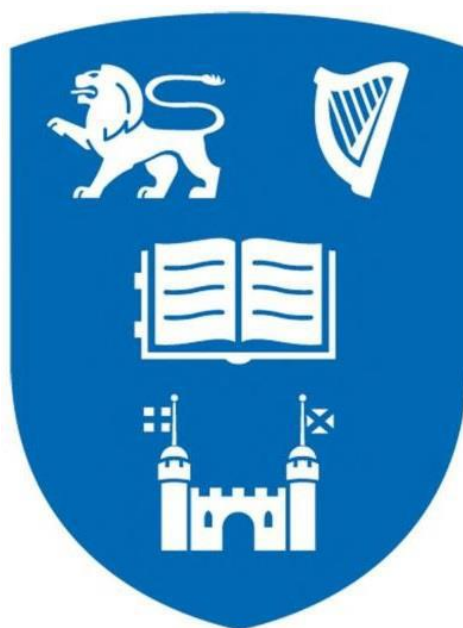


Synthetic Approaches towards Photoactive Metal-Organic Frameworks



*A thesis submitted to the University of Dublin for the degree of
Doctor of Philosophy*

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2021*

Declaration

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Summary

Metal-organic frameworks (MOFs) are a class of hybrid inorganic-organic materials. They are composed of metal-containing units linked by organic linkers through strong bonds, forming high dimensional frameworks. MOFs are exciting materials for their designability and exceptional porosity, leading to a wide range of potential industrial applications. In particular, applications related to light driven transformations and energy technologies as photocatalytic conversions and fuel cells have made them objects of extensive academic study. The tunability of MOFs towards these potential applications is guided by an approach known as reticular synthesis. The approach emphasises the judicious assembling of rigid molecular building blocks into predetermined networks.

The research outlined in this thesis focuses on the synthesis and characterisation of novel coordination polymers and MOFs with functionalities that can be exploited in light driven chemical transformations and related applications. The first chapter introduces the reader to the subject area of MOFs. It comprises the foundation for the design and synthesis of representative frameworks reported in the literature as well as an overview of potential applications.

Chapter two details the synthesis of a multidentate ligand 4'-(1Himidazo[4,5-f][1,10]phenanthroline-2-yl)-[1,1'-biphenyl]-4-carboxylic acid (HNCP₂) containing N-donors and O-donors from the phenanthroline and a carboxylic acid moieties respectively. The synthesis and structural characterisation of a series of coordination polymers based on various M^{II} metal ions are also described. The work presented on this chapter aimed to understand the impact of synthetic conditions (specifically the use of modulators) on the crystallisation process of coordination polymers derived from phenanthroline based ligands and M^{II} metal ions.

In chapter three, a photoactive, hetero-metallic Co^{II}/Ru^{II}-based MOF with a channel aperture of *ca.* 21 Å, is reported as **Photo-MOF**. The MOF was crystallised from Co^{II} salt and a phenanthroline-based tritopic metallo-ligand [Ru(HNCP)₃](PF₆)₂ (named **H₃L^{Ru}**) in the presence of a modulator. The photophysical properties of the MOF are derived from the Ru^{II} nodes giving rise to emission centred at *ca.* 620 nm and relatively long triplet ³MLCT lifetimes. In addition to the optical attributes, the 1H-imidazo [4,5-f][1,10]-phenanthroline ligand imparts structural functionality to the MOF which is composed of alternating Co^{II}- and Ru^{II}-based nodes. The framework maintains its integrity upon removal of constitutional solvent and shows gas sorption behaviour that is characteristic of mesoporous materials promoting high CO₂ sorption capacities and selectivity over N₂.

Electrochemical synthesis of the obtained material was used as an alternative synthetic pathway. The deposition method allowed us to functionalise a conductive substrate through an energy-efficient process in reduced reaction time. The characterisation of the obtained thin film confirms the identity of the film as microporous layers of **Photo-MOF**, which is corroborated by structural characterisation as well as photophysical and imaging studies.

Chapter four contains the optimised synthetic pathway of a novel organic ligand 5-((4-([2,2':6',2''-terpyridin]-4'-yl)phenyl)ethynyl)isophthalic acid (H_2TpyPEI) and a ditopic Ru^{II} metallo-ligand $\text{H}_2\text{L}^{\text{Ru}}$ crystallographically identified as $[\text{Ru}(\text{H}_2\text{TpyPEI})\text{Tpy}](\text{PF}_6)_2$. The metallo-ligand comprises a $[\text{Ru}(\text{tpy})_2]^{2+}$ moiety that has been reported as an efficient photosensitiser used in light-driven, hydrogen evolution reaction. Photophysical studies performed on metallo-ligand reveal relatively intense absorption in the visible region. $\text{H}_2\text{L}^{\text{Ru}}$ was employed in the synthesis of a 2D heterometallic $\text{Mn}^{\text{II}}/\text{Ru}^{\text{II}}$ -MOF, which is comprised of $\{[\text{Ru}(\text{tpy})_2]\}$ as light-harvesting unit and a $\{\text{Mn}_2(\text{COO})_4\}$ dinuclear cluster with unsaturated metal sites that combined can act as photocatalytic active platform.

Chapter five conveys a preliminary study on the impact of the use of structurally related organic ligands on the frameworks topology. Two carboxylate-based ligands: isophthalic acid (H_2IP) and an asymmetrically elongated, trifunctional polycarboxylate derivative (H_3CPEIP) were used in the synthesis of two Co^{II} -MOFs **5.1** and **5.2** respectively. The structures crystallise at corresponding synthetic conditions and contain an identical dinuclear Co^{II} cluster. **5.2** incorporates an additional mononuclear cluster that forms in presence of the third carboxylate functionality. As expected both structures exhibit 2D layered architectures with unblocked channels. **5.1** exhibits smaller triangular and larger hexagonal channels and a topology typically classified as a Kagomé lattice while **5.2** presents a novel topology which is characterised by the vertex symbol $(4.6^2) \cdot (4^2.6^2.8^2)$.

Chapter six provides concluding remarks and offers an outline of possible future studies related to applications of the presented materials in photocatalysis.

Finally, chapter seven provides detailed experimental procedures and characterisation of all the compounds and intermediates described throughout the thesis.

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Abbreviations

BBC	4,4',4''-[Benzene-1,3,5-triyl-tris(benzene-4,1-diyl)]tribenzoate
BDC	1,4-Benzenedicarboxylic acid
H ₂ BDPB	1,4-Bis[(3,5-dimethyl)pyrazol-4-yl]-benzene
BET	Brunauer–Emmett–Teller
BTB	1,3,5-Tris(4-carboxyphenyl)benzene
BTC	1,3,5-Benzene tricarboxylate)
BTE	4,4',4''-(Benzene-1,3,5-triyl-tris(ethyne-2,1-diyl))tribenzoate
BTEI	5,5',5''- Benzene-1,3,5-triyltris(1-ethynyl-2-isophthalate)
H ₃ BTT	1,3,5-benzenetristetrazol-5-yl
BPDC	Biphenyl-4,4'-dicarboxylate
BPY	2,2'-Bipyridine
CSD	Cambridge Structural Database
CV	Cyclic voltammetry
DCM	Dichloromethane
DCBPY	4,4'-Dicarboxy-2,2'-bipyridine
DEF	N,N-Diethylformamide
DFT	Density functional theory
DMF	Dimethylformamide
DOBDC	2,5-Dioxido-1,4-benzenedicarboxylate
DOT	Dioxidoterephthalate
DTOA	Dithiooxamidato
Et ₃ N	Triethylamine
FBA	Fluorobenzoic acid

FLIM	Fluorescence-lifetime imaging microscopy
FTIR	Fourier-transform infrared
FTO	Fluorinated tin oxide
H ₄ BPTC	3,3',4,4'-Benzophenone tetracarboxylate acid
HKUST	Hong Kong University of Science and Technology
H ₂ IP	Isophthalic acid
H ₃ CPEIP	1.1.2.5-(4-Carboxyphenyl) ethynyl) isophthalic acid
H ₂ QPTB	3,4-Dicarboxyl-(30,40-dicarboxylazophenyl)
IR	Infrared
J	Coupling constant
L	Ligand
LC	Ligand centred
M	Multiplet
Meim	2-Methyl-1H-imidazole
Me ₂ TpyPEI	Dimethyl 5-((4-([2,2':6',2''-terpyridin]-4'-yl)phenyl)ethynyl)isophthalate
MeOH	Methanol
MLCT	Metal-to-ligand charge transfer
MOF	Metal-organic framework
MOP	Metal-organic polyhedra
MS	Mass spectrometry
NA	Numerical aperture
NMR	Nuclear magnetic resonance
m/z	Mass-to-charge ratio
PCN	Porous coordination networks

PL	Photoluminescence
Por	Porphyrin
Por-PP	Meso-tetrakis-(4-carboxybiphenyl)porphyrin
Por-PTP	Meso-tetrakis-(4-((phenyl)ethynyl)benzoate)porphyrin
ppm	parts per million
ppy	2-Phenylpyridine
PS	Photosensitiser
Py-XP	(Pyrene-1,3,6,8-tetrayl)tetrakis(2',5'-dimethyl[1,1'-biphenyl]-4-carboxylic acid)
PXRD	Powder X-ray diffraction
Qt	Quartet
RCSR	Reticular chemistry structure resource
s	Singlet
SBB	Secondary building block
SBU	Secondary building unit
SCXRD	Single Crystal X-ray Diffraction
SDCA	4,4'-stilbenedicarboxylate
t	Triplet
TATB	4,4',4''-s-Triazine-2,4,6-triyl-tribenzoic
TCPP	Tetrakis(4-carboxyphenyl)porphyrin
TFA	Trifluoroacetic acid
THT	Tetrahydrothiophene
TMA	Trimesic acid
TP	Tetramethylbutane-1,4-diammonium bis(4-amino benzoate)
TPDC	Terphenyl dicarboxylate

Tpy	Terpyridine
TRPL	Time-resolved photoluminescence
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TTPY	4'-Tolylterpyridyl
UV-Vis	Ultraviolet–visible
XRD	X-ray Diffraction

Chapter 1

Introduction

1. Introduction

1.1. Introduction to metal-organic frameworks

There has been a rapid increase in interest in the field of metal-organic frameworks (MOFs) since the early pioneering work of Robson and co-workers in the 1990s, when structural ideas for the design and construction of infinite frameworks resembling scaffolding were presented.² MOFs are coordination compounds which extend through repeating coordination entities in two or three dimensions combining inorganic and organic moieties through relatively strong bonds.³ The inorganic portion of these materials can be composed of single metal ions, coordination clusters, chains, layers or polyhedra, while oxygen and nitrogen atoms provide the most common donors within the organic linkers.⁴ These metal-organic materials can also be defined as extended porous structures with one extraordinary feature arising from the possibility of structural design and synthetic rationality. Tailoring of the size and environment of the pores is performed by selecting ligands that possess a pre-determined shape and particular functionality.⁵

In contrast, porous molecular materials are composed of discrete organic or metal-organic molecules where the molecular subunits are not connected by strong intermolecular bonds, such as coordination bonds.⁶ Metal-organic polyhedra (MOPs) or coordination cages are also discrete molecular coordination assemblies having well-defined cage-like structures and confined cavities, and may provide a class of porous molecular materials.⁷ Unlike MOFs, MOPs are not infinite networks. They are discrete, molecular metal-organic molecular entities that are generally soluble in homogeneous media, depending on the chemical nature of the molecular entity.⁸ A hierarchy scheme that is in-line with IUPAC-recommended definitions and that defines MOFs as a class of compound distinguishable from 1D coordination polymers is shown in Fig. 1.1.⁹

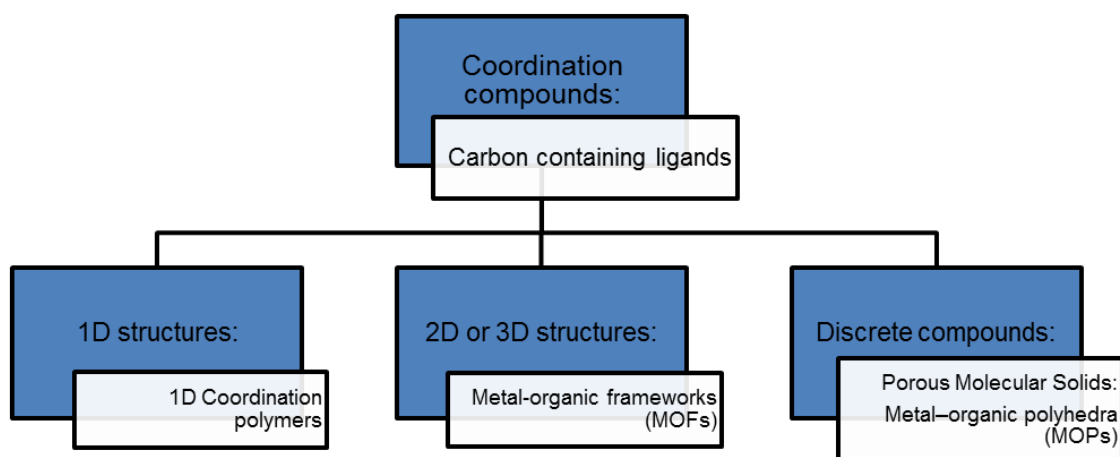


Figure 1.1: Schematic hierarchy of coordination polymers, adapted from ref. 9.

One major advantage of MOFs is the possibility to control connectivity, structure and pore dimension by varying the nature of ligands and metal ions. Functionalisation of the pores can also be achieved by choosing preferred coordination geometries of the metal ions and by the incorporation of ligands with the desired functionalities. Additionally, the well-organised environment and the crystalline nature of these materials, provide useful platforms to apply concepts of supramolecular chemistry. These concepts are used in the assembling of molecules into structures that are suitable for applications in gas storage, separation and purification, heterogeneous catalysis, sensing and photochemical applications.¹⁰⁻¹⁵

1.2. Design and synthesis of metal-organic frameworks

1.2.1. The network approach

For a rational synthetic approach towards tailored solids, it is convenient to reduce intricate structures into simple networks. For that, the visualisation of structures as nets, is of great importance allowing a simplified and more facile understanding of the way the components in a MOF arrange themselves. Additionally, this understanding provides a way of controlling the arrangement of the components and thus, potentially influencing the properties of the final material.

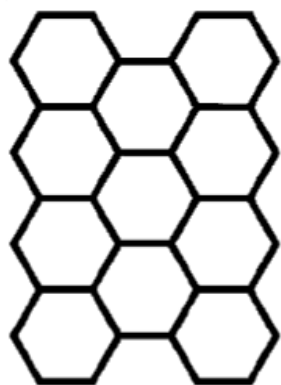


Figure 1.2: Representation of simplified 2D (6,3) net.¹

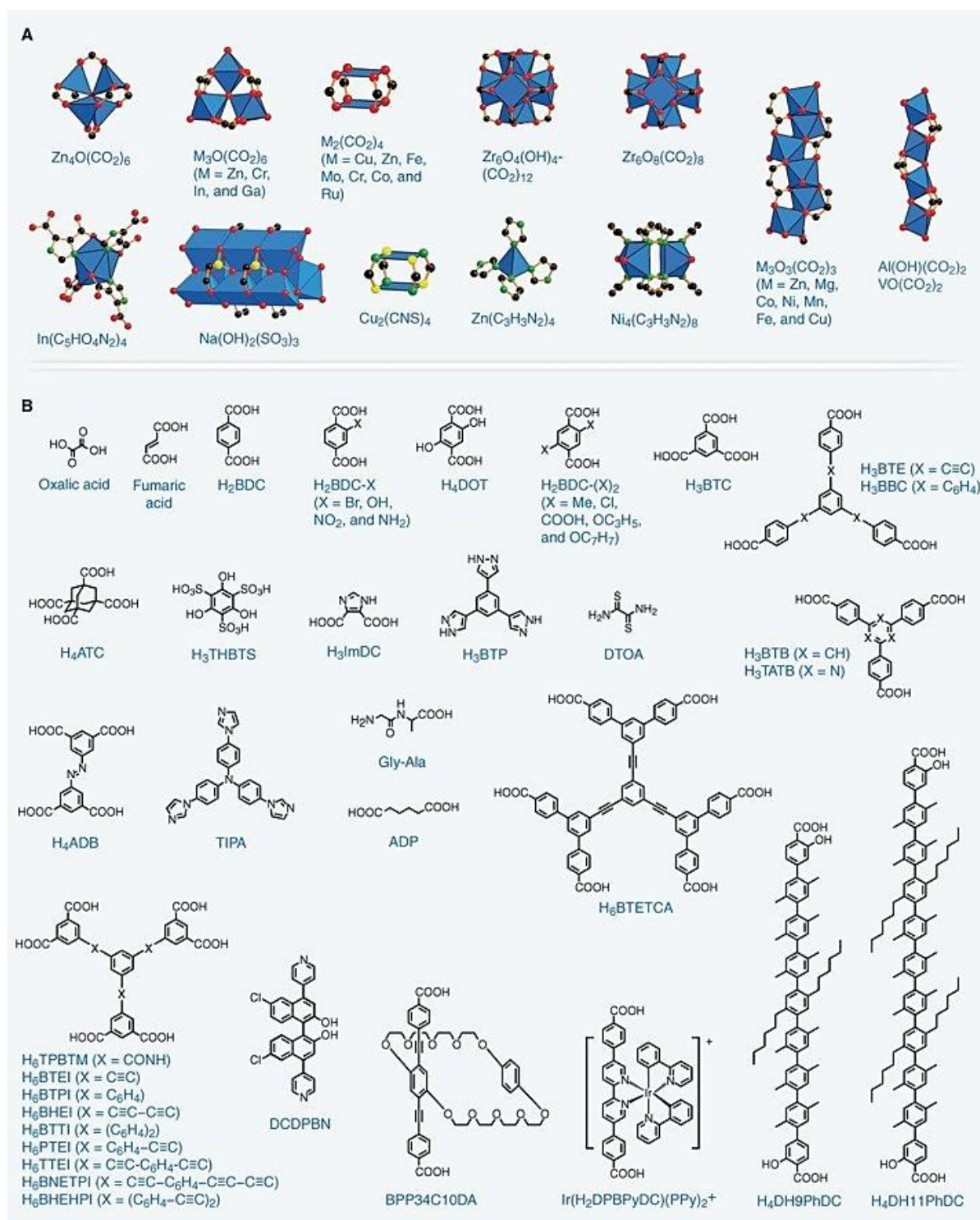
The net approach was initially developed by Wells using purely inorganic compounds.¹⁶ According to his concept, a net is defined as an infinity array of nodes, whereby each node is connected to three or more other nodes by linkers. Linkers are by definition 2-connecting and nodes are at least 3-connecting.¹

The connectivity (topology) of a net can be represented through the general (n,p) notation. In that representation n is the number of nodes in the smallest closed circuits in the net and p is the number of connections to other nodes that radiate from any centre (Fig.1.2).¹

Later Robson applied this concept to coordination polymers and related extended structures.¹⁷ In his analysis using the net approach, a crystal structure of an extended metal-organic material could be reduced to nodes and their connectivity forming a network. Nodes can be metal ions or coordination clusters and organic ligands which are nowadays often described as secondary building units (SBUs). SBUs impart directionality^{5, 13} and can be further defined as rigid molecular building blocks that maintain structural integrity upon the formation of a framework.^{18, 19}

The *in situ* formation of a given SBU provides a viable approach for the design of extended structures through reticular synthesis, a process that can be described as the judicious assembling of rigid molecular building blocks into predetermined networks.⁵ The targeted network can be deconstructed into nodes and links as the examples shown

in Figure 1.3. Often the topologies of the resulting structures relate to those of purely inorganic default structures like **pcu**, **qom**, **tbo**, **ntt** and **etb** nets.



Yaghi and co-workers were pioneers in demonstrating the principles of designing rigid frameworks based on predetermined SBUs.²¹ MOF-5 was synthesised in 1999 and contains a carboxylate-stabilised, tetranuclear $\{\text{Zn}_4\text{O}(\text{COO})_6\}$ SBU composed of four vertex-sharing $\{\text{ZnO}_4\}$ tetrahedra (Fig. 1.4A). The carboxylate carbon atoms of the six stabilising carboxylate moieties define this unit as an SBU with octahedral topology that assembles in the presence linear terephthalate linkers into a simple cubic net (Fig. 1.4B).

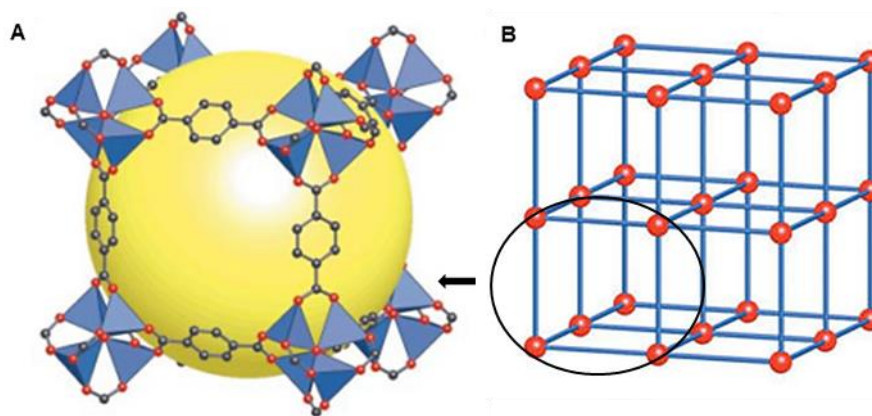


Figure 1.4: Structure of MOF-5, the yellow sphere represents the volume of the pore (A); Representation of the topology of the structure as a simple cubic net (B); Colour code: O, red; C grey; Metal-oxygen derived polyhedra, blue.⁵

Later, isorecticular expansion was further used as an important design tool to synthesise series of MOFs with increasing pore sizes and added functionalities that maintain the same topology.²² The expansion is achieved through use of extended versions of a parent organic linkers. The concept was firstly exemplified by Yaghi and co-workers resulting in the synthesis of $\{\text{Zn}_4\text{O}(\text{CO}_2)_6\}$ -based MOFs. In addition to isorecticular MOF-5 analogues, Yaghi and co-workers demonstrated the principle using Zn-based MOFs with **qom** topology that are stabilised by various extended tritopic ligands [$\text{Zn}_4\text{O}(\text{BTB})_2$], MOF-177; [$\text{Zn}_4\text{O}(\text{BTE})_2$], MOF-180 and [$\text{Zn}_4\text{O}(\text{BBC})_2$], MOF-200 (Fig. 1.5A).^{20, 23} A second classic example of a representative SBU is the well-known dinuclear ‘paddlewheel’ unit which defines a square planar inorganic secondary building unit. It assembles in the presence of tri-functional, triangular trimesate ligands into a MOF, [$\text{Cu}_3(\text{BTC})_2$] with **tbo** topology and which is generally denoted as HKUST-1²⁴. The most pronounced isorecticular expansion of HKUST-1 was achieved with BBC (4,4',4''-[benzene-1,3,5-triyl-tris(benzene-4,1-diyl)]tribenzoate) generating [$\text{Cu}_3(\text{BBC})_2$], MOF-399²⁵ (Fig. 1.5B).

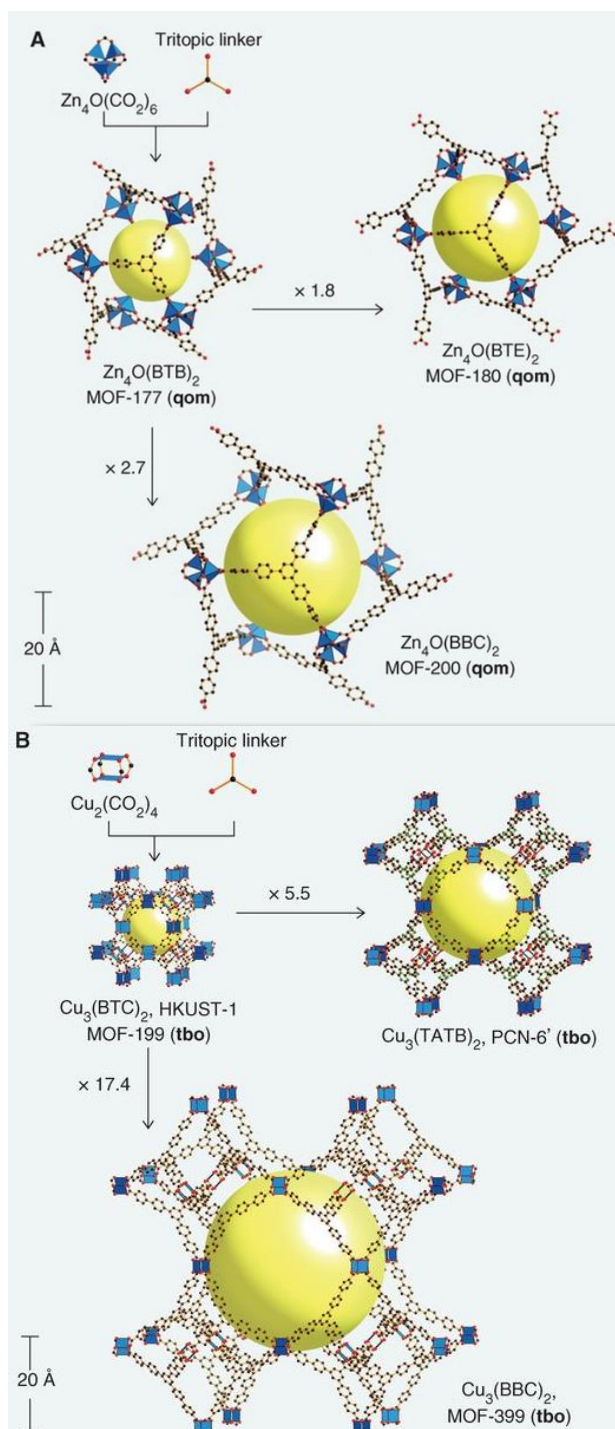


Figure 1.5: Selected examples highlighting the principle of isoreticular expansion for MOFs; The isoreticular expansion of archetypical MOFs resulting from discrete inorganic SBUs when combined with tritopic organic linkers to obtain frameworks with qom topology (A) and tbo-type (B) nets; Colour code: C, black; O, red; Metal-electron donor derived polyhedra, blue; Numbers above each arrow represent the degree of volume expansion from the smallest framework²⁰

Zhou and co-workers also constructed an isorecticular series of such dicopper, paddlewheel-based MOFs, abbreviated as PCN-61, PCN-66 and PCN-68^{26, 27} whereby a systematic ligand extension results in enlarged surface areas. However, the activation process which involves the removal of constitutional solvent molecules upon heating and application of negative pressures, caused these highly augmented structures to collapse due to prevailing capillary forces upon desolvation.²⁸ Zhou *et al.* further reported a strategy for stabilising MOFs with high surface areas by introducing mesocavities with micro-windows; the resulting materials are more robust and retain crystallinity after the removal of guest molecules.²⁶ The surface areas were increased by ligand extension as a result of the increased size of the mesocavities.

The use of well-defined reaction conditions was primordial for the in situ formation of cationic SBUs with specific geometries and consequently for the formation of pre-determined extended structures. Differently, anionic SBUs (organic linkers) are synthesised prior to the synthesis of the MOFs through the use of sophisticated synthetic methods.²⁹ The potential for variation of organic linkers and inorganic SBUs allowed for the preparation of thousands of new extended MOF-type compounds, resulting in an exponential increase of structurally characterised compounds that were reported in the past decades (Fig. 1.6).

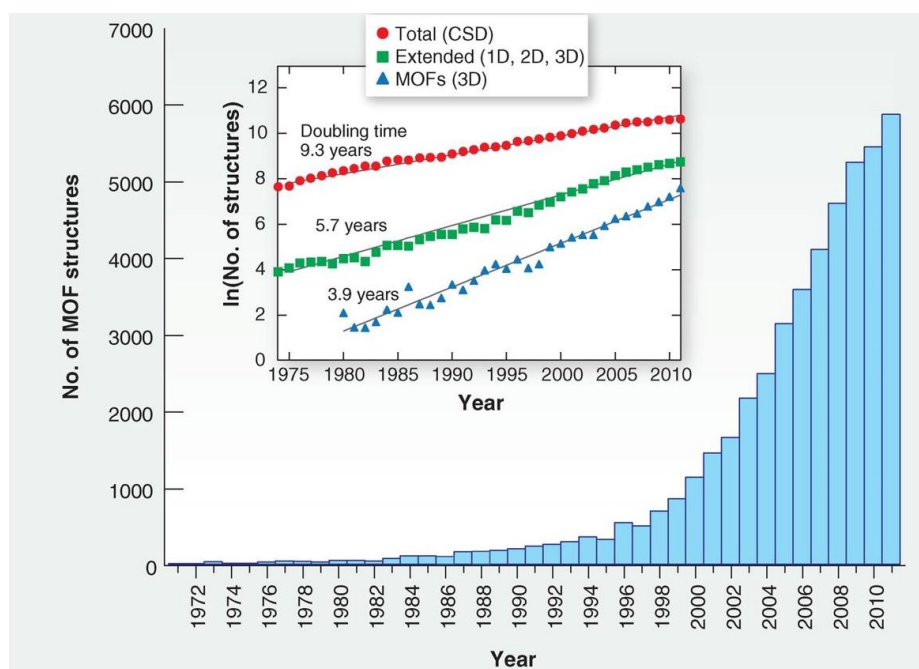


Figure 1.6: Number MOFs reported in the Cambridge Structural Database (CSD) from 1971 to 2011. Inset: Similar increasing trend in the number of all structure types during the same period.²⁰

In recent years Zr-based MOFs were extensively investigated due to their hydrolytic stability. The $\{Zr_6O_4(OH)_4(CO_2)_{12}\}$ unit was first reported in UiO-66, UiO-67 and UiO-68 as a 12-connected SBU that revealed highest connectivity found in a MOF. The inorganic ‘brick’ was described as the key to the exceptional stability towards solvents and mechanical pressure of such Zr-MOFs. The series of related isorecticular structures was expanded by increasing the length of the linkers. BDC, BPDC and TPDC were used as linkers for UiO-66, UiO-67 and UiO-68, respectively as shown in Figure 1.7.³⁰

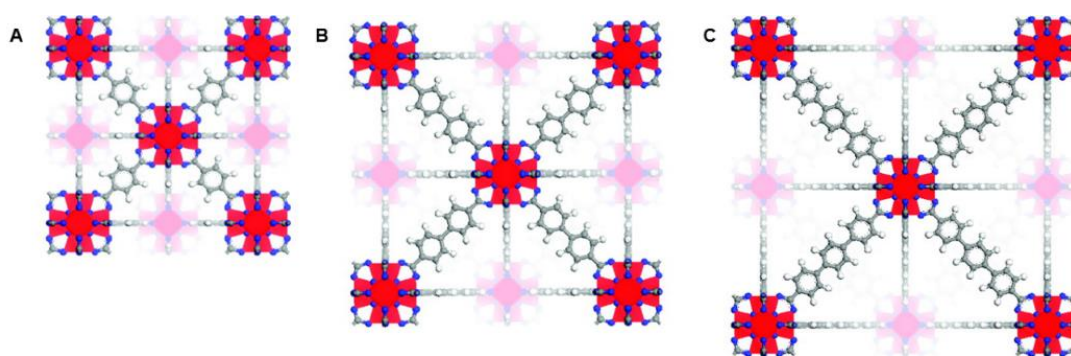


Figure 1.7: Isorecticular Zr-MOFs containing extended organic carboxylates; BDC, UiO-66, (A), BPDC, UiO-67 (B) and TPDC, UiO-68 (C) as linkers; Colour code: Zr, red; O, blue; C, grey; H, white.³⁰

1.2.2. Synthetic methods

The translation of MOFs synthesis into potential industrial applications relies on the efficiency of manufacturing these materials in bulk. In recent years, several approaches for addressing prospective scale-up methods have been considered. Modern approaches include electrochemical, microwave and mechanochemical syntheses. Figure 1.8 shows the timeline of synthetic processes for MOFs and related materials established in the last twenty years.³¹

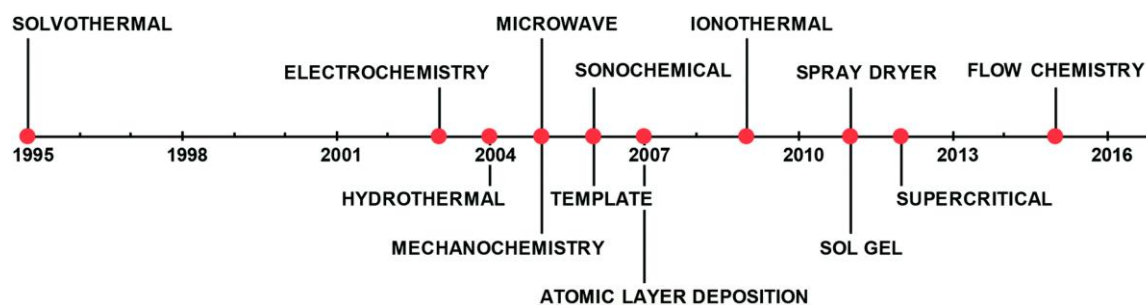


Figure 1.8: A timeline of synthetic approaches for the synthesis of MOFs.³¹

However, it must be noted that the scale-up of MOF production is challenging as the synthesis of individual MOF families requires specific conditions due to the variety of composition and functionality of the materials. This section, we will focus on selected efficient conventional and contemporary synthetic processes to MOFs that can lead to reduced reaction times. Thus, aspects of solvothermal, electrochemical, microwave and mechanochemical synthesis will be described.

1.3. Solvothermal synthesis

Solvothermal synthesis of crystalline microporous MOFs was initially applied Yaghi and co-workers in 1995 to prepare archetype MOFs³² and it is currently the most used synthetic technique to MOFs in research laboratories around the world.³¹ A solvothermal reaction takes place in a closed vessel above the boiling point of the chosen solvent and under autogenous pressure.^{33, 34} The high reaction temperatures used in solvothermal conditions have a strong influence on crystallinity as well as the morphology of the crystals. Additionally, higher temperatures are crucial to attain suitable reaction rates when kinetically inert reactants are used.³⁵

1.3.1. Choice of solvent in solvothermal synthesis

The use of solvents that have high boiling points is preferable, as those are relatively stable to the high temperatures where partially or completely soluble, otherwise insoluble, reagents can form extended networks.³⁶ Dialkylamides, such as DMF and DEF are especially desirable due their polarity and their ability to impart stabilisation effects to reagents and intermediates in the reaction mixture. Those solvents are also known for their partial hydrolytic decomposing upon heating as highlighted by Equation 1.2.2.1.³⁷



As a result of the high temperatures applied in solvothermal synthesis, decomposition products, such as dialkylammonium were reported to influence the self-assembly process of MOFs and it has been postulated that those products template the formation of the networks. The amide solvent decomposition often facilitates the formation of charged network structures whereby ammonium ions can act as counterions of the compounds.^{38, 39} Nevertheless, although dialkylamides have shown desirable properties for the synthesis of MOFs, the decomposition process also brings the risk of synthesising undesired products and mixtures which often contain simple metal formats.

1.3.2. Up-scaling process in solvothermal synthesis

Despite the high academic interest in MOFs that reveal properties that can lead to promising applications, the scaling-up process remains a challenge and hence, very few materials were produced in bulk to explore industrial applications.^{11, 31, 40} The main obstacle is due to the fact that crystallisation under solvothermal conditions relies on the nucleation processes that occur at the reactor vessel surface. When up-scaling the reaction, and consequently the reactor vessel, the surface to volume ratio decreases, reducing the efficiency of the synthetic method. Additional problems result from the difficulty of obtaining phase-pure products and long reaction times.³³

1.4. Electrochemical deposition on conductive surfaces

MOF thin films have been recently synthesised utilising the preparation strategies developed for thin films of zeolites or other porous materials.⁴¹ There are two main synthetic approaches for the preparation of MOF thin films: *in-situ* and *ex-situ* deposition. Deposition processes involving self-assembly (solvothermal and electrochemical growth) are covered by the *in-situ* method. The *ex-situ* method requires the MOFs to be pre-synthesised and deposited.⁴² MOFs are obtained *via* a self-assembly process that can be explored to create thin films through layer deposition methods.⁴¹ Table 1.1 compiles an up-to-date list of MOFs synthesised through different deposition methods.⁴¹⁻⁴⁴

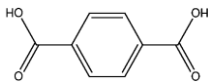
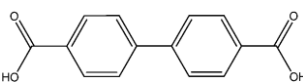
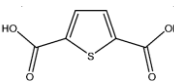
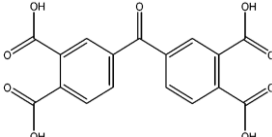
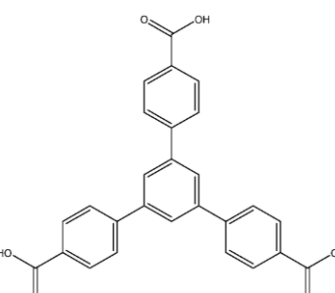
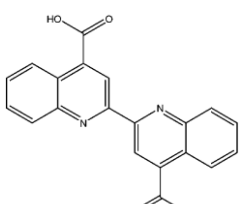
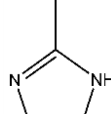
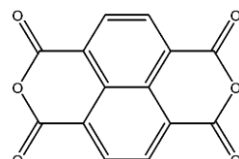
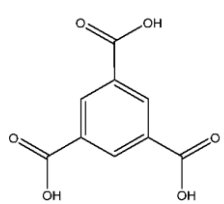
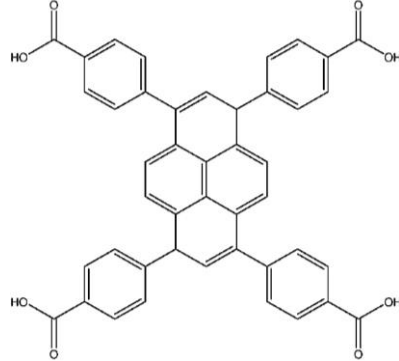
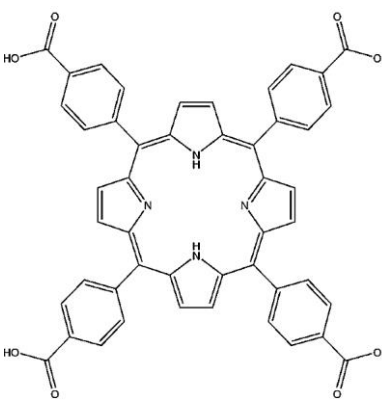
The *in situ* electrochemical approach represents a particularly interesting technique to deposit microporous layers on top of conductive substrates. The electro-synthetic process can be scaled up and was proved to be an efficient method for the industrial synthesis of MOFs.^{31, 45, 46} In contrast to conventional methods, as solvothermal, it reduces synthesis

time as well as allowing some control over the morphology of the material. It can be achieved either through the addition of metal salts to the solution, or through electrochemical delivery of metal ions through the oxidation of metal in a solution containing the ligand. MOF layers can then be formed in short time frames (30 minutes or less) by applying a voltage. The thickness of the film can be controlled by variation of solvent and concentration of the solution as well as the voltage and frequency of the applied current.^{41, 47} Most importantly, the cathodic electrodeposition generates accumulation of anions near the conductive surface causing ligand deprotonation. This method limits MOF formation to the electrode and allows a more controlled synthesis when compared to other methods.⁴⁸ Thin films of archetypical MOFs as HKUST-1, MOF-5 and ZIF-8 have been electrochemically synthesised and reproduced in different synthetic conditions. Morphology, photochemical and mechanical properties of these materials have been extensively investigated with prospective applications in photochemistry, sensing and as solar cells.^{42, 43, 49-51}

Table 1.1: Summary of recently reported MOF thin films and membranes. MOFs in bold letters have been obtained through electrochemical deposition.

MOF	Metal node	Linker*	References
HKUST-1	Cu	BTC	47, 49, 50, 52-57
UiO-66	Zr	BDC	52, 58, 59
UiO-67	Zr	BPDC	60, 61
NU-901	Zr	TBAPy	62
NU-1000	Zr	TBAPy	52, 63-65
MOF-525	Zr	TCPP	66, 67
MOF-5	Zn	BDC	48, 68-72
MOF-177	Zn	BTB	68
Zn-MOF	Zn	NDI	73
MIL-96	In	BTC	74
CPM-5	In	BTC	75
MIL-100	In	BTC	75
MIL-100	Fe	BTC	49
Li-doped MIL-100	Fe	BDC	76
MIL-100	Al	BTC	54
MIL-53	Al	BDC	54
MOF-3	Zn	NH ₂ -BDC	70
MOF-10	Zn	BPDC	70
ZIF-L	Zn	Hmim	77
ZIF-8	Zn	Hmim	54, 78, 79
Ru MOF	Ru	BTC	80
DA/L2-MOF	Zn	TCPP	81
Ir-Zn _e -MOF	Ir-Zn	DCBPY	82
Ln-MOF	Eu	BQDC	83
Ln-MOF	Eu	BPTC	43, 84
Ln-MOF	Eu	TDC	85
Ln-MOF	Gd, Tb	BTC	86
Ln-MOF	Eu–Tb	BTC	87
Ln-MOF	Tb	BTC	88

Table 1.2: Ligands and their names, cited from Table 1.1.

Abbreviation	H ₂ BDC	H ₂ BPDC	H ₂ TDC
Name	Benzene dicarboxylic acid	Biphenyl dicarboxylic acid	Thiophene-2,5-dicarboxylic acid
Structure			
Abbreviation	H ₄ BPTC	H ₃ BTB	H ₂ BQDC
Name	Benzophenone-3,3',4,4'-tetracarboxylic acid	4,4',4''-Benzene-1,3,5-triyl-tribenzoic acid	2,2'-Biquinoline-4,4'-dicarboxylic acid
Structure			
Abbreviation	Hmim	NDI-ATZ	H ₃ BTC
Name	2-Methylimidazole	1,4,5,8-Naphthalenetetracarboxylic-di-aminotetrazole	1,3,5-Benzenetricarboxylic acid
Structure			
Abbreviation	H ₄ TBAPy	H ₄ TCPP	
Name	1,3,6,8-Tetrakis(p-benziuc)pyrene	Tetrakis(4-carboxyphenyl)porphyrin	
Structure			

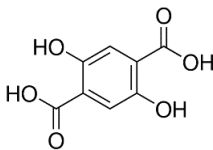
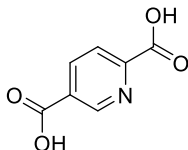
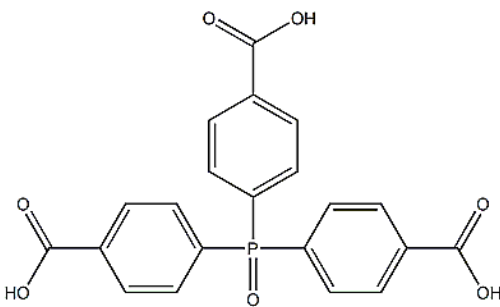
1.5. Microwave synthesis

Microwave irradiation is a widely utilised source of energy to promote chemical reactions in organic synthesis and has, in recent years, been used for the synthesis of MOFs and other inorganic materials.^{31, 89-91} It is regarded as an inexpensive and efficient nonconventional heating method and involves in the use of electromagnetic radiation whose wavelengths of 1 mm to 1 m correlate to an energy that locates between that of radio and infrared waves.^{89, 92} Microwave synthesis is based on the interaction of these waves with polar molecules in a solvent. It differs from the conventional solvothermal method as the irradiation interacts directly with the reactants resulting in faster heating rates. While in conventional solvothermal synthesis the initial crystallisation process generally occurs on the walls of the reactor vessel, in microwave synthesis it occurs in hot spots that are formed due to the direct heating of the solvent molecules. In consequence, the crystallisation process tends to be faster often generating smaller sized, microcrystalline particles. Water and ethanol mixtures are commonly used for this synthetic approach.^{31, 89, 93} A list of representative MOFs that can be synthesised using microwave methods is provided in Table 1.3, particle sizes were measured from SEM images.⁸⁹

Table 1.3: Representative MOFs synthesised using microwave methods.

MOF	Metal node	Linker	Particle Size	Ref.
MOF-5	Zn	BDC	20-25 μm	94
HKUST-1	Cu	BTC	~ 10 μm	95
IRMOF1/2/3	Zn	BDC	--	96
MIL-101	Cr	BDC	40-80 nm	97
MIL-88	Fe	BDC	20 nm	98, 99
MIL-53/MIL-47	Al, Cr, Fe, V	BDC	0.5-2 μm	100-102
MIL-100/110/96	Al	BTC	--	103
MIL-140B	Zr	NDC	--	104
MOF-77	Zn	BTB	--	105
MOF-74	Mg	DOT	--	106
IRMOF-74	Co	DHTP	--	93
Ln-MOF	La, Pr	PYDC	--	107
Ln-MOF	Y, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	TPO	--	108
CPO-27	Zn, Co, Ni	DHTP	5-7 μm	109

Table 1.4: Additional ligands and their names, cited from Table 1.3.

Abbreviation	H ₄ DOT/ H ₄ DHTP	H ₂ PYDC
Name	2,5-Dihydroxyterephthalic acid	2,5-Pyridinedicarboxylic acid
Structure		
Abbreviation	H ₃ TPO	
Name	Tris-(4-carboxylphenyl)phosphineoxide	
Structure		

1.6. Mechanochemical synthesis

Mechanochemical methods involve chemical reactions induced and sustained by the use of mechanical force, for instance by grinding in ball mills.¹¹⁰ The technique is widely for industrial mineral processing¹¹¹ purposes and has recently expanded into inorganic chemistry for the synthesis of metal complexes¹¹² and coordination compounds.¹¹³⁻¹¹⁵

This solvent-free synthetic approach is reported as one of the most environmentally friendly process to produce MOFs.¹¹⁰ Besides the green-chemistry appeal, the main advantage of the method derives from its reproducibility.¹¹⁶ However, mechanochemical synthesis has a considerable up-scaling limitation as it constitutes a batch processing technique with a relatively low production rate.³¹ It is also worth noting that despite being a solvent-free synthesis, purification of the obtained products may still require the use of solvents as by products and reactant components often remain enclosed within the porous materials.¹¹⁷ Notably, HKUST was successfully synthesised through this method by grinding together the reactants for 15 minutes without any applied heating.¹¹⁸ Other representative MOFs that can be synthesised using microwave methods are ZIF-8,^{119, 120} MOF-74,¹²¹ UiO-66,¹²² MOF-5,¹²³ MOF-14,^{124, 125} MIL-101¹²⁶ and MIL-78¹²⁷.

1.7. Properties and applications

Porous materials have had a preeminent role in the development of materials and devices for adsorption,¹²⁸⁻¹³⁰ catalysis,¹³¹ separation¹³² and storage^{10, 133}. Amongst other porous solids as activated carbons, zeolites and different porous polymers, MOFs have been well-established as the most chemical diverse class of porous materials. Such diversity allows tunability and design of structures that can be used not only as adsorbents, but also for applications in light harvesting, photocatalysis and molecular sensing.¹³⁴

Table 1.5 summarises a direct comparison of the properties of different classes of emerging porous materials according to important criteria such as porosity, crystallinity, stability, diversity and designability. Very high surface areas have been achieved in MOFs with pores sizes up to 9.8 nm in diameter.¹³⁵ MOFs are generally crystalline and relatively thermally stable, nevertheless, they can be unstable to water and collapse upon activation as a result of their very low density.^{20, 134}

Table 1.5: Comparison of selected porous materials; Adapted from ref. ¹³⁴.

Property	Zeolites	Organic polymers	Molecular solids	MOFs
Porosity*	Microporous/ mesoporous	Mostly microporous	Mostly microporous	Ultraporous** / mesoporous
Crystallinity	Typically high/ can be amorphous	Moderate to high	Typically high/ can be amorphous	Typically high
Stability	Excellent	Poor to High	Poor	Poor to good
Diversity	High; new structures can be based on known zeotypes	High, but less developed than MOFs	Low	Very high
Designability	Excellent	Excellent	Poor	Excellent
Summary	Developed but still actively growing area	Considerably less developed than MOFs	New area, good results specific molecular separations	Established and highly active field

*Microporous: pores < 2 nm; mesoporous: pores in the range of 2-50 nm.

***Ultraporous* refers to a material comprising micropores or mesopores with high surface area (*ca.* 3700 m²/g).¹³⁶

1.7.1. Porosity

Porosity is one of the most interesting properties of MOFs as it can promote interesting applications for gas storage and gas separation as well as catalysis. The synthesis of MOFs with ultrahigh porosity (high surface areas) relies on an increase in storage space per weight of the material and can be achieved by the use of extended organic linkers.²⁰ The high surface areas of MOFs is advantageous as it maximises the density of open metal sites per volume and allows for easy access of substrates to potential active sites.^{137, 138}

Interpenetration often occurs when the large space within the individual frameworks (caused by the use of extended linkers) induces two or more frameworks to mutually intertwine without forming connecting covalent bonds. The use of rod-shaped SBUs and linkers with arbitrary lengths provides periodicity in the formation of the frameworks and is reported as an efficient strategy to avoid interpenetration and increase porosity.^{20, 139}

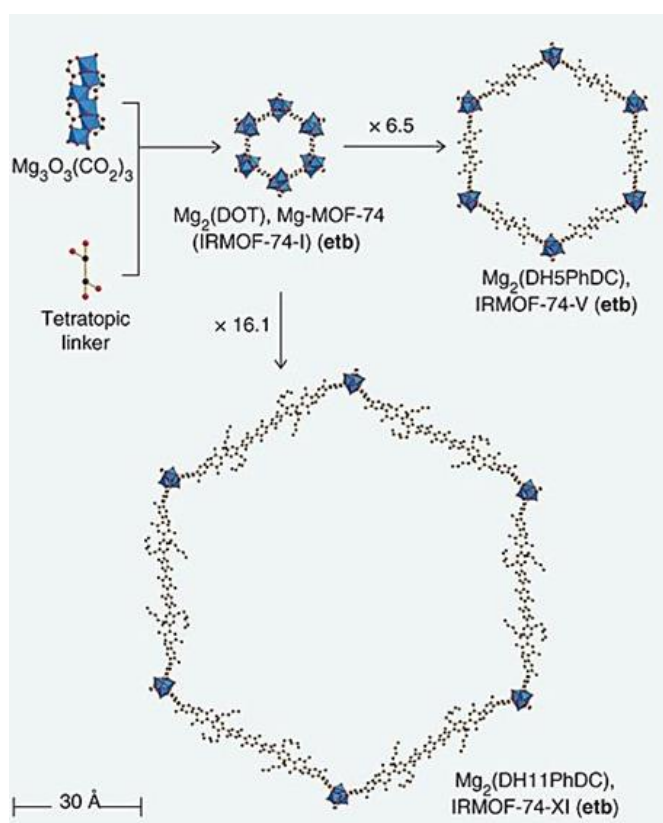


Figure 1.9: Isorecticular expansion of MOF-74 using a rod-shaped inorganic SBU and progressively longer organic linkers; Numbers above each arrow represent the degree of volume expansion in relation to the initial archetype framework.²⁰

A successful implementation of this strategy was achieved by the isorecticular expansion of MOF-74^{139, 140} to progressively form larger mesoporous cavities. Pore apertures in the range of 14 to 98 Å were achieved for the series of isorecticular MOFs (named IRMOF-74-I to XI) with **etb** topology.¹³⁵ The original structure of the archetype MOF has the formula $[\text{Mg}_2(2,5\text{-DOT})]$ where DOT is the stabilising dioxidoterephthalate ligand. This ligand was expanded, progressively adding phenyl rings to the original ligand backbone and combining the extended linker with the rod-like inorganic SBU (Fig. 1.9).

A chronological representation of the progress in the synthesis of typical conventional porous materials and MOFs to form ultrahigh-porosity MOFs and their surface areas can be seen in Figure 1.10. The graph demonstrates that surface areas of 3780 m²/g are achievable in MOF-177 $[\text{Zn}_4\text{O}(\text{BTB})_2]$ ¹⁴¹ in addition to 4530 m²/g and 6240 m²/g in MOF-200 $[\text{Zn}_4\text{O}(\text{BBC})_2]$ and MOF-210 $[(\text{Zn}_4\text{O})_3(\text{BTE})_4(\text{BPDC})_3]$ respectively.²³ Remarkably, the judicious use of extended alkyne-based tritopic ligands resulted in the synthesis of NU-110 $[\text{Cu}_3(\text{BHEHPI})]$ with a surface area of 7140 m²/g.¹⁴²

All surface area values are given as BET (Brunauer–Emmett–Teller) surface areas estimated from gas adsorption measurements and determined using the linear region of the N₂ isotherm measured at 77 K.^{20, 143}

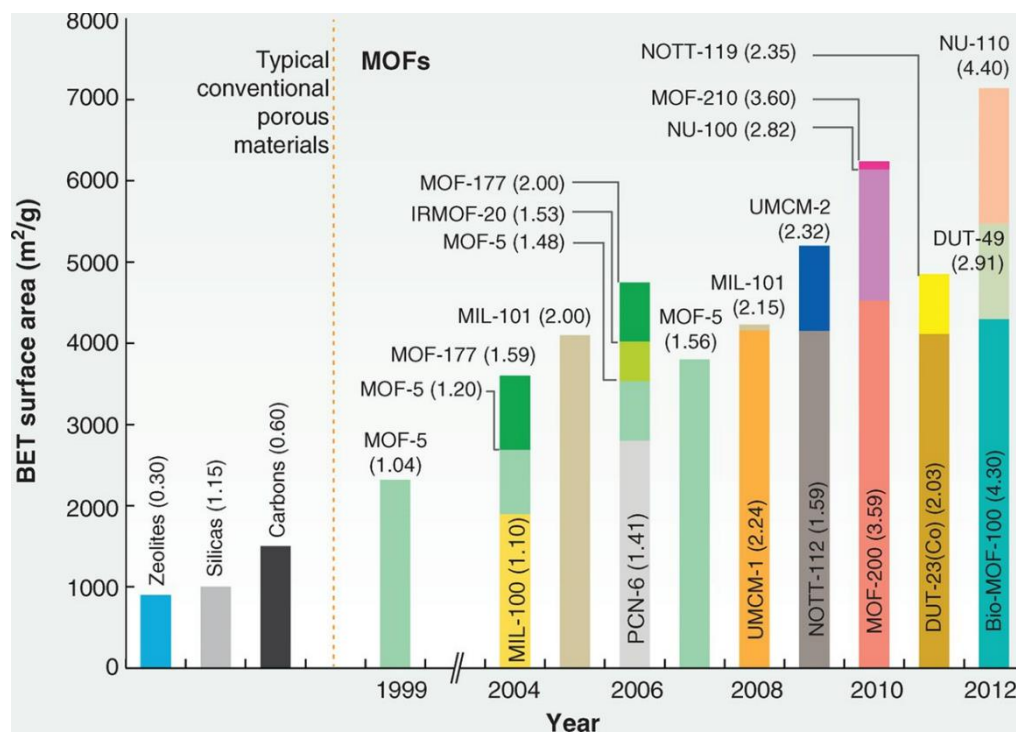


Figure 1.10: Chronological representation of the progression the synthesis of ultrahigh-porosity MOFs. The values in parentheses represent the pore volume in cm³/g.²⁰

1.7.2. Gas storage

Gas storage applications are very often associated in the literature with the development of clean, sustainable energy concepts and capture of harmful greenhouse gases. These applications are thoroughly related to societal aspects of life such as environmental protection and energy utilisation.¹⁰ Alleviating the greenhouse effect is targeted by studies involving porous materials for CO₂ capture,¹⁴⁴⁻¹⁴⁶ whereas the widespread use of clean energy can be associated with H₂ and CH₄ storage.¹⁴⁷ Multiple characterisation techniques show that the polar nature of SBUs leads to strong interactions with adsorbate molecules¹⁴⁸⁻¹⁵¹ confirming the importance of the judicious selection of building units when designing MOFs for gas storage.

1.7.2.1. CO₂ storage

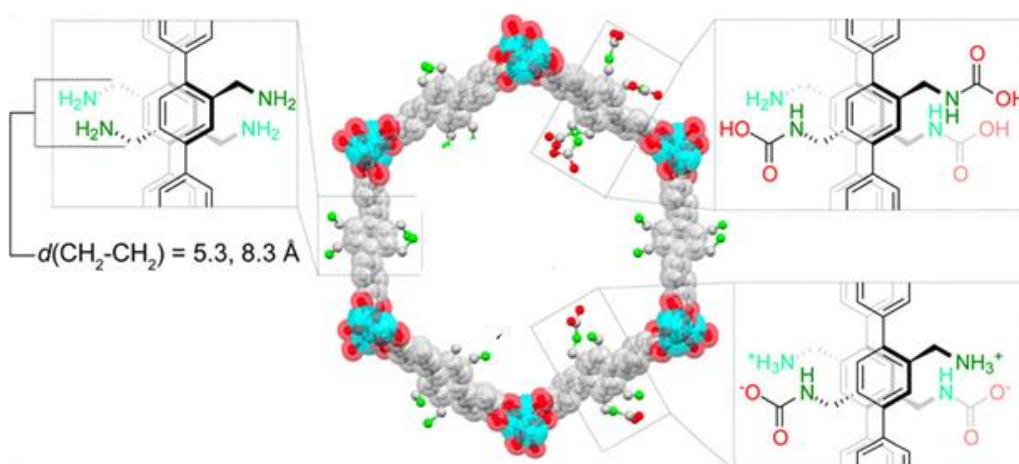
Taking into account the kinetic diameter of a CO₂ molecule (0.33 nm)¹⁵² MOFs with suitable pore sizes can be designed through ligand choice to function as efficient adsorbents.¹⁰ The previously discussed MOF-74 and its isorecticular series¹³⁵ have exhibited excellent CO₂ sorption capacities with one of the best known uptake characteristics observed for Mg-IRMOF-74.^{153, 154} Highly selective CO₂ uptake was exhibited by PCN-88¹⁵⁵, a MOF containing a dicopper paddlewheel SBU with unsaturated coordination sites. Some other examples of MOF materials with promising CO₂ uptakes are MOF-5,¹⁵⁶ MOF-177,¹⁴¹ MIL-101¹⁵⁷ and SIFSIX-2-Cu¹⁵⁸. Table 1.6 summarises the CO₂ capacities of these representative MOFs and other porous reference materials.

Table 1.6: CO₂ capacities for representative MOFs and other porous materials.

Material	CO ₂ Capacity (mmol/g)	Ref.
Zeolite 13X	2.41 (0.1 bar, 298 K)	159
Activated Carbon	0.20 (0.1 bar, 298 K)	160
MOF-5	1.50 (1.0 bar, 298 K)	94
MOF-177	1.81 (1.0 bar, 298 K)	161
MIL-101	2.33 (1.0 bar, 298 K)	162
PCN-88	4.20 (1.0 bar, 298 K)	155
Mg-MOF-74	4.10 (1.0 bar, 298 K)	153
SIFSIX-2-Cu	5.44 (1.0 bar, 298 K)	158

Further functionalisation of the chemical environment of the pores with amine groups have applied as a strategy to demonstrate enhanced CO₂ capture. Alkylamine functionalities covalently bonded to the linkers of MOF-74 to produce IRMOF-74-III-(CH₂NH₂)₂¹⁶³ (Fig. 1.11A) facilitate CO₂ uptake at low partial pressures through a chemisorption mechanism. To show that CO₂ binds in a chemisorptive fashion and to confirm the reversibility of the process, CO₂ isotherms were measured after different activation conditions (Fig. 1.11B). The material shows a maximum CO₂ adsorption capacity of 67 cm³ g⁻¹ at 800 Torr.

A



B

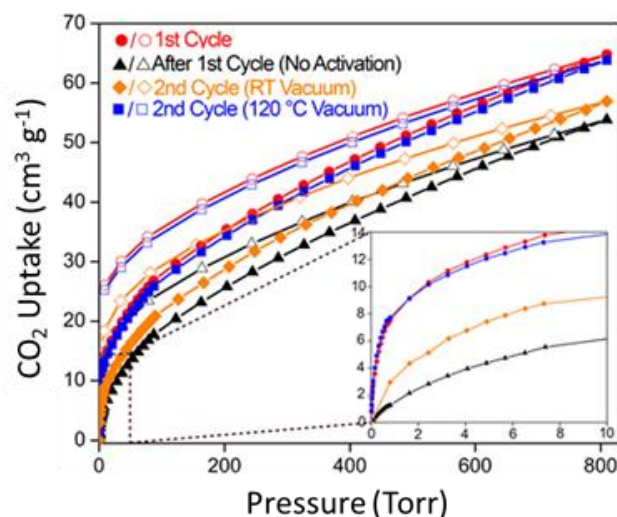


Figure 1.11: Structural model of IRMOF-74-III-(CH₂NH₂)₂ viewed down the crystallographic *c*-axis (A); CO₂ isotherms for IRMOF-74-III-(CH₂NH₂)₂ subjected to different activation processes (B); Inset: Expansion of the low pressure range.¹⁶³

1.7.2.2. Hydrogen storage

Hydrogen gas molecules generally do not experience the attractive forces from pore surfaces in the void spaces of large-pore MOFs. Consequently MOFs with large pores are not desirable for H₂ storage at low/moderate pressures and the functionality of organic linkers has only little influence on hydrogen adsorption behaviour. This phenomena stems from the low polarizability of the H₂ molecules.^{10, 164, 165}

Tailored void sizes and incorporation of metal clusters with labile sites within the structures have been applied to improve H₂ uptakes in MOFs. The well-known MOF-177 and MOF-5 structures have pronounced H₂ cryo-temperature storage capacities of 7.5 wt % at 70 bar and 10 wt % at 100 bar respectively, and were amongst the first MOFs whose H₂ adsorption characteristics were investigated.^{20, 23, 166} The {Zn₄O(CO₂)₆}₄-based MOF-210 with the compositional formula [Zn₄O(BTE)₄/3(BPDC)] exhibits hydrogen adsorption capacities as high as 9.0 wt % at 56 bar and 15 wt % at 80 bar.²³

All the reported uptakes are based on physisorption interactions and were obtained at 77 K (cryo-temperature adsorption). Room temperature H₂ adsorption in MOFs at satisfactory quantity remains a challenge as the absence of a permanent dipole moment of the H₂ molecule leads to limited interactions with MOF channels.¹⁰

1.7.2.3. Methane storage

Methane is the most abundant component of natural gas and which remains a predominant energy source.¹⁶⁷ When compared to compressing and liquefying natural gas, the use of adsorbents can optimise large scale transportation and utilisation of methane in the gaseous state once it allows for storage at room temperature.¹⁶⁸ MOFs have been investigated extensively as adsorbents; the studies suggests that apart from geometrical factors, van der Waals and electrostatic interactions are the defining factors that influence the methane capacities of MOFs.¹⁰ Table 1.7 shows methane uptakes for a list of representative MOFs.

Table 1.7: CH₄ capacities for representative MOFs.

Material	CH ₄ Uptake (cm ³ /cm ³)	Ref.
Ni-MOF-74	260 (65 bar, 298 K)	¹⁶⁹
Co-MOF-74	249 (65 bar, 298 K)	¹⁶⁹
Mg-MOF-74	200 (35 bar, 298 K)	¹⁶⁹
Zn-MOF-74	188 (35 bar, 298 K)	¹⁷⁰
Mn-MOF-74	176 (35 bar, 298 K)	¹⁷⁰
NU-135	176 (35 bar, 298 K)	¹⁷¹
NU-125	182 (35 bar, 298 K)	¹⁷²
NOTT-107	196 (35 bar, 298 K)	¹⁷³
HKUST-1	227 (35 bar, 298 K)	^{172, 174}

MOFs containing open metal sites allow electrostatic interactions between individual methane molecules and the framework.¹⁶⁹ Such effects are exemplified by the CH₄ uptakes of Ni-MOF-74 (230 cm³/cm³ at 298 K and 35 bar and 260 cm³/cm³ at 298 K and 65 bar), which is amongst the highest total volumetric capacity for MOFs and the highest for the M-MOF-74 (M = Mg, Zn Mn, Ni and Co) series.¹⁷⁰ Considering each open metal site is occupied by one CH₄ molecule, an estimated volumetric uptake of 172 cm³/cm³ was expected based on the quantity of available open nickel sites.¹⁶⁹ The experimental adsorption behaviour was consequently attributed to the high densities of open metal sites and the strong polarising ability of Ni²⁺ ions.

Van der Waals forces, differently from electrostatic interactions, often result in modest frameworks interactions with CH₄ molecules. Nevertheless, the strength and extent of the interactions can be tuned by the pore size and shape of the adsorbent.¹⁰ A high working capacity/total uptake ratio for HKUST was reported by Yildirim and co-workers. The reported gravimetric total methane uptake and working capacity at 298 K are 227 cm³/cm³ (35 bar) and 190 cm³/cm³ (5–65 bar), respectively.¹⁷² The high working capacity/total uptake ratio indicates that the interaction between adsorbed methane molecules and the framework is relatively weak. Direct binding of one CH₄ molecule may possible at each metal site,¹⁷⁵ however those electrostatic interactions only account for a small fraction of the total uptake. The observed uptake substantiates that van der Waals interactions are the dominant force accounting for the methane storage in the material.^{10, 169}

1.7.3. Gas separation

Gas separations processes using MOFs rely on two main aspects: the chemical affinity for the targeted gas and the size of the pores within the material. Potential gas selectivity is often estimated based on experimental and simulated single-gas isotherms using a given porous MOF as adsorbent.²⁰

The first example of dynamic separation using a microporous MOF was achieved by Chen *et al.* using $[\text{Zn}_2(\text{BDC})_2(\text{BPY})]$ denoted as MOF-508.¹⁷⁶ For this purpose a gas-chromatographic column was filled with a powder of MOF-508 and used for the separation of alkanes. Successful separation using MOF-508 was achieved as a result of tuning the pore size of the microporous material to obtain 1D channels with cross-sectional diameters comparable to the sizes of the alkane molecules.¹⁷⁶

Electrochemically synthesised HKUST (referred to as Cu-BTC-MOF) was used in gas separation, demonstrating the removal of sulphur components from methane. Separation occurred in a bed reactor vessel containing granular Cu-BTC-MOF. The gas in the reactor effluent was analysed by gas chromatography to confirm the removal of tetrahydrothiophene (THT) for the mixture. Interestingly, the colour of the MOF changed from blue to green due to the adsorption of the THT molecules at the unsaturated metal sites present in the Cu-SBU of the MOF.⁴⁶

Fe-MOF-74 $[\text{Fe}_2(\text{DOT})]$ was also used in a gas-chromatographic column to achieve the separation of hydrocarbons present in natural gas. Evaluation of adsorption capacities for targeted hydrocarbons was obtained by collecting single component data from experimental isotherms for methane, ethane, ethylene, acetylene, propane and propylene. Fe-MOF-74 isotherms demonstrated strong affinity of the material for the unsaturated hydrocarbons acetylene, ethylene, and propylene. The material exhibited excellent performance for separation of ethylene/ethane and propylene/propane mixtures with selectivities of 2.1 and 15 respectively. Analogously to Cu-BTC-MOF, the affinity between Fe-MOF-74 and the hydrocarbons was explained by means of interactions with the open metal sites present in the MOF SBU as seen in Figure 1.12).¹⁷⁷

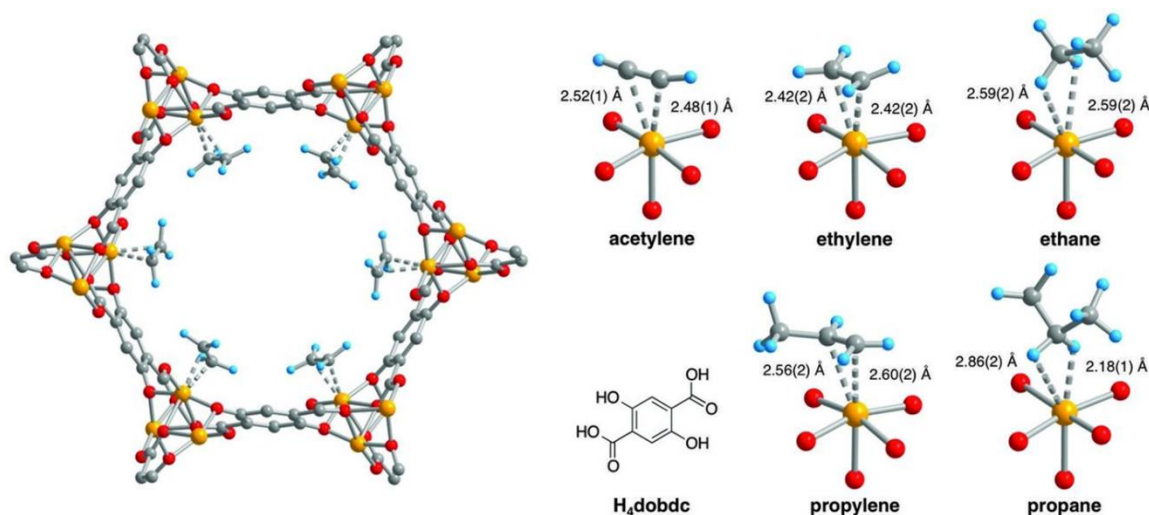


Figure 1.12: A portion of the structure of Fe-MOF-74. Hydrocarbon molecules bound to open coordination sites at each Fe^{II} centre were simulated using DFT methods. Colour Code: Fe, orange; O, red; C, grey; H, blue.¹⁷⁷

More recently, SIFSIX materials in which layered 2D pyridyl based MOFs are pillared by inorganic hexafluorosilicate ions were used to demonstrate how pore size and pore chemistry control can be tuned for acetylene/ethylene separation.¹⁷⁸ The hexafluorosilicate sites exhibit preferential binding of acetylene molecules through cooperative host-guest and guest-guest interactions from a 1/99 C₂H₂/C₂H₄ mixture. SIFSIX-2-Cu adsorbs high quantities of C₂H₂ under very low pressures and exhibits the highest C₂H₂/C₂H₄ selectivity amongst SIFSIX materials (39.7 to 44 from 283 to 303 K). SIFSIX-1-Cu also displays significant selectivities towards C₂H₂ (7.1 and 10.6 at 283 to 303 K, respectively), which are higher than values obtained for NOTT-300¹⁷⁹ (2.2 - 2.5) and Fe-MOF-74¹⁷⁷ (2.1).¹⁷⁸

The flue gases, generated in contemporary power plants are mainly composed of CO₂ and N₂. In that context, CO₂/N₂ gas separation is a relevant application for MOFs in the interest of post-combustion capture at higher temperatures.¹⁴⁴ Mg-MOF-74 is a notable example of an adsorbent with apparent potential for CO₂/N₂ separation due to its high CO₂ uptake behaviour at relatively low partial pressure, resulting in capacities of 5.28 mmol/g at 0.15 bar.^{154, 180} The uptakes, as previously discussed, stem from the strong interaction of its coordinatively unsaturated metal sites with CO₂ molecules.¹⁸¹ However, the high density of open metal sites also allows for interactions with H₂O molecules. As

a result, there is a dramatic decrease of selectivity towards CO₂ when the material is exposed to moisture.¹⁰

An alternative approach towards MOFs with high CO₂ over N₂ selectivity was provided by Chen and co-workers who synthesised microporous MOF with potential for CO₂ capture at ambient conditions.¹⁸² UTSA-16 (Fig. 1.13) is a 3D MOF with **dia** topology. Its structure incorporates {Co₄O₄} clusters and ionic K⁺ linkers resulting in heteronuclear M-O-M connections. The MOF contains 3.3 x 5.4 Å² channels and exhibits a BET surface area of 628 m² g⁻¹. Its CO₂ uptake is 160 cm³/cm³ at 296 K and 1 bar and a high CO₂/N₂ selectivity of ca. 314.7 at ambient conditions is reported. The uptake and high selectivity towards CO₂ were attributed to the pore size of the compound and hydrogen bonding interactions of CO₂ with terminal coordinated H₂O molecules.¹⁸³

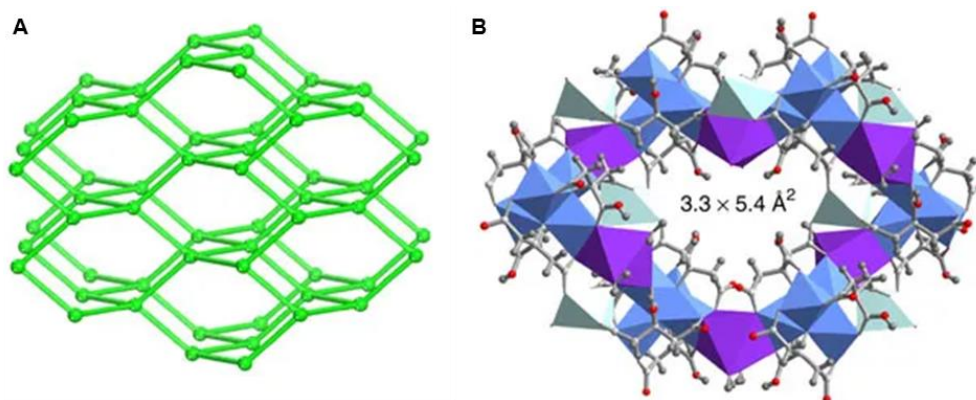


Figure 1.13: The dia topology of UTSA-16 (A); Representation of the window with the dimensions of 3.3×5.4 Å². . Colour Code: Co polyhedra, blue; K, red; O, red; C, light grey; H, dark grey.¹⁸²

Zaworotko and co-workers have used sorption experiments for capture of CO₂ from CO₂/N₂/H₂O gas mixtures. Representative MOFs, such as HKUST-1, MOF-74 and SIFSIX-3 were used as adsorbents. HKUST-1 and Mg-MOF-74 showed diminished adsorption performance in the presence of water vapour, suggesting occupancy of open sites by water molecules and possible degradation by exposure to humidity. The strongest performance was observed for SIFSIX-3 (ca. 60 cm³ g⁻¹ CO₂ at 293 K and 1 atm); the CO₂ uptake of the sample that was exposed to moisture, remained nearly unaffected when compared to the pristine sample.¹⁸⁴ The selective CO₂ capture from CO₂/N₂/H₂O gas mixtures exhibited by SIFSIX-3 was mainly attributed to its pore size (3.84 Å).¹⁸³ The CO₂ selectivity of SIFSIX-3 was also investigated using a CO₂/N₂:10/90 mixture at 298 K at atmospheric pressure and resulted in a value of 495.¹⁵⁸

1.7.4. Catalysis

Porosity, crystallinity, diversity and designability as well as the high density of active sites within their structures, make MOFs advantageous platforms for catalysis.²⁰ Fujita *et al.* reported the first example of catalysis in an extended framework in 1994. It involved a 2D square network material composed of Cd^{II} and 4,4'-bipyridine linkers and that promoted the cyanosilylation of aldehydes.¹⁸⁵

Catalytic activity was observed within the pores of HKUST-1 upon activation. Removal of coordinated solvent molecules of the material leads to exposure of open metal sites. The metal sites can act as Lewis acid catalyst for the isomerisation of terpene derivatives.¹⁸⁶ Similar Lewis acid catalytic behaviour was exhibited by Cr-MIL-101, $[\text{Cr}_3\text{OH}(\text{H}_2\text{O})_2\text{BDC}_3]\cdot\text{H}_2\text{O}$ ¹⁸⁷ and the microporous MOF, Mn-BTT, $[\text{Mn}_3[(\text{Mn}_4\text{Cl})_3\text{BTT}_8(\text{CH}_3\text{OH})_{10}]_2]$ ¹⁸⁸ (H_3BTT = 1,3,5-benzenetristetrazol-5-yl) whereby the catalytic activity was achieved upon ligand removal and exposing a catalytic site.

Oxidation of alkenes and the hydrolysis of esters was achieved by exploring host-guest interactions within the pores of HKUST and Cr-MIL-101, respectively. Polyoxometalates were encapsulated utilising electrostatic interactions to the inorganic SBUs of the MOFs and applied as heterogeneous catalysts in the hydrolysis of esters and oxidative desulfurization processes.^{189, 190} In addition, palladium nanoparticles were also incorporated within Cr-MIL-101 to promote cross-coupling reactions.¹⁹¹

More recently, a bimetallic water-stable MOF ($\text{NH}_2\text{-MIL-88B}(\text{Fe}_2\text{Ni})$) was synthesised on the surface of a highly conducting 3D macroporous nickel foam. The composite was reported as highly efficient, stable catalyst for water oxidation. The catalytic activity was accredited to the open metal sites in the bimetallic $\{\text{Fe}_2\text{Ni}(\mu_3\text{-O})(\text{COO})_6(\text{H}_2\text{O})_3\}$ clusters present in the MOF.¹⁹² The use of MOFs as oxidation and reduction catalysts recently was reviewed by Kang *et al.*¹⁹³ A list of representative MOFs with catalytic activity is provided in Table 1.8.

Table 1.8: List of representative MOFs with coordinatively unsaturated metal sites used in catalytic reactions. Adapted from ref. 14.

MOF	Formula*	Catalytic reactions	Ref.
MIL-101(Cr)	$[\text{Cr}_3\text{OH}(\text{H}_2\text{O})_2\text{O}(\text{BDC})_3]$	Cyanosilylation of aldehydes, oxidation of hydrocarbons and sulphides, cycloaddition of CO_2 and epoxides	187, 194-196
MIL-101(Fe)	$[\text{Fe}_3\text{F}(\text{H}_2\text{O})_2\text{O}(\text{BTC})_2]$	Friedel–Crafts benzylation, oxidation of hydrocarbons, ring-opening of epoxides, oxidation of thiophenol to diphenyldisulfide.	197-199
MIL-53(Al)	$[\text{Al}_2(\text{BDC})_3]$	Reduction of carbon–carbon multiple bonds	200
MOF-74 (Co)	$[\text{Co}_2(\text{DOT})(\text{H}_2\text{O})]$	Cycloaddition of CO_2 and epoxides	201
HKUST-1	$[\text{Cu}_3(\text{BTC})_2]$	Cyanosilylation of aldehydes, isomerisation of terpene derivatives, cyclopropanation of olefins	186, 202-205
UiO-66	$[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BDC})_6]$	Aldol condensation reactions, cyclisation of citronellal	206-208
ZIF-8	$[\text{Zn}(\text{L}^{\text{I}})_2]$	Cycloaddition of CO_2 and epoxides	209
MFU-1	$[\text{Co}_4\text{O}(\text{L}^{\text{II}})_3]$	Oxidation of hydrocarbons	210

* L^{I} = 2-methyl-1H-imidazole* $\text{H}_2\text{L}^{\text{II}}$ = 1,4-Bis[(3,5-dimethyl)pyrazol-4-yl]-benzene

1.7.5. Photocatalysis

The percentage of the solar energy reaching the Earth's surface corresponding to the UV region is about 4 % and about 46 % corresponds to the visible region of the electromagnetic spectrum.²¹¹ The energy influx from the sun is unlimited and sustainable, which makes solar energy an appealing energy source. Green plants harvest solar energy in order to convert CO₂ and water into carbohydrates. This process is known as photosynthesis and requires a relatively high amount of energy (endergonic transformation).²¹² The first reported example of artificial photosynthesis was achieved in 1978 by Fujishima and Honda.²¹³ They reported water splitting by TiO₂ through UV radiation. Molecular, homogeneous dyes and photocatalysts as [(Ru(bpy)₃)³⁺]²¹⁴ and *cis,cis*-[(bpy)₂(H₂O)Ru^{III}ORu^{III}(H₂O)(bpy)₂]⁴⁺²¹⁵ were also developed with the objective of mimicking the natural photosynthetic process.²¹⁶⁻²²¹ These homogeneous systems had the advantage of increased catalytic selectivity or binding affinity towards targeted substrates when compared to metal oxides. The selectivity could be tailored through the modification of the organic ligands however, deactivation (for instance through formation of dimeric species) and solubility limitations resulted in drawbacks. Additionally, the use of multiple components (i.e. photosensitiser, catalyst, sacrificial reductant) and their random distribution in solution can be a limiting factor to the dye activity and electron transfer to the catalytical centre.^{137, 222}

In the context of photocatalytic materials, *first generation* MOFs¹³⁷ are defined as materials with high internal surface areas and chemical features (i.e., binding affinity, redox properties and acid/base character) that lead to selectivity of a given substrate targeted for photocatalysis. An example of a functionalised *first generation* MOF was reported in 2011 by Lin and co-workers.²²³ In their work, catalytically efficient Ir, Re, and Ru complexes were incorporated into UiO-67³⁰ [Zr₆O₄(OH)₄(BPDC)₆] through a doping process. The resulting MOFs were isostructural to the parent UiO-67 framework and were found effective for water oxidation and CO₂ reduction catalysts. However, FTIR studies on the recovered functionalised UiO-67 revealed that carbonyl moieties detached from the complexes leading to the degradation of the MOF backbone during consecutive catalytic cycles. The loss of {C=O} stretching vibrations on the recovered solid was accompanied with a loss of catalytic activity.¹³⁷

Second generation, photoactive MOFs¹³⁷ can be defined as MOFs that efficiently absorb light in the visible region. Synthetic approaches to such optically efficient frameworks include: (i) organic modification, by encapsulating or integrating an organic chromophore into the framework and (ii) inorganic modification, by integrating optically efficient inorganic SBUs into the MOF. A persistent challenge for increasing efficiency of *second generation* MOFs is associated with the fact that not every photon absorbed by the system can be transferred to a substrate or catalytically active centre. Thus, the efficiency of these systems is somewhat limited.

Photoactive *third generation* MOFs combine optical and electronic efficiency as well as catalytic selectivity towards a targeted substrate and permanent high porosity. One approach that has been utilised in the production of photoactive *third generation* MOFs involves the introduction (not grafting) of a molecular photosensitiser moiety into the MOF framework. In this strategy, optical efficiency is achieved by an incorporated photosensitiser that exhibits visible light absorption and prolonged excited state lifetimes.^{137, 224}

Recently Yan *et al.*²²⁵ synthesised an interpenetrated Eu-Ru(phen)₃-MOF (Fig. 1.14A) that features dinuclear {Eu^{III}₂} complexes (Fig. 1.14B) and {Ru(phen)}₃-derived metallo-ligands. 2-Fluorobenzoic acid (2-FBA), was used as a modulator in the solvothermal synthesis stabilising a the framework compound that has the constitutional formula (NO₃)₂[Eu₂(μ₂-H₂O)(H₂O)₃(L)₂].2(2-FBA⁻)·22H₂O. (L = Ru(phen)₃-derived metallo-ligand). The material absorbs visible light causing the photo-excitation of the Ru^{II}-based metallo-ligand which prompts the reduction of the dinuclear {Eu^{III}}₂ moiety to {Eu^{II}}₂. The active sites present in the dinuclear {Eu^{II}}₂ unit efficiently catalyse CO₂ reduction to formate in a two-electron reduction process (Fig. 1.14C).²²⁵ A list of MOFs with photocatalytic activity towards CO₂ reduction is shown on Table 1.9.

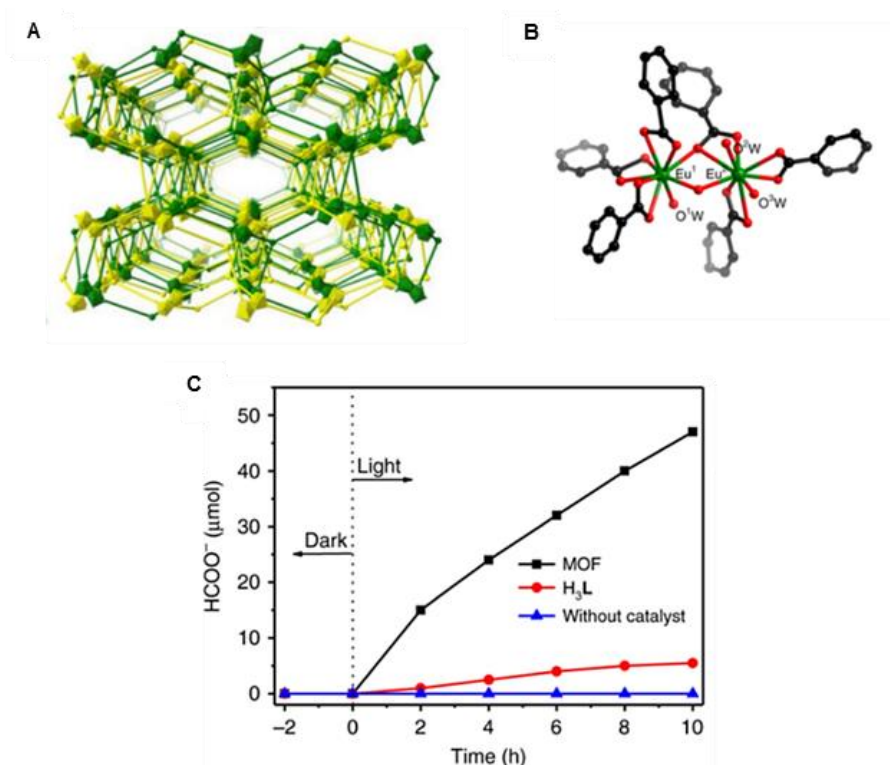


Figure 1.14: Topology representation of the Eu-Ru(phen)₃-MOF, yellow/green colours indicate interpenetrated frameworks (A); Chemical structure of the dinuclear {Eu₂} SBU (B); Time profiles of the photocatalytic CO₂ reduction to formic acid: H₃L represents the Ru-based metallo-ligand (C).²²⁵

Table 1.9: List of representative MOFs used in visible-light driven CO₂ reduction.

MOF	Catalytic Site	Formula*	Ref.
Zr-SDCA-NH ₂	Zr-O cluster	[Zr ₆ O ₄ (OH) ₄ (L ^I) ₆]	226
MIL-101	Fe-O cluster	Fe ₃ O(OH ₂) ₃ L ^{II} Cl	227
NH ₂ -MIL-101	Fe-O cluster	Fe(OH)(L ^{II}) 0.3L ^{II}	227
NH ₂ -MIL-125	Ti-O cluster	Ti ₈ O ₈ (OH) ₄ (L ^{II}) ₆	228
NH ₂ -UiO-66	Zr-O cluster	Zr ₆ O ₄ (OH) ₄ (L ^{II}) ₆	229
PCN-222	Zr-O cluster	Zr ₆ (μ ₃ -OH) ₈ (OH) ₈ (L ^{III}) ₂	230
NNU-28	Zr-O cluster	Zr ₆ O ₄ (OH) ₄ (L ^{IV}) ₆	231
Ir-CP	Ir-O cluster	[Ir(ppy) ₂ (L ^V) ₂][OH]	232

*H₂L^I = 2,2'-Diamino-4,4'-stilbenedicarboxylic acid;

*H₂L^{II} = 2-Aminoterephthalic acid;

*H₂L^{III} = Tetrakis(4-carboxyphenyl)porphyrin;

*H₂L^{IV} = 4,4'-(Anthracene-9,10-diylbis(ethyne-2,1-diyl))dibenzoic acid

*H₂L^V = 2,2'-Bipyridine-4,4'-dicarboxylic acid; ppy = 2-Phenylpyridine

1.8. Objectives of this project

The general aim of this research project was to develop synthetic concepts to novel MOFs that may incorporate photoactive moieties and nodes in their framework structures. Thus, the ultimate objective was directed towards the synthesis of photoactive 3rd generation MOFs whereby the photophysical properties were set-out to be investigated. Overall, the research project strives towards the design of new, porous metal-organic materials that may conceptually be capable to promote for light driven chemical transformations and ultimately be exploited for sustainable energy, ‘solar-fuel’-related applications. Initially, the scientific attention was set-out to be directed towards the synthesis of polypyridyl- or phenanthroline-based ligands that would lend itself to the formation of Ru-based metallo-ligands and could potentially be exploited as nodes in the formation of heterometallic MOFs. Figure 1.15 highlights the organic ligands, the investigated metallo-ligands and their abbreviations.

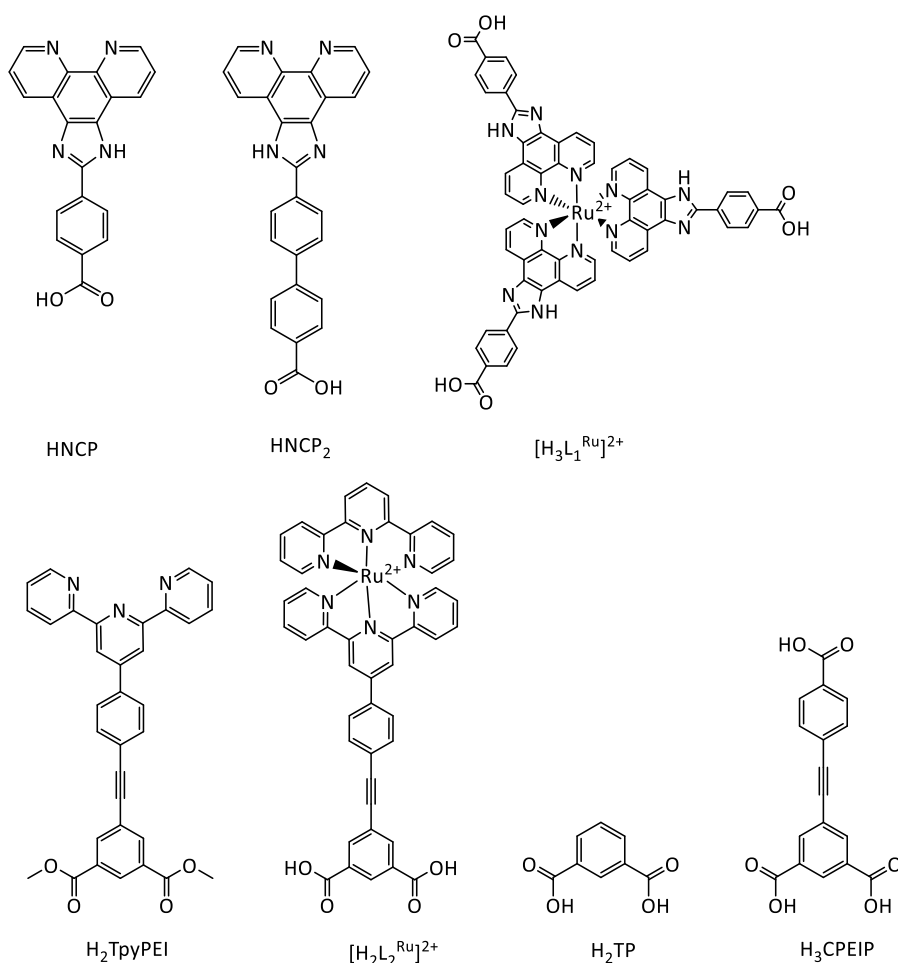


Figure 1.15: Organic ligands and metallo-ligands exploited as linkers in the formation of heterometallic MOF.

The initial part of the study as described in the following chapter 2 focused on the use of phenanthroline-based ligands that incorporate both N- and O- functionalities and the investigation of the crystallisation processes for the formation of coordination polymers. Particular emphasis was given to the coordination chemistry and supramolecular interactions that derive from the use of the extended 4'-(1-Himidazo[4,5-f][1,10]phenanthrolin-2-yl)-[1,1'-biphenyl]-4-carboxylate (NCP_2^{2-}) ligand that was employed to stabilise Zn^{II} , Co^{II} and Cd^{II} based coordination polymers.

In Chapter 3, the coordination chemistry of a tritopic metallo-ligand $\text{H}_3\text{L}_1^{\text{Ru}}$ which also contains a phenanthroline moiety is described. The applied synthetic strategy consisted in using the N-donors as binding sites for Ru^{II} ions to generate a $[\text{Ru}(\text{phen})_3]^{2+}$ chromophore that relates to the vastly studied $[\text{Ru}(\text{bpy})_3]^{2+}$ complex. The main synthetic objective was to use the light-harvesting functionality to form a predesigned stable MOF. To achieve the synthetic objective, a self-assembly strategy was employed^{5, 233} as a design tool to pursue to obtain a novel light-harvesting MOF with unblocked channels. Furthermore, we aimed to explore alternative electrochemical approaches to synthesise light harvesting MOF films allowing the functionalisation of conductive surfaces.

A novel ditopic metallo-ligand containing a polypyridyl based $[\text{Ru}(\text{tpy})_2]^{2+}$ chromophore moiety was also targeted with the objective of constructing photoactive MOFs. $\text{H}_2\text{L}_2^{\text{Ru}}$ Was synthesised via a multi-step synthetic approach. Solution studies to characterise the photophysical behaviour of $\text{H}_2\text{L}_2^{\text{Ru}}$ aimed to indicate how effective the chromophore moiety is within the metallo-ligand. We set out to perform the preparation, structural and physicochemical characterisation of light-harvesting MOFs that include potentially catalytically active clusters with labile coordination sites as SBUs.

This research project also addressed the question of how MOFs can be modularly modified through organic ligand variation. We aimed to explore ligand systems that can modularly be extended and whose functionality be varied. The carboxylate moieties in these systems were expected to react with oxophilic metal ions and clusters to stabilise extended MOFs and coordination polymers. N-donor moieties were expected to stabilise softer metal ions. We aimed to use Co^{II} SBUs for the preparation of the MOFs as Co^{II} species are known to show promising activities to promote redox-catalytic transformations.²³⁴⁻²³⁹

1.9. References

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Chapter 2

Synthesis of phenanthroline-based
coordination polymers

2. Synthesis of phenanthroline-based coordination polymers

2.1. Introduction

The choice of organic ligands and synthetic conditions have a great impact on the design and synthesis of MOFs with versatile structures. Key attributes can be imparted to the structure determined by size, shape, rigidity, and conformation and substituent groups of the selected linkers.¹⁻³ Rigidity is a particularly advantageous characteristic for the preparation of open-framework structure with applications involving host-guest interactions for instance in areas of gas adsorption, separations and sensing.⁴⁻⁶

Multidentate linkers containing O- and N-donors can display a variety of coordination modes that can result in MOFs with diverse topologies.⁷ 1,10-Phenanthroline derivatives functionalised with aromatic carboxylic acid groups are notably interesting for the development of MOFs with luminescent behaviour as those linkers function as absorbing sensitizers.⁸ 2-(4-Carboxyphenyl)imidazo[4,5-f]-1,10-phenanthroline (HNCP) has both a phenanthroline moiety and a carboxylic acid moiety, and has been used previously for the construction of robust MOFs and other coordination polymers.⁸⁻¹¹ The long conjugated structure of HNCP give rise to $\pi - \pi$ stacking interactions and can potentially impart rigidity to a framework. Selected coordination modes for NCP and HNCP can be seen in Figure 2.1.

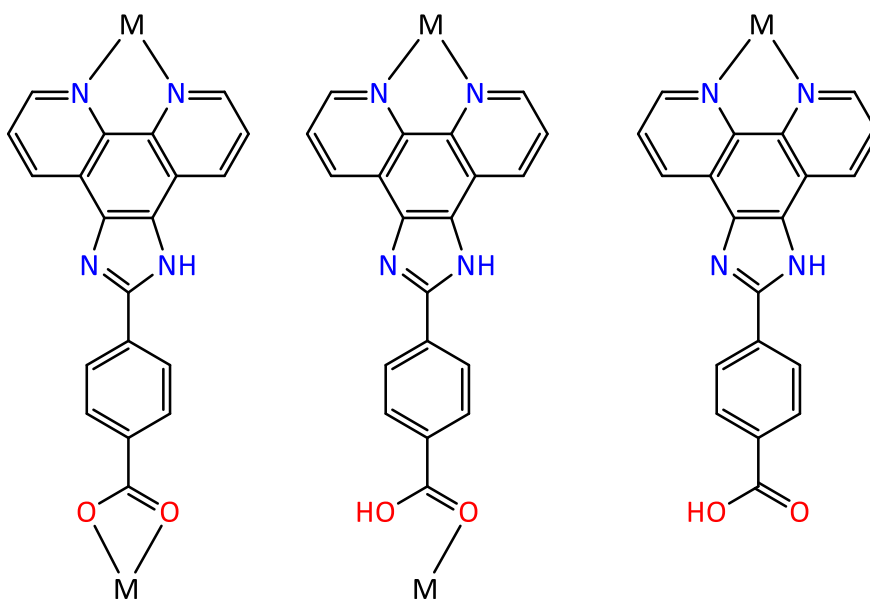


Figure 2.1: Selected coordination modes for HNCP; Adapted from ref. 1.

Mineralisers allow for a higher level of control over product crystallization and are commonly used in MOF synthesis. They can act as bases in the deprotonation equilibria during nucleation and crystal growth, influencing size and morphology of the resulting crystals.¹²⁻¹⁴ By adding modulators containing the same chemical functionality as the chosen linkers to a given reaction mixture (i.e. carboxylic acids), these can compete with the organic linkers in order to coordinate with the metal ions during nucleation.¹⁵ Moreover, those modulators can be used in synthesis to improve crystal growth and to direct the formation of targeted polymeric structures.¹⁶⁻¹⁸

2.2. Synthesis of organic linker

Noncovalent interactions, such as $\pi - \pi$ stacking, are important adhesive and cohesive forces that can favour the crystallisation process.¹⁹ With the aim of increasing potential $\pi - \pi$ interactions, an extended version of the HNCP ligand, containing an additional phenyl ring, 4'-(1Himidazo[4,5-f][1,10]phenanthroline-2-yl)-[1,1'-biphenyl]-4-carboxylic acid (HNCP₂) (Fig. 2.2), was synthesised. HNCP₂ was synthesised in two steps involving the synthesis of 1,10-phenanthroline-5,6-dione, and the subsequent formation of an imidazole ring with 4'-formyl-[1,1'-biphenyl]-4-carboxylic acid.

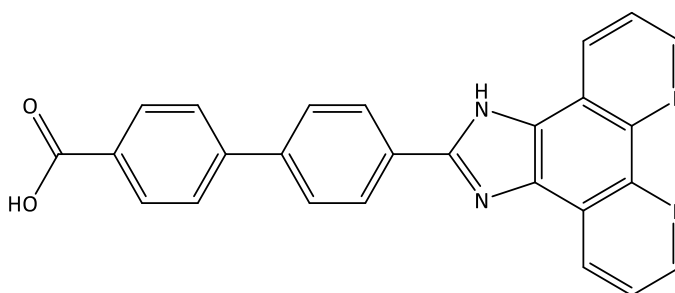
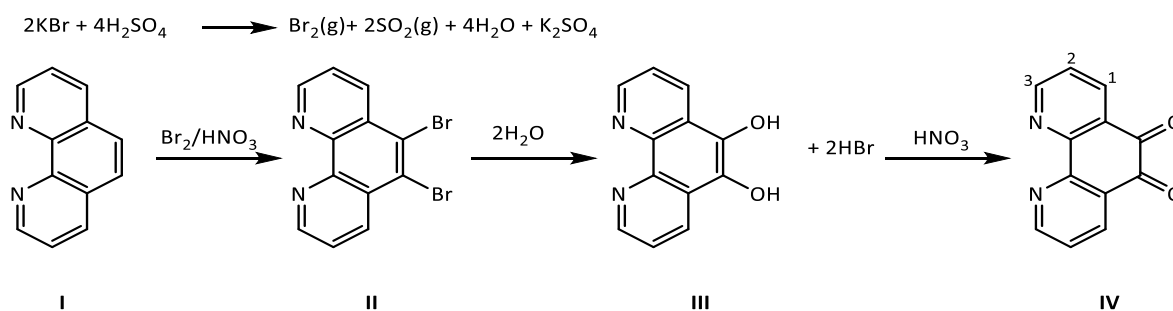


Figure 2.2: The multidentate HNCP₂ ligand, an extended version of HNCP.

1,10-Phenanthroline-5,6-dione (phendione) (**IV**) was synthesised according to literature procedure.²⁰ Primarily, bromine gas is generated *in-situ* by the reaction of KBr and H₂SO₄ with HNO₃. The generated Br₂ gas then acts as a Lewis acid in the electrophilic aromatic bromination of 1,10-phenanthroline (**I**). The brominated product (**II**) undergoes a hydrolysis reaction *via* an S_N2 mechanism to yield a 1,2-diol product (**III**).²¹ The phendione is then generated by the oxidation of the diol product by nitric acid as shown in Scheme 2.1. Typical yields of 65% of **IV** were achieved.



Scheme 2.1: One-pot synthetic route to 1,10-phenanthroline-5,6-dione: Redox reaction to yield Br₂ followed by bromination of phenanthroline, hydrolysis to diol and oxidation to dione.

The ^1H -NMR spectrum of **IV** (Fig. 2.3) reveals signals at 9.00 ppm, 8.40 ppm and 7.68 ppm which are attributed to the H- atoms in the phenanthroline and in agreement with the literature.²⁰

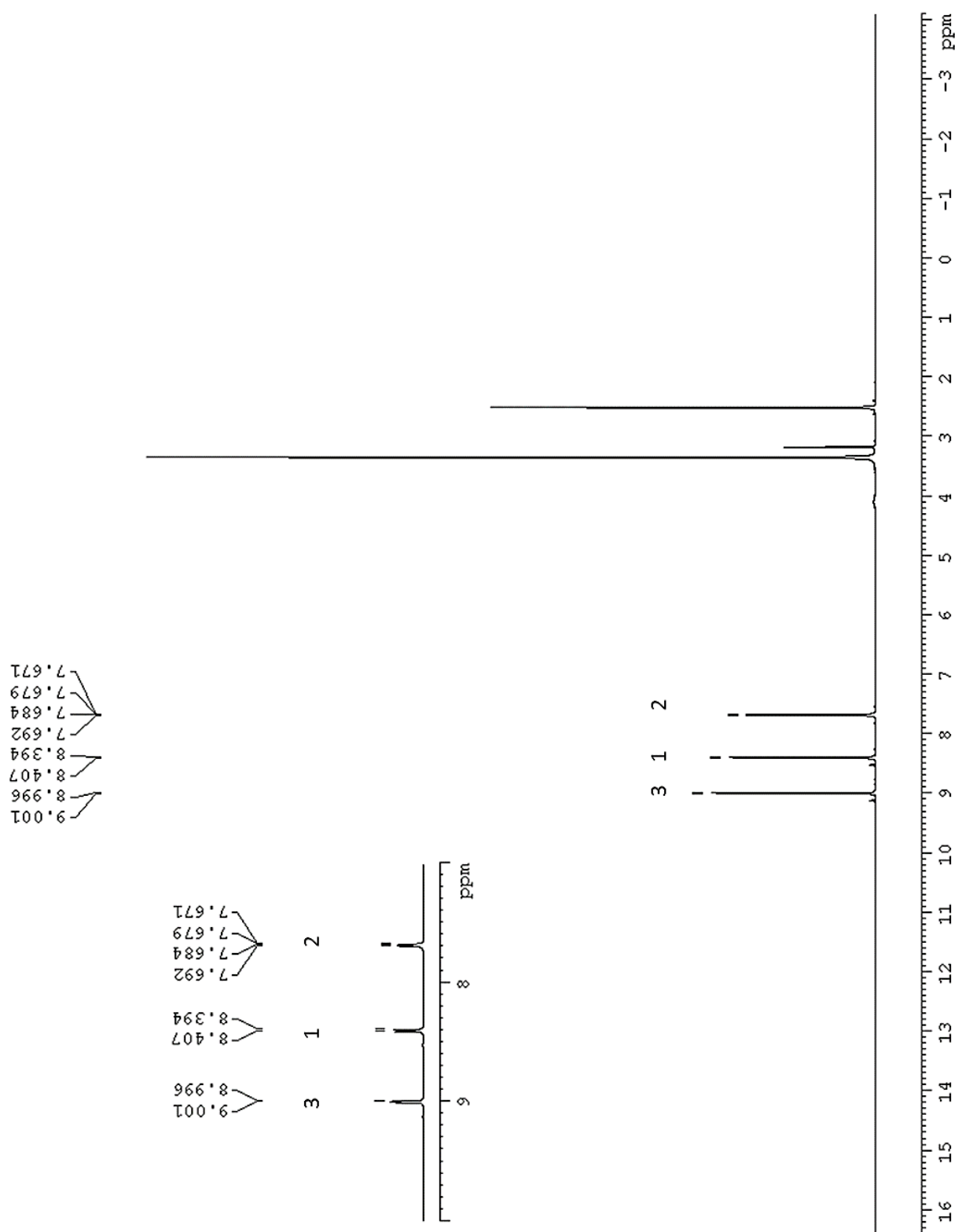
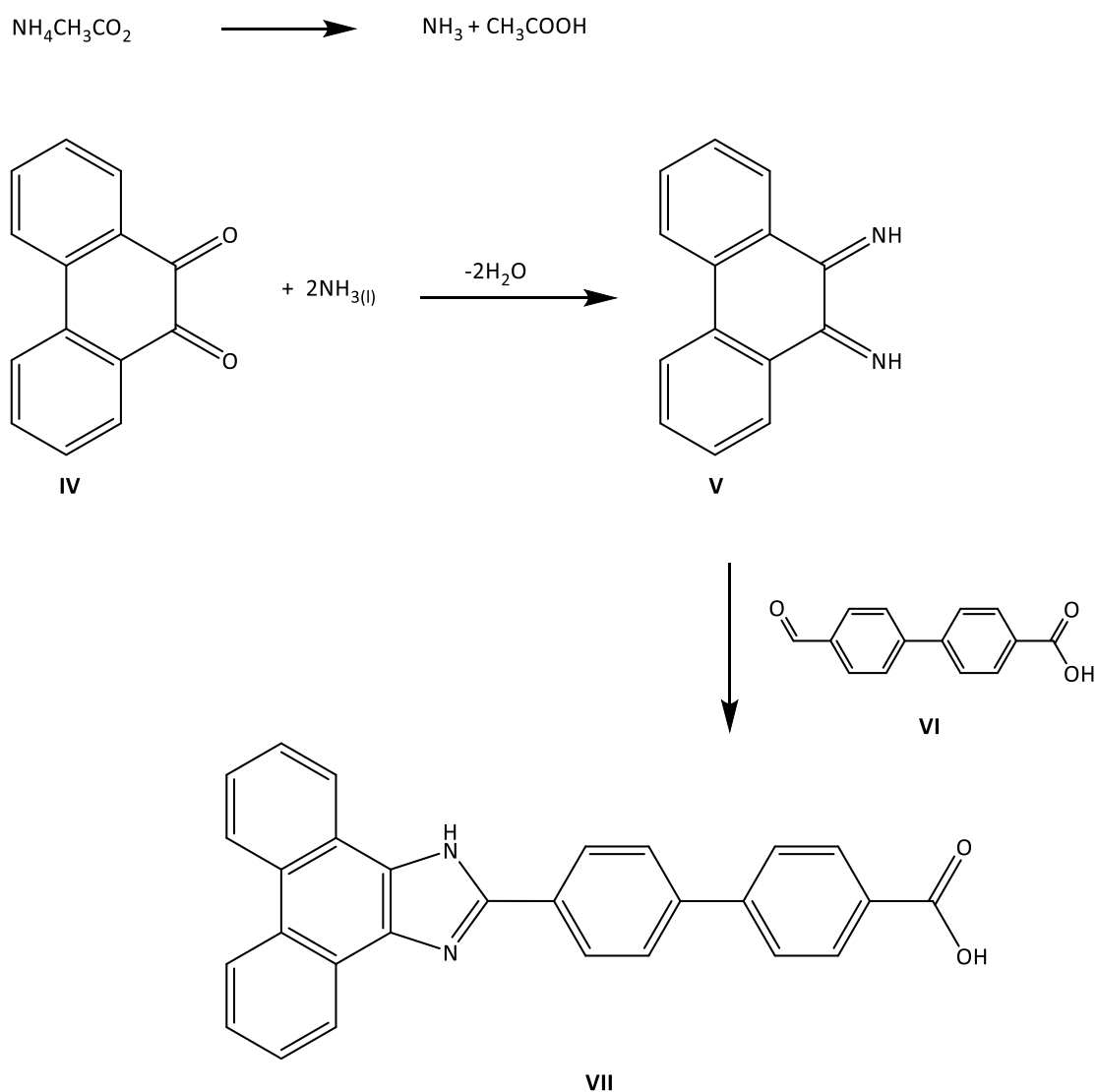


Figure 2.3: ^1H -NMR spectrum of **IV** in d_6 -DMSO.

To generate the imidazole ring present in HNCP₂, the Debus-Radziszewski method²² was used to facilitate the reaction between **IV** and the aldehyde group in 4'-formyl-[1,1'-biphenyl]-4- carboxylic acid (**VI**). The original method involves the reaction between a 1,2-diketone and an aldehyde to cyclise involving a diimide intermediate (**V**), in the presence of dry ammonia in EtOH solution.²² Better yields can be achieved by the use of the Davidson modification²³ of this procedure, where ammonium acetate (NH₄CH₃CO₂) is the source of nitrogen instead of dry ammonia and acetic acid (CH₃COOH) is used as solvent. Scheme 2.2 shows the modified Debus-Radziszewski condensation reaction between a dicarbonyl moiety and the aldehyde used in the synthesis of HNCP₂ (**VII**).



Scheme 2.2: Modified Debus-Radziszewski condensation reaction used in the synthesis of HNCP₂.

The region of the ^1H NMR spectrum, characteristic for aromatic moieties, features signals that result from phenanthroline-derived H-atoms and which are common to both **IV** and **VII**. These signals are observed at chemical shifts of 9.05 and 8.97 ppm for **VII**. The H-atoms on the phenyl ring of the benzoic acid functionality, exhibit signals at 8.44 ppm and 8.01 ppm. The H-atoms on the central phenyl ring of **VII** exhibit signals at 8.07 and 7.90 ppm. The assigned signals are in close agreement with the parent molecule (HNCP) spectrum (Fig. 2.4).^{24, 25}

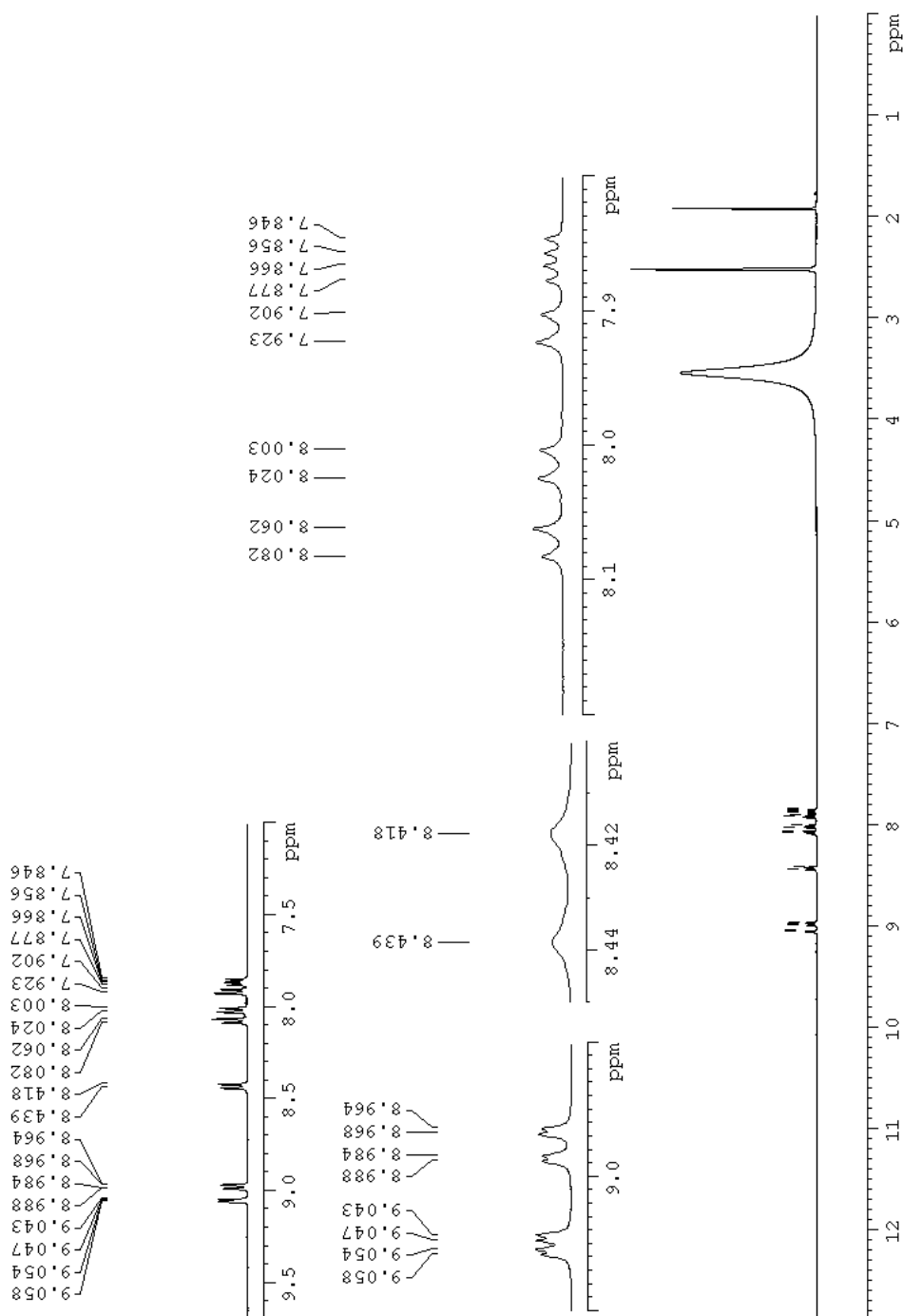


Figure 2.4: ^1H -NMR spectrum of VII in d_6 -DMSO.

FTIR spectroscopy was also carried out to characterise the extended ligand HNCP₂ (**VII**), and revealed signals characteristic of aromatic, conjugated compounds with carboxylic acid functionalities (Fig. 2.5). Broad bands between 3000 and 3500 cm⁻¹ derive from O – H stretches engaged in hydrogen bonds, the N – H vibrations of the imidazole functionality and C – H vibrations of aromatic organic moieties.^{26, 27} The O – H stretches involving hydrogen bonds most likely result in the broad region down to 2600 cm⁻¹. The band at 1710 cm⁻¹ can be assigned to the C = O vibrations of the free carboxylic acid group. Bands between 1620 cm⁻¹ and 1320 cm⁻¹ are due to aromatic C = C and C = N stretching frequencies and N – H bending vibrations.²⁸ The sharp well defined weak band at 1505 cm⁻¹ is characteristic of phenanthroline based ligands as well as the strong band at 850 cm⁻¹ which is assigned to the central ring of phenanthroline.²⁹ The medium intense band observed at 1274 cm⁻¹ most likely arises from the symmetric C – O stretch of the acid functionality.

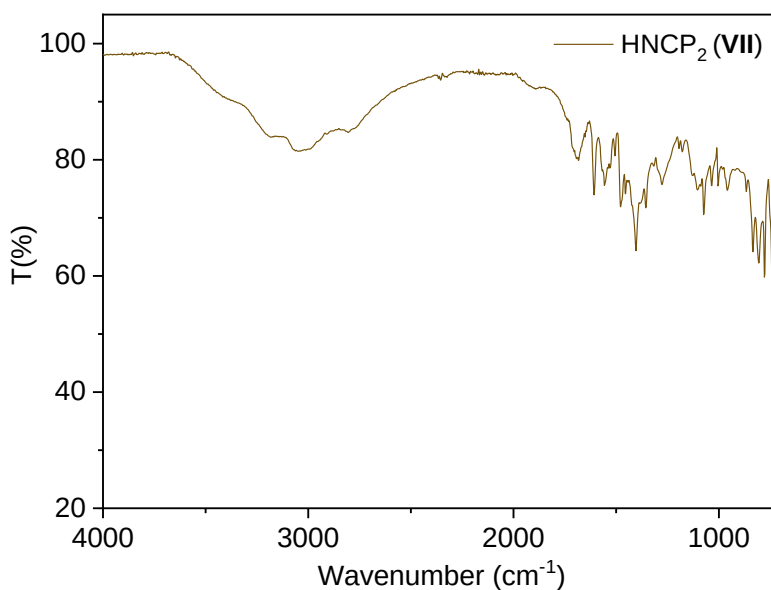


Figure 2.5: FTIR spectrum of VII.

Synthesis of the coordination polymers

Following the successful synthesis of HNCP₂, work then began on exploring the synthesis of coordination compounds and supramolecular structures based on this ligand. The synthetic approach involved the application of solvothermal reaction conditions and the use of hydrochloric acid and acetic acid as modulators. Crystallographic data was acquired by Friedrich Steuber and Dr. Lauren Macreadie and the structures were solved and refined by Dr Brendan Twamley and Dr. Amal Cherian.

2.3. [Co(HNCP₂)(NCP₂)]Cl·2DMF (2.1)

Compound **2.1** was synthesised in a DMF/HCl (20:1 v:v, 4.5 mL) mixture containing HNCP₂ and Co(NO₃)₂·6H₂O. The reaction mixture was heated at 120 °C for two days. Yield: 7.5 mg (0.0075 mmol, 65 %). The coordination compound crystallises in the triclinic space group $P\bar{1}$ with half a formula unit comprising the asymmetric unit. The crystal structure contains a six-coordinate Co^{II} complex, with a distorted octahedral coordination geometry. Each Co^{II} centre is coordinated to four organic ligands. These ligands bind to the Co^{II} metal centre through either monodentate coordination of an O-donor atom or bidentate coordination of the nitrogen donor atoms of the phenanthroline moiety in a *cis* geometry (Fig. 2.6).

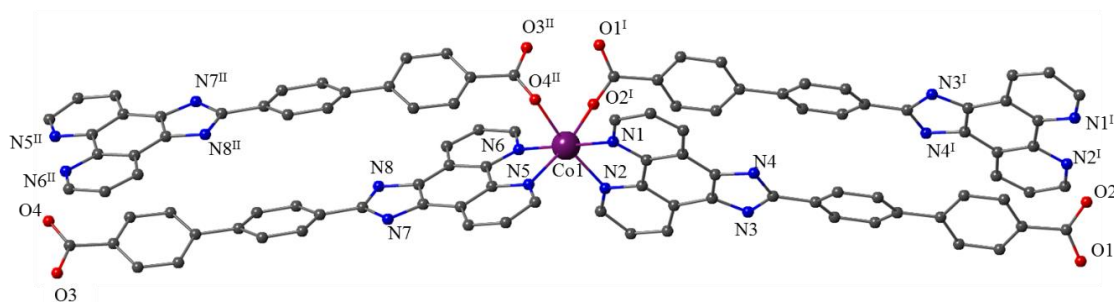


Figure 2.6: Coordination environment of the Co^{II} centre in the crystal structure of [Co(HNCP₂)(NCP₂)]Cl·2DMF, the metal centre is connected to HNCP₂ and NCP₂[−] ligands. Colour code: Co purple, C grey, O red, N blue, H atoms omitted for clarity; Symmetry codes: (I) 2-x, 2-y, 2-z (II) -1-x, -1-y, -1-z.

The HNCP and NCP[−] ligands in **2.1** exhibit identical binding modes. The nitrogen donor atoms from the phenanthroline moiety display asymmetrical bidentate chelation to the

Co^{II} centre, with all the Co – N bond lengths varying in the range of 2.090(4) – 2.124(4) Å. Such relative asymmetric coordination and similar approximate bond distances were observed for [Co₂(phen)₄(Hdczpb)₂]₂·5H₂O and [Co(H₃bptc)₂(phen)₂]. Those coordination polymers contain carboxylic acids and 1,10-phenanthroline as ligands as well as Co centres with very similar coordination environment to Co(1).^{30, 31}

Bond lengths can be used to confirm oxidation states of metal centres through Bond Valence Sum (BVS) analysis. BVS is defined as:

$$BVS = \sum \exp \frac{(R_0 - R_i)}{b} \quad (2.3.1.1)$$

In equation 5.4.1.1, R_0 represents an idealised bond length for a given pair of atoms, R_i represents the observed bond length, and b represents an empirical constant which is typically 0.37 Å.³²

BVS analysis confirms that the Co centre in 2.1 adopts the oxidation state +II (Table 2.1).

Table 2.1: Crystallographically-determined bond lengths for the Co(1) centre in 2.1, along with the assignment of the oxidation state as determined by Bond Valence Sum (BVS) analysis.

Metal Atom	Bonded Atom	Bond Length (Å)	BVS	Oxidation State
Co(1)	N(1)	2.084(4)	1.70	+II
	N(2)	2.113(4)		
	N(5)	2.124(4)		
	N(6)	2.090(4)		
	O(1)	2.150(3)		
	O(3)	2.121(3)		

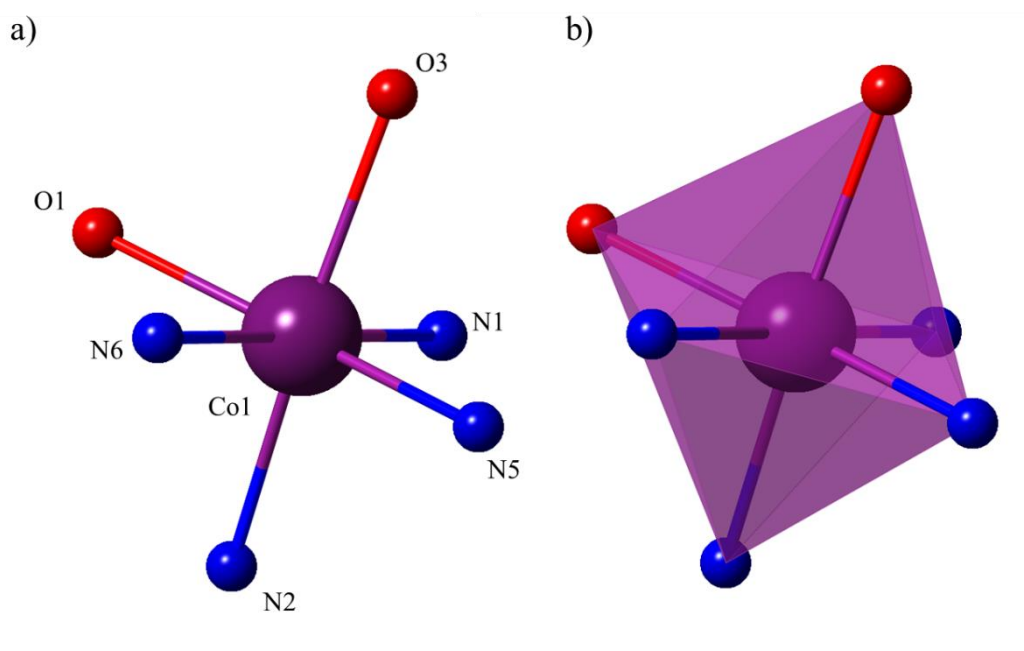


Figure 2.7: Co^{II} coordination environment in [Co(HNCP₂)(NCP₂)]Cl·2DMF (a); Polyhedral representation of the distorted octahedral coordination geometry (b); Colour code: Co purple, O red, N blue.

A monodentate binding mode is exhibited by the carboxylate O-donor atoms of the HNCP₂/NCP[−] ligands. The Co – O bond lengths are 2.150(3) Å for Co(1) – O(1) and 2.121(3) Å for Co(1) – O(3) and are in close agreement with bond distances reported for compounds containing similar SBUs (Fig. 2.7).³³⁻³⁵

The distorted nature of the octahedral coordination geometry of the Co^{II} centre is confirmed by the bond angles. The bond angles O(3) – Co(1) – N(2) and O(1) – Co(1) – N(5) of 168.41(8) and 170.0(5), respectively, deviate from the ideal octahedral angle of 180°. The O(3) – Co(1) – N(1) and O(3) – Co(1) – N(6) angles of 90.13(7)° and 90.56(5)°, respectively, show relatively small deviations from the ideal angle of 90°. Selected bond angles are displayed in Table 2.2.

Table 2.2: Selected bond lengths (Å) and angles (°) for 2.1.

Atoms	Angles (°)	Atoms	Angles (°)
O(3) – Co(1) – N(2)	168.41(8)	N(1) – Co(1) – N(2)	78.75(15)
O(1) – Co(1) – N(5)	170.0(5)	N(6) – Co(1) – N(5)	78.99(15)
O(3) – Co(1) – N(1)	90.13(7)	O(3) – Co(1) – N(6)	90.56(5)

Intramolecular hydrogen bonding prevails in **2.1**, involving the O(2) – H···O(4) structural motif of adjacent carboxylate groups that bind in *cis* arrangement of the octahedral Co^{II} environment (Fig 2.8). The observed distance between the H(16) and O(4) is 1.661(3) Å which is indicative of a strong H-bond interaction; the corresponding O(2) – O(4) distance is 2.481(5) Å. The ligand connectivity results in a 1D bilayered polymer structure that extends in the crystallographic [111] direction (Fig 2.9).

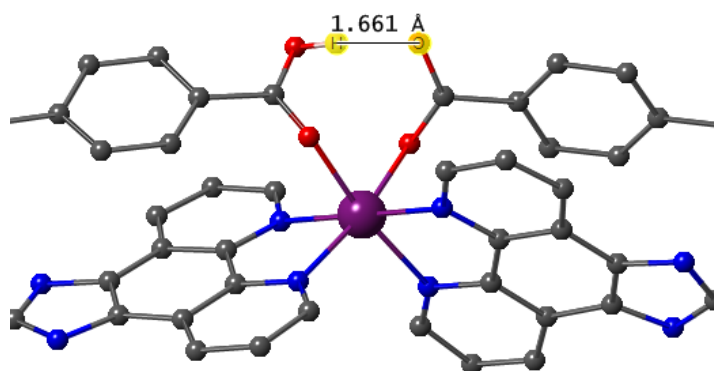


Figure 2.8: Intramolecular H-bonded motif in $[\text{Co}(\text{HNCP}_2)(\text{NCP}_2)]\text{Cl}\cdot 2\text{DMF}$; other hydrogen atoms were omitted for clarity.

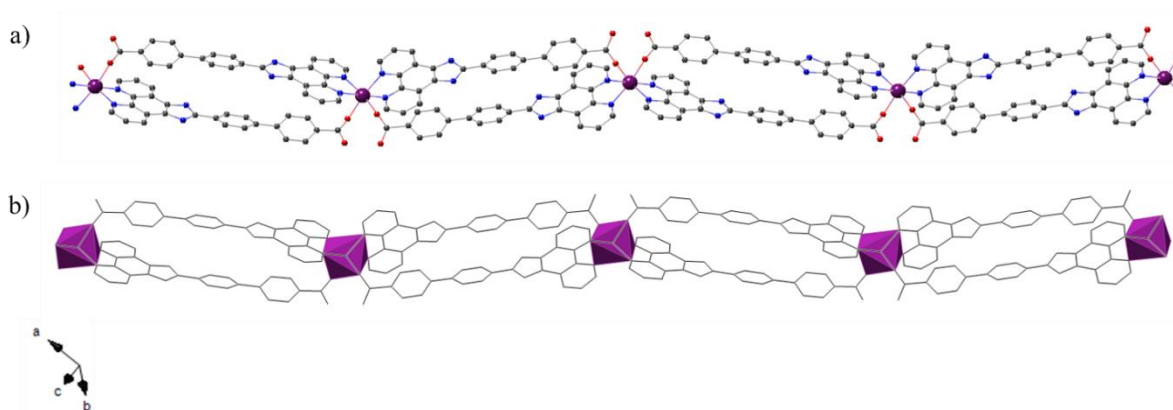


Figure 2.9: Polymeric, bilayered chain in 2.1 (a); Polyhedral representation of the Co^{II} coordination environments in $[\text{Co}(\text{HNCP}_2)(\text{NCP}_2)]\text{Cl}\cdot 2\text{DMF}$ (b); Colour code: Co purple, C grey, O red, N blue, H atoms omitted for clarity.

The Cl^- counter ion influences the overall crystal packing. It interacts with the imidazole H – atom *via* $\text{Cl}^- \cdots \text{H} - \text{N}$ interactions and locates between two neighbouring chains (Fig. 2.10). The closest phenyl centroid distances between two parallel aligned ligands within the chain motifs are 3.524(3) Å, hence fall within the range of moderately strong $\pi - \pi$ interactions.³⁶

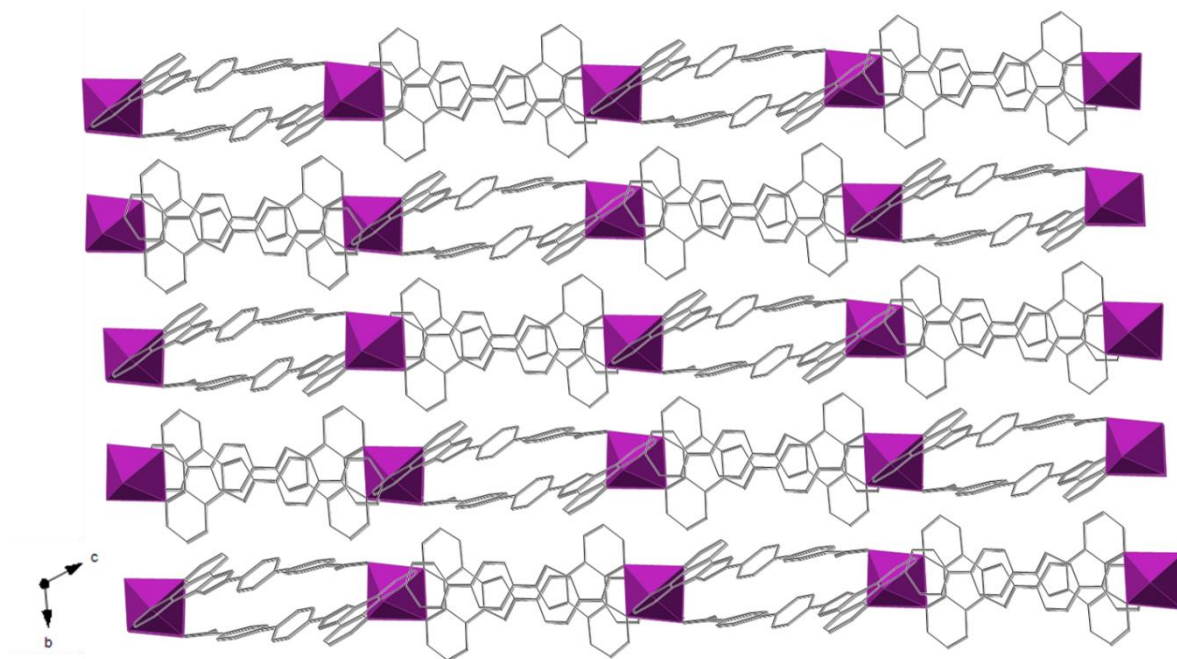


Figure 2.10: Packing arrangement of 1D chains in $[\text{Co}(\text{HNCP}_2)(\text{NCP}_2)]\text{Cl}\cdot 2\text{DMF}$ as seen along the crystallographic a -axis. H atoms omitted for clarity.

Table 2.3: Crystal data and structure refinement for 2.1.

Identification code	2.1
Empirical formula	C ₅₅ H ₃₈ ClCoN ₉ O ₅
Formula weight/ g mol ⁻¹	999.32
Temperature/K	100
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> /Å	12.9564(14)
<i>b</i> /Å	13.3112(14)
<i>c</i> /Å	14.9380(16)
α /°	108.232(5)
β /°	108.086(4)
γ /°	102.024(5)
Volume/Å ³	2188.9(4)
<i>Z</i>	2
ρ_{calc} /cm ³	1.516
μ /mm ⁻¹	0.519
<i>F</i> (000)	1030.0
Crystal size/mm ³	0.2 × 0.1 × 0.06
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	5.098 to 50.966
Index ranges	-15 ≤ <i>h</i> ≤ 15, -15 ≤ <i>k</i> ≤ 16, -17 ≤ <i>l</i> ≤ 18
Reflections collected	17822
Independent reflections	8072 [<i>R</i> _{int} = 0.1014, <i>R</i> _{sigma} = 0.1754]
Data/restraints/parameters	8072/60/623
Goodness-of-fit on <i>F</i> ²	1.024
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0853, <i>wR</i> ₂ = 0.1957
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1793, <i>wR</i> ₂ = 0.2388
Largest diff. peak/hole / e Å ⁻³	1.68/-1.36

2.3.1. Further characterization of 2.1

The FTIR spectrum for compound **2.1** (Fig. 2.11) is characteristic for a coordination compound that contains carboxylate-functionalised phenanthroline-based ligands. The strong peak at *ca.* 1690 cm^{-1} is due to the (C = O) stretch in the DMF molecules, the presence of constitutional solvent is in agreement with the crystal structure. The spectrum also revealed band at *ca.* 1716 cm^{-1} that can be assigned as the protonated carboxylic acid functionality. The vibration for $\nu(\text{C} - \text{N})$ and $\nu(\text{C} - \text{O})$ can be assigned to strong bands at 1087 cm^{-1} and 1014 cm^{-1} . The frequencies corresponding to the symmetric and asymmetric stretching vibrations of the carboxylate moiety are assigned to signals at 1362 cm^{-1} and 1568 cm^{-1} . The latter is in close agreement with the signal observed for $[\text{Co}(\text{O}_2\text{CMe})\text{NH}_3)_5]$ that also exhibits unidentate coordination mode.³⁷ A Deacon-Phillips value $\Delta = \nu_{\text{as}}(\text{CO}_2) - \nu_{\text{s}}(\text{CO}_2) = 206\text{ cm}^{-1}$ is consistent with the observed binding mode.^{38,39} Generally the expected C – H and N – H vibrations $> 3000\text{ cm}^{-1}$ only occur in low intensity.

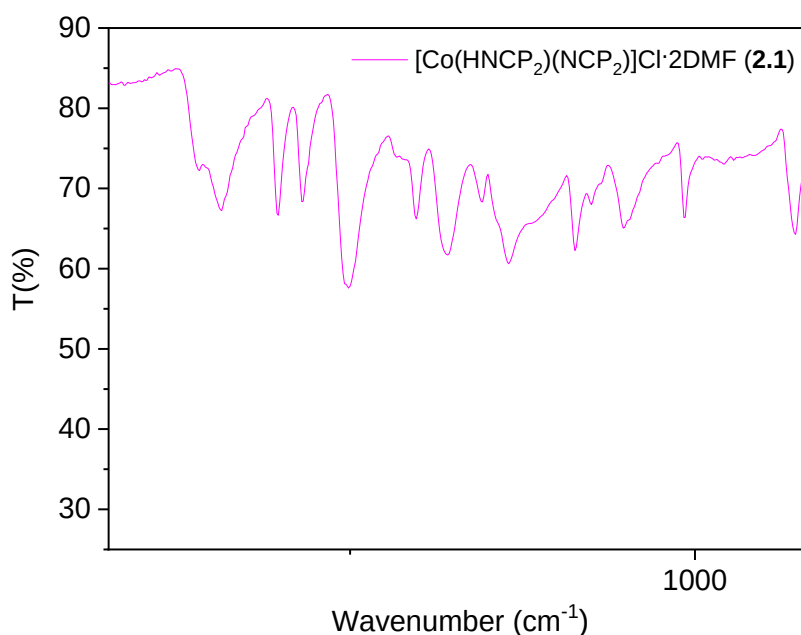


Figure 2.11: FTIR spectrum of 2.1.

The thermal stability of **2.1** was also evaluated by thermogravimetric analysis in an air atmosphere, revealing stability up to *ca.* 200 °C upon which the compound undergoes degradation (Fig. 2.12). An initial step corresponding to the loss of the two constitutional DMF molecules commences at *ca.* 150°C and corresponds to the loss of *ca.* 14 % of the sample weight. Further, the compound decomposes in two major degradation events centred at 200 and 275°C.

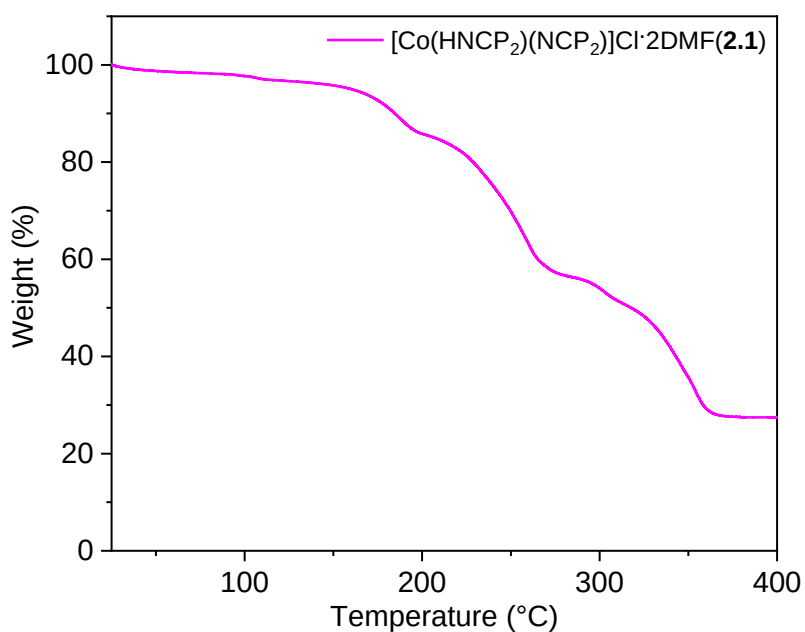


Figure 2.12: Thermogravimetric analysis for 2.1.

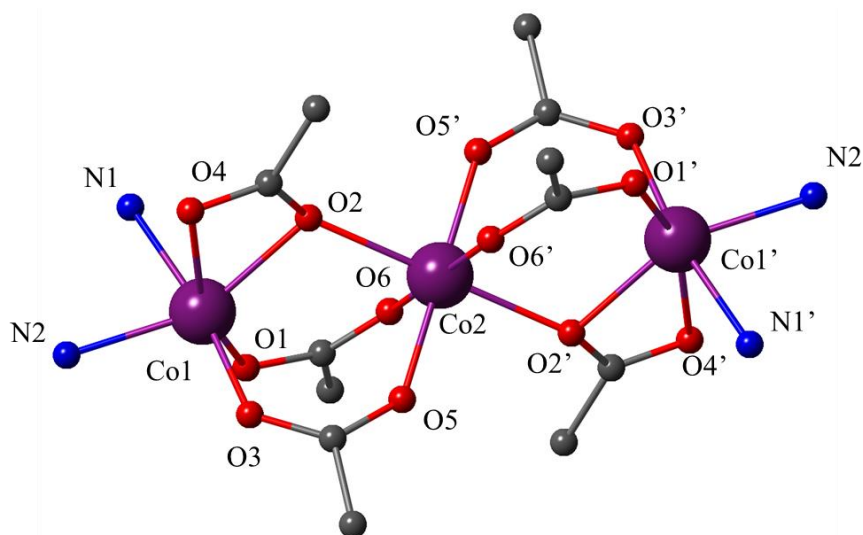


Figure 2.14: Core structure of the linear trinuclear Co^{II} unit showing the coordination environment of the three metal centres and the coordination modes of the acetate ligands; the latter involve bidentate, monodentate bridging and bidentate chelating modes. Colour code: Co purple, C grey, O red, N blue, H atoms omitted for clarity. Symmetry code: 3-x, 1-y, 3-z.

The terminal Co(1) atom and its symmetry equivalent Co(1'), are six coordinate, adopting a distorted octahedral binding geometry (Fig. 2.15). One HNCP_2 ligand coordinates to each terminal Co^{II} centre exhibiting bidentate coordination through the nitrogen donor atoms while the oxygen donor atoms of the carboxylate groups remain protonated. The Co – N bonds reveal bond lengths of 2.086(2) and 2.154(2) Å, which are in agreement with reported Co^{II} phenanthroline complexes.⁴⁰⁻⁴² The coordination environment is completed by the coordination to the previously discussed acetate groups. The corresponding bond lengths vary in a close range showing values of 2.043(18) and 2.044(18) Å for Co(1) – O(2) and Co(1) – O(4) and symmetry equivalents. BVS analysis confirms that Co(1) is in oxidation state +II (Table 2.4).

The highly distorted nature of octahedral coordination geometry of the terminal Co^{II} ions can be exemplified by analysing the bond angles involving the Co(1) centre. The $\text{N}(1) - \text{Co}(1) - \text{N}(2)$ and $\text{O}(2) - \text{Co}(1) - \text{O}(3)$ angles of $77.75(8)^\circ$ and $95.97(7)^\circ$, respectively, deviate from the ideal angle of 90° .

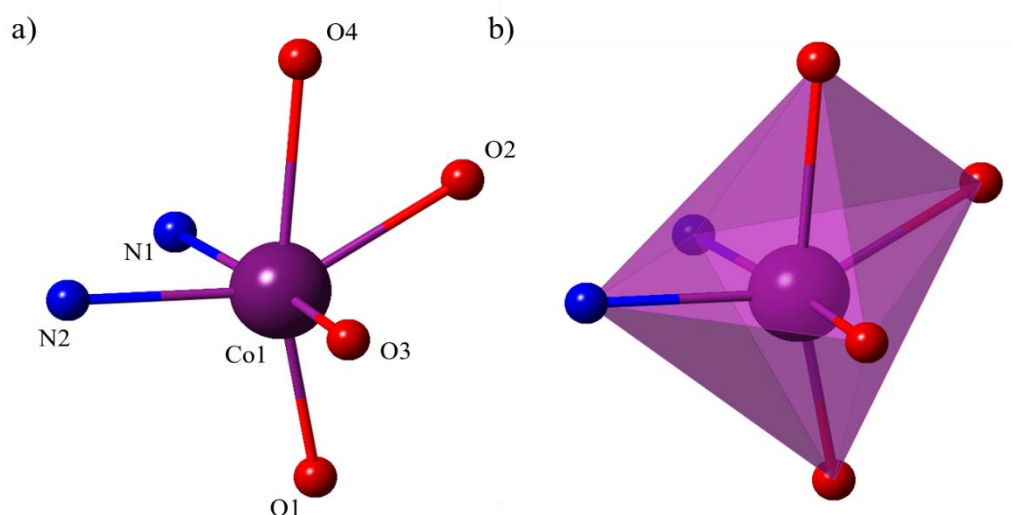


Figure 2.15: Coordination environment for the terminal Co^{II} atoms in $[\text{Co}_3(\text{HNCP}_2)_2(\text{OAc})_6] \cdot \text{DMF}$ (a); Polyhedral representation of the distorted octahedral coordination geometry (b); Colour code: Co purple, O red, N blue, H atoms omitted for clarity; Symmetry code: 3-x, 1-y, 3-z.

Table 2.4: Crystallographically-determined bond lengths for the Co(1) centre in 2.2, along with their oxidation state as determined by Bond Valence Sum (BVS) analysis.

Metal Atom	Bonded Atom	Bond Length (Å)	BVS	Oxidation State
Co(1)	N(1)	2.154(2)	1.80	+II
	N(2)	2.086(2)		
	O(3)	2.021(18)		
	O(2)	2.043(18)		
	O(4)	2.044(18)		
	O(1)	2.337(2)		

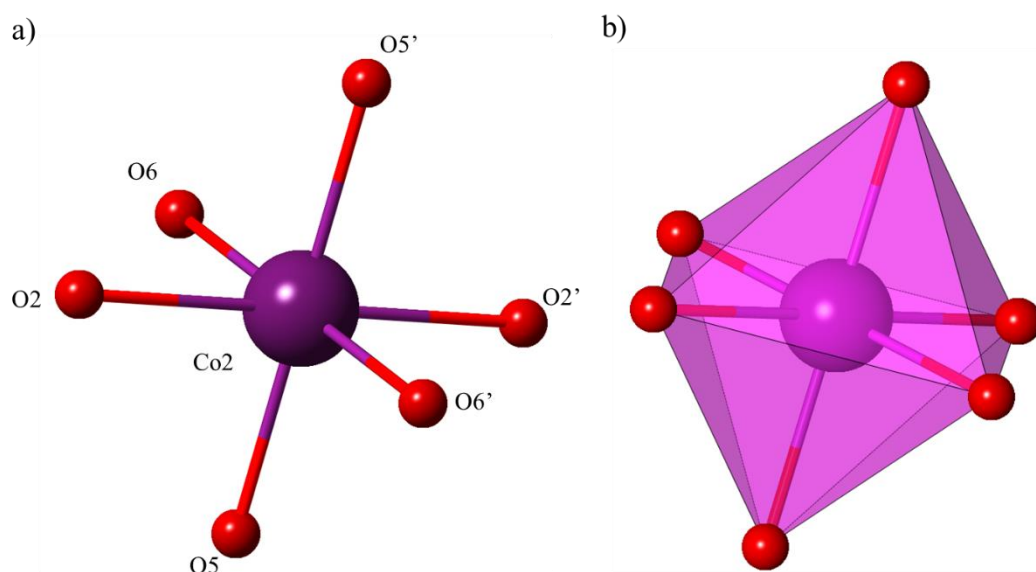


Figure 2.16: Coordination environment of the central Co^{II} ion in $[\text{Co}_3(\text{HNCP}_2)_2(\text{OAc})_6]\cdot\text{DMF}$ (a); Polyhedral representation of the distorted octahedral coordination geometry(b); Colour code: Co purple, O red; Symmetry code: 3-x, 1-y, 3-z.

The central Co(2) centre adopts a relatively symmetrical octahedral coordination environment which entirely comprises O-donor atoms of the acetate ligands (Fig. 2.16). The Co – O bonds reveal bond lengths that vary from 2.337(2) Å to 2.021(18) Å. BVS analysis confirms that Co(2) also adopts the oxidation state +II (Table 2.5).

Table 2.5: Crystallographically-determined bond lengths for the Co(2) centre in 2.2, along with its oxidation state as determined by Bond Valence Sum (BVS) analysis.

Metal Atom	Bonded Atom	Bond Length (Å)	BVS	Oxidation State
Co(2)	O(6)	2.154(2)	1.80	+II
	O(6')	2.086(2)		
	O(5)	2.021(18)		
	O(5')	2.043(18)		
	O(2)	2.044(18)		
	O(2')	2.337(2)		

The relatively symmetric coordination environment also relates from the fact that the atom locates on an inversion centre within the crystal structure of 2.2. The slight distortion

of the octahedral coordination geometry of the Co(2) atom within **2.2** is characterised by the bond angles of O(5) – Co(2) – O(2) and O(5) – Co(2) – O(6) of 91.00(4)° and 91.2(5)°, respectively. These are in close agreement with the ideal angle of 90°. Selected angles in **2.2** are summarised in Table 2.6.

Table 2.6: Selected bond angles (°) for 2.2 Symmetry code: 3-x, 1-y, 3-z.

Atoms	Angles (°)	Atoms	Angles (°)
N(1) – Co(1) – N(2)	77.75(8)	O(5) – Co(2) – O(2)	91.00(4)
N(1) – Co(1) – O(1)	88.60(6)	O(5) – Co(2) – O(6)	91.20(5)
O(3) – Co(1) – O(1)	95.97(7)	O(5) – Co(2) – O(5')	180.00(8)
O(4) – Co(1) – O(3)	91.93(4)	Co(1) – O(2) – Co(2)	110.81(8)
		Co(1) – Co(2) – Co(1)	180.00(12)

The presence of intermolecular H-bonds involving the H-atoms of the carboxylic acid groups and the oxygen atoms of the bridging acetate groups may contribute to the stabilisation of the structure (Fig. 2.17). The H...OH distance is approximately 1.85 Å which indicates the presence of relatively strong H – bond interactions.

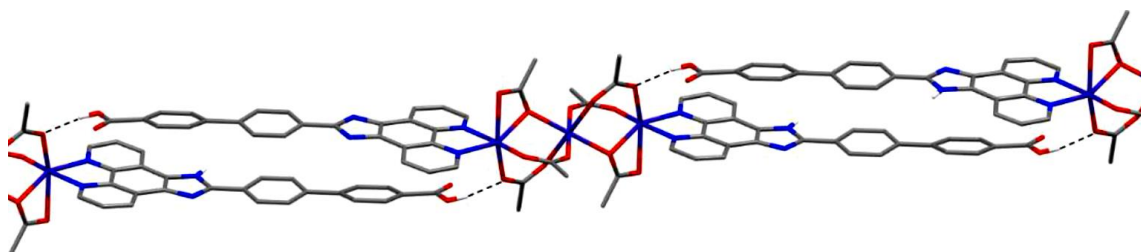


Figure 2.17: The packing of [Co₃(HNCP₂)₂(OAc)₆] molecules via intermolecular H-bonds involving the H-atoms of the carboxylic acid groups and the oxygen atoms of the bridging acetate group; structure viewed in the direction of the crystallographic *c*-axis. Hydrogen atoms not participating in hydrogen bonding and DMF molecules were omitted for clarity.

The packing arrangement of the molecular entities in **2.2** can be seen in Figure 2.18 in which the trinuclear units are portrayed in perspective along the crystallographic *c*-axis. The closest intermolecular distance between centroid positions of phenanthroline and phenyl moieties within the packing arrangement is *ca.* 3.68 Å, suggesting rather weak $\pi - \pi$ interactions that stabilise the packing arrangement.

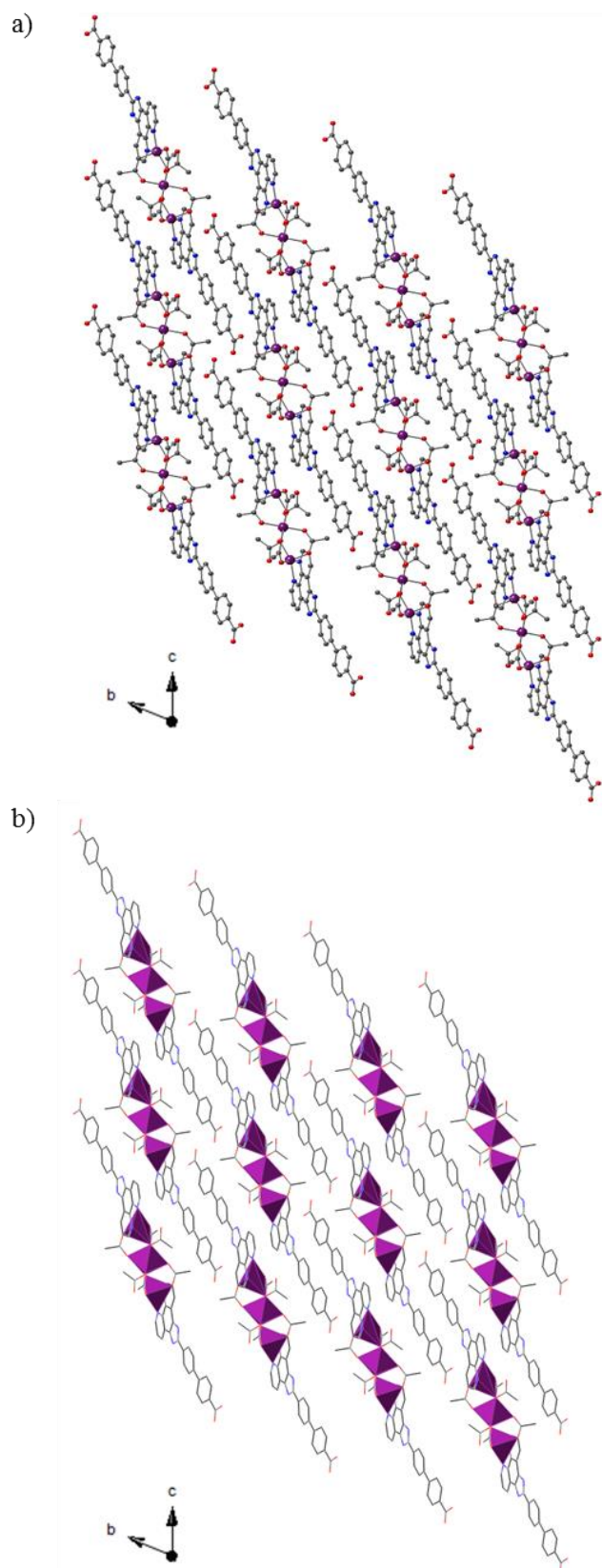


Figure 2.18: Packing arrangement for $[\text{Co}_3(\text{HNCP}_2)_2(\text{OAc})_6] \cdot \text{DMF}$ with view in the direction of the crystallographic a-axis (a); Polyhedral representation of the CoII coordination environment (b); Colour code: Co purple, O red, N blue, H atoms and DMF molecules omitted for clarity.

The discrete nature of the trinuclear complexes can be clearly observed by the packing arrangement as shown with view in the crystallographic *b*- and *c*-axes (Fig. 2.19).

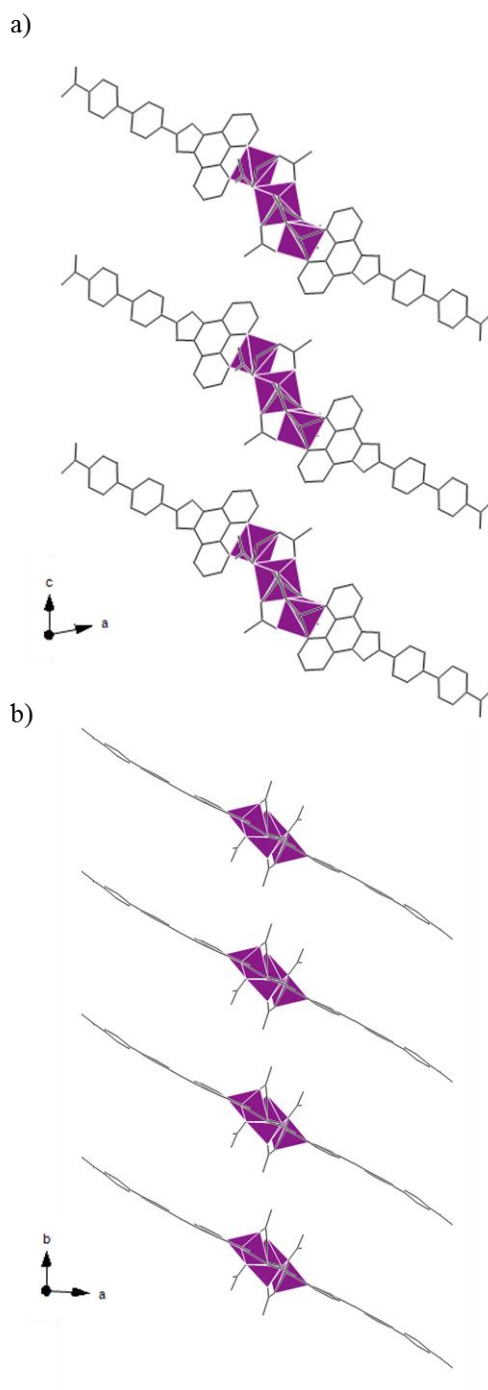


Figure 2.19: Polyhedral representation and packing arrangement of the trinuclear complexes in $[\text{Co}_3(\text{HNCP}_2)_2(\text{OAc})_6]\cdot\text{DMF}$; views in the direction of the crystallographic *b*-axis (a) and *c*-axis (b); Colour code: Co purple, C grey, H, O and N atoms as well as DMF molecules omitted for clarity.

Table 2.7: Crystal data and details of the structure determination for 2.2.

Identification code	2.2
Empirical formula	C ₇₀ H ₆₄ Co ₃ N ₁₀ O ₁₈
Formula weight/g mol ⁻¹	1510.10
Temperature/K	220
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> /Å	8.5478(11)
<i>b</i> /Å	14.0205(19)
<i>c</i> /Å	14.8150(19)
α /°	97.086(9)
β /°	104.092(8)
γ /°	105.751(8)
Volume/Å ³	1622.9(4)
<i>Z</i>	1
ρ_{calc} /cm ³	1.543
μ /mm ⁻¹	6.639
<i>F</i> (000)	779
Crystal size/mm ³	0.3 × 0.2 × 0.2
Radiation	CuK α (λ = 1.54178)
2 Θ range for data collection/°	3.141 to 68.165
Index ranges	-10 ≤ <i>h</i> ≤ 10, -16 ≤ <i>k</i> ≤ 16, -17 ≤ <i>l</i> ≤ 17
Reflections collected	13576
Independent reflections	5743 [<i>R</i> _{int} = 0.0538, <i>R</i> _{sigma} = 0.0819]
Data/restraints/parameters	5743/0/457
Goodness-of-fit on <i>F</i> ²	1.465
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.2183, <i>wR</i> ₂ = 0.4681
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.2648, <i>wR</i> ₂ = 0.5048
Largest diff. peak/hole / e Å ⁻³	1.165/-1.269

2.4.1. Further characterisation of 2.2

Characteristically, the IR spectrum of a dried sample of compound **2.2** (Fig. 2.20) contains a signal at 1710 cm^{-1} which originates from the $\nu(\text{C}=\text{O})$ vibrations of the non-coordinating carboxylic acid functionalities of the HNCP₂ ligands that retain their H-atoms.^{26, 28} Broad asymmetric carboxylate stretches of the acetate ligands appear in the IR spectrum at *ca.* 1580 cm^{-1} . An additional band occurs at 1400 cm^{-1} which may be assignable to the symmetric $\nu(\text{C}-\text{O})$ stretch. Deacon-Phillips values $\Delta = \nu_{\text{as}}(\text{CO}_2) - \nu_{\text{s}}(\text{CO}_2) = 180\text{ cm}^{-1}$ were found are in agreement with the *syn*, *syn*-bidentate bridging mode of the acetate ligands in the trinuclear complexes.³⁸ The spectrum also reveals bands in the range of 1240 cm^{-1} to 1100 cm^{-1} assigned to $\nu(\text{C}-\text{N})$ and $\nu(\text{C}-\text{N})$.

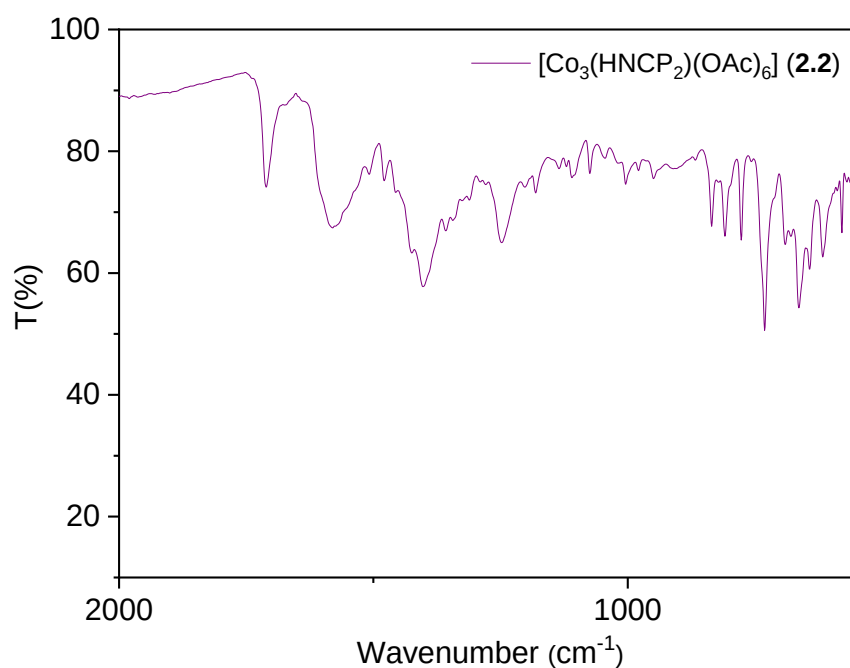


Figure 2.20: FTIR spectrum of 2.2.

The thermal stability of a dried sample **2.2** was evaluated by thermogravimetric analysis in an air atmosphere (Fig. 2.21). Under these experimental conditions, compound **2.2** decomposes in two thermogravimetric steps. An initial step is observed between 100-230 °C and corresponds to the loss of *ca.* 22 % of the sample weight. The first step most likely can be assigned to loss of the acetate groups.⁴³ The second and last step starting at *ca.* 275°C is due to the oxidation of the organic ligand residues.

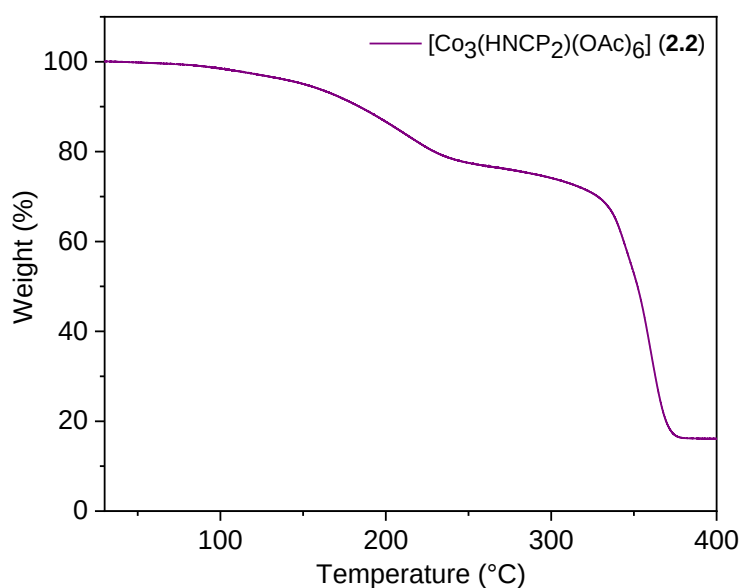


Figure 2.21: Thermogravimetric analysis for 2.2.

2.5. $[\text{Zn}^{\text{II}}(\text{NCP}_2)\text{Cl}]$ (**2.3**)

$[\text{Zn}^{\text{II}}(\text{NCP}_2)\text{Cl}]$ (**2.3**) was prepared by the reaction of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with HNCP_2 in DMF solution, in the presence of aqueous HCl (2M). Cubic yellow crystals of **2.3** were obtained by heating the reaction mixture at 120 °C for two days. The material was characterised by single crystal X-ray diffraction measurements. **2.3** crystallises in the monoclinic space group $P2_1/c$, and consists of 1D coordination polymers composed of mononuclear Zn^{II} SBUs whereby one formula unit comprises the asymmetric unit. The Zn^{II} ion is five-coordinate, adopting a distorted square pyramidal coordination geometry. Two NCP_2^- ligands coordinate to the metal centre, one exhibiting bidentate coordination through the nitrogen donor atoms and the other exhibiting bidentate coordination through oxygen donor atoms of the carboxylate group. The coordination environment is then completed by the coordination of one chloride ion located in the apical position (Fig. 2.22).

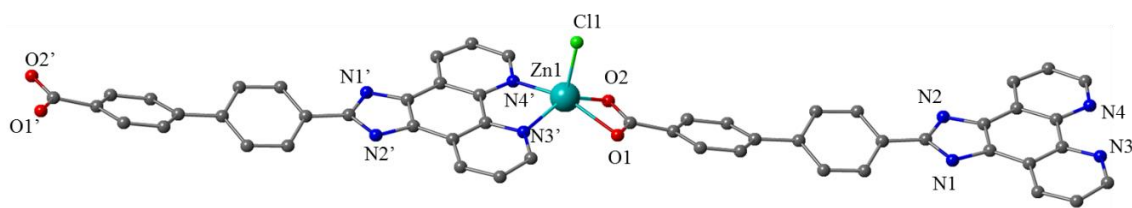


Figure 2.22: Coordination environment of the Zn^{II} centre in the crystal structure of $[\text{Zn}^{\text{II}}(\text{HNCP}_2)\text{Cl}]$; the metal centre is connected to two NCP_2^- ligands; a chloride ion completes the square pyramidal coordination environment. Colour code: Zn turquoise, C grey, O red, N blue, H atoms omitted for clarity; Symmetry code: $1+x, +y, 1+z$.

The Zn^{II} centre adopts a relatively symmetric square pyramidal, five-coordinate binding environment. The $\text{Zn} - \text{N}$ bonds reveal bond lengths of 2.057(3) and 2.088(3) Å which are in agreement with comparable phenanthroline or bipyridine complexes reported in the literature.⁴⁴⁻⁴⁶

BVS analysis confirms that the $\text{Zn}(1)$ centre in **2.3** is in oxidation state +II (Table 2.8)

Table 2.8: Crystallographically-determined bond lengths for the zinc centre in 2.3, along with their oxidation state as determined by Bond Valence Sum (BVS) analysis.

Metal Atom	Bonded Atom	Bond Length (Å)	BVS	Oxidation State
Zn(1)	N(3)	2.088(3)	2.009	+II
	N(4)	2.057(3)		
	O(1)	2.208(2)		
	O(3)	2.033(2)		
	Cl(1)	2.293(9)		

The unit involves O,O'-chelation of the carboxylate moiety of the NCP_2^- to the Zn(1) centre. The corresponding bond lengths of 2.033(2) and 2.208(2) Å are agreement with those of other reported series of new Zn^{II} complexes with flufenamic acid and pyridine containing an equivalent SBU.⁴⁷ The observed Zn – Cl bond length is 2.293(9) Å, which is also in agreement with reported five-coordinated Zn^{II} complexes.^{45, 47}

The distorted nature of the square pyramidal coordination is exemplified by the bond angles involving the central Zn^{II} ion (Fig. 2.23) Indeed, N(4) – Zn(1) – N(3) and O(3) – Zn(1) – O(1) angles of 80.64(10)° and 62.41(9)°, respectively, deviate from the ideal angle of 90°. The five coordinate geometry index τ_5 is defined as:

$$\tau_5 = \frac{\alpha_1 + \alpha_2}{60^\circ} \quad (2.5.1)$$

where α_1 and α_2 represent the largest and second largest bond angles within the inner coordination sphere, respectively. The geometry index for an ideal square pyramid is $\tau_5 = 0$ and for an ideal trigonal bipyramidal polygon, it is $\tau_5 = 1$. A value of $\tau_5 = 0.03$ indicates a minor distortion from a square pyramidal coordination mode.⁴⁸ Selected bond angles in 2.3 are summarised in Table 2.9.

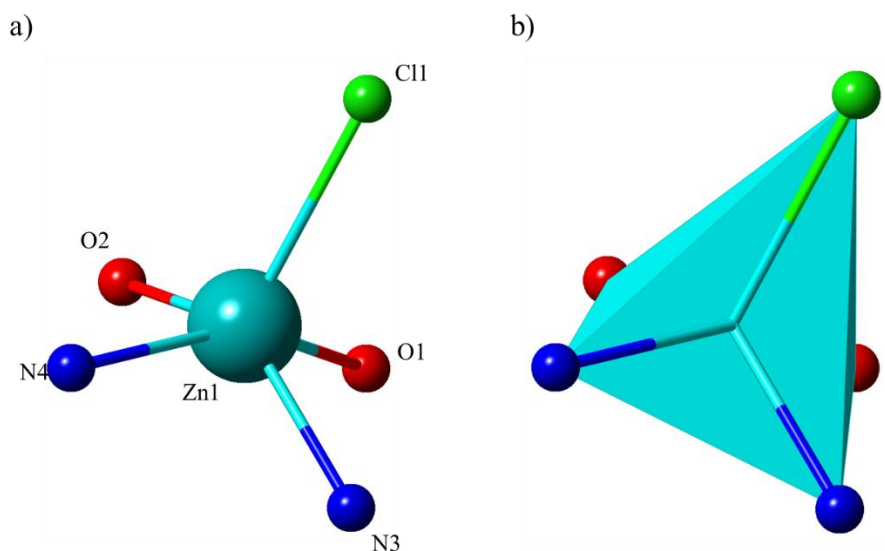


Figure 2.23: Zn^{II} coordination environment in $[\text{Zn}^{\text{II}}(\text{NCP}_2)\text{Cl}]$ (a); Polyhedral representation of the Zn^{II} coordination geometry (b); Colour code: Zn turquoise, O red, N blue, Cl green, H atoms omitted for clarity.

Table 2.9: Selected bond angles ($^\circ$) for 2.3.

Atoms	Angles($^\circ$)	Atoms	Angles($^\circ$)
O(1) – Zn(1) – Cl(1)	104.19(4)	N(4) – Zn(1) – N(3)	80.64(10)
N(3) – Zn(1) – O(1)	96.11(9)	O(2) – Zn(1) – O(1)	62.41(9)
Cl(1) – Zn(1) – N(3)	102.23(7)	O(1) – Zn(1) – Cl(1)	101.25(7)

The connectivity of the organic ligands and the mononuclear Zn^{II} SBUs in compound **2.3** results in chains, whereby the 1D polymeric structure extend parallel to the *c*-axis as seen in Figure 2.24.

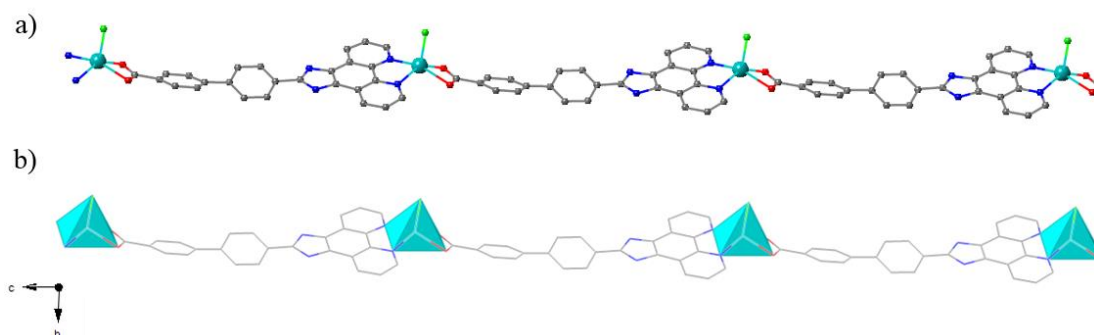


Figure 2.24: 1D polymeric chain formed through the bridging of Zn^{II} SBUs as seen in the direction of the crystallographic *a*-axis (a); Polyhedral representation of the zinc complexes in the chain (b); Colour code: Zn turquoise, C grey, O red, N blue, H atoms omitted for clarity.

The Cl^- present in the coordination sphere of the Zn^{II} centres influence the supramolecular packing of the structure. $\text{N} - \text{H} \cdots \text{Cl}$ interactions prevail approximately in the direction of the crystallographic *b*-axis and promote the formation of double chain motifs.

Within the double chain motif the orientation of the Zn centres alternates 180° (Fig. 2.25 and Fig/ 2.27), facilitating the interaction between the Cl atoms and the $\text{N} - \text{H}$ moieties of the imidazole rings. The observed $\text{N} - \text{H} \cdots \text{Cl}$ distance of *ca.* 2.263(7) Å is consistent with strong $\text{N} - \text{H} \cdots \text{Cl}$ H-interactions reported for supramolecular networks where those secondary interactions lead to 2D architectures.⁴⁹

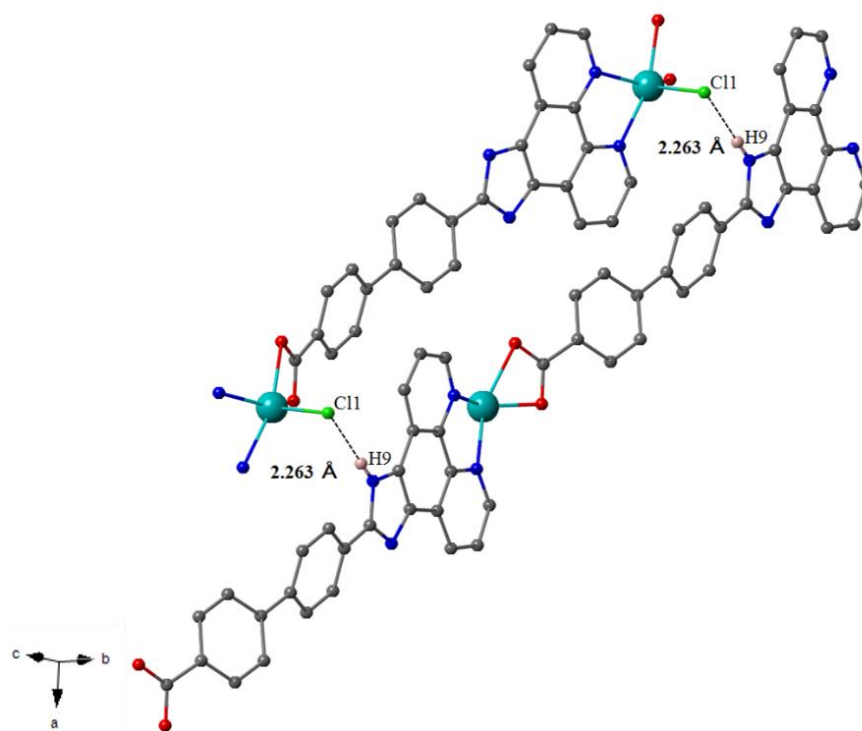


Figure 2.25: The observed N – H...Cl H-interactions give rise to an N...Cl distance of *ca.* 2.26 Å. Colour code: Zn turquoise, C grey, O red, N blue, H atoms omitted for clarity.

The closest observed phenanthroline-phenyl centroid distances within the double chain motif account for 3.934(3) Å, thus may fall within the range of weak $\pi - \pi$ interactions.³⁶ These interactions are facilitated by the layered packing arrangement exhibited by the structure, as seen in Figures 2.26 and 2.27.

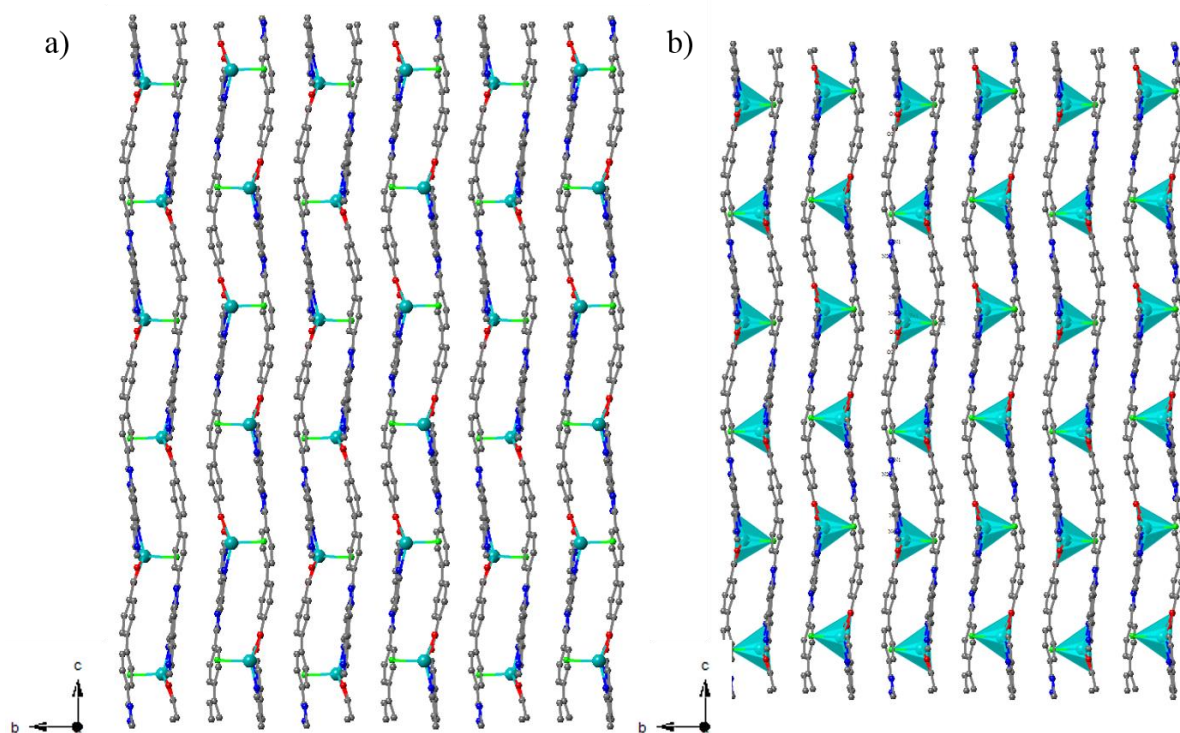


Figure 2.26: 1D chains packing arrangement for $[\text{Zn}^{\text{II}}(\text{NCP}_2)\text{Cl}]$ as seen along the crystallographic a -axis showing; Colour code: Zn turquoise, C grey, O red, N blue, H atoms omitted for clarity.

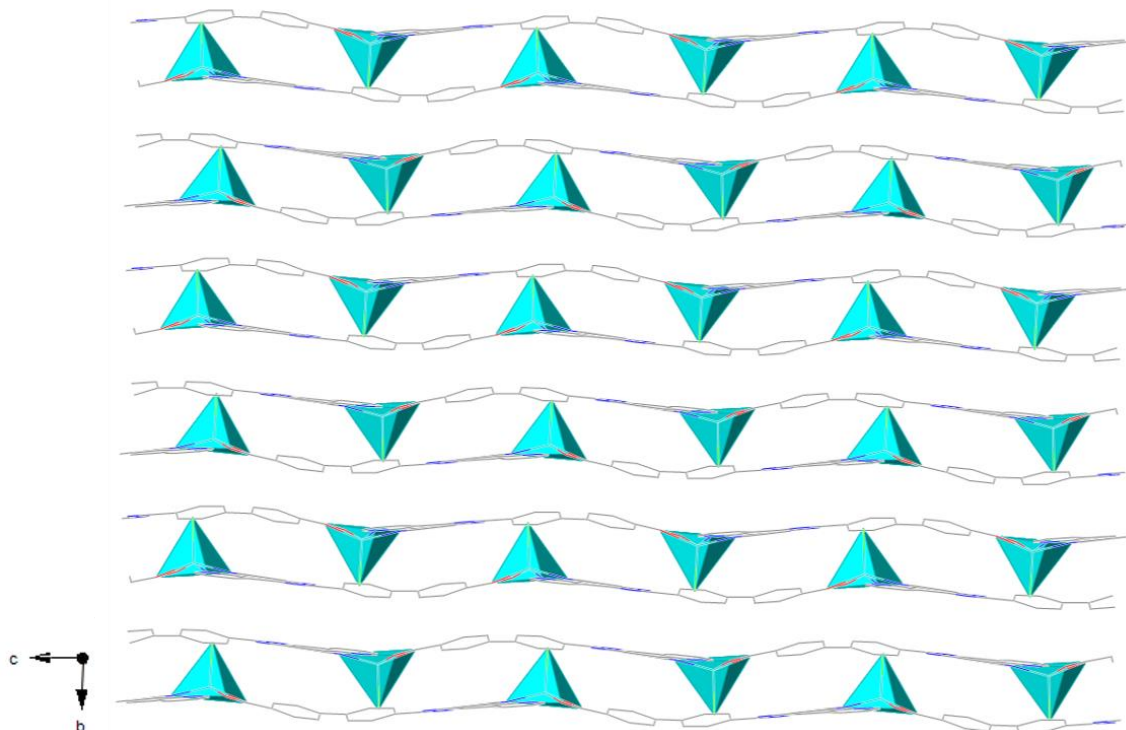


Figure 2.27: 1D chains within the packing arrangement of $[\text{Zn}^{\text{II}}(\text{NCP}_2)\text{Cl}]$ as seen along the crystallographic a -axis.

Table 2.10: Crystal data and structure refinement for 2.3.

Identification code	2.3
Empirical formula	C ₂₆ H ₁₅ ClN ₄ O ₂ Zn
Formula weight/ g mol ⁻¹	516.24
Temperature/K	100
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	9.7799(2)
<i>b</i> /Å	12.5085(3)
<i>c</i> /Å	16.9268(4)
α /°	90
β /°	90.5800(10)
γ /°	90
Volume/Å ³	2070.58(8)
<i>Z</i>	4
ρ_{calc} /cm ³	1.656
μ /mm ⁻¹	1.350
<i>F</i> (000)	1048.0
Crystal size/mm ³	0.2 × 0.15 × 0.1
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	5.288 to 55.25
Index ranges	-12 ≤ <i>h</i> ≤ 12, -16 ≤ <i>k</i> ≤ 16, -22 ≤ <i>l</i> ≤ 22
Reflections collected	36874
Independent reflections	4805 [<i>R</i> _{int} = 0.0779, <i>R</i> _{sigma} = 0.0402]
Data/restraints/parameters	4805/0/307
Goodness-of-fit on <i>F</i> ²	1.019
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0483, <i>wR</i> ₂ = 0.1314
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0739, <i>wR</i> ₂ = 0.1467
Largest diff. peak/hole / e Å ⁻³	0.68/-1.23

2.5.1. Further characterization of 2.3.

FTIR spectroscopy was carried out on a sample of compound **2.3** (Fig. 2.28). The carboxylate moiety of NCP_2^- coordinates to the Zn^{II} centre in a chelating mode. Signals at 1084 cm^{-1} and 1016 cm^{-1} can be assigned to $\nu(\text{C} - \text{N})$, and $\nu(\text{C} - \text{O})$ vibrations. The vibrational frequency at 1652 cm^{-1} results from the asymmetric carboxylate stretch. The corresponding symmetric C – O stretch can be assigned to the band at 1500 cm^{-1} . This assignment gives rise to a Deacon-Phillips value $\Delta = \nu_{\text{as}}(\text{CO}_2) - \nu_{\text{s}}(\text{CO}_2) = 152\text{ cm}^{-1}$, which is in agreement with the observed chelating binding mode.^{38, 50} The broad band centred at 1360 cm^{-1} is likely to derive from a combination of unresolved aromatic skeletal C = C and C = N stretching frequencies and N – H bending stretches.

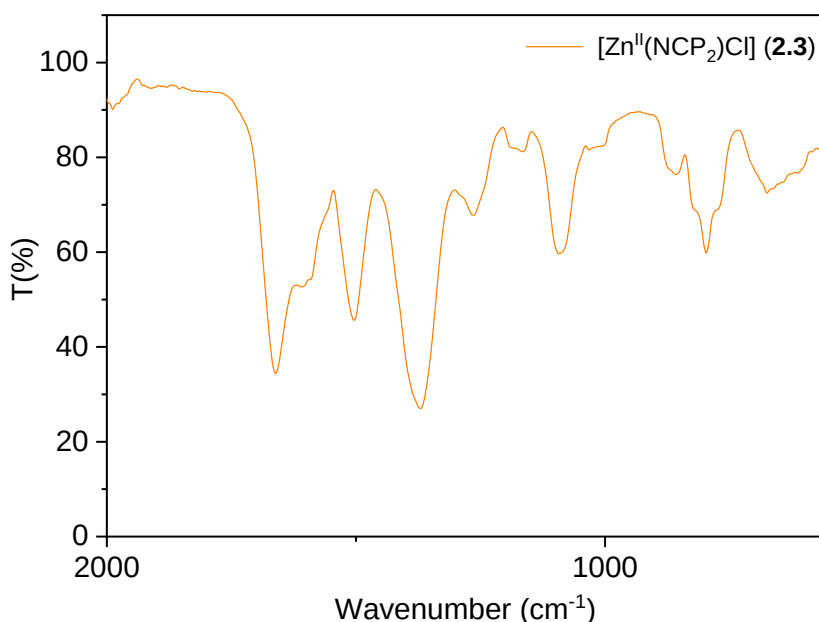


Figure 2.28: FTIR spectrum of 1.3.

The thermal stability of **2.3** was evaluated by thermogravimetric analysis under air atmosphere (Fig. 2.29). Analysis reveals thermal stability up to *ca.* 340 °C whereby the majority of the framework undergoes oxidative degradation above 405 °C. The combined decomposition values result in a weight loss of *ca.* 83% and correspond to the combustion of the organic ligand (theoretical 80%).

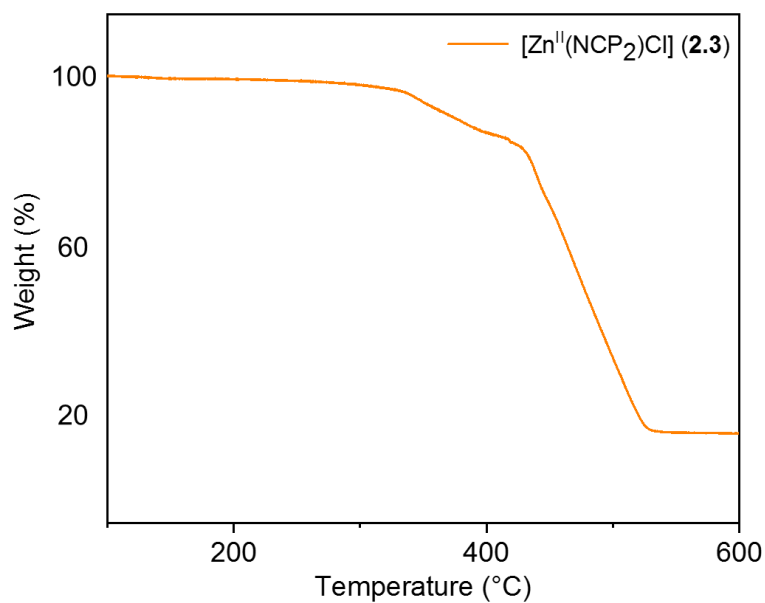


Figure 2.29: Thermogravimetric analysis of 2.3.

2.6. $[\text{Zn}^{\text{II}}(\text{HNCP}_2)(\text{NCP}_2)](\text{OH})$ (**2.4**)

$[\text{Zn}^{\text{II}}(\text{HNCP}_2)(\text{NCP}_2)](\text{OH})$ (**2.4**) was prepared by the reaction of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with HNCP_2 in a DMF/ H_2O (1:1 v:v, 1.0 mL) mixture. Yellow needles of **2.4** were obtained by heating the reaction mixture at 120 °C for four days. The material was characterised by single crystal X-ray diffraction measurements. The structure of $[\text{Zn}^{\text{II}}(\text{HNCP}_2)(\text{NCP}_2)](\text{OH})$ (**2.4**) is structurally closely related to the previously described structure of $[\text{Co}(\text{HNCP}_2)(\text{NCP}_2)]\text{Cl} \cdot 2\text{DMF}$ (**2.1**). In contrast to **2.1**, **2.4** contains a hydroxide ion instead of a chloride counter ion. It crystallises in the triclinic space group $P\bar{1}$, and consists of bilayer-type coordination chains containing a mononuclear Zn^{II} SBU with half a formula comprising the asymmetric unit. The Zn^{II} ion is six-coordinate, adopting a distorted octahedral coordination geometry. Four organic ligands coordinate to a central Zn^{II} centre, with two ligands exhibiting bidentate coordination through the nitrogen donor atoms and two exhibiting monodentate coordination through the oxygen donor atom of the carboxylates in a *cis* geometry (Fig. 2.30).

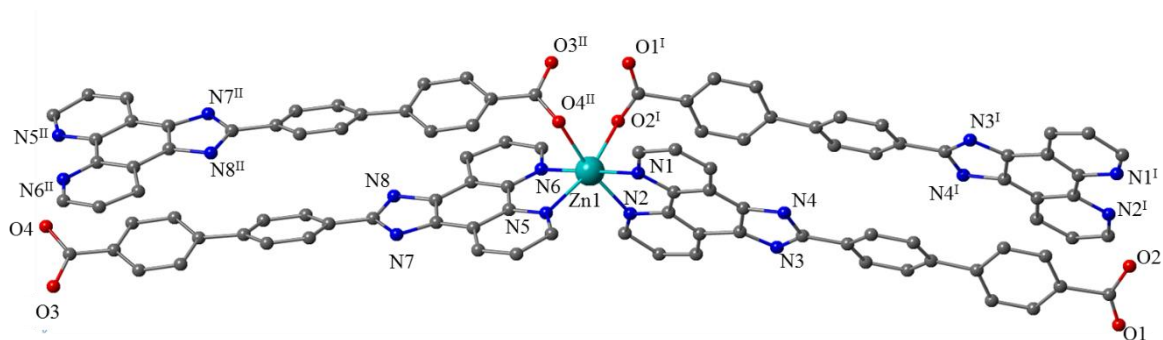


Figure 2.30: Coordination environment of Zn^{II} , in the crystal structure of $[\text{Zn}^{\text{II}}(\text{HNCP}_2)(\text{NCP}_2)](\text{OH})$; the Zn^{II} centre is connected to four HNCP_2 ligands. Colour code: Zn turquoise, C grey, O red, N blue, H atoms omitted for clarity; Symmetry codes: (I) 2-x, 2-y, 2-z (II) -1-x, 1-y, -z.

Similarly to **2.1**, each Zn^{II} centre in the HNCP ligands display bidentate chelation of the nitrogen donor atoms from the phenanthroline moiety to the Zn^{II} centre, with all the $\text{Zn}-\text{N}$ bond lengths in the range of 2.098(6) – 2.155(7) Å (Fig. 2.31). This slightly asymmetric coordination and approximate bond distances were observed for $[\text{Zn}_4(\text{adc})_3(\text{bpz})_6(\text{HCOO})_2] \cdot 2\text{H}_2\text{O}$ (adc = 9,10-anthracenedicarboxylate and bpz = bipyridophenazine), a coordination complex that contains a similar SBU.⁵¹ BVS analysis confirms that Zn centre in **2.4** resides in the oxidation state +II (Table 2.11).

Table 2.11: Crystallographically-determined bond lengths for the zinc centre in 2.4, along with the assignment of the oxidation state as determined by Bond Valence Sum (BVS) analysis.

Metal Atom	Bonded Atom	Bond Length (Å)	BVS	Oxidation State
Zn(1)	N(1)	2.139(7)	1.753	+II
	N(2)	2.098(6)		
	N(5)	2.155(7)		
	N(6)	2.116(3)		
	O(2)	2.159(3)		
	O(4)	2.290(2)		

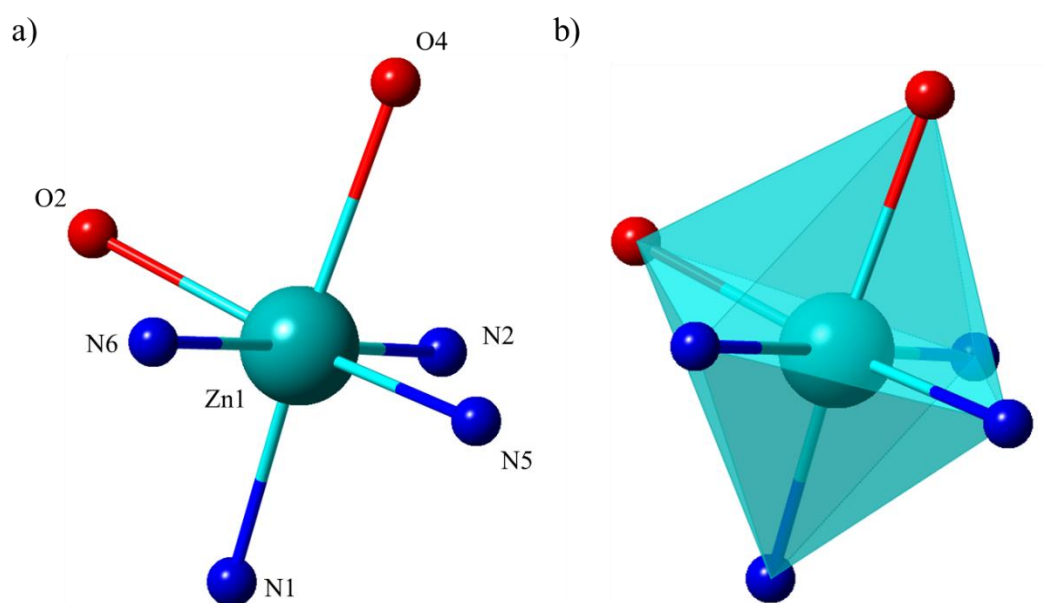


Figure 2.31: Zn^{II} coordination environment in [Zn^{II}(HNCP₂)(NCP₂)](OH) (a); Polyhedral representation of the distorted octahedral geometry (b); Colour code: Zn turquoise, O red, N blue.

The distorted nature of the octahedral coordination geometry of the Zn^{II} centres can be clarified by analysis of the bond angles involving the metal centre. Equivalently to **2.1**, the bond angles $\text{O}(2) - \text{Zn}(1) - \text{N}(5)$ and $\text{O}(4) - \text{Zn}(1) - \text{N}(1)$ of $163.9(8)^\circ$ and $167.6(9)^\circ$ deviate from the ideal octahedral angle of 180° whilst the $\text{N}(6) - \text{Zn}(1) - \text{N}(2)$ angle is in close agreement with the ideal angle. The $\text{O}(4) - \text{Zn}(1) - \text{N}(2)$ and $\text{O}(2) - \text{Zn}(1) - \text{N}(2)$ of $89.1(8)^\circ$ and $92.3(7)^\circ$, respectively, show small deviation from the ideal angle of 90° . Selected bond angles are summarised in Table 2.12.

Table 2.12: Selected bond lengths (Å) and angles (°) for $[\text{Zn}^{\text{II}}(\text{HNCP}_2)(\text{NCP}_2)](\text{OH})$.

Atoms	Angles(°)	Atoms	Angles(°)
$\text{O}(2) - \text{Zn}(1) - \text{N}(6)$	87.5(9)	$\text{O}(4) - \text{Zn}(1) - \text{O}(2)$	87.6(7)
$\text{O}(2) - \text{Zn}(1) - \text{N}(2)$	92.3(7)	$\text{O}(4) - \text{Zn}(1) - \text{N}(2)$	89.1(8)
$\text{O}(2) - \text{Zn}(1) - \text{N}(5)$	163.9(8)	$\text{O}(4) - \text{Zn}(1) - \text{N}(6)$	91.8(6)
$\text{O}(4) - \text{Zn}(1) - \text{N}(1)$	167.6(9)	$\text{O}(4) - \text{Zn}(1) - \text{N}(5)$	85.3(6)
$\text{N}(6) - \text{Zn}(1) - \text{N}(2)$	179.1(8)		

The carboxylate O-donor atoms of HNCP_2 coordinate to the Zn^{II} centre in a monodentate fashion. The $\text{Zn} - \text{O}$ bond lengths are $2.159(3)$ Å for $\text{Zn}(1) - \text{O}(2)$ and $2.290(2)$ Å for $\text{Zn}(1) - \text{O}(4)$ and are in agreement with corresponding Zn^{II} crystal structures.⁵²⁻⁵⁶ As in **2.1**, the close proximity of the carboxylate O-atoms $\text{O}(1)$ and $\text{O}(3)$ suggests that the observed binding arrangement is stabilised by a relatively strong H-bond between these atoms. The $\text{O}(1) - \text{O}(3)$ distance is $2.526(3)$ Å.

The ligand coordination gives rise to a structure that consists of bilayered 1D strands that polymerize as shown in Figure 2.32.

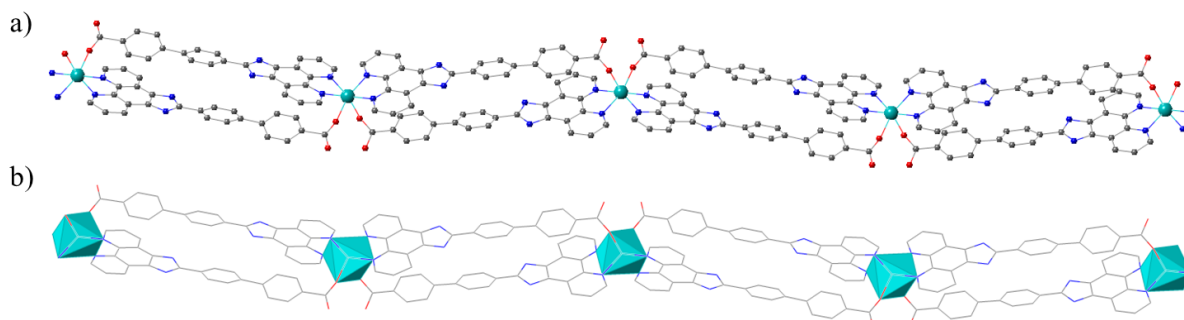


Figure 2.32: Polymeric chains in 2.4 (a); Polyhedral representation of the Zn^{II} -based SBU in the chain structure (b); Colour code: Zn turquoise, C grey, O red, N blue, H atoms omitted for clarity.

The charge of the 1D chains is most likely balanced by a hydroxide ion, as other potential counter ions could not be identified by crystallography. As for **2.1**, significant electron density is located next to the imidazole moiety between neighbouring chains. However this position could not be refined as a Cl^- ion.

The assumed charge balancing hydroxide counter ion in **2.4**, strongly interacts with the imidazole H-atoms *via* H-bonds (Fig. 2.33). The $\text{N}\cdots\text{O}-\text{H}$ and $\text{N}-\text{H}\cdots\text{O}-\text{H}$ bond distances are 2.69 Å and 1.82 Å, respectively. Other supramolecular structures containing such H-bonded hydroxide counter ions have previously been reported.⁵⁷⁻⁶¹

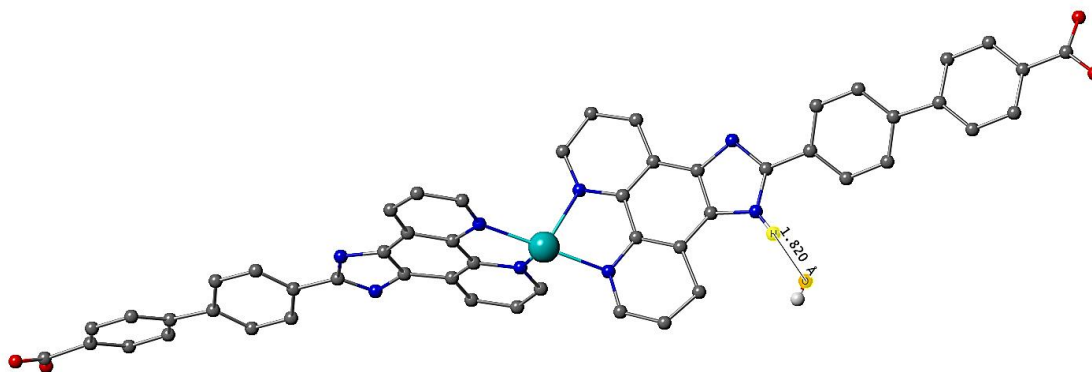


Figure 2.33: Asymmetric unit of $[\text{Zn}^{\text{II}}(\text{HNCP}_2)(\text{NCP}_2)](\text{OH})$ showing the charge balancing hydroxide counter ion; Colour code: Zn turquoise, C grey, O red, N blue, H pink; other hydrogen atoms were omitted for clarity.

The polymeric 1D chains pack relatively densely in the crystal structure (Fig.2.34). The closest intra-chain phenyl-phenyl centroid distances of the phenanthroline moieties account for *ca.* 3.5 Å, and thus can be classified as moderately strong $\pi-\pi$ interactions.³⁶

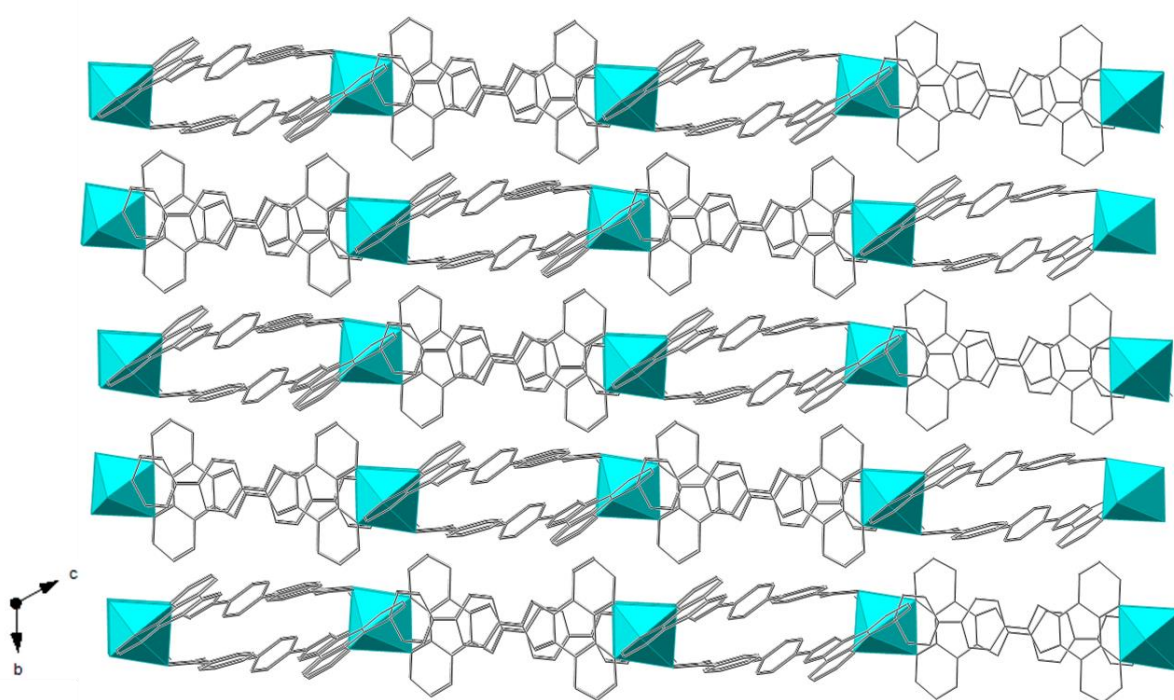


Figure 2.34: Packing arrangement of 1D chains in $[\text{Zn}^{\text{II}}(\text{HNCP}_2)(\text{NCP}_2)](\text{OH})$, as seen in the direction of the crystallographic *a*-axis.

Table 2.13: Crystal data and structure refinement for 2.4.

Identification code	2.4
Empirical formula	C ₅₂ H ₃₂ N ₈ O ₅ Zn
Formula weight/ g mol ⁻¹	914.26
Temperature/K	100
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> /Å	13.310(7)
<i>b</i> /Å	13.376(6)
<i>c</i> /Å	14.473(7)
α /°	110.18(3)
β /°	108.69(3)
γ /°	101.63(3)
Volume/Å ³	2145.2(19)
<i>Z</i>	4
ρ_{calc} /g/cm ³	1.415
μ /mm ⁻¹	1.295
<i>F</i> (000)	940.0
Crystal size/mm ³	0.5 × 0.2 × 0.1
Radiation	CuK α (λ = 1.54178)
2 Θ range for data collection/°	7.186 to 82.6
Index ranges	-11 ≤ <i>h</i> ≤ 11, -11 ≤ <i>k</i> ≤ 11, -12 ≤ <i>l</i> ≤ 12
Reflections collected	12127
Independent reflections	2719 [<i>R</i> _{int} = 0.3325, <i>R</i> _{sigma} = 0.3340]
Data/restraints/parameters	2719/383/521
Goodness-of-fit on <i>F</i> ²	0.973
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.1321, <i>wR</i> ₂ = 0.3055
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.2637, <i>wR</i> ₂ = 0.3936
Largest diff. peak/hole / e Å ⁻³	0.94/-0.64

2.6.1. Further characterization of 2.4

Compound **2.4** is structurally closely related to **2.1** and reveals a very similar IR spectrum as a result of their similar crystal structures (Fig. 2.35). The broad region above 2600 cm^{-1} is characteristic of O – H vibrations involved in relatively strong hydrogen bonds. This is in agreement with the C = O vibrational signal that appears as a shoulder at *ca.* 1724 cm^{-1} and most likely derives from the protonated carboxylic acid functionality engaging in the intramolecular H-bonding.²⁸ Signals at 1098 cm^{-1} and 1020 cm^{-1} are most likely from $\nu(\text{C} - \text{N})$, and $\nu(\text{C} - \text{O})$ vibrations. The signal at *ca.* 1686 cm^{-1} corresponds to the asymmetric C = O stretches of the carboxylate functionality of the deprotonated organic ligand that acts as H-bond acceptor. The symmetric C – O vibrations give rise to a signal at 1337 cm^{-1} which is in very good agreement with values expected for the observed unidentate coordination mode of carboxylate based ligands.^{38,39}

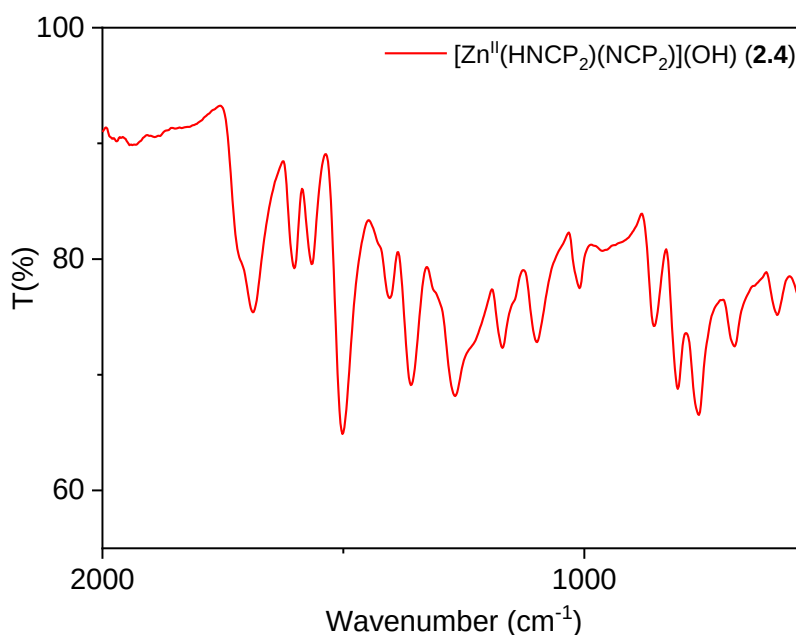


Figure 2.35: FTIR spectrum of 2.4.

The thermal stability of **2.4** was evaluated by thermogravimetric analysis in an air atmosphere (2.36). The compound undergoes oxidative degradation commencing at 265 °C. This degradation broadly occurs in by three major steps centred at 265, 325 and 466 °C. The latter two steps result from the total oxidation of the organic ligand residues most likely resulting in zinc oxide.

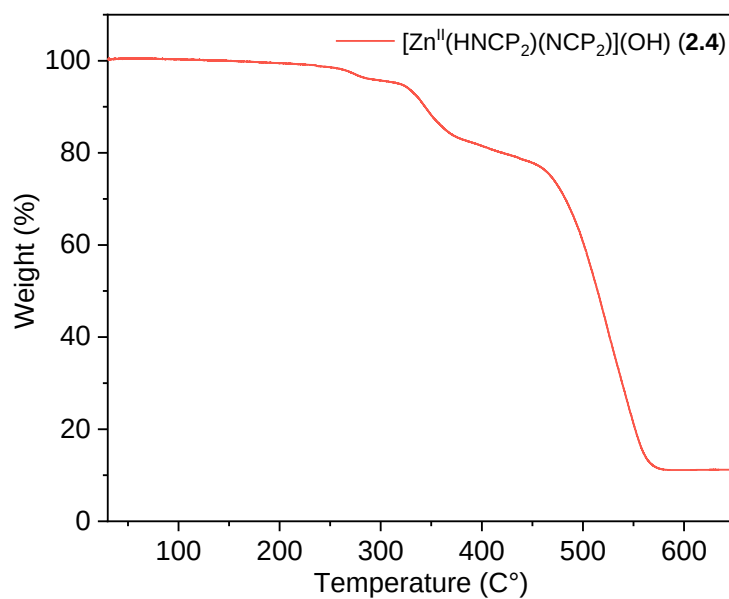


Figure 2.36: Thermogravimetric analysis of 2.4.

2.7. $[\text{Cd}_2(\text{NCP}_2)\text{Cl}_3(\text{DMF})]$ (2.5)

$[\text{Cd}_2(\text{NCP}_2)\text{Cl}_3(\text{DMF})]$ (2.5) was prepared by the reaction of $\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$ with HNCP_2 in a $\text{DMF}/\text{HCl}_{\text{aq}}$ (10:1 v:v) solvent mixture. Yellow needles of 2.5 were obtained by heating the reaction mixture to 120 °C for two days. The material was characterised by single crystal X-ray diffraction measurements.

The compound crystallises in the monoclinic space group $P2_1/c$, and consists of polymeric entities in which two parallel aligned 1D Cd^{II} based chains are bridged via NCP^{2-} ligands composed of dinuclear Cd^{II} units. Within the asymmetric unit of the structure (Fig. 2.37), one NCP^{2-} ligand coordinates to two symmetry-independent Cd^{II} centres. The organic ligand exhibits bidentate coordination through the nitrogen donor atoms as well as a chelating and bridging coordination mode involving the oxygen donor atoms of the carboxylate group.

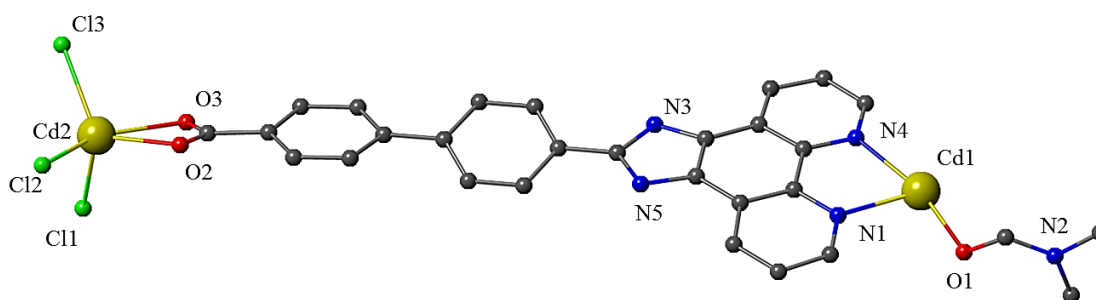


Figure 2.37: Asymmetric unit of compound 2.5 in the crystal structure of $[\text{Cd}_2(\text{NCP}_2)\text{Cl}_3(\text{DMF})]$.

The binding behaviour of the organic ligand is replicated through the structure whereby the two organic motifs are symmetry related by inversion symmetry. Figure 2.38 shows the coordination behaviour of the two symmetry-independent Cd^{II} atoms Cd(1) and Cd(2) which are bridged by one chloride ion, Cl(1), and one oxygen atom O(3) of the carboxylate group of the organic ligand.

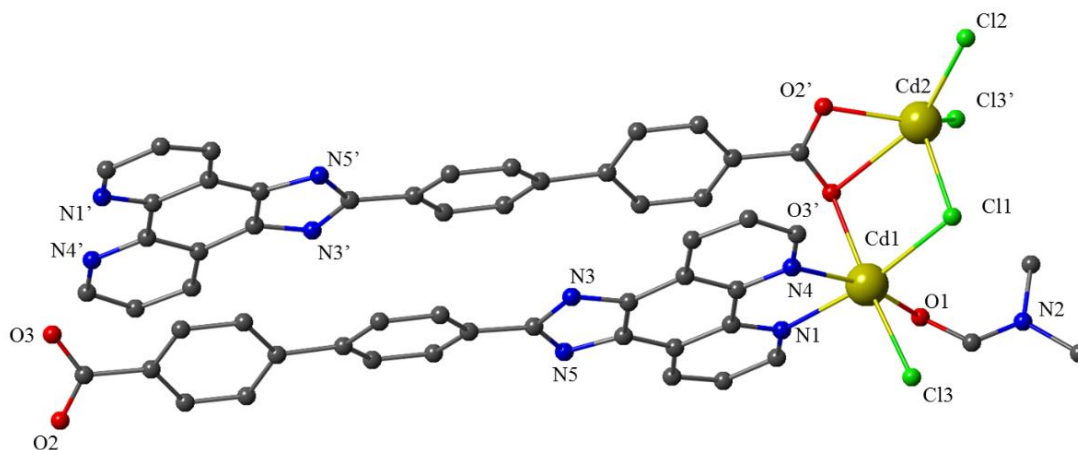


Figure 2.38: Coordination environment of two crystallographically independent Cd^{II} centres in the crystal structure of [Cd₂(NCP₂)Cl₃(DMF)]; Colour code: Cd yellow, C grey, O red, N blue, Cl green. H atoms omitted for clarity. Symmetry code: 1-x, 1-y, 1-z.

The six-coordinate Cd(1) atom adopts a distorted octahedral coordination geometry (Fig. 2.39). The organic ligand facilitates an asymmetric bidentate N,N' chelation exhibiting Cd(1) – N bond lengths of 2.291(4) and 2.334(5) Å. The coordination environment also comprises of two non-equivalent chlorine ligands, each bridging Cd(1) to two, symmetry-related neighbouring 5-coordinate Cd(2) and Cd(2') ions. The observed bond lengths are 2.434(16) Å for Cd(1) – Cl(3) and 2.068(18) Å for Cd(1) – Cl(3). Additionally, the coordination sphere contains two oxygen atoms. One oxygen atom O(3), derives from the carboxylate moiety of the ligand and further acts as a bridge to the neighbouring Cd(2) atom. The Cd(1) – O(3) bond length is 2.439(4) Å. The second oxygen atom originates from a coordination to a DMF molecule. The observed Cd(1) – O(1) bond distance is 2.305(4) Å. Table 2.14 highlights selected bond distances for Cd(1).

Table 2.14: Crystallographically-determined bond lengths for the Cd(1) centre in 2.5.

Metal Atom	Bonded Atom	Bond Length (Å)
Cd(1)	Cl(1)	2.068(18)
	Cl(3)	2.434(16)
	O(3)	2.439(4)
	O(1)	2.305(4)
	N(4)	2.332(5)
	N(1)	2.291(4)

The distorted nature of the octahedral coordination geometry of the Cd(1) centre can be visualised by examination of bond angles involving the metal centre. Indeed, the bond angles $\text{N}(1) - \text{Cd}(1) - \text{Cl}(1)$ and $\text{O}(3) - \text{Cd}(1) - \text{Cl}(3)$, of $170.04(15)^\circ$ and $173.79(9)^\circ$ respectively, deviate from the ideal octahedral angle of 180° . The angles of $\text{O}(3) - \text{Cd}(1) - \text{N}(1)$ and $\text{O}(3) - \text{Cd}(1) - \text{O}(1)$, of $86.88(15)^\circ$ and $94.19(15)^\circ$ respectively, show small deviation from the ideal angle of 90° . Selected angles that characterise the binding geometry of Cd(1) in 2.5 are given in Table 2.15.

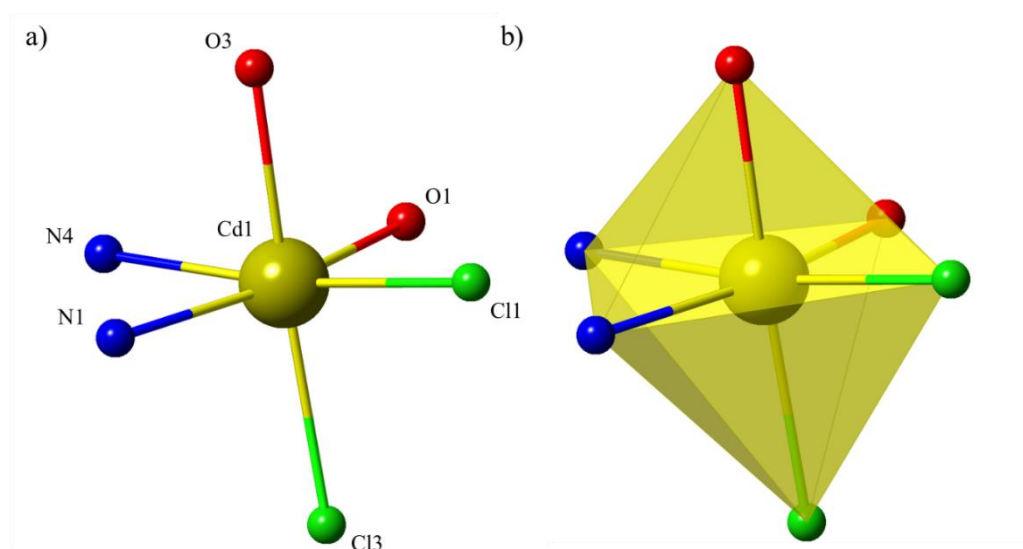


Figure 2.39: Coordination environment of Cd(1) in $[\text{Cd}_2(\text{NCP}_2)\text{Cl}_3\text{DMF}]$ (a); Polyhedral representation of the distorted octahedral geometry (b); Colour code: Cd yellow, C grey, O red, N blue, Cl green.

The structure of **2.5** also features a five coordinate Cd^{II} centre (Fig. 2.40). This $\text{Cd}(2)$ centre adopts a highly distorted trigonal bipyramidal coordination geometry. As mentioned above, it shares both, $\mu\text{-Cl}$ - and $\mu\text{-O}$ -bridging atoms with $\text{Cd}(1)$ whereby bond lengths of 2.518(18) Å for $\text{Cd}(2) - \text{Cl}(3)$ and 2.605(4) Å for $\text{Cd}(2) - \text{O}(3)$ are observed. The carboxylate group of NCP_2^- displays distorted asymmetric O, O' chelation to $\text{Cd}(2)$. This results in bond lengths of 2.229(4) Å and 2.605(4) Å for $\text{Cd}(2) - \text{O}(2)$ and $\text{Cd}(2) - \text{O}(3)$, respectively. Similar bridging behaviour of O and Cl atoms and Cd – Cl/O bond distances are observed in a Cd-MOF containing a bipyridinium carboxylate ligand (L) reported as $[\text{Cd}_{1.5}(\text{L})(\text{Cl})_2] \cdot 2\text{H}_2\text{O}$. The framework is described as a two dimensional double-layer structure packed by $\pi - \pi$ interactions and also contains carboxylate groups that display chelating and bridging tridentate coordination mode.⁶²

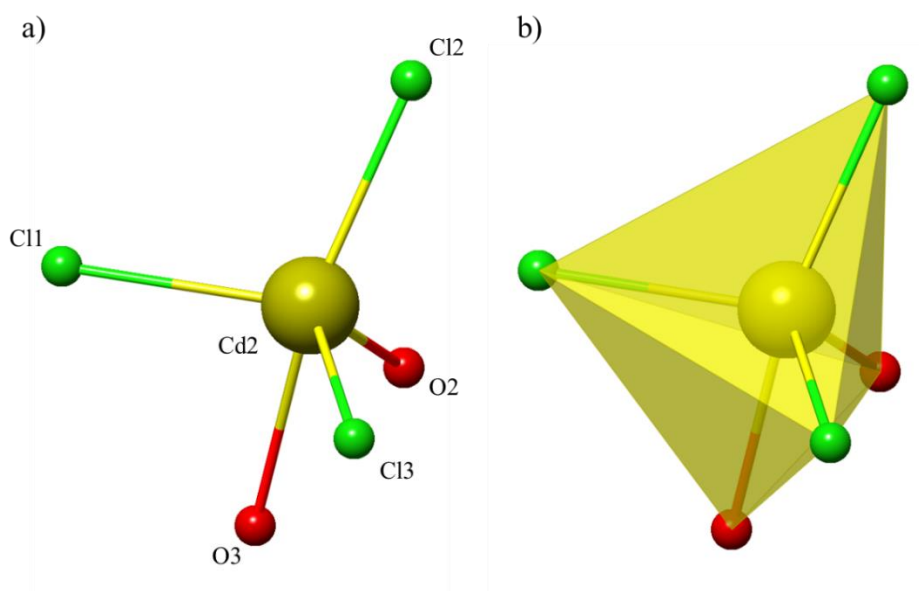


Figure 2.40: Coordination environment of $\text{Cd}(2)$ in $[\text{Cd}_2(\text{NCP}_2)\text{Cl}_3\text{DMF}]$ (a); Polyhedral representation of the distorted trigonal bipyramidal coordination environment (b); Colour code: Colour code: Cd yellow, O red, Cl green.

Table 2.15: Crystallographically-determined bond lengths for the Cd(2) centre in 2.5.

Metal Atom	Bonded Atom	Bond Length (Å)
Cd(2)	Cl(1)	2.489(17)
	Cl(3)	2.518(18)
	Cl(2)	2.452(15)
	O(3)	2.605(4)
	O(2)	2.229(4)

The five coordinate geometry index was calculated for the coordination sphere of the Cd(2) centre. A value of $\tau_5 = 0.90$ indicates a moderate distortion from the ideal trigonal bipyramidal coordination environment.⁴⁸ Selected bond angles in **2.5** are summarised in Table 2.16.

Table 2.16: Selected bond angles (°) for 2.5.

Bond Angles	Angles (°)	Bond Angles	Angles (°)
O(3) – Cd(1) – O(1)	94.19(15)	O(2) – Cd(2) – O(3)	54.18(13)
N(1) – Cd(1) – Cl(1)	170.04 (13)	Cl(2) – O(3) – Cl(3)	108.51(6)
Cl(1) – Cd(1) – Cl(3)	91.12(6)	Cl(2) – Cd(2) – Cl(1)	106.01(6)
O(3) – Cd(1) – Cl(3)	173.79(9)	Cl(2) – Cd(2) – O(2)	100.14(11)
N(1) – Cd(1) – N(4)	73.09(15)	Cd(1) – O(3) – Cd(2)	97.86(13)
O(3) – Cd(1) – N(4)	86.28(15)	Cd(2) – Cl(1) – Cd(1)	113.92(6)
O(3) – Cd(1) – N(1)	86.88(15)	Cd(2) – Cl(3) – Cd(1)	97.70(6)

The dinuclear symmetry-independent subunit within **2.5** is then connected to the next unit through a Cl(3) atom (located on a C2 axis) to form a 1D Cd^{II}-based chain that extends in the direction of the crystallographic *a*-axis (Fig. 2.41).

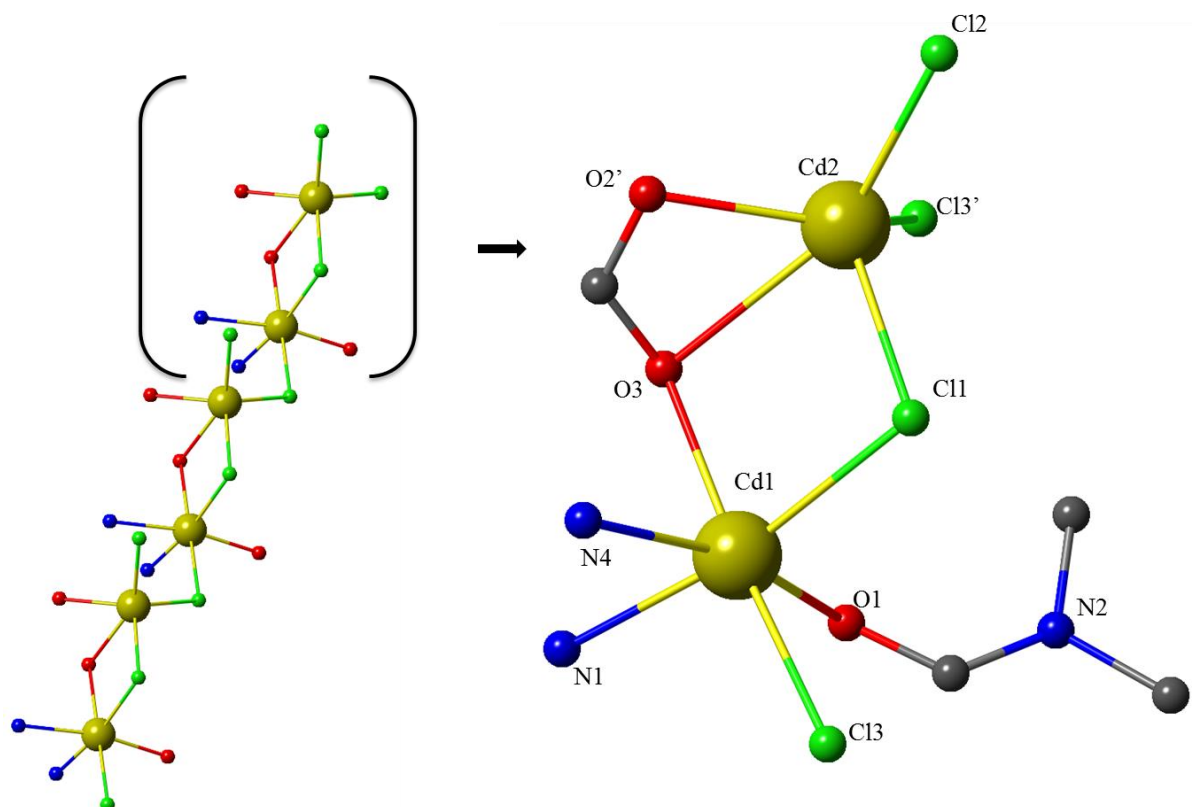


Figure 2.41: Polymeric chain formed by the dinuclear symmetry-independent subunit that extends in the direction of the crystallographic *a*-axis. Colour code: Cd yellow, C grey, O red, N blue, Cl green, H atoms omitted for clarity. Symmetry code: 1-*x*, 1-*y*, 1-*z*.

Two parallel aligned chains are connected through the organic ligands each of which is rotated by 180° with respect to the next. Within these chain motifs phenanthroline-phenyl $\pi - \pi$ interactions prevail giving rise to ring centroid-centroid distances of *ca.* 3.50 Å. These 1D assemblies pack in the crystal structure of **2.5**, to give a herring bone-type packing motif that is characterised by 2₁ screw symmetry, whereby the screw axis is extends parallel to the crystallographic *b*-axis (Fig. 2.42 and 2.43).

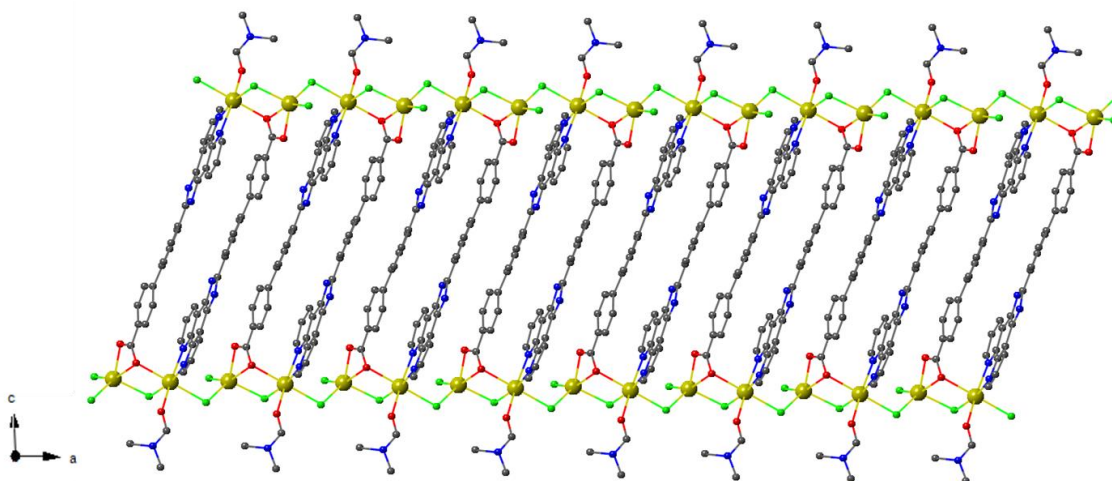


Figure 2.42: 1D polymeric chain formed through bringing chlorides ions and O-donor atoms of the organic ligands. Colour code: Colour code: Cd yellow, C grey, O red, N blue, Cl green, H atoms omitted for clarity.

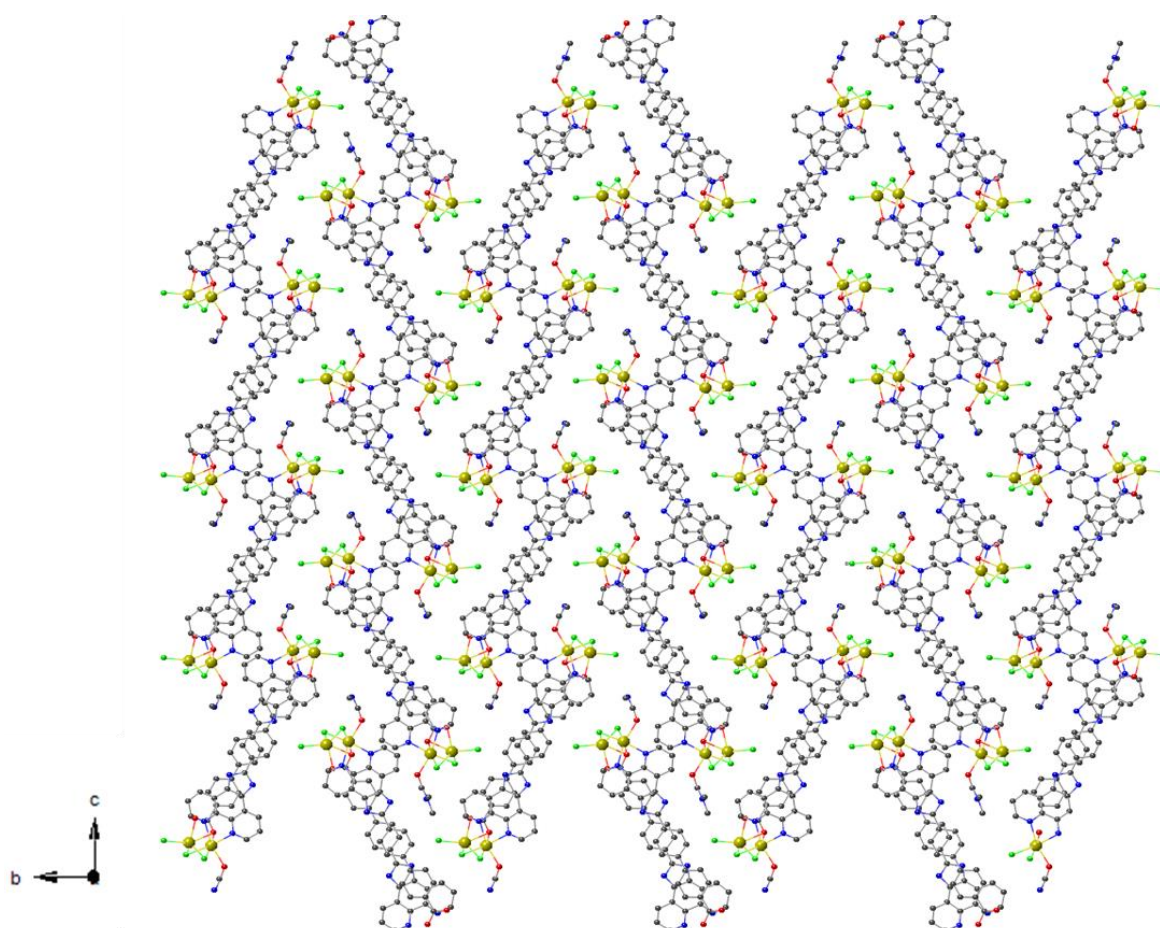


Figure 2.43: Packing arrangement of the polymeric chains in $\text{Cd}_2(\text{NCP}_2)\text{Cl}_3\text{DMF}$ as seen along the crystallographic a -axis. Cd yellow, C grey, O red, N blue, Cl green, H atoms omitted for clarity.

Table 2.17: Crystal data and structure refinement for 2.5.

Identification code	2.5
Empirical formula	C ₂₉ H ₂₂ Cd ₂ Cl ₃ N ₅ O ₃
Formula weight	819.69
Temperature/K	100
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	7.168(2)
<i>b</i> /Å	24.405(5)
<i>c</i> /Å	16.301(3)
α /°	90.00(3)
β /°	95.75(3)
γ /°	90.00(3)
Volume/Å ³	2837.1(11)
<i>Z</i>	1
ρ_{calc} /cm ³	1.917
μ /mm ⁻¹	1.824
<i>F</i> (000)	1604.0
Crystal size/mm ³	0.13 × 0.03 × 0.02
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	3.014 to 52.112
Index ranges	-8 ≤ <i>h</i> ≤ 8, -30 ≤ <i>k</i> ≤ 30, -19 ≤ <i>l</i> ≤ 20
Reflections collected	42835
Independent reflections	5584 [<i>R</i> _{int} = 0.1045, <i>R</i> _{sigma} = 0.0781]
Data/restraints/parameters	5584/0/385
Goodness-of-fit on <i>F</i> ²	0.987
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0446, <i>wR</i> ₂ = 0.0761
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0881, <i>wR</i> ₂ = 0.0866
Largest diff. peak/hole / e Å ⁻³	1.05/-0.89

2.7.1. Further characterisation of 2.5

FTIR spectroscopy was carried out on a sample of compound **2.5** and revealed bands above 3000 cm^{-1} characteristic of C – H stretches in aromatic compounds (Fig. 2.44).²⁸ Asymmetric $\nu(\text{C} - \text{O})$ stretching vibration of the carbonyl moieties of the coordinated DMF molecules and carboxylate functionalities result in bands at *ca.* 1660 cm^{-1} and 1504 cm^{-1} , respectively. A strong signal at 1574 cm^{-1} may derive from the $\nu(\text{C} = \text{N})$ vibration.^{27, 63} The symmetric $\nu(\text{C} - \text{O})$ stretching vibration of the carboxylate group occur at 1384 cm^{-1} . A Deacon-Phillips value $\Delta = \nu_{\text{as}}(\text{CO}_2) - \nu_{\text{s}}(\text{CO}_2) = 146\text{ cm}^{-1}$ is in close agreement with the bridging geometry exhibited by the carboxylate functionalities in **2.5**.^{38, 64, 65}

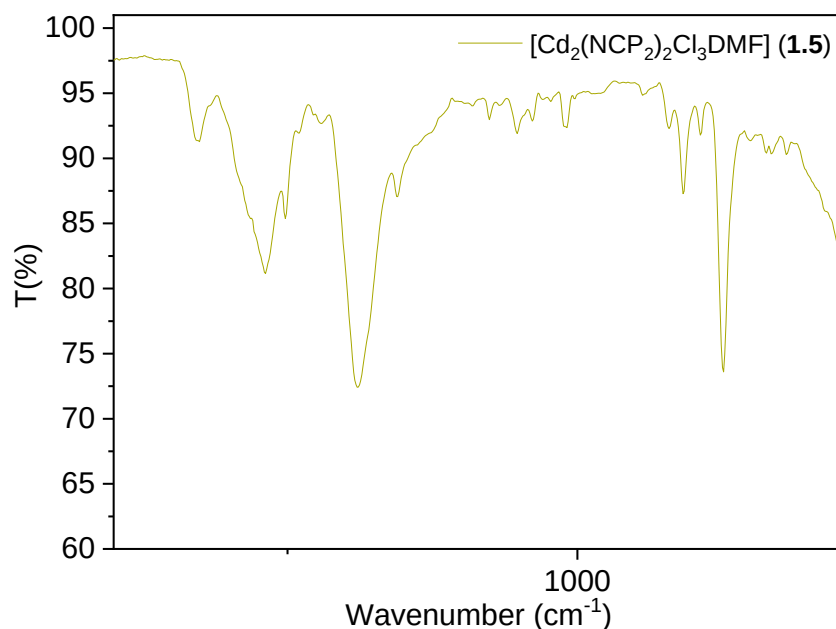


Figure 2.44: FTIR spectrum of 2.5.

The thermal stability of **2.5** was evaluated by thermogravimetric analysis in an air atmosphere (Fig. 2.45). An initial weight loss of *ca.* 17.5% between room temperature and 120°C can be attributed to the loss of solvent associated with the freshly prepared sample and the loss of coordinated DMF molecules. The organic ligand undergoes oxidative degradation above 340°C most leading to a weight loss of 52% during the thermogravimetric step. This process most likely leads to a Cd^{II} based oxide.

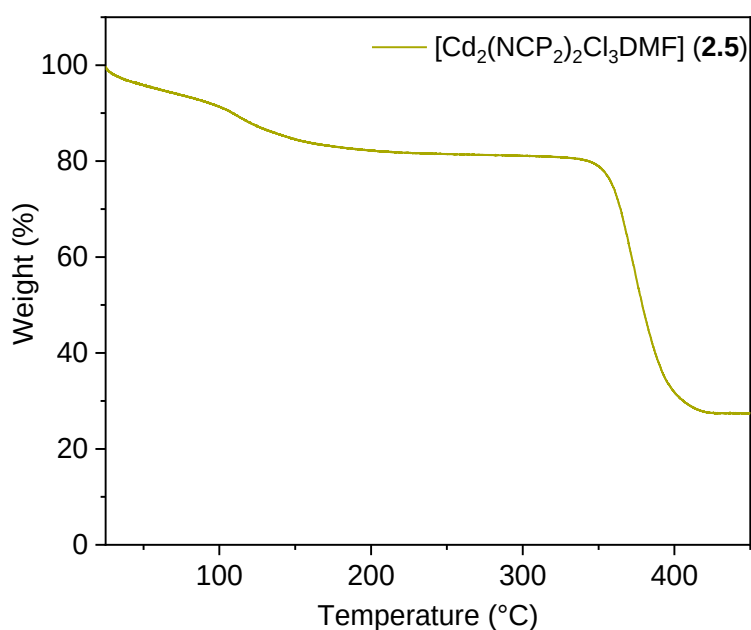


Figure 2.45: Thermogravimetric analysis of 2.5.

2.8. Conclusion

A novel phenanthroline based ligand, 4'-(1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl)-[1,1'-biphenyl]-4-carboxylic acid (HNCP₂), was prepared. The new ligand is an extended version of HNCP, and whose functionalities provide O- and N-donors that facilitate a variety of coordination modes when binding to transition and main group metal ions. Additionally the phenyl ring increases potential $\pi - \pi$ interactions that can stabilise the supramolecular assembly within the crystal structures.

Solvothermal conditions were employed with the aim of studying the coordination behaviour of HNCP₂. Optimization of crystal growth was achieved by varying three main parameters: nature of the metal salt, solvent system and mineralizer/acid while maintaining reaction temperature, metal-ligand ratio (M:L) and reaction time. Five novel compounds were synthesised. These include four coordination polymers and one discrete trinuclear Co^{II} coordination complex. Their corresponding crystal structures were determined *via* single x-ray diffraction. The structures demonstrate that the ligand systems favours the formation of lower dimensional structures whereby the phenanthroline moiety exhibits a strong chelating ability. The carboxylate functionality of the ligand system can facilitate the bridging between metal ions. Selected reaction conditions used during this work are presented on Table 2.18.

One observes that crystal growth is mostly favoured by the use of solvent systems composed of DMF and an acid. Acetic acid acts a modulator, competing with the organic linkers in order to coordinate with the metal ions during nucleation and crystal growth. Both, hydrochloric acid and acetic acid, however can also provide ligands to stabilise the resulting coordination compounds.

As observed in compound **2.2**, the acetate groups bridge Co^{II} ions to form a molecular trinuclear complex instead of a polymeric structure. HCl was also employed as a modulator whereby it is expected to shift the equilibrium towards the carboxylic acids rather than their deprotonated carboxylates and thus, slowing down the formation of a product and improving crystal growth.¹² The aqueous acid can provide a source of chloride ions that may provide terminal or bridging ligands in **2.3** and **2.5**, respectively.

The HNCP₂ ligand system is particularly interesting as it combines harder carboxylate functionalities with a softer set of N-donor atoms of the phenanthroline moiety. Thus the ligand system may be used for the formation of mixed metal compounds involving harder

and softer metal ions. Particularly interesting are $\text{Ru}(\text{phen})_3]^{2+}$ related structures that may possibly be prepared with such ligand systems and which can give rise to interesting photophysical properties.⁶⁶

Such phenanthroline-based ligands may provide a viable option in the construction of robust, permanently porous MOFs that are stabilised by efficient Ru^{II} chromophore moieties.

Table 2.18: Reaction conditions employed in solvothermal reactions using HNCP2; Highlighted conditions yielded compounds 2.1, 2.2, 2.3, 2.4 and 2.5.

Metal Salt	Solvent system	Modulator	Reaction temperature	Time	Result
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	MeCN	--	120 °C	48 h	Amorphous material
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	DMF	--	120 °C	48 h	Amorphous material
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	DMF	HCl	120 °C	48 h	Orange needles (2.1)
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	DMF	CH_3COOH	120 °C	48 h	Cubic brown crystals (2.2)
$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	DMA	--	120 °C	48 h	Amorphous material
$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	DMA/EtOH	--	120 °C	48 h	Amorphous material
$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	DMF	HCl	120 °C	48 h	Cubic yellow crystals (2.3)
$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	DMF/ H_2O	--	120 °C	48 h	Yellow needles (2.4)
$\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$	DMF	--	120 °C	48 h	Amorphous material
$\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$	DMF	HCl	120 °C	48 h	Yellow needles (2.5)

2.9. References

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Chapter 3

Synthesis of a hetero-metallic $\text{Co}^{\text{II}}/\text{Ru}^{\text{II}}$ -
based MOF

3. Synthesis of a hetero-metallic Co^{II}/Ru^{II}-based MOF

3.1. Introduction

Many resulting metal-organic framework structures are amenable to chemical functionalization, whereby possible applications derive from the intrinsic porosity, high number of active sites per unit volume and high diffusion coefficients.¹⁻³ These materials can demonstrate how size, shape, charge and functional group availability influences guest binding and performances in gas storage, separation and catalysis.⁴⁻⁶ Particularly intriguing are photoactive, ‘3rd or even 4th generation MOFs’⁷ that can impact on areas including artificial photosynthesis,⁸ photo-catalysis,⁹ sensor materials,¹⁰ light-emitting¹¹ or smart flexible materials.^{12, 13}

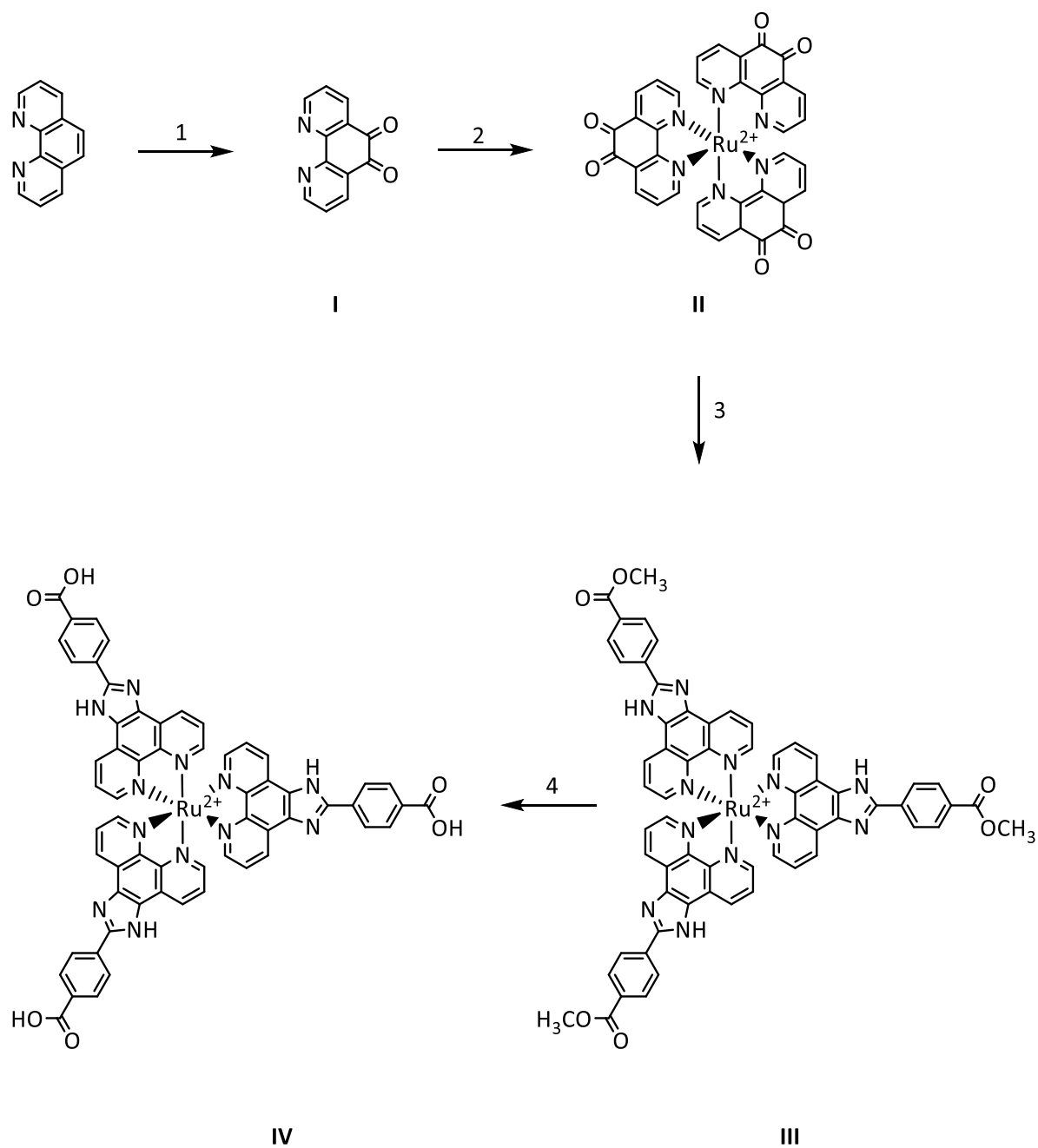
Considering the exceptional scientific interest in these areas, it is surprising that Ru^{II}/polypyridyl complexes have rarely been employed as SBUs of permanently porous, crystalline MOFs containing large unblocked openings.^{14, 15} Ru^{II} complexes generally reveal high molar absorptivities and strongly luminesce at room temperature whereby the excited state manifold of the metal-to-ligand charge transfer (MLCT) states have intensively been investigated.^{16, 17} The quantum efficiencies of the systems, *e.g.* in photo-electrochemical cells or in photocatalysis (H₂ or O₂ evolution; CO₂ reduction) rely on satisfactory excited state lifetimes and electron- and energy-transfer processes.¹⁸

In order to preserve the polypyridyl coordination environment of Ru^{II} upon incorporation into a framework, bifunctional pyridyl-carboxylate ligands are typically used, and a bimetallic MOF is constructed using another metal centre as the structure directing unit when bound by carboxylate groups.^{19, 20} Generally, when Ru/pyridyl complexes or other analogous photosensitizers (PS) are incorporated into the framework structures of MOFs, quenching of the lifetime and fast energy/electron transfer processes are observed.²¹⁻²³ Such quenching effects are desirable for several applications, including heterogeneous oxidation/reduction catalysis at secondary catalytic nodes or for dye-sensitised solar cell fabrication.²⁴⁻²⁶ The significance of {Ru/pyridyl} nodes as hopping intermediates for energy transfer has been demonstrated using Zn^{II}-containing MOFs.²³ Further, noteworthy are UiO-type MOFs in which Ru- or Ir/pyridyl nodes connect {Zr₆O₄(OH)₄(CO₂)₁₂} units and that can be applied for the photocatalytic CO₂ reduction and the oxidation of organic substrates.²⁷ Similarly Ru^{II}/Eu^{II}-based MOFs can be applied as photosensitizing materials for CO₂ reduction.²¹

In this chapter, the synthesis and photochemical properties a photoactive, MOF, [Co^{II}L^{Ru}]⁺TFA that is characterised by accessible, tubular 1D channels with large pore aperture, are described. The synthetic approach employs the racemic propeller-like metallo-ligand [H₃L^{Ru}]²⁺ that directs the assembly into a honeycomb, **hcb** topology with alternating Co^{II}- and Ru^{II}-based nodes of Δ and Λ helicity. Interestingly, the light-harvesting and emission spectral properties of the metallo-ligands are maintained in the framework structure, and significant lifetime quenching is observed. **Photo-MOF** reveals structural stability, permanent porosity (which is rare for MOFs with this large pore aperture) and shows selectivity for CO₂ over N₂. It is further noteworthy that the incorporation of the PS facilitates heat dissipation in the solid material resulting in an increased photo-stability of **Photo-MOF** in comparison to [H₃L^{Ru}](PF₆)₂.

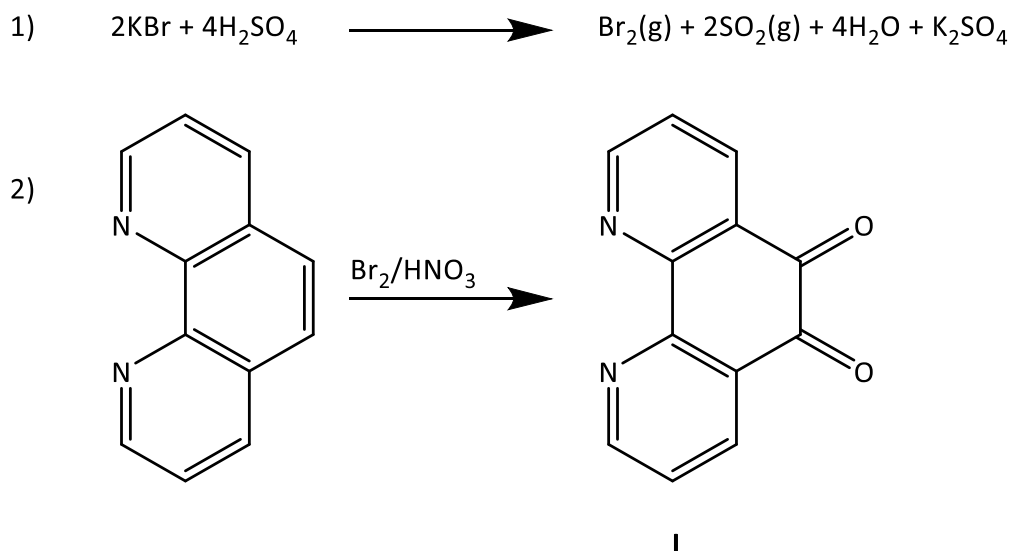
3.2. Synthesis of the tritopic Ru^{II} metallo-ligand [H₃L^{Ru}](PF₆)₂

The tritopic Ru^{II} metallo-ligand [H₃L^{Ru}](PF₆)₂ (scheme 3.1) featuring a carboxylate-derivative of 1*H*-imidazo [4,5-*f*][1,10]-phenanthroline, was synthesised in four steps involving the synthesis of 1,10-phenanthroline-5,6-dione, coordination of 1,10-phenanthroline-5,6-dione to Ru(DMSO)₄Cl₂ followed by a modified Debus-Radziszewski reaction²⁸ and ester hydrolysis to introduce the phenylcarboxylate functionality. Schemes 3.1-3.2 summarise the applied synthetic sequence.



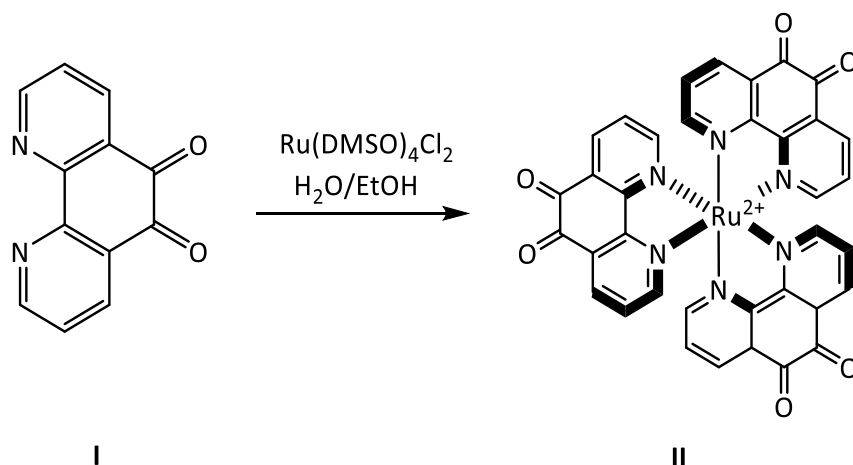
Scheme 3.1: Synthetic procedure used in the synthesis of the metallo-ligand $[H_3L_1^{Ru}](PF_6)_2$ (IV) (steps 1-4 are described in the following sections).

Step 1: The synthesis of 1,10-phenanthroline-5,6-dione (**I**) was adapted from a procedure reported in the literature.²⁹ Sulphuric acid and nitric acid were dropwise added to one equivalent of 1,10-phenanthroline and approximately seven equivalents of potassium bromide. The approach was accompanied by the generation of bromine gas. In the first stage, electrophilic aromatic bromination of 1,10-phenanthroline is achieved by Br₂ gas, created *in-situ* through the reaction of KBr and H₂SO₄ with HNO₃ acting as a Lewis acid.²⁹ The 1,2-diol is produced from the hydrolysis of the brominated product *via* an S_N2 mechanism. The desired product **I** is then generated when the diol is oxidised by HNO₃ as shown in Scheme 1. Typical yields of 65% of **I** were achieved.



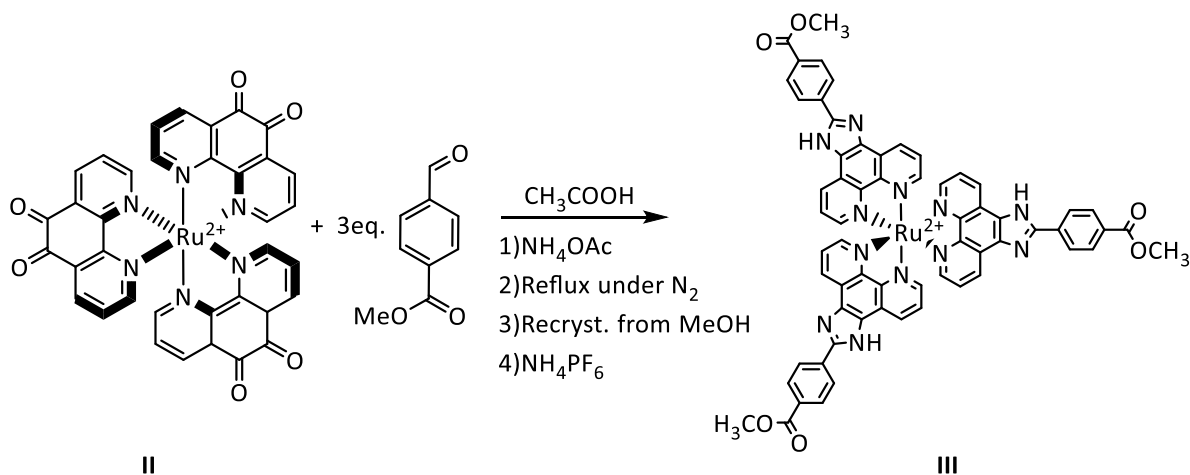
Scheme 3.2: Synthesis of 1,10-phenanthroline-5,6-dione: Redox reaction of HBr with H₂SO₄ to yield Br₂ (1); Bromination of phenanthroline, *in-situ* hydrolysis to diol and oxidation to dione (2).

Step 2: [Ru(phendione)₃]Cl₂ (**II**) was prepared according to a literature procedure.³⁰ For this purpose, one equivalent of Ru(DMSO)₄Cl₂ and approximately three equivalents of 1,10-phenanthroline-5,6-dione were dissolved in a H₂O/EtOH mixture and refluxed for 12 hours. The resulting product of the reaction, [Ru(phendione)₃]Cl₂ (**II**), is a dark complex and was obtained at *ca.* 84 % yield.

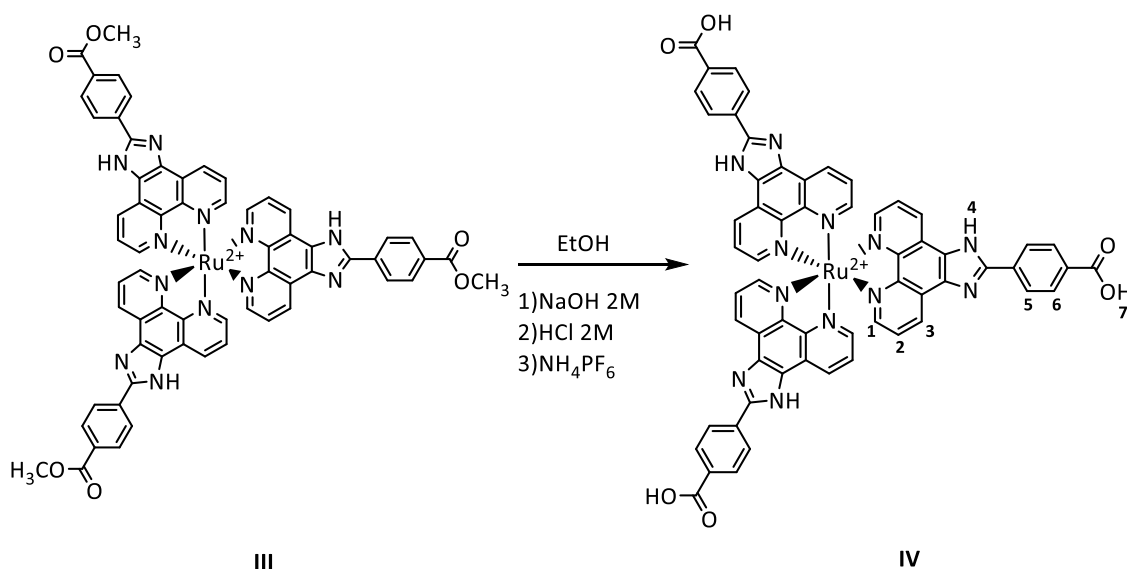


Scheme 3.3: Synthesis of [Ru(phendione)₃]Cl₂ (phendione = 1,10-phenanthroline-5,6-dione) (II).

Step 3: The introduction of the phenylcarboxylate functionality was achieved *via* a modification of the Debus-Radziszewski reaction. The Debus-Radziszewski method²⁸ is a well established approach that yields an imidazole ring through a reaction between a desired aldehyde and 1,10-phenanthroline-5,6-dione. It has been studied since the 19th century and has been commercially used to produce a wide range of imidazole-containing products.³¹ A proposed mechanism involves the cyclisation through the interaction of a 1,2-diketone and an aldehyde with a diimide intermediate. Ammonia in an EtOH solution is traditionally used. To improve yields, however, the Davison modification³¹ was chosen and ammonium acetate in acetic acid was used. Thus, one equivalent of **II**, three equivalents methyl 4-formylbenzoate and excess ammonium acetate were reacted under reflux for 12 hours in acetic acid under N₂ atmosphere. The resulting crude solid was dissolved in methanol upon which the addition of a saturated aqueous solution of ammonium hexafluorophosphate led to the precipitation of the desired product [Ru(MeNCP)₃](PF₆)₂ (**III**). Yields of *ca.* 72 % were achieved using this approach.

Scheme 3.4: Synthesis of [Ru(MeNCP)₃](PF₆)₂ (III).

Step 4: For the final step, a deprotection procedure was carried out using basic hydrolysis of the ester groups. The reaction was carried out refluxing **III** in ethanol and an aqueous 2M sodium hydroxide solution. The reaction mixture was then acidified with a 2M hydrochloric acid solution. Precipitation of the final product, [Ru(HNCP)₃](PF₆)₂ or [H₃L^{Ru}](PF₆)₂ (**IV**) was achieved by dropwise addition of ammonium hexafluorophosphate. Compound **IV** was obtained in a yield of 85%.

Scheme 3.5: Synthesis of [H₃L^{Ru}](PF₆)₂ (IV); Basic hydrolysis of the ester groups used as deprotection procedure for the metallo-ligand.

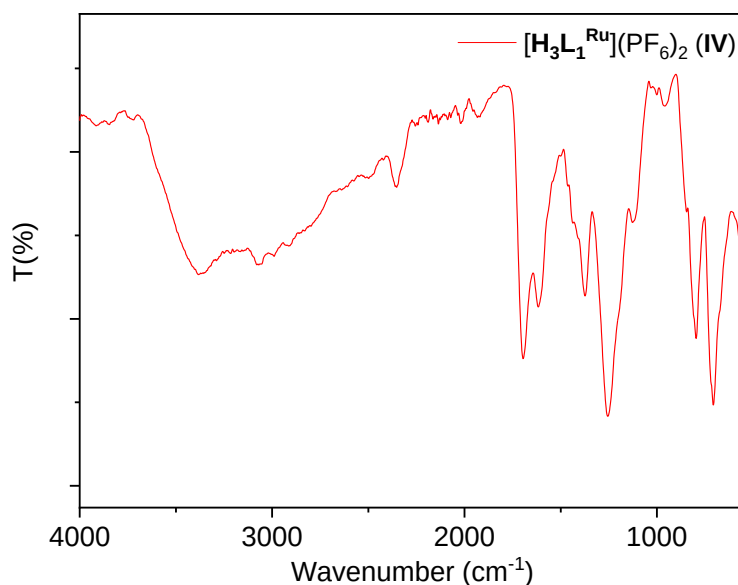


Figure 3.1: FTIR spectrum of $[\text{H}_3\text{L}_1\text{Ru}](\text{PF}_6)_2$ (IV).

FTIR spectroscopy was carried out revealing bands characteristic of aromatic and highly conjugated compounds (Fig. 3.1). The signal at *ca.* 1710 cm^{-1} can be assigned to the C = O vibrations of the free carboxylic acid groups. Bands between 1610 cm^{-1} and 1330 cm^{-1} are due to aromatic C = C and C = N stretching frequencies. The weak absorption frequencies at 576 cm^{-1} and 566 cm^{-1} result from the coordination of the phenanthroline nitrogen atoms of the organic ligands to central Ru^{II} atom.³² The shoulder at *ca.* 840 cm^{-1} confirms the presence of PF₆³³ the weak band around 2360 cm^{-1} is most likely due to the presence of CO₂.

3.3. NMR Characterisation of [H₃L^{Ru}](PF₆)₂ (IV)

The metallo-ligand was characterized through ¹H, ¹³C and ¹³C¹H-COSY-NMR. The analysis of (IV) in deuterated DMSO proved to be challenging due to solubility issues. The ¹H-NMR spectrum (Fig. 3.2) reveals signals at 9.12 ppm, 7.82 ppm, 8.53 ppm and 14.98 ppm which are attributed to the H-atoms in the phenanthroline portion of the ligand. Signals at 8.08 ppm and 8.19 ppm arise from the H-atoms at the aromatic benzoate moiety. The intense signals at 3.38 ppm and 2.50 ppm are singlets due to the presence of residual solvent, water and dimethyl sulfoxide respectively. Figure 3.3 shows the two-dimensional ¹³C¹H-COSY spectrum of the metallo-ligand. The spectrum shows coupling of the H-atoms in the aromatic region with signals at 130.02 ppm to 151.09 ppm in the ¹³C-NMR spectrum. It is evident that the NMR ¹H-signals at 8.53 ppm and 7.82 ppm do not have any correlation with aromatic benzoate rings, and consequently, arise from the phenanthroline moiety. The ¹³C-NMR spectrum, shows a signal at 167.30 ppm, which is attributed to the carbon atoms of the carboxylate moiety. The signals in the range of 152.06 ppm to 130.02 ppm can be assigned to carbon atoms at the benzoate rings of the complex, whereas 128.90 ppm to 126.79 ppm can be assigned to the carbons of the phenanthroline portion (Fig. 3.4). All the assigned signals are in close agreement with spectra of similar complexes that were recently reported in the literature.²¹

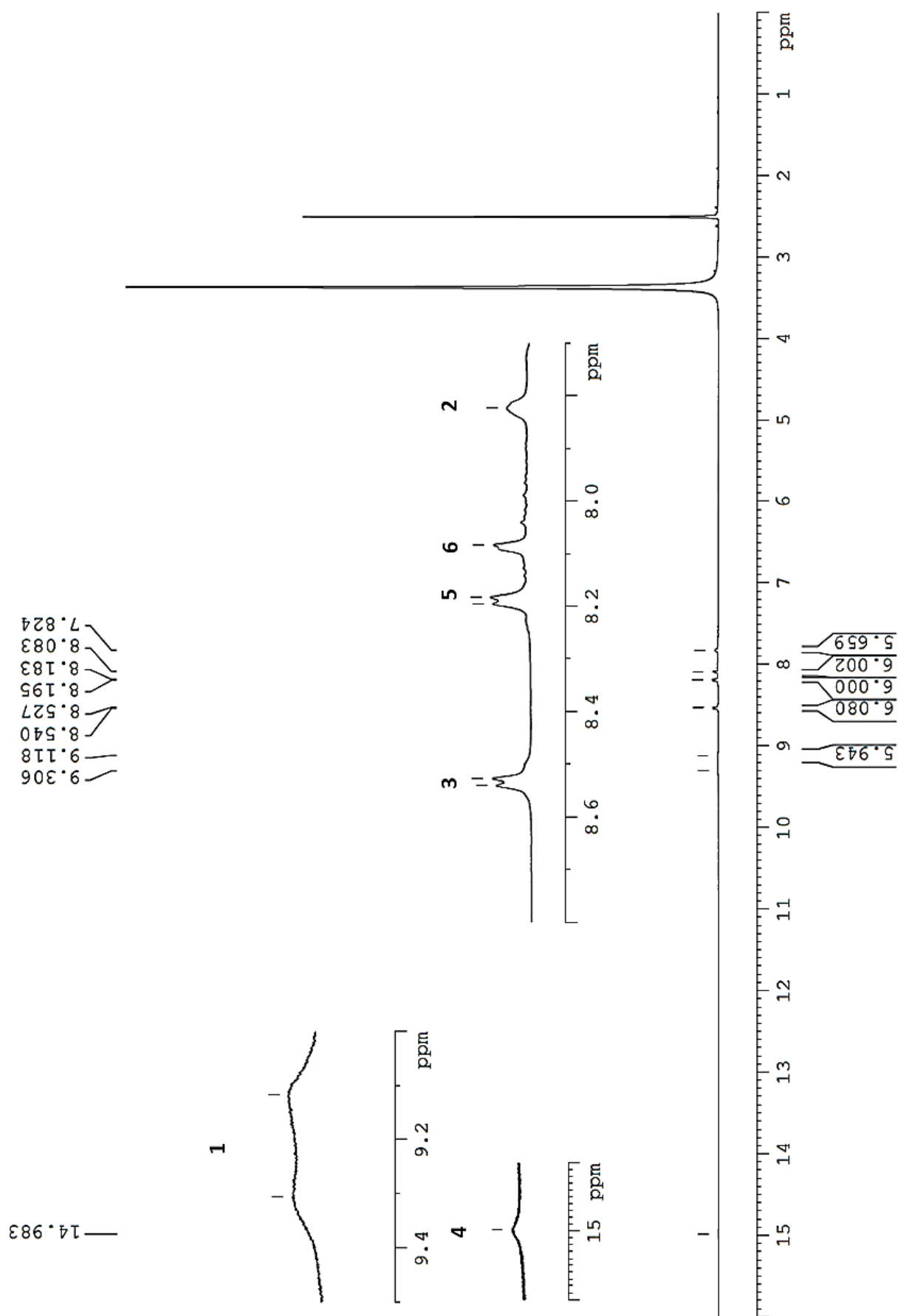


Figure 3.2: ¹H-NMR spectrum of [H₃L₁Ru](PF₆)₂ (IV) in d₆-DMSO.

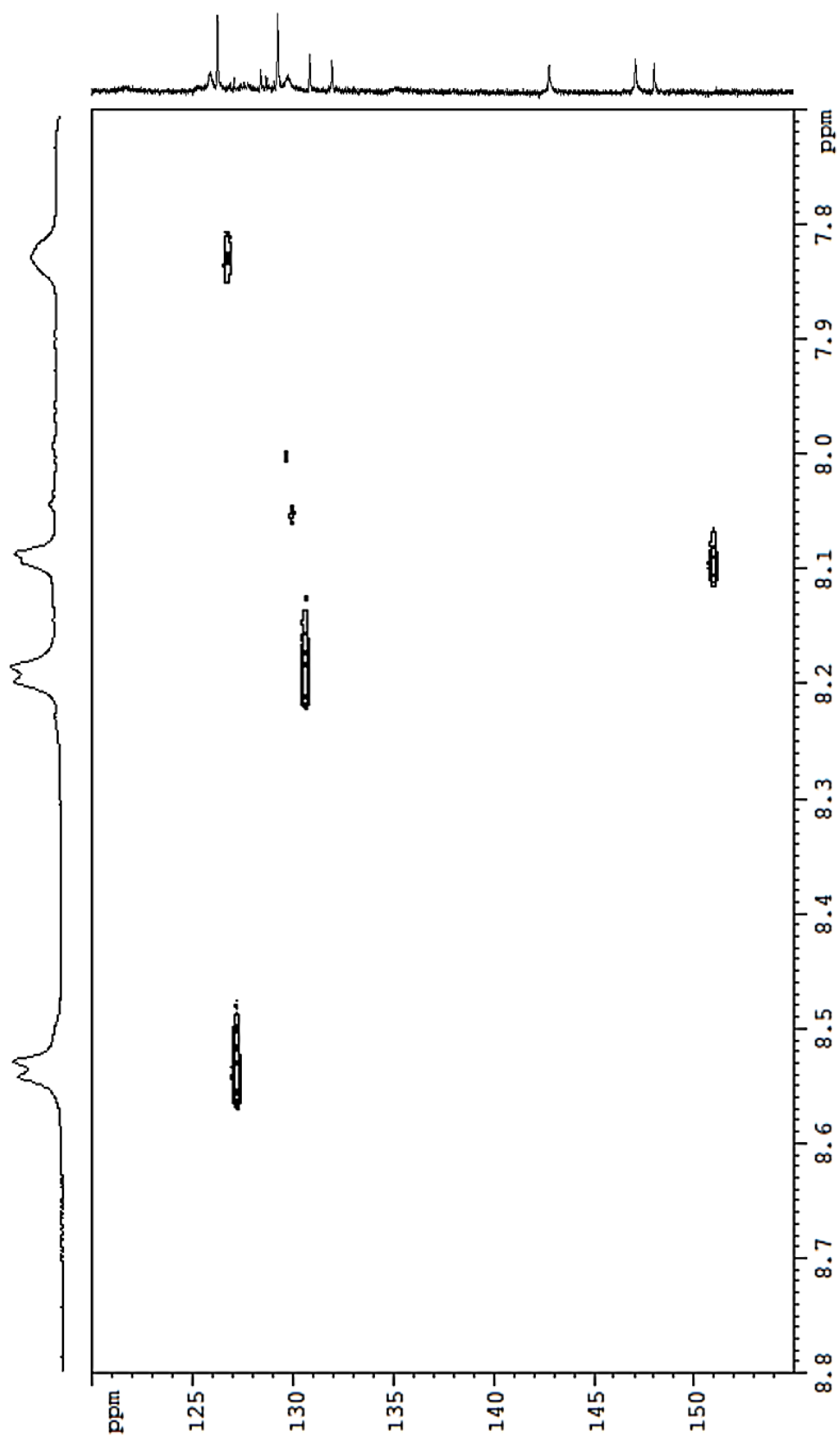


Figure 3.3: ¹³C¹H-COSY spectrum (600 MHz) of [H₃L₁^{Ru}](PF₆)₂ (IV) in d₆-DMSO.

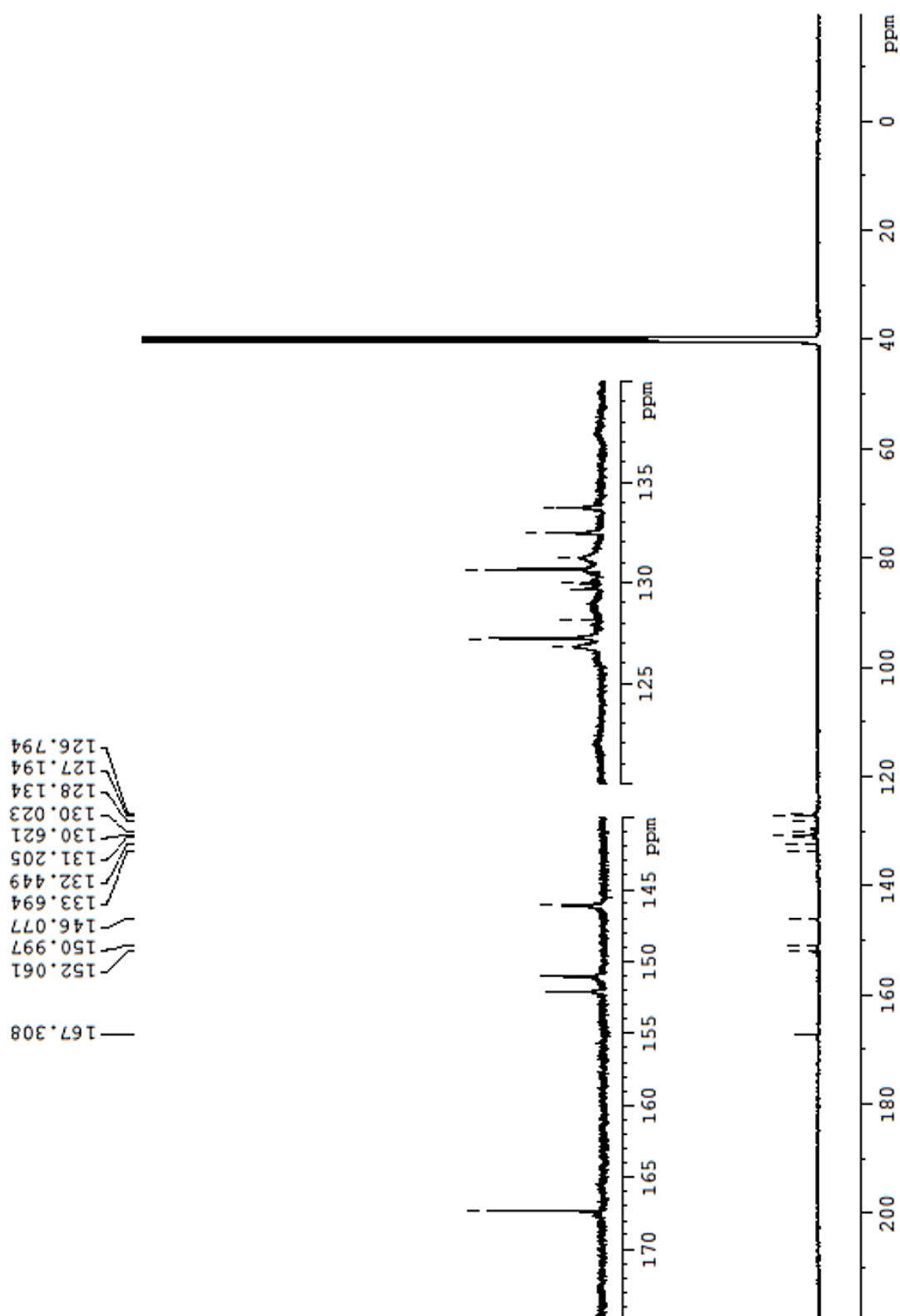


Figure 3.4: ¹³C-NMR spectrum of [H₃L₁^{Ru}](PF₆)₂ (IV) in d₆-DMSO.

3.4. Photophysical characterisation of complex (IV)

In order to achieve efficient solar light absorption by the targeted MOFs, it is important to design struts that exhibit a spectral satisfactory overlap with that of the solar spectrum. Solution absorption spectra can provide a starting point for selecting the right struts or linkers for light harvesting purposes.¹⁴

Photophysical characterisation of **IV** was performed at room temperature in two different degassed solvent systems (CH₃CN and DMF). UV-visible adsorption and emission spectra were obtained as seen in Figures 3.5 and 3.6, despite solubility issues. The absorption spectra in both CH₃CN and DMF reveal typical bands characteristic for Ru^{II}/polypyridyl complexes.^{34, 35} However, there are slight detectable differences due to solubility differences in the two solvent systems as well as differences arising from the characteristic UV solvent cutoff.³⁶

Analysis carried out in CH₃CN reveal ligand-centred $\pi - \pi^*$ transitions in the UV region at *ca.* 200 - 350 nm with intense bands at $\lambda_{\text{max}} = 295$ nm and 330 nm (Fig. 3.5a) which marginally redshifted (4–7 nm) in their band position when compared to [Ru(bpy)₃]²⁺,¹⁶ and in close agreement with spectra of related Ru(II) complexes reported in the literature.³⁷⁻³⁹ In the visible region, relatively intense broad absorption bands arise from the spin-allowed metal-to-ligand charge transfer (MLCT) transitions. This band can be assigned to d - π^* transitions and is present at *ca.* 490 nm. The observed MLCT transition is marginally blueshifted when compared to similar complexes reported in the literature.^{38, 40, 41} Photoluminescence data from CH₃CN solution were collected, in addition to the absorption spectrum of the complex, at room temperature. The excitation within the spectral region of the MLCT band was followed by an emission centred at 605 nm, which is close to that of [Ru(phen)₃]²⁺ and [Ru(bpy)₃]²⁺.^{16, 42} The emission spectra agree well with complexes presenting the same chromophore^{42, 43}, and are red shifted when compared to other derivative Ru(II) transition metal complexes (Fig. 5b).^{44, 45}

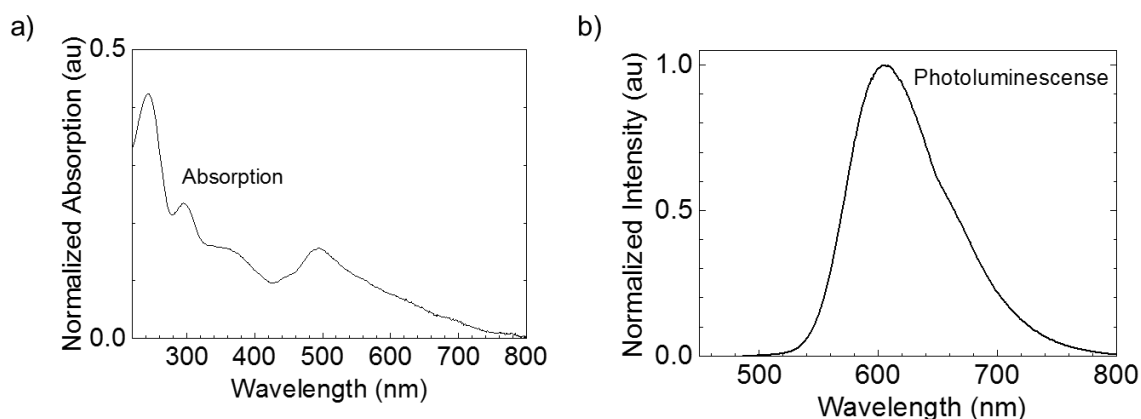


Figure 3.5: Normalized UV-vis (a) and emission (b) spectra of [H₃L₁Ru]²⁺ (IV) in CH₃CN.

Bands in the UV-Vis absorption spectra are characteristic for {Ru/phenanthroline} species were also found for analyses carried out in DMF. Bands giving rise to ligand-centred transitions at *ca.* 300 nm and relatively intense broad absorbance bands in the region of 420–480 nm are observed (Fig. 3.6a). The latter can be assigned to characteristic broad absorption of Ru²⁺-centred MLCT transitions.^{16, 46} All reported bands and assignments are in agreement with reported data carried out in the corresponding solvent systems and temperature.^{21, 47}

Emission studies were also performed in DMF whereby the compound was found to induce an intense emission at room temperature (Fig. 3.6b). The photoluminescence spectrum in DMF is centred at approximately 615 nm. This is slightly blue shifted (4 nm) compared to [Ru(bpy)₃]²⁺, and in close agreement with [Ru(phen)₃]²⁺ and similar complexes reported in the literature.^{16, 21, 42}

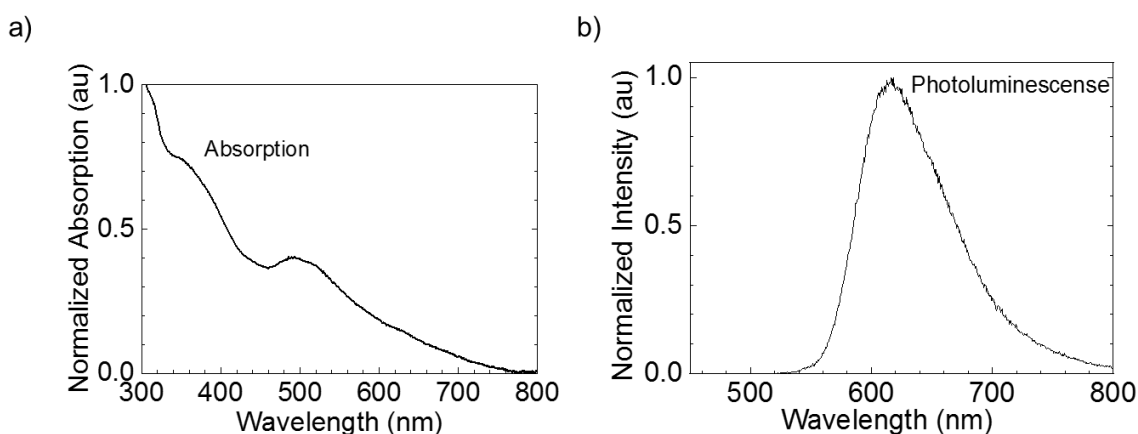


Figure 3.6: Normalized UV-vis (a) and emission (b) spectra of [H₃L₁Ru]²⁺ (IV) in DMF.

3.5. Synthesis of Photo-MOF [Co(Ru(HNCP)₃)(CF₃CO₂)]. (HTFA)₅12H₂O)

Photo-MOF forms reproducibly under solvothermal conditions in DMF during the reaction between [H₃L^{Ru}]²⁺ and Co(NO₃)₂·6H₂O at a mole ratio of 1:10 in the presence of trifluoroacetic acid (HTFA). The reactant mixture was sonicated at room temperature for 10 minutes, during which both reactants dissolved resulting in a deep, red solution. On heating at 120 °C for 72 hours, orange needles were obtained. Crystals were separated manually. Crystallographic data was acquired by Dr Brendan Twamley and the structures were solved and refined by Dr Nian- Yong.

3.6. Structural characterisation of Photo-MOF

Single-crystal X-ray studies demonstrate that **Photo-MOF** crystallises in the trigonal space group $P\bar{3}1c$, whereby the asymmetric unit comprises of 1/6 of the Ru^{II} and Co^{II} atoms and ½ of the organic ligand derivative. The homoleptic Ru^{II} complex [L^{Ru}]⁻ is maintained in the framework structure whereby each carboxylate moiety links to a Co^{II} centre directing the assembly into a layered hexagonal topology (Fig. 3.7).

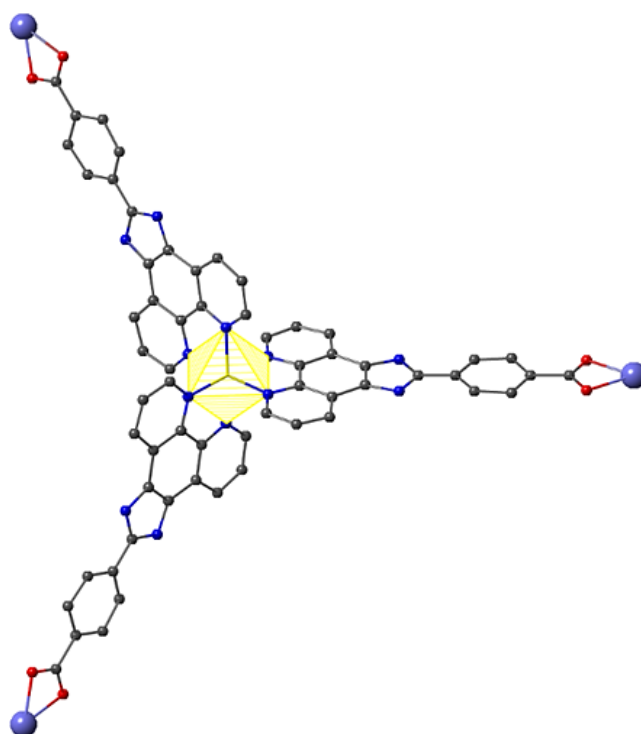


Figure 3.7: Propeller-like metallo-ligand within Photo-MOF that directs the assembly into a hexagonal topology.

The Co^{II} centres in **Photo-MOF** adopt octahedral coordination environments, each coordinated by three bidentate, chelating carboxylate functionalities that derive from three different [**L**₁^{Ru}][−] SBUs. (Fig. 3.8). The corresponding bond lengths of 2.094(7) Å are in agreement with those of other reported cobalt carboxylate complexes.⁴⁸⁻⁵¹

The distorted nature of the octahedral coordination geometry of the Co^{II} ion is exemplified by the bond angles involving the Co^{II} metal centre. There are four different O(1) – Co(1) – O(1) angles involving symmetry generated O-donors of 162.7(4)°, 90.4(4)°, 104.5(2)° and 62.4(4)°. Those angles deviate significantly from the ideal angles of 180° and 90° and highlight the distorted nature of the coordination environment

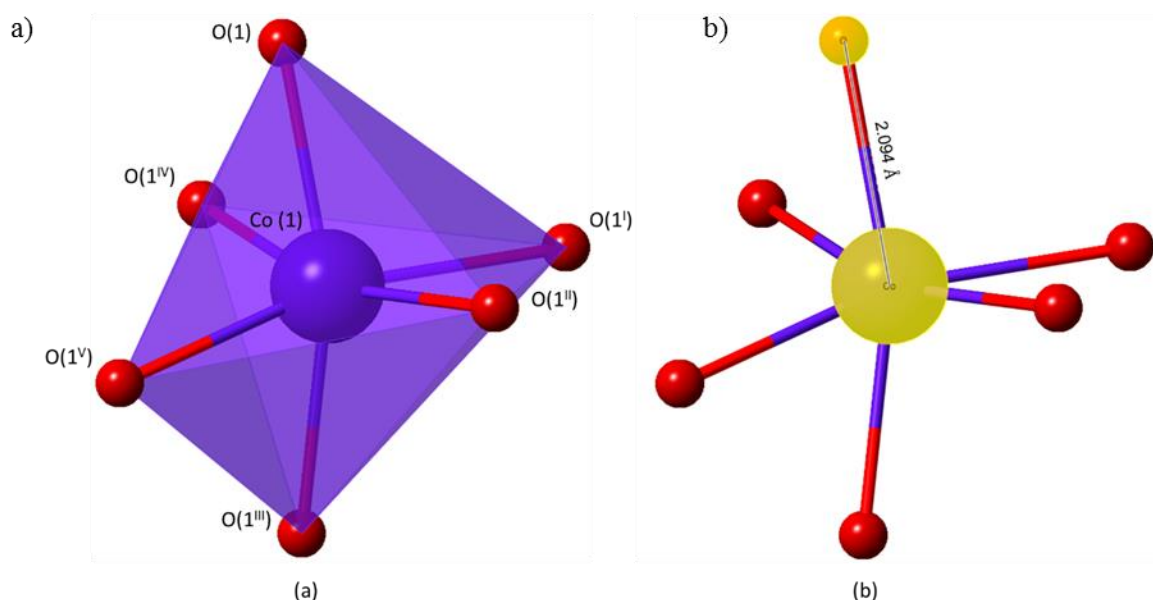


Figure 3.8: Polyhedral representation of the coordination environment of the Co^{II} centres in Photo-MOF (a); Coordination environment of the Co^{II} centres with indicated Co(1) – O(1) bond distance (b); Symmetry codes: (I) $x, x - y, 1.5 - z$; (II) x, y, z ; (III) $1 - x + y, 1 - x, z$; (IV) $1 - y, x - y, z$.

In contrast, the Ru^{II} centre in the metallo-ligand adopts a rather symmetric octahedral coordination environment (Fig. 3.9). The coordination sphere is completed by crystallographically identical nitrogen atoms. The Ru–N bonds reveal bond lengths of 2.02(9) Å which are in agreement with similar complexes in the literature.⁵²⁻⁵⁵ The observed N(1)-Ru(1)-N(1) angles are 86.4(4)°, 96.0(1) and 176.8(5)° which closely corresponds to the octahedral geometry. Selected bond distances and angles in **Photo-**

MOF are summarised in Table 3.1. Similarly to the O-donors of the Co(II) environment, all positions of the N-atoms are symmetry-related.

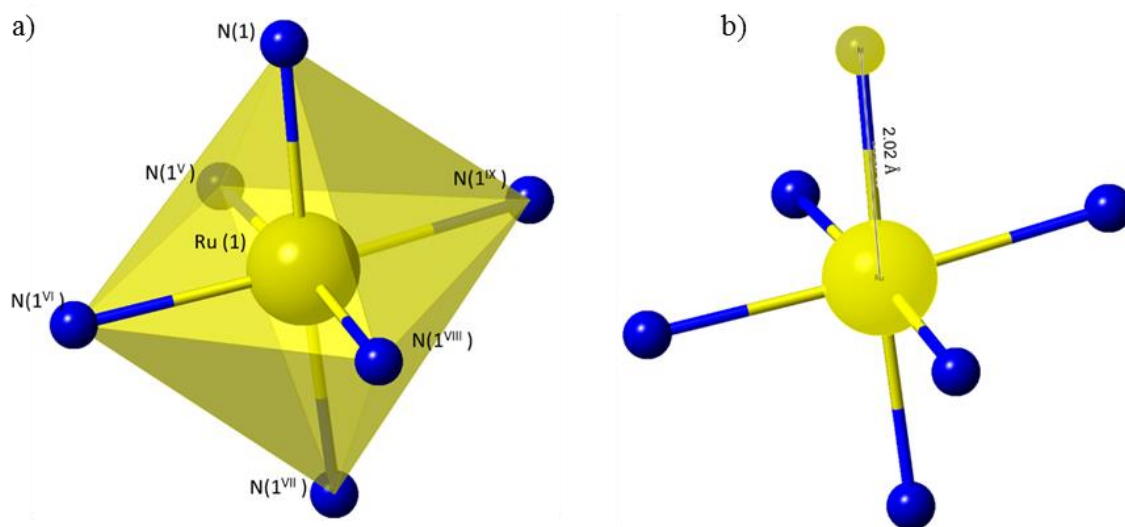


Figure 3.9: Polyhedral representation of the coordination environment of the RuII centres in Photo-MOF (a); Coordination environment of the RuII centres with indicated Ru(1) – N(1) bond distance (b). Symmetry codes: (V) $x, -1 + y, -1 + z$; (VI) $1 - y, -x, 0.5 - z$; (VII) $+ y - x, -x, -1 + z$.

Table 3.1: Selected bond distances and angles for 1. Symmetry codes: (I) $x, x - y, 1.5 - z$; (II) x, y, z ; (III) $1 - x + y, 1 - x, z$; (IV) $1 - y, x - y, z$; (V) $x, -1 + y, -1 + z$; (VI) $1 - y, -x, 0.5 - z$; (VII) $+ y - x, -x, -1 + z$.

Atoms	Distances (Å)	Atoms	Angles(°)
Ru(1) – N(1)	2.02(9)	O(1) – Co(1) – O(1 ^I)	90.4(4)
Co(1) – O(1)	2.09(7)	O(1) – Co(1) – O(1 ^{II})	104.5(2)
		O(1) – Co(1) – O(1 ^{III})	162.7(4)
		O(1) – Co(1) – O(1 ^{IV})	62.4(4)
		N(1) – Ru(1) – N(1 ^V)	86.4(4)
		N(1) – Ru(1) – N(1 ^{VI})	96.0(1)
		N(1) – Ru(1) – N(1 ^{VII})	176.8(5)

Thus, the tris-bidentate coordination geometry of both, the {Co^{II}/carboxylate} and {Ru^{II}/phenanthroline} SBUs, results in structurally similar nodes with D₃ point group symmetry that can be resolved into Δ and Λ enantiomers depending on their helicity. The extended structure results in 2D hexagonal layers composed of alternating Co^{II} and Ru^{II}

nodes of opposite handedness. The layers pack in the direction of the crystallographic *c*-axis in an *ABAB* fashion, involving π -CH and π -NH interactions to form hexagonal channels (Fig. 3.10)

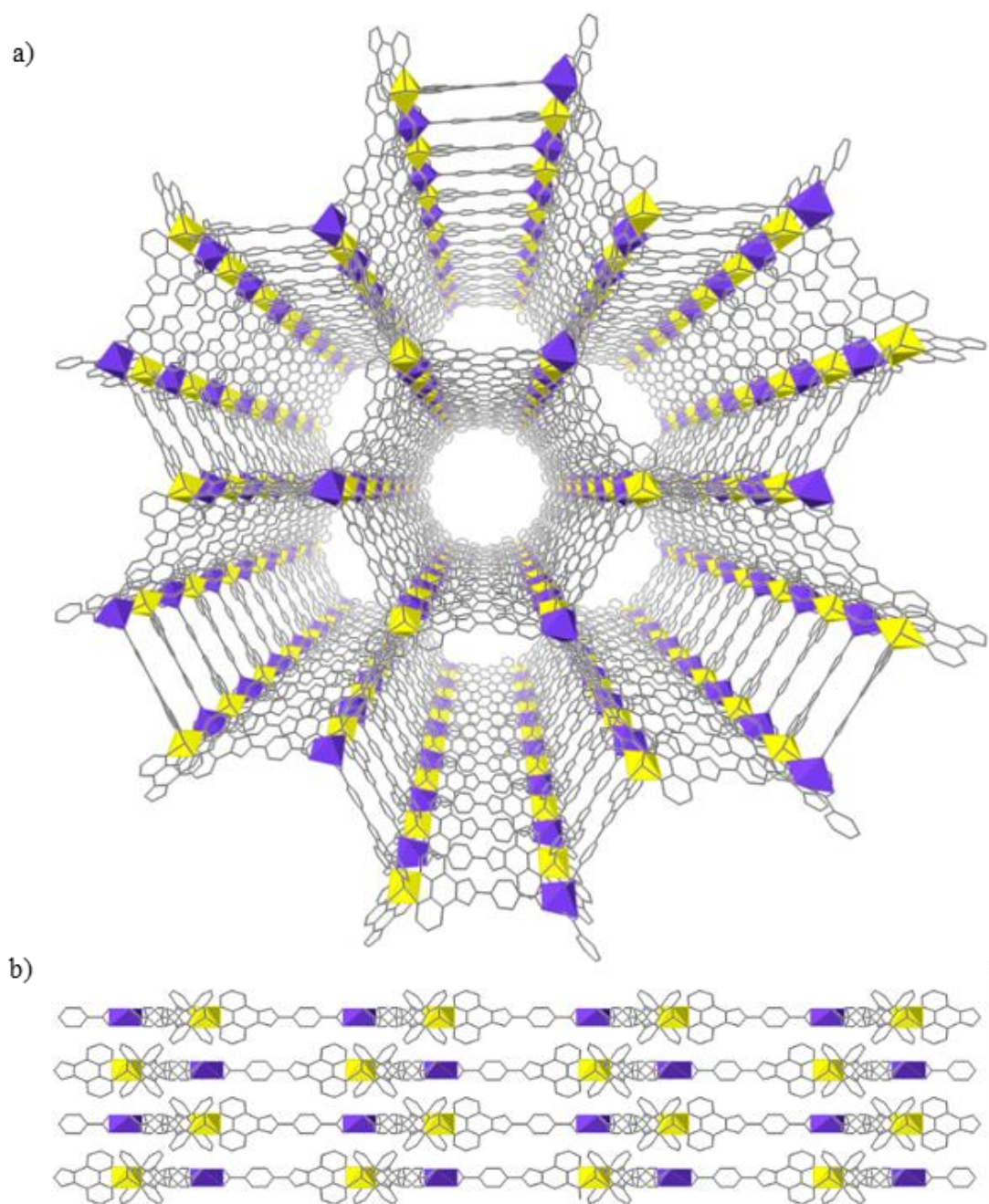


Figure 3.10: A representation of the 2D MOF (1) viewed down the crystallographic *c*-axis showing the channels within the structure (a); and *a*-axis showing the different 2D layers that constitute Photo-MOF (b).

Particularly noteworthy is the large channel aperture that is characterized by cross-sectional diameters of *ca.* 21 Å (Fig. 3.11) which is ideal for encapsulation and rapid diffusion of guest molecules, and potential applications as heterogeneous catalysis, drug-delivery and small bio-molecule/protein encapsulation.⁵⁶⁻⁶¹ The stereochemistry of the individual nodes and the geometry of the channels are characterised by the symmetry operation of an improper S_3 axis which coincides with the centre of the channels and combines the C_3 rotation with a reflection through a plane perpendicular to this rotational axis.

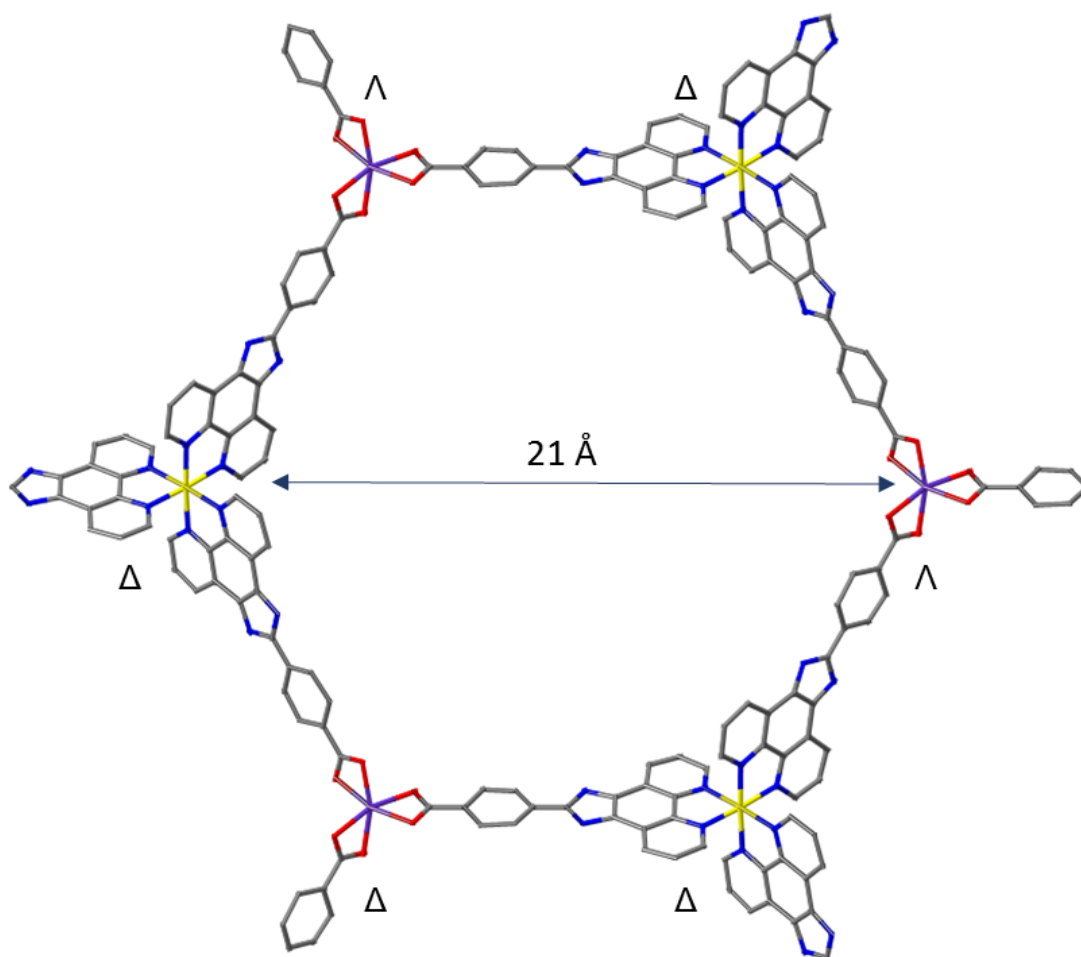


Figure 3.11: Pore aperture of 21 Å and alternating helicities through the channels of Photo-MOF viewed down the crystallographic *c*-axis.

The structure is thus linked into two dimensional plane sheets based on 3-connected SBUs and 3-connected metallo-ligands. The overall net type is a honeycomb **hcb** net with an overall point symbol of 6^3 and an extended point symbol of [6.6.6] (Fig. 3.12)

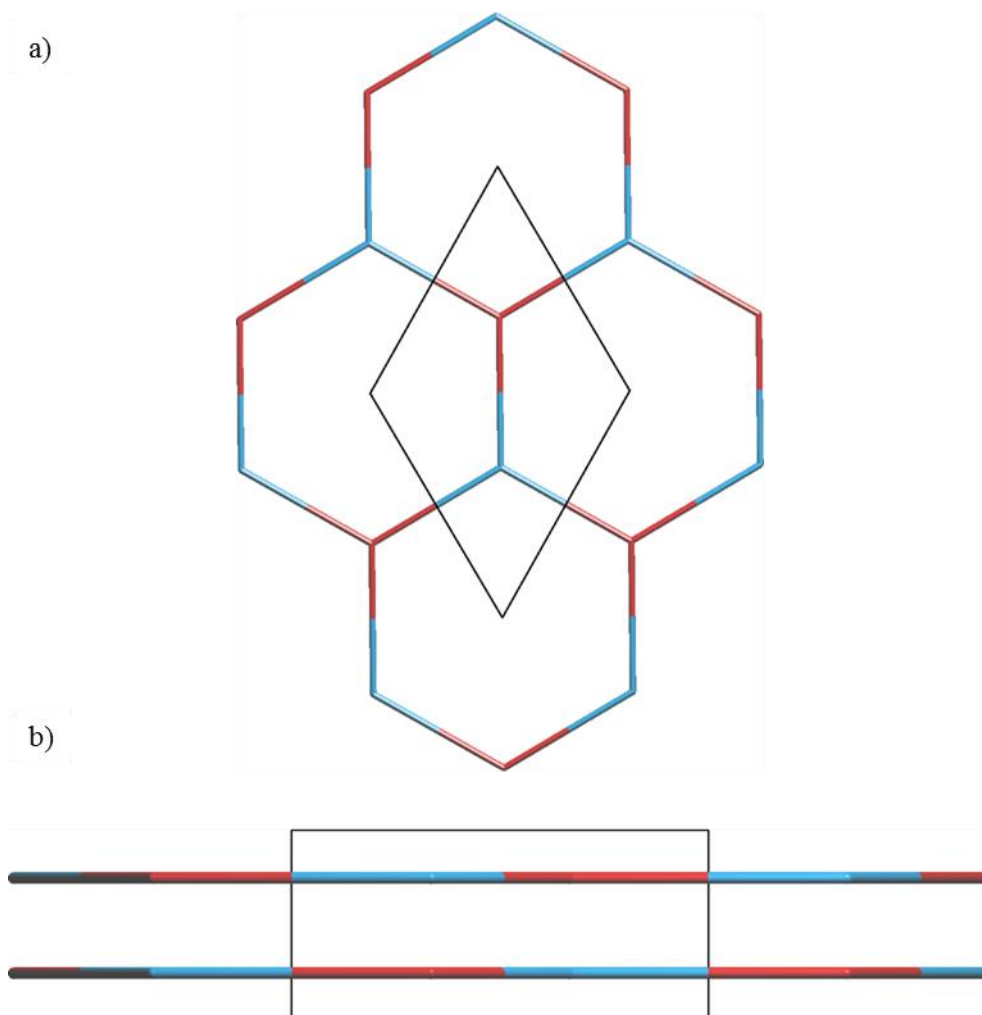


Figure 3.12: The topological reduction of Photo-MOF into an hcb network along the crystallographic c -axis (a); and a -axis (b). 3-connected nodes representing metallo-ligands are in red. Also 3-connected nodes representing $\{\text{CoC}_3\text{O}_6\}$ SBU are in blue.

Table 3.2: Crystal data and structure refinement for Photo-MOF.

Identification code	Photo-MOF
Empirical formula	C ₆₀ CoH ₃₃ N ₁₂ O ₆ Ru (C ₂ F ₃ O ₂) *
Formula weight/ g mol ⁻¹	1291.00
Temperature/K	100
Crystal system	trigonal
Space group	$P\bar{3}1c$
a/Å	26.645(4)
b/Å	26.645(4)
c/Å	10.542(21)
α /°	90
β /°	90
γ /°	120
Volume/Å ³	6482(2)
Z	2
ρ_{calc} mg/m ³	0.661
μ /mm ⁻¹	2.237
F(000)	1302.0
Crystal size/mm ³	0.12 × 0.08 × 0.05
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	1.915 to 52.844
Index ranges	-26 ≤ h ≤ 27, -27 ≤ k ≤ 27, -10 ≤ l ≤ 10
Reflections collected	54055
Independent reflections	2508 [R _{int} = 0.1939]
Data/restraints/parameters	2508 / 0 / 124
Goodness-of-fit on F ²	1.056
Final R indexes [I >= 2 σ (I)]	R ₁ == 0.1010, wR ₂ = 0.2370
Final R indexes [all data]	R ₁ = 0.1793, wR ₂ = 0.2388
Largest diff. peak/hole / e Å ⁻³	1.239/-0.461

* One trifluoroacetate (C₂F₃O₂) has been added to the CIF formula for charge balance.

The phase-purity of the bulk sample was confirmed by powder X-ray diffraction (PXRD) analysis conducted in glass capillaries (Fig. 3.13). The experimental PXRD pattern of an as-synthesized **Photo-MOF** sample was compared to a powder pattern calculated from the single crystal XRD data. The calculated data was obtained using Olex2 software.⁶² The comparison between the experimental and calculated patterns can be seen in Figure 10. The experimental pattern is characterised by signals that appear at $2\theta = 3.85^\circ$, 6.60° and 10.21° . The matching powder patterns indicate phase purity of the bulk sample and supports the accuracy of the refined crystallographic model.

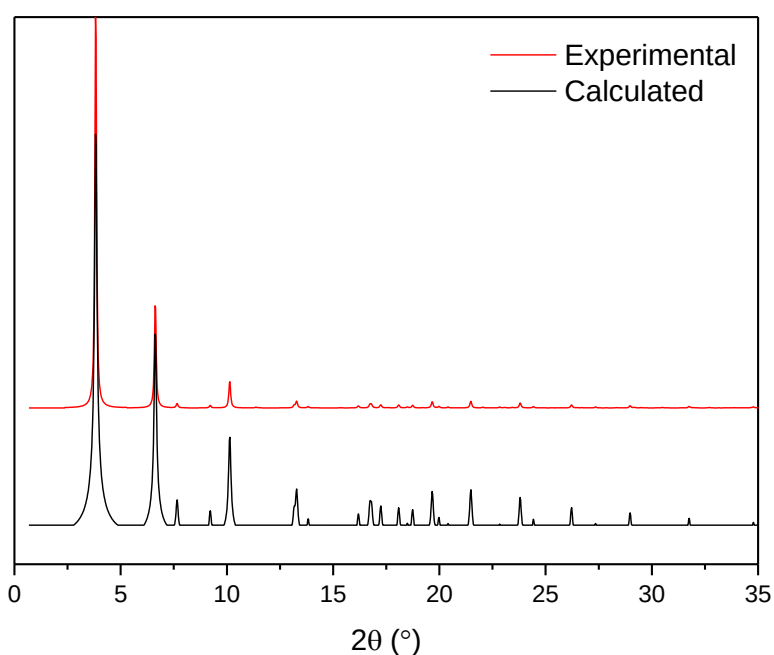


Figure 3.13: Powder X-ray Diffraction (PXRD) pattern for Photo-MOF and calculated pattern.

FTIR spectroscopy was also carried out, and revealed bands characteristic of aromatic and highly conjugated compounds (Fig. 3.14). Bands between 1620 cm⁻¹ and 1330 cm⁻¹ are due to aromatic C=C and C=N stretching frequencies and the different carboxylate binding modes in **Photo-MOF**. Frequencies corresponding to the symmetric and asymmetric stretching vibrations of the carboxylate group in a chelating bidentate mode are assigned to signals at 1599 cm⁻¹ and 1536 cm⁻¹. A Deacon-Phillips value $\Delta = \nu_{\text{as}}(\text{CO}_2) - \nu_{\text{s}}(\text{CO}_2) = 57 \text{ cm}^{-1}$ is characteristic for the observed bidentate binding mode.⁶³⁻⁶⁵ The weak absorption frequencies at 576 cm⁻¹ and 566 cm⁻¹ result from the coordination of the bipyridine nitrogen atoms of the organic ligands to central ruthenium(II) atom.³² The broad signal centred at *ca.* 3500 cm⁻¹ is due to hydrogen bonded DMF molecules present in the framework channels. The weak band at around 2360 is most likely due to the presence of CO₂.

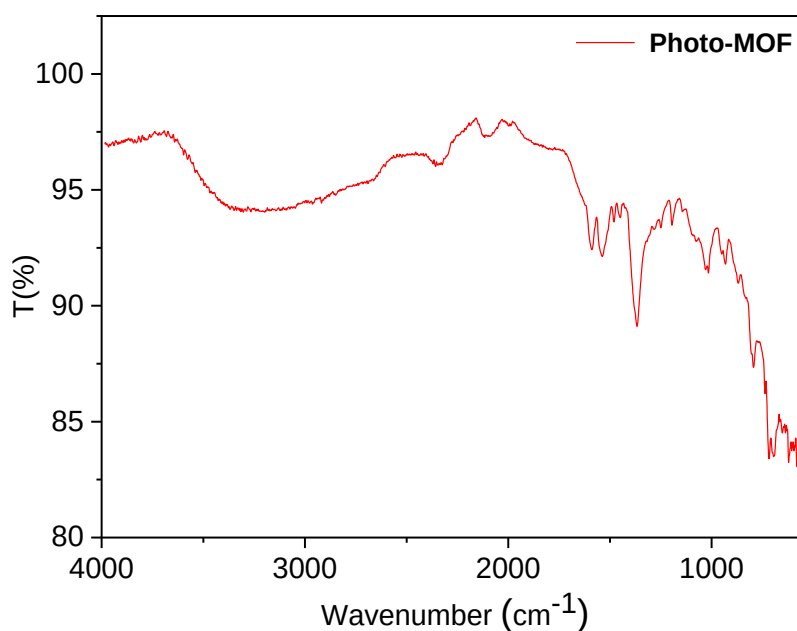


Figure 3.14: FTIR spectrum of Photo-MOF.

3.7. Further characterisation of Photo-MOF

Concerning the identification of the counter ion of **Photo-MOF**, single-crystal X-ray studies were not conclusive as the charge balancing ions were disordered within the large channels of the structure. Further characterisation of the MOF was carried out in pursuance of elucidating the nature of the counter ion. Solid-state NMR spectroscopy, is an important analytical method for structure elucidation providing an alternative characterisation method for insoluble compounds. This technique can also be valuable to determine relative element quantities in addition to identification of a specific chemical environment.⁶⁶⁻⁶⁸

Solid-state NMR experiments of **Photo-MOF** samples were carried out using a Bruker DPX 400 spectrometer at frequencies of 400 MHz for the ¹³C, ³¹P and ¹⁹F nuclei, respectively. Data was collected using 20 mg of the material which was activated by subjecting the sample to vacuum for 12 hours at 150 °C to remove any constitutional solvent molecules. Additionally, a ¹⁹F-NMR spectrum of an as-synthesized sample that contained solvent molecules in the channels, was obtained.

The ¹³C-NMR spectrum of the activated sample (Fig. 3.15) shows very intense broadening due to the presence of paramagnetic Co^{II} ions. The paramagnetic Co^{II} ions, also prevent the appearance of resonance signals that derive from carboxylate moieties (162-190 ppm). Relatively strong signals that result from the aromatic residues of the organic ligand can be observed in the range of 108 to 170 ppm and are in agreement with literature values.^{69, 70}

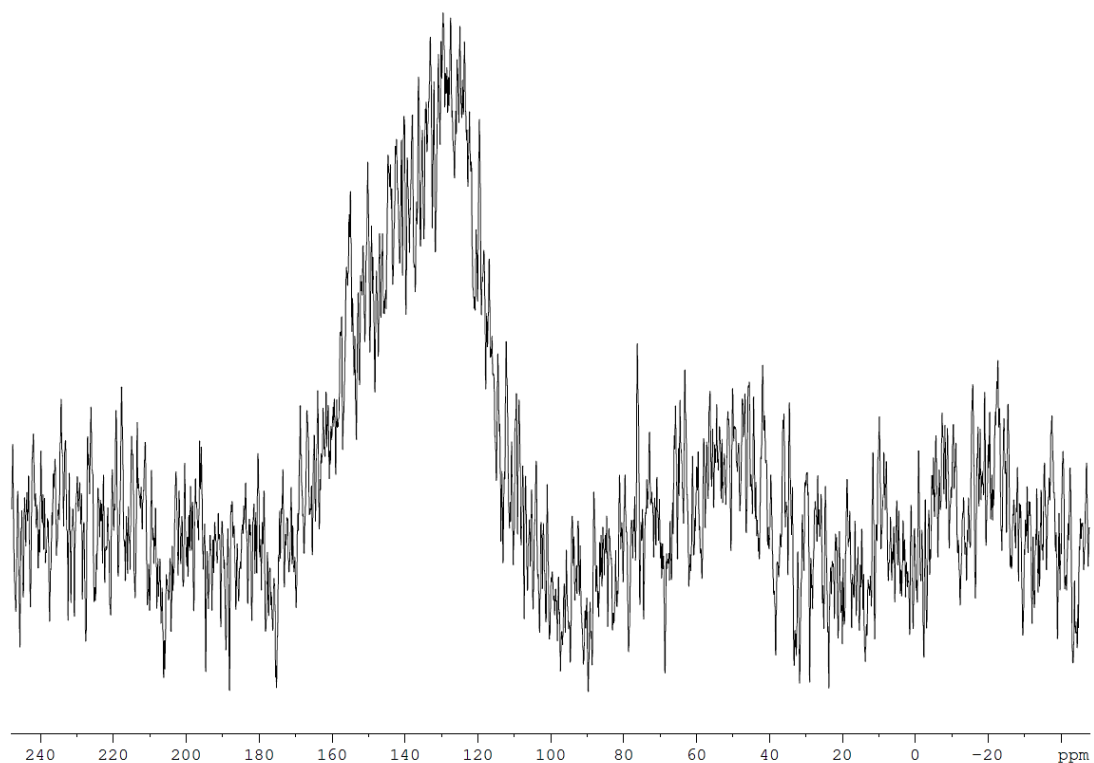


Figure 3.15: Solid-state ¹³CNMR (400 MHz) spectrum of an activated sample of Photo-MOF. Sample was activated under vacuum at 150 °C for 24 hrs.

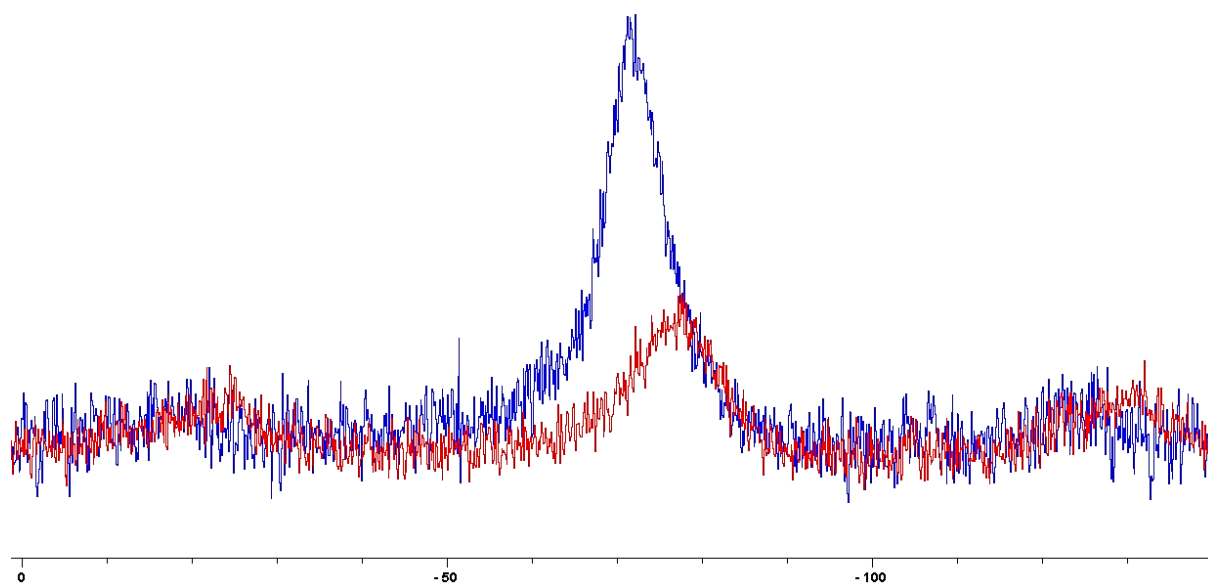


Figure 3.16: Solid-state ¹⁹F-NMR (400 MHz) spectrum of Photo-MOF; as-synthesized (blue) and activated (red).

Figure 3.16 shows ¹⁹F-NMR spectra of the activated and as-synthesized samples. Both spectra show a typical single resonance at *ca.* -75.9 ppm corresponding to the fluorine environment in trifluoroacetic acid (HTFA) or trifluoroacetate (TFA) molecules that are contained in the material. NMR shifts are in agreement with HTFA/TFA shifts reported in the literature.⁷¹ The ratio between the areas of the two signals are indicative for the relative fluorine content of each sample. It is observed that the fluorine quantity is reduced by a factor of *ca.* 5 after the activation procedure.

The Ru(II) metallo-ligand used in the synthesis of the framework was obtained as a salt containing hexafluorophosphate counter anions. ³¹P NMR spectroscopy was carried out to investigate the possibility of PF₆⁻ species (expected at *ca.* $\delta = -145$ ppm)⁷² present as counter ions in the pores of the structure after activation. The ³¹P NMR spectrum (Fig. 3.17) does not display any resonance signals confirming the absence of PF₆⁻ anions within the structure. Thus the NMR analyses suggest that trifluoroacetate anions act as counterions of the cationic framework structure whilst additional trifluoroacetic acid molecules locate in the channels of the MOF. This assignment is further consistent microanalytical data.

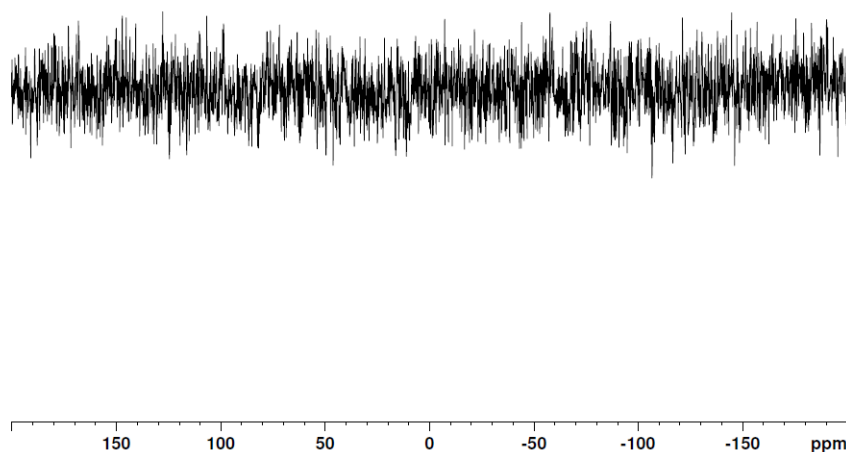


Figure 3.17: Solid-state ³¹P-NMR (400 MHz) spectrum of Photo-MOF confirming the absence of possible PF₆⁻ counterions in the structure.

Energy Dispersive X-Ray Spectroscopy (EDX) measurements were carried out using samples of **Photo-MOF** which were deposited on carbon tabs for elemental analysis (Fig. 3.18). The experiment was performed at an acceleration voltage of 20 keV and revealed

an average Ru/Co atomic ratio of 1:0.93, which is in close agreement with crystallographic data of the material.

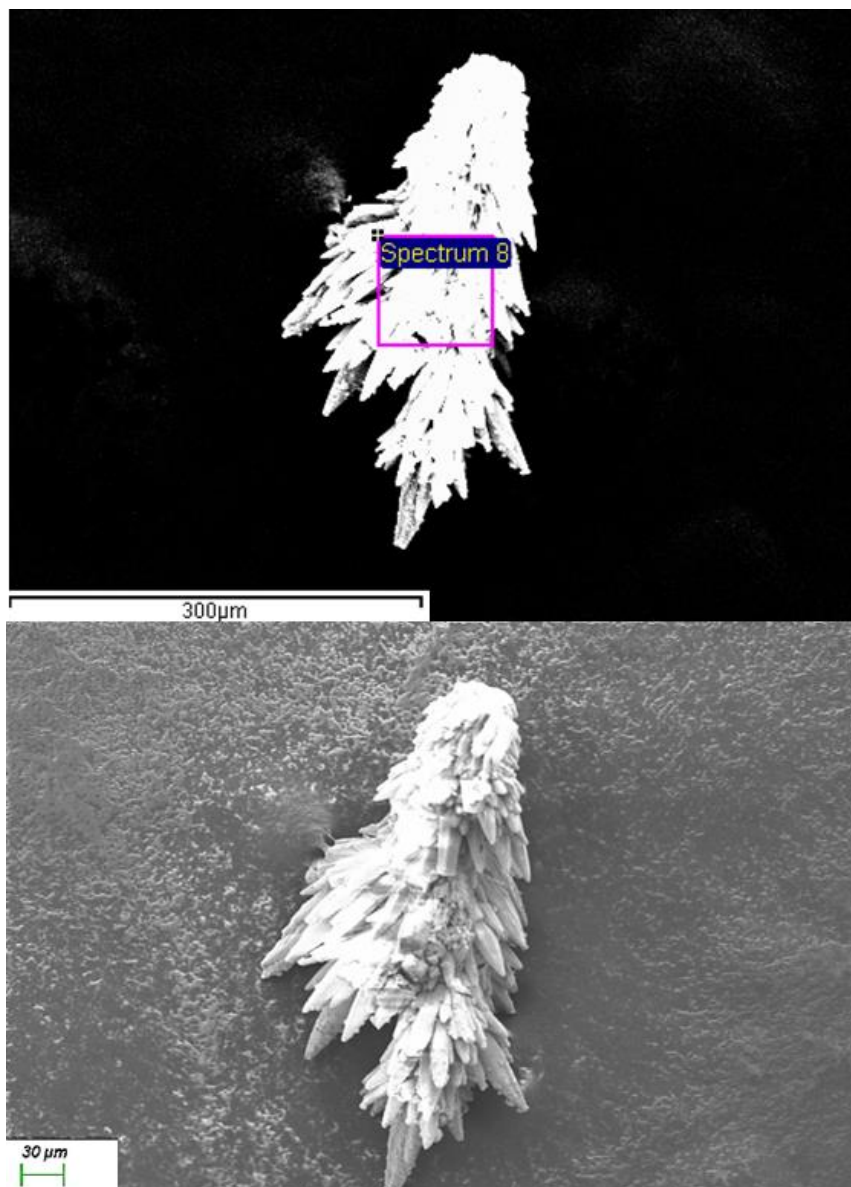


Figure 3.18: Dispersive X-ray (EDX) elemental analysis of Photo-MOF.

Scanning Electron Microscopy (SEM) analysis was also performed on a freshly synthesized sample of **Photo-MOF**. The sample was mounted on adhesive carbon tape and coated with gold for imaging purposes (Fig. 3.19). Individual crystals of **Photo-MOF** reveal a needle-like morphology forming characteristic agglomerates. The observed crystal sizes vary and individual crystals have typical lengths of 95 μm and widths of 4 μm. It is further noteworthy that the layered nature of the material is somewhat also

represented in the morphology of the crystals, which reveal layers/lines that arrange perpendicular to the long crystal axis.

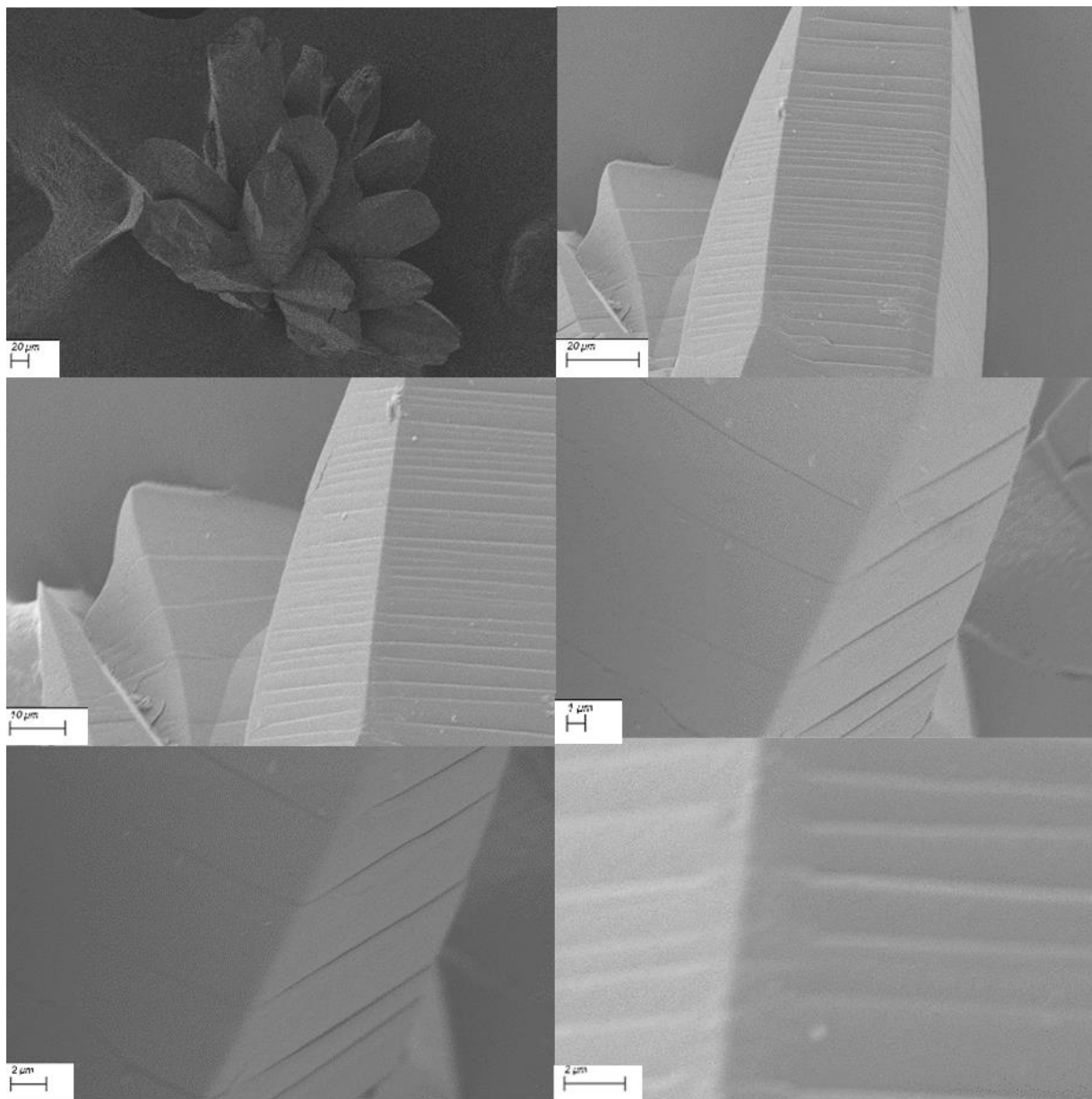


Figure 3.19: Scanning Electron Microscopy (SEM) images displaying layered pattern of the crystals of Photo-MOF.

3.8. Thermogravimetric analysis

The thermal stability of a freshly prepared crystalline sample of **Photo-MOF** was investigated. Thermogravimetric analysis (TGA) was carried out under nitrogen atmosphere in the temperature range of 25 to 500 °C. The experiment revealed that **Photo-MOF** undergoes a decomposition pathway that follows three main steps (Fig. 3.20). The primary step between 20°C and approximately 100°C shows a weight loss of *ca.* 46 % due to the loss of constitutional solvent molecules trapped in the pores of the framework. The degradation of the counterions and the organic ligand can be observed above 250 °C and it is followed by further degradation above 330 °C, resulting, most likely, in the formation of a metal oxide material and possibly residual amorphous carbon.

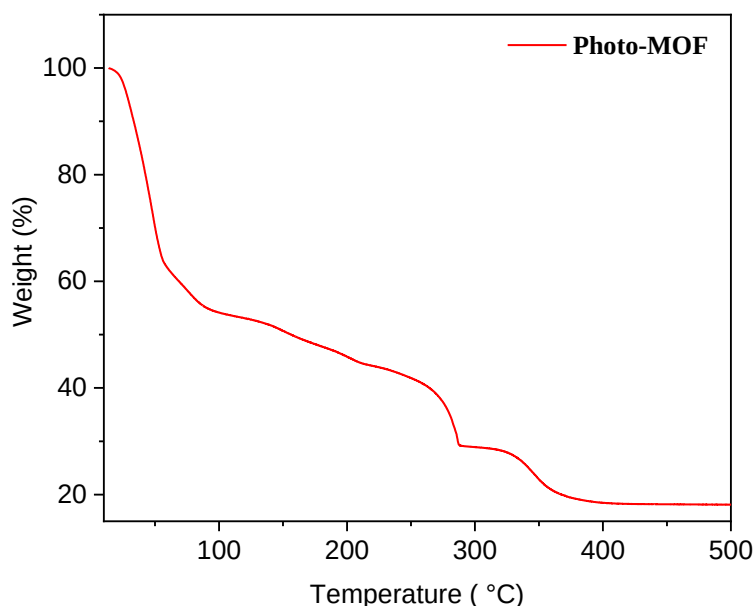


Figure 3.20: Thermogravimetric analysis of Photo-MOF showing the percentage weight loss upon increasing temperature.

3.9. Gas adsorption studies

Volumetric gas adsorption isotherms of an activated sample of **Photo-MOF** were recorded in the 0 – 1 bar pressure range using a Quantachrome Autosorb-iQ gas analyser. For this purpose 65 mg of a dried methanol exchanged sample was placed in a pre-dried and weighed glass cell. The sample was subjected to vacuum and activated at 150 °C under secondary vacuum for 12 hours to remove any constitutional solvent molecules. The accurate weight of the activated sample was measured prior to analysis.

3.9.1. N₂ adsorption studies

N₂ adsorption at 77 K (Fig. 3.21) using **Photo-MOF** as adsorbent confirmed structural integrity of the framework structure upon activation. **Photo-MOF** shows relatively high N₂ uptake at 77 K. The adsorption-desorption isotherms reveal type IV(b) behaviour, characterized by rather steep adsorption at low relative pressures followed by a step at a relative pressure of *ca.* 0.1 whereby no hysteresis effects are observed during the adsorption/desorption cycle.^{73,74} The characteristic step is consistent with the presence of small mesopores of *ca.* 2 nm in diameter, in which capillary condensation of N₂ takes place.⁷⁵

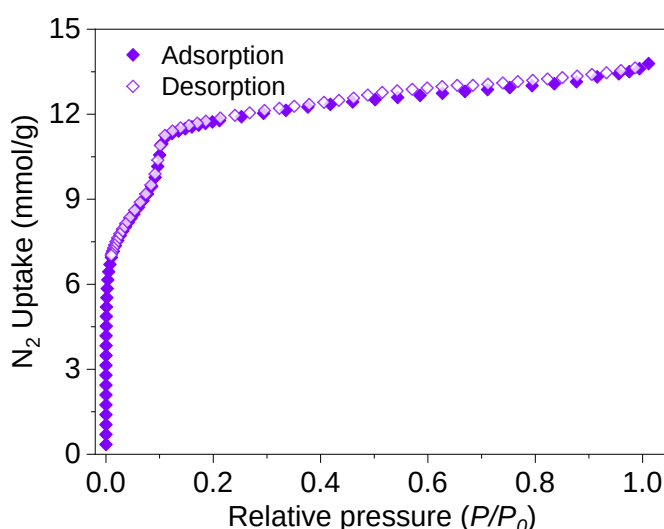


Figure 3.21: N₂ adsorption (filled symbols) and desorption (open symbols) isotherms at 77 K using Photo-MOF as adsorbent.

The N₂ adsorption behaviour of the metallo-ligand at 77 K was also investigated (Fig. 3.22). The sample was activated using the same process that was used for **Photo-MOF**. The experiment was carried out to characterise the metallo-ligand and for consistency to provide comparable data to **Photo-MOF**. The resulting N₂ isotherm measured at 77 K is essentially characteristic of a non-porous adsorbent.

A comparison of the N₂ adsorption capacities of **Photo-MOF** and the metallo-ligand is shown in Figure 3.23. The data confirms that the metallo-ligand does not present sorption capacities.

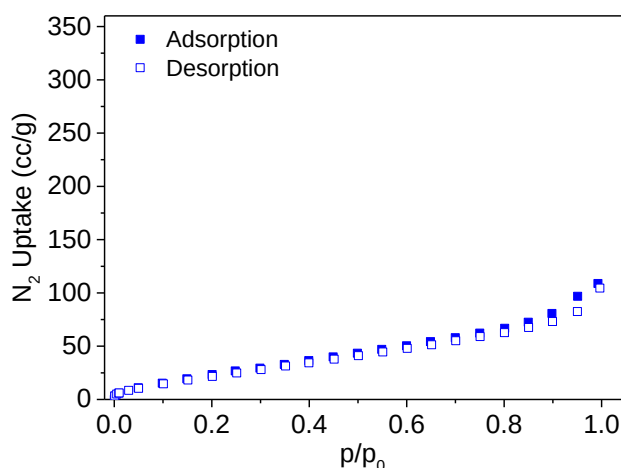


Figure 3.22: N₂ adsorption (filled symbols) and desorption (open symbols) isotherms at 77 K using metallo-ligand [H₃L₁^{Ru}](PF₆)₂ as adsorbent.

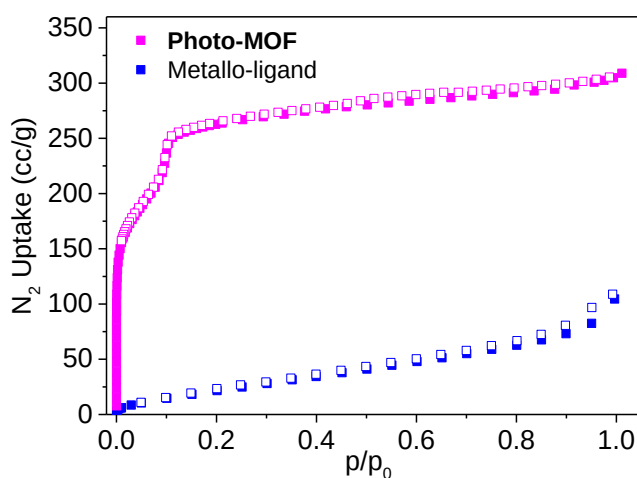


Figure 3.23: N₂ adsorption (filled symbols) and desorption (open symbols) isotherms at 77 K using of Photo-MOF (magenta) and the metallo-ligand (blue) as adsorbent.

3.9.2. BET surface area determination

The BET (Brunauer–Emmett–Teller) surface area of **Photo-MOF** and the metallo-ligand [H₃L^{Ru}](PF₆)₂ was determined using the linear region of the N₂ isotherm at 77 K prior to the pore filling step. Equation 3.9.2.1 was used for the analysis of the experimental data.⁷⁶

$$\frac{1}{W((P_0/P) - 1)} = \frac{1}{W_m C} + \frac{C - 1}{W_m C} (P/P_0) \quad (3.9.2.1)$$

Where P is the equilibrium pressure of the adsorbate (N₂) and P_0 is the saturation pressure of the adsorbate at 77 K, W is the weight of gas adsorbed at relative pressure, P/P_0 and W_m is the weight of adsorbate considering a monolayer of surface coverage. The BET constant, C , is related to the energy of adsorption in the first adsorbed layer and an indication of the magnitude of the absorbent/adsorbate interactions.^{76, 77}

The BET equation required linear plots of $1/(W((P_0/P) - 1))$ against P/P_0 using **Photo-MOF** and the metallo-ligand as adsorbents and nitrogen as adsorbate. The BET plots result in straight lines and are shown in Figures 3.24 and 3.25. The value of the slope, $s = (C - 1)/(W_m C)$ and the intercept, $i = 1/(W_m C)$, were used to calculate the weight of the monolayer W_m and the BET constant C .

The BET surface area (S_{BET}) was then calculated from the total surface area (S_{total}) using equations 3.9.2.2 and 3.9.2.3,

$$S_{BET} = \frac{S_{total}}{w} \quad (3.9.2.2)$$

$$S_{total} = \frac{W_m N A_{cs}}{M} \quad (3.9.2.3)$$

where w is the weight of the sample of adsorbent, N is Avogadro's number and M is the molar mass of the adsorbate. The cross-sectional area (A_{cs}) for a close-packed nitrogen monolayer at 77 K is 16.2 Å².

A BET surface area of *ca.* 910 m²/g and total pore volume of 0.478 cm³/g (using the Gurvich rule)⁷⁸ were found for **Photo-MOF**. The BET surface area calculated for the metallo-ligand was found to be of only 50.17 m²/g which is not significant when compared to the surface area of the MOF. The calculations confirmed that the adsorption properties of the material are intrinsic to the framework. Structure of **Photo-MOF**.

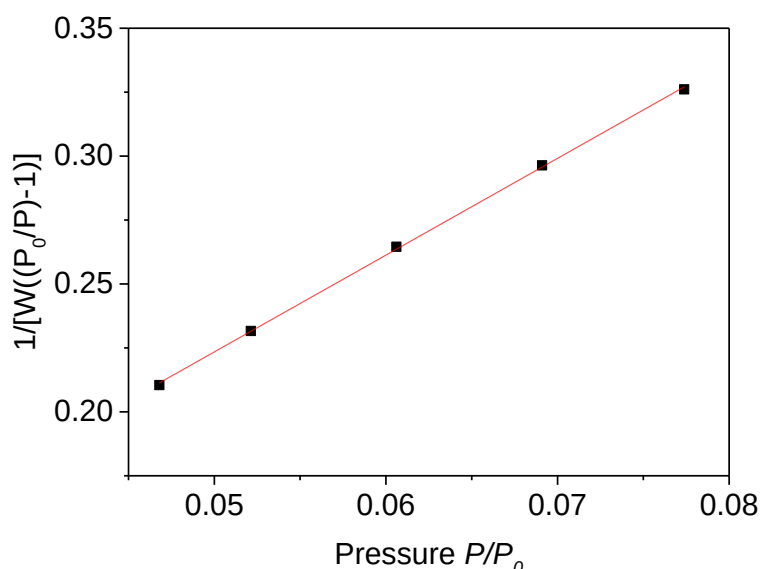


Figure 3.24: Multi-point BET fit for Photo-MOF as adsorbent.

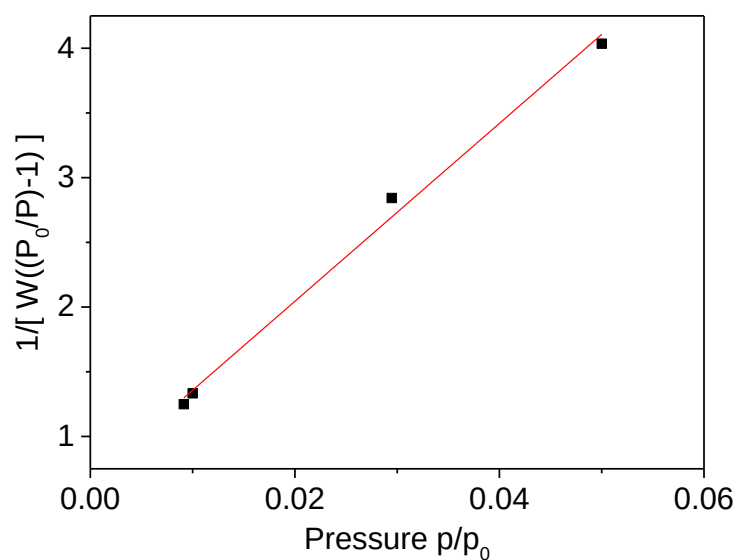


Figure 3.25: Multi-point BET fit for [H₃L^{Ru}](PF₆)₂ as adsorbent.

3.9.3. DFT calculations to evaluate the pore-size distribution

Gas adsorption measurements can provide a fingerprint of the microstructure of adsorbents. The pore size distribution is particularly useful information that can be obtained specifically from nitrogen adsorption at 77 K. Most applied analysis methodologies rely on the fact that capillary condensation occurring in a particular pore is directly related to the size of that pore and thus, the condensation pressure can be used as an indicator of a particular pore size.⁷⁹ Density Functional Theory (DFT) can be used as a practical method for determining pore size distribution. When used for simple pore geometries like the cylindrical pores observed in **Photo-MOF**, the DFT method is particularly accurate as the experimental capillary condensation pressures relate to a specific singular geometry resulting in converging simulation results.^{80,81}

DFT calculations were performed using the Quantachrome ASiQwin software and the N₂ isotherms measured at 77 K, in order to determine the pore size distribution of the **Photo-MOF**. The model used for the calculations is the non-local density functional theory (NLDFIT) equilibrium model⁸² for cylindrical pores that was developed for carbon-based materials. The fitting of the experimental data is presented in Figure 3.26.

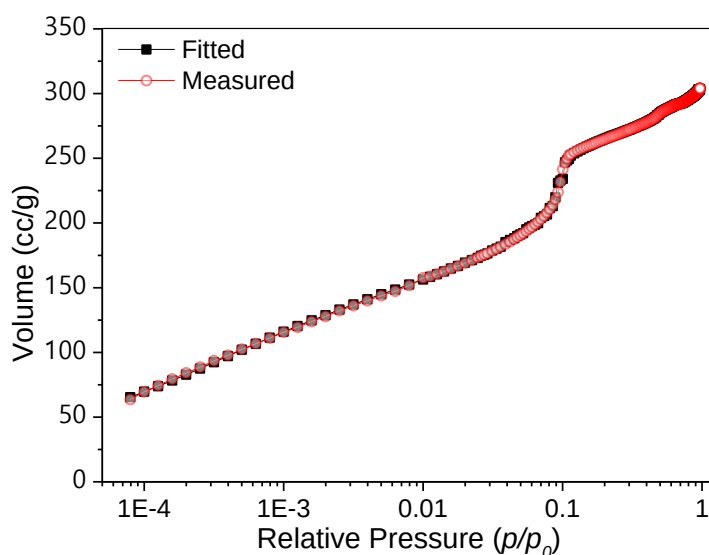


Figure 3.26: DFT fitting for Photo-MOF.

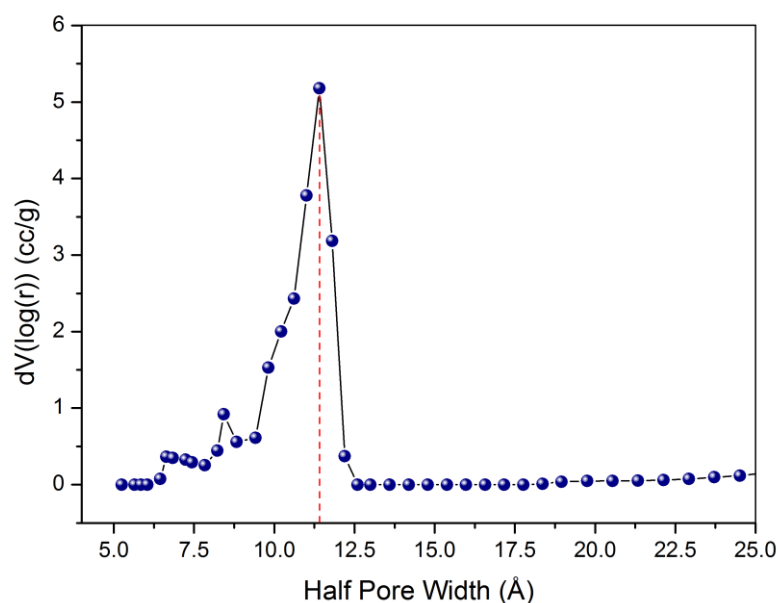


Figure 3.27: Pore size distribution of Photo-MOF calculated by DFT method.

As previously discussed, the small step observed in the nitrogen sorption graph (Fig. 3.27) at a relative pressure of *ca.* 0.1 is indicative of the presence of small mesopores in the material.⁷⁵ This assessment is confirmed by the DFT calculations. The calculated half pore width of 11.4 Å (Fig. 3.11) classifies **Photo-MOF** as a borderline material between classical microporous and the mesoporous materials.⁷⁶ DFT calculations confirm the prevalence of small mesopores of *ca.* 2 nm within the structure.

3.9.4. CO₂ adsorption studies

CO₂ adsorption isotherms were measured at three different temperatures (278 K, 293 K and 308 K) as shown in Figure 3.28. The same activation procedure as for the N₂ sorption studies were applied. Higher adsorption capacities were obtained at lower temperatures, as expected. At 278 K, the lowest applied experimental temperature, the CO₂ uptake is 63.09 cc/g at 1 bar. This storage capability is *ca.* 24% higher than at room temperature (CO₂ uptake at 293 K of 50.60 cc/g). The experiment also reveals that **Photo-MOF** adsorbs CO₂ reversibly which indicates the absence of chemisorption processes under the applied experimental conditions.

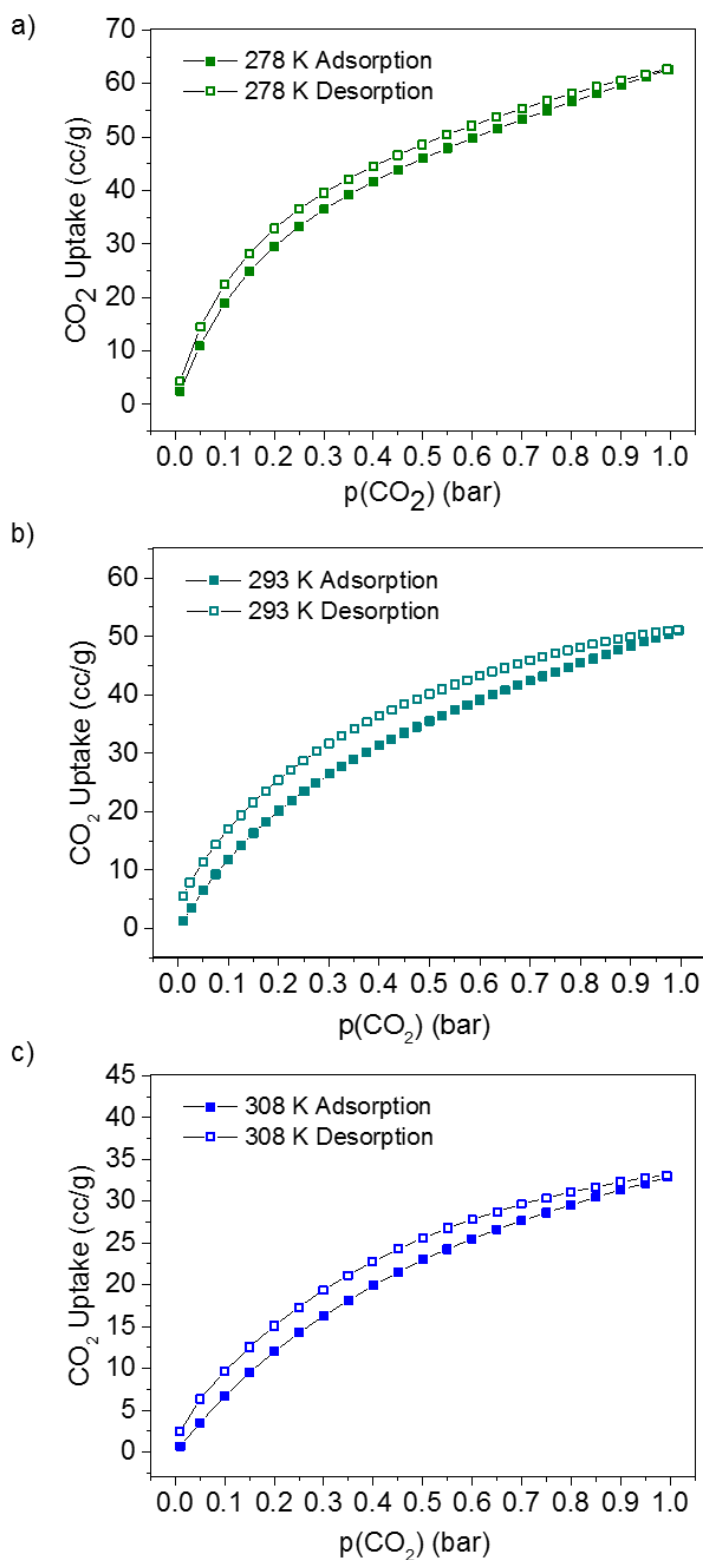


Figure 3.28: CO₂ adsorption (filled symbols) and desorption (open symbols) isotherms at 278 K (a); 293 K (b); and 308 K (c) using Photo-MOF as adsorbent.

3.9.5. CO₂/N₂ selectivity calculations

Aiming to investigate the CO₂/N₂ selectivity capabilities of **Photo-MOF**, the adsorption isotherm of N₂ was measured at 293 K using **Photo-MOF** as adsorbent. The obtained data was then compared to the CO₂ uptake at the same temperature (Fig. 3.29). The adsorption storage capacities at 1 bar for CO₂ and N₂ are 2.28 mmol/g and 0.244 mmol/g, respectively.

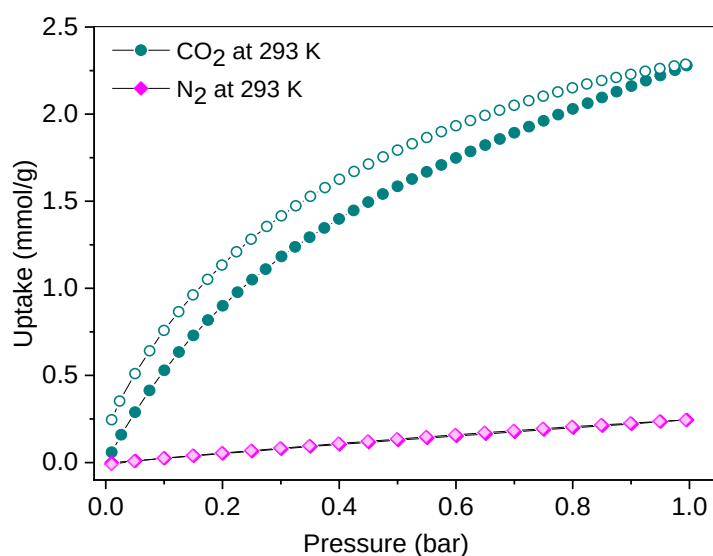


Figure 3.29: CO₂ and N₂ adsorption (filled symbols) and desorption (open symbols) isotherms at 293 K and 293 K for Photo-MOF.

In order to accurately determine the CO₂/N₂ selectivity of **Photo-MOF**, the experimental single-gas isotherms were simulated using Henry and Langmuir models. These models were selected in order to give the best fits while minimizing the number of parameters. Respectively, the pure CO₂ and N₂ isotherms were fitted using the following models:

$$q_{model,CO_2}(p_{CO_2}) = \frac{q_{s,CO_2} b_{CO_2} p_{CO_2}}{1 + b_{CO_2} p_{CO_2}} + K_{H,CO_2} p_{CO_2} \quad (3.9.5.1)$$

$$q_{model,N_2}(p_{N_2}) = K_{H,N_2} p_{N_2} \quad (3.9.5.2)$$

To quantify the quality of the fitting, the mean relative deviations were calculated for each isotherm as:

$$D(\%) = \frac{100}{N} \sum_{i=1}^N \frac{|q_{exp}(i) - q_{model}(i)|}{q_{exp}(i)} \quad (3.9.5.3)$$

In these equations, q represents the uptake while q_s is the maximum uptake, b is the energetic parameter and N is the number of experimental values for the considered isotherm. The Henry constant is represented by K_H .

Figure 3.30 compares the experimental and simulated isotherms of CO₂ and N₂ at 293 K measured on **Photo-MOF**. Table 3.2 reports the parameters that were used for the simulations and the mean relative deviations.

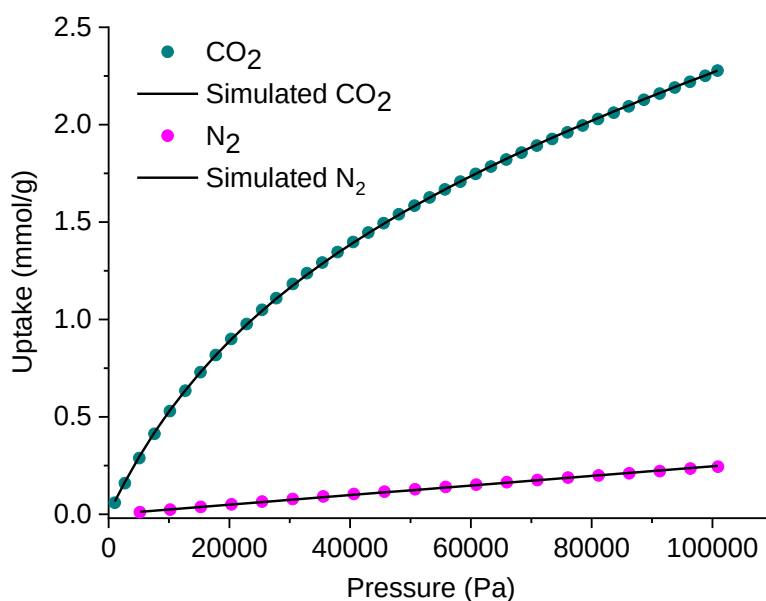


Figure 3.30: Data fitted to experimental CO₂ and N₂ adsorption isotherms measured at 293 K for Photo-MOF.

The CO₂/N₂ selectivity was calculated by dividing the slopes, of the simulated isotherms, in the Henry region:

$$S_{CO_2/N_2} = \frac{q_{s,CO_2} b_{CO_2} + K_{H,CO_2}}{K_{H,N_2}} = 26.72 \quad (3.9.5.4)$$

Table 3.3: Isotherms parameters and deviation.

Compound	K _H (mmol g ⁻¹ Pa ⁻¹)	q _s (mmol g ⁻¹)	b(Pa ⁻¹)	D(%)
CO ₂	7.92 x 10 ⁻⁶	1.9797	2.92 x 10 ⁻⁵	3.12
N ₂	2.46 x 10 ⁻⁶	-	-	0.75

Thus, **Photo-MOF** reveals a CO₂/N₂ selectivity of 26.7 suggesting preferential CO₂-framework interactions within the 1-D channels of the framework. This relatively high selectivity is somewhat surprising as the channel/pore sizes in Photo-MOF cannot give rise to preferential uptake characteristics based on geometrical features and the different kinetic radii of the adsorbates. The observed behaviour can be due to dipolar CO₂ interactions with the imidazole functionality of the organic ligands.⁸³⁻⁸⁶

3.10. Photophysical characterisation of Photo-MOF

To evaluate the role of the Ru^{II} centre's ability as a photosensitizer, UV-Vis absorption, spectral photoluminescence and time-resolved photoluminescence studies were performed using both, the metallo-ligand [H₃L^{Ru}](PF₆)₂ and **Photo-MOF**.

Bands at *ca.* 200-300 nm in the UV-Vis absorption spectra of the metallo-ligand and the MOF are characteristic for {Ru/phenanthroline} species, giving rise to ligand-centred transitions (Fig. 2a).^{34, 35} Broad absorbance bands at *ca.* 480 nm can be assigned to ¹MLCT transitions^{16, 87, 88} and demonstrate that excitation energies of the chromophore are only slightly altered in **Photo-MOF** in comparison to the metallo-ligand (Fig.3.31).

From a perspective of efficient use of solar light, there is widespread demand for visible-light active photosensitisers. The absorption spectrum of **Photo-MOF** shows that a larger photon absorption region of the solar spectrum⁸⁹ compared to porphyrin-based MOFs.^{14 25, 90} **Photo-MOF** also exhibit broader MLCT bands than [Ru(bpy)₃]²⁺ complexes that were encapsulated within the UiO-67^{20, 91, 92} and where the MOF functions more as an inert physical scaffold rather than a light-harvesting framework.

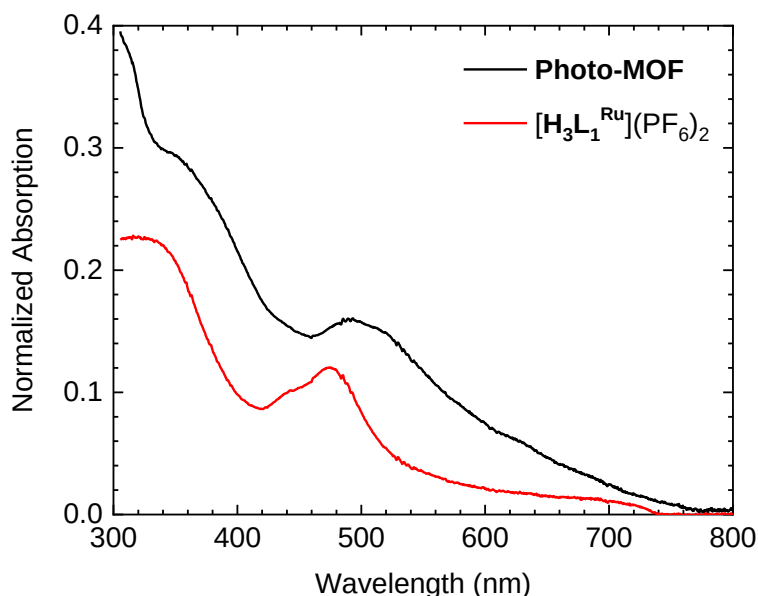


Figure 3.31: Normalised absorption spectra of Photo-MOF and [H₃L^{Ru}](PF₆)₂.

The photoluminescence spectra of metallo-ligand $[\text{H}_3\text{L}_1^{\text{Ru}}](\text{PF}_6)_2$ and **Photo-MOF** were recorded at an excitation wavelength of $\lambda_{\text{ex}} = 405$ nm (Fig. 3.32). The spectrum of **Photo-MOF** is centred at approximately 620 nm and shows evidence of a stronger shoulder on the lower wavelength side of the spectrum when compared to the metallo-ligand as a result of the binding to of the Co^{II} ions.

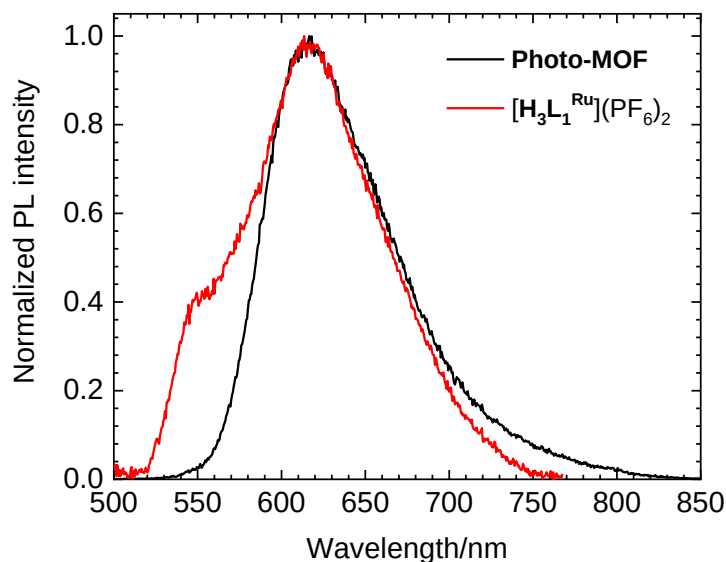


Figure 3.32: Normalised photoluminescence (PL) spectra of Photo-MOF and the metallo-ligand ($\lambda_{\text{ex}} = 405$ nm).

As previously discussed, MOFs that exhibit photoluminescence can be exploited in sensing applications as luminescent probe materials.⁹³ The photoluminescence spectrum of **Photo-MOF** is similar to those of other heterometallic MOFs such as a Ru-In-based MOF that also incorporates a propeller-like metallo-ligand based on the $[\text{Ru}(\text{bpy})_3]^{2+}$ moiety as a chromophore.⁹⁴ The material was employed for the sensing of explosives due to its luminescent properties. However, very small pore size and channel diameters within the framework hampered the encapsulation of the analytes. As a porous framework, **Photo-MOF** can encapsulate guest molecules allowing for a variety of diverse sensing mechanisms. Moreover, MOFs with similar photoluminescent behaviour and lower surface areas have been exploited for sensing of toxins,⁹⁵ humidity,⁹⁶ temperature^{97,98} and oxygen.⁹⁹

Time-resolved photoluminescence decays (recorded at $\lambda_{\text{emis}} = 600$ nm with an excitation power of 20 μW) for **Photo-MOF** and the metallo-ligand are shown in Figure 3.33 and highlight the reduced photoluminescence decay lifetime for **Photo-MOF** in comparison to the uncomplexed metallo-ligand. The studies emphasise that the native photophysical properties of $[\text{H}_3\text{L}_1^{\text{Ru}}](\text{PF}_6)_2$ are maintained in **Photo-MOF**, whereby coordination to Co^{II} ions gives rise to electron/energy transfer processes throughout the network structure. This is consistent with a predominant Dexter mechanism for energy transfer in MOFs.¹⁴

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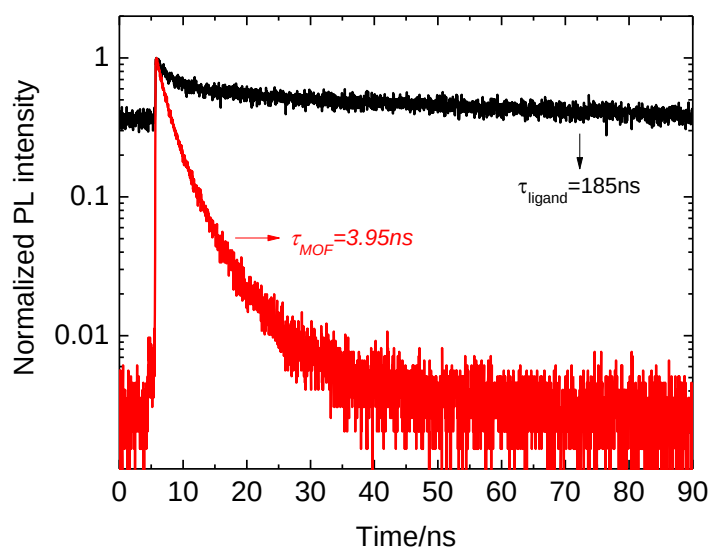


Figure 3.33: Normalised time-resolved photoluminescence decays of Photo-MOF (red) and the metallo-ligand (black) measured at $\lambda_{\text{emis}} = 600$ nm ($\lambda_{\text{ex}} = 405$ nm). Measurements conducted in DMF dispersions.

Spectrally time-resolved photoluminescence decays were measured using five bandpass filters with centre wavelengths across the photoluminescence spectra. These reveal that the lifetime of the ³MLCT state of the metallo-ligand is consistently reduced upon coordination to Co^{II} ions in **Photo-MOF**. Increased average lifetimes were observed for longer emission wavelengths, and an average luminescence decay lifetime of *ca.* 20 ns for $\lambda_{\text{emis}} = 750$ nm (Fig. 3.34) was obtained for **Photo-MOF**. Bioexponential behaviour in DMF suspension was observed for both the MOF and the metallo-ligand.

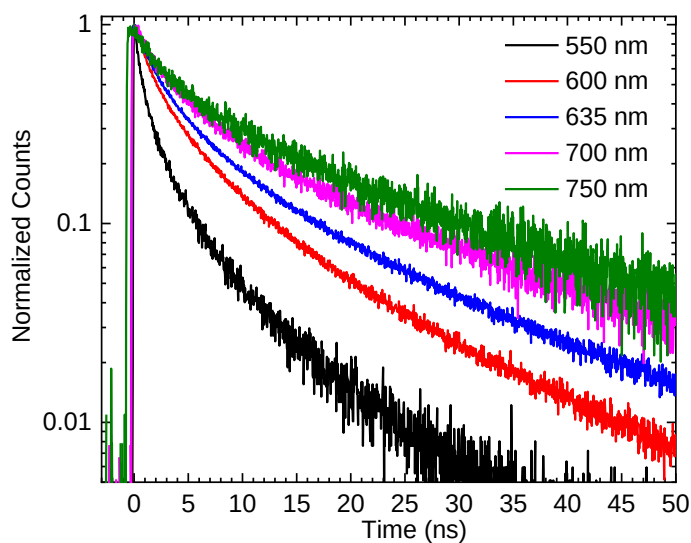


Figure 3.34: Normalised time-resolved photoluminescence decays of Photo-MOF measured at 5 different central emission wavelengths using 10 nm bandpass filters ($\lambda_{\text{ex}} = 405$ nm).

The dependence of the integrated lifetimes and peak intensities of Photo-MOF on the laser power at the excitation wavelength of $\lambda_{\text{ex}} = 405$ nm, were investigated. The spectrally resolved data is presented in Figure 3.35. The measurements confirm spectral and power dependence of the lifetimes and peak intensities whereby the lifetimes and intensities generally increase linearly with the energy of the incident laser light. Regarding spectrally resolved lifetimes, higher values were recorded at $\lambda_{\text{emis}} = 635$ nm and lowest values were observed at $\lambda_{\text{emis}} = 550$ nm (Fig. 3.35a). A different trend can be seen for the spectrally resolved peak intensities (Fig. 3.35b) where the results at $\lambda_{\text{emis}} = 550$ nm and 700 nm partially overlap, and lower intensity were obtained at $\lambda_{\text{emis}} = 750$ nm. The power dependence trends for the lifetimes and peak intensities are equivalent at the five different central emission wavelengths used in the experiment. Thus, varying the laser power between 0.02 μW and 2.00 μW results in the increase of the lifetime by a factor of approximately 100. Similarly the peak intensities increase by a factor of 60 upon power variation.

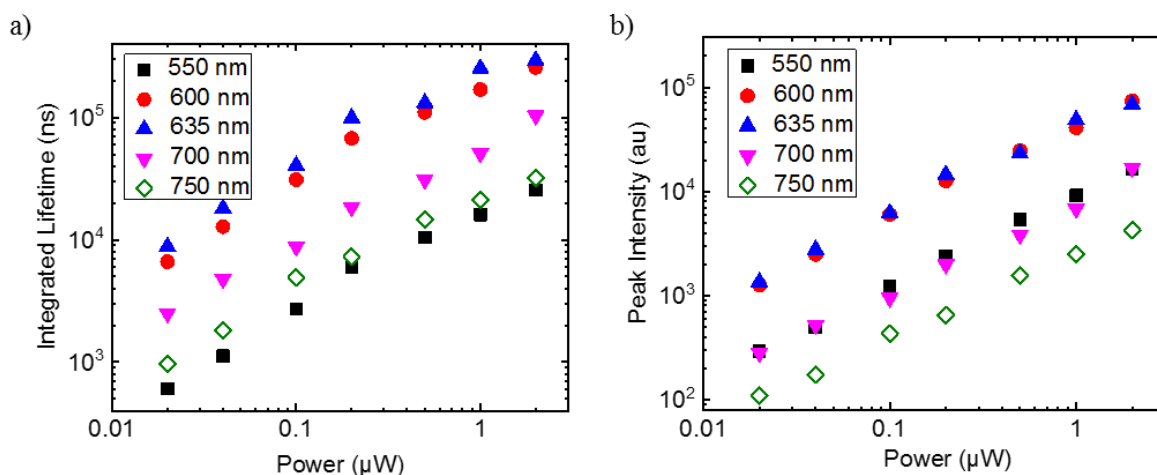


Figure 3.35: Dependence of the lifetimes (a) and peak intensities (b) on the laser power at the excitation wavelength of $\lambda_{\text{ex}} = 405$ nm.

Fluorescence lifetime imaging microscopy (FLIM) was applied to solid-state samples to demonstrate the uniform distribution of fluorophores within the material and evaluate the opto-thermal stability of **Photo-MOF**. Interestingly, whilst the solid material of $[\text{H}_3\text{L}_1^{\text{Ru}}](\text{PF}_6)_2$ undergoes rapid degradation upon exposure to the higher power laser excitation, no detectable damage is noticed for crystals of **Photo-MOF**. This can be attributed to the lower density of chromophores per unit volume and possibly to the inherent structural integrity of **PhotoMOF** or the heat dissipation throughout the network (Fig. 3.36a and 3.36b).

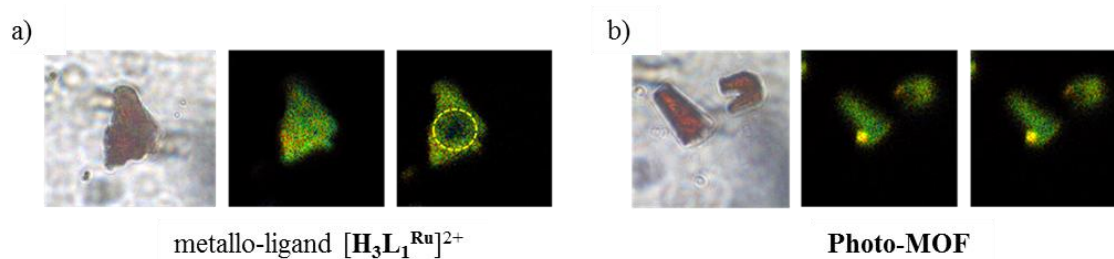


Figure 3.36: Optical and fluorescence-lifetime imaging microscopy (FLIM) images of solid state $[\text{H}_3\text{L}_1^{\text{Ru}}](\text{PF}_6)_2$ (a) and **Photo-MOF (b) before and after excitation with 4 microWatt excitation at 405 nm respectively; The FLIM images are in false-colour with each colour representing a lifetime, and the brightness of the colour representing the intensity; The damaged area for $[\text{H}_3\text{L}_1^{\text{Ru}}](\text{PF}_6)_2$ is the highlighted by yellow circle; The FLIM images are measured using $\lambda_{\text{ex}} = 405$ nm; Scan time: 300 s; Spot-size ca. 430 nm.**

3.11. Electrochemical deposition of Photo-MOF thin films

There are appealing applications for the use of porous MOFs as coatings once these materials have pores and can behave as molecular hosts. Molecules can be trapped in the pores in order to change optical and/or catalytic properties of the surface. The coating itself can also behave as a membrane or filter for those molecules.¹⁰⁰ Microporous layers of MOFs have been successfully implemented for gas separation^{101, 102} and sensing devices for humidity,¹⁰³ oxygen and glucose.¹⁰⁴

Crystal growth optimization is commonly accomplished by the slow introduction of base equivalents to undertake ligand deprotonation. In solvothermal synthesis that can be achieved with the in situ formation of dialkylamines from dialkylformamides.¹⁰⁵⁻¹⁰⁷ In a bulk reaction medium, nucleation and growth of MOF crystals occur indiscriminately on any surface exposed to this medium, rather than a specified surface, and controlling the morphology of the material is consequently challenging.¹⁰⁷ In this context, the development of alternative synthetic techniques are important for controlled MOF assembly.

3.11.1. Experimental procedure

The experiment on the cathodic deposition was run according to literature procedure, a schematic representation of the apparatus is shown on Figure 3.37.^{100, 108} A process of optimization of the procedure was carried out by tuning electrolyte composition, changing solvent system (amounts of the mineralizer present in the conventional synthesis), and by applying different voltages in order to create a continuous film completely adhered to the substrate. The optimized electrolyte used is consistent with the solvothermal synthesis of **Photo-MOF** and was composed of 5.5 g L⁻¹ [H₃L^{Ru}](PF₆)₂, 14.5 g L⁻¹ Co(NO₃)₂·6H₂O, and 11 g L⁻¹ NaBF₄ used as supporting electrolyte. The solvent system used was DMF/TFA (50:1, vol %). A three electrode set-up with a CH potentiostat (CH instruments, 600D) was employed. Fluorinated Tin Oxide (FTO) glass were used as working electrodes and platinum grids were used as counter electrode. Ag/Ag(Cryptand)⁺ electrode was made according to literature procedure and used as reference.¹⁰⁹ After synthesis the samples were gently splashed with acetone to wash away the reaction mixture, dried layers of the electrochemically synthesized material can be seen in Figure 3.38.

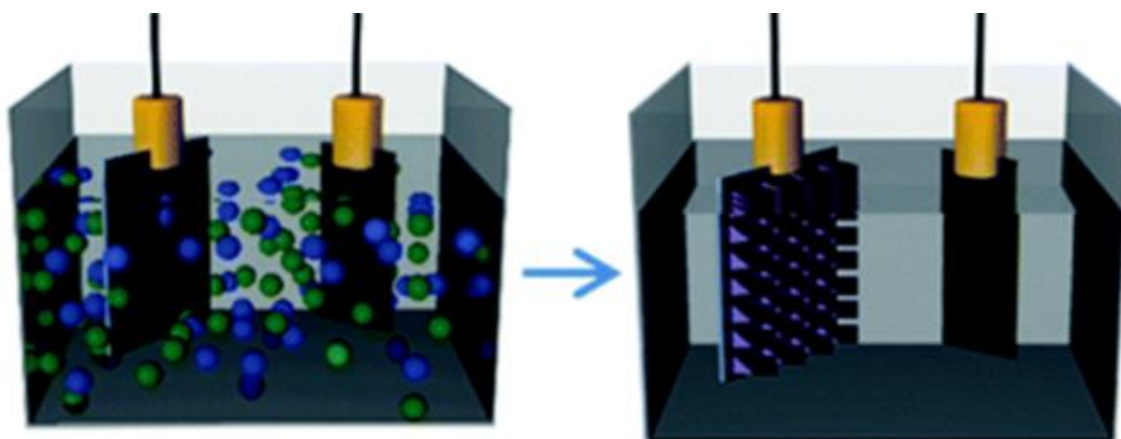


Figure 3.37: Simplified schematic representation of the electro-synthetic method; Adapted from ref. ¹⁰⁸.

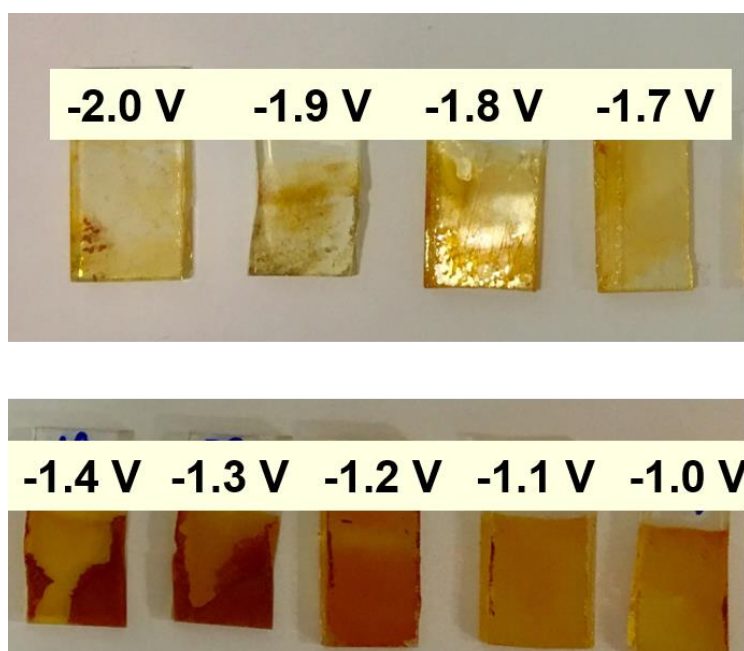


Figure 3.38: Images of Photo-MOF samples synthesised cathodically by applying -2.0 V to -1.0 V vs reference.

Raman and IR spectroscopy have been employed to confirm the structural identity of the electrochemically deposited material.

The IR spectra of the electrochemically synthesized material showed bands characteristic of **Photo-MOF** with symmetric and asymmetric carboxyl stretch signals, typical of bidentate carboxylate moieties present in the structure and previously discussed in this chapter. An overlay of both spectra can be seen in Figure 3.39.

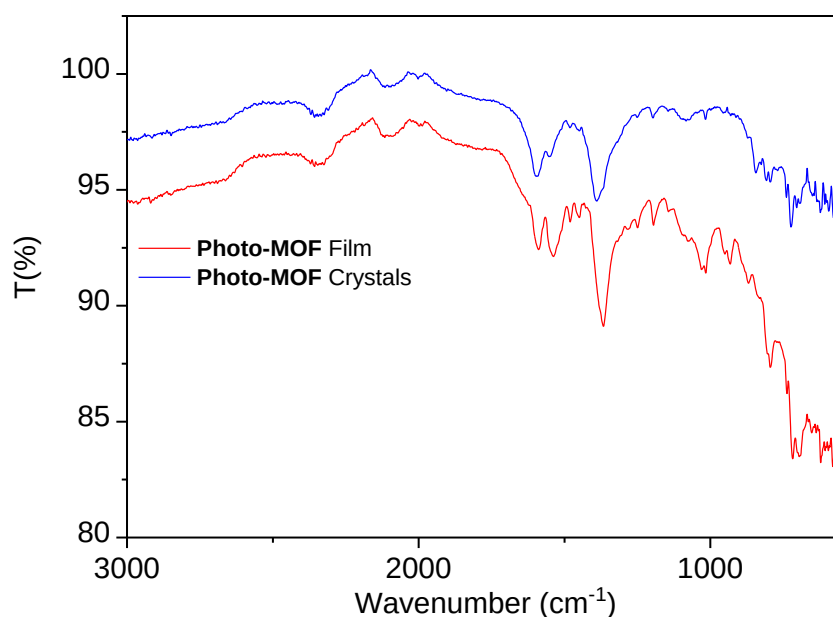


Figure 3.39: FTIR spectrum of crystalline (black) and electrochemically synthesized (red) Photo-MOF.

In Figure 3.40 Raman spectra of the clean FTO glass, crystalline sample of **Photo-MOF** and electrochemically synthesized sample of **Photo-MOF** is shown. The spectra indicates both materials have the same chemical structure. Intense bands at 1614 cm⁻¹ can be assigned to C=N while mildly intense bands at 1552 cm⁻¹ correspond to heteroaromatic rings. Mildly intense bands at 100-1100 cm⁻¹ are consistent with the presence of aromatic rings. Interestingly, weak bands at 787 cm⁻¹ are present and indicates the presence of C-F species due to the nature of the counter-ion previously detected by solid state NMR and elemental analysis on **Photo-MOF**. Additionally, bands below 650 cm⁻¹ usually arise from inorganic and metal-organic groups.¹¹⁰

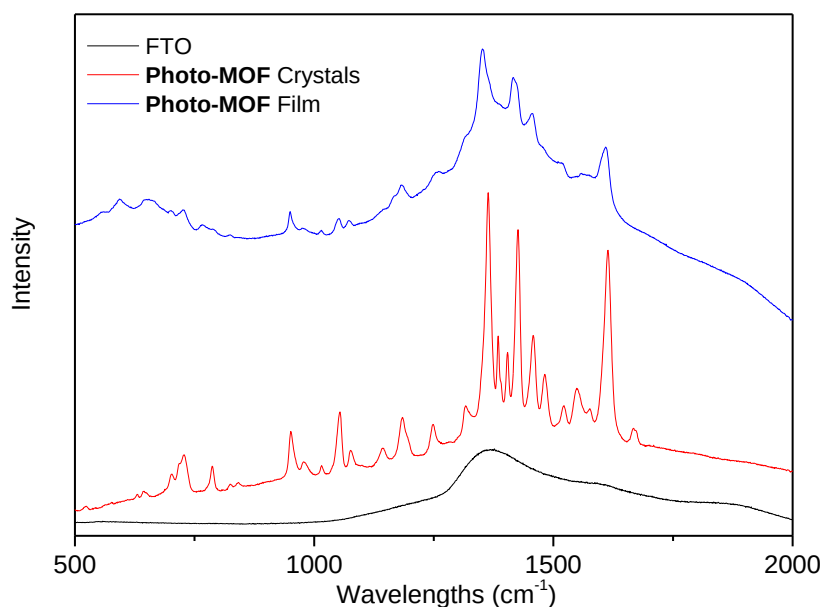


Figure 3.40: Overlay of Raman spectra of crystalline (red) and electrochemically synthesized film (blue) of Photo-MOF and the FTO glass slide (black) background.

The results for Raman and FTIR spectroscopy were consistent for the different films shown in Figure 3.38. The films were synthesized under different applied voltages using the same electrolyte.

Energy Dispersive X-Ray Spectroscopy (EDX) measurements were carried out on **Photo-MOF** thin films. The FTO containing a thin film was mounted on adhesive carbon tape for elemental analysis. The experiment was performed at an acceleration voltage of 10 keV confirmed the presence of Co and Ru throughout the thin films.

3.11.2. SEM studies of Photo-MOF thin films

Scanning Electron Microscopy (SEM) analysis was also performed on electrochemically synthesized samples of **Photo-MOF**. Two FTOs containing **Photo-MOF** films synthesized at -2.0 V and at -1.0 V were mounted on adhesive carbon tape and coated with gold for imaging purposes.

Figure 3.41 show the image obtained for **Photo-MOF** film electrochemically synthesized at -1.0 V. The images review that the MOF layer is relatively evenly deposited through the surface (Fig. 3.41a). Higher magnification image of the same FTO (Fig. 3.41b) shows that the compound does not retain the morphology exhibited by the MOF synthesised under solvothermal conditions, instead, it forms a film of aggregated polycrystalline material. The particles have a diameter of approximately 0.32 μm and adopt an spherical morphology.

Further, the images of the thin film synthesized at -2.0 V (Fig. 3.41c and d) show the existence of small individual crystals with needle-like morphology similar to the ones observed for solvothermally synthesized **Photo-MOF**. The observed crystal sizes vary and individual crystals have typical lengths of 20 μm and widths of 2 μm . The crystals are approximately five times smaller in length than the crystals obtained by solvothermal synthesis. Also differently from the solvothermally synthesized **Photo-MOF**, the electrochemically synthesized crystals do not grow in aggregates and are not easily seen with the assistance of optical microscopy.

The results suggests that increase in the voltage provides higher concentration of polycrystalline material and the formation of a thicker film. The same effect was observed in the electro-synthesis of HKUST-1¹¹¹⁻¹¹³ and, in accordance with nucleation theory,¹¹⁴ can be explained by the increase in the concentration of metal ions near the substrate surface.

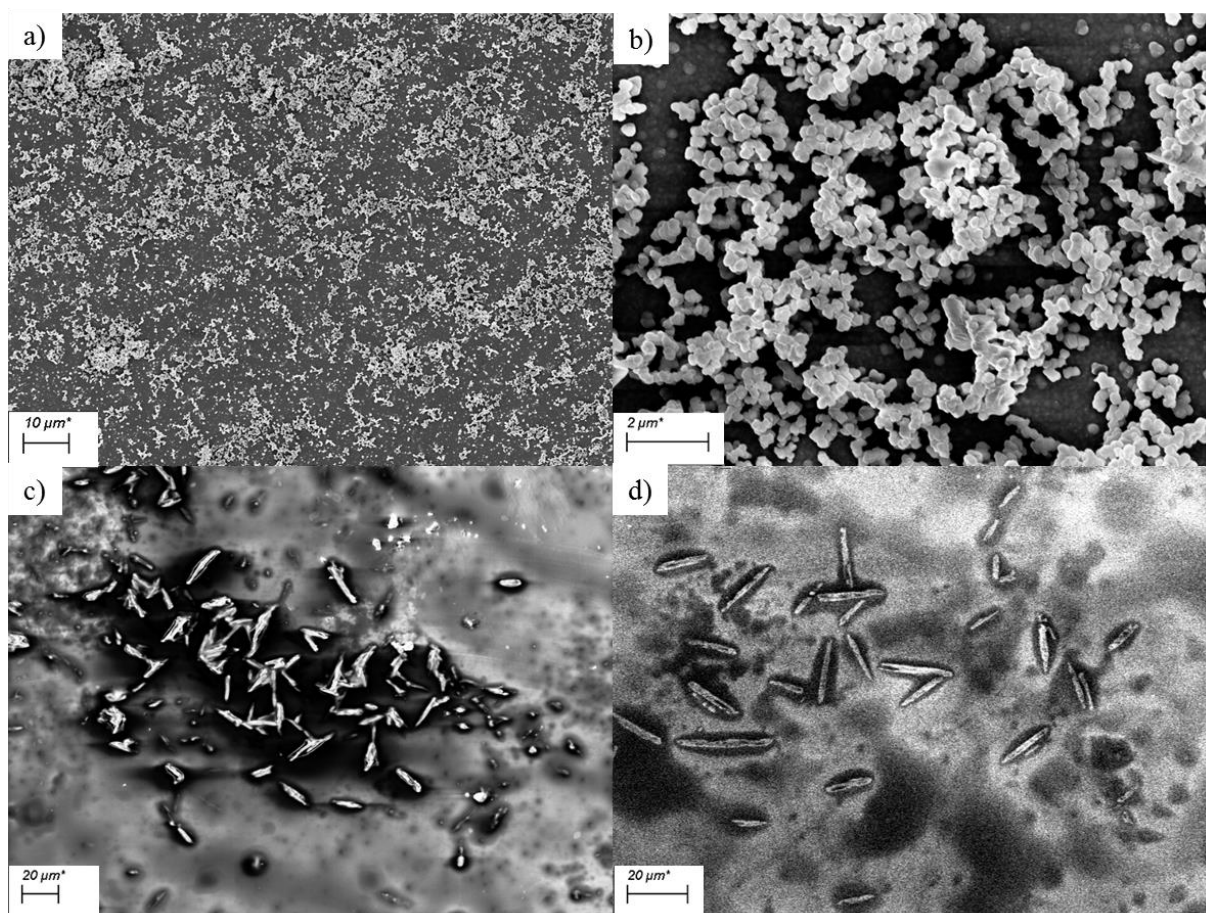


Figure 3.41: Scanning Electron Microscopy (SEM) images of FTO containing electrochemically synthesized Photo-MOF); Film synthesised cathodically by applying -2.0 V vs ref. (a) and (b); Film synthesised cathodically by applying -1.0 V vs ref. (c) and (d).

3.11.3. Photophysical characterisation of Photo-MOF thin films

UV-Vis absorption, spectral photoluminescence and time-resolved photoluminescence studies were performed on electrochemically synthesized films of **Photo-MOF**. Two different film samples were selected for measurements. The films were distinguished based on the applied voltage and their continuousness/uniformity. Sample **A** was synthesised cathodically by applying -1.4V and yielded a discontinuous thick film; sample **B** was synthesised applying -1.1V generating a continuous film (Fig. 3.42).

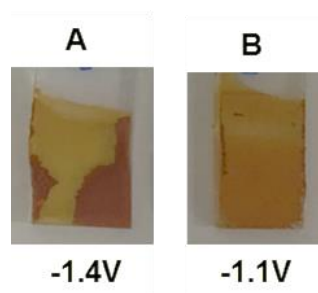


Figure 3.42: Images of selected films of Photo-MOF. Discontinuous film (Sample A) was synthesised cathodically by applying -1.4V (a) and continuous film (Sample B) was synthesised cathodically by applying -1.1V (b).

Time-resolved photoluminescence measurements were performed using a PicoQuant Microtime 200 time-resolved confocal microscope system using an excitation of 90 ps pulses at a wavelength of 405 nm with a repetition rate of 10 MHz and an integration time of 4 ms per pixel. The laser spot size was approximately 430 nm. The sample was excited through a 40x objective (NA = 0.65) and the photoluminescence excitation (PLE) and photoluminescence (PL) was collected through the same objective. The excitation power used for the spectral dependence measurements was 0.2 μ W. The photoluminescence spectra (PL) were recorded for an excitation wavelength of 405 nm. All scans were performed over 5 μ m x 5 μ m square areas (Fig. 3.43).

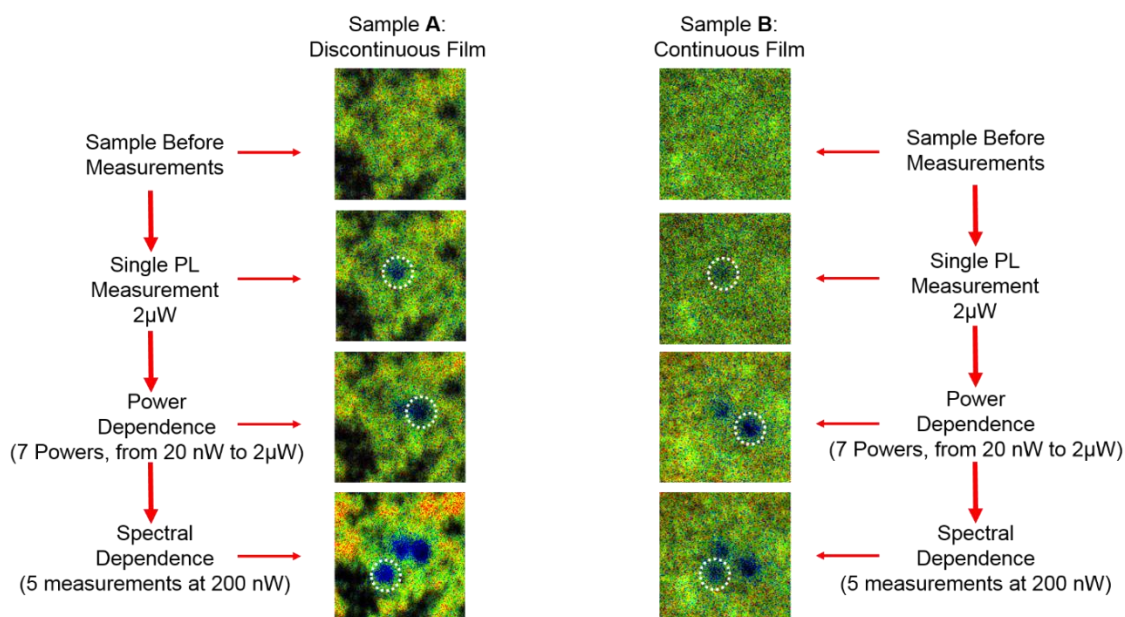


Figure 3.43: FLIM images of samples A and B before and after excitation with 4 microWatt excitation at 405 nm, respectively. The FLIM images are in false-colour with each colour representing a lifetime, and the brightness of the colour representing the intensity. The damaged areas are highlighted by yellow circles.

Fluorescence-lifetime imaging microscopy (FLIM) images show the chromophore distribution over portions of samples **A** and **B** before and after several excitation processes. The samples were excited for photoluminescence as well as power and spectral dependence studies. Both film samples of **Photo-MOF** were damaged by optical excitation, nevertheless, film **A** shows less regular distribution of chromophores. This is due to the discontinuity of the film and consequent uneven distribution of chromophores present in $[\text{H}_3\text{L}_1^{\text{Ru}}]^{1-}$ and incorporated into the framework.

Samples **A** and **B** display very similar absorption and photoluminescence properties. Differences are most likely related to the difference in film uniformity. Thicker regions of film **A** proved to be challenging to measure due to the high optical density and opacity of the film, resulting in noisier spectra.

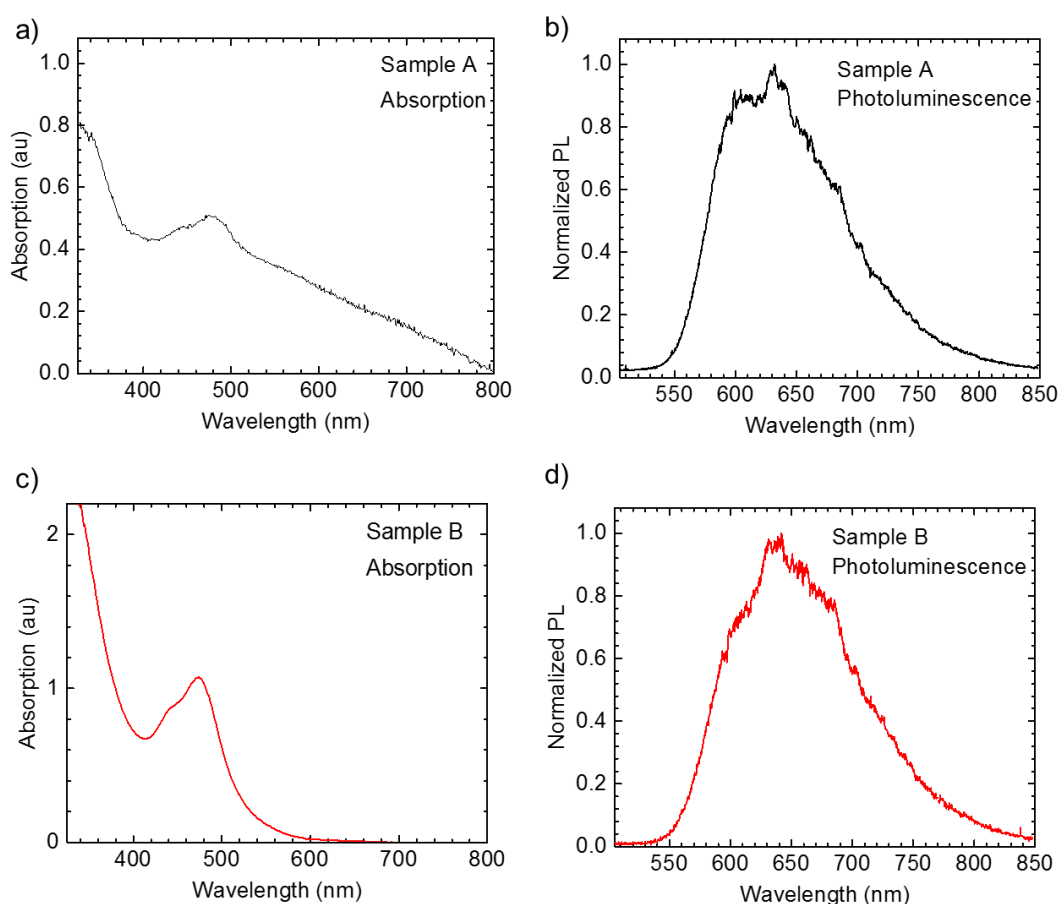


Figure 3.44: Optical characterisation of Photo-MOF continuous film (sample B); Absorption (a); photoluminescence (b); and normalized photoluminescence spectra of A and B in solid state;

Photo-MOF films absorption spectra feature characteristic broad absorbance bands at *ca.* 480 nm (Fig. 3.44a and 3.44c) and are consistently observed for the crystalline samples of **Photo-MOF**. Those bands can be assigned to MLCT transitions^{38, 40, 41} and demonstrate that excitation energies of the chromophore are not altered in the films in comparison to the crystalline samples. The difference in intensities of the absorption can

be attributed to film thickness and regularity. The resulting differences can be related to different concentration of chromophores per square areas of the film.

The emission spectra are both centred at approximately 637 nm (Fig.3.44b and 3.44d) and is in close agreement with emission of crystalline samples of **Photo-MOF**.

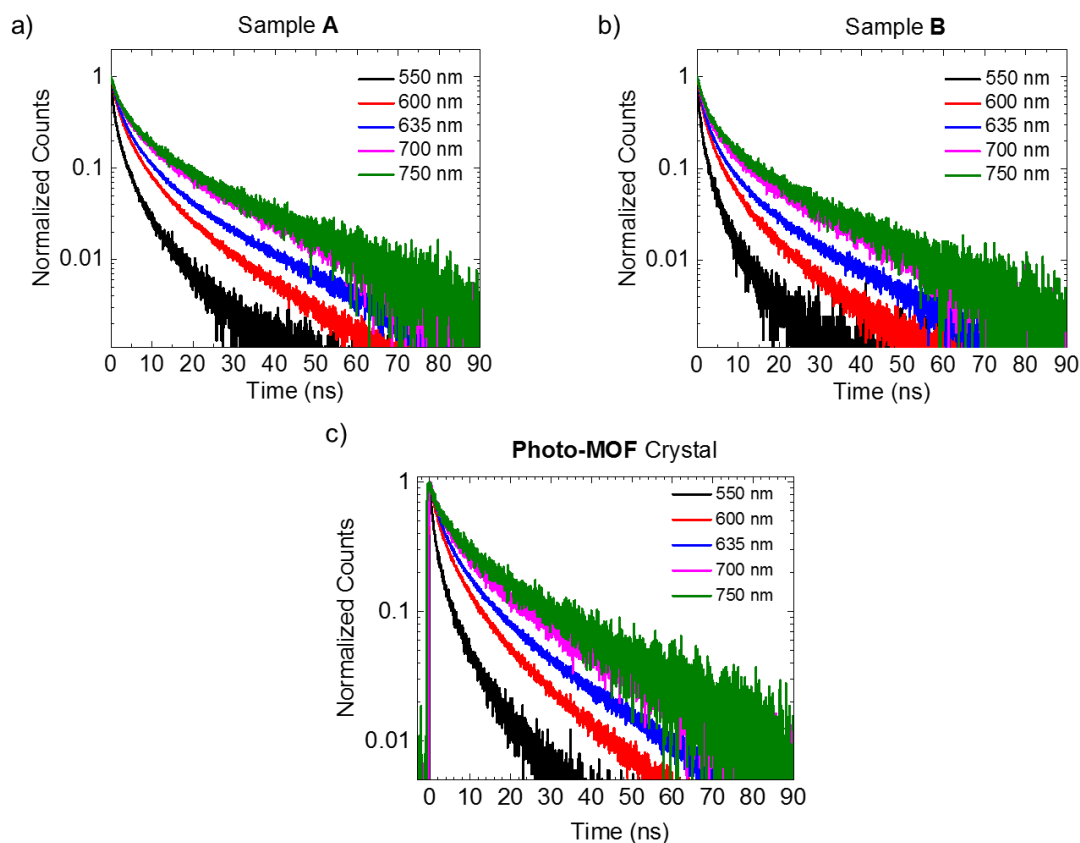


Figure 3.45: Luminescence decays of films A (a) and B (b) and crystalline sample of Photo-MOF (c) measured at 5 different central emission wavelengths using 10 nm bandpass filters.

The photoluminescence decays for films **A** and **B** and a crystalline sample of **Photo-MOF** were measured over the first 90 ns at five central emission wavelengths using 10 nm bandpass filters (Fig. 3.45). Increased average lifetimes were observed for longer emission wavelengths for all samples, and an average luminescence decay lifetime of ca. 20 ns for $\lambda_{\text{emis}} = 750$ nm. Importantly, no significant quenching of the triplet ³MLCT state is observed for the films when compared to the crystalline sample, indicating that the chromophores occupy very similar environments in the two materials. The

photoluminescence decay curves recorded at the five different emission wavelengths show that the films and the crystalline samples present very similar decay kinetics over the whole emission wavelength range.

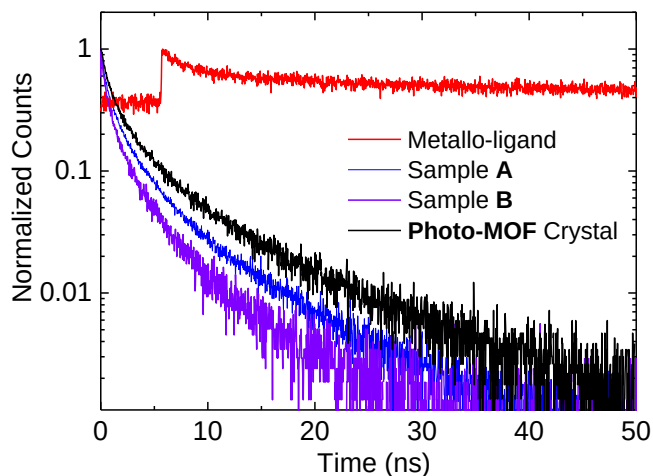


Figure 3.46: Normalised time-resolved photoluminescence decays of the metallo-ligand (red), of films A (blue) and B (purple) and crystalline sample of Photo-MOF (black).

Figure 3.46 shows the luminescence decay traces of the metallo-ligand, the films and a crystalline sample of **Photo-MOF** over the first 50 ns. Consistent decay curves can be observed for the films and the crystalline samples of **Photo-MOF** whereas the metallo-ligand displays a flat line behaviour.

The free metallo-ligand presents a much longer lifetime, *ca.* 90 ns, and slower decay when compared to **Photo-MOF** in both forms (film or crystalline material), this could be potentially explained by interactions with the cobalt centres.

Through examination of the decay curves, absorption and emission spectra it is possible to conclude that the material synthesized through electrochemical deposition on FTO substrates have very similar optical and photophysical behaviour to the crystallographically characterized compound.

3.11.4. Cyclic voltammetry studies

As previously discussed, photoexcited ruthenium polypyridyl complexes and their analogues can be used to drive processes initiated by electron transfer. These photoexcited complexes have electrochemical potentials that lie within a range that can perform chemical transformations initiated by light absorption.¹¹⁵⁻¹¹⁸

In the context of coupling photo-induced electron-transfer properties of photoactive materials to electrochemically driven transformations, electrochemistry is an important tool to investigate reactions involving electrons once it can relate the flow of electrons to chemical change.¹¹⁹ It can also help the comprehension of which reactions could be better photosensitised using **Photo-MOF** as a sensitizer by elucidating how high of a thermodynamic barrier can be crossed.

Cyclic voltammetry (CV) is a useful electrochemical technique employed to study reduction and oxidation processes. In order to determine the redox potential for **Photo-MOF** a CV experiment was carried out. A three electrode set-up with a Bio-logic VSP potentiostat (a Bio-logic VSP instruments, 600D) was employed. **Photo-MOF** on a FTO was employed as working electrode. Platinum mesh was used as counter electrode. Ag/AgNO₃ electrode was made according to literature procedure and used as reference.¹⁰⁹ The electrolyte solution was composed of 0.1 M tetrabutylammonium hexafluorophosphate (NBu₄PF₆) as supporting electrolyte in 20 ml of acetonitrile (CH₃CN).

A cyclic voltammogram is presented in Figure 3.47 for the CV of **Photo-MOF** electro-synthesised on a FTO electrode. The recorded peaks can be assigned to the Ru³⁺/Ru²⁺ redox pair of the metal centre in the positive region.

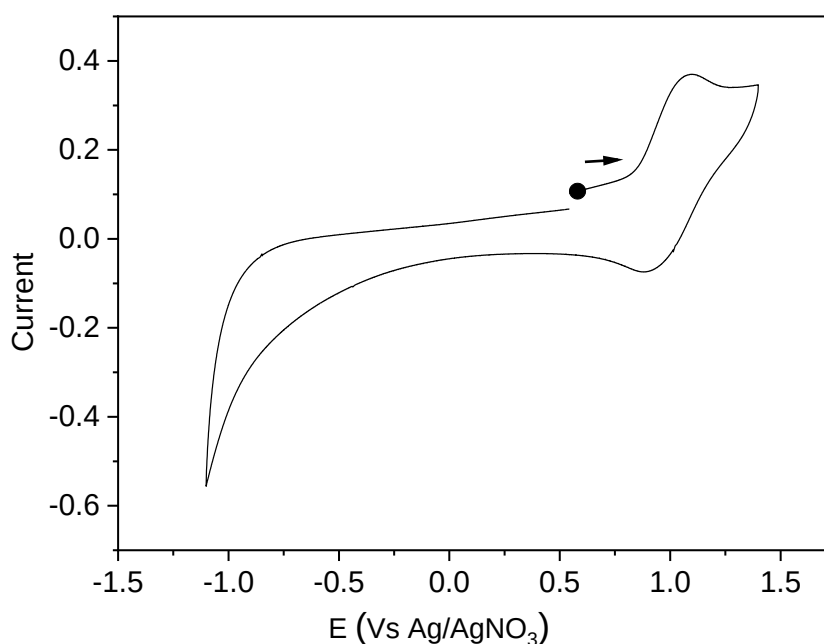


Figure 3.47: CV of Photo-MOF/FTO electrode in an acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate (NBu₄PF₆) as electrolyte at a scan rate of 500 mV s⁻¹.

The potential of the redox pair within the film of **Photo-MOF/FTO** as the working electrode, at a scan rate 500 mV s⁻¹ was calculated according to Equation 3.11.4.1:

$$E_{1/2} (V) = (E_{pa} + E_{pc})/2 \quad (3.11.4.1)$$

Where $E_{1/2}$ is the average potential between E_{pa} (anodic peak) and E_{pc} (cathodic peak).

The obtained result of $E_{1/2} = +0.97$ V vs Ag/AgNO₃ is in close agreement with the calculated potential for [Ru(bpy)₃]²⁺ found in the literature.¹²⁰ This result was somewhat foreseen as [Ru(bpy)₃]²⁺ is analogous to [Ru(phen)₃]²⁺ parent molecule.¹¹⁵ For [Ru(bpy)₃]²⁺ a wave at +0.97 V vs Ag/AgNO₃ is assigned to Ru³⁺/Ru²⁺ redox process as well as three successive reversible reductions that happens in the organic moiety at -1.60 V, -1.80 V and -2.07 V.^{120, 121}

Electrochemical reversibility refers to the electron transfer kinetics.¹¹⁹ Regarding the reversibility of the redox process in **Photo-MOF**/FTO, the peak-to-peak separation (ΔE_p) was calculated according to equation 1.12.2 at 25 °C:

$$\Delta E_p \text{ (mV)} = (E_{pc} - E_{pa}) \quad (3.11.4.2)$$

Chemical and electrochemical reversibility process is confirmed when the peak-to-peak separation (ΔE_p) is 59 mV.¹²² A value of 210 mV was found for **Photo-MOF**/FTO, indicating quasi-reversibility of the redox pair, this may be caused by a reduction of the charge transfer from the MOF to the FTO and might indicate that, the [Ru(phen)₃]²⁺ moiety transfer electrons to throughout the network structure.²¹

3.12. Conclusion

Well-defined structures, porosity and chemical diversity are important assets of MOFs as a family of porous functional materials. A mesoporous MOF with well-chosen struts, can be used as a great platform for light-harvesting functionality.¹²³ We worked towards those attributes by exploring a driven self-assembly strategy as a design tool. Chelating nitrogen donor ligands were pre-organised in an octahedral metal complex, giving directionality to the formation of the framework of **Photo-MOF**. The principles of supramolecular chemistry were applied to design a MOF with a specific type of channel, due to geometrically prefixed phenanthroline based ligands. These ligands function as bridging linkers, provide strong coordination bonds to metals and impart rigidity to the framework, resulting in a stable permanently porous MOF.¹²⁴⁻¹²⁶

Photo-MOF can be described as a functionalised version of the topologically related MOF-74,¹²⁷ where pore/channel modifications successfully increased gas sorption capacities and porosity (Fig. 3.48a). The experimentally determined surface area is high in comparison to previously synthesized heterometallic MOFs, which feature large pore apertures that often collapse upon removal of solvent molecules due to structural rearrangement.²¹ Moreover, those materials often present solvent molecules coordinated to the metal centre, which leads to instability and increases the likelihood of loss of structural integrity.¹²⁸⁻¹³¹ The structural attributes of **Photo-MOF** promote relatively high CO₂ storage capacity and selectivity over N₂ equal to 26.7, suggesting preferential CO₂-framework interactions within the 1-D channels of the framework.

Photophysical studies emphasise that the photophysical properties of the free metallo-ligand, as indicated from absorption and emission spectra, are maintained in the framework. However, coordination to Co^{II} ions gives rise to electron/energy transfer processes throughout the network structure that can be exploited for photo-catalysis and photo-electrochemical studies. Furthermore **Photo-MOF** also comprises an efficient chromophore (Fig. 3.48b) that exhibits broad absorbance in the visible range, which results in the production of a relatively long-lived excited state.

The layered nature of the material facilitated electrochemical synthetic studies. The method used is an alternative synthetic route used in industry to produce MOFs in reduced time compared to solvothermal synthesis methods.¹³² The successful functionalization of conductive surfaces through the production of a MOF thin-film reduces unpredictability

by limiting MOF formation to the electrode and allows for a more controlled synthesis when compared to other methods.¹⁰⁷ Structural, photophysical and optical characterisation carried out indicate that the thin-films formed are consistent with **Photo-MOF**.

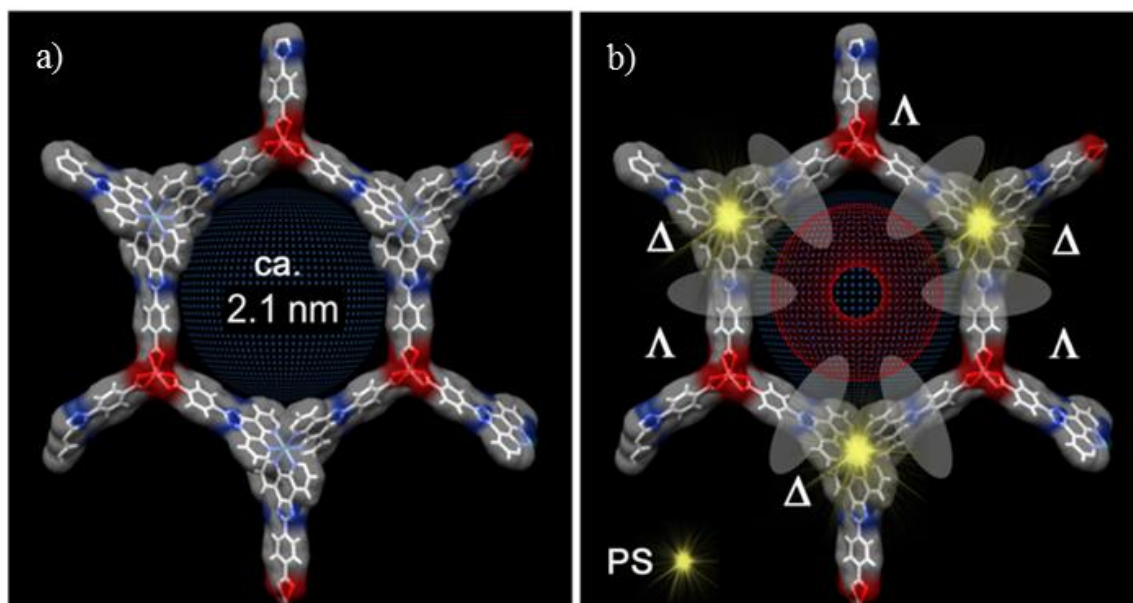


Figure 3.48: Hexagonal channel in [001] direction in Photo-MOF highlighting the aperture that is characterized by a diameter of *ca.* 21 Å. (a) and the key attributes of Photo-MOF, including Ru^{II}/phenanthroline-based photosensitisers; nodes with D₃ point symmetry of opposite helicity and imidazole-based binding sites (b).

3.13. References

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Chapter 4

Synthesis of a hetero-metallic $\text{Mn}^{\text{II}}/\text{Ru}^{\text{II}}$ -
based MOF

4. Synthesis of a hetero-metallic Mn^{II}/Ru^{II}-based MOF

4.1. Introduction

A synthetic approach to synthesise light-harvesting MOFs may utilise struts that absorb light in the visible or near infrared region of the solar spectrum. In contrast with organic molecules that tend to absorb only photons in the ultraviolet (UV),¹⁻⁴ ruthenium/pyridyl-based bridging metallo-ligands exhibit a strong, broad absorbance in the visible range.^{5,6} Following the absorption process, these ligands often can facilitate the stabilisation of relatively long-lived excited states which makes them suitable building blocks for the construction of MOFs used in visible light-driven photocatalysis.^{7,8}

The photophysical properties of Ru^{II} polypyridyl complexes can be modulated by the nature of the ligands coordinated to the metal centre. Ru complexes incorporating tridentate polypyridine ligands have extensively been exploited for the design of well characterized supramolecular architectures, due to a facile *para*-substitution at the central pyridyl ring and the absence of optical isomers upon coordination.⁹⁻¹²

Combining Ru^{II} polypyridyl struts and catalytically active clusters with labile coordination sites as secondary building units (SBUs) can be used to catalyse useful and unique organic reactions that are initiated by visible light irradiation.¹³⁻¹⁵ Within these systems, the incorporated Ru-polypyridine photosensitizers serve as antenna for the metal clusters in long range energy transfer *via* a series of sequential Dexter energy transfer events.¹ Interestingly, it has been reported that energy transfer is faster in MOFs containing light-harvesting metallo-ligands as SBUs than in MOFs which only physically encapsulate those chromophores and that the photo-excited framework is capable of engaging in electron transfer with guest species.¹⁶⁻¹⁸ Finally, design and synthesis of MOFs with precise arrangement of a photo-sensitizer and catalytic active SBUs can be an attractive strategy for further studies of rapid long-range energy transfer with applications in light-harvesting and photocatalysis.

With these promising applications in mind, we sought to synthesise a photoactive MOF comprising a Ru-terpyridine strut and a potentially catalytically active transition metal cluster.

4.2. Synthesis of organic linker Me_2TpyPEI

To fulfil the aim of creating photoactive struts for photocatalytic MOFs, a new dimethyl 5-((4-([2,2':6',2''-terpyridin]-4'-yl)phenyl)ethynyl)isophthalate (Me_2TpyPEI) was designed and synthesized as a precursor (Fig. 4.1). The presence of nitrogen donors provides a tridentate binding site, favourable to the formation of homo- and heteroleptic octahedral ruthenium complexes.^{10, 18} In addition, the two ester groups at the tail end of the ligand can be hydrolysed into free carboxylic acids and, when reacted with oxophilic metal ions, undergo *in situ* deprotonation and form potentially catalytically active clusters with labile coordination sites. These sites can act as secondary building units (SBUs) for the synthesis of photoactive MOFs.^{19, 20}

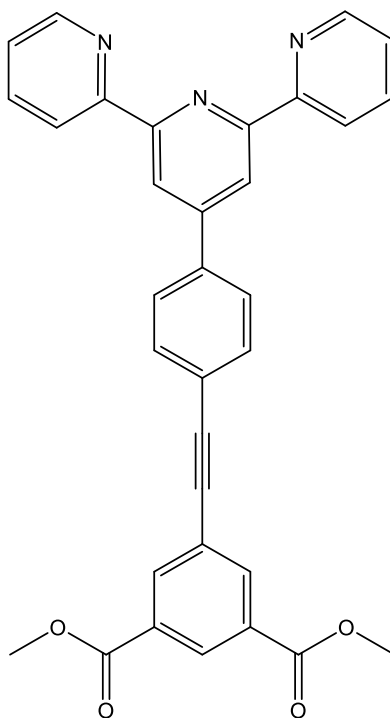
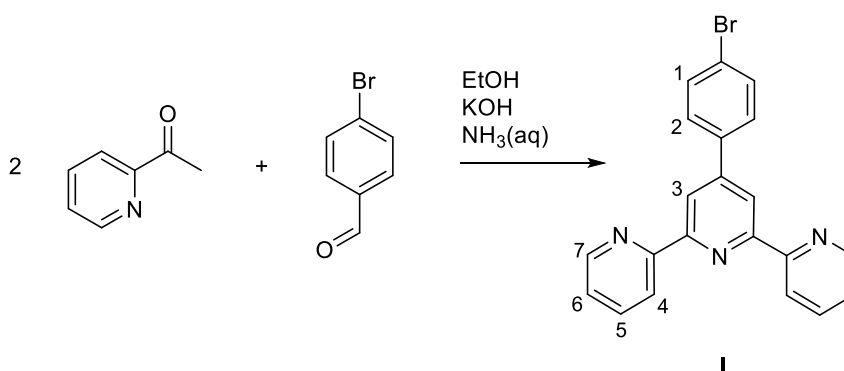


Figure 4.1: Pro-ligand Me_2TpyPEI used for the synthesis of Ru^{II} complexes.

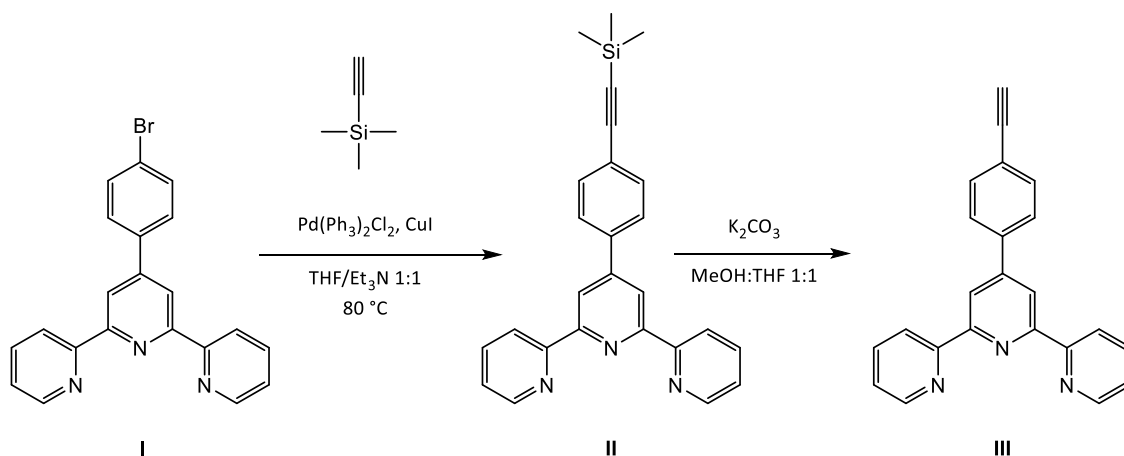
The pro-ligand was synthesized in the three steps involving the synthesis of 4'-([4-bromophenyl]-2,2':6',2''-terpyridine and two subsequent coupling reactions to introduce the acetylenic and ester groups.

4'-(4-Bromophenyl)-2,2':6',2''-terpyridine was synthesized according to a literature procedure.²¹ The product was obtained through a Kröhnke-type reaction²² (Scheme 4.1) whereby two equivalents of 2-acetylpyridine reacted with 4-bromobenzaldehyde *via* a base-mediated aldol condensation. This yields an α , β -unsaturated ketone, which further reacts with another equivalent of 2-acetylpyridine giving a 1,5-diketone through a Michael addition.²³ The diketone intermediate was then allowed to form the central pyridine ring using aqueous ammonia as the nitrogen source. An average yield of 65% of the target compound was obtained.



Scheme 4.1: Synthetic procedure for 4'-(4-bromophenyl)-2,2':6',2''-terpyridine.

The ¹H NMR spectrum of **I** (Fig. 4.2) shows signals characteristic of aromatic and terpyridine moieties. It features signals between 8.78 ppm and 8.68 ppm as well as signals at 7.92 and 7.40 ppm that result from terpyridine-derived H-atoms. The H-atoms on the B-substituted? phenyl ring exhibit signals at 7.82 and 7.67 ppm in the aromatic region. An additional signal at approximately 7.26 ppm is due to residual H-atoms chloroform molecules.²⁴ The assigned signals are in good agreement with the spectrum of the reported molecule.²¹



Scheme 4.2: Synthetic procedure for 4'-(4-ethynylphenyl)-2,2':6',2''-terpyridine (III).

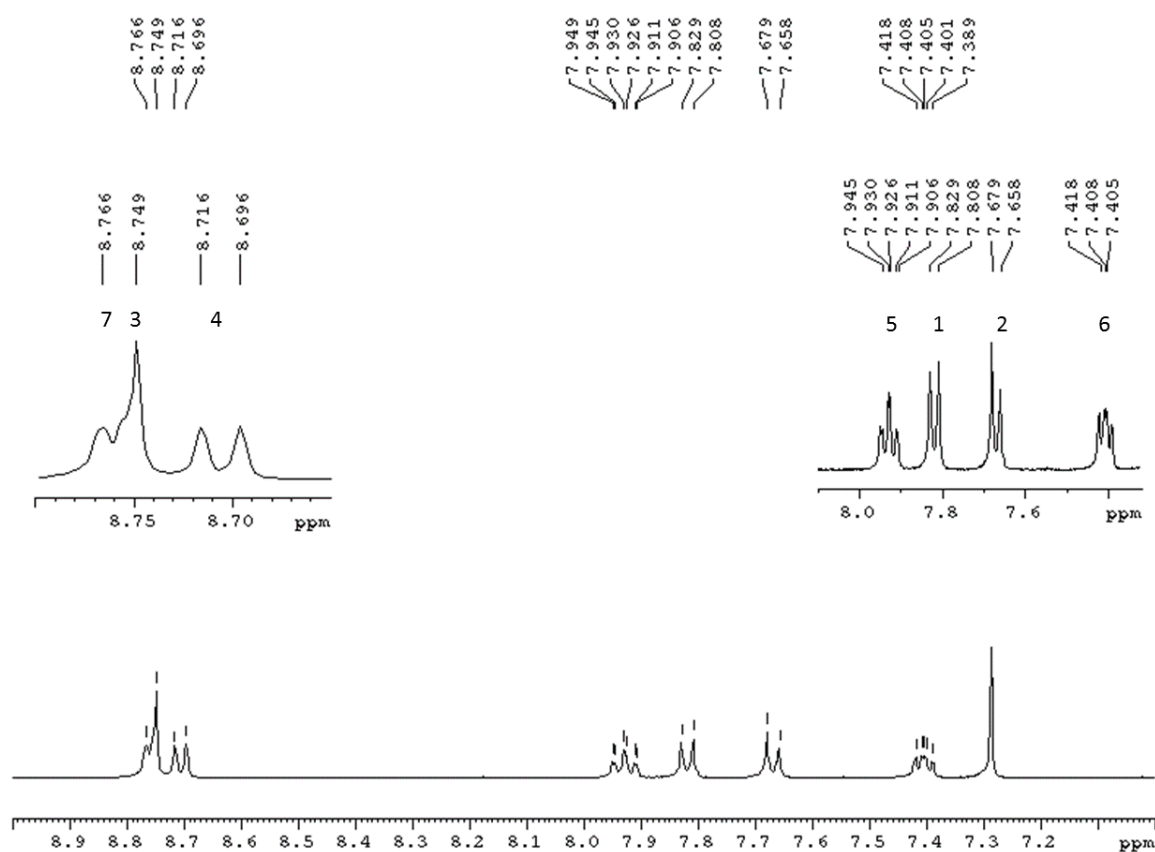
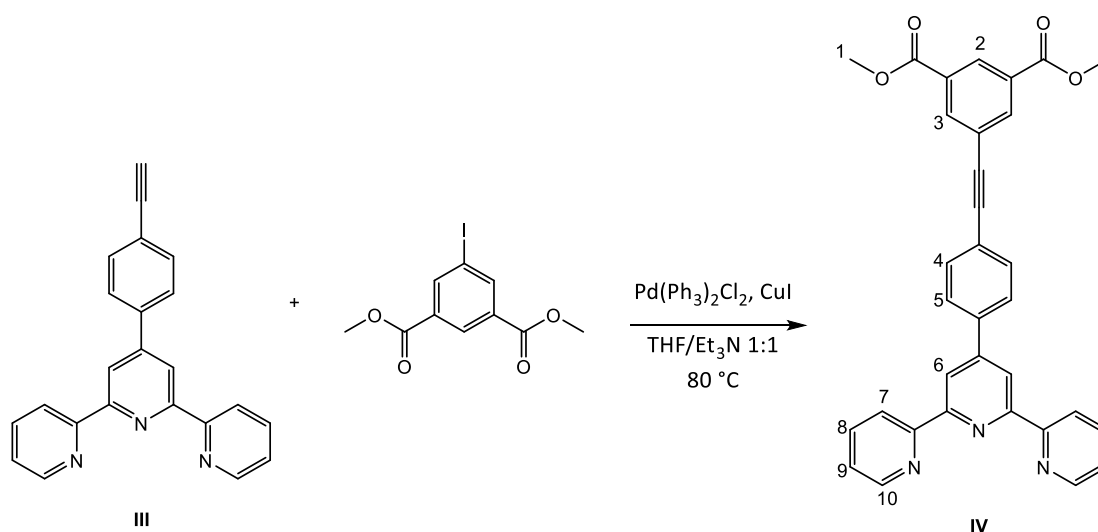


Figure 4.2: ^1H NMR spectrum of 4'-(4-bromophenyl)-2,2':6',2''-terpyridine (I) in CDCl_3 .

The second step (scheme 4.2) in the synthesis of Me₂TpyPEI involved a Sonogashira coupling reaction²⁵ using 4'-(4-bromophenyl)-2,2':6',2''-terpyridine (**I**) and (trimethylsilyl)acetylene to form 4'-(4-((trimethylsilyl)ethynyl)phenyl)-2,2':6',2''-terpyridine (**II**). The latter, **II**, was subjected to a deprotection procedure to remove the trimethylsilyl group generating a terminal alkyne in 4'-(4-ethynylphenyl)-2,2':6',2''-terpyridine (**III**). An additional Sonogashira reaction (scheme 4.3) using compound **III** and dimethyl 5-iodoisophthalate produces the desired product **IV** at an average yield of 60%.



Scheme 4.3: Synthetic procedure for Me₂TpyPEI (IV**).**

The ¹H NMR spectrum of **IV** (Fig. 4.3) reveals signals at 8.80 ppm, 8.77 ppm, 8.72 ppm and 8.67 ppm that result from the hydrogen atoms in the terpyridine moiety. Additionally, the spectrum shows a signal at *ca.* 7.9 ppm that arises as an apparent multiplet. This signal is assigned as the overlap of a triplet from H₈ and a doublet from H₄ in the terpyridine moiety and the central phenyl ring respectively. The signal at 7.72 ppm is due to the H₅ atom, also present in the central phenyl group. The singlets observed at 8.67 ppm and 8.42 ppm are due to the H-atoms in the terminal phenyl group and the signal at 4.00 ppm derives from the ester groups..

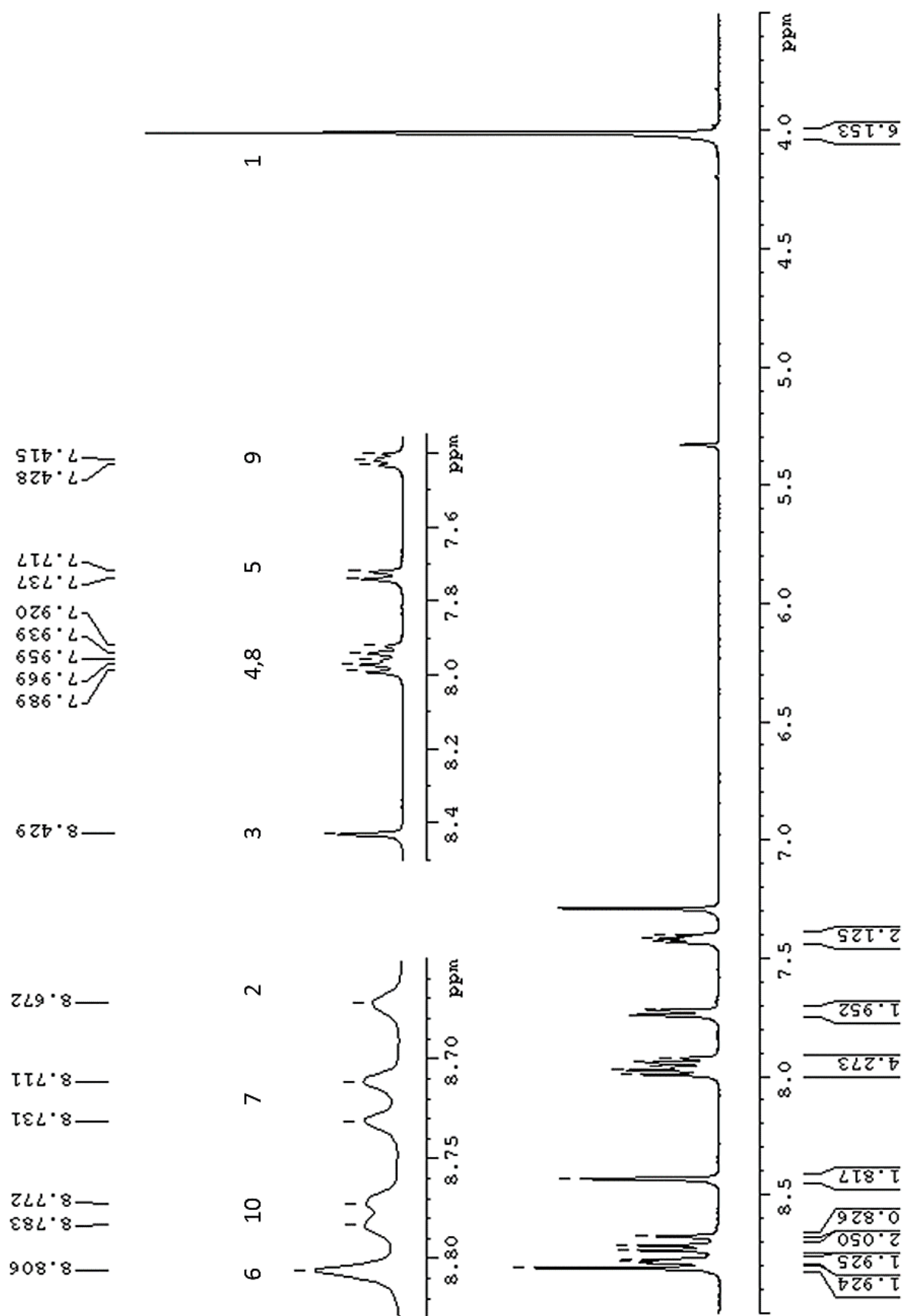
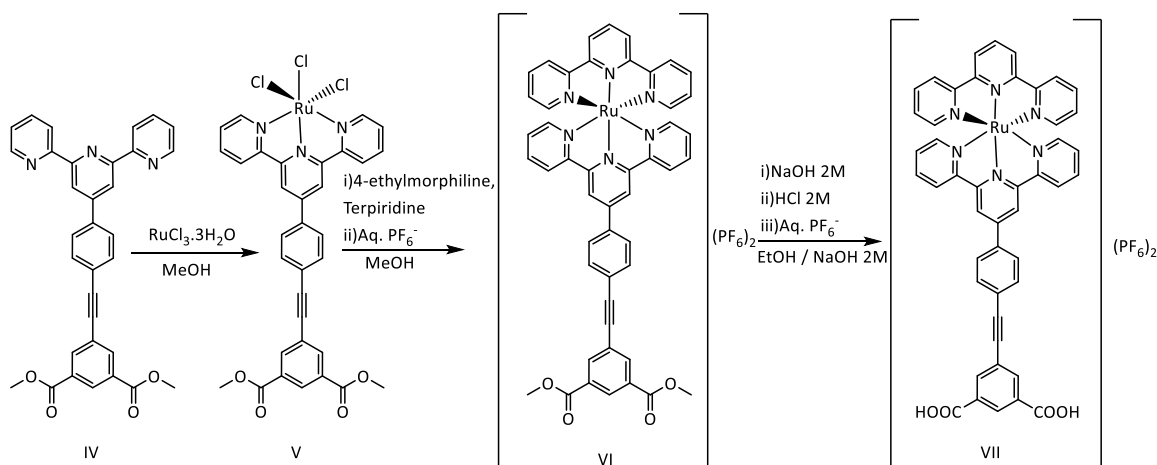


Figure 4.3: ¹H NMR spectrum of Me₂TpyPEI (IV) in CDCl₃.

4.3. Synthesis of the ditopic Ru^{II} metallo-ligand [H₂L₂^{Ru}](PF₆)₂

The ditopic Ru^{II} metallo-ligand [H₂L₂^{Ru}]²⁺ features the multidentate organic ligand H₂TpyPEI (**IV**) and a terpyridine moiety as capping ligand. It was synthesised in three steps according to a modified literature procedure²⁶ (Scheme 4.4). The first step of the synthesis was achieved by refluxing Me₂TpyPEI (**IV**) and RuCl₃·3H₂O in MeOH. [Ru(Me₂TpyPEI)Cl₃] (**V**) was obtained at an average yield of 56%. The second step of the synthesis involved the addition of a reducing agent, (4-ethylmorpholine) to a reaction mixture of **V** and terpyridine in MeOH. The obtained product, **VI**, was further deprotected through basic hydrolysis of the ester functional groups to produce the desired product [Ru(H₂TpyPEI)Tpy](PF₆)₂ (**VII**) with an average yield of 62% (step from **V** to **VII**).



Scheme 4.4: Synthetic procedure for Ru^{II} metallo-ligand [H₂L₂^{Ru}](PF₆)₂ (**VII**).

The FTIR spectrum of compound **VII** (Fig. 4.4) shows bands characteristic of aromatic, conjugated compounds containing carboxylic acid functionalities. The broad signal at *ca.* 3450 cm⁻¹ can be assigned to O – H stretches involving hydrogen bonds. A signal centred at *ca.* 3073 cm⁻¹ arise from C – H vibrations of the aromatic ligand moieties.^{27, 28} The intense signal at 1722 cm⁻¹ is due to the C = O vibrations of the carboxylic acid group. Bands between 1660 cm⁻¹ and 1310 cm⁻¹ are due to aromatic C = C and C = N stretches.²⁹ The intense band observed at 1246 cm⁻¹ most likely arises from the C – O stretch of the acid functionality. The weak band at *ca.* 835 cm⁻¹ confirms the presence of PF₆⁻ ions and the sharp absorption frequencies at 788 cm⁻¹ and 650 cm⁻¹ result from the coordination of the terpyridine nitrogen atoms to the Ru atom.^{30, 31}

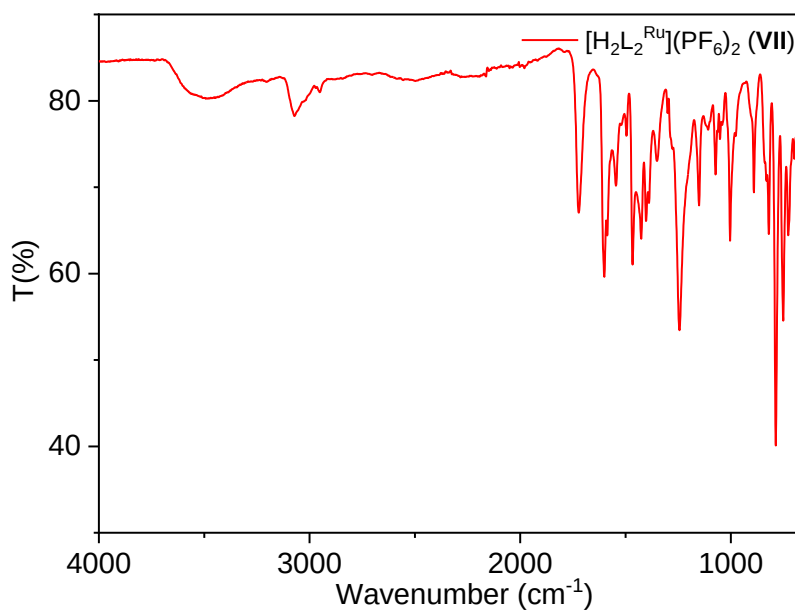


Figure 4.4: FTIR spectrum of VII.

4.3.1. Photophysical Characterisation

Photophysical characterisation of Me₂TpyPEI (**IV**), [Ru(Me₂TpyPEI)Cl₃] (**V**) and H₂L₂^{Ru}]²⁺ (**VII**) was performed at room temperature in degassed dichloromethane solutions. Normalised absorption spectra of the three compounds can be seen in Figures 4.5a to 4.5c. Additionally, a photoluminescence spectrum was obtained for the metallo-ligand **VII** as shown in Figure 4.5d.

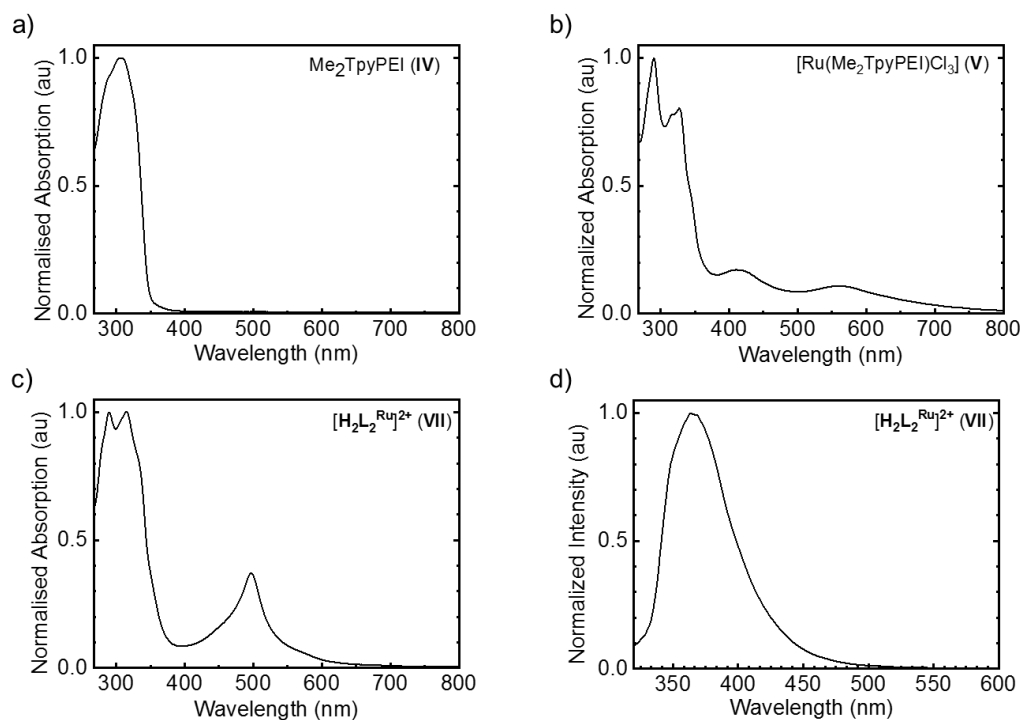


Figure 4.5: Normalised UV-vis spectra of Me₂TpyPEI (IV**)(a), [Ru(Me₂TpyPEI)Cl₃] (**V**) (b), (**VII**) (c) and the normalised photoluminescence spectrum of H₂L₂^{Ru}]²⁺ ($\lambda_{\text{ex}} = 298 \text{ nm}$) (d) in dichloromethane solution at 293 K.**

Bands characteristic of terpyridyl species and their ruthenium complexes were observed in the UV-vis absorption spectra for compounds **IV**, **V** and **VII**. The pro-ligand **IV** (Fig. 4.5a) shows a strong absorption band at $\lambda = 307 \text{ nm}$ which can be assigned to the $\pi-\pi^*$ intra-ligand transition. The absorption maximum of this type of is influenced only marginally by changes of the solvent polarity²⁶ and agrees with terpyridine species reported in the literature.^{26, 32} The absorption band is red-shifted compared to that of 4'-phenyl-2,2':6',2''-terpyridine (278 nm in dichloromethane),³³ 4'-(4-methoxyphenyl)-2,2':6',2''-terpyridine (285 nm in dichloromethane),³³ and 4'-([1,1'-biphenyl]-4-yl)-2,2':6',2''-terpyridine (289 nm in ethanol).³⁴ The fact that **IV** absorbs at higher wavelength

in comparison to previously reported terpyridines is due to the increased electron conjugation and delocalization caused by the addition of the diphenylacetylene moiety. This decrease of the energy gap between the bonding and antibonding π -orbitals affects this ligand-centred (LC) transition giving rise to the bands centred at longer wavelengths.^{26, 32} Additionally, the rigidity of the conjugated linkage between the diphenylacetylene moiety and the central pyridyl ring of the terpyridine fragment can also affect the absorbance in this region, consequently shifting the signal to a longer wavelength.³⁵

Significant changes are observed in the UV-vis spectrum upon complexation reactions of Me₂TpyPEI, RuCl₃·3H₂O and terpyridine to form **V** and **VII** (Fig. 4.5b and 4.5c). As expected, the UV region of the absorption spectra of the three compounds are dominated by spin-allowed ligand centred (LC) π - π^* transitions centred at *ca.* 320 nm. The two transitions at 290 nm and 320 nm observed for **V** and **VII** involve intra-ligand excitations from the diphenylacetylene moiety to the terpyridine framework. Compound **VII** also exhibits typical metal to ligand charge-transfer (MLCT) transitions in the visible region of the spectra as shown in Figure 4.5c. The MLCT bands for **VII** are observed at 497 nm and are in close agreement to other reported Ru^{II}/terpyridine species.^{26, 36} Compound **V** shows a different absorption behaviour when compared to compound **VII** (Fig. 4.5b). *d-d* transitions are experimentally observed for transition metal complexes due to the mixing of *d*- and *p*-orbitals, however the intensity depends on the violation of this selection rule.³⁷ The weak absorption band observed at *ca.* 410 nm in the spectrum of **V** arises from MLCT and is in accordance with results reported in the literature for heteroleptic Ru^{III} complexes.^{38, 39} The weak band at 569 nm in the spectrum of **V** is characteristic of *d-d* transitions, which are less intense as they are Laporte-forbidden, and also due to the low energy gap between the *t*_{2g} and *e*_g orbitals when compared to the energy gap between ground and excited states of the charge transfer bands.³⁷ In the spectrum of compound **VII** (Fig. 4.5c) this weak transition is not directly observed because of an overlap with the relatively intense MLCT band.

Upon excitation at the wavelengths of the absorption maximum of **VII** at $\lambda_{\text{ex}} = 298$ nm in dichloromethane, a single intense band is observed in the recorded emission spectrum, indicating that the fluorescence involves only one excited state.²⁶ The photoluminescence spectrum of **VII** is centred at approximately 360 nm. The recorded emission is red-shifted when compared to [Ru(tpy)₂](PF₆)₂ and [Ru(tpy)(ttpy)](PF₆)₂.^{36, 40}

The photoluminescence excitation spectrum at higher wavelengths ($\lambda_{\text{ex}} = 500 \text{ nm}$) does not display any emission band, indicating a non-radiative decay from the MLCT excited state.

4.3.2. Crystal structure of ditopic Ru^{II} metallo-ligand $[\text{H}_2\text{L}_2^{\text{Ru}}](\text{NO}_3)_2 \cdot 2\text{DMF}$ (**3.1**)

Single crystals suitable for X-ray diffraction were grown upon recrystallization of compound **VII**. The recrystallized compound was identified as $[\text{H}_2\text{L}_2^{\text{Ru}}](\text{NO}_3)_2 \cdot 2\text{DMF}$ (**3.1**) and was obtained from DMF in the presence of a nitrate salt. Compound **3.1** crystallises in the trigonal crystal system in the space group $P\bar{1}$ as a DMF solvate with two counter ions per formula unit. The nitrates replace the hexafluorophosphate anions observed in **VII**, providing charge balance and most likely facilitating crystallisation of **3.1**. The crystal structure reveals that the three rings of the 2,2';6',2''-terpyridine ligand are slightly out of plane. As expected, the Ru^{II} centre displays an octahedral coordination environment in **3.1**, with the three nitrogen donors of the substituted terpyridine ligands completing the coordination sphere. (Fig. 4.6).

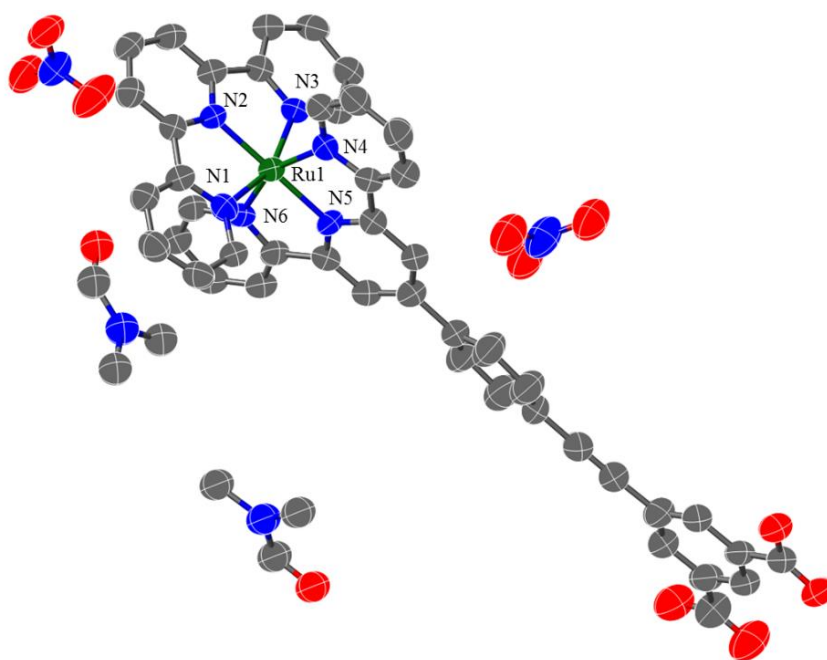


Figure 4.6: View of Ru^{II} metallo-ligand $[\text{H}_2\text{L}_2^{\text{Ru}}](\text{NO}_3)_2 \cdot 2\text{DMF}$ (**3.1**) including solvent molecules (DMF) and counter ions (NO_3^-); Colour code: Ru green, C grey, O red, N blue, H atoms omitted for clarity.

The Ru – N bond lengths within the complex are very similar (Table 4.1). The Ru – N(2) and Ru – N(5) bond lengths to the central ring of the tridentate ligands are slightly shorter than the other Ru – N bond lengths to the terminal rings. This fact is most likely due to the rigidity of the ligands that prevents all three nitrogen atoms of the same terpyridine moiety from approaching the ruthenium centres equally closely.⁴¹ The bond distances, as well as the rigidity effect observed for **3.1** are in close agreement with the ones observed for [Ru(tpy)₂]²⁺-based complexes with different substituents on the terpyridine ligands.⁴¹ BVS analysis confirmed that the Ru(1) centre adopts the oxidation state +II.

Table 4.1: Crystallographically-determined bond lengths for the Ru(1) centre in **3.1, along with the oxidation state as determined by Bond Valence Sum (BVS) analysis.**

Metal Atom	Bonded Atom	Bond Length (Å)	BVS	Oxidation State
Ru(1)	N(1)	2.089(5)	2.25	+II
	N(2)	1.982(5)		
	N(3)	2.083(6)		
	N(4)	2.081(6)		
	N(5)	1.993(5)		
	N(6)	2.084(6)		

The N – Ru – N angles deviate from linearity with values of 178.2(2)°, 157.2(2)°, and 158.1(2)° for N(2) – Ru(1) – N(5), N(4) – Ru(1) – N(6) and N(3) – Ru(1) – N(1), respectively. The N(3) – Ru(1) – N(6) angle deviates only slightly from the ideal angle of 90° with the value of 90.2(2)°. In contrast, the N(1) – Ru(1) – N(2) and N(2) – Ru(1) – N(3) angles display a large deviation revealing values of 79.3(2)° and 90.2(2)°. Selected angles for **3.1** are summarised in Table 4.2.

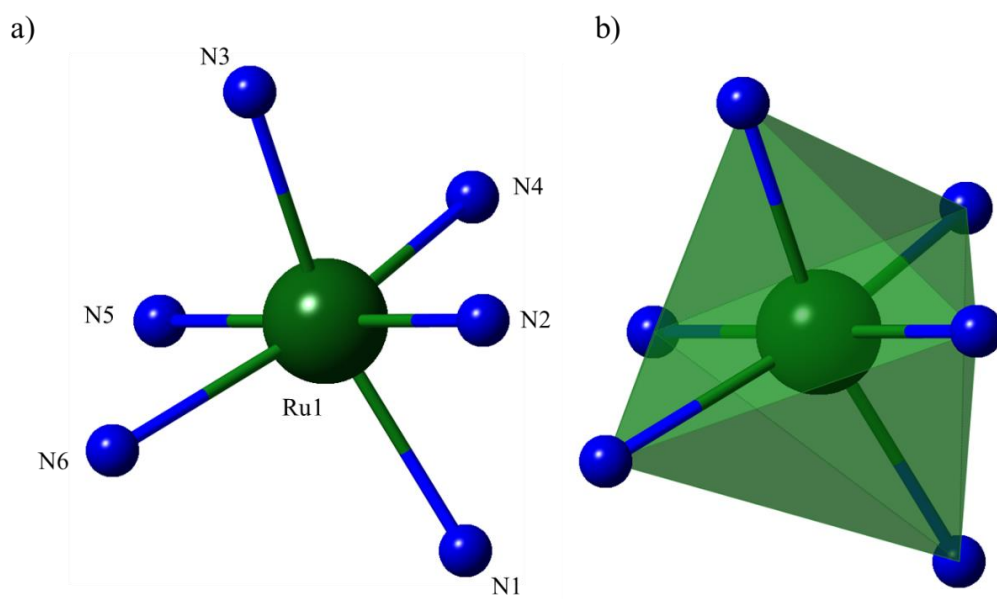


Figure 4.7: a) Coordination environment of the central Ru^{II} ion in the metallo-ligand [H₂L₂Ru](NO₃)₂·2DMF (3.1), b) Polyhedral representation of the distorted octahedral coordination geometry. Colour code: Ru green, N blue.

Table 4.2: Selected bond lengths (Å) and angles (°) for 3.1.

Atoms	Angles (°)	Atoms	Angles (°)
N(2) – Ru(1) – N(5)	178.1(3)	N(1) – Ru(1) – N(2)	79.3(2)
N(4) – Ru(1) – N(6)	157.2(2)	N(2) – Ru(1) – N(3)	78.8(2)
N(3) – Ru(1) – N(1)	158.1(2)	N(3) – Ru(1) – N(6)	90.2(2)

Table 4.3: Crystal data and structure refinement for 3.1.

Identification code	3.1
Empirical formula	C ₅₂ H ₄₀ N ₁₀ O ₁₂ Ru
Formula weight/ g mol ⁻¹	1098.0200
Temperature/K	100
Crystal system	Triclinic
Space group	P $\bar{1}$
a/Å	9.0072(5)
b/Å	14.5446(6)
c/Å	20.6625(10)
α /°	73.862(3)
β /°	77.928(4)
γ /°	84.734(4)
Volume/Å ³	2541.1(2)
Z	2
ρ_{calc} /g/cm ³	1.393
μ /mm ⁻¹	3.086
F(000)	1092
Crystal size/mm ³	0.13 × 0.08 × 0.02
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	3.165 to 68.687
Index ranges	-10 ≤ h ≤ 10, -17 ≤ k ≤ 16, -24 ≤ l ≤ 24
Reflections collected	28838
Independent reflections	9239 [R_{int} = 0.0733]
Data/restraints/parameters	9239 / 63 / 628
Goodness-of-fit on F ²	1.019
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0952, wR_2 = 0.2439
Final R indexes [all data]	R_1 = 0.1230, wR_2 = 0.2724
Largest diff. peak/hole / e Å ⁻³	1.431/-0.802

Synthetic approach towards hetero-metallic MOFs

Following the successful synthesis of the Ru^{II} metallo-ligand [H₂L₂^{Ru}]²⁺, numerous attempts were made towards the assembly of hetero-metallic MOFs for potential photocatalytic applications. We aimed to synthesize a framework structure that integrates the {Ru^{II}/tpy}= chromophore and transition metal clusters containing labile sites. The synthetic approach involved the use of reaction mixtures that consisted of [H₂L₂^{Ru}]²⁺ and Mn metal salts in DMF/HTFA mixtures. Data collection and refinement of the structures were done by Dr Brendan Twamley.

4.4. [Mn₂Cl₂(L₂^{Ru})₂][MnCl₄]·DMF (3.2)

The coordination compound [Mn₂Cl₂(L₂^{Ru})₂][MnCl₄]·DMF (**3.2**) forms under solvothermal conditions in DMF/HTFA 50:1 v:v, 1.0 mL) during the reaction between [H₂L₂^{Ru}]²⁺ and MnCl₂·4H₂O at a molar ratio of 1:3. Sonication at room temperature ensured that all reactants were dissolved prior to the reaction, yielding a red clear solution. Red crystals were obtained upon heating the reaction mixture at 120 °C for 72 hours.

Single-crystal X-ray studies demonstrate that compound **3.2** crystallises in the monoclinic space group *C2/c*. The heteroleptic Ru^{II} complex L₂^{Ru} is maintained within the framework structure. The MOF is constructed from dinuclear M^{II} carboxylate units {Mn₂(COO)₄} that are connected to four ditopic metallo-ligands in the extended solid (Fig. 4.8).

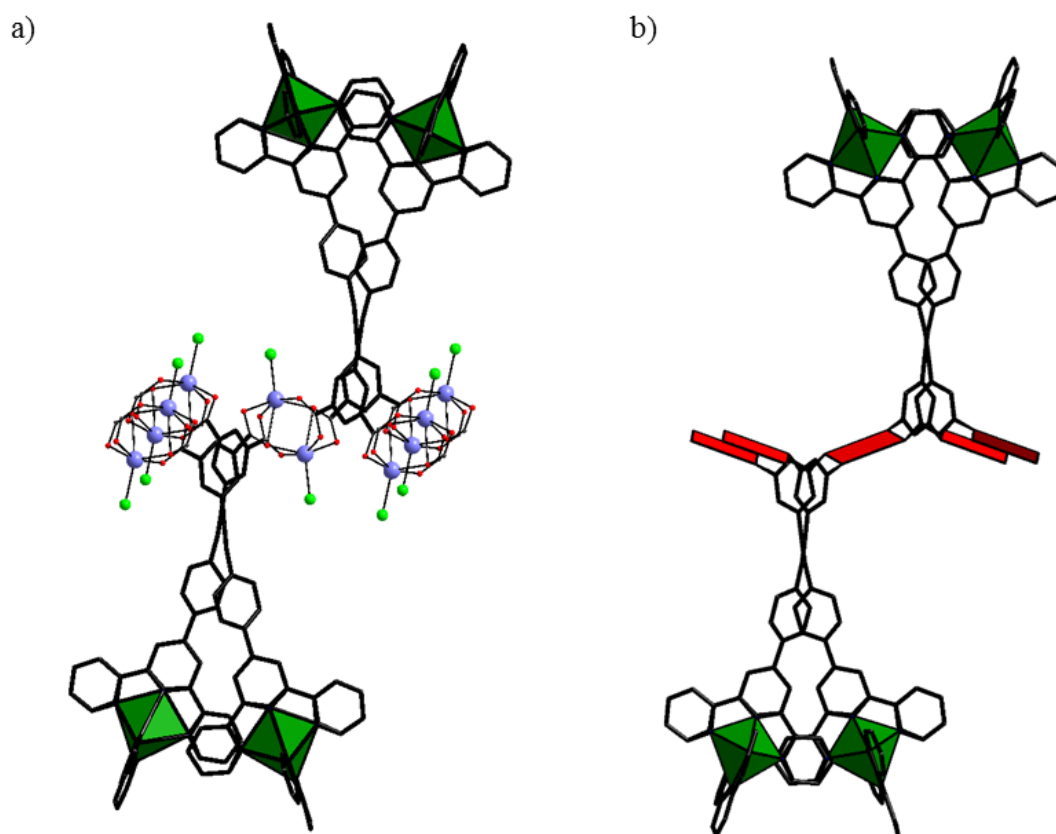


Figure 4.8: View of $[\text{Mn}_2\text{Cl}_2(\text{L}_2^{\text{Ru}})_2][\text{MnCl}_4]\cdot\text{DMF}$ (3.2) showing Ru^{II} metallo-ligand $[\text{H}_2\text{L}_2^{\text{Ru}}]$ motifs and the dinuclear unit that defines the $\{\text{Mn}_2(\text{COO})_4\}$ SBU (a); Square nodes defined by the carbon atoms of the carboxylate donor bridges b); Colour code: Ru and N green polyhedra, C black, O red, Mn purple, $\{\text{Mn}_2(\text{COO})_4\}$ red square; Charge-balancing $[\text{MnCl}_4]^{2-}$ ions, constitutional solvent molecules and H atoms omitted for clarity.

Within the dinuclear unit and each Mn^{II} centre is coordinated by four oxygen atoms originating from four different carboxylate ligands giving rise to a *syn, syn* bidentate bridging mode. The unit in 3.2 is characterised by inversion symmetry whereby the inversion element is located in the centre of the dinuclear unit. The axial positions of the square pyramidal coordination polyhedra of the Mn^{II} centres are occupied by chloride ions. The carbon atoms of the carboxylate donor bridges define the geometry of the resulting node as a square (Fig. 4.9). This SBU closely relates to a ‘paddlewheel’ unit present in the crystal structures of well-studied MOFs as HKUST – 1,⁴² MOF-505,⁴³ MOF-2⁴⁴ and the NOTT series.^{45, 46}

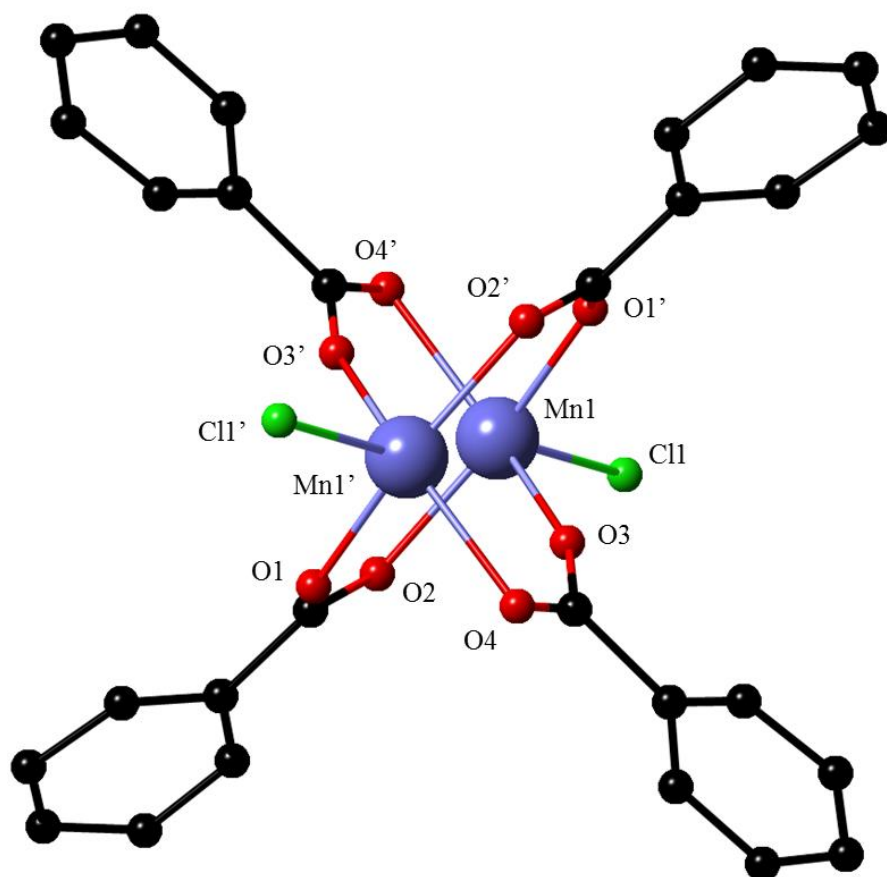


Figure 4.9: Dinuclear paddlewheel-type motif present in $[\text{Mn}_2\text{Cl}_2(\text{L}_2^{\text{Ru}})_2][\text{MnCl}_4]\cdot\text{DMF}$ (**3.2**); Colour code: C black, O red, Mn purple, Cl green; H atoms omitted for clarity; Symmetry codes: $1/2 - x$; $3/2 - y$; $-z$.

The Mn^{II} centres in **3.2** adopt square pyramidal coordination environments. The corresponding Mn – O bond lengths vary between 2.144(9) to 2.265(9) Å and 2.361(4) Å for Mn(1) – Cl(1). The observed bond lengths are in close agreement with a Mn-MOF featuring a dinuclear paddlewheel units with chloride ligands located in the apical positions.⁴⁷ The square pyramidal coordination geometry of Mn^{II} ions displays a slightly distorted arrangement. This effect is exemplified by the bond angles involving the metal centre whereby the O(3) – Mn(1) – O(2) and O(1') – Mn(1) – O(4') angles are of 81.1(3)° and 83.2(4)°, respectively and deviate from the ideal angle of 90°. Selected bond distances and angles in **3.2** are summarised in Table 4.4.

Table 4.4: Selected bond lengths (Å) and angles (°) for [Mn₂Cl₂(L₂Ru)₂][MnCl₄]·DMF (3.2); Symmetry codes: 1/2 - x; 3/2 - y; -z.

Atoms	Distances (Å)	Atoms	Angles(°)
O(1) – Mn(1)	2.129(9)	Cl(1) – Mn(1) – O(1')	100.1(3)
O(2) – Mn(1)	2.144(9)	Cl(1) – Mn(1) – O(2)	102.3(3)
O(3) – Mn(1)	2.195(10)	Cl(1) – Mn(1) – O(3)	102.7(3)
O(4) – Mn(1)	2.265(9)	O(3) – Mn(1) – O(2)	81.1(3)
Cl(1) – Mn(1)	2.361(4)	O(1') – Mn(1) – O(4')	83.2(4)

The connectivity of the L₂^{Ru} metallo-ligands and the dinuclear Mn^{II} paddlewheel nits in compound **3.2** results in 2D sheets with L₂^{Ru} moieties located above and below the plane of the sheet. The polymeric structure extends approximately in parallel to the crystallographic *bc*-plane (Fig. 4.10)

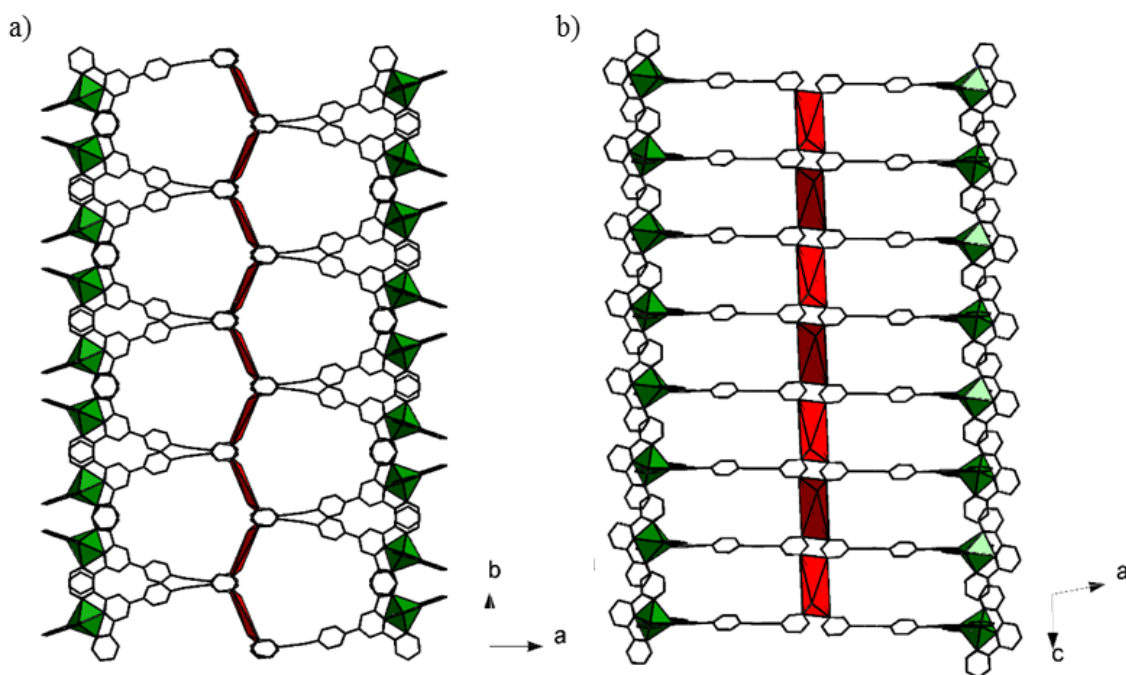


Figure 4.10: 2D sheets featured in [Mn₂Cl₂(L₂^{Ru})₂][MnCl₄]·DMF (3.2) with L₂^{Ru} moieties above and below the plane. Colour code: Ru and N green polyhedra, C black, {Mn₂(COO)₄} red square; H atoms omitted for clarity.

The 2D sheets shown in Figure 4.11 interdigitate in the [001] direction. The L₂^{Ru} metallo-ligands of each sheet alternate 180° resulting a dense arrangement and intercalation of the {Ru(tpy)₂} and {Mn₂(COO)₄} SBUs.

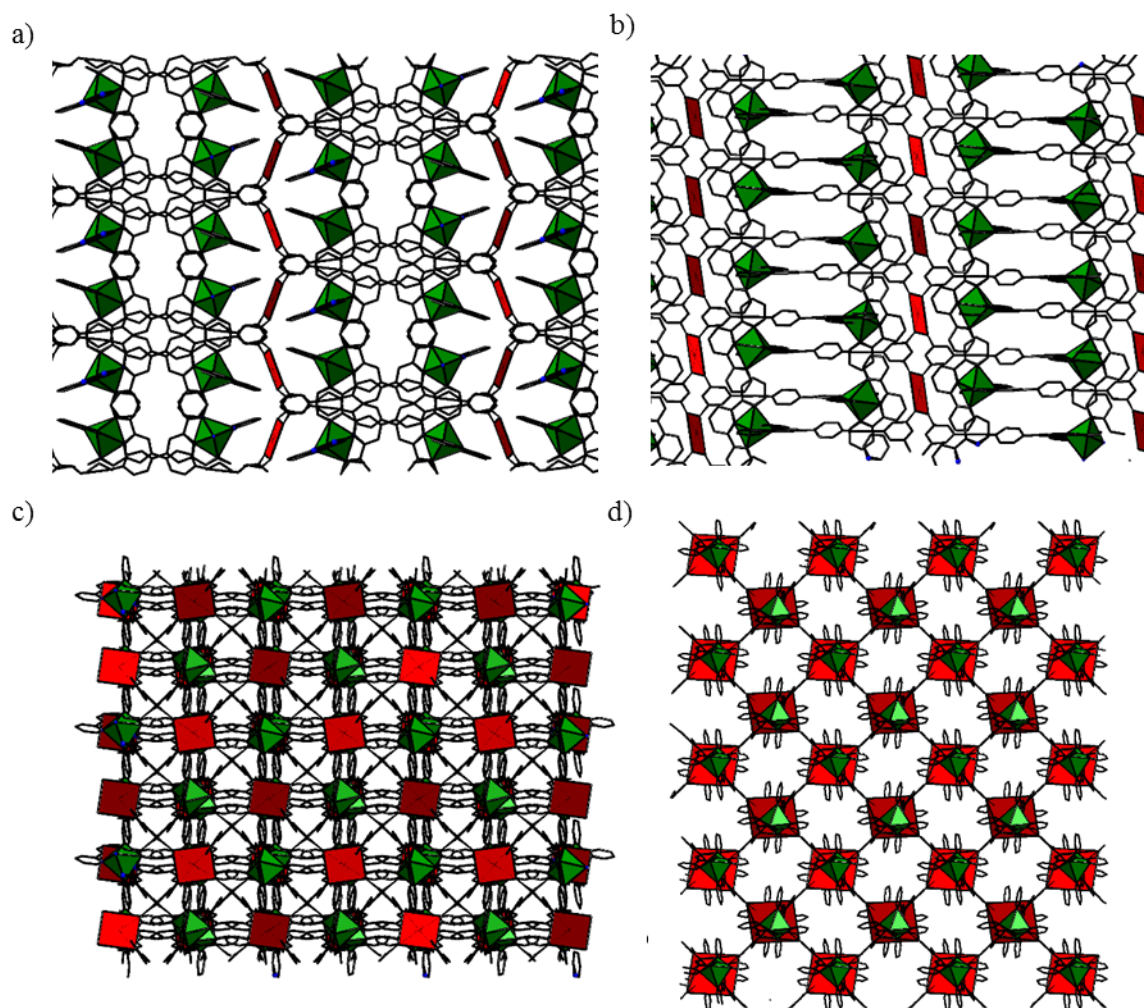


Figure 4.11: Interdigitation of sheets in $[\text{Mn}_2\text{Cl}_2(\text{L}_2^{\text{Ru}})_2][\text{MnCl}_4] \cdot \text{DMF}$ (3.2) as seen along the crystallographic b -axis (a) and c -axis (b); Packing arrangement showing proximity of the $\{\text{Ru}(\text{tpy})_2\}$ and $\{\text{Mn}_2(\text{COO})_4\}$ SBUs (c); Simplified representation of the close arrangement of the SBUs (d); Colour code: Ru and N green polyhedra, C black, $\{\text{Mn}_2(\text{COO})_4\}$ red square; H atoms omitted for clarity.

The terminal terpyridine group of the metallo-ligand composes the $\{\text{Ru}(\text{tpy})_2\}$ moiety. This moiety adds light-harvesting functionality to the material. Directionality and connectivity is exclusively facilitated by the $\{\text{Mn}_2(\text{COO})_4\}$ SBU. As previously discussed, the SBU functions as a 4-connected node by linking to four L_2^{Ru} metallo-ligands resulting in a uninodal net. This connectivity generates a 2D (4)-connected network with an overall point symbol of 4^4 and an extended point symbol of $[4.4.4]$. This topology is classified as a square lattice, typically abbreviated by the RCSR symbol **sql**. Within each sheet the $\{\text{Mn}_2(\text{COO})_4\}$ SBUs display a zigzag pattern slightly in and out in relation to a mean $[110]$ plane (Fig. 4.12)

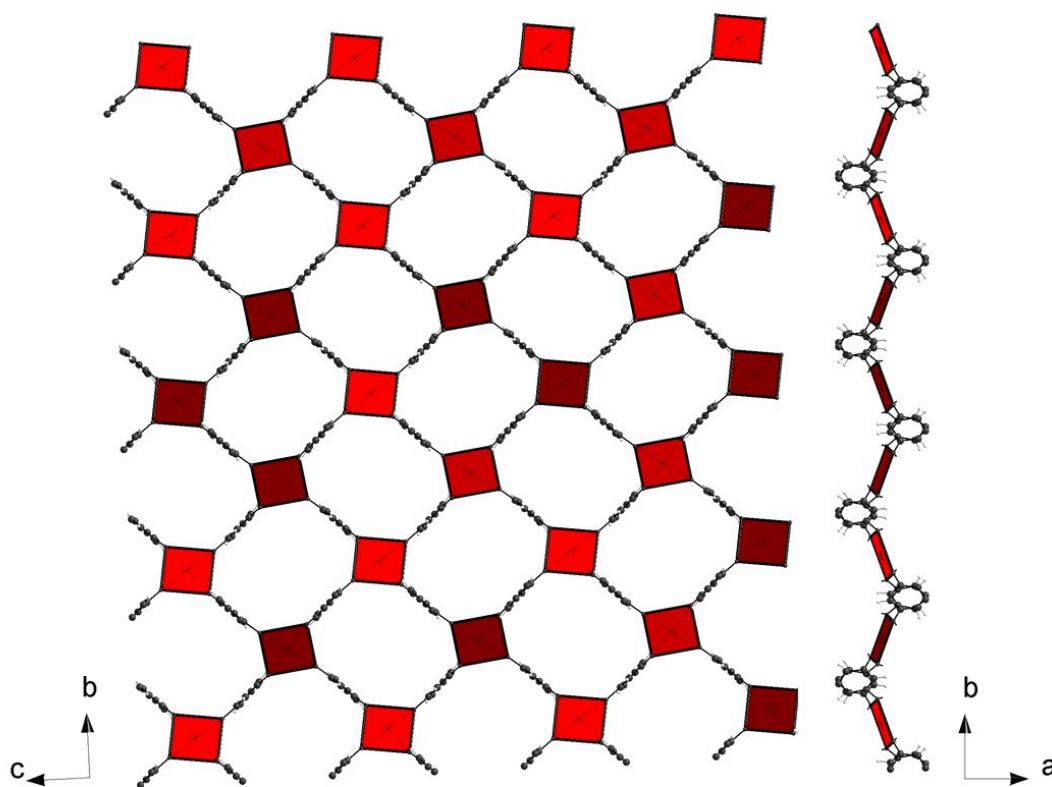


Figure 4.12: 4-connected uninodal net viewed down the a -axis (a); Schematic representation of the zigzag pattern of the connected SBUs in each sheet, viewed down the c -axis (b).

Table 4.5: Crystal data and structure refinement for 3.2.

Identification code	3.2
Empirical formula	C ₉₅ H ₆₃ Cl ₆ Mn ₃ N ₁₃ O ₉ Ru ₂
Formula weight/ g mol ⁻¹	2110.2801
Temperature/K	100
Crystal system	Monoclinic
Space group	C2/c
a/Å	43.930(3)
b/Å	13.1872(9)
c/Å	15.3053(10)
α/°	90
β/°	100.032
γ/°	90
Volume/Å ³	8731.0(10)
Z	2
ρ _{calc} /mg/cm ³	1.529
μ/mm ⁻¹	7.823
F(000)	4034
Crystal size/mm ³	0.09 × 0.06 × 0.04
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	2.043 to 56.116
Index ranges	-47 ≤ h ≤ 47, -14 ≤ k ≤ 14, -16 ≤ l ≤ 16
Reflections collected	5691
Independent reflections	5691 [R _{int} = 0.0613, R _{sigma} = 0.0601]
Data/restraints/parameters	5691/ 2 /506
Goodness-of-fit on F ²	1.075
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.1080, wR ₂ = 0.2707
Final R indexes [all data]	R ₁ = 0.1521, wR ₂ = 0.3124
Largest diff. peak/hole / e Å ⁻³	2.735/-1.241

4.4.1. Further characterisation of 3.2

The IR spectrum of compound **3.2** (Fig. 4.13) reveals strong absorptions in the region 1600–1500 cm⁻¹. The lack of the signal at approximately 1720 cm⁻¹ confirms the absence of starting materials. The shoulder at *ca.* 1687 cm⁻¹ might arise from the carbonyl stretch in constitutional DMF. Correspondingly to **VII**, the signal at *ca.* 3078 cm⁻¹ arises from C – H vibrations of the aromatic ligand moieties^{27,28} The asymmetric vibration modes of the carboxylate moieties are observed at 1600 cm⁻¹ and 1550 cm⁻¹ with the corresponding symmetric vibrations are attributed to the bands centred at 1402 cm⁻¹ and 1350 cm⁻¹

Deacon-Phillips values of 198 cm⁻¹ and 200 cm⁻¹ are consistent with the observed bidentate bridging mode of the carboxylates.^{48, 49} The assignments of the symmetric and asymmetric vibrations and the calculated delta values are in agreement with those obtained for a paddlewheel manganese carboxylate MOF structure reported in the literature.⁴⁷

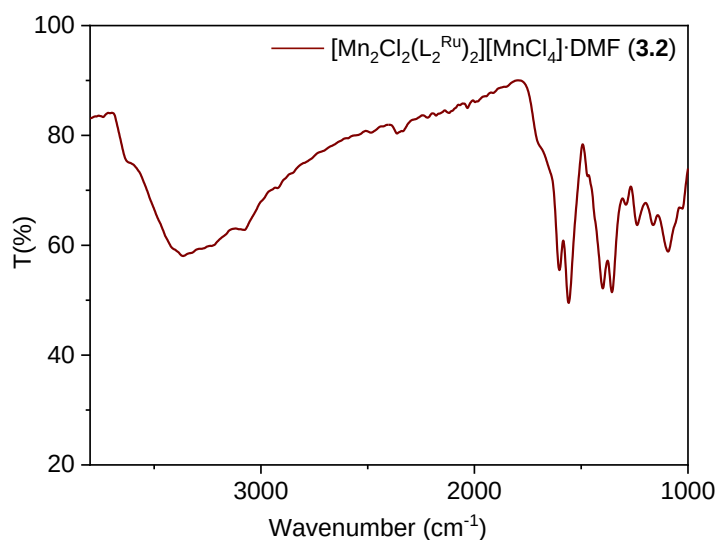


Figure 4.13: FTIR spectrum of 3.2.

The thermal stability of **3.2** was evaluated by thermogravimetric analysis under air atmosphere (Fig. 4.14). An initial weight loss of *ca.* 15.0 % between room temperature and 120°C can be attributed to the loss of solvent associated with the freshly prepared sample and constitutional DMF. Analysis reveals thermal stability up to *ca.* 200 °C whereby the majority of the framework undergoes oxidative degradation due to the organic ligand above 250 °C.

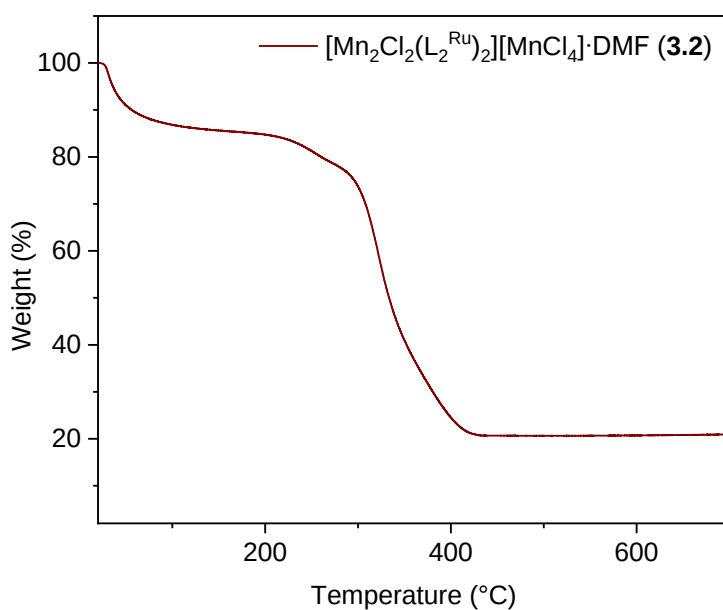


Figure 4.14: Thermogravimetric analysis of 3.2.

4.5. Conclusion

During the course of the project, synthetic approaches to novel, extended organic ligands that contain terpyridyl and carboxylate moieties were developed. These systems were designed to provide a synthetic pathway to incorporate photosensitizers as struts into potentially photocatalytic MOFs. The ligand synthesis was achieved in good yields using Sonogashira coupling reactions. To construct photoactive struts the heteroleptic ruthenium complex $[\text{H}_2\text{L}_2^{\text{Ru}}](\text{PF}_6)_2$ was successfully synthesized. Photophysical studies were performed for the metallo-ligand and its intermediates in order to evaluate the properties of these compounds. The experiments involved UV-vis absorption and photoluminescence studies. The results demonstrate that the organic precursor, pro-ligand **IV**, absorbs light in the UV region whilst the coordination complexes **V** and the hydrolysed carboxylic acid derivative **VII** show MLCT absorptions in the visible region. **VII** shows relatively intense absorption in the visible region when compared to **IV** and **V** and a single band is observed in its emission spectrum. The obtained results confirm that the photophysical properties were successfully improved by complexation of **IV** with a Ru^{III} salt and subsequent reduction of the metal centre to Ru^{II}, by addition of a second terpyridine moiety in the presence of a reducing agent. Therefore, solution experiments indicated that **VII** was a suitable linker to be used in the construction of a MOF for light-harvesting related applications. $\text{H}_2\text{L}_2^{\text{Ru}}$ was also crystallographically characterised as $[\text{H}_2\text{L}_2^{\text{Ru}}](\text{NO}_3)_2 \cdot 2\text{DMF}$ and employed in the synthesis of a Mn^{II}-based MOF $[\text{Mn}_2\text{Cl}_2(\text{L}_2^{\text{Ru}})_2][\text{MnCl}_4]$ (**3.2**). Compound **3.2** features dinuclear Mn paddlewheel motifs that function as 4-connected nodes to form 2D sheets with L_2^{Ru} moieties located above and below the [100] plane. The interdigitation of the sheets results in proximity between $\{\text{Mn}_2(\text{COO})_4\}$ and $\{\text{Ru}(\text{tpy})_2\}$ moieties. Furthermore, the retained structural integrity of the photosensitizer metallo-ligands and the existence of labile sites within the Mn-based SBU within the framework are noteworthy and may be exploitable in future investigations of visible light-driven photocatalytic reactions.

4.6. References

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Chapter 5

Synthesis of Co^{II}-based MOFs

5. Synthesis of Co^{II}-based MOFs

5.1. Introduction

The possibility of varying the pore size and nature of MOFs without changing the underlying connectivity of their framework gave rise to the principle of isorecticular chemistry. This principle has been applied in the synthesis of MOFs with large pore apertures and low densities.^{1,2} The approach requires the use of a secondary building unit (SBU) to direct the assembly of ordered frameworks. This can be achieved through the use of expanded versions of a parent organic linker containing the same functional groups.³

Coupling reactions have been used extensively as a reliable method for the synthesis of acetylenic materials.⁴⁻⁸ The Sonogashira coupling method is particularly interesting as it allows the cross-coupling of terminal acetylenes with sp²-hybridised carbon-based halides.^{7, 8} This reaction can be used as a viable method of producing planar rigid molecules that function as rigid organic units. These rigid building blocks can retain geometrical features throughout the synthesis of a MOF to form the predesigned solid-state frameworks.⁹

In order to have a targeted dimensionality in a MOF it is essential to select organic linkers with appropriate functional groups. Polycarboxylates are the most commonly used anionic linkers and have been widely employed for the synthesis of MOFs, and are particularly interesting as they have been reported to be highly reactive towards condensation metal ions under solvothermal conditions.^{10, 11}

We aim to explore ligands that can modularly be extended and whose functionality be varied. The carboxylate moieties are expected to react with oxophilic metal ions and cluster units to stabilise extended MOFs. We set out to use Co^{II} SBUs for the preparation of the MOFs. Co^{II} coordination clusters are known to show interesting reactivities as oxidation catalysts.¹²⁻¹⁶

5.2. Organic ligands

The research described in this chapter, aimed to study the coordination modes of two related organic ligands for the synthesis of Co^{II}-based MOFs. The chosen linkers were isophthalic acid (commercially available) and an extended trifunctional derivative, 5-((4-carboxyphenyl) ethynyl) isophthalic acid) (H₃CPEIP) (Fig. 5.1).

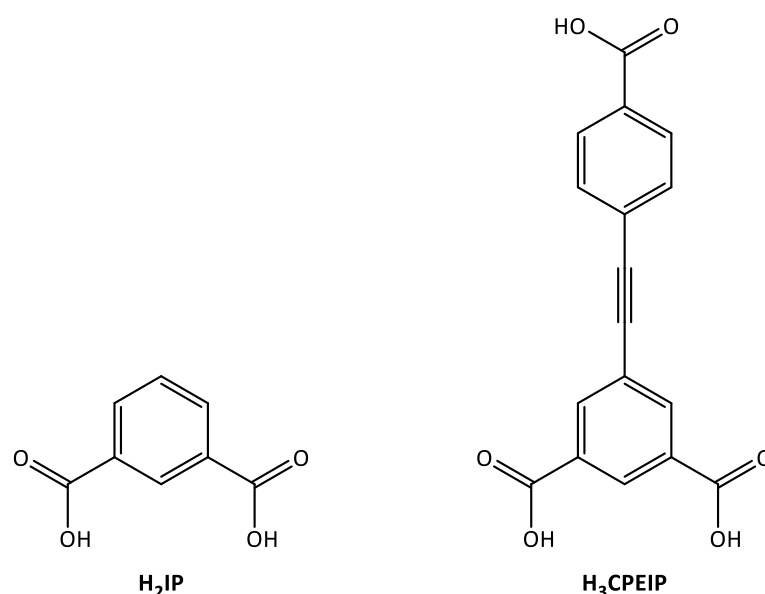


Figure 5.1: Organic ligands used in the synthesis of Co^{II}-based MOFs: isophthalic acid (H₂IP) and 5-((4-carboxyphenyl) ethynyl) isophthalic acid) (H₃CPEIP).

1,3-Benzenedicarboxylic acid or commonly referred to as isophthalic acid (H₂IP) is a C₂ symmetrical dicarboxylate ligand that, together with its derivatives, has been widely investigated in the synthesis of several microporous MOFs.¹⁷⁻²³ Selected, commonly observed coordination modes for this linker are represented in Figure 5.2.

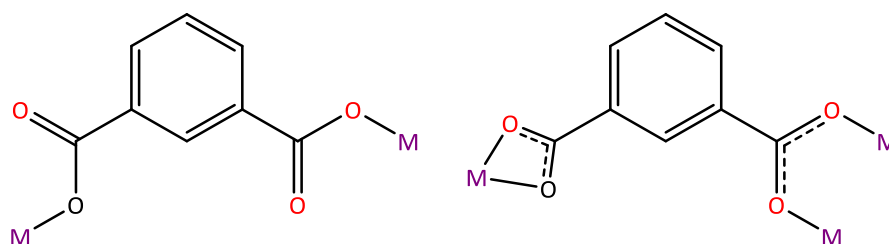
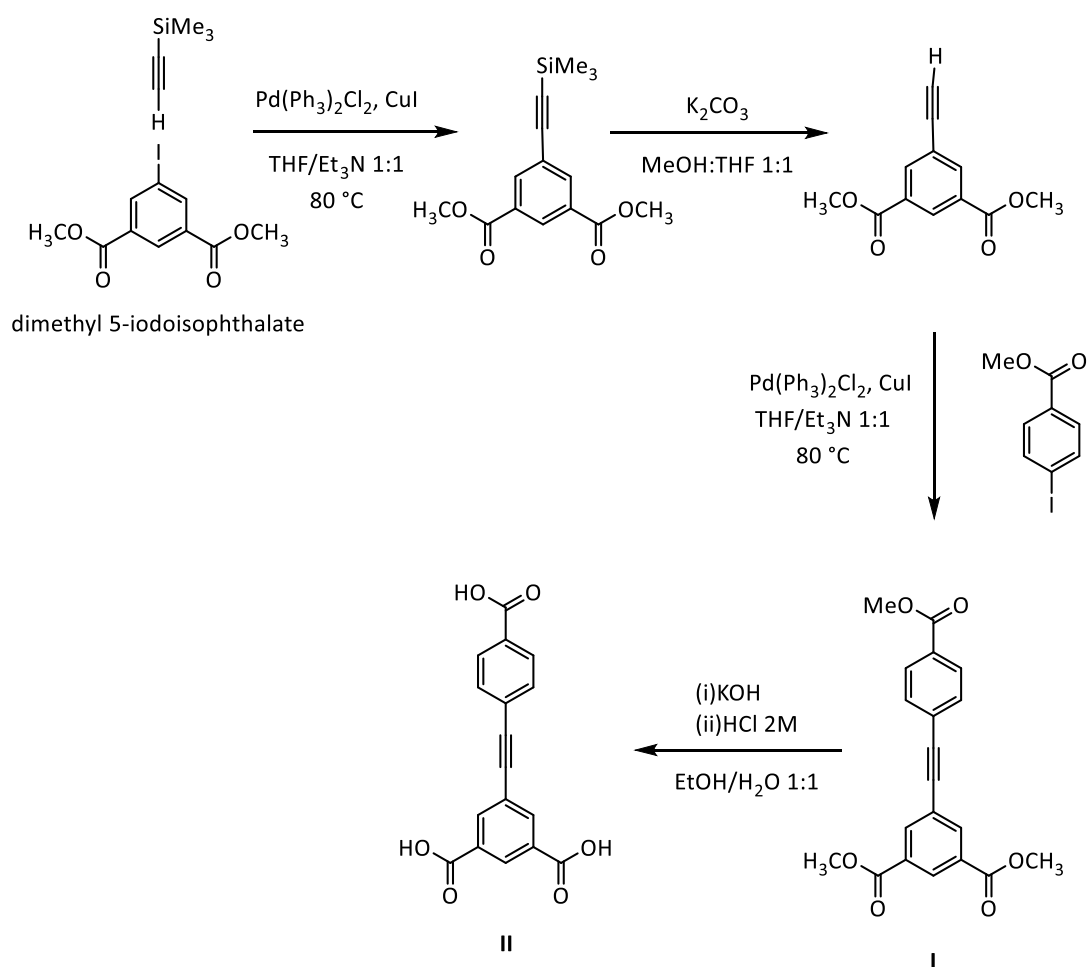


Figure 5.2: Selected coordination modes for 1,3-benzenedicarboxylate (IP²⁻); Adapted from ref. 24.

H₃CPEIP is an asymmetrical organic ligand with three carboxylate functionalities. Asymmetric linkers are especially interesting because they can adopt a variety of coordination modes that result in diversity of topologies who often structurally relate to those obtained with higher symmetric analogues²⁵

5.3. Synthesis of 5-(4-carboxyphenyl) ethynyl) isophthalic acid (H₃CPEIP)

H₃CPEIP (**II**) was synthesised according to an adapted literature procedure (Scheme 5.1).²⁶ The synthesis was carried out by Sonogashira cross-coupling reaction⁸ using ethynyltrimethylsilane and dimethyl 5-iodoisophthalate as reactants, followed by another cross-coupling reaction to introduce an additional benzoate group, giving dimethyl 5-(4-(methoxycarbonyl)phenyl)ethynyl isophthalate (Me₃CPEIP, **I**). Compound **I** was deprotected through basic ester hydrolysis. An average yield of *ca.* 58 % of compound **II** was obtained.



Scheme 5.1: Synthetic route to H₃CPEIP (**II**).

The ligand was characterised through ¹H-NMR and ¹³C-NMR spectroscopy. The analysis of **II** was carried out in deuterated dimethyl sulfoxide (d₆-DMSO). The ¹H-NMR spectrum (Fig. 5.3) reveals signals at 8.47 ppm, 8.30 ppm, 8.00 ppm and 7.77 ppm which are attributed to the aromatic H-atoms. The ¹³C-NMR spectrum (Fig. 5.4) shows signals at 90.6 ppm and 90.3 ppm attributed to acetylene carbon atoms and 167.1 ppm and 166.2 ppm attributed to the carboxylate-derived carbon atoms. Signals between 136.2 to 123.4 ppm are assigned to the carbon atoms of the aromatic ligand moieties.

The obtained ¹H-NMR and ¹³C-NMR spectra for **II** are in agreement with reported spectra of H₃CPEIP in d₆-DMSO.²⁷

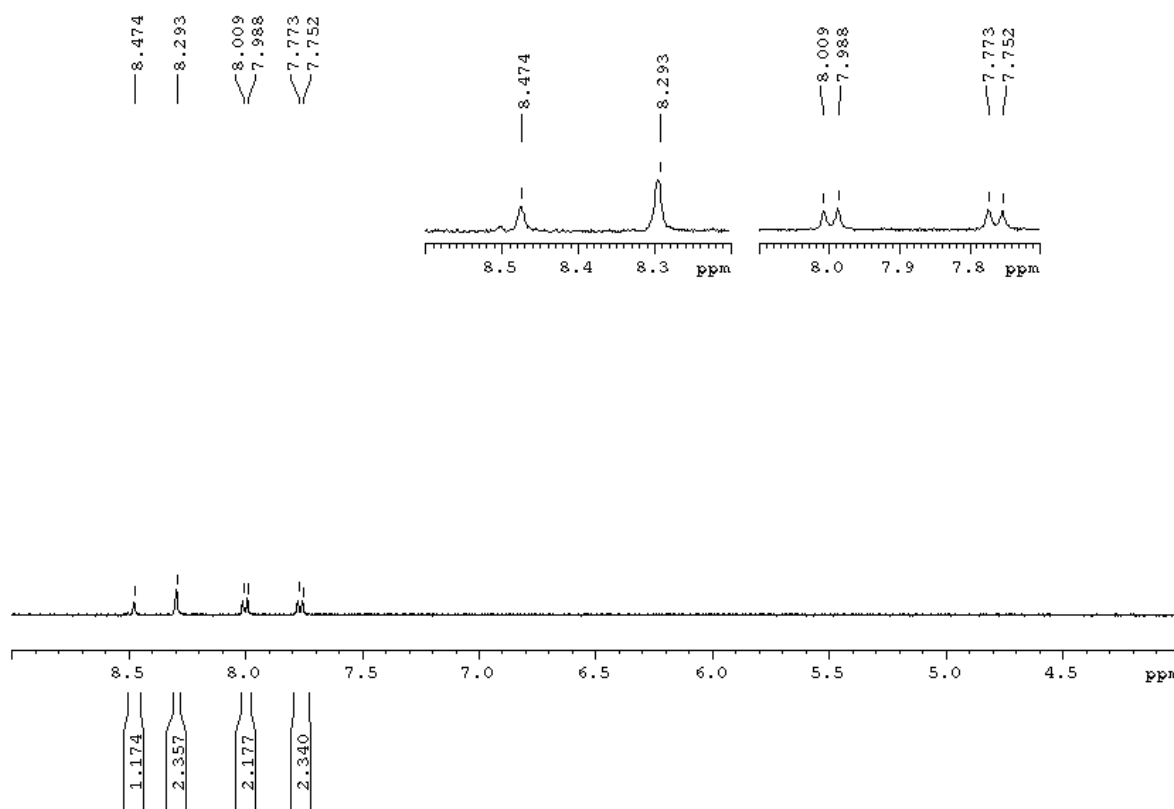


Figure 5.3: ¹H-NMR spectrum (600 MHz, d₆-DMSO) of H₃CPEIP (II).

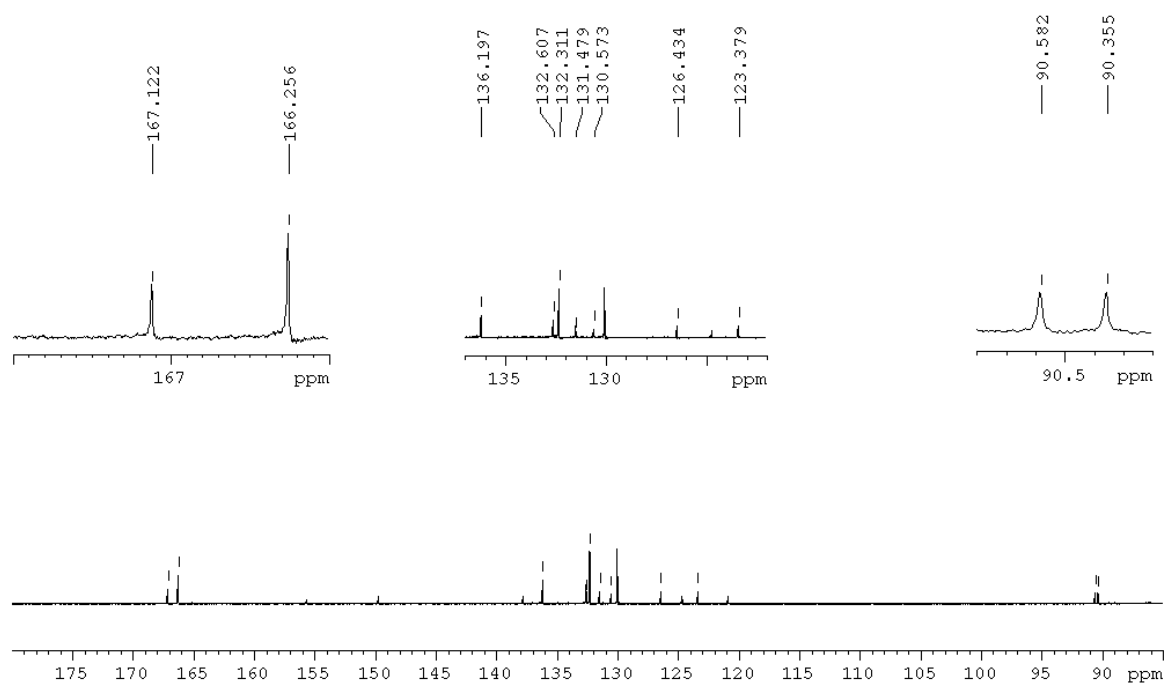


Figure 5.4: ¹³C-NMR spectrum (600 MHz, d₆-DMSO) of H₃CPEIP (II).

5.4. Novel metal-organic frameworks:

Two novel 2D MOFs were synthesised, [Co(IP)Py₂].2MeOH (**5.1**) and [Co₃(CPEIP)₂Py₆(H₂O)₂].3MeOH (**5.2**). The compounds were synthesised through the reaction of equimolar quantities of organic ligand (H₂IP for **5.1** and H₃CPEIP for **5.2**) and Co(NO₃)₂·6H₂O under solvothermal conditions in a MeOH/pyridine solvent mixture (1.0 mL: 0.5 mL). The structures of the two MOFs contain structurally similar dinuclear SBUs. Data collection and refinement of the structures were done by Dr Brendan Twamley.

5.4.1. [Co(IP)Py₂].2MeOH (**5.1**)

Compound **5.1** was crystallographically identified as [Co(IP)Py₂].2MeOH. It was prepared by the reaction of Co(NO₃)₂·6H₂O with H₂IP in MeOH solution, in the presence of aqueous pyridine (Py). The compound crystallizes in the trigonal crystal system in the space group *R*-3. It contains a dinuclear building unit composed of two crystallographically identical six-coordinated Co^{II} ions. An inversion centre is situated in the centre of the dinuclear unit. The two Co^{II} atoms within the dinuclear unit are doubly bridged by two *syn, syn* bidentate carboxylate moieties that are derived from two IP²⁻ ligands, and adopt distorted octahedral coordination geometries. Co(1) and its symmetry equivalent Co(1') are further coordinated by chelating carboxylate moieties of two IP²⁻ ligands. The coordination spheres are completed by two *trans*-located pyridine ligands located in the apical positions as shown in Figure 5.5. Each dinuclear unit is stabilised by four carboxylate moieties derived from four organic ligands.

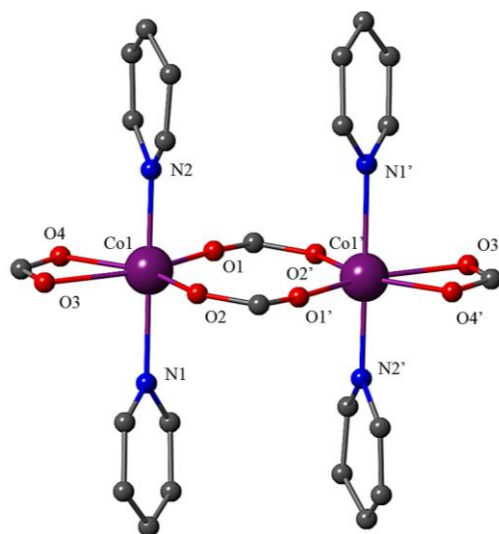


Figure 5.5: Dinuclear unit in 5.1. Colour code: Co purple, C grey, O red, N blue, H atoms omitted for clarity; Symmetry code: 1/3-x, 2/3-y, 2/3-z.

The bond lengths involving the O-donor atoms of the bidentate chelating ligand are 2.037(5) Å and 2.274(6) Å for Co(1) – O(3) and Co(1) – O(4), respectively. Similar bond lengths were observed for Co – O in [Co₃(H₂O)₆(TMA³⁻)(TMA²⁻)(TMA¹⁻)]·2H₂O, a {Co^{II}/trimesic acid}-based coordination polymer where the carboxylate moieties also display bidentate chelating mode.²⁸ The Co(1) – O bond lengths involving the bridging carboxylate moieties are 1.994(7) and 2.203(5) Å. The two pyridine ligands which complete the coordination environment of the Co^{II} centre form Co(1) – N(1) and Co(1) – N(2) bonds, with bond lengths of 1.930(2) Å and 2.270(2) Å, respectively. The Co – O and Co – N bond distances in **5.1** are in close agreement with the Co – O and Co – N distances in a coordination polymer reported as [Co(tbip)(bipy)]_n containing a very similar dinuclear unit.²⁴

BVS analysis confirms that the Co(1) centre in **5.1** is in oxidation state +II (Table 5.1)

Table 5.1: Crystallographically-determined bond lengths for the Co(1) centre in 5.1, along with their oxidation state as determined by Bond Valence Sum (BVS) analysis.

Metal Atom	Bonded Atom	Bond Length (Å)	BVS	Oxidation State
Co(1)	O(1)	1.994(7)	1.71	+II
	O(2)	2.203(5)		
	O(3)	2.037(5)		
	O(4)	2.274(6)		
	N(1)	2.270(2)		
	N(2)	1.930(2)		

The distorted nature of octahedral coordination geometry of the Co^{II} ions can be exemplified by the bond angles involving Co(1). The O(1) – Co(1) – O(2) and O(4) – Co(1) – O(3) angles of 112.18(8)° and 60.26(5)°, respectively, deviate from the ideal angle of 90°.

Nonetheless, the N(1) – Co(1) – O(2) and N(1) – Co(1) – O(4) angles of 93.10(5)° and 90.25(7)°, respectively are close to the ideal angles. Selected bond angles in **5.1** are summarised in Table 5.2.

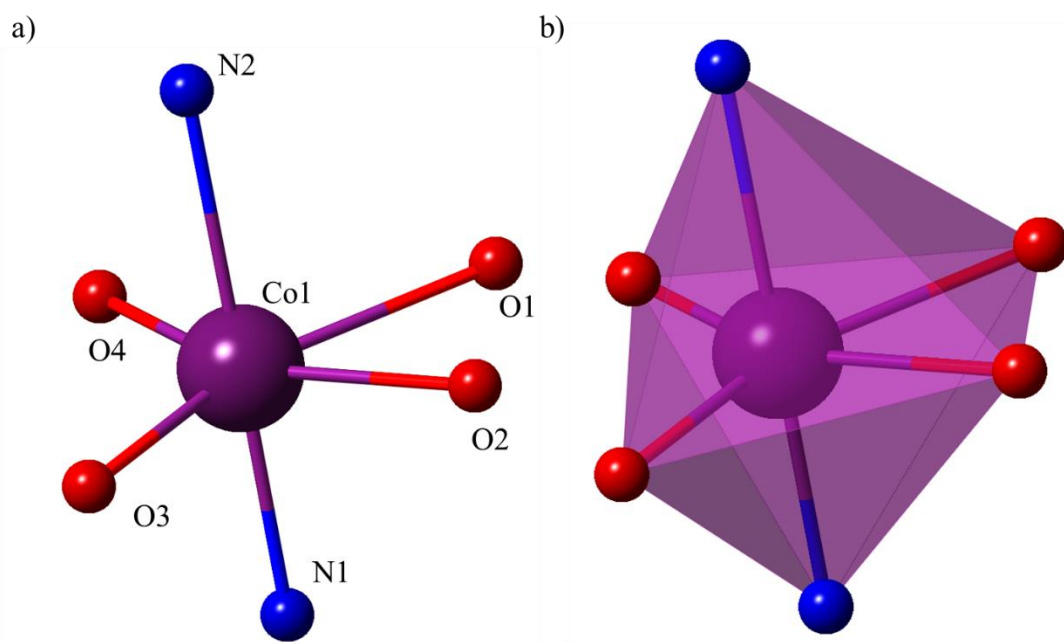


Figure 5.6: Co^{II} coordination environment in 5.1 (a); Polyhedral representation of the distorted square pyramidal geometry (b); Colour code: Co purple, O red, N blue.

Table 5.2: Selected bond angles (°) for compound 5.1.

Atoms	Angles(°)	Atoms	Angles(°)
O(1) – Co(1) – O(2)	112.18 (8)°	N(1) – Co(1) – O(3)	93.74(4)
O(4) – Co(1) – O(3)	60.26 (5)°	N(1) – Co(1) – O(1)	85.87(9)
N(1) – Co(1) – O(2)	93.10(5)°	O(2) – Co(1) – O(3)	95.31(3)
N(1) – Co(1) – O(4)	90.25(7)°	O(1) – Co(1) – O(4)	92.24(7)

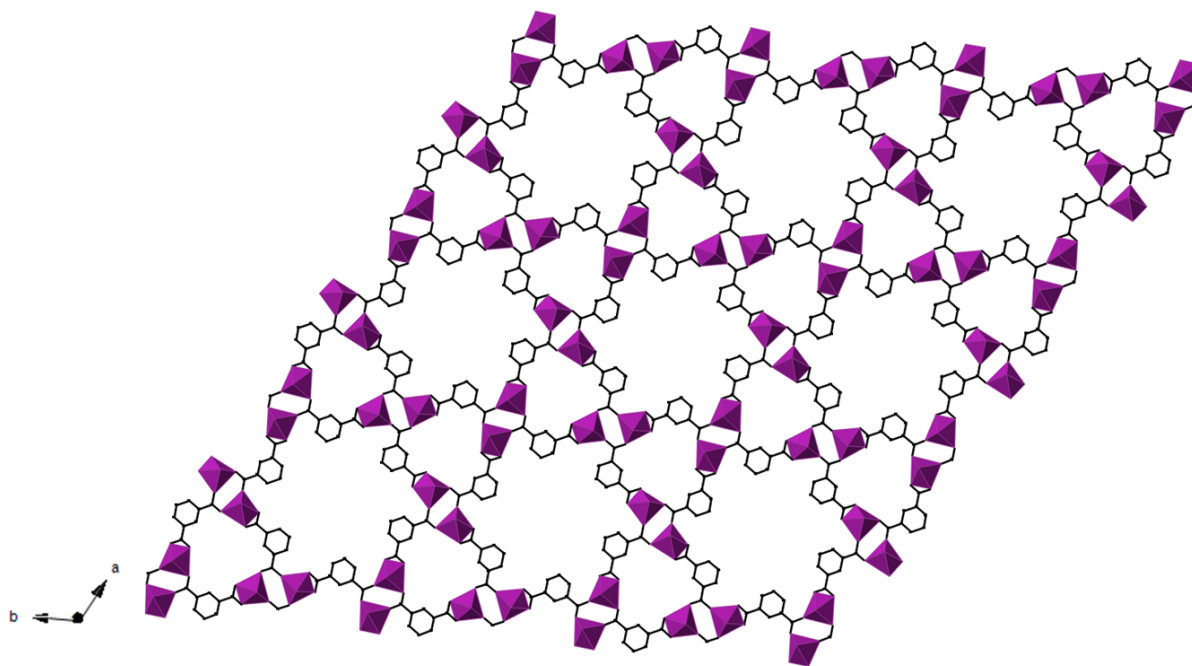


Figure 5.7: View of the structure of 5.1 viewed in the direction of the crystallographic c -axis showing the arrangement of the hexagonal and triangular channels.

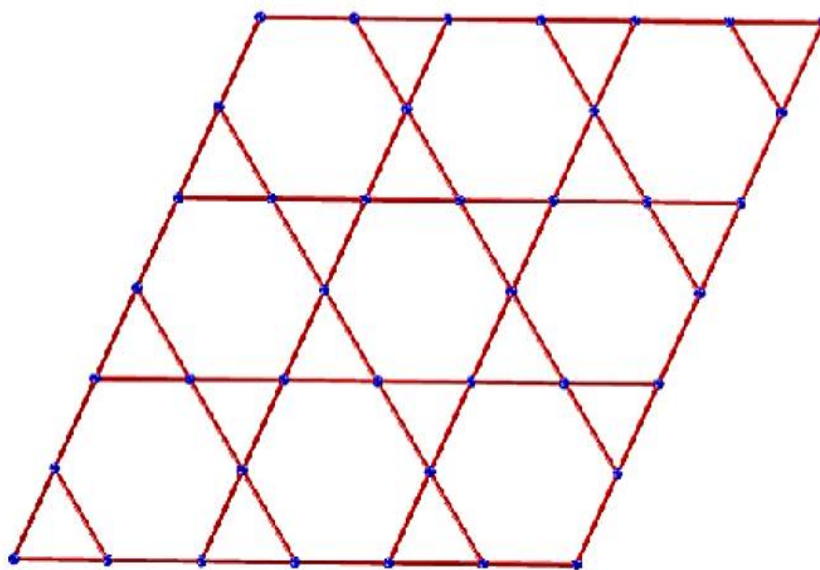


Figure 5.8: Nodal representation of the (3.6.3.6) Kagomé type lattice of 5.1.

Each IP²⁻ ligand in **5.1** connects two dinuclear units, whereby one carboxylate moiety acts as a bidentate bridging group and the second group binds terminally as a chelating functionality. The observed binding arrangement results in 2D sheets that extend parallel to the crystallographic *ab*-plane (Fig. 5.7) forming smaller triangular and larger hexagonal openings. Each hexagonal ring is delimited by six triangular rings. This topology is typically classified as a Kagomé lattice, typically abbreviated by the the RCSR symbol **kgm** (Fig. 5.8).^{29, 30} The 2D sheets in the structure pack directly on top of each other forming smaller triangular and larger hexagonal channels with cross-sectional diameters of *ca.* 20.6 Å and 9.6 Å, respectively.

The pyridine moieties in **5.1** bind perpendicular to the sheets; the packing of the sheets in the direction of the crystallographic *c*-axis results in an interdigitated arrangement (Fig. 5.9). The interlayer distance observed is *ca.* 10.54 Å.

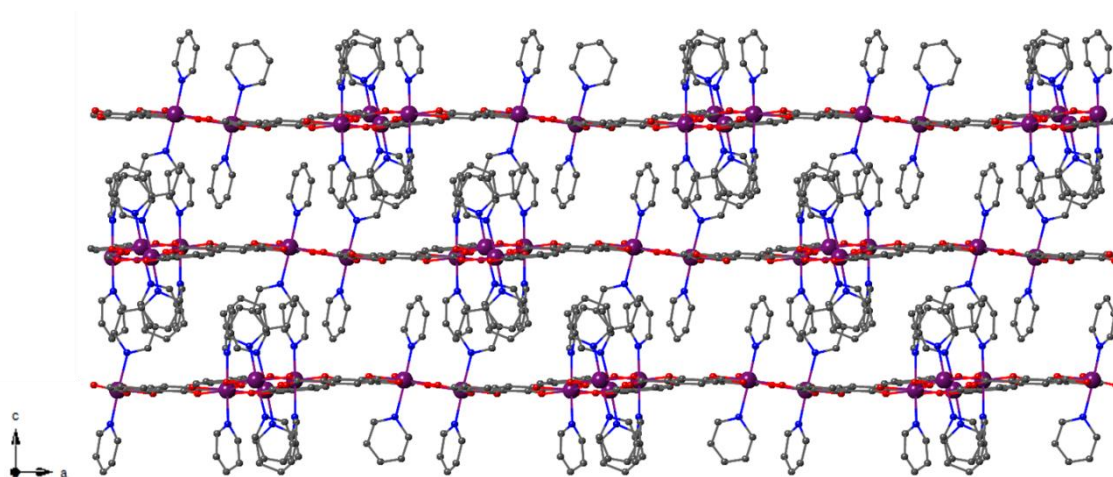


Figure 5.9: Packing arrangement in **5.1** gives rise to sheets that are shown with view in the direction of the crystallographic *c*-axis.

Table 5.3: Crystal data and structure refinement for 5.1.

Identification code	5.1
Empirical formula	C ₂₁ H ₂₇ CoN ₂ O ₆
Formula weight/ g mol ⁻¹	462.388
Temperature/K	100
Crystal system	trigonal
Space group	<i>R</i> -3
<i>a</i> /Å	22.9823(10)
<i>b</i> /Å	22.9823(10)
<i>c</i> /Å	22.9777(18)
α /°	90
β /°	90
γ /°	120
Volume/Å ³	10510.5(12)
<i>Z</i>	6
ρ_{calc} /cm ³	1.084
μ /mm ⁻¹	5.924
<i>F</i> (000)	3510.0
Crystal size/mm ³	0.10 × 0.1 × 0.08
Radiation	CuK α (λ = 1.54178)
2 Θ range for data collection/°	5.874 to 139.834
Index ranges	-25 ≤ <i>h</i> ≤ 27, -24 ≤ <i>k</i> ≤ 25, -21 ≤ <i>l</i> ≤ 24
Reflections collected	12583
Independent reflections	4082 [<i>R</i> _{int} = 0.0613, <i>R</i> _{sigma} = 0.0601]
Data/restraints/parameters	4082/342/339
Goodness-of-fit on <i>F</i> ²	1.076
Final <i>R</i> indexes [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0815, <i>wR</i> ₂ = 0.2450
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1103, <i>wR</i> ₂ = 0.2719
Largest diff. peak/hole / e Å ⁻³	1.26/-0.42

5.4.1.1. Further characterisation of 5.1

FTIR spectroscopy was carried out on a sample of compound **5.1** and revealed bands characteristic of similar coordination polymers reported in the literature (Fig. 5.10).^{24, 31, 32} The broad band centred at 3400 cm⁻¹ most likely derives from O – H vibrations in constitutional solvent molecules that are located in the channels of the MOF. The signal at 3056 cm⁻¹ is likely caused by C – H vibrations of the aromatic ring moieties in IP²⁻. The asymmetric vibrations of the carboxylate groups appear at 1586 and 1570 cm⁻¹. The corresponding symmetric C – O vibrations occur at 1480 and 1463 cm⁻¹. The occurrence of these signals agrees with the observed binding modes of the carboxylate groups.³³ The sharp strong signal at 1441 cm⁻¹ can be assigned to C = N stretch in the pyridine ring.³⁴

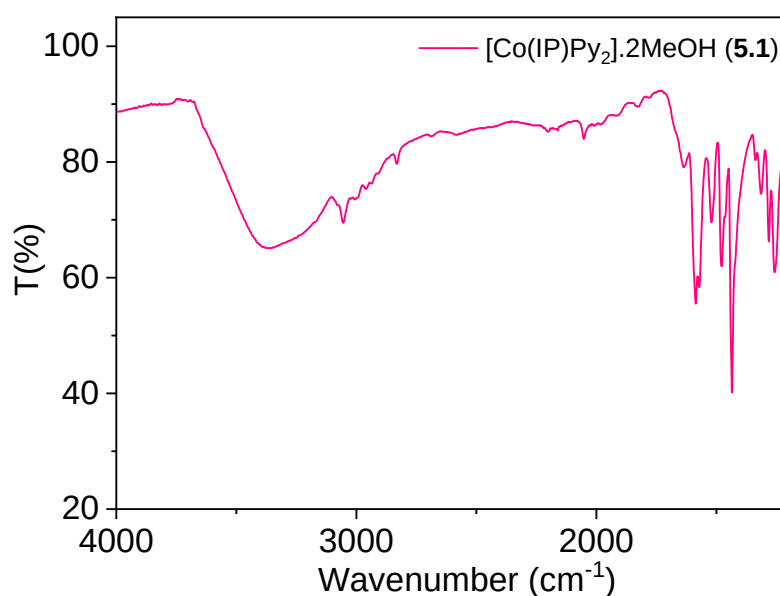


Figure 5.10: FTIR spectrum of 5.1.

The thermal stability of a freshly prepared crystalline sample of **5.1** was investigated in an air atmosphere, in the temperature range of 25 to 500 °C. The initial mass loss of 10% between 30 and 60 °C can be assigned the loss of constitutional solvent (methanol) molecules present in the channels of the MOF. TGA analysis (Fig. 5.11) reveals that framework structure undergoes decomposition in two consecutive steps. A step in the range between 100 °C to 220 °C correspond to a mass loss of *ca.* 15% weight. The oxidation of the organic carboxylate ligand can be observed above 400 °C resulting, most likely, in the formation of cobalt oxide materials, i.e. Co₃O₄.

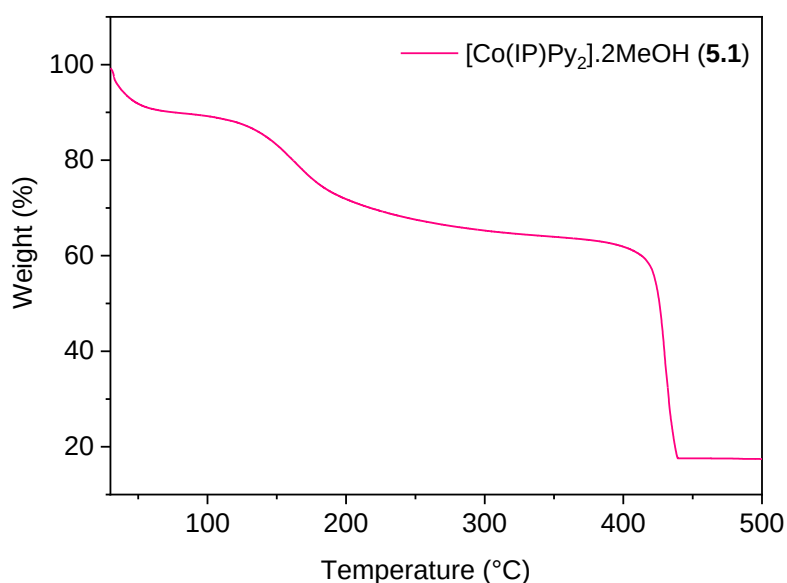


Figure 5.11: Thermogravimetric analysis of 5.1.

5.4.2. [Co₃(CPEIP)₂Py₆(H₂O)₂]-3MeOH (5.2)

Compound **5.2** crystallises in the triclinic space group *P*-1 and consists of dinuclear and mononuclear building units (Fig. 5.12). The structure contains three six-coordinated Co^{II} centres, two Co^{II} centres in a dinuclear unit (Co1 and its symmetry equivalent Co1') and one further crystallographically independent Co^{II} centre in the mononuclear unit, Co(2). The observed dinuclear unit is structurally very similar to that in **5.1**. An inversion centre is situated in the centre of the dinuclear unit. The two Co^{II} centres within the dinuclear unit are doubly bridged by two *syn, syn* bidentate carboxylates from the CPEIP³⁻ ligands to form a distorted octahedral coordination polyhedron. Co(1) is further coordinated by a chelating carboxylate moiety of a CPEIP³⁻ ligand. The coordination spheres are completed by two *trans* located pyridine ligands.

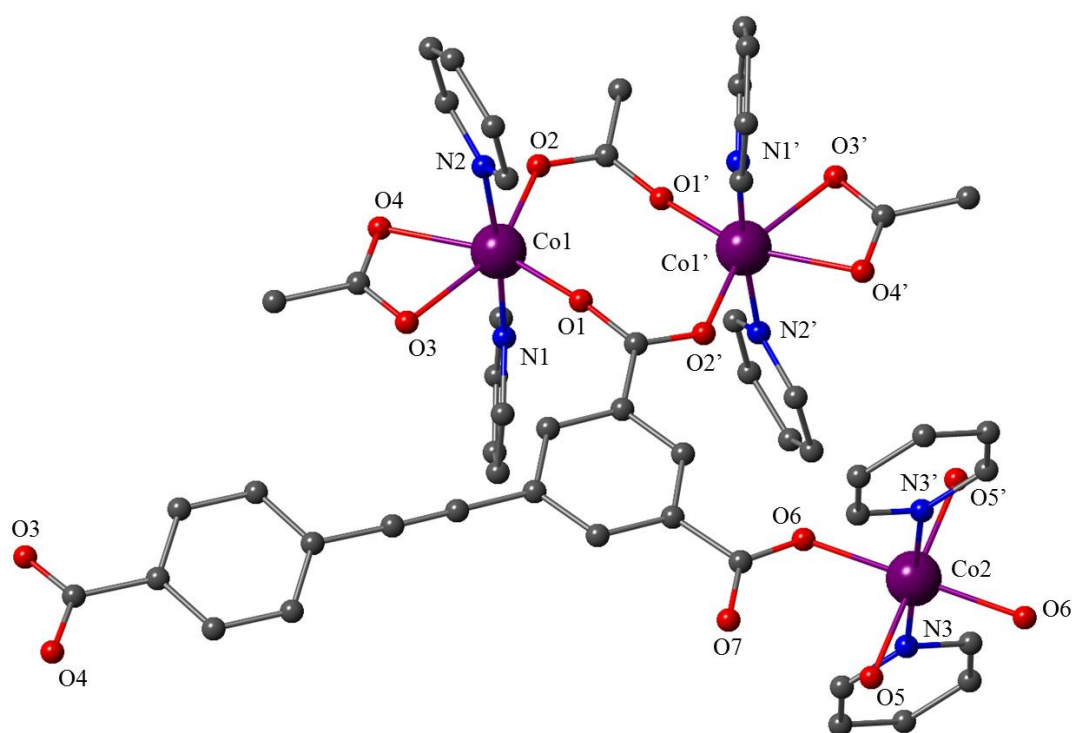


Figure 5.12: Crystal structure of the mono- and dinuclear units in [Co₃(CPEIP)₂Py₆(H₂O)₂]-3MeOH ; H atoms omitted for clarity; Colour code: Co purple, C grey, O red, N blue; Symmetry code: -x, 2-y, 2-z.

In the dinuclear unit (Fig. 5.13) one of the three coordinating CPEIP³⁻ ligands provides two oxygen donors and displays symmetrical bidentate chelation with bond lengths of 2.167(3) to 2.187(4) Å for Co(1) – O(3) and Co(1) – O(4) respectively. The two Co^{II} centres are bridged through a chelating CPEIP³⁻ ligand with bond lengths of 1.994(4) to 2.008(4) Å for Co(1) – O(1) and Co(1) – O(2) respectively. The observed Co – O bond distances are in agreement with Co – O bridging carboxylates bond distances previously reported.^{24, 35, 36} The Co(1) – N(2) and Co(1) – N(1) have bond lengths of 2.155(11) to 2.153(5) Å respectively. BVS analysis confirms that the Co(1) centre in 5.2 is in oxidation state +II (Table 5.4).

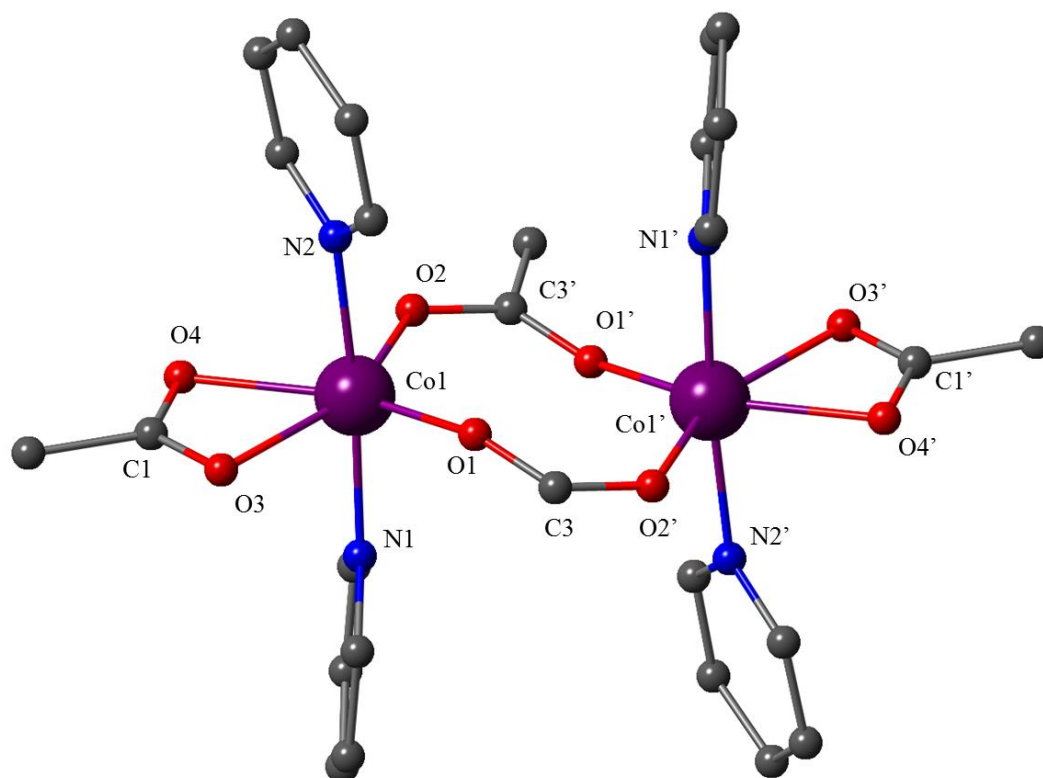
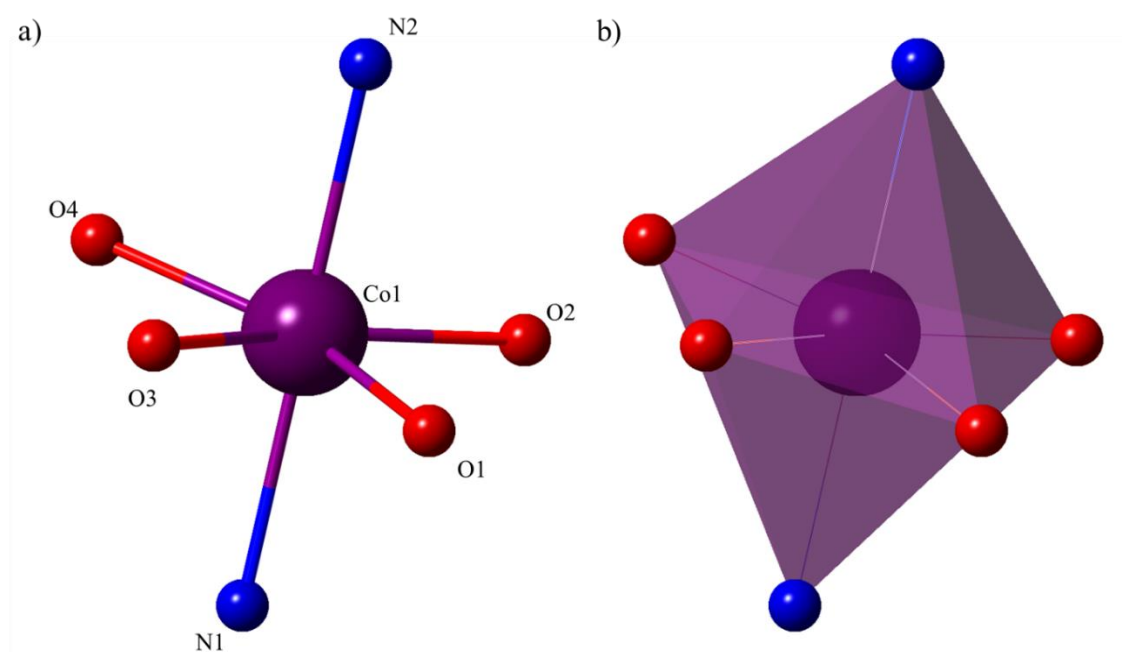


Figure 5.13: Crystal structure of the dinuclear subunit of 5.2 showing the coordination environment of Co(1); Colour code: Co purple, C grey, O red, N blue; H atoms omitted for clarity. Symmetry code: $-x, 2-y, 2-z$.

Table 5.4: Crystallographically-determined bond lengths for the Co(1) centre in 5.2, along with their oxidation state as determined by Bond Valence Sum (BVS) analysis.

Metal Atom	Bonded Atom	Bond Length (Å)	BVS	Oxidation State
Co(1)	O(1)	1.994(4)	1.70	+II
	O(2)	2.008(4)		
	O(4)	2.187(4)		
	O(3)	2.167(3)		
	N(1)	2.153(5)		
	N(2)	2.155(11)		

**Figure 5.14: Co^{II} coordination environment in 5.2 (a); Polyhedral representation of the distorted square pyramidal geometry (b); Colour code: Co purple, O red, N blue.**

An O(4) – C(1) – O(3) angle of 120.9(5)° is observed for the chelating carboxylates in **5.2**. The distorted nature of octahedral coordination geometry of the Co^{II} ions can be exemplified by the bond angles involving the Co(1) centre (Fig. 5.14). The O(4) – Co(1) – O(3) and O(2) – Co(1) – O(1) angles of 60.50(14)° and 120.9(5)° respectively, deviate from the ideal angle of 90°. The deviation is very comparable with the angles observed in **5.1**. Nonetheless, the N(4) – Co(1) – O(4) and N(4) – Co(1) – O(3) angles of 87.15(9)° and 91.83(3)°, respectively, are close to the ideal angle.

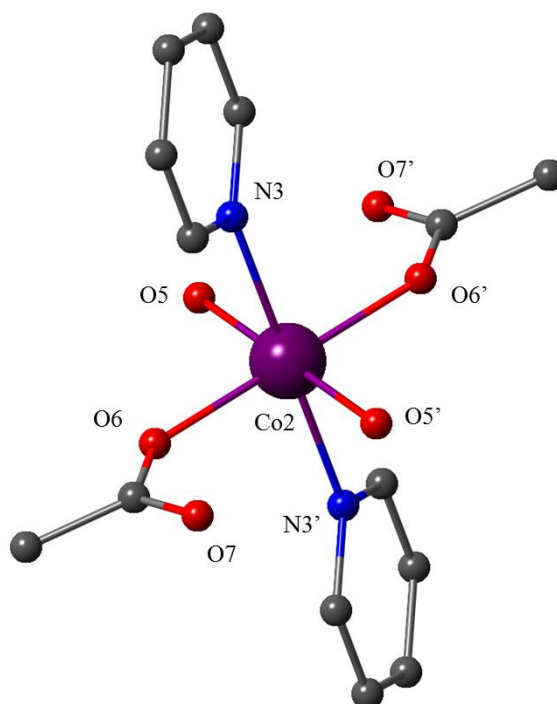


Figure 5.15: Mononuclear subunit of 5.2; Colour code: Co purple, O red, N blue, H atoms omitted for clarity; Symmetry code: -x, 2-y, 2-z.

Co(2) of the mononuclear subunit (Fig. 5.15) also adopts a distorted octahedral coordination environment and is located on an inversion centre. The coordination sphere is composed of two *trans* located carboxylate O-donors: O6 and O6' of two different CPEIP ligands, two *trans* located water molecules and two pyridine molecules. Each of the two CPEIP³⁻ ligands coordinate to Co(2) with a Co(2) – O(6) bond length of 2.051(4) Å.

The two remaining equatorial positions are occupied by oxygen donors from water molecules, the Co(2) – O(5) bond lengths of 2.121(7) Å. The coordination environment of the Co(2) centre is completed by two axial nitrogen donors provided by pyridine ligands, the Co(2) – N(3) bond lengths of 2.308(16) Å.

The bond distances involving Co(2) are in close agreement with those observed for [Co(C₉H₇O₅)₂(C₁₀H₈N₂)₂(H₂O)₂]·4H₂O³⁷ and [Co(C₇H₅O₃)₂(C₆H₆N₂O)₂(H₂O)₂]³⁸. Those Co^{II} complexes feature a mononuclear subunit very similar to the one observed in compound 5.2.

Additionally, BVS analysis confirms that the Co(2) centre in 5.2 is in oxidation state +II (Table 5.5).

Table 5.5: Crystallographically-determined bond lengths for the Co(2) centre in 5.2, along with their oxidation state as determined by Bond Valence Sum (BVS) analysis.

Metal Atom	Bonded Atom	Bond Length (Å)	BVS	Oxidation State
Co(2)	O(6)	2.051(4)	1.76	+II
	O(5)	2.121(7)		
	N(3)	2.308(16)		
	O(6')	2.051(4)		
	O(5')	2.08(3)		
	N(3')	2.034(8)		

The four oxygen donors in the coordination sphere of Co(2) are arranged within the square plane of the resulting octahedron. As the Co(2) atom is located on an inversion centre, the resulting coordination environment is almost undistorted and almost ideal 180° and 90° angles are observed. Selected angles in 5.2 are summarised in Table 5.6.

Table 5.6: Selected bond angles (°) for compound 5.2.

Atoms	Angles(°)	Atoms	Angles(°)
O(4) – C(1) – O(3)	120.9(5)	O(1) – C(2) – O(3)	123.8(5)
O(4) – Co(1) – O(3)	60.50(14)	O(6) – Co(2) – O(6)	180.00(14)
O(2) – Co(1) – O(1)	113.10(16)	O(6) – Co(2) – O(5)	90.2(2)
N(4) – Co(1) – O(4)	87.15(9)	O(6) – Co(2) – N(3)	90.6(6)
N(4) – Co(1) – O(4)	91.83(3)		

Each CPEIP³⁻ ligand connects two dinuclear units and one mononuclear unit to form sheets that extend approximately 45° to the crystallographic *bc*-plane (Fig. XX). These sheets pack in a relatively dense fashion once the pyridine moieties that bind perpendicular to the sheets interdigitate exhibiting the same arrangement of compound 5.1 (Fig. 5.16). The observed interlayer distance for 5.2 is *ca.* 10.4 Å.

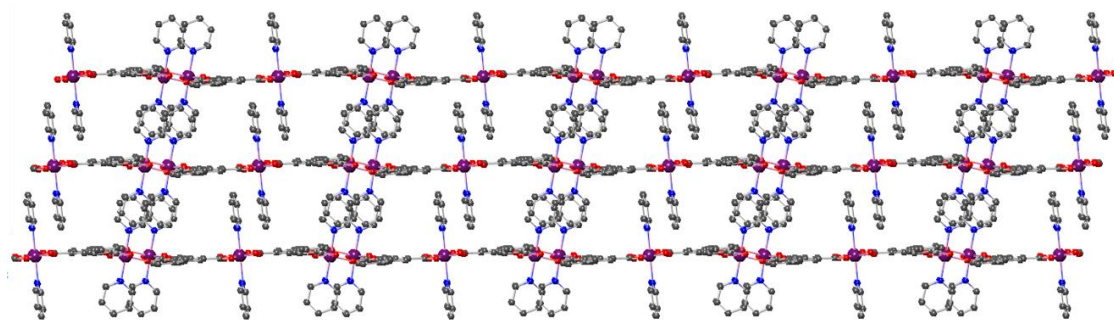


Figure 5.16: Packing arrangement for compound 5.2 viewed down the *a*-axis, sheets grown diagonally to the plane defined by *b*- and *c*-axis.

Despite this interdigitating arrangement, the packing results in two kinds of channels that extend in the direction of the *a*-axis. The crystallographically determined void volume is 720 Å³, which corresponds to *ca.* 36% of the unit cell volume (Fig. 5.17).

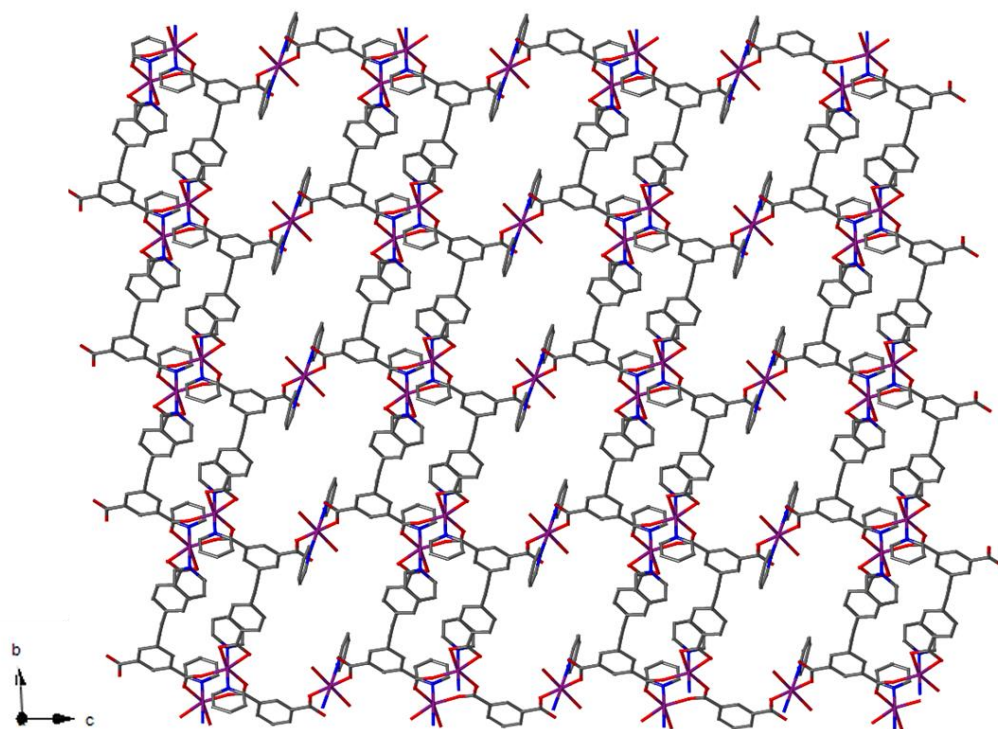


Figure 5.17: Packing arrangement for compound 5.2 view of the channels along the *a*-axis.

Topological analysis was also performed, highlighting that the polymer represents an unprecedented layered structure. The layer-net has a short vertex symbol: $(4.6^2) \cdot (4^2 \cdot 6^2 \cdot 8^2)$ as represented in Figure 5.18. Each layer presents two different types of nodes. The triangular ligands are represented as 3-connected nodes, and the dinuclear subunits acts as 4-connected node involving four ligand moieties. The structure exhibits two different types of channels with diameter openings of *ca.* 22.4 Å and 15.12 Å.

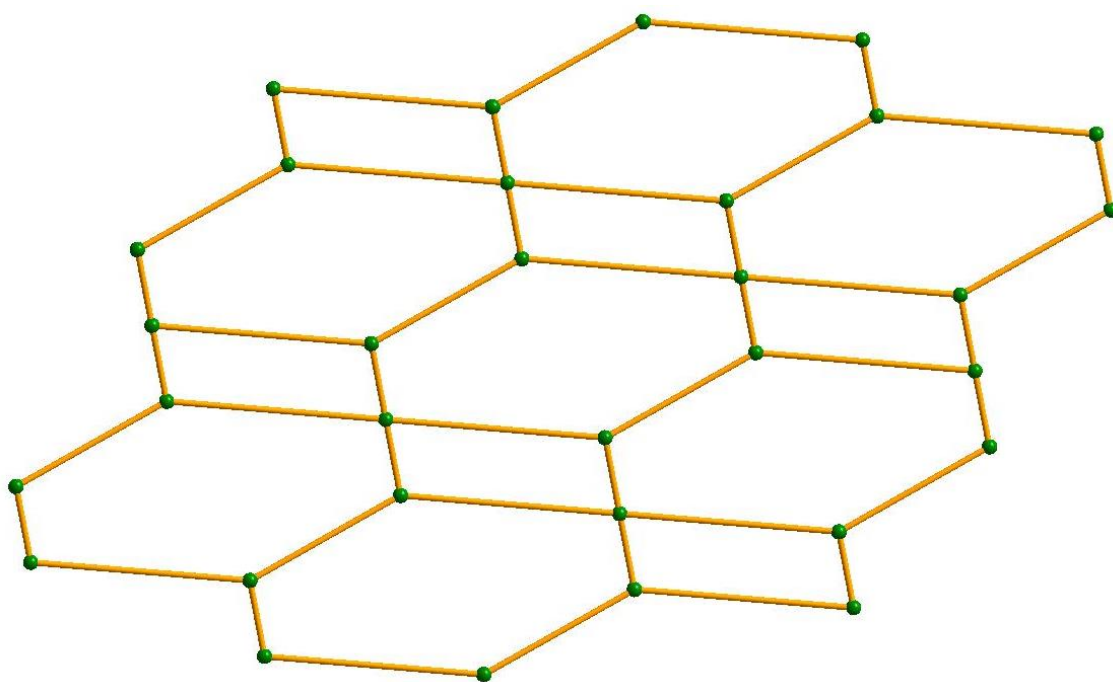


Figure 5.18: Topological representation of 5.2 with short vertex symbol: $(4.6^2) \cdot (4^2 6^2 8^2)$.

Table 5.7: Crystal data and structure refinement for 5.2.

Identification code	5.2
Empirical formula	C ₆₀ H ₆₂ Co ₃ N ₆ O ₁₇
Formula weight/ g mol ⁻¹	1400.05
Temperature/K	100
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> /Å	11.0214(11)
<i>b</i> /Å	11.4112(11)
<i>c</i> /Å	17.2429(17)
α /°	94.327(4)
β /°	102.228(4)
γ /°	93.945(4)
Volume/Å ³	2105.3(4)
<i>Z</i>	1
ρ_{calc} /cm ³	0.969
μ /mm ⁻¹	0.631
<i>F</i> (000)	628.0
Crystal size/mm ³	0.27 × 0.14 × 0.07
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	4.932 to 50.998
Index ranges	-13 ≤ <i>h</i> ≤ 13, -13 ≤ <i>k</i> ≤ 13, -20 ≤ <i>l</i> ≤ 20
Reflections collected	23768
Independent reflections	7731 [<i>R</i> _{int} = 0.0829, <i>R</i> _{sigma} = 0.1042]
Data/restraints/parameters	7731/13/341
Goodness-of-fit on <i>F</i> ²	1.053
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0810, <i>wR</i> ₂ = 0.2292
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1346, <i>wR</i> ₂ = 0.2601
Largest diff. peak/hole / e Å ⁻³	1.39/-0.62

5.4.2.1. Further characterisation of 5.2

The FTIR spectrum of compound **5.2** (Fig. 5.19) shows a weak band at *ca.* 3070 cm⁻¹ and a broad signal at 3400 cm⁻¹ that, correspondingly to **5.1**, can be assigned to C – H stretching from the aromatic ligand and N – H stretching in the pyridine ring.³⁹ The vibration for the asymmetric stretching vibrations of the carboxylate moiety displaying unidentate coordination mode can be assigned to a strong signal at 1621 cm⁻¹,⁴⁰ and the strong signal at 1439 cm⁻¹ can be assigned to stretching vibrations from pyridine ring.³⁴ The spectrum also shows band patterns that can be seen in the 1600-1300 cm⁻¹ ring stretching region and are characteristic of heterocyclic compounds such as pyridine.³⁹ The remaining signals between 1610 and 1350 cm⁻¹ and the symmetric and asymmetric stretches of the carboxylate moieties engaging in chelating and bridging binding modes could not be precisely assigned.

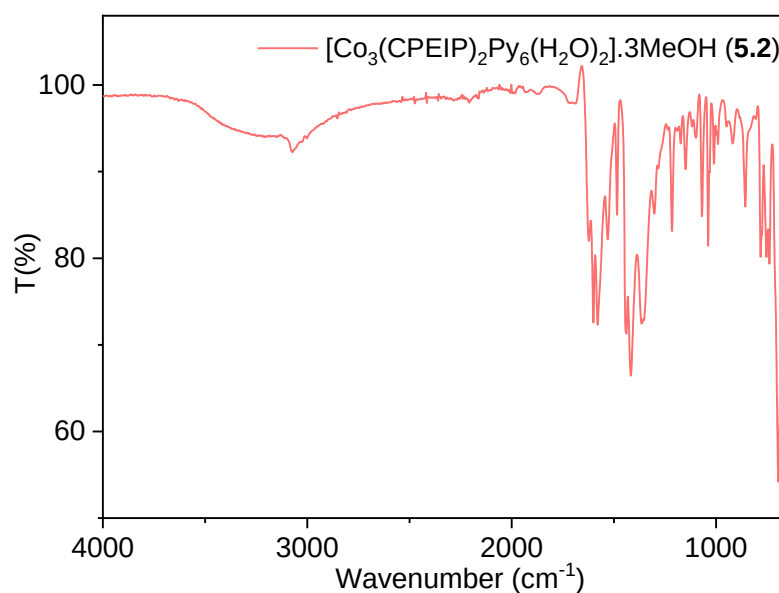


Figure 5.19: FTIR spectrum of 5.2.

The thermal stability of a freshly prepared crystalline sample of **5.2** was investigated in an air atmosphere, in the temperature range of 25 to 500 °C. TGA analysis (Fig. 5.20) reveals that **5.2** undergoes a decomposition pathway in two steps. The first thermogravimetric step correspond to *ca.* 40% mass loss, it is observed between 25-220 °C. This mass loss can be attributed to the loss of constitutional solvent guest molecules and coordinated H₂O and pyridine molecules. The oxidation of the organic ligand can be observed above 360 °C resulting, most likely, in the formation of metal oxide materials.

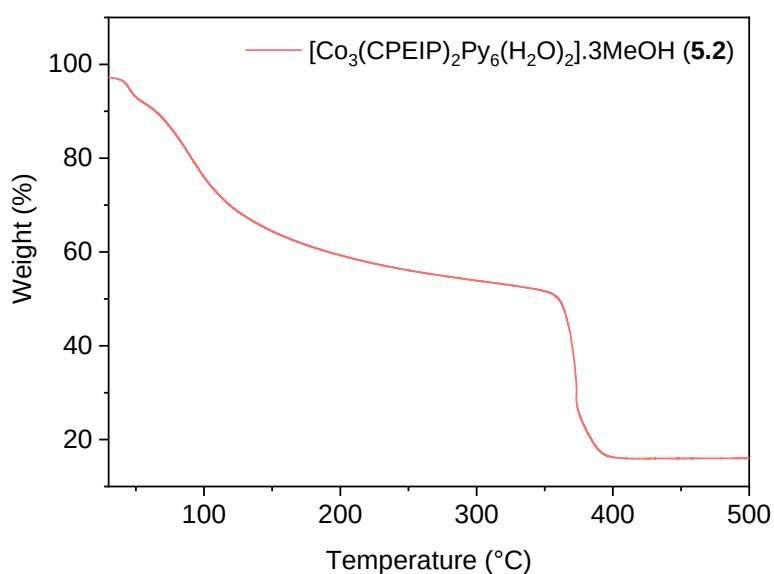


Figure 5.20: Thermogravimetric analysis of 5.2.

5.5. Conclusion

The aim of this chapter was to synthesize new metal-organic frameworks (MOFs) with labile coordination sites for structural and topological studies. To accomplish this, reticular chemistry principles were implemented using two carboxylate-based ligands: isophthalic acid (H₂IP) and an asymmetrically elongated, trifunctional polycarboxylate derivative (H₃CPEIP).

Two MOFs containing two crystallographically identical dinuclear Co^{II} SBUs were formed in the presence of IP and H₃CPEIP, namely compounds **5.1** and **5.2** respectively. Compound **5.2** contains additionally mononuclear Co^{II} SBUs that form in presence of the third carboxylate functionality. Both, **5.1** and **5.2** exhibit 2D layered architectures with pyridine moieties that coordinate perpendicular to the sheets to form interdigitated arrangements throughout the crystal structures. Compound **5.1** exhibits smaller triangular and larger hexagonal openings and a topology typically classified as a Kagomé lattice. Compound **5.2** presents a novel layered structure which is characterized by the vertex symbol (4.6²)·(4²·6²·8²). Despite the constitutional similarity of **5.1** and **5.2**, these two compounds present rather different topologies but similar packing arrangement of the 2D sheets.

5.6. References

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Chapter 6

Experimental

6. Experimental

6.1. Materials and Methods

Reagents: All chemicals and solvents were purchased from Sigma-Aldrich Chem. Co. Ltd., Alfa Aesar or Acros Organics and were used as received. Solvents were supplied by internal solvent suppliers and were used as received without further purification. Methanol and ethanol were of technical grade quality and acetonitrile, dichloromethane (DCM) and dimethylformamide (DMF) were of HPLC grade quality, except where otherwise noted. Water was deionised before use.

NMR Spectroscopy: ^1H and ^{13}C NMR, spectra were recorded on a Bruker DPX 400 spectrometer operating at 400 MHz by Dr. John O'Brien and Dr. Manuel Rüther. Samples were prepared by dissolving in suitable deuterated solvents. Standard abbreviations for spectra are used here: s, singlet; d, doublet; t, triplet; qt quartet; q, quaternary; m, multiplet; br, broad; J, coupling constant.

IR Spectroscopy: Infrared spectroscopy was recorded on a PerkinElmer Spectrum One FT-IR spectrometer using a universal attenuated total reflectance (ATR) sampling accessory. Data was collected and processed using Spectrum v5.0.1 (2002 PerkinElmer Instrument LLC) software. Samples were measured with a scan rate of 25 scans per minute with a resolution of 4 cm^{-1} in the range $4000\text{-}650\text{ cm}^{-1}$. The following listed symbols were used to describe the spectra: w weak; m medium; st strong; s shoulder; b broad.

Mass Spectrometry: Mass spectrometry was carried out on a Micromass LCT Electrospray mass spectrometer by Dr. Martin Feeney and Dr. Gary Hessman. Samples were diluted in HPLC grade solvents. MALDI spectra were acquired using a Waters Maldi Q-Tof Premier in negative mode using DCTB (trans-2-[3-4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile) as a MALDI matrix. MassLynx 4.1 software and mMass software were used to carry out the analysis. ESI mass spectra were acquired using a Micromass time of flight mass spectrometer (tof), interfaced to a Waters 2690 HPLC. Masses were recorded over the range 100-1000 m/z.

Thermogravimetric Analysis: Thermogravimetric analysis (TGA) was carried out using a Perkin Elmer Pyris-1 thermogravimetric analyser under air atmosphere. The instrument was previously calibrated using nickel and iron standards. Measurements were carried out in the range 25 -700 °C at a heating rate of 1 °C per minute in a ceramic crucible.

Elemental Analysis: Elemental Carbon, Hydrogen and Nitrogen (CHN) analysis was performed by Ronan Crowley using an Exeter Analytical CE 440 at the Analytical Laboratory, School of Chemistry and Chemical Biology, University College Dublin.

Powder XRD: Powder XRD measurements were carried out on a Bruker D2 Phaser using a low-background silicon sample holder. Data were gathered between $2\theta = 3^\circ$ and $2\theta = 35^\circ$.

Single-Crystal X-Ray Diffraction Analysis: Single crystal X-ray Diffraction data were collected by Dr. Brendan Twamley, Dr. Amal Cherian Kathalikkattil, Dr. Nian-Yong Zhu, Dr. Lauren Macreadie and Friedrich Steuber. All diffraction data were collected using a Bruker APEX-II Duo dual-source instrument using graphite-monochromated Mo K α ($\lambda = 0.71073 \text{ \AA}$) or microfocus Cu K α ($\lambda = 1.54178 \text{ \AA}$) radiation. Datasets were collected using ω and ϕ scans with the samples immersed in oil and maintained at a constant temperature of 100 K using a Cobra cryostream. The data were reduced and processed using the Bruker APEX suite of programs. Multi-scan absorption corrections were applied using SADABS. The diffraction data were solved using SHELXT and refined by full-matrix least squares procedures using SHELXL-2015 within the OLEX-2 GUI.

UV-visible and Photoluminescence Spectroscopy: Solution-state UV-vis absorption spectroscopy measurements were performed in DMF using matched quartz cuvettes with an optical path lengths of 1 cm. Absorption spectra were recorded on Lambda35 UV/vis spectrometer with a wavelength range of 250-800 nm and a scan rate of 600 nm min⁻¹. Baseline correction measurements were used for all spectra and all data was processed via OriginPro 9.1 SR0 (2015). The photoluminescence spectra were recorded with an excitation wavelength of 300 and 405 nm. The absorption spectra and photoluminescence spectra of the MOF samples were measured using a suspension of the MOF (3 mg) in DMF (3 mL) and were measured using a Cary 50 UV-vis spectrophotometer. Time-resolved photoluminescence (TRPL) measurements of the MOF and the metallo-ligands in DMF were performed using a PicoQuant Microtime 200 time-resolved confocal

microscope system using an excitation of 90 ps pulses at a wavelength of 405 nm with a repetition rate of 10 MHz and an integration time of 4 ms per pixel. The laser spot size was ~430 nm. The sample was excited through a 40x objective (NA = 0.65) and the photoluminescence was collected through the same objective. A 40 nm bandpass filter centre on 600 nm was used. Solid state measurements were performed by Dr Xia Zhang from the School of physics.

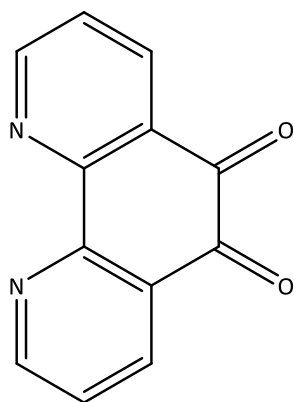
The Fluorescence Lifetime Imaging (FLIM): Scans on the solid-state samples were performed using the PicoQuant Microtime 200 under the same conditions that were applied for the photoluminescence decay measurements. Solid state samples of the MOF and the metallo-ligand were used for the measurements.

Solvothermal Synthesis: Solvothermal synthesis was carried out using Parr stainless steel reactor autoclave with 23 ml Teflon inserts or in 1.5 ml sealed vials, both placed in a UN30 Memmert chemical heating oven. The samples were subjected to a slow gradual cooling period (average 5 hours). Alternatively, syntheses were carried out in an aluminium heating block in 4.5 mL sealed vials, and the vials were cooled down over a period of 4 hours.

Gas Sorption Analyses: Gas adsorption isotherms were obtained from data collected by Dr Debobroto Sensharma and Dr Sebastien Vaesen. Measurements were performed on an activated sample and were recorded in the 0 - 1 bar pressure range using a volumetric method using a Quantachrome Autosorb iQ instrument. For this purpose 65 mg of a dried CH₃OH-exchanged samples were placed in a pre-dried and weighed glass cell. The sample was subjected to vacuum and activated at 200 °C under secondary vacuum for 12 hours to remove any constitutional solvent molecules. The cryo-temperature adsorption measurements were performed at 77 K using a liquid nitrogen bath. The accurate weight of the activated sample was measured prior to analysis. Gas adsorption measurements were performed using CP grade N₂ and CO₂ provided by BOC Ireland.

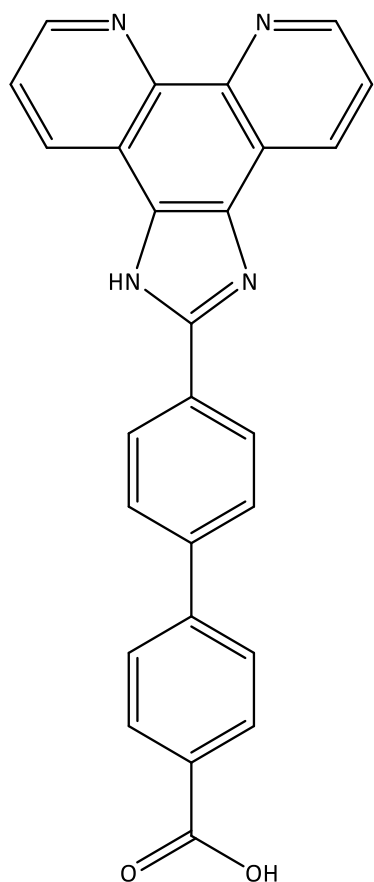
6.2. Synthetic Procedures

6.2.1. Synthesis of 1,10-Phenanthroline-5,6-dione



1,10-Phenanthroline-5,6-dione was synthesized using an adapted literature procedure.¹ 1,10-Phenanthroline (7.50 g, 41.62 mmol) and potassium bromide (36.65 g, 307.98 mmol) were placed in a 3-neck round bottom flask in an ice bath. Sulfuric acid (97 %, 150 mL, at 0 °C) and nitric acid (66%, 60 mL) were added to the flask sequentially through dropwise addition. The reaction was heated to 80 °C for 1.5 hours and to 100 °C for a further 3.5 hours. The solution was cooled to room temperature and poured onto ice, accompanied by a colour change from orange to green. The pH of the solution was raised to *ca.* 6 using an aqueous solution of sodium carbonate and the residual sodium salt precipitate was removed *via* filtration and washed with DCM until the precipitate was colourless. The aqueous layer was subsequently extracted with DCM, the organic layer was dried over MgSO₄, filtered and the solvent removed under reduced pressure. The resulting compound was recrystallised from hot methanol to yield needle-shaped yellow crystals. Yield of 1,10-phenanthroline-5,6-dione: 5.69 g (27.05 mmol, 65%). ¹H NMR (400 MHz, d₆-DMSO): δ (ppm) = 9.00 (2H, d, J_1 = 3.06), 8.40 (2H, d, J_1 = 7.39), 7.68 (2H, dd, J_1 = 7.82 Hz J_2 = 7.46 Hz); ¹³C NMR (400 MHz, d₆-DMSO): δ (ppm) = 177.8, 154.3, 152.3, 135.7, 129.1, 125.2.

6.2.2. Synthesis of 2-(4-Carboxyphenyl-biphenyl)imidazo[4,5-f]1,10-phenanthroline (HNCP₂)



1,10-Phenanthroline-5,6-dione (2.84 g , 13.52 mmol) was dissolved in acetic acid (100 mL) with 4'-formyl-[1,1'-biphenyl]-4-carboxylic acid (3 g, 13.26 mmol). The temperature of the mixture was increased to 100 °C and stirred for 30 min, to which an excess of ammonium acetate (approx. 25 eq.) was added while stirring at 120 °C for 2 hours. The reaction system was reduced to room temperature and water was added to precipitate out the crude product. The crude product was filtered and washed with water, acetone, and diethyl ether to yield the final product. Yield: 3.66 g (8.78 mmol 65 %). ¹H NMR (d₆-DMSO); δ (ppm) = 9.05 (2H, dd), 8.97 (2H, dd), 8.44 (2H, d), 8.07 (2H, d), 8.01 (2H, d) 7.90 (2H, d), 7.26 (2H, q); ¹³C NMR (d₆-DMSO); δ (ppm) = 127.21, 167.95, 150.26, 147.87, 143.63, 142.21, 140.11, 130.00, 129.81, 129.58, 127.44, 126.29, 126.48, 123.37; IR (ATR) $\tilde{\nu}/\text{cm}^{-1}$ 3460 (w) (ar CH st), 3050 (w) (O – H) 1710 (m) (C = O st),

1620 (m), 1320 (m), 1505 (s), 805 (m) cm^{-1} .

6.2.3. Synthesis of [Co(HNCP₂)(NCP₂)]Cl·2DMF (2.1)

HNCP₂ (15.0 mg, 0.023 mmol) was added to a solution of Co(NO₃)₂·6H₂O (17.2 mg, 0.046 mmol) in 4.5 mL of DMF/HCl (20:1) and gradually dissolved after heating to 120 °C for 48 hours in an aluminium heating block. The solution was cooled to room temperature over 4 hours. The product was isolated as orange needles. The resulting orange crystals were suitable for single crystal XRD analysis. Yield: 7.5 mg (0.0075 mmol, 65 %). Analysis calculated for C₅₅H₃₈ClCoN₉O₅ (%) C, 67.43; H, 3.37; N, 12.10; Found: C, 66.87; H, 3.69, N, 12.03. IR (ATR): $\tilde{\nu}$ = 1568 (m) (CO_{2asym}), 1362 (s) (CO_{2sym}), 1690 (s), 1716 (s) (C = O st), 1087 (m), 1014 (w) cm⁻¹.

6.2.4. Synthesis of [Co₃(HNCP₂)₂(OAc)₆]·DMF (2.2)

HNCP₂ (15.0 mg, 0.023 mmol) was added to a solution of Co(NO₃)₂·6H₂O (17.2 mg, 0.046 mmol) in 4.5 mL of DMF/CH₃COOH (3:1) and gradually dissolved after heating to 120 °C for 48 hours in an aluminium heating block. The solution was cooled to RT over 4 hours. The product was isolated as cubic brown crystals. The resulting orange crystals were suitable for single crystal XRD analysis. Yield: 10 mg (0.006 mmol, 57 %). Analysis calculated for C₇₀H₆₄Co₃N₁₀O₁₈ (%) C, 55.36; H, 3.70; N, 8.22; Found: C, 55.16; H, 3.88, N, 7.83. IR (ATR): $\tilde{\nu}$ = 1710 (m) (C = O st), 1580 (m) (CO_{2asym}), 1400 (s) (CO_{2sym}), 1240 (w), 1100 (w) cm⁻¹.

6.2.5. Synthesis of [Zn^{II}(NCP₂)Cl] (2.3)

HNCP₂ (3.0 mg, 0.004 mmol) was added to a solution of Zn(NO₃)₂·6H₂O (1.0 mg, 0.003 mmol) 1.0 mL of DMF/HCl (20:1, v/v) and gradually dissolved after heating to 120 °C for 48 hours. The solution was cooled to room temperature over 4 hours. The product was isolated as yellow, cubic crystals. The resulting crystalline material was suitable for single crystal XRD analysis. Yield: 1.03 mg (0.002 mmol, 73 %). Analysis calculated for C₂₆H₁₅ClN₄O₂Zn (%) C, 60.49; H, 2.93; N, 10.85; Found: C, 60.15; H, 3.43, N, 10.5. IR (ATR): $\tilde{\nu}$ = 1652 (s) (CO_{2asym}), 1500 (s) (CO_{2sym}), 1360 (s-broad) (CN), 1084 (w) cm⁻¹.

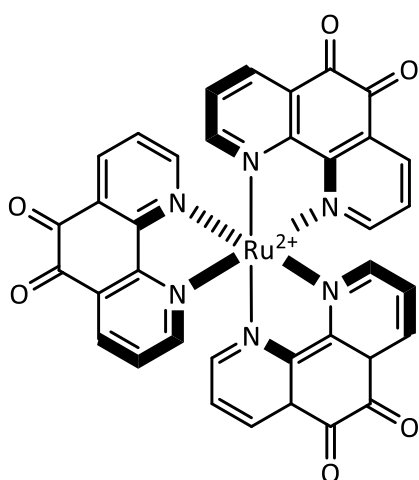
6.2.6. Synthesis of $[\text{Zn}^{\text{II}}(\text{HNCP}_2)(\text{NCP}_2)](\text{OH})$ (2.4)

HNCP_2 (3.0 mg, 0.004 mmol) was added to a solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.0 mg, 0.003 mmol) in 1.0 mL of $\text{DMF}/\text{H}_2\text{O}$ (1:1, v/v) and gradually dissolved after heating to 120 °C for 48 hours. The solution was cooled to room temperature over 4 hours. The product was isolated as yellow crystalline needles suitable for single crystal XRD analysis. Yield: 1.24 mg (0.0014 mmol, 68 %). Analysis calculated for $\text{C}_{52}\text{H}_{32}\text{N}_8\text{O}_5\text{Zn}$ (%) C, 68.31; H, 3.53; N, 12.26; Found: C, 68.50; H, 4.1, N, 12.17. IR (ATR): $\tilde{\nu} = 2600$ (s-broad) (OH), 1686 (s) ($\text{CO}_{2\text{asymm}}$), 1337 (m) ($\text{CO}_{2\text{symm}}$), 1724 (m) (C = O st), 1098 (w), 1020 (w) cm^{-1} .

6.2.7. Synthesis of $[\text{Cd}_2(\text{NCP}_2)\text{Cl}_3(\text{DMF})]$ (2.5)

HNCP_2 (15.0 mg, 0.023 mmol) was added to a solution of $\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$ (12.5 mg, 0.046 mmol) in 4.5 mL of DMF/HCl (10:1, v/v) and gradually dissolved after heating to 120 °C for 48 hours in an aluminium heating block. The solution was cooled to room temperature over 4 hours. The product was isolated as cubic yellow crystals suitable single crystal XRD analysis. Yield: 10.6 mg (0.013 mmol, 58 %). Analysis calculated for $\text{C}_{116}\text{H}_{84}\text{Cd}_8\text{Cl}_{12}\text{N}_{20}\text{O}_{12}$ (%) 42.55; H, 2.59; N, 12.99; Found: C, 41.89 H, 3.23, N, 12.2. IR (ATR): $\tilde{\nu} = 3400$ (w) (ar CH st) 1660 (m) ($\text{CO}_{2\text{asymm}}$), 1384 (s) ($\text{CO}_{2\text{symm}}$), 1574 (m) (CN), 1504 (w), 750 (s) cm^{-1} .

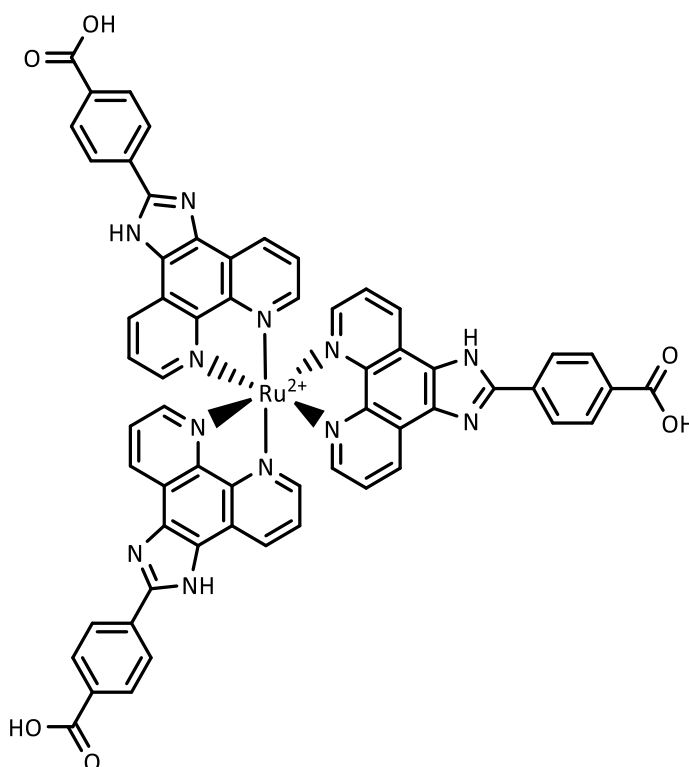
6.2.8. Synthesis of $[\text{Ru}(\text{phendione})_3]\text{Cl}_2$ (Phendione = 1,10-phenanthroline-5,6-dione)



The Ru^{II} complex of 1,10-Phenanthroline-5,6-dione, $[\text{Ru}(\text{phendione})_3]\text{Cl}_2$, was prepared according to a literature procedure.² For this purpose, $[\text{Ru}(\text{DMSO})_4\text{Cl}_2]$ (305 mg, 0.63 mmol) and 1,10-Phenanthroline-5,6-dione (453 mg, 2.16 mmol) were dissolved in 10 mL of $\text{H}_2\text{O}/\text{EtOH}$ (1:1, v/v). The reaction mixture was then refluxed for 6 hours after which the product was isolated by centrifugation. Residual solvent was removed through evaporation,

resulting in a dark compound, $[\text{Ru}(\text{phendione})_3]\text{Cl}_2$. Yield: 425.8 mg (0.520 mmol, 84%). ^1H NMR (400 MHz, CD_3CN): δ (ppm) = 7.73 (6H, dd, $J_1 = J_2 = 5.5$ Hz), 8.18 (6H, d, $J_1 = 8.0$ Hz), 8.61 (4H, d, $J_1 = 8.0$ Hz,).

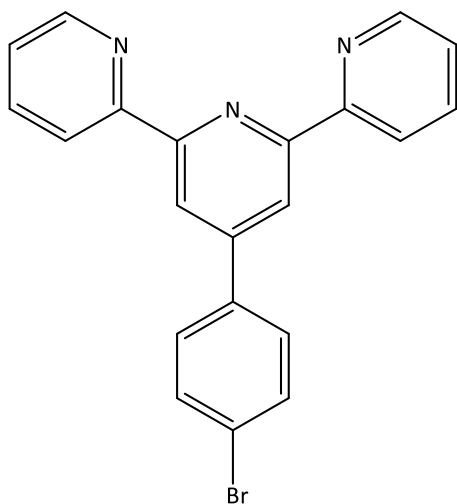
6.2.9. Synthesis of $[\text{Ru}(\text{HNCP})_3](\text{PF}_6)_2/[\text{H}_3\text{L}_2^{\text{Ru}}](\text{PF}_6)_2$



$[\text{H}_3\text{L}_1^{\text{Ru}}](\text{PF}_6)_2$ was prepared according to an adapted literature procedure.³ $[\text{Ru}(\text{phendione})_3]\text{Cl}_2$ (83 mg, 0.104 mmol), methyl 4-formylbenzoate (51.00 mg, 0.312 mmol) and NH_4OAc (160 mg, 2.08 mmol) were dissolved in 10 mL of glacial acetic acid. The reaction mixture was then heated at 80 °C for 8 hours under N_2 atmosphere followed by solvent evaporation. The resulting product was dissolved in methanol. The addition of saturated aqueous solution of ammonium hexafluorophosphate led to the precipitation of the product. The obtained compound was then deprotected *via* basic hydrolysis by dissolving it in ethanol (30 mL) and aqueous NaOH (2 M, 5 mL) and heating the reaction mixture at reflux for 3 hours. The volatiles were then removed by evaporation under reduced pressure. The residue was dissolved in 100 mL of water and acidified to *ca.* pH 3 using 2 M HCl until precipitation of the product which was followed by vacuum filtration. Yield: 78.55 mg (0.062 mmol, 60%). Analysis calculated for $\text{C}_{60}\text{H}_{36}\text{N}_{12}\text{O}_6\text{RuP}_2\text{F}_{12}$: C, 51.04; H, 2.57; N, 11.90 Found: C 51.75, H 3.00, N 10.72. IR(ATR): $\tilde{\nu}$ = 1698 (s) ($\text{CO}_{2\text{asym}}$), 1690 (s) ($\text{CO}_{2\text{sym}}$), 1574 (w), 1526 (w), 1514 (w), 1482 (w), 1451 (w), 1426(w), 1365 (m) (CN), 1316 (m), 1272 (m), 1244 (m), 1194 (w), 1117 (w), 1012 (w), 957 (w), 868 (w), 831 (w), 809 (s), 719 (s) (PF_6), 682 (m), 666 (s), 651 (w), 556 (w), 527 (w) cm^{-1} ; ^1H NMR (600 MHz, d_6 -DMSO): δ (ppm) = 14.98 (m, 3H), 9.31 (3H, m), 9.12 (6H, m), 8.53 (6H, d, $J_1 = 8.5$ Hz), 8.19 (6H, d, $J_1 = 6.8$ Hz), 8.08 (6H, m) 7.82 (6H, m). ^{13}C NMR (600 MHz, d_6 -DMSO): δ (ppm) = 167.9, 152.1, 151.0, 146.1, 133.7, 132.4, 131.2, 130.6, 130.0, 128.1, 127.2, 126.8.

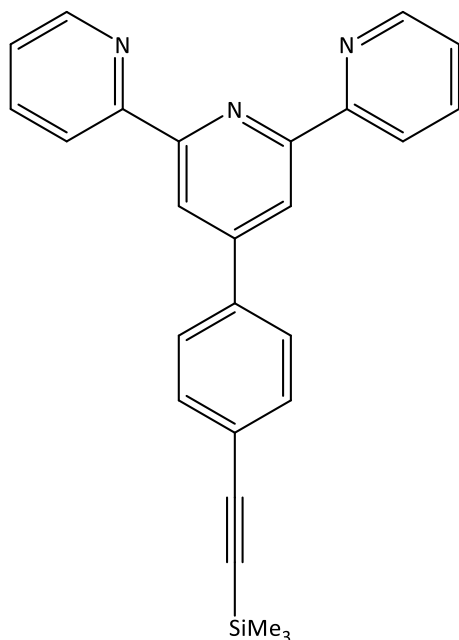
6.2.10. Synthesis of [Co(Ru(HNCP)₃)(CF₃CO₂⁻)]·5(HTFA)·12H₂O/Photo-MOF

Co(NO₃)₂·6H₂O (29.00 mg, 0.1 mmol) and [H₃L^{Ru}](PF₆)₂ (11 mg, 0.01 mmol) were added to a 2 mL vial with a silicon cap and dissolved in 1.5 mL of DMF/TFA (50:1, v/v) solution. The reaction mixture was sonicated at room temperature for 10 minutes, during which both reactants dissolved resulting in a deep, red solution. The vial was placed in a 20 mL Teflon-lined autoclave heated at 120 °C. Upon heating for 72 hours, orange needles were observed. Yield: 10.46 mg (0.005 mmol, 50 %). Analysis calculated for C₇₂CoF₁₈H₆₂N₁₂O₃₀Ru (as synthesized including 1 CF₃CO₂⁻, 5 CF₃CO₂H and 12 H₂O guest molecules) (%): C 41.63, H 3.01, N 8.09 Found: C 41.14, H 2.60, N 8.35. Yield: 10.46 mg (0.005 mmol, 50 %). ¹⁹F NMR: δ (ppm) = 72.3 ; IR(ATR): $\tilde{\nu}$ = 1599 (s-broad) (CO₂asymm), 1536 (s-broad) (CO₂symm), 1477 (w), 1453 (w), 1428 (w), 1365 (s-broad) (CN), 1316 (m), 1282 (w), 1248 (w), 1192 (m), 1144 (w), 1029 (w), 948 (w), 870 (w), 798 (s), 717 (s), 690 (m), 653 (w), 624 (w), 604 (w), 590 (w), 578 (w), 566 (w) cm⁻¹.

6.2.11. Synthesis of 4'-(4-Bromophenyl)-2,2':6',2''-terpyridine

4'-(4-Bromophenyl)-2,2':6',2''-terpyridine was synthesized according to a procedure reported in the literature.⁴ 4-Bromobenzaldehyde (3.70 g, 20.0 mmol) was dissolved in ethanol (100 mL). 2-Acetylpyridine (4.80 mL, 40.0 mmol) was then added. This was followed by the addition of potassium hydroxide pellets (85 %) (3.08 g, 40 mmol). Aqueous ammonia (35 %), (52 mL) was then added to the stirred solution. This reaction mixture was left to stir for 12 hours at RT. The

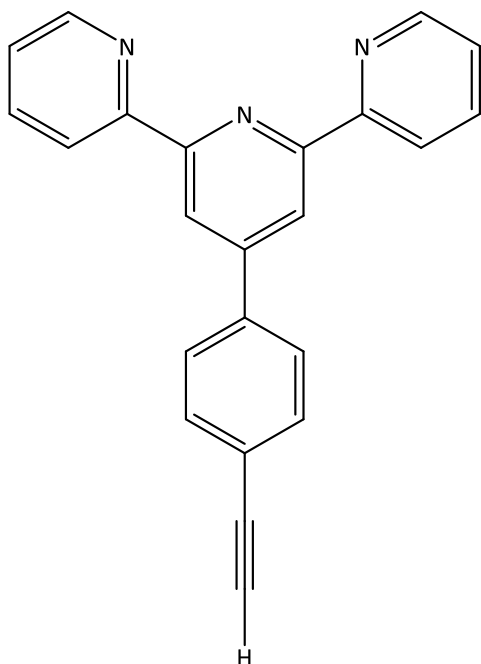
solution was filtered using a glass sintered funnel, and the solids were washed with ice cold ethanol. The precipitate was recrystallized from hot ethanol to give a white crystalline powder. Yield: 5.05 g (13.00 mmol 65 %). HRMS: 388.0453 ([M + H]⁺. C₂₁H₁₅N₃Br⁺ requires 388.0453). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.76 (2H, d, ³J_{HH} = 8 Hz), 8.74 (2H, s), 8.71 (2H, d, ³J_{HH} = 8 Hz), 7.9 (2H, td, ³J_{HH} = 8 Hz, ⁴J_{HH} = 2 Hz), 7.8 (2H, d, ³J_{HH} = 8 Hz), 7.67 (2H, d, ³J_{HH} = 8 Hz), 7.4 (2H, m).

6.2.12. Synthesis of 4'-((4-((Trimethylsilyl)ethynyl)phenyl)-2,2':6',2''-terpyridine.

4'-((4-((Trimethylsilyl)ethynyl)phenyl)-2,2':6',2''-terpyridine was synthesized according to reported procedure found in the literature.⁵ Trimethylsilylacetylene (2.27 mL, 16.0 mmol) was added to a stirred solution of 4'-(4-Bromophenyl)-2,2':6',2''-terpyridine (5.63 g, 14.5 mmol) in degassed THF (27.0 mL) with N₂ gas flow. It was then further purged three times alternating between vacuum and nitrogen for 20 minutes. Triethylamine (6.7 mL) was added and the solution again was degassed for 20 minutes. PdCl₂(PPh₃)₂ (0.30 g, 0.43 mmol) and CuI (165

mg, 0.87 mmol) were added. The solution was heated under reflux at 80 °C for 12 hours. It was left to cool to room temperature before filtering through a glass sintered crucible. The filtrate was then washed first with 30 mL of a saturated NH₄Cl solution and then with 30 mL of saturated brine solution. The organic fraction was extracted with DCM and dried with MgSO₄. Column chromatography was performed through silica column using DCM as eluting solvent. Fractions containing the product were combined and the solvent was evaporated off. A brown oil was obtained. It was further dissolved in MeOH (10 mL), which was then left in the freezer for 5 hours. A light brown precipitate was collected from the solution. This was filtered through a glass sintered crucible and dried overnight in an oven at 80 °C. The product was recrystallised from MeOH, resulting in a yellow crystalline product. Yield = 3.29 g (8.12 mmol 56 %). HRMS: 406.1738 ([M + H]⁺. C₂₆H₂₄N₃Si requires 406.1740). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.77 (4H, s), 8.72 (2H, d, ³J_{HH} = 8 Hz), 7.9 (4H, m, ³J_{HH} = 8 Hz), 7.6 (2H, d, ³J_{HH} = 8 Hz), 7.4 (2H, t, ³J_{HH} = 8 Hz), 0.3 (9H, s).

6.2.13. Synthesis of 4'-(4-Ethynylphenyl)-2,2':6',2''-terpyridine

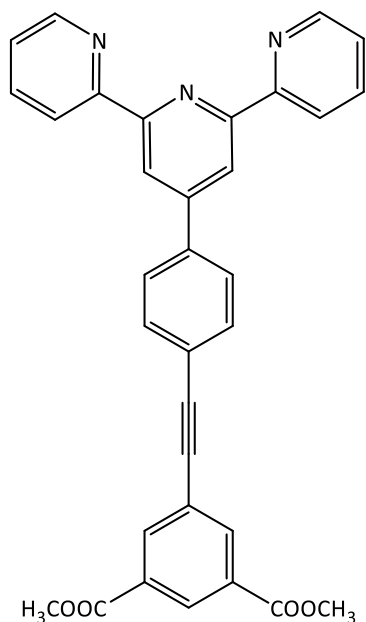


The deprotection was achieved by following literature procedure⁵:

4'-4-((Trimethylsilyl)ethynyl)phenyl)-2,2':6',2''-terpyridine (2.62 g, 6.5 mmol) was dissolved in a MeOH:THF (1:1, v/v) solution (20 mL). Excess of solid anhydrous K_2CO_3 was then added to the reaction mixture. The mixture was left to stir for 30 minutes and was filtered through a plug of silica eluting with DCM. The eluent was washed a saturated brine solution. $MgSO_4$ was used as drying agent and solvent removal was subsequently performed. Yield = 1.30 g (3.9

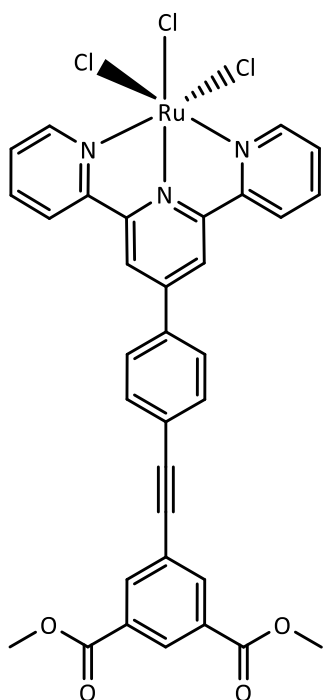
mmol 60 %). HRMS: 334.1339 ($[M + H]^+$, $C_{23}H_{16}N_3$ requires 334.1344). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.78 (4H, d), 8.72 (2H, d, $3J_{HH} = 8$ Hz), 7.9 (3H, m), 7.8 (1H, d, $3J_{HH} = 12$ Hz), 7.6 (2H, dd, $J = 8$ and 2 Hz).

6.2.14. Synthesis of Dimethyl 5-((4-([2,2':6',2''-terpyridin]-4'-yl)phenyl)ethynyl)isophthalate (Me₂TpyPEI)



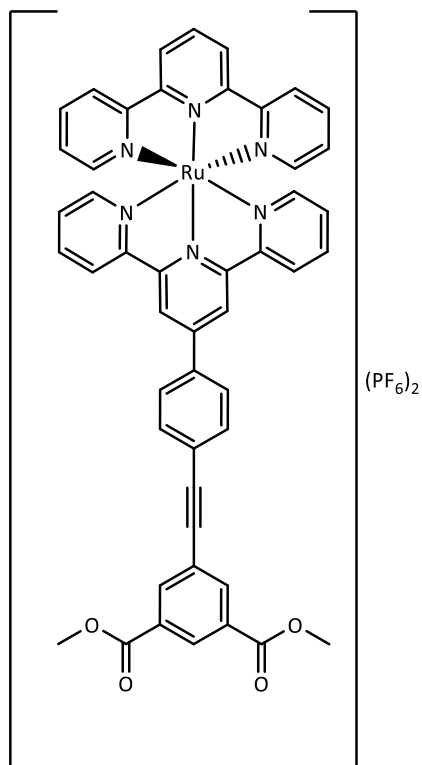
A modified procedure that was used for the synthesis of 4'-(4-Ethynylphenyl)-2,2':6',2''-terpyridine was followed, substituting the ethynyltrimethylsilane for dimethyl 5-iodoisophthalate (1.25 g, 4.00 mmol). After refluxing the reaction mixture for 12 hours, the solvent was removed under vacuum. Deionized H₂O (50 mL) was added to the flask and left to stir for 15 minutes. DCM (75 mL) was then added and again was left to stir for another 15 minutes. Extraction of the product was performed using THF, the organic layer extract was later filtered through a glass sintered funnel. The organic layer was washed with saturated solutions of ammonium chloride and brine. It was dried using MgSO₄ and solvent was removed. A light yellow solid was obtained and further recrystallized with MeOH. Yield: 1.26 g (2.40 mmol 60 %) HRMS: 526.1760 ([M + H]⁺. C₃₃H₂₄N₃O₄ requires 526.1767), ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.8 (2H, s), 8.78 (2H, d, *J* = 4 Hz), 8.73 (2H, d, ³*J*_{HH} = 8 Hz), 8.6 (1H, s), 8.4 (2H, s), 7.98 (2H, d, ³*J*_{HH} = 8 Hz), 7.93 (2H, t, ³*J*_{HH} = 8 Hz), 7.7 (2H, d, ³*J*_{HH} = 8 Hz), 7.4 (2H, t, ³*J*_{HH} = 8 Hz), 4 (6H, s). UV-vis λ_{max} /nm 307 (ε = 4.48 × 10⁴ M⁻¹ cm⁻¹).

6.2.15. Synthesis of [Ru(Me₂TpyPEI)Cl₃]



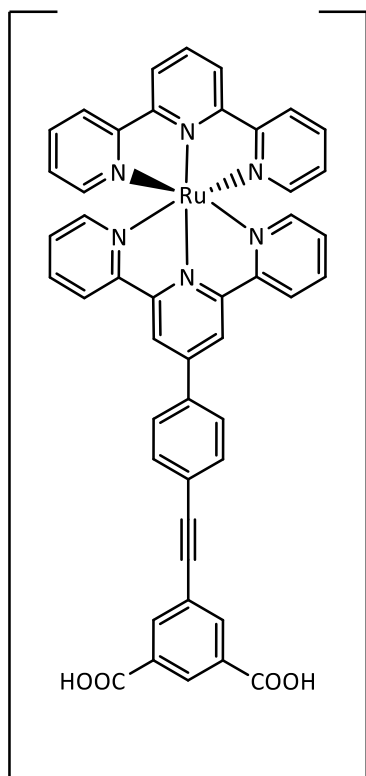
A reaction mixture containing Me₂TpyPEI (200 mg, 0.38 mmol), RuCl₃·3H₂O (100 mg, 0.38 mmol) and MeOH (40 mL) was heated under reflux, stirring for 12 hours. Following filtration, the precipitate was washed with water and secondly with diethyl ether. The drying process was carried out by leaving the obtained product in a chemical oven at 70 °C for one hour. 1.1.1. [Ru(Me₂TpyPEI)Cl₃] was obtained as a red dry solid. Yield: 156 mg (0.21 mmol, 56 %). FT-IR (ATR) $\bar{\nu}/\text{cm}^{-1}$ 3071 (w) (ar C-H st), 1722 (m) (C=O st), 1601 (m), 1466 (m), 1244 (s), 787 (s) (C-H). UV-vis $\lambda_{\text{max}}/\text{nm}$ 290 (ϵ $4.48 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), 327 (ϵ $0.85 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), 410 (ϵ $0.75 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), 569 (ϵ $0.65 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).

6.2.16. Synthesis of [Ru(Me₂TpyPEI)Tpy](PF₆)₂



[Ru(Me₂TpyPEI)Cl₃] (129 mg, 0.18 mmol) and terpyridine (41 mg, 0.18 mmol) were suspended in MeOH (20.0 mL). 20 drops of N-ethylmorpholine was added. The solution was heated under reflux for 12 hours. The solution was allowed to cool to room temperature before adding excess aqueous ammonium hexafluorophosphate, which resulted in the formation of a red precipitate. The red precipitate was filtered and washed with water twice and further washed with diethyl ether. Yield = 159 mg (0.14 mmol, 77 %). FT-IR (ATR) $\bar{\nu}/\text{cm}^{-1}$ 3027 (w) (ar C-H st), 1725 (s) (C = O st), 1601 (m), 1231 (s), 1004 (m), 820 (s), 725 (s) (C – H bending). UV-vis $\lambda_{\text{max}}/\text{nm}$ 291 (ϵ $4.48 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), 316 (ϵ $4.48 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), 497 (ϵ $2.15 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).

6.2.17. Synthesis of $[\text{Ru}(\text{H}_2\text{TpyPEI})\text{Tpy}](\text{PF}_6)_2/[\text{H}_2\text{L}_2^{\text{Ru}}](\text{PF}_6)_2$



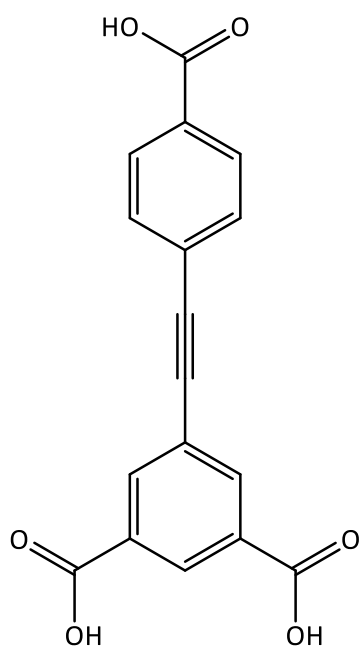
Aqueous NaOH (2 M, 5 mL) was added to a solution of $[\text{Ru}(\text{Me}_2\text{TpyPEI})\text{Tpy}](\text{PF}_6)_2$ (136 mg, 0.13 mmol) in acetonitrile (30 mL). This reaction mixture was heated at reflux overnight. HCl (2 M, 5 mL) was added after the solution had cooled down to room temperature.

Excess ammonium hexafluorophosphate was added to the reaction mixture causing precipitation of the desired product. The precipitate was collected by filtration and re-dissolved in approximately 10 mL of HPLC grade DCM. The resulting solution was filtrated and the solid residue was discarded. Addition of diethyl ether to the DCM solution caused the precipitation of a red solid, which was

isolated by a third filtration. Yield = 131 mg (0.12 mmol 90 %). Analysis calculated for $\text{C}_{46}\text{H}_{30}\text{F}_{12}\text{N}_6\text{O}_4\text{P}_2\text{Ru}$: C, 49.25; H, 2.70; N, 7.49 Found: C 51.53, H 3.1, N 8.1. ^1H NMR (600 MHz, CDCl_3): δ (ppm) = 9.50 (4H, s), 9.10 (4H, d, $J = 4$ Hz), 7.56 (4H, d, $^3J_{\text{HH}} = 8$ Hz), 8.72 (2H, s), 8.42 (4H, s), 7.40 (4H, d, $^3J_{\text{HH}} = 8$ Hz), 8.08 (4H, t, $^3J_{\text{HH}} = 8$ Hz), 8.00 (4H, d, $^3J_{\text{HH}} = 8$ Hz), 7.28 (4H, t, $^3J_{\text{HH}} = 8$ Hz). IR (ATR) $\bar{\nu}/\text{cm}^{-1}$ 3450 (w) (ar C – H st), 3073 (w) (O – H) 1722 (m) (C = O st), 1660 (m), 1310 (m), 1246 (s), 835 (w) cm^{-1} . UV-vis $\lambda_{\text{max}}/\text{nm}$ 290 ($\epsilon 5.52 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), 320 ($\epsilon 4.48 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), 497 ($\epsilon 2.15 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).

6.2.18. Synthesis of $[\text{Mn}_2\text{Cl}_2(\text{L}_2^{\text{Ru}})_2][\text{MnCl}_4]$ (4.2)

$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (5.00 mg, 0.03 mmol) and $[\text{H}_2\text{L}_2^{\text{Ru}}](\text{PF}_6)_2$ (11 mg, 0.01 mmol) were added to a 2 mL glass vial and dissolved in 1.0 mL of DMF/TFA (50:1, v/v) solution. The reaction mixture was sonicated at room temperature for 10 minutes, during which both reactants dissolved. The vial was placed in a 20 mL Teflon-lined autoclave and put in an oven and heated at 120 °C. Upon heating for 72 hours, red crystals were obtained and separated manually. Yield: 8.15 mg (0.004 mmol, 80 %). IR (ATR): $\tilde{\nu} = 3400$ (s-broad) ($\text{CO}_{2\text{asymm}}$), 1550 (s) ($\text{CO}_{2\text{symm}}$), 1350 (s), 1360 (s-broad), 1600 (s), 1402 (s-broad), cm^{-1} .

6.2.19. Synthesis of H₃CPEIP (5-((4-Carboxyphenyl) ethynyl) isophthalic acid)

H₃CPEIP was synthesized according to literature procedure.⁶ A flask purged with N₂ was charged with Ethyl-4-iodobenzoate (2.47 g, 8.95 mmol), Pd(PPh₃)₂Cl₂ (168.5 mg, 0.24 mmol) and CuI (77.4 mg, 0.41 mmol). Following the addition of reactants, a mixture of degassed tetrahydrofuran (40 mL) and triethylamine (40 mL) was added. After stirring for approximately 30 minutes, diethyl-5-ethynylbenzoate (2 g, 8.13 mmol) was added. The solution was stirred at room temperature for 12 hours. The resultant mixture was evaporated to dryness. Extraction was performed using DCM. The DCM solution containing the product was filtered and dried over MgSO₄.

After filtration the the solvent was removed by evaporation under reduced pressure. The resulting solid residue was recrystallized from ethyl acetate and lastly dried under vacuum at 40 °C for 8 hours. Yield = 1.59 g (4.7 mmol, 57.8 %). The product was further deprotected upon dissolution in 80 mL of a THF/H₂O mixture (1:1, v/v), and addition of KOH (4.14 g, 73.8 mmol). The mixture was the further heated under reflux for 12 hours. The solvent was removed by evaporation under reduced pressure. Following the residue was dissolved in 100 mL of water and further acidified to pH~2-3 using HCl (1M). The resulting solution was subsequently stirred for 3 hours at room temperature and cooled down in an ice bath. A white precipitate was recovered by filtration, washed with water, and dried under vacuum at 40 °C for 8 hours. Yield: 1.31 g (4.25 mmol, 90.5 %). NMR in agreement with the literature⁶: ¹H NMR (d₆-DMSO); δ (ppm) = 8.47 (1H, s, ArH), 8.30 (2H, s, ArH), 8.00 (2H, d, J=8 Hz, ArH), 7.77 (2H, d, J=8.5 Hz, ArH). ¹³C NMR (d₆-DMSO) δ (ppm) =: 167.1, 166.2, 136.2, 132.6, 132.5, 131.5, 130.6, 126.2, 123.4, 90.6, 90.3.⁶

6.2.20. Synthesis of [Co(IP)Py₂].2MeOH (5.1)

H₂IP (14.62 mg, 0.088 mmol) and Co(NO₃)₂.6H₂O (25.61 mg, 0.088 mmol) was dissolved in MeOH/pyridine (1.0 mL : 0.5 mL) and added to a 1.5 mL glass vial. The mixture was sonicated for 15 minutes and added to a 23 mL Teflon insert. The Teflon insert was placed inside a Parr stainless steel reactor autoclave and heated at 100 °C for 48 hours. Pink crystals were obtained. The crystals were separated manually and washed with MeOH. Yield: 4.14 mg (0.009 mmol, 10 %). Analysis calculated for C₂₁H₂₇CoN₂O₆ (%) C, 54.55; H, 5.89; N, 6.06; Found: C, 54.33; H, 6.05, N, 5.85. IR (ATR): $\tilde{\nu}$ = 3056 (w) (ar CH st), 3400 (s-broad) (OH), 1586 (m) (CO_{2asym}), $\tilde{\nu}$ = 1570 (m) (CO_{2asym}), 1480 (s) (CO_{2sym}), 1463 (s) (CO_{2sym}), 1441 (m) (CN st) cm⁻¹.

6.2.21. Synthesis of [Co₃(CPEIP)₂Py₆(H₂O)₂] (5.2)

H₃CPEIP (27.28 mg, 0.088 mmol) and Co(NO₃)₂.6H₂O (25.61 mg 0.088 mmol) were dissolved in MeOH/pyridine (1.0 mL: 0.5 mL) and added to a 1.5 mL glass vial. The mixture was sonicated for 15 minutes and add to a 23 mL Teflon insert. The Teflon insert was placed inside a Parr stainless steel reactor autoclave and heated at 100 °C for 48 hours. Pink crystals were obtained. The crystals were separated manually and washed with MeOH. Yield: 14 mg (0.010 mmol, 35 %). Analysis calculated for C₆₀H₆₂Co₃N₆O₁₇ (%) 54.76; H, 4.75; N, 6.39; Found: C, 54.12; H, 5.23, N, 6.02. IR (ATR): $\tilde{\nu}$ = 3070 (w) (ar CH st), 3400 (s-broad) (OH), 1621 (m) (CO_{2asym}), $\tilde{\nu}$ = 1610 (m) (CO_{2asym}), 1439 (s) (CO_{2sym}), 1350 (s) (CO_{2sym}), 1439 (s) cm⁻¹.

6.3. References

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7. Conclusions and outlook

This research project aimed to synthesise a range of MOFs whose functionalities may be exploited for light-driven chemical transformations and related applications. To address this aim, recently developed approaches in supramolecular chemistry was employed which allowed for the assembly of three types of organic ligands and Co-, Mn-, Zn- and Cd-based building units into MOFs and coordination polymers. Analysis of the topologies of the resulting coordination polymers and MOFs was also carried out.

In particular, the use of phenanthroline based ligands (HNCP₂) was explored, as this ligand provides harder carboxylate functionalities in addition to a softer set of N-donor atoms. Supramolecular synthesis using this ligand resulted in the structurally related coordination polymers **2.1** to **2.5**. The main recurrent structural features in these compounds were the presence of strong $\pi - \pi$ interactions and packing arrangements. These features resulted in parallel aligned chains formed by the organic ligands, which are rotated by 180° with respect to one another. Additionally, an important synthetic strategy was developed during the course of the synthesis. The approach focused on the use of solvent systems composed of DMF and an acid. The addition of acids improved the solubility of starting materials in the reaction mixture, favoured the formation of crystals suitable for X-ray diffraction and, most importantly, acted as modulators in the synthesis.

Using the synthetic and structural insights acquired during the research conducted with compounds **2.1** to **2.5**, we aimed to generate a stable MOF with the potential to be exploited for sustainable energy and ‘solar-fuel’-related applications. The novel crystalline material, **Photo-MOF** was designed to contain mesoporous cavities, display stability upon activation and contain functionalities that relate to the well-studied chromophore, [Ru(bpy)₃]²⁺. To the best of our knowledge, these attributes have not yet been reported for a single material. **Photo-MOF** displays crystallinity, permanent porosity and high CO₂ storage capacity. Regarding the light-harvesting properties, the photophysical properties of the free phenanthroline based metallo-ligand (**H₃L₁^{Ru}**) are maintained in the framework with absorption recorded in the visible range. The absorption and photoluminescence behaviour of both Photo-MOF and the free ligand, **H₃L₁^{Ru}** are comparable to the behaviour of [Ru(bpy)₃]²⁺. An average luminescence decay lifetime of *ca.* 20 ns was obtained for **Photo-MOF**. Photoluminescence lifetime is

reduced for the chromophore within the framework, indicating that coordination to Co^{II} ions gives rise to electron/energy transfer processes throughout the network structure.

Having established the conventional solvothermal synthetic method for the preparation of **Photo-MOF**, work began to explore alternative, improved ways to produce the material in bulk and with reduced time and costs, with the intention of approximating the synthesis of our material to industrial synthetic methods. An electrochemical synthetic method was used in which an electrolyte containing Co ions and $\text{H}_3\text{L}_1^{\text{Ru}}$ self-assembled as thin films that were consistently identified as **Photo-MOF**. Photophysical studies confirmed the properties of the films were nearly identical to the conventionally synthesised material, with the same decay lifetime observed for the chromophore upon coordination to the Co^{II} ions. Further examination of the thin films by imaging studies showed that, at specific voltages, crystal morphology is maintained throughout the films. Comparison of characterisation data strongly indicates the successful functionalisation of conductive surfaces through the electrochemical deposition of **Photo-MOF**. The electrochemical method allowed us to acquire additional information on the behaviour of the material. Cyclic voltammetry performed on the electrochemically synthesised films revealed quasi-reversibility of the redox pair $\text{Ru}^{3+}/\text{Ru}^{2+}$ within the framework of **Photo-MOF**.

In order to explore different synthetic pathways towards metallo-ligands and to obtain a diversity of Ru-polypyridine photosensitisers incorporated to our MOFs, a second type of strut was designed and synthesised. Differently from $\text{H}_3\text{L}_1^{\text{Ru}}$, the ditopic Ru^{II} metallo-ligand $\text{H}_2\text{L}_2^{\text{Ru}}$ comprises a $[\text{Ru}(\text{tpy})_2]^{2+}$ moiety and the optimised synthetic strategy involved the synthesis of an organic precursor. The precursor was extended through a coupling reaction and featured a tridentate coordination site. $\text{H}_2\text{L}_2^{\text{Ru}}$ absorbs in the visible, however further photoluminescence studies revealed that the MLCT excited state decays non-radiatively.

The metallo-ligand was successfully incorporated into a 2D Mn^{II} -MOF ($[\text{Mn}_2\text{Cl}_2(\text{L}_2^{\text{Ru}})_2][\text{MnCl}_4]$, **4.2**). Interestingly, structural integrity of the metallo-ligand $\text{H}_2\text{L}_2^{\text{Ru}}$ is maintained in the framework and results in an interdigitation arrangement with $\{[\text{Ru}(\text{tpy})_2]^{2+}\}$ moieties above and below the plane formed by the MOF sheets. Further, compound **4.2** contains a $\{\text{Mn}_2(\text{COO})_4\}$ paddlewheel, which has great potential as

catalytically active centre due to the presence of labile binding sites occupied by chloride ions.

Compounds **5.1** and **5.2** were synthesised with the objective of understanding the impact of using structurally related organic ligands in MOF synthesis. A reticular chemistry strategy was used, in which related symmetrical and asymmetrical organic ligands were subjected to the same reaction conditions (solvent system, reaction time and temperature, ratios) to yield two novel MOFs containing two crystallographically identical SBUs. Compound **5.2** was obtained using the extended asymmetric organic ligand. The tritopic ligand provided an additional coordination site resulting in a unique SBU containing two appended labile sites. The existence of the additional SBU results in an additional node and consequently different topologies. Compound **5.1** displays smaller triangular-shaped channels and larger hexagonal-shaped channels while **5.2** displays hexagonal and rectangular channels. Despite the differences in cluster nuclearity, number of labile sites and topologies, the two MOFs have very similar layered packing arrangements with interlayer distances of 10.54 Å and 10.4 Å for compounds **5.1** and **5.2** respectively.