
by

Amy J. Cairns

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy
Department of Chemistry
College of Arts and Sciences
University of South Florida

Major Professor: Mohamed Eddaoudi, Ph.D.
Michael J. Zaworotko, Ph.D.
Brian Space, Ph.D.
Juergen Eckert, Ph.D.

Date of Approval: June 4, 2010

Keywords: metal-organic frameworks, gas storage, isosteric heats of adsorption, supermolecular building blocks

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Dedication

To my family for their continuous support throughout this journey
Acknowledgements

First and foremost, I would like to take this opportunity to express my sincere appreciation towards my Ph.D. advisor, Dr. Mohamed Eddaoudi for providing me with the opportunity to conduct research under his supervision and for his continuous financial support, inspiration, and guidance throughout my graduate career at USF.

I would also like to acknowledge the rest of my committee members – Drs. Michael J. Zaworotko, Brian Space, and Juergen Eckert for their countless discussions, positive input, and helpful suggestions concerning the research presented in this dissertation and for taking valuable time out of their busy schedules to serve on my dissertation examination committee. Special thanks to Dr. Anthony Coleman for agreeing to chair my dissertation defense and taking the time to fly all the way from France. In particular, many thanks to Dr. Juergen Eckert for his help with the inelastic neutron scattering (INS) experiments and for his expertise, patience, and limitless hours of discussion during our beam time at the Institut Laue-Langevin (ILL) in Grenoble, France. Special thanks to Drs. Lukasz Wojtas, Victor Kravtsov, Gregory McManus, and Mohamed Alkordi for single-crystal data collection and Dr. Matthias Thommes (Quantachrome Instruments) for assisting with sorption experiments. Last but certainly not least, I would like to extend my heartfelt gratitude to all the past and present students and post-doctoral fellows in the research groups of Drs. Eddaoudi, Zaworotko, and Space, as well as, all members of the SMMARTT team.
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<th>Full Name</th>
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<tr>
<td>H₄-ABTC</td>
<td>3,3',5,5'-azobenzenetetracarboxylic acid</td>
</tr>
<tr>
<td>H₄-BIPATC</td>
<td>Benzoimidephenanthroline tetracarboxylic acid</td>
</tr>
<tr>
<td>H₃ImDC</td>
<td>4,5-imidazoledicarboxylic acid</td>
</tr>
<tr>
<td>BTC</td>
<td>1,3,5-benzenetricarboxylic acid</td>
</tr>
<tr>
<td>BTB</td>
<td>1,3,5-tris(4-carboxyphenyl)benzene</td>
</tr>
<tr>
<td>BDC</td>
<td>Benzenedicarboxylate</td>
</tr>
<tr>
<td>5-NH₂BDC</td>
<td>5-aminoisophthalic acid</td>
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<tr>
<td>H₃TZI</td>
<td>Tetrazolylisophthalic acid</td>
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<td>CH₃CN</td>
<td>Acetonitrile</td>
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<tr>
<td>H₂O</td>
<td>Water</td>
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<tr>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N'-Dimethylformamide</td>
</tr>
</tbody>
</table>
DMA$^+$ ........................................................................................................ Dimethylammonium

DMA ........................................................................................................... $N,N'$-Dimethylacetamide

DEF ......................................................................................................... $N,N'$-Diethylformamide

HNO$_3$ .................................................................................................. Nitric acid

HCl ........................................................................................................... Hydrochloric acid

CH$_2$Cl$_2$ ............................................................................................... Dichloromethane

CH$_3$Cl .................................................................................................. Chloroform

NMP ........................................................................................................ N-Methylpyrrolidone

Py ........................................................................................................... Pyridine

TEA ........................................................................................................... Triethylamine

DEA ........................................................................................................... Diethylamine

TeaBr ....................................................................................................... Tetraethylammonium Bromide

TeaCl ....................................................................................................... Tetraethylammonium Chloride

TMAN .................................................................................................. Tetramethylammonium Nitrate

HMTA ..................................................................................................... Hexamethylenetetramine

IMI .......................................................................................................... Imidazole

PIP ............................................................................................................ Piperazine
MOM ........................................................................................................... Metal-Organic Material
MOF ........................................................................................................... Metal-Organic Framework
CP ........................................................................................................... Coordination Polymer
MOP ........................................................................................................... Metal-Organic Polyhedra
MOC ........................................................................................................... Metal-Organic Cube
ZMOF .................................................................................................... Zeolite-like Metal-Organic Framework
ZIF ........................................................................................................... Zeolitic Imidazolate Framework
COF ........................................................................................................... Covalent-Organic Framework
MBB ........................................................................................................... Molecular Building Block
SBB ........................................................................................................... Supermolecular Building Block
SBU ........................................................................................................... Secondary Building Unit
BU .............................................................................................................. Building Unit
TBU ........................................................................................................... Tetrahedral Building Unit
TeBU ...................................................................................................... Tertiary Building Unit
nMR ........................................................................................................... n Member Rings
FT-IR ...................................................................................................... Fourier Transform Infrared
PXRD ...................................................................................................... Powder X-ray Diffraction
Structural Diversity in Crystal Chemistry: Rational Design Strategies Toward the Synthesis of Functional Metal-Organic Materials (MOMs)

Amy J. Cairns

ABSTRACT

Metal-Organic Materials (MOMs) represent an important class of solid-state crystalline materials. Their countless attractive attributes make them uniquely suited to potentially resolve many present and future utilitarian societal challenges ranging from energy and the environment, all the way to include biology and medicine. Since the birth of coordination chemistry, the self-assembly of organic molecules with metal ions has produced a plethora of simple and complex architectures, many of which possess diverse pore and channel systems in a periodic array. In its infancy however this field was primarily fueled by burgeoning serendipitous discoveries, with no regard to a rational design approach to synthesis.

In the late 1980s, the field was transformed when the potential for design was introduced through the seminal studies conducted by Hoskins and Robson who transcended the pivotal works of Wells into the experimental regime. The construction of MOMs using metal-ligand directed assembly is often regarded as the origin of the molecular building block (MBB) approach, a rational design strategy that focuses on the self-assembly of pre-designed MBBs having desired shapes and geometries to generate
structures with intended topologies by exploiting the diverse coordination modes and geometries afforded by metal ions and organic molecules.

The evolution of the MBB approach has witnessed tremendous breakthroughs in terms of scale and porosity by simply replacing single metal ions with more rigid inorganic metal clusters whilst preserving the inherent modularity and essential geometrical attributes needed to construct target networks for desired applications. The work presented in this dissertation focuses upon the rational design and synthesis of a diverse collection of open frameworks constructed from pre-fabricated rigid inorganic MBBs (i.e. $[\text{M(CO}_2\text{)}_4]$, $[\text{M}_2(\text{RCO}_2\text{)}_4]$, $[\text{M}_3\text{O(RCO}_2\text{)}_6]$, $\text{MN}_3\text{O}_3$, etc), supermolecular building blocks (SBBs) and 3-, 4- and 6-connected organic MBBs. A systematic evaluation concerning the effect of various structural parameters (i.e. pore size and shape, metal ion, charge, etc) on hydrogen uptake and the relative binding affinity of H$_2$-MOF interactions for selected systems is provided.
Chapter 1. Introduction to Metal-Organic Materials:  
Historical Perspectives, Design Principles, and Potential Applications

1.1 Preamble

“What could we do with layered structures with just the right layers? What would the properties of materials be if we could really arrange the atoms the way we want them? They would be very interesting to investigate theoretically. I can’t see exactly what would happen, but I can hardly doubt that when we have some control of the arrangement of things on a small scale we will get an enormously greater range of possible properties that substances can have, and of different things that we can do”

Richard P. Feynman

1.1.1. Nanoscale Materials and Devices

Nanoscience represents a highly diverse and interdisciplinary field of science that is concerned with the study and manipulation of chemical and biological structures and/or devices within limited dimensions, more specifically in the range of 1 to 100 nanometers (nm). The ability to have a certain degree of control over matter at the atomic and molecular level often leads to the emergence of attractive properties and unique phenomena that are fundamentally different from that observed in bulk systems. This notion of extreme miniaturization is nothing short than astounding when one considers that one nanometer is equivalent to one billionth, $10^{-9}$, of a meter. To put this size scale into perspective, a common reference would be to compare the relative size of marble versus that of the Earth!!
The prolific “nano” vision provided by physicist Richard Feynman in his legendary talk at the meeting of the American Physical Society in 1959 entitled “There’s Plenty of Room at Bottom” is widely regarded as the birthplace of the fundamental concepts featured within the realm of nanotechnology or nanoscience, i.e. concepts pertaining to the controllable manipulation of matter at the atomic level. Several significant discoveries toward the latter half of the 20th century helped to jump start this every growing field. These include but are not limited to, the invention of the scanning tunneling (STM) and atomic force microscopes (AFM), development of cluster chemistry, and the synthesis of carbon nanotubes and fullerenes.2, 3

The assortment of top-down design methods employed by engineers to construct miniaturized devices has undoubtedly led to exceptional results but this strategy becomes less viable and more cumbersome in the nanoscale regime. Rational top-town design, bottom-up synthetic approaches developed by materials scientists, chemists, and biologists is an attractive alternative to generate prefabricated nanostructures which exhibit fine-tunable features and properties. They therefore have demonstrated immense potential to be utilized in a myriad of pertinent applications (e.g. gas storage and separation, magnetism, drug delivery, etc). All of the structures presented in this dissertation in fact, i.e. metal-organic materials (MOMs), fall into the second category whereby rational design strategies were employed to target functional solid-state crystalline materials with intended topologies based on the self-assembly judiciously chosen molecular building blocks (MBBs).
1.1.2. Solid State Chemistry

1.1.2.1. Crystalline versus Amorphous Solids

All matter is capable of forming a solid phase in the presence of the appropriate conditions (i.e. sufficiently cooled). The vast majority of these solids adhere to one or more crystalline phases, while others can be classified as being amorphous solids (e.g. glass, polystyrene, etc). The terms crystal and amorphous in fact come from the Greek words meaning “ice or clear ice” (krustallos) and “without form” (amorphos), respectively. Crystalline materials are defined as having long range order and therefore the solid consists of a regular repeating array of atoms, molecules, or ions arranged in an orderly periodic fashion. Amorphous materials on the other hand consist of random molecules with no long range order.

1.1.2.2. Single-Crystal X-ray Diffraction (SCD)

The discovery of X-radiation also known as X-rays by W. C. Röntgen (1895) was a pivotal scientific discovery and paved the way for fundamental developments in many fields, particularly crystallography. X-rays are a form of electromagnetic radiation with a sufficiently small wavelength; that is, in the range of 10 to 0.01 nm. This limit can be further subdivided into soft (λ = 10 – 0.10 nm) and hard X-rays (λ = 0.10 – 0.01 nm) based upon their penetrating abilities. Hard X-rays are ideally suited for atomic level structural characterization (i.e. crystal structures) because this range is comparable to the distance of chemical bonds. Crystallography was developed shortly after the discovery of X-rays as a result of the collective contributions of many inspirational scientists including M. V. Laue, R. J. Haüy, W. H. Miller, J. Hessel, A. Bravais, W. H. Bragg, W. L. Bragg.
and many others. In a typical experiment, a beam of X-rays were passed through a crystalline sample to produce a diffraction pattern on a photographic plate. It was shown that the observable spots could only be caused by diffraction of short wavelengths due to the resultant spatial arrangement of the atoms in the crystal. Diffraction patterns were significantly improved over the years as a result of the development of better X-ray sources. The field was truly revolutionized however when the CCD detector and computers were introduced. This is evidenced by the fact that data acquisition and structure solution for small molecule organics has become rather standard practice for present day crystallographers.

I would like to highlight a few relevant crystallographic terms that are commonly used in solid state chemistry, as several will be used throughout this dissertation. A diffraction pattern having a sufficient number of useable spots is needed to deduce the position of the atoms relative to each other in three spatial directions. A crystal structure is therefore delimited by a point lattice which is characterized by specific lengths (Å) and angles (°) referred to as, a, b, c, and α, β, γ, respectively. The smallest possible repeating unit that can be used to construct the entire lattice using these parameters and only translation is denoted as the unit cell. The unit cell of a crystal can fall into one of seven crystal systems and these include (1) cubic, (2) tetragonal, (3) orthorhombic, (4) monoclinic, (5) triclinic, (6) hexagonal, and (7) trigonal. They can be further subdivided into 14 Bravais lattices and 230 space groups and thus represent the only ways identical objects can be arranged in an infinite lattice.
1.1.2.3. Crystal Packing: Role of Intermolecular Interactions

Molecular recognition of complimentary molecular building blocks (MBBs) is largely responsible for the self-assembly of atoms to yield functional molecular assemblies. An excellent example to illustrate this concept is base pairing of the nucleotides in the double helix of DNA. Note that molecular synthesis is concerned with the making and breaking of intra-molecular covalent bonds (e.g. organic chemistry), while the manipulation of weak non-covalent intermolecular interactions between two or more molecular entities (e.g. in solution or the solid state) is encompassed within the realm of supramolecular chemistry, defined as “chemistry beyond the molecule” by Jehn Marie Lehn who won the Nobel prize (1987) for his significant contributions to this area.10

Crystal packing and in many cases the resultant properties of a material are indeed governed by the existence of attractive and repulsive intermolecular interactions. It is therefore imperative to have a fundamental understanding of the nature of these forces in order to target potential made-to-order molecular assemblies. A comparison of some of the commonly encountered intermolecular forces and their approximate energies is provided in Table 1.1. Note that the weak energetics exhibited by these forces often makes it difficult to predict the outcome of the assembly. The hydrogen bond however is certainly recognized as the most important force due to its robustness and directionality (i.e. predictable nature). This is not to say that other forces are not present, as it is rare to observe a single force in a single molecular system.
Table 1.1. Comparison of some intermolecular forces.10

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Energy (kJ/mol)</th>
<th>Description</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion-Ion</td>
<td>100 – 350</td>
<td>Electrostatic interaction between two oppositely charged ions</td>
<td>Na⁺ Cl⁻</td>
</tr>
<tr>
<td>Ion-Dipole</td>
<td>50 – 200</td>
<td>Bonding of an ion with a lewis base</td>
<td>[Na(H₂O)₆]⁺</td>
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<tr>
<td>Coordinate covalent bond</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen Bond</td>
<td>4 – 120</td>
<td>Attraction of a hydrogen atom on an electronegative atom to a dipole on a neighboring atom</td>
<td>DNA double helix</td>
</tr>
<tr>
<td>D-H⋯A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>π–π stacking</td>
<td>&lt; 50</td>
<td>Occurs between electron-delocalized systems</td>
<td>graphite</td>
</tr>
<tr>
<td>Dipole-dipole</td>
<td>5 – 50</td>
<td>Alignment of one polar molecule with another</td>
<td>acetone</td>
</tr>
<tr>
<td>London dispersion</td>
<td>1 – 10</td>
<td>Always present (i.e. arises from polarization)</td>
<td>noble gases</td>
</tr>
</tbody>
</table>

1.1.2.4. The Cambridge Structural Database

The Cambridge Structural Database (CSD) is available to users as a systems software package provided by The Cambridge Crystallographic Data Center (CCDC).11 It includes user friendly programs that are capable of search and informational retrieval (ConQuest), structure visualization (Mercury), numerical analysis (Vista), and database creation (PreQuest). The CSD is comprised of over 500,000 structures which have been solved using X-ray and neutron diffraction methods (Figure 1.1.). As of February 1ˢᵗ, 2010 in fact the database includes bibliographic, chemical, and crystallographic information for 503,268 organic and metal-organic compounds from a collection of open publications in the literature and private submissions.
Each entry deposited into the CSD is assigned a unique reference code consisting of six alphabetical letters (e.g. MABJUV) and is sometimes accompanied by a two-digit number (e.g. MABJUV01). This indicates either data collection using a different temperature(s), radiation source, experimental conditions, or the same structure reported in a different journal or published by another authors. The CSD is widely regarded as a vital research tool for crystal engineers. Most notably perhaps because (1) it is extremely useful at providing a current inventory of published crystal structures and is a critical feature as the number of reported structures continues to expand, (2) each entry provides pertinent structural information concerning the preferred metal-ligand coordination environments, and (3) when used correctly it can be used to gain insights into the role of intermolecular interactions in different systems and how it governs the overall crystal packing. It is important to mention that the CSD does not store information related to the following, polypeptides and polysaccharides with more than 24 units, oligonucleotides, inorganic structures, or metal alloys. Researchers can therefore refer to the RCSB Protein
Data Bank to obtain experimentally determined structures of proteins, nucleic acids, and complex assemblies.\textsuperscript{13, 14} While the Inorganic Crystal Structure Database (ICSD) features over 125,000 data entries accompanied by the 3D atomic coordinates of inorganic crystal structures dating back as far as 1913.\textsuperscript{15} Crystallographic data for metals, including alloys, intermetallics and minerals can be obtained from the CRYSTMET database.\textsuperscript{16}

1.2. Metal-Organic Materials (MOMs): Historical Perspectives

Metal-organic assemblies (MOAs) sustained by coordinate covalent bonds have been constructed over the years from the reaction of neutral or charged organic ligands with an assortment of metal cations. This process has resulted in the formation of a diverse collection of discrete and extended structures. In its infancy however little was understood about this field and no rational design strategies were implemented to construct functional solid state materials possessing targeted properties that would make them suitable for applications. This all changed in the late 1980s with the pivotal works by Hoskins and Robson. The following section will provide a scope of the history in this area and highlight select examples of significant developments that helped to shape this area to what is today.

1.2.1. Inclusion Compounds

Metal-cyanide compounds are amongst the earliest reports of MOAs, as evidenced by Prussian blue (PB) compounds and Hofmann clathrates. PB is indeed the oldest \textit{synthetic} coordination compound. The blue pigment was synthesized in Berlin in the early 1700s\textsuperscript{17} but initially its composition was unknown but it was believed to be a
mixed valence complex consisting of either iron(III) hexacyanoferrate (II) or iron(II) hexacyanoferrate (III). The simplest and most reliable approach to deduce this information would be to grow single crystals and obtain the crystal structure. PB however has a low solubility which hampers crystal growth. Keggin and Miles therefore used powder X-ray diffraction (PXRD) to deduce the first cubic structural model (1936). Ludi and co-workers (1972) later reported the first crystal structure of PB and confirmed that it is indeed a mixed-valance iron(III) hexacyanoferrate (II) complex. The framework is comprised of octahedral metal centers bridged through linear cyano-based ligands with a general formula of, Fe₄[Fe(CN)₆]₃ₓH₂O (x = 14-16).

The intense blue color of PB naturally led to its utility in dye-related applications (e.g. inks). Host-guest chemistry applications also became apparent after it was discovered that it could act as a molecular sieve; that is, the framework can be fully dehydrated and reversibly adsorb small molecules without comprising the structural integrity of the material. Accordingly, PB became known as a prototypical framework because the octahedral metal could be readily substituted for an array of mixed valence transition metal ions and clusters. This generated a multitude of compounds represented by the general formula, Mₙ[Mₙ(CN)₆]ₙₓH₂O (Figure 1.2.). Note that these analogues constitute a family of complex-based magnetic materials, many of which possess interesting high-temperature molecular magnetic properties that can be fine tuned through judicious choice of pre-designed molecular building blocks.
Research interest pertaining to another family of metal-cyanide compounds with unique inclusion properties occurred parallel to studies on PB and its analogs, that is, the Hofmann clathrate (1897) named after its founder Karl Andreas Hofmann. The layered network is built-up from alternating square-planar and octahedral Ni(II) metal ions. Each cyano group of [Ni(CN)]\(^{4-}\) is coordinated to the octahedral Ni cation along the equatorial plane through the nitrogen to reveal a layered network comprised of tetragonal sheets formulated as Ni(NH\(_3\))\(_2\)Ni(CN)\(_4\) 2C\(_6\)H\(_6\). The optimal interlayer separation coupled with the relative position of the coordinated NH\(_3\) ligands permits the encapsulation of benzene molecules and an assortment of other suitable guest molecules. Iwamoto and co-workers and others explored an assortment of synthetic strategies (e.g. amine and metal substitutions) to construct novel Hofmann-type analogs (Figure 1.3.). The proposed strategies were successful and yielded isostructural compounds having the general formula M(NH\(_3\))\(_2\)M'\((\text{CN})_4\) 2G (M = Co, Ni, Cu, Zn, Cd, Mn, or Fe; M' = Ni, Pd, or Pt; G = C\(_4\)H\(_4\)S, C\(_4\)H\(_4\)N, C\(_6\)H\(_6\), C\(_6\)H\(_5\)NH\(_2\), or C\(_{12}\)H\(_{10}\)).
The repertoire of modular solid state materials also led to the development of a specific class of inclusion compounds regarded as *Werner-type complexes*, named after Alfred Werner. Note that he proposed the octahedral configuration of transition metal complexes and is largely responsible for developing the basis of modern coordination chemistry. He in fact received the Nobel Prize in Chemistry in 1913 for his outstanding contributions. This family of compounds are generally expressed as $\text{MX}_2\text{A}_4\text{G}$, where $M$ represents a divalent metal cation which typically assumes an octahedral coordination environment (*e.g.* Zn, Ni, Cd, Co, Cr, Cu, Fe, Mn, *etc*), $X$ represents an anionic ligand (*e.g.* CN$^-$, Cl$^-$, Br$^-$, I$^-$, NCS$^-$, NCO$^-$, NO$_3^-$, NO$_2^-$, *etc*), $A$ refers to a neutral pyridine-based ligand (*e.g.* 4,4-bipyridine, pyrazine, 4-picoline, 4-phenylpyridine, *etc*), and lastly $G$ refers to a guest molecule trapped in the framework (Figure 1.4.).$^{32, 33}$

**Figure 1.3.** Ball-and-stick representations of a Hofmann-type clathrate: (left) Tetragonal sheet comprised of octahedral and square-planar metal centers, Cd$_4$(NH$_3$)$_2$ and Ni(CN)$_4$, respectively; and (right) Piperizine molecules trapped between the layers. Hydrogen atoms and water molecules have been omitted for clarity. Color Code: Cd = yellow; Ni = green; N = blue; and C = gray.$^{31}$
Figure 1.4. Examples of MX₂A₄ Werner-type complexes: (a) X=Cl⁻, A=pyridine; (b) X= NCS⁻, A=3,5-lutidine; (c) X=NCS⁻, A=4,4'azo-bis(4-pyridyl).

Early serendipitous discoveries concerning metal-cyanide compounds and Werner-type complexes clearly exposed unique modular prototypes that are amenable to design and therefore paved the way for fruitful opportunities concerning the development of functional MOAs. Nevertheless, the design and synthesis of coordination polymers assembled from pre-designed molecular building blocks (MBBs) was not envisioned until the late 1980s through the revolutionary discoveries reported by Robson and Hoskins.

1.3. Rational Assembly of MOMs from Expanded Nitrogen-Donor Ligands

“One approach to crystal engineering that we have been developing is first to choose as a geometrical/topological model one of a number of simple 3D nets such as diamond (all centers tetrahedral), α-Po (all centers octahedral), rutile (octahedral and trigonal centers in a 1:2 proportions) and so on, and then try to revise ways of chemically linking together molecular building blocks with a functionality and a stereochemistry appropriate to the chosen net.”

Richard Robson

Robson et al. embarked on a clever sequence of experiments to demonstrate the possibility of rational construction of infinite scaffolding-like structures (e.g. coordination polymers) built-up from pre-selected inorganic and organic MBBs. The overall concept is rather simple and in hindsight it is somewhat surprising that it took
experimentalists so long to prove this notion, given the amount of knowledge available concerning the simplification and topological assessments of nets provided by A. F. Wells. That notwithstanding, the node and spacer approach clearly marked the origin of the MBB approach and laid the foundations for the discovery of a plethora of predicted novel MOMs of unprecedented scale and functionality.

Simple MBBs (i.e. regular polygons and polyhedral) offer a high degree of structural diversity but in the absence of structure directing agents (SDAs) their self-assembly predominately yields high-symmetry networks, termed default nets, i.e. preferred by nature. For example, cubic and hexagonal diamond nets are both uninodal 4-connected nets comprised of tetrahedral nodes bridged by linear carbon-carbon rod-like bonds (i.e. spacers). The default net for the assembly of tetrahedral building units (TBUs) is cubic diamond (dia) and thus it is more cumbersome to form hexagonal diamond (lon) because it is less symmetric. It was envisioned that a hybrid network assembled from an assortment of predesigned MBBs could generate similar nets with appreciably larger cavities and windows and consequently render them well suited for many applications (e.g. as catalysts or molecular sieves).

Several different synthetic strategies were proposed to mimic the MBBs in an attempt yield expanded nets with the same underlying topologies. These include, (1) reaction of simple bifunctional linear spacers (e.g. CN\(^{-}\), 4,4\(^{\prime}\)-bipyridine, etc) with metal centers that have a preference to adopt tetrahedral coordination environments, and/or (2) vice versa wherein more complex molecules represent the tetrahedral center (e.g. tetrasubstituted tetraphenyl methane and silane analogues) connected through linear centers (e.g. Ag\(^{+}\),Cu\(^{+}\)). The versatile coordination geometries afforded by metal ions
coupled with the repertoire of organic molecules offers unlimited possibilities for a large collection of discrete and extended MOMs. Metal-cyanide chemistry in fact offers one of the simplest bifunctional linear molecules, CN\(^-\). Reaction of CN\(^-\) with a divalent metal cation (\textit{i.e.} \(\text{Zn}^{2+}, \text{Cd}^{2+}\)) indeed resulted in the formation of the \textbf{dia} network. Despite the modest length of the carbon-nitrogen bond the framework was still interpenetrated and therefore the available free volume was significantly reduced. Cubic diamond is a self-dual net and therefore catenation is commonly observed, particularly in instances where longer or flexible organic linkers are employed. Depending on the desired application however this feature may be regarded as an advantage or a limitation. Studies have shown that the degree of interpenetration can be controlled, to some extent, or completely avoided by fine-tuning the experimental parameters. These include, (1) introducing neutral or charged SDAs (\textit{e.g.} metal cations, organic templates, counter ions, \textit{etc}) into the reaction medium (Figure 1.5.), (2) varying the length and functionality of the organic spacers, and (3) temperature control in the case of solvothermal synthesis.
The success of this approach in terms of its feasibility and versatility was extended to include complex building blocks. The deliberate design and *in situ* synthesis of a cationic *dia* MOA constructed from the assembly of 4,4′,4″,4‴-tetracyanotetraphenylmethane ligands with Cu(I) cations was a significant achievement by Robson and co-workers (Figure 1.6.).

**Figure 1.5.** (Left) Non-interpenetrating anionic MOM with *dia* topology constructed from Zn(II) and Cu(I) tetrahedral building blocks. TMA cations, shown in space-filling representation, reside in each of the adamantane cavities to balance the charge. Hydrogen atoms have been omitted for clarity. Color Code: Zn = yellow; Cu = green; N = blue; and C = gray. (Right) Schematic representation of the cubic diamond topology.  

**Figure 1.6.** Schematic representation the first *dia* MOA constructed a complex organic MBBs: (a) Tetrahedral metal ion coordination environment, Cu(I); (b) Tetrahedral molecular building block, 4,4′,4″,4‴-tetracyanotetraphenylmethane; and (c) Fragment of the \{Cu[I(C_6H_4CN)_4]\}^+.
MOA. All hydrogen atoms and solvent molecules are omitted for clarity. Color code: Cu = green; C = gray; N = blue.39

The modularity, mild synthetic conditions, and ease of crystallization presented by this class of crystalline materials therefore prompted a wide spread research interest in this area. The innovative crystal engineers subsequently expanded their studies to include linear neutral nitrogen-donor ligands such as 4,4'-bipyridine and its derivatives (Figure 1.7.).45-49 The resultant networks in this case are predisposed to be cationic due to the fact that the organic ligands are neutral and the metal cations are positively charged. Thus, charge balance is often provided by anionic counter ions in the form of BF$_4^-$, PF$_6^-$, NO$_3^-$, SiF$_6^{2-}$, etc located in the framework lattice.

![Figure 1.7. Examples of polytopic nitrogen-donor ligands: (left to right) imidazole (IMI); hexamethylenetetramine (HMTA); 4,4'-bipyridine (BIPY); 9, 10-bis(4-pyridyl)anthracene; 1,2,4,5-tetra(4-pyridyl)benzene; and 2,4,6-tris(4-pyridyl)-1,3,5-triazine.](image)

1.3.1. Supramolecular Polygons

The utilization of linear spacers with monodentate coordination modes dictate that the underlying topology will be governed by the preferred coordination environment around the metal center. It is possible however to employ chelating moieties (e.g. EN, 1,10-Phen, 2,2'-BIPY, etc) to cap the metal centers and thereby control the coordination
environment and direct the topology. These arrangements commonly form molecular squares, triangles, etc. The first metal-organic molecular square was in fact reported by Fujita and co-workers in 1990\textsuperscript{50} and since then metal-organic polygons akin to an equilateral triangle, square, pentagon and hexagon have become well documented in the literature.

Initial studies focused upon reacting linear bipyridine-\textit{type} ligands with an assortment of transition metals that adopt predictable coordination geometries. The ligand therefore constitutes the edges of the polygon, while the inorganic MBB is positioned at the vertices to define the angle and control the overall geometry (Figure 1.8.). Studies were also conducted by Stang and co-workers to pursue the modular nature of this system.\textsuperscript{51-53} The field therefore expanded to include a series of analogous molecular squares, as well as, other molecular polygons synthesized using an assortment of diamine capping ligands and ditopic nitrogen-based ligands.\textsuperscript{54-57}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure1.png}
\caption{(left) First metal-organic molecular square, [Pd(BIPY)(En)]\textsubscript{4}\textsuperscript{8+};\textsuperscript{51} (right) an example of a molecular triangle, [Pd(BIPY)(Tmen)]\textsubscript{3}\textsuperscript{6+}.\textsuperscript{55} Hydrogen atoms and counterions are omitted for clarity. Color code: Pd = green; C = gray; N = blue.}
\end{figure}
1.3.2. Angular Nitrogen-Donor Ligands

A tremendous amount of structural diversity resulted by introducing angularity into the organic components via ligand design, i.e. non-linear polytopic pyridyl-based ligands.\textsuperscript{58-63} Angularity not only imparts directionality but also allows for the formation of $n$-connected nodes where $n$ typically ranges between 2 and 6 and thus building units with different shapes are feasible targets. Nitrogen-based ligands such as pyrimidine, IMI, HMTA and others have proven to facilitate the formation of nets having topologies and properties akin to traditional inorganic zeolites. Substitution of the oxide anions (O\textsuperscript{2-}) for angular organic ligands whilst maintaining the optimal M-L-M angle (i.e. close to 145°) permits edge expansion and decoration and has therefore generated zeolite-like MOFs (ZMOFs) with enlarged cavities and channels.\textsuperscript{62, 64-67} The construction of MOMs from simple TBUs commonly forms dia nets and therefore devising pathways to overcome has proven challenging.\textsuperscript{68} A possible explanation is likely associated with the labile nature (flexibility) of the metal-nitrogen coordinate bond.

1.3.3. Nitrogen-Based Metal Clusters

MOAs constructed from single-metal ions that are flexible in nature, i.e. bipyridine-type coordination polymers, are often less robust than metal clusters and therefore exploiting their porosity for desired applications can be challenging. Alternative pathways have therefore been recently devised to alleviate this issue by employing polytopic nitrogen-based ligands that are capable of coordinating to metal ions in a bis-monodentate fashion to generate rigid metal clusters (Figure 1.9.). This ligand class belongs to the azole family and is therefore identified as 5-membered heterocyclic nitrogen
containing systems. These include pyrazoles (N$_2$C$_3$R), triazoles (N$_3$C$_2$R), and tetrazoles (N$_4$CR).$^{69-75}$

![Figure 1.9](image)

**Figure 1.9.** (a) $\mu_3$-oxo-centered trinuclear cluster, [M$_3$O(N$_3$CR)$_3$(H$_2$O)$_3$]; (b) Dinuclear paddlewheel-like cluster, [M$_2$(N$_2$CR)$_3$(H$_2$O)$_6$]; (c) M$_4$Cl(N$_4$CR)$_8$L$_4$ tetranuclear cube-like cluster; (d) [M$_3$(N$_4$CR)$_6$(H$_2$O)$_6$] trinuclear cluster; (e) [M$_3$O(N$_2$CR)$_3$] trinuclear cluster; (f) Prototypical example of a 3-periodic sod-type MOM constructed from a M$_4$Cl(N$_4$CR)$_8$L$_4$ (M= Cu or Mn) clusters and a triangular ligand, H$_3$TPT-3tz. Hydrogen atoms and solvent molecules have been omitted for clarity. Color Code: M = green; C = gray; N = blue; Cl = yellow; and O = red.$^{76}$ **Note:** The yellow sphere located inside the cavity represents the largest sphere that can fit inside taking into account van der Waals radii.

### 1.4. Construction of MOMs from Carboxylate-Based Ligands

The last decade has witnessed an explosive increase in the synthesis and characterization of MOMs, particularly frameworks constructed from carboxylate-based organic ligands (Figure 1.10.).$^{77-87}$ The wide spread interest in this class of linkers is due
in part to (1) their ability to accommodate various coordination modes, e.g. bidendate, monodentate, bis-monodentate, etc; a feature that is not permitted with nitrogen-based bipyridine- or cyano-type ligands, (2) ability to form rigid and directional metal clusters with fixed geometries by conforming to the bis-monodentate coordination mode, and (3) the negatively charged carboxylate groups (i.e. \( \text{RCO}_2^- \)) often preclude the need for charge balancing counter ions.

**Figure 1.10.** Select examples of polytopic carboxylate-based organic ligands used to construct MOMs.

A few of the commonly employed metal carboxylate clusters (i.e. generated *in situ*) that have proven to be useful in the construction of MOFs are illustrated in Figure 1.11. Each metal cluster can be simplified into a geometric entity by connecting the points of extension, i.e. via the carboxylate carbon atoms, to reveal a so-called secondary building unit, which is a term borrowed from zeolites. A large number of discrete metal clusters are in fact available in the chemist toolbox but the organic linker must have the appropriate functionalities built-in to facilitate the requisite geometry and rigidity upon
coordination. Prior to isolating a cluster in an extended structure, the next step is to identify the appropriate synthesis conditions which consistently lead to its formation once the MBBs have been modified, i.e. to produce structures having the same underlying topology but different pore metrics and functionality. This step has indeed proven to be a contemporary challenge but once this step is accomplished then the design of target networks can truly be envisioned.

Figure 1.11. Examples of rigid metal carboxylate-based MBB clusters used to construct MOFs, each of which can be translated into geometrical shapes [SBU(s)]: (a) Dimetal tetracarboxylate cluster, often regarded as the “paddlewheel” M₂(RCO₂)₄L₂ forms either a square or octahedral SBU; (b) Basic chromium acetate trimetal cluster M₃(RCO₂)₆L₃ represents a trigonal prismatic SBU; and (c) Basic zinc acetate cluster, Zn₄O(RCO₂)₆ forms an octahedral SBU. Color Code: C = gray; O = red; M= green.

The versatile and predictable nature of the MBB approach is still preserved in the case of carboxylate-based ligands whereby different ligands can be utilized to construct discrete and extended structures with fine-tunable pore sizes, shapes, and functionality. An excellent example to illustrate the concept of reticular chemistry is represented by the
archetypical MOF-5 (or IRMOF-1) synthesized by Yaghi and co-workers from prefabricated basic zinc acetate, [Zn₄O(RCO₂)₆], and ditopic 1,4-BDC MBBs that reticulate to form a primitive cubic structure (Figure 1.12.a).⁸⁴

Figure 1.12. Two examples of IRMOFs constructed from linear carboxylate-based ligands and the 6-connected basic zinc acetate, [Zn₄O(RCO₂)₆] metal cluster: (a) MOF-5 (IRMOF-1); and (b) IRMOF-11. Hydrogen atoms and solvent molecules have been omitted for clarity; Color Code: Zn = green; C = gray; and O = red.

The attractive structural features of MOF-5; that is, being exceptionally rigid and highly porous provided a unique prototype to embrace a conglomeration of novel properties through the synthesis of isoreticular analogs (Figure 1.12b). Note that hydrogen sorption studies conducted on MOF-5 were the first to be reported for this class of materials. It therefore paved the way for the development of sixteen additional IRMOFs through variation of the chemical composition, functionality, and dimensions. Kitagawa and co-workers on the other hand were the first to report the adsorption of small gaseous molecules such as CH₄, N₂, and O₂ gases at ambient temperature (1997),⁸⁸ while Eddaoudi and co-workers were the first to confirm and study permanent
microporosity with MOF-2 using N₂ and CO₂ gas adsorption measurements at 78 K and 195 K, respectively.

The dimetal tetracarboxylate “paddlewheel” MBB, [M₂(RCO₂)₄L₂], is a ubiquitous inorganic MBB in crystal chemistry (see chapters 3 and 4). The first example of a polymeric material assembled from linked paddlewheel MBBs was reported by O’Connor and Malsen (1966) whereby a 1-periodic coordination polymer containing succinic acid of formula, [Cu₂(succinate)₂(H₂O)₂]ₙ. Yaghi and co-workers later reported the synthesis of MOF-2 and then in 1999 the synthesis of HKUST-1 was reported by Williams and co-workers. From this point onward the field of MOF chemistry concerning paddlewheel MBBs was transformed (i.e. in extended structures), due in part to the outstanding contributions from O. M. Yaghi and M. J. Zaworotko.

In 2001 these groups independently reported on the design and synthesis of a discrete spheroid-like metal-organic polyhedral (MOP) built-up from copper paddlewheel MBBs and \( m \)-BDC units, coined the nanoball and MOP-1 by Zaworotko et al. and Yaghi et al., respectively (Figure 1.13.). The modular nature afforded by this prototype lead to the development of a series of decorated nanoscale analogs. This was accomplished by functionalizing the 5-position of the \( m \)-BDC moiety with various substituents (i.e. SO₃⁻, ΩOH, ΩOCH₃, ΩOC₁₂H₂₅, etc). It was also demonstrated that extended suprasupermolecular networks could be isolated by employing the metal-organic small rhomibhexahedra as nanoscale nodes (supermolecular building blocks, SBBs).
Figure 1.13. (a) Ball-and-stick representation of the neutral nanoball or MOP-1, \([\text{Cu}_2(m\text{-BDC})_4]_{12}\); (b) Schematic representation reveals a small rhombihexahedron consisting of vertex-linked square SBUs. The 5-position of the \(m\text{-BDC}\) unit lies on the vertices of the SBB and is highlighted in orange. Color Code: C = gray; O = red; and Cu = green. All hydrogen atoms and solvent molecules are omitted for clarity.

The \(\mu_3\)-oxygen-centered TMBB, \([\text{M}_3\text{O}(\text{RCO}_2)_6(\text{L})_3]\), is an ideal rigid and directional MBB used to target nets whose vertex figures indicate the need for a 6-connected node having trigonal prismatic geometry. Note that oxo-bridged trimers are common in transition-metal chemistry, i.e. for discrete complexes, but are less documented in the case of extended networks, particularly for \(p\)-block metal ions (see Chapter 2).\(^{98}\) Férey and co-workers have in fact exploited the diversity of the TMBB with an assortment of transition metal cations and organic struts to isolate robust MOFs with interesting properties, e.g. high porosity and breathing effects as a consequence of framework flexibility. Perhaps most notably, are the two highly porous MIL compounds with zeotypic giant pores and augmented \textbf{mtn} topology, coined MIL-100 and MIL-101 (M = Materials of Institut Lavoisier).\(^{85,86}\) In the crystal structure of the former the chromium-based TMBBs are linked through 1,3,5-benzeneetricarboxylic acid (BTC), while in the latter BTC is substituted for 1,4-benzenedicarboxylic acid (BDC). This arrangement therefore reveals a supertetraheral building block (Figure 1.14.). Both MIL-
100 and -101 have remarkably large cage dimensions of 25 Å and 34 Å, respectively and huge Langmuir surface areas of 3100 m²/g and 5600 m²/g, respectively and thus are good candidates for many applications.

![Figure 1.14](image)

Figure 1.14. Select fragments from the crystal structures of (a) MIL-100; and (b) MIL-101, which form a supertetrahedral building block that can be rationalized as a super tetrahedral building unit (center).

1.5. Hybrid Ligand Design: MOMs Constructed from Hetero-Functional Linkers

The previous sections highlighted the modularity offered by MOMs as a function of ligand design, i.e. independently employing nitrogen- and oxygen-based organic ligands. A natural transition is therefore to combine these functional groups into a single entity to form a hetero-functional organic linker (Figure 1.15.). The existence of more than one type of heteroatom or functional group is considered advantageous because these moieties offer the potential to facilitate the formation of rigid and directional mixed metal-ligand coordination environments and thus different geometries and shapes can theoretically be isolated. Mono- or polytopics ligands comprised solely of either nitrogen- or oxygen-donor atoms predominately bond to metal cations yielding one type of coordination environment and therefore uninodal and binodal networks are commonly observed.
Hetero-functional ligands can sustain a variety of building blocks and therefore can be used to target more complex architectures (e.g. tertiary or even quaternary nets). Eddaoudi and co-workers in fact isolated a novel 3-perioidic tertiary net by reacting a bifunctional tetrazolate ligand, 5-tetrazoleisophthalic acid (TZI) with Cu(NO₃)₂·2.5H₂O. The cationic 3-periodic MOF is built-up from two types of inorganic MBBs and an organic MBB (Figure 1.16.). Viewing the structure as the assembly 24-connected rhombicuboctahedral building units linked together through 3-connected trigonal nodes results in a (3,24)-connected MOF with rht topology (see chapter 4).
Figure 1.16. Illustration of the (3,24)-connected rht-MOF: (a) Hetero-functional ligand yields a trigonal $[\text{Cu}_3\text{O}(\text{N}_4\text{CR})_3]$ MBB and $[\text{Cu}_2(\text{RCO}_2)_4]$ paddlewheel MBBs; (b) Tiling representation.

Hetero-functional ligands possessing chelating moieties, i.e. carboxylate and nitrogen groups, can also be used to control the coordination environment around single-metal ions. This concept involves saturation of the metal center through the formation of hetero-chelating rings. This type of arrangement precludes the coordination of unwanted solvent/guest molecules and therefore renders the single-metal node rigid and directional. Design strategies pertaining to the single-metal-ion-based MBB approach was introduced by Eddaoudi and co-workers as a reliable to target robust metal-organic assemblies (MOAs) with single metal ions located at the vertices.$^{105}$ This concept is based on the fact that the aromatic nitrogen atoms will direct the framework topology, while the carboxylate moieties located in the $\alpha$-position relative to the nitrogen will complete the coordination sphere and lock the metal ion into position through the formation of 5-membered chelating rings. The resultant single-metal-ion based MBBs are therefore of the type $\text{MN}_x(\text{CO}_2)_y$ where M represents a 6 to 8 coordinate metal cation, x refers to the number of hetero-chelating moieties, and y refers to the number of ancillary (bridging)
donor atoms. The success of this approach is evidenced by the large number of structures reported by Eddaoudi and co-workers, which have been deliberately constructed from predesigned rigid and directional MBBs using hetero-chelating ligands. For example, a discrete octahedron ($M_6L_{12}$), metal-organic cubes ($M_8L_{12}$), 2-periodic kagomé lattice, and a 3-periodic diamondoid net.$^{99,106}$

A particular subset of MOMs (i.e. ZMOFs) deserves special attention. The versatility of the single-metal-ion-based MBB approach permitted the assembly of non-default networks with topologies akin to inorganic zeolitic (e.g. rho-, sod-, usf-, ast-, aco-, and lta-ZMOFs).$^{64-67,100}$ This was carried out by employing judiciously chosen MBBs that translate into 4-connected tetrahedral building units. The rigid and directional TBUs adhere to the desired M-L-M angle of ~145° observed in zeolites. Decoration and/or expansion via the organic functionality affords extra-large cavities that are fine-tunable (Figure 1.17.).

![Figure 1.17. Ball-and-stick and schematic representations of (left) rho-ZMOF comprised of 8-coordinate InN$_4$O$_4$ MBBs (= InN$_4$ TBUs) and (right) sod-ZMOFs comprised of 6-connected InN$_4$O$_2$ MBBs (= InN$_4$ TBUs). Both compounds were constructed using an angular ditopic hetero-functional ligand, 4,5-imidazoledicarboxylic acid (H$_3$-ImDC).$^{64}$](image)
1.6. Identification and Classification of MOMs: Topological Descriptors

Several notations have been implemented over the years to classify nets, many of which are widely reported to date. These terms however are used interchangeably and thus misused by researchers, as exemplified in hundreds of manuscripts published in ACS and RSC journals since 2000.\textsuperscript{107} The following sub-chapters will provide an overview of the commonly used topological notations and symbols. An outline of their advantages and limitations will be provided accompanied by relevant examples.

1.6.1. Point Symbols and Schl{"a}fli Notation

The topological descriptors used to describe a net are derived from graph theory and therefore in a mathematical sense a net can be rationalized as a special kind of graph.\textsuperscript{108} In the context of MOMs, researchers commonly report the growth of a net as being 0-dimensional (discrete), 1-dimensional, 2-dimensional, or 3-dimensional. For example, metal-organic polyhedra (MOPs) are often regarded as 0-dimensional architectures, while the metal-organic analog of the \textbf{dia} net is viewed as a 3-dimensional structure. This convention is in fact misleading because all atoms and molecules are indeed 3-dimensional. It is therefore more precise to use the term \textit{n}-periodic to refer to the independent directions of a net and thus MOP would be regarded as 0-periodic structures.

Early topological assessments of nets were primarily developed by A. F. Wells, who analyzed and classified a great number of nets based on their connectivity using a simple \((n, p)\) notation. This description is related to geometrical principles and mathematical descriptors.\textsuperscript{40, 109-114} Accordingly, Wells dissected a net into the assembly of
nodes (vertices) connected through spacers (edges) and tried to identify the polygons that were apparent as a consequence of these linkages. Note that a metal ion is often regarded as a node and the organic ligand represents the edge (bond) to link a pair of vertices and therefore permits the growth of the net. In cases of higher coordination (e.g. metal clusters) it is often easier to simplify the group of nodes into a single node (Figure 1.18.). The connectivity of the vertices is dependent upon the node and spacer assignment and therefore more than one topological outcome may be possible for a given structure.

Figure 1.18. (left) Tetravalent basic zinc acetate cluster, \([\text{Zn}_4\text{O(RCO}_2\text{)}_6]\) simplified into a 6-connected node (right) via the points of extension.

In Wells’ notation, the \(n\) term refers to the number of edges of the faces of a polygon in the net and \(p\) refers to the number of edges that meet at each of the vertices. For example, a 2-periodic tetragonal sheet could be given the symbol (4,4) which implies a 4-connected net comprised of 4-membered rings (MRs) that meet at each vertex (Figure 1.19a.). A honeycomb lattice is therefore assigned a symbol of (6,3) because it is a 3-connected net with the shortest ring at each angle being a 6-MR (Figure 1.19b.).
The $(n,p)$ system is quite efficient for simple nets but it has limitations in the sense that it does not uniquely describe a net. It also becomes less reliable and more complicated for higher connected nets. Wells was aware of this shortcoming and in some instances assigned a letter to follow the $(n,p)$ nomenclature as a way of providing a topological distinction. For example, Wells referred to the 3-connected nets of the Si atoms in SrSi$_2$ (srs) and ThSi$_2$ (ths) structures as (10,3)-a and (10,3)-b, respectively. Although the use of a letter descriptor is useful, it does not provide any topological distinction between the nets and thus more descriptive approaches were needed.

Wells therefore introduced a topological descriptor that he called a point symbol. In this sense, each net is comprised of a certain number of nodes and each $n$-connected node has $N=\lfloor n(n-1)/2 \rfloor$ angles surrounding it. The shortest cycle between the first and last vertex defined as $(x_1, x_2, \ldots, x_{n-1}, x_1)$ must be identified at each angle. A point symbol is expressed in the form of $A^a.B^b.C^n \ldots$ etc, where $A < B < C$, and so forth. The upper-case letter denotes the size of the shortest cycle circuits contained at each angle and the superscripts refer to the number of shortest circuits at that specific angle. For example, the uninodal 4-connected dia net has 6 equivalent angles at each node and the shortest...
cycle circuit is 6 and therefore the point symbol is 6⁶. Likewise, the aforementioned (10,3)-a net would be assigned a point symbol of 10³ because it has 3 equivalent angles at each node and the shortest cycle circuit is 10.

Now is an appropriate time to introduce another symbol widely used in the literature, Schlāflī symbols, which appear in the form of a \(\{p,q,r,\ldots\}\) notation and are applied to regular 2- and 3-periodic tilings. In its simplest form, a \(p\)-sided regular polygon is represented as \(\{p\}\). For example regular polygons such as triangles, squares, and pentagons would be assigned a Schlāflī symbol of \{3\}, \{4\}, and \{5\}, respectively. Whereas, a regular polyhedron would be represented by the notation \(\{p, q\}\) because it is assembled from \(q\)-regular \(p\)-gon faces that meet at each vertex. An excellent example to illustrate this notation is represented by the five Platonic solids which include: tetrahedron \{3,3\}, cube \{4,3\}, octahedron \{3,4\}, icosahedron \{3,5\}, and dodecahedron \{5,3\}. A tetrahedron accommodates three triangles at its vertices, while three squares meet at each of the vertices in a cube and therefore have Schlāflī symbols of \{3,3\} and \{4,3\}, respectively (Figure 1.20.).

![Figure 1.20. Schematic representation of two Platonic solids: (left) Tetrahedron; and (right) Cube.](image)

Similarly, a tetragonal sheet and honeycomb lattice would be assigned a symbol of \{4,4\} and \{6,3\} because each plane is assembled from tiles of squares and hexagons,
respectively. This notation can also be applied to regular 3-periodic tilings in the form of a \( \{p, q, r\} \) Schläfli symbol whereby \( r \{p,q\} \)'s meet at each edge. For instance, \( \{4,3,4\} \) would symbolize a cubic lattice comprised of four cubes around each edge and corresponds to the primitive cubic (pcu) net. Unfortunately, point symbols and Schläfli symbols are often applied interchangeably in the literature which leads to confusion and misrepresentation. A recent article by O’Keeffe and co-workers addresses this issue and the authors urge researchers to restrict the usage of Schläfli symbol to regular tilings in 2- and 3-periodic nets, while point symbols should only be applied to 3-periodic nets and not used interchangeably with Schläfli symbol or circuit symbol.\(^{116}\) Although the aforementioned notations are quite useful, they are accompanied by limitations. The problem arises when one must distinguish between two or more nets having the same point or Schläfli symbol.

### 1.6.2. Extended Schläfli Notation and Vertex Symbols

In an attempt to resolve the ambiguity between similar nets, a more descriptive group of terms were introduced, i.e. long (extended) Schläfli symbols and vertex symbols (O’Keeffe). Both notations are widely reported in the literature but the key distinction lies in the use of the term “cycle” versus “ring”. In contrast to a cycle, a ring is a more specific type of cycle which is not the sum of two smaller cycles and does not contain any shortcuts (Figure 1.21.).\(^{116}\)
Figure 1.21. A schematic to illustrate the difference between strong rings, rings, and cycles: (left) 4-cycle that is a strong ring, (middle) 12-cycle that is the sum of a 6- and 8-cycle, thus is not a ring, and (right) A 12-cycle that is the sum of a 6-, 8-, and 4-cycle but not of just 2 cycles and therefore is a ring (not a strong ring).

The sequence is expressed in the form of $A_aB_bC_n\ldots$ etc, in both cases where the upper-case letter refers to the size of the “shortest cycle” (extended Schläfli symbol) or “ring” (O’Keefe) contained at each angle and the subscripts refer to the number of shortest cycles / rings at the respective angle. The key distinction to be made here between short and long notation is the latter computes the number of cycles at each of the respective angles. The use of vertex symbols is currently the most informative and commonly used notation to classify MOMs because the extended Schläfli notation can be misleading. Because a cycle is not always the shortest distance between the starting and ending point and can lead to inaccurate results.

The vertex symbol computed for each node often provides enough information to make a decisive topological distinction. For example, Wells’ (10,3)-a and (10,3)-b nets can be uniquely identified through the use of vertex symbols: $10_5.10_5.10_5$ and $10_2.10_4.10_4$, respectively. Yet there are exceptions, as in cubic (crystabolite; dia) and hexagonal (longstalite; lon) diamond which both are uninodal 4-connected nets possessing the same vertex symbol of, $6_2.6_2.6_2.6_2.6_2$. This notation implies that each of the 4-connected nodes are surrounded by 6 angles and each angle contains two 6-membered rings that meet at the vertex but does not provide enough information to uniquely identify the net.
1.6.3. Coordination Sequence

In order to topologically distinguish between the dia and lon nets, one must further determine the coordination sequence (CS) of each node. According to O’Keeffe et al. a CS consists of a sequence of numbers \((n_1, n_2, n_3, \ldots, nk, \ldots)\) in which the \(k\)th term is the number of nodes in the shell \(k\) that are connected to nodes in shell \(k-1\). In short it refers to the number of neighbors surrounding each node as the structure grows. The CS of dia up to \(k = 10\) is 4, 12, 24, 42, 64, 92, 124, 162, 204, 252, etc (Table 1.2.). In this case, the [CS(0)] refers to the 4-connected node which has a set of 4 nearest neighbors, this subsequently generates the first shell [CS(1)]. These nodes are then linked to set of 12 nearest neighbors, further extended to 24, and so on. There is no specific limit for the \(k\)th term but typically computer software programs determine this value up to \(k = 10\). The sum of the CS is regarded as the topological density \((Td_{10})\) and reveals the total number of vertices in the \(k\)th subshell. The computed coordination sequence for dia and lon up to \(k = 10\) reveals a difference at the third neighbor, thereby illustrating the topological difference between these nets. The topological density determined for each net, reveals lon is denser than dia having values of 1027 and 981, respectively.

Table 1.2. Coordination sequence computed up to \(k = 10\) for the cubic and hexagonal diamond nets.117

<table>
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<th>cs3</th>
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Difference

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<th>10</th>
<th>12</th>
</tr>
</thead>
</table>

35
Likewise, in 2003, a similar observation was reported by Zaworotko and co-workers between two fundamentally different supramolecular isomers of \([\text{M}_2(\text{bdc})_2(\text{L})_2]_n\). Both nets possess the same novel point symbol \((6^5.8)\) and vertex symbol \((6.6.6.6.6.\star)\) but were determined to have a different CS. Note that an asterisk is present in the VS because no ring is contained at that angle but there is always a cycle, hence the point symbol of \((6^5.8)\). An in-depth topological study confirmed that one of the nets had a similar connectivity to the 4-connected CdSO\(_4\) net and was classified as having \textit{cds} topology. Interestingly, the other net was identified as adopting an unprecedented network topology, coined \textit{usf}–1.\(^{118}\)

Vertex symbols are more informative topological descriptors than point symbols. Nevertheless, for nets that possess higher coordination numbers it is much more practical to report the point symbol as oppose to the vertex symbol. For example, Eddaoudi and co-workers were the first to report a \((3,24)\)-connected MOM having \textit{rht} topology and there are 276 angles around the 24-connected node!!! As you can imagine, reporting the vertex symbol for this node would not only be time consuming but extremely complex. It is therefore more appropriate to report the point symbol, \((4^3.8)(4^{72}.6^{132}.8^{72})\). Alternatively, similar nets may have the same coordination sequence but different vertex symbols. This is attested in two zeolite nets, \textit{lta} (Linda A) and \textit{rho}. The CS for both nets up to \(k = 10\) is 4, 9, 17, 28, 42, 60, 81, 105, 132, 162, and 641; therefore both nets have a topological density of 641. However, the nets are indeed unique as they possess different vertex symbols of 4.6.4.6.4.8 and 4.4.4.6.8.8 for \textit{rho} and \textit{lta}, respectively.
1.6.4. Tiling and Transitivity

A powerful tool implemented for the systematic enumeration of structures is to describe the net in terms of the tiling that it carries because each tiling can encode valuable information (e.g. transitivity, natural tiling, duals, etc), all of which contribute to the understanding of existing nets and development of future target structures. Tiling representations for 2-periodic lattices appear in the form of edge-to-edge tiles that cover a plane, for instance covering a plane with equivalent hexagons would reveal a regular tiling for the (6,3) honeycomb lattice. Tilings for 3-periodic nets on the other hand consist of an assortment of face-to-face tiles that fill space through the formation of generalized polyhedra or cages (Figure 1.22.). A visualization of the tiling that carries at net can provide a clearer picture of the open channels and cages present in the structure; however, in complex networks the tiling may be less appropriate and look like nothing more than a collage of colors and shapes.

Figure 1.22. Tiling representation and face symbols for two zeolite nets: (left) lta $3[4^4] + [4^6.6^8]$ + $[4^{12}.6^8.8^6]$; and (right) rho $3[4^8.8^2] + [4^{12}.6^8.8^6]$.

Most nets adopt a so-called natural tiling which consists of the smallest possible tiles and thus it is uniquely suited to describe a particular net. Computer software
packages are available to determine (TOPOS)\textsuperscript{119} and visualize (3dt)\textsuperscript{120} the natural tiling by applying the following restrictions in the calculation: (a) each tile must carry the maximum symmetry for that net and (b) all faces must represent strong, essential rings. Consequently, a *face symbol* is generated for each tiling which reveals the ratio and composition of the tile in the form of \([A^a.B^b….etc]\). One may recall that this notation looks quite similar to that used for point symbols. Nonetheless, the meaning is quite different and refers to *a* faces that are A-membered rings (MRs), *b* faces that are B-rings, *etc*. For example, the face symbol for the \textbf{Ita} net could be broken down as follows: \(3[4^6] + [4^6.6^8] + [4^{12}.6^8.8^6]\) \(\rightarrow\) the tiling contains three different tiles in a ratio of 3:1:1. The largest tile, an \(\alpha\)-cage, is assembled from twelve 4-MRs, eight 6-MRs, and six 8-MRs. Each of the 6-MRs are shared faces with a \(\beta\)-cage comprised of six 4-MRs and eight 6-MRs. Likewise, the 4-MRs of the \(\beta\)-cage share all faces with the cube tile comprised of six 4-MRs.

A valuable property obtained from tiling is a measure of its *regularity* which is categorized in terms of transitivity, \(pqrs\). This notation specifies the number of kinds of vertices (*p*), edges (*q*), faces (*r*), and tiles (*s*) in a 3-periodic network. Alternatively, since 2-periodic nets do not contain tiles, it is expressed as \(pqr\). MOMs that possess lower numerical transitivities have a higher degree of regularity and are therefore regarded as highly feasible targets in crystal chemistry and are easier to access synthetically. Thus, the assembly of flexible building blocks, in the absence of structure directing agents, frequently leads to the formation of a so called, *default* net.\textsuperscript{121}

Each vertex in a net can be simplified into a geometrical building unit by replacing a single vertex with a group of vertices (augmentation) by connecting the points
of extension to reveal a vertex figure/coordination figure. The most regular MOMs have transivities of 1111 which means they are vertex-, edge-, face-, and tile-transitive. The vertex figures of these nets correspond to regular polygons or polyhedron, specifically a triangle, tetrahedron, square, octahedron, or cube. There are exactly five regular 3-periodic default nets: srs (triangle), dia (tetrahedron), nbo (square), pcu (octahedron), and bcu (cube). Alternatively, the 12-coordinated fcu net has a transitivity of 1112 because it is comprised of a quasiregular polyhedron (cuboctahedron) which generates two kinds of holes in the structure and leads to the formation of two different tiles – tetrahedron and octahedron. Semi-regular nets are vertex- and edge-transitive, represented by a transitivity of 11rs with \( r > 1 \). Edge-transitive nets are attractive targets in crystal chemistry. In fact, many MOMs are assembled from two different vertex figures linked together through a common edge.\(^{121}\)

1.6.5. Reticular Chemistry Structure Resource (RCSR) Database

The RCSR\(^{117}\) is a comprehensive database developed by O’Keeffe and co-workers. It is dedicated to facilitating the rapid development of reticular chemistry and is comprised of over 1600 entries from known chemical compounds and crystal structure predictions ranging from 0- to 3-periodic architectures. RCSR is modeled after the zeolite database and therefore a three-letter nomenclature system was adopted. The key distinction between these codes is that all RCSR symbols are lower case bold as oppose to the upper case symbols used in the zeolite database.\(^{122}\) The symbols help to alleviate confusion between nets because nets are associated with different names (e.g. Laves net, (10,3)-a, Y*, etc). The RCSR letter code assigned to this uninodal 3-connected net is
therefore srs because it is the Si net in SrSi₂. When applicable, the nets are assigned a symbol based on their relation to zeolites, for instance LTA (Zeolite-A) is given the RCSR symbol lta. Many of the symbols reported in the database are in fact derived from their relation to minerals such as diamond (dia), Niobium Oxide (nbo), Platinum Sulfide (pts), Quartz (qtz), etc. In special circumstances however nets with unprecedented topologies maybe assigned a symbol that is named after a person, such as the med net, named after Professor Mohamed Eddaoudi.

The database is user friendly whereby a known crystal net can be located either by searching for the symbol, name, keyword(s), modifiers, and/or bounds (i.e. density, td₁₀, kinds of vertex, edge, face, etc). Perhaps most importantly, each entry is unique and reveals valuable crystallographic information (i.e. unit cell parameters) and topological details including the vertex symbol, and coordination sequence for each crystallographically independent node. Furthermore, information pertaining to the natural tiling and transitivity of a net is available for 3-periodics structures accompanied with a file in a coordinates of vertices in faces (cdg) that can be visualized using a useful tiling and analysis program (3dt) design by Olaf Delagado-Friedrichs.¹²⁰

1.7. Properties and Potential Applications of MOMs

The unique structural and chemical features that are characteristic of MOMs separate them from other solid state materials and so the field has witnessed an exponential growth concerning interest in their physical and chemical properties. The attractive features include but are not limited to, (1) hybrid inorganic-organic components allow for a high degree of modularity whereby the choice of metal ion, as well as, the
length and functionality of the organic linker can often be modified while maintaining the geometry of the MBBs; (2) varying degrees of dimensionality are possible, e.g. discrete, 2-, and 3-periodic; (3) decoration and expansion of traditional zeolite nets topologies using the single-metal-ion-based MBB approach has proven to yield ZMOFs with fine-tunable pores and enlarged cavities; (4) many open structures are known to exhibit high surface areas, pore volumes, and low framework densities; (5) open metal centers have shown to enhance H₂-MOF binding interactions and thus lead to higher $Q_{st}$ (at low loading); (6) typically facile and inexpensive synthetic protocols with high yields; and (7) many structures are thermally and chemically stable.

Academic and industrial researchers from across the world have therefore placed a particular focus on investigating the potential utility of these materials in desired applications. The national meeting of the American Chemical Society in fact held a special symposium in 2008 comprised of invited speakers devoted to this topic, entitled: “Metal-Organic Frameworks: What are they good for?” A themed issue of Chemical Society Reviews (Title: Metal-Organic Frameworks) also emphasized this topic whereby 18 peer-reviewed articles were published concerning design principles, molecular modeling, and various applications of which MOMs are well suited. Examples of some applications included, gas storage (e.g. H₂, CH₄, etc), selective gas adsorption and separation, drug delivery, catalysis, post-synthetic modifications, sensing, magnetism, and thin films. Studies concerning the storage and binding affinity of hydrogen, methane, and carbon dioxide gases in selected MOFs is the focus of this dissertation. Accordingly, details concerning other applications are beyond the scope of this discussion and can be found in the cited themed issue on MOFs and references therein.
1.8. Potential Clean Energy Alternative: Bridging the Interface between Hydrogen Storage and On-Board Applications

The rapid expenditure of non-renewable petroleum-based fossil fuels coupled with escalating environmental concerns (e.g. global warming and air pollution) has drawn considerable interest worldwide on a both scientific and societal level. The industrial and transportation sectors are the two primary consumers of fossil fuels and therefore this demand is not expected to subside in the future as the global population continues to increase. The United States currently relies heavily on foreign countries to fulfill this quota and from an economical perspective this is dangerous because it can lead to price fluctuations and supply disruptions. This dilemma has prompted researchers from a range of disciplines to work together towards the rational development of alternative renewable energy technologies that will alleviate the harmful side effects brought by the consumption of fossil fuels, yet preserve or even exceed their optimal energy output.

Vehicles powered by battery, hybrid, and fuel-cell technologies are currently used by many individuals to reduce their carbon footprint. This technology certainly offers improvements over traditional methods but it is not an ultimate solution to the problem because fuel-cells partially rely on the use of fossil fuels to power the internal combustion engine. Nissan however plans to launch the LEAF this year which is a 100 % electric car and therefore has zero emissions. It has an estimated driving range of 100 miles before recharging and is thus well suited for city commuters.

An attractive energy alternative that has gained much momentum in recent years is the use of hydrogen as an energy carrier for potential on-board applications. Although hydrogen is the simplest and most abundant chemical element on earth, less than 1 % is fact available in the form of a pure gas. It is therefore often extracted
from domestic resources (e.g. water, biomass, hydrocarbons) by means of chemical processes. The use of hydrogen as an energy carrier offers many advantages over gasoline and diesel fuel, perhaps most notable that it is 100% carbon-free which means it is clean burning, with only water as a byproduct. It also has an outstanding gravimetric mass energy density which is almost three times that of liquid hydrocarbons: 142 MJ kg⁻¹ versus 44.5 MJ kg⁻¹. Significant drawbacks however hinder its utility especially with regards to identifying cost-effective and safe storage technologies. Note that molecular hydrogen exists as an extremely volatile gas at ambient temperatures and therefore it has a very low volumetric energy density, which is much too low for practical applications (i.e. \( d_{\text{H}_2} = 0.08988 \text{ kg m}^{-3} \) at STP versus gasoline \(~700 \text{ kg m}^{-3}\)). To put this number into perspective, 5 kg of hydrogen gas occupies a volume of 60 m³ at room temperature and atmosphere pressures!

In order to facilitate the potential widespread commercialization of hydrogen-fueled light weight vehicles the Bush administration implemented the Hydrogen Fuel Initiative in 2003. The US Department of Energy (DoE) introduced the Energy Efficiency and Renewable Energy (EERE) and Fuel Cells Technologies (FCT) program to provide funding to universities, as well as, industrial and government agencies in order to accelerate the research and development in this area. The program focuses on many factors including hydrogen production, delivery, storage, infrastructure, and safety concerns. The DoE has therefore developed a specific set of technical targets (Table 1.3.) that span across numerous storage parameters.
Table 1.3. Select “revised” technical targets (September 2009) as set forth by the US Department of Energy (DoE) for on-board hydrogen storage systems in light-duty vehicles.

<table>
<thead>
<tr>
<th>Storage parameter</th>
<th>Units</th>
<th>2010</th>
<th>2015</th>
<th>Ultimate</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>System Gravimetric Capacity:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Usable, specific-energy from H₂ (net useful energy/max system mass)</td>
<td>kWh / kg</td>
<td>1.5</td>
<td>1.8</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>(kg H₂/kg system)</td>
<td>(0.045)</td>
<td>(0.055)</td>
<td>(0.075)</td>
</tr>
<tr>
<td><strong>System Volumetric Capacity:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Usable energy density from H₂ (net useful energy/max system volume)</td>
<td>kWh/L</td>
<td>0.9</td>
<td>1.3</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>(kg H₂/L system)</td>
<td>(0.028)</td>
<td>(0.040)</td>
<td>(0.070)</td>
</tr>
<tr>
<td><strong>Storage system cost and fuel cost</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$/kWh net</td>
<td>TBD a</td>
<td>TBD</td>
<td>TBD</td>
<td>TBD</td>
</tr>
<tr>
<td>$/kg H₂</td>
<td>TBD</td>
<td>TBD</td>
<td>TBD</td>
<td>TBD</td>
</tr>
<tr>
<td>$/gge at pump</td>
<td>3-7</td>
<td>2-6</td>
<td>2-3</td>
<td></td>
</tr>
<tr>
<td><strong>Durability/Operability</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Operating ambient temperature</td>
<td>ºC</td>
<td>-30/50</td>
<td>-40/60</td>
<td>-40/60</td>
</tr>
<tr>
<td>• Min/max delivery temperature</td>
<td>ºC</td>
<td>-40/85</td>
<td>-40/85</td>
<td>-40/85</td>
</tr>
<tr>
<td>• Cycle life (1/4 tank to full) Cycle life variation</td>
<td>Cycles</td>
<td>1000</td>
<td>1500</td>
<td>1500</td>
</tr>
<tr>
<td>• Maximum delivery pressure from a tank</td>
<td>bar (abs)</td>
<td>12</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>• Refueling rate for 5-kg of H₂</td>
<td>min</td>
<td>4.2</td>
<td>3.3</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>(kg H₂/min)</td>
<td>(1.2)</td>
<td>(1.5)</td>
<td>(2.0)</td>
</tr>
</tbody>
</table>

a To be determined.

These targets serve as criteria for candidate materials if they are to be used as alternative fueling systems for on-board hydrogen storage systems in light-duty vehicles. Every five years the targets are re-examined and adjusted according to the progress made in terms of the development. If a material was to meet or exceed all of these parameters it would essentially provide the same efficiency as current gasoline tanks.
1.8.1. Conventional Hydrogen Storage Technologies: Advantages and Limitations

Current hydrogen storage technologies involve storing large quantities of H\textsubscript{2} gas in compressed steel cylinders at elevated pressures (5000 – 10000psi), as well as, sufficiently cooling the gas below its critical temperature so that it becomes liquefied, i.e. cryogenic storage. Both methods have limitations concerning on-board applications. Compressed tanks store hydrogen at elevated pressures and therefore pose neither obvious safety concerns, while liquefaction of hydrogen is not cost-effective nor energy efficient. Note that the latter is still used in space technology and related applications but it must be contained in well insulated and pressurized vessels to avoid loss through evaporation\textsuperscript{136}. In summary, these methods are plagued by limited storage densities as a result of the added weight (e.g. insulation) and this will in turn prevent them from reaching the technical targets. Ongoing studies are however being conducted to develop hybrid compressed/liquefied storage systems (i.e. lower pressures and warmer temperatures) because this approach would be deemed safer and reduce the amount of H\textsubscript{2} lost from constant boil off.

1.8.2. Potential Hydrogen Storage Materials

In an effort to overcome the limitations imposed by compressed and cryogenic hydrogen storage technologies researchers are exploring the potential of solid-state materials to remedy this problem by storing hydrogen in or on the surface of wide range of materials via physisorption (reversible), chemisorption (irreversible), and/or spill-over processes\textsuperscript{128, 133, 137-139}. The relative strength of the binding affinity of dihydrogen with the adsorbent will ultimately dictate which mechanism is observed and play a decisive role in
determining the uptake capacity and reversibility of the system. A tank containing a porous material (adsorbent) loaded with hydrogen would in theory store the same amount of gas in less volume and at lower pressures.

Materials that are currently being explored and developed as viable hydrogen storage materials (HSMs) include metal hydrides, complex hydrides, carbon-based compounds, zeolites, and MOFs. Each of the proposed platforms offer a unique set of advantages but in many cases are plagued by severe limitations that impede their development for practical on-board applications. The revised DoE targets for 2010 stipulate that a viable HSM storing 5 kg of H\textsubscript{2} must have a gravimetric and volumetric storage capacity of 4.5 wt\% of H\textsubscript{2} and 0.028 kg L\textsuperscript{-1}, respectively and should reversibly adsorb/desorb H\textsubscript{2} under moderate pressures in the temperature range of -30 to 50\textdegree C, and permit a driving range of greater than 300 miles (480 km), as highlighted above in Table 1.3.\textsuperscript{135} It is important to bear in mind however that these targets include all system components such as the tank, regulators, valves, piping, mounting brackets, insulation, cooling capacity, etc. The actual storage capacity of the adsorbent must therefore exceed these values to compensate for the loss due to infrastructure. Not to mention that the tank must be durable and the re-fueling process must be safe, fast, and as efficient as currently gasoline tanks. These targets become even more demanding for 2015.

1.8.2.1. Chemical \textit{versus} Physical Adsorption

Adsorption can be subdivided into two categories based upon the relative strength of interaction between the adsorbate and the host (\textit{e.g.} adsorbent); that is, chemical (irreversible) and physical (reversible) adsorption. The former, commonly referred to as
chemisorption is associated with strong adsorbate-adsorbent interactions (e.g. > 50 kJ mol\(^{-1}\)). The estimated binding energy is therefore similar in magnitude to the strength of a chemical bond that is ionic or covalent in nature.\(^{140}\) The adsorption process often takes place at elevated temperatures (i.e. above the critical temperature of the adsorbate) and frequently leads to very high isosteric heats of adsorption (\(Q_{st}\)) values (i.e. too high for vehicular applications). This is because the mechanism involves the making (adsorption) and subsequent breaking (desorption) of chemical bonds. Unfavorable temperature, pressure, and/or chemical reaction conditions may therefore be required to remove the adsorbate and could compromise the structural integrity of the adsorbent.

The other adsorption category encompasses physisorbent materials. This particular class of compounds is well-known to exhibit facile reversibility because the adsorption process is governed by rather weak intermolecular interactions (e.g. ~ 4 to 8 kJ mol\(^{-1}\)). The so-called van der Waals forces, i.e. dispersion and London forces\(^{141}\) are the most prevalent types of forces in physisorption but others can also be present and include ion-dipole, ion-induced dipole, dipole-dipole, and quadrupole interactions.\(^{140,142}\) This technique is well suited for surface area, pore volume, and pore size distribution determinations because the adsorbed phase is free to migrate on the surface and completely fill the pores.

### 1.8.2.2. Proposed Chemisorption-Based Adsorbents

Metallic and chemical hydrides fall into the chemisorption category and therefore are often associated with very high binding affinities which lead to issues with refueling due to irreversibility\(^ {143-146}\) Fully reversible adsorption of hydrogen accompanied by high
volumetric capacities has indeed been observed in some metallic hydrides but their high framework densities often lead to gravimetric storage capacities that are far too low to meet technical targets. Complex hydrides have demonstrated good gravimetric energy densities but are plagued by slow kinetics and unfavorable desorption temperatures. Reports have shown that hybrid materials comprised of both metallic and complex hydrides offer superior performance. Full reversibility is achieved along with good kinetics and gravimetric uptake capacities; however, desorption at elevated temperatures is still a reoccurring problem.

1.8.2.3. Hydrogen Storage in Physisorption-Based Materials

The fastest way to charge and discharge hydrogen from an adsorbent ideally is to keep it in its molecular form, i.e. using physisorption-based materials. The most extensive amount of research in this area has focused on the storage of dihydrogen in carbon-based materials, zeolites, and permanently porous MOFs.72, 133, 147-151 The latter class of solid-state crystalline materials has received considerable interest since the first reported H₂ uptake by Yaghi and co-workers in 2003 (i.e. MOF-5).152 In order to achieve high uptake capacities that will satisfy the DoE technical targets the optimal binding affinity is estimated to be in the range of 15 to 20 kJ mol⁻¹. A compromise must therefore be made with respect to the binding affinity observed in physis- and chemisorption-based materials. A promising hydrogen storage candidate must exhibit lower H₂-MOF binding energies than those observed in dissociative chemisorption in order to sustain the reversibility and fast kinetics but exhibit a significant increase in binding energy must be sustained over
what is classically observed for physisorption-based materials in order to adequately store large amounts of hydrogen.

1.9. Key Factors which Govern \( \text{H}_2 \) Binding in MOFs: Literature Summary and Future Outlook

Permanently porous MOFs are well suited to potentially circumvent the \( \text{H}_2 \) storage challenge. This is due to their extensive list of attractive features, which include modularity, high surface areas and \( \text{H}_2 \) uptake capacities (at 77 K), low framework densities, and moderate chemical/thermal stabilities. Several promising avenues have been pursed in recent years to increase the \( \text{H}_2 \)-MOF binding interactions, while maintaining high surface areas and low framework densities. These include, most notably: (1) Embedding coordinatively unsaturated metal sites into the MOF via the framework backbone (\( e.g. \) using inorganic or organic MBBs);\(^{153} \) (2) Optimizing the pore dimensions (\( e.g. < 1 \text{ nm} \));\(^{98} \) (3) Incorporation of highly polarizable moieties into the framework;\(^{154} \) and (4) Inclusion of an electrostatic field by having a charged framework (\( e.g. \) extraframework cations/anions).\(^{155-157} \) Each pathway has attracted considerable attention because the \( Q_{st} \) determined for these systems is estimated to be in the range of 7 to 13 \( \text{kJ mol}^{-1} \). This is an improvement over the 5 \( \text{kJ mol}^{-1} \) benchmark (\( e.g. \) MOF-5).

Few reports however embark on this challenge in a systemic fashion and this makes it exceedingly difficult to independently evaluate the contribution of each parameter towards the overall \( \text{H}_2 \)-MOF binding affinity. The design of potential made-to-order hydrogen storage candidates is therefore critically dependent on gaining a detailed chemical understanding of the preferential binding sites of molecular hydrogen in these frameworks in a systematic fashion (see Chapter 2).
1.9.1. Importance of High Surface Area

The rational construction of porous MOFs with high anticipated apparent surface areas is a crucial parameter to maintain throughout the design process. A large accessible surface facilitates more H₂-MOF interactions and in doing affords an increased number of binding affinities. This will ultimately contribute to improving the overall performance of the MOF. The abundance of sorption data available for MOFs in the literature reveals a direct correlation between surface area and pore volume; that is, MOFs with high surface areas often have large corresponding pore volumes (Figure 1.23.). For example, NOTT-116 published be Schroder and co-workers with \textbf{rht} topology has an apparent BET surface of 4664 m²/g and a pore volume that is estimated to be 2.17 cm³ g⁻¹.\textsuperscript{158} MOFs with large pore volumes however rarely reach saturation at lower pressures (\textit{e.g.} 1 atm) but often reveal outstanding gravimetric uptake capacities at higher pressures (\textit{i.e.} compressibility factor). The highest surface area reported for a MOF (\textit{i.e.} as of May 2010) is UMCM-2 synthesized by Matzger and co-workers.\textsuperscript{159} Apparent BET and Langmuir surface areas were determined to be 5200 and 6060 m²/g, respectively. Note that since 2004 this field has witnessed unprecedented breakthroughs in terms of reported surface areas (\textit{e.g.} MOF-177, MIL-101, NOTT-116) which implies the limits have not yet been realized for these materials.\textsuperscript{86, 158, 160}
Select examples of MOFs having apparent surface areas greater than 3000 m$^2$/g is provided in Table 1.4. Note that the calculated framework density for MOFs is often inversely proportional with respect to the surface area and pore volume whereby higher surface area materials predominantly have lower densities. The data presented below clearly reveals that MOFs with high surface areas are dominated by neutral frameworks having low densities. Yet, those with smaller pores and potential open metal sites reveal enhanced H$_2$-MOF interactions as evidenced by the larger isosteric heat of adsorption (at low loading), as will be discussed below.
Table 1.4. Select examples of MOFs with high surface areas.

<table>
<thead>
<tr>
<th>refMOF</th>
<th>Inorganic</th>
<th>Organic</th>
<th>C&lt;sup&gt;a&lt;/sup&gt;</th>
<th>P.S. (Å)</th>
<th>S.A. (m&lt;sup&gt;2&lt;/sup&gt;/g)</th>
<th>H&lt;sub&gt;2&lt;/sub&gt; Uptake&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Q&lt;sub&gt;st&lt;/sub&gt; (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>159UMCM-2&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Zn&lt;sub&gt;2&lt;/sub&gt;O(CO&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;6&lt;/sub&gt;</td>
<td>BTB; T&lt;sup&gt;2&lt;/sup&gt;DC</td>
<td>N</td>
<td>~14-30</td>
<td>5200</td>
<td>6060</td>
<td>1.3</td>
</tr>
<tr>
<td>160MOF-177</td>
<td>Zn&lt;sub&gt;2&lt;/sub&gt;O(CO&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;6&lt;/sub&gt;</td>
<td>BTB</td>
<td>N</td>
<td>~10-15</td>
<td>4746</td>
<td>5640</td>
<td>1.25</td>
</tr>
<tr>
<td>161UMCM-1</td>
<td>Zn&lt;sub&gt;2&lt;/sub&gt;O(CO&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;6&lt;/sub&gt;</td>
<td>BTB; p-BDC</td>
<td>N</td>
<td>~14-32</td>
<td>4730</td>
<td>4160</td>
<td>N.R.</td>
</tr>
<tr>
<td>159NOTT-116&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Cu(CO&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;L&lt;sub&gt;2&lt;/sub&gt;</td>
<td>ATPB</td>
<td>N</td>
<td>~13-24</td>
<td>4664</td>
<td>N.R.</td>
<td>9.2</td>
</tr>
<tr>
<td>162MIL-101&lt;sup&gt;g&lt;/sup&gt;</td>
<td>Cu(CO&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;L&lt;sub&gt;2&lt;/sub&gt;</td>
<td>p-BDC</td>
<td>N</td>
<td>~29-34</td>
<td>4240</td>
<td>5500</td>
<td>2.5</td>
</tr>
<tr>
<td>163, 164IRMOF-20</td>
<td>ZnO(CO&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;6&lt;/sub&gt;</td>
<td>T&lt;sup&gt;2&lt;/sup&gt;DC</td>
<td>N</td>
<td>~15-20</td>
<td>4024</td>
<td>4593</td>
<td>1.35</td>
</tr>
<tr>
<td>165PCN-66&lt;sup&gt;h&lt;/sup&gt;</td>
<td>Cu(CO&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;L&lt;sub&gt;2&lt;/sub&gt;</td>
<td>NTEI</td>
<td>N</td>
<td>~13-20</td>
<td>4000</td>
<td>4600</td>
<td>N.R.</td>
</tr>
<tr>
<td>166, 167IRMOF-1</td>
<td>ZnO(CO&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;6&lt;/sub&gt;</td>
<td>p-BDC</td>
<td>N</td>
<td>~10-15</td>
<td>3800</td>
<td>4400</td>
<td>1.32</td>
</tr>
<tr>
<td>168NOTT-112&lt;sup&gt;f&lt;/sup&gt;</td>
<td>Cu(CO&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;L&lt;sub&gt;2&lt;/sub&gt;</td>
<td>TPB</td>
<td>N</td>
<td>~13-20</td>
<td>3800</td>
<td>N.R.</td>
<td>2.30</td>
</tr>
<tr>
<td>82PMOF-2</td>
<td>Cu(CO&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;L&lt;sub&gt;2&lt;/sub&gt;</td>
<td>TEPB</td>
<td>N</td>
<td>~13-20</td>
<td>3730</td>
<td>4180</td>
<td>2.21</td>
</tr>
<tr>
<td>97rht-1</td>
<td>Cu&lt;sub&gt;2&lt;/sub&gt;O(N&lt;sub&gt;2&lt;/sub&gt;Cr)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>TZI</td>
<td>C</td>
<td>~13-20</td>
<td>2847</td>
<td>3223</td>
<td>2.4</td>
</tr>
<tr>
<td>169PCN-6</td>
<td>Cu(CO&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;L&lt;sub&gt;2&lt;/sub&gt;</td>
<td>TATB</td>
<td>N</td>
<td>~10-15</td>
<td>N.R.</td>
<td>3800</td>
<td>1.90</td>
</tr>
<tr>
<td>164IRMOF-6</td>
<td>ZnO(CO&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;6&lt;/sub&gt;</td>
<td>o-DCB</td>
<td>N</td>
<td>~10-15</td>
<td>2476</td>
<td>3263</td>
<td>1.48</td>
</tr>
</tbody>
</table>

<sup>a</sup>Overall charge on the framework, where N refers to neutral, A is anionic, and P is cationic; <sup>b</sup>H<sub>2</sub> uptake measured at 77 K and 1 atm; <sup>c</sup>University of Michigan Crystalline Material; <sup>d</sup>Not reported; <sup>e</sup>Nottingham; <sup>f</sup>Isoreticular Metal-Organic Framework; <sup>g</sup>Porous Coordination Network. Abbreviations: BTB = 1,3,5-benzenetribenzoate; T<sup>2</sup>DC = thieno[3,2-b]thiophene-2,5-dicarboxylate; p-BDC = 1,4-benzenedicarboxylate; ATPB = 1,3,5-tris(3,5-dicarboxylphenylethynyl)benzene; NTEI = 5,5',5''-(4,4',4''-nitrilotris(benzene-4,1-diyl)tris(ethylene-2,1-diyl)trisophthalate; TPB = 1,3,5-tris(p-phenyldicarboxyl)benzene; TEPB = 1,3,5-tris(3,5-dicarboxylphenylethynyl)benzene; TZI = 5-tetrazolylate; TATB = 4,4',4''-s-triazine-2,4,6-triyltribenzoate; o-DCB = 1,2-dihydrocyclobutabenzen-3,6-dicarboxylate.

1.9.2. Design Strategies to Incorporate Potential Open Metal sites into MOFs

Experimental and computational studies have shown that a high concentration of potentially accessible open-metal binding sites, i.e. multinuclear clusters, enhances Q<sub>st</sub> in MOFs at low loading. This is therefore a sought after feature because it facilitates higher gravimetric H<sub>2</sub> uptake capacities at lower pressures (see Table 1.5.). The impregnation of coordinately unsaturated metal centers into MOFs, whether in the form of intra- or extra-framework metal cations often leads to stronger binding sites due in part to favorable metal-H<sub>2</sub> orbital interactions and enhanced electrostatic interactions. The organic components on the other hand are believed to have less of an effect, with binding energies in the range of ~4 – 5 kJ mol<sup>1</sup>. Note that the contemporary challenge is to
synthesize a MOF that also maintains these favorable binding interactions at higher loadings (see Chapter 2).

Table 1.5. Select examples of MOFs to highlight the relationship between $Q_{st}$ and accessible to potential open-metal centers.

<table>
<thead>
<tr>
<th>ref</th>
<th>Material</th>
<th>Inorganic MBB</th>
<th>Surface Area (m²/g)</th>
<th>$H_2$ Uptakeb</th>
<th>$Q_{st}$b (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>170</td>
<td>Ni₃(DHTP)</td>
<td>rod-like Ni clusters</td>
<td>N.R.</td>
<td>N.R.</td>
<td>2.0</td>
</tr>
<tr>
<td>171</td>
<td>[Cd₆(TZ)₉]NO₃</td>
<td>Cd₆(TZ)₉</td>
<td>310</td>
<td>338</td>
<td>0.75</td>
</tr>
<tr>
<td>172</td>
<td>Co₃[(Mn₄Cl₃)(BTT)₈]·1.7CoCl₂</td>
<td>Co₃[Mn₄Cl₃(N₄CR)₈]</td>
<td>2096</td>
<td>2268</td>
<td>2.12</td>
</tr>
<tr>
<td>173</td>
<td>NaNi₅(OH)(SIP)₂</td>
<td>Na₅Ni₅O₃₄</td>
<td>700</td>
<td>N.R.</td>
<td>0.94</td>
</tr>
<tr>
<td>174</td>
<td>Fe₃[(Mn₄Cl₃)(BTT)₈]·FeCl₂</td>
<td>Fe₃[Mn₄Cl₃(N₄CR)₈]</td>
<td>2033</td>
<td>2201</td>
<td>2.21c</td>
</tr>
<tr>
<td>175</td>
<td>Mn₃[(Mn₄Cl₃)(BTT)₈(CH₃OH)₁₀]₂</td>
<td>Mn₃[Mn₄Cl₃(N₄CR)₈]</td>
<td>2057</td>
<td>2230</td>
<td>2.20c</td>
</tr>
<tr>
<td></td>
<td>MIL-101</td>
<td>[Cr₇OF(CO₂)₆]</td>
<td>4230</td>
<td>5500</td>
<td>2.5</td>
</tr>
<tr>
<td>98</td>
<td>[Cu₆O(TZI)₃]NO₃</td>
<td>[Cu₄(CO₂)₄]; Cu₉O(N₄CR)₃</td>
<td>2847</td>
<td>3223</td>
<td>2.4</td>
</tr>
<tr>
<td>176</td>
<td>Ni₂.₇₅Mn₀.₂₅[(Mn₄Cl₃)(BTT)₈]₂</td>
<td>Ni₃;Mn₀.₂₅ [Mn₄Cl₃(N₄CR)₈]</td>
<td>2110</td>
<td>2282</td>
<td>2.29a</td>
</tr>
<tr>
<td>71</td>
<td>Zn₃(BDT)₃</td>
<td>Zn₃(BDT)₃</td>
<td>640</td>
<td>N.R.</td>
<td>1.46</td>
</tr>
<tr>
<td>72</td>
<td>Mn₃(BDT)₃</td>
<td>Mn₃(BDT)₃</td>
<td>290</td>
<td>N.R.</td>
<td>0.97</td>
</tr>
<tr>
<td>163</td>
<td>Zn₃(DHTP)</td>
<td>rod-like Zn clusters</td>
<td>783</td>
<td>1132</td>
<td>1.77</td>
</tr>
<tr>
<td>164</td>
<td>Cu₃(BTC)₂</td>
<td>[Cu₂(CO₂)₄]</td>
<td>1507</td>
<td>2175</td>
<td>2.5</td>
</tr>
<tr>
<td>165</td>
<td>[In₃O(ABTC)₁.₅]NO₃</td>
<td>In-MBB</td>
<td>N.R.</td>
<td>1417</td>
<td>2.6a</td>
</tr>
</tbody>
</table>

aPore size; bHydrogen uptake capacity at 77 K and 1 atm; cIsosteric heat of adsorption at low loading; d at 1.2 bar. **Abbreviations:** DHTP = 2,5-dihydroxyterephthlate; TZ = tetrazolate; BTT = 1,3,5-benzenetristetrazolate; SIP = 5-sulfoisophthalate; TZI = 5-tetrazolylate; BDT = 1,4-benzeneditetrazol-5-yl; BTC = 1,3,5-benzenetricarboxylate; ABTC = 3,3',5,5'-azobenzenetetracarboxylate.

An urgent need exists for the development of various platforms so that the overall effect of the metal ion can be truly assessed in a systematic fashion. In many cases a MOF that exhibits a high $Q_{st}$ may also contain other key parameters that promote stronger interactions (*i.e.* narrow pores, electrostatic field, *etc*). This is exemplified in the case of soc-MOF which exhibits an exceptional $H_2$ uptake capacity of 2.61 wt % at 1.2 atm and 77 K. The high uptake is in agreement with the constancy observed in $Q_{st}$ and most importantly it is maintained at 6.5 kJ mol⁻¹ even at higher loadings. Eddaoudi and
co-workers attribute to the potential open In-TMBB metal centers, narrow pores, and higher localized charge density in the channels (see Chapter 2).98, 174

To date, three different strategies are actively being pursued by researchers to incorporate accessible open-metal binding sites into MOFs. These include, (1) the synthesis of solvent-containing MOFs whereby the metal-bound solvent molecules on the inorganic MBB (e.g. H2O, DMF, MeOH, etc) can be removed post-synthetically via thermal and/or solvent exchange techniques to produce unsaturated metal centers,87, 153 (2) introducing metal cations into the framework backbone by utilizing metallated organic-based bridging ligands (e.g. metalloporphyrins, crown ethers, salen-type ligands, etc),175-177 and (3) the synthesis of charged frameworks in which case the extra-framework cations can be substituted for metal ions or metallated complexes (i.e. anionic MOFs).72, 155

The first approach is certainly the most exploited strategy used by experimentalists, especially since the latter have only been recently developed. In addition to selecting a suitable strategy, the type of metal cation is very important because the binding affinity of molecular hydrogen can vary significantly from one metal ion to the next. Specific characteristics that must be taken into consideration include the charge, atomic radius, and the classification of the metal (e.g. s-, d-, p-, or f-block). Studies suggest that alkali-based metals are unlikely to satisfy the optimal Qst demand at room temperature, yet monovalent transition metals may lead to binding energies that are in fact too strong (i.e irreversible) for on-board applications. The most explored group of metal ions are the dicationic first row transition metal ions and select s- and p-block metals (e.g. Na⁺, Li⁺, Mg²⁺, Al³⁺). Note that the highest H₂ uptake recorded for a MOF is
comprised of dicationic copper centers (i.e. paddlewheel). Accordingly, PCN-12 has an apparent BET and Langmuir surface area that is estimated to be 1943 and 2425 m²/g, respectively and a corresponding pore volume of 0.94 cm³ g⁻¹. The neutral MOF adsorbs 3.05 wt % of H₂ at 77 K and 1 atm. The Qst was not reported for the this material but the authors attribute the high uptake to presence of open copper metal sites and the efficient packing of the spheroid-like building blocks.

1.9.2.1. Extra-framework Approaches: Ion-Exchange and Metal Doping

The relative binding strength of metal-hydrogen interactions has been systematically evaluated in ion-exchanged zeolites for many years. For example, temperature-dependent infrared spectroscopy measurements carried out on Li⁺, Na⁺, and K⁺ ion exchanged zeolites (e.g. ZSM-5, Ferrierite) confirm that the interaction energy is strongest for Na⁺ than the others. High framework densities associated with zeolite frameworks coupled with their lack of modularity render them unsuitable for hydrogen storage applications. Eddaoudi and co-workers however conducted similar studies using anionic ZMOFs as platforms. The charge balancing extra-framework organic cations (e.g. DMA⁺) present in the enlarged cavities were readily exchanged for Li⁺ and Mg²⁺ ions, which resulted in improved Qst over the parent compound (e.g. Li > Mg) and more importantly as much as a 50% increase compared to neutral MOFs. Unlike their inorganic counterparts, ZMOFs are not thermally stable at elevated temperatures (i.e. > 300°C) and therefore the metal ions are still hydrated. Accordingly, the authors associated the enhanced isosteric heat of adsorption to the presence of an electrostatic field in the cavities resultant from the metal ions.
A comprehensive ion-exchange study was conducted by Long and co-workers to investigate the effect of metal cation on H\textsubscript{2} binding affinities in a sodalite-type platform formulated as, \[(\text{Mn}_4\text{Cl}_3\text{BTT}_8\text{CH}_3\text{OH})_{10}\]\textsubscript{2}. Exchange with metal chloride salts resulted in the formation of an isostructural series of mix-metal MOFs, 
\(\text{M}_3[(\text{Mn}_4\text{Cl}_3\text{BTT}_8\text{CH}_3\text{OH})_{10}]_2\cdot\text{xMCl}_2\) where \(\text{M} = \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Fe}^{2+}\). The isosteric heats of adsorption for these MOFs were estimated to be in the range of 8.5 kJ mol\textsuperscript{-1} to 10.5 kJ mol\textsuperscript{-1} with the Cu analog being the lowest and Co the highest.\textsuperscript{172} Hupp and co-workers on the hand introduced a novel strategy by doping a neutral pillared MOF with Li\textsuperscript{+} cations. The results were encouraging whereby the H\textsubscript{2} uptake was increased from 0.93 wt % to 1.63 w% (77 K; 1 atm). This was found to be in agreement with the isosteric heat of adsorption, which revealed an increased over the full pressure range.\textsuperscript{182}

1.9.2.2. Experimental Techniques: Detection of Metal-H\textsubscript{2} Binding in MOFs

Many strategies have been developed in recent years to incorporate potential open metal binding sites into MOFs. Only a handful of these studies however use experimental techniques to unequivocally prove that the metal centers are indeed open binding sites and thus accessible to molecular hydrogen. The possibility that hydrogen can in fact bind to a metal center in molecular form was discovered in 1984 by Kubas in the complex [W(CO)\textsubscript{3}Pr\textsubscript{3}(H\textsubscript{2})].\textsuperscript{183} The formation of such a side-on \(\eta_2, \sigma\)-H\textsubscript{2} complex was confirmed with various experimental and theoretical techniques, including for example, single-crystal neutron diffraction studies. Following this extremely significant discovery many analogous transition metal \(\sigma\)-H\textsubscript{2} complexes have been reported, where it must be
noted that oxidative addition of the H₂ to the metal, and hence binding as hydrides, is still far more common.¹⁸⁴, ¹⁸⁵

### 1.9.2.2.1. SCD, FT-IR, and Low-temperature Powder Neutron Diffraction Studies

Some experimental techniques that have been employed to provide evidence of an open metal center include single-crystal X-ray diffraction (SCD), infrared (IR) spectroscopy, low-temperature powder neutron diffraction studies, and inelastic neutron scattering (INS) experiments. Yaghi and co-worker were the first to investigate the presence of accessible open metal sites by using SCD studies. The authors collected SCD data on the hydrated and dehydrated forms of the porous MOF-11 with pts topology.¹⁸⁶ The framework is built-up from copper tetracarboxylate MBBs and therefore has two potential open metal sites per MBB. Indeed, the crystal structure of the dehydrated form revealed no evidence of coordinated axial aqua ligands and the structure was more relaxed as compared to the hydrated form. Bordiga and co-workers were however the first to confirm binding of molecular hydrogen to open metal sites in a MOF, i.e. HKUST-1 formulated as [Cu₃(BTC)₂], which is also assembled from copper paddlewheel MBBs.¹⁸⁷ This was carried using IR spectroscopy whereby a stretching band at 4100 cm⁻¹ in the IR spectrum confirmed the presence of a metal-H₂ interaction (i.e. physisorbed). Note however that this type of interaction is nothing like that observed in the Kubas complexes and is nothing more than a physisorbed interaction.

More extensive studies in recent years have focused on the use of low-temperature neutron powder diffraction experiments by determining the M⁺⁺-D₂ distances. Results on HKUST-1 and revealed 6 different binding sites, with the accessible
square pyramidal copper site being the most favorable, i.e. Cu$^{2+}$-$D_2$ distance of 2.39 Å.

Long and co-workers carried out a systematic study of metal on H$_2$-MOF interactions in two isostructural MOFs with sodalite-type topology and formulated as, HM[(M$_4$Cl)$_3$(BTT)$_8$]$_3$.5HCl, where M = Mn or Cu. M$^{2+}$-$D_2$ distance of 2.27 Å and 2.47 Å for the Mn$^{2+}$ and Cu$^{2+}$ analogs, respectively, were found in neutron powder diffraction data. This evidence suggests that hydrogen will bind more strongly in the Mn analog and is therefore anticipated to have a higher $Q_{st}$ for H$_2$ at low loadingsw. Indeed, sorption experiments confirmed that the $Q_{st}$ was higher for Mn analog (10.1 kJ mol$^{-1}$) compared to the copper-based framework (9.5 kJ mol$^{-1}$). It is noteworthy to mention that $Q_{st}$ for the copper analog was more constant over the entire coverage because of the presence of a higher concentration of open metal sites. This is because the manganese analog cannot be fully dehydrated owing to the presence of residual methanol ligands.

A neutron scattering study of the zinc analog of MOF-74 (i.e. CPO-27) found a rather long Zn$^{2+}$-$D_2$ distances of 2.6 Å, which is in accord with the lower $Q_{st}$ of 8.8 kJ mol$^{-1}$ as compared to complexes with shorter M$^{x+}$-$D_2$ bond lengths. D$_2$-D$_2$ distance between neighboring adsorbed molecules were determined to be 2.85 Å which is rather short in view of the fact that the distance between H$_2$ molecules in the solid state is 3.6 Å. This finding therefore does suggest that open metal centers lead to more dense packing of hydrogen in these systems. Cheetham and co-workers explored the Ni$^{2+}$-$D_2$ interactions via INS studies in two microporous phosphate- and sulfoisophthalate-based frameworks. Both TPD studes and INS spectra an unusually strong interaction of hydrogen with Ni in accord with the high value of $Q_{st}$ of 10.4 kJ mol$^{-1}$. 

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1.10. Inelastic Neutron Scattering (INS)

Neutrons can be used in a wide variety of scattering techniques to investigate the bulk properties and surrounding chemical environment of materials in condensed phases. Neutrons are neutral subatomic particles and interact directly with atomic nuclei rather than the electrons. Scattering of neutrons is a function of this neutron-nuclear interaction, and it has an irregular variation through the periodic table, whereas the intensity of the scattering in photon-based techniques depends upon the number of electrons (i.e. in X-ray diffraction) or their polarizability or the resulting dipole moment (in optical spectroscopy). For example, it can be difficult to obtain information for light atoms such as hydrogen, which has the largest neutron scattering cross section of any element (Figure 1.24.). Neutrons are unique scattering probes in the sense that both of their energies and wavelengths match, respectively, excitations and interatomic dimensions found in condensed matter. They can, therefore be used in diffraction experiments, i.e. elastic scattering (as X-rays) and in a variety of spectroscopies, i.e. inelastic scattering, to study dynamics of molecules over a very large range of timescales. In the latter case the neutron can either lose energy by exciting a vibrational, or rotational mode in the solid in the scattering process, or gain energy from de-excitation of such a mode.

INS maybe regarded as the most sensitive spectroscopic tool for determining the affinity of adsorbed H₂ at various binding sites in porous materials. This is based on the fact that the lowest transition between the rotational energy levels of the bound H₂ molecule is extremely sensitive to the surroundings which give rise to the barrier to rotation. Neutrons can observe the rotational transitions associated with a change in the total nuclear spin of the hydrogen molecule, which is not normally possible using optical
spectroscopy. A change in the nuclear spin (I) coincides with a change in the molecular rotational quantum number (J) and is forbidden in optical spectroscopy because photons are unable to couple to nuclear spins.\(^{189}\)

**Figure 1.24.** Schematic illustration of select elements and the deuterium isotope to emphasize the cross sections due to neutron scattering (coherent = blue; incoherent = purple) and absorption (green).\(^{190}\)

The rotational transitions observed in an INS spectrum can tentatively be assigned using a phenomenological model for the rotational energy levels. We use the model previously described by Eckert and co-workers for rotation in a simple double-minimum potential with two angular degrees of freedom, which has just one parameter, namely the barrier height, \(V_2\), to be determined from the observed transitions.\(^{98, 191}\) In the absence of a barrier to rotation the energy levels of the hydrogen molecule are quantized and given by \(BJ(J+1)\) whereby \(B\) is the rotational constant (7.35 meV or 59.6 cm\(^{-1}\)) and \(J\) the rotational quantum number. The lowest transition for the free rotor is the *ortho*- to *para*- \(\text{H}_2\) transition which occurs at 14.7 meV (119 cm\(^{-1}\) = 2\(B\)). Introduction of a barrier to rotation from guest-host interactions results in a hindered rotation, which lifts some or all
of the degeneracy of the higher levels (Figure 1.25.). We have chosen to simply label the energy levels sequentially (0, 1, 2, etc.) as the exact attribution (m_j sublevels) is not trivial, and depends on the form of the actual rotational potential energy surface.

**Figure 1.25.** Schematic of the rotational energy level diagram for a dihydrogen molecule with two rotational degrees of freedom, under the influence of a hindering potential (Courtesy of Dr. Eckert at UCSB).

The 0-1 transition decreases very strongly with increasing barrier height as it may be regarded as a rotational tunneling transition. The tunneling probability is always smaller for larger barriers, whereas the higher transitions (torsional oscillator) increase with barrier height. A smaller value for the 0-1 transition therefore suggests a stronger interaction of H_2 with the host. We can associate different sets of observed transitions with particular binding sites when we carry out a series of experiments as a function of H_2 loading, related to know structural features in the material, and thereby assess the relative strengths of different binding sites. This type of INS experiment has the potential to provide critical insights in terms of rationalizing which structural and chemical
features contribute to favorable hydrogen interactions with the host material. Efforts are underway to obtain rotational potential energy surfaces directly from ab-initio calculations for a given binding site, and then to calculate the expected rotational and translational transition directly using quantum dynamics. This will make it possible to use the INS data to give direct and quantitative information of the interactions of H₂ at particular sites, and thereby direct efforts in synthesis in very specific ways.

1.11. Other Applications: MOFs as Platforms for the Capture, Sequestration and Separation of Gases

1.11.1. Methane Storage

The movement towards a potential hydrogen-based economy is certainly the most practical solution from both an environmental and economic standpoint. Methane however is also regarded as attractive substitute for gasoline and diesel fuels because of its high volatility (e.g. dissociates quickly in the event of a spill) and the byproducts from the combustion process contain less carbon dioxide emissions than conventional hydrocarbon fuel sources. Methane is very abundant, non-toxic, and the principle component in natural gas (87 % by volume). The reoccurring problem however is that it also exists as a gas at ambient temperatures and standard pressures. This feature therefore hinders its utility in on-board storage applications. Accordingly, the development of a safe, efficient, and cost-effective storage system is of the utmost importance. Note that a vehicle powered by adsorbed natural gas must have an energy density that is at least equivalent to the commercially available compressed natural gas powered vehicles.¹⁹³,¹⁹⁴ The US DoE methane storage target is 180v(STP)/v, which represents the equivalent volume (cm³) of methane stored per volume of the adsorbent at near ambient temperature

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and pressures under 35 bar. A variety of porous adsorbents have been explored for their potential to serve as suitable methane storage media (e.g. zeolites, activated carbons, single-walled carbon nanotubes, and MOFs). The results are promising, yet an adsorbent that adequately stores significant amounts of both methane and hydrogen has not been isolated and therefore remains a contemporary challenge. The highest absolute methane adsorption capacity is exhibited by a MOF (PCN-14) which indeed surpasses the DoE target by 28 % by storing 230v(STP)/v at 290K and 35 bar. It is assembled from two types of nanoscopic cages (octahedral and cuboctahedral) comprised of copper paddlewheel inorganic building blocks which are linked together through an anthracene backbone. The assembly of the two 4-connected nodes results in the formation of a neutral 3-periodic MOF having nbo topology. The presence of coordinately unsaturated metal sites and enlarged pores having small window apertures contributes to an unprecedented isosteric heat of adsorption, i.e. $Q_{st}$ 30 to 35 kJ mol$^{-1}$. It is noteworthy to mention that certain carbon-based adsorbents have also exceeded the DoE target; however, they exhibit very weak adsorbate-adsorbent interactions and it is difficult to enhance these interactions.

1.1.1.2. Storage and/or Sequestration of Carbon Dioxide

The combustion of fossils fuels generates the most abundant greenhouse gas; that is, carbon dioxide (CO$_2$). In 2005 alone the United States independently released 11 billion metric tonnes of CO$_2$ into the atmosphere, 1/3 of which was from power plants and other large point sources. Amid escalating environmental concerns (e.g. global warming) the DoE introduced the Carbon Sequestration Program (CSP) in 1997 to
promote the research and development of high scale cost-effective CO$_2$ capture technologies. The ultimate goal of this program is to significantly reduce large scale CO$_2$ gas emissions (by 2012) through the development of a fossil fuel conversion system that efficiently captures at least 90% of the gas (in the pure form). Once isolated and captured the gas would be compressed and then transported to an underground storage site for disposal or recycled for use in chemical processes, enhancement of oil recovery, and/or enhancement of coal bed methane production. Note that it is vital for all of these steps to accomplished whilst simultaneously being efficient and cost effective; that is, with a maximum of 10-20% increase in production costs. The most expensive step of the entire process is estimated to be the capture process, which represents three-fourths the cost of the entire system. Methods have been proposed and explored to capture CO$_2$ via pre-combustion, post-combustion, or via oxy-combustion; each of which are characterized by specific advantages and limitations.

The most prevalent industrial adsorbents currently used to sequester CO$_2$ via post-combustion from flue gas streams are so-called chemical (e.g. monoethanolamine, MEA) and physical solvents (e.g. Selexol) which are utilized at low and high pressures, respectively. These solvent methods are expensive and pose an environmental challenge for large scale CO$_2$ sequestration due to potential solvent degradation and loss during the operation process. Some large point sources also dilute CO$_2$ with N$_2$ using air fired combustors but this method is not ideal and better separation methods must be devised. Scientists are therefore exploring alternative CO$_2$ sequestration systems that are highly efficient, practical, and cost-effective. Some of the proposed concepts include low-temperature distillation, gas separation membranes functionalized with mobile or fixed
amine carriers, mineralization, biological-based capture systems, absorption and adsorption (physical and chemical).\textsuperscript{205, 206}

Porous MOFs with high surface areas represent an attractive class of solid adsorbents that are well suited to potentially remedy this problem. An optimal adsorbent must therefore be designed to possess the following traits: (1) high gas selectivity for CO\textsubscript{2} in a mixed gas stream, (2) high adsorption capacity, (3) high stability (\textit{e.g.} in the presence of contaminants), (4) favorable equilibrium and kinetics, (5) ease of regeneration, and (6) of course be cost effective. The underlying mechanisms that govern adsorption-based gas separation processes are not fully understood. Numerous studies however have proven that the molecular sieving effect, thermodynamic equilibrium effect, kinetic effect, and/or quantum sieving effect can independently or collectively play a dominant role in governing the overall selectivity process.\textsuperscript{207} An increasing number of rigid and flexible MOFs have been evaluated in recent years for their CO\textsubscript{2} storage capabilities.\textsuperscript{59, 208-213} The results of these studies are encouraging, as illustrated in Table 1.6., but still of hundreds if not thousands of MOFs have yet to be tested.
Table 1.6. CO₂ adsorption capacities (e.g. low and high) for selected MOFs.

<table>
<thead>
<tr>
<th>Material</th>
<th>S. A. (m²/g)</th>
<th>Framework Features</th>
<th>P. S. (Å)</th>
<th>Max. CO₂ Uptake</th>
<th>Exp. Conditions (T K, P bar)</th>
<th>Qtc (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>214MOF-177</td>
<td>4750</td>
<td>high porosity; large cavities</td>
<td>11 x 17</td>
<td>33.5 mmol g⁻¹</td>
<td>298, 42</td>
<td>298, 50</td>
</tr>
<tr>
<td></td>
<td>5640</td>
<td>OMS²; large cages; small window apertures</td>
<td>C: 25 x 29; W: 5.5 x 8.6</td>
<td>40.0 mmol g⁻¹</td>
<td>304, 50</td>
<td></td>
</tr>
<tr>
<td>215MIL-100</td>
<td>1900</td>
<td>mesoporous cages with small window apertures</td>
<td>C: 29 x 34; W: 12 x 16</td>
<td>18.0 mmol g⁻¹</td>
<td>304, 50</td>
<td></td>
</tr>
<tr>
<td>215MIL-101c</td>
<td>4100</td>
<td>1-D circular channels decorated with F⁻ anions</td>
<td>~4.4</td>
<td>3.4 mmol g⁻¹</td>
<td>304, 50</td>
<td></td>
</tr>
<tr>
<td>216MIL-102</td>
<td>N. R.</td>
<td>42.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HKUST-1</td>
<td>1154</td>
<td>OMS²; high porosity</td>
<td>5 and 15</td>
<td>10.7 mmol g⁻¹</td>
<td>298, 42</td>
<td>35</td>
</tr>
<tr>
<td>IRMOF-1</td>
<td>3800</td>
<td>high porosity</td>
<td>12 x 15</td>
<td>21.7 mmol g⁻¹</td>
<td>298, 35</td>
<td>N.R.</td>
</tr>
<tr>
<td>IRMOF-3</td>
<td>1568</td>
<td>amino functionalized pores</td>
<td>10 x 15</td>
<td>18.7 mmol g⁻¹</td>
<td>298, 35</td>
<td>N.R.</td>
</tr>
<tr>
<td>IRMOF-6</td>
<td>2516</td>
<td>alkyl functionalized pores</td>
<td>10 x 15</td>
<td>21.7 mmol g⁻¹</td>
<td>298, 35</td>
<td>N.R.</td>
</tr>
<tr>
<td>IRMOF-11</td>
<td>2096</td>
<td>catenated</td>
<td>7 x 12</td>
<td>14.7 mmol g⁻¹</td>
<td>298, 35</td>
<td>N.R.</td>
</tr>
<tr>
<td>215Bio-MOF-11</td>
<td>1040</td>
<td>narrow pores with lewis basic sites</td>
<td>~5.2</td>
<td>6.0 mmol g⁻¹</td>
<td>298, 35</td>
<td>45</td>
</tr>
<tr>
<td>174In soc-MOF</td>
<td>N.R.</td>
<td>narrow pores; high localized charge density</td>
<td>&lt; 10</td>
<td>9.0 mmol g⁻¹</td>
<td>298, 25</td>
<td>28.5</td>
</tr>
<tr>
<td>213ZIF-78</td>
<td>620</td>
<td>polar functional group; small windows</td>
<td>C: ~ 7.1; W: ~ 3.8</td>
<td>6.0 mmol g⁻¹</td>
<td>298, 1</td>
<td>N.R.</td>
</tr>
<tr>
<td>213ZIF-69</td>
<td>950</td>
<td>Large pores and large windows</td>
<td>C: ~ 12.4; W: ~ 5.9</td>
<td>37.6 cm³ g⁻¹</td>
<td>Or 82.6 L/L</td>
<td>298, 1</td>
</tr>
</tbody>
</table>

a Apparent surface area; b Average pore size; c Isosteric heat of adsorption at low loading; and d Open metal sites.

Similar to hydrogen storage there is a continuous quest to find the optimal balance between a maximum adsorption capacity and favorable isosteric heat of adsorption. The highest amount of CO₂ adsorbed in a MOF to date at room temperature is 33.5 mmol g⁻¹ and 40.0 mmol g⁻¹ at 42 bar and 50 bar, respectively for MOF-177. To put these numbers into perspective the highest gravimetric CO₂ adsorption capacity for a zeolite...
material is 7.4 mmol g⁻¹ at 32 bar and room temperature (zeolite 13X),²¹⁸ while for a carbon-based material (MAXSORB) it is 25.0 mmol g⁻¹ at 35 bar and room temperature.²¹⁹ Several MOFs exhibit high adsorption capacity for pure CO₂ as shown above. The adsorption behavior however can be significantly altered when the material is exposed to a mixture of gases and thus the adequate purification and separation of specific gases is of paramount importance for their potential utility in industrial applications. Dynamic adsorption measurements in the form of kinetic breakthrough curves are commonly employed to quantify and assess the adsorption behavior of solid adsorbents with respect to multi-component gas mixtures. The methodology behind this type of experiment separates the gases based on their affinity towards the adsorbent; that is, the gas mixture is introduced to a column that is packed with the adsorbent and the mixture is circulated until equilibrium is established. Those gases with a strong affinity for the adsorbent will be retained in the column, while weakly bound gases will be permitted to pass through. The adsorbed phase can be readily released in a controlled fashion via mild heating. A numerical value for selectivity (separation factor) can be then be extrapolated from these curves and correlated to the pore structure and composition of the adsorbent.

The current state of the art industrial separation technologies utilize general-purpose filters composed of activated carbon beds that are impregnated with metal salts (e.g. Cu, Zn, Ag, Mo). This class of adsorbents is efficient for some systems but it is not transferrable to all systems and their lack of modularity is impedes future optimization. The unique attributes afforded by MOFs circumvent these limitations and systematic breakthrough studies carried out by Yaghi and co-workers, amongst others, demonstrates
the importance of pore structure and functionality for adequate gas separation using this class of adsorbents. For example, it was shown that IRMOF-3 exhibits an 18 fold increase in ammonia dynamic capacity over MOF-5 upon exposure to a mixture of eight challenge cases (ammonia, ethylene oxide, chlorine, carbon monoxide, sulfur dioxide, dichloromethane, and tetrahydrothiophene). The vast number of MOFs synthesized versus those that have been tested for their selective gas adsorption and separation capabilities is not comparable. We therefore anticipate that future studies in this area will be fruitful and lead to unprecedented results.


Porous compounds are delimited by an interconnected network of pores or voids. The vast majority of solid-state materials can therefore be described as having some degree of porosity because many contain open channels and/or cavities. Permanently porous solids however encompass a unique subset of porous materials whereby the structural integrity of the framework is maintained even after the complete removal of all guest molecules. Due to their inherent porosity, they are uniquely suited for a plethora of potential applications ranging from gas storage and separation, catalysis, drug delivery, etc. In order to optimize the performance of these materials in practical applications it is imperative to perform a comprehensive textual characterization, in addition to, a systematic study to evaluate their adsorption properties (e.g. surface area, pore volume, pore size). Numerous experimental techniques are available to assess these features (e.g. small angle x-ray and neutron scattering, NMR-methods, mercury porosimetry, gas adsorption, etc) but the applicability of each method is highly dependent on a length
factor. Each method is therefore not universal for the entire pore size regime. Gas adsorption is widely recognized as a reliable, convenient, and cost-effective technique that is commonly employed to characterize porous materials because it permits a full evaluation of pore sizes ranging from micro- to macropores (from 0.35 nm up to 100 nm). Note that the amount of gas adsorbed is critically dependent upon several experimental and structural parameters which include the absolute temperature, pressure, and the interaction potential ($E$) between the vapor (adsorbate) and the surface (adsorbent).

1.12.1. Exploiting the Porosity of MOFs: Protocols for Sample Activation

An ongoing challenge for experimentalists is to identify a suitable protocol to fully activate porous MOFs, so that the experimental values agree well with computational and/or SCD studies. This is a prerequisite step in order to take advantage of the porosity whilst avoiding collapse of the framework. Several activation methods are currently available but each system often behaves differently and therefore what works for one material may not work for the next.

MOFs that display permanent porosity are predominately activated via solvent exchange; that is, the higher boiling point guest molecules residing in the channels/cages are exchanged for volatile solvents (e.g. DCM, EtOH, (CH$_3$)$_2$CO, CH$_3$CN, etc). In a typical experiment, 30 – 100 mg of the as-synthesized material is washed and then soaked in the chosen solvent for an unspecified amount of time (e.g. 1 – 7 days). This step is predominately carried out at room temperature but mild heating has been used to speed up the equilibrium process. The low boiling point guest molecules can then be
removed from the MOF using relatively mild evacuation procedures \(i.e.\) heating under vacuum). The success of this approach is evidenced by the larger number of highly porous MOFs reported that were activated using solvent exchange but still occasionally fails for many compounds.\textsuperscript{153}

Promising alternatives have been proposed to circumvent this challenge in solvent-containing MOFs and demonstrate great promise. In one method, Hupp and co-workers introduced a hybrid technique consisting of liquid activation followed by supercritical drying (ScD) using CO\textsubscript{2} activation.\textsuperscript{221} The authors observe up to 1200\% increase over traditional liquid and thermally assisted evacuation protocols. Note that ScD is often used in the preparation of silica aerogels, organosilicates, and polymer synthesis because it is an effective way to remove liquids in a controlled fashion without comprising the structural integrity of the material.\textsuperscript{222} This method is therefore uniquely suited to enhance access to the internal surface area of solvent-containing MOFs by because the fluid can be removed by reducing the surface tension in the material. In this context, the preferred gas of choice is CO\textsubscript{2} because it is cheap and more importantly it becomes supercritical under mild conditions \(T_c = 31^\circ\text{C}; P = 73\ \text{atm}\). A similar concept, yet less explored, was introduced by Lin and co-workers (2009) whereby the higher boiling point solvents were exchanged with solvents that can be removed via freeze-drying \(i.e.\) benzene.\textsuperscript{223} In this sense the liquid phase is precluded owing to the direct gas to solid transition. In summary, the enormous internal surface areas offer by this emerging classes of crystalline materials is critically dependent on development and identification of proper activation procedures that are unique for a particular material.
1.12.2. Classification of Adsorption Isotherms

An adsorption isotherm provides a relationship between the amount of gas adsorbed per gram of solid as a function of pressure at a constant temperature (i.e. boiling point of the adsorbate). Volumetric and gravimetric sorption measurements are the two most popular techniques currently used to determine the amount of gas adsorbed in a porous material. The shape of the isotherm is dependent upon the relative strength of the adsorbate-adsorbent and adsorbate-adsorbate interactions and therefore it reveals important structural information. This is because these interactions are governed by the size, shape, and chemical composition of the framework. The sorption behavior is also affected by the experimental conditions, i.e. the temperature relative to the boiling point of the adsorbate. This is due to the fact that differences in temperature (i.e. sub- and supercritical) will invoke changes in the thermodynamic states of the pore and bulk fluid phases (see Chapter 2).

In 1985, the International Union of Pure and Applied Chemistry (IUPAC) recognized the need for an efficient and universal classification system regarding the terminology, classification, and interpretation of sorption isotherms. As a subjective guide to researchers IUPAC therefore proposed to classify pore sizes based on the diameter of the pore. The limits were divided into three categories: (1) Micropores (2 nm or less); (2) Mesopores (2 nm to 50 nm); and (3) Macropores (> 50 nm). With regards to sorption behavior, porous materials fall into one of the six types of adsorption isotherms (Figure 1.26.). A fully reversible Type I isotherm is characteristic of microporous materials whereby the adsorption process is restricted to only a few molecular layers and is exemplified in the case of many MOFs, zeolites, porous oxides, and activated carbons.
These isotherms are predominantly collected using nitrogen and argon as adsorbates at their corresponding boiling temperature of 77 K and 87 K, respectively. With respect to shape, the curve is concave with respect to the P/P₀ axis and reaches a plateau as P/P₀ approaches 1. This therefore allows for the determination of the surface area and pore volume of the material. Note that the steepness and high uptakes (micropore filling) observed in the isotherm at low pressures is attributed to strong adsorbate-adsorbent interactions.

Figure 1.26. IUPAC classification of sorption isotherms.²²⁴

A reversible Type II isotherm denotes a non-porous or macroporous material. The overall shape is concave with respect to the P/P₀ axis at low pressures but it exhibits an inflection point or knee (e.g. point B) at higher pressures. This point is believed to indicate the transition from mono- to multilayer coverage. The amount adsorbed does not
reach a plateau as $P/P_0$ approach 1 and therefore materials that fall into this category possess such large pores that monolayer-multilayer coverage is not restricted.

The reversible Type III isotherm adopts a shape that is completely convex to the $P/P_0$ axis and is rarely observed in the literature. The adsorption behavior is primarily influenced by adsorbate-adsorbate interactions and less on the attractive adsorbate-adsorbent interactions (i.e. as observed in Type I). This is evidenced by the horizontal slope with respect to the $P/P_0$ axis at low pressure, which signifies rather weak fluid-wall interactions. At higher pressures the amount adsorbed increases at an exponential rate and thus reflects the importance of strong fluid-fluid interactions.

Mesoporous materials commonly exhibit the Type IV isotherm, which is accompanied by a distinct hysteresis loop thereby indicating that the adsorption process is not fully reversible. This loop results from pore (capillary) condensation and is observed when the adsorbate reaches a liquid-like state at pressures below the saturation pressure ($P_0$) of the bulk fluid. The general shape resembles a Type II isotherm (at lower pressures) due to the presence of a knee but following micropore filling the mesopores become saturated at higher pressures. This is indicated by the observed plateau in the isotherm as $P/P_0$ approach 1.

The Type V isotherm can be rationalized as a combination of the Types III and IV isotherms. It resembles the former with respect to the weak fluid-wall interactions, yet it is similar to the latter due to the presence of pore condensation. It is noteworthy to mention this type is rarely observed for porous materials, i.e. as for Type III. Lastly, the reversible Type VI isotherm is unique as compared to the aforementioned isotherms because each adsorbed layered is reflected in the form of *stepwise* multilayer adsorption.
The relative height and definition of each step is dependent upon the surface chemistry of the adsorbent, adsorptive, and the temperature. Each step represents the monolayer capacity for the respective adsorbed layer and typically remains constant for two to three layers. The type of isotherm is characteristic of adsorption on a uniform non-porous adsorbent, as exemplified by the adsorption of argon or krypton on graphitized carbon at a temperature of 77 K (i.e. below the boiling point of the adsorptive).

1.12.3. Surface Area Analysis

1.12.3.1. Adsorbate Selection

The standard adsorbate used for surface area analysis is nitrogen at its boiling temperature of 77 K. Alternative probe molecules have however been proposed and are often more reliable such as Ar at 87 K. The cross-sectional area of the adsorptive is also an important parameter to consider because its size can be affected by the surrounding environment. For example, the customary cross-sectional value for nitrogen at 77.35 K is 0.162 nm² but when it is exposed to a hydroxlated surface this values is significantly reduced to 0.135 nm². This discrepancy arises from the fact that nitrogen has a permanent quadruple moment and has the potential to interact with specific groups on the surface of the adsorbent. To overcome this limitation alternative probe molecules have been investigated with similar kinetic diameters to nitrogen and most notably include, argon (0.34nm), carbon dioxide (0.33nm), and methane (0.38nm) (see Chapter 2). Note that argon adsorption at 87.3 K is a more reliable probe molecule for pore size and surface area analysis because it does not have a quadruple. It therefore does not interact with specific sites on surface and high resolution data can be collected in a timely
fashion. The pores are then filled at higher relative pressures in the case of argon (Figure 1.27.).

![Figure 1.27.](image)

Figure 1.27. Semi-logarithmic plot of the low pressure sorption data collected for indium soc-MOF using nitrogen (red) and argon (blue) as adsorptives at 77.3 K and 87.3 K, respectively shown to highlight the differences in pore filling ranges. (i.e. $10^{-7} < P/P_0 < 10^{-5}$ for N$_2$ and $10^{-5} < P/P_0 < 10^{-3}$ for Ar).\textsuperscript{174}

1.12.3.2. Langmuir and BET Theories

The two most recognized methods for determining the apparent surface area (m$^2$/g) is determined by applying the Langmuir\textsuperscript{225} and/or BET theories\textsuperscript{226} (i.e. within the appropriate pressure region). The former theory assumes that the adsorbate covers the surface of the adsorbent with only one layer (i.e. monolayer coverage) and therefore the surface area can be obtained by experimentally determining the total number of adsorbed molecules that are required to completely cover the surface. The shortcomings of this approach are encountered when one considers the mechanism or sequence of adsorption on the surface. At low pressures the stronger binding sites on the surface will favor adsorbate coverage over the lower energetic sites and therefore subsequent layers will
surely form before monolayer coverage is complete. This has the potential to lead to uncertainties with respect to the number of adsorbed molecules and thus the surface area. The experimentally determined surface area will therefore be underestimated as compared to the theoretical values. The Langmuir equation can be written as follows:\textsuperscript{140}

\[
\frac{P}{W} = \frac{1}{KW_m} + \frac{P}{W_m}
\]

where \( P \) represents the equilibrium pressure of the adsorbate, \( K \) is the Langmuir constant, and \( W \) and \( W_m \) refer to the adsorbed weight and monolayer weight, respectively. A plot of \( \frac{P}{W} \) versus \( P \) should ideally reveal a straight line. The slope and intercept correspond to \( \frac{1}{W_m} \) and \( \frac{1}{KW_m} \), respectively. Once a solution is determined for the monolayer weight, the total surface area, \( S_t \), can be computed using the equation given below, where \( A_x \) is the cross-sectional area of the adsorbate, \( \bar{N} \) is Avogadro’s number, and \( \bar{M} \) is the molecular weight of the adsorbate.

\[
S_t = N_mA_x = \frac{W_m\bar{N}A_x}{\bar{M}}
\]

Three scientists by the names of Brunauer, Emmett, and Teller modified Langmuir’s theory by accounting for multilayer adsorption, referred to as the BET theory (1938). This method can be used for surface area analysis of nonporous and mesoporous materials but strictly speaking it is not appropriate for microporous materials. The reason for this is that it is difficult to distinguish between monolayer coverage and micropore filling and therefore is more of an \textit{apparent} or \textit{estimated} surface area when reporting on microporous materials. This theory does however account for surface area analysis up to three layers of adsorption, which is not possible with the Langmuir model. Surface area
analysis using the BET method involves two steps. The weight of the monolayer ($W_m$) must first be derived by transforming the adsorption isotherm into a linear BET plot, i.e. consisting of a slope and intercept. The simplified form of the BET equation can be written as follows:\(^{140}\)

\[
\frac{1}{W} \left[ \frac{P}{P_0} - 1 \right] = \frac{1}{W_mC} + \frac{C - 1}{P_0W_mC} \left[ \frac{P}{P_0} \right]
\]

where $W$ is the adsorbed weight, $W_m$ is the weight of the monolayer, and $C$ is an empirical constant. The latter value reflects the relative strength of the attractive adsorbate-adsorbent interactions and must always be positive (i.e. negative value is not physical). A negative result implies that the BET plot is outside the reasonable pressure range. A plot of $\frac{1}{W} \left[ \frac{P}{P_0} - 1 \right]$ versus $\frac{P}{P_0}$ typically yields a straight line; that is, if it is applied in the appropriate pressure region. The classical BET range of $\frac{P}{P_0}$ is between 0.05 and 0.35 atm and therefore the equations for the slope ($s$) and intercept ($i$) are represented as

\[
s = \frac{C - 1}{W_mC} \quad \text{and} \quad i = \frac{1}{W_mC},
\]

respectively. Combining these equations and solving for the weight of the monolayer generate the following expression: $W_m = \frac{1}{s + i}$. While a solution for $C$ is expressed as $c = \frac{s}{i} + 1$. The second and last step involves determining the total BET surface area using the expression below (i.e. as described for the Langmuir theory). It is noteworthy to mention the specific surface area is predominantly reported in the literature, meaning the total surface area divided by the weight of the sample.

\[
S_t = \frac{W_mC A_x}{M}
\]
To reiterate, the success of the BET theory for microporous materials lies in choosing the appropriate relative pressure range to generate a linear BET plot. It must therefore display a positive value for C and the term \( n \left( 1 - \frac{p}{p_0} \right) \) must continuously increase with respect to \( \frac{p}{p_0} \). Failure to do so will certainly lead to inaccurate BET surface area analysis. To illustrate the importance of selecting the optimal pressure range, two BET plots were generated for indium soc-MOF using the argon adsorption data collected at 87 K (Figure 1.28.). Data points selected within the classical BET range (0.05 and 0.35 atm) do not yield a straight line. The apparent surface area was estimated to be 891.5 m\(^2\)/g and the value for C is negative. Moreover, the points lie in the decreasing portion with respect to \( n \left( 1 - \frac{p}{p_0} \right) \). Deleting the points above 0.04 atm however generate a linear plot with a positive value for C and a surface area of 1148.3 m\(^2\)/g. Note that this value is 13% higher than if the classical BET range is applied.
Figure 1.28. BET plots for indium soc-MOF derived from the argon adsorption data collected at 87 K: (a) a plot of $n \left( 1 - \frac{p}{p_0} \right)$ versus $\frac{p}{p_0}$, where $n$ is the amount adsorbed; (b) BET plot in the classical relative pressure range; and (c) a linear BET plot generated by deleting all point above 0.04 atm.\(^{174}\)

1.12.4. Pore volume and Pore size Analysis

Experimental pore volume and pore sizes of porous materials are routinely obtained from high resolution adsorption isotherms, i.e. using nitrogen (77 K) or argon (87 K). It is assumed that the pores are filled with a liquid-like fluid after micropore filling and therefore the easiest way to determine the pore volume is to correlate the
amount adsorbed at higher relative pressures (e.g. in the plateau region) by applying the following equation:\textsuperscript{140}

\[ V_{\text{liq}} = \frac{P_a V_{\text{ads}} V_m}{RT} \]

where \( V_{\text{liq}} \) represents the volume of the liquid adsorptive contained in the pores, \( P_a \) and \( T \) are the ambient temperature and pressure, \( R \) is the gas constant, \( V_{\text{ads}} \) is the volume of adsorbate adsorbed, and \( V_m \) is the molar volume of the liquid adsorbate (e.g. \( 34.7 \text{ cm}^3 \text{ g}^{-1} \) for nitrogen).

Insights into pore size analysis (e.g. using a pore size distribution) can be conducted by applying a variety of classical macroscopic and modern approaches. The Dubinin-Raduschkevitch (D-R) method is based on Polanyi’s potential theory and is one of the classical approaches for pore volume and pore size analysis.\textsuperscript{227-230} This equation is not reliable for heterogeneous microporous adsorbents and therefore a linear fit for the adsorption data cannot be obtained. This is because the points are taken within a limited pressure range. To overcome this limitation the Dubinin-Asthakov (D – A) equation was developed because to be applicable over a much wider pressure range.\textsuperscript{231} It does not however account for adsorbate-adsorbent interactions, which are particularly important to consider in the case of microporous materials. This therefore paved the way for the development of the Horvath-Kawazoe (H-K) method because it recognizes that the relative size and shape of the pore has a direct effect on the adsorption properties.\textsuperscript{232} A limitation which impedes the success of this approach is that it is only applies to pores with a slit-like shape and it still assumes the properties of the fluid are identical to that of the bulk liquid. This assumption can lead to uncertainties in the pore size and volume analysis because it does not rationally describe the micropore filling process.\textsuperscript{140} The
Saito-Foley method was therefore developed to account for cylindrical-like pores (e.g. zeolites).²³³

The most advanced methods currently available for pore size analysis of both micro- and mesoporous materials are based on statistical mechanics; that is, Density Functional Theory (DFT), Monte Carlo (MC) simulation, and Molecular Dynamics (MD).²³⁴,²³⁵ A more accurate pore size can be obtained using these methods because they recognize that the thermodynamic state of the liquid is affected by the size and shape of the pore. Accordingly, the NLDFT method can be applied to extrapolate this data but it is imperative to choose the appropriate kernel in the sense that chosen kernel must be in agreement with the experimental data. A suitable kernel is evaluated based on the following parameters: (1) type of adsorptive and temperature (e.g. nitrogen at 77 K); (2) Pore geometry (e.g. cylindrical, spherical, slit-like pores); and lastly (3) Type of adsorbent (e.g. oxidic/zeolite, carbonaceous, silica).

The importance of choosing the appropriate NLDFT kernel is shown in Figure 1.29, whereby the semi-logarithmic plot of the experimental argon (87.3 K) isotherm for indium soc-MOF (with cylindrical-like pores) is compared to the NLDFT-Fit using both the oxidic/zeolite and carbonaceous models. Note that the surface chemistry of MOFs is more comparable to zeolites as oppose to carbonaceous materials. The semi-logarithmic plot of the experimental data therefore appears to be in better agreement with the oxidic/zeolite method. This is confirmed from the corresponding pore size distribution plot which reveals a pore size of 6.1 Å and 12 Å for the oxidic/zeolite and carbon models, respectively. The estimated diameter of the channels in soc-MOF as calculated from the crystal structure is approximately 10 Å (point to point and not considering van der Waals
radii). This specific NLDFT method therefore provides a very accurate assessment of the experimental pore size.

Figure 1.29. (a) Semi-logarithmic plot of the experimental argon (87.3 K) isotherm for indium soc-MOF with cylindrical-like pores compared to the NLDFT-Fit using both the oxidic/zeolite and carbonaceous models and (b) Corresponding pore size distribution.174

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2.1. Introduction

Self–assembly of molecular building blocks (MBBs) with prefabricated shapes, geometries, and functionality that are amenable to design from first principles, have proven to facilitate the construction of discrete and extended functional solid-state crystalline materials with specific functionalities.1-8 The success of this approach is exemplified by the burgeoning number of metal-organic polyhedra (MOPs), metal-organic frameworks (MOFs), covalent organic frameworks (COFs), and coordination polymers, reported in the literature on a daily basis.9-15 The MBB approach is a rational top-down design, bottom-up synthetic strategy and thus is inherently modular and predictable (to a certain degree). Potential made-to-order MOMs can therefore be targeted for their ability to exhibit desired properties by employing the appropriate MBBs that possess the warranted structural and chemical attributes.

The unique inorganic-organic hybrid nature, a characteristic feature of MOMs, together with effective design strategies, i.e. reticular chemistry, and facile synthesis makes it possible to construct rigid and directional pre-designed MBBs of varying connectivity by exploiting the diverse coordination modes and geometries provided by metal ions and organic molecules. From a design perspective, inorganic and organic MBBs can be translated into building units (BUs) that are analogous to geometrical
shapes. The BU is defined by connecting the points of extension of the respective building block via the carboxylato carbon atom. The vertex figure (or coordination figure) of the original $n$-connected node(s) is thereby revealed and this representation corresponds to the augmented conformation of the net.\textsuperscript{16} Inorganic MBBs (i.e. metal clusters) which are typically formed \textit{in situ} and organic MBBs are therefore targeted prior to the assembly process for the desired shape, geometry, and directionality necessary to augment a specific predicted net. Highly symmetrical building blocks with 3-, 4-, and/or 6-connectivity are commonly exploited in solid-state chemistry, as their vertex figures correspond to regular polygons and/or polyhedra such as those depicted in Figure 2.1.\textsuperscript{17-22}

![Figure 2.1. Commonly employed inorganic and organic MBBs and their corresponding augmented forms: (a) BTEC organic MBB, square BU; (b) [Zn$_4$O(RCO$_2$)$_6$] MBB, octahedral SBU; (c) BTC organic MBB; triangular BU; and (d) [M$_3$O(RCO$_2$)$_6$(H$_2$O)$_3$] trimer MBB (TMBB), trigonal prismatic SBU.](image)

Porous MOFs have gained much momentum in recent years as a promising class of solid-state materials to be utilized as potential hydrogen storage mediums (host) for onboard vehicular applications.\textsuperscript{11, 23-26} MOMs are ideal physisorption-based candidates
because by their very nature they exhibit fast kinetics and fully reversible adsorption/desorption isotherms. Molecular hydrogen can therefore be readily released under mild conditions (in contrast to chemisorption methods). Several MOFs have certainly exceeded expectations whereby unprecedented surface areas, uptake capacities, and $Q_{st}$ values have been reported. Many key obstacles however must be overcome before a hydrogen-based economy can become an efficient and safe alternative fuel to fulfill future energy demands.

A significant limitation which impedes the development of MOFs as potential solid-state hydrogen storage materials is dominated by weak binding affinities between molecular hydrogen and the constituents of the framework, i.e. typically in the range of $\sim 5 – 8$ kJ mol$^{-1}$. These fundamental interactions predominately arise from a collective group of forces; that is, van der Waals, charge-quadrupole, and induction forces. To date no porous physisorbent based material has in fact concomitantly sustained the optimal binding energy ($15 – 20$ kJ mol$^{-1}$) and uptake capacity required for on-board applications. In their present state it is therefore impossible for these materials to store adequate amounts of hydrogen at operable temperatures and pressures. It is this very reason why it is imperative to devise pathways to increase the H$_2$ binding energies in a systematic fashion to afford stronger binding affinities via structural and chemical modifications (see Chapter 1).

We sought to gain a better understanding of the preferential binding of hydrogen in porous MOFs by conducting a systematic adsorption study by synthesizing an isostructural series of MOFs having soc topology ($=\text{square octahedron}$). The MOFs described herein, 1 – 5, were constructed from the self-assembly of predesigned 6-
connected oxygen-centered metal trimer molecular building blocks (TMBBs) having trigonal prismatic geometry and a 4-connected rectangular-planar tetracarboxylate organic ligand (3,3′,5,5′-azobenzenetetracarboxylic acid, H₄-ABTC). To the best of our knowledge, these compounds represent the only examples of MOFs having soc topology. The unique features offered by the prototypical platform include: (1) Narrow pores (< 1 nm); (2) Higher localized charge density; and (3) Accessibility to potential vacant metal sites. All of these parameters are recognized in literature as a means to improve the binding energy of hydrogen in MOFs; however, systematic studies that independently evaluate the effect of each parameter remain scarce.²⁰, ⁴³, ⁴⁴ It therefore seems highly plausible that the rational construction of a MOF having a large surface area and bearing the aforementioned characteristics would represent an ideal candidate to permit the attainment of the DoE systems targets for H₂ uptake at operable temperatures and pressures.

An increasing number of MOFs are being constructed in recent years using rigid and flexible tetracarboxylate organic ligands, with the nbo, pts, and lvt nets being predominately observed.⁴⁵-⁴⁸ A dominant factor which prevents the formation of the soc net using other tetracarboxylate ligands is the relative scale and geometry of the ligand. To generate a MOF with soc topology using a longer ligand would require expansion in both directions (x and y). This is because the faces of the cuboidal cages are delimited by the ligands, which are oriented perpendicular with respect to the neighboring face. The H₄-ABTC ligand was therefore deliberately chosen for this project to link the TMBBs because the distance between the azo moieties is precisely the right size to connect the opposing m-BDC units of neighboring trimers. It is important to note however that the
soc net is the most symmetrical outcome for the assembly of octahedral and square BUs. In our case, H₄-ABTC is not a perfect square and the inorganic MBB exhibits trigonal prismatic geometry which is certainly not octahedral. Accordingly, the rectangular geometry of the ligand causes elongation along one direction which thereby permits the formation of trigonal prismatic BUs as oppose to octahedral BUs but the coordination sequence is still a match to soc topology.

The structural description provided in this chapter coupled with the sorption and INS data will reveal that the unique structural features offered by this platform provide valuable insights for enhancing H₂-MOF interactions. Accordingly, fine-tuning these features to further enhance these interactions plays an important role in governing the maximum uptake capacity and enthalpy of adsorption. The results will independently assess the effect of the following parameters on H₂-MOF interactions using the cationic soc-MOF as a platform: (1) Effect of metal cation whereby the TMBB has the potential to be replaced with different metal cations (e.g. In, Al, Cr, Mn, Fe, Ni, etc) to generate accessible open-metal centers and lower framework densities; (2) Fine-tuning the extra-framework counter ions which are confined in the cuboidal cage (e.g. NO₃⁻, Cl⁻, Br⁻, etc); and (3) Effect of polarizability via the incorporation of decorated TMBBs; that is, one of the axial sites is occupied by a halide which thereby leaves the cuboidal cage anion-free. These modifications were accomplished in situ, while preserving the structural integrity of the frameworks.
2.2. Results and Discussion

The first MOF possessing soc topology was isolated from the solvothermal reaction of H$_4$-ABTC with In(NO$_3$)$_3$·2H$_2$O in a DMF/CH$_3$CN solution in the presence of piperazine.$^{20}$ This led to the formation of orange polyhedral crystals, characterized and formulated by elemental microanalysis and SCD studies as {[In$_3$O(ABTC)$_{1.5}$(H$_2$O)$_3$](NO$_3$)(H$_2$O)$_3$}, (I). The purity of I was confirmed by similarities between the experimental and calculated powder X-ray diffraction (PXRD) patterns (Appendix B). Compound I crystallizes in the cubic space group $P-43n$ with $a = 22.4567(11)$ Å and has a unit cell volume of $11325.0(10)$ Å$^3$. The 3-periodic framework is built up from $\mu_3$-oxygen-centered indium TMBBs whereby each indium cation adopts an octahedral coordination environment (Figure 2.2.). The equatorial plane of the TMBB is occupied by four deprotonated carboxylate oxygen atoms ($d_{\text{In-O}} = 2.162(2)$ Å) from four independent ABTC$^{4+}$ ligands, each of which coordinate in a bis-monodentate fashion. A terminal aqua ligand ($d_{\text{In-O}} = 2.173(6)$ Å) and a central $\mu_3$-oxo anion ($d_{\text{In-O}} = 2.040(3)$ Å) are bound in the axial positions and complete the coordination sphere of the metal cation, [InO$_5$(H$_2$O)]. The central oxo anion ($O^2-$) is located on a threefold axis and unites the three indium octahedra, which leads to three planar In-(μ$_3$-O)-In angles of 120°.
Each pair of indium centers are bridged together via two independent ABTC$^{4-}$ ligands that coordinate to each indium in a bis-monodentate fashion through the carboxylato oxygen atoms. Each TMBB is linked together by six separate organic linkers to result in the formation of a novel 3-periodic structure. In 1, each indium atom is trivalent and the \( \mu_3 \)-oxo anion contributes a negative two charge and therefore this yields an overall cationic framework (+1 per formula unit). The charge balance is provided by disordered extra-framework nitrate, [NO$_3$]$^-$, anions which statistically occupy two
positions on the three fold axis with an equal probability of being located at either position. The nanometer-scale carcerand-like cage therefore encapsulates a total of four $[\text{NO}_3^-]$ ions. The cage is cube-like in shape and is delimited by six ABTC$^+$ ligands and eight TMBBs, which occupy the faces and vertices of the cage, respectively. Each cage is shared between eight neighboring cages via the TMBBs and thereby reveals a periodic array of connected cages and infinite intersecting channels resembling a bcc arrangement. The cage is comprised of small window apertures that measure approximately 4.612 Å x 2.431 Å, taking into considering van der Waals radii. Consequently, the $[\text{NO}_3^-]$ anions are trapped due to steric hindrance and so the cage remains inaccessible to guest molecules in the absence of external forces, i.e. pressure.

As eluted to in the introduction and the title of this chapter, all compounds described herein possess the same connectivity; that is, they all have soc topology. The TMBB can be rationalized as a 6-connected trigonal prismatic building unit and can be regarded as a pseudo-octahedron. The 4-connected node is represented by the organic MBB, H$_4$-ABTC, which is rationalized as rectangular-planar node, or pseudo-square. Accordingly, the assembly of such 4- and 6-connected nodes results in the formation of an edge-transitive 3-periodic network with soc topology. Compound 1 exhibits an interesting pore system because it contains two well-defined types of infinite channels, namely an intersecting hydrophobic and hydrophilic channel system (Figure 2.3.).
Figure 2.3. Select fragment from the crystal structure of 1 to emphasize the packing of the cages and highlight the two types of intersecting channels. The green tubular rods run through the hydrophobic channels, while the pink tubular rods run through the hydrophilic channels. Color code: In = green; C = gray; N = blue; O = red. Hydrogen atoms, solvent molecules, and [NO₃]⁻ anions are omitted for clarity.

The relative span of the cage is estimated to be 10 Å, while the channels measure approximately 6.5 Å. The hydrophilic channel system sustains a polar environment due to the presence of aqua ligands bound in the axially positions of the indium centers. The water molecules are directed inward towards these channels and participate in hydrogen bonding with other guest water molecules located in these channels. The hydrophobic channels however were determined to be completely guest-free in the as-synthesized material.

2.2.1. Low Pressure Adsorption Measurements for 1.

The interesting structural and chemical features of 1, that is, narrow pores with higher localized charge density and potentially accessible open-metal binding sites,
prompted us to investigate the gas storage properties of 1. The total solvent accessible volume was obtained using the PLATON software by summing the voxels that are more than 1.2 Å away from the framework. For 1, it was determined to be approximately 57.2% of the unit cell volume. Gas-sorption studies were conducted on the fully evacuated sample following exchange in CH₃CN for a period of 36 h. The exchanged sample was loaded into a 6-mm sample cell (dry) and evacuated at room temperature for 24 h and then gradually heated to 135°C for 8 h to afford the desolvated form of 1. The permanent porosity was confirmed by the nitrogen sorption isotherm collected at 77 K. It revealed a fully reversible Type I isotherm, which is characteristic of microporous materials. The apparent Langmuir surface area was estimated to be 1417 m²/g with a corresponding experimental pore volume of 0.50 cm³·g⁻¹. This value agrees very well with the theoretical value of 0.51 cm³·g⁻¹. The hydrogen capacity was assessed at atmospheric pressures and temperatures of 77 K and 87 K (Figure 2.4a.). Regardless of the fact that 1 has a moderate free volume and exhibits a lower surface area as compared to other MOFs (i.e. > 3000 m²/g) it was still able to store a significant amount of H₂. It was found to store up to 2.61 wt% at 77 K and 895 Torr (1.2 atm), as shown in Figure 2.4b.
Figure 2.4. Sorption data collected on 1: (a) Nitrogen sorption isotherm at 77 K; (b) Hydrogen sorption isotherm at 77 K and 87 K; and (c) Isosteric heat of adsorption for H₂.

The ability of 1 to adsorb such high amounts of H₂ indicates a higher density of H₂ in the pores (i.e. 0.05 g cm⁻³) and therefore the bulk properties of the H₂ adsorbed in 1 changed from that of a gas to resemble that of a liquid-like state (0.0708 g cm⁻³ at 20 K). The fact that 1 is able to achieve this density at 77 K and atmosphere pressures is interesting and most likely driven by the overlap of potential energy fields from the narrow pore dimensions, which facilitate strong adsorbate-adsorbent interactions. In
addition to the collective contributions from the residual charge density from the extra-framework nitrates anions and accessibility to potentially vacant In(III) metal binding sites.

The corresponding isosteric heat of adsorption for H$_2$ was calculated from the 77 K and 87 K H$_2$ sorption data, up to 1.8% loading of H$_2$ per sorbent weight and determined to be 6.5 kJ mol$^{-1}$ (Figure 2.4c.) The $Q_{st}$ is higher than values reported for porous carbon materials, yet similar to those reported for an assortment of MOFs. This may not seem all that significant at low coverage but it is remarkable that it is maintained even at higher loadings. This observation can be attributed to a significant averaging of the binding sites which is a unique feature that is rarely observed in MOFs. In most reported cases $Q_{st}$ is significantly lower at higher coverage as compared to low loadings because the structural and chemical features of the MOF become less accessible to the adsorbate (i.e. open-metal sites, organic functionality, counter ions, etc). In other words, the stronger H$_2$-MOF binding sites become fully occupied at lower loadings and thus are less accessible at higher loadings which cause $Q_{st}$ to decrease.

2.2.2. Inelastic Neutron Scattering (INS) Studies for 1.

Owing to the fact 1 can adequately store such high amounts of H$_2$ and sustain the H$_2$-MOF interactions even at higher loadings illustrates the importance of potential vacant metal sites, higher localized charge density, and pore dimensions on the energetics of sorbed H$_2$ molecules in MOFs. INS experiments were therefore carried out on 1 in order to gain a better understanding of the preferential H$_2$-MOF sorption sites in this material. This technique is well suited to probe H$_2$ interactions because it is sensitive to
the chemical environment of the host material that causes the hindered rotational transitions of the adsorbed hydrogen molecules (see Chapter 1).\textsuperscript{50-55}

The INS experiments conducted on 1 were carried out on the QENS spectrometer (neutron energy loss) at the Institute Pulsed Neutron Source at Argonne National Laboratory. Approximately 2g of the fully exchanged and evacuated sample was transferred to an aluminum sample holder, sealed under a He atmosphere, and connected to an external gas dosing system. A “blank” spectrum was first collected on 1 in the absence of hydrogen. It was then warmed to approximately 70 K and hydrogen was adsorbed \textit{in-situ} at various loadings equivalent to one, two, three, five, and seven H\textsubscript{2} molecules per indium atom. The sample was then cooled to 15 K for data collection to observe the respective interactions of molecular hydrogen with the framework.

The INS spectra for H\textsubscript{2} in 1 reveals reasonably well-defined peaks even at the lowest loading (1 H\textsubscript{2}/In), i.e. after subtracting the blank spectrum. Multiple peaks are observed in the spectra, even at the initial loading of 1 H\textsubscript{2}/In. This is indicative of multiple binding sites which are occupied simultaneously and is evidenced by the observable peaks in the range of 12 to 16 meV and another at 25.3 meV (Figure 2.5.). Note that the In-TMBB, [In\textsubscript{3}O(RCO\textsubscript{6})], contains three potentially vacant metal sites and therefore one would predict to observe only one peak at the lowest loading since the interaction of H\textsubscript{2} with a metal center ought to be the strongest. Conversely, the occupancy of multiple sites in MOFs having no vacant metal sites is expected as the binding energies are typically within a close range. Nevertheless, the presence of multiple sites at the lowest loading is in accord with the overall consistency observed in the isosteric heat of adsorption for 1, which is maintained up to 1.8 wt% of H\textsubscript{2}.  

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The relative peak positions (Table 2.1) in the INS spectra of 1 were assigned on the basis of the phenomenological model (see section 2.3.2.). It is important to keep in mind that a hindered transition observed at lower energy is caused by a higher barrier to rotation with respect to H₂. This indicates a stronger interaction which means that particular binding site(s) should be occupied first (at lower loadings). In the case of 1, the most intense bands are labeled as the 0-1 and 0-2 transitions which correspond to weakly bound (physisorbed) H₂ at different sites in the backbone of the framework. In lieu of the previous discussion concerning the barrier to rotation, the potentially vacant indium site was tentatively assigned (in 2007) as the peak located at 25.3 meV. This corresponds to the 0 – 2 transition for weakly bound H₂. It is noteworthy to mention that due to computational advances speculation currently surrounds the origin of this peak. The original phenomenological model may not have been appropriate for this system (i.e. over simplified). The presence of a 0 – 2 transition stipulates that the 0 – 1 transition must be present at 4.8 meV. The relatively low value of this observed rotational transition (i.e.}
high barrier to rotation) suggests a stronger overall interaction as compared to the other 0-1 transitions observed at 12.7 and 14.1 meV.

**Table 2.1.** Tentative rotational transitions (meV) assigned for the hydrogen adsorbed at different sites on 1.

<table>
<thead>
<tr>
<th>Transition</th>
<th>0-1</th>
<th>0-2</th>
<th>1-2 (calcd)</th>
<th>Barrier (V/B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sites</td>
<td>4.8</td>
<td>25.3</td>
<td>20.5</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td>12.7</td>
<td>15.9</td>
<td>3.2</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td>13.3</td>
<td>15.4</td>
<td>2.1</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>14.1</td>
<td>15.0</td>
<td>1.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Additional Sites</td>
<td>11.8</td>
<td>16.4</td>
<td>4.6</td>
<td>1.55</td>
</tr>
<tr>
<td></td>
<td>11.2</td>
<td>16.9</td>
<td>5.7</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>-9.5</td>
<td>18.3</td>
<td>8.7</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Accordingly, we speculate that the latter transitions arise from interactions associated with the weaker binding sites near the cationic TMBB; while the former peak arises from interactions with the organic components of the framework (*i.e.* carboxylates, azo bridge, phenyl moieties). This assumption was supported following the addition of 3 H$_2$/In because the intensity of the non-indium sites increased owing to subsequent filling of H$_2$. There was little change however in the relative intensity of the peak assigned to the vacant indium site. This indicates the stronger binding site is predominately occupied after the initial loading.

When the dosage of H$_2$ is subsequently increased to 5 H$_2$/In the aforementioned non-indium binding sites did not gain intensity but instead they became overshadowed by new peaks at even lower energies than those observed after loadings of 1 and 3 H$_2$/In, as highlighted in the difference spectra in Figure 2.6. The fact that non-indium sites become populated at higher loadings is not surprising and is often observed in MOFs.41, 44, 50 The
astonishing observation is that these binding sites correspond to stronger non-indium interactions (higher barrier to rotation) than those observed in lower loadings whereby the H<sub>2</sub>-MOF interactions are typically weak in nature. It is important to mention that <i>in situ</i> loading of 5 H<sub>2</sub>/In and higher surpass 1.8 wt% of H<sub>2</sub> and approaches the maximum uptake capacity of 2.61 wt% at 77 K and 1.2 atm. This is relevant to the discussion because we hypothesize that these additional binding sites become available <i>only</i> at higher loading due to pressure induced interactions within the isolated nanometer-scale cuboidal cages which house the nitrate ions.

![Figure 2.6](image)

**Figure 2.6.** Difference spectra calculated for 1 between 3H<sub>2</sub>/In – 1H<sub>2</sub>/In and 5H<sub>2</sub>/In and 3H<sub>2</sub>/In.

At lower loadings (<i>i.e.</i> 1 and 3 H<sub>2</sub>/In) we speculate that the H<sub>2</sub> is unable to overcome the sorption kinetic-energy diffusion barrier to facilitate access into the cage owing to the steric constraints imposed by the window apertures. Thus, at lower loadings H<sub>2</sub> is preferentially occupied at the vacant indium centers and throughout the intersecting channel system. At higher loadings however the framework is subject to elevated levels
of H$_2$ (compressibility factor) and the isolated cages become accessible near the entrances of the cage. The increased local pressure of H$_2$ allows the kinetic barrier to be overcome and permits access to the once inaccessible cage. The confined dimensions of the cavity coupled with the higher localized charge density induced from the nitrate ions and the proximal distance to the cationic TMBBs promote stronger sorption sites and thus correspond to increased H$_2$-MOF interactions. This evidenced by the strong binding sites in the INS at higher loadings (5 H$_2$/In). These findings support the elevated density of H$_2$ (0.05 g cm$^{-3}$) observed in the pores at 77 K and atmospheric pressures.

### 2.2.3. High Resolution Physical Adsorption Measurements: A Systematic Benchmark Study on 1.

In order to explore the vast potential of 1, as well as, other MOFs for existing and novel applications (e.g. gas storage and separation) it is imperative to fully characterize the materials using a combination of experimental techniques such as X-ray diffraction and physical adsorption. The data provides essential structural details that compliment the quantitative physisorption measurements concerning the surface area, porosity, relative pore size, as well as, the relative strength of the adsorbate-MOF interactions. This therefore allows for a reliable assessment concerning the adsorption capacity and surface energetics with respect to different adsorptives for gas storage and separation applications. The preliminary low pressure gas sorption data collected on 1 using nitrogen and hydrogen as adsorptives revealed promising results, as discussed above. This prompted us to conduct a comprehensive and systematic physical adsorption study to evaluate the uptake capacity and $Q_{st}$ of 1 using a variety of adsorptives (i.e. H$_2$, CH$_4$, and CO$_2$) over a wide range of temperatures and pressures. High resolution hydrogen
isotherms were collected for 1 at three closely spaced temperatures of 87 K, 97 K, and 107 K. These measurements were performed in order to validate the previously reported $Q_{\text{st}}$ of 6.5 kJ mol$^{-1}$.

The reason for choosing the aforementioned adsorptives was twofold: (1) We were interested in assessing their reliability as alternative probe molecules for pore size and surface area analysis as compared to traditional adsorptives (*i.e.* nitrogen and argon); and (2) the uptake capacity can be evaluated as a function of temperature (*e.g.* sub- to supercritical range) whereby the impact of choosing alternative thermodynamic states of the pore and bulk fluid states can be identified.

### 2.2.3.1. Adsorption Characterization using H$_2$ and CH$_4$ as Adsorptives

The Clausius-Clapeyron expression is quite effective and routinely used to calculate $Q_{\text{st}}$ in MOFs and other porous materials. Values derived from this expression however using just two experimental temperatures are associated with a high degree of uncertainty. To provide the most accurate result this method requires at least three adsorption isotherms collected in a closely spaced temperature range. High resolution low pressure volumetric hydrogen adsorption isotherms were therefore collected on 1 at 87 K, 97 K, and 107 K (Figure 2.7.). All three isotherms are indeed fully reversible with the highest capacity observed at 87 K. The heats of adsorption for H$_2$, derived from these isotherms show a slight deviation in the region of low loading but are very close to the expected value of 6.5 kJ mol$^{-1}$. The consistency is maintained across this temperature regime, even at high loadings and therefore validates our previous measurements.
Figure 2.7. (a) Low pressure volumetric hydrogen adsorption isotherms for 1 collected at 87, 97, and 107 K and (b) Corresponding isosteric heats of adsorption for H₂.

The overall shape of an adsorption isotherm is influenced by many factors, one of which experimental conditions, such as the temperature and pressure at which the measurement is performed. This is because these parameters effect the observed states of the pore and bulk fluid phases of the adsorptive. For example, a classical Type I argon isotherm collected at 87 K \(T_c(Ar) = 151\) K will fill the pores of a framework with a liquid-like state at lower pressures, which is indicative of the observed plateau following saturation. A hydrogen isotherm collected at 87 K \(T_c(H_2) = 33.3\) K however will not fill the pores in a liquid-like state at this temperature until higher pressures because you are above the critical temperature of H₂. An excellent example to illustrate the dependence of thermodynamic states of pore and bulk fluid phases on the overall shape of an isotherm is shown in Figure 2.8. for methane and hydrogen adsorption isotherms collected at 107 K.
Figure 2.8. Adsorption isotherms for I collected at 107 K using methane and hydrogen as adsorptives illustrated in the linear display and (left) semi-logarithmic plot to highlight the adsorption behavior at low pressures (right).

The critical temperature of methane is 190 K and therefore at this experimental temperature it is considered to be subcritical, while hydrogen is in a supercritical state because it is above its critical temperature. This explains why methane fills the pores in a liquid-like state as evidenced by the observed plateau (typical of a Type I behavior), while the H₂ adsorption isotherm exhibits a linear fit as a function of pressure. The overall shape of the methane adsorption isotherm is analogous to that observed for a Type I nitrogen or argon adsorption isotherm collected at 77 K and 87 K, respectively and therefore it is possible to extrapolate surface area and pore volume information. Note that methane is a non polar molecule and therefore has no dipole or quadrupole moment. Accordingly, methane should in theory be a reliable probe molecule for textural characterization because it will not give rise to specific interactions with functional groups on the surface of the adsorbent (i.e. similar to Ar). The pore volume calculated from the methane adsorption at 0.95 atm (0.45 cm³ g⁻¹) is close to that calculated from the argon isotherm at 87 K (0.47 cm³ g⁻¹). This result confirms that a methane adsorption
isotherm collected at 107 K can also be employed to gain meaningful information pertaining to pore volume and porosity.

2.2.3.2. Polar and Non-polar Adsorptives: CO$_2$ versus CH$_4$ Adsorption Studies

The CO$_2$ and CH$_4$ sorption capabilities of 1 were assessed in the temperature range of 273 K to 323 K and pressures up to 3 MPa (30 atm). This was achieved by using two instruments, namely a high resolution volumetric apparatus in combination with a gravimetric instrument equipped with a magnetic suspension balance. The data points collected at relative pressures ranging from $10^{-5}$ to $10^{-2}$ were measured on the volumetric instrument, while data collection at higher pressures was obtained using the magnetic suspension balance. Since the isotherms were collected at high pressures it is necessary to distinguish between surface excess adsorption ($n^\sigma$) and absolute adsorption ($n_A$) which are related by the following expression: $N_{ex} = N_{ads} - \rho_{bulk}V_{ads}$. The aforementioned values can differ substantially at higher temperatures and pressures, which is in contrast to sorption at lower temperatures and pressures.

The quantity of gas that is experimentally measured using standard physical adsorption measurements (i.e. volumetric or gravimetric techniques) provides the amount of surface excess gas adsorbed (not the absolute value). For simplicity, at very low temperatures (i.e. the boiling point of the adsorptive) the amount of gas adsorbed can be rationalized as a two phase model. This means that the gas adsorbed at the surface does not experience the same type of environment or interactions as the gas located further away from the surface. An adsorbed phase is considered to coexist with the bulk phase at lower pressures because the gas molecules will initially accumulate (adsorb) on the
surface as a dense monolayer. At higher pressures however multilayer coverage occurs and a liquid-like density builds up on the surface owing to strong interactions with the surface of the adsorbent as \( P_0 \) is approached -- a gas and liquid-like phase thereby co-exist.\(^{37,56,61}\) At very low temperatures the density of the gas is insignificant compared to the density of the bulk phase near the surface. The surface excess is therefore roughly equivalent to the adsorbed amount and there is no need to differentiate between these two values. At higher pressures however this analogy is false because there is a significant difference in the density between the bulk gas phase and the adsorbed phase at the surface.

The *absolute* adsorbed amount of CO\(_2\) was calculated for 1 from the surface excess using two different approaches. The first method is more applicable to systems with narrow pores, as in the case of soc-MOF. It relies on the assumption that the volume adsorbed in the system is fixed. The volume adsorbed therefore is correlated to the pore volume as determined from argon or nitrogen adsorption isotherms at 77 K and 87 K, respectively. The equation used to calculate the absolute adsorbed amount is based on the following equality below, where \( \rho_g \) refers to the molar density of the bulk gas at the experimental temperature and pressure, \( V_p \) is the corresponding pore volume, and \( n^\sigma \) represents the experimentally determined surface excess adsorbed amount.

\[
n_A = n^\sigma + \rho_g V_p
\]

If one assumes however that the volume of the adsorbed phase is not fixed and varies as a function of the density of the adsorbed phase, then the following expression is revealed whereby the density of the adsorbed and gas phase is considered.\(^{37}\)

\[
N_{ex} = N_{ads} - \rho_{bulk}V_{ads} \quad \Rightarrow \quad N_{ex} = N_{ads}/[1-(\rho_{bulk}/\rho_{bulk})].
\]
The absolute adsorbed amount of CO₂ for 1 was determined by employing both methods using a pore volume of 0.50 cm³/g (N₂ isotherm) and assuming the adsorbed CO₂ was in a liquid-like phase owing to the fact that the experimental conditions (273 K) were conducted below the critical temperature of CO₂ (T_c = 304.1 K). Both methods in fact are in good agreement. The pore volume obtained from the absolute adsorption isotherm at 273 K was determined to be 0.44 cm³ g⁻¹, which agrees with the aforementioned pore volumes obtained using nitrogen (0.50 cm³ g⁻¹), argon (0.47 cm³ g⁻¹), and methane (0.45 cm³ g⁻¹). The work described herein therefore demonstrates that a variety of adsorptives can be employed as probe molecules to extrapolate meaning porosity information if the experiment is conducted at the appropriate temperature. However, since the values are in such good agreement across all adsorptives it only stands to reason that Ar adsorption at 87 K is an adequate probe to be employed over the others. This is due to convenience, reliability, and because it does not have a quadrupole moment and thus is not expected to give rise to specific interactions with most surfaces and ions (contrary to N₂ and CO₂).

The uptake capacity of 1 for CO₂ and CH₄, plotted as surface excess and absolute amounts adsorbed, is shown in Figure 2.9. These plots clearly demonstrate how the excess and absolute adsorbed values deviate as a function of pressure. We predicted that 1 would exhibit stronger adsorbate-adsorbent interactions for the adsorption of CO₂ and thus have a higher uptake capacity as compared to CH₄. The reason being that CO₂ has a quadruple moment and 1 exhibits narrow pores, higher localized charge density, and vacant In(III) centers. This should lead to stronger binding sites and enhance the H₂-MOF interactions. Methane on the other hand is a non-polar molecule with no dipole or
quadruple moment. Indeed, 1 does adsorb more CO$_2$ than CH$_4$ at temperatures ranging from 273 K to 323 K up to pressures of 30 atm. The steep rise observed at low loadings in the CO$_2$ adsorption isotherm, as compared to CH$_4$, indicates that CO$_2$ has a strong affinity for the surface of the MOF.

![Figure 2.9](image_url)

**Figure 2.9.** (a) Surface excess and absolute amounts of CO$_2$ adsorbed for 1 at 273, 298, and 323 K; and (b) Surface excess and absolute amounts of CH$_4$ adsorbed for 1 over the same temperature range.

The isosteric heats of adsorption calculated from the CO$_2$ and CH$_4$ adsorption isotherms at three closely spaced temperatures confirms that CO$_2$ has a stronger binding affinity for the MOF adsorption sites in 1 as compared to CH$_4$. For CO$_2$ it is 28.5 kJ mol$^{-1}$ versus 18.8 kJ mol$^{-1}$ in the case of CH$_4$ (Figure 2.10.). In contrast to the Qst obtained from the hydrogen adsorption isotherm at low pressures, these values do not remain constant at higher loadings but instead slightly increase. At low loading the interaction energy is primarily influenced by adsorbate-adsorbent interactions but at higher pressures adsorbate-adsorbate interactions becomes dominant and is facilitated by the narrow pores.
Figure 2.10. (a) A comparison between the absolute CO2 and CH4 adsorption isotherms for 1 as a function of pressure to illustrate the differences in uptake capacity; and (b) Isosteric heat of adsorption for CO2 and CH4.

The maximum uptake capacity observed for CO2 and CH4 in 1 is higher than those values reported for zeolites but still lower than those reported for other MOFs.62-64 The current record holder for the maximum amount of CO2 stored in a MOF is MOF-177 which adsorbs 33.5 mmol g\(^{-1}\) and 40.0 mmol g\(^{-1}\) of CO2 at 42 bar and 50 bar, respectively.62 While in the case of methane storage, Zhou and co-workers reported the synthesis of a compound that surpasses the DoE targets and stores 230v(STP)/v at 290 K and 35 bar.65

The ability of 1 to efficiently separate CO2 from CH4 was investigated as a function of temperature (273 K to 323 K) and pressure (0 to 3 MPa), as shown in Figure 2.11. Since the critical temperature of CO2 is 304.1 K, it is highly plausible that it fills the pores in a liquid-like state. Alternatively, the critical temperature of CH4 is 190 K therefore it will remain in the supercritical state across the temperature range and is not
expected to fill the pores in this fashion. The loading ratio of CO$_2$/CH$_4$ was predicted to be the highest at 273 K and the lowest at 323 K and equivalent pressures whereby more CO$_2$ should be adsorbed when it is in a liquid-like state. Indeed, the loading ratio is the highest at 273K in the low pressure region (below 0.3 MPa) and decreases with increasing pressure. This finding implies that in the pressure range of $<$0.3 MPa and 273 K compound 1 is more efficient at CO$_2$/CH$_4$ separation. Above this pressure there is a crossing of the loading curves whereby the loading ratio at 323 K is the highest. The reason for this stems from the fact that at high pressures the supercritical phase CO$_2$ is more compressible than for the liquid-like state whereas the thermodynamic state of CH$_4$ remains constant throughout the entire temperature range.

![Figure 2.11](image_url)

**Figure 2.11.** Evaluation of 1 to separate CO$_2$ and CH$_4$ as a function of temperature and pressure: (a) Loading ratio of CO$_2$/CH$_4$ up to pressures of 3 MPa (30 atm); and (b) Zoomed in plot up to 0.3 atm to emphasize the behavior of the loading ratio at low loadings.

In summary, the data presented herein suggests that efficient CO$_2$/CH$_4$ separation at high pressures is more favorable at temperatures above the bulk critical temperature while at low pressures ($<$ 3 MPa) the temperature should be maintained well below the
critical temperature of CO₂. This observation further validates our hypothesis that different thermodynamic states of adsorbed phases can drastically affect the amount adsorbed at the same pressure. In conclusion, the high resolution physical adsorption data discussed in this section provides a systematic evaluation of the temperature dependency of H₂, CH₄, and CO₂ adsorption over a wide range of temperatures and pressures in a robust MOF, 1. The results are both informative and encouraging but more importantly emphasize the importance of identifying different thermodynamic states of pore and bulk fluid phases because this can substantially affect the adsorption behavior, uptake capacity, and surface energetics of the material.

2.2.4. Isostructural Series of soc-MOF Analogs: Prototypical Platform to Conduct Systematic H₂-MOF Interaction Studies

The structural analysis of 1 coupled with the high resolution physical adsorption measurements and INS data reveals that high uptakes of hydrogen along with favorable H₂-MOF interactions are attainable when the appropriate structural and chemical features are incorporated into the MOF. Thus, the importance of potential open-metal binding sites and narrow pores (< 1nm) with higher localized charged density was highlighted in the context of gas storage and separation applications. In the ongoing quest towards the development of an optimal hydrogen storage material, we sought to gain a better understanding of the preferential binding of hydrogen in porous MOFs by conducting a systematic adsorption study using soc-MOF as a prototypal platform.
2.2.4.1. Iron-Based TMBBs

Herein, we report on the design and synthesis of two isostructural MOFs constructed from Fe-TMBB and H₄-ABTC. The reaction of H₄-ABTC with FeSO₄·2H₂O under solvothermal conditions in a mildly acidic solution containing DMF/H₂O/chlorobenzene affords a orange cube-shape microcrystalline material, formulated as \([\text{Fe}_3(\text{ABTC})_{1.5}(\text{H}_2\text{O})_3](\text{NO}_3)(\text{H}_2\text{O})_{0.67}\), (2) determined using SCD studies. The as-synthesized material is not homogenous; it is accompanied by an unidentified brown powder that we speculate to be iron oxide. The impurity can be readily removed to afford a homogenous phase by repeatedly washing the as-synthesized sample with DMF, as confirmed by the similarities between the calculated and experimental PXRD patterns (Appendix B). SCD studies, as well as, XPRD patterns confirmed that compound 2 is isostructural to 1. The 3-periodic framework is built up from the same organic MBBs (i.e. ABTC⁺) as used in 1 but each octahedral metal center of the TMBB is replaced by a lighter Fe(III) metal cation, [FeO₅(H₂O)]. The trimers are linked together by six independent ABTC⁺ ligands (d_{Fe-O} = 2.005 Å to 2.018 Å), each of which are comprised of three Fe octahedra that share one central \(\mu_3\)-oxo anion. The trimer is located on the three fold axis and yields Fe-(\(\mu_3\)-O)-Fe units at angles of 120° (d_{Fe-O} = 1.923 Å).

Iron has an open-shell electron configuration and therefore it can adopt different spin states, which means the metal ion can adopt different oxidation states. In the crystal structure of 2, each Fe atom is trivalent, the \(\mu_3\)-oxo anion and deprotonated ABTC ligand contribute a negative two and four charge, respectively. The crystallographic assignment of \(\mu_3\)-O and Fe(III) was based on literature precedents. This yields an overall cationic
framework (+1 per formula unit) whereby disordered extra-framework nitrate, \([\text{NO}_3^-]\), anions are anchored in the corners of the carcerand-like cage in a tetrahedral arrangement and provide charge balance. The anions statistically occupy two positions on the three fold axis with an equal probability of being located at either position (as observed in 1). The anions are unable to escape this cavity owing to electrostatics and steric hindrance (window dimensions: 5.139 Å x 7.639 Å point to point). The relative scale of the cage in 2 is comparable to that of 1 and thus has an effective diameter of approximately 10.437 Å and the intersecting channels have an estimated diameter of 6.004 Å.

During the course of these studies, \(\text{H}_4\)-ABTC was reacted with an assortment of iron salts in an attempt to establish a series of Fe-based soc-MOF analogs. This platform would allow us to systematically evaluate the contribution of charge balancing anions (i.e. \(\text{NO}_3^-, \text{Cl}^-, \text{Br}^-, \text{OH}^-\), etc) on \(\text{H}_2\)-MOF interactions by fine-tuning the localized charge density. A mixed valence Fe soc-MOF analog would also afford a neutral MOF and thus the overall contribution from the charge density could be investigated. The following iron salts were employed in this study: \(\text{FeSO}_4 \cdot 6\text{H}_2\text{O}, \text{FeCl}_2\) (anhydrous), \(\text{FeCl}_2 \cdot 4\text{H}_2\text{O}, \text{FeBr}_2, \text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}\), as well as, ferrocene. A brief list of the extensive experimental parameters which were adjusted during the course of this project include the metal-to-ligand ratio, solvent polarity, structure directing agents (SDAs), concentration, temperature, and pH.

Indeed, reaction between \(\text{H}_4\)-ABTC and \(\text{FeCl}_2\) in a \(\text{DMF}/\text{H}_2\text{O}/\text{chlorobenzene}\) solution in the presence of warm diluted \(\text{HCl}\) yields orange homogenous microcrystalline material with cube-shape morphology. The purity of the as-synthesized material was confirmed by similarities between the experimental and calculated PXRD patterns.
(Appendix B). The as-synthesized material, stable and insoluble in H₂O and common organic solvents, was characterized by elemental microanalysis and SCD studies and formulated as \([\text{[Fe}_3(\text{ABTC})_{1.5}\text{(H}_2\text{O})_3\text{]}\cdot(\text{Cl})]_3\), \((3)\). In the crystal structure of \(3\), each Fe-based TMBB adopts the same coordination environment as that observed in compounds \(1\) and \(2\), \([\text{Fe}_3\text{O}(\text{CO}_2)_6\text{(H}_2\text{O})_3\text{]}\). Each Fe cation is trivalent and thus charge balance for the cationic framework is provided by chloride ions (Cl⁻), as oppose to nitrate ions. Note that in this case it is impossible for the charge to be balanced by nitrate ions because there is no nitrate source in the starting materials. The chloride assignment was also supported by the halide elemental microanalysis studies which detected chloride ions in the sample. The disordered chloride ions are located in the cavities but statistically occupy three positions about the three fold axis with equal probability. In other words the disordered nitrate ions in \(2\) are substituted for chloride ions in \(3\) (Figure 2.12.). As observed in the previous analogs, the chloride ions are unable to escape owing to steric hindrance (window dimensions: 7.599 Å x 5.133 Å; point to point and excluding van der Waal radii). The two types of narrow channels; that is, the hydrophobic and hydrophilic have similar diameters, which are estimated to be 6.024 Å.
2.2.4.2. Decorated TMBBs: Incorporation of Coordinated Halide Anions

The solvothermal reaction of H₄-ABTC and InCl₃ or InBr₃ in separate vials containing solutions of DMF/EtOH/H₂O and DMF/CH₃CN/H₂O, respectively yields orange homogenous microcrystalline materials. In both cases, the morphology of the as-synthesized samples is cube-shape. The as-synthesized compounds were characterized by SCD studies and formulated as \{[In₃(ABTC)₁.₅(Cl)(H₂O)₂](H₂O)₅.₃₅\} \(^{4}\) and \{[In₃(ABTC)₁.₅(Br)(H₂O)₂](H₂O)₆.₂₅\} \(^{5}\), respectively. Indeed, \(^{4}\) and \(^{5}\) are isostructural compounds and crystallize in the cubic P-4₃n space group with a = 22.4570(3) Å and a = 22.4530(4) Å, respectively. The location of the charge balancing counter ions is different in this set of soc-MOF analogs as compared to compounds \(^{1}\) – \(^{3}\). In the previous soc-MOF structures the nitrate and chloride anions were encapsulated in the cages but in \(^{4}\) and \(^{5}\) the halide ions are not located in the cages. The anions are coordinated in the apical
position on the In-TMBB (1 halide per trimer) to reveal a so-called decorated TMBB.

Note that oxo-bridged indium trimers are scarce, with only three structures in the Cambridge Structural Database (CSD: February, 2010). Two of which are reported by Eddaoudi and co-workers. Similarly, the 3-periodic structure of 4 is built-up from indium TMBBs which contain three indium-centered octahedra that share one central \( \mu_3 \)-oxo anion, In-(\( \mu_3 \)-O)-In angles of 120° (\( d_{\text{In-O}} = 2.045(2) \) Å). Crystallographic analysis shows that one of the three apical positions is occupied by a chloride ion (Cl\(^-\)), which is disordered over the three apical sites with an equal probability of being at either position (\( d_{\text{In-Cl}} = 2.460(4) \) Å). The two remaining apical positions are saturated by aqua ligands (\( d_{\text{In-O}} = 2.164(2) \) Å) to afford a [In\(_3\)O(CO\(_2\))\(_6\)(Cl)(H\(_2\)O)\(_2\)] TMBB. Note that the presence of a halide ion coordinatively bound in the axial position is unprecedented for indium-based TMBBs.

The crystal structure of 5 reveals a similar coordination environment, except the apical chloride ion is replaced by a bromide ion (Br\(^-\)), which is also disordered over the three apical sites with an equal probability of being located at either of the positions (\( d_{\text{In-Br}} = 2.619 \) Å). Thus, the assembly of eight [In\(_3\)O(RCO\(_2\))\(_6\)(Br)(H\(_2\)O)\(_2\)] TMBBs and twelve ABTC\(^+\) organic ligands delimit the anion-free cuboidal cage, as depicted in Figure 2.13. The relative size of the channels in 4 and 5 must be reported within a range owing to the fact the halide ions are delocalized over the three apical sites. Accordingly, in the crystal structure of 4 and 5 the estimated diameter of the channels can range in size from 3.333 Å to 5.952 Å and 2.867 Å to 5.966 Å, respectively depending on the location of the halide ions. The approximate dimensions of the window apertures of the cuboidal cages in 4 and
5 measure 4.562 Å \( \times \) 7.622 Å and 4.590 Å \( \times \) 7.626 Å, respectively (point to point and excluding van der Waals radii).

![Figure 2.13](image)

Figure 2.13. Select fragments from the crystal structure of 5: (a) Ball-and-stick representation of the indium-based TMBB, \([\text{In}_3\text{O}(\text{RCO}_2)_6(\text{Br})(\text{H}_2\text{O})_2]\); (b) Ball-and-stick representation of the anion-free cuboidal cage. Color code: In = green; C = gray; N = blue; O = red; Br = purple. Hydrogen atoms and solvent molecules are omitted for clarity. The yellow sphere represents the largest sphere that can fit inside the cage (~10.137 Å in diameter), considering van der Waals radii.

2.2.4.3. Low Pressure Gas Adsorption Measurements

The total solvent-accessible free volume for compounds 2 – 5 was calculated to be 55.5 %, 58.9 %, 59.2 %, and 58.5 %. The set of isostructural \textit{soc}-MOFs described herein, 1 – 5, made it possible for us to independently evaluate the effect of each of the following structural parameters on \( \text{H}_2\)-MOF binding interactions: (1) Accessibility to potential open-metal binding sites (In \textit{versus} Fe); (2) The impact of localized charge
density by utilizing different extra-framework anions (NO$_3^-$ versus Cl$^-$); and (3) The effect of polarizing substituents (Cl$^-$ versus Br$^-$).

2.2.4.3.1. Evaluating the Effect of Open Metal Binding Sites on H$_2$-MOF Interactions

In order to assess the sorption properties of the Fe-based soc-MOF with extra-framework nitrates, 2, the guest molecules were exchanged with CH$_3$CN. The orange microcrystalline sample was air dried and loaded into a 6-mm glass sample cell, where it was initially outgassed at room temperature for 12 h and then gradually heated to 135°C for 8 h. TGA spectra for the as-synthesized and exchanged samples indicate that 2 is indeed thermally stable above 135°C (Appendix C). We decided however to proceed with a full sorption study at 135°C in order to gain insights into the nature of the axial aqua ligands. Most notable the question was if they were bound at this temperature or removed to yield open Fe binding sites. Since iron interacts more strongly with water than indium (d$_{Fe-O}$ = 2.060 Å; d$_{In-O}$ = 2.173 Å), we anticipated that elevated temperatures would be required to ensure complete removal of the axial ligands.

The argon sorption isotherm collected at 87 K is of Type I isotherm, which is characteristic of permanently porous microporous materials (Figure 2.14a.). BET and Langmuir surface areas were estimated to be 1381 m$^2$/g and 1678 m$^2$/g and the total pore volume was found to be 0.563 cm$^3$/g (P.V.$^{\text{theo}}$ = 0.570 cm$^3$ g$^{-1}$). The internal pore diameter, 6.42 Å, was obtained from a cylindrical NLDFT pore model assuming an oxidic (zeolite) surface (Figure 2.14b.). This value agrees reasonably well with the accessible pore diameter of the cylindrical-like channels in 2, which have an estimated diameter of 6.085 Å.
Figure 2.14. (a) Argon sorption isotherm at 87 K for 2, \{Fe(NO_3)_3 soc-MOF\}, after evacuation at 135°C; and (b) Pore size distribution in 2 calculated from the Ar isotherm (~6.42 Å).

The hydrogen sorption capacity for 2, measured at 77 K and 87 K and atmospheric pressures, was determined to be as high as 2.17 wt % of H_2 (Figure 2.15a.) and the $Q_{st}$ was determined to reach a maximum of 6.50 kJ mol$^{-1}$ at low loading. This value decreased slightly to 5.80 kJ mol$^{-1}$ at higher loading (e.g. 1.5 % per weight). As illustrated in Figure 2.15b., $Q_{st}$ at low loading is similar for 1 and 2. The lower than expected $Q_{st}$ (at low loading) and the gradual decline observed in 2, may indicate that some of the coordinated water molecules are still bound to the axial positions of the Fe-TMBB. The cationic cluster would be less polarizable and contribute less towards the ionic character of the MOF because the iron sites are not open and thus less accessible to H_2.
Heating the exchanged sample, 2, to elevated temperatures (175°C / 8h) did indeed result in a significant change in the appearance of the crystalline sample; that is, 2 changed color from orange to dark brown when heated from 135°C to 175°C. This observation coupled with the TGA data leads us to believe that 2 is desolvated and thus the water molecules should be removed from the axial positions in the Fe-TMBB. Argon sorption studies on 2 at 175°C at 87 K revealed BET and Langmuir surface areas were estimated to be 1701 m²/g and 2061 m²/g, respectively. The corresponding pore volume and pore size were determined to be 0.687 cm³·g⁻¹ and 6.42 Å, respectively. As illustrated in Figure 2.16., compound 2 certainly adsorbs more argon after evacuation at 175°C as compared to 135°C and a significant increase in the pore volume is observed. This data coupled with the observable color change upon heating helps to support the argument that higher temperatures are needed to remove the coordinated water molecules in 2.
An evaluation of the H$_2$ sorption properties at 175°C revealed that 2 can store higher amounts of H$_2$, up to 2.62 wt % at 77 K and atmospheric pressure and approaches saturation (Figure 2.17a.). This is indicative of the near liquid density of the sorbed hydrogen in the pores (0.04 g cm$^{-3}$). Interestingly, the isosteric heat of adsorption was calculated to be 7.84 kJ mol$^{-1}$ at low loading, which is noticeably higher as compared to the 135°C data for both 1 and 2 (Figure 2.17b.). In contrast to 1, the isosteric heat of adsorption is not constant at higher loadings and gradually decreases to an estimated value of 5.82 kJ mol$^{-1}$, which is comparable to the 135°C $Q_{st}$ data calculated for 2. This result implies that the binding sites in 2 are not homogenous (averaged) up to the experimental loading capacity. This is not overly surprising because it is known that vacant Fe binding sites facilitate stronger H$_2$-MOF interactions than open In binding sites and thus the binding sites are not expected to be homogenous. Note that at higher loadings the heat of adsorption is not all that different between 1 and 2 and therefore if multiple hydrogen sorption isotherms were collected on 2 at three or more closely related temperatures (i.e. 77, 87, and 97 K) it may reveal little difference.
Figure 2.17. (a) Hydrogen sorption isotherm at 77 K and 87 K for 2, \{Fe(NO_3)_3, soc-MOF\}, after evacuation at 175°C; and (b) Isosteric heat of adsorption for 2 after evacuation at 135°C and 175°C compared to the Qst for 1, \{In(NO_3)_3, soc-MOF\}, after evacuation at 135°C.

The enhanced H_2-MOF interactions at lower loadings may therefore be attributed to: (1) the electric field created by the positively charged and highly polarizable open Fe coordination sites on the TMBBs; and (2) Accessibility to the windows of the cage, which is geometrically proximal to all of the dominantly charged components.

2.2.4.3.2. Contributions from Different Extra-framework Anions: Cl^- versus NO_3^-.

The importance of open coordination metal sites and the choice of metal cation employed can have a significant effect on the H_2 sorption properties of a material. The former was exemplified in the previous section by comparing the Qst of 2 after evacuation at 135°C and 175°C, while the significance of the latter was demonstrated by reporting higher Qst values for the iron versus the indium analog at low loading. Unfortunately, devising pathways to satisfy the DoE technical targets is not as simple as just fine-tuning the choice of metal center. In this context, compounds 2 and 3 are ideally
suited to evaluate the overall effect regarding the type of extra-framework counter ions on H2-MOF interactions in the charged soc-MOFs. Both compounds are constructed from the same Fe-based TMBBs and ABTC\textsuperscript{4+} organic MBBs and therefore contain the same number of potential open Fe binding sites. The two MOFs differ however with respect to the type of tetrahedrally positioned counter ions in nanometer-scale cavity; that is, nitrate anions in 2 and chloride anions in 3.

In order to assess the sorption properties 3 the guest molecules were exchanged with CH\textsubscript{3}CN for 3 days. The orange microcrystalline sample was air dried and loaded into a 6-mm glass sample cell, where it was initially outgassed at room temperature for 28 h. Subsequently, the hydrogen sorption properties were investigated so that a similar comparison could be made with respect to the accessibility of the potential open Fe sites (\textit{i.e.} RT evacuation \textit{vs.} elevated temperatures). The estimated BET and Langmuir surface areas were determined to be 1006 m\textsuperscript{2}/g and 1117 m\textsuperscript{2}/g, respectively (N\textsubscript{2} isotherm) with a corresponding pore volume of 0.418 cm\textsuperscript{3} g\textsuperscript{-1} (P.V.\textsubscript{theo} = 0.619 cm\textsuperscript{3} g\textsuperscript{-1}). It was evidenced that 3 stores up to 1.75 wt % of H\textsubscript{2} at 77 K and atmospheric pressures. The \(Q_{st}\) was calculated to be in the range of 6.50 kJ mol\textsuperscript{-1} and 5.80 kJ mol\textsuperscript{-1}, which is identical to 2 after heating to 135\textdegree C (Figure 2.18.). The lower than expected values can be attributed to improper sample activation due to the presence of axial water ligands on the Fe TMBBs, as previously demonstrated in the case of 2.
These results raise an important question – Do the counter ions provide any contribution towards enhancing the polarizability of the ionic framework below the optimal evacuation temperature? Computational studies provide valuable insights to help answer this question. Indeed, Space and co-workers have demonstrated that a high dipole population is localized inside the carcerand-like capsule near the window aperture. The authors ascribe this high dipole population to the relative position of the window with respect to the dominantly charged components (ABTC^+, In-TMBB, and nitrate ions). With respect to H_2-MOF interactions, a hydrated TMBB would not only reduce the contributions from the metal sites but restrict accessibility to the windows of the cage. Thus, we speculate the overall contribution from the counter ions would have a reduced effect if the TMBB is hydrated.

In order to fully assess the porosity of 3 the sample was heated to 165°C for 8h. During the evacuation process the microcrystalline sample changed color from orange to dark brown, similar to that observed in the case of 2. The apparent BET and Langmuir
surface areas were calculated from the Ar sorption isotherm at 87 K and estimated to be 1648 m$^2$/g and 1969 m$^2$/g, respectively. The corresponding pore volume and pore size were estimated to be 0.65 cm$^3$ g$^{-1}$ and 6.42 Å, respectively (Figure 2.19.).

Figure 2.19. Sorption studies for 3,$\{\text{FeCl}_3\ \text{soe-MOF}\}$, after evacuation at 165°C: (a) Argon sorption isotherm at 87 K; and (b) Pore size distribution calculated from the Ar isotherm (~6.42 Å) by applying a cylindrical NLDFT pore model assuming an oxidic/zeolite surface.

Hydrogen sorption studies revealed 3 adsorbs up to 2.53 wt% at 77 K and atmospheric pressures, while the associated isosteric heat of adsorption was estimated to reach a maximum of $q = 7.10$ kJ mol$^{-1}$ at lower loadings (Figure 2.20.). The heat of adsorption for 3 after evacuation at 165°C shows increased H$_2$-MOF interactions at low loading as compared to the $Q_{st}$ after room temperature evacuation. This observation suggests that the axial ligands on the Fe-TMBB were removed. The total number of potential open Fe sites is the same in 2 and 3 and thus a direct comparison can be made with respect to the extra-framework counter ions. Also, the relative size of the channels and cages is nearly identical in both structures and the density of the desolvated frameworks is similar having calculated values of 0.975 g cm$^{-3}$ and 0.952 g cm$^{-3}$ for 2 and
The chloride ion would be expected to be more polarizable than a nitrate ion on account of the fact that the negative charge is localized on one atom as oppose to being distributed over four atoms. We therefore expected the presence of chloride ions in 3 would lead to a higher dipole population and thereby promote stronger H₂-MOF interactions. However, this is not the case and the heat of adsorption was higher in 2 at low loadings.

Figure 2.20. (a) Hydrogen sorption isotherm at 77 K and 87 K for 3, \{FeCl₃ soc-MOF\}, after evacuation at 175°C; and (b) Isosteric heat of adsorption for 3 after evacuation at 165°C compared to the Qst for 3 after evacuation at 175°C.

These findings can be rationalized by noting the relative size of the counter ions. A nitrate ion is by far larger than a chloride ion so that nitrates occupy more space in the cage than the chloride ions. The nitrate ions should therefore be more accessible to H₂ via the windows than the chloride ions in the desolvated MOFs.
2.2.4.3.3. Polarizability Effects via Decorated Indium-based TMBBs

The two MOFs described herein are constructed from decorated In-TMBBs whereby one of the axial positions of each TMBB in 4 and 5 contain a disordered chloride ion and bromide ion, respectively. The aforementioned halides have the same formal charge of negative one but differ in size (R_{Cl^-} = 181 pm ; R_{Br^-} = 196 pm) and thus polarizability (Br^- > Cl^-). The desolvated forms of 4 and 5 will possess one less potential metal binding site as compared to compounds 1 – 3 and for that reason the cavity is anion-free. They therefore represent an ideal pair of compounds to determine if minor structural and chemical modifications in pore structure, i.e. size and localized charge density, influence the H₂-MOF preferential binding sites.

The solvent activation protocol carried out on 4 and 5 was similar to that used for the previous compounds whereby the as-synthesized samples were exchanged in CH₃CN for 4 to 7 days. The activated microcrystalline samples were outgassed at room temperature for 8 h and then gradually heated to 135°C and 145°C for 8 h in the case of 4 and 5, respectively. The apparent BET and Langmuir surface areas of the evacuated form of 4 were estimated to be 1244 m²/g and 1494 m²/g, respectively (Figure 2.21a.). The specific pore volume of 0.50 cm³ g⁻¹ agrees reasonably well with the theoretical pore volume that is estimated to be 0.53 cm³ g⁻¹. The internal pore diameter, calculated from the Argon adsorption isotherm at 87 K, shows that the majority of the accessible pores exhibit a diameter of 6.12 Å (Figure 2.21b.), which is comparable to that determined for 1. At first glance is may seem surprising that 1 and 4 have similar experimental pore sizes owing to the fact that the hydrophilic pores of 4 are decorated with chloride ions. However, it is important to consider that each TMBB only contains one chloride per
trimer and therefore on average the pores are not expected to be substantially different in size.

Figure 2.21. Sorption studies for 4, \{InCl$_3$ soc-MOF\}, after evacuation at 135°C: (a) Argon sorption isotherm at 87K; (b) Pore size distribution obtained from a cylindrical NLDFT pore model assuming an oxidic/zeolite surface (~6.12 Å and 7.15 Å).

In the case of 4, the pore size distribution does reveal an additional peak, albeit very small, at approximately 7.2 Å. The relative peak height indicates that the majority of the pores do not adhere to this diameter. There is uncertainty surrounding the origin of this peak because it is neither in agreement with the dimensions of the channels calculated from the crystal structure nor the dimensions of the cage (if Ar could enter). Alternatively, it would be more understandable if the peak was located below 6.1 Å owing to the reduced pore dimensions imposed by the disordered chloride ions. The H$_2$ sorption uptake of 4 was explored and it was found to adsorb 2.04 wt % at 77 K and atmospheric pressures (Figure 2.22a.), which is significantly lower than the capacities reported for compounds 1 – 3. The isosteric heat of adsorption for 4 was calculated to be in the range of 6.79 kJ mol$^{-1}$ to 5.93 kJ mol$^{-1}$ at low and high loadings, respectively
(Figure 2.22b.). To further validate this result, the sample was subsequently heated to 200°C to ensure complete removal of the axial water molecules (2 per trimer). Indeed, the sample adsorbed similar amounts of H₂ (2.03 wt %) at 200°C and the isosteric heat of adsorption was in good agreement with the data at 135°C having a range of 6.53 kJ mol⁻¹ to 6.04 kJ mol⁻¹ (Figure 2.22b.).

Figure 2.22. (a) Hydrogen sorption isotherm at 77 K and 87 K for 4, {InCl₃-soc-MOF}, after evacuation at 135°C; and (b) Isosteric heat of adsorption of H₂ for 4 after evacuation at 135°C and 200°C.

The heat of adsorption is comparable to 2 and 3 at higher loadings; meaning it is not completely flat as observed in the case of 1. A plausible explanation to account for this result could be associated with the anion-free cage. The bound chloride ions that are delocalized on the cationic cluster may lead to a lower dipolar population as compared to the extra-framework anions in a confined space, 1 – 3. Strictly speaking it is difficult to make a direct comparison between the Qst of 1 and 4 because more than one parameter has been modified: (1) compound 4 has less potential open metal sites than 1 (2 versus 3); and (2) the carcerand cage has is anion-free in 4.
Gas adsorption studies conducted on 5 using argon and hydrogen as adsorbates revealed similar behavior as that reported for 4. The desolvated form of 5 was found to exhibit apparent BET and Langmuir surface areas of 1237 m²/g and 1486 m²/g, respectively. The experimentally determined pore volume of 0.4986 cm³ g⁻¹ agrees very well with the theoretical value that is estimated to be 0.50 cm³ g⁻¹. The pore size distribution was comparable to 4 whereby the internal diameter of the majority of the pores measure 6.12 Å while a small percentage exhibits a width of 7.16 Å.

![Figure 2.23](image)

**Figure 2.23.** Sorption studies for 5, {InBr₃ soc-MOF}, after evacuation at 145°C: (a) Argon sorption isotherm at 87 K; (b) Pore size distribution obtained from a cylindrical NLDFT pore model assuming an oxidic/zeolite surface (~6.12 Å and 7.16 Å).

The framework densities for the desolvated forms of 4 and 5 are very similar having values of 1.09 g cm⁻³ and 1.14 g cm⁻³, respectively. Therefore, it was not overly surprising that 5 was found to adsorb 1.95 wt % of H₂ at 77 K and atmospheric pressures (Figure 2.24). The isosteric heat of adsorption for 5 was determined from the 77 K and 87 K H₂ adsorption isotherms after evacuation at 145°C and 200°C. In both cases a maximum of \( q = 7.00 \text{ kJ mol}^{-1} \) and \( 6.72 \text{ kJ mol}^{-1} \) was recorded at low loadings for the
aforementioned temperatures, respectively. These results demonstrate that having a bromide versus a chloride ion coordinated in the apical position of the TMBB has little if any effect on the H₂-MOF interactions at low loading, as illustrated in Figure 2.24c.

![Figure 2.24](image_url)

**Figure 2.24.** (a) Hydrogen sorption isotherm at 77 K and 87 K for 5, {InBr₃ soc-MOF}, after evacuation at 145°C; (b) Isosteric heat of adsorption for 5 after evacuation at 145°C and 200°C; and (c) Isosteric heat of adsorption of H₂ for 5 compared with 4, {InCl₃ soc-MOF}.

The fact that the $Q_{st}$ curves for 4 and 5 is similar to compounds 1 – 3 is interesting because the former contain one less potential open metal site per TMBB and the carcerand cage contains no anions. We may conclude that the added polarizability and
modest pore size reduction from the halide ions is large enough to compensate for the loss of one open In-TMBB binding site and localized charge density associated with the cuboidal cage of 1.

2.2.5. Validity of the Isosteric Heats of Adsorption via Computational Studies

Space and co-workers assisted us in this study by fitting the hydrogen sorption isotherms collected at 77 and 87 K, i.e. for compounds 2 – 5, to a function in order to determine if the experimentally determined \( Q_{st} \) was appreciably higher at low loadings as we observed. It is important to recall that all data points below \( P/P_0 \) equal to \( 10^{-3} \) were deleted for the \( Q_{st} \) curves shown above because at such low pressures there is a high degree of uncertainty between the two temperatures. Accordingly, in trying to fit the experimental data to their parameterized model Space et al. also observed significant discrepancies at very low coverage, i.e. it was not a linear fit, and therefore many points had to be deleted. The resultant curves shown in Figure 2.25. do not reveal a significant difference between the analogs. It does however show the same trend as we observed experimentally; that is, \( Q_{st} \) decreases according to the following trend \( \text{Fe(NO}_3)_3 (2) > \text{FeCl}_3 (3) > \text{InBr}_3 (4) > \text{InCl}_3 (3) \).
2.2.6. INS Studies: Insights into the H₂-MOF Preferential Binding Sites in 2 and 4

INS spectra were collected for compounds 2 and 4 on the direct geometry IN5 spectrometer at the Institut Laue-Langevin in Grenoble, France. For these specific experiments an incident wavelength of 2 Å was used in order to access a significantly large energy transfer range in neutron energy loss. In doing so however this resulted in a rather modest energy resolution for the spectra. Prior to conducting the measurements, both samples were activated (CH₃CN) on site and evacuated using the same protocol as noted in the sorption experiments above. The INS spectra for 2 and 4, collected after the first in situ loading of H₂, is shown in Figure 2.26. for 1 H₂ / trimer, [Fe₃O(RCO₂)₆] (2) and [In₃O(RCO₂)Cl] (4). This loading corresponds to 1/3 H₂ per Fe and 1/2 H₂ per In, respectively.
Figure 2.26. INS spectra (T = 4.3 K) corresponding to 1 H$_2$ per trimer of 2 \{Fe(NO$_3$)$_3$ soc-MOF\}, (red) and 4 \{InCl$_3$ soc-MOF\} (green) in neutron energy loss over the range: (a) From 1 – 17 meV; and (b) enlarged range below 12 meV.

An appreciable difference is observed between the spectra at this loading, which is precisely the range whereby a noticeable difference is observed in the experimentally determined isosteric heat of adsorption. That is, the $Q_{st}$ at low loading is appreciably greater for 2 than the indium analogs (1, 4, and 5). The low-energy region of the
spectrum provides useful insights to understand the underlying interactions at this loading because those peaks located at lower energy indicate a higher barrier to rotation and thus correspond to stronger binding sites (lower frequency transitions). A careful inspection of the low-energy region of the spectrum for 2 reveals two well-defined peaks at 7.7 meV and 10 meV. Compound 4 however does not have clearly visible peaks in this region. As eluted to previously, the lower rotational transition frequencies are associated with high barrier (rotational tunneling) and therefore a stronger interaction is observed in the case of H₂ with Fe than compound 4.

The second set of loadings corresponding to 3 and 2/3 H₂ per formula unit in the case of 2 and 4, respectively (Figure 2.27.) correspond to filling of the metal binding sites. The pair of peaks observed in 2 (7.7 meV and 10 meV) show a commensurate increase in intensity, while a weak, and rather broad band appears in the spectrum of 4 at approximately 8 meV. The aforementioned peaks observed in 2 show a parallel increase in intensity that is comparable to the H₂ adsorbed at open –metal binding sites in the Ni-, Co-, and Mg-CPO-27 analogs of MOF-74.⁶⁷
Accordingly, these peaks can be assigned as two related rotational transitions\textsuperscript{68} for H\textsubscript{2} at the Fe binding site. The broad peak observed in the spectrum of 4 can therefore be tentatively assigned to H\textsubscript{2} binding sites near the chloride ion located in the apical position of the indium-based TMBB. This assignment is in accord with a very similar band observed in ZIF-68 whereby the organic ligand was functionalized by replacing a hydrogen atom for a chloro substituent.\textsuperscript{69} Accordingly, the INS data presented herein explicitly demonstrate that it is the Fe-binding sites in 2 which are responsible for the enhancement of \(Q\)st at low loadings relative to that of the indium analogs. At higher loading, the INS spectra for 2 and 4 are similar and reveal strong albeit broad bands at subsequent loadings in the region above 10 meV, which may be resolved into three peaks (Figure 2.28.).

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure227.png}
\caption{INS spectra (T = 4.3 K) of 3 H\textsubscript{2} per trimer in 2 \{Fe(NO\textsubscript{3})\textsubscript{3} soc-MOF\} (black) and 3/2 H\textsubscript{2} per trimer in 4 \{InCl\textsubscript{3} soc-MOF\} (yellow) in neutron energy loss over the range from 1 to 12 meV.}
\end{figure}
Figure 2.28. INS spectra (T = 4.3 K) to emphasize the differences at higher loading in neutron energy loss over the range from 1 to 12 meV: (a) Compound 2, \{Fe(NO_3)_3 soc-MOF\}, shown after loadings of 2, 6, 18, and 30 mmol which are represented in red, green, blue, and yellow respectively; (b) Compound 4 \{InCl_3 soc-MOF\} at loadings corresponding 1.3, 2.7, 12, and 20 mmol of H_2 represented in red, blue, green, and yellow, respectively.

It is important to take into consideration that the modest energy resolution available from this type of instrument when used with a short incident wavelength, 2 Å, will not resolve fine structure in these bands, as was possible on the QENS instrument at
IPNS used in previous measurements. In previous studies, we assigned peaks in this frequency region to weaker binding sites between the TMBB and the organic components of the framework; that is, carboxylate, azo, and phenyl moieties. At low loading the INS spectra appear to be fairly similar in this region for both compounds, i.e. one may discern three peaks at 13.3, 14.4 and 15.6 meV for compound 2, and 12.6, 14.5 and 15.6 meV for 4. The two highest frequency transitions (higher energy region of the spectra) are likely to be related, and thus arise from similar sites. Note that at higher loadings in 2, the lower frequency transition (13.3 meV) shifts to even lower frequency (12.1 meV) when the loading is increased to the equivalent of 2 H₂ per Fe. A similar, yet less pronounced, effect was observed in the parent indium-based soc-MOF compound, 1. A plausible explanation to account for this observation can be explained by noting that in both 1 and 2 the carerand-like cage encapsulates four nitrate anions, which are statically occupy two positions on the three fold axis with an equal probability of being located in either position (see section 2.2.4.1.), whereas this cage is anion-free in 4. It is thereby apparent, that hydrogen can be forced into the partially nitrate filled cage at high loadings, whereas this cage simply fills gradually (peak at 12.6 meV, shifts slightly to 12.0 meV at high loadings) in 4.

2.3. Experimental Section

2.3.1. Materials and Methods

Unless otherwise noted, all MOMs discussed in the following chapters were synthesized and characterized by Amy J. Cairns in Prof. Mohamed Eddaoudi’s research group in the Department of Chemistry at the University of South Florida (USF) according
to the outlined experimental methods and procedures. Please note that compound 1 was first synthesized by Professor Yunling Liu when he was a post doctoral fellow in Prof. Mohamed Eddaoudi’s research group at USF. My contribution focused on preparing 1 for gas sorption measurements, collecting sorption data, and preparing bulk quantities of 1 for INS experiments.

2.3.2. Instrumentation and Software

Single-crystal X-ray diffraction (SCD) data were collected on a Bruker AXS SMART-APEX CCD diffractometer using MoKα radiation (λ = 0.71073 Å) or CuKα radiation (λ = 1.54178 Å) operated at 2000 W power (50 kV, 40 mA). The frames were integrated using the SAINT software package\textsuperscript{70} with a narrow frame algorithm. The structures were solved using direct methods and refined by full-matrix least-squares on|\(F|\)^2. The SHELXTL 5.1 program package\textsuperscript{71} was used for all crystallographic calculations. The crystallographic data reported in the following chapters were primarily and solved by Dr. Lukasz Wojtas. Assistance was also graciously Dr. Gregory J. McManus, Dr. Derek Beauchamp, and Mr. Mohamed Alkordi in the Department of Chemistry at the University of South Florida and Dr. Victor Kravtsov at the Institute of Applied Physics of Academy of Science of Moldova. The crystallographic data for compound 2 was collected at the Small Molecule Crystallography Beamline (11.3.1) at the Advanced Light Source in Berkley, California by Dr. Paul Forster from the University of Las Vegas in Nevada. Complete lists of crystallographic tables are included in Appendix A.
X-ray Powder Diffraction (XRPD) measurements were carried out at room temperature on a Bruker AXS D8 Advance 50kV instrument using a 40mA for CuKα (λ = 1.5418 Å), with a scan speed of 1°/min and a step size of 0.02° in 2θ. Calculated XRPD patterns were produced using the PowderCell 2.4 software\textsuperscript{72} and/or Materials Studio MS Modeling version 4.0.\textsuperscript{73} See Appendix B for a comparison between calculated and experimental XRPD patterns.

Conventional thermogravimetric analyses (TGA) were performed under N\textsubscript{2} and recorded on a Perkin Elmer Precisely STA6000 thermogravimetric analyzer. TGA profiles are included in Appendix C.

Volumetric gas sorption studies performed at the University of South Florida (USF) were conducted on a fully automated micropore gas analyzer Autosorb-1 MP (Quantachrome Instruments) at relative pressures up to 1 atm. The cryogenic temperatures were controlled using liquid nitrogen and liquid argon at temperatures of 77 K and 87 K, respectively. Gravimetric gas sorption studies were performed by Mr. Ryan Luebke in the Department of Chemistry at the University of South Florida on a VTI MB-300 GHP (gravimetric high pressure analyzer) gas adsorption instrument up to a pressure of 19,000 Torr at temperatures ranging from 273 to 298 K. High resolution physical adsorption experiments were performed on 1 using argon, hydrogen, methane and carbon dioxide as adsorptives. The low pressure measurements were collected on a volumetric adsorption analyzer equipped with a novel cryostat (Quantachrome Instr. / Oxford Instr.) from 0 to 0.1 MPa over a wide range of temperatures (77 – 323 K). While, high pressure gravimetric adsorption measurements were measured on 1 from 273 K to 323 K on a Rubotherm GmbH instrument equipped with a magnetic suspension balance up to
pressures of 50 MPa. The high resolution sorption data was collected and analyzed by our collaborators at Quantachrome Instruments (M. Thommes and E.B. Celer) in Boynton Beach, FL and our collaborators at the Institut für Nichklassische Chemie (J. Moellmer and R. Staudt) in Leipzig, Germany.

INS spectra of hydrogen adsorbed on 1 were collected by Drs. Juergen Eckert and Jarrod Eubank on the quasielastic neutron spectrometer (QENS) spectrometer at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory (ANL). High resolution INS spectra of hydrogen adsorbed on compounds 2 and 4 were obtained on the cold-neutron time-of-flight IN5 spectrometer at the high-flux reactor located at the Institut Laue-Langevin (ILL) in Grenoble, France. The experiments were carried out by Dr. Juergen Eckert, Peter Georgiev, and Amy Cairns. All spectra were analyzed using the LAMP software. The observed binding sites in the INS spectra were tentatively assigned using a two-dimensional phenomenological model previously described by Eckert and co-workers. That is, for simplicity, the model assumes H₂ to be a hindered rotor that is subjected to a barrier to rotation with 2 angular degrees of freedom in a simple double-minimum potential. The transitions for the hindered rotor occur between different energy levels (i.e. 0, 1, 2, etc) with increasing energy and are therefore labeled as (0 – 1), (0 – 2), etc transitions. Accordingly, in the absence of a barrier to rotation the H₂ molecule is permitted to rotate freely and the lowest transition for H₂ occurs at 14.7 meV (or 119 cm⁻¹ = 2B) and is observed for the para- and ortho-H₂. Alternatively, when H₂ is introduced to a host material (i.e. MOF) that exhibits various structural and functional features, the H₂ molecules are subjected to a barrier that hinders the rotation. This partially lifts the degeneracy of the J = 1 level and the lowest transition frequency
for the hindered rotor between $J = 0$ and $J = 1$, regarded as the 0 – 1 transition, decreases exponentially as the barrier height is increased. Thus, a 0-1 transition at lower energy is the direct result of a higher barrier to rotation and is indicative of a stronger interaction at that particular binding site. It is imperative to point out that these energy values are not equivalent to the rotation quantum number $J$ because it is not applicable to the hindered rotor, only the free rotor.

Atomic Absorption (AA) experiments were carried out on a Varian Spectra AA 100 instrument, with the help of Mr. Farid Nouar in the Department of Chemistry at the University of South Florida.

Total solvent-accessible volumes were determined using PLATON software by summing voxels more than 1.2 Å away from the framework.

Materials Studio MS Modeling version 4.0 was used for the graphical structural analysis. A topological evaluation for each compound was performed using Topos software. Subsequently, the topological terms were compared to those present in the literature and the RCSR database. For known topologies, the three-letter symbols adopted by Prof. Michael O’Keeffe are used (e.g. pts represents the topology for the Platinum Sulfide net). Tiling representations were evaluated using 3dt software.

### 2.3.3. Synthesis and Characterization

All chemicals and solvents used in the preparation of compounds 1 - 5 were of reagent grade and used without further purification.
Figure 2.29. Synthetic strategy followed for the preparation of 3,3',5,5'-azobenzenetetracarboxylic acid (H₄-ABTC). Reagents and Conditions: (i) H₂O / NaOH / stir for 30 min; (ii) slow addition of hot glucose (aq) and bubble air through the solution for 24 h; (iii) filter the precipitate; dissolve in a minimal amount of H₂O; acidify to pH = 1 using 12 M HCl.

Preparation of 3,3',5,5'-azobenzenetetracarboxylic acid, H₄-ABTC: The product was synthesized according to a modified procedure from the literature. In a typical reaction, (9.5g, 0.045mol) of 5-nitroisophthalic acid was gradually added to a round bottom flask (r.b.f) containing 120 mL of H₂O and (25g, 0.63mol) of NaOH pellets. Concomitantly, (50g, 0.28mol) of D(+)Glucose was dissolved in 75mL of H₂O, the dissolving process was aided by heating the solution. The hot aqueous glucose solution was added dropwise to the mixture over a 1 h period. During the addition process, many color changes are observed; that is, the mixture is initially yellow but as more glucose is added the solution changes color to orange, then to a deep red, and finally upon full addition the solution appears almost black with a hint of orange. To facilitate the azo coupling reaction, a constant flow of air is bubbled through the mixture for approximately 24 h. This causes the sodium salt of the ligand to crash out of solution in the form of a yellow precipitate. The precipitate was dissolved in a minimal amount of H₂O to yield a transparent deep orange solution whereby the final product is isolated by acidification to pH = 1 using 12M HCl. The orange product was filtered, washed thoroughly with ice cold water, and air-dried. Note: No further purification is required.
Synthesis of \{[\text{In}_3(\text{ABTC})_{1.5}(\text{H}_2\text{O})_3]\cdot(\text{NO}_3)(\text{H}_2\text{O})_3\}_n, (1). A solution of In(NO_3)_3\cdot2\text{H}_2\text{O} (22.0mg, 0.065mmol) and H_4-\text{ABTC} (16.6mg, 0.044mmol) in 1 mL DMF, 1 mL CH_3CN, 0.100 mL piperizine (0.4 M in DMF), and 0.300 mL warm HNO_3 (3.5M in DMF) was prepared in a 20 mL scintillation vial. The solution was heated to 85°C for 16h, after which orange polyhedra-shaped crystals were obtained. Crystals of 1 were harvested and air-dried. The as-synthesized material is insoluble in H_2O and common organic solvents. (Yield: 28.0 mg, 95.6 %). Elemental analysis calcd (%) for 1, C_{24}H_{21}N_4O_{22}In_3: C 27.15, H 1.99, N 5.28; found: C 27.32, H 2.51, N 5.18.

Synthesis of \{[\text{Fe}_3(\text{ABTC})_{1.5}(\text{H}_2\text{O})_3]\cdot(\text{NO}_3)(\text{H}_2\text{O})_{0.67}\}_n, (2). A solution of FeSO_4\cdot6\text{H}_2\text{O} (30.0mg, 0.11mmol) and H_4-\text{ABTC} (12.9mg, 0.036mmol) 1 mL DMF, 1 mL H_2O, 0.5 mL chlorobenzene, and 0.300 mL HNO_3 (3.5M in DMF) was prepared in a 20 mL scintillation vial. The solution was heated at a constant rate of 1.5°C/min to 85°C and held for 12h, then cooled at a constant rate of 1.0°C/min to room temperature. The as-synthesized sample was purified through repeated washings with DMF solvent, revealing small cube-shaped crystals that are insoluble in water and common organic solvents. Crystals of 2 were harvested and air-dried. (Yield: 10.2 mg, 33.0 %).

Synthesis of \{[\text{Fe}_3(\text{ABTC})_{1.5}(\text{H}_2\text{O})_3]\cdot(\text{Cl})\}_n, (3). A solution of FeCl_2 (13.7mg, 0.1 mmol) and H_4-\text{ABTC} (12.9mg, 0.034mmol), 1 mL DMF, 1 mL H_2O, 0.5 mL chlorobenzene, and 0.450 mL of warm HCl (3.5 M in DMF) was prepared in a 20 mL scintillation vial. The solution was heated at a constant rate of 1.5°C/min to 85°C and held for 12h, then cooled at a constant rate of 1.0°C/min to room temperature resulting in orange cube-shaped crystals. The as-synthesized crystals are insoluble in water and
common organic solvents. Crystals of 3 were harvested and air-dried. (Yield: 14.2 mg, 52.9 %).

**Synthesis of** $\{[\text{In}_3(\text{ABTC})_{1.5}(\text{Cl})(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})_{5.35}\}_n$, (4). A solution of InCl$_3$ (30.0mg, 0.14mmol) and H$_4$-ABTC (24.3mg, 0.068mmol) in 1 mL DMF, 1 mL ethanol, and 0.5 mL H$_2$O was prepared in a 20 mL scintillation vial. The solution was heated to 85°C for 12h, and pure orange cube-shaped crystals were obtained. Crystals of 4 were harvested and air-dried. The crystals were found to be insoluble in H$_2$O and common organic solvents. (Yield: 26.2 mg, 52.9 %).

**Synthesis of** $\{[\text{In}_3(\text{ABTC})_{1.5}(\text{Br})(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})_{6.25}\}_n$, (5). A solution of InBr$_3$ (49.6mg, 0.14mmol) and H$_4$-ABTC (24.1mg, 0.067mmol) in 1 mL DMF, 1 mL CH$_3$CN, and 0.5 mL H$_2$O was prepared in a 20 mL scintillation vial. The solution was heated to 85°C for 12h and pure orange cube-shape crystals were obtained. Crystals of 5 were harvested and air-dried. (Yield: 23.4 mg, 44.7 %) and found to be insoluble in H$_2$O and common organic solvents.

2.4. Summary and Conclusions

In summary, the rational design and synthesis of an isostructural series of MOFs with soc topology, 1 – 5, permitted a methodical hydrogen sorption study to be conducted in which case some factors that govern H$_2$ binding were isolated. To gain a better understanding of the sorption sites within select compounds (1, 2, and 4), the sorption data was complimented by INS studies. Collectively, the data obtained from these measurements provide valuable insights into the preferential H$_2$-MOF interactions as a direct consequence of varying specific structural and chemical components. This study
independently evaluated the effect of three key parameters: (1) Metal cation (In \textit{versus} Fe) in two MOFs whose structure and composition differ only with respect to the choice of metal center; (2) Contributions from extra-framework counter ions (NO$_3^-$ \textit{versus} Cl$^-$) housed in a confined space in two Fe-based MOFs; and (3) Contributions from polarizability via decorated In-TMBBs (Cl$^-$ \textit{versus} Br$^-$).

Table 2.2. Selected sorption data for compounds 1 – 5.

<table>
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<tr>
<th>Cpd</th>
<th>Evac.$^a$ (°C)</th>
<th>$d_{\text{nom}}$ (g/cm$^3$)</th>
<th>BET/Langmuir$^b$ (m$^2$/g)</th>
<th>P.V.$_{\text{exp}}$ (cm$^3$/g)</th>
<th>P.V.$_{\text{theo}}^d$ (cm$^3$/g)</th>
<th>P.S.$_{\text{exp}}^e$ (Å)</th>
<th>% H$_2$$^c$ (77 K)</th>
<th>H$_2$ (g/L)</th>
<th># H$_2$/Metal$^f$</th>
<th>$Q_{\text{st}}$$^g$ (kJ/mol)</th>
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<td>7.84</td>
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<td>1648 / 1969</td>
<td>0.66</td>
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<td>$\sim$0.55 (P) $\sim$0.53 (M.S)</td>
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<tr>
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<td>1.95</td>
<td>22.2</td>
<td>3.13</td>
<td>6.86</td>
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</tbody>
</table>

$^a$Evacuation temperature of the exchanged samples; $^b$Apparent BET and Langmuir surface areas obtained from the Ar sorption isotherms at 87 K, except for 1 which was determined from the N$_2$ isotherm at 77 K; $^c$BET surface area was not reported for 1; $^d$Theoretical pore volume calculated using PLATON (P) and Materials Studio (M.S.) using argon probe; $^e$Hydrogen uptake (wt %) at 77 K and 724 Torr; $^f$The unit cell of each compound contains 24 metal cations; $^g$Isosteric heat of adsorption for H$_2$ at low loading.

With regards to the choice of metal cation, it was demonstrated that potentially open Fe cationic TMBBs facilitate stronger H$_2$-MOF interactions at low loading as compared to the indium analogs. This was evidenced by the notable increase in the isosteric heats of adsorption; that is, 6.50 kJ mol$^{-1}$ and 7.84 kJ mol$^{-1}$ for 1 and 2, respectively. Since compound 2 is constructed from Fe metal cations (MW$_{Fe} = 55.85$ g
mol\(^{-1}\); MW\(_{in} = 114.82\) g mol\(^{-1}\)) this affords a lighter framework density and thus a larger pore volume and surface area. These structural features coupled with the enhanced interaction of Fe with H\(_2\) led to a higher uptake of H\(_2\) at 77 K and 723 Torr as compared to 1 and is supported by INS data.

The types of extra-framework anions were found to play a role as demonstrated in two Fe-based MOFs, 2 and 3. The materials have similar framework densities, pore sizes and volumes but differ with respect to the type of anion located in the cage. Compound 2 having four disordered nitrate ions was found to exhibit a higher Q\(_{st}\) at low loading as compared to 3 having disorder chloride ions. Indeed, compound 2 was found to have a higher Q\(_{st}\) and adsorbs slightly more H\(_2\) than observed in the case of 3.

The effect polarizability and to a lesser extent pore size was assessed via the incorporation of decorated In-TMBBs. This study revealed an insignificant difference by having one bromide ion coordinated in the apical position of each trimer versus a chloride ion. This conclusion, based on the sorption data, is further supported by the INS data collected on 4 which did not reveal well-defined peaks at lower transitional frequencies (below 10 meV). Compound 5 exhibits a slightly higher framework density than 4 due to the increased molecular weight from the bromide and thus it adsorbs less H\(_2\) at 77 K and atmospheric pressures. However, its larger atomic radius and higher polarizability afforded a slightly higher isosteric heat of adsorption as compared to the chloride analogue.

In conclusion, we have shown that the soc-MOF platform is well suited to achieve high uptake capacities in which case the H\(_2\)-MOF interactions are maintained even at higher loadings. Nevertheless, the chemical changes described herein afforded minor
changes in \(Q_{st}\) and therefore we are still far away from satisfying the DoE targets. We are currently exploring alternative avenues to increase the uptake capacity and \(Q_{st}\) by designing isoreticular soc-MOF analogs using expanded square-planar tetracarboxylate organic ligands. The relative scale imposed by such ligands would result in the formation of larger cages and would therefore allow for encapsulation studies to be conducted, i.e. metal complexes. This could be interesting for gas storage and/or sensing applications.

2.5. References


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Chapter 3. Structural Diversity of 4-Connected Nodes: Serendipity versus Predictability in Crystal Chemistry

3.1. Synthesis of 2-Periodic Metal-Organic Materials

3.1.1. Introduction

Metal-organic materials (MOMs) are widely recognized as a unique class of solid-state crystalline materials. They exhibit superior fine-tunable structural and chemical features which make them ideally suited for many desired applications (e.g. gas storage and separation, magnetism, drug delivery, etc). The molecular building block (MBB) approach has proven to be remarkably successful at producing modular MOMs with a certain degree of predictability that range from discrete (0-periodic), 1-, 2-, to 3-periodic, as described in Chapter 1. In this chapter we will address the significance and versatility of such MBBs for the construction of 2-periodic MOMs, with an emphasis on structures having kgm and sql topology.

Layered networks are naturally more complex than 1-periodic structures because the latter are delineated by chain-like structures having at most 2-connected nodes and thus the geometry (angularity) around each node governs the formation of the net. The geometry around each node is equally important in the realm of 2-periodic networks but the existence of two spatial directions supports the formation of n-connected nodes where n is greater than 2. This modification facilitates the formation of geometrical shapes (e.g. building units; BUs) through the self-assembly of the n-connected nodes. In the context
of MOMs, the overall shape and packing motif of the layers can lead to the formation of channels and/or cavities, which will have a profound effect on the properties of the material (e.g. porosity, magnetism).

Layered structures have a rich history with clay-like materials and graphite being two well-known examples.²⁴, ²⁵ Some of the earliest reports of metal-organic analogues were inclusion compounds based on metal-cyanide compounds,²⁶ more specifically Prussian blue (PB) compounds and Hofmann clathrates (see Chapter 1).²⁷-²⁹ One of the fascinating features of this broad class of materials is their ability to trap guest molecules between neighboring layers through the expansion and/or contraction of the layers. The intercalated guest molecules can be incorporated into the host lattice as a means to control the overall packing of the layers (e.g. AAA, ABAB, ABC, etc) and the relative distance between neighboring layers. Hence the chemical composition and functionality of the framework, as well as, the packing motif provides a useful strategy for controlling and optimizing the porosity of these materials.

3.1.1.1. Topological Perspective: Regular and Semi-Regular Plane Tilings

Two-periodic metal-organic architectures are commonly referred to as layered or sheet structures. This analogy stems from the fact that the underlying topology of the net is described by planar networks. In order to evaluate the topology of a framework, it must be reduced into its simplest components; that is, the assembly of \( n \)-connected nodes connected through edges (spacers). In this context the plane can be enclosed (covered) by convex polygons to reveal a tiling representation that is unique for that particular net. In most cases the product of the self-assembly process yields the simplest and most
symmetric nets. There exists three exclusive regular plane nets or Platonic tilings. Their transitivity is described by [111] which denotes one type of vertex-, edge-, and tile. As illustrated in Figure 3.1., these tilings include: the (3,6)-hexagonal lattice which is assembled from 6-connected nodes to reveal triangular tiles, the (4,4)-square grid lattice composed of 4-connected nodes which assemble to afford square tiles, and the (6,3)-honeycomb lattice comprised of 3-connected nodes and hexagonal tiles.

![Figure 3.1. Tiling representation of the three exclusive regular [111] plane nets: (left) (3,6) hexagonal lattice (**hxl**); (middle) (4,4) square grid lattice (**sqg**); and (right) (6,3) honeycomb lattice (**hcb**).](image)

The regularity of a given net is reduced for systems composed of more than one type of convex polygon whose vertices intersect whereby an increased level of topological complexity is introduced. Accordingly, a sub-class of plane tilings which warrant special attention is the semi-regular (Archimedean) nets and there are exactly eight tilings in this group (Figure 3.2.). A diverse collection of 2-periodic nets exist, a few of which have been highlighted here. In particular, the edge-transitive nets must be emphasized because this group of nets is salient to crystal chemistry. There are precisely five 2-periodic edge-transitive nets: the three regular nets, the quasi-regular **kgm** net, and the Kagomé dual (**kgd**; isohedral tiling). The results described below will highlight the
versatility and significance of the **sql** and **kgm** nets by reporting the design and synthesis of several decorated metal-organic architectures having the noted topologies.

![Figure 3.2](image.png)

**Figure 3.2.** Tiling representation of the semi-regular plane nets constructed from two or more regular polygons. Top (left to right): (4.8^2) *fes* or *sql-a*; (3.12^2) *hca*; (3^2.4.3.4) *tts*; (3^2.4^2) *cem*. Bottom (left to right): (3.4.6.4) *htb*; (4.6.12) *fxt*; (3^4.6) *fsz*; (3.6.3.6) *kgm*.32

### 3.1.1.2. Design Principles and Applications: Nanoscale Kagomé and Square Grid Lattices

Metal-organic materials with **kgm** topology are attractive targets because of their properties, which include potential magnetism applications in resulting from spin frustration.22, 33-38 The Kagomé lattice is a uninodal net (vertex transitive) comprised of 4-connected square planar nodes and thus the self-assembly of suitable MBBs can lead to the formation of this layered network with (3.6.3.6) topology. This particular sequence of numbers indicates that the **kgm** net is comprised of two sets of triangular and hexagonal convex polygons, which meet at each 4-connected node.39 The triangular polygons are vertex-linked and thus delimit the hexagonal polygon. The tiling representations of the **kgm** and **sql** nets provide a blueprint for the rational design of nanoscale metal-organic...
analogue. Thus, the self-assembly of pre-fabricated MBBs with the necessary geometric attributes have the potential to generate analogous nets under the appropriate reaction conditions. A clever design strategy was introduced by Zaworotko and co-workers to target such nets by utilizing nanoscale SBUs \((n\text{SBUs})\).\(^{21, 22, 40-42}\) The authors demonstrated that square and triangular \(n\text{SBUs}\) can be formed via the self-assembly of vertex-linked regular molecular squares (Figure 3.3.).

![Figure 3.3. Schematic illustration of the two nanoscale SBUs that can be generated by linking molecular squares through \(m\)-BDC type ligands: (a) Square \(n\text{SBU}\) comprised of four square SBUs; and (b) Triangular \(n\text{SBUs}\) comprised of three square SBUs.](image)

The dimetal tetracarboxylate, \([\text{M}_2(\text{RCO}_2)_4\text{L}_2]\), MBB is commonly employed to construct a diverse collection of MOMs, which require a 4-connected square planar building unit.\(^{43-46}\) This analogy stems from the fact that connecting the points of extension of the paddlewheel MBB reveals a molecular square, when viewed down the 4-fold axis (Figure 3.4.). In a similar vein, a linear spacer and octahedral building unit are attainable if only the axial positions represent the points of extension or if all six positions are extension points, respectively. This particular MBB can be readily synthesized and thus is a ubiquitous metal cluster in solid-state chemistry as exemplified by the extensive number of crystal structures reported in the CSD (over 1600!). Transition metal ions predominately form this cluster, specifically Cu, Rh, Ru, and Mo. The inherent modularity and rigidity afforded by the paddlewheel MBB renders it an
ideal building block in crystal design: (1) the metal cations can be readily substituted; (2) the carboxylato ligands can be varied; and (3) the axial positions can be easily altered.

**Figure 3.4.** (left) Dimetal tetracarboxylate, $[\text{M}_2(\text{RCO}_2)_4\text{L}_2]_n$, “paddlewheel” building block, which can be regarded as (right) a square building unit when viewed down the 4-fold axis.

Zaworotko and co-workers in fact demonstrated that triangular and square $n$SBUs can be generated by linking these molecular squares at their vertices using rigid ditopic organic ligands (e.g. $m$-BDC). The natural angularity imposed by the relative position of the carboxylate groups dictates that such ligands are predisposed to link the squares at a 120° angle. The versatility and predictability of linking square paddlewheel MBBs with $m$-BDC and its derivatives is exemplified by the large collection of discrete nanoballs (triangular and square $n$SBUs),$^{41, 47, 48}$ Kagomé lattices (triangular $n$SBUs),$^{22, 49}$ and 2-periodic tetragonal (square $n$SBUs) lattices.$^{21, 42}$ Hence, the aforementioned MOMs are excellent examples of supramolecular isomerism whereby more than one type of network is generated from the same MBBs.

In the context of this discussion, the Kagomé lattice is assembled from alternating bowl-shaped triangular $n$SBUs. This arrangement of atoms leads to the formation of small triangular and large hexagonal cavities having van der Waals dimensions of approximately 7.804 Å and 15.751 Å, respectively (Figure 3.5a,c.). The amplitude between the layers and their overall packing can be influenced by ligand functionality,
non-covalent interactions, template-effects, steric hindrance, etc. A higher degree of diversity is possible in the tetragonal square grid structure with respect to the orientation of the molecular squares in the nSBUs (Figure 3.5b,d.) whereby the square grid is constructed from both the cone and 1,3-alternate forms. This leads to the formation of uniform rectangular-shaped channels in which each bowl has an outer diameter of approximately 9.024 Å and a depth of 8.412 Å. Such topological differences have the potential to lead to rather different porosities and magnetic properties.

Figure 3.5. Examples of Kagomé and Square Grid MOMs constructed from m-BDC and $[\text{Cu}_2(\text{RCO}_2)_4\text{L}_2]$ MBBs: (a-b) Space-filling representation of a single 2-periodic layer in a Kagomé and tetragonal square grid structure, respectively, viewed down the z-axis; (c) Schematic illustration of the Kagomé lattice which is comprised of 6- and 3-membered rings; and (d) Schematic illustration of the tetragonal square grid lattice comprised of solely 4-membered rings. Color Code: C = gray; O = red; hydrogen = white; and Cu = green. The 5-position of the BDC moiety is highlighted in purple.
3.1.1.3. Taxonomy of Calixarene-like MOMs

The resultant bowl-shape of the square \( n \)SBU bears a striking resemblance to the conformation adopted by calixarene compounds (\( e.g. \) calix[4]arene). It was therefore shown that tetragonal square grid structures, amongst others, can form analogous metal-organic atropisomers in the solid state.\(^{42}\) Calixarenes are macrocyclic compounds derived from the assembly of aromatic and alkyl components.\(^{50,51}\) They are routinely synthesized via a condensation reaction by combining \( N \) equivalents of phenol, resorcinol, or pyrogallol with \( N \) equivalents of an aldehyde. Typically, phenol is reacted with formaldehyde while the substituted phenyl components require larger aldehydes (\( e.g. \) acetaldehyde).\(^{52}\) The resultant bowl-shape cavities facilitate the encapsulation of guest molecules and thus this class of compounds represent an ever growing field in supramolecular Host:Guest chemistry.\(^{53-57}\)

Atropisomerism is a form of isomerism that can occur in systems when free rotation about the \( sp^3 \) carbon-carbon bond is significantly hindered.\(^{58}\) This can invoke the formation of different stereoisomers, i.e. compounds having the sample chemical composition but differs only in their arrangement in space. This form of isomerism is predominately observed in biaryls, porphyrins, and calixarene-based materials. The four possible atropisomerisms of a calix[4]arene identified by Gutsche\(^{54}\) (Figure 3.6.).\(^{59-63}\)
Figure 3.6. The four types of atropisomers of calix[4]arene: (a) Cone; (b) Partial cone; (c) 1,2-alternate; and (d) 1,3-alternate.

The basis for this nomenclature arises from the orientation of neighboring arene units. In the cone arrangement, all arene units are directed upward, while having one arene directed downward affords the partial cone. The 1,2- and 1,3-alt newates correspond to cis- and alternating arenes directed downward, respectively. The organic MBBs used to construct the 2- and 3-periodic structures presented in this chapter are all derived from 1,3-BDC ligands. Accordingly, this type of terminology will be utilized throughout this chapter to described networks that are independently assembled from clusters of four square and tetragonal building units, as well as, triangular nSBUs.

3.1.2. Results and Discussion

3.1.2.1. Decorated Kagomé Lattice

Herein, we contribute to the collection of decorated metal-organic 2-periodic Kagomé lattices by reporting the serendipitous discovery of compound 6, \([\text{Cu}_2(5-\text{NH}_2\text{BDC})_2(\text{H}_2\text{O})_2]\), with kgm topology. The goal of this project was in fact to synthesize an isoreticular series of porous 3-periodic MOFs having nbo topology, whose
cross-linked layers mimic the connectivity of the \textbf{kgm} lattice. A so-called ligand-to-ligand pillaring design strategy was employed to connect the adjacent layers in an attempt to systematically control the resultant pore size (along the z-direction) by using an assortment of \textit{m}-BDC derived tetracarboxylate organic ligands. The linkers were functionalized in the \textit{m}-position to precisely fuse the neighboring layers. A detailed discussion of this design strategy will be provided in the following section. The rationale behind this methodology stems from the fact that planar networks exhibit modular interlayer distances and the packing arrangement of these layers (\textit{e.g.} AAA, ABAB, ABC, \textit{etc}) in the solid state is predominately controlled by non-covalent intermolecular interactions between guest molecules. Thus covalent cross-linking of neighboring layers through pre-designed tetracarboxylate organic ligands of various lengths and functionality is expected to facilitate the formation of highly porous 3-periodic MOFs with tunable pore dimensions.

The tetracarboxylate organic ligand employed in this study, \textit{5,5'}-\{benzene-1,4-diylbis[(\textit{E})methylidylenenitrilo]}benzene-1,3-dicarboxylic acid (H$_4$-ImTC) is shown in Figure 3.7. Mild solvothermal reaction between H$_4$-ImTC and Cu(NO$_3$)$_2$.2.5H$_2$O however yields a 2-periodic \textbf{kgm} net instead of the expected 3-periodic \textbf{nbo} structure. There are several possible explanations to account for this outcome: (1) the aqueous reaction conditions may have promoted the imine functionality to undergo a hydrolysis reaction which liberated 5-NH$_2$BDC as a product, and/or (2) the final product was contaminated with unreacted starting material in the form of 5-NH$_2$BDC.
We were unable to reproduce these crystals using $\text{H}_4\text{-ImTC}$ and therefore the next logical step was to focus on the reaction of 5-NH$_2$BDC with copper. Indeed, mild solvothermal reaction of 5-NH$_2$BDC with Cu(NO$_3$)$_2$·2.5H$_2$O in a DMF/CH$_3$CN solution in the presence of triethylamine (TEA) yields homogenous green hexagonal crystals, designed as compound 6. The crystal structure revealed a 2-periodic network similar to that of the parent Kagomé structure.\textsuperscript{22} Accordingly, the network is built up from copper paddlewheel building blocks, whereby each copper ion exhibits the expected square pyramidal geometry ($d_{\text{Cu-Cu}} = 2.630$ Å). The equatorial plane is occupied by four independent carboxylato oxygen atoms that bridge the dinuclear copper ions in a bis-monodentate fashion ($d_{\text{Cu-O}} = 1.950$ Å, 1.971 Å), while aqua ligands lie in the axial positions ($d_{\text{Cu-O}} = 2.110$ Å) to yield the CuO$_5$ primary building block. The self-assembly of the triangular $n$SBU$s$ affords an infinite nanoscale Kagomé lattice sustained by large hexagonal cavities and small triangular cavities (Figure 3.8.). The estimated window dimensions of the aforementioned cavities are 15.751 Å (6.138 Å vdw sphere) and 5.174 Å, respectively. The approximate depth the hexagonal and triangular cavities is 9.072 Å and 10.600 Å, respectively which roughly corresponds to the interlayer separation.
The natural curvature imparted by the angularity in the functionalized $m$-BDC ligand promotes efficient packing of the undulating layers (AAA) with an effective interlayer separation of 10.600 Å. Each of the layers interact through N-H$\cdots$O hydrogen bonding interactions (distance is 1.749 Å); that is, aqua ligands are positioned between the layers which serve as a bridge. Thus, each aqua ligand participates in N-H$\cdots$O hydrogen bonding with two N-H groups located on different phenyl rings in neighboring layers (Figure 3.9.).
3.1.2.2. Synthesis of an Anionic Tetragonal Square Grid Lattice from Tetrahedral MBBs

The natural angularity imparted by \( m \)-BDC is not a prerequisite for the synthesis of tetragonal square grid structures. These networks have also been constructed using linear ditopic ligands, such as 1,4-BDC\(^{19} \) and others.\(^{42, 64} \) In a similar vein, the vertex figure of the inorganic MBB does not have to be a perfect square to facilitate the formation of a square grid lattice. Mild solvothermal reaction between 5-NH\(_2\)BDC and In(NO\(_3\))\(_6\)H\(_2\)O in a DMF/H\(_2\)O solution indeed yields a tetragonal square grid lattice, formulated by SCD studies as, \([\text{In}(5-\text{AmBDC})_2\cdot\text{(DMA)}\cdot\text{(DMF)}]_n\), (7). It must be noted that the reaction conditions employed in the synthesis of 7 promote a condensation reaction, which converts the amine functionality into the amide derivative. Amides are routinely synthesized in organic synthesis via the reaction of a carboxylic acid with an amine. The general reaction mechanism is outlined in Figure 3.10. Under appropriate reaction conditions, DMF frequently decomposes to liberate DMA cations and formic acid as bi-products. We therefore hypothesize that 5-AmBDC was formed via a
condensation reaction between formic acid and the amine group on 5-NH₂BDC following the decomposition of DMF. To the best of our knowledge, compound 7 represents the first example of a MOM constructed using this ligand (CSD update: February 2010).

![Figure 3.10](image)

**Figure 3.10.** A general reaction mechanism for the direct synthesis of amides via a condensation reaction between a carboxylic acid and an amine.⁶⁵

Each indium metal ion in the crystal structure of 7 is surrounded by four independent 5-AmBDC ligands, which coordinate to each In(III) cation through the carboxylato groups in a bidentate fashion. A 4-connected In(RCO₂)₄ MBB is thereby revealed having In−O distances in the range of 2.141 Å to 2.562 Å (Figure 3.11a.). The O−In−O angles are in the range of 83.084° to 165.769°, which significantly deviate from an ideal tetrahedral arrangement. Thus, each In(III) metal ion is said to adopt a distorted tetrahedral configuration. Each independent angular 5-AmBDC ligand bridges two In(III) centers and thus the assembly of the 4-connected nodes results in the generation of 4-membered windows to give an overall sql topology. A square nSBU consisting of four vertex-linked tetrahedral building units is thereby obtained.
Figure 3.11. X-ray crystal structure of 7: (a) In(RCO2)₄ MBB which can be viewed as a 4-connected node; (b) Ball-and-stick representation of the tetragonal sheets which pack in an ABAB fashion down the z-axis; and (c) The layers interact via offset face-to-face π-π interactions through the phenyl rings of 5-AmBDC. Color Code: C = gray; O = red; N = blue; hydrogen = white; and In = green. The channels are represented by the undulating yellow columns.

The 1,3-alternate conformation is the only isomer observed in 7 and therefore the four dicarboxylate ligands orient in an alternating fashion. The anionic layers propagate in the xy-plane and stack in an ABAB fashion along the z-axis with an interlayer separation of approximately 6.660 Å. The rectangular-shaped channels have an estimated diameter of 6.110 Å. Non-covalent intermolecular interactions govern the overall packing arrangement of the layers. These include offset face-to-face π-π interactions and hydrogen bonding interactions. In the case of the former, the two opposing metal carboxylate groups in the inorganic MBB are facing downward while these groups in the subsequent layers are directed upward. An offset face-to-face π-π interaction occurs
between neighboring phenyl moieties and an N-H…O hydrogen bonding interaction (2.006 Å) is observed between the amide functionality of one layer and a carbonyl oxygen atom of the next layer. Disordered DMF solvent molecules reside between the layers, as well as, DMA+ for charge balance.

3.1.3. Experimental Section

3.1.3.1. Materials and Methods

All materials and methods are described in Chapter 2, unless otherwise noted. The H4-ImTC ligand was prepared by Mohamed Alkordi.

3.1.3.2. Synthesis and Characterization

**Synthesis of [Cu2(5-NH2BDC)2(H2O)2]n, (6).** A solution of Cu(NO3)2·2.5H2O (23.3mg, 0.10mmol), 5-aminoisophthalic acid (5-NH2BDC) (36.2mg, 0.20mmol), DMF (0.5mL), CH3CN (1mL), triethylamine (0.2mL, 1M in DMF), and HNO3 (0.2mL, 3.5M in DMF) was prepared in a 20 mL scintillation vial. The solution was heated to 85°C for 12 hours followed by additional heating to 105°C for 23 hours to afford homogenous green hexagonal crystals. Homogenous green crystals of 6 were harvested and air-dried. The as-synthesized material was determined to be insoluble in H2O and common organic solvents.

**Synthesis of [In(5-AmBDC)2·(DMA)(DMF)]n, (7).** A solution of In(NO3)2·6H2O (69.1mg, 0.23mmol), 5-NH2BDC (41.7mg, 0.23mmol), DMF (1mL), H2O (1mL) and HNO3 (0.3mL, 3.5M in DMF) was prepared in a 20 mL scintillation vial. The solution was heated to 85°C for 12 hours followed by additional heating to 105°C for
23 hours and 115°C for 23h hours, after which colorless block shape crystals were obtained. Crystals of 7 were harvested and air-dried. The as-synthesized material was determined to be insoluble in H₂O and common organic solvents; however, the crystals do degrade upon exposure to aqueous media.

3.2. From 2-Periodic Layers to 3-Periodic Frameworks: Pillaring as a Design Strategy

3.2.1. Introduction

The previous section highlighted the significance, complexity, and structural diversity of 2-periodic architectures. This information provides a solid foundation for the transition into and development of a specific class of 3-periodic MOMs regarded as pillared frameworks. It is important to note that layered structures possess interesting properties and are useful for many applications as note above; however, their inability to enclose space often limits their development in a wide range of porosity related applications. A logical approach to circumvent this shortcoming is to merge the attractive features of 2- and 3-periodic frameworks into one class of material; that is, to bridge the layers through judiciously chosen organic MBBs (e.g. pillars) to form fine-tunable cavities and/or channel systems that have the potential to adsorb gases and/or organic molecules.

The diverse topologies adopted by layered structures lead to fundamental changes in pore size and shape, as exemplified by supramolecular isomerism whereby more than one superstructure can be isolated from the same MBBs (e.g. nanoball, kgm, and sql structures). Moreover, each topological class represents a modular platform where the metal cation or organic component(s) can be readily varied to give charged or neutral
isostructural or isoreticular analogs, respectively. These types of platforms are urgently needed in order to systematically evaluate the effect of each parameter on gas-MOF interactions.

Thousands of layered structures have been documented as a result of both serendipitous discoveries and rational design strategies (e.g. MBB approach). We have therefore instituted a plan which specifically targets 3-periodic MOMs whose layers are based upon the \textit{sqi} and \textit{kgm} topologies. The reason was twofold: (1) the fundamental differences in pore shape and size and (2) predictability because these nets are proven to be readily constructed from a wide range of different chemical components. The pillaring approach provides a unique pathway to incorporate these desired features into 3-periodic frameworks. Gas sorption studies could then be conducted in a systematic fashion using a series of modular microporous MOM platforms to independently discern the impact of pore size/shape, chemical functionality, and charge.

3.2.1.1. Pillaring Strategy: Design Principles

Layered structures can in principle be pillared into 3-periodic MOMs via the inorganic or organic building blocks by choosing pre-designed spacer/pillar moieties that can fulfill geometrical (\textit{e.g.} size, angles, \textit{etc}) criteria and at the same time adhere to the coordination environment around the metal center. There are at least three ways to pillar layers, which are categorized based on the location of the pillar in the layer: (1) axial-to-axial; (2) axial-to-ligand; and (3) ligand-to-ligand (Figure 3.12.). The dimetal tetracarboxylate “paddlewheel” MBB is well suited for all three types of pillaring
because it commonly forms layered structures when reacted with ditopic carboxylate-based organic molecules.

![Diagram of pillared layers](image)

**Figure 3.12.** Schematic representation to illustrate the three possible design strategies to pillar 2D layers into 3D frameworks: the purple, blue, and yellow pillars independently represent the axial-to-axial, axial-to-ligand, and ligand-to-ligand strategies, respectively.

Linear bipyridyl-based organic moieties are ideally suited to connect collimated layers via the axial-to-axial positions on the paddlewheel MBB (Figure 3.13.).\textsuperscript{66-74} This form of pillaring can take place *in situ* by combining all necessary chemical components in a one-pot reaction or by using a post-synthetic approach whereby the layers are first synthesized and subsequently pillared.
Figure 3.13. Select examples of bipyridyl-based organic ligands (left to right): pyrazine; 1,4-diazabicyclo[2.2.2.]octane; 4,4'-bipyridine; 1,2-di(pyridine-4-yl)ethane-1,2-diol; and N,N'-di(4-pyridyl)1,4,5,8-naphthalenetetracarboxyldiimide.

Axial-to-ligand pillaring on the hand is regarded as a hybrid method because the eclipsed layers are covalently cross-linked by judiciously chosen bifunctional organic moieties. One type of functional group forms the necessary metal cluster and thus bridges the clusters to form the infinite layer, such as a decorated isophtalate unit. The role of the other functionality (e.g. pyridyl-type) is to pillar the layers via the 5-position of the isophtalate unit to the axial position of the metal cluster in the neighboring layer (Figure 3.14.). Eddaoudi and co-workers have demonstrated the versatility and predictability of this approach by pillaring sql and kgm lattices using 5-(4-pyridinylmethoxy)-isophtalate (PMOI). To the best of our knowledge, this design strategy has not previously been observed in the literature.⁷⁵
The pillared structures described herein are of the ligand-to-ligand type. The layers are therefore fused together in an eclipsed fashion through a functionalized tetracarboxylate organic bridge. There are several examples of highly porous MOFs constructed using this approach. The type of tetracarboxylate pillar employed, whether it be rigid, flexible, or bulky in nature can lead to structural diversity as a direct consequence of ligand design.

3.2.2. Results and Discussion

The ligand-to-ligand pillaring method was used to design and synthesize a diverse collection of open 3-periodic architectures, whose layers are based upon the kgm and sql lattices. The tetracarboxylate organic ligands (e.g. the pillars) employed in these studies are shown in Figure 3.15.
Figure 3.15. Tetracarboxylate organic ligands utilized for the ligand-to-ligand pillaring strategy: (left) H₄-ABTC; (middle) H₄-BIPATC; and (right) H₄-BAYTC.

The rational assembly of open 3-periodic MOMs based upon the aforementioned lattices generates several platforms that possess various pore sizes and shapes, due to their connectivity and relative scale and functionality of the pillars. These platforms therefore (in theory) provide a systematic pathway to attain high surface area materials whereby the effect of metal cation, pore size and shape, and ligand functionality can be evaluated with respect to the gas adsorption properties (e.g. uptake capacity and Qst). A major obstacle however which impeded these studies was improper sample activation and therefore obtaining the expected results proved to be very challenging, as will be discussed below.

3.2.2.1. Isoreticular MOFs with nbo Topology: Pillared Kagomé Layers

The solvothermal reaction of H₄-ABTC and Cu(NO₃)₂·2.5H₂O, Zn(NO₃)₂·6H₂O, or MnCl₂ in separate vials containing solutions of DMF/CH₃CN/IMI, DEF/CH₃CN, and DMF/CH₃CN/HMTA, respectively generates crystalline material in high yield. The as-synthesized compounds were characterized by SCD studies and determined to be
isostructural frameworks (Appendix A). The following structural description will only pertain to the copper analogue which was formulated as \([\text{Cu}_2(\text{ABTC})(\text{H}_2\text{O})_2]_n\), (8).

The crystal structure of 8 is built-up from dicoppertetracarboxylate MBBs by bridging two Cu(II) cations with four deprotonated carboxylate moieties from the ABTC ligand to reveal a \([\text{Cu}_2(\text{RCO}_2)_4(\text{H}_2\text{O})_2]\) paddlewheel configuration (\(d_{\text{Cu}-\text{Cu}}=2.675\) Å). Each Cu(II) cation adopts a square pyramidal coordination environment. The equatorial plane is defined four oxygen atoms from four independent ABTC\(^{4+}\) ligands, which coordinate through the carboxylato groups in a bis-monodentate fashion (\(d_{\text{Cu}-\text{O}}=1.927, 1.927, 1.915, 1.915\) Å). The axial position is occupied by an aqua ligand (\(d_{\text{Cu}-\text{O}}=2.155\) Å). Each ABTC\(^{4+}\) ligand is linked to four paddlewheel MBBs and vice versa; therefore both the inorganic and organic MBBs can be reduced to 4-connected nodes. Augmentation of the aforementioned nodes reveals square and rectangular-planar building units, respectively. A topological assessment was performed using the TOPOS software\(^{82}\) and the vertex symbol and coordination sequence were calculated to be \([6(2).6(2).6(2).6(2).8(2).8(2)]\) and 4, 12, 28, 50, 76, 110, 148, 194, 244, and 302, respectively. This confirms that the 4-connected 3-periodic framework possesses \text{nb}0 topology.

The topology of 8 can be delineated as a neutral 3-periodic pillared MOM constructed from 2-periodic layers that are connected by covalently cross-linked ABTC\(^{4+}\) pillars. A space-filling representation of 8 viewed along the \(x\)-axis illustrates this concept (Figure 3.16.). The undulating layers propagate along the \(xy\)-plane and are pillared diagonally to neighboring layers through ABTC\(^{4+}\) via the 5-position of the diisophthalate units. A select fragment of the layer reveals it has the same connectivity as the (3.6.3.6)
Kagomé lattice. The pillared Kagomé network, 8, is constructed from the self-assembly of alternating bowl-shaped triangular cavities having a “cone” confirmation, [Cu$_2$(ABTC)(H$_2$O)$_2$]$_3$. Hexagonal channels having a 1,3,5-alternate conformation are thereby revealed (Figure 3.16c.). The relative diameters of the metalla[3]calix and metalla[6]calix are predetermined by the geometry of the paddlewheel MBB and the distance between the carboxylato moieties on the BDC unit and therefore have an estimated diameter of 3.387 Å and 7.606 Å, respectively.

Figure 3.16. Space-filled views from the x-ray crystal structure of 8: (a) Viewed along the x-axis to highlight the undulating 2-D layers (shown in black); (b) Select fragment of one Kagomé layer which propagates in the xy-plane (the triangular and hexagonal cavities are highlighted with black circles); (c) Layers are pillared along the z-axis; (d) Two metal-organic calixarene-like conformations observed in 1: cone and 1,3,5-alternate. Color Code: C = gray; O = red; N = blue; hydrogen = white; and Cu = green. All solvent molecules and axial aqua ligands are removed for clarity, as well as, hydrogen atoms in figures (a) and (c).
The centroids of the diisophthalate benzene ring were chosen as the points of extension to reveal a square SBU. Triangular \( n \)SBUs are obtained by linking three square SBUs at their vertices. These nanosized triangles then self-assemble at their vertices to create a 2D Kagomé lattice with infinite undulating layers (Figure 3.17.).

Figure 3.17. Schematic representation of the arrangement of the \( n \)SBUs in the 2D Kagomé layer: (top) Triangle bowl-shaped \( n \)SBU are formed by the assembly of three vertex-linked molecular squares, which are formed by linking together the centroids of the BDC units; (bottom) the natural curvature of the BDC ligand leads to the formation of undulating layers.

The Kagomé layers can be covalently pillared into 3-periodic frameworks in two ways: (1) pillaring a triangle to a triangle and a hexagon to a hexagon (e.g. AAA face-to-face packing); or (2) pillaring a triangle to a hexagon (e.g. ABAB offset face-to-face packing). The former arrangement requires that the ligand have some degree of flexibility because the BDC units would be directed out of plane. Ligand flexibility is not required in the latter case and therefore a planar rigid ligand is well suited to facilitate this geometrical conformation. In the crystal structure of 8, the layers are connected through a triangle-to-hexagon conformation. Layer A is covalently cross-linked to layer B through three \( \text{ABTC}^{4-} \) ligands in the following way: three BDC moieties of the cone triangular
building block in layer A are directed downward to three BDC moieties directed upward in the 1,3,5-alternate hexagon in layer B. Layer A and B are thus connected via the 5-position of the BDC moiety through the azo moiety.

The pillared layers generate two types of cages with stoichiometries of \([\text{Cu}_{12}(\text{ABTC})_{12}]\) and \([\text{Cu}_{24}(\text{ABTC})_{6}]\), denoted as cage I and II, respectively (Figure 3.18). The dimensions of each cage are proportional to the relative size \(\text{ABTC}^{4-}\). Cage I is sphere-like in shape and is assembled from six paddlewheel MBBs and twelve ligands, while cage II is elongated and comprises twelve paddlewheel MBBs and six ligands.

**Figure 3.18.** Two types of cages whose dimensions are predetermined by the relative size of the \(\text{ABTC}^{4-}\) ligand: (a) Spheroid-like cage, \([\text{Cu}_{12}(\text{ABTC})_{12}]\); (b) Elongated cylindrical-like cage, \([\text{Cu}_{24}(\text{ABTC})_{6}]\); (c) Schematic nSBU representation of the spheroid cavity; (d) The elongated cavity (highlighted in blue) results from the packing arrangement of the spheroid-like cavity. Color Code: C = gray; O = red; N = blue; hydrogen = white; and Cu = green.
The cages are delimited by two types of intersecting windows defined as A and B. The overall shape can be correlated with the connections between adjacent paddlewheel MBBs. This thereby reveals an overall triangular arrangement. The estimated size of the internal cavity in cage I is 9.522 Å and it has 8 windows which lead to its interior, two of which are TYPE A and 6 are TYPE B. The former window is defined by the cone arrangement (equilateral triangle) and thus the dimensions (~3.387 Å) are not dependent on the length of ABTC$^4$. On the other hand, type B is defined by isosceles triangles whereby the two equivalent edges represent the ligand and the third edge is occupied by one BDC moiety. Thus, the window dimension is predetermined by the length of ABTC$^4$. The Cu····Cu separation between adjacent paddlewheel MBBs is 6.457 Å, while the estimated diameter of the window is 7.397 Å. The eight triangular windows described herein are shared between cage B, which passes through three layers. The internal cavity of this cage is estimated to be 11.891 Å and the vertical distance of measures approximately 22.633 Å.

Isoreticular MOMs can be generated in a similar manner using elongated pillars to yield non-interpenetrated networks with nanoscopic cages. It is noteworthy to mention that nbo is a dual net (i.e. bcu) and thus interpenetration is possible. The structure described above however, 8, does not favor interpenetration because the effective diameter of the regular triangular window is too small to allow the penetration of a pillar(s). It is possible however for an organic spacer to penetrate the isosceles windows but the ligand would have to be quite long and this could be avoided by functionalizing the pillar with bulky substituents.
3.2.2.2. Enroute to Larger Functionalized Cavities and Higher Surface Area: 
Pillared Kagomé Lattices from Expanded Tetracarboxylate Ligands

The organic pillars described in this section are two polyphenyl tetracarboxylate 
ligands of varying length and functionality, i.e. H₄-BAYTC and H₄-BIPATC. The 
resultant MOMs therefore has the same number of potential unsaturated metal centers but 
the size and functionality of the pillar would directly affect the pore size and shape. A 
systematic gas sorption study could then, in theory, be conducted to evaluate the effect of 
pore structure and metal cation on the uptake capacity and gas-MOF interactions.

Solvothermal reaction between H₄-BAYTC and Cu(NO₃)₂·2.5H₂O in a mildly 
acetic solution consisting of DMF and chlorobenzene in the presence of 
tetrabutylammonium bromide (TBABr) yields blue-green microcrystalline material with 
parallelepiped morphology. The as-synthesized compound, which is insoluble in H₂O and 
common organic solvents, was characterized and formulated by single-crystal X-ray 
diffraction studies as \{[Cu₂(BAYTC)(H₂O)₂]\}ₙ, (11). Compound 11 crystallizes in the 
rhombohedral R-3m space group with a = 15.527(3) Å, b = 18.527(3) Å, c = 54.221(1) Å 
and a unit cell volume of 16117(5) Å³. The crystal structure has a framework comprised 
of the same inorganic MBBs as compound 8, i.e. the paddlewheel MBB (d_{Cu1-Cu1}=2.659 
Å). A topological evaluation confirmed that 11 exhibits the same nbo network topology 
as compounds 8-10 but the structures differ with respect to the pore sizes because of the 
length of the pillars. Similarly, the undulating Kagomé layer propagates in the xy-plane 
and its windows are unaffected by the length of the organic ligand (Figure 3.19.).
The two cages generated from pillaring the layers with BAYTC$^{+}$ have the same metal-to-ligand ratio as observed in 8, [Cu$_{12}$(BAYTC)$_{12}$] and [Cu$_{24}$(BAYTC)$_{6}$] for cage I and II, respectively (Figure 3.20.). The relative span of BAYTC$^{+}$ (16.430 Å) *versus* ABTC$^{+}$ (9.283 Å) leads to the generation of much larger cavities.
Cage I in 11 can accommodate a van der Waals sphere with an estimated diameter of 12.974 Å. In both structures the size of the intersecting triangular windows (TYPE A) are roughly the same in both structures. The isosceles window (TYPE B), which can be viewed along the x- or y-axis, has an estimated edge and length that span 6.697 Å and 13.030 Å, respectively. The increased length of the pillar makes cage II to be much more elongated with a distance from the top layer to the third layer of ~38.312 Å. It can however only accommodate a van der Waals sphere with a diameter of ~9.833 Å because of the bottle-neck shape.

The inherent modularity of the MBB approach also facilitates fine-tuning of the interior cavities and windows through the use of judiciously chosen pillars with desired built-in functionality. These parameters can then be modified by employing functionalized organic ligands whose substituents range from bulky to small, electron-donating to electron-withdrawing, etc. The H₄-BIPATC pillar is well suited for this purpose, i.e. to link the Kagomé because it is comprised of a naphthalene moiety that is decorated with four oxygen atoms. Reaction of H₄-BIPATC with Cu(NO₃)₃·2.5H₂O in a mildly acidic solution consisting of DMF and chlorobenzene indeed results in the formation of blue-green microcrystalline material having a polyhedral morphology. The as-synthesized material was characterized using single-crystal X-ray diffraction studies and formulated as \{[Cu₂(BIPATC)(H₂O)₂]\}, (12). The crystal structure of 12 features a 3-periodic pillared Kagomé network consisting of infinite Kagomé layers \{[Cu₂(R-BDC)₂(L)₂]₃ \}_n that are covalently cross-linked through BIPATC⁺.

The coordination environment is identical to that observed in 8-11 but one paddlewheel MBBs has a terminal aqua ligand located in the axial positions (d_{Cu-O} =
2.165, 2.274 Å), while the apical sites on the second MBB are occupied by a DMF molecule (dCu-O = 2.171 Å). There are two crystallographically independent BIPATC$_4^+$ ligands: one type coordinates to four aqua paddlewheel MBBs and the other coordinates to both an aqua and DMF paddlewheel MBB in a trans fashion. The 1,3-BDC moieties remain coplanar but steric hindrance between neighboring hydrogen atoms causes the naphthalene-based moiety to twist perpendicular to the plane having an estimated dihedral angle of 82.2° and 72.9° (Figure 3.21.).

![Figure 3.21. Crystal structure of 12: (top) Each BIPATC$^+$ coordinates to four paddlewheel MBBs and the naphthalene-based moiety twists out of plane; (bottom) Space-filling view down the y-axis. Color Code: C = gray; O = red; N = blue; and Cu = green.](image)

The dimensions of the cages and windows are directly affected by the conformation of BIPATC$^+$. Accordingly, the spheroid-like cage has a larger interior cavity as compared to the previous compounds and thus can accommodate a van der Waals sphere with an estimated diameter of 15.164 Å. Access to the interior is only permitted through the isosceles windows and the dimensions are significantly reduced as
compared to compound 8 and 11 because the naphthalene moiety is in the plane of the window. The length and width of the small window apertures are 12.250 Å and 3.94 Å, respectively. The elongated cavity has a vertical distance of ~36.432 Å and it largest diameter can fit a van der Waals sphere of ~11.838 Å (Figure 3.22.).

![Figure 3.22. Two types of cages in 12: (left) Spheroid-like cage, [Cu_{12}(BIPATC)_{12}]; and (right) Elongated cylindrical-like cage, [Cu_{24}(BIPATC)_{6}]. Color Code: C = gray; O = red; and Cu = green.]

3.2.2.3. Pillared Tetragonal Square Grid Networks

The reaction of H$_4$-BIPATC with Cu(NO$_3$)$_2$·2.5H$_2$O in a DMA/H$_2$O solution with a minimal amount of pyridine generates homogenous microcrystalline material in high yield. The parallelepiped shaped crystals were characterized and formulated by single-crystal X-ray diffraction studies as \([\{\text{Cu}_5(\text{BIPATC})(\text{DMA})_2\}\cdot n\text{H}_2\text{O}:x\text{solvent}\] (13). The purity of 13 was confirmed by similarities between the calculated and experimental X-ray powder diffraction (XRPD) patterns (Appendix B). The crystal structure of 13 reveals a 3-periodic framework consisting of pillared tetragonal square grid layers. The layers are built-up from dinuclear paddlewheel MBBs consisting of two copper ions bridged through four deprotonated carboxylato groups of the diisophthalate units in the
BIPATC ligand, \([\text{Cu}_2(\text{RCO}_2)_4(\text{DMA})_2]_n\) \((d_{\text{Cu-Cu}} = 2.665 \text{ Å})\). The BDC-linked moieties adopt the “1,2-D” configuration whereby two adjacent meta-carboxyl groups are directed downward and thus the square grid layer adopts the 1,2-alternate conformation. The SBUs do not assemble to form a cone-shaped square nSBU due to pronounced twisting of the adjacent moieties (Figure 3.23.). Two opposing molecular squares lie in the same plane while the adjacent molecular squares are directed upward and downward, respectively to form \([\text{Cu}_2(m-\text{BDC})_4]_4\).

**Figure 3.23.** (left) “1,2-D” configuration associated with the BDC-linked SBU in 13, which can be interpreted as a square building unit by choosing the centroids of the benzene ring as the points of extension; (right) A cluster of four squares vertex-linked at 120° through 1,3-BDC reveals nanoscale square nSBUs. Color Code: C = gray; O = red; and Cu = green.

The nanosized square nSBUs in turn self-assemble at their vertices into a corrugated square grid lattice that propagates in the \(xz\)-plane and is pillared along the \(y\)-axis through BIPATC\(^{4+}\) to give a 3-periodic framework with intersection channels (Figure 3.24.). The geometrical conformation of the nSBUs facilitates the formation of an infinite intersecting channel system. These channels are decorated with naphthalene moieties (dihedral angle: 86.13°) and thus the dimensions are reduced as compared to a coplanar polyphenyl backbone. When viewed down the \(y\)-axis it resembles a zigzag channel because the “1,2-D” conformation in one layer is connected with the opposing layer which is directed upward and vice versa.
The effective dimensions of the grids have an edge length of 6.574 Å and diagonal length of 12.407 Å. The grids are covalently cross-linked by BIPATC$^+$ with an interlayer separation which corresponds to the relative scale of the pillar, ~15.537 Å. From a topological perspective, the coordination sequence and vertex symbol of the 4-connected node was determined to be 4, 10, 24, 44, 72, 104, 144, 188, 240, 296 and [4.4.(8)4.8(8).8(8)], respectively which corresponds to the lvt network topology. Space-filling views of 13 (Figure 3.25.) highlight the intersecting channel system. To the best of our knowledge, no tetracarboxylate pillared structures having lvt have been reported in the literature.
3.2.2.4. Potential Gas Storage Applications

Compounds 8-13 represent three modular platforms which, in principle, can be used to systematically assess adsorbate-MOF interactions by varying specific structural components. They can be categorized and used to evaluate the effect of the following parameters: (1) Metal cation (Cu, Zn, and Mn) in an isostructural \textit{nbo} series of MOMs constructed from ABTC pillars; (2) Pore size and functionality by varying the pillar (ABTC vs. BAYTC vs. BIPATC) in an isoreticular series of MOMs having \textit{nbo} topology; (3) Pore shape and size between two MOMs having \textit{nbo} (triangular windows and cages) and \textit{lvt} (rectangular-shaped channels) topology. Unfortunately, sample activation proved to be very challenging for all compounds due either to framework collapse or improper solvent system.
Indeed, the effect of metal cation could not be evaluated because 9 and 10 collapse upon removal of the solvent molecules. This was confirmed by PXRD patterns because no peaks were observed, as is characteristic of an amorphous material. Framework collapse is commonly observed for porous MOMs constructed from paddlewheel building blocks comprised with transition metals other than copper. A possible explanation for this observation is instability of the inorganic MBB upon removal of the axial ligands for metals which do not undergo a Jahn-Teller distortion.

The copper analogue, 8, was exchanged in acetone for 36 hours and evacuated at 100°C for 12 hours. The solvent-accessible volume for 8 was determined to be 70.9% and the apparent BET and Langmuir surface areas were for 8 determined to be 882 m²/g and 1239 m²/g, respectively (Figure 3.26a.). These values are significantly lower than anticipated because the calculated surface area is estimated to be 3004 m²/g. The H₂ uptake capacity at 723 torr and 77 K was found to be 1.41 wt% (Figure 3.27b.). The isosteric heat of adsorption at low loading begins at approximately 6.8 kJ mol⁻¹ and decreases slightly at higher loading to ~5 kJ mol⁻¹.
Two other research groups independently published the same structure, 8, at about the same time. They used different solvent activation procedures which resulted in higher surface area values. Zhou and co-workers reported apparent BET and Langmuir surface area values of 1407 m$^2$/g and 1779 m$^2$/g using a combined methanol and DCM exchange protocol. $^{80}$ Suh and co-workers heated the hydrated sample of 8 to 170$^\circ$C to remove the axial aqua ligands and obtained an apparent Langmuir surface area of 2850 m$^2$/g. $^{78}$ Suh et al. noted that they could not reproduce the sorption data published by Zhou et al. These reports further support the importance of proper sample activation and reproducibility in order to obtain reliable sorption data.

The effect of pore size and functionality could in principle be addressed in compounds 8, 11, and 12 which are constructed from the dicopper paddlewheel MBBs but with different pillars – ABTC$^{4-}$, BAYTC$^{4-}$, and BIPATC$^{4-}$, respectively. Compound 12 unfortunately could not be activated and consequently a tentative comparison can only be made between 8 and 11. Table 3.1., provides a summary of the cage dimensions and
window apertures for compounds 8-12. The incorporation of a longer organic ligand is a logical design strategy to obtain MOMs with higher surface areas and larger pore volumes.

**Table 3.1.** Comparison of the cages and window dimensions between compounds 8, 11, and 12 having nbo topology.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cage Dimensions (Å)</th>
<th>Window Dimensionsd (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Type I^a</td>
<td>Type II^bc</td>
</tr>
<tr>
<td>8; [Cu2(ABTC)]</td>
<td>9.522</td>
<td>11.891; 22.633</td>
</tr>
<tr>
<td>11; [Cu2(BAYTC)]</td>
<td>12.974</td>
<td>9.833; 38.312</td>
</tr>
<tr>
<td>12; [Cu2(BIPATC)]</td>
<td>15.164</td>
<td>11.838; 36.432</td>
</tr>
</tbody>
</table>

^a^ The largest van der Waals sphere that can fit inside the spheriod-shape cage; ^b^ The largest van der Waals sphere that can fit inside the elongated cage; ^c^ The vertical length of the Type II cage; ^d^ Aperture dimensions of the isosceles windows shared between cage types I and II.

The cage and window dimensions of 8, 11, and 12 correlate with the length and functionality of the organic ligands. As expected, 8, has the smallest cages and windows and 11 and 12 are comparable in size. The window dimensions in 12 are significantly reduced due to twisting of the naphthalene moiety. The steric conformation of 12 accommodates a larger van der Waals sphere in cage I and decorates the interior cavity of cage II which can be advantageous in terms of increasing gas-MOF interactions.

The large solvent-accessible volume for 11 (78.5%) was determined by summing voxels more than 1.2 Å away from the framework using PLATON software. The estimated BET and Langmuir surface areas determined from the N2 sorption were 2055 m²/g and 2499 m²/g, respectively. The H2 uptake capacity was determined to be 1.71 wt % at 722 torr and 77 K, Figure 3.27. Compound 11 has a larger pore volume than 8; therefore, it is expected to adsorb more H2, particularly at high pressure.
Figure 3.27. Sorption data for 11: (a) Nitrogen sorption isotherm at 77 K; and (b) Hydrogen sorption isotherm at 77 K.

A summary of the sorption data collected on 8 and 11 is provided in Table 3.2. A comparison between the experimental and calculated surface area values implies further studies are needed to optimize the porosity of these materials. Ongoing studies are exploring alternative solvent activation methods such as the use of supercritical CO2 activation.

Table 3.2. Sorption data for compounds 8, 11, and 12.

<table>
<thead>
<tr>
<th>Cpd</th>
<th>F. V. a (%)</th>
<th>Simulated S.A. b (m²/g)</th>
<th>Experimental S. A. (m²/g)</th>
<th>H₂ Uptake (%) c</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>70.9</td>
<td>3004</td>
<td>882</td>
<td>1239</td>
</tr>
<tr>
<td>11</td>
<td>78.5</td>
<td>4991</td>
<td>2055</td>
<td>2499</td>
</tr>
<tr>
<td>12</td>
<td>69.2</td>
<td>3124</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
</tbody>
</table>

| 8   | 70.9        | 3004                     | 882                        | 1239            | 1.41 |
| 11  | 78.5        | 4991                     | 2055                       | 2499            | 1.71 |
| 12  | 69.2        | 3124                     | N.A.                       | N.A.            |     |

a Estimated solvent-accessible free volume calculated using PLATON software; b calculated accessible surface area determined using the Cygwin software package; c H₂ uptake at 722 torr; N.A. refers to not applicable due to sample activation problems.

Sample activation issues encountered with compound 12 impeded the studies of the effect of pore shape (lvt versus nbo topologies) on gas-MOF interactions. However,
preliminary sorption studies were carried out on the pillared square grid structure, 13, with a solvent-accessible volume of 64.4%. The as-synthesized sample was exchanged in a variety of volatile solvents such as CH₃CN, CH₃Cl, DCM, THF, and (CH₃)₃CO but none were effective, as shown by the low surface area values (e.g. below 500 m²/g). We decided to take a different approach and exchange the crystals in a bulkier solvent having a moderate boiling point. The as-synthesized sample was exchanged in chlorobenzene for 4 days and evacuated at 110°C for 12h. The resultant sorption data did show an improvement over the other solvent systems. The argon sorption isotherm for 13 was a fully reversible type I isotherm, characteristic of microporous materials. The estimated BET and Langmuir surface areas are 1052 m²/g and 1308 m²/g, respectively, which is appreciably lower than the calculated surface area of 2621 m²/g. The H₂ uptake capacity of 13 was found to be as much as 1.73 wt % at 77 K and 722 Torr. The isosteric heat of adsorption is very similar to that observed in 8. At low loading the enthalpy of adsorption is 6.60 kJ mol⁻¹ and it decreases slightly to 5.76 kJ mol⁻¹ at higher loadings of H₂ (Figure 3.28.).
While compound 13 possesses larger cages than 8; however, the increased functionality of the BIPATC ligand facilitates stronger gas-MOF interactions which results in a trade off with respect to Qst. The enthalpy of adsorption was thereby maintained despite the fact the dimensions of the cages were increased. Figure 3.29d. depicts the CO$_2$ sorption isotherms measured at 0°C and 25°C, respectively. The full reversibility of these isotherms further supports the microporosity of the material, as
outlined by the Type I isotherm. The saturation capacity is reached at relatively low pressures (~ 4 atm) which can be attributed to the narrow pore size. The maximum amount of CO₂ stored in 13 is 31.3 wt% and 27.1 wt% at 0°C and 25°C, respectively. These values are comparable to some of the best performing zeolites, yet lower than some of the recorder holder MOMs. The shape of the sorption isotherm is influenced by many factors, one of which is functional groups. Accordingly, we may speculate that the interesting structural features in 13, namely narrow pores and carbonyl moieties promote favorable CO₂-MOF interactions. This hypothesis is supported by the relatively steep rise in the isotherm at low loading.

3.2.2.5. Lanthanide-Based lvt-MOMs

The 15 elements from lanthanum to lutetium are termed lanthanides and constitute the f-block group of metals. Rare earth metals have received less attention than the transition and main group elements for the design of MOMs. The main reason for this is their cost and the lack of control over the coordination number and geometry about the metal center. Lanthanides possess unique spectroscopic properties and thus MOMs constructed from such metals have the potential to be used in a variety of sensing and related applications. MOMs are commonly constructed from transition metal cations with coordination numbers ranging from 2 to 6 and in some cases up to 8 (e.g. Cadmium) has been reported. Rare earth metals have larger atomic radii and so higher coordination numbers are possible. They are therefore ideally suited to target nets where the vertex figure presents the need for higher connectivity.
Lanthanides ions are hard acids and have a high affinity for hard donor ligands containing oxygen or hybrid oxygen-nitrogen atoms. It is therefore important for the ligand to have an adequate number of donor atoms. Otherwise the coordination sphere will become saturated with solvent molecules. This could be considered as an advantage or a limitation: the coordinated solvent molecules could potentially be removed to expose open metal centers but the inorganic MBB may become unstable upon removal of the ancillary ligands and cause the framework to collapse. H$_4$-ABTC was reacted as part of this project with an assortment of lanthanides metal salts such as erbium, ytterbium, cerium, europium, and terbium using a diverse set of reaction conditions. The objective was to isolate robust 3-periodic MOFs having a high degree of potential coordinately unsaturated metal sites for gas storage studies.

Solvothermal reaction between H$_4$-ABTC and Yb(NO$_3$)$_3$·5H$_2$O in a mildly acidic solution of DMF/CH$_3$CN with a minimal amount of piperazine (PIP) generates yellow homogenous microcrystalline material. Microcrystalline material was also isolated under similar reaction conditions from the reaction of H$_4$-ABTC with Er(NO$_3$)$_3$·5H$_2$O from a solution containing DMF/CH$_3$Cl/PIP. The as-synthesized materials, which were determined to be insoluble in H$_2$O and common organic solvents, and were characterized and formulated by SCD studies as $\{[\text{Yb}_2(\text{ABTC})(\text{NO}_3)_2(\text{DMF})_4]\}_n$ (14) and $\{[\text{Er}_2(\text{ABTC})(\text{NO}_3)_2(\text{DMF})_4]\}_n$ (15), respectively. Compounds 14 and 15 were determined to be isostructural frameworks based on similar unit cell parameters (Appendix A). The crystal structure of 14 reveals a 3-periodic framework built-up from dinuclear ytterbium MBBs consisting of two crystallographically equivalent ytterbium
ions bridged through two deprotonated carboxylato ABTC moieties ($d_{Yb-Yb} = 5.180 \, \text{Å}$), see Figure 3.29.

**Figure 3.29.** Select fragments from the X-ray crystal structure of 14: (left) 4-connected inorganic MBB, $[\text{Yb}_2(\text{ABTC})(\text{NO}_3)_2(\text{DMF})_4]_n$; and (right) Each ABTC$^{4+}$ ligand is connected to four inorganic MBBs. C = gray; O = red; N = blue; and Yb = green. All hydrogen atoms are omitted for clarity.

Each trivalent ytterbium ion is 8-coordinate and is bound to four carboxylato atoms: one ABTC$^{4+}$ ligand coordinates in a bidentate fashion ($d_{Yb-O} = 2.383 \, \text{Å}, 2.326 \, \text{Å}$) and two ABTC$^{4+}$ ligands are bridged between the metals in a bis-monodentate fashion ($d_{Yb-O} = 2.181 \, \text{Å}, 2.215 \, \text{Å}$). The remainder of the coordination sphere is occupied by two oxygen atoms from two DMF molecules ($d_{Yb-O} = 2.259 \, \text{Å}, 2.249 \, \text{Å}$) and two bidentate oxygen atoms from a nitrate ion ($d_{Yb-O} = 2.417 \, \text{Å}, 2.374 \, \text{Å}$). The inorganic metal cluster is linked to four ABTC$^{4+}$ ligands and *vice versa*. The assembly of these two 4-connected nodes results in the generation of a cationic MOM with lvt topology. The charge balanced is provided by the coordinated nitrate ($\text{NO}_3^-$) ions. The inorganic MBBs form a chain-like arrangement and propagate in the $xz$-plane. This unit is pillared along the $y$-axis through ABTC$^{4+}$ to afford a 3-periodic MOM with rectangular-shaped intersecting channels (Figure 3.30.).
Figure 3.30. Select fragments from the X-ray crystal structure of 14: (left) 4-connected inorganic MBB, [Yb2(ABTC)(NO3)2(DMF)4]n; and (right) Each ABTC4+ ligand is connected to four inorganic MBBs and vice versa. C = gray; O = red; N = blue; and Yb = green. All hydrogen atoms and coordinated DMF molecules are omitted for clarity.

The coordinated DMF molecules and nitrate ions are directed towards these channels. The largest channel, viewed along the z-axis, has an estimated diameter of 16.792 Å by 5.465 Å. The total solvent-accessible free volumes for the desolvated forms of 14 and 15 are estimated to be 62.7 % and 62.1 %, respectively. The interesting structural features of these charged frameworks are potential open metal sites (4 per metal cluster), open channels, and moderate free volumes. In an attempt to exploit the porous features of 14 and 15 the as-synthesized samples were exchanged in a variety of volatile solvents. Unfortunately, the BET surface area values were always 0 m²/g. A plausible explanation to account for this observation is that upon removal of the coordinated DMF molecules the metal cluster becomes flexible which leads to the
collapse of the framework or that a suitable solvent exchange protocol has not been discovered.

3.2.2.6. Default versus Non-Default Structures in Crystal Chemistry: MOMs Assembled from Tetrahedral and Rectangular Building Units

Inorganic and organic chemistries offer a vast repertoire of MBBs with varying connectivities, which can be utilized to construct target networks with desired properties. Despite the large number of structural possibilities, it is a general thesis that only a small fraction of simple high-symmetry nets will be generated via the self-assembly of simple building blocks. These nets are therefore often regarded as so-called default nets and are particularly salient to crystal chemistry. In the context of this discussion, binodal edge-transitive nets (Table 3.3.) represent an interesting class of networks; that is, networks assembled from two types of vertices and one type of edge.

Table 3.3. Select examples of binodal edge-transitive nets.\textsuperscript{90}

<table>
<thead>
<tr>
<th>Coord. Number</th>
<th>Vertex Figure</th>
<th>Symbol</th>
<th>Tiles</th>
<th>Transitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,4</td>
<td>triangle; square</td>
<td>pto</td>
<td>3[8^4]+[8^6]</td>
<td>2122</td>
</tr>
<tr>
<td>3,4</td>
<td>triangle; rectangle</td>
<td>tbo</td>
<td>2[6^6]+3[8^4]+[6^4.8^6]</td>
<td>2123</td>
</tr>
<tr>
<td>3,4</td>
<td>triangle; tetrahedron</td>
<td>bor</td>
<td>[6^4]+[6^4.8^6]</td>
<td>2122</td>
</tr>
<tr>
<td>3,4</td>
<td>triangle; tetrahedron</td>
<td>ctn</td>
<td>2[8^8]+3[8^3]</td>
<td>2122</td>
</tr>
<tr>
<td>3,6</td>
<td>triangle; octahedron</td>
<td>pyr</td>
<td>[6^6]+2[6^3]</td>
<td>2112</td>
</tr>
<tr>
<td>3,2,4</td>
<td>triangle; rhombicuboctahedron</td>
<td>rht</td>
<td>6[4^2]+2[4^6]+[4^12]</td>
<td>2123</td>
</tr>
<tr>
<td>4,4</td>
<td>square; tetrahedron</td>
<td>pts</td>
<td>[8^8]+[4^2.8^6]</td>
<td>2132</td>
</tr>
<tr>
<td>4,4</td>
<td>square; tetrahedron</td>
<td>pth</td>
<td>[4.8^2]+[8^4]</td>
<td>2132</td>
</tr>
<tr>
<td>4,6</td>
<td>square; octahedron</td>
<td>soc</td>
<td>[4^2]+3[4^4.8^6]</td>
<td>2122</td>
</tr>
<tr>
<td>4,8</td>
<td>tetrahedron; cube</td>
<td>flu</td>
<td>[4^12]</td>
<td>2111</td>
</tr>
<tr>
<td>6,6</td>
<td>octahedron; trigonal prism</td>
<td>nia</td>
<td>[4^12]+[4^8]</td>
<td>2122</td>
</tr>
</tbody>
</table>

The default net for the assembly of solely 4-connected square planar nodes is nbo (vertex-transitive); however, the simplest and most symmetrical linkage of 4-connected tetrahedral and square planar nodes (in a 1:1 ratio) affords the binodal pts (cooperite) net,
which is derived as the edge-net of the CdSO$_4$ (cds) uninodal net. Alternatively, the less symmetrical variant of pts; that is, the hexagonal pth network is also a plausible outcome for the assembly of such MBBs and is derived from the 4-connected quartz (qzt) uninodal net. The pts net is topologically equivalent to Platinum Sulfide whereby the planar node (i.e. Pt) forms PtS$_4$ rectangles and the tetrahedral node (i.e. S) forms SPt$_4$ tetrahedra. Significant advances in crystal chemistry have made it possible to attain decorated networks by replacing these nodes with suitable MBBs, as exemplified by several reports of MOFs having the pts topology.$^{91, 92}$ Prefabricated MBBs are thus chosen prior to the assembly process for their desired shape, geometry, and directionality which are prerequisites to augment an anticipated net.

The overall objective of this project was to design rigid architectures that support permanent porosity to be utilized in potential gas storage applications, as well as, ion-exchange studies. The pts net is an ideal synthetic target for such purposes because of its open channel system. Furthermore, this net is not self-dual and therefore interpenetration is less likely when using long pillars. These structural characteristics coupled with the inherent modularity afforded by MOFs permits the designer to fine-tune both the inorganic and organic MBBs to favor the formation of decorated pts nets with diverse pore dimensions, functionality, and charge.

3.2.2.6.1. MOFs Constructed from $p$-block Metal Centers

The reaction of H$_4$-ABTC with InCl$_3$ under mild solvothermal conditions indeed yields orange homogeneous crystals having a polyhedral morphology (16). The purity of the as-synthesized compound was confirmed by comparison of the experimental and
calculated PXRD patterns. The microcrystalline material, which was found to be insoluble in H₂O and common organic solvents, was characterized and formulated by single-crystal X-ray diffraction studies as \{[\text{In(ABTC)}]·(\text{DMA})\}_n (16). Compound 16 was not initially isolated in a homogenous phase, however. Prior to optimizing the reaction conditions the vial contained a mixture of two phases, i.e. crystals with both polyhedral and plate-like morphologies were observed. SCD studies confirmed that the plate-like phase was in fact a supramolecular isomer of 16, which was characterized and formulated as \{[\text{In(ABTC)}]·(\text{DMA})\}_n, (17). Many experimental protocols were pursed in an attempt to obtain a pure phase of 17 but were unsuccessful.

The single-crystal structure of 16 is a 3-periodic pts-MOF constructed from [\text{In(RCO}₂)_₄] inorganic MBBs bridged by the tetracarboxylate organic MBB, ABTC⁺ (Figure 3.31.) Each In(III) is surrounded by four independent carboxylate groups which coordinate to the metal ion in a bidentate fashion. This results in a distorted tetrahedral coordination environment with In−O distances ranging from 2.068 Å to 2.314 Å and O−In−O angles ranging from 82.088° to 94.595°. Each deprotonated ABTC ligand coordinates to four individual indium ions and thus acts as a rectangular-planar 4-connected node. Since each indium center is trivalent, this yields an overall anionic framework. Charge balance is provided by dimethylammonium cations (DMA⁺) located in the channels.
Figure 3.31. Schematic representation of 16 and 17: (center) In(RCO₂)₄ and H₄-ABTC MBBs which can be viewed as tetrahedral and rectangular building units, respectively; (left) ball-and-stick and augmented representation of 16; and (right) ball-and-stick and augmented representation of 17. Color Code: C = gray; O = red; N = blue; and In = green. The infinite channels are represented by the green and purple columns.

The crystal structure of 17 is built up from two crystallographically independent In(III) metal centers. Both are surrounded by four independent carboxylate groups. Each ABTC⁺ ligand coordinates to In(III) in a bidentate fashion to generate 4-connected [In(RCO₂)₄] MBBs having distorted tetrahedral geometry. It is worth noting that compound 17 is comprised of two types of inorganic MBBs which are differentiated based on the spacial orientation of the BDC-moiety around the metal centers. One type of [In(O₂CR)₄] MBB and thus adopts a so-called “1,3-D” conformation whereby two opposite meta-carboxyl groups are directed downward (same as that observed in 16). The second MBB resembles a “3-D” conformation, i.e. three of the four meta-carboxyl groups are facing downward. Both inorganic MBBs adopt a distorted tetrahedral geometry with
In-O distances ranging from 2.136 Å to 2.483 Å and 2.136 Å to 2.386 Å, respectively.

Two crystallographically independent ABTC ligands are present in 17 and both coordinate to four individual indium ions: three “1,3-D” conformations and one “3-D” surround each ligand. The propagation of the 4-connected tetrahedral and rectangular-planar nodes leads to the formation of an anionic 3-periodic framework with an unprecedented network topology. DMA⁺ cations in the channels balance the charge.

A topological distinction was made using the TOPOS software package whereby the coordination sequence was determined up to \( k = 10 \) (Table 3.4). The vertex symbols of the two independent nodes in 16 are 4.4.8(2).8(2).8(8).8(8) and 4.4.8(7).8(7).8(7).8(7). Compound 17 on the other hand is more complex and contains four independent vertices with corresponding VSs of 4.4.8(2).8(2).8(8).8(8), 4.6(2).6(2).8(8).8(2).8(2), 4.4.6.8(7).6.8(7), 4.6(2).6.8(7).6.8(7).6.8(7). The degree of regularity can be described based on the transitivity of the net which is 2132 and 4896 for 16 and 17, respectively. The network topology of compound 17 is therefore less regular than 16 and not classified as an edge-transitive net.

Table 3.4. Coordination sequence up to \( k = 10 \) determined for 16 and 17.

<table>
<thead>
<tr>
<th>net</th>
<th>vertex</th>
<th>cs₁</th>
<th>cs₂</th>
<th>cs₃</th>
<th>cs₄</th>
<th>cs₅</th>
<th>cs₆</th>
<th>cs₇</th>
<th>cs₈</th>
<th>cs₉</th>
<th>cs₁₀</th>
<th>cum₁₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>pts</td>
<td>V1</td>
<td>4</td>
<td>10</td>
<td>24</td>
<td>42</td>
<td>64</td>
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<td>124</td>
<td>162</td>
<td>204</td>
<td>252</td>
<td>979</td>
</tr>
<tr>
<td></td>
<td>V2</td>
<td>4</td>
<td>10</td>
<td>24</td>
<td>42</td>
<td>64</td>
<td>90</td>
<td>124</td>
<td>162</td>
<td>204</td>
<td>250</td>
<td>975</td>
</tr>
<tr>
<td>novel</td>
<td>V1</td>
<td>4</td>
<td>10</td>
<td>24</td>
<td>46</td>
<td>70</td>
<td>100</td>
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<td>230</td>
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<td>1078</td>
</tr>
<tr>
<td></td>
<td>V2</td>
<td>4</td>
<td>11</td>
<td>26</td>
<td>45</td>
<td>71</td>
<td>102</td>
<td>140</td>
<td>182</td>
<td>228</td>
<td>283</td>
<td>1093</td>
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<tr>
<td></td>
<td>V3</td>
<td>4</td>
<td>10</td>
<td>25</td>
<td>47</td>
<td>72</td>
<td>101</td>
<td>137</td>
<td>180</td>
<td>230</td>
<td>284</td>
<td>1091</td>
</tr>
<tr>
<td></td>
<td>V4</td>
<td>4</td>
<td>11</td>
<td>25</td>
<td>43</td>
<td>69</td>
<td>101</td>
<td>139</td>
<td>181</td>
<td>228</td>
<td>282</td>
<td>1084</td>
</tr>
</tbody>
</table>
The structure of 17 can, for a better understanding of the framework topology, be rationalized as a pillared 3-periodic MOM constructed from 2-periodic tetragonal square grid layers (Figure 3.32).

**Figure 3.32.** Select fragments from the crystal structure of 17: (a-b) Illustration of the two 4-connected indium MBBs, [In(RCO₂)₄]₄; (c) Ball-and-stick presentation viewed along the x-axis to show the three types of channels as highlighted by the green, purple, blue, and yellow column; (d) CPK presentation of the 2-D undulating tetragonal layer viewed down the z-axis. Color Code: C = gray; O = red; N = blue; and In = green. Hydrogen atoms and guest molecules are omitted for clarity.

The existence of the “3-D” conformation in 17 is the structure directing feature which facilitates the formation of the novel net, as oppose to the pts network topology, 16. The enhanced curvature (because of position 4) of the “3-D” conformation cause the cones to alternate and thus infinite undulating layers are obtained. The neighboring layers are pillared by ABTC⁺ (along the z-direction) via a ligand-to-ligand approach to generate
the pillared 3-periodic MOF. This arrangement reveals an interesting channel system consisting of four types of infinite narrow pores. The curvature resulting from the “3-D” MBB conformation gives rise to an undulating channel system along the z-direction with a diameter of approximately 6.526 Å. These channels are intersected along the x-direction by the 5-membered ring channels that are highlighted in blue (~6.661 Å). Moreover, 1D 4-membered rectangular and square-like channels also run along this axis and measure 6.135 Å x 10.093 Å and 6.902 Å x 4.206 Å, respectively.

Compound 16, on the other hand, is solely comprised of the “1,3-D” conformation (Figure 3.33.). For this reason the tetragonal square grid layers are not undulating and the bridged layers make this a 3-periodic MOF with infinite and regular 3D channel system with regular channels.

![Figure 3.33. Select fragments from the crystal structure of 16: (a) Illustration of the indium MBB, [In(RCO₂)₄] whereby two ABTC ligands are directed upward and two downward; (b) Ball-and-stick presentation to show the three types of channels, as highlighted by the green, pink, and yellow columns; (c) CPK view of the 2-D tetragonal layer viewed down the z-axis. Color Code: C = gray; O = red; N = blue; and In = green. All hydrogen atoms and guest molecules are omitted for clarity.](image)
The 4-membered ring channels directed down the z-axis measure approximately 6.468 Å in diameter and are intersected by the 4-membered ring channel which is rectangular in shape (7.088 Å x 6.468 Å) (purple column in Figure 3.33.). The aforementioned channel is further intersected by another small 4-membered ring channel which is square-like in shape (4.473 Å x 4.147 Å) (yellow column in Figure 3.33.).

3.2.2.6.2. Compound 16: Prospective Properties

The interesting structural features of 16, namely a large solvent-accessible free volume (70.2 %) and the anionic character and infinite channel system of intersecting narrow pores, prompted us to assess the gas sorption and ion-exchange properties of this material. We were equally as interested in investigating these properties in 17, but were unable to do so because isolating a pure phase was problematic. Future studies will therefore be devoted to isolating a homogenous phase of 17.

We attempted to investigate the gas sorption properties of 16 by conducting initial studies on the as-synthesized sample, as well as, the as-synthesized crystals soaked in a variety of low boiling point organic solvents. The list of solvents included acetonitrile, dichloromethane, chloroform, ethanol, benzene, ether, tetrahydrofuran. Unfortunately, we were unable to obtain a suitable solvent activation protocol for this system as the apparent BET surface areas were only in the range of 120 to 280 m²/g, which is much lower than we anticipated. The unexpected porosity data can be attributed to: (1) improper sample activation and/or (2) framework collapse under vacuum. The latter explanation is less likely because we anticipate the [In(RCO₂)₄] MBB to be rigid and thus enhance the robustness of the framework. This has been observed in permanently porous pts and pth...
MOFs synthesized by Eddaoudi and co-workers using 1,2,3,4-BTEC, as well as, a indium-based MOF synthesized by Schröder and co-workers with pts topology.

We also explored the potential of exchanging the DMA$^+$ organic cations for a variety of mono-, di-, and trivalent metal cations. The purpose of this study was to assess the H$_2$-MOF interactions in this system as a function of varying the extraframework metal cation, if suitable solvent activation methods could be found. The data would then be compared with the parent compound comprised of solely DMA$^+$ cations. A sample of 16 (activated in ethanol) was therefore exchanged in a variety of metal stock solutions, as summarized in Table 3.5.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Concentration$^a$</th>
<th>Duration$^b$</th>
<th>Stability</th>
<th>Color Change</th>
<th>Ratio</th>
<th>S.A.$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>0.5; 0.1</td>
<td>24</td>
<td>N</td>
<td>yellow powder</td>
<td>N.M.</td>
<td>N.M.</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>0.5</td>
<td>24</td>
<td>Y</td>
<td>no change</td>
<td>2.05:1</td>
<td>129</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.5</td>
<td>24</td>
<td>Y</td>
<td>no change</td>
<td>1.73:1</td>
<td>0</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>0.5</td>
<td>24</td>
<td>Y</td>
<td>orange to green</td>
<td>1.25:1</td>
<td>351</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>1.0</td>
<td>24</td>
<td>Y</td>
<td>deep orange</td>
<td>1.75:1</td>
<td>257</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>1.0</td>
<td>24</td>
<td>Y</td>
<td>no change</td>
<td>1.45:1</td>
<td>398</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>0.5; 0.1</td>
<td>5 min</td>
<td>N</td>
<td>xtals dissolve</td>
<td>N.M.</td>
<td>N.M.</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>0.5; 0.1</td>
<td>10 min</td>
<td>N</td>
<td>xtals dissolve</td>
<td>N.M.</td>
<td>N.M.</td>
</tr>
</tbody>
</table>

$^a$Concentration (Molarity); $^b$Duration in hours (unless otherwise noted); $^c$BET surface area (m$^2$/g) measured on the NOVA instrument; N. R. refers to not measured due instability after metal exchange.

The trivalent metal salts immediately attacked the framework and dissolved the crystals within minutes. Results obtained for those samples exchanged with mono- and divalent metals were more encouraging, except for the sodium sample which rapidly lost crystallinity. The atomic absorption data collected on the Cu$^{2+}$, Co$^{2+}$, and Ni$^{2+}$ exchanged samples revealed the DMA$^+$ cations were almost completely replaced by the aforementioned metal salts. The estimated BET surface areas for the Cu$^{2+}$, Co$^{2+}$, and Ni$^{2+}$
exchanged samples were found to be 351, 257, and 398 m²/g, respectively. These results are lower than that obtained with the parent compound. Future studies are therefore needed to explore alternative activation methods for this material, such as the use of supercritical CO₂ activation.

3.2.2.7. Strategy to Incorporate Unsaturated Metal Centers into MOFs via Organic Building Blocks: Porphyrin-Based Metalloligands

Computational and experimental studies have shown that the incorporation of unsaturated metal centers into porous MOFs enhances H₂-MOF interactions, as demonstrated by an increase in the isosteric heat of adsorption (often observed at low loadings). A considerable effort is therefore being made to incorporate this particular property into MOFs in conjunction with other important characteristics (e.g. high surface area and localized charge density, optimal pore sizes, low framework density, etc).¹

The most common approach is to create a high concentration of exposed metal sites into the framework of MOFs by the design and synthesis of solvated MOFs constructed from inorganic MBBs that contain coordinated solvent molecule(s) bound to the metal center. This strategy is often most effective for porous MOFs constructed from rigid MBBs (e.g. metal clusters) because single-metal-ion based MBBs are frequently too labile to support permanent porosity, once the solvent molecules are removed. Another powerful strategy for creating additional metal centers, which may however, be hydrated is derived from examples in inorganic zeolites. Eddaoudi and co-workers utilized the anionic rho-ZMOF as a platform to evaluate the H₂-MOF interactions as a function of extra-framework metal cationic complexes. The presence of an electrostatic field induced from the hydrated metal cations was indeed found to enhance the sorption energetics and
led to an increase in the isosteric heat of adsorption.\textsuperscript{95} Incorporation of metal centers in MOMs now includes the organic components whereby additional binding sites are created within the ligand in the form of metal fragments and/or chelated metal centers, as for example in MOFs assembled from salen-type and porphyrin-based ligands.\textsuperscript{66, 68, 96-99}

We are interested in using tetracarboxylate porphyrin-based organic ligands (Figure 3.34.) as a pathway to create metal binding centers within the framework backbone of 3-periodic MOFs with\textsuperscript{pts} topology. This approach could generate a platform with a high concentration of exposed metal sites whereby the effect of metal cations on \(\text{H}_2\)-MOF interactions could be evaluated in a systematic fashion if successful. The metal sites could be incorporated into the MOF via the framework backbone and/or extra-framework cations. In the latter case, the porphyrin functionality could be metallated with an assortment of metal cations by using pre- or post-synthetic modification techniques and in the form the extra-framework organic cations could be exchanged for different metal cations.

\textbf{Figure 3.34.} Porphyrin-based linkers used in this study: (left) 5,15-bis(2,6-dibromophenyl)-10,20-bis(3,5-dicarboxyphenyl)porphyrin, (\(\text{H}_4\)-TCBrPP); (right) 5,10,15,20-tetrakis(4-carboxy)-2\(1H/23H\)-porphine (\(\text{H}_4\)-TCPP).
Reaction of H$_4$-TCBrP with In(NO$_3$)$_3$·6H$_2$O in a mildly acidic solution containing DMF/H$_2$O/2,6-lutidine yields purple crystals with cube-shape morphology. The as-synthesized compound was characterized by single-crystal X-ray diffraction studies and formulated to be \{[In(TCBrPP)(H$_2$O)-DMA]\}$n$, 18. The crystal structure of 18 reveals a 3-periodic (4,4)-connected MOF constructed from mononuclear [In(RCO$_2$)$_4$] nodes that are bridged by the tetracarboxylate TCBrP$^{4-}$ porphyrin-based ligand. Each In(III) metal ion is seven-coordinate and binds to oxygen centers from four carboxylato moieties and one terminal aqua ligand to form a square pyramidal coordination geometry. Four independent deprotonated TCBrP ligands occupy the equatorial plane: opposing ligands coordinate to In(III) through the carboxylato groups in a bidentate (d$_{\text{In-O}} =$ 2.194 to 2.322 Å) and monodentate fashion (d$_{\text{In-O}} =$ 2.020 to 2.109 Å), respectively, and an aqua ligand (d$_{\text{In-O}} =$ 2.234 Å) completes the coordination sphere in the axial position. The conformation around the inorganic MBB can be rationalized as “3-D” because three of the four meta-carboxyl groups are facing downward (Figure 3.36.); however, in order to make the pts net the “1,3-D” conformation is desired. When only the points of extension are considered, the geometry around the inorganic MBB resembles a distorted tetrahedron. As a general theme presented throughout this section, the MOF can be dissected as a 3-periodic framework comprised of pillared 2-D tetragonal square grid layers. The layers are assembled from alternating cones which measure approximately 7.461 Å in diameter, as illustrated in Figure 3.35b. The distance between each layer is relative to the length of the pillar; that is, approximately 9.971 Å as measured from the 5-position of the BDC unit on neighboring layers.
Figure 3.35. Select fragments from the crystal structure of 18: (a) “3-D” conformation; and (b) Upon deleting the pillars, TCBrP, 2-periodic tetragonal square grid layers are revealed, as viewed down the $z$-axis. Color Code: C = gray; O = red; N = blue; Br = brown; and In = green. The purple atom located in the 5-position of the BDC unit represents the point of extension of the pillar. All hydrogen atoms and guest molecules are omitted for clarity.

Each TCBrP$^+$ ligand binds to four separate In(III) metal ions which is thus regarded as a 4-connected node. The assembly of the two types of 4-connected nodes leads to the formation of a 3-periodic MOF with nia-4,4-Pbca topology. The framework is anionic because the porphyrin unit is not metallated in the as-synthesized material and each indium metal ion is trivalent. The charge is balanced by disordered DMA$^+$ cations located in the interconnected irregular shaped channels. The relative size of the channels is significantly reduced because the porphyrin is oriented perpendicular to the BDC unit with a dihedral angle of 53.92°. The observed conformation results from steric hindrance which takes place between the neighboring hydrogen atoms on the BDC and pyridyl units, similar to that observed with BIPATC. The bromo-functionalized phenyl moieties are also twisted with respected to the porphyrin with a dihedral angle of 82.50°. The infinite channels are decorated by the porphyrin-based group and have approximate diameters of 7.268 Å and 5.356 Å (green and purple column, respectively; Figure 3.36). The total solvent-accessible free volume for 18 corresponds to approximately 35.4 % of the unit cell volume.
Figure 3.36. X-ray crystal structure of 18: (a) TCBPP\(^{+}\) organic MBB which coordinates to four \([\text{In(RCO}_{2})_4(\text{H}_2\text{O})]\) inorganic MBBs and thus can be viewed as 4-connected rectangular and distorted tetrahedral building units, respectively; (b) Ball-and-stick and schematic representation viewed along the y-axis to highlight the two types of infinite channels shown with green and purple columns; (c) Ball-and-stick and schematic representation viewed along the x-axis to show the undulating conformation of the 2-D layers. Color Code: C = gray; O = red; N = blue; Br = brown; and In = green. All hydrogen atoms and guest molecules are omitted for clarity.

From a topological perspective the assembly of the two 4-connected nodes did not yield the pts net. Instead the framework adopts a topology of a new subnet that is derived from a net with a large net relation graph (NRG). The binodal network can be topologically described as nia-4,4-Pbca having a transitivity of [2474] and thus is not an edge-transitive net. The 4-connected inorganic and organic nodes have a coordination sequence up to \(k = 10\) of 4, 11, 27, 52, 81, 117, 161, 210, 266, 332 and 4, 11, 27, 51, 81, 116, 161, 209, 266, 329, respectively. These sequences correspond to vertex symbols of \([4.6.6.8(6).6.8(6)]\) and \([4.6.6.8.6.8(7)]\), respectively. This net is rarely observed in MOMs and to the best of our knowledge, only two other MOFs exist with this network topology.
This is in addition to one hydrogen bonded network (CSD ref codes: NEHMET, WINJOS, CEJRUE).

While our objective was to isolate MOFs with pts topology using the porphyrin-based ligands presented, we have shown in this section that this was not the case. This unexpected result raises important questions such as: (1) why do some nets occur more frequently? Or (2) why is it that some nets rarely or never occur in nature? A general answer is that nature prefers to form the simplest nets with the highest symmetry. The connectivity observed in compound 18 is an excellent example of a rare net but this raises the question of why the pts net did not form? A plausible explanation may be the steric hindrance brought about by the twisted conformation of the porphyrin. The relative size of the 4-membered ring channels along the z-direction (square grid tetragonal layers) in a pts net constructed from 1,3-BDC organic linkers is somewhat predetermined by the BDC units. Formation of the target net might be blocked if bulky substituents, such as the porphyrin unit, are directed inward towards the channel, as opposed to lying in the plane of the BDC unit, this could prevent the formation of the target net.

We report a 3-periodic porphyrin-based MOF having an unprecedented topology. Despite many attempts no crystalline material could however be isolated with H₄-TCPP. The anionic character of 18 offers the potential for post-synthetic modification experiments whereby the extraframework metal cations are exchanged for different metal ions. In a similar vein, post-synthetic modification is feasible with the porphyrin unit because it is not metallated in the as-synthesized compound. This material may therefore be of interest for potential catalysis applications.
3.2.2.8. MOFs with pts Topology Constructed from Mono- and Bimetallic Transition Metal Centers

Solvothermal reaction between \( \text{H}_4\text{-ABTC} \) and \( \text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} \) or \( \text{Cd(NO}_3\text{)}_2\cdot4\text{H}_2\text{O} \) in a mildly acidic mixture containing DMF/CH\(_3\)CN/H\(_2\)O and DMF/NMP yields crystalline samples with a polyhedral morphology. The as-synthesized compounds were characterized by single-crystal X-ray diffraction studies and formulated to be

\[
\{(\text{Co}_4(\text{ABTC})_2(\text{DMF})_2(\text{EtOH})_3)\cdot(\text{EtOH})_4\cdot\text{H}_2\text{O}\}_n, \quad (19), \quad \text{and}
\]

\[
\{(\text{Cd}_2(\text{ABTC})(\text{DMF})_3)(\text{DMF})_3\cdot(\text{H}_2\text{O})_5\}_n, \quad (20), \quad \text{respectively. Compound 19 crystallizes in the P2(1)2(1)2(1) space group and belongs to the orthorhombic crystal system with a = 13.514(3) Å, b = 13.766(3) Å, c = 45.290(8) Å. Compound 19 was determined to be isostructural to 20 with a = 23.516(0) Å, b = 15.120(7) Å, c = 12.859(7) Å.}

The crystal structure of 19 is that of a 3-periodic network built-up from bimetallic \( \text{Co}_2(\text{RCO}_2)_4(\text{DMF})(\text{EtOH}) \) and \( \text{Co}_2(\text{RCO}_2)_4(\text{DMF})(\text{EtOH})_2 \) building blocks, which are linked through ABTC\(^{4-}\) units to exhibit a “1,3-D” conformation. The only difference between the aforementioned inorganic MBBs is the number of coordinated solvent molecules; otherwise, the geometry around the Co(II) cations and thus the points of extension are the same. Four deprotonated ABTC ligands coordinate to Co1 and Co2, in each cluster, by means of the carboxylato oxygen atoms (Figure 3.37.).
The coordination environment around Co1 consists of six oxygen atoms: one ligand coordinates in a bidentate fashion ($d_{\text{Co-O}} = 2.097$ and 2.217 Å), two coordinate in a bis-monodentate fashion ($d_{\text{Co-O}} = 2.026$ and 2.085 Å; $d_{\text{Co-O}} = 2.008$ and 1.936 Å) and serve as a bridge between Co1 and Co2, and the coordination sphere is completed by one ABTC ligand which coordinates in a bidentate fashion ($d_{\text{Co-O}} = 2.243$ Å) and simultaneously is bridged to Co2 via the deprotonated hydroxyl moiety ($d_{\text{Co-O}} = 2.058$ Å). Each Co2 metal cation adopts a square pyramidal geometry. The equatorial plane is occupied by two carboxylato oxygen atoms from two independent ligands which coordinate in a bis-monodentate ($d_{\text{Co-O}} = 2.085$ Å) and bifurcated bis-monodentate
fashion \( d_{\text{Co-O}} = 2.058 \, \text{Å} \), respectively. The remaining equatorial sites contain oxygen atoms from coordinated DMF and ethanol solvent molecules \( d_{\text{Co-O}} = 2.100 \, \text{Å} \) and \( d_{\text{Co-O}} = 1.969 \, \text{Å} \). This axial sites is occupied by one deprotonated ligand which coordinates to Co2 in a bis-monodentate fashion \( d_{\text{Co-O}} = 1.936 \, \text{Å} \).

The bimetallic Co(II) clusters can be viewed as 4-connected nodes having distorted tetrahedral geometry, if all the coordinated solvent molecules are disregarded. Each tetrahedral building unit is linked by four separate rectangular-planar building units to form a decorated 3-periodic MOF with \textit{pts} topology. The overall charge is neutral on account of the Co(II) bimetallic cluster in contrast to the indium-based \textit{pts} net (compound 16). The infinite channel system is analogous to that described for compound 16; however, the rectangular \( (4.985 \times 7.526 \, \text{Å}) \) and rhombic-like \( (5.480 \times 10.193 \, \text{Å}) \) channels are filled with coordinated and guest DMF and ethanol molecules that are directed towards the interior of the channels. The total solvent-accessible free volumes calculated for 19 and 20 is estimated to be 70.9 and 71.4 %, respectively (coordinated and guest solvent molecules were omitted for this calculation).

We were unable to study the gas-sorption properties of these materials because the as-synthesized and solvent exchanged samples did not exhibit permanently porosity, as confirmed by a BET surface area of 0 m\(^2\)/g. The XPRD pattern following sorption analysis did not reveal any peaks which is indicative of framework collapse. These results are not surprising, as many MOFs constructed from inorganic MBBs with a high degree of coordinated solvent molecules becomes less rigid upon solvent removal. It was our goal to circumvent this shortcoming through the design and synthesis of compound 16,
which is constructed from rigid single-metal-ion based inorganic MBBs (section 3.2.3.3.1.).

The primary objective of this project was to react H₄-ABTC with variety of transition metal cations (e.g. Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd) which are capable of maintaining an octahedral coordination environment. The target was to generate an isoreticular series of MOFs with \textit{soc} (= square octahedron) topology – see Chapter 2 for a detailed explanation. A serious challenge in the synthesis of such compounds is to uncover the optimal reaction conditions that can \textit{always} lead to the formation of a target MBB, such as the reactions conditions which consistently lead to the formation of the oxo-centered metal trimer cluster. During the course of this work, the following experimental parameters were adjusted in an attempt to favor the formation of this trimeric MBB: M:L ratio, concentration, polarity, acidity, temperature, alternative counter ions, and various SDAs. The TMBB was only isolated for In(III) and Fe(III) metal cations, while Co, Ni, Cu, Zn, Cd complexes predominately formed 4-connected nodes with square-planar or tetrahedral geometries having \textit{nbo} and \textit{pts} topologies, respectively.

It was therefore not very surprising that the solvothermal reaction of H₄-ABTC with Co(NO₃)₂·6H₂O or Mn(OAc)₃·2H₂O under mildly acidic conditions lead to the formation of two isostructural MOFs with \textit{pts} topology. The as-synthesized compounds were characterized by single-crystal X-ray diffraction studies and formulated to be \{[(Co(H-ABTC)(H₂O)₂)]ₙ, 21, and \{[(Mn(H-ABTC)(H₂O)₂)]ₙ, 22, respectively. The former compound was determined to crystallize in the P2₁/c space group with \(a = 11.024(3) \, \text{Å}, \, b = 22.005(4) \, \text{Å}, \, c = 9.691(9) \, \text{Å}. \) Similarly, compound 22 crystallizes in the
C2/c space group with a = 11.117(8) Å, b = 22.102(5) Å, c = 9.722(6) Å. A crystallographic analysis of 21 revealed that its structure is built up from 4-connected single-metal ion [Co(RCO2)4] building blocks, which adopt the “1,3-D” conformation. Four independent BDC moieties of the ABTC ligands are positioned in the same plane, which is in contrast to other MOFs in which the opposing BDC groups are oriented perpendicular to the plane. Four deprotonated ABTC ligands thus coordinate to each Co(II) metal center through the carboxylato oxygen atoms: the equatorial plane is occupied by two independent ligands coordinated in a cis-monodentate fashion (d_{Co-O} = 2.064 and 2.093 Å), and two disordered DMF molecules (d_{Co-O} = 2.082 and 2.101 Å), while the axial sites are occupied by two additional ligands which are also coordinated in a monodentate fashion (d_{Co-O} = 2.062 and 2.104 Å), as shown in Figure 3.38a. The inorganic MBB can be interpreted as a 4-connected MBB, if the DMF molecules are neglected, with a see-saw or a highly distorted tetrahedral geometry. The self-assembly of the two 4-connected MBBs results in an anionic 3-periodic MOF with pts topology. Charge is balance is provided by DMA⁺ cations, which are located in the infinite rectangular channels that measure approximately 4.6 x 7.3 Å in diameter (Figure 3.38b-c.).
Figure 3.38. Select fragments from the crystal structure of 21: (a) [Co(ABTC)_4(DMF)_2], which can be viewed as a 4-connected node with a see-saw or highly distorted tetrahedral geometry; (b) Ball-and-stick representation of the infinite rectangular channels that run along the z-axis; (c) Schematic representation of the 4-connected building units down the z-axis. All hydrogen atoms and solvent molecules are omitted for clarity. Color Code: C = gray; O = red; N = blue; and Mn = green. The open channels are highlighted with the green columns.

The underlying connectivity observed in 21 and 22 is the same but the presence of a mono- versus bimetallic MBB influences the packing of the pillared 2-D layers along the y-axis. The conformation of the BDC units in 21, which are all being parallel to the plane, thus prevents the formation of 2-D tetragonal square grid layers. Each layer is comprised of 4-membered rings, constructed from two opposing BDC units which interact with neighboring layers in a zig-zag fashion. Gas-sorption properties of 21 and 22 could not be investigated since neither of the MOFs retained their crystallinity upon the removal of coordinated solvent and guest molecules.
3.2.3. Experimental Section

3.2.3.1. Materials and Methods

All materials and methods are described in Chapter 2, unless otherwise noted. A detailed synthesis of H$_4$-ABTC is described in Chapter 2. The tetracarboxylate porphyrin-based organic ligand, H$_4$-TCBrP, was synthesized by Chungsik Kim in Dr. Peter Zhang’s lab at the University of South Florida and H$_4$-BAYTC was synthesized by Bao Zhong in Dr. Graham Bodwell’s lab at Memorial University in St. John’s, Newfoundland.

3.2.3.2. Synthesis and Characterization

![Figure 3.39](image)

**Figure 3.39.** A schematic to illustrate the cocrystal controlled solid-state synthesis (C$^3$S$^3$) of benzoimidephenanthroline tetracarboxylic acid (H$_4$-BIPATC). Reagents and Conditions: (i) DMF, (ii) Grind the solids together (uniform purple color), and (iii) Δ = 180°C for 1 hr.

**Preparation of benzoimidephenanthroline tetracarboxylic acid, H$_4$-BIPATC:**

5-Aminoisophthalic acid (1.81g, 10mmol) and 1,4,5,8-naphthalenetetracarboxylic dianhydride (1.34g, 5mmol) were ground together using a mortar and pestle in a minimal amount of DMF (~0.150mL). The homogenous purple solid was heated at 180°C for approximately 1 hr and cooled to room temperature to yield a yellow powder. The as-synthesized product does not require additional purification steps; however, if desired the solid can be refluxed in DMF overnight if additional purification is deemed necessary.
Synthesis of \{[Cu_2(ABTC)(H_2O)_2]\}_n, (8). A mixture of Cu(NO_3)_2·2.5H_2O (8.8mg, 0.070mmol), H_4-ABTC (12.1mg, 0.034mmol), DMF (0.5mL), CH_3CN (1mL), H_2O (0.5mL), and HMTA (0.15mL, 1M in DMF) was prepared in a 20 mL scintillation vial. The solution was heated to 85°C for 12 hours and cooled to room temperature. Orange cube-shaped crystals of 8, which were found to be insoluble in H_2O and common organic solvents, were harvested and air-dried.

Synthesis of \{[Zn_2(ABTC)(H_2O)_2]\}_n, (9). A mixture of Zn(NO_3)_2·6H_2O (8.8mg, 0.070mmol), H_4-ABTC (12.1mg, 0.034mmol), DEF (1mL) was prepared in a 20 mL scintillation vial. The solution was heated to 85°C for 12 hours and cooled to room temperature. Orange cube-shaped crystals of 9, which were found to be insoluble in H_2O and common organic solvents, were harvested and air-dried.

Synthesis of \{[Mn_2(ABTC)(H_2O)_2]\}_n, (10). A mixture of MnCl_2 (8.8mg, 0.070mmol), H_4-ABTC (12.1mg, 0.034mmol), DMF (0.5mL), CH_3CN (1mL) and HMTA (0.15mL, 1M in DMF) was prepared in a 20 mL scintillation vial. The solution was heated to 85°C for 12 hours and cooled to room temperature. Orange cube-shaped crystals of 10, which were found to be insoluble in H_2O and common organic solvents, were harvested and air-dried.

Synthesis of \{[Cu_2(BAYTC)(H_2O)_2]\}_n, (11). A mixture of Cu(NO_3)_2·2.5H_2O (20.0mg, 0.086mmol), H_4-BAYTC (15.4mg, 0.035mmol), DEF (1mL), chlorobenzene (1mL), tetrabutylammonium bromide (0.2mL, 1M in H_2O), and HNO_3 (0.0mL, 3.5M in DMF) was prepared in a 20 mL scintillation vial and subsequently heated to 85°C for 12 hours and cooled to room temperature to afford green parallelepiped crystals. The as-
synthesized crystals of 11 were harvested, air-dried, and determined to be insoluble in H₂O and common organic solvents.

**Synthesis of \{[Cu₂(BIPATC)(H₂O)₂]ₙ\}, (12).** A mixture of Cu(NO₃)₂·2.5H₂O (35.8mg, 0.20mmol), H₄-BIPATC (31.2mg, 0.20mmol), DMF (1mL), CH₃CN (1mL) and guanidine nitrate (0.2mL, 1M in DMF) was prepared in a 20 mL scintillation vial. The solution was heated to 85°C for 12 hours followed by additional heating to 105°C for 23 hours and 115°C for 23h hours. Each of the heating cycles were increased at rate of 1.5°C/minute and cooled to room temperature at a rate of 1.0°C/minute. Green hexagonal crystals of 12 were harvested and air-dried. The as-synthesized material was determined to be insoluble in H₂O and common organic solvents.

**Synthesis of \{[Cu₂(BIPATC)(H₂O)₂]ₙ\}, (13).** A mixture of Cu(NO₃)₂·2.5H₂O (11.6mg, 0.050mmol), H₄-BIPATC (28.5mg, 0.052mmol), DMA (1mL), H₂O (1mL) and pyridine (0.1mL, 1M in DMF) was prepared in a 20 mL scintillation vial. The solution was heated to 85°C for 12 hours followed by additional heating to 105°C for 23 hours and 115°C for 23h hours. Green parallelepiped crystals of 13 were harvested and air-dried. The as-synthesized material was determined to be insoluble in H₂O and common organic solvents.

**Synthesis of \{[Yb₂(ABTC)(NO₃)₂(DMF)₄]ₙ\}, (14).** A mixture of Yb(NO₃)₃·5H₂O (50.0mg, 0.11mmol), H₄-ABTC (7.97mg, 0.022mmol), DMF (1mL), CH₃CN (1mL), PIP (0.15mL, 1M in DMF), and HNO₃ (0.15mL, 3.5M in DMF) was prepared in a 20 mL scintillation vial. The solution was heated to 85°C for 12 hours followed by additional heating to 105°C for 23 hours and cooled to room temperature. Orange block-shaped
crystals of \textbf{14}, which were found to be insoluble in H\textsubscript{2}O and common organic solvents, were harvested and air-dried.

**Synthesis of \{[\text{Eb}\textsubscript{2}(ABTC)(NO\textsubscript{3})\textsubscript{2}(DMF)\textsubscript{4}]\}_n, (15).** A mixture of Er(NO\textsubscript{3})\textsubscript{3}·5H\textsubscript{2}O (50.0mg, 0.11mmol), H\textsubscript{4}-ABTC (8.08mg, 0.022mmol), DMF (1mL), CH\textsubscript{3}Cl (0.5mL), PIP (0.2mL, 1M in DMF), and HNO\textsubscript{3} (0.15mL, 3.5M in DMF) was prepared in a 20 mL scintillation vial. The solution was heated to 85°C for 12 hours followed by additional heating to 105°C for 23 hours and cooled to room temperature. Orange block-shaped crystals of \textbf{15}, which were found to be insoluble in H\textsubscript{2}O and common organic solvents, were harvested and air-dried.

**Synthesis of \{[\text{In}(ABTC)·(DMA)]_n\}_n, (16).** A mixture of InCl\textsubscript{3} (22.1mg, 0.10mmol), H\textsubscript{4}-ABTC (35.8mg, 0.10mmol), DMF (1mL), NMP (0.5mL), H\textsubscript{2}O (0.5mL) and HNO\textsubscript{3} (0.45mL, 3.5M in DMF) was prepared in a 20 mL scintillation vial and heated to 85°C for 12 hours and cooled to room temperature. Orange polyhedral crystals of \textbf{16}, which were found to be insoluble in H\textsubscript{2}O and common organic solvents, were harvested and air-dried.

**Synthesis of \{[\text{In}(ABTC)·(DMA)]_n\}_n, (17).** A mixture of InCl\textsubscript{3} (30.0mg, 0.14mmol), H\textsubscript{4}-ABTC (24.4mg, 0.07mmol), DMF (1mL), ethanol (0.5mL), H\textsubscript{2}O (0.5mL) and HNO\textsubscript{3} (0.45mL, 3.5M in DMF) was prepared in a 20 mL scintillation vial and heated to 85°C for 12 hours and cooled to room temperature to afford a heterogeneous mixture of \textbf{16} and \textbf{17}. Despite many trials, a homogenous phase of \textbf{17} could not be isolated.

**Synthesis of \{[\text{In}(TCBrPP)(H\textsubscript{2}O)\textsubscript{2}]·DMA\}_n, (18).** A mixture of In(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O (3.24mg, 0.011mmol), H\textsubscript{4}-TCBrPP (3.00mg, 0.003mmol), DMF (1mL), H\textsubscript{2}O (1mL), 2,6-lutidine (0.1mL in 1M DMF), and HNO\textsubscript{3} (0.25mL, 3.5M in DMF) was prepared in a 20
mL scintillation vial. The solution was heated to 85°C for 12 hours and cooled to room temperature whereby red cube-shaped crystals were obtained. The as-synthesized crystals of 18 were harvested, air-dried, and determined to be insoluble in H2O and common organic solvents.

Synthesis of \{[Co₄(ABTC)₂(DMF)₂(EtOH)₃]·(EtOH)₄(H₂O)}ₙ, (19). A mixture of Co(NO₃)₂.6H₂O (15.0mg, 0.052mmol), H₄-ABTC (9.23mg, 0.03mmol), DMF (1mL), CH₃CN (1.5mL), H₂O (0.25mL), and HNO₃ (0.15mL, 3.5M in DMF) was prepared in a 20 mL scintillation vial. The solution was heated to 85°C for 12 hours followed by additional heating to 105°C for 23 hours and cooled to room temperature. Purple polyhedral crystals of 19 were harvested and air-dried. The as-synthesized material was determined to be insoluble in H₂O and common organic solvents.

Synthesis of \{[Cd₄(ABTC)₂(DMF)₂(EtOH)₃]ₙ, (20). A mixture of Cd(NO₃)₂.4H₂O (30.8mg, 0.1mmol), H₄-ABTC (11.6mg, 0.03mmol), DMF (1mL), NMP (1mL), and HNO₃ (0.15mL, 3.5M in DMF) was prepared in a 20 mL scintillation vial. The solution was heated to 85°C for 12 hours followed by additional heating to 105°C for 23 hours and cooled to room temperature. Orange polyhedral crystals of 20 were harvested and air-dried. The as-synthesized material was determined to be insoluble in H₂O and common organic solvents.

Synthesis of \{[Co(ABTC)(H₂O)₂]ₙ, (21). A mixture of Co(NO₃)₂·6H₂O (29.1mg, 0.10mmol), H₄-ABTC (9.23mg, 0.03mmol), DMF (1mL), CH₃CN (1mL), and H₂O (0.25mL) was prepared in a 20 mL scintillation vial and subsequently heated to 85°C for 12 hours and cooled to room temperature to afford pink plate-shaped crystals. The
as-synthesized crystals of 21 were harvested, air-dried, and determined to be insoluble in H$_2$O and common organic solvents.

**Synthesis of $\{[\text{Mn(ABTC)}(\text{H}_2\text{O})_2]\}_n$, (22).** A mixture of Mn(OAc)$_3$·2H$_2$O (20.0mg, 0.074mmol), H$_4$-ABTC (17.8mg, 0.05mmol), DMF (1mL), H$_2$O (1mL) and HNO$_3$ (0.3mL, 3.5M in DMF) was prepared in a 20 mL scintillation vial. The solution was heated to 85°C for 12 hours and cooled to room temperate to afford pale orange plate-shaped crystals. The as-synthesized crystals of 22 were harvested, air-dried, and determined to be insoluble in H$_2$O and common organic solvents.

### 3.3. Summary and Conclusions

A series of MOMs built up from solely 4-connected nodes have been described. The majority of the structures presented in this chapter were in fact targeted and therefore exemplify the power of the MBB approach. Several of the structures did, however, form by accident but are also interesting in their own regard. Three nets in particular were the focus of this study; that is, the nbo, lvt, and pts nets. The resultant MOMs were isolated with a ligand-to-ligand pillaring strategy by employing suitable tetracarboxylate organic spacers (e.g. H$_4$-ABTC, H$_4$-BIPATC, and H$_4$-BAYTC) in conjunction with inorganic MBBs having the appropriate geometry needed to yield the target net. We have thereby shown that covalently cross-linking kgm and sql layers with a rigid ligand results in 3-periodic MOMs with nbo and lvt topology, respectively. Although both of these nets are constructed from 4-connected nodes their channel systems are significantly different in that the form is comprised of two types of cages while the latter is exhibits regular channels. A platform has thus been established on the basis of which the effects from
metal cation, pore size, and pore shape can be evaluated with respect to H$_2$-MOF interactions. Sample activation problems did, however, impede these studies but efforts are underway to explore alternative activation protocols (e.g. ScD CO$_2$ activation). Gas sorption properties of the anionic indium-based pts-MOF were investigated but the values were much lower than anticipated. It will, therefore, be necessary to study this problem in more detail to determine if the MOF collapses under vacuum or if it is just a matter of identifying an optimal activation protocol. Future work will focus upon synthesizing 4-connected MOMs based upon flexible tetracarboxylate ligands. This would allow for an elevated degree of diversity via ligand design which may otherwise be unattainable with the use of rigid spacers.

3.4. References


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Chapter 4. From Molecular Building Blocks to Supermolecular Building Blocks: Highly Connected MOMs that Possess a Superior Level of Hierarchical Complexity

4.1. Covalent Cross-Linking of Nanoscale Faceted Polyhedra

4.1.1. Introduction

The evolvement of the node-and-spacer approach into the MBB approach is widely recognized as a powerful design strategy for the rational construction of functional solid-state MOMs (e.g. metal-organic polyhedra, coordination polymers, metal-organic frameworks, etc). This is exemplified by the burgeoning academic and industrial interest in this class of materials.\(^1\) An exceptional feature offered by this strategy is that the desired functionality and directionality can be introduced into the inorganic and organic building blocks at the molecular level, prior to the assembly process, to generate modular MOMs that are uniquely suited for a wide range of pertinent applications (see Chapter 1). The transition from single metal MBBs to enlarged rigid metal clusters with 3-, 4-, and/or 6-connectivity therefore provided a heightened degree of predictability and more importantly an attractive pathway to target highly porous MOFs with increased surface areas and larger pore volumes.

The relative size of metal clusters \textit{versus} single metal ions has undoubtedly led to unprecedented breakthroughs in terms of scale and porosity. It remains however a challenge to absolutely predict which net will form once the MBBs self-assemble. This is because more than one net can often be isolated from a combination of building blocks.
For example, the self-assembly of tetrahedral and triangular SBUs has the potential to form augmented networks with **ctn** or **bor** topology but other nets are also possible (see Chapter 5). Furthermore, metal ions often adhere to more than one type of coordination geometry and thus the corresponding building units can possess different shapes. This is exemplified in the case of indium whereby 4-connected single metal ions MBBs or 6-connected metal clusters have been observed having tetrahedral and trigonal prismatic building units, respectively and therefore MOMs with different topologies are generated (see Chapters 2 and 3). Due to the numerous topological possibilities for a given combination of building blocks one once must not take the term “design” too literally at this stage. A review article published by Yaghi and co-workers in 2005 addresses the issue of ambiguity by stating the following: “*We believe that a structure can be truly designed when a specific building block leads to a specific predetermined structure, which is only possible for that building block. Such structures fall into the highest level, which in essence conceives the construction of a net from a building block that codes specifically and only for that net.*”

Accordingly, nets whose vertex figures designate the need for high connectivity are ideal targets to serve as nodes for the construction of extended frameworks. This is due, in part, because fewer nets are likely to form based on the combination of complex building blocks and the enhanced structural and directional information is already built-in to the MBBs to facilitate the formation of a specific network. This higher level of complexity therefore offers greater potential toward prediction, design, and synthesis of prospective made-to-order MOMs with unprecedented pore metrics. Such structural features are required for many important applications, as will be discussed below.
In crystal chemistry the deliberate construction of MOMs from prefabricated nodes with high connectivity is less prevalent than basic MBBs. It is an ongoing synthetic challenge to target such nets using traditional MBBs, \textit{i.e.} with connectivity $\leq 8$, because the necessary MBBs are often far more complex than the connectivity offered by organic ligands and multinuclear clusters. Zaworotko and co-workers therefore initiated a clever design strategy in 2004 to overcome the limitations of scale and connectivity imposed by traditional MBBs and SBUs by engaging in a form of suprasupermolecular chemistry using metal-organic polyhedra (MOP) as nodes. The authors demonstrated the feasibility of employing highly symmetric nanoscale metal-organic nanoballs, \textit{i.e. small rhombihexahedra} ([Cu$_2$(m-BDC)$_2$L$_2$]$_{12}$), as nodes for the construction of extended networks with intended topologies. The discrete spheroid-like nanoballs exhibit $O_h$ symmetry and are assembled from 12 copper paddlewheel building blocks (\textit{i.e.} closed faces) which in turn reveal 8 triangular and 6 square accessible windows. The prototypical nanoball is therefore uniquely suited to act as a rigid and directional node because the peripheral sites can be decorated through the axial metal sites and/or the meta position of the $m$-BDC ligand to yield extended architectures. The underlying topology of these nets is therefore governed by which face/window facilitates the connection to adjacent nanoballs. The 4-connected diamondoid nets, 6-connected octahedral or tetragonal nets, or 8-connected \textbf{bcc} nets are therefore suitable targets. Substitution of the meta-hydrogen atom on the BDC ligand for a sulfonate group indeed resulted in the formation of decorated anionic nanoballs having 24 sulfonate moieties located at the vertices. The crystal packing of the nanoballs resembles a \textbf{bcc} arrangement sustained by double cross-linking whereby 16 sulfonate moieties of one nanoball are bridged to an
adjacent nanoball through the axial positions of 16[Cu(methoxypyridine)₄]²⁺ cations.⁶

This connectivity therefore yields a 3-periodic MOM built-up from discrete MOP (Figure 4.1a-b.). Shortly thereafter, Zaworotko et al. generated a pcsu arrangement of nanoballs sustained by quadruple covalent cross-linking of each of the 24-connected nodes. This was accomplished using a flexible tetracarboxylate organic ligand, 1,3-bis(5-methoxy-1,3-benzene dicarboxylic acid)benzene (Figure 4.1c-d.).⁷

**Figure 4.1.** (a) Ball-and-stick representation of the sulfonated nanoball; (b) Schematic representation of the bcc packing of nanoballs, which is facilitated by double cross-linking; (c) Select fragment from pcsu net of nanoballs viewed along the b, c axes, which is sustained by quadrupole covalent cross-linking to six nanoballs; (d) Schematic to illustrate the pcsu packing of nanoballs.

The realization that MOP can be employed as nanoscale nodes to target specific nets represents the next generation of building blocks, coined supermolecular building
blocks (SBBs) by Eddaoudi and Zaworotko et al. in 2008. Recall that SBUs are assembled from MBBs and therefore connecting the points of extension of SBBs reveals a tertiary building unit (TeBU), which corresponds to the vertex figure of that particular net. Pre-designed SBBs therefore accolade existing design strategies and offer an exceptional degree of hierarchical structural complexity to construct higher connected and functional 3-periodic MOMs that are otherwise unattainable via simple MBBs and SBUs.

The SBB approach offers many advantages over traditional design strategies because the remarkable scale attainable by SBBs guarantees that the relative size of the resultant material will be enhanced since SBBs are considerably larger than their SBU counterparts. Prior to the assembly process the relative cavity dimensions of the SBBs can be controlled and functionalized to ensure that the desired features are present in the resultant material. This will be, in part, determined by the cross-linker positioned at each of the vertices. The SBBs often have narrow accessible window apertures that permit the passage of small molecules into the hollow interior micropore cavity, which simultaneously hinders the formation of interpenetrated nets.

4.1.1.1. Classification of Metal-Organic Polyhedra

Many examples of MOPs having 8, 12, 20, and 24 vertices have been reported in the literature. They therefore represent ideal synthetic targets to serve as nanoscale nodes in the construction of extended nets that indicate the need for higher connectivity, as exemplified above. The design and synthesis of a particular subset of MOPs are graciously inspired by a specific class of solids called the Platonic solids. The convex
polyhedra are assembled from edge-sharing regular polygons wherein all faces are congruent polygons that meet at the same angles with the same number of polygons at each vertex (Figure 4.2.). They are therefore described as being vertex-, edge-, and face-transitive regular polyhedra and have the lowest possible transitivity of [1111] due to the highest degree of regularity.

Figure 4.2. Schematic representation of the five regular Platonic Solids (left to right): Tetrahedron, hexahedron (cube), octahedron, dodecahedron, and icosahedron.

The implementation of design strategies that consistently form supramolecular polygons provided the foundations for the development of more complex structures akin to specific classes of polyhedra (see Chapter 1). In a similar manner, early reports of MOPs were constructed by adopting a molecular paneling approach and this gave rise to a diverse collection of cage-like compounds (e.g. molecular tetrahedra, octahedra, etc). An immense number of metal-organic nanostructures have also been constructed from carboxylate-based and heterofunctional organic ligands which exhibit similar cage-like characteristics (Figure 4.3.). The windows and accessible interior cavities have the potential to offer unique host-guest chemistry applications and the restricted cavity dimensions of these nanoscale polyhedra have shown to promote chemical reactions that are otherwise not observed in less confined environments. MOPs possessing peripheral functionalities can be further employed as SBBs to construct unprecedented extended MOMs, as will be discussed below.
A large number of MOPs on the other hand can be classified as Archimedean in nature because they are assembled from two or more types of polygons that meet at identical vertices as oppose to just one type of face. They are therefore regarded as semi-regular vertex-transitive polyhedra (Figure 4.4.). The simplest and most widely reported Archimedean polyhedron is the truncated tetrahedron, also known as the augmented form of the regular tetrahedron. Many examples of MOPs related to truncated octahedron, cuboctahedron, truncated cuboctahedron and others have also been reported.
Lastly, a class of polyhedra that are derived from both the Platonic and Archimedean solids must be highlighted as they are well-represented in the literature and are particularly salient to the results described in this chapter. These uniform polyhedra are classified as *faceted polyhedra* because they are sustained by vertex-linking of one or more types of regular polygons which meet at identical vertices. The polygons comprising this group assemble in such a way so that none of their edges are shared. This is in contrast to the aforementioned purely convex polyhedra. Accordingly, polyhedra that are comprised of both closed faces (convex polygons) and open (concave) windows are thereby revealed. There are nine *faceted polyhedra*, all generated from regular polygonal faces (*e.g.* square, triangle, pentagon) and open windows (Figure 4.5.).
4.1.2. Results and Discussion

A particular group of faceted polyhedra that are assembled from solely square polygons will be the focus of this section. They are suitable synthetic targets to be exploited as SBBs because the ubiquitous dimetal tetracarboxylate, $[\text{M}_2(\text{RCO}_2)_4]$ paddlewheel MBB, defined as a square SBU is readily accessible in crystal chemistry. This is exemplified by the over 1600 crystal structures reported in the Cambridge Structural Database (CSD) that are built up from this particular MBB. The assembly of vertex-linked square polygons oriented at 90°, 120°, and 144° angles has the potential to afford the following faceted polyhedra, the cubohemioctahedron (12 vertices), small rhombihexahedron (24 vertices), and small rhombidodecaheron (60 vertices), respectively (Figure 4.6.). Employing a suitable spacer moiety to link each of the aforementioned vertices will, in theory, be a governing factor for determining the formation of one polyhedron over the other.
Figure 4.6. Three uniform faceted polyhedra that can be generated via linking of molecular squares only: (left) cubohemioctahedron, (middle) small rhombihexahedron, (right) small rhombidodecahedron.

The first examples of MOMs containing only vertex-linked square SBUs was based on a molecular small rhombihexahedron, also known as the nanoball, truncated cuboctahedron or rhombicuboctahedron (MOP-1). The crystal structure is built up from copper paddlewheel MBBs that link at 120° through the carboxylate moieties of \( m \)-BDC (see Chapter 1). Further studies revealed the outer surface of the prototypical MOP could be fine tuned via decoration of the \( m \)-BDC unit and/or the axial metal sites to yield multiple derivatives that exhibit unique properties and molecular weights of at least 6 kDa. To be the best of our knowledge, a molecular form of the small rhombidodecahedron has not yet been synthesized as a discrete or extended entity.

We report herein the first example of a MOF rationalized as the assembly of metal-organic cubohemioctahedral SBUs, generated in situ, as cuboctahedral TeBU to construct an edge-transitive 12-connected MOF, as oppose to discrete molecules or ions. The \( m \)-BDC derived tetracarboxylate organic ligand, i.e. H₄-ABTC, is precisely located at the vertices of the vertex figure and thereby permits covalent cross-linking to adjacent SBUs to generate a 12-connected MOF having \( \text{fcu} \) topology, i.e. the only quasi-regular net. A (3,24)-connected \( \text{rht} \) MOF was also targeted using the SBB approach by linking metal-organic small rhombihexahedral SBUs through tritopic hexacarboxylate organic
ligands. This particular SBB was targeted because the TeBU corresponds to the requisite 24-connected rhombicuboctahedral vertex figure. The trigonal building units are positioned exactly at the 24 vertices to facilitate the construction of this anticipated net (Figure 4.7.).

![Figure 4.7.](right) Tiling representation of the (3,24)-connected rht net; and (right) augmentation of the 24- and 3-connected nodes reveals rhombicuboctahedron and triangular vertex figures.

Note that the hexacarboxylate organic ligands, containing three \( m \)-BDC moieties, were judiciously chosen to be analogous to the trigonal \( m \)-BDC units generated from the inorganic \([\text{Cu}_3\text{O(N}_4\text{CR)}_3]\) trimer MBBs in the original (3,24)-connected rht net (i.e. \textit{rht}-1) as previously reported by our group (Figure 4.8.).\textsuperscript{33} The data presented in this chapter will attempt to convey that molecular analogs of the \textit{fcu} and \textit{rht} nets represent unique prototypical platforms. The cavities and bulk properties of the materials can be fine tuned via judicious substitution of the metal ions and organic ligands to yield an isoreticular series of functional MOFs. They are therefore ideal systems to analyze and correlate a large number of structure-property relationships (e.g. gas storage).
4.1.2.1. Structural Analysis: 12-connected fcu nets

Reaction of H$_4$-ABTC with Ni(NO$_3$)$_2$·6H$_2$O in a DMF/HNO$_3$ solution, in the presence of HMTA, yields green homogeneous crystals with a cube-shape morphology. The purity of the as-synthesized compound was confirmed by similarities between the experimental and calculated PXRD patterns (Appendix B). The microcrystalline material was found to be insoluble in H$_2$O and common organic solvents. It was characterized and formulated by single-crystal X-ray diffraction studies as [Ni$_2$(ABTC)·(H$_2$O)$_3$]$_n$, (23). The crystal structure is built up from centrosymmetric [Ni$_6$(ABTC)$_{12}$]$^{12-}$ anions and therefore a novel anionic metal-organic cubohemioctahedral SBB is revealed (Figure 4.9.). Each SBB is covalently cross-linked to twelve adjacent SBBs through the meta position of the rigid diisophthalate tetracarboxylate ligand, ABTC$^4-$ which thereby leads to the formation of a 3-periodic network with fcu topology. A pure phase of the cobalt analogue of 23, 24,
can also be prepared under mild solvothermal conditions via the reaction of H$_4$-ABTC with Co(NO$_3$)$_2$·6H$_2$O to yield homogenous red crystals with a truncated cube-shape morphology.

Figure 4.9. (left) Schematic representation of the cubohemioctahedron assembled from square polygons sustained by a 90° vertex connection; Prototypical metal-organic cubohemioctahedron [M$_6$(bdc)$_{12}$]$^{12-}$ SBB in ball and stick (middle) and space-filling modes (right). Color code: M (Ni, Co) = green; C = gray; O = red. All hydrogen atoms and the decorated metal site have been omitted for clarity.

The inorganic MBB in 23, assembled from two octahedrally coordinated Ni(II) cations, adopts a pseudo-paddlewheel conformation. Four independent ABTC$^4-$ ligands coordinate to Ni1 in a monodentate fashion through the carboxylato oxygen atoms along the equatorial plane ($d_{\text{Ni-O}} = 2.02$ to 2.12 Å; O⋯Ni⋯O angle of 89.9°), while the axial positions are occupied by aqua ligands ($d_{\text{Ni-O}} = 2.00$ to 2.08 Å). Charge balance for the anionic metal-organic cubohemioctahedron is provided by a crystallographically disordered Ni(II) cation, Ni2, which bridges one of the axial aqua ligands and two of the four carboxylato moieties (Ni⋯μ$_2$-O distance of 1.98 Å; $d_{\text{Ni-O}} = 1.48$ Å) (Figure 4.10.). From a topological perspective, Ni2 is not a point of extension and therefore plays no decisive role in governing the underlying topology of the network. Since the decorated metal site is symmetrically disordered across the four carboxylato moieties this appears to
facilitate crystallization in the Fm-3 space group. Taking into consideration the decorated metal site, a cubohemiocahedron SBB of formula M_{12}L_{6} is thereby revealed.

![Figure 4.10](image)

**Figure 4.10.** Ball and stick representation of the inorganic MBB in 23: (left) octahedral coordination environments about Ni1 and the symmetrically disordered Ni2 cation; (right) Ni2 metal center shown without disorder.

The cubohemiocahedron SBB has inner cavity dimensions of ca. 8.7 Å and the relative size of this cavity is essentially predetermined by the distance between the carboxylate groups in ABTC^{4+}. Much larger tetrahedral and octahedral cavities are unveiled as a direct consequence of linking the nanoscale SBBs (Figure 4.11.). The truncated octahedral cage consists of six inorganic MBBs which occupy the vertices of the octahedron, viewed as square faces, linked together by twelve ABTC^{4+} ligands. The ligand therefore constitutes the edges of the octahedron and reveals idealized triangular windows proportional to the dimensions of the ligand. The octahedral cavity is cross-shaped and exhibits an internuclear distance of 23.3 Å. Suitable guest molecules can enter this cavity via the accessible triangular windows that measure approximately 7.4 Å. The tetrahedral cavity is comprised of smaller window apertures, 4.9 Å, which lead into a cavity with an internuclear distance of approximately 18.9 Å.
Figure 4.11. (a) Fragment of the single-crystal structure of 23 comprised of (b) cubohemioctahedral; (c) tetrahedral; and (d) truncated octahedral cavities. Hydrogen atoms, decorated metal site, and solvent molecules are omitted for clarity. Color code: Ni = green; C = gray; O = red.

MOMs are commonly simplified by dissecting the networks into an assembly of $n$-connected nodes. The frameworks are subsequently classified based upon the underlying topology adopted by that particular net. This assessment is critically dependent upon the MBB assignments because this will ultimately determine the points of extension that govern the growth of the net. In lieu of this anomaly, most structures can be interpreted in more than one yet equally acceptable ways. This often leads to more than one topological possibility, as exemplified by in the case of 23 and 24. One way of rationalizing the topology of 23 is to view the spheroid SBB as a 12-connected node.
Augmentation reveals a cuboctahedron vertex figure which corresponds to the vertex figure of the \textit{fcu} net.\textsuperscript{34} Each SBB is linked to 12 adjacent SBBs to generate the observed face-centered cubic, \textit{fcu}, network (Figure 4.12a-b.).

\begin{figure}[h]
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\includegraphics[width=\textwidth]{a}
\caption{(a) Augmented 12-connected \textit{fcu} topology; (b) Tiling representation of the \textit{fcu} net comprised of two types of tiles; (c) Schematic of the augmented \textit{nbo} network; and (d) Tiling view of the \textit{nbo} net consisting of one type of tile.}
\end{subfigure}
\end{figure}

An \textit{nbo} type network on the other hand is revealed if the carbon bearing the carboxylato groups are deemed the points of extension. In this case, the inorganic and organic MBBs are represented as two distinct 4-connected nodes which correspond to square and rectangular building units, respectively. The assembly of $M_{12}L_6$ moieties would therefore
be regarded as the assembly of squares, rectangles, and hexagons, generating cages resembling those in the zeolite structure sodalite, SOD (Figure 4.12c-d.).

4.1.2.2.1. Properties

Both the enlarged cavities and potential open metal sites exhibited by 23 and 24 encouraged us to investigate their H₂ uptake capacity. We found that 23 can store 0.6 wt% of H₂ at 77 K and 1 atm, whereas, 24 could not be activated despite trying a variety of protocols (e.g. solvent exchange and supercritical CO₂ activation). We also carried out preliminary spectroscopic studies to investigate the feasibility of exchanging the decorated SBB metal site for different metal cations. The UV-Vis spectra however did not show any evidence of exchange as no shift in the maxima was observed between the exchanged samples as compared to the parent compound. It is noteworthy to mention that Zaworotko and co-workers reported the synthesis of an isoreticular fcu framework built-up from cubohemiocahedral SBBs that were covalently cross-linked using an expanded tetracarboxylato ligand, BIPATC⁴⁻.³⁵ The relative span of the ligand facilitated the formation of enlarged cavities (> 3nm) comprised of a similar inorganic MBB (M = Co or Ni) as 23, which did readily undergo full metal exchange for Cu.

4.1.2.2. Structural and Topological Analysis: (3,24)-connected rht nets from Hexatopic Organic Ligands

Mild solvothermal reaction of H₆-PTMOI with Cu(NO₃)₂·2.5H₂O in a DMF/NMP mixture yields a blue homogenous microcrystalline material in 86% yield with truncated octahedron morphology. The purity of the material was confirmed by similarities between calculated and experimental PXRD patterns (Appendix B). The as-synthesized
compound, which is insoluble in H₂O and common organic solvents, was characterized and formulated by single-crystal X-ray diffraction studies as {[Cu₅(PTMOI)(H₂O)₃]}ₙ, (25). Zinc, cobalt, and manganese analogs of 25, 26 – 28, were also successfully isolated in crystalline forms under similar reaction conditions and therefore support the versatility of the approach as a function of varying the metal cation. Compounds 26 – 28 are insoluble in common organic solvents; however, the crystals rapidly degrade in air and aqueous environments. For that reason, the purity of the bulk samples could not be confirmed. SCD data collected on several crystals harvested from independent vials confirmed compounds 25 – 28 are indeed isostructural frameworks with rht topology. The only structural difference between the aforementioned networks is the metal ion and therefore the following structural description will pertain to 25.

Compound 25 crystallizes in the cubic Fm-3m space group with a = 41.4786(3) Å and a unit cell volume of 71,362.9(9) Å³. The crystal structure exhibits a 3-periodic network built up from copper paddlewheel MBBs, whereby each copper ion exhibits the expected square pyramidal geometry. The equatorial plane is occupied by four independent carboxylate oxygen atoms that bridge the dinuclear copper ions in a bis-monodentate fashion, while an aqua ligand lies in the axial position, CuO₅. The natural 120° angle subtended by the three angular m-BDC units of the C₃-symmetric hexatopic ligand, PTMOI⁶⁻, facilitates the assembly of vertex-linked molecular squares (Figure 4.13top.).
Twelve [Cu$_2$(RCO$_2$)$_4$] paddlewheel MBBs assemble in a cis fashion to generate the anticipated neutral metal-organic SBBs with 24-vertices, which are generated in situ as rhombicuboctahedral tertiary building units (TeBUs). Note that since the SBB is indeed comprised of both open windows and closed faces, it can be represented as a nanoscale small rhombihexahedra consisting of 12 vertex-linked, not edge shared, square SBUs (Figure 4.13middle.). Each SBB is covalently cross-linked to twelve adjacent SBBs.
through the triconnected coplanar isophthalate BDC units of the hexatopic ligand, regarded as a triangular building unit (Figure 4.13bottom.). This results in an edge-transitive (3,24)-connected MOF with rht topology. This topology was in fact only recently reported by Delgado-Friedrichs and O’Keeffe to be the sole edge transitive net for the assembly of rhombicuboctahedral and trigonal BUs.\textsuperscript{36}

The overall neutral framework is comprised of three distinct types of open polyhedral cages (Figure 4.14.). Covalent cross-linking of the SBBs (cage A) through PTMOI\textsuperscript{6} permits the formation of tetrahedral and octahedral cavities referred to as cages B and C, respectively. The largest cage, C, is defined by 8 triangular organic MBBs and 24 [Cu\textsubscript{2}(RCO\textsubscript{2})\textsubscript{4}] inorganic MBBs. The inner cavity dimensions of this cage are large enough to accommodate a van der Waals sphere measuring approximately 16.624 Å and it is surrounded by 6 truncated cuboctahedra cages and 8 tetrahedral-like cages. The truncated cuboctahedral cage, comprised of 12 [Cu(RCO\textsubscript{2})\textsubscript{4}] MBBs, exhibits an internuclear distance of approximately 13.069 Å and is surrounded by six large cages and eight tetrahedral-like cages. While the tetrahedral-like cage can accommodate a van der Waals sphere measuring approximately 10.460 Å and is assembled from 12 [Cu(RCO\textsubscript{2})\textsubscript{4}] MBBs and 4 PTMOI\textsuperscript{6} ligands; consequently, each of these cages are bordered by four truncated cuboctahedra and four of the largest cages.
The results reported so far in this section have addressed the modularity and predictability of the SBB approach by showing that isostructural \textbf{rht} analogues can indeed be readily obtained under similar reaction conditions by merely replacing the copper ions with different dicationic transition metals such as zinc, cobalt, and manganese. MOFs with this particular connectivity have demonstrated great promise as potential hydrogen storage systems because of the unique structural features of the \textbf{rht} network, which include (1) high surface area, (2) large free volume, (3) low framework density, (4) potential open metal sites and (5) large open windows and cavities. Once proper activation procedures have been developed, compounds 25 – 28 are expected to be an ideal series of materials to analyze and correlate the contribution of potential open metals sites on framework dihydrogen interactions.
Isoreticular rht MOFs assembled from expanded tritopic organic ligands can therefore be targeted to achieve even higher surface areas and larger pore volumes. An elongated $C_3$-symmetric hexacarboxylate organic ligand, H$_6$-ABPTMOI, was therefore designed to mimic the connectivity and geometry of H$_6$-PTMOI. We predicted that each of the 4-connected square planar [M$_2$(RCO$_2$)$_4$] nodes would assemble with each of the $m$-BDC units whereby one ABPTMOI$^{6-}$ ligand is shared between three truncated cuboctahedra to generate a trigonal 3-connected node with an estimated edge length of 24.6 Å (Figure 4.15.).

![Figure 4.15. Tritopic hexacarboxylate organic ligands (L$^{6-}$) employed in this study: (left) PTMOI$^{6-}$ spans ~13.6 Å, these dimensions can be substantially increased to ~24.6 Å as demonstrated in ABPTMOI$^{6-}$ (right).](image)

MOFs constructed from flexible elongated organic ligands commonly form interpenetrated networks but porous MOFs constructed from SBBs are in fact less likely to exhibit interpenetration when using such ligands due the relative window dimensions of the SBB. Accordingly, solvothermal reaction of H$_6$-ABPTMOI and Zn(NO$_3$)$_2$·6H$_2$O in a DMF/NMP solution yields a orange homogenous microcrystalline material in 81% yield with a truncated octahedron morphology, (29). The connectivity of 29 is the same as that observed in 25-28 but ligand expansion permits the formation of much larger
tetrahedral and octahedral cages (Figure 4.16.). The diameter and windows of the truncated cuboctahedral cage are relatively consistent for all the compounds (i.e. ~13 Å) because the dimensions are delimited by the scale of the inorganic MBBs and the 120° angle between the $m$-BDC units.

![Figure 4.16. Ball-and-stick representation of two of the three cages in 29: (a) Tetrahedral-like cage can accommodate a van der Waals sphere that measures approximately 17.138 Å; and (b) Largest cage is estimated to 27.199 Å in diameter. Color code: Zn = green; C = gray; O = red; N = blue. Hydrogen atoms and solvent molecules are omitted for clarity.](image)

As exemplified in the previous section of this chapter, the topological assessment of a net can come in many flavors. Likewise, the present isoreticular frameworks, 25 – 29, can also be interpreted as novel (3,3,4)-connected ternary net based on the assembly of three different building units to afford a trinodal $n$-connected net (Figure 4.17.).
The 4-connected paddlewheel MBBs (i.e. square vertex figure) are linked to four trigonal nodes (i.e. three m-BDC units) which constitute one of the 3-connected nodes. Three of these nodes surround the central benzene ring of the ligand at 120°, which delimits the second 3-connected vertex. The connectivity of the decorated nets of 25-29 can also be rationalized as related to Zeolite A with \( \text{Ita} \) topology; that is, assembled from \( \alpha \)- and \( \beta \)-cages and d4r or the reo-e net comprised of rhombicuboctahedron, cuboctahedron, and d4Rs.\(^{34, 37}\)
4.1.2.2.1. Gas Sorption Measurements for Compound 25

The total solvent-accessible volume calculated for 25 is estimated to be 74% of the unit cell volume\textsuperscript{38} and the calculated density for the desolvated framework was found to be 0.615 g cm\textsuperscript{-3}. The high free volume and low density paired with the unique structural features of this framework, i.e. the large accessible windows leading to the large open cavities with potential open metal sites therefore prompted us to investigate the gas sorption properties of this MOF. The sorption data is compared to the copper TZI (rht-1) MOF which exhibits a higher framework density, larger cavities, and potentially a higher concentration of open metal sites. This was done as a comparative study to evaluate the effect of these structural parameters on H\textsubscript{2} uptake and isosteric heat of adsorption.

Gas sorption investigations were carried out on the fully evacuated sample after exchanging the crystals in methanol for a period of 72 h. The activated blue crystalline material was loaded into a 6mm sample cell (slightly wet), initially evacuated at room temperature for a period of 6 h, then gradually heated to 95°C for 12 h and lastly heated to 115°C and held for 6 h. The permanent porosity of 25 was confirmed by the argon sorption isotherm collected at 87 K which reveals a pseudo- type I isotherm (Figure 4.18.). The overall shape of the isotherm is characteristic of a material containing both micropores and larger pores that approach the mesoporous range. This is in accord with the calculated dimensions of cages A – C.
The smaller cages undergo micropore filling at lower pressures, i.e. below 0.01, while a second slope appears in the range of 0.01 to 0.1 atm. This is due to gradual mesopore filling of the largest cage but note that saturation is still not achieved at 1 atm. The small hysteresis loop that is apparent in the desorption isotherm implies that the adsorbate cannot be removed from the framework as readily as it enters and therefore stronger adsorbate-MOF binding sites are likely responsible. This type of behavior is not observed in rht-1 and hexatopic organic-based rht analogs reported previously by other groups.\textsuperscript{39-41} It is unlikely that the hysteresis is due to the copper metal sites because the aforementioned analogues are also comprised of the same [Cu\textsubscript{2}(RCO\textsubscript{2})\textsubscript{4}] inorganic MBBs. It is plausible however that under vacuum the seemingly rigid PTMOI\textsubscript{6}-hexatopic ligand undergoes a structural change around the methoxy groups whereby the relative size/shape of the windows and cavities is altered and as a result hinders the desorption of the adsorbate. Note that this is purely speculation and further experiments are required to validate this hypothesis.
The apparent BET and Langmuir surface areas of 25 were estimated to be 1688 and 1105 m$^2$/g, respectively. The corresponding total pore volume was estimated to be 0.572 cm$^3$/g. The experimental data is not however in agreement with the calculated values, i.e. half of what we anticipate. This implies that either the sample was not fully activated or the framework partially collapses under vacuum. The calculated pore volume of 25 is estimated to be 1.20 cm$^3$/g, while the anticipated BET surface area computed for this compound was found to be 3601 m$^2$/g.

The CO$_2$ sorption capabilities of 25 were tested on the methanol exchanged sample following evacuation at 115°C for 6 h. The permanent porosity of the material was once again confirmed by the pseudo-type I adsorption isotherms which were collected at 0°C and 25°C (Figure 4.19). The overall shapes of the isotherms reveal a step rise in the lower pressure region. This step rise is due to stronger adsorbate-MOF interactions which may be associated with the potential open copper sites. The maximum CO$_2$ uptake capacity of 25 at 25 atm is 42 and 79 wt% at 25°C and 0°C, respectively. The large accessible cavities and accessible windows permit saturation at higher pressures in the 25°C isotherm but this is not observed at 0°C. A hysteresis is observed upon desorption in both isotherms, and is particularly apparent in the isotherm collected at 0°C. This could be attributed to framework flexibility but as previously stated this is only speculation. Second slope is observed for pressures between 7 to 10 atm and 10 to 16 atm in the 0°C and 25°C isotherm, respectively which is similar to that observed in the argon isotherm at 87 K (i.e. mesopore filling).

The overall shapes of the isotherms reveal a step rise in the lower pressure region. This step rise is due to stronger adsorbate-MOF interactions which may be associated with the potential open copper sites. The maximum CO$_2$ uptake capacity of 25 at 25 atm is 42 and 79 wt% at 25°C and 0°C, respectively.
Figure 4.19. (a) CO$_2$ sorption isotherms measured at 0°C and 25°C on compound 25 after exchange in methanol; and (b) CO$_2$ sorption isotherm measured at 25°C to emphasize the steep rise at low loading and filling in the largest cages that approach the mesoporous range at higher pressures.

Interestingly, the second slope does not appear in the same pressure range in the two isotherms. In order to provide an accurate assessment of this behavior, a more informative full sorption study must be completed. Meanwhile, I speculate that at 0°C and higher pressures the framework becomes flexible in nature which would further support the presence of the third slope observed for pressures between 20 to 25 atm. The pronounced hysteresis loop remains constant during desorption from 25 atm to approximately 13 atm and decreases steadily until it closes at approximately 2 atm.

The sorption studies reported herein concerning the CO$_2$ storage capacity of 25 shows great promise for the rht platform as a potential CO$_2$ storage medium. This compound is however subjected to an unidentified pressure and/or temperature dependent structural change which we have not observed in similar materials (at 25°C). This highlights the importance of generating and identifying highly favorable sites of interaction between the gas and material to establish pertinent structure-function
relationships. Ongoing studies are directed towards investigating the reason for the unexpected CO$_2$ sorption behavior.

The hydrogen uptake capacity for 25, evaluated at 77 K and 87 K at atmospheric pressures, revealed that it can adsorb 1.9 wt% of H$_2$ (Figure 4.20a.). The isosteric heat of adsorption, up to 1.4 % loading of H$_2$ per sorbent weight, has an estimated value of 9.7 kJ mol$^{-1}$ at low loading (Figure 4.20b.). Note that the $Q_{st}$ for 25 is appreciably larger than that observed for porous carbon materials and higher than most neutral MOFs. Nevertheless, the heat of adsorption is not maintained at higher loadings, evidenced by the decrease to 6.0 kJ mol$^{-1}$. This is in accord with pore filling of the larger cavities at higher loading.

![Figure 4.20](image.png)

Figure 4.20. Sorption measurements for 25 following activation in methanol: (a) Hydrogen sorption isotherms at 77 K and 87 K; and (b) Isosteric heat of adsorption for H$_2$.

We proceeded to try alternative activation protocols to fully activate 25 since the sorption data was much lower than we anticipated. Accordingly, the as-synthesized crystals were exchanged in a variety of other solvents such as: EtOH, CH$_3$CN, CHCl$_3$, CH$_2$Cl$_2$, THF, and acetone. Despite repeated attempts, the estimated BET surface areas
did not exceed the original values (i.e. MeOH exchange). It is a well known fact that open MOFs are often plagued by activation problems. Confronted with these challenges, I turned to supercritical drying (ScD) in the form of CO₂ activation as an alternative approach (see Chapter 1). This form of sample activation causes less surface tension than traditional thermal evacuation techniques and therefore is more likely to preserve the structural integrity of the MOF.⁴²

The as-synthesized crystals were exchanged in anhydrous methanol for 7 days, transferred to a plastic holder and placed in the CO₂ activation chamber. The blue microcrystalline material was then repeatedly washed with liquid CO₂, taken to its critical point (T = 31°C, P = 73 atm), held for 45 min, and finally set to vent/bleed out slowly over a 12 h period. The deep purple crystals (dry) were loaded into a 6 mm sample cell, evacuated at room temperature for 12 h and heated to 115°C for 6 h. The argon isotherm exhibits similar behavior as determined for the MeOH exchanged sample and thus the apparent BET and Langmuir surface areas are 1676 and 1088 m²/g, respectively with a corresponding total pore volume of only 0.56 cm³ g⁻¹ (Figure 4.21a.).
The maximum H$_2$ uptake for 25 at 77 K and atmospheric pressures was determined to be 1.87 wt% with an estimated $Q_{st}$ of 9.5 kJ mol$^{-1}$ at low loadings (Figure 4.21b-c.). The ScD CO$_2$ activation method there did not enhance the sorption properties of this material. In fact, it was virtually identical to that of the methanol exchanged sample. A comparison between the isosteric heats of adsorption between 25 and the
original Cu-TZI rht MOF (rht-1) reveals similar behavior at low loading, i.e. approximately 9.5 kJ mol\(^{-1}\) for both compounds. At higher loadings however the \(Q_{st}\) decreases more rapidly in rht-1. This is perhaps driven by the larger dimensions of the tetrahedral-\textit{like} and largest cavity. It is noteworthy to mention that this is somewhat counterintuitive because rht-1 is comprised of two inorganic MBBs and therefore has a higher concentration of potential open-copper binding centers. A possible explanation to account for this unexpected result may be that some of the copper sites in rht-1 are still saturated and thus higher evacuation temperatures are needed to fully desolvate the copper centers. Infrared spectroscopy and/or low-temperature powder neutron diffraction studies should be conducted on both compounds in order to prove or disprove the evidence of H\(_2\) binding to the copper centers, as was first evidenced in the case of HKUST-1, soon followed by other MOFs (see Chapter 1). A more accurate comparison concerning the expected binding affinities observed in these and related materials could then be conducted. It is important to mention that compounds 26 – 29 were subjected to gas sorption measurements but all exhibited poor sorption behavior; this is the surface area values never exceeded 80 m\(^2\)/g for any of the compounds. This could be attributed to inadequate sample activation or the dimetal paddlewheel MBBs comprised of Mn\(^{2+}\), Co\(^{2+}\), and Zn\(^{2+}\) are unstable following the removal of the axial ligands; whereas, dicopper complexes are more readily stabilized by the Jahn-Teller effect.

In summary, this section has addressed the unique traits of the rht network and highlighted the potential benefits this platform offers to reticular chemistry and gas storage applications. That is, larger surface areas and free volumes can be easily achieved via ligand expansion while avoiding interpenetrated nets. Optimal activation of these
materials however poses a significant challenge and must be overcome but in principle such values are attainable.

4.1.3. Experimental Section

4.1.3.1. Materials and Methods

All materials and methods are described in Chapter 2, unless otherwise noted. The azo-derived hexatopic organic ligand, 1,3,5-tris(5’-[(E)-(p-phenyloxy)diazenyl]benzene-1,3-dicarboxylic acid) benzene (H₆-ABPMTOI) was prepared by Mohamed Alkordi. For clarification purposes, the original synthesis of compounds 25 and 26 was carried out by an undergraduate student in the Eddaoudi group (Matthew Hight) but pure phases could not be isolated. Following his graduation, I started working on this project and purified these compounds and later synthesized 27 and 28 under similar reaction conditions.

4.1.3.2. Synthesis and Characterization

Figure 4.22. Synthetic strategy followed for the preparation of 1,3,5-tris(5-methoxy-1,3-benzene dicarboxylic acid)benzene (H₆-PTMOI). Reagents and Conditions: (i) DMF / KI / K₂CO₃ / Δ = 100°C for 1h, (ii) add H₂O and filter, (iii) NaOH / H₂O / MeOH / Δ = 50°C for 12h / HCl, pH = 1.
Preparation of 1,3,5-tris(5-methoxy-1,3-benzene dicarboxylic acid)benzene methyl ester: The product was synthesized according to a modified procedure from the literature. In a typical reaction, (12.7g, 0.06mol) of dimethyl-5-hydroxyisophthalate was dissolved in 250mL of DMF. A catalytic amount of KI (74mg, 4.4mol) was added to the solution followed by (26g, 0.26mol) K$_2$CO$_3$. The solution was then heated to 100°C for 1 hour. Subsequently, (2.88g, 0.008mol) of 1,3,5-tris(bromomethyl)benzene was dissolved in 10mL of DMF and added dropwise to the mixture and allowed to heat at 100°C for an additional hour and then cooled to room temperature. Approximately 800mL of water was added to the solution and the resulting white precipitate was filtered, washed thoroughly with ice cold water, and air-dried. **Note:** No further purification is required.

Preparation of 1,3,5-tris(5-methoxy-1,3-benzene dicarboxylic acid)benzene, H$_6$-PTMOI: In a typical hydrolysis reaction, the methyl ester product isolated from the previous step was added to a round bottom flask containing 250mL of methanol. Subsequently, an aqueous NaOH solution (6g in 60mL H$_2$O) was added to this mixture and then refluxed at 50°C for 12 hours. The solution was acidified to pH = 1 using 15M HCl. The precipitate was separated by filtration, washed with cold H$_2$O, and air-dried.

Synthesis of {[Ni$_2$(ABTC)(H$_2$O)$_3$]}$_n$, (23). A solution of Ni(NO$_3$)$_2$.6H$_2$O (15mg, 0.05mmol), H$_4$-ABTC (9.24mg, 0.025mmol), DMF (1mL), HMTA (0.1mL, 1M in H$_2$O), and HNO$_3$ (0.4mL, 3.5M in DMF) was prepared in a 20 mL scintillation vial. The solution was heated to 85°C increasing at a rate of 1.5°C/minute, held for 12 hours, and cooled to room temperature at a rate of 1.0°C. Green cube-shaped crystal of 23, which were found to be insoluble in H$_2$O and common organic solvents, were harvested and air-dried.

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Synthesis of \([\text{Co}_2(\text{ABTC})(\text{H}_2\text{O})_3]_n\), (24). A solution of \(\text{Co(NO}_3)_2\cdot6\text{H}_2\text{O}\) (29.1mg, 0.1mmol), \(\text{H}_3\text{-ABTC}\) (9.23mg, 0.025mmol), DMF (1mL), ethanol (1.5mL), \(\text{H}_2\text{O}\) (0.25mL), and HNO\(_3\) (0.3mL, 3.5M in DMF) was prepared in a 20 mL scintillation vial. The solution was heated to 85°C increasing at a rate of 1.5°C/minute, held for 12 hours, and cooled to room temperature at a rate of 1.0°C. Red cube-shaped crystal of 24, which were found to be insoluble in \(\text{H}_2\text{O}\) and common organic solvents, were harvested and air-dried.

Synthesis of \([\text{Cu}_3(\text{PTMOI})(\text{H}_2\text{O})_3]_n\), (25). A solution of \(\text{Cu(NO}_3)_3\cdot2.5\text{H}_2\text{O}\) (19.5mg, 0.084mmol), \(\text{H}_6\text{-PTMOI}\) (37mg, 0.056mmol), DMF (1mL), and \(\text{H}_2\text{O}\) (1mL) was prepared in a 20 mL scintillation vial. The solution was heated to 85°C for 12 hours followed by additional heating to 105°C for 23 hours and 115°C for 23h hours. Each of the heating cycles were increased at rate of 1.5°C/minute and cooled to room temperature at a rate of 1.0°C/minute. Green polyhedral crystals of 25 were harvested and air-dried. The as-synthesized material was determined to be insoluble in \(\text{H}_2\text{O}\) and common organic solvents.

Synthesis of \([\text{Zn}_3(\text{PTMOI})(\text{H}_2\text{O})_3]_n\), (26). A solution of \(\text{Zn(NO}_3)_3\cdot6\text{H}_2\text{O}\) (12.5mg, 0.042mmol), \(\text{H}_6\text{-PTMOI}\) (18.5mg, 0.028mmol), DMF (1mL), and NMP (1mL) was prepared in a 20 mL scintillation vial. The solution was heated to 85°C for 12 hours and cooled to room temperature at a rate of 1.0°C/minute. Colorless polyhedral crystals of 26 were harvested and air-dried. The as-synthesized material is insoluble in \(\text{H}_2\text{O}\) and common organic solvents.

Synthesis of \([\text{Mn}_3(\text{PTMOI})(\text{H}_2\text{O})_3]_n\), (27). A solution of \(\text{Mn(NO}_3)_2\cdotx\text{H}_2\text{O}\) (35.8mg, 0.2mmol), \(\text{H}_6\text{-PTMOI}\) (37mg, 0.056mmol), DMF (1mL) and NMP (1mL) were
combined in a 20 mL scintillation vial and heated to 85°C for 12 hours followed by additional heating to 105°C for 23 hours. Both heating cycles were increased at rate of 1.5°C/minute and cooled to room temperature at a rate of 1.0°C/minute. Colorless polyhedral crystals of 27 were harvested and air-dried. The as-synthesized material is insoluble in H₂O and common organic solvents.

**Synthesis of \{[Co₃(PTMOI)(H₂O)₃]\}_n, (28).** A solution of Co(NO₃)₂·6H₂O (24.4mg, 0.084mmol), H₆-PTMOI (37mg, 0.056mmol), DMF (1mL), and NMP (0.5mL) was prepared in a 20 mL scintillation vial. The solution was heated to 85°C for 12 hours followed by additional heating to 105°C for 23 hours and subsequently cooled to room temperature at a rate of 1.0°C/minute. Red cube-shaped crystal of 28, which were found to be insoluble in H₂O and common organic solvents, were harvested and air-dried.

**Synthesis of \{[Zn₃(ABPTMOI)(H₂O)₃]\}_n, (29).** A solution of Zn(NO₃)₂·6H₂O (12.5mg, 0.042mmol), H₆-ABPTMOI (27mg, 0.028mmol), DMF (1mL) and NMP (1mL) was prepared in a 20 mL scintillation vial. The solution was heated to 85°C for 12 hours followed by heating to 105°C for 23 hours heating increasing at rate of 1.5°C/minute and cooled to room temperature at a rate of 1.0°C/minute. Orange cube-shaped crystal of 29, which were found to be insoluble in H₂O and common organic solvents, were harvested and air-dried.

4.2. Rational Directed Assembly of Finite Metal-Organic Cubes (MOCs): A Viable Pathway to Target Zeolite-like Metal-Organic Frameworks (ZMOFs)

4.2.1. Introduction

Zeolites are typically defined as purely inorganic aluminosilicate microporous crystalline materials. They are constructed from corner-sharing [AlO₄]²⁻ and [SiO₄]⁴⁻
tetrahedra bridged at an approximate T-O-T angle of 145° (Figure 4.23.). The incorporation of a trivalent metal ion (e.g. Al\(^{3+}\)) into the silicate network generates anionic frameworks whereby additional metal ions and/or cationic organic molecules reside within the cavities/channels for charge balance. The assembly of simple tetrahedral building units (TBUs) generates a diverse range of open and robust 3-periodic structures. They may possess large cavities and uni- or multi-dimensional pore systems or channels, as exemplified by the extensive number of different frameworks (over 170) recognized by the IZA.\(^{37}\)

![Figure 4.23.](image)

**Figure 4.23.** Ball and stick representation of corner-sharing [AlO\(_4\)]\(^{5-}\) and [SiO\(_4\)]\(^{4-}\) tetrahedra bridged via O\(^2-\) at a T-O-T angle of ~145°. Color Code: Al = green; Si = yellow; O = red.

The frameworks are differentiated based on a number of factors such as cage dimensions, channel system, ring sizes, framework and topological densities, *etc.* Many synthetic protocols, therefore, rely on the use of an assortment of structure directing agents (e.g. alkyl ammonium salts) to provide charge balance as well as a certain degree of control over the resultant pore dimensions. The cationic templates are often readily exchanged through post-synthetic techniques for an assortment of guest molecules and/or metal ions.

Zeolites occur in a hydrated form and exhibit varying degrees of reversible dehydration owing to their exceptional thermal stability, as indicated by their name which translates into “boiling stone”. This unique class of compounds comes in two flavors
namely naturally occurring and synthetic structures. Over 40 naturally occurring zeolite frameworks are known,\textsuperscript{37} however, their use in commercial and industrial applications is often limited because they are rarely isolated in a pure phase and obtaining bulk quantities can be challenging. An alternative strategy implemented to overcome some of these limitations is focused upon the design and synthesis of topologically equivalent synthetic zeolites that possess unique properties akin to the natural analogues. In addition, this approach offers feasible synthetic pathways to construct a plethora of novel zeolite structures and/or hypothetical zeolite structures\textsuperscript{44} with intrinsic features that have the potential to address pertinent scientific and societal needs (Figure 4.24.).

![Zeolite Frameworks](image)

**Figure 4.24.** Schematic illustration of some naturally occurring and synthetic zeolite frameworks which exhibit versatile pore structures that render them suitable materials for many commercial and industrial applications: (left) Faujasite, FAU (middle) Linde Type A, LTA; and (right) ZSM-5, MFI.

Zeolites are the largest class of commercially available functional porous materials. Specific applications include, but are not limited to, ion-exchange (e.g. water softening and purification), shape-selective catalysis (e.g. petrochemical cracking), drug delivery and separation and removal of gases and solvents.\textsuperscript{45-55} A severe limitation, which impedes the development and applicability of purely inorganic zeolites, is the inherent lack of organic functionality. Generally speaking, this restricts the pore dimensions and
makes it difficult to extend the size beyond the “1 nm prison”.\textsuperscript{56} Because of this shortcoming, zeolites have proven to be unsuitable for some applications, such as molecular magnetism, hydrogen storage (due to high framework density), and separation/catalysis/encapsulation of large molecules.

In recent years, our group and others have strived to develop rational methodologies for the deliberate construction of functional MOMs that possess zeolitic topologies with fine tunable properties that exceed the boundaries of traditional inorganic zeolites.\textsuperscript{57-65} Zeolite-like metal-organic frameworks (ZMOFs) represent a perfect merger between two classes of materials, namely MOFs and zeolites. The increased tunability and functionality, along with the porosity and facile preparation methods of MOFs are combined with the typical anionic character exhibited by their zeolite analogues. Like their counterparts ZMOFs lack interpenetration but do contain extra-large cavities which renders them ideal platforms for cationic exchange and encapsulation of large organic molecules and molecular complexes. ZMOFs are an emerging class of materials that are attractive for a much wider range of potential applications, such as but not limited to, sensing, ion-exchange, catalysis, magnetism, and gas storage/sequestration.

Rational synthesis of MOMs with zeolitic topologies remains a significant scientific challenge because the assembly of non-directional and flexible TBUs in combination with flexible ditopic organic ligands predominantly yields MOMs having the default cubic diamond topology (\textit{dia}).\textsuperscript{34} Our group has demonstrated that non-default structures, such as zeolites, can be targeted by employing the single-metal-ion-based MBB approach.\textsuperscript{57, 58, 65} Accordingly, this strategy permits the formation of the necessary MBBs (e.g. MN\textsubscript{4}O\textsubscript{4}, MN\textsubscript{4}O\textsubscript{2}) which are regarded as rigid and directional TBUs via the
combination of angular heterofunctional organic ligands (e.g. H$_3$ImDC) with 6 or 8-coordinated metal ions. In the construction of ZMOFs, the angular ligands are judiciously chosen so that the nitrogen atom is part of the aromatic ring to direct the framework topology and the carboxylate moieties are located in the α-position relative to the nitrogen atom to sustain the rigidity of the resultant framework by means of the formation of rigid heterochelated five-membered rings (Figure 4.25.).

![Figure 4.25. An example of a ZMOF constructed using the single-metal-ion-based MBB approach: (right) Fragment of rho-ZMOF shown in ball and stick and node-and-spacer representations; composed of (left) InN$_4$O$_4$ MBBs which can be viewed as InN$_4$ TBUs. Color code: In = green; C = gray; N = blue; O = red.]

A particular subset of zeolite nets possessing LTA, AST, ACO, and ASV topologies share a common composite building unit comprised of eight tetrahedra linked together in a cube-like arrangement referred to as a double 4-ring, d4R.$^{37}$ A d4R is analogous to a specific type of Platonic solid, namely a hexahedron (cube) and thus gives rise to a highly symmetric metal-organic cube (MOC). As previously reported by us, finite and rigid MOP possessing appropriately positioned peripheral functionalities can be further employed as SBBs to construct extended MOFs. The ability to control the connectivity between SBBs offers the potential for structural diversity in the sense that
MOCs can be connected via the edge and/or vertex in a linear or tetrahedral manner to
generate an assortment of structures. Furthermore, the modular nature of MOMs permits
functionalization of the SBBs (e.g. interior and/or exterior) whereby topologically
identical or novel architectures can be constructed.

The single-metal-ion-based MBB approach has been shown by our group to be a
successful design strategy to control the coordination number and thus geometry to afford
discrete MOCs via the self-assembly of $\text{fac-MN}_3(\text{CO}_2)_3$ MBBs with a ditopic
heterofunctional organic ligand (Figure 4.26a-b.).$^\text{4, 66}$ The peripheral carboxylate oxygen
atoms embedded into the MOC, via the ligand, have the potential to participate in
hydrogen bonding interactions with or without metal-coordination with neighboring
cubes.$^\text{67, 68}$ Thus, MOCs can be employed as SBBs for the directed assembly and
deliberate construction of MOMs based on edge-transitive 8-connected nets and having
zeolite-like topologies (Figure 4.26c-d.). MOCs linked at the vertex in a linear fashion
could afford ZMOFs having LTA- and ASV-like topologies; while a vertex-connection
via tetrahedral nodes has the potential to form ACO- and AST-like topologies.
Figure 4.26. Examples of ZMOFs closely related to edge-transitive 8-connected nets synthesized using H$_3$ImDC as an organic linker: (a) Single metal-ion-based $\text{fac-MN}_3(CO_2)_3$ MBBs facilitate the assembly of (b) Finite MOCs which can be utilized as 8-connected SBBs to generate (c) Left to right: LTA-, ACO-, and AST-like topologies which are closely related to the reo-, bcu-, and flu-like edge-transitive nets, respectively.

The aforementioned zeolite nets, i.e. LTA, ASV, ACO, and AST, are particularly interesting in reticular chemistry as their nets correspond to the augmented conformation of the edge-transitive 8-connected nets reo, scu, bcu, and flu, respectively. To be more specific, reo is a semi-regular binodal net; bcu is a regular net and the default net for the
assembly of cube-like vertex figures; scu and flu are both (4,8)-connected nets, as outlined in the introductory chapter of this dissertation. The construction of functional solid state crystalline materials with just one type of edge makes life much easier for the synthetic chemist as there are fewer experimental parameters to take into consideration. This subclass of nets are highly feasible targets, since existing or predicted edge-transitive nets can serve as blueprints for the generation of a plethora of compounds having the same topology but with a different chemical composition.

Herein, I will demonstrate the utilization of MOP, MOCs, as SBBs by reporting the deliberate design and construction of an ast-ZMOF sustained by vertex- and edge-connected SBBs related to the (4,8)-connected edge-transitive flu-like net.

4.2.2. Results and Discussion

Solvothermal reaction of H3ImDC with Mn(NO3)2·6H2O in a DMF / CH3CN solution, in the presence of guanidine nitrate, yields homogeneous red polyhedral crystals. The purity of the microcrystalline material was confirmed by similarities between the calculated and experimental PXRD patterns (Appendix B). The as-synthesized compound, which was determined to be insoluble in H2O and common organic solvents, was characterized and formulated using SCD studies as 

\[ \{[\text{Mn}_8(\text{ImDC})_8(\text{HImDC})_4]\text{Mn}_4(\text{DMF})_8(\text{H}_2\text{O})_3(\text{guanidinium})_8} \}, (30). \]

The crystal structure of 30 reveals a 3-periodic network constructed from edge- and vertex-connected MOCs, generated in situ, wherein each anionic MOC formulated as 

\[ [\text{Mn}_8(\text{ImDC})_8(\text{HImDC})_4]^{16-} \]

is comprised of four doubly and eight triply deprotonated imidazoledicarboxylate exo-ligands that coordinate to eight Mn\(^{2+}\) ions located at the
vertices of each MOC. Three independent ditopic heterofunctional \( \text{H}_n\text{ImDC} \) ligands coordinate to each of the \( \text{Mn}^{2+} \) ions in a bis(bidentate) fashion through N-, O-heterocoordination, forming the essential \( \text{fac-MN}_3(\text{CO}_2)_3 \) MBB needed to construct a MOC. Each ligand constitutes the edges of the cube and bridges two individual \( \text{Mn}^{2+} \) ions by forming two rigid five-membered chelate rings coplanar with the imidazole ring which reinforce the rigidity and directionality of the assembly by locking the metal into position.

The regularity of the cube is akin to that of an ideal cube with \( \text{Mn}^{2+} \text{Mn} \) distances along the edges of the cube of 6.525 Å and \( \text{Mn}^{2+} \text{Mn}^{2+} \text{Mn} \) angles of 90° (Figure 4.27.). The presence of excess manganese and guanidinium ions not only provides charge balance to the framework but permits vertex-to-vertex and edge-to-edge connection to twelve adjacent cubes through the peripheral oxygen atoms of the \( \text{H}_n\text{ImDC} \) ligand, to reveal an extended zeolite-like framework possessing ast topology. Each of the twelve edge connections occur though a \( \text{Mn}^{2+} \) ion that adopts an octahedral coordination environment whereby four carboxylate oxygen atoms (\( d_{\text{Mn-O}} = 2.13 \) Å) from two \( \text{ImDC} \) ligands of two independent MOCs lie along the equatorial plane while disordered DMF molecules in the axial positions saturate the coordination sphere of the metal (\( d_{\text{Mn-O}} = 2.16 \) Å).
Figure 4.27. (a) Ball and stick representation of the single-crystal structure of 30 which reveals edge-to-edge connections through octahedrally coordinated Mn$^{2+}$ ions; (b) vertex-to-vertex connections occur through charge-assisted H-bonding between guanidinium ions which link four MOCs through (c) a supramolecular tetrahedron represented in yellow; (d) six MOCs (red tile) assemble to generate the AST-cage (green tile). Hydrogen atoms and solvent molecules are omitted for clarity Color code: Mn, orange; C, gray; N, blue; O, red.

The vertex-to-vertex intermolecular connections however are sustained by charge-assisted hydrogen bonds that occur between four guanidinium cations and carboxylate oxygen atoms located at the vertices (N-H…O distances of 2.92 to 3.00 Å) of neighboring cubes. The cations are uniquely situated to represent a supramolecular tetrahedron and play an influential role in governing the overall outcome of the assembly. Hence, each tetrahedron and can be simplified into a 4-connected tetrahedral node that extends to four
neighboring MOCs via the vertices to generate a 3-periodic network possessing the zeolite-like AST topology.

As previously mentioned, a similar approach can be used to target binodal edge-transitive nets whereby the MOC is regarded as an 8-connected node instead of a d4R. The 8-connected nodes are therefore linked together through the 4-connected tetrahedral nodes, to reveal a binodal edge-transitive (4,8)-connected net represented by the flu (Figure 4.28.). It is noteworthy to mention, the flu net is the dual of the only quasi-regular net, a uninodal 12-connected fcu net, described in the first section of this chapter.

![Diagram](image)

**Figure 4.28.** (a) MOC and tetrahedron represented as 8- and 4-connected nodes, respectively which self-assembly to form (b) a binodal edge-transitive flu-like net.

The total solvent-accessible volume for 30 was obtained using the PLATON software by summing the voxels that are more than 1.2 Å away from the framework which revealed an estimated free-volume of 48.3%. The approximate diameter of the AST-cage is 15 Å; however, the 6-membered ring windows which lead to the interior of the cavity are severely obstructed by the presence of the guanidinium ions which form supramolecular H-bonded panels that span much of the window aperture. Nevertheless,
we proceeded to investigate the potential gas sorption properties of this material. Despite numerous attempts to activate the compound, BET surface area values were only found to be in the range of 10 to 25 m$^2$/g. The PXRD pattern collected on these samples after sorption did not show any peaks, indicating collapse of the framework. It is conceivable that the edge-directed Mn$^{2+}$ ions become unstable upon evacuation if the axial ligands are removed and contributes to the framework collapse.

The same design strategy as detailed above was used to construct similar nets, lead by Mohamed Alkordi (ast-ZMOFs) and Jacilynn Brant (Ita-ZMOF), whereby the octahedral metal ions were substituted for an assortment of metal ions which include Co, Cd, In, and Zn. Likewise, the supramolecular tetrahedron formed via the assembly of guanidinium ions can readily be replaced by analogous monovalent metal clusters (i.e. K$^+$, Na$^+$, Cs$^+$) to generate isoreticular edge- and vertex-connected nets. The results described herein, therefore highlight the versatile nature and accessibility of this approach toward the construction of ZMOFs based on different octahedrally coordinated metal ions. Work is in progress to investigate the potential of these materials for host-guest applications for catalysis and/or small molecule sensing and to expand the structure library to include novel ZMOFs based on the directed assembly of the readily accessible MOCs using an assortment of functional ditopic organic ligands and metal ions.

**4.2.3. Experimental Section**

**4.2.3.1. Materials and Methods**

All materials and methods are described in Chapter 2, unless otherwise noted.
4.2.3.2. Synthesis and Characterization

**Synthesis of \([\text{Mn}_{12}(\text{guanidinium})_{8}(\text{ImDC})_{8}(\text{HImDC})_{4}]^{\cdot}(\text{DMF})_{8}(\text{H}_{2}\text{O})_{3}]_{n}, (30)\).**

A solution of Mn(NO$_3$)$_2$·6H$_2$O (35.8mg, 0.20mmol), H$_3$ImDC (31.2mg, 0.20mmol), DMF (1mL), CH$_3$CN (1mL) and guanidine nitrate (0.2mL, 1M in DMF) was prepared in a 20 mL scintillation vial. The solution was heated to 85°C for 12 hours followed by additional heating to 105°C for 23 hours and 115°C for 23h hours. Each of the heating cycles were increased at rate of 1.5°C/minute and cooled to room temperature at a rate of 1.0°C/minute. Red polyhedral crystals of 30 were harvested and air-dried (Yield: 13.6 mg, 22.7 %). The as-synthesized material was determined to be insoluble in H$_2$O and common organic solvents.

4.3. Summary and Conclusions

The work reported in this chapter further supports the evolution of the MBB approach by introducing the next generation of MOMs that are deliberately constructed from externally functionalized rigid and directional MOP, termed as SBBs. They are ideal nodes to be exploited in the construction of target nets where the vertex figures allocate the need for high connectivity. Furthermore, expanded non-interpenetrated nets are readily obtained due to the narrow window dimensions of the SBB, which in turn provides enhanced stability to the overall framework.

This chapter outlined several examples of 3-periodic MOMs built-up from discrete MOP. They can be divided into two classifications based on the SBBs employed; namely two prototypical platforms based upon linking nanoscale *faceted polyhedra* and another platform sustained by linking metal-organic cubes which are related to
hexahedra. The first study provided two examples of 12-connected MOFs with fcub topology. The frameworks are sustained by rigid cross-linking of cubohemioctahedral SBBs, \([\{M_2(ABTC)\cdots(H_2O)_3\}]_n\) where M = Ni or Co, through a tetracarboxylate organic ligand, ABTC\(^4\). Work is in progress to synthesize isostructural and isoreticular anionic fcub nets with large cavities in which case the decorated metal site is to be substituted for extra-framework organic cations (e.g. alkylammonium ions) or charged complexes (e.g. porphyrin-based molecules). The incorporation of extra-framework cations of varying size and functionality is a practical strategy to tune the pore size of these materials. If successful, these materials could be useful in gas storage and/or catalytic applications.

The second study focused on the synthesis of (3,24)-connected MOFs with rht topology. Small rhombihexadral SBBs where covalently cross-linked through a tritopic hexacarboxylate organic ligand, PTMOI\(^6\). This strategy therefore afforded a series of isostructural compounds formulated as \([\{M_3(PTMOI)(L)_3\}]_n\) where M = Cu\(^{2+}\), Zn\(^{2+}\), Co\(^{2+}\), Mn\(^{2+}\). The uniqueness of the rht network to the practice of reticular chemistry was exemplified by reporting the deliberate construction of an expanded isoreticular analogue formulated as \([\{Zn_3(ABPTMOI)(H_2O)_3\}]_n\). Future studies for this neutral platform will be devoted to finding the appropriate conditions to make these materials porous. This would permit a systematic analysis to be conducted in order to correlate the dihydrogen interactions as a function of both varying the metal cation and size of the cages. Concurrent work will also focus on impregnating these MOFs with enlarged metal complexes, as well as, exploring the possibility of generating anionic organic-based rht-MOFs by coordinating halide ions in the apical position of the paddlewheel MBB.
In the last study, predesigned finite MOCs were employed as rigid and directional SBBs. This provides a reliable pathway to target to specific zeolite nets comprised of the composite d4R building unit, while simultaneously generating nets based on edge-transitive nets. Work related to this project is in progress to explore the potential of constructed ZMOFs as hosts for molecules with applications in catalysis and/or small molecule sensing. Additionally, we are extending this approach further to construct novel ZMOFs based on the directed assembly of the readily accessible MOCs.68

In conclusion, the developed SBB methodologies delineated throughout this chapter provide a unique and modular pathway to access complex structures. This approach offers new horizons for solid state materials in terms of chemical functionality, scale, and structural diversity that are otherwise unattainable using basic MBBs and SBUs.

4.4. References


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Chapter 5. Tuning Pore Size via Charged Metal-Organic Frameworks: Pathway to Enhance Adsorbate-MOF Interactions

5.1. Introduction

Porous materials, specifically MOFs, are widely recognized as an interesting class of solid-state adsorbents for use in applications such as gas storage and sequestration, as evidenced throughout this dissertation.\(^1\)\(^-\)\(^3\) A contemporary challenge in the context of hydrogen storage is to significantly increase the adsorbate-MOF interactions, i.e. by factors of 3 – 5 over traditional physisorbents, while maintaining a high free volume and low framework density. These traits are imperative in order to facilitate high uptake capacities that will ultimately satisfy the DoE technical targets at working pressure and temperatures. Several key parameters have shown great promise towards increasing the sorption energetics in MOFs (see chapter 1 and 2); two of which are in fact the relative pore size and the presence of a strong electrostatic field. Synthetic strategies that therefore allow for control over these features in a systematic fashion are particularly salient to reticular chemistry.

One method that has been explored to study the effects of pore size is so-called interpenetration, also known as framework catenation, whereby one or more nets are entangled within a single network.\(^4\)\(^-\)\(^6\) Note that early reports often regarded this feature as an undesirable outcome for gas storage applications due to mitigation in the free volume and an increase in the framework density. In recent years however partitioning the empty

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space using this approach has endured success in that higher surface areas and isosteric heats of adsorption have been attained.\textsuperscript{7-12} A limitation to this strategy however lies in the fact that it is often difficult to control the degree of interpenetration and factors which influence its formation remain generally unclear. Furthermore, for some nets it is strictly forbidden all together such as in the case of ZMOFs.\textsuperscript{13} Reports on anionic ZMOFs and other charged MOFs have therefore shown that occupying the large open space with extra-framework cations (\textit{e.g.} hydrated metal ions or organic cations) leads to an electrostatic field with charged-induced forces and therefore enhances $Q_{st}$.\textsuperscript{1, 14-22}

The objective of this project was therefore to design a charged and robust structural prototype that would permit facile modifications to the pore metrics and functionality through the use of different extra-framework organic cations (Figure 5.1.). This would serve as a dual feature whereby the organic cations could also be substituted for an array of metal cations. Note that depending on the window dimensions of the resultant MOF, the organic cations may also be introduced into the MOF using post-synthetic exchange techniques.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.1.png}
\caption{Examples of targeted extra-framework alkylammonium organic cations (left to right): Dimethylammonium (DMA$^+$), diethylammonium (DEA$^+$), triethylammonium (TEA$^+$), and tetrabutylammonium (Bu$_4$N$^+$).}
\end{figure}

In this sense, charged frameworks offer a significant advantage over neutral MOFs because it is often easier to fine-tune the pore features using post-synthetic
exchange techniques as oppose to finding the appropriate reaction conditions to synthesize an isoreticular or isostructural MOF. In planning the synthesis we chose to use tetrahedral and triangular building units (BUs) because they are less likely deform in the assembly process due to their rigidity and so we anticipated the resultant MOF would also be robust.\textsuperscript{23} The self-assembly of tetrahedral and planar triangular BUs has the potential to form an infinite number of nets. In the absence of structure directing effects however nets with \textbf{ctn} and \textbf{bor} topology are most likely to form by linking the nodes through one kind of edge. The reason being that they are the most symmetric structures for the assembly of the aforementioned MBBs,\textsuperscript{24} i.e. edge-transitive. They are in fact ideal targets for this study because they possess large cavities.\textsuperscript{25}

In terms of finding the suitable MBBs, Eddaoudi and co-workers have already confirmed the feasibility of generating rigid single-metal ion TBUs with $p$-block metal cations (\textit{i.e.} In$^{3+}$)\textsuperscript{26} and therefore we chose to target this group of metals to represent the tetrahedral MBB. A trivalent node in conjunction with a trivalent organic linker would afford a charged framework and so we chose to bridge the tetrahedral MBBs with 1,3,5-benzenetricarboxylic acid (H$_3$BTC) because it is a rigid MBB and its vertex figure corresponds to a planar triangular BU. The diverse coordination geometries sustained by BTC (Figure 5.2.) has afforded a wide range of MOMs with intriguing topologies and fascinated properties, as evidenced by the hundreds of reported structures in the literature.\textsuperscript{27-34} In order to form the targeted (3,4)-connected nets it is vital that the three carboxylate moieties in H$_3$BTC coordinate to the metal ion in either a bidentate fashion or monodentate fashion. This is difficult to control however as BTC has many permutations
(Figure 5.2.) and slight variations in the reaction conditions can lead to an unprecedented results (i.e. quaternary net)

![Figure 5.2. Examples of common coordination modes generated by BTC.](image)

5.2. Results and Discussion

5.2.1. Porous Anionic MOFs with ctn Topology: Structural Description

Reaction of H$_3$-BTC with InBr$_3$ in a DMF/CH$_3$CN solution in the presence of tetraethylammonium chloride (TEACl) indeed yields colorless tetrahedral-shape crystals characterized and formulated using single-crystal diffraction studies as,

$\{[\text{In(BTC)}_{1.33}]\cdot\text{DMA}\}_n$ (31). The purity of the as-synthesized material was confirmed by similarities between the calculated and experimental PXRD patterns (Appendix B). In the crystal structure of 31, each indium ion is coordinated to eight carboxylate oxygen atoms
from four independent deprotonated BTC ligands. This configuration affords a rigid single metal ion MBB, In(RCO₂)₄ (d_{In-O} = 2.114 to 2.374 Å) which can be portrayed into the expected TBU. Each independent trivalent BTC anion is coordinated to three In(III) ions in a bidentate fashion and is therefore regarded as a 3-connected node (Figure 5.3.). The assembly of these 3- and 4-connected nodes generates a microporous anionic 3-periodic MOF with ctn (C₃N₄) topology. Charge balance for 31 however can potentially come from two different extra-framework organic cations; that is, dimethylammonium cations (DMA⁺) due to thermal decomposition of DMF or tetraethylammonium cations (TEA⁺) from the SDA.

**Figure 5.3.** Ball-and-stick and schematic representation of the ctn analogs, 31 and 32. Top: the 3- and 4-connected organic and inorganic MBBs can be rationalized as triangular and tetrahedral BUs, respectively. Bottom: MBBs self-assemble to yield anionic 3-periodic MOFs with a complex intersecting channel system. Color Code: Ga = yellow; In = green; C = gray; O = red. All hydrogen atoms and guest molecules are omitted for clarity.
The crystal structure of the indium-based ctn-MOF, 31, revealed too much disorder in the channels and thus it was not possible to definitively confirm the presence of one cation over the other. Preliminary metal exchange studies nevertheless lead me to believe that DMA\(^+\) cations are present in 31 due to the rapid rate of the exchange, as will be discussed below. Note that other solvent systems were pursued in an attempt to avoid the presence of DMA\(^+\) cations (e.g. DMSO). This was carried out in conjunction with an assortment of larger alkylammonium-based SDAs, such as but not limited to diethylamine (DEA), triethylamine (TEA), tetrapropylamine (Pr\(_4\)N), tetraethylamine (Et\(_4\)N), and tetrabutylamine (Bu\(_4\)N). Attempts to rationally fine-tune the pore dimensions in 31 were not successful but studies carried out on another \(p\)-block metal cation (\(i.e.\) Ga\(^{3+}\)) offered encouraging results.

Accordingly, reaction of H\(_3\)BTC with Ga(NO\(_3\))\(_3\)\(\cdot\)xH\(_2\)O in a DMA/butanol solution in the presence of TEACL generates colorless polyhedral crystals. The as-synthesized material was characterized and formulated using single-crystal diffraction studies as, \{[Ga(BTC)\(_{1.33}\)]\(_n\)\(\cdot\)DMA\}\(_n\) (32). The crystal structure of 32 therefore reveals the same network topology as 31 (\(i.e.\) ctn) but in this case each Ga(III) ion is 4-coordinate due its smaller atomic radius and thus each BTC\(^3-\) ligand is coordinated to three gallium centers in a monodentate fashion (Figure 5.3.). The same dilemma concerning the organic source for the charge balance is encountered in 32 because DMA can also decompose into DMA\(^+\), while TEA\(^+\) could also be present. Reaction between H\(_3\)BTC and Ga(NO\(_3\))\(_3\)\(\cdot\)xH\(_2\)O in a DMF/butanol solution also generates colorless microcrystalline material, which was determined to be another ctn analog (33). This was confirmed by comparing similarities between the experimental PXRD patterns (Appendix B). Charge balance in this case must
therefore be provided by extra-framework DMA$^+$ cations because there is no other source. Two more ctn analogs were isolated using a similar approach and contain DEA$^+$ (34) and Bu$_4$N$^+$ (35). They were generated by reacting H$_3$BTC with Ga(NO$_3$)$_3$·xH$_2$O in a DEF/butanol solution and DMSO/butanol solution in the presence of tetrabutylammonium bromide (TBABr), respectively.

Despite the high symmetry of the In- and Ga-based ctn-MOFs (i.e. 31 and 32), the pore system is quite complex. It is possible to simplify the structure into four independent intersecting channels, which form a repeating array of [M$_6$(BTC)$_{11}$]$^6$- cage-like units where M refers to indium or gallium (Figure 5.4.). The apical positions of the cage are defined by two parallel BTC$_3^-$ moieties oriented in an eclipsed fashion with an interlayer separation that is estimated to be 5.472 Å and 5.255 Å in 31 and 32, respectively. The BTC$_3^-$ ligands coordinate to six independent M(III) centers, three on the top and bottom and are bridged through three BTC$_3^-$ ligands located in the equatorial plane. The relative dimensions of the cage are significantly enhanced due to the presence of three additional equatorial M(III) ions. These are connected in a bidentate mode via two BTC$_3^-$ units. A large triangular-shape cage is thereby revealed having a 3-fold rotation axis (i.e. $C_3$ symmetry). The relative dimensions of this large cage are reflected in the edge length which is estimated to measure 16.236 Å and 15.927 Å for 31 and 32, respectively with accessible windows that range from approximately 6.74 to 7.55 Å. The total accessible free volume to solvent molecules and charge balancing organic cations in 31 and 32 was calculated to be 66.7 % and 63.1 %, respectively. Note that gallium has a smaller atomic radius than indium and therefore exhibits slightly smaller dimensions.
In summary, the direct synthesis of five porous anionic ctn-MOFs housing size-tunable extra-framework organic cations in the channels was reported. It is important to mention that during the course of these studies two other groups reported on this work (i.e. indium analogs only).\textsuperscript{15, 30} This therefore demonstrates the facile experimental protocols and modularity to which the pore metrics can be modified in these materials by simply employing cations of varying size and functionality. All of the compounds described above were isolated using direct synthesis; however, it is entirely possible that extra-framework cations of suitable size can be introduced via post-synthetic methods. In principle, these MOFs therefore represent prototypical platforms that provide a unique opportunity to investigate the impact of pore size on the gas adsorption properties (e.g. adsorbent-adsorbent interactions).

5.2.1.1. Properties: Preliminary Gas Sorption and Metal Ion Exchange Studies

The anionic nature, large accessible cages, and high thermal and chemical stability (i.e. $> 300^\circ$C) exhibited by these ctn-MOFs permits the incorporation of a wide
range of fine-tunable extra-framework cations \( i.e. \) organic or metal ions). Preliminary
gas adsorption studies carried out on the indium and gallium analogs having either DMA\(^+\)
or TEA\(^+\) extra-framework cations residing in the cages are discussed below. Note that
ongoing investigations are being conducted with similar analogs. Due to time constraints
and the high demand for the gas adsorption analyzer they could not be included in this
dissertation.

In order to assess the sorption properties of the indium ctn-MOF, 31, the guest
molecules were exchanged with ethanol for 3 days. The colorless microcrystalline sample
was then air dried and loaded into a 6-mm sample cell, initially outgassed at room
temperature for 8 h and then gradually heated to 280°C for 3 h. PXRD patterns confirmed
that the framework does not change after evacuation (Appendix B). TGA spectra for the
as-synthesized and exchanged samples indicate that 31 is indeed stable up to 400°C
(Appendix C). The exceptional thermal stability displayed by this compound is a feature
rarely observed in MOFs and likely attributed to the rigid MBBs in conjunction with the
intricate pore structure. This is interesting because it offers the potential for dehydrating
the extra-framework metal cations to generate accessible open-metal binding sites, \( i.e. \)
analogous to zeolites. This has proven to be problematic in fact for many reported anionic
MOFs owing to the lower thermal stability of the framework, \( i.e. \) at temperatures required
to fully dehydrate the metal ions.

The nitrogen and argon adsorption isotherms collected at 77 K and 87 K,
respectively reveal Type I behavior but saturation is not reached at 1 atm (Figure 5.5.).
BET and Langmuir surface areas were estimated from the Ar isotherm to be 515 \( m^2/g \)
and 851 \( m^2/g \) and the total pore volume was found to be 0.23 \( cm^3/g \) (at \( P/P_0 = 0.60 \)). The
internal pore diameter of 5.52 Å and 7.93 Å was obtained from both a cylindrical and spherical NLDFT pore model, respectively assuming an oxidic (zeolite) surface. The lower than expected pore volume may be attributed to the location of the alkylammonium cations in the cage and/or improper sample activation. Note that in both cases a hysteresis loop is observed in the desorption isotherms and therefore the adsorbate is irreversibly sorbed in 31. The loop closes at lower relative pressures in the N₂ isotherm as compared to Ar, which is likely associated with the fact that N₂ has a larger kinetic diameter and dipole moment, i.e. can lead to interactions with the surface of the MOF. This is in agreement with the slightly lower values obtained from the N₂ isotherm.

Figure 5.5. N₂ and Ar sorption isotherm for 31 collected at 77 K and 87 K, respectively.

The hydrogen sorption capacity for 31, measured at 77 K and 87 K and atmospheric pressures revealed a moderate uptake of 1.2 wt % of H₂ (Figure 5.6a.). The $Q_{st}$ was calculated to be 7.39 kJ mol⁻¹ and found to be nearly constant at higher loadings, which is indicative of averaging of the binding sites (Figure 5.6b.). Since compound 31 contains no open-indium binding sites the consistency observed in the $Q_{st}$ can be
attributed to the presence of an electrostatic field and the reduced pore size due to the presence of the alkylammonium cations (i.e. DMA⁺ or TEA⁺). Ongoing studies are therefore focused upon identifying which cation is present and synthesizing other analogs with larger cations, i.e. using direct and post-synthetic techniques.

Figure 5.6. Gas sorption studies for the indium ctn-MOF, 31: (a) N₂ and Ar sorption isotherm at 77 K and 87 K, respectively; (b) H₂ sorption data at 77 K and 87 K; and (c) isosteric heat of adsorption for H₂.

Gas sorption studies carried out on the gallium ctn-MOF after exchange in ethanol and evacuated at 280°C revealed different behavior with regards to the N₂ and Ar isotherms (Figure 5.7a.), i.e. the MOF selectively adsorbs Ar over N₂. It is important to note that the identity of the extra-framework organic cation is also under speculation in 32, i.e. either DMA⁺ or TEA⁺. The cage and window dimensions in compounds 31 (In) and 32 (Ga) are very similar and therefore I believe that it is possible that DMA⁺ and TEA⁺ cations are present in the cages, respectively. The larger size of the latter cation could hinder accessibility into the cage, depending on its location, and help to explain the hysteresis observed in the desorption for both adsorbates. Since N₂ has a larger kinetic
diameter than Ar and has a dipole moment is not surprising that it adsorbed less, that is, if the windows are indeed blocked. The BET and Langmuir surfaces areas estimated from the Ar isotherm at 87 K are 256 and 368 m$^2$/g, which are lower than expected. The H$_2$ isotherm however is fully reversible and has a maximum uptake of 1.5 wt % at 77 K (Figure 5.7b.). This is in accord with what we expect because the gallium analog has a lower framework density.

Figure 5.7. Gas sorption studies for a gallium ctn-MOF, 32: (a) N$_2$ and Ar sorption isotherm at 77 K and 87 K, respectively; (b) H$_2$ sorption data at 77 K and 87 K; and (c) Isosteric heats of adsorption for H$_2$ in 32 compared with the indium analog (31).
The isosteric heats of adsorption for 31 and 32 are in fact quite comparable but the latter deviates initially at higher loadings (Figure 5.7c.). This result was unexpected because if 32 does indeed have smaller pores due to the presence of the extra-framework organic cations then one would expect the $Q_{st}$ to be higher across the entire range. A possible explanation to account for this may in fact have nothing to do with cations, meaning the non-coordinated carboxylate oxygen atoms from BTC$^{3-}$ may interact with N$_2$ and hinder is mobility in the MOF. Future studies will be carried to confirm the identity of the extra-framework cation because without this key bit of information a true comparison between 31 and 32 cannot be conducted.

Post-synthetic metal ion exchange studies were carried out on 31 to assess the feasibility of substituting the organic cations for various mono-, di-, and trivalent metal ions (Table 5.1.). Note that similar studies were also done with 32 but the exchange process could not be quantified because a gallium lamp is needed for the Atomic Absorption (AA) instrument to deduce the metal ratios. Exchange studies carried out with trivalent metal ions, i.e. Cr$^{3+}$ or Fe$^{3+}$, were not successful for 31 and 32 because the ions instantly attack the ethanol exchanged MOF. In an attempt to alleviate this issue the concentration of the stock solution was reduced, as well as, the duration of the exchange but the crystals still degraded to powder. The divalent metal ion exchange studies however revealed promising results in which case the colorless crystals changed color almost instantly and remained crystalline even after exchange for 15 h in the stock solution. The AA experiments for the Cu$^{2+}$ and Co$^{2+}$ exchanged samples of 31 revealed full exchanges, while the Ni$^{2+}$ and Mg$^{2+}$ analogs were determined to be partially exchanged. The BET surface areas were measured for select samples on the NOVA
surface area analyzer but the results are not that significant at this stage and further studies are required to make meaningful conclusions. In short, we have demonstrated that full metal ion exchange is feasible using the robust cttn platform but the surface areas are lower than expected and therefore much effort is needed to optimize the activation conditions. The PXRD patterns are in good agreement with the as-synthesized and calculated patterns and therefore the unexpected results are not attributed to framework collapse (Appendix B). Accordingly, it would be beneficial to this study to collect SCD data of the exchanged samples to confirm their location in the MOF.

Table 5.1. Summary of the metal cation exchange studies carried out on 31, which is tentatively formulated as [In_{12}(BTC)_{16}]^{12-}·12DMA*

<table>
<thead>
<tr>
<th>Metal</th>
<th>Conc. a (M)</th>
<th>Duration</th>
<th>Stability b</th>
<th>Color Change</th>
<th>Ratio In³⁺:M²⁺</th>
<th># of Cations</th>
<th>Surface Area c (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>0.1</td>
<td>12-15 h</td>
<td>Y</td>
<td>colorless</td>
<td>N.R.</td>
<td>N.R.</td>
<td>N.R.</td>
</tr>
<tr>
<td>Li⁺</td>
<td>0.5</td>
<td>12-15 h</td>
<td>Y</td>
<td>colorless</td>
<td>N.R.</td>
<td>N.R.</td>
<td>20 – 32</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.5</td>
<td>12-15 h</td>
<td>Y</td>
<td>colorless</td>
<td>5.5:1</td>
<td>2</td>
<td>282</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>0.5</td>
<td>12-15 h</td>
<td>Y</td>
<td>light blue</td>
<td>1.88:1</td>
<td>6</td>
<td>76 – 118</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>0.5</td>
<td>12-15 h</td>
<td>Y</td>
<td>light green</td>
<td>2.75:1</td>
<td>4</td>
<td>410</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>0.5</td>
<td>12-15 h</td>
<td>Y</td>
<td>light red</td>
<td>1.76:1</td>
<td>6</td>
<td>12</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>0.1; 0.5</td>
<td>5 min</td>
<td>N</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>0.1; 0.5</td>
<td>15 min</td>
<td>N</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

*aConcentration of the metal stock solution; bYes (Y) or no(N) refers to the stability of the crystals after exchange; cBET surface area measured on the NOVA instrument after evacuation at 200°C.

5.2.2. Novel Quaternary Net formed by Self-Assembly of Triangles (2), Tetrahedral, and Trigonal Prismatic Building Units

A vast number of 3-periodic MOMs can be categorized as uninodal nets (*i.e.* vertex transitive) 35,36 The best examples are the five regular nets with a transitivity of [1111] and include the srs, dia, nbo, pcu, and bcu nets.37 They therefore correspond to
the default nets for the assembly of triangles, tetrahedra, squares, octahedra, and cubes, respectively and are thus constructed from one type of polygon or polyhedra. Binodal nets on the other hand offer more diversity since they are built-up from two different nodes. The (3,4)-connected nets are excellent examples to illustrate this concept because employing the simplest of MBBs (e.g. regular polygon/polyhedra) can afford very different structures. For example, the assembly of squares that are exclusively linked to triangles and vice versa can afford nets with Pt$_3$O$_4$ ($\text{pto}$) and twisted boracite ($\text{tbo}$) topology, while linking tetrahedra to only triangles and vice versa can lead to the formation of the boracite ($\text{bor}$) and C$_3$N$_4$ ($\text{ctn}$) nets, as demonstrated above for the latter case.

The MBB approach can also be used to target tertiary nets that consist of three different vertex-linked polygons or polyhedra. The rational design and synthesis of nets having more than two nodes is a considerable synthetic challenge because the reaction of unifunctional ligands with metal ions predominantly leads to the formation of one type of metal chromophore in given structure. To overcome this limitation one must therefore either (1) use a metal cation that has the potential to adopt multiple coordination modes (e.g. Zn), (2) employ a bifunctional organic ligand that will facilitate the formation of MBBs with different geometries (e.g. azolates), and/or (3) introduce two different ligands into the reaction scheme. Zaworotko and co-workers were in fact the first to demonstrate the feasibility of isolating tertiary nets from simple MBBs by synthesizing USF-3 and USF-4, both of which are built-up from triangular, square, and tetrahedral MBBs and exhibit unprecedented network topologies. The novel nets are therefore represented by the topological acronyms USF which stand for University of South Florida. The
triangular MBB is represented by a BTC anion, while the square and tetrahedral MBBs are based on different zinc chromophores. An interesting feature is that the exclusive formation of one net over the other can be precisely controlled using template effects. The authors later extended this simple strategy by reporting on the synthesis of USF-5, a 3-periodic copper-based MOM also built-up from triangles, squares, and pseudo-tetrahedral MBBs.\(^4\)\(^3\) Note that in this case the authors used a bifunctional ligand (i.e. 5-aminoisophthalic acid) to promote the formation of geometrically and chemically diverse metal coordination environments as oppose to using a metal ion with many chromophores. The success of this one-pot MBB approach has witnessed success in as evidenced by reports on other novel (3,4)-connected nets,\(^4\)\(^4\),\(^4\)\(^5\) as well as, ternary MOFs constructed from a range of geometrically different MBBs.\(^3\)\(^1\),\(^4\)\(^6\)

### 5.2.2.1. Structural Description of 36

Herein, we extend this simple strategy to the next hierarchical level by reporting on the serendipitous discovery a 3-periodic MOF comprised of four types of MBBs. This framework therefore represents a quaternary MOF and was in fact isolated while trying to synthesize an indium-based MOF with bor topology. To the best of our knowledge, this represents the first example of a MOF built-up from four different polygons or polyhedra; that is, trigonal prismatic, tetrahedral, and two topologically different triangles. Reaction of H\(_3\)BTC with In(NO\(_3\))\(_3\)·\(\chi\)H\(_2\)O in a NMP/DMF solution in the presence of TEABr affords colorless polyhedral crystals formulated by SCD diffraction studies as, \([[\text{In}_{30}(\text{O}_4)(\text{BTC})_{24}(\text{HCOO})_4\text{Br}_6])_n\) (36). The structure is complex as shown in ball-and-stick and polyhedral representations (Figure 5.8.). It is comprised of three crystallographically independent 3-connected BTC\(^3\)- anions which display the following
coordination environments: (1) adjacent carboxylate moieties bridge to two In(III) ions in a bidentate fashion and the third is coordinated to another In in a bis(monodentate) fashion, referred to as BTC1 coordination mode; (2) adjacent carboxylate moieties bridge to two In in a monodentate fashion and the third also bridges to another In(III) in a bis(monodentate) fashion, BTC2; and (3) all carboxylate moieties coordinate to six In(III) ions in a bis(monodentate fashion) in BTC3.

Figure 5.8. Optical image and select fragments from the crystal structure of 36 including the corresponding vertex figures when augmented. (Left) The four MBBs include BTC, [In(RCO2)4], [In3O(RCO2)6(Br)], and [In3O(RCO2)3(HCOO)6(Br)]. (Right) SBUs for each of the inorganic and organic MBBs. (Middle) the assembly of the $n$-connected nodes (where $n = 3, 4$, and 6) yields a porous 3-periodic MOF comprised of 3 types of cages. Color Code: In = green, C = gray, O = red, Br = pink.
Three independent indium ions are present in the crystal structure of 36. In1 is coordinated to four oxygen atoms, that is, two from BTC1 and BTC2, respectively. This reveals a [In(RCO₂)₄] MBB and reveals a TBU. In2 on the other hand displays an octahedral coordination geometry in which case three octahedra, [InO₅], are bridged through a central µ₃-oxo anion to generate a trimer MBB. Each In is linked to six BTC3 ligands and thereby reveals a trigonal prismatic building unit (TPBU). The coordination mode exhibited by In3 on the other hand is unprecedented and so is regarded as a pseudo-TMBB. Each indium in latter case coordinates to two oxygen atoms from BTC³⁻ bound in the cis position of the equatorial plane, while the opposing positions are occupied by oxygen atoms from two formic acid ligands. Each octahedral MBB is however still linked through a central µ₃-oxo anion and thus when augmented reveals a triangular BU.

The four vertices of the supertetrahedral building block (i.e. ST1) are occupied by the 6-connected TMBBs while the ligand (i.e. BTC3) is located at the four faces of the SBB. Each corner is thereby bridged to six In(III) carboxylate-based tetrahedral MBB, [In(RCO₂)₄] through three BTC1 ligands to reveal four cages that are hexagonal in shape, referred to as cage C. Accordingly, this cage is delimited by 6 tetrahedral MBBs which are positioned in the equatorial plane bridged through 6 deprotonated BTC2 ligands to the 6-connected pseudo-trimer MBBs located in the axial positions. The four hexagonal cages are united through a second supertetrahedral MBB (i.e. ST2) which links the pseudo-TMBBs through formic acid. The ST2 cage is therefore delimited by 4 pseudo-TMBBs located at the vertices and 12 deprotonated formic acid ligands (FA) lie in the faces of the cage (i.e. two per face). A summary of the selected features of 36 in terms of the pores sizes and window dimensions is provided in Table 5.2. Note that according to
the crystallographic data, the indium ions that make up cage B (i.e. ST2) are partially occupied and therefore the pseudo-TMBB is disordered over the four positions with an equal probability of being located at either position.

Table 5.2. Selected structural features of compound 36.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Topology</td>
<td>novel</td>
</tr>
<tr>
<td>Crystallographic data</td>
<td>Cubic; Fd-3m; a = 50.5457 Å; V = 129138 Å³</td>
</tr>
<tr>
<td># Independent In(III) ions</td>
<td>3</td>
</tr>
<tr>
<td># Independent BTC³⁻ anions</td>
<td>3</td>
</tr>
<tr>
<td>Density</td>
<td>1.003 g cm⁻³</td>
</tr>
<tr>
<td>Supertetrahedron (ST1) – Cage A</td>
<td></td>
</tr>
<tr>
<td>• Edge length</td>
<td>9.902 Å</td>
</tr>
<tr>
<td>• Internal diameter</td>
<td>7.918 Å</td>
</tr>
<tr>
<td>• Window dimensions</td>
<td>4.707 Å x 7.538 Å</td>
</tr>
<tr>
<td>Supertetrahedron (ST2) – Cage B</td>
<td></td>
</tr>
<tr>
<td>• Edge length</td>
<td>7.015 Å</td>
</tr>
<tr>
<td>• Internal diameter</td>
<td>7.314 Å</td>
</tr>
<tr>
<td>• Window dimensions</td>
<td>4.167 Å x 6.369 Å</td>
</tr>
<tr>
<td>Hexagonal-shape Cage C</td>
<td></td>
</tr>
<tr>
<td>• Edge length</td>
<td>8.627 Å</td>
</tr>
<tr>
<td>• Internal diameter</td>
<td>13.295 Å</td>
</tr>
<tr>
<td>• Window dimensions</td>
<td>7.422 Å x 9.134 Å</td>
</tr>
<tr>
<td>Cage D</td>
<td></td>
</tr>
<tr>
<td>• Internal diameter</td>
<td>7.790 Å</td>
</tr>
<tr>
<td>• Window dimensions</td>
<td>7.780 Å x 11.765 Å</td>
</tr>
</tbody>
</table>

Note: all measurements are point-to-point and do not include van der Waals radii between adjacent atoms.

Each indium ion is trivalent in 36 and thus yields an overall cationic MOF. The charge is broken down as follows with respect to each In carboxylate-based MBB: [In(BTC)₁₃]⁻¹, [In₃O(BTC)₂]⁺¹, and [In₃O(BTC)(FA)₁₅]⁺¹ for the tetrahedral, TMBB, and pseudo-TMBB, respectively. Charge balance for the cationic MOF is provided a coordinated bromide ion that is coordinated in the apical position of the TMBB (d_{In–Br} = 2.558 Å). The ion is disordered over the three positions with an equal probability of being
located at their site. From a topological perspective compound 36 can be simplified as
consisting of 3,4,12,12-connected nodes, which corresponds to BTC, tetrahedral MBB,
ST1, and ST2 respectively. Topological analysis performed using TOPOS software
confirms the frameworks unprecedented topology, as defined by the unique coordination
sequences and vertex symbols (Table 5.3. and 5.4.).

Table 5.3. Coordination sequence for the independent nodes in 36.
Node

cs1

cs2

cs3

cs4

cs5

cs6

cs7

cs8

cs9

cs10

In(RCO2)4
BTC
BTC
ST1
ST2

4
3
3
12
12

8
17
17
24
24

48
28
28
48
48

70
79
78
38
38

138
80
81
132
144

102
191
182
156
156

268
162
155
300
288

246
341
353
206
206

482
277
282
468
456

342
567
565
360
360

Table 5.4. Vertex symbols for the independent nodes in 36.
Node

Vertex Symbol

In(RCO2)4
BTC
BTC

[6.6.6.6.6(2).6(2)]
[6(2).6(2).6(2)]
[6(2).6(2).6(2)]

ST1

ST2

[6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.8.8.8.8.8.8.8.8.8.8.8.8.*.*.*.*.*.*.*.
*.*.*.*.*.*.*.*.*.*.*.*.*.*.*.*.*.*.*.*.*.*.*]
Point Symbol: {6^24;8^12;10^24;12^6}
8.8.8.8.8.8.8.8.8.8.8.8.8.8.8.8.8.8.8.8.*.*.*.*.*.*.*.*.*.*.*.*]
Point Symbol: {6^18;8^36;12^12}

The transitivity of this net is [5444] and therefore it is comprised of 5 types of
nodes, 4 edges, 4 faces, and 4 types of tiles. In many cases the natural tiling that carries a
net provides a clearer view of the structure in terms of understanding the connectivity of
the cages and/or channels by having a polyhedral illustration. This is not the case
however for 36 (Figure 5.9.). Note that TOPOS recognizes the BTC ligands as being 2
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independent nodes but from a geometrical perspective they are both triangular BUs and therefore in our assessment we regard them as being identical (i.e. quaternary net) with respect to the types of BUs present in 36.

![Tiling representation of 36, 5[6^6] + 2[6^9].](image)

**Figure 5.9.** Tiling representation of 36, 5[6^6] + 2[6^9].

### 5.2.2.2. Properties: Preliminary Gas Sorption Studies

Although compound 36 was not predicted, it certainly possesses desirable structural features which offer much potential from a gas storage point of view. This MOF in fact contains many of the key parameters that are suggested to increase $Q_{st}$; that is, a significant number of accessible open metal sites (indium-based TMBBs), the framework is charged and thereby induces an electrostatic field into the cavities, charge balance is provided by polarizable bromide ions, has a moderate solvent-accessible free volume of 63 %, and the pore size is rather narrow (see Table 5.1.). Compound 36 was exchanged in CH$_3$CN for 5 days and its sorption properties assessed after evacuation at 115°C for 9 h. The Ar sorption studies carried out at 87 K on 36 did not reveal a typical
Type I isotherm, in the sense that it does not reach saturation and it displays a small hysteresis in the desorption isotherm (Figure 5.10a.).

![Figure 5.10. Gas sorption studies for compound 36: (a) Ar sorption isotherm at 87 K; (b) H₂ sorption data at 77 K and 87 K; and (c) Isosteric heats of adsorption for H₂.](image)

This may be explained by improper sample activation or a heterogeneous sample and current studies are focused on addressing this issue. The apparent BET and Langmuir surface areas are estimated to be 540 and 748 m²/g with a corresponding pore volume of 0.26 cm³ g⁻¹. Note that obvious structural and chemical differences exist between 36 and
the ctn-MOFs discussed above. Nevertheless, the H$_2$ uptake capacity at 77 K for was found to be similar, 1.2 wt % (Figure 5.10b.). The $Q_{st}$ was also comparable within the range of 7.4 to 5.7 kJ mol$^{-1}$ at low and high loadings, respectively (Figure 5.10c.). These findings therefore point towards the importance of pore size and charged frameworks towards achieving enhanced binding affinities in these materials but more importantly the materials presented herein demonstrate that such interactions can be maintained even at higher loadings.

5.3. Experimental Section

5.3.1. Materials and Methods

All chemicals and solvents used in the preparation of compounds 31 – 36 were of reagent grade and used without further purification.

5.3.2. Synthesis and Characterization

**Synthesis of $\{[(\text{In(BTC)}_{1.33})\cdot\text{DMA}]_n\}$, (31).** A solution of InBr$_3$ (17.7mg, 0.05mmol) and BTC (21.0mg, 0.1mmol), DMF (1.0mL), CH$_3$CN (0.5mL), and tetraethylammonium chloride (TEACl) (0.1mL, 1M in H$_2$O) were placed in a 20 mL scintillation vial which was sealed, heated to 85$^\circ$C for 12h, and then cooled to room temperature. Colorless tetrahedral-shape crystals of 31 were harvested and air-dried. The as-synthesized material was determined to be insoluble in H$_2$O and common organic solvents.

**Synthesis of $\{[(\text{Ga(BTC)}_{1.33})\cdot\text{DMA}]_n\}$, (32).** A solution of Ga(NO$_3$)$_3$·$x$H$_2$O (12.8mg, 0.05mmol), BTC (21.0mg, 0.05mmol), DMA (0.5 mL), butanol (1.0 mL), and
TEACl (0.1 mL, 1M in H2O) was prepared in a 20 mL scintillation vial, which was sealed and heated to 85°C for 12h and then to 105°C for 24h and cooled to room temperature. Colorless tetrahedral-shape crystals of 32, which were found to be insoluble in H2O and common organic solvents, were harvested and air-dried.

**Synthesis of \{[(Ga(BTC)1.33]·DMA]\}ₙ, (33).** A solution of Ga(NO₃)₃·xH₂O (12.8mg, 0.05mmol), BTC (21.0mg, 0.05mmol), DMF (0.5 mL) and butanol (1.0 mL) was prepared in a 20 mL scintillation vial. The solution was then sealed and heated to 85°C for 12h, 105°C for 24h, and 115°C for 24h and cooled to room temperature. Colorless tetrahedral-shape crystals of 33, which were found to be insoluble in H₂O and common organic solvents, were harvested and air-dried.

**Synthesis of \{[(Ga(BTC)1.33]·DEA]\}ₙ, (34).** A solution of Ga(NO₃)₃·xH₂O (12.8mg, 0.05mmol), BTC (21.0mg, 0.05mmol), DEF (0.5 mL) and butanol (1.0 mL) was prepared in a 20 mL scintillation vial. The solution was then sealed and heated to 85°C for 12h followed by additional heating to 105°C for 24h and 115°C for 23h. Colorless tetrahedral-shape crystals of 34, which were found to be insoluble in H₂O and common organic solvents, were harvested and air-dried.

**Synthesis of \{[(Ga(BTC)1.33]·Bu₄N]\}ₙ, (35).** A solution of Ga(NO₃)₃·xH₂O (12.8mg, 0.05mmol), BTC (21.0mg, 0.05mmol), DMSO (0.5 mL) and butanol (1.0 mL), and tetrabutylammonium bromide (TBABr; 1M in H₂O) was prepared in a 20 mL scintillation vial. The solution was then sealed and heated to 85°C for 12h, 105°C for 24h, and 115°C for 23h and cooled to room temperature. Colorless tetrahedral-shape crystals of 35 were harvested and air-dried. The as-synthesized material was found to be insoluble in H₂O and common organic solvents.
Synthesis of \( \{\text{In}_{30}(\text{O})_4(\text{BTC})_2(\text{HCOO})_4\text{Br}_6\}_{n}, \) (36). A solution of \( \text{In(NO}_3\text{)}_3\cdot x\text{H}_2\text{O} \) (19.5mg, 0.05mmol), BTC (10.5mg, 0.05mmol), DMF (0.5mL), NMP (0.5mL), tetraethylammonium bromide (TEABr; 0.3mL, 1M in H\(_2\)O), and warm HNO\(_3\) (0.3mL, 3.5M in DMF) was prepared in a 20 mL scintillation vial. The solution was heated to 85\(^\circ\)C for 12h and cooled to room temperature to yield colorless polyhedral crystals. The as-synthesized crystals, 36, were isolated and air-dried and determined to be insoluble in H\(_2\)O and common organic solvents.

5.4. Summary and Conclusions

The work conducted in the first part of this chapter focused on the rational synthesis of anionic (3,4)-connected nets. Structures possessing ctn and bor topologies were specifically targeted for this study because we anticipated that the frameworks would be robust and contain large cavities. The objective of this study was to incorporate extra-framework organic cations of varying size and functionality into the cavities as a means to control the pore size and study the effects on adsorbate-MOF interactions. We deliberately selected rigid and directional prefabricated tetrahedral and triangular MBBs in the form of \([\text{M(RCO}_2\text{)}_4]\) and H\(_3\)BTC, respectively. Studies aimed at isolating charged MOFs with bor topology were not successful. The latter is a viable synthetic target but I believe that was not successful at finding the appropriate reaction conditions to generate this structure.

A series of anionic indium- and gallium-based 3-periodic MOFs with ctn topology were isolated housing different extra-framework alkylammonium cations in the cavities, i.e. DMA\(^+\), DEA\(^+\), TEA\(^+\), and Bu\(_4\)N\(^+\). Preliminary metal ion exchange studies
confirmed the feasibility of substituting the organic cations of suitable size for an array of
divalent metal ions. A significant challenge however was encountered when trying to
determine the identity of the cation using SCD studies. A high degree of disorder in the
cavities made it impossible to confirm which alkylammonium cation was there in
instances where more than one cation could be present, i.e. DMA$^+$ or TEA$^+$. To alleviate
this issue DMF solvent was avoided from the reaction conditions and in doing so charged
balance could only be provided by the chosen template. Preliminary sorption studies were
carried out on the In and Ga ctn-MOFs having either DMA$^+$ or TEA$^+$ cations in the
cavities. Note that at this stage it is difficult to make any reliable conclusions since it is
unknown which counter ion is located in the cavity. The isosteric heats of adsorption
nevertheless were similar for both compounds and an interesting feature observed in both
was the consistency in $Q_{st}$ at low and high loadings, i.e. $\sim 7$ kJ mol$^{-1}$. This plateau is
indicative of a significant averaging of the binding sites in these MOFs which therefore
can be attributed to the presence of an electrostatic field and the relative pore size.

The second part of this chapter revealed a serendipitous discovery that was in fact
isolated while trying to synthesize an indium-based MOF with bor topology. The porous
MOF has a novel topology and is built-up from four different types of MBBs.
Accordingly, we have classified it as a quaternary MOF and to the best of our knowledge
it is unprecedented for MOFs. It is therefore an excellent proof of principle in that
complex MOFs can indeed be obtained from simple MBBs and we anticipate that this
strategy will lead to other modular structures.

In summary, the ctn-MOFs presented in this chapter represent ideal molecular
platforms for which systematic adsorbate-MOF interactions can be conducted. Future
studies for this project will focus on completing full sorption studies on each of the alkylammonium analogs to assess the contributions of pore size on $Q_{st}$. Sorption studies can be concurrently carried out on the metal exchanged samples to assess differences in $Q_{st}$ as a function of varying the metal. This has the potential to be afford very interesting results owing to the high stability of the ctn-MOFs (i.e. $> 300^\circ$C). Moreover, studies can be also be done to investigate the feasibility of isolating isoreticular ctn- or bor-MOFs with enlarged cavities by using H$_3$BTB. This would therefore allow for the encapsulation of even large alkylammonium cations and even metal complexes.

5.5. References


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7519-7521.
2007, 5212-5213.
Chapter 6. Conclusions and Prospects for Future Studies

6.1. Summary

The research presented in this dissertation focused upon the rational construction of 3-periodic porous MOMs with a particular emphasis on gaining insights into the structure-property relationships that govern H$_2$-MOF interactions. It is imperative to the advancement of this field to have a detailed chemical understanding of these binding affinities at the molecular level in order to design potential made-to-order MOMs bearing the desired features that would meet future DoE targets for hydrogen storage in mobile applications. Herein, we have shown that highly porous MOFs may be capable of reaching these targets; however; these capacities are currently only achievable at low temperatures (i.e. 77 K). Nevertheless, pertinent information can be extrapolated from these studies and several of the necessary components have been identified that lead to improvements in the sorption energetics in these materials. This is certainly a step in the right direction and therefore to achieve the optimal binding energies at working temperatures and pressure it is a general thesis that an ideal physisorbent-based MOM must strike a comprise between having a high surface area, large pore volume, narrow pore dimensions, and low framework density.

The MOMs described here were isolated by employing a top down design bottom up synthesis approach. Prior the assembly process a collection of pre-designed MBBs was therefore specifically targeted for their requisite shape, geometry and directionality
necessary to augment a given anticipated net. In this context, the notion of design is not an exact science in the sense that a combination of building blocks often encodes for more than one net. Accordingly, these studies also led to serendipitous discoveries, which are nevertheless interesting in their own right. Note that functional molecular analogs of such nets were deliberately targeted for their anticipated properties, i.e. exhibit large/small cages or channels, etc.

The evolution of the MBB approach was evidenced whereby the transition from MOFs constructed from single metal ion nodes to highly symmetric multinuclear metal clusters was provided. The ability to targets nets which are exclusive to a combination of MBBs was a significant achievement and thereby represents the next hierarchical level (i.e. supramolecular building blocks) of design because it offers great potential towards prediction and synthesis of resultant structures. Briefly, this dissertation has contributed to reticular chemistry in the following ways:

(i) An isostructural series of cationic 3-periodic MOFs with soc topology have been deliberately prepared from the self-assembly of 6-connected In- and Fe-based $\mu_3$-oxygen centered trigonal prismatic MBBs with a 4-connected rectangular planar ligand, $\text{H}_4\text{-ABTC}$. This established a modular platform bearing unique structural and chemical features, i.e. accessible open metal centers and narrow pores with higher localized charge density. A systematic gas sorption study complimented by INS studies on selected compounds was conducted to gain insights into the preferential $\text{H}_2$-MOF interactions as a function of varying the metal center (e.g. In versus Fe), extra-framework counter ions (e.g. $\text{NO}_3^-$ versus $\text{Cl}^-$), and polarizability (e.g. $\text{Br}^-$ versus $\text{Cl}^-$). Exceptional $\text{H}_2$ uptake capacities at 77 K and 1 atm were reported and the $Q_{st}$ values at low loading revealed a
stronger interaction in the case of the Fe analogs as oppose to the In structures. The differences however were not all that substantial (≈ 1 kJ mol⁻¹) but it is important to emphasize that these values were even maintained at high loadings for all analogs. This feature is rarely observed in other materials in the sense that $Q_{st}$ decreases significantly at higher loadings.

(ii) A platform of 4-connected 3-periodic neutral MOMs has been generated by employing a pillaring design strategy. Readily accessible layered structures (e.g. Kagomé and tetragonal lattices) which exhibit different pore shapes and sizes were covalently cross-linked using rigid diisophthalate tetracarboxylate pillars (e.g. $H_4$-ABTC, $H_4$-BIPATC, and $H_4$-BAYTC). Accordingly, the pillared Kagomé and tetragonal lattices afforded MOMs with nbo and lvt topology, respectively while the assembly of tetrahedral and square BUs led to the formation of the pts net. The former platform, in theory, permits a systematic sorption studies to be conducted whereby the effect of metal cation, pore size and shape on H₂-MOF interactions could be independently assessed. The frameworks however were plagued by activation issues and therefore further studies are needed to address this issue.

(iii) A higher level of structural complexity was delineated through the introduction of SBBs in the form of MOP (i.e. small rhombihexahedron and cubohemiocatledron), in which case the corresponding vertex figure represents a tertiary building unit. The relationship between the SBB and a specific net illustrates the potential to derive pathways for the construction of 3D MOFs from SBBs that when rigidly cross-linked are uniquely suited for a particular net. That such SBBs can be exploited to form MOFs via a crystal engineering approach implies that polyhedral SBBs are amenable to
crystal design approaches that facilitate the generation of nets that cannot be readily obtained using traditional MBBs, that the limit of scale has not yet been realized and that a high degree of fine-tunability will be feasible for such materials. Future work will focus upon the properties of the \textbf{fcc} and \textbf{rht} platforms with regards to their gas storage, catalytic and sensing capabilities.

(iv) The direct synthesis of a series of porous anionic In- and Ga-based MOFs with \textbf{ctn} topology was reported. Charge balance is provided in the form of various-sized extra-framework organic cations, which were shown to be readily exchanged for divalent metal ions. Accordingly, this system provides a pathway to fine-tune the pore metrics of these materials as to influence the gas sorption behavior. Unfortunately, due to lack of instrument time we were unable to complete this study and no correlation between the sorption properties and the size of the organic cation was provided. Nevertheless, preliminary gas sorption studies did reveal constant $Q_{st}$ values estimated to be 7.0 kJ mol$^{-1}$, at both low and high loadings for the In- and Ga-based analogs. These tentative results therefore support the effects and pore size and electrostatic on H$_2$-MOF interactions, as these MOFs do not contain any open metal sites. We anticipate that larger organic cations will lead to enhanced binding affinities. Finally, to the best of our knowledge we reported the first example of a 3-periodic MOF constructed from four different types of MBBs and therefore is rationalized as a quaternary MOF.

6.2. Future Prospects

This dissertation has highlighted a handful of extended structures but in the big picture they represent only a diminutive percentage of the many thousands of structures
that have been reported to date. Without a doubt, this field has witnessed tremendous
success in a short period of time concerning advancements in design, as evidenced by the
transition towards targeted functional MOMs with intended properties. If the field
continues to expand at this alarming pace and scientists continue to be creative then it
surely is a conceivable thought that made-to-order MOMs will be a way of the future.

In my personal opinion, future research studies should place a primary focus on
conducting a comprehensive evaluation of existing structures to understand their potential
properties and surface chemistry (e.g. in-depth adsorption characterization studies),
particularly with regards to sample activation. Significant advancements in recent years
in the computational area would be a nice compliment to aid in these studies. This
dissertation is an example of this concept whereby a pool of structures was reported but it
contains many incomplete studies. In hindsight, it would be have much more informative
to focus on a particular set of platforms because this would ultimately provide more
meaningful information and provide a clearer vision as to which direction to move
forward.
Appendix A. Crystal data and structure refinement for Select Compounds

Table A.1. Compound 1 \{In(NO_3)_3 soc-MOF\}.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification Code</td>
<td>1</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{24}H_{21}In_{3}N_{4}O_{22}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1061.91</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Cubic, P-43n</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>\begin{align*} a &amp;= 22.4567(11) \text{ Å} \ \alpha &amp;= 90^\circ \end{align*}</td>
</tr>
<tr>
<td>Volume</td>
<td>11325.0(10) Å</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>8, 1.246 Mg/m^3</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>1.270 mm(^{-1})</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.03° to 25.01°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-15 \leq h \leq 15, 0 \leq k \leq 18, 1 \leq l \leq 26</td>
</tr>
<tr>
<td>Reflections collected / unique / observed</td>
<td>3352 / 1819 [R(int) = 0.0572]</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F^2</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>3334 / 6 / 210</td>
</tr>
<tr>
<td>Goodness-of-fit on F^2</td>
<td>1.039</td>
</tr>
<tr>
<td>Final R indices [I &gt; 2σ(I)]</td>
<td>R_1 = 0.0680, wR_2 = 0.1760</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R_1 = 0.0855, wR_2 = 0.1844</td>
</tr>
</tbody>
</table>
Appendix A (continued)

Table A.2. Compound 2 \{Fe(NO_3)_3 \text{soc}-MOF\}.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification Code</td>
<td>2</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{24}H_{16.33}Fe_{3}N_{4}O_{19.67}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>842.95</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.77090 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Cubic, P-43n</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 21.9524(6) Å, α = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>10579.0(5) Å</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>8, 1.059 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>1.078 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>3389</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.01 x 0.01 x 0.01 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>3.77° to 27.55°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-6 ≤ h ≤ 26, -24 ≤ k ≤ 10, -7 ≤ l ≤ 25</td>
</tr>
<tr>
<td>Reflections collected / unique / observed</td>
<td>12785 / 2945 [R(int) = 0.0700]</td>
</tr>
<tr>
<td>Completeness to theta = 27.55</td>
<td>99.3 %</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9893 and 0.9893</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>2945 / 4 / 149</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.064</td>
</tr>
<tr>
<td>Final R indices [I &gt;2σ(I)]</td>
<td>R1 = 0.0471, wR2 = 0.1265</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0534, wR2 = 0.1293</td>
</tr>
<tr>
<td>Absolute structure parameter</td>
<td>0.08(3)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.532 and -0.608 e.A⁻³</td>
</tr>
</tbody>
</table>
### Table A.3. Compound 3 \{FeCl$_3$ soc-MOF\}.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification Code</td>
<td>3</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C$<em>{24}$ H$</em>{15}$ Cl Fe$_3$ N$<em>3$ O$</em>{16}$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>804.39</td>
</tr>
<tr>
<td>Temperature</td>
<td>225(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Cubic, P-43n</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>$a = 21.8720(9)$ Å, $\alpha = 90^\circ$</td>
</tr>
<tr>
<td>Volume</td>
<td>10463.2(7) Å $^3$</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>8, 1.021 Mg/m$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>7.477 mm$^{-1}$</td>
</tr>
<tr>
<td>F(000)</td>
<td>3224</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.04 x 0.04 x 0.04 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.86$^\circ$ to 64.98$^\circ$</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>$-17 \leq h \leq 25$, $-17 \leq k \leq 7$, $-24 \leq l \leq 10$</td>
</tr>
<tr>
<td>Reflections collected / unique / observed</td>
<td>12512 / 2672 [R(int) = 0.0980]</td>
</tr>
<tr>
<td>Completeness to theta = 64.98</td>
<td>98.0 %</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.7541 and 0.7541</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F$^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>2672 / 0 / 147</td>
</tr>
<tr>
<td>Goodness-of-fit on F$^2$</td>
<td>1.016</td>
</tr>
<tr>
<td>Final R indices [$I &gt; 2\sigma(I)$]</td>
<td>$R1 = 0.0621$, $wR2 = 0.1665$</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>$R1 = 0.0917$, $wR2 = 0.1804$</td>
</tr>
<tr>
<td>Absolute structure parameter</td>
<td>0.025(14)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.399 and -0.329 e.Å$^{-3}$</td>
</tr>
</tbody>
</table>
Table A.4. Compound 4 \{InCl$_3$ soc-MOF\}.

<table>
<thead>
<tr>
<th>Identification Code</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{24}$ H$</em>{23.70}$ Cl In$_3$ N$<em>3$ O$</em>{20.35}$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1059.69</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Cubic, P-43n</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>$a = 22.4570(3)$ Å, $\alpha = 90^\circ$</td>
</tr>
<tr>
<td>Volume</td>
<td>$11325.4(3)$ Å$^3$</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>8, 1.243 Mg/m$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>10.603 mm$^{-1}$</td>
</tr>
<tr>
<td>F(000)</td>
<td>4124</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.10 x 0.10 x 0.10 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>5.57$^\circ$ to 68.14$^\circ$</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>$-24 \leq h \leq 26$, $-24 \leq k \leq 26$, $-16 \leq l \leq 23$</td>
</tr>
<tr>
<td>Reflections collected / unique / observed</td>
<td>27765 / 3412 [R(int) = 0.0688]</td>
</tr>
<tr>
<td>Completeness to theta = 68.14</td>
<td>99.2 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.4169 and 0.4169</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F$^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>3412 / 0 / 175</td>
</tr>
<tr>
<td>Goodness-of-fit on F$^2$</td>
<td>1.053</td>
</tr>
<tr>
<td>Final R indices [$I &gt; 2\sigma(I)$]</td>
<td>R1 = 0.0385, wR2 = 0.1116</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0417, wR2 = 0.1139</td>
</tr>
<tr>
<td>Absolute structure parameter</td>
<td>0.000(15)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.906 and -0.637 e.A$^{-3}$</td>
</tr>
</tbody>
</table>
### Table A.5. Compound 5 \{InBr$_3$ soc-MOF\}

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification Code</td>
<td>5</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C$<em>{24}$ H$</em>{25.50}$ Br$_3$ N$<em>3$ O$</em>{21.25}$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1120.34</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Cubic, P-43n</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 22.4530(4) Å</td>
</tr>
<tr>
<td>Volume</td>
<td>11319.4(3) Å</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>8, 1.315 Mg/m$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>11.021 mm$^{-1}$</td>
</tr>
<tr>
<td>F(000)</td>
<td>4340</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.10 x 0.10 x 0.10 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>4.82° to 67.40°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-25 $\leq$ h $\leq$ 24, -25 $\leq$ k $\leq$ 18, -15 $\leq$ l $\leq$ 26</td>
</tr>
<tr>
<td>Reflections collected / unique / observed</td>
<td>24026 / 3334 [R(int) = 0.0771]</td>
</tr>
<tr>
<td>Completeness to theta = 67.40</td>
<td>98.5 %</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.4053 and 0.4053</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F$^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>3334 / 6 / 182</td>
</tr>
<tr>
<td>Goodness-of-fit on F$^2$</td>
<td>1.076</td>
</tr>
<tr>
<td>Final R indices indices [$I &gt; 2\sigma(I)$]</td>
<td>R1 = 0.0391, wR2 = 0.1121</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0426, wR2 = 0.1145</td>
</tr>
<tr>
<td>Absolute structure parameter</td>
<td>0.002(14)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.816 and -0.523 e.A$^{-3}$</td>
</tr>
</tbody>
</table>
Table A.6. Compound 6 \{kgm\ lattice\}.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification Code</td>
<td>6</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C16 H14 Cu2 N2 O10</td>
</tr>
<tr>
<td>Formula weight</td>
<td>521.38</td>
</tr>
<tr>
<td>Temperature</td>
<td>293(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Hexagonal, P-3</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>(a = 18.521(3) \text{ Å} \quad \alpha = 90^\circ)</td>
</tr>
<tr>
<td></td>
<td>(b = 18.521(3) \text{ Å} \quad \beta = 90^\circ)</td>
</tr>
<tr>
<td></td>
<td>(c = 10.594(2) \text{ Å} \quad \gamma = 120^\circ)</td>
</tr>
<tr>
<td>Volume</td>
<td>3147.2(9) Å(^3)</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>3, 0.901 Mg/m(^3)</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>1.049 mm(^{-1})</td>
</tr>
<tr>
<td>F(000)</td>
<td>846</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.10 x 0.05 x 0.03 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.27(^\circ) to 25.02(^\circ)</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>(-11 \leq h \leq 18, -16 \leq k \leq 21, -8 \leq l \leq 12)</td>
</tr>
<tr>
<td>Reflections collected / unique / observed</td>
<td>6115 / 3698 [R(int) = 0.0742]</td>
</tr>
<tr>
<td>Completeness to theta = 25.02(^\circ)</td>
<td>99.2 %</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9692 and 0.9024</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on (F^2)</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>3698 / 0 / 149</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>0.786</td>
</tr>
<tr>
<td>Final R indices ([I &gt; 2\sigma(I)])</td>
<td>(R1 = 0.0728, \text{wR}2 = 0.1550)</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>(R1 = 0.1247, \text{wR}2 = 0.1676)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.810 and -0.517 e.A(^{-3})</td>
</tr>
</tbody>
</table>
## Table A.7. Compound 7 {sql lattice}.

<table>
<thead>
<tr>
<th>Identification Code</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C23 H25 In N4 O11</td>
</tr>
<tr>
<td>Formula weight</td>
<td>648.29</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, C2/c</td>
</tr>
</tbody>
</table>
| Unit cell dimensions| a = 15.533(3) Å \(\alpha = 90^\circ\)  
b = 12.515(2) Å \(\beta = 90.254(3)^\circ\) 
c = 13.320(3) Å \(\gamma = 90^\circ\) |
| Volume              | 2588.9(9) Å³ |
| Z, Calculated density| 4, 1.663 Mg/m³ |
| Absorption coefficient | 0.981 mm⁻¹ |
| F(000)              | 1312 |
| Crystal size        | 0.10 x 0.10 x 0.10 mm |
| Theta range for data collection | 2.09° to 25.25° |
| Limiting indices    | -18 \(\leq h \leq 17\), -5 \(\leq k \leq 15\), -15 \(\leq l \leq 15\) |
| Reflections collected / unique / observed | 5129 / 2216 [R(int) = 0.0322] |
| Completeness to theta = 25.25° | 95.1 % |
| Max. and min. transmission | 0.9083 and 0.9083 |
| Refinement method   | Full-matrix least-squares on F² |
| Data / restraints / parameters | 2216 / 0 / 195 |
| Goodness-of-fit on F² | 1.016 |
| Final R indices \([I > 2\sigma(I)]\) | R1 = 0.0325, wR2 = 0.0834 |
| R indices (all data) | R1 = 0.0378, wR2 = 0.0863 |
| Largest diff. peak and hole | 0.604 and -0.512 e.A⁻³ |
Table A.8. Compound 8 \{Cu(ABTC)\}_m-MOF\}.

<table>
<thead>
<tr>
<th>Identification Code</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{24}H_{9}Cu_{3}N_{3}O_{15}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>769.96</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Rhombohedral, R-3m</td>
</tr>
</tbody>
</table>
| Unit cell dimensions| a = 22.9196(8) Å \(\alpha = 90^\circ\)  
b = 22.9196(8) Å \(\beta = 90^\circ\)  
c = 19.9060(7) Å \(\gamma = 120^\circ\) |
| Volume              | 9055.8(5) Å³ |
| Z, Calculated density | 6, 0.847 Mg/m³ |
| Absorption coefficient | 1.567 mm⁻¹ |
| F(000)              | 2286 |
| Crystal size        | 0.10 x 0.10 x 0.10 mm |
### Table A.9. Compound 9 \{Zn(ABTC) nbo\}.

<table>
<thead>
<tr>
<th>Identification Code</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C27.33 H6 N4.33 O10.67 Zn2</td>
</tr>
<tr>
<td>Formula weight</td>
<td>696.44</td>
</tr>
<tr>
<td>Temperature</td>
<td>293(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
</tbody>
</table>
| Unit cell dimensions| a = 21.8708(2) Å \( \alpha = 90^\circ \)  
                      | b = 19.4600(2) Å \( \beta = 99.1640(10)^\circ \)  
                      | c = 29.3141(3) Å \( \gamma = 90^\circ \) |
| Volume              | 12317.0(2) Å³ |
| Z, Calculated density| 12, 1.127 Mg/m³ |
| Absorption coefficient| 1.854 mm⁻¹ |
| F(000)              | 4148 |
| Crystal size        | 0.10 x 0.08 x 0.08 mm |
| Theta range for data collection | 2.35° to 67.41° |
| Limiting indices    | -25 \( \leq h \leq 25 \), -22 \( \leq k \leq 22 \), -35 \( \leq l \leq 33 \) |
| Reflections collected / unique / observed | 106455 / 21700 [R(int) = 0.0715] |
| Completeness to theta = 67.41° | 97.9 % |
| Max. and min. transmission | 0.8658 and 0.8363 |
| Refinement method   | Full-matrix least-squares on F² |
| Data / restraints / parameters | 21700 / 0 / 847 |
| Goodness-of-fit on F^² | 1.047 |
| Final R indices \([I > 2\sigma(I)]\) | R1 = 0.0906, wR2 = 0.2639 |
| R indices (all data) | R1 = 0.1045, wR2 = 0.2768 |
| Largest diff. peak and hole | 1.298 and -1.630 e.A⁻³ |
Appendix A (continued)

**Table A.10. Compound 11 \{Cu(BAYTC)_{nbo}\}.**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Identification Code</strong></td>
<td>11</td>
</tr>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C_{26}H_{10}Cu_{2}O_{10}</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>609.44</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>293(2) K</td>
</tr>
<tr>
<td><strong>Wavelength</strong></td>
<td>0.71073 Å</td>
</tr>
<tr>
<td><strong>Crystal system, space group</strong></td>
<td>Rhombohedral, R-3m</td>
</tr>
<tr>
<td><strong>Unit cell dimensions</strong></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>15.527(3) Å</td>
</tr>
<tr>
<td>α</td>
<td>90°</td>
</tr>
<tr>
<td>b</td>
<td>18.527(3) Å</td>
</tr>
<tr>
<td>β</td>
<td>90°</td>
</tr>
<tr>
<td>c</td>
<td>54.221(1) Å</td>
</tr>
<tr>
<td>γ</td>
<td>120°</td>
</tr>
<tr>
<td><strong>Volume</strong></td>
<td>16117(5) Å³</td>
</tr>
<tr>
<td><strong>Z, Calculated density</strong></td>
<td>9, 0.565 Mg/m³</td>
</tr>
<tr>
<td><strong>Absorption coefficient</strong></td>
<td>0.614 mm⁻¹</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>2736</td>
</tr>
<tr>
<td><strong>Crystal size</strong></td>
<td>0.25 x 0.18 x 0.15 mm</td>
</tr>
<tr>
<td><strong>Theta range for data collection</strong></td>
<td>3.85° to 25.02°</td>
</tr>
<tr>
<td><strong>Limiting indices</strong></td>
<td>-10 ≤ h ≤ 15, -10 ≤ k ≤ 21, -62 ≤ l ≤ 64</td>
</tr>
<tr>
<td><strong>Reflections collected / unique / observed</strong></td>
<td>12739 / 3439 [R(int) = 0.1141]</td>
</tr>
<tr>
<td><strong>Completeness to theta = 25.02°</strong></td>
<td>98.6 %</td>
</tr>
<tr>
<td><strong>Max. and min. transmission</strong></td>
<td>1.00 and 0.474</td>
</tr>
<tr>
<td><strong>Refinement method</strong></td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td><strong>Data / restraints / parameters</strong></td>
<td>3439 / 0 / 97</td>
</tr>
<tr>
<td><strong>Goodness-of-fit on F²</strong></td>
<td>1.458</td>
</tr>
<tr>
<td><strong>Final R indices [I &gt; 2σ(I)]</strong></td>
<td>R1 = 0.1304, wR2 = 0.4094</td>
</tr>
<tr>
<td><strong>R indices (all data)</strong></td>
<td>R1 = 0.1889, wR2 = 0.4416</td>
</tr>
<tr>
<td><strong>Largest diff. peak and hole</strong></td>
<td>1.407 and -0.517 e.A⁻³</td>
</tr>
</tbody>
</table>
Appendix A (continued)

<table>
<thead>
<tr>
<th>Table A.11. Compound 12 {Cu(BIPATC) nbo}.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification Code</td>
</tr>
<tr>
<td>Empirical formula</td>
</tr>
<tr>
<td>Formula weight</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Wavelength</td>
</tr>
<tr>
<td>Crystal system, space group</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
</tr>
<tr>
<td>a = 32.461(12) Å</td>
</tr>
<tr>
<td>b = 18.024(6) Å</td>
</tr>
<tr>
<td>c = 19.748(7) Å</td>
</tr>
<tr>
<td>Volume</td>
</tr>
<tr>
<td>Z, Calculated density</td>
</tr>
<tr>
<td>Absorption coefficient</td>
</tr>
<tr>
<td>F(000)</td>
</tr>
<tr>
<td>Crystal size</td>
</tr>
<tr>
<td>Theta range for data collection</td>
</tr>
<tr>
<td>Limiting indices</td>
</tr>
<tr>
<td>-28 ≤ h ≤ 28, -10 ≤ k ≤ 16, -17 ≤ l ≤ 17</td>
</tr>
<tr>
<td>Reflections collected / unique / observed</td>
</tr>
<tr>
<td>Completeness to theta = 18.53</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
</tr>
<tr>
<td>Refinement method</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
</tr>
<tr>
<td>Final R indices [ I &gt; 2σ(I) ]</td>
</tr>
<tr>
<td>R indices (all data)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
</tr>
</tbody>
</table>
Table A.12. Compound 13 \{\text{Cu(BIPATC) lvt-MOF}\}.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Identification Code</td>
<td>13</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C38 H28 Cu2 N4 O23</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1035.72</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Orthorhombic, Imma</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 15.209(1) Å , (\alpha = 90^\circ)</td>
</tr>
<tr>
<td></td>
<td>b = 36.441(3) Å , (\beta = 90^\circ)</td>
</tr>
<tr>
<td></td>
<td>c = 10.324(1) Å , (\gamma = 90^\circ)</td>
</tr>
<tr>
<td>Volume</td>
<td>5721.8(9) Å³</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>4, 1.202 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>1.542 mm(^{-1})</td>
</tr>
<tr>
<td>F(000)</td>
<td>2104</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.10 x 0.10 x 0.10 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>4.85(^{\circ}) to 67.64(^{\circ})</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-17 (\leq h \leq 13), -41 (\leq k \leq 43), -10 (\leq l \leq 12)</td>
</tr>
<tr>
<td>Reflections collected / unique / observed</td>
<td>12397 / 2685 [R(int) = 0.0479]</td>
</tr>
<tr>
<td>Completeness to theta = 67.64</td>
<td>97.7%</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.8611 and 0.8611</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F(^2)</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>2685 / 0 / 213</td>
</tr>
<tr>
<td>Goodness-of-fit on F(^2)</td>
<td>1.102</td>
</tr>
<tr>
<td>Final R indices ([I &gt; 2\sigma(I)])</td>
<td>R1 = 0.0574, wR2 = 0.1603</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0705, wR2 = 0.1722</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.631 and -0.424 e.A(^{-3})</td>
</tr>
<tr>
<td>Identification Code</td>
<td>14</td>
</tr>
<tr>
<td>---------------------</td>
<td>----</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C28 H34 Yb2 N8 O18</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1116.69</td>
</tr>
<tr>
<td>Temperature</td>
<td>298(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, C2/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 27.703(1) Å, α = 90°, b = 9.325(4) Å, β = 121.379(2)°, c = 21.117(1) Å, γ = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>4657(4) Å³</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>4, 1.678 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>4.072 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>2280</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.07 x 0.06 x 0.05 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.72° to 25.23°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-32 ≤ h ≤ 32, -11 ≤ k ≤ 11, -13 ≤ l ≤ 25</td>
</tr>
<tr>
<td>Reflections collected / unique / observed</td>
<td>11745 / 4150 [R(int) = 0.1267]</td>
</tr>
<tr>
<td>Completeness to theta = 25.23°</td>
<td>98.4 %</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>1.000 and 0.074</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>4150 / 0 / 272</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>0.905</td>
</tr>
<tr>
<td>Final R indices [I &gt; 2σ(I)]</td>
<td>R1 = 0.0609, wR2 = 0.1389</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.1331, wR2 = 0.1742</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>1.496 and -1.876 e Å⁻³</td>
</tr>
</tbody>
</table>
Table A.14. Compound 15. \{Er(ABTC) \textit{lvt-MOF}\}.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification Code</td>
<td>15</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C31 H34 Er2 N9 O22</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1219.19</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, C2/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>[a = 27.953(3) \text{ Å} \quad \alpha = 90^\circ]</td>
</tr>
<tr>
<td></td>
<td>[b = 9.299(1) \text{ Å} \quad \beta = 121.923(2)^\circ]</td>
</tr>
<tr>
<td></td>
<td>[c = 21.288(2) \text{ Å} \quad \gamma = 90^\circ]</td>
</tr>
<tr>
<td>Volume</td>
<td>4697.0(9) Å³</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>4, 1.724 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>3.634 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>2380</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.40 x 0.30 x 0.20 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.25° to 28.31°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-35 ≤ h ≤ 17, -12 ≤ k ≤ 12, -23 ≤ l ≤ 27</td>
</tr>
<tr>
<td>Reflections collected / unique / observed</td>
<td>11877 / 4881 [R(int) = 0.0235]</td>
</tr>
<tr>
<td>Completeness to theta = 28.31°</td>
<td>83.3 %</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>1.000 and 0.464</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>4881 / 0 / 274</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.171</td>
</tr>
<tr>
<td>Final R indices ([I &gt; 2\sigma(I)])</td>
<td>R1 = 0.0466, wR2 = 0.1354</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0566, wR2 = 0.1791</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>2.123 and -1.984 e.A⁻³</td>
</tr>
</tbody>
</table>
### Table A.15. Compound 16 \{In(ABTC) pts-MOF\}.

<table>
<thead>
<tr>
<th>Identification Code</th>
<th>16</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C18 H8 In N3 O8</td>
</tr>
<tr>
<td>Formula weight</td>
<td>509.09</td>
</tr>
<tr>
<td>Temperature</td>
<td>293(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, C2</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>(a = 14.778(3) \text{ Å} ) (\alpha = 90^\circ)</td>
</tr>
<tr>
<td></td>
<td>(b = 13.081(3) \text{ Å} ) (\beta = 102.37(3)^\circ)</td>
</tr>
<tr>
<td></td>
<td>(c = 21.597(4) \text{ Å} ) (\gamma = 90^\circ)</td>
</tr>
<tr>
<td>Volume</td>
<td>4078.0(14) Å³</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>4, 0.826 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>4.863 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>992</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.20 x 0.20 x 0.20 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.09° to 49.99°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>(-13 \leq h \leq 14, -10 \leq k \leq 12, -21 \leq l \leq 19)</td>
</tr>
<tr>
<td>Reflections collected / unique / observed</td>
<td>6487 / 3318 [R(int) = 0.0619]</td>
</tr>
<tr>
<td>Completeness to theta = 49.99°</td>
<td>94.9 %</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.4430 and 0.4430</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>3318 / 1 / 28</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.217</td>
</tr>
<tr>
<td>Final R indices ([I &gt; 2\sigma(I)])</td>
<td>R₁ = 0.1122, wR² = 0.2762</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.1194, wR² = 0.2878</td>
</tr>
</tbody>
</table>
### Table A.16. Compound 17 \{In(ABTC) novel-MOF\}.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification Code</td>
<td>17</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C18 H8 In N3 O8</td>
</tr>
<tr>
<td>Formula weight</td>
<td>509.09</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, P21/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 9.926(2) Å                           α = 90°</td>
</tr>
<tr>
<td></td>
<td>b = 35.737(7) Å                          β = 98.088(4)°</td>
</tr>
<tr>
<td></td>
<td>c = 23.401(5) Å                          γ = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>8218(3) Å</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>8, 0.820 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>4.826 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>1984</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.10 x 0.10 x 0.10 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>3.82° to 67.81°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-10 ≤ h ≤ 11, -41 ≤ k ≤ 42, -27 ≤ l ≤ 27</td>
</tr>
<tr>
<td>Reflections collected / unique / observed</td>
<td>62551 / 14220 [R(int) = 0.1266]</td>
</tr>
<tr>
<td>Completeness to theta = 67.81°</td>
<td>95.5%</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.6440 and 0.6440</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>14220 / 0 / 494</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>0.956</td>
</tr>
<tr>
<td>Final R indices (I &gt; 2\sigma(I))</td>
<td>R1 = 0.0750, wR2 = 0.1976</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.1324, wR2 = 0.2229</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>1.304 and -1.560 e.A⁻³</td>
</tr>
</tbody>
</table>
### Appendix A (continued)

Table A.17. Compound 18. {porphyrin-based MOF}.

<table>
<thead>
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<th><strong>Identification Code</strong></th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C48 H20 Br4 In N4 O9</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>1231.14</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>100(2) K</td>
</tr>
<tr>
<td><strong>Wavelength</strong></td>
<td>1.54178 Å</td>
</tr>
<tr>
<td><strong>Crystal system, space group</strong></td>
<td>Orthorhombic, Pbca</td>
</tr>
</tbody>
</table>
| **Unit cell dimensions**| a = 26.734(17) Å, α = 90°  
   | b = 13.358(9) Å, β = 98.088(4)°  
   | c = 33.07(2) Å, γ = 90° |
| **Volume**              | 11810(13) Å³ |
| **Z, Calculated density** | 8, 1.385 Mg/m³ |
| **Absorption coefficient** | 6.771 mm⁻¹ |
| **F(000)**              | 4776 |
| **Crystal size**        | 0.04 x 0.02 x 0.02 mm |
| **Theta range for data collection** | 2.67° to 33.53° |
| **Limiting indices**    | -19 ≤ h ≤ 18, -9 ≤ k ≤ 9, -23 ≤ l ≤ 21 |
| **Reflections collected / unique / observed** | 8766 / 2238 [R(int) = 0.1783] |
| **Completeness to theta = 33.53°** | 98.4 % |
| **Max. and min. transmission** | 0.8765 and 0.7734 |
| **Refinement method**   | Full-matrix least-squares on F² |
| **Data / restraints / parameters** | 2238 / 0 / 290 |
| **Goodness-of-fit on F²** | 0.802 |
| **Final R indices [I > 2σ(I)]** | R1 = 0.0545, wR2 = 0.0939 |
| **R indices (all data)** | R1 = 0.1252, wR2 = 0.1103 |
| **Largest diff. peak and hole** | 0.378 and -0.302 e.A⁻³ |
Table A.18. Compound 19 \{Co₂(ABTC) pts-MOF\}.

<table>
<thead>
<tr>
<th>Identification Code</th>
<th>19</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₅₂ H₇₀ Co₄ N₆ O₂₆</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1430.87</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Orthorhombic, P₂₁₂₁₂₁</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>13.514(3) Å</td>
</tr>
<tr>
<td>b</td>
<td>13.766(3) Å</td>
</tr>
<tr>
<td>c</td>
<td>45.290(8) Å</td>
</tr>
<tr>
<td>Volume</td>
<td>8426(3) Å³</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>4, 1.353 Mg/m³</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.10 x 0.10 x 0.10 mm</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.053</td>
</tr>
<tr>
<td>Final R indices [I &gt; 2σ(I)]</td>
<td>R₁ = 0.0365, wR2 = 0.0997</td>
</tr>
</tbody>
</table>
### Table A.19. Compound 21. {Co(ABTC) pts-MOF}.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification Code</td>
<td>21</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C22 H22 Co N4 O10</td>
</tr>
<tr>
<td>Formula weight</td>
<td>561.37</td>
</tr>
<tr>
<td>Temperature</td>
<td>293(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, P21/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 11.024(4) Å, α = 90°</td>
</tr>
<tr>
<td></td>
<td>b = 22.005(7) Å, β = 105.094(6)°</td>
</tr>
<tr>
<td></td>
<td>c = 9.692(3) Å, γ = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>2270.1(13) Å³</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>4, 1.643Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>6.541 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>1156</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.15 x 0.10 x 0.06 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>4.02° to 38.77°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-8 ≤ h ≤ 8, -17 ≤ k ≤ 17, -7 ≤ l ≤ 7</td>
</tr>
<tr>
<td>Reflections collected / unique / observed</td>
<td>5015 / 1240 [R(int) = 0.0907]</td>
</tr>
<tr>
<td>Completeness to theta = 38.77°</td>
<td>97.8 %</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.6949 and 0.4403</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>1240 / 0 / 154</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.086</td>
</tr>
<tr>
<td>Final R indices [I &gt;2σ(I)]</td>
<td>R₁ = 0.0679, wR₂ = 0.1596</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.1242, wR₂ = 0.1804</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.521 and -0.381 e.A⁻³</td>
</tr>
</tbody>
</table>
### Table A.20. Compound 22. \{Mn(ABTC) pts-MOF\}.

<table>
<thead>
<tr>
<th>Identification Code</th>
<th>22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C19 H13 Mn N4 O9</td>
</tr>
<tr>
<td>Formula weight</td>
<td>497.01</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, C2/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 11.178(4) Å α = 90°</td>
</tr>
<tr>
<td></td>
<td>b = 22.103(7) Å β = 104.284(6)°</td>
</tr>
<tr>
<td></td>
<td>c = 9.723(3) Å γ = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>2327.9(13) Å³</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>4, 1.544 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.632 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>1084</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.1 x 0.1 x 0.1 mm</td>
</tr>
</tbody>
</table>
### Table A.21. Compound 23 {Ni(ABTC) fcc-MOF}.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification Code</td>
<td>23</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C18 H12 Ni2 N2 O11</td>
</tr>
<tr>
<td>Formula weight</td>
<td>549.68</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Cubic, Fm-3</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>( a = 22.340(7) ) Å ( \alpha = 90^\circ )</td>
</tr>
<tr>
<td>Volume</td>
<td>30782.0(12) Å³</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>96, 0.660 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.757 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>6125</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.10 x 0.10 x 0.10 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.30° to 19.98°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-30 ( \leq h \leq 18 ), -30 ( \leq k \leq 30 ), -30 ( \leq l \leq 29 )</td>
</tr>
<tr>
<td>Reflections collected / unique / observed</td>
<td>19812 / 1153 [R(int) = 0.1212]</td>
</tr>
<tr>
<td>Completeness to theta = 19.98</td>
<td>88.5 %</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9631 and 0.9631</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>1153 / 5 / 62</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.111</td>
</tr>
<tr>
<td>Final R indices ( I &gt; 2\sigma(I) )</td>
<td>( R_1 = 0.1432, wR2 = 0.3462 )</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>( R_1 = 0.1575, wR2 = 0.3575 )</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.887 and -0.851 e.A⁻³</td>
</tr>
</tbody>
</table>
### Table A.22. Compound 25 \{Cu(PTMO) rht-MOF\}.

<table>
<thead>
<tr>
<th>Identification Code</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C33 H18 Cu3 O18</td>
</tr>
<tr>
<td>Formula weight</td>
<td>893.09</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Cubic, Fm-3m</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 41.4786(3) Å, α = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>71362.9(9) Å³</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>32, 0.665 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>1.115 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>14304</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.10 x 0.10 x 0.10 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.84° to 58.55°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-45 ≤ h ≤ 33, -45 ≤ k ≤ 42, -37 ≤ l ≤ 45</td>
</tr>
<tr>
<td>Reflections collected / unique / observed</td>
<td>40041 / 2529 [R(int) = 0.1454]</td>
</tr>
<tr>
<td>Completeness to theta = 58.55</td>
<td>99.9 %</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.8967 and 0.8967</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>2529 / 0 / 45</td>
</tr>
<tr>
<td>Goodness-of-fit on F^²</td>
<td>1.032</td>
</tr>
<tr>
<td>Final R indices [I &gt;2σ(I)]</td>
<td>R1 = 0.1172, wR2 = 0.3004</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.1390, wR2 = 0.3213</td>
</tr>
<tr>
<td>Absolute structure parameter</td>
<td>0.002(13)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.807 and -0.972 e.A⁻³</td>
</tr>
</tbody>
</table>
### Table A.23. Compound 26 {Zn(PTMOI) rht-MOF}.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification Code</td>
<td>26</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C40.50 H18 N2.50 O18 Zn3</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1023.68</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Tetragonal, I4/m</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 29.271(2) Å, α = 90°</td>
</tr>
<tr>
<td></td>
<td>b = 29.271(2) Å, β = 105.094(6)o</td>
</tr>
<tr>
<td></td>
<td>c = 41.637(3) Å, γ = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>35674(4) Å³</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>16, 0.762 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>1.275 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>8200</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.05 x 0.05 x 0.05 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.84° to 39.08°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-12 ≤ h ≤ 23, -22 ≤ k ≤ 23, -22 ≤ l ≤ 31</td>
</tr>
<tr>
<td>Reflections collected / unique / observed</td>
<td>23763 / 4903 [R(int) = 0.0470]</td>
</tr>
<tr>
<td>Completeness to theta = 39.08°</td>
<td>93.8 %</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9390 and 0.9390</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>4903 / 0 / 262</td>
</tr>
<tr>
<td>Goodness-of-fit on F^2</td>
<td>1.147</td>
</tr>
<tr>
<td>Final R indices [I &gt; 2σ(I)]</td>
<td>R1 = 0.0877, wR2 = 0.2579</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0979, wR2 = 0.2721</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.813 and -0.634 e.A⁻³</td>
</tr>
</tbody>
</table>
**Appendix A (continued)**

<table>
<thead>
<tr>
<th>Table A.24. Compound 29 {Cu(ABPTMOI) rht-MOF}.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Identification Code</strong></td>
</tr>
<tr>
<td><strong>Empirical formula</strong></td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
</tr>
<tr>
<td><strong>Wavelength</strong></td>
</tr>
<tr>
<td><strong>Crystal system, space group</strong></td>
</tr>
<tr>
<td><strong>Unit cell dimensions</strong></td>
</tr>
<tr>
<td><strong>Volume</strong></td>
</tr>
<tr>
<td><strong>Z, Calculated density</strong></td>
</tr>
<tr>
<td><strong>Absorption coefficient</strong></td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
</tr>
<tr>
<td><strong>Crystal size</strong></td>
</tr>
<tr>
<td><strong>Theta range for data collection</strong></td>
</tr>
<tr>
<td><strong>Limiting indices</strong></td>
</tr>
<tr>
<td><strong>Reflections collected / unique / observed</strong></td>
</tr>
<tr>
<td><strong>Completeness to theta = 33.53°</strong></td>
</tr>
<tr>
<td><strong>Max. and min. transmission</strong></td>
</tr>
<tr>
<td><strong>Refinement method</strong></td>
</tr>
<tr>
<td><strong>Data / restraints / parameters</strong></td>
</tr>
<tr>
<td><strong>Goodness-of-fit on F^2</strong></td>
</tr>
<tr>
<td><strong>Final R indices [I &gt;2σ(I)]</strong></td>
</tr>
<tr>
<td><strong>R indices (all data)</strong></td>
</tr>
<tr>
<td><strong>Largest diff. peak and hole</strong></td>
</tr>
</tbody>
</table>
### Table A.25. Compound 30 \{Mn ast-ZMOF\}.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification Code</td>
<td>30</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C86 H120 Mn12 N56 O60</td>
</tr>
<tr>
<td>Formula weight</td>
<td>3664.56</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Cubic, (Fm)-3</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>(a = 26.291(6) \text{ Å} \quad \alpha = 90^\circ)</td>
</tr>
<tr>
<td>Volume</td>
<td>18172(7) Å</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>4, 1.313 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.888 mm(^{-1})</td>
</tr>
<tr>
<td>F(000)</td>
<td>6999</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.10 x 0.10 x 0.10 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.19° to 20.43°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>(-25 \leq h \leq 6, -21 \leq k \leq 13, -3 \leq l \leq 25)</td>
</tr>
<tr>
<td>Reflections collected / unique / observed</td>
<td>3669/817 [R(int) = 0.04101]</td>
</tr>
<tr>
<td>Completeness to theta = 20.43°</td>
<td>98.0 %</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9165 and 0.9165</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on (F^2)</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>816 / 4 / 103</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>1.245</td>
</tr>
<tr>
<td>Final R indices ([I &gt;2\sigma(I)])</td>
<td>(R1 = 0.0841, \text{ wR2} = 0.2320)</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>(R1 = 0.0952, \text{ wR2} = 0.2416)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.339 and -0.464 e.A(^{-3})</td>
</tr>
</tbody>
</table>
## Table A.26. Compound 31 {In(BTC) ctn-MOF}.

<table>
<thead>
<tr>
<th>Identification Code</th>
<th>31</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C14 H10 In N O8</td>
</tr>
<tr>
<td>Formula weight</td>
<td>435.05</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Cubic, I-43d</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 20.417(2) Å, (\alpha = 90^\circ)</td>
</tr>
<tr>
<td>Volume</td>
<td>8511.2(17) Å³</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>12, 1.019 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.857 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>2568</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.20 x 0.20 x 0.20 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>3.16° to 24.69°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-22 ≤ h ≤ 7, -16 ≤ k ≤ 16, -1 ≤ l ≤ 24</td>
</tr>
<tr>
<td>Reflections collected / unique / observed</td>
<td>3692 / 1207 [R(int) = 0.0425]</td>
</tr>
<tr>
<td>Completeness to theta</td>
<td>49.99°</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9192 and 0.9192</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>1207 / 0 / 49</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.054</td>
</tr>
<tr>
<td>Final R indices ([I &gt; 2\sigma(I)])</td>
<td>R1 = 0.0489, wR2 = 0.1255</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0654, wR2 = 0.1322</td>
</tr>
<tr>
<td>Absolute structure parameter</td>
<td>0.03(9)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.421 and -0.289 e.A⁻³</td>
</tr>
</tbody>
</table>
### Table A.27. Compound 32 \{Ga(BTC)$_{ctn}$-MOF\}

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification Code</td>
<td>32</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C$<em>{14}$ H$</em>{12}$ Ga$_1$ N$<em>1$ O$</em>{11}$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>439.97</td>
</tr>
<tr>
<td>Temperature</td>
<td>173(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Cubic, I-43d</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>$a = 19.982(6)$ Å, $a = 90^\circ$</td>
</tr>
<tr>
<td>Volume</td>
<td>7978(4) Å$^3$</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>12, 1.116 Mg/m$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>1.077 mm$^{-1}$</td>
</tr>
<tr>
<td>F(000)</td>
<td>2704</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.20 x 0.20 x 0.20 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.88$^\circ$ to 20.78$^\circ$</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>$-12 \leq h \leq 3$, $-8 \leq k \leq 18$, $-3 \leq l \leq 19$</td>
</tr>
<tr>
<td>Reflections collected / unique / observed</td>
<td>1403 / 519 [R(int) = 0.1293]</td>
</tr>
<tr>
<td>Completeness to theta = 20.78$^\circ$</td>
<td>96.1%</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9000 and 0.9000</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F$^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>519 / 0 / 61</td>
</tr>
<tr>
<td>Goodness-of-fit on F$^2$</td>
<td>1.160</td>
</tr>
<tr>
<td>Final R indices [$I &gt; 2\sigma(I)$]</td>
<td>R1 = 0.0996, wR2 = 0.1760</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.1430, wR2 = 0.1995</td>
</tr>
<tr>
<td>Absolute structure parameter</td>
<td>0.02(10)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.248 and -0.228 e.A$^{-3}$</td>
</tr>
</tbody>
</table>
### Table A.28. Compound 36 \{In(BTC) novel-MOF\}.

<table>
<thead>
<tr>
<th>Identification Code</th>
<th>36</th>
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</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C2040 H672 Br48 In240 O1536</td>
</tr>
<tr>
<td>Formula weight</td>
<td>81146.26</td>
</tr>
<tr>
<td>Temperature</td>
<td>293(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Cubic, Fd-3m</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 50.546(5) Å, α = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>129138(22) Å³</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>1, 1.043Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>1.475 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>38640</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.04 x 0.04 x 0.04 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.09° to 20.84°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-18 ≤ h ≤ 50, -43 ≤ k ≤ 40, -27 ≤ l ≤ 50</td>
</tr>
<tr>
<td>Reflections collected / unique / observed</td>
<td>40013 / 3168 [R(int) = 0.1504]</td>
</tr>
<tr>
<td>Completeness to theta = 20.84°</td>
<td>99.2 %</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9433 and 0.9433</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>3168 / 18 / 213</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.096</td>
</tr>
<tr>
<td>Final R indices [I &gt;2σ(I)]</td>
<td>R1 = 0.0946, wR2 = 0.2226</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.1186, wR2 = 0.2392</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>1.237 and -1.047 e.A⁻³</td>
</tr>
</tbody>
</table>
Appendix B. Powder X-ray Diffraction (PXRD) Patterns for Select Compounds

Figure B.1. PXRD pattern for compound 1, \{\text{In(NO}_3\text{)}_3 \text{soc-MOF}\}.

Figure B.2. PXRD pattern for compound 2, \{\text{Fe(NO}_3\text{)}_3 \text{soc-MOF}\}.
Appendix B (Continued)

Figure B.3. PXRD pattern for compound 4, \{InCl$_3$ soc-MOF\}.

Figure B.4. PXRD pattern for compound 5, \{InBr$_3$ soc-MOF\}.
Appendix B (Continued)

Figure B.5. PXRD pattern for compound 6, \{Cu kgm-MOM\}.

Figure B.6. PXRD pattern for compound 8, \{Cu(ABTC) nbo-MOF\}.
Figure B.7. PXRD pattern for compound 9, \{\text{Zn(ABTC) nbo-MOF}\}.

Figure B.8. PXRD pattern for compound 13, \{\text{Cu(BIPATC) lvt-MOF}\}.
Appendix B (Continued)

**Figure B.9.** PXRD pattern for compound 14, \{Yb(ABTC) lvt-MOF\}.

**Figure B.10.** PXRD pattern for compound 15, \{Er(ABTC) lvt-MOF\}.
Appendix B (Continued)

Figure B.11. PXRD pattern for compound 16, \{\text{In(ABTC) pts-MOF}\}.

Figure B.12. PXRD pattern for compound 18, \{\text{porphyrin-based MOF}\}.
Appendix B (Continued)

Figure B.13. PXRD pattern for compound 23, \{\text{Ni(ABTC) fcu-MOF}\}.

Figure B.14. PXRD pattern for compound 24, \{\text{Co(ABTC) fcu-MOF}\}.
Appendix B (Continued)

Figure B.15. PXRD pattern for compound 25, \{Cu(PTMOI) rht-MOF\}.

Figure B.16. PXRD pattern for compound 26, \{Zn(PTMOI) rht-MOF\}.
Appendix B (Continued)

Figure B.17. PXRD pattern for compound 29, \{Mn ast-ZMOF\}.

Figure B.18. PXRD pattern for compound 31, \{In ctn-MOF\}.
Figure B.19. PXRD pattern for compound 32, \{Ga ctn-MOF\}.
Appendix C. TGA for Select Compounds

Figure C.1. Compound 1, \{In(NO_3)_3 soc-MOF\}, as-synthesized in DMF.

Figure C.2. Compound 1, \{In(NO_3)_3 soc-MOF\}, exchanged in CH_3CN.
Appendix C (Continued)

**Figure C.3.** Compound 2, {Fe(NO$_3$)$_3$ soc-MOF}, as-synthesized in DMF.

**Figure C.4.** Compound 2, {Fe(NO$_3$)$_3$ soc-MOF}, exchanged in CH$_3$CN.
Figure C.5. Compound 3, \{FeCl_3 soc-MOF\}, as-synthesized in DMF.

Figure C.6. Compound 3, \{FeCl_3 soc-MOF\}, exchanged in CH_3CN.
Figure C.7. Compound 4, \{InCl$_3$ soc-MOF\}, as-synthesized in DMF.

Figure C.8. Compound 4, \{InCl$_3$ soc-MOF\}, exchanged in CH$_3$CN.
Appendix C (Continued)

Figure C.9. Compound 5, \{InBr$_3$ soc-MOF\}, as-synthesized in DMF.

Figure C.10. Compound 5, \{InBr$_3$ soc-MOF\}, exchanged in CH$_3$CN.
Figure C.11. Compound 6, \{Cu kgm-MOF\}, as-synthesized in DMF.

Figure C.12. Compound 7, \{In sql-MOF\}, as-synthesized in DMF.
Figure C.13. Compound 8, \{\text{Cu(ABTC) nbo-MOF}\}, as-synthesized in DMF.

Figure C.14. Compound 9, \{\text{Zn(ABTC) nbo-MOF}\}, as-synthesized in DEF.
Figure C.15. Compound 13, \{Cu(BIPATC) lvt-MOF\}, as-synthesized in DMA.

Figure C.16. Compound 13, \{Cu(BIPATC) lvt-MOF\}, exchanged in chlorobenzene.
Figure C.17. Compound 14, \{\text{Yb(ABTC) lvt-MOF}\}, as-synthesized in DMF.

Figure C.18. Compound 15, \{\text{Er(ABTC) lvt-MOF}\}, as-synthesized in DMF.
Appendix C (Continued)

Figure C.19. Compound 16, \{\text{In(ABTC) pts-MOF}\}, as-synthesized in DMF.

Figure C.20. Compound 18, \{\text{porphyrin- based MOF}\}, as-synthesized in DMF.
Appendix C (Continued)

Figure C.21. Compound 19, \{\text{Co}_2(\text{ABTC})\text{pts-MOF}\}, as-synthesized in DMF.

Figure C.22. Compound 20, \{\text{Cd}_2(\text{ABTC})\text{pts-MOF}\}, as-synthesized in DMF.
Appendix C (Continued)

Figure C.23. Compound 21, \{Co(ABTC) pts-MOF\} in DMF.

Figure C.24. Compound 22, \{Mn(ABTC) pts-MOF\} in DMF.
Figure C.25. Compound 23, \{\text{Ni(ABTC) fcc-MOF}\}, as-synthesized in DMF.

Figure C.26. Compound 24, \{\text{Co(ABTC) fcc-MOF}\}, as-synthesized in DMF.
Appendix C (Continued)

Figure C.27. Compound 25, \{Cu(PTMOI) rht-MOF\}, as-synthesized in DMF.

Figure C.28. Compound 25, \{Cu(PTMOI) rht-MOF\}, exchanged in methanol.
Appendix C (Continued)

Figure C.29. Compound 26, \{Zn(PTMOI) \textit{rht}-MOF\}, as-synthesized in DMF.

Figure C.30. Compound 27, \{Mn(PTMOI) \textit{rht}-MOF\}, as-synthesized in DMF.
Appendix C (Continued)

Figure C.31. Compound 28, \{Co(PTMOI) rht-MOF\}, as-synthesized in DMF.

Figure C.32. Compound 30, \{Mn(ImDC) ast-MOF\}, as-synthesized in DMF.
Appendix C (Continued)

Figure C.33. Compound 31, \{In(BTC) ctn-MOF\}, as-synthesized in DMF.

Figure C.34. Compound 31, \{In(BTC) ctn-MOF\}, exchanged in CH$_3$CN.
Figure C.35. Compound 32, \{Ga(BTC) ctn-MOF\}, as-synthesized in DMF.

Figure C.36. Compound 32, \{Ga(BTC) ctn-MOF\}, exchanged in ethanol.
Figure C.37. Compound 36, \{In(BTC) novel-MOF\}, as-synthesized in DMF.
About the Author

Amy J. Cairns was born in Sydney, Nova Scotia in 1981 and received her BSc in chemistry (with honors) from Saint Mary’s University in 2004. As undergraduate student she was granted the opportunity to be a research assistant in the laboratory of Dr. Hilary A. Jenkins. From 2001 – 2004 she worked on numerous projects related to the synthesis and characterization of nitrogen-based metal-organic materials (MOMs). In August 2004, Amy was admitted to the Ph.D. program at USF and joined Dr. Mohamed Eddaoudi’s research group. Her research interests pertain to the design, synthesis, and characterization of functional MOMs with an emphasis on investigating their potential utility in pertinent applications (e.g. gas storage and separation).

She is a member of the American Chemical Society (ACS) and as a result of her work and collaborations has co-authored 5 publications in peer-reviewed journals and has several other manuscripts in preparation. During her studies at USF she had the opportunity to travel to local, regional, and national conferences for which she made a total of 8 oral or poster presentations. In 2006, she received a travel award from the International Center for Materials Research (ICMR) to attend a two week summer school on porous materials at UC Santa Barbara. She also had the chance in 2009 to visit the Institut Laue-Langevin (ILL) in Grenoble, France to conduct inelastic neutron scattering (INS) experiments on two porous metal-organic frameworks (MOFs) that she synthesized.