) Electrochemical synthesis method, and (g) Solvothermal synthesis method. *Figure reprinted (adapted) with permission from Sharanyakanth, P. S.; Radhakrishnan, M. Synthesis of metal-organic frameworks (MOFs) and its application in food packaging: A critical review. Trends Food Sci. Technol. 2020, 104, 102–116. Copyright (2020) Elsevier.*⁵²

1.2. MOF Design

In the formation of the MOF coordination bonds, the organic ligands act as Lewis bases, donating their lone pair of electrons to the metal centers, which act as Lewis acids.⁵⁴ A crucial aspect of constructing MOFs is the careful selection or design of organic ligands to achieve the desired structures and functions.⁵⁵ Various polytopic organic ligands with carboxylate, pyridyl, amine, sulfonate and phosphonate donor groups are used in MOF synthesis.^{55,56} Polycarboxylates and polypyridyls are widely utilised due to their strong binding capabilities with metal ions and their adjustable lengths and geometries.⁵⁵



Scheme 1.1. Selected coordination modes of carboxylate groups.

Carboxylate groups exhibit versatile coordination modes, such as monodentate terminal or bridging, chelating, and chelating-bridging (Scheme 1.1), with each oxygen atom being a donor capable of binding to one, two, or even three metal ions, leading to diverse MOF structures and topologies.⁵⁵ Additionally, carboxylate groups form

stable coordination bonds with metal ions and therefore contribute to the high stabilities of MOFs in accordance with Pearson's hard-soft, acid-base (HSAB) principle.⁵⁷ This is further reinforced in zirconium-carboxylate MOFs, where the strong interactions between the hard acid Zr^{4+} ions and the hard base oxygen atoms in carboxylate groups form stable Zr-O clusters, resulting in high chemical and thermal stability of the MOFs.

In contrast, pyridyl-type ligands typically exhibit simpler coordination modes and weaker binding strength, often resulting in less stable MOFs than those formed with carboxylates.⁵⁵ Despite their weaker binding and charge neutrality, pyridyl ligands can contribute to the formation of MOFs that exhibit reasonable stability under certain conditions.^{57,58} For example, pyridyl ligands are classified as softer ligands, forming more stable interactions with softer metals like Zn^{2+} or Ni^{2+} and other low-valent metal cations.⁵⁷ These interactions, although classified as soft, do not imply that the frameworks are less stable. Some pyridyl-based MOFs have comparable chemical and thermal stabilities to carboxylate-based MOFs and perform better under extreme pH conditions.

Organic ligands can be classified, based on their flexibility, into rigid, semi-rigid and flexible types and based on their charge into neutral, anionic, and cationic types.^{54,59} Carboxylic acids are neutral but become negatively charged when deprotonated, facilitating interaction with positively charged metal centers.⁵⁴

1.2.1. Mixed-Ligand MOFs

MOFs may incorporate only one ligand (a single-ligand MOF) or more than one chemically distinct ligands (a mixed-ligand MOF), with the latter type often pursued to

enhance the MOF's properties imparted by their differences.⁶⁰ Mixed-ligands that have more than two types of ligands have also been observed.^{58,61} In mixed-ligand MOF design strategies, ligands with different lengths, geometries, and diverse functional groups are incorporated into MOFs to combine multiple functionalities within the same framework.⁵⁷ This approach is attractive because it allows for fine tuning and control of the internal environment and associated properties of mixed-ligand MOFs. Mixed-ligand design in MOF synthesis offers several advantages over single-ligand strategies, including the ability to regulate topology, enhance framework flexibility, and create diverse coordination modes.⁵⁸

In mixed-ligand MOF synthesis, different ligands coordinate with the metals synergistically, resulting in a cooperative interaction that inhibits the formation of single-ligand MOFs.^{58,62} One effective strategy for constructing mixed-ligand MOFs is to combine polycarboxylic acid ligands with bipyridine ligands due to the complementary nature of their acid-base interactions.^{54,63} This combination leverages the strengths of both ligand types to enhance the stability and functionality of MOFs. Neutral bipyridine ligands bind to metal ions as rod-like bidentate connectors, while polycarboxylic ligands can adopt anionic or neutral (not deprotonated) forms, providing various coordination modes with metals.⁶³

Among MOFs that utilise mixed bipyridine and carboxylic acid ligands, pillared-layer MOFs have garnered significant attention because their channel sizes can be easily adjusted by modifying the pyridyl pillar ligands or their derivatives.⁵⁴ For example, the hydrothermal reaction of terephthalic acid (H_2tp), 4,4'-bipyridine (bpy), and Zn^{2+} results in a 2-fold interpenetrated 3D¹ MOF $[Zn(tp)(bpy)]_n$, which features parallelogram-like

¹3D refers to "3-periodic" as used in this thesis.

$[\text{Zn}(\text{tp})]_n$ sheets interconnected by bpy pillars (Figure 1.5).⁶³ A range of bpy derivatives with extended and varied lengths is synthesised by incorporating spacers between the pyridyl groups of bpy.

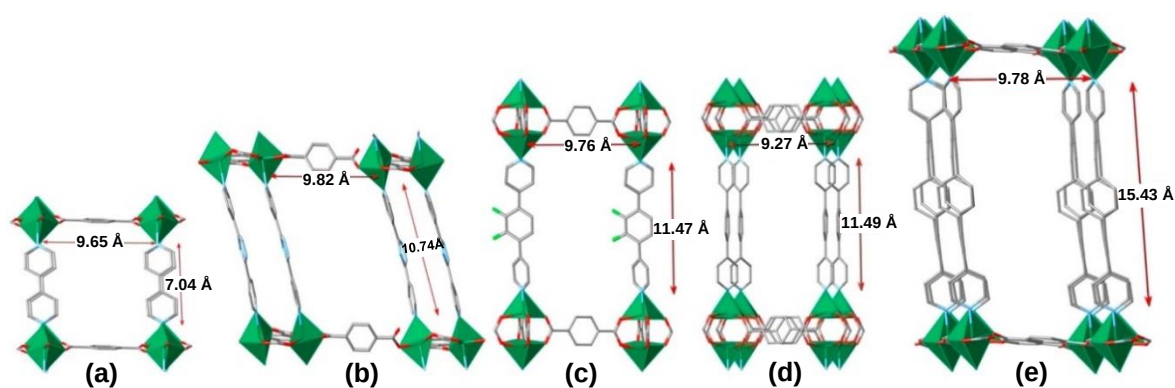


Figure 1.5. Schematic illustration of various cubic frameworks pillared by (a) 4,4'-bipyridine (bpy), (b) 1H-3,5-bis(4-pyridine)-1,2,4-triazole (4,4'-bpt), (c) 1,4-bis(4-pyridine)benzene (bpb), (d) 2,3-difluoro-1,4-bis(4-pyridine)benzene (dfbpb), and (e) 1,4-bis(4-pyridineethynyl)benzene (bpeb). *Figure reprinted (adapted) with permission from Du, M.; Li, C.; Liu, C.; Fang, S. Design and construction of coordination polymers with mixed-ligand synthetic strategy. Coord. Chem. Rev. **2013**, 257, 1282–1305. Copyright (2013) Elsevier.*⁶³

1.3. Reticular Design of MOFs

Many MOF structures are frequently discovered by chance. However, scientists have long been striving to intentionally design and assemble these structures at the molecular level.^{64,65} Over the past two decades, reticular synthesis has been extensively utilised in predicting and designing various MOF structures.^{66,67} Reticular synthesis involves assembling carefully designed rigid molecular building blocks into predetermined crystalline structures held together by strong bonds.⁶⁸ This precision has enabled scientists to predict and control the properties of the resulting MOF

structures, such as pore size, functionality, and overall architecture.⁶⁹ As a result, MOF structures can be tailored for specific applications.³⁴ The three essential elements for reticular design are building blocks, targeted nets, and isorecticular chemistry.⁶⁶

1.3.1. Building Blocks

The crystal chemistry of MOFs provides a powerful platform for tailoring desired properties and functionalities at the design stage.⁷⁰ By strategically pre-selecting building blocks, it becomes possible to encode desired structural and geometrical information that guides the formation of a targeted underlying net during the assembly process. These building blocks are broadly classified into two categories: molecular building blocks (MBBs) and supermolecular building blocks (SBBs).⁶⁶

Utilising the MBB approach has been an effective strategy for designing and constructing MOFs.^{71,72} The MBBs can serve as secondary building units (SBUs), which are described as clusters of metal (M) ions that are not connected directly through metal-metal bonds but rather indirectly through oxygen (M-O-M) and oxygen-carbon-oxygen (M-O-C-O-M) bonds.^{73,74} These SBUs are connected by the remaining organic components of the ligands to form the desired MOF structures.^{68,71}

SBUs emerged as a solution to the challenges faced by researchers in the late 1980s and 1990s when attempting to build porous coordination networks using assemblies of single metal ions and neutral donor ligands.^{65,74} These early structures aimed to accommodate guest solvent molecules but often collapsed irreversibly upon their removal due to the structural fragility of coordination geometries based on single metals.⁷⁴

The discovery and use of SBUs provided a breakthrough.⁶⁵ SBUs introduce thermodynamically and mechanically stable coordination environments by utilising chelation and the bridging of multidentate ligands, such as carboxylates and phosphates, which effectively link the SBUs and enhance the overall stability of the structures.^{65,74,75} Typically, SBUs are not directly introduced into the reaction; instead, they form in situ under specific synthetic conditions.⁷⁶ Figure 1.6 illustrates examples of common SBUs found in MOFs. The SBUs are incorporated into MOFs by linking the carboxylate carbons with organic units. They can also be linked through the replacement of terminal ligands. The effectiveness of an SBU in constructing open frameworks depends on its rigidity and the directionality of its bonding, which need to be consistently maintained throughout the assembly process.

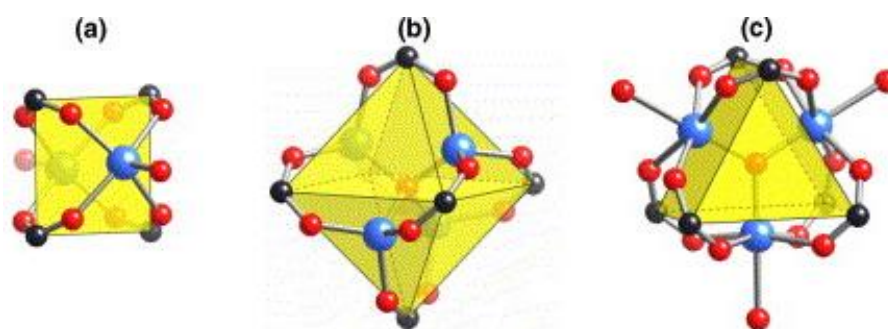


Figure 1.6. SBUs commonly found in MOFs: (a) square "paddlewheel" with two terminal ligand sites, (b) octahedral "basic zinc acetate" cluster, and (c) trigonal prismatic oxo-centred trimer with three terminal ligand sites. Metals are depicted as blue spheres, carbon as black spheres, and oxygen as red spheres. *Figure reprinted (adapted) with permission from Rowsell, J. L.; Yaghi, O. M. Metal–organic frameworks: a new class of porous materials. Microporous mesoporous mater. 2004, 73, 3–14. Copyright (2004) Elsevier.*⁷⁶

MOF-5 is one of the first examples of a rigid framework based on M-O-C-O-M SBUs (Figure 1.7).^{33,68} Its structure features $\text{Zn}_4\text{O}(\text{CO}_2)_6$ units, consisting of four ZnO_4 tetrahedra sharing a common vertex and six carboxylate carbon atoms forming an octahedral SBU.⁶⁸ These SBUs are linked by phenyl groups (the remainder of the terephthalate ligand), creating a cubic network where the vertices represent the octahedral SBUs, and the edges are the phenyl struts. The rigid SBUs and benzene ligands provide MOF-5 with exceptional porosity and stability. The structure retains its rigidity due to the strong metal-oxygen bonds and the geometric properties of the SBUs. This design ensures that the framework does not collapse upon removal of guest molecules.

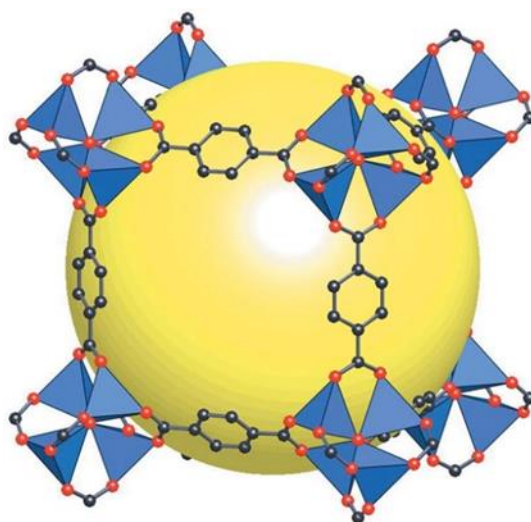


Figure 1.7. MOF-5 structure depicted with ZnO_4 tetrahedra (blue polyhedra) connected by benzene dicarboxylate ligands (O in red and C in black), forming an extended 3D cubic framework. The yellow sphere represents the largest sphere that can occupy the pores. *Reprinted (adapted) with permission from Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. Reticular synthesis and the design of new materials. Nature* **2003**, 423, 705–714. Copyright (2003) Macmillan Magazines.⁶⁸

The concept of SBBs emerged as a complementary strategy to the MBB approach, enabling the construction of more complex and highly connected MOFs. SBBs are larger, pre-organized units formed from the assembly of smaller MBBs, typically 3- or 4-connected building blocks.⁷⁰ They offer an ordered design strategy that incorporates a higher degree of symmetry, connectivity, and pre-encoded structural information, making them essential for achieving novel framework architectures.

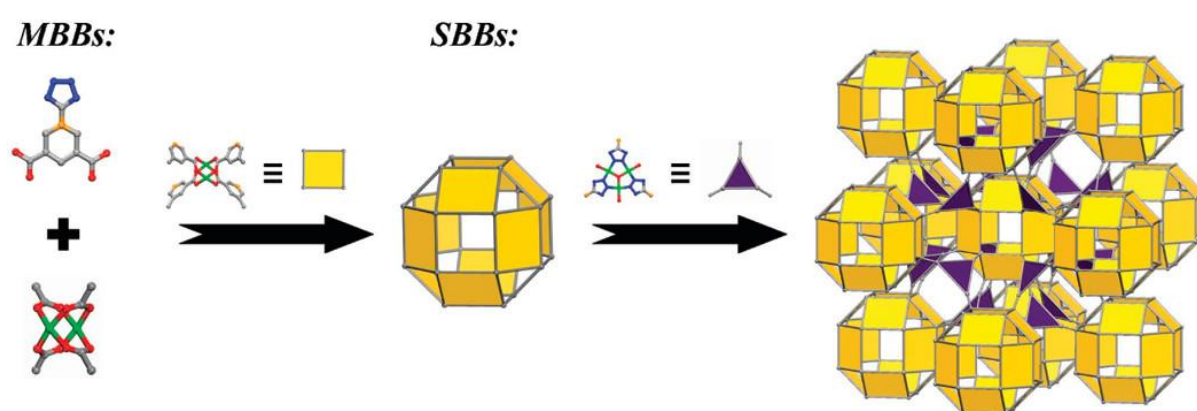


Figure 1.8. Formation strategy from MBBs to SBBs to MOF. Reprinted (adapted) with permission from Nouar, F.; Eubank, J. F.; Bousquet, T.; Wojtas, L.; Zaworotko, M. J.; Eddaoudi, M. *Supramolecular building blocks (SBBs) for the design and synthesis of highly porous metal-organic frameworks*. *J. Am. Chem. Soc.* **2008**, 130, 1833–1835. Copyright (2008) American Chemical Society.⁷⁷

SBBs address the challenges associated with creating MOFs of high connectivity (≥ 8), which are often too intricate to be constructed using simple organic ligands or multinuclear clusters.^{70,77} Instead, the SBB approach uses assemblies such as metal-organic polyhedra (MOP), where individual MBBs associate into larger, more elaborate units that retain their integrity during the assembly of the final framework (Figure 1.8). This method has enabled the design of MOFs with unprecedented

connectivity, such as **rht**-MOFs, **gea**-MOFs, and **fcu**-MOFs, using 24-, 18-, and 12-connected MOPs as SBBs, respectively.^{70,78,79,80}

1.3.2. Targeted nets (Topology)

A crucial aspect of reticular chemistry is deconstructing structures into their underlying nets (framework topology), where the structures are viewed as connected links and vertices (nodes).^{81,82} This approach is beneficial for simplifying, understanding, comparing, and predicting the structures of crystalline open-framework materials where the arrangement of atoms determines the pore size, shape, and volume.⁸³ The process of deconstructing MOF structures into their underlying topology begins with identifying the SBUs. MOFs consist of two or more SBUs, which fall into two broad categories: (a) metal-containing units that may vary from single metal atoms to infinite groups such as rods or layers, and (b) polytopic organic ligands, which may also include metal atoms, as in the case of a porphyrin.⁸¹ Typically, the metal-containing SBUs are finite units, with points of extension, forming well-defined geometric shapes such as squares or octahedrons. The points of extension are the interfaces of the inorganic (SBUs) and organic (remainder of the organic ligands) components, e.g., the carboxylate carbon atoms in carboxylate MOFs.^{68,82,83} The SBUs are connected via these extension points into periodic frameworks.⁸¹

The underlying topology of the framework is represented by a periodic net where solid spheres serve as vertices of the net, whilst the lines connecting these vertices are the edges (ligands) (Figure 1.9).⁸⁴ The vertices and ligands simplify how the MOF structure extends in 1-, 2- or 3-dimensions. The vertices could consist of single atoms or centroids of larger units, such as polynuclear metal oxide clusters.⁸² Vertices may

also be the centroids of ligands if they are not ditopic, i.e., if the ligands have more than two sites of ligation (Figure 1.10).⁸³ It is seen as redundant to assign the centroids of ditopic ligands, such as terephthalate, as vertices since this will not change the connectivity of the net. Most MOFs possess underlying nets with minimal transitivity, characterised by the fewest number of unique vertices and edges compatible with their local structure. This includes iconic MOFs such as MOF-5 and HKUST-1, which have transitivity values of 1 1 and 2 1, respectively. In the latter case, the centroid of the tricarboxylate ligand is also assigned as a node, hence there are two unique types of nodes.

Various commonly occurring nets are stored in databases such as Reticular Chemistry Structure Resource (RCSR), ToposPro, and Systre.⁸⁵ These nets are typically identified by three-letter, lowercase bold symbols or symbols with extensions such as

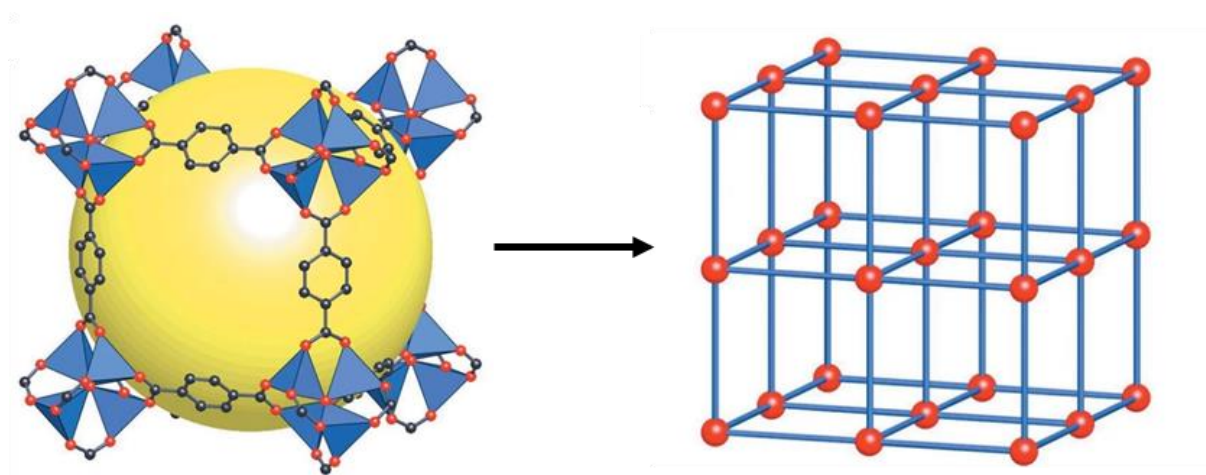


Figure 1.9. (Left) MOF-5. (Right) The corresponding underlying primitive cubic (**pcu**) net with $\text{Zn}_4\text{O}(-\text{CO}_2)_6$ SBUs as vertices and ditopic terephthalate ligands as edges. Reprinted (adapted) with permission from Yaghi, O. M.; O’Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Reticular synthesis and the design of new materials*. *Nature* **2003**, 423, 705–714. Copyright (2003) Macmillan Magazines Ltd.⁶⁸

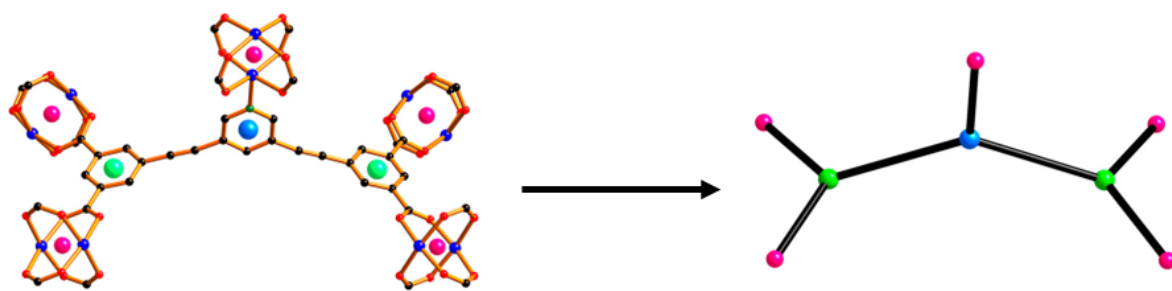


Figure 1.10. (Left) The tetracarboxylate ligand in PMOF-3 and its adjoining $\text{Cu}_4(-\text{CO}_2)_4$ paddle wheel SBUs. (Right) The corresponding nodes and ligands of the underlying net. Reprinted (adapted) with permission from Li, M.; Li, D.; O’Keeffe, M.; Yaghi, O. M. *Topological analysis of metal–organic frameworks with polytopic linkers and/or multiple building units and the minimal transitivity principle*. *Chem. Rev.* **2014**, 114, 1343–1370. Copyright (2014) American Chemical Society.⁸⁶

abc-d, as assigned to entries in the RCSR.^{85,87} Symbols such as **pcu** (primitive cubic), **fcu** (face-centered cubic), and **dia** (diamond) are based on their structures, while some others are derived from mineral names. However, most topology symbols are assigned randomly.⁸² For example, MIL-53 features a square (**sql**) net and MOF-74 features a honeycomb (**hcb**) net (Figure 1.11).⁸³ Nets serve as blueprints for predefined frameworks used in the design and construction of materials in reticular chemistry.⁶⁶ Edge-transitive nets, characterised by a single type of edge, are crucial in MOF design, providing reliable design targets and foundational blueprints for creating more complex nets. This approach has facilitated the intentional construction of many isorecticular (same topology) MOFs.^{69,87}

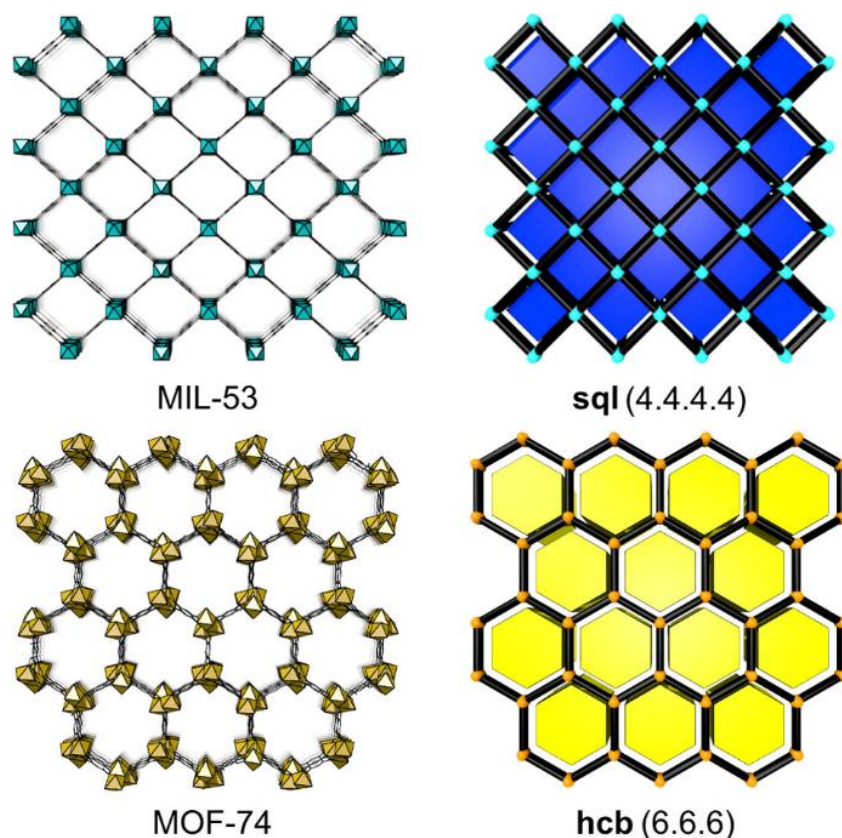


Figure 1.11. Selected rod-based MOFs and their corresponding 2-periodic nets that describe how the rods are packed. Included examples are MIL-53 with a square (**sql**) net and MOF-74 with a honeycomb (**hcb**) net. *Reprinted (adapted) with permission from Inge, A. K.; Köppen, M.; Su, J.; Feyand, M.; Xu, H.; Zou, X.; O’Keeffe, M.; Stock, N. Unprecedented topological complexity in a metal–organic framework constructed from simple building units. J. Am. Chem. Soc. **2016**, 138, 1970–1976. Copyright (2016) American Chemical Society.*⁸³

1.3.3. Isorecticular Chemistry

Isorecticular chemistry is a powerful strategy that involves deliberately modifying a MOF's pore size, volume, or functionality without changing its underlying topology.³⁵ This approach enables the construction of highly porous MOFs by carefully expanding the pore size and volume while preserving the original topology, leading to the development of new functional materials with distinctive properties.⁸⁸

1.3.3.1. Isoreticular Design Strategies

Isoreticular design strategies involve modifying, replacing, expanding, and contracting building blocks to achieve specific properties and applications.⁶⁶

Building block modification and substitution

Modifying and substituting building blocks are crucial strategies for introducing various functional groups into MOFs, thereby enhancing their tailored properties for specific applications.⁶⁶ Building block modification involves introducing functional groups before or after material synthesis. Pre-designed functional groups are often incorporated into organic ligands to target specific functionalities. For instance, isostructural rare-earth **fcu**-MOFs were synthesised using the bulky ligand 1,4-naphthalenedicarboxylate (1,4-NDC) to restrict pore access.⁸⁹ This resulted in a contracted triangular window aperture, which enhanced selectivity for CO₂/N₂ and CO₂/CH₄ separations compared to the parent **fcu**-MOF that utilised the 2-fluoro-4-(1H-tetrazol-5-yl)benzoate (FTZB) ligand.^{89,90}

Substitution of building blocks within MOFs after their initial synthesis represents another critical strategy for achieving desired properties.⁶⁶ This involves replacing existing building blocks with other pre-designed inorganic or organic counterparts. For example, solvent-assisted ligand exchange (SALE) was employed to substitute the 9-Å *meso*-1,2-di(4-pyridyl)-1,2-ethanediol (dped) pillars in a pillared-paddlewheel MOF structure, **SALEM-5** [Zn₂(Br-tcpb)(dped)] (tcpb = 1,2,4,5-tetrakis(4-carboxylatophenyl)benzene), with longer organic ligands (Figure 1.12).⁹¹ Initially, the 11-Å 2,3,5,6-tetramethyl-1,4-bis(4-pyridyl)benzene (tmbpb) ligand was used, resulting in **SALEM-6**. Subsequent experiments replaced

dped with even longer pillars of 14-Å naphthalene bis(pyridin-4-yl) (nbp) and 17-Å 4,4'-((2,3,5,6-tetramethyl-1,4-phenylene)bis(ethyne-2,1-diyl))dipyridine (tmbebp), yielding **SALEM-7** and **SALEM-8**. The incorporation of longer ligands expanded the pore size of the resulting MOFs.

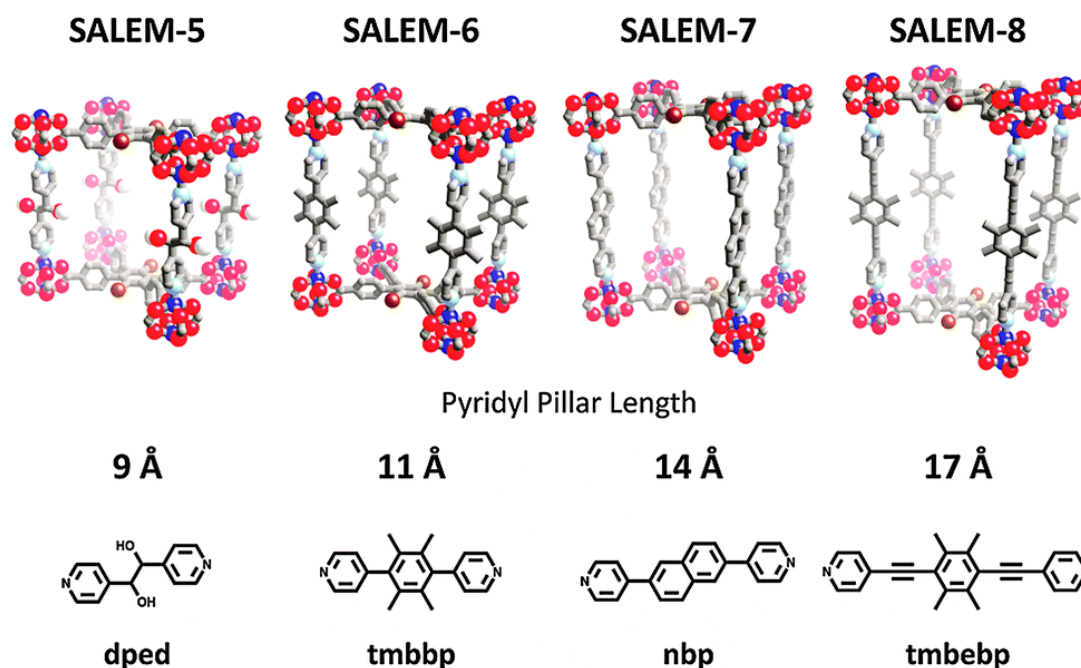
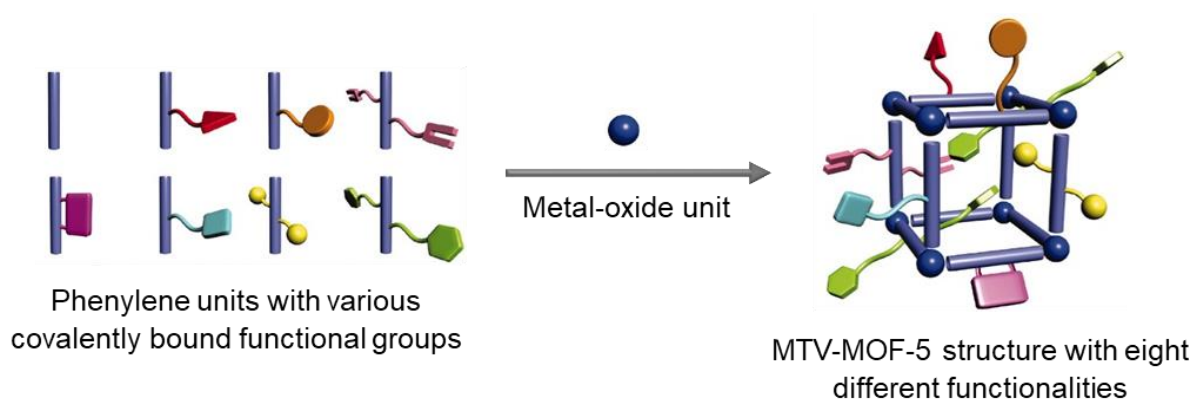


Figure 1.12. Increasing pore dimensions in a series of isorecticular pillared-paddlewheel MOFs synthesised through SALE. The length in Å denotes the dipyrindyl ligand length incorporated into the parent MOF **SALEM-5** during SALE. Reproduced from Deria, P.; Mondloch, J. E.; Karagiaridi, O.; Bury, W.; Hupp, J. T.; Farha, O. K. *Beyond post-synthesis modification: evolution of metal–organic frameworks via building block replacement*. *Chem. Soc. Rev.* **2014**, 43, 5896–5912, with permission from the Royal Society of Chemistry.⁹²

The multivariate (MTV) approach

The multivariate (MTV) approach in MOFs involves incorporating multiple functional groups or metal atoms into a single MOF structure, thereby enhancing the material's

versatility and functionality.⁶⁶ This approach was first demonstrated using the MOF-5 platform, which contains terephthalate ligand (denoted as A in the original study), by incorporating up to eight different functionalised A-type ligands, each with distinct functional groups, such as -NH_2 (B), -Br (C), -(Cl)_2 (D), -NO_2 (E), $\text{-(CH}_3)_2$ (F), $\text{-C}_4\text{H}_4$ (G), $\text{-(OC}_3\text{H}_5)_2$ (H), and $\text{-(OC}_7\text{H}_7)_2$ (I), into the same structure.⁹³ Scheme 1.2 illustrates this concept of multivariate incorporation within the MOF-5 framework. A notable member of this series, MTV-MOF-5-EHI, comprising a mixture of three functionalised terephthalic ligands: -NO_2 (E), $\text{-(OC}_3\text{H}_5)_2$ (H), and $\text{-(OC}_7\text{H}_7)_2$ (I), exhibited significant improvements in gas adsorption properties. Specifically, it demonstrated up to 400% better selectivity for CO_2 over CO compared with the unfunctionalised MOF-5, due to the synergistic interaction of multiple functional groups within the pore environment (Figure 1.13).



Scheme 1.2. Schematic representation of the synthesis of MTV-MOF-5. *Reproduced from Deng, H.; Doonan, C. J.; Furukawa, H.; Ferreira, R. B.; Towne, J.; Knobler, C. B.; Wang, B.; Yaghi, O. M. Multiple functional groups of varying ratios in metal-organic frameworks. Science* **2010**, 327, 846-850, with permission from American Association for the Advancement of Science.⁹³

Reports also exist on multi-metal MTV-MOFs.^{94,95} For example, up to ten different metals were introduced into the rod building blocks of MOF-74, resulting in variants

such as M2M-, M4M-, M6M-, M8M-, and M10M-MOF-74, where the number indicates the number of different metals involved.⁹⁴ The presence of multiple metals within a single MOF framework creates unique catalytic, electronic, and optical properties due to the synergistic effects of the different metals.^{95,96}

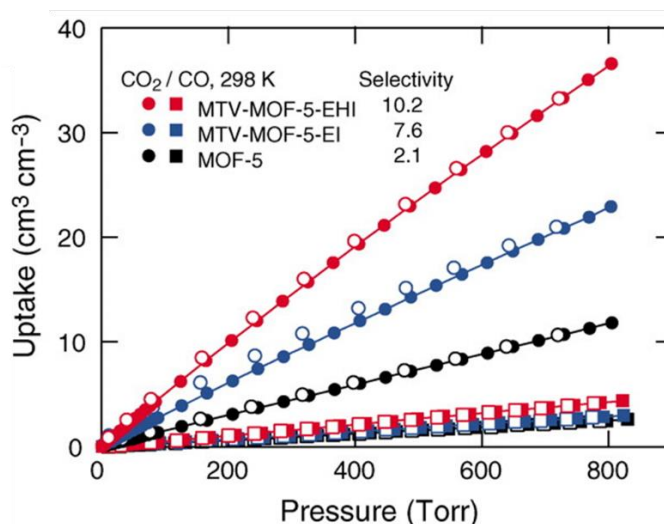


Figure 1.13. Adsorption Isotherms of CO₂ (circles) and CO (squares) on MTV-MOF-5-EI (blue), MTV-MOF-5-EHI (red), and MOF-5 (black) at 298 K. Reproduced from Deng, H.; Doonan, C. J.; Furukawa, H.; Ferreira, R. B.; Towne, J.; Knobler, C. B.; Wang, B.; Yaghi, O. M. Multiple functional groups of varying ratios in metal-organic frameworks. *Science* **2010**, 327, 846–850, with permission from American Association for the Advancement of Science.⁹³

Building block expansion and contraction

The expansion and contraction of building blocks in MOFs have primarily focused on organic ligands because incorporating metal atoms to create larger clusters while maintaining the same geometry remains challenging.⁶⁶ Isoreticular expansion, an effective strategy for achieving materials with larger pore volumes, involves extending the length of a ligand while retaining its symmetry and geometry.^{90,97,98} This method

typically uses rigid groups, such as acetylene or phenylene, to ensure the topology remains unchanged.⁹⁹ Consequently, this approach has resulted in notable families of MOFs with progressively increasing pore sizes.^{99,100,101} For instance, in the IR-MOF family reported by Yaghi *et.al.*, the initial ligand, 1,4-benzenedicarboxylic acid (BDC), was replaced with biphenyl-4,4'-dicarboxylic acid (BPDC) in IR-MOF-10 and terphenyl-4,4'-dicarboxylic acid (TPDC) in IRMOF-16 (Figure 1.14).^{68,69} This substitution resulted in fixed pore diameters expanding from 18.5 Å in IRMOF-1, to 24.5 Å in IRMOF-10 and 28.8 Å in IRMOF-16. Similarly, this strategy was applied to UiO-66, leading to the synthesis of MOFs UiO-67 and UiO-68, with the largest cage diameters of 11 Å, 16 Å, and 25.6 Å, respectively (Figure 1.15).^{99,101}

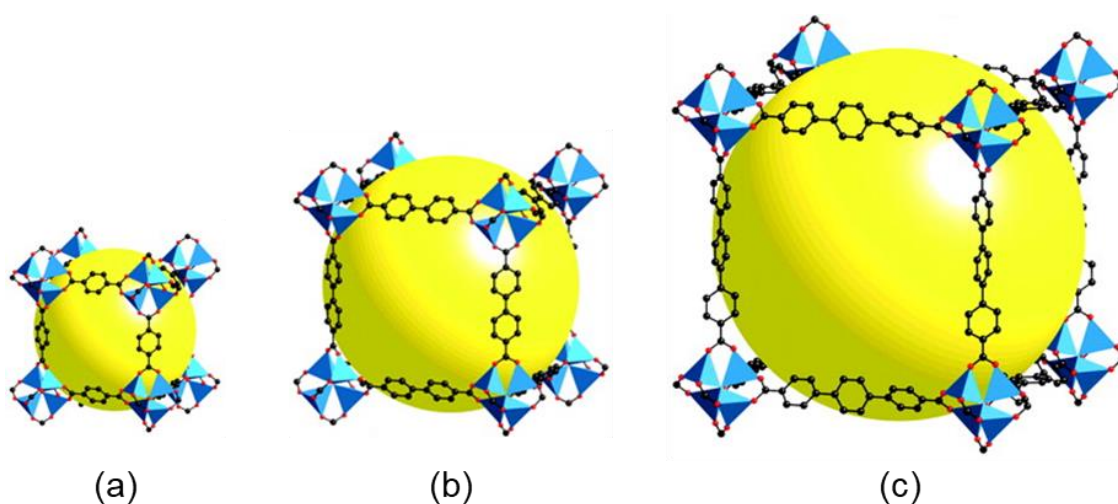


Figure 1.14. Crystal structures of (a) IRMOF-1, (b) IRMOF-10, and (c) IRMOF-16. The yellow sphere represents the largest sphere that can occupy the pores. *Reproduced from Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. Systematic design of pore size and functionality in isorecticular MOFs and their application in methane storage. Science* **2002**, 295, 469–472, with permission from American Association for the Advancement of Science.⁶⁹

On the other hand, the contraction of building blocks can produce materials with smaller pore-aperture sizes, making them suitable for separating small molecules and potentially resulting in more stable structures.⁶⁶ An example of isorecticular contraction is demonstrated with the synthesis of a rare-earth **fcu**-MOF using fumaric acid as the ligand.¹⁰² This approach involved substituting a longer ligand, such as 1,4-naphthalenedicarboxylate, with the shorter fumarate (fum) ligand, resulting in a significant reduction of the pore aperture size. The resultant Y-fum-**fcu**-MOF and Tb-fum-**fcu**-MOF exhibited fine-tuned triangular windows that facilitated the separation of branched paraffins from normal paraffins.

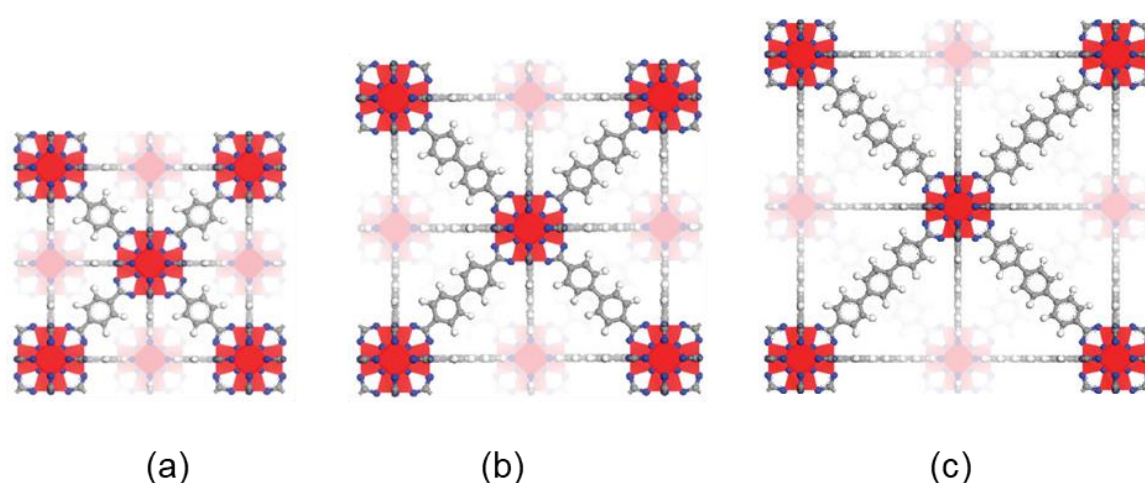


Figure 1.15. Crystal structures of (a) UiO-66, (b) UiO-67, and (c) UiO-68. *Reprinted (adapted) with permission from Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. A new zirconium inorganic building brick forming metal organic frameworks with exceptional stability. J. Am. Chem. Soc. **2008**, 130, 13850–13851. Copyright (2008) American Chemical Society.*¹⁰¹

1.4. Periodicity vs Dimensionality

The terms " n -periodic" and " n -dimensional" nets are often confused but represent distinct concepts.¹⁰³ n -periodic refers specifically to translational symmetry in n -independent directions, indicating that a structure is infinite in those directions. In contrast, n -dimensionality describes the spatial embedding of the net, i.e., the dimensions in which its vertices are located, regardless of whether the structure is infinite or finite. For instance, a polynuclear cluster may span three-dimensional space and thus be considered 3D in dimensionality, but if it lacks translational symmetry, it is 0-periodic. Although the terminology " n -dimensional" (e.g., 0D, 1D, 2D, 3D) is commonly used, the term " n -periodic" is preferred here to provide a more rigorous classification of extended structures in the context of crystal engineering.¹⁰⁴ As illustrated in the literature, a 3D object can be 0-periodic (finite cluster), 1-periodic (tube), 2-periodic (layer), or 3-periodic (framework), depending on its symmetry and connectivity.¹⁰⁵ Thus, periodicity provides a clearer and more precise description of network topology in coordination polymers and MOFs.

1.5. Porosity

Porosity is a crucial characteristic of MOFs and is significant in determining their utility and performance in various applications. MOF porosity refers to the ability to maintain a porous structure even when guest molecules are absent.⁵⁷ This means that when guest molecules are removed under vacuum, the pore structure remains intact, ensuring permanent porosity. Barbour offers a practical and comprehensive understanding of porosity, attempting to avoid the complexities often found in legal definitions.¹⁰⁶ Barbour suggests a straightforward definition, emphasising

demonstrating permeability and that the host framework should be largely unaffected by guest removal and uptake.

Barbour categorises porosity into three types: conventional porosity, virtual porosity, and porosity "without pores". Conventional porosity allows for the removal or exchange of guest molecules without damaging the host framework's structural integrity. Virtual porosity involves deleting certain atoms or molecules from the crystal structure's data file and generating a packing diagram to reveal large channels, which are then claimed to be pores. Porosity "without pores" refers to porosity with lattice voids but lacking atomic-scale channels connecting these voids.¹⁰⁶ An example is *p*-*tert*-butylcalix[4]arene, which forms a low-density polymorph with a discrete lattice

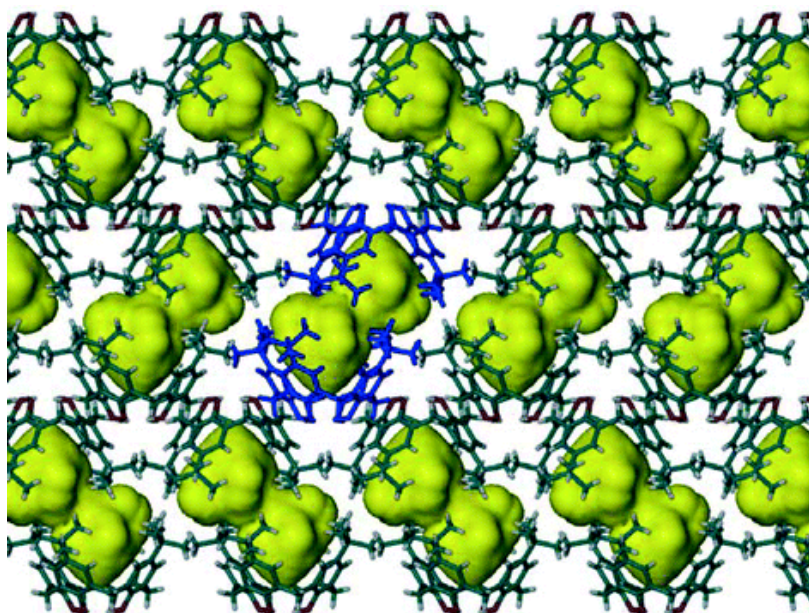


Figure 1.16. Two-dimensional packing arrangement of calixarenes. *Figure reprinted (adapted) with permission from Barbour, L. J. Crystal porosity and the burden of proof. Chem. Commun. 2006, 1163–1168. Copyright (2006) Royal Society of Chemistry.*¹⁰⁶

voids of about $235 \text{ \AA}^3$ but no visible interconnecting channels (Figure 1.16).^{106,107} Despite this, the structure can incorporate guest molecules such as vinyl bromide through a single-crystal-to-single-crystal transformation (SCSC), suggesting a form of dynamic porosity where the crystal structure adapts to include guest molecules without conventional pores.¹⁰⁷

MOFs, along with zeolites and activated carbons, are porous materials categorised based on pore size into three types, according to the IUPAC definition, namely microporous materials (pore diameters up to 2.0 nm), mesoporous materials (pore sizes between 2.0 and 50.0 nm), and macroporous materials (pore sizes exceeding 50.0 nm).¹⁰⁸ The term "pore size" refers to the width between two opposite walls, while porosity is defined as "the ratio of the volume of pores and voids to the total volume of the solid".^{109,110} The porosity of MOF was initially explored in the 1990s by forcing gas molecules into their cavities under high pressure.^{38,111} However, to prove permanent porosity, measuring reversible gas sorption isotherms at low temperatures and pressure is necessary.³⁸ This sorption process is quantitatively described using sorption isotherms, which show the amount of gas adsorbed by the material at a chosen temperature as a function of pressure.¹¹² The measurement of nitrogen and carbon dioxide isotherms of a 2-periodic zinc terephthalate MOF provided the first evidence of permanent porosity for a MOF.^{38,113}

IUPAC conventions classify the pore sizes, often derived from gas sorption isotherms, to demonstrate the relationship between porosity and sorption.^{108,112,114} This classification of sorption isotherms indicates the porosity of materials according to six types, namely those which are microporous (type I), nonporous or macroporous (types II, III, and VI), and mesoporous (types IV and V) adsorbents (Figure 1.17).^{108,112} Type I isotherm is concave to the P/P_0 (relative pressure; P = absolute pressure of the

gas and P_0 = saturation pressure of the gas) axis, and the adsorbed amount reaches a limiting value as P/P_0 approaches 1.¹⁰⁸ This isotherm is characteristic of microporous materials where adsorption is limited to a few molecular layers. The isotherm shows high uptake at low pressures due to narrow pore widths and high adsorption potential. Type I isotherm is commonly observed in microporous materials. Type II isotherm, often observed in non-porous or macroporous adsorbent, features an inflection point, where monolayer coverage is complete and multilayer adsorption begins. Type III isotherm, which is convex to the P/P_0 axis and lacks an inflection point, indicates weak adsorbate-adsorbent interactions and significant adsorbate-adsorbate interactions.

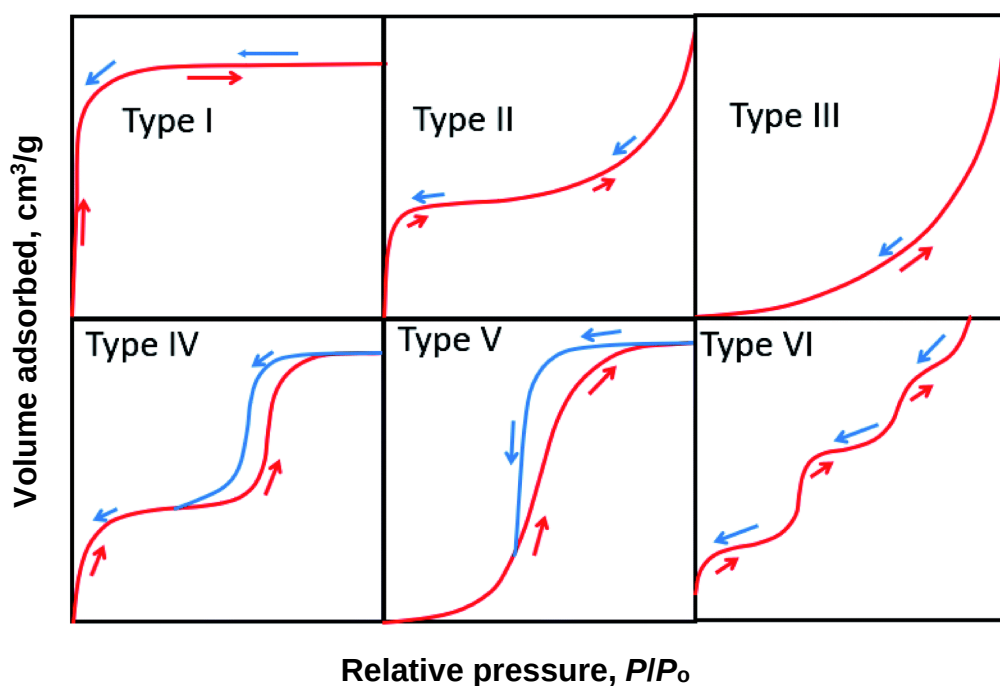


Figure 1.17. The six types of physisorption isotherms as classified by IUPAC. *Figure reprinted (adapted) with permission from Kumar, K. V.; Gadipelli, S.; Wood, B.; Ramisetty, K. A.; Stewart, A. A.; Howard, C. A.; Brett, D. J.; Rodriguez-Reinoso, F. Characterization of the adsorption site energies and heterogeneous surfaces of porous materials. J. mater. Chem. A* **2019**, 7, 10104-10137. Copyright (2019) Royal Society of Chemistry.¹¹⁵

Type IV isotherm is characteristic of mesoporous materials and is marked by a hysteresis loop associated with capillary condensation and a plateau at high P/P_0 , indicating complete pore filling. The initial part of this isotherm involves monolayer-multilayer adsorption similar to Type II isotherm. Type V isotherm also shows pore condensation and hysteresis, but the initial adsorption behaviour resembles Type III, indicating relatively weak adsorbent-adsorbate interactions. Type VI isotherms represent stepwise multilayer adsorption on a uniform, non-porous surface, dependent on the homogeneity of the adsorbent surface, the adsorptive and the temperature. While the IUPAC classification is comprehensive for rigid materials, Zaworotko *et al.* extended these concepts to flexible microporous materials, which exhibit dynamic structural transformations under external stimuli such as gas pressure or temperature.^{116,117} These materials challenge traditional isotherm classifications as their pore geometries change during adsorption, leading to "stepped" or "S-shaped" isotherms caused by breathing or swelling.¹¹⁶ Zaworotko introduced Type F-I to F-V isotherms to describe these behaviours (Figure 1.18). Type F-I and F-II represent gradual or sudden transitions from small to large pores, respectively, while Type F-III and F-IV describe transformations from non-porous (closed) to porous (open) phases, occurring either gradually or abruptly. Type F-V, on the other hand, describes materials with a "shape memory effect," where the open phase persists after desorption and requires specific external stimuli, such as heat or vacuum, to revert to the closed phase.^{116,117}

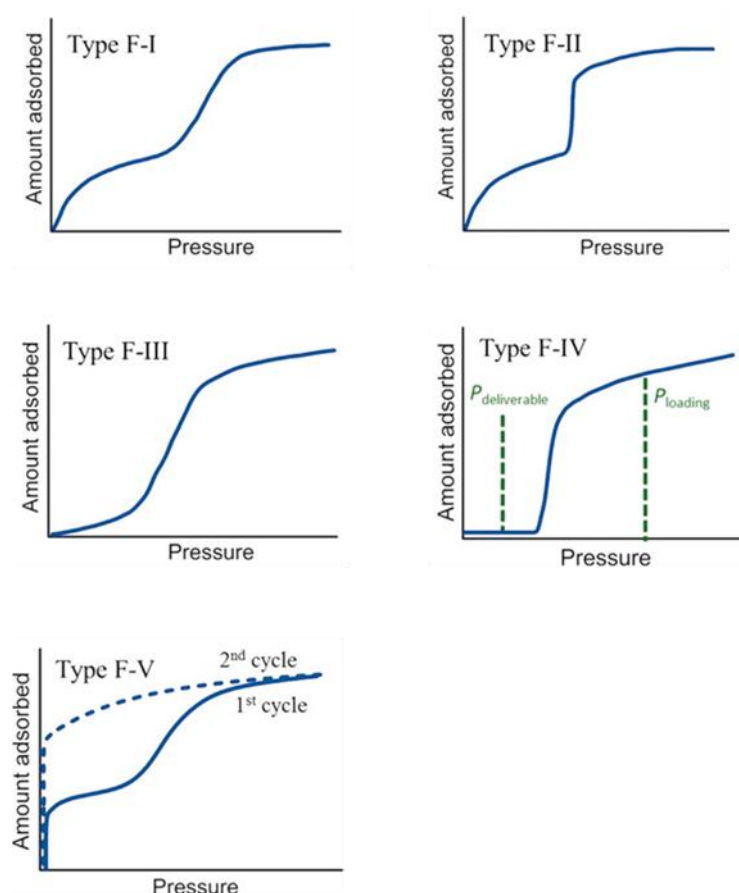


Figure 1.18. Proposed categorisation of isotherm profiles for flexible microporous materials, from Type F-I to F-V. *Figure reprinted (adapted) with permission from Yang, Q.; Lama, P.; Sen, S.; Lusi, M.; Chen, K.; Gao, W.; Shivanna, M.; Pham, T.; Hosono, N.; Kusaka, S. Reversible switching between highly porous and nonporous phases of an interpenetrated diamondoid coordination network that exhibits gate-opening at methane storage pressures. Angew. Chem., Int. Ed. **2018**, 57, 5684–5689. Copyright (2018) Germany Chemical Society.*¹¹⁶

1.6. Interpenetration

Designing MOFs with high porosity has been a major focus in MOF research due to their potential for high storage capacities. Achieving ultrahigh porosity requires increasing the material's storage space per unit mass.³⁸ To this end, utilising longer organic ligands can create larger storage spaces and provide more adsorption

sites.^{38,69,100,118} However, these expanded spaces within the crystal frameworks often lead to interpenetration, which reduces porosity and compromises performance.^{38,119} Interpenetration, a specific type of entanglement, occurs when two or more independent frameworks grow and intertwine within the same crystal lattice, forming a network that cannot be separated without breaking chemical bonds.^{38,120,121,122,123} This phenomenon typically occurs when elongated organic ligands in the framework promote self-catenation, as the frameworks prefer to fill voids rather than maintain large empty spaces.¹²² Typically, the void spaces in a MOF are filled with additional template molecules such as solvents, cations, or anions.^{124,123} However, in some instances, the growth of secondary networks is essential to occupy the large voids, leading to interpenetration.¹²⁴ Interpenetration networks are categorised as N -fold ($N \geq 2$) networks according to the number of entangled nets within the overall packing structure.¹²³ Interpenetration has traditionally been seen as disadvantageous due to the resulting reduction in surface areas and pore sizes.¹²² However, its significance has been recognised, highlighting its role in providing greater stability, rigidity, and improved separation capabilities in MOF frameworks.^{125,126} Interpenetration enhances framework stability through close interactions, including supramolecular interactions such as hydrogen bonding, π - π stacking, and van der Waals forces.¹²⁷ These interactions can significantly improve the interaction between the pore surface and guest molecules. Additionally, interpenetration can facilitate CO₂ uptake, leading to an increased isosteric heat of adsorption.^{127,128} This improvement in CO₂ adsorption can be attributed to the stepwise filling of pores and the inherent flexibility of the framework.^{127,129} Interpenetration in MOFs can also improve their hydrogen storage and separation ability.¹³⁰

1.7. Classification of MOFs

In 1998, Kitagawa and Kondo classified MOF materials into three categories, namely first-generation, second-generation, and third-generation, based on the response of their frameworks to guest removal (Figure 1.19).¹³¹ First-generation MOFs typically become nonporous after the removal of guest molecules.^{132,133} Their frameworks collapse irreversibly, displaying nonpermanent porosity due to their dependence on the presence of guest molecules, a behaviour often observed in charged frameworks

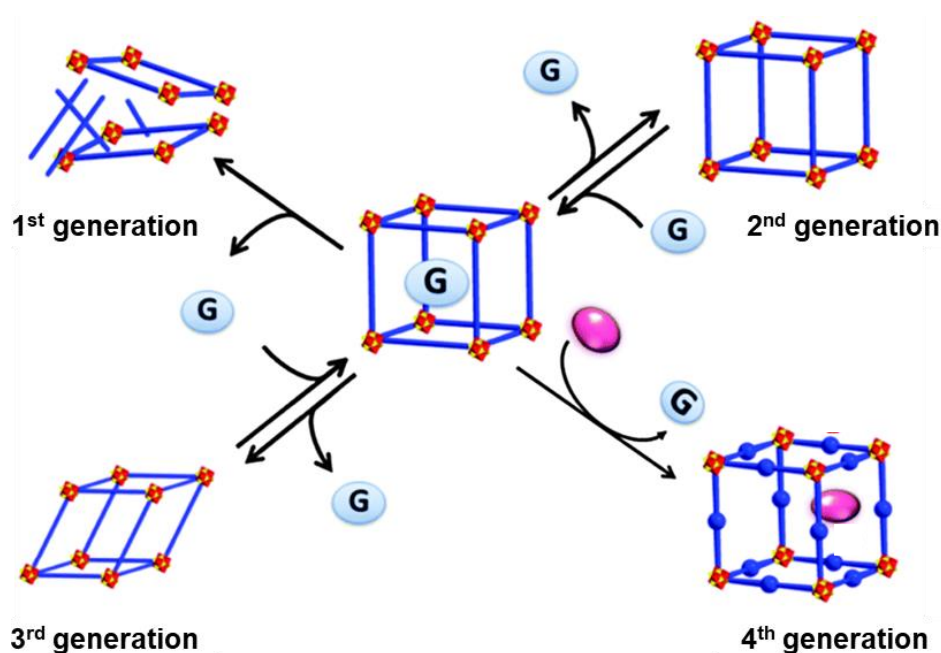


Figure 1.19. Classification of MOFs: 1st, 2nd, 3rd, and 4th generation MOFs upon removal of guest solvent. *Figure reprinted (adapted) with permission from Liu, J.; Chen, L.; Cui, H.; Zhang, J.; Zhang, L.; Su, C. Applications of metal–organic frameworks in heterogeneous supramolecular catalysis. Chem. Soc. Rev. 2014, 43, 6011–6061. Copyright (2014) Royal Society of Chemistry.*¹³³

filled with counter anions. On the contrary, second-generation MOFs are characterised by permanent porosity and retention of the original framework structure after guest removal, typically exhibiting Type I adsorption isotherms, similar to neutral and

zeolite-like MOFs. Third-generation MOFs are flexible and dynamic, capable of responding to guest exchange or external stimuli such as temperature, pressure, light, and mechanics, including chemical, physical, light or magnetic inducers.^{133,134} These flexible MOFs are also referred to as soft porous crystals, spring-like, sponge-like, flexible, or dynamic MOFs.¹³⁴ These frameworks exhibit "stepped" or "S-shaped" adsorption isotherms.¹³² As defined by Liu *et al.*, fourth-generation MOFs (Figure 1.19) are porous materials with modifiable pore size and chemistry through postsynthetic modification. These MOFs maintain their underlying topology and structural integrity during various post-modifications.¹³³

1.8. Single-Crystal-to-Single-Crystal (SCSC)

Transformations in MOFs

SCSC transformations have garnered significant interest in crystal engineering.^{135,136,137} These transformations occur when a single crystal undergoes structural changes due to exposure to solvent, heat, light, or mechanochemical forces, resulting in transformed products (Figure 1.20).^{138,139} Such structural transformations lead to changes in physical properties such as crystal colour, porosity, chirality, conductivity, magnetism, optics, and luminescence.¹³⁸ They also affect coordination number, geometry, and dimensionality.¹³⁹ SCSC transformations are particularly fascinating because they can produce unique products that are difficult to create through conventional synthetic methods and allow for the direct visualisation of changes in the molecular structure before and after the transformation process.¹³⁹ However, achieving SCSC transformations remains challenging, as it is difficult for crystals to simultaneously cleave and form chemical bonds in multiple directions in the

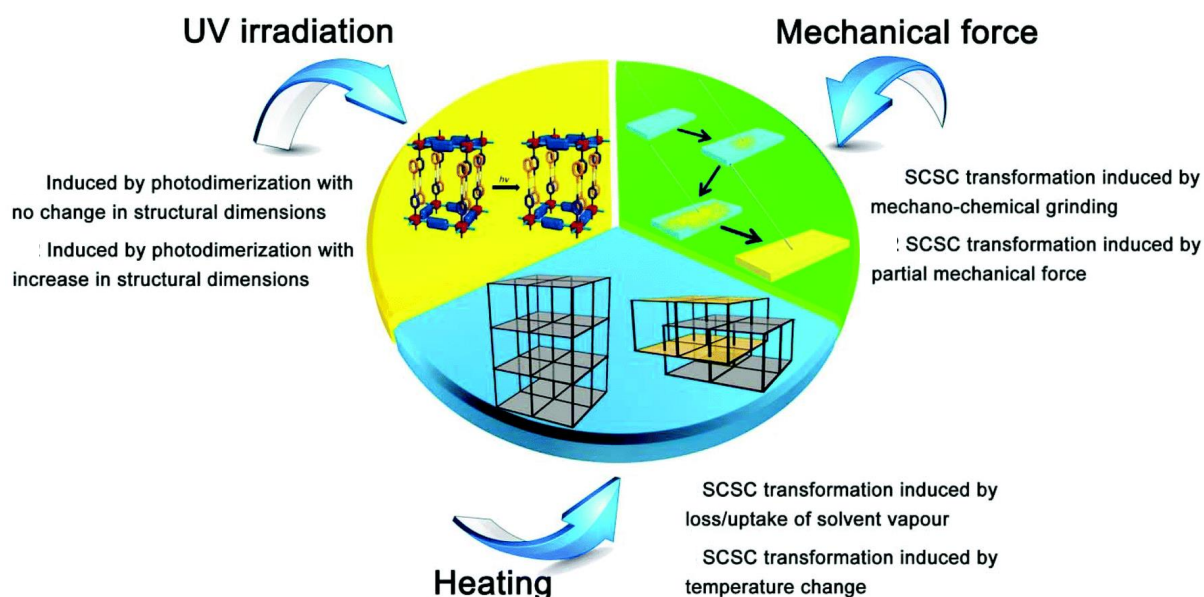


Figure 1.20. Diagram illustrating the classification of SCSC transformations. *Figure reprinted (adapted) with permission from He, W.; Li, S.; Lan, Y. Liquid-free single-crystal to single-crystal transformations in coordination polymers. Inorg. Chem. Front. 2018, 5, 279-300. Copyright (2018) Royal Society of Chemistry.*¹³⁸

solid state.¹⁴⁰ As a result, many MOFs fail to retain their single crystallinity during the transformation process. Nevertheless, the phenomenon has been increasingly observed in certain cases.^{136,141,142} Bon *et al.* report an example of a SCSC transformation in the flexible porous coordination polymer $[\text{Zn}_2(\text{BPnDC})_2(\text{bpy})]_n$ (BPnDC = benzophenonedicarboxylate), a twofold, interpenetrated flexible framework also known as SNU-9 (Seoul National University), during its activation process (Figure 1.21).¹⁴³ This activation results in significant structural transformations, including the rearrangement of Zn–O bonds and changes in the coordination environment of Zn atoms. During this process, the unit cell volume of SNU-9 contracts by nearly 28% compared to its as-synthesised, open structure. The coordination geometry of the Zn1 atom changes from a distorted octahedral to a

strongly distorted square-pyramidal geometry. Additionally, the solvent-accessible volume of the unit cell decreases from 40.8 to 12.8%.

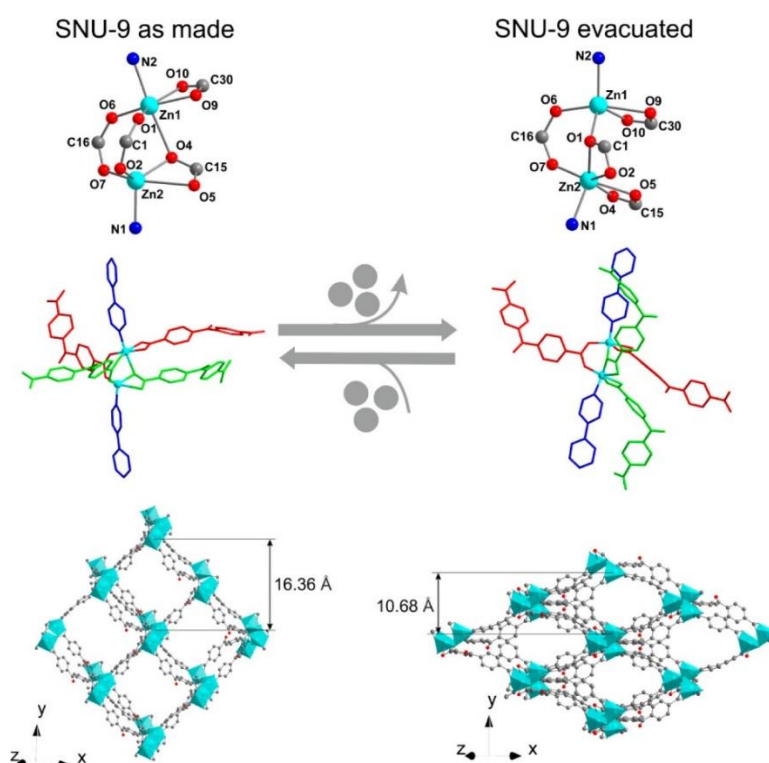


Figure 1.21. Crystal structure of SNU-9 in its as-made (left) and evacuated (right) phases: SBU geometry (top), arrangement of ligands around SBUs (middle), and a view of a single framework along the [101] direction (bottom). *Reprinted (adapted) with permission from Bon, V.; Senkovska, I.; Wallacher, D.; Többsens, D. M.; Zizak, I.; Feyerherm, R.; Mueller, U.; Kaskel, S. In situ observation of gating phenomena in the flexible porous coordination polymer $\text{Zn}_2(\text{BPnDC})_2(\text{bpy})$ (SNU-9) in a combined diffraction and gas adsorption experiment. *Inorg. Chem.* **2014**, 53, 1513–1520. Copyright (2014) American Chemical Society.¹⁴³*

1.9. Gas Sorption

Gas sorption is a process by which gas molecules interact with the surface of the solid material. This interaction can be categorised into two types, namely physisorption and

chemisorption.¹⁴⁴ Physisorption occurs when an adsorbable gas (adsorptive) comes into contact with the surface of the adsorbent. The intermolecular forces involved in physisorption include attractive dispersion forces, short-range repulsive forces, and specific molecular interactions such as polarisation, field-dipole, and field gradient-quadrupole interactions. Physisorption is generally characterised by weaker, reversible interactions due to the absence of activation energy requirements and minimal interaction energies involved.¹⁴⁵ Chemisorption, on the other hand, involves the formation of chemical bonds between the adsorptive and the adsorbent.¹⁴⁴ In materials such as MOFs, porous carbons, and zeolites, gases adhere to the surface of pores through physisorption.¹⁴⁶ Physisorption isotherms represent the amount of gas adsorbed versus the relative pressure.¹⁰⁸ The IUPAC recommendations classify those isotherms into six types, each reflecting different adsorption behaviours and pore structures, as discussed in **section 1.6**.

One class of materials that has gained significant attention in gas sorption studies is MOFs. Their exceptionally high surface areas and tunable pore sizes make them ideal candidates for gas sorption applications. Studying gas sorption in MOFs is crucial for understanding surface properties, including surface area and the nature of adsorption sites. A widely used technique for determining the specific surface area of MOFs is the Brunauer-Emmett-Teller (BET) method, which analyses gas adsorption data.^{144,145} Typically, gases such as nitrogen and argon are used at cryogenic temperatures (77 K and 87 K, respectively) in these analyses because they are less reactive and provide reliable measurements of the adsorbent's specific surface area.¹⁴⁴ Several MOFs have demonstrated the capability to adsorb various gases, including greenhouse gases and toxic gases (e.g. CO₂, NO_x, SO₂, NH₃ and H₂O) and energy gases (e.g. H₂ and

CH₄).^{147,148,149} However, only CO₂, H₂, and H₂O sorption are discussed, as they are the only gases tested in this study.

1.9.1. Carbon Dioxide Sorption

The global greenhouse effect has resulted in significant challenges, such as rising temperatures, melting glaciers, sea-level rise, and accelerated species extinction.^{24,150} CO₂, mainly produced by human activities such as electricity generation, industrial production, and transportation, is a primary greenhouse gas responsible for these changes.¹⁵¹ As a result, reducing CO₂ emissions from power plants and industrial facilities has become increasingly important. There is a growing global interest in CO₂ capture and storage technologies, with adsorption emerging as an effective method

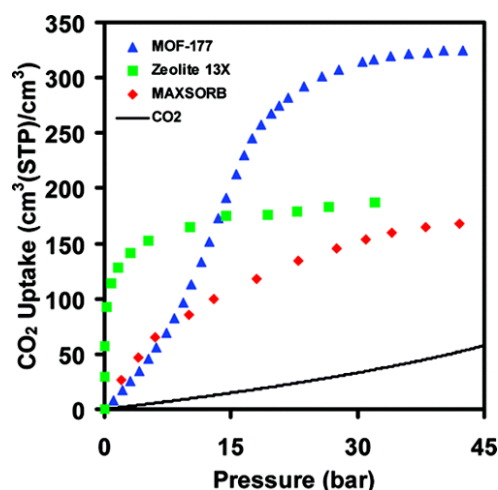


Figure 1.22. Comparison of the volumetric CO₂ capacity: crystalline MOF-177 (blue) vs. zeolite 13X pellets (green), MAXSORB carbon powder (red), and pressurised CO₂ (black). Reprinted (adapted) with permission from Millward, A. R.; Yaghi, O. M. *Metal-organic frameworks with exceptionally high capacity for storage of carbon dioxide at room temperature.* *J. Am. Chem. Soc.* **2005**, 127, 17998–17999. Copyright (2005) American Chemical Society.¹⁵⁴

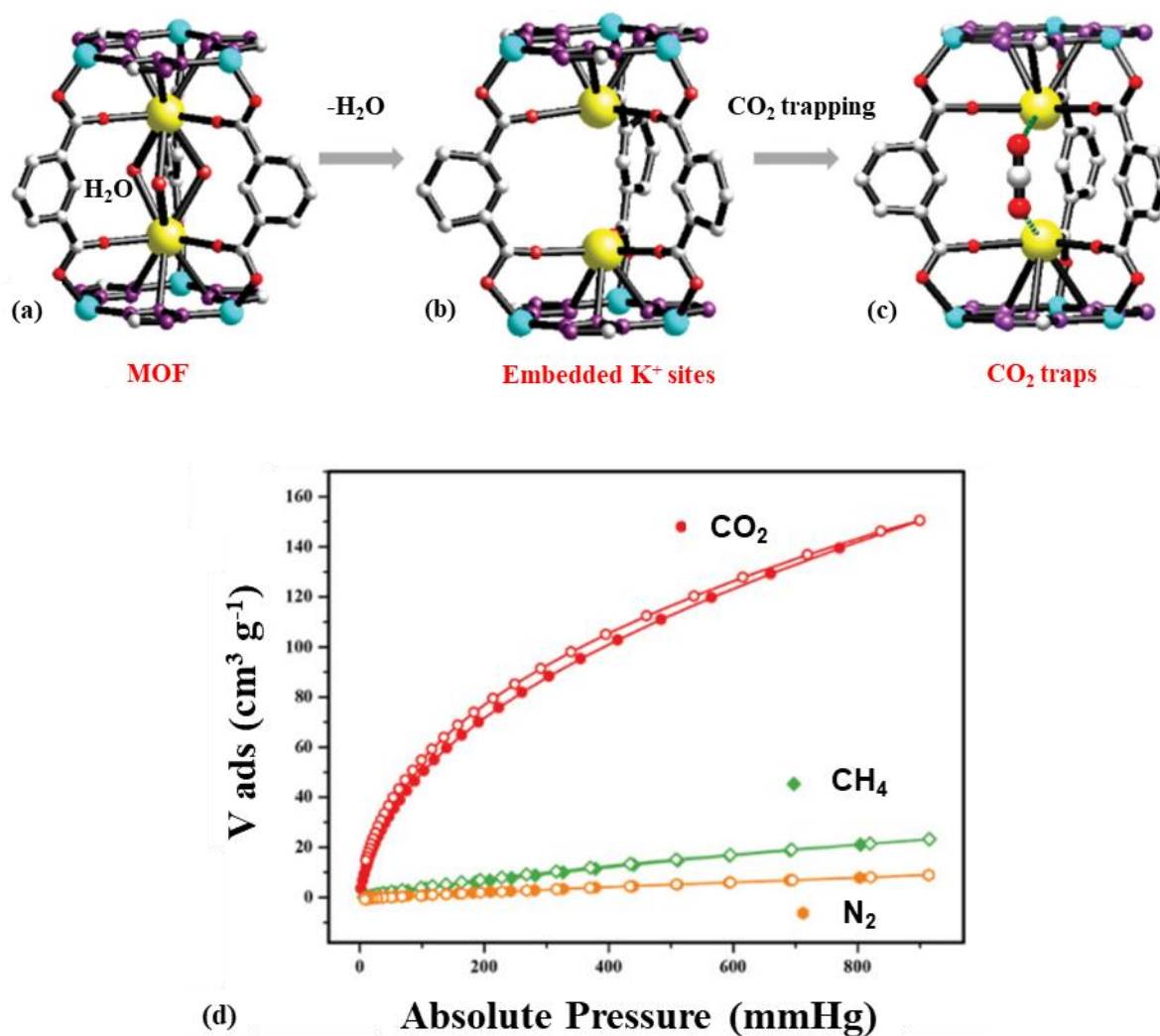


Figure 1.23. Structural differences in the environment of K⁺ in (a) NKU-521 (as-synthesised), (b) NKU-521a (activated form), (c) NKU-521a-CO₂ (from molecular simulation). (d) Sorption isotherms of CO₂, CH₄, and N₂ for NKU-521a at 273 K. *Figure reprinted (adapted) with permission from Li, N.; Chang, Z.; Huang, H.; Feng, R.; He, W.; Zhong, M.; Madden, D. G.; Zaworotko, M. J.; Bu, X. Specific K binding sites as CO₂ traps in a porous MOF for enhanced CO₂ selective sorption. Small* **2019**, 15, 1900426. Copyright (2019) Germany Chemical Society.¹⁵⁷

due to its cost efficiency, low energy demands, and versatility across various conditions.^{150,151,152,153} MOFs are ideal for CO₂ capture and storage due to their high crystallinity, large surface areas, exceptional porosity, and customisable and

adaptable structures.^{69,91,93,101,154} They may outperform traditional adsorbents like zeolite or activated carbon (Figure 1.22).¹⁵⁴

The strength of interactions between MOFs and CO₂ molecules is crucial for enhancing CO₂ uptake, particularly at low pressures.¹⁵⁵ Modifying the chemical and physical properties of MOFs can increase these interactions. MOFs offer various sites that enhance their adsorption capacities and selectivities towards CO₂.^{155,156} Structural features and functional modifications such as open metal sites, Lewis basic sites, polar functional groups, hydrophobicity and flexible frameworks allow for more control over tailorability.¹⁵⁵ For example, Li *et al.* showed that immobilising unsaturated alkali metal sites in NKU-521 enhances CO₂ adsorption.¹⁵⁷ K⁺ cations integrated into a trinuclear Co²⁺-tetrazole coordination motif, exposed to the pores after the removal of coordinated water molecules, acted as CO₂ traps, significantly boosting sorption capacity and selectivity over gases such as CH₄ and N₂ (Figure 1.23). Lu *et al.* reported another effective strategy using HHU-5, a MOF featuring free tetrazolyl groups.¹⁵⁸ These groups enhance CO₂ adsorption due to their uncoordinated nitrogen atoms, acting as electron-rich sites that attract the electropositive carbon atoms of CO₂ molecules to form Lewis acid-base pairs. HHU-5 also demonstrates selective CO₂ adsorption over N₂ and CH₄.

A critical parameter in evaluating MOF performance in CO₂ capture is the isosteric heat of adsorption (Q_{st}), which measures the interaction strength between CO₂ molecules and the MOF pore surface and reflects the energy required for adsorbent regeneration.¹⁵⁶ Q_{st} is determined from adsorption isotherms measured at various temperatures, usually between 273 K and 298 K.^{128,159} Representing the heat released

during the exothermic adsorption process, Q_{st} is conventionally reported as a positive value ($Q_{st} = -\Delta H_{ads}$).¹⁶⁰ Higher Q_{st} values indicate stronger CO₂-MOF interactions and usually correlate with higher adsorption capacity but require more energy for desorption, while lower Q_{st} values mean weaker interactions and easier regeneration.¹⁵⁶ The ideal Q_{st} for CO₂ capture is between 35 and 50 kJ mol⁻¹ to minimise regeneration cost.^{156,161}

1.9.2. Hydrogen Sorption

The focus on developing carbon-neutral alternatives to fossil fuels, mainly for automotive transportation, has intensified due to concerns about escalating atmospheric CO₂ levels and their irreversible ecological impact.¹⁶² Fuel-cell systems, particularly hydrogen fuel cells, are considered promising replacements for gasoline and diesel engines due to hydrogen's high energy efficiency, non-toxic nature, and minimal environmental footprint.^{162,163,164} However, the widespread adoption of hydrogen faces challenges, notably its very low volumetric energy density under ambient conditions (0.0813 g L⁻¹ at 298 K and 1 bar).^{165,166} This necessitates either high-pressure compression, which requires significant energy input to compress hydrogen to pressures of up to 700 bar, or cryogenic storage, which involves cooling hydrogen to extremely low temperatures (-253°C) to liquify it, a process that is both energy-intensive and complex.^{164,165} Consequently, the goal is to overcome these obstacles by developing lightweight, cost-effective materials capable of efficiently storing hydrogen near ambient conditions, ideally matching or exceeding liquid hydrogen density.^{162,167}

MOFs, known for their high surface area and favourable adsorption properties, have been thoroughly investigated for hydrogen storage applications.^{40,145,168} Hydrogen uptake measurements in MOFs are typically conducted at 77 K and 1 atm due to the availability of gas adsorption equipment suited to these conditions, in particular relating to pressure.¹⁶⁹ While these conditions provide an initial assessment of a MOF's hydrogen sorption capability, they are far from the real-world conditions under which hydrogen storage systems must operate.

Recent advancements in instrumentation have enabled high-pressure sorption measurements at room temperature, aligning more closely with practical application requirements.¹⁶⁹ The U.S Department of Energy has established ambitious targets for onboard hydrogen storage systems to advance hydrogen as a viable energy carrier. These targets include a gravimetric capacity of 0.055 kg/kg and a volumetric capacity of 0.040 kg L⁻¹ by 2025, and ultimately 0.065 kg/kg and 0.050 kg L⁻¹, applicable at ambient temperatures (-40 to 85 °C) and pressures below 12 bar.¹⁷⁰ For MOFs, achieving these goals remains challenging due to weak hydrogen binding at room temperature, where solid-gas interaction energies are comparable to thermal vibration energies, resulting in low uptake (<1 wt%). In contrast, at 77 K, the interaction between hydrogen and MOFs strengthens significantly, leading to enhanced uptake.

Optimising hydrogen storage in MOFs involves a multi-faceted approach that integrates pore size engineering, ligand modification, impregnation, catenation strategies, utilisation of open metal sites, and selection of lighter metals.^{167,171} In the porous coordination network (PCN) series of MOFs studied by Yuan *et al.*, PCN-61, which has the smallest pore diameter, exhibited the highest hydrogen uptake capacity of 2.25 wt % in the low-pressure region (<1 bar) compared to PCN-66 (1.79 wt%) and PCN-68 (1.87 wt%) with larger pores.¹⁷² This shows that MOFs with pore diameter

close to the kinetic diameter of hydrogen molecules (2.89 Å) are more effective for hydrogen adsorption at low pressure, due to enhanced interactions between the adsorbed hydrogen molecules and the pore walls.¹⁴⁶ Thus, adjusting pore diameter can enhance the hydrogen storage capacity of MOFs.

1.9.3. Water Sorption

Water is undeniably the most essential resource for life on Earth. Despite its apparent abundance, only 2.5% of Earth's water is fresh, with most of it locked in glaciers (68.7%) and groundwater (30.1%).^{173,174} This limited availability leaves a significant portion of the global population experiencing water stress. Ocean water, constituting 96.5% of the Earth's water, requires energy-intensive desalination, which is impractical for many regions.^{173,175} Atmospheric water vapour, amounting to 10% of freshwater resources, offers a potential solution.

Technologies for harvesting this atmospheric water include fog collectors and adsorption-based systems.^{173,174} Fog collectors, however, are geographically limited by their need for high humidity. Adsorption-based systems show more promise, but current desiccants like calcium chloride (CaCl_2) and silica gel are energy-intensive to regenerate.^{173,176} This highlights the need for new adsorbents. MOFs are promising candidates due to their customisable structure, which can be optimised for high water stability, tailored hydrophilicity, and adjustable pore sizes.¹⁷³ While initial MOFs were unstable in water,^{177,178,179} the development of new classes of MOFs constructed from high-valence metal ions such as Cr^{3+} , Al^{3+} , Zr^{4+} , and Ti^{4+} has improved their hydrolytic stability, making them suitable for water-related applications.^{180,181,182} This enhanced

stability is primarily due to high-valence metal ions forming stronger bonds with the ligand, making it more resistant to water attack.^{183,184}

Several key criteria have been identified for designing effective MOFs for water capture.^{185,186} Firstly, hydrothermal stability is critical, as MOFs must withstand exposure to water in both liquid and vapour forms. Secondly, MOFs should exhibit steep uptake isotherms at specific relative pressures (Figure 1.24), enabling efficient adsorption and desorption of water with minimal changes in pressure or temperature. Thirdly, a large water working capacity is required for greater efficiency during cycles, allowing for higher uptake and release of water per unit of MOF. Additionally, the

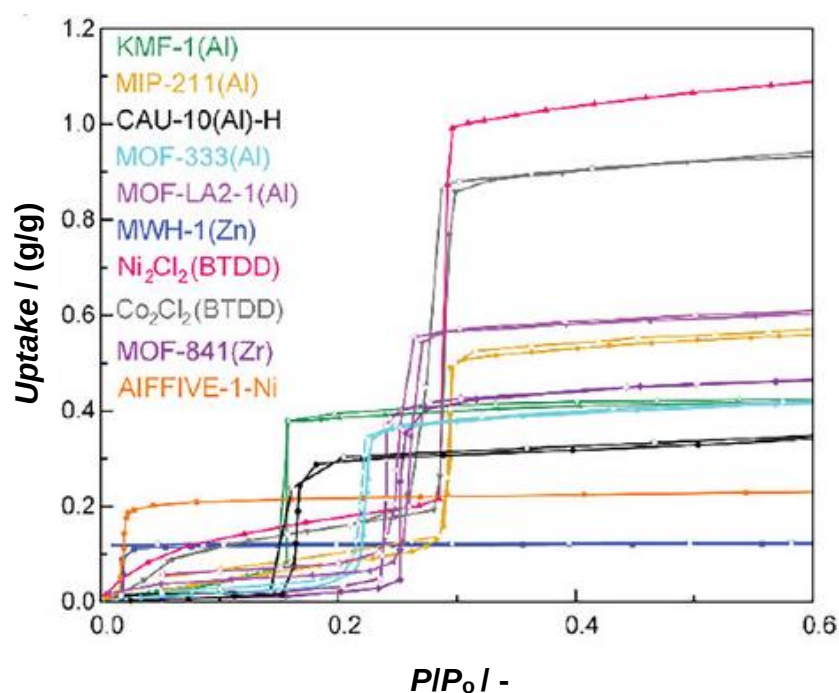


Figure 1.24. Gravimetric uptake isotherms of selected MOFs: water adsorption (solid symbols) and desorption (open symbols) with very steep uptake at various relative pressures at 298 K. *Figure reprinted (adapted) with permission Zhang, B.; Zhu, Z.; Wang, X.; Liu, X.; Kapteijn, F. Water adsorption in MOFs: structures and applications. Adv. Fun. Mater. 2023, 2304788. Copyright (2023) Germany Chemical Society.*¹⁸⁶

adsorption-desorption hysteresis should be tailored to a specific application, with minimal or no hysteresis preferred for atmospheric water harvesting and controlled hysteresis beneficial for indoor humidity regulation. High cycling durability is essential to prevent performance degradation due to repeated water adsorption and desorption. Finally, fast adsorption-desorption kinetics, along with effective mass and heat transport, are necessary to achieve energy efficiency and ensure rapid performance without compromising thermal diffusivity. Furukawa and co-workers reported on a series of Zr(IV)-based MOFs to evaluate their water sorption properties.¹⁸⁵ Among them, MOF-801-P and MOF-841 demonstrated high water uptake at low relative pressures, stability over multiple adsorption/desorption cycles, and easy regeneration at room temperature, making them the best performers based on these criteria. These criteria depend on factors such as the organic ligands and functional groups, the inorganic building unit, the shape and size of the cavities, and the arrangement and flexibility of the frameworks.¹⁸⁰ For example, the Zr-adip MOF, which includes nitrogen functional groups, demonstrates significantly improved water uptake capacities at low relative pressures and maintains high efficiency in water adsorption and desorption cycles, significantly outperforming its unfunctionalised counterpart, MIP-200.¹⁸⁷ This improvement is primarily attributed to nitrogen incorporation into its organic ligands, which enhances their hydrophilicity and introduces extra binding sites that facilitate weak hydrogen-bonding interactions with water molecules, particularly effective at lower pressures.

1.10. Motivation

The development of MOFs has significantly advanced the field of crystal engineering, offering innovative solutions for gas storage, separation, and catalysis due to their exceptional porosity, structural tunability, and functional versatility. This study aims to contribute to this growing field by exploring mixed-ligand and single-ligand strategies for synthesising MOFs using diverse organic ligands and transition metals, focusing on their structural and functional properties.

Mixed-ligand systems are particularly promising as they offer increased opportunities to construct MOFs with diverse and complex topologies. Carboxylate and pyridyl ligands have been extensively studied, offering numerous advantages in mixed-ligand frameworks, as discussed in **section 1.3**. While significant focus has been placed on pyridyl donor ligands such as 4,4'-bipyridine and its derivatives, mixed-ligand MOFs incorporating functional neutral ligands with oxygen donor sites have been less explored.¹⁸⁸ Pyridine *N*-oxide (pyO) ligands present distinctive advantages over pyridine-type ligands: (a) oxygen is a harder donor than nitrogen; (b) pyO can bridge multiple metal centers, whereas pyridyl nitrogen typically coordinates to one; (c) pyO ligands act as longer spacers, promoting the formation of more porous frameworks; and (d) they exhibit high coordination ability with various transition metals, even at low pH values.^{188,189}

Building upon previous work conducted in the Oliver laboratory, where a rigid two-periodic zinc-based mixed-ligand MOF was synthesised using 1,3,5-benzenetricarboxylic acid and 4,4'-bipyridine-*N,N'*-dioxide, this study investigates the potential of 1,3-bis(4-pyridyl)propane-*N,N'*-dioxide (bppdo) in combination with isophthalic acid (H₂ia) as ligands (Figure 1.25).¹⁹⁰ The previous MOF

exhibited isolated voids and cooperative structural changes during SCSC dehydration and rehydration processes, demonstrating the dynamic behaviour of such systems. Bppdo was chosen for its flexibility, stemming from the propylene unit that links the two pyridine *N*-oxide groups.^{191,192} This flexibility allows for multiple conformations (Figure 1.26), maximising void space in the resulting structures and enabling dynamic

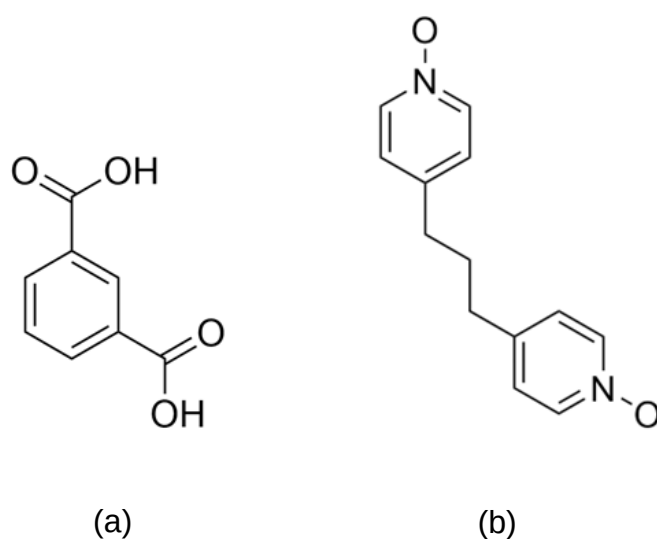


Figure 1.25. Chemical structure of (a) isophthalic acid (H₂ia) and (b) 1,3-bis(4-pyridyl)propane-*N,N'*-dioxide (bppdo).

behaviour. In contrast, H₂ia was selected for its polycarboxylate nature, which is known to provide a high degree of rigidity, chemical durability, and thermal stability.¹⁹³ Its diverse coordination modes (monodentate, chelating, bridging, etc.) upon deprotonation, make it well-suited for constructing stable MOFs. Notably, bppdo has been underexplored in mixed-ligand MOFs, with only 12 structures reported in the Cambridge Structural Database (CSD) thus far.¹⁹⁴

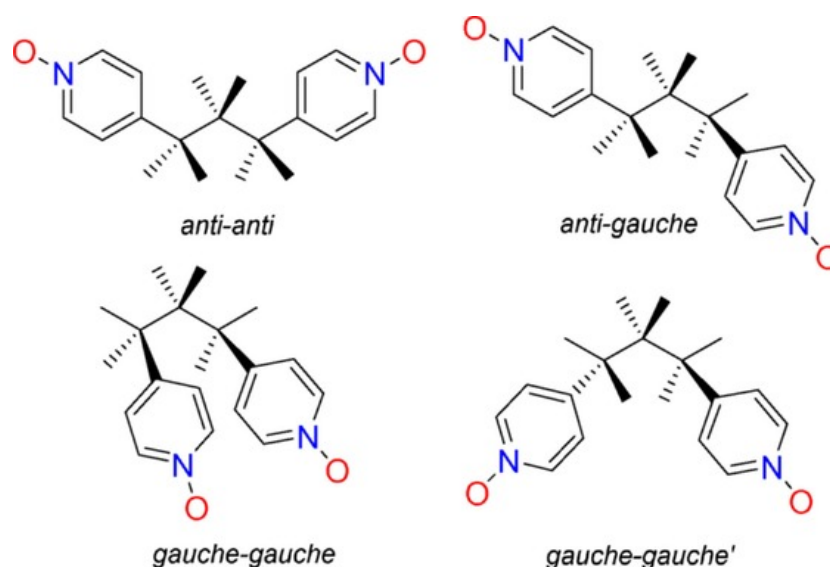


Figure 1.26. Possible conformations of bppdo.¹⁹¹

In addition to mixed-ligand strategies, this study employs a single-ligand strategy using the fluorinated ligand 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) ($H_2hfipbb$) (Figure 1.27). This ligand features a $C(sp^3)$ fluorinated spacer and polar $-CF_3$ groups, which induces a bent configuration that facilitates the formation of helical networks and in some cases, self-interpenetrating structures.^{195,196} The highly polar $-CF_3$ groups may enhance gas sorption properties, particularly for CO_2 , due to their large quadrupolar moment.¹⁹⁷ Moreover, their hydrophobic nature enhances structural resistance to moisture.

Studies have demonstrated the crucial role of solvent templating in determining the structural outcomes of MOFs synthesised with $H_2hfipbb$.^{128,198} Solvent effects are known to influence factors such as layer stacking, degree of interpenetration, and void volume, providing an opportunity to fine-tune MOF properties. Additionally, the choice of metal center plays a significant role in defining MOF stability and functionality.

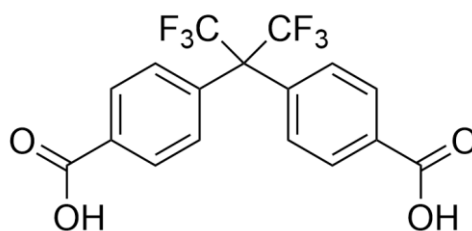


Figure 1.27. Chemical structure of 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (H₂hfipbb).

This study is motivated by the opportunity to leverage solvent templating and metal salt effects to create MOFs with tailored topologies and functionalities. It investigates how variations in solvent type and metal coordination chemistry influence structural features such as interpenetration, void volume, and adsorption behaviour. This comprehensive approach not only aims to expand the understanding of solvent and metal salt effects in MOF synthesis but also to develop advanced MOFs with enhanced stability and sorption properties.

This ligand was selected not only for its promising structural and functional characteristics, but also to build upon prior work conducted in our laboratory, where the influence of solvent templating on interpenetration and gas sorption behaviour was explored using MOFs constructed from the ligand H₂hfipbb.¹²⁸

Metals such as cobalt (II) and manganese (II) ions will be employed to facilitate the formation of robust and versatile mixed-ligand MOFs, while Zn(II) ions will be used for the formation of single-ligand MOFs. These transition metals were chosen due to their ability to form a wide range of coordination geometries (tetrahedral, square-pyramidal, octahedral etc.,).¹⁵ Initially, a wider range of transition metals was screened during the synthesis phase; however, only Co, Mn, and Zn produced crystalline, phase-pure materials with sufficient stability and structural integrity suitable for detailed

characterization and analysis. This final selection reflects both the synthetic feasibility and the relevance of the resulting materials for the goals of this work.

1.11. Objectives

The main objectives of the study presented in this thesis are to:

- Prepare mixed-ligand MOFs using isophthalic acid (H_2ia) in combination with 1,3-bis(4-pyridyl)propane-*N,N'*-dioxide (bppdo) and Co(II) or Mn(II) metal ions.
- Prepare single-ligand MOFs using 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) ($H_2hfipbb$) as a functionalised dicarboxylic ligand and Zn(II) metal ion.
- Characterise the synthesised compounds through X-ray diffraction and thermal analysis techniques.
- Examine the gas sorption capabilities of the synthesised compounds.

Chapter 2:

Experimental Methods

This chapter provides an overview of the metal salts and organic ligands used in MOF synthesis. It discusses the synthetic methods and analytical techniques employed for MOF characterization, including instrumentation for X-ray diffraction, hot-stage microscopy, thermogravimetric analysis, differential scanning calorimetry, and gas sorption studies. Additionally, the software tools used for solving, refining, and analysing crystal structures are described.

2.1. Starting Materials

The metal salts cobalt(II) nitrate hexahydrate (purity >98%), manganese(II) nitrate tetrahydrate (> 97% purity) and zinc(II) nitrate hexahydrate (98% purity), along with the organic ligands 1,3-benzenedicarboxylic acid (99% purity), also known as isophthalic acid, and 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (98% purity) were purchased from Merck (Germany). The ligand 1,3-bis(4-pyridyl)propane-*N,N'*-dioxide was synthesised from 1,3-bis(4-pyridyl)propane according to the literature method.¹⁹⁹ Yield: 62%. Solvents, including *N,N'*-dimethylformamide (99.8% purity), *N,N'*-dimethylacetamide (99% purity), ethanol (99% purity), methanol (99% purity) and deionised water, were used for MOF synthesis. All solvents, except deionised water (obtained from a Milli-Q water purification system), were purchased from Merck. All chemicals were used as received without further purification.

2.2. General Synthesis Procedures

MOFs were synthesised using two distinct methods: (1) solvothermal synthesis, and (2) two-step synthesis involving a solvothermal reaction followed by slow evaporation crystallization. Brief descriptions of these methods are provided below, with complete synthetic details for each compound included in the relevant chapters.

2.2.1. Solvothermal Synthesis

Ligands and metal salts were dissolved in separate solvents before combining the solutions. The resulting mixture was transferred to either a glass vial or aluminium

autoclave, sealed tightly, and heated in an oven at a specific temperature for one to three days. Crystals formed during this heating period.

2.2.2. Solvothermal Synthesis with Slow Evaporation

The ligands and metal salts were first dissolved in separate solvents and then combined. The resulting mixture was transferred to a glass tube, sealed tightly, and heated in an oven at a specific temperature for three days. After heating, the solution was removed from the oven, transferred into a glass vial, and left undisturbed on the benchtop at room temperature. Crystallization of the MOF occurred through the slow evaporation of the solvent.

2.3. X-ray Diffraction

2.3.1. Single-Crystal X-ray Diffraction (SCXRD) Analysis

Crystal structure determination provided valuable information, including atomic types, atomic connectivity, interatomic distances and angles, intermolecular interactions, and symmetry operations within the crystal. This was achieved using the non-destructive single-crystal X-ray diffraction (SCXRD) technique, which required high-quality well diffracting crystals. A suitable single crystal was selected, removed from the mother liquor, and immediately covered in Paratone N oil (Exxon Chemical Co., TX, USA) in order to prevent solvent loss.²⁰⁰ The crystal was then mounted on a nylon loop attached to a rigid holder and placed on the goniometer head.

In addition to standard SCXRD analysis, variable-temperature SCXRD (VT-SCXRD) was employed to observe structural changes under controlled temperature variations,

including processes such as desolvation and rehydration, without physically removing the crystal from the instrument. For this analysis, a fresh crystal was selected and glued directly onto a specialized holder to prevent movement during the experiment. Unlike the standard method, the crystal was not covered in oil, allowing it to remain exposed to the ambient environment within the diffractometer chamber.

Preliminary unit cell determination was first carried out at room temperature to assess whether this was consistent with the subsequent unit cell obtained for low temperature full data collection and in this manner to assess for possible phase changes upon cooling. The measured unit cell parameters were compared against entries in the Cambridge Crystallographic Database (CSD) to determine whether these matches those of any existing deposited crystal structures before proceeding with full data collection.¹⁹⁴

Unit cell determinations and data collections were carried out on a Bruker D8 VENTURE single crystal X-ray diffractometer (Madison Wisconsin, U.S.A) using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) generated at 50 kV and 1.4 mA. The crystals were cooled to 100 K using a nitrogen vapour stream, with the temperature controlled by an Oxford Cryostream-800 (Oxford Cryosystems Ltd, Oxford, U.K.). Data reduction and unit cell refinement were carried out using the SAINT-Plus program.²⁰¹ The X-ray diffraction data were corrected for Lorentz-polarization effects and scaled for absorption effects using the SADABS program.²⁰²

The XPREP program was used to suggest the initial space group, based on the *hkl* data, and also for preparation of the input file for structure solution via SHELXT.²⁰³ The latter program was accessed via the crystallographic suite OLEX2 interface,²⁰⁴ which also allowed refinement to proceed using the full-matrix least-squares method, based

on F^2 values against all reflections, including anisotropic displacement parameters for all non-H atoms, as implemented in SHELXL-2019/3.²⁰⁵ Where necessary, often due to disorder, various restraints and constraints were employed to ensure chemically reasonable structures and stabilise refinement. The RIGU restraint promoted directional similarity between the anisotropic displacement parameters (ADPs) of bonded atoms, particularly for those with high thermal motion. SIMU was used to ensure similar ADPs for neighbouring atoms within a specified distance, especially in disordered molecules with poor electron density. The EADP constraint applied identical ADPs to chemically equivalent or disordered atoms, while the DANG restraint maintained chemically reasonable "1,3 distances" with a default tolerance of ± 0.02 Å. DFIX ensured bond lengths adhered to known chemical expectations, restraining distances with a default tolerance of ± 0.02 Å. The FLAT restraint enforced planarity in aromatic rings, correcting deviations caused by poor data. Finally, the SADI restraint ensured similarity in bond lengths for chemically equivalent or symmetry-related bonds, maintaining consistent geometry in disordered regions.

After all non-hydrogen atoms had been placed and refined satisfactorily with isotropic temperature factors, they were refined anisotropically. All hydrogen atoms were placed using riding models with isotropic thermal factors 1.2 or 1.5 times that of their parent atoms. OLEX2 also allowed visualization of the structures during the refinement process.²⁰⁴

2.3.2. Powder X-ray Diffraction (PXRD)

For each compound, a CIF or SHELX RES file, which contained the atomic coordinates, was opened in the program Mercury.²⁰⁶ Subsequently, Mercury was used

to calculate an idealised PXRD pattern using the same wavelength ($\lambda = 1.5406 \text{ \AA}$) as used during the experimental measurements. The calculated pattern was then compared to the experimentally obtained PXRD pattern to assess whether the single crystal accurately represents the bulk material. Furthermore, PXRD was utilised to ascertain whether the desired product has been obtained in subsequent experiments. The PXRD experiments were performed on a Bruker D2 Phaser (2nd generation) benchtop diffractometer (Billerica, Massachusetts, U.S.A) equipped with a 1D LynxEye detector, using Cu K α -radiation ($\lambda = 1.5406 \text{ \AA}$) generated at 30 kV and 10 mA. All the samples were finely ground and placed on a silicon zero-background sample holder. Scans were conducted over a $4 - 40^\circ 2\theta$ range, with a step size rate of $0.016^\circ \text{ s}^{-1}$, and a primary beam path slit width of 0.6 mm.

2.3.3. Variable-Temperature Powder X-ray Diffraction (VT-PXRD)

VT-PXRD experiments were conducted in order to investigate the impact of solvent removal on sample crystallinity at varying temperatures. This was required since it is preferable for the porous framework to maintain its structure after solvent removal. The VT-PXRD patterns provided insight into the crystalline phases and long-range order of the analysed materials as the temperature increased. This experiment was performed on a Bruker D8 Advance X-ray diffractometer (Billerica, Massachusetts, U.S.A) fitted with a LynxEye detector, using Cu K α -radiation ($\lambda = 1.5406 \text{ \AA}$) generated at 30 kV and 40 mA. Scans were conducted over a $4 - 40^\circ 2\theta$ range, with a step size rate of $0.016^\circ \text{ s}^{-1}$. The sample preparation process entailed gently grinding a substantial amount of the product to ensure even filling of the metal sample holder. Throughout the experiment, the sample was kept under vacuum conditions, except during the initial PXRD measurement and final exposure to air. The PXRD under

vacuum was recorded immediately after the vacuum was established, with no prolonged holding time prior to data collection.

2.4. Thermal Analysis

In this study, three distinct thermal analysis techniques were used: thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and hot-stage microscopy (HSM). These techniques were used to determine various thermal properties, including desolvation, melting, phase changes, and compound decomposition.

2.4.1. Thermogravimetric Analysis (TGA)

TGA was used to determine the percentage mass loss of the sample as a function of temperature. This analysis aimed to determine the number of guest molecules per asymmetric unit present in the crystal structure. Furthermore, it enabled the characterization of the thermal stability and decomposition behaviour of the framework. To prepare for the TGA experiments, crystals were removed from the mother liquor and thoroughly dried on filter paper to remove surface solvents. Subsequently, samples, weighing between 2 – 8 mg, were placed in an open platinum crucible and loaded in the TA instrument. The samples were then subjected to a consistent heating rate of 10 °C min⁻¹, ranging from ~15 to 500 – 550 °C, while being purged with dry nitrogen gas at a flow rate of 60 mL min⁻¹. These TGA experiments were conducted using a TA-Q500 Thermogravimetric Analyser from TA instruments, and the acquired data were analysed with the Universal Analysis 2000 software.

2.4.2. Differential Scanning Calorimetry (DSC)

DSC is a technique that measures the difference in heat flow between the sample and a reference pan while maintaining the same temperature of both pans as a function of temperature. This heat flow difference is represented as either endothermic troughs or exothermic peaks. DSC is a valuable tool for determining the enthalpy associated with thermal events such as desolvation, melting, recrystallizations, solid-solid phase transitions, and sample decomposition.

Before conducting the DSC analysis, the sample was first dried on filter paper to remove the surface solvent. The sample, ranging in mass from ~1 to 2 mg, was then placed in an aluminium pan with a vented lid. The pan was subsequently loaded into a TA Discovery DSC 25 instrument and subjected to a consistent heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$, within a temperature range of 25 to 350 – 400 $^{\circ}\text{C}$, under a dry nitrogen purge gas flow rate of 60 mL min^{-1} . Data obtained from the DSC experiments were analysed using the TRIOS software from TA instruments. Samples were not heated to the point of decomposition during the analysis in order to prevent sample spillage that could damage the instrument's thermocouple. As a result, no direct comparisons with regard to decomposition events recorded on the HSM or TGA instruments could be made.

2.4.3. Hot Stage Microscopy (HSM)

HSM experiment was performed to visualise and study various thermal events such as desolvation, melting, phase transitions, and compounds. In this study, HSM primarily serves the purpose of observing thermal desolvation and decomposition processes. To identify the desolvation phase, the sample was immersed in silicone oil,

which allowed the observation of bubbling, indicative of solvent loss. Another sign of desolvation was the potential transformation of initially clear crystals into an opaque state due to partial solvent loss. The opacification of crystals also indicated the loss of monocrystallinity, but not necessarily the total loss of crystallinity as these could still be polycrystalline. The temperatures at which these physical changes occurred during heating were compared to the thermal events measured using TG and DSC analysis. Notably, the temperatures of the thermal events observed in HSM often differed from those detected in TG and DSC analysis, possibly owing to variations in equipment configurations and the particle size of the analysed sample.

During the experiment, the samples were placed on a cover slip under a small amount of silicone oil and subjected to the heating process. This was accomplished using a Linkam THM600 hot stage and Linkam TP92 temperature control unit mounted on a Nikon SMZ-10 stereoscopic microscope. Images were captured at different temperatures with the assistance of a real-time ThorLabs Digital colour video camera, operated through the ThorCam software. The heating rate used was $10\text{ }^{\circ}\text{C min}^{-1}$, with the temperature range depending on the MOF, varying between 22 to $500\text{ }^{\circ}\text{C}$.

2.5. Gas Sorption Studies

Gas sorption studies were conducted to investigate the adsorption capacity of the compounds with respect to gases, such as nitrogen, carbon dioxide and hydrogen. Additionally, water vapour sorption experiments were performed on the same compounds. All gas and vapour sorption experiments were carried out using a Micromeritics 3Flex Surface Area Analyser. To ensure uniform surface area contacts, each sample was homogenised through grinding and weighed within the range of 45 to

80 mg. For all compounds, the sample preparation involved degassing by subjecting them to *in situ* heating at either 120 or 200 °C under vacuum for about 2 hours on the 3Flex analyser before analysis. This rigorous degassing procedure was employed to remove any solvent within the compounds, as the analysis required an empty framework. CO₂ sorption experiments were conducted at various temperatures to determine the isosteric heat of adsorption (Q_{st}). The sorption of hydrogen was carried out at 77 K. N₂ sorption, conducted at 77 K, was used to ascertain the Brunauer-Emmett-Teller (BET) surface area. A Micromeritics water bath was used for experiments conducted within the temperature range of 273 to 298 K, while a liquid nitrogen bath was used for experiments conducted at 77 K. To perform gas sorption experiments at 195 K, a slurry was created using a mixture of dry ice and acetone to achieve the low temperature. All experiments were conducted at low pressures, as the equipment has a maximum measurement capacity of ~1 bar. Subsequent analysis of the sorption isotherms was conducted using the 3Flex Micromeritics software.

2.6. Computer Packages

The Cambridge Structural Database (CSD), accessed through ConQuest, played a significant role in verifying the novelty of the synthesised structures.¹⁹⁴ Additionally, the CSD was utilised to obtain literature compounds with similar structural motifs to the compounds presented in this thesis. The X-SEED program served as a graphical interface for additional programs like POV-RAY and LAYER.²⁰⁷ LAYER was useful in investigating and identifying systematic absences in the intensity data collected to confirm the space group suggested by XPREP visually. Meanwhile, POV-RAY in X-SEED and MERCURY were used to generate high-quality images depicting

molecular structure and crystal packing.²⁰⁶ MERCURY also proved valuable in determining the free void space within the porous framework, using a grid spacing of 0.3 Å and a probe radius of 1.2 Å. Additionally, it was employed to calculate the root-mean-square (RMS) deviation of overlayed structures. In parallel, the program PLATON was used to extract molecular parameters and geometrical data.²⁰⁸

2.7. Appendices

Table 2.1: Crystallographic file types that can be found in the appendices.

File Extensions	Contents
.hkl	Reflection data
.res	SHELX coordinate data
.lis	PLATON output file – geometrical parameters
.cif	Crystallographic information file
.pdf	CheckCif report

Chapter 3:

Co/Mn Mixed-Ligand MOFs

This chapter presents the characterisation of synthesised mixed-ligand metal-organic frameworks (MOFs) formed with isophthalic acid and 1,3-bis(4-pyridyl)propane-*N,N'*-dioxide as ligands. The frameworks, $[\text{Co}_3(\text{ia})_3(\text{bppdo})(\text{MeOH})]_n \cdot n(\text{DMF})$ (**1**) and $[\text{Mn}_3(\text{ia})_3(\text{bppdo})(\text{MeOH})]_n \cdot n(\text{DMF})$ (**2**), are isorecticular and isostructural 2-periodic frameworks, synthesised using Co^{2+} and Mn^{2+} ions, respectively, with the same ligand combination. Comprehensive characterization was conducted using X-ray diffraction techniques (SCXRD, VT-SCXRD, PXRD, and VT-PXRD) and thermal analysis methods (HSM, TGA, and DSC). The chapter is divided by characterisation technique with each section discussing the analytical findings for each compound. Additionally, the frameworks were evaluated for their gas and water vapour sorption properties.

3.1. Synthesis

3.1.1. Preparation of $[\text{Co}_3(\text{ia})_3(\text{bppdo})(\text{MeOH})]_n \cdot n(\text{DMF})$ (**1**)

The organic ligands, isophthalic acid (17 mg, 0.10 mmol) and 1,3-bis(4-pyridyl)propane-*N,N'*-dioxide (22 mg, 0.10 mmol) were dissolved in a solvent mixture of 4.0 mL MeOH and 4.0 mL DMF. The metal salt, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (28 mg, 0.10 mmol), was dissolved in 1.0 mL H_2O in a separate vial. Both solutions were combined and stirred for 10 min at room temperature to give a pale-pink solution. Purple, plate-shaped crystals suitable for X-ray diffraction were obtained after heating the solution in an oven at 90 °C for 48 hours. The yield was 68% (based on Co), which was calculated based on the crystalline material obtained.

3.1.2. Preparation of $[\text{Mn}_3(\text{ia})_3(\text{bppdo})(\text{MeOH})]_n \cdot n(\text{DMF})$ (**2**)

A synthetic procedure analogous to that described for **1** was employed, with the only difference being the use of the metal salt $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (24 mg, 0.096 mmol). After the solutions were combined, the resulting clear solution was transferred into an autoclave and subsequently placed inside an oven. Following a 24 h heating period at 90 °C, light-brown, plate-shaped crystals were obtained. The yield was 45% (based on Mn), which was calculated based on the crystalline material obtained.

3.2. Single Crystal X-ray Diffraction Analysis

3.2.1. Structure Description

Single-crystal X-ray diffraction analysis reveals that **1** and **2** have similar unit cell parameters, both crystallizing in the monoclinic crystal system with the $P2_1/c$ space

group (Table 3.1). They are isostructural, with nearly identical atomic coordinates, and isorecticular, sharing the same network topology. At 100 K, the asymmetric units (ASUs) of both structures consist of three metal cations, designated as M1, M2, and M3 (where M = Co²⁺ in **1** and Mn²⁺ in **2**), three fully deprotonated, bridging isophthalic acid ligands (H₂ia), one neutral bridging 1,3-bis(4-pyridyl)propane-*N,N'*-dioxide (bppdo) ligand, one coordinated MeOH molecule, and one uncoordinated DMF molecule (Figure 3.1).

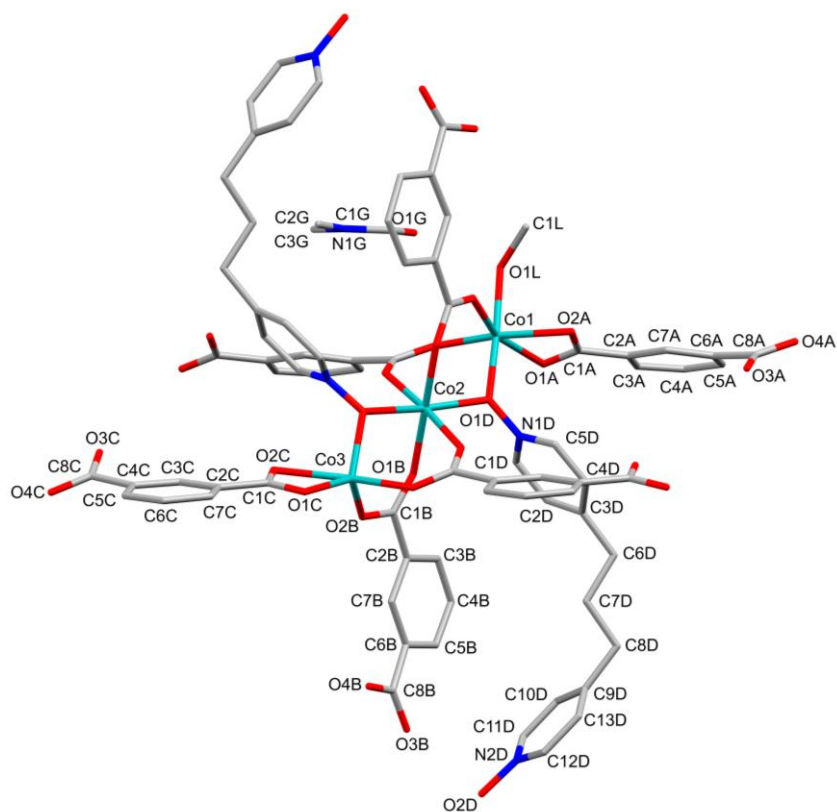
The bppdo ligand adopts a stable *anti-anti* conformation about the propylene group.¹⁹¹ The three unique metal ions form a linear trinuclear metal cluster, where M1 and M2 ions adopt distorted octahedral geometries, while M3 exhibits a distorted square pyramidal geometry.

The M1 ion coordinates to two oxygen atoms from two separate bridging bidentate carboxylate groups ($\mu_2\text{-}\eta^1\text{:}\eta^1$) and two oxygen atoms from a chelating carboxylate group ($\eta^1\text{:}\eta^1$) in the equatorial positions, as well as one bridging oxygen atom ($\mu_2\text{-}\eta^2$) from a bppdo ligand and one oxygen atom from a methanol molecule in the axial positions. The central M2 ion coordinates to four oxygen atoms from four distinct bidentate bridging carboxylate groups ($\mu_2\text{-}\eta^1\text{:}\eta^1$) in the equatorial positions and two bridging oxygen atoms ($\mu_2\text{-}\eta^2$) from separate bppdo ligands in the axial positions. In contrast, the M3 ion coordinates to two oxygen atoms from two distinct bidentate bridging carboxylate groups ($\mu_2\text{-}\eta^1\text{:}\eta^1$), two oxygen atoms from a chelating carboxylate group ($\eta^1\text{:}\eta^1$) in the equatorial positions, and one bridging oxygen atom ($\mu_2\text{-}\eta^2$) from a bppdo ligand in the axial position.

Table 3.1. Crystal Data and Refinement Parameters for **1** and **2**.

	1	2
ASU formula	C ₄₁ H ₃₇ Co ₃ N ₃ O ₁₆	C ₄₁ H ₃₇ Mn ₃ N ₃ O ₁₆
Formula weight	1004.52	992.55
Temperature / K	100(2)	100(2)
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> / Å	10.0908(5)	10.1712(5)
<i>b</i> / Å	21.5274(10)	21.8779(12)
<i>c</i> / Å	18.5847(8)	18.6405(11)
α / °	90	90
β / °	93.415(2)	92.579(2)
γ / °	90	90
Volume / Å ³	4030.0(3)	4143.8(4)
<i>Z</i>	4	4
ρ / g cm ⁻³	1.656	1.591
μ / mm ⁻¹	1.301	0.978
<i>F</i> (000)	2052	2028
Crystal size (mm ³)	0.144 × 0.098 × 0.065	0.133 × 0.085 × 0.085
2 θ range for data collection / °	4.374 to 56.724	4.318 to 52.976
Index ranges	-13 ≤ <i>h</i> ≤ 13, -27 ≤ <i>k</i> ≤ 28, -24 ≤ <i>l</i> ≤ 23	-12 ≤ <i>h</i> ≤ 12, -27 ≤ <i>k</i> ≤ 27, -23 ≤ <i>l</i> ≤ 23
Reflections collected	106954	139386
Independent reflections	10059 [<i>R</i> _{int} = 0.0495, <i>R</i> _{sigma} = 0.0249]	8562 [<i>R</i> _{int} = 0.1017, <i>R</i> _{sigma} = 0.0384]
Data/restraints/parameters	10059/0/572	8562/3/574
Goodness-of-fit on <i>F</i> ²	1.321	1.205
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0782, <i>wR</i> ₂ = 0.1623	<i>R</i> ₁ = 0.0818, <i>wR</i> ₂ = 0.1658
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0817, <i>wR</i> ₂ = 0.1638	<i>R</i> ₁ = 0.0966, <i>wR</i> ₂ = 0.1720
Largest diff. peak/hole / e Å ⁻³	0.97/-0.94	1.18/-0.88

(a)



(b)

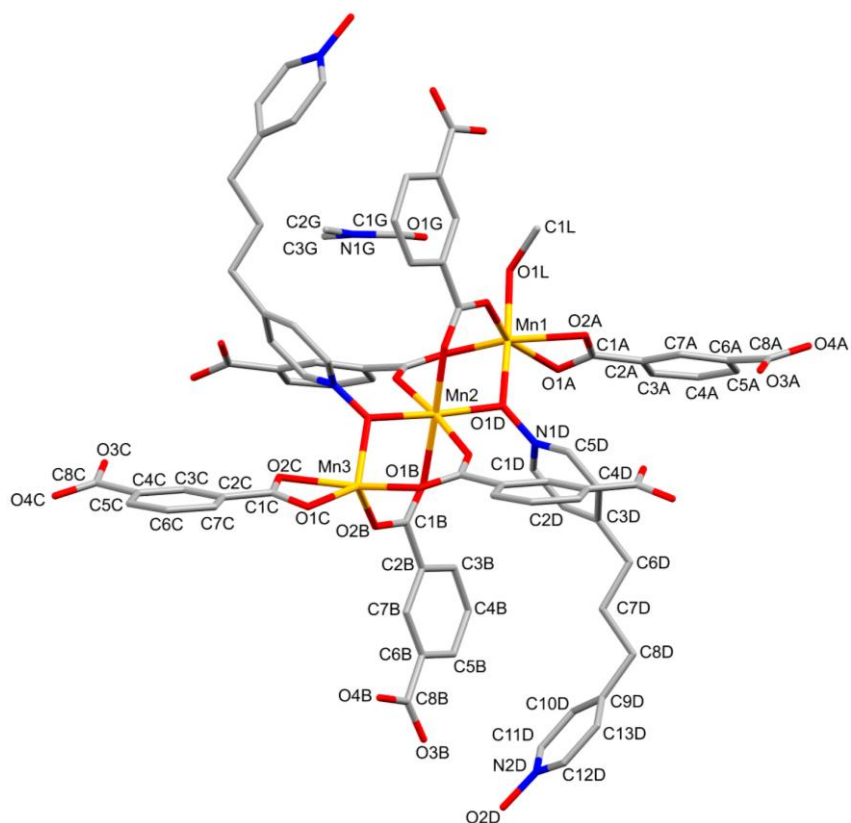


Figure 3.1. The coordination environment of the three unique metal ions: (a) Co^{2+} in **1** and (b) Mn^{2+} ions in **2**. Hydrogen atoms are omitted for clarity, and only atoms of the ASU are labelled.

Table 3.2: Selected bond lengths (Å) around each of the three Co²⁺ ions **1**.

Bond	Length (Å)	Bond	Length (Å)
Co1–O1A	2.183(3)	Co2–O3C	2.099(3)
Co1–O1D	2.082(4)	Co2–O2D	2.192(3)
Co1–O1L	2.180(4)	Co2–O3B	2.043(4)
Co1–O2A	2.118(3)	Co3–O1C	2.037(4)
Co1–O4A	2.009(3)	Co3–O2B	1.967(4)
Co1–O4B	2.011(4)	Co3–O2C	2.221(4)
Co2–O1B	2.082(4)	Co3–O4C	1.972(3)
Co2–O1D	2.122(3)	Co3–O2D	1.988(4)
Co2–O3A	2.096(3)		

Table 3.3: Selected bond lengths (Å) around each of the three Mn²⁺ cations in **2**.

Bond	Length (Å)	Bond	Length (Å)
Mn1–O1A	2.288(4)	Mn2–O3C	2.175(4)
Mn1–O1D	2.145(4)	Mn2–O2D	2.256(4)
Mn1–O1L	2.223(4)	Mn2–O3B	2.120(4)
Mn1–O2A	2.180(4)	Mn3–O1C	2.176(4)
Mn1–O4A	2.071(4)	Mn3–O2B	2.035(5)
Mn1–O4B	2.074(4)	Mn3–O2C	2.210(4)
Mn2–O1B	2.150(4)	Mn3–O4C	2.040(4)
Mn2–O1D	2.210(4)	Mn3–O2D	2.083(4)
Mn2–O3A	2.172(4)		

The M–O bond lengths range from 1.967(4) to 2.221(3) in **1** (Table 3.2), and 2.035(5) to 2.288(4) in **2** (Table 3.3), which are consistent with bond lengths observed in related Co₃/Mn₃ cluster SBUs.^{209,210,211,212} The positive charge (6+) of the three M²⁺ ions in both MOFs is balanced by the negative charge (6-) of the three fully deprotonated H₂ia ligands.

3.2.2. Crystal Packing

Each trinuclear unit in both **1** and **2** connects to four neighbouring trinuclear units via four isophthalate (ia) ligands along the *a*-axis and two ia and two bppdo ligands along the *b*-axis, forming a 2-periodic framework (Figure 3.2). Viewed edge-on, these 2-periodic frameworks stack in an interdigitated ABAB arrangement along the *c*-axis, creating channels between adjacent frameworks where DMF molecules reside (Figure 3.3). The coordinated MeOH molecules are orientated toward the channels containing uncoordinated DMF molecules.

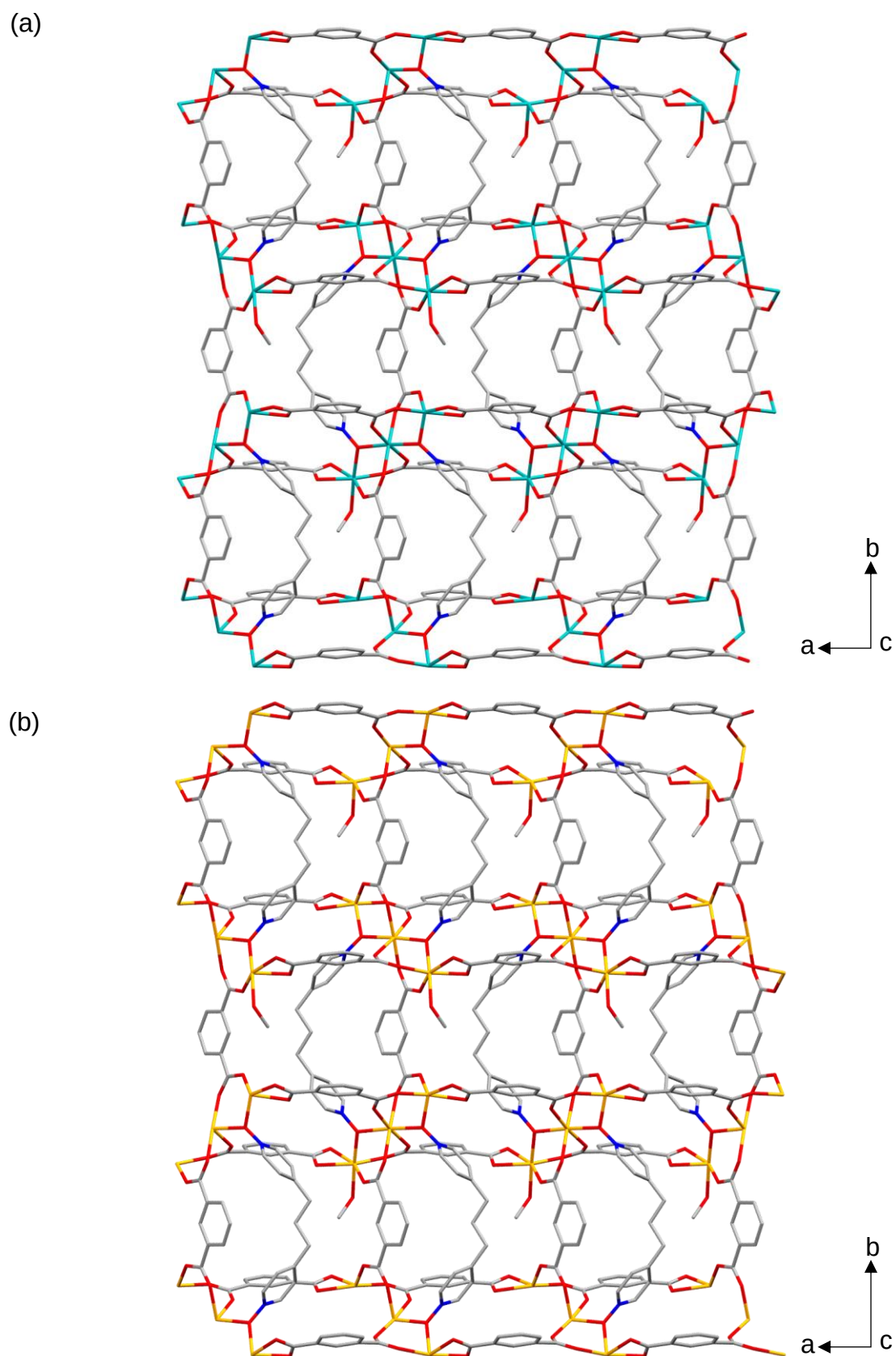


Figure 3.2. Extension of the 2-periodic frameworks along the a - and b -axis in (a) **1** and (b) **2**.

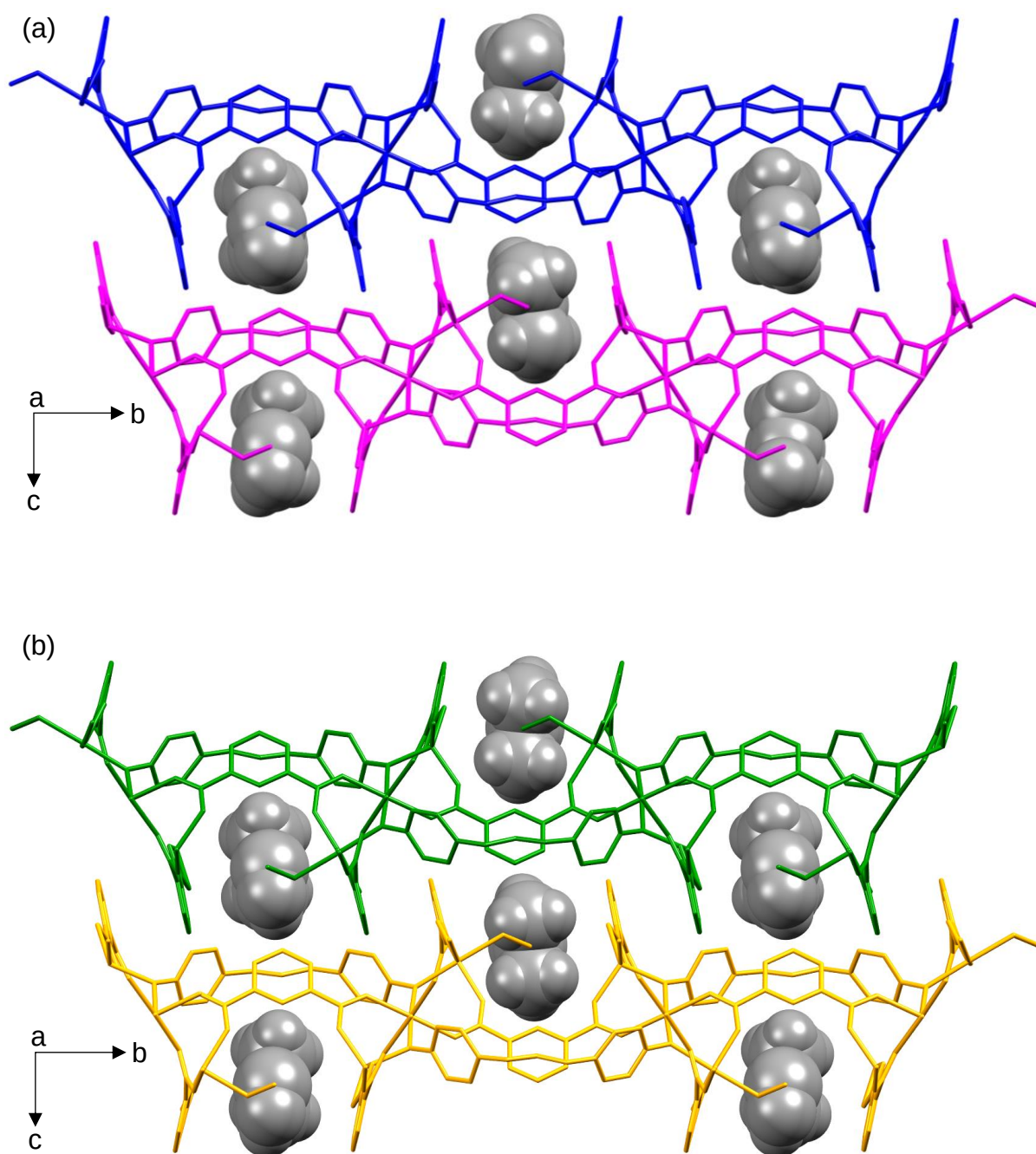


Figure 3.3. Colour-coded 2-periodic frameworks stacked along the *c*-axis, with uncoordinated DMF molecules shown in grey in a space-filling mode for (a) **1** and (b) **2**.

3.3. Thermal Analysis

3.3.1. Thermogravimetric and Differential Scanning Calorimetry Analysis

TGA and DSC analysis were conducted to investigate the thermal stability of **1** and **2**. The TGA and DSC thermograms for both MOFs show similar behaviour upon heating (Figure 3.4). The TGA thermograms indicate a single-step mass loss for **1** and **2** in the temperature ranges of 18 – 301 and 22 – 314 °C, respectively. The experimental mass losses are 11.1% for **1** (calculated 10.5%) and 11.0% for **2** (calculated 10.6%), confirming the removal of one uncoordinated DMF molecule within the cavity and one coordinated MeOH molecule per ASU. The derivative mass curves for both MOFs support the observed solvent loss, each showing a single peak.

The appearance of a single-step mass loss, despite the presence of two different types of solvent molecules, likely arises from structural constraints within the MOF. The coordinated MeOH molecules appear to block the pore channels (refer to Figure 3.3), preventing the uncoordinated DMF from escaping until the coordinated solvent detaches. This leads to the simultaneous release of both solvent types in a single thermal event.

After desolvation, the decomposition onset temperature is 361 °C for **1** and 347 °C for **2**, indicating relatively high thermal stability for both MOFs. Although the decomposition onset occurs at a slightly lower temperature for **2**, its total decomposition is completed at higher temperature than of **1**, suggesting greater stability at elevated temperature. The DSC thermograms for **1** and **2** display prominent, broad endothermic peaks at higher temperatures, with onset at 141 and

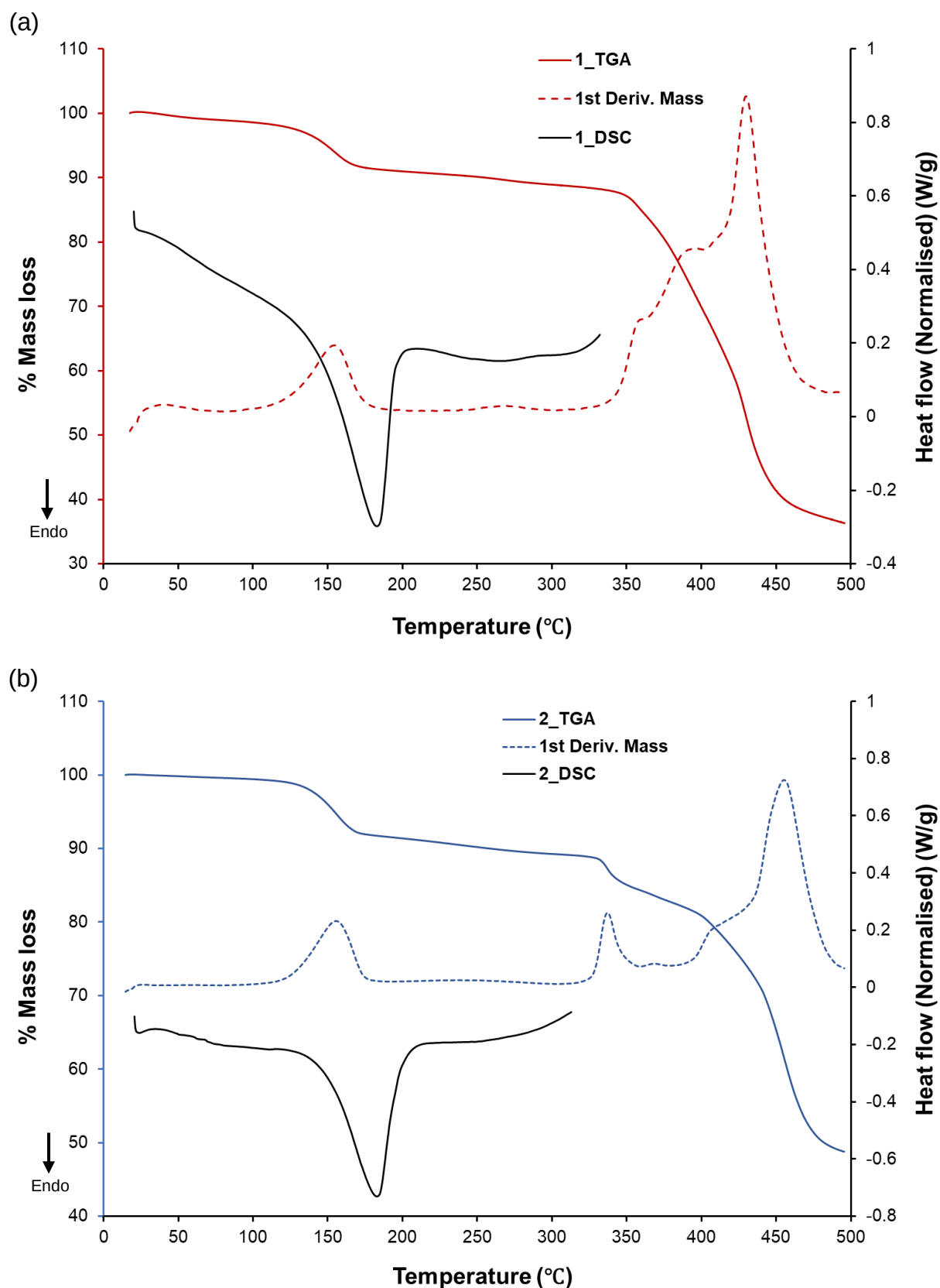


Figure 3.4. Overlay of the TGA thermogram, its first derivative mass, and the DSC thermogram of (a) **1** and (b) **2**.

146 °C, respectively. These peaks correspond to the mass loss of both the uncoordinated DMF and coordinated MeOH in each MOF. The DSC analysis was stopped at the onset of decomposition for all MOFs analysed, to prevent contamination of the instrument cell that would be caused by spillage of the sample (decomposition often causes frothing of the sample).

3.3.2. Hot Stage Microscopy

Crystals of **1** were placed on a microscope slide and covered in silicone oil to observe thermal events, including the loss of monocrystallinity, desolvation, and decomposition over a temperature range from 24 to 400 °C (Figure 3.5). As the temperature increased from 160 to 238 °C, the crystals gradually darkened, with bubbling observed at 238 °C, indicating the release of uncoordinated DMF and coordinated MeOH molecules from the MOF.

This observation aligns with the findings from TGA and DSC analysis. The colour change likely reflects a change in the coordination environment around the Co^{2+} ion, such as the coordinated MeOH molecule being released.²¹³ The crystals continued darkening as heating progressed until they fully decomposed at 400 °C. Notably, no cracking occurred during heating or desolvation, and the crystals retained transparency, suggesting that desolvation may occur through a single-crystal-to-single-crystal (SCSC) transformation.

Similarly, crystals of **2** were placed on a microscope slide and covered with silicone oil to observe thermal events across a temperature range from 22 to 400 °C (Figure 3.6). At room temperature, the crystals were golden in colour. Between 116 and 190 °C, the crystals gradually lightened, indicating the release of uncoordinated DMF and coordinated MeOH molecules from the MOF, consistent with the TGA and DSC

results. Unlike crystals of **1**, no bubbles formed during solvent release, likely because the process did not generate enough pressure to form gas bubbles in the silicone oil. Starting at 300 °C, the crystals began to darken again, indicating the onset of decomposition, and they continued to darken until full decomposition occurred at 400 °C. Similarly to **1**, the crystals of **2** showed no cracking during heating or desolvation, and they retained transparency, suggesting an SCSC transformation during desolvation.

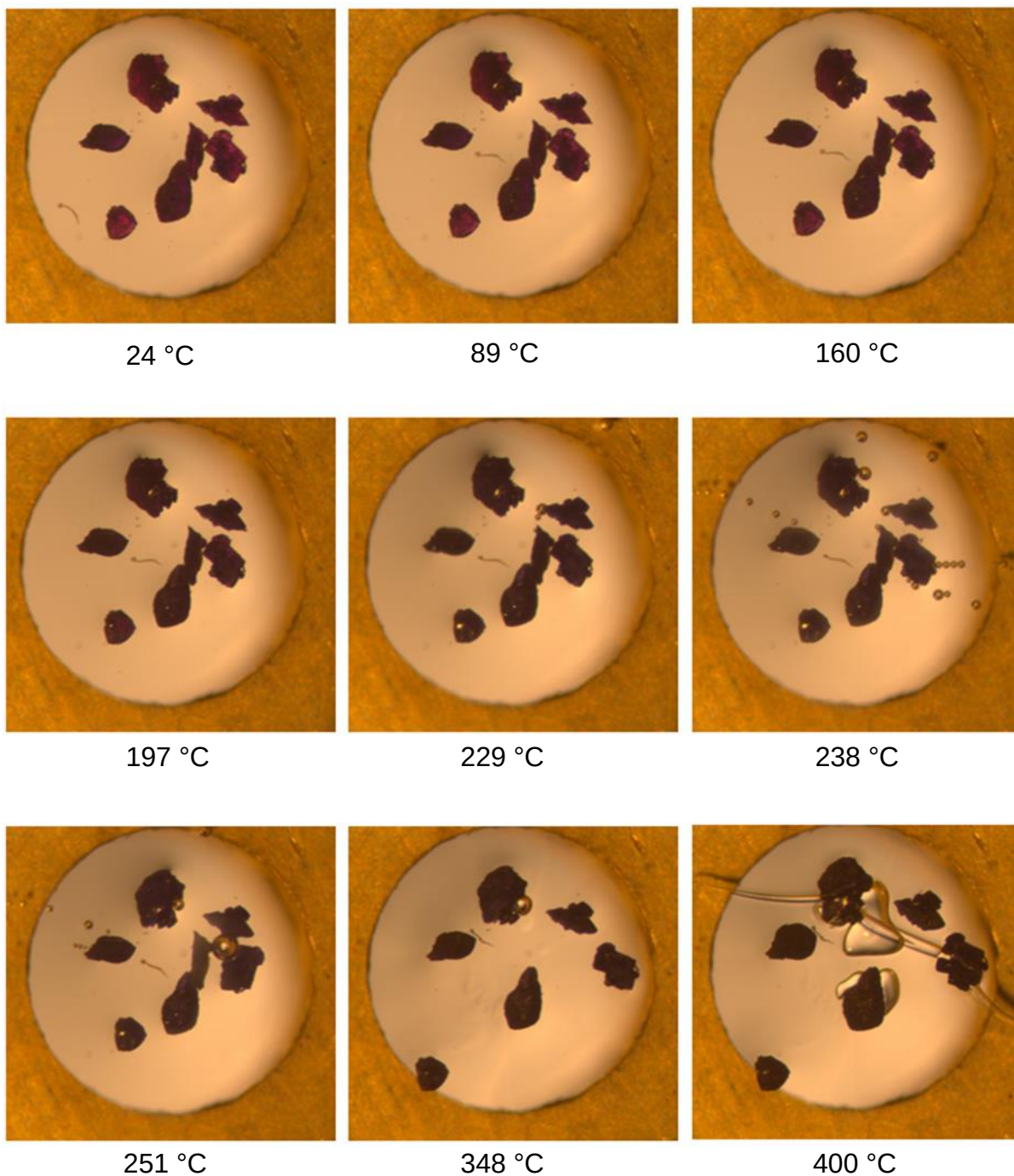


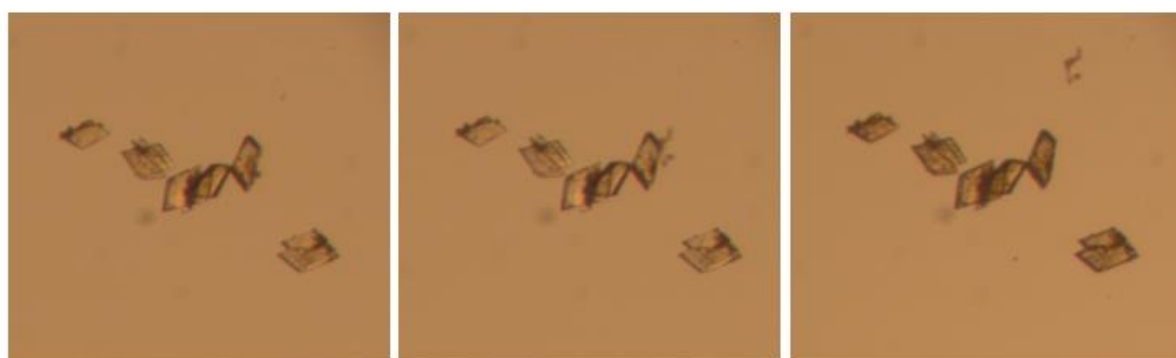
Figure 3.5. HSM images of crystals of **1** heated from 24 to 400 °C.



22 °C

95 °C

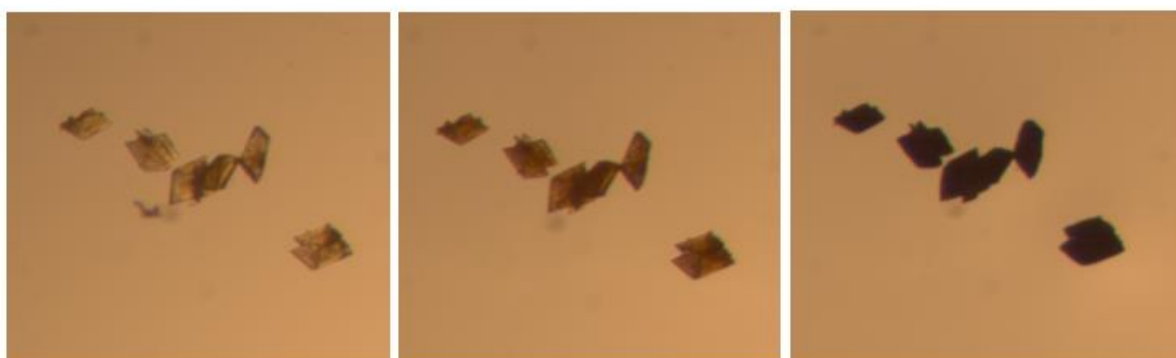
116 °C



132 °C

150 °C

190 °C



300 °C

355 °C

400 °C

Figure 3.6. HSM images of crystals of **2** heated from 22 to 400 °C.

3.4. Desolvation Studies

3.4.1. Single-Crystal-to-Single-Crystal Desolvation Studies

HSM studies showed that crystals of **1** and **2** retained some transparency during desolvation, suggesting the possibility of SCSC transformations. Such transformation could allow structural determination of the desolvated MOFs. To investigate this, successive data collections were performed on the same crystals of **1** and **2** at 298, 323, and 373 K. After desolvation, additional data collections were conducted at 473, 298, and 195 K on the desolvated crystals, referred to as **1'** and **2'**, respectively. Variable-temperature single-crystal X-ray diffraction (VT-SCXRD) data for **1/1'** and **2/2'** are provided in Tables 3.4 and 3.5, respectively.

Changes in the unit cell parameters upon desolvation indicate that the process may involve conformational changes within the 2-periodic frameworks, shifts in their relative positions, or a combination of both. For each crystal, a detailed comparison shows that the ASUs at 298, 323, and 373 K closely overlay with the ASU at 100 K, with root-mean-square (RMS) deviations of 0.042, 0.046, and 0.055 Å, respectively, for **1** and 0.067, 0.081, and 0.011 Å, respectively, for **2** (Figure 3.7).

At 473 K, both structures undergo complete solvent loss via an SCSC transformation (Figure 3.8). Overlay comparisons of the ASUs at 298 and 473 K reveal substantial structural changes beyond those due to solvent loss, as indicated by the significantly higher RMS deviations of 0.91 Å for **1/1'** and 0.85 Å for **2/2'** (Figure 3.9). This transformation also results in changes to the direction of the unit cell axes, as shown in the overlay images in Figure 3.9. At this elevated temperature, the C-labeled ia ligand rotates by 64° in **1'** and 59° in **2'** relative to its mean plane orientation at 298 K. In **1'**, this rotation increases the Co3-O1C bond distance from 2.043(2) to 2.505(6) Å,

Table 3.4: VT-SCXRD crystal data and refinement parameters for **1**.

	1 (298 K)	1 (323 K)	1 (373 K)	1' (473 K)	1' (298 K)	1' (195 K)	1W
ASU formula	C ₄₁ H ₃₇ C ₀₃ N ₃ O ₁₆	C ₄₁ H ₃₇ C ₀₃ N ₃ O ₁₆	C ₄₁ H ₃₇ C ₀₃ N ₃ O ₁₆	C ₃₇ H ₂₆ C ₀₃ N ₂ O ₁₄	C ₃₇ H ₂₆ C ₀₃ N ₂ O ₁₄	C ₃₇ H ₂₆ C ₀₃ N ₂ O ₁₄	C ₃₇ H _{31.34} C ₀₃ N ₂ O _{16.67}
Formula weight	1004.52	1004.52	1004.52	899.39	899.39	899.39	947.49
Temperature / K	298	323	373	473.00	298	195	298
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁
<i>a</i> / Å	10.0916(6)	10.0864(5)	10.0834(6)	10.8548(15)	10.7823(14)	10.750(2)	9.7706(6)
<i>b</i> / Å	21.6091(13)	21.6091(11)	21.6155(13)	21.417(3)	21.428(3)	21.444(4)	20.8585(14)
<i>c</i> / Å	18.7736(10)	18.7958(9)	18.8539(10)	16.112(2)	16.025(2)	15.995(3)	10.0670(7)
α / °	90	90	90	90	90	90	90
β / °	93.3040(10)	93.2590(10)	93.1660(10)	91.724(3)	91.346(3)	91.202(3)	111.505(2)
γ / °	90	90	90	90	90	90	90
Volume / Å³	4087.2(4)	4090.1(4)	4103.1(4)	3744.0(9)	3701.5(8)	3686.1(12)	1908.8(2)
<i>Z</i>	4	4	4	4	4	4	2
ρ / g.cm⁻³	1.632	1.631	1.626	1.596	1.614	1.621	1.648
μ / mm⁻¹	1.282	1.281	1.277	1.385	1.401	1.407	1.368
<i>F</i>(000)	2052.0	2052.0	2052.0	1820.0	1820	1820.0	963
Crystal size (mm³)	0.199 × 0.186 × 0.042	0.199 × 0.186 × 0.042	0.199 × 0.186 × 0.042	0.199 × 0.186 × 0.042	0.199 × 0.186 × 0.042	0.199 × 0.186 × 0.042	0.199 × 0.186 × 0.042
2θ range for data collection / °	2.876 to 50.7	2.874 to 50.7	2.868 to 50.694	3.164 to 50.794	3.174 to 50.854	3.178 to 50.654	4.768 to 50.818
Index ranges	-12 ≤ <i>h</i> ≤ 12, -26 ≤ <i>k</i> ≤ 26, -22 ≤ <i>l</i> ≤ 22	-12 ≤ <i>h</i> ≤ 12, -26 ≤ <i>k</i> ≤ 26, -22 ≤ <i>l</i> ≤ 22	-12 ≤ <i>h</i> ≤ 12, -26 ≤ <i>k</i> ≤ 26, -22 ≤ <i>l</i> ≤ 22	-13 ≤ <i>h</i> ≤ 13, -25 ≤ <i>k</i> ≤ 25, -19 ≤ <i>l</i> ≤ 19	-12 ≤ <i>h</i> ≤ 13, -25 ≤ <i>k</i> ≤ 25, -19 ≤ <i>l</i> ≤ 19	-12 ≤ <i>h</i> ≤ 12, -25 ≤ <i>k</i> ≤ 25, -19 ≤ <i>l</i> ≤ 18	-8 ≤ <i>h</i> ≤ 11, -25 ≤ <i>k</i> ≤ 25, -12 ≤ <i>l</i> ≤ 12
Reflections collected	45834	45569	45958	29587	26082	31592	28689
Independent reflections	7476 [<i>R</i> _{int} = 0.0388, <i>R</i> _{sigma} = 0.0253]	7485 [<i>R</i> _{int} = 0.0397, <i>R</i> _{sigma} = 0.0258]	7502 [<i>R</i> _{int} = 0.0403, <i>R</i> _{sigma} = 0.0263]	6839 [<i>R</i> _{int} = 0.0880, <i>R</i> _{sigma} = 0.0841]	6683 [<i>R</i> _{int} = 0.0877, <i>R</i> _{sigma} = 0.0866]	6697 [<i>R</i> _{int} = 0.1049, <i>R</i> _{sigma} = 0.0808]	6963 [<i>R</i> _{int} = 0.0372, <i>R</i> _{sigma} = 0.0319]
Data/restraints/parameters	7476/0/572	7485/0/572	7502/0/572	6839/0/505	6683/0/505	6697/0/505	6963/702/478
Goodness-of-fit on <i>F</i>²	1.179	1.187	1.145	1.108	1.067	1.063	1.137
Final <i>R</i> indexes [<i>I</i> ≥ 2σ (<i>I</i>)]	<i>R</i> ₁ = 0.0377, <i>wR</i> ₂ = 0.0826	<i>R</i> ₁ = 0.0385, <i>wR</i> ₂ = 0.0865	<i>R</i> ₁ = 0.0403, <i>wR</i> ₂ = 0.0907	<i>R</i> ₁ = 0.0659, <i>wR</i> ₂ = 0.1279	<i>R</i> ₁ = 0.0577, <i>wR</i> ₂ = 0.1075	<i>R</i> ₁ = 0.0533, <i>wR</i> ₂ = 0.0982	<i>R</i> ₁ = 0.0713, <i>wR</i> ₂ = 0.1925
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0442, <i>wR</i> ₂ = 0.0856	<i>R</i> ₁ = 0.0453, <i>wR</i> ₂ = 0.0896	<i>R</i> ₁ = 0.0483, <i>wR</i> ₂ = 0.0946	<i>R</i> ₁ = 0.1469, <i>wR</i> ₂ = 0.1563	<i>R</i> ₁ = 0.1259, <i>wR</i> ₂ = 0.1343	<i>R</i> ₁ = 0.1102, <i>wR</i> ₂ = 0.1191	<i>R</i> ₁ = 0.0734, <i>wR</i> ₂ = 0.1937
Largest diff. peak/hole / e Å⁻³	0.44/-0.39	0.46/-0.38	0.56/-0.38	0.51/-0.33	0.50/-0.41	0.53/-0.50	0.77/-0.88

Table 3.5: VT-SCXRD crystal data and refinement parameters for **2**.

	2 (298 K)	2 (323 K)	2 (373 K)	2' (473 K)	2' (298 K)	2' (195 K)	2W
ASU formula	C ₄₁ H ₃₇ Mn ₃ N ₃ O ₁₆	C ₄₁ H ₃₇ Mn ₃ N ₃ O ₁₆	C ₃₇ H ₂₆ Mn ₃ N ₂ O ₁₄	C ₃₇ H ₂₆ Mn ₃ N ₂ O ₁₄	C ₃₇ H ₂₆ Mn ₃ N ₂ O ₁₄	C ₃₇ H ₂₆ Mn ₃ N ₂ O ₁₄	C ₃₇ H ₂₇ Mn ₃ N ₂ O ₁₆
Formula weight	992.55	992.55	992.55	887.42	887.42	887.42	923.45
Temperature / K	298	323	373	473	298	195	298
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁
<i>a</i> / Å	10.1824(8)	10.1833(10)	10.203(5)	10.889(2)	10.921(2)	10.8473(18)	10.0694(16)
<i>b</i> / Å	22.0016(18)	22.010(2)	22.132(12)	21.303(5)	21.367(4)	21.233(4)	20.715(3)
<i>c</i> / Å	18.8050(15)	18.8315(18)	19.013(10)	16.622(4)	16.658(3)	16.551(3)	10.0741(17)
α / °	90	90	90	90	90	90	90
β / °	92.323(2)	92.260(2)	92.104(10)	91.782(4)	91.545(4)	91.486(3)	113.433(5)
γ / °	90	90	90	90	90	90	90
Volume / Å³	4209.4(6)	4217.5(7)	4290(4)	3854.1(15)	3885.8(14)	3810.9(11)	1928.0(6)
<i>Z</i>	4	4	4	4	4	4	2
ρ / g.cm⁻³	1.566	1.563	1.537	1.529	1.517	1.547	1.591
μ / mm⁻¹	0.963	0.961	0.945	1.037	1.029	1.049	1.044
<i>F</i>(000)	2028	2028	2028	1796	1796	1796	938
Crystal size (mm³)	0.197 × 0.154 × 0.05	0.197 × 0.154 × 0.05	0.197 × 0.154 × 0.05	0.197 × 0.154 × 0.05	0.197 × 0.154 × 0.05	0.197 × 0.154 × 0.05	0.197 × 0.154 × 0.05
2θ range for data collection / °	2.85 to 50.694	2.848 to 51.29	2.826 to 50.698	3.108 to 50.698	3.1 to 49.424	3.12 to 49.426	4.826 to 50.762
Index ranges	-12 ≤ <i>h</i> ≤ 12, -26 ≤ <i>k</i> ≤ 26, -22 ≤ <i>l</i> ≤ 22	-12 ≤ <i>h</i> ≤ 12, -26 ≤ <i>k</i> ≤ 26, -22 ≤ <i>l</i> ≤ 22	-12 ≤ <i>h</i> ≤ 12, -26 ≤ <i>k</i> ≤ 26, -22 ≤ <i>l</i> ≤ 22	-13 ≤ <i>h</i> ≤ 12, -25 ≤ <i>k</i> ≤ 25, -20 ≤ <i>l</i> ≤ 19	-12 ≤ <i>h</i> ≤ 11, -25 ≤ <i>k</i> ≤ 23, -19 ≤ <i>l</i> ≤ 19	-12 ≤ <i>h</i> ≤ 12, -24 ≤ <i>k</i> ≤ 24, -19 ≤ <i>l</i> ≤ 19	-11 ≤ <i>h</i> ≤ 12, -24 ≤ <i>k</i> ≤ 20, -11 ≤ <i>l</i> ≤ 12
Reflections collected	36937	37090	25106	40463	21897	27471	11468
Independent reflections	7705 [<i>R</i> _{int} = 0.0610, <i>R</i> _{sigma} = 0.0498]	7922 [<i>R</i> _{int} = 0.0624, <i>R</i> _{sigma} = 0.0523]	7829 [<i>R</i> _{int} = 0.0808, <i>R</i> _{sigma} = 0.0806]	7044 [<i>R</i> _{int} = 0.0765, <i>R</i> _{sigma} = 0.0564]	6497 [<i>R</i> _{int} = 0.0855, <i>R</i> _{sigma} = 0.0882]	6380 [<i>R</i> _{int} = 0.0849, <i>R</i> _{sigma} = 0.0794]	5523 [<i>R</i> _{int} = 0.0574, <i>R</i> _{sigma} = 0.0950]
Data/restraints/parameters	7705/0/572	7922/0/574	7829/24/563	7044/707/439	6497/707/445	6380/707/445	5523/723/459
Goodness-of-fit on <i>F</i>²	1.226	1.23	1.186	1.218	1.184	1.194	1.157
Final <i>R</i> indexes [<i>I</i> ≥ 2σ (<i>I</i>)]	<i>R</i> ₁ = 0.0789, <i>wR</i> ₂ = 0.1409	<i>R</i> ₁ = 0.0800, <i>wR</i> ₂ = 0.1416	<i>R</i> ₁ = 0.1039, <i>wR</i> ₂ = 0.1909	<i>R</i> ₁ = 0.1479, <i>wR</i> ₂ = 0.3178	<i>R</i> ₁ = 0.1500, <i>wR</i> ₂ = 0.2952	<i>R</i> ₁ = 0.1521, <i>wR</i> ₂ = 0.3113	<i>R</i> ₁ = 0.1080, <i>wR</i> ₂ = 0.2378
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1015, <i>wR</i> ₂ = 0.1482	<i>R</i> ₁ = 0.1073, <i>wR</i> ₂ = 0.1503	<i>R</i> ₁ = 0.1428, <i>wR</i> ₂ = 0.2054	<i>R</i> ₁ = 0.1913, <i>wR</i> ₂ = 0.3384	<i>R</i> ₁ = 0.2065, <i>wR</i> ₂ = 0.3202	<i>R</i> ₁ = 0.2000, <i>wR</i> ₂ = 0.3346	<i>R</i> ₁ = 0.1614, <i>wR</i> ₂ = 0.2635
Largest diff. peak/hole / e Å⁻³	0.61/-0.80	0.61/-0.69	0.60/-0.72	0.81/-0.55	1.18/-0.65	1.48/-0.72	0.71/-0.50

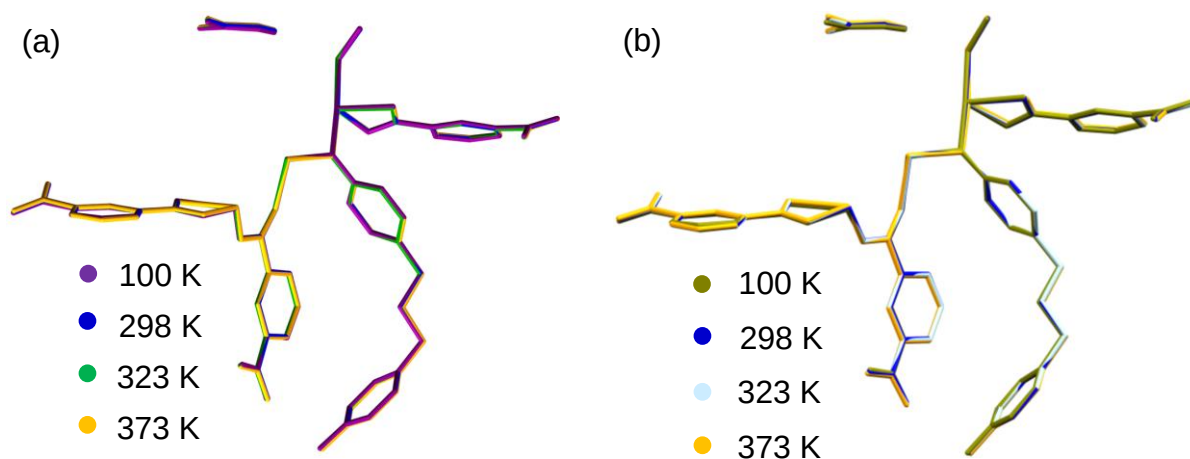


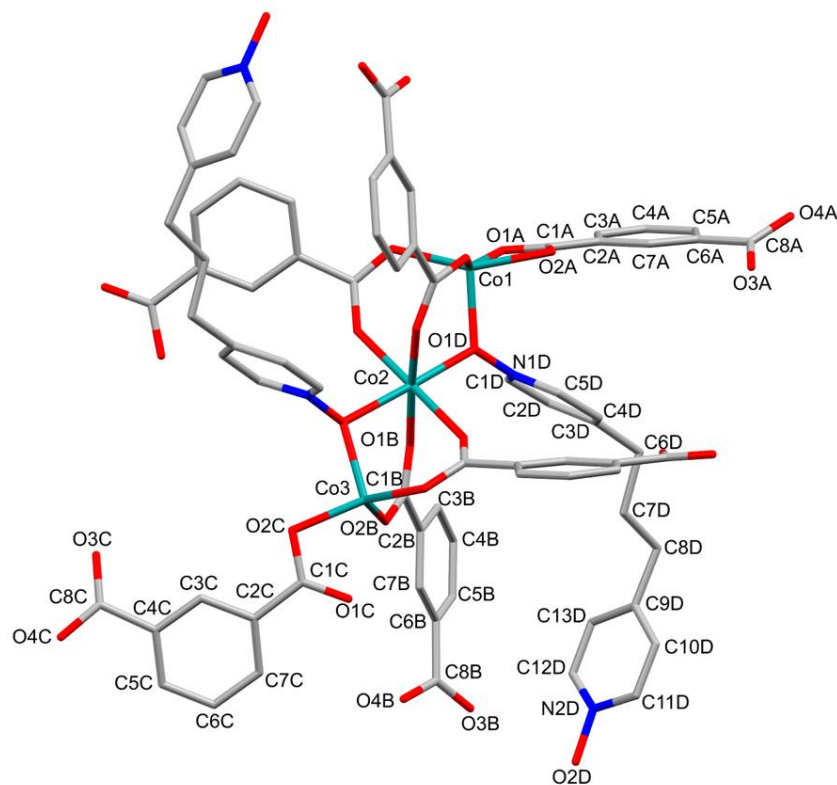
Figure 3.7. Color-coded overlays of the ASUs of structures at 100 to 373 K for (a) **1** and (b) **2**. Hydrogen atoms are omitted for clarity.

breaking the coordination bond and changing the coordination mode of the carboxylate group from bidentate chelating ($\eta^1:\eta^1$) to monodentate (η^1). This also changes the coordination geometry from a distorted square pyramidal to a distorted tetrahedral form (Figures 3.1a and 3.8a). In contrast, the carboxylate group in **2'** retains its bidentate chelating mode, due to a smaller Mn3-O1C distance increase from 2.182(4) to 2.285(12) Å, maintaining the distorted square pyramidal geometry (Figures 3.1b and 3.8b).

The loss of the coordinated MeOH molecule at 473 K in both **1** and **2** leads to a shift in the coordination environment geometry of the Co1 metal ion in **1'** and the Mn1 metal ion in **2'**, changing from a distorted octahedral to a distorted square pyramidal geometry (Figures 3.1 and 3.8). Upon cooling to 298 K and then to 195 K, the ASUs of **1'** and **2'** closely overlay with those at 473 K, showing RMS deviations of 0.048 and 0.071 Å for **1'**, respectively, and 0.055 and 0.070 Å for **2'**, respectively (Figures 3.10).

After desolvation, the crystals of **1'** and **2'** were left on the diffractometer at room temperature (~25 °C) for 24 h without a flow of dry air, allowing them to adsorb water

(a)



(b)

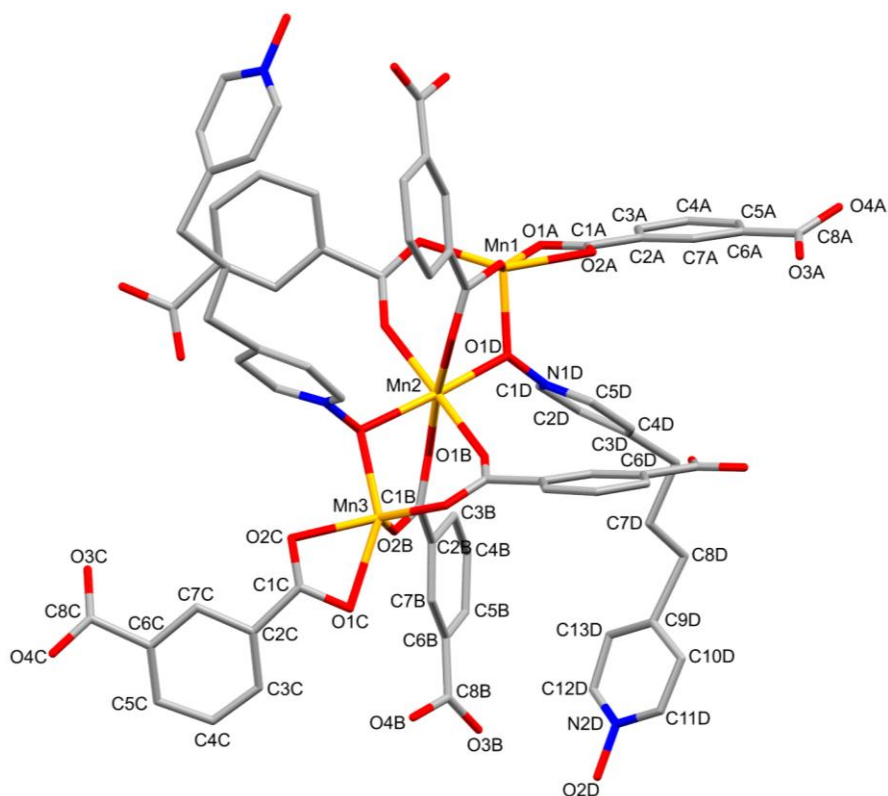


Figure 3.8. The coordination environment of the three unique metal ions: (a) Co^{2+} in **1** and (b) Mn^{2+} ions in **2** at 473 K. Hydrogen atoms are omitted for clarity, and only atoms in the ASU are labelled.

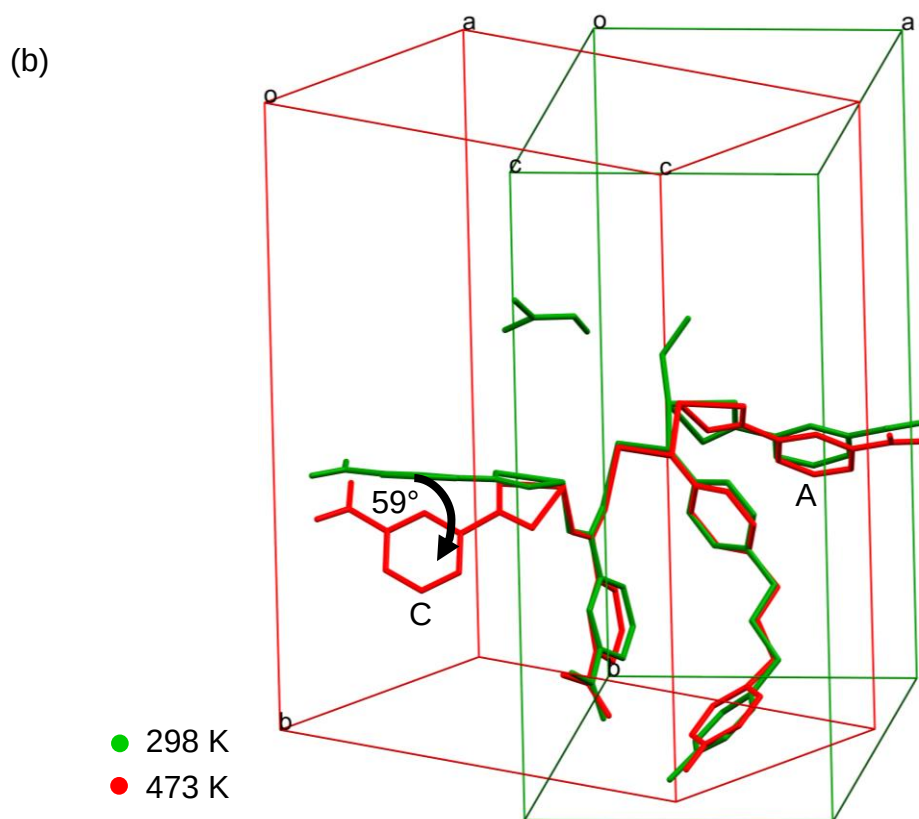
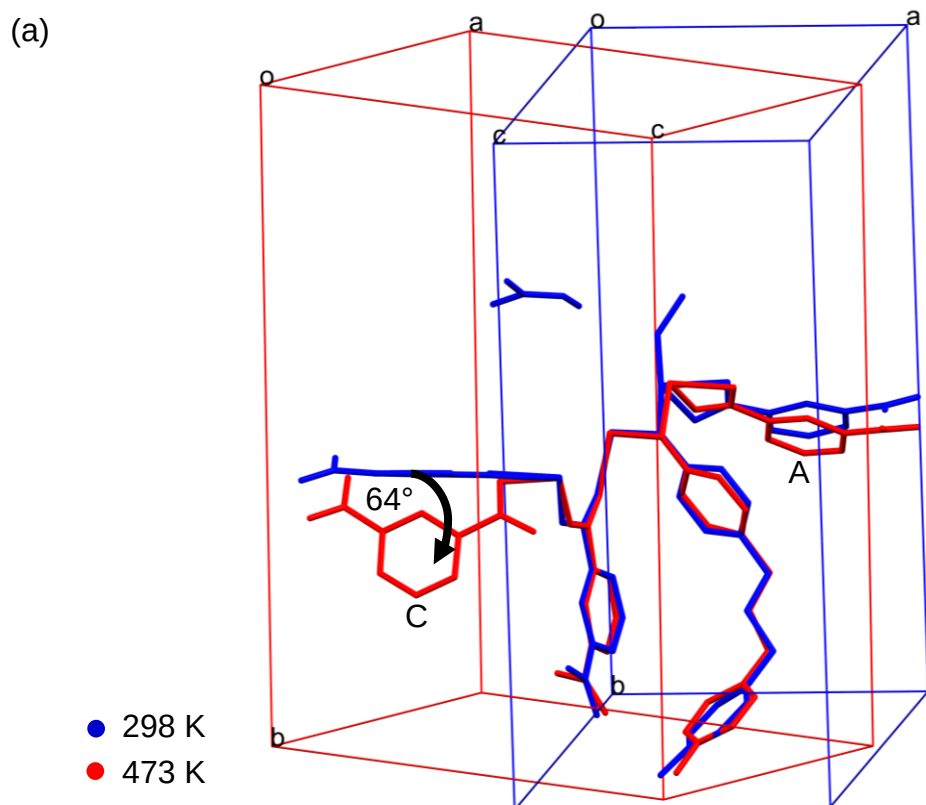


Figure 3.9. Color-coded overlays of the ASUs of structures at 298 and 473 K for (a) **1** and (b) **2**. Hydrogen atoms are omitted for clarity.

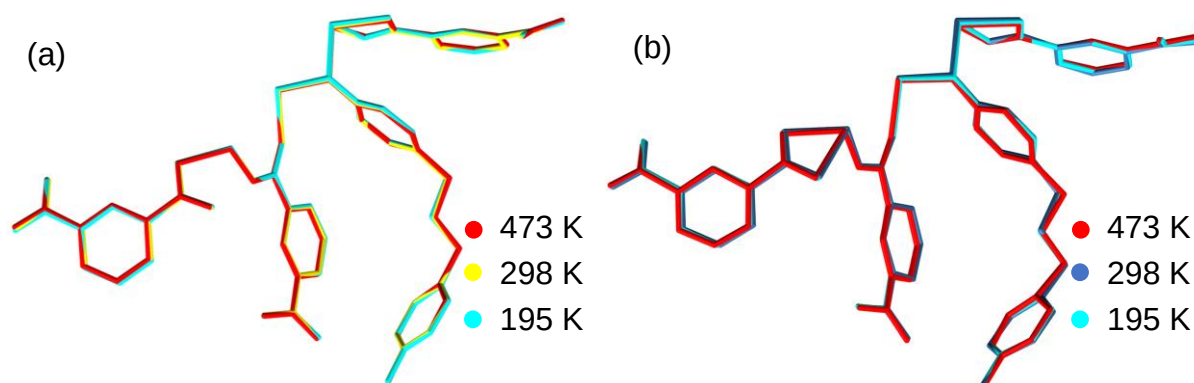


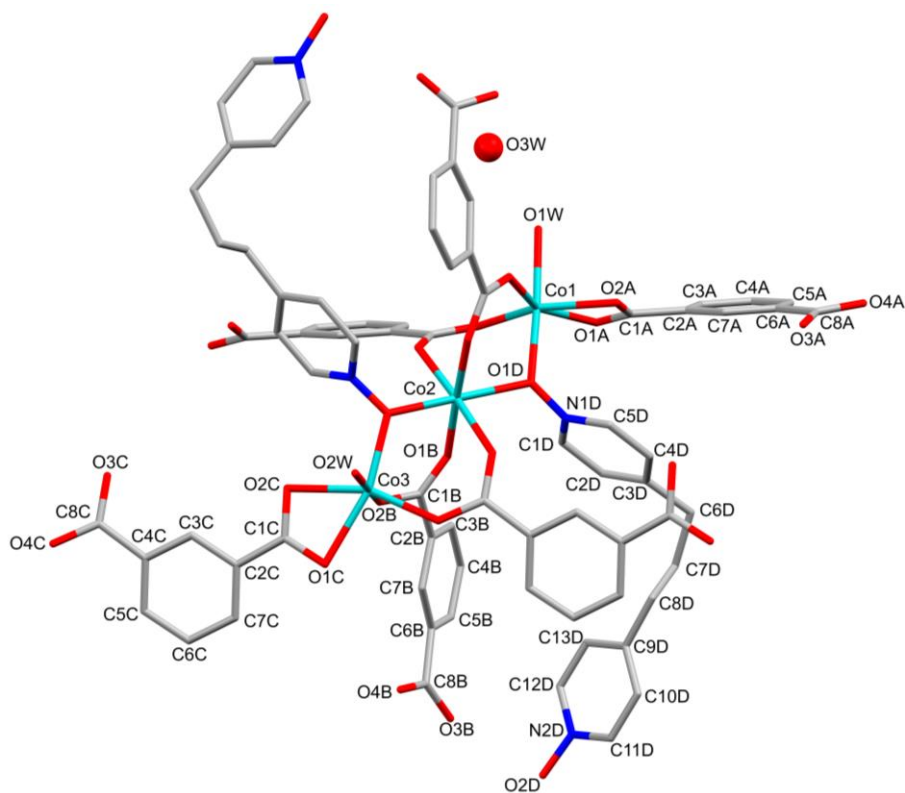
Figure 3.10. Colour-coded overlays of the ASUs of desolvated structures at 473, 298, and 195 K for (a) **1'** and (b) **2'**. Hydrogen atoms are omitted for clarity.

from the atmosphere. Subsequent SCXRD analysis confirmed that both desolvated crystals had adsorbed water, forming the hydrated phases **1W** and **2W** for the Co-based and Mn-based MOFs, respectively. Hydration induces further conformational changes in the 2-periodic framework, as evidenced by changes in unit cell parameters (Tables 3.4 and 3.5). This transformation is fully reversible, as the crystals return to their desolvated structure upon reheating and dehydration, as confirmed by a full structure determination.

In **1W**, three distinct positions are identified for the sorbed water molecules, two coordinated to the metal center and one uncoordinated in the cavity (Figure 3.11a). In contrast, **2W** shows only two coordinated water molecules, occupying positions similar to those in **1W** (Figure 3.11b).

In both structures, the O1W atom coordinates to the metal center (Co1/Mn1) that was previously bonded to the methanol molecule, while O2W coordinates to the Co3/Mn3 metal ion, forming an additional coordination bond that was absent in the as-synthesized structures. The coordination environment around the Co1/Mn1 metal centres, initially distorted octahedral (6-coordinate) in the as-synthesized state,

(a)



(b)

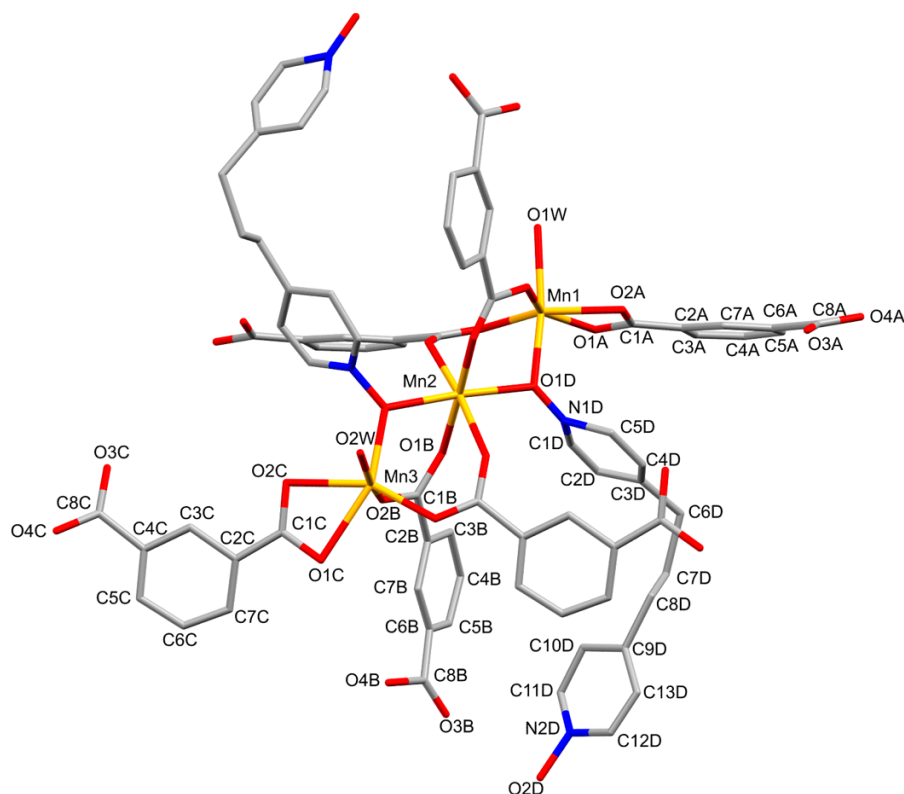


Figure 3.11. The coordination environment of the three unique metal ions: (a) Co^{2+} in **1W** and (b) Mn^{2+} ions in **2W** at 298K. Hydrogen atoms are omitted for clarity, and only atoms in the ASU are labeled.

transitions to distorted square pyramidal (5-coordinate) upon desolvation and then returns to distorted octahedral geometry (6-coordinate) upon hydration. Similarly, Co3/Mn3 transitions from distorted square pyramidal (5-coordinate) in the as-synthesized form to distorted tetrahedral (4-coordinate) in the desolvated state for Co3 due to one of the Co3-O bonds involving the chelating carboxylate group breaking (Mn3 remains 5-coordinate), and then to distorted octahedral (6-coordinate) upon hydration. In **1W**, the Co3-O bond that broke during desolvation reforms upon hydration.

RMS deviations for ASU overlays of **1W** and **2W** with their 298 K desolvated structures are 0.57 and 0.42 Å, respectively (Figure 3.12). Notably, the overlays also show that the structural change due to hydration causes a reorientation of the unit cell.

Further evidence of structural adaptation to water sorption includes slight rotations of the phenyl rings in the A and B ligands around the phenyl-carboxylate C-C bond, further altering their orientations in the hydrated structures. Furthermore, the conformation of the propylene spacer in the bppdo ligand (circled in black in Figure 3.12) shifts from a stable *anti-anti* conformation to a less stable *anti-gauche* form upon hydration (Scheme 3.1).¹⁹¹ This transformation demonstrates the flexibility of the ligand as it adapts conformationally to structural changes induced by water sorption. The conformational change also disrupts *n*-glide symmetry and, consequently, the inversion symmetry, resulting in the lower-symmetry but chiral space group $P2_1$ describing the crystallographic symmetry. Changes in the extended structures, i.e., beyond the ASUs, that occur during the transformations from as-synthesized to desolvated to hydrated states can be tracked by identifying conformational changes within the 2-periodic frameworks, which may be the result of relative shifts of adjacent 2-periodic frameworks.

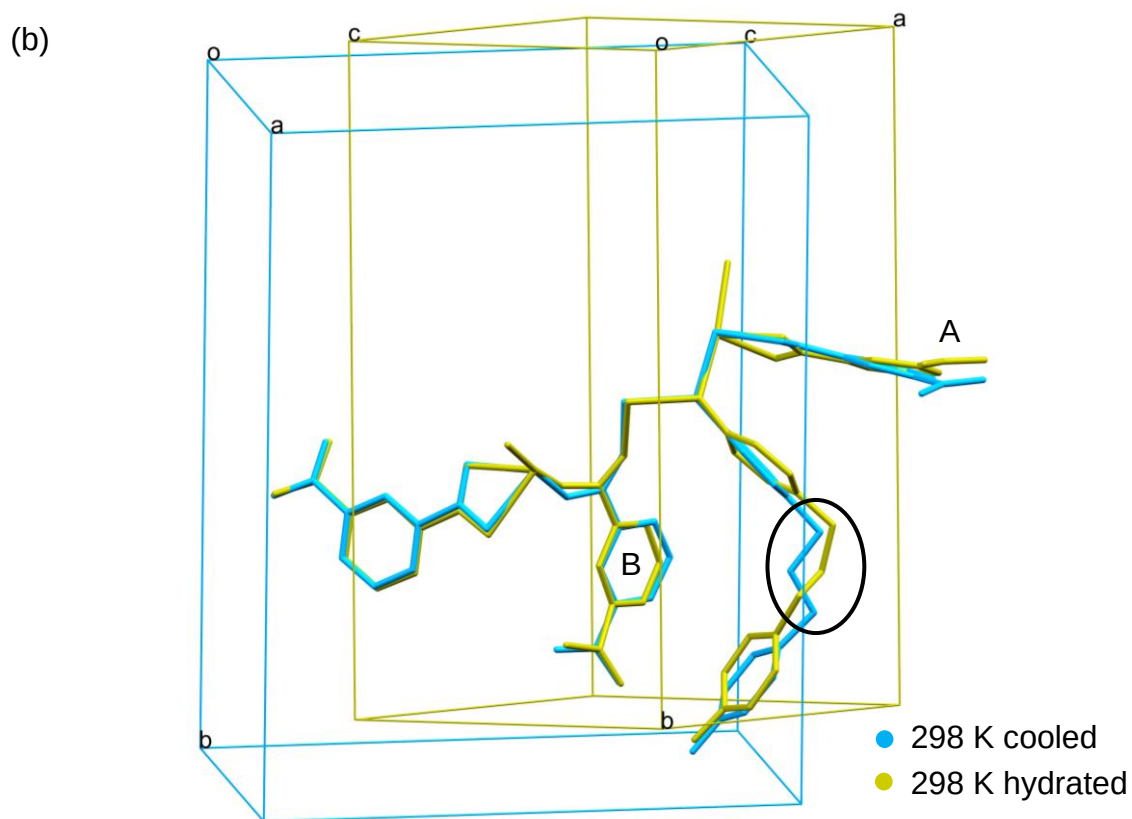
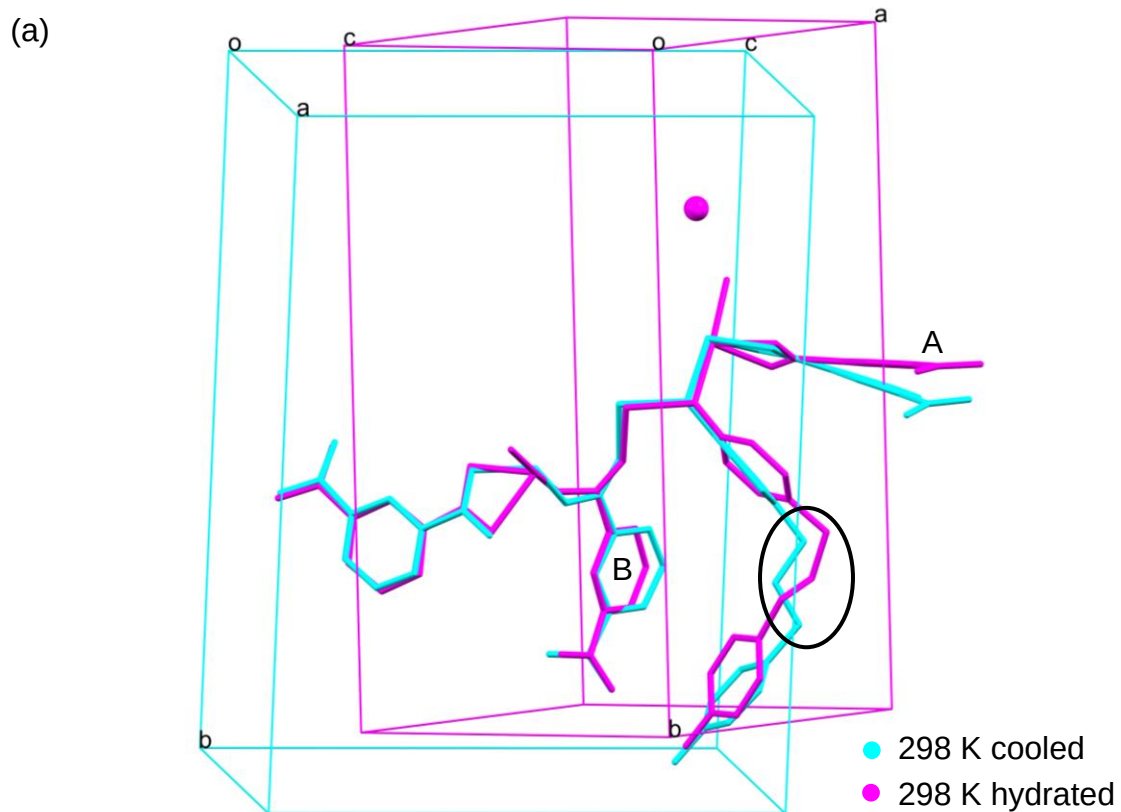
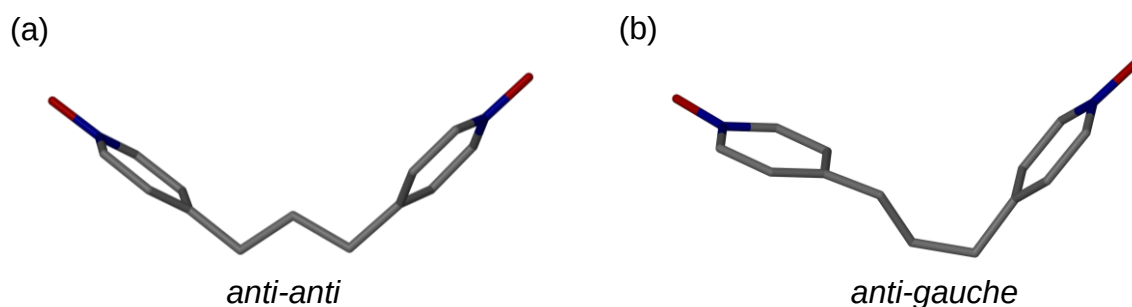


Figure 3.12. Color-coded overlays of the ASUs of desolvated structures at 298 K and hydrated forms at 298 K for (a) **1** and (b) **2**. Hydrogen atoms are omitted for clarity.



Scheme 3.1. Conformations of bppdo ligand in (a) **1/2**, **1'/2'** and (b) **1W/2W**.

Significant conformational changes are evident in the colour-coded ia ligands (pink for **1/1'/1W** and green for **2/2'/2W**) in Figure 3.13. For instance, along the [100] direction in **1** and **2**, there is one ia ligand per periodic repeat distance. In **1'/2'**, however, this repeat distance doubles (now along the crystallographic [101] direction according to the new unit cell orientation with respect to the structure) due to the rotation of alternating ia ligands, leading to two ia ligands per repeat distance. In **1W** and **2W**, all ia ligands are rotated, resulting, again, in one ia ligand per repeat distance along the now [001] direction.

These transformations can also be represented through a topological simplification of the structure, using the centroids of the trinuclear metal units, the ia ligands aromatic rings, and the propylene spacer of the bppdo ligands as three distinct nodes to represent the topology of the 2-periodic frameworks (Figure 3.14). Here, the trinuclear metal centroid, shaded in blue, acts as an 8-connected node, linked to six surrounding ia ligand centroids (shaded green) and two bppdo propylene groups (shaded orange), which serve as 2-connected nodes bridging the trinuclear clusters. These topological representations reveal shifts in the “equatorial” ia ligand centroids due to the rotation of the C-labeled ia ligand, although the framework topologies remain unchanged since the connectivities of nodes are not affected.

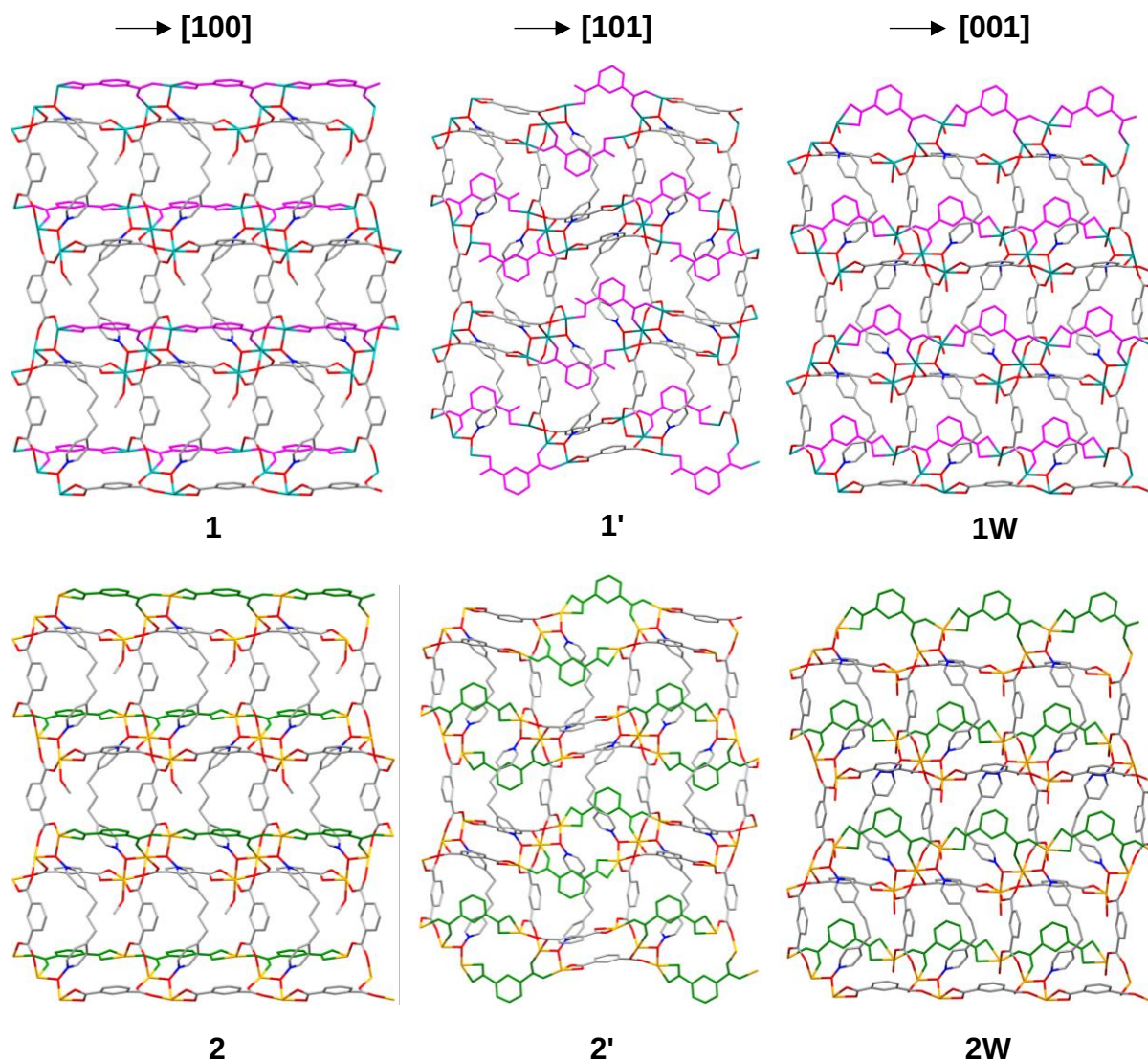


Figure 3.13. Face-on views of the 2-periodic frameworks of **1** and **2** along the [100] (left), [101] (middle), and [001] (right) directions, showing the structural transformations from as-synthesised to desolvated and subsequently hydrated forms. The top row represents **1/1'/1W**, and the bottom row represents **2/2'/2W**. The colour-coded ia ligands (pink for **1** and green for **2**) highlight the unique ia ligand that undergoes rotation during the desolvation process.

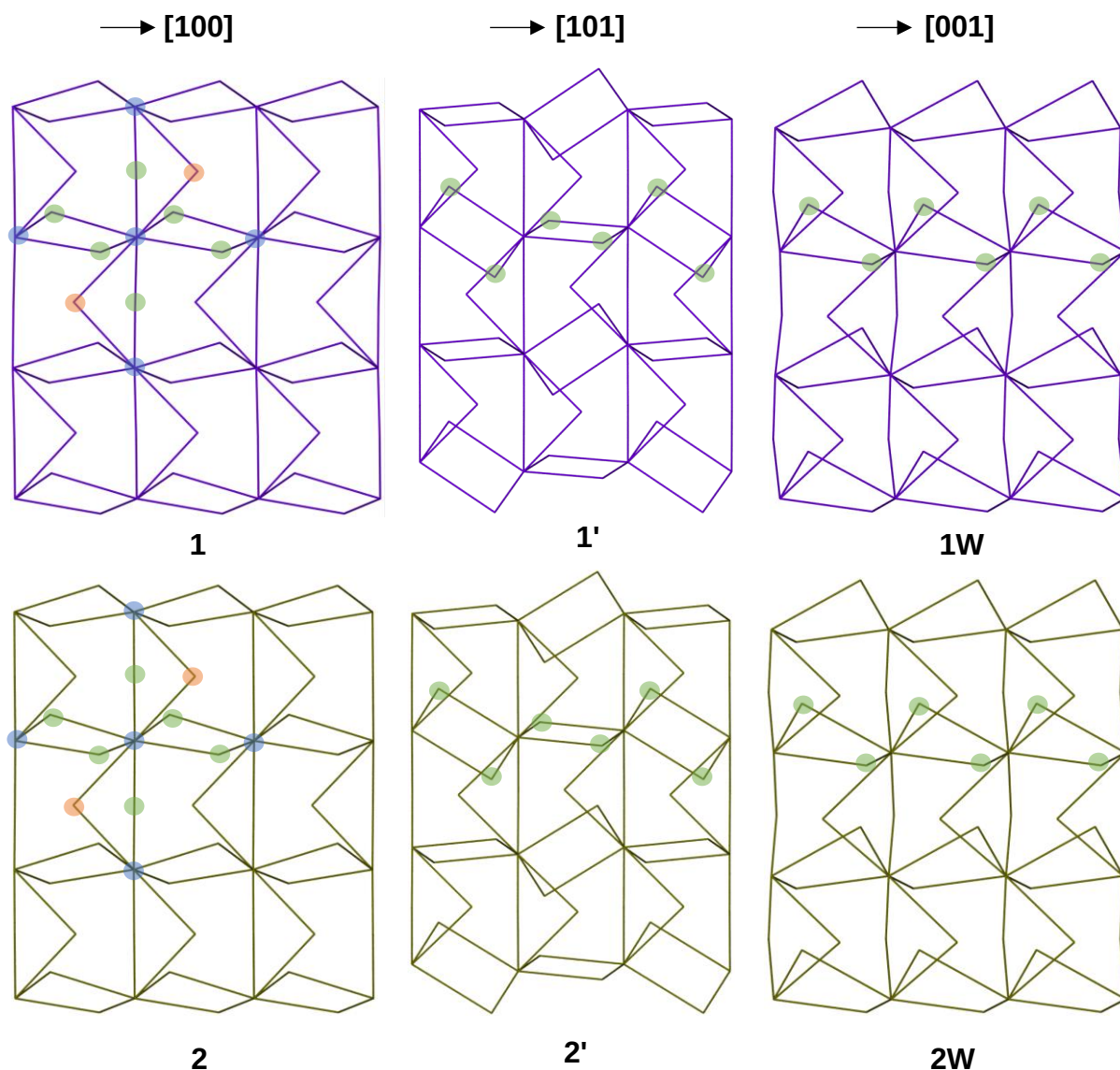


Figure 3.14. Face-on views of topological representations of the 2-periodic frameworks for **1** and **2** along the $[100]$ (**left**), $[101]$ (**middle**), and $[001]$ (**right**) directions, showing the structural transformations from as-synthesised to desolvated and hydrated forms. Selected centroids of the trinuclear metal nodes and the ia and bppdo ligands are shaded. The top row represents **1/1'/1W**, and the bottom row represents **2/2'/2W**.

3.4.2. Hydrogen Bonding

Changes in the relative positions of the 2-periodic frameworks during transformations from as-synthesized to desolvated to hydrated states, can be indicated by shifts in interframework hydrogen-bonding interactions, although these may also be affected by the conformational changes within the frameworks.

No strong hydrogen bonds exist between adjacent 2-periodic frameworks in **1/1'** and **2/2'**. However, five distinct, weaker C–H...O bonds are present at various temperatures, i.e., they are not necessarily present simultaneously (Table 3.6 and Figure 3.15a-g). Among these, the C1D–H1D...O1A hydrogen bond, linking the aromatic ring of a bppdo ligand to a carboxylate oxygen on an ia ligand, is consistently observed across all temperatures in both the solvated and desolvated structures of **1** and **2**.

The C12D–H12D...O1C bond, which similarly links parts of neighbouring frameworks as C1D–H1D...O1A, is present up to 373 K in both **1** and **2** but breaks at 473 K due to rotation of the C-labeled ia ligand in the desolvated structures. Another hydrogen bond, C4B–H4B...O1L, linking the aromatic ring of the B-labeled ia ligand to the oxygen atom of a methanol molecule on an adjacent framework, is only observed in **1** and only at 100 K.

At 473 K, a new hydrogen bond, C3A–H3A...O1B, forms, linking the aromatic ring of an ia ligand to a neighbouring carboxylate group in both **1'** and **2'**, and remains upon cooling. Another hydrogen bond, C2D–H2D...O4C, linking the aromatic ring of a bppdo ligand to the carboxylate group of an ia ligand, appears in **2'** at 473 K and remains upon cooling, but only appears in **1'** when its crystal is cooled.

Table 3.6: Selected hydrogen bond distances and angles at various temperatures for the solvated and desolvated forms of **1** and **2**, as obtained from PLATON.

Donor– H···Acceptor	MOF	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)	Symmetry operators
C1D–1D···O1A						
100 K	1	0.95	2.40	3.152(5)	135	-x, 2-y, 1-z
	2	0.95	2.36	3.121(7)	137	-x, 2-y, 1-z
298 K	1	0.93	2.44	3.184(4)	137	1-x, 1-y, 2-z
	2	0.93	2.42	3.172(7)	138	-x, 2-y, 1-z
323 K	1	0.93	2.44	3.188(4)	137	1-x, 1-y, 2-z
	2	0.93	2.43	3.178(7)	137	-x, 2-y, 1-z
373 K	1	0.93	2.45	3.201(4)	137	1-x, 1-y, 2-z
	2	0.93	2.48	3.218(10)	137	3-x, 1-y, -z
473 K	1'	0.93	2.43	3.167(9)	136	-x, 1-y, 2-z
	2'	0.93	2.39	3.161(11)	140	-x, 1-y, 2-z
298 K cooled	1'	0.93	2.41	3.120(8)	134	-x, 1-y, 2-z
	2'	0.93	2.39	3.161(11)	140	-x, 1-y, 2-z
195 K cooled	1'	0.95	2.38	3.097(5)	132	-x, 1-y, 2-z
	2'	0.95	2.35	3.129(11)	139	-x, -y, 2-z
C12D–H12D···O1C						
100 K	1	0.95	2.16	3.055(6)	156	1/2+x, 5/2-y, 1/2+z
	2	0.95	2.17	3.065(7)	156	-x, 2-y, 1-z
298 K	1	0.93	2.23	3.107(4)	157	1/2+x, 3/2-y, 1/2+z
	2	0.93	2.23	3.124(7)	161	1/2+x, 5/2-y, 1/2+z
323 K	1	0.93	2.24	3.113(4)	157	1/2+x, 3/2-y, 1/2+z
	2	0.93	2.25	3.144(7)	162	1/2+x, 5/2-y, 1/2+z

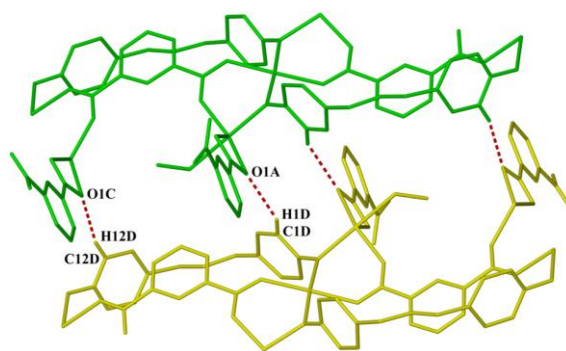
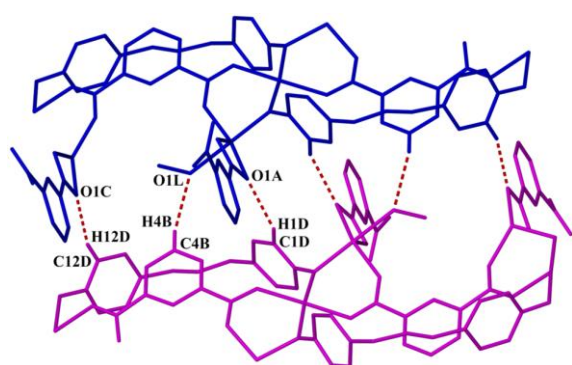
Donor– H···Acceptor	MOF	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)	Symmetry operators
C12D–H12D···O1C						
373 K	1	0.93	2.25	3.129(4)	156	1/2+x, 3/2-y, 1/2+z
	2	0.93	2.27	3.168(11)	161	1/2+x, 3/2-y, 1/2+z
C4B–H4B···O1L						
100 K	1	0.95	2.59	3.510(7)	164	-x, 2-y, 1-z
C3A–H3A···O1B						
473 K	1'	0.93	2.43	3.167(9)	136	-x, 1-y, 2-z
	2'	0.93	2.58	3.297(10)	135	-x, 1-y, 2-z
298 K cooled	1'	0.93	2.51	3.251(6)	137	-x, 1-y, 2-z
	2'	0.93	2.57	3.294(11)	135	-x, 1-y, 2-z
195 K cooled	1'	0.95	2.45	3.215(5)	137	-x, 1-y, 2-z
	2'	0.95	2.51	3.249(10)	134	-x, 1-y, 2-z
C2D–H2D···O4C						
473 K	2'	0.93	2.53	3.417(14)	160	x, y, 1+z
298 K cooled	1'	0.93	2.58	3.496(8)	167	x, y, 1+z
	2'	0.93	2.54	3.437(15)	163	x, y, 1+z
195 K cooled	1'	0.95	2.56	3.492(6)	169	x, y, 1+z
	2'	0.95	2.49	3.409(14)	163	x, y, 1+z
O1W–H1WA···O3W						
298 K exposed	1W	0.89	2.03	2.49(3)	111	x, y, z
O1W–H1WB···O3W						
298 K exposed	1W	0.90	2.16	2.49(3)	101	x, y, z

Donor– H...Acceptor	MOF	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (°)	Symmetry operators
O2W–H2WA...O1A						
298 K exposed	1W	0.88	2.17	2.78(2)	125	-1+x, y, z
	2W	0.86(9)	2.12(10)	2.86(4)	145(8)	-1+x, y, z
O2W–H2WB...O4A						
298 K exposed	1W	0.88	2.55	3.01(2)	113	-1+x, y, 1+z
O3W–H3WA...O1C						
298 K exposed	1W	0.86	2.12	2.68(2)	123	1-x, -1/2+y, 1-z
O3W–H3WB...O4C						
298 K exposed	1W	0.84	2.09	2.77(3)	137	1-x, -1/2+y, 2-z
C1D–H1D...O2W						
298 K exposed	1W	0.93	2.45	3.004(19)	118	1+x, y, z
	2W	0.93	2.20	2.77(4)	119	1+x, y, z
C2D–H2D...O3W						
298 K exposed	1W	0.93	2.30	3.23(3)	176	2-x, 1/2+y, 1-z
C12D–H12D...O1A						
298 K exposed	2W	0.93	2.58	3.36(2)	141	2-x, 1/2+y, 1-z

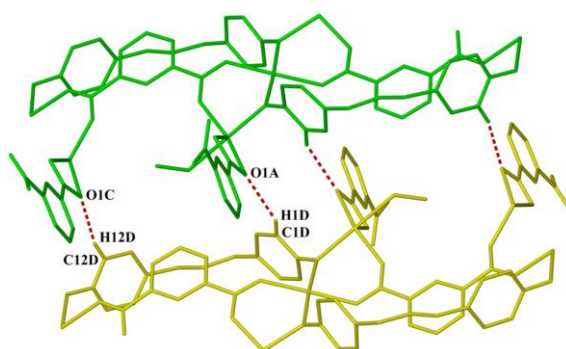
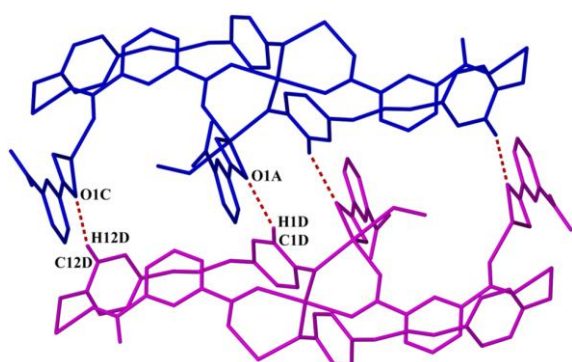
In the hydrated structures, **1W** and **2W**, eight and three distinct interframework hydrogen bonds, respectively, are present (Table 3.6 and Figure 3.15h). Interestingly, none of the hydrogen bonds observed in **1** or **1'** are found in **1W**, which predominantly contains strong hydrogen bonds. A coordinated water molecule forms two strong hydrogen bonds with an uncoordinated water molecule (O1W–H1WA...O3W and O1W–H1WB...O3W). This uncoordinated water molecule further forms additional strong hydrogen bonds with carboxylate oxygen atoms on neighbouring framework

(O3W–H3WA···O1C and O3W–H3WB···O4C). These interactions, along with the weaker C2D–H2D···O3W bond connecting a bppdo aromatic ring to the O3W water molecule, allow O3W to act as a bridge between two adjacent frameworks. The coordinated water molecule O2W forms two strong hydrogen bonds with carboxylate groups on ia ligands (O2W–H2WA···O1A and O2W–H2WB···O4A) and one weaker hydrogen bond with a bppdo aromatic ring (C1D–H1D···O2W) on an adjacent framework.

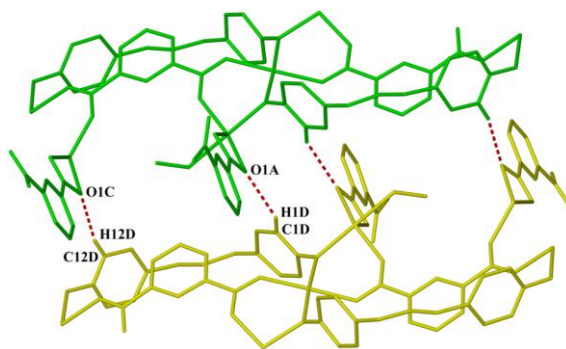
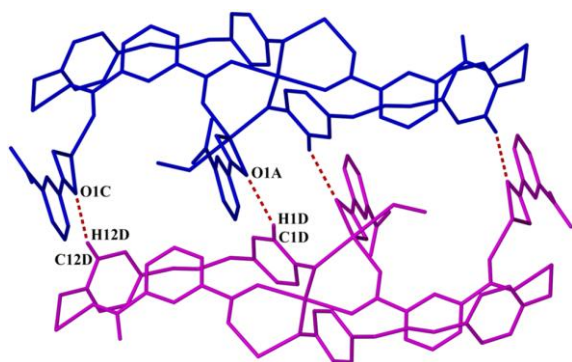
In **2W**, only O2W participates in hydrogen bonding with an adjacent framework, acting as both a hydrogen bond donor to carboxylate oxygen (O2W–H2WA···O1A, also found in **1W**) and an acceptor from the bppdo ring (C1D–H1D···O2W, also seen in **1W**). An interframework hydrogen bond present in the solvated structure (C12D–H12D···O1C in **1** and **2**) reappears in the hydrated structure of **2W** as C12D–H12D···O1A, which was not the case for **1W**.



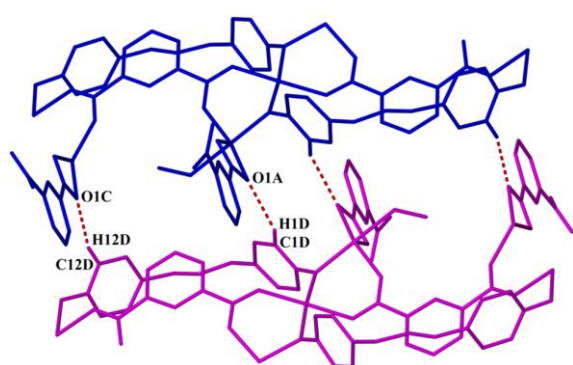
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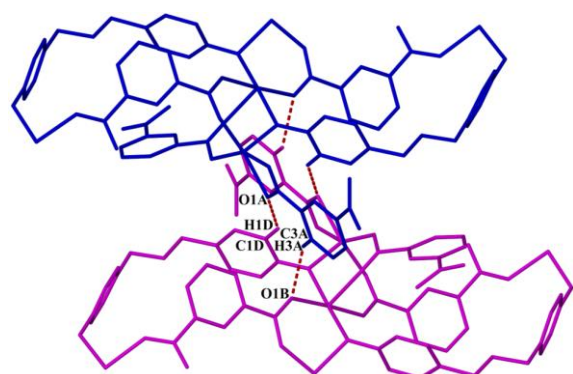
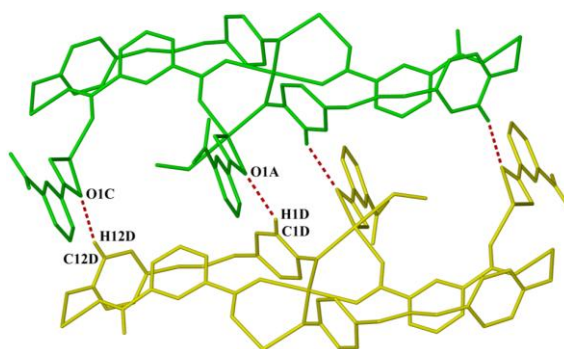
(b)



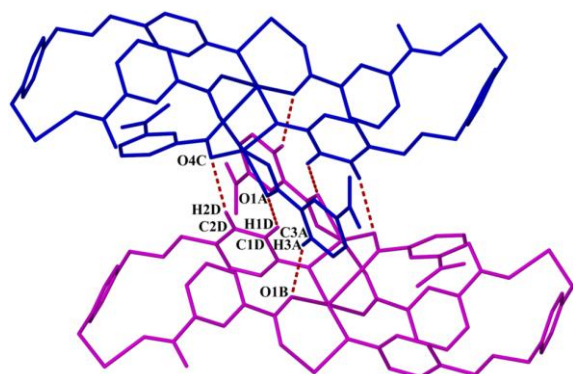
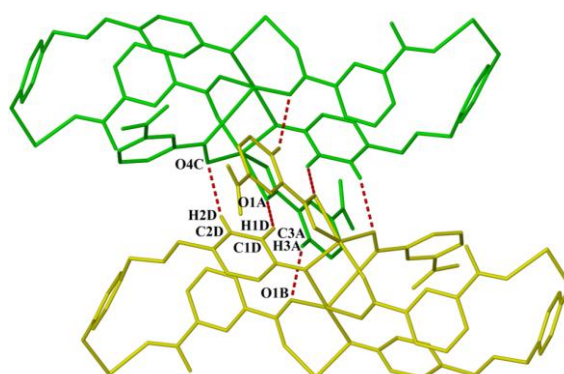
(c)



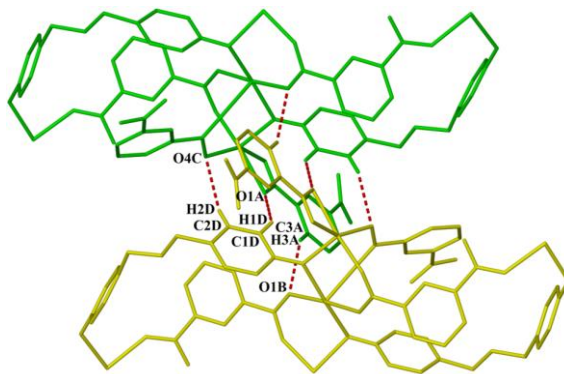
(d)



(e)



(f)



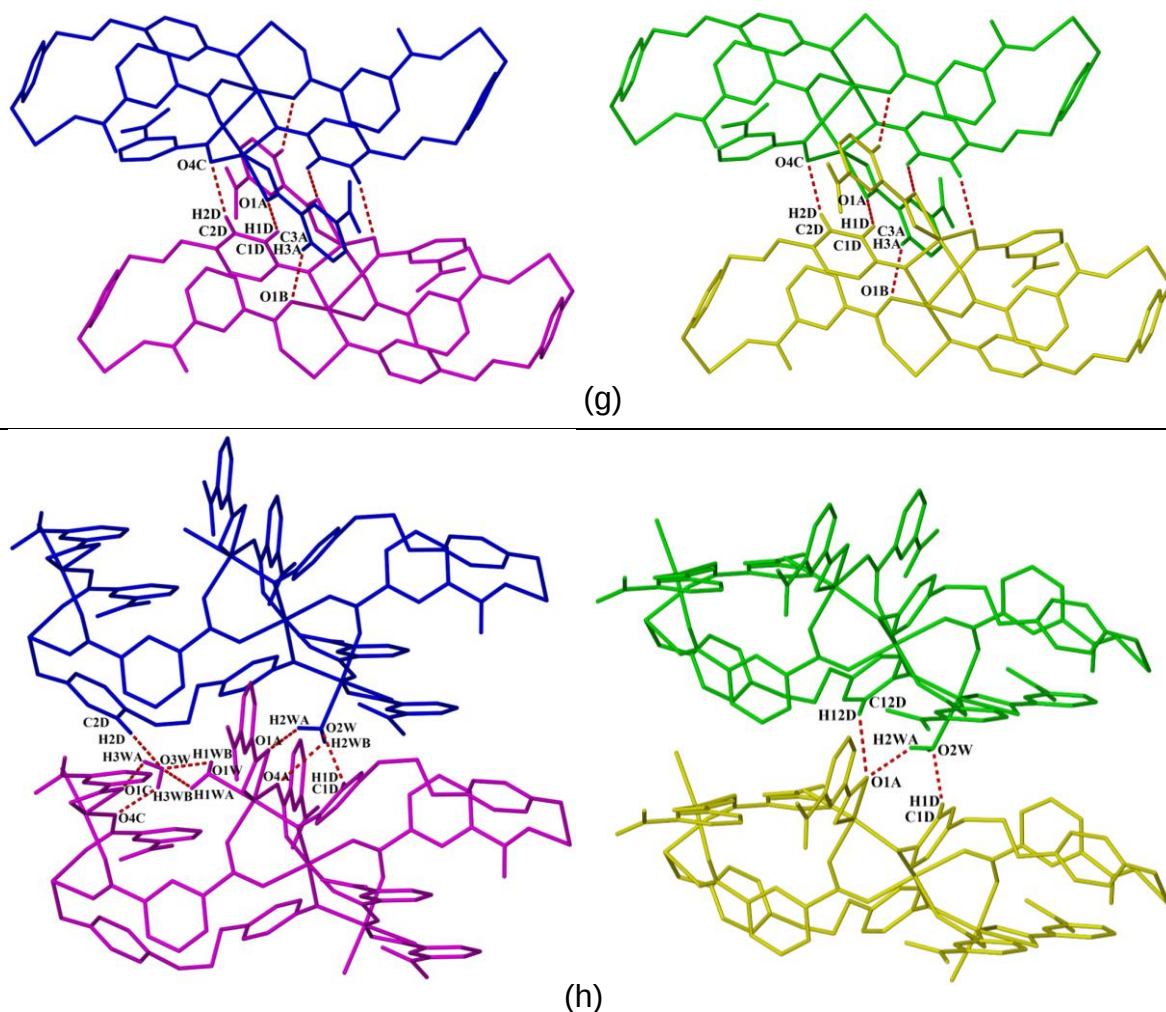


Figure 3.15. Hydrogen bonds (indicated in red) between neighbouring 2-periodic frameworks, with colour coding to distinguish frameworks **1** (blue and pink) and **2** (green and yellow). Interframework hydrogen bonds present at various temperatures: (a) 100 K, (b) 298 K, (c) 323 K, (d) 373 K, (e) 473 K, (f) 298 K cooled, (g) 195 K cooled, and (h) 298 K exposed. Only hydrogen atoms involved in these bonds are shown, and unique donor, hydrogen, and acceptor atoms for each bond are labelled.

3.4.3. Void Space Analysis

The potential void spaces in the as-synthesized structures, after removing solvent molecules by deleting the coordinates of MeOH and DMF in the 298 K structure, are 21.6% for **1** and 22.3% for **2** (Table 3.7). These voids form parallel, 1D channels

(Figure 3.16 (Left)). However, upon actual desolvation at 298 K, the void spaces shrink significantly to 3.7% for **1'** and 5.7% for **2'** (Table 3.7). This substantial reduction in void volume is due to the rotation of C-labeled ia ligands, which extend into cavities previously occupied by solvent molecules. Consequently, the void spaces after desolvation are significantly smaller, with ~6- and 4-fold reductions for **1'** and **2'**, respectively, resulting in isolated pockets (Figure 3.16 (middle)). Notably, the potential void spaces of the hydrated forms, **1W** and **2W**, are 4.2% and 3.0%, respectively, also

Table 3.7. Potential (for **1**, **2**, **1W** and **2W**) and actual (for **1'** and **2'**) void spaces for the solvated and desolvated forms, respectively.

Structure and temperature of analysis	Percent void volume per unit cell (%)	Absolute void space per unit cell and ASU	Description of void space
<u>298 K (solvent deleted)</u>			
1	21.6	884.3/221.1	channels
2	22.3	940.5/235.1	channels
<u>473 K</u>			
1'	4.0	151.3/37.8	isolated voids
2'	5.5	211.6/52.9	isolated voids
<u>298 K cooled</u>			
1'	3.7	137.4/34.4	isolated voids
2'	5.7	221.7/55.4	isolated voids
<u>195 K cooled</u>			
1'	3.6	134.0/33.5	isolated voids
2'	4.8	182.7/45.7	isolated voids
<u>298 K exposed (solvent deleted)</u>			
1W	4.2	80.15/40.1	isolated voids
2W	3.0	58.47/29.2	isolated voids

appearing as isolated pockets. This suggests that these structures might accommodate larger guest molecules, since the as-synthesized structures had much larger, potential void spaces (Table 3.7 and Figures 3.16 (right)). The retention of crystallinities after the desolvation and rehydration processes also indicates that these transformations involve cooperative structural adjustments.

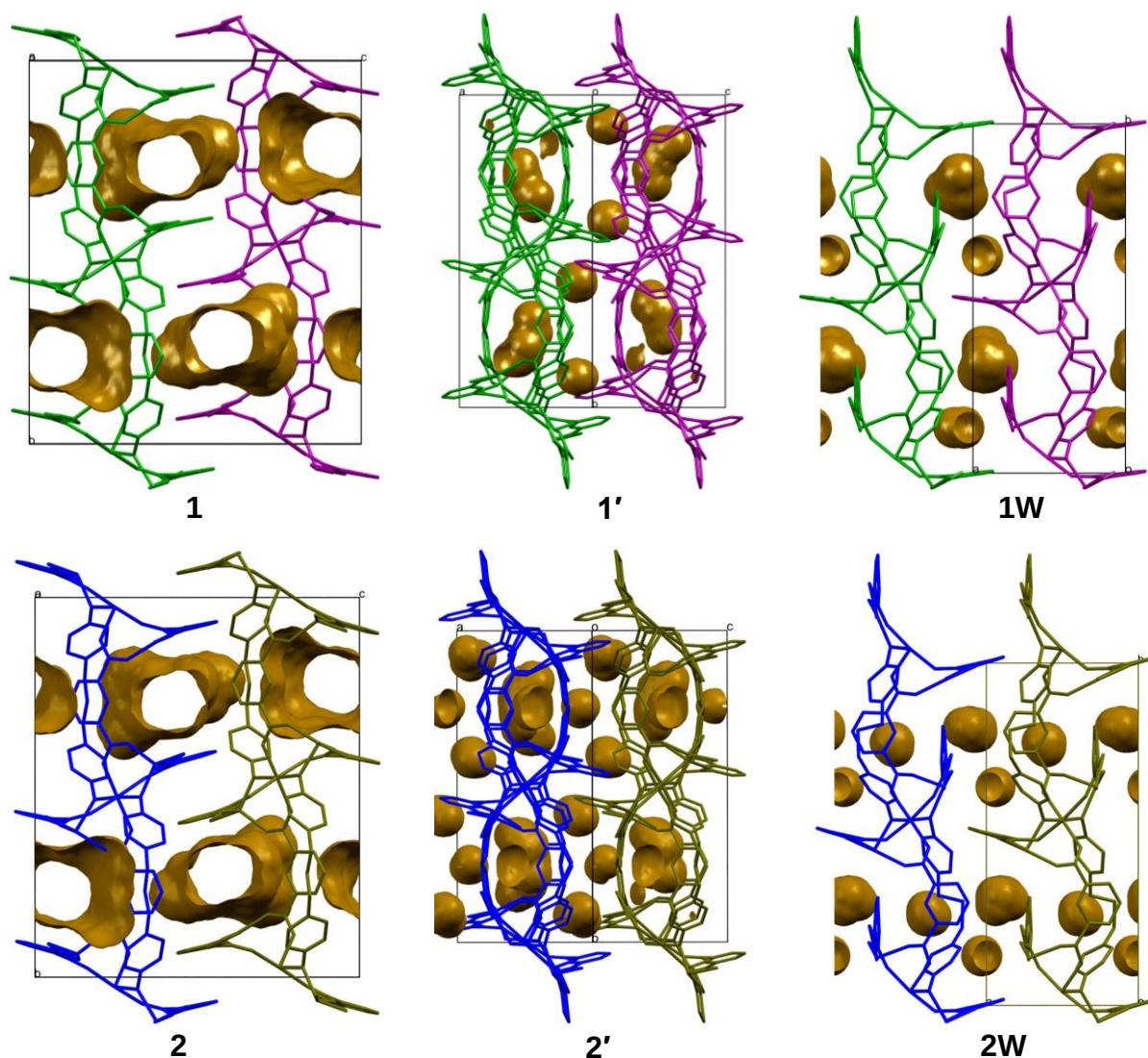


Figure 3.16. Views of channels/isolated voids in **1** and **2** at 298 K: The top row represents **1/1'/1W**, and the bottom row represents **2/2'/2W**. **(Left)** Void spaces when solvent molecules are artificially removed from the as-synthesized structures; **(middle)** actual void spaces after desolvation; **(right)** void spaces in the hydrated structures, with water molecules artificially removed.

3.5. Variable-Temperature Powder X-ray Diffraction (VT-PXRD) Studies

VT-PXRD patterns for **1** and **2**, measured at room temperature and ambient pressure, agree closely with their respective calculated patterns (Figure 3.17), indicating high phase purity and confirming that the single crystal structure is representative of the bulk sample. All VT-PXRD patterns display a broad peak in the $6 - 8^\circ 2\theta$ range (highlighted in grey), an artefact caused by the sample stage. Additionally, the Co(II)-based MOF patterns exhibit a high background due to Co ion fluorescence when copper radiation is used.

VT-SCXRD analysis revealed that both **1** and **2** fully desolvated by 473 K. However, the calculated PXRD patterns at 100 K and 473 K are very similar, suggesting that conformational changes upon desolvation, evident from VT-SCXRD analysis, are not easily detectable using VT-PXRD. Nonetheless, subtle changes are visible in the VT-PXRD patterns, particularly in the $9.5 - 11^\circ$ and $18 - 21.5^\circ 2\theta$ ranges (shaded in blue), indicate these structural changes.

After cooling to 298 K and exposing the desolvated samples (**1'** and **2'**) to the atmosphere, the PXRD patterns show minor differences within the $16 - 17.5^\circ 2\theta$ range (shaded in green) compared to the patterns obtained under vacuum. These patterns closely match the calculated patterns for the hydrated forms, **1W** and **2W**, indicating water absorption from the atmosphere. In the case of **1**, a visual colour change from a dark purple (desolvated) to pink upon cooling and air exposure provides additional evidence of hydration (Figure 3.18). Conversely, no colour change was observed for **2**. In a separate experiment, both **1** and **2** were desolvated using the TGA equipment and then exposed to air for 10 minutes. The subsequent TGA thermograms showed

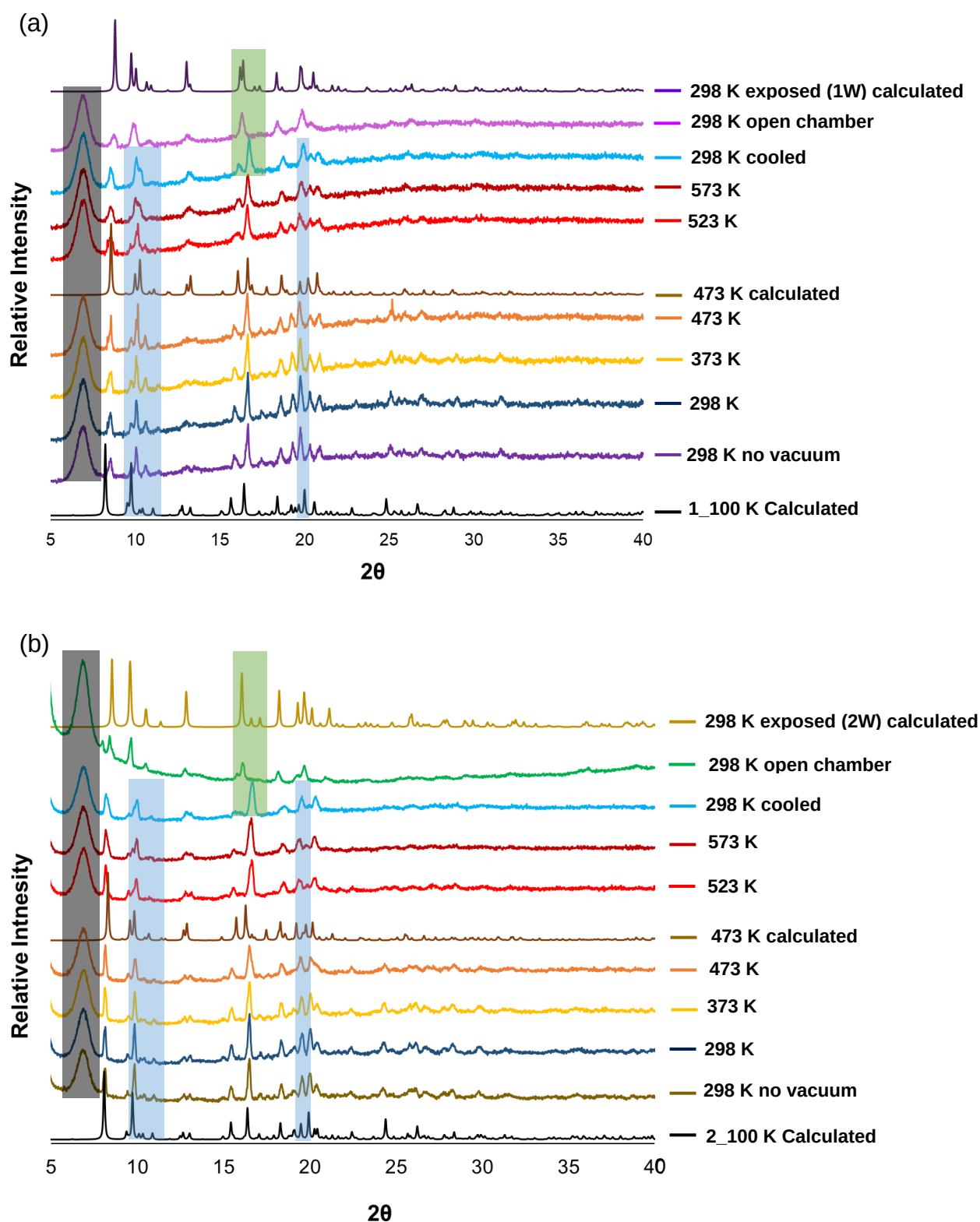


Figure 3.17. VT-PXRD patterns for the bulk powder samples of (a) **1** and (b) **2**. For comparison, calculated PXRD patterns from VT-SCXRD structures at selected temperatures are included. Blue and green shaded areas highlight regions where changes in the VT-PXRD patterns occur.

mass losses of 5.2 and 6.0% for **1** and **2**, respectively, corresponding to approximately three water molecules per ASU (Figure 3.19).

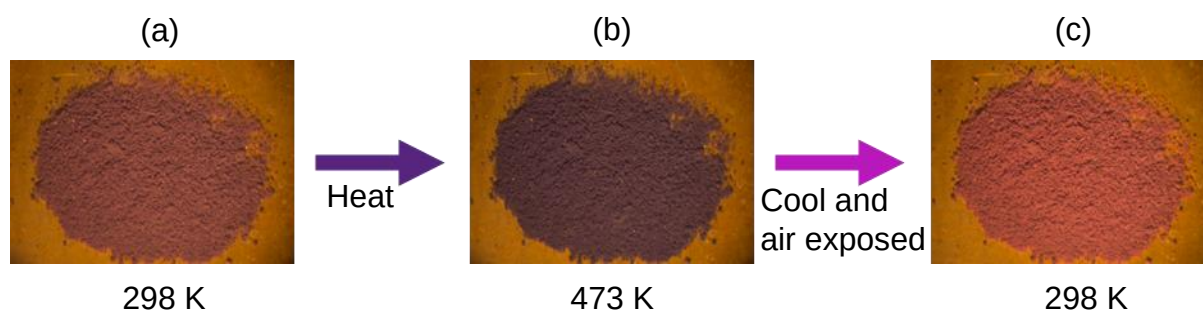


Figure 3.18. Colour changes in crystal powder of the (a) as-synthesised, (b) desolvated, and (c) hydrated structure of **1**.

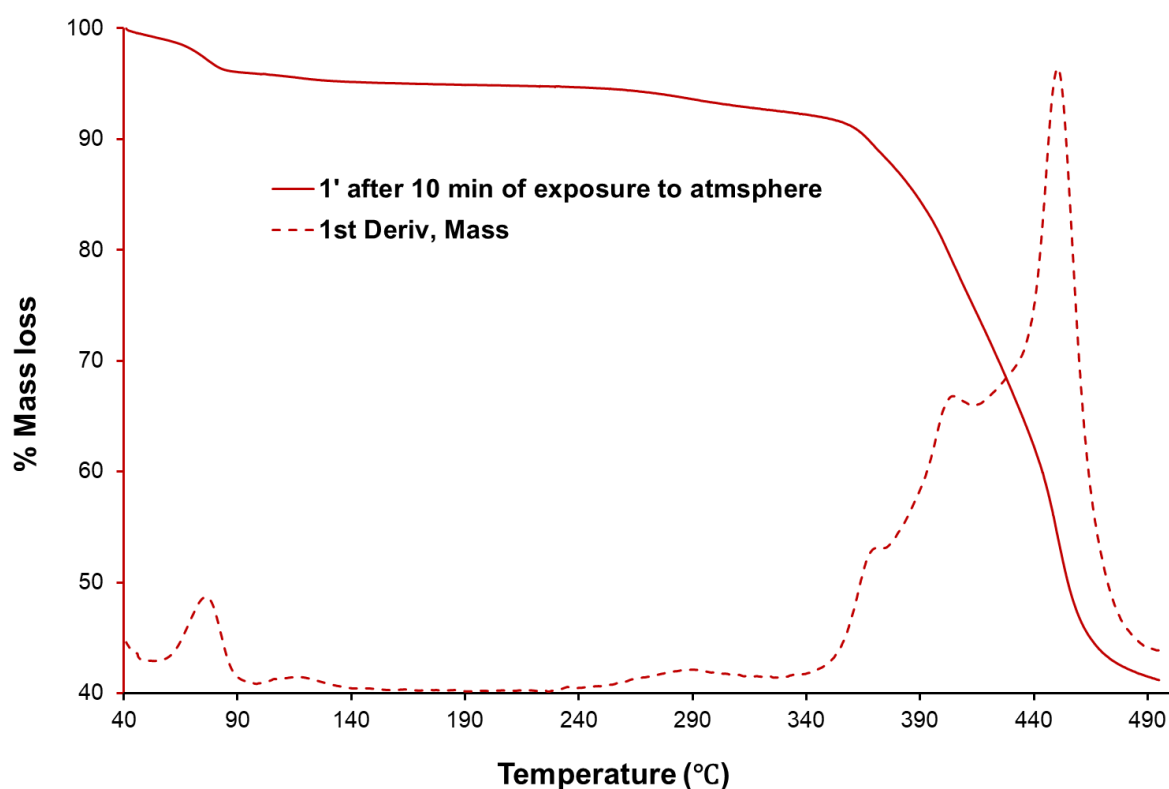


Figure 3.19. TGA thermogram and the first derivative of mass for **1**, showing evidence of water adsorption when desolvated **1** was exposed to the atmosphere.

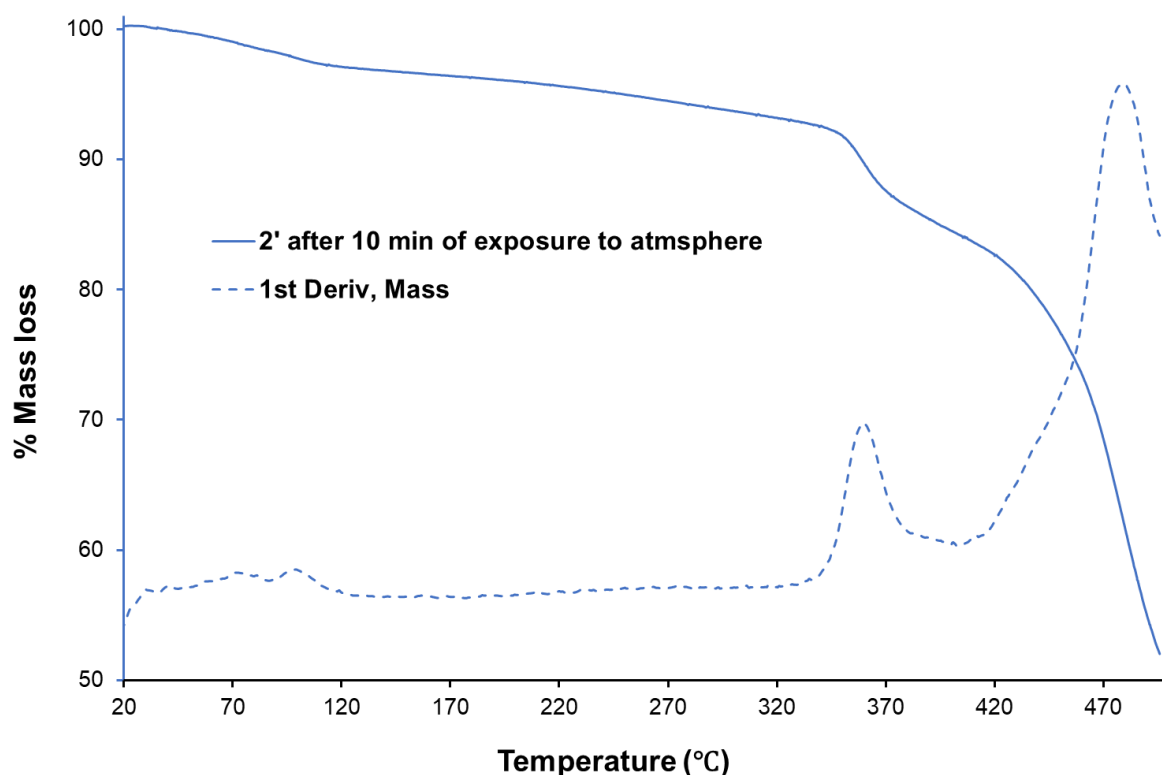


Figure 3.20. TGA thermogram and the first derivative of mass for **2**, showing evidence of water adsorption when desolvated **2** was exposed to the atmosphere.

3.6. Gas Sorption Studies

Although the actual void spaces in **1'** and **2'** are relatively small (3.7% and 5.7% at 298 K, and 3.6% and 4.8% at 195 K, respectively), the flexibility observed in these structures during VT-SCXRD studies served as motivation to explore their gas and vapour sorption behaviours. The activation of **1** and **2** were performed by heating the samples under vacuum *in situ* at 120 °C for 2 h prior to the commencement of the analysis.

3.6.1. Nitrogen and Hydrogen Sorption

Due to small accessible voids, **1'** and **2'** showed no sorption for nitrogen or hydrogen. Since neither sample showed uptake of N₂, BET surface areas could not be measured.

3.6.2. Carbon Dioxide (CO₂) Sorption

CO₂ sorption studies for **1'** and **2'** were conducted at 298 K and 195 K. At 298 K, both **1'** and **2'** show low CO₂ sorption (~ 1.2 cm³ (STP) g⁻¹ for **1'** and ~ 2.0 cm³ (STP) g⁻¹ for **2'**). However, at 195 K, both MOFs exhibit significantly increased CO₂ sorption despite similar void spaces at both 298 and 195 K (Figure 3.20). For **2'**, the 195 K sorption isotherm has a near-typical type-I shape, with a steep initial positive slope at low pressure that gradually decreases while remaining positive until reaching maximum sorption at the highest pressure. Notably, the positive slope of the isotherm of **2'** decreases until a small increase appears at 474 mmHg, followed by another slope decrease until reaching maximum sorption at 716 mmHg (34.2 cm³ (STP) g⁻¹, corresponding to 1.35 CO₂ molecules per ASU). The desorption curve shows an 11% hysteresis, calculated using the method by Barbour *et al.*²¹⁴

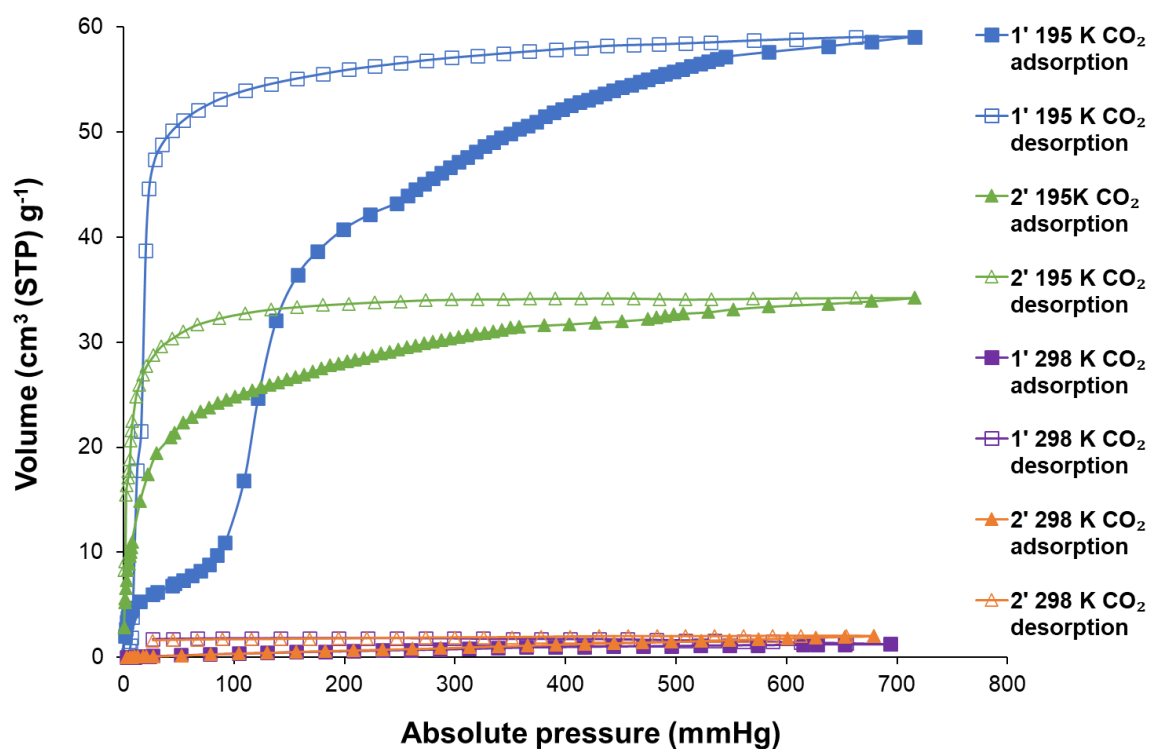


Figure 3.21. CO₂ sorption isotherms for **1'** and **2'** at 298 K and 195 K.

In contrast, **1'** displays a step-shaped isotherm (type-F-I isotherm), which is characteristic of a gradual structural transformation from a less open to a more open phase, at 195 K. After an initial slope decrease, a slope increase is observed at 54 mmHg ($7.4 \text{ cm}^3 \text{ (STP) g}^{-1}$ equivalent to 0.30 CO₂ molecules per ASU), which then decreases at the inflection point at 121 mmHg ($24.7 \text{ cm}^3 \text{ (STP) g}^{-1}$ equivalent to 0.99 CO₂ molecules per ASU) after which it exceeds the sorption of **2'**. Another slope increase occurs at 247 mmHg ($43.2 \text{ cm}^3 \text{ (STP) g}^{-1}$ corresponding to 1.74 CO₂ molecules per ASU), before gradually decreasing again, reaching maximum sorption at 716 mmHg ($59.1 \text{ cm}^3 \text{ (STP) g}^{-1}$ equivalent to 2.37 CO₂ molecules per ASU). A significant hysteresis of 22% is observed upon desorption. The stepwise shape of **1'** isotherm indicates pressure-triggered gate-opening structural changes, which expands the void space and enhances sorption capacity.^{215,216,217}

VT-SCXRD analysis shows that both **1'** and **2'** have very limited and isolated void spaces (33.5 and 45.6 Å^3 per ASU, respectively), as determined using Mercury, which are insufficient to accommodate CO₂ molecules. Thus, both frameworks have to undergo structural adaptations at the start of CO₂ sorption (although inflection points were not observed at the very low pressures), with the stepped isotherm in **1'** indicating further transformation at higher pressures. This is consistent with the fact that **1'**, while having a similar initial void space to **2'** and nearly identical initial structure, demonstrates nearly double the CO₂ sorption of **2'**, indicating a higher degree of structural flexibility.

3.6.3. Water Vapour Sorption

The water vapour sorption isotherms for both **1'** and **2'** resemble their CO₂ sorption profiles at 195 K (Figure 3.21). Initially, **1'** shows lower water sorption than **2'**, with a

slope increase at $P/P_0 = 0.10$ ($26.5 \text{ cm}^3 \text{ (STP) g}^{-1}$ corresponding to 1.06 water molecules per ASU) and a decrease at the inflection point of $P/P_0 = 0.14$ ($34.5 \text{ cm}^3 \text{ (STP) g}^{-1}$ corresponding to 1.39 water molecules per ASU). At $P/P_0 = 0.19$ ($48.7 \text{ cm}^3 \text{ (STP) g}^{-1}$ corresponding to 1.95 water molecules per ASU), **1'** surpasses **2'** in sorption, reaching its maximum sorption at $P/P_0 = 0.76$ ($74.4 \text{ cm}^3 \text{ (STP) g}^{-1}$ corresponding to 2.99 water molecules per ASU).

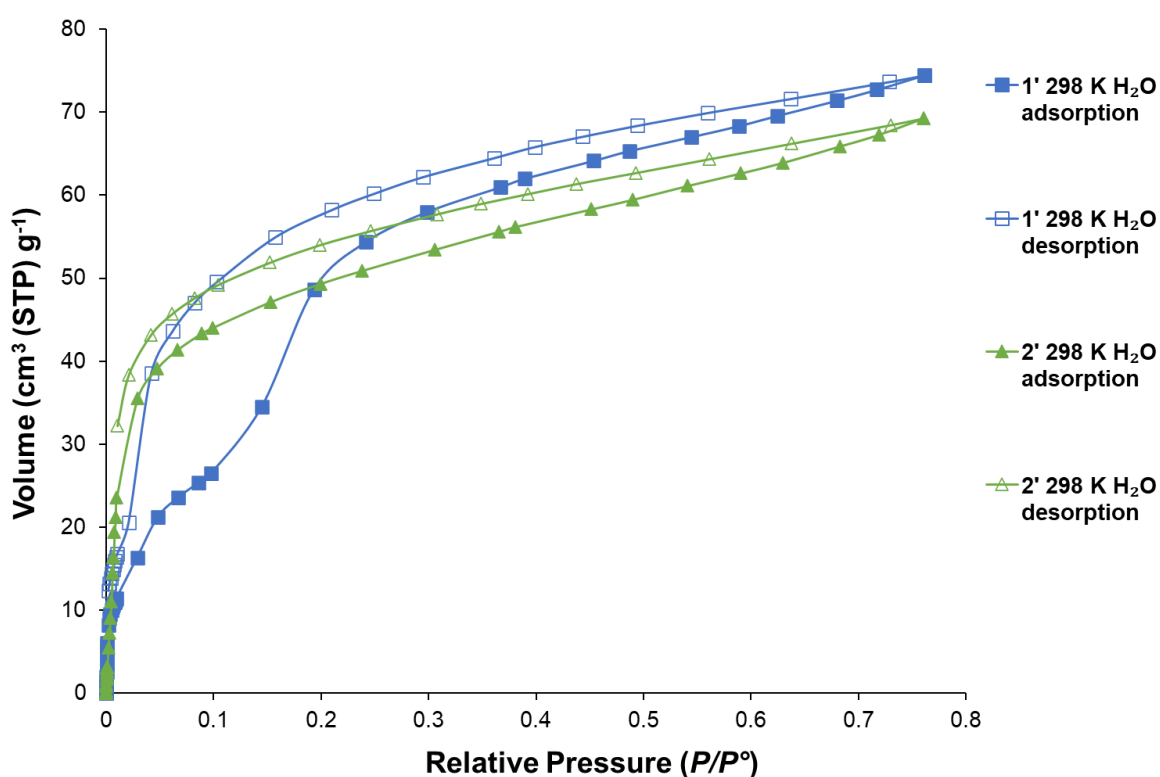


Figure 3.22. Water vapor sorption isotherms for **1'** and **2'** at 298 K.

For **2'**, the maximum sorption is slightly lower, occurring at $P/P_0 = 0.76$ ($69.3 \text{ cm}^3 \text{ (STP) g}^{-1}$ corresponding to 2.75 water molecules per ASU). Similar to CO_2 desorption, the hysteresis in **1'** (11%) is nearly twice that of **2'** (6%). The number of water molecules adsorbed per ASU aligns with those observed in the crystal structures

of **1W** and **2W**, except for the third water molecule that was not located in **2W**. This discrepancy is attributed to the experimental differences between single-crystal *in situ* water sorption and water vapour sorption studies, with vapour sorption allowing for exposure to higher water vapour pressures than were present in the atmosphere. Single crystal *in situ* water sorption studies identified the location of the sorbed water molecules as one uncoordinated and two coordinated water molecules.

3.7. Summary

Two 2-periodic mixed-ligand MOFs, which are both isorecticular and isostructural, have been synthesised, featuring linear trinuclear Co₃ and Mn₃ clusters in **1** and **2**, respectively. These MOFs were synthesized using the unique combination of isophthalic acid and 1,3-bis(4-pyridyl)propane-*N,N'*-dioxide ligands. Both frameworks exhibit temperature-induced dynamic behaviour, undergoing single-crystal-to-single-crystal transformations during desolvation and hydration processes, resulting in significant changes in void space volumes. During these transformations, the ia ligand rotates upon desolvation, while the bppdo ligand undergoes a conformational change from the stable *anti-anti* form to the less stable *anti-gauche* form upon water sorption. This behaviour highlights the different roles these ligands play in response to external stimuli, demonstrating the flexibility and adaptability of these MOFs. Furthermore, both frameworks display high CO₂ selectivity over N₂ at low temperatures. Despite structural similarities between the desolvated forms **1'** and **2'**, their adsorption behaviour differs, **1'** displays a three-step CO₂ adsorption process (type-F-I sorption isotherm) at 195 K, with a pronounced hysteresis during desorption, indicating a greater susceptibility to pressure-induced structural changes. In contrast, **2'** exhibits a near-typical type-I isotherm shape. Additionally,

water vapour sorption at 298 K reveals that both desolvated MOFs have a strong affinity for water, which also induces structural transformations in **1'** and **2'**.

Among the two MOFs, **1'** demonstrates superior adsorption performance, with higher maximum CO₂ and water vapour sorption at low temperatures and a distinct multi-step adsorption behaviour that reflects its greater structural flexibility. This flexibility enables pressure-triggered gate-opening, expanding void space and enhancing sorption capacity. Conversely, **2'** shows a more rigid framework with lower sorption and less hysteresis, as indicated by its typical type-I isotherm.

Chapter 4:

Zn Single-Ligand MOFs

This chapter discusses the characterisation of synthesised single-ligand MOFs. The ligand used, 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (H_2hfipbb), led to the formation of two pairs of Zn(II)-based, 2-periodic MOFs. The first pair, $[\text{Zn}(\text{hfipbb})(\text{MeOH})]_n \cdot n(\text{MeOH})_{0.5}$ (**3**) and $[\text{Zn}(\text{hfipbb})(\text{EtOH})]_n \cdot n(\text{EtOH})_{0.5}$ (**4**), were synthesised using methanol (MeOH) and ethanol (EtOH) as solvents, respectively, resulting in doubly interpenetrated structures. The second pair, $[\text{Zn}_2(\text{hfipbb})_2(\text{DMF})_2]_n \cdot n(\text{DMF})_4$ (**5**) and $[\text{Zn}_4(\text{hfipbb})_4(\text{DMA})_4]_n \cdot n(\text{DMA})_8 \cdot n(\text{H}_2\text{O})$ (**6**), were formed using *N,N'*-dimethylformamide (DMF) and *N,N'*-dimethylacetamide (DMA) as solvents, respectively, leading to non-interpenetrated structures. The MOFs were fully characterised by X-ray diffraction techniques (SCXRD, PXRD, VT-PXRD) and thermal analysis methods (HSM, TGA, and DSC). This chapter also provides a detailed comparison of their gas sorption properties.

4.1. Synthesis

4.1.1. Preparation of $[\text{Zn}(\text{hfipbb})(\text{MeOH})]_n \cdot n(\text{MeOH})_{0.5}$ (**3**)

The ligand, 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (38 mg, 0.10 mmol) was dissolved in 0.50 ml of DMF. In a separate vial, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (30 mg, 0.10 mmol) was dissolved in 4.5 ml MeOH. The two solutions were combined and stirred for 10 min at room temperature, yielding a clear solution. This solution was transferred into an autoclave and placed in an oven. Clear, plate-shaped crystals, suitable for X-ray diffraction, were obtained after heating at 90 °C for 72 hours. The yield was 61% (based on Zn), which was calculated based on the crystalline material obtained.

4.1.2. Preparation of $[\text{Zn}(\text{hfipbb})(\text{EtOH})]_n \cdot n(\text{EtOH})_{0.5}$ (**4**)

The synthesis of **4** followed the same procedure as for **3**, with EtOH replacing MeOH. This substitution resulted in the formation of crystals isomorphous to those of **3**. The yield was 64% (based on Zn), which was calculated based on the crystalline material obtained.

4.1.3. Preparation of $[\text{Zn}_2(\text{hfipbb})_2(\text{DMF})_2]_n \cdot n(\text{DMF})_4$ (**5**)

The ligand, 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (38 mg, 0.10 mmol) was dissolved in 4.0 ml of DMF. In a separate vial, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (30 mg, 0.10 mmol) was dissolved in 1.0 ml DMF. The solutions were combined and stirred for 10 min at room temperature to form a clear solution. This solution was transferred into a 10 ml glass tube and heated at 90 °C. After 48 hours, the tube was removed from the oven and the solution was transferred to a vial to stand at room temperature. Colourless,

plate-shaped crystals, suitable for X-ray diffraction, were obtained by slow evaporation of the solvent after 48 hours. The yield was 35% (based on Zn), which was calculated based on the crystalline material obtained.

4.1.4. Preparation of $[\text{Zn}_4(\text{hfipbb})_4(\text{DMA})_4]_n \cdot n(\text{DMA})_8 \cdot n(\text{H}_2\text{O})$ (**6**)

The ligand, 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (38 mg, 0.10 mmol) was dissolved in 3.0 ml of DMA and 1.0 ml MeOH. In a separate vial, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (30 mg, 0.10 mmol) was dissolved in 1.0 ml DMA. The two solutions were combined and stirred for 10 min at room temperature, yielding a clear solution. This solution was transferred into an autoclave and placed in an oven. Clear, rectangular-shaped crystals suitable for X-ray diffraction were obtained after heating at 90 °C for 72 hours. The yield was 68% (based on Zn), which was calculated based on the crystalline material obtained.

4.2. Single Crystal X-Ray Diffraction Analysis of **3**

4.2.1. Structure Description

Single crystal X-ray diffraction analysis reveals that **3** crystallises in the orthorhombic crystal system with space group *Pccn* (Table 4.1). The ASU contains one Zn^{2+} ion, a fully deprotonated 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (H_2hfipbb) ligand, one coordinated and one uncoordinated MeOH molecule with a site occupancy factor (sof) of 0.50 (Figure 4.1a). The uncoordinated MeOH molecule is positioned near a 2-fold rotation axis, necessitating its half occupancy. The Zn^{2+} ions form binuclear SBUs, where each Zn center adopts a distorted square pyramidal geometry

(Figure 4.1b). This coordination is stabilised by the formation of a paddlewheel structure, which imposes geometric constraints commonly observed in MOFs containing Zn^{2+} .^{218,219} In the paddlewheel SBU, the equatorial positions are occupied by four bidentate bridging carboxylate oxygen atoms from four different hfipbb ligands,

Table 4.1. Crystal Data and Refinement Parameters for **3**.

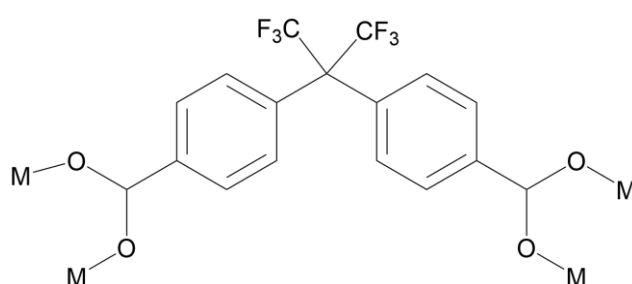
ASU formula	$\text{C}_{18.5}\text{F}_6\text{O}_{5.5}\text{ZnH}_{14}$
Formula mass	503.67
Temperature / K	100
Crystal system	orthorhombic
Space group	<i>Pccn</i>
<i>a</i> / Å	25.722(3)
<i>b</i> / Å	6.9466(11)
<i>c</i> / Å	23.062(4)
α / °	90
β / °	90
γ / °	90
Volume / Å ³	4120.9(11)
<i>Z</i>	8
ρ / g cm ⁻³	1.624
μ / mm ⁻¹	1.275
<i>F</i> (000)	1952.0
Crystal size (mm ³)	0.13 × 0.12 × 0.09
2 Θ range for data collection / °	3.87 to 56.164
Index ranges	-34 ≤ <i>h</i> ≤ 34, -9 ≤ <i>k</i> ≤ 9, -30 ≤ <i>l</i> ≤ 30
Reflections collected	130652
Independent reflections	5011 [<i>R</i> _{int} = 0.1095, <i>R</i> _{sigma} = 0.0351]
Data/restraints/parameters	5011 / 12 / 293
Goodness-of-fit on <i>F</i> ²	1.064
Final <i>R</i> indexes [<i>I</i> ≥ 2σ (<i>I</i>)]	<i>R</i> ₁ = 0.1135, <i>wR</i> ₂ = 0.2894
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1379, <i>wR</i> ₂ = 0.3178
Largest diff. peak/hole / e Å ⁻³	10.88 / -1.28

Table 4.2. Paddlewheel Zn...Zn distance and bond lengths involving Zn²⁺ cations in **3**.

Bond	Length (Å)	Bond	Length (Å)
Zn1...Zn1	2.901	Zn1–O2	2.015(5)
Zn1–O1	2.038(6)	Zn1–O4	2.014(5)
Zn1–O1S	1.978(4)	Zn1–O3	2.034(6)

4.2.2. Crystal Packing

In **3**, each paddlewheel unit connects to four adjacent paddlewheel clusters via the bridging hfipbb ligands, whose carboxylate groups adopt a bidentate bridging coordination mode (Scheme 4.1). This arrangement forms undulating, 2-periodic frameworks parallel to the *bc* plane that stacks along the *c*-axis, with large, rhombus-like windows (Figure 4.2a). The short and long diagonals of the rhombic windows, measured between the centroids of the binuclear Zn²⁺ subunits at the corners, are 13.9 and 23.1 Å, corresponding to *2b* and *c*, respectively, in terms of unit cell axis lengths.

**Scheme 4.1.** Bridging coordination mode of hfipbb²⁻ ligand in **3**.

When viewed along the *c*-axis, the framework resembles a zig-zag chain due to the bent conformation of the hfipbb ligands (Figure 4.2b). The large windows in one framework allow another framework to be entwined with it, forming a 2-fold parallel

interpenetrated 2-periodic (Figure 4.3 and 4.4). When viewed along the *b*-axis, these interpenetrated 2-periodic bilayers contain diamondoid-shaped channels, which are occupied by MeOH molecules (Figure 4.5). The frameworks stack in an interdigitated ABAB sequence along the *a*-direction, with a separation distance of 12.9 Å between bilayers. The coordinated MeOH molecules are orientated perpendicular to the channels, pointing towards the neighbouring 2-periodic frameworks.

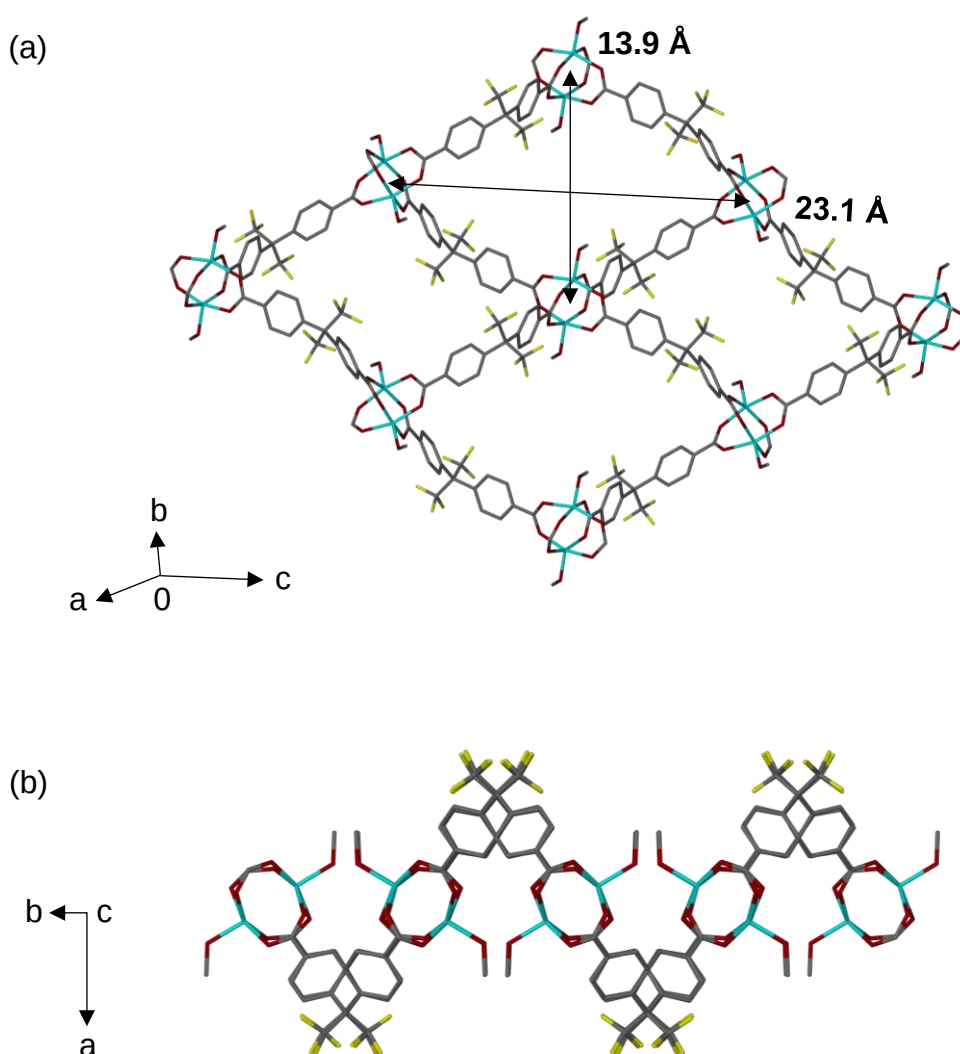


Figure 4.2. (a) Oblique view of the 2-periodic framework of **3**, indicating the dimensions of the rhombic windows. (b) View of the 2-periodic framework of **3** along the *c*-axis. Uncoordinated solvent molecules and hydrogen atoms are omitted for clarity.

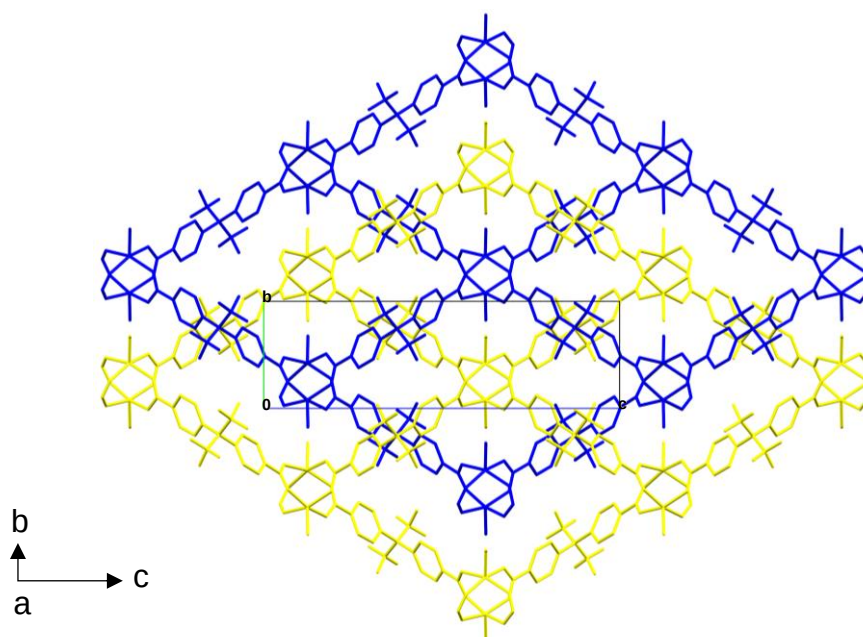


Figure 4.3. Colour-coded representation of the 2-fold parallel interpenetrated frameworks of **3**, viewed along the *a*-axis. Uncoordinated solvent molecules and hydrogen atoms are omitted for clarity.

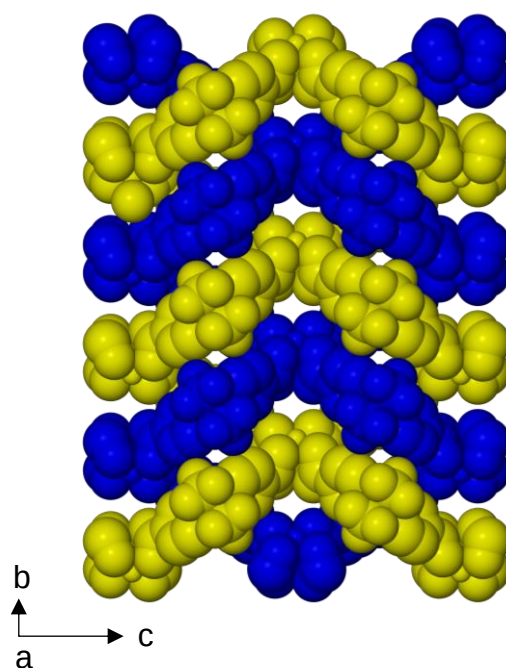


Figure 4.4. Colour-coded, space-filling representation of the interpenetrated, interwoven 2-periodic frameworks viewed along the *a*-axis in **3**. Uncoordinated solvent molecules and hydrogen atoms are omitted for clarity.

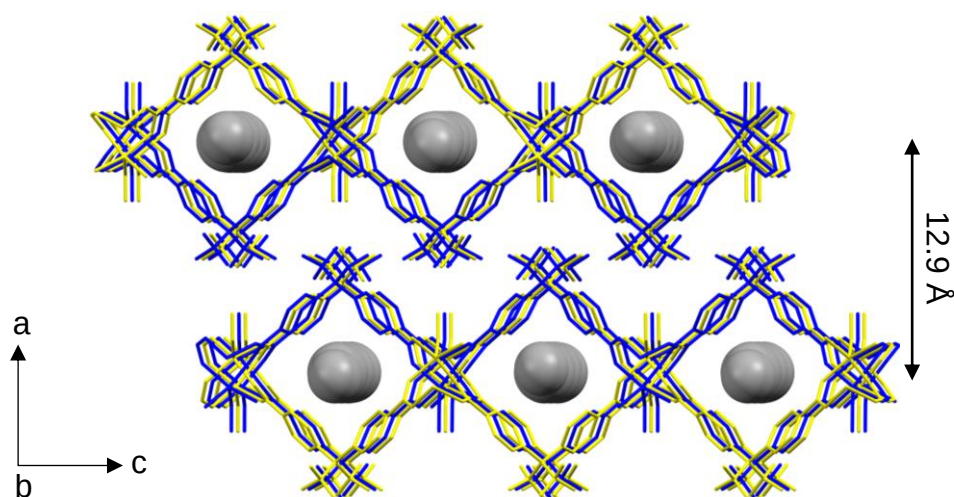


Figure 4.5. 2-periodic 2-fold interpenetrated frameworks in **3**, colour-coded and stacked along the *a*-axis, with a stacking distance of 12.9 Å, indicated by a line. Uncoordinated MeOH molecules are shown in space-filling mode (grey), with hydrogen atoms omitted for clarity.

4.2.3. Hydrogen Bonding

The interpenetrated frameworks in **3** are connected by hydrogen bonding (Figure 4.6 and Table 4.3). These framework...framework hydrogen bonds occur between two interpenetrated frameworks, with no interactions observed between 2-periodic frameworks from adjacent layers. The interpenetrated frameworks are connected by strong O–H...O bonds (O1S–H1S...O1 and O1S–H1S...O3) formed between the coordinated MeOH molecules and the carboxylate groups of the hfipbb ligands. Weaker C–H...F interactions (C4–H4...F1 and C12–H12...F6) are also present between the aromatic ring and fluorine atoms of the hfipbb ligands.

While this discussion focuses only on hydrogen bonds between the interpenetrated frameworks, hydrogen bonds within the individual frameworks also exist and are detailed in the .lis file supplied as supplementary information.

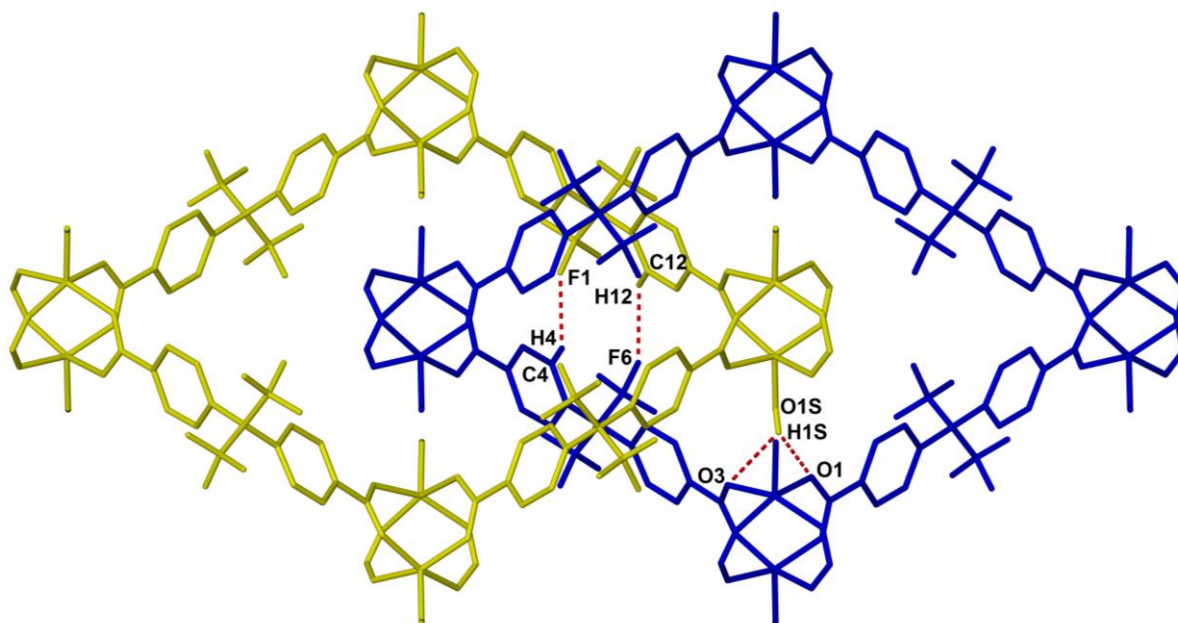


Figure 4.6. Hydrogen bonding in **3**, showing interactions between the interpenetrated 2-periodic frameworks.

Table 4.3. Hydrogen bond distances, angles, and symmetry operators for **3**.

Donor–H···Acceptor	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)	Symmetry operators
O1S–H1S···O1	0.78	2.02	2.7668(5)	159	$\frac{1}{2}-x, \frac{1}{2}-y, z$
C4–H4···F1	0.93	2.51	3.1389(5)	125	$x, 1+y, z$

4.3. Desolvation Studies

4.3.1. Thermal Analysis

4.3.1.1. Thermogravimetric and Differential Scanning Calorimetry Analysis

The thermal stability of **3** was quantitatively analysed using TGA and DSC. TGA measurements were performed on crystalline samples of **3** over a temperature range of 16 to 550 °C (Figure 4.7). The analysis revealed a single mass loss of 10.7%

(calculated 9.5%) between 50 and 200 °C, corresponding to the release of both coordinated and uncoordinated MeOH molecules. This observation is supported by the derivative mass curve, which displays a single peak.

The DSC thermogram further supports this finding, showing a sharp endothermic peak with an onset temperature of 111 °C and a peak temperature of 148 °C. The framework remains stable up to approximately 430 °C, beyond which decomposition occurs.

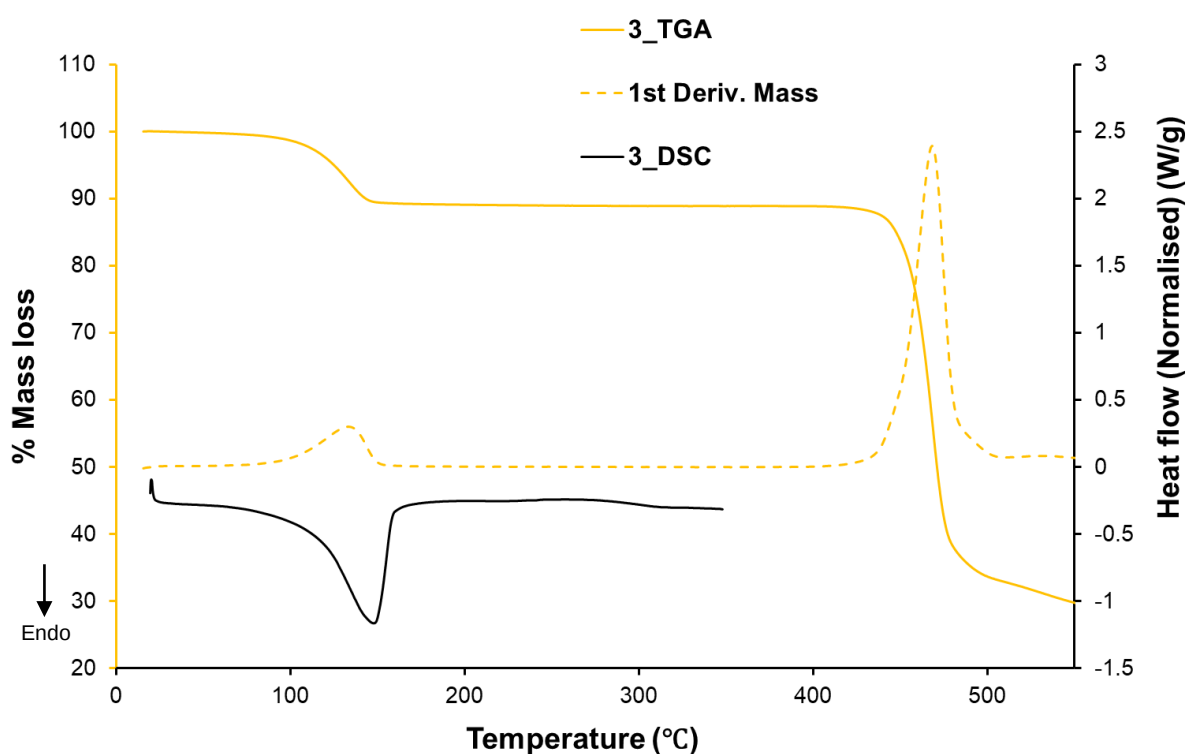


Figure 4.7. Overlay of the TGA thermogram, its first derivative mass, and the DSC thermogram of **3**.

4.3.1.2. Hot Stage Microscopy

The thermal events observed in the HSM experiment occurred at slightly different temperatures compared to the TG and DSC analyses, likely due to the differences in the experimental setup geometry.

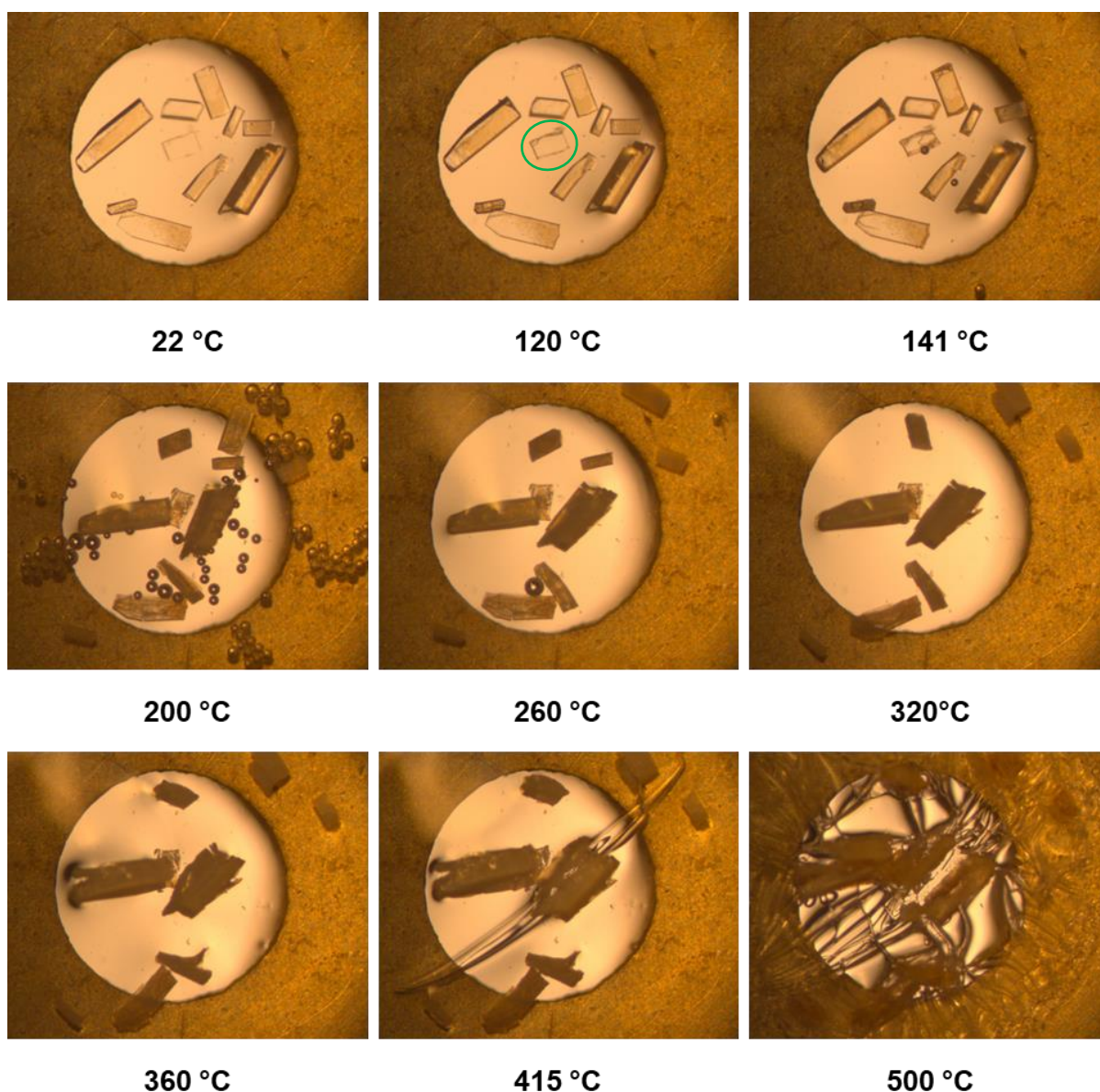


Figure 4.8. HSM images of **3** from 22 – 500 °C.

Crystals of **3** were placed on a microscope slide and covered in silicone oil to observe thermal events such as monocrystallinity loss, desolvation, and decomposition between 22 to 500 °C (Figure 4.8). Desolvation began at 120 °C, as evidenced by cracks on the crystal surface (indicated by a circle in the 120 °C image), followed by bubbling at 141 °C, indicating further solvent release. By 200 °C, the crystals became opaque, signifying the loss of monocrystallinity, and bubbling intensified, suggesting rapid solvent release. Disintegration of the crystals began at this temperature, with

bubbling persisting until 260 °C. The solvent release between 120 and 260 °C indicates the loss of both coordinated and uncoordinated MeOH molecules, as confirmed by TGA data. Disintegration of the crystals continued until complete decomposition occurred at 500 °C.

4.3.2. Water Exchange Studies

We attempted to obtain the single crystal structure of the desolvated form of **3** through SCSC transformations in order to gain structural insights into its behaviour during gas sorption studies. However, heating crystals of **3** resulted in the formation of polycrystalline material, preventing the direct observation of the desolvated phase using SCXRD. In order to overcome this, we explored an indirect approach using water-exchange phases. Crystals of **3**, soaked in water for 24 hours, underwent complete replacement of MeOH ligand molecules with water, as confirmed by SCXRD analysis. These water-exchanged crystals are hereinafter referred to as **3W**. The single crystal data and refinement parameters for **3W** are provided in Table 4.4.

Remarkably, while the MeOH molecules in the channels were removed, no water molecules were found to occupy these channels, indicating that the interior of the channels is hydrophobic (Figure 4.9). Attempts to desolvate **3W** *in situ* on the single-crystal X-ray diffractometer were unsuccessful, as heating again led to polycrystalline material. Nonetheless, the structure of **3W** provides valuable insights into the desolvated phase of **3**. Specifically, the 2-periodic layers in **3W** are shifted closer to each other due to the smaller size of the water ligand compared to the MeOH ligand, with a 1.8 Å reduction in the interlayer distance. This observation suggests that, in the fully desolvated phase, the 2-periodic layers may shift even closer together. This behaviour aligns with previous findings in 2-periodic Cu-based MOFs, where

exchanging ligated DMF molecules with water led to relative shifts of neighbouring 2-periodic layers, followed by even more pronounced shifts upon the removal of ligated water molecules.¹²⁸

Table 4.4. Crystal Data and Refinement Parameters for **3W**.

ASU formula	C ₁₇ H ₁₀ F ₆ O ₅ Zn
Formula mass	473.62
Temperature / K	100
Crystal system	monoclinic
Space group	<i>P2₁/n</i>
<i>a</i> / Å	12.675(3)
<i>b</i> / Å	6.9121(14)
<i>c</i> / Å	20.933(4)
α / °	90
β / °	93.439(6)
γ / °	90
Volume / Å ³	1830.7(6)
<i>Z</i>	4
ρ / g cm ⁻³	1.718
μ / mm ⁻¹	1.428
<i>F</i> (000)	944
Crystal size (mm ³)	0.534 × 0.074 × 0.067
2 θ range for data collection / °	3.898 to 56.984
Index ranges	-16 ≤ <i>h</i> ≤ 16, -9 ≤ <i>k</i> ≤ 9, -27 ≤ <i>l</i> ≤ 27
Reflections collected	34890
Independent reflections	4570 [<i>R</i> _{int} = 0.0723, <i>R</i> _{sigma} = 0.0485]
Data/restraints/parameters	4570/0/245
Goodness-of-fit on <i>F</i> ²	1.108
Final <i>R</i> indexes [<i>I</i> ≥ 2σ (<i>I</i>)]	<i>R</i> ₁ = 0.1727, <i>wR</i> ₂ = 0.3932
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1863, <i>wR</i> ₂ = 0.4030
Largest diff. peak/hole / e Å ⁻³	10.10/-1.69

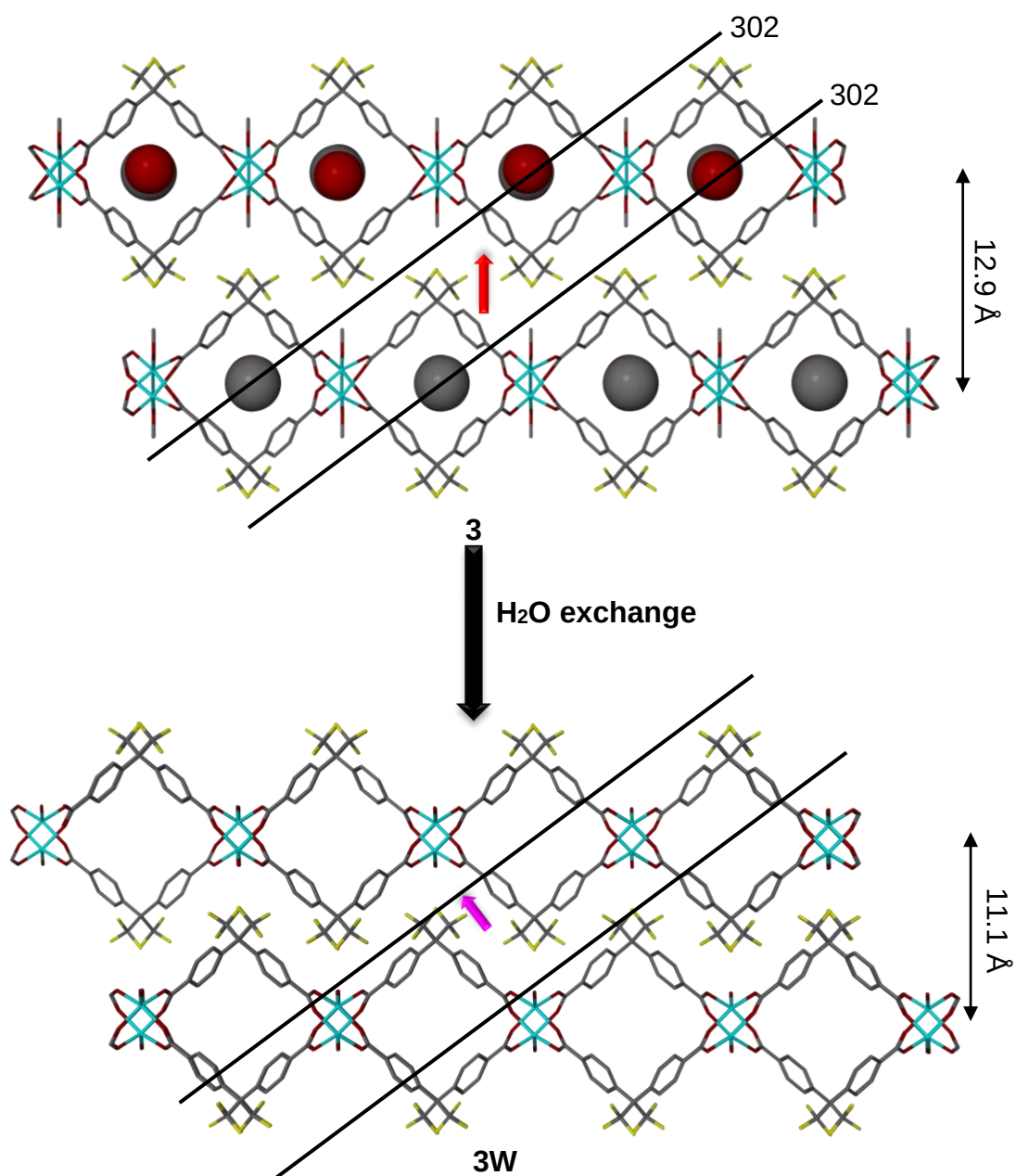


Figure 4.9. Crystal packing diagrams illustrating the ligand exchange transition from **3** to **3W**. The (302) planes in **3** are shown along the *b*-axis with the red arrow indicating the possible vertical movement of the 2-periodic layers. In **3W**, the pink arrow indicates the orthogonal direction relative to the equivalent set of planes in **3**. Hydrogen atoms are omitted for clarity.

Consistent with this, the calculated PXRD pattern of **3** shows that the peaks at 6.9 and 12.9° 2θ, corresponding to the 200 and 302 planes, respectively, either disappear or are significantly reduced in the calculated pattern of **3W** (Figure 4.10). The most

notable change is the sharp decrease in the intensity of the 12.9° 2θ peak, indicating the closer shift of neighbouring 2-periodic layers during the transition from **3** to **3W**. This behaviour can be explained by examining the 302 planes in the structure of **3** (Figure 4.9). In **3**, the metals on both neighbouring layers are positioned halfway along the planes. In **3W**, as the layers move closer together, the metals in one layer shift orthogonally, positioning closer to the planes. This partial shift causes destructive X-ray interference, though not complete, resulting in the reduction in the intensity of the 12.9° 2θ peak in the PXRD pattern of **3W**.

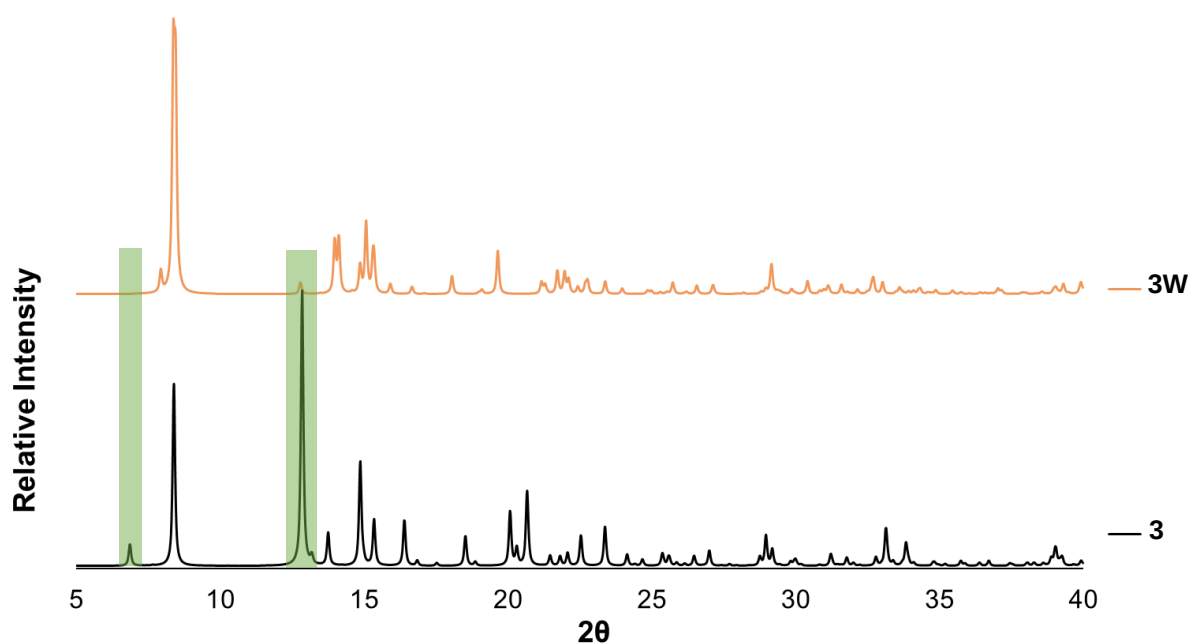


Figure 4.10. Calculated PXRD patterns of **3** and **3W**, with key changes in peak intensities highlighted by green-shaded bars.

4.3.3. Variable-Temperature Powder X-Ray Diffraction Studies

The VT-PXRD pattern of **3** at 25°C and ambient pressure (~ 1 atm) closely matches the calculated pattern (Figure 4.11). This close match confirms the phase purity of the

synthesised material and shows that the single crystal is representative of the bulk sample. However, the peaks at 18.6 and 20.0° 2 θ (marked by red stars) are either absent or reduced in intensity in the 25 °C experimental PXRD pattern compared to the calculated pattern, likely due to preferred orientation effects. Additionally, the peak at 6.8 ° 2 θ (marked by a blue star) in the calculated pattern is obscured in the experimental VT-PXRD patterns by a broad background peak in the 6-8° 2 θ region. This is attributed to an artefact from the sample stage, making it difficult to evaluate the peak's behaviour accurately.

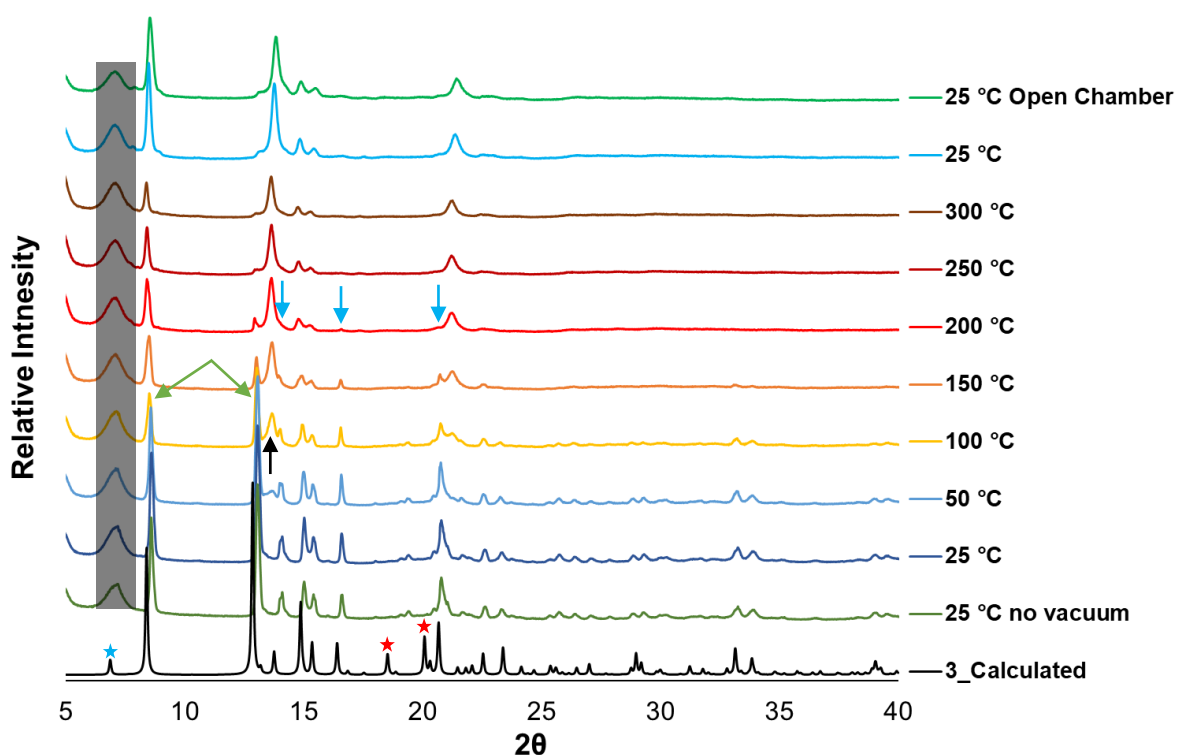


Figure 4.11. Calculated and VT-PXRD patterns of **3** from 25 to 300 °C under vacuum, followed by cooling back to 25 °C, and finally after exposure to air at 25 °C.

Structural changes become evident at 100 °C in the VT-PXRD pattern, with the appearance of a new peak at 13.6° 2 θ (indicated by a black arrow) and reduced intensities of the prominent peaks at 8.5 and 12.9° 2 θ (indicated by green arrows), indicating the onset of desolvation. As the temperature increases to 150 °C, the new peak at 13.6° 2 θ becomes more pronounced, while existing peaks continue to decrease in intensity, suggesting further structural changes due to desolvation. At 200 °C, the peaks at 14.0, 16.6, and 20.8° 2 θ (indicated by blue arrows) disappear and the peak at 12.9° 2 θ weakens further, indicating further solvent loss. By 250 °C, the peak at 12.9° 2 θ disappears, marking the structure's transition to its final desolvated phase. No further changes are observed up to 300 °C.

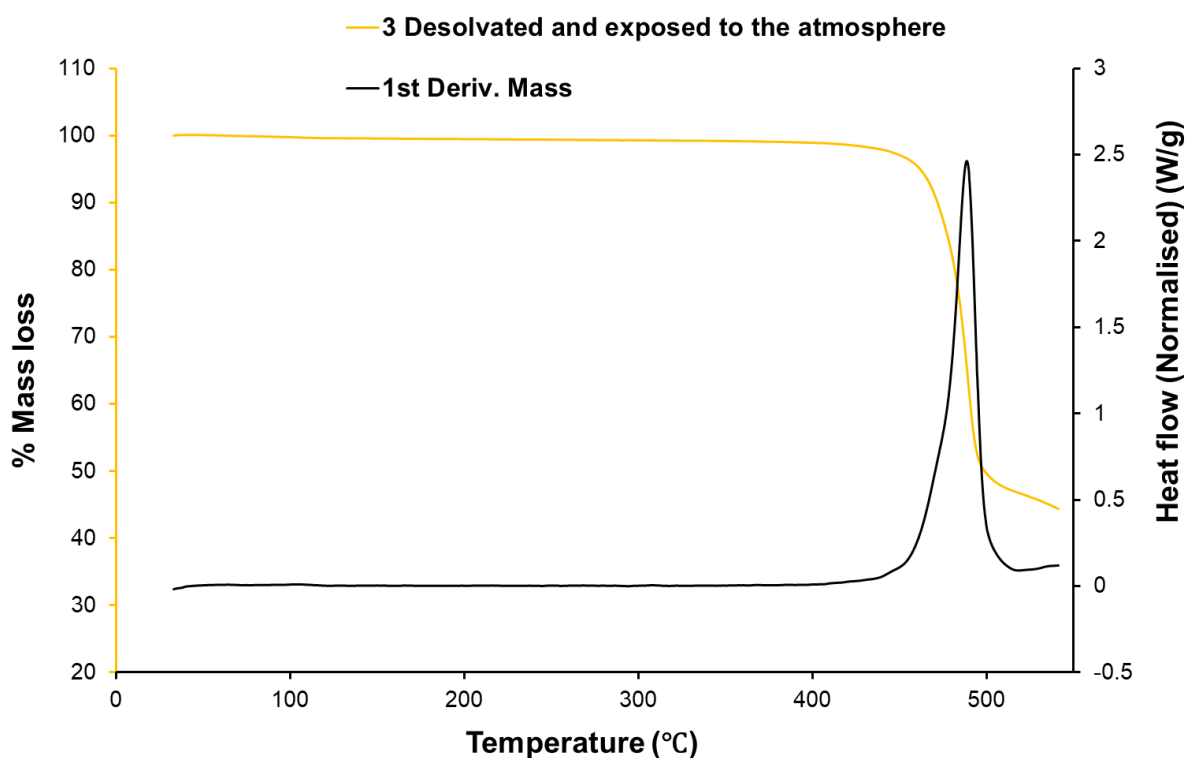


Figure 4.12. TGA thermogram of **3** after desolvation and 24-hour exposure to the atmosphere, along with its first derivative mass curve.

The structural changes involve neighbouring layers in the 2-periodic framework moving closer to each other as ligated MeOH molecules are removed. This is evidenced by the progressive reduction in the intensity of the prominent peak at $12.9^\circ 2\theta$ with increasing temperature, consistent with observations from the water-exchange analysis. Upon cooling to 25°C , the pattern remains unchanged, but peak intensities increase, indicating improved crystallinity due to reduced thermal vibrations. HSM analysis revealed the loss of monocrystallinity during the heating process. However, VT-PXRD results confirm that overall crystallinity is retained, suggesting that the sample transitions to a polycrystalline state upon desolvation.

When the desolvated sample is exposed to air for 24 hours, no structural changes are observed, as the pattern remains consistent. This is further supported by the TGA thermogram of the desolvated sample exposed to air (Figure 4.12), which shows no mass loss until decomposition, indicating that the unsaturated metal sites do not adsorb atmospheric water vapour.

4.3.4. Void Space Analysis

The void space characteristics of **3** were analysed using MERCURY after the artificial removal of uncoordinated solvent molecules.²⁰⁵ Observations from the hydrated form, **3W**, suggest that the 2-periodic layers in **3** may shift closer together following the loss of ligated solvent. As a result, only the channels previously occupied by uncoordinated solvent molecules are accessible as potential voids. Analysis of **3** reveals the presence of 1D continuous channels running along the *b*-axis (Figure 4.13). These channels account for 12.9% of the unit cell volume, corresponding to a potential void space of $530.2 \text{ \AA}^3$ per unit cell.

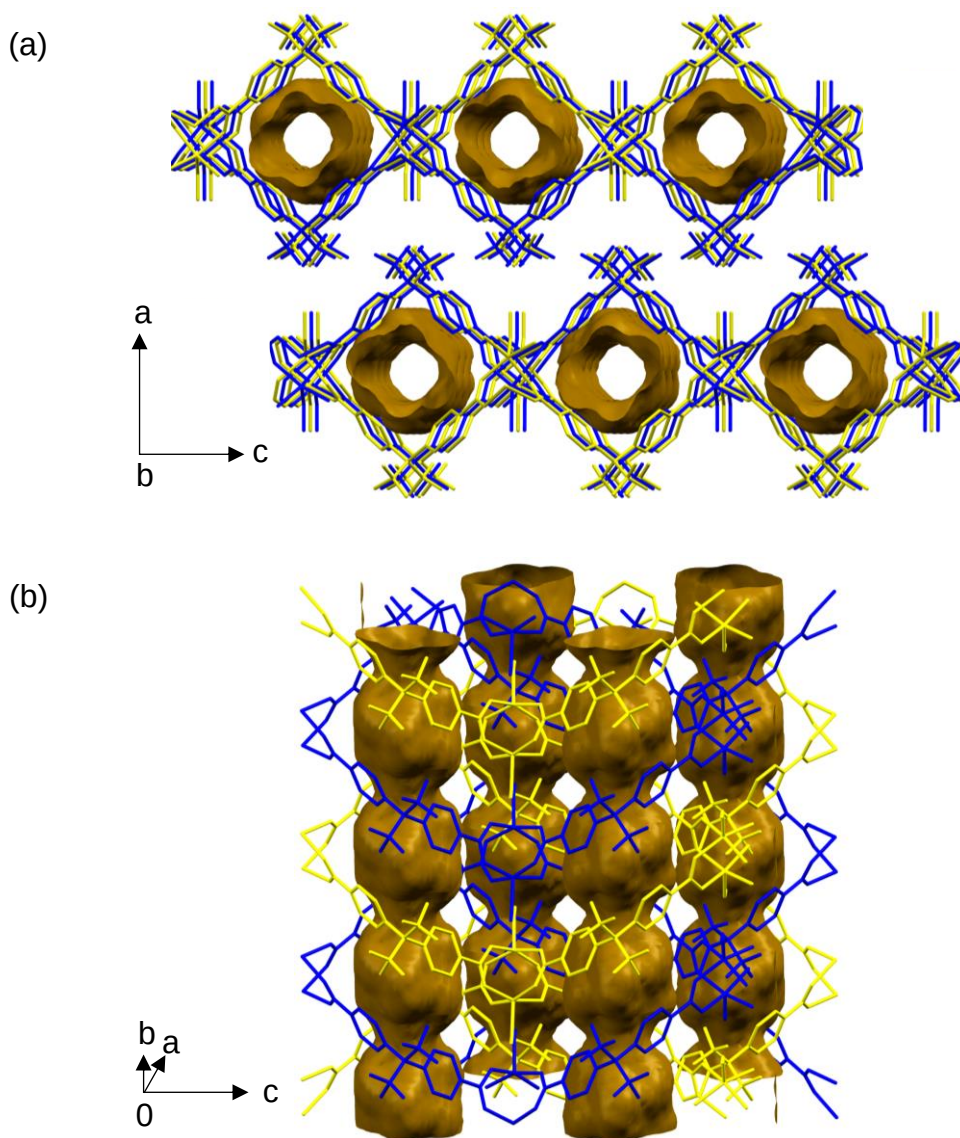


Figure 4.13. (a) Void spaces in **3**, with uncoordinated solvent molecules artificially removed, showing 1D channels along the *b*-axis. (b) Side-view of the 1D channels that form along the *b*-direction. Hydrogen atoms are omitted for clarity.

4.4. Single Crystal X-Ray Diffraction Analysis of **4**

4.4.1. Structure Description

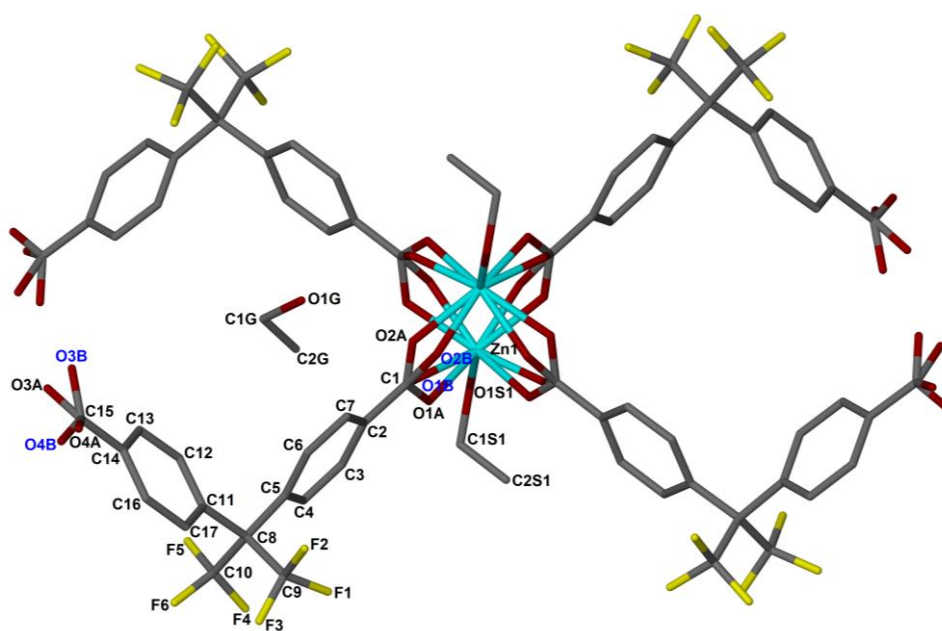
4 crystallizes in the monoclinic crystal system with space group *C2/c* (Table 4.5). The ASU comprises one Zn^{2+} ion, a fully deprotonated H_2hfipbb ligand exhibiting disorder, one coordinated EtOH molecule, and one uncoordinated EtOH molecule with half

occupancy (Figure 4.14a). The uncoordinated EtOH molecule is positioned near a 2-fold rotation axis, necessitating its half occupancy. Disorder in the hfipbb ligand is present at the carboxylate groups, where the oxygen atoms are disordered over two

Table 4.5. Crystal Data and Refinement Parameters for **4**.

ASU formula	C ₂₀ H ₁₇ F ₆ O _{5.5} Zn
Formula mass	524.71
Temperature / K	100
Crystal system	monoclinic
Space group	<i>C2/c</i>
<i>a</i> / Å	29.5482(15)
<i>b</i> / Å	6.9610(4)
<i>c</i> / Å	23.8623(12)
α / °	90
β / °	119.905(2)
γ / °	90
Volume / Å ³	4254.6(4)
<i>Z</i>	8
ρ / g cm ⁻³	1.638
μ / mm ⁻¹	1.239
<i>F</i> (000)	2120.0
Crystal size (mm ³)	0.19 × 0.18 × 0.15
2 Θ range for data collection / °	3.624 to 56.612
Index ranges	-39 ≤ <i>h</i> ≤ 39, -9 ≤ <i>k</i> ≤ 9, -31 ≤ <i>l</i> ≤ 31
Reflections collected	113366
Independent reflections	5298 [<i>R</i> _{int} = 0.0392, <i>R</i> _{sigma} = 0.0123]
Data/restraints/parameters	5298 / 24 / 345
Goodness-of-fit on <i>F</i> ²	1.066
Final <i>R</i> indexes [<i>I</i> ≥ 2σ (<i>I</i>)]	<i>R</i> ₁ = 0.0396, <i>wR</i> ₂ = 0.1148
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0418, <i>wR</i> ₂ = 0.1167
Largest diff. peak/hole / e Å ⁻³	1.58 / -0.64

(a)



(b)

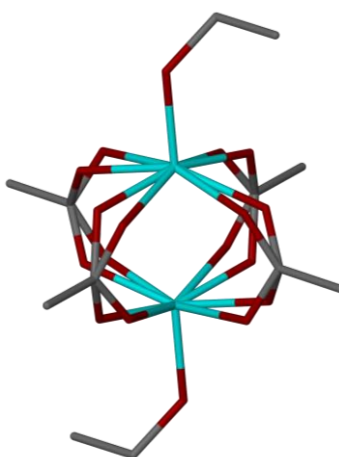


Figure 4.14. (a) Coordination environment around the Zn²⁺ ion of **4**, with only atoms of the ASU labelled. (b) Paddlewheel SBU present in **4**. Hydrogen atoms are omitted for clarity.

positions, each with half occupancy, as these positions cannot coexist simultaneously. The Zn²⁺ ions form binuclear paddlewheel SBUs, with each Zn center adopting a distorted square pyramidal geometry (Figure 4.14b). The equatorial positions are occupied by four bridging bidentate carboxylate oxygen atoms from four different

hfipbb ligands, while the axial positions are occupied by the oxygen atoms of the ligated EtOH molecules. The Zn–O bond lengths range from 1.9800(1) – 2.0778(1) Å, slightly longer than those observed in **3**, and the paddlewheel Zn···Zn separation is 2.936 Å (Table 4.6).

The hfipbb ligand in **4** adopts a bent conformation similar to that in **3**, with an angle of 70.3° between the plane of its two benzene rings, compared to 67.7° in **3**. This slight difference in the ligand's conformation may influence the void spaces within the channels that are formed. The 2+ charge on the Zn²⁺ ion is balanced by the 2- charge on the fully deprotonated H₂hfipbb ligand.

Table 4.6. Zn···Zn distances and bond lengths involving Zn²⁺ cations in **4**.

Bond	Length (Å)	Bond	Length (Å)
Zn1···Zn1	2.936	Zn1–O3B	2.0778(1)
Zn1–O1S1	1.9942(1)	Zn1–O2A	2.1102(1)
Zn1–O1A	2.0650(1)	Zn1–O2B	2.0020(1)
Zn1–O1B	1.9800(1)	Zn1–O4A	1.9922(1)
Zn1–O3A	2.0723(1)	Zn1–O4B	2.0622(1)

4.4.2. Crystal Packing

The 2-periodic framework of **4** retains the undulating arrangement parallel to the *bc* plane and the zig-zag chain appearance along the *c*-axis, similar to **3** (Figure 4.15). However, the rhombic windows in **4** are slightly larger, measuring 13.9 and 23.9 Å, compared to 13.9 and 23.1 Å in **3**. These dimensions are also, as in the case of **3**, *2b* and *c* in terms of unit cell lengths. As in **3**, the large windows in **4** enable a 2-fold

parallel interpenetration of the frameworks, forming interpenetrated 2-periodic bilayers with diamondoid-shaped channels (Figure 4.16 and 4.17). In **4**, the channels are occupied by EtOH molecules, replacing the MeOH molecules in **3** (Figure 4.18).

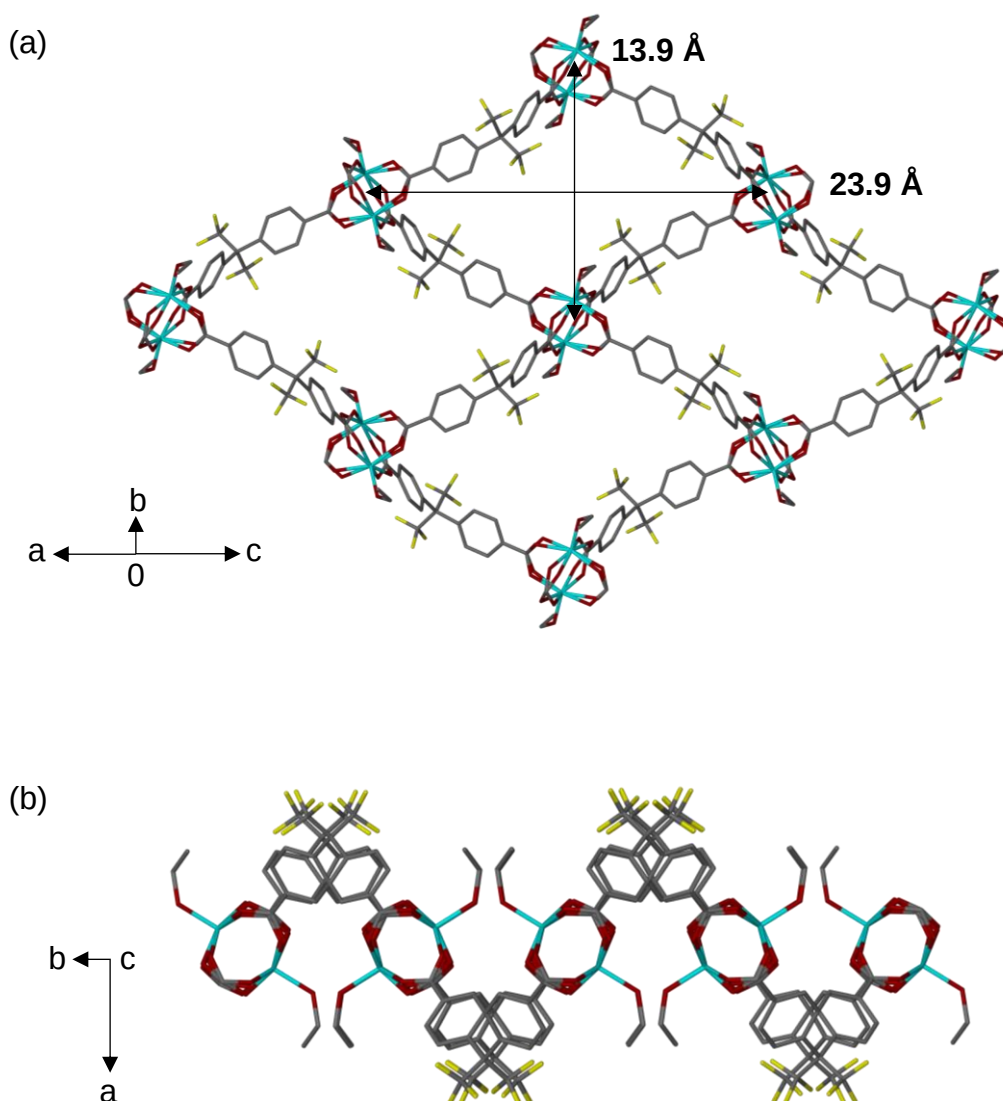


Figure 4.15. (a) The 2-periodic framework of **4** along the *bc* plane with dimensions of the rhombic windows. (b) View of the 2-periodic framework of **4** along the *c*-axis. Uncoordinated solvent molecules and hydrogen atoms are omitted for clarity.

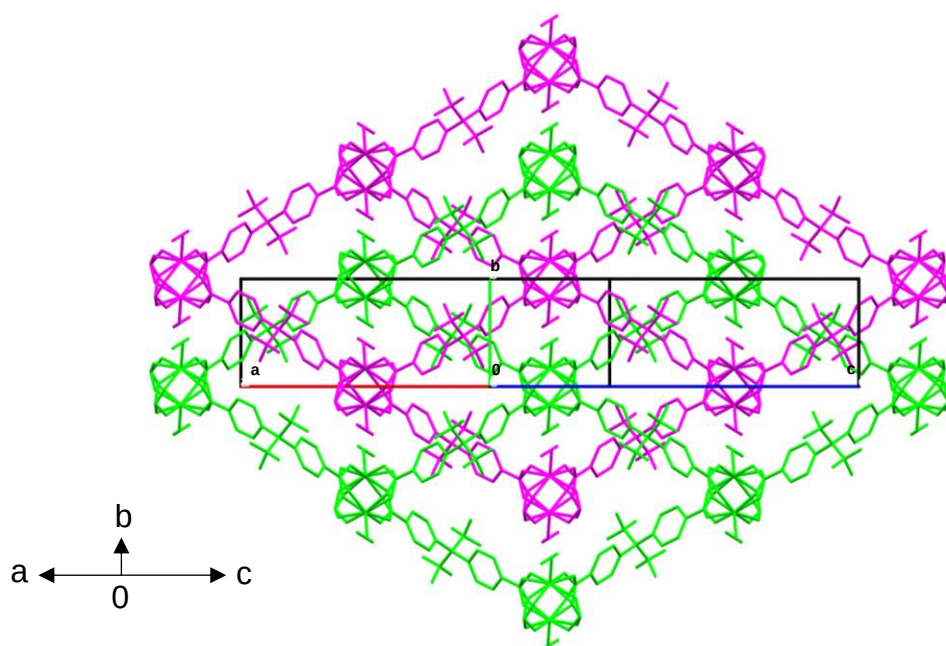


Figure 4.16. View of the 2-fold parallel interpenetration of **4** in the *bc* plane. Uncoordinated solvent molecules and hydrogen atoms are omitted for clarity.

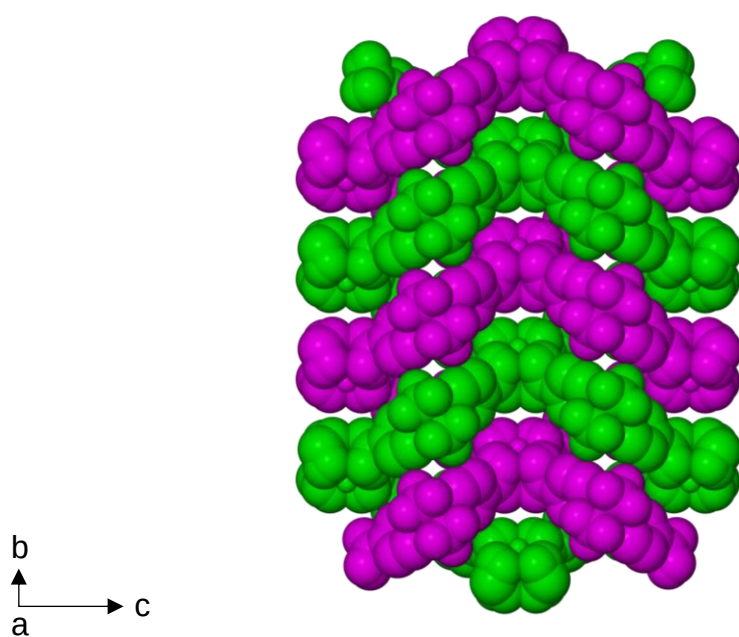


Figure 4.17. Colour-coded space-filling representation of the interwoven bilayer framework viewed along the *a*-axis in **4**. Uncoordinated solvent molecules and hydrogen atoms are omitted for clarity.

The interdigitated ABAB stacking of the bilayers along the *a*-direction exhibits a slightly reduced separation distance of 12.8 Å compared to 12.9 Å in **3**. The ligated EtOH molecules are orientated perpendicular to the channels, pointing towards the neighbouring 2-periodic frameworks, similar to the orientation of MeOH molecules in **3**.

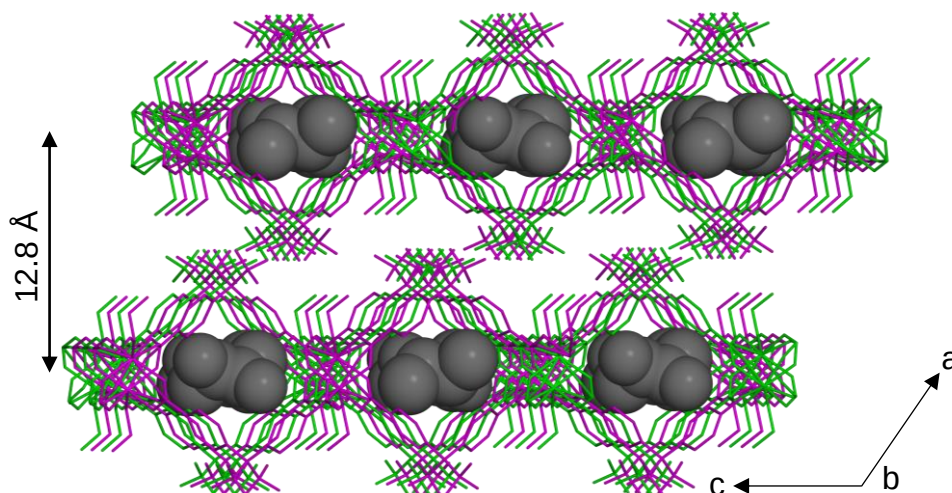


Figure 4.18. 2-periodic interpenetrated frameworks in **4**, colour-coded and stacked along the *a*-axis, with a stacking distance of 12.8 Å, indicated by a line. Uncoordinated MeOH molecules are shown in space-filling mode (grey), with hydrogen atoms omitted for clarity.

4.4.3. Hydrogen Bonding

In **4**, three types of intermolecular hydrogen bonds are present: framework...framework, solvent...framework, and solvent...solvent (Figure 4.19 and Table 4.7). The framework...framework hydrogen bonds occur between two interpenetrated frameworks, with no interactions observed between adjacent 2-periodic frameworks. These frameworks are linked by strong O–H...O bonds (O1S1–H1S1...O2B, O1S1–H1S1...O3A, and O1S1–H1S1...O3B) between the coordinated EtOH molecules and the carboxylate groups of the hfipbb ligands on a

Table 4.7. Hydrogen bond distances, angles, and symmetry operators for **4**.

Donor– H···Acceptor	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)	Symmetry operators
O1S1–H1S1···O2B	0.85(2)	2.45(3)	2.841(4)	109(3)	x, 1+y, z
O1S1–H1S1···O3A	0.85(2)	1.86(2)	2.699(4)	167(3)	x, 2-y, -1/2+z
O1S1–H1S1···O3B	0.85(2)	2.47(2)	3.308(5)	167(2)	x, 2-y, -1/2+z
O1G–H1G···O2A	0.84	2.10	2.894(13)	158	x, y, z
O1G–H1G···O4A	0.84	2.59	3.006(19)	112	1-x, 1+y, 3/2-z
C4–H4···F2	0.95	2.49	3.119(3)	124	x, 1+y, z
C1G–H1GB···O1G	0.99	1.80	2.74(2)	157	1-x, y, 3/2-z
C2G–H2GA···O1B	0.98	2.49	3.021(8)	114	x, y, z
C2G–H2GA···O3B	0.98	2.01	2.979(9)	169	1-x, 1+y, 3/2-z
C12–H12···O1G	0.95	2.50	3.267(16)	138	1-x, y, 3/2-z

4.5. Desolvation Studies

Attempts were unsuccessful to obtain the single-crystal structure of the desolvated form of **4** through crystal heating. Similarly, the water-exchange method, which was successful for **3**, failed for **4**. Although crystals of **4** remained stable in water, no ligand exchange occurred even after several days. Consequently, no water-exchanged structure could be obtained to provide structural insights into its behaviour during gas sorption studies.

4.5.1. Thermal Analysis

4.5.1.1. Thermogravimetric and Differential Scanning Calorimetry Analysis

The thermal behaviour of **4** was analysed using TGA and DSC. TGA conducted on crystalline samples over a temperature range of 32 – 543 °C revealed a single mass loss of 13.3% (calculated 13.2%) between 50 and 200 °C, corresponding to the removal of coordinated and uncoordinated EtOH molecules (Figure 4.20). This mass loss is confirmed by the derivative mass curve, which shows a single peak.

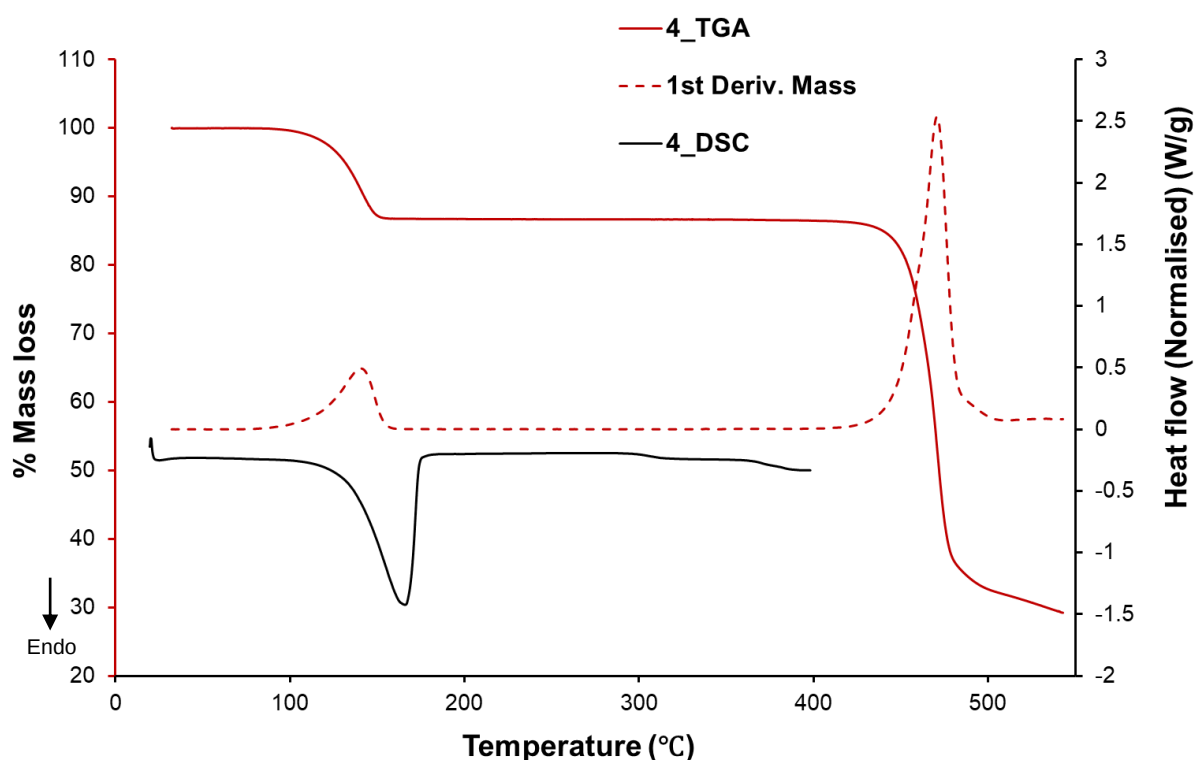


Figure 4.20. Overlay of the TGA thermogram, its first derivative mass, and the DSC thermogram of **4**.

The DSC thermogram shows a distinct endothermic peak with an onset temperature of 134 °C and a peak temperature of 166 °C, both higher than those observed for **3**.

This indicates stronger EtOH-framework interactions compared to the MeOH-framework interactions in **3**, consistent with the greater number of hydrogen bonds observed in **4**. As a result, disrupting the interactions in **4** requires more energy than in **3**. The framework of **4** remains stable until around 430 °C, after which decomposition occurs. The similar thermal stability of the desolvated phases of **3** and **4** suggests that the structural integrity of the frameworks is not significantly influenced by the type of solvent molecule present before desolvation.

4.5.1.2. Hot Stage Microscopy

Crystals of **4** were placed on a microscope slide and covered in silicone oil to observe thermal events from 23 to 500 °C (Figure 4.21). The first signs of desolvation appeared at 137 °C, with surface cracks observed on the crystal (indicated by arrows in the 137 °C image). The crystals turned opaque at 161 °C, suggesting the loss of monocrystallinity due to solvent release. As the temperature increased, the crystals became increasingly opaque, indicating further solvent release. Unlike the behaviour of MeOH in crystals of **3**, no rapid bubbling occurred during the release of EtOH in **4**, likely because the release did not generate enough pressure to form gas bubbles in the silicone oil. Browning began at 400 °C, and complete decomposition occurred at 500 °C. The desolvation observed between 137 and 161 °C corresponds to the release of both coordinated and uncoordinated EtOH molecules, as confirmed by TGA. Compared to **3**, the crystals of **4** displayed greater physical stability during desolvation, retaining their integrity without disintegration until decomposition.

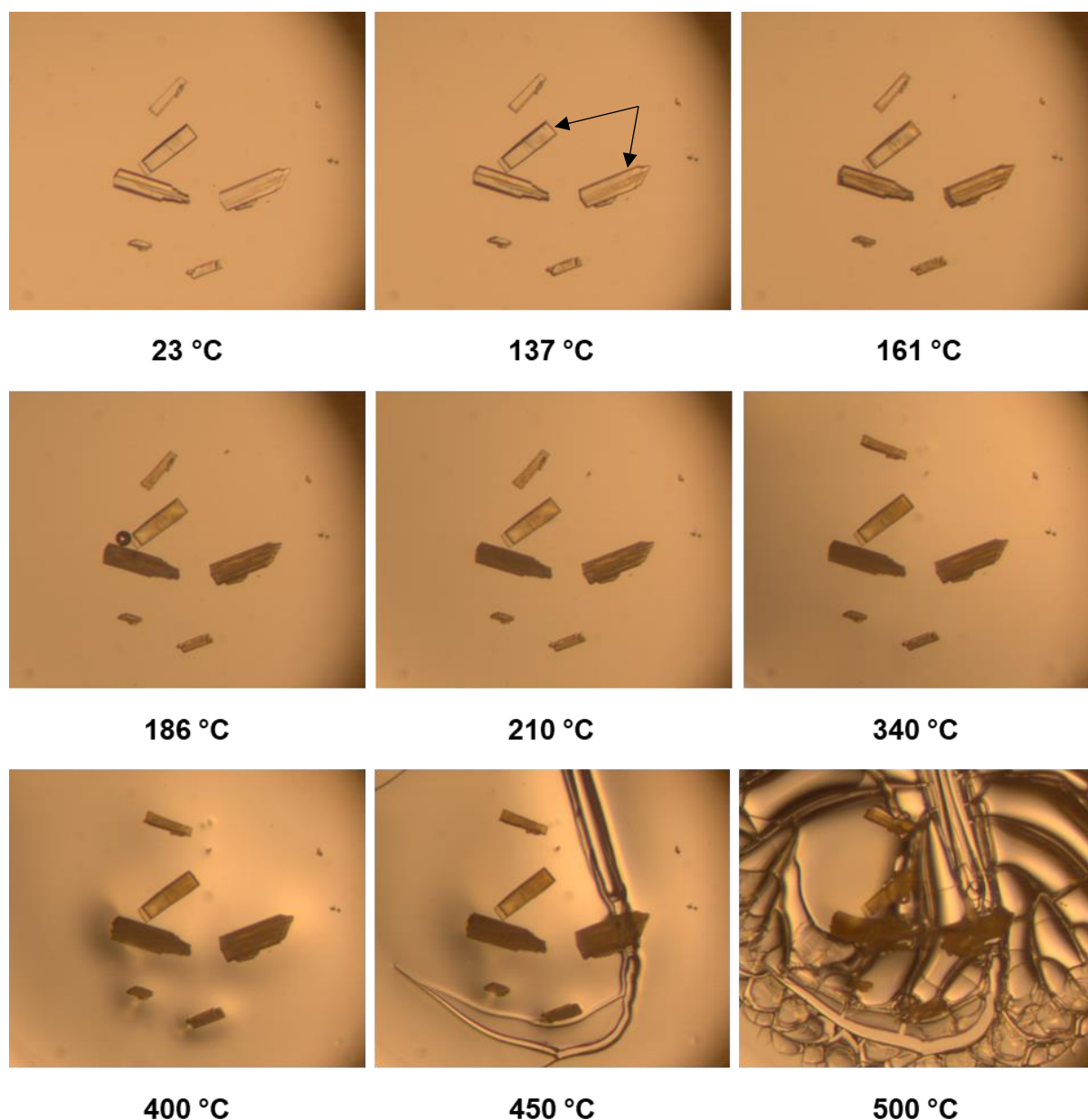


Figure 4.21. HSM images of **4** from 23 – 500 °C.

4.5.2. Variable-Temperature Powder X-Ray Diffraction Studies

The VT-PXRD pattern of **4** closely matches the calculated pattern at 25 °C and ambient pressure (~1 atm) (Figure 4.22). The close match confirms the phase purity of **4** and verifies that the single crystal accurately represents the bulk sample. Similar to the case of **3**, the peak at $6.7^\circ 2\theta$ (marked by a red star) in the calculated pattern is obscured in the experimental VT-PXRD patterns by a broad background peak in the

6-8° 2 θ range. This artefact makes it difficult to accurately assess the behaviour of this peak.

At 100 °C, a new shoulder peak at 8.4° 2 θ (indicated by a black arrow) emerges, marking the onset of a phase transition associated with solvent loss. At 150 °C, the overall peak intensity decreases, while peaks at 8.4 and 13.4° 2 θ (marked by black stars) increase, reflecting further structural changes linked to continued solvent loss. At 200 °C, peaks at 8.6, 16.3, 19.1, 19.5, and 20.1° 2 θ (indicated by blue arrows) disappear, indicating continued desolvation. By 250 °C, a peak at 12.1 ° 2 θ (indicated by green arrow) also disappears, and the structure reaches its final phase, with no further changes observed up to 300 °C. The pattern remains consistent upon cooling back to 25 °C, indicating the stability of the final desolvated phase.

Interestingly, the desolvated phase of **4** shows a PXRD pattern similar to that of desolvated **3** (Figure 4.23), despite differences in their calculated PXRD patterns arising from the presence of different crystal packing arrangement. This similarity suggests that both structures rearrange to the same or similar structure upon desolvation. However, **3** qualitatively exhibits a higher peak-to-background ratio than **4**, likely indicating a higher degree of crystallinity in **3** compared to **4**.

In **4**, as in **3**, the removal of the ligated solvent appears to cause the 2-periodic layers to move closer together, as evidenced by the disappearance of the prominent 12.1° 2 θ peak at 250 °C in the VT-PXRD pattern. This peak corresponds to the 40 $\bar{2}$ set of planes, where the trifluoromethyl groups of the 2-periodic frameworks are located in the as-synthesised structure (Figure 4.24).

The disappearance of the 40 $\bar{2}$ planes in the desolvated phase suggest that neighbouring 2-periodic layers shift orthogonally to this plane as they draw closer

together. Such a shift would reposition the trifluoromethyl groups of one layer to approximately halfway between the original $40\bar{2}$ planes, resulting in destructive X-ray interference and the disappearance of the 12.1° 2θ peak.

Similar to **3**, exposure of the desolvated sample to air for 24 hours caused no changes in the PXRD pattern. Additionally, the TGA thermogram of the desolvated sample exposed to air shows no mass loss until decomposition (Figure 4.25). These results indicate that the unsaturated metal sites in **4**, like those in **3**, do not adsorb atmospheric water vapour.

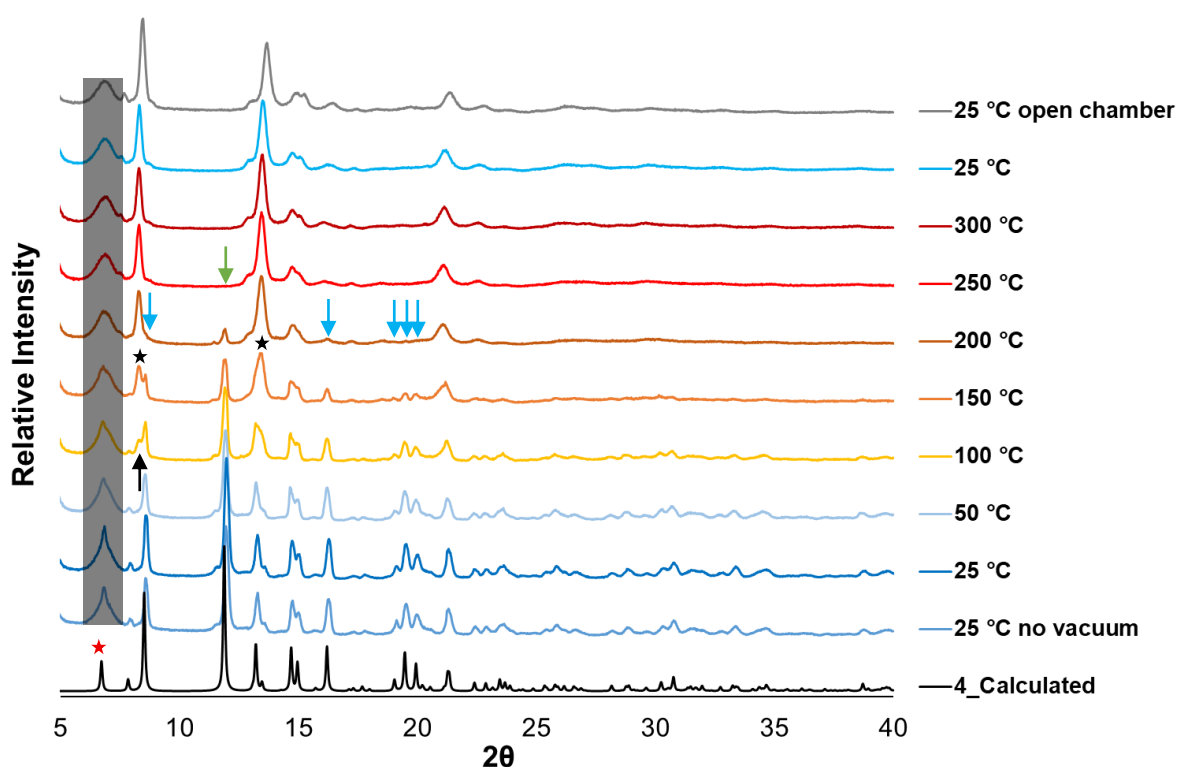


Figure 4.22. Calculated and VT-PXRD patterns of **4** from 25 to 300 °C under vacuum, followed by cooling back to 25 °C, and finally after exposure to air at 25 °C.

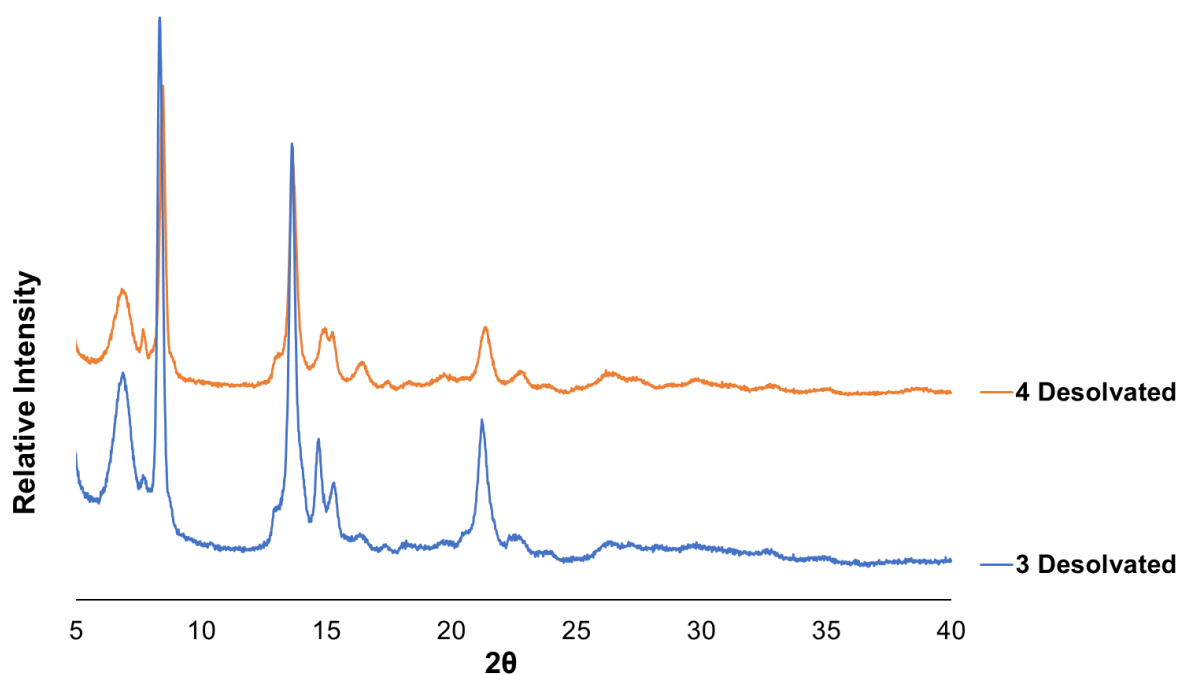


Figure 4.23. PXRD patterns of the desolvated structure of **3** and **4**.

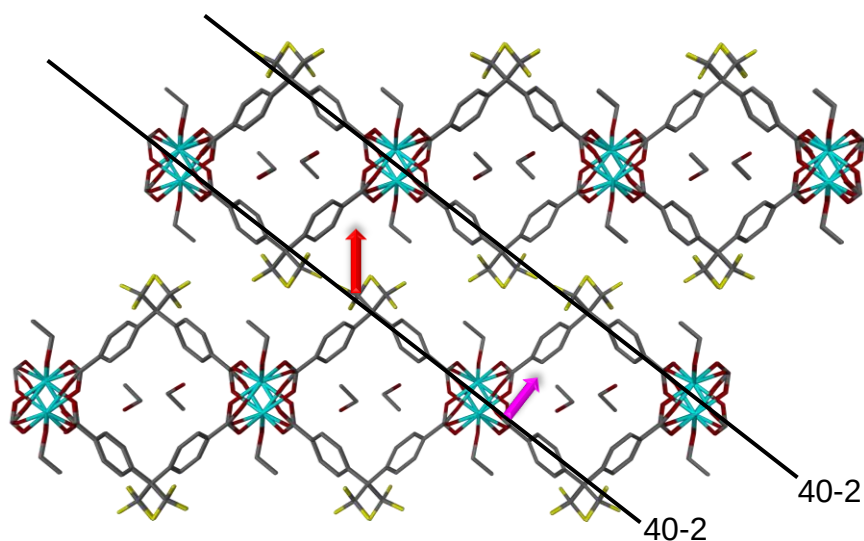


Figure 4.24. $(40\bar{2})$ planes of **4** viewed along the b -axis. The pink arrow represents the direction orthogonal to the $(40\bar{2})$ planes, while the red arrow indicates the potential vertical movement of a neighbouring 2-periodic layer. This movement contributes to the reduction in the intensity of the 12.1° 2θ peak observed in the higher temperature VT-PXRD patterns. Hydrogen atoms are omitted for clarity.

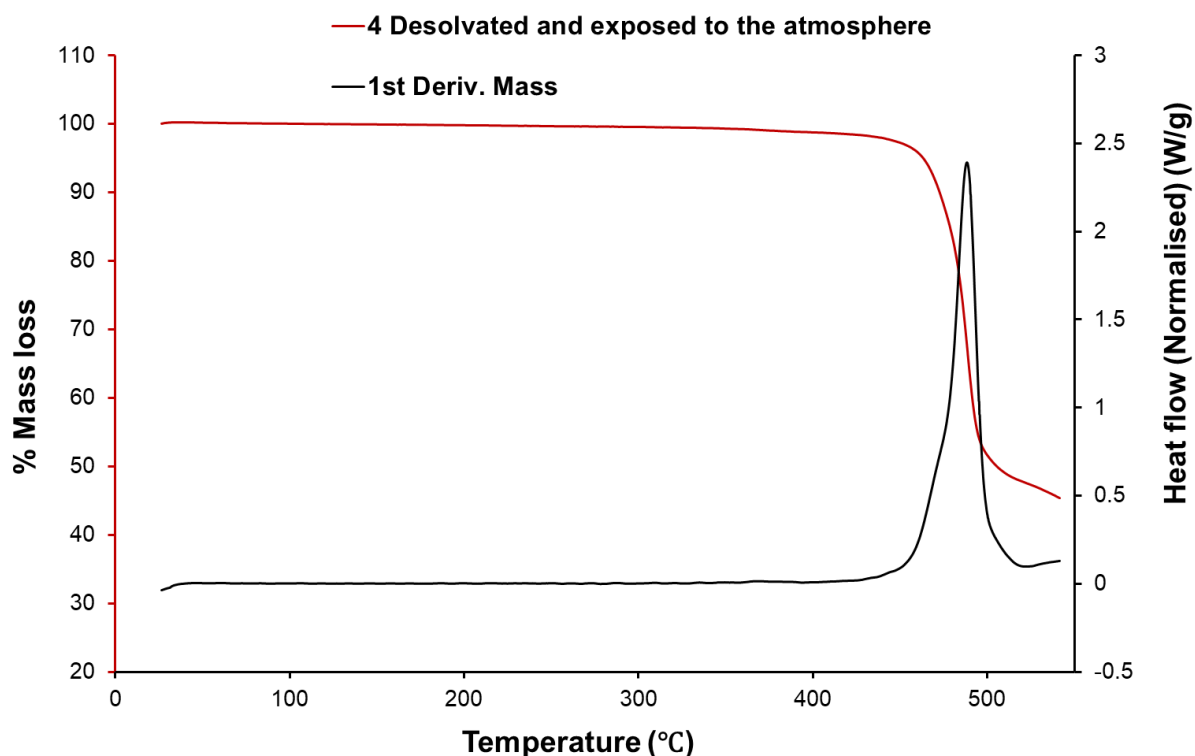


Figure 4.25. TGA thermogram of **4** after desolvation and 24-hour exposure to the atmosphere, along with its first derivative mass curve.

4.5.3. Void Space Analysis

The void space characteristics of **4** were analysed following the artificial removal of uncoordinated solvent molecules. As indicated by the VT-PXRD patterns, the 2-periodic layers shift during the removal of ligated solvent molecules. Consequently, the potential void space of the structure is determined by the channels that initially contain the uncoordinated solvent molecules.

Analysis using MERCURY revealed the presence of 1D continuous channels running along the *b*-axis, similar to those observed in **3** (Figure 4.26). These channels account for 12.0% of the unit cell volume, corresponding to the potential void space of 511.1 Å³. Interestingly, this void space is slightly smaller than that of **3**, despite being occupied by EtOH molecules, which are larger than the MeOH molecules present in **3**.

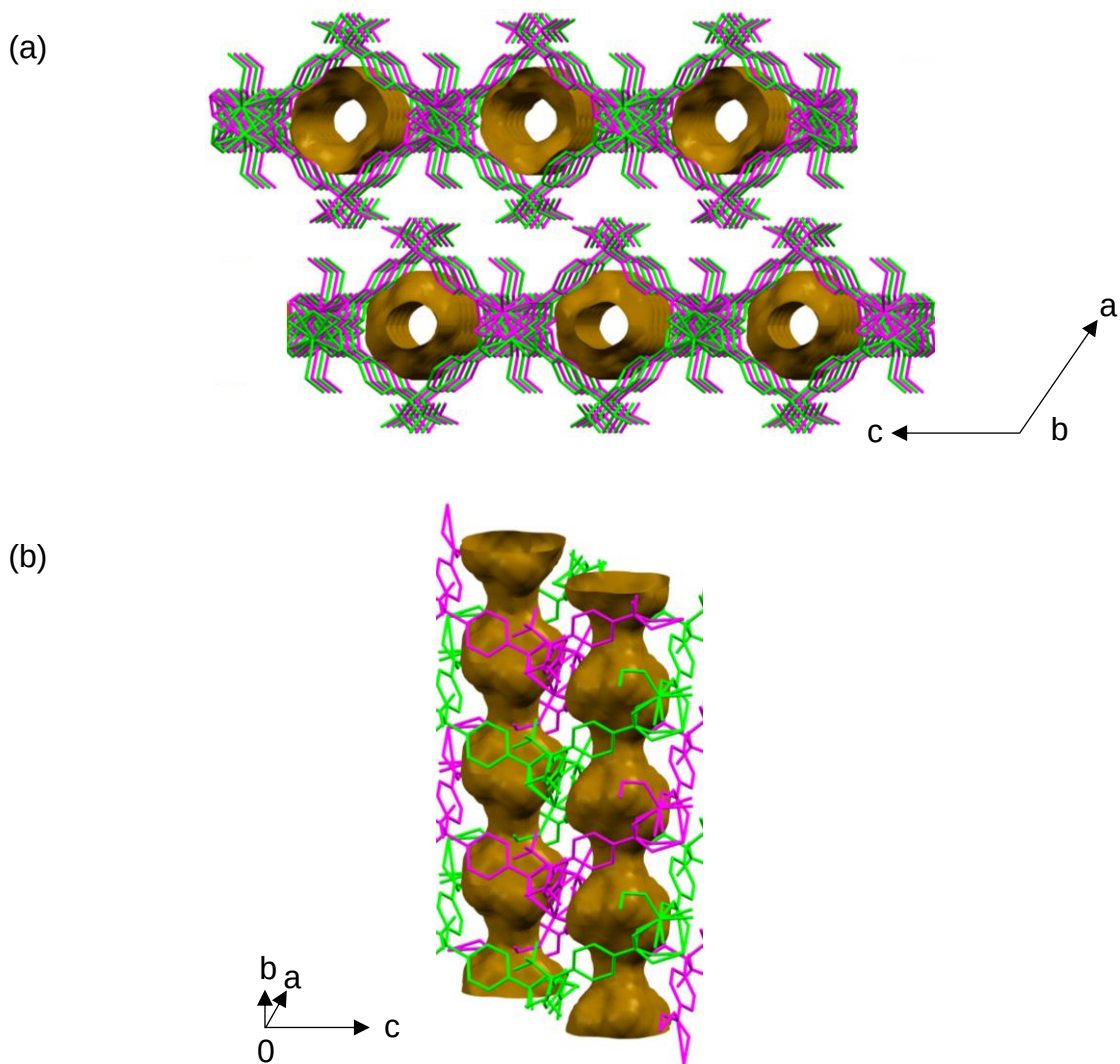


Figure 4.26. (a) Void spaces in **4**, with uncoordinated solvent molecules artificially removed, showing 1D channels along the *b*-axis. (b) Side-view of the 1D channels that form along the *b*-direction. Hydrogen atoms are omitted for clarity.

4.6. Single Crystal X-Ray Diffraction Analysis of **5**

4.6.1. Structure Description

Single crystal X-ray diffraction analysis reveals that **5** crystallizes in the monoclinic crystal system with space group $P2_1/c$ (Table 4.8). While **3** and **4** each contain a single crystallographically distinct Zn^{2+} ion, the ASU of **5** contains two distinct Zn^{2+} ions, two

Table 4.8. Crystal Data and Refinement Parameters for **5**.

ASU formula	C ₅₂ H ₅₈ F ₁₂ N ₆ O ₁₄ Zn ₂
Formula mass	1349.78
Temperature / K	100
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> / Å	25.976(2)
<i>b</i> / Å	10.5720(9)
<i>c</i> / Å	24.749(2)
α / °	90
β / °	116.683(3)
γ / °	90
Volume / Å ³	6072.8(10)
<i>Z</i>	4
ρ / g cm ⁻³	1.476
μ / mm ⁻¹	0.892
<i>F</i> (000)	2768.0
Crystal size (mm ³)	0.249 × 0.061 × 0.056
2 θ range for data collection / °	4.234 to 52.744
Index ranges	-31 ≤ <i>h</i> ≤ 32, -12 ≤ <i>k</i> ≤ 13, -30 ≤ <i>l</i> ≤ 30
Reflections collected	62531
Independent reflections	12395 [<i>R</i> _{int} = 0.0731, <i>R</i> _{sigma} = 0.0618]
Data/restraints/parameters	12395 / 132 / 769
Goodness-of-fit on <i>F</i> ²	1.198
Final <i>R</i> indexes [<i>I</i> ≥ 2σ (<i>I</i>)]	<i>R</i> ₁ = 0.1119, <i>wR</i> ₂ = 0.2188
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1356, <i>wR</i> ₂ = 0.2286
Largest diff. peak/hole / e Å ⁻³	1.33 / -1.70

fully deprotonated H₂hfipbb ligands, two coordinated DMF molecules, and four uncoordinated DMF molecules (Figure 4.27a).

Each Zn²⁺ ion in **5** forms a binuclear paddlewheel SBU, similar to those in **3** and **4**, with Zn centers adopting a distorted square pyramidal geometry (Figure 4.27b). The

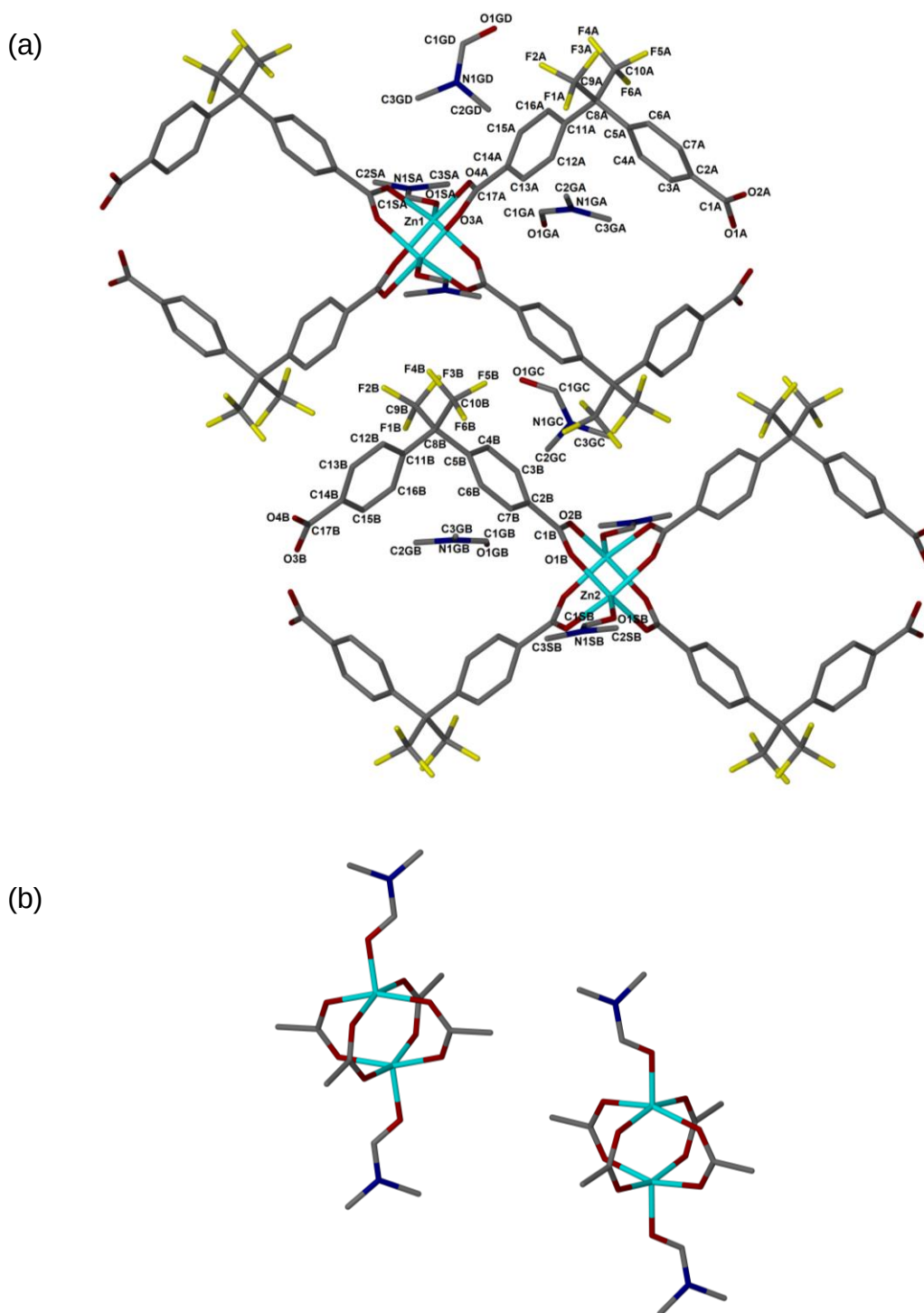


Figure 4.27. (a) Coordination environment around the Zn^{2+} ions of **5**, with only atoms of the ASU labelled. (b) Paddlewheel SBUs present in **5**. Hydrogen atoms are omitted for clarity.

equatorial positions are coordinated by four bridging bidentate carboxylate oxygen atoms from four distinct hfipbb ligands, while the axial positions are occupied by the oxygen atoms of the ligated DMF molecules. The Zn–O bond lengths (1.9772(2) to 2.0663(2) Å) are comparable to those in **3** and **4**, while the paddlewheel Zn⋯Zn separations, measure at 2.930 and 2.921 Å for the two paddlewheels, are slightly larger than in **3** but similar to those in **4** (Table 4.9). The hfipbb ligands in **5** exhibit bent conformations with angles of 68.6° and 70.7° between their two benzene rings. These angles fall between those observed in **3** (67.7°) and **4** (70.3°), highlighting the subtle changes in the ligand conformations.

The 4+ charge on the two Zn²⁺ ions is balanced by the 4- charge of the two fully deprotonated H₂hfipbb ligands.

Table 4.9. Paddlewheel Zn⋯Zn distance and bond lengths involving Zn²⁺ cations in **5**.

Bond	Length (Å)	Bond	Length (Å)
Zn1⋯Zn1	2.930	Zn1–O2A	2.0308(2)
Zn2⋯Zn2	2.921	Zn2–O1B	2.0511(2)
Zn1–O1SA	1.9793(2)	Zn2–O1SB	1.9772(2)
Zn1–O4A	2.0322(2)	Zn2–O4B	2.0437(2)
Zn1–O1A	2.0362(2)	Zn2–O2B	2.0098(2)
Zn1–O3A	2.0663(2)	Zn2–O3B	2.0281(2)

4.6.2. Crystal Packing

5 retains the undulating, 2-periodic framework motif seen in **3** and **4**, characterised by large, rhombus-like windows (Figure 4.28a). The rhombic windows in **5**, measuring

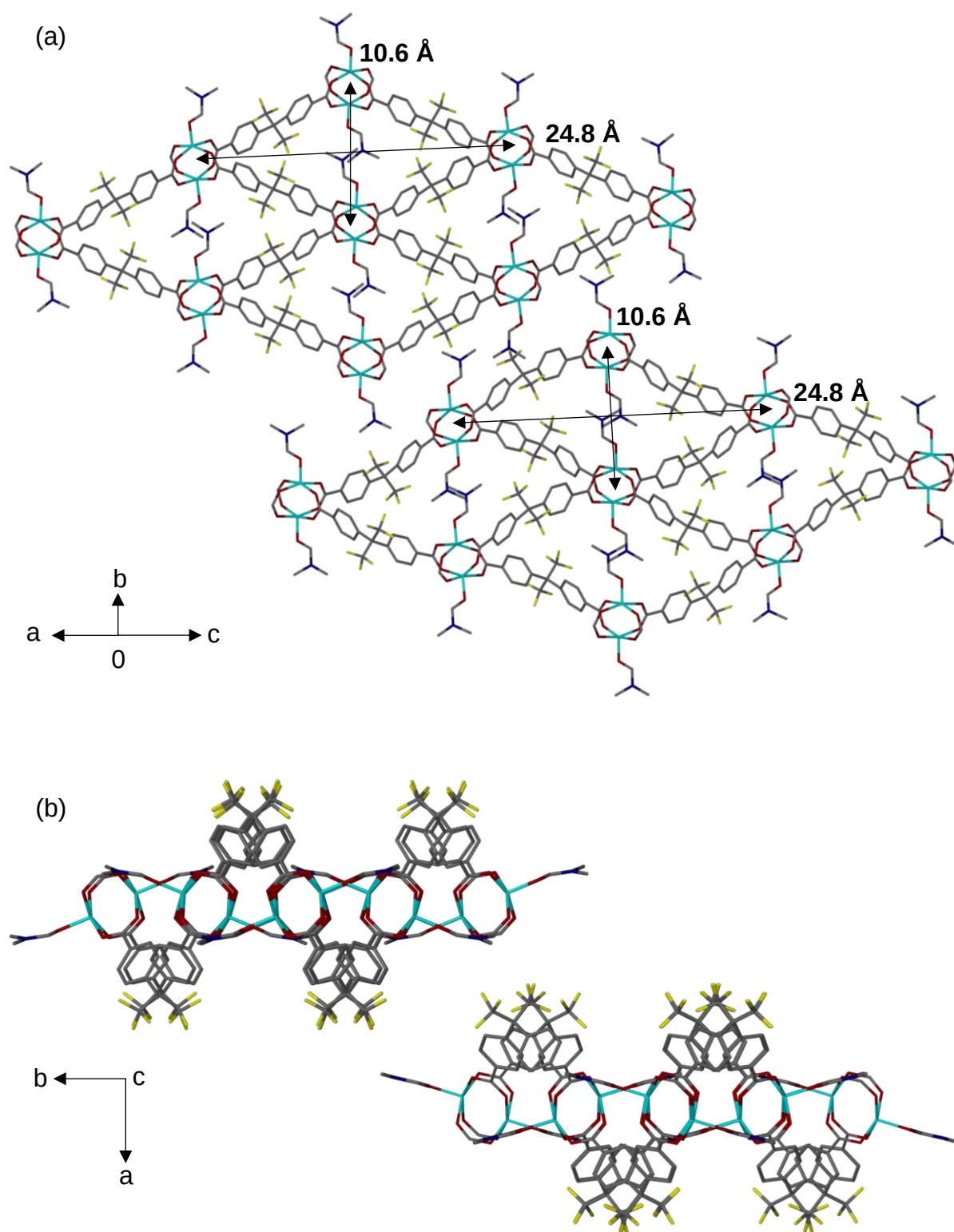


Figure 4.28. (a) Two unique 2-periodic frameworks of **5** in the *bc* plane with dimensions of the rhombic windows. (b) View of the 2-periodic frameworks of **5** along the *c*-axis. Uncoordinated solvent molecules and hydrogen atoms are omitted for clarity.

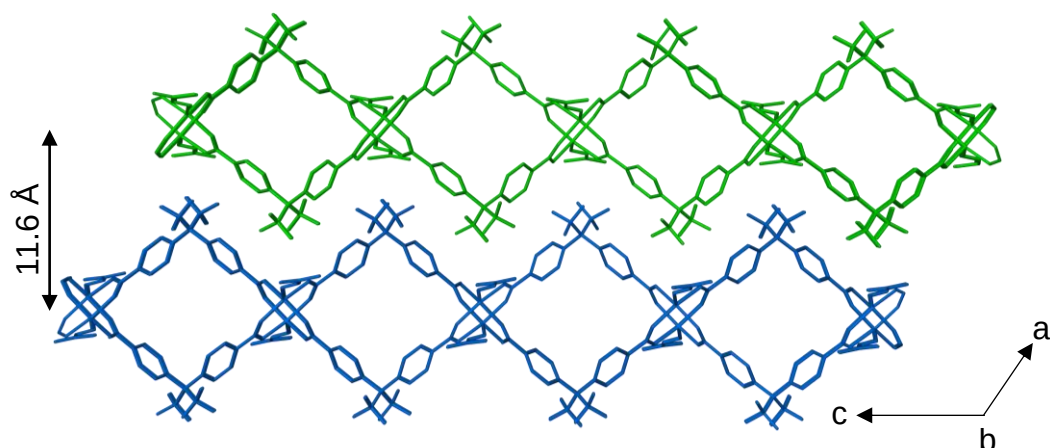


Figure 4.29. Colour-coded, non-interpenetrated 2-periodic frameworks in **5**, stacked along the *a*-axis with a stacking distance of 11.6 Å, indicated by a line. Uncoordinated solvent molecules and hydrogen atoms are omitted for clarity.

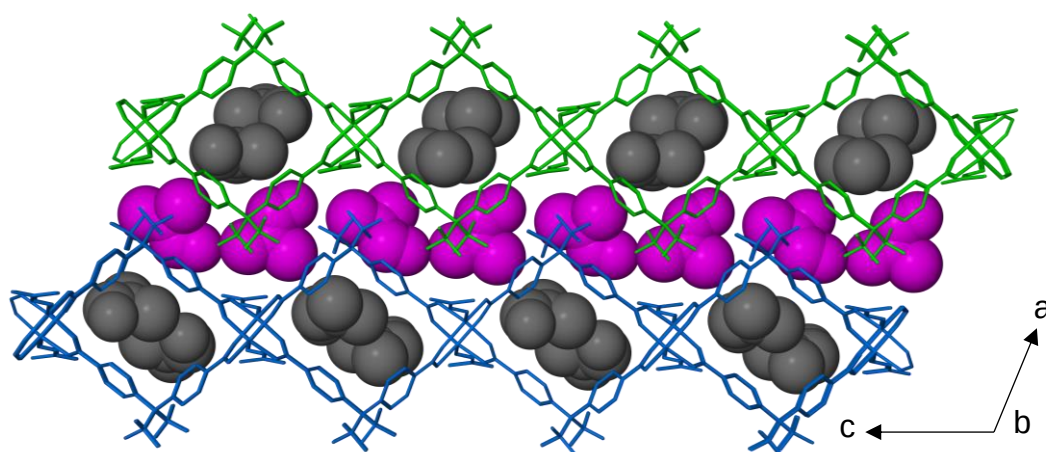


Figure 4.30. View of the non-interpenetrated 2-periodic frameworks in **5** along the *b*-axis, showing uncoordinated DMF molecules (grey) in the channels and DMF molecules (pink) between neighbouring frameworks in space-filling mode. Hydrogen atoms are omitted for clarity.

10.8 and 24.8 Å, respectively, are narrower along the one diagonal compared to those in **3** (13.9 and 23.1 Å) and **4** (13.9 and 23.9 Å). When viewed along the *c*-axis, the zig-zag chain appearance is similar to that of **3** and **4** (Figure 4.28b). However, unlike the interpenetrated bilayer structures in **3** and **4**, **5** features two neighbouring,

crystallographically distinct, non-interpenetrated 2-periodic frameworks. These frameworks stack in an interdigitated ABAB sequence along the *a*-direction, with a separation distance of 11.6 Å, significantly shorter than the 12.9 Å in **3** and 12.8 Å in **4** (Figure 4.29).

The diamondoid-shaped channels in **5** are occupied by DMF molecules, as MeOH and EtOH molecules occupy the channels in **3** and **4**, respectively (Figure 4.30). Additionally, **5** contains uncoordinated DMF molecules between the adjacent frameworks, a feature absent in **3** and **4**. Moreover, the ligated DMF molecules in **5** are orientated perpendicular to the stacking direction of the neighbouring 2-periodic frameworks. This orientation contrasts with the ligated solvent orientations in **3** and **4**, where MeOH and EtOH molecules, respectively, point towards neighbouring frameworks along the stacking direction. The perpendicular orientation of the DMF molecules in **5** reduces steric hindrance between adjacent frameworks, enabling closer stacking and contributing to the smaller inter-framework separation distance observed in **5** compared to **3** and **4**.

4.6.3. Hydrogen Bonding

In **5**, the hydrogen bonds interaction includes framework...framework and solvent...framework hydrogen bonds (Figure 4.31 and Table 4.10). Unlike in **3** and **4**, these framework...framework hydrogen bonds interaction occurs between neighbouring 2-periodic frameworks. The frameworks are linked by three weaker C-H...F interactions (C2SA-H2SB...F3B, C2GC-H2GA...F3A, and C3SB-H3SF...F2A) between the coordinated DMF molecules and the fluorine atoms of the hfipbb ligand. Among the two unique uncoordinated DMF molecules in the channel, only one forms weaker C-H...O interactions with one of the unique

frameworks (C12A-H12A...O1GA). Additionally, one of the unique uncoordinated DMF molecules between neighbouring frameworks interacts with one of the frameworks via weaker C-H...F bonds (C2GC-H2GA...F3A). The hydrogen bonds in **5** are fewer than in **4**, indicating weaker interactions between the solvent molecules and the framework in **5** compared to **4**.

Intramolecular interactions are also present in this structure and are detailed in the .lis file, given as part of the supplementary information.

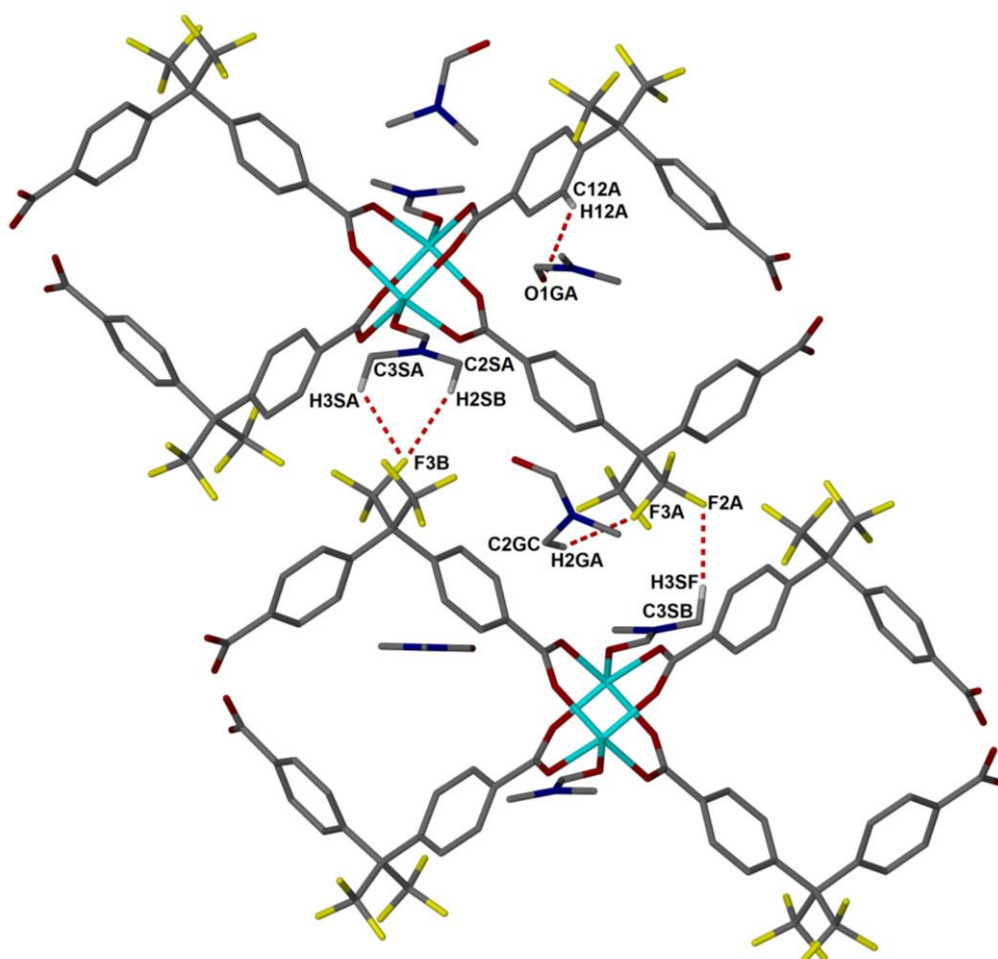


Figure 4.31. Hydrogen bonding in **5**, showing interactions between the neighbouring 2-periodic frameworks and solvent molecules.

Table 4.10. Hydrogen bond distances, angles, and symmetry operators for **5**.

Donor–H···Acceptor	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)	Symmetry operators
C3SA–H3SA···F3B	0.98	2.46	3.1517(3)	127	-x, 1-y, 1-z
C2SA–H2SB···F3B	0.98	2.43	3.189(18)	134	-x, 1-y, 1-z
C2GC–H2GA···F3A	0.98	2.49	3.321(13)	142	-x, 3/2+y, 1/2-z
C12A–H12A···O1GA	0.95	2.59	3.296(15)	132	x, -1+y, z
C3SB–H3SF···F2A	0.98	2.38	3.35(2)	170	-1+x, -1/2-y, -1/2+z

4.7. Desolvation Studies

Efforts to determine the single crystal structure of the desolvated form of **5** through heating proved unsuccessful. In contrast to **3**, where the water-exchange process was effective, this method was not feasible for **5** due to the crystals' instability in water. Consequently, no solvent exchange was achieved, and a water-exchanged structure could not be obtained to shed light on its behaviour during gas sorption experiments.

4.7.1. Thermal Analysis

4.7.1.1. Thermogravimetric and Differential Scanning Calorimetry Analysis

The thermal stability of **5** was examined using TGA and DSC. TGA analysis was performed on crystalline samples over a temperature range of 25 to 542 °C (Figure 4.32). A mass loss of 32.6% (calculated 32.5%) was observed between 50 and 300 °C, corresponding to the removal of both coordinated and uncoordinated DMF

molecules. This mass loss is further supported by the derivative mass curve, which shows a single peak.

The DSC thermogram exhibits an endothermic peak with an onset temperature of 126 °C and a peak temperature of 132 °C. The onset temperature is lower than that of **4**, indicating weaker DMF interactions compared to EtOH in **4**. This trend is consistent with the fewer hydrogen bonds observed in **5** compared to **4**, suggesting that disrupting the interactions in **5** requires less energy than in **4**. The framework of **5** remains stable up to around 430 °C, at which point decomposition begins. This thermal stability is comparable to that of **3** and **4**, further indicating that the structural integrity of the frameworks is not significantly affected by the type of solvent molecule present prior to desolvation.

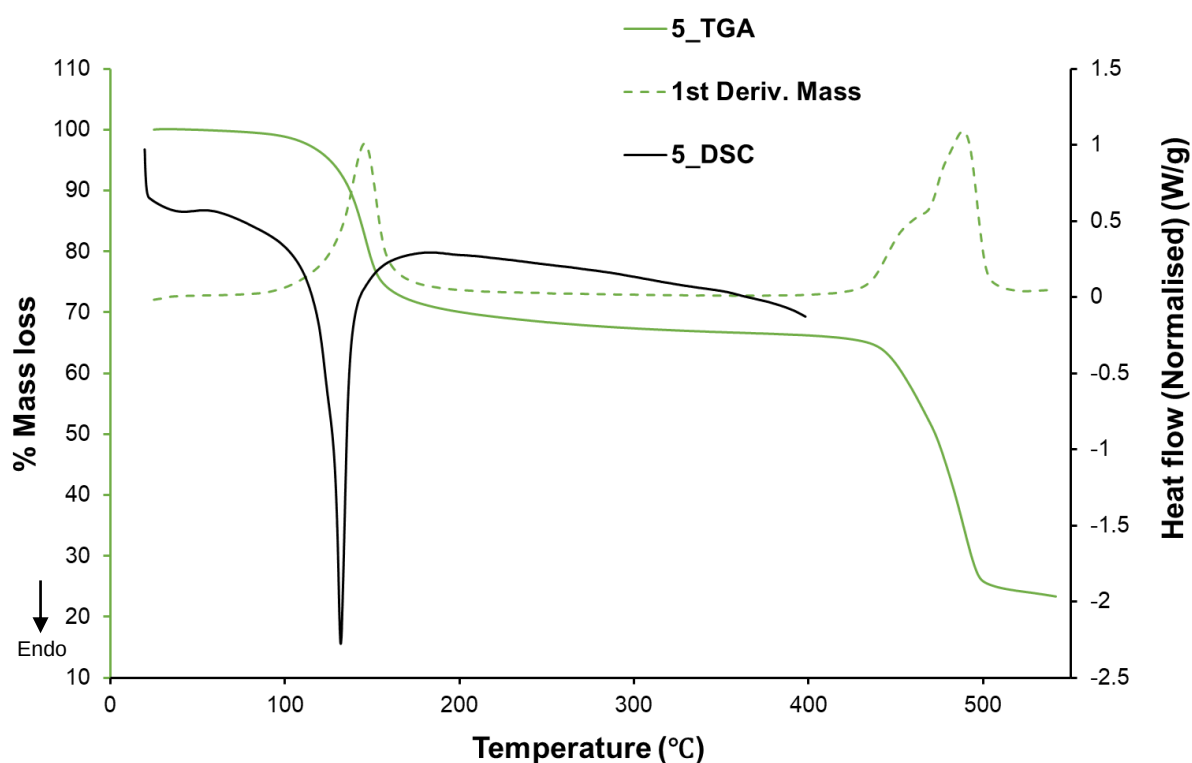


Figure 4.32. Overlay of the TGA thermogram, its first derivative mass, and the DSC thermogram of **5**.

4.7.1.2. Hot Stage Microscopy

A crystal of **5** was placed on a microscope slide and covered with silicone oil to observe thermal events between 24 and 500 °C (Figure 4.33). Between 24 and 274 °C, minimal physical changes were observed, except for minor cracks on the surface of the crystal; however, the crystal remained intact throughout this range. These observations suggest that solvent release occurred with the retention of monocrystallinity. Unlike **3** and **4**, the crystal of **5** did not turn opaque, further indicating the retention of monocrystallinity. At 387 °C, the crystal began turning brown, signalling the onset of

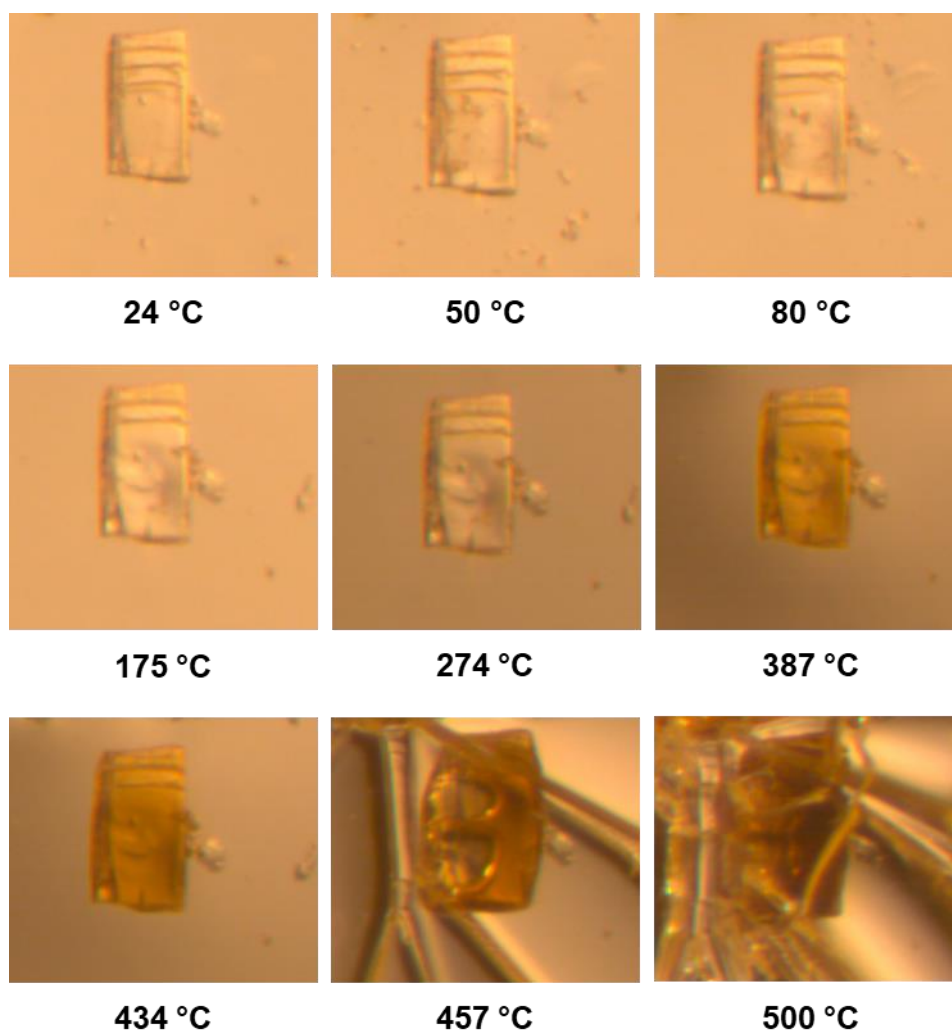


Figure 4.33. HSM images of **5** from 24 – 500 °C.

decomposition, and by 500 °C, the crystal had fully decomposed. The HSM observations suggest that **5** possesses the most robust crystal morphology during thermal treatment. The solvent release occurred with minimal physical disruption, and the crystal remained intact and transparent, indicating superior stability compared to both **3** and **4**.

4.7.2. Variable-Temperature Powder X-Ray Diffraction Studies

The VT-PXRD pattern of **5** at 25 °C under ambient pressure (~1 atm) matches the calculated pattern (Figure 4.34). This close agreement confirms the phase purity of the synthesised sample and establishes that the single crystal is representative of the bulk material.

Upon exposure to vacuum at 25 °C, structural changes are evident in the VT-PXRD patterns. Peaks in the 12.8 – 14.3° and 17.8 – 23.1° 2 θ ranges (circled in black in the ‘no vacuum’ PXRD pattern) disappear, while new broad peaks emerge at 13.7 and 21.3° 2 θ (indicated by black arrows). These changes are attributed to solvent loss. At 50 °C, prominent peaks at 9.3 and 10.8° 2 θ (indicated by red arrows) disappear, marking the transition of **5** to its final desolvated phase.

Notably, the desolvation-induced structural changes in **5** occur at lower temperatures than those observed in **3** and **4**. This difference arises from the nature of the solvent molecules in these MOFs. In **3** and **4**, only ligated solvent molecules are present between the layers, and the layers do not shift until these strongly bound molecules are removed at higher temperatures. In contrast, the structure of **5** contains uncoordinated DMF molecules between the layers. The weaker interactions of the uncoordinated DMF molecules with the framework facilitate their loss and the

subsequent layer shifts at much lower temperatures under vacuum. The structure remains relatively crystalline up to 300 °C and retains this crystallinity upon cooling back to 25 °C.

Unlike in **3** and **4**, the removal of DMF solvent molecules between neighbouring 2-periodic layers causes the layers to move closer together because these are uncoordinated. This structural change is evidenced by the disappearance of the prominent 9.2 and 10.8° 2 θ peaks at 50 °C, corresponding to the 011 and 30 $\bar{2}$ set of planes, respectively. For instance, analysis of the 30 $\bar{2}$ set of planes in the as-synthesised structure reveals that the trifluoromethyl groups in two crystallographically equivalent neighbouring 2-periodic frameworks (colour-coded green) are located on the same plane (Figure 4.35).

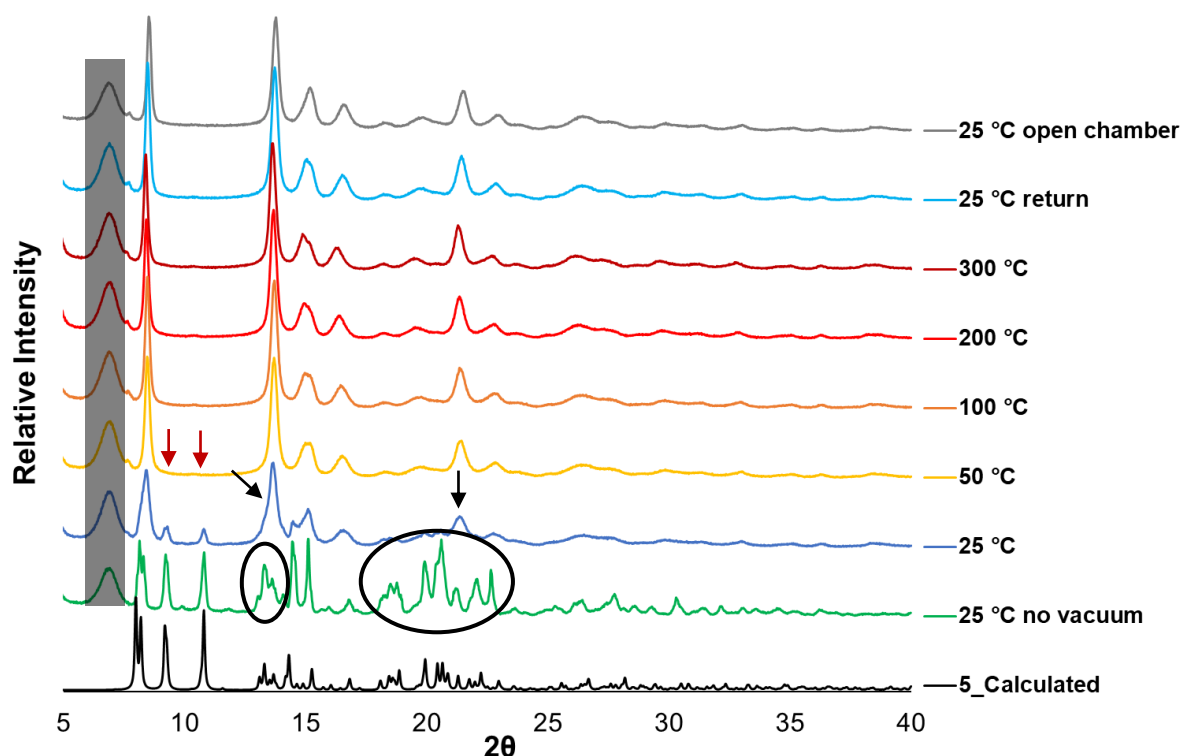


Figure 4.34. Calculated and VT-PXRD patterns of **5** from 25 to 300 °C under vacuum, followed by cooling back to 25 °C, and finally after exposure to air at 25 °C.

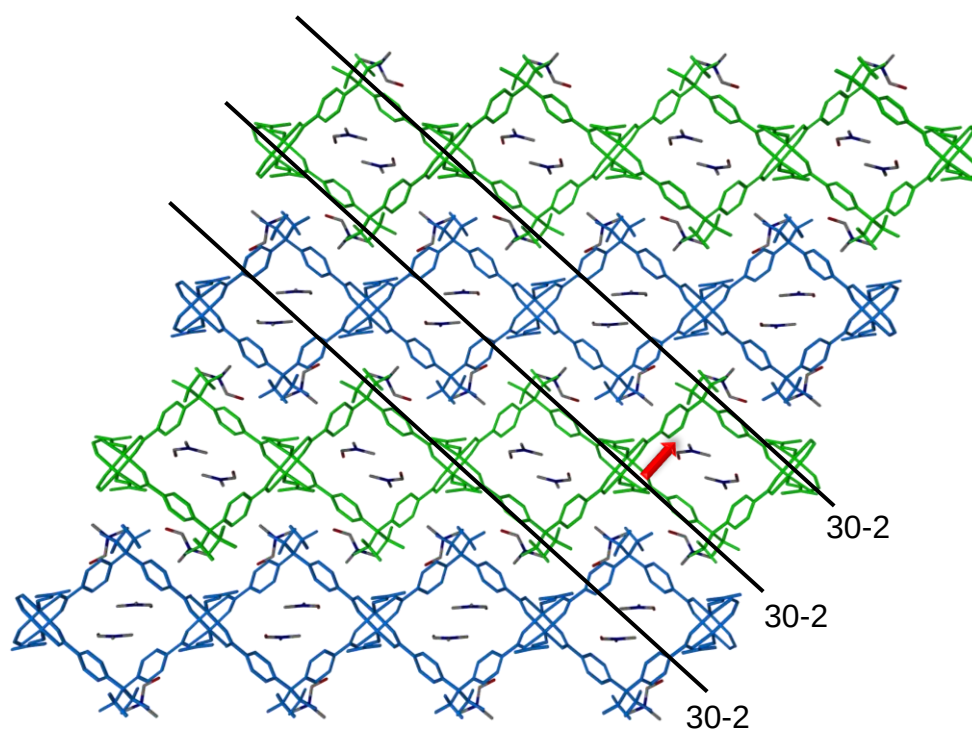


Figure 4.35. $(30\bar{2})$ planes in **5** viewed along the b -axis. The red arrow represents the direction orthogonal to the $(30\bar{2})$ planes.

In the desolvated phase, the disappearance of the $30\bar{2}$ planes suggests that neighbouring 2-periodic layers shift orthogonally to this plane as they draw closer together. This shift repositions the trifluoromethyl groups of one layer to a position approximately halfway between the original $30\bar{2}$ planes, resulting in destructive X-ray interference and the disappearance of the 10.8° 2θ peak.

Similar to **3** and **4**, exposure of the desolvated sample of **5** to air for 24 hours results in no changes to the PXRD pattern. In addition, the TGA thermogram of the desolvated sample exposed to air shows no mass loss until decomposition (Figure 4.36). This indicates that the unsaturated metal sites in **5** do not adsorb atmospheric water vapour. As in **3** and **4**, this behaviour is attributed to the contraction of the 2-periodic layers upon removal of ligated DMF molecules, leaving no voids for atmospheric water to ligate to the metal centers.

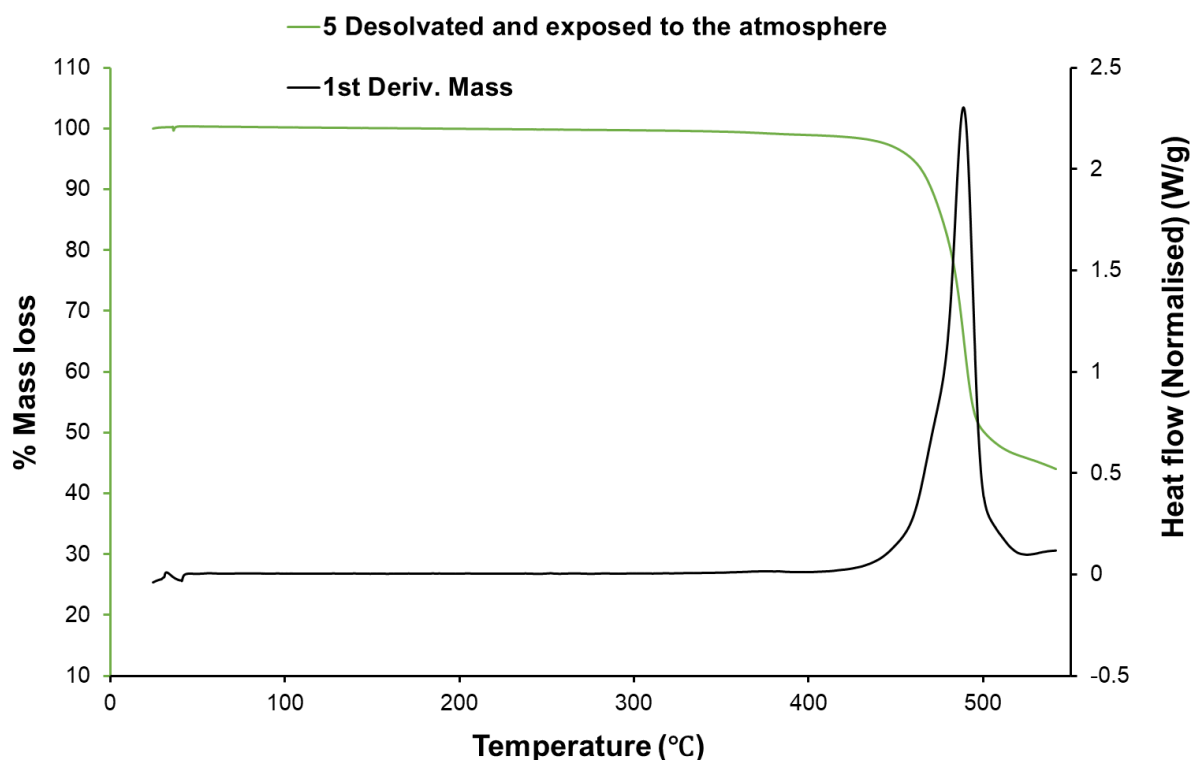


Figure 4.36. TGA thermogram of **5** after desolvation and 24-hour exposure to the atmosphere, along with its first derivative mass curve.

4.7.3. Void Space Analysis

Similar to **3** and **4**, the VT-PXRD patterns of **5** indicated that the 2-periodic layers move closer together upon desolvation, as both the coordinated and uncoordinated solvent molecules between the layers are removed. This contraction reduces the void space accessible within the structure to only the channel void space. Following the artificial removal of uncoordinated solvent molecules in the channels, analysis using MERCURY revealed the presence of 1D continuous channels running along the *b*-axis, akin to those observed in **3** and **4** (Figure 4.37). These channels account for 24.2% of the unit cell volume, corresponding to a potential void space of 1467.2 Å³. This void space is significantly larger than those of **3** and **4**, consistent with **5** being non-interpenetrated, as opposed to **3** and **4** which both have 2-fold interpenetrated structures. Additionally, the larger void space in **5** is attributed to the presence of DMF

molecules occupying the channels, which are bulkier compared to the MeOH and EtOH molecules occupying the channels in **3** and **4**, respectively.

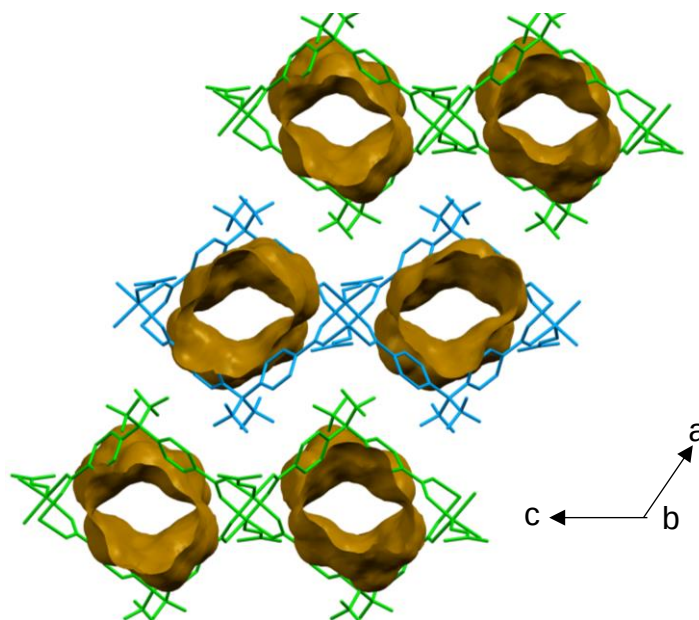


Figure 4.37. 1D channels in **5** formed along the *b*-axis, with channel-only solvents artificially removed. Hydrogen atoms are omitted for clarity.

4.8. Single Crystal X-Ray Diffraction Analysis of **6**

4.8.1. Structure Description

Single crystal X-ray diffraction analysis reveals that **6** crystallizes in the monoclinic crystal system with space group *Cc* (Table 4.11). While **3**, **4**, and **5** each contain one or two crystallographically distinct Zn^{2+} ions, the ASU of **6** is more complex, containing four distinct Zn^{2+} ions, four fully deprotonated H_2hfipbb ligands, four coordinated DMA molecules, eight uncoordinated DMA molecules, and one uncoordinated water molecule (Figure 4.38a).

Table 4.11. Crystal Data and Refinement Parameters for **6**.

ASU formula	C ₁₁₆ H ₁₄₂ F ₂₄ N ₁₂ O ₂₉ Zn ₄
Formula mass	2885.89
Temperature / K	100
Crystal system	monoclinic
Space group	Cc
<i>a</i> / Å	32.069(3)
<i>b</i> / Å	19.9228(15)
<i>c</i> / Å	25.856(4)
α / °	90
β / °	126.648(3)
γ / °	90
Volume / Å ³	13254(2)
<i>Z</i>	4
ρ / g cm ⁻³	1.446
μ / mm ⁻¹	0.823
<i>F</i> (000)	5960.0
Crystal size (mm ³)	0.28 × 0.19 × 0.16
2 θ range for data collection / °	3.774 to 56.672
Index ranges	-42 ≤ <i>h</i> ≤ 42, -26 ≤ <i>k</i> ≤ 26, -34 ≤ <i>l</i> ≤ 34
Reflections collected	264879
Independent reflections	32912 [<i>R</i> _{int} = 0.0495, <i>R</i> _{sigma} = 0.0286]
Data/restraints/parameters	32912/59/1693
Goodness-of-fit on <i>F</i> ²	1.023
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0430, <i>wR</i> ₂ = 0.1057
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0449, <i>wR</i> ₂ = 0.1071
Largest diff. peak/hole / e Å ⁻³	0.97/-0.63

Each Zn²⁺ ion in **6** forms a binuclear paddlewheel SBU, similar to those in **3**, **4**, and **5**, with Zn²⁺ centers adopting a distorted square pyramidal geometry (Figure 4.38b). The equatorial positions are coordinated by four bridging bidentate carboxylate oxygen atoms from four distinct hfipbb ligands, while the axial positions are occupied by the

oxygen atoms of the ligated DMA molecules. The Zn–O bond lengths range from 1.9684(3) to 2.0686(3) Å, and the Zn···Zn separations are 3.015 and 2.985 Å for the two paddlewheels, slightly larger than those observed in **3** and **4** but similar to those in **5** (Table 4.12).

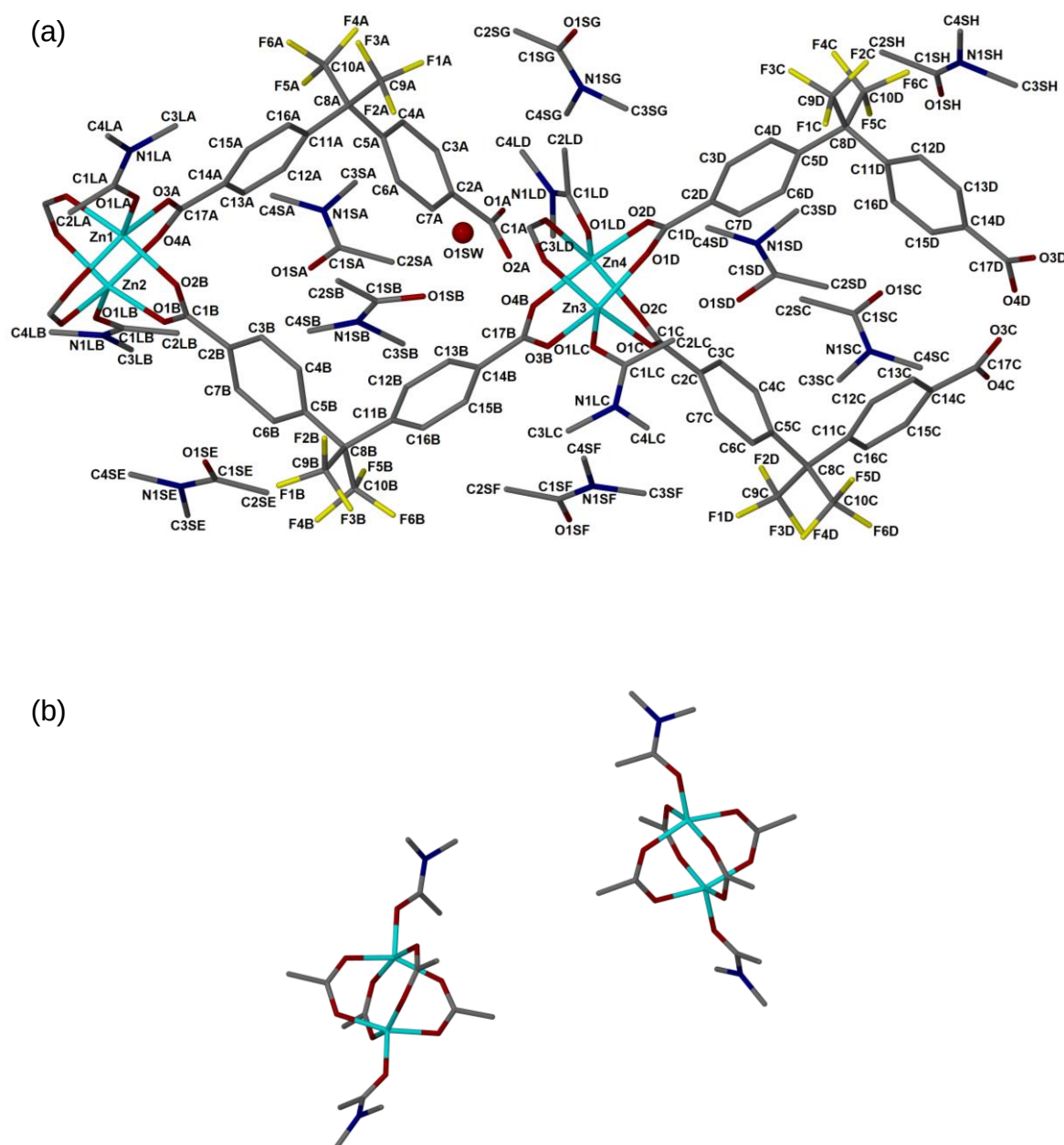


Figure 4.38. (a) Coordination environment around the Zn²⁺ ions of **6**, with only atoms of the ASU labelled. (b) Paddlewheel SBUs present in **6**. Hydrogen atoms are omitted for clarity.

The hfipbb ligands in **6** exhibit bent conformations, with angles of 75.5°, 75.8°, 78.1° and 79.8° between their two benzene rings. These angles are larger than those observed in **3**, **4**, and **5**, indicating a less pronounced bending conformation. The 8+ charge on the four Zn²⁺ ions is balanced by the 8- charge of the four fully deprotonated H₂hfipbb ligands.

Table 4.12. Zn···Zn distances and bond lengths involving Zn²⁺ cations in **6**.

Bond	Length (Å)	Bond	Length (Å)
Zn1···Zn2	3.015	Zn2–O4A	2.0508(3)
Zn3···Zn4	2.985	Zn3–O1D	2.0455(3)
Zn1–O1A	2.025(3)	Zn3–O1LC	1.9684(3)
Zn1–O2B	2.038(3)	Zn3–O3B	2.0375(3)
Zn1–O1LA	1.9796(3)	Zn3–O4D	2.0255(3)
Zn1–O3C	2.0477(3)	Zn3–O1C	2.0386(3)
Zn1–O3A	2.0338(3)	Zn4–O1LD	1.9702(3)
Zn2–O1B	2.0296(3)	Zn4–O2D	2.0440(3)
Zn2–O2A	2.0233(3)	Zn4–O3D	2.0395(3)
Zn2–O1LB	1.9742(3)	Zn4–O4B	2.0686(3)
Zn2–O4C	2.0322(3)	Zn4–O2C	2.0198(3)

4.8.2. Crystal Packing

6 retains the undulating, 2-periodic framework motif observed in **3**, **4**, and **5**, characterised by large, rhombus-like windows (Figure 4.39a). However, unlike in **3**, **4**, and **5**, where the windows are uniform in size, **6** features two unique rhombic windows

with slightly different dimensions: 9.45 and 25.86 Å and 10.49 and 25.86 Å along the *b*-direction. These dimensions are smaller than the corresponding windows in **3** (13.9 and 23.1 Å), **4** (13.9 and 23.9 Å), and **5** (10.8 and 24.8 Å). The unique window sizes in **6** are a result of crystallographically distinct hfipbb ligands, which show variations in their bending conformations. Viewed along the *c*-axis, the zig-zag chain

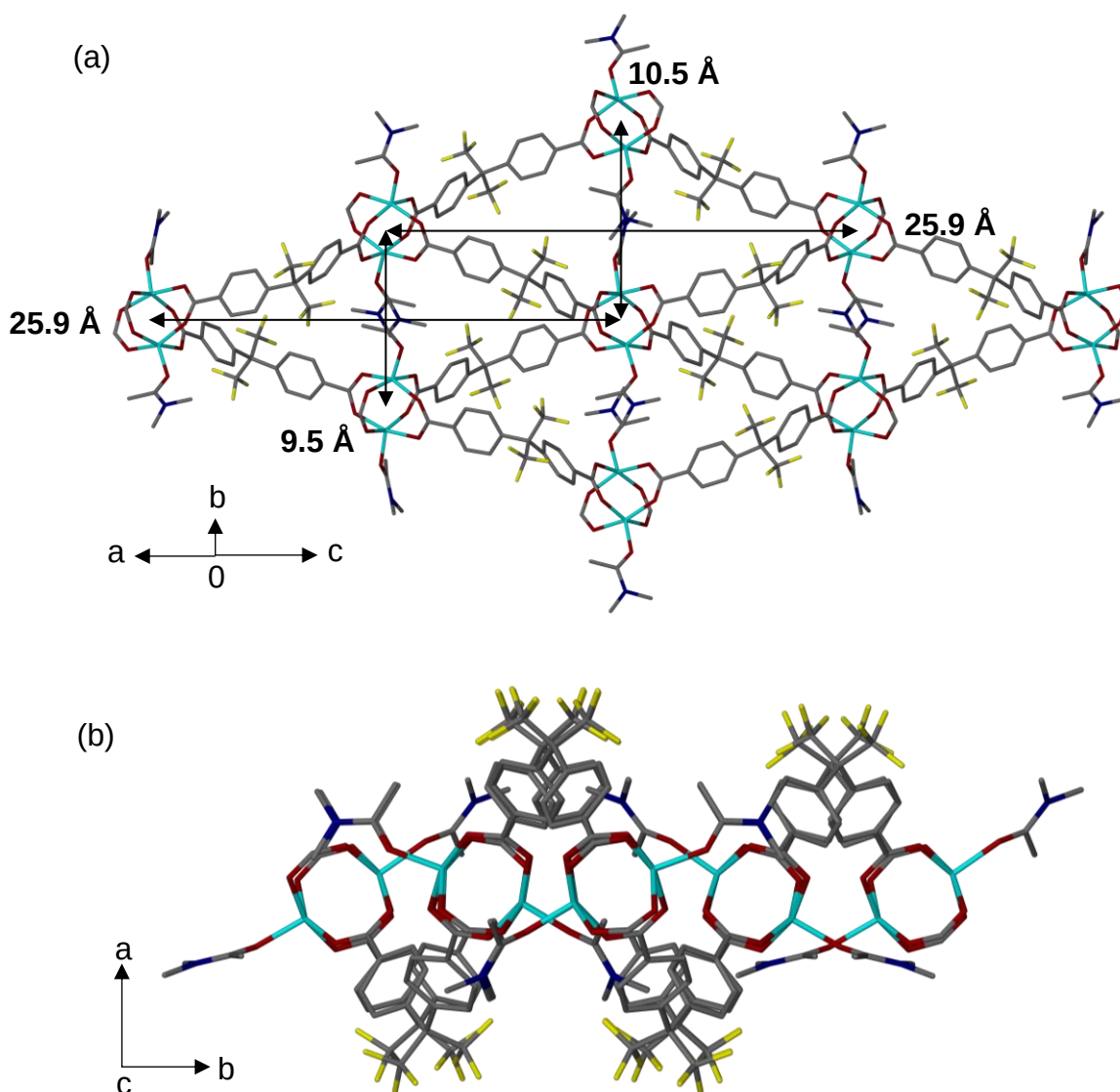


Figure 4.39. (a) The 2-periodic framework of **6** in *bc* plane with dimensions of the rhombic windows. (b) View of the 2-periodic framework of **6** along the *c*-axis. Uncoordinated solvent molecules and hydrogen atoms are omitted for clarity.

appearance remains evident (Figure 4.39b). Like **5**, **6** features a non-interpenetrated 2-periodic framework. The neighbouring 2-periodic frameworks in **6** stacks in an interdigitated ABAB sequence along the *a*-direction, with a separation distance of 12.9 Å (Figure 4.40). This distance is longer than in **5** (11.6 Å) but comparable to those in **3** (12.9 Å) and **4** (12.8 Å). The diamondoid-shaped channels in **6** are occupied by DMA and water molecules, contrasting with the MeOH, EtOH, and DMF molecules occupying the channels in **3**, **4**, and **5**, respectively (Figure 4.41). Additional uncoordinated DMA molecules are situated between adjacent frameworks. The ligated DMA molecules in **6** are slightly inclined toward the adjacent frameworks, unlike the perpendicular orientation of the ligated DMF molecules in **5**. This orientation contributes to a larger inter-framework separation distance in **6** compared to **5**, while remaining similar to those in **3** and **4**.

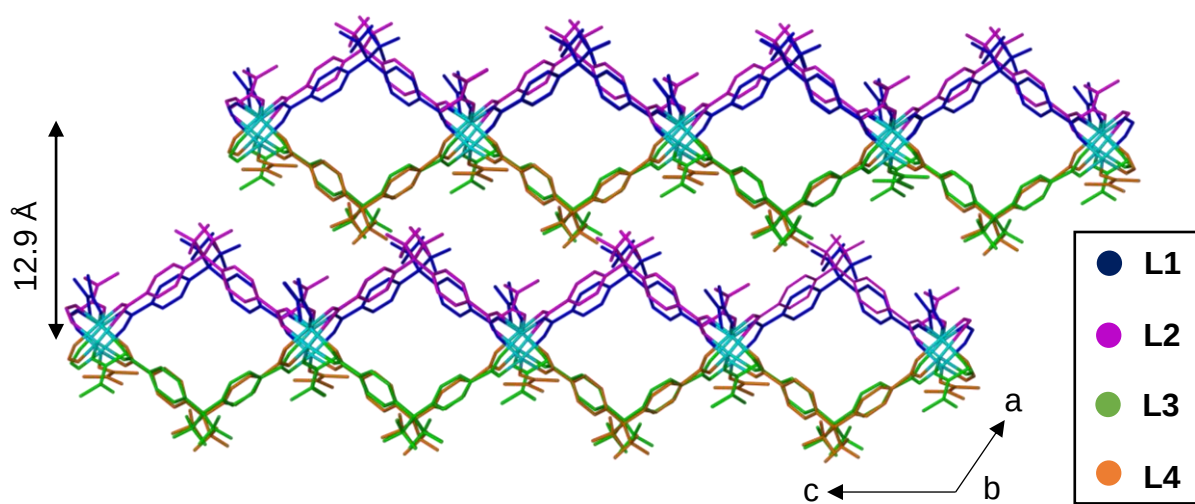


Figure 4.40. 2-periodic, non-interpenetrated frameworks in **6**, stacked along the *a*-axis with a stacking distance of 12.9 Å, indicated by a line. The distinct hfpbb ligands (L) are shown in different colours: L1 (blue), L2 (pink), L3 (green), and L4 (orange). Uncoordinated solvent molecules and hydrogen atoms are omitted for clarity.

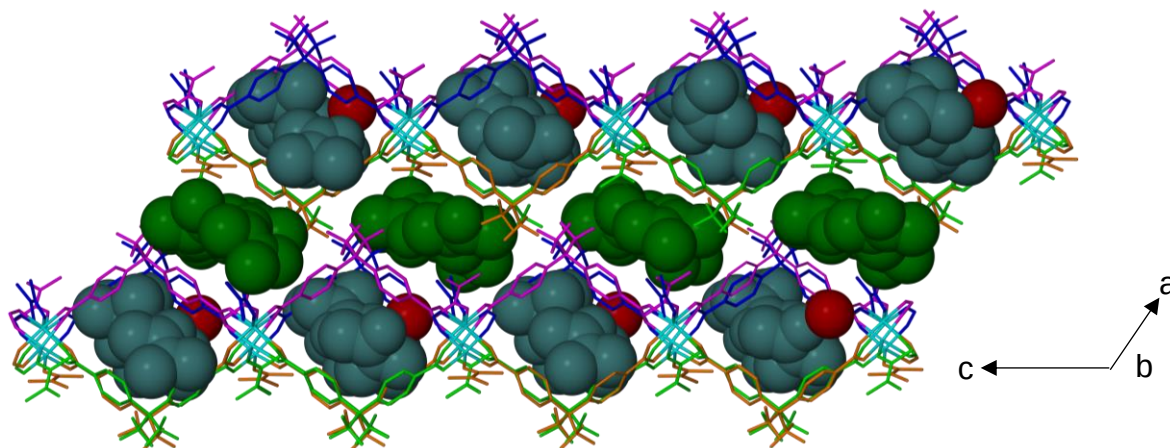


Figure 4.41. View of the colour-coded, non-interpenetrated 2-periodic frameworks in **6** along the *b*-axis. Uncoordinated DMA (blue) and water (red) molecules filling the channels within the framework, and DMA (green) molecules occupying the space between adjacent frameworks, are shown in space-filling mode. Hydrogen atoms are omitted for clarity.

4.8.3. Hydrogen Bonding

In **6**, both solvent...solvent and solvent...framework hydrogen bonds are present (Figure 4.42 and Table 4.13). Unlike in **5**, no hydrogen bonding occurs between neighbouring frameworks in **6**. Within the channel, a strong O-H...O bond is observed between the uncoordinated water molecule and both the uncoordinated DMA (O1SW-H1SA...O1SB) and the framework (O1SW-H1SB...O4B). The uncoordinated DMA molecules located between the 2-periodic frameworks interact with the framework through a series of seven weaker C-H...O and C-H...F bonds (C3A-H3A...O1SH, C4A-H4A...O1SH, C6C-H6C...O1SG, C7B-H7B...O1SE, C12D-H12D...O1SF, C2SE-H2SD...F3C, and C2SH-H2SR...F6D). Additionally, two weaker C-H...O interactions (C4SE-H4SE...O1SF, and C3SF-H3SH...O1SG) occur between the uncoordinated DMA molecules located between the 2-periodic frameworks.

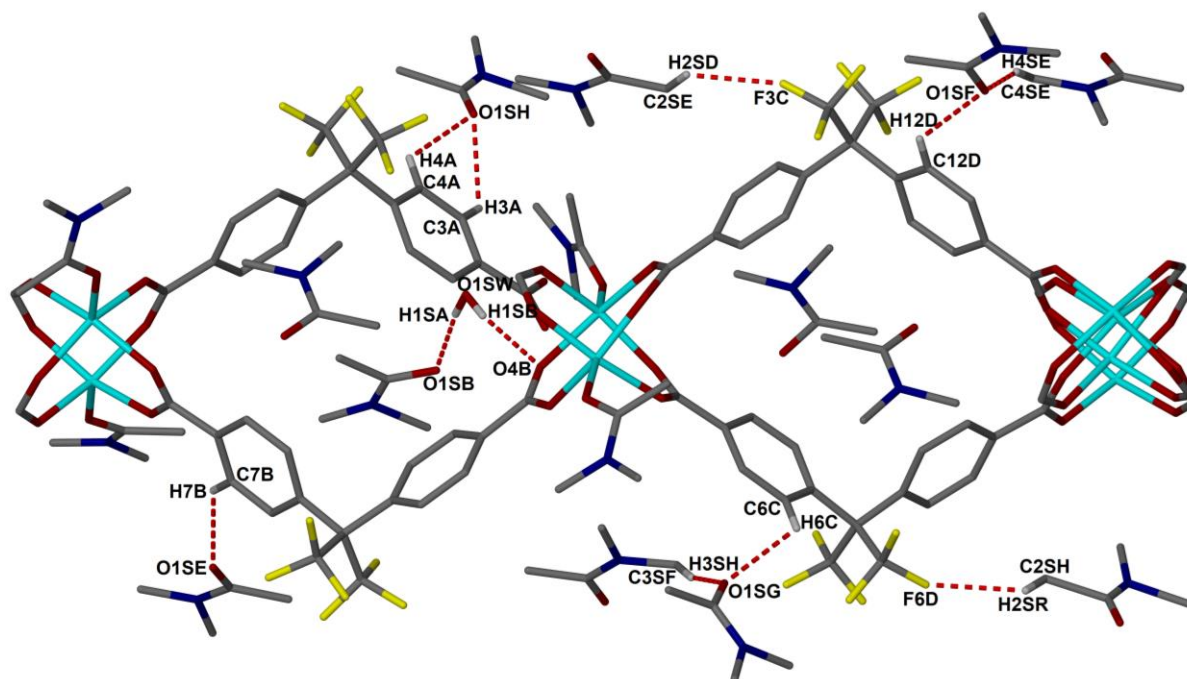


Figure 4.42. Hydrogen bonding in **6**, showing the interactions between uncoordinated water and DMA molecules, and their interactions with the framework.

Unlike in **4** and **5**, no hydrogen bonds are observed between ligated solvent molecules and either the framework or other solvent molecules. Furthermore, some of the unique uncoordinated DMA molecules exhibit no hydrogen bonding interactions, indicating weaker overall interactions between the solvent molecules and the framework compared to **4** and **5**.

Intramolecular interactions are also present in this structure and are detailed in the .lis file, provided in the supplementary information.

Table 4.13. Hydrogen bond distances, angles, and symmetry operators for **6**.

Donor–H···Acceptor	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)	Symmetry operators
O1SW–H1SA···O1SB	0.85	2.03	2.877(9)	171	x, y, z
O1SW–H1SB···O4B	0.85	2.27	3.109(6)	170	x, y, z
C3A–H3A···O1SH	0.93	2.52	3.101(9)	121	x, 1–y, $\frac{1}{2}+z$
C4A–H4A···O1SH	0.93	2.56	3.120(9)	119	x, 1–y, $\frac{1}{2}+z$
C6C–H6C···O1SG	0.93	2.58	3.128(9)	118	$-\frac{1}{2}+x$, $\frac{1}{2}-y$, $-\frac{1}{2}+z$
C7B–H7B···O1SE	0.93	2.46	3.195(7)	136	x, y, z
C12D–H12D···O1SF	0.93	2.59	3.220(8)	126	$\frac{1}{2}+x$, $-\frac{1}{2}+y$, z
C4SE–H4SE···O1SF	0.96	2.55	3.468(8)	159	x, 1–y, $\frac{1}{2}+z$
C2SE–H2SD···F3C	0.96	2.47	3.106(9)	124	$-\frac{1}{2}+x$, $\frac{1}{2}+y$, z
C3SF–H3SH···O1SG	0.96	2.53	3.459(8)	164	$-\frac{1}{2}+x$, $\frac{1}{2}-y$, $-\frac{1}{2}+z$
C2SH–H2SR···F6D	0.96	2.54	3.203(9)	126	$\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$

4.9. Desolvation Studies

Efforts to obtain the single crystal structure of the desolvated form of **6** through heating failed. Similar to **5**, the instability of **6** in water prevented the application of the solvent exchange process. As a result, no structural insights could be gained through water exchange.

4.9.1. Thermal Analysis

4.9.1.1. Thermogravimetric and Differential Scanning Calorimetry Analysis

The thermal stability of **6** was examined using TGA and DSC. TGA analysis, performed on a crystalline sample of **6** over a temperature range of 22 to 542 °C, showed a single mass loss of 35.9% (calculated 36.9%) between 50 and 250 °C (Figure 4.43). This loss is attributed to the removal of both uncoordinated and coordinated DMA molecules. This observation is supported by the derivative mass curve, which shows a single peak.

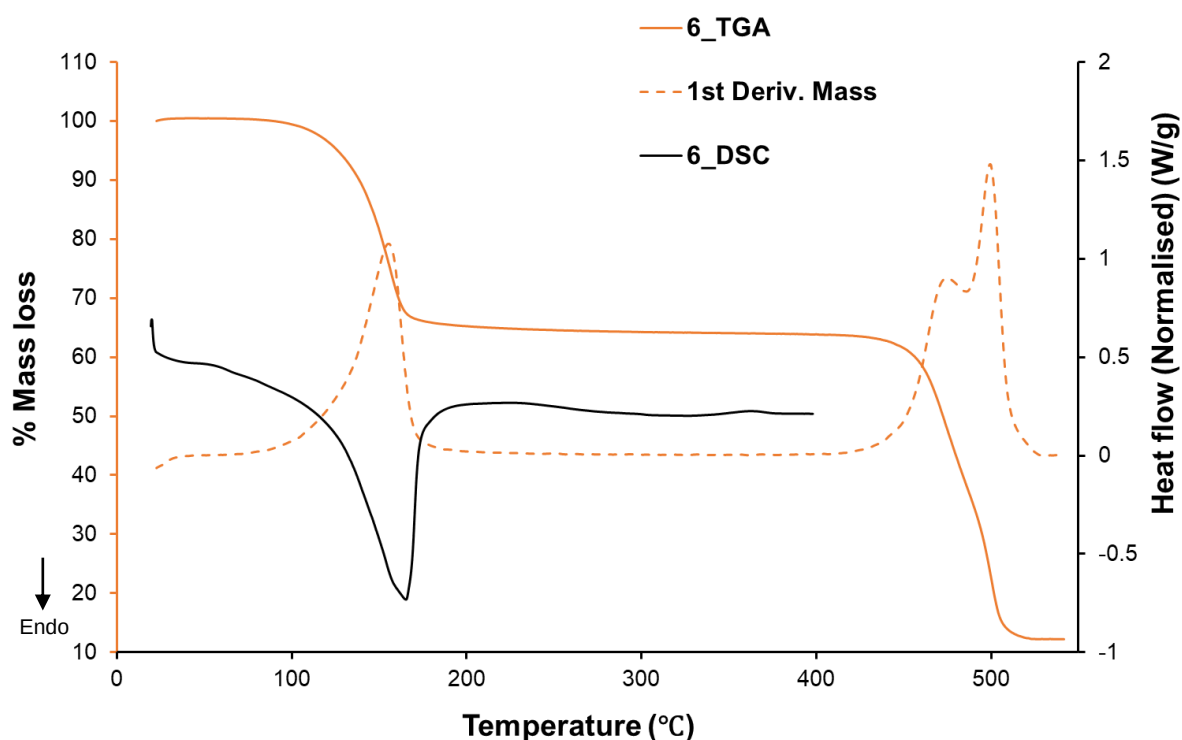


Figure 4.43. Overlay of the TGA thermogram, its first derivative mass, and the DSC thermogram of **6**.

The DSC thermogram displays a sharp endothermic peak with an onset of 123 °C and a peak temperature of 165 °C. The onset temperature is lower than those observed

for **4** and **5** but higher than that for **3**, indicating weaker DMA–interactions compared to the EtOH and DMF interactions in **4** and **5**, respectively, but stronger than the MeOH interactions in **3**. This trend aligns with the observed hydrogen bonding patterns, where **6** shows weaker interactions than in **4** and **5** but stronger than in **3**, suggesting that disrupting the interactions in **6** requires less energy than in **4** and **5** but more than in **3**. The framework of **6** remains stable until approximately 430 °C, after which decomposition occurs. This stability is comparable to that of **3**, **4**, and **5**, further supporting the conclusion that the structural integrity of the frameworks is not significantly affected by the type of solvent molecule present prior to desolvation.

4.9.1.2. Hot Stage Microscopy

Crystals of **6** were placed on a microscope slide and covered in silicone oil to observe thermal events between 24 to 500 °C (Figure 4.44). At 84 °C, the crystals began to turn opaque, as indicated by decolouration at the edges, suggesting the onset of solvent loss and the loss of monocrystallinity. As the temperature increased, the opacity spread, and by 130 °C, the crystals started to disintegrate. This disintegration was followed by bubbling at 190 °C, indicating further solvent loss. At 318 °C, the crystals started turning brown, marking the onset of decomposition. By 500 °C, the crystals had completely decomposed. When compared to **3**, **4**, and **5**, **6** exhibited a less robust crystal morphology under thermal treatment. Unlike **5**, **6** showed an earlier onset of opacity and disintegration. Additionally, while **3** and **4** also turned opaque during solvent release, the disintegration of **6** progressed more rapidly. These observations highlight that the crystal morphology of **6** is less stable under heating conditions compared to **5**, **4**, and **3**, with earlier and more pronounced changes during thermal events.

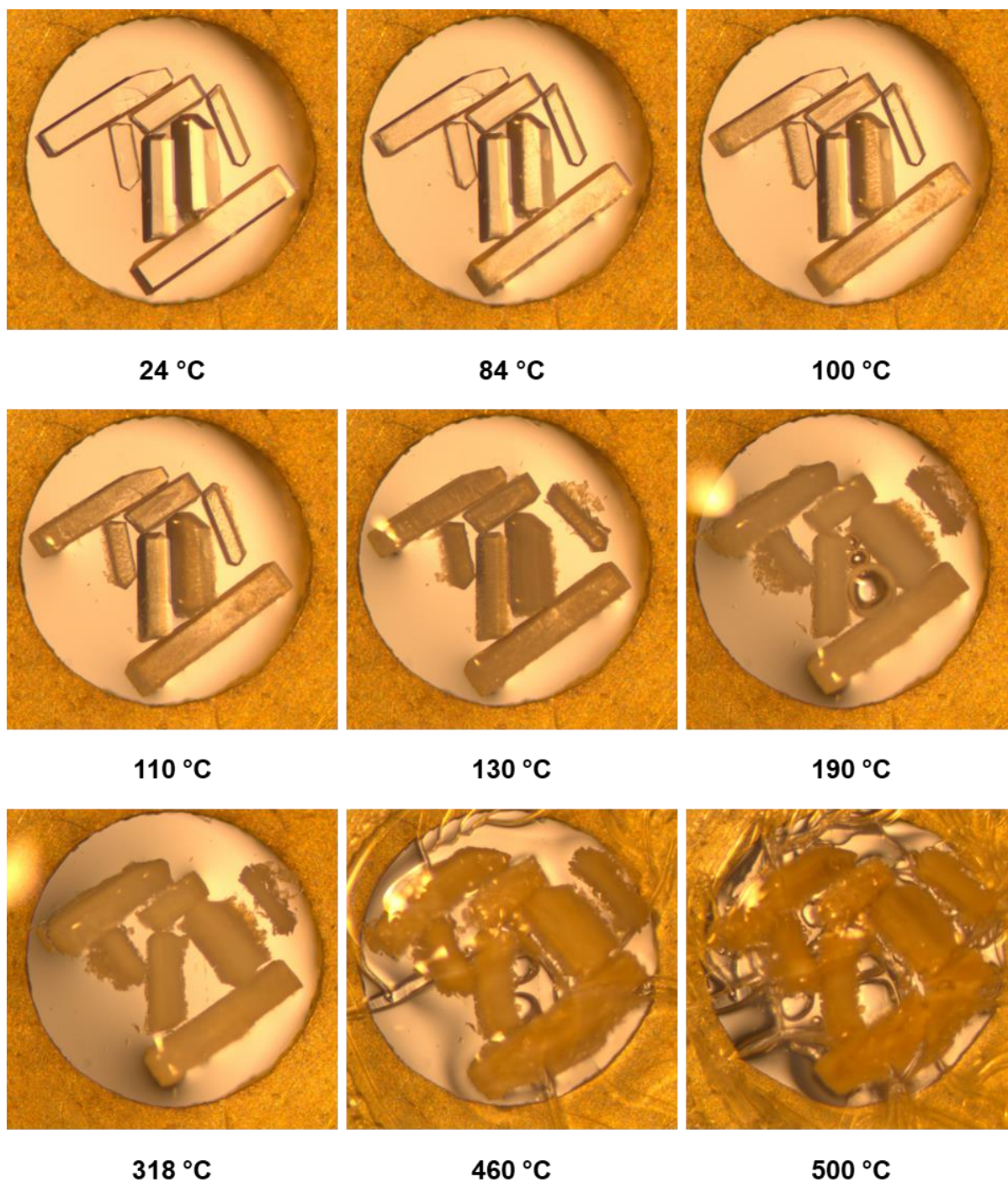


Figure 4.44. HSM images of **6** from 24 – 500 °C.

4.9.2. Variable-Temperature Powder X-Ray Diffraction Studies

The VT-PXRD pattern of **6** at 25 °C and ambient pressure (~1 atm) closely matches the calculated pattern, confirming the phase purity and that the single crystal represents the bulk material (Figure 4.45). Desolvation of **6** proceeds through an

intermediate phase between 25 and 50 °C, indicated by the disappearance of several peaks (indicated by green arrows) and the emergence of new ones (marked by red stars). By 50 °C, more peaks disappear (indicated by black arrows), and others either intensify (indicated by red arrows) or diminish (indicated by black circles), indicating structural changes due to solvent loss. The final phase is established at 75 °C, with no further changes up to 300 °C, and the pattern remains stable upon cooling to 25 °C.

The desolvated phase of **6** exhibits a PXRD pattern that closely matches that of desolvated **5**, despite differences in their calculated PXRD patterns due to the presence of different solvent molecules in their structures (Figure 4.46). This indicates

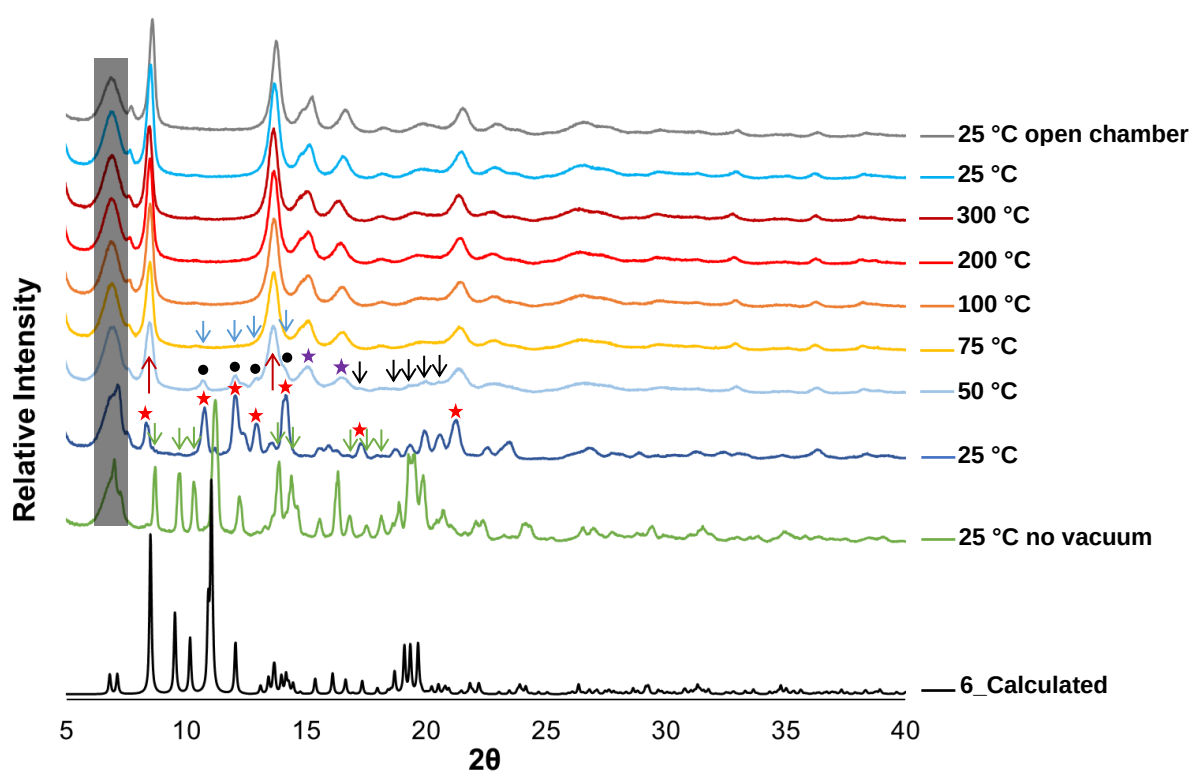


Figure 4.45. Calculated and VT-PXRD patterns of **6** from 25 °C to 300 °C under vacuum, followed by cooling back to 25 °C, and finally after exposure to air at 25 °C.

similar 2-periodic framework stacking transitions during desolvation. Qualitatively, **5** exhibits a higher peak-to-background ratio than **6**, which likely indicates a higher degree of crystallinity in **5** compared to **6**.

When compared to the desolvated phases of **3** and **4**, the PXRD patterns of desolvated **5** and **6** show overall similarities but differ in specific peak profiles. Notable differences include the peaks between 14.0 and $16.0^\circ 2\theta$ and the peak at $\sim 16.6^\circ 2\theta$ (shaded in blue), which is absent or significantly reduced in the PXRD patterns of desolvated **3** and **4** (Figure 4.46).

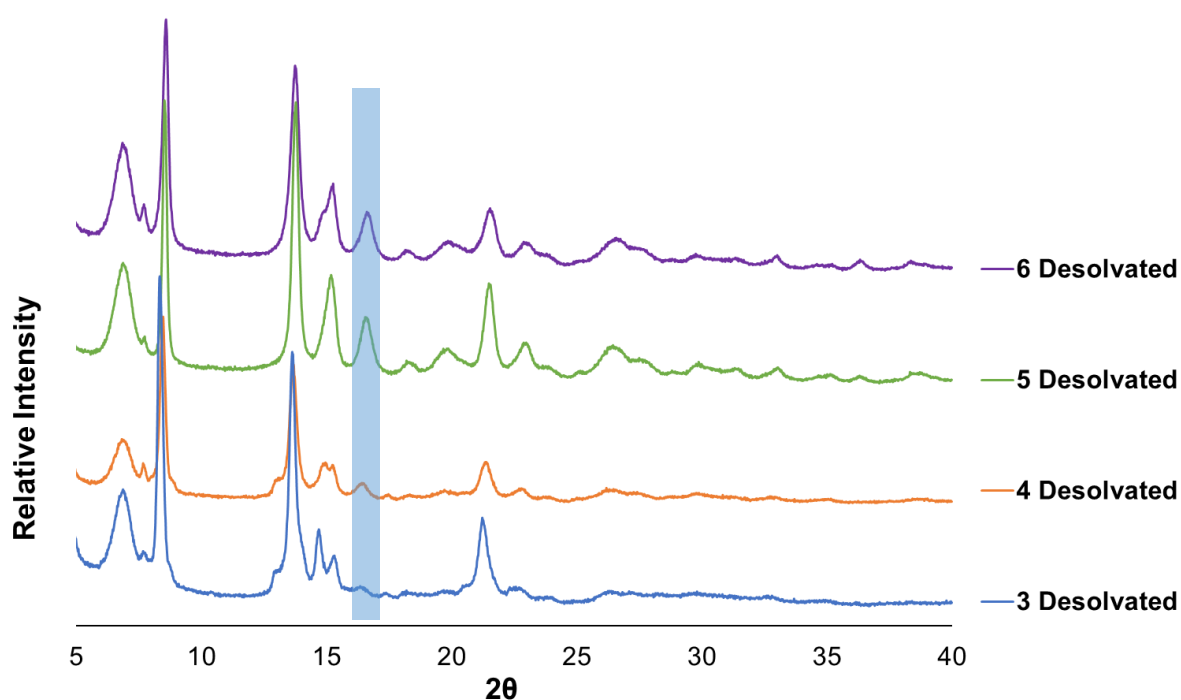


Figure 4.46. PXRD patterns of the desolvated structure of **5** and **6**.

These differences likely arise from the structural interpenetration observed in **3** and **4**, which is absent in **5** and **6**. Despite this distinction, the overall similarities in the PXRD patterns of the desolvated phases of **3**, **4**, **5**, and **6** suggest that these MOFs undergo

similar structural transitions upon desolvation, specifically involving the 2-periodic layers moving closer together as solvent molecules between the layers are removed.

In the VT-PXRD analysis of **6**, three prominent peaks disappeared sequentially at different temperatures, indicating that the coordinated and uncoordinated DMA molecules are removed gradually over time. In contrast, the peaks in **5** disappeared simultaneously, suggesting a faster desolvation process.

The prominent peak at $11.0^\circ 2\theta$, corresponding to the $40\bar{2}$ planes, disappeared first at 25°C under vacuum, likely reflecting the removal of uncoordinated DMA molecules between the layers. This removal causes shifts, as seen in the as-synthesised structure, where the trifluoromethyl groups on adjacent 2-periodic frameworks align along the same path parallel to the $40\bar{2}$ planes (Figure 4.47). As the uncoordinated DMA molecules are removed, these shifts may misalign the trifluoromethyl groups on one layer with those on neighbouring layers, causing them to shift orthogonally to the

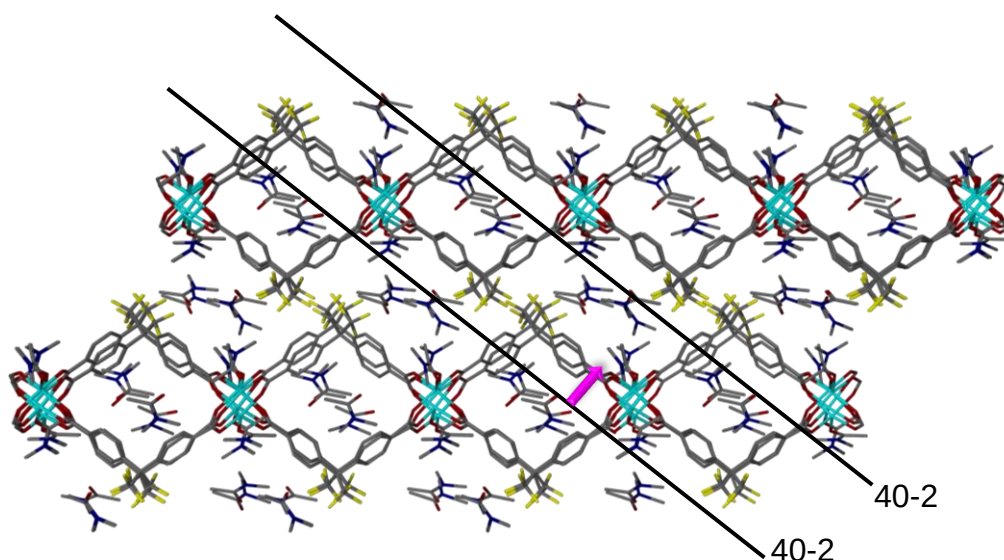


Figure 4.47. $(40\bar{2})$ planes of **6** viewed along the b -axis. The pink arrow represents the direction orthogonal to the $(40\bar{2})$ planes. Hydrogen atoms are omitted for clarity.

planes. This misalignment results in destructive X-ray interference, leading to the disappearance of the 11.0° 2θ peak.

Similar to **3**, **4**, and **5**, exposing the desolvated sample of **6** to air for 24 hours caused no changes in the PXRD pattern. Furthermore, TGA data showed no mass loss until decomposition (Figure 4.48). This indicates that the unsaturated metal sites in **6** do not adsorb atmospheric water vapour.

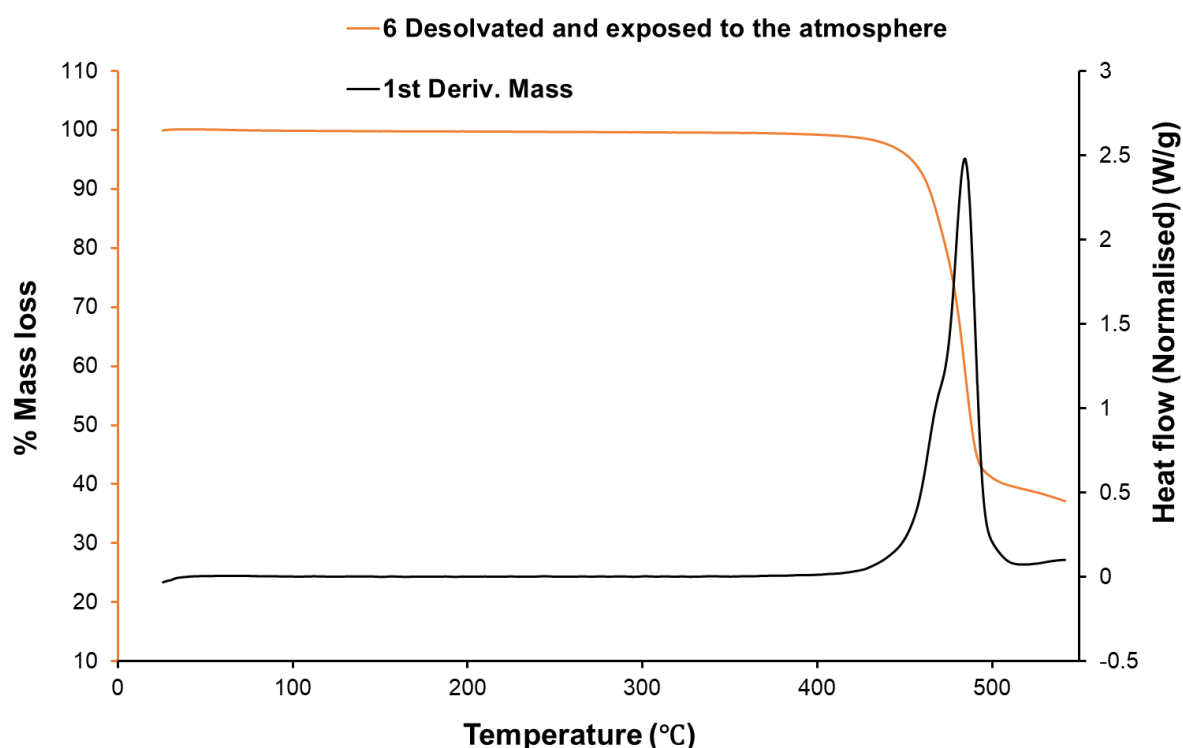


Figure 4.48. TGA thermogram of **6** after desolvation and 24-hour exposure to the atmosphere, along with its first derivative mass curve.

As with **5**, the thermal events observed in the VT-PXRD analysis for **6** occurred at lower temperatures than those in the TGA analysis. This discrepancy can again be attributed to the nature of the solvent molecules in the MOF. The structure of **6** contains uncoordinated DMA molecules between the layers. The weaker interactions

of these uncoordinated DMA molecules with the framework facilitate their removal and the subsequent layer shifts at much lower temperatures under vacuum, similar to the behaviour observed in **5**.

4.9.3. Void Space Analysis

The VT-PXRD patterns of **6** showed that the 2-periodic layers move closer together upon desolvation, as the coordinated and uncoordinated DMA solvent molecules between the layers are removed. This contraction similarly reduces the void space accessible within the structure to only the channel void space. Upon artificial removal of uncoordinated solvent molecules in the channels, analysis using MERCURY

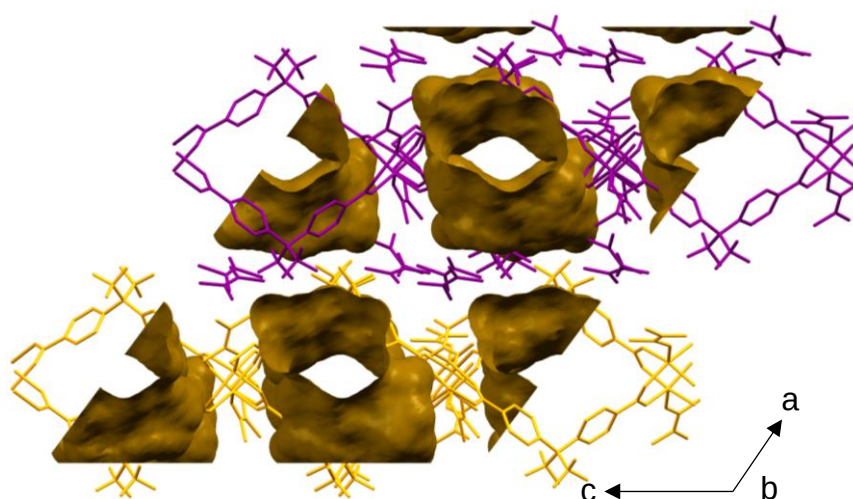


Figure 4.49. 1D channels in **6** formed along the *b*-axis, with channel-only solvents artificially removed.

identified 1D channels running along the *b*-axis, as observed in **3**, **4**, and **5** (Figure 4.49). These channels account for 25.4% of the unit cell volume, corresponding to a potential void space of 3363.4 Å³. This void space is the largest compared to **3**, **4**, and **5**. The larger void volume in **6** arises from its non-interpenetrated framework and the larger size of DMA solvent molecules

compared to the DMF, EtOH, and MeOH molecules present in **5**, **4**, and **3**, respectively.

4.10. Gas Sorption Studies

Gas and water vapour sorption experiments were conducted on the activated samples of **3** – **6** (denoted as **3'**, **4'**, **5'**, and **6'**) to evaluate their ability to adsorb various gases (N₂, H₂, and CO₂) and water vapour. Despite interpenetration in **3'** and **4'**, there remain voids to include solvents, hence adsorption studies were taken up for **3'** and **4'** as well because the solvent molecules could be removed to create void spaces. These experiments also provided data for calculating the Brunauer-Emmett-Teller (BET) surface area from N₂ sorption and the CO₂ Q_{st} value for each MOF. The activation process for **3** – **6** involved heating the samples at 200 °C under vacuum for 2 hours before conducting the sorption experiments with CO₂ (at 195 K, 273 K, 288 K and 298 K), N₂ (at 77 K), H₂ (at 77 K) and water vapour (at 298 K).

4.10.1. N₂ Sorption

N₂ sorption at 77 K was performed to confirm the permanent porosity and measure the BET surface areas of **3'** – **6'**. Each activated compound exhibits a Type-I isotherm for N₂ sorption, with the maximum sorption capacity following the order: **5'** > **6'** > **4'** > **3'** (Figure 4.50). At ~ 750 mmHg, the sorption maxima for **5'**, **6'**, **4'**, and **3'** were measured as 110.1, 87.5, 57.5, and 28.7 cm³ (STP) g⁻¹, respectively, which correspond to 2.24, 1.78, 1.17, 0.58 CO₂ molecules per Zn²⁺-hfipbb²⁻ unit (Table 4.14). The calculated BET surface areas from these isotherms are 340, 233, 224, and 110 m² g⁻¹ for **5'**, **6'**, **4'**, and **3'**, respectively (Table 4.14).

Interestingly, the observed maximum sorption capacity order (**5'** > **6'** > **4'** > **3'**) deviates from the expected trend (**6'** > **5'** > **3'** > **4'**), which is based solely on the potential void

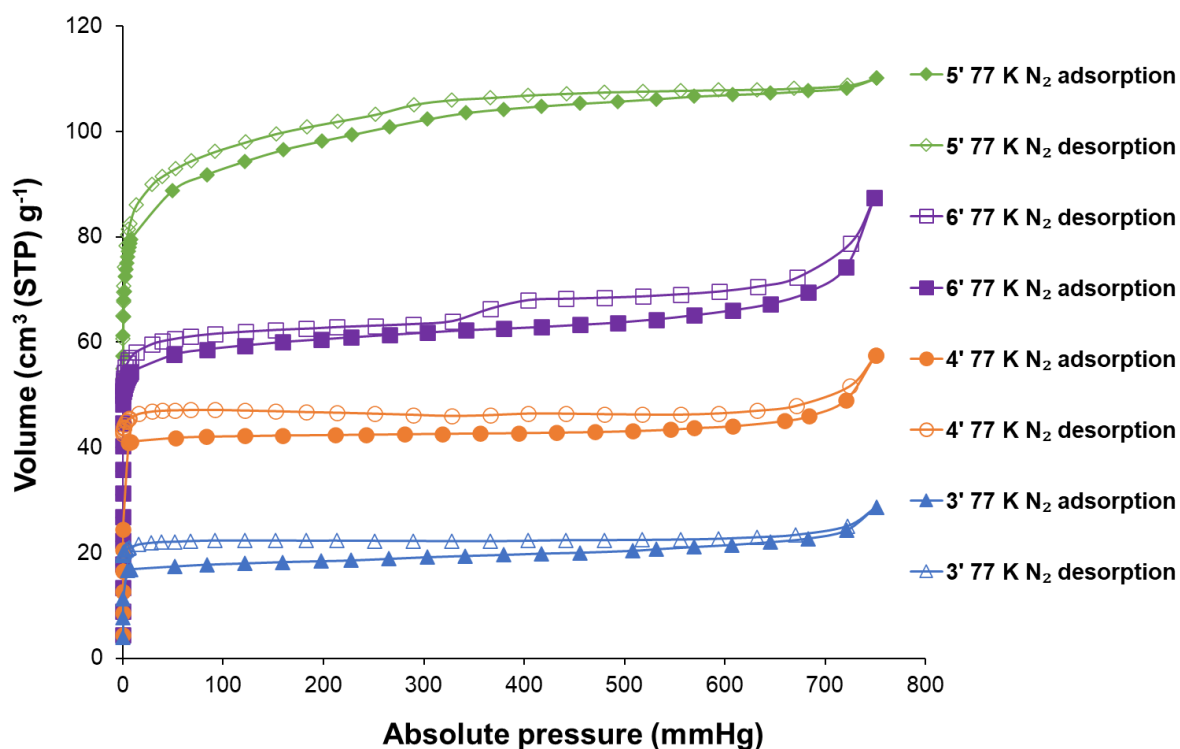


Figure 4.50. Adsorption and desorption isotherms for N₂ sorption for **3'** – **6'** at 77 K.

Table 4.14. N₂ quantity and N₂ molecules adsorbed per Zn²⁺-hfipbb²⁻ unit at 77 K and BET surface area for **3'** – **6'**.

	N ₂ adsorption amount (cm ³ (STP) g ⁻¹)	N ₂ molecules adsorbed per Zn ²⁺ -hfipbb ²⁻ unit	BET surface area (m ² g ⁻¹)
3'	28.7	0.58	110
4'	57.5	1.17	224
5'	110.1	2.24	340
6'	87.5	1.78	233

space within the channels (Table 4.15). This expected trend assumes that, upon solvent removal, layers of the 2-periodic frameworks shift closer together, restricting voids to within the channels. Despite **4'** and **3'** having similar potential void spaces, **4'** exhibits ~ 2 times the N₂ sorption of **3'**. Similarly, in the non-interpenetrated pair, **5'** shows ~ 1.5 times the N₂ sorption of **6'**. This indicates that other factors beyond void space, such as crystallinity, could be more dominant in influencing N₂ sorption capacity. For instance, **5'** qualitatively exhibits a higher degree of crystallinity than **6'** (refer back to Figure 4.46), which may support its superior sorption performance. However, although **3'** shows a slightly higher degree of crystallinity than **4'**, it exhibits lower N₂ sorption, suggesting that additional factors, such as pore accessibility, may also influence sorption behaviour. Additionally, all compounds exhibit slight hysteresis in their desorption isotherms.

Table 4.15. Percentage (%) potential void spaces for **3** – **6**, with channel-only solvent molecules artificially removed.

	Percentage (%) potential void space with channel-only solvent molecules removed
3	12.9
4	12.0
5	24.2
6	25.4

4.10.2. H₂ Sorption

The H₂ sorption maxima at 77 K and ~ 800 mmHg follow the order: **5'** > **4'** > **6'** > **3'**, with uptake values of 72.1, 57.8, 55.6, and 53.0 cm³ (STP) g⁻¹, respectively. These values correspond to 1.47, 1.17, 1.13, and 1.08 H₂ molecules per Zn²⁺-hfipbb²⁻ unit,

respectively (Figure 5.51 and Table 4.16). All isotherms exhibit Type-I behaviour with slight hysteresis. The sorption order slightly deviates from that observed for N₂ sorption, as **4'** displays a slightly higher uptake than **6'**. The maximum sorption capacities of **4'**, **6'**, and **3'** are relatively similar, and all three MOFs show high sorption at lower pressures, which suggests strong adsorbent-adsorbate interactions. In contrast, **5'** shows lower sorption at lower pressures, lagging behind **4'**, **6'**, and **3'**. However, at ~245 mmHg, **5'** surpasses **4'**, which had the highest uptake at lower pressures and reaches its maximum sorption capacity of 72.1 cm³ (STP) g⁻¹, which is 1.25 times greater than the maximum uptake of **4'**.

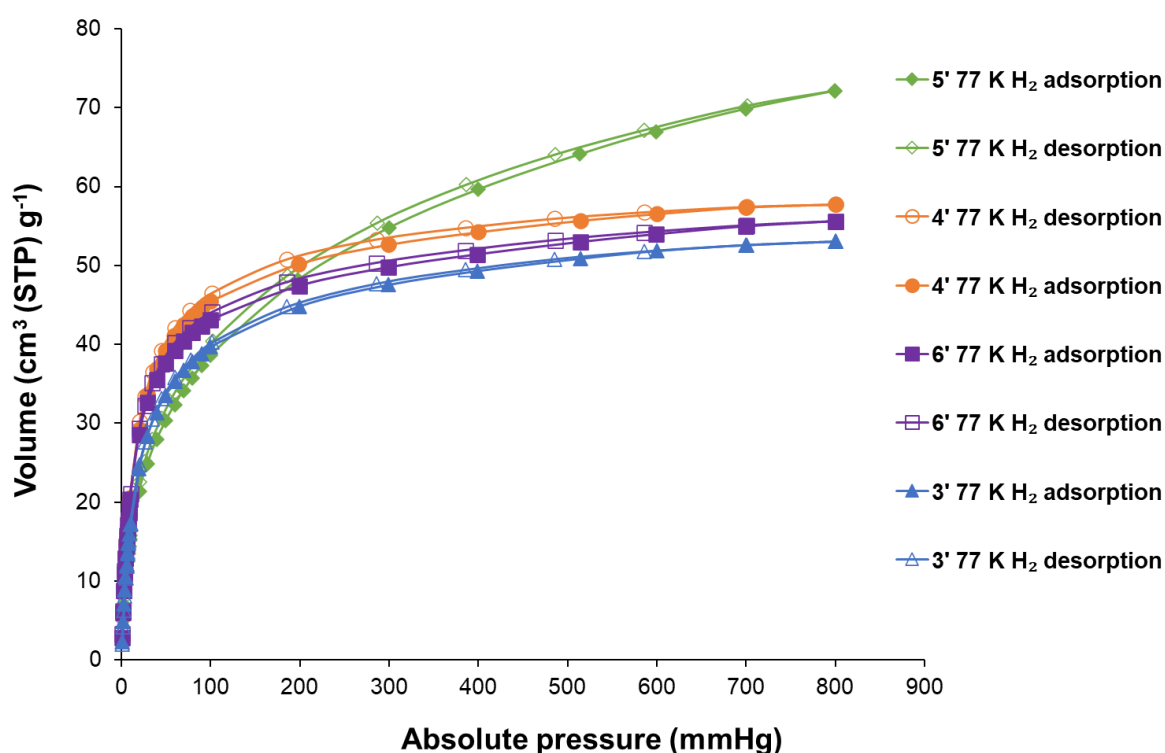


Figure 4.51. Adsorption and desorption isotherms for H₂ sorption for **3'** – **6'** at 77 K.

The lower sorption of **5'** at lower pressures could indicate weaker adsorbent-adsorbate interactions compared to the other MOFs. However, at higher pressures, **5'** outperforms the others, likely due to its higher degree of crystallinity compared to **4'**,

6', and **3'**. Interestingly, **4'** and **3'**, despite having significantly less potential void space than **6'**, display similar H₂ sorption behaviour. This might be attributed to specific binding sites within the framework of **4'** and **3'** that interact more favourably with H₂.

Table 4.16. H₂ quantity and H₂ molecules adsorbed per Zn²⁺-hfipbb²⁻ unit at 77 K for **3'** – **6'**.

	H ₂ adsorption amount (cm ³ (STP) g ⁻¹)	H ₂ molecules adsorbed per Zn ²⁺ -hfipbb ²⁻ unit
5'	72.1	1.47
4'	57.8	1.17
6'	55.6	1.13
3'	53.0	1.08

4.10.3. CO₂ Sorption

The CO₂ sorption of **3'** – **6'** were evaluated at 195, 273, 288, and 298 K. Sorption isotherms at 273, 288, and 298 K were used to determine the Q_{st} values.

The CO₂ sorption maxima follow a trend similar to that observed for H₂ sorption: **5'** > **4'** ~ **6'** > **3'** at all temperatures. The sorption maxima for **3'** – **6'** at 298, 288, 273 and 195 K are listed in Table 4.17. At 298 K (Figure 4.52), 288 K (Figure 4.53), and 273 K (Figure 4.54), all CO₂ isotherms exhibit Type-I behaviour with no hysteresis. The sorption capacities of **4'** and **6'** are nearly identical across all temperatures, consistent with their behaviour in H₂ sorption.

At 195 K, **4'** and **6'** exhibit type-I isotherms, while **3'** and **5'** initially display type-I isotherms, followed by inflection points at ~325 and 500 mmHg, respectively (Figure 4.55). After these inflection points, **3'** shows a slight increase in sorption, whereas **5'** displays a more substantial increase, reaching maximum sorption

Table 4.17. CO₂ quantity and CO₂ molecules adsorbed per Zn²⁺-hfipbb²⁻ unit for **3'**– **6'** at 298 – 195 K.

T (K)		P (mmHg)	CO ₂ adsorption amount (cm ³ (STP) g ⁻¹)	CO ₂ molecules adsorbed per Zn ²⁺ -hfipbb ²⁻ unit
298 K	5'	801	22.5	0.46
	4'		16.8	0.34
	6'		16.7	0.34
	3'		14.0	0.28
288 K	5'	800	25.0	0.51
	4'		21.3	0.43
	6'		21.2	0.43
	3'		17.2	0.35
273 K	5'	784	28.4	0.58
	4'		27.8	0.57
	6'		27.5	0.55
	3'		25.3	0.51
195 K	5'	701	84.6	1.72
	4'		65.3	1.33
	6'		65.6	1.33
	3'		58.9	1.20

capacities of 58.9 and 84.6 cm³ (STP) g⁻¹ at 701 mmHg, respectively. These values correspond to 1.20 and 1.72 CO₂ molecules per Zn²⁺-hfipbb²⁻ unit, respectively. The

inflection points observed in **3'** and **5'** suggest structural flexibility, which allows them to have increased CO₂ uptake. Similar to H₂ sorption behaviour, **5'** shows weaker adsorbent-adsorbate interactions at low pressures, initially lagging behind the other MOFs. However, it surpasses **4'** at ~95 mmHg, reaching a maximum sorption capacity of 84.6 cm³ (STP) g⁻¹, which is 1.30 times higher than that of **4'**. The superior CO₂ sorption performance of **5'** can be attributed to its high crystallinity and structural flexibility. The observed inflection point indicates the ability of its framework to open up and adsorb more CO₂ compared to other MOFs. Upon desorption, **5'** exhibits slight hysteresis.

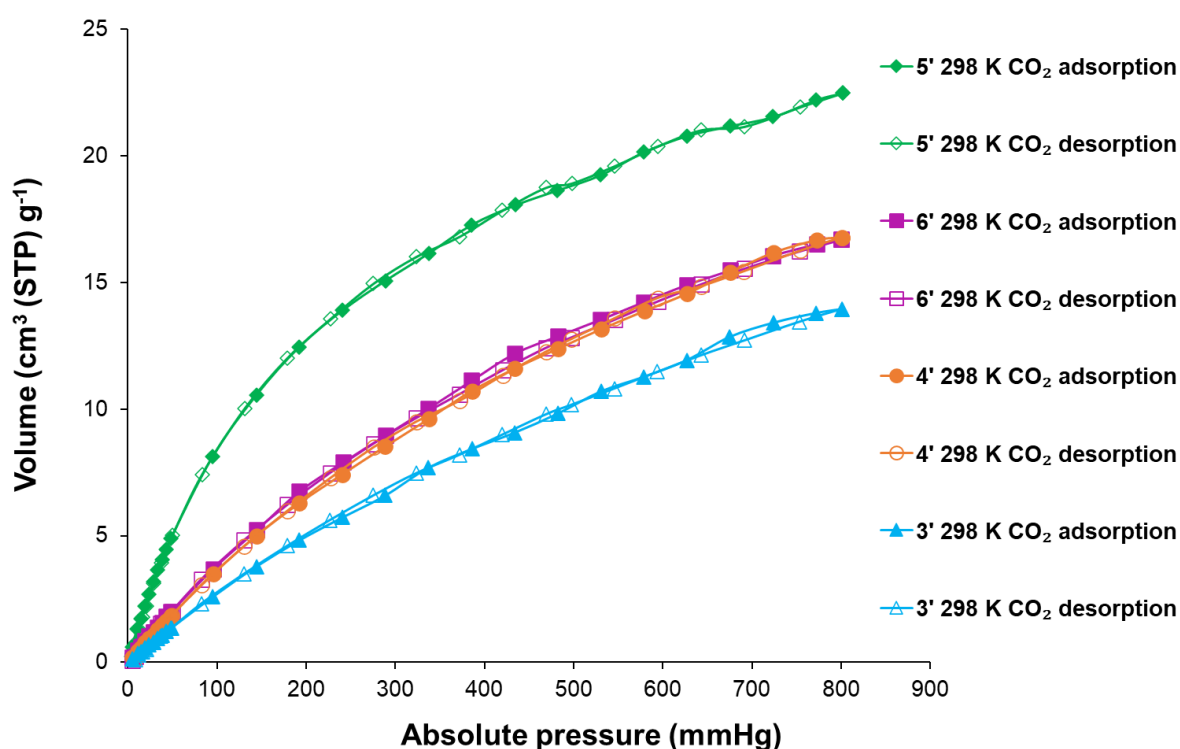


Figure 4.52. Adsorption and desorption isotherms for CO₂ sorption for **3'** – **6'** at 298 K.

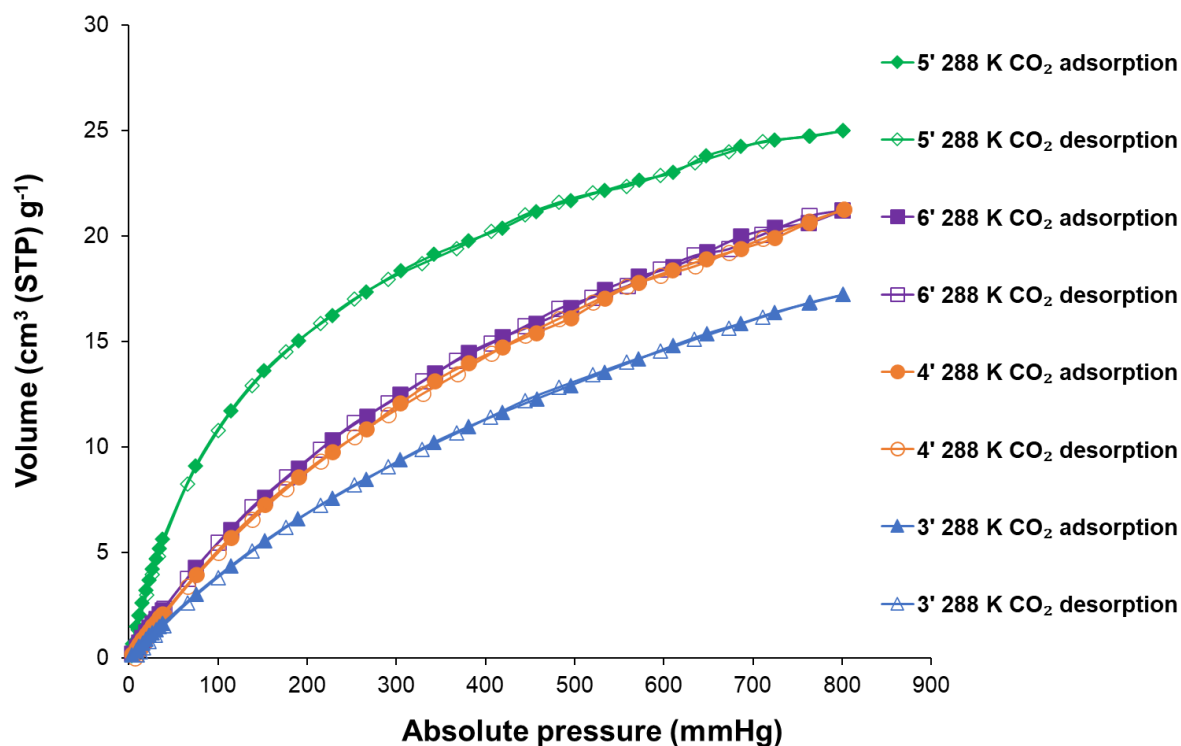


Figure 4.53. Adsorption and desorption isotherms for CO₂ sorption for **3' – 6'** at 288K.

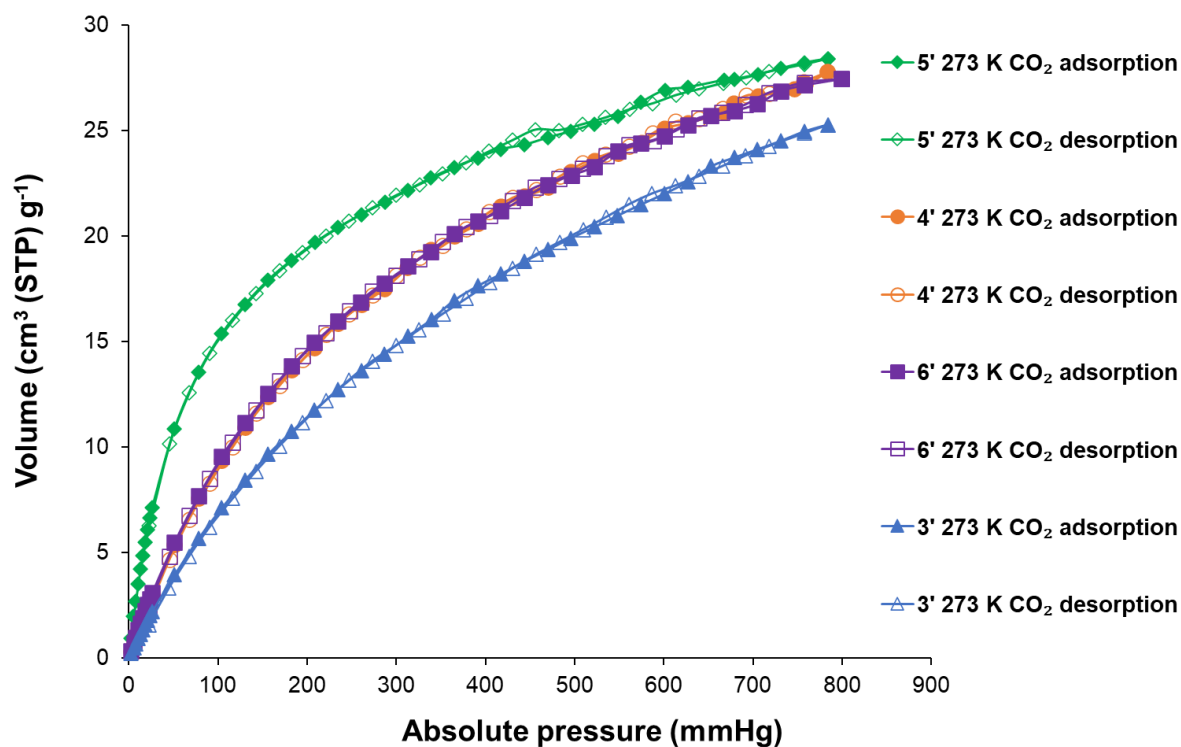


Figure 4.54. Adsorption and desorption isotherms for CO₂ sorption for **3' – 6'** at 273 K.

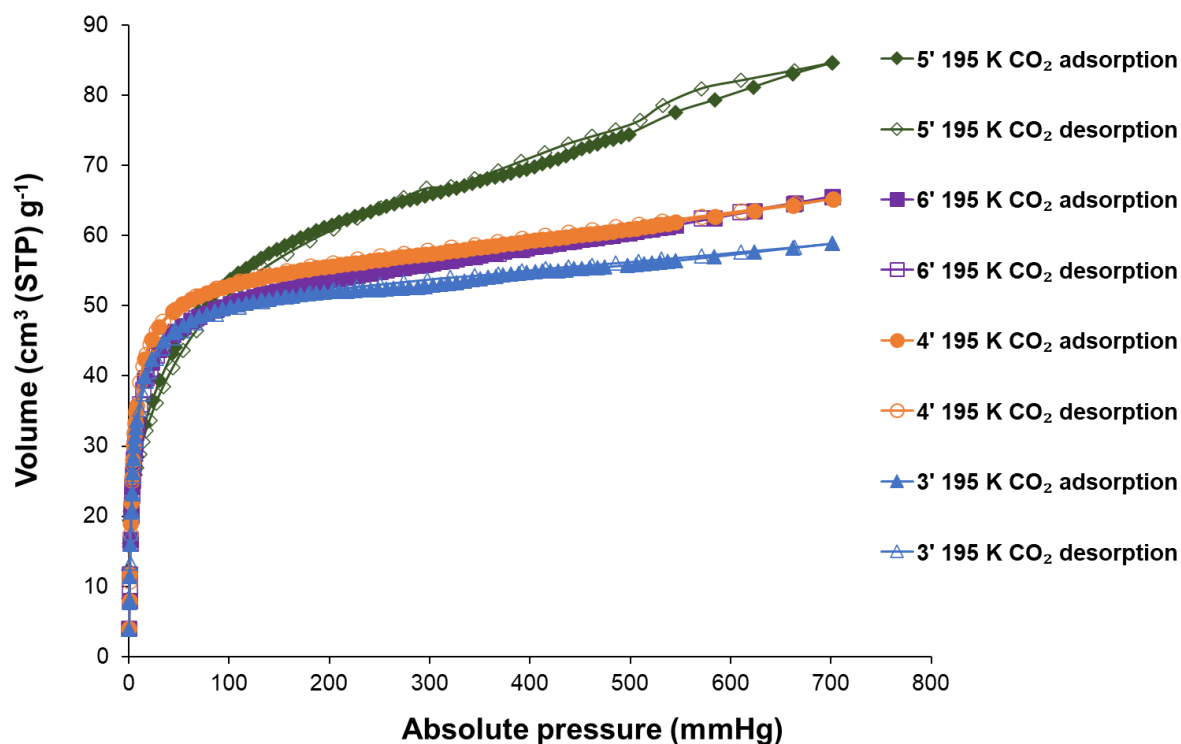


Figure 4.55. Adsorption and desorption isotherms for CO₂ sorption for **3'** – **6'** at 195 K.

The Q_{st} values for **3'**, **4'**, **5'** and **6'** were determined based on CO₂ sorption experiments conducted at 273, 288, and 298 K (Figure 4.56). The average Q_{st} values for **3'** and **6'** are similar, measuring 29.8(0.8) and 29.7(0.3) kJ mol⁻¹, respectively, within their respective loading ranges (Table 4.18). In contrast, the Q_{st} values for **4'** and **5'** are 30.8(0.7) and 28.7(0.4) kJ mol⁻¹, respectively. The Q_{st} values follow the order: **4'** > **3'** ~ **6'** > **5'**, which is inconsistent with the order of the observed sorption capacities.

Although **4'** exhibits the highest Q_{st} , indicating the strongest CO₂-framework interactions, it does not achieve the highest CO₂ sorption capacity and instead ranks below **5'**. Its strong interactions, however, explain its comparable CO₂ sorption capacity to **6'**, despite **4'** having a smaller potential void space. In contrast, the

relatively low Q_{st} of **5'**, despite its high CO₂ sorption capacity, suggests weaker CO₂-framework interactions. This disparity is compensated by **5'**'s high crystallinity and structural flexibility, enabling it to adsorb significantly more CO₂, especially at high pressures, outperforming **4'**. For **3'** and **6'**, their similar Q_{st} values indicate comparable binding interactions with CO₂. However, **6'** archives a slightly higher CO₂ sorption capacity than **3'** due to its larger potential void space. This highlights the complex relationship among adsorbate-adsorbent binding strength, void space, and crystallinity in determining the sorption performance of these MOFs.

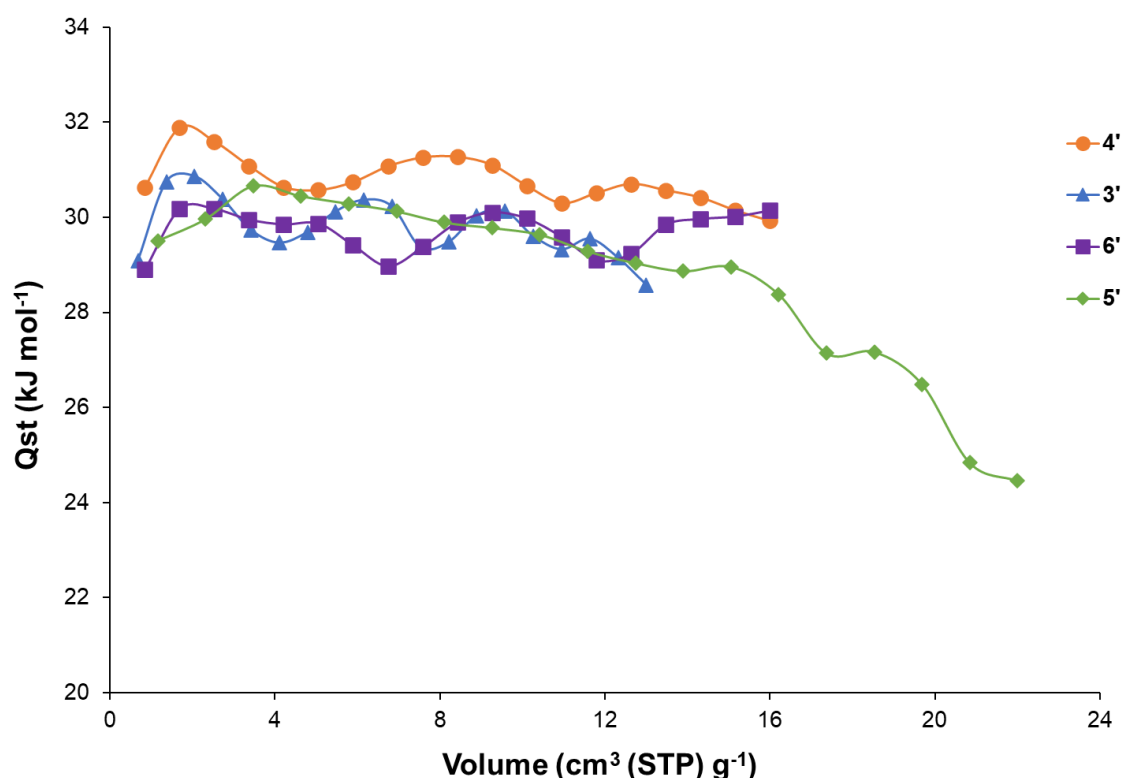


Figure 4.56. Q_{st} values for **3'** – **6'** calculated across different loading ranges using isotherms from 273 – 298 K. Maximum loading ranges correspond to the highest adsorption values from the 298 K isotherms, which showed the lowest overall sorption among the tested temperatures for each activated MOF.

Table 4.18. Q_{st} for **3'** – **6'** determined from CO₂ isotherms over the 273 – 298 K temperature range.

	3'	4'	5'	6'
load range (cm ³ (STP) g ⁻¹)	0.68 – 13.0	0.84 – 16.0	1.15 – 22.0	0.84 – 16.0
average Q_{st} (kJ mol ⁻¹) ^a	29.8(0.8) ^a	30.8(0.7) ^a	28.7(0.4) ^a	29.7(0.3) ^a

^aValues in brackets represent the average uncertainties in Q_{st} , calculated at each loading point by the Micromeritics 3Flex software, and are not standard deviations of the Q_{st} values.

4.10.4. Water Vapour Sorption

The water vapour sorption maxima at $P/P_0 \sim 0.8$ follow the order **6'** > **3'** > **4'** >> **5'**, with values of 24.3, 19.9, and 14.4 cm³ (STP) g⁻¹ for **6'**, **3'**, and **4'**, respectively, which correspond to 0.49, 0.40, and 0.29 H₂O molecules per Zn²⁺-hfipbb²⁻ unit, respectively (Figure 4.57 and Table 4.19). Surprisingly, despite **5'** exhibiting the highest sorption capacities for N₂, CO₂, and H₂ compared to **6'**, **3'**, and **4'**, it shows negligible water sorption, with minimal uptake (~ 0.49 cm³ (STP) g⁻¹). This suggests that the pores of **5'** are significantly more hydrophobic than those of **3'**, **4'**, and **6'**, which contrasts with its strong performance for other gases.

Interestingly, none of the MOFs display a sharp increase in water vapour sorption at lower pressures. This probably indicates that water molecules simultaneously coordinate with uncoordinated metal sites and fill the channels (or the spaces between 2-periodic layers), or that access to the unsaturated metal sites is limited. Upon desolvation, **3'**, **4'**, and **6'** exhibit significant hysteresis, with calculated values of 35.4, 28.9, and 28.5%, respectively, according to the formula used by Barbour *et al.*²¹⁴

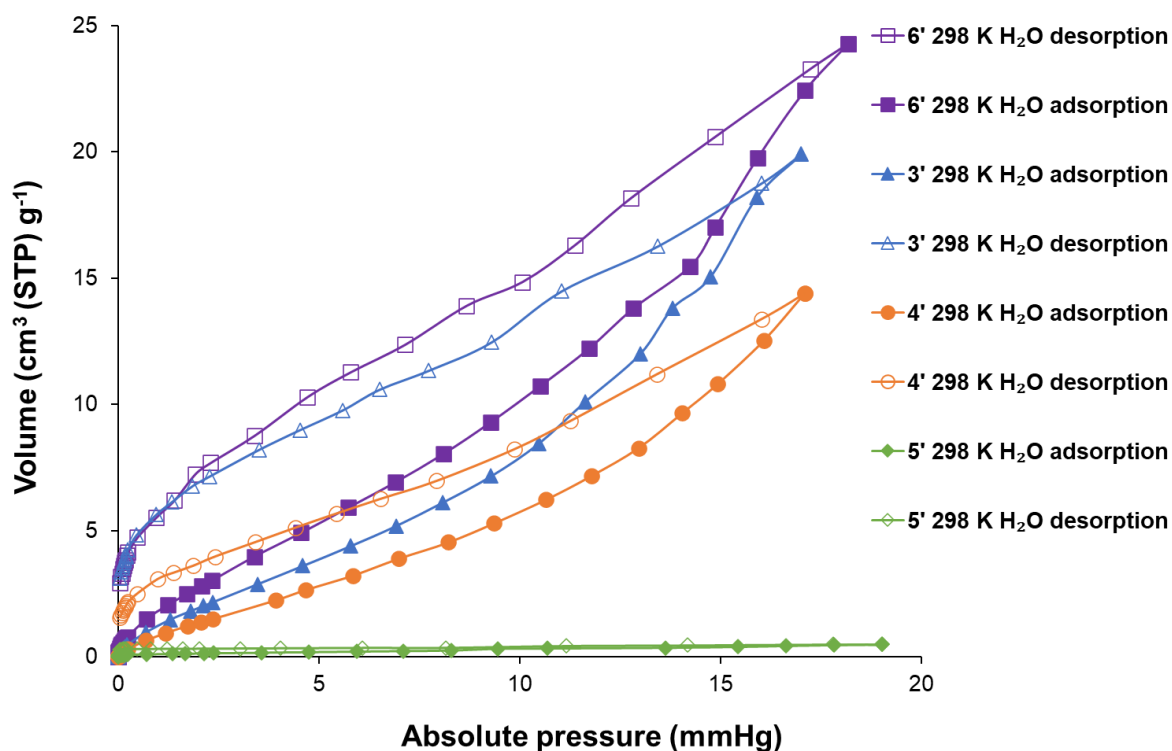


Figure 4.57. Adsorption and desorption isotherms for water vapour sorption at 298 K for **3'** – **6'**.

Table 4.19. H₂O vapour quantity and H₂O molecules adsorbed per Zn²⁺ -hfipbb²⁻ unit for **3'** – **6'** at 298 K.

	H ₂ O vapour adsorption amount (cm ³ (STP) g ⁻¹)	H ₂ O molecules adsorbed per Zn ²⁺ -hfipbb ²⁻ unit
3'	19.9	0.40
4'	14.4	0.29
5'	0.49	-
6'	24.3	0.49

4.11. Comparison of Sorption with Similar MOFs

In this chapter, we have synthesised four closely related 2-periodic MOFs (**3** – **6**) using Zn²⁺, the partially fluorinated ligand 4,4'-(hexafluoroisopropylidene)bis(benzoic acid),

and either MeOH, EtOH, DMF, or DMA as solvents. Our findings revealed that the use of alcohol solvents (MeOH and EtOH) resulted in 2-periodic, doubly interpenetrated MOFs (**3** and **4**), whereas the use of formamide (DMF) and acetamide (DMA) solvents produced non-interpenetrated MOFs (**5** and **6**).

A literature review reveals that these MOFs have analogous structures differing only in the metal ion used. For example, **3** and **4** are similar to structures reported by Leszczyński and Lewiński *et al.*,¹⁹⁸ which contain Cu²⁺ ions instead of Zn²⁺. Calculated PXRD patterns generated using Mercury confirm the structural similarity between **3** and its Cu-based counterpart [**Cu(hfipbb)·MeOH**], as well as between **4** and its Cu-based counterpart [**Cu(hfipbb)·EtOH**], as evidenced by their closely related PXRD patterns (Figure 4.58a and b). For simplicity, **3** and **4**, along with the Cu-based structures reported by Leszczyński and Lewiński *et al.* are referred to as **3(IP)** (IP = interpenetrated), **4(IP)**, **Cu(hfipbb)·MeOH(IP)**, and **Cu(hfipbb)·EtOH(IP)**, respectively, throughout this section.

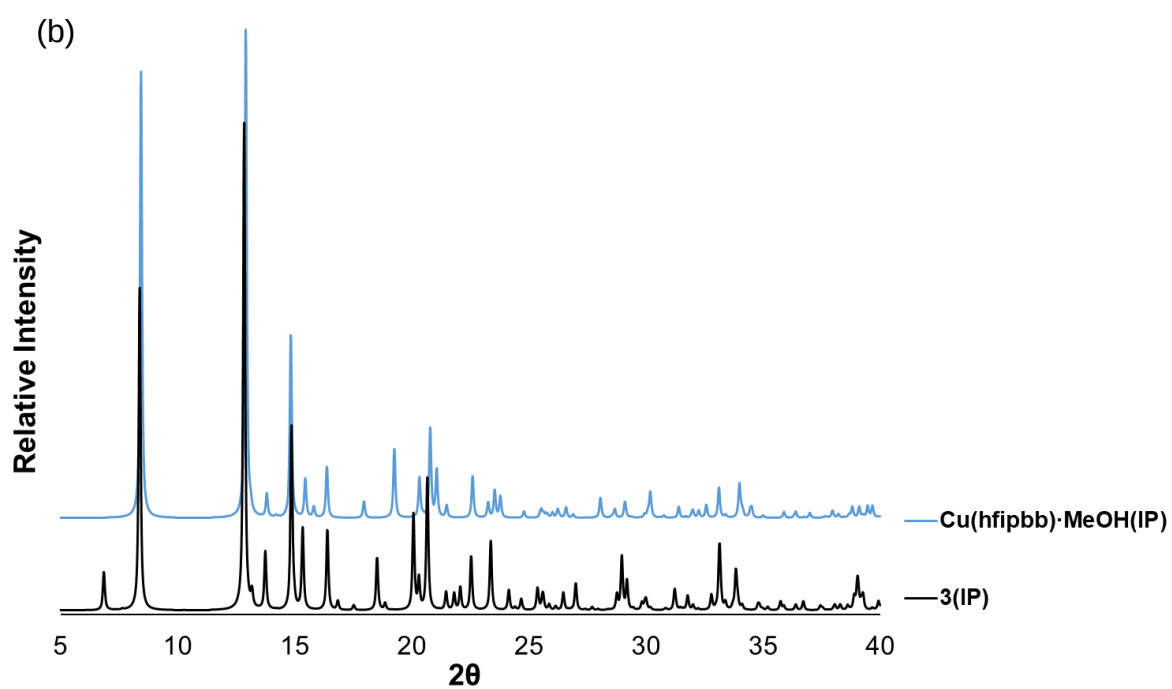
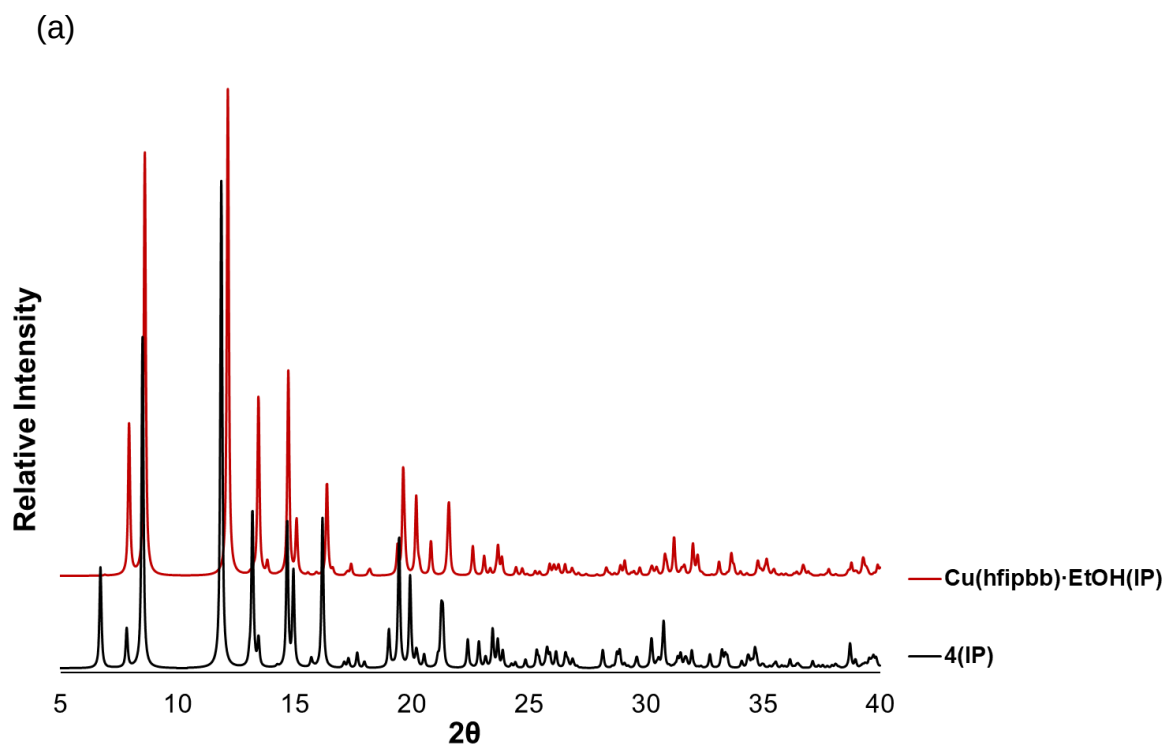


Figure 4.58. Calculated PXRD patterns of (a) **3(IP)** and **Cu(hfipbb)·MeOH(IP)** and, (b) **4(IP)** and **Cu(hfipbb)·EtOH(IP)**.

Similarly, **5** has both non-interpenetrated and doubly interpenetrated Cu-based counterparts. The non-interpenetrated structure, $[\text{Cu}_2(\text{hfipbb})_2(\text{DMF})_2]_n \cdot n(\text{DMF})_4$, reported in Lungelo Bambiso's MSc thesis,²²⁰ closely resembles **5**, as confirmed by their nearly superimposable PXRD patterns (Figure 4.59a). The doubly interpenetrated structure reported by Chatterjee *et al.*,¹²⁸ $[\text{Cu}(\text{hfipbb})(\text{DMF})]_n \cdot 0.5(\text{DMF})_n$, is isorecticular with **5**. However, due to the difference in degree of interpenetration, no PXRD comparison is provided. Similarly, **6** has an analogous non-interpenetrated structure, $[\text{Cu}_3(\text{hfipbb})_3(\text{DMA})_3]_n \cdot 6(\text{DMA})_n \cdot 2(\text{H}_2\text{O})_n$, also reported by Chatterjee *et al.*,¹²⁸ which aligns closely with **6**, as confirmed by PXRD patterns (Figure 4.59b).

For simplicity, we refer to **5** and **6** as **5(NIP)** (NIP = non-interpenetrated) and **6(NIP)**, respectively. Bambiso's structure, $[\text{Cu}_2(\text{hfipbb})_2(\text{DMF})_2]_n \cdot n(\text{DMF})_4$ is depicted as **Cu(hfipbb)DMF(NIP)**, while Chatterjee *et al.*'s structures, $[\text{Cu}(\text{hfipbb})(\text{DMF})]_n \cdot 0.5(\text{DMF})_n$ and $[\text{Cu}_3(\text{hfipbb})_3(\text{DMA})_3]_n \cdot 6(\text{DMA})_n \cdot 2(\text{H}_2\text{O})_n$, are referred to as **Cu(hfipbb)DMF(IP)** and **Cu(hfipbb)DMA(NIP)**, respectively.

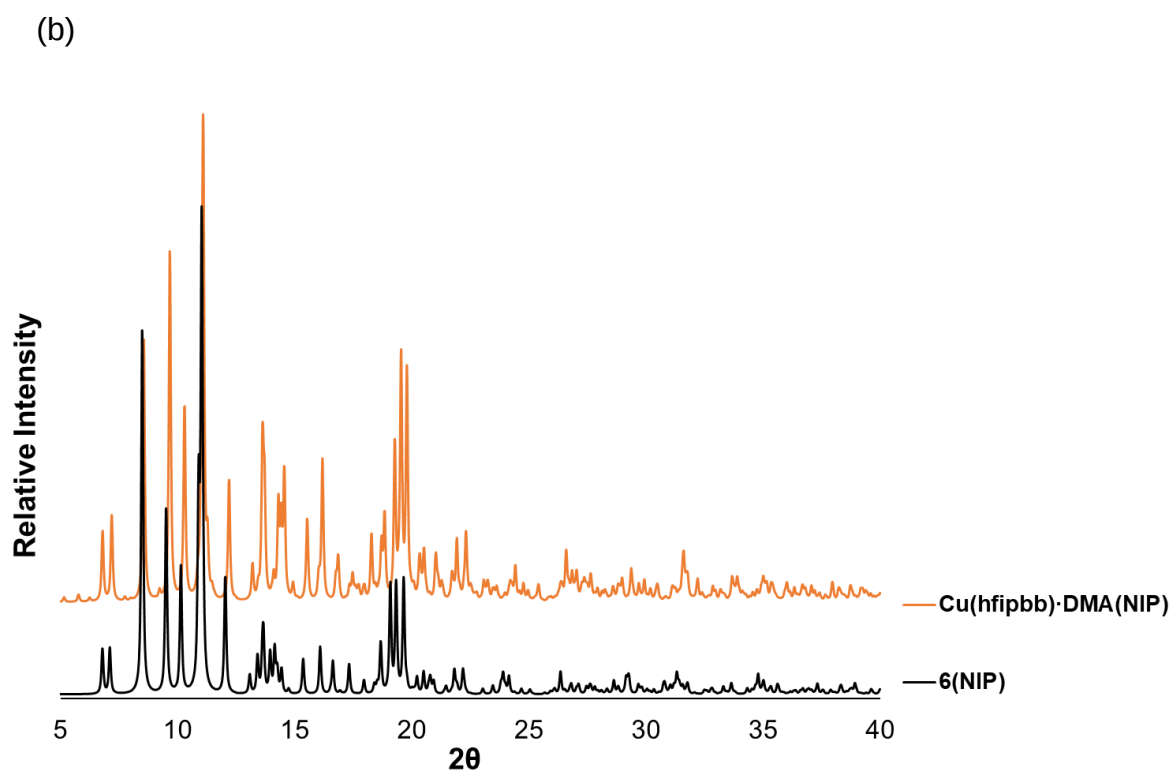
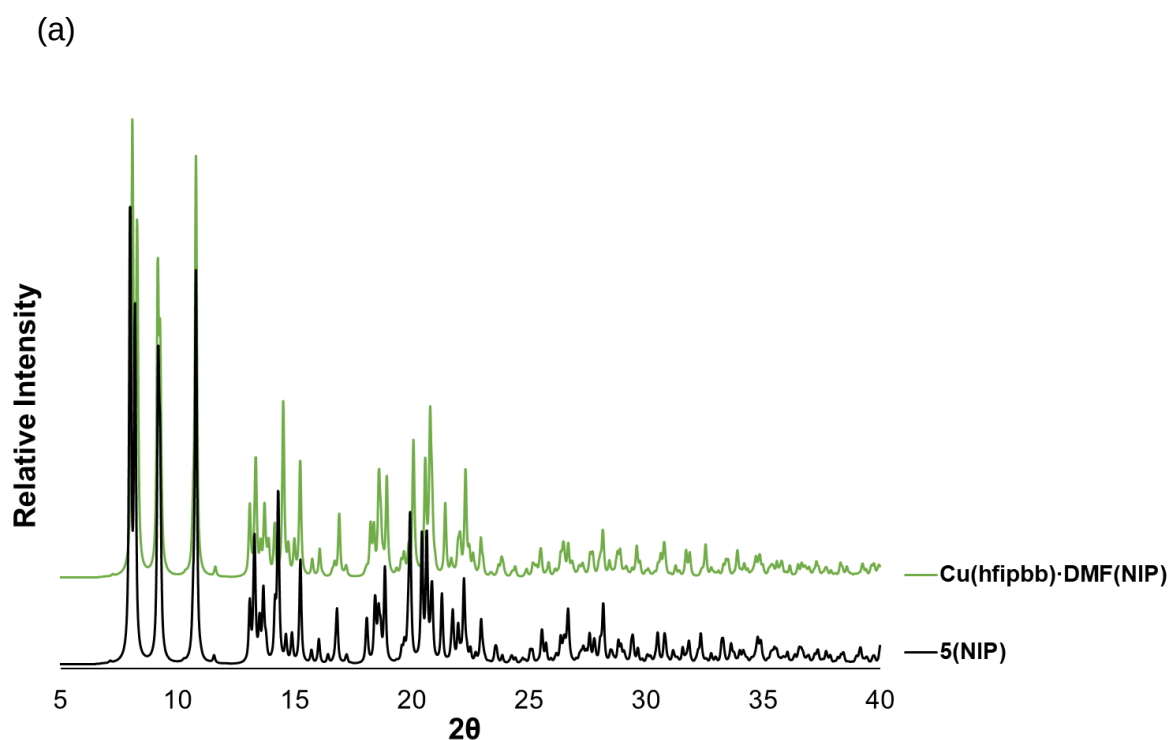


Figure 4.59. Calculated PXRD patterns of (a) **5(NIP)** and **Cu(hfipbb)·DMF(NIP)** and, (b) **6(NIP)** and **Cu(hfipbb)·DMA(NIP)**.

4.11.1. Void Space Comparison

The comparison of potential void spaces (Table 4.20), considering only the channel void spaces based on the assumption that the layers of the 2-periodic frameworks shift closer together upon solvent removal (leaving voids exclusively within the channels), reveals consistent trends in both interpenetrated and non-interpenetrated MOFs. For interpenetrated structures, **Cu(hfipbb)·MeOH(IP)** exhibit a slightly larger void space (13.5%) compared to **3(IP)** (12.9%), and **Cu(hfipbb)·EtOH(IP)** similarly shows a slightly larger void space (12.4%) compared to **4(IP)** (12.0%). These similarities are consistent with the analogous structural designs of the Zn- and Cu-based frameworks, as their metal centers and ligands adopt nearly identical geometries.

Table 4.20. Percentage potential void space for **3(IP)**, **4(IP)**, **5(NIP)**, **6(NIP)** and their Cu-based counterparts.

Description	Percentage (%) potential void space with channel-only solvent removed
3(IP)	12.9
Cu(hfipbb)·MeOH(IP)	13.5*
4(IP)	12.0
Cu(hfipbb)·EtOH(IP)	12.4*
5(NIP)	24.2
Cu(hfipbb)·DMF(NIP)	22.6
Cu(hfipbb)·DMF(IP)	10.7
6(NIP)	25.4
Cu(hfipbb)·DMA(NIP)	18.4

An asterisk (*) denotes void space values calculated by the author using Mercury, as these were not specified in the original publication.

For non-interpenetrated structures, **6(NIP)** has the largest potential void space (25.4%), followed by **5(NIP)** (24.2%). Both outperform than their Cu-based counterparts, **Cu(hfipbb)·DMA(NIP)** (18.4%) and **Cu(hfipbb)·DMF(NIP)** (22.6%). The interpenetrated Cu-based MOF, **Cu(hfipbb)·DMF(IP)**, has the lowest potential void space (10.7%), consistent with the reduced void space expected from interpenetration.

4.11.2. Gas Sorption Comparison

N₂ Sorption

Zn-based MOFs significantly outperform Cu-based MOFs in N₂ adsorption, with higher sorption values observed across all Zn-based frameworks (Table 4.21). The superior performance of Zn-based MOFs can be attributed to their higher degree of crystallinity upon desolvation, as revealed by VT-PXRD analysis (Figure 4.60). The greater crystallinity of the Zn-based MOFs could reflect a more rigid and stable framework that better preserves the ordered pore structure, potentially facilitating greater accessibility for N₂ molecules. Due to the low N₂ adsorption capacities of the Cu-based MOFs, BET surface areas were not determined, preventing direct comparison with the Zn-based MOFs.

Table 4.21. Reported gas and water vapour sorption properties for **3(IP)**, **4(IP)**, **5(NIP)**, **6(NIP)** and their Cu-based 2-periodic counterparts.

Description	N ₂ (77 K)	H ₂ (77 K)	CO ₂ (195 K)	CO ₂ (298 K)	H ₂ O (298 K)
3(IP)	0.58	1.08	1.20	0.28	0.40
Cu(hfipbb)·MeOH(IP)	~0.30	~0.65	-	~0.45	-
4(IP)	1.17	1.17	1.33	0.34	0.29
Cu(hfipbb)·EtOH(IP)	~0.40	~0.53	-	~0.34	-
5(NIP)	2.24	1.47	1.72	0.46	~0
Cu(hfipbb)·DMF(NIP)	~0	1.23	1.45	0.39	1.12
Cu(hfipbb)·DMF(IP)	~0	1.05	3.58	0.71	0.92
6(NIP)	1.78	1.13	1.33	0.34	0.49
Cu(hfipbb)·DMA(NIP)	~0	0.91	1.15	0.26	1.21

All sorption values for gases and water vapour are presented in terms of gas or water molecules per M²⁺-hfipbb²⁻ unit (M = Zn/Cu) for better comparison. A dash (“-”) indicates that the value was not provided in the original article. A tilde (“~”) precedes a calculated estimate made by the author of this thesis where, in the original publication, a maximum sorption value was not reported but a sorption graph was provided.

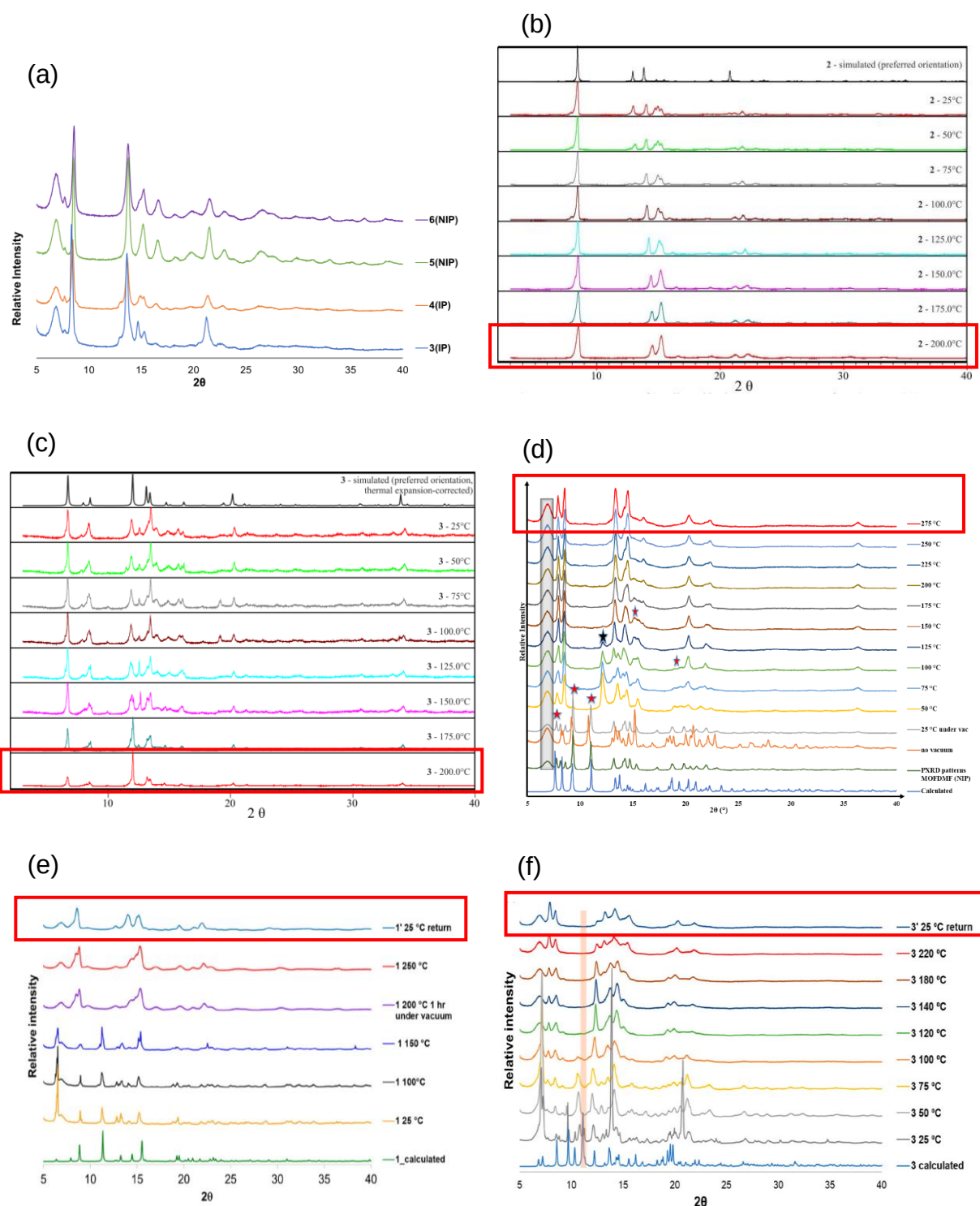


Figure 4.60. (a) PXR patterns of the desolvated structure **3(IP)**, **4(IP)**, **5(NIP)**, and **6(NIP)**. VT-PXR patterns of (b) $\text{Cu(hfipbb)·MeOH(IP)}$,¹⁹⁸ (c) $\text{Cu(hfipbb)·EtOH(IP)}$,¹⁹⁸ (d) $\text{Cu(hfipbb)·DMF(NIP)}$,²²⁰ (e) $\text{Cu(hfipbb)·DMF(IP)}$,¹²⁸ and (f) $\text{Cu(hfipbb)·DMA(NIP)}$,¹²⁸ obtained from their original publication, with the final desolvated phase for each highlighted by a red box.

H₂ Sorption

In H₂ sorption, Zn-based MOFs again show superior adsorption (Table 4.21), particularly **3(IP)** (1.08 H₂ molecules per Zn²⁺-hfipbb²⁻ unit) and **4(IP)** (1.17 H₂ molecules per Zn²⁺-hfipbb²⁻ unit) compared to their Cu-based counterparts, **Cu(hfipbb)·MeOH(IP)** and **Cu(hfipbb)·EtOH(IP)** (~0.65 and 0.53 H₂ molecules per Cu²⁺-hfipbb²⁻ unit, respectively). Notably, this trend persists despite the slightly larger potential void spaces in Cu-based MOFs, suggesting that void space alone is not the primary determinant of H₂ adsorption. Instead, the enhanced performance of Zn-based frameworks may be attributed to stronger Zn-H₂ interactions. H₂ sorption isotherms support this conclusion, showing a steeper increase in H₂ sorption at lower pressures than their Cu-based counterparts, which is indicative of stronger H₂-MOF interactions in Zn-based frameworks.

Among non-interpenetrated MOFs, **5(NIP)** achieves the highest H₂ adsorption (1.47 H₂ molecules per Zn²⁺-hfipbb²⁻ unit), surpassing both **Cu(hfipbb)·DMF(NIP)** (1.23 H₂ molecules per Cu²⁺-hfipbb²⁻ unit) and **Cu(hfipbb)·DMF(IP)** (1.05 H₂ molecules per Cu²⁺-hfipbb²⁻ unit). The larger potential void space of **5(NIP)** compared to its Cu-based counterparts directly correlates with its higher adsorption capacity. Similarly, **6(NIP)** exhibits higher H₂ adsorption (1.13 H₂ molecules per Zn²⁺-hfipbb²⁻ unit) than **Cu(hfipbb)·DMA(NIP)** (0.91 H₂ molecules per Cu²⁺-hfipbb²⁻ unit), which aligns with its larger potential void space.

Interestingly, Cu-based MOFs display significant hysteresis during H₂ desorption, unlike their Zn-based counterparts. This suggests that although Cu-based MOFs adsorb less H₂, they retain it more strongly.

CO₂ Sorption

CO₂ adsorption results reveal subtle differences between Zn- and Cu-based MOFs (Table 4.21). At 298 K, **Cu(hfipbb)·MeOH(IP)** adsorbs more CO₂ (~0.45 CO₂ molecules per Cu²⁺-hfipbb²⁻ unit) than **3(IP)** (0.28 CO₂ molecules per Zn²⁺-hfipbb²⁻ unit), and **Cu(hfipbb)·EtOH(IP)** matches the performance of **4(IP)** (~0.34 CO₂ molecules per Cu²⁺/Zn²⁺-hfipbb²⁻ unit). The interpenetrated Cu-based MOF, **Cu(hfipbb)·DMF(IP)**, displays the highest CO₂ adsorption (0.71 CO₂ molecules per Cu²⁺-hfipbb²⁻ unit), surpassing all non-interpenetrated Zn-based MOFs (**5(NIP)** (0.46 CO₂ molecules per Zn²⁺-hfipbb²⁻ unit) and **6(NIP)** (0.34 CO₂ molecules per Cu²⁺-hfipbb²⁻ unit)) despite its smaller potential void space. Among the non-interpenetrated Cu-based MOFs, **Cu(hfipbb)·DMF(NIP)** and **Cu(hfipbb)·DMA(NIP)**, exhibit CO₂ adsorption capacities of 0.39 and 0.26 CO₂ molecules per Cu²⁺-hfipbb²⁻ unit, respectively, which are both less than their Zn-based counterparts.

At 195 K, CO₂ sorption measurements were not available for **Cu(hfipbb)·MeOH(IP)** and **Cu(hfipbb)·EtOH(IP)**, so no comparison can be made with **3(IP)** and **4(IP)**. Among MOFs measured at this temperature, **Cu(hfipbb)·DMF(IP)** again shows the highest uptake (3.58 CO₂ molecules per Cu²⁺-hfipbb²⁻ unit), followed by **5(NIP)** (1.72 CO₂ molecules per Zn²⁺-hfipbb²⁻ unit) and **Cu(hfipbb)·DMF(NIP)** (1.45 CO₂ molecules per Cu²⁺-hfipbb²⁻ unit). **6(NIP)** adsorbs more CO₂ than **Cu(hfipbb)·DMA(NIP)**, with values of 1.33 and 1.15 CO₂ molecules per Zn²⁺/Cu²⁺-hfipbb²⁻ unit, respectively.

Notably, **Cu(hfipbb)·DMF(IP)** adsorbs more CO₂ despite having a smaller void space than **5(NIP)**. The authors have attributed this high sorption capacity to the flexibility of

its interpenetrated structure, as evidenced by a two-step adsorption isotherm with a very steep second increase and the large extent of hysteresis during desorption, indicating that the MOF holds onto CO₂ molecules more tightly. In comparison, **5(NIP)** exhibits a nearly Type-I isotherm with a much less pronounced inflection point, minimal structural changes, and little hysteresis, reflecting its significantly reduced flexibility relative to its Cu-based counterpart. Even non-interpenetrated **Cu(hfipbb)·DMF(NIP)** shows two-step adsorption and significant hysteresis, though its sorption is lower than **5(NIP)**, suggesting that Cu-based MOFs exhibit greater flexibility than the Zn-based counterpart.

The Q_{st} values offer deeper insight into the strength of CO₂ adsorption interactions. However, Q_{st} values were not reported for **Cu(hfipbb)·MeOH(IP)** and **Cu(hfipbb)·EtOH(IP)**, so no comparison is made with **3(IP)** and **4(IP)**. Among the measured MOFs, Cu-based MOFs generally exhibit higher Q_{st} values, reflecting stronger CO₂-framework interactions (Table 4.22). **Cu(hfipbb)·DMF(IP)** has the highest Q_{st} value (31.8 kJ mol⁻¹), followed closely by **Cu(hfipbb)·DMF(NIP)** (31.7 kJ mol⁻¹), both surpassing the Q_{st} of **5(NIP)** (28.7 kJ mol⁻¹). Interestingly, **6(NIP)** (29.7 kJ mol⁻¹) shows slightly weaker CO₂ adsorption interactions compared to its Cu-based counterpart, **Cu(hfipbb)·DMA(NIP)** (30.2 kJ mol⁻¹), despite **6(NIP)** adsorbing more CO₂. This suggests that the increased adsorption capacity of **6(NIP)** is likely due to its larger void space, which accommodates more CO₂, rather than stronger adsorption interactions.

Table 4.22. Comparison of Q_{st} values for **3(IP)**, **4(IP)**, **5(NIP)**, **6(NIP)** with Cu-based counterparts from literature.

Description	Average Q_{st} (kJ mol ⁻¹)
3(IP)	29.8
Cu(hfipbb)·MeOH(IP)	-
4(IP)	30.8
Cu(hfipbb)·EtOH(IP)	-
5(NIP)	28.7
Cu(hfipbb)·DMF(NIP)	31.7
Cu(hfipbb)·DMF(IP)	31.8
6(NIP)	29.7
Cu(hfipbb)·DMA(NIP)	30.2

A dash ("-") indicates that the value was not reported in the original publication.

H₂O Vapour Sorption

Cu-based MOFs outperform Zn-based MOFs in water vapour sorption. The water vapour uptake values follow the trend: **Cu(hfipbb)·DMA(NIP) > Cu(hfipbb)·DMF(NIP) > Cu(hfipbb)·DMF(IP) > 6(NIP) > 3(IP) > 4(IP) >> 5(NIP)**, with corresponding adsorption values of 1.21, 1.12, 0.92, 0.49, 0.40, 0.29 and ~0 H₂O molecules per M²⁺-hfipbb²⁻ unit, respectively, (Table 4.21).

Notably, Cu-based MOFs exhibit higher water vapour adsorption than their Zn-based counterpart. This is likely due to differences in the mode of interaction between water molecules and the metal centers in Cu- and Zn-based MOFs. For instance, Cu-based MOFs show a steep uptake of water vapour at low pressure, indicating strong adsorption at unsaturated Cu²⁺ metal sites. In contrast, no steep uptake is observed

in the Zn-based MOFs, indicating restriction to the unsaturated Zn^{2+} metal sites. Interestingly, while **5(NIP)** shows negligible water adsorption, its Cu-based counterpart, **Cu(hfipbb)·DMF(NIP)**, demonstrates substantial water sorption, adsorbing more than one water molecule per Cu^{2+} -hfipbb $^{2-}$ unit.

4.12. Summary

Two pairs of Zn(II)-based, 2-periodic single-ligand MOFs were synthesised using 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) as the ligand. The first pair, $[\text{Zn}(\text{hfipbb})(\text{MeOH})]_n \cdot n(\text{MeOH})_{0.5}$ (**3**) and $[\text{Zn}(\text{hfipbb})(\text{EtOH})]_n \cdot n(\text{EtOH})_{0.5}$ (**4**), formed doubly interpenetrated frameworks, while the second pair, $[\text{Zn}_2(\text{hfipbb})_2(\text{DMF})_2]_n \cdot n(\text{DMF})_4$ (**5**) and $[\text{Zn}_4(\text{hfipbb})_4(\text{DMA})_4]_n \cdot n(\text{DMA})_8 \cdot n(\text{H}_2\text{O})$ (**6**), featured non-interpenetrated structures.

VT-PXRD experiments revealed that all MOFs underwent structural changes upon solvent removal, leading to shifts in their 2-periodic layers. Among them, **5** exhibited the highest degree of crystallinity in its desolvated phase.

Although **5** had the second largest potential void space, it exhibited the highest sorption capacity for N_2 , H_2 , and CO_2 , attributed to its superior crystallinity. However, it showed negligible water vapour sorption, indicating a hydrophobic nature. Despite having a smaller potential void space than **6**, **4'** displayed comparable H_2 and CO_2 sorption, likely due to stronger interactions with gas molecules, as evidenced by its steep H_2 uptake at lower pressures and higher Q_{st} values for CO_2 . **6'** exhibited the highest water vapour sorption with pronounced hysteresis, likely due to its larger potential void space. **3'** on the other hand, displayed the highest hysteresis percentage

in water vapour sorption, indicating strong interactions with the water molecules, further supported by its ability to undergo water exchange.

A comparison with structurally analogous Cu-based MOFs highlighted key differences in gas sorption behaviour. Zn-based MOFs generally outperformed their Cu-based counterparts in N₂ and H₂ adsorption, with **5'** showing remarkably high N₂ uptake. However, Cu-based MOFs exhibited stronger interactions with CO₂, as evidenced by their two-step CO₂ adsorption isotherms, significant hysteresis, and higher Q_{st} values. Cu-based MOFs again outperform their Zn-based counterparts for water vapour sorption, likely due to stronger interactions with unsaturated metal sites.

Chapter 5:

Summary and Future Work

This chapter summarises the key findings of this research project and discusses potential future work. A total of six 2-periodic MOFs were synthesised and fully characterised, including two mixed-ligand MOFs and four single-ligand MOFs. Comprehensive characterisation was achieved through X-ray diffraction studies and thermal analysis. Additionally, gas and water vapour sorption experiments were conducted to evaluate the sorption properties of all the MOFs. The chapter also highlights directions for future research, building on the results obtained in this study.

5.1. Summary

5.1.1. Mixed-ligand MOFs (1 and 2)

Two novel mixed-ligand MOFs, $[\text{Co}_3(\text{ia})_3(\text{bppdo})(\text{MeOH})]_n \cdot n(\text{DMF})$ (**1**) and $[\text{Mn}_3(\text{ia})_3(\text{bppdo})(\text{MeOH})]_n \cdot n(\text{DMF})$ (**2**), were synthesised via solvothermal methods using isophthalic acid and 1,3-bis(4-pyridyl)propane-*N,N'*-dioxide (bppdo) as ligands. Cobalt(II) metal salt was used for **1**, while manganese(II) was used for **2**. Single-crystal analysis revealed that both MOFs adopt isorecticular and isostructural 2-periodic frameworks, as evidenced by their similar unit cell parameters and connectivity through linear trinuclear clusters. The frameworks stack in an interdigitated fashion and incorporate coordinated MeOH and uncoordinated DMF solvent molecules. Thermal analysis (TGA and DSC) showed that both MOFs are stable up to 347 - 361 °C.

VT-SCXRD was performed at 298, 323, 373, 473, 298, and 195 K to investigate structural changes during desolvation and subsequent exposure to atmospheric moisture. These analyses confirmed SCSC transformation with temperature-induced dynamic behaviour. During desolvation, the isophthalate ligands rotated, causing a significant reduction in void space, from 21.6 and 22.3% for **1** and **2**, respectively, to 3.7 and 5.7% for the desolvated structures (**1'** and **2'**). Additionally, upon exposure to the atmosphere, the bppdo ligand underwent a conformational shift from the *anti-anti* to the less stable *anti-gauche* form, demonstrating the adaptability of the frameworks to external stimuli.

Despite reduced void spaces after desolvation, both MOFs exhibited substantial gas sorption properties. CO₂ sorption at 195 K revealed distinct behaviours: **1'** exhibited a stepwise adsorption profile indicative of pressure-induced gate-opening effects, while

2' displayed a typical type-I isotherm. **1'** achieved nearly double the CO₂ uptake of **2'**, attributed to the greater flexibility of the Co-based framework. Water vapour sorption at 298 K also highlighted the structural responsiveness of both frameworks, with **1'** showing higher water uptake and hysteresis compared to **2'**.

The study underscores the dynamic nature and structural adaptability of these MOFs, with particular emphasis on their potential for gas capture applications, especially CO₂ storage. The Co-based MOF demonstrated superior flexibility and performance compared to the Mn-based MOF.

5.1.2. Single-ligand MOFs (3, 4, 5 and 6)

Four Zn(II)-based, 2-periodic single-ligand MOFs were synthesised using 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (H₂hfipbb) as the ligand. These MOFs include, [Zn(hfipbb)(MeOH)]_n·n(MeOH)_{0.5} (**3**), [Zn(hfipbb)(EtOH)]_n·n(EtOH)_{0.5} (**4**), [Zn₂(hfipbb)₂(DMF)₂]_n·n(DMF)₄ (**5**) and [Zn₄(hfipbb)₄(DMA)₄]_n·n(DMA)₈·n(H₂O) (**6**). Single crystal analysis confirmed that all four MOFs have 2-periodic frameworks connected by binuclear paddlewheel SBUs. Interpenetration occurs in **3** and **4** but is absent in **5** and **6**. **3** and **4** incorporate ligated solvent molecules between their layers, as well as uncoordinated solvent molecules in their channels. In contrast, **5** and **6** contain ligated solvent molecules between the layers and uncoordinated solvent molecules both between the layers and in the channels.

Thermal analysis (TGA and DSC) revealed that all MOFs remained stable up to approximately 430 °C, indicating that the structural integrity of the frameworks is not significantly affected by the type of solvent molecule present before desolvation.

VT-PXRD analysis showed that both interpenetrated and non-interpenetrated frameworks undergo structural changes upon desolvation. These changes shift the 2-periodic layers, limiting the potential void spaces to the channel. Interestingly, although the as-synthesised MOFs exhibit different PXRD patterns due to the presence of different solvents, they display similar PXRD patterns in their desolvated phase. This suggests that during desolvation, they transition into similar phase, where the 2-periodic layers shift closer together. Notably, **5** exhibits the highest degree of crystallinity in its desolvated phase compared to the others. Water-exchange studies in **3** provided insight into structural rearrangements occurring during solvent removal. **3** was the only framework that allowed for the replacement of coordinated methanol with water molecules while retaining its monocrystallinity.

Gas sorption analysis revealed distinct adsorption behaviours among the MOFs. **5** exhibited the highest gas uptake for N₂, H₂, and CO₂, despite having the second-largest potential void space, attributed to its superior crystallinity. However, **5** showed negligible water vapour sorption, indicating strong hydrophobicity. Interestingly, **4'** displayed comparable H₂ and CO₂ adsorption to **6'**, despite having a smaller void space. This was attributed to stronger framework-gas interactions, as evidenced by its sharp increase in H₂ uptake at lower temperatures and higher Q_{st} values for CO₂, indicating a stronger interaction with gas molecules. **6'** exhibited the highest water vapour uptake, accompanied by significant hysteresis, likely due to its larger void space. Meanwhile, **3'** displayed the highest percentage of hysteresis in water sorption, suggesting strong water-framework interactions, consistent with its ability to undergo water exchange.

A comparison with structurally analogous Cu-based MOFs highlighted key differences in gas sorption properties. Zn-based MOFs generally outperformed Cu-based MOFs

in N₂ and H₂ adsorption, with **5'** showing particularly high N₂ uptake. However, Cu-based MOFs exhibited stronger interactions with H₂ and CO₂, as indicated by their two-step CO₂ adsorption isotherms, pronounced hysteresis, and higher Q_{st} values. Additionally, Cu-based MOFs demonstrated superior water vapour sorption, likely due to stronger interactions with unsaturated metal sites.

5.2. Final Remarks and Future Work

5.2.1. Conclusions

This study successfully synthesised and characterised two novel mixed-ligand Co(II)/Mn(II)-based MOFs and four single-ligand Zn(II)-based MOFs, providing valuable insights into their structural adaptability, thermal stability, and gas sorption properties. The mixed-ligand MOFs demonstrated dynamic structural behaviour, with the Co-based framework exhibiting enhanced flexibility during sorption, making it a promising candidate for adaptive sorption-based applications.

For the Zn(II)-based MOFs, the findings highlight the critical influence of structural features, interpenetration, and solvent coordination on their thermal stability and adsorption behaviour. Framework crystallinity, flexibility, and gas interactions played key roles in performance, with **5** achieving the highest uptake for N₂, H₂, and CO₂. A comparison with Cu-based analogues further underscored the tunability of MOF properties based on metal selection, where Zn-based MOFs generally showed higher gas uptake, whereas Cu-based MOFs exhibited greater flexibility and stronger framework-gas interactions.

5.2.2. Future Work

Future research on **1** and **2** could focus on determining the precise location of CO₂ within the MOF framework to enhance understanding of the adsorption mechanism and factors influencing hysteresis. Investigating structural changes during CO₂ adsorption and desorption may provide valuable insights into host-guest interactions and adsorption pathways, contributing to the development of more efficient sorbent materials. For **3**, **4**, **5**, and **6**, future studies should aim to obtain the crystal structures of the activated phases of the MOFs, with particular emphasis on **5**, which exhibited a higher degree of crystallinity. This was not achievable in the present study due to the small crystal size of **5**, which precluded VT-SCRXD experiments. However, further investigations into the crystal structures of the activated phases are warranted, as they could reveal subtle structural features that influence sorption properties.

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