SYNTHESIS OF METAL-ORGANIC FRAMEWORKS FROM STRUCTURE-
DIRECTING IPTYCENYL LIGANDS

by

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Abstract

Metal-organic frameworks (MOFs) are of great interest as hydrogen storage materials for use in vehicles. A series of triptycene-containing and pentiptycene-containing organic ligands was synthesized, characterized and used for MOF formation. A total of five unique triptycene-containing MOFs (TMOFs) and three pentiptycene-containing MOFs (PMOFs) were synthesized and examined using X-ray diffraction studies. Although the structure of each MOF was unique, structural adaptations to incorporate the rigid, bulky, structure-directing ligand into the framework were observed. For example, in some cases extended pseudo-[Zn₄O]⁶⁺ secondary building units (SBUs) were present in order to distort the framework to allow the ligand to coordinate. Reaction conditions also proved to be important in determining the dimensionality of MOF. It was shown that slight modifications of the reaction conditions using the same organic ligand could produce a 1-D, 2-D, and 3-D framework with different SBUs. The use of a ditopic bridging ligand, such as 4,4’-bipyridine, can also be used to increase the dimensionality of a structure. This protocol was used in converting 1-D chain structures and 2-D sheet structures into 2-D sheet structures and 3-D pillared structures, respectively. The overall functional groups in the ligand backbone can also have an adverse effect in the MOF structure. It was found that flexible linkages often led to collapse of the framework structure, whereas rigid linkages led to more robust structures. Extension along the carboxylate axis was also found to be important for iptycene incorporation. Unfortunately such extensions often led to close-packed or interpenetrated systems, which diminished porosity in the framework. Lastly, the long-range ordering of a MOF structure was predicted using modelling of powder X-ray diffraction (PXRD) peaks. When no single-crystal data were obtained, the PXRD
data could suggest whether a material had a hexagonal structure or cubic structure. In all cases thermal stability studies were carried out and it was found that these TMOF and PMOF materials were thermally stable up to 400 °C.

These iptycene-containing materials had been highlighted as potential hydrogen storage materials due to the potential for high aromatic surface areas and well-defined pore structure. As a result, nitrogen adsorption experiments were conducted on several of the robust frameworks to assess surface area. In each case, low surface areas were found.
Preface

In all chapters, Dr. Mark MacLachlan acted in a supervisory role. Many of the single crystal X-ray diffraction (SCXRD) experiments were initially solved by Dr. Brian O. Patrick, however I carried out most of the refinements, with help from Peter Frischmann and Nicholas White.

A portion of Chapter 1 has been previously published as: A. K. Crane, M. J. MacLachlan, “Portraits of Porosity: Porous Structures Based on Metal Salen Complexes.” Eur. J. Inorg. Chem., 2012, 1, 17-30. I was the principal author of this work and co-edited it with Dr. Mark MacLachlan.

A version of Chapter 2 has been previously published as: A. K. Crane, B. O. Patrick, M. J. MacLachlan, “New metal-organic frameworks from triptycene: structural diversity from bulky bridges.” Dalton Trans., 2013, 42, 8026-8033. I was the principal author of this work and co-edited it with Dr. Mark MacLachlan. I carried out all of synthesis experiments in Chapter 2, including growing all crystals. Some of the SCXRD structural refinements on TMOF-1 and TMOF-2a were performed by Peter Frischmann. Some of the SCXRD structural refinements TMOF-1, TMOF-2b and TMOF-2c were performed by Dr. Brian O. Patrick. I performed all other characterization experiments reported in Chapter 2, and wrote this chapter with input from Dr. MacLachlan.

A version of Chapter 3 has been previously published as: A. K. Crane, E. Y. L. Wong, M. J. MacLachlan, “Metal-organic frameworks from novel flexible triptycene- and pentiptycene-based ligands.” CrystEngComm., 2013, 15, 9811-9819. I was the principal author of this work and co-edited it with Dr. Mark MacLachlan. Elaine Y. L. Wong carried all synthesis experiments and most characterization experiments of dimethyl triptycene-1,4-benzyloxydicarboxylate, triptycene-1,4-benzyloxydicarboxylic acid, TMOF-3, TMOF-3-bipy, and TMOF-4, including growing all crystals. Additionally, Dr. Brian O. Patrick aided with the crystallographic data by solving each
structure, and providing guidance throughout the refinement process. I carried out all other synthesis and characterization experiments reported in Chapter 3, including growing crystals of pentiptycene-6,13-benzyloxydicarboxylic acid and PMOF-1 and wrote this chapter with input from Dr. MacLachlan.

A version of Chapter 4 will be submitted for publication after completion of this thesis as: A. K. Crane, N. White, M. J. MacLachlan, “Metal-organic frameworks from extended, conjugated triptcene- and pentiptycene-based ligands.” I will be the principal author of this work, and will co-edit it with Dr. Mark MacLachlan. I carried out all synthesis experiments of dimethyl triptcene-1,4-ethynylphenyldicarboxylate, triptcene-1,4-ethynylphenyldicarboxylic acid, TMOF-5, dimethyl pentiptycene-6,13-ethynylphenyldicarboxylate, pentiptycene-6,13-ethynylphenyldicarboxylic acid, PMOF-2a, PMOF-2b and PMOF-3, including growing all crystals. Additionally, Dr. Brian O. Patrick aided with the crystallographic data by running the PMOF-3 experiment, and solving each structure. All crystallographic refinements were carried out by Dr. Nicholas White. I carried out all other characterization experiments reported in Chapter 4 and wrote this chapter with input from Dr. MacLachlan.
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List of Symbols and Abbreviations

Å = Angstrom

BTU = British thermal unit

δ = chemical shift

Δ = heat

Mtoe = million tonnes of oil equivalent

Ppm = parts per million

psi = pounds per square inch

$T_g$ = glass transition temperature

$cm^{-1}$ = wave number

wt% = weight percent

AB = ammonia borane

BDC = benzene dicarbonxylate

BET = Brunauer-Emmett-Teller

bipy = bipyridine

BiPyTz = bis(4-pyridyl)-s-tetrazone

BP = British Petroleum

$n$-BuLi = $n$-butyllithium

CCDC = Cambridge Crystallographic Data Centre

CcH$_2$ = cryo-compressed hydrogen

cH$_2$ = compressed hydrogen
CPK = Corey-Pauling-Koltun

CPMAS = cross-polarization magic angle spinning (CPMAS)

CTAB = cetyltrimethylammonium bromide

DCM = dichloromethane

DEF = $N,N$-diethylformamide

DMF = $N,N$-dimethylformamide

DMSO = dimethylsulfoxide

EA = elemental analysis

EV = electric vehicle

FTIR = Fourier-transform infrared

GHG = greenhouse gas

H-K = Horvath-Kawazoe

HRMS = high resolution mass spectrometry

IMFV = internal molecular free volume

IR = infrared

IRMOF = isoreticular metal-organic framework

LCH$_2$ = liquid carrier hydrogen

LH$_2$ = liquid hydrogen

LOHC = liquid organic hydrogen carrier

MIL = materials from Institut Lavoisier

MOF = metal-organic framework

MOF-IP = metal-organic framework-iptycene phthalocyanine

MS = mass spectrometry
NMR = nuclear magnetic resonance
PET = poly(ethylene terephthalate)
PHEV = plug-in hybrid electric vehicles
PhCl = chlorobenzene
PIM = polymer of intrinsic microporosity
PM3 = parameterized model 3
PMOF = pentiptycene metal-organic framework
PPE= poly(phenylene vinylene)
PPV = poly(phenylene ethynylene)
PXRD = powder X-ray diffraction
PyPv = bis(4-pyridyl)dimethoxy-p-phenylenedivinylene
ref = reference
salphen = N,N-phenylene-bis-(salicylimine)
SBU = secondary building unit
SCXRD = single-crystal X-ray diffraction
SWNT = single-walled carbon nanotubes
TDC-MOF = triptycenedicarboxylate metal-organic framework
TGA = thermogravimetric analysis
THF = tetrahydrofuran
TMOF = triptycene metal-organic framework
UBC = University of British Columbia
US-DOC-NOAA = United States Department of Commerce National Oceanic and Atmospheric Administration
US-DOE = United States Department of Energy

US-EIA = United States Energy Information Administration

XRD = X-ray diffraction
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To all of my amazing sisters Guiding
Chapter 1: Introduction*

More than ever before the activities of modern society rely on the use of energy. In fact, global energy consumption has grown by 2.3% annually\(^1\) over the last decade (Figure 1.1(a)).\(^1\) Given that the current major source of energy is burning hydrocarbon fossil fuels, society will likely face a time when energy demand exceeds supply. Fossil fuels are known to be non-renewable energy sources that continue to fuel our energy needs. However, estimates show the depletion of oil and gas will occur within the next 40 years, and coal within 110 years at current consumption rates.\(^2\) In addition, a shifting away from fossil fuels has started to gain popularity due to the environmental impact of hydrocarbon combustion. As the world faces the challenges of accelerated global warming due to the presence of elevated levels of greenhouse gases (GHGs),

especially carbon dioxide (CO₂, Figure 1.1(b)),³ it is vitally important to look towards greener methods of energy production. Therefore, in order to sustain the global energy demand, other renewable sources of energy must be investigated.

Solar, wind and hydroelectric energy have been suggested as viable options for static energy supplies, such as residential and industrial electricity. However, the transportation sector still poses a challenge when considering alternative energy (Figure 1.2) due to the constraints of having a mobile system.⁴ Current efforts to replace oil and gasoline engines with cleaner natural gas and biodiesel have been mildly successful in certain applications, yet do not eliminate CO₂ as a by-product. Additionally, in the case of natural gas vehicles, current methane oxidation catalysts do not show overall high efficiency, resulting in unused methane escaping in the exhaust gas of the vehicle.⁵ This has further environmental impact, as methane is a far more potent greenhouse gas than CO₂.⁶

Figure 1.1 (a) Global primary energy consumption (b) Mean global CO₂ concentrations based on marine surface data. (a) Graph produced from BP data ref. 1. (b) Graph produced from US-DOC-NOAA data ref. 3.
Similarly, electric vehicles (EVs) have enjoyed growing popularity. EVs are powered by rechargeable batteries and have no exhaust emissions, but many models can only be driven approximately 100 miles per charging cycle. This is sufficient for inner city driving, which accounts for 90% of all US-household vehicle trips, but not for longer trips. As a result, plug-in hybrid electric vehicles (PHEVs) are more common to date. These vehicles are equipped with both an electric motor that is powered by a rechargeable battery, and an internal combustion engine fuelled by gasoline. Cooperation between both engines allows for longer trips to be made with an overall reduction of exhaust emissions. Regardless, gasoline is still required in PHEVs and all forms of EVs rely on charging the car from an electrical outlet. Therefore, the net environmental benefit of using EVs is reduced due to the fact that 68% of electricity in the US is currently generated through the consumption of hydrocarbons (Figure 1.3).
Figure 1.3 Sources of US electricity generation in 2013.
Graph produced from US-EIA data ref. 9: Table 1.1 and Table 1.1A.

Hydrogen fuel cell cars, while not currently commercially available, have been heralded by many to be the future of transportation powered by alternative energy.\textsuperscript{10} Hydrogen gas has a very high energy content, providing 146 MJ kg\textsuperscript{-1} compared to 46 MJ kg\textsuperscript{-1} for gasoline.\textsuperscript{11} Additionally, production and use of hydrogen gas can be viewed as being a renewable, cyclic process, where water can be split to give hydrogen and oxygen gas then consumed in the engine of a vehicle to reproduce the water with no additional by-products.
1.1 Obstacles Facing Hydrogen Gas as an Energy Currency

Many obstacles still remain before hydrogen gas can be used in high demand in the automotive industry. Unlike fossil fuels, if hydrogen gas is to be used in the energy sector it must first be produced through chemical means and stored until the time it will be used. This makes hydrogen gas an energy currency rather than a fuel.\textsuperscript{12} Current hydrogen production technologies involve steam reforming of hydrocarbons and electrolysis. Figure 1.4 shows that 48 out of 50 Mt of hydrogen gas produced annually comes from a hydrocarbon source.\textsuperscript{14} Once again, with fossil fuels at the backbone of world hydrogen gas production, net environmental benefit of hydrogen fuelled vehicles is minimized. Fortunately, research in the photocatalytic water-splitting electrolysis has gained momentum since the mid-1990s.\textsuperscript{13} In these systems, solar energy is used to facilitate the electrolysis of water to hydrogen and oxygen gas without the use of a hydrocarbon feedstock.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{hydrogen_production_consumption.png}
\caption{World hydrogen (a) production and (b) consumption; 2008 estimate. Graphs produced from Carbon Counts data ref.14.}
\end{figure}
Therefore it is evident that before hydrogen fuel cell vehicles become commercially viable further research must be done in order to optimize the production, transportation, and storage of hydrogen gas, in addition to its use in electrochemical fuel cells. This work addresses the storage of hydrogen gas only.

1.1.1 Storage of Hydrogen Gas

When considering issues involving hydrogen storage in a vehicle, many aspects must be taken into account. For example, there needs to be a net benefit from the added weight of the hydrogen storage tank versus the energy content of the hydrogen stored inside. To this end, the United States Department of Energy (US-DOE) has outlined hydrogen storage targets for use in the transportation sector. These targets include both volumetric and gravimetric components and current technologies including compression, absorption and adsorption have been plotted against these capacities in Figure 1.5. The current capacity goals for hydrogen storage tanks are 5.6 wt% and 40 g/L hydrogen content by 2015, with ultimate goals of 7.5 wt% and 70 g/L hydrogen content.\textsuperscript{15}
Figure 1.5 US-DOE hydrogen gas storage targets, including many materials currently being investigated as viable options. Reprinted with permission from ref. 15. Copyright © 2010 US Department of Energy.

The current standard for the storage of hydrogen gas is through compression methods to give compressed hydrogen (cH2), liquid hydrogen (LH2) and cryo-compressed hydrogen (CcH2). While these routes allow for some of the highest storage capacities, as seen in LH2 and CcH2, problems arise when considering the engineering involved in incorporating a large and specialized storage tank into a commercial vehicle. Pressurized hydrogen systems are also unfavourable due to public perception and issues of safety. In addition, an overall energy penalty occurs during the compression of hydrogen gas; up to 10-15% of the energy content is needed to achieve gas compression, while an energy deficit of 30% results from liquefaction. Therefore a shift to more
moderate pressure conditions is viewed as advantageous and has led to the development of several materials for this application.\textsuperscript{17}

1.1.1.1 Liquid Organic Carriers

Liquid organic hydrogen carriers (LOHCs; refer to LCH\textsubscript{2} in Figure 1.5) are organic liquids that directly absorb hydrogen gas through hydrogenation reactions.\textsuperscript{18} For such carriers to be effective, dehydrogenation (i.e. hydrogen release) must not be too endothermic otherwise release is not observed at moderate temperatures. Incorporation of heteroatoms and fused ring systems can aid with this thermodynamic requirement.\textsuperscript{19} Furthermore, these systems must work in conjunction with a catalyst in order to overcome the kinetic barrier associated with the hydrogenation/dehydrogenation process.

There are many examples of LOHCs,\textsuperscript{20} however heterocyclic aromatic hydrocarbons such as \textit{N}-ethylcarbazole (1)\textsuperscript{19(b),21} have shown the most promise. For example, perhydro-\textit{N}-ethylcarbazole (2) has a hydrogen storage capacity of 5.8 wt\% (Scheme 1.1). In this case, reversible hydrogenation/dehydrogenation can take place with the use of Ru/LiAlO\textsubscript{2} and Pd/LiAlO\textsubscript{2} catalysts, respectively, and show no degradation of the LOHC after 5 cycles.

\textbf{Scheme 1.1} Reversible hydrogenation/dehydrogenation of \textit{N}-ethylcarbazole (1) to perhydro- \textit{N}-ethylcarbazole (2)

\begin{center}
\includegraphics[width=\textwidth]{Scheme_1.png}
\end{center}
1.1.1.2 Metal and Chemical Hydrides

Metal hydrides and chemical hydrides\textsuperscript{22} rely on the reversible incorporation of hydrogen into a crystalline lattice, first by chemisorption onto the surface of the material, followed by diffusion into the crystal lattice (Figure 1.6).\textsuperscript{23} Metal hydrides have strong chemical interactions between hydrogen and the remaining metal ion lattice, therefore higher temperatures are required for hydrogen release from the material. Furthermore, metal hydrides are quite dense. This is both advantageous, as it allows for volumetric capacity targets to be met, and detrimental, as the increased weight of the overall system renders the materials non-competitive for gravimetric targets. While this can be addressed through the use of light metal hydrides, such as NaAlH\textsubscript{4} and AlH\textsubscript{3} (alane), it is evident from Figure 1.5 that gravimetric capacities remain a pertinent issue. Light-weight dopants, such as titanium, can be used to further decrease the mass of metal hydrides as well as increase activity.\textsuperscript{24} Additionally, complex metal hydrides, such as amide and borohydride compounds have shown increased gravimetric uptake (Figure 1.7).
Figure 1.6 (a) Mechanism of chemisorption. (b) Incorporation of hydrogen into hydrides through (i) surface chemisorption followed by (ii-iv) diffusion and absorption. Image (b) Reprinted with permission from ref. 23. Copyright (c) 2014 US Department of Energy.

One simple example is sodium borohydride (NaBH₄; Figure 1.7(a)). Upon reaction with water, NaBH₄ can release 4 equivalents of hydrogen. Commercial systems based on NaBH₄/H₂O slurries report a gravimetric capacity of 4 wt%. More complicated systems include lithium nitride (Li₃N; Figure 1.7 (b)), which can take up two equivalents of hydrogen gas to obtain lithium amide (LiNH₂) and lithium hydride (LiH) in a 1:2 ratio at 200-250 °C. This system has an overall gravimetric capacity of 9.3 wt%, and shows a 6.3 wt% release of hydrogen below 200 °C under
vacuum. Also, calcium borohydride (Ca(BH$_4$)$_2$; Figure 1.7 (c)) can release 9.0 wt% hydrogen at temperatures around 400 °C (9.6 wt% theoretical capacity). Regeneration of the Ca(BH$_4$)$_2$ can occur with the incorporation of a dopant catalyst (TiCl$_3$ or Pd) at 400-440 °C and 700 bar. Finally, using a magnesium borohydride amine system (Mg(BH$_4$)$_2$•2NH$_3$; Figure 1.7(d)) a maximum storage capacity of 16.0 wt% was found. Unfortunately, even after heating to over 400 °C only 13.1 wt% hydrogen was released.

(a) $\text{NaBH}_4 + 2 \text{H}_2\text{O} \rightleftharpoons \text{NaBO}_2 + 4 \text{H}_2$

(b) $\text{Li}_2\text{N} + 2 \text{H}_2 \rightleftharpoons \text{Li}_2\text{NH} + \text{LiH} + \text{H}_2 \rightleftharpoons \text{LiNH}_2 + 2 \text{LiH}$

(c) $3 \text{Ca(BH}_4)_2 \rightleftharpoons \text{CaB}_6 + 2 \text{CaH}_2 + 10 \text{H}_2$

(d) $\text{Mg(BH}_4)_2 \cdot 2\text{NH}_3 \rightleftharpoons \text{MgH}_2 + 2 \text{BN} + 6 \text{H}_2$

**Figure 1.7** Examples of metal complex metal hydride systems.

Shifting to even lower mass systems has seen the development of “chemical” hydrides, in which covalent bonds are cleaved between the heteroatom and hydrogen. While this deals with the issue of gravimetric capacity, it introduces even higher activation barriers for hydrogen release. Several non-metal systems have been highlighted in Figure 1.8, however none is as favourable as ammonia-borane (AB) and related systems (Figure 1.8(f)). These materials see a mixture of amine Lewis bases with borane Lewis acids that are stable, non-flammable, and non-explosive at ambient conditions. In the case of AB, a theoretical maximum of 19.1 wt% hydrogen can be liberated if all three equivalents of available hydrogen are evolved. This however would leave the resulting product as boron nitride, which is an unstable species. Therefore hydrogen loss is limited
to two equivalents, giving an overall 13.06 wt% capacity of hydrogen. The synthesis of many AB derivatives have been investigated for their high theoretical gravimetric capacities (ranging from 4.7-13.6 wt%, Figure 1.9). It is thought that these derivatives could be used in combination with AB to help enhance the system’s hydrogen capacity and stabilize the resultant products.\(^{30}\)

Figure 1.8 Potential chemical hydride systems.
<table>
<thead>
<tr>
<th>well-defined liquid systems</th>
<th>potential reversible systems</th>
<th>high capacity exothermic systems</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical Structure</strong></td>
<td><strong>Theor. ( \text{H}_2 ) capacity (wt%)</strong></td>
<td><strong>Chemical Structure</strong></td>
</tr>
<tr>
<td>3</td>
<td>5.6</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>4.7</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>4.7</td>
<td>9</td>
</tr>
<tr>
<td>6</td>
<td>4.7</td>
<td></td>
</tr>
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</tbody>
</table>

![Figure 1.9](image_url) Synthetic targets for AB derivatives (3-14) and their associated theoretical gravimetric hydrogen capacities.\textsuperscript{30(c)}

1.1.1.3 Sorbent Materials

While all methods previously reviewed require the formation and cleavage of hydrogen-atom bonds, sorption methods rely solely on van der Waals interactions between the surface of the material and diatomic hydrogen (Figure 1.10). These materials thus must have high surface areas.
in order to maximize hydrogen storage. Common sorption materials include carbon-based sorbents, zeolites, and metal-organic frameworks.\textsuperscript{31}

![Physisorption](image)

**Figure 1.10** Mechanism of surface physisorption.

Carbon-based sorbents can range from activated carbon systems, such as type AX-21 seen in Figure 1.5 to more well-defined systems such as carbon nanotubes. Single-walled carbon nanotubes (SWNTs) were first highlighted as hydrogen storage materials by Dillon et al. in 1997.\textsuperscript{32(a)} Here bundles of 7-14 SWNTs of 12 Å diameter were tested for hydrogen adsorption giving 5-10 wt% gravimetric capacity. This was a remarkable value as it far exceeded (by 2.5-5 times) the expected value for close-packed tube filling alone. This could be explained by the presence of hydrogen adsorption not only inside the SWNTs, but also adsorbed to the outer wall in between individual tubes in each bundle. Unfortunately, limited reproducibility hinders the wide-spread use of SWNTs as a hydrogen storage agent.\textsuperscript{33}

Like activated carbon, zeolites are known for their adsorbent properties and have also been examined for hydrogen storage. In general, however, zeolites are not competitive with other
hydrogen storage agents, providing volumetric capacities of less than 0.8 L/g.\textsuperscript{34} Furthermore, it was determined that most of the hydrogen adsorption within the material was occurring in the smaller sodalite cages of the structures, not the larger $\alpha$-cages.\textsuperscript{35} The poor performance of zeolites as hydrogen storage materials is likely due to their high mass density (much like metal hydrides) and poor interactions between the adsorbent hydrogen molecules and the zeolite walls.

Hybrid materials such as metal-organic frameworks seem to overcome some of these obstacles. Here, well defined porous materials are formed through the synthesis of organic linker molecules and binding metals or metal clusters. This allows for carbon sorbent-like surface interactions, as well as well-defined pore systems for hydrogen diffusion. In fact, \textit{MOF-177}, was the first material to rival CcH\textsubscript{2} in terms of hydrogen storage capacity (Figure 1.5).\textsuperscript{15,56}

\section*{1.2 Metal-Organic Frameworks}

Coordination polymers and networks formed by the coordination of multidentate ligands to metal ions or metal-containing nodes, known as secondary building units (SBUs), can afford 1-D, 2-D, or 3-D extended structures with interesting properties. Metal-organic frameworks (MOFs) can be defined as coordination polymers with an open framework containing potential voids.\textsuperscript{36} There has been a great deal of interest in the production of MOFs since the properties of each MOF material may be tuned by modifying the properties of the precursor components. A wide variety of applications have been proposed, including gas storage,\textsuperscript{37} chemical sensing,\textsuperscript{38} catalysis,\textsuperscript{39} biomedical imaging,\textsuperscript{40} and drug delivery.\textsuperscript{41} The use of a solvothermal synthetic route
has also led to highly reproducible materials where framework topology can be controlled with pore and channel sizes as variables.

This is achieved by linking ligands of various sizes to metal-containing SBUs. In general, metal choice and reaction conditions dictate which SBU is observed, and thus the overall topology of the network. Consequently, several SBUs have been observed in MOF synthesis; the $[\text{Zn}_4(\mu_4-O)]^{6+}$ (or $[\text{Zn}_4O]^{6+}$) SBU, however, has shown predominance in carboxylate-containing ligands and often produces isoreticular cubic MOFs that have the same overall topology with the overall composition $[\text{Zn}_4(\mu_4-O)(\text{O}_2\text{CR})_6]$ (Figure 1.11). As a result, properties such as pore size, surface area, and rigidity can be tuned for particular applications with some predictability.

![Zn4O(CO2)6](image)

**Figure 1.11** $[\text{Zn}_4(\mu_4-O)(\text{O}_2\text{CR})_6]^{6+}$ SBU that gives an overall cubic topology in MOFs. Reprinted with permission from ref. 81. Copyright © 2010 AAAS.

### 1.2.1 Rigid Isoreticular MOFs

One of the simplest ligands used in the construction of MOFs is 1,4-benzenedicarboxylate (BDC). Yaghi and co-workers reacted H$_2$-BDC (15) with Zn(NO$_3$)$_2$ under various conditions to achieve 2-D and 3-D network solids (Scheme 1.2). Using a mild vapor-diffusion method of
triethylamine/toluene into a DMF/toluene solution of the precursors yields **MOF-2** (16), a 2-D square paddlewheel grid structure with a capped dinuclear zinc SBU.\(^{45}\) However, harsher solvothermal conditions can be applied to the same precursors in DMF to give **MOF-5** (17), a 3-D framework with a simple cubic topology where \([\text{Zn}_4\text{O}]^{6+}\) clusters are bridged by BDC.\(^{46}\) The porosity and structure of **MOF-5** is remarkable and it has been studied extensively due to its ease of production, high surface area, and well-defined pore structure.\(^{47}\)

Adding functional groups to the \(\text{H}_2\)-BDC scaffold proved not to affect the overall topology of the **MOF-5** framework. Consequently, Yaghi and co-workers constructed a cubic isoreticular MOF series (IRMOFs, Figure 1.12) showing that implementation of a \([\text{Zn}_4\text{O}]^{6+}\) cluster with analogous BDC ligands always resulted in a cubic lattice. Additional functional groups had little effect on the observed porosity of the material (as measured by Langmuir surface area, Table 1.1). This is just one of many examples of such IRMOF series that have been reported in the literature.\(^{43}\)

---

**Scheme 1.2 Synthesis of MOF-2 (16) and MOF-5 (17).** Portions of this image are reprinted with permission from ref. 44. Copyright © 2003 Nature Publishing Group.
Figure 1.12  Isoreticular MOF (17-28) series derived from $\text{H}_2$-BDC (15) and analogues (29-39) and $[\text{Zn}_4\text{O}]^{6+}$ to give porous materials of cubic topology. Portions of this image are reprinted with permission from ref. 43(a). Copyright © 2002 AAAS.
Table 1.1 Comparison of accessible surface area through IRMOF series.

<table>
<thead>
<tr>
<th>IRMOF (compound)</th>
<th>SAAccessible (m² g⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (17)</td>
<td>3558</td>
<td>48</td>
</tr>
<tr>
<td>2 (18)</td>
<td>2461&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>3 (19)</td>
<td>2850&lt;sup&gt;b&lt;/sup&gt;</td>
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</tr>
<tr>
<td>6 (22)</td>
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<td>1750&lt;sup&gt;c&lt;/sup&gt;</td>
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</tr>
<tr>
<td>16 (28)</td>
<td>6038</td>
<td>51</td>
</tr>
</tbody>
</table>

<sup>a</sup>SABET.<br>
<sup>b</sup>Surface area after drying with supercritical CO₂.<br>
<sup>c</sup>SA<sub>Langmuir</sub>.

### 1.2.2 Flexible Isoreticular MOFs

Moving away from zinc based systems, Férey <i>et al.</i> have been using H<sub>2</sub>-BDC (15) in conjunction with aluminum and chromium salts in order to create isostructural compounds known as MIL-53 (40; Scheme 1.3).<sup>52</sup> These frameworks have a hydroxide-bridged chain of chromium(III) centres coordinated to the BDC ligand in a zig-zag fashion. These contacts expand and contract upon the introduction of guest molecules such as H<sub>2</sub>-BDC, water, and DMF (Figure 1.13). As a result, these MOFs are often referred to as “breathable MOFs,” as they have the ability to undergo structural changes without framework degradation in the solid state.

Breathable MOFs can also be constructed with a flexible component built into the ligand. One example is the complexation of 41 with zinc nitrate hexahydrate, using 4,4ʹ-bipyridine (42) as organic pillars between complexes (43, Scheme 1.4).<sup>53</sup> In this case, the 3-D nature of the MOF comes from the tetrahedral nature of the ligand (Figure 1.14). Furthermore, the pore sizes allow
for selective separation of CO₂ from a mixture of gases including H₂ and N₂. The CO₂ adsorption/desorption curves for this framework show a molecular gateway opening pressure. This means that at a particular pressure, a solid-state structural expansion occurs to allow more adsorbent to enter the system (as well as a contraction as adsorbent leaves the system). Also, powder X-ray diffraction (PXRD) patterns suggest expansion and contraction of the framework without collapse. Other reports of flexible MOFs and related structures have been investigated.⁵⁴

![Scheme 1.3 Synthesis of MIL-53 (40).](image)

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![Figure 1.13 Evidence of structural changes in the solid state upon guest inclusion/exclusion for MIL-53 (40).](image)

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Scheme 1.4 Synthesis of MOF 43 from tetrahedral flexible ligand 41.

Figure 1.14 MOF, 43, containing flexible ligand 41 with overall 3-D solid-state structure. Each sheet pictured here is also pillared by 4,4′-bipyridine (42), which has been omitted for clarity.
1.2.3 Application of MOFs for Hydrogen Gas Storage

One of the most promising applications of MOFs is storage of small molecules such as hydrogen (H$_2$) and methane (CH$_4$). This is primarily due to the extraordinary surface areas of MOFs (Table 1.2). For example, MOF-5, one of the simplest MOFs, has a Langmuir surface area of 4400 m$^2$ g$^{-1}$ and H$_2$ uptake of 53 mg g$^{-1}$ at 77 K.$^{55}$ By changing from a traditional ditopic ligand like H$_2$-BDC to the tritopic ligand 44 (Scheme 1.5(a)), a more complex topology can be achieved in MOF-177 (45, Figure 1.15(b)).$^{56}$ This results in a larger Langmuir surface area of 7300 m$^2$ g$^{-1}$ and H$_2$ uptake of 73 mg g$^{-1}$.$^{57}$ MOF-210 (48, Scheme 1.5(b) and Figure 1.15(c)) is synthesized by using a mixed ligand system of ditopic ligand 47 and tritopic ligand 46. This MOF has a Langmuir surface area of 10400 m$^2$ g$^{-1}$ and H$_2$ uptake of 86 mg g$^{-1}$, one of the largest ever reported. Recent successes in the development of MOFs have illustrated the tremendous diversity and capacity for tuning the surface area and porosity of these materials.$^{58}$ Moreover, the importance of rigid ligands with high electron density achieved through addition of aromatic rings and conjugation has been further displayed in these examples.

<table>
<thead>
<tr>
<th>MOF</th>
<th>$S_{\text{Langmuir}}$ (m$^2$ g$^{-1}$)</th>
<th>$S_{\text{BET}}$ (m$^2$ g$^{-1}$)</th>
<th>Pore Volume (cm$^3$ g$^{-1}$)</th>
<th>Void Volume (%)</th>
<th>H$_2$ Uptake (mg g$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOF-5 (17)</td>
<td>4400</td>
<td>3800</td>
<td>1.55</td>
<td>79</td>
<td>71 (52)$^{57}$</td>
<td>80</td>
</tr>
<tr>
<td>MOF-177 (45)</td>
<td>7300</td>
<td>4500</td>
<td>1.89</td>
<td>83</td>
<td>73</td>
<td>56, 57</td>
</tr>
<tr>
<td>MOF-210 (48)</td>
<td>10400</td>
<td>6240</td>
<td>3.60</td>
<td>89</td>
<td>86</td>
<td>81, 43(b)</td>
</tr>
</tbody>
</table>
Scheme 1.5 Synthesis of highly porous MOFs. (a) MOF 177 (45) (b) MOF-210 (48).

Figure 1.15 Comparison of solid state structures of highly porous MOFs. (a) MOF-5 (17) (b) MOF-177 (45) (c) MOF-210 (48).
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(b-c) Reprinted with permission from ref. 81. Copyright © 2010 AAAS.
1.3 Iptycenes

The iptycene family of molecules is characterized by the presence of aromatic rings held rigidly about a bicyclo[2.2.2]octatriene bridgehead system.\textsuperscript{59} This is seen quite clearly in the smallest member of the iptycene family, triptycene 49. First reported in 1942,\textsuperscript{60} triptycene consists of three benzene rings fixed 120° to one another, resembling the shape of a propeller. Larger iptycene compounds such as pentiptycenes (50-51), heptiptycenes (52-54), noniptycenes (55-57), nonadecaipntyocene (58) and supertriptycene (59) can be obtained through the addition of further bridgehead scaffolds and arene planes in a dendritic fashion (Figure 1.16). Larger polycyclic arene groups such as naphthalene, anthracene or pyrene can also be appended to the bridgehead scaffold in place of benzene to achieve a greater size (53).

1.3.1 Synthesis of Iptycene Molecules

1.3.1.1 Synthesis of Triptycene

Original synthetic routes to triptycene involved the Diels-Alder reaction of para-benzoquinone with anthracene followed by a multi-step chemical modification procedure to yield triptycene in very low yield (Scheme 1.6). By the mid-1950s Wittig and Ludwig\textsuperscript{61} were using reactive benzyne intermediates in the Diels-Alder reaction with anthracene to develop a one-pot synthesis for the compound. Through the screening of various benzyne intermediates it was found...
Figure 1.16 Examples of iptycene molecules (49-59).
that the decomposition of benzenediazonium-2-carboxylate would facilitate the Diels Alder addition to anthracene with the highest yield (30%). Soon after, it was reported that anthranilic acid derivatives could lead to the desired diazonium carboxylate, and hence the benzyne intermediate in situ, giving yields of 70-80% as long as one of the precursors was in excess (Scheme 1.7).

Scheme 1.6 First reported synthesis of triptycene (49) from anthracene (60) and p-benzoquinone (61).

Scheme 1.7 Synthesis of triptycene (49) from anthracene (60) and the in situ formation of a benzyne from anthranilic acid (68).
1.3.1.2 Synthesis of Pentiptycene

Similar to triptycene, the synthesis of pentiptycene also proceeds via a benzyne intermediate reacting with anthracene. The first successful synthesis of pentiptycene was reported in 1974 by Skarche and Shalaev, where 2-aminotriptycene (70) was used to ultimately form a benzyne for reaction with anthracene in a three step process (Scheme 1.8). This procedure, however, suffered from low yields of both the amino-triptycene preparation and the subsequent steps, providing an overall yield of 10%. A one-pot synthesis followed shortly after in 1981 when Hart and co-workers reported that pentiptycene could be produced in 94% yield by treating a mixture of excess anthracene and 1,2,4,5-tetrabromobenzene in toluene with a hexanes solution of n-butyllithium (n-BuLi) at room temperature (Scheme 1.9). Here, sequential dehalogenation to form benzyne species allows for two-fold Diels-Alder addition of anthracene to the benzene ring giving the para-pentiptycene, which henceforth will be referred to simply as pentiptycene.

Scheme 1.8 Synthesis of para-pentiptycene (50; pentiptycene) from 2-aminotriptycene (70).

Scheme 1.9 Synthesis of pentiptycene (50) from reaction of anthracene (60) with the diaryne formed from 1,2,4,5-tetrabromobenzene (73) and n-BuLi.
1.3.1.3 Synthesis of Larger Iptycenes

Reports of larger iptycene compounds are far fewer in number than those for the smaller triptycene and pentiptycene. Symmetric heptiptycene 52 was synthesized by Huebner et al. in 20% yield by treating compound 74 with \( n \)-BuLi (Scheme 1.10). \(^{67}\) Other asymmetric extended heptiptycene analogues have been produced through the use of polyaromatic arene bridges such as compound 53 in Figure 1.16. \(^{68}\) This method proved to be quite useful as it led Hart and co-workers to the synthesis of the first noniptycene compound. \(^{69}\) This symmetric noniptycene (also referred to as tritriptycene) was achieved through a step-wise Diels-Alder approach whereby the arene planes were added sequentially until a total of nine were installed (Scheme 1.11). The late 1990s saw a renewed interest in large iptycene molecules, particularly iptycene quinones. Reports from Zhu and Chen showcase a variety of heptiptycene quinones as well as two noniptycene quinones exhibiting both a U-shaped and zig-zag spatial arrangement. \(^{70}\)

![Scheme 1.10 Synthesis of heptiptycene (52).](image-url)
Scheme 1.11 Synthesis of dendritic noniptycene (55).

Other dendritic iptycenes have also been reported. For example, nonadeca-iptycene, a $D_{3h}$-symmetric molecule, was produced in 2% yield from the reaction depicted in Scheme 1.12. This iptycene, which effectively adds six triptycene moieties to a heptiptycene scaffold results in the formation of two cavities located on both the top and bottom of the central benzene ring.

Scheme 1.12 Synthesis of dendritic nonadeca-iptycene (58) and a side view of a 3-D model of 58 showing the cavity on top and bottom of the structure. Portions of this image are reprinted with permission from ref. 71. Copyright © 1990 American Chemical Society.
Pentadecaipytene, or supertriptycene, has also been reported by Hart and co-workers.\textsuperscript{72} Also a $D_{3h}$ symmetric iptycene molecule, supertriptycene (59) has a triptycene core decorated with three ortho-pentiptycene units after a multi-step synthesis (Scheme 1.13). Although X-ray diffraction quality crystals of 59 were obtained, the structure remains unsolved due to the presence of solvent in the large areas of void space inherent to the structure of the molecule.

\textbf{Scheme 1.13} Synthesis of supertriptycene (59)
1.3.2 Materials Applications of Iptycene-Containing Molecules

Owing to their rigid design, iptycene molecules possess an internal molecular free volume (IMFV). This molecular property arises from the 120° fixed angle about the bridgehead unit, creating a structure-directing environment for the aromatic planes of the molecule.\(^73\) In crystals, this void space is often filled with guest molecules (generally solvent) or appendages from the iptycene molecules themselves. Intermolecular interactions, such as π-π stacking, are observed in the solid-state structure and give rise to long-range order of the iptycene molecules, as well as a well-defined pore system and large degree of void space. For example, this is observed in the solid state structure of compound 55 (tritiptycene) where void space is minimized by the arene rings stacking to give hexagonal channels that are filled by disordered solvent molecules (Figure 1.17(a)).\(^69\) Furthermore, this tendancy to fill void space in the solid state has been shown to distort the structure of the molecule, as seen in the solid-state structure of heptiptycene 52 (Figure 1.17(b))\(^74\) where the blade of one molecule is nested into the cleft of an adjacent molecule. This causes the cleft to widen and distort the rigid bridgehead system away from its ideal 120° arrangement. Furthermore, a channel of chlorobenzene solvent molecules exists between networks of nested iptycene molecules.

Much of the research into iptycene-containing molecules has been geared towards using these void spaces in host-guest chemistry; both molecular separation and storage are potential applications. Several notable examples of functionalized discrete molecules can be described.\(^75-78\) Furthermore, iptycene motifs have been incorporated into macromolecular polymeric systems for
various applications. In adding iptycene structural units to an extended system, amplification of
the materials properties for further use in host-guest chemistry can be achieved.

(a)

(b)

Figure 1.17 Packing motifs observed in iptycene molecules to minimize void space. Examples
given include (a) Tritriptycene (55) and (b) heptiptycene (52).
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(b) Reprinted with permission from ref. 74. Copyright © 1995 Elsevier.
1.3.2.1 Molecular Cages

Many of the reports involving host-guest iptycene systems arise from linking two triptycene molecules through polyether moieties. In doing so, rigidity is maintained in the system through the 120° cleft of the triptycene molecules. Selective guest binding to the two pseudo-crown ether motifs can then occur. Scheme 1.14 illustrates the first of such molecular cages reported by Zong and Chen in 2006. Once synthesized, complexation with various paraquat guests (Figure 1.18(a-c)) showed 1:1 or 1:2 host:guest binding within the crown ether bridged cavity depending on the paraquat functionality. Further binding studies of positively charged secondary ammonium salts (Figure 1.18(d-f)) were performed on the ditriptycene-poly-crown ether molecular cage 86 in order to produce 1:2 host:guest binding with pseudorotaxane structures in solution and the solid state.

Scheme 1.14 Synthesis of ditriptycene-poly-crown ether molecular cage 86.
**Figure 1.18** Host-guest chemistry of poly-crown ether ditriptycene molecular cages 
(a-c) Paraquat substrates used as binding guests for 86 (d-f) Secondary ammonium salts substrates used as binding guests for 86 (g-i) Molecular hand-cuff motif observed in bissditriptycene-poly-crown ether host 90.

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(e-f) Reprinted with permission from ref. 75(b). Copyright © 2006 American Chemical Society.

(h-i) Reprinted with permission from ref. 76. Copyright © 2010 Wiley-VCH Verlag GmbH & Co. KGaA.
These macrocyclic cages can also be extended to give a bis-ditriptycene-poly-crown ether host (90). As expected, this host can bind up to 4 paraquat guests per host molecule. Moreover, the use of an extended bis-secondary ammonium salt gave rise to a “molecular hand-cuff” motif that could be both locked and unlocked through switching of acidic and basic conditions (Figure 1.18(g-i)).

Switching from cationic to anionic guests required the use of a different bridging component. In 2008, Chen and co-workers reported the first nitrogen-bridged triptycene-containing azacalixarene macrocycles. Upon synthesis of these macrocycles (Scheme 1.15), both the cis and trans isomers of the macrocycles were observed. Using NMR spectroscopy and X-ray diffraction it was determined that the cis isomer adopted a highly symmetric structure both in solution and the solid state. The trans isomer, however, was observed to be asymmetric. The solid-state structures also show each of these macrocycles having significant cavities for host-guest interactions. These macrocycles were used to complex squaraine derivatives (95) to give [2]pseudorotaxane and [2]rotaxane structures (Figure 1.19(a)) through both a threading scheme, as well as by in situ formation of the macrocycle in the presence of the guest. In the solid state, asymmetric channels were observed for the cis macrocycles while tubular channels were observed for the trans macrocycles. The shapes of these channels arise from the axle from one [2]rotaxane molecule interacting with the axle from an adjacent [2]rotaxane in a non-covalent fashion (Figure 1.19(b)).
Scheme 1.15 Synthesis of triptycene-containing azacalixarenes 93/94 and squaraine complexes 96/97.

Figure 1.19 Solid-state extended structures of complex (a) 96e and (b) 97d. Reprinted with permission from ref. 77(c). Copyright © 2010 Wiley-VCH Verlag GmbH & Co. KGaA.
1.3.2.2 Discrete Iptycene Metal Complexes

MacLachlan and co-workers have probed the effect of introducing triptycene functionalities to Ni(salphen) systems (Figure 1.20) for the purpose of creating amorphous, porous solids for H₂ uptake. Comparing complexes containing up to six triptycene functionalities with simple Ni(salphen) structures, it was found that the addition of a triptycene moiety greatly enhanced the observed surface areas of the materials. This alone, however, was not the only factor to be considered; addition of Ni(salphen) units also produced a large increase in the accessible surface area. Interestingly, the N₂ adsorption isotherms for these materials did not match any of those outlined by IUPAC recommendations. Instead, large hysteresis is observed, which is characteristic of capillary condensation in mesoporous materials (Figure 1.21).

As these solids show pore sizes in the microporous regime, it is likely that this hysteresis is caused by the swelling of the solid as the adsorbate pushes the individual molecules apart. In this system, where no significant interactions are expected between the individual molecules, such hysteresis could prove beneficial for gas storage applications. The solid-state structure of 102a (Figure 1.22) confirms that large void spaces are present (occupied by free solvent molecules). Furthermore, close packing is prevented because of the presence of the triptycene functionalities with no significant interactions between individual molecules.
Figure 1.20 Triptycene-containing Ni(salphen) complexes 98-103.
Figure 1.21 (a) $N_2$ adsorption/desorption isotherm and (b) $H_2$ adsorption/desorption isotherm for 103. ● : adsorption; ▽ : desorption.
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Figure 1.22 Solid-state structure of 102a showing (a) free solvent in the IMFV of the molecule and (b) the packing of individual molecules.
Reprinted with permission from ref. 78. Copyright © 2009 Wiley-VCH Verlag GmbH & Co. KGaA.
Table 1.3 Structure summary and properties of Ni(salphen) complexes.\[a]\n
<table>
<thead>
<tr>
<th></th>
<th># salphen units</th>
<th># triptycene units</th>
<th>IMFV (%)[b]</th>
<th>Surface Area[c] (m² g⁻¹)</th>
<th>H₂ adsorption (cm³ g⁻¹)[d]</th>
<th>Weight H₂ adsorbed (%)[d]</th>
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</thead>
<tbody>
<tr>
<td>98a</td>
<td>1</td>
<td>0</td>
<td>46.5</td>
<td>Null[e]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>98b</td>
<td>1</td>
<td>0</td>
<td>67.7</td>
<td>Null[e]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>99</td>
<td>1</td>
<td>2</td>
<td>76.5</td>
<td>40, 61</td>
<td>6.7</td>
<td>0.1</td>
</tr>
<tr>
<td>100a</td>
<td>1</td>
<td>1</td>
<td>79.6</td>
<td>Null[d]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100b</td>
<td>1</td>
<td>1</td>
<td>76.4</td>
<td>146, 233</td>
<td>21.2</td>
<td>0.2</td>
</tr>
<tr>
<td>101</td>
<td>1</td>
<td>3</td>
<td>74.2</td>
<td>216, 311</td>
<td>52.4</td>
<td>0.5</td>
</tr>
<tr>
<td>102a</td>
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<td>1</td>
<td>72.5</td>
<td>174, 253</td>
<td>49.8</td>
<td>0.4</td>
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<tr>
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<td>84.3</td>
<td>0.8</td>
</tr>
<tr>
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<td>7</td>
<td>84.6</td>
<td>403, 592</td>
<td>121.0</td>
<td>1.1</td>
</tr>
</tbody>
</table>

[a] Data originally reported in ref. 78 [b] Calculated using CPK models with idealized geometry from PM3 calculations. [c] BET and Langmuir surface areas, respectively, determined from N₂ adsorption at 77 K. [d] Measured at 1 atm, at 77 K. [e] N₂ isotherm shows that the error is disproportionately high due to low adsorption and, consequently, the surface area data is unreliable.

Surprisingly, the surface areas determined by N₂ adsorption were not effective predictors as to which solids would show the highest H₂ adsorption (Table 1.3). For example, compound 102b showed the highest surface area, while compound 103 had the highest H₂ adsorption, 1.1 wt%, which is competitive with primitive MOF systems studied for H₂ storage.\[81\] One possible explanation for this result is the size difference between N₂ molecules and H₂ molecules, i.e., H₂ molecules can access more void spaces than N₂ molecules. Another possible explanation is that the increased H₂ adsorption is associated with the increased number of arene rings in compound.
103 (21) when compared with compound 102b (9). Increasing the density of arene rings in a system has previously been shown to have a large effect on the ability of a material to adsorb H₂ gas.⁵⁵

1.3.2.3 Non-Conjugated Iptycene Polymers

In the late 1960s the first examples of iptycene-containing polymers were reported through the work of Klanderm and Faber⁸² and Hoffmeister et al.⁸³ In an attempt to raise the glass transition temperature (T_g), Klanderm and Faber incorporated a rigid triptycene moiety into poly(ethylene terephthalate) (PET) through the use of 9,10-bis(hydroxymethyl)triptycene (104) or 9,10-bis(carbethoxy)triptycene (106) as one of the monomeric units (Figure 1.23). Using increasing mole percent of 104 in conjunction with ethylene glycol (105) gave modified PET of increasing T_g from 89 °C to 170 °C. Shortly thereafter Hoffmeister et al. used a series of bridgehead functionalized triptycene compounds to synthesize an array of modified polymers such as polyesters, polyurethanes, polyamides, and polyoxadiazoles. In particular the triptycene-containing polyesters and polyamides formed were found to be colourless and thermally stable, with thermal decomposition temperatures between 310 °C and 460 °C in air.

Figure 1.23 Monomeric units used in various mole ratios to produce modified PET.
It wasn’t until the early 1990s that triptycene polymer chemistry moved away from using bridgehead-functionalized analogues. In 1994, Akutsu and co-workers used the asymmetric triptycenediamine 108 with a number of different diacyl dichlorides (Scheme 1.16). The premise behind the construction of these polymers was to enhance polyamide solubility while preserving the high thermal stability of the polymer through the use of a rigid asymmetric unit. This was achieved for polyamides, as well as polyarylates and poly(ether ketone)s in 1997. While these polymers afforded improved solubility and high thermal stability, they were found to be semi-crystalline and still exhibited overall low solubility.

![Scheme 1.16 Synthesis of triptycene-containing polymer 110.](image)

In 2006, Swager and co-workers began an extensive research program involving iptycene-containing non-conjugated polymers. The first of these to be reported utilized packing of the rigid triptycene units with long-chain aliphatic regions (Scheme 1.17), giving an overall woven structure. This polymer contained both rigid and flexible motifs, and as a result maintained some degree of freedom for polymer chains to move relative to one another (Figure 1.24). It was found that by using this approach the triptycene-containing polymers (113a) had improved stiffness and
ductility when compared to an analogous polyester reference (113b), and enhanced values for Young’s modulus (by three times), strength (by three times), and strain to failure (by 20 times).  

Scheme 1.17 Synthesis of triptycene-containing polymer 113.

Figure 1.24 Comparison of polymer interaction under various strain conditions. Note the triptycene derivatives show enhanced interactions under strain allowing for higher polymer strength compared to triptycene-free analogues. Reprinted with permission from ref. 86(a) Copyright © 2006 American Chemical Society.
1.3.2.4 Conjugated Iptycene Polymers

The first rigid, highly conjugated iptycene-containing polymers were reported by Swager and co-workers in 1998. Here, pentiptycene units were incorporated into a poly(phenylene ethynylene) (PPE) polymer (Scheme 1.18). The bulky, rigid pentiptycene units, prevent π-π stacking between polymer chains. This disrupts excimer formation in the solid state and enhances solubility of the polymer, allowing thin-films to be cast from solution. The thin films showed an unprecedented high sensitivity to electron deficient aryl analytes, in particular trinitrotoluene, dinitrotoluene and benzoquinone. Uptake of the analyte results in fluorescence quenching (Figure 1.25), making these polymers ideal as chemical sensors, especially for volatile explosives.

Scheme 1.18 Synthesis of pentiptycene-containing polymer 116.

In 2001, Swager and co-workers reported triptycene-containing analogues of poly(phenylene vinylene) (PPV) (Figure 1.26). Once again it was observed that the added bulk of the iptycene unit allowed for higher solubility of the polymer, as well as increased molecular weights. Excimer formation was once again prohibited between polymer chains, particularly when a pendant chromophore unit was also incorporated within the polymer (such as fluorene; 120).
Figure 1.25 Host-guest interaction between pentiptycene-containing poly(phenylene ethynylene) polymers and small analytes. Reprinted with permission from ref. 87(a). Copyright © 1998 American Chemical Society.

Figure 1.26 Examples of triptycene-containing conjugated polymers.
1.3.2.5 Microporous Iptycene Polymers

Recently, McKeown and co-workers reported the synthesis of amorphous triptycene-containing polymers of intrinsic microporosity (Trip-PIMs). Early reports of such polymers note the high surface areas (1416 m² g⁻¹) and high affinity for hydrogen adsorption (1.68 wt% at 1 bar/77 K and 2.8 wt% at 10 bar/77 K). Altering the functionalization of the bridgehead group afforded a series of analogous Trip-PIMs (Scheme 1.19). McKeown reported in 2010 that the surface area, and hence the amount of H₂ uptake could be altered, with the maximum observed value being for the isopropyl derivative: 1.83 wt% at 1 bar/77 K and 3.1 wt% at 10 bar/77 K. It should be noted that at 10 bar/77 K, 60% of the estimated H₂ capacity is being utilized.

![Scheme 1.19 Synthesis of triptycene-containing polymers of intrinsic microporosity.](image)

1.3.2.6 Iptycene-Containing Coordination Polymers

Very few examples of coordination polymers or metal-organic frameworks (MOFs) that incorporate iptycene units have been reported. The first of these reports was in 2006 when Chong
et al. used phenazine-functionalized triptycene derivatives to coordinate copper(I) ions in the solid state, creating coordination polymers with solvent-accessible void space (127 and 130, Scheme 1.20).91 It was demonstrated that these materials can be used to remove benzene derivatives from contaminated water.

Scheme 1.20 Synthesis of triptycene-containing Cu(I) coordination polymers (a) 127 and (b) 130. Portions of this scheme are reprinted with permission from ref. 91(a). Copyright © 2006 American Chemical Society.
As another method to incorporate triptycene into frameworks, Roy et al. investigated the use of phenanthroline-extended triptycenes (133) as bridging ligands. Upon reacting these with metal cyanides, 1-D coordination polymers (134) were obtained rather than 3-D frameworks (Scheme 1.21).

**Scheme 1.21** Synthesis of 1-D coordination polymers 134 with phenanthroline-extended triptycenes as bridging ligands, 133.

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Triptycene has also been incorporated into amorphous 3-D coordination frameworks (MOF-IPs) by combining zinc acetate with 2,3,6,7,10,11-hexacyanotriptycene (136) in quinoline (Scheme 1.22). This material was found to have a Brunauer-Emmett-Teller (BET) surface area of 621 m$^2$ g$^{-1}$, Horvath-Kawazoe (H-K) pore size distribution of 5.0-9.0 Å (maximum at 6.0 Å), and 1.15 wt% H$_2$ uptake at 77 K and 1 atm. Given that the H$_2$ storage capacity of MOF-IPs is comparable to that of other triptycene-containing gas storage agents, this confirms that the increased number of adsorptive sites on the extra arene rings remain available even after framework assembly.
Similarly, McKeown and co-workers built upon their former Trip-PIMs system by also incorporating a zinc phthalocyanine-based core (138; Figure 1.27). In doing so, McKeown was able to transform Trip-PIMs into a more rigid, crystalline microporous material with similar topologies to zeolites.

**Scheme 1.22** Synthesis of 3-D coordination frameworks (MOF-IPs).
Another strategy for incorporating triptycene into coordination polymers is through functionalization and MOF formation. Here, triptycene molecules that are functionalized with carboxylate groups are oriented opposite one another used to create linear ligands. Vagin et al. used triptycene-9,10-dicarboxylic acid (139) where substitution occurs at the bridgehead carbons (Scheme 1.23). When 139 is treated with zinc nitrate in DMF or DEF, triptycene dicarboxylate MOFs (TDC-MOFs) observed had dinuclear zinc square paddlewheel SBUs capped by two coordinating solvent molecules. In a similar experiment, a TDC-MOF was synthesized containing two different SBUs. Both gave a distorted three-bladed triangular paddlewheel structure that was bridged by an additional 139 ligand in order to provide hexagonal channels in a 3-D pillared arrangement. In an attempt to achieve other 3-D structures, reactions using the same components as the original TDC-MOFs were carried out in the presence of an additional ditopic ligand, such
as 4,4’-bipyridine (bipy, 42), bis(4-pyridyl)-s-tetrazone (BiPyTz, 140), or bis(4-pyridyl)dimethoxy-p-phenylenedivinylene (PyPV). The additional ligand displaced the coordinated solvent molecules that restricted the network to only two dimensions, resulting in a 3-D pillared framework. Using a pillaring approach prevents interpenetration in the solid state structure, and increases the stability of the desolvated material for host-guest and gas storage applications.96

**Scheme 1.23** Synthesis of solid-state triptycene-containing MOFs from proligand 139. Portions of this scheme are reprinted with permission from refs. 95. Copyright © 2008, 2009 Wiley-VCH Verlag GmbH & Co. KGaA.
1.4 Goals and Scope of this Thesis

The goal of this thesis is to develop new iptycene-containing MOFs, study their structure in the solid state, and investigate their ability to store H₂ gas. By incorporating iptycene derivatives in the framework, formation of high surface area, open frameworks was expected. It was predicted that IMFV of iptycenes would allow for additional surface area and porosity to the void space that arises from network formation.

Herein, the synthesis and characterization of three generations of iptycene-containing ligands for the purpose of MOF formation (Figure 1.28) is discussed. The rational design behind these ligands was to introduce steric bulk into the ligand system in an attempt to open up additional channels and pores while incorporating more regions with exposed aromatic rings. It was expected that this would allow for more hydrogen gas to enter the system, and give an enhanced surface area for hydrogen adsorption.

Chapter 2 describes the first generation iptycene-containing ligands. These were designed to be triptycene and pentiptycene analogues of 1,4-BDC (145). Formation of bulky MOFs isoreticular to MOF-5 was expected. From this work, it was found that triptycene-containing ligand 145 gave two different 3-D MOFs at ambient versus solvothermal conditions. Furthermore, at solvothermal conditions a mixture of MOF isomers was observed, all with pseudo-[Zn₄O]⁶⁺ SBUs, allowing extra space in the lattice for incorporation of the bulky iptycenyl clefts.

Chapter 3 outlines the second generation of iptycene-containing ligands which were designed to lengthen the MOF edge axis through the use of a flexible moiety. Through this structural modification less interference of the iptycenyl clefts with the pore structure of the MOF
was expected, as well as access to further pore space through a solid-to-solid transition due to the flexible moiety. From this work the first pentiptycene-containing MOF was isolated showing a 3-D structure with ligand 148 and a pseudo-[Zn_{4}O]^{6+} SBU. Also, a series of 1-D, 2-D, and 3-D triptycene-containing MOFs was synthesized with ligand 147 by altering the solvothermal reaction conditions. Overall stability of these MOFs was good, however in some cases structure collapse was observed upon removal of solvent due to the flexible linkages.

Finally, in Chapter 4 a third generation of iptycene-containing ligand was designed and synthesized, this time not only with extension along the ligand backbone, but also through rigid conjugated linkages (ethynylene groups). It was predicted that adding a rigid linkage would prevent collapse of the frameworks as often observed in the second-generation MOFs. Crystalline material was isolated for both ligands 149 and 150, however only single crystals of MOFs containing 150 were suitable for single-crystal X-ray diffraction (SCXRD). Initial results gave two 2-D square-paddlewheel MOF structures that had DMF and H_{2}O as capping ligands. Attempts at bridging the 2-D sheets with ditopic 4,4’-bipyridine ligands gave a slightly different pillared grid-like 3-D structure. Each of these MOF materials showed good thermal stability up to 400 °C, however suffered from loss of crystallinity upon solvent removal. From the experiments with ligand 149 a crystalline solid was obtained and characterized by powder X-ray diffraction (PXRD) and thermal gravimetric analysis (TGA). In this case, modelling of the observed PXRD peaks corresponded to an overall hexagonal structure.
Figure 1.28 Series of iptycene containing ligand targets for MOF formation.
Chapter 2: Synthesis and Characterization of First-Generation Iptycene-Containing MOFs†

2.1 Introduction

2.1.1 Abstract

Four distinct triptycene-containing metal-organic frameworks (MOFs), including three that are structural isomers, were synthesized and characterized. Structural isomerism was observed in the secondary building units (SBUs) of TMOF-2 (154) giving rise to no fewer than three distinct [Zn₄O]₆⁺ clusters. Structural integrity upon guest solvent removal was confirmed using powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA), but gas adsorption experiments revealed low surface area. Triptycenyl groups incorporated into MOFs appear to enhance structural diversity, but also crowd the pores of the MOF, reducing accessible surface area.

† A version of this chapter has been published: Reproduced in part with permission from Crane, A. K.; Patrick, B. O., MacLachlan, M. J., “New metal-organic frameworks from triptycene: structural diversity from bulky bridges,” Dalton Trans., 2013, 42, 8026-8033. Copyright © 2013 Royal Society of Chemistry.
2.1.2 Background

Using the isoreticular MOF (IRMOF) series developed by Yaghi and co-workers\textsuperscript{43} as inspiration, Synthesis of porous, cubic MOF containing highly rigid and shape-persistent iptycenyl units was targeted. Proligands 145 and 146 were designed as bulky analogues to 1,4-BDC (15) which maintain the para orientation of the carboxylic acid groups (Figure 2.1). It has been shown that adding additional functional groups to linear dicarboxylate ligands does not have an effect on the overall topology of the resulting MOF structure. Instead, enhanced surface areas and large pore sizes have been observed.\textsuperscript{43a} With the addition of iptycenyl clefts, it was expected that a structure containing open pore network would result, with larger pores and enhanced surface area as the structure expands to incorporate such a large ligand into the MOF. It was predicted that the addition of extra aromatic rings to the ligand would generate structure with high affinity for H\textsubscript{2} gas physisorption. This prediction originated from work reported by Yaghi and co-workers in 2003 that suggested highly conjugated organic ligands can increase the overall gravimetric H\textsubscript{2} gas storage capacity of the MOF.\textsuperscript{55-57, 97}

![Figure 2.1](image_url)  

\textbf{Figure 2.1} Series of iptycene-containing ligand targets analogous to 15.
In this chapter the synthesis and characterization of a new triptycene-containing dicarboxylate ligand is reported, and its incorporation into zinc-based metal-organic frameworks is explored. It was found that the conditions used to crystallize the MOFs strongly influenced the product, leading to unique frameworks with distinct SBUs. Four different metal-organic frameworks incorporating the triptycene-1,4-dicarboxylate ligand have been characterized by single-crystal X-ray diffraction (SCXRD). The stability and porosity of the materials were also investigated.

2.2 Discussion

2.2.1 Synthesis of Triptycene-1,4-dicarboxylic Acid

Triptycene-1,4-dicarboxylic acid (145) was synthesized as shown in Scheme 2.1 by analogy to methods previously used to make other carboxylic acid-functionalized triptycenes.\(^9^8\) Reaction of 3,6-dimethylanthranilic acid and isoamyl nitrite produces a diazonium salt. This decomposes \textit{in situ} to give the benzyne required for the Diels-Alder addition to anthracene producing 1,4-dimethyltriptycene (152). Oxidation with KMnO\(_4\) under basic conditions gave the desired dicarboxylic acid (145) in 93% yield. The \(^1\)H NMR resonances of the bridgehead protons of triptycene derivatives are diagnostic features, and in the case of 145 a single resonance is observed at \(\delta\) 5.93 ppm in DMSO-\(d_6\).
Scheme 2.1 Synthesis of triptycene-1,4-dicarboxylic acid (145).

2.2.2 TMOF-1: Synthesis and Structure

Compound 145 was used as a precursor to form MOFs. The carboxylic acid groups in 145 are situated para to one another on a single aromatic ring, similar to their arrangement in 15, so I expected that this compound would lead to a structure closely related to MOF-5 with [Zn₄O]⁶⁺ SBUs.

The first attempt to produce a MOF was through a vapour-diffusion method (Scheme 2.2), in which pyridine slowly diffused from a toluene solution into a DMF solution containing 145 and three equivalents of Zn(NO₃)₂ • 6H₂O. A single crystal suitable for X-ray diffraction analysis was obtained after several months. The resulting crystal structure of this substance, named TMOF-1 (153), revealed a 3-D network that contains three different SBUs with a [Zn₄(μ₃-OH)₂]⁶⁺ cluster at the core (Figure 2.2). Each [Zn₄(μ₃-OH)₂]⁶⁺ cluster is surrounded by six ligands (145*, the conjugate base of 145) in either bridging or monodentate fashion to give the overall formula [Zn₄(μ₃-OH)₂](μ₂-RCOO⁻)₄(RCOO⁻)₂. The difference in each SBU arises from the geometries at the Zn centres in the cluster, as well as the arrangement of solvent molecules coordinated to the Zn centres.
Figure 2.2 Solid-state structure of TMOF-1 (153):
(a-b) [Zn₄(μ₃-OH)₂](μ₂-RCOO⁻)₄(H₂O)₂ SBU.
(c-d) [Zn₄(μ₃-OH)₂](μ₂-RCOO⁻)₄(RCOO⁻)₂(DMF)₂ SBU.
(e-f) [Zn₄(μ₃-OH)₂](μ₂-RCOO⁻)₄(RCOO⁻)₂(H₂O)₂(DMF)₂ SBU.
(g) Packing of 3-D MOF network with three “ladder-type” SBUs along the c-axis.
Non-coordinated solvent molecules and hydrogen atoms have been omitted for clarity.
Carbon = black, oxygen = red, nitrogen = blue, zinc = pink.
Scheme 2.2 Synthesis of TMOF-1 (153).

The first cluster (Figure 2.2(a-b)) contains two pairs of distinct Zn environments: two tetrahedral and two trigonal bipyramidal. The tetrahedral Zn centres are bound to one $\mu_3$-OH$^-$ oxygen, two bridging carboxylates and one monodentate carboxylate ligand. This motif most closely resembles the Zn centres observed in the common $[\text{Zn}_4(\mu_4-O)]^{6+}$ SBU, typical of MOF-5. The two five-coordinate (trigonal bipyramidal) Zn centres of this SBU are each coordinated to both $\mu_3$-OH$^-$ oxygen atoms, two bridging carboxylates, and a neutral H$_2$O ligand in an axial position. These aqua ligands were confirmed based on the Zn-O bond lengths observed from the X-ray structure. From X-ray diffraction data, it was observed that a typical Zn-O bond length is 1.91 Å-1.95 Å. In the Zn-$\mu_3$-OH$^-$ cluster observed here, the Zn-O bonds range from 2.00-2.12 Å. In the aqua complex, the Zn-O bond length is 2.05-2.15 Å. These values are consistent with other crystallographic data in the literature.

The second SBU (Figure 2.2(c-d)) in TMOF-1 is structurally similar to the first, also containing two pairs of Zn centres in distinct coordination environments. Once again, it was observed a tetrahedral $\text{Zn}(\mu_3$-OH$^-)(\mu_2$-RCOO$^-)_{2}$ for two of the Zn centres. The other two Zn ions are five-coordinate with a DMF molecule coordinated. These Zn centres have distorted square pyramidal geometry where the neutral ligand is in an equatorial position.
The third and final Zn cluster (Figure 2.2(e-f)) in TMOF-1 also has two distinct coordination environments for pairs of Zn ions. Again, two of the ions have the previously observed tetrahedral Zn(μ₃-OH)(μ₂-RCOO⁻)₂(RCOO⁻) environment. The second Zn environment in this cluster, however, has expanded to a 6-coordinate system where both a H₂O and DMF ligand are found in the coordination sphere. These two ligands are situated cis to one another. This is most likely due to the distortion of the core [Zn₄(μ₃-OH)(μ₂-RCOO⁻)₄(RCOO⁻)₂] cluster to incorporate extra solvent ligands as the network distorts from a cubic lattice in attempts to accommodate the bulky triptycene unit appended to the dicarboxylate ligand. The presence of a μ₃-OH⁻ instead of the anticipated μ₄-O²⁻ ligand within the cluster of TMOF-1 suggested that harsher conditions would be needed to achieve a more compact SBU.

### 2.2.3 TMOF-2: Synthesis and Structure

Scheme 2.3 shows the solvothermal reaction of 145 and Zn(NO₃)₂•6H₂O in DMF, which yielded a white microcrystalline solid where powder X-ray diffraction showed an X-ray diffraction pattern distinct from TMOF-1. This material was termed TMOF-2 (154), but initially the structure was not identified. Fortunately, single crystals of TMOF-2 were eventually obtained from the solvothermal reaction in DMF and study it by SCXRD. In fact, three isomeric 3-D MOFs (TMOF-2a/154a, TMOF-2b/154b and TMOF-2c/154c), were obtained from the same reaction mixture and characterized by SCXRD (Figure 2.3)!
Scheme 2.3 Synthesis of TMOF-2 (154).

The structures of all three isomeric MOFs are similar; They are 3-D networks with SBUs that are similar to [Zn₄O]⁶⁺ SBUs, having four zinc centres bridged by an oxo-ligand and six carboxylate linkages, but not all of the zinc centres have tetrahedral coordination environments. Instead, the SBUs in TMOF-2a, TMOF-2b and TMOF-2c are distorted from the expected [Zn₄O]⁶⁺ SBU to accommodate the bulky, rigid triptycene moieties. As a result the coordination of two additional DMF solvent molecules per SBU is observed. Several attempts were made to modify the synthesis slightly in order to achieve SBUs without neutral solvent coordinated, but each attempt yielded only one of these three isomeric structures.
Figure 2.3 Solid-state structure of TMOF-2 (154) isomers:

(a-b) TMOF-2a (154a): [Zn₄O(DMF)₂]⁶⁺ SBU and packing along the b-axis.
(c-d) TMOF-2b (154b): [Zn₄O(DMF)₂]⁶⁺ SBU and packing along the b-axis.
(e-f) TMOF-2c (154c): [Zn₄O(DMF)₂]⁶⁺ SBU and packing along the b-axis.

Non-coordinated solvent molecules and hydrogen atoms have been omitted for clarity.
Carbon = black, oxygen = red, nitrogen = blue, zinc = pink.

The SBU of TMOF-2a has three tetrahedral and one octahedral Zn centre, where the extra coordination sites in the axial and equatorial positions are occupied by two solvent (DMF) molecules in a cis fashion (Figure 2.3(a)). This SBU is common to all three isomeric frameworks, with slight distortions observed in each (Figure 2.4). In addition to this SBU, TMOF-2b has a second SBU with two 4-coordinate (tetrahedral) and two five-coordinate Zn centres. For the two five-coordinate Zn centres, one has trigonal bipyramidal geometry with one DMF bound equatorially, and the other has a distorted square pyramidal geometry with a DMF molecule bound equatorially (Figure 2.3(c)). In this particular SBU, the DMF molecules are positioned parallel to
one another on adjacent Zn centres, as opposed to in the same Zn environment. **TMOF-2c** contains yet another isomeric SBU. In this case, the SBU again has two tetrahedral and two five-coordinate Zn centres. In this structure, the five-coordinate Zn centres are still adjacent to one another, but both are in a distorted square pyramidal geometry with the DMF molecules bound in equatorial positions and pointing away from one another with a $O_{\text{DMF}}$–Zn–$O_{\text{DMF}}$ bond angle of 115.7° (Figure 2.3(e)).

![Figure 2.4 Overlay of octahedral Zn centre observed in SBU common to all three isomers of TMOF-2 (154).](image)

**Figure 2.4** Overlay of octahedral Zn centre observed in SBU common to all three isomers of TMOF-2 (154).

TMOF-2a (154a) = blue, TMOF-2b (154b) = red, TMOF-2c (154c) = green.

Figure 2.5 shows the powder X-ray diffraction patterns of two different samples of TMOF-2 and simulated PXRD patterns of TMOF-2a, TMOF-2b and TMOF-2c. Many of the major diffraction peaks occur at similar 2θ values (for example 4.1-4.3°, 7.2-7.3°, 9.8-10.0°), making decomposition of the pattern for TMOF-2 into its components quite difficult. However, the PXRD patterns of bulk TMOF-2 clearly indicate that the samples are crystalline and appear to contain mostly TMOF-2a, but other isomers (perhaps even ones that are not yet isolated) may also be present.
Before gas adsorption studies could be carried out on the material, desolvation of the porous framework was required. A bulk sample of TMOF-2 was used for this study and any changes to its structure were tracked by PXRD (Figure 2.6) and thermogravimetric analysis (TGA; Figure 2.7). The TGA trace performed on the as-synthesized bulk material shows first a loss of encapsulated solvent molecules (between 130 and 280 °C), and decomposition of the organic components (above 415 °C). This sample then went through a series of soaking and evacuation steps including soaking in DMF for 24 h, soaking in dichloromethane for 24 h, and finally evacuation in vacuo at 120 °C.
Figure 2.6 PXRD patterns of bulk TMOF-2 (154) as-synthesized, after soaking in DMF, after soaking in DCM, and after drying in vacuo at 120 °C.

Figure 2.7 TGA traces of bulk TMOF-2 (154) as-synthesized, after soaking in DMF, after soaking in DCM, and after drying in vacuo at 120 °C.
After each step, PXRD patterns showed minimal structural changes had occurred, except during the final step when an additional peak at $2\theta = 3.45^\circ$ is observed in the PXRD pattern. This peak is likely observed due to a completely desolvated lattice, while the overall framework remains intact. The removal of solvent from the network is also indicated by the TGA traces, showing only a 5% mass loss up to 290 °C following the final evacuation step. This corresponds to only one remaining coordinated DMF molecule per SBU. As there is no loss in crystallinity observed in the PXRD patterns, the removal of coordinated solvent from the SBU does not disrupt the overall structure of the framework. Furthermore, after exposure of the dried bulk sample of TMOF-2 to air for several days, no decomposition was observed. Upon exposure to air, [Zn₄O]⁶⁺ SBU s are known to undergo hydrolysis,¹⁰² but the hydrophobic triptycenyl groups in TMOF-2 appear to help prevent degradation of the lattice. After desolvation of the MOF, N₂ adsorption/desorption experiments were conducted and it was found that the bulk, crystalline material did not have a high surface area. Given that MOF-5, a close analogue to TMOF-2, is known for its high surface area, it appears that the presence of the triptycene subunit prevents N₂ from entering the framework.

2.2.4 Attempted Synthesis of Pentiptycene-6,13-dicarboxylic Acid

Next a pentiptycene analogue of 1,4-BDC (15) was highlighted as a synthetic target in order to evaluate its effect on the lattice structure. The synthesis of pentiptycene-containing proligand 146 was attempted using the same strategy as proligand 145 (Scheme 2.4). Synthesis of 6,13-dimethylpentiptycene (156) was prepared using a literature procedure,¹⁰³ but oxidation of 156 to the desired 146 proligand was not achieved. Oxidants such as KMnO₄ (basic), CrO₃, and
K$_2$Cr$_2$O$_7$ were examined, but only starting material was ever obtained. It was speculated that the poor solubility of the very hydrophobic precursor 156 was responsible for its lack of reactivity, so biphasic oxidation experiments were attempted with cetyltrimethylammonium bromide (CTAB) and/or tetrabutylammonium bromide as phase-transfer agents between a basic aqueous phase and DCM. Once again, 156 resisted oxidation to the desired dicarboxylic acid 146.

Scheme 2.4 Proposed synthesis of pentiptycene-6,13-dicarboxylic acid (146).

Alternative synthetic approaches to obtain compound 146 were also unsuccessful (Scheme 2.5). For example, it was predicted that by changing the methyl groups to larger ethynyl groups, steric crowding of the 6,13-substituents by the iptycyl clefts would be avoided. While solubility of this compound in the typical pyridine/H$_2$O solution did not pose a problem, no oxidation was found to occur in this procedure. Finally, dehalogenation of compound 159 with $n$-BuLi followed by quenching with dry ice (solid CO$_2$) was pursued. $^1$H NMR spectra of the crude mixtures of intermediate 159 contained singlets at $\delta$ 5-6 ppm characteristic of a bridgehead system, however isolation of pure product by column chromatography was never achieved.
Alternative syntheses attempted to obtain 146.

Scheme 2.5 Alternative syntheses attempted to obtain 146.

2.3 Conclusions

Synthesis of a new triptycenedicarboxylic acid was carried out from which several 3-D triptycene-MOFs that differed through the framework’s ability to incorporate a bulky, rigid, shape-persistent ligand were obtained. Slight variations in the reaction conditions of the MOF synthesis led to different SBUs and thus significantly affect the structure of the MOF. In the vapour-diffusion synthesis, a MOF that was not fully coordinated through the carboxylic acid bridges was observed, giving a MOF with lowered symmetry. However, through solvothermal synthesis, a robust MOF series was synthesized with pseudo-[Zn₄O]-(DMF)₂ isomeric SBUs. Unfortunately, the presence of the bulky triptycene groups prevented gas from entering into the pores for adsorption to the material, and no appreciable surface area was recorded.
2.4 Experimental

2.4.1 General

3,6-Dimethylantranilic acid was synthesized by a literature procedure. Other reagents were obtained from standard suppliers, and used without further purification unless otherwise specified. All reactions were carried out under air unless otherwise specified. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AV400 spectrometer. $^{13}$C NMR spectra were recorded using a proton decoupled pulse sequence. $^1$H and $^{13}$C NMR spectra were calibrated to the residual protonated solvent at $\delta$ 7.27 ppm and $\delta$ 77.23 ppm, respectively, for CDCl$_3$, at $\delta$ 5.32 ppm and $\delta$ 54.00 ppm, respectively, for CD$_2$Cl$_2$ or at $\delta$ 2.50 ppm and $\delta$ 39.51 ppm, respectively for DMSO-$d_6$. IR spectra were obtained neat with a Thermo Nicolet 6700 FT-IR with a Smart Orbit attenuated total reflectance (ATR) accessory. Electron impact (EI) mass spectra were obtained at the UBC Microanalytical Services Laboratory using a double focussing mass spectrometer (Kratos MS-50) coupled with a MASPEC data system with EI operating conditions of source temperatures 120-180°C and ionization energy of 70 eV. Elemental analyses (C, H, N) were performed at the UBC Microanalytical Services Laboratory. Melting points were obtained on a Fisher-John’s melting point apparatus and corrected according to the appropriate calibration. Single crystal X-ray diffraction (SCXRD) experiments were performed on a Bruker X8 APEX CCD with MoK$\alpha$ radiation or a Bruker APEX DUO with MoK$\alpha$ or CuK$\alpha$ radiation as specified in Appendix D.1-D.4. Powder X-ray diffraction (PXRD) experiments were performed on a Bruker D8 Advance with CuK$\alpha$ sealed tube X-ray source and a NaI scintillation detector. PXRD pattern simulations
were performed with the SCXRD data in the CCDC Mercury software. Thermogravimetric analysis data was obtained using a Perkin Elmer TGA6 instrument. Gas (N₂) adsorption data were obtained at 77 K using a Micromeritics ASAP 2010 analyzer.

Gas adsorption experiments were carried out on a bulk sample of desolvated TMOF-2. Desolvation was achieved over a series of steps, and structural modifications were monitored by PXRD. Prepared TMOF-2 was crushed to a fine powder then soaked for 24 h in fresh DMF. This sample was recovered by suction filtration, then soaked for 24 h in dichloromethane. Once again, the sample was recovered by suction filtration and placed under vacuum at 120 °C for 24 h. This afforded desolvated TMOF-2, which was then tested for gas adsorption.

2.4.2 Procedures and Data

2.4.2.1 1,4-Dimethyltriptycene (152)

A solution of anthracene (60, 0.18 g, 1.0 mmol) in 1,2-dichloroethane (6 mL) was heated at reflux. Simultaneously, a solution of 3,6-dimethylantranilic acid (151, 0.33 g, 0.20 mmol) in THF (5 mL) and a solution of isoamyl nitrite (0.5 mL, 4 mmol) in 1,2-dichloroethane (5 mL) were added drop-wise over 4 h. The mixture was then heated at reflux for 3 h. After cooling to r.t., the solvent was evaporated to leave a yellow oily residue. Column chromatography on silica gel (hexanes followed by DCM:hexanes = 1:9) gave pure product 152 as a white solid (0.19 g, 0.67 mmol, 67%).
Data for compound 152: mp 255-256 °C; $^1$H NMR (400 MHz, CDCl$_3$) 2.49 (s, 6H), 5.67 (s, 2H), 6.74 (s, 2H), 7.00 (dd, $J = 5.3$ and 3.2 Hz, 4H), 7.40 (dd, $J = 5.2$ and 3.1 Hz, 4H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) 18.6, 50.8, 123.8, 125.3, 126.5, 129.6, 134.3, 145.7 ppm; MS $m/z$ (relative intensity) 282 (M$^+$, 100); IR (cm$^{-1}$) 3069, 3036, 3009, 2974, 1497, 1490, 1455, 1376, 1199, 1185, 1164, 1113, 1021, 987, 809, 791, 770, 747, 638, 551, 501, 460; EA calcd for C$_{22}$H$_{18}$: C, 93.57%, H, 6.43%. Found: C, 93.32%, H, 6.43%.

### 2.4.2.2 Triptycene-1,4-dicarboxylic Acid (145)

A solution of 1,4-dimethyltriptycene (152, 0.100 g, 0.354 mmol), pyridine (10 mL) and H$_2$O (7 mL) was heated at reflux. Solid KMnO$_4$ (10 equiv. per methyl group) was added portion-wise over 48 h. The brown mixture was then heated at reflux for 12 h. After cooling to r.t., the precipitated MnO$_2$ was removed by filtration and washed with H$_2$O (25 mL) and pyridine (10 mL). The filtrate was concentrated to approximately half its original volume and then acidified with conc. HCl to form a white precipitate. The precipitate was collected by filtration, washed with H$_2$O (10 mL) and acetone (1 mL). Drying under vacuum at 100 °C gave the pure product 145 as a white solid (0.113 g, 0.330 mmol, 93%).

Data for compound 145: mp > 300 °C; $^1$H NMR (400 MHz, DMSO-$d_6$) 6.75 (s, 2H), 7.05 (dd, $J = 5.4$ and 2.9 Hz, 4H), 7.46 (dd, $J = 5.1$ and 3.2 Hz, 4H), 7.56 (s, 2H), 13.45 (br, 2H) ppm; $^{13}$C NMR (100 MHz, DMSO-$d_6$) 49.3, 124.2, 125.5, 129.6, 144.5, 147.5, 167.7 ppm; MS $m/z$ (relative intensity) 342 (M$^+$, 100); IR (cm$^{-1}$) 3042, 3022, 2644, 2516, 1679, 1569, 1404, 1271, 1184, 1170, 924, 778, 681, 638, 633, 468; EA calcd for C$_{22}$H$_{14}$O$_4$: C, 77.18%, H, 4.12%. Found: C, 77.27%, H, 4.31%.
2.4.2.3 TMOF-1 (153)

In a small vial, a solution of 145 (0.011 g, 0.032 mmol) and Zn(NO$_3$)$_2$$\cdot$6H$_2$O (0.027 g, 0.091 mmol) in DMF (1 mL) and chlorobenzene (1 mL) was prepared. In a large vial, a 1% v/v pyridine/toluene solution (1 mL) was added, along with the small vial. Slow vapour diffusion occurred over several months to afford a single clear colourless crystal suitable for X-ray diffraction.

2.4.2.4 TMOF-2 (154)

A solution of 145 (0.100 g, 0.292 mmol) and Zn(NO$_3$)$_2$$\cdot$6H$_2$O (0.261 g, 0.876 mmol) in DMF (10 mL) was prepared and transferred to a 23 mL Teflon-lined autoclave. The reaction vessel was sealed and heated to 110 ºC for 60 h. Programmed cooling (0.1 ºC/min from 110 ºC to 25 ºC) afforded clear, colourless, crystalline solids (0.107 g, 0.0592 mmol, 61%). Single crystals suitable for X-ray diffraction were isolated and used in structural elucidation of TMOF-2a, TMOF-2b, and TMOF-2c. Confirmation of sample crystallinity throughout the bulk sample was performed using PXRD.

Data for TMOF-2: IR (cm$^{-1}$) 3065, 1574, 1478, 1387, 1185, 818, 797, 766, 746, 690, 637, 550, 481; EA calcd for [Zn$_4$O(1,4-TDC)$_3$]•DMF•7 H$_2$O: C, 55.33%, N, 0.94%, H, 3.84%. Found: C, 55.29%, N, 0.59%, H, 3.33%.
2.4.3 Crystallography

Complete SCXRD refinement details may be found in Appendix D.1-D.4.\textsuperscript{107}

2.4.3.1 TMOF-1 (153)

Crystal data for TMOF-1: C\textsubscript{168}H\textsubscript{166}N\textsubscript{12}O\textsubscript{44}Zn\textsubscript{8}, 3580.08 g mol\textsuperscript{-1}; triclinic, space group: P\textbar{}1, \(a = 21.898(3) \text{ Å}, b = 22.149(3) \text{ Å}, c = 24.663(3) \text{ Å}, \alpha = 109.978(7)^\circ, \beta = 109.835(7)^\circ, \gamma = 104.489(7)^\circ, V = 9875.8(7) \text{ Å}^3, Z = 2, T = 100 \text{ K}, F(000) = 3983, \rho_{\text{calcd}} = 1.33 \text{ g cm}^{-3}, \mu(\text{Mo K}\alpha) = 1.059 \text{ mm}^{-1}(\lambda = 0.71073 \text{ Å}), 189824, \) measured reflections, 57091 independent reflections (\(R_{\text{int}} = 0.072\), 2299 refined parameters, \(R_1 = 0.077\) for \(I > 2\sigma(I)\), and \(wR_2 = 0.276, \text{GOF} = 1.044. \text{CCDC 918432.}

2.4.3.2 TMOF-2a (154a)

Crystal data for TMOF-2a: C\textsubscript{87}H\textsubscript{84}N\textsubscript{7}O\textsubscript{20}Zn\textsubscript{4}, 1809.09 g mol\textsuperscript{-1}; monoclinic, space group: P\textsubscript{2}_{1}/c, \(a = 19.556(5) \text{ Å}, b = 16.330(5) \text{ Å}, c = 25.573(5) \text{ Å}, \beta = 91.097(5)^\circ, V = 8165.2(4) \text{ Å}^3, Z = 4, T = 90 \text{ K}, F(000) = 3739, \rho_{\text{calcd}} = 1.47 \text{ g cm}^{-3}, \mu(\text{Mo K}\alpha) = 1.238 \text{ mm}^{-1}(\lambda = 0.71073 \text{ Å}), 32208 \) measured reflections, 10441 independent reflections (\(R_{\text{int}} = 0.087\), 1111 refined parameters, \(R_1 = 0.149\) for \(I > 2\sigma(I)\), and \(wR_2 = 0.356, \text{GOF} = 1.110. \text{CCDC 918433.}

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2.4.3.3  TMOF-2b (154b)

Crystal data for TMOF-2b: C_{316}H_{61}N_{9}O_{61}Zn_{16}, 5865.5 g mol^{-1}; monoclinic, space group: P2_1, a = 23.310(2) Å, b = 15.341(2) Å, c = 23.684(2) Å, β = 113.845(3)°, V = 7746.2(1) Å^3, Z = 4, T = 90 K, F(000) = 3023, \rho_{\text{calc}} = 1.27 g cm^{-3}, \mu(\text{Mo Ka}) = 1.284 mm^{-1} (\lambda = 0.71073 Å), 119076 measured reflections, 31729 independent reflections (R_{int} = 0.072), 1914 refined parameters, R_1 = 0.075 for I > 2\sigma(I), and wR_2 = 0.222, GOF = 1.034. CCDC 918434.

2.4.3.4  TMOF-2c (154c)

Crystal data for TMOF-2c: C_{87}H_{85}N_{7}O_{20}Zn_{4}, 1810.10 g mol^{-1}; tetragonal, space group: P4_32_12, a = b = 25.502(2) Å, c = 50.469(4) Å, α = β = γ = 90°, V = 32823(4) Å^3, Z = 16, T = 90 K, F(000) = 14976, \rho_{\text{calc}} = 1.47 g cm^{-3}, \mu(\text{Cu Ka}) = 1.966 mm^{-1} (\lambda = 1.54 Å), 178548 measured reflections, 29024 independent reflections (R_{int} = 0.054), 1109 refined parameters, R_1 = 0.069 for I > 2\sigma(I), and wR_2 = 0.194, Flack parameter = 0.03(3), GOF = 1.054. CCDC 918435.
Chapter 3: Synthesis and Characterization of Second-Generation Iptycene-Containing MOFs‡

3.1 Introduction

3.1.1 Abstract

Four distinct iptycene-containing MOFs were synthesized and characterized using two new organic ligands. By varying the reaction conditions a series of 1-D, 2-D, and 3-D frameworks was synthesized with a range of secondary building units (SBUs) using the same triptycene-derived ligand. Furthermore, the first example of a pentiptycene-containing MOF is reported as an interpenetrated 3-D framework containing pseudo-[Zn₃O]⁶⁺ clusters. The structural integrity of the MOFs upon guest solvent removal varies depending on the framework, and was tracked using powder X-ray diffraction and thermogravimetric analysis. Gas adsorption experiments were conducted on the robust frameworks and revealed no appreciable surface area. Iptycenyl groups

‡ A version of this chapter has been published: Reproduced in part with permission from Crane, A. K.; Wong E. Y. L., MacLachlan, M. J., “Metal-Organic Frameworks from Novel Flexible Triptycene- and Pentiptycene-Based Ligands,” CrystEngComm., 2013, 15, 9811-9819. Copyright © 2013 Royal Society of Chemistry.
and flexible moieties incorporated into the MOF ligand system appear to enhance structural
diversity, but also crowd the pores of the MOF or facilitate framework collapse upon solvent
removal, reducing accessible surface area.

3.1.2 Background

In the previous chapter, the use of triptycene-1,4-dicarboxylate ligands in MOF synthesis
was examined. As the orientation of the carboxylate groups in this precursor is identical to that
in 15, formation of a structure isoreticular to MOF-5 with the integration of iptycenyl clefts along
each edge was expected. Instead, structurally isomeric MOFs were isolated from the solvothermal
synthesis containing pseudo-[Zn₄O]⁶⁺ SBUs with extra solvent molecules incorporated. It was
postulated that the steric bulk of the triptycene component was forcing the structure to adopt
unusual SBUs, thus inhibiting formation of the anticipated porous isoreticular MOFs.

With these results in mind, extension of the axis of the triptycene ligand using flexible ether
linkages was investigated. It was predicted that extension of the edges of the framework would
make room for the iptycenyl clefts such that they would no longer pose steric hindrance of guest
molecules in the porous network. Furthermore, any steric interactions may potentially be overcome
by the addition of a flexible unit that could undergo crystal-to-crystal changes upon host gas
uptake. Accordingly, a second generation of iptycene-containing ligands was synthesized and
designed (Figure 3.1). These proligands have two additional aromatic rings along the 1,4-axis that
can act as H₂ gas adsorption sites. Also, it was predicted that the addition of oxymethylene units
would allow for framework flexibility. This would be advantageous in allowing the framework to
undergo a solid-state structural shift as gas molecules pass into the channels of the materials, circumventing the presence of bulky triptycenyl units. Such flexible or “breathable” MOFs have been explored for host uptake first by Férey in MIL-53.52

Figure 3.1 Second generation iptycene-containing ligand targets for MOF synthesis.

Chapter 3, highlights the successful synthesis of triptycene- and pentiptycene-containing proligands 147 and 148, respectively. Proligand 147 was then used to produce a series of 1-D (TMOF-3), 2-D (TMOF-3-bipy), and 3-D (TMOF-4) MOFs by varying the solvothermal reaction conditions to give rise to different SBUs. Such correlation between reaction conditions and MOF structure has also been observed by Yaghi and co-workers in the MOF-2/MOF-5 system.45-46 In addition, proligand 148 was used to synthesis the first reported example of a pentiptycene-containing MOF (PMOF-1). This 3-D MOF has a pseudo-[Zn₄O]⁶⁺ SBU similar to those observed in the isomeric TMOF-2 system. The stability and porosity of the materials were also investigated.
3.2 Discussion

3.2.1 Synthesis of Triptycene-1,4-benzyloxydicarboxylic Acid

The synthesis of proligand 147 (the acid form of dicarboxylate 147*) begins with a Williamson ether synthesis of the corresponding methyl ester (162). 1,4-Triptycenedione (161) which tautomerizes in situ to give 1,4-triptycanediol (Scheme 3.1), is reacted with 2 equivalents of 160 to give 162 in 38% yield. Hydrolysis of the methyl ester groups then gave the desired dicarboxylic acid 147 in 97% yield. Both the methyl ester 162 and dicarboxylic acid 147 were purified by recrystallization to give crystals suitable for SCXRD (Figure 3.2).

Scheme 3.1 Synthesis of triptycene-1,4-benzyloxydicarboxylic acid (147).

In the solid-state molecular structure of 162, the two aromatic rings that are tethered to the triptycene group by ether linkages are nearly coplanar with the corresponding ring of triptycene (Figure 3.2(a-b)). In compound 147, on the other hand, the rings are twisted at angles of 78° and
63° relative to the aromatic ring of the triptycene moiety (Figure 3.2(c)). Furthermore, the molecule crystallizes as an infinite chain with strong hydrogen-bonding between the carboxylic acid groups (Figure 3.2(d-e)). This is supported by the Fourier-transform infrared (FTIR) spectrum (Appendix C.2) which contains a doublet at 2672 cm\textsuperscript{-1} and 2552 cm\textsuperscript{-1}, diagnostic overtones and combination bands of linear carboxylic acid dimers.\textsuperscript{110}

![Diagram of molecular structures](image)

**Figure 3.2** Solid-state structures of (a-b) 162 and (c-e) 147 as determined by SCXRD analysis. Non-coordinated solvent molecules and disordered fragments have been omitted for clarity. Carbon = black, oxygen = red, hydrogen = white, zinc = pink.
3.2.2 TMOF-3: Synthesis and Structure

Proligand 147 was reacted with zinc salts under solvothermal conditions to afford several different MOFs. In the first set of conditions, a DMF solution of 147 and three equivalents of Zn(NO$_3$)$_2$•6H$_2$O was heated to 110 °C for 72 h in a Teflon-lined autoclave (Scheme 3.2). Following controlled cooling of the solution, single crystals suitable for SCXRD were isolated and the structure of TMOF-3 (163) was elucidated (Figure 3.3). This structure proved to be 1-D chains of macrocycles, which are each formed by two molecules of 147* (deprotonated 147) bonded to two dinuclear zinc SBUs in a square paddlewheel formation (Figure 3.3). The SBUs are shared between two of the macrocycles in the chain. These SBUs were also capped by dimethylamine, a common decomposition product of the DMF solvent (Figure 3.3(a)). The double-chain structure observed in TMOF-3 is analogous to that observed in tremolite$^{111}$, an inosilicate, and has been observed in other coordination polymers and MOFs.$^{112}$

Scheme 3.2 Synthesis of TMOF-3 (163).
Figure 3.3 Solid-state structure of TMOF-3 (163) as determined by SCXRD analysis.
(a) Dimethylamine-capped square paddlewheel dinuclear Zn$^{2+}$ SBU,
(b) individual 1-D linear chains showing two SBUs bridged by two bent ligands,
(c) packing of 1-D chains as viewed along $a$-axis.
Non-coordinated solvent molecules, disordered fragments and hydrogen atoms have been
omitted for clarity. Carbon = black, oxygen = red, nitrogen = blue, zinc = pink

Preparation of the bulk solid of TMOF-3 for nitrogen adsorption experiments included
immersion in DMF (24 h) then DCM (24 h), followed by drying in vacuo at 120 °C. Structural
changes of the bulk sample were tracked by thermogravimetric analysis (TGA; Figure 3.4(a)) and
powder X-ray diffraction (PXRD; Figure 3.4(b)) experiments. Overall, few changes were observed
during the solvent removal process; a slight shift to higher angle was observed by PXRD in the
peaks at $2\theta = 5.5\text{-}6.5^\circ$, likely due to a slight shrinkage of the lattice. The TGA traces of TMOF-3
as-synthesized and after soaking for 24 h in DMF show a mass loss at 120 °C corresponding to
encapsulated DMF solvent molecules. The mass loss at 300 °C corresponds to the capping dimethylamine ligands, and decomposition of the organic ligand occurs at 400 °C. This thermal stability of TMOF-3 is comparable to other similar MOFs that incorporate triptycene. Following desolvation, the N₂ adsorption of the bulk sample was analyzed, but the surface area was low.

![Figure 3.4](image)

**Figure 3.4** (a) TGA traces of bulk TMOF-3 (163) as-synthesized (red), after soaking in DMF (blue), and after drying *in vacuo* at 120 °C (green) and (b) PXRD patterns of bulk TMOF-3 as simulated from SCXRD (black), as-synthesized (red), after soaking in DMF (blue), and after drying *in vacuo* at 120 °C (green).

### 3.2.3 TMOF-3-*bipy*: Synthesis and Structure

In the structure of TMOF-3, it is apparent that the presence of capping dimethylamine ligands prohibit extradimensional growth of the framework. In order to expand the dimensionality of the structure, 4,4′-bipyridine (42) was added to the reaction in an effort to bridge the 1-D square paddlewheel chains into 2-D sheets. The use of a 1:1 mixture of DMF and chlorobenzene allowed
for competitive binding of the 4,4′-bipyridine against dimethylamine, a common thermal decomposition product of DMF. After 72 h of heating at 110 °C, TMOF-3-bipy was isolated as a crystalline solid (Scheme 3.3). SCXRD experiments confirmed that the 1-D chains of TMOF-3 were indeed bridged by the 4,4′-bipyridine capping agent in TMOF-3-bipy (Figure 3.5). This bridging, however, caused a disruption in the square paddlewheel motif observed in the structure of TMOF-3. Thus, a dinuclear zinc SBU was observed in TMOF-3-bipy, where one of the two carboxylate ligands are bound in a monodentate fashion, two carboxylate ligands are bridging the zinc centres, and the 4,4′-bipyridine ligands are “capping”. This give an overall SBU of bridged trigonal bipyramidal zinc centres (Figure 3.5(a)).

![Scheme 3.3 Synthesis of TMOF-3-bipy (163b).](image-url)
Figure 3.5 Solid-state structure of TMOF-3-\textit{bipy} (163b) as determined by SCXRD analysis.  
(a) 4,4´-bipyridine capped dinuclear Zn$^{2+}$ SBU,  
(b) individual 1-D linear chains showing two SBUs bridged by two bent ligands,  
(c) packing of 1-D chains as viewed along $b$-axis.  
Non-coordinated solvent molecules, disordered fragments, and hydrogen atoms have been omitted for clarity. Carbon = black, oxygen = red, nitrogen = blue, zinc = pink.

3.2.4 TMOF-4: Synthesis and Structure

In the reaction of 147 with 4,4´-bipyridine to form TMOF-3-\textit{bipy}, the use of chlorobenzene as a non-coordinating co-solvent appeared to suppress the coordination of dimethylamine to the metal centres. Therefore this solvent combination was used in an attempt to construct a 3-D MOF. In this reaction, a 1:1 mixture of DMF and chlorobenzene was used as
before, but without the coordinating ligand 4,4'-bipyridine (Scheme 3.4). TMOF-4 (164) was obtained as a crystalline powder and several crystals were suitable for SCXRD analysis. The structure of TMOF-4 is shown in Figure 3.6.

![Scheme 3.4 Synthesis of TMOF-4 (164).](image)

There are many interesting aspects to this TMOF-4. First, the SBU is not the anticipated [Zn₄O]⁶⁺ octahedral unit commonly observed, nor is it a distorted pseudo-[Zn₄O]⁶⁺ as often observed in sterically-hindered triptycene-containing MOFs. Instead, a [Zn₇(OH)₃]¹¹⁺ SBU was observed in which there are 12 bridging carboxylate ligands. In order to account for the charge balance of the MOF, one of these 12 carboxylates must be protonated, although the location of this proton could not be determined from the SCXRD data.
Figure 3.6 Solid-state structure of TMOF-4 (164) as determined by SCXRD analysis.
(a) \([\text{Zn}_7(\text{OH})_3]^{11+}\) octahedral SBU, (b) double-strutted nature of 147* arranged around the SBU,
(c) individual framework as viewed along the \(a\)-axis,
(d) packing of 3-D frameworks as viewed along \(a\)-axis.
Non-coordinated solvent molecules, disordered fragments, and hydrogen atoms have been omitted for clarity. Carbon = black, oxygen = red, nitrogen = blue, zinc = pink.

The 12 triptycenyl ligands are arranged around the SBU to give a double-strutted MOF; that is to say that instead of one ligand bridging each SBU in all directions, there are two. These two ligands exhibit \(\pi-\pi\) stacking of the central triptycene moiety, as well as the extended benzoate rings, with Ar-Ar distances of 3.7-3.8 Å. Double- or multiply-strutted MOFs have been observed in a few cases,\(^{113}\) but not any with long bridging ligands. Looking along a given axis, it can also be noted that the ligand set twists 90° each time it passes through a SBU. Lastly, this structure consists of two interpenetrating networks. Despite this, large void spaces are still evident in the solid-state structure of the MOF (Figure 3.6). Nitrogen adsorption studies were not conducted on this material due to insufficient yields of the product.
3.2.5 Synthesis of Pentiptycene-6,13-benzyloxydicarboxylic Acid

Having demonstrated that the flexible triptycene-containing ligand 147 can form MOF structures, incorporation of pentiptycene into a MOF was carried out by a similar strategy. It was predicted that the MOF could have substantial porosity and surface area by taking advantage of the intrinsic free volume in pentiptycene. Pentiptycene-based compound 148 was obtained by a similar route to compound 147, starting from pentiptycene-6,13-diol\(^{114}\) \((165;\) Scheme 3.5). A single crystal of proligand 148 was obtained, and its structure was determined by SCXRD. Figure 3.7 shows the molecular and extended structure of 148. As expected, 148 extends in a hydrogen-bonded chain (verified by IR spectroscopy, which shows the diagnostic carboxylic acid dimer peaks at 2665 cm\(^{-1}\) and 2540 cm\(^{-1}\); Appendix C.9).\(^{110}\) Also, from the solid-state packing it can be seen that the aromatic ring of the benzoic acid moiety is interdigitated between the wings of the pentiptycene of an adjacent molecule.

![Scheme 3.5 Synthesis of pentiptycene-6,13-benzyloxydicarboxylic acid (148).](image)
Figure 3.7 Solid-state structure of 148 as determined by SCXRD analysis. Non-coordinated solvent molecules and disordered fragments have been omitted for clarity. Carbon = black, oxygen = red, hydrogen=white, zinc = pink.

3.2.6 PMOF-1: Synthesis and Structure

The reaction of proligand 148 with Zn(NO$_3$)$_2$•6 H$_2$O under solvothermal conditions in DMF was investigated (Scheme 3.6). Following programmed cooling (0.1 °C/min), a solution was recovered in which colourless crystals appeared after several days. SCXRD analysis of the product revealed the first structure of a pentiptycene-containing MOF, PMOF-1 (167; Figure 3.8). This MOF is composed of a 3-D structure containing a pseudo-[Zn$_4$O]$^{6+}$ SBU. In this SBU, a tetrahedral $\mu_4$-bridging $O^{2-}$ ligand is surrounded by three tetrahedral zinc centres and one octahedral zinc centre. Also, five of the coordinated ligand carboxylate units are $\mu_2$-COO$^-$ bridging ligands, leaving
the sixth in a $\mu_1$-COO$^-$ monodentate binding fashion. This leaves three coordination sites on the octahedral zinc centre for solvent coordination; these are occupied by two DMF molecules and a water molecule. The framework itself is open and highly porous in a 3-D near-cubic network. However, the MOF network is triply interpenetrated to give a dense framework (Figure 3.8(c)).

Scheme 3.6 Synthesis of PMOF-1 (167).
Figure 3.8 Solid-state structure of PMOF-1 (167) as determined by SCXRD analysis. 
(a) pseudo-$[\text{Zn}_4\text{O}]^{6+}$ cluster (b) individual framework as viewed along the $c$-axis, 
(c) packing of 3-D framework as viewed along $c$-axis. 
Non-coordinated solvent, disordered fragments and hydrogen atoms have been omitted for clarity. Carbon = black, oxygen = red, nitrogen = blue, zinc = pink.
Removal of the guest solvent molecules in PMOF-1 was attempted and monitored by PXRD (Figure 3.9). After soaking the crystals in DMF for 24 h, PXRD indicates that the structure remains intact. However, after solvent exchange in DCM, the framework loses crystallinity. This collapse is likely due to movement about the flexible components in the ligand, as pseudo-[Zn₄O]⁶⁺ SBUs have proven stable to solvent removal in previous triptycene MOF examples.¹⁰⁹ Attempts to resolvate the lattice and restore crystallinity by reintroducing the crystals to DMF were unsuccessful.

![Figure 3.9 PXRD patterns of bulk PMOF-1 (167) as simulated by SCXRD (black), as-synthesized (red), after soaking in DCM (orange).](image)

### 3.3 Conclusions

Three distinct MOFs of varying dimensionality using a triptycene-containing ligand with a flexible ether moiety were synthesized. Each structure contained a different SBU that generated
distinct 1-D, 2-D and 3-D structures. Although collapse of these MOFs was not observed upon solvent removal, low surface areas were measured by N₂ gas sorption analysis. Furthermore, the first example of a pentiptycene-containing MOF was presented. In this case, an analogue of a pseudo-[Zn₄O]⁶⁺ SBU was observed similar to those seen in our previous work with triptycene containing MOFs. Efforts to exploit the porosity in this new material were unsuccessful owing to framework collapse upon solvent removal. Overall, these results demonstrate new methods to fashion metal-organic frameworks containing rigid and bulky triptycene- and pentiptycene-based components.

3.4 Experimental

3.4.1 General

All reactions were carried out under air unless otherwise specified. ¹H and ¹³C NMR spectra were recorded on a Bruker AV400 spectrometer. ¹³C NMR spectra were recorded using a proton decoupled pulse sequence. ¹H and ¹³C NMR spectra were calibrated to the residual protonated solvent at δ 7.27 ppm and δ 77.23 pm, respectively, for CDCl₃, at δ 2.50 and δ 39.51, respectively, for DMSO-d₆, or at δ 5.32 and δ 53.84, respectively, for CD₂Cl₂. IR spectra were obtained neat with a Thermo Nicolet 6700 FT-IR with a Smart Orbit attenuated total reflectance (ATR) accessory. Electron impact (EI) mass spectra were obtained at the UBC Microanalytical Services Laboratory using a double focussing mass spectrometer (Kratos MS-50) coupled with a MASPEC data system with EI operating conditions of source temperatures 120-180°C and
ionization energy of 70 eV. Elemental analyses (CHN) were performed at the UBC Microanalytical Services Laboratory. Melting points were obtained on a Fisher-John’s melting point apparatus and corrected according to the appropriate calibration. Single crystal X-ray diffraction (SCXRD) experiments were performed on a Bruker X8 APEX CCD with MoKα radiation or a Bruker APEX DUO with MoKα or CuKα radiation as specified in Appendix D.5-D.10. Powder X-ray diffraction experiments were performed on a Bruker D8 Advance with CuKα sealed tube X-ray source and a NaI scintillation detector. PXRD pattern simulations were performed with the SCXRD data in the CCDC Mercury software. Thermogravimetric analysis data was obtained using a Perkin Elmer TGA6 instrument. Gas (N₂) adsorption data were obtained at 77 K using a Micromeritics ASAP 2010 analyzer.

Gas adsorption experiments were carried out on a bulk sample of desolvated TMOF-3 and PMOF-1. Desolvation was achieved over a series of steps, and structural modifications were monitored by PXRD. Prepared samples were crushed to a fine powder then soaked for 24 h in fresh DMF. This sample was recovered by suction filtration, then soaked for 24 h in DCM. Once again, the sample was recovered by suction filtration. In the case of PMOF-1, structure collapse occurred at this stage and no further steps were attempted. For TMOF-3, the remaining sample was placed under vacuum at 120 °C for 24 h. This afforded a desolvated framework, which were then tested for gas adsorption.
3.4.2 Procedures and Data

3.4.2.1 Synthesis of Dimethyl Triptcene-1,4-benzyloxydicarboxylate (162)

A solution of 160 (0.241 g, 1.05 mmol) and KI (0.029 g, 0.18 mmol) was prepared in acetone (20 mL) and added dropwise to a refluxing (80 °C) mixture of 161 (0.100 g, 0.350 mmol) and K₂CO₃ (0.218 g, 1.58 mmol) in acetone (40 mL). The resulting mixture was heated at reflux for 24 h. After cooling to room temperature, the solvent was removed by rotary evaporation and the yellow solid was dissolved in DCM and gravity filtered through filter paper to remove any insoluble salts. After removing the solvent by rotary evaporation, the solid yellow residue was purified using column chromatography on silica gel (DCM:hexanes = 1:1 > DCM) to give a pure product as a white solid 162 (0.20 g, 0.40 mmol, 38%). Recrystallization from DCM/hexanes provided colourless tablet crystals suitable for SCXRD analysis.

Data for compound 162: mp 229-231 °C; ¹H NMR (400 MHz, CDCl₃) 3.96 (s, 6H), 5.10 (s, 4H), 5.95 (s, 2H), 6.48 (s, 2H), 7.01 (dd, J = 5.38 and 2.93 Hz, 4H), 7.41 (dd, J = 5.38 and 3.42 Hz, 4H), 7.54 (d, J = 8.31 Hz, 4H), 8.10 (d, J = 8.31 Hz, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) 47.8, 52.4, 70.9, 111.0, 124.0, 125.3, 127.1, 129.9, 130.1, 136.4, 142.9, 145.7, 148.5, 167.1 ppm; MS m/z (relative intensity) 582 (M⁺, 100); IR 3017, 2950, 1713, 1614, 1498, 1265, 1230, 1173, 1107, 846, 748, 731, 636 (cm⁻¹); EA calc’d for C₃₈H₃₀O₆: C, 78.33%; H, 5.19%. Found: C, 78.05%, H, 5.11%. 

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3.4.2.2 Synthesis of Triptycene-1,4-benzylxydicarboxylic Acid (147)

Compound 162 (0.100 g, 0.172 mmol) was added to a solution of NaOH (0.035 g, 0.875 mol) in THF (10 mL) and H₂O (10 mL). The mixture was heated to reflux (110 °C) for 1 h. After cooling to room temperature, conc. HCl was added in excess to yield a white precipitate. The white solid was collected by filtration and air dried overnight (0.092 g, 0.17 mmol, 97%). Recrystallization from THF provided colourless needle-shaped crystals suitable for SCXRD analysis.

Data for compound 147: mp >300 °C; ¹H NMR (400 MHz, DMSO-d₆) 5.20 (s, 4H), 5.96 (s, 2H), 7.00 (dd, J = 5.38 and 2.93 Hz, 4H), 7.46 (dd, J = 5.38 and 3.42 Hz, 4H), 7.61 (d, J = 8.31 Hz, 4H), 7.96 (d, J = 8.31 Hz, 4H), 12.94 (s, 2H) ppm; ¹³C NMR (100 MHz, DMSO-d₆) 46.7, 69.7, 111.2, 123.8, 125.0, 127.2, 129.5, 130.1, 135.3, 142.6, 145.3, 147.5, 167.1 ppm; MS m/z (relative intensity) 554 (M⁺, 100); IR 3017, 2975, 2672, 2552, 1682, 1617, 1500, 1293, 1262, 1176, 1070, 779, 750, 745 (cm⁻¹). HRMS calcd for C₃₆H₂₆O₆ ([M⁺] 554.1729, found 554.1727.

3.4.2.3 Synthesis of TMOF-3 (163)

A solution of 147 (0.101 g, 0.182 mmol) and Zn(NO₃)₂•6H₂O (0.159 g, 0.535 mmol) in DMF (10 mL) was prepared and transferred to a 23 mL Teflon-lined autoclave. The reaction vessel was sealed and heated to 110 °C for 72 h. Programmed cooling (0.1 °C min⁻¹ from 110 °C to 25 °C) afforded clear, colourless crystalline solids (0.065 g, 0.091 mmol, 46%). Single crystals
suitable for X-ray diffraction were isolated and used in structural elucidation of TMOF-3 (163). Confirmation of structure uniformity throughout the bulk sample was performed using PXRD. Analysis was obtained after the desolvation procedure.

Data for TMOF-3: IR (cm\(^{-1}\)) 2904, 1646, 1607, 1557, 1487, 1405, 1229, 1113, 1070, 1017, 853, 744, 718; EA calcd for Zn\(_2\)(HN(CH\(_3\))\(_2\))(147\(^*\))\(_2\)2CH\(_2\)Cl\(_2\)•3H\(_2\)O: C, 60.44%, N, 1.81%, H, 4.68%. Found: C, 60.42%, N, 1.68%, H, 4.15%.

### 3.4.2.4 Synthesis of TMOF-3-bipy (163b)

A solution of 147 (0.049 g, 0.090 mmol), 4,4′-bipyridine (0.046 g, 0.29 mmol), and Zn(NO\(_3\))\(_2\)•6H\(_2\)O (0.082 g, 0.28 mmol) in DMF (5 mL) and chlorobenzene (5 mL) was prepared and transferred to a 23 mL Teflon-lined autoclave. The reaction vessel was sealed and heated to 110 °C for 48 h. Programmed cooling (0.1 °C min\(^{-1}\) from 110 °C to 25 °C) was followed by transfer to 20 mL glass vial. This sample was allowed to stand for 48 h after which clear, colourless crystalline solids began to form on the vial walls. Single crystals suitable for X-ray diffraction were isolated and used in structural elucidation of TMOF-3-bipy (163b). Confirmation of structure uniformity throughout the bulk sample was performed using PXRD. Analysis was obtained after the desolvation procedure.

Data for TMOF-3-bipy: IR (cm\(^{-1}\)) 3350, 2854, 2323, 1600, 1489, 1297, 1261, 1112, 1070, 1048, 1017, 853, 805, 766, 749, 722, 638; EA calcd for Zn\(_2\)(bipy)(147\(^*\))\(_2\)•4DMF•4PhCl•8H\(_2\)O: C, 63.14%, N, 4.60%, H, 5.30%. Found: C, 63.18%, N, 3.58%, H, 4.44%.
3.4.2.5 Synthesis of TMOF-4 (164)

A solution of 147 (0.051 g, 0.092 mmol) and Zn(NO₃)₂•6H₂O (0.083 g, 0.28 mmol) in DMF (5 mL) and chlorobenzene (5 mL) was prepared and transferred to a 23 mL Teflon-lined autoclave. The reaction vessel was sealed and heated to 110 °C for 48 h. Programmed cooling (0.1 °C min⁻¹ from 110 °C to 25 °C) followed by transfer to 20 mL glass vial occurred. This sample was allowed to stand for 48 h after which clear, colourless crystalline solids began to form on the vial walls. Single crystals suitable for X-ray diffraction were isolated and used in structural elucidation of TMOF-4 (164). Confirmation of structure uniformity throughout the bulk sample was performed using PXRD. Analysis was obtained after the desolvation procedure.

Data for TMOF-4: IR (cm⁻¹) 2917, 1608, 1553, 1487, 1259, 1228, 1161, 1111, 1069, 1017, 852, 763, 720, 638; EA calcd for [Zn₇(OH)₃](147*)₅(147*H)•2DMF•4PhCl•13H₂O: C, 63.46%, N, 0.60%, H, 4.50%. Found: C, 63.51%, N, 0.60%, H, 3.95%.
3.4.2.6 Synthesis of Dimethyl Pentiptycene-6,13-benzyloxydicarboxylate (166)

A mixture of methyl 160 (1.50 g, 6.54 mmol), KI (0.193 g, 1.16 mmol), K$_2$CO$_3$ (1.40 g, 10.1 mmol) and 165 (1.01 g, 2.18 mmol) was prepared in acetone (200 mL) and set to reflux (80 °C) for 7 days. After cooling to room temperature, the solvent was removed by rotary evaporation. The yellow solid was dissolved in DCM and gravity filtered through filter paper to remove any insoluble salts. After removing the solvent by rotary evaporation, the solid yellow residue was purified using column chromatography on silica gel (DCM : hexanes = 1 : 1 > DCM) to give a pure product as a white solid (0.80 g, 1.0 mmol, 48%).

Data for compound 166: $^1$H NMR (400 MHz, CD$_2$Cl$_2$) 3.99 (s, 6H), 5.06 (s, 4H), 5.68 (s, 4H), 6.94 (dd, $J$ = 5.1 and 3.2 Hz, 6H), 7.26 (dd, $J$ = 5.1 and 3.2 Hz, 8H), 7.77 (d, $J$ = 8.3 Hz, 4H), 8.22 (d, $J$ = 7.8 Hz, 4H) ppm; $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) 48.9, 52.7, 77.5, 124.1, 125.8, 128.1, 130.6, 130.8, 137.4, 143.1, 145.6, 146.5, 167.2 ppm; MS m/z (relative intensity) 758 (M$^+$, 100); IR (cm$^{-1}$) 3016, 2972, 2870, 1716, 1461, 1251, 1009, 750, 553; HRMS calcd for C$_{52}$H$_{38}$O$_6$Na ([M+Na]$^+$) 781.2566, found 781.2589.
3.4.2.7 Synthesis of Pentiptycene-6,13-benzyloxydicarboxylic Acid (148)

Compound 166 (0.155 g, 0.204 mmol) was added to a solution of NaOH (0.46 g, 0.012 mol) in THF (15 mL) and H₂O (15 mL). The mixture was heated to reflux overnight (12 h). After cooling to room temperature, conc. HCl was added in excess to yield a white precipitate. The white solid was collected by filtration and dried overnight in vacuo (0.13 g, 0.18 mmol, 87%). Recrystallization from THF/hexanes provided colourless rectangular crystals suitable for SCXRD analysis.

Data for compound 148: mp >300 °C; ¹H NMR (400 MHz, DMSO-d₆) 5.02 (s, 4H), 5.78 (s, 2H), 6.94 (dd, J = 5.1 and 3.2 Hz, 8H), 7.36 (dd, J = 5.4 and 3.4 Hz, 8H), 7.88 (d, J = 8.3 Hz, 4H), 8.15 (d, J = 7.8 Hz, 4H), 13.08(s, 2H) ppm; ¹³C NMR (100 MHz, DMSO-d6) 47.5, 76.7, 123.6, 125.1, 128.4, 129.8, 130.7, 136.5, 141.9, 144.8, 145.5, 167.2 ppm; MS m/z (relative intensity) 730 (M⁺, 100); IR (cm⁻¹) 3020, 2973, 2665, 2540, 1687, 1613, 1459, 1041, 748, 552. HRMS calcd for C₅₀H₃₃O₆ ([M–H]⁺) 729.2277, found 729.2265.

3.4.2.8 Synthesis of PMOF-1 (167)

A solution of 148 (0.105 g, 0.144 mmol) and Zn(NO₃)₂•6H₂O (0.129 g, 0.434 mmol) in DMF (10 mL) was prepared and transferred to a 23 mL Teflon-lined autoclave by filtering the solution through a puck of celite. The reaction vessel was sealed and heated to 110 °C for 72 h. Programmed cooling (0.1 °C min⁻¹ from 110 °C to 25 °C) afforded a clear, orange solution which was transferred to stoppered glass vials. After 24 h, clear, colourless crystalline solids began to
form in the vial (0.066 g, 0.028 mmol, 59%). Single crystals suitable for X-ray diffraction were isolated and used in structural elucidation of PMOF-1 (167). Confirmation of structure uniformity throughout the bulk sample was performed using PXRD.

Data for PMOF-1: IR (cm\(^{-1}\)) 2929, 1652, 1597, 1480, 1253, 1184, 1099, 819, 797, 768, 749.

### 3.4.3 Crystallography

Complete SCXRD refinement details may be found in Appendix D.5-D.11.\(^{107}\)

#### 3.4.3.1 Dimethyl Triptycene-1,4-benzyloxydicarboxylate (162)

Crystal data for 162: C\(_{38}\)H\(_{30}\)O\(_{6}\), 582.65 g mol\(^{-1}\); monoclinic, space group: C\(_{2}\)/c, \(a = 0.9859(10)\) Å, \(b = 16.4295(8)\) Å, \(c = 9.2328(4)\) Å, \(\alpha = 90^\circ, \beta = 114.3400(10)^\circ, \gamma = 90^\circ, V = 900.4(2)\) Å\(^3\), \(Z = 4\), \(T = 90(2)\) K, \(F(000) = 1224, \rho_{calc} = 1.334\) g cm\(^{-3}\), \(\mu(\text{Mo K}\alpha) = 0.090\) mm\(^{-1}\) (\(\lambda = 0.71073\) Å), 33845 measured reflections, 4253 independent reflections (\(R_{int} = 0.0328\)), 200 refined parameters, \(R_1 = 0.0380\) for \(I > 2\sigma(I)\), and \(wR_2 = 0.1055\), GOF = 1.013. CCDC 950967.

#### 3.4.3.2 Triptycene-1,4-benzyloxydicarboxylic Acid (147)

Crystal data for 147: C\(_{36}\)H\(_{26}\)O\(_{6}\)•THF, 626.67 g mol\(^{-1}\); triclinic, space group: P\(-1\), \(a = 19.063(2)\) Å, \(b = 19.875(2)\) Å, \(c = 19.898(2)\) Å, \(\alpha = 92.131(2)^\circ, \beta = 112.476(2)^\circ, \gamma = 112.500(2)^\circ, \)

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\[ V = 6285.6(13) \, \text{Å}^3, \, Z = 8, \, T = 90(2) \, \text{K}, \, F(000) = 2640, \, \rho_{\text{calc}} = 1.324 \, \text{g cm}^{-3}, \, \mu(\text{Mo K}\alpha) = 0.090 \, \text{mm}^{-1} \quad (\lambda = 0.71073 \, \text{Å}), \] 107574 measured reflections, 33613 independent reflections \((R_{\text{int}} = 0.0352)\), 1767 refined parameters, \(R_1 = 0.0733\) for \(I > 2\sigma(I)\), and \(wR_2 = 0.2376, \text{GOF} = 1.031\). CCDC 950966.

### 3.4.3.3 Pentiptycene-6,13-benzyloxydicarboxylic Acid (148)

Crystal data for 148: \(C_{50}H_{34}O_6\cdot2\text{THF} \cdot \text{hexane}, \) 961.21 g mol\(^{-1}\); monoclinic, space group: \(P2_1/c, \) \(a = 11.335(5) \, \text{Å}, \, b = 14.854(5) \, \text{Å}, \, c = 15.823(5) \, \text{Å}, \, \alpha = 90^\circ, \, \beta = 106.140(5)^\circ, \, \gamma = 90^\circ, \, V = 2559.1(16) \, \text{Å}^3, \, Z = 2, \, T = 100(2) \, \text{K}, \, F(000) = 1024, \, \rho_{\text{calc}} = 1.247 \, \text{g cm}^{-3}, \, \mu(\text{Mo K}\alpha) = 0.081 \, \text{mm}^{-1} \quad (\lambda = 0.71073 \, \text{Å}), \) 23637 measured reflections, 5931 independent reflections \((R_{\text{int}} = 0.0546)\), 352 refined parameters, \(R_1 = 0.0879\) for \(I > 2\sigma(I)\), and \(wR_2 = 0.2769, \text{GOF} = 1.037\). CCDC 950968.

### 3.4.3.4 TMOF-3 (163)

Crystal data for TMOF-3: \(C_{38}H_{31}NO_6\text{Zn} \cdot 3\text{DMF}, \) 882.33 g mol\(^{-1}\); triclinic, space group: \(P-1, \) \(a = 8.5277(6) \, \text{Å}, \, b = 16.9942(12) \, \text{Å}, \, c = 17.4044(12) \, \text{Å}, \, \alpha = 113.501(4)^\circ, \, \beta = 101.299(4)^\circ, \, \gamma = 95.990(4)^\circ, \, V = 2221.0(3) \, \text{Å}^3, \, Z = 2, \, T = 90(2) \, \text{K}, \, F(000) = 926, \, \rho_{\text{calc}} = 1.318 \, \text{g cm}^{-3}, \, \mu(\text{Mo K}\alpha) = 0.613 \, \text{mm}^{-1} \quad (\lambda = 0.71073 \, \text{Å}), \) 26585 measured reflections, 8086 independent reflections \((R_{\text{int}} = 0.0543)\), 609 refined parameters, \(R_1 = 0.0767\) for \(I > 2\sigma(I)\), and \(wR_2 = 0.2357, \text{GOF} = 1.036\). CCDC 950970.
3.4.3.5  TMOF-3-bipy (163b)

Crystal data for TMOF-3-bipy: (C_{46}H_{32}N_{2}O_{6}Zn)_{4}·3DMF·5Cl-Bz, 3878.67 g mol\(^{-1}\); triclinic, space group: P-1, a = 11.3952(7) Å, b = 16.0546(9) Å, c = 25.1653(16) Å, α = 84.376(4)°, β = 82.666(4)°, γ = 78.759(4)°, V = 4465.9(5) Å\(^3\), Z = 1, T = 90(2) K, F(000) = 2005, ρ\(_{\text{calc}}\) = 1.438 g cm\(^{-3}\), μ(Cu Kα) = 1.938 mm\(^{-1}\) (λ = 1.54178 Å), 41065 measured reflections, 15214 independent reflections (R\(_{\text{int}}\) = 0.0629), 1358 refined parameters, R\(_1\) = 0.0798 for I > 2σ(I), and wR\(_2\) = 0.2343, GOF = 1.031. CCDC 950971.

3.4.3.6  TMOF-4 (164)

Crystal data for TMOF-4: C_{216}H_{148}O_{39}Zn_{7}, 3825.18 g mol\(^{-1}\); trigonal, space group: R-3c, a = 33.48(2) Å, b = 33.48(2) Å, c = 105.59(7) Å, α = 90°, β = 90°, γ = 120°, V = 102497(125) Å\(^3\), Z = 12, T = 90(2) K, F(000) = 23544, ρ\(_{\text{calc}}\) = 0.743 g cm\(^{-3}\), μ(Cu Kα) = 0.883 mm\(^{-1}\) (λ = 1.54178 Å), 8726 measured reflections, 8726 independent reflections (R\(_{\text{int}}\) = 0.000), 788 refined parameters, R\(_1\) = 0.1166 for I > 2σ(I), and wR\(_2\) = 0.3755, GOF = 1.266. CCDC 950972.

3.4.3.7  PMOF-1 (167)

Crystal data for PMOF-1: (C_{156}H_{110}N_{2}O_{22}Zn_{4})_{2}·5H_{2}O·12DMF, 6219.33 g mol\(^{-1}\); triclinic, space group: P-1, a = 18.978(5) Å, b = 23.170(5) Å, c = 23.477(5) Å, α = 87.730(5)°, β = 68.378(5)°, γ = 68.299(5)°, V = 8861(4) Å\(^3\), Z = 1, T = 90(2) K, F(000) = 3232, ρ\(_{\text{calc}}\) = 1.164 g
cm$^{-3}$, $\mu$(Mo Kα) = 0.602 mm$^{-1}$ ($\lambda = 0.71073$ Å), 84 407 measured reflections, 22 294 independent reflections ($R_{int} = 0.0535$), 2004 refined parameters, $R_1 = 0.0958$ for I > 2σ(I), and $wR_2 = 0.291$, GOF = 1.081. CCDC 950969.
Chapter 4: Synthesis and Characterization of Third Generation Iptycene-Containing MOFs

4.1 Introduction

4.1.1 Abstract

Two conjugated, iptycene-containing, organic ligands were synthesized for incorporation into zinc-containing MOFs. A 2-D pentiptycene-containing, square-paddlewheel MOF was first synthesized and characterized. By changing the reaction conditions slightly, the capping ligand could be changed, but the long-range order and packing of the 2-D sheets by π-π interactions remained intact. A 3-D pillared pentiptycene-containing MOF was also synthesized and characterized. In this material, 2-D sheets containing two different SBUs were pillared by ditopic 4,4´-bipyridine ligands to give a 3-D structure. Finally, a triptycene-containing crystalline material was synthesized, though the exact structure could not be determined. Each of these materials showed good thermal stability up to 400 °C.
4.1.2 Background

In the previous chapter, the use of triptycene-1,4-benzyloxydicarboxylate ligands in MOF synthesis was examined. As the orientation of the carboxylate groups in this precursor are in a para position like 15, formation of a structure isoreticular to MOF-5 with the integration of iptycenyl clefts along each edge was expected. Furthermore, the use of oxymethylene units provided not only extension along the 1,4-axis, but also a flexible moiety to allow for solid-state crystal-to-crystal transformations. A series of 1-D, 2-D and 3-D MOFs was produced with a wide range of varying SBUs. From this series, the importance of reaction conditions was realized, while the MOFs were not suitable for adsorption due to collapse and poor reproducibility. The first pentiptycene-containing MOF, PMOF-1, was also synthesized. It proved to have a 3-D framework containing pseudo-[Zn₄O]⁶⁺ SBUs with extra solvent molecules incorporated, much like in TMOF-2 of Chapter 2. Despite production of a 3-D structure, the framework was triply interpenetrated and densely packed. This, combined with the collapse of the framework upon solvent removal, made it a poor candidate for adsorption studies.

Moving forward, extension of the axis of the triptycene ligand using rigid ethynyl linkages was investigated. Knowing that extension of the edges of the framework could make space for the iptycenyl clefts, yet flexible linkages posed additional problems, rigid, conjugated groups were substituted for the flexible unit. Therefore, a third generation of iptycene-containing ligands was synthesized and designed (Figure 4.1). Like the second generation, these proligands have two additional aromatic rings along the molecular axis that can act as H₂ gas adsorption sites. The difference however, arises from the addition of ethynylene spacers that would allow a rigid
framework with conjugation along the entire backbone. This would be advantageous as there is literature precedence to incorporate extended conjugation into the ligands of the MOF framework.\textsuperscript{56} Such ethynylene bridges have been explored for hydrogen storage applications by Yaghi in MOFs such as MOF-210.\textsuperscript{43(b)}

Chapter 4 highlights the successful synthesis of triptycene- and pentiptycene-containing proligands \textbf{149} and \textbf{150}, respectively. Proligand \textbf{150} was then used to produce a 2-D (PMOF-2) with a square-paddlewheel SBU. Depending on the conditions, different capping ligands could be observed giving the same overall 2-D sheet interactions and long-range packing, as observed in the differences between PMOF-2\textsuperscript{a} and PMOF-2\textsuperscript{b}. In order to extend the framework, PMOF-3 was then synthesized, using 4,4’-bipyridine (\textbf{42}) as a bridging ligand. This method of framework extension is used commonly throughout other works\textsuperscript{95} and was observed in structure TMOF-2-\textit{bipy} in Chapter 3 of this thesis. In addition, proligand \textbf{149} was used to synthesize a crystalline material TMOF-5. Although single crystals of this material were isolated, they were not suitable for X-ray diffraction, leaving the structure of this material unknown. The stability and porosity of the materials was also investigated.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4.1.png}
\caption{Third generation iptycene-containing ligands for MOF synthesis.}
\end{figure}
4.2 Discussion

4.2.1 Synthesis of Pentiptycene-6,13-ethynylphenyldicarboxylic Acid

Pentiptycene-6,13-ethynylphenyldicarboxylate (150) was synthesized as shown in Scheme 4.1. Compound 168 was synthesized following a literature procedure\textsuperscript{87(b)} then underwent a Sonogashira coupling with methyl \textit{para}-iodobenzoate (168). Following purification by silica gel column chromatography (1:1 DCM:hexanes), compound 169 was obtained as a pure, white powder in 44% yield. Saponification of the ester functional groups in compounds 169 to the corresponding carboxylic acids occurred by reaction with base in THF/H\textsubscript{2}O. After refluxing for 12 hours, the solution was then cooled and water was added to dissolve all solids. Acidification followed, allowing for the carboxylic acid to precipitate and be isolated as a pure white powder in quantitative yield. The solid was washed with methanol and hexanes and left to air dry. The \textsuperscript{1}H NMR resonances of the bridgehead protons of pentiptycene derivatives are diagnostic features, and in the case of 150 a single resonance is observed at \(\delta\) 6.04 ppm in DMSO-\textit{d}_6. In addition, the Fourier-transform infrared (FTIR) spectrum (Appendix C.13) indicates the formation of linear carboxylic acid dimers due to the presence of the diagnostic doublet at 2678 cm\textsuperscript{-1} and 2540 cm\textsuperscript{-1}.\textsuperscript{110}
Scheme 4.1 Synthesis of pentiptycene-6,13-ethynylphenyldicarboxylic acid (150).

4.2.2 PMOF-2: Synthesis and Structure

Proligand 150 was reacted with three equivalents of Zn(NO₃)₂•6H₂O in DMF under solvothermal conditions at 110 °C. After programmed cooling at a rate of 0.1 °C/min, a white solid crystalline material resulted. From this mixture, crystals suitable for X-ray diffraction were found and the solid-state structure of PMOF-2a (170a) was elucidated (Figure 4.2). The MOF consisted of a square-paddlewheel SBU bridged by four ligands 150* (the deprotonated analogue of 150). Capping each of the zinc ions in the paddlewheel was a molecule of DMF. This gave a 2-D grid-like sheet of 24.8 Å x 24.8 Å square pores with regions of π-conjugation open for adsorption. In addition, each ligand along the edge of the square deviates slightly from a linear geometry, possessing a torsion angle of approximately 14° out of the plane. This is consistent with analogous molecules previously reported.¹¹⁶(b) Such an open framework would be desirable for hydrogen gas storage applications. Unfortunately, each 2-D sheet was close packed in the structure, and stacking was observed in an A-B-C fashion. Each layer was positioned such that the middle pentiptycene
moiety underwent a π-π stacking interaction (3.4 – 3.6 Å) with an orthogonal pentiptycene from an adjacent sheet from above and below (Figure 4.2(b-c)). Overall, this gave a densely packed structure of 2-D sheets (Figure 4.2(e)) whereby all open pore channels are blocked by the SBU of an adjacent 2-D sheet. This was a discouraging result, as it was observed in Chapter 2 and Chapter 3 that structures where pore channels generally have low surface areas.

In an attempt to lower the concentration of coordinating DMF in solution and therefore allow 3-D growth of a MOF, the solvothermal reaction was repeated with a 1:1 solution of chlorobenzene and DMF (Scheme 4.3). Keeping all other reaction conditions the same, the resulting reaction mixture once again gave a white, crystalline solid with single crystals suitable for X-ray diffraction. Upon structure elucidation of this material, it was found to be analogous to PMOF-2a, with two H₂O molecules capping the square-paddlewheel SBU instead of two DMF molecules (Figure 4.3). This material, referred to as PMOF-2b (170b), also showed a tightly packed structure of 2-D sheets. This structure followed the same A-B-C packing motif of the sheets, and was organized due to π-π interactions (3.4 – 3.6 Å; Figure 4.3(b-c)) between the pentiptycene moieties of orthogonal ligands in adjacent 2-D sheets.
Scheme 4.2 Synthesis of PMOF-2a (170a).

Scheme 4.3 Synthesis of PMOF-2b (170b).
Figure 4.2 Solid-state structure of PMOF-2a (170a) as determined by SCXRD analysis.
(a) DMF-capped square paddlewheel dinuclear Zn$^{2+}$ SBU,
(b-c) π-π stacking between pentiptycene moieties of adjacent sheets,
(d) single 2-D MOF sheet, (e) packing of 2-D MOF sheets in A-B-C pattern
Carbon = black, oxygen = red, nitrogen = blue, zinc = pink
Figure 4.3 Solid-state structure of PMOF-2b (170b) as determined by SCXRD analysis.
(a) H$_2$O-capped square paddlewheel dinuclear Zn$^{2+}$ SBU,
(b-c) π-π stacking between pentiptycene moieties of adjacent sheets,
(d) single 2-D MOF sheet, (e) packing of 2-D MOF sheets in A-B-C pattern
Carbon = black, oxygen = red, nitrogen = blue, zinc = pink
Comparing the simulated PXRD patterns of PMOF-2a and PMOF-2b, it is clear that the two structures are very similar. For example, the FTIR spectra (Figure 4.4) of the two samples match almost perfectly, with the exception of the bands at 2359 cm\(^{-1}\) and 2335 cm\(^{-1}\) in PMOF-2a, which correspond to the N-C(methyl) stretch of the DMF capping ligands. When comparing the simulated powder X-ray diffraction (PXRD; Figure 4.5(a)) patterns, it is observed that peaks at \(2\theta = 5.3^\circ, 6.48^\circ, 8.74^\circ, 10.09^\circ, 10.72^\circ, 10.87^\circ, 13.02^\circ\) are common to both structures. For the experimental PXRD patterns, while diminished crystallinity is seen for both samples (discussion to follow), peaks at \(2\theta = 5.3^\circ, 9.2^\circ, 10.3^\circ, 14.2-15.4^\circ, 20.6^\circ\) remain common to both materials.

![FTIR spectra of PMOF-2a and PMOF-2b](image)

**Figure 4.4** FTIR spectra of PMOF-2a (170a) and PMOF-2b (170b).
In previous work by Garcia-Garibay and co-workers, iptycene-containing molecules with a similar design were used as crystalline molecular rotors.\textsuperscript{116} In these molecules, 1,4-diethynylbenzene was the rotator, while the capping pentiptycene molecules served as stators – the reverse motif as is observed in 150.\textsuperscript{116(a)} These molecules can be observed as rotors as the aromatic rings go in and out of conjugation as a function of rotation. The solid-state structure of this molecule shows a similar packing motif as PMOF-2a and PMOF-2b, whereby \( \pi-\pi \) interactions are observed between adjacent molecules. In the case of the rotors, such interactions were unfavourable as they prevented the central benzene ring from rotating as it was stabilized by an adjacent pentiptycene stator. As a result, the more crystalline the sample, the less rotation was observed in the cross-polarization magic angle spinning (CPMAS) \( ^{13}\text{C} \) NMR spectrum. In further studies into a molecular dirotor analogous to 150,\textsuperscript{116(b)} once again it was observed that a benzene rotator and the pentiptycene stator of an adjacent molecule were stacked by \( \pi-\pi \) interactions. In this case, however, the large amount of solvent between each layer of rotors provided a localized region of fluid, and aided in rotation dynamics improving upon the initial design. Similar packing
interactions are observed in PMOF-2a and PMOF-2b, however in these materials the packing is between pentiptycene clefts of adjacent sheets, not with the ethynylbenzene rotator unit. Consequently, it is proposed that these molecules may show good rotation about the ethynyl bridges, providing not just a molecular rotor, but a network of rotors.

The bulk samples of PMOF-2a and PMOF-2b were then isolated in order to probe structure uniformity throughout the sample and thermal stability. PXRD experiments were conducted and compared to the patterns simulated from the SCXRD data (Figure 4.6). From the PXRD pattern of bulk PMOF-2a it can be determined that the sample is overall crystalline, due to the large peaks at 2θ = 10-12° and 2θ = 20-22°. For PMOF-2b, peaks at 2θ = 5.3° and 2θ = 10-12° are observable in both traces. Given that the SCXRD data had undergone measures to remove encapsulated, non-coordinating solvent from the structure while the bulk samples had not, deviations in the PXRD patterns were thought to be a result of these methods. Therefore each sample was soaked in DCM for 8 hours then air dried for 4 hours in an attempt to displace any guest solvent molecules. After this “desolvation” step the PXRD experiments were conducted again. Unfortunately, upon solvent exchange and loss, samples lost much of their crystallinity. This may be due to the collapse of the ordered A-B-C packing motif observed in the SCXRD upon solvent removal.
Figure 4.6 PXRD patterns of bulk (a) PMOF-2a (170a) and (b) PMOF-2b (170b) as-synthesized and after soaking in DCM.

Peak broadening is observed for many of the desired peaks in both samples, likely caused by microstrain broadening. Microstrain broadening occurs from lattice strains when the unit cell is displaced about their normal position. William and Stokes characterized this relationship and found that the peak width is directly proportional to the weighted average strain observed in the crystalline sample. Several factors including non-uniform lattice distortions and faulting, give rise to solid-solution inhomogeneity and poor crystallinity. Non-uniform lattice distortions arise when a crystallographic plane has a distribution of d-spacing values, rather than just a single value. This distribution of d-spacing values presents itself as an averaged, broadened peak in the PXRD pattern. In these materials, non-uniform lattice distortions could arise due to the presence of disordered guest solvent molecules within the lattice pores. Faulting occurs when twinning defects are observed, or when there is a disruption in layered packing patterns (example: ABCABCABCCBACBACBA). Given that this is a layered structure with an A-B-C packing motif, faulting could easily account for peak broadening as well. Crystal size also plays a role in peak broadening. The relationship between crystallite size and peak broadening can be seen in the
Scherrer Equation.\textsuperscript{118} This relationship states that peak width is inversely proportional to the crystal size. Handling the sample in the SCXRD study, it was clear that the observable crystalline particles were often too small to attempt a SCXRD experiment.

Thermal stability of the materials was also investigated by TGA (Figure 4.7). When considering \textbf{PMOF-2a}, the trace for the material as-synthesized shows a sizable weight loss from 100\% to 90\% from 30 °C to 200 °C. This corresponds to the loss of approximately 5-6 solvent molecules per formula unit. This value reflects the same overall solvent content that was removed from the SCXRD data by \textit{SQUEEZE} of approximately 40 non-hydrogen atoms, or 8 DMF molecules, per formula unit. Next a weight loss of 6\% occurs from 200 °C to 300 °C which corresponds to the loss of two coordinated DMF molecules. Finally thermal decomposition begins at approximately 400 °C, which is consistent with other iptycene-containing MOFs discussed in Chapter 2 and Chapter 3. Examining the TGA trace of bulk desolvated \textbf{PMOF-2a}, no major weight loss is observed until 200 °C, where a 2\% weight loss is seen corresponding to two coordinated DMF molecules. Once again, thermal decomposition of the organic components of the framework occurs at 400 °C. \textbf{PMOF-2b} shows very similar traces to \textbf{PMOF-2a}. In the as-synthesized material, a weight loss of 18\% occurred from 30 °C to 200 °C, corresponding once again to the loss of encapsulated solvent molecules. Assuming this solvent to be DMF, it can be estimated that 4-5 DMF molecules are lost per formula unit at this time. Given that the SCXRD \textit{SQUEEZE} data suggests that electron density for approximately 30 non-hydrogen atoms, or 6 DMF molecules, per formula unit was removed, this is likely a good estimate. Going from 200 °C to 300 °C, a weight loss of 2\% was observed corresponding to two coordinated H\textsubscript{2}O molecules. When comparing to the desolvated sample, a loss of only 2\% is observed around 200 °C, corresponding only to the two coordinated H\textsubscript{2}O molecules. In both samples, thermal degradation occurs at 400 °C, which is
consistent with PMOF-2a and other iptycene-containing MOFs discussed in Chapter 2 and Chapter 3.

**Figure 4.7** TGA traces of bulk (a) PMOF-2a (170a) and (b) PMOF-2b (170b) as-synthesized and after soaking in DCM.

### 4.2.3 PMOF-3: Synthesis and Structure

In a second attempt to synthesize a MOF with a 3-D structure, 4,4'-bipyridine (42) was used as a ditopic bridging ligand. In this case, it was expected that 42 would displace the monotopic capping ligands observed in PMOF-2a and PMOF-2b and the resulting MOF would have a 3-D pillared structure. The reaction was carried out solvothermally in 1:1 DMF:chlorobenzene (Scheme 4.4). After programmed cooling at a rate of 0.1 °C/min, the resulting mixture consisted of a yellow crystalline solid in solution. Single crystals suitable for X-ray diffraction were isolated and the solid-state structure of PMOF-3 (171) was determined (Figure 4.8). This structure did indeed show pillared 2-D sheets, giving an overall 3-D MOF. However, the individual sheets are
quite different than those observed in PMOF-2a and PMOF-2b. Here, two different SBUs are observed. The first, as expected, is a square-paddlewheel capped by the 4,4'-bipyridine pillars. The second however, consists of a trinuclear zinc cluster. The centre zinc ion is octahedral in geometry and surrounded by four bridging carboxylate oxygen atoms and two μ2-NO₃⁺ oxygen atoms. The outer zinc ions are five-coordinate with a distorted trigonal bipyramidal geometry. Each of these zinc ions is bonded to two bridging carboxylate oxygen atoms, the two μ2-NO₃⁺, an additional DMF molecule and the bridging 4,4'-bipyridine pillars. All together the framework exists as alternating SBUs, bridged by 150° ligands to give a 2-D grid-like sheet with square holes, that was then pillared by 4,4'-bipyridine. The resulting space was 24.8 Å x 24.8 Å x 11.0 Å rectangular pore with a volume of 6765 Å³. In addition, the 4,4'-bipyridine pillars are each twisted with a torsion angle approximately 40° out of the plane.

**Scheme 4.4** Synthesis of PMOF-3 (171).
Figure 4.8 Solid-state structure of PMOF-3 (171) as determined by SCXRD analysis. (a) 4,4'-bipyridine-capped square paddlewheel dinuclear Zn$^{2+}$ SBU, (b) trinuclear Zn$^{2+}$ nitrate cluster SBU, (c-d) single 2-D sheet bridged by 4,4'-bipyridine pillars, (d) full structure showing two sheets (red and blue) bridged by 4,4'-bipyridine (green). Carbon = black, oxygen = red, nitrogen = blue, zinc = pink

Bulk sample uniformity was then probed by PXRD (Figure 4.9(a)). PMOF-3 as-synthesized showed good crystallinity, matching the simulated pattern for angles of 2θ larger than 10°; lower angle peaks were not observed. This could be caused by the large pores in the structure (as solved by SCXRD) being filled with uncoordinated solvent molecules. According to the SCXRD SQUEEZE protocol, 130 non-hydrogen atoms were removed from each formula unit of the framework! This could correspond to approximately 26 DMF molecules per formula unit. Looking at the TGA trace (Figure 4.9(b)) of the PMOF-3 sample as-synthesized, a large weight loss of 20% is observed from 30 °C to 200 °C. This would correspond to the loss of 16 DMF
molecules from the lattice per formula unit. A 3% weight loss at approximately 300 °C can be attributed to the loss of two coordinated DMF molecules. At 400 °C the first weight loss corresponds to the loss of four 4,4´-bipyridine molecules, and is then followed by a shoulder at 475 °C corresponding to the decomposition of the rest of the organic material. Looking at the desolvated bulk PMOF-3 sample, loss of crystallinity is observed by PXRD. The TGA trace shows a weight loss of 10% from 30 °C to 100 °C, likely due to the presence of DCM in the material. This is followed by a weight loss of 3% at approximately 300 °C corresponding to the loss of two coordinated DMF molecules. Lastly, like the as-synthesized sample, at 400 °C a weight loss corresponding to the loss of four 4,4´-bipyridine molecules, is then followed by a shoulder at 475 °C corresponding to the decomposition of the remaining organic material.

**Figure 4.9** (a) PXRD patterns and (b) TGA traces of bulk PMOF-3 (171) as-synthesized and after soaking in DCM.
4.2.4 Synthesis of Triptycene-1,4-ethynlyphenyldicarboxylic Acid

Triptycene-1,4-ethynlyphenyldicarboxylate (149) was synthesized as shown in Scheme 4.5. Compound 172 was synthesized following a literature procedure\textsuperscript{88(a)} then underwent a Sonogashira coupling with methyl para-iodobenzoate (168). Following purification by silica gel column chromatography (1:1 DCM:hexanes) compound 173 was obtained as a pure, white powder in 36% yield. Saponification of the ester groups in compounds 173 to the corresponding carboxylic acids occurred by reaction with base in THF/H\textsubscript{2}O. After heating to reflux for 12 hours, the solution was then cooled and acidified, allowing for the carboxylic acid to precipitate and be isolated as a pure white powder in 91% yield. The solid was washed with methanol and hexanes and left to air dry.

The \textsuperscript{1}H NMR resonances of the bridgehead protons of triptycene derivatives are diagnostic features, and in the case of 149 a single resonance is observed at δ 6.13 ppm in DMSO-\textit{d}_6. In addition, the Fourier-transform infrared (FTIR) spectrum (Appendix C.13) indicated the formation of linear carboxylic acid dimers due to the presence of the diagnostic doublet at 2666 cm\textsuperscript{-1} and 2533 cm\textsuperscript{-1}.\textsuperscript{110}

\textbf{Scheme 4.5} Synthesis of triptycene-1,4-ethynlyphenyldicarboxylic acid (149).
4.2.5 TMOF-5: Attempts at Synthesis and Structure

In an attempt to synthesize a MOF with proligand 149, a solvothermal reaction was conducted with three equivalents of Zn(NO$_3$)$_2$•6H$_2$O in DMF at 110 °C (Scheme 4.6). After programmed cooling at a rate of 0.1 °C/min, a white solid crystalline material, presumably TMOF-5 (174), had formed. Observing this material under a microscope, it was clear that single crystals were present in the mixture, however all were too small to conduct X-ray diffraction studies.

Bulk sample studies were conducted using PXRD, and thermal stability was probed using TGA (Figure 4.10). The bulk sample of TMOF-5 showed poor crystallinity, as was expected by observation of the sample by microscope. More importantly, however, the peaks that were present did not match with any of the PMOF-2a or PMOF-2b peaks, leading to the conclusion that this material is not isoreticular and has a different framework structure. Upon desolvation of the sample by soaking in DCM for eight hours, the sample retained the same level of crystallinity, with peaks
at 2θ = 4.5°, 8.4° and 8.9° becoming sharper and better defined. This suggests that while the framework structure cannot be elucidated, the structure is robust and does not collapse as seen with PMOF-2a and PMOF-2b. Looking at the TGA traces, as expected a large weight loss is observed below 200 °C. This is most likely due to the loss of encapsulated non-coordinating solvent within the lattice of the material, as observed in PMOF-2a, PMOF-2b, and PMOF-3. Thermal decomposition of the material’s organic components does not begin until approximately 420 °C, which is consistent with other materials in the TMOF and PMOF series.

![Image](image.png)

Figure 4.10 (a) PXRD patterns and (b) TGA traces of bulk TMOF-5 (174) as-synthesized and after soaking in DCM.

For the desolvated material, a small weight loss is apparent lower than 200 °C, once again probably due to the loss of encapsulated non-coordinating solvent. Following that there is no major weight loss until the material undergoes thermal decomposition at 420 °C. The lack of any other weight loss features indicates that unlike in PMOF-2a, PMOF-2b, and PMOF-3, there are no capping ligands (DMF or H₂O) present in the structure of the TMOF-5 material, further supporting the formation of a different framework than those previously observed with these ligand analogues.
Further investigation of the structure included modelling the PXRD peaks for a simple cubic and hexagonally packed structure (Table 4.1). From the data, it was found that the overall structure likely has a 3-D hexagonal structure. This is unsurprising as there is literature support hexagonal packed structures like this based on the rod/node model. For series of larger ligands it seems production of a hexagonal lattice, like IRMOF-62, is favoured over cubic IRMOF lattice like MOF-5. Given that 150 is 19.6 Å long (measuring from the centre of each C atom in the carboxylate groups) and longer than butadiynedibenzoic acid used in IRMOF-62 it is predicted that TMOF-5 has a similar topology.

<table>
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<th>Plane (hkl)</th>
<th>Hexagonal Packing</th>
<th>Cubic Packing</th>
<th>Experimental d-spacing</th>
<th>Experimental 2θ (°)</th>
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<td>19.7</td>
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<td>13.9</td>
<td>11.5</td>
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<td>210</td>
<td>7.4</td>
<td>8.8</td>
<td>6.1</td>
<td>13</td>
</tr>
</tbody>
</table>

\[ a_0 = 2d_{100}/\sqrt{3} \quad b_0 = d_{100} \]

4.3 Conclusions

Two distinct pentiptycene-containing MOFs were synthesized using an extended iptycene-containing ligand with a rigid ethynyl moiety. The first structure had a 2-D square-paddlewheel structure with either DMF or H₂O capping the dinuclear zinc SBU. The second structure showed bridging of a similar 2-D sheet with two different SBUs. In both cases, collapse of the MOFs occurred after solvent exchange of DMF to DCM. Using the triptycene-containing analogue, a
crystalline material was produced but the structure could not be elucidated. Through PXRD and TGA experiments it was determined that this material was most likely a 3-D MOF with a hexagonal structure. Due to the ligand length (19.6 Å) a shift for a hexagonal lattice over the cubic lattice of MOF-5 is commonly observed. Furthermore, this material was stable to desolvation and showed high thermal stability up to 420 °C. Overall, these results demonstrate that very large and bulking ligands can be incorporated into well-ordered MOFs.

4.4 Experimental

4.4.1 General

All reactions were carried out under air unless otherwise specified. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AV400 spectrometer. $^{13}$C NMR spectra were recorded using a proton decoupled pulse sequence. $^1$H and $^{13}$C NMR spectra were calibrated to the residual protonated solvent at $\delta$ 7.27 and $\delta$ 77.23, respectively, for CDCl$_3$, or at $\delta$ 2.50 and $\delta$ 39.51, respectively, for DMSO-$d_6$. IR spectra were obtained neat with a Thermo Nicolet 6700 FT-IR with a Smart Orbit attenuated total reflectance (ATR) accessory. Electron impact (EI) mass spectra were obtained at the UBC Microanalytical Services Laboratory using a double focussing mass spectrometer (Kratos MS-50) coupled with a MASPEC data system with EI operating conditions of source temperatures 120-180°C and ionization energy of 70 eV. Elemental analyses (CHN) were performed at the UBC Microanalytical Services Laboratory. Melting points were obtained on a Fisher-John’s melting point apparatus and corrected according to the appropriate calibration.
Single crystal X-ray diffraction (SCXRD) experiments were performed on a Bruker X8 APEX CCD with MoKα radiation or a Bruker APEX DUO with MoKα or CuKα radiation as specified in Appendices D.12-D.14. Powder X-ray diffraction (PXRD) experiments were performed on a Bruker D8 Advance with CuKα sealed tube X-ray source and a NaI scintillation detector. PXRD pattern simulations were performed with the SCXRD data in the CCDC Mercury software. Thermogravimetric analysis data was obtained using a PerkinElmer Simultaneous Thermal Analyzer (STA) 6000. Gas (N2) adsorption data were obtained at 77 K using a Micromeritics ASAP 2010 analyzer.

4.4.2 Procedures and Data

4.4.2.1 Dimethyl Pentiptycene-6,13-ethynylphenyldicarboxylate (169)

A 100 mL schlenk flask was charged with 30 mL of diisopropylamine and 30 mL of toluene under a flow of nitrogen. The solvent was then purged of gases via the freeze-pump-thaw method. Once the solvent returned to room temperature compound 157 (1.035 g, 2.163 mmol), Pd(PPh3)4 (0.121 g, 0.104 mmol), CuI (0.038 g, 0.27 mol), and methyl p-iodobenzoate (1.663 g, 6.346 mmol) was added under N2 flow. The vessel was then sealed, and heated to 70-80 °C for 7 days. The mixture was cooled to room temperature and the solvent was removed by rotary evaporation. The brown residue was purified by column chromatography (1:1 DCM:Hexanes), resulting in a white solid (0.689 g, 44.1%).
Data for compound 169: mp: decomposed $> 300 \, ^\circ\text{C}$; $^1\text{H}$ NMR (400 MHz, CDCl$_3$) 4.03 (s, 6H), 5.89 (s, 4H), 6.98 (dd, $J = 5.3$ and 3.2 Hz, 8H), 7.41 (dd, $J = 5.3$ and 3.2 Hz, 8H), 7.87 (d, $J = 8.5$ Hz, 4H), 8.22 (d, $J = 8.5$ Hz, 4H) ppm; $^{13}\text{C}$ NMR (100 MHz, CDCl$_3$) 52.33, 52.39, 87.76, 96.17, 123.88, 15.40, 127.93, 129.84, 130.02, 131.73, 144.30 144.63, 166.52 ppm; MS $m/z$ (relative intensity) 746 (M$^+$, 100); IR 3066, 3043, 2966, 2945, 1718, 1603, 1457, 1431, 1403, 1381, 1275, 1173, 1105, 1017, 964, 854, 766, 751, 739, 692, 672, 600, 568, 526 (cm$^{-1}$); EA calc’d for 169, C$_{54}$H$_{34}$O$_4$: C, 86.84 %, H, 4.59 %. Found: C, 86.48 %, H, 4.57 %.

4.4.2.2 Pentiptycene-6,13-ethynlyphenyldicarboxylic Acid (150)

A 25 mL round-bottomed flask was charged with 10 mL THF and 5 mL H$_2$O. Compound 169 (0.302 g, 0.404 mmol) was added, followed by NaOH (0.801 g, 20.0 mmol). This mixture was allowed to stir and reflux at 110 $^\circ\text{C}$ overnight (12 hours). The reaction mixture was cooled to room temperature and 10 mL of H$_2$O was added to dissolve all solids. Conc. HCl$_{(aq)}$ was added by pipette until the solution was acidic (pH ~1) and white solid had precipitated. This white solid (0.261 g, 90 %) was collected by vacuum filtration and was washed with H$_2$O, MeOH, and hexanes.

Data for compound 150: mp: decomposed $> 300 \, ^\circ\text{C}$; $^1\text{H}$ NMR (400 MHz, CDCl$_3$) 6.04 (s, 4H), 6.99 (dd, $J = 5.1$ and 3.2 Hz, 8H), 7.53 (dd, $J = 5.4$ and 3.42 Hz, 8H), 8.17 (m, 8H), 13.30 (br, 2H) ppm; $^{13}\text{C}$ NMR (100 MHz, CDCl$_3$) 51.21, 86.11, 96.99, 113.84, 124.01, 125.39, 126.40, 129.61, 131.09, 132.34, 144.32, 166.81 ppm; MS $m/z$ (relative intensity) 582 ([M-H]$^-$, 100); IR 3065, 3019, 2891, 2678, 2540, 1687, 1607, 1458, 1434, 1312, 1292, 1173, 1151, 1125, 1019.
926, 851, 766, 755, 690, 672, 570, 553, 509, 447 (cm\(^{-1}\)); EA calc’d for \(150\cdot\frac{1}{2}\) H\(_2\)O, C\(_{52}\)H\(_{31}\)O\(_{4.5}\): C, 85.81 %, H, 4.29 %. Found: C, 85.98 %, H, 4.26 %.

### 4.4.2.3 PMOF-2a (170a)

A solution of \(150\) (0.0513 g, 0.0714 mmol) and Zn(NO\(_3\))\(_2\)\(\cdot\)6H\(_2\)O (0.0632 g, 0.212 mmol) in DMF (10 mL) was prepared and transferred to a 23 mL Teflon-lined autoclave by filtering the solution through a puck of celite. The reaction vessel was sealed and heated to 110 °C for 72 h. Programmed cooling (0.1 °C min\(^{-1}\) from 110 °C to 25 °C) afforded a clear, yellow solution with white crystalline solids (0.045 g, 0.014 mmol, 74%). Single crystals suitable for X-ray diffraction were isolated and used in structural elucidation of PMOF-2a (171a).

Data for PMOF-2a: IR (cm\(^{-1}\)) 3411, 2929, 2359, 2335, 1651, 1601, 1548, 1457, 1381, 1320, 1253, 1195, 1175, 1150, 1093, 1016, 864, 845, 801, 781, 754, 697, 673, 660, 600, 569, 515, 482.

### 4.4.2.4 PMOF-2b (170b)

A solution of \(150\) (0.0498 g, 0.0692 mmol) and Zn(NO\(_3\))\(_2\)\(\cdot\)6H\(_2\)O (0.0624 g, 0.210 mmol) in DMF (5 mL) and chlorobenzene (5 mL) was prepared and transferred to a 23 mL Teflon-lined autoclave by filtering the solution through a puck of celite. The reaction vessel was sealed and heated to 110 °C for 72 h. Programmed cooling (0.1 °C min\(^{-1}\) from 110 °C to 25 °C) afforded a
clear, yellow solution with white crystalline solids (0.029 g, 0.0096 mmol, 55%). Single crystals suitable for X-ray diffraction were isolated and used in structural elucidation of PMOF-2b (171b).

Data for PMOF-2b: IR (cm\(^{-1}\)) 3418, 2929, 1651, 1601, 1548, 1457, 1379, 1320, 1254, 1195, 1176, 1150, 1093, 1016, 864, 845, 781, 754, 697, 673, 6000, 568, 514, 486.

4.4.2.5 PMOF-3 (171)

A solution of 150 (0.0487 g, 0.0678 mmol), 42 (0.0135 g, 0.086 mmol), and Zn(NO\(_3\))\(_2\)•6H\(_2\)O (0.0679 g, 0.228 mmol) in DMF (5 mL) and chlorobenzene (5 mL) was prepared and transferred to a 23 mL Teflon-lined autoclave by filtering the solution through a puck of celite. The reaction vessel was sealed and heated to 110 °C for 72 h. Programmed cooling (0.1 °C min\(^{-1}\) from 110 °C to 25 °C) afforded a clear, yellow solution with yellow crystalline solids (0.034 g, 0.0049 mmol, 58%). Single crystals suitable for X-ray diffraction were isolated and used in structural elucidation of PMOF-3 (172). Confirmation of structure uniformity throughout the bulk sample was performed using PXRD.

Data for PMOF-3: IR (cm\(^{-1}\)) 3431, 2971, 1651, 1645, 1603, 1551, 1457, 1403, 1384, 1174, 1094, 864, 781, 747, 673, 568, 487.

4.4.2.6 Dimethyl Triptycene-1,4-ethynylphenyldicarboxylate (173)

A 25 mL schlenk flask was charged with 5 mL of diisopropylamine and 5 mL of toluene under a flow of nitrogen. The solvent was then purged of gases via the freeze-pump-thaw method.
Once the solvent returned to room temperature compound 172 (0.450 g, 1.49 mmol), Pd(PPh$_3$)$_4$ (0.088 g, 0.076 mmol), CuI (0.016 g, 0.11 mol), and methyl p-iodobenzoate (1.158 g, 4.42 mmol) was added under N$_2$ flow. The vessel was then sealed, and heated to 70-80 °C for 6 days. The mixture was cooled to room temperature and the solvent was removed by rotary evaporation. The brown residue was purified by column chromatography (1:1 DCM:Hexanes), resulting in a white solid (0.306 g, 36.0 %).

Data for compound 173: mp: decomposed > 300 °C; $^1$H NMR (400 MHz, CDCl$_3$) 3.98 (s, 6H), 5.99 (s, 2H), 7.06 (dd, $J = 5.5$ and 3.1 Hz, 4H), 7.19 (s, 2H), 7.49 (dd, $J = 5.5$ and 3.1 Hz, 4H), 7.73 (d, $J = 8.5$ Hz, 4H), 8.13 (d, $J = 8.5$ Hz, 4H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) 51.87, 52.01, 85.99, 93.08, 118.12, 123.80, 125.25, 127.58, 127.81, 129.38, 129.53, 131.31, 144.09, 147.19, 166.21 ppm; MS $m/z$ (relative intensity) 582 (M$^+$, 100); IR 3070, 3044, 2993, 2948, 1705, 1601, 1510, 1456, 1438, 1429, 1403, 1279, 1190, 1171, 1107, 1016, 966, 856, 814, 788, 747, 696, 683, 546, 478, 451 (cm$^{-1}$); EA calc’d for 173, C$_{40}$H$_{26}$O$_4$: C, 84.19 %, H, 4.59 %. Found: C, 83.95 %, H, 4.48 %.

4.4.2.7 Triptycene-1,4-ethynylphenyldicarboxylic Acid (149)

A 25 mL round-bottomed flask was charged with 7 mL THF and 3 mL H$_2$O. Compound 173 (0.261 g, 0.457 mmol) was added, followed by NaOH (0.447 g, 11.2 mmol). This mixture was allowed to stir and reflux at 110 °C overnight (12 hours). The reaction mixture was cooled to room temperature and 10 mL of H$_2$O was added to dissolve all solids. Conc. HCl(aq) was added by pipette until the solution was acidic (pH ~1) and white solid had precipitated. This white solid
(0.226 g, 91 %) was collected by vacuum filtration and was washed with H₂O, MeOH, and hexanes.

Data for compound 149: mp: decomposed > 300 °C; ¹H NMR (400 MHz, DMSO-d₆) 6.13 (s, 2H), 7.07 (dd, J = 5.4 and 2.9 Hz, 4H), 7.30 (s, 2H), 7.61 (dd, J = 5.4 and 2.9 Hz, 4H), 7.93 (d, J = 8.3 Hz, 4H), 8.07 (d, J = 8.3 Hz, 4H), 13.23 (br, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) 51.08, 88.78, 93.84, 117.77, 124.24, 125.58, 126.35, 128.16, 129.61, 130.93, 131.99, 144.13, 147.58, 166.73 ppm; MS m/z (relative intensity) 541([M-H]⁻, 100); IR 3072, 3018, 2974, 2666, 2533, 1661, 1604, 1425, 1314, 1293, 1171, 1018, 940, 854, 821, 768, 704, 690, 640, 558, 520, 493 (cm⁻¹); EA calc’d for 149•1/3 H₂O, C₃₈H₂₂.₆₇O₄.₃₃: C, 84.20 %, H, 4.16 %. Found: C, 83.26 %, H, 4.09 %.

4.4.2.8 TMOF-5 (174)

A solution of 149 (0.0511 g, 0.0942 mmol) and Zn(NO₃)₂•6H₂O (0.0839g, 0.282 mmol) in DMF (10 mL) was prepared and transferred to a 23 mL Teflon-lined autoclave by filtering the solution through a puck of celite. The reaction vessel was sealed and heated to 110 °C for 72 h. Programmed cooling (0.1 °C min⁻¹ from 110 °C to 25 °C) afforded a clear, yellow solution with white crystalline solids (0.051 g).

Data for TMOF-5: IR (cm⁻¹) 2929, 1659, 1601, 1544, 1476, 1458, 1406, 1385, 1252, 1175, 1161, 1093, 1016.862, 808, 780, 707, 639, 587, 517, 474.
4.4.3 Crystallography

Complete SCXRD refinement details may be found in Appendix D.12-D.14.107

4.4.3.1 PMOF-2a (170a)

Crystal data for PMOF-2a: C_{52}H_{30}O_{5}Zn, 800.15 g mol^{-1}; monoclinic, space group: C 2/m, a = 17.128(8) Å, b = 35.003(16) Å, c = 11.620(5) Å, α = 90°, β = 119.498(5)°, γ = 90°, V = 6064(5) Å³, Z = 4, T = 90(2) K, F(000) = 1648, ρ_{calcd} = 0.876 g cm^{-3}, μ(Mo Kα) = 0.438 mm^{-1} (λ = 0.71073 Å), 15801 measured reflections, 5093 independent reflections (R_{int} = 0.076), 266 refined parameters, R₁ = 0.0904 for I > 2σ(I), and wR₂ = 0.2537, GOF = 0.9876.

4.4.3.2 PMOF-2b (170b)

Crystal data for PMOF-2b: C_{55}H_{35}NO_{5}Zn, 855.23 g mol^{-1}; monoclinic, space group: P 2_{1}/n, a = 11.5165(9) Å, b = 33.108(3) Å, c = 15.3490(14) Å, α = 90°, β = 103.074(6)°, γ = 90°, V = 5700.7(9) Å³, Z = 4, T = 90(2) K, F(000) = 1768, ρ_{calcd} = 0.997 g cm^{-3}, μ(Cu Kα) = 0.909 mm^{-1} (λ = 1.54178 Å), 57455 measured reflections, 8245 independent reflections (R_{int} = 0.085), 559 refined parameters, R₁ = 0.0747 for I > 2σ(I), and wR₂ = 0.1986, GOF = 0.9929.
4.4.3.3  PMOF-3 (171)

Crystal data for PMOF-3: C_{234}H_{142}N_{8}O_{24}Zn_{5}, 3776.50 g mol\(^{-1}\); triclinic, space group: P-1, a = 17.2471(19) Å, b = 18.932(3) Å, c = 21.340(2) Å, α = 88.588(10)°, β = 73.431(7)°, γ = 66.759(8)°, V = 6106.1(14) Å\(^3\), Z = 1, T = 90(2) K, F(000) = 1944, \(\rho_{\text{calc}} = 1.027\) g cm\(^{-3}\), \(\mu(\text{Cu K}\alpha) = \)1.003 mm\(^{-1}\) (\(\lambda = 1.54178\) Å), 12477 measured reflections, 8955 independent reflections (\(R_{\text{int}} = 0.080\)), 1222 refined parameters, \(R_1 = 0.1673\) for I > 2σ(I), and \(wR_2 = 0.3903\), GOF = 0.9888.
Chapter 5: Conclusions

Throughout this work, the overall goal was to synthesize new iptycene-containing MOFs as potential candidates for gas adsorption and hydrogen gas storage. The design of the ligands was simple: to incorporate triptycene and pentiptycene moieties into the ligands, and therefore along the edges of the framework. In doing so, it was hoped that enhanced properties such as high crystallinity, stability, pore sizes and surface areas would result. The iptycenyl clefts would add a structure-directing element to the framework, causing pore channels to open, while also providing additional aromatic adsorption sites. Later, extension of the molecular dicarboxylate axis was investigated in order to alleviate some of the steric crowding of the MOFs. This was carried out using additional aromatic rings linked through both flexible and rigid spacers. In these cases, resulting frameworks were found to be more open, consisting of large areas of void space. Unfortunately, these materials were also found to be interpenetrated and densely packed, eliminating the pore structure observed in a single framework.

Strategies used to complete this research focused on attempting to create a rational-design protocol for each framework. After synthesizing TMOF-1, it was decided that moving from vapour diffusion to solvothermal reaction conditions would be advantageous due to improved reproducibility and reaction yields. This then allowed for the production of crystalline TMOF-2 in bulk quantities. TMOF-2 was studied by SCXRD, PXRD, TGA and nitrogen adsorption experiments, and was found to be a mixture of isomorphic MOFs consisting of a pseudo-[Zn₄O]⁶⁺ cluster. The material proved to be stable in air, upon solvent removal from the pores, and up to
415°C. Unfortunately, the material showed a low surface area likely due to the blockage of pore channels by the bulky iptycenyl clefts.

In an effort to overcome this steric crowding within the framework extension along the dicarboxylate molecular axis was achieved. The first attempt to do so was with oxymethylene spacers and additional aromatic rings. The rationale behind this design was to provide additional areas of aromaticity while increasing the edge length with a flexible moiety. The advantage of a flexible moiety was to give rise to the possibility of forming a “breathable MOF”, whereby structural transformations take place in the solid state to incorporate guest molecules. Using a triptycene-based ligand, TMOF-3 was synthesized as a 1-D chain of ligands coordinated to a dimethylamine-capped square paddlewheel SBU. Due to the flexibility of the ligands, this chain had an internal square pore. Layers of these 1-D chains then packed into an open lattice with space accessible to guest molecules. The stability of this material was investigated, it was found that the structure underwent contraction, but not collapse, upon solvent removal and was thermally stable up to 400 °C. Since dimethylamine is a decomposition product of the DMF solvent used at high temperature, reproducibility in this synthesis proved to be problematic.

To overcome the formation of lower dimensional frameworks, a ditopic bridging ligand, 4,4´-bipyrididine, was used to displace capping ligands in the square paddlewheel SBU with pillars between adjacent chains. This led to the formation of TMOF-3-bipy. Once again, the triptycene containing flexible ligand have a set of 1-D chains with a trigonal bipyramidal SBU. In this case however, in place of a monodentate capping ligand was the ditopic pillaring ligand. This gave rise to an overall 2-D structure with long range ordering of the zig-zag sheets.

Still unsatisfied with the formation of 1-D and 2-D frameworks, a different solvent system was used in an attempt to dilute the concentration of coordinating solvent in the reaction solution.
This could discourage the formation of solvent-containing SBUs, like those previously observed with the iptycene ligands. The resulting material TMOF-4 was synthesized and showed a \([\text{Zn}_7\text{(OH)}_3]^{11+}\) SBU supporting 12 triptycene-containing ligands in a double-strutted octahedral fashion. This remarkable 3-D structure had large pores accessible; unfortunately, the structure also displayed two-fold interpenetration, lowering the amount of space available for guest molecules.

Shifting toward the pentaptycene-containing flexible ligand, the first pentaptycene-containing MOF, PMOF-1 was successfully synthesized. In this framework, pseudo-\([\text{Zn}_4\text{O}]^{6+}\) clusters were present much like those observed in TMOF-2, giving a 3-D structure. All pore space within this structure was filled, as it exhibited three-fold interpenetration, leading to a densely packed material. Furthermore, this material was found to collapse upon solvent exchange from DMF to DCM. This can be linked to the presence of flexible moieties that allow for the ligands to contract irreversibly upon solvent removal. Lastly, as observed in TMOF-2, reproducibility in the synthesis of this material proved to be a challenge.

To combat issues of framework collapse a final set of ligands was synthesized, this time using a rigid ethynyl spacer between aromatic rings. Using the pentaptycene analogue, PMOF-2a and PMOF-2b were synthesized and characterized as 2-D grid-like sheets resulting from a dinuclear-zinc square paddlewheel SBU with DMF and H\(_2\)O capping, respectively. Each sheet had 24.8 Å x 24.8 Å square pores that were blocked by adjacent sheets as the material exhibited a layered A-B-C packing motif. An attempt at increasing the dimensionality of the framework by bridging the 2-D sheets with 4,4’-bipyridine proved successful and PMOF-3 was synthesized. In this framework alternating square paddlewheel SBUs and \([\text{Zn}_3\text{(DMF)}_2\text{(NO}_3)_2]^{14+}\) clusters were created a grid-like 2-D sheet that was then pillared to give an overall 3-D framework with a 24.8 Å x 24.8 Å x 11.0 Å rectangular pore. Stability studies were carried out on each of these materials.
Fortunately, each framework was thermally stable up to 400°C, however loss of crystallinity was observed upon solvent exchange from DMF to DCM.

Finally, a robust material TMOF-5 was synthesized using the triptycene-containing rigid ligand. Thermally stable up to 425 °C and able to undergo solvent exchange from DMF to DCM, this material gave a PXRD pattern that suffered from peak broadening, likely due to small crystallite size and non-uniform lattice defects. However, in the absence of SCXRD data, hexagonal lattice packing was identified as the overall framework topology through fitting of the PXRD peaks. While none of the TMOF and PMOF structures elucidated to date have shown this topology, it is known that longer ligands tend to adopt a hexagonal framework rather than the simple cubic network of MOF-5.

Throughout this project, many challenges of MOF synthesis were faced and approached using these rational design methods. Often, altering the reaction conditions by changing the solvent system or using a mixed ligand tactic could increase the dimensionality of a framework, creating collections of structurally similar MOFs. Other problems, such as synthesis reproducibility and scale-up, remain a challenge. For these issues, dedication to detail and perseverance were often the best tactics.
References


8 US Department of Transportation Federal Highway Administration, Policy Information: Highway Finance Data and Information, Figure 4-5. Percent of Trips and Vehicle Miles by Trip Length. http://www.fhwa.dot.gov/policyinformation/pubs/pl08021/fig4_5.cfm (accessed May 7, 2014).


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Appendices

Appendix A - $^1$H NMR Spectra

A.1 1,4-Dimethyltriptycene (152)

$^1$H NMR spectrum of 1,4-dimethyltriptycene, 152 (CDCl$_3$, 298K). The peak at 1.538 ppm is residual water in the solvent.
A.2 Triptycene-1,4-dicarboxylic Acid (145)

$^1$H NMR spectrum of triptycene-1,4-dicarboxylic acid, 145 (DMSO-$d_6$, 298K). The peak at 3.36 ppm is residual water and 2.54 ppm is residual dimethyl sulfoxide in the solvent.
A.3 Dimethyl Triptycene-1,4-benzyloxydicarboxylate (162)

\[ \text{CO}_2\text{CH}_3 \]

\[ \text{CHLOROFORM-d} \]

1H NMR spectrum of dimethyl triptycene-1,4-benzyloxydicarboxylate, 162 (CDCl\textsubscript{3}, 298K). The peak at 1.589 ppm is residual water in the solvent.
A.4 Triptycene-1,4-benzyloxydicarboxylic Acid (147)

\[ \text{Chemical Shift (ppm)} \\
\text{DMSO-d}_6 \\
2.495 \quad 2.500 \quad 2.504 \\
3.348 \\
5.196 \\
5.964 \\
6.703 \\
7.008 \\
7.454 \\
7.604 \\
7.625 \\
7.954 \\
7.975 \\
12.920 \\
\]

\(^1\text{H NMR spectrum of triptycene-1,4-benzyloxydicarboxylic acid, 147 (DMSO-d}_6, 298K). The peak at 3.348 ppm is residual water and 2.54 ppm is residual dimethyl sulfoxide in the solvent.\)
A.5 Dimethyl Pentiptycene-6,13-benzyloxydicarboxylate (166)

\[ \text{Chemical Shift (ppm) } \]

\[ \text{DICHLOROMETHANE-d}_2 \]

- 1.576
- 3.989
- 5.058
- 5.320
- 5.678
- 6.930
- 6.937
- 6.942
- 6.950
- 7.251
- 7.260
- 7.265
- 7.272
- 7.760
- 7.780
- 8.214
- 8.234

\[ \text{H NMR spectrum of dimethyl pentiptycene-6,13-benzyloxydicarboxylate, 166 (CD}_2\text{Cl}_2, 298\text{K).} \]

\[ \text{The peak at 1.576 ppm is residual water in the solvent.} \]
A.6 Pentiptycene-6,13-benzyloxydicarboxylic Acid (148)

![Chemical Structure of 148](image)

$^1$H NMR spectrum of pentiptycene-6,13-benzyloxydicarboxylic acid, 148 (DMSO-$d_6$, 298K). The peak at 3.3-3.4 ppm is residual water and 2.5 ppm is residual dimethyl sulfoxide in the solvent.
A.7 Dimethyl Triptycene-1,4-ethynylphenylidicarboxylate (173)

\[ \text{Chemical Shift (ppm)} \]

1H NMR spectrum of dimethyl triptcnye-1,4-ethynylphenylidicarboxylate, 173 (CDCl\textsubscript{3}, 298K).

The peak at 1.538 ppm is residual water in the solvent.
A.8 Triptycene-1,4-ethynylphenyldicarboxylic Acid (149)

The peak at 3.3-3.4 ppm is residual water and 2.5 ppm is residual dimethyl sulfoxide in the solvent.
A.9 Dimethyl Pentiptycene-6,13-ethynylphenyldicarboxylate (169)

The peak at 1.538 ppm is residual water in the solvent.
A.10 Pentiptycene-6,13-ethynylphenyldicarboxylic Acid (150)

\[
\begin{align*}
&\text{CO}_2\text{H} \\
&\text{CO}_2\text{H}
\end{align*}
\]

1H NMR spectrum of pentiptycene-6,13-ethynylphenyldicarboxylic acid, 150 (DMSO-\text{d}_6, 298K). The peak at 3.3-3.4 ppm is residual water and 2.5 ppm is residual dimethyl sulfoxide in the solvent.
Appendix B - $^{13}$C NMR Spectra

B.1 1,4-Dimethyltriptycene (152)

$^{13}$C NMR spectrum of 1,4-dimethyltriptycene, 152 (CDCl$_3$, 298K).
B.2 Triptycene-1,4-dicarboxylic Acid (145)

$\text{CO}_2\text{H}$

145

$\text{CO}_2\text{H}$

$^{13}$C NMR spectrum of triptycene-1,4-dicarboxylic acid, 145 (DMSO-$d_6$, 298K).
B.3 Dimethyl Triptycene-1,4-benzylxydicarboxylate (162)

\[ \begin{array}{c}
\text{CO}_2\text{CH}_3 \\
\text{O} \\
\text{O} \\
\text{CO}_2\text{CH}_3 \\
\end{array} \]

Chemical Shift (ppm):

- 47.200
- 51.822
- 70.402
- 76.361
- 76.681
- 77.000
- 110.403
- 123.478
- 124.755
- 126.595
- 129.575
- 135.824
- 142.392
- 145.129
- 147.911
- 166.536

13C NMR spectrum of dimethyl triptycene-1,4-benzylxydicarboxylate, 162 (CDCl₃, 298K).
B.4 Triptycene-1,4-benzyloxydicarboxylic Acid (147)

13C NMR spectrum of triptycene-1,4-benzyloxydicarboxylic acid, 147 (DMSO-d6, 298K).
B.5 Dimethyl Pentiptycene-6,13-benzyloxydicarboxylate (166)

\[
\text{\begin{tabular}{c}
\text{CO}_2\text{CH}_3 \\
\text{O} \\
\text{162} \\
\text{CO}_2\text{CH}_3
\end{tabular}}
\]

\[13^C\text{ NMR spectrum of dimethyl pentiptycene-6,13-benzyloxydicarboxylate, 162 (CD}_2\text{Cl}_2, 298K).\]

169
B.6 Pentiptycene-6,13-benzyloxydicarboxylic Acid (148)

\[ \text{\begin{center}
\includegraphics[width=\textwidth]{148_pentiptycene.png}
\end{center}} \]

\[ ^{13} \text{C NMR spectrum of pentiptycene-6,13-benzyloxydicarboxylic acid, 148 (DMSO-d6, 298K).} \]
B.7  Dimethyl Triptycene-1,4-ethynylphenyldicarboxylate (173)

\[ \text{CO}_2\text{CH}_3 \]

13C NMR spectrum of dimethyl triptycene-1,4-ethynylphenyldicarboxylate, 173 (CDCl\(_3\), 298K).
B.8 Triptycene-1,4-ethynylphenyl dicarboxylic Acid (149)

\[
\begin{align*}
\text{CO}_2\text{H} & \quad \text{CO}_2\text{H} \\
\text{149} & \\
\end{align*}
\]

$^{13}$C NMR spectrum of triptycene-1,4-ethynylphenyl dicarboxylic acid, 174 (DMSO-$d_6$, 298K).
B.9  Dimethyl Pentiptycene-6,13-ethynylphenyldicarboxylate (169)

13C NMR spectrum of dimethyl pentiptycene-6,13-ethynylphenyldicarboxylate, 169 (CDCl3, 298K).
B.10 Pentiptycene-6,13-ethynylphenyldicarboxylic Acid (150)

$\text{CO}_2\text{H}$

150

$\text{CO}_2\text{H}$

$^{13}$C NMR spectrum of pentiptycene-6,13-ethynylphenyldicarboxylic acid, 150 (DMSO-$d_6$, 298K).
Appendix C - IR Spectra

C.1 1,4-Dimethyltriphyene (152)

IR spectrum of 1,4-dimethyltriphyene, 152.
C.2 Triptycene-1,4-dicarboxylic Acid (145)

IR spectrum of triptycene-1,4-dicarboxylic acid, 145.
IR spectrum of bulk TMOF-2 after dried under vacuum at 120 °C.
C.4 Dimethyl Triptycene-1,4-benzyloxydicarboxylate (162)

IR spectrum of dimethyl triptycene-1,4-benzyloxydicarboxylate, 162.
C.5 Triptycene-1,4-benzyloxydicarboxylic Acid (147)

IR spectrum of triptycene-1,4-benzyloxydicarboxylic acid, 147.
C.6 TMOF-3 (163)

IR spectrum of bulk TMOF-3 after being dried under vacuum at 120 °C.
IR spectrum of bulk TMOF-3-\textit{bipy} after being dried under vacuum at 120 °C.
IR spectrum of bulk TMOF-4 after being dried under vacuum at 120 °C.
C.9 Dimethyl Pentiptycene-6,13-benzyloxydicarboxylate (166)

IR spectrum of dimethyl pentiptycene-6,13-benzyloxydicarboxylate, 166.
C.10 Pentiptycene-6,13-benzyloxydicarboxylic Acid (148)

IR spectrum of pentiptycene-6,13-benzyloxydicarboxylic acid, 148.
IR spectrum of bulk PMOF-1 after being dried under vacuum at 120 °C.
C.12 Dimethyl Triptycene-1,4-ethynylphenyldicarboxylate (173)

IR spectrum of dimethyl triptycene-1,4-ethynylphenyldicarboxylate, 173.
C.13 Triptycene-1,4-ethynlyphentldicarboxylic Acid (149)

IR spectrum of triptycene-1,4-ethynlyphenyldicarboxylic acid, 149.
IR spectrum of bulk TMOF-5 as synthesized.
C.15 Dimethyl Pentiptycene-6,13-ethynylphenyldicarboxylate (169)

IR spectrum of dimethyl pentiptycene-6,13-ethynylphenyldicarboxylate, 169.
C.16 Pentiptycene-6,13-ethynlyphenyldicarboxylic Acid (150)

IR spectrum of pentiptycene-6,13-ethynlyphenyldicarboxylic acid, 150.
IR spectrum of bulk PMOF-2a as synthesized.
C.18 PMOF-2b (170b)

IR spectrum of bulk PMOF-2b as synthesized.
IR spectrum of bulk PMOF-2b as synthesized.
Appendix D - Crystallographic Data

D.1 TMOF-1 (153)

Crystals of TMOF-1 suitable for X-ray diffraction were grown by slow vapour-diffusion occurred over 2 months. A suitable crystal of TMOF-1 was mounted on a glass fibre with oil by Dr. Peter Frischmann. All measurements were made on a Bruker X8 APEX diffractometer at 173 ± 1 K using graphite monochromated Mo Kα radiation (0.71073 Å). Data were collected to a maximum 20 value of 30.09° in a series of φ and ω scans in 0.50° oscillations with 20 s exposures. Of the 189824 reflections that were collected, 57091 were unique (R_int = 0.072); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package. Data were corrected for absorption effects using a multi-scan technique (SADABS), with max and min transmission coefficients of 0.809 and 0.483, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods by Dr. Peter Frischmann. Structure solutions were refined using the SHELXL software by Angela Crane, Dr. Brian Patrick and Dr. Peter Frischmann. Disorder and partial occupancy is present in solvent DMF molecules and water molecules filling the void space left by the porous structure. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions but not refined. The final cycle of full matrix least-squares refinement on F^2 was based on 57091 reflections and 2299 variable parameters and converged (largest parameter shift was 9.883 per esd).
D.2 TMOF-2a (154a)

Crystals of TMOF-2a suitable for X-ray diffraction were grown by slowly cooling a dimethylformamide solution heated to 110 °C in a sealed Parr pressure vessel. A suitable crystal of TMOF-2a was mounted on a glass fibre with oil by Dr. Peter Frischmann. All measurements were made on a Bruker APEX DUO diffractometer at 183 ± 1 K using graphite monochromated Mo Kα radiation (0.71073 Å). Data were collected to a maximum 2θ value of 22.52° in a series of φ and ω scans in 0.50° oscillations with 60 s exposures. Of the 32208 reflections that were collected, 10441 were unique (R_{int} = 0.087); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package.\textsuperscript{107(b)} Data were corrected for absorption effects using a multi-scan technique (SADABS),\textsuperscript{107(c)} with max and min transmission coefficients of 0.996 and 0.858, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods\textsuperscript{107(d)} by Dr. Peter Friscmann. Structure solutions were refined using the SHELXL software\textsuperscript{107(a)} by Angela Crane and Dr. Peter Frischmann. Disorder is present in solvent DMF molecules filling the void space left by the porous structure. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions but not refined. The final cycle of full matrix least-squares refinement on F^2 was based on 10441 reflections and 1111 variable parameters and converged (largest parameter shift was 5.314 per esd).
D.3 TMOF-2b (154b)

Crystals of TMOF-2b suitable for X-ray diffraction were grown by slowly cooling a dimethylformamide solution heated to 110 °C in a sealed Parr pressure vessel. A suitable crystal of TMOF-2b was mounted on a glass fibre with oil by Angela Crane. All measurements were made on a Bruker APEX DUO diffractometer at 183 ± 1 K using graphite monochromated Mo Kα radiation (0.71073 Å). Data were collected to a maximum 2θ value of 26.32° in a series of φ and ω scans in 0.50° oscillations with 30 s exposures. Of the 119076 reflections that were collected, 31729 were unique (R_int = 0.072); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package. Data were corrected for absorption effects using a multi-scan technique (SADABS), with max and min transmission coefficients of 0.975 and 0.813, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods by Dr. Brian Patrick. Structure solutions were refined using the SHELXL software by Angela Crane and Dr. Brian Patrick. All non-hydrogen atoms were refined anisotropically. Disorder is present in solvent DMF molecules filling the void space left by the porous structure. All hydrogen atoms were included in calculated positions but not refined. The final cycle of full matrix least-squares refinement on F² was based on 31729 reflections and 1914 variable parameters and converged (largest parameter shift was 0.107 per esd).
D.4 TMOF-2c (154c)

Crystals of TMOF-2c suitable for X-ray diffraction were grown by slowly cooling a
dimethylformamide solution heated to 110 °C in a sealed Parr pressure vessel. A suitable crystal
of TMOF-2c was mounted on a glass fibre with oil by Angela Crane. All measurements were
made on a Bruker APEX DUO diffractometer at 183 ± 1 K using graphite monochromated Cu Kα
radiation (1.54178 Å). Data were collected to a maximum 2θ value of 67.17° in a series of φ and
ω scans in 0.50° oscillations with 20 s exposures. Of the 178548 reflections that were collected,
29024 were unique (R_int = 0.054); equivalent reflections were merged. Data were collected and
integrated using the Bruker SAINT software package.\textsuperscript{(b)} Data were corrected for absorption
effects using a multi-scan technique (SADABS),\textsuperscript{(c)} with max and min transmission coefficients
of 0.813 and 0.725, respectively. The data were corrected for Lorentz and polarization effects. The
structure was solved by direct methods\textsuperscript{(d)} by Dr. Brian Patrick. Structure solutions were refined
using the SHELXL software\textsuperscript{(a)} by Angela Crane and Dr. Brian Patrick. Disorder and partial
occupancy is present in solvent DMF molecules filling the void space left by the porous structure.
All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in
calculated positions but not refined. The final cycle of full matrix least-squares refinement on F²
was based on 29024 reflections and 1109 variable parameters and converged (largest parameter
shift was 0.128 per esd).
D.5 Dimethyl Triptycene-1,4-benzyloxydicarboxylate (162)

Crystals of 162 suitable for X-ray diffraction were grown by slow evaporation from DCM/hexanes. A suitable crystal of 162 was mounted on a glass fibre with oil by Angela Crane. All measurements were made on a Bruker APEX DUO diffractometer at 90 ± 2 K using graphite monochromated Mo Kα radiation (0.71073 Å). Data were collected to a maximum 2θ value of 60.078° in a series of φ and ω scans in 0.50° oscillations with 3 s exposures. Of the 33845 reflections that were collected, 4253 were unique (Rint = 0.0328); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package.\(^\text{107(b)}\) Data were corrected for absorption effects using a multi-scan technique (SADABS),\(^\text{107(c)}\) with max and min transmission coefficients of 1.0090 and 0.9674, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods\(^\text{107(d)}\) by Dr. Brian Patrick. Structure solutions were refined using the SHELXL software\(^\text{107(a)}\) by Angela Crane. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions but not refined. The final cycle of full matrix least-squares refinement on F^2 was based on 4253 reflections and 200 variable parameters and converged. (largest parameter shift was 0.001 per esd).
D.6 Triptycene-1,4-benzylxydicarboxylic Acid (147)

Crystals of 147 suitable for X-ray diffraction were grown by slow evaporation from THF. A suitable crystal of 147 was mounted on a glass fibre with oil by Joanna De Witt and Dr. Brian Patrick. All measurements were made on a Bruker APEX DUO diffractometer at 90 ± 2 K using graphite monochromated Mo Kα radiation (0.71073 Å). Data were collected to a maximum 2θ value of 58.39° in a series of φ and ω scans in 0.50° oscillations with 20 s exposures. Of the 107574 reflections that were collected, 33613 were unique (R_{int} = 0.0352); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package.\(^{107(b)}\) Data were corrected for absorption effects using a multi-scan technique (SADABS),\(^{107(c)}\) with max and min transmission coefficients of 1.015 and 0.833, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods\(^ {107(d)}\) by Joanna De Witt and Dr. Brian Patrick. Structure solutions were refined using the SHELXL software\(^ {107(a)}\) by Joanna De Witt and Angela Crane. Disorder and partial occupancy is present in solvent THF molecules filling the void space left by the porous structure. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions but not refined. The final cycle of full matrix least-squares refinement on F^2 was based on 33613 reflections and 1767 variable parameters and converged. (largest parameter shift was 0.001 per esd).
D.7 TMOF-3 (163)

Crystals of TMOF-3 suitable for X-ray diffraction were grown by slow cooling a DMF solution of 147 and Zn(NO₃)₂•6H₂O in a sealed Parr pressure vessel. A suitable crystal of TMOF-3 was mounted on a glass fibre with oil by Angela Crane. All measurements were made on a Bruker APEX DUO diffractometer at 90 ± 2 K using graphite monochromated Mo Kα radiation (0.71073 Å). Data were collected to a maximum 2θ value of 51.08° in a series of φ and ω scans in 0.50° oscillations with 30 s exposures. Of the 26585 reflections that were collected, 8086 were unique (Rint = 0.0543); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package.¹⁰⁷(b) Data were corrected for absorption effects using a multi-scan technique (SADABS),¹⁰⁷(c) with max and min transmission coefficients of 0.9526 and 0.8142, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods¹⁰⁷(d) by Dr. Brian Patrick. Structure solutions were refined using the SHELXL software¹⁰⁷(a) by Angela Crane. Disorder and partial occupancy is present in framework and solvent DMF and water molecules filling the void space left by the porous structure. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions but not refined. The final cycle of full matrix least-squares refinement on F² was based on 8086 reflections and 604 variable parameters and converged. (largest parameter shift was 0.001 per esd).
D.8 TMOF-3-bipy (164)

Crystals of TMOF-3-bipy suitable for X-ray diffraction were grown by slow cooling a DMF solution of 147, 4,4′-bipyridine, and Zn(NO₃)₂•6H₂O in a sealed Parr pressure vessel. A suitable crystal of TMOF-3-bipy was mounted on a glass fibre with oil by Angela Crane. All measurements were made on a Bruker APEX DUO diffractometer at 90 ± 2 K using graphite monochromated Cu Kα radiation (1.54178 Å). Data were collected to a maximum 2θ value of 131.305° in a series of φ and ω scans in 0.50° oscillations with 5 s exposures. Of the 41065 reflections that were collected, 15214 were unique (R_{int} = 0.0629); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package.¹⁰⁷(b) Data were corrected for absorption effects using a multi-scan technique (SADABS),¹⁰⁷(c) with max and min transmission coefficients of 0.6786 and 0.5143, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods¹⁰⁷(d) by Dr. Brian Patrick. Structure solutions were refined using the SHELXL software¹⁰⁷(a) by Angela Crane. Disorder and partial occupancy is present in the framework and solvent DMF, chlorobenzene, and water molecules filling the void space left by the porous structure. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions but not refined. The final cycle of full matrix least-squares refinement on F² was based on 15214 reflections and 1358 variable parameters and converged. (largest parameter shift was 0.030 per esd).
D.9 TMOF-4 (165)

Crystals of TMOF-4 suitable for X-ray diffraction were grown by slow cooling a 1:1 DMF:PhCl solution of 147 and Zn(NO$_3$)$_2$•6H$_2$O in a sealed Parr pressure vessel. A suitable crystal of TMOF-4 was mounted on a glass fibre with oil by Angela Crane. All measurements were made on a Bruker APEX DUO diffractometer at 90 ± 2 K using graphite monochromated Cu K$\alpha$ radiation (1.54178 Å). Data were collected to a maximum 2θ value of 112.605° in a series of φ and ω scans in 0.50° oscillations with 120 s exposures. Of the 8726 reflections that were collected, 8726 were unique ($R_{\text{int}} = 0.000$); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package.$^{107(b)}$ Data were corrected for absorption effects using a multi-scan technique (SADABS),$^{107(c)}$ with max and min transmission coefficients of 1.193 and 0.854, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods$^{107(d)}$ by Dr. Brian Patrick. Electron density resulting from disordered solvent molecules was removed using an OLEX$^{120}$ solvent mask. Structure solutions were refined using the SHELXL software$^{107(a)}$ by Angela Crane. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions but not refined. The final cycle of full matrix least-squares refinement on F$^2$ was based on 8726 reflections and 788 variable parameters and converged. (largest parameter shift was 0.000 per esd).
D.10 Pentiptycene-6,13-benzyloxydicarboxylic Acid (148)

Crystals of 148 suitable for X-ray diffraction were grown by slow evaporation from THF/hexanes. A suitable crystal of 148 was mounted on a glass fibre with oil by Angela Crane. All measurements were made on a Bruker X8 APEX CCD diffractometer at 100 ± 2 K using graphite monochromated Mo Kα radiation (0.71073 Å). Data were collected to a maximum 2θ value of 54.97° in a series of φ and ω scans in 0.50° oscillations with 10 s exposures. Of the 23637 reflections that were collected, 5931 were unique (R_{int} = 0.0546); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package. Data were corrected for absorption effects using a multi-scan technique (SADABS) with max and min transmission coefficients of 0.9879 and 0.8935, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods by Dr. Brian Patrick. Structure solutions were refined using the SHELXL software by Angela Crane. Disorder and partial occupancy is present in solvent hexane molecules filling the void space left by the porous structure. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions but not refined. The final cycle of full matrix least-squares refinement on F^2 was based on 5931 reflections and 352 variable parameters and converged. (largest parameter shift was 0.005 per esd).
Crystals of PMOF-1 suitable for X-ray diffraction were grown by slow cooling a DMF solution of 148 and Zn(NO₃)₂•6H₂O in a sealed Parr pressure vessel. A suitable crystal of PMOF-1 was mounted on a glass fibre with oil by Angela Crane. All measurements were made on a Bruker APEX DUO diffractometer at 90 ± 2 K using graphite monochromated Mo Kα radiation (0.71073 Å). Data were collected to a maximum 2θ value of 49.802° in a series of φ and ω scans in 0.50° oscillations with 30 s exposures. Of the 84407 reflections that were collected, 22294 were unique (R_int = 0.0535); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package. Data were corrected for absorption effects using a multi-scan technique (SADABS), with max and min transmission coefficients of 0.887 and 0.752, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods by Dr. Brian Patrick. Structure solutions were refined using the SHELXL software by Angela Crane. Disorder and partial occupancy is present in solvent DMF and water molecules filling the void space left by the porous structure. Modelling such solvent molecules was performed to partially account for electron density in the void spaces. Further electron density was removed using OLEX solvent mask. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions but not refined. The final cycle of full matrix least-squares refinement on F² was based on 22294 reflections and 2167 variable parameters.
D.12 PMOF-2a (170a)

Crystals of PMOF-2a suitable for X-ray diffraction were grown by slow cooling a DMF solution of 150 and Zn(NO₃)₂•6H₂O in a sealed Parr pressure vessel. A suitable crystal of PMOF-2a was mounted on a glass fibre with oil by Angela Crane. All measurements were made on a Bruker APEX DUO diffractometer at 90 ± 2 K using graphite monochromated Cu Kα radiation (0.71073 Å). Data were collected to a maximum 2θ value of 49.048° in a series of φ and ω scans in 0.50° oscillations with 60 s exposures. Of the 57455 reflections that were collected, 8245 were unique (R_int = 0.085); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package.¹⁰⁷(b) Data were corrected for absorption effects using a multi-scan technique (SADABS),¹⁰⁷(c) with max and min transmission coefficients of 1.00 and 0.633, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods¹⁰⁷(d) by Dr. Brian Patrick. Structure solutions were refined using the SHELXL software¹⁰⁷(a) by Dr. Nicholas White. Disorder and partial occupancy is present of solvent molecules filling the void space left by the porous structure were removed using PLATON SQUEEZE.¹⁰⁷(e) All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions but not refined. The final cycle of full matrix least-squares refinement on F² was based on 57455 reflections and 559 variable parameters.
D.13 PMOF-2b (170b)

Crystals of PMOF-2b suitable for X-ray diffraction were grown by slow cooling a 1:1 DMF:chlorobenzene solution of 150 and Zn(NO₃)₂•6H₂O in a sealed Parr pressure vessel. A suitable crystal of PMOF-2b was mounted on a glass fibre with oil by Angela Crane. All measurements were made on a Bruker APEX DUO diffractometer at 90 ± 2 K using graphite monochromated Cu Kα radiation (0.71073 Å). Data were collected to a maximum 2θ value of 119.698° in a series of φ and ω scans in 0.50° oscillations with 10 s exposures. Of the 57455 reflections that were collected, 8245 were unique (R_{int} = 0.085); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package. Data were corrected for absorption effects using a multi-scan technique (SADABS), with max and min transmission coefficients of 1.00 and 0.803, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods by Dr. Brian Patrick. Structure solutions were refined using the SHELXL software by Dr. Nicholas White. Disorder and partial occupancy is present of solvent molecules filling the void space left by the porous structure were removed using PLATON SQUEEZE. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions but not refined. The final cycle of full matrix least-squares refinement on F² was based on 57455 reflections and 559 variable parameters.
D.14 PMOF-3 (171)

Crystals of PMOF-3 suitable for X-ray diffraction were grown by slow cooling a DMF solution of 150, 4,4’-bipyridine and Zn(NO$_3$)$_2$·6H$_2$O in a sealed Parr pressure vessel. A suitable crystal of PMOF-3 was mounted on a glass fibre with oil by Dr. Brian Patrick. All measurements were made on a Bruker APEX DUO diffractometer at 90 ± 2 K using graphite monochromated Cu Kα radiation (1.54178 Å). Data were collected to a maximum 2θ value of 102.22° in a series of φ and ω scans in 0.50° oscillations with 60 s exposures. Of the 12477 reflections that were collected, 8955 were unique (R$_{int}$ = 0.080); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package.$^{107(b)}$ Data were corrected for absorption effects using a multi-scan technique (SADABS),$^{107(c)}$ with max and min transmission coefficients of 1.00 and 0.662, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods$^{107(d)}$ by Dr. Brian Patrick. Structure solutions were refined using the SHELXL software$^{107(a)}$ by Dr. Nicholas White. Disorder and partial occupancy is present of solvent molecules filling the void space left by the porous structure were removed using PLATON SQUEEZE.$^{107(e)}$ All non-hydrogen atoms were refined anisotropically. The final cycle of full matrix least-squares refinement on F$^2$ was based on 12477 reflections and 1222 variable parameters.