

Imperial College London

**Silicon-Based Hexacarboxylic Acids and Their Application
in Metal-Organic Frameworks**

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A Thesis Submitted in Partial Fulfilment of the Requirements for the

Degree of

DOCTOR OF PHILOSOPHY

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September 2025

Declaration of Originality

I hereby declare that the work presented in this thesis is my own, carried out in the Department of Chemistry at Imperial College London between October 2021 and September 2025. This work has not been submitted, either in whole or in part, for the award of any other degree at this or any other university. All external works used in this thesis have been properly cited within the text, and a complete reference list is provided in the References section. Appropriate rights and permissions have been obtained where necessary.

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Abstract

Metal-Organic Frameworks (MOFs) represent a rapidly expanding class of crystalline materials characterised by their tuneable porosity and modular design. These materials offer exceptional versatility in both structure and function, making them attractive candidates for a wide range of applications. The development of new MOFs depends greatly on the design of novel organic linkers, as they play a crucial role in determining both the structure and the properties of the resulting frameworks. Chapter 1 introduces MOF chemistry, covering its historical background, key design and synthesis strategies, activation and characterisation methods, and the use of organosilicon multicarboxylic acids ($n_{\text{COOH}} \geq 3$) in MOF synthesis. Chapter 2 outlines the synthetic approaches toward organosilicon multicarboxylic acids and details the preparation of organosilicon hexacarboxylic acids featuring different cores and functional groups. Ten hexacarboxylic acid compounds were synthesised and characterised using various techniques. Chapter 3 introduces hydrogen-bonded organic frameworks (HOFs), presenting notable examples based on multicarboxylic acids and discussing the X-ray crystal structures of hexacarboxylic acid compounds prepared in this study that form HOFs. Chapter 4 explores the use of **L1-H₆** and **L4-H₆** in 3D MOF synthesis. Eleven novel 3D MOFs were synthesised by treating **L1-H₆** with a variety of metals, including trivalent, divalent and monovalent metals. These reactions yielded MOFs with a range of topologies, including rare **nia** and **fsy** nets. In addition, the reaction of **L4-H₆** with $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ afforded **L4-In** with **nia** topology, isorecticular to **L1-In**. The use of water stable **L1-Fe** and **L1-Fe-Cl** MOFs as adsorbents for phosphate and perfluorooctanoic acid (PFOA) removal from aqueous solutions is described in Chapter 5. **L1-Fe-Cl** showed higher adsorption capacities for phosphate (27.18 mg/g) than **L1-Fe**, and an outstanding capacity for PFOA (795 mg/g), and excellent

recyclability. These findings confirm the potential of **L1-Fe**-based MOFs as efficient adsorbents for the removal of phosphate and PFOA from contaminated water sources.

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Acknowledgement

First, I would like to thank my sponsor, Kuwait University, for supporting me throughout my PhD journey, as well as the Kuwaiti Cultural Office at the Kuwait Embassy in London. Without their support, pursuing a PhD would have remained only a dream.

I would also like to express my deepest gratitude to my supervisors, Dr. Robert Davies and Prof. Paul Lickiss, for their continuous support, valuable advice, careful proofreading of this thesis, and for always being there for me since day one. I am also thankful to the former members of the Davies group, Dr. Luke Delmas, Dr. Shouyi Tian and Dr. Nudrat Mubarik, for helping me settle into the laboratory and for their helpful advice regarding this project whenever I needed. I would also like to thank my colleague Fauzi Abdilah and all the members of the Davies group for creating a supportive and enjoyable lab environment.

Special thanks to Dr. Peter Horton from the UK National Crystallographic Service for solving the crystal structures, Peter Haycock for the NMR service, Malgorzata Puchnarewicz for her assistance with mass spectrometry, and Dr. Patricia Curry for the BET analysis service.

Finally, my deepest thanks go to my parents, siblings, and friends for their endless love, encouragement, and belief in me from the very beginning of this journey. I am also very grateful to my fiancée, soon to be my wife, she has been one of my greatest motivations and inspirations to work hard and complete this degree.

List of abbreviations

AcOH	Acetic Acid
AFMOFs	Amide-Functionalised Metal–Organic Frameworks
ATR	Attenuated Total Reflection
Ar	<i>p</i> -carboxyphenyl (<i>p</i> -C ₆ H ₄ CO ₂ H)
BDC	Benzenedicarboxylic Acid
BET	Brunauer–Emmett–Teller
BPY	4,4'-Bipyridine
Bu	Butyl
CCDC	Cambridge Crystallographic Data Centre
CSD	Cambridge Structural Database
DEF	<i>N,N</i> -Diethylformamide
DMA	<i>N,N</i> -Dimethylacetamide
DMF	<i>N,N</i> -Dimethylformamide
DMSO	Dimethyl Sulfoxide
DVS	Dynamic Vapour Sorption
EI	Electron Impact Ionization
Eq.	Equivalents
ESI	Electrospray Ionization
Ex situ	Outside the original environment
FTIR	Fourier-Transform Infrared Spectroscopy
HMBC	Heteronuclear Multiple Bond Correlation
HOF	Hydrogen-Bonded Organic Framework
In situ	Within the original environment
IR	Infrared Spectroscopy

IRMOF	Isorecticular Metal–Organic Framework
IUPAC	International Union of Pure and Applied Chemistry
MC	Mechanochemical
Me	Methyl group
MeCN	Acetonitrile
MeOH	Methanol
MOF	Metal–Organic Framework
M.p.	Melting Point
MS	Mass Spectrometry
MW	Microwave-Assisted
NMP	<i>N</i> -Methyl-2-pyrrolidone
NMR	Nuclear Magnetic Resonance
OMe	Methoxy group
PABA	<i>p</i> -Aminobenzoic Acid
<i>p</i>	<i>para</i>
PXRD	Powder X-ray Diffraction
RT	Room Temperature
SBU	Secondary Building Unit
SC	Sonochemical
TCPS	Tetrakis(<i>p</i> -carboxyphenyl)silane
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
UV–vis	Ultraviolet–Visible Spectroscopy
XRD	X-ray Diffraction

Chapter 1: Introduction

1.1 Background

Metal-organic frameworks (MOFs), also referred to as porous coordination polymers (PCPs), are a class of crystalline materials built from metal-based nodes, often called secondary building units (SBUs), which are linked together through coordinate covalent bonds to afford porous two-dimensional (2D) or three-dimensional (3D) structures.¹ MOFs are well known for their potential void spaces within their structures. Solvent molecules initially occupy these pores and the removal of these molecules under dynamic vacuum can activate the MOF and can result in materials with large surface area (up to 10000 mg²/g) and permanent porosity.²⁻⁵ These empty pores can subsequently host a wide range of guest molecules. Moreover, the structural and functional tuneability of MOFs, achieved through linker modification, incorporation of open metal sites, and variation in metal ions or linker geometry, contributes to their exceptional versatility.⁶ As a result, MOF chemistry has become one of the fastest-growing areas in chemistry, with applications including gas storage and separation, drug delivery, chemical sensing, water purification, catalysis, and many others.⁷⁻¹⁸

1.1.1 Historical Development of MOFs

The development of MOFs can be traced back to 1989, when Hoskins and Robson synthesised one of the earliest coordination polymers (CPs) by linking [Cu(NCCH₃)₄]⁺ units with 4,4',4'',4'''-tetracyanotetraphenylmethane.¹⁹ They proposed that connecting tetrahedral or octahedral metal centres with rod-like organic linkers could lead to the formation of infinite networks featuring potential cavities. This structure-directed approach of designed materials is well known in zeolite chemistry.²⁰ The pioneering work of Hoskins and Robson in assembling metal ions with organic molecular building blocks laid the groundwork for the development of

porous coordination polymers, later termed metal-organic frameworks. Building on this concept, they expanded their research to prepare and investigate a series of 3D frameworks using similar design principles with metal centres such as Zn, Cd, and Cu.²¹ These foundational efforts led to what Kitagawa later described as the first generation of MOFs,²² characterised by rigid frameworks and non-accessible pores. MOFs of this generation lacked permanent porosity, as the removal of guest molecules (e.g., solvents) typically resulted in framework collapse and structural decomposition.

Yaghi and co-workers were the first to introduce the term “metal-organic frameworks” in 1995, when they reported the hydrothermal synthesis of a 3D Cu(I)-based MOF. This structure consisted of Cu(I) centres linked by rod-like 4,4'-bipyridine ligands, forming six identical, interpenetrated porous frameworks.²³ Shortly thereafter, Yaghi and colleagues investigated the selective adsorption behaviour of a thermally stable and porous Co-based MOF, constructed from Co(II) and 1,3,5-benzenetricarboxylate (BTC).²⁴ The framework exhibited remarkable selectivity towards aromatic molecules and demonstrated thermal stability up to 350 °C, which was unusual at the time. This high stability was attributed to the use of a multidentate linker such as BTC, bearing three carboxylate groups, which significantly enhanced both the thermal stability and rigidity of the framework. Furthermore, π - π stacking interactions between coordinated pyridine ligands and included guest pyridine molecules contributed to the material's rigidity and selective adsorption characteristics.²⁴ These findings sparked a surge of interest in MOF chemistry, particularly in frameworks assembled from metal-carboxylate clusters, and these developments ultimately led to the 2025 Nobel Prize being awarded to Robson, Kitagawa, and Yaghi.

Building on this progress, a Zn-based MOF, known as MOF-2, was synthesised in 1998. This material exhibits a 2D microporous network composed of 1,4-benzenedicarboxylate (BDC) linkers bridging Zn(II) paddlewheel units in a di-monodentate fashion.²⁵ MOF-2 was the first

MOF reported to possess permanent porosity, with calculated Langmuir surface areas of 270 m²/g and 310 m²/g. It also retained its structure during guest uptake, anion exchange, and even in the absence of guest molecules, making it a representative example of early second-generation MOFs.

A landmark advancement in the field came with the solvothermal synthesis of MOF-5 (also known as IRMOF-1) by Yaghi and co-workers.²⁶ This MOFs exhibits a cubic 3D structure constructed from Zn₄O(CO₂)₆ secondary building units and BDC linkers, inspired by metal–carboxylate cluster chemistry (Figure 1). The Zn-based MOF exhibited outstanding porosity, with a calculated pore volume of 0.54–0.61 cm³/cm³ (via the Dubinin–Radushkevich equation) and a Langmuir surface area of approximately 2900 m²/g, surpassing that of most porous crystalline zeolites at the time.²⁶ This breakthrough has driven a substantial increase in the number of studies focused on stable MOFs, and since then, they have emerged as one of the most dynamic and rapidly evolving fields in chemistry, with over 100,000 reported MOFs encompassing a wide range of topologies, pore sizes, and functional properties.²⁷

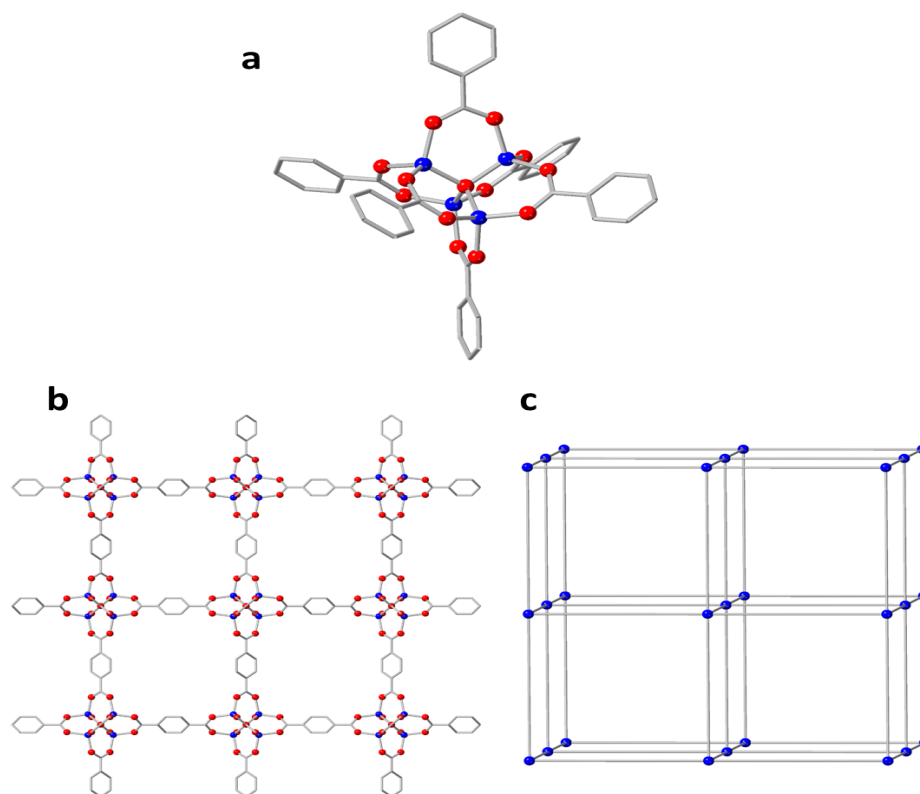


Figure 1: Crystal structure of MOF-5: (a) the Zn_4O cluster for MOF-5 coordinated by the terephthalate linkers; (b) a portion of the extended structure of MOF-5; (d) a topological representation of the **pcu** network showing how the organic and inorganic SBUs are connected in space, with the 6-connected Zn nodes shown in blue. Hydrogen atoms have been omitted for clarity. Colour scheme: Zn, blue; O, red; C, grey. Figure redrawn using CrystalMaker software and crystal data published by Yaghi and co-workers (CSD refcode: SAHYIK).²⁶

1.1.2 MOF Design and Synthesis

As scientific interest in MOFs has grown, so has the need to develop diverse and efficient synthetic strategies to expand the library of MOF structures. When designing a MOF synthesis strategy, several key factors must be considered, as they directly influence the framework's formation, topology (which describes how organic and inorganic components are connected in space),²⁸ and final properties. These factors include the type and functionality of the organic linker, the coordination geometry and oxidation state of the metal ions, the coordination mode

of the linker, the possible network topologies based on geometric compatibility, and the synthetic conditions, such as solvent, temperature, pH, and reaction time, as well as the kinetics and thermodynamics of crystallisation.²⁹ A comprehensive understanding of these factors enables a more rational and predictable approach to MOF synthesis.²⁸

A fundamental principle in the rational design of MOFs is identifying the targeted network topology and selecting the appropriate building blocks required for its construction. This approach forms the basis of reticular synthesis, which involves assembling rigid, pre-defined building units into well-ordered frameworks through strong coordinate covalent bonds, enabling the predictable construction of complex crystalline networks.^{28,30}

One of the earliest and most influential strategies within the framework of reticular chemistry is isorecticular design. This method involves the use of linkers that maintain the same connectivity as those in an existing MOF but vary in length or functionalisation. Such modifications allow for systematic tuning of the pore size and surface area, while preserving the original topology and coordination geometry.³¹ A pioneering example was demonstrated by Yaghi and co-workers, who replaced the linear dicarboxylate BDC linker in MOF-5 (IRMOF-1) with longer analogues.³² This gave rise to the IRMOF series, a family of isorecticular frameworks with expanded pore sizes and tuneable functionality, all retaining the same cubic topology (Figure 2).

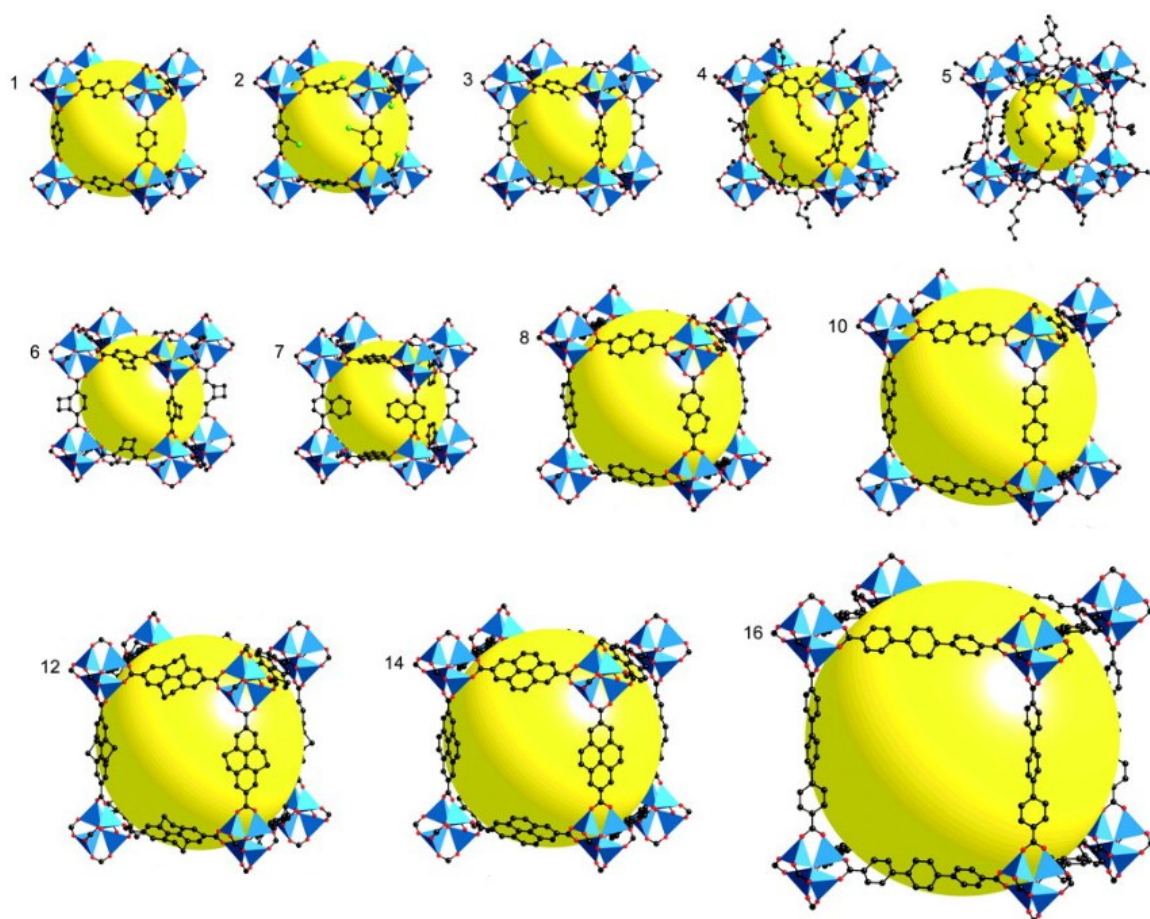


Figure 2: Crystal structures of IRMOF-*n* (*n* = 1–7, 8, 10, 12, 14, and 16). The doubly interpenetrated IRMOF-9, 11, 13, and are not shown here. Colour scheme: Zn, blue polyhedral; O, red spheres; C, black spheres; Br, green spheres in 2; amino-groups, blue spheres in 3. The yellow spheres indicate the largest van der Waals spheres that can fit inside the cavities without touching the framework. H atoms are omitted for clarity. Reproduced from Ref. ³² with permission.

Although isorecticular expansion is typically achieved by elongating the organic linker, variations of the metal ion can also afford isostructural MOFs, as long as the resulting secondary building units maintain the same geometry and connectivity. This has been demonstrated in some cases where different metals can produce isostructural MOFs. For example, the structure of the Cu-based MOF HKUST-1 has been replicated using Zn^{2+} , Fe^{2+} , and Cr^{2+} , yielding frameworks with identical topology and metal cluster geometry, thereby achieving isorecticular expansion through metal substitution.^{33–38}

While these strategies have proven effective for constructing new members of known MOF families, their ability to direct the formation of entirely new structures or topologies is limited. Moreover, in the early years of MOF development, only a few isorecticular series were known, and the discovery of novel frameworks often required careful optimisation of reaction conditions. To address these limitations and expand structural diversity, a variety of synthetic methods has been developed over the past few decades to assemble SBUs and linkers under different conditions. These include conventional solvothermal synthesis, microwave-assisted (MW) synthesis, electrochemical (EC) synthesis, sonochemical (SC) synthesis, and mechanochemical (MC) synthesis.³⁹ These methods differ in terms of reaction conditions, energy input, scalability, and their influence on crystallinity and morphology of the resulting materials.

The term “conventional synthesis” typically refers to reactions performed using standard electric heating methods, without the use of parallel or accelerated reaction techniques.²⁹ This method is the most widely adopted for constructing MOF materials and involves treating organic ligands with metal salts in a single solvent or a mixture of solvents at a controlled temperature. Based on the solvent type, conventional synthesis can be classified as either solvothermal or hydrothermal. In solvothermal synthesis, organic solvents are used, which may be protic (e.g., methanol, ethanol) or aprotic (e.g., DMF, DMA, DMSO, MeCN, NMP, or toluene).⁴⁰ Solvent mixtures are also frequently employed to improve the solubility of starting materials or to influence reaction outcomes. In contrast, hydrothermal synthesis uses water as the solvent.⁴¹ Typically, these reactions are carried out in sealed vessels to allow heating above the solvent’s boiling point, creating autogenous pressure. Reactions at temperatures above 400 K generally require Teflon-lined stainless-steel autoclaves, while lower-temperature reactions can be conducted in glass vials.⁴¹

Temperature is a critical parameter in conventional MOF synthesis, as it influences both nucleation and crystal growth by affecting both kinetic and thermodynamic parameters. Based on the temperature and pressure used, conventional synthesis may also be classified into solvothermal synthesis, which is conducted above the boiling point of the solvent with autogenous pressure,⁴² and non-solvothermal synthesis, which is carried out at or below the solvent's boiling point under ambient pressure.^{29,43}

The solvothermal method is particularly valued for its simplicity, high yields, and its ability to produce high-quality single crystals suitable for structural analysis via single-crystal X-ray diffraction (SCXRD).³⁹ Several parameters can significantly influence crystal quality and formation. These include the concentration of the metal salt and organic ligand, the choice of solvent or solvent mixture, the presence of modulating agents, the reaction temperature and time, as well as the cooling rate and stirring speed.⁴⁴ Among these, solvent selection is especially crucial, as it not only influences solubility and morphology but also affects the coordination behaviour of the metal ions, which may determine the dimensionality and topology of the resulting MOF.^{45,46} For example, Parise and co-workers investigated the role of various solvents, including water, DMF, ethanol, and methanol, on the synthesis of magnesium based MOFs under identical solvothermal conditions.⁴⁷ Their study demonstrated that the solvent's ability to coordinate with metal centres can directly influence the structural dimensionality and topology of the resulting framework. Water (followed by DMF), for example, strongly coordinated with Mg^{2+} ions outcompeting the linker molecules. The presence of terminally coordinated solvent molecules also reduced the dimensionality of the coordination network by blocking potential extension pathways. In contrast, ethanol and methanol exhibited weaker coordination abilities in the presence of DMF. As a result, solvent mixtures such as DMF/ethanol or DMF/methanol/ethanol (1:1 and 1:1:1, respectively) facilitated the formation of 3D structures. The use of DMF was also associated with enhanced

solubility and promoted faster deprotonation of the linker. Taken together, these findings highlight a key limitation of hydrothermal synthesis, as the high hydration energies of metal ions can lead to water outcompeting ligands for coordination at metal centres, thereby inhibiting framework assembly and reducing structural diversity.

Achieving precise control over crystallisation kinetics remains essential for guiding the growth of high-quality MOF crystals, which is critical for structural characterisation by techniques such as X-ray diffraction (XRD).²⁹ One of the most important advances in MOF synthesis has been the introduction of modulating agents. These modulators, typically monodentate acids or bases, influence the coordination environment during framework formation, slowing nucleation and promoting controlled crystal growth. Frequently reported modulator examples include monodentate carboxylic acids such as benzoic acid, formic acid, and acetic acid.⁴⁸ Modulators can also be used to tune MOF properties and pore sizes, thereby increasing their potential for various applications.^{31,49} Their effect on MOF synthesis was first demonstrated by Tsuruoka *et al.* in 2009, who employed acetic acid as a modulating agent to directly influence coordination equilibria and control the crystal growth of nanosized PCP crystals [$\{\text{Cu}_2(\text{ndc})_2(\text{dabco})\}_2$] (ndc = 1,4-naphthalene dicarboxylate; dabco = 1,4-diazabicyclo-[2.2.2]octane).⁵⁰

In addition, modulators can interact with either the metal nodes or organic linkers, forming the basis of controlled MOF assembly. If the modulator contains coordinating functional groups (e.g., COOH for example) similar to those on the linker, it can compete for coordination sites on the metal ions during framework formation. This competition significantly affects nucleation kinetics, thereby influencing crystal growth, morphology, particle size, and porosity.⁴⁹ Furthermore, acidic or basic modulators alter the pH of the reaction medium, which in turn affects linker deprotonation. For example, acidic modulators lower pH and slow deprotonation, thus favouring slower nucleation and improved crystallinity.^{49,51} Additionally,

the competition between inorganic acid modulators and ligands may contribute to the charge balance within the forming framework, further influencing self-assembly.⁵² These interactions are typically reversible, and a slower rate of framework formation allows the system to maintain equilibrium, minimizing defects and promoting high-quality crystal growth.⁵³

Modulator concentration is also important, as higher concentrations typically yield larger, high-quality crystals, possibly through *in situ* metal–modulator complexes that regulate metal ion availability.³¹ Schaate *et al.* demonstrated this by showing that increasing benzoic acid concentration led to larger Zr-MOF crystals (UiO-66, UiO-67, UiO-68).^{31,54} However, excessive modulator can inhibit metal–ligand coordination, hindering nucleation and preventing MOF formation. The morphology and size of MOF crystals are critical to their performance in various applications, such as drug delivery, gas adsorption and separation. For example, large, high-quality crystals are ideal for single-crystal X-ray diffraction (SCXRD), whereas nanoscale MOFs are better suited for biomedical applications.⁵⁵ While modulators can effectively influence the shape and size of MOF crystals, they may also lead to the formation of undesired metal clusters or impure products. This highlights the importance of carefully selecting both the type and concentration of modulator to achieve the desired MOF structure and properties.

Beyond solvothermal methods, a variety of additional synthetic strategies have been developed for MOF synthesis. Microwave-Assisted (MW) synthesis is one of the alternative synthesis methods of MOFs where energy is introduced using microwave irradiation.²⁹ It is known to be used in organic chemistry as well as to prepare nanosized metal oxides and zeolites.^{56,57} This method involves the use of microwaves to generate efficient heat through its interaction with mobile electric charges, such as polar solvent ions or molecules. In MW synthesis, the starting materials are dissolved in a suitable solvent and usually placed in a sealed Teflon-lined vessel in a microwave reactor for a specific time. The microwave radiation interacts with the

permanent dipole moments of polar molecules in the mixture which continuously attempt to realign with the rapidly changing electromagnetic field, thereby increasing the system's temperature and kinetic energy.⁴⁰ MW synthesis is also known for enabling rapid crystallisation, the preparation of nanoscale MOFs, high energy efficiency, and improved product purity.^{29,58} Some examples of MOFs prepared using MW method include Cr-MIL-100,⁵⁹ which was the first MW synthesis of a MOF, MIL-100(Fe),⁶⁰ MIL-101(Fe),⁶¹ MOF-177,⁶² and HKUST-1.⁶³ However, achieving precise control over reaction time, temperature, irradiation power remains a challenge and a limitation of the MW synthesis. This is due to differences between instruments and the inability of different instruments to deliver identical reaction conditions, which affects reproducibility.⁵⁸

Electrochemical (EC) synthesis is another alternative method for the preparation of MOFs. This approach was first employed in the synthesis of HKUST-1 by Mueller *et al.* in 2005.⁶⁴ During the synthesis, they aimed to eliminate anions such as perchlorate, nitrate, or chloride, which pose challenges in large-scale production. In EC synthesis, instead of using metal salts, metal ions are introduced into the reaction medium via anodic dissolution.²⁹ The medium contains both a conducting salt and the organic linker. Protic solvents are typically used, as they prevent metal deposition on the cathode, although hydrogen gas is generated as a byproduct. Alternatively, compounds such as acrylonitrile, maleic or acrylic esters can be used, as they are more readily reduced. EC synthesis offers additional industrial advantages, including the potential for continuous synthesis processing and achieving higher solid yields than to conventional reactions. However, in a comparison between HKUST-1 synthesised electrochemically and that produced by conventional methods, the electrochemically synthesised product exhibited inferior quality, as evidenced by thermogravimetric analysis (TGA), elemental analysis, and gas sorption measurements.⁶⁵ This reduction in quality was attributed to the possible entrapment of linker molecules or conducting salts within the

framework's pores during crystallisation. Additionally, other examples where the electrochemical method has been employed include the synthesis of several Zn- and Cu-based MOFs, such as $[\text{Zn}(\text{1,3-BDC})_{0.5}(\text{bzim})]$ (bzim = benzimidazole) and $[\text{Cu}_3(\text{HHTP})_2]$ (HHTP = 2,3,6,7,10,11-hexahydroxytriphenylene), as well as a few Al-based MOFs.^{66–68}

Sonochemical (SC) synthesis has been widely utilized in MOF chemistry. It was first applied in 2008 when Qiu *et al.* reported the rapid preparation of nanocrystals of a Zn-based MOF, $[\text{Zn}_3(\text{BTC})_2] \cdot 12\text{H}_2\text{O}$, using ultrasonic irradiation.⁶⁹ In this method, MOFs are synthesised by applying sound waves, typically ranging from 20 kHz to 10 MHz.⁷⁰ The reaction is generally carried out in a Pyrex reactor equipped with a sonicator probe and adjustable power settings, into which a mixture of metal salt and organic linker is introduced. This technique relies on ultrasonic waves to induce acoustic cavitation, a phenomenon where microbubbles form, grow, and collapse violently within the liquid medium. This collapse generates localized hotspots with extremely high temperatures (approximately 4000–5000 K) and pressures (up to 1000 bar), which facilitate the rapid nucleation and crystallisation of fine MOF particles.⁷¹ Compared to conventional solvothermal synthesis, the sonochemical approach is simpler (when equipment such as a sonicator probe is available), more energy-efficient, cost-effective, and environmentally friendly.²⁹ Son *et al.* were the first to prepare high-quality MOF-5 crystals using this method.⁷² Using NMP as the solvent, crystals of 5–25 μm were obtained within 30 min, a significant reduction compared to the 24 h required in solvothermal synthesis. Notably, both MOF-5 samples, prepared via sonochemical and solvothermal methods, exhibited nearly identical physical properties. Additionally, the sonochemical method was employed to synthesise nanocrystalline HKUST-1 ($\text{Cu}_3(\text{BTC})_2$) powder (10–40 nm) in just 5 min.⁷³ By extending the reaction time to 10 min, larger crystals (50–200 nm) and improved yields were achieved. However, further increases in reaction time had no significant effect on the size of the MOF nanocrystals. Notably, when the reaction time was extended to 90 min, the larger

crystals disappeared and nanoballs (20–80 nm) were formed, resulting in a change in the structure of $\text{Cu}_3(\text{BTC})_2$, as confirmed by XRD analysis. Although the SC method holds great promise, its reproducibility remains a concern. Variations in equipment can result in inconsistent ultrasonic power delivery. Moreover, prolonged sonication without temperature control can cause the reaction temperature to rise, potentially affecting the consistency and reliability of experimental outcomes, as well as the formation of the resulting MOF.

Another method for the preparation of MOFs is mechanochemical (MC) synthesis which involves mechanical breakage of intermolecular bonds, followed by chemical transformation.⁷⁴ In this method, a metal salt and an organic ligand are mechanically ground together, typically using a ball mill, without the use of solvent. The resulting solid mixture is then gently heated to remove volatile byproducts, such as water, generated during the reaction.⁴⁵ In 2006, Pichon *et al.* reported the first use of the MC method in MOF synthesis, yielding the microporous framework $[\text{Cu}(\text{INA})_2]$ (INA = isonicotinic acid).⁷⁵ In their study, copper acetate and isonicotinic acid were ground together for 10 min without solvent or applied heat, affording a robust 3D MOF. Since then, several MOFs have been synthesised using MC methods, including HKUST-1,⁷⁶ MOF-14,⁷⁷ MOF-74,⁷⁸ MOF-5,⁷⁹ and MIL-101(Cr).⁸⁰ This method is environmentally friendly, time-efficient, and enables solvent-free syntheses at ambient temperature, which is particularly advantageous when the use of organic solvents is undesirable.⁸¹ However, limitations of MC synthesis include reduced pore volume and lower crystallinity in the resulting MOFs.⁴⁰

The methods described above represent the most commonly employed techniques for MOF synthesis. However, alternative methods such as diffusion methods, ionothermal synthesis, chemical vapor deposition, and spray-drying have also been reported in the literature.^{82–86}

1.1.3 Activation and Characterisation of MOFs

1.1.3.1 Activation

As mentioned in section 1.1, guest molecules, typically solvents, unreacted linkers, or modulators, may become trapped within the pores of MOFs during synthesis. These must be removed to access the internal pore structure and achieve permanent porosity. The process in which guest molecules are removed without disrupting the structural integrity or porosity of the framework is referred to as “activation”.⁸⁷ This step can be particularly challenging when dealing with solvents such as DMF, DEF, or water, which have high boiling points and surface tension. During their transition from liquid to gas, these solvents can generate significant capillary forces, which may partially or completely collapse the MOF structure.⁸⁸ As a result, experimentally measured surface areas and pore volumes often fall below the theoretical values predicted from crystallographic data, frequently due to incomplete or ineffective activation. Therefore, careful attention must be given to the activation process to ensure complete removal of solvent molecules and the preservation of porosity. To address this, several activation techniques have been developed, including conventional heating under vacuum, solvent-exchange, supercritical CO₂ drying, freeze-drying, and chemical treatments, all aimed at efficiently removing guest molecules while maximizing porosity and surface area.

Conventional activation, which involves the application of heat under vacuum, is one of the most widely used methods for activating porous materials such as zeolites, carbons, and MOFs. For example, MOFs like UiO-66 and MIL-101(Cr) have been successfully activated using this method, achieving high surface areas of 1070 m²/g and 4100 m²/g, respectively.^{89,90} These activated MOFs have also demonstrated excellent thermal and chemical stability. However, researchers have often encountered problems such as complete loss of crystallinity (as a worst-case scenario) and reduced porosity following activation. This degradation is likely to be due

to the generation of significant surface tension and capillary forces during solvent removal, which can exceed the moderate coordination bond strengths that stabilise many MOFs.⁸⁸ As a result, alternative activation strategies were necessary in order to achieve the high internal surface areas and porosities that these materials can theoretically offer.

MOFs can be activated via solvent-exchange as an alternative strategy. This technique involves replacing high-boiling-point solvents, such as DMF or water, with lower-boiling-point solvents like CHCl_3 or MeOH. Solvents with lower surface tension and lower boiling points exhibit weaker intermolecular interactions, making them easier to remove under milder conditions, specifically vacuum and lower temperatures, since they generate less capillary force during activation.⁸⁸ This technique was first demonstrated to be effective by Yaghi and co-workers on MOF-5.²⁶ In their study, DMF and chlorobenzene were fully exchanged with chloroform, and all chloroform molecules were subsequently removed from the pores within 3 h at ambient temperature. Complete removal of guest molecules was confirmed by ^{13}C NMR spectroscopy, mass spectrometry, elemental microanalysis, and thermogravimetric analysis. Importantly, the framework retained its crystallinity after activation and exhibited thermal stability up to 300 °C. The resulting activated MOF displayed a Langmuir surface area of approximately 2900 m^2/g .

Nelson *et al.* further demonstrated the effectiveness of solvent-exchange as an activation method in their studies on IRMOF-3 and IRMOF-16.⁹¹ When activated directly using conventional methods, IRMOF-3 exhibited a BET surface area of only 10 m^2/g , while IRMOF-16 showed no N_2 uptake. However, after exchanging DMF with CHCl_3 prior to activation, the surface areas increased significantly to 1800 m^2/g and 470 m^2/g for IRMOF-3 and IRMOF-16, respectively. It is worth noting that, despite possessing much larger pore sizes, IRMOF-16 exhibits a significantly lower BET surface area than IRMOF-3 due to the reduced mechanical rigidity of its highly extended linker, which makes the framework more prone to partial pore collapse, structural distortion, and incomplete solvent removal during activation.

To ensure complete solvent-exchange, it is advisable to wash the bulk MOF sample thoroughly with the synthesis solvent to remove any residual impurities or unreacted linkers, which may otherwise remain trapped within the pores.^{90,92} Additionally, prolonged soaking of the MOF in the exchange solvent, typically overnight, is recommended to facilitate effective solvent replacement. Although solvent-exchange has proven effective in many cases, the resulting materials may still exhibit porosity values lower than those predicted from single-crystal data.

Activation using supercritical carbon dioxide (scCO₂) presents an effective alternative to conventional heating/vacuum methods, particularly when solvent-exchange is unsuccessful or leads to framework collapse. This method is considered milder, as it avoids the liquid-to-gas phase transition of the guest solvent. Instead, the solvent passes through a supercritical phase, which eliminates surface tension and thereby minimizes capillary forces that could otherwise damage the MOF structure.⁹² This approach involves initially replacing the guest molecules with a solvent that is miscible with liquid CO₂, such as ethanol or methanol. The solvent is then gradually replaced with liquid CO₂ under a pressure exceeding 73 atm over the course of 2 h. Subsequently, the temperature is raised above CO₂'s supercritical point (31 °C), transitioning the system into the supercritical phase with the MOF pores filled with scCO₂. Finally, the supercritical CO₂ is slowly released by carefully venting the apparatus while maintaining the temperature above the critical threshold, thereby avoiding surface tension and preserving the structural integrity of the framework. Activation using scCO₂ has become widely adopted due to its efficiency, affordability, and scalability.^{3,88,91,93–97} Nelson *et al.* were the first to demonstrate the effectiveness of this technique for MOF activation. For example, IRMOF-3 achieved a BET surface area of 2850 m²/g using scCO₂ activation, significantly higher than the 10 m²/g obtained through conventional heating and vacuum, and even surpassing the 1800 m²/g achieved via solvent-exchange.⁹¹ Similarly, IRMOF-16 exhibited a BET surface area of 1910 m²/g following scCO₂ activation, compared to that obtained using the solvent-exchange

method (470 m²/g). Notably, flow-based supercritical CO₂ activation, where scCO₂ is continuously flowed over crystals solvated in DMF, has been explored as a potentially faster and more scalable alternative. Despite the benefits of this technique, it requires specialized equipment and involves higher operational costs.^{92,98}

Activation by benzene freeze-drying is another developed method for activating MOFs. This technique helps preserve the framework integrity by avoiding the liquid-to-gas phase transition and the associated capillary forces. In this method, the MOF sample is first solvent-exchanged and soaked in benzene. It is then subjected to multiple freeze–thaw cycles, typically by cooling to 0 °C followed by warming to room temperature. After the final cycle, the sample is placed under vacuum at a temperature and pressure below benzene’s triple point. As the sample is gradually warmed under reduced pressure, the benzene undergoes sublimation, transitioning directly from solid to gas, thereby bypassing the liquid–gas phase change that can lead to structural collapse.⁸⁸ Ma *et al.* demonstrated the effectiveness of this technique in activating two isorecticular Cu-based MOFs, [Cu₂(H₄L)(H₂O)₂] and [Cu₂(H₄L’)(H₂O)₂], where H₄L = methanetetra(*p*-benzoic acid) and H₄L’ = methanetetra(biphenyl-*p*-carboxylic acid).⁹⁹ Both MOFs retained crystallinity and exhibited BET surface areas of 1560 and 1020 m²/g, respectively, significantly higher than those obtained by solvent-exchange (526 and 791 m²/g). Moreover, He *et al.* showed that freeze-drying can also be performed using cyclohexane instead of benzene.¹⁰⁰ In their study, the BET surface area of the Zn-based MOF FIR-3, constructed from a nanosized tris((4-carboxyl)phenyl)durylamine ligand, increased from 24 m²/g using conventional solvent-exchange to 497 m²/g following freeze–cyclohexane drying.

Other MOF activation techniques, such as chemical treatment and microwave activation, have also been reported in the literature. For example, treatment of PCN-222 (also known as MOF-545) with concentrated hydrochloric acid, followed by thermal activation under vacuum, was successful in removing unreacted ligands and benzoate ions trapped within the pores, resulting

in a significant increase in the framework's pore volume and surface area.^{101,102} A similar approach was used to cleave coordinated benzoate ions from the Zr_6 nodes in NU-1000, leading to effective activation of the MOF.¹⁰³ Unlike neutral molecules, coordinated benzoate anions lack sufficient volatility and therefore cannot be removed from the pores or coordination sites by heating alone. In such cases, chemical treatment provides an effective strategy for MOF activation. However, for this method to be applicable, the MOF must exhibit acid stability to prevent decomposition during the treatment process. Additionally, microwave activation has been demonstrated as an effective technique. For example, Kalinovsky *et al.* applied this method to MOFs such as UiO-66 and DUT-84 by soaking the samples in water, followed by microwave heating at 150 °C to remove residual modulators.¹⁰⁴ While this technique is particularly effective for MOFs that are both thermally and water stable, it may not always achieve complete removal of guest species from the pores.

1.1.3.2 Characterisation

Understanding the fundamental structural features of MOFs and their derivatives, such as crystallinity, porosity, and specific surface area, is crucial for optimising their performance. To assess crystallinity and phase purity, X-ray diffraction (XRD) is a primary characterisation technique, with single-crystal X-ray diffraction (SCXRD) and powder X-ray diffraction (PXRD) being the most commonly used methods. SCXRD is a well-established technique that allows for the precise determination of crystal structures at the atomic or subatomic level, including accurate bond lengths and angles, with precision down to sub-Angstrom levels.^{105,106} In this technique, data are often collected at low temperatures to reduce atomic thermal vibrations, enabling the acquisition of high-resolution structural information.

MOF crystals, which are inherently porous, typically consist of well-ordered framework atoms alongside more disordered species, often guest molecules occupying the pores.¹⁰⁵ Positional

disorder may also be observed in terminal ligands or functional groups projecting into the pores. When the atomic positions of guest molecules cannot be reliably determined due to severe disorder, solvent masking may be used as a last resort. This technique estimates the total electron density in the void space and accounts for it as bulk disordered solvent, thereby improving refinement stability and minimizing structural errors while preserving the accuracy of the framework model. If solvent masking is applied, it is crucial that the crystallographic information files (CIFs) clearly document its use. Beyond locating metal ions, organic linkers, and guest molecules in the cavities, SCXRD is also used to monitor structural changes in MOFs before and after treatments, such as thermal activation, gas sorption, and host–guest interactions as reported in the literature.^{107–110} However, SCXRD requires high-quality, sufficiently large single crystals, which can be challenging to obtain.

Consequently, PXRD is widely used as an alternative method to evaluate the bulk crystallinity and phase purity of MOF samples. Proper sample preparation is essential for obtaining reliable PXRD data, as it can significantly affect the resulting diffraction pattern. To perform PXRD analysis, the powdered MOF sample is typically loaded onto a flat sample holder, commonly made of glass, plastic, or aluminium, using enough to minimize background interference from the holder.^{92,106} However, when only a small amount of material is available, low-background silicon holders are recommended. It is also advisable to grind the sample prior to loading to achieve uniform particle size and reduce preferred orientation effects.¹⁰⁵ Additionally, the sample must be positioned at the correct height, as any deviation can introduce errors in the recorded peak positions.

Phase purity of the bulk material can be assessed by comparing the experimental PXRD pattern with a simulated or calculated pattern, either derived from SCXRD data or through computational modelling.^{111,112} Once crystallinity is confirmed, structural information such as unit cell dimensions, crystallite size, and lattice parameters can be extracted from the PXRD

data.¹¹² Moreover, PXRD is frequently employed to evaluate the structural integrity of MOFs after activation and other post-synthetic treatments, and to monitor changes following adsorption experiments.^{113,114}

The exceptionally high surface area and permanent porosity of MOFs are among their most defining characteristics, making them highly attractive to researchers across various scientific fields. Adsorption isotherms are commonly used to determine surface area, average pore size, pore volume, and pore size distribution, with nitrogen (N₂) gas adsorption at 77 K being the most widely applied technique.⁹² In a typical N₂ adsorption isotherm experiment, the amount of N₂ gas adsorbed is measured at different relative pressures (p/p_0), often starting as low as 10^{-7} to 10^{-5} , at the boiling point of nitrogen.¹⁰⁵ To obtain a reliable isotherm, it is essential to ensure both sufficient sample mass and complete activation of the MOF, which can be confirmed using PXRD. Following activation, samples are degassed, typically at temperatures ranging from 120 to 150 °C, depending on the MOF and the synthesis solvent used, to ensure complete removal of trapped guest molecules from the pores (see activation methods above).^{115,116} Subsequently, the MOF sample is cooled to 77 K and exposed to controlled doses of N₂ gas. Once temperature and pressure reach equilibrium, the adsorption data are collected by increasing relative pressure until the surface becomes fully saturated. Following this, N₂ is gradually removed to generate the desorption data.¹⁰⁶

According to the International Union of Pure and Applied Chemistry (IUPAC), adsorption isotherms are categorized into six distinct types based on their shapes, which helps in classifying porous materials.¹¹⁷ Type I isotherms are typically observed in microporous MOFs with pore sizes below 2 nm and are indicative of monolayer adsorption (e.g. MOF-5).^{106,118,119} Type II isotherms typically describe adsorption on non-porous or macroporous materials (pore size > 50 nm), where strong adsorbate–adsorbent interactions and multilayer adsorption are commonly observed.^{120,121} Type III isotherms are observed when interactions between

adsorbate molecules are stronger than those between the adsorbate and adsorbent. Type IV isotherms are characteristic of mesoporous materials (pore sizes between 2–50 nm), showing monolayer and multilayer adsorption followed by capillary condensation at higher pressures.¹²¹ Type V isotherms also occur in mesoporous materials with capillary condensation, but where weak interactions between the adsorbent and adsorbate dominate.¹⁰⁶ Finally, Type VI isotherms are rare and associated with materials having highly uniform surface structures, displaying stepwise multilayer adsorption behaviour.¹²²

The Brunauer–Emmett–Teller (BET) and Langmuir theory are the most common method for apparent surface area calculations.^{123,124} The BET theory is well-suited for determining the surface area of most MOFs, as they typically allow for multilayer gas adsorption. On the other hand, the Langmuir model applies exclusively to monolayer adsorption and therefore often leads to significant overestimations of the surface area of many MOFs.⁹²

The BET equation is given by:

$$\frac{\left(\frac{p}{p_0}\right)}{n \left(1 - \frac{p}{p_0}\right)} = \frac{1}{n_m C} + \frac{C - 1}{n_m C} \left(\frac{p}{p_0}\right)$$

In this equation, n represents the amount of nitrogen gas adsorbed, p is the equilibrium pressure, p_0 is the saturation pressure of nitrogen, n_m is the monolayer adsorption capacity, and C is the BET constant. To determine the BET surface area, a graph of $[(p/p_0)/n(1 - p/p_0)]$ against p/p_0 is plotted and analysed. To determine surface area accurately using the BET plot, a linear region must be chosen according to the criteria established by Sing and co-workers.¹²⁵ These include: (i) the C value must be positive, (ii) the product $n(1 - p/p_0)$ should increase monotonically as p/p_0 increases, (iii) the monolayer capacity (n_m) should occur within the measured pressure range, and (iv) the value of p/p_0 at which monolayer coverage occurs should closely match the calculated value of $1/(\sqrt{C} + 1)$.¹²⁵ Once the appropriate linear range is identified, the slope and

intercept of the line can be used to calculate the apparent BET surface area, the monolayer capacity (n_m), and the BET constant (C). It is also important to note that the term “estimated/apparent BET surface area” is often used when it is challenging to differentiate clearly between monolayer and multilayer adsorption, particularly in microporous MOFs, where selecting an appropriate linear region for BET analysis can be difficult.¹²⁶ However, in 2022, Fairen-Jimenez and co-workers developed a computational method known as BET Surface Identification (BETSI), which enhances the accuracy and reproducibility of BET surface area determination in nanoporous materials.¹²⁷ The BETSI algorithm systematically assesses all potential linear fitting regions within an adsorption isotherm using the Rouquerol criteria (mentioned above) and objectively identifies the most appropriate region for BET analysis.

In addition, several methods are used to study pore volume and pore size distribution in MOFs, among which the density functional theory (DFT) method is the most widely employed.¹²⁸ This method is particularly suitable for analysing micropores (< 2 nm) and mesopores close to 2 nm in size. When applied to a pure MOF sample, the appearance of unexpected pore sizes may indicate the presence of structural defects, such as missing or additional linkers or metal nodes. However, caution should be exercised when interpreting pore size distribution data, as simulated distributions may not always accurately represent the actual structure of the material. Discrepancies can arise due to structural changes, incomplete activation, or limitations inherent in the chosen analytical model. Pore size distributions predicted from X-ray crystallographic data can serve as a useful reference. Moreover, the total pore volume can be estimated by measuring the amount of gas adsorbed as the relative pressure (p/p_0) approaches 1.0.

Beyond the techniques discussed above, various analytical methods are available to characterise MOFs across different properties. For example, atomic force microscopy (AFM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) are

commonly employed to study the morphology and crystal size of MOFs, with AFM also offering insights into their mechanical properties. Furthermore, techniques such as fluorescence microscopy, electron paramagnetic resonance (EPR), and positron annihilation spectroscopy (PAS) have been used for detecting crystal defects, vacancies, and understanding the nature of these defects. Thermogravimetric analysis (TGA) is used to assess the thermal stability of MOFs, and in some cases, to estimate pore volume, while aqueous stability testing evaluates the structural stability of MOFs when subjected to water and varying pH environments. Nuclear magnetic resonance (NMR) spectroscopy can also be utilized to determine the bulk purity of MOF samples and quantify linker ratios in mixed-linker systems. Both solution-state NMR, typically performed on digested MOF samples, and solid-state NMR, conducted directly on the intact framework, have been effectively used for these purposes. Additional information on these and other characterisation techniques is available in the literature.^{92,105,129}

1.2 Organosilicon Carboxylic Acids for MOF Synthesis

1.2.1 Background

What makes MOFs unique compared to traditional porous sorbents such as zeolites and activated carbons is their tuneable properties. These can be controlled by selecting from a wide variety of organic linkers with different functionalities.¹³⁰ This highlights the importance of choosing an appropriate linker, as it plays a critical role in both the synthesis and final properties of the resulting MOF. Furthermore, by modifying parameters such as the linker's shape, length, functional groups, and the ratio of linkers to metal ions, it is possible to tailor the pore size, morphology, and internal surface characteristics of the framework to suit specific applications.¹³¹ Moreover, the overall structure and topology of a MOF is largely determined

by the geometry and connectivity of its organic linker. Even slight changes to the linker, such as size and shape, can lead to the formation of a wide range of distinct network topologies.¹³²

The focus of this thesis is the synthesis of novel, organosilicon multicarboxylic acids for MOF construction. MOFs assembled from these linkers feature robust metal–carboxylate secondary building units, which provide enhanced thermodynamic stability through strong coordination between anionic carboxylate groups and metal cations.¹³¹ These linkers also promote the formation of polynuclear inorganic clusters, which further reinforce the structural integrity of the framework. Additionally, highly connected carboxylate SBUs enhance framework rigidity and promote permanent porosity, both of which are key features for many MOF applications. Studies have also shown that highly connected linkers can produce robust frameworks with significant porosity.^{132–135} Furthermore, the negative charges on carboxylate linkers help neutralize the positive charges of metal clusters, often resulting in frameworks free of charge-balancing counterions, as these would otherwise occupy the pores. Moreover, the use of carboxylate linkers enables a degree of predictability in MOF topology, as the geometry of both the linker and the metal node can be considered prior to synthesis. This is possible because the coordination chemistry of many metal–carboxylate clusters, such as polynuclear metal acetates, is well-known, allowing for the targeted and predictable design of MOFs.^{132,136,137}

Planar aromatic carboxylic acid linkers, in particular di-, tri-, and tetracarboxylic acids, have been extensively studied since the emergence of MOFs, and they continue to be a central focus of MOF research today, with some examples illustrated in Figure 3. While these linkers can form 3D frameworks when coupled with suitable metal clusters, their inherently planar geometry often limits the construction of fully three-dimensional structures.¹³⁶ As a result, increasing attention has been directed toward the use of tetra-substituted carbon-based linkers in MOF synthesis. Several examples, including tetraphenylmethane- and adamantane-based

linkers, have been reported in the literature.^{99,138–144} However, the synthesis of such linkers is often complicated, highlighting the need for the design and development of new linkers for MOF construction. Alternatively, tetravalent silicon-based linkers have demonstrated significant potential in the construction of MOFs.

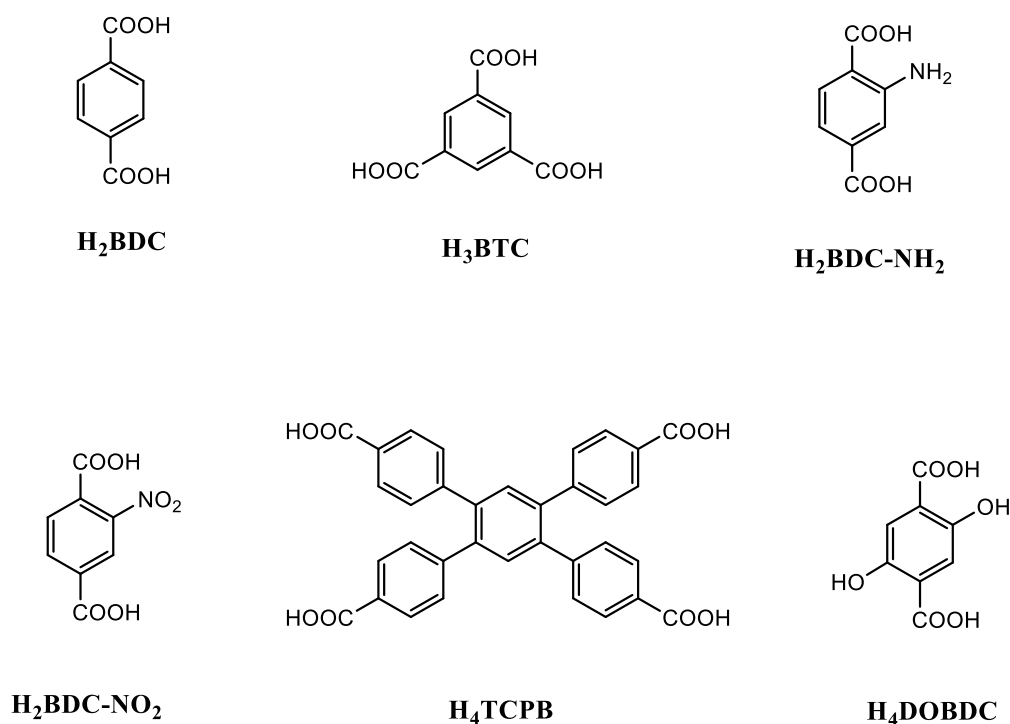


Figure 3: Examples of widely used carboxylic acids in MOF synthesis.

In 1997, Tilley *et al.* reported the first tetrahedral organosilicon ligand, tetrakis(*p*-cyanophenyl)silane ($\text{Si}(p\text{-C}_6\text{H}_4\text{CN})_4$, Figure 4), used in the construction of coordination polymers.¹⁴⁵ The silicon-based linker was treated with AgO_3SCF_3 or AgPF_6 as metal precursors, leading to the formation of two distinct structures. Coordination between the tetrahedral linkers and Ag(I) ions resulted in the assembly of 3D networks composed of interpenetrated double layers. Although the resulting materials exhibited limited stability, the study demonstrated that Si-centred tetrahedral building units can be incorporated successfully into 3D coordination frameworks.

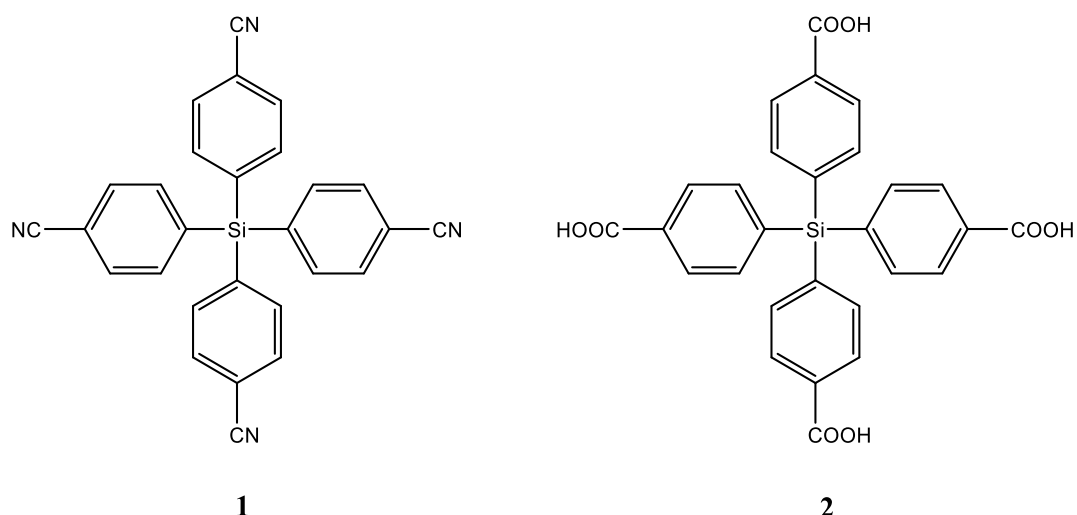


Figure 4: Structure of tetrakis(*p*-cyanophenyl)silane (**1**), and tetrakis(*p*-carboxyphenyl)silane (TCPS-H₄) (**2**).

In the same year, Lambert *et al.* reported the synthesis of another silicon-centred tetrahedral linker, tetrakis(*p*-carboxyphenyl)silane (TCPS-H₄) (**2**).¹⁴⁶ This compound was synthesised through a simple two-step reaction. In the first step, a lithium derivative of 4-bromotoluene was reacted with tetrachlorosilane to yield tetra(4-tolyl)silane. This intermediate was then oxidised using potassium permanganate in pyridine to afford the final TCPS-H₄ product, where “H₄” indicates the four carboxylic acid hydrogens. Single crystals suitable for X-ray analysis were obtained by recrystallisation from acetic acid. SCXRD analysis showed that the material crystallised as a co-crystal of **2** with acetic acid; three of the carboxylic acid groups formed dimeric hydrogen bonds with neighbouring TCPS-H₄ molecules, while the fourth group hydrogen-bonded to an acetic acid molecule. As a result, extension of the 2D polymeric sheet into a 3D diamondoid network was hindered due to the interaction of the fourth carboxylic acid group with acetic acid. Nevertheless, these findings revealed the potential of TCPS-H₄ as a building block for constructing 3D frameworks and subsequently inspired numerous studies on organosilicon compounds for the synthesis of 2D and 3D coordination networks.^{147–154}

In 2007, Yaghi and co-workers reported the preparation of a 3D covalent organic framework via the condensation reaction of Si(*p*-C₆H₄B(OH)₂)₄.¹⁵⁵ A year later, Lambert *et al.* used TCPS-

H₄ (**2**) and tetrakis(4-carboxyphenyl)germanium (**4**) in the synthesis of 3D MOFs (Figure 5).¹⁵³ These compounds retained the tetrahedral geometry offered by compound **3** but replaced the central carbon atom with silicon and germanium to produce compounds **2** and **4**, respectively.

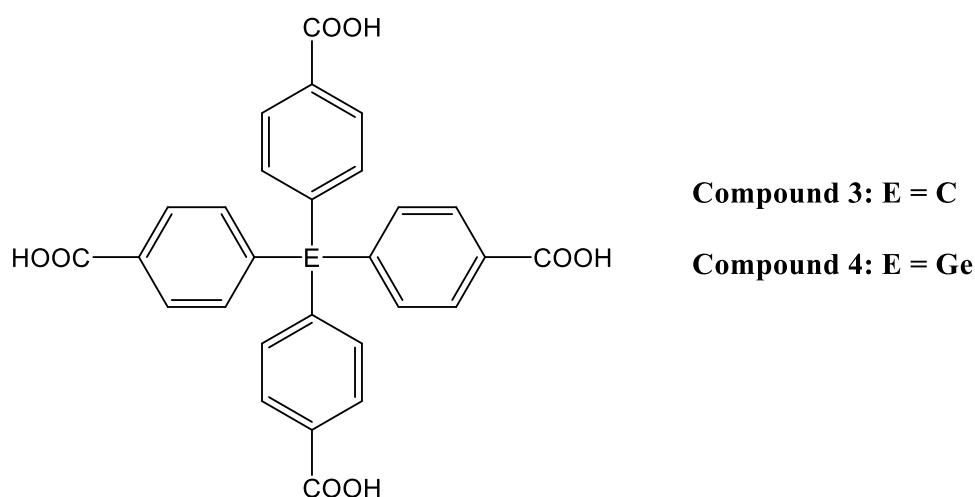


Figure 5: Structure of compounds **3** and **4**.

Both linkers were treated with zinc nitrate hexahydrate in a DMF/EtOH/water solvent mixture at 75 °C for three days to give two distinct MOFs, Si₄A-Zn and Ge₄A-Zn. Interestingly, although both MOFs were synthesised under identical conditions and used linkers of the same geometry, they exhibited different structures, not only from each other but also from the Zn(II)-based MOF constructed from compound **3**, known as MOF-36. For example, MOF-36 contains square-planar dinuclear zinc-oxo clusters. In contrast, Si₄A-Zn consists of zinc-oxo chains formed by two zinc atoms with differing geometries, while Ge₄A-Zn contains linear zinc-oxo clusters composed of three zinc atoms with two distinct geometries. In addition, the secondary building unit in Si₄A-Zn adopts a distorted tetrahedral geometry, whereas in Ge₄A-Zn, the zinc centres exhibit an eight-coordinate bipyramidal geometry.¹⁵³ These differences are likely attributed to the more open geometry arising from the elongation of the E–C bond going from carbon to germanium, demonstrating that even slight structural modifications of the organic ligand can provide access to new MOF topologies.

In the same year, Davies *et al.* reported the synthesis of three novel Zn(II)-based MOFs derived from the reaction of silicon-centred carboxylic acids, including TCPS-H₄, with zinc nitrate hexahydrate.¹⁵⁴ The dicarboxylic acid linker Me₂Si(*p*-C₆H₄CO₂H)₂ yielded a 2D layered network built from bent silicon-based nodes and 1D zinc hydroxo chains. Another 2D structure was obtained from the tricarboxylic linker MeSi(*p*-C₆H₄CO₂H)₃, consisting of distorted octahedral tetranuclear SBUs linked by trigonal-pyramidal silicon-centred nodes. Finally, when TCPS-H₄ was treated with Zn(II) in a 1:1 DMA/water mixture at 100 °C for 18 h, conditions different from those used by Lambert and co-workers, a novel 3D interpenetrated network was formed. This framework comprised tetrahedral silicon-based nodes linked to distorted tetrahedral binuclear Zn-based SBUs, whereas the structure reported by Lambert *et al.* featured rod-like SBUs cross-linked by the tetra-anionic TCPS linker.

Together, the studies by Lambert and Davies demonstrated the potential of silicon-based linkers in MOF design and synthesis. Since then, organosilicon linkers, particularly TCPS-H₄, have attracted growing interest. Numerous 3D MOFs incorporating TCPS or other silicon-centred linkers have been developed, featuring a wide range of metals such as Zn, Cu, Cd, Co, Al, Mn, and Zr, and exhibiting diverse topologies, including **PtS**, **flu**, **dia**, **sra**, **nia**, **fsy** and **alb/P**. Notable examples of these MOFs will be discussed in the following sections.

1.2.2 3D MOFs Derived From TCPS-H₄

In most cases, when TCPS-H₄ is the only linker used in MOF synthesis, it undergoes complete deprotonation to form the tetra-anionic ligand TCPS, which acts as a rigid, extended connector capable of cross-linking both discrete and polymeric secondary building units.^{153,154,156–172} Following the successful synthesis of the 3D Zn(II)-based MOF (IMP-5) using TCPS-H₄, Davies *et al.* extended their work by coupling the same tetracarboxylate linker with a series of other metal centres, including Cd²⁺, Mn²⁺, Cu²⁺, and Zn²⁺, resulting in six novel 3D

microporous MOFs.¹⁵⁶ Among them, IMP-8Cd and IMP-8Mn were synthesised using the same protocol as IMP-5 and were found to be isostructural. Both frameworks feature infinite linear metal–carboxylate chains running along the [100] direction, cross-linked by the TCPS (Figure 6). Moreover, they exhibit small accessible channels, within which non-coordinated DMA molecules reside. The solvent-accessible void volumes were calculated by PLATON,¹⁷³ following the removal of coordinated water and uncoordinated DMA, were found to be 1954.5 Å³ (45.9%) for IMP-8Cd and 1907.3 Å³ (46.1%) for IMP-8Mn. Additionally, both MOFs demonstrated thermal stability when desolvated under dynamic vacuum at 100 °C. Interestingly, when TCPS-H₄ was treated with Cd(NO₃)₂·4H₂O in the same solvent system but under slightly altered conditions (70 °C for 6 days), a different 3D Cd-based MOF (IMP-10) was obtained. Unlike IMP-8Cd and IMP-8Mn, which feature infinite metal–carboxylate chains, IMP-10 was constructed from a discrete trinuclear Cd-based SBU. The resulting structure feature channels along the [001], [010], and [100] directions, with the largest window measuring 6 × 3.5 Å² (along [001]). Upon theoretical removal of non-coordinated [Me₂NH₂]⁺ ions and solvent molecules using PLATON,¹⁷³ the solvent-accessible volume was calculated to be 5381.9 Å³ per unit cell, corresponding to 54.3% of the unit cell volume.

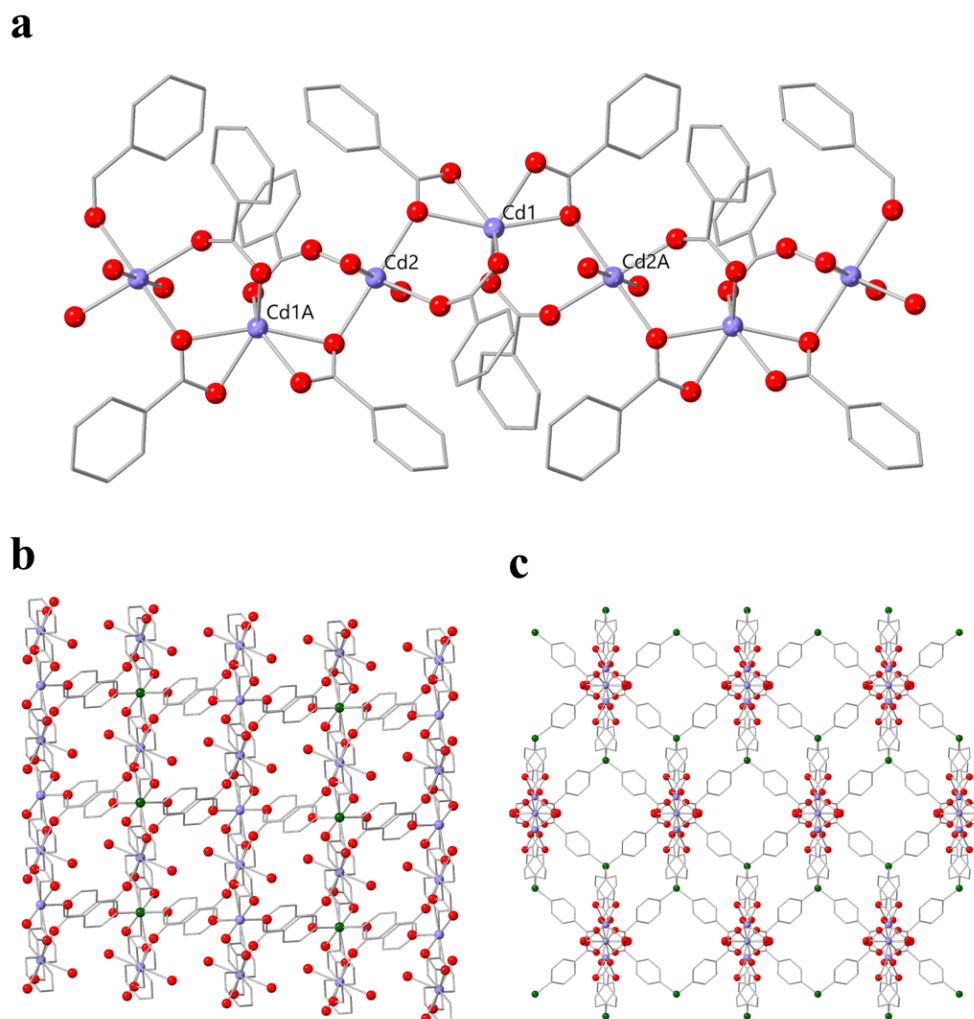


Figure 6: Crystal structure of IMP-8Cd: (a) the coordination environment in the linear Cd(II) carboxylate infinite chains; (b) a section of the network viewed along the *b* axis; (c) a section of the network viewed along the *c* axis. H atoms and non-coordinated solvent molecules have been omitted for clarity. Colour scheme: Cd(II), purple; oxygen, red; carbon, gray; silicon, dark green. Figure drawn using the crystal structure data published by Davies *et al.* (CSD refcode: ENISOK).¹⁵⁶

In several instances, modulators have been employed in the synthesis of 3D MOFs constructed from TCPS- H_4 .^{156,162,164,165} Among the six 3D MOFs reported by the Davies group, a copper(II)-based MOF, IMP-9, has garnered significant attention.¹⁵⁶ IMP-9 was synthesised by treating TCPS- H_4 with copper(II) nitrate in a 1:1 mixture of DMA and water in a sealed vial at 80 °C, with the addition of concentrated HCl as a modulator. This modulated synthesis yielded blue crystals of $[Cu_2(TCPS)(H_2O)_2] \cdot (DMA)_{12}$ (IMP-9). The resulting 3D framework features

a discrete bimetallic secondary building unit (Figure 7). This metal cluster consists of two Cu(II) ions bridged by four carboxylate groups in a di-monodentate fashion and axially coordinated by two water molecules. This arrangement forms a paddlewheel-type SBU with square planar geometry, which is a common motif in Cu(II) carboxylate-based MOFs.¹³⁷ TCPS linkers connect these SBUs, resulting in a 3D network with a **PtS** topology. IMP-9 was found to be isostructural to $[\text{Cu}_2(\mathbf{3}^4)(\text{H}_2\text{O})_2] \cdot (\text{DEF})_6(\text{H}_2\text{O})_2$, previously prepared by Ma *et al.*, with both frameworks adopting the same topology.⁹⁹ This demonstrates that silicon-based linkers can directly replace carbon-based ones, allowing for the construction of isostructural MOFs. IMP-9 also exhibited high porosity, with a PLATON calculated void volume of 2718.0 Å³ per unit cell (equivalent to 73.8% of the total cell volume), after the removal of coordinated water and non-coordinated DMA molecules. This high porosity underscores the material's potential for gas storage applications. Moreover, the structural integrity of IMP-9 was preserved after desolvation by heating under dynamic vacuum at 100 °C for 8 h, further highlighting its robustness. Subsequently, in 2013, Zhou and co-workers recognized the potential of IMP-9 and considered it worthy of further investigation due to its high purity and significant porosity. Their gas sorption analysis revealed a Type I isotherm, with a BET surface area of 601 m²/g. Although this was lower than the predicted surface area of 4162 m²/g reported by Goldsmith *et al.*,¹⁷⁴ the discrepancy may be attributed to incomplete activation. Gas uptake studies showed that IMP-9 could adsorb 80.56 cm³/g of CO₂ and 22.60 cm³/g of CH₄ at 273 K and 1.08 bar. Additionally, hydrogen uptake was measured at 156.13 cm³/g at 77 K and 1.08 bar, indicating promising performance for gas storage, especially considering the low cost of synthesis. This high uptake is attributed to the strong interactions between gas molecules and the accessible metal sites, as well as the presence of unsaturated metal centres created by the removal of axial water molecules during activation.¹⁵⁷

It is also worth noting that, in the same year, Goldsmith *et al.* studied the gas uptake properties of several promising MOFs and predicted their theoretical total hydrogen storage capacities.¹⁷⁴ Among them was IMP-9, which exhibited outstanding potential hydrogen uptake, with a calculated total gravimetric density of 10.2 g H₂/g MOF and a volumetric density of 58.7 g H₂/L.

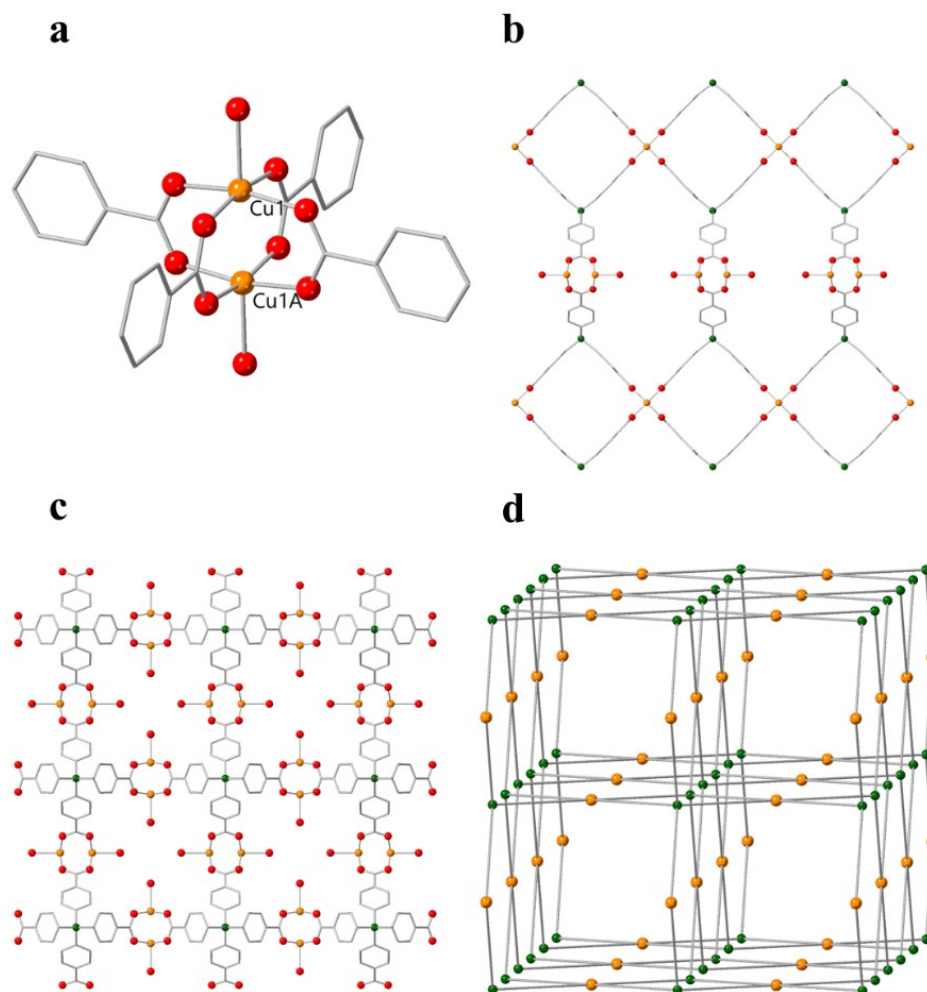


Figure 7: Crystal structure of IMP-9: (a) the coordination environment about the Cu-based paddle-wheel SBU; (b) a section of the network viewed along *a* axis; (c) a section of the network viewed along *c* axis; (d) a topology diagram of IMP-9 showing the **PtS** net with Cu-based nodes in orange and silicon-based nodes in dark green. H atoms and non-coordinated solvent molecules have been omitted for clarity. Colour scheme: Cu(II), orange; oxygen, red; carbon, gray; silicon, dark green. Figure drawn using the crystal structure data of IMP-9 published by Davies *et al.* (CSD refcode: ENITAX).¹⁵⁶

Guo *et al.* also emphasized that silicon-based linkers can be employed in the synthesis of stable 3D MOFs.¹⁶⁴ In their study, hydrofluoric acid (HF) and formic acid were used as modulators to synthesise the first aluminium-based MOFs constructed from TCPS, namely AITCS-1 and AITCS-2, respectively. This modulated synthesis yielded large single crystals of both AITCS-1 and AITCS-2. Unlike the zigzag aluminium oxide chains present in AITCS-1, the Al^{3+} ions in AITCS-2 are all six-coordinated and are cross-linked by the tetrahedral linker to form spiral chains running along the *c* axis (Figure 8). AITCS-2 exhibits permanent porosity, with a BET surface area of 1506 m^2/g , and shows high CO_2 and CH_4 uptake capacities at 273 K and 1 bar. Both MOFs were found to be stable across a wide pH range (pH 1–11) for 24 h, with AITCS-1 demonstrating additional stability in aqua regia.

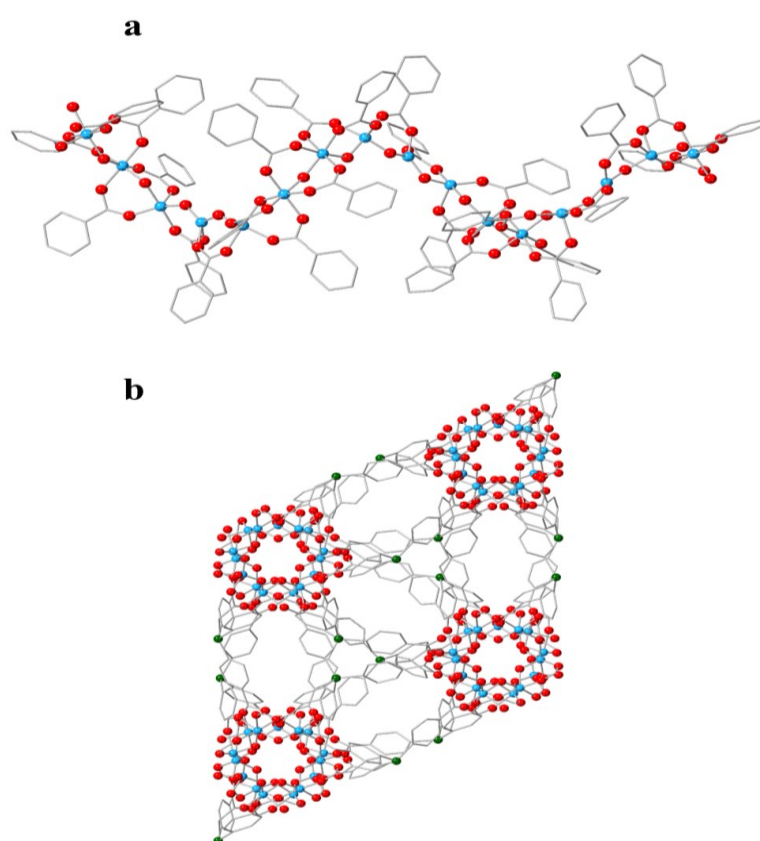


Figure 8: Crystal structure of AITCS-2: (a) the Al^{3+} spiral chain, (b) a section of the extended structure of AITCS-2 along *c* axis. H atoms have been omitted for clarity. Colour scheme: Al(III), sky-blue; oxygen, red; carbon, gray; silicon, dark green. Figure drawn using the crystal structure data of AITCS-2 published by Guo *et al.* (CSD refcod: CEMLIS).¹⁶⁴

It is also worth noting that there are several instances where TCPS-H₄ has been employed alongside nitrogen-donor linkers (Figure 9) to construct MOFs. For example, Gao and co-workers utilized a combination of TCPS-H₄ and 1-(tetrazo-5-yl)-4-(triazol-1-yl)benzene (TTB) to synthesise 3D Co(II)- and Zn(II)-based MOFs.¹⁵⁹ The Zn-based MOF exhibited an apparent BET surface area of 593.8 m²/g. Yang *et al.* also successfully synthesised three water-stable, isostructural, two-fold interpenetrated paddlewheel MOFs by treating TCPS-H₄ and 4,4'-bipyridine (BPY) with CoCl₂·6H₂O, Ni(NO₃)₂·6H₂O, and Cu(NO₃)₂·6H₂O.¹⁷⁵ SCXRD analysis revealed that each paddlewheel SBU comprises two metal ions and four carboxylate groups. BPY coordinates axially to two paddlewheel units, while each TCPS ligand connects to four such SBUs. These MOFs demonstrated good hydrogen uptake and moderate CO₂ and CH₄ storage capacities.

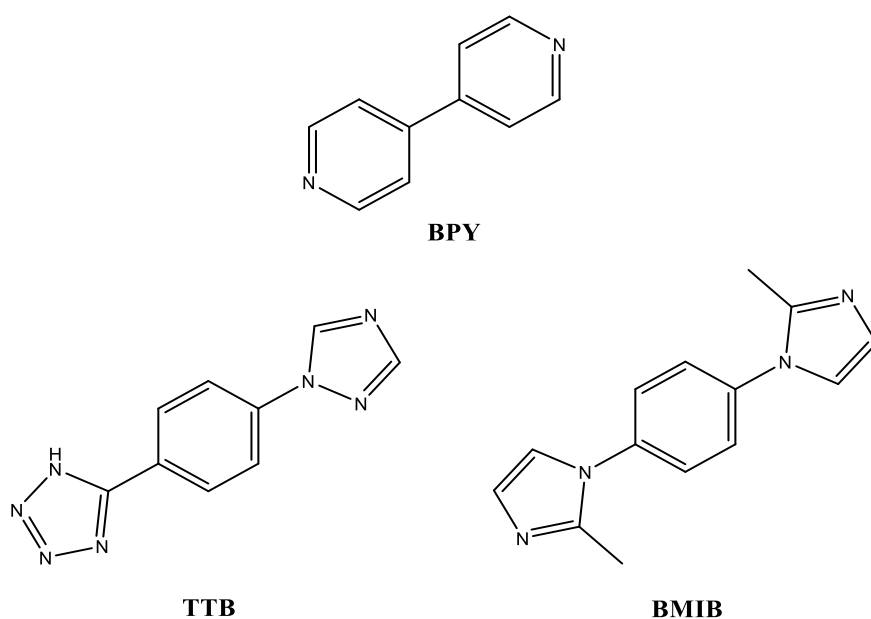


Figure 9: Examples of N-donor co-ligands used with Si-based ligands in MOF synthesis.

Furthermore, Wu and co-workers employed mixed ligands of TCPS-H₄ and 1,4-bis(2-methylimidazol-1-yl)benzene (BMIB) to construct a moisture-stable, microporous 3D Ni(II)-MOF with the formula [Ni₂(TCPS)(BMIB)₂], (Ni-1), and a water-stable, non-porous 2D MOF with the formula [Ni₂(TCPS-H₂)₂(BMIB)₂]·H₂O, (Ni-2·H₂O).¹⁷⁶ The authors suggested that the

enhanced stability of Ni-2 compared to Ni-1 is likely due to its lower porosity, which restricts water molecules from accessing and reacting with M–O and M–N bonds. Ni-1 displayed a BET surface area of 825 m²/g and a notable H₂ uptake of 1.43 wt% at 77 K and 1 atm. In contrast, Ni-2 showed only a CO₂ uptake of 2.1 mL/g at 298 K and 1 bar, consistent with its lower porosity.

1.2.3 Other Organosilicon Multicarboxylic Acids in MOFs

The effective use of TCPS-H₄ in affording 3D MOFs with interesting properties has motivated the development of various organosilicon carboxylate linkers, which have since been employed in MOF synthesis. Silicon-based linkers stand out for their ease of synthesis compared to their carbon analogues.^{154,177,178} In addition, the flexible bond angles at the silicon centre and longer Si–aryl bonds enable the formation of frameworks with a variety of architectures. Their high connectivity, ease of modification, and tuneable chemical properties further facilitate the construction of MOFs with diverse structures and novel topologies. Moreover, there has been significant interest in highly branched linkers, particularly those derived from multicarboxylic acid compounds ($n_{\text{COOH}} \geq 3$), due to their ability to form frameworks with enhanced stability and tuneable properties, arising from their strong coordination ability and versatile, predictable binding modes.^{132,179} In addition, the increased number of extension points enables the formation of highly connected and porous frameworks.¹³² highly branched carboxylate linkers can also adopt a greater variety of conformations and give rise to a wider range of topologies than ditopic linkers. Moreover, the topologies typically formed by tetra- and hexacarboxylate linkers can result in varied pore types and accessible metal sites, both of which influence the adsorption behaviour of these MOFs. For example, MOFs synthesised with hexacarboxylate linkers are among the most promising materials for gas adsorption offering some of the highest surface areas and pore volumes reported within the MOF field, such as NU-109 and NU-110.³

Incorporating organosilicon cores into multicarboxylic acid compounds, can provide an ideal combination of flexibility and directional binding, enhancing both the structural robustness and porosity of the resulting materials, while also expanding the range of accessible MOF topologies. However, despite this potential, highly branched organosilicon carboxylic acids, particularly those with six or more carboxylic acid groups ($n_{\text{COOH}} \geq 6$), remain relatively rare in the literature. This section highlights organosilicon multicarboxylic acids used in the synthesis of 3D MOFs, with particular emphasis on hexacarboxylic acids, which are the primary focus of this study.

1.2.3.1 Organosilicon Tricarboxylate Linkers

Several variations of TCPS- H_4 have been developed, where the silicon-based compound incorporates three carboxylic acid groups (Figure 10). In 2016, Liu *et al.* employed one such tripodal tricarboxylic acid (**5**) in the synthesis of two 3D uranyl-based MOFs.¹⁸⁰ They reported that different coordination modes between the ligand and the uranium centres led to the formation of MOFs with distinct topologies. Two years later, the same group used this linker in combination with N-donor co-ligands, including 2,2'-bipyridine (BIPY), 4,4'-di(1H-imidazol-1-yl)-1,1'-biphenyl (BIP), and 1,4-di(1H-imidazol-1-yl)benzene (DIB), to synthesise a series of two-fold interpenetrated MOFs. Photoluminescence analysis revealed that each framework exhibited characteristic emissions from the uranyl centers.¹⁸¹

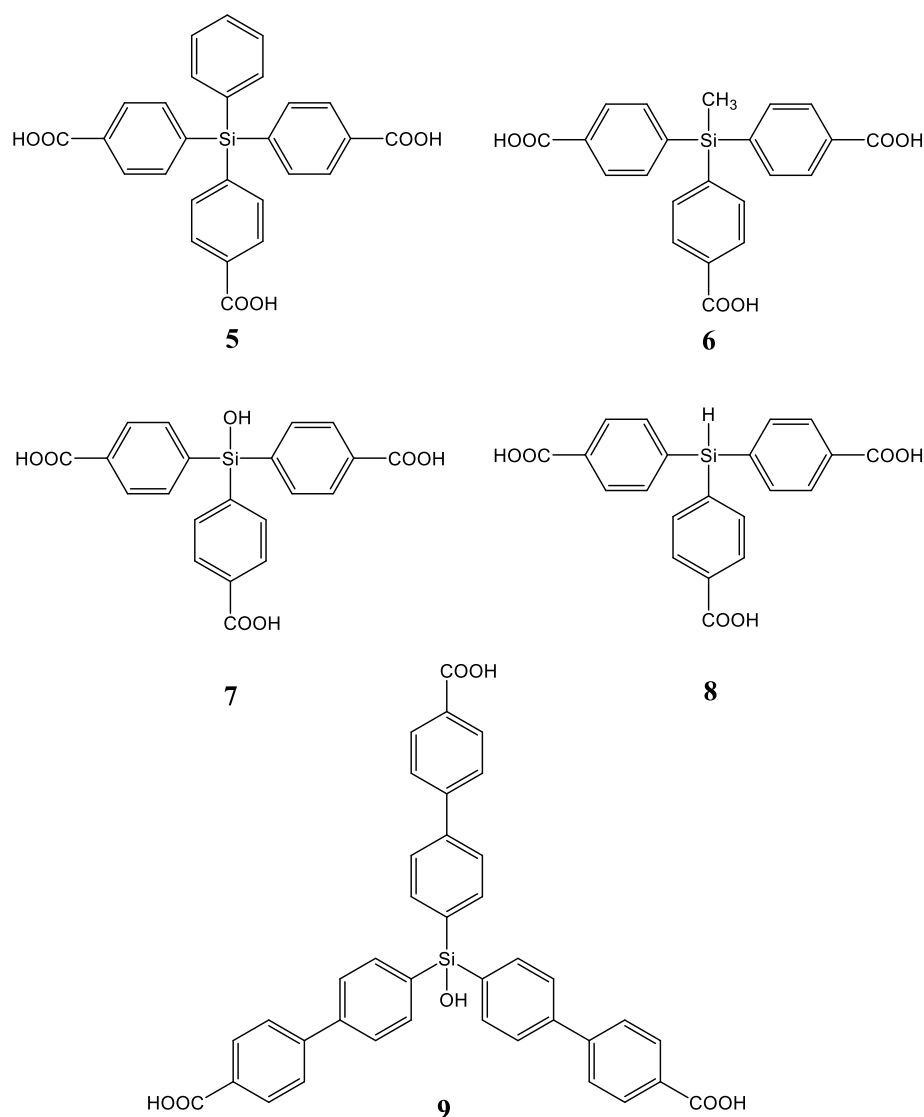


Figure 10: Structures of organosilicon tricarboxylic acids used in MOF synthesis.

Compound **6** is a structural analogue of TCPS-H₄ in which one of the benzoic acid groups is replaced by a methyl group.¹⁵⁴ Wang *et al.* reported a 3D Cd-based MOF with a two-fold interpenetrated network, which was constructed using this linker.¹⁸² Photoluminescence studies revealed that this MOF exhibits exceptional sensing performance for Fe³⁺ ions and acetone, highlighting its potential as a luminescent sensor.

The Davies group later employed the same linker in the synthesis of three alkali metal-based MOFs: IMP-24, IMP-25, and IMP-26.¹⁷¹ IMP-24 was prepared by treating the tricarboxylic acid (**6**) with LiNO₃, while IMP-25 and IMP-26 were obtained as a mixture from the reaction

of compound **6** with NaNO₃. The Li-based MOF adopts a chiral framework composed of helical lithium chains, cross-linked by the anionic ligand derived from compound **6**, forming a 3D network. Tricarboxylate linkers often afford helical structures, as their tendency to adopt monodentate coordination modes promotes helix formation when assembled with metal nodes.¹⁸³ In contrast, IMP-25 is constructed from an unusual 3D Na-based node, whereas IMP-26 features 1D sodium-based rods extending along three distinct crystallographic directions.

The tricarboxylic acid silanol derivative (**7**) represents another class of functional linkers, distinguished by the presence of an Si–OH group. The silanol group serves as a hydrogen bond donor and provides an opportunity for further functionalisation. Delmas *et al.* reported the synthesis of a Zn-based MOF (IMP-19) by treating compound **7** with Zn(NO₃)₂·6H₂O.¹⁸⁴ The resulting framework features tetrametallic clusters of four Zn atoms connected by two μ_3 -OH bridges. These SBUs are linked by the tricarboxylate linker to form 2D polymeric sheets with a **kgd** topology. When hydrogen bonding interactions between the peripheral silanol group from an adjacent layer and the uncoordinated carboxylate oxygen atom of the monodentate carboxylate group on a neighbouring linker are considered, the 2D sheets further extend into a 3D network with **flu** topology.

Li and co-workers synthesised two hydrogen-bonded MOFs, SiMOF-1 and SiMOF-2,¹⁸⁵ by treating the hydrosilane-based tricarboxylic acid **8** with Zn²⁺ and Mn²⁺, which underwent *in situ* transformation from Si–H to Si–OH, as confirmed by FTIR spectroscopy. SiMOF-1, which is identical to IMP-19 (as confirmed by SCXRD), exhibited improved crystallinity after activation compared to IMP-19. The Mn-based SiMOF-2 also displayed permanent porosity and a significant CO₂ uptake of 55.5 cm³/g at 273 K, despite having a modest BET surface area of 560 m²/g. Ma *et al.* reported another tripodal silanol-functionalised tricarboxylic acid (**9**), which was used to construct a novel 3D Cu-based MOF, SDU-9.¹⁸⁶ The structure of SDU-9 is

composed of four types of 12-rings (each consisting of six Cu(II)-based SBU) catenated strongly together, forming a framework with exceptionally high topological density.

1.2.3.2 Organosilicon Tetracarboxylate Linkers

Among all multicarboxylic acids ($n_{\text{COOH}} \geq 3$), tetracarboxylic acids are the most commonly encountered and widely used in MOF synthesis. Beyond TCPS- H_4 , a few other organosilicon tetracarboxylic acids have been reported and explored for MOF synthesis (Figure 11). In 2009, Wenzel *et al.* reported the synthesis of PCN-12-Si, a 3D Cu-based MOF constructed from binuclear Cu paddlewheel units linked by a non-linear tetra-anionic linker derived from **10**.¹⁸⁷ PCN-12-Si was found to be isorecticular with PCN-12 (which was built with 5,5'-methylene-di-isophthalate), but with a slightly larger unit cell, due to the longer Si- C_{Ar} bond in linker **10** compared to the C_{CH_2} - C_{Ar} bond in 5,5'-methylene-di-isophthalate. Gas sorption studies revealed a remarkable hydrogen uptake of 2.6 wt% at 1 bar for the activated PCN-12-Si. Using the same linker, Sun and colleagues prepared another Cu-based MOF comprising $[\text{Cu}_2(\text{CO}_2)_4]$ -type paddlewheel clusters. This material showed impressive H_2 , CH_4 , and CO_2 uptake at ambient pressure, along with strong catalytic performance for CO_2 fixation under mild conditions.¹⁸⁸

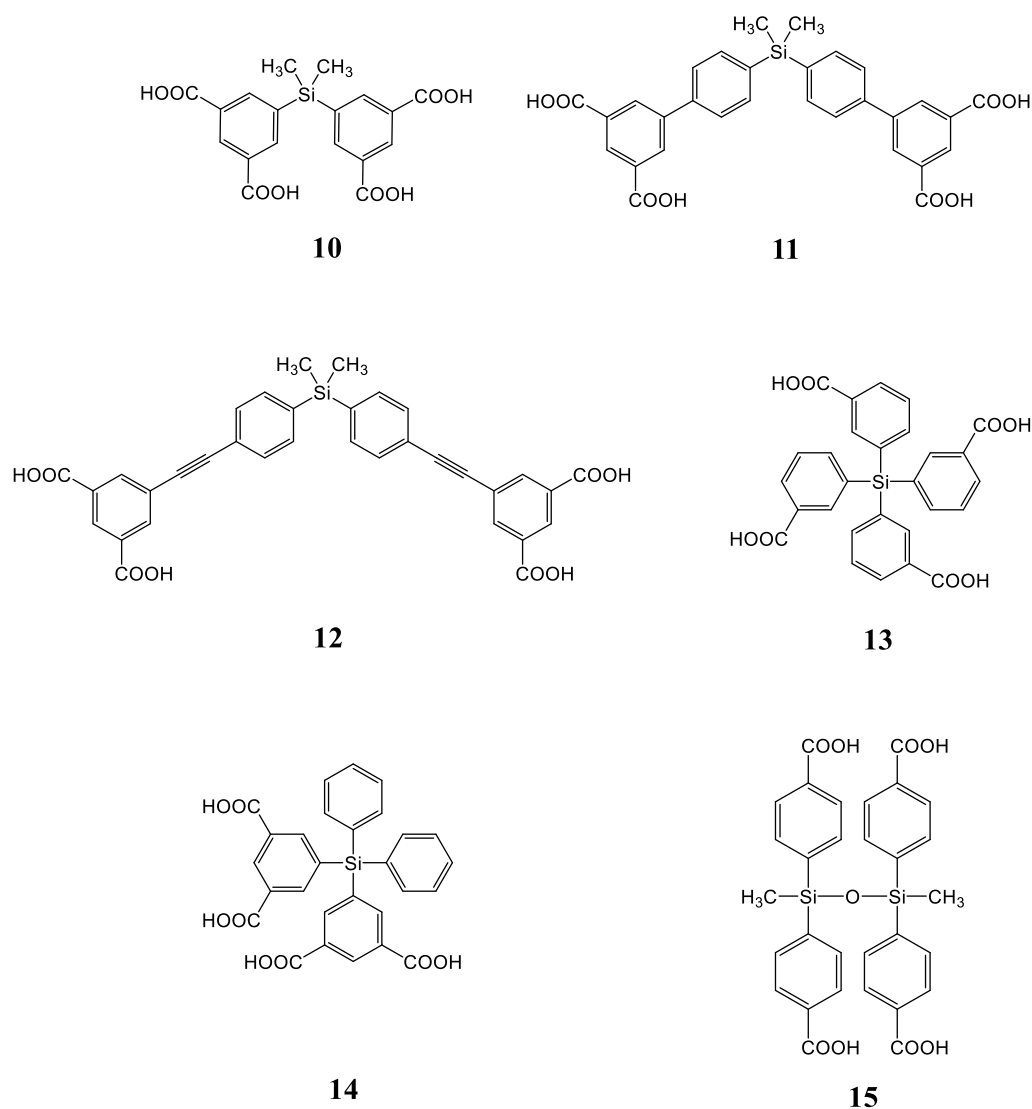


Figure 11: Structures of organosilicon tetracarboxylic acids used in MOF synthesis.

Förba and co-workers modified compound **10** by extending each side arm with an additional phenylene ring to produce compound **11**, introducing isophthalic acid moieties that enhance connectivity and can result in novel framework topologies.¹⁸⁹ Treating compound **11** with copper(II) nitrate trihydrate led to the formation of UHM-6, a two-fold interpenetrated MOF with a **zmj** net. This MOF displayed a BET surface area of 1200 m²/g, an H₂ uptake of 1.8 wt% at 77 K and 1 bar, and CO₂ uptake of 3.3 mmol/g at 273 K. Based on their report, the extension has resulted in a framework with larger voids but different topology. Building on this study, the same group extended compound **11** further with a C≡C unit between the phenyl rings to produce **12**.¹⁹⁰ This compound was used to construct a non-interpenetrated Cu-based MOF with

chs topology (UHM-7). Despite exhibiting slightly higher surface area ($1290 \text{ m}^2/\text{g}$), UHM-7 showed lower H_2 , CH_4 , and CO_2 uptake than UHM-6.

Compound **13** is another TCPS- H_4 analogue, with COOH groups in the *meta*-position. Zhao *et al.* used this compound to prepare a 3D Cd-based MOF with a rare **flu** topology.¹⁹¹ Additionally, Sun and co-workers developed a silicon-based tetracarboxylic acid (**14**) that combines isophthalic and non-functionalised units. Using this tetra-acid, they have successfully prepared a novel Cd(II)-based MOF with strong photoluminescence at ambient temperature.¹⁹²

Water stability is essential for MOFs intended for gas separation, carbon capture, and water purification. The hydrophobic nature of silicones is well known, and research has shown that introducing silicon-based units into MOF systems through functionalising the SBUs can reduce their affinity for water.¹⁹³ In addition, incorporating hydrophobic substituents, such as $-\text{CH}_3$, can further enhance their hydrophobicity. Motivated by this, Davies and co-workers developed a siloxane-based tetracarboxylic acid (**15**) bearing $-\text{CH}_3$ groups and employed it to synthesise two isostructural MOFs, IMP-32-Zr and IMP-32-Hf, which represent the first Zr/Hf-based MOFs constructed from siloxane-based linkers.¹⁹⁴ In both MOFs, the tetra-acid linker is fully deprotonated, with each carboxylate group binding to a different metal cluster. IMP-32-Zr comprises 8-connected Zr_6O_8 clusters (Figure 12) and adopts the rare **scu** topology. Both MOFs were demonstrated to be water stable with very low water affinity, as confirmed by dynamic vapor sorption (DVS) analysis. They also exhibited BET surface areas of $1135 \text{ m}^2/\text{g}$ and $1001 \text{ m}^2/\text{g}$, respectively, and showed promising CO_2 adsorption capacities of 5.9 wt% (IMP-32-Zr) and 5.2 wt% (IMP-32-Hf).

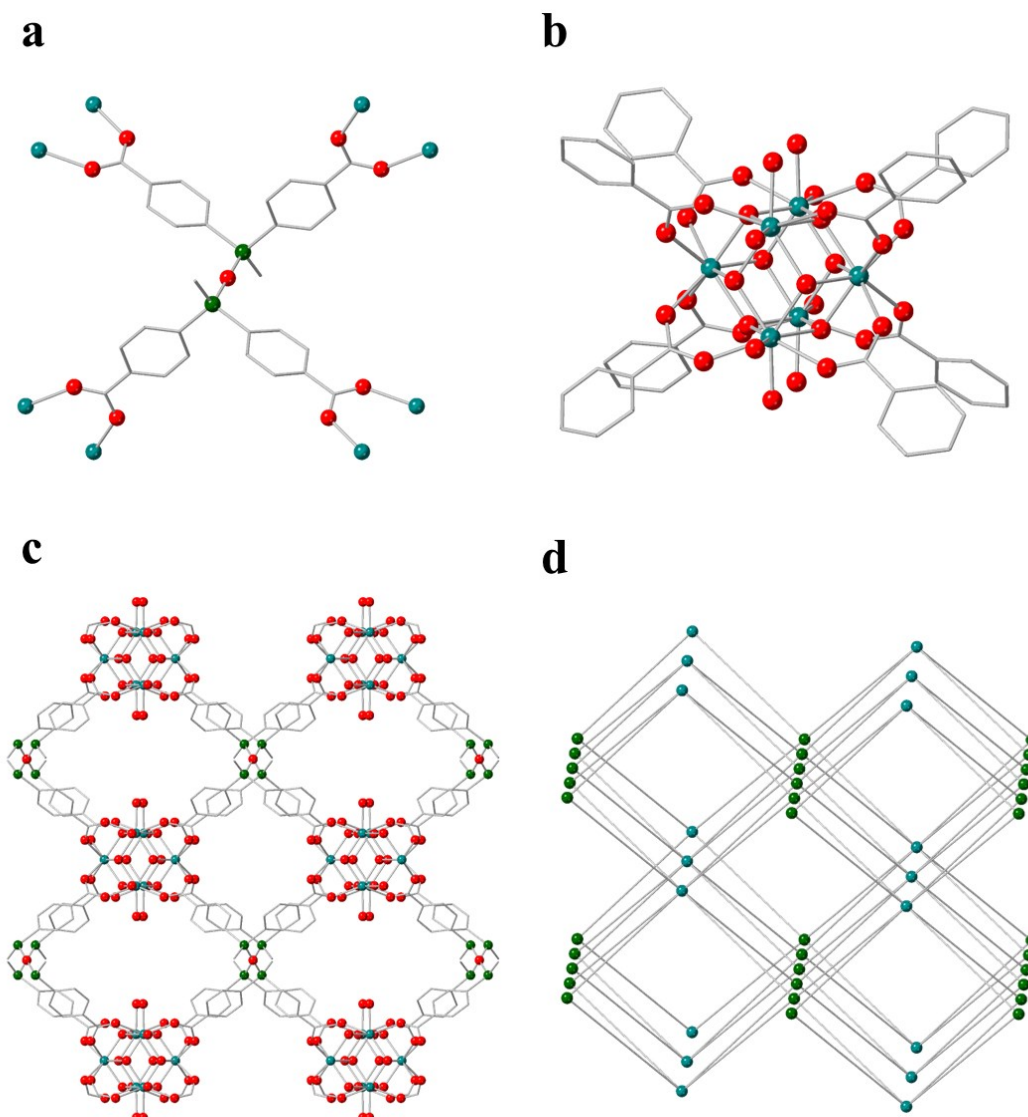


Figure 12: IMP-32-Zr structure: (a) linker environment of **11**; (b) the 8-connected Zr_6O_8 cluster; (c) a portion of the packing structure of IMP-32-Zr viewed along the crystallographic a axis, (d) a topology diagram of IMP-32-Zr diagram showing the **scu** network with Zr-based nodes in dark cyan and silicon-based nodes in dark green. H atoms are omitted for clarity. Colour scheme: Zirconium, dark cyan; oxygen, red; carbon, gray; silicon, dark green. Figure drawn using the crystal structure data of IMP-32-Zr published by Davies and co-workers (CSD refcode: PUQJAP).¹⁹⁴

1.2.3.3 Hexacarboxylate Linkers

While tri- and tetracarboxylic acids are more commonly employed in MOF synthesis, hexacarboxylic acids remain relatively rare and less frequently encountered in the literature. However, their unique structural and functional characteristics make them particularly attractive for the design of highly porous, stable, and multifunctional MOFs. Hexacarboxylate ligands offer high connectivity and large size, resulting in an increased distance between metal nodes and a greater number of metal–ligand bonds, both of which facilitate the formation of robust and highly porous frameworks.¹³² These linkers have also shown strong potential in the construction of MOFs with exceptional thermal and hydrolytic stability. For example, NU-1500-Cr, synthesised from a rigid hexacarboxylate linker, exhibits high porosity and excellent hydrolytic stability, along with remarkable water vapor uptake.¹⁹⁵ Furthermore, the synthesis of NU-110 and NU-1501 (Figure 13) using hexacarboxylate linkers has been reported, with both MOFs exhibiting BET surface areas exceeding 7000 m²/g, placing them among the highest surface area MOFs reported to date.^{2,3} It is worth noting that this high porosity can be further enhanced through linker elongation strategies, which have been extensively studied in hexacarboxylate-based MOFs.^{196,197} Such strategies facilitate the development of isorecticular frameworks with enlarged pore sizes, higher surface areas, and optimised properties tailored to specific application requirements.¹⁹⁸

Hexacarboxylate-based MOFs are also promising candidates for gas separation and storage applications. For example, ZJNU-62 demonstrates excellent selectivity for C₂ hydrocarbons and CO₂ over methane under ambient conditions, highlighting its potential for natural gas purification.¹⁹⁹ Moreover, Li and co-workers reported the synthesis of two **rht**-type MOFs prepared using hexacarboxylate ligands functionalised with acylamide groups.²⁰⁰ Both MOFs exhibited high CO₂ uptake (157 wt%) at 20 bar and 273 K, along with good selectivity for CO₂ over methane and nitrogen.

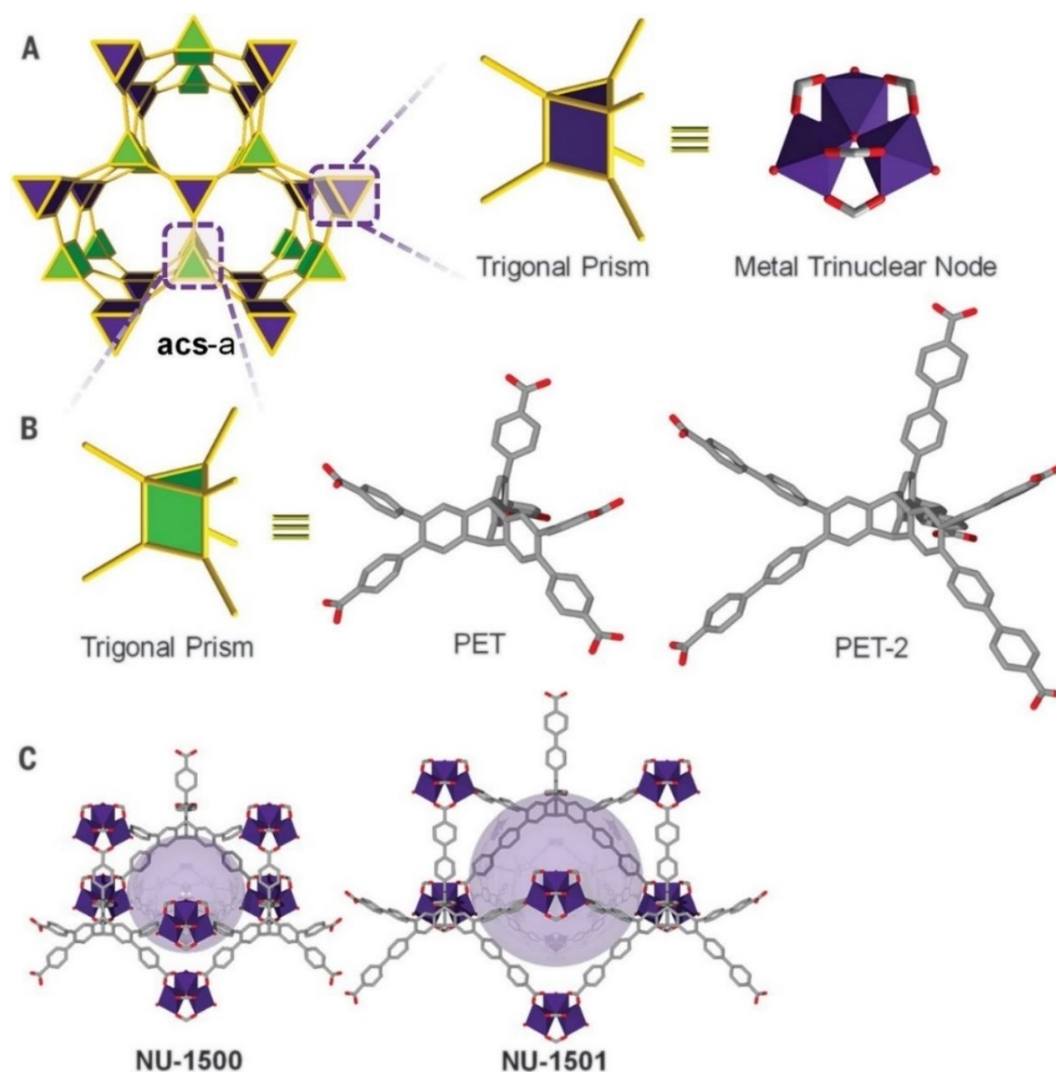


Figure 13: (A) schematic illustration of the 6-connected **acs** net in NU-1501-M (M = Fe and Al); (B) triptycene-based organic ligands PET and PET-2 used for the preparation of NU-1500 and NU-1501, respectively; (C) schematic representation of NU-1500 and NU-1501. Colour scheme: C, gray; metal polyhedron, Northwestern University (NU) purple; O, red. H atoms are omitted for clarity. Reproduced from Ref. ² with permission.

Interestingly, most reported hexacarboxylic acid linkers form MOFs with **rht** topology,^{3,201} offering a higher degree of predictability compared to MOF synthesis using tri- and tetracarboxylic acid linkers. In addition, **rht**-type networks are highly desired for developing stable MOFs with large pores and high surface areas.¹³² These networks are also known for their tuneability, the presence of multiple cavity types, and a high density of open metal sites, all of which increase their potential for gas storage and separation applications. Other rare

topologies have also been reported, with the resulting MOFs exhibiting promising gas storage performance. For example, the **ntt**-type MOF UTSA-61, constructed from 1,3,5-tris(3,5-di(4-carboxyphenyl)phenyl)benzene, demonstrated both high methane uptake and working capacity, making it a promising adsorbent for on-board methane storage.²⁰² Similarly, UTSA-20, synthesised using 3,3',3'',5,5',5''-benzene-1,3,5-triyl-hexabenzoic acid (H₆BHB), adopts a rare **zyg** topology, and exhibits a high methane uptake capacity.²⁰³

Furthermore, JUC-103 and JUC-104 are constructed from a hexadentate linker (Me-TDCPB) featuring three methyl groups on a central phenyl ring.²⁰⁴ This linker is capable of adopting both octahedral and trigonal prismatic geometries when coordinated with Zn₄O and Pb₆ clusters, respectively, leading to the formation of JUC-103 and JUC-104 (Figure 14). JUC-103 exhibits remarkable ethane uptake and efficiently separates ethane from nitrogen, while JUC-104 adopts a rare (6,12)-connected CaSi₂-type topology.

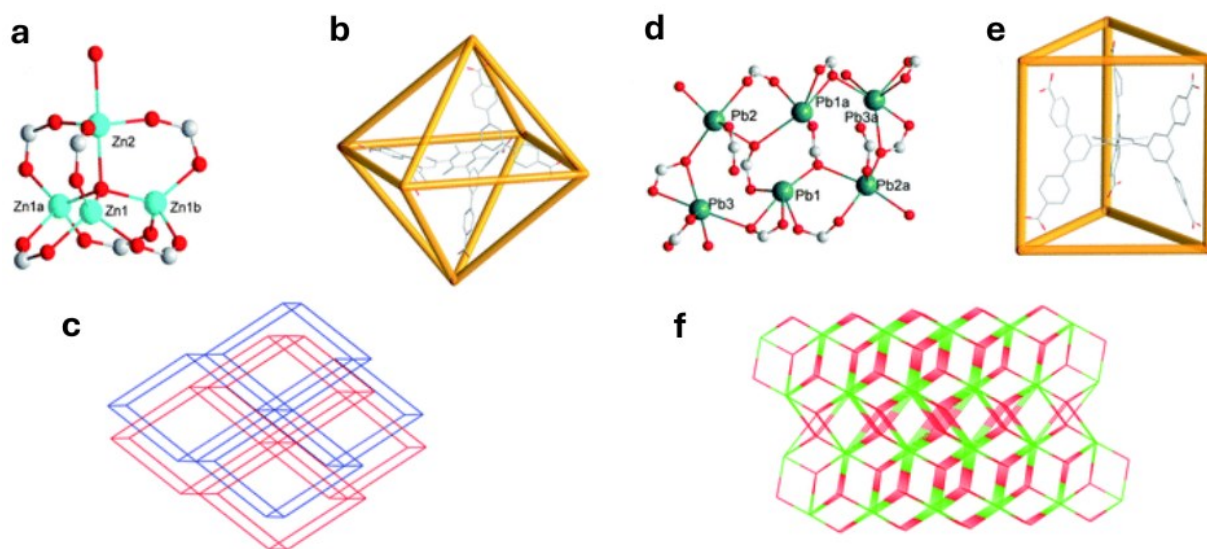


Figure 14: (a) the Zn₄-based SBU in JUC-103; (b) the octahedral geometry of Me-TDCPB; (c) topological representation of JUC-103; (d) The Pb₆-based SBU in JUC-104; (e) the trigonal prismatic geometry of Me-TDCPB; (f) topological representation of JUC-104. Reproduced from Ref. ²⁰⁴ with permission.

1.2.3.3.1 Organosilicon Hexacarboxylate Linkers

As discussed earlier in this chapter, silicon-based linkers are attractive candidates for the development of novel MOF materials. However, while the majority of reported organosilicon carboxylate MOFs are constructed from di-, tri-, and tetracarboxylate linkers, those derived from hexacarboxylate linkers remain extremely rare, with fewer than ten 3D structures reported in the literature, underscoring the significant potential for further discovery in this area.

In 2012, Zhao *et al.* reported three novel Si-based hexacarboxylic acids (**16–18**, Figure 15), designed with varying functional groups, hydroxyl (–OH), methyl (–CH₃), and isobutyl (–CH₂CH(CH₃)₂), on the central silicon atom.²⁰⁵ These hexa-acids were employed in the synthesis of isorecticular Cu-based MOFs, SDU-6, SDU-7, and SDU-8, respectively, all displaying permanent porosity and remarkable BET surface areas of 2826, 2713, and 2516 m²/g. Among them, SDU-6, functionalised with a hydroxyl group, exhibited the highest hydrogen uptake of 21.5 mg/g at 77 K and 1 bar, attributed to enhanced dipole–induced dipole interactions. It also showed a significant CH₄ uptake of 172 cm³/cm³ at 35 bar. These results highlight how incorporating strong polar groups such as –OH can significantly improve gas adsorption, while also demonstrating the potential of hexacarboxylate silicon-based linkers for constructing MOFs with high surface areas.

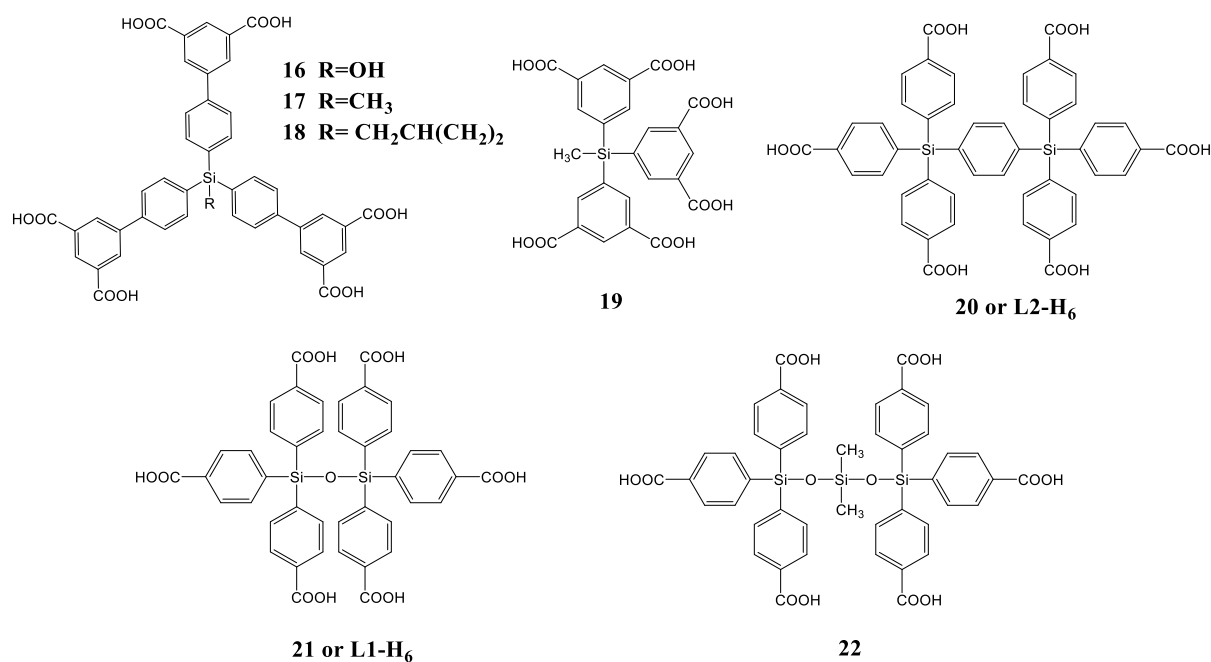


Figure 15: Structures of organosilicon hexacarboxylic acids used in MOF synthesis.

Sun and co-workers also reported a novel silicon-centred hexacarboxylic acid (**19**), which was used to construct a 3D Cd-based MOF containing CdO_6 clusters.²⁰⁶ This MOF exhibited excellent chemical stability in a wide range of organic solvents, such as DMA, DMF, *n*-butanol, acetone, chloroform, *n*-hexane, methanol, and ethanol, and showed promising luminescence properties for sensing *n*-butanol and acetone.

Davies and co-workers developed a novel phenylene-cored hexacarboxylic acid (**20**, also referred to as **L2-H₆** in this thesis). Owing to its rigid backbone and the desired *pseudo*-octahedral arrangement of its carboxylic acid groups, this hexa-acid linker is advantageous for MOF synthesis.²⁰⁷ The reaction of **L2-H₆** with $Zn(NO_3)_2 \cdot 6H_2O$ yielded IMP-15, which was found to be isorecticular to MOF-5. The 3D MOF is composed of $[Zn_4O]^{6+}$ clusters, with each node coordinated by six di-monodentate carboxylate groups. These Zn-based units assemble with **L2** ions to afford a **pcu** network (Figure 16). In addition, BET analysis of nitrogen adsorption at 77 K indicated a surface area of 1230 m²/g. This work demonstrated the potential of hexadentate organosilicon linkers in replacing metal-based SBUs, offering a novel approach

for isorecticular design with reduced metal loading (IMP-15 contains half the number of metal ions compared to the isorecticular MOF-5) and enhanced gravimetric storage capacity.

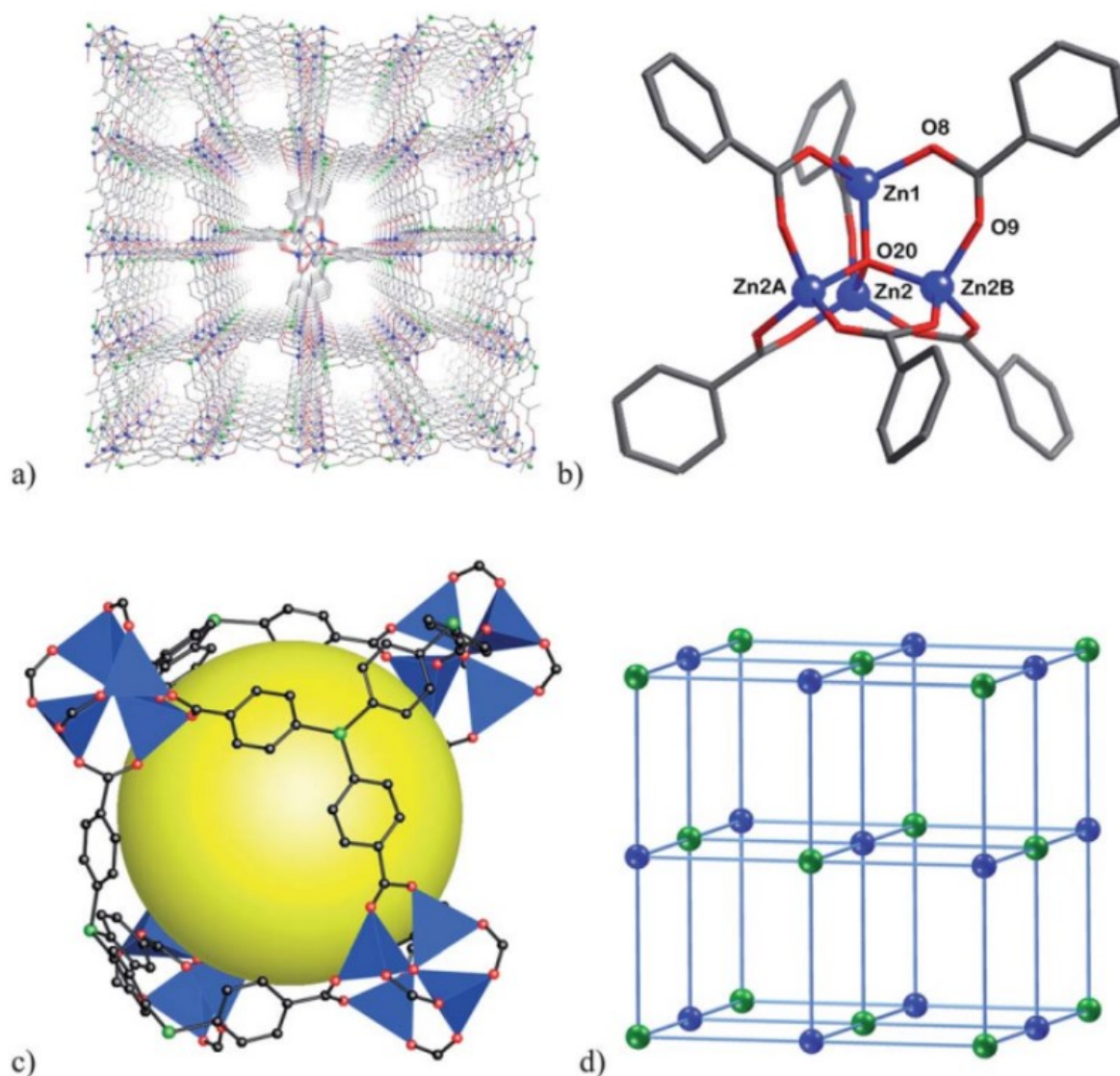


Figure 16: Crystal Structure of IMP-15: (a) a portion of the packing structure of IMP-15; (b) the coordination environment of the Zn_4O cluster; (c) One of the pores in IMP-15; (d) a topological illustration of IMP-15 showing the **pcu** network with Zn SBU nodes in blue, and the silicon-based nodes in green. H atoms and non-coordinated solvent molecules are omitted for clarity. Colour scheme: Zn, blue; O, red; C, grey; Si, green. Reproduced from Ref. ²⁰⁷ with permission.

Continuing their focus on highly branched silicon-based linkers, the Davies group introduced two additional organosilicon hexacarboxylic acids (**21** and **22**, Figure 15), both of which exhibit unusual hydrogen-bonded structures (see Chapter 3 for further details).^{184,208} The hexa-acid **21** (also referred to as **L1-H₆** in this thesis) is based on a disiloxane core and presents a *pseudo*-octahedral arrangement of carboxylate groups. Davies and co-workers have employed the hexadentate disiloxane linker in MOF synthesis by coupling it with a variety of metal precursors. Initially, the treatment of **L1-H₆** with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ afforded IMP-18, a porous 3D MOF composed of discrete bimetallic Zn paddlewheel units linked together by **L1**, forming a rare **fsy** topology (Figure 17).¹⁸⁴ This marked the first 3D MOF synthesised using a disiloxane-based linker. Building on this, the group synthesised three additional MOFs, IMP-28, IMP-29, and IMP-30, by treating **L1-H₆** with Cd^{2+} , Ce^{3+} , and Y^{3+} , respectively.²⁰⁹ These frameworks consisted of discrete metal clusters cross-linked by **L1**, affording 3D polymeric structures with solvent-filled channels. IMP-28 and IMP-29 exhibit rare **nia** and **fsh**, topologies, respectively. Furthermore, the same group prepared IMP-31, a MOF with **mog** topology, by combining **L1-H₆**, 4,4'-bipyridine, and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, emphasising the capability of organosilicon hexacarboxylate linkers in producing uncommon MOF topologies.

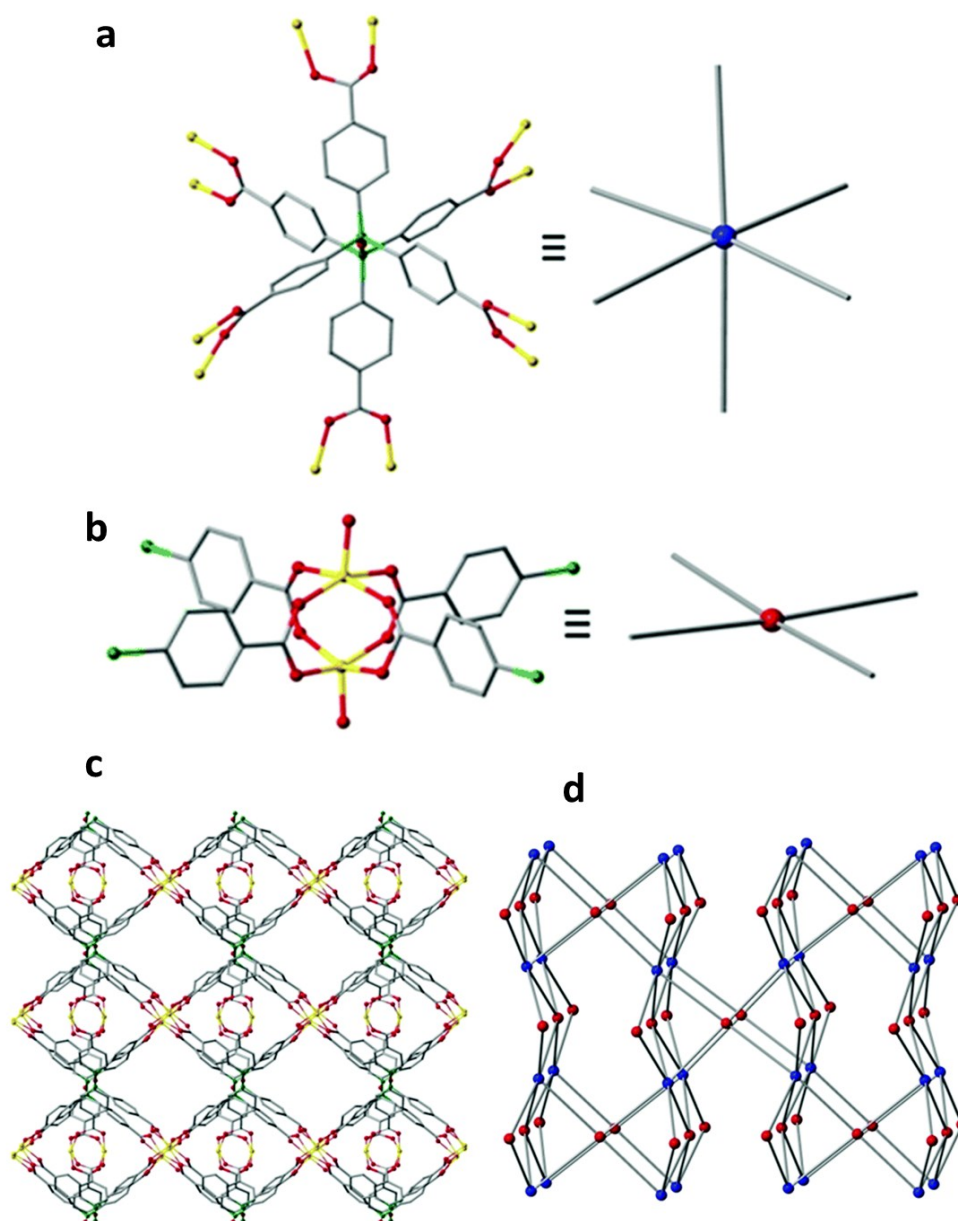


Figure 17: Crystal structure of IMP-18: (a) the coordination mode of **L1** in the IMP-18; (b) the binuclear zinc paddlewheel SBUs within IMP-18; (c) a portion of IMP-18 viewed along the *b* axis, solvent molecules and hydrogen atoms have been omitted for clarity; (d) a simplified schematic of the **fsy** topology, showing the 4-connected zinc SBU nodes in red and the 6-connected silicon-based linker nodes in blue. Colour scheme: Zn, gold; O, red; C, grey; Si, green. Reproduced from Ref. ¹⁸⁴ with permission.

Davies and co-workers continued their investigation into the use of organosilicon hexacarboxylate linkers for MOF synthesis by employing compound **22**.²⁰⁸ This compound features a trisiloxane core that imparts a degree of flexibility, enabling the adjustment in

backbone geometry (bending or stretching) to optimise coordination to metal nodes, which is advantageous for MOF design. Linker **22** was treated with Mn^{2+} and Zn^{2+} to yield porous, 3D MOFs (IMP-20 and IMP-21, respectively), both incorporating Si–O–Si–O–Si backbones. IMP-20 consists of discrete trimetallic nodes bridged by fully deprotonated hexacarboxylate linker derived from **22**, forming a 3D network with **PtS** topology. IMP-21 is composed of trimetallic Zn-based rod units linked together by the hexacarboxylate linker. Although trisiloxane-based MOFs remain rare, they merit further exploration, as the central silicon atom offers an ideal site for additional functionalisation, such as incorporating of hydroxyl groups, which could lead to the development of MOFs with unique properties.²⁰⁸

In addition to tri-, tetra-, and hexacarboxylate organosilicon linkers, dicarboxylate organosilicon linkers have also been employed in MOF synthesis. These often form 2D frameworks, with some demonstrating notable CO_2 adsorption selectivity.^{154,171,210–221} A limited number of MOFs constructed from penta-, octa-, and dodecacarboxylate linkers have been reported in the literature. Among these, some exhibit high thermal or hydrolytic stability, while others demonstrate promising performance in gas adsorption, separation, or sensing applications.^{222–231} However, to the best of our knowledge, no examples of penta- or dodecacarboxylate organosilicon linkers have yet been reported in MOF synthesis. Notably, You and co-workers reported the use of an octacarboxylate organosilicon linker to construct 3D Cu-, Cd-, and Zn-based MOFs, with the Cu-MOF exhibiting promising CO_2/CH_4 separation performance.²³² As far as we are aware, these MOFs remain the only reported examples of 3D frameworks constructed from octacarboxylate organosilicon linkers.

It is also worth to note that MOF structures incorporating $[\text{SiF}_6]^{2-}$ anions are not discussed in this thesis as the focus is limited to organosilicon compounds.²³³ In addition, organosilicon linkers featuring other coordinating groups such as phosphonates, pyridines, azolates,

thioethers, or nitriles have also been used in MOF synthesis; however, these fall outside the scope of this study. Examples of such MOFs can be found in the literature.^{149,156,234–244}

1.3 Linker Elongation via Amide Functionalisation for Enhanced Gas Storage and Separation

The inherent porosity of MOFs makes them highly advantageous for a wide range of applications. In particular, their use in gas storage strongly depends on both their porosity and accessible surface area. As mentioned in Section 1.2.3.3, a common strategy to enhance porosity is linker elongation, which enables the construction of isorecticular MOFs with increased pore sizes and higher surface areas.^{198,245–247} For example, in PCN-66, elongating the hexacarboxylate linker significantly increased both the surface area and pore dimensions.¹⁹⁶ A similar effect was observed in the NOTT framework series built with hexacarboxylate linkers, where linker extension led to improved H₂ adsorption.²⁴⁸

In addition, the incorporation of guest-accessible functional groups into MOFs can further improve their gas storage and separation performance. The amide group –OCNH–, which contains both hydrogen-bond donor and acceptor functionalities, has been widely employed in MOF design to introduce functional organic sites within the channels (Figure 18).^{249–252} These functional groups promote stronger host–guest interactions, enabling enhanced gas uptake through hydrogen bonding and dipole–quadrupole moment interactions. As a result, amide-functionalised MOFs (AFMOFs) have been widely explored for CO₂ capture.^{253–258}

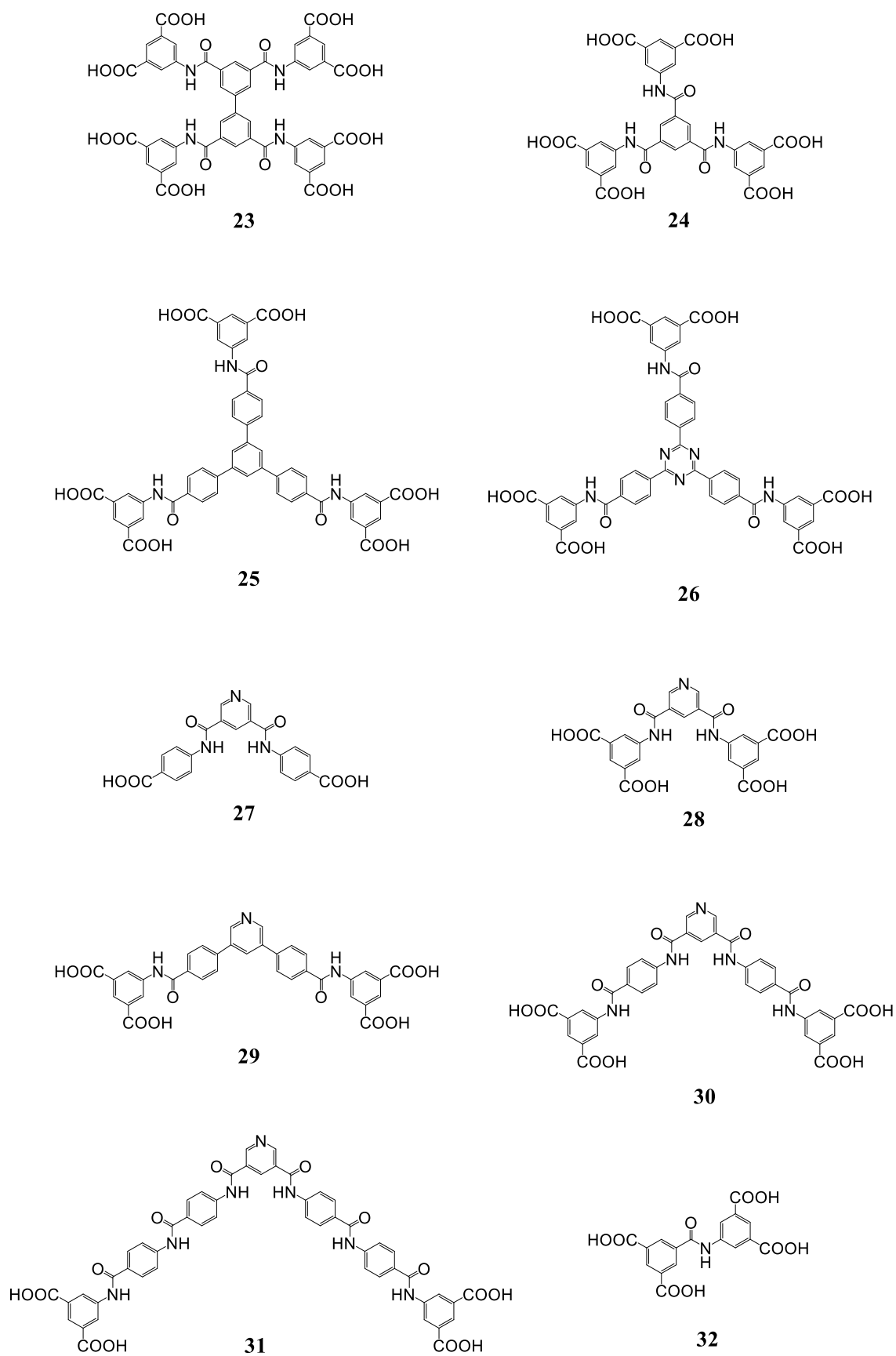


Figure 18: Some examples of amide-functionalised multicarboxylic acid linkers used in MOF synthesis.

Schröder and co-workers investigated gas adsorption in a Cu(II)-based 3D MOF (MFM-188), constructed from a tetra-amide linker (**23**) and bimetallic paddlewheel nodes.²⁵³ The activated MFM-188 exhibited a high BET surface area of 2568 m²/g and one of the highest gravimetric CO₂ uptakes reported, 120 cm³/g (23.7 wt%) at 298 K and 1 bar, as well as a high C₂H₂ uptake of 232 cm³/g (27.0 wt%). Neutron diffraction and inelastic neutron scattering studies confirmed that CO₂ binds cooperatively to both the open metal sites and amide groups within the framework, which contribute significantly to its outstanding gas uptake performance.

Linker elongation via incorporation of amide groups has emerged as an effective strategy for improved stability, porosity and functional properties of the resulting frameworks. The flexibility and polar nature of amide functionalities can also allow them to form hydrogen bonds and enable the discovery of new MOFs with novel topologies. Building on this concept, Bai and co-workers synthesised a series of robust amide-functionalised MOFs using amide-extended multicarboxylic acid linkers.^{255–257,259} Their approach, which included inserting amide groups between two phenyl rings within the linker, resulted in MOFs exhibiting a variety of topologies (**rht**, **txt**, **nbo**, **pcu**, **agw**, and **pbz**) and enhanced gas separation and storage properties.²⁵⁵ For example, an **rht**-type MOF synthesised using the amide-extended hexacarboxylic acid **24** exhibited superior CO₂ uptake and selectivity over N₂ and CH₄ compared to its non-amide analogue (PCN-61).¹⁹⁶ In addition, compounds **25** and **26**, yielded isorecticular mesoporous **rht**-type MOFs with high CO₂ selectivity and capacity.²⁰⁰

Furthermore, mesoporous amide-functionalised pyridine-carboxylate MOFs with rare **pbz** and **txt** topologies (NJU-Bai9 and NJU-Bai21, respectively) were prepared using compounds **27** and **28**.^{258,260} In a subsequent study, Chen and co-workers introduced phenyl spacers to extend compound **28** into **29**, which was then used to construct the 3D MOF PCN-124-stu (stu = Shantou University).²⁵² This MOF exhibited higher porosity, larger pore sizes, and a greater surface area compared to NJU-Bai21 (also known as PCN-124). Moreover, PCN-124-stu(Cu)

demonstrated excellent chemical, thermal, and water stability, along with selective CO₂/CH₄ adsorption. This selectivity is attributed to specific interactions between CO₂ molecules and the active sites within the framework, particularly the coordinatively unsaturated metal centres and amide functional groups.

Further modification of compound **28** by introducing additional amide groups yielded **30** and **31**, which were used to construct the highly porous isorecticular MOFs NJU-Bai22 and NJU-Bai23 (Figure 19).²⁵⁷ These frameworks featured mixed micro- and mesoporosity and exhibited enhanced water stability, attributed to the higher density of hydrophilic amide groups. Both MOFs demonstrated exceptional surface areas (e.g. 5142 m²/g for NJU-Bai23), high CO₂ uptake at high pressure, and remarkable CO₂/N₂ and CO₂/CH₄ selectivity. The same group also reported NJU-Bai49, an AFMOF with **soc** topology constructed from [Sc₃(μ₃-O)(COO)₆] clusters and linker **32**.²⁵⁶ This MOF displayed exceptional thermal and chemical stability alongside highly selective CO₂ capture. The remarkable selectivity is attributed to the presence of both amide functionalities and open metal sites, as supported by GCMC simulation results.

In conclusion, amide-functionalisation, which can be achieved through relatively simple and cost-effective methods (as will be discussed in Chapter 2), represent an effective strategy for linker elongation, leading to the formation of isorecticular MOFs with enhanced porosity and improved gas adsorption and separation performance. However, to the best of our knowledge, no MOFs have been reported to date using organosilicon-based linkers bearing –OCNH– amide groups, highlighting a promising and unexplored direction for future research.

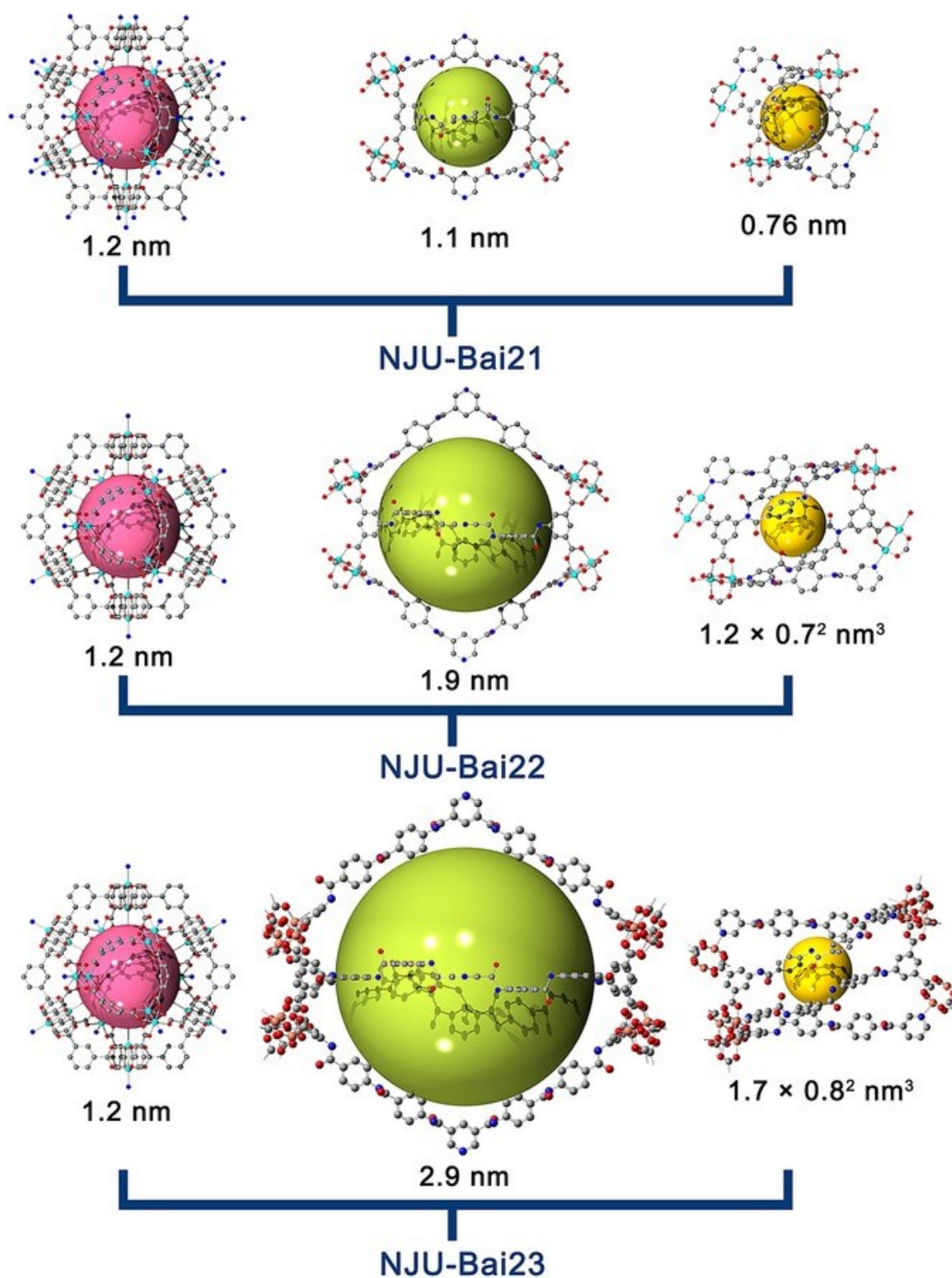


Figure 19: Isoreticular expansion of **txt**-type MOFs leading to pore size variation from micro- to mesopores. Reproduced from Ref. ²⁵⁷ with permission.

1.4 Aims and Objectives

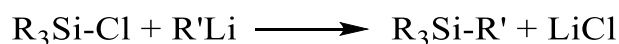
This chapter reviewed the historical development of MOF chemistry, including key aspects of synthesis, activation, and characterisation methods. It also discussed the successful incorporation of organosilicon multicarboxylic acids into MOF synthesis and the advantages they offer. The introduction of amide functionalities provides an effective strategy for generating isorecticular MOFs with enhanced porosity and improved adsorption performance. These functionalities may also create additional opportunities for hydrogen bonding, thereby leading to more robust hydrogen-bonded organic frameworks (HOFs). Furthermore, the incorporation of a disiloxane linkage allows the linker to adopt unusual geometries, often resulting in MOFs with uncommon topologies, and in some cases has been shown to afford water-stable frameworks.

The aim of this study is to expand the family of highly branched organosilicon carboxylic acids, particularly hexacarboxylic acids, and to explore their use in MOF synthesis, which remains an underexplored area in MOF research. The synthesised compounds will be characterised using ^1H , ^{13}C , and ^{29}Si NMR spectroscopy, mass spectrometry, and IR spectroscopy. Their crystal structures will also be determined by single-crystal X-ray diffraction to assess their ability to form HOFs, provided that suitable crystals can be obtained.

Moreover, the study aims to employ these acids in the construction of novel 3D MOFs with rare topologies. The resulting MOFs will be evaluated for their thermal and water stability, as well as their gas sorption properties. Those demonstrating water stability will be investigated further as adsorbents for the removal of phosphate and perfluorooctanoic acid (PFOA) from aqueous solutions.

Chapter 2: Synthesis of Organosilicon Hexacarboxylic Acids

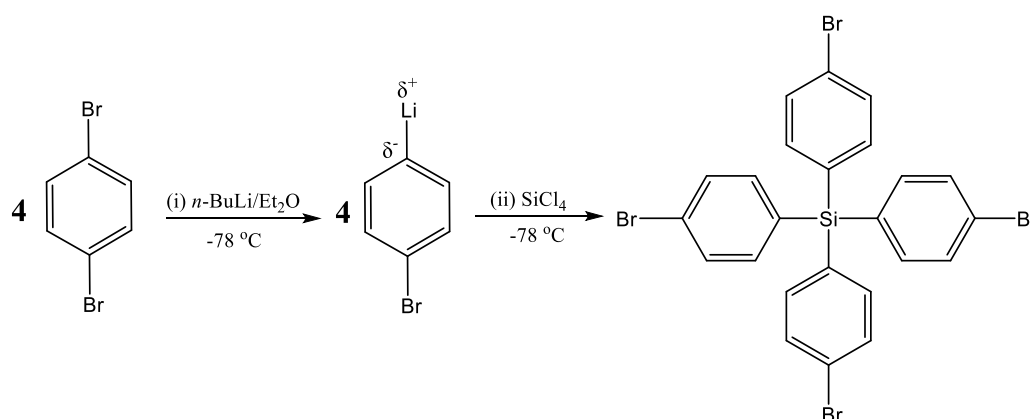
As discussed in Chapter 1, the synthesis of silicon-based multicarboxylic acids offers a practical alternative to the more challenging preparation of structurally similar carbon-centred multicarboxylic acids. Their distinct chemical properties enable more accessible and efficient synthetic routes; for example, the Si–Cl bond is significantly more reactive than the C–Cl bond, and nucleophilic substitution at silicon centres is generally simple, making the organosilicon compounds more synthetically accessible. In addition, silicon's larger atomic radius compared to carbon leads to longer Si–X bond lengths (C–C = 1.54 Å, Si–C = 1.87 Å),¹⁷⁸ greater bond angle flexibility, and reduced molecular rigidity. Moreover, due to its lower electronegativity ($\chi_{\text{Si}} = 1.9$, $\chi_{\text{C}} = 2.5$), silicon forms more polar bonds with halogens (Si–X) than carbon does (C–X), resulting in increased reactivity of silicon halides towards carbon-centred nucleophiles.^{178,261} Furthermore, the availability of low-lying empty d orbitals in silicon, which can act as acceptor orbitals for electron density from the incoming nucleophile, plays a key role in lowering the kinetic barrier to nucleophilic substitution.^{178,262} This helps explain why silicon halides readily undergo nucleophilic substitution with organolithium reagents to form Si–C bonds (Equation 1), a process not observed in analogous carbon halides.



Equation 1: Reaction of chlorosilanes with organolithium reagents.

To understand the chemistry involved in the synthesis of organosilicon carboxylic acids, the preparation of tetrakis(4-carboxyphenyl)silane (TCPS- H_4) serves as a representative and well-studied example.¹⁵⁴ TCPS- H_4 is synthesised in a two-step process. The first step involves the well-established monolithiation of 1,4-dibromobenzene using *n*-butyllithium (*n*-BuLi).^{163,263,264} The resulting kinetically favoured monolithiated aryllithium intermediate then

readily attacks the electrophilic $\text{Si}^{\delta+}$ centre of silicon tetrachloride, yielding moisture- and air-stable tetrakis(4-bromophenyl)silane and lithium chloride as a byproduct (Equation 2).

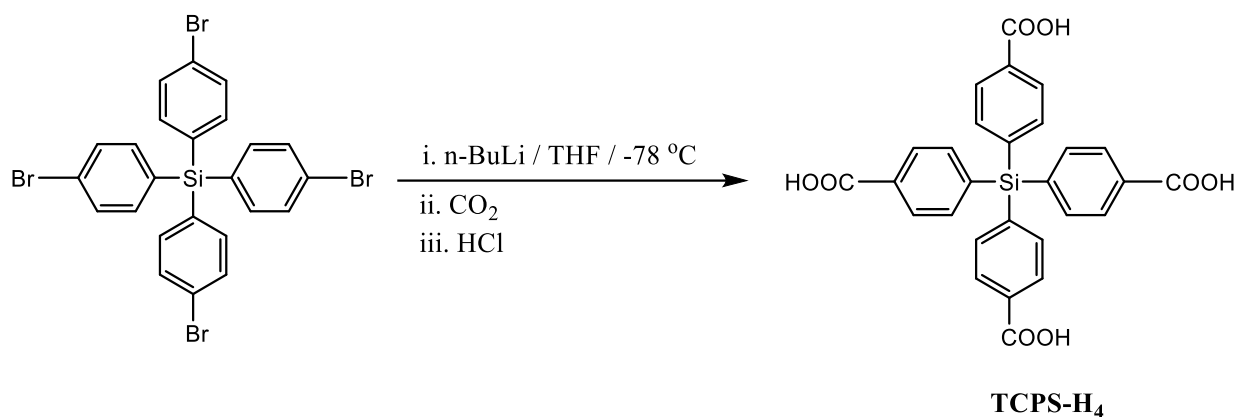


Equation 2: Synthesis of tetrakis(*p*-bromophenyl)silane.

A wide variety of highly branched silicon-based compounds can be synthesised using this lithiation strategy with different commercially available silicon precursors, which react similarly with organolithium reagents, but at different rates ($\text{Si-Cl} > \text{Si-OR} > \text{Si-H}$).²⁶¹ Subsequently, tetrakis(*p*-bromophenyl)silane is converted into TCPS-H₄ through a carboxylation reaction (Equation 3). In this step, *n*-BuLi is used to lithiate the four aryl groups, after which carbon dioxide is bubbled through the reaction mixture, allowing the aryllithium intermediates to attack the electrophilic carbon of CO₂ and form lithium carboxylate salts. Upon quenching with hydrochloric acid, these salts are protonated to yield TCPS-H₄. Both lithiation and carboxylation steps are performed under an inert atmosphere and at -78 °C to protect the air- and moisture-sensitive *n*-BuLi and to prevent decomposition. This method is compatible with a broad range of bromophenyl-substituted compounds and can be employed in the synthesis of various carboxylic acid compounds.

It is also worth mentioning that TCPS-H₄ can be synthesised from the parent *p*-tolyl compound, tetrakis(4-methylphenyl)silane, by oxidation with KMnO₄ or Cr₂O₃, as reported in the literature.^{158,265} This synthetic route eliminates the need for an inert atmosphere during the

carboxylation step and is advantageous when the tolyl-substituted precursor is stable and commercially available.

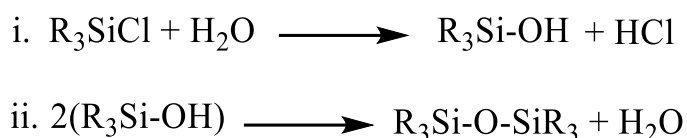


Equation 3: Synthesis of tetrakis(*p*-carboxyphenyl)silane (TCPS-H₄).

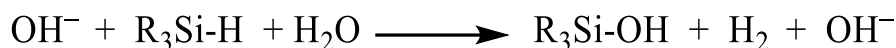
2.1 Synthesis of L1-H₆

Since most organosilicon multicarboxylic acids used in 3D MOF synthesis feature four organic groups bonded to a central silicon atom via Si–C bonds, 3D MOFs incorporating Si–O linkages remain rare in the literature.^{184,186,209,232} Similarly, siloxane-based hexacarboxylic acids are underexplored, and this was one of the main motivations for our interest in synthesising this type of compound.

Silanols and siloxanes can be synthesised via the hydrolysis of halosilanes, as illustrated in Equation 4. In the first step, the reaction of chlorosilanes with water results in the replacement of chlorine atoms by hydroxyl groups, yielding silanols and releasing HCl as a by-product. The resulting silanol products can then undergo condensation to form symmetrical disiloxanes. Alternatively, the hydrolysis of hydrosilanes can also produce silanols, with hydrogen gas (H₂) generated as a by-product, as shown in Equation 5.²⁶⁶ When hydrosilanes are hydrolysed in the presence of alkali metal hydroxides, the reaction strongly favours condensation to give siloxane products.



Equation 4: (i) Hydrolysis of halosilanes to afford silanols; (ii) the condensation of silanols to form disiloxanes.



Equation 5: Hydrolysis of hydrosilanes to afford silanols.

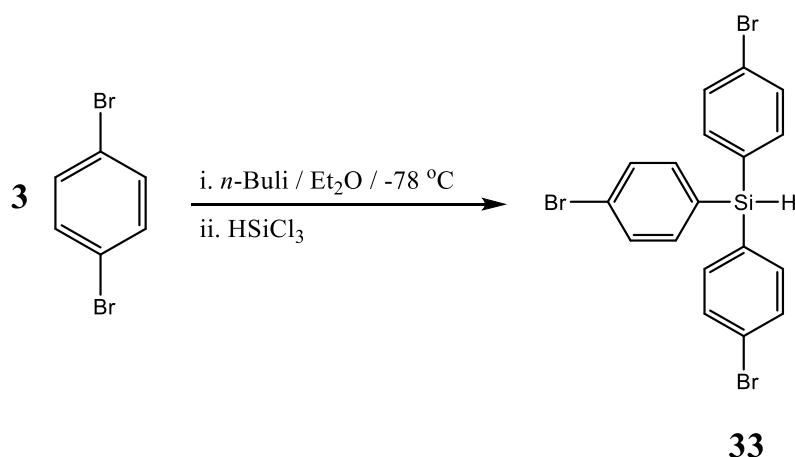
Hydrosilanes are generally less reactive than halosilanes (as mentioned previously in this Chapter), making them more stable and less prone to hydrolysis. This stability is advantageous for synthesising various bromophenyl-substituted organosilicon hydrides. These hydrides can be prepared using commercially available chlorosilanes that contain Si–H bonds, such as trichlorosilane, as shown in Equation 6. Moreover, the number of aryl branches in the resulting hydrides can be tailored by selecting chlorosilane precursors with specific numbers of non-reactive hydrocarbon groups (e.g. CH₃). Thus, by choosing from a broad range of commercially available chlorosilanes, it is possible to control how many aryl groups are introduced onto the silicon atom in the final molecule.



Equation 6: Synthesis of organosilicon hydrides from chlorosilanes with Si-H functionality.

Tris(*p*-bromophenyl)silane (**33**) was synthesised using trichlorosilane (HSiCl₃) as the silicon precursor (Equation 7). This compound is known and its preparation served as the initial step in the synthesis of hexa(4-carboxyphenyl)disiloxane (**L1-H6**).^{184,264,267,268} The synthesis began with the monolithiation of 1,4-dibromobenzene using *n*-BuLi at –78 °C. Since HSiCl₃ can react with organolithium reagents via both its Si–Cl and Si–H bonds, controlling the stoichiometry

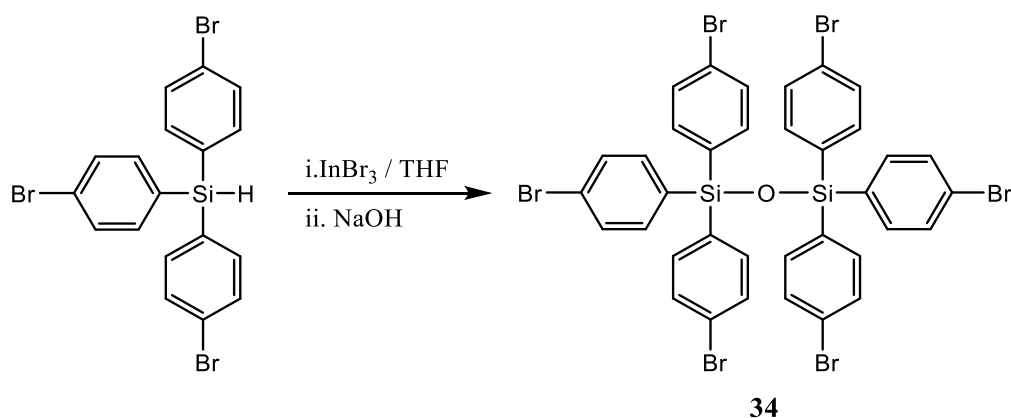
is crucial. Accordingly, three equivalents of *p*-bromophenyllithium were used per molecule of trichlorosilane to selectively substitute all three Si–Cl bonds while preserving the Si–H bond in the product. The *p*-bromophenyllithium solution was then added slowly, via cannula, dropwise to the trichlorosilane solution at $-78\text{ }^{\circ}\text{C}$ to maintain an excess of Si–Cl bonds throughout the reaction.



Equation 7: Synthesis of tris(*p*-bromophenyl)silane (**33**).

The hydrosilane was characterised using ^1H , ^{13}C , ^{29}Si NMR and IR spectroscopy. As expected, a singlet was observed at 5.41 ppm in the ^1H NMR spectrum, corresponding to the Si–H proton. The ^1J coupling constant for ^{29}Si –H was found to be 204 Hz, with the associated satellite peaks observed in the spectrum. The ^{13}C NMR spectrum showed four signals, consistent with the four distinct carbon environments in the structure of compound **33**. In the ^{29}Si NMR spectrum, a single resonance was observed at -18.27 ppm , which corresponds to the Si–H group and confirms the expected chemical environment of the silicon atom. IR spectroscopy further supported the presence of the Si–H bond, with a characteristic stretching band observed at 2139 cm^{-1} . Additional spectral data are provided in Chapter 7 (Experimental), and all spectra are available in the Supplementary Information (SI). The characterisation results are in excellent agreement with literature values,²⁶⁴ confirming the successful synthesis of the silane **33**.

In the second step of preparing **L1-H₆**, the silane **33** was converted into hexa(4-bromophenyl)disiloxane (**34**) (Equation 8) by treatment with InBr₃, followed by the slow addition of NaOH, affording the disiloxane compound.

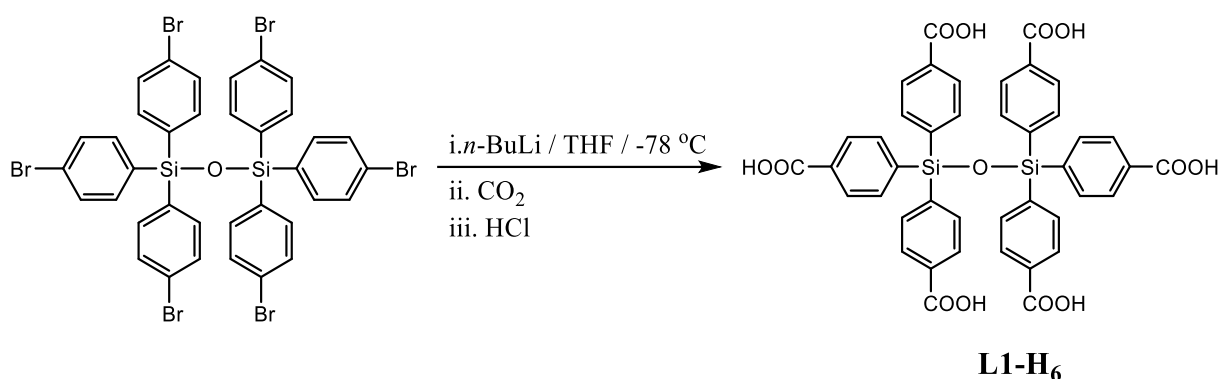


Equation 8: Synthesis of hexa(4-bromophenyl)disiloxane (**34**).

The absence of the Si–H signal in the ¹H NMR spectrum of compound **34** confirmed successful transformation, accompanied by aromatic proton shifts to 7.47 and 7.24 ppm. Additionally, the IR spectrum showed a distinct Si–O–Si stretch at 1088 cm^{−1}, confirming the formation of the disiloxane linkage.²⁶⁹ ²⁹Si NMR spectroscopy also supported this, showing a single resonance at −17.39 ppm. These characterisation data are in excellent agreement with previously reported literature values for compound **34**,¹⁸⁴ confirming the synthesis of the compound.

The carboxylation conditions described earlier in this chapter (used in TCPS-H₄ synthesis) were employed in the final step of **L1-H₆** synthesis to prevent cleavage of the siloxane linkage by the organolithium reagent and to preserve the integrity of the disiloxane moiety in **L1-H₆** (Equation 9).²⁷⁰ The hexacarboxylic acid compound was prepared starting with the reverse addition of *n*-BuLi, where the aryl halide solution was added dropwise into a solution of *n*-BuLi, to ensure an excess of the organolithium reagent and achieve complete lithiation of all six aryl groups. To promote full lithiation, several modifications were made to the protocol reported by Davies and co-workers:¹⁸⁴ eight equivalents of *n*-BuLi were used instead of six,

and after the dropwise addition of the solution of compound **34**, the reaction flask was warmed to 0 °C and held at that temperature for 5 minutes. Lithiation was followed by carboxylation, carried out at -78 °C to maintain CO₂ solubility and promote complete carboxylation.²⁷¹ Finally, the hexacarboxylic acid was obtained by treating the resulting lithium carboxylate salt with hydrochloric acid.



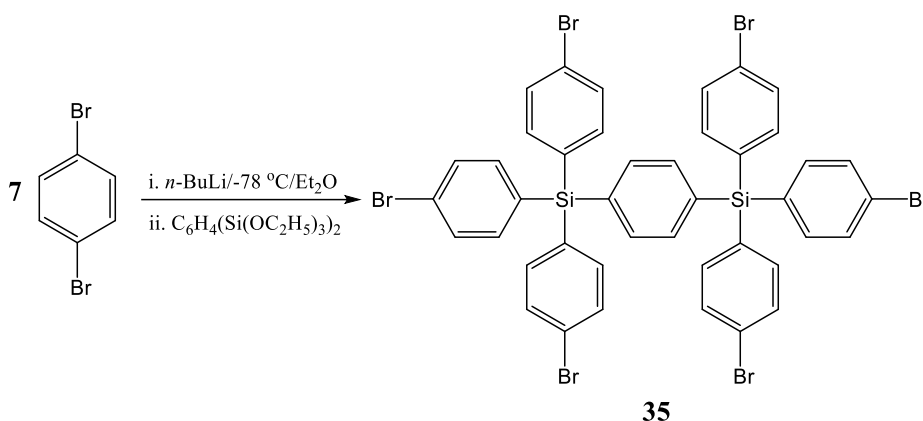
Equation 9: Synthesis of hexa(4-carboxyphenyl)disiloxane (**L1-H₆**).

L1-H₆ was characterised using ¹H, ¹³C, and ²⁹Si NMR spectroscopy, as well as IR spectroscopy and mass spectrometry. In the ¹H NMR spectrum, a new broad singlet appeared at 13.14 ppm, confirming the presence of carboxylic acid protons. This was further supported by the ¹³C NMR spectrum, which exhibited a characteristic carboxylic acid signal at 167.6 ppm, and by the IR spectrum, which showed a broad O–H stretching band at 2880 cm⁻¹, and a sharp C=O stretch at 1689 cm⁻¹. Moreover, the ²⁹Si NMR spectrum of **L1-H₆** displayed a single signal at -18.95 ppm, characteristic of the two silicon atoms in the siloxane linkage. ESI-MS analysis revealed the expected [M–H]⁻ ion at m/z = 797.1166, in excellent agreement with the calculated value (m/z = 797.1152). Taken together, the characterisation data presented above and in the Experimental section are consistent with those previously reported by Davies and co-workers,¹⁸⁴ indicating successful synthesis of **L1-H₆**. In addition, the crystal structure of this compound has been reported in the literature and will be discussed in Chapter 3.¹⁸⁴

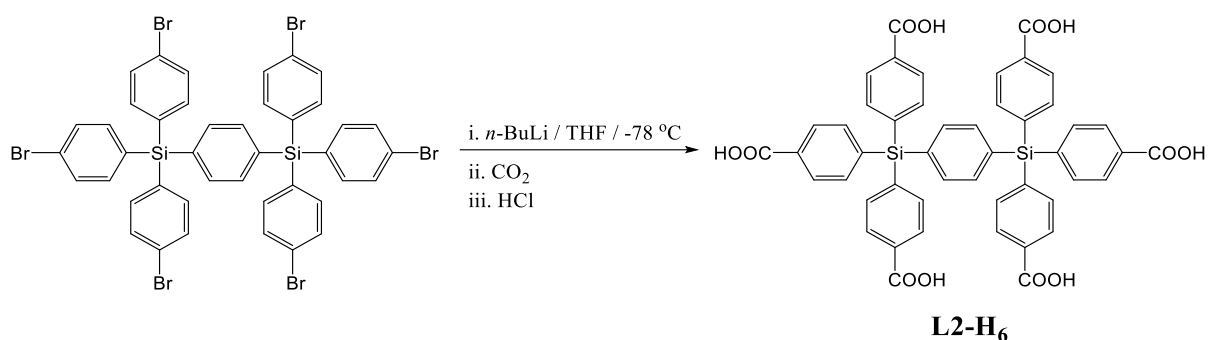
2.2 Synthesis of **L2-H₆** and **L3-H₆**

As mentioned earlier in this chapter, a diverse library of silicon-based compounds can be synthesised with relative ease by selecting from a wide range of commercially available chlorosilanes. 1,2-bis(tris(4-carboxyphenyl)silyl)benzene (**L2-H₆**) and 1,2-bis(tris(4-carboxyphenyl)silyl)ethane (**L3-H₆**) were synthesised via bromophenyl intermediates, both following the same general synthetic route but using different silicon-containing precursors. **L2-H₆** was prepared according to the synthetic protocol reported by Davies and co-workers,²⁰⁷ while **L3-H₆** had been synthesised previously in our group by Robertson,²⁷² and that procedure was adapted for this work.

The synthesis of **L2-H₆** began with the monolithiation of 1,4-dibromobenzene using *n*-BuLi. The reaction mixture was then warmed to 0 °C to ensure complete lithiation, followed by the dropwise addition of 1,4-bis(triethoxysilyl)benzene. This afforded a white precipitate as the aryllithium intermediate attacked the Si–O bonds of the bis(triethoxysilyl)benzene (Equation 10). The reaction was quenched with water, yielding 1,4-bis(tris(4-bromophenyl)silyl)benzene (**35**) as a white solid. Subsequently, compound **35** was carboxylated, following the same procedure used for **L1-H₆**, to afford **L2-H₆** (Equation 11).



Equation 10: Synthesis of 1,4-bis(tris(4-bromophenyl)silyl)benzene (**35**).



Equation 11: Synthesis of 1,2-bis(tris(4-carboxyphenyl)silyl)benzene (**L2-H₆**).

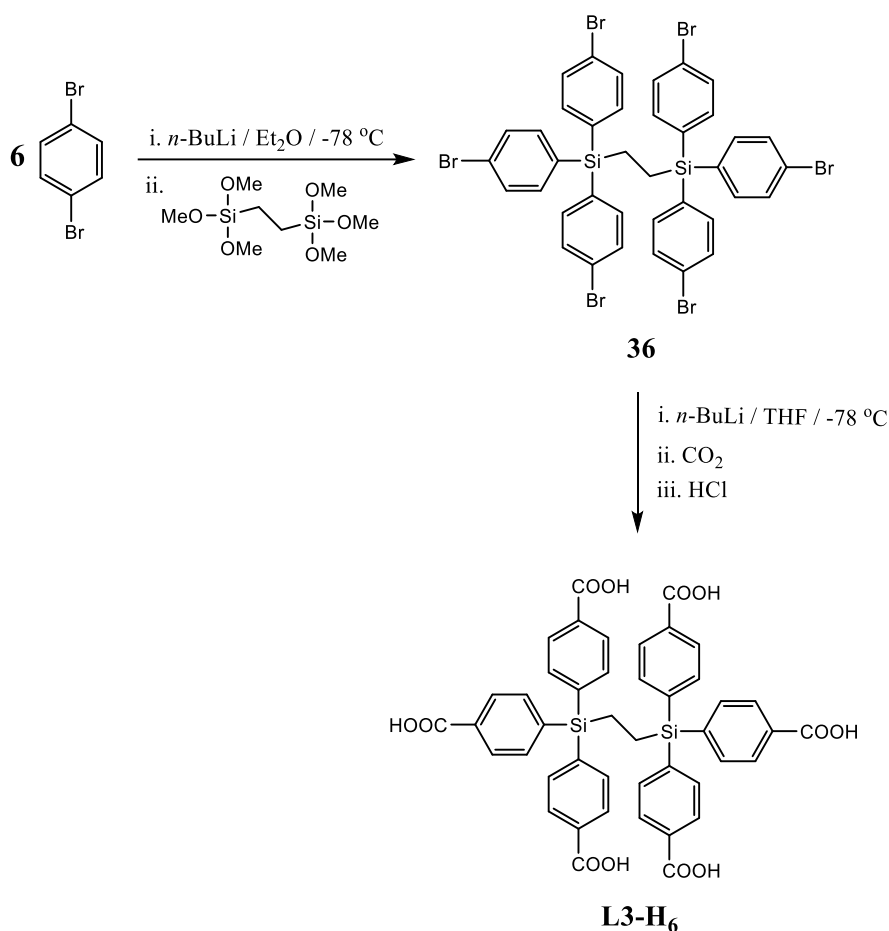
The two compounds were characterised by ^1H , ^{13}C , ^{29}Si NMR, and IR spectroscopy. For compound **35**, the ^1H NMR spectrum, showed two doublets at 7.55 and 7.38 ppm, each integrating for 12 protons, corresponding to the aromatic protons of the *para*-substituted bromophenyl rings. In addition, a singlet at 7.53 ppm was observed and assigned to the central aromatic protons of the bridging 1,4-phenylene unit. The ^{13}C NMR spectrum of compound **35** exhibited six aromatic carbon signals in the range of 125–138 ppm. The two signals at 135.64 ppm and 135.16 ppm correspond to the ipso carbons (aryl, C–Si) and the hydrogen-bearing aromatic carbons of the bridging aryl ring, respectively.²⁰⁷ These signals confirm the presence of the disilylphenyl core in compound **35**. The remaining peaks at 137.71, 131.61, 131.46, and 125.40 ppm are attributed to the secondary and tertiary carbons of the bromophenyl groups. Moreover, the ^{29}Si NMR spectrum displayed a single signal at –13.87 ppm, consistent with tetraaryl-substituted silicon atoms, further supporting the symmetric silicon environment in compound **35**. The IR spectrum showed Si–C stretching band at $\sim 805\text{ cm}^{-1}$, and a band at 1129 cm^{-1} , which corresponds to the Si–C₆H₄–Si linkage.^{207,269} Altogether, these spectroscopic data confirmed the successful formation of compound **35**.

In the ^1H NMR spectrum of **L2-H₆**, a broad singlet at 13.14 ppm (absent in the spectrum of **35**) was observed, corresponding to the carboxylic acid protons. In addition, the ^{13}C NMR spectrum of **L2-H₆** exhibited a distinct signal at 167.6 ppm, consistent with carboxylic acid carbon atoms, and confirmed the successful conversion of the aryl bromide groups into benzoic acid groups.

This was further supported by FTIR spectroscopy, in which **L2-H6** showed a broad O–H stretching band around 2987 cm^{-1} and a strong C=O stretch at 1688 cm^{-1} , both of which were absent in the spectrum of compound **35**. The Si–C₆H₄–Si band was also observed at 1127 cm^{-1} . Additionally, the ^{29}Si NMR spectrum displayed a single signal at -15.15 ppm , corresponding to the silicon atoms in the Si–C₆H₄–Si linkage. Mass spectrometry (ESI– mode) was also employed for further characterisation of **L2-H6**. The observed $[\text{M}-\text{H}]^-$ ion at $m/z = 857.1529$ closely matches the calculated value of 857.1516 for C₄₈H₃₄O₁₂Si₂, confirming the complete substitution of all six bromo groups with carboxylic acid functionalities.

All data obtained for compounds **35** and **L2-H6** were consistent with previously reported values,²⁰⁷ supporting the successful synthesis of both compounds. It is worth noting that only a few MOFs have been synthesised using linkers containing a Si–C₆H₄–Si motif.^{207,273–276} To the best of our knowledge, **L2-H6** is the only hexacarboxylic acid compound featuring a Si–C₆H₄–Si linkage that has afforded a MOF.²⁰⁷ In addition to its rarity, **L2-H6** exhibits inherent rigidity and a desirable *pseudo*-octahedral arrangement of its carboxylic acid groups.²⁰⁷ Given its rare connectivity, and favourable geometry, **L2-H6** serves as a promising candidate for MOF construction, and with a potential for further development through linker extension and isorecticular design to access novel frameworks with enhanced porosity and functionality.

1,2-Bis(tris(4-bromophenyl)silyl)ethane (**36**) was prepared using 1,4-bis(triethoxysilyl)ethane as the precursor, with the reaction, work up and observations being the same as compound **35** (Equation 12). Compound **36** was then carboxylated to form **L3-H6**.



Equation 12: Synthesis of 1,2-bis(tris(4-carboxyphenyl)silyl)ethane (**L3-H₆**).

Compound **36** was characterised by ¹H, ¹³C, ²⁹Si NMR, and IR spectroscopy. The ¹H NMR spectrum exhibited a singlet at 1.31 ppm, corresponding to the methylene (–CH₂–CH₂–) protons bridging the two silicon centres. The ¹³C NMR spectrum displayed five signals, consistent with the expected number of carbon environments in the molecule. Notably, the signal at 5.25 ppm confirmed the presence of aliphatic methylene carbons in the Si–CH₂–CH₂–Si linkage. The ²⁹Si NMR spectrum showed a single sharp signal at –8.72 ppm, corresponding to triaryl-substituted silicon centres within the Si–CH₂–CH₂–Si linkage. Together, these key characterisation data, along with those presented in the Experimental section (Chapter 7), confirm the successful synthesis and purity of the bromophenyl intermediate (**36**).

On the other hand, structural confirmation of the hexa-acid **L3-H₆** was achieved through ¹H, ¹³C, and ²⁹Si NMR spectroscopy, IR spectroscopy, and mass spectrometry. The presence of carboxylic acid protons was confirmed by a singlet at 13.09 ppm in the ¹H NMR spectrum. A singlet at 1.48 ppm was attributed to the methylene protons of the central Si-CH₂-CH₂-Si linkage. The ¹³C NMR spectrum further supported the successful conversion of aryl bromides to carboxylic acid moieties, with a distinct signal at 167.69 ppm corresponding to the carbonyl carbon of the -COOH groups. In the ²⁹Si NMR spectrum, a single signal was observed at -9.41 ppm, consistent with the equivalent silicon environments in the Si-CH₂-CH₂-Si linkage.

The IR spectrum revealed a broad O-H stretch at 2979 cm⁻¹ and a strong C=O stretch at 1687 cm⁻¹, both characteristic of carboxylic acids and absent in the spectrum of compound **36**. Finally, mass spectrometry (ESI- mode) showed a deprotonated molecular ion [M-H]⁻ at m/z = 809.1531, in excellent agreement with the calculated value of 809.1516 for C₄₄H₃₄O₁₂Si₂, confirming the full substitution of all six bromine atoms with carboxylic acid groups.

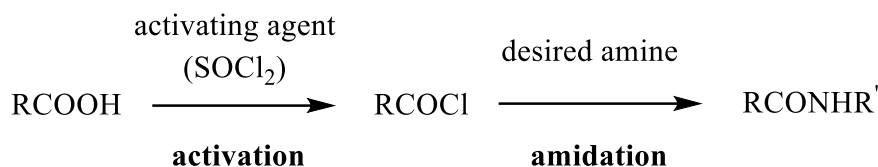
Taken together, the characterisation data of compounds **36** and **L3-H₆** showed good agreement with previously reported values and with those of other known compounds featuring Si-CH₂-CH₂-Si linkage.^{272,277} This consistency, together with the characterisation data, confirms the successful synthesis of compounds **36** and **L3-H₆**. It should be noted that the Si-CH₂-CH₂-Si unit offers enhanced flexibility and spatial adaptability compared to rigid aromatic cores,^{278,279} promoting the formation of a wider variety of structures. However, MOFs constructed using a linker with a Si-CH₂-CH₂-Si core remain extremely rare in the literature, with most reported examples employing bipodal pyridyl Si-based ligands.²⁷⁸

2.3 Amide-Extended Organosilicon Hexacarboxylic Acids

As discussed in Chapter 1.3, carboxylate linkers can undergo further functionalisation with amide groups, affording extended-reach linkers that can lead to MOFs with enhanced performance and selectivity in applications such as gas adsorption and separation. The amide functionality can be introduced by reacting the terminal carboxylic acid groups of the compound with amines to form amides.²⁸⁰ In addition, the amide group is particularly attractive due to its dual functional nature, providing both N–H and C=O sites capable of engaging in hydrogen bonding and dipole–quadrupole interactions. These features can significantly enhance the linker’s affinity for CO₂ and various ionic species, improving adsorption efficiency and selectivity.²⁸¹ Moreover, the amide-extension reaction is practical, cost-effective, and typically offers high yields. Accordingly, the parent organosilicon hexacarboxylic acids **L1-H₆**, **L2-H₆**, and **L3-H₆** were extended with an amide linkage to form **L4-H₆**, **L5-H₆**, and **L6-H₆**. This section presents the synthetic procedures and key characterisation data for the novel amide-functionalised organosilicon hexacarboxylic acids developed in this study.

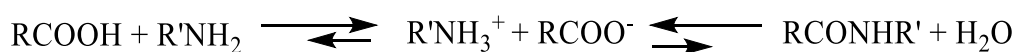
2.3.1 Synthesis of **L4-H₆**, **L5-H₆**, and **L6-H₆**

The hexacarboxylic acids described in Sections 2.1 and 2.2 were extended by introducing one amide linkage per aryl arm using a two-step synthetic process. In the first step, the carboxylic acid groups were converted to acyl chlorides using thionyl chloride. This was followed by an amidation reaction with 4-aminobenzoic acid, yielding the amide-functionalised compound (Equation 13). During the activation step, the carboxylic acid is converted into an acid chloride by replacing the hydroxyl group with a chlorine atom at the acyl carbon, forming a reactive intermediate. This acyl chloride then readily undergoes nucleophilic attack by the amine group of 4-aminobenzoic acid, facilitating the formation of amide bonds.²⁸²



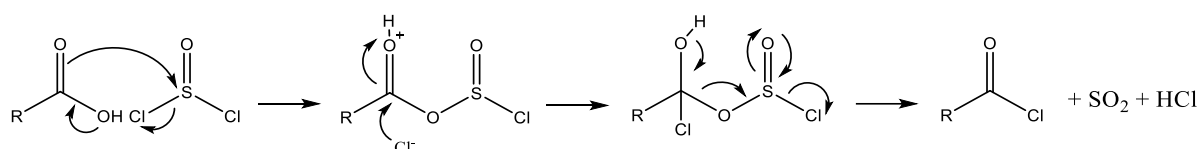
Equation 13: Amide-extension process: activation of the carboxylic acid followed by amidation to form an amide.

To gain a deeper insight into this process, it is important to note that the formation of an amide bond between a carboxylic acid and an amine is a condensation reaction. Initially, an acid–base reaction between the amine and the carboxylic acid forms a thermodynamically stable carboxylate salt, as the equilibrium of the condensation reaction typically favours hydrolysis rather than amide formation (Equation 14).²⁸² Direct condensation of the salt can be carried out at high temperatures (160–180 °C) to form amides,²⁸³ but such conditions may affect the functional integrity of the compound. Therefore, the carboxylic acid is commonly activated by replacing its hydroxyl group with a better leaving group, such as halides, esters, imidazoles, or azides, to facilitate nucleophilic attack by the amine.²⁸⁴



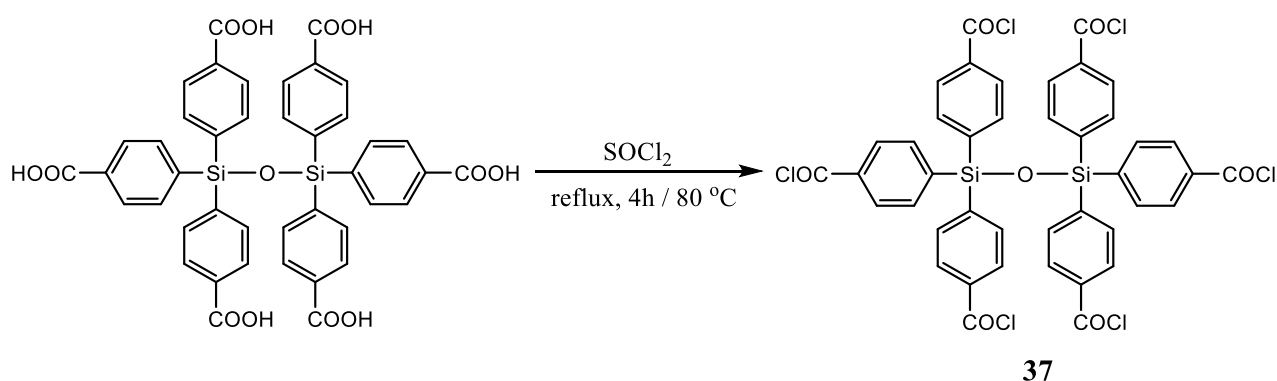
Equation 14: Amide bond formation.

Activation of carboxylic acids to form acyl chlorides is a well-established and cost-effective method.²⁸⁵ This conversion can be achieved using a variety of common reagents, including thionyl chloride, phosphorous trichloride, oxalyl chloride, phosphorous pentachloride, and phosphorus oxychloride.^{284,286–288} These reagents typically form HCl and SO₂ as by-products, as shown in Equation 15. Once the acyl chloride is formed, it can then be coupled with an amine to yield the corresponding amide product.



Equation 15: Nucleophilic substitution mechanism to activate the carboxylic acid and form an acyl chloride using thionyl chloride (SOCl₂).^{282,289}

Applying these key synthetic strategies, **L1-H6** was activated using an excess of commercially available thionyl chloride (140 equivalents) to ensure complete conversion of all carboxylic acid groups into acyl chlorides (Equation 16). The reaction was carried out under reflux at 80 °C for 4 h in an inert atmosphere to prevent moisture from hydrolysing the acyl chlorides back to the parent carboxylic acids.



Equation 16: Preparation of hexa(4-acylchlorophenyl)disiloxane (**37**).

After reflux, the mixture was cooled to room temperature, and the excess thionyl chloride was removed via vacuum distillation rather than rotary evaporation due to its highly corrosive nature. The reaction flask was connected to a solvent trap immersed in liquid nitrogen and attached to the Schlenk line vacuum to condense and collect volatile by-products. This process afforded hexa(4-acylchlorophenyl)disiloxane (**37**) as an off-white solid. The same method was employed to synthesise acyl chlorides **38** and **39** (Figure 20), with the reaction conditions, work-up, and observations remaining consistent.

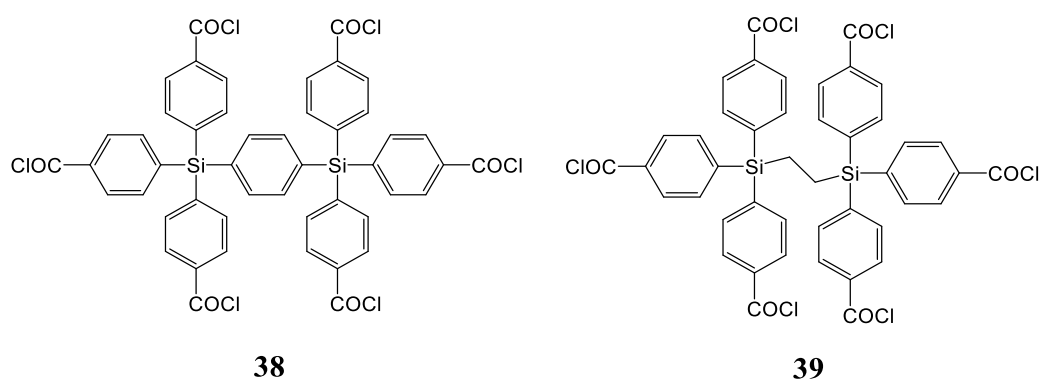


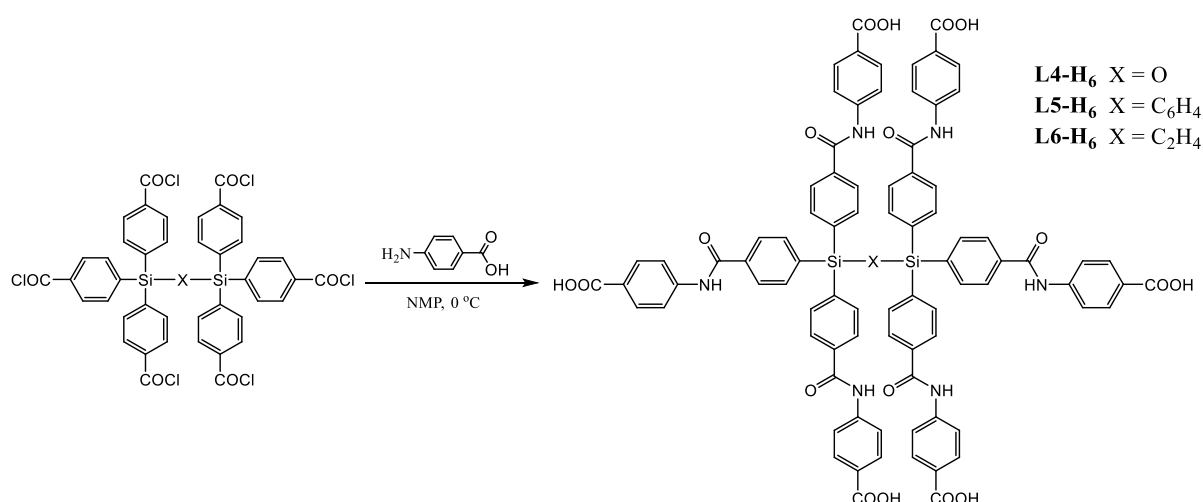
Figure 20: Structures of acyl chlorides **38** and **39**.

The three novel acyl chlorides were characterised by ^1H , ^{13}C , and ^{29}Si NMR, as well as IR spectroscopy. The absence of the carboxylic acid proton signals in the ^1H NMR spectra, along with the disappearance of the O–H stretching band in the IR spectra of all three compounds, confirmed the successful conversion of carboxylic acid groups to acyl chlorides. In the IR spectrum of compound **37**, the C=O stretch appeared sharply at 1771 cm^{-1} , accompanied by a strong adjacent peak at 1735 cm^{-1} . This is attributed to Fermi resonance, in which the overtone of a strong aromatic C–H bending vibration (typically observed around $900\text{--}800\text{ cm}^{-1}$) couples with the carbonyl stretch, commonly seen in aromatic acyl chlorides.²⁹⁰ This phenomenon was also evident in the IR spectra of compounds **38** and **30**, with corresponding C=O stretches at 1772 and 1735 cm^{-1} , and at 1772 and 1734 cm^{-1} , respectively.

In the ^{13}C NMR spectra, the carbonyl carbon signal appeared downfield at 167.44 ppm for compound **37**, 167.59 ppm for **38**, and 167.54 ppm for **39**, consistent with the strong electron-withdrawing inductive effect of the chlorine atom in the acyl group. The rest of the characterisation data are provided in the Experimental section (Chapter 7).

Following the successful chlorination reactions, the resulting acyl chlorides were treated with excess 4-aminobenzoic acid, which served both as the coupling agent and to neutralise the HCl by-product. The reaction was carried out in anhydrous *N*-methyl-2-pyrrolidone (NMP) as the solvent and conducted under an inert atmosphere to prevent hydrolysis of the starting materials.

The acyl chloride was added to the 4-aminobenzoic acid solution maintained at 0 °C, in order to reduce the reactivity of the acyl chloride and prevent side reactions. The mixture was then stirred for 30 minutes at 0 °C, followed by 1 h at ambient temperature. This reaction occurs through nucleophilic acyl substitution, where the lone pair of the amine attacks the electrophilic carbon of the acyl chloride. Upon quenching the reaction with cold water, an off-white precipitate formed immediately. The solid was collected by suction filtration and washed thoroughly with warm water to remove any residual 4-aminobenzoic acid and NMP. Using this method, adapted from Maldar and co-workers,²⁶⁵ **L4-H₆**, **L5-H₆**, and **L6-H₆** were successfully obtained as off-white solids (Equation 17).



Equation 17: Synthesis of **L4-H₆**, **L5-H₆**, and **L6-H₆** via amidation.

L4-H₆, **L5-H₆**, and **L6-H₆** were fully characterised using by ¹H, ¹³C, ²⁹Si NMR spectroscopy, IR spectroscopy, and mass spectrometry. For **L4-H₆**, the formation of the amide bond was confirmed by the presence of a singlet corresponding to the amide proton at 10.62 ppm in the ¹H spectrum (Figure 21). A carboxylic acid proton signal was also observed at 12.77 ppm. The aromatic protons appeared as a multiplet (8.02–7.90 ppm) and a doublet (7.72 ppm) within the typical aryl region. The assignment of these protons was confirmed by 2D NMR (COSY) analysis and supported by integration values. The ¹³C NMR spectrum showed ten different

carbon environments, consistent with the expected structure. In addition, the carboxylic acid carbon was found at 167.38 ppm, while the amide carbonyl carbon appeared at 166.21 ppm. Moreover, the aryl carbon peaks (sp^2 hybridized) were observed in the range of 120-144 ppm. The ^{29}Si NMR spectrum showed a single peak at -19.09 ppm, confirming the presence of one silicon environment (Si–O–Si).

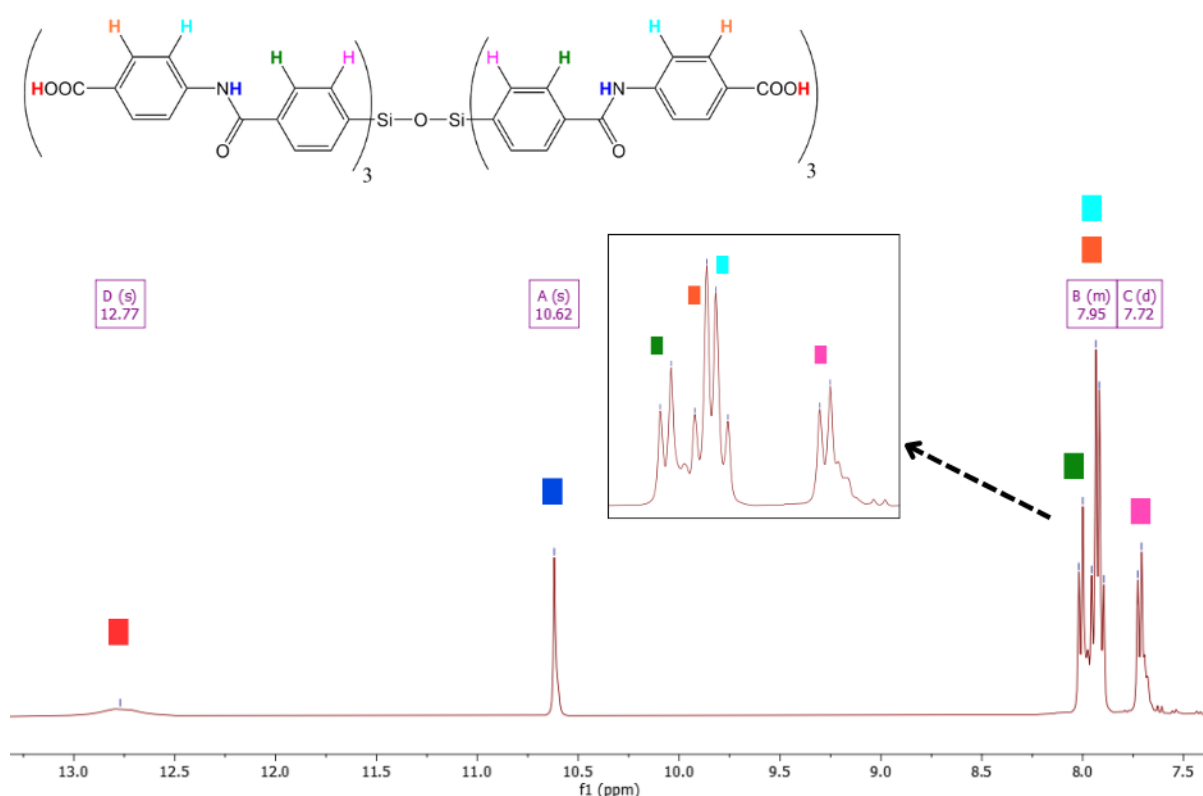


Figure 21: ^1H NMR (DMSO- d_6) spectrum of **L4-H6**.

The IR spectrum of **L4-H6** (Figure 22) displayed overlapping broad bands in the range 2600–3500 cm^{-1} , corresponding to O–H (from the carboxylic acid), N–H (from the amide group), and aromatic C–H stretches. Two carbonyl stretches were observed at 1679 cm^{-1} and 1595 cm^{-1} , assigned to the carboxylic acid and amide C=O groups, respectively. A sharp band at 1087 cm^{-1} confirmed retention of the Si–O–Si linkage. Additionally, aromatic C–C stretching and both in-plane and out-of-plane C–H bending vibrations were observed at 1516 cm^{-1} , 1171 cm^{-1} and

726 cm^{-1} , respectively. Electrospray ionization mass spectrometry (ESI+) further supported the successful synthesis of **L4-H₆**, with the observed $[\text{M}+\text{H}]^+$ ion at $m/z = 1513.3470$ closely matching the calculated value of 1513.3530.

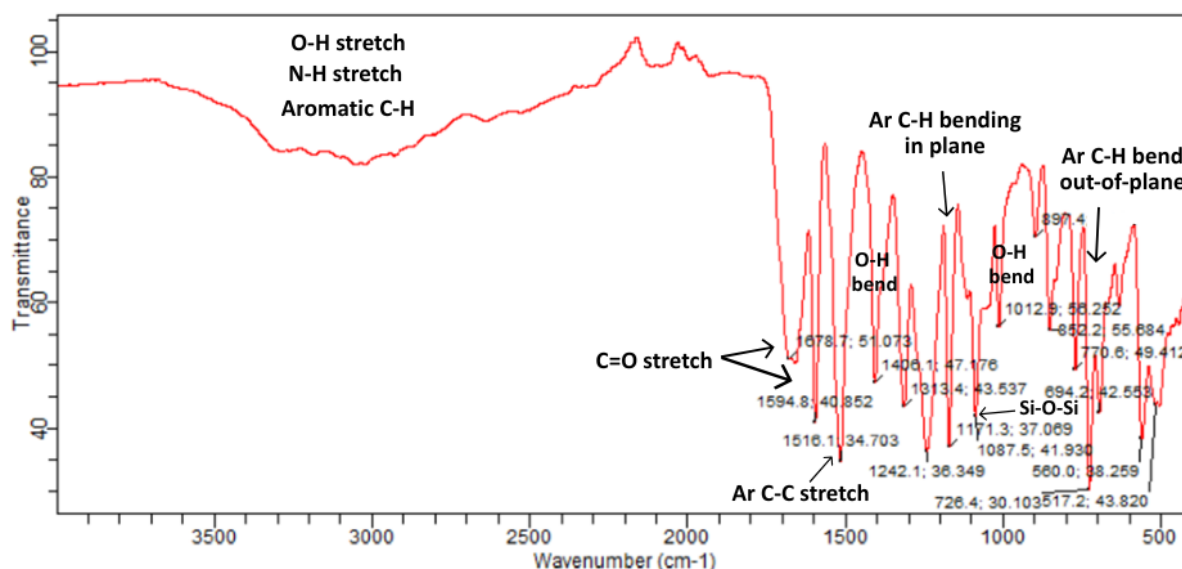


Figure 22: IR spectrum of **L4-H₆**

The ^1H NMR spectrum of **L5-H₆** displayed distinct singlets at 12.72 ppm and 10.66 ppm, corresponding to the carboxylic acid and amide protons, respectively. The aromatic proton signals appeared as a doublet at 8.05 ppm and two multiplets: one in the region of 7.91–7.97 ppm and another in the 7.75–7.70 ppm region. The ^{13}C NMR spectrum showed an amide carbonyl carbon signal at 166.44 ppm, while the carboxylic acid carbonyl appeared at 167.39 ppm. The aromatic carbon signals appeared in the expected range of 119–144 ppm. In the ^{29}Si NMR spectrum, a single peak was observed at –15.18 ppm, consistent with the presence of a single silicon environment in the molecule ($\text{Si}-\text{C}_6\text{H}_4-\text{Si}$).

In the IR spectrum, three broad overlapping bands between 3500 and 2500 cm^{-1} were attributed to O–H, N–H, and aromatic C–H stretching vibrations. Two distinct C=O stretching bands were observed at 1680 cm^{-1} (carboxylic acid) and 1595 cm^{-1} (amide), confirming the presence of

both functionalities. Additionally, a Si–C₆H₄–Si stretch was identified at 1128 cm⁻¹, which indicates the presence of the preserved silanetetraaryl linkage. Finally, electrospray ionization mass spectrometry (ESI⁻) further confirmed the synthesis and the purity of **L5-H6** as the observed [M–H]⁻ peak at m/z = 1571.3750 closely matched the calculated value of 1571.3743 for C₉₀H₆₄O₁₈Si₂.

For **L6-H6**, the ¹H NMR spectrum showed a carboxylic acid proton at 12.78 ppm and an amide N–H proton at 10.62 ppm. The aromatic protons appeared as a multiplet at 7.90–8.01 ppm and a doublet at 7.68 ppm, while the CH₂–CH₂ protons were observed as a singlet at 1.61 ppm. The ¹³C NMR spectrum supported the successful functionalisation, displaying the carboxylic acid and amide carbon signals at 167.40 ppm and 166.48 ppm, respectively, with the aromatic carbon signals in the expected range between 119 and 144 ppm. The ²⁹Si NMR spectrum showed a single sharp signal at –9.31 ppm, which also supports the presence of the Si–CH₂–CH₂–Si linkage. IR spectroscopy further confirmed the successful amidation reaction, with overlapping broad bands between 3500–2600 cm⁻¹ attributed to O–H, N–H, and aromatic C–H stretching, alongside distinct carbonyl stretches at 1655 cm⁻¹ (COOH) and 1593 cm⁻¹ (amide). Electrospray ionization mass spectrum (ESI⁺) showed a molecular ion peak at m/z = 1525.3856, in excellent agreement with the calculated value of 1525.3894 for [M+H]⁺, confirming the expected molecular composition of **L6-H6**. It is worth noting that electrospray ionisation mass spectrometry was performed in both positive and negative ion modes to account for the presence of multiple ionisable functional groups within the molecule. In ESI⁺ mode, protonation of basic sites, particularly amide –NH groups, leads to the formation of [M+H]⁺ species, often giving strong molecular ion signals. In contrast, ESI⁻ mode is more suitable for acidic functionalities such as carboxylic acid and hydroxyl groups, which readily undergo deprotonation to generate [M–H]⁻ ions. As the studied compounds contain both amide and carboxylic acid functionalities, ionisation was observed in both modes. Comparison of the

positive- and negative-ion spectra allowed identification of the molecular ion with the highest signal intensity and improved confidence in molecular mass assignment. Where appropriate, isotope patterns observed in the negative-ion spectra further supported the charge state and composition of the detected species.

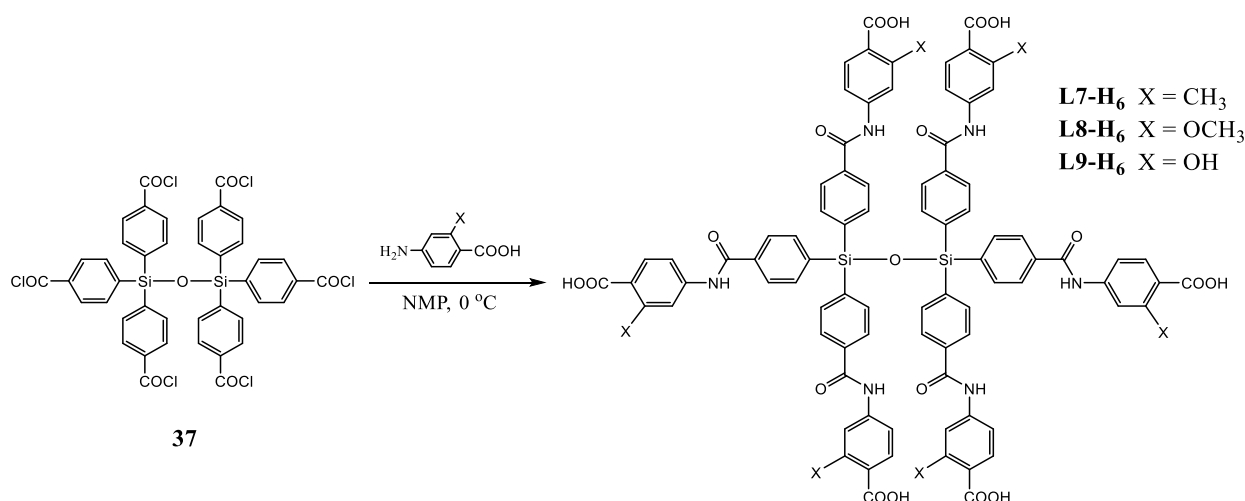
The crystal structures of **L4-H₆**, **L5-H₆**, and **L6-H₆** have been determined and are discussed in Chapter 3. These compounds are novel and, to the best of our knowledge, represent extremely rare examples of organosilicon amide-functionalised carboxylic acid compounds.

2.3.2 Synthesis of **L7-H₆**, **L8-H₆**, and **L9-H₆**

Silicon-based linkers offer remarkable structural tunability, allowing for the straightforward introduction of diverse functional groups to tailor their properties. As demonstrated in the previous section, amide functionalities can be easily incorporated to afford amide-extended compounds. Beyond this, additional modifications can be achieved by introducing various side groups, such as $-\text{CH}_3$, $-\text{OMe}$, and $-\text{OH}$, which can significantly influence the properties of the linker and enhance the performance of the resulting MOFs in targeted applications. For example, incorporating hydrophobic groups like $-\text{CH}_3$ near the coordination sites (e.g., at the *ortho*-position of aromatic rings) can improve the overall hydrophobicity of the MOF, shielding coordination bonds from hydrolytic degradation. This enhancement is particularly beneficial for adsorption and sensing applications.^{291,292} In contrast, hydroxyl groups are known to increase chemical functionality due to their high electronegativity and ability to participate in hydrogen bonding, thereby offering promise for adsorption applications.^{293,294} These groups can also act as both hydrogen bond donors and Lewis bases, enabling strong interactions with various guest molecules such as CO_2 and SO_2 through hydrogen bonding and electron donor–acceptor mechanisms. In addition, hydroxyl functionalities facilitate electron transfer and binding interactions with metal ions, which is valuable for environmental and biomedical

applications.²⁹⁵ Moreover, functional groups such as methoxy and hydroxyl, when introduced alongside carboxylate groups, can offer additional coordination sites for metal ions or be involved in diverse supramolecular interactions.^{296–299} These functionalities promote greater structural diversity, enabling better control over MOF topology, interpenetration, and host-guest interactions.^{300–302} Furthermore, the electron-rich oxygen atoms in these groups enhance dipole–quadrupole interactions with guest molecules such as CO₂, thereby increasing adsorption selectivity.^{293,303,304} In addition, the incorporation of methoxy groups can lead to more robust frameworks with enhanced thermal stability.^{296,297}

Building on these advantages and following the successful synthesis of **L4-H₆**, **L5-H₆**, and **L6-H₆** via coupling with 4-aminobenzoic acid, the precursor compound **37** was further treated with a series of amino benzoic acids bearing side groups, –CH₃, –OMe, and –OH. This afforded a new series of amide-functionalised organosilicon hexacarboxylic acids, **L7-H₆**, **L8-H₆**, and **L9-H₆**, respectively (Equation 18).



Equation 18: Synthesis of **L7-H₆**, **L8-H₆**, and **L9-H₆** via amidation.

L7-H₆ was prepared by coupling compound **37** with 4-amino-2-methylbenzoic acid, following the same amidation method and reaction conditions described previously in Section 2.3.1. The preparation of **L7-H₆** was confirmed by ¹H, ¹³C, and ²⁹Si NMR spectroscopy, as well as IR

spectroscopy and mass spectrometry. In the ^1H NMR spectrum, a sharp singlet at 2.53 ppm and a corresponding signal at 22.35 ppm in the ^{13}C NMR spectrum confirmed the presence of the methyl substituent on the aromatic rings.²⁹² The carboxylic acid and amide N–H protons were observed at 12.54 ppm and 10.49 ppm, respectively. Both the aromatic proton and carbon signals appeared within their expected regions, with the protons observed as two multiplets and a doublet between 7.66–8.01 ppm in the ^1H NMR spectrum, and the carbon signals detected between 117–143 ppm in the ^{13}C NMR spectrum. In addition, the amide and carboxylic acid carbonyl carbons appeared at 166.09 ppm and 168.47 ppm, respectively.

The IR spectrum of **L7** displayed broad absorptions between 2700–3500 cm^{-1} , corresponding to overlapping O–H and aromatic C–H stretches. The methyl C–H stretch, typically found below 3000 cm^{-1} , appeared to be overlapped by the O–H and aromatic C–H bands. Distinct carbonyl stretching vibrations were detected at 1664 cm^{-1} (COOH) and 1582 cm^{-1} (amide). Additional bands were observed at 1448 cm^{-1} and 1390 cm^{-1} , which correspond to the methyl bending modes, providing another evidence for the presence of the aromatic methyl group. An Si–O–Si stretch appeared at 1079 cm^{-1} , confirming the integrity of the disiloxane core. Furthermore, the ESI– mass spectrum of **L7** showed a $[\text{M} - \text{H}]^-$ ion at $m/z = 1595.4357$, in a good agreement with the calculated value of 1595.4318.

Compound **37** was also coupled with 4-amino-2-methoxybenzoic acid and 4-amino-2-hydroxybenzoic acid in NMP to afford **L8-H₆** and **L9-H₆**, respectively. **L8-H₆** was synthesised following the same aminolysis procedure and workup protocol as described for **L7-H₆** (Equation 17), with similar observations. The synthesis of **L9-H₆** followed the same method but required some modifications. Upon quenching the reaction with cold water, the solution became cloudy pink, and a pale pink precipitate formed, resulting in an initial low yield of 24%. To improve the yield, hydrochloric acid was added to the filtrate, followed by overnight

cooling at -5°C . This treatment successfully induced further precipitation, increasing the overall yield to 64%. After washing with warm water, the solid turned off-white.

L8-H₆ and **L9-H₆** were characterised by ^1H , ^{13}C , and ^{29}Si NMR spectroscopy as well as IR spectroscopy and mass spectrometry. For **L8-H₆**, the methoxy protons appeared as a sharp singlet at 3.80 ppm in the ^1H NMR spectrum. The carboxylic acid proton peak was also observed at 12.38 ppm, while the amide proton appeared at 10.55 ppm. In addition, the aromatic protons appeared as two multiplets at 8.02–7.97 and 7.73–7.65 ppm, and as a doublet at 7.47 ppm, all within the expected aromatic region. In the ^{13}C NMR spectrum, a signal was observed at 56.06 ppm, corresponding to the methoxy carbon. Moreover, the carboxylic acid and amide carbonyl carbons were detected at 166.96 ppm and 166.19 ppm, respectively. The ^{29}Si NMR spectrum of **L8-H₆** exhibited a single peak at -19.08 ppm, consistent with the disiloxane linkage.

In the IR spectrum of **L8-H₆**, the methyl C–H stretch was observed around 2950 cm^{-1} , while broad overlapping bands between 2500 and 3400 cm^{-1} corresponded to $-\text{OH}$ and $\text{N}-\text{H}$ stretching. Two distinct carbonyl stretches appeared at 1659 cm^{-1} (carboxylic acid) and 1589 cm^{-1} (amide), while the methoxy C–O stretch appeared at 1249 cm^{-1} . The Si–O–Si stretching was observed at 1078 cm^{-1} , confirming its structural integrity. Furthermore, ESI-MS analysis of **L8-H₆** showed a peak at $m/z = 845.1970$, matching the calculated value for the doubly deprotonated, doubly charged species $[\text{M}-2\text{H}]^{2-}$ ($m/z = 845.1970$). The charge state was confirmed by the isotopic peak spacing of $\sim 0.5\text{ Da}$, consistent with a doubly charged species. Altogether, these characterisation data confirm the successful synthesis of the **L8-H₆**.

For **L9-H₆**, the ^1H NMR spectrum displayed three singlet signals at 10.55, 11.36, and 13.76 ppm, corresponding to the amide, *ortho*-hydroxyl, and carboxylic acid protons, respectively. The aromatic region exhibited two doublets at 7.98 and 7.31 ppm, a singlet at 7.52 ppm, and a multiplet at 7.77–7.66, with integration values consistent with the structure of **L9-H₆**. The ^{13}C

NMR spectrum further supported the formation of **L9-H₆**, showing distinct signals for the carboxylic acid carbon at 172.06 ppm, the amide carbonyl at 166.37 ppm, and the hydroxyl-bearing aromatic carbon at 162.41 ppm. The presence of the hydroxyl group was also supported by IR spectroscopy, which showed a broad O–H stretching band around 2965 cm⁻¹. Two carbonyl stretches were observed at 1656 cm⁻¹ (carboxylic acid) and 1596 cm⁻¹ (amide), along with a Si–O–Si stretch at 1079 cm⁻¹. In addition, the ²⁹Si NMR spectrum of **L9-H₆** showed a single peak at –10.58 ppm, corresponding to the disiloxane linkage. Moreover, mass spectrometric analysis (ESI–) revealed a [M–H][–] peak at m/z = 1607.3085, in an excellent agreement with the calculated value of 1607.3074.

Some residual NMP signals were still visible in the ¹H NMR spectra (below 3 ppm), indicating solvent impurities. Attempts to recrystallise **L8-H₆** and **L9-H₆** for improved purity and for SCXRD analysis were unsuccessful. Nonetheless, all spectroscopic and analytical data presented above and in Chapter 7 confirm the successful synthesis of both compounds. All compounds described in this section are novel and represent an important addition to the rare family of amide-functionalised organosilicon carboxylic acid compounds.

2.4 Synthesis of **L10-H₆**

As described in Section 2.1, hydrosilanes can undergo hydrolysis in the presence of excess alkali metal hydroxide to produce silanols. These silanols can subsequently react with halosilanes to generate siloxanes, which serve as intermediates for the synthesis of siloxane-based carboxylic acid compounds through subsequent carboxylation reactions. This strategy is applicable not only to disiloxanes but also to trisiloxanes, which can be synthesised via the reaction of triorgano-substituted silanols with dialkyldichlorosilanes, typically in the presence of a non-nucleophilic base such as pyridine, which acts as a hydrogen halide acceptor. This method has proven effective; for example, Davies and co-workers reported the synthesis of a

novel trisiloxane-centered hexacarboxylic acid linker (compound **22**, Figure 15, Chapter 1).²⁰⁸

In their study, tris(4-bromophenyl)silanol was treated with pyridine and then reacted with dimethyldichlorosilane to yield the corresponding trisiloxane. The resulting intermediate was lithiated using six equivalents of *n*-BuLi, followed by carboxylation with CO₂ and acidic workup, affording compound **22**.

Siloxane-based compounds exhibit highly desirable properties, including structural flexibility, low toxicity, and excellent thermal stability.³⁰⁵ Moreover, incorporating siloxane-based linkers into MOFs can enhance hydrophobicity, thermal stability, and reduce chemical reactivity.^{184,306,307} Longer siloxane backbones offer added flexibility which may lead to interesting structures. Additionally, hydrophobic substituents such as –CH₃ can further increase the hydrophobic nature of the linkers.¹⁹⁴ In particular, the presence of Si–CH₃ groups or tetramethyldisiloxane moieties plays a crucial role in improving framework stability by protecting the structure from degradation upon exposure to water.^{194,306} Despite these advantages, tetrasiloxane multicarboxylate linkers remain extremely rare in the literature. Notably, Deshmukh *et al.* reported three novel cyclotetrasiloxane scaffolds bearing peripheral 3-pyridyl functional groups, which were used to construct 1D Zn- and Ag-based MOFs and a 2D Cu-based MOF exhibiting thermochromic luminescence behaviour (Figure 23).³⁰⁸ However, to the best of our knowledge, there are no reported examples of 3D MOFs constructed from tetrasiloxane-based linkers.

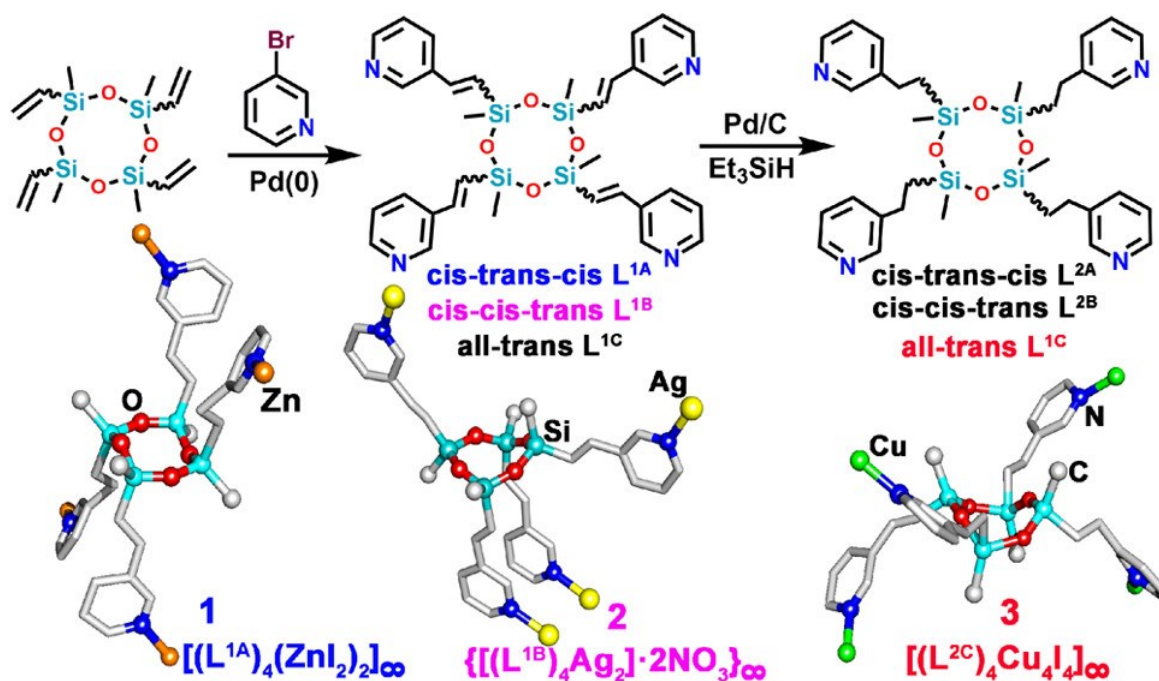
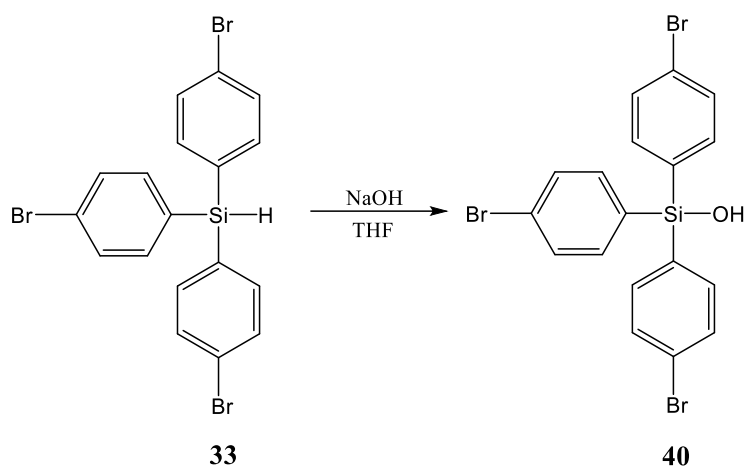


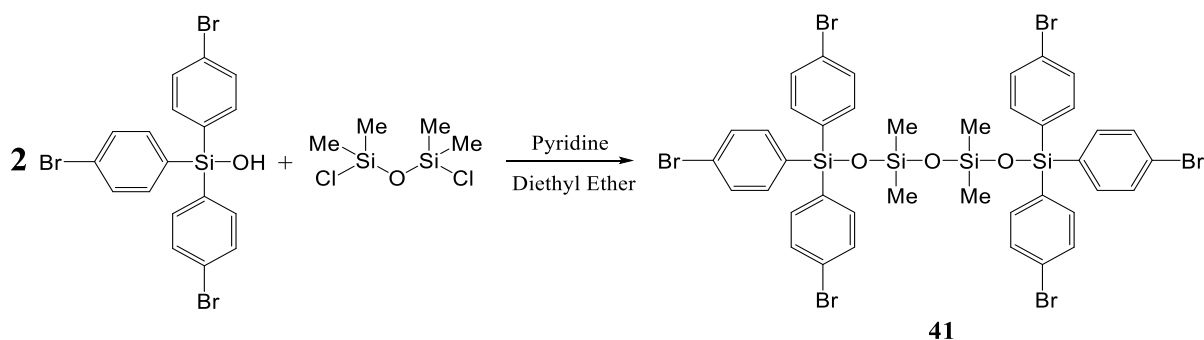
Figure 23: Cyclotetrasiloxane scaffolds bearing peripheral 3-pyridyl used in MOF synthesis. Reproduced from Ref. ³⁰⁸ with permission.

Motivated by the above, **L10-H₆** was synthesised following the general strategy used for compound **22** by Davies *et al.*,²⁰⁸ but employing 1,3-dichloro-1,1,3,3-tetramethyldisiloxane in place of dimethyldichlorosilane. First, tris(4-bromophenyl)silanol (**40**) was obtained by hydrolysing compound **33** (prepared in Section 2.1) with NaOH, as shown in Equation 19. This compound is known and was resynthesised in this study following the procedure reported by Davies and co-workers.²⁰⁸ Compound **40** was characterised by ¹H, ¹³C, and ²⁹Si NMR and IR spectroscopy, and the data matched literature values, confirming successful synthesis.²⁰⁸ In particular, the disappearance of the Si–H peak and the emergence of a new singlet at 2.87 ppm (Si–OH proton) in the ¹H NMR spectrum were key indicators. The IR spectrum further supported this with a broad O–H stretch at 3168 cm^{−1} and a Si–O stretch at 1066 cm^{−1}. It is worth mentioning that compound **40** can also be prepared via an alternative method using dibromobenzene and tetrachlorosilane, as reported by Sun and co-workers, where selective hydrolysis of Si–Cl bonds yields the silanol.¹⁸⁶



Equation 19: Preparation of tris(4-bromophenyl)silanol (**40**).

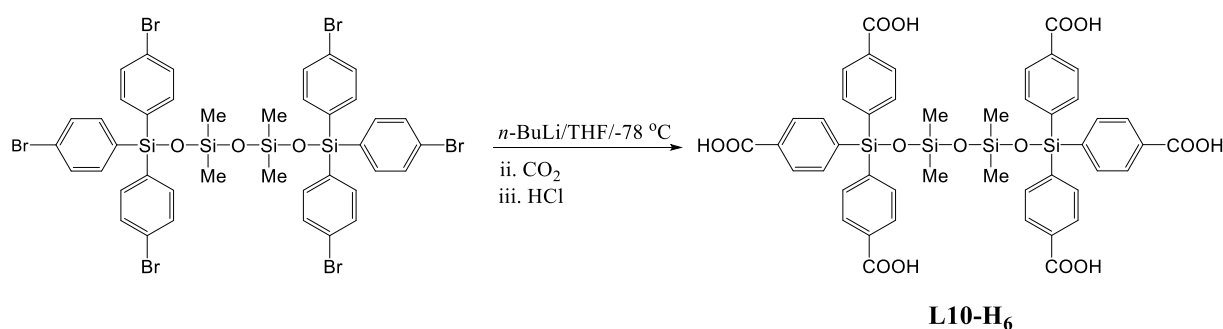
In the next step, two equivalents of the silanol were reacted with 1,3-dichloro-1,1,3,3-tetramethyldisiloxane via nucleophilic substitution in the presence of pyridine to afford the *p*-bromophenyl-substituted tetrasiloxane, compound **41** (Equation 20).



Equation 20: Synthesis of compound **41**.

The successful formation of the tetrasiloxane **41** was confirmed by a singlet peak for Si–CH₃ at 0.01 ppm in the ¹H NMR spectrum and at 1.22 ppm in the ¹³C NMR spectrum.^{208,309} The ²⁹Si NMR spectrum displayed two distinct signals at –18.76 ppm (Ar₃Si) and –21.37 ppm (Me₂Si), confirming the presence of two silicon environments. The IR spectrum indicated disappearance of the broad O–H band and appearance of a Si–CH₃ stretch at 1259 cm^{–1} and Si–O stretch at 1060 cm^{–1}. It is worth noting that, this compound is novel and represents a rare example of a functionalised phenyl-substituted tetrasiloxane derivative.

Finally, **L10-H₆** was synthesised via carboxylation and acidic workup using the same protocol applied for the other hexacarboxylic linkers prepared in Sections 2.1 and 2.2, as shown in Equation 21.



Equation 21: Synthesis of L10-H₆.

The carboxylic acid formation was confirmed by peaks at 12.18 ppm (¹H NMR) and 167.83 ppm (¹³C NMR), corresponding to the carboxylic acid proton and carbonyl carbon, respectively. In addition, a singlet peak was observed at −0.03 ppm in the ¹H NMR spectrum, corresponding to the Si–methyl protons. The ²⁹Si NMR spectrum showed signals at −18.16 (Ar₃Si) and −22.65 ppm (Me₂Si), consistent with the expected structure of **L10-H₆**. In the IR spectrum, the appearance of an O–H stretch at 3050 cm^{−1}, along with retained Si–CH₃ and Si–O stretches at 1258 and 1096 cm^{−1}, respectively, further supported the formation of the tetrasiloxane-based acid. Mass spectrometry (ESI+) also confirmed the molecular formula of **L10-H₆**, with the [M+H]⁺ ion observed at m/z = 947.1724, in excellent agreement with the calculated value of m/z = 947.1679.

L10-H₆ was recrystallised from a methanol/acetic acid mixture, and the resulting crystal structure was successfully resolved and is discussed in Chapter 3. Notably, tetrasiloxane compounds with terminal Ar₃Si groups are extremely rare in the literature.^{309,310} **L10-H₆** is a novel compound and, to the best of our knowledge, represents the first example of a carboxylic

acid compound based on a tetrasiloxane core, according to the Cambridge Structural Database as of the April 2025 update.

2.5 Conclusion

The synthesis of a diverse series of organosilicon hexacarboxylic acids was described in this chapter. By functionalising the parent hexacarboxylic acids, it was possible to generate extended compounds and introduce different substituents, including $-\text{CH}_3$, $-\text{OMe}$, and $-\text{OH}$, using convenient synthetic routes. These compounds were characterised using a range of analytical techniques, including NMR spectroscopy, IR spectroscopy, and mass spectrometry. In addition, the crystal structures of several compounds were determined by SCXRD and will be discussed in detail in Chapter 3. **L4-H₆**–**L10-H₆** are novel compounds and represent a significant expansion of the organosilicon hexacarboxylic acid family. Moreover, these compounds have a strong potential for the construction of HOFs and MOFs, which will be investigated in Chapters 3 and 4.

Chapter 3: Hydrogen-Bonded Organic Frameworks

3.1 Introduction

Hydrogen-bonded organic frameworks (HOFs) are a class of crystalline materials constructed from discrete organic molecules that assemble into 1D, 2D, or 3D structures.³¹¹ They are structurally related to coordination polymers and MOFs, but differ from covalent organic frameworks (COFs), which are held together by strong covalent bonds. In contrast, HOFs are primarily assembled through relatively weak, non-covalent intermolecular hydrogen bonds.³¹² These weak and reversible hydrogen bonding interactions endow HOFs with several unique features. For example, they can be synthesised under very mild conditions and easily recycled through simple recrystallisation.³¹³ Additionally, the flexible and weak nature of hydrogen bonds allows HOFs to adopt a variety of structural forms.³¹⁴ However, this poses a challenge because activating the framework by removing solvent from the pores can lead to structural rearrangement, often reducing pore size or causing complete loss of porosity.³¹⁵ This instability makes the design and synthesis of highly stable HOFs particularly demanding.

HOF crystals can be synthesised using various established methods such as liquid/vapor diffusion, evaporation or cooling crystallisation, and electrophoretic deposition (particularly for thin-film HOFs).³¹⁶ Nevertheless, due to their inherently weak hydrogen bonds, enhancing the stability and maintaining permanent porosity remains a key objective in HOF research. Effective strategies include the use of organic building blocks with multiple hydrogen bonding sites and incorporating additional intermolecular interactions, such as π - π stacking, which can be facilitated by employing planar organic building blocks with π -conjugated systems.³¹⁷

Interestingly, while interpenetration of HOF networks can reduce the accessible pore volume, it often leads to enhanced framework stability.^{314,317-319} This is because interpenetrated structures are generally more thermodynamically favourable than their non-interpenetrated

counterparts.³²⁰ By adopting such structural strategies, enhanced stability has been successfully developed.^{321–325} Moreover, owing to the unique properties discussed above, HOFs have garnered considerable attention for their potential in a wide range of applications, including gas sorption,^{325–327} gas separation,^{326,328,329} proton conductivity,^{330,331} sensing,^{323,332–334} and catalysis.^{313,335–337}

Research on HOFs confirms that the choice of building units and functional binding sites significantly influences both the stability and performance of these materials.³¹⁴ Their assembly fundamentally relies on the formation of hydrogen bonds between organic components, commonly referred to as synthons. A wide variety of hydrogen bonding synthons have been investigated for HOF construction, including carboxylic acids, diaminotriazine (DAT), imidazole, pyridine, and others (Figure 24).^{328,338–342} Among these, carboxylic acids have emerged as particularly promising building blocks due to their versatile binding modes, high directionality, and strong hydrogen bonding capabilities.³⁴³ Accordingly, this chapter focuses on multicarboxylic acid-based HOFs and presents several notable examples. It also discusses the crystal structures of some organosilicon compounds prepared in this study that form HOFs.

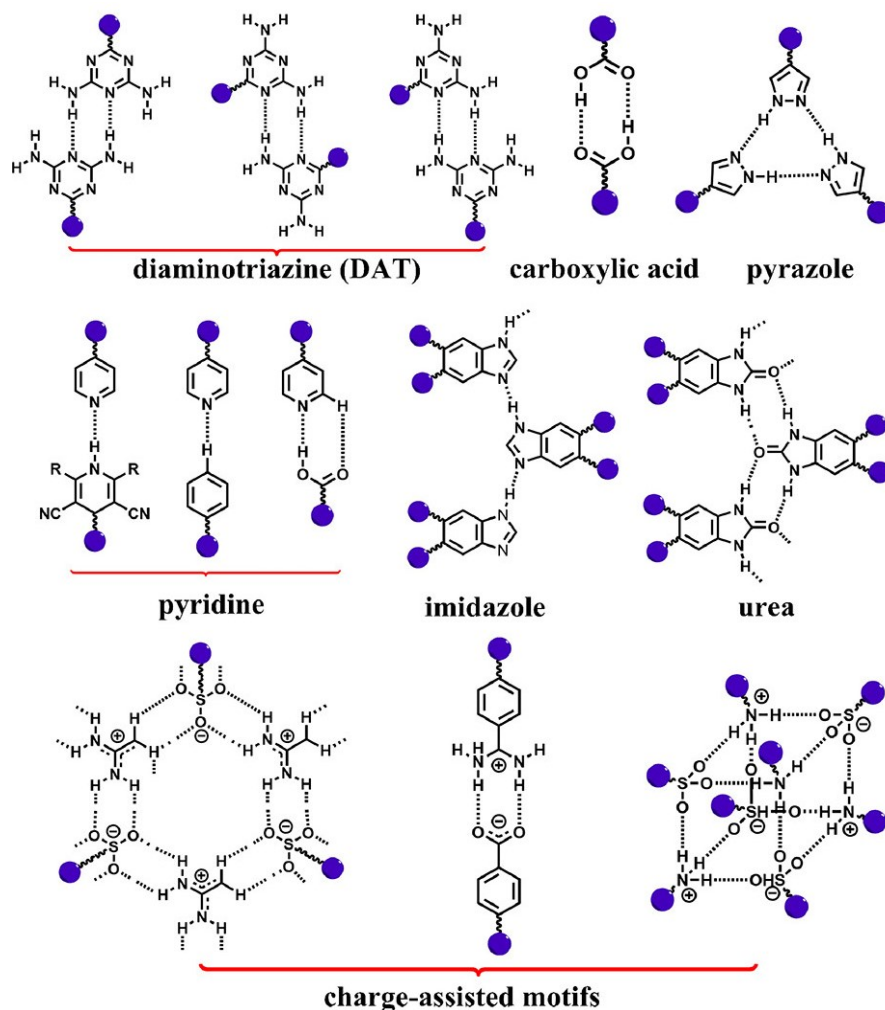


Figure 24: H-bonding motifs used for the building of porous HOFs. Reproduced from Ref. ³¹⁹ with permission.

3.2 Carboxylic Acid-Based HOF Systems

The carboxylic acid group is one of the most common and simplest motifs used in constructing HOFs due to its high directionality and strong hydrogen bonding interactions ($\text{O}-\text{H}\cdots\text{O}$).³⁴⁴ In addition, the aromatic backbones bearing these groups have the potential to engage in π - π stacking, providing further stabilisation of the framework. In solution, carboxyl groups readily self-assemble into carboxylic acid dimers through hydrogen bonding between adjacent COOH groups (Figure 25), typically with $\text{O}\cdots\text{O}$ distances of ~ 2.77 Å and $\text{O}-\text{H}\cdots\text{O}$ angles ranging from 170° to 180° in most cases, facilitating the formation of highly stable frameworks.^{316,345}

These dimers are widely employed in HOF design because of their linearity and structural predictability.³⁴⁶

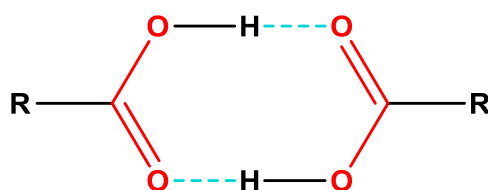


Figure 25: Dimeric H-bonding interaction formed between two carboxylic acid groups.

One of the earliest examples of a carboxylic acid-based hydrogen-bonded framework was reported by Duchamp and Marsh in 1969 using 1,3,5-benzenetricarboxylic acid (trimesic acid, TMA).³⁴⁷ In this structure, self-complementary hydrogen-bonded dimers formed a 2D hexagonal (**hcb**) network. Later, in 1988, Ermer described a 3D HOF constructed solely through hydrogen bonding from adamantane-1,3,5,7-tetracarboxylic acid, which adopted a five-fold interpenetrated **dia** topology.³⁴⁸ Although neither of these early examples exhibited accessible void space due to interpenetration, they provided foundational insights into using directional hydrogen bonding for HOF design. Notably, the successful formation of TMA frameworks demonstrated that symmetric multicarboxylic acids can enable the construction of 3D HOFs. Since then, many guest-inclusion hydrogen-bonded networks with 1D, 2D, and 3D architectures have been developed.^{320,349}

Kobayashi *et al.* reported a 2D hexagonal HOF assembled from carboxylic acid dimers of hexakis(4-carboxyphenyl)benzene (HCPB), featuring triangular cavities (15.2 Å per side) occupied by guest molecules (Figure 26).³⁵⁰ Despite the absence of interpenetration, the structure lacked permanent porosity and long-term stability. Nevertheless, it demonstrated how planar, C₆-symmetric multicarboxylic acids can form extended hydrogen-bonded frameworks with large internal cavities, highlighting their potential in host–guest chemistry and porous material design.

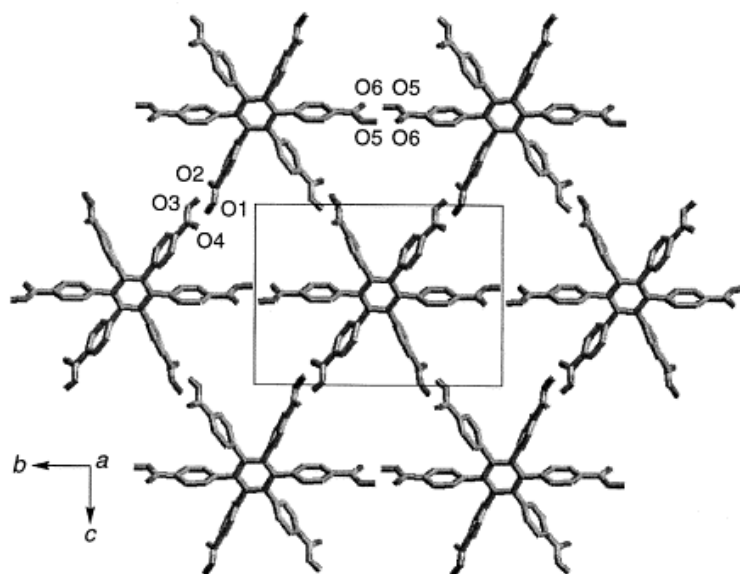


Figure 26: 2D hexagonal hydrogen-bonded network of hexakis(4-carboxyphenyl)benzene. Guest molecules are omitted for clarity. Reproduced from Ref. ³⁵⁰ with permission.

A major advancement in HOF porosity was achieved by Hong *et al.* through the introduction of π - π interactions in HOFs.³⁵¹ They reported HOF-TCBP, constructed from 3,3',5,5'-tetrakis(4-carboxyphenyl)-1,1'-biphenyl. Similar to the tetrahedral adamantane-based HOF first prepared by Ermer in 1988, HOF-TCBP formed a five-fold interpenetrated 3D **dia**-type network (Figure 27). However, HOF-TCBP exhibited permanent porosity, exceptional thermal and water stability, and a high BET surface area of 2066 m²/g upon activation, with easy regeneration by dissolving the material in an appropriate solvent followed by rotary evaporation. The remarkable stability is attributed to a combination of robust hydrogen bonding networks and strong π - π stacking interactions, making it a promising candidate for light hydrocarbon separation and purification.

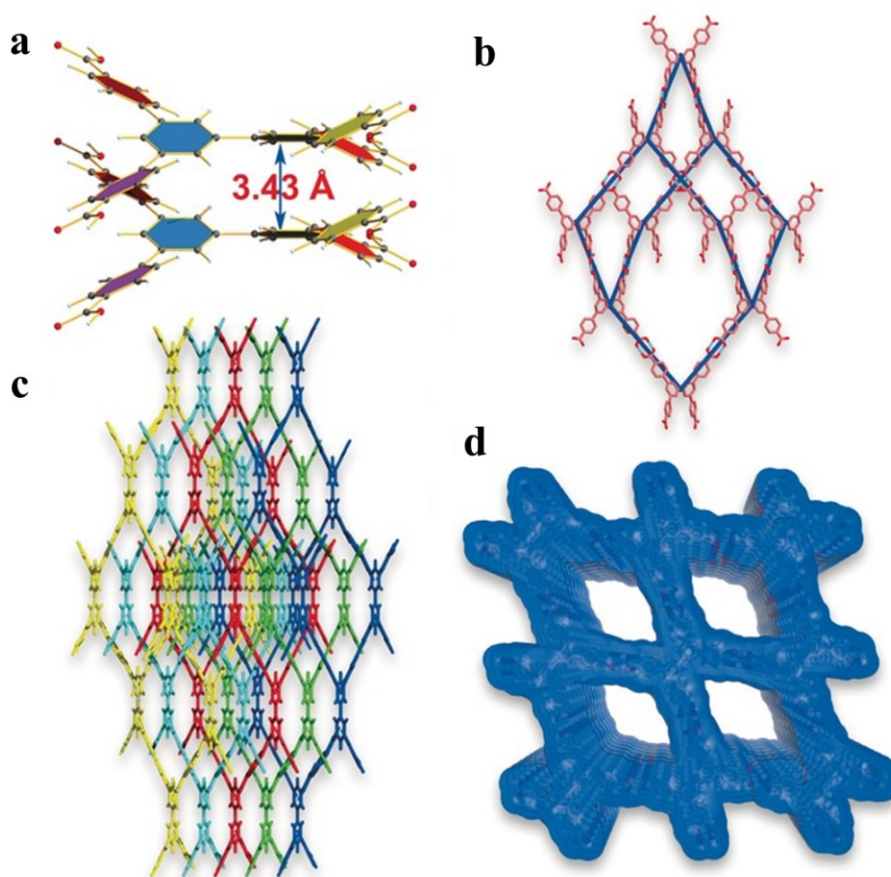


Figure 27: Crystal structure of HOF-TCBP: (a) face-to-face π – π stacking interactions; (b) **dia**-type network; (c) five-fold interpenetrated **dia** framework; (d) connolly surface representation highlighting the 1D channels oriented along the a axis. Reproduced from Ref. ³⁵¹ with permission.

Cao and co-workers further demonstrated the effectiveness of π – π interactions in the development of PFC-1, synthesised from 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene (H_4TBAPy), a planar, π -conjugated molecule bearing four terminal carboxylic acid groups.³⁵² The resulting structure consisted of 2D **sql** layers stacked via π – π interactions (interlayer distance: 3.338 Å). PFC-1 displayed a surface area of 2122 m²/g and became the first HOF applied in the delivery of multiple cancer therapeutics. In a follow-up study, the same group reported PFC-2, a five-fold interpenetrated HOF with **nbo** topology formed from another pyrene-based tetracarboxylic acid.³⁵³ PFC-2 featured exceptionally large channels and demonstrated potential for fuel gas purification and separation of C_2H_2/C_2H_4 from CH_4 .

Farha and co-workers later reported a series of stable HOFs with **sql** topology using pyrene-based tetracarboxylic acids, including HOF-101, which is structurally equivalent to PFC-1.³²⁴ Through functionalization of the phenyl rings with ortho-substituted groups (CH₃, F, NH₂), they prepared three isostructural variants: HOF-101-CH₃, HOF-101-NH₂, and HOF-101-F.³⁵⁴ Crystal structures revealed 2D layers connected by intermolecular hydrogen bonds, stacking in an AA pattern with π - π interactions between adjacent tectons. These assemblies formed 1D channels ($\sim$ 2 nm wide), with functional groups oriented toward the channel interior, providing tunability for specific adsorption applications (Figure 28).

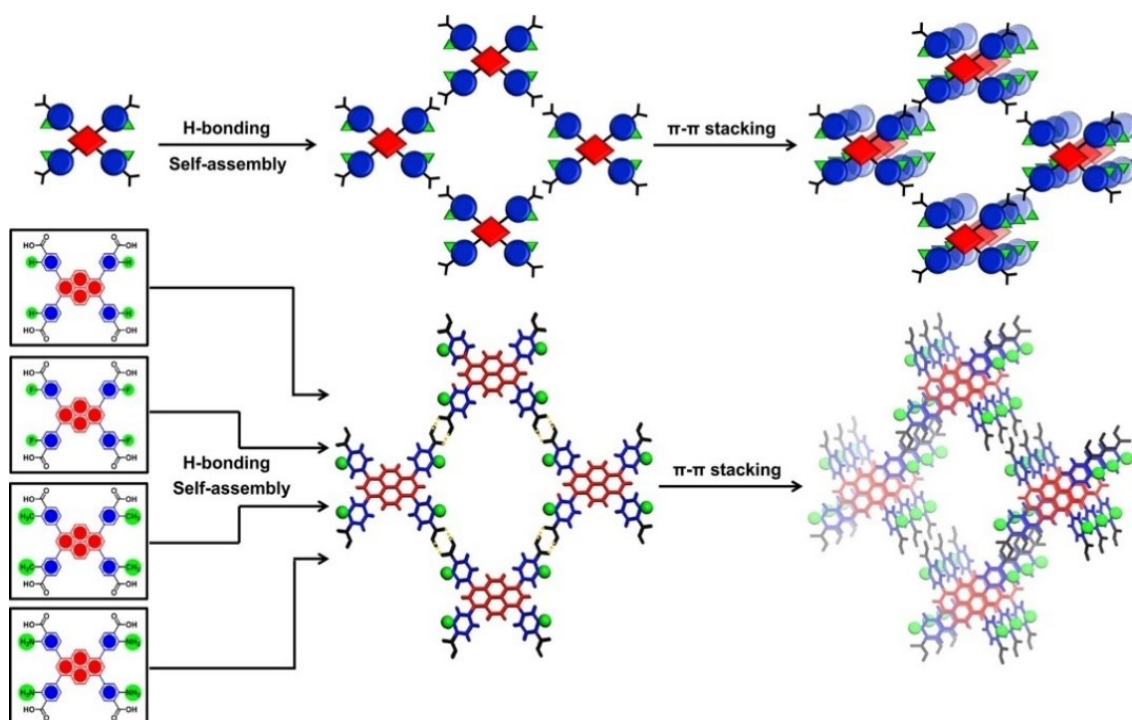


Figure 28: Schematic illustration of the self-assembly of HOF materials from various tectons. Reproduced from Ref. ³⁵⁴ with permission.

Hisaki and co-workers developed several isostructural HOFs using C₃-symmetric, cyclic π -conjugated linkers bearing three 4,4'-dicarboxy-*o*-terphenyl groups.^{323,355–357} These porous frameworks exhibited potential in chemical sensing and organic light-emitting device (OLED) applications. In a related study, Hisaki's group demonstrated that 3D HOFs could be achieved by conformationally controlling extended carboxylic acid linkers.³⁵⁸ Using hexakis(4-

carboxyphenyl)hexaazatriphenylene (CPHAT), a non-planar π -conjugated heterocycle with six terminal COOH groups, they obtained CPHAT-1 by slow evaporation from a DMF/1,2,4-trichlorobenzene (TCB) solution at 100 °C. CPHAT-1 is a four-fold interpenetrated, highly stable 3D HOF with **pcu** topology, featuring an infinite helical structure. Notably, it retained crystallinity and represents the first HAT-based HOF with permanent porosity. The activated material exhibited a CO₂-based BET surface area of 649 m²/g and an uptake of 137 cm³/g at 0.99 bar. In a subsequent study, extending the arms of the hexacarboxylic linker in CPHAT-1 yielded CBPHAT-1a, an isostructural HOF with an increased BET surface area of 1288 m²/g.³⁵⁹

Stoddart and co-workers further expanded the HOF landscape by assembling **acs**-topology frameworks using a triptycene-based hexacarboxylic acid.³⁶⁰ They demonstrated that interpenetration in these structures could be tuned via crystallisation conditions. The activated materials showed permanent porosity with BET surface areas exceeding 1100 m²/g.

In a recent study, Bu and co-workers reported two eight-connected, blue-emitting, carboxylic acid-based 3D HOFs with two-fold interpenetrated **bct** topologies, inspired by the principles of reticular chemistry.³⁶¹ These frameworks featured large pores ($7.8 \times 11.6 \text{ \AA}^2$ and $8.4 \times 16.2 \text{ \AA}^2$) and demonstrated the ability to absorb fluorescent molecules such as diketopyrrolopyrrole (DPP) and 9-anthraldehyde (AnC), leading to the formation of white light-emitting (WLE) composites with promising potential for use in white light-emitting diodes (WLEDs).

3.3 Organosilicon Multicarboxylic Acid HOFs

While several 1D hydrogen-bonded supramolecular polymers based on organosilicon carboxylic acids have been reported in the literature, examples of 2D or 3D HOFs derived from such compounds remain rare.^{362–365} Moreau and co-workers reported the synthesis of the carboxylic acid POSS derivative octa[2-(*p*-carboxyphenyl)ethyl] silsesquioxane, which self-assembles into a 3D HOF. In this HOF, silsesquioxanes cages bearing eight carboxylic acid groups interconnect via dimeric hydrogen bonding to form the extended framework.³⁶⁴ Bassanetti *et al.* reported another example of 3D HOF, TCF-2, obtained by crystallising TCPS-H₄.³⁶⁶ Since acetic acid was found to inhibit the extension of TCPS-H₄ into a 3D framework (as discussed in Section 1.2.1),¹⁴⁶ crystallisation in this study was instead carried out by layering *n*-hexane over a THF solution of TCPS-H₄. The resulting TCF-2 structure featured a 3D channel network, in which each TCPS-H₄ molecule connected to four neighbours through eight hydrogen bonds formed by carboxylic acid dimers. The framework adopted a six-fold interpenetrated **dia** topology with significant solvent-accessible pores (Figure 29).

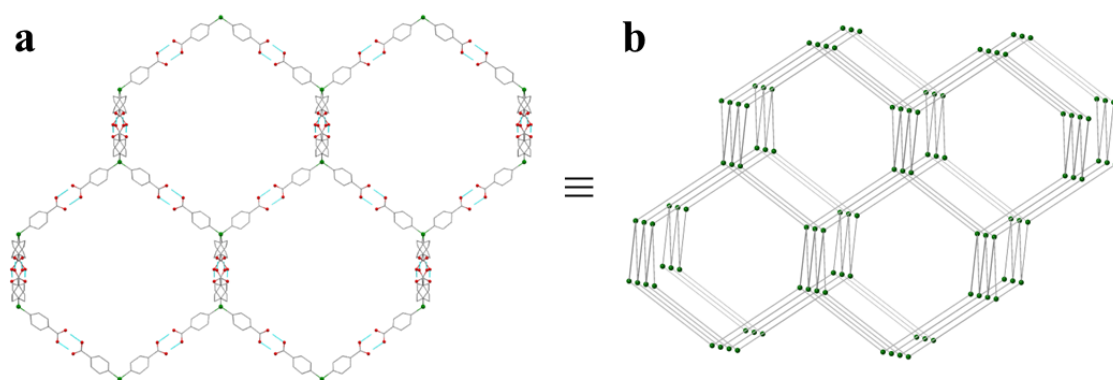


Figure 29: Crystal structure of TCF-2: (a) cross-section of the extended TCF-2 structure viewed along the *b* axis, showing TCF-2 molecules connected via dimeric H-bonding; (b) topological representation of the **dia** network, with Si-based ligand nodes shown in green. H atoms are omitted for clarity. Colour scheme: O, red; C, grey; Si, green; hydrogen bonds represented by blue dashed lines. Figure was drawn using published crystal data from Bassanetti *et al.* (CSD refcode: RIJHUQ).³⁶⁶

As mentioned in Chapter 1.2.3, Davies and co-workers reported several rare multicarboxylic silicon-based HOFs.^{184,194,207,208} One such example is compound **15** (see Figure 11 in Chapter 1),¹⁹⁴ which was crystallised via slow evaporation of a methanol/acetic acid mixture. The rotational freedom around the Si–O bonds, along with the flexible Si–O–Si bond angle, allows the compound to adjust the orientation of its carboxylic acid groups to optimise dimeric hydrogen bonding with adjacent molecules, promoting the formation of an extended network.¹⁹⁴ As a result, the structure exhibit two crystallographically distinct tetra-acid molecules with differing geometries: one with a bent disiloxane linkage, and the other with a linear disiloxane linkage. These molecules interconnect via dimeric hydrogen bonds to form a quadruply interpenetrated 3D framework with **mog** topology.

L1-H₆ represents a rare example of a hexacarboxylic acid with a *pseudo*-octahedral arrangement of carboxylic acid groups.¹⁸⁴ Single crystals of **L1-H₆** were obtained from a methanol/acetic acid mixture. The unit cell contains three independent siloxane molecules: two of these are crystallographically distinct and exhibit linear siloxane linkages, while the third adopts a slightly bent conformation with an Si–O–Si bond angle of 170.76(18)°, consistent with the 140–180° range reported for acyclic disiloxane structures.³⁴⁵ The **L1-H₆** molecules are linked via dimeric hydrogen bonding, giving rise to a triply interpenetrated 3D **pcu** framework (Figure 30). Within this structure, 1D polymeric chains of H-bonded **L1-H₆** molecules were found to occupy the network voids.

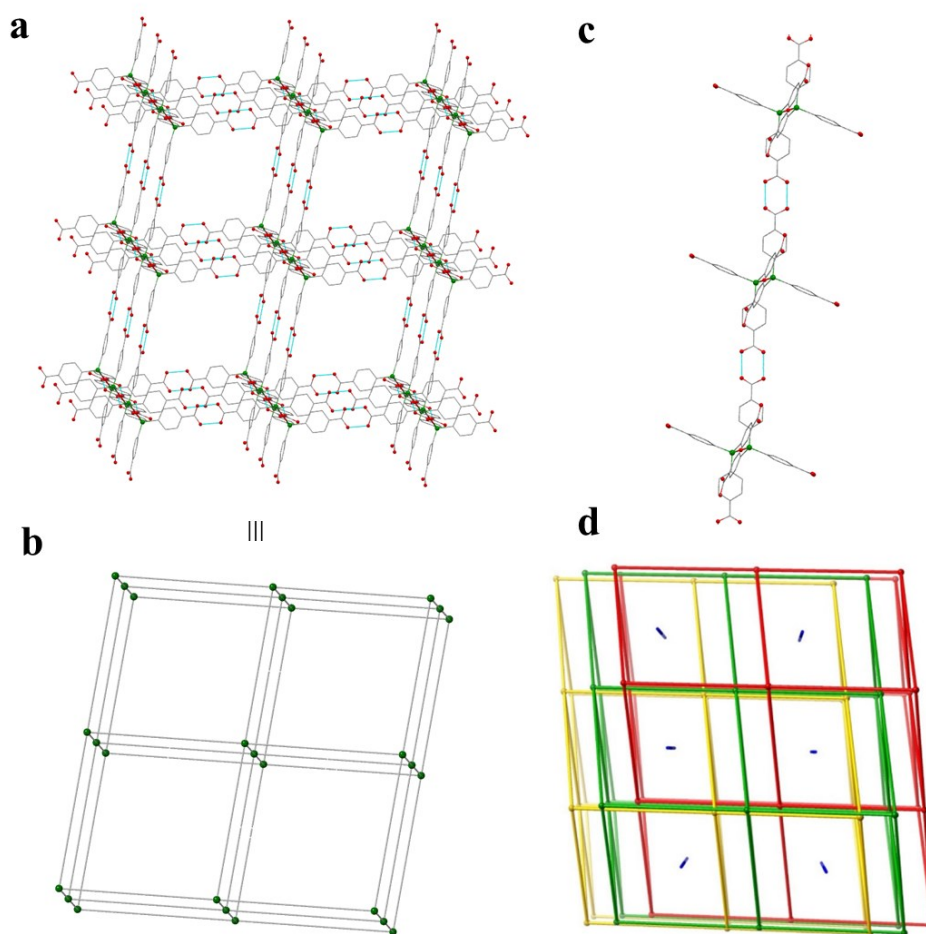


Figure 30: Crystal structure of **L1-H₆**: (a) a portion of the 3D **pcu** net formed by H-bonded **L1-H₆** molecules; (b) the corresponding topology diagram (c) 1D polymeric chains of linear H-bonded **L1-H₆** molecules; (d) a topological illustration of the three interlocked **pcu** networks, showing 1D chains occupying the pores along the [101] crystallographic direction. H atoms are omitted for clarity. (a), (b), and (c) were drawn using published crystal data from Davies and co-workers (CSD refcode: ZENHUY).¹⁸⁴ (d) was reproduced from Ref. ¹⁸⁴ with permission.

Another example is the trisiloxane hexacarboxylic acid (**22**), which is an extended version of **L1-H₆** with an additional [–O–Si–] unit.²⁰⁸ This extension resulted in a U-shaped Si–O–Si–O–Si backbone, in contrast to the nearly linear Si–O–Si arrangement observed in **L1-H₆**. All carboxylic acid groups in compound **22** participate in hydrogen bonding, either with neighbouring **22** molecules or with acetic acid, forming an unusual 2D hydrogen-bonded network composed of interlinked, rod-like molecular bundles. In addition, unusual parallel

orientation of two acid groups on each ligand molecule gives rise to a distinctive set of quadruple hydrogen bonds observed between certain molecules, as illustrated in Figure 31. Notably, the formation of a 3D network is hindered by the presence of acetic acid, which caps the remaining uncoordinated carboxylic acid groups and thereby prevents further aggregation of the corrugated 2D layers.²⁰⁸

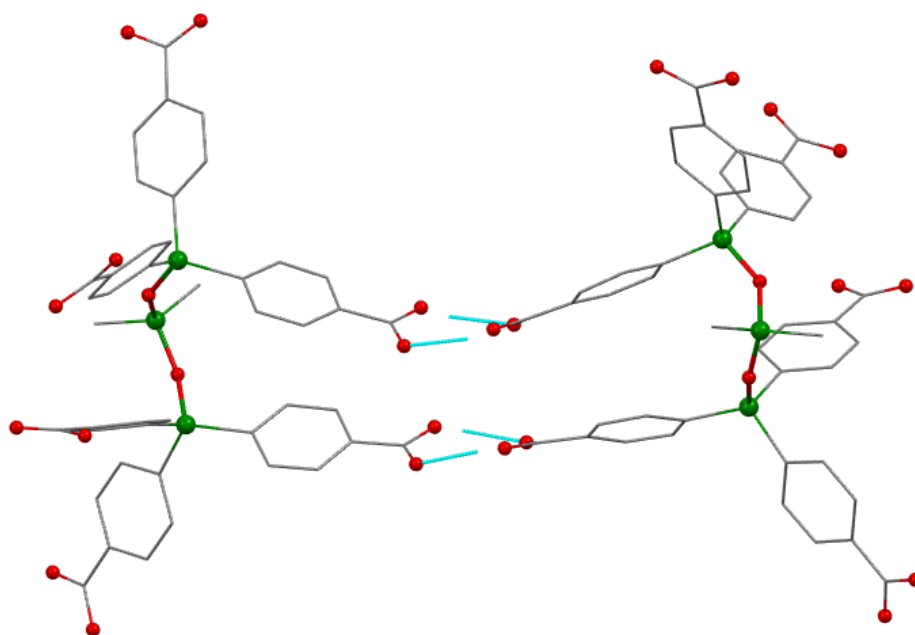
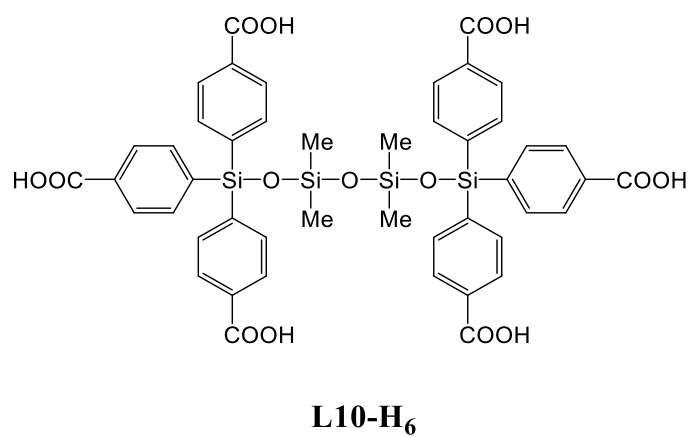


Figure 31: Quadruple hydrogen bonds observed in between adjacent **22** molecules. H atoms are omitted for clarity. Figure was drawn using published crystal data from Davies and co-workers (CSD refcode: UFOZEX).²⁰⁸

The highly branched organosilicon carboxylic acid compounds synthesised and discussed in Chapter 2 also show promise for assembling HOFs through hydrogen bonding interactions involving their carboxylic acid groups. Additionally, the presence of amide functionalities in the linker arms offers further opportunities for hydrogen bonding, which can lead to more robust HOFs, as demonstrated by Wu and co-workers.³⁶⁷ Inspired by this, the studies reviewed in this chapter, and the growing interest in organosilicon multicarboxylic acid HOFs, the crystal structures of several compounds presented in Chapter 2 (Figure 32) have been investigated and will be discussed in detail in the remainder of this chapter.



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3.4 Structure of **L4-H₆·2MeOH·2H₂O**

Amide functionalization of **L1-H₆** over two reaction steps afforded **L4-H₆** (see section 2.3.2), which was slowly recrystallised from methanol to yield colourless, lath-shaped crystals. The crystal structure was determined by single-crystal X-ray diffraction, revealing that **L4-H₆** crystallises in the monoclinic space group *I*2/*a* (No. 15). Similar to **L1-H₆**, **L4-H₆** exhibits a *pseudo*-octahedral arrangement of six carboxylic acid and amide groups, representing another rare example of an organosilicon hexacarboxylic acid linker with a highly desirable geometry for MOF construction. The asymmetric unit comprises one **L4-H₆** molecule, two methanol molecules, and two water molecules, and the unit cell contains eight such units. In contrast to the **L1-H₆** structure, where the Si–O–Si linkage is linear in two siloxane molecules and slightly bent in a third (angle = 170.76(18)°), all **L4-H₆** molecules in the unit cell feature bent siloxane linkages with an Si–O–Si angle of 151.8(2)°. This value falls within the typical range of 140–180° reported for acyclic disiloxanes in the literature.^{184,194,345} Disiloxanes with strongly bent Si–O–Si angles (<140°) are also known in the literature.^{368,369}

L4-H₆ molecules are interconnected through intermolecular hydrogen bonding involving both carboxylic acid and amide groups (Figure 33). Solvent molecules also participate in hydrogen bonding with neighbouring **L4-H₆** molecules. For example, one water molecule bridges three adjacent **L4-H₆** molecules (at O4, O12, and O16 sites) via hydrogen bonding through a methanol–water cluster (Figure S1), while the other water molecule bridges two **L4-H₆** molecules by connecting an amide nitrogen (N3) and a carboxyl oxygen (O9).

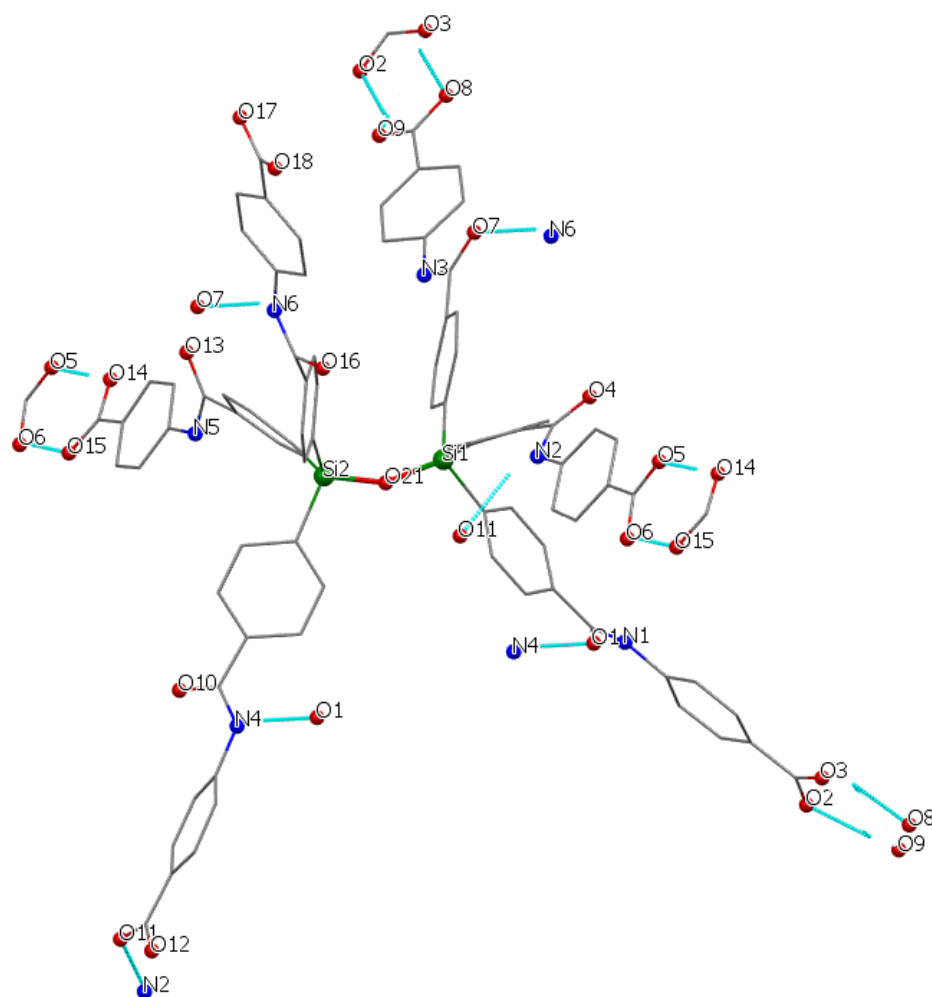


Figure 33: Coordination environment of **L4-H6** in the framework, showing H-bonding interactions with neighbouring **L4-H6** molecules. H atoms and solvent molecules are removed for clarity. Colour scheme: O, red; C, grey; Si, green; N, blue. H-bonds are shown by a cyan line.

Five of the six carboxylic acid groups in each **L4-H6** molecule are involved in hydrogen bonding. Four COOH groups form dimeric hydrogen bonds with four neighbouring **L4-H6** molecules, exhibiting O $\cdots$ O distances between 2.554–2.699 Å and O–H $\cdots$ O angles between 140.69° and 169.31°, values that are consistent with typical carboxylic acid dimer interactions in HOFs.³¹⁶ The fifth COOH group acts as a hydrogen bond donor (O12) to a bridging water molecule and as an acceptor (O11) from an amide NH group (N2) of a neighbouring **L4-H6**. The remaining COOH group does not participate in hydrogen bonding, though it may engage

in weak interactions with any disordered solvent that could not be fully modelled crystallographically and was removed by the SQUEEZE routine of PLATON.³⁷⁰ It is worth noting that solvent masking analysis revealed the presence of nine methanol and two water molecules per asymmetric unit. Therefore, the complete formula can be written as **[L4-H₆(MeOH)₂(H₂O)₂]·9MeOH·2H₂O**.

Five out of the six amide groups in **L4-H₆** also engage in hydrogen bonding. Four of these function as both donors and acceptors. For example, the amide groups at N1 and N3 donate to solvent molecules and accept hydrogen bonds through their carbonyl oxygens (O1 and O7, respectively) from neighbouring **L4-H₆** molecules. The amide group at N2 donates a hydrogen bond to the carbonyl oxygen (O11) of a carboxylic acid group in another **L4-H₆** molecule, with an N···O distance of 2.896 Å (consistent with the average bonding distance of N–H···O interaction),³¹⁶ and an N–H···O angle of 158.56°. The amide groups at N4 and N6 form hydrogen bonds to carbonyl oxygens (O1 and O7, respectively) of the same neighbouring **L4-H₆**, with distances of 2.881 Å and 3.359 Å, and corresponding angles of 165.72° and 162.49°. Additionally, the carbonyl oxygen at O16 (from N6) accepts a hydrogen bond from a bridging water molecule. Finally, the amide group at N5 does not participate in any hydrogen bonding with neighbouring **L4-H₆** molecules or solvent molecules. In total, each **L4-H₆** molecule connects to eight neighbouring **L4-H₆** molecules via hydrogen bonding, five through carboxylic acid groups and three through amide groups.

The self-assembly of **L4-H₆** molecules into a 3D HOF involves several distinct hydrogen-bonding interactions. **L4-H₆** molecules adopt a side-by-side arrangement linked through pairs of amide–amide N–H···O hydrogen bonds (2.881 Å and 3.359 Å), forming continuous arrays (Figure 34). It is worth noting that a similar side-by-side hydrogen-bonded mode has been reported by Wu and co-workers in the amide-functionalised HOF MTHOF-1.³⁶⁷ Four adjacent arrays connect via dimeric H-bonds to form a hydrogen-bonded net, which further extends

through carboxyl–amide hydrogen bonds to produce a chiral net. Both nets continue to interconnect to afford a potentially porous 3D HOF (Figure 35), exhibiting square solvent-accessible channels visible along the *b* axis. After theoretical removal of coordinated and non-coordinated solvent molecules, the solvent-accessible void volume was estimated using Mercury to be 7324 Å³,³⁷¹ corresponding to 35% of the unit cell volume (30% with coordinated solvent molecules). This represents a significant increase in porosity compared to the parent **L1-H6** HOF, which exhibits a void volume of 1037 Å³ (22% of the unit cell volume).

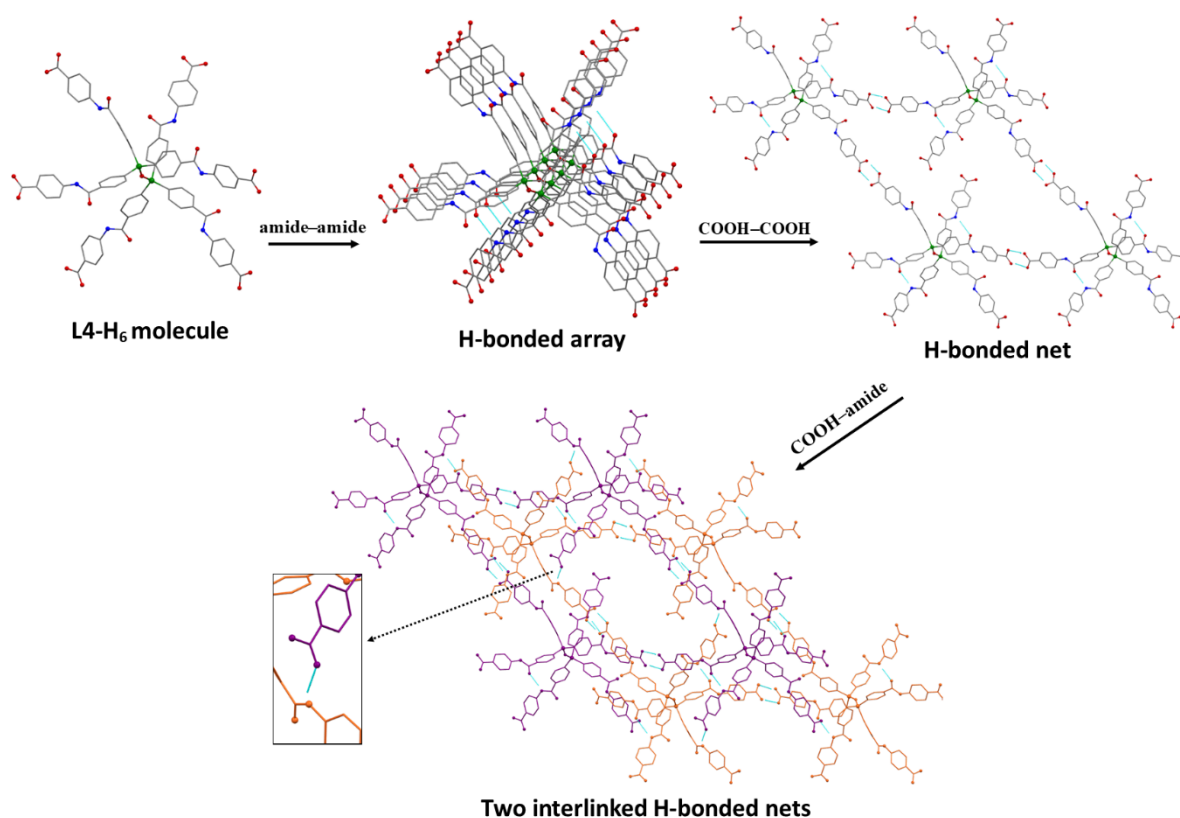


Figure 34: The self-assembly pathway from a single **L4-H6** molecule to two interlinked hydrogen-bonded nets (shown in purple and orange).

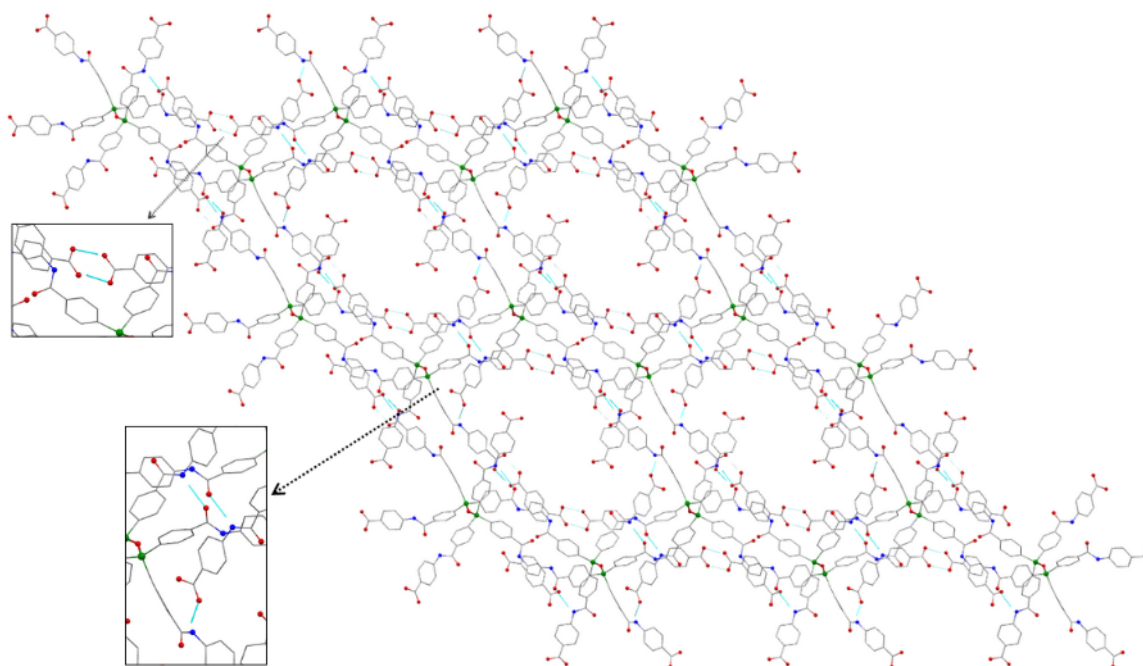


Figure 35: A portion of the packing structure of **L4-H₆** viewed along the *b* axis. H atoms and coordinated solvent molecules are removed for clarity. The three types of H-bonds in **L4-H₆** are shown in cyan.

3.5 Structure of L5-H₆

Extending the carboxyphenyl arms of **L2-H₆**, which is based on a central Si–C₆H₄–Si unit, with amide groups afforded **L5-H₆**. Single colourless blade-shaped crystals of **L5-H₆** were obtained by slow recrystallisation from methanol. **L5-H₆** crystallises in the triclinic space group *P*-1 (No. 2). The asymmetric unit contains two crystallographically distinct half-molecules of **L5-H₆**, each located on an inversion centre and belonging to a different **L5-H₆** molecule. Application of the inversion symmetry generates two complete crystallographically distinct **L5-H₆** molecules, **A** and **B** (Figure 36). The two tris(*p*-benzamidecarboxyphenyl)silyl groups adopt a staggered conformation relative to each other when viewed along the central Si–C₆H₄–Si axis. As a result, the six carboxylic acid groups are arranged in a *pseudo*-octahedral geometry, similar to that observed in **L1-H₆**, **L2-H₆**, and several other hexaphenyl disilicon-based compounds.^{184,207,372,373}

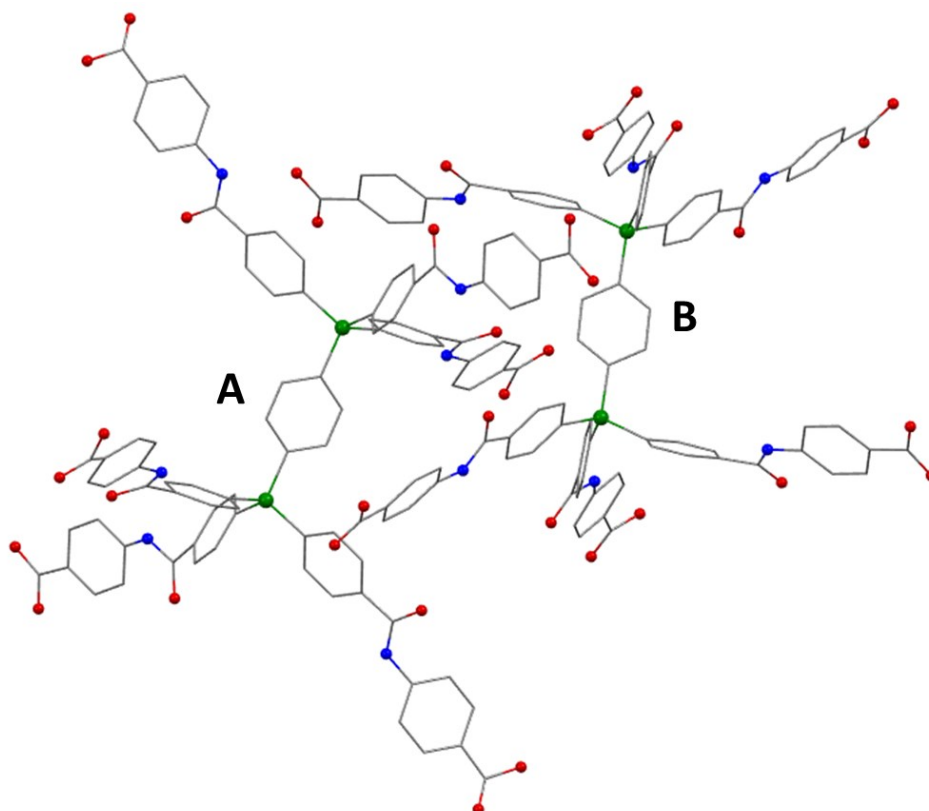


Figure 36: The two crystallographically distinct **L5-H₆** molecules, **A** and **B**.

In the crystal structure of **L5-H₆**, the two crystallographically distinct molecules, **A** and **B**, exhibit different hydrogen bonding interactions that together construct a 3D HOF. Out of the six carboxylic acid groups in molecule **A**, four are involved in intermolecular hydrogen bonding. Two of these form classical carboxylic acid dimers with COOH groups from two different neighbouring **A** molecules, exhibiting O $\cdots$ O distances of 2.69(2) Å and O–H $\cdots$ O angles of 167(9)°. The remaining two hydrogen-bonded COOH groups act as acceptors for NH groups of adjacent **B** molecules. The remaining two COOH groups do not participate in any observable hydrogen bonding. Among the six amide groups in molecule **A**, four engage in hydrogen bonding, all acting as donors. Each pair of donor amides forms two hydrogen bonds with two acceptor groups on the same neighbouring **B** molecule, with N $\cdots$ O distances ranging from 2.81(2) to 2.885(19) Å (mean 2.849 Å), and N–H $\cdots$ O angles ranging from 133.1(6)° to 165.1(5)° (mean 152.6°). The remaining two amide groups do not appear to participate in hydrogen bonding. In total, molecule **A** connects to six neighbouring **L5-H₆** molecules via hydrogen bonds, four through its COOH groups and two through its amide groups.

In contrast, only two COOH groups in molecule **B** are involved in hydrogen bonding. These act as acceptors, forming hydrogen bonds with amide NH donors from neighbouring **A** molecules. The remaining four COOH groups do not engage in any H-bonding. Four of the six amide groups in molecule **B** participate in hydrogen bonding: two act as donors to carboxylic acid carbonyls of adjacent **A** molecules, and two act as acceptors from other amide NH groups. Notably, in each case, the acceptor COOH and amide group on molecule **B** form hydrogen bonds with functional groups on the same neighbouring **A** molecule, forming a paired hydrogen bond interaction with a single neighbour. In total, each **B** molecule connects to four neighbouring **A** molecules via hydrogen bonding, two via its COOH groups (as acceptors) and two via its amide groups (as both donor and acceptor).

The self-assembly process from the two crystallographically distinct molecules to the 3D HOF involves the interaction between **A** and **B** molecules to form what can be best described as a discrete cage-like assembly, in which four **A** molecules hydrogen bond to a central **B** molecule. These cages interconnect to form an infinite supramolecular chain through dimeric COOH $\cdots$ COOH interactions between the antiparallel arms of adjacent **A** molecules (Figure 37). This hydrogen-bonded chain extends diagonally within the *bc* plane through dimeric hydrogen bonding, approximately along the [0 1 1] crystallographic direction. It is worth noting that **A** molecules are linked through dimeric hydrogen bonding, while **B** molecules do not form direct hydrogen bonds with each other.

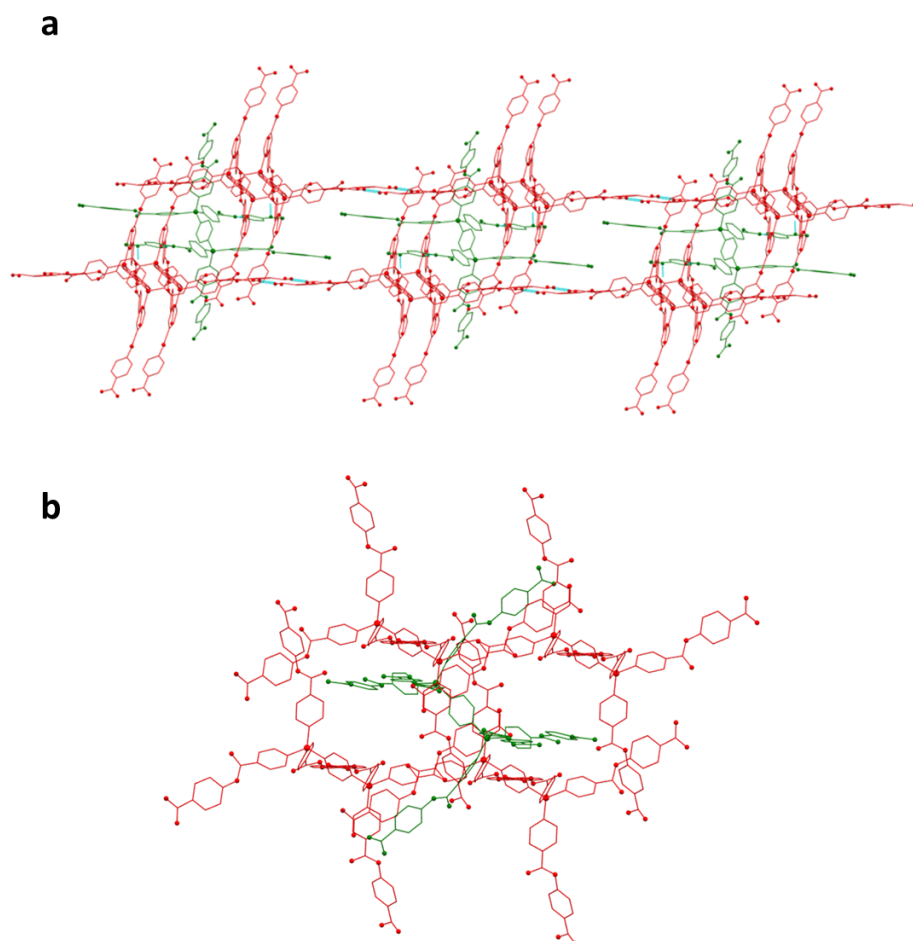


Figure 37: (a) Assembly of **L5-H₆** molecules into a hydrogen-bonded polymeric array; (b) view along the array axis. **A** molecules are shown in red, **B** in green, and hydrogen bonds are shown in cyan.

In addition to hydrogen bonding, π - π stacking interactions are observed between aromatic rings of **A** and **B** molecules within the chain. These interactions are characterised by a centroid-to-centroid distance of 3.776 Å, a lateral offset (slippage) of 1.538 Å, and an interplanar angle of 8.43°, which fall within the typical range for offset face-to-face π - π stacking interactions.³⁷⁴ Such interactions further stabilise the packing of the supramolecular chains and enhance the cohesion of the overall structure. Upon expansion of the packing, the hydrogen-bonded chains interconnect through the available COOH and amide groups of **A** molecules (via carboxyl–amide interactions) to form a densely packed 3D HOF (Figure 38). The structure exhibits solvent-accessible voids, which are estimated using Mercury to occupy 27% of the unit cell volume.³⁷¹

It is also worth noting that solvent masking analysis using PLATON/SQUEEZE revealed the presence of twelve disordered methanol molecules per **L5-H6** molecule,³⁷⁰ which were not modelled explicitly. This yields an overall sum formula of [**L5-H6**] $\cdot$ 12MeOH.

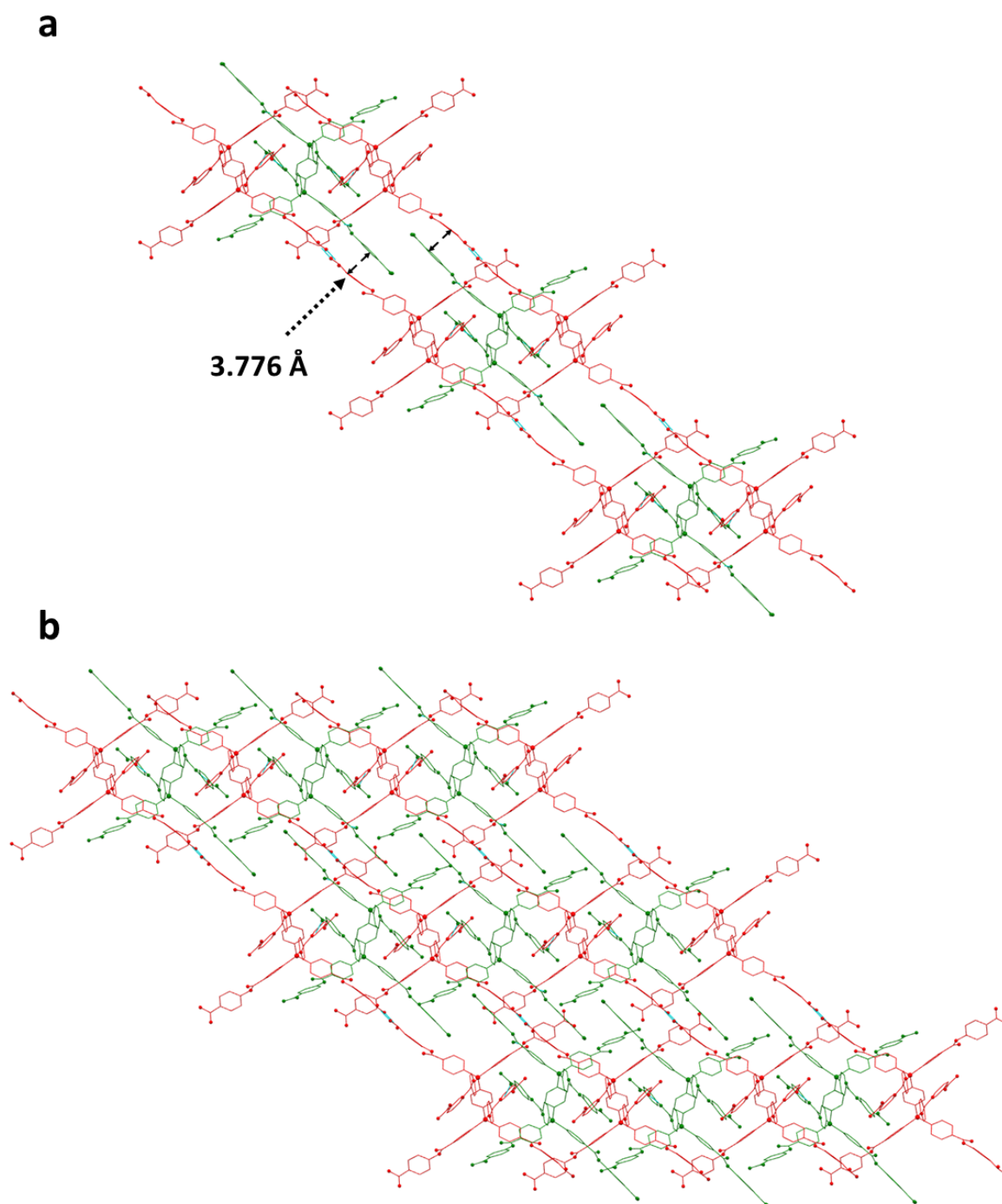


Figure 38: (a) Cross-section of a single hydrogen-bonded array of **L5-H6** molecules viewed along the *a* axis; (b) a portion of packing diagram of **L5-H6** viewed along the *a* axis. Hydrogen atoms are omitted for clarity. **A** molecules are shown in red, **B** in green; hydrogen bonds are shown in cyan, and π – π interactions in black.

3.6 Structure of **L6-H₆**

Single colourless plate-shaped crystals of **L6-H₆** were rapidly obtained by crystallisation from methanol. **L6-H₆** crystallises in the monoclinic space group $C2/c$ (No. 15), with the asymmetric unit containing half an **L6-H₆** molecule located on an inversion centre ($Z' = 0.5$). This indicates that only half of the formula unit is present in the asymmetric unit, while the other half is generated through crystallographic symmetry. Solvent masking analysis (SQUEEZE) indicated the presence of eighteen methanol molecules per formula unit,³⁷⁰ which were subsequently removed. Therefore, the resulting moiety formula is [**L6-H₆**] $\cdot 18\text{MeOH}$.

L6-H₆ adopts a trans-planar conformation of the $\text{Si}-\text{C}_2\text{H}_4-\text{Si}$ linkage, with a measured $\text{Si}-\text{C}-\text{C}-\text{Si}$ dihedral angle of 180° . The $\text{C}-\text{C}-\text{Si}$ bond angle is $117.2(4)^\circ$, slightly larger than the ideal tetrahedral angle of 109.5° . Such widening is commonly observed in $\text{Si}-\text{C}_2\text{H}_4-\text{Si}$ -based compounds with two trisubstituted silicon ends,^{277,375–377} likely due to steric repulsion between the bulky substituents on the silicon atoms, which is relieved by increasing the bond angle. Each silicon atom in **L6-H₆** is bonded to three *p*-benzamidicarboxyphenyl groups, forming two trisubstituted silicon ends. This results in a hexacarboxylic acid structure bearing six amide groups, capable of participating in hydrogen bonding through both the carboxyl and amide groups. In addition, the two tris(*p*-benzamidicarboxyphenyl)silyl groups adopt a staggered conformation relative to each other when viewed along the central $\text{Si}-\text{C}_2\text{H}_4-\text{Si}$ axis. Consequently, the carboxylic acid groups in **L6-H₆** are arranged in a *pseudo*-octahedral geometry, which is consistent with the conformation observed in **L1-H₆**, **L2-H₆**, and **L5-H₆**.

L6-H₆ molecules are connected through intermolecular hydrogen bonding involving both carboxylic acid and amide functional groups. In each **L6-H₆** molecule, four out of six carboxylic acid groups participate in hydrogen bonding, forming carboxylic acid dimers with four neighbouring **L6-H₆** molecules (Figure 39). The $\text{O}\cdots\text{O}$ distances range from $2.605(4)$ Å

to 2.674(5) Å, and the corresponding O–H···O angles fall between 158.3° and 163.0°. The remaining two carboxylic acid groups (top left and bottom right in Figure 39), do not appear to engage in hydrogen bonding.

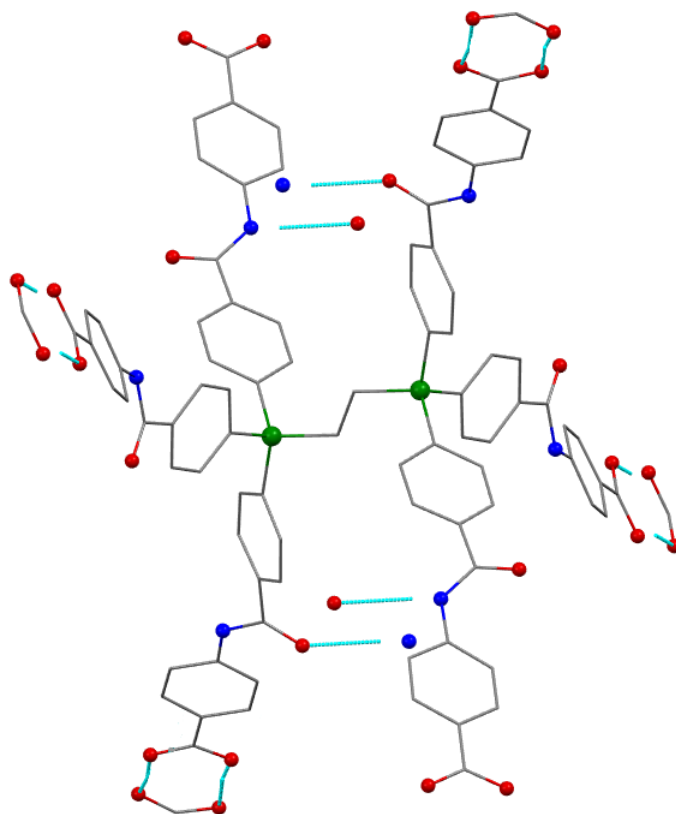


Figure 39: Crystal structure of a single **L6-H₆** molecule showing four COOH groups involved in dimeric H-bonding and four amide groups forming H-bonds with adjacent amide groups. H atoms are omitted for clarity. Colour scheme: Si (green), O (red), C (grey), N (blue). H-bonds are represented by cyan lines.

Additionally, four of the six amide groups per **L6-H₆** molecule are involved in intermolecular hydrogen bonding. Two act as hydrogen bond donors to the amide carbonyl groups of one neighbouring **L6-H₆** molecule, while the other two function as acceptors from amide NH groups of a second neighbouring **L6-H₆** molecule. These interactions exhibit N···O distances of 3.044(6) Å and an N–H···O angle of 167.0°. The remaining two amide groups (right and left arms, Figure 39) do not participate in hydrogen bonding. As a result, each **L6-H₆** molecule

is connected to six neighbouring **L6-H₆** molecules through hydrogen bonds involving both carboxylic acid and amide groups (Figure 40).

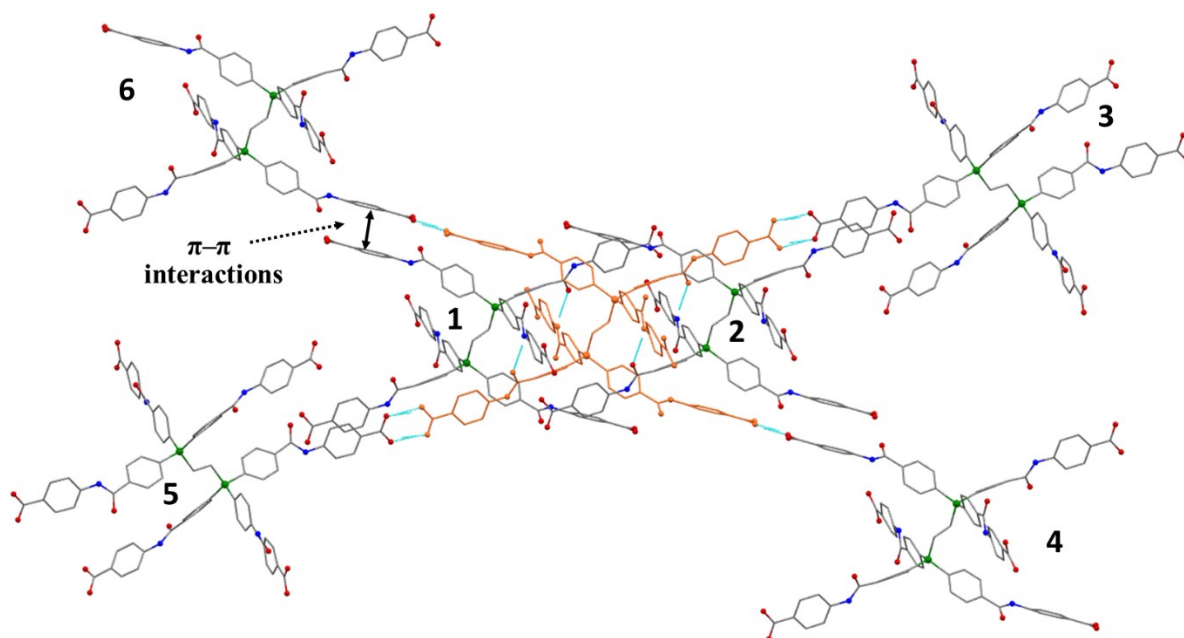


Figure 40: Connectivity of a single **L6-H₆** molecule (shown in orange) to six neighbouring **L6-H₆** molecules (labelled 1–6) via intermolecular hydrogen bonds. π – π interactions are also present between adjacent aromatic rings.

Hydrogen bonding involving the amide groups alone drives an infinite extension of **L6-H₆** molecules along the crystallographic *a* axis. This forms a continuous hydrogen bonds array in which the hexa-acid molecules adopt a parallel, back-to-face arrangement (Figure 41). Each **L6-H₆** molecule is aligned such that its Si–C₂H₄–Si plane is parallel to those of its neighbours, with a consistent interplanar spacing of 6.379 Å.

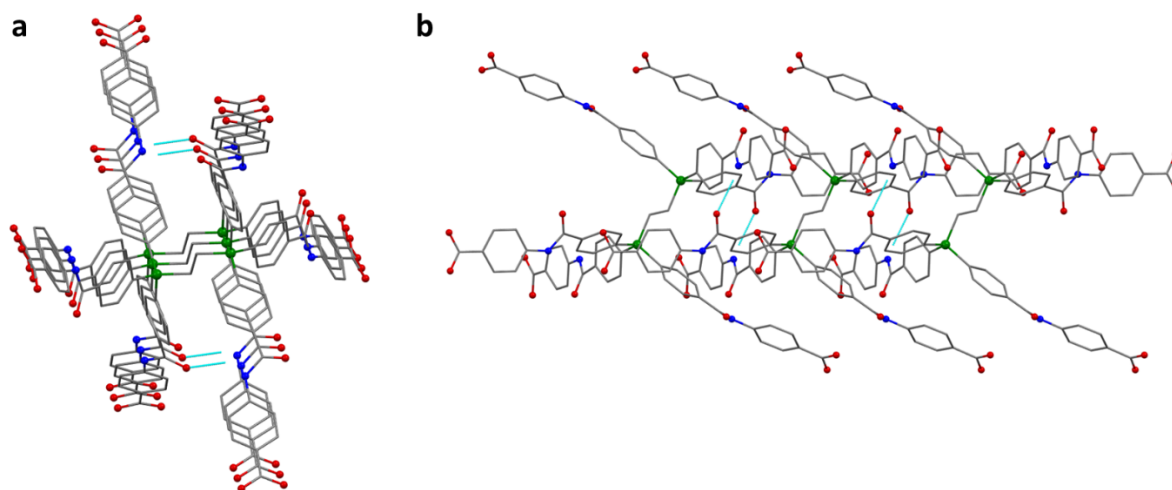


Figure 41: Cross-section of the back-to-face hydrogen-bonded array formed by extending **L6-H6** via its amide groups only: (a) viewed along the *a* axis (which is also along the hydrogen-bonded array); (b) viewed along the *c* axis.

Adjacent arrays interconnect via dimeric hydrogen bonding involving the four available carboxylic acid groups of each **L6-H6** molecule, resulting in a 3D HOF stabilised by both amide- and carboxyl-derived hydrogen bonding (Figure 42a). Additional stabilisation arises from π - π interactions observed between adjacent aromatic rings of the *p*-benzamidocarboxyphenyl groups, characterised by a centroid-to-centroid distance of 3.794 Å, indicative of significant face-to-face stacking within the crystal structure. Rectangular solvent-accessible channels (14 x 10 Å²) are observed in the structure running along the *a* axis. Void volume calculations performed using Mercury revealed a solvent-accessible volume of approximately 4153 Å³ per unit cell,³⁷¹ corresponding to 37% of the unit cell volume. This significant porosity highlights the potential of the framework for guest uptake and adsorption-related applications. Topologically, the framework can best be described as a **pcu** net when each **L6-H6** molecule is simplified to a 6-connected node centred on the Si-C₂H₄-Si linkage, as shown in Figure 42b.

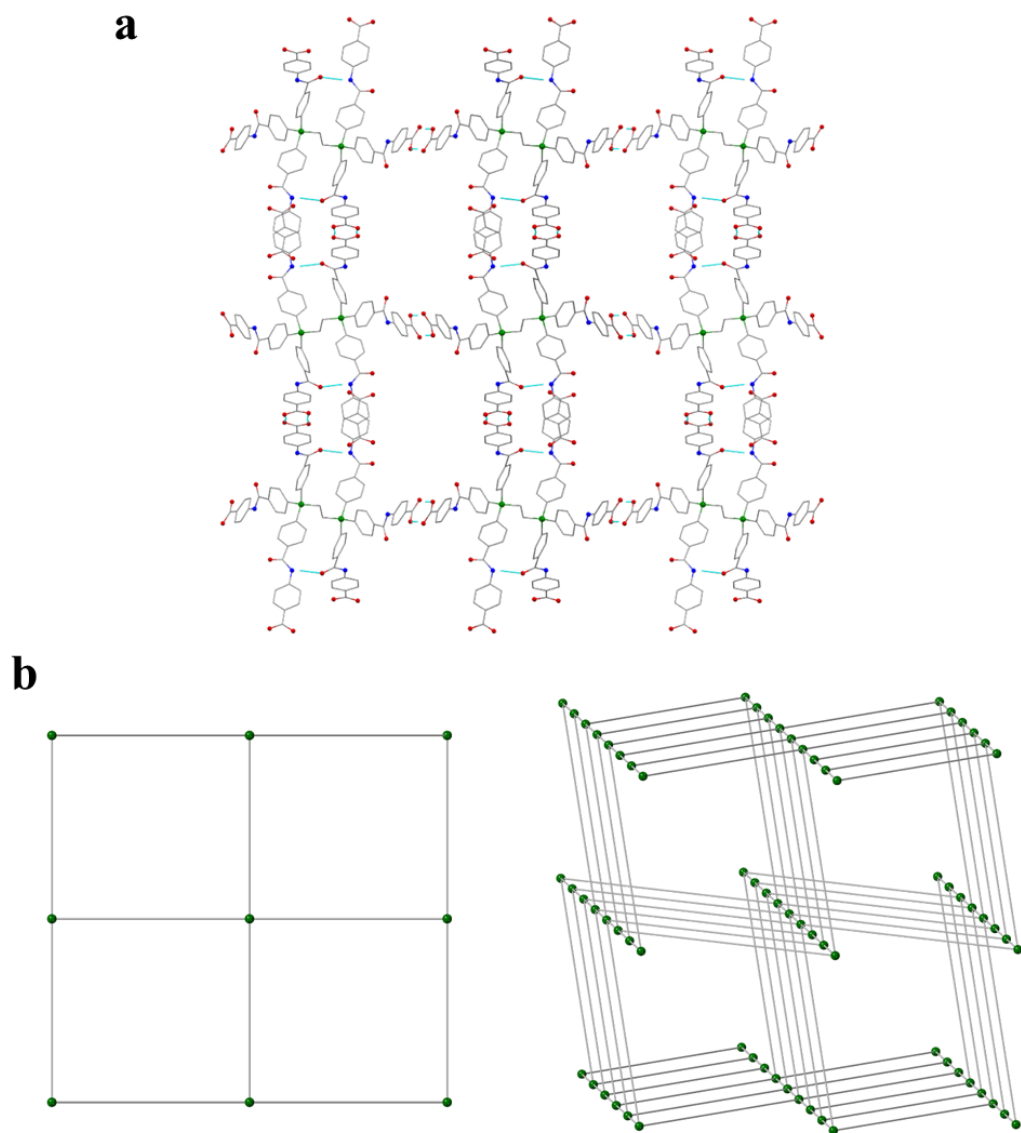


Figure 42: (a) A portion of packing diagram of **L6-H₆** viewed along the *a* axis; (b) the corresponding topological representation of the **pcu** net along *a* axis, showing the 6-connected **L6-H₆** nodes in green.

3.7 Structure of (L10-H₆)₂·AcOH

L10-H₆ was synthesised by formally extending a Si–O–Si disiloxane core with two additional [–O–Si–] units, forming a tetrasiloxane backbone. Slow evaporation from a methanol/acetic acid mixture yielded single colourless plate-shaped crystals suitable for structural analysis. SCXRD revealed that **L10-H₆** crystallises in the triclinic space group *P*-1 (No. 2), with two crystallographically independent **L10-H₆** molecules (**A** and **B**) present in the asymmetric unit, along with one resolved acetic acid molecule (Figure 43). Notably, solvent mask analysis indicated the presence of an additional six acetic acid and three methanol molecules per unit cell, which were not modelled crystallographically.

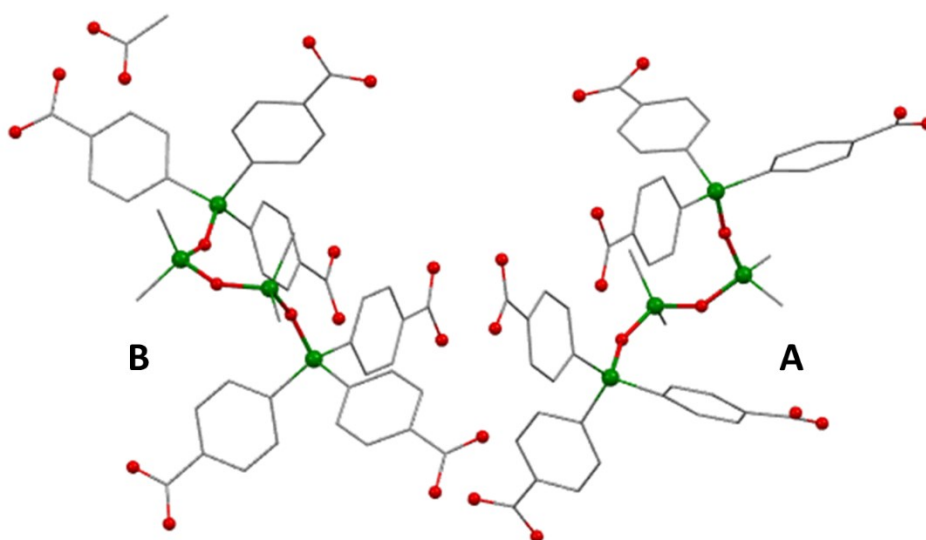


Figure 43: The asymmetric unit of **L10-H₆**, showing two distinct **L10-H₆** molecules (**A** and **B**) and one acetic acid molecule.

Each **L10-H₆** molecule contains six carboxyphenyl arms arranged around the tetrasiloxane core in a distorted trigonal prismatic geometry. The central dimethylsilyl units within the core adopt a tetrahedral geometry, while the overall tetrasiloxane backbone exhibits a non-linear, twisted conformation. This non-linearity and twisted conformation were also observed in the trisiloxane-based linker (**33**) described in Section 3.3.²⁰⁸ It is worth noting that a planar

tetrasiloxane backbone was previously observed in a hexaphenyl tetramethyltetrasiloxane compound reported by Pannel and co-workers, featuring a dihedral angle of 180.00° .³⁰⁹ Cyclic tetrasiloxane cores have also been reported in the literature.^{236,378,379}

The dihedral angles between the four silicon atoms in molecules **A** and **B** are 71.35° and 91.79° , respectively. Each Si–O–Si linkage exhibits a bent geometry, with angles ranging from $141.25(19)^\circ$ to $168.12(18)^\circ$, and an average angle of 149.95° , in agreement with the values commonly observed in siloxane compounds.³⁶⁸ The bent Si–O–Si angles and the dihedral angles between silicon atoms suggest conformational flexibility of the tetrasiloxane backbone in **L10-H6**. Compared to **L1-H6** and **L4-H6**, the Si–O–Si linkages in **L10-H6** display greater angular flexibility due to reduced steric crowding around each Si–O–Si unit, which in turn influences how the compound assembles in the solid state, as it allows adjustment of the carboxylic acid group orientations, thereby optimising dimeric hydrogen bonding with neighbouring molecules to generate an extended structure.

Each terminal silicon atom is bonded to three carboxyphenyl moieties, resulting in a total of six hydrogen bond donor/acceptor sites per molecule. All six COOH groups participate in dimeric hydrogen bonding interactions. The observed O $\cdots$ O distances range from $2.559(3)$ to $2.694(3)$ Å, with O–H $\cdots$ O angles from 162.1° to 174.0° , consistent with strong hydrogen bonding commonly found in carboxylic acid-based HOFs. Each **A** molecule forms dimers with six COOH groups of adjacent **L10-H6** molecules (Figure 44a), including two rare quadruple hydrogen bonding motifs arising from the unusual parallel arrangement of some of the carboxylic acid groups in each **L10-H6** molecule. Each motif involves two COOH groups from molecule **A** and two from a neighbouring **L10-H6** molecule. On the other hand, molecule **B** forms dimers involving six COOH groups, connecting to four adjacent **L10-H6** molecules and one acetic acid molecule (Figure 44b). In addition, only one quadruple hydrogen bonding motif

is observed for **B**. However, the hydrogen bonding is limited to the *bc* plane and does not extend in three dimensions, preventing the formation of a 3D HOF (*vide infra*).

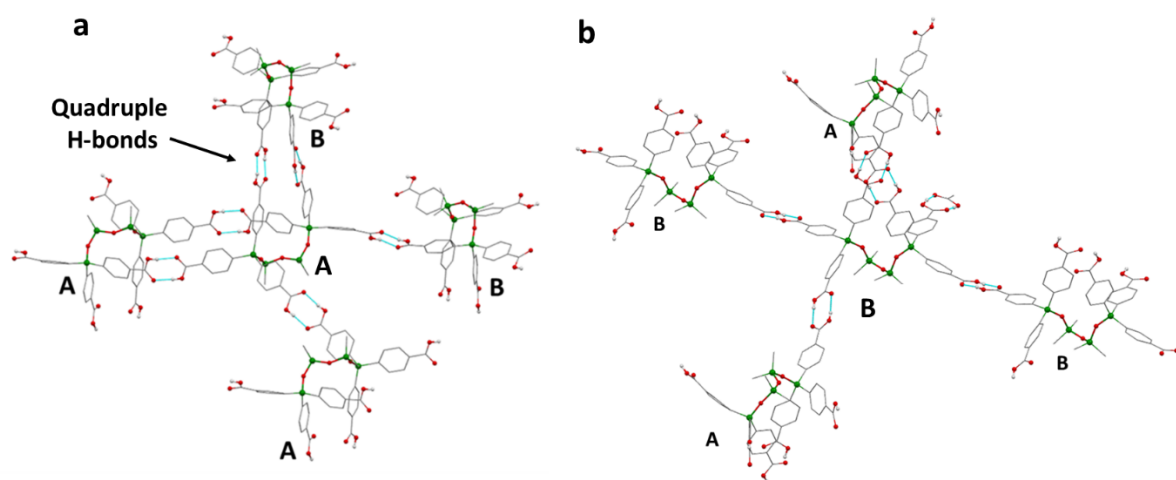


Figure 44: (a) Dimeric H-bonding between a central **A** molecule and adjacent ligand molecules; (b) H-bonding between a central **B** molecule and its neighbouring molecules, including one acetic acid molecule. Colour scheme: Si, green; O, red; and C, grey. Carboxylic acid hydrogens are shown in off-white; all other hydrogen atoms are omitted for clarity. H-bonds are shown in cyan lines.

A molecules are linked via intermolecular dimeric hydrogen bonding to form 1D polymeric chains (Figure 45a), while **B** molecules self-assemble into 1D hydrogen-bonded chains composed of oval units (Figure 45b). These units are stabilised by quadruple H-bonds. Both chains run along the *b* axis and are further interconnected by additional hydrogen bonds, resulting in a 2D structure held entirely by dimeric hydrogen bonds (Figure 46). However, the formation of a 3D framework is inhibited by the presence of acetic acid molecules, which cap the remaining uncoordinated carboxylic acid groups (Figure 46a). This capping prevents further extension along the *c* axis, thereby restricting the structure to two dimensions. To the best of our knowledge, **L10-H₆** represents the first example of a tetrasiloxane-based carboxylic acid HOF. Solvent-accessible voids are visible along the *a* axis and their volume was calculated using the Pore Analyser in Mercury to occupy approximately 15% of the unit cell volume (19%

after theoretical removal of acetic acid). In comparison with the 2D trisiloxane-based HOF reported by Davies and co-workers (**22**),²⁰⁸ which is non-porous, extension of the trisiloxane linkage by an additional –Si–O– unit resulted in a 2D HOF with potential porosity.

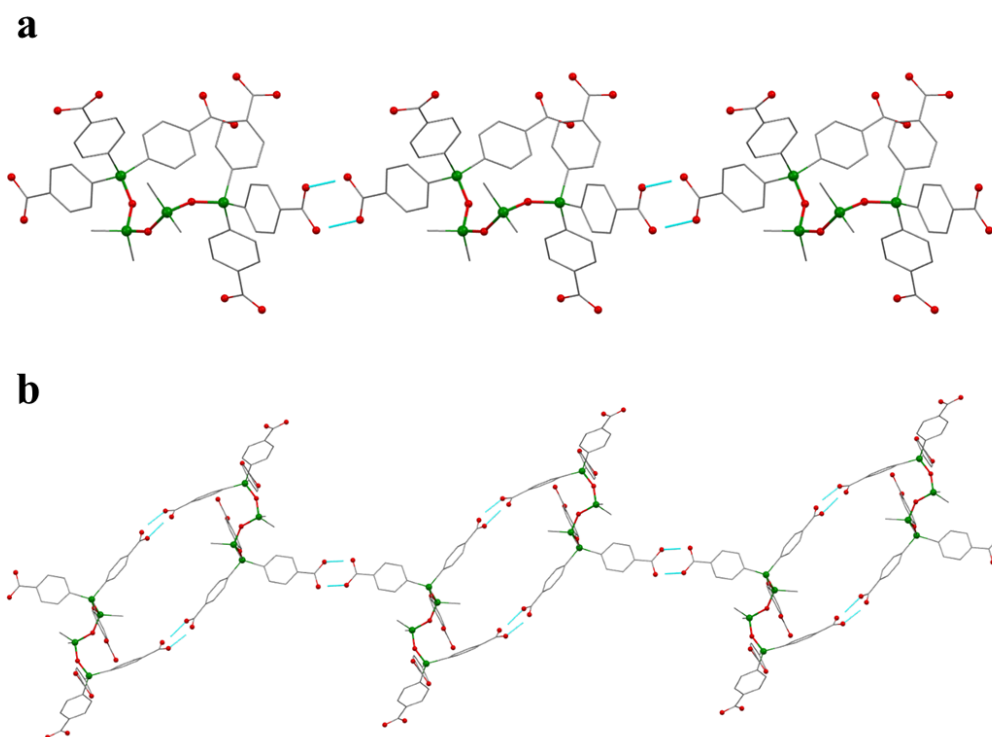


Figure 45: (a) Organization of **A** molecules into 1D supramolecular polymeric chains; (b) 1D polymeric chain of oval units assembled from **B** molecules.

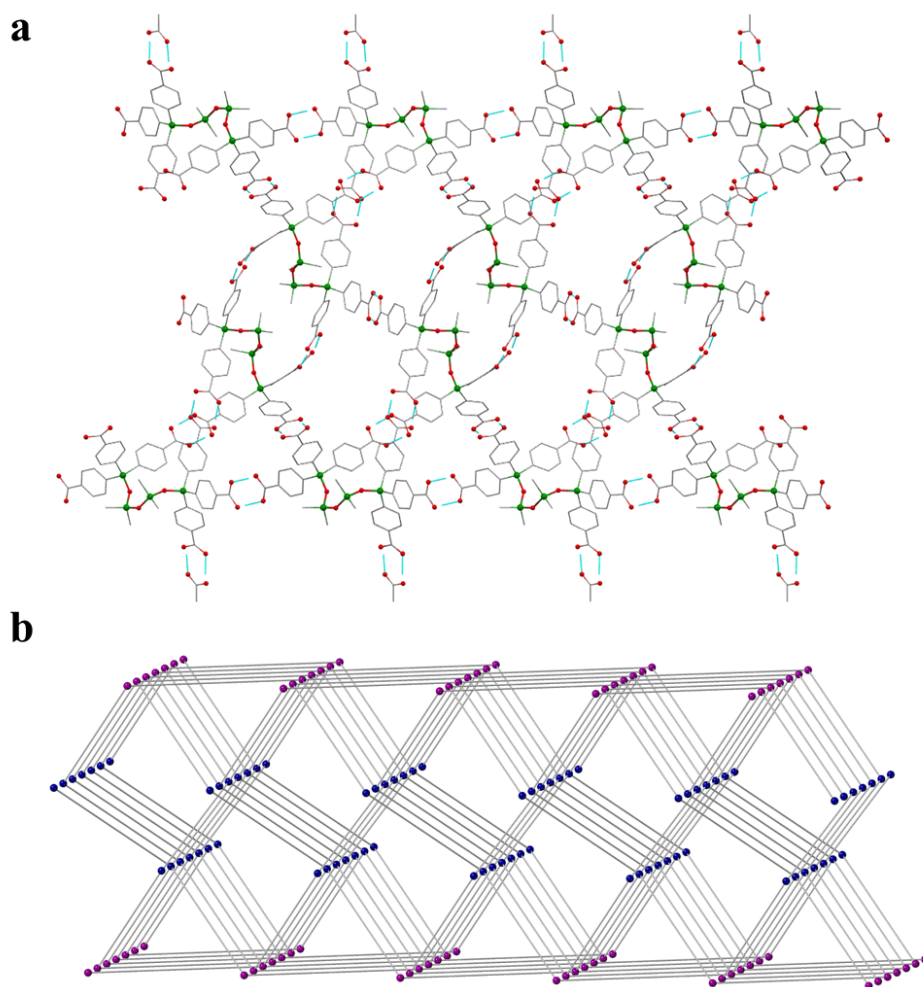


Figure 46: (a) A portion of the packing diagram of **L10-H₆** viewed along the *a* axis, showing acetic acid molecules positioned at the top and bottom ends, which prevent further extension along the *c* axis; (b) topological representation of the framework, where **L10-H₆** molecules are simplified to 4-connected nodes. **A** nodes are shown in purple, and **B** nodes in blue.

3.8 Conclusion

The potential of the organosilicon hexacarboxylic acids prepared in this thesis to form HOFs was investigated in this chapter. All compounds were recrystallised under mild conditions using methanol or mixtures of methanol and acetic acid. The amide-functionalised acids **L4-H₆** to **L6-H₆** assembled into 3D HOFs linked by hydrogen bonding from both carboxyl and amide groups. The tetrasiloxane acid **L10-H₆** crystallised as a 2D HOF held together solely by dimeric hydrogen bonds. This HOF represent the first example of a tetrasiloxane-based carboxylic acid HOF. All HOFs described in this chapter exhibit carboxylic acid dimeric hydrogen bonding, while additional stabilisation in **L5-H₆** and **L6-H₆** arose from face-to-face π - π interactions between aryl groups. In the case of **L10-H₆**, the presence of coordinated acetic acid molecules prevented extension into a 3D HOF. This highlights the importance of exploring recrystallisation solvents other than acetic acid as a promising direction for future work. All HOFs described in this chapter are novel, represent a significant expansion of the organosilicon hexacarboxylic acid family, and exhibit potential porosity. In particular, **L4-H₆** and **L6-H₆** warrant further investigation for adsorption studies, as their promising porosity may prove advantageous for gas storage and separation applications. Moreover, the unusual arrangement of the carboxylic acid groups observed across all described structures may present unique opportunities in MOF synthesis, enabling the design of frameworks with novel topologies.

Chapter 4: The use of **L1-H₆** and **L4-H₆** in 3D MOF Synthesis

The focus of research in this thesis is on highly branched organosilicon carboxylic acids. Linkers derived from these compounds possess distinctive properties that facilitate the construction of 3D frameworks.^{154,156,163,184,194,207–209,241,242} As mentioned in Chapter 1, MOFs constructed from such linkers exhibit several desirable characteristics, including enhanced framework stability and access to a broad range of topologies. In addition, compounds featuring siloxane linkages are known for their enhanced flexibility, low toxicity, and excellent thermal stability.^{194,305} Incorporating siloxane units or siloxane-based linkers into MOFs can also improve hydrophobicity.^{184,193,194,306,307,380–383} Despite these advantages, 3D MOFs prepared using siloxane-based linkers, particularly hexadentate ones, remains relatively rare.^{209,244}

Earlier in this thesis, we discussed the synthesis of the siloxane-based hexacarboxylic acid **L1-H₆** and its structure.¹⁸⁴ Most of the reported MOFs constructed using this compound display a rare and highly desirable *pseudo*-octahedral arrangement of carboxylate groups.^{184,209} Additionally, the application of **L1-H₆** in MOF synthesis led to the formation of several novel 3D frameworks with diverse topologies,²⁰⁹ including uncommon ones such as **nia**, **fsy**, and **fsh**. Motivated by the above, we further investigated the use of the **L1-H₆** for constructing 3D MOFs by treating it with various metal salts under solvothermal conditions. As a result, eleven new 3D MOFs were synthesized successfully. Among them was an In-based MOF (**L1-In**), which had previously been prepared by a former PhD student in our group.³⁸⁴ Four of the novel MOFs synthesized in this study were found to be isostructural with **L1-In**; therefore, the crystal structure of the In-based MOF will be discussed in this chapter. As described in Chapter 2, linker elongation of **L1-H₆** was achieved by introducing an amide linkage into each of the six arms, producing **L4-H₆**. This amide-extended linker was also investigated for 3D MOF synthesis, and afforded **L4-In**. The crystal structures, topologies, thermal and water stability,

as well as gas adsorption properties, for many of the synthesised MOFs have been investigated and are presented in this chapter.

4.1 Isostructural Series of Trivalent Metal MOFs Built from **L1**

Indium-based MOFs have recently attracted significant research interest owing to their versatile coordination modes, and fascinating topological architectures.³⁸⁵ **L1-In** was re-synthesised in this study following the synthetic protocol adapted from Delmas.³⁸⁴ **L1-H₆** was treated with $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in a 1:1 mixture of DMF and MeCN with concentrated HNO_3 at 80 °C in a screw-cap vial for 42 h, yielding colourless tear-shaped crystals of **L1-In**. The crystal structure of **L1-In** was determined by SCXRD and identified as $[\text{In}_3(\mu_3\text{-O})(\text{L1})(\text{H}_2\text{O})_3] \cdot \text{NO}_3 \cdot 5\text{DMF}$. This MOF crystallises in the trigonal space group $P\bar{3}1c$ (No. 163), with the asymmetric unit consisting of three indium(III) ions bridged by a central oxide anion and coordinated to a fully deprotonated **L1** hexacarboxylate linker with staggered aryl groups (along the Si–O–Si axis). Notably, the Si–O–Si linkage in **L1-In** adopts a bent geometry with an angle of 152.1(16)°, which is unusual compared to other reported MOFs incorporating **L1** in which the siloxane unit is either linear or close to linear.^{184,209}

The **L1-In** framework is cationic, with the positive charge presumably balanced by non-coordinating nitrate ions residing within the pores.³⁸⁴ The presence of nitrate ions in the pores has also been observed in other reported In-based MOFs constructed from tetracarboxylate ligands.^{386,387} As shown in Figure 47, **L1-In** forms a porous 3D MOF comprising In_3O clusters crosslinked by **L1**. The three indium atoms in each In_3O cluster are linked by a central μ_3 -bridging oxide anion and six bridging di-monodentate ($\mu_2\text{-}\eta^1\text{:}\eta^1$) carboxylate groups from different **L1** ligands, with In–O bond lengths ranging from 1.94 to 2.39 Å, and an average of 2.17 Å. In addition, each indium ion has four equatorial coordination sites occupied by

carboxylate oxygen atoms and two axial sites, one coordinated to a water molecule and the other to the central μ_3 -oxide anion.

Topological analysis on **L1-In** was performed by simplifying the **L1** hexa-anion to an octahedral 6-connected point node centred on the central oxygen of the disiloxane linkage, while the indium-based SBU was reduced to a 6-connected node with trigonal prismatic geometry. Together, these nodes form a rare **nia** network, as shown in Figure 47d. It is worth noting that Zhu and co-workers have reported a cationic MOF (JUC-101) with the same **nia** topology, constructed from a phenylene-based octahedral linker and the same In_3O cluster present in **L1-In**.³⁸⁸ Additionally, as mentioned in Chapter 1, a Cd-based MOF (IMP-28) with the same topology was reported by Davies and co-workers, which was also constructed using **L1**.²⁰⁹ Although **L1-In** and IMP-28 are not crystallographically isostructural, they share the same underlying net connectivity. Notably, **L1-In** exhibits a significantly greater distortion from ideal octahedral geometry compared to the Cd-based cluster in IMP-28, which features a linear Si–O–Si linkage. Furthermore, examples of **nia**-topology MOFs constructed from octahedral linkers and trigonal prismatic SBUs remain rare in the literature.^{209,388–391}

The **L1-In** framework exhibits solvent-accessible channels, with the largest window size measuring approximately $5 \times 5 \text{ \AA}^2$ along the *b* axis. PLATON estimated the solvent-accessible void volume in **L1-In** to occupy 46% of the unit cell volume, upon theoretical removal of solvent molecules.³⁸⁴

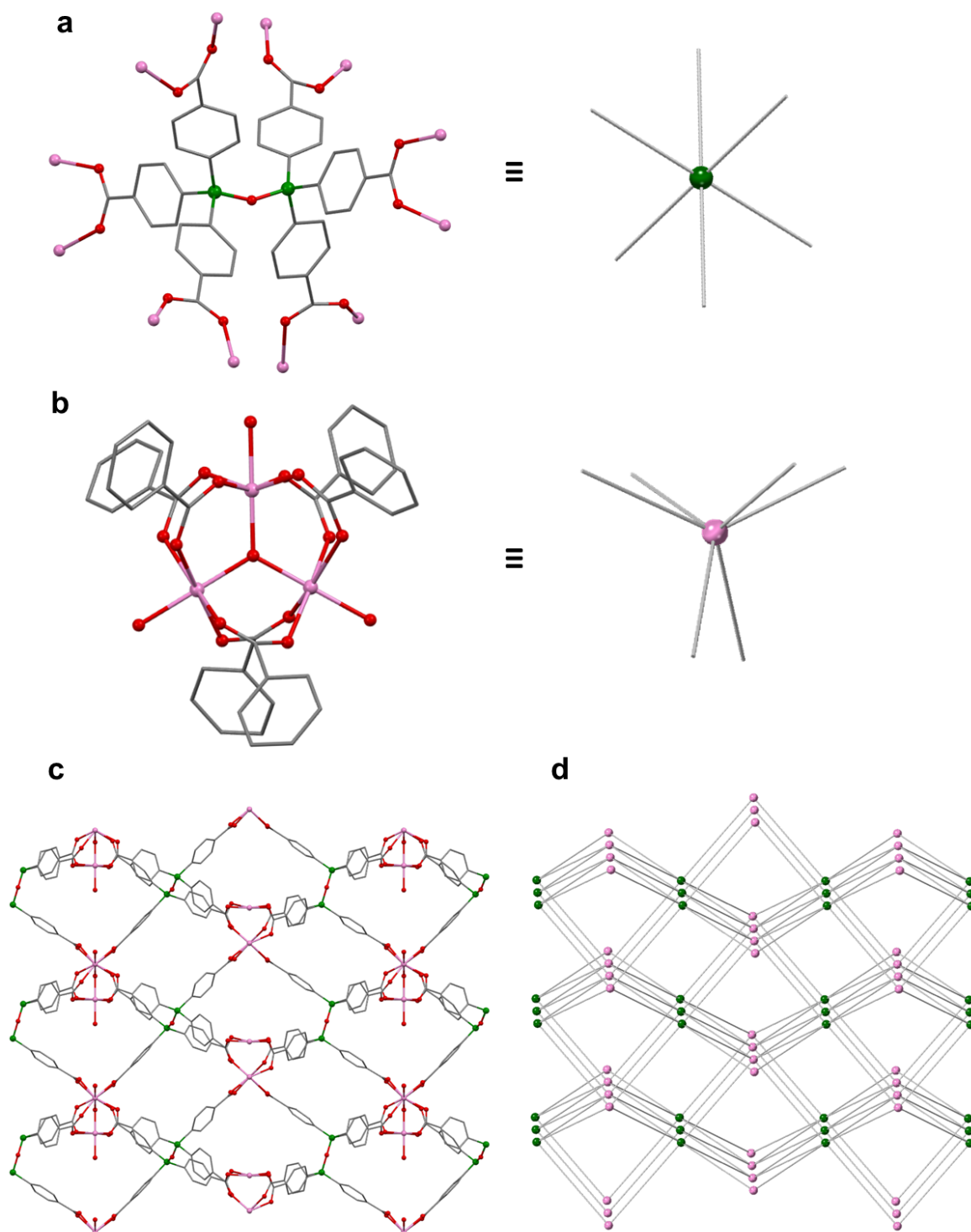


Figure 47: Crystal structure of **L1-In**: (a) coordination environment of **L1** in **L1-In**; (b) the In_3O -based cluster in **L1-In**; (c) a portion of the packing structure of **L1-In** viewed along the *b* axis; (d) a topological illustration of the **nia** net, showing the 6-connected In-based SBU nodes in pink, and the 6-connected Si-based nodes in green. Colour scheme: Si, green; O, red; C, grey; In, pink; H, pale pink. All H atoms have been omitted for clarity. Figure redrawn using the unpublished SCXRD data reported by Delmas.³⁸⁴

Following the synthesis of **L1-In**, **L1-H6** was treated with $\text{Ga}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ using the same solvent system and acid modulator under identical reaction conditions, yielding powder products of **L1-Ga**, **L1-Al**, and **L1-Fe**, respectively. In addition, because nitrate anions are assumed within the pores of the **L1-In** framework, thereby potentially limiting surface area and pore volume, the incorporation of a smaller counterion (in terms of ionic radii), Cl^- , was considered to assess whether this might result in increased accessible porosity. Accordingly, **L1-H6** was also treated with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ under the same reaction conditions, but using 1M HCl as the modulator, producing an orange-brown powder (**L1-Fe-Cl**).

The measured PXRD patterns of **L1-M** ($\text{M} = \text{In}^{3+}$, Fe^{3+} , Ga^{3+} , and Al^{3+}) and **L1-Fe-Cl** exhibit good agreement with the simulated (calculated) pattern of **L1-In**, (Figure 48), confirming the purity of the bulk samples and that all of these MOFs are isostructural. While the **L1**-based MOFs reported by Davies and co-workers exhibited decomposition and complete loss of porosity upon isolation and air drying,²⁰⁹ the trivalent metal MOFs described in this section remained stable under similar conditions. This observation motivated further investigations into their stability and gas adsorption properties. Thermogravimetric analysis under a nitrogen atmosphere showed gradual solvent loss followed by decomposition beginning at approximately 350 °C for **L1-Ga** (Figure S6). In contrast, the other MOFs in the series showed higher thermal stability, with decomposition onsets around 380 °C for **L1-In**, **L1-Fe** and **L1-Fe-Cl**, and ~450 °C for **L1-Al**,

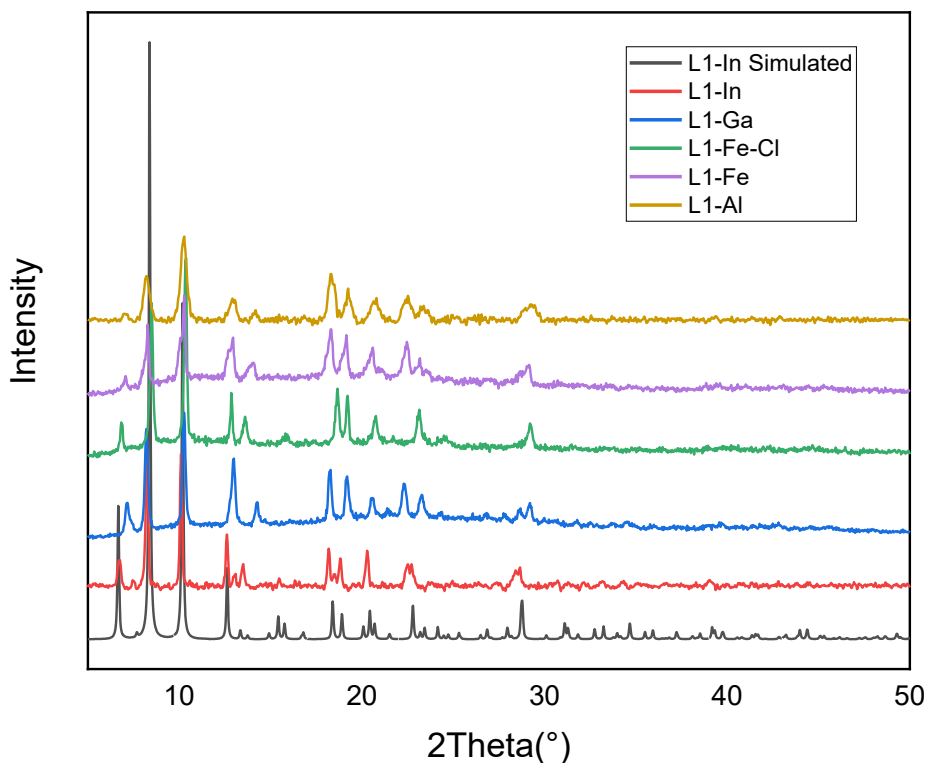


Figure 48: PXRD results of **L1-M** (**M** = In^{3+} , Fe^{3+} , Ga^{3+} , and Al^{3+}) and **L1-Fe-Cl**. The simulated pattern of **L1-In** was calculated using Mercury from the SCXRD data reported by Delmas.^{371,384}

An activated sample of each MOF was prepared for N_2 sorption analysis by washing and soaking in MeCN for 24 h, followed by drying at 40 °C under dynamic vacuum overnight. The samples were then degassed *ex situ* at 100 °C for 12 h, followed by *in situ* degassing at 120 °C for 4 h. Nitrogen sorption studies at 77 K revealed reversible Type I adsorption isotherms for **L1-In**, **L1-Ga**, **L1-Fe**, and **L1-Fe-Cl**, indicative of microporosity (Figure 49). In contrast, **L1-Al** exhibits a hybrid isotherm (Type I/IV) with a sharp uptake at low relative pressures ($p/p_0 < 0.05$) due to micropore filling, typical of a Type I isotherm, followed by a gradual increase at higher relative pressures with a hysteresis loop, characteristic of a Type IV isotherm and suggesting the presence of mesopores within the sample.³⁹² The BET surface areas were

calculated and are listed in Table 1, with **L1-Al** exhibiting the highest value among the series. Additionally, the incorporation of Cl^- anions in **L1-Fe-Cl**, rather than NO_3^- , resulted in a higher surface area, as predicted. Moreover, the CO_2 adsorption performance of **L1-Al**, **L1-Fe-Cl**, and **L1-Fe** was evaluated at 298 K across a pressure range of 0–1 bar. All four materials showed reversible Type I isotherms (Figure 50), with CO_2 uptake capacities of 8.67, 7.01, and 5.04 wt% at 1 bar, respectively.

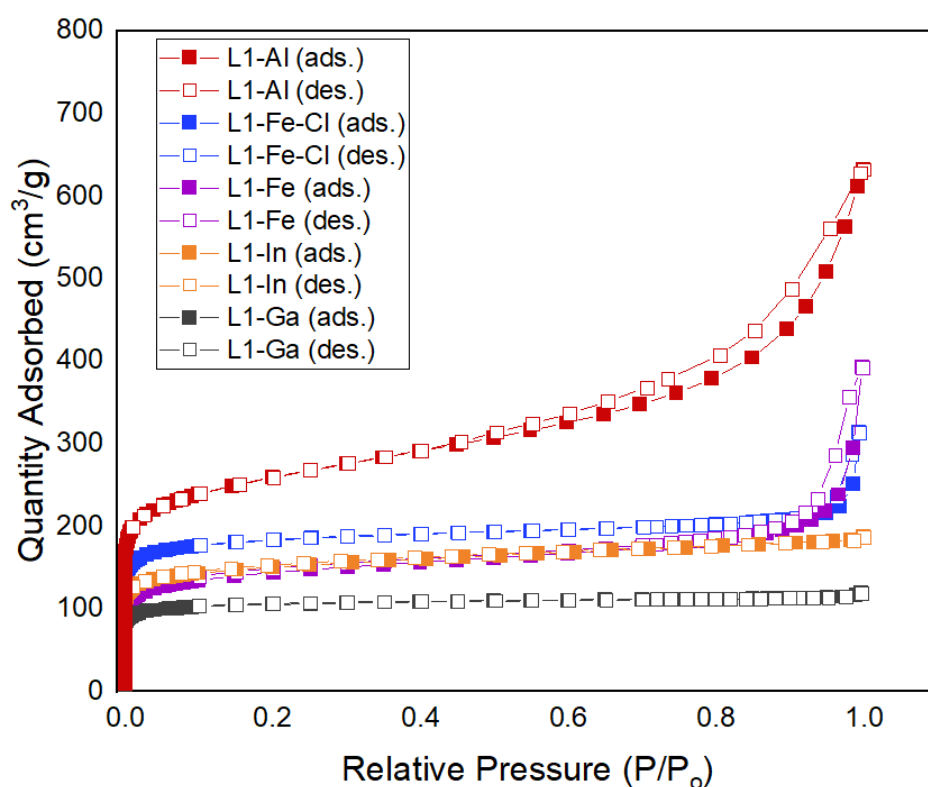
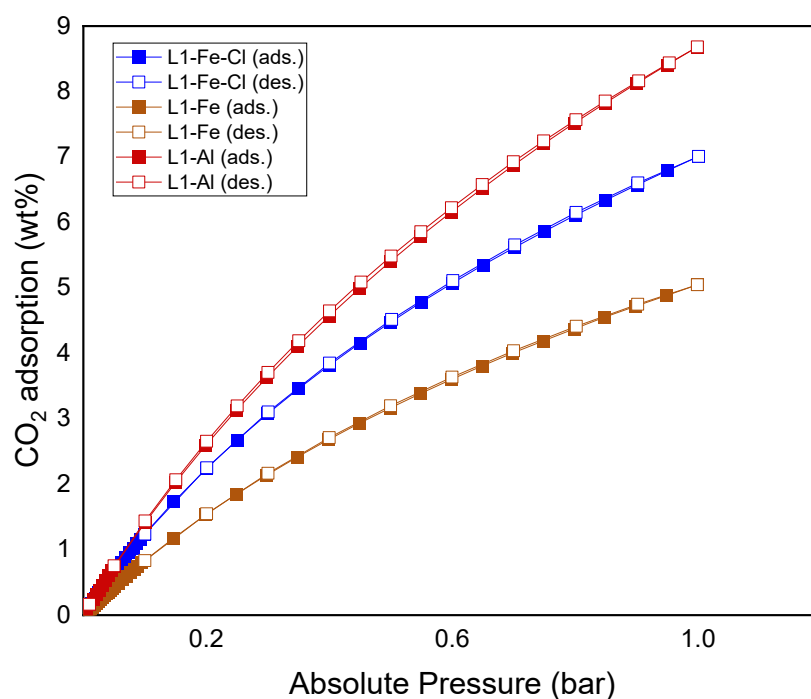


Figure 49: N_2 adsorption isotherms (77 K) for an activated sample of **L1-In**,³⁸⁴ **L1-Ga**, **L1-Al**, **L1-Fe**, and **L1-Fe-Cl**.

Table 1: Calculated BET surface areas of the prepared MOFs.

MOF	BET surface area (m ² /g)
L1-Al	935
L1-Fe-Cl	670
L1-Fe	566
L1-In	570
L1-Ga	382

**Figure 50:** CO₂ sorption isotherms (298 K) for activated samples of **L1-Al**, **L1-Fe-Cl**, and **L1-Fe**.

The water stability of the MOF series was evaluated by soaking the samples in deionised water at room temperature for 24 h. PXRD analysis showed that **L1-In**, **L1-Ga**, and **L1-Al** lost their crystallinity under these conditions (Figure S2), indicating degradation in water. In contrast,

both Fe-based MOFs maintained their crystallinity even after 144 h in water (Figures 51 and 52). They also remained crystalline after soaking in water at 60 °C for 24 h and across a wide pH range (pH 0.3–12). These results indicate that both Fe-based MOFs exhibit excellent hydrolytic stability and could be promising candidates for applications requiring stability in aqueous environments, such as the removal of phosphate ions and per- and polyfluoroalkyl substances (PFAS) from contaminated water, and this will be described in Chapter 5.

Notably, according to the April 2025 update of the Cambridge Structural Database, there are no previously reported siloxane-based MOFs incorporating In, Ga, Al, or Fe. Therefore, this series represents a valuable contribution to the limited number of known siloxane-based MOFs. In addition, while the majority of reported MOFs are not stable in water,^{306,393} **L1-Fe**, and **L1-Fe-Cl** mark important additions to the family of water-stable MOFs.

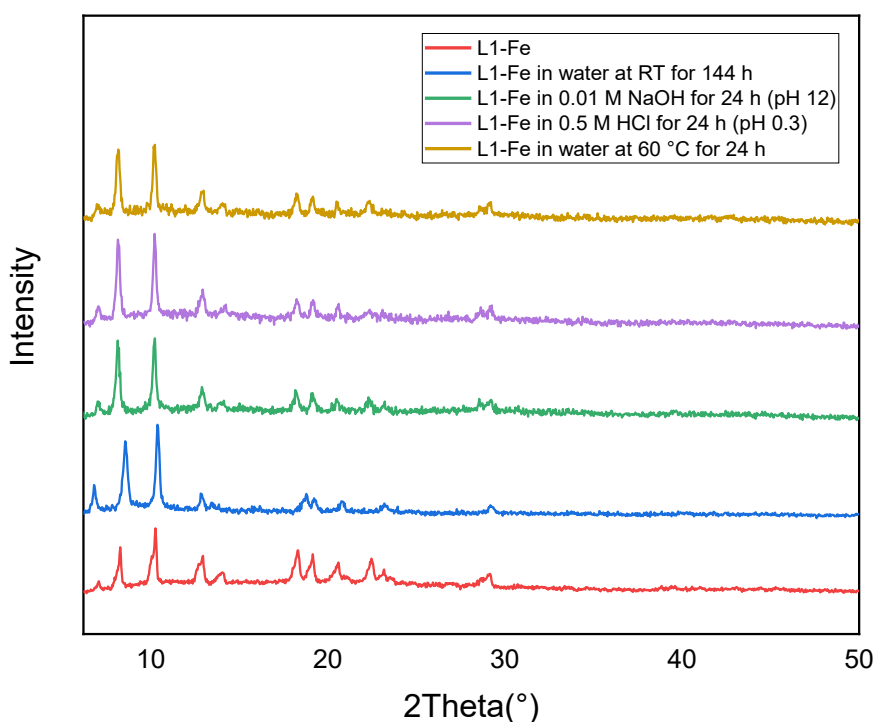


Figure 51: PXRD patterns of **L1-Fe** measured under neutral, acidic, and basic conditions.

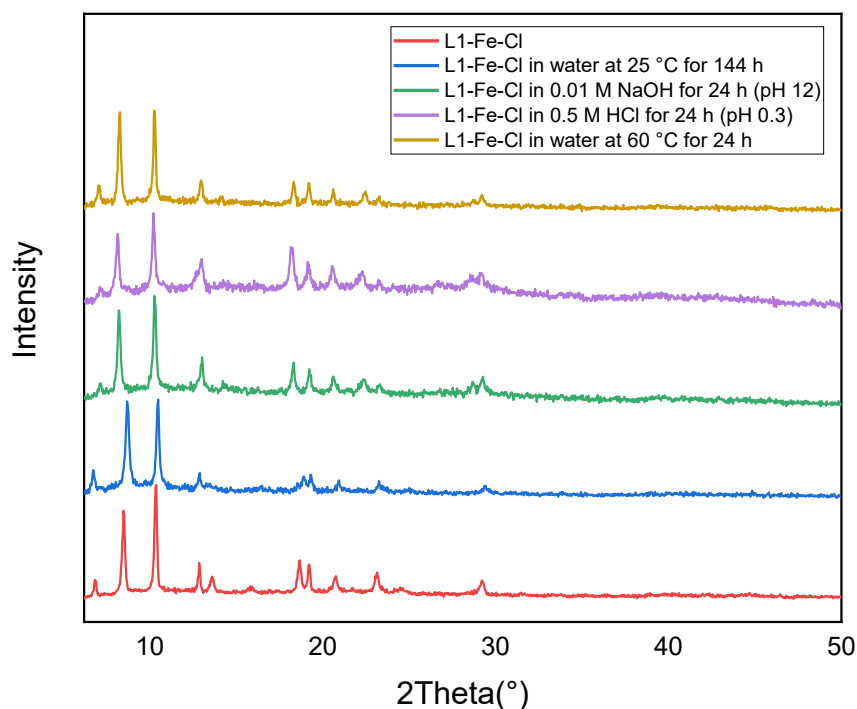


Figure 52: PXRD patterns of **L1-Fe-Cl** measured under neutral, acidic, and basic conditions.

4.2 Lanthanide MOFs (**L1-Tb** and **L1-Eu**) Built from **L1**

MOFs constructed from rare earth elements, including the lanthanides, as well as scandium (Sc) and yttrium (Y), can exhibit unique structures and properties due to the high coordination numbers and distinctive optical characteristics of these elements.³⁹⁴ As a result, lanthanide-containing MOFs have attracted significant attention, with numerous studies exploring their potential in applications such as chemical sensing,^{395–397} gas adsorption,³⁹⁸ drug delivery,^{399,400} catalysis,⁴⁰¹ and beyond.^{402–404}

L1-H₆ was treated with terbium nitrate ($\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) in a solvent mixture of DMF (2 mL) and water (0.5 mL) at 80 °C in a sealed vial for 42 h, forming colourless blade-shaped single crystals of **L1-Tb**. These crystals were characterised by SCXRD and determined to have the overall formula $[\text{Tb}_2(\text{L1})(\text{H}_2\text{O})_4] \cdot 4\text{DMF} \cdot 6\text{H}_2\text{O}$. Notably, only four coordinated water

molecules were modelled crystallographically, while four DMF and six water molecules, estimated to reside in the pores, were removed using the SQUEEZE routine in PLATON.³⁷⁰

L1-Tb crystallises in the triclinic space group *P*-1 (No. 2). The asymmetric unit contains half **L1** anion, and one Tb (III) ion connected to two coordinating water molecules, with the central siloxane oxygen atom located on inversion centre. **L1** adopts an octahedral arrangement of carboxylate groups around the siloxane core, featuring a linear Si–O–Si linkage ($\angle \text{Si–O–Si} = 180.0^\circ$).

L1-Tb is a 3D MOF constructed from discrete bimetallic Tb-based clusters and fully deprotonated **L1** ligands (Figure 53). Each ligand binds to six different bimetallic Tb-based SBUs through its carboxylate groups. The two Tb(III) ions in the SBU are bridged by two μ_2 - $\eta^1:\eta^1$ carboxylate groups, where one oxygen atom from each carboxylate coordinates to one metal centre. In addition, each Tb(III) ion is bound to two chelating (η^2) carboxylate groups, where both oxygen atoms from each carboxylate coordinate to the same metal ion. Overall, this results in a 6-connected SBU that links to six distinct linkers, with Tb–O bond lengths ranging from 2.305(11) to 2.510(2) Å (average 2.41 Å). Each Tb(III) ion also coordinates to two water molecules, as shown in Figure 53b.

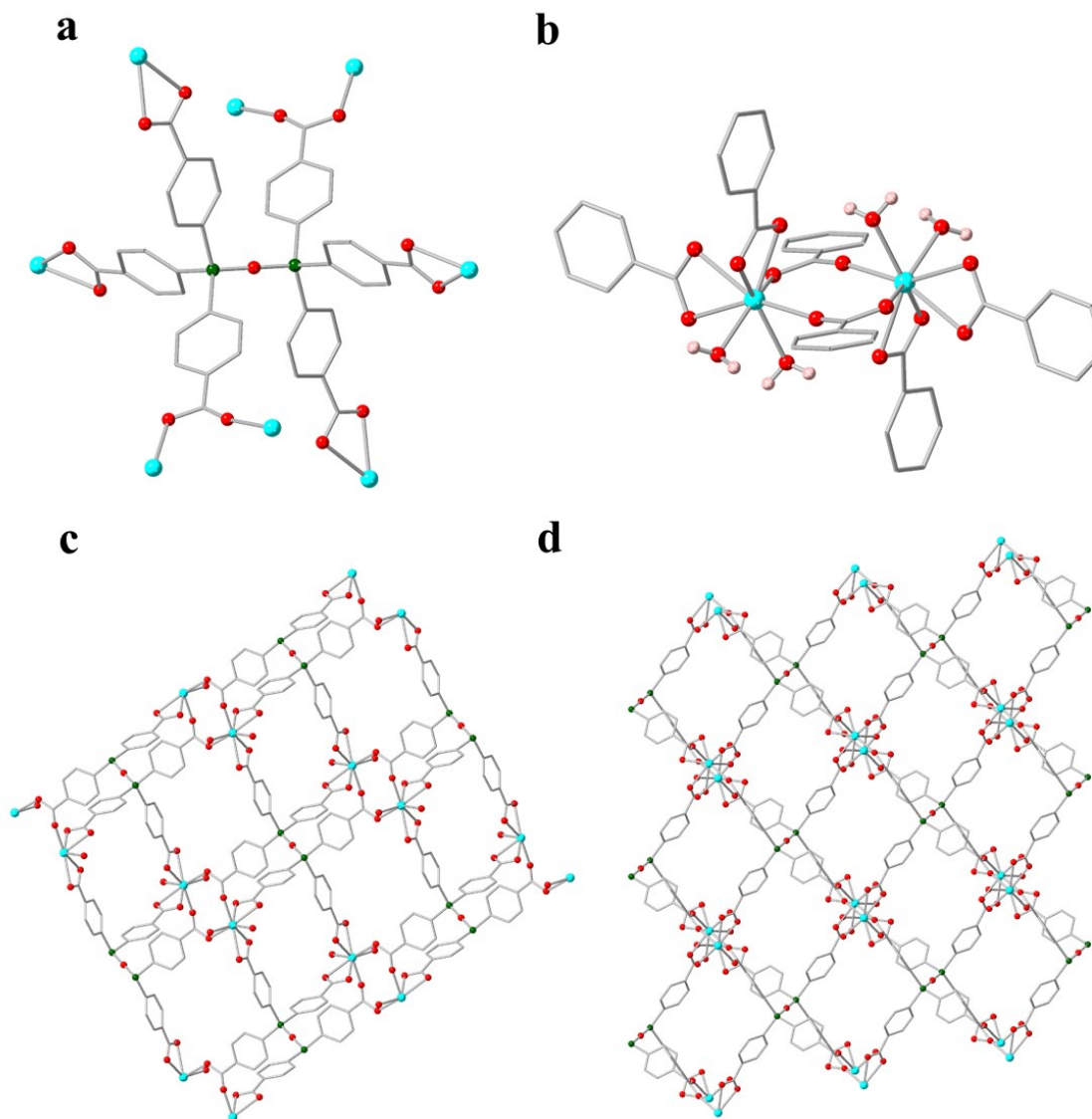


Figure 53: Crystal structure of **L1-Tb**: (a) the coordination environment of **L1** within the **L1-Tb** framework; (b) the binuclear Tb-based cluster; (c) a portion of the packing structure viewed along the crystallographic *a* axis; and (d) along the *b* axis. Colour scheme: Si, green; O, red; C, grey; Tb, cyan; H, pale pink. All hydrogen atoms are omitted in (a), (c), and (d) for clarity.

When both **L1** and the Tb SBU are reduced to octahedral 6-connected point nodes, a 3D **pcu** underlying net is afforded (Figure 54a). An alternative topological interpretation of **L1-Tb** involves replacing the 6-connected **L1** node with two 4-connected vertices centred on each of the terminal silicon atoms of siloxane linkage, to afford a rare 4,6-connected **fsh** topology (Figure 54b).^{209,405–408} **L1-Tb** was found to be isostructural to the reported Y-based MOF (IMP-

30), constructed from **L1**,²⁰⁹ with both MOFs sharing the same topology, crystallising in the same space group, and exhibiting very similar unit cell parameters. This is further supported by PXRD analysis, as the simulated patterns for both MOFs are in excellent agreement (Figure 55). While the bulk sample of IMP-30 decomposed upon isolation and air drying, PXRD measurements of the bulk **L1-Tb** sample confirmed its stability under the same conditions, with a good agreement between the experimental pattern and simulated one (Figure 55).

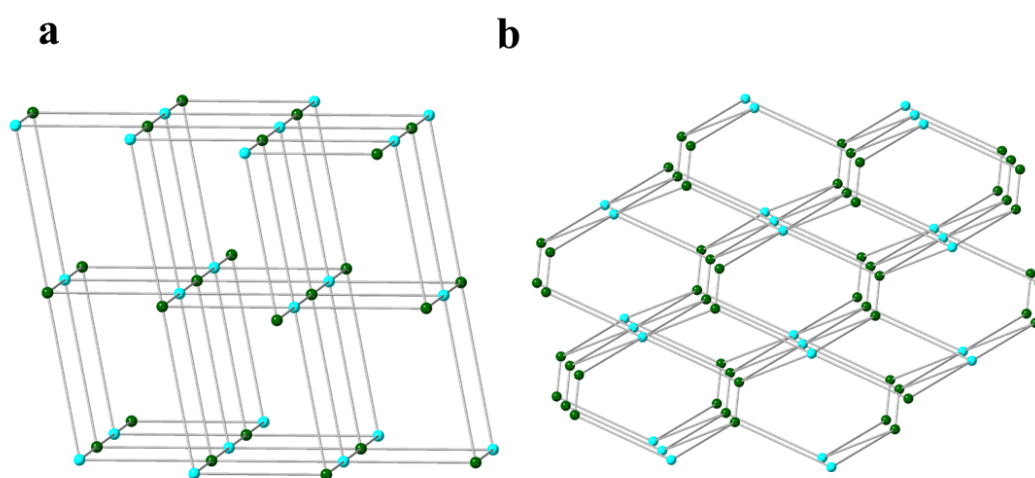


Figure 54: (a) Topological illustration of the **pcu** net in **L1-Tb**, where **L1** is simplified to a 6-connected node; (b) the **fsh** net in **L1-Tb**, where **L1** is represented as two conjoined tetrahedral nodes. Si-based nodes are shown in green, while the 6-connected Tb SBU nodes are shown in cyan.

Additionally, **L1-Tb** exhibited excellent thermal stability, as shown by TGA (Figure S7), with no decomposition observed until approximately 500 °C. The framework has solvent-accessible channels visible along all three crystallographic axes, with the largest window measuring approximately $6 \times 8 \text{ \AA}^2$ along the *a* axis. Mercury analysis of the theoretically desolvated framework indicates that the solvent-accessible voids occupy 58% of the unit cell volume.³⁷¹ These findings encouraged further porosity analysis; however, gas sorption studies on an activated sample of **L1-Tb** (activated under dynamic vacuum at 60 °C overnight) revealed a

low BET surface area of 9.07 m²/g (at 77 K under N₂) and a CO₂ uptake of 2.46 wt% at 1 bar (Figures S14 and S15). These unexpectedly low values were attributed to framework collapse, most likely occurring during degassing at 100-120 °C, as confirmed by PXRD on the post-BET sample (Figure S3).

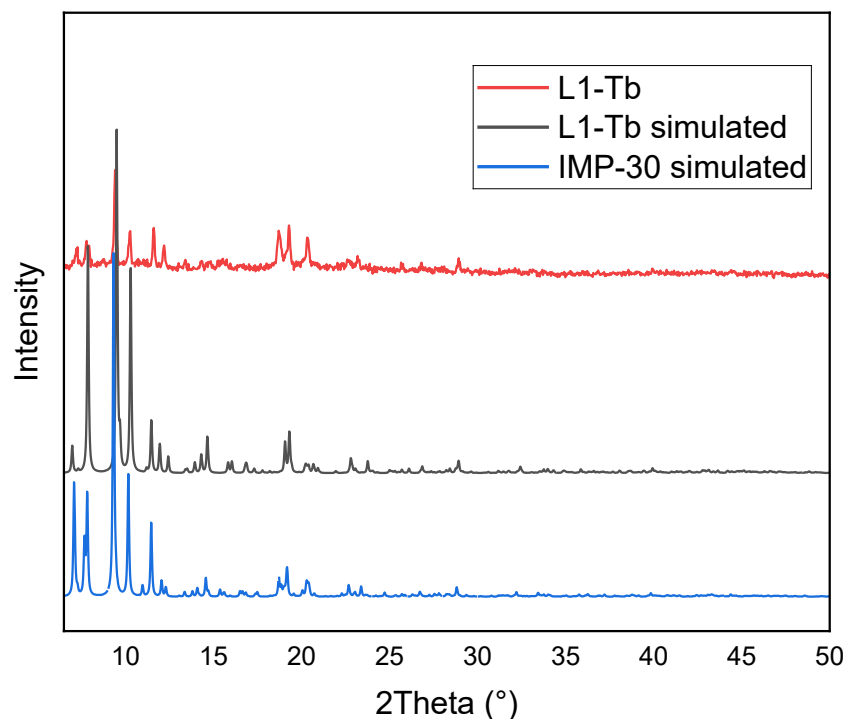


Figure 55: Comparison of the PXRD pattern of bulk **L1-Tb** with the simulated patterns of **L1-Tb** and IMP-30. The simulated pattern of IMP-30 is based on the published SCXRD data reported by Davies and co-workers (CSD refcode: NIQPAH).²⁰⁹

Following the successful synthesis of **L1-Tb**, **L1-H₆** was treated with Eu(NO₃)₃·6H₂O using the same synthetic protocol, affording high-quality, colourless rectangular crystals (**L1-Eu**). Comparison of the PXRD pattern of **L1-Eu** with the simulated pattern of **L1-Tb** suggests that they possess different structures (Figure 56). Furthermore, TGA of **L1-Eu** showed good thermal stability up to 420 °C, after which decomposition begins (Figure S8). Although time constraints prevented further characterisation of the Eu-based MOF, this material merits

additional studies (e.g., SCXRD and gas adsorption studies on both MOFs). In addition, Tb- and Eu-based MOFs are known to exhibit characteristic luminescent properties, with green and red emissions in the solid state under UV excitation, respectively.^{395,409} This highlights their potential for sensing applications, such as the detection of Pb^{2+} ions, perfluorooctanoic acid (PFOA), or phosphate ions in aqueous solutions.^{397,410,411} When exposed to UV light, the bulk samples of **L1-Tb** and **L1-Eu** exhibited bright green and red luminescence, respectively, visible to the naked eye (Figure S105). This suggests promising direction for future investigation on both MOFs. To the best of our knowledge, no Tb- or Eu-based MOFs constructed using a siloxane-based linker have been reported to date; thus, **L1-Tb** and **L1-Eu** represent significant additions to the family of siloxane-based MOFs.

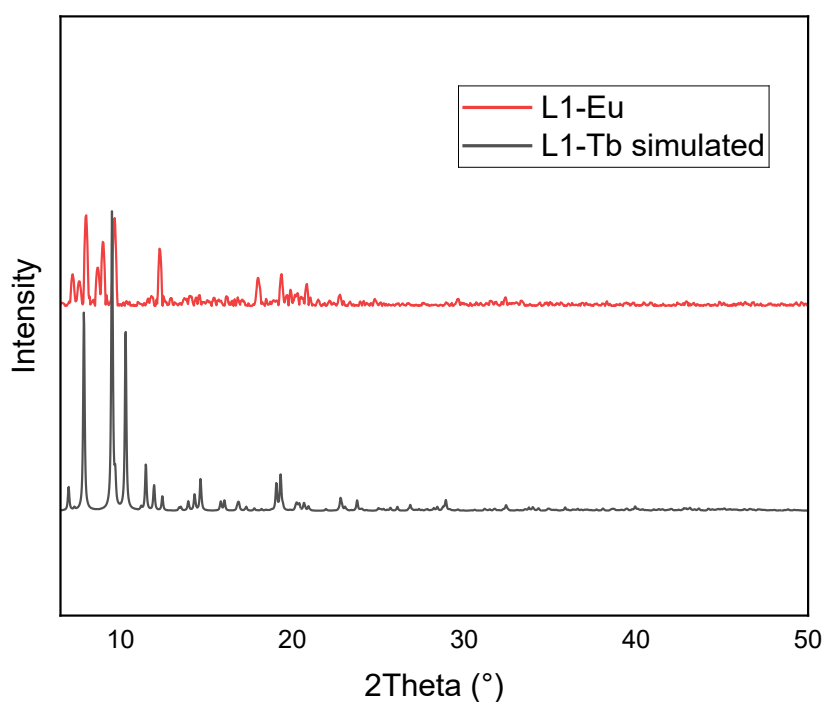


Figure 56: Comparison of the PXRD pattern of bulk **L1-Eu** with the simulated patterns of **L1-Tb**.

4.3 A Cu Paddlewheel-Based MOF (**L1-Cu**) with *fsy* Topology Built from **L1**

L1-H₆ was treated with Cu(NO₃)₂·3H₂O in a 1:1 mixture of DMF and MeCN in the presence of HNO₃ in a sealed glass vial. The mixture was heated for 42 h at 80 °C, and after slow cooling to room temperature over 6 h, plate shaped pale greenish blue crystals of **L1-Cu** were formed. The cooling period and amount of modulator used were key in producing suitable single crystals of **L1-Cu** for SCXRD analysis as several attempts with less than 6 h cooling and less HNO₃ failed and resulted with either a blue powder or a clear solution. The crystal structure of **L1-Cu** was determined by SCXRD analysis and identified as [Cu₃(**L1**)(H₂O)₂]·4DMF·10H₂O. **L1-Cu** crystallises in the orthorhombic space group *Cmmm* (No. 65). Similar to **L1-In**, the siloxane linkage is bent, with an Si–O–Si angle of 164(3)°. In addition, the aryl groups are staggered, with the six carboxylate groups arranged in a *pseudo*-octahedral geometry.

L1-Cu framework is built from Cu paddlewheel nodes linked by the fully deprotonated **L1** linker (Figure 57). The hexa-anion coordinates to six different bimetallic Cu-based SBUs through its six carboxylate groups. The two Cu atoms in each paddlewheel node are held together by four di-monodentate carboxylate groups from four different **L1** ligands, with C–O bond distances in the range 1.916(6)–1.975(8) Å. This results in a square planar paddlewheel SBU, which is seen often in Cu(II) carboxylate MOFs and many other transition metal carboxylate MOFs.^{38,137,156,184,203,412–414} In addition, the Cu paddlewheel connects to two axial coordinating water molecules pointing towards the centre of the pores. Topologically, when **L1** is reduced to a 6-connected node and Cu paddlewheel is reduced to a 4-connected node, a rare *fsy* net is afforded (Figure 57d).^{415–417} It is worth noting that **L1-Cu** is topologically equivalent to IMP-18, previously reported by Davies and co-workers,¹⁸⁴ which consists of a 4-connected square planar Zn paddlewheel and the same 6-connected disiloxane linker (**L1**).

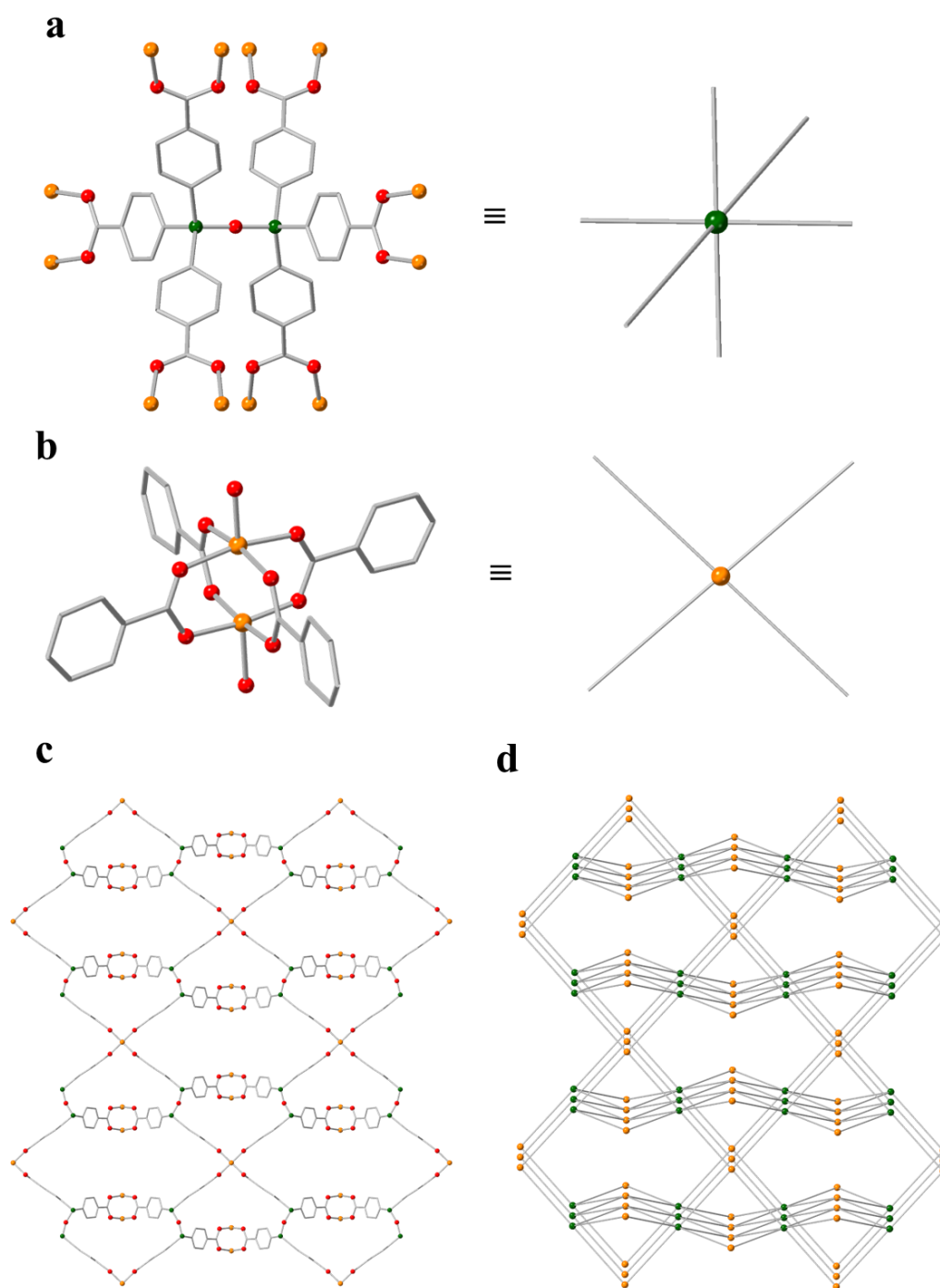


Figure 57: Crystal structure of **L1-Cu**: (a) Coordination environment of **L1** in the **L1-Cu** framework; (b) the Cu(II) paddlewheel SBU; (c) a portion of the packing structure of **L1-Cu** viewed down the *c* axis; (d) a topological illustration of the **fsy** net, showing the 6-connected Cu SBU nodes in orange, and the 6-connected Si-based nodes in green. Colour scheme: Si, green; O, red; C, grey; Cu, orange. H atoms are omitted for clarity; coordinated and non-coordinated DMF/water molecules are omitted in (c).

TGA of a bulk sample of **L1-Cu** (Figure S9) indicates that the MOF remains thermally stable up to approximately 280 °C, beyond which decomposition begins. The **L1-Cu** framework features solvent-accessible channels visible along all three crystallographic axes, with the largest window measuring approximately $7 \times 24.5 \text{ \AA}^2$ along the *c* axis (Figure 57c). After theoretical removal of both coordinated and non-coordinated solvent molecules, Mercury estimated the solvent-accessible void volume in **L1-Cu** to be $5745 \text{ \AA}^3$ per unit cell ($8761.8(8) \text{ \AA}^3$), corresponding to 65% of the unit cell volume.³⁷¹ Pore analysis in Mercury also revealed a theoretical network-accessible surface area of $2640 \text{ m}^2/\text{g}$.³⁷¹ This moderately large void volume highlights the potential of **L1-Cu** for adsorption studies, including gas uptake and related applications.

In addition, Cu paddlewheel-based MOFs are well known for their stability upon removal of axial ligands (such as water) through heating.^{38,418–420} As mentioned above, the two axial water molecules in **L1-Cu** project directly into the channels, and their theoretical removal increases the solvent-accessible void volume. Dehydration of the MOF may also generate open metal sites, which can enhance hydrogen sorption by increasing the binding energy between hydrogen and the exposed, electron-rich metal centres.^{421–423} Motivated by this, **L1-Cu** was subjected to dehydration by heating at 100 °C under dynamic vacuum overnight. Interestingly, after 15 minutes, a colour change from turquoise to dark blue was observed (Figure 58), which is likely due to a change in the coordination environment of the Cu centres upon loss of the axial water ligands. When exposed to air, the original turquoise colour returned within 15 mins, likely due to re-coordination of water molecules. This behaviour is consistent with that observed in HKUST-1,³⁸ where a similar colour change occurs upon dehydration at the same temperature, and reversible dehydration is likewise reported for other Cu-based MOFs.^{424,425}

Moreover, PXRD analysis of bulk **L1-Cu** shows good agreement with the simulated pattern generated from SCXRD data using Mercury, indicating the purity of the bulk sample (Figure

59). In addition, PXRD collected after the dehydration treatment confirmed that crystallinity was retained. Assuming dehydration is achieved, the resulting open (coordinatively unsaturated) metal sites are advantageous for applications including gas uptake, separation, and chemical sensing, suggesting promising directions for future investigation of **L1-Cu**.^{156,426,427} Overall, **L1-Cu** represents a significant addition to both the siloxane-based and hexacarboxylate MOF families. To the best of our knowledge, it is the first example of a 3D Cu(II)-based MOF constructed using a siloxane-based linker.

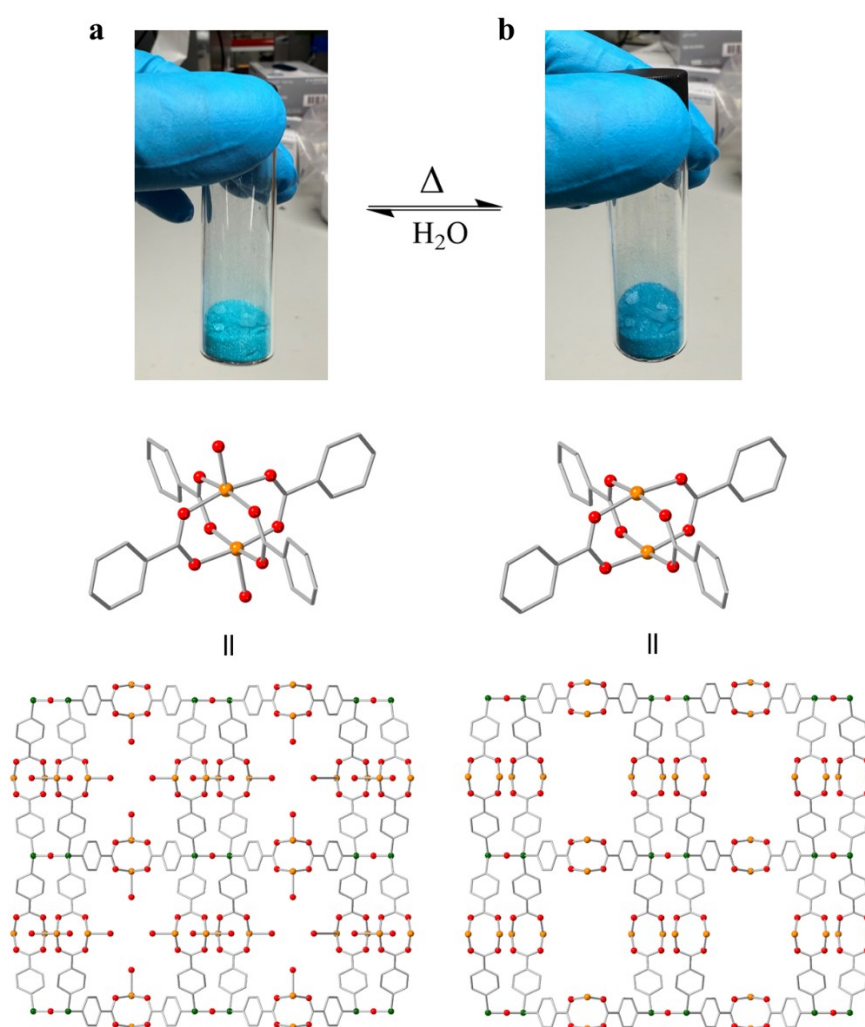


Figure 58: (a) Image of the fresh **L1-Cu** sample (top), the Cu paddlewheel SBU and a portion of the packing structure before removal of water molecules, viewed along the *b* axis (bottom); (b) Image of **L1-Cu** after heating at 100 °C for 15 minutes, with the expected structure of the Cu cluster and the **L1-Cu** packing diagram upon dehydration (bottom).

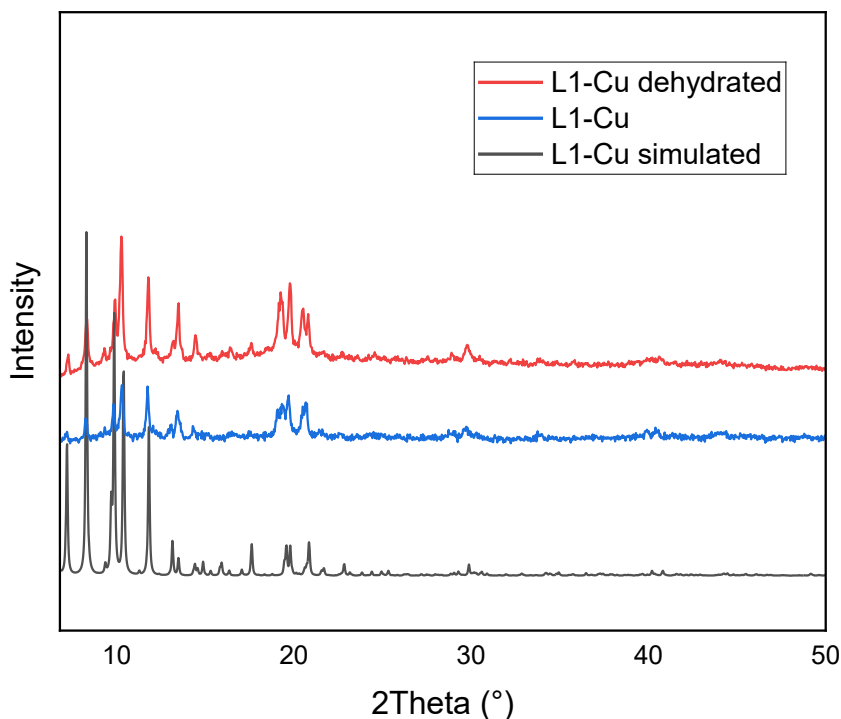


Figure 59: PXRD patterns of **L1-Cu** before and after dehydration.

4.4 Monovalent Alkali Metal-based MOFs Derived from **L1-H₆**

4.4.1 An Li-Based MOF Featuring an Extended Li SBU

Reaction of **L1-H₆** with LiNO₃ in DMF afforded colourless petal-shaped crystals of **L1-Li** with the formula [Li₁₀(**L1-H**)₂(DMF)₅]·DMF. **L1-Li** crystallises in the monoclinic space group *P*21/*c* (No. 14). The asymmetric unit contains one **L1-H** ligand coordinated to five Li atoms, with one carboxyphenyl arm remaining protonated (at O6, see Figure 60). One side arm of the linker is disordered, and a disordered network of DMF molecules coordinates to lithium ions associated with this arm. Additionally, a well-resolved DMF molecule is coordinated to Li2 on one of the ordered arms. The siloxane linkage is nearly linear with Si–O–Si angle of

178.53(12)°, and the aryl rings are staggered, resulting in the six carboxylate groups adopting a *pseudo*-octahedral arrangement.

While Li carboxylate MOFs commonly form structures based on infinite Li–O chains,^{428–431} **L1-Li** features an unusual extended Li-based SBU that runs from Li1 to Li1', and coordinates to twelve different **L1-H** linkers (Figure 60). This SBU consist of two Li₅-based subunits. Two of the twelve carboxylate groups that coordinates to the extended SBU (O8+O9 and O8'+O9') form μ_4 bridges, with each oxygen bridging two Li atoms (Li2, Li3+Li3', Li5 and Li2', Li3'+Li3, Li5, respectively), thus connecting the two subunits. This results in an 8-membered Li–O–C–O–Li–O–C–O ring at the centre of the SBU, which is common in Li carboxylate chain-based MOFs.⁴³¹ The carboxylate groups O12+O13 and O12'+O13' also form μ_4 bridges, where one oxygen of each group (O12 and O12') coordinates to a single Li atom, and the other (O13 and O13') coordinates to three Li atoms. Moreover, four carboxylate groups (O2+O3, O4+O5, O2'+O3' and O4'+O5') form μ_3 bridges, where one oxygen of each group (O2, O2', O4, and O4') binds to one Li and the other (O3, O3', O5, and O5') bridges two Li atoms. The O10+O11 and O10'+O11' groups form μ_2 bridges connecting Li4 to Li1 and Li4' to Li1', respectively. The remaining two carboxylate groups, O6+O7 and O6'+O7', coordinate monodentately to one Li atom via O7 and O7' oxygen atoms. Notably, the free OH groups in **L1-H** linkers (at O6 and O6', Figure 60) engage in hydrogen bonding with neighbouring carboxylate oxygen atoms (O11 and O11'), with O...O distances of 2.566 Å, which is also observed in other reported MOFs.^{432,433} Additionally, one DMF molecule is coordinated to each Li2 and Li2', while disordered DMF molecules bind to Li5 and Li5' and block the pores (Figure 61a). Therefore, upon successful removal of DMF molecules, increased porosity is anticipated (Figure 61b).

Topologically, since **L1-H** connects to six different Li-based SBUs, it can be reduced to a 6-connected node, while the Li₁₀-based SBU is simplified to a 12-connected node, resulting in an unusual 12,6-connected network (Figure 62).

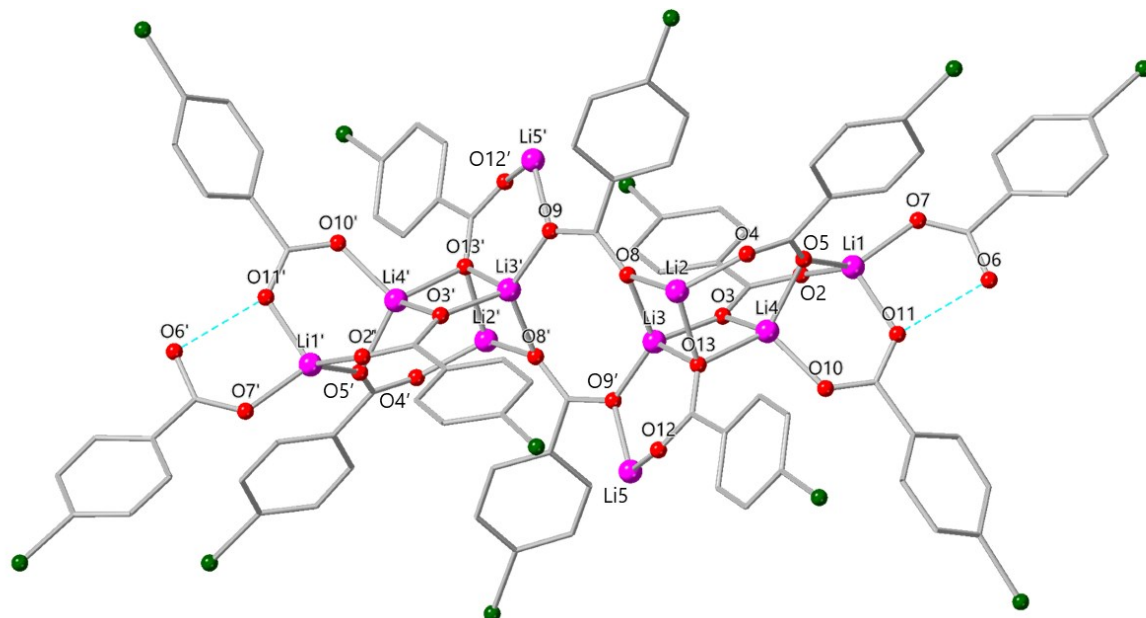


Figure 60: Ball-and-stick representation of the Li-based SBU in **L1-Li**. Colour scheme: Si, green; O, red; C, grey; Li, magenta. Hydrogen bonds are shown as dashed cyan lines. Hydrogen atoms are omitted for clarity.

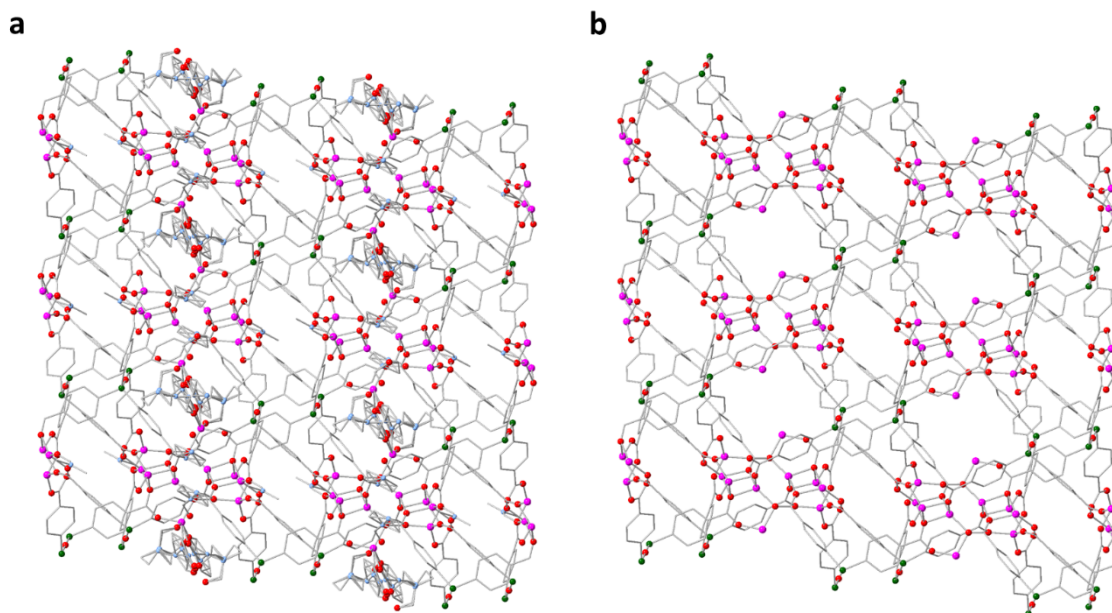


Figure 61: A portion of packing diagram of **L1-Li** viewed along the *b* axis: (a) including coordinated DMF molecules; (b) with solvent molecules removed.

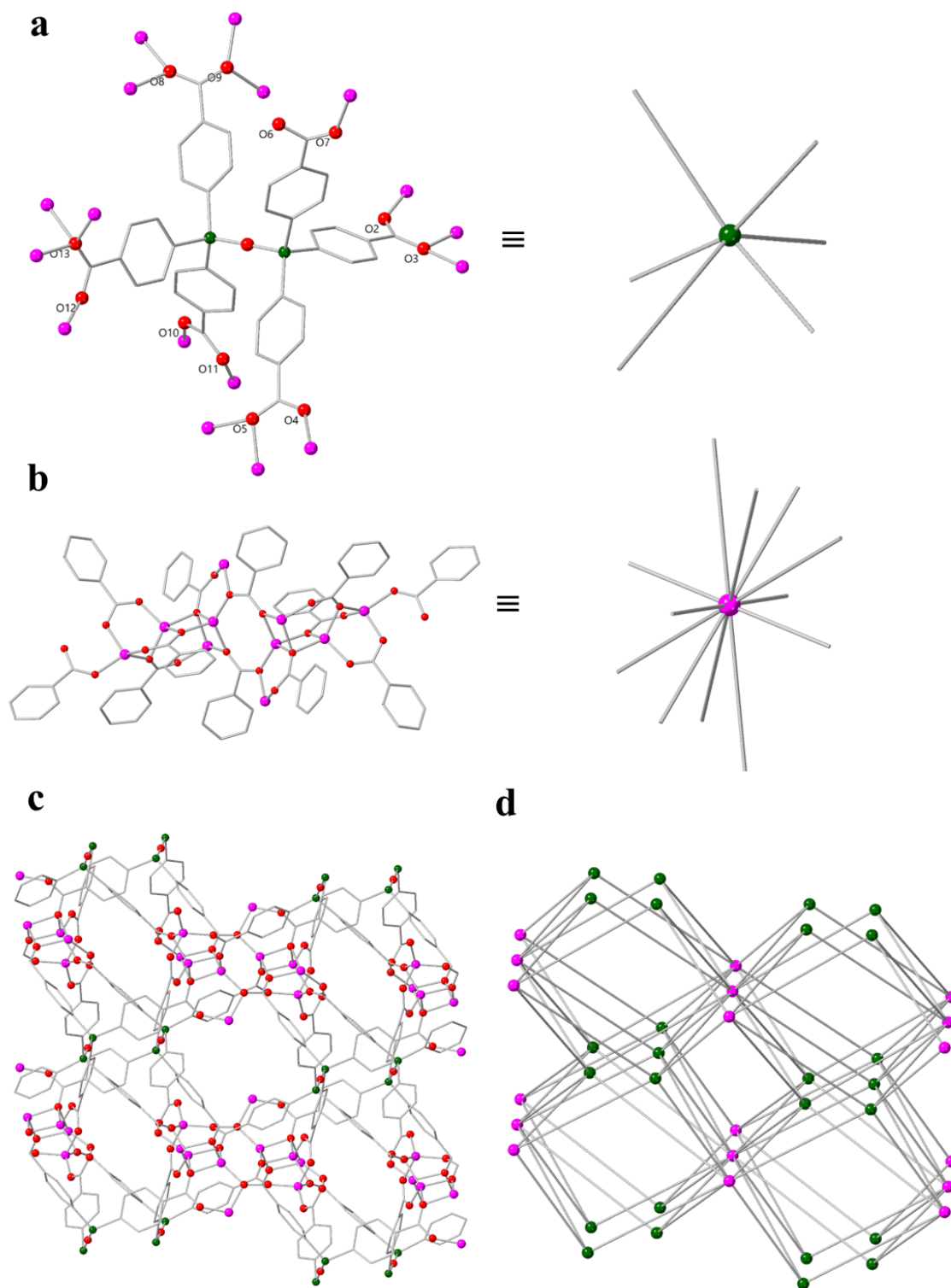


Figure 62: Crystal structure of **L1-Li**: (a) the coordination environment of **L1-H** in the framework; (b) the Li_{10} -based SBU in **L1-Li**; (c) a portion of the packing structure of **L1-Li** viewed along the *b* axis; (d) a topological illustration of the (12,6)-coordinated net, showing the 12-connected Li SBU nodes Li magenta, and the 6-connected Si-based nodes in green. Colour scheme: Si, green; O, red; C, grey; Li, magenta; H, pale pink. H atoms, coordinated and non-coordinated solvent molecules are omitted for clarity.

The framework features solvent-filled channels, with the largest window measuring approximately $5 \times 6 \text{ \AA}^2$ along the b axis. TGA under a nitrogen atmosphere revealed that the framework remains stable up to approximately 390°C , with a 20% mass loss between $30\text{--}265^\circ\text{C}$ corresponding to the loss of coordinated and non-coordinated DMF molecules (Figure S10). After theoretical removal of all solvent molecules, Mercury estimated the solvent-accessible voids to occupy 35% of the unit cell volume. PXRD analysis of the bulk sample showed good agreement with the simulated pattern (Figure 63).³⁷¹ Notably, two low-angle peaks at 8.3° and 7.5° observed in the simulated pattern are absent in the experimental pattern. Aside from these differences, the experimental and simulated patterns align well.

An activated sample of **L1-Li** was prepared for N_2 sorption analysis by heating under dynamic vacuum at 70°C overnight, followed by *ex situ* degassing at 100°C for 12 h and *in situ* degassing at 120°C for 4 h. Although **L1-Li** retained its crystallinity after activation, N_2 sorption analysis (at 77 K) indicated that the activated sample was non-porous. PXRD analysis performed after BET measurements confirmed that the framework remained crystalline (Figure 63), suggesting that the lack of porosity may be due to the presence of DMF molecules not removed during the activation process, thereby blocking N_2 adsorption. Therefore, it may be worthwhile to modify the activation protocol, for example, by increasing the activation temperature or duration, or by employing a different technique, to ensure complete solvent removal and potentially achieve higher porosity before concluding that the MOF is truly non-porous.

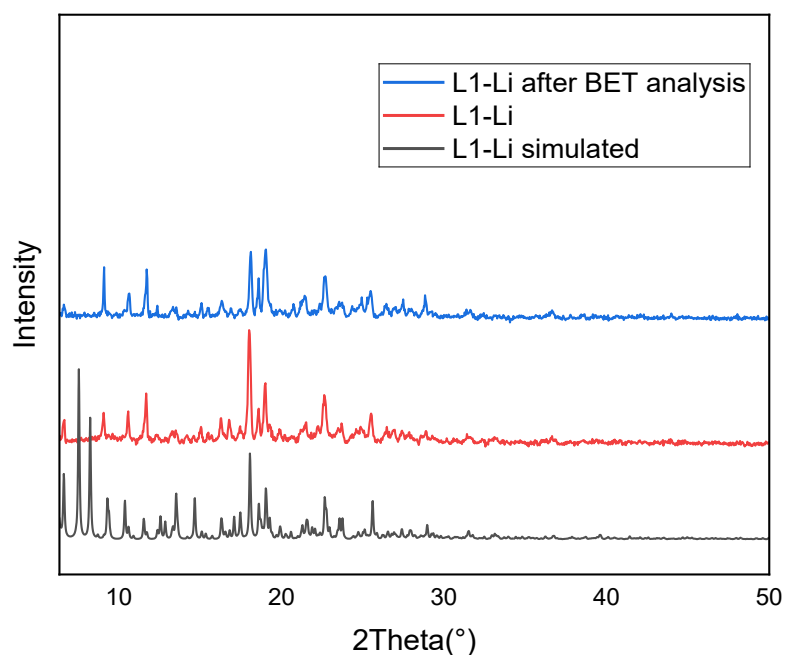


Figure 63: PXRD patterns of bulk **L1-Li** before and after gas sorption measurements, compared with the simulated pattern generated from the SCXRD structure in Mercury.³⁷¹

4.4.2 A Na-Based MOF (**L1-Na**) with *nia* Topology

The reaction of **L1-H₆** with NaNO₃ in DMF afforded colourless needle-shaped single crystals of [Na₃(**L1-H₃**)(DMF)₆] (**L1-Na**). The Na-based MOF crystallises in the trigonal space group *P*-31 $\bar{c}$ (No. 163). The siloxane linkage is linear, with the six carboxylate groups arranged in an octahedral geometry. The asymmetric unit (*Z'* = 1/12) contains a fragment of an O–Si–carboxyphenyl arm, two crystallographically distinct Na ions, and one DMF molecule. The linker is only partially deprotonated, with three of its arms protonated.

L1-Na forms a 3D framework constructed from **L1-H₃** linkers and trimetallic Na-based SBUs. Each **L1-H₃** linker connects to six different Na-based clusters, while each Na₃ cluster connects to six independent **L1-H₃** ligands. The Na-based node consists of three Na⁺ ions, one central

and two crystallographically equivalent terminal Na⁺ ions, that are not directly bonded to each other. The central Na⁺ ion is bridged to each terminal Na⁺ by three μ_2 -carboxylate oxygens, with an average Na–O distance of 2.39 Å. Notably, the protonated carboxylic acid groups engage in hydrogen bonding with the free carboxylate oxygens on neighbouring linkers (Figure 64b), with O $\cdots$ O distances of 2.424(4) Å. Additionally, each terminal Na⁺ ion coordinates to three DMF molecules pointing towards the centre of the pores.

From a topological perspective, the trimetallic Na cluster can be simplified as a distorted trigonal prismatic 6-connected node, while **L1-H₃** can be simplified as an octahedral 6-connected node. This yields a rare (6,6)-connected **nia** topology (Figure 64). To the best of our knowledge, **L1-Na** represents the first Na-based MOF with a **nia** topology.

The **L1-Na** framework features solvent-filled voids, with the largest channel measuring approximately $7 \times 12 \text{ Å}^2$ along the *a* and *b* axes. Coordinated DMF molecules were observed to occupy these pores, as shown in Figure 65. Thermogravimetric analysis of **L1-Na** revealed a gradual mass loss between 45 and 200 °C, attributed to the release of coordinated DMF molecules, followed by framework decomposition beginning around 420 °C (Figure S11). Upon theoretical removal of all solvent molecules, the solvent-accessible void volume was calculated using Mercury to be 47% of the unit cell volume.³⁷¹ PXRD analysis showed excellent agreement between the bulk sample and the simulated pattern of **L1-Na**, confirming both crystallinity and phase purity (Figure 66). Mercury also predicted a network-accessible surface area of 1679 m²/g. However, nitrogen sorption analysis (at 77 K) on an activated **L1-Na** sample indicated non-porous material. PXRD analysis on **L1-Na** sample after BET analysis confirmed that the lack of porosity is not due to framework decomposition during analysis (Figure 66). Instead, it is likely attributed to incomplete removal of solvent molecules during activation, which could block the channels and hinder nitrogen access.

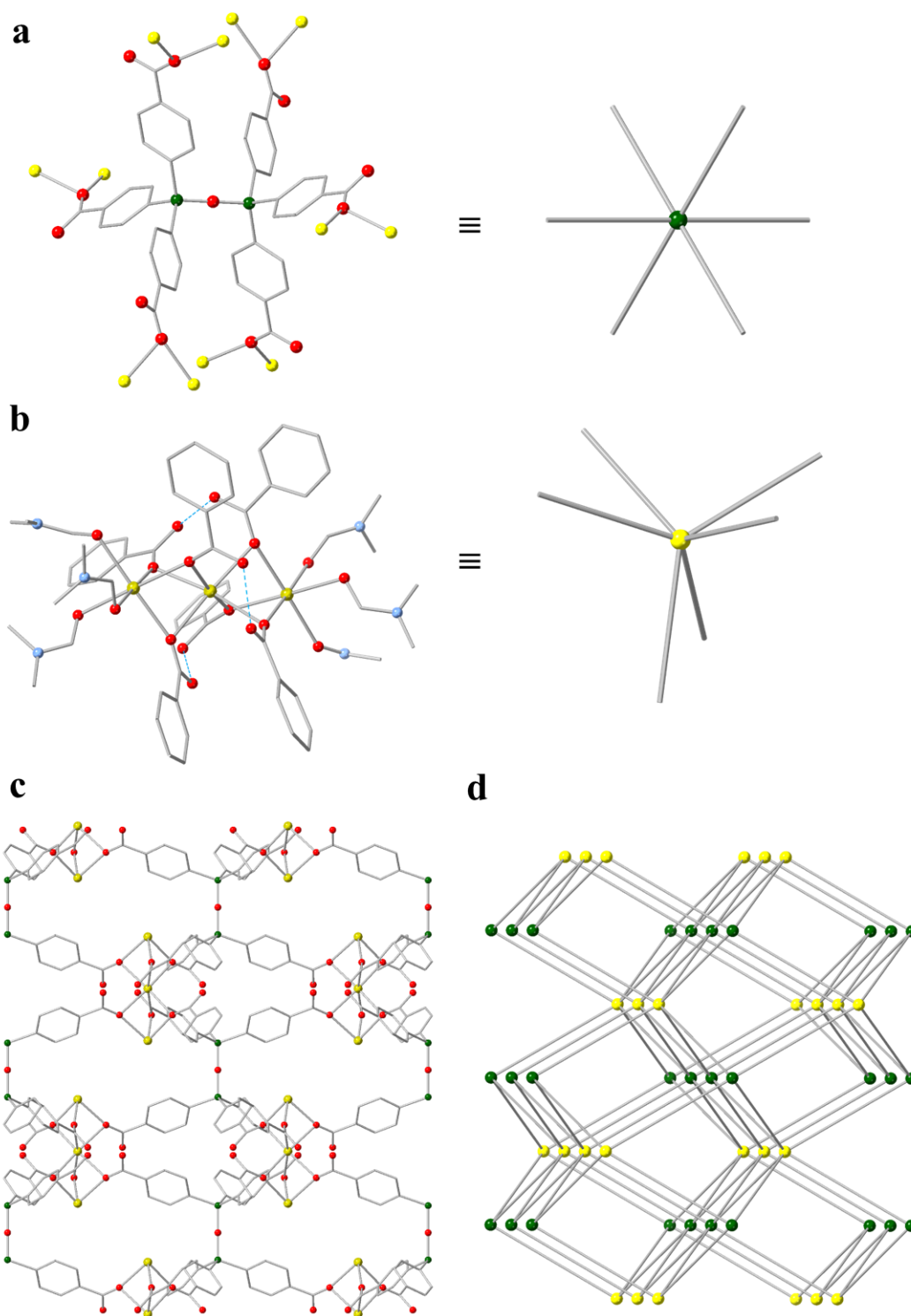


Figure 64: Crystal structure of **L1-Na**: (a) coordination environment of **L1-H₃** in **L1-Na**; (b) the trinuclear Na-based cluster; (c) a portion of the packing structure of **L1-Na** viewed along the *a* axis; (d) a topological illustration of the **nia** net, showing the 6-connected Na SBU nodes in yellow, and the 6-connected Si-based nodes in green. Colour scheme: Si, green; O, red; C, grey; Na, yellow; N, light blue. H-bonds are shown as dashed cyan lines. All H atoms have been omitted for clarity. DMF molecules are omitted in (c) for clarity.

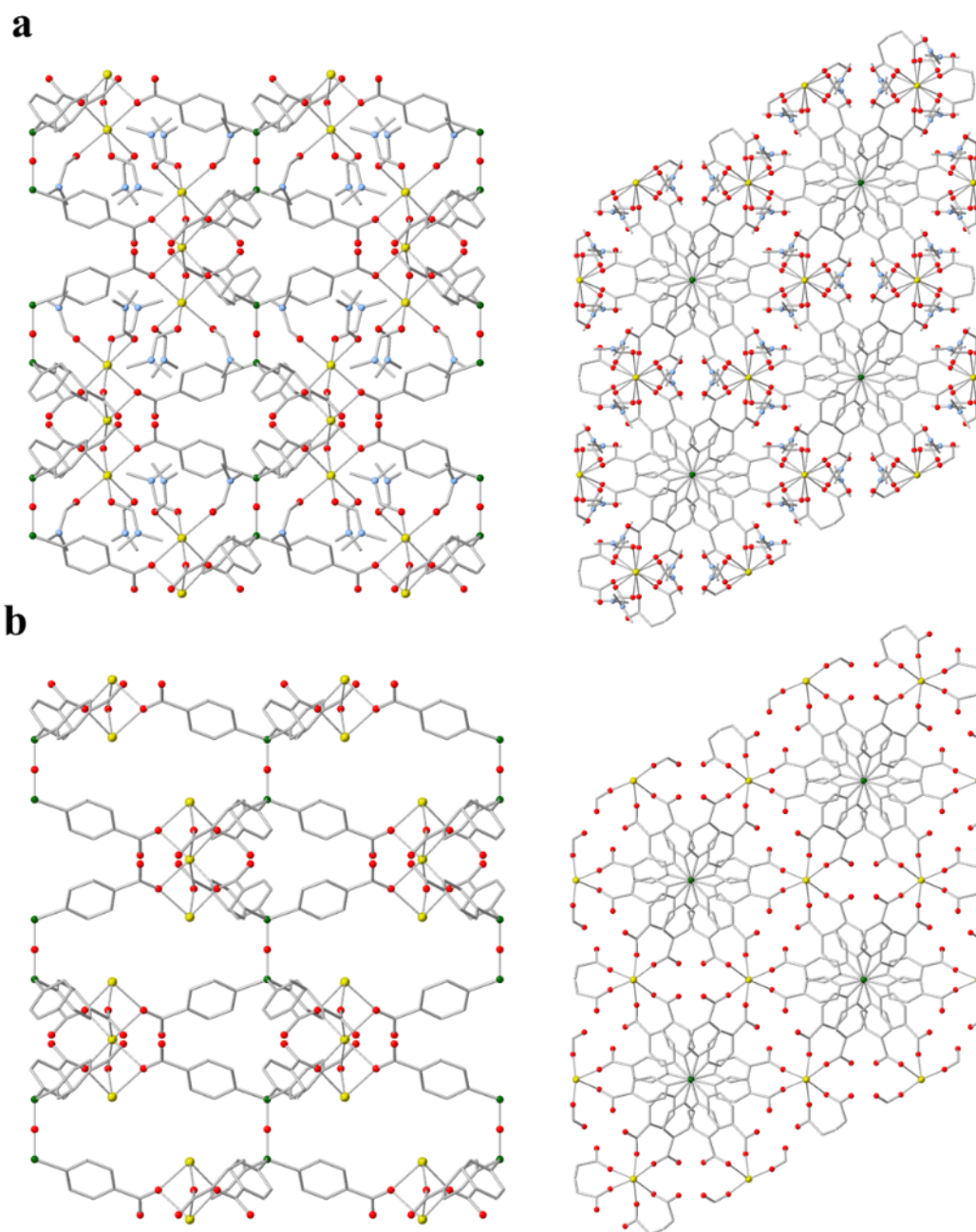


Figure 65: (a) A portion of the packing structure of **L1-Na** viewed along the *a* axis (left) and the *c* axis (right); (b) after the theoretical removal of coordinated DMF molecules.

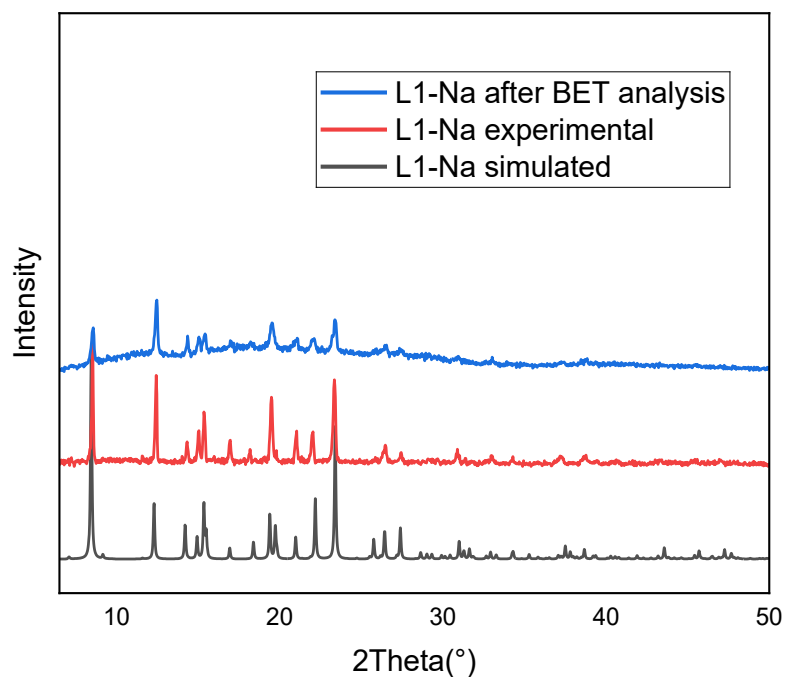


Figure 66: PXRD patterns of bulk **L1-Na** before and after gas sorption measurements, compared with the simulated pattern generated from the SCXRD structure in Mercury.³⁷¹

4.4.3 A K-Based MOF (**L1-K**) with *nia* Topology

The treatment of **L1-H₆** with KNO₃ in DMF afforded colourless block-shaped crystals of [K₂(**L1-H₄**)(H₂O)₃]·6DMF (**L1-K**). SCXRD analysis revealed that **L1-K** crystallises in the trigonal space group *P31c* (No. 159). The siloxane core in **L1-K** is bent, with an Si–O–Si angle of 164.0(8)°, and the aryl arms are staggered along the Si–O–Si axis, with the six carboxylate groups adopting a *pseudo*-octahedral confirmation. The asymmetric unit contains one di(*p*-carboxyphenyl)disiloxane unit, two coordinated K⁺ ions and one coordinated water molecule. It is also worth noting that solvent masking was used and indicated the presence of six DMF molecules per asymmetric unit.³⁷⁰ In addition, to achieve charge balance of the structure, an additional hydrogen atom is required and has been included in the formula above. However,

this hydrogen could not be located crystallographically and is expected to be disordered over several carboxylate sites.

The **L1-K** framework is comprised of binuclear K-based clusters linked by six different **L1-H4** linkers, with an average K–O distance of 2.963 Å. The two K⁺ are bridged by three μ_2 -carboxylate oxygens, and the cluster further connects to three water molecules (pointing towards the pores) through one of its metal ions. Similar to **L1-Na**, the three carboxylic acid groups in each linker participate in H-bonding with the free carboxylate oxygens on adjacent linkers (Figure 67b), with O $\cdots$ O distances of 2.470(3) Å.

Topological analysis of **L1-K** was performed by simplifying the silicon-based linkers and the bimetallic K SBUs into 6-connected nodes, forming a **nia** net, which makes **L1-K** the first K-based MOF with **nia** topology. In comparison with **L1-Na**, **L1-K** exhibits a very similar structure, with nearly identical trigonal cell metrics (see Table S3), the main differences being the space group and the metal SBU. Although the two frameworks contain different metal centres, **L1-Na** features a trimetallic Na₃ SBU coordinated to DMF molecules, whereas **L1-K** contains a bimetallic K₂ SBU coordinated to water molecules, their connectivity is preserved, with each SBU acting as a 6-connected octahedral node and adopting the same **nia** topology, as shown on the right-hand side of Figures 64 and 67. Furthermore, the PXRD patterns of **L1-K** and **L1-Na** are in good agreement (Figure 68). Therefore, the two MOFs are considered isorecticular.

The **L1-K** structure exhibits solvent-accessible voids, with the largest channel measured to be about 7×12 Å² along the crystallographic *a* and *b* axes. In addition, voids analysis using Mercury estimates the solvent-accessible void volume to be 56% of the unit cell volume.³⁷¹ The TGA curve of **L1-K** (Figure S12) shows a gradual weight loss between 30–200 °C, corresponding to the removal of coordinated water and non-coordinated DMF molecules. The material remains thermally stable up to the onset of decomposition, which begins around

420 °C. These findings encouraged nitrogen sorption analysis; however, although the predicted network-accessible surface area is 1679 m²/g,³⁷¹ **L1-K** showed the same N₂ adsorption results as **L1-Li** and **L1-Na** (at 77 k), suggesting that the material is non-porous.

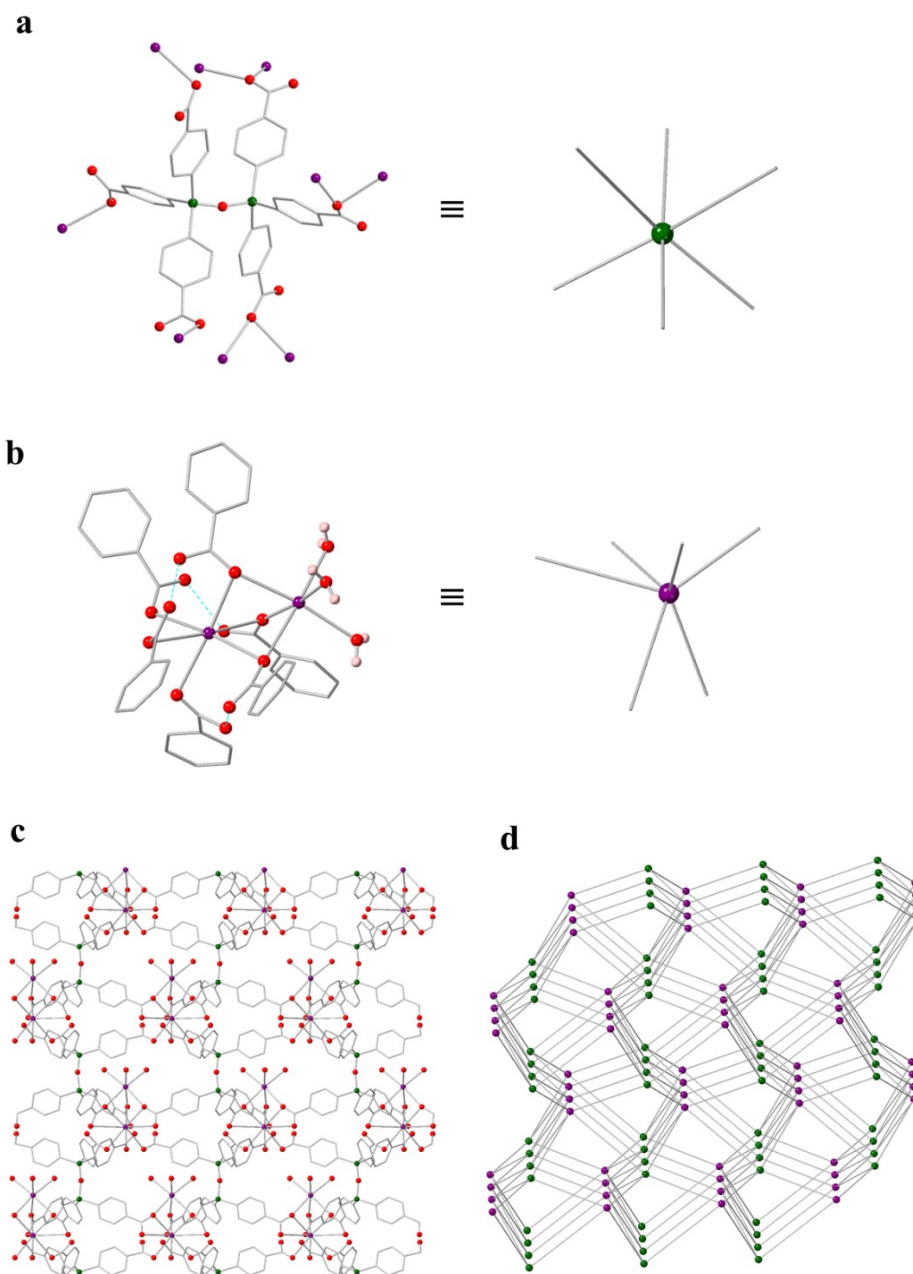


Figure 67: Crystal structure of **L1-K**: (a) coordination environment of **L1-H₄** in **L1-K**; (b) K-based SBU; (c) portion of the packing structure along *a* axis; (d) topological illustration of the **nia** net in **L1-K**, showing the 6-connected K SBU nodes in dark purple, and the 6-connected Si-based nodes in green. Colour scheme: Si, green; O, red; C, grey; K, dark purple; H, pale pink. H-bonds are shown as dashed cyan lines. All H atoms (except those of water molecules in b) have been omitted for clarity.

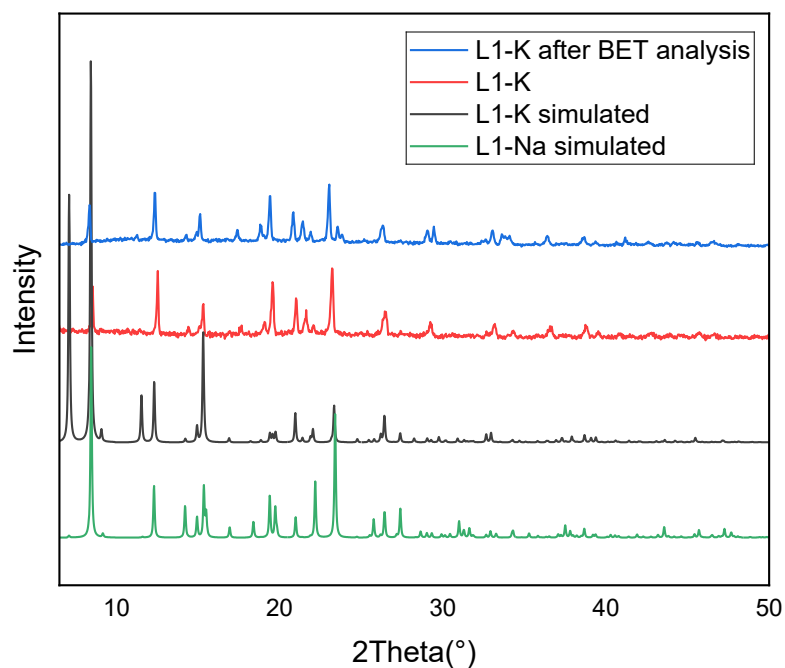


Figure 68: PXRD patterns of bulk **L1-K** before and after gas sorption measurements, compared with the simulated patterns of **L1-K** and **L1-Na**.

It is worth noting that the preparation of alkali metal MOFs with permanent porosity remains challenging in the literature, owing to the strong tendency of solvent molecules, typically water and DMF, to coordinate with these metals.^{434–436} In addition, many such MOFs are sensitive to pore evacuation and often collapse upon removal of organic solvents residing in the pores and/or coordinated ligands.^{437–439} Nevertheless, the Na-based MOF reported by Wang and co-workers, HIAM-111, achieved permanent porosity while preserving crystallinity after removal of both coordinated and non-coordinated solvents.⁴³⁵ This MOF was activated by solvent-exchange to acetone followed by thermal activation. Remarkably, HIAM-111 exhibited a BET surface area of 1561 m²/g, which is outstanding for a Na-MOF. More recently, the same group reported a series of robust alkali metal MOFs (HIAM-112-Na/K/Rb) with BET surface areas exceeding 1300 m²/g.⁴³⁶ These were activated by soaking in ethanol for 3 days, followed by heating under dynamic activation at 150 °C for 12 h. These findings encourage further

investigation into the porosity of the alkali metal MOFs described in this section, with future studies considering modified activation protocols and alternative techniques (e.g., solvent exchange, supercritical CO₂ drying).

4.5 Amide-Functionalised Indium-Based MOF with *nia* Topology Built from **L4**

L4-H₆ was treated with In(NO₃)₃·5H₂O in a 1:1 mixture of DMF and MeCN, and in the presence of concentrated HNO₃ and heated at 80 °C for 42 h in a screw-cap vial, producing colourless blade-shaped crystals of **L4-In**. Single-crystal X-ray diffraction identified the crystals as [In₃(μ₃-O)(**L4**)(H₂O)₃]·NO₃·12DMF·6H₂O. **L4-In** crystallises in the trigonal space group *P*-31 $\bar{c}$ (No. 163). The asymmetric unit contains three indium(III) ions linked by a central μ₃-oxide anion and coordinated to an **L4** linker with six fully deprotonated carboxylic acid groups. As observed in **L1-In**, the Si–O–Si unit shows a bent geometry with an angle of 163(2)°. The framework is also cationic, with the positive charge most likely balanced by non-coordinating nitrate anions occupying the pores.

The structure consists of trimetallic In-based clusters interconnected by **L4** linkers (Figure 69). Each In₃O cluster contains three indium atoms bridged by a central μ₃-oxide anion and coordinated by six μ₂-η¹:η¹ carboxylate groups from the linkers, with In–O bond lengths ranging from 1.95 to 2.48 Å. Each indium(III) ion is coordinated equatorially by four carboxylate oxygen atoms, while the axial positions are occupied by a water molecule and the μ₃-oxide anion. Topological analysis reduces the **L4** linker to a 6-connected node (by placing a centroid at the centre of the disiloxane linkage) and the In-based SBU to a trigonal prismatic 6-connected node, resulting in a rare *nia* topology (Figure 69d). To the best of our knowledge, **L4-In** is the first amide-functionalised disiloxane-based MOF.

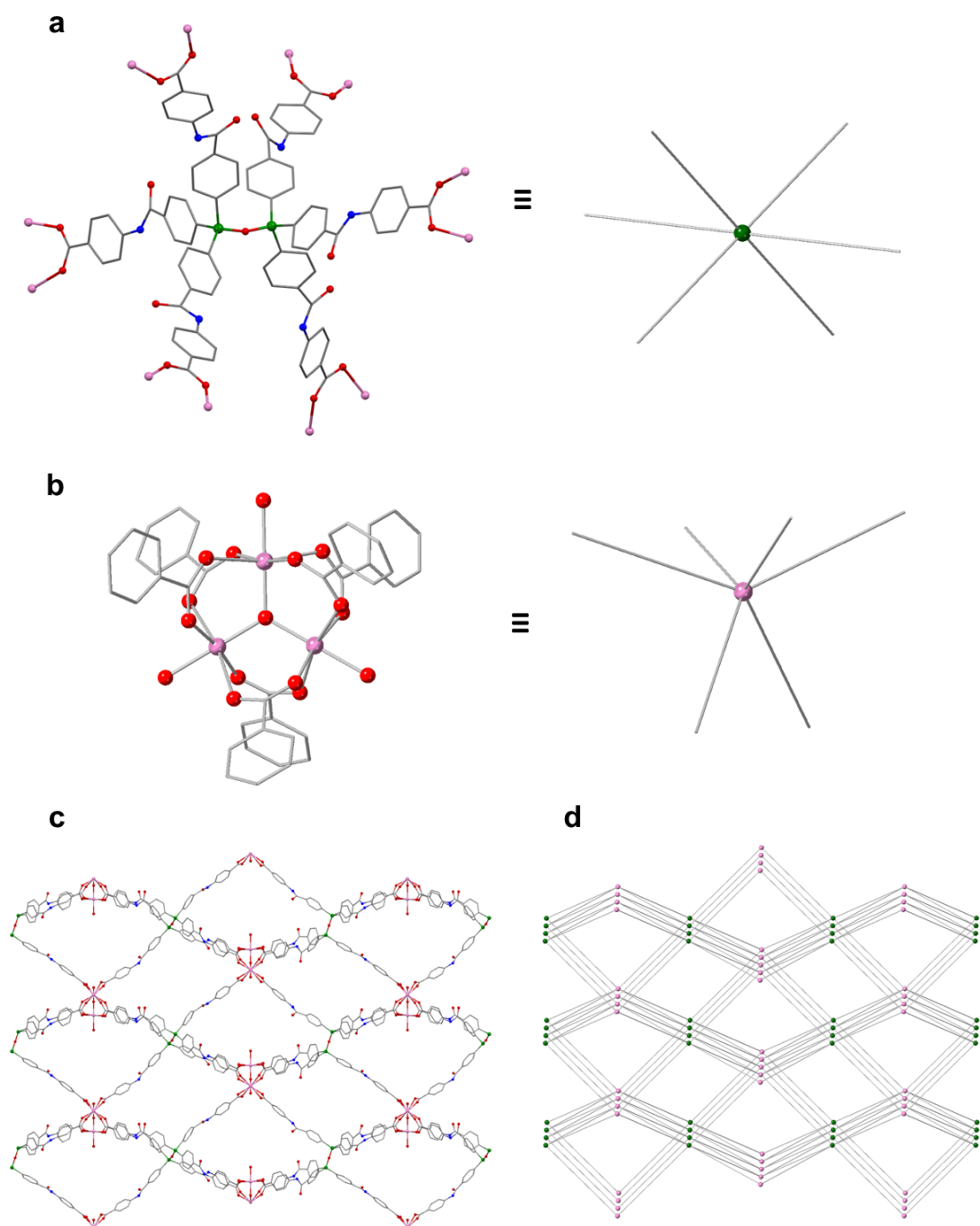


Figure 69: Crystal structure of **L4-In**: (a) the coordination environment of **L4** in **L4-In**; (b) the In_3O -based cluster; (c) a portion of the packing structure of **L1-In** along the *b* axis; (d) a topological illustration of the **nia** net, showing the 6-connected In-based SBU nodes in pink, and the 6-connected Si-based nodes in green. Colour scheme: Si, green; O, red; C, grey; In, pink; H, pale pink. All H atoms have been omitted for clarity.

The **L4-In** framework features solvent-accessible channels, with the largest window measuring approximately $12 \times 12 \text{ \AA}^2$ along the *b* axis. The TGA curve of **L4-In** (Figure S13) displayed a thermal stability up to approximately 380 °C, after which decomposition began. Upon theoretical removal of coordinated and non-coordinated solvent molecules, Mercury estimated the remaining voids to occupy 82% of the unit cell volume (total volume: 16259.3(15) $\text{\AA}^3$).³⁷¹

In comparison with **L1-In**, introducing an amide linkage into each of the six arms of **L1** increased the arm length from 6.63 $\text{\AA}$ in **L1** to 13.06 $\text{\AA}$ in **L4**. As demonstrated by the SCXRD analysis of **L4-In**, treating **L4-H₆** with the same metal salt under identical reaction conditions afforded a MOF isorecticular to **L1-In** with significantly enlarged channels. This confirms the successful reticular expansion of **L1-In** through amide incorporation. Mercury also predicted a network-accessible surface area of 4035 m^2/g .³⁷¹ Such high porosity is critical for applications such as gas adsorption and strongly motivated further investigations into the stability and sorption properties of **L4-In**. However, PXRD analysis of the bulk **L4-In** sample after isolation and air drying indicated poor air stability (Figure 70). In addition, **L4-In** lost crystallinity upon activation under dynamic vacuum at 40 °C; therefore, no further studies were carried out on this material.

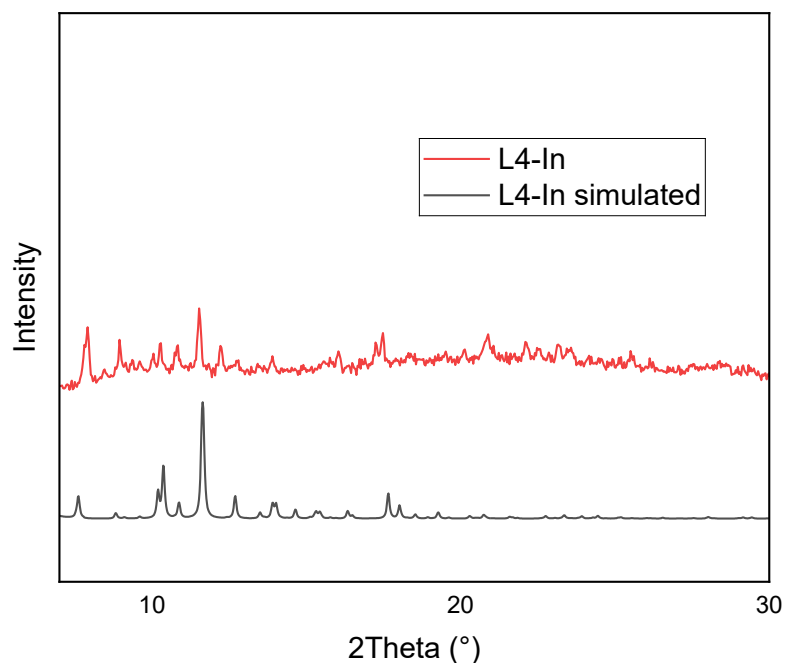
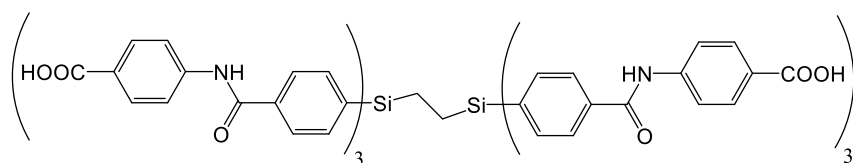


Figure 70: PXRD pattern of bulk **L4-In**, compared with the simulated pattern generated using Mercury.³⁷¹

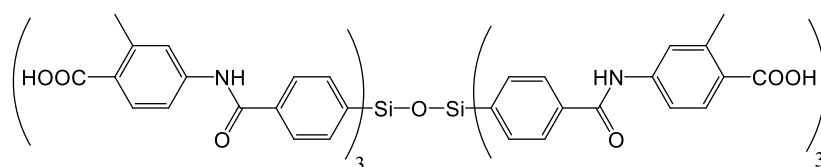
4.5 Attempted MOF Synthesis using Other Linkers

The other hexacarboxylic acids (**L5-H₆**–**L10-H₆**) prepared and described in Chapter 2 were investigated for MOF synthesis using a variety of metal precursors such as In, Fe, Cu, Zn, and Tb (see Table S4), under varying conditions; however, most attempts were not promising, yielding either powders that were found to be non-crystalline by PXRD or crystals unsuitable for SCXRD analysis. Some attempts were more promising and warrant further investigation. For example, treatment of **L6-H₆** (Figure 71) with In(NO₃)₃·5H₂O in a 1:1 mixture of DMF and MeCN with the addition of HNO₃ at 80 °C produced colourless tear-shaped crystals (**L6-In**). PXRD of the bulk sample confirmed that crystallinity was retained throughout the isolation procedure and after overnight airdrying (Figure S4). However, time constraints prevented

further stability tests and SCXRD characterisation. The treatment of **L7-H₆** with $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ under the same conditions afforded colourless needle-shaped crystals, but PXRD showed loss of crystallinity upon isolation and air drying, highlighting the challenge of forming stable In-based MOFs from amide-extended disiloxane linkers. Accordingly, no further studies were carried out on this material.



L6-H₆



L7-H₆

Figure 71: Structures of **L6-H₆** and **L7-H₆**.

4.6 Conclusion

The hexacarboxylic acid **L1-H₆** was employed in MOFs synthesis, affording 10 novel 3D MOFs based on trivalent or divalent or monovalent metals. This linker was found to undergo complete deprotonation when treated with divalent and trivalent metals, but incomplete deprotonation with alkali metals, demonstrating its broad coordination versatility. In most cases, the disiloxane linkage adopts a bent conformation. The hexacarboxylate linker also adopts a rare *pseudo*-octahedral arrangement of carboxylic acids with staggered Ar₃Si groups (along the Si–O–Si axis). This has led to the formation of MOFs with uncommon topologies such as **nia**, **fsy**, and **fsh**, which represent a significant expansion to the family of hexacarboxylate MOFs that is known to exhibit a limited range of topologies (typically **rht**).

The treatment of **L1-H₆** with a various trivalent metal precursors yielded a series of novel isostructural MOFs, including an Al-based MOF that showed the highest thermal stability (up to 450 °C), BET surface area (935 m²/g at 77 K) and CO₂ uptake (9.07 wt% at 298 K, 1 bar) among the series. In addition, the Fe-based MOFs displayed a remarkable water stability making them promising candidates for applications such as phosphate and PFOA removal, which are investigated in Chapter 5. **L1-Tb** and **L1-Eu** represent rare examples of lanthanide MOFs built from an organosilicon hexacarboxylate linker, with potential for sensing applications. **L1-Cu**, with the rare **fsy** topology, showed reversible dehydration while preserving crystallinity. Although gas sorption studies have not been conducted on this material, this represents a direction for future work. Treatment of the same hexa-acid with alkali metal nitrates (Li, Na, and K) afforded three novel MOFs, including two isorecticular frameworks with **nia** topology. Although these alkali metal MOFs showed non porosity when studied for N₂ sorption, modifying the activation protocol or using alternative techniques may fully activate these MOFs and achieve permanent porosity, given their remarkable thermal stability.

Finally, reticular expansion of **L1-In** via amide incorporation yielded **L4-In** with **nia** topology. This MOF represents the first example of an amide-functionalised siloxane-based MOF. Although this extension strategy has resulted in increased pore size and porosity (as calculated by Mercury), PXRD analysis on **L4-In** revealed poor air stability and decomposition upon drying under mild conditions. Overall, MOFs described in this chapter are significant additions to the rare family of organosilicon hexacarboxylate MOFs.

Although initial attempts to incorporate the other hexa-acid acid linkers into MOFs were unsuccessful, future work should continue to focus on expanding the range of MOFs to include all synthesized linkers by employing a variety of metal precursors and reaction conditions, which may lead to interesting 3D MOF structures owing to their distinct silicon backbones, multifunctionality, and the presence of side groups ($-\text{CH}_3$, $-\text{OMe}$, or $-\text{OH}$) in some of these linkers. It would also be worthwhile to investigate coupling **L4-H₆** and **L7-H₆** with other metals apart from indium (e.g., Cu(II), Fe(III), Zr(IV)) to target more stable frameworks.

Chapter 5: Fe-Based MOFs for Phosphate and PFOA Capture

5.1 Phosphate Removal from Water using MOFs

Phosphorus is an essential nutrient for living organisms and an important component in fertilizers.⁴⁴⁰ It plays a key role in the growth of the cells and in the production of DNA and RNA.⁴⁴¹ However, the widespread use of fertilizers in agriculture has resulted in increased phosphate concentrations in surface waters as rain and irrigation can wash away excess phosphate from the soil, carrying it into nearby water bodies through agriculture runoff.^{440,442} Additionally, wastewater from households and industries also increases phosphate levels in aquatic systems. This rise in phosphate concentrations promotes the overproduction of toxic algal blooms, which degrades water quality and leads to eutrophication.⁴⁴³ Therefore, removing excess phosphate from water is crucial for protecting the environment from the harmful effects of eutrophication.

In addition to its environmental consequences, phosphate discharge is subject to increasingly strict regulatory control worldwide. Water and wastewater treatment authorities are legally required to limit phosphorus concentrations in treated effluents to prevent eutrophication of downstream rivers, lakes, and other natural water bodies. International guidelines and regional regulations typically restrict total phosphorus concentrations in discharged wastewater, with recommended limits commonly ranging from 0.05 to 1.0 mg/L.^{444,445} Exceeding these limits can result in financial penalties and long-term environmental damage. Consequently, water companies and wastewater treatment facilities face growing legal and economic pressure to implement efficient and reliable phosphate removal technologies capable of meeting discharge standards.

Various techniques have been employed to remove phosphate from contaminated water bodies, including adsorption,⁴⁴⁶ biological treatment,⁴⁴⁷ precipitation,^{448,449} membrane technology,⁴⁵⁰

and crystallisation.^{451–454} Among these, adsorption is considered the most effective due to its low cost, operational simplicity, environmental friendliness, ability to remove pollutants to ultra-low levels, and high adsorption capacities.^{440,455,456}

An ideal phosphate adsorbent should possess a high surface area, excellent adsorption capacity and selectivity, chemical and thermal stability, and good recyclability.^{453,457} To meet these criteria, a wide range of phosphate removal adsorbents have been explored including graphene oxide,⁴⁵⁸ mesoporous silicon nanoparticles,⁴⁵⁹ organic polymers,⁴⁶⁰ and activated carbons.⁴⁶¹ Nonetheless, these materials usually exhibit poor selectivity towards phosphate due to nonspecific interactions between adsorbents and phosphate ions.⁴⁵³ As a result, incorporating metals such as Al, Fe, Zr, or La into adsorbent materials has become a widely adopted strategy, owing to the strong and selective interactions between these metal sites and phosphate ions in solution.^{442,462,463} Metal oxides/hydroxides have also been investigated as phosphate adsorbents; however, their performance is frequently limited in the presence of competing anions, leading to a reduction in adsorption capacity.^{462,464–466}

MOFs have attracted considerable interest as solid adsorbents due to their unique properties including large surface area, and permanent porosity. They have shown strong adsorption performance in the removal of various water pollutants, such as organic dyes,⁴⁶⁷ heavy metal ions,^{468,469} phenols,⁴⁷⁰ and humic acid,^{471,472} with some examples achieving higher removal capacities and efficiencies than conventional adsorbents such as activated carbons.^{469,473} Moreover, MOFs can be readily functionalised and modified through the use of different organic linkers, further enhancing their surface area and adsorption capacity. Although more than 100,000 MOF structures have been reported, only a very small fraction have been investigated as phosphate adsorbents. Examples include La-based,^{474,475} Zr-based,^{463,476,477} Ce-based,^{478–480} and Fe-based MOFs.^{442,472,481,482} These materials display effective performance in phosphate capture, which can be attributed to strong interactions between phosphate ions and

saturated or unsaturated metal centres in the framework, as well as the presence of functional groups such as amines or carboxylic acids, in addition to their high surface area.⁴⁸³

UiO-66 type MOFs have been widely studied for phosphate uptake due to their high stability and ability to remove pollutants.^{484,485} Lin *et al.* reported the use of Zr-based MOFs, including UiO-66 and UiO-66-NH₂, for phosphate removal from water and urine, showing high adsorption capacity and selectivity toward phosphate over other anions such as bromate, nitrite, and nitrate.⁴⁸⁶ UiO-66-NH₂ showed higher adsorption capacity (92 mg/g compared to 85 mg/g at 20 °C for UiO-66 at 20 °C) attributed to the presence of amine groups, which provide additional adsorption sites for phosphate ions (Figure 72). Under acidic conditions, the –NH₂ groups in UiO-66-NH₂ are protonated to –NH₃⁺ groups, thereby increasing the electrostatic attraction between the adsorbent and the negatively charged phosphate species (HPO₄²⁻ and H₂PO₄⁻) and enhancing adsorption capacity.⁴⁵³ Furthermore, UiO-66 and UiO-66-NH₂ MOFs were shown to be easily recyclable and reusable using a 1% NaCl solution, achieving up to 85% regeneration efficiency.⁴⁸⁶ In addition, doping UiO-66-NH₂ with cerium resulted in Ce-UiO-66-NH₂, which demonstrated outstanding performance as a phosphate adsorbent, with a maximum adsorption capacity ($q_{\max}$) of 211.86 mg/g.⁴⁸⁷ This improvement is attributed to the higher number of active sites in Ce-UiO-66-NH₂, which facilitated ligand exchange between Ce/Zr–OH groups and phosphate ions, thereby enhancing selectivity and adsorption efficiency.⁴⁵³

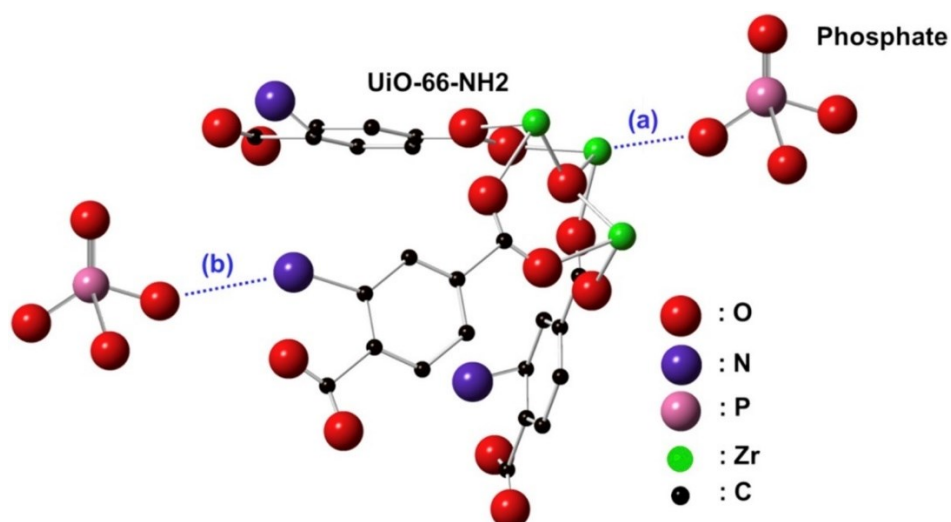


Figure 72: Proposed adsorption mechanisms of phosphate on UiO-66 and UiO-66-NH₂: (a) electrostatic interactions between Zr metal sites and O atoms of phosphate; (b) additional electrostatic interactions in UiO-66-NH₂ between the primary amine groups of the linker and O atoms of phosphate. Reproduced from Ref. ⁴⁸⁶ with permission.

Zhao and co-workers demonstrated that tuning the particle size of UiO-66 can significantly enhance phosphate removal efficiency and sorption kinetics.⁴⁸⁸ They synthesised three UiO-66 samples of varying sizes, UiO-66-1, UiO-66-2, and UiO-66-3, in increasing order of size (30–70 nm, 400–500 nm, and 1.0–1.3 μm , respectively), by modifying the amount of acetic acid and the reaction time during solvothermal synthesis. All three samples exhibited impressive phosphate adsorption capacities, with uptake increasing as particle size decreased. UiO-66-1, the smallest of the series, achieved the highest capacity at 415 mg/g (at pH 7), surpassing most previously reported phosphate adsorbents. Furthermore, these MOFs demonstrated strong phosphate removal performance in complex real water samples, highlighting their potential for practical, real-world applications.

While most MOFs with phosphate adsorption capabilities are microporous, Wu *et al.* recently synthesised a novel UiO-66-NH₂ MOF with hierarchical porosity using MOF-5 as a template.⁴⁸⁹ The resulting HUiO-66-NH₂(X) retained the structural integrity of the microporous UiO-66-NH₂ framework while incorporating a large number of mesopores. Additionally,

HUiO-66-NH₂-HTC exhibited an excellent maximum adsorption capacity ($q_{\max}$) of 226.7 mg/g, alongside impressive reusability. Despite these advances, there remains a need for more environmentally friendly, cost-effective and selective phosphate adsorbent alternatives.

Fe-based MOFs have attracted attention as being promising adsorbents for phosphate due to high abundance of Fe in the earth's crust, environment friendly nature, low cost and low toxicity, desirable physicochemical properties, high surface area and stability.^{442,490} These MOFs exhibit strong affinity between saturated or unsaturated Fe metal sites and phosphate ions, and can adsorb phosphate primarily through ligand exchange with surface hydroxyl groups and electrostatic interactions, which are pH-dependent.^{472,482,483} Additionally, many Fe-based MOFs, such as MIL-101(Fe),⁴⁸² possess large surface areas and high pore volumes, further enhancing their potential for phosphate capture.

Xie *et al.* have investigated the phosphate removal performance of two Fe-based MIL-101 MOFs, MIL-101(Fe) and NH₂-MIL-101(Fe), in both aqueous solutions and real eutrophic water samples at pH 7.⁴⁸² These MOFs were synthesized via a simple solvothermal method and exhibited high adsorption capacities, reaching 107.70 mg/g for MIL-101(Fe) and 124.38 mg/g for NH₂-MIL-101(Fe). The enhanced performance of NH₂-MIL-101(Fe) was attributed to the amine group, which facilitated stronger interactions with phosphate ions. Both materials displayed rapid phosphate uptake, strong selectivity over competing anions such as bromide, chloride, nitrate, and sulphate, and maintained effective removal efficiency in real eutrophic water samples. Furthermore, they demonstrated excellent reusability, highlighting their potential for practical water treatment applications.

Subsequently, Nehra *et al.* synthesized MIL-100(Fe) using trimesic acid via hydrothermal synthesis and evaluated its performance in removing phosphate from eutrophic water samples.⁴⁷² MIL-100(Fe) achieved a maximum phosphate adsorption capacity of 93.6 mg/g at pH 4 and room temperature, attributed to electrostatic interactions between the partially

positively charged Fe sites and negatively charged phosphate species. Its effectiveness was further confirmed in six real eutrophic water samples (Figure 73), where adsorption efficiency was found to depend on the initial phosphate concentration, with the highest efficiency observed for the tap water sample. However, the presence of co-existing ions in the samples reduced phosphate removal efficiency due to competitive adsorption.

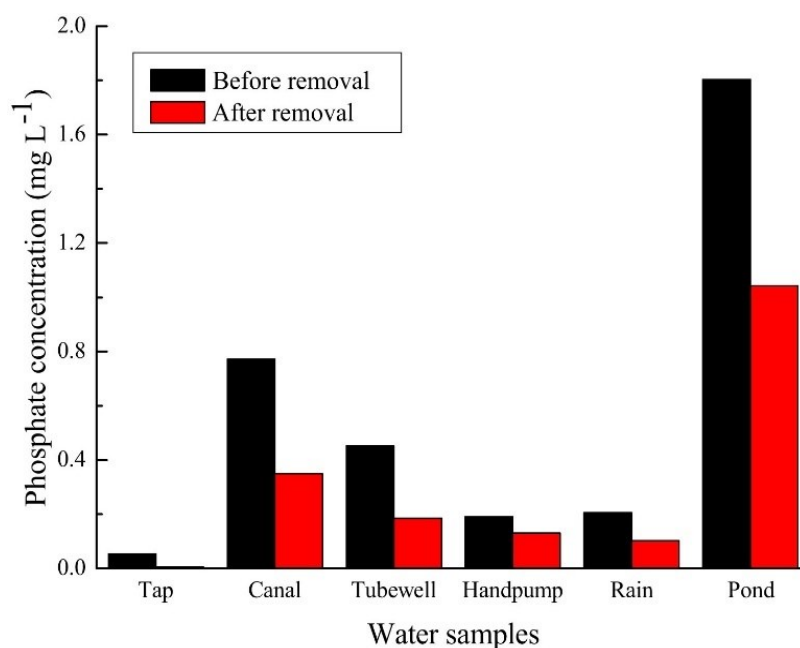


Figure 73: Phosphate removal efficiency of MIL-100(Fe) from six real water samples (Adsorbent, 70 mg; V = 1 L; pH = 7). Reproduced from Ref. ⁴⁷² with permission.

Building on the studies by Xie *et al.* and Nehra *et al.* on iron-based MOFs for phosphate removal from aqueous solutions, Chi and co-workers developed a hybrid composite adsorbent, MIL-101(Fe)/sugarcane bagasse (SCB), which demonstrated high selectivity toward phosphate, enhanced stability, and a significantly higher adsorption capacity (211 mg/g at pH 5.3) compared to MIL-101(Fe) (158 mg/g) under the same conditions.⁴⁸¹ This highlights the preparation of hybrid composite adsorbents as an effective approach for improving both their stability and adsorption performance, thereby enhancing their suitability for practical applications.

5.2 PFOA Removal from Water using MOFs

While phosphate contamination is a critical environmental issue, it is not the only threat to water quality. Another class of emerging contaminants receiving increasing attention is per- and polyfluoroalkyl substances (PFAS). PFAS are synthetic aliphatic compounds consisting of molecules that are either fully or partially fluorinated.⁴⁹¹ They contain hydrophobic carbon–fluorine (C–F) bonds, among the strongest covalent bonds in organic chemistry, with bond energies reaching up to 488 kJ/mol.^{110,492} This extraordinary bond strength contributes to the exceptional chemical and thermal stability of PFAS, which has led to their widespread use as surfactants in various industries and products, including medicine, electronics manufacturing, packaging, cosmetics, and the production of polytetrafluoroethylene. They are also incorporated into water-, oil-, and stain-repellent coatings for textiles and food packaging, and are used in aqueous film-forming foams for fire suppression.^{493–496} However, PFAS are often referred to as "forever chemicals" due to their environmental persistence, arising from the remarkable strength of their C–F bonds.^{110,496} As a result of their extensive global use and resistance to degradation, PFAS have become significant contaminants in water bodies, posing serious risks to both environmental and human health.⁴⁹⁷

Among PFAS compounds, the long-chain variant perfluorooctanoic acid (PFOA), which has a high water solubility of ~9.5 g/L due to its hydrophilic carboxylic acid group,^{110,495} is the most commonly used PFAS.^{496,498} The International Agency for Research on Cancer (IARC) has identified a strong link between PFOA exposure and testicular and kidney cancers.⁴⁹⁸ In 2024, the U.S. Environmental Protection Agency (EPA) finalised the first legally enforceable national drinking water standards for six per- and polyfluoroalkyl substances, including PFOA. The Maximum Contaminant Levels (MCLs) for PFOA was set at 4 ng/L, in response to growing concerns about its harmful effects on human health and the environment.⁴⁹⁹

A range of methods has been explored to address PFAS contamination; however, traditional approaches, including bioremediation, UV disinfection, and electrocoagulation, have proven challenging due to the high chemical stability and hydrophilicity of PFAS, along with their typically low concentrations in water.⁴⁹⁶ Recent advances have introduced more effective strategies, including adsorption,^{110,493,497,500} electrochemical oxidation,⁵⁰¹ photocatalysis,⁵⁰² bioremediation,⁵⁰³ and some others.⁵⁰⁴ Among these, adsorption remains the most widely used technique for PFAS removal, owing to its simplicity, cost-effectiveness, and high efficiency.^{110,493,496}

Compared with other porous materials, MOFs have emerged as ideal candidates for PFAS removal due to their unique structural features and exceptional porosity. Research into using MOFs as innovative adsorbents for PFAS removal from water began in 2015, when Yu and co-workers investigated PFOA adsorption on MIL-101Cr-based MOFs, reporting high adsorption capacities ranging from 290 to 754 mg/g.⁵⁰⁵ This notable performance prompted further studies on various MOFs for PFAS removal, including ZIF-8,⁵⁰⁶ UiO-66,⁵⁰⁷ MIL-101-Fe,⁵⁰⁸ MIL-100-Fe,⁵⁰⁸ NU-1000,⁵⁰⁹ PCN-999,¹¹⁰ and UiO-66-N(CH₃)₃⁺,⁵¹⁰ with most work focusing on the adsorption of PFOA and PFOS in water.^{497,509,511,512}

Zhang and co-workers investigated the PFOA adsorption performance of three Fe-based MOFs: Fe-BTC, MIL-100-Fe, and MIL-101-Fe.⁵⁰⁸ This was the first study to report PFOA adsorption using Fe-based MOFs. The adsorption capacities were 418 mg/g for Fe-BTC, 349 mg/g for MIL-100(Fe), and 370 mg/g for MIL-101(Fe), all of which were higher than those of other MOFs evaluated in the same study, such as Ce-BTC (210 mg/g), Mn-BTC (130 mg/g), and Cu-BTC (95 mg/g), indicating a stronger affinity between PFOA and Fe-based MOFs. Additionally, the effect of pH on the adsorption of PFOA by the three Fe-based MOFs was investigated over the range of 3–11, with the adsorption capacities found to decrease as pH increased (Figure 74). This trend was attributed to electrostatic repulsion between the

negatively charged surface of the Fe-based MOFs (at higher pH) and the deprotonated PFOA molecules. At low pH, however, the carboxyl group of PFOA can engage in hydrogen bonding with the protonated Fe-based MOFs, resulting in higher adsorption capacities. These findings highlight the significant influence of pH on the surface properties and protonation state of functional groups in the MOFs. Other parameters such as initial PFOA concentration, and MOF dosage was also found to affect adsorption performance of the Fe-based MOFs. For instance, increasing the dosage of Fe-BTC led to a higher removal efficiency of PFOA from the aqueous solution. Similarly, as the initial concentration of PFOA increased, the adsorption capacity also increased. Based on the reported results, the removal rate was most strongly affected by pH, followed by adsorbent dosage, and then the initial concentration.

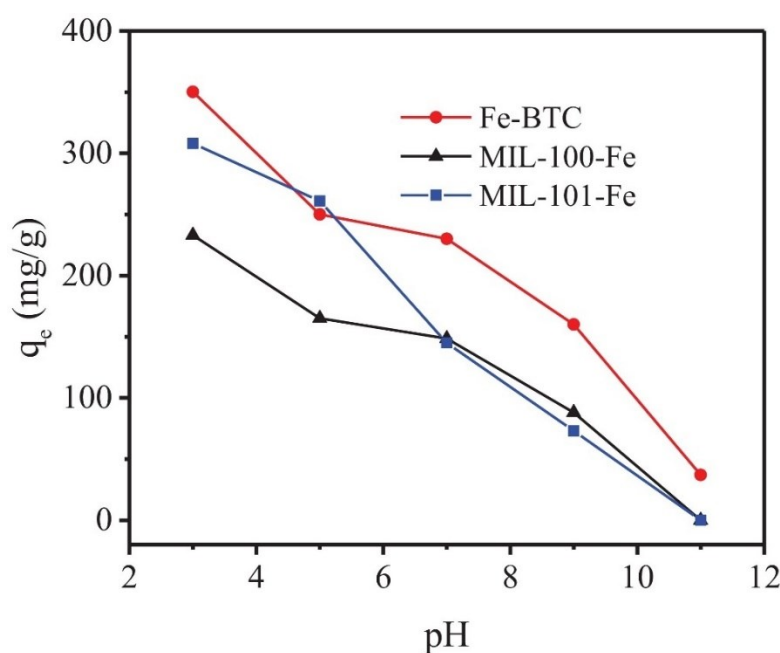


Figure 74: Influence of pH on PFOA adsorption by Fe-based MOFs. Reproduced from Ref. ⁵⁰⁸ with permission.

Four years later, Liang *et al.* have reported the synthesis of a zirconium-based MOF, PCN-999 (Figure 75).¹¹⁰ This MOF was constructed via linker desymmetrization and contained two types of metal-based clusters: Zr_6 and biformate-bridged $(Zr_6)_2$ units. PCN-999 is the first MOF built using an eight-connected $(Zr_6)_2$ SBU, providing multiple coordination sites for PFOA binding.

Additionally, PCN-999 features a unique hierarchically porous architecture consisting of two types of one-dimensional channels along the a axis: hexagonal mesopores (~ 22 Å) and rhombic micropores (~ 12 Å), as shown in Figure 75d. Owing to this hierarchical structure, as well as its excellent thermal, chemical, and water stability (conferred by strong Zr–O bonds), PCN-999 demonstrated an exceptional PFOA adsorption capacity of 1089 mg/g in water at an equilibrium concentration of 3911 ppm (Figure 76). This remains one of the highest reported PFOA adsorption capacity among all adsorbent materials, including MOFs. Furthermore, PCN-999 exhibited rapid adsorption kinetics, high selectivity toward PFOA over co-existing ions (e.g. Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Fe^{3+} , Al^{3+} , Mn^{2+} , Zn^{2+} , Cl^- , NO_3^- , SO_4^{2-} , and CH_3COO^-), and excellent recyclability.

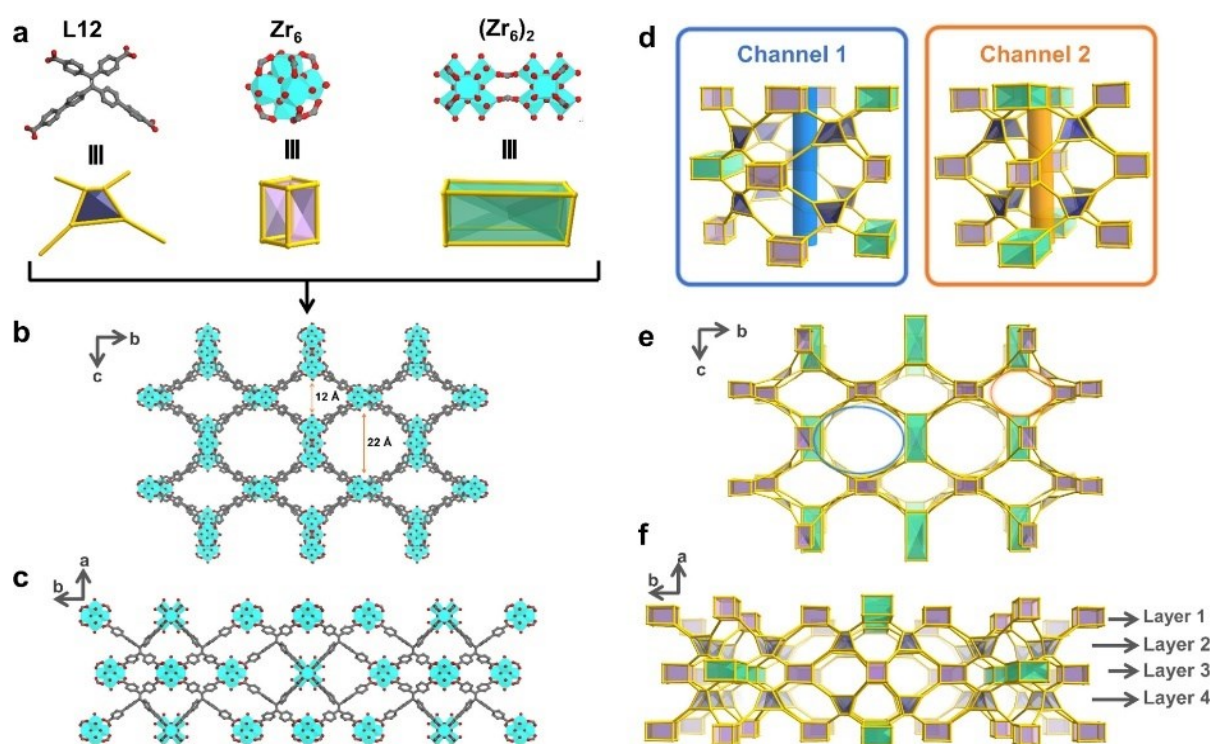


Figure 75: (a) Ligand used in PCN-999 synthesis and the two types of metal clusters; (b) a portion of the packing structure along the a axis and (c) c axis; (d) topological illustration showing two types of 1D channels, viewed along the (e) a axis and (f) c axis. Colour scheme: C, grey; O, red; Zr, cyan. H atoms are omitted for clarity. Reproduced from Ref. ¹¹⁰ with permission.

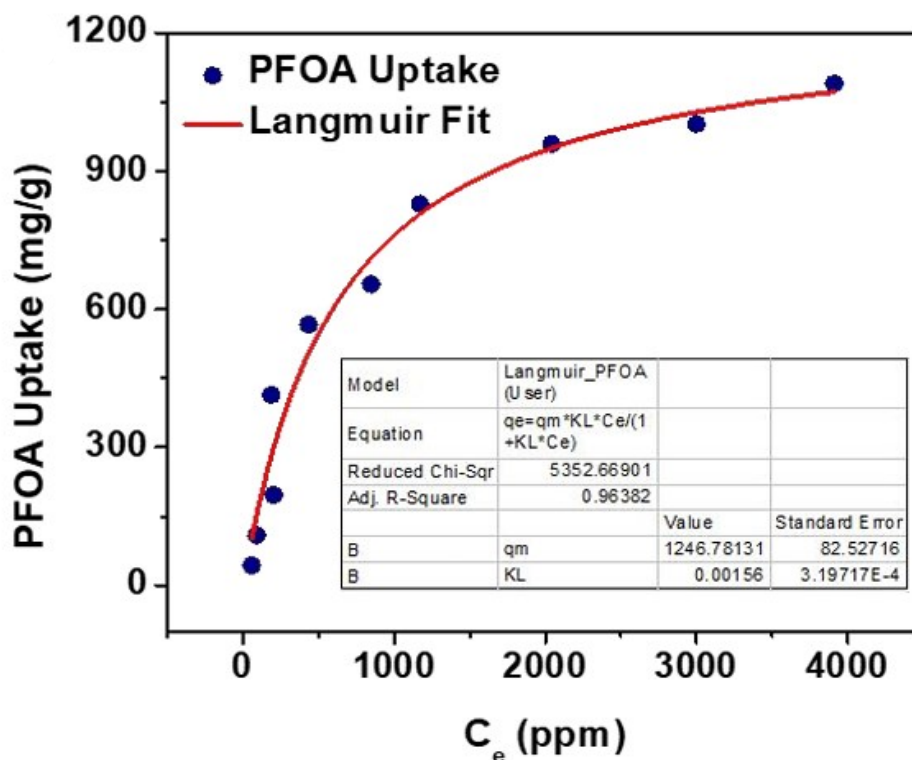


Figure 76: Langmuir plot of the isotherm for PFOA adsorption on PCN-999. The isotherm was derived from experimental data obtained using initial concentrations of PFOA between 100 and 5000 ppm and subsequently fitted to the Langmuir model. Reproduced from Ref. ¹¹⁰ with permission.

Recently, Zang and co-workers reported $\text{UiO-66-N}(\text{CH}_3)_3^+$,⁵¹⁰ a MOF capable of both efficient removal and fluorescent detection of PFOA from water, synthesised via post-synthetic modification of $\text{UiO-66-NH}_2(\text{Zr})$ with methyl iodide. The introduction of the cationic ammonium group in $\text{UiO-66-N}(\text{CH}_3)_3^+$ led to markedly enhanced electrostatic interaction with anionic PFOA, and as a result the material combined high adsorption capacity with improved selectivity. In an adsorption experiment using an adsorbent dosage of 500 mg/L in a 1000 ppm PFOA solution, an uptake of 665 mg/g was achieved within 30 min. In addition, the adsorption capacity of $\text{UiO-66-N}(\text{CH}_3)_3^+$ was estimated by the Langmuir model to be 1178 mg/g, higher than most previously reported adsorbent materials, including MOFs. Notably, the remarkable performance was maintained in the presence of salts commonly found in real water samples

(such as MgCl_2 , CaCl_2 , KCl , Na_2SO_4 , $\text{Zn}(\text{NO}_3)_2$). Performance was also evaluated under environmentally related and scalable conditions (20 mg/L of adsorbent; 50 ppb PFOA), under which 99% removal was achieved within 5 min. $\text{UiO-66-N}(\text{CH}_3)_3^+$ also displayed excellent stability and reusability, highlighting potential for practical real-world water treatment applications.

5.3 L1-Fe-based MOFs for Phosphate and PFOA Removal

Water stability is a critical factor for the effective application of MOFs in the removal of phosphate and PFOA from contaminated water. Water-stable MOFs are defined as those that retain their crystallinity and porosity after exposure to water, as confirmed by comparative PXRD and BET analyses. Although several water-stable MOFs have been reported, the majority display poor stability in aqueous environments, limiting their practical applicability and underscoring the need for further discovery in this area.³⁹³

Highly connected organosilicon carboxylate linkers, due to their hydrophobicity, structural integrity, synthetic accessibility, and ease of modification, are promising candidates for constructing such stable frameworks.^{184,194} In particular, we have found that **L1-H₆** facilitated the formation of water-stable MOFs when coordinated with Fe(III)-based precursors (as described in Chapter 4), potentially enhancing their suitability for phosphate and PFOA removal.

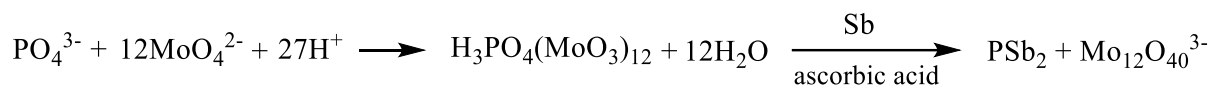
Motivated by these considerations, as well as the findings presented in Sections 5.1 and 5.2 and the limited availability of stable Fe-based MOFs for phosphate and PFOA adsorption, we investigated the performance of **L1-Fe** and **L1-Fe-Cl**. These MOFs are cationic (which may enhance interactions with phosphate anions and PFOA), permanently porous, and exhibit remarkable water stability, demonstrating strong potential for efficient phosphate and PFOA capture. As mentioned in this chapter, adsorption offers a convenient, cost-effective, and

environmentally friendly approach that can achieve high uptake capacities. For these reasons, it was adopted for both phosphate and PFOA removal studies.

5.3.1 L1-Fe-based MOFs for Phosphate Capture

5.3.1.1 The Molybdenum Blue Method

The molybdenum blue method, originally developed by Murphy and Riley and later modified in several studies, is the most widely used technique for determining phosphate concentrations in aqueous solutions.^{513–515} This method involves the formation of 12-molybdophosphoric acid, which is subsequently reduced in the presence of antimony, typically using ascorbic acid or stannous chloride, to produce the intensely coloured molybdenum blue complex (Equation 22). The intensity of the colour is directly proportional to the concentration of orthophosphate ions incorporated into the complex. The resulting blue solution can then be measured colorimetrically at a wavelength of 880 nm to quantify the phosphate concentration. Ascorbic acid is generally preferred over stannous chloride as the reducing agent because it produces a more stable colour and is less sensitive to variations in temperature and salt concentrations. However, it is important to note that the use of ascorbic acid results in a relatively slow rate of colour development. Therefore, phosphate concentration measurements must be taken only after full colour development to avoid analytical errors.⁵¹⁵ Notably, there are several factors that can significantly influence the formation rate of the phosphomolybdenum blue complex, including reagent concentrations, reactant stoichiometry, and the temperature of the final solution.⁵¹⁵ Taking all these considerations into account, the ascorbic acid-based molybdenum blue method was adopted in this study to determine phosphate concentrations in solution before and after treatment with **L1-Fe** and **L1-Fe-Cl** adsorbents.



Equation 22: The general reaction for the determination of phosphate using the molybdenum blue method.⁵¹⁶

5.3.1.2 Phosphate Adsorption Experiment using L1-Fe and L1-Fe-Cl

The phosphate adsorption performance of **L1-Fe** and **L1-Fe-Cl** was studied in different batch experiments. In each experiment, 15 mg of the MOF was added to 15 mL of phosphate solution (10–100 mg/L) in a Falcon tube to investigate the effect of initial adsorbate concentration on adsorption capacity. The tubes were agitated at 250 rpm for 4 h using a rotatory shaker. Following treatment, the solutions were filtered, and the concentration of phosphate in the filtrate was determined using the molybdenum blue spectrophotometric method.⁵¹⁴ Phosphate concentrations were analysed using UV-vis spectrophotometry, with absorbance measured at 880 nm.

The initial and equilibrium concentration, C_i and C_e , of phosphate in aqueous solutions was calculated using the Beer-Lambert law,⁵¹⁷ which is commonly employed to determine analyte concentrations in liquid samples. The Beer-Lambert law can be expressed as:

$$A = -\log_{10} \frac{P}{P_0} = \epsilon bc$$

where A is the absorbance of the sample solution, P_0 and P are the incident and transmitted radiant powers (intensities), respectively, ϵ is the absorptivity or the extinction coefficient, b is the length of the beam in the absorbing medium (in this case 10 mm), and c is the concentration of the absorbing species.

The phosphate removal efficiency was then calculated using the following equation:⁵¹⁸

$$\text{Removal efficiency (\%)} = \frac{C_i - C_e}{C_i} \times 100$$

where C_i and C_e represent the initial and equilibrium metal ion concentration (mg/L), respectively.

The phosphate removal efficiency was consistently higher for **L1-Fe-Cl** compared to **L1-Fe**, as shown in Figure 77. This was expected, given its higher BET surface area (670 m²/g) compared to **L1-Fe** (566 m²/g). In addition, the smaller counter-anion in **L1-Fe-Cl** (Cl⁻, relative to NO₃⁻ in **L1-Fe** in terms of ionic radii) is likely held less strongly and therefore more readily displaced,^{519,520} facilitating anion exchange adsorption of phosphate which may be the primary mechanism. Phosphate removal efficiency was also found to be inversely dependent on the initial phosphate concentration. For both MOFs, removal percentages increased as the phosphate concentration decreased from 100 to 10 mg/L. This trend is typical for adsorption systems, where a higher ratio of available adsorption sites to phosphate ions at lower concentrations facilitates more effective phosphate removal from solution.⁴⁷²

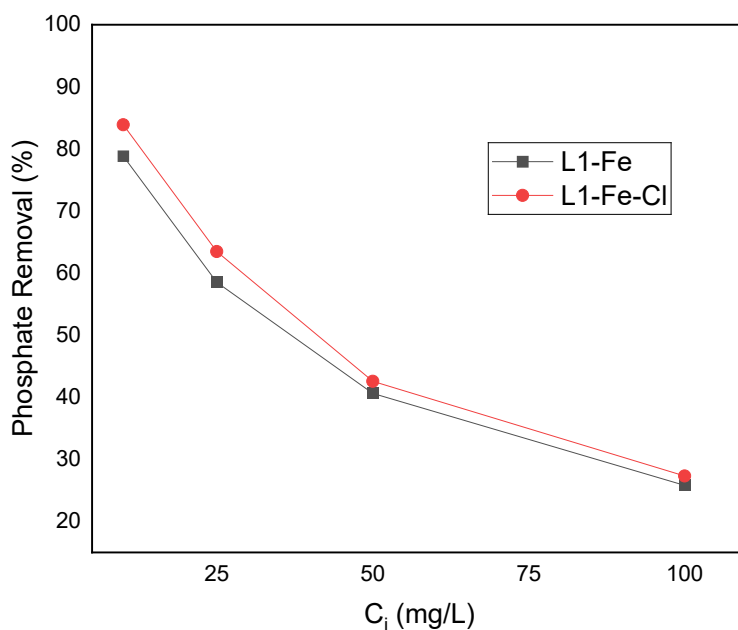


Figure 77: Phosphate removal efficiency (%) of **L1-Fe** and **L1-Fe-Cl** by adsorbate concentration (MOF, 15 mg; $V = 15$ mL, extraction time: 4 h).

Additionally, a mass balance equation was employed to calculate the equilibrium adsorption capacity (q , mg/g),⁴⁶⁹ as expressed by the following formula:

$$q_e = \frac{V}{m} (C_i - C_e)$$

where V is the volume of the adsorbate solution (L), and m is the mass of the adsorbent (g).

The Langmuir and Freundlich isotherm models were applied to fit the experimental equilibrium data.^{124,521} These models are commonly used to describe the adsorption behaviour of adsorbents and to understand the relationship between the adsorption capacity and the equilibrium adsorption in solution. The Langmuir model assumes monolayer adsorption on a homogeneous surface with a finite number of identical adsorption sites. The maximum adsorption capacity ($q_{\max}$) is reached when all sites are occupied, preventing further adsorption. The linear form of the Langmuir equation is given by:

$$\frac{C_e}{q_e} = \frac{1}{q_m \times K_L} + \frac{1}{q_m} C_e$$

where K_L ($L \cdot mg^{-1}$) is the Langmuir adsorption constant, related to the affinity of the adsorbate for the adsorbent.¹²⁴

In contrast, the Freundlich model describes adsorption on heterogeneous surfaces, where varying adsorption energies lead to multilayer adsorption.^{521,522} Due to the presence of sites with differing affinities, the model does not define a clear maximum adsorption capacity. The Freundlich model equation is given as:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$$

where K_f is the Freundlich adsorption capacity constant (mg/g), and $1/n$ is the adsorption intensity constant.⁴⁷²

Experimental data were found to fit the Langmuir model better than the Freundlich model (Figures 78 and 79), with high correlation coefficients (R^2) exceeding 0.99 for both **L1-Fe** and **L1-Fe-Cl**. Based on Langmuir analysis, the calculated maximum adsorption capacities (q_{max}) were 27.95 mg/g for **L1-Fe** and 28.71 mg/g for **L1-Fe-Cl**, with experimentally observed capacities of 25.53 and 27.02 mg/g at equilibrium concentrations of 73.39 and 71.27 mg/L , respectively.

In comparison, the Freundlich model produced slightly lower R^2 value of 0.985 and 0.984, respectively. Although the adsorption data were also described by the Freundlich model, the higher R^2 values associated with the Langmuir model indicate that it provides a more suitable representation of the adsorption behaviour. This suggests that the adsorption process predominantly involves monolayer surface interactions. Notably, several other MOF-based adsorbents for phosphate reported in the literature have also demonstrated adsorption behaviour that can be described by both the Langmuir and Freundlich isotherm models.^{479,482,486}

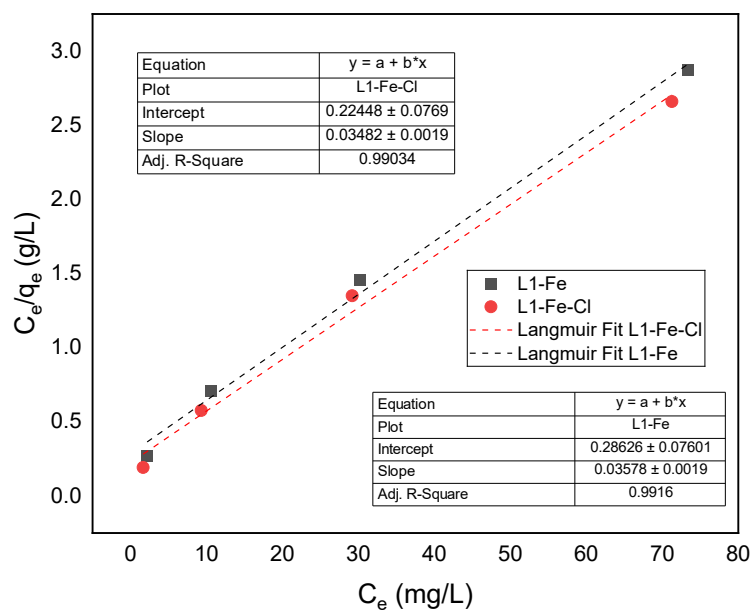


Figure 78: Linear Langmuir plots of the isotherms for phosphate adsorption on **L1-Fe** and **L1-Fe-Cl**.

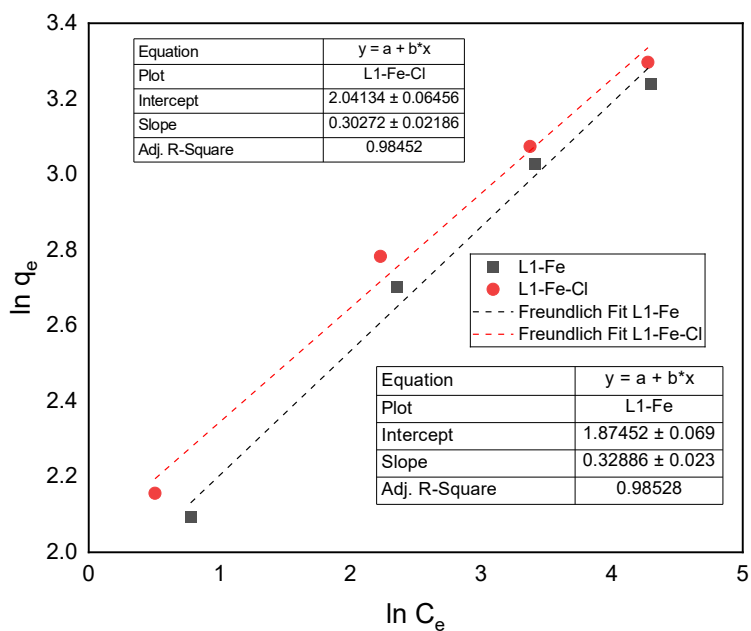


Figure 79: Linear Freundlich plots of the isotherms for phosphate adsorption on **L1-Fe** and **L1-Fe-Cl**.

Furthermore, the Langmuir separation factor (R_L) was calculated to determine the nature of the adsorption interaction, whether it is linear ($R_L = 1$), irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), or unfavourable ($R_L > 1$). The separation factor is expressed by the following equation:⁵²³

$$R_L = \frac{1}{1 + K_L \times C_i}$$

As shown in Figure 80, R_L values decreased with increasing initial phosphate concentration but remained between 0 and 1 across the studied range, confirming that the adsorption process was favourable. Additionally, the $1/n$ parameter in the Freundlich isotherm offers insight into the nature of adsorbent–adsorbate interactions.⁴⁷⁹ According to the Freundlich plot (Figure 79), $1/n$ values of 0.33 (**L1-Fe**) and 0.30 (**L1-Fe-Cl**) were obtained, indicating favourable adsorption ($0 < 1/n < 1$).

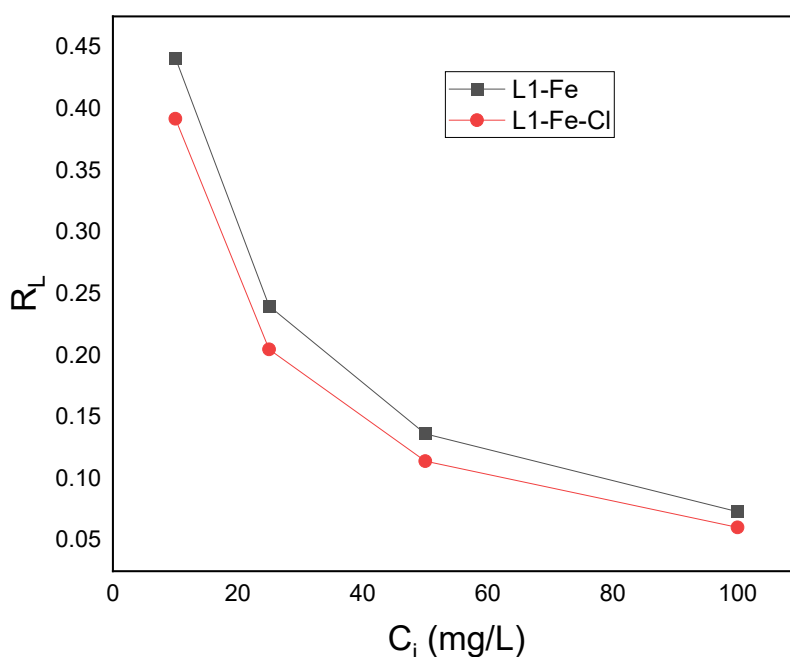


Figure 80: Plot of separation factor (R_L) with respect to initial phosphate concentrations (C_i).

Although linear regression methods are widely used in phosphate adsorption studies,^{472,482,522} they encounter problems related to inconsistent error structures, resulting mainly from axis transformations of dependent variables. As reported by Bhaskar and co-workers,⁵²⁴ nonlinear regression methods are generally more reliable, as they avoid such distortions. Therefore, the experimental data were also analysed using the nonlinear Langmuir model (Figure 81). Although the correlation coefficients slightly decreased to ~ 0.98 , the data remained consistent with Langmuir behaviour. The maximum capacities determined nonlinearly were 26.72 mg/g for **L1-Fe** and 27.18 mg/g for **L1-Fe-Cl**, values that aligned more closely with the experimental data. In addition, the isotherms clearly show that the equilibrium adsorption capacity (q_e) increases with increasing equilibrium phosphate concentration (C_e), indicating enhanced phosphate uptake as its availability in solution rises.

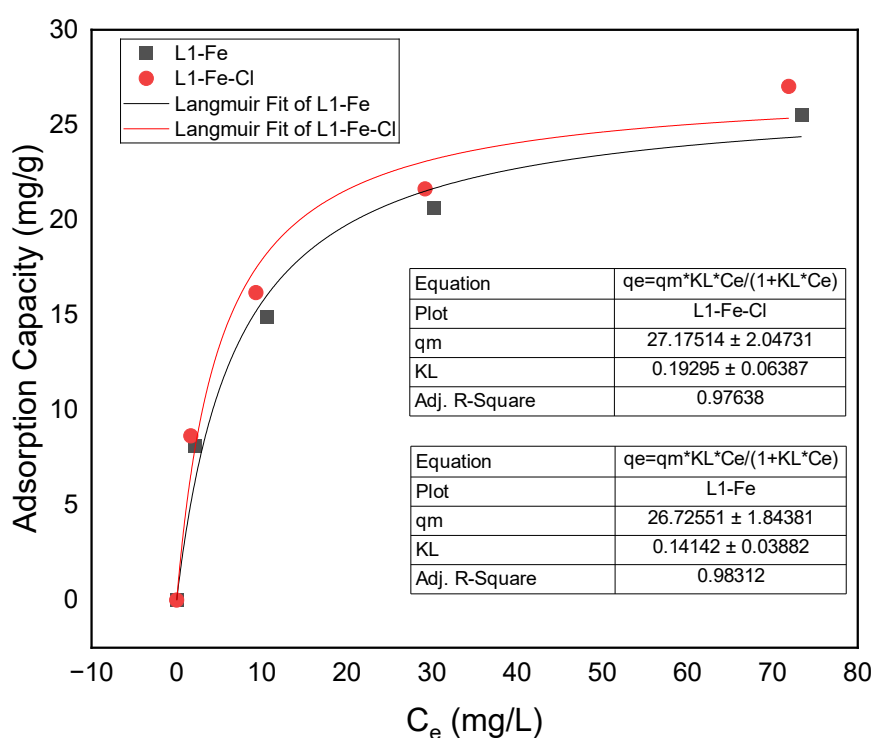


Figure 81: Nonlinear Langmuir plots of the isotherms for phosphate adsorption on **L1-Fe** and **L1-Fe-Cl**.

5.3.1.3 Recyclability L1-Fe-Based MOFs for Phosphate Adsorption

The recyclability of the Fe-based MOFs was evaluated through regeneration experiments conducted over three adsorption–desorption cycles. For each cycle, the used MOF material was regenerated by soaking in a 10 mL of 0.1% sodium chloride (NaCl) solution overnight. After treatment, the MOFs were thoroughly washed with water, dried, and reused in subsequent phosphate adsorption tests. The regeneration efficiencies of **L1-Fe** and **L1-Fe-Cl** after four cycles are presented in Figure 82. While a noticeable decrease in adsorption capacity was observed after the first regeneration cycle, both materials retained considerable phosphate removal efficiency, maintaining values above 65%. In addition, both MOFs retained their crystallinity after the adsorption–desorption cycles, as confirmed by PXRD. These results demonstrate the robustness of these MOFs and confirm that they can be easily recycled and reused multiple times for phosphate capture.

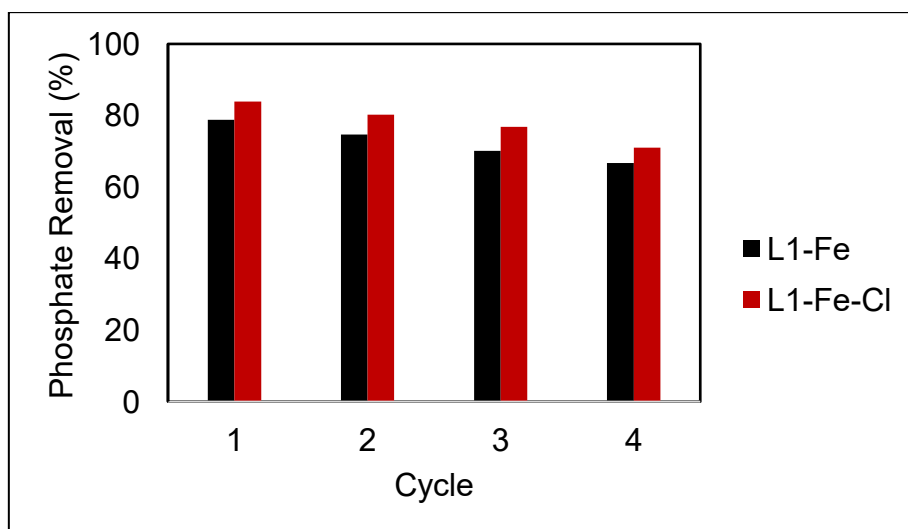


Figure 82: Recyclability tests in phosphate adsorption on **L1-Fe** and **L1-Fe-Cl** in 10 mg/L solution.

While the adsorption capacities of **L1-Fe** and **L1-Fe-Cl** are modest compared to many MOF-based adsorbents reported in the literature (Table 2), both materials have demonstrated effective phosphate uptake and the potential for multiple reuse cycles through a cost-effective

regeneration method. Moreover, given that water stability, affordable regeneration techniques, and selectivity toward phosphate ions remain key challenges in the development of MOF-based adsorbents,⁴⁵³ further investigation of **L1-Fe** and **L1-Fe-Cl** is needed. Future studies could explore the effects of adsorbent dosage and pH on adsorption capacity (which may lead to improved performance), as well as their selectivity in the presence of competing ions and adsorption kinetics, to evaluate their behaviour better and enhance their potential for practical phosphate removal applications.

Table 2: Reported phosphate adsorption capacities of different MOF adsorbents.

MOF	pH	Adsorption capacity (mg/g)	Reference
UiO-66	8	415	488
0.2La-UiO-66	7	348.82	525
La-UiO-66	7	348.43	525
La-MOF-808	9	287.71	526
NH ₂ -MIL101(Al)	5.5	243	483
Ce-UiO-66-NH ₂	3-9	211.86	487
MIL-101(Fe)/SCB ₃	5.3	211	481
Ce-BDC	4.5	179	480
MIL-101(Fe)	5.3	158.10	481
NH ₂ -MIL-101(Fe)	7	124.38	482
UiO-66-Br	4	132.50	527
UiO-66-NO ₂	4	117.70	527
NH ₂ -MIL-101 (Fe)	2-11	94.34	483
MIL-100(Fe)	7	93.60	472
ZIF-67	6.82	92.43	528
St ⁺ @UiO-66	2–5.5	80	477
UiO-66-3	2-7	73.15	529
HCl-NH ₂ -UiO-66	2	65.55	530
ZIF-8	2.8	38.22	531
L1-Fe-Cl	5.5	27.18	This work
L1-Fe	5.5	26.72	This work

Table 2 – *continued*

MOF	pH	Adsorption capacity (mg/g)	Reference
MIL-101@Zr	6.5	21.28	466
MFC@UiO-66	2	16.95	532
Fe ₃ O ₄ @NH ₂ -MIL-101(Fe)	7	9.11	533

5.3.2 PFOA Adsorption using L1-Fe-Based MOFs

PFOA adsorption experiments on **L1-Fe** and **L1-Fe-Cl** were carried out following a modified protocol from Liang *et al.*,¹¹⁰ selected for its convenience and ability to produce high efficiency with rapid kinetics. 10 mg of the MOF was dispersed in 10 mL of PFOA solution (800–3000 ppm) prepared using Milli-Q water. After being agitated for 3 days at room temperature using a rotary shaker, the solutions were filtered and the residual PFOA concentrations in the filtrates were quantified by ¹⁹F NMR spectroscopy by integrating the PFOA signal relative to a fluorinated internal standard of known concentration (e.g., 4-trifluoroethanol).

L1-Fe-Cl consistently exhibited higher PFOA removal efficiency compared to **L1-Fe** (Figure 83); therefore, it was further evaluated over a broader concentration range (100–3000 ppm). As shown in Figure 84, the removal efficiency increased with decreasing initial PFOA concentration, reaching > 99% at 100 ppm (Figures 84, and S102). This aligns with the trend previously observed for phosphate adsorption (see Figure 77). Furthermore, the IR spectra of **PFOA@L1-Fe-Cl** and **PFOA@L1-Fe** confirmed the successful loading of PFOA (Figures S45 and S46), as both spectra displayed new absorption bands at ~1235, ~1202 and ~1144 cm⁻¹, attributed to the –CF₂ asymmetric stretching, –CF₃ asymmetric stretching, and –CF₂ symmetric stretching vibrations, respectively.^{510,534} Moreover, the IR data provide preliminary insight into the Fe-based MOFs/PFOA adsorption mechanism. For example, no noticeable shift

was observed in the symmetric carboxylate stretch of the coordinated linker ($\sim 1405\text{ cm}^{-1}$) after adsorption, suggesting that anion exchange is more likely the primary adsorption mechanism rather than ligand exchange. However, further studies using additional techniques (e.g. SCXRD, molecular electrostatic potential, XPS) are required to confirm the mechanism involved.

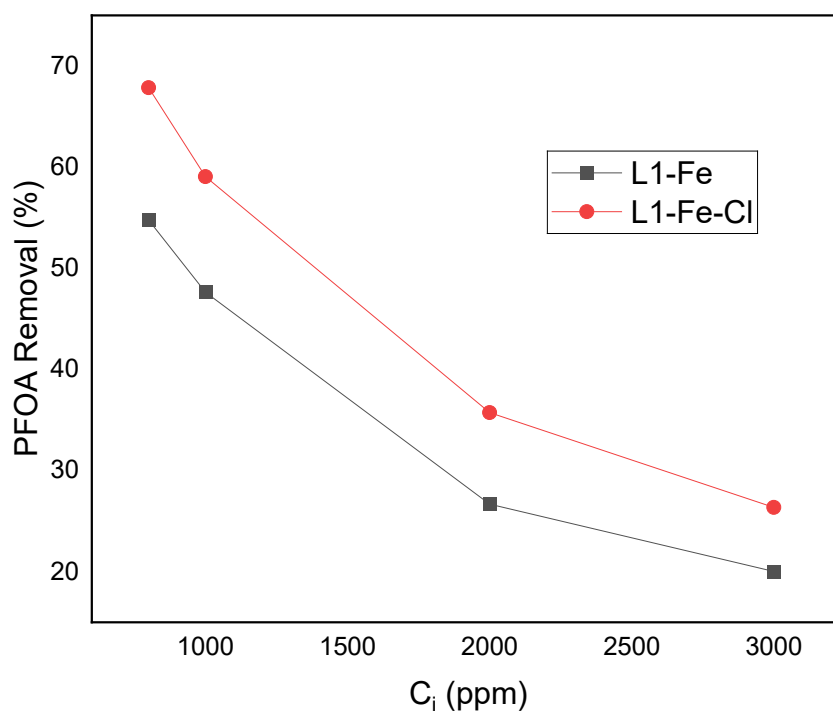


Figure 83: Percentage PFOA removal (%) of L1-Fe-Cl and L1-Fe by adsorbate concentration (MOF, 10 mg; $V = 10\text{ mL}$, extraction time: 72 hours).

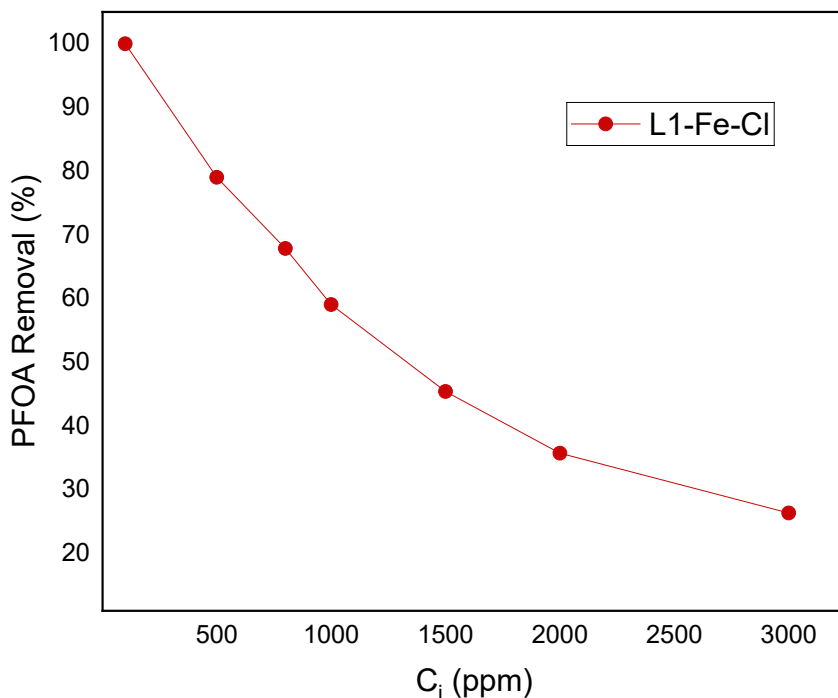


Figure 84: Percentage PFOA removal (%) of **L1-Fe-Cl** by adsorbate concentration (MOF, 10 mg; V = 10 mL, extraction time: 72 hours).

To gain deeper insight into the adsorption behaviour of **L1-Fe-Cl**, equilibrium isotherms were plotted from experimental data obtained across a PFOA concentration range of 100–3000 ppm. The adsorption data showed an agreement with the Langmuir isotherm model (Figure 85a), with a correlation coefficient value (R^2) of 0.978, whereas the Freundlich model (Figure 85b) gave a slightly lower correlation ($R^2 = 0.969$). This suggests that PFOA adsorption on **L1-Fe-Cl** follows a monolayer adsorption process rather than multilayer adsorption. According to the Langmuir isotherm, the maximum theoretical adsorption capacity (q_m) was 795 mg/g (1.92 mmol/g), closely matching the experimental value of 791 mg/g (1.91 mmol/g) at an equilibrium concentration of 2209.1 ppm. To the best of our knowledge, this is among the highest PFOA adsorption capacities reported for MOF-based adsorbents, outperforming most previously studied MOFs, including Fe-based MOFs with higher surface areas such as MIL-101(Fe) and

MIL-100(Fe) (Table 3), as well as other adsorbents like zeolites,^{535,536} MWNTs,⁵³⁷ and FCX4-P.⁵³⁸

Inspired by this outstanding performance, the adsorption kinetics were investigated, revealing that equilibrium was achieved within 10 h. Fitting the data to the *pseudo*-second-order model gave a high adsorption rate constant ($k_2 = 2.92 \times 10^{-3} \text{ g mg}^{-1} \text{ h}^{-1}$) and an excellent correlation coefficient ($R^2 = 0.99$) (Figure 86). This reflects a faster adsorption process than that of PCN-999,¹¹⁰ which is among the highest reported adsorption capacities in the literature. However, some MOF-based adsorbents, such as MIL-101(Cr), MIL-101(Cr)-QDMEN,⁵⁰⁵ and UiO-66-N(CH₃)₃⁺,⁵¹⁰ displayed even higher k_2 values and faster kinetics.

Another adsorption experiment was also conducted to investigate the effect of increasing the adsorbent dosage on PFOA adsorption efficiency. When the adsorbent-to-adsorbate ratio was raised from 1:1 to 5:1 (10 mg of MOF in 2 mL of a 1000 ppm PFOA solution), **L1-Fe-Cl** achieved nearly complete removal (~100%) within 24 h (Figure 87). This result further highlights the effectiveness of **L1-Fe-Cl** as an adsorbent for PFOA.

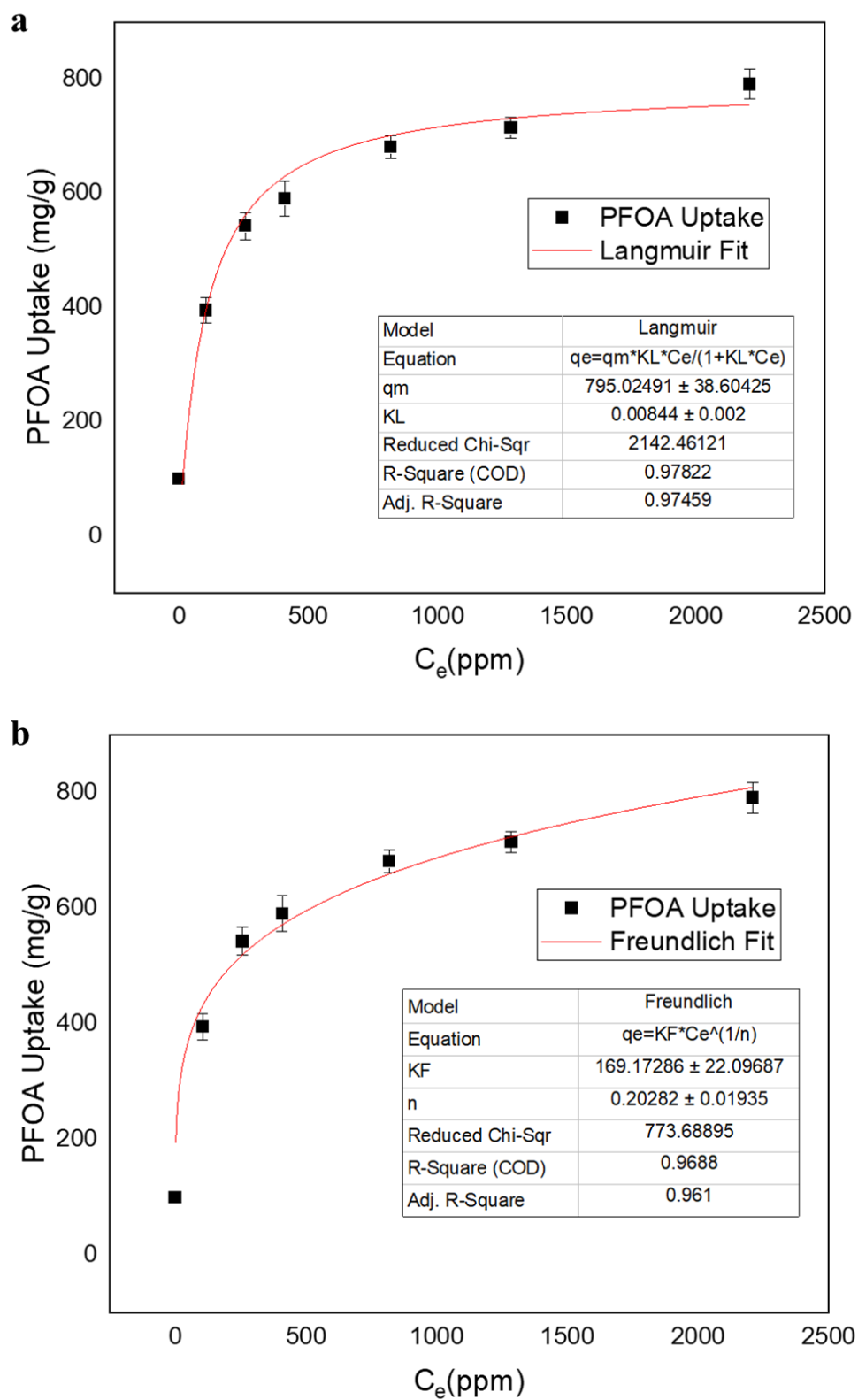


Figure 85: Langmuir (a) and Freundlich (b) plots of the isotherms for PFOA adsorption on **L1-Fe-Cl**.

Table 3: PFOA adsorption capacity of different reported MOF adsorbents.

MOF adsorbent	PFOA adsorption capacity (mg/g)	Reference
UiO-66-N(CH ₃) ₃ ⁺	1178	510
PCN-999	1089	110
L1-Fe-Cl	795	This work
MIL-101-Cr-QDMEN	753.5	505
UiO-67	743	512
NW-101	698.4	539
PCN-1002	632	294
MIL-101-Cr-DMEN	534	505
NU-1000	507	509
MIL-101-Cr-NMe ₂	493	505
UiO-66-F4	467	507
MIL-101-Cr	460	505
F-MOF	420	540
Fe-BTC	418	508
UiO-66	388	507
MIL-101-Fe	370	508
MIL-100-Fe	349	508
MIL-101-Cr-NH ₂	290	505
ZIF-L	243.8	506
ZIF-8	177.2	506
MIL-100(Al)	131.58	511
MIL-125-NH ₂	42	541
W-101	42.7	539
ZIF-7	21.5	506
C-101	12.3	539
PVA@UiO-66/GO	9.90	542

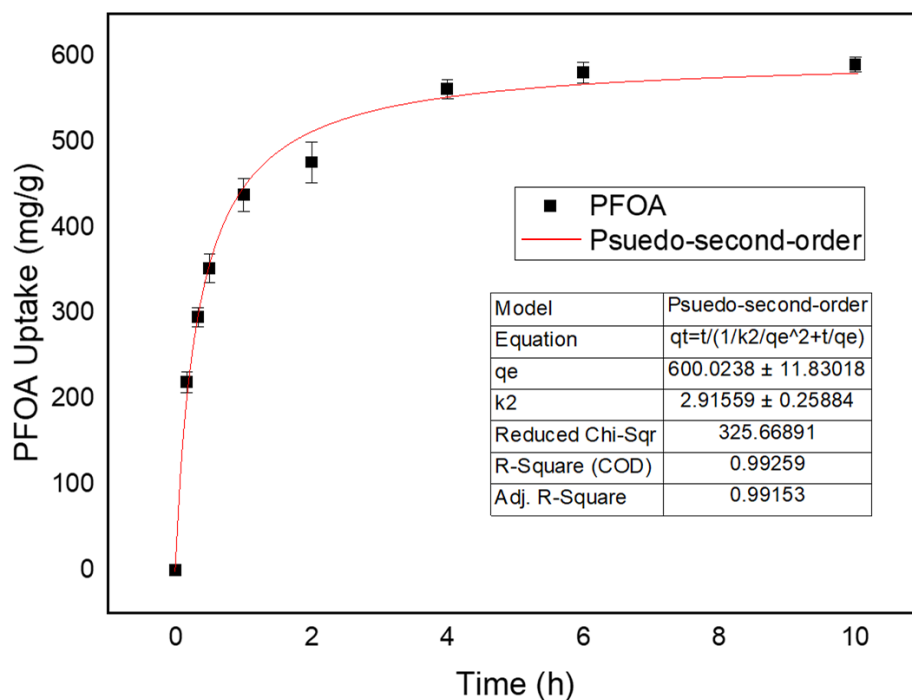


Figure 86: Sorption kinetics of PFOA into **L1-Fe-Cl** with an initial concentration of 1000 ppm, fitted with a *pseudo*-second-order model.

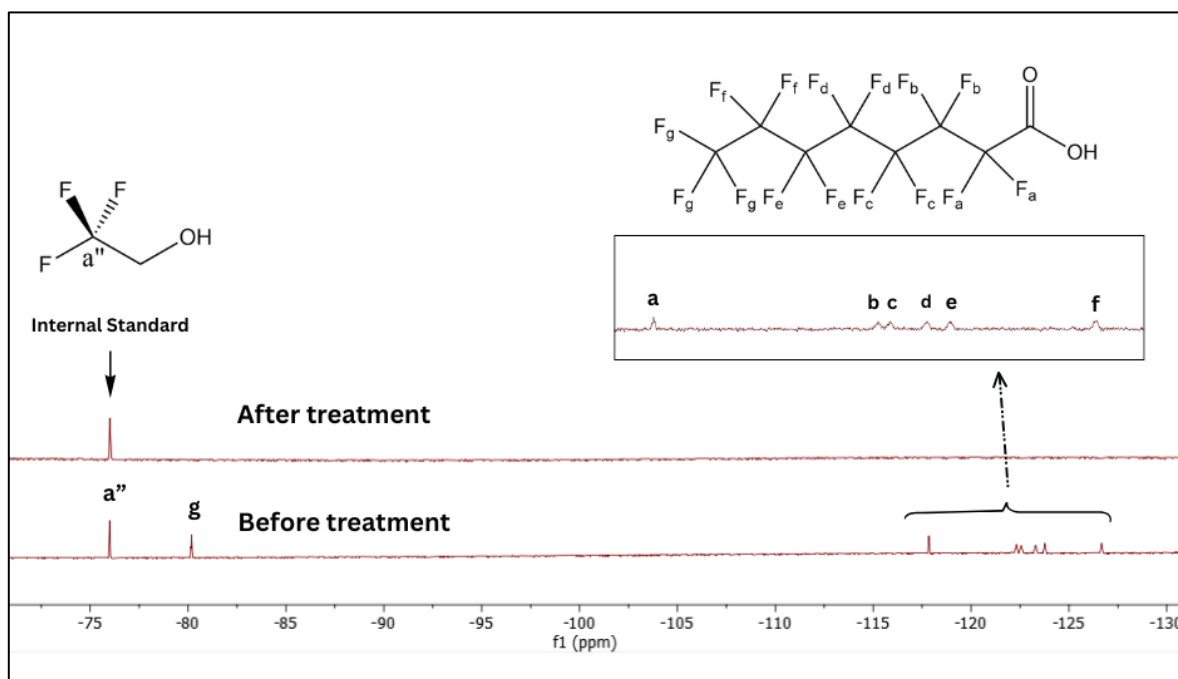


Figure 87: ^{19}F NMR spectra of the PFOA solution with an initial concentration of 1000 ppm before and after being treated with **L1-Fe-Cl**. Note: 4-Trifluoroethanol was used as an internal standard. (MOF, 10 mg; $V = 2$ mL, extraction time: 24 h).

5.3.2.1 Regeneration of the Adsorbent

The reusability of **L1-Fe-Cl** was evaluated through four successive adsorption–desorption cycles. After each adsorption cycle, the used MOF was regenerated by soaking in a 9:1 mixture of methanol (9 mL) and 1% NaCl solution (1 mL) at room temperature for 30 h. The material was then thoroughly rinsed with methanol, dried, and reused in subsequent PFOA adsorption experiments.

Remarkably, the MOF maintained about 95% of its initial adsorption capacity after the fourth cycle (Figure 88). In addition, PXRD analysis confirmed that the crystalline structure was preserved throughout the recycling process (Figure 89). These results indicate excellent reusability and structural integrity of **L1-Fe-Cl** and highlight the potential of this MOF as a robust, efficient, and reusable MOF adsorbent for removal of persistent perfluorinated pollutants such as PFOA from contaminated water.

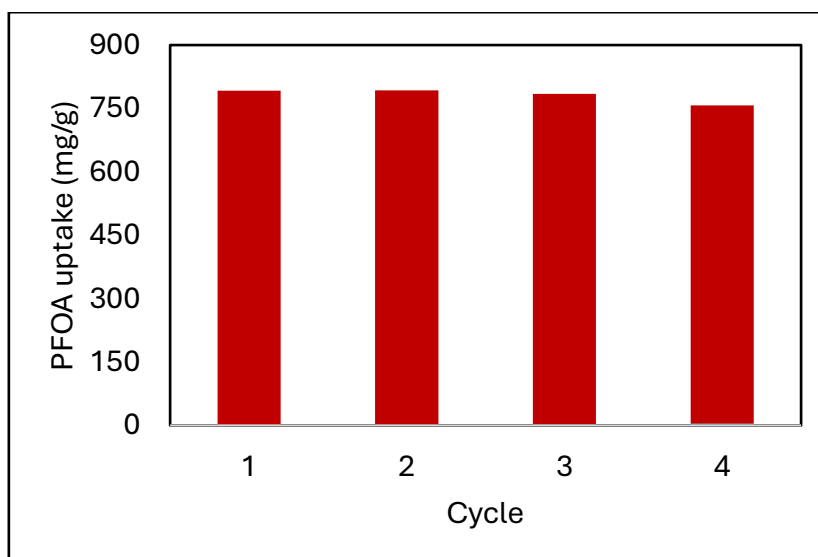


Figure 88: Recyclability tests in PFOA adsorption on **L1-Fe-Cl**.

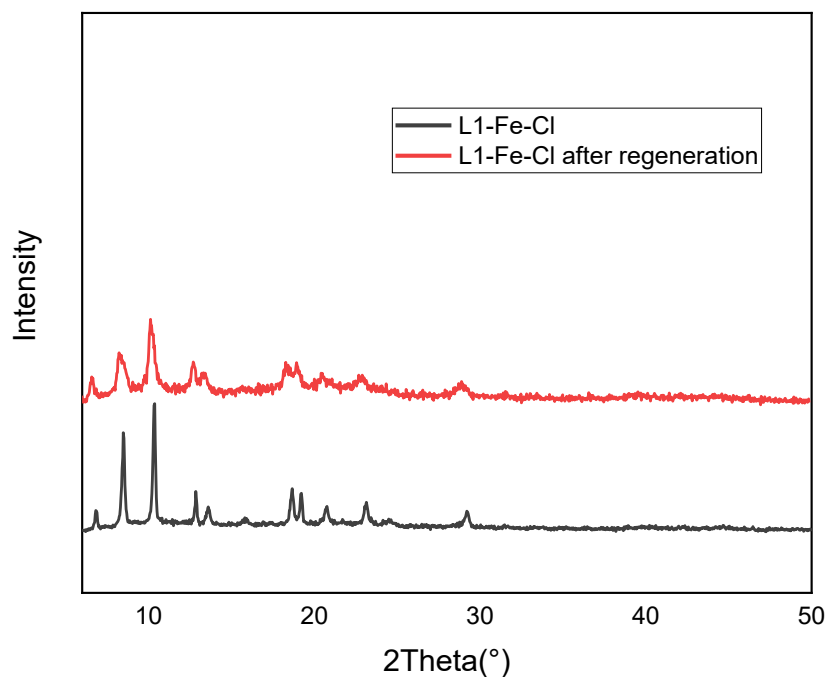


Figure 89: PXRD Pattern **L1-Fe-Cl** before and after four PFOA adsorption–desorption cycles.

5.4 Conclusion

L1-Fe and **L1-Fe-Cl** were investigated for phosphate and PFOA removal from aqueous solutions, with both materials displaying effective performance. **L1-Fe-Cl** exhibited higher removal efficiencies than **L1-Fe**, achieving phosphate and PFOA uptakes of 27.18 mg/g and 795 mg/g, respectively. To the best of our knowledge, the adsorption capacity of **L1-Fe-Cl** for PFOA is the among the highest reported to date. The adsorption behaviour of these Fe-based MOFs followed the Langmuir isotherm model, indicating a monolayer adsorption process. Moreover, **L1-Fe-Cl** demonstrated rapid kinetics, with the data fitting well to a *pseudo*-second-order model. Both materials also showed good recyclability over multiple phosphate adsorption–desorption cycles. For PFOA, a slight modification to the regeneration protocol enabled **L1-Fe-Cl** to maintain excellent performance over four adsorption–desorption cycles.

Given this remarkable performance, both materials merit further investigation. This should include investigating the adsorption mechanism, assessing performance across pH, evaluating selectivity in the presence of co-existing ions, and testing in real contaminated water samples. Such studies will provide deeper insight into their potential for real-world applications in water purification and environmental remediation.

Chapter 6: Conclusions and Future Work

Highly branched organosilicon carboxylic acids, particularly organosilicon hexacarboxylic acids, have been previously underexplored despite the advantages they offer for HOF and MOF applications. The work in this thesis seeks to address this with the report of ten organosilicon hexacarboxylic acids (**L1-H₆** to **L10-H₆**) which were prepared using a variety of synthetic approaches, seven of which are novel and previously unreported (**L4-H₆** to **L10-H₆**). These novel compounds include a series of six hexacarboxylic acids containing additional amide group functionalities (**L4-H₆**–**L9-H₆**), and a rare tetrasiloxane-based acid (**L10-H₆**). Functionalisation of the parent hexacarboxylic acids (**L1-H₆**, **L2-H₆**, and **L3-H₆**) enabled the preparation of new, extended-reach linkers and allowed the introduction of various substituents, such as –CH₃, –OMe, or –OH, using straightforward and convenient synthetic approaches. The multifunctionality of these compounds is advantageous for forming HOFs and MOFs and could lead to improved performance in applications such as gas adsorption and separation and water purification.

The ability of these novel compounds to form HOFs was investigated in this thesis, with four of the compounds shown to form porous 2D or 3D HOFs upon recrystallisation under mild conditions. Three amide-functionalised compounds, **L4-H₆**, **L5-H₆**, and **L6-H₆**, assembled into 3D HOFs in which both carboxylic acid and amide groups are involved in hydrogen bonding. Classical carboxylic acid dimeric hydrogen bonds, together with amide–amide and carboxylic acid–amide hydrogen bonds, were observed within these HOFs, with additional stabilisation in **L5-H₆** and **L6-H₆** arising from π – π interactions between aryl groups. Although linker elongation often leads to interpenetration, no interpenetration was observed in these structures. Among the three amide-functionalised HOFs, **L4-H₆** and **L6-H₆** displayed remarkable porosity, with solvent-accessible volumes of 35% and 37% of the unit cell, respectively

(calculated for the theoretically desolvated structures). Such porosity is advantageous for applications including gas uptake and separation. In addition, the free COOH and amide groups in these HOFs can potentially interact with guest molecules through hydrogen bonding and dipole–quadrupole moment, strengthening host–guest interactions and thereby enhancing adsorption capacity and selectivity. Furthermore, the variety of hydrogen-bonding interactions from amide and carboxyl groups present in all the novel HOFs is likely to contribute to their robustness. Therefore, these frameworks hold great potential and merit further studies regarding their stability and gas sorption properties.

In comparison with the parent, interpenetrated **L1-H₆** HOF (Figure 90), amide extension of **L1-H₆** to give **L4-H₆** increased the length of each aryl arm from 6.63 Å in **L1-H₆** to 13.06 Å in **L4-H₆** (~97% increase). This resulted in a significantly higher porosity, with the solvent-accessible void volume increasing from 1037 Å³ in **L1-H₆** (22% of the unit cell) to 7324 Å³ in **L4-H₆** (35% of the unit cell). These observations highlight amide extension of organosilicon hexacarboxylic acids as an effective strategy for obtaining non-interpenetrated HOFs with increased porosity.

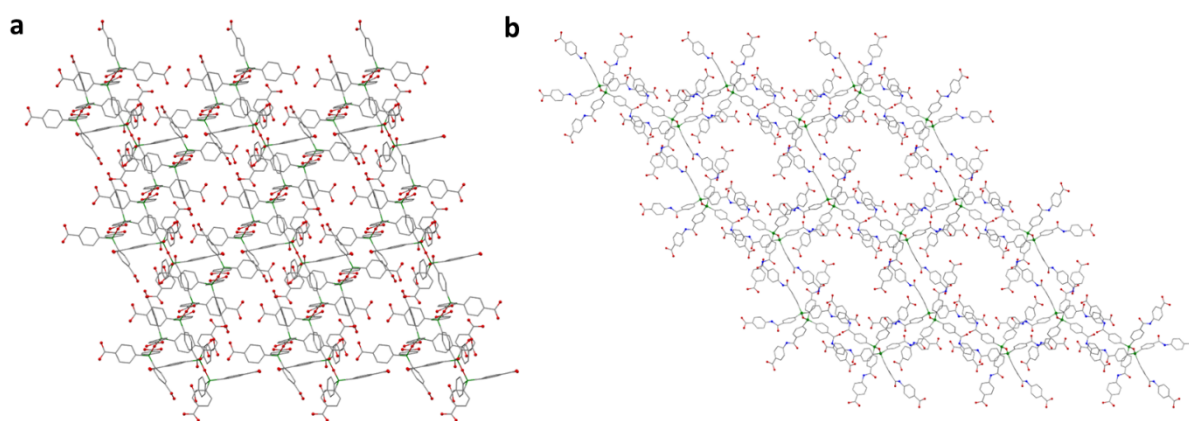


Figure 90: Comparison of the crystal structures of **L1-H₆** and **L4-H₆** HOFs: (a) a portion of the packing structure of **L1-H₆** viewed along the *b* axis; (b) a portion of the packing structure of **L4-H₆** viewed along the *b* axis.

In contrast to the amide-functionalised compounds, **L10-H₆** assembled into a 2D HOF held together entirely by dimeric hydrogen bonds. This HOF represent an extremely rare example of a tetrasiloxane-based HOF. The structure also contains coordinated acetic acid molecules, which appear to restrict the assembly to two dimensions; therefore, exploring alternative recrystallisation solvents is a promising route to afford a 3D HOF.

Importantly, these findings demonstrate that amide functionalisation of organosilicon hexacarboxylates is a powerful strategy that increases linker reach, introduces directional hydrogen bond donors and acceptors, and suppresses interpenetration, collectively enabling the formation of potentially porous, non-interpenetrated HOFs. These results also establish a clear design principle for the future construction of HOFs based on multifunctional silicon-containing linkers. Furthermore, further work should focus on recrystallising **L7-H₆**, **L8-H₆**, and **L9-H₆**, as they may form interesting HOFs owing the presence of $-\text{CH}_3$, $-\text{OMe}$, and $-\text{OH}$ substituents in their structures, respectively.

The versatility of **L1** was demonstrated by its ability to coordinate to a variety of metal clusters, from monovalent to trivalent, affording eleven new 3D MOFs. **L1** adopts a *pseudo*-octahedral arrangement of carboxylic acids, with staggered Ar_3Si groups (along the $\text{Si}-\text{O}-\text{Si}$ axis), leading to uncommon MOF topologies, such as **nia**, **fsh**, and **fsy**. Some of these MOFs were isostructural based on In^{3+} , Ga^{3+} , Al^{3+} , and Fe^{3+} . The **L1-Fe**-based MOFs exhibit excellent water stability, highlighting their potential for environmental applications such as phosphate and PFOA removal. **L1-Tb** and **L1-Eu** are rare examples of lanthanide MOFs derived from an organosilicon hexacarboxylate linker, and show promise for sensing, emitting green and red luminescence under UV excitation.

Treating **L1-H₆** with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ afforded the first example of a 3D Cu(II)-based MOF built from a siloxane-based linker (**L1-Cu**). This MOFs adopts a rare **fsy** topology, with solvent-accessible voids volume of 65% of the unit cell (after theoretical removal of solvent

molecules). **L1-Cu** shows reversible dehydration while preserving crystallinity, suggesting opportunities for future gas sorption studies. The same hexacarboxylate linker also yielded a series of alkali metal MOFs with interesting structures. The preparation of stable alkali-metal MOFs with 3D dimensionality remains a significant challenge in the literature, due to their strong tendency to bind with polar solvents. A successful strategy reported in the literature to overcome this challenge is the use of highly connected linkers,^{435,436} as they facilitate coordination of metal centres to organic linkers rather than to solvent molecules. A similar approach was employed in the synthesis of **L1-Li** and the two isorecticular **nia**-type MOFs, **L1-Na** and **L1-K**, all of which exhibit 3D structures and notable thermal stability. However, the activation protocol employed was not effective in removing both coordinated and non-coordinated solvent molecules for gas sorption studies, which hindered pore accessibility. Therefore, optimising this protocol, either by increasing the activation temperature or by employing alternative methods (e.g., solvent-exchange or scCO₂ drying), should be explored to achieve complete solvent removal and enhanced accessible porosity.

Furthermore, reticular expansion of **L1-In** via amide insertion afforded **L4-In** with the same rare **nia** topology (Figure 91), representing the first amide-functionalised siloxane-based MOF. Although **L4-In** exhibits poor stability, its increased pore sizes and higher porosity (as estimated by Mercury) encourage further investigation of **L4** with other metal-oxide SBUs, such as Cu²⁺, Fe³⁺, and Zr⁴⁺ as these units are frequently targeted in MOF synthesis due to their thermal, chemical, and water stabilities. Silicon-based linkers have also been shown to be compatible with these SBUs both in this thesis and in the literature.^{156,194}

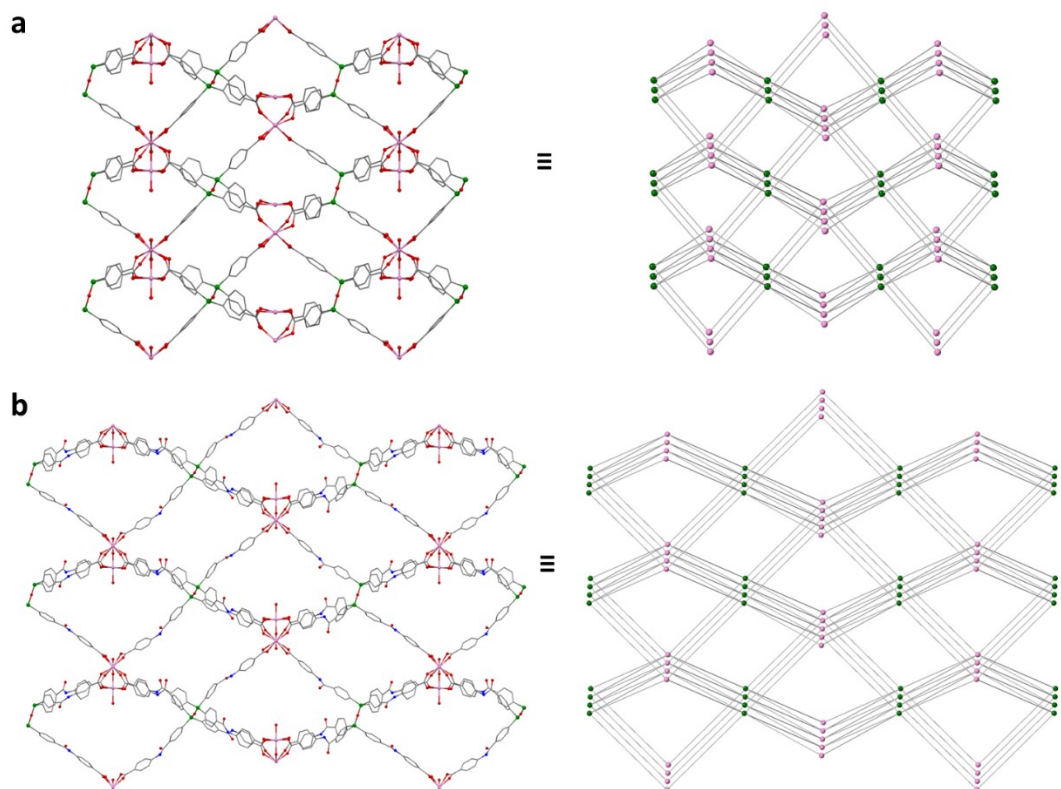


Figure 91: Comparison of the crystal structures of **L1-In** and **L4-In** HOFs: (a) a portion of the packing structure of **L1-In** viewed along the *b* axis, and the corresponding topological diagram of the **nia** net; (b) a portion of the packing structure of **L4-In** along the *b* axis, and the corresponding **nia** net.

Taken together, the new MOFs described in this thesis represent a significant addition to the scarce family of organosilicon hexacarboxylate frameworks. The successful incorporation of **L1** into a wide range of metal clusters demonstrates that organosilicon hexacarboxylate linkers are versatile and able to form uncommon topologies, accommodate diverse SBUs, and impart water stability, particularly in Fe-based systems, positions this linker family as a valuable building block for the rational design of functional MOFs beyond traditional aromatic carboxylates. Although initial efforts to incorporate the other hexa-acid linkers into MOFs were unsuccessful, highlighting the challenges associated with synthesising amide-functionalised organosilicon linkers, future studies should focus on broadening the scope by employing diverse metal precursors and synthetic conditions. Such approaches may lead to new 3D

structures driven by the distinct silicon backbones, multifunctionality, and additional groups ($-\text{CH}_3$, $-\text{OMe}$, $-\text{OH}$) present in these linkers. In addition, treating the amide-functionalised compounds with metals beyond indium (e.g., Fe^{3+} , Cu^{2+}) may offer a promising route to more robust and stable frameworks, as this class of linkers has shown limited compatibility with indium in forming stable MOFs. Furthermore, **L10-H₆** (Figure 92), owing to the presence of dimethylsiloxane units, holds potential in affording hydrophobic MOFs. The tetrasiloxane backbone also displays some flexibility, which enables the linker to adjust its geometry by bending or stretching to optimise coordination with metal nodes. This merits further investigation, as it may lead to MOFs with novel structures and properties.

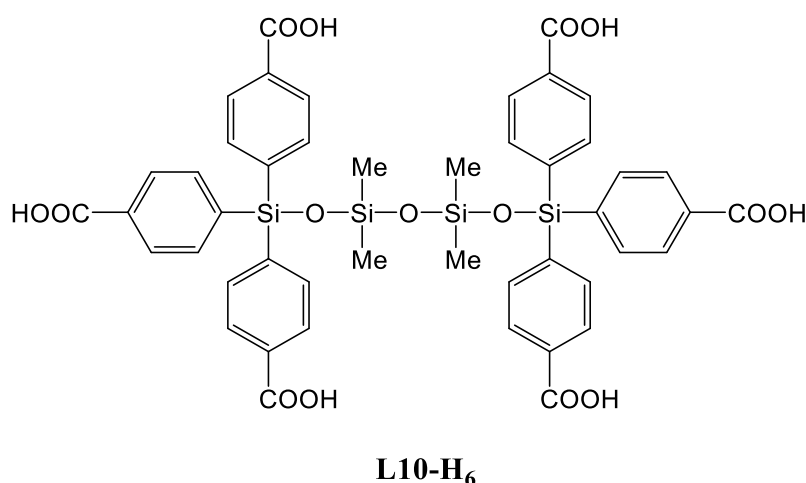


Figure 92: Structure of **L10-H₆**.

The excellent water stability of **L1-Fe** and **L1-Fe-Cl** has encouraged investigation into their performance in phosphate and PFOA removal from water. Both materials have shown effective adsorption of phosphate and PFOA from aqueous solutions. **L1-Fe** and **L1-Fe-Cl** achieved maximum phosphate adsorption capacities of 27.95 mg/g and 28.71 mg/g, respectively. For PFOA, **L1-Fe-Cl** displayed outstanding performance with an adsorption capacity of 795 mg/g, ranking this MOF among the highest performing PFOA adsorbent materials

reported to date. The Fe-based MOF have also shown excellent recyclability over multiple adsorption–desorption cycles, following easy regeneration protocol.

These results motivate further investigation of both materials, as this would provide deeper insight into their potential for real-world applications. In particular, future studies should explore the adsorption mechanisms involved using a variety of characterization techniques (e.g. SCXRD, molecular electrostatic potential, XPS), their performance across different pH values, selectivity in the presence of co-existing ions, and efficiency in real contaminated water samples. The findings of this thesis also demonstrate the potential of organosilicon MOFs for environmental applications and encourage broader investigation into organosilicon carboxylate MOFs as adsorbents for phosphate and PFOA, as this area remains underexplored. Furthermore, the incorporation of additional functional groups, such as $-\text{CONH}-$, $-\text{NH}_2$, or cationic ammonium groups, may represent an effective strategy for improved adsorption performance.

Chapter 7: Experimental

7.1 Materials and General Methods

All starting materials were commercially available and purchased from Sigma-Aldrich, Fluorochem, Thermo Fisher Scientific, or Avantor, and were used without further purification. Dry solvents were obtained from a PureSolv multi-solvent drying system and stored under a nitrogen atmosphere. All references to "H₂O" or "water" throughout the experiments, reactions, and work-up procedures refer to Milli-Q grade deionized water. Anhydrous reactions were conducted in glassware pre-dried at 120 °C overnight and carried out under inert conditions using a Schlenk line connected to house nitrogen. Reaction temperatures of –78 °C and 0 °C were achieved using dry ice-acetone and ice-water baths, respectively. MOF synthesis reactions were conducted in either a Memmert UFE500 programmable oven or a Grant Instruments QBH2 heating block.

¹H, ¹³C, ²⁹Si, and ¹⁹F NMR spectra were recorded on a Bruker Avance III spectrometer, at frequencies 400 MHz, 101 MHz, 80 MHz, 377 MHz, respectively. ¹H NMR spectra were recorded using standard short-run setting, ¹³C NMR spectra were obtained in a long-run and 1380 scans setting, ²⁹Si NMR spectra were recorded with inverse-gated ¹H decoupling, and ¹⁹F NMR spectra were collected with a 55 s relaxation delay. NMR spectral analysis was carried out using MestReNova software.⁵⁴³ Infrared (IR) spectra were obtained using an Agilent Cary 630 FTIR spectrometer over a wavenumber range of 4000–400 cm⁻¹. Mass spectrometry was performed using electrospray ionization (ESI) by Malgorzata Puchnarewicz.

Powder X-ray diffraction (PXRD) patterns were recorded using a Bruker D2-Phaser diffractometer with Cu-K α radiation (λ = 1.5418 Å), in the 2 θ range of 5–50°, with a 0.2 s scan rate. MOF samples were air-dried overnight and finely ground before analysis. The raw data files (.raw) were converted to .csv format using PowDLL Converter software for subsequent

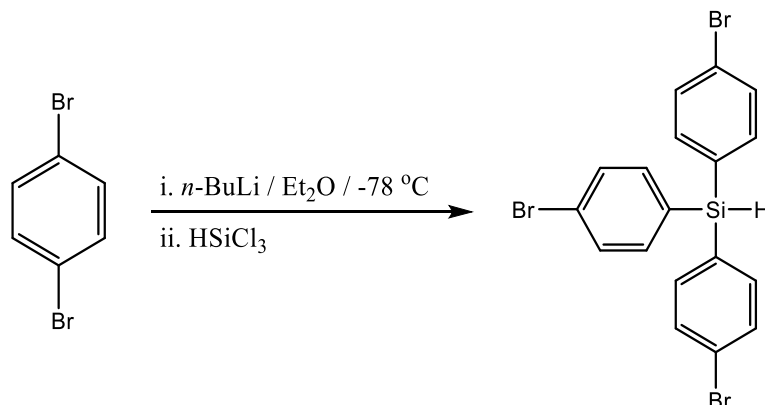
analysis.⁵⁴⁴ Simulated patterns were generated from single-crystal data using Mercury software.³⁷¹ Single-crystal X-ray diffraction (SCXRD) was carried out by Dr. Peter Horton at the UK National Crystallography Service (NCS) using Rigaku FRE+ or Rigaku 007HF diffractometers. Topological analyses were performed using TopCryst.⁵⁴⁵

Thermogravimetric analysis (TGA) was performed using a PerkinElmer TGA 8000 under nitrogen flow (50 mL/min). Samples were heated from 30 to 800 °C at 5 °C/min. Brunauer–Emmett–Teller (BET) measurements were performed using a Micromeritics 3Flex porosity analyzer. N₂ adsorption isotherms were collected at 77 K, and CO₂ adsorption/desorption isotherms at 298 K. Samples were degassed overnight at 100 °C using an external system, followed by *in-situ* degassing at 120 °C for 4 h under 0.1 mmHg vacuum. Surface areas were calculated using the BET method.¹²³

Universal UV Lamp (CAMAG, Typ TL-900/U) was used to visually examine the luminescence of the bulk lanthanide-based MOF samples under UV light ($\lambda = 254$ nm). UV-vis spectra for phosphate adsorption studies were recorded using a Cary 5000 UV-Vis-NIR spectrophotometer. Measurements were performed in Hellma® high-performance quartz cuvettes with a 10 mm path length, 3500 μ L chamber volume, and a spectral range of 200–2500 nm. The shaker used for the phosphate and PFOA adsorption experiments was a Rotamax 120 from Heidolph.

7.2 Preparation of L1-H₆

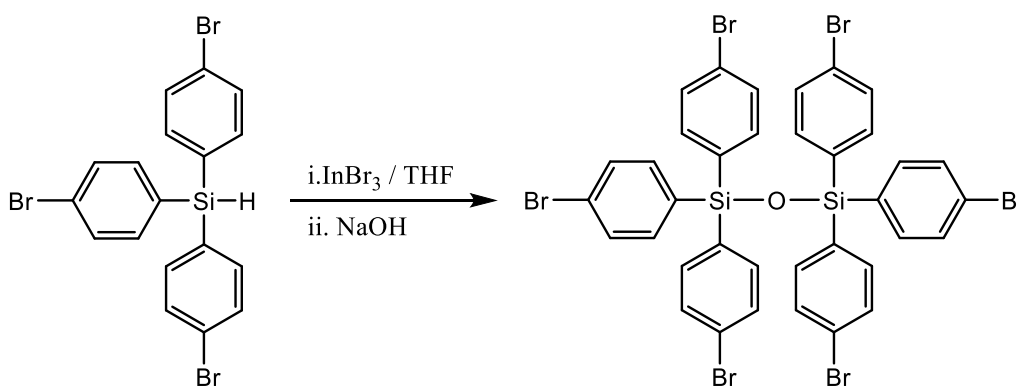
Tris(4-bromophenyl)silane (33)



1,4-Dibromobenzene (10.0 g, 42 mmol) was dissolved in anhydrous diethyl ether (75 mL) under a nitrogen atmosphere in a 250 mL two-neck round-bottomed flask and cooled in an acetone–dry ice bath. The flask was kept immersed for 15 min to ensure the temperature reached $-78\text{ }^{\circ}\text{C}$ (measured using a thermometer) before the addition of *n*-BuLi. A 2.5 M solution of *n*-BuLi in hexane (17 mL, 42 mmol) was added dropwise over 30 min, during which a white precipitate formed. The resulting mixture was stirred for 2 h at $-78\text{ }^{\circ}\text{C}$. The dry ice–acetone bath was then replaced with an ice–water bath to raise the temperature to $0\text{ }^{\circ}\text{C}$ gradually, resulting in a clear solution as the precipitate dissolved. The lithiated mixture was transferred via cannula into a second two-neck round-bottomed flask containing a solution of HSiCl₃ (1.4 mL, 14 mmol) in anhydrous diethyl ether (5 mL), also under a nitrogen atmosphere and cooled to $-78\text{ }^{\circ}\text{C}$. A white precipitate formed during the addition. The reaction mixture was stirred overnight, gradually warming to room temperature. The reaction was quenched with water (30 mL), and the organic layer was collected. The aqueous layer was washed with diethyl ether (30 mL), and the combined organic extracts were dried over anhydrous MgSO₄ and concentrated under reduced pressure using a rotary evaporator. The resulting wet white solid was recrystallised from hot hexane, affording tris(4-bromophenyl)silane as white needle-like

crystals, which were collected by suction filtration and washed with cold hexane (2×5 mL): 5.31 g (78 %). M.p.: 110-111 °C (lit.: 110.5 °C)²⁶⁴; ^1H NMR (CDCl_3): δ (ppm) = 7.56 (d, J = 8 Hz, 6 H, Ar-H), 7.40 (d, J = 8 Hz, 6 H, Ar-H), 5.41 (s, 1 H, Si-H; ^{29}Si satellites, $J(^{29}\text{Si}-^1\text{H})$ = 204 Hz); ^{13}C NMR (CDCl_3): δ (ppm) = 137.2, 131.6, 131.0, 125.4; ^{29}Si NMR (CDCl_3): δ (ppm) = -18.27; IR (ATR): ν (cm^{-1}) = 2139, 1566, 1475, 1375, 1110, 1062, 1005, 816, 772, 718, 513.

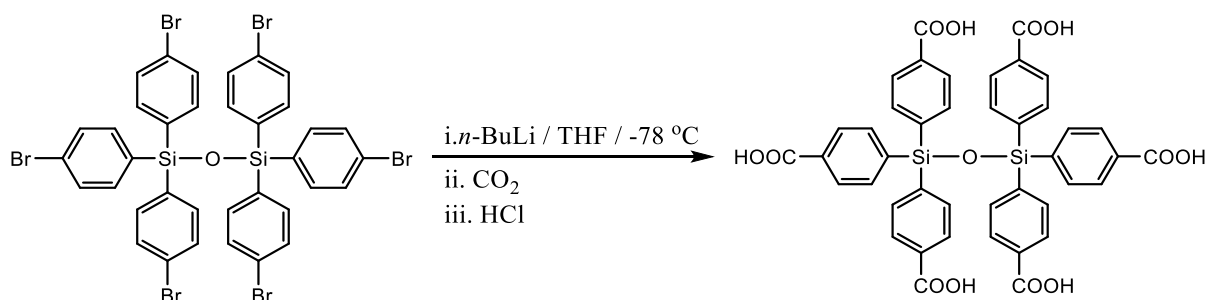
Hexa(4-bromophenyl)disiloxane (34)



Tris(4-bromophenyl)silane (4.0 g, 8 mmol) was dissolved in THF (20 mL) in a round-bottomed flask. Indium(III) bromide (0.4 g, 1 mmol) was then added, and the resulting mixture was stirred for 10 min. An aqueous solution of NaOH (4 M, 1.5 mL, 6 mmol) was added dropwise, during which a white precipitate formed. The reaction mixture was stirred at ambient temperature overnight. The liquid phase was decanted into another round-bottomed flask to separate the colourless solution from the white solid deposited on the walls of the flask. The solution was concentrated to approximately 5 mL using a rotary evaporator. Hot chloroform (40 mL) was then added, and the mixture was washed with water (14 mL). The organic layer was collected, gently warmed, and methanol (40 mL) was added. The solution was left to cool to room temperature, and a white crystalline solid (**34**) precipitated immediately, which was collected by suction filtration and washed with methanol (2×5 mL): 2.87 g (71 %). M.p.: > 240 °C (lit. 294.5-296 °C)¹⁸⁴; ^1H NMR (CDCl_3): δ (ppm) = 7.47 (d, J = 8 Hz, 12 H, Ar-H), 7.24 (d, J = 8 Hz, 12 H, Ar-H); ^{13}C NMR (CDCl_3): δ (ppm) = 136.4, 132.6, 131.4, 125.8; ^{29}Si NMR

(CDCl₃): δ (ppm) = -17.39; IR (ATR): ν (cm⁻¹) = 1568, 1476, 1373, 1114, 1088, 1061, 1005, 809, 730.

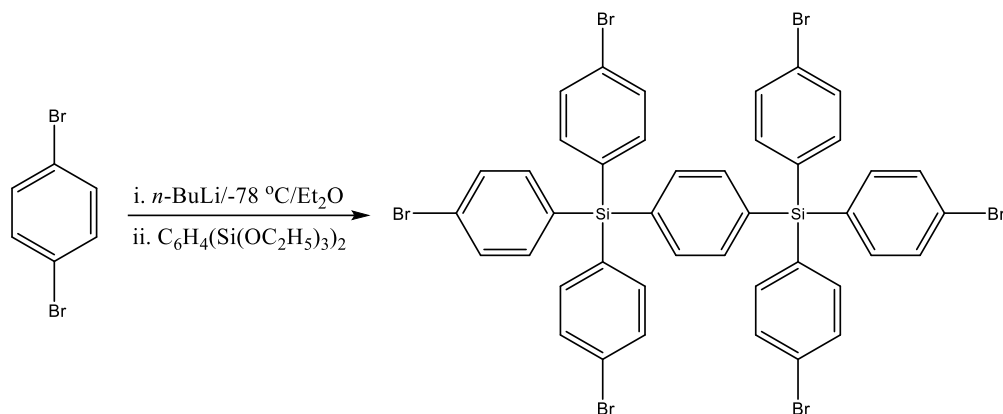
Hexa(4-carboxyphenyl)disiloxane (**L1-H₆**)



Hexa(4-bromophenyl)disiloxane (1.0 g, 1 mmol) was dissolved in anhydrous THF (15 mL) in a two-neck round-bottomed flask under a nitrogen atmosphere. This solution was added dropwise to a second flask containing 2.5 M *n*-BuLi (3.4 mL, 8.5 mmol) in anhydrous THF (30 mL) at -78 °C under nitrogen. A pink colour developed during the addition, which gradually faded and disappeared. The reaction mixture was stirred for 1.5 h, after which carbon dioxide was bubbled through for 3 h. The mixture was then allowed to stir overnight while warming slowly to ambient temperature. The reaction was quenched with 1 M HCl (10 mL), and the organic layer was collected. After solvent removal via rotary evaporation, a white solid was obtained, washed with ethyl acetate (2 × 5 mL), and dried overnight to afford **L1-H₆**: 0.65 g (79 %). M.p.: > 240 °C (lit. > 240 °C)¹⁸⁴; ¹H NMR (DMSO-*d*₆): δ (ppm) = 13.14 (s, 6 H, COOH), 7.91 (d, *J* = 8 Hz, 12 H, Ar-H), 7.56 (d, *J* = 8 Hz, 12 H, Ar-H); ¹³C NMR (DMSO-*d*₆): δ (ppm) = 167.6, 138.9, 135.2, 133.4, 129.2; ²⁹Si NMR (DMSO-*d*₆): δ (ppm) = -18.95; IR (ATR): ν (cm⁻¹) = 2880, 1689, 1553, 1497, 1389, 1283, 1094, 1014, 841, 759, 701, 552, 488; MS (ESI⁻): C₄₂H₂₉N₆O₁₃Si₂ [M-H]⁻: calcd. *m/z* = 797.1152, found *m/z* = 797.1166.

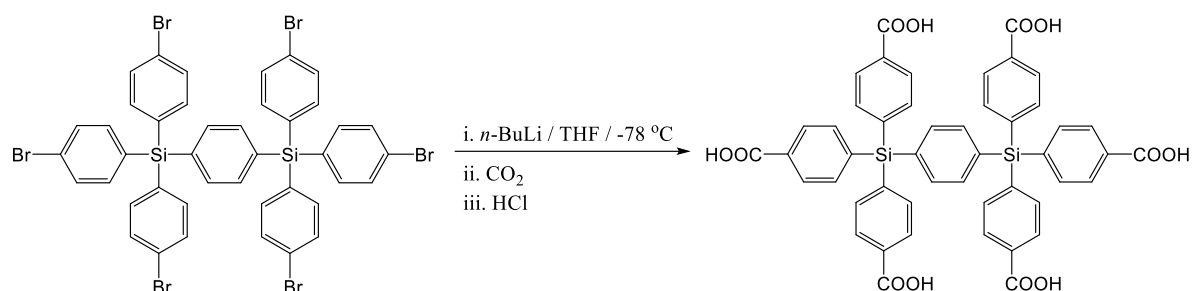
7.3 Preparation of L2-H₆ and L3-H₆

1,4-Bis(tris(4-bromophenyl)silyl)benzene (**35**)



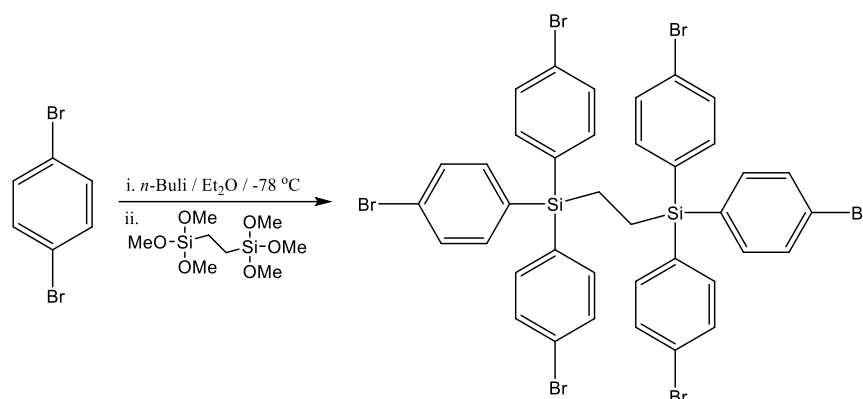
1,4-Dibromobenzene (8.3 g, 35 mmol) was dissolved in dry diethyl ether (30 mL) under a nitrogen atmosphere, and the reaction mixture was placed in an acetone–dry ice bath to cool to $-78\text{ }^{\circ}\text{C}$. A 2.5 M solution of *n*-BuLi in hexane (14 mL, 35.28 mmol) was added dropwise, and the resulting mixture was stirred for 2 h, during which a white suspension formed. The suspension was then placed in an ice bath at $0\text{ }^{\circ}\text{C}$, resulting in the formation of a colourless solution. 1,4-Bis(triethoxysilyl)benzene (2 mL, 5.04 mmol) was added dropwise, and the reaction mixture was stirred overnight while gradually warming to room temperature. The reaction was quenched with water (10 mL), leading to the formation of a white precipitate. The crude solid was collected by filtration, washed with cold water ($3 \times 10\text{ mL}$), and recrystallised from hot ethyl acetate to yield a white crystalline solid (**35**): 1.94 g (44 %). M.p.: $129\text{--}133\text{ }^{\circ}\text{C}$ (lit., $129\text{--}133\text{ }^{\circ}\text{C}$)²⁰⁷; ¹H NMR (CDCl₃): δ (ppm) = 7.55 (d, $J = 8\text{ Hz}$, 12 H, Ar-H), 7.53 (s, 4 H, SiC₆H₄Si), 7.38 (d, $J = 8\text{ Hz}$, 12 H, Ar-H); ¹³C NMR (CDCl₃): δ (ppm) = 137.7, 135.6, 135.0, 131.6, 131.5, 125.4; ²⁹Si NMR (CDCl₃): δ (ppm) = -13.87; IR (ATR): ν (cm⁻¹) = 1568, 1476, 1375, 1129, 1063, 105, 805, 727, 534, 475.

1,4-Bis(tris(4-carboxyphenyl)silyl)benzene (**L2-H₆**)



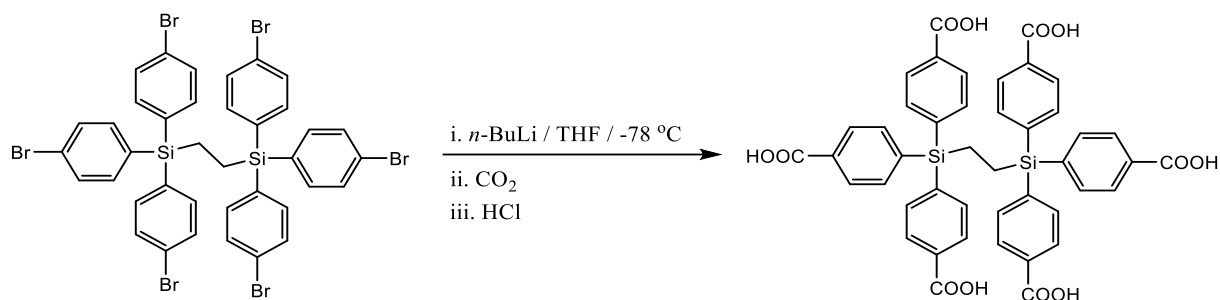
1,4-Bis(tris(4-bromophenyl)silyl)benzene (1 g, 0.96 mmol) was dissolved in anhydrous THF (15 mL) under a nitrogen atmosphere. This solution was added dropwise to a solution of *n*-BuLi (2.69 mL, 6.72 mmol, 2.5 M in hexane) in anhydrous THF (25 mL) maintained at $-78\text{ }^{\circ}\text{C}$ and stirred for 1.5 h. Carbon dioxide was then bubbled through the mixture for 3 h at $-78\text{ }^{\circ}\text{C}$, resulting in the formation of a white suspension. The reaction mixture was allowed to stir overnight while gradually warming to room temperature. The reaction was quenched with 1 M HCl (2 mL), and the precipitate was isolated by filtration, dissolved in 1 M NaOH, and subsequently reprecipitated with 2.5 M HCl. The resulting white solid was washed with water and chloroform and dried overnight under dynamic vacuum to afford **L2-H₆**: 0.773 g (94 %). M.p.: $> 240\text{ }^{\circ}\text{C}$ (lit., $> 300\text{ }^{\circ}\text{C}$)²⁰⁷; ^1H NMR (DMSO- d_6): δ (ppm) = 13.14 (s, 6 H, COOH), 8.00 (d, $J = 8\text{ Hz}$, 12 H, Ar-H), 7.63 (s, 4 H, SiC₆H₄Si), 7.60 (d, $J = 8\text{ Hz}$, 12 H, Ar-H); ^{13}C NMR (DMSO- d_6): δ (ppm) = 167.6, 138.2, 136.6, 136.1, 132.9, 129.3; ^{29}Si NMR (DMSO- d_6): δ (ppm) = -15.15; IR (ATR): ν (cm^{-1}) = 2987, 1688, 1597, 1552, 1497, 1386, 1231, 1183, 1127, 1088, 1015, 847, 807, 697, 547; MS (ESI-) C₄₈H₃₄O₁₂Si₂ [M-H]⁻: calcd. m/z = 857.1516, found m/z = 857.1529.

1,2-Bis(tris(4-bromophenyl)silyl)ethane (36)



1,4-Dibromobenzene (10 g, 42 mmol) was dissolved in dry diethyl ether (75 mL) under a nitrogen atmosphere. The reaction mixture was cooled to $-78\text{ }^{\circ}\text{C}$ in a dry ice–acetone bath. A 2.5 M solution of *n*-BuLi in hexane (17 mL, 42 mmol) was added dropwise, and the resulting mixture was stirred for 2 h, forming a white suspension. The suspension was then warmed to $0\text{ }^{\circ}\text{C}$, yielding a clear solution. A solution of 1,4-bis(trimethoxysilyl)ethane (2.77 mL, 7 mmol) in dry diethyl ether (5 mL) was added dropwise, and the reaction mixture was stirred overnight, gradually warming to room temperature. The reaction was quenched with water (6 mL), resulting in the formation of a white precipitate. The crude solid was collected by Büchner filtration, washed with water ($3 \times 10\text{ mL}$) and cold methanol ($3 \times 10\text{ mL}$), and recrystallised from hot ethyl acetate to yield the white crystalline product (**36**): 5.11 g (71 %). M.p.: $> 240\text{ }^{\circ}\text{C}$; ^1H NMR (CDCl_3): δ (ppm) = 7.3 (d, $J = 8\text{ Hz}$, 12 H, Ar-H), 7.27 (d, $J = 8\text{ Hz}$, 12 H, Ar-H), 1.31 (s, 4 H, Si-CH₂-CH₂-Si); ^{13}C NMR (CDCl_3): δ (ppm) = 136.98, 132.16, 131.48, 125.19, 5.25; ^{29}Si NMR (CDCl_3): δ (ppm) = -8.72; IR (ATR): ν (cm^{-1}) = 1571, 1548, 1478, 1377, 1141, 1109, 1066, 810, 810, 728, 537, 492.

1,2-Bis(tris(4-carboxyphenyl)silyl)ethane (**L3-H₆**)

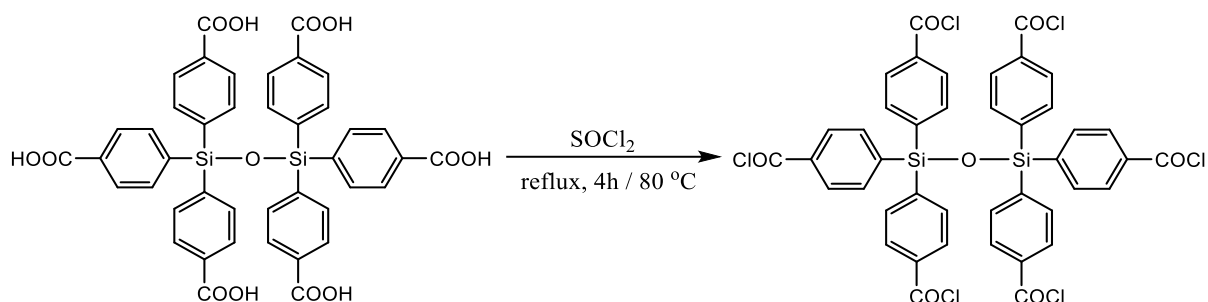


1,2-Bis(tris(4-bromophenyl)silyl)ethane (2.0 g, 1.97 mmol) was dissolved in dry THF (30 mL) under a nitrogen atmosphere and added dropwise to a solution of *n*-BuLi (6.30 mL, 15.75 mmol, 2.5 M in hexane) in dry THF (40 mL) cooled to $-78\text{ }^{\circ}\text{C}$. The reaction mixture was stirred for 1.5 h, after which carbon dioxide was bubbled through the solution for 3 h. The mixture was then stirred overnight, allowing it to warm to room temperature gradually. The reaction was quenched with 1 M HCl (15 mL), and the organic layer was collected and concentrated using a rotary evaporator. The crude product was recrystallised from ethyl acetate, and the pure compound was precipitated by the addition of hexane (**L3-H₆**): 1.29 g (81 %). M.p.: $> 240\text{ }^{\circ}\text{C}$; ^1H NMR (DMSO- d_6): δ (ppm) = 13.09 (s, 6 H, COOH), 7.96 (d, $J = 8\text{ Hz}$, 12 H, Ar-H), 7.57 (d, $J = 8\text{ Hz}$, 12 H, Ar-H), 1.48 (s, 4 H, Si-CH₂-CH₂-Si); ^{13}C NMR (DMSO- d_6): δ (ppm) = 167.69, 139.28, 135.93, 132.68, 129.20; ^{29}Si NMR (DMSO- d_6): δ (ppm) = -9.41; IR (ATR): ν (cm^{-1}) = 2979, 1687, 1598, 1552, 1498, 1388, 1285, 1131, 1091, 759, 704, 473; MS (ESI-) C₄₄H₃₄O₁₂Si₂ [M-H]⁻: calcd. m/z = 809.1516, found m/z = 809.1531.

7.4 Preparation of Amide-Extended Carboxylic Acids

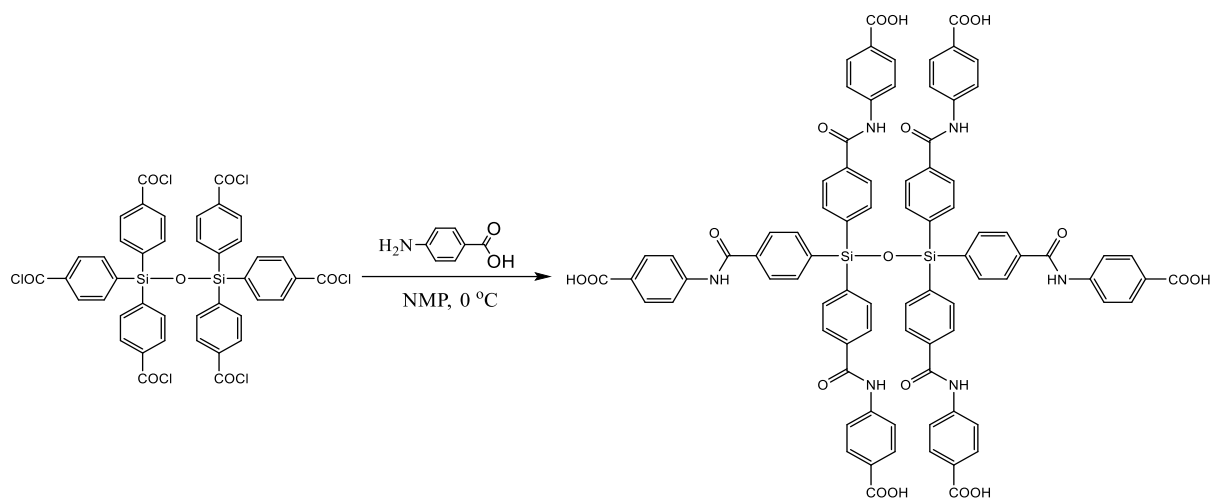
7.4.1 Preparation of L4-H₆, L5-H₆, L6-H₆

Hexa(4-acylchlorophenyl)disiloxane (**37**)



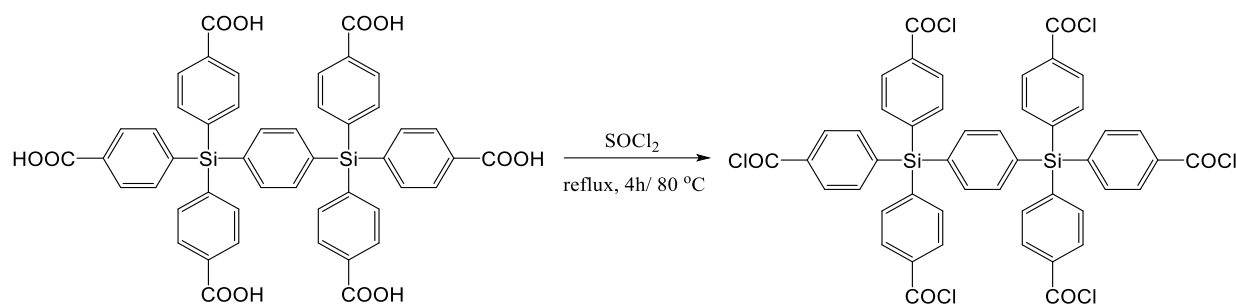
L1-H₆ (0.301 g, 0.390 mmol) was refluxed in thionyl chloride (3.97 mL, 54.6 mmol) under an N_2 atmosphere for 4 h at $80\text{ }^\circ\text{C}$. Excess SOCl_2 was removed under reduced pressure. The resulting white solid was collected and washed with dry hexane to give compound **37**: 0.30 g (87 %). ^1H NMR (DMSO-d_6): δ (ppm) = 7.91 (d, $J = 8\text{ Hz}$, 12 H, Ar-H), 7.59 (d, $J = 8\text{ Hz}$, 12 H, Ar-H); ^{13}C NMR (DMSO-d_6): δ (ppm) = 167.44, 138.95, 135.21, 133.17, 129.24; ^{29}Si NMR (DMSO-d_6): δ (ppm) = -18.97; IR (ATR): ν (cm^{-1}) = 1771, 1735, 1551, 1591, 1385, 1204, 1175, 1108, 1019, 870, 820, 711, 647, 572.

Hexa(4-carboxyphenyl-4-benzamide)disiloxane (L4-H₆)



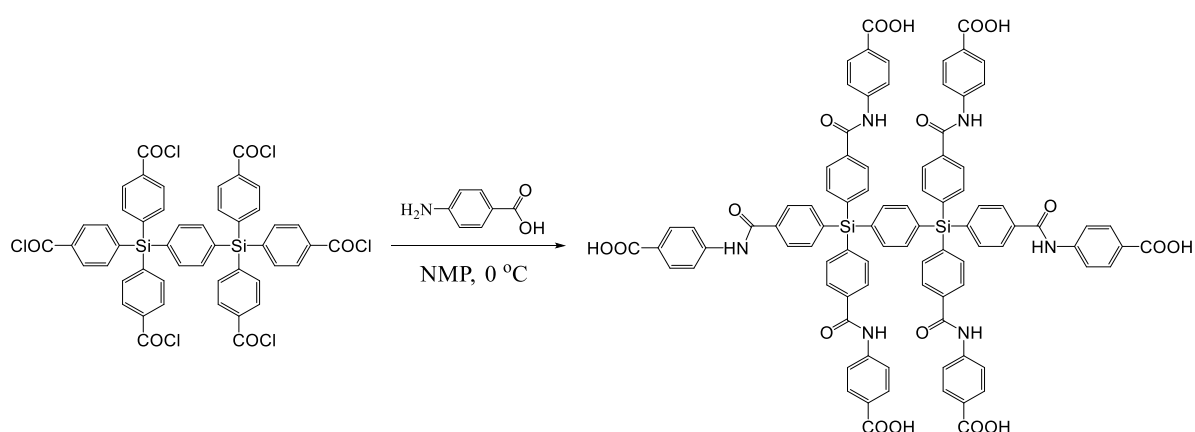
4-Aminobenzoic acid (0.584 g, 4.26 mmol) was fully dissolved in NMP (10 mL) and cooled in an ice bath to 0 °C. Hexa(4-acylchlorophenyl)disiloxane (0.25 g, 0.284 mmol) was then added, and the resulting mixture was stirred for 30 min at 0 °C, followed by 1 h at ambient temperature. The reaction mixture was poured into a flask containing ice-cold water, resulting in the immediate formation of a white precipitate. The solid was collected by suction filtration, washed with water, and dried under vacuum to give to give **L4-H₆**: 0.37 g (82 %); ¹H NMR (DMSO-d₆): δ (ppm) = 12.77 (s, 6 H, COOH), 10.62 (s, 6 H, N-H), 8.02-7.90 (m, 36 H, Ar-H), 7.72 (d, *J* = 8 Hz, 12 H, Ar-H); ¹³C NMR (DMSO-d₆): δ (ppm) = 167.38, 166.21, 143.55, 138.02, 137.30, 135.01, 130.72, 128.03, 126.14, 120.00; ²⁹Si NMR (DMSO-d₆): δ (ppm) = -19.09; IR (ATR): ν (cm⁻¹) = 3053, 1679, 1595, 1516, 1406, 1313, 1242, 1171, 1087, 1013, 897, 852, 770, 726, 560, 517; MS (ES⁺) C₈₄H₆₁N₆O₁₉Si₂ [M+H]⁺: calcd. *m/z* = 1513.3530, found *m/z* = 1513.3470.

1,4-Bis(tris(4-acylchlorophenyl)silyl)benzene (**38**)



L2-H₆ (0.403 g, 0.469 mmol) was refluxed in thionyl chloride (4.10 mL, 56.44 mmol) under a nitrogen atmosphere at 80 °C for 4 h. The excess SOCl₂ was then removed under reduced pressure. The product was obtained as a white solid, which was then washed with dry hexane to give compound **38**: 0.395 g (87 %). ¹H NMR (DMSO-d₆): δ (ppm) = 8.00 (d, *J* = 8 Hz, 12 H, Ar-H), 7.63 (s, 4 H, SiC₆H₄Si), 7.60 (d, *J* = 8 Hz, 12 H, Ar-H); ¹³C NMR (DMSO-d₆): δ (ppm) = 167.6, 138.2, 136.6, 136.1, 132.9, 129.3; ²⁹Si NMR (DMSO-d₆): δ (ppm) = -15.14; IR (ATR): ν (cm⁻¹) = 1772, 1735, 1590, 1550, 1385, 1128, 1205, 1177, 870, 831, 706.

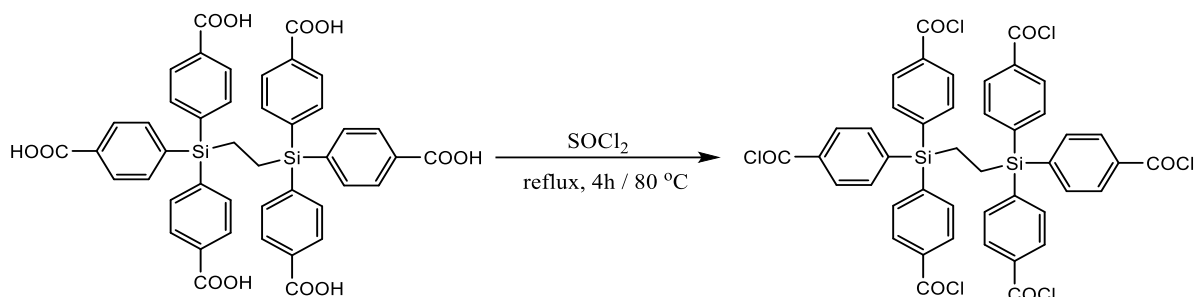
1,4-Bis(tris(4-carboxyphenyl-4-benzamide)silyl)benzene (**L5-H₆**)



4-Aminobenzoic acid (0.663 g, 4.837 mmol) was fully dissolved in NMP (10 mL) and cooled in an ice bath to 0 °C. 1,4-Bis(tris(4-acylchlorophenyl)silyl)benzene (0.312 g, 0.322 mmol) was then added, and the resulting mixture was stirred for 30 min at 0 °C, followed by 1 h at ambient

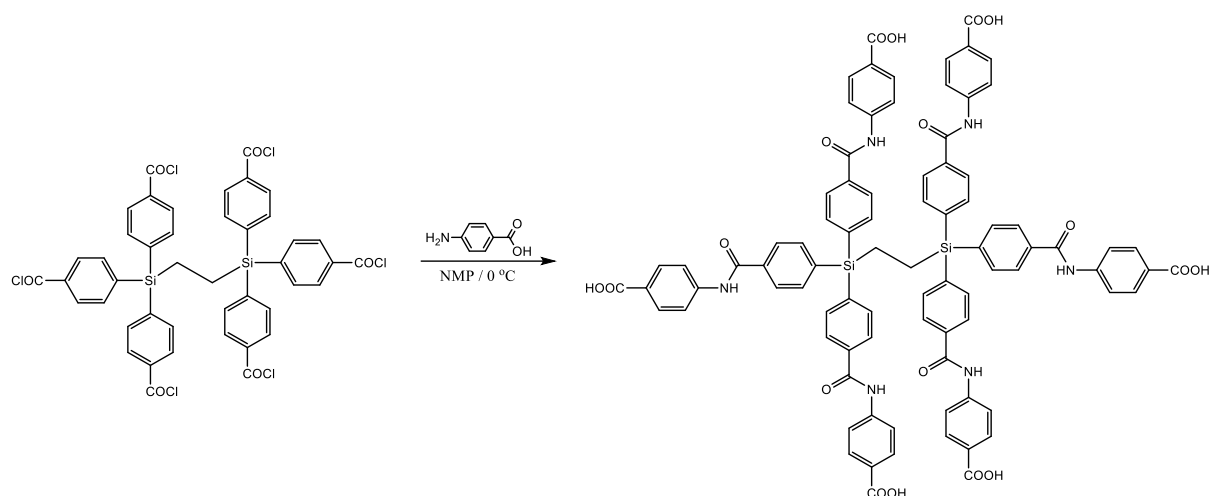
temperature. The mixture was poured into a flask containing ice-cold water, resulting in the immediate formation of a white precipitate. The solid was collected by suction filtration, washed with water, and dried under vacuum to give **L5-H₆**: 0.296 g (92 %). ¹H NMR (DMSO-*d*₆): δ (ppm) = 12.72 (s, 6 H, COOH), 10.66 (s, 6 H, N-H), 8.05 (d, *J* = 8 Hz 12H), 8.06-7.91 (m, 24 H, Ar-H), 7.75-7.70 (m, 16 H, Ar-H); ¹³C NMR (DMSO-*d*₆): δ (ppm) = 167.39, 166.44, 143.63, 137.06, 136.43, 136.11, 130.75, 128.00, 126.10, 119.94; ²⁹Si NMR (DMSO-*d*₆): δ (ppm) = -15.18 ppm; IR (ATR): ν (cm⁻¹) = 3057, 1680, 1595, 1517, 1406, 1313, 1241, 1172, 1128, 1085, 1015, 723; MS (ESI-) C₉₀H₆₄O₁₈Si₂ [M-H]⁻: calcd. *m/z* = 1571.3743, found *m/z* = 1571.3750

1,2-Bis(tris(4-acylchlorophenyl)silyl)ethane (**39**)



L3-H₆ (0.301 g, 0.371 mmol) was refluxed in thionyl chloride (3.78 mL, 52.04 mmol) under a nitrogen atmosphere at 80 °C for 4 h. The excess SOCl₂ was removed under reduced pressure, and the resulting white solid was collected and washed with dry hexane (**39**): 0.287 g (84 %). ¹H NMR (DMSO-*d*₆): δ (ppm) = 7.93 (d, *J* = 8 Hz, 12 H, Ar-H), 7.54 (d, *J* = 8.2 Hz, 12 H, Ar-H), 1.45 (s, 4 H, Si-CH₂-CH₂-Si); ¹³C NMR (DMSO-*d*₆): δ (ppm) = 167.54, 139.32, 135.94, 132.50, 129.18, 4.76; ²⁹Si NMR (DMSO-*d*₆): δ (ppm) = -9.45; IR (ATR): ν (cm⁻¹) = 1772, 1734, 1590, 1550, 1387, 1206, 1174, 1140, 1101, 866, 829, 759, 704.

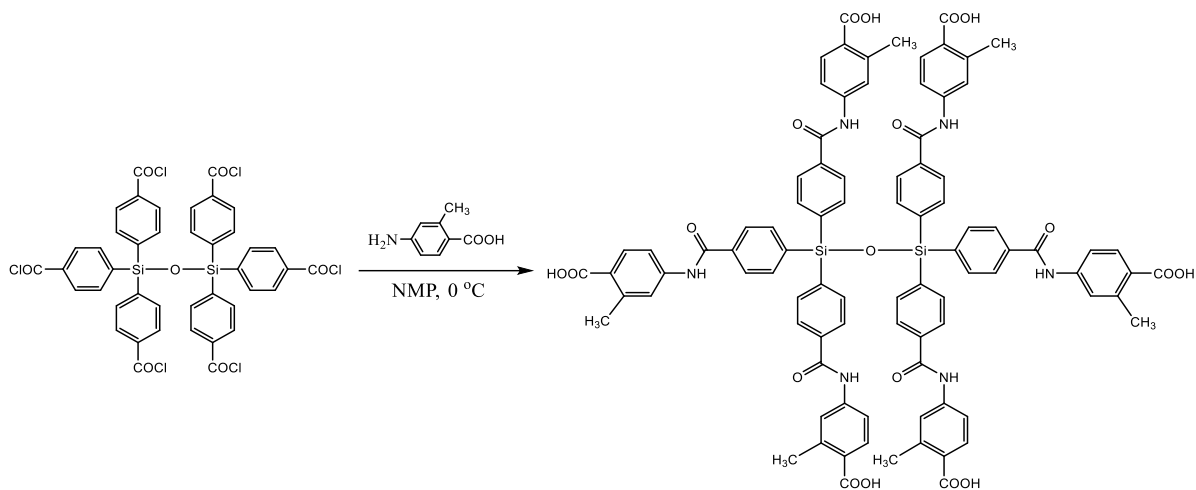
1,2-Bis(tris(4-carboxyphenyl-4-benzamide)silyl)ethane (L6-H₆)



4-Aminobenzoic acid (0.557 g, 4.07 mmol) was fully dissolved in NMP (10 mL) and cooled in an ice bath to 0 °C. 1,2-Bis(tris(4-acylchlorophenyl)silyl)ethane (0.250 g, 0.271 mmol) was then added, and the resulting mixture was stirred for 30 min at 0 °C followed by 1 h at ambient temperature. The reaction mixture was poured into a flask containing ice-cold water, immediately forming a white precipitate. The product was collected by suction filtration, washed with water, and dried under vacuum to give **L6-H₆**: 0.327 g (79 %). ¹H NMR (DMSO-d₆): δ (ppm) = 12.78 (s, 6 H, COOH), 10.62 (s, 6 H, N-H), 8.01-7.90 (m, 36 H, Ar-H), 7.68 (d, *J* = 8, 12 H, Ar-H), 1.61 (s, 4 H, Si-CH₂-CH₂-Si); ¹³C NMR (DMSO-d₆): δ (ppm) = 167.40, 166.48, 143.64, 138.19, 136.74, 135.82, 130.73, 127.90, 126.09, 119.96; ²⁹Si NMR (DMSO-d₆): δ (ppm) = -9.31 ppm; IR (ATR): ν (cm⁻¹) = 3057, 1655, 1593, 1515, 1407, 1241, 1172, 1087, 725; MS (ES⁺) C₈₆H₆₅N₆O₁₈Si₂ [M+H]⁺: calcd. *m/z* = 1525.3894, found *m/z* = 1525.3856.

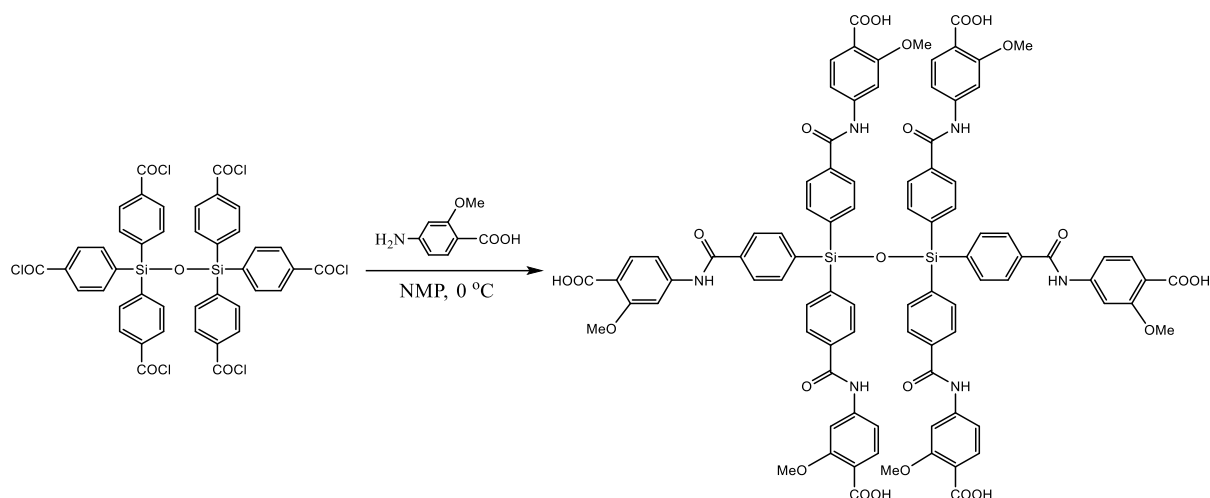
7.4.2 Preparation of L7-H₆, L8-H₆, L9-H₆

Hexa(4-carboxy-2-methylphenyl-4-benzamide)disiloxane (L7-H₆)



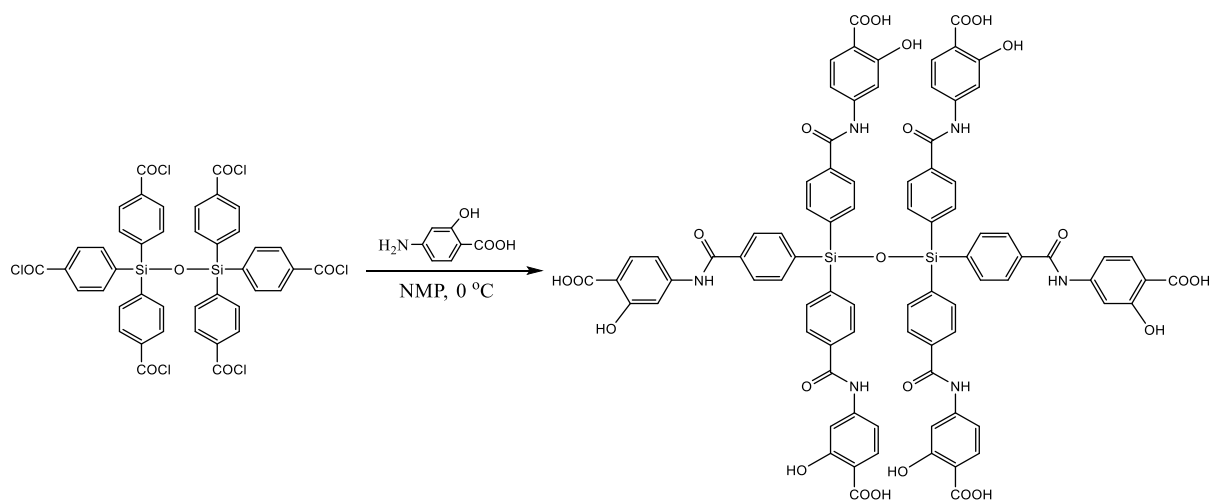
4-Amino-2-methylbenzoic acid (0.375 g, 2.475 mmol) was fully dissolved in NMP (15 mL) and cooled in an ice bath to 0 °C. Hexa(4-acylchlorophenyl)disiloxane (0.15 g, 0.165 mmol) was then added, and the resulting mixture was stirred for 30 min at 0 °C, followed by 1 h at ambient temperature. The reaction mixture was poured into a flask containing ice-cold water, immediately forming an off-white precipitate. The solid was collected by suction filtration, washed with water, and dried under vacuum to give **L7-H₆**: 0.224 g (85 %). ¹H NMR (DMSO-d₆): δ (ppm) = 12.54 (s, 6 H, COOH), 10.49 (s, 6 H, N-H), 7.99 (m, *J* = 9, 12 H, Ar-H), 7.87 (d, 6 H, *J* = 8 Hz, Ar-H), 7.75-7.67 (m, 24 H, Ar-H), 2.53 (s, 18 H, CH₃); ¹³C NMR (DMSO-d₆): δ (ppm) = 168.47, 166.09, 142.50, 140.96, 137.99, 137.28, 135.00, 132.06, 127.97, 125.51, 122.87, 117.57, 22.35; ²⁹Si NMR (DMSO-d₆): δ (ppm) = -19.01; IR (ATR): ν (cm⁻¹) = 3250, 1664, 1603, 1582, 1523, 1390, 1243, 1079, 721, 557; MS (ESI-) C₉₀H₇₂N₆O₁₉Si₂ [M-H]⁻: calcd. *m/z* = 1595.4318, found *m/z* = 1595.4357.

Hexa(4-carboxy-2-methoxyphenyl-4-benzamide)disiloxane (L8-H₆)



4-Amino-2-methoxybenzoic acid (0.414 g, 2.475 mmol) was fully dissolved in NMP (20 mL) and cooled in an ice bath to 0 °C. Hexa(4-acylchlorophenyl)disiloxane (0.15 g, 0.165 mmol) was then added, and the resulting mixture was stirred for 30 min at 0 °C, followed by 1 h at ambient temperature. The reaction mixture was poured into a flask containing ice-cold water, immediately forming an off-white precipitate. The solid was collected by suction filtration, washed with water, and dried under vacuum to give **L8-H₆**: 0.226 g (81 %). ¹H NMR (DMSO-d₆): δ (ppm) = 12.38 (s, 6 H, COOH), 10.55 (s, 6 H, N-H), 8.02-7.97 (m, 12 H, Ar-H), 7.73-7.65 (m, 24 H, Ar-H), 7.47 (d, 6 H, *J* = 8 Hz, Ar-H), 3.80 (s, 18 H, -OCH₃); ¹³C NMR (DMSO-d₆): δ (ppm) = 166.96, 166.19, 159.71, 144.20, 138.04, 137.25, 135.02, 132.62, 127.97, 115.92, 111.75, 104.13, 56.05; ²⁹Si NMR (DMSO-d₆): δ (ppm) = -19.08; IR (ATR): ν (cm⁻¹) = ~3300, 2950, 1659, 1589, 1525, 1400, 1250, 1172, 1078, 1015, 840, 775, 719, 558; MS (ESI-) C₉₀H₇₂N₆O₂₅Si₂ [M-H]⁻: calcd. *m/z* = 1691.4013; *m/z*, C₉₀H₇₂N₆O₂₅Si₂ [M-2H]²⁻: calcd. *m/z* = 845.1970 found *m/z* = 845.1970 ([M-2H]²⁻).

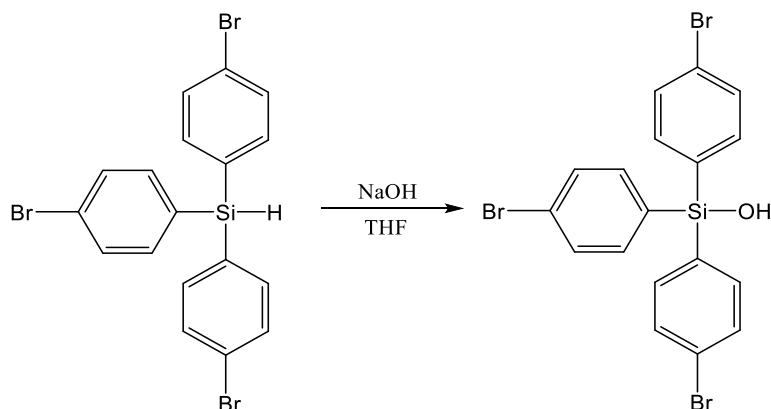
Hexa(4-carboxy-2-hydroxyphenyl-4-benzamide)disiloxane (**L9-H₆**)



4-Amino-2-hydroxybenzoic acid (0.379 g, 2.475 mmol) was fully dissolved in NMP (15 mL) and cooled in an ice bath to 0 °C. Hexa(4-acylchlorophenyl)disiloxane (0.15 g, 0.165 mmol) was then added, and the resulting mixture was stirred for 30 min at 0 °C and for 1 h at ambient temperature. The reaction mixture was poured into a flask containing ice-cold water, followed by the addition of HCl (4 mL, 2.5 M). After overnight cooling at -5 °C, a pink precipitate formed, which was collected by suction filtration. Upon washing with warm water, the solid turned off-white and was subsequently dried under vacuum to give **L9-H₆**: 0.170 g (64 %). ¹H NMR (DMSO-*d*₆): δ (ppm) = 13.76 (s, 6 H, COOH), 11.36 (s, 6 H, O-H), 10.54 (s, 6 H, N-H), 7.98 (d, *J* = 8 Hz, 12 H, Ar-H), 7.77-7.66 (m, 18 H, Ar-H), 7.53 (s, 6 H, Ar-H), 7.31 (d, *J* = 9 Hz, 6 H, Ar-H); ¹³C NMR (DMSO-*d*₆): δ (ppm) = 172.06, 166.37, 162.41 145.88, 138.06, 137.24, 134.99, 131.35, 128.05, 111.66, 108.62, 107.49; ²⁹Si NMR (DMSO-*d*₆): δ (ppm) = -10.58; IR (ATR): ν (cm⁻¹) = 2965, 1656, 1596, 1503, 1402, 1281, 1221, 1156, 1079, 1012, 784, 724, 558; MS (ESI-) C₈₄H₆₀N₆O₂₅Si₂ [M-H]⁻: calcd. *m/z* = 1607.3074, found *m/z* = 1607.3085, [M-2H]²⁻: calcd. *m/z* = 803.1501, found *m/z* = 803.1505.

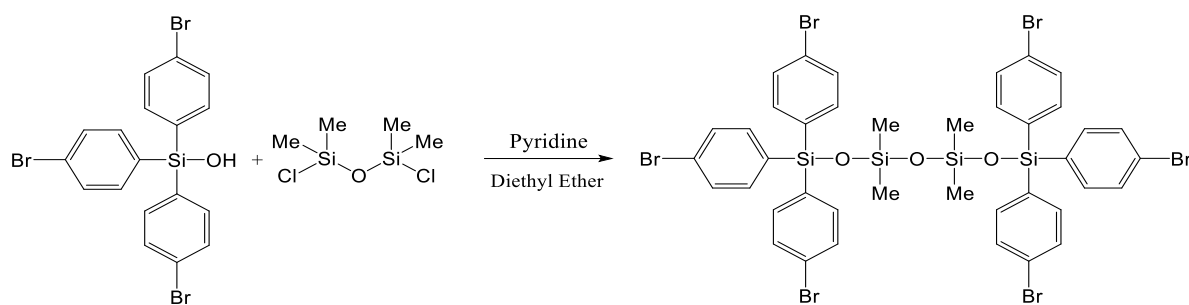
7.5 Preparation of L10-H₆

Tris(4-bromophenyl)silanol (**40**)



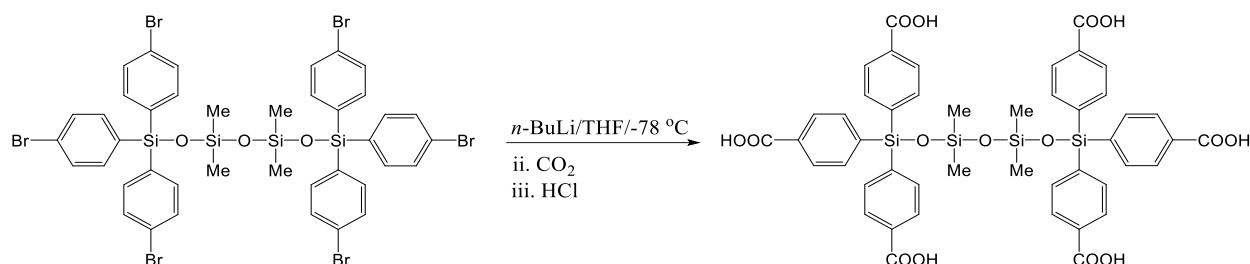
A solution of tris(4-bromophenyl)silane (8.0 g, 16 mmol) in THF (80 mL) was treated with 4 M NaOH (4.8 mL, 19.2 mmol) and stirred overnight. The reaction mixture was then concentrated to approximately 10 mL, followed by the addition of chloroform (50 mL) and 1 M HCl (30 mL). The organic layer was collected, dried over MgSO₄, and concentrated using a rotary evaporator to afford a colourless oil. Hot hexane (80 mL) was added to the residue, and the solution was allowed to stand, yielding colourless needles (**40**), which were collected by suction filtration: 5.91 g (72 %). M.p.: 125-127 °C (lit. 125-127 °C)²⁰⁸; ¹H NMR (CDCl₃): δ (ppm) = 7.56 (d, *J* = 8.3 Hz, 6 H, Ar-H), 7.44 (d, *J* = 8 Hz, 6 H, Ar-H), 2.87 (s, 1 H, Si-OH); ¹³C NMR (CDCl₃): δ (ppm) = 136.40, 132.89, 131.41, 125.73; ²⁹Si NMR (CDCl₃): δ (ppm) = -12.64; IR (ATR): ν (cm⁻¹) = 3168, 1571, 1478, 1377, 1117, 1066, 1009, 835, 802, 733.

1,1,1,7,7,7-hexakis(4-bromophenyl)-3,3,5,5-tetramethyltetrasiloxane (41)



Tris(4-bromophenyl)silanol (4.0 g, 7.80 mmol) was dissolved in diethyl ether (50 mL), and dry pyridine (2.0 mL, 24.72 mmol) was added. The solution was stirred for 5 min at room temperature, then cooled to 0 °C before Me₂SiCl₂ (0.76 mL, 3.88 mmol) was added dropwise. The reaction mixture was stirred overnight, gradually warming to ambient temperature. The reaction was quenched with water (30 mL), and the organic layer was separated and extracted with diethyl ether (3 × 20 mL). The combined organic extracts were dried over MgSO₄ and concentrated using a rotary evaporator to afford a colourless oil. The oil was dissolved in hot hexane, allowed to stand, and placed in the fridge overnight. The resulting white solid (**41**) was collected by suction filtration: 1.66 g (37 %). M.p.: 185-188 °C; ¹H NMR (CDCl₃): δ (ppm) = 7.49 (d, *J* = 8 Hz, 12 H, Ar-H), 7.36 (d, *J* = 8 Hz, 12 H, Ar-H), 0.01 (s, 12 H, Si-CH₃); ¹³C NMR (CDCl₃): δ (ppm) = 136.31, 133.45, 131.28, 125.47, 1.22; ²⁹Si NMR (CDCl₃): δ (ppm) = -18.76 (Ar₃Si), -21.37 (Me₂Si); IR (ATR): ν (cm⁻¹) = 1570, 1477, 1375, 1259, 1185, 1119, 1060, 1004, 841, 801, 729, 592.

1,1,1,7,7,7-hexakis(4-carboxyphenyl)-3,3,5,5-tetramethyltetrasiloxane (L10-H₆)



Compound **41** (1.0 g, 0.865 mmol) was dissolved in anhydrous THF (30 mL) in a 2-neck round-bottomed flask under a nitrogen atmosphere. This solution was added dropwise into a second flask containing 2.5 M *n*-BuLi (2.08 mL, 5.19 mmol) in anhydrous THF (35 mL) at -78 °C under nitrogen. The reaction mixture was stirred for 1.5 h, after which carbon dioxide was bubbled through the solution for 3 h. The mixture was then stirred overnight, gradually warming to room temperature. The reaction was quenched with 1 M HCl (15 mL), and the mixture was concentrated using a rotary evaporator, yielding a white crystalline solid (**L10-H₆**): 0.61 g (74 %). M.p.: > 240 °C; ¹H NMR (DMSO-*d*₆): δ (ppm) = 12.19 (s, 6 H, COOH), 7.94 (d, *J* = 8 Hz, 12 H, Ar-H), 7.62 (d, *J* = 8 Hz, 12 H, Ar-H), -0.03 (s, 12 H, Si-CH₃); ¹³C NMR (DMSO-*d*₆): δ (ppm) = 167.83, 139.57, 134.95, 133.82, 129.12, 1.40; ²⁹Si NMR (DMSO-*d*₆): δ (ppm) = -18.16 (Ar₃Si), -22.65 (Me₂Si); IR (ATR): ν (cm⁻¹) = 3050, 2846, 2652, 2530, 2111, 1688, 1600, 1554, 1550, 1498, 1390, 1319, 1286, 1258, 1184, 1096, 1033, 1011, 841, 798, 762, 760, 698; MS (ES⁺) C₄₆H₄₃N₆O₁₅Si₄ [M+H]⁺: calcd. *m/z* = 947.1679, found *m/z* = 947.1724.

7.6 MOF Synthesis

L1-In

L1-H₆ (20 mg, 26 μmol) and $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (60 mg, 156 μmol) were placed in a 7 mL polypropylene screw-cap glass vial. Subsequently, a 1:1 mixture of DMF (2.5 mL) and MeCN (2.5 mL) and concentrated nitric acid (0.1 mL) were added to the vial. The vial was tightly sealed with its screw lid, and the mixture was then sonicated in an ultrasonic bath for 3 min, giving a clear solution. The vial was placed in a programmable oven and was gradually heated to 80 °C over 2 h. The vial was then heated for 42 h at the same temperature, followed by cooling to room temperature over 3 h. Colourless tear-shaped crystals were obtained (**L1-In**). IR (ATR): ν (cm^{-1}) = 2926, 1649, 1577, 1533, 1497, 1386, 1252, 1099, 861, 770, 724.

L1-Ga

L1-H₆ (20 mg, 26 μmol) and $\text{Ga}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (54 mg, 156 μmol) were placed in a 7 mL polypropylene screw-cap glass vial. Subsequently, a 1:1 mixture of DMF (2.5 mL) and MeCN (2.5 mL) and concentrated nitric acid (0.1 mL) were added to the vial. The vial was tightly sealed with its screw lid, and the mixture was then sonicated in an ultrasonic bath for 3 min, giving a clear solution. The vial was placed in a programmable oven and was gradually heated to 80 °C over two h. The vial was then heated for 42 h at the same temperature, followed by cooling to room temperature over 3 h. **L1-Ga** was obtained as a white powder. IR (ATR): ν (cm^{-1}) = 2911, 1622, 1544, 1503, 1470, 1409, 1303, 1101, 825, 773, 729.

L1-Al

L1-H₆ (20 mg, 26 μ mol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (59 mg, 156 μ mol) were placed in a 7 mL polypropylene screw-cap glass vial. Subsequently, a 1:1 mixture of DMF (2.5 mL) and MeCN (2.5 mL) and concentrated nitric acid (0.1 mL) were added to the vial. The vial was tightly sealed with its screw lid, and the mixture was then sonicated in an ultrasonic bath for 3 min, giving a clear solution. The vial was placed in a programmable oven and was gradually heated to 80 °C over 2 h. The vial was then heated for 42 h at the same temperature, followed by cooling to room temperature over 3 h. **L1-Al** formed as a white gel which, when subjected to low pressure (oil pump), afforded a white powder. IR (ATR): ν (cm^{-1}) = 2924, 1639, 1548, 1501, 1436, 1383, 1261, 1101, 850, 777, 724.

L1-Fe

L1-H₆ (20 mg, 26 μ mol) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (63 mg, 156 μ mol) were placed in a 7 mL polypropylene screw-cap glass vial. Subsequently, a 1:1 mixture of DMF (2.5 mL) and MeCN (2.5 mL) and concentrated nitric acid (0.1 mL) were added to the vial. The vial was tightly sealed with its screw lid, and the mixture was then sonicated in an ultrasonic bath for 3 min, giving a clear solution. The vial was placed in a programmable oven and was gradually heated to 80 °C over 2 h. The vial was then heated for 42 h at the same temperature, followed by cooling to room temperature over 3 h. Orange-brown powder was obtained (**L1-Fe**). IR (ATR): ν (cm^{-1}) = 2920, 1658, 1599, 1543, 1498, 1405, 1211, 1104, 856, 791, 725.

L1-Fe-Cl

L1-H₆ (20 mg, 26 μ mol) and FeCl₃·6H₂O (42 mg, 156 μ mol) were placed in a 7 mL polypropylene screw-cap glass vial. Subsequently, a 1:1 mixture of DMF (2.5 mL) and MeCN (2.5 mL), and 1 M HCl (0.1 mL) were added to the vial. The vial was tightly sealed with its screw lid, and the mixture was then sonicated in an ultrasonic bath for 3 min, giving a clear solution. The vial was placed in a programmable oven and was gradually heated to 80 °C over 2 h. The vial was then heated for 42 h at the same temperature, followed by cooling to room temperature over 3 h. Orange-brown powder was obtained (**L1-Fe-Cl**). IR (ATR): ν (cm⁻¹) = 2927, 1653, 1597, 1541, 1498, 1405, 1101, 1017, 849, 769, 725.

L1-Tb

L1-H₆ (10 mg, 13 μ mol) and Tb(NO₃)₃·6H₂O (49 mg, 113 μ mol) were placed in a 7 mL polypropylene screw-cap glass vial. Subsequently, DMF (2 mL) and water (0.5 mL) were added to the vial. The vial was tightly sealed with its screw lid, and the mixture was then sonicated in an ultrasonic bath for 3 min, giving a clear solution. The vial was placed in a programmable oven and was gradually heated to 80 °C over 3 h. The vial was then heated for 42 h at the same temperature, followed by cooling to room temperature over 3 h. Colourless blade-shaped crystals were isolated by suction filtration (**L1-Tb**). IR (ATR): ν (cm⁻¹) = 2929, 1648, 1576, 1522, 1497, 1400, 1381, 1252, 1100, 1015, 855, 773, 729.

L1-Eu

L1-H₆ (10 mg, 13 μ mol) and $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (50 mg, 113 μ mol) were placed in a 7 mL polypropylene screw-cap glass vial. Subsequently, DMF (2 mL) and water (0.5 mL) were added to the vial. The vial was tightly sealed with its screw lid, and the mixture was then sonicated in an ultrasonic bath for 3 min, giving a clear solution. The vial was placed in a programmable oven and was gradually heated to 80 °C over 3 h. The vial was then heated for 42 h at the same temperature, followed by cooling to room temperature over 3 h. Colourless rectangular-shaped crystals were isolated by suction filtration (**L1-Eu**). IR (ATR): ν (cm^{-1}) = 2928, 1649, 1578, 1522, 1497, 1400, 1383, 1252, 1100, 1015, 852, 773, 731.

L1-Cu

L1-H₆ (20 mg, 26 μ mol) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (37 mg, 156 μ mol) were placed in a 7 mL polypropylene screw-cap glass vial. Subsequently, a 1:1 mixture of DMF (2.5 mL) and MeCN (2.5 mL) and concentrated nitric acid (0.2 mL) were added to the vial. The vial was tightly sealed with its screw lid, and the mixture was then sonicated in an ultrasonic bath for 3 min, giving a clear solution. The vial was placed in a programmable oven and was gradually heated to 80 °C over 2 h. The vial was then heated for 42 h at the same temperature, followed by cooling to room temperature over 6 h. Greenish blue plate-shaped crystals were obtained (**L1-Cu**). IR (ATR): ν (cm^{-1}) = 3070, 1700, 1577, 1526, 1498, 1388, 1187, 1100, 1015, 848, 770, 729.

L1-Na

L1-H₆ (38 mg, 49 μmol) and NaNO_3 (25 mg, 294 μmol) were placed in a 7 mL polypropylene screw-cap glass vial. DMF (2 mL) was added, the vial was sealed tightly, and the mixture was stirred for 2 h at room temperature. The mixture was then placed in a heating block and heated at 140 °C for 96 h. Colourless needle-shaped crystals were obtained (**L1-Na**). IR (ATR): ν (cm^{-1}) = 2924, 1653, 1540, 1497, 1386, 1255, 1097, 1013, 848, 768, 701.

L1-Li

L1-H₆ (38 mg, 49 μmol) and LiNO_3 (20 mg, 294 μmol) were placed in a 7 mL polypropylene screw-cap glass vial. DMF (2 mL) was added, the vial was sealed tightly, and the mixture was stirred for 2 h at room temperature. The mixture was then placed in a heating block and heated at 140 °C for 96 h. Colourless petal-shaped crystals were obtained (**L1-Li**). IR (ATR): ν (cm^{-1}) = 2925, 1664, 1603, 1541, 1497, 1381, 1320, 1299, 1101, 1018, 851, 777, 729, 706.

L1-K

L1-H₆ (38 mg, 49 μmol) and KNO_3 (30 mg, 294 μmol) were placed in a 7 mL polypropylene screw-cap glass vial. DMF (2 mL) was added, the vial was sealed tightly, and the mixture was stirred for 2 h at room temperature. The mixture was then placed in a heating block and heated at 140 °C for 96 h. Colourless block-shaped crystals were obtained (**L1-K**). IR (ATR): ν (cm^{-1}) = 2924, 1664, 1549, 1497, 1384, 1254, 1098, 1012, 770, 701.

L4-In

L4-H₆ (39 mg, 26 μ mol) and $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (60 mg, 156 μ mol) were placed in a 7 mL polypropylene screw-cap glass vial. Subsequently, a 1:1 mixture of DMF (2.5 mL) and MeCN (2.5 mL) and concentrated nitric acid (0.1 mL) were added to the vial. The vial was tightly sealed with its screw lid, and the mixture was then sonicated in an ultrasonic bath for 3 min, giving clear solution. The vial was placed in a programmable oven and was gradually heated to 80 °C over 2 h. The vial was then heated for 42 h at the same temperature, followed by cooling to room temperature over 3 h. Colourless blade-shaped crystals were obtained (**L4-In**). IR (ATR): ν (cm^{-1}) = 3284, 2930, 1647, 1597, 1521, 1498, 1387, 1314, 1249, 1176, 1088, 1013, 857, 781, 732.

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Supplementary Information (SI)

HOFs and MOFs Crystallographic Data

Table S1. Crystallographic Data of the HOFs described in Chapter 3.

Compound	L4-H ₆	L5-H ₆	L6-H ₆	L10-H ₆
Formula	C ₉₅ H ₁₁₂ N ₆ O ₃₄ Si ₂	C ₁₀₂ H ₁₁₂ N ₆ O ₃₀ Si ₂	C ₁₀₄ H ₁₃₆ N ₆ O ₃₆ Si ₂	C ₅₁ H ₅₃ O ₂₀ Si ₄
$D_{calc.}/\text{g cm}^{-3}$	1.232	1.316	1.258	1.345
m/mm^{-1}	0.993	0.112	0.986	1.669
Formula Weight	1938.08	1958.219	2102.36	1091.29
Colour	colourless	colourless	colourless	colourless
Shape	lath-shaped	blade-shaped	plate-shaped	plate-shaped
Size/mm ³	0.260×0.040×0.010	0.090×0.050×0.025	0.160×0.140×0.020	0.190×0.060×0.015
T/K	100(2)	30(2)	100(2)	100(2)
Crystal System	monoclinic	triclinic	monoclinic	triclinic
Space Group	$I2/a$	$P-1$	$C2/c$	$P-1$
$a/\text{\AA}$	44.9472(17)	15.8485(4)	8.8350(3)	8.65810(10)
$b/\text{\AA}$	9.7251(2)	16.4134(4)	36.7881(16)	17.1794(2)
$c/\text{\AA}$	49.0557(10)	20.1625(6)	34.1620(8)	38.1669(5)
α°	90	75.226(3)	90	78.1330(10)
β°	102.947(3)	77.048(2)	90.310(3)	88.9190(10)
γ°	90	85.980(2)	90	76.0570(10)
$V/\text{\AA}^3$	20897.9(10)	4941.9(2)	11103.3(7)	5389.15(12)
Z	8	2	4	4
Z'	1	1	0.5	2
Wavelength/ $\text{\AA}$	1.54178	0.68890	1.54178	1.54178
Radiation type	Cu K α	Synchrotron	Cu K α	Cu K α
Q_{min}°	1.848	1.46	2.402	2.367
Q_{max}°	70.068	25.50	70.783	75.230
Measured Refl's.	95956	65849	79854	43305
Indep't Refl's	19540	19260	10459	43305
Refl's $I \geq 2\sigma(I)$	10398	8176	6280	35055
R_{int}	0.0910	0.0788	0.0675	N/A
Parameters	1422	1523	593	1230
Restraints	3368	5957	1120	0
Largest Peak	0.917	1.3107	0.338	0.506
Deepest Hole	-0.350	-0.5945	-0.334	-0.386
GooF	1.048	1.1574	1.114	1.034
wR_2 (all data)	0.3228	0.3993	0.3166	0.1917
wR_2	0.2802	0.3421	0.2856	0.1819
R_I (all data)	0.1512	0.1886	0.1231	0.0801
R_I	0.1000	0.1141	0.0944	0.0664

Table S2. Crystallographic Data of the MOFs described in Chapter 3.

Compound	L1-In	L4-In	L1-Tb	L1-Cu
Formula	$[\text{In}_3(\mu_3\text{-O})(\text{L1})(\text{H}_2\text{O})_3] \cdot \text{NO}_3 \cdot 5 \text{DMF}$	$[\text{In}_3(\mu_3\text{-O})(\text{L4})(\text{H}_2\text{O})_3] \cdot \text{NO}_3 \cdot 12\text{DMF} \cdot 3\text{H}_2\text{O}$	$[\text{Tb}_2(\text{L1})(\text{H}_2\text{O})_4] \cdot 4\text{D MF} \cdot 6\text{H}_2\text{O}$	$[\text{Cu}_3(\text{L1})(\text{H}_2\text{O})_2] \cdot 4\text{D MF} \cdot 10\text{H}_2\text{O}$
$D_{\text{calc.}}/\text{g cm}^{-3}$	1.351	0.593	1.361	1.184
m/mm^{-1}	7.635	0.236	1.918	0.757
Formula Weight	1645.87	2901.21	1583.17	1562.03
Colour	colourless	colourless	colourless	pale greenish blue
Shape	prism, tear	blade-shaped	blade-shaped	plate-shaped
Size/ mm^3	$0.090 \times 0.050 \times 0.045$	$0.200 \times 0.060 \times 0.050$	$0.150 \times 0.080 \times 0.030$	$0.110 \times 0.070 \times 0.010$
T/K	100(2)	30(2)	100(2)	30.15
Crystal System	trigonal	trigonal	triclinic	orthorhombic
Space Group	$P\text{-}31c$	$P\text{-}31c$	$P\text{-}1$	$Cmmm$
$a/\text{\AA}$	13.2739(7)	20.0207(9)	11.5950(7)	24.5592(11)
$b/\text{\AA}$	13.2739(7)	20.0207(9)	13.3618(7)	27.199(2)
$c/\text{\AA}$	26.5092(12)	46.8397(12)	14.1945(7)	13.1168(5)
a°	90	90	65.202(5)	90
b°	90	90	76.094(5)	90
g°	120	120	79.935(5)	90
$V/\text{\AA}^3$	4045.1(5)	16259.3(15)	1931.0(2)	8761.8(8)
Z	2	2	1	4
Z'	0.16667	0.166667	0.5	0.25
Wavelength/ $\text{\AA}$	1.54184	0.68890	0.71075	0.6889
Radiation type	Cu K_α	Synchrotron	Mo K_α	Synchrotron
Q_{min}°	3.334	1.686	2.231	1.451
Q_{max}°	68.225	22.241	27.485	26.572
Measured Refl's.	26158	114695	48769	31153
Indep't Refl's	2474	7529	8838	5396
Refl's $I \geq 2 \sigma(I)$	1424	2239	6535	2047
R_{int}	0.0606	0.0540	0.0470	0.1421
Parameters	395	868	467	170
Restraints	1129	2083	1281	274
Largest Peak	0.485	0.771	3.462	1.552
Deepest Hole	-0.435	-0.268	-0.920	-0.913
GooF	0.971	1.090	1.031	1.190
wR_2 (all data)	0.2267	0.3920	0.2858	0.4479
wR_2	0.1982	0.3223	0.2651	0.4092
R_I (all data)	0.0881	0.1771	0.1093	0.2104
R_I	0.0692	0.1223	0.0940	0.1493

Table S3. Crystallographic Data of the alkali metal MOFs described in Chapter 4.

Compound	L1-Li	L1-Na	L1-K
Formula	[Li ₁₀ (L1-H) ₂ (DMF) ₅]·DMF	[Na ₃ (L1-H ₃)(DMF) ₆]	[K ₂ (L1-H ₄)(H ₂ O) ₃]·6DMF
$D_{calc.}/\text{g cm}^{-3}$	1.263	1.147	1.300
m/mm^{-1}	1.162	1.186	0.229
Formula Weight	2083.56	1303.4	1366.64
Colour	colourless	colourless	colourless
Shape	petal-shaped	needle-shaped	block-shaped
Size/mm ³	0.100×0.070×0.025	0.240×0.030×0.020	0.085×0.070×0.050
T/K	100.00(10)	100(2)	100(2)
Crystal System	monoclinic	trigonal	trigonal
Space Group	$P2_1/c$	$P-31c$	$P31c$
$a/\text{\AA}$	14.42220(10)	14.3853(6)	14.3708(3)
$b/\text{\AA}$	16.21530(10)	14.3853(6)	14.3708(3)
$c/\text{\AA}$	23.64560(10)	19.2834(6)	19.4711(5)
a°	90	90	90
b°	97.6980(10)	90	90
g°	90	120	120
$V/\text{\AA}^3$	5479.93(6)	3455.8(3)	3482.43(17)
Z	4	1	2
Z'	1	0.083333	0.333333
Wavelength/ $\text{\AA}$	1.54178	1.54178	0.6889
Radiation type	Cu K α	Cu K α	Synchrotron
Q_{min}°	3.092	4.225	1.586
Q_{max}°	73.685	73.830	36.008
Measured Refl's.	195235	24314	67588
Indep't Refl's	10859	2219	11407
Refl's $I \geq 2 \sigma(I)$	9464	1816	4903
R_{int}	0.0405	0.0466	0.0495
Parameters	1012	189	322
Restraints	2123	389	960
Largest Peak	0.957	0.538	0.506
Deepest Hole	-0.393	-0.400	-0.194
GooF	1.038	1.134	0.932
wR_2 (all data)	0.2278	0.2025	0.2494
wR_2	0.2199	0.1937	0.1962
R_I (all data)	0.0771	0.0758	0.1340
R_I	0.0707	0.0661	0.0674

MOF synthesis (Failed Attempts)

Table S4. Failed attempts in MOF synthesis.

Compound	Metal salt	L:M (mol ratio)	Solvent	Modulator	T (°C)	Time (h)
L1-H ₆	Co(NO ₃) ₂ ·6H ₂ O	1:6	1:1 DMA/water	-	100	18
L1-H ₆	Co(NO ₃) ₂ ·6H ₂ O	1:6	1:1 DMF/MeCN	-	80	42
L1-H ₆	MnNO ₃ ·4H ₂ O	1:6	1:1 DMA/water	-	100	18
L2-H ₆	In(NO ₃) ₃ ·5H ₂ O	1:6	1:1 DMF/MeCN	0.1 mL HNO ₃	80	42
L2-H ₆	In(NO ₃) ₃ ·5H ₂ O	1:3	1:1 DMF/MeCN	0.1 mL HNO ₃	80	42
L2-H ₆	In(NO ₃) ₃ ·5H ₂ O	1:6	1:1 DMF/MeCN	0.1 mL HNO ₃	100	42
L2-H ₆	Fe(NO ₃) ₃ ·9H ₂ O	1:6	1:1 DMF/MeCN	0.1 mL HNO ₃	80	42
L3-H ₆	In(NO ₃) ₃ ·5H ₂ O	1:6	1:1 DMF/MeCN	0.1 mL HNO ₃	80	42
L3-H ₆	Fe(NO ₃) ₃ ·9H ₂ O	1:6	1:1 DMF/MeCN	0.1 mL HNO ₃	80	42
L3-H ₆	FeCl ₃ ·6H ₂ O	1:6	1:1 DMF/MeCN	0.1 mL 1M HCl	80	42
L4-H ₆	Cu(NO ₃) ₂ ·3H ₂ O	1:6	1:1 DMF/MeCN	0.1 mL HNO ₃	80	42
L4-H ₆	Cu(NO ₃) ₂ ·3H ₂ O	1:6	1:1 DMF/MeCN	0.05 mL HNO ₃	80	42
L4-H ₆	Cu(NO ₃) ₂ ·3H ₂ O	1:6	1:1 DMA/water	0.1 mL cHCl	80	72
L4-H ₆	Cu(NO ₃) ₂ ·3H ₂ O	1:6	1:1 DMF/water	0.1 mL cHCl	80	72
L4-H ₆	Cu(NO ₃) ₂ ·3H ₂ O	1:6	1:1 DMF/water	0.05 mL cHCl	80	72
L4-H ₆	Cu(NO ₃) ₂ ·3H ₂ O	1:6	1:1 DMA/water	0.2 mL cHCl	80	72
L4-H ₆	Cu(NO ₃) ₂ ·3H ₂ O	1:6	1:1 DMA/water	0.15 mL cHCl	80	72
L4-H ₆	Cu(NO ₃) ₂ ·3H ₂ O	1:6	1:1 DMA/water	0.2 mL 1M HCl	80	72
L4-H ₆	Cu(NO ₃) ₂ ·3H ₂ O	1:6	1:1 DMA/water	0.1 mL 1M HCl	80	72
L4-H ₆	Cu(NO ₃) ₂ ·3H ₂ O	1:6	1:1 DMA/water	0.05 mL 1M HCl	80	72
L4-H ₆	Cu(NO ₃) ₂ ·3H ₂ O	1:6	1:1 DMA/water	0.1 mL cHCl	80	42
L4-H ₆	Tb(NO ₃) ₃ ·6H ₂ O	1:6	4:1 DMF/water	-	80	42
L4-H ₆	Tb(NO ₃) ₃ ·6H ₂ O	1:6	4:1 DMF/water	0.1 HNO ₃	80	42
L4-H ₆	Fe(NO ₃) ₃ ·9H ₂ O	1:6	1:1 DMF/MeCN	0.1 mL HNO ₃	80	42
L4-H ₆	FeCl ₃ ·6H ₂ O	1:6	1:1 DMF/MeCN	0.1 mL 1M HCl	80	42
L5-H ₆	In(NO ₃) ₃ ·5H ₂ O	1:6	1:1 DMF/MeCN	0.1 mL HNO ₃	80	42
L5-H ₆	Zn(NO ₃) ₃ ·6H ₂ O	1:6	1:1 DMF/water	-	100	24
L5-H ₆	Zn(NO ₃) ₃ ·6H ₂ O	1:6	1:1 DMF/water	-	100	48
L5-H ₆	Zn(NO ₃) ₃ ·6H ₂ O	1:3	1:1 DMF/water	-	100	24
L5-H ₆	Zn(NO ₃) ₃ ·6H ₂ O	1:6	1:1 DMA/water	-	100	24
L5-H ₆	Fe(NO ₃) ₃ ·9H ₂ O	1:6	1:1 DMF/MeCN	0.1 mL HNO ₃	80	42
L5-H ₆	FeCl ₃ ·6H ₂ O	1:6	1:1 DMF/MeCN	0.1 mL 1M HCl	80	42
L6-H ₆	Fe(NO ₃) ₃ ·9H ₂ O	1:6	1:1 DMF/MeCN	0.1 mL HNO ₃	80	42
L6-H ₆	FeCl ₃ ·6H ₂ O	1:6	1:1 DMF/MeCN	0.1 mL 1M HCl	80	42
L6-H ₆	Tb(NO ₃) ₃ ·6H ₂ O	1:6	4:1 DMF/water	-	80	42
L6-H ₆	Tb(NO ₃) ₃ ·6H ₂ O	1:6	4:1 DMF/water	0.1 HNO ₃	80	42
L6-H ₆	NaNO ₃	1:6	2 mL DMF	-	140	96
L6-H ₆	Tb(NO ₃) ₃ ·6H ₂ O	1:6	4:1 DMF/water	0.1 HNO ₃	80	42
L9-H ₆	In(NO ₃) ₃ ·5H ₂ O	1:6	1:1 DMF/MeCN	0.1 mL HNO ₃	80	42
L10-H ₆	Cu(NO ₃) ₂ ·3H ₂ O	1:6	1:1 DMF/MeCN	0.2 mL HNO ₃	80	42
L10-H ₆	Cu(NO ₃) ₂ ·3H ₂ O	1:6	1:1 DMA/Water	0.1 mL cHCl	80	72
L10-H ₆	Cu(NO ₃) ₂ ·3H ₂ O	1:6	1:1 DMA/Water	0.2 mL cHCl	80	72
L10-H ₆	In(NO ₃) ₃ ·5H ₂ O	1:6	1:1 DMF/MeCN	0.1 mL HNO ₃	80	42
L10-H ₆	Zn(OAc) ₂	1:6	2.8 mL DMF/300 μL acetic acid	0.1 mL HNO ₃	80	42

Additional SCXRD Figures

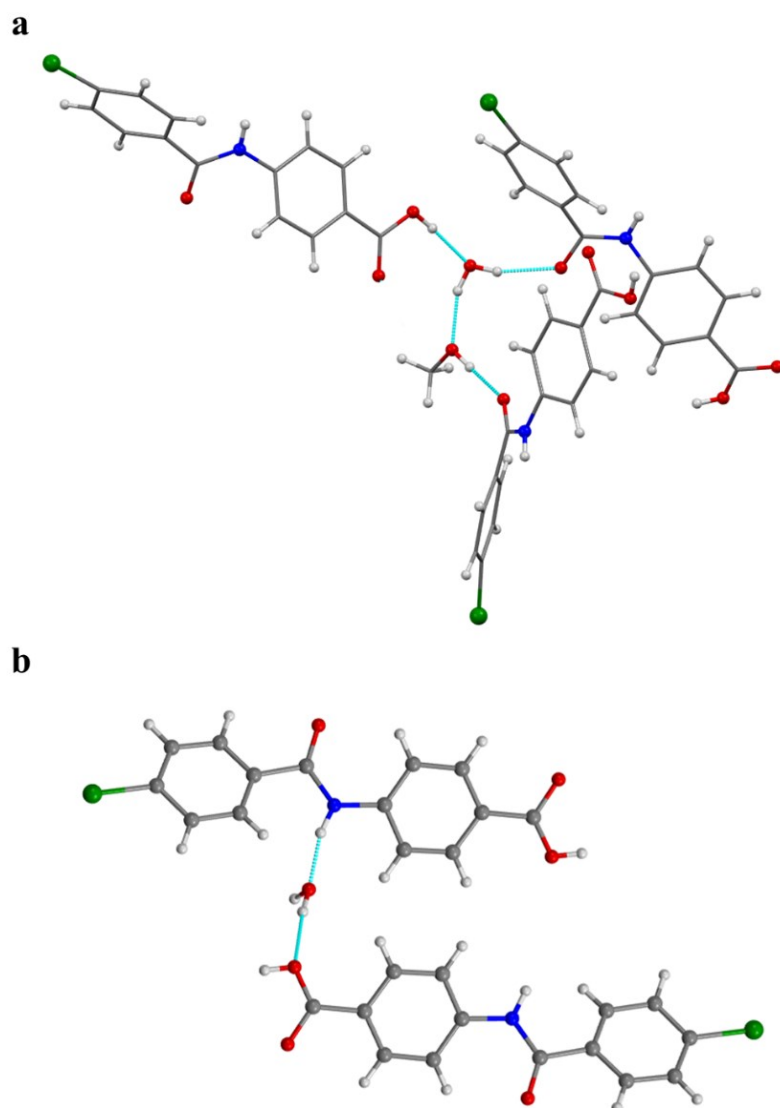


Figure S1. Coordinating solvent molecules in **L4-H₆** HOF: (a) methanol-water cluster bridging three different **L4-H₆** molecules; (b) water molecule bridging two different **L4-H₆** molecules. Colour scheme: O, red; C, grey; Si, green; N, blue; H, off-white. H-bonds are shown by a cyan line.

PXRD Patterns for MOF Samples

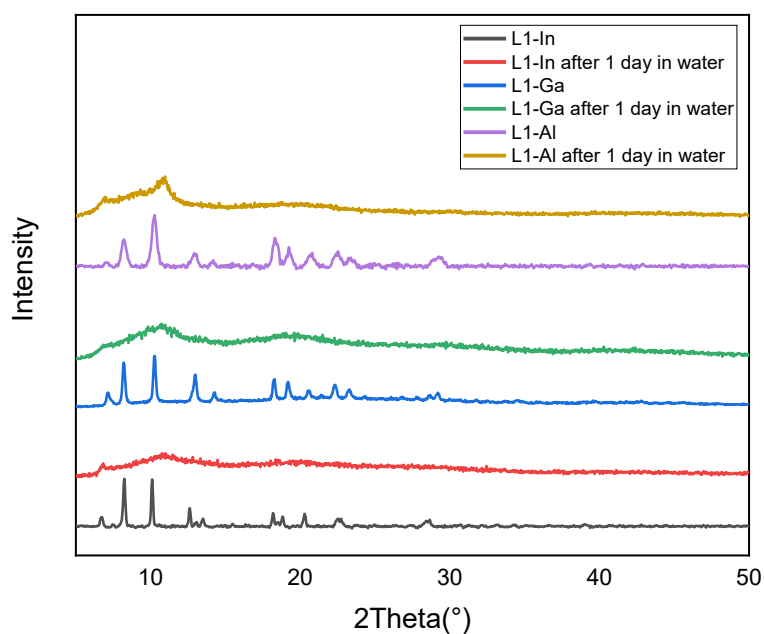


Figure S2: PXRD pattern of **L1-In**, **L1-Ga**, and **L1-Al** before and after being soaked in water for 24 h.

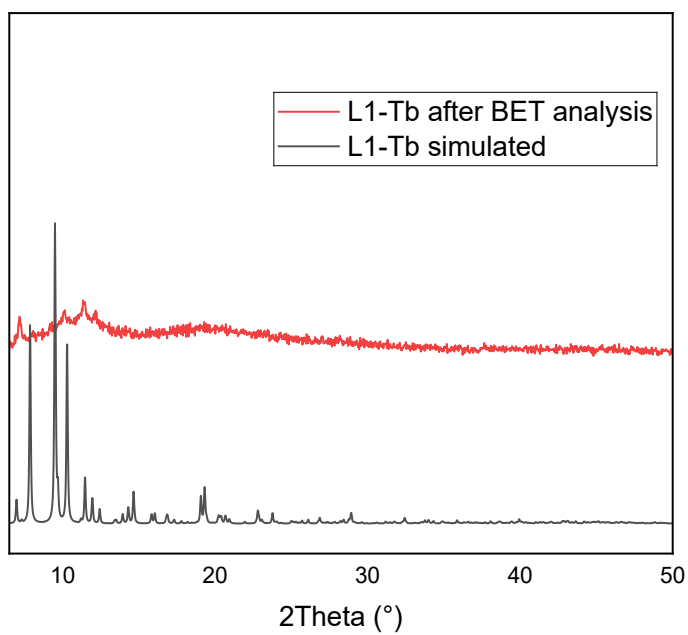


Figure S3: PXRD pattern on **L1-Tb** after gas sorption studies.

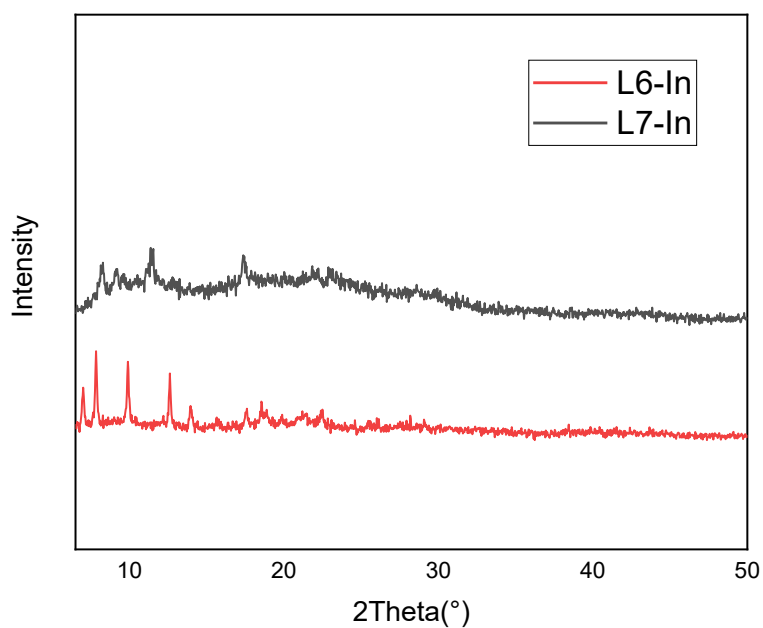


Figure S4: PXRD patterns of bulk **L9-In** and **L7-In** after air drying for 24 h.

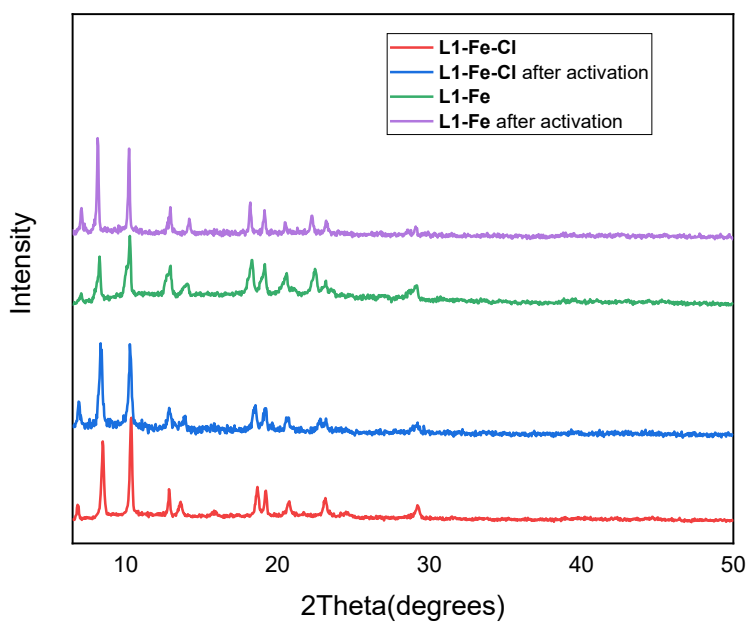


Figure S5: PXRD Patterns of both **L1-Fe** and **L1-Fe-Cl** before and after activation for adsorption experiment.

TGA Plots for MOF Samples

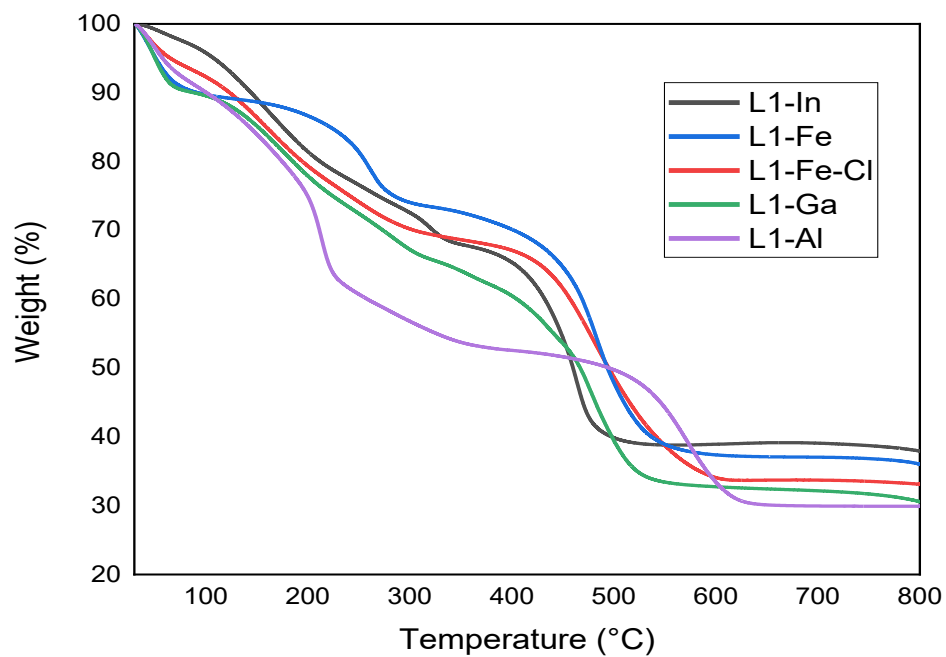


Figure S6: TGA plot under nitrogen for **L1-M** ($M = \text{In}^{3+}$, Fe^{3+} , Ga^{3+} , and Al^{3+}) and **L1-Fe-Cl**.

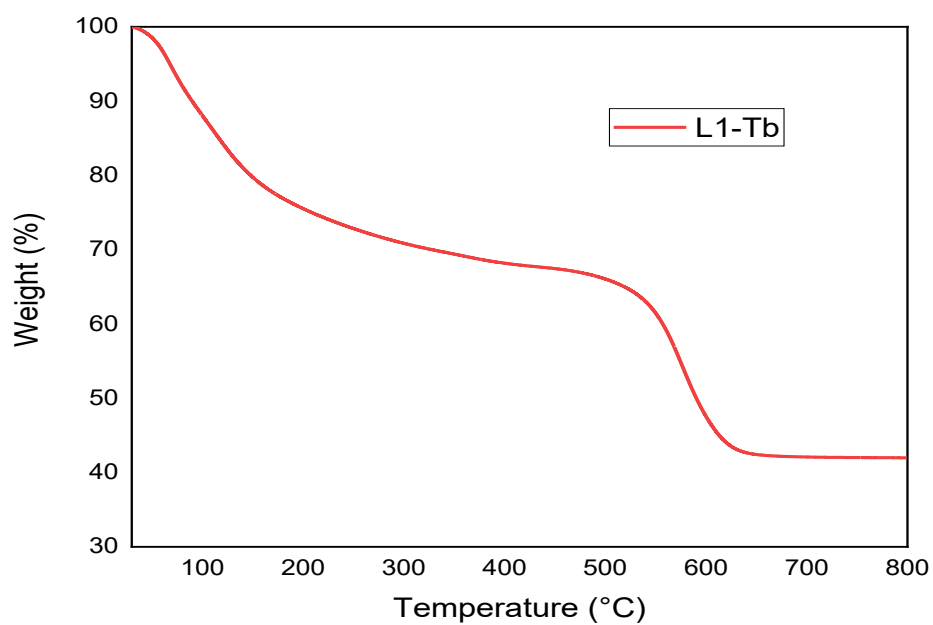


Figure S7: TGA curve of **L1-Tb**.

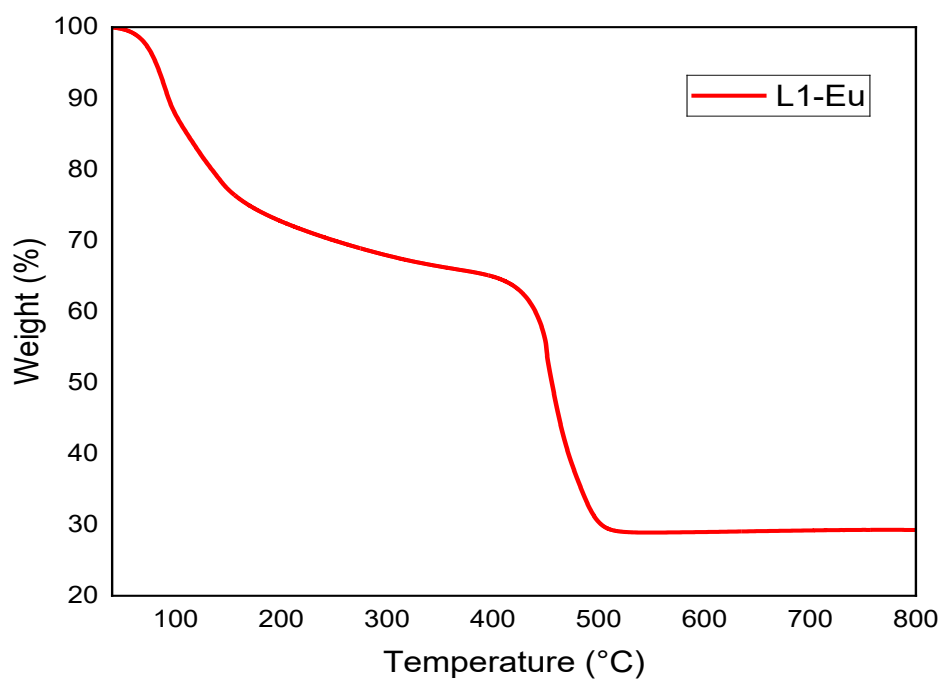


Figure S8: TGA curve of **L1-Eu**.

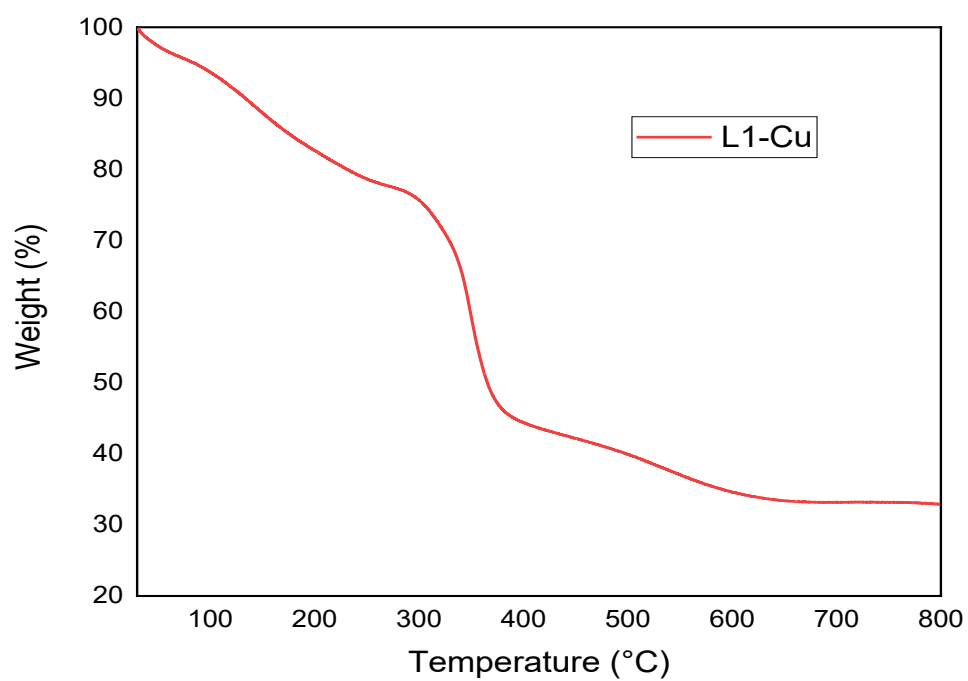


Figure S9: TGA curve of **L1-Cu**.

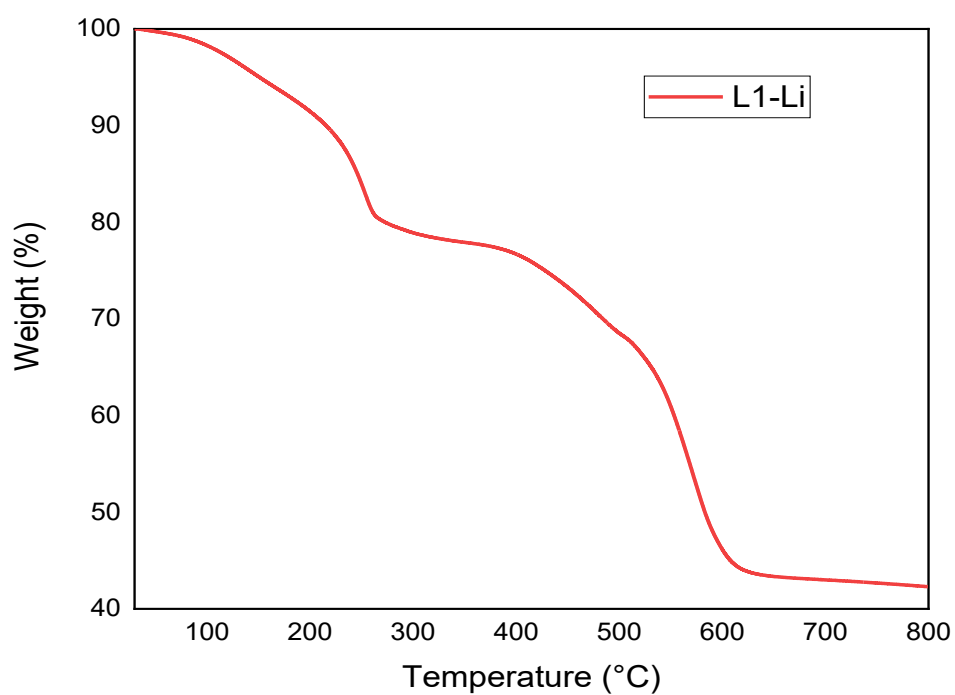


Figure S10: TGA curve of **L1-Li**.

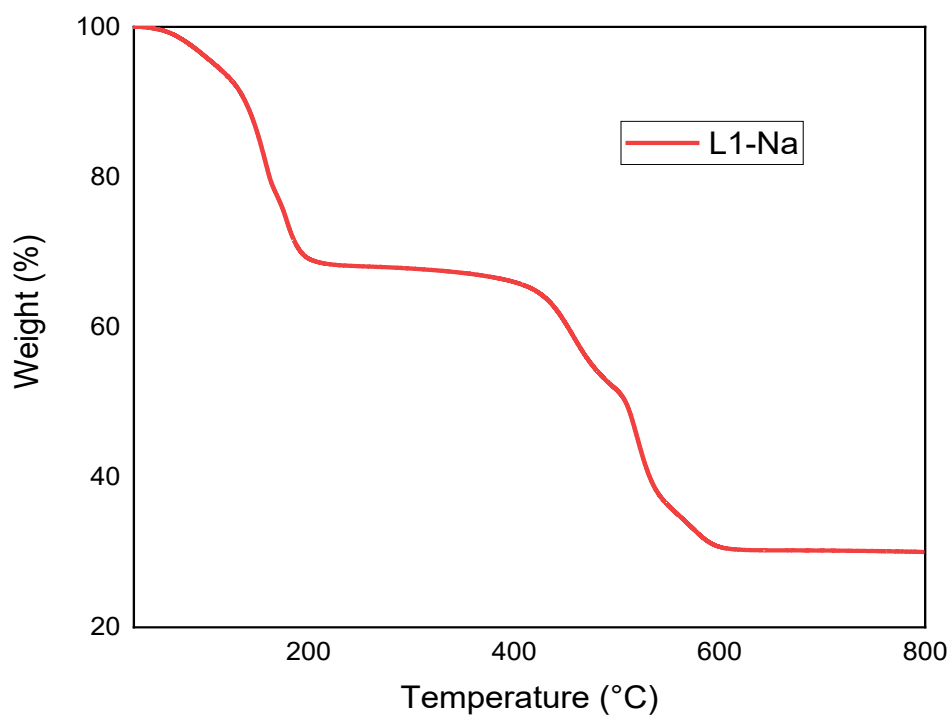


Figure S11: TGA curve of **L1-Na**.

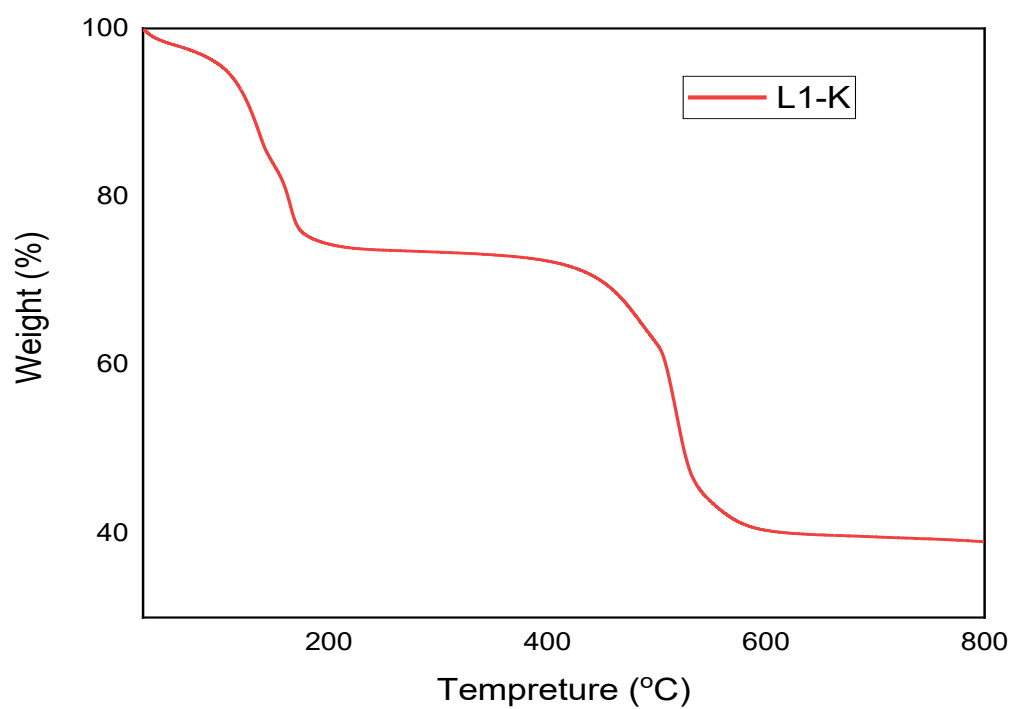


Figure S12: TGA curve of **L1-K**.

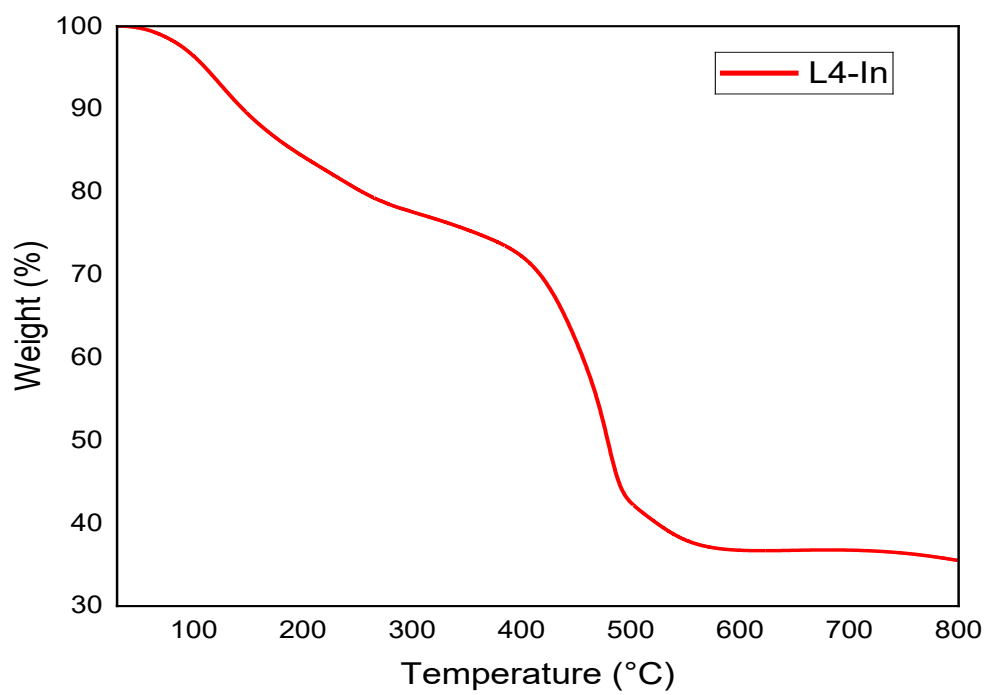


Figure S13: TGA curve of **L4-In**.

Gas Adsorption Isotherms

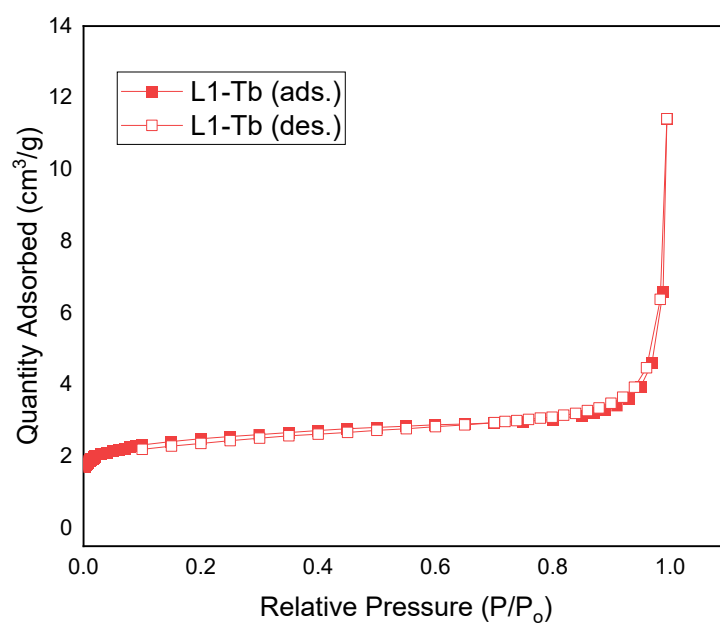


Figure S14: N₂ adsorption isotherms (Type I) for an activated sample of **L1-Tb** (at 77 K)

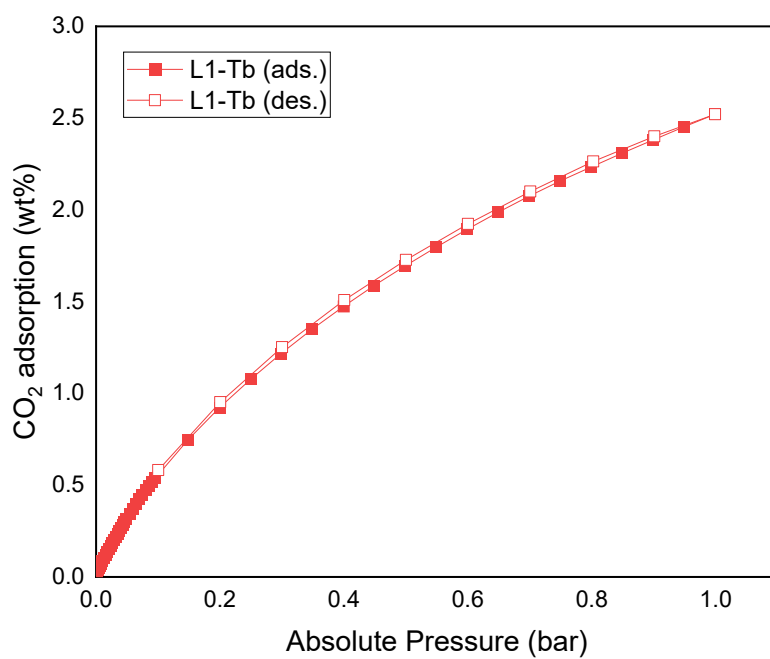


Figure S15: CO₂ sorption isotherm (Type I) for an activated sample of **L1-Tb** (at 298 K).

FTIR Spectra

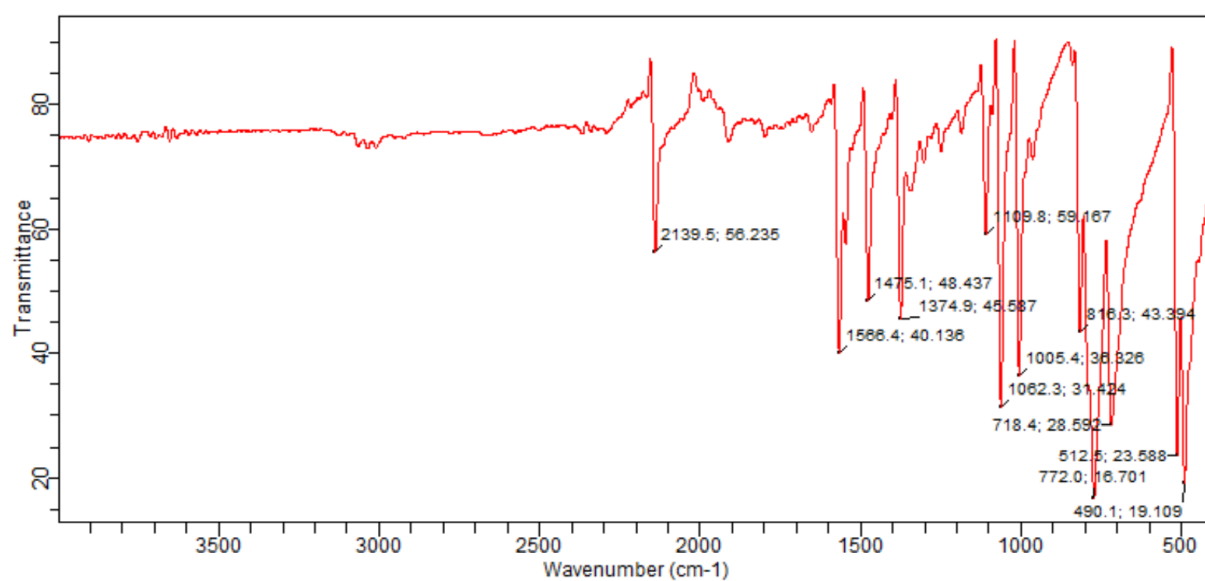


Figure S16: IR spectrum of tris(4-bromophenyl)silane (**33**).

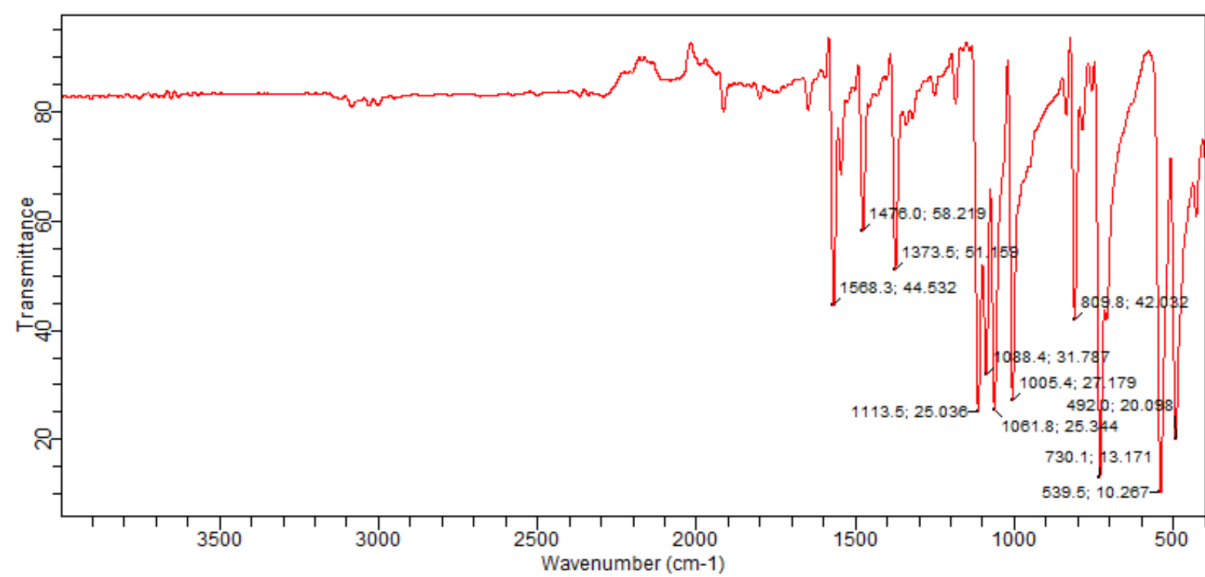


Figure S17: IR spectrum of hexa(4-bromophenyl)disiloxane (**34**).

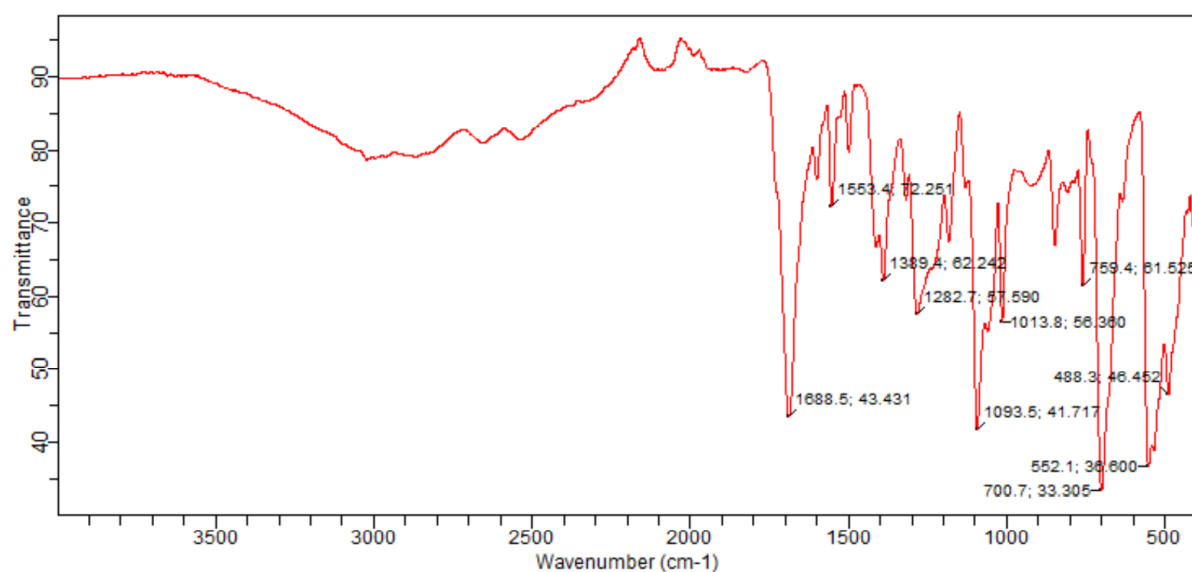


Figure S18: IR spectrum of hexa(4-carboxyphenyl)disiloxane (**L1-H₆**).

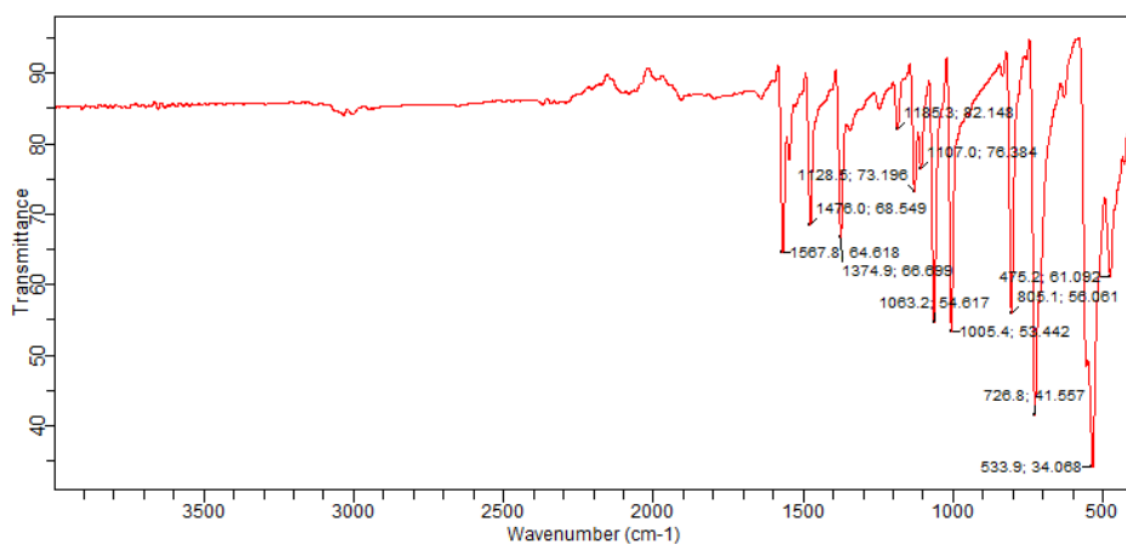


Figure S19: IR spectrum of 1,4-bis(tris(4-bromophenyl)silyl)benzene (**35**).

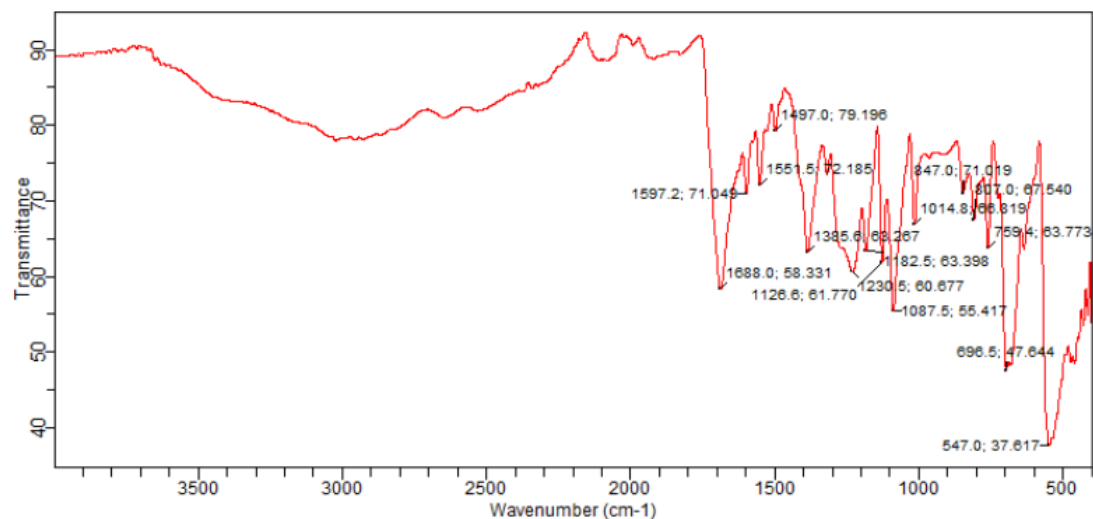


Figure S20: IR spectrum of 1,4-bis(tris(4-carboxyphenyl)silyl)benzene (**L2-H₆**).

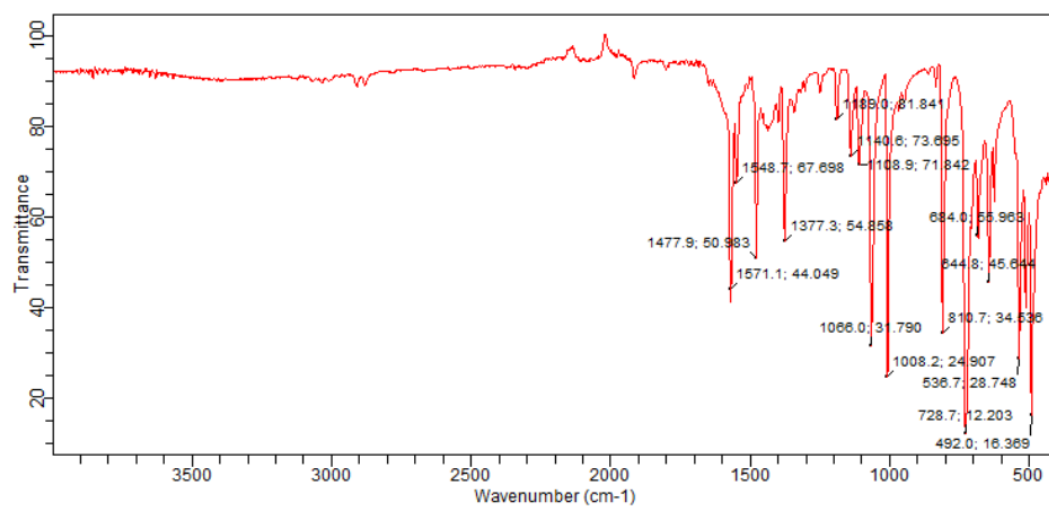


Figure S21: IR spectrum of 1,2-bis(tris(4-bromophenyl)silyl)ethane (**36**).

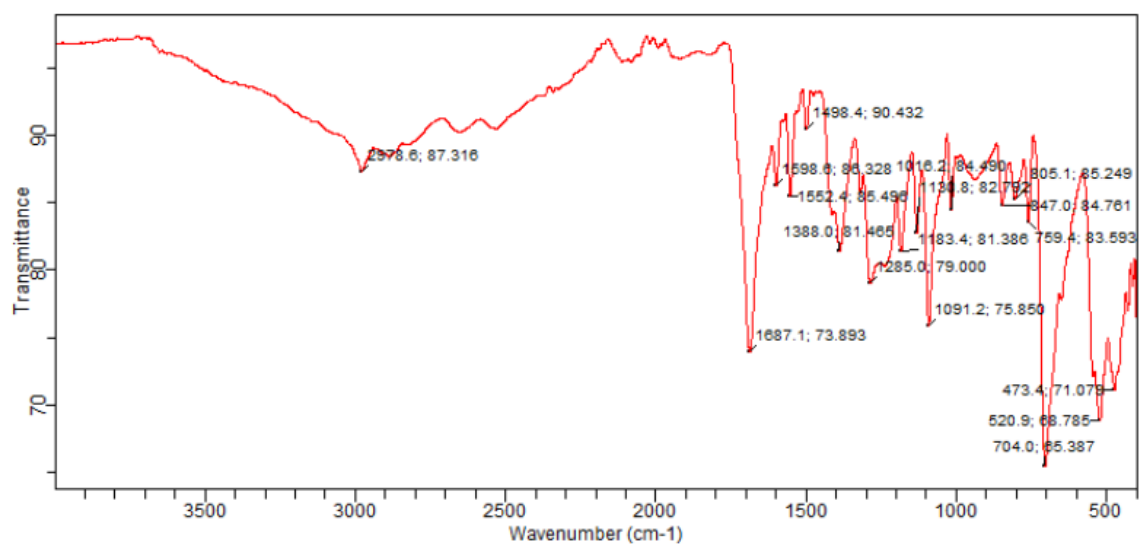


Figure S22: IR spectrum of 1,2-bis(tris(4-carboxyphenyl)silyl)ethane (**L3-H₆**).

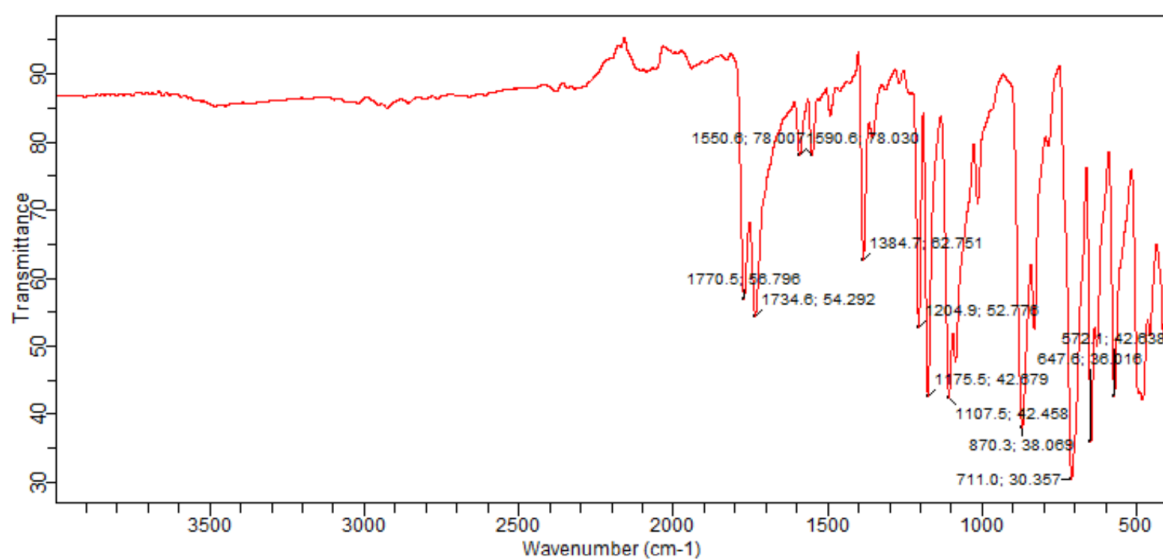


Figure S23: IR spectrum of hexa(4-acylchlorophenyl)disiloxane (**37**).

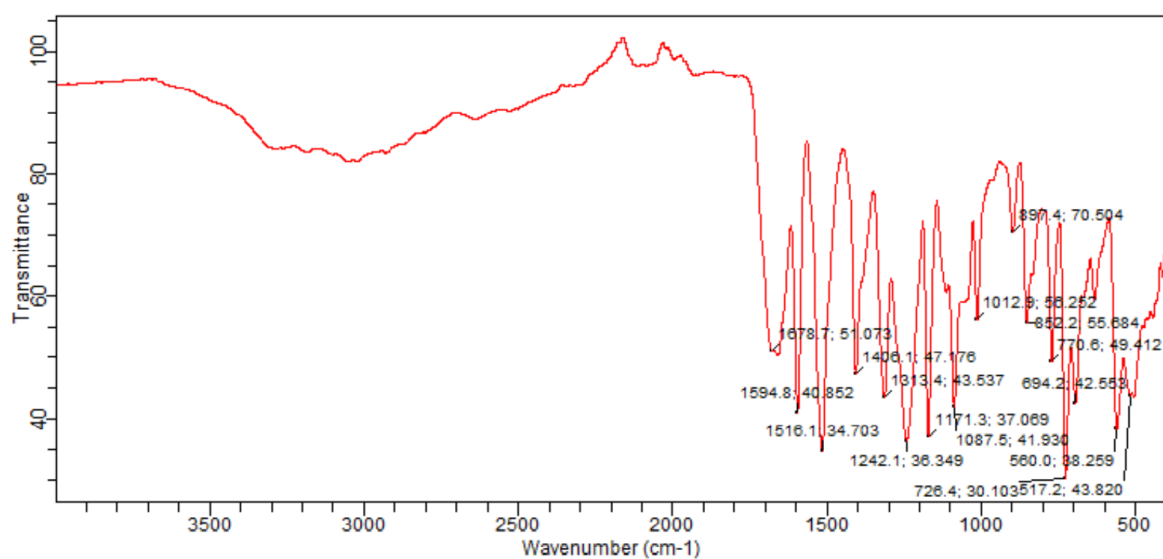


Figure S34: IR spectrum of hexa(4-carboxyphenyl-4-benzamide)disiloxane (L4-H₆).

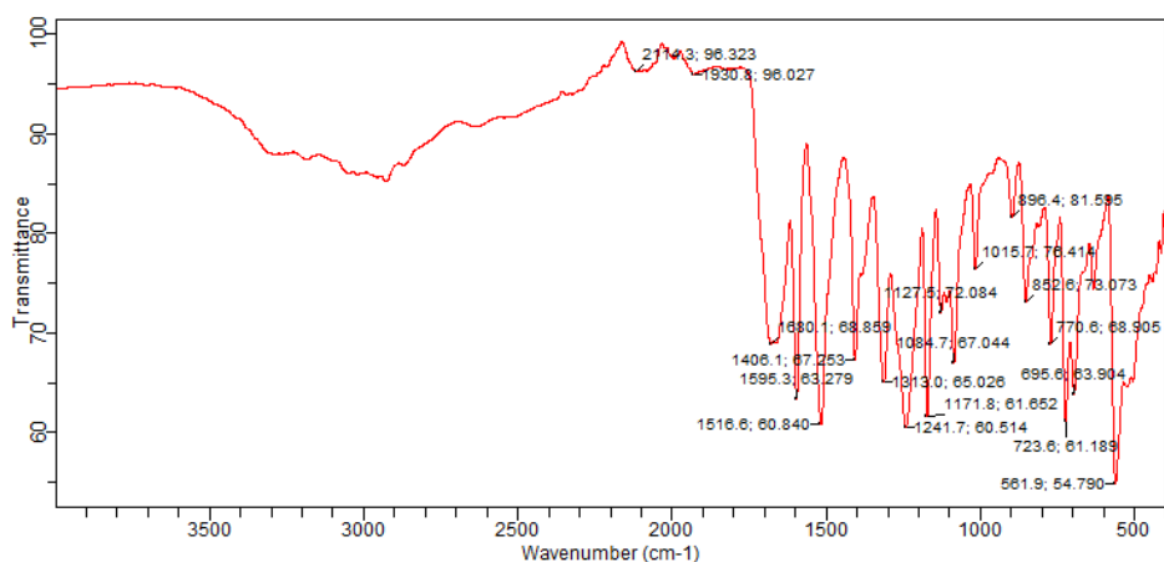


Figure S25: IR spectrum of 1,4-bis(tris(4-carboxyphenyl-4-benzamide)silyl)benzene (L5-H₆).

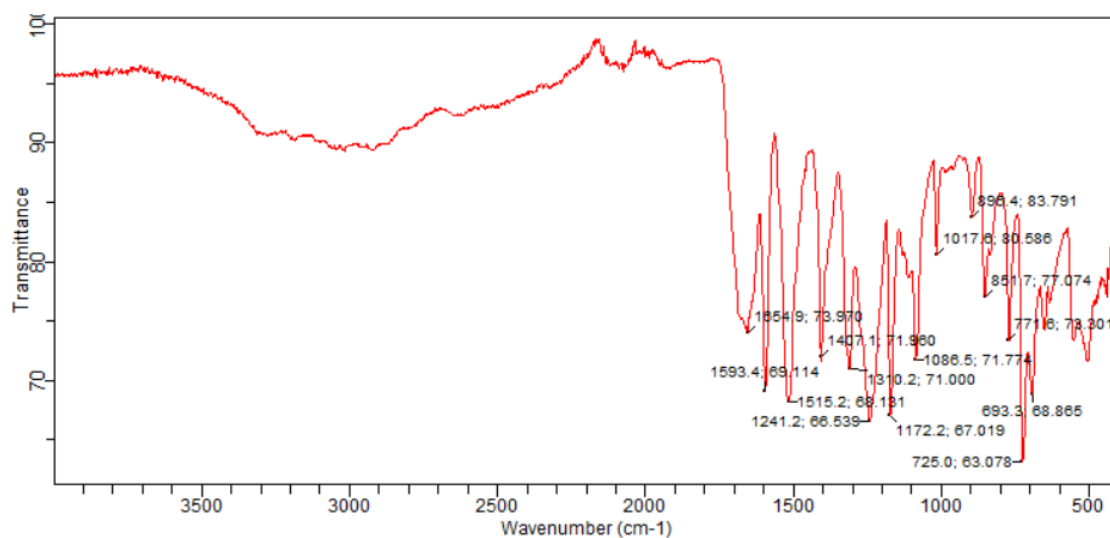


Figure S26: IR spectrum of 1,2-bis(tris(4-carboxyphenyl-4-benzamide)silyl)ethane (**L6-H₆**).

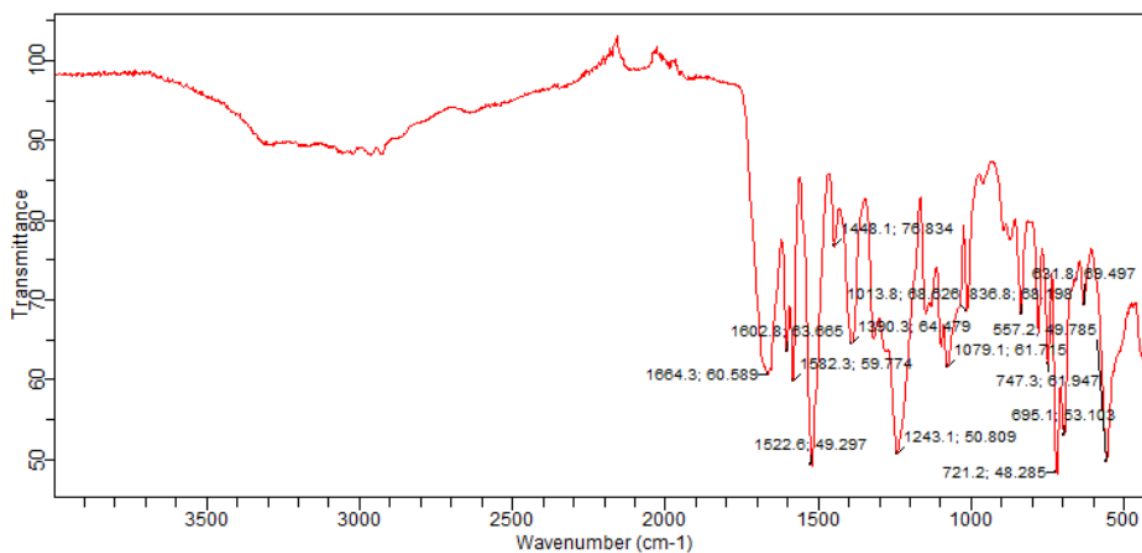


Figure S27: IR spectrum of hexa(4-carboxy-2-methylphenyl-4-benzamide)disiloxane (**L7-H₆**).

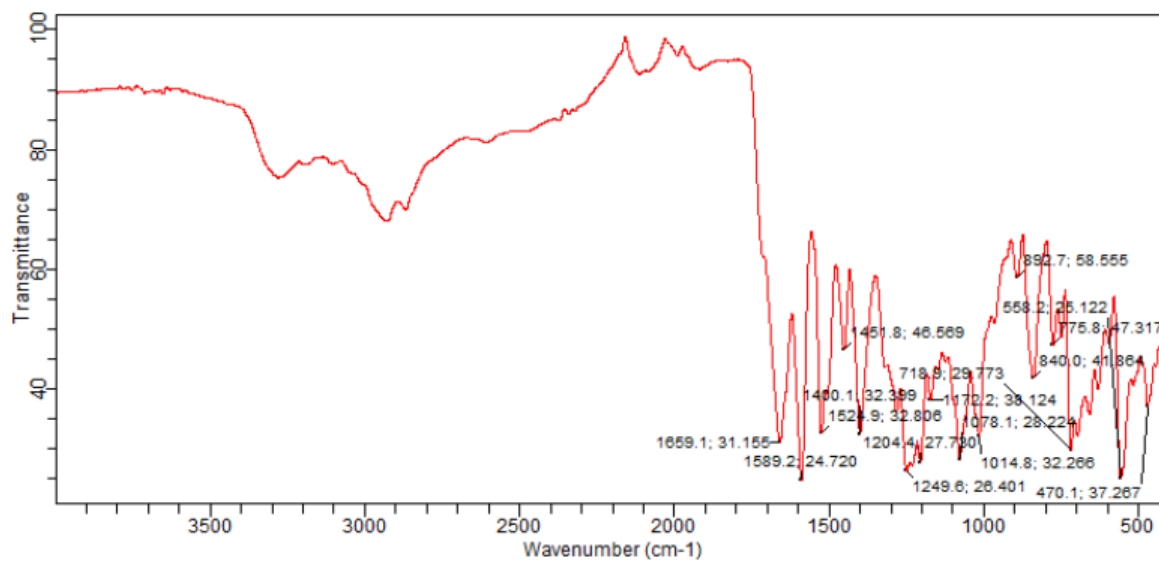


Figure S28: IR spectrum of hexa(4-carboxy-2-methoxyphenyl-4-benzamide)disiloxane (**L8-H₆**).

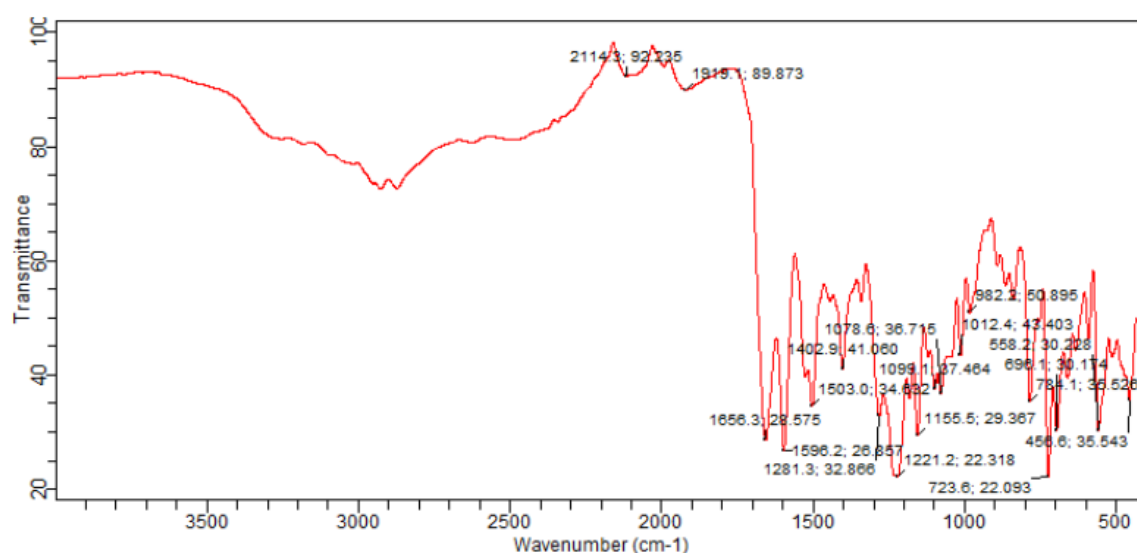


Figure S29: IR spectrum of hexa(4-carboxy-2-hydroxyphenyl-4-benzamide)disiloxane (**L9-H₆**).

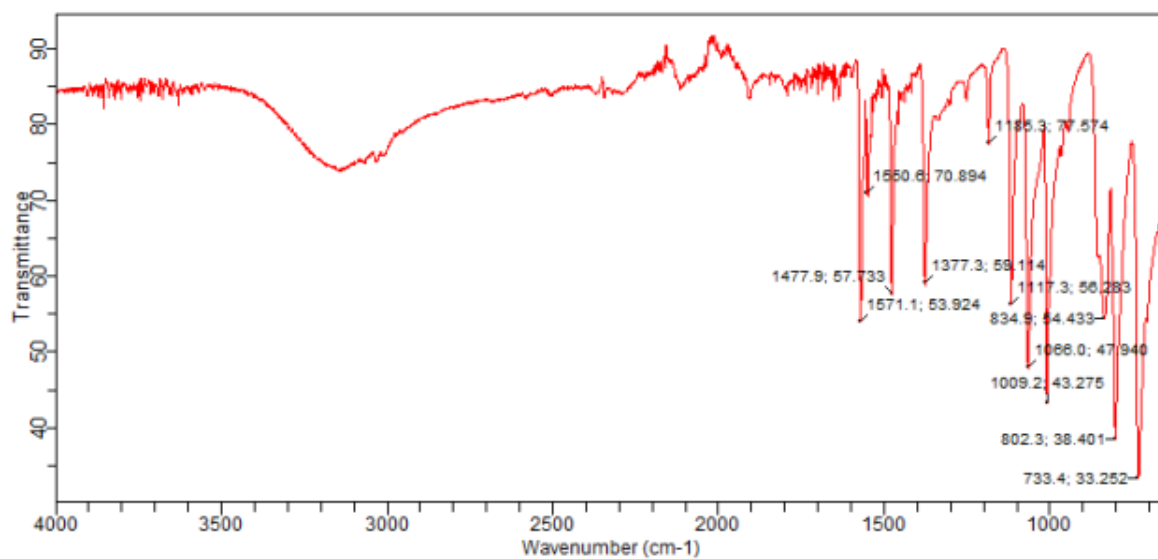


Figure S30: IR spectrum of tris(4-bromophenyl)silanol (**40**).

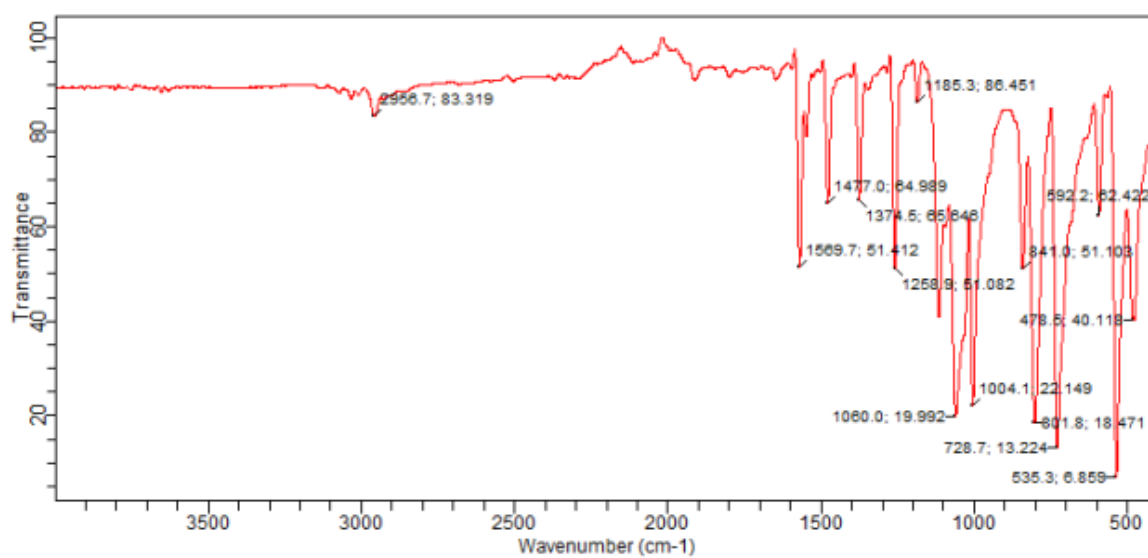


Figure S31: IR spectrum of 1,1,1,7,7,7-hexakis(4-bromophenyl)-3,3,5,5-tetramethyltetrasiloxane (**41**).

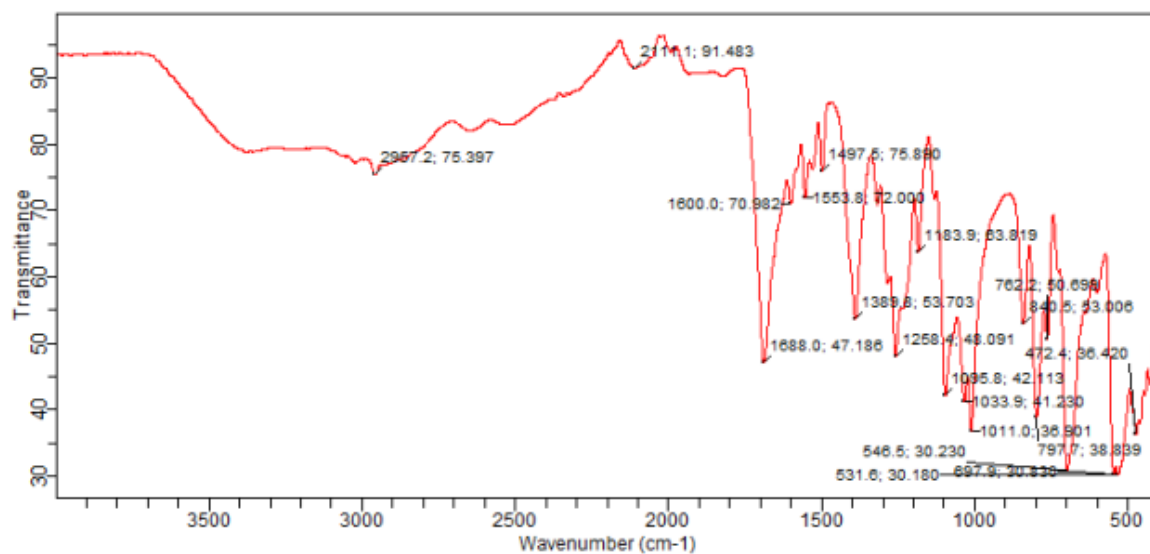


Figure S32: IR spectrum of 1,1,1,7,7,7-hexakis(4-carboxyphenyl)-3,3,5,5-tetramethyltetrasiloxane (**L10-H₆**).

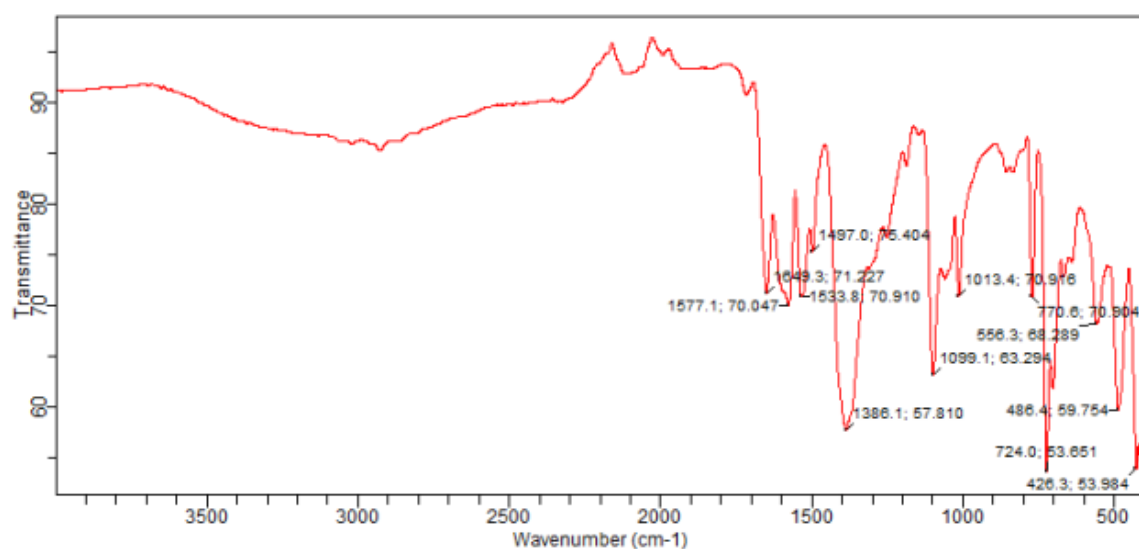


Figure S33: L1-In IR spectrum.

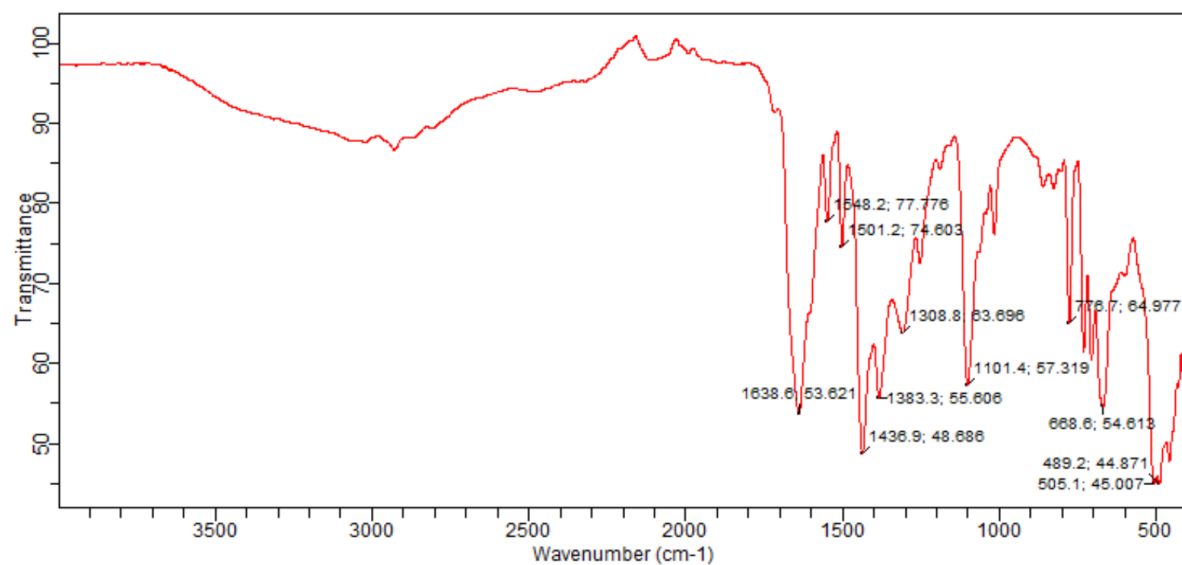


Figure S34: L1-Al IR spectrum.

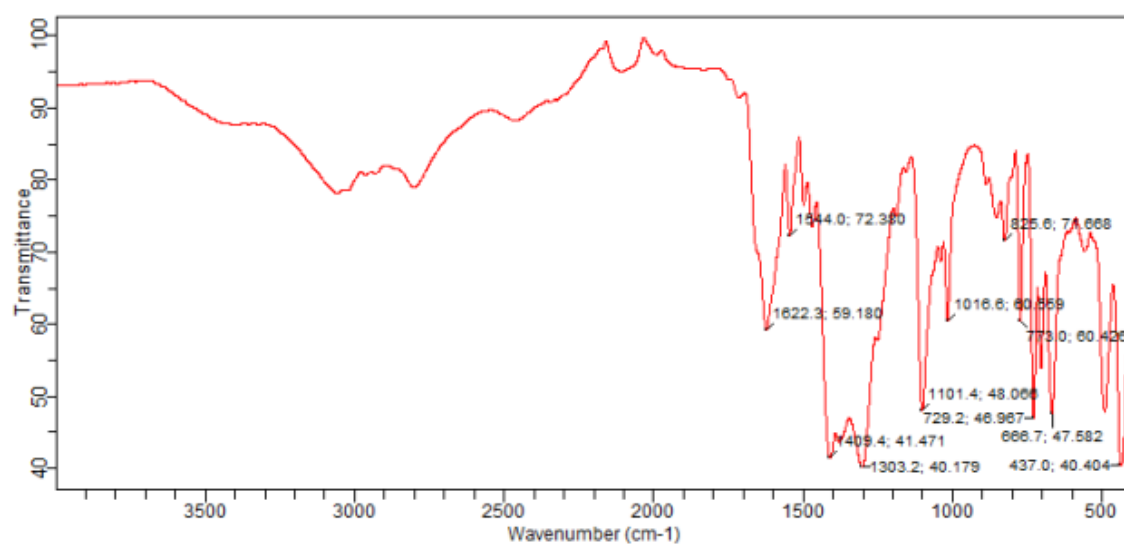


Figure S35: L1-Ga IR spectrum.

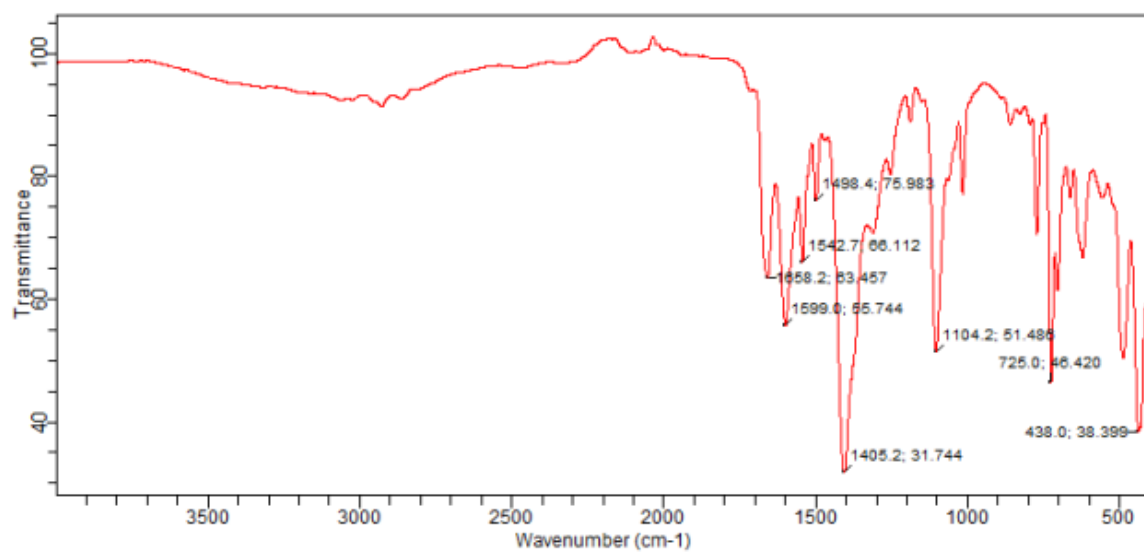


Figure S36: L1-Fe IR spectrum.



Figure S37: L1-Fe-Cl IR spectrum.

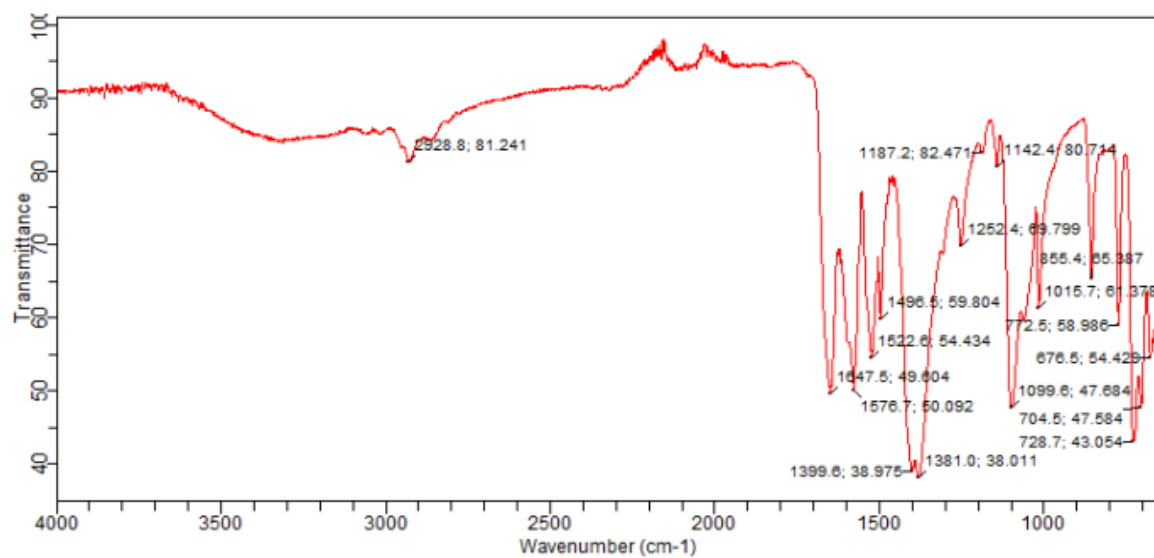


Figure S38: L1-Tb IR spectrum.

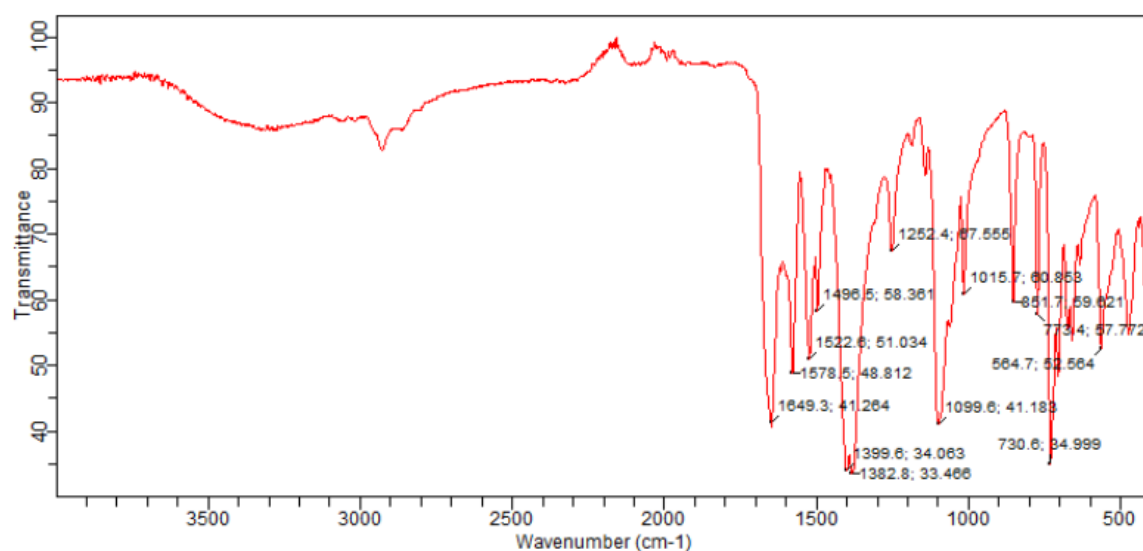


Figure S39: L1-Eu IR spectrum.

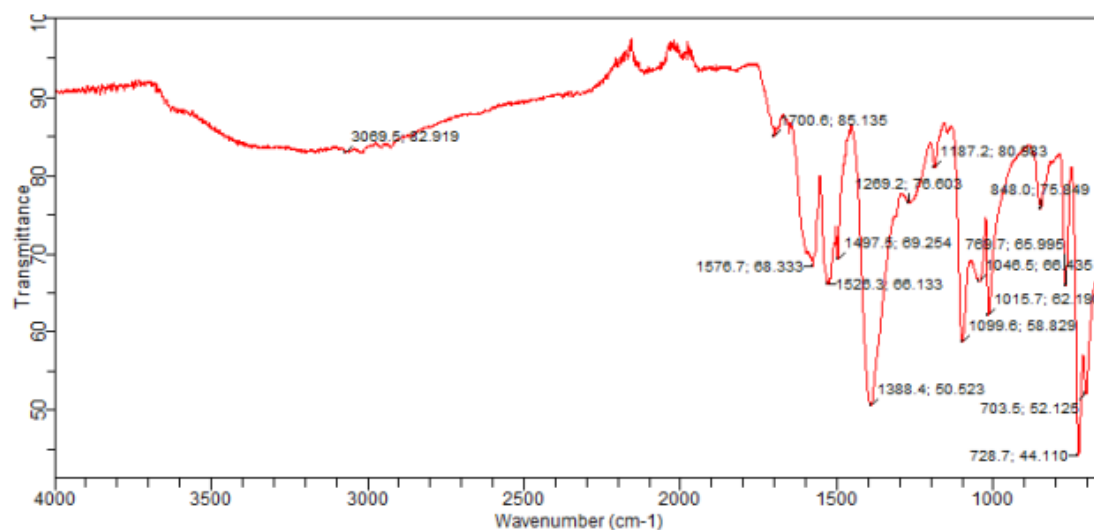


Figure S40: L1-Cu IR spectrum.

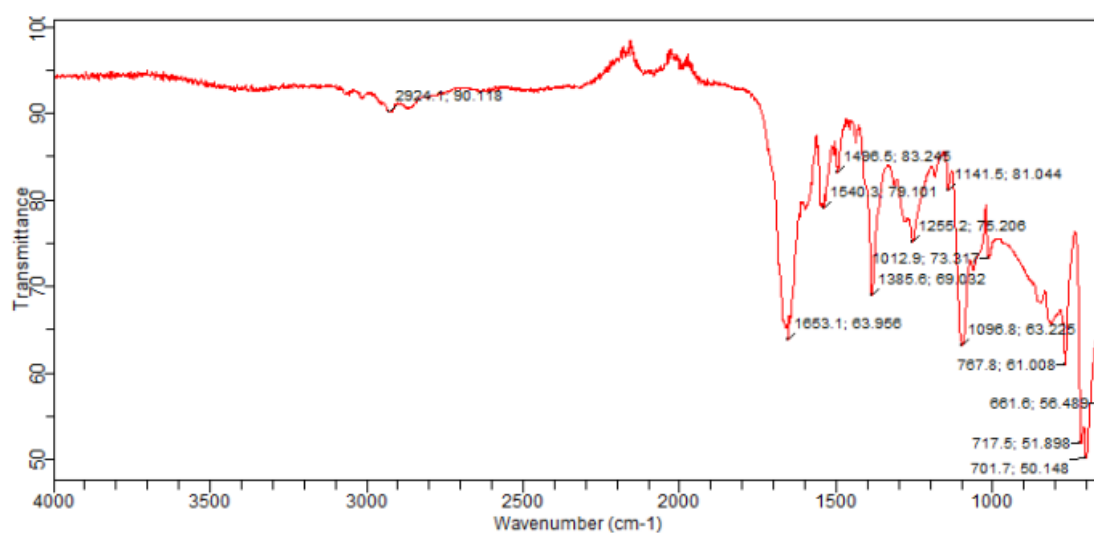


Figure S41: L1-Na IR spectrum.

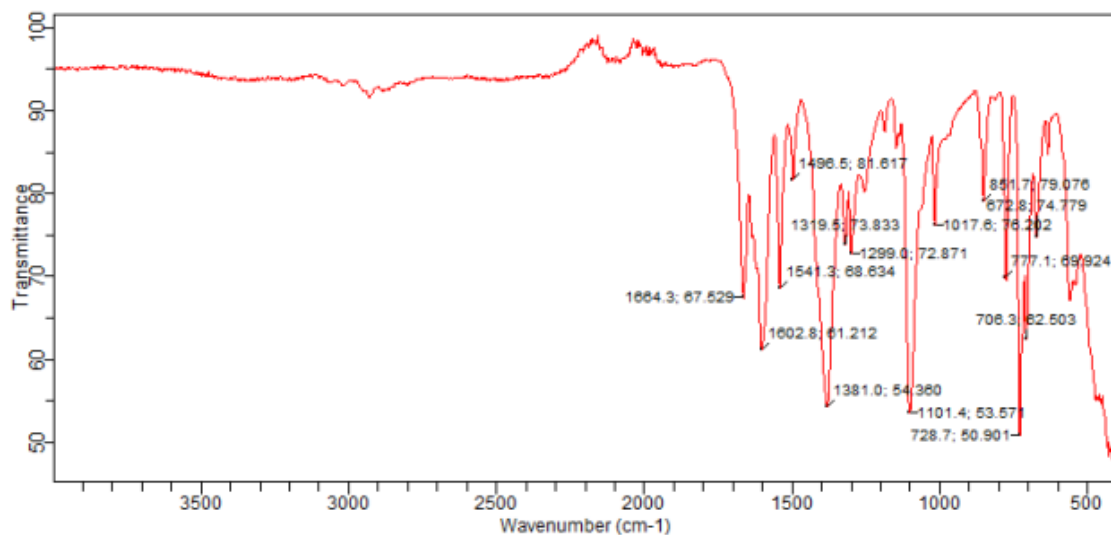


Figure S42: L1-Li IR spectrum.

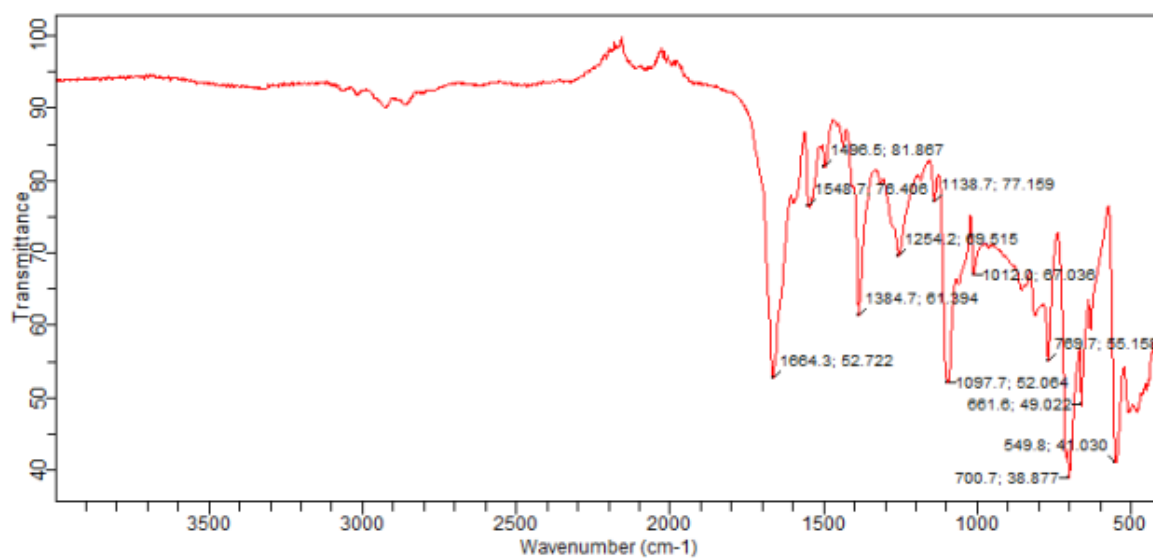


Figure S43: L1-K IR spectrum.

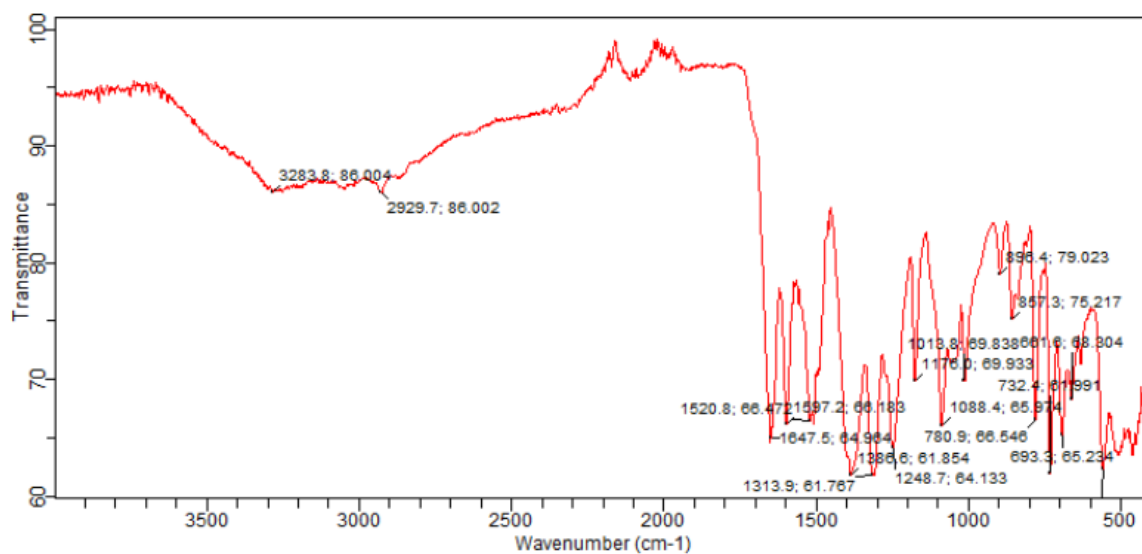


Figure S44: L4-In IR spectrum.

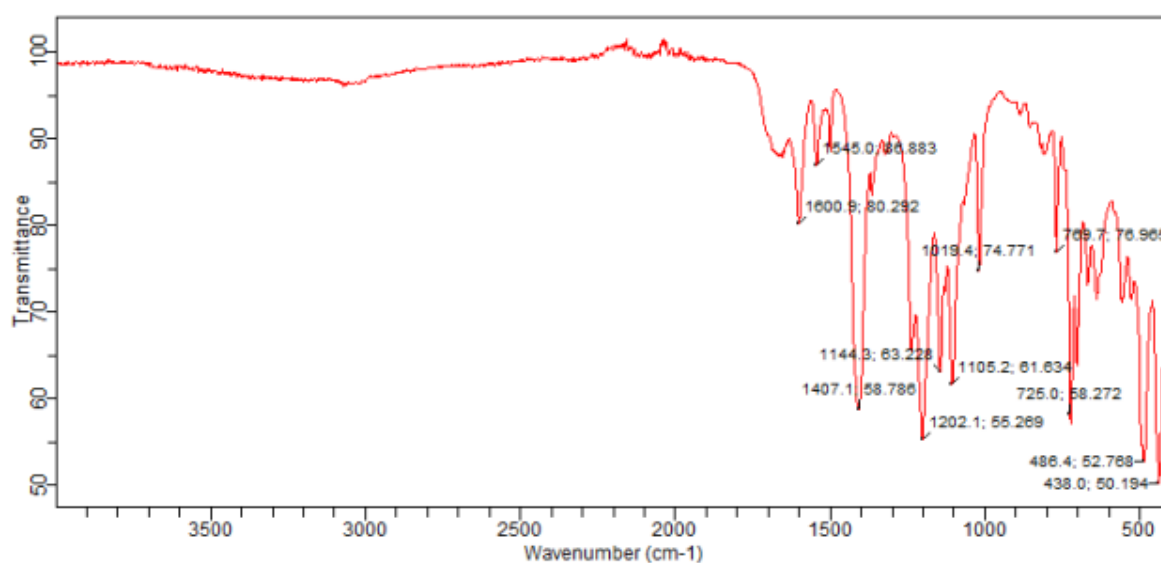


Figure S45: IR spectrum of PFOA@L1-Fe-Cl.

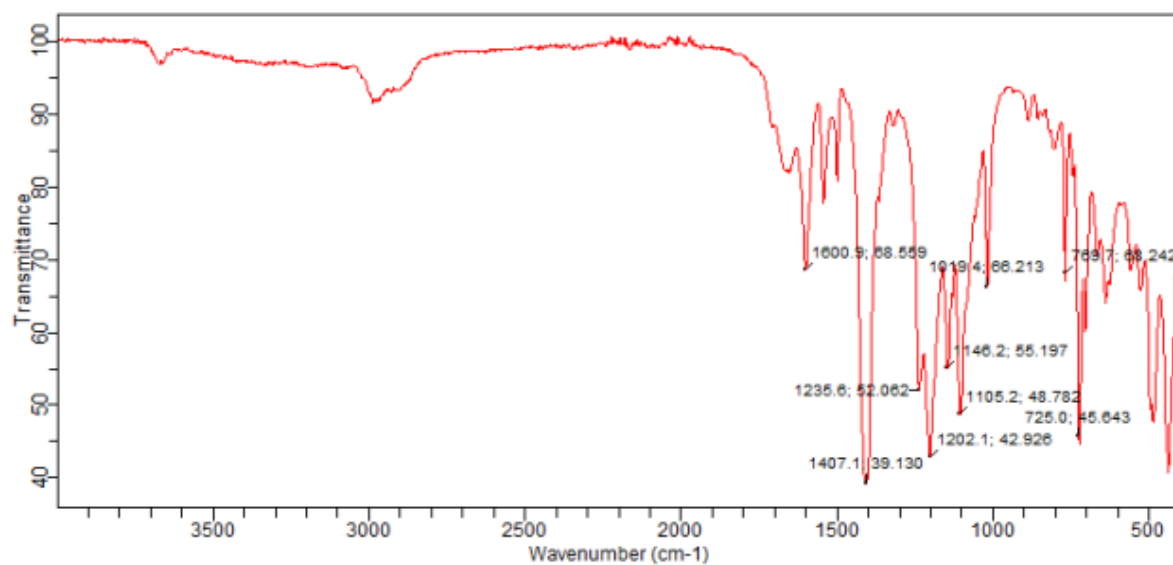


Figure S46: IR spectrum of PFOA@L1-Fe.

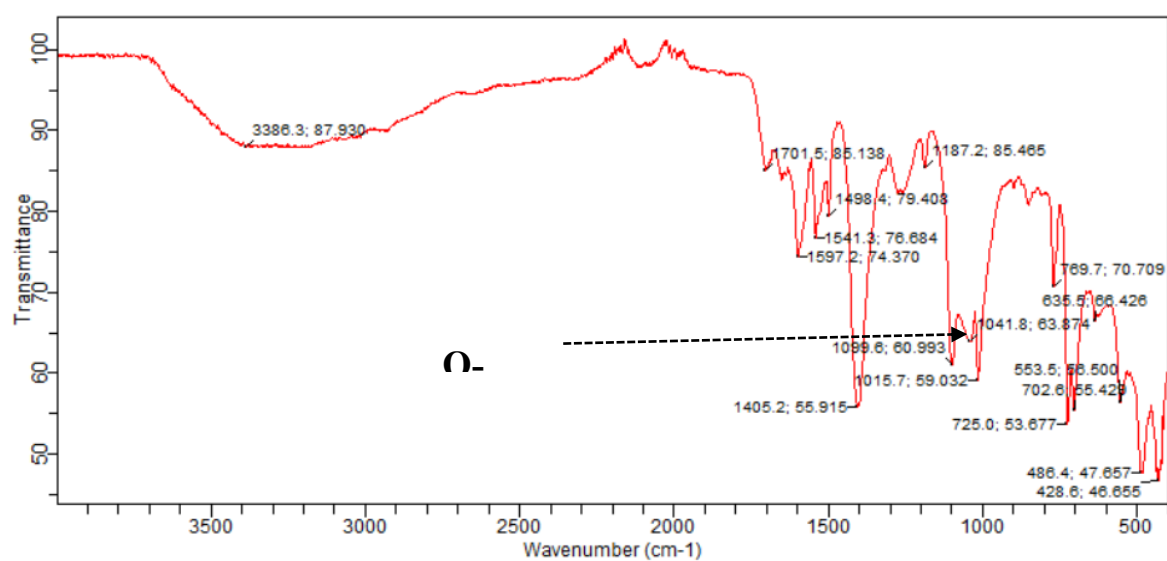


Figure S47: IR spectrum of L1-Fe-Cl after phosphate adsorption.

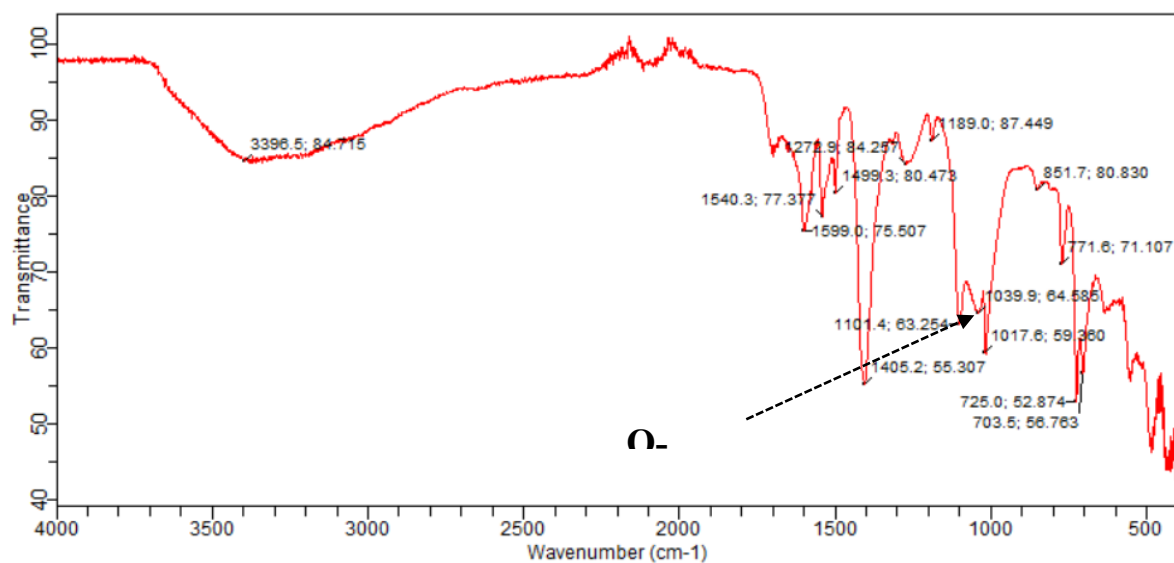


Figure S48: IR spectrum of L1-Fe after phosphate adsorption.

NMR Spectra

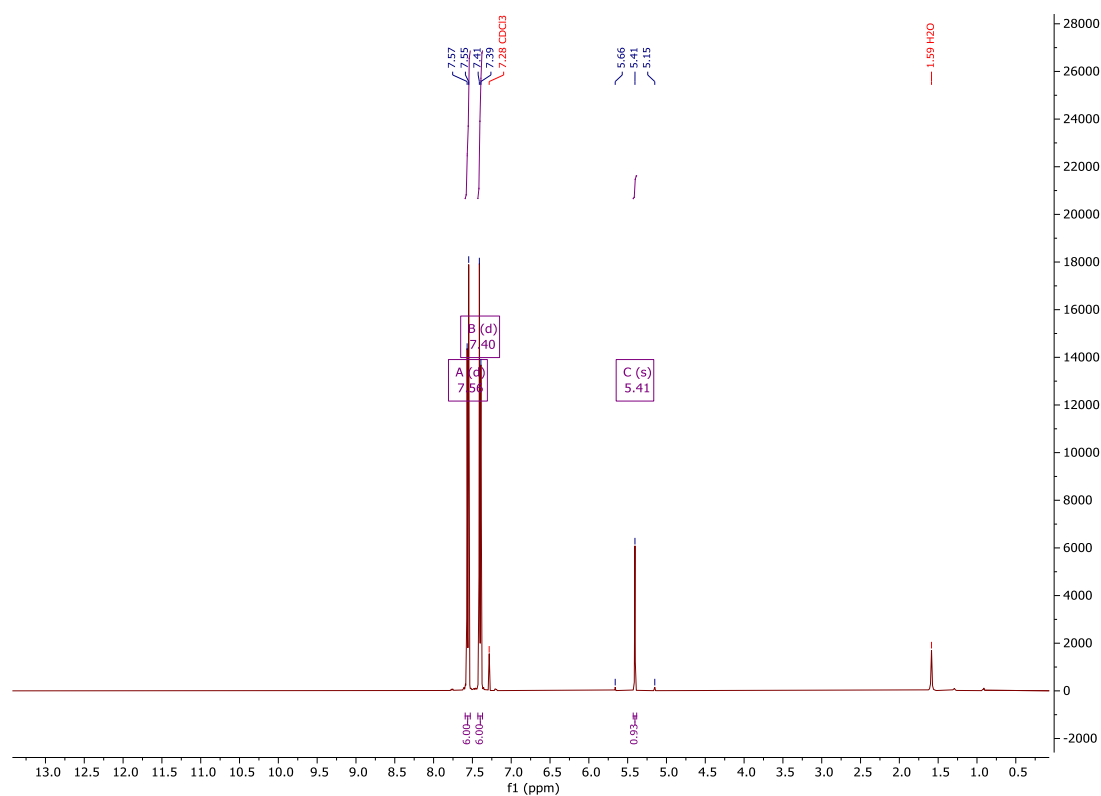


Figure S49: ¹H NMR spectrum of tris(4-bromophenyl)silane (**33**).

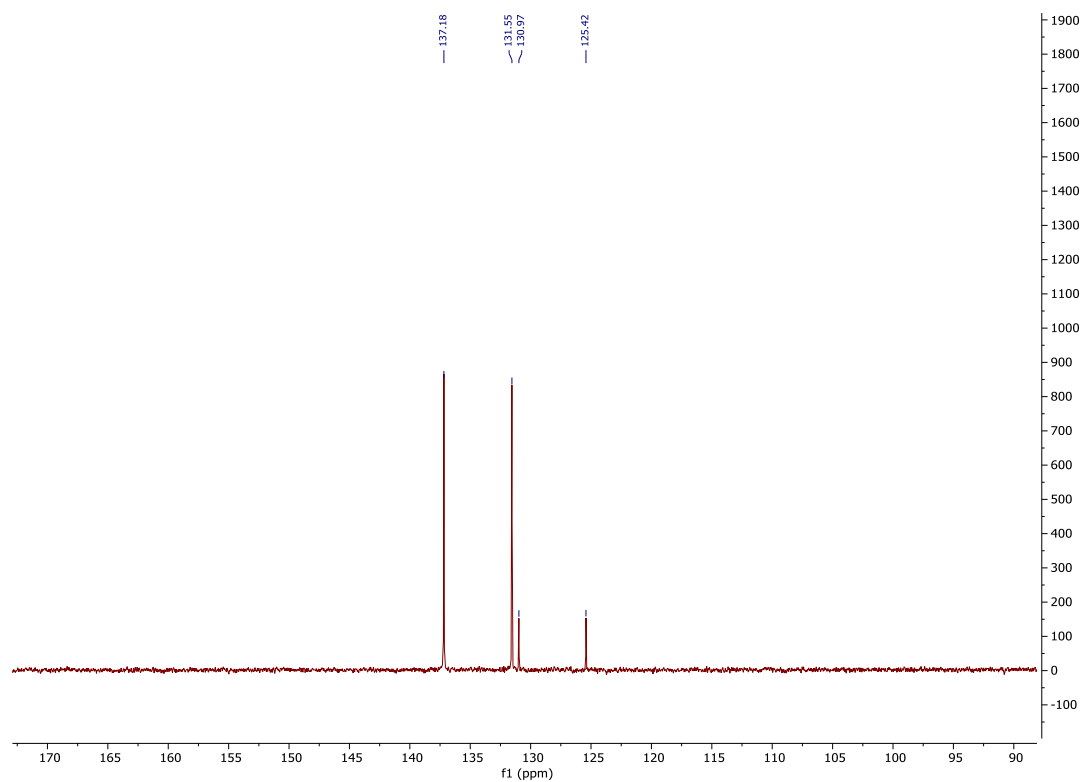


Figure S50: ¹³C NMR spectrum of tris(4-bromophenyl)silane (**33**).

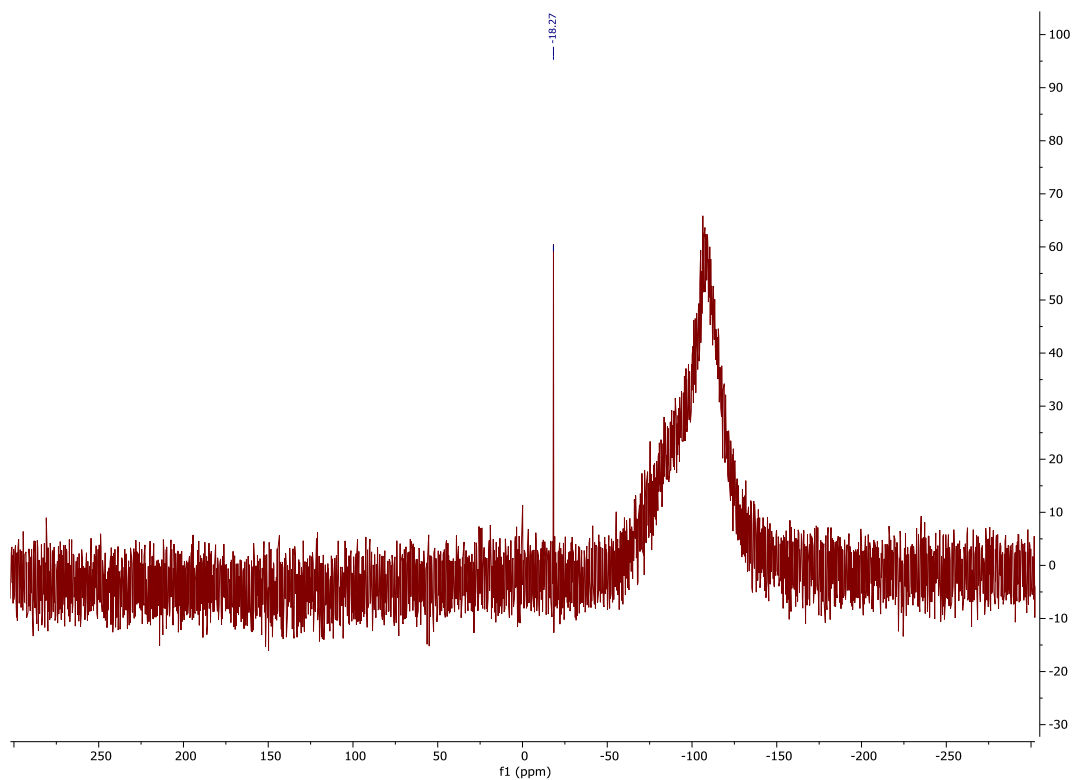


Figure S51: ^{29}Si NMR spectrum of tris(4-bromophenyl)silane (**33**).

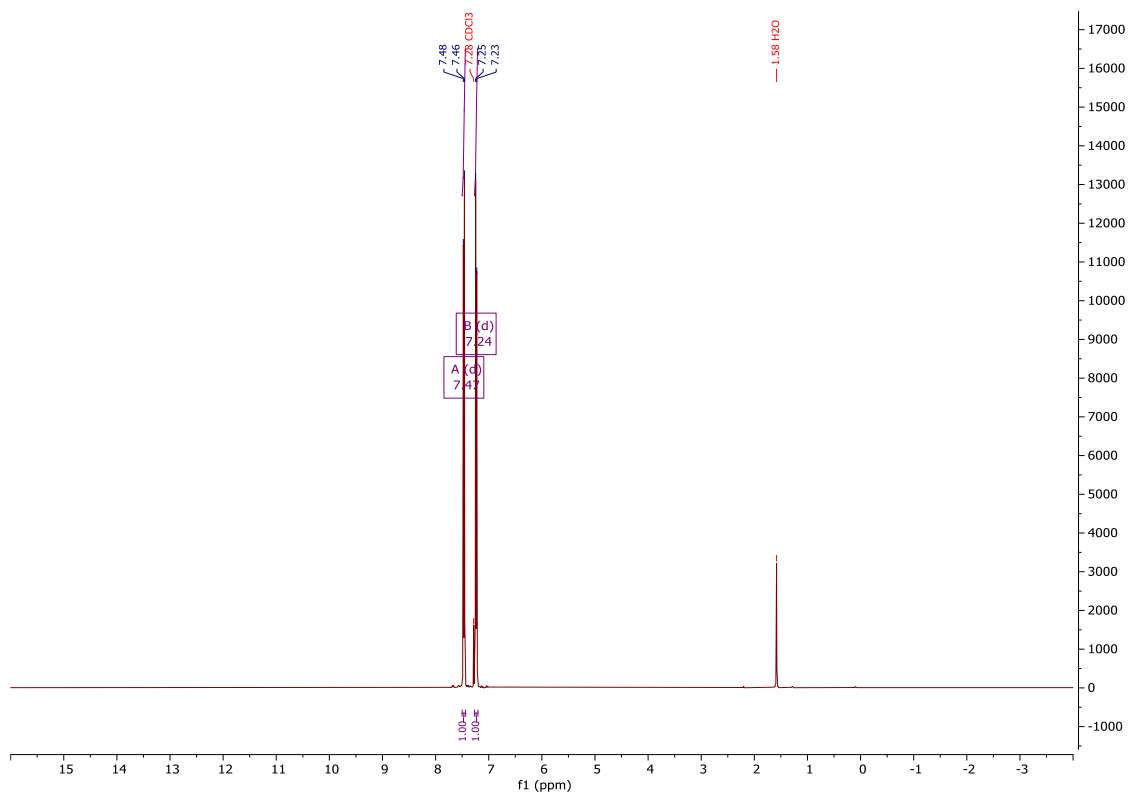


Figure S52: ^1H NMR spectrum of hexa(4-bromophenyl)disiloxane (**34**).

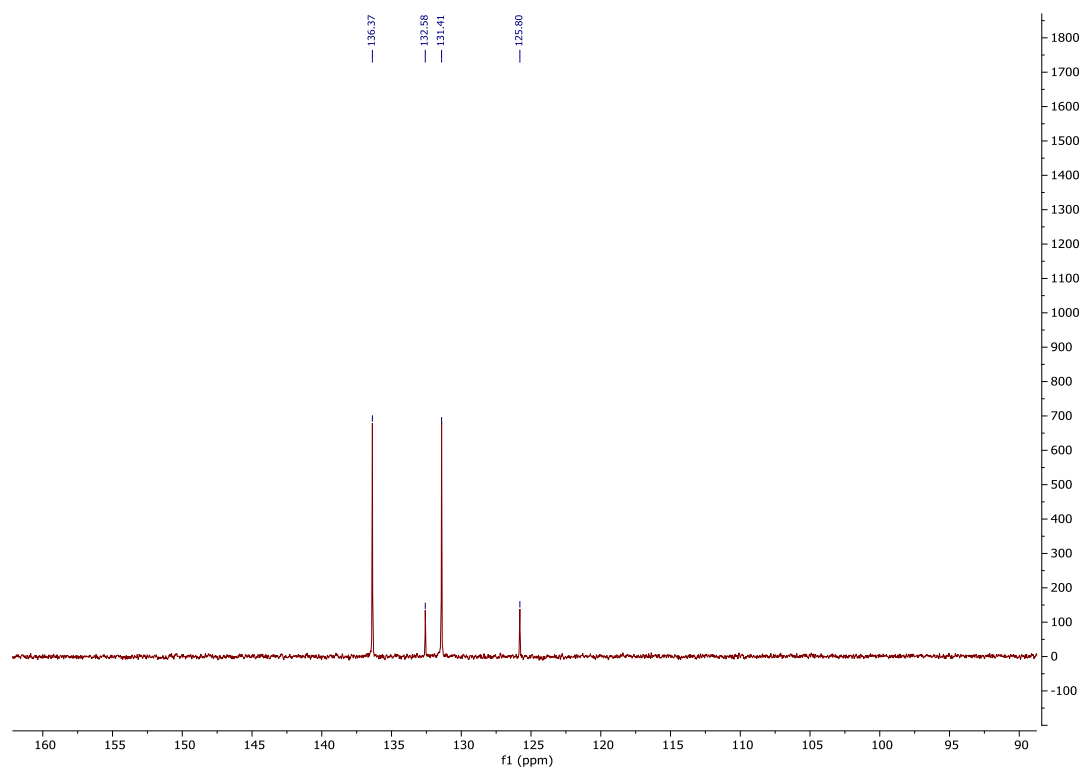


Figure S53: ^{13}C NMR spectrum of hexa(4-bromophenyl)disiloxane (34).

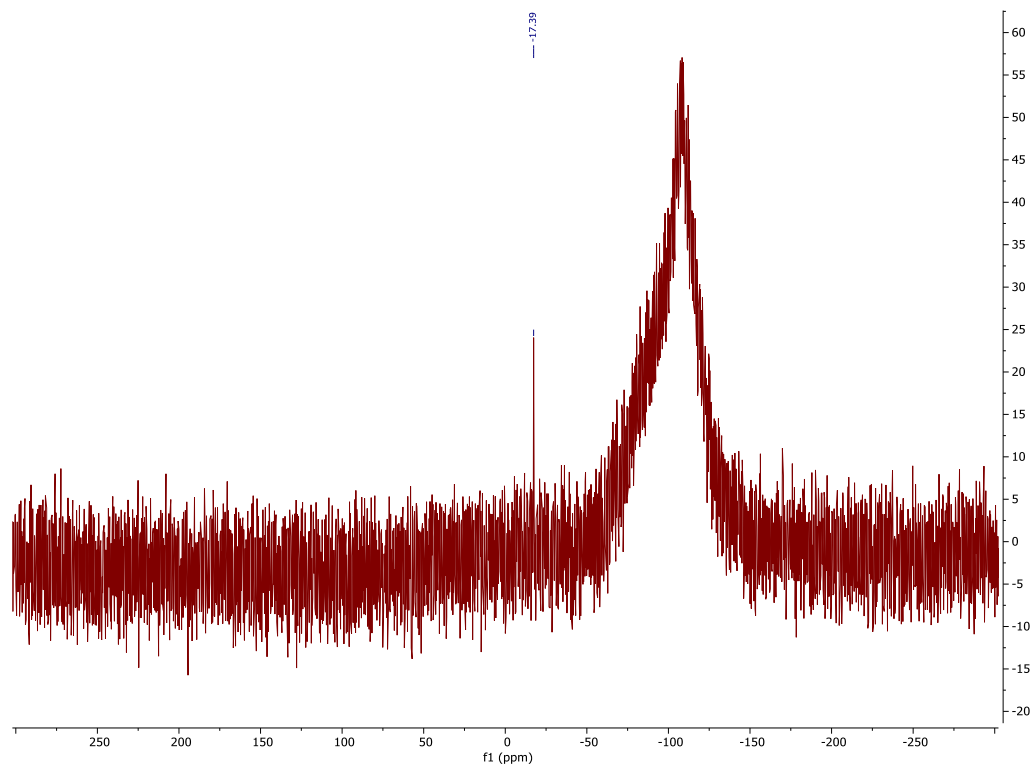


Figure S54: ^{29}Si NMR spectrum of hexa(4-bromophenyl)disiloxane (34).

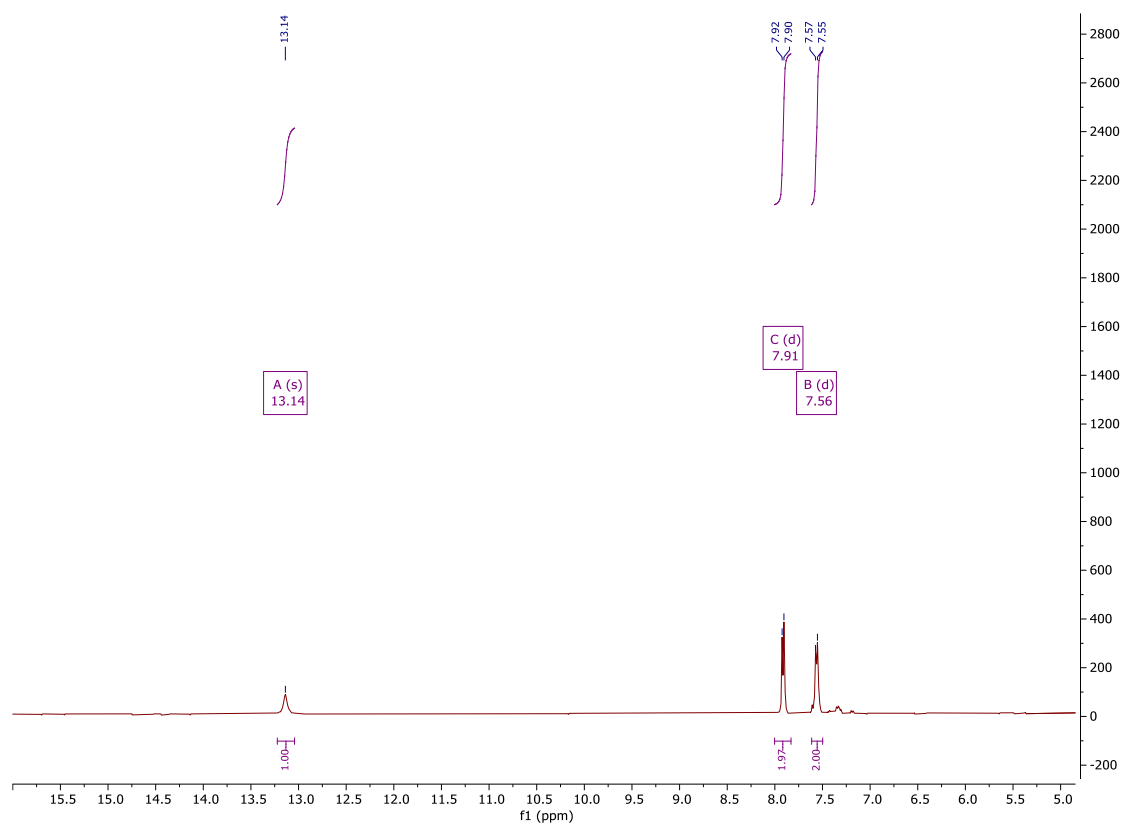


Figure S55: ¹H NMR spectrum of hexa(4-carboxyphenyl)disiloxane (L1-H₆).

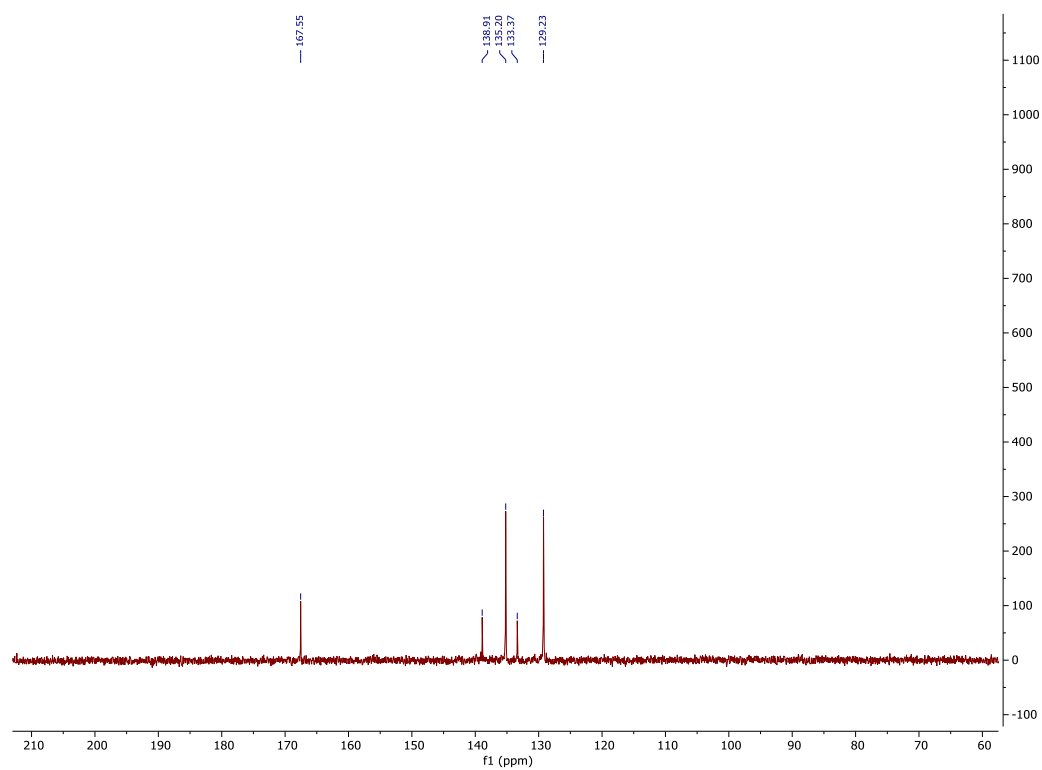


Figure S56: ¹³C NMR spectrum of hexa(4-carboxyphenyl)disiloxane (L1-H₆).

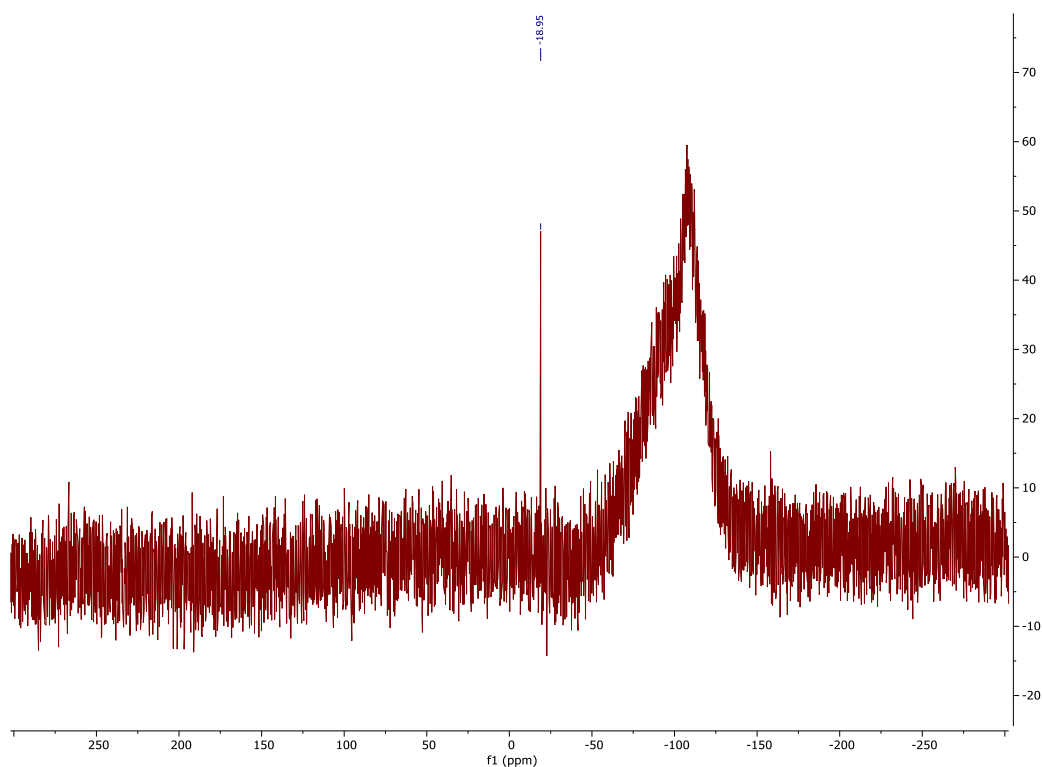


Figure S57: ^{29}Si NMR spectrum of hexa(4-carboxyphenyl)disiloxane (**L1-H₆**).

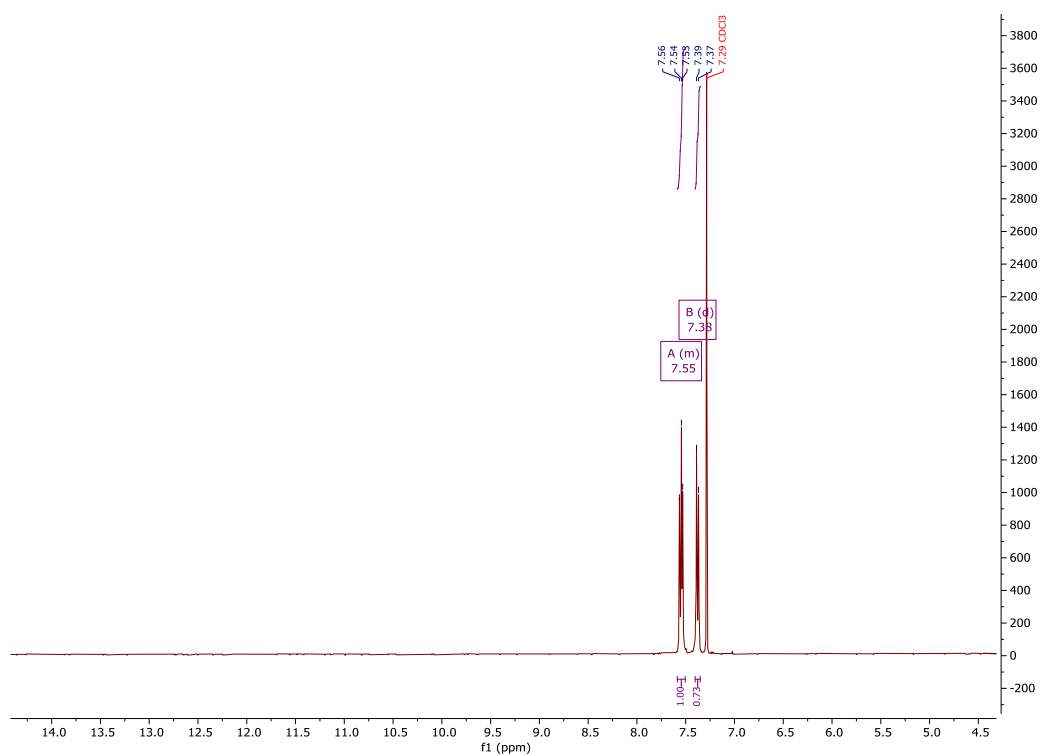


Figure S58: ^1H NMR spectrum of 1,4-bis(tris(4-bromophenyl)silyl)benzene (**35**).

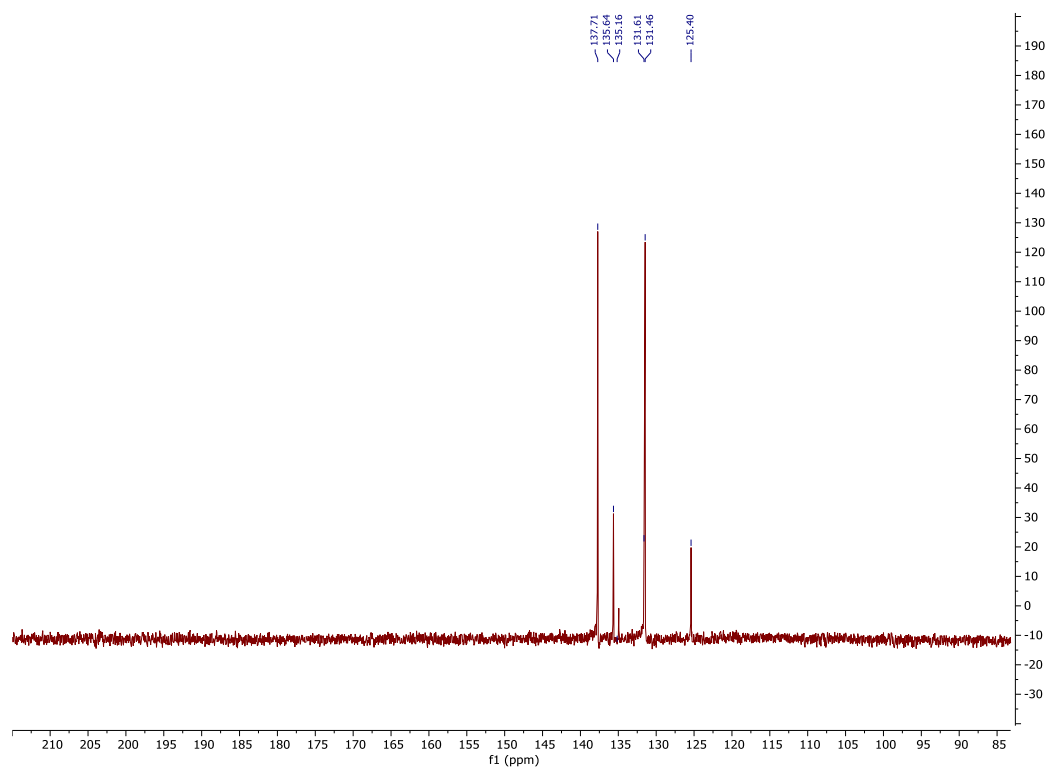


Figure S59: ¹³C NMR spectrum of 1,4-bis(tris(4-bromophenyl)silyl)benzene (**35**).

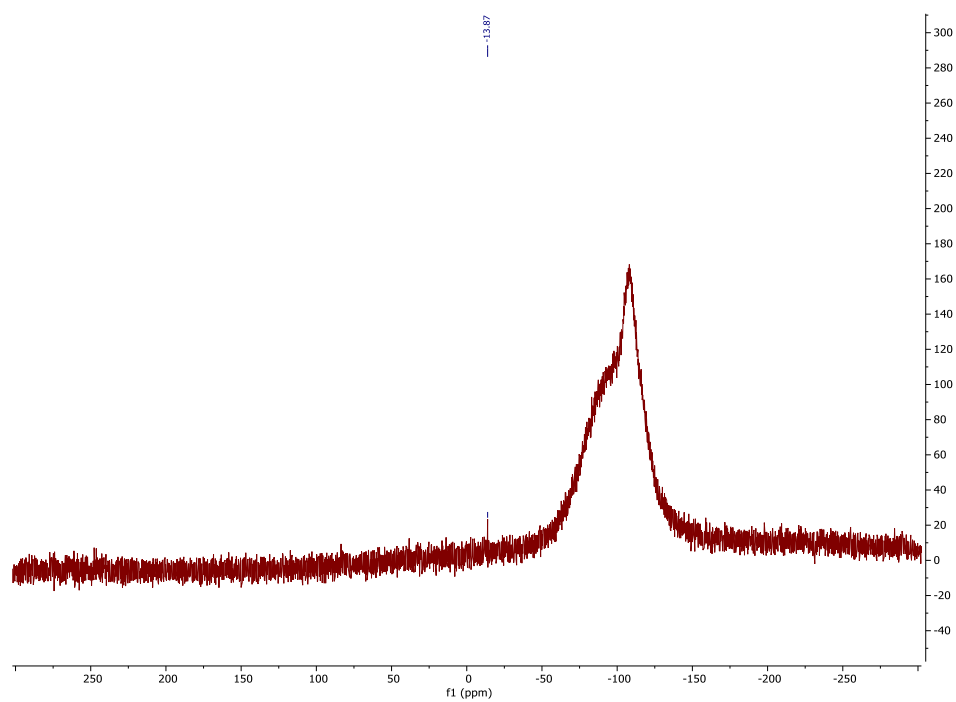


Figure S60: ²⁹Si NMR spectrum of 1,4-bis(tris(4-bromophenyl)silyl)benzene (**35**).

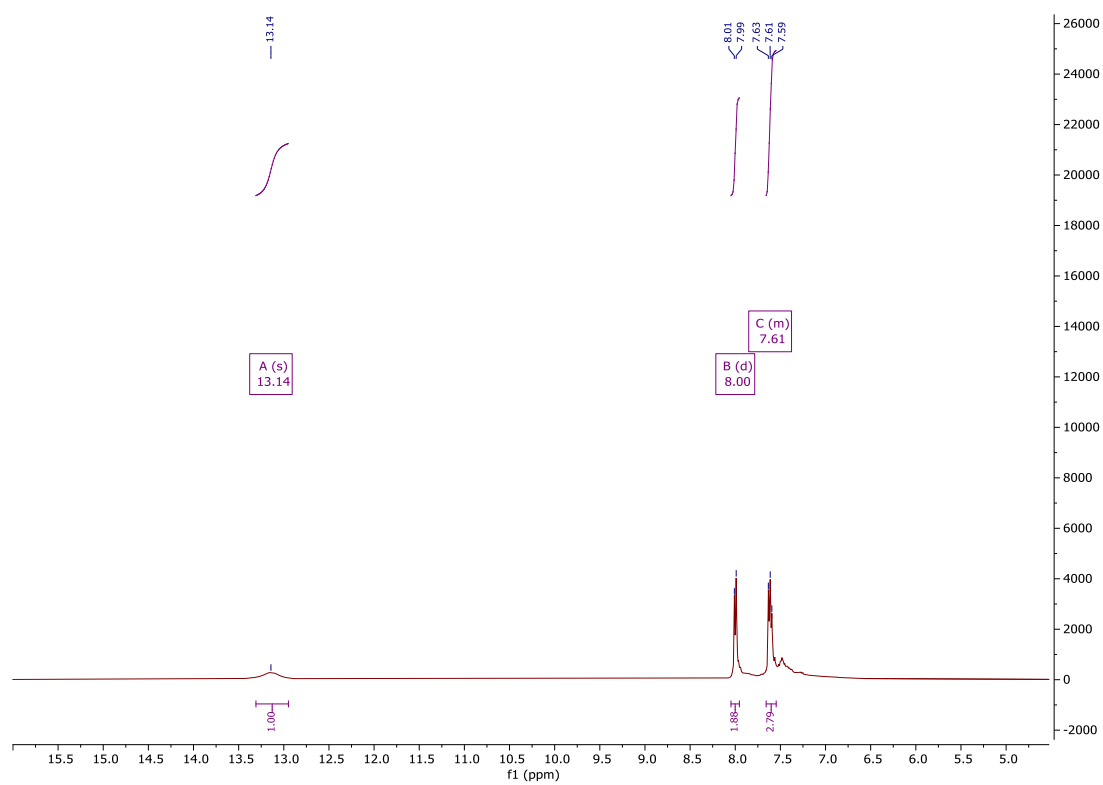


Figure S61: ^1H NMR spectrum of 1,4-bis(tris(4-carboxyphenyl)silyl)benzene (L2-H₆).

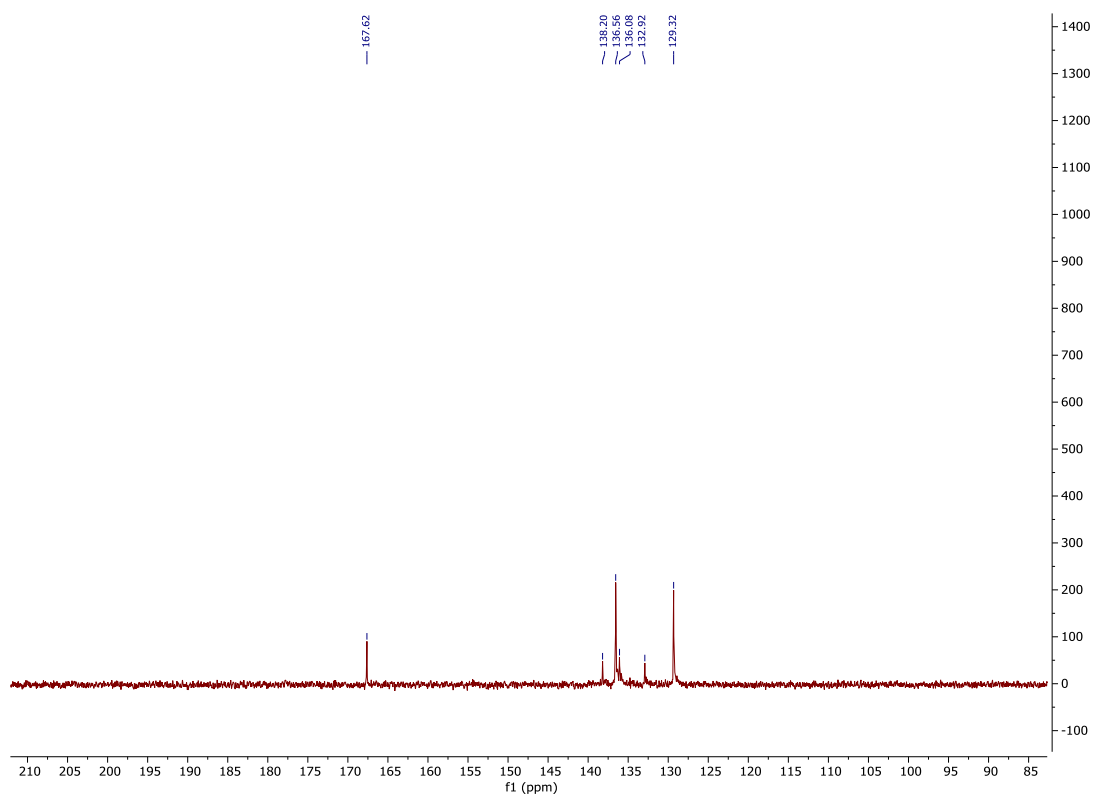


Figure S62: ^{13}C NMR spectrum of 1,4-bis(tris(4-carboxyphenyl)silyl)benzene (**L2-H₆**).

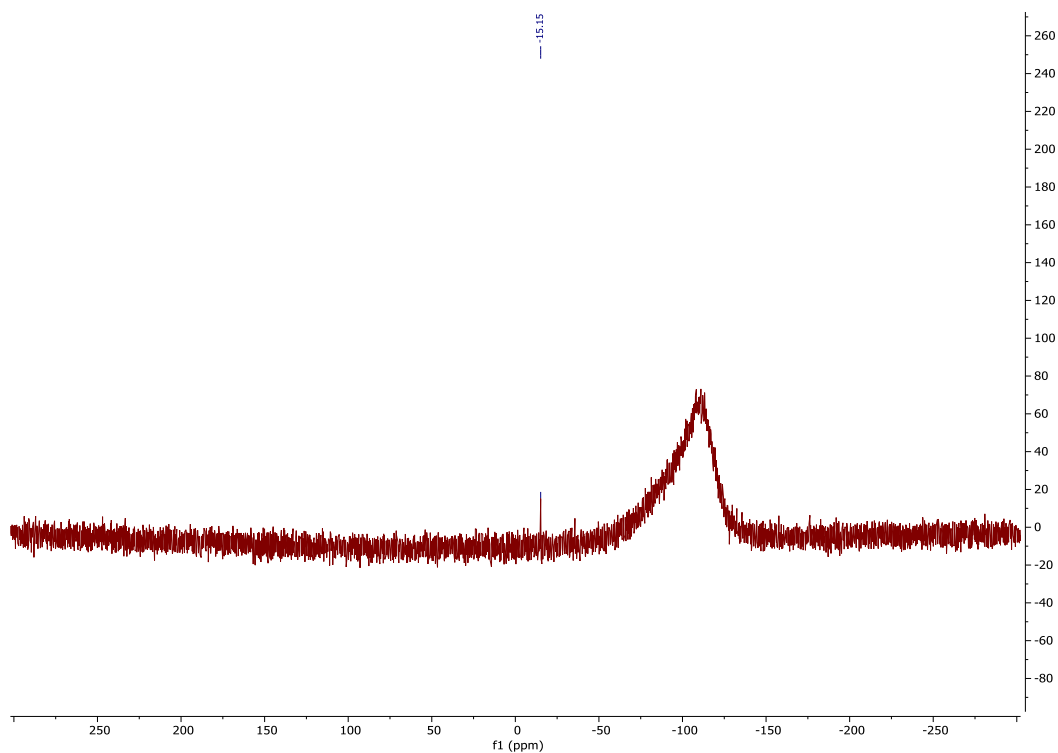


Figure S63: ^{29}Si NMR spectrum of 1,4-bis(tris(4-carboxyphenyl)silyl)benzene (**L2-H₆**).

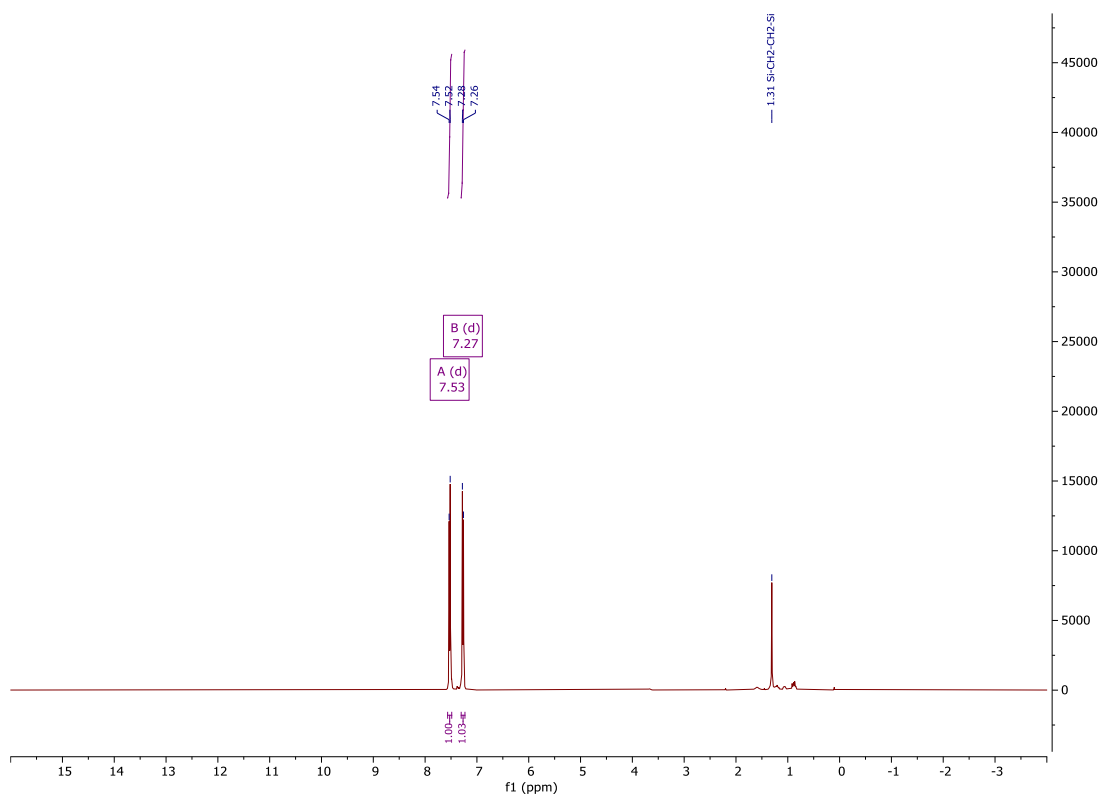


Figure S64: ¹H NMR spectrum of 1,2-bis(tris(4-bromophenyl)silyl)ethane (**36**).

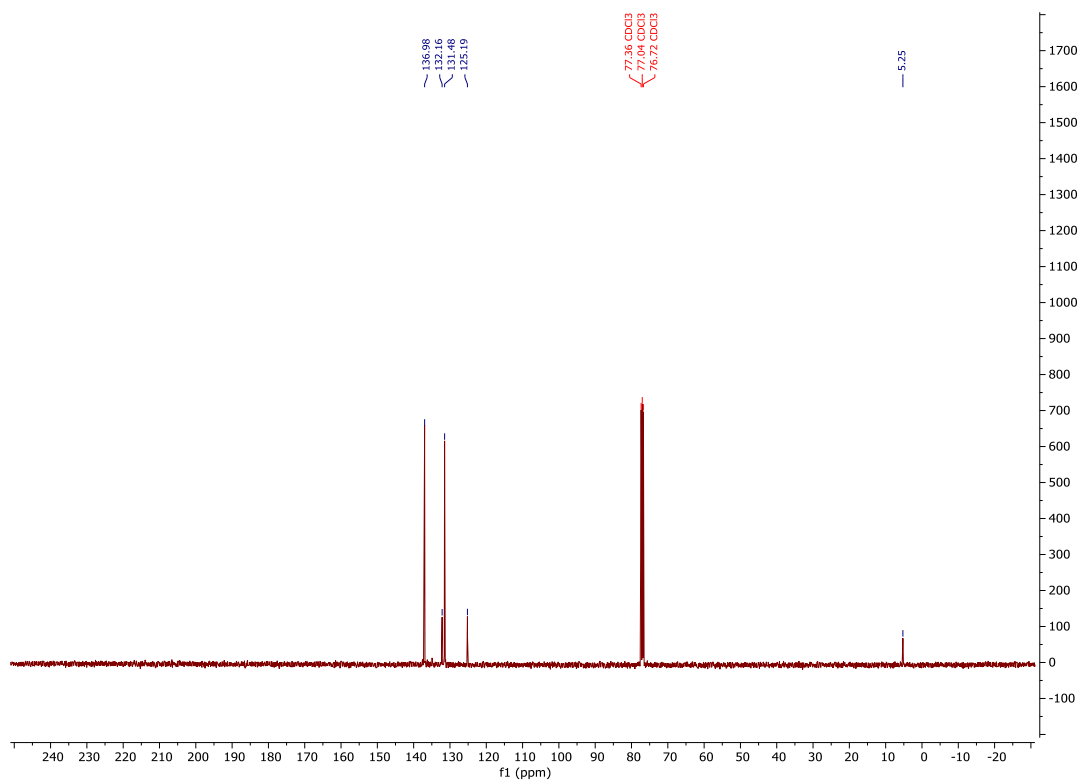


Figure S65: ¹³C NMR spectrum of 1,2-bis(tris(4-bromophenyl)silyl)ethane (**36**).

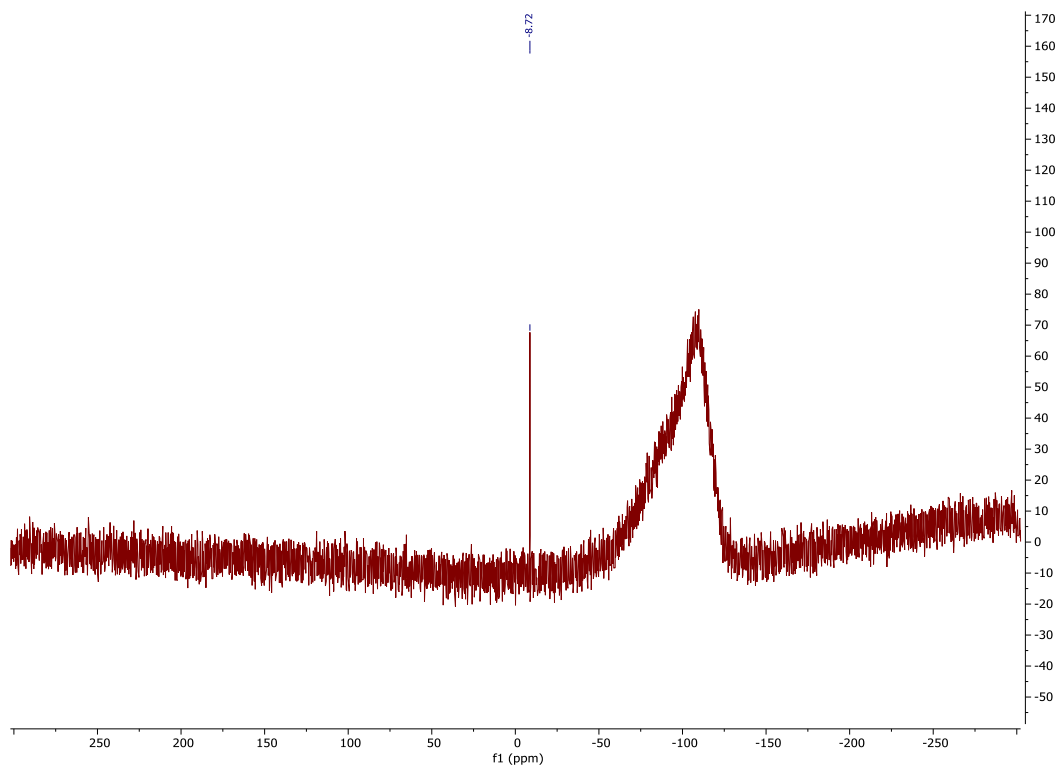


Figure S66: ^{29}Si NMR spectrum of 1,2-bis(tris(4-bromophenyl)silyl)ethane (**36**).

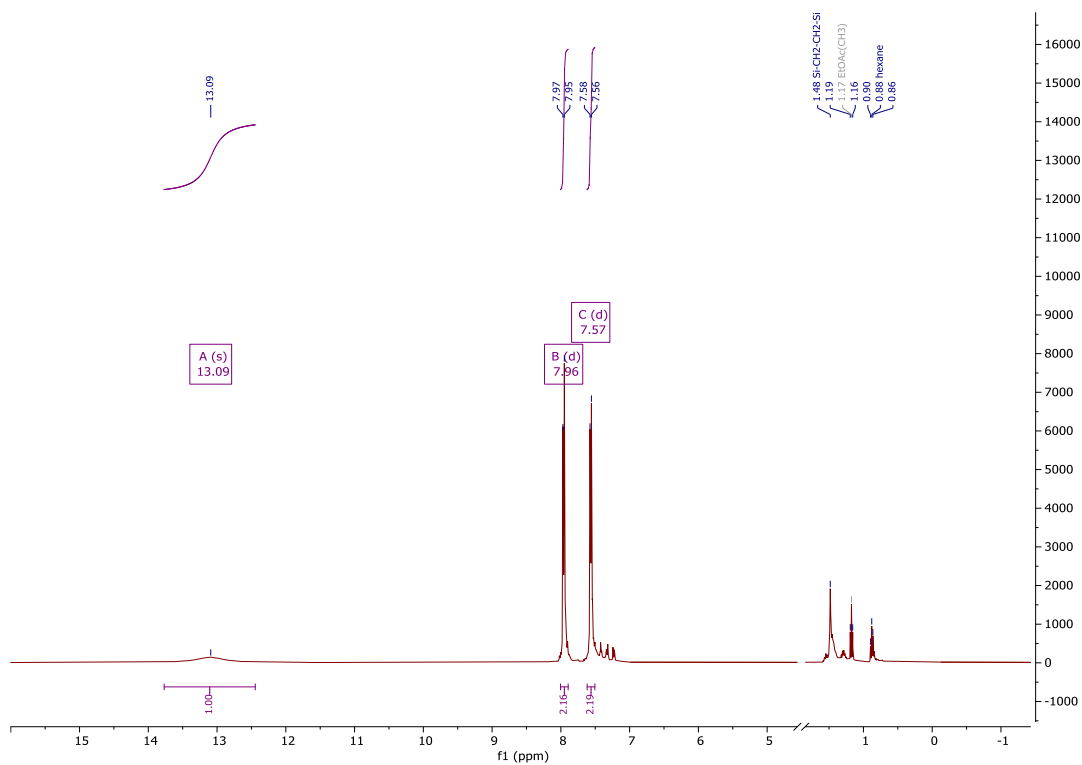


Figure S67: ^1H NMR spectrum of 1,2-bis(tris(4-carboxyphenyl)silyl)ethane (**L3-H₆**).

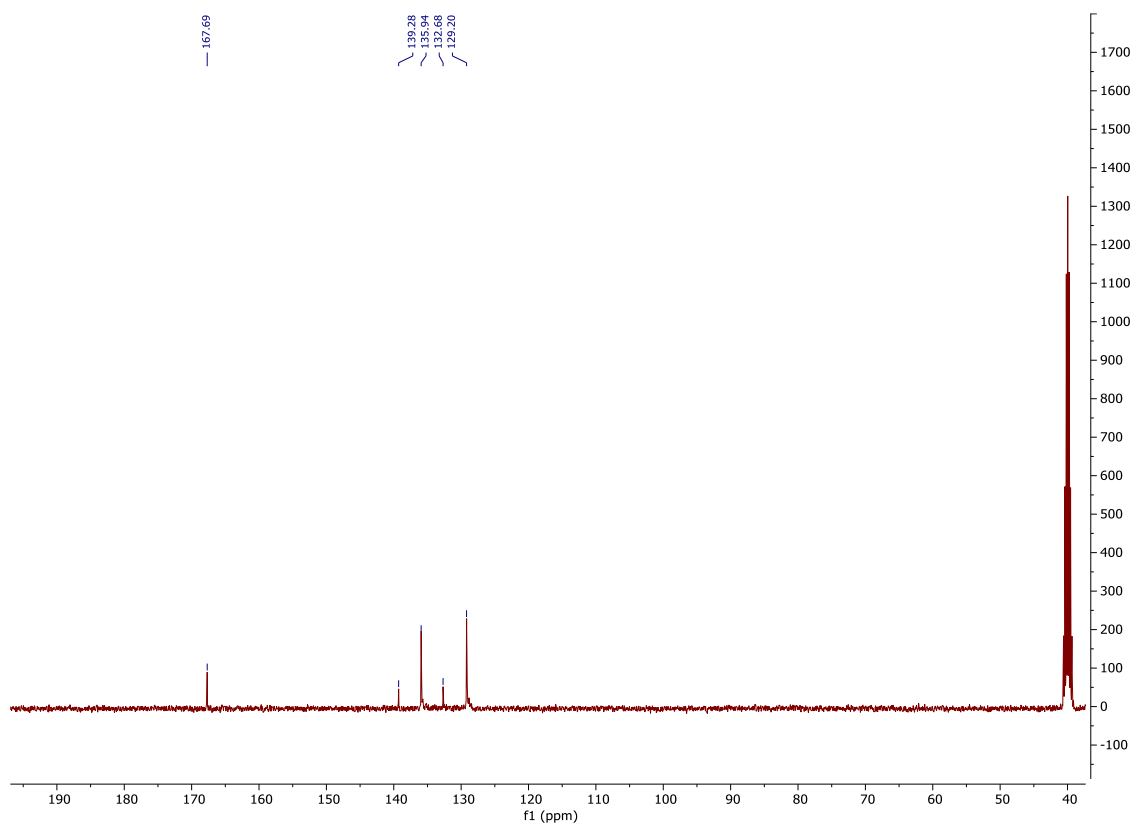


Figure S68: ^{13}C NMR spectrum of 1,2-bis(tris(4-carboxyphenyl)silyl)ethane (**L3-H₆**).

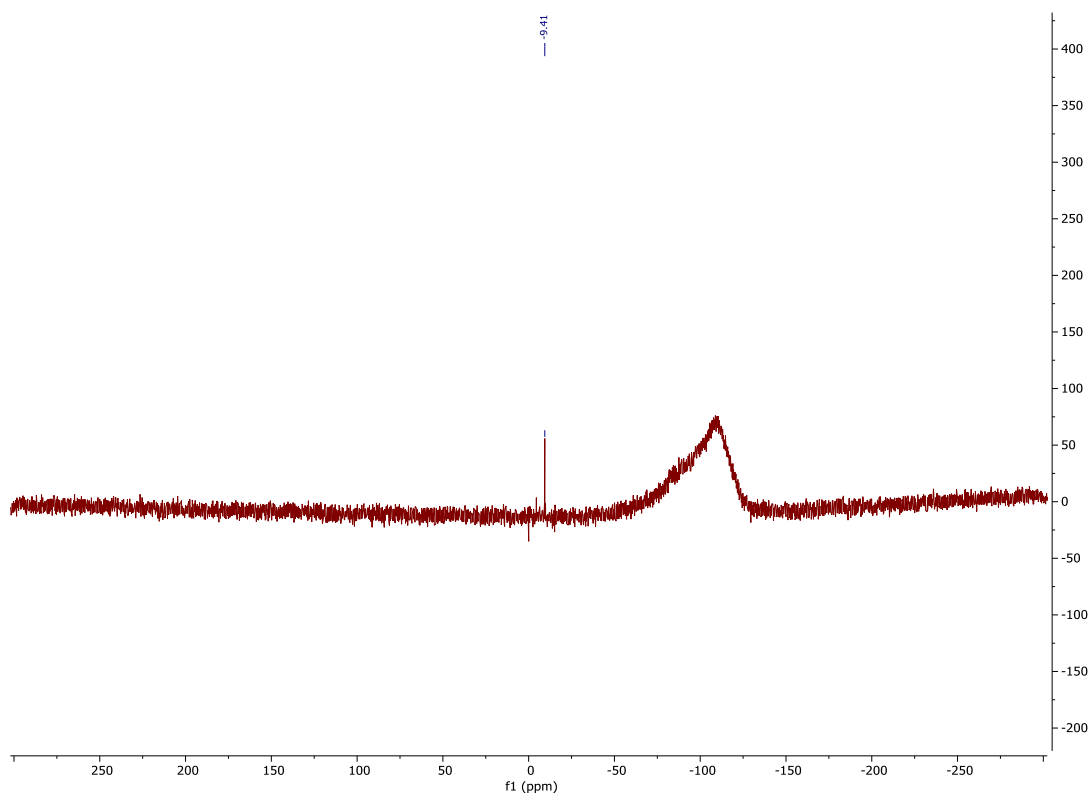


Figure S69: ^{29}Si NMR spectrum of 1,2-bis(tris(4-carboxyphenyl)silyl)ethane (**L3-H₆**).

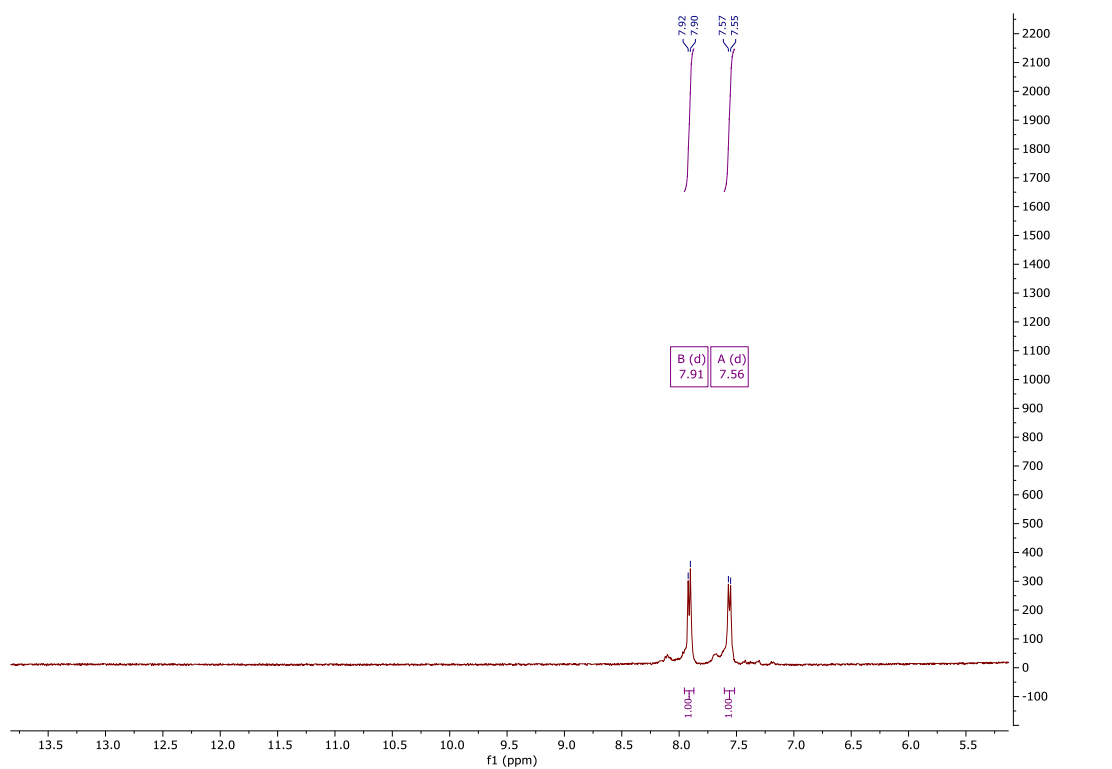


Figure S70: ¹H NMR spectrum of hexa(4-acylchlorophenyl)disiloxane (**37**).

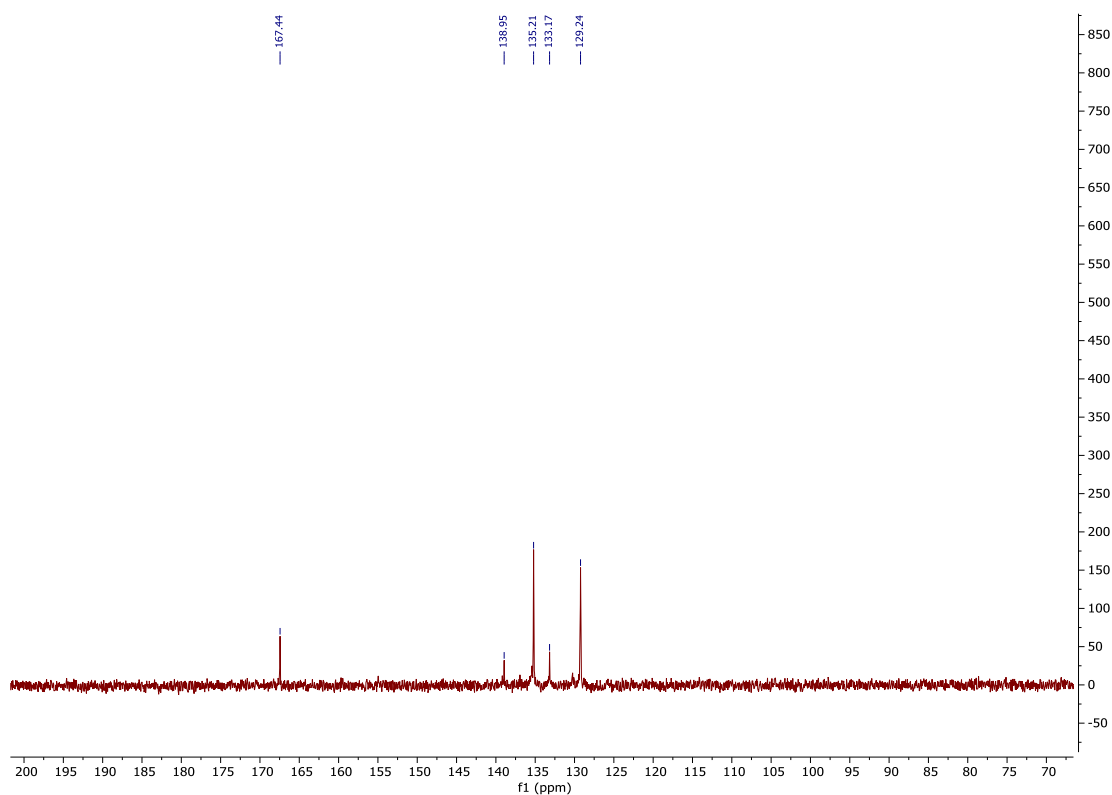


Figure S71: ¹³C NMR spectrum of hexa(4-acylchlorophenyl)disiloxane (**37**).

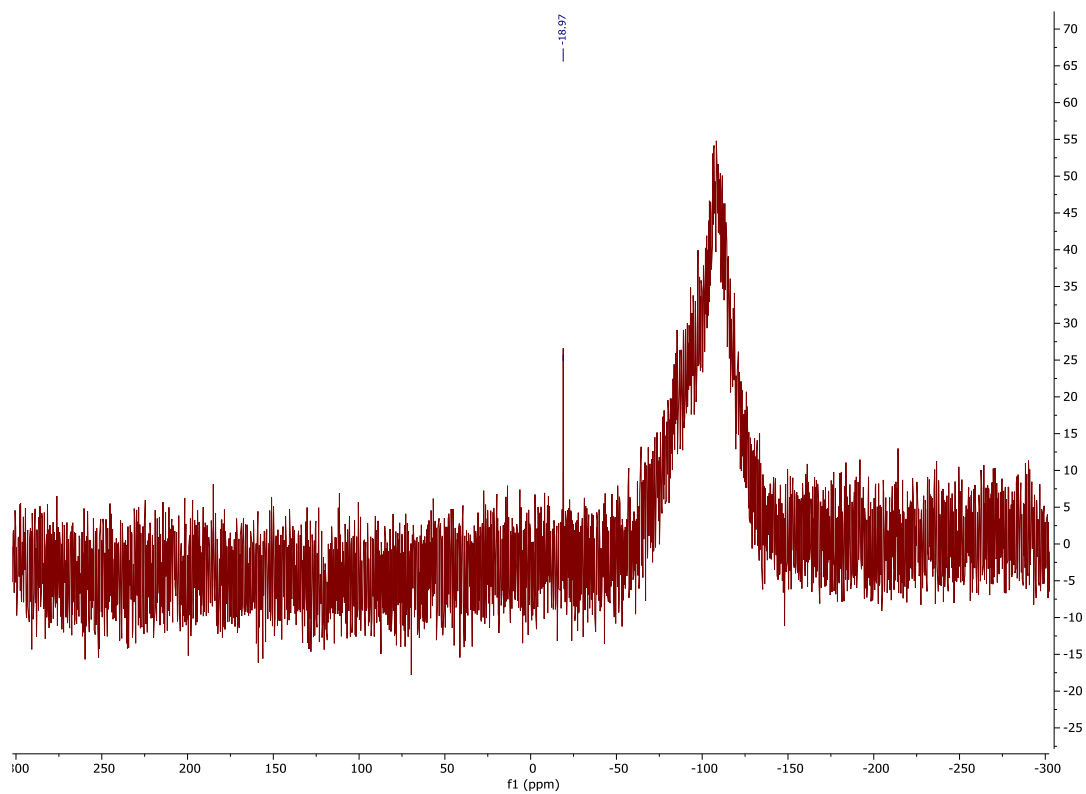


Figure S72: ^{29}Si NMR spectrum of hexa(4-acylchlorophenyl)disiloxane (**37**).

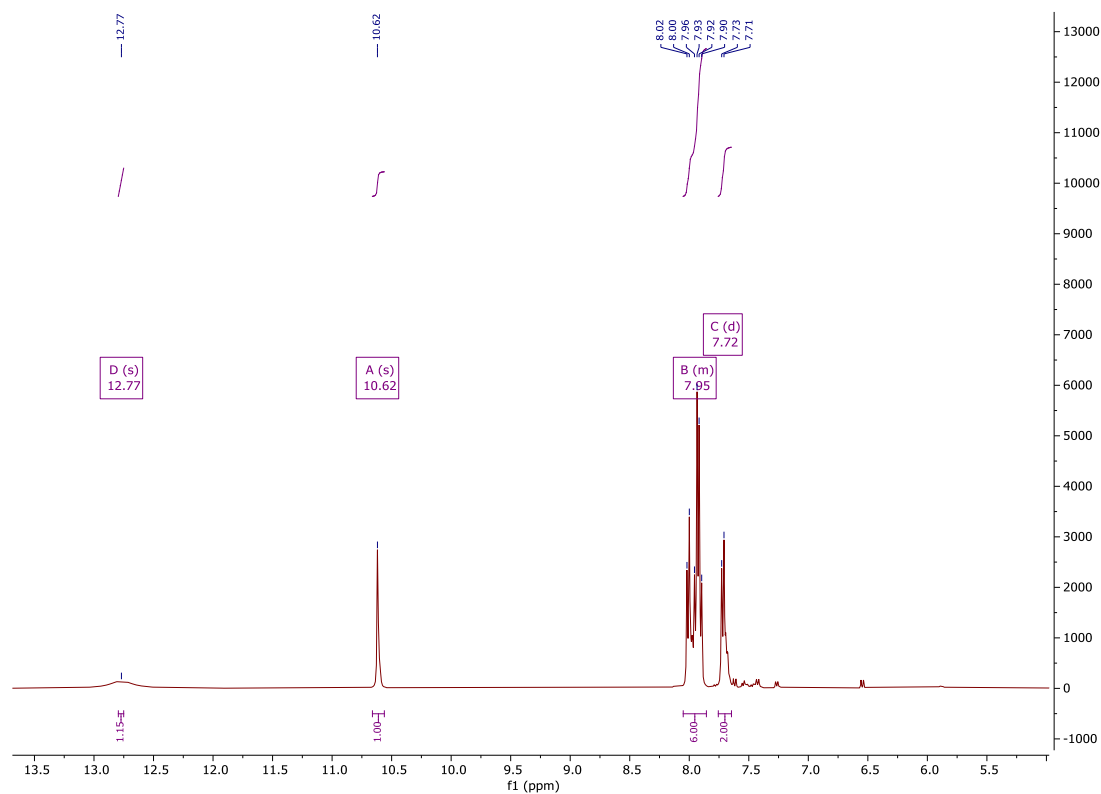


Figure S73: ^1H NMR spectrum of hexa(4-carboxyphenyl-4-benzamide)disiloxane (**L4-H₆**)

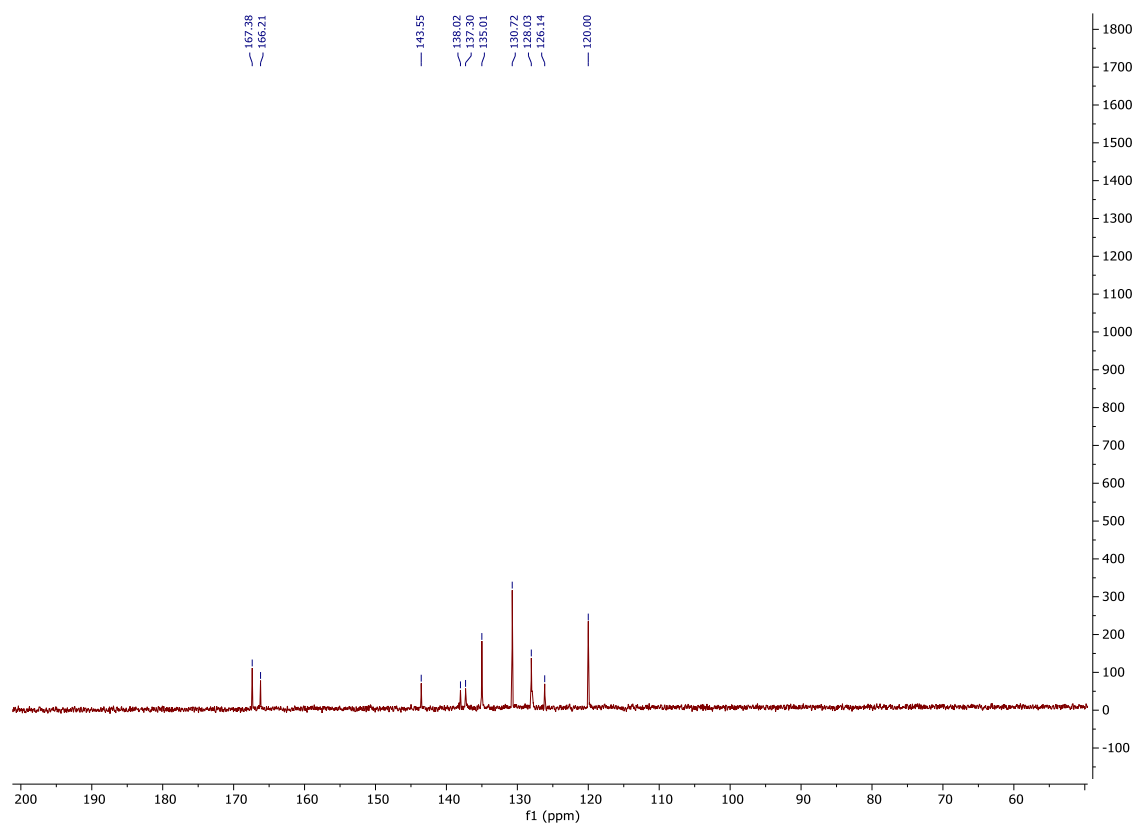


Figure S74: ¹³C NMR spectrum of hexa(4-carboxyphenyl-4-benzamide)disiloxane (L4-H₆).

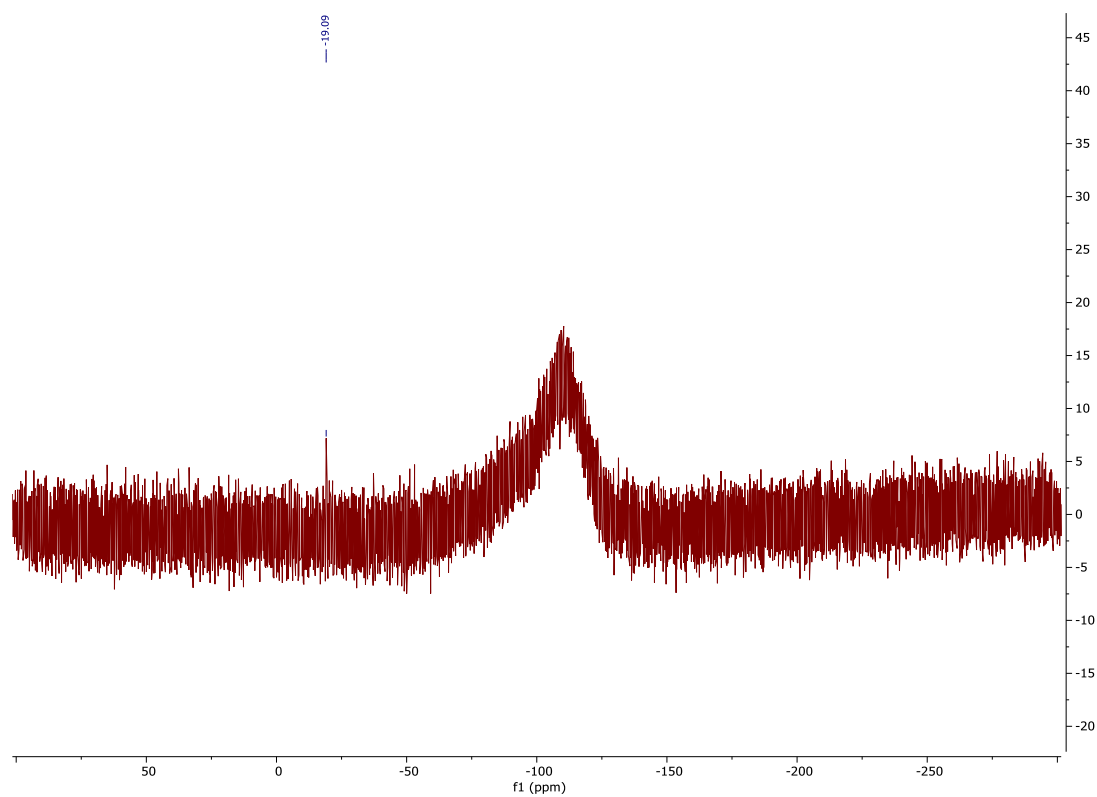


Figure S75: ²⁹Si NMR spectrum of hexa(4-carboxyphenyl-4-benzamide)disiloxane (L4-H₆).

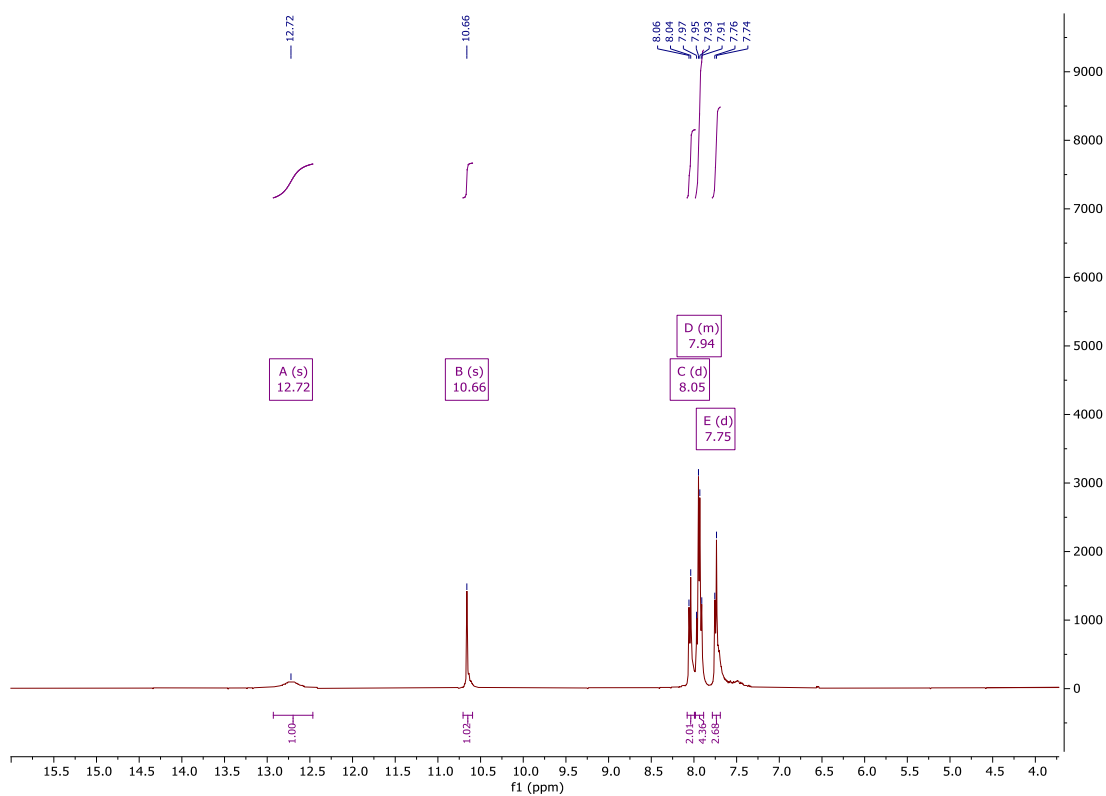


Figure S76: ¹H NMR spectrum of 1,4-bis(tris(4-carboxyphenyl-4-benzamide)silyl)benzene (L5-H₆).

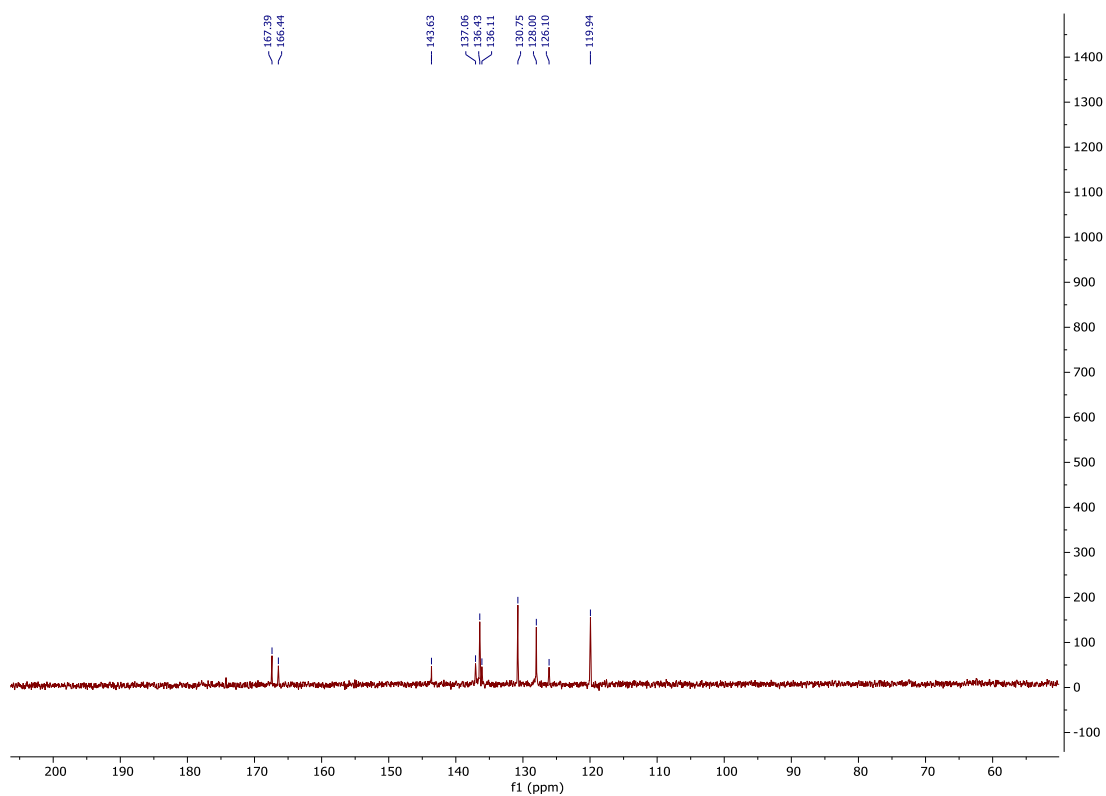


Figure S77: ¹³C NMR spectrum of 1,4-bis(tris(4-carboxyphenyl-4-benzamide)silyl)benzene (L5-H₆).

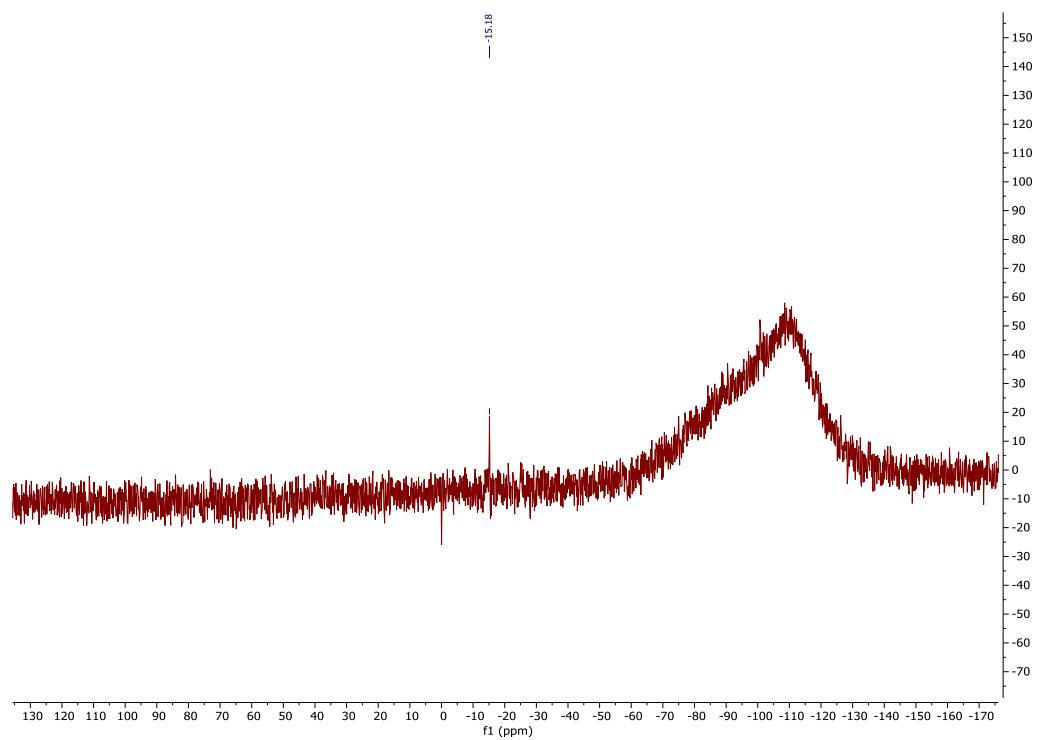


Figure S78: ^{29}Si NMR spectrum of 1,4-bis(tris(4-carboxyphenyl-4-benzamide)silyl)benzene (**L5-H₆**).

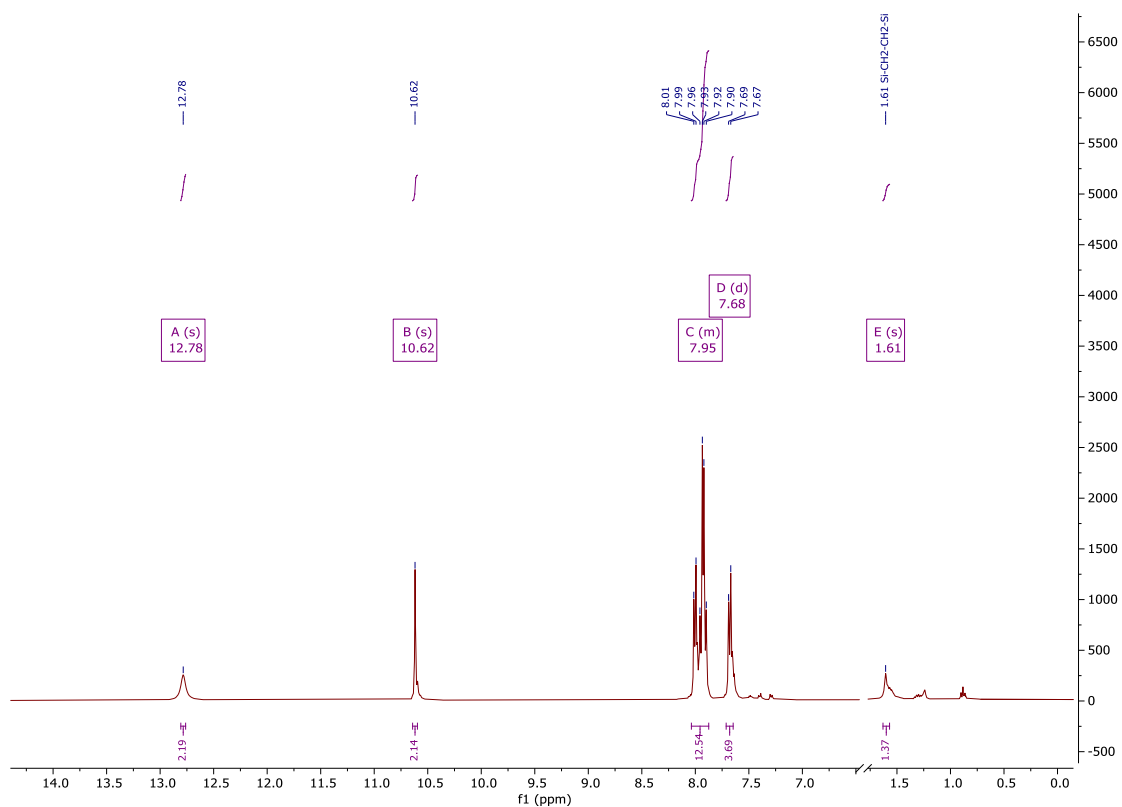


Figure S79: ^1H NMR spectrum of 1,4-bis(tris(4-carboxyphenyl-4-benzamide)silyl)benzene (L6-H₆).

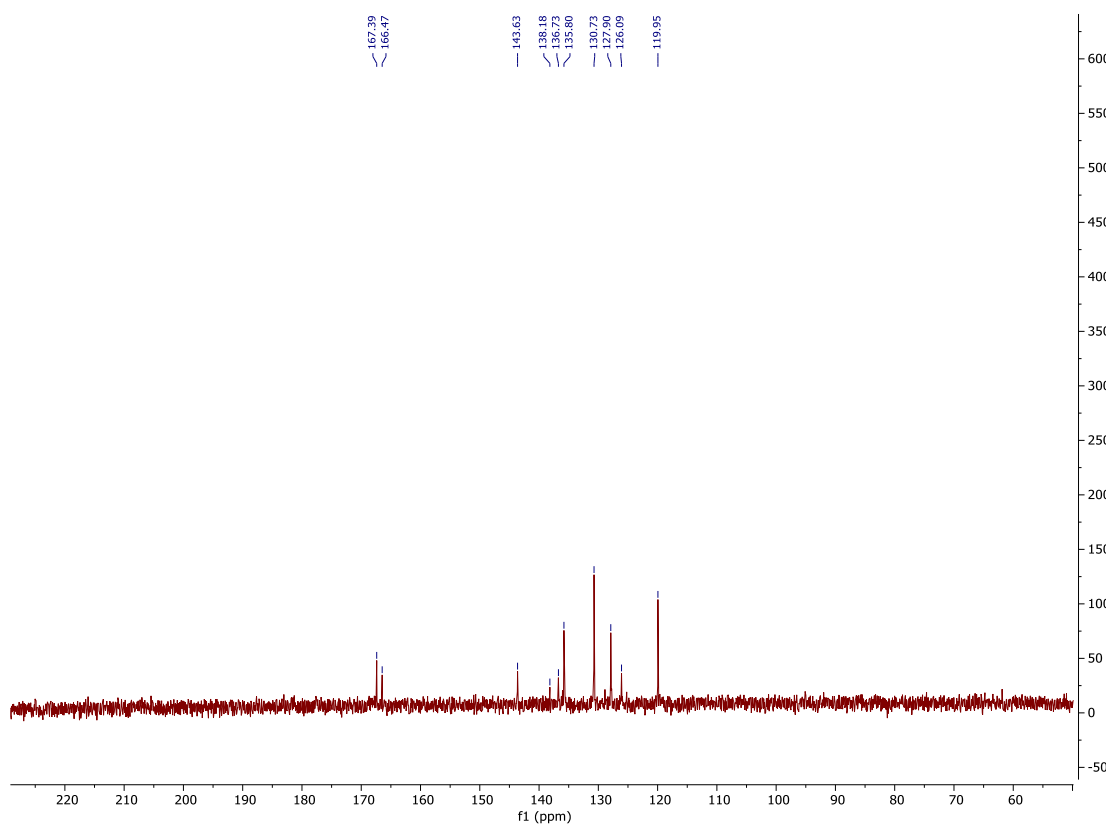


Figure S80: ^{13}C NMR spectrum of 1,2-bis(tris(4-carboxyphenyl-4-benzamide)silyl)ethane (L6-H₆).

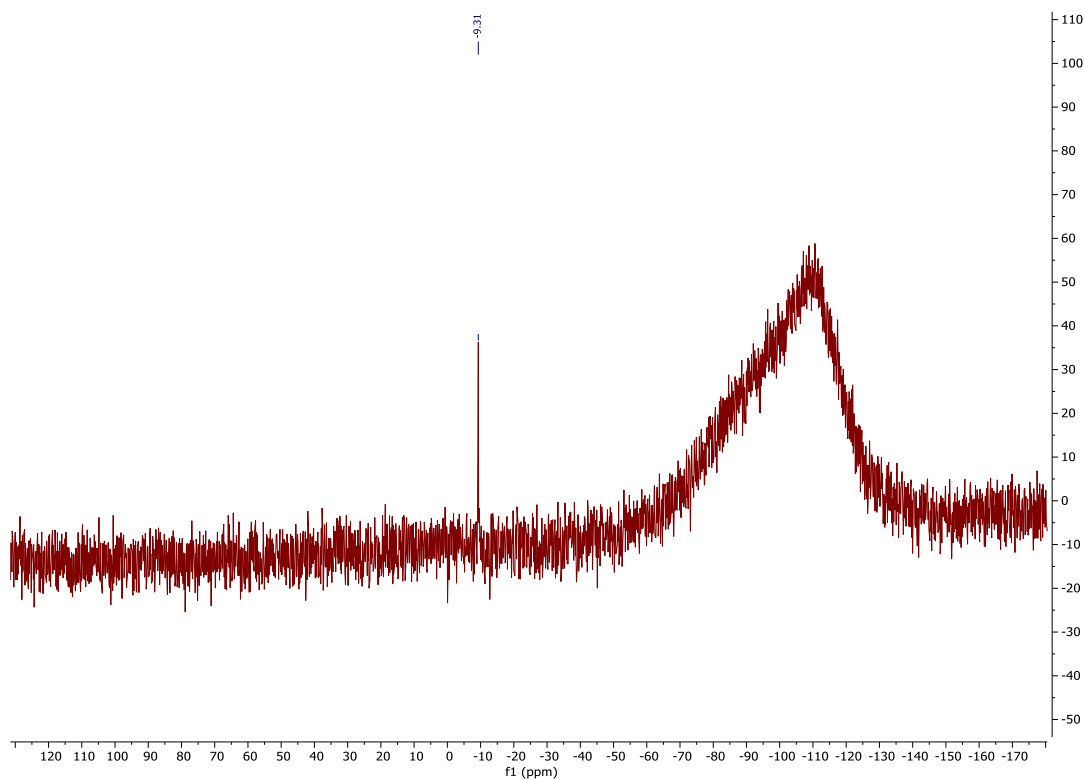


Figure S81: ^{29}Si NMR spectrum of 1,2-bis(tris(4-carboxyphenyl-4-benzamide)silyl)ethane (L6-H₆).

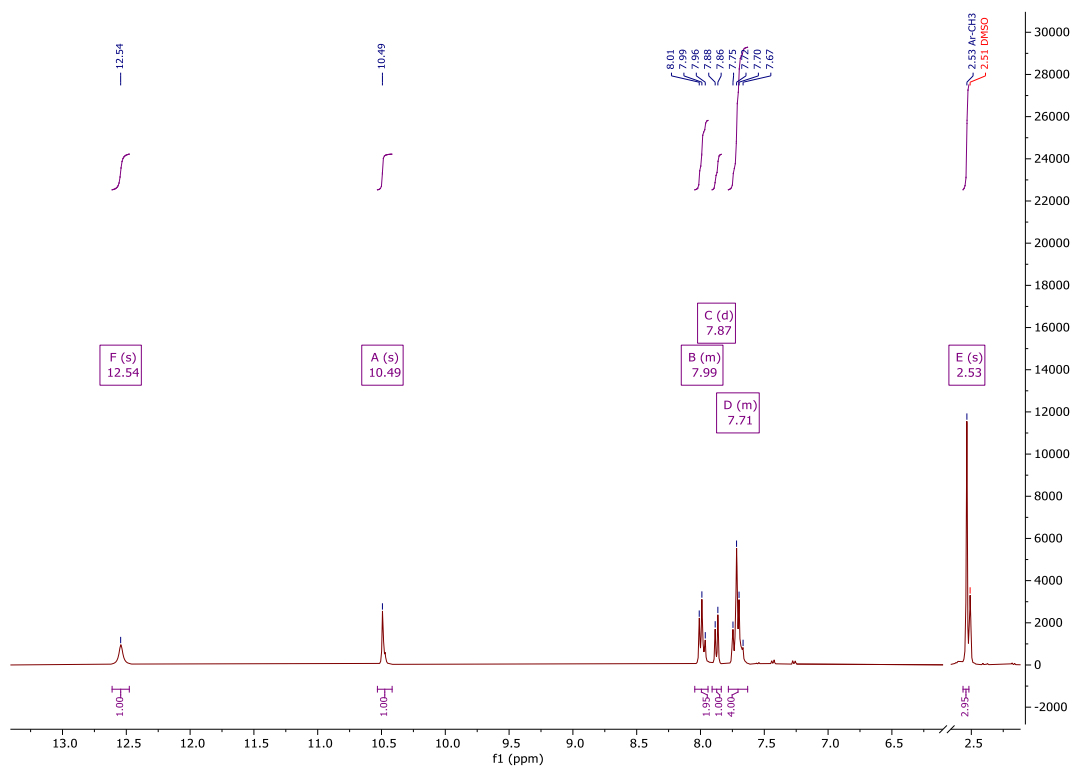


Figure S82: ^1H NMR spectrum of hexa(4-carboxy-2-methylphenyl-4-benzamide)disiloxane (L7-H₆).

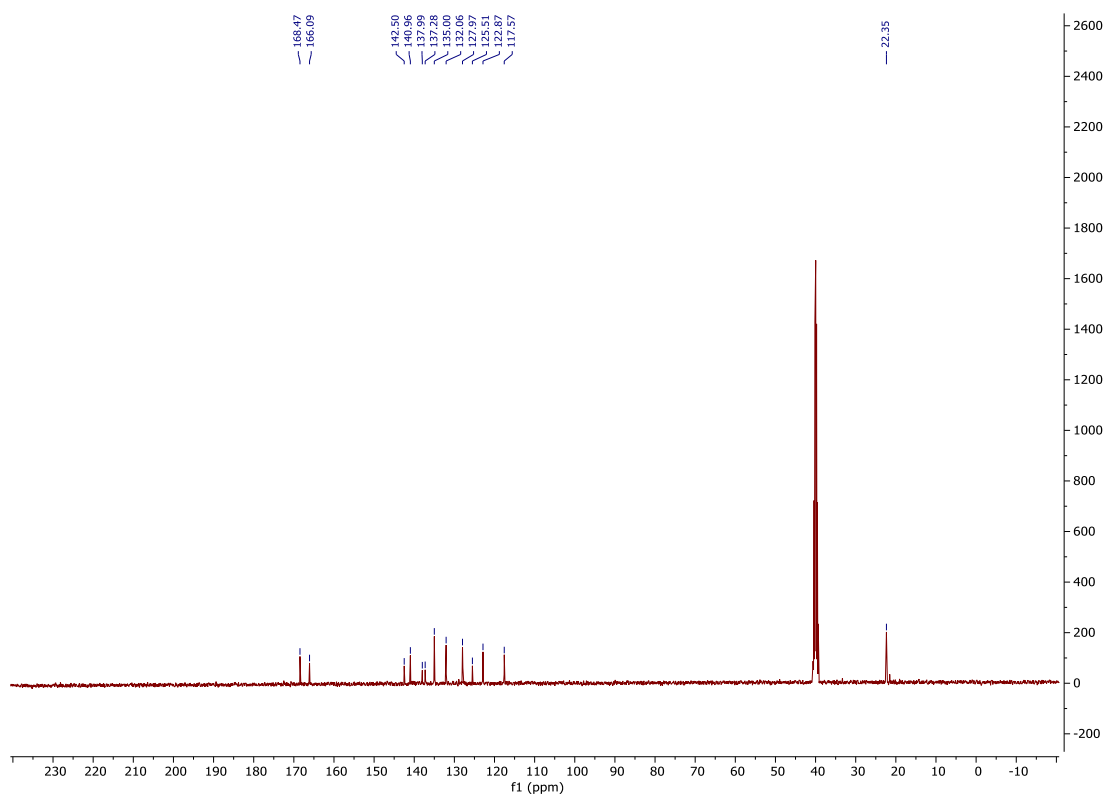


Figure S83: ^{13}C NMR spectrum of hexa(4-carboxy-2-methylphenyl-4-benzamide)disiloxane (L7-H₆).

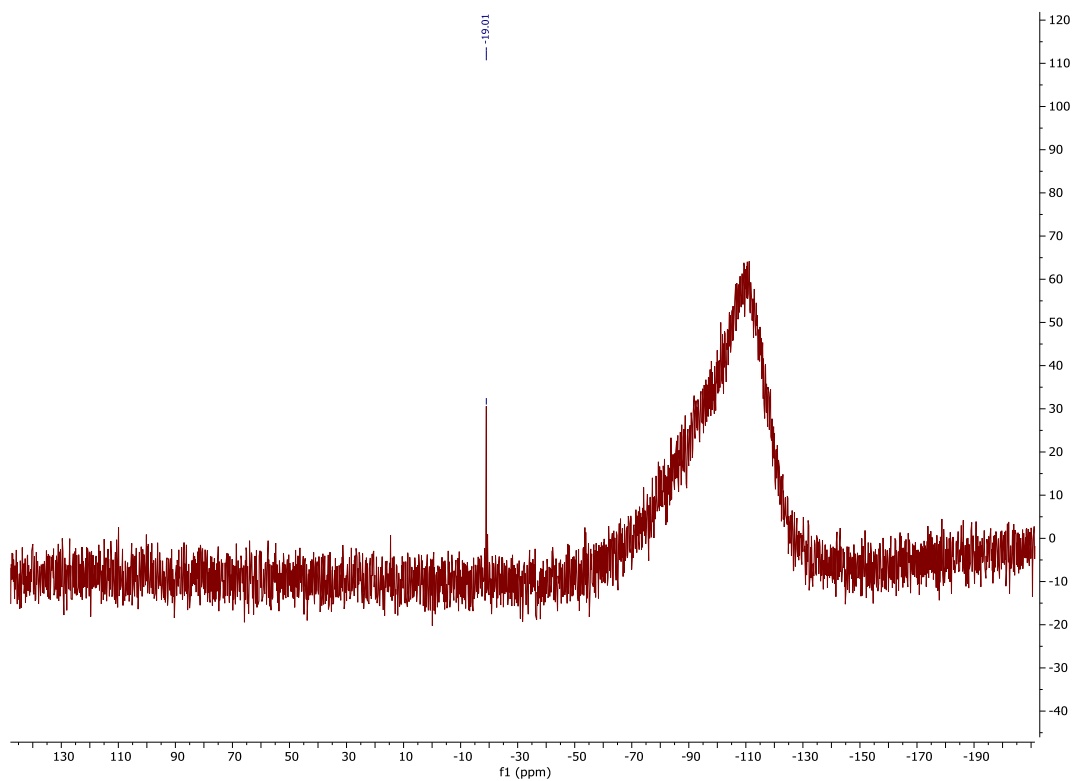


Figure S84: ^{29}Si NMR spectrum of hexa(4-carboxy-2-methylphenyl-4-benzamide)disiloxane (L7-H₆).

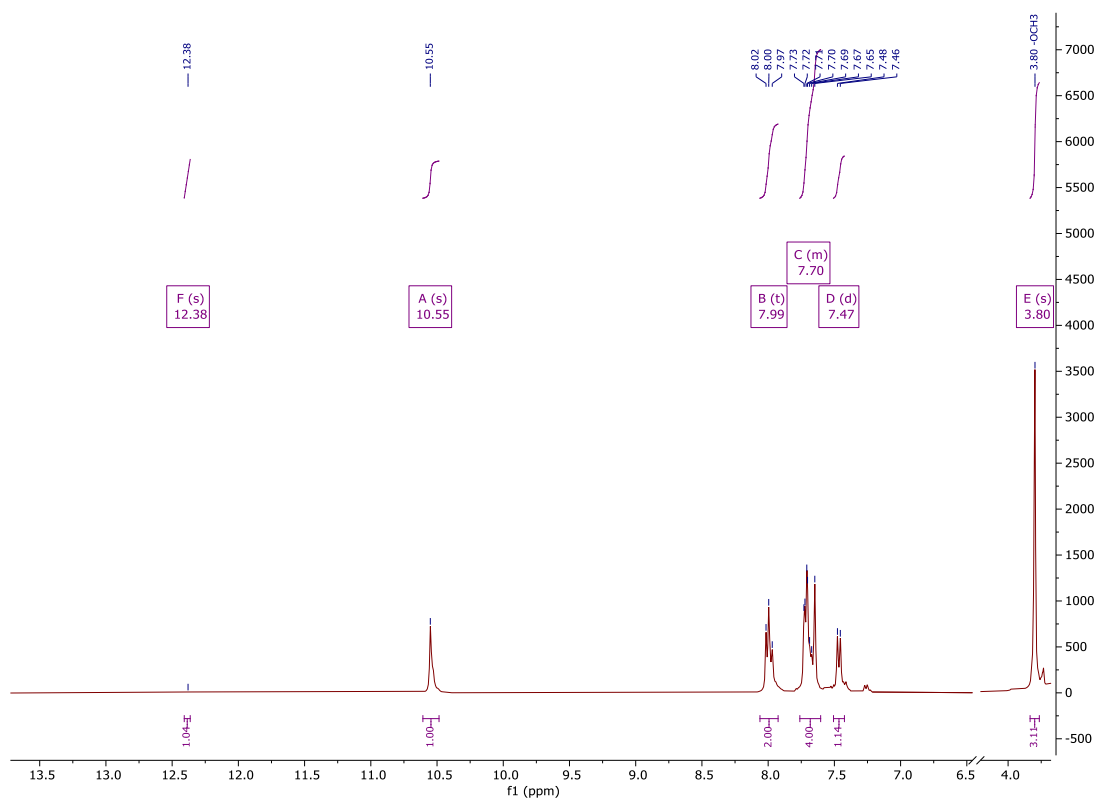


Figure S85: ¹H NMR spectrum of hexa(4-carboxy-2-methoxyphenyl-4-benzamide)disiloxane (L8-H₆).

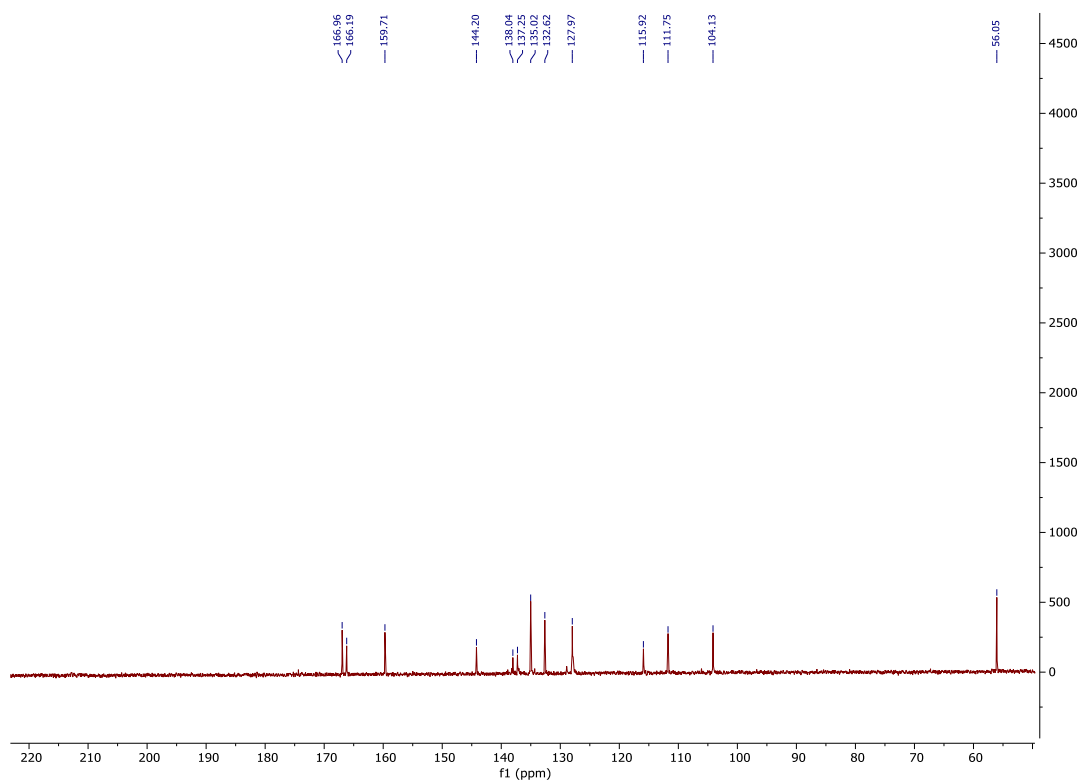


Figure S86: ¹³C NMR spectrum of hexa(4-carboxy-2-methoxyphenyl-4-benzamide)disiloxane (L8-H₆).

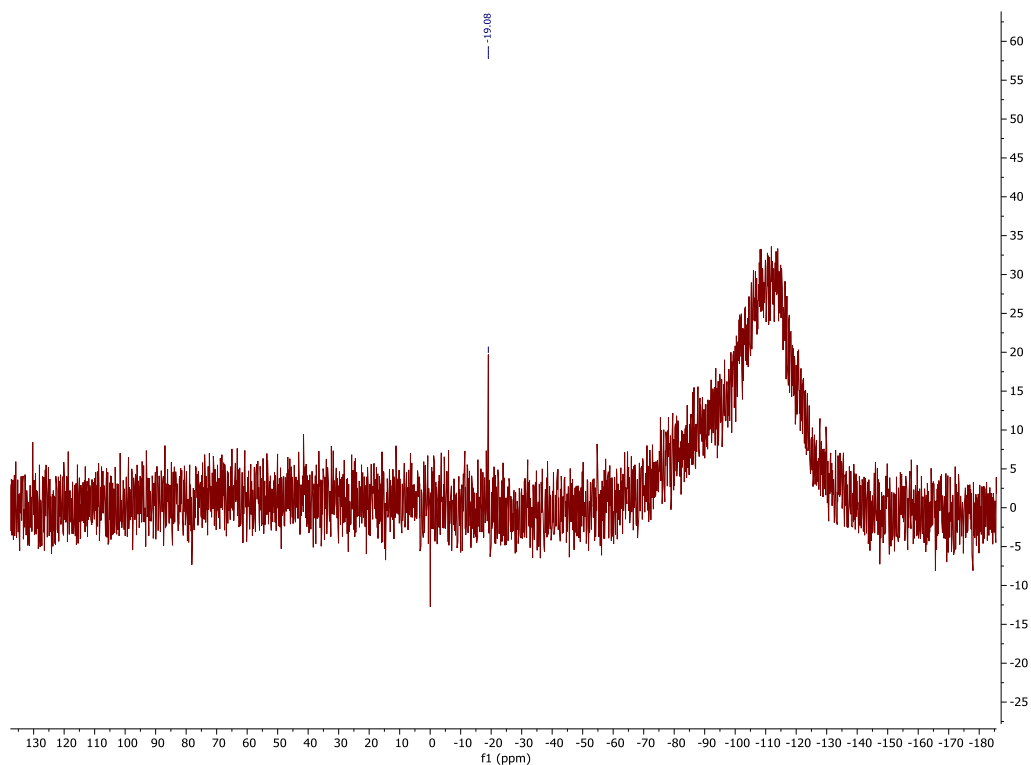


Figure S87: ^{29}Si NMR spectrum of hexa(4-carboxy-2-methoxyphenyl-4-benzamide)disiloxane (**L8-H₆**).

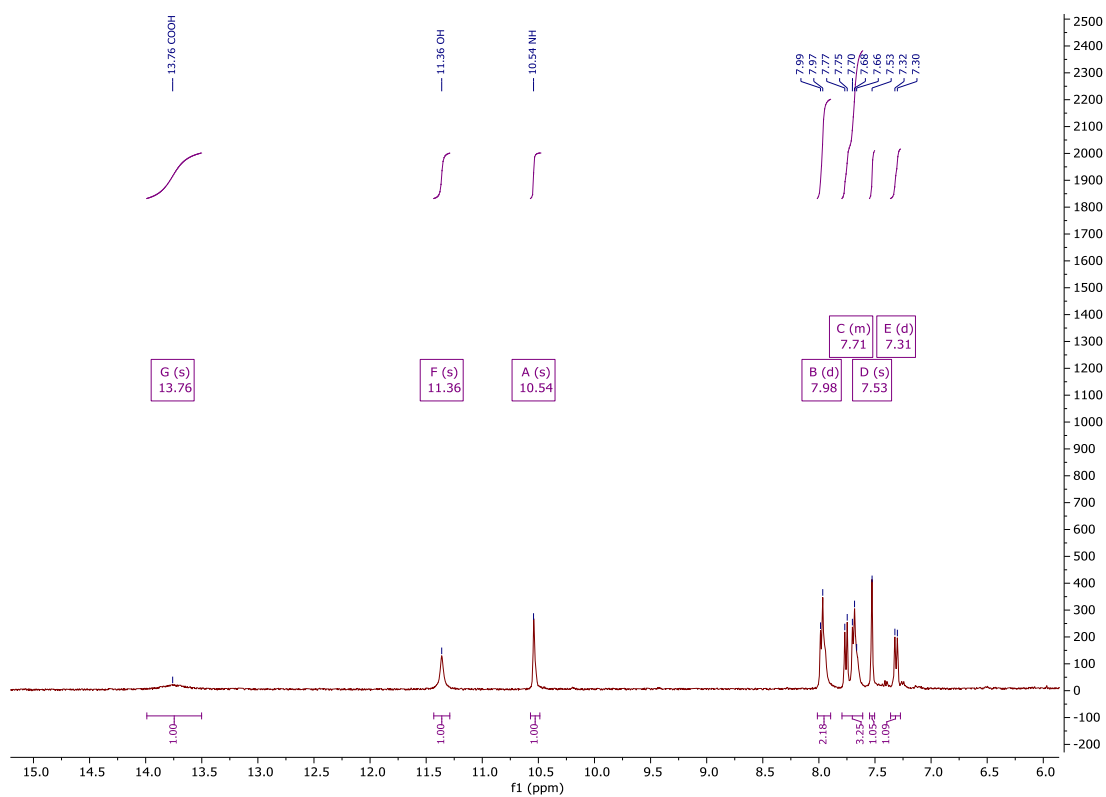


Figure S88: ^1H NMR spectrum of hexa(4-carboxy-2-hydroxyphenyl-4-benzamide)disiloxane (**L9-H₆**).

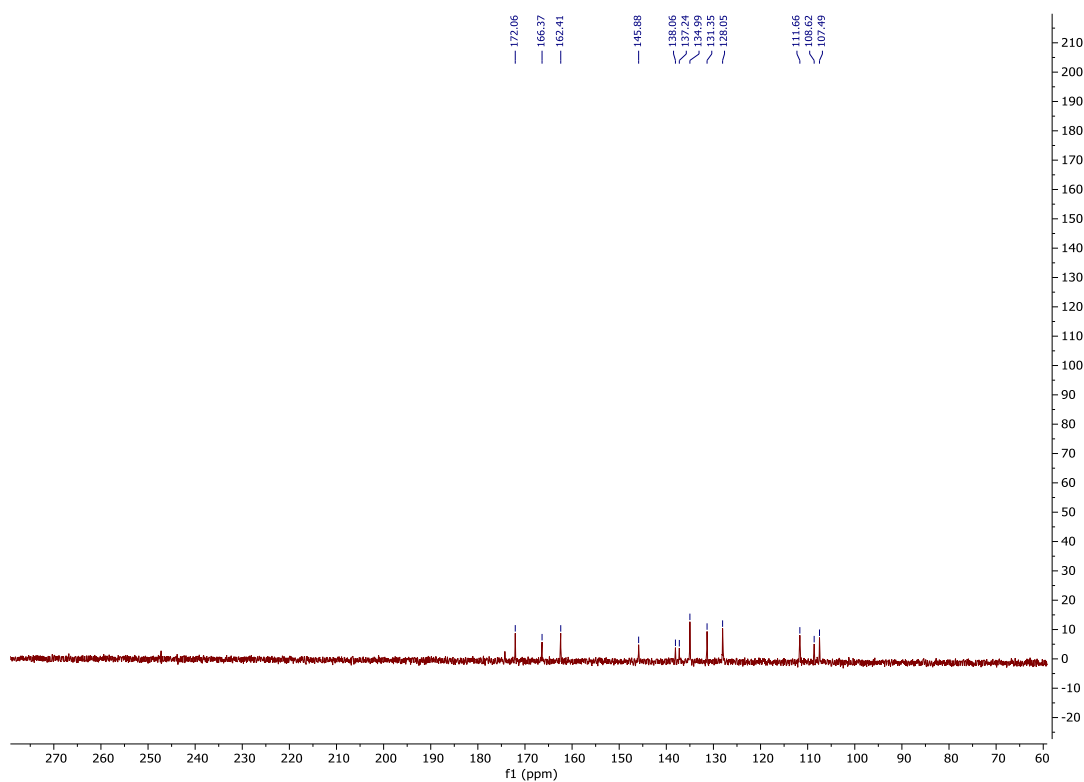


Figure S89: ^{13}C NMR spectrum of hexa(4-carboxy-2-hydroxyphenyl-4-benzamide)disiloxane (**L9-H₆**).

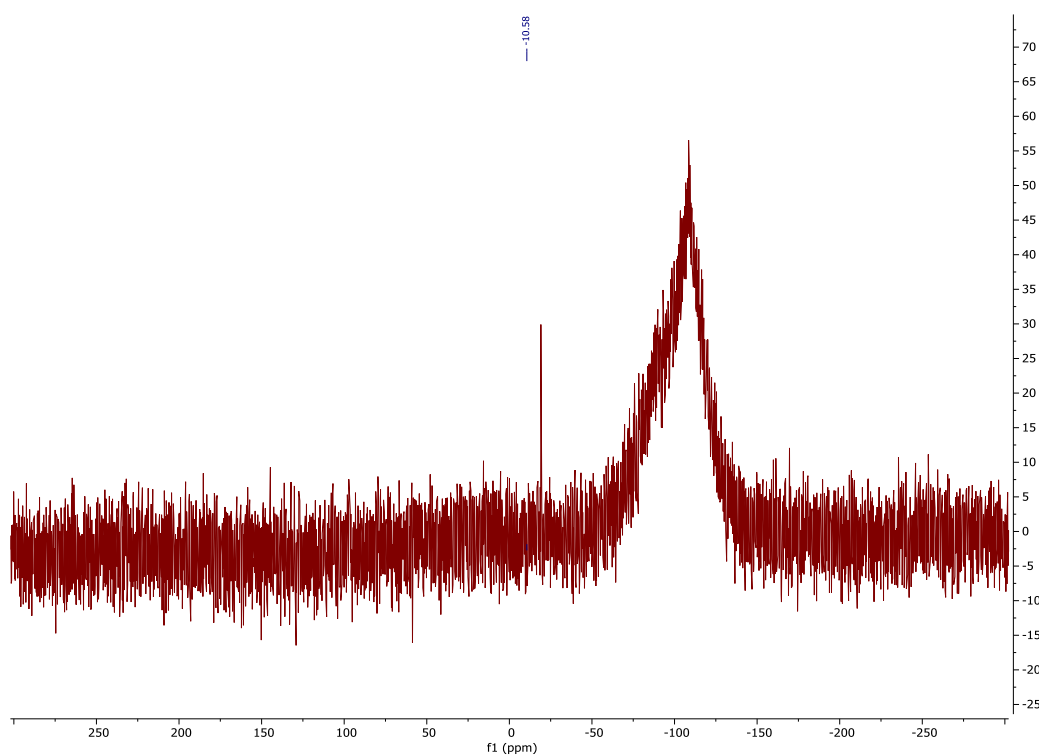


Figure S90: ^{29}Si NMR spectrum of hexa(4-carboxy-2-hydroxyphenyl-4-benzamide)disiloxane (**L9-H₆**).

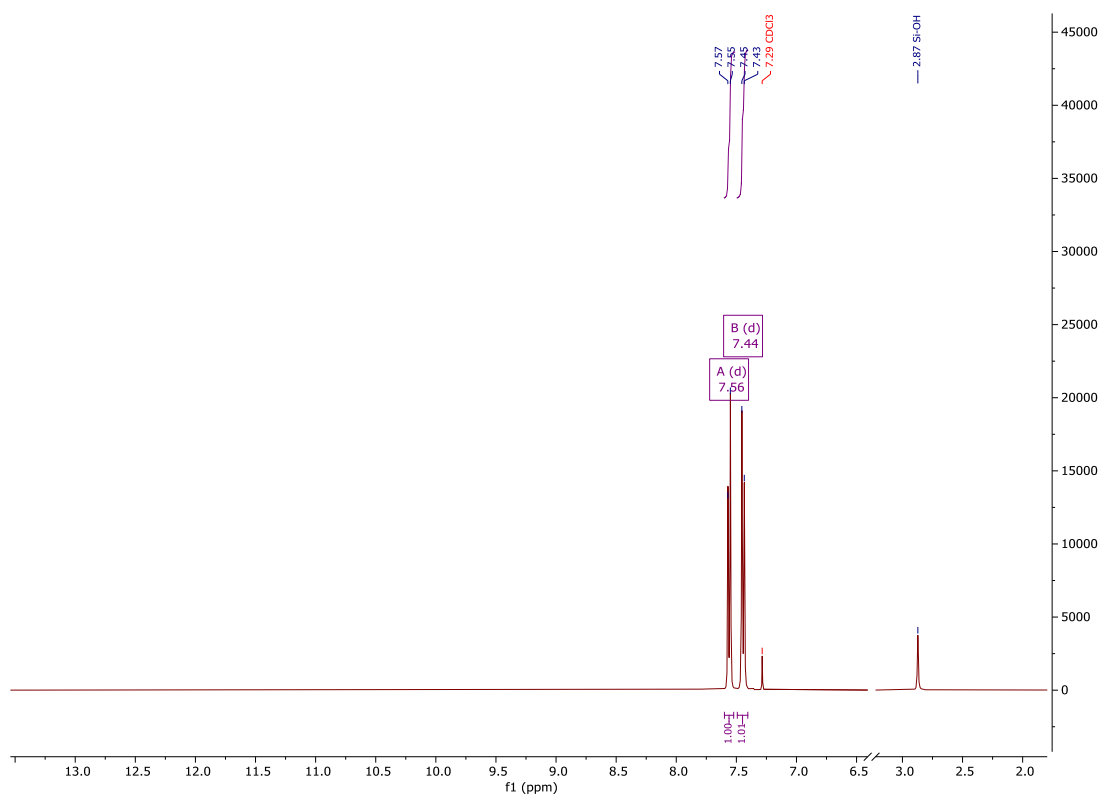


Figure S91: ¹H NMR spectrum of tris(4-bromophenyl)silanol (**40**).

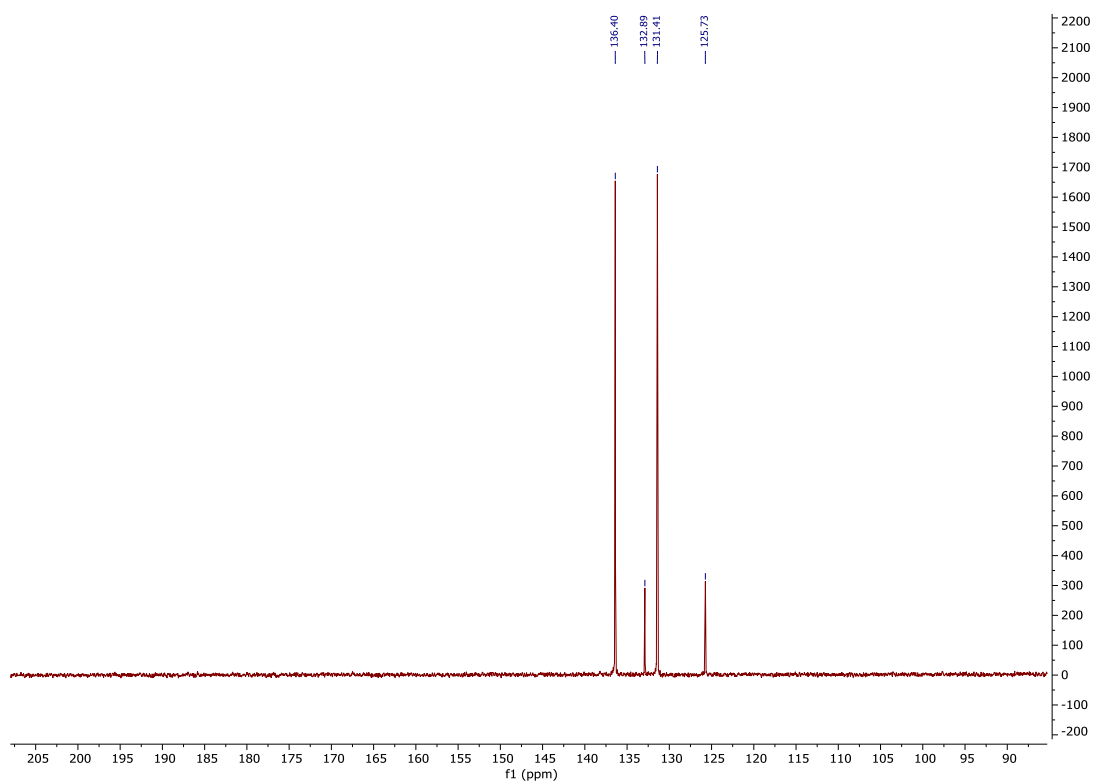


Figure S92: ¹³C NMR spectrum of tris(4-bromophenyl)silanol (**40**).

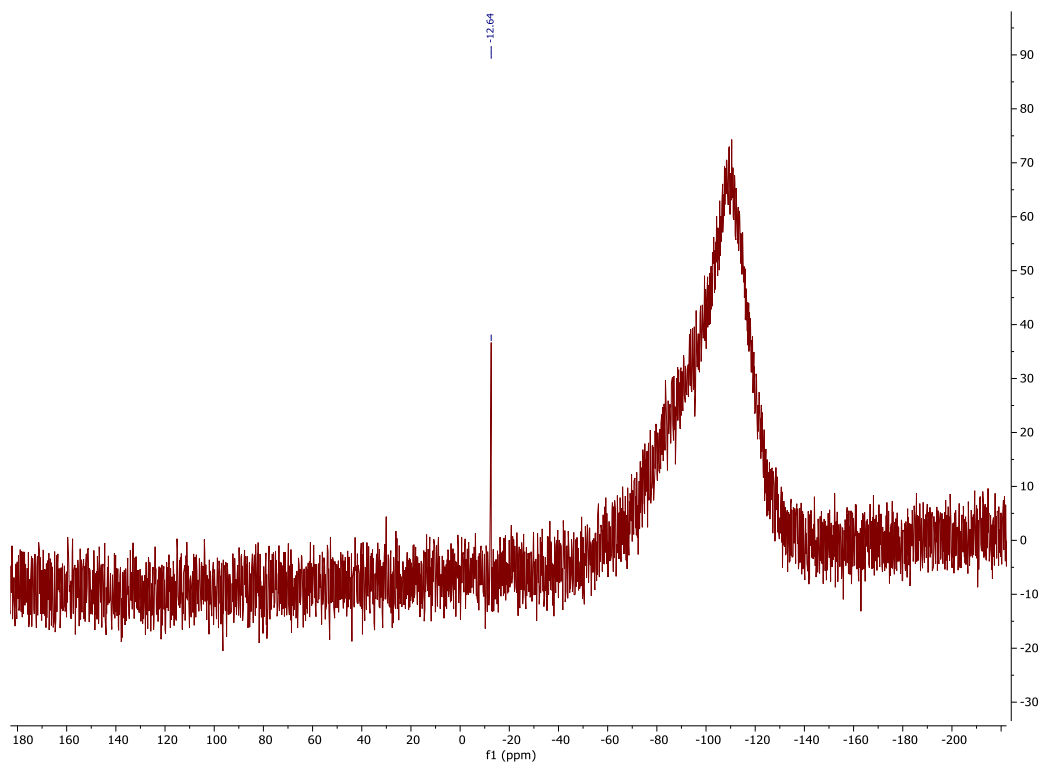


Figure S93: ^{29}Si NMR spectrum of tris(4-bromophenyl)silanol (**40**).

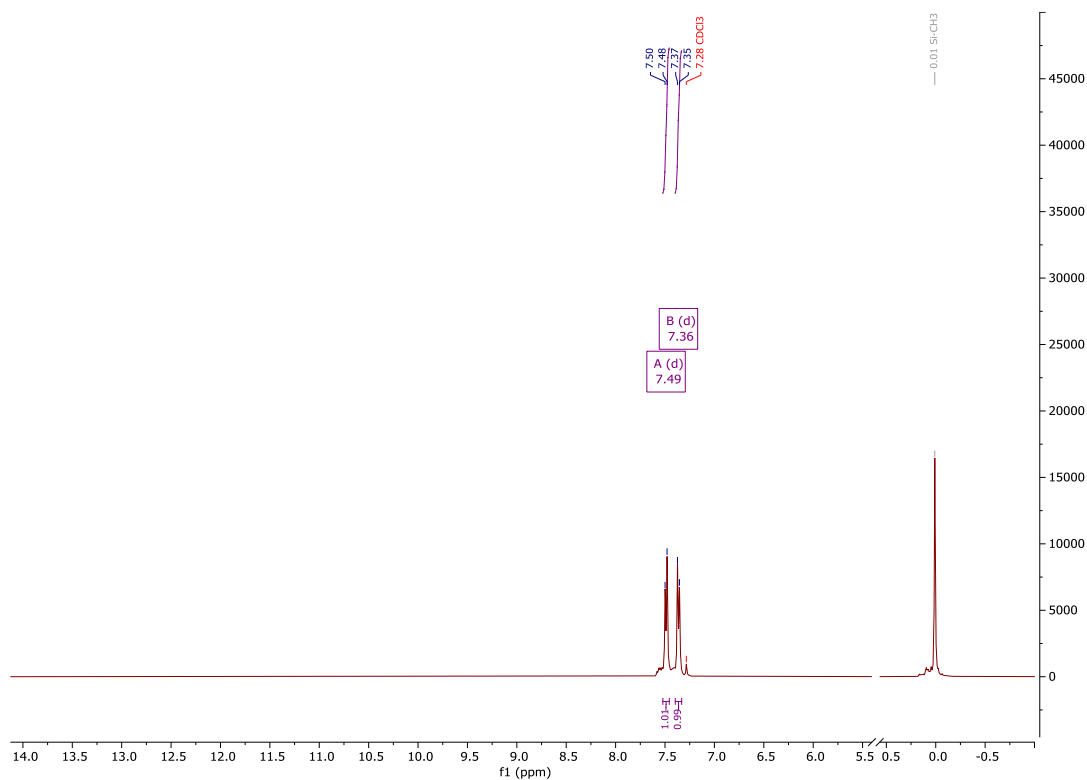


Figure S94: ^1H NMR spectrum of 1,1,1,7,7,7-hexakis(4-bromophenyl)-3,3,5,5-tetramethyltetrasiloxane (**41**).

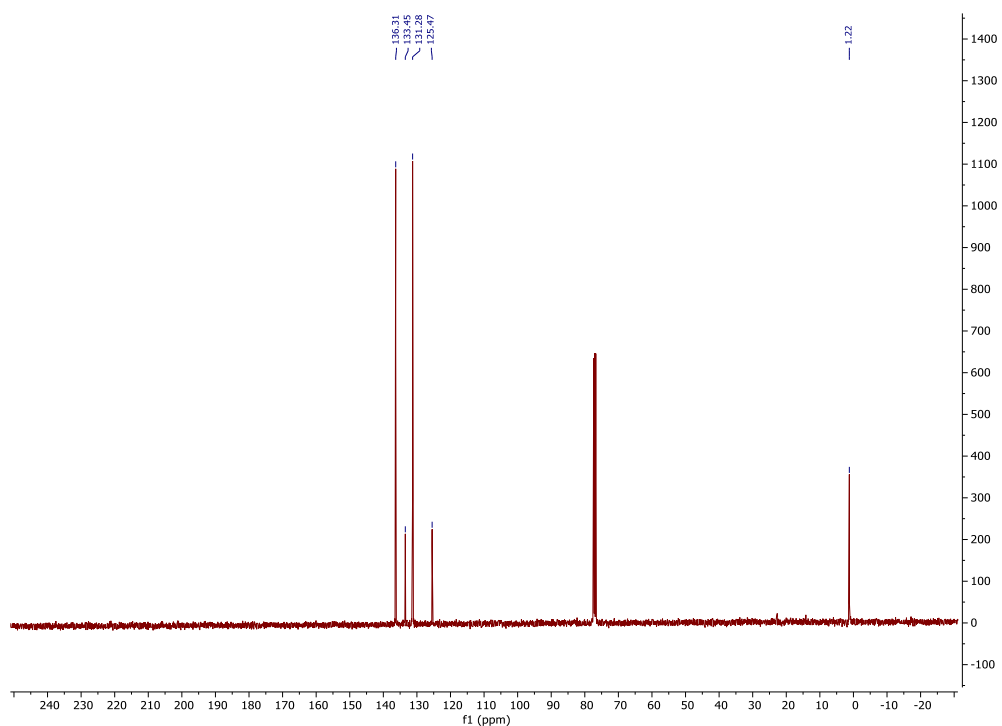


Figure S95: ^{13}C NMR spectrum of 1,1,1,7,7,7-hexakis(4-bromophenyl)-3,3,5,5-tetramethyltetrasiloxane (**41**).

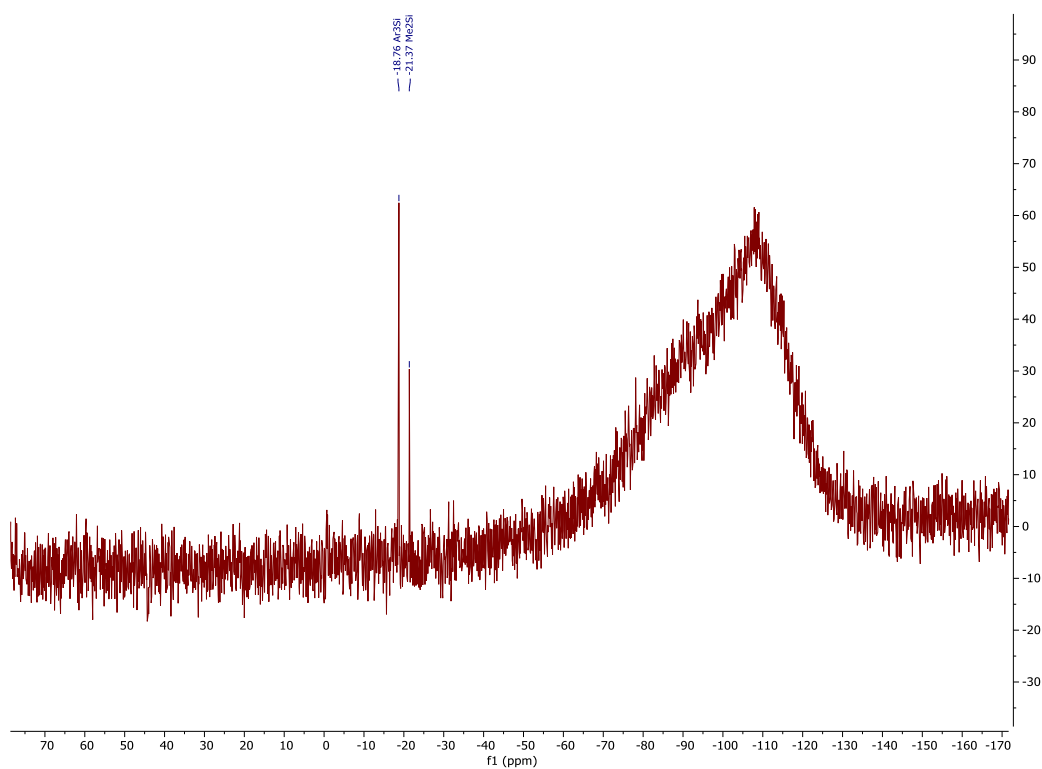


Figure S96: ^{29}Si NMR spectrum of 1,1,1,7,7,7-hexakis(4-bromophenyl)-3,3,5,5-tetramethyltetrasiloxane (**41**).

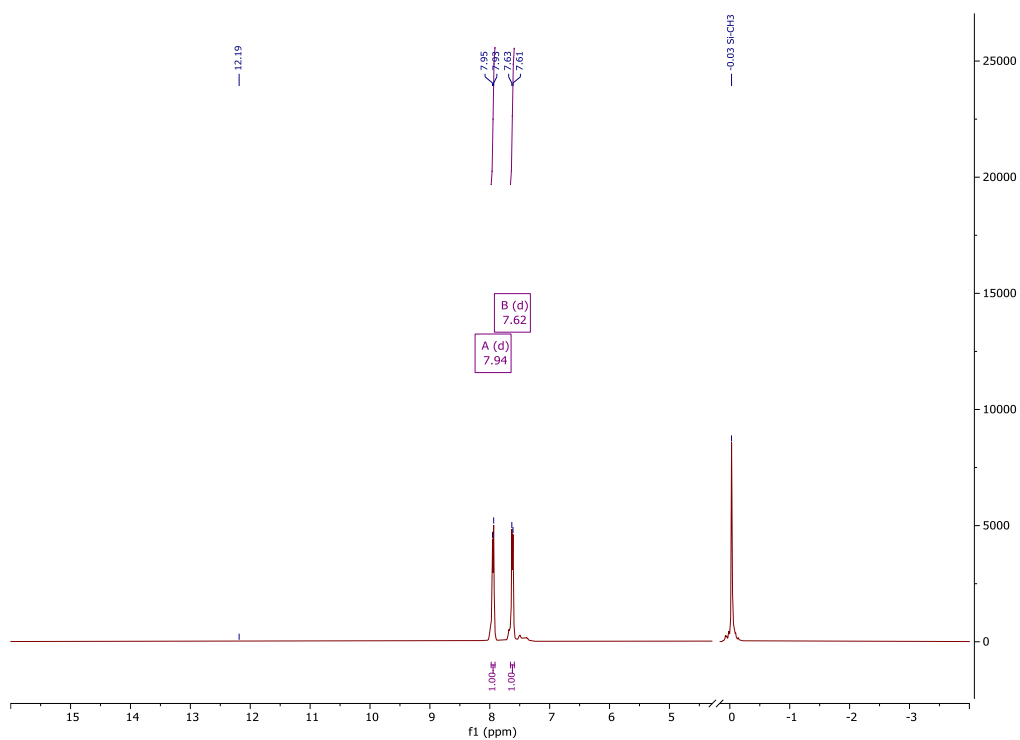


Figure S97: ¹H spectrum of 1,1,1,7,7,7-hexakis(4-carboxyphenyl)-3,3,5,5-tetramethyltetrasiloxane (L10-H₆).

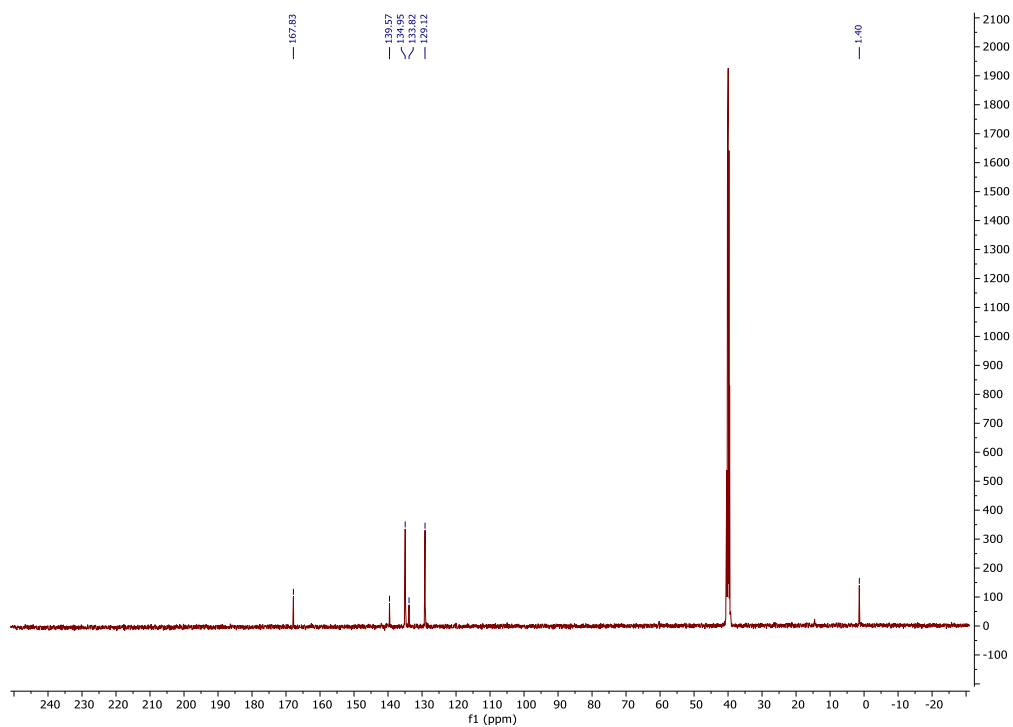


Figure S98: ¹³C spectrum of 1,1,1,7,7,7-hexakis(4-carboxyphenyl)-3,3,5,5-tetramethyltetrasiloxane (L10-H₆).

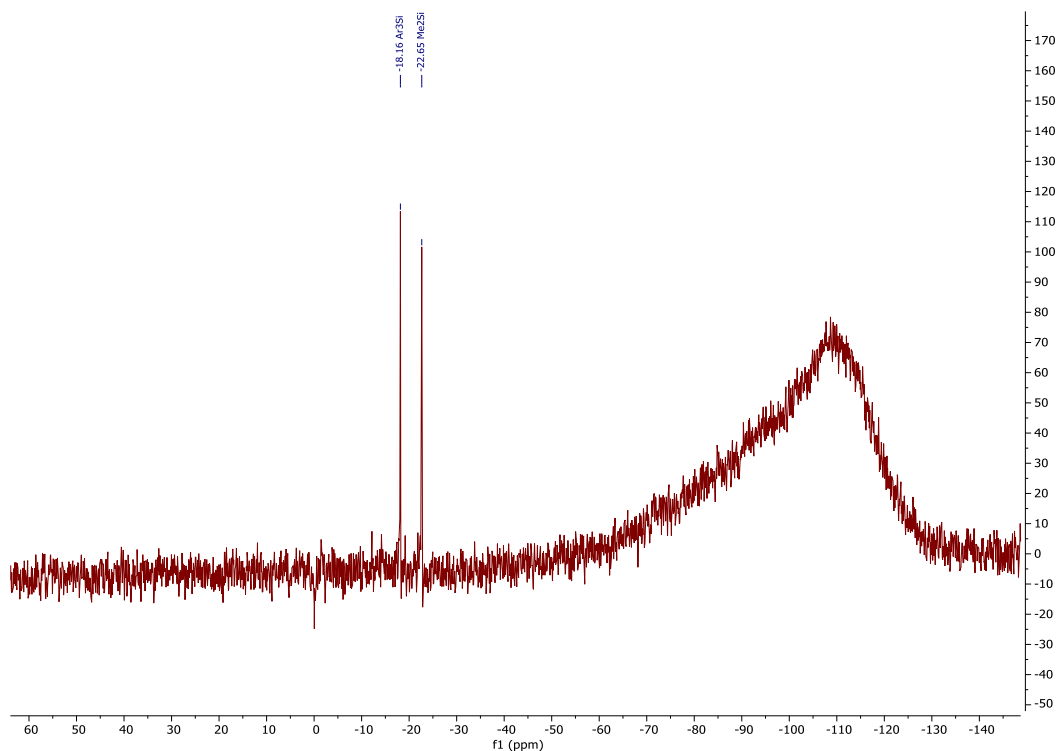


Figure S99: ^{29}Si spectrum of 1,1,1,7,7,7-hexakis(4-carboxyphenyl)-3,3,5,5-tetramethyltetrasiloxane (**L10-H₆**).

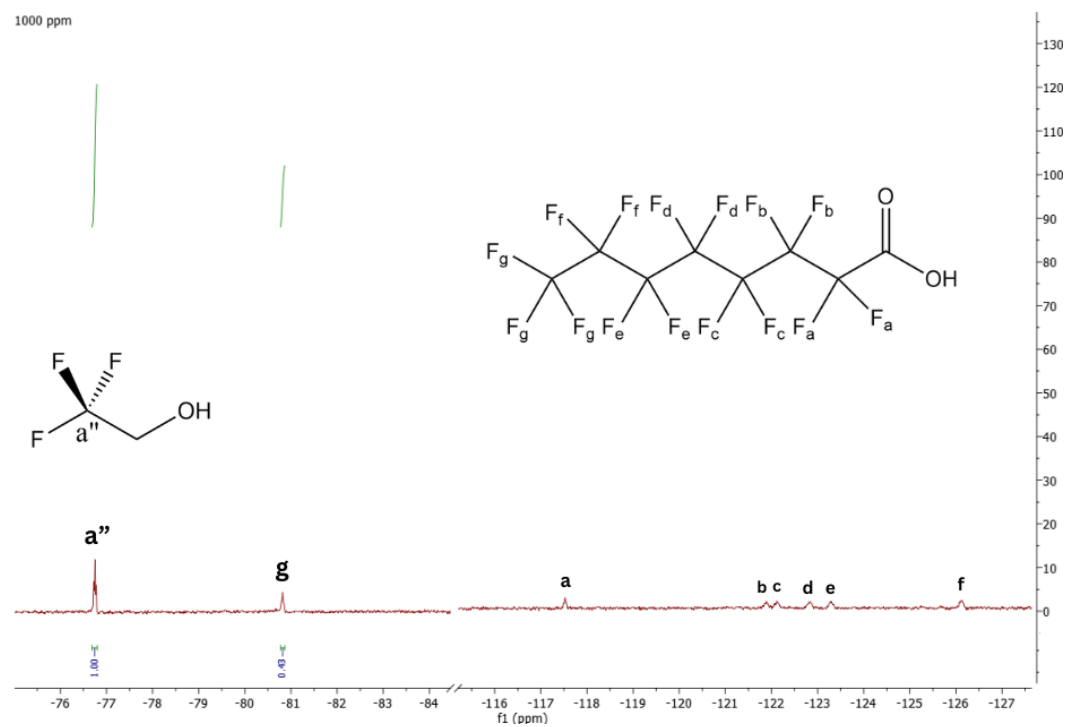


Figure S100: ^{19}F NMR Spectrum of the filtrate after immersing **L1-Fe-Cl** in 1000 ppm PFOA solution for 3 days. Noted: 4-Trifluoroethanol was used as an internal standard.

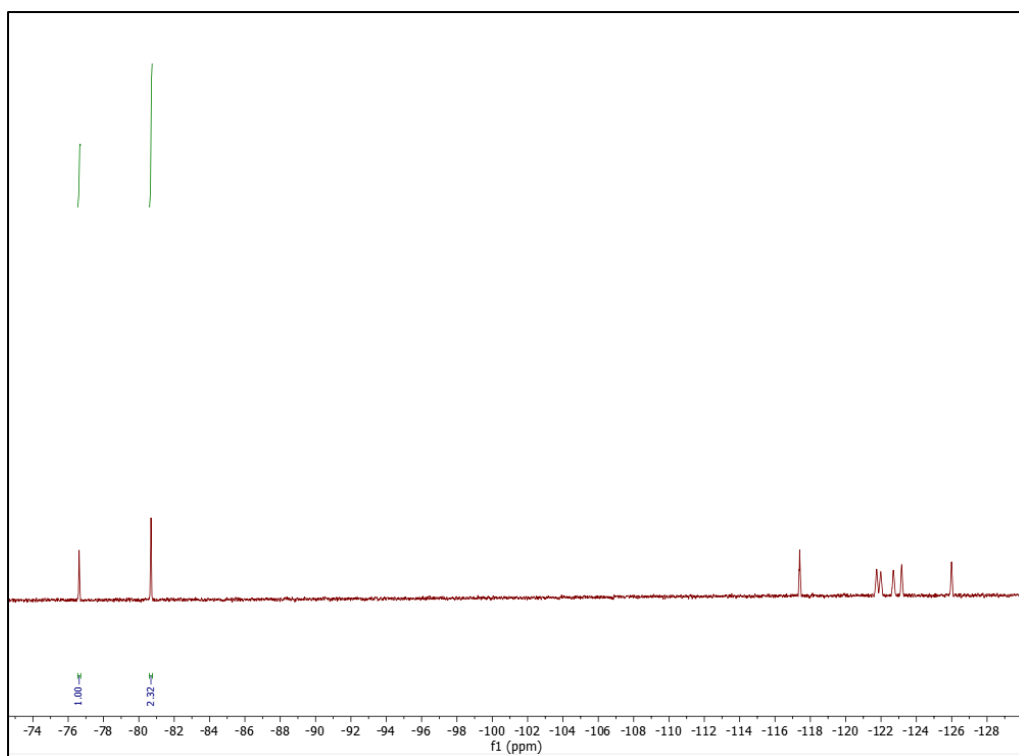


Figure S101: ^{19}F NMR Spectrum of the filtrate after immersing **L1-Fe-Cl** in 3000 ppm PFOA solution for 3 days. Noted: 4-Trifluoroethanol was used as an internal standard.

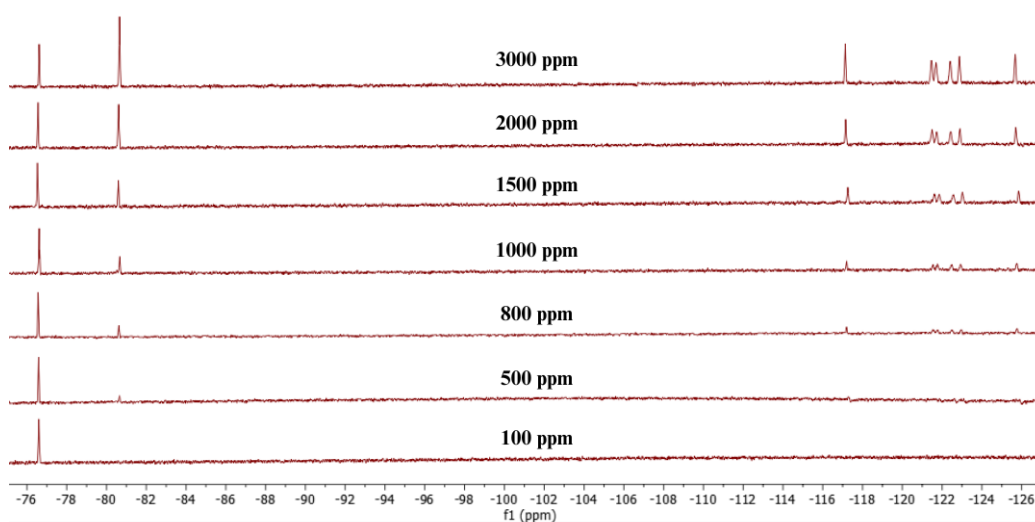


Figure S102: ^{19}F NMR Spectra of the filtrate after immersing **L1-Fe-Cl** in different PFOA solution with concentrations in the range of 100-3000 ppm for 3 days. Note: 4-Trifluoroethanol was used as an internal standard.

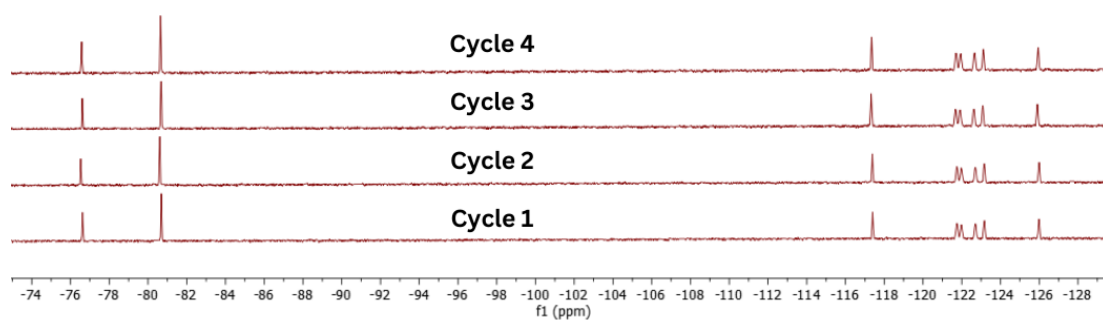


Figure S103: ^{19}F NMR spectra of the filtrate after five PFOA adsorption–desorption cycles on **L1-Fe-Cl**. Noted: 4-Trifluoroethanol was used as an internal standard.

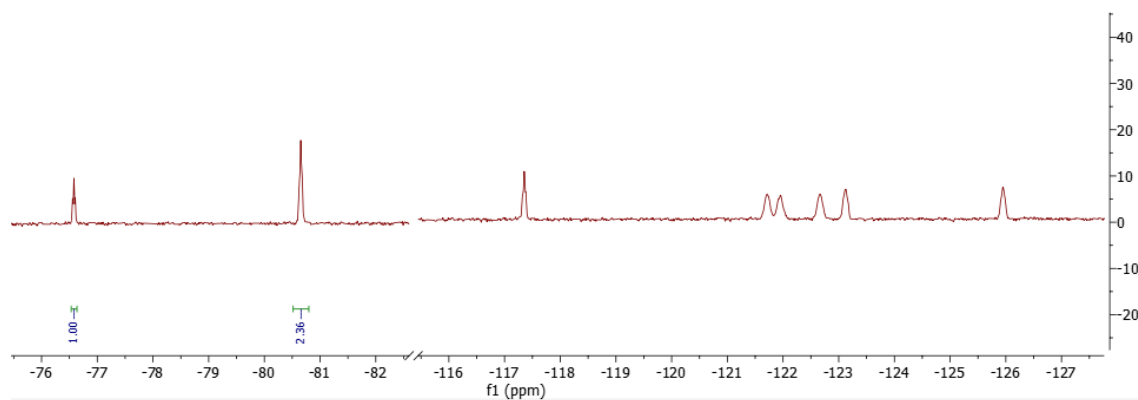
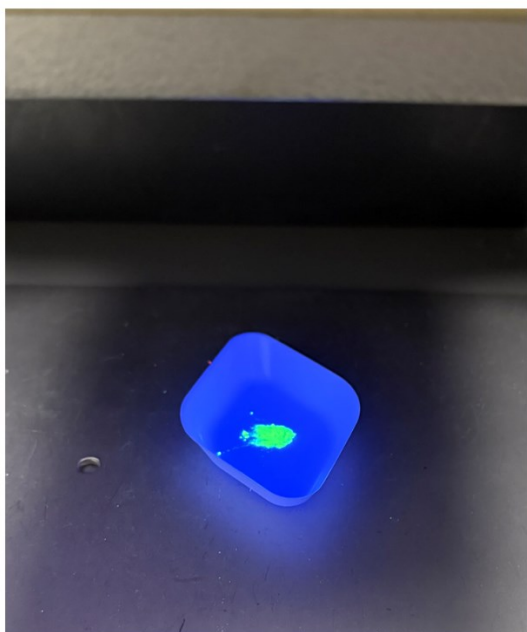


Figure S104: ^{19}F NMR spectra of the filtrate after the fourth PFOA adsorption–desorption cycle on **L1-Fe-Cl**.

L1-Tb and L1-Eu under UV Light

a



b

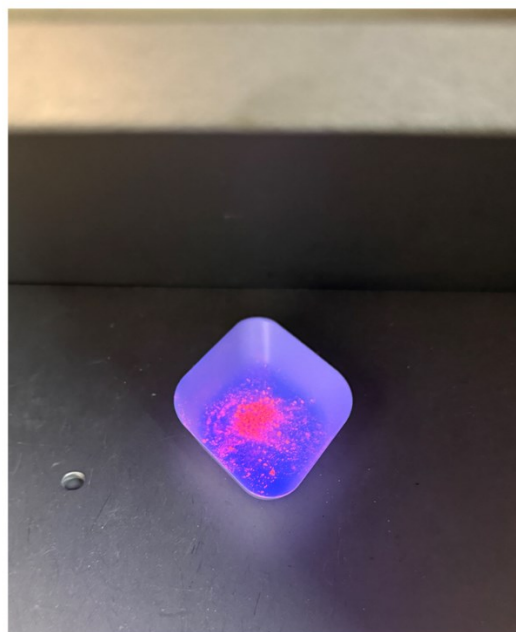


Figure S105. Images of bulk samples of (a) **L1-Tb** and (b) **L1-Eu** under UV light ($\lambda = 254$ nm).

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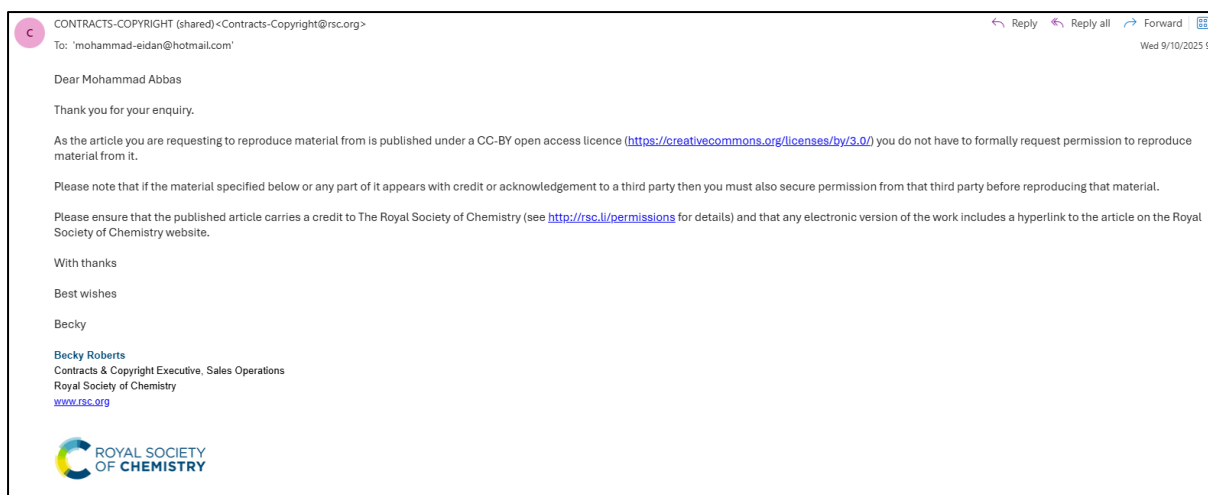
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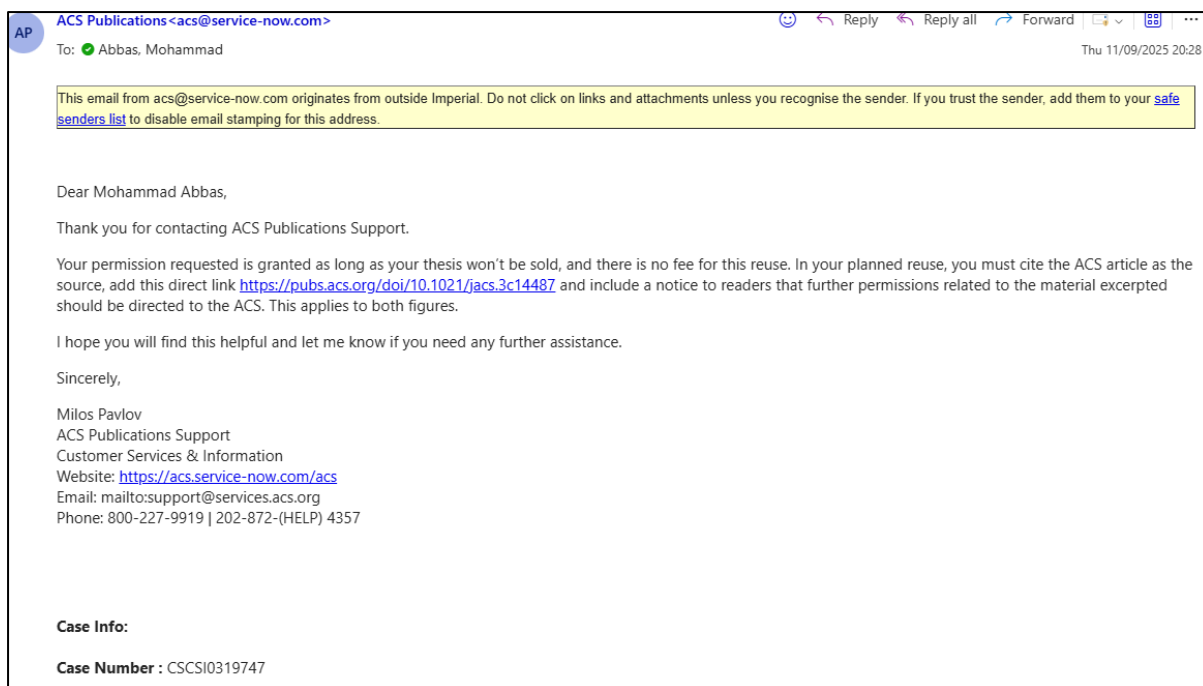
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