2008

Structural diversity in metal-organic materials

Gregory J. McManus

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Structural Diversity in Metal-Organic Materials

by

Gregory J. McManus

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

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Date of Approval:
July 9th, 2008

Keywords: crystal structure, coordination polymer, crystal engineering, supramolecular isomerism, topology

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Dedication

To my parents
Acknowledgments

First and foremost, I would like to express my sincere appreciation to my advisor Dr. Michael Zaworotko for the opportunity to conduct research under his supervision and for his guidance throughout my experience at USF.

In addition, I would like to thank Dr. Mohamed Eddaoudi, Dr. Julie Harmon, Dr. Travis Holman, and Dr. Srikanth Hariharan for their time and serving on my examination committee.

I would also like to thank Dr. Randy Larsen and Dr. Victor Kravtsov for their helpful insights into physical chemistry and crystallography.

I would like to thank all the members of Dr. Zaworotko and Dr. Eddaoudi labs past and present throughout my time at USF especially John Perry, Jason Perman, Zhenqiang Wang, and Amy Cairns.
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Structural Diversity in Metal-Organic Materials

Gregory J. McManus

ABSTRACT

The interest in metal-organic materials namely, coordination polymers and metal-organic frameworks has risen dramatically over the past few years. To a certain extent this interest is a consequence of the realization chemists have discovered how to play a form of molecular Lego® in which metal cations or metal clusters represent the bricks (or nodes) and organic ligands such as 4,4-bipyridine (bipy) or benzene-dicarboxylate represents the glue (or spacers). The “node-and-spacer” approach to self-assembly can be invoked in such a manner that a plethora of infinite architectures and discrete polyhedra can be generated from geometric principles, some of which are unprecedented in either natural or synthetic materials. The research presented within this dissertation primarily involves the use of coordination chemistry and supramolecular chemistry in the context of synthesizing metal-organic materials and deals with how subtle variations in reactants and procedures can have dramatic effects upon the materials formed. The effect of aromatic guest molecules on the crystal packing of 1D and 2D “metal-4,4’-bipyridine” coordination polymers has been addressed in terms of structural analysis and fluorescence spectroscopy. The phenomena of supramolecular isomerism resulting from the use of metal-carboxylate clusters as building blocks for a variety of metal-organic
materials will be discussed. Finally, an analysis of the Host:Guest and suprasupermolecular properties of discrete nanostructures will be provided.
Chapter 1

Introduction

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.”

R. Feynman

1.1.1. Nanoscience

Nanoscience has emerged as a central science providing a means for the union of various aspects of biology, chemistry, and physics. In terms of chemistry the driving force behind this development has been materials science which deals with the relationship between the structure of materials at atomic or molecular scale and their macroscopic properties. Over the past few decades we have witnessed an enormous deal of miniaturization resulting from different methodologies used to fabricate microelectronics. This top-down approach employed by engineers to develop smaller and smaller devices has up until now provided outstanding results, however, this top-down approach has drastic limitations for dimensions smaller than 100 nm (i.e. the nanoscale). Chemists are currently in an enviable position to exploit an alternative
strategy for the development of technology at the nanoscale, the bottom-up approach involves using nanoscale objects (molecules) to assemble nanostructures.

1.1.2. Solid State Chemistry

At the center of materials science is solid state chemistry which deals with the synthesis, characterization, and structural analysis of amorphous and crystalline materials. Solid state compounds represent an important class of materials and have been utilized for a variety of applications including: superconductors; magnets; non-linear optics; luminescent materials; and hydrogen storage materials.

An amorphous solid such as, window glass or polystyrene are materials in which there is no long-range order of the positions of the atoms. In the context of this research we are primarily interested in crystalline materials which are composed of ordered arrays of atoms and molecules within solids. The ultimate goal of solid state chemistry would be to make Feynman’s infamous quote a reality. Of course, the study of crystalline materials does not necessarily affords chemists the opportunity to arrange atoms anyway we desire but through x-ray crystallography we can at least take the initial step and determine exactly how these atoms and molecules are arranged in the materials which we do developed. In this regard, we can obtain a greater understanding of inter and intra molecular interactions in term of crystal packing which can potentially afford us some degree of control over the composition of these solid state materials.

As previously mentioned one of the most powerful tools available for the characterization of crystalline materials involves x-ray crystallography. In 1895 Wilhelm Roentgen, a German physicist discovered X-rays and subsequently won the first Nobel
prize in Physics (1901) for his discovery. Although the main use of x-rays is in medicine, x-ray diffraction is also very important in spectroscopy and as a basis for x-ray crystallography. In 1914, another German scientist named Max von Laue also won a Nobel Prize in Physics for his discovery that crystals can diffract x-rays. The following year in 1915 two British scientists Sir William Henry Bragg and William Lawrence Bragg won another Nobel Prize in Physics for their services in the analysis of crystal structures by means of x-rays.

1.1.3. The Cambridge Structural Database

The Cambridge Structural Database (CSD) is the world’s leading depository of small molecule organic and metal-organic crystal structures. Currently more than 435,000 crystal structures studied by x-ray or neutron diffraction which yield 3D atomic coordinate data for at least all non-H atoms have been deposited in the CSD either through publication in the open literature or via private communication to the CSD. Since the early 1970’s there has been a rapid increase in the number of structures published in the CSD (Figure 1.1), a great deal of this is due to improvements in single crystal x-ray diffraction studies. Structural solution via x-ray diffraction has been around for less than a century and it used to take weeks, months, or even years for a crystallographer to solve a crystal structure. It has only been because of recent technological improvements within the past few decades that single crystal x-ray diffraction has become a practical and accessible method of solid state characterization – in fact, under ideal conditions data can be collected and a crystal structure can be solved within a matter of hours.
In recent years the CSD has become invaluable for solid state chemists. In addition to serving as an inventory of the literature, if used properly the CSD can provide insight into intermolecular interactions and their role in crystal packing. It can tell inorganic chemists how predominant a particular metal cluster might be in the literature or the coordination tendencies of various ligands. Pharmaceutical chemists can analyze the hydrogen bonding capabilities of various functional groups which could be present in a drug molecule. The most important thing to note is that the CSD can provide a plethora of information to a solid state chemist provided the proper inquiry is asked in the proper manner.

1.2 Supramolecular Chemistry

“chemistry beyond the molecule”

Lehn$^6$-$^7$
1.2.1 Intermolecular Interactions

Supramolecular chemistry is primarily concerned with the study of non-covalent intermolecular interactions between molecules primarily in solution and the solid state. Although these forces (hydrogen bonding, π-π stacking, dipole-dipole, London dispersion) individually may not as strong as the covalent bonds (150-600 kJ/mol) within the molecules themselves (Table 1.1) they can have a profound effect upon crystal packing and the properties of a material (i.e. the lower density of ice compared to water or the binding of base pairs in DNA). Unfortunately, considering these forces are individually so weak, especially in the case of the van der Waals forces it is often impossible to control or predict how they will affect crystal packing of a material.

Table 1.1 Strength of various intermolecular forces.

<table>
<thead>
<tr>
<th>Force</th>
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<td>50-200</td>
</tr>
<tr>
<td>Hydrogen Bond</td>
<td>1-160</td>
</tr>
<tr>
<td>π – π stacking</td>
<td>&lt;50</td>
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<tr>
<td>Dipole-Dipole</td>
<td>3-4</td>
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<tr>
<td>London dispersion</td>
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1.2.2 Host:Guest Chemistry

Host:Guest chemistry is one of the most topical areas of supramolecular chemistry. It involves the formation of inclusion compounds in which one molecule
“host” forms a cavity in which a smaller “guest” is located. Host molecules which have been extensively studied include calixarenes, cyclodextrins, cucurbiturils, porphyrins, crown ethers, zeolites, and cryptophanes. These inclusion compounds can encompass a large number of materials from extended lattice structures possessing open channels and or cavities where the guest molecule(s) can be removed or exchanged to clathrates where the guest molecule(s) are trapped or encapsulated within the host cavity.

1.2.3 Crystal Engineering

“Crystal engineering is the understanding of intermolecular interactions in the context of crystal packing and in the utilization of such understanding in the design of new solids with desired physical and chemical properties”

Gautam Desiraju

Within the realm of supramolecular chemistry, resides the discipline of crystal engineering (i.e. design of crystalline solids), a field initiated by Schmidt in the context of organic solid-state photochemistry and vastly expanded in the 1980’s by the works of Etter and Desiraju through the use of the CSD to study hydrogen bonding, and subsequently extended into the realm of metal-organic coordination polymers through the initial work of Robson in the early 1990’s and Zaworotko in subsequent years. Typically the objective of a crystal engineer is to isolate a targeted coordination or hydrogen bonded framework, molecule, or synthon. In order to accomplish this, one carefully selects the appropriate combination of building blocks (i.e. transition metal ions, metal clusters, organic molecules) that will allow for molecular recognition, (i.e. the formation of metal-ligand bonds or complementary hydrogen bonded synthons), and
invoke the proper geometry and dimensionality that could allow for targeted structure to be generated. Of course, more often than not the design aspect of the experiment can be the trivial part and actually having the building blocks assemble the way they were designed to can be problematic and depends upon a variety of experimental conditions including the choice of: solvent(s); counter ions; templates; and reaction conditions including: temperature; pressure; time; heating/cooling rates; and pH. Fortunately, as the field matures and the literature grows scientists are slowly getting a grasp on how these systems work but there is still much progress to be made.

1.2.4 Supramolecular Isomerism

“...the existence of more than one type of network superstructure for the same molecular building blocks...”

Zaworotko15

In addition to the large selection of transition metals are the almost endless combinations created through the use of coordinating organic ligands which can be pre-selected for specific shapes, sizes, and properties and then derivatized at will, fine tuning structural and functional features of these modular coordination polymers. This large diversity in both the metal ion node and the organic ligand spacer, inherent to the modular nature of these metal-organic frameworks, ultimately manifests itself as supramolecular isomerism15.

The consequences of supramolecular isomerism are significant, not merely in the sense that it represents a bona fide scientific challenge that is both little understood and
even less studied to date, but are especially so for the concept of crystal engineering. Since the bulk properties of solids are critically dependent upon structure, any realization of the goals of crystal engineering, i.e. the rational design of functional materials, will require not only an understanding, but ultimately some level of control over supramolecular isomerism. Supramolecular isomerism in metal-organic materials can roughly be divided into four classes which parallel those of isomerism types found at the molecular level; structural isomerism in which the chemical components remain the same but a different superstructure exists (Figure 1.2), conformational isomerism which deals with the conformational changes possible in flexible ligands, catenane isomerism which addresses the possibility of different degrees of interpenetration within otherwise identical networks, and optical isomerism which becomes possible when networks crystallize in chiral space groups.

**Figure 1.2** Supramolecular isomers generated from identical building blocks: a) 0D square; b) 1D zigzag chain; and 3) 1D helix.
1.3 Metal-Organic Materials

Metal-organic coordination polymers have been the subject of a great deal of attention in recent years (Figure 1.3). Resulting from the field still in its infancy a number of terms have often been used interchangeably to describe these structures the most common being metal-organic frameworks/networks/materials, coordination polymers, and inorganic/organic hybrid materials. To a certain extent this interest is a consequence of the realization that metal-organics provide chemists with a degree of control over solid-state structure and properties. In a sense, it can be asserted that chemists have discovered how to play a form of molecular Lego® in which metal cations represent the bricks (or nodes) and organic ligands represent the glue (or spacers). The “node-and-spacer” approach to self-assembly can be invoked in such a

Figure 1.3 Occurrence of the term “Coordination Polymer” in the titles and abstracts of entries in SciFinder Scholar.
manner that a plethora of infinite architectures\textsuperscript{23-30} and discrete polyhedra\textsuperscript{31-36} can be generated from geometric principles, some of which are unprecedented in either natural or synthetic materials.\textsuperscript{37-42} Coordination polymer nodes are ideally suited for being used as “bricks” for generation of self-assembled structures for the following reasons: they are invariably based upon previously reported discrete coordination compounds; they can be afforded \textit{via} self-assembly, which typically makes them facile and inexpensive to synthesize, often in one-step with high yield; such structures are inherently modular since they contain at least two components, affording diversity of compositions since both the node and the spacer can be modified without loss of overall topology. Open framework structures can be designed from first principles and the chemist can therefore gain precise control over cavities and channels, making them particularly useful for selective sorption of small molecules;\textsuperscript{43-47} coordination polymers can contain active chromophores in both components;\textsuperscript{48-52} and the presence of guest molecules can invoke functionality or influence the properties of coordination polymers.\textsuperscript{53-57}

Depending upon geometric constraints imposed by the metal and/or the ligand, as well as their intrinsic chemical properties, it is possible to select molecular components, which are likely to self-assemble in a predictable fashion to generate structures predisposed to exhibit desirable properties including porosity\textsuperscript{58-66}, magnetism\textsuperscript{67-70}, catalysis\textsuperscript{71-73} and luminescence\textsuperscript{74-76}.

They can be prepared from a wide range of metals and they exhibit a rich degree of superstructural diversity. For example, bipy has commonly been coordinated to metals in 1:1, 1:1.5, 1:2, and 1:3 metal:ligand ratios; 1:1 stoichiometry can afford molecular polygons or chains (zig-zag, linear or helical); 1:1.5 stoichiometry can form 1-D ladder
structures; 1:2 stoichiometry can generate 2-D square grid or 3-D diamondoid topologies; and 1:3 stoichiometry has been shown to produce a 3-D cubic framework (Figure 1.4).

Figure 1.4 Schematic representation of metal-organics: using metal “nodes” (red) and organic “spacers” (blue) to construct 1-D, 2-D, and 3-D metal-organic networks: a) cubic; b) cubic diamond; c) hexagonal diamond; d) square grid; e) ladder; f) zigzag; g) helix.
Chapter 2

Exciplex Fluorescence in Metal-Bipy Coordination Polymers

2.1 The History of Metal-Bipy Coordination Polymers

In the context of coordination polymers, those that are sustained by 4,4’-bipyridine (bipy) spacers or extended versions of bipy (e.g. 4,4’-(1,2-ethanediyl)bis-pyridine and 4,4’-(1,2-ethenediyl)bis-pyridine) are amongst the earliest and most widely studied class of coordination polymers.\textsuperscript{77-83} A search of the CSD V5.29 (Nov. 2007 + 1 update) of all coordination polymers propagated through transition metal to nitrogen polymeric bonds (TR-N) produces 9853 hits. In 41\% (4001 hits) of those crystal structures the N-atom belongs to a pyridine based ligand and if the search is refined even further it is evident that in 28\% (1140 hits) of those structures the pyridine based ligand is in fact 4,4’-bipyridine. These statistics show the significance of pyridine and more specifically bipy in the evolution of coordination polymers.

2.1.1 0-D Metal-Bipy Structures

In 1990, using NMR analysis, Fujita\textsuperscript{84} reported the first metal-organic molecular square (also referred to as a molecular box) consisting of Pd\textsuperscript{2+} cations coordinated to two bipy ligands with the corners of the squares capped of by ethylenediamine (en) ligands (uncoordinated nitrate anions balance the charge). A few years later Stang\textsuperscript{85-86} reported the first crystal structure of one of these \{[Pd(bipy)(en)]\textsubscript{4}\}\textsuperscript{8+} molecular squares (Figure 2.1a) as well as a series of related molecular squares where he substituted bipy for other
linear ditopic pyridine based ligands. Around this same time Fujita\textsuperscript{87} reported that a minor side product was present during their synthesis of the \{[Pd(bipy)(en)]\textsubscript{4}\}\textsuperscript{8+} molecular squares which they hypothesized was a molecular triangle of formula \{[Pd(bipy)(en)]\textsubscript{3}\}\textsuperscript{6+}, the crystal structure of which was recently confirmed by Mizuno (Figure 2.1b).\textsuperscript{88}

\textbf{Figure 2.1} 0D Molecular Polygons: a) Fujita’s \{[Pd(bipy)(en)]\textsubscript{4}\}\textsuperscript{8+} molecular square; b) Fujita’s [Pd(bipy)(en)]\textsubscript{3}\textsuperscript{6+} molecular triangle.

\subsection*{2.1.2 1-D Metal-Bipy Structures}

The first report of a 4,4’-bipyridine coordination polymer was published in 1982 when Kubel and Strahle were able to use bipy to link Co(dimethylglyoxime)\textsubscript{2} units into a

\textbf{Figure 2.2} 1-D coordination polymers: a) the 1\textsuperscript{st} bipy coordination polymer – a linear chain; b) 1-D zigzag chain; and c) 1-D ladder.
linear 1-D \([\text{Co(dimethylglyoxime)}_2(\text{bipy})]_n\) chain (Figure 2.2a).\(^9^9\) A large number of bipy coordination polymers are of the 1-D variety which can include linear\(^9^0-9^3\), zigzag\(^9^4-9^6\) (Figure 2.2b), and helical chains\(^9^7\), as well as molecular antenna\(^9^8-1^0^2\), ladder\(^1^0^3-1^0^6\) (Figure 2.2c), and railroad networks.\(^1^0^7\)

### 2.1.3 2-D Metal-Bipy Structures

A number of 2-D metal-bipy coordination polymers have been reported to date including square grids, rectangular grids and bilayer structures. The first example of a metal-bipy 2-D square grid coordination polymer was reported by Robson in 1990 and is often credited as the seminal paper applying the principles of crystal engineering to the construction of metal-organic materials (Figure 2.3a).\(^1^0^8\) Since then there have been many reports of both interpenetrated and non-interpenetrated metal-bipy square grid structures in the literature. They have been synthesized from a number of metal cations and incorporating a variety of different guest molecules.\(^1^0^9-1^1^0\) As mentioned previously 2-D metal-bipy rectangular grids can also be generated involving the use of a shorter or longer dipyridyl based ligand in addition to 4,4′-bipyridine.\(^1^1^1-1^1^2\) The final example of a 2-D
metal-bipy coordination polymer is the bilyar structure which consists of a set of 1-D chains arranged in a parallel fashion connected orthogonally through bipy ligands to another set of 1-D chains (Figure 2.3b).\textsuperscript{123-127}

\textbf{2.1.4 3-D Metal-Bipy Structures}

Although reports of 3-D metal-bipy coordination polymers have been much less common than 1-D and 2-D structures there are still a few examples. There have been multiple reports of 3-D topologies based upon 3-connected nodes\textsuperscript{128-132} and 4-connected nodes\textsuperscript{133-135} (Figure 2.4a). Another well established method for preparing 3-D metal-bipy structures was initially reported by Zaworotko \textit{et al.} where they demonstrated that it was possible to pillar 2-D metal-bipy square grids together through SiF\textsubscript{6} anions (Figure 2.4b).\textsuperscript{136} The porosity of these pillared architectures were subsequently studied by Kitagawa (although Kitagawa’s compound was prepared using a Cu(II) salt whereas Zaworotko’s compound was prepared using a Zn(II) salt.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figures/figure2.4.png}
\caption{3-D coordination polymers: a) diamondoid network; b) square grid networks pillared together through SiF\textsubscript{6} anions.}
\end{figure}
2.2 Pyrene in Metal-Bipy coordination polymers

2.2.1 Solid-state Characteristics of Pyrene

Pyrene (Figure 2.5a), has been extensively studied as a fluorescent probe because of its many interesting photophysical properties and also because of its relatively long fluorescence lifetime. The crystal structure of pyrene was first reported in 1965 and consists of pyrene dimers held together through face-to-face π-π interactions which pack together in a herringbone pattern (Figure 2.5b).

![Figure 2.5](image)

**Figure 2.5** Solid state packing of pyrene: a) pyrene; b) herringbone packing of pyrene dimers.

2.2.2 Fluorescence Characteristics of Pyrene

In a homogeneneous solution at relatively low concentrations, pyrene molecules ($\lambda_{\text{excit}} = 310-340$ nm) have an interesting fluorescence emission spectrum with as many as five sharp high intensity peaks between 350-430 nm emerging from differences in vibronic band intensities (Figure 2.6a). The emission measured in this region of the spectrum is from monomer emission of pyrene molecules, i.e., individual non-interacting pyrene molecules. It has been reported my Nakajima that the relative intensities of the various peaks within the monomer emission are strongly dependent upon the solvent
environment. It has also been shown that the fluorescent intensity ratio of the third peak (I_{III}) (which occurs around 381 nm) to that of the first peak (I_{I}) (which arises at approximately 370 nm), is directly related to the polarity of the solvent medium. A I_{III}/I_{I} value of less than one is usually indicative of a polar environment and I_{III}/I_{I} values of greater than one can give evidence of a nonpolar hydrocarbon environment.\textsuperscript{147}

When two pyrene molecules come into contact they have the potential to form a dimer; this occurs if the face of one pyrene molecule binds to the face of a neighboring pyrene to form a sandwich-like structure through π-π interactions.\textsuperscript{148} When fluorescence excitation occurs, one pyrene molecule absorbs the original photon and becomes promoted to the excited state. However, the other pyrene molecule in the dimer cannot absorb the same photon and thus remains in the ground state. The resulting excited/ground state complex is referred to as an excimer ("exc(i)mer"). Pyrene excimers have a broad fluorescence emission at a wavelength [\lambda_{\text{em}} 430-540 nm (Figure 2.6b)] much higher than the monomer emission of pyrene. This is expected as the energy gap between excited and ground states of the excimer would be smaller, due to part of the

\textbf{Figure 2.6} Fluorescence characteristics of pyrene: a) fluorescence emission of pyrene monomer in solvents of varying polarity; b) fluorescence emission of pyrene dimer.
dimer still being in the ground state. The maximum $\lambda_{em}$ from the excimer emission as well as the intensity ratio of excimer to monomer emission ($I_E / I_M$) can reveal extremely useful information concerning the pyrene molecule’s environment.\(^{149}\)

In the same manner that pyrene can form a sandwich-like dimer with other pyrene molecules, it is also possible for pyrene molecules to form similar complexes with other planar aromatic molecules. Similar to the pyrene excimer discussed earlier, the pyrene molecule in these complexes has the potential to be promoted to an excited state producing an exciplex (“exci(ted com)plex”) in which the molecular complex is in contact with both the excited and ground electronic states.

\subsection*{2.2.3 Pyrene as a Guest in Metal-Bipy Coordination Polymers}

Previously, we reported the use of pyrene, a well studied highly polarity-sensitive fluorescent probe as a guest molecule to study the environment within metal-bipy coordination polymers and to investigate how large aromatic guests can influence the topology and/or crystal packing of coordination polymers.\(^{150}\) Resulting from the well-known ability of transition metal cations to quench the fluorescence emission of aromatic hydrocarbons the metal cation chosen for these studies was Zn(II) as it possesses a $d^{10}$ electronic configuration and therefore does not significantly quench the fluorescence emission of pyrene.

In this contribution we have prepared a number of Zn-bipy coordination polymers of 1-D ladder and 2-D square grid topologies containing pyrene guest molecules in addition to other smaller aromatic guest molecules (i.e., benzene, toluene, $p$-xylene, chlorobenzene, and $o$-dichlorobenzene). These structures have been characterized by
single crystal x-ray diffraction and their intrinsic host:guest interactions have been studied in the solid-state via time-resolved and steady-state fluorescence spectroscopy. Herein we report some insight upon the influence of the network environment upon the fluorescence properties of pyrene and of the pyrene molecules upon the crystal packing of the coordination polymers.

2.3 Mixed Aromatics Guests in Metal-Bipy Coordination Polymers

2.3.1 1D Ladder Structures

Compounds 1-4 form isostructural 1-D ladder coordination polymers, [Zn(bipy)$_{1.5}$(NO$_3$)$_2$], with pyrene intercalated between adjacent ladders and an aromatic solvent molecule (1 = benzene, 2 = toluene, 3 = p-xylene, 4 = chlorobenzene) located in the cavity of the [Zn(bipy)$_{1.5}$(NO$_3$)$_2$] ladders (Figure 2.7a). Each Zn(II) cation in 1-4 is coordinated to three bipyridine ligands (Zn–N bond distances: 2.107 – 2.168 Å) and two bidentate nitrate anions (Zn-O bond distances: 2.180 – 2.498 Å) which generates an overall neutral framework. Although the coordination sphere appears to be seven coordinate, it may be regarded as possessing a trigonal bipyramidal geometry if the nitrates are assumed to occupy only one coordination site each. These distances are expected since statistically identical distances have been observed in the related discrete complex [Co(pyridine)$_3$(NO$_3$)$_2$]. In compounds 1-4 the torsion angle between the planes of the pyridyl rings in the bipy ligands lies within the range of 23.98° – 31.66°; such values are consistent with the bimodal distribution of torsion angles exhibited by crystal structures that contain bipy bridging two metals in the CSD. The 1-D ladders
propagate along the a axis and stack next to each other along the c axis forming 2-D sheets of parallel ladders which are held together through weak C-H···O hydrogen bonds (range of bond distances measured between the C and O atoms and angles in 1-4: 3.005 – 3.295 Å; 108.3° – 126.6°) between the bipys and the nitrates of adjacent ladders. These distances and angles are well within the normal ranges for C-H···O hydrogen bonds.\textsuperscript{153-156}

Along the b axis the 2-D sheets of ladders pack in an ABAB fashion with pyrene intercalated between the layers. The guest molecules interact through arene:pyrene edge-

Figure 2.7 Crystal structure of 1, the Zn-bipy-pyrene-benzene coordination polymer, illustrating: a) the 1-D Zn-bipy ladder coordination polymer and the single benzene included in each cavity; b) the 2-D [(benzene):(pyrene)]\textsubscript{n} non-covalent network sustained by edge-to-face C-H···π interactions (benzene and pyrene shown in gold and green respectively); and c) interpenetration of the non-covalent network as shown in “b” and the 1-D Zn-bipy ladders (pictured in red and blue).
to-face C-H···π stacking to form a 2-D non-covalent sheet as shown for compound 1 in Figure 2.7b (bond distances measured from the arene carbon in addition to the methyl carbons in compounds 2 and 3 to the mean plane of the pyrene range from 3.429 – 3.740 Å); these distances are within expected values for C-H···π interactions. The non-covalent array can be interpreted as a (6:3) network if it is assumed the node of the network is the center of gravity between adjacent pyrene molecules and a neighboring aromatic solvent molecule. The interpenetration observed between the [(arene):(pyrene)2]n non-covalent sheets and the Zn-bipy 1-D ladders can best be described as parallel/parallel inclined interpenetration (Figure 2.7c). The pyrene molecules interact with the bipy ligands oriented parallel to the a axis through face-to-face π-π stacking to form an infinite array of π-π stacked bipy:pyrene along the b axis (Figure 2.8). In compounds 1-4 the distances between the centroids of the bipy moieties

![Figure 2.8](image)

**Figure 2.8** Face-to-face bipy:pyrene π...π stacking interactions in 1. Bipy ligands which interact with pyrene are highlighted in green. Benzene guest molecules show in gold for clarity and interact with pyrene and bipy ligands through C-H···π interactions (nitrate anions have been omitted for clarity).
and the mean plane of the pyrene molecules are between 3.46 – 3.63 Å; which would be expected for π-π interactions.\textsuperscript{160-164} These results are strikingly different than our previous report of a Zn-bipy ladder and pyrene which resulted in a discrete 2:1 bipy:pyrene complex.\textsuperscript{150} Synthetically the only discernible difference between this previous example and the compounds presented herein are the presence of other aromatic benzene-like solvents in 1-4. The actual influence the aromatic solvents have on generating 1-4 is currently unknown, moreover the reaction and nucleation mechanisms of most coordination polymers are currently poorly understood.

\textit{2.3.2 2D Square Grid Structure}

Compound 5 forms a 2-D square grid coordination polymer, [Zn(bipy)$_2$(NO$_3$)$_2$], with pyrene intercalated between the 2-D sheets and two $o$-dichlorobenzene ($o$-DCB) molecules located in each of the square cavities (Figure 2.9a). The Zn(II) cations in 5 possess an octahedral geometry coordinated by four bipyridine ligands (Zn–N bond distances: 2.129 – 2.200 Å) and two monodentate nitrate anions (Zn-O bond distance: 2.165 Å) generating an overall neutral framework. Crystallographically there are two unique bipy ligands in compound 5 with torsion angles of 0.0° and 27.442° between the pyridyl rings.\textsuperscript{152} The 2-D square grids exhibit a Type C packing (as described in reference 15) with an interlayer separation of 8.164 Å and pyrene intercalated between the layers. The layers also interact through weak C-H···O hydrogen bonds (bond distances measured between the C and O atoms and angles: 3.165 Å; 148.8°) between the bipy’s and the nitrate’s of adjacent 2-D layers. The square cavities are large enough (Zn-Zn bond distances: 11.374 – 11.472 Å) to accommodate two $o$-DCB molecules which interact with
the planar bipy ligands through face-to-face π-π stacking to form a 2:1 $o$-DCB:bipy sandwich complex (Figure 2.10); the distance between the centroid of the bipy moiety and the mean plane of the $o$-DCB molecule is 3.418 Å. The guest molecules interact through pyrene:$o$-DCB edge-to-face C-H···π stacking to form a 2-D non-covalent sheet as shown in Figure 2.9b (bond distances measured from the pyrene carbon to the mean plane of the $o$-DCB: 3.541 Å); this distance is within expected values for C-H···π interactions. The non-covalent array can be interpreted as a (6:3) network if it is assumed the node of the network is the midpoint of this pyrene:$o$-DCB C-H···π bond. The

![Figure 2.9](image)

**Figure 2.9** Crystal structure of 5, the Zn-bipy-pyrene-$o$-DCB coordination polymer, illustrating: a) the 2-D square grid coordination polymer and the two $o$-DCB included in each cavity; b) the 2-D [(($o$-DCB)$_2$:pyrene)$_n$] non-covalent network sustained by edge-to-face C-H···π interactions ($o$-DCB and pyrene shown in gold and green respectively); and c) interpenetration of the non-covalent network as
interpenetration observed between the \([(\sigma\text{-DCB})_2:(\text{pyrene})]\) non-covalent sheets and the \([\text{Zn(bipy)}_2(\text{NO}_3)_2]\) square grids can also be described as the parallel/parallel inclined interpenetration (Figure 2.9c). The pyrene molecules interact with the planar bipy ligands through bipy:pyrene edge-to-face C-H···π stacking (bond distances measured from the bipy carbon to the mean plane of the pyrene: 3.669 – 3.712 Å); these distances are expected for C-H···π interactions.\(^{157-159}\)

**Figure 2.10** Edge-to-face bipy:pyrene C-H···π interactions in 5. Bipy ligands which interact with pyrene are highlighted in green. \(\sigma\text{-DCB}\) guest molecules are shown in gold for clarity and interact with pyrene through C-H···π interactions and bipy ligands through π-π stacking and C-H···π interactions (nitrate anions have been omitted for clarity).

### 2.3.3 Fluorescence Characterization

As discussed in our initial paper on the Zn-bipy-pyrene coordination polymer in the absence of aromatic solvent guest, two fluorescence bands can be observed from these compounds. One of these, in the 350 to 425 nm region, is clearly assignable to pyrene monomer emission, while the other, in the 400 to 700 nm region, is assigned to 2:1 pyrene:bipy exciplex emission.\(^\text{150}\) We now have evidence that this observed monomer emission arises from pyrene adsorbed to the surface of the coordination polymer surface,
and that the pyrene intercalated within the layers of this coordination polymer gives rise solely to exciplex emission. Emission spectra collected using samples synthesized many months previously showed no evidence of monomer emission. However, if these same samples were freshly crushed, then the monomer emission is clearly observed. Increased monomer emission could also be observed by leaving the sample in the fluorimeter for several hours, exposed to the 320 nm excitation light. This is clearly illustrated in Figure 2.11, which shows an expanded monomer region, and compares the results obtained for a previously prepared sample used as is and freshly crushed and exposed to UV. We hypothesize that freshly prepared samples of this coordination polymer contain significant amounts of pyrene monomers adsorbed to the surface, which disappear through sublimation over a period of time. Crushing a sample releases more pyrene

![Figure 2.11](image)

**Figure 2.11** Monomer emission spectrum of the Zn-bipy-pyrene coordination polymer (excitation wavelength 310 nm, emission shown in the monomer emission region): a) freshly crushed and repeatedly UV-exposed; and b) powder prepared several months prior to measurement of spectrum.
molecules, which again adsorb to the surface. Continued exposure to UV light also must break down the coordination polymer structure to some degree, again releasing pyrene monomers. Thus, only the observed exciplex band can be used to characterize the coordination polymer; the $I_{III}/I_1$ vibronic band ratio of the observed monomer$^{165}$ cannot be used to determine the polarity of the local environment of the pyrene intercalated within the coordination polymer, as was previously reported.

Strong fluorescence emission was observed from all five of the Zn-bipy-pyrene coordination polymers with aromatic solvent guests (weak monomer bands of varying intensities relative to the exciplex bands were also observed, and assigned as discussed above). Figure 2.12 shows the emission spectra for compounds 1 and 5, namely those with benzene and $o$-DCB as guests. Table 2.1 lists the observed fluorescence maxima for compounds 1-5, for four (or in two cases five) different synthesis trials.

![Figure 2.12](image.png)

**Figure 2.12** Full emission spectrum of the Zn-bipy-pyrene coordination polymers (excitation wavelength 310 nm): a) 5 ($o$-DCB); and b) 2 (toluene).
In the cases of compounds 2 (toluene) and 4 (chlorobenzene), excellent consistency was obtained, with $\lambda_{F,max}$ values of 517 ± 2 and 523 ± 3 nm, respectively. These values are slightly blue-shifted compared to that of 540 nm obtained for the original Zn-bipy-pyrene coordination polymer (*i.e.* with included methanol solvent). In the case of compound 3 (*p*-xylene), four of the five samples gave similar results, with an average $\lambda_{F,max}$ of 521 ± 1 nm, consistent with the results of 2 and 4. One trial, however, gave a significantly blue-shifted spectrum, with a $\lambda_{F,max}$ of 475 nm, suggesting perhaps a different structure. In the case of compound 5 (*o*-DCB), a significantly blue shifted exciplex emission was observed, with a $\lambda_{F,max}$ of 459 ± 2 nm. In one trial, a second type of crystal were observed, which appeared darker, and which gave a different fluorescence maximum of 509 nm (similar to that for 2 and 4). In the case of compound 1 (benzene), great inconsistencies were observed, with some trials showing $\lambda_{F,max}$ values above 500 nm (similar to 2 and 4), others around 460 nm (similar to 5); and one trial showing two types of crystals, one of each type.

Table 2.1. Fluorescence emission of compounds 1-5. Wavelength maxima ($\lambda_{F,max}$, in nm) for the Zn-bipy-pyrene coordination polymers with aromatic solvent guests.

<table>
<thead>
<tr>
<th>aromatic guest</th>
<th>Trial #1</th>
<th>Trial #2</th>
<th>Trial #3</th>
<th>Trial #4</th>
<th>Trial #5</th>
<th>Avg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 – benzene</td>
<td>513</td>
<td>456</td>
<td>477</td>
<td>476/505</td>
<td>505</td>
<td>-</td>
</tr>
<tr>
<td>2 – toluene</td>
<td>517</td>
<td>519</td>
<td>515</td>
<td>517</td>
<td>-</td>
<td>517 ± 2</td>
</tr>
<tr>
<td>3 – <em>p</em>-xylene</td>
<td>520</td>
<td>520</td>
<td>475</td>
<td>522</td>
<td>521</td>
<td>521 ± 1*</td>
</tr>
<tr>
<td>4 – CB</td>
<td>525</td>
<td>525</td>
<td>519</td>
<td>522</td>
<td>-</td>
<td>523 ± 3</td>
</tr>
<tr>
<td>5 – <em>o</em>-DCB</td>
<td>460</td>
<td>461</td>
<td>458/509</td>
<td>457</td>
<td>-</td>
<td>459 ± 2**</td>
</tr>
</tbody>
</table>

*Trial 3 excluded.
**Second value for Trial 3 excluded.
Similar results were obtained for the fluorescence lifetimes $\tau_F$, as shown in Table 2.2. In one case (trial #3 with 3), a two-exponential decay curve was required to fit the data, however in all other cases the decay curves fit well to a single exponential function. Compounds 1, 3, and 4 (with the exception of one trial) all had $\tau_F$ on the order of 74 ns, whereas compound 5 (o-DCB) had a much shorter $\tau_F$ of 43 ns. Although it is possible that this significant decrease in lifetime was caused by the external heavy atom effect of the two chlorines on this solvent, no decrease of any size is observed in compound 4 (chlorobenzene). We therefore conclude that it must be a result of a difference in structure. Again, compound 1 (benzene) showed great inconsistencies, with some trials giving compounds with $\tau_F$ in the range of 72 – 78 ns and others around 42 ns.

Table 2.2. Fluorescence lifetimes of compounds 1-5. ($\tau_F$, in ns) of the Zn-bipy-pyrene coordination polymers with aromatic solvent guests.

<table>
<thead>
<tr>
<th>aromatic guest</th>
<th>Trial #1</th>
<th>Trial #2</th>
<th>Trial #3</th>
<th>Trial #4</th>
<th>Trial #5</th>
<th>Avg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 – benzene</td>
<td>72</td>
<td>28/41</td>
<td>42</td>
<td>51/61</td>
<td>78</td>
<td>-</td>
</tr>
<tr>
<td>2 – toluene</td>
<td>71</td>
<td>75</td>
<td>70</td>
<td>80</td>
<td>-</td>
<td>74 ± 5</td>
</tr>
<tr>
<td>3 – p-xylene</td>
<td>76</td>
<td>74</td>
<td>22^\dagger</td>
<td>87</td>
<td>71</td>
<td>77 ± 7*</td>
</tr>
<tr>
<td>4 – CB</td>
<td>73</td>
<td>73</td>
<td>68</td>
<td>75</td>
<td>-</td>
<td>72 ± 3</td>
</tr>
<tr>
<td>5 – o-DCB</td>
<td>42</td>
<td>42</td>
<td>44/68</td>
<td>44</td>
<td>-</td>
<td>43 ± 1**</td>
</tr>
</tbody>
</table>

\^\dagger 2-exp fit
*Trial 3 excluded.
** Second value for Trial 3 excluded.

These fluorescence results are consistent with the structural results described in the previous section, namely that coordination polymers 1-4 containing benzene, toluene, p-xylene, and chlorobenzene all exhibit 1-D ladder architectures, while 5 with o-DCB exhibits a 2-D square grid architecture. This difference in structure is clearly manifested in the fluorescence results, with the 1-D ladder structures having $\lambda_{F,max}$ values around 520
nm and $\tau_F$ values around 74 ns, whereas the square grid structures have $\lambda_{F,\text{max}}$ values around 460 nm and $\tau_F$ values around 43 ns. This is very significant, as it illustrates that the exciplex emission can be used diagnostically to indicate the type of architecture obtained in these coordination polymers, with distinctive fluorescence maxima and lifetimes observed for these two very different structures. The variable results from trial to trial observed in the case of 1, which showed maxima and lifetimes in both ranges, suggest that for this solvent, both architectures are possible. Thus, the formation of these two structures in this particular case must be very similar in terms of both kinetics and thermodynamics, and which structure is obtained in a given trial must depend on slight variations in experimental conditions, such as concentrations of all the components, and the aromatic solvent:methanol ratio. This was also observed, to a much lesser extent, in the case of 3 ($p$-xylene), which gave results consistent with a square grid structure in one of the five trials, and in the case of 5 ($o$-DCB), which gave results consistent with both square grid and 1-D ladder structures in one trial (but not in the other three trials).

The nature of the pyrene emission observed can be further investigated by comparing the excitation spectrum of these compounds to that of pyrene in solution; this yields information about the nature of the emitting state. These excitation spectra are shown in Figure 2.13. Whereas the excitation spectrum of pyrene in methanol solution reproduces very nicely the absorption spectrum (not shown), that of compounds 2 (toluene) and 5 ($o$-DCB) are clearly red-shifted and relatively broad and featureless, indicative of the formation of a ground state charge transfer complex. This shows that pyrene is complexed in these compounds even in the ground state, and that the exciplex is formed by direct excitation of this complex, and not by the solution mechanism of
excitation of a monomer followed by complexation of the excited state species with a
ground state species. Furthermore, the excitation spectrum of 2 (toluene) is significantly
more red-shifted than 5 (o-DCB), supporting our proposal on the difference in the nature
of the pyrene complexation in the 1-D ladders vs. 2-D square grid structures. Excitation
of such a ground state charge transfer complex could potentially lead to photo-induced
electron transfer in these compounds.

In the case of the 1-D ladders in 1-4, the observed exciplex emission can be
assigned to an infinite array of bipy:pyrene exciplexes, which differs from our previous
report of a Zn-bipy ladder and pyrene which resulted in a discrete 2:1 bipy:pyrene
complex. In contrast, the present 1-D ladders have a net bipy:pyrene ratio of 1:1, and it is
interesting to note that in this case the pyrene emission is not as strongly red-shifted (520
nm) as was the case in those previously reported 2:1 exciplexes (540 nm). Figure 2.8

\[\text{Figure 2.13 Excitation spectra of pyrene in methanol [-----] and the Zn-bipy-
pyrene coordination polymers 5 (o-DCB) [-----] and 2 (toluene) [------] as
guests. The emission wavelengths monitored were 380 nm, 430 nm, and 502
nm, respectively.}\]
clearly shows how the pyrene and bipy are \( \pi \)-stacked on top of each other and thus how an exciplex can form upon excitation of the pyrene fluorophore. This is an ideal arrangement to maximize the \( \pi-\pi \) interactions;\textsuperscript{157-159} this then leads to exciplex formation upon excitation of the ground state pyrene in the bipy:pyrene complex, in an analogous way to a previous report of excimer/exciplex formation upon excitation of van der Waals dimers of aromatic molecules.\textsuperscript{166-167} This mechanism also precludes the observation of monomer emission from these structures, since every pyrene is complexed. The observed emission maximum of \textit{ca.} 520 nm compares well to that of other reported pyrene exciplexes, including a 1:1 dimethylaniline:pyrene exciplex with a reported emission maximum of 496 nm,\textsuperscript{168} and with a reported 2:1 4,4'-bis(dimethylamino)diphenylmethane triplex, which had an emission maximum of 590 nm.\textsuperscript{169} Furthermore, there have been cases of the formation of exciplexes between bipy and other fluorescent probes reported, for example that between bipy and a phenanthroline-based macrocycle in a rotaxane structure.\textsuperscript{170}

In the case of \textbf{5} (\( o \)-DCB) square grid, however, a different assignment of the observed 460 nm emission is required. As can be seen from Figure 2.10, there is no face-to-face interaction of pyrene with any of the aromatic moieties in this structure, including bipy, \( o \)-DCB, or neighboring pyrenes. In this case, the red-shifted emission observed may be the result of a T-shaped exciplex, in which the bipy hydrogens interact with the pyrene \( \pi \)-electrons in an edge-to-face manner, \textit{i.e.} a C-H\textendash{}\( \pi \) interaction. This possibility is clearly shown in Figure 2.10; bond distances measured from the bipy carbon to the mean plane of the pyrene range from 3.669 – 3.712 Å but are well within expected distances for C-H\textendash{}\( \pi \) interactions. This interaction can be considered a very weak hydrogen bond and
would be expected to be a much weaker interaction than $\pi-\pi$ stacking, and this is consistent with the significantly smaller degree of red-shifting of the pyrene emission observed in this case: 460 vs. 520 nm. There have been numerous examples of such edge-to-face C-H···$\pi$ interactions between aromatic species reported in the recent literature.$^{171-176}$ In fact, a critical survey of $\pi$-interactions in metal complexes with aromatic ligands containing nitrogen concludes that in only a limited number of cases does near perfect face-to-face alignment occur, and that in many reported structures the interaction in fact occurs through off-set face-to-face or edge-to-face interactions.$^{177}$ As shown in Figure 2.10 these o-DCB solvent molecules in the cavity also interact with pyrene, in a similar way as bipy as described above, through pyrene:o-DCB edge-to-face C-H···$\pi$ stacking (bond distances measured from the pyrene carbon to the mean plane of the o-DCB: 3.541 Å). It is this combination of bipy and o-DCB edge-to face stacking with pyrene that results in the observed red-shifted pyrene emission. This is a very complex and unique pyrene emitting state. Furthering this complicated electronic structure, the o-DCB molecules also interact with the planar bipy ligands through face-to-face $\pi-\pi$ stacking, forming 2:1 o-DCB:bipy sandwich complexes (Figure 2.10); the distance between the centroid of the bipy moiety and the mean plane of the o-DCB molecule is 3.418 Å. As noted above, the net effect of all of these edge to face interactions on the pyrene is significantly less than that of the face to face interactions with bipy observed in the 1D ladder structures.

2.4 Conclusions
A series of fluorescent Zn-bipy coordination polymers have been prepared with pyrene intercalated between the layers and aromatic solvent molecules incorporated within the cavities defined by the Zn-bipy coordination. The type of structure obtained depends on the nature of the enclathrated solvent molecule: in the case of benzene, toluene, \( p \)-xylene, and chlorobenzene, a 1-D ladder architecture was obtained, whereas in the case of \( o \)-DCB, a 2-D square grid architecture was obtained. The fluorescence of these compounds is diagnostic of the structure: the 1-D ladder compounds had fluorescence maxima around 520 nm and fluorescence lifetimes around 70 ns, whereas the square grid compounds had fluorescence maxima around 460 nm and fluorescence lifetimes around 40 ns. In the case of benzene, the fluorescence of various samples varied between these two sets of values, suggesting that either type of structure can be obtained in this case. In the case of the 1-D ladder structures, the emission is easily assignable to an extended 1:1 bipy:pyrene exciplex network, which results from direct excitation of the corresponding ground state complex. In the case of the 2-D square grid structures, face-to-face interaction of pyrene with a second aromatic species does not occur, so the observed red-shifted emission is assigned to exciplex formation resulting from direct excitation of pyrene interacting with the hydrogens along the bipy and \( o \)-DCB edges. The edge to face interactions in the 2-D square grid structures results in significantly lower red-shifting of the pyrene exciplex emission as compared to the face to face interactions in the 1-D ladder structures.

2.5 Experimental
2.5.1 Syntheses

All materials were used as received; solvents were purified and dried according to standard methods.

**Synthesis of** \([\text{Zn(bipy})_{1.5}(\text{NO}_3)_2] \cdot \frac{1}{2} \text{benzene} \cdot \text{pyrene}\) \(_n\) (1). Light yellow-brown crystals of 1 were obtained within a week in a 44% yield from slow diffusion via layering a methanol solution (15.0mL) of zinc nitrate hexahydrate (147mg, 0.49mmol) onto a methanol solution (10.0mL) of 4,4'-bipyridine (156mg, 1.0mmol), pyrene (405mg, 2.0mmol) and benzene (5.0mL, 56mmol) in a 40 mL vial which was subsequently capped and allowed to remain undisturbed at room temperature until diffusion was completed.

**Synthesis of** \([\text{Zn(bipy})_{1.5}(\text{NO}_3)_2] \cdot \frac{1}{2} \text{toluene} \cdot \text{pyrene}\) \(_n\) (2). Light yellow-brown crystals of 2 were obtained within a week in a 35% yield from slow diffusion via layering a methanol solution (15.0mL) of zinc nitrate hexahydrate (148mg, 0.50mmol) onto a methanol solution (10.0mL) of 4,4'-bipyridine (156mg, 1.0mmol), pyrene (404mg, 2.0mmol) and toluene (5.0mL, 47mmol) in a 40 mL vial which was subsequently capped and allowed to remain undisturbed at room temperature until diffusion was completed.

**Synthesis of** \([\text{Zn(bipy})_{1.5}(\text{NO}_3)_2] \cdot \frac{1}{2} \text{p-xylene} \cdot \text{pyrene}\) \(_n\) (3). Light yellow-brown crystals of 3 were obtained within a week in a 56% yield from slow diffusion via layering a methanol solution (15.0mL) of zinc nitrate hexahydrate (147mg, 0.49mmol) onto a methanol solution (10.0mL) of 4,4'-bipyridine (154mg, 0.99mmol), pyrene (406mg, 2.0mmol) and p-xylene (5.0mL, 40mmol) in a 40 mL vial which was subsequently capped and allowed to remain undisturbed at room temperature until diffusion was completed.
Synthesis of \{[Zn(bipy)_{1.5}(NO_3)_2] \cdot \frac{1}{2}\text{chlorobenzene} \cdot \text{pyrene}\}_n (4). Light yellow-brown crystals of 4 were obtained within a week in a 51\% yield from slow diffusion via layering a methanol solution (15.0mL) of zinc nitrate hexahydrate (148mg, 0.50mmol) onto a methanol solution (10.0mL) of 4,4'-bipyridine (157mg, 1.01mmol), pyrene (407mg, 2.01mmol) and chlorobenzene (5.0mL, 49mmol) in a 40 mL vial which was subsequently capped and allowed to remain undisturbed at room temperature until diffusion was completed.

Synthesis of \{[Zn(bipy)_2(NO_3)_2] \cdot 2\text{o-dichlorobenzene} \cdot \text{pyrene}\}_n (5). Light yellow-brown crystals of 5 were obtained within a week in a 42\% yield from slow diffusion via layering a methanol solution (15.0mL) of zinc nitrate hexahydrate (146mg, 0.49mmol) onto a methanol solution (10.0mL) of 4,4'-bipyridine (157mg, 1.01mmol), pyrene (403mg, 1.99mmol) and o-dichlorobenzene (5.0mL, 44mmol) in a 40 mL vial which was subsequently capped and allowed to remain undisturbed at room temperature until diffusion was completed.

2.5.2 X-ray Crystallography

Single crystals suitable for X-ray crystallographic analysis were selected following examination under a microscope. Intensity data were collected on a Bruker-AXS SMART APEX/CCD diffractometer using Mo_{Kα} radiation (\(\lambda = 0.7107\ \text{Å}\)). The data were corrected for Lorentz and polarization effects and for absorption using the SADABS program (SAINT). The structures were solved using direct methods and refined by full-matrix least-squares on |F|^2 (SHELXTL).
**Table 2.3. Crystallographic data for compounds 1-5.**

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2.5.3 Fluorescence Spectroscopy

All fluorescence measurements were performed using a front-face solid sample emission configuration. Powdered samples were adhered to a 45° aluminum support (the base of which was a 1×1 cm square to fit a standard spectrometer cuvette holder), using double-sided adhesive tape. Fluorescence spectra were measured on a Photon Technologies International LS-100 luminescence spectrometer, with excitation and emission monochromator bandpasses set at 3 nm and an excitation wavelength of 310 nm (at this wavelength, only pyrene absorbs the excitation light: neither bipy nor any of the benzene-derived guests absorb at 310 nm). Excitation spectra were recorded using the same condition, with the emission wavelength set at an appropriate wavelength based on the corresponding emission spectrum. Time-resolved fluorescence was measured on the same samples using a Photon Technologies International Timemaster fluorescence lifetime spectrometer. This instrument measures fluorescence decay curves using the stroboscopic technique;¹⁸¹ resulting decay curves were fit to one-or two-exponential decay functions using supplied deconvolution software. Excellent fits were obtained, as indicated by the very good $\chi^2$ statistical test values obtained (which should be close to 1 for a good fit result): an average $\chi^2$ value of 1.11 for the five samples in trial 1, and an overall average of 1.27 for all trials.
3.1 [M₂(RCO₂)₄L₂] Square Paddlewheel

The dimetal tetracarboxylate \(^{182}\) “paddlewheel” molecular building block (MBB) also referred to as a secondary building unit (SBU) is a ubiquitous metal cluster that is present in the CSD in approximately 1652 structures involving 23 transition metals, most prominently with Cu, Mo, Ru, and Rh cations (the discrepancy between the 1636 structures analyzed in Table 5 and the 1652 reported in the CSD is due to a small number of mixed metal paddlewheel clusters). It is clear that the structural and functional

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Table 3.1. CSD analysis of paddlewheel dimetal tetracarboxylate. Analysis of the dimetal present in all crystal structures containing the \([M₂(RCO₂)_4]_n\) “paddlewheel” (in black), analysis of dimetal present in all polymeric “metal-organic” crystal structures containing the \([M₂(RCO₂)_4]_n\) “paddlewheel” (in red).
versatility of the $[M_2(\text{RCO}_2)_4L_2]$ cluster makes this a particularly attractive SBU: the metal cation can be substituted; the carboxylate moiety has many permutations; and the axial ligand can be varied almost at will.

Two approaches have thus far been delineated for the use of this cluster as a building block: as a linear spacer when coordination occurs at the axial positions, \textsuperscript{183-185} or as a molecular square linked at the vertices (as suggested when viewing the paddlewheel down the four-fold axis as in Fig. 18).\textsuperscript{186-191} In fact, of the 1652 paddlewheel structures, 391 (24 \%) are present in polymeric crystal structures employing one or both of these approaches.

\textbf{Figure 3.1.} $[M_2(\text{RCO}_4)_2L_2]_n$ “paddlewheel” when viewed down the 4-fold axis can be interpreted as a molecular square.

The first example of the $[M_2(\text{RCO}_2)_4L_2]$ paddlewheel in a polymeric crystal structure was reported in 1966 by O’Connor and Maslen when they used succinic acid and Cu(II) to form a one-dimensional coordination polymer chain $[\text{Cu}_2(\text{succinate})_2(\text{H}_2\text{O})_2]_n$, (Figure 3.2a).\textsuperscript{192} In 1998, Eddaoudi and Yaghi were the first to introduce the idea of systematically linking these clusters through a linear dicarboxylate to generate a porous 2D square grid metal-organic framework (Figure 3.2b).\textsuperscript{193} Shortly thereafter in 1999, Williams \textit{et al.} demonstrated that 3D extended frameworks could be generated by linking these molecular squares with a triangular benzene-1,3,5-
Recent efforts by our group have focused upon linking together vertices of these molecular squares through their carboxylate groups with rigid angular organic spacers such as benzene-1,3-dicarboxylate (bdc) which is predisposed to link the squares at an angle of 120°. By introducing slight variations in reaction conditions we have demonstrated that the molecular squares can assemble into clusters of three or four, to

tricarboxylic acid linker (Figure 3.2c).

![Figure 3.2](image)

**Figure 3.2** Early metal-carboxylate coordination polymers: a) 1D coordination polymer \([\text{Cu}_2(\text{succinate})_2(\text{H}_2\text{O})_2]_n\), the first example linked paddlewheel building blocks; b) 2D MOF-2 tetragonal sheet \([\text{Cu}_2(1,4-bdc)_2(\text{H}_2\text{O})_2]_n\); c) 3D HKUST metal-organic framework \([\text{Cu}_3(1,4-bdc)_2(\text{H}_2\text{O})_3]_n\). (axial H2O ligands have been deleted for clarity).

![Figure 3.3](image)

**Figure 3.3** nanoscale Secondary Building Units (nSBUs'): linking paddlewheel molecular square at their vertices to form; a) triangular (cluster of three) and b) square (cluster of four) (nSBUs Intl).
form triangular and square nanoscale secondary building units (nSBU’s) (Figure 3.3).

We have previously demonstrated that the linking of these of square paddlewheel MBB’s with bdc can facilitate the assembly of discrete 0D and extended 2D and 3D structures. These structures can be decorated using bdc ligands derivatized at the 5-position on the benzene ring (5-R-bdc) and that many of the structures previously reported for Cu(II)\(^{195-199}\) are feasible when using Zn(II)\(^ {200}\) which has only been observed in 26 (1.5 %) of the 1652 dimetal tetracarboxylate paddlewheel structures reported in the CSD. In this contribution we demonstrate how three supramolecular isomers based on dizinc tetracarboxylate SBU and bdc have been obtained: (a) 2D sheet structures based on square nSBUs only, \([\text{Zn}_2(bdc)_2(L)_2]^4_n\), (b) 2D sheet structure based on triangular nSBUs only, \([\text{Zn}_2(bdc)_2(L)_2]^3_n\) (Kagomé lattice), (c) 3D structure with a 6\(^5.8\) topology, \([\text{Zn}_2(bdc)_2(L)_2]^n\).

3.2 Tetragonal Square Grid Structures

3.2.1 Calixarenes and Atropisomerism

Calixarenes are macrocyclic compounds prepared via condensation of \(n\) molecules of formaldehyde and \(n\) molecules of phenol, which results in \(n\) phenyl rings bridged by \(n\) methylene groups. The size of the resulting calixarene is specified in its name by inserting the number \(n\) in brackets between \(\text{calix}\) and \(\text{arene}\). Thus, a cyclic tetramer is designated calix[4]arene. Calixarenes have been shown to behave as excellent host molecules and have demonstrated a propensity for complexing small guest
molecules in their bowl-shaped cavities and thus remain a topical area of research in the context of supramolecular Host:Guest chemistry.\textsuperscript{201-208}

Atropisomerism\textsuperscript{209} is a form of stereoisomerism that results when rotation around a single covalent bond is hindered enough as to allow for the isolation of different isomers. This phenomenon has been documented in a variety of systems including porphyrins, biaryls, and calixarenes. There are four possible atropisomers of calix[4]arenes\textsuperscript{210-214} that have been designated by Gutsche\textsuperscript{201} as the cone, partial cone, 1,2-alternate and 1,3-alternate (Figure 3.4).\textsuperscript{215-218} In the cone conformation, all arenes point up and form a cone-like structure, whereas in the partial cone three arenes point up and one points down, similarly in the 1,2-alternate and 1,3-alternate either neighboring or opposite arenes are oriented in the same direction.

![Figure 3.4](image)

\textbf{Figure 3.4} The four atropimers of calix[4]arene: a) cone, (b) partial cone; c) 1,2-alternate; and d) 1,3-alternate.

Due to the curvature of the square nSBU imparted by the angularity of the bdc ligands, it can be regarded as being a metal-organic calix, or a “metallo[4]calix”, where the CH\textsubscript{2} bridging groups have been replaced by the paddlewheel cluster. Metallocalixarenes are metal-organic analogous of the organic calixarenes that result
from the assembly of metal nodes and organic spacers. Examples based on Pt(II) and Pd(II) complexes of 2-hydroxypyrimidine have been shown to resemble calix[4]arenes in their shape, conformation and chemical properties.

Compounds 6-8 are supramolecular isomeric 2D sheet structures that result from the self-assembly of square nSBUs only. In this series of compounds four SBUs are linked in an angular fashion by bdc ligands and the resulting nSBU therefore possess curvature and, in principle, torsional flexibility. Close examination of the square nSBU reveals that it resembles a calix[4]arene in its shape and ability to adopt different conformations. Structures 6-8 are polymeric structures based on the metal-organic calix-like monomeric nSBUs shown in Figure 3.5.

**Figure 3.5.** The four metallo-calix[4]arene atropisomers observed in compounds 6-8: a) cone, (b) partial cone; c) 1,2-alternate; and d) 1,3-alternate.

### 3.2.2 Cone / 1,3-Alternate

Compound 6a, \([\{\text{Zn}_2(\text{bdc})_2(\text{pyridine})_2\}\cdot\text{benzene}\}_n\), and Compound 6b, \([\{\text{Zn}_2(\text{bdc})_2(4\text{-methoxypyridine})_2\}\cdot\text{benzene}\cdot2\text{ethanol}\}_n\), are polymeric structures which consist of two of these atropisomer units, the cone and 1,3-alternate which alternate in an undulating fashion throughout the structure (Figure 3.6). In 6a the cone has an outer diameter of 1.14 nm (measured from the center of one bdc benzene ring to the center of an opposite bdc benzene ring within the cone) and a depth of 0.84 nm
(measured from the center of a line joining the bottom carbon atoms on opposite axial ligands to the midpoint of a line joining the top carbon atoms on opposite bdc moieties) whereas in 6b the depth of the cone is increased to 1.10 nm due to the increased size of the 4-methoxypyridine axial ligand in 6b compared to pyridine in 6a. The 2D sheets stack in an ABAB arrangement along the Z-axis so that the cones of one layer sit inside the 1,3-alternate nSBUs of the adjacent layer where the interlayer separation is 0.81 nm in 6a and is increased to 0.98 nm in 6b. Disordered benzene guest molecules occupy both types of cavities associated within each nSBU and disordered ethanol solvent is also present in 6b.

**Figure 3.6** Crystal structure of 6a: a) undulating 2D tetragonal sheet, (b) assembly of square nSBU’s to generate 2D tetragonal sheet; c) crystal structure of compound 6a showing the presence of adjacent cone and 1,3-alternate metallo-calix atropisomers (axial pyridine ligands have been deleted for clarity except for N atom pictured in blue); d) ABAB packing of tetragonal sheets along z-axis.
3.2.3 Partial Cone

Compound 7, \([\text{Zn}_2(\text{bdc})_2(2\text{-picoline})_2] \cdot 2 \text{nitrobenzene}\)_n, consists of the partial cone nSBUs self-assembling into an undulating sheet structure (Figure 3.7). The outer diameter of the partial cone (measured from the center of the benzene rings on opposite bdc ligands which are oriented in the same direction – the other set of bdc ligands by default have to be oriented in opposite directions) is 0.96 nm and the depth is 0.81 nm (measured from the center of a line joining the carbon atoms in the 5-position on opposite bdc ligands which are oriented in the same direction and the midpoint between the carbon atom of the bdc ligand oriented in the opposite direction and the 3-position carbon atom of the 2-picoline axial ligands). Two disordered nitrobenzene molecules are also present in the cavity of each partial cone. The polymeric sheets stack eclipsed AAA along the x-axis so that the partial cones sit inside one another with an interlayer separation of ca. 1.06 nm.

Figure 3.7 Crystal structure of 7: a) showing the presence of partial cone (axial 2-picoline ligands have been deleted for clarity except for N atom pictured in blue); b) AAA packing of tetragonal sheets along x-axis.
Thermogravimetric analysis of 7 demonstrates a weight loss at approximately 175 °C which corresponds by weight to the loss of nitrobenzene guest molecules and 2-picoline axial ligands. Although we have not been able to confirm the resulting structure we propose that the [Zn$_2$(bdc)$_2$]$n$ partial cone tetragonal sheet is still in tact and appears to be thermally stable up to approximately 300 °C before decomposing.

3.2.4 1,2-Alternate

Compounds 8a-f, {[Zn$_2$(bdc)$_2$(L)$_2$]}$_n$, (Figure 3.8) (L = 4-picoline for 8a and 8b; 3,5-lutidine for 8c and 8d; 4-methoxypyridine for 8e and isoquinoline for 8f), in these polymers the 1,2-alternate nSBUs assemble into undulating sheets in which the cavities of the nSBUs can host a variety of guest molecules including: o-dichlorobenzene for 8a, 8d and 8f; nitrobenzene for 8b; and benzene for 8c and 8e. The polymeric sheets propagate along the YZ-plane and stack in an ABAB fashion along the x-axis where the interlayer separations range from 0.94 to 1.02 nm depending upon the axial coordinating ligand.

Figure 3.8 Crystal structure of 8a: a) showing the presence of partial cone (axial ligands have been deleted for clarity except for N atom pictured in blue); b) ABAB packing of tetragonal sheets along x-axis.
Thermogravimetric analysis of 8a demonstrates a weight loss at approximately 200 °C which corresponds by weight to the loss of o-dichlorobenzene guest molecules and 4-picoline axial ligands. Thermogravimetric analysis of 8f demonstrates a weight loss at approximately 250 °C which corresponds by weight to the loss of o-dichlorobenzene guest molecules and isoquinoline axial ligands. Although we have not been able to confirm the resulting structures of 8a and 8f we propose that the \([\text{Zn}_2(\text{bdc})_2]_n\)

1,2-alternate tetragonal sheet is still in tact and appears to be thermally stable up to approximately 350 °C before decomposing.

3.2.5 Decorated Tetragonal Sheets

It has been demonstrated in the literature that these tetragonal sheets can be decorated by using substituted bdc ligands. In fact the cone / 1,3-alternate tetragonal sheet has recently been reported with 5-methyl-benzene-1,3-dicarboxylic acid\textsuperscript{226} and the 1,2-alternate tetragonal sheet has been prepared from 5-hydroxy-benzene-1,3-

![Figure 3.9 Crystal structure of 9:](image)

a) showing the presence of the 1,2-alternate (axial ligands have been deleted for clarity except for N atom pictured in blue); b) Na\textsuperscript{+} cations serve to link the anionic tetragonal sheets together in an AAA packing motif along x-axis.
dicarboxylic acid$^{227}$ and 5-amino-benzene-1,3-dicarboxylic acid$^{228}$ We have demonstrated that a decorated 1,2-alternated tetragonal sheet can be prepared from 5-sulfo-benzene-1,3-dicarboxylic acid monosodium salt. Compound 9, $\left\{\left[Zn_2\left(5-SO_3-bdc\right)_2\text{(quinoline)}_2\right]^{2-}\cdot 2\left[Na^+\right]\cdot 2\text{ quinoline} \cdot o\text{-dichlorobenzene}\right\}_n$, (Figure 3.9), represents to the best of our knowledge the first example of an anionic tetragonal sheet. The overall charge of the framework is balanced by the presence of sodium cations located between the 2D layers which stack in an eclipsed AAA fashion with an interlayer separation of 1.57 nm.

In the previously discussed tetragonal sheet structures the carboxylates of the bdc ligands were either planar with the benzene ring or very close to it. There have also been reports of 2D tetragonal sheets prepared from other angular non planar dicarboxylate ligands which end up distorting the nSBU’s to the point where they can no long be effectively described as metallo-calixarenes such as, thiophene-2,5-dicarboxylic acid$^{190}$, 2,4,5,6-benzene-1,3-dicarboxylic acid$^{229}$, and camphoric acid$^{230}$. Herein, we report two closely related tetragonal sheets prepared by linking copper paddlewheel building blocks with 1,3-phenylenedicarboxylic acid (1,3-pda) (Figure 3.9a). In 1,3-pda the carboxylates can

![Figure 3.10](image)

**Figure 3.10** a) 1,3-phenylenedicarboxylic acid (1,3-pda); b) *trans* orientation of carboxylates in 1,3-pda observed in 10a; c) *cis* orientation of carboxylates in 1,3-pda observed in 10b.
rotate freely around the sp$^3$ carbon atom and we observed the _trans_ (Figure 3.9b) and _cis_ (Figure 3.9c) configuration of this ligand in compounds 10a and 10b respectively.

Compound 10a, \{[Cu$_2$(1,3-pda)$_2$(4-methoxypyridine)$_2$] • nitrobenzene\}$\_n$, (Figure 3.11a-b), shows the distorted square nSBU obtained from linking copper paddlewheel clusters with the _trans_ configuration of the 1,3-pda ligands and the resulting 2D tetragonal sheet which stack in an eclipsed fashion along the x-axis with an interlayer separations of 1.00 nm. Compound 10b, [Cu$_2$(1,3-pda)$_2$(4-methoxypyridine)$_2$]$\_n$ (Figure 3.11c-d), shows the distorted square nSBU obtained from linking copper paddlewheel clusters with the _cis_ configuration of the 1,3-pda ligands and the resulting 2D tetragonal sheet which stack in an eclipsed fashion along the x-axis with an interlayer separations of 1.26 nm.

*Figure 3.11* Crystal structures of 10a and 10b: a) square nSBU present in the crystal structure of compound 10a; b) 2D distorted tetragonal sheet in 10a; c) a) square nSBU present in the crystal structure of compound 10b; d) 2D distorted tetragonal sheet in 10b.
3.3 2D Kagomé Structures

3.3.1 Zn(II) Kagomé

Compound 11, \([\text{Zn}_2(\text{bdc})_2(4\text{-methoxypyridine})_2 \cdot \text{methanol}]_n\), results from the self-assembly of triangular nSBUs into a 2D sheet structure. The resulting structure has a topology that is an example of a Kagomé lattice.\(^{231}\) A Kagomé lattice is a spin-frustrated lattice where spins are located on the vertices of triangles. There are few examples of molecular Kagomé lattices\(^{232-234}\) and we have recently reported the first example of a nanoscale Kagomé lattice based on the Cu(II) SBU.\(^{236-237}\) Zn(II) produces the same topology where Zn\(_2\) dimers are positioned at the lattice points and are bridged by the bdc

![Figure 3.12](image)

**Figure 3.12** Kagome lattice: a) 2D undulating Kagome, (b) assembly of triangular nSBU’s to generate 2D Kagome sheet; c) line view of Kagome lattice assembled from corner sharing of triangles; d) crystal structure of compound 11 (axial pyridine ligands have been deleted for clarity except for N atom pictured in blue).
ligands, thereby generating large hexagonal cavities within the layer (Figure 3.12). The bowl-shaped nSBUs pack eclipsing one another thereby generating hexagonal channels with effective diameter of 0.93 nm. The resulting 2D sheet is undulated due to the curvature of the nSBU imparted by the angularity of the bdc ligand. It is important to note that this lattice would not have magnetic properties since Zn(II) is a d^{10} ion.

### 3.3.2 Decorated Kagomé

Similar to the tetragonal sheets, it is also possible to use substituted bdc ligands to decorate these Kagomé lattices. An example of which was reported by Zaworotko et. al. in 2004 when they used a bdc ligand substituted the 5-position of the bdc ligand with a 5-O-benzyl group. However, a number of decorated Kagomé lattices have been obtained by the Zaworotko group (Figure 3.13).

![Figure 3.13 Substituted bdc ligands used to obtain decorated Kagomé lattices in the Zaworotko group, from left to right: –NO$_2$; -SO$_3$; -Br; -phenyl; -tert-butyl; -O-C$_6$H$_{13}$; -O-benzyl; -NH$_2$.](image)
Compound 12, $\text{[Cu}_2\text{(5-t-butyl-bdc)}_2\text{(isoquinoline)}_2]_n$, (Figure 3.14), is a Kagomé lattice in which the 5-position of the bdc ligand is substituted with a tert-butyl group. The 5-t-buty1-bdc ligand and the axial coordinating isoquinoline ligand on the SBU are disordered in this structure. The packing pattern is the same as in the original Kagomé as the layers are eclipsed with an interlayer separation of 1.22 nm along the z-axis.

![Figure 3.14](image)

**Figure 3.14** a) crystal structure of 12 (axial ligands have been deleted for clarity except for N atom pictured in blue); b) AAA packing of Kagome sheets along z-axis.

Compound 13, $\{[[\text{Cu}_2\text{(5-SO}_3\text{-bdc)}_2\text{(4-methoxypyridine)(methanol)}][\text{Cu}_2\text{(5-SO}_3\text{-bdc)}_2\text{(methanol)}]_2]_{0.5}\}^3\cdot 2 \text{[Na]}^+ \cdot [4\text{-methoxypyridium}]^+ \cdot \text{nitrobenzene} \cdot 2 \text{(methanol)} \cdot 2 \text{(H}_2\text{O})\}_n$, (Figure 3.15) is a Kagomé lattice in which an anionic sulfonate group is substituted at the 5-position of the bdc ligand. This results in an anionic Kagomé lattice with the charge being balanced by sodium counter ions. All our previous Kagomé lattices have had trigonal crystal systems whereas, 13 is of lower monoclinic symmetry. Part of the reason for the lower symmetry is that 13 is the first example of a Kagomé lattice with different $\text{[Cu}_2\text{(RCO}_2\text{)}_4\text{(L)}_2]$ SBUs present. Two thirds of the SBUs in the structure have one MeOH and one 4-methoxypyridine coordinated at opposite axial sites on the SBU, while the remaining third of the SBUs only have MeOH coordinating at the
axial positions. The packing of the layers in 13 is also different than the original Kagomé as they pack in an ABAB pattern with an interlayer separation of 1.07 nm.

Figure 3.15. a) crystal structure of 13 (axial ligands have been deleted for clarity except for N atom pictured in blue); b) ABAB packing of Kagome sheets along z-axis.

3.4 “USF-1” Structure

Compound 14, \([\text{Zn}_2(\text{bdc})_2(\text{quinoline})_2]_4\)_n, is an excellent example of how supramolecular isomerism can afford structural diversity as 14 is a completely unpredictable product which results from supramolecular isomerism. The structures previously discussed in this chapter all form highly predictable patterns and as previously mentioned can be interpreted as molecular squares linked at their vertices. However, analysis of 14 as a 3D collection of molecular squares provides little insight into the topology of the network. By reducing the paddlewheel clusters to a series of 4-connected distorted square planar nodes and the bdc ligands to linear spacers the network topology can be delineated through analyzing the connectivity of these square planar nodes.
While the most easily recognizable structure associated with the assembly of square planar nodes is a 2D square grid structure there exists a variety of 3D network topologies which can be generated from square planar nodes, namely those based upon minerals such as, NbO, CdSO$_4$, and the quartz dual net (Figure 3.16). In the context of coordination polymers Batten$^{238}$ and Yaghi$^{190}$ have each recently reported novel networks constructed from square planar nodes. The circuit symbol 6$^5$.8 for 14 can be defined by considering the six angles associated with a 4-connected node. Along five of those angles a six membered circuit is the shortest path that can be completed starting and finishing along the two edges associated with each angle. Whereas, an eight membered circuit is the shortest circuit which can be completed by starting and finishing from the

![Figure 3.16](image-url) Topologies generated from 4-connected square planar nodes: a) square grid; b) NbO; c) CdSO$_4$; d) compound 14.
two edges associated with the sixth angle. The circuit symbol $6^5 8$ for $\textbf{14}$ is especially interesting as CdSO$_4$ also possess the same circuit symbol, although these two networks are clearly not the same. The difference in these topologies becomes apparent when the Schlafli (vertex) notation$^{239}$ of each topology is compared. For example, $(6,6,6,6_2,\infty)$ is the Schlafli notation for CdSO$_4$ whereas for $\textbf{14}$ the notation is $(6_2,6_2,6_2,6_3,6_3,6_2,\infty)$. This form of notation represents the shortest ring associated with each angle, the terms ring and circuit should not be confused as a ring can be defined as a particular type of circuit which cannot be “short-circuited” back to the original starting node. A symbol such as, “$6_2$” is representative of two separate six membered rings being present along a specified angle whereas, “$6_3$” would be representative of three distinct six membered rings. The “$\infty$” symbol represents that no ring is present along the edges associated with this angle or in other words the shortest circuit which exists along this angle can be short circuited back to the starting point. This structure is representative of a novel topology which was previously unknown for networks constructed from 4-connected square planar nodes.

Thermogravimetric analysis of $\textbf{14}$ demonstrates a weight loss at approximately 250 °C which corresponds by weight to the loss of quinoline axial ligands. Compound $\textbf{14}$ then appears to be thermally stable up to approximately 350 °C.

3.5 Conclusions

This is an excellent example of supramolecular isomerism as three dramatically different metal-organic architectures (2D tetragonal sheets, 2D Kagomé sheets, and 3D USF-1) which have been prepared from the same set of square building blocks linked though their vertices through an angular spacer. Supramolecular atropisomerism is even
evident in the various tetragonal sheet structures. The tetragonal and Kagomé sheets can readily be decorated with various functional groups, we demonstrated that both Cu(II) and Zn(II) can be utilized as the metal cation, in some instances the guest molecules can be changed, and through careful selection of the axial coordinating ligand we are able to obtain slight control over the packing distances between these layers.

3.6 Experimental

3.6.1 Syntheses

All materials were used as received; solvents were purified and dried according to standard methods.

**Synthesis of \{[Zn₂(bdc)₂(pyridine)₂] • benzene\}_n (6a).** Colorless crystals of 6a were obtained within days in a 3.5% yield from slow diffusion via layering an ethanolic solution (10.0mL) of benzene-1,3-dicarboxylic acid (82mg, 0.49mmol) and zinc (II) nitrate hexahydrate (150mg, 0.50mmol) through an ethanolic layer (10.0mL) onto an ethanolic solution (10.0mL) of pyridine (0.12mL, 1.6mmol) and benzene (2.0mL).

**Synthesis of \{[Zn₂(bdc)₂(4-methoxypyridine)₂] • benzene • 2 ethanol\}_n (6b).** Compound 6b was synthesized by refluxing an ethanolic solution (20.0mL) of benzene-1,3-dicarboxylic acid (42mg, 0.25mmol), benzoic acid (30mg, 0.24mmol), zinc (II) nitrate hexahydrate (150mg, 0.50mmol), benzene (2.0mL) and 4-methoxypyridine (0.2mL, 2.0mmol) for 3 hours at 70 °C. Colorless crystals were obtained within a few hours after the solution was allowed to cool to room temperature.
Synthesis of $\{[\text{Zn}_2(\text{bdc})_2(2\text{-picoline})_2] \cdot 2 \text{nitrobenzene}\}_n$ (7). Colorless crystals of 7 were obtained within days in a 14% yield from slow diffusion via layering a methanolic solution (10.0mL) of benzene-1,3-dicarboxylic acid (84mg, 0.50mmol) and zinc (II) nitrate hexahydrate (150mg, 0.50mmol) through a methanolic layer (10.0mL) onto a methanolic solution (10.0mL) of 2-picoline (0.15mL, 1.7mmol) and nitrobenzene (2.0mL). X-ray powder diffraction (XPD) was obtained for 7 and the major diffraction peaks obtained from the bulk experimental sample match the major peaks from the calculated powder pattern.

Synthesis of $\{[\text{Zn}_2(\text{bdc})_2(4\text{-picoline})_2] \cdot \text{o-dichlorobenzene}\}_n$ (8a). Colorless crystals of 8a were obtained within days in a 6.1% yield from slow diffusion via layering a methanolic solution (20.0mL) of benzene-1,3-dicarboxylic acid (166mg, 0.999mmol) and zinc (II) nitrate hexahydrate (297mg, 0.998mmol) through a methanolic layer (10.0mL) onto a methanolic solution (10.0mL) of 4-picoline (0.30mL, 3.4mmol) and o-dichlorobenzene (2.0mL). X-ray powder diffraction (XPD) was obtained for 8a and the major diffraction peaks obtained from the bulk experimental sample match the major peaks from the calculated powder pattern.

Synthesis of $\{[\text{Zn}_2(\text{bdc})_2(4\text{-picoline})_2] \cdot \text{nitrobenzene}\}_n$ (8b). Colorless crystals of 8b were obtained within days in a 28% yield from slow diffusion via layering a methanolic solution (20.0mL) of benzene-1,3-dicarboxylic acid (166mg, 0.999mmol) and zinc (II) nitrate hexahydrate (297mg, 0.998mmol) through a methanolic layer (10.0mL) onto a methanolic solution (10.0mL) of 4-picoline (0.30mL, 3.4mmol) and nitrobenzene (2.0mL).
**Synthesis of \([\text{Zn}_2\text{(bdc)}_2(3,5\text{-lutidine})_2] \cdot \text{benzene}\)\(_n\) (8c).** Colorless crystals of 8c were obtained within days in a 47% yield from slow diffusion via layering a methanolic solution (10.0mL) of benzene-1,3-dicarboxylic acid (84mg, 0.50mmol) and zinc (II) nitrate hexahydrate (150mg, 0.50mmol) through a methanolic layer (10.0mL) onto a methanolic solution (10.0mL) of 3,5-lutidine (0.17mL, 1.7mmol) and benzene (2.0mL).

**Synthesis of \([\text{Zn}_2\text{(bdc)}_2(3,5\text{-lutidine})_2] \cdot \text{o-dichlorobenzene}\)\(_n\) (8d).** Colorless crystals of 8d were obtained within days in a 32% yield from slow diffusion via layering a methanolic solution (10.0mL) of benzene-1,3-dicarboxylic acid (84mg, 0.50mmol) and zinc (II) nitrate hexahydrate (150mg, 0.50mmol) through a methanolic layer (10.0mL) onto a methanolic solution (10.0mL) of 3,5-lutidine (0.17mL, 1.7mmol) and o-dichlorobenzene (2.0mL).

**Synthesis of \([\text{Zn}_2\text{(bdc)}_2(4\text{-methoxypyridine})_2] \cdot \text{benzene}\)\(_n\) (8e).** Colorless crystals of 8e were obtained within days in a 19% yield from slow diffusion via layering an ethanolic solution (10.0mL) of benzene-1,3-dicarboxylic acid (82mg, 0.49mmol) and zinc (II) nitrate hexahydrate (150mg, 0.50mmol) through an ethanolic layer (10.0mL) onto an ethanolic solution (10.0mL) of 4-methoxypyridine (0.15mL, 1.3mmol) and benzene (2.0mL).

**Synthesis of \([\text{Zn}_2\text{(bdc)}_2(\text{isoquinoline})_2] \cdot \text{o-dichlorobenzene}\)\(_n\) (8f).** Colorless crystals of 8f were obtained within days in a 38% yield from slow diffusion via layering a methanolic solution (10.0mL) of benzene-1,3-dicarboxylic acid (84mg, 0.50mmol) and zinc (II) nitrate hexahydrate (150mg, 0.50mmol) through a methanolic layer (10.0mL) onto a methanolic solution (10.0mL) of isoquinoline (0.18mL, 1.3mmol) and o-
dichlorobenzene (2.0mL). X-ray powder diffraction (XPD) was obtained for 8f and the major diffraction peaks obtained from the bulk experimental sample match the major peaks from the calculated powder pattern.

**Synthesis of \([\text{Zn}_2(5\text{-SO}_3\text{-bdc})_2(\text{quinoline})_2]^2\cdot 2 [\text{Na}]^+ \cdot 2 \text{quinoline} \cdot o\text{-dichlorobenzene}]_n\) (9).** Colorless crystals of 9 were obtained from slow diffusion via layering a methanolic solution (10.0mL) of 5-sulfo-benzene-1,3-dicarboxylic acid monosodium salt (134mg, 0.50mmol) and zinc (II) nitrate hexahydrate (148mg, 0.50mmol) through a methanolic layer (10.0mL) onto a nitrobenzene solution (10.0mL) of quinoline (0.18mL, 1.5mmol).

**Synthesis of \([\text{Cu}_2(1,3\text{-pda})_2(4\text{-methoxypyridine})_2] \cdot \text{nitrobenzene}]_n\) (10a).** Green crystals of 10a were obtained from slow diffusion via layering a methanolic solution (2.0mL) of 1,3-phenylenediacetic acid (20mg, 0.10mmol) and copper (II) nitrate hemipentahydrate (23mg, 0.10mmol) through a methanolic layer (2.0mL) onto a methanolic solution (3.0mL) of 4-methoxypyridine (0.30mL, 3.0mmol) and nitrobenzene (1.0mL).

**Synthesis of \([\text{Cu}_2(1,3\text{-pda})_2(4\text{-methoxypyridine})_2]_n\) (10b).** Green crystals of 10b were obtained from slow diffusion via layering a methanolic solution (2.0mL) of 1,3-phenylenediacetic acid (20mg, 0.10mmol) and copper (II) nitrate hemipentahydrate (23mg, 0.10mmol) through a methanolic layer (2.0mL) onto a methanolic solution (3.0mL) of 4-methoxypyridine (0.30mL, 3.0mmol).

**Synthesis of \([\text{Zn}_2(\text{bdc})_2(4\text{-methoxypyridine})_2] \cdot \text{methanol}]_n\) (11).** Colorless crystals of 11 were obtained from slow diffusion via layering a methanolic solution (10.0mL) of benzene-1,3-dicarboxylic acid (82mg, 0.49mmol) and zinc (II) nitrate
hexahydrate (150mg, 0.50mmol) through a methanolic layer (10.0mL) onto a nitrobenzene solution (10.0mL) of 4-methoxypyridine (0.15mL, 1.5mmol).

**Synthesis of** \([\text{Cu}_2(5\text{-t-butyl-bdc})_2(\text{isoquinoline})_2]_n\) (12). Green crystals of 12 were obtained from slow diffusion by placing a methanolic solution (5.0mL) of isoquinoline (0.07mL, 0.6mmol) and nitrobenzene (4.0mL) in a small vial which is itself placed within a larger vial. A methanolic solution (4.0mL) of 5-tert-butyl-benzene-1,3-dicarboxylic acid (44mg, 0.20mmol) and copper (II) nitrate hemipentahydrate (47mg, 0.20mmol) is then placed in the bottom of the large vial. A methanol buffer solution (10.0mL) is layered onto the copper/acid solution until the contents of both vials are in contact with the methanol buffer.

**Synthesis of** \([[\text{Cu}_2(5\text{-SO}_3\text{-bdc})_2(4\text{-methoxypyridine})(\text{methanol})][\text{Cu}_2(5\text{-SO}_3\text{-bdc})_2(\text{methanol})_2]_{0.5}\]

\(\cdot 2\ [\text{Na}]^+ \cdot [4\text{-methoxypyridinium}]^+ \cdot \text{nitrobenzene} \cdot 2\ (\text{methanol})

\(\cdot 2\ (\text{H}_2\text{O}))_n\) (13). Green crystals of 13 were obtained from slow diffusion via layering a methanolic solution (10.0mL) of 5-sulfo-benzene-1,3-dicarboxylic acid monosodium salt (270mg, 1.01mmol) and copper (II) nitrate hemipentahydrate (115mg, 0.494mmol) through a methanolic layer (10.0mL) onto a methanolic solution (10.0mL) of 4-methoxypyridine (0.20mL, 2.0mmol) and nitrobenzene (2.0mL).

**Synthesis of** \([\text{Zn}_2(\text{bdc})_2(\text{quinoline})_2]_n\) (14). Colorless crystals of 14 were obtained within a days in a 13% yield from slow diffusion via layering a methanolic solution (20.0mL) of benzene-1,3-dicarboxylic acid (166mg, 0.999mmol) and zinc (II) nitrate hexahydrate (297mg, 0.998mmol) through a methanolic layer (10.0mL) onto a methanolic solution (10.0mL) of quinoline (0.24mL, 1.7mmol) and nitrobenzene (2.0mL). X-ray powder diffraction (XPD) was obtained for 14 and the major diffraction
peaks obtained from the bulk experimental sample match the major peaks from the calculated powder pattern.

3.6.2 X-ray Crystallography

Single crystals suitable for X-ray crystallographic analysis were selected following examination under a microscope. Intensity data were collected on a Bruker-AXS SMART APEX/CCD diffractometer using Mo$_{K\alpha}$ radiation (\(\lambda = 0.7107 \, \text{Å}\)).$^{178}$ The data were corrected for Lorentz and polarization effects and for absorption using the SADABS program (SAINT).$^{179}$ The structures were solved using direct methods and refined by full-matrix least-squares on |F|$^2$ (SHELXTL).$^{180}$
Table 3.2. Crystallographic data for compounds 6-14.

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<td>0.10x0.10x0.05</td>
<td>0.20x0.20x0.20</td>
<td>0.30x0.10x0.10</td>
<td>0.40x0.40x0.20</td>
</tr>
<tr>
<td><strong>θ range for data collection, deg</strong></td>
<td>1.51 to 28.28</td>
<td>2.07 to 28.28</td>
<td>1.93 to 28.26</td>
<td>1.96 to 28.26</td>
</tr>
<tr>
<td><strong>Limiting indices</strong></td>
<td>-25&lt;=h&lt;=25</td>
<td>-22&lt;=h&lt;=25</td>
<td>-14&lt;=h&lt;=12</td>
<td>-24&lt;=h&lt;=24</td>
</tr>
<tr>
<td></td>
<td>-25&lt;=k&lt;=24</td>
<td>-22&lt;=k&lt;=25</td>
<td>-25&lt;=k&lt;=25</td>
<td>-16&lt;=k&lt;=16</td>
</tr>
<tr>
<td></td>
<td>-13&lt;=l&lt;=20</td>
<td>-13&lt;=l&lt;=12</td>
<td>-23&lt;=l&lt;=25</td>
<td>-18&lt;=l&lt;=19</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>33447</td>
<td>22848</td>
<td>24385</td>
<td>13748</td>
</tr>
<tr>
<td><strong>Unique reflections</strong></td>
<td>3612</td>
<td>4397</td>
<td>4931</td>
<td>7080</td>
</tr>
<tr>
<td><strong>R(int)</strong></td>
<td>0.0765</td>
<td>0.0427</td>
<td>0.0388</td>
<td>0.0237</td>
</tr>
<tr>
<td><strong>Completeness to θ</strong></td>
<td>98.4 %</td>
<td>96.9 %</td>
<td>97.0 %</td>
<td>94.9 %</td>
</tr>
<tr>
<td><strong>Absorption correction</strong></td>
<td>multi-scan</td>
<td>multi-scan</td>
<td>multi-scan</td>
<td>multi-scan</td>
</tr>
<tr>
<td><strong>Max. and min. transmission</strong></td>
<td>1.000 and 0.865</td>
<td>1.000 and 0.779</td>
<td>1.000 and 0.721</td>
<td>1.000 and 0.662</td>
</tr>
<tr>
<td><strong>Data/ restraints/parameters</strong></td>
<td>3612 / 0 / 186</td>
<td>4397 / 0 / 229</td>
<td>4931 / 0 / 396</td>
<td>7080 / 2 / 435</td>
</tr>
<tr>
<td><strong>Goodness-of-fit on F²</strong></td>
<td>1.051</td>
<td>0.959</td>
<td>1.189</td>
<td>1.041</td>
</tr>
<tr>
<td><strong>Final R indices [I&gt;2sigma(I)]</strong></td>
<td>R₁ = 0.0534</td>
<td>wR₂ = 0.1311</td>
<td>R₁ = 0.0522</td>
<td>wR₂ = 0.1503</td>
</tr>
<tr>
<td></td>
<td>wR₂ = 0.1503</td>
<td>R₁ = 0.0557</td>
<td>wR₂ = 0.1475</td>
<td>R₁ = 0.0338</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>wR₂ = 0.0849</td>
<td>R₁ = 0.0347</td>
</tr>
<tr>
<td><strong>R indices (all data)</strong></td>
<td>R₁ = 0.0748</td>
<td>wR₂ = 0.1425</td>
<td>R₁ = 0.0690</td>
<td>wR₂ = 0.1633</td>
</tr>
<tr>
<td></td>
<td>wR₂ = 0.1633</td>
<td>R₁ = 0.0652</td>
<td>wR₂ = 0.1524</td>
<td>R₁ = 0.0347</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>wR₂ = 0.0855</td>
<td>R₁ = 0.0347</td>
</tr>
<tr>
<td><strong>Large diff. peak and hole, e•Å⁻³</strong></td>
<td>1.243, -0.920</td>
<td>1.020, -0.451</td>
<td>1.203, -0.651</td>
<td>0.622, -0.458</td>
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<tr>
<td></td>
<td>8b</td>
<td>8c</td>
<td>8d</td>
<td>8e</td>
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<td>---------------</td>
<td>-----------------------------------------</td>
<td>-----------------------------------------</td>
<td>-----------------------------------------</td>
<td>-----------------------------------------</td>
</tr>
<tr>
<td><strong>Empirical formula</strong></td>
<td>( C_{34}H_{27}N_{3}O_{10}Zn_{2} )</td>
<td>( C_{34}H_{27}N_{3}O_{10}Zn_{2} )</td>
<td>( C_{34}H_{27}Cl_{2}N_{2}O_{8}Zn_{2} )</td>
<td>( C_{34}H_{28}N_{2}O_{10}Zn_{2} )</td>
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<tr>
<td><strong>Formula weight</strong></td>
<td>768.33</td>
<td>751.38</td>
<td>820.26</td>
<td>755.32</td>
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<td><strong>Temperature</strong></td>
<td>100(2)</td>
<td>100(2)</td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>Cc</td>
<td>C2/c</td>
<td>C2/c</td>
<td>C2/c</td>
</tr>
<tr>
<td><strong>a, Å</strong></td>
<td>19.796(2)</td>
<td>19.206(2)</td>
<td>18.8097(17)</td>
<td>19.291(7)</td>
</tr>
<tr>
<td><strong>c, Å</strong></td>
<td>14.8457(18)</td>
<td>14.3339(18)</td>
<td>14.3915(13)</td>
<td>13.864(5)</td>
</tr>
<tr>
<td><strong>α, deg</strong></td>
<td>90°</td>
<td>90°</td>
<td>90°</td>
<td>90°</td>
</tr>
<tr>
<td><strong>β, deg</strong></td>
<td>116.064(2)°</td>
<td>109.542(2)°</td>
<td>109.109(2)°</td>
<td>114.797(6)°</td>
</tr>
<tr>
<td><strong>γ, deg</strong></td>
<td>90°</td>
<td>90°</td>
<td>90°</td>
<td>90°</td>
</tr>
<tr>
<td><strong>V, Å³</strong></td>
<td>3240.7(7)</td>
<td>3386.8(7)</td>
<td>3366.6(5)</td>
<td>3263(2)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td><strong>ρ_{calcd}, g•cm^{-3}</strong></td>
<td>1.575</td>
<td>1.474</td>
<td>1.618</td>
<td>1.538</td>
</tr>
<tr>
<td><strong>μ, mm^{-1}</strong></td>
<td>1.544</td>
<td>1.471</td>
<td>1.641</td>
<td>1.532</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>1568</td>
<td>1544</td>
<td>1672</td>
<td>1544</td>
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<tr>
<td><strong>Crystal size, mm</strong></td>
<td>0.60x0.40x0.30</td>
<td>0.20x0.10x0.05</td>
<td>0.20x0.10x0.10</td>
<td>0.20x0.05x0.05</td>
</tr>
<tr>
<td><strong>θ range for data collection, deg</strong></td>
<td>2.02 to 28.25</td>
<td>1.92 to 28.34</td>
<td>1.93 to 28.24</td>
<td>1.91 to 23.27</td>
</tr>
<tr>
<td><strong>Limiting indices</strong></td>
<td>-24&lt;=h&lt;=26 -25&lt;=h&lt;=13 -24&lt;=h&lt;=16 -21&lt;=h&lt;=21</td>
<td>-15&lt;=k&lt;=16 -16&lt;=k&lt;=17 -17&lt;=k&lt;=14 -14&lt;=k&lt;=14</td>
<td>-18&lt;=l&lt;=19 -16&lt;=l&lt;=19 -18&lt;=l&lt;=8 -12&lt;=l&lt;=15</td>
<td></td>
</tr>
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<td><strong>Reflections collected</strong></td>
<td>9716</td>
<td>10274</td>
<td>6391</td>
<td>6724</td>
</tr>
<tr>
<td><strong>Unique reflections</strong></td>
<td>5974</td>
<td>3963</td>
<td>3202</td>
<td>2354</td>
</tr>
<tr>
<td><strong>R(int)</strong></td>
<td>0.0257</td>
<td>0.0538</td>
<td>0.0226</td>
<td>0.0567</td>
</tr>
<tr>
<td><strong>Completeness to θ</strong></td>
<td>94.2 %</td>
<td>93.5 %</td>
<td>86.8 %</td>
<td>99.9 %</td>
</tr>
<tr>
<td><strong>Absorption correction</strong></td>
<td>multi-scan</td>
<td>multi-scan</td>
<td>multi-scan</td>
<td>none</td>
</tr>
<tr>
<td><strong>Max. and min. transmission</strong></td>
<td>1.000 and 0.609</td>
<td>1.000 and 0.749</td>
<td>1.000 and 0.671</td>
<td>none</td>
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<tr>
<td><strong>Data/ restraints/ parameters</strong></td>
<td>5974 / 2 / 444</td>
<td>3963 / 0 / 219</td>
<td>3302 / 0 / 264</td>
<td>2354 / 0 / 218</td>
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<tr>
<td><strong>Goodness-of-fit on F²</strong></td>
<td>1.032</td>
<td>1.022</td>
<td>1.048</td>
<td>1.130</td>
</tr>
<tr>
<td><strong>Final R indices [I&gt;2sigma(I)]</strong></td>
<td>R1 = 0.0359 wR2 = 0.0931</td>
<td>R1 = 0.0442 wR2 = 0.0954</td>
<td>R1 = 0.0322 wR2 = 0.0817</td>
<td>R1 = 0.0867 wR2 = 0.1727</td>
</tr>
<tr>
<td><strong>R indices (all data)</strong></td>
<td>R1 = 0.0376 wR2 = 0.0944</td>
<td>R1 = 0.0606 wR2 = 0.1031</td>
<td>R1 = 0.0362 wR2 = 0.0837</td>
<td>R1 = 0.1040 wR2 = 0.1819</td>
</tr>
<tr>
<td><strong>Large diff. peak and hole, e•Å⁻³</strong></td>
<td>0.662, -0.444 0.588, -0.687 0.535 and -0.363</td>
<td>0.755, -0.707</td>
<td></td>
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<tr>
<td></td>
<td>8f</td>
<td>9</td>
<td>10a</td>
<td>10b</td>
</tr>
<tr>
<td>----------------------</td>
<td>----------------</td>
<td>----------------</td>
<td>----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td><strong>Empirical formula</strong></td>
<td>$C_{40}H_{26}Cl_2N_2O_8Z$</td>
<td>$C_{40}H_{34}Cl_2Na_2O_4$</td>
<td>$C_{37}H_{20}Cu_2N_2O_12$</td>
<td>$C_{37}H_{30}Cu_2N_2O_{10}$</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>864.27</td>
<td>1346.65</td>
<td>821.71</td>
<td>729.66</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>100(2)</td>
<td>100(2)</td>
<td>298(2)</td>
<td>100(2)</td>
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<tr>
<td><strong>Crystal system</strong></td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>C2/c</td>
<td>P2(1)/c</td>
<td>P2(1)/c</td>
<td>P2(1)/c</td>
</tr>
<tr>
<td><strong>a, Å</strong></td>
<td>20.416(3)</td>
<td>15.6981(13)</td>
<td>9.9976(18)</td>
<td>12.5592(15)</td>
</tr>
<tr>
<td><strong>b, Å</strong></td>
<td>13.2052(18)</td>
<td>13.4044(11)</td>
<td>10.4299(18)</td>
<td>12.4669(16)</td>
</tr>
<tr>
<td><strong>c, Å</strong></td>
<td>13.8901(9)</td>
<td>13.8988(11)</td>
<td>17.736(3)</td>
<td>10.3218(13)</td>
</tr>
<tr>
<td><strong>α, deg</strong></td>
<td>90°</td>
<td>90°</td>
<td>90°</td>
<td>90°</td>
</tr>
<tr>
<td><strong>β, deg</strong></td>
<td>109.477(2)°</td>
<td>94.7850(10)°</td>
<td>97.902(3)°</td>
<td>109.948(2)°</td>
</tr>
<tr>
<td><strong>γ, deg</strong></td>
<td>90°</td>
<td>90°</td>
<td>90°</td>
<td>90°</td>
</tr>
<tr>
<td><strong>V, Å$^3$</strong></td>
<td>3530.4(8)</td>
<td>2914.4(4)</td>
<td>1831.8(6)</td>
<td>1519.2(3)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td><strong>$\rho_{calcd}$, g•cm$^{-3}$</strong></td>
<td>1.626</td>
<td>1.535</td>
<td>1.490</td>
<td>1.595</td>
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<tr>
<td><strong>μ, mm$^{-1}$</strong></td>
<td>1.569</td>
<td>1.072</td>
<td>1.226</td>
<td>1.463</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>1752</td>
<td>1364</td>
<td>840</td>
<td>748</td>
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<tr>
<td><strong>Crystal size, mm</strong></td>
<td>0.20x0.10x0.10</td>
<td>0.30x0.20x0.10</td>
<td>0.15x0.12x0.08</td>
<td>0.15x0.11x0.07</td>
</tr>
<tr>
<td><strong>θ range for data collection, deg</strong></td>
<td>1.87 to 28.25</td>
<td>2.00 to 28.32</td>
<td>2.06 to 25.10</td>
<td>1.72 to 25.02</td>
</tr>
<tr>
<td><strong>Limiting indices</strong></td>
<td>-26&lt;=h&lt;=26</td>
<td>-20&lt;=h&lt;=10</td>
<td>-11&lt;=h&lt;=11</td>
<td>-14&lt;=h&lt;=14</td>
</tr>
<tr>
<td></td>
<td>-8&lt;=k&lt;=16</td>
<td>-17&lt;=k&lt;=17</td>
<td>-7&lt;=k&lt;=12</td>
<td>-14&lt;=k&lt;=8</td>
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<td>-17&lt;=l&lt;=17</td>
<td>-18&lt;=l&lt;=18</td>
<td>-21&lt;=l&lt;=20</td>
<td>-12&lt;=l&lt;=11</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>10475</td>
<td>18167</td>
<td>9383</td>
<td>6732</td>
</tr>
<tr>
<td><strong>Unique reflections</strong></td>
<td>4104</td>
<td>6810</td>
<td>3236</td>
<td>2641</td>
</tr>
<tr>
<td><strong>R(int)</strong></td>
<td>0.0534</td>
<td>0.0241</td>
<td>0.0465</td>
<td>0.0439</td>
</tr>
<tr>
<td><strong>Completeness to θ</strong></td>
<td>93.8 %</td>
<td>99.7 %</td>
<td>99.2 %</td>
<td>98.4 %</td>
</tr>
<tr>
<td><strong>Absorption correction</strong></td>
<td>multi-scan</td>
<td>multi-scan</td>
<td>multi-scan</td>
<td>multi-scan</td>
</tr>
<tr>
<td><strong>Max. and min. transmission</strong></td>
<td>1.000 and 0.693</td>
<td>1.000 and 0.815</td>
<td>1.000 and 0.550</td>
<td>1.000 and 0.746</td>
</tr>
<tr>
<td><strong>Data/ restraints/ parameters</strong></td>
<td>4104 / 0 / 262</td>
<td>6810 / 0 / 383</td>
<td>3236 / 0 / 236</td>
<td>2641 / 0 / 208</td>
</tr>
<tr>
<td><strong>Goodness-of-fit on $F^2$</strong></td>
<td>1.093</td>
<td>1.038</td>
<td>1.051</td>
<td>1.051</td>
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<tr>
<td><strong>Final R indices [I&gt;2sigma(I)]</strong></td>
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<td>R1 = 0.0796</td>
<td>R1 = 0.0531</td>
<td>R1 = 0.0436</td>
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<td>wR2 = 0.1993</td>
<td>wR2 = 0.2107</td>
<td>wR2 = 0.1538</td>
<td>wR2 = 0.0933</td>
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<td><strong>R indices (all data)</strong></td>
<td>R1 = 0.1120</td>
<td>R1 = 0.0841</td>
<td>R1 = 0.0792</td>
<td>R1 = 0.0566</td>
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<td>wR2 = 0.2140</td>
<td>wR2 = 0.2147</td>
<td>wR2 = 0.1656</td>
<td>wR2 = 0.0984</td>
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<td><strong>Large diff. peak and hole, e•Å$^{-3}$</strong></td>
<td>1.926, -0.725</td>
<td>2.847, -1.713</td>
<td>1.021, -0.286</td>
<td>0.552, -0.374</td>
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64
<table>
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<th>11</th>
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<td><strong>Empirical formula</strong></td>
<td>C₂₉H₂₉N₂O₁₇Zn₂</td>
<td>C₃₁H₂₆Cu₂N₂₆₅O₈₆₇</td>
<td>C₄₆H₂₁Cu₂N₃Na₂O₃</td>
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<tr>
<td><strong>Formula weight</strong></td>
<td>709.26</td>
<td>935.78</td>
<td>1444.44</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>100(2)</td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Trigonal</td>
<td>Trigonal</td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P-3m1</td>
<td>P-3</td>
<td>C2/c</td>
</tr>
<tr>
<td><strong>a, Å</strong></td>
<td>18.9565(8)</td>
<td>18.5627(10)</td>
<td>18.351(2)</td>
</tr>
<tr>
<td><strong>b, Å</strong></td>
<td>18.9565(8)</td>
<td>18.5627(10)</td>
<td>18.351(2)</td>
</tr>
<tr>
<td><strong>c, Å</strong></td>
<td>11.1246(9)</td>
<td>12.1635(13)</td>
<td>21.498(3)</td>
</tr>
<tr>
<td><strong>α, deg</strong></td>
<td>90°</td>
<td>90°</td>
<td>90°</td>
</tr>
<tr>
<td><strong>β, deg</strong></td>
<td>90°</td>
<td>90°</td>
<td>100.151(2)°</td>
</tr>
<tr>
<td><strong>γ, deg</strong></td>
<td>120°</td>
<td>120°</td>
<td>90°</td>
</tr>
<tr>
<td><strong>V, Å³</strong></td>
<td>3462.0(3)</td>
<td>3629.7(5)</td>
<td>12486(3)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>3</td>
<td>3</td>
<td>8</td>
</tr>
<tr>
<td><strong>ρ_calcd, g•cm⁻³</strong></td>
<td>1.021</td>
<td>1.284</td>
<td>1.537</td>
</tr>
<tr>
<td><strong>µ, mm⁻¹</strong></td>
<td>1.080</td>
<td>0.933</td>
<td>1.216</td>
</tr>
<tr>
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3.6.3 Thermogravimetric Analysis

Thermogravimetric analysis for 7 and 8e was performed under nitrogen at a fixed heating rate of 25 °C/min on a Perkin Elmer STA 6000 Simultaneous Thermal Analyzer. Thermogravimetric analysis for 8a and 14 was performed under nitrogen as a dynamic scan at a maximum heating rate of 50 °C/min on a TA Instrument TGA 2950 Hi-Res.

Figure 3.17 TGA of Compound 7 - {[Zn₂(bdc)₂(2-picoline)₂] • 2 nitrobenzene}

\[
\begin{align*}
\text{Zn}^{2+} &= 65.38 \text{ g/mol} \\
b\text{dc}^{2-} &= 164.10 \text{ g/mol} \\
2\text{-picoline} &= 93.13 \text{ g/mol} \\
nitrobenzene &= 123.11 \text{ g/mol} \\
{[\text{Zn}_2(\text{bdc})_2(2\text{-picoline})_2] \cdot 2\text{ nitrobenzene}} &= 891.44 \text{ g/mol}
\end{align*}
\]

Theoretical Weight Loss:

\[
\frac{(2\text{-picoline})_2 \& (\text{nitrobenzene})_2}{([\text{Zn}_2(\text{bdc})_2(2\text{-picoline})_2] \cdot 2\text{ nitrobenzene})} \times 100 = 48.51 \%
\]

Experimental Weight Loss:

\[
13.095 / 30.679 = 42.68 \%
\]
**Figure 3.18** TGA of Compound 8a – \{[\text{Zn}_2(\text{bdc})_2(4\text{-picoline})_2] \cdot \text{o-dichlorobenzene}\}_n

\[\text{Zn}^{2+} = 65.38 \text{ g/mol}\]

\[\text{bdc}^{2-} = 164.10 \text{ g/mol}\]

\[4\text{-picoline} = 93.13 \text{ g/mol}\]

\[\text{o-dcb} = 147.00 \text{ g/mol}\]

\[\{[\text{Zn}_2(\text{bdc})_2(4\text{-picoline})_2] \cdot \text{o-dcb}\} = 792.22 \text{ g/mol}\]

**Theoretical Weight Loss:**

\[
(\text{4-picoline})_2 \& \text{o-dcb} / \{[\text{Zn}_2(\text{bdc})_2(4\text{-picoline})_2] \cdot \text{o-dcb}\} \times 100 = 42.07 \%
\]

**Experimental Weight Loss:**

38.70 %
**Figure 3.19** TGA of Compound 8f – \{[Zn_2(bdc)_2(isoquinoline)_2] \cdot o\text{-dichlorobenzene}\}_n

Zn^{2+} = 65.38 \text{ g/mol}

bdc^{2-} = 164.10 \text{ g/mol}

isoquinoline = 129.16 \text{ g/mol}

o-dcb = 147.00 \text{ g/mol}

\{[Zn_2(bdc)_2(isoquinoline)_2] \cdot o\text{-dcb}\} = 864.28 \text{ g/mol}

**Theoretical Weight Loss:**

\((\text{isoquinoline})_2 \cdot o\text{-dcb} / \{[Zn_2(bdc)_2(isoquinoline)_2] \cdot o\text{-dcb}\} \times 100 = 46.90 \%\)

**Experimental Weight Loss:**

\(18.679 / 42.863 = 43.58 \%\)
Figure 3.20 TGA of Compound 14 – \([\text{Zn}_2(\text{bdc})_2(\text{quinoline})_2]_n\)

\[
\begin{align*}
\text{Zn}^{2+} & = 65.38 \text{ g/mol} \\
\text{bdc}^{2-} & = 164.10 \text{ g/mol} \\
\text{quinoline} & = 129.16 \text{ g/mol} \\
[\text{Zn}_2(\text{bdc})_2(\text{quinoline})_2] & = 717.28 \text{ g/mol}
\end{align*}
\]

Theoretical Weight Loss:

\[
(\text{quinoline})_2 / [\text{Zn}_2(\text{bdc})_2(\text{quinoline})_2] \times 100 = 36.10 \%
\]

Experimental Weight Loss:

36.49 %
3.6.4 X-Ray Powder Diffraction (XPD)

High resolution X-ray Powder Diffraction (XPD) data were recorded on a Bruker D8 Advance X-Ray diffractometer at 20kV, 5mA for Cu Kα (λ = 1.5418 Å), with a scan speed of 0.5 sec/step (1°/min) and a step size of 0.05° in 2θ at room temperature.

Figure 3.21 XPD of Compound 7 – \{[Zn_2(bdc)_2(2-picoline)_2] \cdot 2 nitrobenzene\}_n
Figure 3.22 XPD of Compound 8a – $\{[\text{Zn}_2(\text{bdc})_2(4\text{-picoline})_2] \cdot o\text{-dichlorobenzene}\}_n$

![Graph showing the XPD of Compound 8a.](image1)

Figure 3.23 XPD of Compound 8f – $\{[\text{Zn}_2(\text{bdc})_2(\text{isoquinoline})_2] \cdot o\text{-dichlorobenzene}\}_n$

![Graph showing the XPD of Compound 8f.](image2)
Figure 3.24 XPD of Compound 14 – [Zn$_2$(bdc)$_2$(quinoline)$_2$],
Chapter 4

Structural Diversity in Metal-Carboxylate Chemistry

4.1 Introduction

The coordination chemistry and coordination environment around transition metals can be dependent upon a variety of experimental conditions. Whether or not a ligand will coordinate to a single metal ion or partake in the formation of metal clusters can often be very hard to control. As previously discussed the ubiquitous square \([M_2(RCO_2)_4(L)_2]\) paddlewheel cluster can readily be formed from Cu(II) ions and although carboxylates can coordinate to Cu(II) in a variety of ways the square paddlewheel remains one of the most common coordination modes in Cu(II)-carboxylate chemistry. On the other hand the coordination chemistry of Zn(II) is much more difficult to control although we have previously demonstrated that the \([M_2(RCO_2)_4(L)_2]\) paddlewheel cluster can readily form from Zn(II) and carboxylates the large degree of structural diversity associated with this metal can make its coordination chemistry difficult to control. This phenomenon can be troublesome when attempting to target a particular structure or framework. However at the same time this form of structural diversity can also lead to a number of unpredictable results which can often prove to be interesting in their own right.

4.2 \([Zn_2(\mu^2-RCO_2)_3(\mu^1-RCO_2)]\) Tetrahedral Metal Clusters
During our attempts to prepare metal-organic materials based upon the Zn(II) paddlewheel and 1,3-bdc we isolated Compound 15, {[Zn$_2$(bdc)$_2$(DMSO)$_2$(H$_2$O)] • 3 DMSO}$_n$, in which the dimetal tetracarboxylate building block formed contained three carboxylates coordinated in a bidentate manner to different Zn(II) ions and another monodentate carboxylate coordinated to just one of the Zn(II) ions (Figure 4.1a). A search of the CSD for this particular zinc cluster provided five hits$^{240-243}$ one of which was actually used to generate a 2D metal-organic framework.$^{244}$

![Figure 4.1 a) [M$_2$(µ$^2$-RCO$_2$)$_3$(µ$^1$-RCO$_2$)] tetrahedral dimetal tetracarboxylate (axially coordinating DMSO and H$_2$O ligands have been removed for clarity); b) tetrahedral building block.](image)

In 15, one of the Zn(II) ions is coordinated to four carboxylates in a tetrahedral environment while the other Zn(II) is coordinated to three carboxylates in an octahedral environment with 2 DMSO molecules and a H$_2$O molecule serving as the remaining ligands. The Zn-Zn distance in the tetrahedral cluster is 3.769 Å which is comparable to the Zn-Zn distance found in the literature.$^{244}$ As a building block this cluster can be interpreted as a distorted tetrahedron (Figure 4.1b) and in 15 these distorted tetrahedrons are linking through the angular bdc ligands to generate a 2D metal-organic framework with a diamondoid topology (Figure 4.2).

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We were also able to isolate this tetrahedral cluster in the presence of the square paddlewheel cluster in compound 16, $\{[\text{Zn}_2(\text{bdc})_2(4\text{-methoxypyridine})][\text{Zn}_2(\text{bdc})_2(4\text{-methoxypyridine})(\text{methanol})]^2\}_{n}$, (Figure 4.3). The Zn(II) ions present in tetrahedral dimetal tetracarboxylate cluster of 16 are 4-coordinate tetrahedral with four coordinating carboxylate groups and 5-coordinate trigonal bipyramidal with three coordinating carboxylate groups and 4-methoxypyridine and methanol ligands completing the coordination sphere. The Zn-Zn distance in the tetrahedral cluster is 3.330 Å compared to 2.937 Å in the square paddlewheel cluster. Each tetrahedral cluster in 16 is linked through bdc to two other tetrahedral clusters and to two square paddlewheel resulting in a 2:1 ratio of tetrahedral clusters to square paddlewheel clusters.

Figure 4.2 a) crystal structure of 15; b) linking of tetrahedral metal cluster through 1,3-bdc; c) idealized diamondoid net assembled from perfect tetrahedrons; d) diamondoid nets assembled in 15 from distorted tetrahedrons.
The topology of 16 can best be described after analyzing the PtS topology which is constructed from a 1:1 ratio of vertex linked squares and tetrahedrons (Figure 4.4). The “truncated PtS” topology observed in 16 and be obtained by selecting a two dimensional cross section of the PtS framework where every square remains linked to four tetrahedrons and then linking the two open vertices of each tetrahedron together.

![Figure 4.3 Crystal structure of 16](image)

**Figure 4.3** Crystal structure of 16: a) bdc ligands (highlighted in various colors) linking the square and tetrahedral dimetal tetracarboxylate clusters; b) 2D metal organic materials in 16.

![Figure 4.4](image)

**Figure 4.4** a) 3D PtS framework assembled from a 1:1 ratio of vertex linked tetrahedrons and squares; b) the 2D “truncated PtS” topology observed in 16 from a 2:1 ratio of vertex lined tetrahedrons and squares.
4.3 $[\text{Zn}_3(\text{RCO}_2)_6]$ Trimetal Hexacarboxylate Clusters

Similarly during our attempts to prepare metal-organic materials based upon the Zn(II) paddlewheel and 1,3-bdc we isolated a series of compounds containing a trizinc hexacarboxylate $[\text{Zn}_3(\text{RCO}_2)_6]$ cluster. A search of the CSD for this particular zinc cluster provided thirteen hits$^{245-253}$ a few of which were actually present in polymeric metal-organic structures.$^{253-255}$ The first structure containing this trizinc hexacarboxylate cluster was compound 17 $\{[\text{Zn}_3(\text{bdc})_3(6\text{-methoxyquinoline})_2] \cdot 6\text{-methoxyquinoline} \cdot \text{methanol}\}_n$, (Figure 4.5). The metal cluster consists of three 4-coordinate tetrahedral Zn(II) ions, the central Zn(II) in the cluster is coordinated by four bidentate carboxylates whereas the other two Zn(II) ions are each coordinated by two bidentate and one monodentate carboxylates with a 4-methoxyquinoline ligand occupying the remaining

Figure 4.5 Crystal structure of 17: a) the $[\text{Zn}_3(\text{RCO}_2)_6]$ cluster in 17; b) cross-linking between clusters through bdc ligands to generate a 3-connected node; c) 2D metal-organic framework in 17 based upon a (6,3)-honeycomb structure.
coordination site. The Zn-Zn distances within this cluster measured from the central Zn ion are 3.390 Å and 3.510 Å. These trizinc hexacarboxylate clusters in 17 behave as 3-connected nodes as they are cross-linked together through bdc to form a 2D (6,3)-honeycomb structure. The dimensions of the cavities generated are approximately 0.90 x 1.77 nm and are filled by 6-methoxyquinoline and methanol guest molecules which themselves are hydrogen bonded together (O-H…N 2.786 Å). Thermogravimetric analysis of 17 demonstrates a weight loss at approximately 200 °C which corresponds by weight to the loss of the methanol and 6-methoxyquinoline guest molecules as well as the two 6-methoxyquinoline ligands. Although we have not been able to confirm the resulting structure we propose that the [Zn₃(bdc)₃]ₙ honeycomb sheet is still in tact and appears to be thermally stable up to approximately 400 °C before decomposing.

We were also able to isolate compound 18, ([Zn₃(1,3-bdc)₃(4-methoxypyridine)₂] ⋅ 2 4-methoxypyridine)ₙ, (Figure 4.6). The metal cluster in 18 consists of a central 6-coordinate octahedral Zn(II) ion coordinated by four bidentate carboxylates and the remaining two carboxylates are coordinated through single bifurcated oxygen atoms. The two exterior Zn(II) ions of the cluster posses a 4-coordinate tetrahedral geometry and each are coordinated by two bidentate carboxylate groups and the bifurcated oxygen atom of another carboxylate with a 4-methoxypyridine ligand occupying the remaining site. The Zn-Zn distances within this cluster measured from the central Zn ion are 3.240 Å and 3.267 Å. The trizinc hexacarboxylate clusters in 18 behave as a 4-connected tetrahedral node as they are cross-linked together through bdc ligands to two other clusters and form a single linkage between two other clusters. The resulting 3D metal-organic framework
possesses a diamondoid topology with 4-methoxypyridine present as a guest within the framework.

![Crystal structure of 18](image)

**Figure 4.6.** Crystal structure of 18: a) the [Zn₃(RCO₂)₆] cluster in 18; b) cross-linking between clusters through bdc ligands to generate a 4-connected tetrahedral node; c) 3D metal-organic diamondoid framework in 18.

We were also able to isolate compound 19, [Zn₃(5-t-butyl-bdc)(methanol)₄]ₙ, (Figure 4.7). The metal cluster in 19 consists of a central 6-coordinate octahedral Zn(II) ion coordinated by four bidentate carboxylates and two methanol ligands. The two exterior Zn(II) ions of the cluster posses a 4-coordinate tetrahedral geometry and each are coordinated by two bidentate and one monodentate carboxylate groups with a methanol ligand ligand occupying the remaining site. The Zn-Zn distances within this cluster measured from the central Zn ion are 3.830 Å and 3.848 Å. The trizinc hexacarboxylate clusters in 19 behave as a 6-connected octahedral node as they are linked together through 5-t-butyl-bdc ligands to six other clusters. The resulting 3D metal-organic framework possesses a cubic topology and no guest or solvent molecules are present.
Thermogravimetric analysis of 19 demonstrates a weight loss at approximately 125 °C which corresponds by weight to the loss of the four methanol ligands. Although we have not been able to confirm the resulting structure we propose that the \([\text{Zn}_3(5\text{-t-butyl-bdc})_3]_n\) cubic framework is still in tact and appears to be thermally stable up to approximately 350 °C before decomposing.

Figure 4.7 Crystal structure of 19: a) the \([\text{Zn}_3(\text{RCO}_2)_6]\) cluster in 19; b) linking between clusters through bdc ligands to generate a 6-connected octahedral node; c) 3D metal-organic cubic framework in 19.

4.4 Ternary Nets

As discussed earlier Wells catalogued network structures in crystals\(^{23}\) and spawned the “node-and-spacer” methodology\(^{256}\) which simplifies design since it reduces MBB’s into topological points and lines. Interpretation and design of nets can also take into account the geometrical shape of the MBB’s by representing nets as vertex-linked polygons or polyhedra (VLPP).\(^{257}\) Topologically the simplest nets are unitary nets.
comprised of only one type of MBB for which the topology of the net is directed by the geometry and arrangement of the MBB’s: (10,3)-a (triangular MBB’s), diamondoid tetrahedral MBB’s), NbO (square MBB’s), and primitive cubic (octahedral MBB’s) nets. The VLPP approach comes into its own for binary nets sustained by pairs of polygonal or polyhedral MBB’s and even the simplest combinations of MBB’s can result in structural diversity as exemplified by (3,4)-connected nets.\(^{191, 194, 258-261}\) Nevertheless, the design of novel topologies remains challenging and is a dominant theme in crystal engineering since new topologies can serve as “blueprints” for the design of new classes of materials. We have proposed a design strategy based upon the VLPP approach for the synthesis of ternary nets sustained by a combination of three distinct polygons or polyhedra\(^{37}\) utilizing zinc (II), which is known to offer structural diversity. Herein, we delineate how 3-

![Molecular Building Blocks used in USF-5](image)

**Figure 4.8** Molecular Building Blocks used in USF-5: a) Molecular building blocks (MBB’s) employed in the 20a: a) 5-NH$_2$-1,3-bdc – triangular MBB; b) Cu$_2$(RCO$_2$)$_2$L$_2$ – square MBB; c) Cu(RCO$_2$)$_2$(RNH$_2$)$_2$L – pseudo-tetrahedral MBB.
connected triangular MBB’s with different coordinating functional groups such as, 5-NH$_2$-1,3-bdc (5-amino-1,3-benzenedicarboxylate)$^{262}$ can promote the formation of two distinct metal centers and a ternary net (Figure 4.8) with a new topology, USF-5: [Cu$_4$(5-NH$_2$-1,3-bdc)$_4$(pyridine)$_2$(H$_2$O)$_2$]$_n$, 20a.

The square MBB utilized in USF-5 (20a) is based upon the paddlewheel dicopper tetracarboxylate, [Cu$_2$(RCO$_2$)$_4$L$_2$]. The Cu(5-NH$_2$-1,3-bdc)$_4$/3(H$_2$O)$_n$. building block in 20a is a pseudo-tetrahedral MBB. The 5-coordinate Cu(RCO$_2$)$_2$(RNH$_2$)$_2$L chromophore is present in over 50 crystal structures in the CSD. USF-5 (20a) is closely related to the previously reported USF-4$^{37}$ in that each triangular MBB is linked to one square MBB and two pseudo-tetrahedral MBB’s which in turn are each linked to four triangular

![Figure 4.9](image)

**Figure 4.9** Crystal structure of 20a: a) triangular 5-NH$_2$-1,3-bdc units linked to one square MBB and two pseudo-tetrahedral MBB’s. b) Crystal structure of 20a viewed down the x-axis in stick representation (pyridine and H$_2$O ligands have been deleted for clarity). c) Schematic representation of 1 in VLPP format viewed down the x-axis.
MBB’s (Figure 4.9). However, USF-5 is significantly different than USF-4 and previously reported (3,4)-connected networks, the long vertex symbols, 
\[(4\cdot8\cdot8)_{4}(8\cdot8\cdot8\cdot8\cdot12\cdot12_{8})_{2} (4\cdot4\cdot8\cdot8\cdot12\cdot13)_{2}\] being hitherto unprecedented.\(^{263-265}\) When the experimental conditions of \(20a\) were altered to utilize 4-picoline instead of pyridine we obtained two products: green crystals \((20b)\) isostructural to with the pyridine ligand replaced for a 4-picoline ligands; and yellow crystals of \([\text{Cu}(5\text{-NH}_2\text{-1,3-bdc})(4\text{-picoline})]_n\), \(21\), (Figure 4.10). The 2-D honeycomb framework of \(21\) is composed of 3-connected 5-NH\(_2\)-1,3-bdc ligands and 5-coordinate Cu (II) metal centers which also serve as 3-connected nodes. A series of Zn(II) analogues of this structure has recently been reported.\(^{266}\)

![Figure 4.10](image)

**Figure 4.10** Crystal structure of \(21\): a) crystal structure of \(21\) in stick representation. b) schematic representation of \(21\) in VLPP format. c) bilayer structure formed from interdigitating 4-picoline ligands on adjacent layers (illustrated as blue and red) of \(21\).

### 4.5 Conclusions

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We have shown how the structural diversity associated with Zn(II)-carboxylate coordination chemistry can lead to the formation of a number of unpredictable yet interesting results. Although this chemistry can be difficult to control it is possible to generate both the square and tetrahedral dizinc tetracarboxylate from the same starting materials and it is even possible to have both cluster present within the same structure. Likewise, through serendipity we were also able to isolate three different trizinc hexacarboxylates metal clusters which were able to be utilized as 3-, 4- and 6-connected nodes to generate 2D and 3D frameworks. Finally, we have demonstrated a second simple strategy for the design of ternary nets, i.e. triangular MBB’s containing different coordinating functional groups (i.e. carboxylates and amines) which promote the formation of geometrically and chemically distinct metal centers.

4.6 Experimental

4.6.1 Syntheses

All materials were used as received; solvents were purified and dried according to standard methods.

Synthesis of \( \{[\text{Zn}_2(\text{bdc})_2(\text{DMSO})_2(\text{H}_2\text{O})] \cdot 3 \text{ DMSO}\}_n \) (15). A white precipitate was obtained from dropwise addition of 2,6-lutidine (0.27mL, 2.3mmol) to a stirred methanolic solution (30mL) of benzene-1,3-dicarboxylic acid (197mg, 1.18mmol) and zinc (II) nitrate hexahydrate (275mg, 0.92mmol). Colorless crystals of 15 were obtained by recrystallizing the white precipitate from DMSO.
Synthesis of \([\text{Zn}_2(\text{bdc})_2(4\text{-methoxypyridine})_2][\text{Zn}_2(\text{bdc})_2(4\text{-methoxypyridine})(\text{methanol})]_2 \cdot \text{methanol}\)_2\(\cdot\) \(n\) \(16\). Colorless crystals of \(16\) were obtained from slow diffusion via layering a methanolic solution (2.0mL) of benzene-1,3-dicarboxylic acid (17mg, 0.10mmol) and zinc (II) nitrate hexahydrate (30mg, 0.10mmol) through a methanolic layer (2.0mL) onto a methanolic solution (2.0mL) of 4-methoxypyridine (0.03mL, 0.3mmol) and hexafluorobenzene (0.5mL)).

Synthesis of \([\text{Zn}_3(\text{bdc})_3(6\text{-methoxyquinoline})_2] \cdot 6\text{-methoxyquinoline} \cdot \text{methanol}\)_\(n\) \(17\). Colorless crystals of \(17\) were obtained from slow diffusion via layering a methanolic solution (10.0mL) of benzene-1,3-dicarboxylic acid (83mg, 0.50mmol) and zinc (II) nitrate hexahydrate (149mg, 0.50mmol) through a methanolic layer (10.0mL) onto a methanolic solution (10.0mL) of 6-methoxyquinoline (0.28mL, 2.0mmol). X-ray powder diffraction (XPD) was obtained for \(17\) and the major diffraction peaks obtained from the bulk experimental sample match the major peaks from the calculated powder pattern.

Synthesis of \([\text{Zn}_3(1,3\text{-bdc})_3(4\text{-methoxypyridine})_2] \cdot 2\ 4\text{-methoxypyridine}\)_\(n\) \(18\). Colorless crystals of \(18\) were obtained from slow diffusion via layering a methanolic solution (10.0mL) of benzene-1,3-dicarboxylic acid (82mg, 0.49mmol) and zinc (II) nitrate hexahydrate (150mg, 0.50mmol) through a methanolic layer (10.0mL) onto a nitrobenzene solution (10.0mL) of 4-methoxypyridine (0.15mL, 1.5mmol).

Synthesis of \([\text{Zn}_3(5\text{-t-butyl-bdc})_3(\text{methanol})_4]_n \cdot \text{methanol}\)_\(n\) \(19\). Colorless crystals of \(19\) were obtained from slow diffusion via layering a methanolic solution (10.0mL) of 5-t-Butyl-benzene-1,3-dicarboxylic acid (111mg, 0.50mmol) and zinc (II) nitrate hexahydrate (150mg, 0.50mmol) through a methanolic layer (10.0mL) onto a benzene
solution (10.0mL) of 4-picoline (0.15mL, 1.5mmol). X-ray powder diffraction (XPD) was obtained for 19 and the major diffraction peaks obtained from the bulk experimental sample match the major peaks from the calculated powder pattern.

**Synthesis of** \([\text{Cu}_4(5-\text{NH}_2-\text{bdc})_4(\text{pyridine})_2(\text{H}_2\text{O})_2]_n (20a)\). Green crystals of 20a form in a 38% yield within one day of layering a 10.0 mL methanolic solution of copper (II) nitrate hemipentahydrate (116 mg, 0.499 mmol) through a 10.0 mL methanol buffer layer onto a 10.0 mL methanolic solution containing 5-amino-1,3-benzenedicarboxylic acid (91 mg, 0.50 mmol) and pyridine (0.12 mL, 1.5 mmol).

**Synthesis of** \([\text{Cu}_4(5-\text{NH}_2-\text{bdc})_4(4-\text{picoline})_2(\text{H}_2\text{O})_2]_n (20b) and [\text{Cu}(5-\text{NH}_2-\text{bdc})(4-\text{picoline})]_n (21)\). Green 20b and yellow 21 crystals form within one day of layering a 10.0 mL methanolic solution of copper (II) nitrate hemipentahydrate (116 mg, 0.499 mmol) through a 10.0 mL methanol buffer layer onto a 10.0 mL methanolic solution containing 5-amino-1,3-benzenedicarboxylic acid (91 mg, 0.50 mmol) and 4-picoline (0.15 mL, 1.5 mmol).

**4.6.2 X-ray Crystallography**

Single crystals suitable for X-ray crystallographic analysis were selected following examination under a microscope. Intensity data were collected on a Bruker-AXS SMART APEX/CCD diffractometer using Mo_Kα radiation (\(\lambda = 0.7107\) Å). The data were corrected for Lorentz and polarization effects and for absorption using the SADABS program (SAINT). The structures were solved using direct methods and refined by full-matrix least-squares on \(|F|^2\) (SHELXTL).
Table 4.1. Crystallographic data for compounds 15-21.

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<td>0.493, -0.351</td>
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3.6.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis for 17 was performed under nitrogen as a dynamic scan at a maximum heating rate of 50 °C/min on a TA Instrument TGA 2950 Hi-Res. Thermogravimetric analysis for 19 was performed under nitrogen at a fixed heating rate of 25 °C/min on a Perkin Elmer STA 6000 Simultaneous Thermal Analyzer.

Figure 4.11 TGA of Compound 17 – \{[Zn_3(bdc)_3(6-methoxyquinoline)_2] \cdot 6-methoxyquinoline \cdot methanol\}_n

Zn^{2+} = 65.38 g/mol

bdc^{2-} = 164.10 g/mol

6-methoxyquinoline = 159.2 g/mol

methanol = 32.04 g/mol

\{[Zn_3(bdc)_3(6-methoxyquinoline)_2] \cdot 6-methoxyquinoline \cdot methanol\} = 1198.08 g/mol
Theoretical Weight Loss:

methanol & 6-methoxyquinoline & (6-methoxyquinoline)₂ / {[Zn₃(bdc)₃(6-methoxyquinoline)₂] • 6-methoxyquinoline • methanol} x 100 = 42.54 %

Experimental Weight Loss: 41.43%

Figure 4.12 TGA of Compound 19 – [Zn₃(5-t-butyl-bdc)₃(methanol)₄]ₙ

Zn²⁺ = 65.38 g/mol
5-t-butyl-bdc²⁻ = 220.22 g/mol
methanol = 32.04 g/mol

[Zn₃(5-t-butyl-bdc)₃(methanol)₄] = 984.96 g/mol

Theoretical Weight Loss:

(methanol)₄ / [Zn₃(5-t-butyl-bdc)₃(methanol)₄] x 100 = 13.01 %

Experimental Weight Loss: 4.888 / 36.855 = 13.26 %
4.6.4 X-Ray Powder Diffraction (XPD)

High resolution X-ray Powder Diffraction (XPD) data were recorded on a Bruker D8 Advance X-Ray diffractometer at 20kV, 5mA for Cu Kα (λ = 1.5418 Å), with a scan speed of 0.5 sec/step (1°/min) and a step size of 0.05° in 2θ at room temperature.

Figure 4.13 XPD of Compound 17 – {[Zn₃(bdc)$_3$(6-methoxyquinoline)$_2$] • 6-methoxyquinoline • methanol}$\_n$
Figure 4.14 XPD of Compound 19 – $[\text{Zn}_3(5\text{-t-butyl-bdc})_3(\text{methanol})_4]_n$
5.1 Introduction

Since the principles of crystal engineering have been applied towards nanoscience the design and synthesis of high molecular weight discrete compounds has blossomed. Many of these organic\textsuperscript{31-32}, metal-organic\textsuperscript{33-36}, and inorganic\textsuperscript{267-268} structures have been obtained via design principles that invoke geometric as well as chemical considerations to generate curvature and enclose space. This has been particularly evident from the numerous nanoscale structures based upon Platonic (regular) and Archimedean (semi-regular) solids (Figure 5.1).\textsuperscript{269}

\textbf{Figure 5.1} The five Platonic and 13 Archimedean solids.
Characteristically these compounds are prepared by one of two approaches: edge-sharing of molecular polygons which affords closed convex polyhedra, whereas, the second method generates open structures that are the edge-skeletons of polyhedra through the connection of appropriately designed molecular vertices by linear bifunctional rod-like ligands. As previously outlined our design principle involves vertex-sharing of molecular polygons (squares) a strategy which is closely related to a previously unexplored third class of uniform polyhedra constructed from linking the vertices of regular polygons. These structures are referred to as faceted polyhedra as they contain both open (concave) and closed (convex) faces.\textsuperscript{270} Of the nine faceted polyhedra Figure 5.2, three can be generated from the assembly of only square polygons and are dependent solely on the angle subtended by the “spacer” moiety which serves to link these squares.

![Figure 5.2](image.png) The nine Faceted polyhedra. The three polyhedra pictured along the bottom consist of only squares.
at their vertices: cubohemiocahedron (90°) < small rhombihexahedron (120°) < small rhombidodecahedron (144°). We have demonstrated that the angle between the carboxylates of the bdc ligand can be used to assemble square paddlewheel SBUs at an angle of 120° to generate infinite coordination polymers. Zaworotko\textsuperscript{271} and Yaghi\textsuperscript{272} demonstrated that the curvature imposed by this ligand also allows for the assembly of twelve paddlewheel SBUs in such a way that they can enclose space to form a discrete nanoscale small rhombihexahedron (Figure 5.3).

Similarly to the 2D tetragonal sheets and Kagomé structures discussed earlier these nanoballs can be decorated with a variety of functional groups by way of using different 5-R-bdc ligands (Figure 5.4). The Zaworotko group has reported hydroxy\textsuperscript{273}, methoxy\textsuperscript{274}, and sulfonated\textsuperscript{274} derivatives. Whereas other groups have reported t-butyl\textsuperscript{275} and a long alkoxy chain derivative\textsuperscript{276-277}. The diameter and molecular weight of these decorated nanoballs can be greatly altered depending upon the 5-R-bdc derivative utilized as the exterior surface of these newly decorated nanoballs possess twenty-four of these
functional groups. The solubility to a certain degree can be controlled, for instance the long alkoxy decorated nanoball is soluble in many common non-polar solvents whereas the hydroxy nanoball is very soluble in methanol. In fact, through a recent study preformed with collaborators we were able to monitor the formation of the hydroxy nanoball in solution and at the same time prove that the nanoball remained in tact while in solution.\textsuperscript{278}

![Figure 5.4](image_url) Decorated nanoballs synthesized in the Zaworotko lab.

### 5.2 Nitro Nanoball

The nitro nanoball $[\text{Cu}_2(5-\text{NO}_2-\text{bdc})_2(L)_2]_{12}$, (Figure 5.5), with twenty-four exterior NO$_2$ groups residing on the exterior surface of the nanoball can be readily
synthesized from Cu(II) and 5-NO$_2$-bdc using a variety of pyridine based coordinating axial ligands as well as different solvents and templates.

![Figure 5.5 Nitro nanoball $[\text{Cu}_2(5-\text{NO}_2\text{-bdc})_2(\text{L})_2]_{12}$, 22.](image)

Nitro-nanoballs 22a-22h were prepared at room temperature via layers from methanol (MeOH) or ethanol (EtOH) solvent with pyridine (py), 3-picoline (3-pic), 4-picoline (4-pic), 3,5-lutidine (3,5-lut) or quinoline (quin) as a base and in 22a-22g nitrobenzene (nb) was present as a template whereas in 2h o-dichlorobenzene (o-dcb) was utilized as a template (Table 5.1). The number of base ligands which coordinate axial to the exterior of these nanoballs varies from 8-11 out of a possible 12 coordination sites.

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The remaining exterior and interior coordination sites are coordinated by methanol / ethanol and H$_2$O. The diameter of these nitro nanoballs varys from 3.50 nm to 3.76 nm depending upon the axial coordinating ligand. Each nanoball has 12 closest neighbors, which form a distorted cuboctahedron and thus emulates cubic close packing (Figure 5.6). The range of distances from the nanoball center to 12 closest neighbors is the widest in 22a and 22b (2.40 nm – 3.09 nm) and this range is the smallest in 22g and 22h (2.43 nm – 2.66 nm).

![Figure 5.6 Cubic close packing in nitro nanoballs.](image)

### 5.2.1 Host:Guest Interactions

The porous nanoball surface can be viewed as association of six metallocalix[4]arene and eight metallocalix[3]arene cone shaped bowls (Figure 5.7). The walls of each bowl is assembled from three or four 5-NO$_2$-bdc ligands and held together with three or four square paddlewheels.
The crystal structure of the nitro nanoball (22a-22g) shows that these bowl shaped cavities can incorporate multiple guest molecules forming huge supramolecular complexes, (Figure 5.8). The molecular mass of the nitro nanoballs is in the range of 7.8-8.3 kDa and depends upon the axial coordinated ligands. The molecular mass of supramolecular inclusion complexes varies from 10.8 to 12.3 kDa and thus guest molecules can consist of 24-36% the supramolecular complexes mass.

![Figure 5.7 Metal-organic metallo-calixarene present in nitro nanoball: a) square metallocalix[4]arene; b) triangular metallocalix[3]arene.](image)

![Figure 5.8 The inclusion complex in 22a-22g.](image)
The aromatic nature of nanoball cavities determines the main scenery of its interaction with the small guest molecules. The solvent nitrobenzene or base molecules are captured in the nanoball pores by stacking interactions with 5-NO$_2$-bdc and coordinated aromatic base moieties, which shape the cavities walls. The solvent molecules inside the cavities can also interact between themselves via face-to-face and edge-to-face stacking interactions. The hetero guests inclusion in one of the square cavities is shown in Figure 5.9. The 3,5-lutidine and nitrobenzene guest molecules are completely included in the cavity and form the double sandwich with two opposite 5-NO$_2$-bdc ligands. Four aromatic moieties take part in the $\pi-\pi$ stacking interactions.

**Figure 5.9** Host:Guest interaction in nitro nanoball metallocalixarenes. Top and side view of inclusion manner of 3,5-lutidine and nitrobenzene molecules intercalate in square nanoball cavity due to face-to-face $\pi-\pi$ stacking interactions of different arene moieties: 5-NO$_2$-bdc, 3,5-lutidine, nitrobenzene and 5-NO$_2$-bdc.

The aromatic guest molecules demonstrate a versatile mode of $\pi-\pi$ stacking interactions with 5-NO$_2$-bdc and coordinated to nanoball exterior aromatic base as well as face to face and edge to face stacking interactions between themselves. The inclusion
mode differs in square and triangular cavities and can also vary in cavities of the same type by number and manner of included guest molecules. Additional representative examples of interactions in square cavities and triangular cavities are provided in Figures 5.10 and 5.11 respectively.

**Figure 5.10** Host:Guest interactions within the square metallo[4]calixarene’s.

**Figure 5.11** Host:Guest interactions within the triangular metallo[3]calixarene’s.
5.2.2 Nitro Nanoball Solubility Studies

Due to the weak of fluorescence emission of 5-NO\textsubscript{2}-bdc it was not possible to analyze the solution stability and formation of the nitro nanoballs in solution as was done with the hydroxy nanoballs. However, we were able to perform qualitative solubility studies on these nitro nanoballs (Table 5.2). Small vials were filled with 2 mL of solvent to which 8-10 mg of solid was added. The following criteria was used to categorize the solubility observed in these system: not soluble – the solid did not go into solution with or without heat; sparingly soluble – a slightly discoloration of the solvent with most of the solid out of solution; partially soluble – approximately 50% of the solid dissolved into solution, solvent color change was observed; soluble – the solid completely dissolved into solution.

Table 5.2 Solubility tests for nitro nanoballs.

<table>
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<tr>
<th>Solvent</th>
<th>22a</th>
<th>22b</th>
<th>22c</th>
<th>22d</th>
<th>22e</th>
<th>22f</th>
<th>22g</th>
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<tr>
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<td>soluble</td>
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<td>soluble</td>
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<td>Chloroform</td>
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<td>partially soluble</td>
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<td>not soluble</td>
<td>not soluble</td>
</tr>
</tbody>
</table>
5.3 Sulfonated Nanoball

These nanoballs are ideally suited for exploitation as nanoscale building blocks since they are predisposed towards further decoration at either the axial metal sites or the bdc ligand. Here, we address decoration of the prototypal nanoball and how it thereby becomes feasible to engage in a form of suprasupermolecular chemistry.\textsuperscript{279}

Compound 23, \(\{[\text{Cu}_2(5-\text{SO}_3\text{-bdc})_2(4\text{-methoxy-pyridine})_{0.50}(\text{MeOH})_{\lambda}(\text{H}_2\text{O})_{1.50-\lambda}][\text{Cu}(4\text{-methoxypyridine})_4]\}_{\lambda}^\bullet[\text{Cu}(4\text{-methoxypyridine})_4]\}_{n}\), forms a sulfonated version of the nanoball (Figure 5.12) which has 24 $\text{SO}_3^-$ groups exposed on the exterior surface of the sphere resulting in an anionic nanoball with a molecular weight of ca. 8.6 kDa, a diameter of 3.6 nm (measured from opposite groups at the periphery), and a molecular volume of ca. 24.4 nm\(^3\). In comparison, the original nanoball has a molecular weight of ca. 6.8 kDa and a molecular volume slightly greater than 10 nm\(^3\).

![Figure 5.12 Sulfonated nanoball (24$^-$ anion).](image)

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They are suitable for coordination to Cu(II) and, in the presence of excess copper (II) nitrate, 16 sulfonate moieties bond to 16 \([\text{Cu(methoxypyridine)}_4]^{2+}\) cations that facilitate crosslinking via axial coordination to a second sulfonate moiety that lies on an adjacent nanoball (Figure 5.13). The Cu-N distances in all the bridging \(\text{CuN}_4\text{O}_2\) moieties fall within an acceptable range (1.98-2.07Å). While the Cu-O distances of the \(\text{CuN}_4\text{O}_2\) moieties which crosslink the nanoballs along the xz plane is within a narrow range (2.38-2.41Å), the Cu-O distances of the remaining 8 cross-linking moieties vary significantly (2.33-2.85Å). The variation in these \(\text{CuN}_4\text{O}_2\) moieties is still consistent with what would be expected for this known chromophore.\(^{280}\) The remaining negative charge of the system is balance by the presence of two \([\text{Cu(4-methoxypyridine)}_4(\text{H}_2\text{O})_2]^{2+}\) cations and 4-methoxypyridium cations that are located in the interstitial spaces. The distance from the center of adjacent nanoballs averages 3.05 nm and reduction of the sulfonated nanoballs to an 8-connect node results in the generation of a bcc network (Figure 5.14). Although a few examples have recently been reported for assembling nanoscale
structures into polymeric compounds\textsuperscript{281-287}, \textbf{23} is the first example of such structure constructed by employing the principles of crystal engineering and suprasupermolecular chemistry. Using the mono-lithium salt of the ligand as opposed to the mono-sodium salt we were able to isolated \textbf{24}, \{[Cu\textsubscript{2}(5-SO\textsubscript{3}-bdc)\textsubscript{2}(methanol)\textsubscript{2}]\textsuperscript{24+} • 24 Li\textsuperscript{+}\}_n, the discrete anionic sulfonated nanoball. Unfortunately, to date we have not been able to located the lithium cations within the crystal structure.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{sulfonated_nanoballs.png}
\caption{Sulfonated nanoballs as an eight connected node and the generation of a bcc network.}
\end{figure}

\textbf{5.4 Conclusions}

Discrete metal-organic nanoballs can readily be prepared and in a similar fashion to the 2D tetragonal and Kagomé sheets can be decorated with various functional groups which can affect. These nanoballs have been shown to be stable in solution and their
solubility can be altered depending upon which functional group they may be decorated with. Their ability to behave as “host” molecules within a host:guest complex has been proven as they square and triangular metallo-calixarene cavities can complex same organic in a variety of ways. Finally, the suprasupramolecular chemistry of these nanoballs can be controlled thus affording them the ability to behave as nanoscale building blocks in the generation of extended metal-organic frameworks.

5.5 Experimental

5.5.1 Syntheses

All materials were used as received; solvents were purified and dried according to standard methods.

**Synthesis of [{[(Cu$_2$(5-NO$_2$-bdc)$_2$)$_{12}$(3,5-lutidine)$_{10}$(MeOH)$_{14}$] • 22 (NB) • (MeOH)}$_n$ (22a).** Blue-green crystals of 22a were obtained in a 22.5% yield from slow diffusion via layering a methanolic solution (10.0mL) of 3,5-lutidine (0.171mL, 1.50mmol) through a methanol layer (8.0mL) onto a methanolic solution (10.0mL) of 5-nitroisophthalic acid (105mg, 0.497mmol), Cu(II) nitrate hemipentahydrate (119mg, 0.512mmol) and nitrobenzene (4.0mL).

**Synthesis of [{[(Cu$_2$(5-NO$_2$-bdc)$_2$)$_{12}$(3,5-lutidine)$_{10}$(EtOH)$_{12}$(H$_2$O)$_2$] • 4 (3,5-lutidine) • 18 (NB) • 8 (EtOH)}$_n$ (22b).** Blue-green crystals of 22b were obtained in a 8.0% from slow diffusion via layering an ethanolic solution (10.0mL) containing 3,5-lutidine (0.171mL, 1.50mmol) through an ethanol layer (8.0mL) onto an ethanolic
solution (10.0mL) of 5-nitroisophthalic acid (90mg, 0.426mmol), Cu(II) nitrate hemipentahydrate (98mg, 0.421mmol) and nitrobenzene (4.0mL).

**Synthesis of** \{[(Cu$_2$(5-NO$_2$-bdc)$_2$)$_{12}$(pyridine)$_{10.44}$(MeOH)$_{13.56}$] • 2 (pyridine) • 28 (NB) • 8 (MeOH) • 6 (H$_2$O)$_n$ (22c). Blue-green crystals of 22c were obtained in a 16.5% from slow diffusion via layering a methanolic solution (10.0mL) containing pyridine (0.122mL, 1.50mmol) through a methanol layer (8.0mL) onto a methanol solution (10.0mL) of 5-nitroisophthalic acid (105mg, 0.497mmol), Cu(II) nitrate hemipentahydrate (119mg, 0.512mmol) and nitrobenzene (4.0mL).

**Synthesis of** \{[(Cu$_2$(5-NO$_2$-bdc)$_2$)$_{12}$(3-picoline)$_{9.4}$(EtOH)$_{14.6}$] • 24 (NB) • 4 (EtOH) • 12 (H$_2$O)$_n$ (22d). Blue-green crystals of 22d were obtained in a 4.9% from slow diffusion via layering an ethanolic solution (10.0mL) containing 3-picoline (0.146mL, 1.50mmol) through an ethanol layer (8.0mL) onto an ethanolic solution (10.0mL) of 5-nitroisophthalic acid (90mg, 0.426mmol), Cu(II) nitrate hemipentahydrate (98mg, 0.421mmol) and nitrobenzene (4.0mL).

**Synthesis of** \{[(Cu$_2$(5-NO$_2$-bdc)$_2$)$_{12}$(4-picoline)$_{11}$(MeOH)$_{11}$(H$_2$O)$_2$] • 28 (NB) • 12 (MeOH)$_n$ (22e). Blue-green crystals of 22e were obtained in a 21.2% from slow diffusion via layering a methanolic solution (10.0mL) containing 4-picoline (0.146mL, 1.50mmol) through a methanol layer (8.0mL) onto a methanol solution (10.0mL) of 5-nitroisophthalic acid (123mg, 0.529mmol), Cu(II) nitrate hemipentahydrate (123mg, 0.529mmol) and nitrobenzene (4.0mL).

**Synthesis of** \{[(Cu$_2$(5-NO$_2$-bdc)$_2$)$_{12}$(4-picoline)$_{9}$(EtOH)$_{3}$(H$_2$O)$_{12}$] • 24 (NB) • 15 (EtOH) • 4 (H$_2$O)$_n$ (22f). Blue-green crystals of 22f were obtained in a 16.9% from slow diffusion via layering an ethanolic solution (10.0mL) containing 4-picoline (0.146mL,
1.50 mmol) through an ethanol layer (10.0 mL) onto an ethanolic solution (10.0 mL) of 5-nitroisophthalic acid (107 mg, 0.507 mmol), Cu(II) nitrate hemipentahydrate (116 mg, 0.499 mmol) and nitrobenzene (4.0 mL).

**Synthesis of** \( \{(\text{Cu}_2(5\text{-NO}_2\text{-bdc})_2)_{12}\text{(quinoline)}_{10}\text{(MeOH)}_{14}\} \cdot 24 \text{ (NB) } \cdot 32 \text{ (MeOH)} \}_n \) (22g). Blue-green crystals of 22g were obtained in a 7.8% from slow diffusion via layering a methanolic solution (10.0 mL) containing quinoline (0.178 mL, 1.50 mmol) through a methanol layer (8.0 mL) onto a methanol solution (10.0 mL) of 5-nitroisophthalic acid (105 mg, 0.497 mmol), Cu(II) nitrate hemipentahydrate (119 mg, 0.512 mmol) and nitrobenzene (4.0 mL).

**Synthesis of** \( \{(\text{Cu}_2(5\text{-NO}_2\text{-bdc})_2)_{12}\text{(quinoline)}_8\text{(MeOH)}_{16}\} \cdot 76 \text{ (MeOH) } \cdot 64 \text{ (H}_2\text{O)} \}_n \) (22h). Blue-green crystals of 22h were obtained in a 7.7% from slow diffusion via layering a methanolic solution (10.0 mL) containing quinoline (0.178 mL, 1.50 mmol) through a methanol layer (8.0 mL) onto a methanol solution (10.0 mL) of 5-nitroisophthalic acid (112 mg, 0.530 mmol), Cu(II) nitrate hemipentahydrate (133 mg, 0.572 mmol) and o-dichlorobenzene (4.0 mL).

**Synthesis of** \( \{(\text{Cu}_2(5\text{-SO}_3\text{-bdc})_2(4\text{-methoxy-pyridine})_{0.50}\text{(MeOH)}_x\text{(H}_2\text{O)}_{1.50-}\text{x)}\}_12 \text{[Cu(4methoxypyridine)_{4}]_s}[\text{Cu(4-methoxy pyridine)_{4}]_2\}_n \) (23). Blue-green crystals of 5i were obtained from slow diffusion via layering a methanolic solution (10.0 mL) of 5-sulfo-benzene-1,3-dicarboxylic acid monosodium salt (135 mg, 0.503 mmol) and copper (II) nitrate hemipentahydrate (115 mg, 0.494 mmol) through a methanolic layer (10.0 mL) onto a methanolic solution (10.0 mL) of 4-methoxypyridine (0.15 mL, 1.5 mmol) and nitrobenzene (2.0 mL). Crystals form within days in 17% yield.
Synthesis of $\{[\text{Cu}_2(5-\text{SO}_3\text{-bdc})_2(\text{methanol})_2]^{24+} \cdot 24 \text{ Li}^+\}_n$ (24). Green crystals of 5i were obtained from slow diffusion via layering a methanolic solution (10.0mL) of 5-sulfo-benzene-1,3-dicarboxylic acid monolithium salt (124mg, 0.49mmol) and copper (II) nitrate hemipentahydrate (232mg, 0.997mmol) through a methanolic layer (10.0mL) onto a methanolic solution (10.0mL) of 4-methoxypyridine (0.15mL, 1.5mmol) and nitrobenzene (2.0mL).

5.5.2 X-ray Crystallography

Single crystals suitable for X-ray crystallographic analysis were selected following examination under a microscope. Intensity data were collected on a Bruker-AXS SMART APEX/CCD diffractometer using $\text{Mo}_\text{K}a$ radiation ($\lambda = 0.7107 \, \text{Å}$). The data were corrected for Lorentz and polarization effects and for absorption using the SADABS program (SAINT). The structures were solved using direct methods and refined by full-matrix least-squares on $|F|^2$ (SHELXTL). All non-hydrogen atoms were refined anisotropically.
### Table 5.3 Crystallographic data for compounds 22-24.

<table>
<thead>
<tr>
<th></th>
<th>22a</th>
<th>22b</th>
<th>22c</th>
<th>22d</th>
<th>22e</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
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<td>C₆₀₀H₄₀₀Cu₂₄N₄₀O₆₀</td>
<td>C₄₃₄H₃₅₄Cu₂₄N₆₂O₂₂₄</td>
<td>C₄₉₀H₄₄₈Cu₂₄N₅₆O₁₆₈</td>
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<td>100(2)</td>
<td>100(2)</td>
<td>293(2)</td>
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<td>Monoclinic</td>
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<td>P-1</td>
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<td>C2/c</td>
<td>C2/m</td>
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<td>24.024(4)</td>
<td>37.926(6)</td>
<td>38.188(3)</td>
<td>26.688(2)</td>
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<td>32.469(2)</td>
<td>27.273(2)</td>
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<td>100.401(3)°</td>
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<td>90°</td>
<td>90°</td>
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<td>90°</td>
<td>90°</td>
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<td>0.10x10x0.05</td>
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<td>1.07 to 22.55</td>
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<td>1.54 to 25.08</td>
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<td><strong>Completeness to θ</strong></td>
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<td>32900 / 454 / 2655</td>
<td>42085 / 155 / 2482</td>
<td>32894 / 121 / 2716</td>
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<td><strong>Goodness-of-fit on R²</strong></td>
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<td>1.131</td>
<td>1.086</td>
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<td><strong>Final R indices [I&gt;2sigma(I)]</strong></td>
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<td>R1 = 0.1470</td>
<td>R1 = 0.0945</td>
<td>R1 = 0.0990</td>
<td>R1 = 0.0877</td>
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<td>wr2 = 0.2924</td>
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<td>R1 = 0.1365</td>
<td>R1 = 0.1466</td>
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<td>wr2 = 0.4181</td>
<td>wr2 = 0.3004</td>
<td>wr2 = 0.3186</td>
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<td>1.991, -0.826</td>
<td>2.160, -1.936</td>
<td>1.349, -0.866</td>
<td>1.153, -0.756</td>
<td>1.770, -0.813</td>
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<td>22f</td>
<td>22g</td>
<td>22h</td>
<td>23</td>
<td>24</td>
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<td>-----</td>
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<tr>
<td><strong>Empirical formula</strong></td>
<td>C₄₁₇H₃₅₅Cu₂₄N₅₅O₂₁₉</td>
<td>C₃₀₈H₁₄₀Cu₂₄N₃₆O₁₉₇</td>
<td>C₅₀₄H₄₅₆Cu₂₄N₂₄O₹₆</td>
<td>C₂₀₉H₁₂₂Cu₁₇N₂₅O₁₃₅S₁₂</td>
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<td><strong>Formula weight</strong></td>
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<td>9909.89</td>
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<td>293(2)</td>
<td>100(2)</td>
<td>100(2)</td>
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<td>Tetragonal</td>
<td>Tetragonal</td>
<td>Monoclinic</td>
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<td><strong>Space group</strong></td>
<td>I₂/m</td>
<td>I₄/m</td>
<td>I₄/m</td>
<td>P2₁/n</td>
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<td><strong>a, Å</strong></td>
<td>26.922(3)</td>
<td>24.4181(19)</td>
<td>24.275(2)</td>
<td>30.4712(11)</td>
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<tr>
<td><strong>b, Å</strong></td>
<td>33.567(4)</td>
<td>24.4181(19)</td>
<td>24.275(2)</td>
<td>46.5263(17)</td>
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<td><strong>c, Å</strong></td>
<td>27.363(5)</td>
<td>40.380(7)</td>
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<td><strong>α, deg</strong></td>
<td>90°</td>
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<td><strong>β, deg</strong></td>
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<td>90°</td>
<td>90°</td>
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<td>90°</td>
<td>90°</td>
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<tr>
<td><strong>V, Å³</strong></td>
<td>24485(6)</td>
<td>24076(5)</td>
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<td>42756(3)</td>
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<td><strong>Z</strong></td>
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<td>2</td>
<td>2</td>
<td>4</td>
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<tr>
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<td>1.514</td>
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<td>1.377</td>
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<tr>
<td><strong>µ, mm⁻¹</strong></td>
<td>1.123</td>
<td>1.122</td>
<td>1.121</td>
<td>0.963</td>
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<tr>
<td><strong>F(000)</strong></td>
<td>11380</td>
<td>9024</td>
<td>10224</td>
<td>15460</td>
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<tr>
<td><strong>Crystal size, mm</strong></td>
<td>0.10x0.10x0.07</td>
<td>0.30x0.20x0.10</td>
<td>0.30x0.20x0.10</td>
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<td><strong>θ range for data collection, deg</strong></td>
<td>1.67 to 25.06</td>
<td>1.67 to 22.64</td>
<td>1.55 to 25.11</td>
<td>0.98 to 22.57</td>
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<td><strong>Limiting indices</strong></td>
<td>-32&lt;=h&lt;=32, -39&lt;=k&lt;=24, -32&lt;=l&lt;=32</td>
<td>-26&lt;=h&lt;=22, -26&lt;=k&lt;=26, -43&lt;=l&lt;=43</td>
<td>-28&lt;=h&lt;=27, -28&lt;=k&lt;=28, -48&lt;=l&lt;=45</td>
<td>-32&lt;=h&lt;=32, -50&lt;=k&lt;=50, -43&lt;=l&lt;=43</td>
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<td><strong>Reflections collected</strong></td>
<td>64779</td>
<td>49980</td>
<td>63348</td>
<td>181062</td>
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<td><strong>Unique reflections</strong></td>
<td>22043</td>
<td>8120</td>
<td>10821</td>
<td>56042</td>
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<td>0.1909</td>
<td>0.1028</td>
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<td><strong>Completeness to θ</strong></td>
<td>99.6 %</td>
<td>99.4 %</td>
<td>99.9 %</td>
<td>99.4 %</td>
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<td>none</td>
<td>none</td>
<td>multi-scan</td>
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<tr>
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<td>none</td>
<td>none</td>
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<td><strong>Data/ restraints/ parameters</strong></td>
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<td>8120 / 78 / 680</td>
<td>10821 / 171 / 748</td>
<td>56042 / 16 / 4392</td>
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<tr>
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<td>0.768</td>
<td>1.568</td>
<td>0.841</td>
<td>1.119</td>
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<tr>
<td><strong>Final R indices [I&gt;2σ(I)]</strong></td>
<td>R1 = 0.0856, wR² = 0.2227</td>
<td>R1 = 0.1426, wR² = 0.4035</td>
<td>R1 = 0.1055, wR² = 0.2748</td>
<td>R1 = 0.1829, wR² = 0.4510</td>
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<tr>
<td><strong>R indices (all data)</strong></td>
<td>R1 = 0.2395, wR² = 0.2558</td>
<td>R1 = 0.1907, wR² = 0.4256</td>
<td>R1 = 0.2163, wR² = 0.3142</td>
<td>R1 = 0.2117, wR² = 0.4676</td>
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<tr>
<td><strong>Large diff. peak and hole, e•Å⁻³</strong></td>
<td>1.101, -0.752, 1.212, -0.714, 1.695, -0.559, 2.622, -0.997</td>
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</table>
6.1 Summary and Conclusions

The research presented within this dissertation is concerned with developing an understanding of the basic principles that govern the supramolecular behaviors of metal-organic materials and gaining an experimental control over the structure and function of these new classes of materials. To summarize, this dissertation has contributed to the following:

i) A series of fluorescent Zn-bipy 1D ladder and 2D square grid metal-organic materials have been prepared with pyrene intercalated between the layers and aromatic solvent molecules incorporated within the cavities defined by the Zn-bipy coordination. The resulting solid state fluorescence could be assigned to the formation of face-to-face a pyrene:bipy exciplex in the 1D ladder structures and an edge-to-face pyrene:bipy exciplex in the 2D square grid structure. These different interactions yield differences in emission maxima and fluorescence lifetimes and could be used as a diagnostic probe of the structure of these materials.

ii) An excellent example of supramolecular isomerism has been provided as three dramatically different metal-organic architectures (2D tetragonal sheets, 2D Kagomé sheets, and 3D USF-1) have been prepared from the same set of [Zn₂(RCO₂)₄] square building blocks linked though their vertices with an angular spacer (bdc). Also, within the series of 2D tetragonal sheet structures a unique form of supramolecular atropisomerism
occurs in the metallo-calixarene like cavities. To the best of our knowledge this is the only example of this phenomena which has been reported in a metal-organic material.

iii) The 2D tetragonal and Kagomé sheets can readily be decorated with various functional groups, we demonstrated that both Cu(II) and Zn(II) can be utilized as the metal cation in most of these structures. In some instances the guest molecules can be changed, and through careful selection of the axial coordinating ligand we are able to obtain slight control over the packing distances between these layers. Even if it is only to a small extent this demonstrated that it is possible for crystal engineers to effect a small degree of control within these systems.

iv) The structural diversity associated with Zn(II)-carboxylate coordination chemistry has been demonstrated as a number of metal-organic materials based upon lesser known tetrahedral dizinc tetracarboxylate \([\text{Zn}_2(\mu^2-\text{RCO}_2)_3(\mu^1-\text{RCO}_2)]\) and trizinc hexacarboxylate \([\text{Zn}_2(\text{RCO}_2)_4]\) clusters which can be utilized as 3-, 4- and 6-connected nodes to generate 2D and 3D frameworks.

v) A second simple strategy for the design of ternary nets has been delineated through utilization of triangular MBB’s containing different coordinating functional groups (i.e. carboxylates and amines) which promote the formation of geometrically and chemically distinct metal centers.

vi) Discrete metal-organic nanoballs can readily be prepared and in a similar fashion to the 2D tetragonal and Kagomé sheets can be decorated with various functional groups which can affect: 1) the solubility of the discrete nanostructures; 2) their ability to behave as “host” molecules within a host:guest complex; and 3) their
suprasupramolecular chemistry and thus the ability to behave as nanoscale building blocks in the generation of extended metal-organic frameworks.

In conclusion, the focal point of this work has been devoted to illuminating basic principles of supramolecular chemistry and crystal engineering in the context of synthesizing metal-organic materials, which could be applicable to a much more broad range of supramolecular materials.

6.2 Future Directions

It is an exciting time to be involved with metal-organic materials as the field continues to grow rapidly with more and more scientists “jumping on the bandwagon”. Advances in single crystal x-ray crystallography and the synthetic methodologies employed to form these materials has made it possible to generate molecules and frameworks the scale of which previously would not have been possible. However, the crux of materials science is not just to prepare novel materials but novel materials with function. The movement to functional metal organic materials has already begun and to date there have been promising results reported in terms of porosity and to a lesser extent catalysis. Although metal-organics with a large degree of porosity and/or catalytic activity are desirable scientists should continually attempt to think outside of the box in an attempt to find the next great usage for metal-organic materials. Eventually it will also be necessary to develop a greater understanding in terms of the formation of these materials and their nucleation processes. For instance, although supramolecular isomerism can lead to an enviable number of interesting products it can also potentially
be problematic if attempting to target one particular isomer and another one inexplicably forms and/or competes with the formation of your targeted structure.

Preliminary magnetic measurements of the decorated Kagomé lattices discussed earlier have demonstrated that the electron withdrawing/donating capability of the various functional groups could provide a small degree of control over the magnetic moment observed in these compounds. Although these metal-organic Kagomé lattices we have developed will most likely never be made into functional magnetic materials the principle that scientists could have a degree of control over the magnetism in these systems could be of great use in related metal-organic magnetic materials.

Whereas much of the focus in terms of metal-organics has revolved around solid state materials and properties there is also a great deal of potential for the discrete metal-organic in terms of solution chemistry. For instance, working with collaborators we were able devise an unconventional methodology for analyzing the formation and stability in solution of the hydroxylated nanoballs developed in the Zaworotko lab.

At the moment the future of metal-organic materials is as bright as ever and the field should continue to flourish as long as researchers continued to be creative.
References


152. There are 190 crystal structures deposited in the CSD containing 4,4’-bipyridine ligands that bridge 2 metals and exhibit pyridyl ring torsion angles which fall within the range of $23.975^\circ$ – $31.664^\circ$. (c) there are 275 crystal structures deposited in the CSD containing 4,4’-bipyridine ligands that bridge 2 metals and exhibit pyridyl ring torsion angles which fall within the range of $0.0^\circ$ – $1.0^\circ$; CSD V5.28 – Nov. 2006 + 1 update.


262. There have been 28 crystal structures containing 5-amino-1,3-benzenedicarboxylate coordinated to metal centers reported in the CSD V5.29 (Nov. 2007 + 1 update) – none of which can be interpreted as a ternary net.


281. A. J. Cairns, J. A. Perman, L. Wojtas, V. Ch. Kravtsov, M. H. Alkordi, M.


About the Author

Gregory J. McManus was born in Prince Edward Island, Canada, in 1980. He received a B.Sc. degree (with honors in chemistry) from the University of Prince Edward Island in 2002. In August 2002, Gregory was admitted to the Ph.D. program at the University of South Florida and joined Dr. Michael J. Zaworotko’s research group. His research interests are mainly focused upon crystal engineering of molecular solids, and particularly, design and synthesis of functional metal-organic framework materials. He is a member of the American Chemical Society and the Canadian Society for Chemistry. He has published 13 scientific papers, including 7 communications and 6 full articles. He has made a total of 17 oral or poster presentations at local, regional, and national, and international conferences. He has received multiple distinctions during graduate school including being awarded the George Bursa award in 2004 which is awarded annually to an outstanding graduate student in the chemistry department at USF. In 2005, he was awarded the Theodore and Venette Askounes Ashford Doctoral Fellowship in Chemistry also awarded annually to an outstanding graduate student in the chemistry department at USF. In 2005 and 2006, he was awarded with a Provost Graduate Teaching Assistant Award which is a designed to recognize the teaching abilities of graduate students from different disciplines all across the University of South Florida.