Design of Metal-Organic Framework Materials Based upon Inorganic Clusters and Polycarboxylates

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Design of Metal-Organic Framework Materials Based upon Inorganic Clusters and Polycarboxylates

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy
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Dedication

To my family
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ABSTRACT

Network structures based upon metal-organic backbones represent a new class of functional materials that can be rationally constructed by employing the concepts of supramolecular chemistry and crystal engineering. The modularity of design strategies, the diversity of prototypal structures, and the dynamic features of networks have afforded great advantages over traditional materials syntheses. The research presented in this dissertation is primarily concerned with developing an in-depth understanding of the basic principles that govern the supramolecular behaviors of metal-organic frameworks and gaining an experimental control over the structure and function of these new classes of hybrid materials.

The use of rigid and angular organic ligands along with transition metal clusters gives rise to a wide variety of novel metal-organic architectures ranging from zero-dimensional nanostructures to three-dimensional frameworks. Gas sorption experiments suggest some of these compounds are potentially useful as porous materials. Conformational analysis of these structural models reveals geometrical foundations for the existence of superstructural diversity. Controlled crystallization experiments further indicate synthetic factors that might determine the formation of supramolecular isomers.
On the other hand, careful selection of more labile organic components leads to flexible metal-organic frameworks exhibiting dynamic characteristics that have not been observed in their rigid counterparts. The guest-dependent switch-on/off of cavities and the ease of fine-tuning their chemical environments demonstrate the effectiveness of such a strategy in the context of generating tailored functional materials.

Discovery and recognition of novel three-periodic metal-organic nets remains a nontrivial exercise. In this context, rigorous topological analysis assists the understanding of complicated nets and application of geometrical principles facilitates designing of new metal-organic structures.

Finally, scaled-up metal-organic frameworks are potentially accessible with the aid of existing prototypical structures and a systematic study on ligand design.
Chapter 1

Introduction

1.1 Preamble: Crystals

1.1.1 Crystals and the Science of Crystals

“These were little plates of ice, very flat, very polished, very transparent, about the thickness of a sheet of rather thick paper...but so perfectly formed in hexagons, and of which the six sides were so straight, and the six angles so equal, that it is impossible for men to make anything so exact.”

René Descartes, 1635

For centuries, the extraordinary beauty of crystals has captivated people’s fondness and curiosities. Snowflakes, diamonds and common salt are familiar examples of crystals and their distinctive and beautiful patterns have sparked the interest of writers, poets, photographers, philosophers, mathematicians, and scientists throughout history. Although it is almost impossible to determine at what point in the history did mankind begin their fascination with crystals, it has been known that as early as 135 B.C., ancient Chinese had recorded their observations of snow as “always six-pointed”. The first attempt to fundamentally understand the nature of a crystal, i.e., to relate the external form or shape of a crystal to its underlying structure, was made in 1611 by Johannes Kepler, who speculated that the hexagonal close-pack of spheres may have something to do with the morphology of snow crystals. Robert Hooke went on to extend this idea to other crystals and show how different shapes of crystals--rhomb, trapezia, hexagons, etc.--could arise from the packing together of spheres and globules. René Just Haüy (also known as Abbé Haüy, 1743-1822) discovered that crystals of the same composition
possessed the same internal nucleus, even though their external forms differed. The now banished *molécules intégrantes* that he persistently used in his original treatise eventually transformed into “unit cells”, the contemporary term to describe the smallest building block of a crystal, and for this reason, he is arguably regarded by some as the father of modern crystallography.

The modern development of the science of crystals, however, began after the discovery of X-ray by W. C. Röntgen in 1895 and, in particular, when Max von Laue demonstrated in 1912 that passage of a narrow beam of X-ray through a crystal of copper sulfate resulted in a pattern of spots on a photographic plate due to the diffraction of very short waves by the crystal. Shortly thereafter, W. H. Bragg (1862-1942) and his son, W. L. Bragg (1890-1971) utilized and extended this diffraction method to determine the arrangement of the atoms within such simple crystalline materials as NaCl, pyrite, fluorite, and calcite. By examining the pattern of X-rays diffracted by various crystals, the Braggs were able to establish the fundamental mathematical relationship between an atomic crystal structure and its diffraction pattern--the Bragg’s Law. Since that time, the improvement of the techniques of X-ray crystallography has resulted in an enormous increase in the store of scientific knowledge of matter in the solid state, with consequent impact on the development of the sciences of physics, chemistry, biology, and geology. Today, hundreds of thousands of crystal structures have been determined for a wide spectrum of molecules ranging from simple inorganic and organic compounds to complex multi-chained proteins and nucleic acids.
1.1.2 The Crystal as Molecular Entity

When cooled sufficiently, the vast majority of substances form one or more crystalline phases, where the atoms, molecules or ions interplay with each other via different kinds of chemical interactions such as covalent, ionic, and metallic bonds. The resulting entities exhibit a regular repeating array of atoms, molecules or ions that extend in three dimensions. Mathematically, these chemical building units can be represented by their centers of gravity and a crystal can be simplified as a three-dimensional lattice based upon an infinite number of points orderly arranged in space and entirely related by symmetry. In reality, however, most atoms, molecules and ions are anisotropic and real crystals often feature defects or irregularities in their ideal arrangements. Interestingly, many of the mechanical, electrical and chemical properties of real crystalline materials are critically dependent upon such defects.

1.1.3 Solid State Chemistry

Solid state chemistry is concerned with the synthesis, structure, properties and applications of solid materials. Whereas some aspects of glasses and other amorphous solids are also quite relevant to solid state chemistry, crystalline materials are generally of paramount importance in most cases, and accordingly crystals and crystallography have been often associated with this subject. Solid state compounds represent an important class of materials with high technological relevance and they have been widely used as key devices, such as superconductors, fast ion conductors, magnets, non-linear optics, luminescent materials, laser materials, and hydrogen storage materials, just to name a few.
Traditional solid state chemistry usually involves the study of inorganic materials including naturally occurring minerals, and large majority of these compounds are non-molecular, i.e., their structures are determined by the manner in which the atoms and ions are packed together in three dimensions. Although the types of elements involved in these non-molecular solids are relatively limited in the periodic table, the structural diversity exhibited by the materials is nevertheless amazingly striking. For example, of the nearly 25,000 known binary compounds there exist at least 100 structure types, and among the estimated 100,000 possible ternary phases, of which only about 5% have been investigated, already more than 700 structure types have been identified and several thousand more might be expected; not to even mention yet those of quaternary and quinary systems.

Historically, the discovery of new solid state compounds, especially those with novel structure types, has largely relied on serendipitous, or at best, empirical processes. The synthesis of extended structure compounds usually takes place at the range of 500°C to 2,500°C and at such high temperatures the control over structure and reactivity is inevitably diminished to a considerable degree. For a long period of time solid state synthesis has been decried as “shake and bake” or “heat and beat”, and there is a widely-held belief that the preparation of new solid-state compounds based on rational design is not possible. However, this situation is gradually being changed and a number of efforts have been devoted to establish a priori synthetic strategies for solid state materials. In particular, two different methods, one of which considers constructing a free energy landscape assisted by computational modeling while the other takes advantage of the
concept of molecular building blocks, point at the future direction of solid state synthesis: materials by design.

1.2 Supramolecular Chemistry

1.2.1 History and Scope

“The relations between toxin and its antitoxin are strictly specific... For this reason it must be assumed that the antipodes enter into a chemical bond which, in view of the strict specificity is most easily explained by the existence of two groups of distinctive configuration - of groups which according to the comparison made by Emil Fischer fit each other ‘like lock and key’.”

Paul Ehrlich, 1908

Although Nature has established its own supramolecular chemistry through billions of years of evolution, the most elegant examples including enzyme-substrate interactions and DNA double helix formation and replication, that of mankind can be only traced back to the late 19th and early 20th century when Paul Ehrlich, the founder of modern chemotherapy, first introduced the idea of receptor while recognizing that molecules do not act if they do not bind. It was Emil Fischer, however, who expressively enunciated the concept of binding selectivity and geometrical complementarity of molecular recognition in his celebrated “lock and key” model. In 1948, H. M. Powell described a series of what he called clathrates--inclusion compounds formed when small molecules, such as methanol, hydrogen sulphide or sulphur dioxide, are completely enclosed in cavities formed by a “host” such as a hydroquinone network. In the 1960’s, Charles J. Pedersen showed that some cyclic polyethers, which he termed crown ethers, bind the alkali ions (i.e., Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺) strongly and selectively. The selectivity is essentially determined by the degree of geometrical match between the cations and the cavities of crown ethers into which the spherical metal ions will fit. This discovery
represents a breakthrough towards the ambition of many chemists (of then and today!): designing and synthesizing organic molecules that mimic the extraordinary functions of biological systems (e.g., enzymes, DNA, etc). Jean-Marie Lehn and Donald J. Cram subsequently each developed increasingly sophisticated organic compounds containing holes and clefts that bind cationic as well as anionic and neutral species even more efficiently and selectively. With this work, Pedersen, Lehn and Cram, who also shared the Nobel Price of Chemistry in 1987, laid the foundations of what is today one of the most active and expanding fields of chemical research--supramolecular chemistry.

Thus, supramolecular chemistry, as coined by Lehn, may be defined as “chemistry beyond the molecule”, i.e., it is the chemistry of molecular assemblies and of the intermolecular bond. Two main tenets, molecular recognition and supramolecular function, lie at the center of understanding the concepts of supramolecular chemistry. Whereas mere binding doesn’t necessarily infer recognition, molecular recognition is generally regarded as a patterned process involving a structurally well-defined set of intermolecular interactions: binding with a purpose. It thus implies the storage, at the supramolecular level, of molecular information associated with their electronic properties, size, shape, number, and arrangement. There are generally two partially overlapping areas encountered in supramolecular chemistry: 1) supermolecules, well-defined, discrete oligomolecular species that result from the intermolecular association of a few components; 2) supramolecular assemblies, polymolecular entities that result from the spontaneous association of a large undefined number of components into a specific phase having more or less well-defined microscopic organization and macroscopic characteristics. More recently, suprasupermolecules, a new class of organized entities
that bridge the gap between the above two, has been delineated.\textsuperscript{22, 23} Therefore
“supramolecular chemistry” is a broad term that concerns the chemistry of all types of
supramolecular entities including the well-defined supermolecules, the extended, more or
less organized, polymolecular associations, and their appropriate combinations.

The breadth and especially the unifying power of the perspectives and conceptual
framework of supramolecular chemistry developed by Lehn as well as other researchers
have become progressively more and more evidenced. In fact, over the past few decades,
supramolecular chemistry has fueled numerous developments at the interfaces with
biology, physics, and engineering, thus giving rise to the emergence and establishment of
supramolecular science and technology.\textsuperscript{24} Nevertheless, although in principle the
molecular recognition events occurring at various levels exhibit similar characteristics, it
is perhaps still quite appropriate to note the significantly different aspects of
supramolecular chemistry that takes place among different physical states of matters.
Notably, the early development of host-guest chemistry was originated from solutions
and the fundamental principles governing solution behaviors of molecular aggregates are
relatively better understood compared to those in the solid state.

1.2.2 Supramolecular Chemistry in Solution

The pioneering examples of synthetic receptors featuring macrocyclic shapes
developed by Pedersen, Lehn and Cram have established the field of host-guest chemistry.
However, two main drawbacks are inherently associated with this early approach: 1) the
construction of host molecules almost exclusively relies upon the tedious and irreversible
covalent synthesis of a single structure; 2) the sizes of holes or cavities exhibited by the
host molecules are relatively small, thus limiting their recognition capabilities to small guest species such as alkali ions. Accordingly, an alternative synthetic strategy that takes advantage of multiple building blocks, reversible self-assembly process, and “weak” intermolecular forces, such as hydrogen bonds and metal coordination, is highly desirable.

The first examples of self-assembled hydrogen-bonded molecular receptors were described by J. Rebek, Jr. in the 1990’s. Two self-complementary molecules assemble to form dimers via an array of hydrogen bonds, giving rise to molecular capsules enclosing either spherical/semispherical or cylindrical cavities (Figure 1.1). Depending on the size and shape of the monomeric species, a wide variety of guests can be included inside the capsules and quite often simultaneous encapsulation of more than one guest molecule has been observed. The electronic and geometric restrictions by the confined space result in some unique and interesting behaviors of the guest molecules. For example, the accommodation of p-quinone and 1, 3-cyclohexadiene inside the “softball” capsule dramatically accelerates the Diels-Alder reaction, whereas the unusual associations of pairs of guests within the cylindrical capsule lead to the discovery
of “social isomerism”. Nevertheless, since only relatively weak intermolecular interactions, i.e., hydrogen bonds, are involved, the formation and disassociation of the capsules is reversible and the systems reach thermodynamic equilibrium rapidly under mild conditions in solution. Thus they require analytical methods that operate on the same timescale (such as NMR spectroscopy and electrospray mass spectrometry). Furthermore, the inclusion complexes do not survive purification by chromatography and few of these encapsulation complexes have been characterized by X-ray crystallography.

Therefore, relatively stable (that is, longer lived but still reversibly formed) encapsulation complexes should be explored by using the stronger forces of metal–ligand interactions. In this regard, Fujita has taken advantage of pyridine-based monodentate ligands and cis-capped square planar transition metal units and developed a series of cationic supramolecular metal-organic aggregates based upon what he has termed the “molecular paneling” approach. In particular, a M₆L₄ type octahedral cage (Figure 1.2) has been shown to possess a cavity large enough to accommodate up to four guest species,

Figure 1.2. Fujita’s octahedral M₆L₄ cage (left) and Raymond’s tetrahedral M₄L₆ cage (right).
which can be used as ideal molecular chambers for mediating chemical reactions such as Diels-Alder reaction, [2+2] cycloaddition, and Wacker oxidation.\textsuperscript{35,36} Most recently, it was demonstrated that an aqueous solution of the octahedral M\textsubscript{6}L\textsubscript{4} cage induces highly unusual regioselectivity in the Diels-Alder coupling of anthracene and phthalimide guests, promoting reaction at a terminal rather than central anthracene ring.\textsuperscript{37}

Raymond’s group uses an alternative strategy, namely, bidentate chelating ligands and octahedral transition metal units, to direct the assembly of a M\textsubscript{4}L\textsubscript{6} type anionic tetrahedral cage (Figure 1.2) and other related molecular containers.\textsuperscript{38-40} The most salient feature of this approach is the presence of homochirality as a result of trisbidentate coordination at each metal center that leads to either $\Delta$ or $\Lambda$ configuration. The chiral environment of the cavity turns out to significantly stabilize otherwise short-lived organometallic intermediates and therefore mediate their reactivity toward other substrates.\textsuperscript{41}

1.3 Crystal Engineering: a Supramolecular Perspective

1.3.1 History and Scope

Although the roots of crystal engineering can be traced at least as far back as the 1930’s, when Pauling defined the chemical bond in both covalent and non-covalent senses,\textsuperscript{42} the term “crystal engineering” was initially introduced by Pepinsky in 1955 in an effort to solve the “phase problem” in crystallography.\textsuperscript{43} However, it was Schmidt who first systematically formulated this idea in the 1970’s in the context of topochemical reactions. He and his co-workers found that the photo-reactivity of dimerizable olefins, such as substituted cinnamic acids, is critically dependent upon the crystal packing of the
molecules; in other words, solid state reactivity is a supramolecular property and is characteristic of an entire assembly of molecules. Schmidt therefore proposed an “empirical” strategy based upon the understanding of intermolecular forces as an approach for the development of organic solid state chemistry, namely, *crystal engineering*.44

In the late 1980’s and early 1990’s, Desiraju intensively investigated weak intermolecular forces such as C-H⋯X and C-H⋯π and the roles they play in the design of organic solids.45-48 Thanks to his efforts, these interactions are now widely accepted as an important part of the whole spectrum of hydrogen bonds that are crucial for crystal packing of molecules. In his monograph titled “Crystal Engineering: the Design of Organic Solids”, Desiraju has defined crystal engineering as “the understanding of intermolecular interactions in the context of designing new solids with desired physical and chemical properties”.49 The elucidation of the concept *supramolecular synthon*,50 a structural unit within a supermolecule which can be formed and/or assembled by known or conceivable synthetic operations involving intermolecular interactions, has afforded reliable strategies for designing and exploiting crystal structures. Indeed, when crystals are conceived as supermolecules *par excellence*, 51, 52 it is perhaps conceptually instructive to consider crystal engineering as synonymous with supramolecular synthesis in solid state.

Interestingly, almost coincident with the establishment of design principles for organic solids, the development of metal-organic compounds and coordination polymers was mainly pushed forward by Robson using a modular “node-and-spacer” approach in the late 1980’s and early 1990’s.53-55 However, these two seemingly isolated areas were
not unified under the same context until 2001 when Zaworotko explicitly delineated their conceptual similarities.\textsuperscript{56} Today crystal engineering has become a paradigm not only for constructing organic and metal-organic solids, but also for the design of organometallic and inorganic structures.

1.3.2 Intermolecular Interactions

Just as molecular synthesis (organic synthesis in particular) is concerned with the breaking and construction of intramolecular covalent bonds, supramolecular synthesis (crystal engineering in particular) is dictated by the re-organization of intermolecular non-covalent interactions. The existence of attractive and repulsive intermolecular forces and their dynamic balance in crystalline solids are responsible for holding individual molecules in an ordered array and maintaining particular crystallographic symmetries. Depending upon their distance-dependence and their directionality, intermolecular interactions can be classified as London dispersion, dipole-dipole interaction, $\pi-\pi$ stacking, hydrogen bond, and coordination bond, with some overlap between them (Table 1.1).

<table>
<thead>
<tr>
<th>Force</th>
<th>Strength (kJ/mol)</th>
<th>Characteristics</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coordination bond</td>
<td>50-200</td>
<td>Occurs between metal ions and molecules with lone pairs</td>
<td>cis-platin hemoglobin</td>
</tr>
<tr>
<td>Hydrogen bond</td>
<td>1-160</td>
<td>Occurs between molecules with O-H, N-H, F-H and C-H bonds</td>
<td>carboxylic dimers DNA</td>
</tr>
<tr>
<td>$\pi-\pi$ stacking</td>
<td>&lt;50</td>
<td>Occurs between electron- delocalized systems</td>
<td>graphite</td>
</tr>
<tr>
<td>Dipole-dipole</td>
<td>3-4</td>
<td>Occurs between polar molecules</td>
<td>acetone</td>
</tr>
<tr>
<td>London dispersion</td>
<td>1-10</td>
<td>Occurs between all molecules; strength depends on size, polarizability</td>
<td>CO$_2$, He</td>
</tr>
</tbody>
</table>
In classical or Werner type coordination compounds, ligands bind to metal ions almost exclusively via donating their lone pair of electrons, resulting in relatively strong metal-ligand binding. One would argue such an interaction should be regarded as a type of covalent linkage because of the strength criterion; however, if considering their donor-acceptor pattern as well as liable and reversible nature, coordination bonds exhibit more intermolecular characteristics and therefore have been enormously exploited in the context of crystal engineering of functional solids.

1.4 Metal-Organic Frameworks

1.4.1 History and Scope

Metal-organic frameworks (MOFs), also known as metal-organic networks, or coordination polymers, represent a new class of compounds containing metal ions linked by organic bridging ligands. The structures resulting from metal-ligand linkages can be discrete zero-dimensional (0D) molecular complexes or infinite one-dimensional (1D), two-dimensional (2D) or three-dimensional (3D) architectures. Whereas the term “coordination polymers” is more commonly referred to the latter, “metal-organic networks” and “metal-organic frameworks” are applicable in a broader context and are interchangeable in most cases.

One of the very first examples of MOFs that have been structurally characterized appeared in 1943, although similar studies can be traced back to as early as the 1930’s. The area of coordination polymers was initially reviewed in 1964 with an emphasis on the preparations. In the early investigations, Prussian blue based on Fe-CN-Fe linkages and its analogues were perhaps among the most systematically studied. Surprisingly,
however, the field of metal-organic frameworks wasn’t prospering until the late 1980’s when Robson initiated the now famous “node-and-spacer” approach$^{55}$ to incorporate both transition metal ions of well-defined coordination geometries and rod-like organic ligands in the design of network materials. Subsequently, the work by Zaworotko,$^{56,59-61}$ Yaghi,$^{62-65}$ and others$^{66-70}$ substantially contributed to the field and it is now so rapidly developing that the number of coordination polymeric compounds has witnessed an exponential growth in the past few years (Figure 1.3).

In Robson’s original node-and-spacer approach, the nets were usually constructed from organic-based linear spacers as well as metal-based nodes that could be square, tetrahedral, octahedral, etc. This strategy, however, can be conveniently extended to a much broader context where both metal centers and organic ligands can appropriately
function as either nodes or spacers. Figure 1.4 illustrates some representative examples of organic ligands with linear/angular, trigonal, and tetrahedral shapes.

![Figure 1.4 Representative examples of organic ligands used in metal-organic frameworks.](image)

### 1.4.2 Design Principles

Metal-organic frameworks exemplify how crystal engineering has become a paradigm for the design of new supramolecular materials. Since the structures are typically composed of at least two components (i.e., metal ions and organic ligands), it appears clear that such components can be pre-selected for their ability to self-assemble. The network structures can therefore be regarded as examples of blueprints for the construction of networks that, in principle, can be generated from a diverse range of chemical components, i.e., they are prototypal examples of modular frameworks.
There exist two different strategies that have been widely used to direct the syntheses of MOFs. The first is the above mentioned node-and-spacer approach in which the building blocks are simplified as topological points and lines and the nets are represented in their appropriate combinations. Wells was regarded as the pioneer of this approach thanks to his systematic studies on the geometrical basis of crystal chemistry.\(^{72-74}\) Although Wells’ initial work was primarily focused upon inorganic crystalline compounds, Robson extrapolated this method into the realm of metal-organic compounds and coordination polymers.\(^{55}\) As revealed by Figure 1.5, the node-and-spacer approach has afforded a diverse array of metal-organic architectures ranging from 0D discrete nanostructures to 3D infinite networks, some of which have no inorganic analogues.
Another approach, also based upon geometrical principles, takes into account the specific shapes of the building blocks and represents nets as being sustained by vertex-linked polygons or polyhedra (VLPP).\textsuperscript{75-78} Notably nets shown in Figure 1.5 can be equally well represented in the VLPP fashion (Figure 1.6). Whereas the node-and-spacer approach appears more straightforward in cases involving linear spacers, VLPP perspective reveals the more fundamental geometrical relationship between various building units.

Figure 1.6 “Vertex-linked Polygons or Polyhedra” (VLPP) representations of metal-organic frameworks: \(a\) 0D nanoball; \(b\) 3D (10,3)-a net; \(c\) 3D diamondoid net; \(d\) 3D primitive cubic net; \(e\) 3D NbO net.
1.4.3 Structural Analysis of Metal-Organic Nets

The employment of geometrical principles not only facilitates the development of reliable design strategies for the synthesis of metal-organic compounds, but also affords an indispensable tool for the recognition and interpretation of some perplexing nets and prediction of novel nets. In this context, Wells introduced a simple notation \((n, p)\) to describe nets, where \(n\) is the number of edges of polygons present in the net and \(p\) the connectedness of the vertices.\(^72\) For example, the planar square grid (Figure 1.5\(f\)) can be represented as \((4, 4)\) and the symbol \((10, 3)\) implies a 3-connected net based upon 10-membered rings (Figure 1.5\(h\)).

Although Wells notation is still widely accepted in the literature, this method inevitably has some limitations due to its over-simplification. For example, the above mentioned symbol \((10, 3)\) in fact represents several distinct 3D nets that are topologically related but nevertheless inherently different. Therefore a more informative system based upon Schläfli symbols, namely, vertex symbols, has been proposed by O’Keeffe.\(^79\) In his terminologies, O’Keeffe defined rings as shortest closed circuits without any shortcuts for each angle at a vertex and used \(A_a\cdot B_b\cdot […]\cdot M_m\) to depict the connectivity of nets, where \(A, B, \ldots, M\) are numbers that represent the ring size and \(a, b, \ldots, m\) are numbers of the respective rings meeting at that angle (subscript “1” is omitted). Thus \(10_5\cdot 10_5\cdot 10_5\) indicates there are five 10-rings at each of the three angles, and \(10_2\cdot 10_4\cdot 10_4\) suggests two 10-rings at the first angle and four 10-rings at each of the other two, whereas in Wells notations, these two nets are designated as \((10, 3)\)-\(a\) and \((10, 3)\)-\(b\) (or \((10, 3)\)-\(d\)), respectively.
It is important to note the following while using Schlafli symbols to describe metal-organic nets: 1) in principle, the concept of vertex symbols is applicable to any types of nets and the number of angles for a \( m \)-connected node can be generically written as \( m \times (m-1)/2 \) (i.e., there exist three angles for each 3-connected node and six angles for each 4-connected node); in reality, however, it is more widely used for three-dimensional nets that are based upon 3-connected or/and 4-connected nodes because the length of vertex symbols dramatically increases as the connectedness of nodes becomes 5 or higher; 2) for the purpose of clarity, the long Schlafli symbol is sometimes replaced by a short one that specifies just the shortest circuit contained in each angle. The vertex symbols for the above two \((10, 3)\) nets can therefore be both simplified as \(10^3\); 3) for 4-connected nodes, the long Schlafli symbols are usually represented in such a way that opposite angles (those not sharing edges) are paired together and the ones with smallest rings are written first; 4) in some cases, where there might not exist any closed \textit{rings} for a certain angle but the shortest \textit{circuits} are still present, the symbol \( \infty \) and the number that represents the size of the shortest circuit will then be used in the long vertex symbols and the short vertex symbols, respectively. For instance, the 4-connected \( \text{CdSO}_4 \) net is designated as \(6\times6\times6\times6\times6\times6\times\infty\) (long vertex symbol) or \(6^5.8\) (short vertex symbol).\(^{80}\)

However, it should be pointed out even applying Schlafli symbols is sometimes not entirely satisfying. For example, although belonging to completely different topologies, the two well-known 4-connected nets, diamond and lonsdaleite (hexagonal diamond), share the same vertex symbols with each other (i.e., \(6_2\times6_2\times6_2\times6_2\times6_2\times6_2\)). It thus follows that a more rigorous way of describing detail topological information of nets is necessary and one of the possible solutions is to take into account the concept of topological
neighbors--a $k$th neighbor of a vertex is the one for which the shortest path to that vertex consists of $k$ edges. Each different kind of vertex in a net has then associated with it a coordination sequence which is the sequence of $n_1, n_2, \ldots, n_k, \ldots$ where $n_k$ is the number of $k$th topological neighbors. Only by considering coordination sequences, for example, it is possible to distinguish between diamond and lonsdaleite nets (Table 1.2).

<table>
<thead>
<tr>
<th>$k$</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>4</td>
<td>12</td>
<td>24</td>
<td>42</td>
<td>64</td>
<td>92</td>
<td>124</td>
<td>162</td>
<td>204</td>
<td>252</td>
</tr>
<tr>
<td>Lonsdaleite</td>
<td>4</td>
<td>12</td>
<td>25</td>
<td>44</td>
<td>67</td>
<td>96</td>
<td>130</td>
<td>170</td>
<td>214</td>
<td>264</td>
</tr>
<tr>
<td>Difference</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>6</td>
<td>8</td>
<td>10</td>
<td>12</td>
</tr>
</tbody>
</table>

1.4.4 Metal-Organic Frameworks as Functional Materials

Early research in MOFs tended to concentrate on synthesis of a wide variety of new compounds with novel topologies and compositions. Although the design of new structures remains highly topical and a significant amount of research efforts are still devoted to the discovery of unprecedented network topologies, the primary motivation in crystal engineering of MOFs has shifted toward constructing materials that possess specific physical properties and supramolecular functions, such as catalysis, gas storage, luminescence, nonlinear optical properties (NLO), and magnetism.

In 1994, Fujita reported a Cd(II)-(4,4'-bipyridine) square grid complex (Figure 1.7) that catalyzes cyanosilylation of aldehydes with a moderate shape specificity. The heterogeneous metal-organic catalyst has recently been shown to also promote cyanosilylation of imines under similar conditions.
although the active sites are mainly around the surface of the catalyst, binding of substrates by hydrophobic grid cavities also accounts for the acceleration of the reactions.\textsuperscript{89} In addition to this pioneering study, examples in which a wide variety of other reactions are catalyzed by MOFs have also been reported recently.\textsuperscript{90-94}

Nevertheless, the most intriguing opportunity provided by MOF materials in this context is their applications in the asymmetric heterogeneous catalysis.\textsuperscript{95-100} Kim and coworkers constructed a 3D porous homochiral MOF using trimeric Zn\textsubscript{3}(\textmu-O) units and enantiopure chiral organic building blocks derived from tartaric acid (Figure 1.8). The material revealed enantioselective catalytic activity for the transesterification of 2, 4-dinitrophenyl acetate with alcohols.\textsuperscript{101} Lin \textit{et al} subsequently reported a family of chiral porous solids based on lamellar lanthanide phosphonates, which have been shown to be capable of catalyzing several organic transformations including cyanosilylation of aldehydes and ring opening of \textit{meso}-carboxylic anhydrides.\textsuperscript{102} Although these early studies were responsible for the rapid growth of the field of asymmetric metal–organic catalysts, their significance in practical applications has been largely hampered by the
low levels of enantiomeric excess ( ~8% and <5%, respectively). Most recently, high enantiomeric excesses have been achieved in the conversions of aldehydes to secondary alcohols (up to 93% ee)\textsuperscript{103} and the asymmetric epoxidation (82% ee)\textsuperscript{104} using homochiral MOFs as enantioselective catalysts.

In addition to facilitating many chemical transformations, the nanoscale space present in MOFs also provides an ideal platform for various physical processes. Whereas traditional porous materials including inorganic solids\textsuperscript{105-106} (e.g., aluminosilicates and aluminophosphates) and carbonaceous compounds\textsuperscript{107-108} have been widely used in commercial applications such as separation and storage, MOFs have only recently emerged as a new class of porous materials.\textsuperscript{62-66, 68-70, 109} Similar to their inorganic counterparts, microporous\textsuperscript{110} MOF materials typically display type I\textsuperscript{111-112} adsorption isotherms (Figure 1.9) due to the micro-filling of guest molecules into the crystallographically well-defined pores in MOFs. It is worth noting that although the terms “porous” and “open framework” have been commonly used in literature to describe MOFs, largely based upon crystallographic evidences only, porosity is actually a property that must be experimentally demonstrated rather than graphically inferred.\textsuperscript{7, 113-114}

![Figure 1.9 Five types of adsorption isotherm, I to V, in the classification of Brunauer, Deming, Deming, and Teller\textsuperscript{111} (BDDT), together with type VI, the stepped isotherm.](image-url)
One of the first examples of true porous MOFs was reported by Moore and Lee in 1995, in which a (10, 3)-b net based MOF exhibits large open channels and remains its structural integrity even upon guest exchange. In two separate reports, Kitagawa and Yaghi further proved that the permanent porosity of MOFs can be experimentally established by gas adsorption isotherms. Following these early studies, a rapidly growing number of other microporous MOFs have appeared and the surface areas of this new class of porous materials have been shown to be as high as 4,500 m$^2$/g, which is almost 5 times that of the best zeolites.

Due to their crystalline, uniform and adjustable micropores, porous MOFs have recently been targeted as potential adsorbents for a wide variety of gases, including CH$_4$, CO$_2$, acetylene, and H$_2$. These gaseous molecules are of significance either as important industrial raw materials, alternative fuels, or greenhouse gases; the development of new methods that can efficiently separate, sequester, or store these gases is therefore both scientifically and technologically relevant. Of particular interest in the past several years has been the idea of using microporous MOFs with high surface areas to store molecular hydrogen in light of an optimistic future of the “hydrogen economy” (also see section 2.1.3).

Whereas inorganic zeolites have been widely used as “molecular sieves” in various industrial and laboratory separation processes, some of the porous MOFs also reveal similar or, in some cases, unprecedented adsorption selectivity (Table 1.3), which can not necessarily be explained based upon the simple size-matching principles. These compounds thus might find unique applications in areas where traditional porous materials are of limit utility.
Table 1.3 Selected microporous MOFs that have shown adsorption selectivity. \(^a\)

<table>
<thead>
<tr>
<th>Compound[^d]</th>
<th>Structural Description</th>
<th>Selectivity [^b](A_1, A_2, …)/(B_1, B_2, …)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er(_2)(PDA)_3</td>
<td>3D framework based on chain-like infinite (Er-COO)(_n) linkages</td>
<td>CO(_2)/(N(_2), Ar)</td>
<td>[149]</td>
</tr>
<tr>
<td>Mn(HCOO)_2</td>
<td>3D diamondoid net based on vertex-sharing tetrahedral (Mn(_2)O(_4)) clusters</td>
<td>(H(_2), CO(_2))/(N(_2), Ar, CH(_4))</td>
<td>[135]</td>
</tr>
<tr>
<td>Cd(pzdc)(azpy)</td>
<td>3D framework based on pillarared layers</td>
<td>(H(_2)O, MeOH, EtOH, THF, Me(_2)CO)/N(_2)</td>
<td>[206]</td>
</tr>
<tr>
<td>Cd(pzdc)(bpee)</td>
<td>3D framework based on pillarared layers</td>
<td>(H(_2)O, MeOH)/(EtOH, THF, Me(_2)CO, N(_2))</td>
<td>[206]</td>
</tr>
<tr>
<td>Gd(imidca)_2</td>
<td>3D framework based on cage-like building units</td>
<td>H(_2)O/(MeOH, CO(_2), O(_2), Ar, N(_2))</td>
<td>[207]</td>
</tr>
<tr>
<td>Mg(_3)(NDC)_3</td>
<td>3D framework based on chain-like infinite (Mg-COO)(_n) linkages</td>
<td>(H(_2), O(_2))/(CO, N(_2))</td>
<td>[171]</td>
</tr>
<tr>
<td>Cu(hfipbb)(^•) (H(<em>2)hfipbb)(</em>{0.5})</td>
<td>3D 2-fold interpenetrated distorted cubic framework based on Cu(_2)(COO)(_4) paddle-wheel clusters</td>
<td>(CH(_3)CH(_2)CH(_3), CH(_3)(CH(_2)(_2)CH(_3))/CH(_3)(CH(_2)(_2)CH(_3))CH(_3)</td>
<td>[208]</td>
</tr>
<tr>
<td>Zn(aip)(BPy/DPE/DPA/DPP)(_{0.5})</td>
<td>2D bilayer structures based on honeycomb lattices</td>
<td>H(_2)/N(_2)</td>
<td>[185]</td>
</tr>
<tr>
<td>Zn(tbip)</td>
<td>3D framework based on chain-like infinite (Zn-COO)(_n) linkages</td>
<td>((CH(_3))(_2)O, MeOH)/Aromatics; (CH(_3))(_2)O/MeOH</td>
<td>[209]</td>
</tr>
<tr>
<td>Cu(BDT)</td>
<td>3D framework based on chain-like infinite (CuN(_2))(_n) linkages</td>
<td>O(_2)/(H(_2), N(_2))</td>
<td>[195]</td>
</tr>
</tbody>
</table>

[^a]: Only examples with adsorption isotherms were selected.  
[^b]: The symbol (A_1, A_2, …)/(B_1, B_2, …) means guests A_1, A_2, … are favored over guests B_1, B_2, …  
[^c]: Acronyms: PDA = 1, 4-phenylendiacetate; pzdc = pyrazine-2,3-dicarboxylate; azpy = 4,4’-azodipyridine; bpee = 1,2-Bis(4-pyridyl)ethene;imidca = 4,5-imidazolodicarboxylate; NDC = 2,6-naphthalenedicarboxylate;H\(_2\)hfipbb = 4,4’-(hexafluoroisopropylidene)bis(benzoic acid);aip = 5-aminoisophthalate; BPy = 4,4’-bipyridine; DPE = 1,2-di(4-pyridylethylene); DPA = 1,2-di(4-pyridylethane); DPP = 1,3-di(4-pyridylpropane); tbip = 5-tert-butylisophthalate; BDT = 1,4-benzenedithetetrazolate.

In addition to the above applications that are primarily based on their microporous architectures, metal-organic network structures have also been demonstrated to show intriguing properties in a wide variety of other areas such as luminescence,\(^{210-211}\) nonlinear optical properties,\(^{212}\) and magnetism,\(^{213}\) which largely rely upon the metal-
ligand interactions. Most significantly, metal-organic materials that combine multiple functionalities have also appeared. 155, 170, 214
Chapter 2
Metal-Organic Frameworks Based Upon Rigid Angular Dicarboxylates

2.1 Introduction

2.1.1 Secondary Building Units (SBUs)

Crystal engineering, and in particular, design strategies that are based upon geometrical principles, provide successful approaches to the synthesis of metal-organic frameworks. Enormous progress has been made in the past decades, giving rise to a large number of aesthetically pleasing and potentially functional coordination polymers.\textsuperscript{56, 63, 65, 68-70, 215} For example, the self-assembly of 4, 4'-bipyridine, a linear spacer, and single-metal ions has afforded, depending upon the coordination geometry of metal ions, a wide variety of superstructures (Figure 2.1).\textsuperscript{56}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.1.png}
\caption{Metal-organic frameworks based upon 4, 4'-bipyridine and mono-metal centers: \textit{a}) 1D chain; \textit{b}) 1D ladder; \textit{c}) 2D square grid; \textit{d}) 3D diamondoid net.}
\end{figure}
Although this “M—N” (M being referred to single metal ion and N pyridyl nitrogen) based approach proves to be extremely successful, it is nevertheless inherently associated with a number of issues that could potentially be of weakness, especially in the context of porous materials. For instance, the single “M—N” interactions are less rigid and in most cases, the pyridyl rings are subject to free rotation around the metal centers, thus limiting the degree of control over the final structures; the presence of anionic species due to the cationic nature of the frameworks significantly reduces available free space of the structure; attempts to evacuate/exchange guests within the pores often result in collapse of the host framework.

In this context, a so-called “secondary building units (SBUs)” strategy has been employed to overcome the above problems. The concept was originally used in zeolite chemistry where SUBs are referred to the common structural motifs occurring in various tetrahedral frameworks. Yaghi and Eddaoudi extended this idea to metal-organic chemistry and re-defined SBUs as molecular complexes or metal clusters that have well-defined and highly symmetric coordination geometries. Of particular interest are the carboxylate-based metal clusters since the metal ions are locked into positions by the carboxylates. Expansion of SBUs by multifunctional ligands, such as 1, 4-benzene-dicarboxylate and 1, 3, 5-benzenetricarboxylate, allows for the construction of neutral open frameworks of high structural stability.

Figure 2.2 The four dimetal tetracarboxylate secondary building units (SBUs).
In the context of this dissertation, we are interested in exploiting four different SBUs, all of which are dimetal tetracarboxylates and have a general formula of $\text{M}_2(\text{RCOO})_4$ (Figure 2.2). SBU I, famously known as the “paddle-wheel” cluster, has been well studied for decades because of its ubiquity and easy accessibility. It is perhaps the most frequently used SBU in MOF chemistry and is present in over 1,300 crystal structures deposited in the Cambridge Structural Database (CSD). As revealed by Figure 2.3, the paddle-wheel pattern is most commonly seen among metals such as Cu, Rh, Ru, and Mo, etc. SBUs II–IV, on the other hand, are far less common than I and remain largely unexploited in the crystal engineering of metal-organic frameworks. Nevertheless, these four types of SBUs are closely related in that they can all be simplified as 4-connected nodes (either planar or tetrahedral) using the node-and-spacer approach, although from the VLPP perspective they are clearly distinguished by their shapes (Figure 2.4). While SBUs III and IV will be discussed in Chapter 4, we primarily focus upon SBU I and II in this Chapter.

Figure 2.3 Distribution of paddle-wheel SBUs I deposited in the Cambridge Structural Database (CSD) among various transition metal ions. Numbers represent the percentages of SBUs for different metals.
2.1.2 Supramolecular Isomerism

In molecular chemistry, it is a well known phenomenon that some elements and compounds exist in more than one form and the presence of various molecular isomers is due to different arrangements of atoms, which can be exemplified by the four different forms of carbon, i.e., diamond, graphite, C_{60}, and carbon nanotube. A direct analogy can be drawn in supramolecular chemistry where some molecules are capable of interacting with their partners in different ways, giving rise to a diverse range of superstructures. In 1997, Zaworotko first recognized superstructural diversity in metal-organic frameworks in which he observed three supramolecular isomers (two of which are schematically shown in Figure 1.5d and 1.5e) resulting from T-shaped metal centers linked by a conformationally labile bidentate ligand in a 1:1.5 stoichiometry. He subsequently defined supramolecular isomerism as “the existence of more than one type of network superstructure for the same molecular building blocks”. Indeed, as illustrated by Figure 1.5, other pairs of nets can also exhibit similar supramolecular isomerism: zigzag chain vs. helix and honeycomb vs. (10, 3)-a net, for example.
The existence of supramolecular isomerism might be seen as a problem from a design perspective since it necessarily implies the difficulty of control over final structures. In this regard, a detail understanding of the factors that could potentially affect the outcome of crystallization, including solvent polarity, templates, and temperatures, is necessary in order to facilitate the selective formation of one isomer over the others. Ironically, it is also possible to view supramolecular isomerism as an opportunity because gaining a better and more fundamental understanding of the factors that influence crystal nucleation and growth will undoubtedly improve the ability to engineer crystalline solids. In addition, if one considers that the bulk properties of crystalline solids are as critically dependent upon the distribution of molecular components within the crystal lattice as the properties of its individual molecular components, it is perhaps quite appropriate, from a material perspective, to regard the occurrence of supramolecular isomers as a huge bonus. In fact, each of the four carbon polymorphs represents an extremely important class of materials in both academic and industrial areas.

Figure 2.5 Schematic illustrations of five supramolecular isomers based upon SBU I and BDC: A) nanoball; B) tetragonal sheet; C) Kagomé lattice; D) USF-1; E) CdSO₄ net.
Our group has previously shown that Cu(II)/Zn(II)-based paddle-wheel SBUs I and angular spacer 1,3-benzenedicarboxylate (BDC) afford an ideal system for the investigation of supramolecular isomerism. Depending upon various crystallization conditions, such as solvents, templates (molecules that might or might not be directly involved in the final structures but participate in some way during the crystallizations), and axial ligands, a total of five supramolecular isomers have been isolated, i.e., 0D nanoballs (A),\textsuperscript{75} 2D tetragonal sheets (B)\textsuperscript{76} and Kagomé lattices (C),\textsuperscript{218} and 3D USF-1 net (D) and CdSO₄ net (E)\textsuperscript{219} (for detail discussions on the geometrical relationships among these supramolecular isomers and other possible supramolecular isomers, see section 2.2.3).

2.1.3 Hydrogen Storage in Metal-Organic Frameworks

Due to its central role in the projected “hydrogen economy”, hydrogen storage has been intensively studied in the past decades and chemists are, as always, actively involved in seeking suitable chemical means to efficiently store molecular hydrogen. In particular, an energy density superior to liquid hydrogen is expected if hydrogen gas can be efficiently adsorbed onto solid materials via either physisorption or chemisorption. Some critical requirements for an ideal hydrogen storage material should include: 1) high volumetric/gravimetric uptake capacity; 2) fast sorption kinetics at practically feasible temperatures and pressures; 3) high tolerance to recycling.\textsuperscript{220} Along these lines, a great deal of efforts have been devoted to the investigation of both metal hydrides (such as NaAlH₄) and carbon-based nanostructures\textsuperscript{222} as potentially suitable hydrogen storage materials. Although both families show their own advantages, however, none of the
current members from these two categories can meet all three requirements described above.

Metal-organic frameworks have only recently emerged as a new class of porous materials. The extremely high surface areas reported for some of the best MOFs have promoted their study as hydrogen storage materials. Although it has only been three years since the first reports appeared, the field is now rapidly developing and a large number of important discoveries have been reported. Table 2.1 summarizes a most up-to-date list of MOFs that have been probed in the context of hydrogen storage.

Table 2.1 Summary of hydrogen adsorption in MOFs.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structural Descriptions</th>
<th>Surface Areas (m²/g); Model</th>
<th>H₂ Uptake (wt %)</th>
<th>Adsorption Conditions (T, P, Method)</th>
<th>References</th>
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</thead>
<tbody>
<tr>
<td>Zn₄O(1,4-BDC)₃, MOF-5/ IRMOF-1</td>
<td>3D cubic framework</td>
<td>3362; Langmuir</td>
<td>1.32</td>
<td>77K, 1 atm, G</td>
<td>[160]</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>RT, 20 bar, G</td>
<td>[157]</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>1.65</td>
<td>RT, 48 atm, G</td>
<td>[159, 165]</td>
</tr>
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<td></td>
<td></td>
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<td>1.38</td>
<td>77K, 0.92 bar, V</td>
<td>[184]</td>
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<td></td>
<td></td>
<td>4171; Langmuir</td>
<td>5.2</td>
<td>77K, 45 bar, V</td>
<td>[187]</td>
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<tr>
<td></td>
<td></td>
<td>4171; Langmuir</td>
<td>1014; Langmuir</td>
<td>1.6</td>
<td>77K, 10 bar, V</td>
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<td></td>
<td></td>
<td></td>
<td>572; BET</td>
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<td></td>
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<td>3080; Langmuir</td>
<td>4.3</td>
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<td></td>
<td></td>
<td>3840; Langmuir</td>
<td>4.7</td>
<td>77K, 50 bar, V</td>
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<td>2296; BET</td>
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<td>1355; Langmuir</td>
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<td></td>
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<td>1021; BET</td>
<td>0.4</td>
<td>RT, 100 bar, V</td>
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<td>1.22</td>
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<td>Zn₄O(2-Br-1,4-BDC)₃, IRMOF-2</td>
<td>3D cubic framework</td>
<td>2544; Langmuir</td>
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<td>2446; BET</td>
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<td>Zn₄O(CBBDC)₃, IRMOF-6</td>
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<td></td>
<td>3263; langmuir</td>
<td>1.48</td>
<td>77K, 1 atm, G</td>
<td>[183]</td>
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<td>Compound</td>
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<td>BET</td>
<td>Adsorption Temperature</td>
<td>Pressure</td>
<td>Reference</td>
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<td>3305; Langmuir</td>
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<td>1818; Langmuir</td>
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<td>77K, 10–16 bar, V</td>
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<td>Zn₄O(BPDC)₃, IRMOF-9</td>
<td>3D two-fold interpenetrated cubic framework</td>
<td>2613; Langmuir</td>
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<td>183</td>
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<td>Zn₄O(HPDC)₃, IRMOF-11</td>
<td>3D two-fold interpenetrated cubic framework</td>
<td>1911; Langmuir</td>
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<td>2337; Langmuir</td>
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<td>4593; Langmuir</td>
<td>6.7</td>
<td>77K, 78 bar, V</td>
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<td>4024; BET</td>
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<td>Zn₄O(DHBDC)₃, MOF-74</td>
<td>3D framework based on 1D infinite SBUs</td>
<td>1132; Langmuir</td>
<td>1.77</td>
<td>77K, 1 atm, G</td>
<td>183</td>
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<td></td>
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<td>783; BET</td>
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<td>1072; Langmuir</td>
<td>2.3</td>
<td>77K, 50 bar, V</td>
<td>187</td>
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<td>Zn₄O(BTB)₂, MOF-177</td>
<td>3D 2-fold interpenetrated framework based on (3,6)-connected topology gom</td>
<td>4526; Langmuir</td>
<td>1.25</td>
<td>77K, 1 atm, G</td>
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<td>5640; Langmuir</td>
<td>7.5</td>
<td>77K, 69 bar, V</td>
<td>187</td>
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<td>Zn₄O(NTB)₃</td>
<td>3D 2-fold interpenetrated framework based on (3,6)-connected pyrite topology</td>
<td>1121; Langmuir</td>
<td>1.9</td>
<td>77K, 1 atm, V</td>
<td>170</td>
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<td>Zn₄O(L₂)₃(DMF)₂</td>
<td>3D distorted cubic framework of 4-fold interpenetration</td>
<td>502; BET</td>
<td>1.12</td>
<td>RT, 48 bar, G</td>
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<td>Zn₄O(L₂)₃</td>
<td>3D distorted cubic framework of 4-fold interpenetration</td>
<td>396; BET</td>
<td>0.98</td>
<td>RT, 48 bar, G</td>
<td>165</td>
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<tr>
<td>Cu₆(BTC)₂, HKUST-1</td>
<td>3D framework based on twisted</td>
<td>1958; Langmuir</td>
<td>3.6</td>
<td>77K, 50 bar, V</td>
<td>190</td>
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<td></td>
<td></td>
<td>1154; BET</td>
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<table>
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<tr>
<th>Compound</th>
<th>Framework Type</th>
<th>Temperature</th>
<th>Pressure</th>
<th>Adsorption</th>
<th>Reference</th>
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<td><strong>BORACITE TOPOLOGY</strong></td>
<td>3D framework based on twisted boracite topology</td>
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<td>Mo$_3$(BTC)$_2$, TUDMOF-1</td>
<td>3D framework based on twisted boracite topology</td>
<td>2010</td>
<td></td>
<td>1.75</td>
<td>77K, 1 atm, V</td>
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<td>Al(OH)(1,4-BDC), MIL-53 (Al)</td>
<td>3D framework based on 1D infinite SBUs</td>
<td>1020</td>
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<td>3.8</td>
<td>77K, 16 bar, V</td>
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<td>Cr(OH)(1,4-BDC), MIL-53 (Cr)</td>
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<td>3.1</td>
<td>77K, 16 bar, V</td>
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<td><strong>Ni(glutarate), MIL-77</strong></td>
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<td>346/313</td>
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<td>77K, 1 atm, V</td>
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<td>[Al$_2$O(OH)$_3$(H$_2$O)$_3$(Al$_2$(OH)$_3$)][BTC]$_6$, MIL-96</td>
<td>3D framework with three types of cages</td>
<td>NA</td>
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<td>1.91</td>
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<td>Cr$_3$F(H$_2$O)$_3$O (BTC)$_2$, MIL-100</td>
<td>3D framework based on supercages</td>
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<td>77K, 1 atm, V</td>
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<td>[Cr$_3$(1,4-BDC)$_3$][F], MIL-101</td>
<td>3D framework based on supercages and MTN topology</td>
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<td>77K, 20 bar</td>
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<td>Cu(hfipbb)$^*$</td>
<td>3D 2-fold interpenetrated distorted cubic framework</td>
<td>NA</td>
<td></td>
<td>1</td>
<td>RT, 48 atm, G</td>
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<td>Co(ox)(bpy)</td>
<td>2D layered network</td>
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<tr>
<td>Ni(ox)(bpy)</td>
<td>2D layered network</td>
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<td>Co$_2$(BPDC)$_3$(bpy) RPM-1</td>
<td>3D 2-fold interpenetrated framework based on 8-connected nodes</td>
<td>922; BET$^*$</td>
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<td>77K, 1 atm, V</td>
<td>[92, 178]</td>
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<tr>
<td>Zn$_2$(BPDC)$_3$(bpy)</td>
<td>3D 2-fold interpenetrated framework based on 8-connected nodes</td>
<td>792; BET$^*$</td>
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<td>77K, 1 atm, V</td>
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<td>Zn$_2$(L$_3$)</td>
<td>3D framework</td>
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<td></td>
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<td>BET Surface Area (m²/g)</td>
<td>BET Adsorption (m²/g)</td>
<td>Temperature (K)</td>
<td>Pressure (atm)</td>
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<td>Mn(HCOO)$_2$</td>
<td>3D framework based on diamondoid net</td>
<td>312.7</td>
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<td>77K, 1 atm, V</td>
<td>[135]</td>
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<td>Mg(HCOO)$_2$</td>
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<td>77K, 1 atm, V</td>
<td>[176]</td>
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<td>Mn(NDC)</td>
<td>3D framework based on 1D infinite SBUs</td>
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<td>0.57</td>
<td>77K, 1 atm, V</td>
<td>[139]</td>
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<td>[NH$_2$(CH$_3$)$_2$]$<em>8$[Fe$</em>{12}$O$_4$(SO$<em>4$)$</em>{12}$(BPDC)$<em>3$(py)$</em>{12}$], IRMOP-51</td>
<td>Discrete polyhedron based on sulfate-capped trimeric SBUs</td>
<td>191/227</td>
<td>0.44</td>
<td>78K, 500 torr, G</td>
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<td>Pd(2-pymo)$_2$</td>
<td>3D framework based on a sodalite topology</td>
<td>600</td>
<td>1.29</td>
<td>77K, 900 torr, V</td>
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<td>Cu(2-pymo)$_2$</td>
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<td>350</td>
<td>0.86</td>
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<td>[152]</td>
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<td>Dy(BTC)</td>
<td>3D framework with 1D infinite SBUs</td>
<td>655</td>
<td>1.32</td>
<td>77K, 1 atm, V (?)</td>
<td>[153]</td>
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<td>Ni(cyclam)(bpyde)</td>
<td>1D linear chains packed in a hexagonal manner</td>
<td>817</td>
<td>1.1</td>
<td>77K, 1 atm, V</td>
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<td>Zn(nip)(bpy)</td>
<td>1D ladder-type structure</td>
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<td>.48</td>
<td>RT, 30 bar, V</td>
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<td>Ni$_2$(bpy)$_3$(NO$_3$)$_4$ (M)</td>
<td>1D ladder-type structure</td>
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<td>0.99</td>
<td>77K, 1 atm, G</td>
<td>[163]</td>
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<td>2D bilayer-type structure</td>
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<td>77K, 1 atm, G</td>
<td>[163]</td>
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<td>416</td>
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<td>77K, 720 mmHg, V</td>
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<td>Rh$_2$[Cu$^{2+}$TPPP]</td>
<td>3D framework based on NbO topology (proposed)</td>
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<td>[166]</td>
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<td>361</td>
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<td>77K, 720 mmHg, V</td>
<td>[167]</td>
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<td>Rh₂[Pd²⁺TCP]</td>
<td>3D framework based on NbO topology (proposed)</td>
<td>387; Langmuir 318; BET</td>
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<td>77K, 720 mmHg, V</td>
<td>[167]</td>
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<td>89K, 1 atm, V</td>
<td>[168]</td>
</tr>
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<td>Zn₄(1,4-BDC)₃(dabco)</td>
<td>3D cubic framework</td>
<td>2090; Langmuir 1450; BET</td>
<td>2.01</td>
<td>78K, 1 atm, V</td>
<td>[164, 169]</td>
</tr>
<tr>
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<td>3D cubic framework</td>
<td>1670; Langmuir 1100; BET</td>
<td>2.08</td>
<td>78K, 1 atm, V</td>
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<td>[169]</td>
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<tr>
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<td>303; Langmuir 200; BET</td>
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<td>77K, 40 bar, V</td>
<td>[196]</td>
</tr>
<tr>
<td>Mg₃(NDC)₂</td>
<td>3D framework with 1D infinite SBUs</td>
<td>190; BET[11]</td>
<td>0.46</td>
<td>77K, 880 torr, V</td>
<td>[171]</td>
</tr>
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<td>Rh(II)₂(bza)₄(pyz)</td>
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<td>352.5; BET</td>
<td>0.81</td>
<td>77K, 1 atm, V</td>
<td>[148, 172]</td>
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<td>1830; Langmuir 1670; BET</td>
<td>2.47</td>
<td>77K, 750 torr, G</td>
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</tr>
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<td>3D framework based on paddle-wheel SBUs and NbO topology</td>
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<td>504.22; Langmuir</td>
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<td>Cu₃(TATB)₂</td>
<td>3D 2-fold interpenetrated framework based on twisted</td>
<td>3800; Langmuir</td>
<td>1.9</td>
<td>77K, 1 atm, V</td>
<td>[188]</td>
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<td>Compound</td>
<td>Structure Description</td>
<td>BET Surface Area</td>
<td>Temperature</td>
<td>Pressure</td>
<td>Ref.</td>
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<td><strong>H₂[Co₄O(TATB)₃]</strong></td>
<td>3D framework based on (3,8)-connected “the” topology</td>
<td>1.53</td>
<td>77 K, 1 atm, V</td>
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<td>3D triangular framework based on 1D infinite SBUs</td>
<td>1.8</td>
<td>77 K, 43 bar, V</td>
<td>[186]</td>
<td></td>
</tr>
<tr>
<td><strong>Zn(aip)(bpy)₀.₅</strong></td>
<td>2D bilayer structures based on honeycomb lattices</td>
<td>NA</td>
<td>77 K, 1 atm, V</td>
<td>[185]</td>
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<td>77 K, 1 atm, V</td>
<td>[185]</td>
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<tr>
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<td><strong>Zn(aip)(dpp)₀.₅</strong></td>
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<td>77 K, 1 atm, V</td>
<td>[185]</td>
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<td><strong>Ni₂(DHBDC)</strong></td>
<td>3D triangular framework based on 1D infinite SBUs</td>
<td>1.8</td>
<td>77 K, 43 bar, V</td>
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<td>3D framework based on heptametallic SBUs</td>
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<td>RT, 71 bar, V</td>
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<td><strong>Zn₃(BDT)₃</strong></td>
<td>3D framework</td>
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<td><strong>Mn₃(BDT)Cl₂</strong></td>
<td>3D framework</td>
<td>0.97</td>
<td>77 K, 880 torr, V</td>
<td>[195]</td>
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<td>3D hexagonal framework based on 1D infinite SBUs</td>
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<td>77 K, 1 atm, G</td>
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<td><strong>Y₂(PYDC)₃</strong></td>
<td>3D hexagonal framework based on 1D infinite SBUs</td>
<td>0.76</td>
<td>77 K, 1 atm, G</td>
<td>[202]</td>
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[¹] Acronyms: 1,4-BDC = 1,4-benzenedicarboxylate; 2-Br-1,4-BDC = 2-bromobenzene-1,4-dicarboxylate; 2-NH₂-1,4-BDC = 2-aminobenzene-1,4-dicarboxylate; CBBDC = bicyclo[4.2.0]octa-1,3,5-triene-2,5-dicarboxylate; NDc = 2,6-naphthalenedicarboxylate; BPDC = 4,4′-biphenyldicarboxylate; HPDC = 4,5,9,10-tetrahydro-2,7-Pyrenedicarboxylate; PDC = pyrene-2,7-dicarboxylate; TMBDC = 2,3,5,6-tetramethyl-1,4-benzenedicarboxylate; TTDC = thieno[3,2-b]thiophene-2,5-dicarboxylate; DHBDC = 2,5-
dihydroxy-1,4-benzenedicarboxylate; **BTB** = 1,3,5-benzenetribenzoate; **NTB** = 4,4',4''-nitrilotrisbenzoate; **L1** = 6,6'-dichloro-2,2'-diethoxy-1,1'-binaphthyl-4,4'-dibenzoate; **DMF** = N,N-dimethylformamide; **L2** = 6,6'-dichloro-2,2'-dibenzyloxy-1,1'-binaphthyl-4,4'-dibenzoate; **BTC** = 1,3,5-benzenetricarboxylate; **H2hfipbb** = 4,4'-(hexafluoroisopropylidene)bis(benzoic acid); **ox** = oxalate; **bpy** = 4,4'-bipyridine; **L3** = 4,4'-bipyridine-2,6,2',6'-tetracarboxylate; **py** = pyridine; **2-pymo** = 2-pyrimidinolate; **cyclam** = 1,4,8,11-tetraazacyclotetradecane; **bpydc** = 2,2'-bipyridyl-5,5'-dicarboxylate; **nip** = 5-nitroisophthalate; **3-pie** = 3-picoline; **pd** = 1,2-propanediol; **TCPP** = 4,4',4'',4'''-(21H,23H-porphine-5,10,15,20-tetrayl)tetrakis benzoate; **pzdc** = pyrazine-2,3-dicarboxylate; **pyz** = pyrazine; **bptc** = 3,3',5,5'-biphenyltetracarboxylate; **L5** = terphenyl-3,3'',5,5''-tetracarboxylate; **TCPPDA** = N,N,N',N'-tetrakis(4-carboxyphenyl)-1,4-phenylenediamine; **TATB** = 4,4',4''-s-triazine-2,4,6-triyltribenzoate; **aip** = 5-aminoisophthalate; **dpe** = 1,2-di(4-pyridyl-ethene); **dpa** = 1,2-di(4-pyridylethane); **dpp** = 1,3-di(4-pyridylpropane); **pda** = p-phenylenediacrylate; **BDT** = 1,4-benzeneditetrazolate; **PYDC** = pyridine-3,5-dicarboxylate.

While it appears clear that hydrogen storage in MOFs has undergone an exponential growth in terms of both the width and the depth of the related studies, the following key observations should also be noted: 1) Both theoretical calculations and experimental results indicate that the saturation uptakes of H₂ in some of the best MOFs fall within the limits of practical utility, 2) In addition to a large total pore volume, acquiring a pore size matching the molecular dimensions of H₂ has been shown to be equally critical in order to achieve a high gravimetric and volumetric uptake; 3) In the lower pressure range, the inorganic metal-carboxylate clusters (especially those with open metal-sites) of MOFs are believed to be the primary interaction sites for...
hydrogen adsorption, \textsuperscript{173, 183, 188-190, 226, 229} whereas in the higher pressure range, where saturation uptakes are likely to be achieved, the organic components seem to be playing a more important role\textsuperscript{177, 187, 190}; \textbf{4)} A recent study demonstrates that MOF samples ground with catalytic amounts of Pt/AC (active carbon) that can cause dissociation/spillover of H\textsubscript{2} exhibit significantly enhanced hydrogen storage capacity even at ambient temperature (298K)\textsuperscript{198-199} Although the detail mechanism that accounts for such a remarkable enhancement remains to be explored, this new methodology deserves particular attention in that it is perhaps one of the very first efforts to take the advantages of both physisorption and chemisorption (Note that the former is primarily responsible for the adsorption of H\textsubscript{2} in MOFs\textsuperscript{70, 181} whereas the latter is the essential mechanism for storing H\textsubscript{2} in metal hydrides\textsuperscript{221}).

Despite the impressive progress that has been made in the past several years, however, the field of hydrogen storage using porous MOFs is perhaps still in the early stage of its development, as indicated by the relatively insignificant amounts of H\textsubscript{2} uptakes under ambient conditions (Table 2.1). In addition, a number of key issues need to be seriously addressed before major breakthroughs can be achieved:

\textbf{1)} The quality and reproducibility of experimental data will have to be improved. It has been noted that some of the published results from independent groups do not necessarily agree with each. For example, incongruous adsorption properties have been observed for the same materials that are either treated differently\textsuperscript{173, 195} or prepared via various routes\textsuperscript{166, 183, 190}. Different adsorption techniques or instrumentations also contribute to the uncertainty of results.
2) Standard protocols for performing sorption experiments, analyzing sorption data and reporting results need to be established. For instance, there currently exist a wide variety of commercial sorption instruments that are either based on gravimetric method or volumetric method, surface areas of the porous MOF materials are analyzed using different gases (e.g., N\textsubscript{2}, CO\textsubscript{2}, Ar, O\textsubscript{2}, etc.) and different models (Langmuir or BET), and various experimental parameters (such as temperatures and pressures) are being used to investigate H\textsubscript{2} uptakes. All of these have made the comparison of adsorption data from independent studies more difficult.

3) Theoretical or empirical models that can accurately describe and precisely predict hydrogen sorption behaviors under a wide range of conditions are still not readily available. Although classical Langmuir model has been frequently applied to describe the H\textsubscript{2} adsorption isotherms in MOFs, special cautions should be exerted when predictions (e.g., estimated saturation H\textsubscript{2} uptakes) based on this theory are made, since micropore filling rather than monolayer coverage is more likely to be the mechanism behind the gas adsorption by porous MOFs and the Langmuir equation will be only of limit utility when the occupancy by H\textsubscript{2} is higher.

2.2 Metal-Organic Frameworks from SBU I and BDC or Its Derivatives:

The fact that 1, 3-benzenedicarboxylate (BDC) is an angular and relatively rigid ligand subtending an angle of 120° has made it an extremely versatile building block. In particular, the presence of two carboxyl groups at the meta-positions affords a unique opportunity for the investigation of supramolecular isomerism. For example, if one considers each individual paddle-wheel SBU I along with the four BDC moieties that are
attached to it, it should be noted that, in principle, there exist four possible configurations in which one of the following situations is applicable: 1) all four meta-carboxyl groups are facing down (or up); 2) two adjacent meta-carboxyl groups are facing down; 3) two opposite meta-carboxyl groups are facing down; and 4) three of the four meta-carboxyl groups are facing down (Figure 2.6). For the sake of simplification, we will designate these as “4D”, “1, 2-D”, “1, 3-D”, and “3D”, respectively. As will become apparent below, the very presence of multiple possible arrangements of the molecular building blocks accounts for the occurrence of some supramolecular isomers that are assembled from BDC and SBU I. It should be pointed out that a CSD survey reveals that while “1, 2-D” is the predominant conformation and a few other examples exist for “4D”, either “1, 3-D” or “3D” has been hardly observed.

2.2.1 Nanoballs

Nanoscale small rhombihexahedra A (cubic phase) are spontaneously formed by the self-assembly of Cu(NO$_3$)$_2$ and H$_2$BDC under appropriate conditions.$^{75}$ As revealed by Figure 2.7a, 12 SBU I’s are convergently bridged by 24 BDC moieties, generating 8
triangular windows and 6 square windows. Note that each of the 12 SBUs adopts the same “4D” conformation described above.

Surprisingly, a closely related form of the nanoballs, i.e., that of hexagonal symmetry, arises from the identical building blocks under slightly different conditions. This supramolecular isomer of A has an equal number of triangular and square windows and, most importantly, the same “4D” arrangement of SBUs also accounts for its discrete architecture. Degradation of the symmetry of SBU I (i.e., the $D_{4h}$ symmetry no long holds) as well as a small distortion of the bridging ligand BDC has been attributed to the formation of this second form. Although visually quite similar, these two compounds can nevertheless be easily distinguished by their connectivities: contrary to the cubic phase which only has one type of node (vertex symbol: $(3\cdot3\cdot4\cdot4)_{12}$), the hexagonal phase is binodal (vertex symbol: $(3\cdot3\cdot4\cdot4)_6(3\cdot4\cdot3\cdot4)_6$).

While structure A and its hexagonal isomer are spectacular molecular complexes on their own right thanks to their discrete architectures and nanoscale cavities, it occurs to us that these nanoballs can serve as the building blocks for constructing architectures of

![Figure 2.7 Ball-and-stick and schematic representations of nanoballs assembled from SBU I and BDC: a) cubic phase; b) hexagonal phase.](image)

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higher hierarchy, i.e., they can act as the nodes of much larger infinite networks. For instance, functionalization on the outer surface of nanoballs, which can be realized on either BDC site or SBU site, allows for the cross-linking of adjacent nanoballs.

Specifically, several design strategies can be applied: if each nanoball is only linked to two adjacent neighbors, a 1D chain is possible to form; when it is tetrahedrally associated with four neighbors, then a super-diamondoid net is readily accessible; similarly, a primitive cubic or body-centered cubic net can be expected by arranging each nanoball to six or eight adjacent nanoballs, respectively.

Indeed, crystals of methoxylated, neutral nanoballs of formula \([\text{Cu}_2(5-\text{MeO-BDC})_2(\text{MeOH})_x(\text{H}_2\text{O})_{1.83-x}]_{12}, \text{I}\), result from the modular self-assembly in MeOH under ambient conditions of 70 molecular components: 24 5-MeO-BDC moieties, 24 Cu(II) cations (from copper (II) nitrate), and 22 coordinated solvent (MeOH or H2O) molecules.\(^{23}\) The molecular mass of each molecule is ca. 6.9 kDa and their molecular volume is ca. 11.5 nm\(^3\). It should be noted the nanoballs in \(\text{I}\) exists in the hexagonal form.

The 24 methoxy moieties are disposed at the exterior of the nanoball, and they are capable of coordinating to metal centers through their ether oxygen atoms. In fact, two methoxy moieties on each nanoball coordinate to axial sites on adjacent nanoballs in such a way that double cross-linking occurs. As revealed in Figure 2.8, this cross-linking also occurs at the opposite face of each nanoball, thereby generating an infinite 1D chain of nanoballs. The Cu-O distances, averaging 2.26 Å, are consistent with expected values and the separation between centers of adjacent nanoballs is 2.15 nm. The manner in which the 1D chains pack can be described as \textit{hexagonal packing of parallel cylinders (rods)}.\(^{79}\) In effect, compound \(\text{I}\) has exemplified the principles of suprasupermolecular chemistry.\(^{22-23}\)
The polyhedron-type metal-organic spherical structures are speculated to be superior for hydrogen storage since they necessarily contain multiple interaction sites for H₂, namely, those within, as well as between, the spheres. Surprisingly, however, we found no appreciable amount of H₂ uptake for the original discrete nanoballs A, presumably because of the loss of the long-range structural regularity upon removal of guest species. Although each individual sphere is likely to remain intact, the collapse of 3D framework due to the weak intermolecular interactions is attributed to the blocking of interior cavities. On the contrary, the framework of the covalently linked methoxy nanoballs 1 is expected to be more robust because of the relatively stronger Cu(II)-ether coordination bonding that are sustaining the 1D nanoball networks. Indeed, 5-point N₂ isotherm at 77K suggests a BET surface area of 351 m²/g for 1 and hydrogen sorption experiments.
performed volumetrically reveals a significant amount of H₂ uptake (0.94 wt%) at 77K and 1 atm, which is favorably comparable to that of most reported MOFs (Table 2.1). The H₂ adsorption-desorption profile represents a type I isotherm (Figure 2.9a), which is characteristic of the uniform and crystalline micropore structures. The small hysteresis between adsorption and desorption traces is attributed to the presence of more than one type of cavities and, perhaps, a slight instrumental fluctuation.

In order to simulate the hydrogen adsorption behavior in I, three different models, namely, Langmuir, Langmuir-Freundlich, and Dubinin-Radushkevich (D-R) equations, are employed and their results are compared in Figure 2.9b–c:

1) Langmuir equation: \( Q/Q_m = (B*P)/(1 + B*P) \); where \( P \) is the pressure, \( Q \) is the amount of adsorption at \( P \), \( Q_m \) is the saturation adsorption, and \( B \) is the adsorption constant. When compared with the mathematic formula \( y = x/(a*x + b) \), which is actually adapted in the simulation (assuming \( y = Q \) and \( x = P \)), the estimated saturation adsorption can be obtained as \( Q_m = 1/a \).

2) Langmuir-Freundlich (L-F): \( Q/Q_m = (B*P^{1/n})/(1 + B*P^{1/n}) \); where \( P \) is the pressure, \( Q \) is the amount of adsorption at \( P \), \( Q_m \) is the saturation adsorption, \( B \) is the adsorption constant, and the value of \( n \) is greater than unity under normal conditions for physical adsorption. When compared with the mathematic formula \( y = a*b*x^{1-c}/(1+b*x^{1-c}) \), which is actually adapted in the simulation (assuming \( y = Q \) and \( x = P \)), the estimated saturation adsorption can be obtained as \( Q_m = a \).

3) Dubinin-Radushkevich (D-R) equations: \( \ln Q = \ln Q_m - (RT/\beta E_0) * (\ln P_0 - \ln P)^2 \), where \( P \) is the pressure, \( P_0 \) is the saturation pressure, \( T \) is the temperature, \( Q \) is the amount of adsorption at \( P \), \( Q_m \) is the saturation adsorption, \( R \) is the gas constant.
(8.314 J/(mol•K)), and $\beta E_0$ is the adsorption energy. When compared with the mathematic formula $y = A + Bx + Cx^2$, which is actually adapted in the simulation (assuming $y = \ln Q$, and $x = \ln P$), the estimated saturation adsorption can be obtained as $Q_m = \exp(A - B^2/(4C))$ and the adsorption energy can be obtained as $\beta E_0 = -RT/C$.

Whereas the classical Langmuir model does not seem to adequately describe the $\text{H}_2$ adsorption isotherm of I, the extended Langmuir-Freundlich equation and the D-R

Figure 2.9 $\text{H}_2$ sorption profiles in I: a) $\text{H}_2$ isotherm of I at 77K; b) Langmuir fit of $\text{H}_2$ isotherm in I; c) Langmuir-Freundlich fit of $\text{H}_2$ isotherm in I; d) Dubinin-Radushkevich fit of $\text{H}_2$ isotherm in I.
equation give much better simulation results, from which an estimated saturation \( \text{H}_2 \) uptake of 4.68 wt\% and 1.39 wt\%, respectively, can be obtained. In addition, the adsorption energy \( \beta E_0 \) is predicted to be 3.13 kJ/mol using the nonlinear D-R equation.

2.2.2 Two-Dimensional Tetragonal Sheets and Kagomé Lattices

Tetragonal sheet \( B^{76} \) and Kagomé lattice \( C^{218} \) represent two of the prototypal two-dimensional structures that can be assembled from angular ligand BDC and square SBU \( I \). While \( B \) is based upon the linking of square cavities that are consisted of four SBUs \( I \), \( C \) is characterized by the presence of triangular windows composed of three SBUs \( I \) (Figure 2.10). Both \( B \) and \( C \) exhibit undulating nature as a result of the 120° angle subtended by

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Figure 2.10 Ball-and-stick representations of prototypal tetragonal sheet (\( a \) and \( b \)) and Kagomé lattice (\( c \) and \( d \)). \( b \) and \( d \) highlight the structural reason for the existence of both isomers.
BDC and the presence of such a curvature is critical for the formation of Kagomé lattices, whereas topologically related tetragonal sheets have been generated from linear spacers such as 1, 4-benzenedicarboxylate. In contrast to the “4D” configurations that are observed in the discrete nanoball structures, both B and C exhibit the “1, 2-D” dispositions, which presumably account for their two dimensionalities.

However, a fundamental question still needs to be raised and answered: what exactly causes the existence of these two isomers since they are built from the same building blocks that adopt similar configurations? Close examination of the two structures suggests that the answer lies in the combined effects of the angular nature of ligand BDC and the reducing symmetry of SBU I. Molecular modeling study using the program Materials Studio indicates that SBUs I in the most symmetric forms of B and C possess $D_{2h}$ symmetry, which is lower than its ideal $D_{4h}$ symmetry. In fact, the dihedral angles between the adjacent two planes defined by the carboxyl groups are not identical. If we designate “D” for the plane that contains a meta-carboxyl group facing downward, and “U” otherwise (Figure 2.10b, d), then the dihedral angles can be written as either $\angle DD$ (same as $\angle UU$!) or $\angle DU$. Notice that in structure B, $\angle DD$ is slightly larger than $\angle DU$, whereas in structure C it is the just opposite. Although such a difference might not seem obvious, it nevertheless dramatically influences the connectivity of the networks and ultimately leads to the generation of two completely different architectures (see the blue motifs shown in Figure 2.10b and 2.10d for an appreciation of this argument).

Whereas the principles of crystal engineering provide reliable blueprints for the construction of prototypal structures, as illustrated by the tetragonal sheets B and Kagomé lattices C, they also afford a great opportunity to chemically functionalize these
model compounds, which might be crucial in terms of improving the material’s performances. As chapter 3 will focus upon a series of tetragonal sheets that are derivatives of B, we discuss two examples of functionalized Kagomé lattices C herein.

Compound 2 of formula \([\{\text{Cu}_2(5\text{-MeO-BDC})_2(4\text{-MeO-Pyridine})_2\}(\text{guest})_x\}^\infty\) was obtained as crystalline materials from an ethanol solution of Cu(NO\(_3\))\(_2\)•2.5H\(_2\)O and 5-MeO-H\(_2\)BDC using 4-MeO-Pyridine as the base and nitrobenzene as the template. In a similar fashion, crystals of compound 3, \([\{\text{Cu}_2(5\text{-Br-BDC})_2(\text{MeOH})_2\}(\text{guest})_x\}^\infty\), was obtained from a methanol solution of Cu(NO\(_3\))\(_2\)•2.5H\(_2\)O and 5-Br-H\(_2\)BDC using pyridine as the base and nitrobenzene as the template. Both compounds manifest 2D Kagomé topology, i.e., they contain triangular cavities as well as hexagonal cavities that result from the linking of triangular units. The size of the triangular and hexagonal cavities in both structures is comparable to 1 \(nm\) and 2 \(nm\), respectively, which is consistent with their parent compound C. However, the crystal structures of compound 2 and 3

![Figure 2.11 Crystal packing of compound 2 (a) and 3 (b). Atoms highlighted in purple are methoxy- (in 2) or bromo- (in 3) groups.](image-url)
significantly differ in the manner in which the networks stack with respect to each other. The 2D Kagomé sheets in 2 eclipse right on top of each other, giving rise to an “AAA” packing, as is also the case in the parent compound; those in 3 are, on the other hand, slipped in the c direction by ca. 33.3%, i.e., every fourth layer repeats, thus resulting in an “ABCABC” sequence (Figure 2.11). The interlayer distances for 2, 3 and C are 11.6Å, 10.4 Å, and 9.9 Å, respectively (Table 2.2), underlining the different sizes of the substituted groups at the 5- position of BDCs.

Table 2.2 Comparison of chemical and structural information for compound 2, 3 and their parent compound.

<table>
<thead>
<tr>
<th>Compound</th>
<th>R (5-R-BDC)</th>
<th>L (axial ligand of SBU)</th>
<th>Space Group</th>
<th>Packing Sequence</th>
<th>Interlayer Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>MeO</td>
<td>4-MeO-Pyridine</td>
<td>P-3</td>
<td>AAA</td>
<td>11.6Å</td>
</tr>
<tr>
<td>3</td>
<td>Br</td>
<td>MeOH</td>
<td>R-3</td>
<td>ABCABC</td>
<td>10.4 Å</td>
</tr>
<tr>
<td>parent</td>
<td>H</td>
<td>Pyridine</td>
<td>P-3Cl</td>
<td>AAA</td>
<td>9.9 Å</td>
</tr>
</tbody>
</table>

Kagomé lattices are an extremely important class of compounds for a number of reasons: 1) Kagomé lattice C is one of the most famous examples of geometrically frustrated topologies, which have been highly pursued by both physicists and chemists;230 2) They are inherently suitable for the generation of multifunctional materials since they are magnetically active and they contain nanoscale cavities and channels; 3) They are modular in nature and they contain multiple sites for steric and/or electronic modification.

Compound 2 and 3 ideally illustrate these features and therefore represent a step forward toward tailored functional materials. Indeed, 5-point N₂ adsorption isotherm at 77K confirms the porosity of compound 2 (BET surface area: ca. 100 m²/g) and hydrogen adsorption experiments that are performed volumetrically reveal an uptake of 0.62 wt%
for 2 at 77K and 1 atm (Figure 2.12a). The simulations using L-F model and D-R model give a saturation adsorption of 2.2 wt% and 1.37 wt%, respectively, whereas D-R model also results in an adsorption energy of 3.04 kJ/mol (Figure 2.12c–d).

2.2.3 Three-Dimensional Structures and Some Predicted Structures

In addition to the zero-dimensional nanoballs and two-dimensional tetragonal sheets and Kagomé lattices, the self-assembly of SBU I and BDC and its derivatives has also resulted in a number of three-dimensional structures, two of which are shown in Figure

Figure 2.12 H₂ sorption profiles in 2: a) H₂ isotherm of 2 at 77K; b) Langmuir fit of H₂ isotherm in 2; c) Langmuir-Freundlich fit of H₂ isotherm in 2; d) Dubinin-Radushkevich fit of H₂ isotherm in 2.
2.13, namely, USF-1 net D and CdSO₄ net E, respectively. Similar to those in the two-dimensional structures B and C, the SBUs in D and E also display “1, 2-D” predispositions. However, in both cases, the configurations of SBUs I are significantly twisted and the carboxylate groups in the ligand BDC are considerably out-of-plane, which explains the higher dimensionality of the resulting structures, as compared to the cases of structures B and C. The differences between D and E, on the other hand, can be rationalized on the basis of the different torsion angles of their SBUs and BDCs. It should be pointed out that D and E represent two examples of 4-connected nets that are both based upon square nodes (Figure 2.5). The vertex symbols can be written as $6_2 \cdot 6_2 \cdot 6_2 \cdot 12_{50} \cdot 6_3 \cdot 6_3$ and $6 \cdot 6 \cdot 6 \cdot 6 \cdot 6 \cdot 6^5$, for D and E, respectively. While CdSO₄ net represents a common topology for a diverse range of metal-organic networks, the connectivity of USF-1 net is truly unprecedented and compound D is thus far the only example that has been observed. 

Figure 2.13 Crystal structures of USF-1 D (a) and CdSO₄ net E (b). Motifs shown in the blue boxes illustrate the distorted “1, 2-D” conformations of SBUs.
We have so far experimentally produced at least 6 different supramolecular isomers (i.e., two forms of nanoballs A, tetragonal sheet B, Kagomé lattice C, USF-1 net D and CdSO₄ net E) that are assembled from SBU I and ligand BDC. A conformational consideration has been invoked to facilitate the rationalization of this remarkable supramolecular isomerism. In summary, SBUs in nanoballs A (including both cubic and hexagonal phases) take up a “4D” configuration, and those in structures B–E belong to a “1, 2-D” conformation. Such a conformational analysis further suggests the possibility of other supramolecular isomers that might be isolated from this system and we will briefly describe below four of these hypothetical structures, which are based upon “1, 3-D” (structure H1), a combination of “1, 2-D” and “1, 3-D” (structure H2), a combination of “4D” and “1, 2-D” (structure H3), and a combination of “3D” and “1, 2-D” (structure H4), respectively (Figure 2.14–2.17).

Structures H1 and H2 are both three-dimensional architectures. The inherent topology of H1 is related to that of the sodalite net seen in both inorganic zeolites and MOFs.²¹⁶,²³⁶-²³⁷ Note that the 1, 3- alternative configuration of SBUs has in effect
rendered each node a pseudo-$S_4$ symmetry (since the SBU only has $D_{2h}$ symmetry), resulting in a tetrahedral framework (Figure 2.14). $H_2$ is based upon a 1:1 mixture of “1, 2-D” and “1, 3-D” nodes and its topology is associated with that of the PtS nets (Figure 2.15). Table 2.3 shows a short summary of the crystallographic data for $H_1$ and $H_2$.

![Image](image-url)

Figure 2.15 Ball-and-stick and schematic representations of hypothetical structure $H_2$. Blue box illustrates a combination of “1, 2-D” and “1, 3-D” configurations of SBUs in the structure.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space Group</th>
<th>a/Å</th>
<th>b/Å</th>
<th>c/Å</th>
<th>$\alpha$/°</th>
<th>$\beta$/°</th>
<th>$\gamma$/°</th>
<th>V/Å³</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_1$</td>
<td>Pn-3m</td>
<td>26.343</td>
<td>26.343</td>
<td>26.343</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>18280.8</td>
</tr>
<tr>
<td>$H_2$</td>
<td>P4$_2$/nmm</td>
<td>18.6273</td>
<td>18.6273</td>
<td>26.3430</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>9140.4</td>
</tr>
</tbody>
</table>

Structures $H_3$ and $H_4$ illustrate two examples of two-dimensional hypothetical structures that can be derived using the same principles of conformational consideration. Interestingly, $H_3$ bears the same connectivity as structure $C$, i.e., that of Kagomé lattices. Nevertheless, it differs from $C$ by the following aspects: 1) $H_3$ is based upon a 1:2 mixture of “4D” and “1, 2-D” nodes, whereas $C$ is purely from “1, 2-D” type nodes; 2) The lattice symmetry of $H_3$ has been reduced to orthorhombic from trigonal seen in $C$; 3)
The two-dimensional sheets of $\textbf{H3}$ exhibit a much more undulating nature than those of $\textbf{C}$ (Figure 2.16). $\textbf{H4}$ is quite an unusual two-dimensional lattice in that it is composed of triangular, square and hexagonal windows due to the presence of its mixed “1, 2-D” and “3D” nodes (Figure 2.17).

Figure 2.16 Perspective and side views of hypothetical structure $\textbf{H3}$ in a ball-and-stick mode. Blue box illustrates a combination of “4D” and “1, 2-D” configurations of SBUs in the structure.

Figure 2.17 Perspective and side views of hypothetical structure $\textbf{H4}$ in a ball-and-stick mode. Blue box illustrates a combination of “1, 2-D” and “3D” configurations of SBUs in the structure.

It is perhaps worth pointing out that there likely exist other possible structures from the same SBU I-BDC system. However, it should also be kept in mind that although these hypothetical structures are of reasonable geometric plausibility, the chemical feasibility of their formations remains unclear.
2.3 Metal-Organic Framework from SBU I and 1, 3-Adamantanedicarboxylate

Similar to BDC, a ligand that subtends an angle of 120°, 1, 3-adamantanedicarboxylate (ADC) represents another rigid and angular dicarboxylato ligand that can be employed in the construction of novel MOFs. In contrast to BDC, however, ADC has a relatively smaller angle which is close to 109°, and the two planes defined by the COO\(^-\) groups are instead not parallel to each other (Figure 2.18a). Accordingly one would expect different types of structures can be assembled from ADC and SBU I.

Indeed, single crystals of \{[Zn\(_2\)(ADC)\(_2\)(Pyridine)\(_2\)](MeOH)\(_2\)\}_\infty, 4, were attained by layering a methanolic solution of H\(_2\)ADC and pyridine onto a methanolic solution of Zn(NO\(_3\))\(_2\)•6H\(_2\)O that contains nitrobenzene as the template. As illustrated in Figure 2.18, the square SBUs I are double-linked by ADC motifs resulting in 1D architecture of

![Figure 2.18 Crystal structures of compound 4: a) ligand ADC; b) the 1D ladder; c) interdigitation of 1D ladders, leading to a 2D sheet; d) packing of 2D sheets (guest molecules MeOH in CPK mode).](image)
molecular ladder topology (Figure 2.18b). These 1D ladders are running along (100) with two different orientations alternatively such that two neighboring ladders have an angle of ca. 107°. Interdigitation occurs between adjacent ladders through face-to-face $\pi\cdots\pi$ interactions ($d_{\text{centroid-centroid}} = 4.3$ Å). As result, an undulating 2D sheet whose mean plane parallels (110) plane is generated by virtue of combining relative strong metal-ligand coordination bonding and weak $\pi\cdots\pi$ interaction (Figure 2.18c). These 2D sheets are further packed into three dimensions in an “ABAB” fashion, therefore producing 1D channels of ca. 4.9 Å × 5.0 Å. Two methanol molecules per SBU occupy this free space and are hydrogen bonding to the carboxylato oxygens of ADC, which presumably further stabilizes the overall structure (Figure 2.18d).

The features of compound 4 are salient from a design perspective: a) The ladder topology exemplifies another pattern in which square building units can be linked to each other; b) The fact that the angular ligand ADC is geometrically compatible with square SBUs I suggests other rigid angular organic linkers as reasonable candidates for the design of novel MOFs; c) In principle, other supramolecular isomers of 4 might as well
be possible. In fact, a cylindrical structure $H_5$, 1D analogue of 2D tetragonal sheets $B$, has been proposed (Figure 2.19).

2.4 Metal-Organic Frameworks from SBU II and BDC or Its Derivatives

The supramolecular isomerism demonstrated above by the SBU I-BDC system has been remarkably impressive, and our conformational analysis reveals the fundamental geometric relationships among the various isomers. As MOFs continue to be intensively exploited in the context of functional materials, an enhanced understanding on the formation of multiple forms of metal-organic compositions becomes especially critical not only from a design perspective, but perhaps even more importantly, from a synthetic perspective. In this context, we have explored the use of another type of dimetal tetracarboxylate, SBU II (Figure 2.2) along with BDC ligands, in order to determine the experimental parameters that might potentially affect supramolecular isomerism. As a result, we have found both templates and axial ligands play an important role in this regard.

Whereas SBU I exemplifies a versatile square building block in terms of generating various MOFs, SBU II can potentially serve as a pseudo-square building block with an ideal symmetry of $C_{2h}$ (Figure 2.4; although the highest possible symmetry for SBU II is $D_{2h}$, it is usually not achievable due to its less rigidity). A CSD analysis indicates the motif of SBU II exists for a wide array of transition metals, although its occurrence is much less often than that of SBU I.

Compound 5, $\{[\text{Zn}_2(\text{BDC})_2(4-\text{PhPy})_4](\text{Benzene})]\infty$ (4-PhPy = 4-Phenylpyridine), was isolated as single-crystalline materials from a methanolic solution of BDC and $\text{Zn(NO}_3)_2\cdot6\text{H}_2\text{O}$ using 4-Phenylpyridine as axial ligand and benzene as template. X-ray
single crystal diffraction reveals a 1D ladder structure in which SBUs II are doubly 
bridged by BDC in a convergent fashion along a single direction, resembling the structure 
of compound 4 (Figure 2.20a). Each of the Zn(II) ions manifests an octahedral 
coordination geometry which is surrounded by two oxygens from one chelating carboxyl 
group, two oxygens from two bridging carboxyl groups, and two nitrogens from two 4-
phenylpyridine ligands. The Zn-O distances fall in the range of 1.991~2.292Å, and Zn-N 
distances average 2.188Å. The elongated aromatic systems of the axial ligands 4-
phenylpyridine engage in multiple $\pi\cdots\pi$ interactions in such a way that interdigitation 
occurs between neighboring ladders, thus generating cavities in which benzene molecules 
inhabit (Figure 2.20b).

![Figure 2.20 1D ladder structure (a) and its packing (b) in compound 5. Benzene guests are shown in a space-filling mode. Blue box illustrates the convergent fashion in which SBUs II are linked by BDC.](image-url)
When replacing benzene with toluene and leaving everything else in the reaction mixture unchanged, colorless crystals of a new form, compound 6 of formula 
\[\left[\text{Zn}_2(\text{BDC})_2(4-\text{PhPy})_4\right](\text{Toluene})_2\] precipitate out. In contrast to the ladder structure of 5, BDC moieties in 6 connect SBUs II in an alternative manner, i.e., divergently, therefore giving rise to a 2D layer structure (Figure 2.21a). The Zn(II) ions maintain an octahedral geometry and the Zn-O distances range from 2.014Å to 2.505Å, somewhat larger than those observed in 5. The Zn-N distances (an average of 2.164Å), on the other hand, are close to or even shorter than those of 5. The interdigitation again occurs between 4-phenylpyridine moieties from adjacent layers with toluene occupying in the interlayer cavities (Figure 2.21b).

5 and 6 might be distinguished from a number of ways, among which is their packing efficiency. Apparently the lower dimensionality of 5 has facilitated a better staking of the bulky 4-phenylpyridyl groups, thus generating cavities of smaller size that can only fit benzene (but not toluene), while the higher dimensionality of 6 seems to prevent the same bulky groups from coming as closely. Retrospectively, therefore,
benzene preferentially induces the formation of 5 whereas toluene is probably a better template for 6 based upon a size-matching principle. That a small variation on the size of templates has such a dramatic effect on the outcome of superstructures underscores the importance of a careful control over crystallization conditions.

Similar tuning effects exerted by axial ligands on supramolecular isomers can also be demonstrated by compound 7 and 8. In this context, we use a substituted BDC, namely, 5-hydroxy-1, 3-benzene-dicarboxylate (5-OH-BDC), to bridge SBUs II. Note that hydroxyl groups are ideally suited for engaging in complementary supramolecular interactions since they are both hydrogen-bond donors and acceptors. Two different pyridine-type bases, namely, 3, 5-lutidine and isoquinoline, are employed as axial ligands in an effort to direct individual crystallization processes while benzene is used as the template in both cases.

Figure 2.22 Crystal structures of 7: a) 1D ladder; b) 2D sheet sustained by complementary hydrogen bonds; and c) the packing of the 2D sheets. Benzene molecules are shown in space-filing mode.
7, \{[\text{Zn}_2(5\text{-OH-BDC})_2(3,5\text{-lutidine})_2](\text{Benzene})_2\}_\infty, is structurally related to 5 in that it also exhibits a 1D ladder topology (Figure 2.22a) and both Zn-O and Zn-N distances are within the expected ranges and comparable to those observed in both 5 and 6. As is contrary to those seen in the previous two compounds, however, each of the Zn(II) ions in 7 displays a tetrahedral geometry which is completed by two oxygens from two bridging carboxyl groups, one oxygen from one mono-dentate carboxyl group and one nitrogen from 3,5-lutidine. As a result, the ladders in 7 are inevitably prone to be undulating and more significantly, such a wavy disposition allows the hydroxyl group (hydrogen-bond donor) and uncoordinated carboxyl oxygen (hydrogen-bond acceptor) on each 5-OH-BDC moiety in close contact with their partners from adjacent ladder in such a way that 2-fold hydrogen bonding occurs between neighboring ladders (Figure 2.22b). These complementary hydrogen bonds thus assemble the 1D ladders into 2D sheets, which in turn pack into 3D architecture and generate both cavities and channels that are occupied by benzene molecules (Figure 2.22c). It should be pointed out, however, that the way the 2D sheets are arranged might be subject to change especially upon guest
release, as suggested by the X-ray powder diffraction (XPD) patterns obtained at ambient conditions.

8, \{[Zn_2(5-OH-BDC)_2(isoquinoline)_3](Benzene)_{1.5}\}_\infty, was isolated when replacing 3,5-lutidine with isoquinoline and the resulting compound bears a close resemblance to 6, i.e., a 2D layer structure. Nevertheless, the coordination of Zn(II) ions in 8 demonstrates somewhat surprising diversity and within each SBU II, one of the two zinc centers assumes a trigonal bipyramidal shape while the other, a trigonal pyramidal. Similar to the situations observed in 7, distortion away from an octahedral geometry results in an uncoordinated carboxyl oxygen on each 5-OH-BDC moiety, which further engages in hydrogen bonding with nearby hydroxyl group within the same 2D sheet (Figure 2.23a).

In short, we have investigated two different approaches that involve careful selection of either templates or axial ligands and that aim to gain a better control on the formation of desired supramolecular isomers. Although more efforts need to be accomplished and still more data need to be collected, our systems clearly suggest a well-founded direction, i.e., supramolecular isomerism is experimentally controllable.

2.5 Summary

This Chapter is focused upon the discussions of the following topics:

1) The concept of secondary building units (SBUs), which are referred to molecular complexes or metal clusters that have well-defined and highly symmetric coordination geometries. Four different SBUs, namely, paddle-wheel square SBU I, pseudo-square SBU II, and tetrahedral SBU III and IV will be exploited in this dissertation.

2) Supramolecular isomerism, which is defined as the existence of more than one type of network superstructure for the same molecular building blocks. In particular, we
have investigated in details the BDC-SBU I system, in which at least 6 different isomeric MOFs are experimentally isolated and a number of predicted structures are potentially possible. The geometrical principles that account for such a large number of supramolecular isomers are proposed. In addition, the influence of experimental parameters (such as templates and bases) on supramolecular isomerism is studied in the BDC-SBU II system.

3) Metal-organic frameworks as functional materials. In particular, the state of the art of hydrogen storage using porous MOFs is discussed in details.

2.6 Experimental

2.6.1 Syntheses

The materials in the synthesis were used as received from reliable commercial sources (Sigma-Aldrich or Fischer Scientific); solvent methanol was purified and dried according to standard methods.

*Synthesis of \([\text{Cu}_2(5\text{-MeO-BDC})_2(\text{MeOH})_x(\text{H}_2\text{O}_{1.83-x})_{12}], \text{1}\)*

Green plate crystals of compound 1 were formed by layering 3mL of a methanol solution containing 5-methoxyisophthalic acid (20 mg, 0.10 mmol) and 2,6-lutidine (0.035 mL, 0.30 mmol) onto 3mL of a methanol/nitrobenzene solution (2:1, v/v) containing Cu(NO₃)₂•2.5H₂O (23 mg, 0.099 mmol). Typical yield of the reaction is ca. 18mg for each vial.

*Synthesis of \([\text{Cu}_2(5\text{-MeO-BDC})_2(4\text{-MeO-Pyridine})_2(\text{guest})_x]_\infty, \text{2}\)*

Compound 2 were obtained by layering 3 mL of an ethanol solution containing 5-methoxyisophthalic acid (20 mg, 0.10 mmol) and 4-methoxypyridine (0.031 mL, 0.30
mmol) onto 3 mL of an ethanol/nitrobenzene solution (2:1, v/v) containing Cu(NO₃)₂•2.5H₂O (23 mg, 0.099 mmol). Some green-blue precipitates appeared immediately and green hexagonal crystals formed at the interlayer boundary within 3 days. Typical yield of the reaction is ca. 14 mg for each vial.

*Synthesis of \([\text{Cu}_2(5-\text{Br-BDC})_2(\text{MeOH})_2](\text{guest})_x\), 3*

Compound 3 were obtained by layering 3 mL of a methanol solution containing 5-bromoisophthalic acid (11 mg, 0.050 mmol) and pyridine (0.012 mL, 0.15 mmol) onto 3 mL of a methanol/nitrobenzene solution (2:1, v/v) containing Cu(NO₃)₂•2.5H₂O (23 mg, 0.10 mmol). Green-blue crystals (mostly twinned) appeared at the interlayer boundary within 3 days. Typical yield of the reaction is ca. 12 mg for each vial.

*Synthesis of \([\text{Zn}_2(\text{ADC})_2(\text{Pyridine})_2](\text{MeOH})_2\)_x, 4*

Compound 4 were obtained by layering 4 mL of a methanol solution containing 1,3-adamantanedicarboxylic acid (112 mg, 0.500 mmol) and pyridine (0.24 mL, 3.0 mmol) onto 5 mL of a methanol/nitrobenzene solution (3:2, v/v) containing Zn(NO₃)₂•6H₂O (149 mg, 0.500 mmol). Colorless crystals appeared at the interlayer boundary within 7 days.

*Synthesis of \([\text{Zn}_2(\text{BDC})_2(\text{4-PhPy})_4](\text{Benzene})\)_x, 5*

Compound 5 were obtained by layering 6 mL of a methanol solution containing isophthalic acid (33 mg, 0.20 mmol) and 4-phenylpyridine (93 mg, 0.60 mmol) onto 6 mL of a methanol/benzene solution (2:1, v/v) containing Zn(NO₃)₂•6H₂O (60 mg, 0.20 mmol). Colorless crystals appeared within 2 weeks. Percent yield: 21% (24 mg).
Synthesis of \([\text{Zn}_2(\text{BDC})_2(4-\text{PhPy})_4](\text{Toluene})_2\) \(_\infty\), \(6\)

Compound \(6\) were obtained by layering 6 mL of a methanol solution containing isophthalic acid (33 mg, 0.20 mmol) and 4-phenylpyridine (93 mg, 0.60 mmol) onto 6 mL of a methanol/toluene solution (2:1, v/v) containing \(\text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\) (60 mg, 0.20 mmol). Colorless prism crystals appeared within 3 days. Percent yield: 38% (33 mg).

Synthesis of \([\text{Zn}_2(5-\text{OH-BDC})_2(3,5-\text{lutidine})_2](\text{Benzene})_2\) \(_\infty\), \(7\)

Compound \(7\) were obtained by layering 20 mL of a methanol solution containing 5-hydroxyisophthalic acid (182 mg, 1.00 mmol) and 3, 5-lutidine (0.342 mL, 3.00 mmol) onto 20 mL of a methanol/benzene solution (3:1, v/v) containing \(\text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\) (297 mg, 1.00 mmol). Colorless needle crystals appeared after 24 hours. Percent yield: 46.7% (185 mg).

Synthesis of \([\text{Zn}_2(5-\text{OH-BDC})_2(\text{isoquinoline})_3](\text{Benzene})_{1.5}\) \(_\infty\), \(8\)

Compound \(8\) were obtained by layering 20 mL of a methanol solution containing 5-hydroxyisophthalic acid (182 mg, 1.00 mmol) and isoquinoline (0.354 mL, 3.00 mmol) onto 20 mL of a methanol/benzene solution (3:1, v/v) containing \(\text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\) (297 mg, 1.00 mmol). Colorless block crystals appeared after 24 hours. Percent yield: 49.0% (244 mg).

2.6.2 Characterizations

Crystal Structure Determination

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 Moka radiation (\(\lambda = 0.7107\) Å). The data were corrected
for Lorentz and polarization effects and for absorption using the SADABS program. The structures were solved using direct methods and refined by full-matrix least-squares on |F|^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions and refined with temperature factors 1.2 times those of their bonded atoms. All crystallographic calculations were conducted with the SHELXTL 5.1 program package. Note: formulas of the compounds discussed in this dissertation are mainly based upon single-crystal diffraction data.

Table 2.4 Crystallographic data for compounds 1–8.

<table>
<thead>
<tr>
<th>Compound</th>
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<th>2*</th>
<th>3</th>
<th>4</th>
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<td>C24H20Cu2N2O12</td>
<td>C18H12.22Br2Cu2O10.67</td>
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<tr>
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\]
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&= 0.0788, \\
wR2 &= 0.4806 \\
&= 0.1127
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\]
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\begin{align*}
1.321 \text{ and } -1.132 \\
1.593 \text{ and } -1.273 \\
0.738 \text{ and } -0.471
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\]
* The poor quality of X-ray diffraction data for 2 and its structural refinement only result in reliable structural models and respective cell parameters.

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| Final R indices | \[ I > 2\sigma(I) \]
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R1 &= 0.0333 \\
wR2 &= 0.0880 \\
R1 &= 0.1440 \\
wR2 &= 0.4073 \\
R1 &= 0.0673 \\
wR2 &= 0.1728 \\
R1 &= 0.0417 \\
wR2 &= 0.0932
\end{align*}
\]
R indices (all data)
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\begin{align*}
R1 &= 0.0382 \\
wR2 &= 0.0912 \\
R1 &= 0.1727 \\
wR2 &= 0.4181 \\
R1 &= 0.1149 \\
wR2 &= 0.2004 \\
R1 &= 0.0570 \\
wR2 &= 0.1002
\end{align*}
\]
Large diff. peak and hole, e·Å\(^{-3}\)
\[
\begin{align*}
0.519 \text{ and } -0.385 \\
2.188 \text{ and } -1.100 \\
0.821 \text{ and } -0.446 \\
0.436 \text{ and } -0.347
\end{align*}
\]
Other Characterizations

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. Low resolution XPD data were recorded on a Rigaku RU15 diffractometer at 30kV, 15mA for Cu Kα (λ = 1.5418 Å), with a scan speed of 1°/min and a step size of 0.05° in 2θ at room temperature. The simulated XRPD patterns were produced using Powder Cell for Windows Version 2.4 (programmed by W. Kraus and G. Nolze, BAM Berlin, © 2000).

Infrared spectra were recorded on a Nicolet Avatar 320 FT-IR spectrometer. Samples of 1 (16.8 mg) and 2 (53.1 mg) are soaked in fresh methanol for ca. 48 hrs before gas sorption experiments. 5-point BET surface areas of both compounds are measured from N2 isotherms at 77K with an Autosorb-1 instrument by Quantachrome Instruments (Boynton Beach, Florida USA), running version 1.2 of the ASWin software package. H2 sorption isotherms are measured volumetrically at 77K using the Autosorb-1 instrument.

![Figure 2.24 Experimental and simulated XPD patterns of 1.](image-url)
Figure 2.25 Experimental and simulated XPD patterns of 5.

Figure 2.26 Experimental and simulated XPD patterns of 6.
Figure 2.27 Experimental and simulated XPD patterns of 7.

Figure 2.28 Experimental and simulated XPD patterns of 8.
Figure 2.29 FT-IR spectrum of 5.

Figure 2.30 FT-IR spectrum of 6.
Figure 2.31 FT-IR spectrum of 7.

Figure 2.32 FT-IR spectrum of 8.
3.1 Introduction

3.1.1 Rigidity vs. Flexibility

Metal-organic frameworks, or coordination polymers, have been intensively investigated in the last decade as new classes of functional materials, in part due to the unique characteristics of metal-ligand interactions, namely, they are relatively strong and highly directional, but also kinetically labile. In addition, the well-established molecular synthetic chemistry has afforded, in the context of constructing hybrid network structures, a wide variety of organic ligands ranging from robust rod-like spacers to conformationally versatile linkers. The modular assembly of these building blocks can therefore be easily fine-tuned by judicious selection of either components and it is perhaps not surprising to encounter the accommodation of both rigidity and flexibility in the same class of compounds.

Metal-organic frameworks that are able to remain intact under intense conditions (such as high temperatures, removal of guest species, etc.) are of high technical importance because of their potential applications in separation, storage, and heterogeneous catalysis (see Chapter 2). In the previous chapter, we focus upon incorporating rigid but angular dicarboxylato ligands into the frameworks, which has been proved to be of success in terms of generating a wide array of supramolecular isomers from simple building blocks.
Recently, attentions have been paid to a novel type of MOFs that are integrated with more flexible structural elements. This new class of compounds are characterized by the dynamic features of their porous architectures and the ability to undergo structural deformations upon external stimuli while maintaining crystallinity of the materials, i.e., they are capable of guest-induced shape-responsive fitting and resemble the degree of induced-fit behavior of bioenzymes such as metalloproteins. An elegant example of dynamic MOFs, in which reversible release and uptake of guest molecules cause substantial changes in the local geometry of metal centers (Fe(II)) and lead to interesting spin crossover properties, has been recently reported (Figure 3.1).

![Figure 3.1 Guest-dependent deformation of a metal-organic framework that leads to spin crossover.](image)

In principle, the resilience of MOFs can be mainly attributed to the flexibility on the molecular level (i.e., flexibility of both metal coordination geometries and ligand conformations) as well as on the supramolecular level (i.e., low energy barriers among multiple arrangements of molecular building blocks). Although it is not unfeasible to
exploit the dynamic aspects of MOFs from both perspectives, we will herein primarily
highlight the influence of ligand conformation on the supramolecular structures.

3.1.2 Conformational Analysis of Organic Ligands: A CSD Survey

As delineated above, the manner in which different parts of a molecular entity are
disposed with respect to each other will have critical impact on the resulting
superstructures; in other words, the intrinsic rigidity or flexibility of MOFs will be in part
dictated by the configurations of organic ligands. Therefore a detailed investigation on
three-dimensional structures of organic functional groups is reasonably justified. In this
respect, Cambridge Structural Database (CSD), a database that houses more than 360,000
organic and metal-organic crystal structures in total and over 330,000 with 3D
coordinates determined,\(^{217}\) provides an ideal platform because a systematic analysis of
structural parameters can be conveniently realized with the aid of appropriate
softwares.\(^{246}\)

In particular, we are concerned with two prototypical ligands, namely, 4, 4'-bipyridine
\((4, 4'-\text{bipy})\) and benzoates/benzoic acids (molecules that contain at least one carboxyl
\(^{56}\) We define torsion angle of 4, 4'-bipy as the dihedral angle between the

---

Figure 3.2 Planes that define the torsion angles of 4, 4'-bipyridine \((a)\) and benzoates/benzoic acids \((b)\).

---
two pyridyl rings and that of benzoates/benzoic acids as the inclination between carboxyl group and benzene ring (Figure 3.2).

In the case of 4, 4'-bipy, while it is obvious that the two pyridyl rings are allowed to have certain degree of free rotations, there exists a clear-cut between the planar and torsional conformations, as indicated by the sharp peaks representing near-zero torsion angles and a much smoother distributions among higher torsion angle regions (Figure 3.3). It is worth noting that far less hits are seen in the range of large torsion angles, although coordinating to metal ions does slightly push such a limit to a higher extent.

![Histograms showing the distributions of torsion angles for both noncoordinated (a) and coordinated (b) 4, 4'-bipyridine.](image)

Similar trends can also be observed in the case of benzoates/benzoic acids, i.e., a large number of hits are narrowed within a small range of relatively low torsion angles and the metal-ligand interactions somehow contribute to the increase of distortions. However, the distributions of torsion angles tend to be more continuous than those of 4,
4’-bipy, indicating a generally higher flexibility for the aromatic carboxylates/carboxylic acids. In particular, we found an even higher degree of distortion for the fluoro-substituted ligands within this family, as compared to aromatic carboxylates/carboxylic acids in general. Interestingly, other halogen-substituted carboxylates/carboxylic acids do not share this same pattern, suggesting an electronic rather than steric reason for the high flexibility of fluorinated ligands (Figure 3.4).

Figure 3.4 Histograms showing the distributions of torsion angles for noncoordinated (a), coordinated (b), fluoro-substituted (c) and other halogen-substituted (d) benzoates/benzoic acids.
3.2 Metal-Organic Frameworks from TFBDC

3.2.1 1D Structures

In the previous chapter, we concentrate upon the use of angular dicarboxylato ligand BDC, which prefers to adopt planar or near-planar conformations. The combination of angularity and rigidity of the ligand has thus far led to a diverse range of MOF structures that are of particular interest from both scientific and technical perspectives. It hence intrigued us as what could be expected if higher flexibility is integrated along with angularity. Our CSD analysis above indicates that fluorinated carboxylates/carboxylic acids are ideal candidates in this regard since the presence of fluorine atoms significantly increases the flexibility of molecules. In this context, we have initiated a systematic investigation on a particular ligand, namely, tetrafluoro-1, 3-benzenedicarboxylate (TFBDC), a fluorinated version of BDC, to explore its use in the context of MOF chemistry.

The solid state structure of H₂TFBDC reveals that of 1D zigzag chain motifs which are sustained by an array of carboxylic dimers (Figure 3.5a). The O•••O distances in each dimer are ca. 2.6Å, well within the anticipated range for such interactions. As expected, the torsion angles of carboxyl planes with respect to the aromatic rings have the values of 39.00 and 41.34°, which are considerably higher than those observed in BDC.

Interestingly, the zigzag chain pattern exhibited in the crystal structure of the free ligand has been literally retained by compound 9, [Cu₂(TFBDC)₂(Py)₄]ₙ, which was obtained from an ethanol solution of Cu(NO₃)₂•2.5H₂O and TFBDC in the presence of pyridine and nitrobenzene. The analogy can be further drawn by comparing the dimeric units seen in 9, which are composed of two Cu(II) centers, two bridging bifurcated
carboxyl oxygens, two mono-dentate carboxyl oxygens and four pyridines, to the carboxylic dimers in the free ligand (Figure 3.5). Each Cu(II) displays a trigonal bipyramidal geometry and the Cu•••Cu distance is as far as 3.44Å, also within the reasonable range expected for this type of chromophore although significantly larger than those seen in SBU I. These dimeric units are doubly bridged by TFBDC moieties to give rise to 1D polymeric chains, which in turn close-pack into three dimensions, excluding nitrobenzene from entering the crystal structure. The centroid-centroid distances of each pair of TFBDCs and pyridines are 4.53Å and 3.98Å, respectively, indicating fairly weak π•••π stacking for the former and moderate one for the latter. It should be noted that similar 1D coordination polymers have also been isolated using BDC and Cu(II) as building blocks; however, they are mostly based upon mono-copper centers and no such dimeric units have been identified in those structures.247

Figure 3.5 1D zigzag chain structures of the ligand H2TFBDC (a) and compound 9 (b).
3.2.2 Guest-Dependent switch-on/-off of Two Types of Cavities in 2D Structures

The flexibility of the ligand TFBDC and its impacts on supramolecular structures not only can be exemplified by the above 1D structures, but more remarkably, as will be specified below, they are also well demonstrated in a series of 2D architectures that are built upon paddle-wheel SBU I and that are closely related to the tetragonal sheets B discussed in Chapter 2.

Compound 10a, \( \{\text{Cu}_2(\text{TFBDC})_2(\text{quinoline})_2\}_\infty \), was acquired as green single-crystalline materials from an ethanol solution of \( \text{Cu(NO}_3)_2\cdot2.5\text{H}_2\text{O} \) and TFBDC using quinoline as the base and relatively large aromatic molecules (such as toluene and xylenes) as the template. X-ray single crystal diffraction study discloses a contracted 2D tetragonal sheet topology for 10a, thanks to a pronounced distorted effect of TFBDC in which the torsion angles of two carboxyl planes are 57.92° and 75.29°, respectively. The fluorinated rings of two opposite TFBDC ligands are facing toward each other (\( d_{\text{centroid-centroid}} = 3.665\text{Å} \)) and they therefore engage in fairly strong \( \pi-\pi \) interactions. Such a short

![Figure 3.6 Crystal structure (a) and crystal packing (b) of compound 10a.](image-url)
contact, however, effectively closes off the potential cavities that would otherwise be available to guest species (Figure 3.6a). Notably, the axial ligand quinolines also participate in, among themselves, considerably strong C-H•••π interactions with the D (distance from C to the aromatic ring) being 3.683Å within each layer and 3.757Å between adjacent layers, respectively. As a result of such efficient close-packing, no inter-layer space exists either and thus 10a can be described as an “apohost” framework (a host framework without guest molecules).70

Such an apohost framework, however, exhibits quite intriguing dynamic characteristics. Indeed, by careful selection of other aromatic templates of appropriate sizes, as compared to those larger ones used in the synthesis of 10a, we are able to open up the potential cavities and introduce guest species into the framework. Even more significantly, crystallographic study demonstrates it is possible to selectively open either intra- or inter-layer free space by means of controlling molecular recognitions.

When employing o-dichlorobenzene instead of toluene or xylanes as the template, we obtained compound 10b, \{[Cu₂(TFBDC)₂(quinoline)₂](o-dichlorobenzene)₀.₅\}∞, as the

Figure 3.7 Crystal structure (a) and crystal packing (b) of compound 10b. The axial ligand (quinoline) is omitted in a) for the purpose of clarity.
major product. Single-crystal X-ray diffraction suggests that 10b retains a very similar 2D architecture as 10a, i.e., a distorted tetragonal sheet. In contrast to 10a, however, guest molecules o-dichlorobenzene enter into the crystal structure of 10b and force to open the intra-layer cavities that are each defined by four SBUs I and four TFDBC moieties (Figure 3.7a). Surprisingly, o-dichlorobenzene occupies only half of these cavities, leaving the other half remain closed. Such a dissymmetric occupancy leads to two remarkably distinct dimensions for the open and closed cavities and their centroid-centroid distances between opposite TFBDC rings vary by more than 2.4 Å (6.793 Å vs. 4.390 Å)! Within the open cavities, each of the crystallographically disordered o-dichlorobenzene molecules is sandwiched by two TFBDCs and the centroid-centroid distance from o-dichlorobenzene to each of the TFBDC rings is 3.397 Å, exactly half of the value 6.793 Å, indicating perfectly parallel π-π interactions between these aromatic systems. It is perhaps of interest to compare the centroid-centroid distances of the closed cavities in 10b (4.390 Å) with those in 10a (3.665 Å) and presumably such a discrepancy can be attributed to the structural distortion of 10b which is induced by the presence of o-dichlorobenzene.

The structural deformations caused by o-dichlorobenzene can be further evidenced by the subtle changes of intra-layer and inter-layer interactions among quinolines. Whereas quinolines within each layer still participate in C-H···π interactions (D = 3.787 Å), only half amount of such interactions prevails because of a much larger separation for the other half (D = 7.106 Å) due to the expansion of the open cavities. The inter-layer interactions between quinolines, on the other hand, manifest an accommodation of both π···π (d_{centroid-centroid} = 3.355 Å and 3.341 Å) and C-H···π bonding.
(D = 3.765 Å), in contrast to the solo appearance of C-H–π interactions in 10a.

Surprisingly, although 10b significantly differs from 10a from a supramolecular perspective, X-ray powder diffraction (XPD) and Thermal Gravimetric Analysis (TGA) experiments indicate that if removed from mother liquor under ambient conditions, 10b quickly undergoes a phase transition, most likely back to 10a, suggesting the thermodynamic instability of the former.

Another form of 10 was also isolated as single-crystalline product when using chlorobenzene as the crystallization template. This new compound, namely, 10c, with a formula of \{[\text{Cu}_2(\text{TFBDC})_2(\text{quinoline})_2](\text{chlorobenzene})_{0.5}\}_\infty, also exhibits a 2D distorted tetragonal sheet topology with an identical network composition as in 10a and 10b. As illustrated in Figure 3.8a, the 2D framework displays a closed mode and the two types of short contacts between opposite TFBDC rings (d_{centroid-centroid} = 4.149 Å and 4.652 Å; see below for an explanation of such a difference) clearly suggest an efficient π–•••π stacking. Quinolines again play an important role in stabilizing each of the 2D layers by engaging

![Figure 3.8 Crystal structure (a) and crystal packing (b) of compound 10c.](image)
in an array of C-H•••π interactions (D = 3.977Å). What makes this structure so unique, however, is the position of chlorobenzene molecules within the metal-organic framework. Instead of going into the intra-layer space as seen in 10b, chlorobenzene is found to be hosted by the inter-layer cavities that are enclosed by quinolines on the sides and TFBDCs from the top and bottom (Figure 3.9a). While these cavities are mainly constructed from quinolines which engage in alternative π•••π stacking (d_{centroid-centroid} = 3.927Å) and C-H•••π bonding (D = 3.576Å and 3.977Å), the entrapped chlorobenzene molecules are sandwiched by TFBDC rings from adjacent layers through two-fold π•••π interactions (d_{centroid-centroid} = 3.998Å). Nevertheless, only half of these inter-layer cavities are occupied by chlorobenzene molecules and the other half remain guest-free (Figure 3.9b). Calculations further suggest a volume of ca. 130Å³ for the first type of cavities, in good accordance with the molecular volume of chlorobenzene (98.5Å³), and a near-zero volume for the second type. One would probably be amazed by the extremely high local molar concentration (ca. 12.8M!) of the enclosed guest species. The alternative
occupancy of the inter-layer cavities by chlorobenzene also accounts for the aforementioned two different centroid-centroid distances observed within each layer in 10c (4.652Å vs. 4.149Å; the former belongs to the ones involved with chlorobenzene) since the interactions between the TFBDC rings and the sandwiched chlorobenzene molecules are driving TFBDC rings slightly away from their opposite partners from the same layer with which they are simultaneously interacting. It is worth noting that both XPD and TGA experiments suggest that complex 10c is much more stable than 10b and the guest species stay in the structure even after removed from mother liquor at ambient conditions.

Compounds 10a–c therefore represent a prototypical example of MOFs that are robust and flexible enough to adjust the frameworks under different environments. It appears clear to us that fluorination on the dicarboxylato ligand plays a critical role in this regard, since the remarkable flexibility of the functionalized frameworks hasn’t been observed in the original MOFs that are derived from the ligand BDC. In contrast to highly rigid MOFs, these new classes of dynamic structures are capable of responding to various host-guest recognition events and accommodating a wide array of guest species, which is especially important in the context of separation, molecular sensing and storage.242-243

Until now, nevertheless, the following questions concerning the host-guest relationships and the diversity of molecular recognitions in compounds 10a–c remain unanswered: 1) why would o-dichlorobenzene only reside in the intra-layer cavity whereas chlorobenzene exclusively stays within the inter-layer cavity, even though these two molecules are electronically and chemically quite similar? 2) Which factors (e.g., energetic or steric effects) determine that only half of the intra-layer or inter-layer
cavities are occupied by guest species? 3) Does the presence of guest molecules in the final structure indicate their pre-organization and subsequent template effects on the formation of the ordered arrays of metal-organic compositions, or is it simply a result of post-synthetic molecular recognitions?

Although further theoretical and experimental investigations are undoubtedly necessary, and a thorough understanding of these questions will largely facilitate the design of future generations of functional materials, we speculate tentative answers to the above as such: 1) Whereas the dimensions of the intra-layer cavities are suitable for both chlorobenzene and o-dichlorobenzene, the limited space enclosed by each of the inter-layer cavities has eliminated the inclusion of slightly larger o-dichlorobenzene; and since structures with guests sitting in the intra-layer cavities have been shown to be less stable, the thermodynamic forces are probably driving chlorobenzene into the inter-layer cavities. In short, steric effects seem to be playing a central role in the case of dichlorobenzene while thermodynamic factors are likely to be the key for the case of chlorobenzene; 2) both the size of guests and the degree of deformation the framework can sustain, among others, decide that only half of the intra- or inter-layer cavities of 10 can be fulfilled by chlorobenzene and dichlorobenzene, respectively. One could imagine complexes of 10 with full occupancy of either type of cavities; however, they are most likely over-distorted and therefore become thermodynamically unstable. In fact, as will be demonstrated below, benzene, a guest of smaller size, is able to fully occupy the intra-layer cavities of a related tetragonal sheet; 3) the existence of apohost 10a implies that the presence of aromatic guests is not indispensable for the formation of the metal-organic network; yet the well-trapped scenario of chlorobenzene as suggested by the
fairly high thermal stability of complex 10c might indirectly indicate the possible template effects of host-guest interplay at the early stages of crystallization.

3.2.3 Functionalization of Inter-layer Cavities in 2D Structures

Thus far we have demonstrated an effective approach, namely, fluorination of organic ligands, for the modification of prototypal MOFs. The introduction of highly electron-negative fluorine atoms on the BDC rings dramatically alters the electronic properties of the ligand and results in a much higher level of framework flexibility. In fact, compounds 10a–c exemplify a new family of compounds with functionalized intra-layer cavities as the dynamic features of these structures are not observed in their unsubstituted counterparts.

Since both intra-layer and inter-layer cavities are potentially amenable to be structurally and chemically fine-tuned in these structures, it is perhaps appropriate to further evaluate the feasibility of using a similar strategy to transform the nature of inter-

![Figure 3.10 Three axial ligands of SBU I used for the functionalization of inter-layer cavities.](image)
layer cavities. Quinoline, a relatively large hydrophobic aromatic system, has been shown to serve as the axial ligand of SBU I and play an important role in the construction of inter-layer cavities in 10a–c. It therefore occurs to us that other types of axial ligands, such as 2-picoline (a hydrophobic but smaller aromatic molecule) and ethanol (a smaller but less hydrophobic and more hydrophilic molecule), might as well be suited to direct the formation of various inter-layer cavities (Figure 3.10).

Indeed, green crystals of 11, \([\text{Cu}_2(\text{TFBDC})_2(\text{EtOH})_2](\text{EtOH})_2(\text{benzene})\)\(\infty\), precipitate from an ethanol solution containing Cu(NO\(\text{3}\))\(2\)•6H\(\text{2O}\), TFBDC, benzene and 2,6-lutidine. Structural analysis based on X-ray single crystal diffraction reveals a familiar 2D distorted tetragonal sheet and contrary to 10b, where only half of the intra-layer cavities are filled with guest species, each of the holes in 11 is inhabited by one benzene molecule that interacts with TFBDC rings through \(\pi\cdots\pi\) stacking (Figure 3.11a; \(d_{\text{centroid-centroid}} = 3.481\text{Å} \text{ and } 3.542\text{Å}\)). Due to the weak coordination ability of 2, 6-lutidine,
solvent molecules ethanol instead coordinate at the axial positions of SBUs I, therefore modifying both steric and electronic environments on the exterior of the 2D networks. As a result, the inter-layer cavities become less hydrophobic and two ethanol molecules (instead of benzene!) are sitting as guests inside each of them. Interestingly, these EtOH guests are hydrogen-bonding with the frameworks in two distinct motifs, one of which only involves the coordinated EtOH while the other takes advantage of both coordinated EtOH and the carboxyl oxygens (Figure 3.12). Four different hydrogen-bond distances ($d_{O•••O} = 2.609\text{Å}, 2.817\text{Å}; 2.633\text{Å}, \text{and } 2.980\text{Å}$) are also well within the anticipated range for this type of interactions.

When replacing uncoordinating 2, 6-lutidine with coordinating 2-picoline and using hexafluorobenzene (HFB) as the template, we obtained another new compound, 12 of formula $\{[\text{Cu}_2(\text{TFBDC})_2(2\text{-picoline})_2](\text{EtOH})_{1.3}(\text{HFB})\}_\infty$. 12 again manifests an alike 2D tetragonal sheet which has found no guests within the intra-layer cavities (Figure 3.13).
The centroid-centroid distance between opposite TFBDC rings is 4.281Å, in good consistence with those of 10c ($d_{\text{centroid-centroid}} = 4.149Å$ and $4.652Å$) but slightly larger than those in 10a ($d_{\text{centroid-centroid}} = 3.665Å$). The use of a smaller axial ligand 2-picoline, as compared to the more bulky quinoline, has resulted in the following salient features concerning the inter-layer cavities: 1) the cavities are not as well-defined as in the case of quinoline and the free space is in fact continuous along one direction, thus in effect transformed into 1D channels; 2) the aromatic molecules (HFB) and solvent species (EtOH) are co-existing as guests within the channels; 3) the average number of guest molecules per SBU I (1 HFB and 1.3 EtOH) is larger than other cases; 4) instead of associating with TFBDC rings, HFB molecules orientate themselves toward 2-picoline moieties in such a way that the pairs participate in face-to-face $\pi\cdots\pi$ stacking ($d_{\text{centroid-centroid}} = 3.632Å$).

Figure 3.13 Crystal structure (a) and packing (b) of 12. Half of 2-picoline ligands and all EtOH guests are crystallographically disordered. Guest molecules (EtOH and HFB) are represented in a CPK mode.
In short, we have illustrated, in addition to the use of fluorinated ligands as flexible structural ingredients, another compelling design element that can be employed to manipulate supramolecular structures and functions, i.e., systematically fine-tuning the chemical nature of the exteriors of 2D MOFs. Since both approaches are based upon well-established supramolecular chemistry and crystal engineering principles, we anticipate them to be of general implications for the design of other useful metal-organic materials.

3.3 Summary

This Chapter is focused upon the discussions of the following topics:

1) Flexible metal-organic frameworks, which are new classes of metal-organic compounds able to respond to the environments (such as release, uptake or exchange of guest species) by adjust their supramolecular architectures. The flexibility of MOFs can be imparted and controlled from the molecular level.

2) Guest-dependent switch-on/off of cavities in a series of distorted 2D tetragonal sheets that are assembled from fluorinated BDC and SBU I. Both intra-layer and inter-layer free spaces can be closed or opened by introducing appropriate guest molecules.

3) Functionalization of metal-organic frameworks by means of substituting axial ligands in the above-mentioned tetragonal sheets.
3.4 Experimental

3.4.1 Syntheses

The materials in the synthesis were used as received from reliable commercial sources (Sigma-Aldrich or Fischer Scientific); solvent methanol was purified and dried according to standard methods.

*Synthesis of \([\text{Cu}_2(\text{TFBDC})_2(\text{Pyridine})_4]_\infty, \mathbf{9}\)*

Compound \(\mathbf{9}\) were obtained by layering 4 mL of an ethanol solution containing 2, 4, 5, 6-tetrafluoroisophthalic acid (169 mg, 0.500 mmol) and pyridine (0.12 mL, 1.50 mmol) onto 4.5 mL of an ethanol/nitrobenzene solution (2.5:2, v/v) containing \(\text{Cu(NO}_3\text{)}_2\cdot2.5\text{H}_2\text{O}\) (116 mg, 0.500 mmol). Blue rod-like crystals formed at the interlayer boundary within 24 hours.

*Synthesis of \([\text{Cu}_2(\text{TFBDC})_2(\text{Quinoline})_2]_\infty, \mathbf{10a}\)*

Compound \(\mathbf{10a}\) were obtained by layering 3.5 mL of an ethanol solution containing 2, 4, 5, 6-tetrafluoroisophthalic acid (23 mg, 0.10 mmol) and quinoline (0.059 mL, 0.50 mmol) onto 3.5 mL of an ethanol/toluene solution (2.5:1, v/v) containing \(\text{Cu(NO}_3\text{)}_2\cdot2.5\text{H}_2\text{O}\) (23 mg, 0.10 mmol). Green block crystals formed at the interlayer boundary within 24 hours.

*Synthesis of \([\text{Cu}_2(\text{TFBDC})_2(\text{quinoline})_2](\text{p-dichlorobenzene})_{0.5}]_\infty, \mathbf{10b}\)*

Compound \(\mathbf{10b}\) were obtained by layering 3.5 mL of an ethanol solution containing 2, 4, 5, 6-tetrafluoroisophthalic acid (23 mg, 0.10 mmol) and quinoline (0.059 mL, 0.50 mmol) onto 3.5 mL of an ethanol/p-dichlorobenzene solution (2.5:1, v/v) containing \(\text{Cu(NO}_3\text{)}_2\cdot2.5\text{H}_2\text{O}\) (23 mg, 0.10 mmol). Green block crystals formed at the interlayer boundary within 24 hours.
Synthesis of $\{[\text{Cu}_2(\text{TFBDC})_2(\text{quinoline})_2]\text{(chlorobenzene)}_{0.5}\}_\infty$, 10c

Compound 10c were obtained by layering 3.5 mL of an ethanol solution containing 2, 4, 5, 6-tetrafluoroisophthalic acid (23 mg, 0.10 mmol) and quinoline (0.059 mL, 0.50 mmol) onto 3.5 mL of an ethanol/chlorobenzene solution (2.5:1, v/v) containing Cu(NO$_3$)$_2$•2.5H$_2$O (23 mg, 0.10 mmol). Green block crystals formed at the interlayer boundary within 24 hours.

Synthesis of $\{[\text{Cu}_2(\text{TFBDC})_2(\text{EtOH})_2]\text{(EtOH)}_2\text{(benzene)}\}_\infty$, 11

Compound 11 were obtained by layering 2.5 mL of an ethanol solution containing 2, 4, 5, 6-tetrafluoroisophthalic acid (23 mg, 0.10 mmol) and 2, 6-lutidine (0.034 mL, 0.30 mmol) onto 2.5 mL of an ethanol/benzene solution (1.5:1, v/v) containing Cu(NO$_3$)$_2$•2.5H$_2$O (23 mg, 0.10 mmol). Green block crystals formed at the interlayer boundary within 24 hours.

Synthesis of $\{[\text{Cu}_2(\text{TFBDC})_2(2\text{-picoline})_2]\text{(EtOH)}_{1.3}\text{(HFB)}\}_\infty$, 12

Compound 12 were obtained by layering 3 mL of an ethanol solution containing 2, 4, 5, 6-tetrafluoroisophthalic acid (23 mg, 0.10 mmol) and 2-picoline (0.030 mL, 0.30 mmol) onto 3 mL of an ethanol/hexafluorobenzene (HFB) solution (5:1, v/v) containing Cu(NO$_3$)$_2$•2.5H$_2$O (23 mg, 0.10 mmol). Green block crystals formed at the interlayer boundary within 24 hours.
3.4.2 Characterizations

Crystal Structure Determination

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 Moka radiation ($\lambda = 0.7107$ Å). The data were corrected for Lorentz and polarization effects and for absorption using the SADABS program. The structures were solved using direct methods and refined by full-matrix least-squares on $|F|^2$. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions and refined with temperature factors 1.2 times those of their bonded atoms. All crystallographic calculations were conducted with the SHELXL 5.1 program package.

Table 3.1 Crystallographic data for compounds 9, 10a–c, 11, 12.

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Other Characterizations

Thermogravimetric analysis was performed under nitrogen at a scan speed of 4°C/min on a TA Instrument TGA 2950 Hi-Res. Low resolution XRPD data were recorded on a Rigaku RU15 diffractometer at 30kV, 15mA for Cu Kα (λ = 1.5418 Å), with a scan speed of 1 or 2°/min and a step size of 0.05° in 20 at room temperature. The simulated XRPD patterns were produced using and Powder Cell for Windows Version 2.4 (programmed by W. Kraus and G. Nolze, BAM Berlin, © 2000).

Figure 3.14 TGA trace of compound 10a.
Figure 3.15 TGA trace of compound 10b.

Figure 3.16 TGA trace of compound 10c.
Figure 3.17 TGA trace of compound 11.

Figure 3.18 Experimental and simulated XPD of compound 10a.
Figure 3.19 Experimental and simulated XPD of compound 10b compared with simulated XPD of 10a.

Figure 3.20 Experimental and simulated XPD of compound 10c.
4.1 Introduction: 3D Nets

In the period of 1954~1976, A. F. Wells published a series of seminar papers\textsuperscript{250-261} to investigate the geometrical basis of crystal chemistry and elaborate general principles for the topological analysis of crystalline inorganic and in some cases, hydrogen-bonded, solids. These systematic studies laid the foundation for a later publication of his famous monograph entitled “Three-Dimensional Nets and Polyhedra”\textsuperscript{72}, which is now widely regarded as the milestone of inorganic structural chemistry. In this book, as well as in a subsequent related study, \textsuperscript{73} Wells systematically (although not completely!) enumerates, based on their connectivity, various 3D nets and analyzes their topological properties. A wide array of 3-connected nets, 3, 4-connected nets, 4-connected nets, and interpenetrated nets are covered in details. In particular, a large number of uniform (meaning all shortest circuits are the same kind) 3-connected nets, including (7, 3) nets, (8, 3) nets, (9, 3) nets, (10, 3) nets, and (12, 3) nets, are the subjects of detail discussions. For example, seven (10, 3) nets, namely, (10, 3)-a ~ g, have been identified by Wells, although it is worth mentioning only the first four are uninodal (bearing just one type of vertices) while the last three are multimodal (bearing more than one type of vertices). Figure 4.1 depicts the connectivity of these four uninodal (10, 3) nets.

It should be noted that a rigorous enumeration of all uniform and uninodal 3-connected nets (52 in total) has been made by Koch and Fischer using the concept of homogenous sphere packings. In Koch & Fischer’s terminology, a sphere-packing type
may be characterized by a symbol $k/m/f/n$, where $k$ is the number of contacts per sphere, $m$ is the number of edges (or vertices) in a shortest closed path of the graph, $f$ designates the crystal family (referring to the highest possible symmetry of a sphere packing of that type) and $n$ is a consecutive number within a class $k/m/f$. More recently, O’Keeffe has developed, based in part on the concept of natural tilings, a hierarchical description of three-periodic nets and proposed a new nomenclature for these structures using lower-

Figure 4.1 Representative examples of uniform and uninodal (10, 3) nets: a) (10, 3)-a net; b) (10, 3)-b net; c) (10, 3)-c net; d) (10, 3)-d net.
Table 4.1 summarizes a list of 11 uniform and uninodal (10, 3) nets that have been studied by Wells, O’Keeffe, and Fischer & Koch.\textsuperscript{72-73, 236, 236}

<table>
<thead>
<tr>
<th>Net</th>
<th>Wells Symbol</th>
<th>O’Keeffe Symbol</th>
<th>Fischer &amp; Koch Symbol</th>
<th>Space Group</th>
<th>Vertex Symbol</th>
<th>Coordination Sequence</th>
<th>Td\textsuperscript{[a]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(10,3)-a</td>
<td>srs</td>
<td>3/10/c1</td>
<td>$I4_1$</td>
<td>10•10•10•10</td>
<td>3, 6, 12, 24, 35, 48, 69, 86, 108, 138</td>
<td>529</td>
</tr>
<tr>
<td>2</td>
<td>(10,3)-b</td>
<td>ths</td>
<td>3/10/t4</td>
<td>$I4_1/amd$</td>
<td>10•10•10•10</td>
<td>3, 6, 12, 24, 38, 56, 77, 102, 129, 160</td>
<td>607</td>
</tr>
<tr>
<td>3</td>
<td>(10,3)-c</td>
<td>bto</td>
<td>3/10/h1</td>
<td>$P6_22$</td>
<td>10•10•10•10</td>
<td>3, 6, 12, 24, 43, 64, 91, 124, 160, 202</td>
<td>729</td>
</tr>
<tr>
<td>4</td>
<td>(10,3)-d</td>
<td>utp</td>
<td>3/10/o1</td>
<td>$Pmna$</td>
<td>10•10•10•10</td>
<td>3, 6, 12, 24, 38, 56, 80, 106, 132, 164</td>
<td>621</td>
</tr>
<tr>
<td>5</td>
<td>--</td>
<td>utj</td>
<td>3/10/t2</td>
<td>$P4_1/nbc$</td>
<td>10•10•10•10</td>
<td>3, 6, 12, 24, 43, 64, 87, 118, 156, 196</td>
<td>709</td>
</tr>
<tr>
<td>6</td>
<td>--</td>
<td>utm</td>
<td>3/10/t5</td>
<td>$I4_1/acd$</td>
<td>10•10•10•10</td>
<td>3, 6, 12, 24, 39, 56, 76, 100, 130, 164</td>
<td>610</td>
</tr>
<tr>
<td>7</td>
<td>--</td>
<td>utn</td>
<td>3/10/t6</td>
<td>$I4_1/acd$</td>
<td>10•10•10•10</td>
<td>3, 6, 12, 24, 39, 70, 108, 159, 206, 260</td>
<td>891</td>
</tr>
<tr>
<td>8</td>
<td>--</td>
<td>uto</td>
<td>3/10/t7</td>
<td>$I4_1/acd$</td>
<td>10•10•10•10</td>
<td>3, 6, 12, 24, 43, 64, 87, 118, 156, 198</td>
<td>711</td>
</tr>
<tr>
<td>9</td>
<td>--</td>
<td>utk</td>
<td>3/10/t3</td>
<td>$P4_22$</td>
<td>10•10•10•10</td>
<td>3, 6, 12, 24, 43, 72, 109, 142, 177, 228</td>
<td>816</td>
</tr>
<tr>
<td>10</td>
<td>--</td>
<td>wix</td>
<td>3/10/h2\textsuperscript{[b]}</td>
<td>$P6_22$</td>
<td>10•10•10•10</td>
<td>3, 6, 12, 24, 39, 60, 87, 112, 137, 168</td>
<td>648</td>
</tr>
<tr>
<td>11</td>
<td>--</td>
<td>wiy</td>
<td>3/10/h3\textsuperscript{[b]}</td>
<td>$P6_22$</td>
<td>10•10•10•10</td>
<td>3, 6, 12, 24, 39, 62, 95, 142, 198, 236</td>
<td>817</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} Tdn is the cumulative sum of the first n shells of topological neighbors.

\textsuperscript{[b]} It was originally written as “3/10/h1” by Fischer & Koch.

Systematic enumeration of 3D nets is especially desirable in the study of zeolites and related materials, of which there are now 167 recognized structural types.\textsuperscript{216} Whereas 3-connected structures represent a relatively small and perhaps simple subclass of the three-periodic nets, a thorough enumeration of 4-connected\textsuperscript{269} and hetero-coordinated nets, such as (3, 4)-connected nets, seems to be more challenging, due to the increased or more complicated connectivity. A catalog of 4-connected nets has been compiled by
Smith, and a number of hetero-coordinated nets (see the discussions on binary and ternary nets in section 4.3) have also been recognized by Wells and O’Keeffe.

4.2 Topological Analysis of Metal-Organic Frameworks

Similar to the inorganic minerals and synthetic zeolites or their related compounds, 3D MOFs can be conveniently conceptualized as geometrical entities that are composed of points and lines of various shapes. Topological analysis on such simplified models has thus greatly facilitated the recognition, interpretation, and comparison of the inherent connectivity of these MOF structures, which might be critical, especially from the materials perspective, in order to establish a well-founded structure-property rationale.

Nevertheless, in our experiences, discovery and recognition of novel three-periodic nets remains a nontrivial exercise and it is not unusual to encounter such cases in the literature where the topologies underlying the MOFs of interest are either wrongfully identified or not identified at all. Therefore we will next discuss some intriguing 3D MOFs that have been synthesized by our laboratory as well as other research groups.

4.2.1 Topological Analysis of Some 3D MOFs from Our Recent Studies

Our laboratory has been actively involved in the discovery of novel MOFs and a number of unprecedented structures were initially reported by us. In this section, we will illustrate the topological features of some interesting 3D MOFs studied by our group in the past decade.
1) [Ag(4,4'-bipy)](NO₃)²⁺

[Ag(4,4'-bipy)](NO₃) was assembled from the linear spacer 4, 4'-bipy and three-coordinate “T-shape” silver ions (an Ag-Ag bond occupies the third coordination site) in a 1:1 stoichiometry. The structure is composed of three interpenetrated networks and only one single framework is shown in Figure 4.2a. The connectivity of the structure can be schematically illustrated by linking the metal nodes while ignoring the organic components (Figure 4.2b). A topological analysis in the simplified model reveals a vertex symbol of “10₂•10₄•10₄” and a coordination sequence of “3, 6, 12, 24, 38, 56, 77, 102, 129, 160”, which correspond to those of a (10, 3)-b net (Table 4.1). Therefore, [Ag(4,4'-bipy)](NO₃) represents one of the very first examples of metal-organic (10,3)-b nets.

Figure 4.2 Topological analysis of [Ag(4,4'-bipy)](NO₃): a) a single framework of the structure; Ag – green, H – gold, N – blue, C – grey; NO₃⁻ is deleted for clarity. b) a schematic illustration.
2) \([\text{Co}(4,4'\text{-bipy})_{1.5}](\text{NO}_3)_2\)\(^{274}\)

Similar to \([\text{Ag}(4,4'\text{-bipy})](\text{NO}_3)_2\), \([\text{Co}(4,4'\text{-bipy})_{1.5}](\text{NO}_3)_2\) is also based upon T-shape nodes and linear spacers and is complicated by three-fold interpenetration as well. However, the T-shape geometry of the vertices in the latter is instead originated from the distorted trigonal bipyramidal configuration of Co(II) centers that are partially capped by \(\text{NO}_3^-\) groups and the stoichiometry between metal ions and ligands appears to be 1:1.5 (Figure 4.2). Using the same topological analysis protocols, it can be confirmed that both vertex symbol and coordination sequence of this MOF match those of a (10, 3)-b net, although it is distorted from the ideal symmetry (Figure 4.1b).

3) \([\text{Zn(BDC)(bpeta)}](\text{solvent})\)\(^{275}\) (BDC = 1, 3-benzenedicarboxylate; bpeta = 1,2-bis(4-pyridyl)ethane; solvent = MeOH, naphthalene or CH\(_2\)Cl\(_2\)).

\(\text{Zn(BDC)(bpeta)}\) is a neural 3D 3-fold interpenetrated MOF based upon tetrahedral Zn(II) centers bridged by two types of organic linkers, BDC and bpeta. A single

Figure 4.3 Topological analysis of \([\text{Co}(4,4'\text{-bipy})_{1.5}](\text{NO}_3)_2\): \(a\) a single framework of the structure; Co – green, H – gold, N – blue, O – red, C – grey; \(\text{NO}_3^-\) is deleted for clarity. \(b\) schematic illustration of the net.
framework of this structure is shown in Figure 4.4a and the inherent architecture of this net bears a close resemblance to that of the 4-connected diamond net since both structures contain similar chair-shape 6-membered rings (Figure 4.4b). Nevertheless, a detail topological study indicates a completely different connectivity for this 3D MOF, as its vertex symbol and coordination sequence are shown to be $6 \cdot 6 \cdot 6 \cdot 6 \cdot 8_3$ and “4, 12, 30, 62, 98, 144, 198, 262, 332, 412”, respectively (see Table 1.2 for a comparison with the diamond net). The topology of this MOF is thus distinct from the diamond net or any other known 4-connected nets and Zn(BDC)(bpeta) is, to the best of our knowledge, the
only example of MOFs that possess this type of linkage (O’Keeffe has termed this
topology as dmp in his under-construction RCSR Database\textsuperscript{236}). It somewhat amazes us
how new types of structures still seem to have found their own way into the reaction vials
of synthetic chemists\textsuperscript{216}, even though tetrahedron-based 4-connected nets have been
intensively studied both theoretically\textsuperscript{72-73, 79, 270} and experimentally\textsuperscript{276} over the years.

4) $[\text{Zn}_2(\text{BTC})_L_2\cdot X]_8[\text{Zn}_2(\text{BTC})_{4/3}L_2]_3$ \textsuperscript{77} (BTC = 1,3,5-benzenetricarboxylate; L =
pyridine or water; X = NO$_3^-$).

The 3D MOF $[\text{Zn}_2(\text{BTC})_L_2\cdot X]_8[\text{Zn}_2(\text{BTC})_{4/3}L_2]_3$ is consisted of two types of
inorganic clusters (i.e., square and triangular paddle-wheel SBUs) in 1:2 ratio which are
linked by the triangular ligand BTC$^{3-}$ (Figure 4.5). The structure has a cubic symmetry
and it was previously interpreted from the perspective of space-filling of faceted

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.5.png}
\caption{Topological analysis of $[\text{Zn}_2(\text{BTC})_L_2\cdot X]_8[\text{Zn}_2(\text{BTC})_{4/3}L_2]_3$: \textit{a)} the crystal structure; Zn –
green, H – gold, N – blue, O – red, C - grey; NO$_3^-$ is deleted for clarity. \textit{b)} a schematic illustration of the
net; the red and green represent 4-connected and 3-connected nodes, respectively.}
\end{figure}
polyhedra.\textsuperscript{77} We will demonstrate here that it is also of interest from a node-and-spacer perspective. Indeed, the structure can be described as an example of class II type (3, 4)-connected nets where 3-connected and 4-connected nodes are not necessarily alternating (whereas in class I type (3, 4)-connected nets, 3-connected nodes are exclusively linked to 4-connected nodes and vice versa; see section 4.3 for more details on the class I).

The long vertex symbol for this net is \((8_2 \cdot 8_2 \cdot 8_2)_{12}(8_2 \cdot 8_2 \cdot 8_2)_{6}(8_2 \cdot 8_2 \cdot 8_2 \cdot 12_4 \cdot 12_4)_{3}\) and the three separate parts represent BTC\textsuperscript{3−}, the triangular SBUs \([\text{Zn}_2(\text{COO})_3]\textsuperscript{+}\), and the square SBUs \(\text{Zn}_2(\text{COO})_4\), respectively, which are in a ratio of 12:8:3. Although both the organic and inorganic 3-connected nodes appear to have the same vertex symbols, they are nevertheless different in a topological sense, as suggested by their distinct coordination sequences:

\[
\text{BTC}^{3−}:\quad 3\quad 7\quad 14\quad 26\quad 38\quad 61\quad 77\quad 110\quad 133\quad 179\quad 649;
\]

\[
[Z\text{Zn}_2(\text{COO})_3]^{+}:\quad 3\quad 6\quad 15\quad 24\quad 42\quad 58\quad 84\quad 100\quad 144\quad 165\quad 642;
\]

\[
\text{Zn}_2(\text{COO})_4:\quad 4\quad 8\quad 16\quad 24\quad 40\quad 52\quad 84\quad 110\quad 148\quad 168\quad 655.
\]

While in the first class (3, 4)-connected nets, the ratio between 3-connected and 4-connected nodes is always 4:3, this is not necessarily the case for the second class, as can be seen from above. It should also be noted that this novel topology has been named by O’Keeffe as tfe in the Database,\textsuperscript{236} where a number of other (3, 4)-connected nets can also be found.

5) \textbf{Zn(nicotinate)}\textsubscript{2}.\textsuperscript{277}

The 3D MOF \(\text{Zn(nicotinate)}\textsubscript{2}\) is one of the supramolecular isomers that are assembled from \(\text{Zn(II)}\) and the angular ligand nicotinate. The \(\text{Zn(II)}\) centers adopt a
distorted octahedral geometry furnished with two chelating carboxylate groups and two pyridyl nitrogens (Figure 4.6a); surprisingly, however, the simplified connectivity of the compound appears to be based upon square nodes (Figure 4.6b). Visual inspection of the structure reveals the presence of both 4-membered and 8-membered rings, whereas topological calculations give a vertex symbol of \(4\cdot4\cdot8_4\cdot8_4\cdot8_8\cdot8_8\) and a coordination sequence of “4, 10, 24, 44, 72, 104, 144, 188, 240, 296”. In fact, the topology behind this net, lvt, as in O’Keeffe’s terminology, has recently been described\(^{264}\) and a number of metal-organic structures (including the one to be discussed in section 4.2.2) have been found to be related to this connectivity.

6) \(\text{M}_2(\text{BDC})_2\text{L}_2\)\(^{219}\) (\(M = \text{Cu(II)}, \text{Zn(II)}, \text{or Co(II)}; \text{L} = \text{quinoline}\)).

The structure of \(\text{M}_2(\text{BDC})_2\text{L}_2\), which is the isomer D of the SBU I-BDC system, has been discussed previously in Chapter 2 (see Figure 2.5D and Figure 2.13a). However, the
unique topological attributes of this structure deserve some further comments. For instance, it should be noted that although the short vertex symbol (6^5·8) was correctly given in the original paper, the proposed long vertex symbol and coordination sequence need to be re-evaluated. A more careful and rigorous topological analysis suggests these values should be corrected as \(6_2\cdot6_2\cdot6_2\cdot\text{1250}\cdot6_3\cdot6_3\) and “4, 12, 26, 50, 92, 138, 200, 264, 344, 426”, respectively. Notice the term 1250 in the vertex symbol and it clearly suggests it would be necessary to use a computer program in order to obtain the correct form of vertex symbol for this complicated network structure.

Another salient feature of this net is that it demonstrates another way in which square nodes can be linked to each other. To this point, this dissertation has shown a myriad of possibilities of incorporating square building blocks into MOF structures, including structure A~E (i.e., nanoballs, tetragonal sheets, Kagomé lattices, USF-1 net, and CdSO\(_4\) net; Figure 2.5), structure H1~H5 (i.e., sodalite net, PtS net, distorted Kagomé lattices, a novel 2D net, and cylindrical structure; Figure 2.14~17, 19), ladder structure (Figure 2.18), NbO net (Figure 1.6e), and lvt net (Figure 4.6). Other possibilities include MOF-112, ROH net, quartz dual net (also called “dense net”), etc., some of which are still yet to be realized in MOF structures.\(^{278}\)

4.2.2 Topological Analysis of Some 3D MOFs from the Literature

As a detail demonstration of our previous argument that discovery and recognition of novel three-periodic nets remains a nontrivial exercise, this section will highlight, from the recent literature, some selected MOF structures whose topological identities have not be appropriately recognized.
1) **Cu$_2$(scp11)$_2$**$^{279}$ (scp11 = N-(2-hydroxybenzyl)-1-aminocyclopentyl-1-carboxylate).

Cu$_2$(scp11)$_2$ is a 3D MOF based upon Cu(II) dimeric units bridged by the reduced Schiff base ligands scp11, which in turn results in tetramers of dimers (Figure 4.7a). If the nodes are chosen at the center of the tetramers, a tetrahedral 4-connected three-periodic net can be constructed (Figure 4.7b). A topological analysis on this model reveals a vertex symbol of $6\cdot6\cdot6\cdot6\cdot6\cdot6$ and a coordination sequence of “4, 12, 26, 48, 76, 110, 146, 192, 244, 302”, which match with those of the so-called lattice complex $S^\ast$ (lcs). Therefore, assignment of a hexagonal diamondoid (or Lonsdaleite) network topology to this compound, as was done in the title of the paper$^{279}$, is questionable.

Ironically, however, the authors did appropriately specify the correct vertex symbol for the structure and point out its link to the complex lattice $S^\ast$. The confusion perhaps comes from the existence of similar hexagonal cages (Figure 4.7a) that are also present in the Lonsdaleite net.

Figure 4.7 Topological analysis of Cu$_2$(scp11)$_2$: a) the crystal structure (only framework atoms are retained for the purpose of clarity); the blue cage highlights the choice of nodes. b) a schematic illustration of the net.
2) [M(L)]X\(^{280}\) (M = Cu(II), Ag(I); L = 2,3,4,5-tetra(4-pyridyl)thiophene; X = BF\(_4^{-}\), SbF\(_6^{-}\), CF\(_3\)SO\(_3^{-}\), PF\(_6^{-}\))

The 3D MOFs [M(L)]X are assembled from tetrahedral metal ions and pseudo-planar tetradentate pyridine-type ligands (Figure 4.8a). The combination of tetrahedral and square nodes results in a three-periodic binodal net (Figure 5.8b). Although both types of nodes share the same short vertex symbols, namely, 4\(^2\).8\(^4\), they nevertheless have different long vertex symbols and coordination sequences (almost identical!), and they therefore are topologically distinguishable from each other.

**Square nodes:** 4\(^4\).8\(^2\).8\(^2\).8\(^8\); 4, 10, 24, 42, 64, 92, 124, 162, 204, 252;

**Tetrahedral nodes:** 4\(^4\).8\(^7\).8\(^7\).8\(^7\); 4, 10, 24, 42, 64, 90, 124, 162, 204, 250.

Even though the authors believed they identified a new “zeolite-like” topology, it becomes quite clear, based on the above topological data, that the inherent connectivity of these MOFs is actually related to the PtS net, which is the prototypal structure for the inorganic mineral cooperite and a number of other metal-organic compounds.\(^{80}\) On the
other hand, none of the known zeolites or their related compounds appears to have shown this type of linkage presumably because of the absence of planar square building blocks in the zeolitic compounds.\textsuperscript{216}

3) \([\text{CdL}_2(\text{H}_2\text{O})_2][\text{ClO}_4]_2\)\textsuperscript{281}(L = (R)-6,6'-dichloro-2,2'-diethoxy-1,1'-binaphthyl-4,4'-bipyridine)

Self-assembly of a chiral bidentate pyridyl ligand and 6-coordinated Cd(II) centers (two \textit{cis} coordination sites are occupied by water molecules) gives rise to 3D frameworks of 3-fold interpenetration (Figure 4.9\textit{a}). The framework can be simplified as a 4-connected net based upon seesaw-shape nodes (Figure 4.9\textit{b}). Notice this net is closely related to the primitive cubic net in that removing two \textit{cis} edges from each node of the

![Figure 4.9](image-url).

latter in an appropriate way will lead to the former. The cis configuration of the metal centers and thus the unique seesaw shape of the vertices have made the authors conclude that “this network topology is different from those of known 4-connected nets enumerated by Wells.” However, our topological calculations suggest that this net is actually a distorted version of the commonly observed quartz net, as confirmed by its vertex symbol (6•6•6•6•8•8•8) and coordination sequence (“4, 12, 30, 52, 80, 116, 156, 204, 258, 318, 1231”).

Nevertheless, this structure is of significance from both topological and materials perspectives (in the context of designing homochiral MOFs) and it raises some interesting questions, such as: a) are other types of 4-connected nets (especially those chiral ones) possible to be generated from seesaw-shape nodes? b) is there any correlation between the handedness of the ligands and that of the resulting chiral MOFs? Specifically, in the present structure, is the handedness of the quartz net (-Q as shown by the reported crystal structure) dictated by the enantiomorphism of the ligand (R)-L? Clearly a systematic study focused on both structures and chirality of a series of homochiral MOFs is necessary to answer these questions.

4) \( \text{Cu}_2(C_{2h}-\text{TCPPDA})(\text{H}_2\text{O})_2 \) (TCPPDA = N,N,N',N'-tetrakis(4-carboxyphenyl)-1,4-phenylenediamine).

TCPPDA is a flexible tetracarboxylate ligand that can adopt either \( C_{2h} \) (rectangular) symmetry or \( D_2 \) (pseudo-tetrahedral) symmetry in the solid state. A 3D MOF results from the linking of the rectangular \( C_{2h}-\text{TCPPDA} \) and the square SBU I (Figure 4.10a). The framework appears as a square-based 4-connected net as a result of the planar geometries
of both organic ligands and metal clusters (Figure 4.10b). Contrary to the conclusion reached by the authors in the original paper, however, the presence of 4-membered rings unambiguously eliminates the possibility of a NbO topology for this structure, since NbO net contains 6-membered and 8-membered rings only. Indeed, our topological analysis suggests that the connectivity of the net corresponds to that of a lvt net (see Figure 4.6b for a comparison).

Finally, as a summary and a convenient future reference, topological data of some important 4-connected nets, including those discussed above, are described below in Table 4.2.
Table 4.2 Some important 4-connected nets.

<table>
<thead>
<tr>
<th>Net</th>
<th>O’Keeffe Symbol</th>
<th>Space Group</th>
<th>Short Symbol</th>
<th>Long Vertex Symbol</th>
<th>Coordination Sequence</th>
</tr>
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<tbody>
<tr>
<td>Diamond</td>
<td>dia</td>
<td>Fd-3m</td>
<td>6(^7)</td>
<td>6(^4)*6(^6)*6(^6)*6(^6)*6(^6)</td>
<td>4, 12, 24, 42, 64, 92, 124, 162, 204, 252</td>
</tr>
<tr>
<td>Lonsdaleite</td>
<td>lon</td>
<td>P6(_3)/mmc</td>
<td>6(^9)</td>
<td>6(^6)*6(^6)*6(^6)*6(^6)*6(^6)</td>
<td>4, 12, 25, 44, 67, 96, 130, 170, 214, 264</td>
</tr>
<tr>
<td>Quartz</td>
<td>qtz</td>
<td>P(_6)22</td>
<td>6(^8)*9</td>
<td>6(^6)*6(^2)*8(^2)*8(_2)*8(_2)</td>
<td>4, 12, 30, 52, 80, 116, 156, 204, 258, 318</td>
</tr>
<tr>
<td>Sodalite</td>
<td>sod</td>
<td>Im-3m</td>
<td>4(^6)*9</td>
<td>4(^4)*6(^6)*6(^6)</td>
<td>4, 10, 20, 34, 52, 74, 100, 130, 164, 202</td>
</tr>
<tr>
<td>RHOs</td>
<td>rho</td>
<td>Im-3m</td>
<td>4(^6)*9(_2)</td>
<td>4(^4)*4(^6)*8(_2)</td>
<td>4, 9, 17, 28, 42, 60, 81, 105, 132, 162</td>
</tr>
<tr>
<td>SrAl(_2)</td>
<td>sra</td>
<td>Imma</td>
<td>4(^6)*8</td>
<td>4(^6)*6(^6)*6(_2)</td>
<td>4, 10, 21, 36, 54, 78, 106, 136, 173, 214</td>
</tr>
<tr>
<td>CrB(_4)</td>
<td>crb</td>
<td>I(_4)/mmm</td>
<td>4(^6)*9</td>
<td>4(^6)*6(^6)*6(_2)</td>
<td>4, 11, 24, 41, 62, 90, 122, 157, 200, 247</td>
</tr>
<tr>
<td>Gismondine</td>
<td>gis</td>
<td>I(_4)/amd</td>
<td>4(^8)*9</td>
<td>4(^4)*4(^8)*8(_2)*8(_2)</td>
<td>4, 9, 18, 32, 48, 67, 92, 120, 150, 185</td>
</tr>
<tr>
<td>Lattice complexes S(^_)</td>
<td>lcs</td>
<td>Ia-3d</td>
<td>6(^5)</td>
<td>6(^6)*6(_2)*6(_2)*6(_2)*6(_2)</td>
<td>4, 12, 26, 48, 76, 110, 146, 192, 244, 302</td>
</tr>
<tr>
<td>Zn(BDC) (bpta)</td>
<td>dmp</td>
<td>P(_4)/mmm</td>
<td>6(^8)</td>
<td>6(^6)*6(_2)*6(_2)*8(_2)</td>
<td>4, 12, 30, 62, 98, 144, 198, 262, 332, 412</td>
</tr>
<tr>
<td>Lattice complexes V(^_)</td>
<td>lcv</td>
<td>I(_4)/32</td>
<td>3(^*)_10(^4)</td>
<td>3(^3)*10(_1)*10(_1)*10(_1)*10(_1)</td>
<td>4, 8, 16, 32, 54, 70, 102, 128, 158, 212</td>
</tr>
<tr>
<td>NbO</td>
<td>nbo</td>
<td>Im-3m</td>
<td>4(^8)*9</td>
<td>6(^6)*6(_2)*6(_2)*8(_2)</td>
<td>4, 12, 28, 50, 76, 110, 148, 194, 244, 302</td>
</tr>
<tr>
<td>CdSO(_4)</td>
<td>cds</td>
<td>P(_4)/mmc</td>
<td>6(^8)</td>
<td>6(^6)*6(_2)*6(_2)*8(_2)</td>
<td>4, 12, 30, 58, 94, 138, 190, 250, 318, 394</td>
</tr>
<tr>
<td>Lattice complex V(^_)</td>
<td>lvt</td>
<td>I(_4)/amd</td>
<td>4(^8)_9</td>
<td>4(^4)*4(^8)_4(^8)_4(^8)_4(^8)</td>
<td>4, 10, 24, 44, 72, 104, 144, 188, 240, 296</td>
</tr>
<tr>
<td>USF-1</td>
<td>usf</td>
<td>R-3c</td>
<td>6(^8)</td>
<td>6(_6)*6(_6)*12(_6)*6(_3)</td>
<td>4, 12, 26, 50, 92, 138, 200, 264, 344, 426</td>
</tr>
<tr>
<td>Quartz dual</td>
<td>qzd</td>
<td>P(_6)22</td>
<td>7(^*)_9</td>
<td>7(_6)*7(_7)*7(_7)*7(_7)</td>
<td>4, 12, 36, 72, 122, 188, 264, 354, 456, 570</td>
</tr>
<tr>
<td>MOF-112</td>
<td>mot</td>
<td>P(_4)/mmm</td>
<td>6(_9)</td>
<td>6(_6)*6(_6)*6(_2)</td>
<td>4, 12, 30, 58, 78, 110, 150, 194, 246, 302</td>
</tr>
<tr>
<td>PtS</td>
<td>pts</td>
<td>P(_4)/mmc</td>
<td>4(_9)*8(_9)</td>
<td>4(_4)*4(_8)_4(_8)_4(_8)_4(_8)</td>
<td>4, 10, 24, 42, 64, 92, 124, 162, 204, 252</td>
</tr>
<tr>
<td>Twisted PtS</td>
<td>ptt</td>
<td>C(_c)cm</td>
<td>4(_6)*8(_9)</td>
<td>4(_6)*6(_6)*8(_8)_8(_8)</td>
<td>4, 11, 27, 48, 77, 111, 154, 200, 252, 311</td>
</tr>
<tr>
<td>Moganite</td>
<td>mog</td>
<td>C(_m)mm</td>
<td>4(_6)*8(_9)</td>
<td>4(_4)*6(_6)*8(_8)_8(_8)_8(_8)</td>
<td>4, 10, 24, 40, 64, 90, 120, 160, 200, 244</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4(_6)*8(_8)</td>
<td>4(_8)_6(_6)*6(_6)</td>
<td>4, 11, 24, 41, 62, 90, 122, 157, 200, 247</td>
</tr>
</tbody>
</table>
4.3 Ternary Nets.

The discussions in the previous sections of this Chapter are primarily focused upon understanding metal-organic framework structures, especially those with more complicated linkages. This has been done mainly from the node-and-spacer perspective, which simplifies molecular building blocks as mathematical points and lines. The advantage of this strategy can be illustrated by the easiness of generating simplified structural models and the convenience of comparing related structures that might seemingly look different. However, such simplification processes typically lead to loss of detail geometrical information on the molecular building blocks that originally sustain the frameworks, while such information might be critically important from a design perspective. Therefore, an alternative approach that takes into account the shape of molecules is desirable. In this regard, we have recently explored the so-called VLPP strategy, which interprets and represents metal-organic nets as being sustained by vertex-linked polygons or polyhedra.\textsuperscript{75-78} It occurs to us that the VLPP approach can be particularly effective and of advantage in cases where multiple polygonal building units are linked to each other.

4.3.1 Unitary and Binary Nets.

From the VLPP point of view, unitary nets are those composed of only one type of polygonal or polyhedral building blocks and they can be exemplified by (10, 3)-a net, diamond net, NbO net, and primitive cubic net, which are based upon triangles, squares, tetrahedra, and octahedra, respectively (Figure 1.6). It is worth noting that even this class
of nets exhibit remarkable structural diversity as both the shape of polygons or polyhedra and the angle subtended by them have a critical influence on the resulting architectures.

The VLPP approach comes into its own for binary nets, that is, nets sustained by pairs of polygonal or polyhedral molecular building blocks. In principle, binary nets (and ternary nets, which will be discussed below) can be divided into two classes: those in which the same type of polygons or polyhedra do not share vertices (class I) and those in which they do (class II). We will, however, mainly focus upon class I type binary (and ternary) nets in this section.

It is perhaps not difficult to envision the multiple possible combinations from which binary nets can be constructed. The above mentioned triangular, square, tetrahedral and octahedral building blocks, for example, can be cross-linked in a wide variety of manners in such a way that all of the following combinations are applicable: triangle-square, triangle-tetrahedron, triangle-octahedron, square-tetrahedron, square-octahedron, and tetrahedron-octahedron. As a result of such diversity, a large number of possible nets can readily form (Table 4.3). Some important binary nets resulting from these combinations are schematically shown in Figure 4.11. These binary nets are of particular interest from both design and synthetic perspectives since triangular, square, tetrahedral, and octahedral shapes are commonly seen and readily available in molecular chemistry. Indeed, a number of interesting MOFs that have been reported are based upon these prototypical architectures.66, 77, 141, 188, 282-290 A discussion on more binary nets and their occurrences can be found in a recent account.268
Figure 4.11 Some important binary nets shown in VLPP format:  

- **a)** Pt$_3$O$_4$ net (triangle-square);  
- **b)** twisted boracite net (triangle-square);  
- **c)** boracite net (triangle-tetrahedron);  
- **d)** cubic C$_3$N$_4$ net (triangle-tetrahedron);  
- **e)** pyrite net (triangle-octahedron);  
- **f)** rutile net (triangle-octahedron);  
- **g)** PtS net (square-tetrahedron);  
- **h)** soc net (square-octahedron);  
- **i)** corundum net (tetrahedron-octahedron).  

Color code: red-triangles; green-squares; yellow-tetrahedra; teal-octahedra.
Table 4.3 Some important binary nets from the combination of triangles, squares, tetrahedra or octahedra.

<table>
<thead>
<tr>
<th>Connectedness</th>
<th>Combination</th>
<th>Resulting Net</th>
<th>O’Keeffe Symbol</th>
<th>Representative Examples in MOFs</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,4</td>
<td>triangle-square</td>
<td>Pt$_3$O$_4$ net</td>
<td>pto</td>
<td>[282]</td>
</tr>
<tr>
<td>3,4</td>
<td>triangle-tetrahedron</td>
<td>Boracite net</td>
<td>bor</td>
<td>[66, 77, 188]</td>
</tr>
<tr>
<td>3,6</td>
<td>triangle-octahedron</td>
<td>Pyrite net</td>
<td>pyr</td>
<td>[283]</td>
</tr>
<tr>
<td>4,4</td>
<td>square-tetrahedron</td>
<td>PtS net</td>
<td>pts</td>
<td>[284]</td>
</tr>
<tr>
<td>4,6</td>
<td>square-octahedron</td>
<td>Co$_3$[Re$_6$Se$_8$(CN)$_6$]$_2$ net</td>
<td>soc</td>
<td>[285]</td>
</tr>
<tr>
<td>4,6</td>
<td>tetrahedron-octahedron</td>
<td>Corundum net</td>
<td>cor</td>
<td>[286, 287]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.3.2 Ternary Nets.

That binary nets can be realized from a wide array of building blocks and their appropriate combinations illustrates how VLPP approach can be applied in the design of modular MOF compounds using two types of molecular shapes. We will demonstrate below that VLPP approach can in fact be extended to ternary nets, that is, those sustained by a combination of three polygons or polyhedra. Most significantly, we have found hierarchical assembly of molecular building blocks leads to some novel MOFs with unprecedented topologies and, at the very least, a higher degree of modularity and fine-tunability toward the structures.

Compound 13, $\{[\text{Zn}_6(\text{btc})_4(\text{isoquinoline})_4(\text{MeOH})](\text{H}_2\text{O})(\text{benzene})_2\}_n$ (USF-3; btc=1,3,5-benzenetricarboxylate), was isolated as colorless crystalline products from a methanolic solution of Zn(NO$_3$)$_2$·6H$_2$O, H$_2$btc, isoquinoline and benzene. The structure of USF-3 was determined by X-ray single-crystal diffraction and it is depicted in Figure 4.12. There are two different Zn(II) chromophores present in USF-3: square paddle-wheel SBU I, and pseudo-tetrahedral dizinctetracarboxylates SBU III (see Figure 2.2), in a 2:1 ratio. SBU III is far less common than the intensively studied SBU I and is
comprised of a binuclear Zn(II) unit, two bridging carboxylates, one bridging oxygen and two chelating carboxylates. Methanol and/or isoquinoline serve as axial ligands in this chromophore. The Zn-Zn distance in SBU I is ca. 2.995Å, which is within the expected range for Zn(II) paddle-wheel SBUs, whereas this distance is significantly larger in SBU III (ca. 3.707Å). Overall, the Zn-O distances are in the range of 1.985(5)─2.295(5)Å (average: 2.082Å) and the Zn-N distances are in the range of 2.003(7)─2.104(3)Å (average: 2.063Å).

Figure 4.12 Crystal structures of USF-3: a) the 3D framework in a stick representation (isoquinoline, benzene and water are deleted for clarity); b) a schematic representation of the structure; c) type I cage; d) type II cage. The cavities are shown in stick mode while the guests (benzene) in CPK mode. Both isoquinoline and benzene are crystallographically disordered. Color scheme: C, grey; H, gold; O, red; N, blue; Zn, green.
Ideally, the combination of btc\(^{3-}\), SBU I and SBU III would generate a net structure with large open channels; however, no such channels are observed in USF-3 because isoquinoline, a bulky molecule, is protruding and blocking the possible channels. As a result, there are two different types of cavities within which disordered benzene molecules are trapped (Figure 4.12c, d). One water molecule per asymmetric unit is also present, which engages in hydrogen bonding with the bridging methanol molecules. Thermal gravimetric analysis (TGA) and X-ray powder diffraction data suggest that USF-3 is stable up to at least 130°C whereas further heating above 180°C leads to collapse of the framework (see Experimental section).

Figure 4.13 Crystal structures of USF-4: a) the 3D framework in a stick representation (isoquinoline, chlorobenzene and methanol are deleted for clarity); b) a schematic representation of the structure; c) the cavity shown in stick mode with the guests (chlorobenzene) in CPK mode. Color scheme: C-grey; H-gold; O-red; N-blue; Zn-green, Cl- turquoise.
Colorless crystalline materials of compound 14, \([\text{Zn}_6(\text{btc})_4(\text{isoquinoline})_4(\text{MeOH})_2](\text{MeOH})_8(\text{chlorobenzene})]_n\) (USF-4), were synthesized by laying a methanolic solution of \(\text{H}_2\text{btc}\) and isoquinoline onto a methanolic solution of \(\text{Zn(NO}_3)_2\cdot6\text{H}_2\text{O}\) and chlorobenzene. As revealed by the single-crystal X-ray diffraction experiment, USF-4 also has two Zn(II) chromophores: a mixture of SBU I and a different pseudo-tetrahedral SBU IV (see Figure 2.2); contrary to USF-3, however, the ratio of SBU I: SBU IV in USF-4 is 1:2 (Figure 4.13a). SBU IV features a binuclear Zn(II) unit, three bridging carboxylates and one monodentate carboxylate. The Zn-Zn distance of SBU I in USF-4 is ca. 2.999Å, comparable to the corresponding value in USF-3; the Zn-Zn distance of SBU IV, on the other hand, is ca. 3.338Å and therefore shorter than that of SBU III in USF-3. Other distances, including Zn-O (average: 2.005Å) and Zn-N (average: 2.030 Å) distances are well within the reasonable ranges.

Similarly to USF-3, USF-4 also has cavities but open channels are precluded by the presence of coordinated isoquinoline molecules (Figure 4.13c); however, as calculated using the program Platon,\(^{291}\) USF-4 possesses a higher free volume than USF-3, 32.2% vs. 19.3%, which hosts methanol and disordered chlorobenzene molecules.

In order to facilitate the understanding of the structures of USF-3 and USF-4, the VLPP approach is employed. Indeed, both compounds can be represented as being sustained by vertex linkage of molecular triangles, squares and tetrahedra in which triangles are exclusively linked to squares or tetrahedra and vice versa (Figure 4.14). The stoichiometry of these three types of building blocks is 4:2:1 for USF-3 and 4:1:2 for USF-4, respectively, therefore retaining the 4:3 ratios for sustaining class I type (3, 4)-connected nets.
Topological analysis indicates that USF-3 and USF-4 are based upon unique connectivity and they represent two examples of hitherto undocumented (3, 4)-connected nets. The long vertex symbols for USF-3 and USF-4 are 

Figure 4.14 VLPP representations of USF-3 and USF-4: a) the structural moieties in USF-3; b) the structural moieties of USF-4; c) VLPP representation of USF-3; d) VLPP representation of USF-4. Color scheme: triangle-red, square-green; tetrahedron-yellow.
(6•6•6)₄(6•6•8•2•8•2•12₂•12₂)₂(6•6•6•8•8•8•8) and (4•6•8•3(6•6•8•2)₂
(6•6•8•8•10•₂•8•8•10•₂)₄, respectively. Therefore, USF-3 can be regarded as an
“intermediate” structure between boracite net (triangle-tetrahedron) and twisted boracite
net (triangle-square), as implied by their vertex symbols and coordination sequences (see
Table 4.4 below). USF-4 represents a more complicated and less symmetric (3, 4)-
connected net.

Table 4.4 Some important (3, 4)-connected nets.

<table>
<thead>
<tr>
<th>Net</th>
<th>Building Blocks</th>
<th>Ratio of Building Blocks</th>
<th>Vertex Symbol</th>
<th>Coordination Sequence</th>
<th>Td₁₈</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt₃O₄</td>
<td>triangles</td>
<td>4</td>
<td>8•S•8•S•5</td>
<td>3, 9, 18, 39, 51, 98, 99, 167, 162, 267</td>
<td>913</td>
</tr>
<tr>
<td></td>
<td>squares</td>
<td>3</td>
<td>8•S•8•S•8•S•8•S•8•4</td>
<td>4, 8, 24, 34, 68, 74, 132, 130, 216, 202</td>
<td>892</td>
</tr>
<tr>
<td>Twisted</td>
<td>triangles</td>
<td>4</td>
<td>6•6•6</td>
<td>3, 9, 15, 33, 45, 82, 90, 153, 150, 241</td>
<td>821</td>
</tr>
<tr>
<td>Boracite</td>
<td>squares</td>
<td>3</td>
<td>6•₂•6•S•8•S•S•12₂•12₂</td>
<td>4, 8, 20, 30, 60, 68, 120, 126, 200, 180</td>
<td>816</td>
</tr>
<tr>
<td>Boracite</td>
<td>triangles</td>
<td>4</td>
<td>6•6•6</td>
<td>3, 9, 15, 33, 45, 84, 90, 152, 150, 240</td>
<td>821</td>
</tr>
<tr>
<td></td>
<td>tetrahedra</td>
<td>3</td>
<td>6•₂•6•S•8•8•8•8</td>
<td>4, 8, 20, 30, 60, 68, 120, 126, 200, 180</td>
<td>816</td>
</tr>
<tr>
<td>Cubic C₃N₄</td>
<td>triangles</td>
<td>4</td>
<td>8•S•8•S•5</td>
<td>3, 9, 18, 41, 48, 92, 96, 167, 162, 269</td>
<td>905</td>
</tr>
<tr>
<td></td>
<td>tetrahedra</td>
<td>3</td>
<td>8•S•8•S•8•S•8•8•4</td>
<td>4, 8, 24, 32, 64, 70, 128, 128, 216, 204</td>
<td>878</td>
</tr>
<tr>
<td>USF-3</td>
<td>triangles</td>
<td>4</td>
<td>6•6•6</td>
<td>3, 9, 15, 33, 45, 84, 90, 152, 150, 238</td>
<td>819</td>
</tr>
<tr>
<td></td>
<td>squares</td>
<td>2</td>
<td>6•₂•6•S•8•S•S•12₂•12₂</td>
<td>4, 8, 20, 30, 60, 68, 120, 126, 200, 180</td>
<td>816</td>
</tr>
<tr>
<td></td>
<td>tetrahedra</td>
<td>1</td>
<td>6•₂•6•S•8•8•8•8</td>
<td>4, 8, 20, 30, 60, 68, 120, 126, 200, 180</td>
<td>816</td>
</tr>
<tr>
<td>USF-4</td>
<td>triangles I</td>
<td>2</td>
<td>4•6•8</td>
<td>3, 8, 14, 34, 41, 77, 81, 137, 139, 227</td>
<td>761</td>
</tr>
<tr>
<td></td>
<td>triangles II</td>
<td>2</td>
<td>6•6•6•8</td>
<td>3, 9, 14, 32, 41, 75, 80, 141, 140, 227</td>
<td>762</td>
</tr>
<tr>
<td></td>
<td>squares</td>
<td>1</td>
<td>6•6•6•S•8•10ols•*</td>
<td>4, 8, 20, 26, 52, 64, 112, 104, 180, 182</td>
<td>752</td>
</tr>
<tr>
<td></td>
<td>tetrahedra</td>
<td>2</td>
<td>4•6•6•6•8•8•10₄</td>
<td>4, 7, 18, 28, 56, 57, 85, 116, 189, 167</td>
<td>747</td>
</tr>
<tr>
<td>USF-5</td>
<td>triangles</td>
<td>4</td>
<td>4•6•8•5</td>
<td>3, 8, 13, 31, 42, 80, 85, 152, 151, 248</td>
<td>813</td>
</tr>
<tr>
<td></td>
<td>squares</td>
<td>1</td>
<td>8•8•8•S•8•S•12₈•12₈</td>
<td>4, 8, 20, 22, 52, 74, 128, 106, 188, 214</td>
<td>816</td>
</tr>
<tr>
<td></td>
<td>tetrahedra</td>
<td>2</td>
<td>4•4•6•8•8•12₁₃</td>
<td>4, 6, 16, 27, 58, 57, 106, 130, 208, 164</td>
<td>776</td>
</tr>
</tbody>
</table>
Interestingly, an alternative interpretation of USF-3, in which only the paddle-wheel SBUs I are represented in VLPP format and btc$^{3-}$ and SBUs III are simply treated as spacers, reveals its close relationship to the tetragonal sheets B discussed in Chapter 2 and 3. Indeed, USF-3 is related to B in that cross-linking of tetragonal sheet layers by SBU III gives rise to USF-3 (Figure 4.15).

Figure 4.15 An alternative interpretation of USF-3 reveals its close relationship to the tetragonal sheets B: a perspective view (left) and a side view (right). SBUs I are shown as squares in VLPP format while SBUs III are shown in ball-and-stick manner.

That USF-3 and USF-4 might have general implications in the context of designing new MOFs can be justified by the following considerations.
1) Although it is established that knowledge of molecular symmetry facilitates the design and synthesis of nets in a systematic manner, until recently this has been limited to unitary or binary nets. USF-3 and USF-4 suggest that the use of three or perhaps even more SBUs could represent a facile approach to the construction of VLPP nets with unprecedented topologies.

In this context, a new Zn(II)-based ternary net, which is closely related to USF-3 and USF-4, has been reported most recently (for convenience, we will call this net “JLU” hereafter). JLU is similarly assembled from the triangular ligand btc$^3^-$, square SBU I, and a new tetrahedral SBU (Figure 4.16a). As in USF-4, the relative ratio between squares and tetrahedra in JLU is also 1:2. Surprisingly, however, the connectivity of JLU turns out to be distinct from either USF-3 or USF-4 (see Table 4.4), and it thus represents another unprecedented (3, 4)-connected net.

![Figure 4.16 Schematic illustrations of the ternary net JLU: a) tetrahedral SBU; b) VLPP representation of JLU.](image)

2) The recent discovery of porous metal-organic structures that are capable of guest induced shape-responsive fitting represent a class of materials that resemble the degree of induced fit behavior of bioenzymes such as metalloproteins. That the formation of
USF-3 and USF-4 is so profoundly dependent upon the presence of guest/template illuminates a possible mechanism for translating structural information from an external medium into the formation of a novel framework.

3) It must be noted that the existence of USF-3, USF-4 and JLU is at least partly a reflection of the tendency for Zn(II) to exhibit multiple coordination geometries and the one-pot reaction employed in their synthesis is unlikely to be successful for other metals. In our opinion, as the number of SBUs increases, synthetic strategies will likely have to focus upon either preformed SBUs (rather than those generated in situ) or organic building blocks that inherently favor the generation of multiple inorganic SBUs. This later approach has recently been used to construct a new ternary net, USF-5, whose connectivity represents yet another unique topology (Figure 4.17; Table 4.4).

Figure 4.17 Schematic illustrations of USF-5: a) molecular building blocks in USF-1; triangle: 5-aminoisophthalate; square: Cu(II) based SBU I; tetrahedron: mono-Cu(II) center; b) USF-5 represented in VLPP format.
4.4 Summary

This Chapter is focused upon the discussions of the following topics:

1) **Three-periodic nets** in the context of metal-organic frameworks. Since a large number of 3D MOFs are based upon 3-connected, 4-connected, or (3, 4)-connected nets, topological data on some of these common nets are given.

2) **Discovery and recognition of novel three-periodic nets remains a nontrivial exercise.** In particular, topologies of some important MOFs in the literature are not properly recognized or identified; therefore, a correct version of analysis on these structures is given.

3) **The approach of “vertex-linked polygons and polyhedra” (VLPP)** turns out to be extraordinarily efficient in revealing the fundamental geometrical features of some complicated MOF structures.

4) **Ternary nets**, which are sustained by three types of polygons or polyhedra, illustrate how appropriate combinations of vertex-linked polygons or polyhedra afford novel topologies that could be prototypal of an even wider range of organic and metal-organic compounds.

4.5 Experimental

4.5.1 Syntheses

The materials in the synthesis were used as received from reliable commercial sources (Sigma-Aldrich or Fischer Scientific); solvent methanol was purified and dried according to standard methods.
Synthesis of USF-3 (13), \{[\text{Zn}_{6}(\text{btc})_4(\text{isoquinoline})_6(\text{MeOH})](\text{H}_2\text{O})(\text{benzene})_2\}_n

A solution of 1,3,5-benzenetricarboxylic acid (140 mg, 0.667 mmol) and isoquinoline (0.350 mL, 3.00 mmol) in methanol (20 mL) was heated gently for ca. 10 min and then carefully layered onto a solution of Zn(NO$_3$)$_2$•6H$_2$O (297 mg, 1.00 mmol) in methanol/benzene (2:1, 20mL). Colorless single crystals formed within 12h under ambient conditions (217 mg, 59.6% yield).

Synthesis of USF-4 (14), \{[\text{Zn}_{6}(\text{btc})_4(\text{isoquinoline})_4(\text{MeOH})_2](\text{MeOH})_8(\text{chlorobenzene})\}_n

A solution of 1,3,5-benzenetricarboxylic acid (70 mg, 0.33 mmol) and isoquinoline (0.177 mL, 1.50 mmol) in methanol (20 mL) was carefully layered onto a solution of Zn(NO$_3$)$_2$•6H$_2$O (149 mg, 0.500 mmol) in methanol/chlorobenzene (2:1, 20mL). Colorless single crystals formed within 12h under ambient conditions (56 mg, 30.9% yield).

4.5.2 Characterizations

Crystal Structure Determination

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 Moka radiation (\(\lambda = 0.7107 \text{ Å}\)). The data were corrected for Lorentz and polarization effects and for absorption using the SADABS program. The structures were solved using direct methods and refined by full-matrix least-squares on |F$^2|$. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions and refined with temperature factors 1.2
times those of their bonded atoms. All crystallographic calculations were conducted with
the SHELXTL 5.1 program package.

Table 4.5 Crystal data and structure refinement for USF-3.

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Table 4.6 Crystal data and structure refinement for USF-4.

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</table>

**Other Characterizations**

Thermogravimetric analysis was performed under nitrogen on TA Instruments TGA 2950 Hi-Res. XRPD data were recorded on a Rigaku RU15 diffractometer at 30kV, 15mA for CuKα (λ = 1.5418 Å), with a scan speed of 1°/min and a step size of 0.05° in 20
at room temperature. Infrared spectra were recorded on a Nicolet Avatar 320 FT-IR spectrometer. Samples of USF-3 and USF-4 were prepared at room temperature (25°C) without heating, or further heated for 5h under vacuum at 80, 130, or 180°C, respectively, before cooling back to room temperature for XRPD and FT-IR experiments.

Figure 4.18  TGA trace of USF-3
Figure 4.19  TGA trace of USF-4

Figure 4.20  X-ray powder diffraction patterns of USF-3 sample prepared at 25°C and those further heated at 80, 130 and 180°C.
Figure 4.21 X-ray powder diffraction patterns of USF-4 sample prepared at 25°C and those further heated at 80, 130 and 180°C.

Figure 4.22 FT-IR spectra of USF-3 sample prepared at 25°C and those further heated at 80, 130 and 180°C.
Figure 4.23 FT-IR spectra of USF-4 sample prepared at 25°C and those further heated at 80, 130 and 180°C.
Chapter 5
Metal-Organic Frameworks Based upon Imide-Type Carboxylato Ligands

5.1 Introduction

The concept of scale chemistry\textsuperscript{294-296} is perhaps not unfamiliar in the context of metal-organic frameworks, especially if one considers the early examples of diamondoid MOFs were typically based upon the idea of replacing short C-C covalent bonds with much longer metal-ligand linkages.\textsuperscript{53, 297} Replacement of single metal ions with SBUs, as has been demonstrated in the previous Chapters, represents another strategy toward scaled-up MOFs (SUMOFs). Indeed, these two approaches have now been further exploited in the search of new generations of porous MOFs with giant pores and extremely high surface areas. For instance, Yaghi and coworkers recently use the concept of isoreticular synthesis to generate a series of porous MOFs, of which the highest percent free volume obtained is up to 91.1\%.\textsuperscript{132} Férey and coworkers, on the other hand, take advantage of the formation of super-cages using simple building blocks to create MOF structures with giant pore sizes.\textsuperscript{119, 223} These results have undoubtedly shown the remarkable merits of both approaches; however, the limitations of these studies are perhaps also obvious. For example, while Férey’s materials are typically polycrystalline and their discovery thus largely relies upon computational models that might not be easily available in other systems, Yaghi’s isoreticular MOFs have thus far been limited to the octahedral $\text{Zn}_4\text{O(COO)}_4$ SBUs and the adoption of long organic linkers in his case seems to require multiple-step and time-consuming organic synthetic procedures.
The previous few Chapters of this dissertation have delineated a general design blueprint for the construction of functional MOF materials using the molecular building block approach. In particular, the assembly of angular ligand BDC and square SBUs I gives rise to a number of supramolecular isomeric structures, including nanoballs A, tetragonal sheets B, and Kagomé lattices C, which have shown interesting properties, such as porosity and magnetism. We therefore envision these prototypical structures as ideal candidates for the design of SUMOFs. Specifically, expanded nanoballs, tetragonal sheets, and Kagomés, decorated nanoballs, and pillared Kagomés (Figure 5.1) will be of interest because of their unique architectures and increased dimensions. From a design

Figure 5.1 Schematic representations of prototypical scaled-up MOFs: a) expanded nanoball; b) decorated nanoball; c) expanded tetragonal sheet; d) expanded Kagomé; e) pillared Kagomé.
perspective, a feasible approach to achieve these SUMOFs is to use elongated analogues of the ligand BDC, BDC derivatives substituted with plate-like moiety, and BDC-based tetracarboxylates, respectively. Along this line, we have initiated a systematic study on the design of new ligands using simple organic condensation reactions.

5.2 Design of Ligands using Imide Reactions

5.2.1 Imide-Type Ligands from Solution Synthesis

Imides are organic compounds that contain the moiety of \( \text{O} - \text{C} - \text{R} - \text{O} \) (R = H or other functional group). They have been widely studied as fluorescence sensors,\(^{298-300}\) and antitumor agents,\(^{301}\) and polyimides are an important class of polymers in industrial.\(^{302}\) Imides are routinely formed via solution methods, typically involving

![Figure 5.2 Selected carboxylic anhydrides (AHs) and primary amines (AMs) for the design of imide-type ligands.](image-url)

Figure 5.2 Selected carboxylic anhydrides (AHs) and primary amines (AMs) for the design of imide-type ligands.
dimethylformamide, from a dicarboxylic acid or its anhydride and a primary amine. Figure 5.2 lists some selected carboxylic anhydrides and primary amines that are relevant in the design of new ligands. We consider imide reactions as particularly suitable for our study for a number of reasons: 1) most anhydrides and amines are inexpensive and readily available in large quantities; 2) the reactions are facile (usually one step) and high yield and the products are easy to be isolated and purified since the by-product is water; 3) the reactions are highly modular in that both anhydrides and amines are subject to change without significantly affecting the reactions, thereby affording the possibility of generating a series of new ligands in a systematic manner.

Thus far, we have synthesized the following eight different new ligands: \( \text{N-(3, 5-dicarboxylphenyl)-1, 8-naphthalimide (L1a)} \), \( \text{N-(3, 5-dicarboxylphenyl)-3-nitro-1, 8-naphthalimide (L1b)} \), \( \text{N-(3, 5-dicarboxylphenyl)-4-sulfo-1, 8-naphthalimide, potassium salt (L1c)} \), \( \text{N, N'-di(3-caboxylphenyl)-1,4,5,8-naphthalenetetracarboxylic diimde (L2a)} \), \( \text{L2b} \), \( \text{L3a} \), \( \text{L3b} \), \( \text{L4} \).

![Figure 5.3 The pre-designed ligands for scaled-up MOFs.](image-url)
$N'$-di(3-carboxyphenyl)-1,2,4,5-benzenetetracarboxylic diimde ($L_2b$), $N'$-di(3, 5-dicarboxyphenyl)-1,4,5,8-naphthalenetetracarboxylic diimde ($L_3a$), $N'$-di(3, 5-dicarboxyphenyl)-1,2,4,5-benzenetetracarboxylic diimde ($L_3b$), and 1,3-bis(N-trimellitoyl)benzene ($L_4$). Typical synthetic procedures to generate these ligands involve heating a DMF solution of the appropriate anhydrides and primary amines at 100°C for 24~48 hours. Spectroscopic methods such as Fourier Transform Infrared (FT-IR) turn out to be particularly convenient in characterizing the products since the carbonyl peaks in the imides are significantly red-shifted as compared to those in the parent anhydrides (see section 5.2.2). Other techniques, such as mass spectrometry, nuclear magnetic resonance (NMR) spectroscopy, and X-ray diffraction are also helpful in assisting the characterizations of these new ligands. In particular, the structure of a pyridine solvate of $L_2a$ has been revealed by single-crystal X-ray diffraction study, which unambiguously confirms the formation of the desired product (Figure 5.4). It should be noted although

![Figure 5.4 Crystal structure of a pyridine solvate of $L_2a$.](image)

the molecules of $L_2a$ exist in a trans configuration in the crystal structure of this solvate, it is reasonable to expect a cis configuration under appropriate conditions because of the flexible nature of the molecule.
With these pre-designed ligands in hand, we are now capable of targeting the above described SUMOFs (Figure 5.1). Specifically, we anticipate ligand \textbf{L1a} and its derivatives \textbf{L1b} and \textbf{L1c} to be ideally suited for the construction of decorated nanoballs. Indeed, model building using the program Materials Studio\textsuperscript{273} indicates the geometrical plausibility of the proposed structure (Figure 5.5). Ligands \textbf{L2a}, \textbf{L2b} and perhaps \textbf{L4} would be reasonable candidates for expanded versions of nanoballs, tetragonal sheets, or Kagomé lattices, whereas ligands \textbf{L3a} and \textbf{L3b} might be important in directing the assembly of pillared Kagomés\textsuperscript{173, 201}. It should be pointed out that new types of SUMOFs are also potentially possible from these nano-sized ligands when combined with various other SBUs.
5.2.2 Imide-Type Ligands from Solid State Synthesis

In the course of our systematic study on ligand design, we surprisingly found some of the imide reactions can be carried out even under solventless conditions. For example, the anhydride \( \text{AH6} \) has been shown to undergo a solid state reaction with the primary amine \( \text{AM1} \), giving rise to ligand \( \text{L2a} \), as indicated by both XPD patterns and IR spectra (Figure 5.6). Typical experimental protocols in the initial attempts of solid state reactions involve dry grinding of stoichiometric amounts of \( \text{AH6} \) and \( \text{AM1} \) and subsequent heating of the grinding mixtures for a few hours.

![Figure 5.6 XPD patterns (left) and FT-IR spectra (right) show the reaction between \( \text{AH6} \) and \( \text{AM1} \) undergoes in solid state.](image)

However, as suggested by the XPD, and to a less extent, FT-IR results, the dry-grinding mixtures are only partially converted to the product \( \text{L2a} \) upon heating in solid state, leaving a significant amount of reactants unreacted. In order to improve the efficiency of the solid state reactions, we introduce during the grinding processes microliter amounts of a series of organic solvents, including cyclohexane, ethyl acetate, toluene, tetrahydrofuran (THF), and \( N, N \)-dimethylformamide (DMF). To our surprise,
whereas all the other solvents execute no appreciable efforts on the course of grinding, the addition of DMF leads to a completely new solid phase characterized by a purple color. Most significantly, this purple solid undergoes a clean conversion to the product \( \text{L2a} \) at elevated temperature. Perhaps even more surprisingly, the imide reaction gradually occurs at room temperature within a period of a week if the purple solid is placed on the bench (Figure 5.7).

![Figure 5.7 XPD patterns (left) and FT-IR spectra show the DMF grind of AH6 and AM1 undergoes a clean conversion to L2a within a few hours upon heating or within a week at room temperature.](image)

Although attempts to make single crystals of the purple phase have not been successful presumably because of its relatively high reactivity, the solid structure of this intermediate is likely related to that of a dioxane solvate of the co-crystal \(^{304}\) AH6•AM1, which has been established by single crystal X-ray diffraction experiment, since the latter also exhibits the characteristic purple color. The crystal structure of the solvate reveals a short distance (ca. 3.17Å) between the aromatic rings of AM1 and AH6 and a short distance (ca. 3.88Å) between the nitrogen from the amino group and the carbon from the
adjacent carbonyl group, which are essentially where the nucleophilic reactions occur (Figure 5.8). While the former distance possibly accounts for the existence of the purple color in the DMF grind (due to strong $\pi-\pi$ interaction and charge transfer), the latter explains its relatively high reactivity because the reacting groups are already pre-aligned in proximity.

![Figure 5.8 Structural moiety in the crystal structure of the dioxane solvate of AH6•AM1 co-crystal.](image)

The significance of the above observations on co-crystal promoted solid state synthesis of new ligands can be appreciated by the following considerations: 1) solid state synthesis potentially affords a green alternative that can circumvent the shortcomings of conventional solution synthesis which typically involves production of large amounts of liquid wastes; 2) with an appropriate choice of solvent, the solvent-drop grinding technique can be highly efficient to facilitate the formation of co-crystals that are otherwise not accessible from dry grinding; 3) although solid state organic synthesis represents a well established area of research, co-crystal promoted solid-state reactions have thus far been essentially limited to photodimerizations and photopolymerizations; our results therefore indicate that other types of organic reactions might as well be feasible using similar strategies.

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5.3 Metal-Organic Frameworks from Pre-designed Imide-Type Carboxylato Ligands

5.3.1 Metal-Organic Framework from Ligand L1a

1, 8-Naphthalic anhydride and its derivatives have been widely used as herbicide safeners and precursors of fluorescent dyes in industry; thus incorporation of this building block into the BDC-based ligands L1a–c will be of interest not only from the design perspective, but also from the materials perspective. In this context, we are able to isolate single crystalline products of a new MOF using ligand L1a and Zn(II) ions.

Figure 5.9 Crystal structures of compound 15: a) the 2D framework; b) tetrahedral SBU in 15; c) a VLPP representation of the 2D framework; d) the packing of 2D sheets. Solvent molecules are deleted for clarity.
Compound 15, [Zn$_2$(L$_{1a}$)$_2$(DMF)$_3$]•(guest)$_x$, is prepared via solvothermal reactions from a mixture of Zn(NO$_3$)$_2$, L$_{1a}$, benzene and DMF in a 1:1:225:776 mole ratio. The structure of 15 is determined by single-crystal X-ray diffraction and as revealed by Figure 5.9, it exhibits a 2D tetragonal sheet topology that is based upon tetrahedral SBUs. The tetrahedral SBU is composed of two Zn(II) ions, four carboxyl groups and three DMF molecules. The two Zn(II) ions are coordinated by two bidentate bridging carboxyl group, one tridentate carboxyl group (one oxygen being monodentate while the other bifurcated), and one chelating carboxyl group (Figure 5.9b). Each of the metal centers therefore has an octahedral or pseudo-octahedral coordination geometry. The Zn(II)-Zn(II) distance is ca. 3.338Å and the Zn(II)-O distances are in the range of 1.969-2.320Å with an average of 2.103Å. Notice this tetrahedral SBU is also observed in the ternary net JLU discussed in Chapter 4 and is closely related to (but not exactly the same with) SBU III and IV seen in USF-3 and USF-4.

The 2D framework, which manifests a certain degree of undulation thanks to the tetrahedral shape of the SBUs and the angularity of the ligand, can be conveniently described as being sustained by vertex-linking of molecular tetrahedra (Figure 5.9c). The plate-like naphthalic imide groups appear to play an important role in directing the packing of the 2D sheets, since they are engaged in with each other face-to-face π-π interactions in such a manner that interdigitation occurs between adjacent layers (Figure 5.9d). Due to the undulating nature of the 2D frameworks, as well as the large dimension of the naphthalic imide group in L$_{1a}$, a large percent of free volume exists between the layers, which are occupied by guest species.
In short, we have demonstrated the incorporation of the pre-designed ligand $L_{1a}$ into a novel 2D MOF. Compound 15 is of importance for the following reasons:

1) It confirms the feasibility of our proposal that plate-like moieties can in principle be used to construct “decorated” SUMOFs;

2) Although the tetragonal sheet topology is usually a collection of planar square (or rectangular) building blocks, the structure of 15 illustrates how appropriate combination of molecular tetrahedra can result in 4-membered rings and thus the tetragonal sheet topology. Nevertheless, one would argue that another 2D 4-connected topology, namely, Kagomé lattice, which is based upon 3- and 6-membered rings (Figure 2.5C), is probably not accessible from tetrahedral units due to the geometrical limitations. The formation of 6-membered rings from tetrahedral units more commonly leads to 3D frameworks such as diamondoid structures.

Although numerous efforts have been attempted trying to assemble ligands $L_{1a-c}$ with the square SBU I, we have not been successful in isolating single-crystalline products of the targeted structures (such as decorated nanoballs).

5.3.2 Metal-Organic Framework from Ligand $L_{2a}$.

Ligand $L_{2a}$, when in a cis configuration, can be regarded as a longer version of the ligand BDC. It is therefore reasonable to anticipate association of $L_{2a}$ and SBU I and thus generation of SUMOFs that are based upon the original prototypal structures. On the other hand, the somewhat different chemical (e.g., containing a larger conjugated system) and structural (e.g., significantly more flexible) nature of $L_{2a}$, as compared to BDC, will
likely to be pronounced in the supramolecular assemblies and new types of MOFs are in principle possible to form.

5.3.2.1 Expanded Tetragonal Sheets

As expected, an expanded version of the tetragonal sheet B has been obtained from the assembly of \( L_2a \) and the paddle-wheel SBU I. Reactions between \( \text{Zn(NO}_3\text{)}_2 \) and \( L_2a \) under various conditions give rise to an array of single crystalline products with different morphologies. For instance, crystals of compound \( 16a, [\text{Zn}_2(L_2a)_2(\text{MeOH/H}_2\text{O})_2](\text{guest})_x, \) are grown from a DMF/MeOH mixture solution of \( \text{Zn(NO}_3\text{)}_2, L_2a, \) and pyridine type base (e.g., pyridine, 2,6-lutidine, 4-methoxypyridine, quinoline, isoquinoline, etc.), whereas compounds \( 16b \) or \( 16c \), both of which can be formulated as \( [\text{Zn}_2(L_2a)_2(\text{DMF})_2](\text{guest})_x \), precipitate in the presence of liquid aromatics from the same reaction mixtures. X-ray single crystal diffraction experiments nevertheless reveal very similar 2D tetragonal sheet architectures for \( 16a-c \) despite their distinct morphologies. However, subtle and yet significant variations, such as shapes of the 2D sheets and the way they pack in 3D, do exist among these three phases (Figure 5.10).

To be more specific, these three structures can be compared in details as following:

1) The ligand \( L_2a \) exists in a \textit{trans} configuration in all three compounds and in each case, the carboxyl groups are almost planar with the phenyl rings. However, while crystallographically there is only one type of \( L_2a \) in \( 16a \), there are two of them in both \( 16b \) and \( 16c \). The torsion angles of the phenyl rings (and thus the carboxyl planes) with
Figure 5.10 2D frameworks and their packings of 16a (a, b), 16b (c, d) and 16c (e, f). Solvent molecules are deleted for clarity.
respect to the naphthalic diimide planes vary from $82.2^\circ$ in 16a to $60.1^\circ$ and $85.7^\circ$ in 16b or $58.5^\circ$ and $85.1^\circ$ in 16c.

2) The cavity sizes of the 2D frameworks in all three compounds are in the range of 2 nm but their shapes differ slightly. Whereas cavities in 16a can be described as ideally rhomboidal (length of edges: 20.486Å; sharp angles: 73.5°), those in 16b and 16c are somewhat distorted and thus less symmetric (lengths of edges: 19.867 & 20.425 Å for 16b; 19.684 & 20.308 Å for 16c; sharp angles: 68.8° for 16b; 67.6° for 16c).

3) The most significant feature that distinguishes 16a from 16b or 16c is perhaps the different manner in which the 2D layers pack with respect to each other. The 2D sheets in 16a repeat themselves in the third direction in an ABAB fashion, thereby generating large channels that are occupied by guest molecules (Figure 5.10). Those in 16b or 16c appear to adopt an ABCDABCD manner, thus considerably reducing the percentage of free volumes. In fact, percent free volume of 60%, 26% and 28% are calculated for 16a, 16b, and 16c, respectively, using the program Platon.291

4) Another interesting difference between 16a and 16b or 16c is the ligand coordinating at the axial position of SBU I. Although in each case, both MeOH (and likely H$_2$O) and DMF are present in the reaction mixture, MeOH or H$_2$O is found to be the axial ligand in 16a whereas DMF fills in this role in 16b and 16c, although reasons for such a variation remain unclear at present.

5) Except their slightly different cell parameters (see Table 5.2&5.3), compound 16b and 16c are almost identical to each other, as suggested from above.

The interesting structural features of compounds 16a–c have promoted us to investigate their thermal stability and possible porosity. Preliminary results suggest
although the crystallinity of the materials is sufficiently maintained even after gas 
sorption experiments (see experimental section), no appreciable N$_2$ uptake has been 
observed, presumably due to the structural rearrangement upon guest release, which 
causes the blocking of open channels.

Another question yet to be answered is concerned with the fundamental driving 
forces that direct the respective formation of the two dramatically distinct supramolecular 
entities, i.e., 16a vs. 16b or 16c. Notice essentially the only variation in the reaction 
mixtures is the absence or presence of aromatic species. Accordingly, it is tempting to 
assume the important role played by these $\pi$-electron rich systems. Unfortunately, due to 
the severe disordering of guest species in the crystal structures, reliable structural models 
of host-guest interactions could not be established at this point, therefore a more detail 
analysis in this regard will not be possible.

As a summary, Table 5.1 lists some important information of 16a–c.

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<td>MeOH or H$_2$O</td>
<td>ABAB</td>
<td>60%</td>
</tr>
<tr>
<td>16b</td>
<td>19.867Åx20.425 Å; 68.8°</td>
<td>60.1° and 85.7°</td>
<td>DMF</td>
<td>ABCDABCD</td>
<td>26%</td>
</tr>
<tr>
<td>16c</td>
<td>19.684Å &amp; 20.308 Å; 67.6°</td>
<td>58.5° and 85.1°</td>
<td>DMF</td>
<td>ABCDABCD</td>
<td>28%</td>
</tr>
</tbody>
</table>

5.3.2.2 Bilayer Structure

Since only the trans configuration of L2a has been observed in 16a–c, it would be 
of interest to obtain the cis configuration because this latter isomer more closely mimics 
the ligand BDC and therefore more likely to direct the formation of the targeted SUMOFs
such as expanded Kagomés and nanoballs. Herein we will show that the cis configuration of L2a is indeed present in a new 2D bi-layer type MOF.

Compound 17, [Zn2(L2a)(isoquinoline)2](guest), precipitates from a mixture of Zn(NO3)2, L2a, isoquinoline, and o-xylene that are dissolved in MeOH/DMF. The crystal structure is determined by X-ray diffraction and as shown in Figure 5.11, it represents a novel 2D bi-layer structure that is composed of paddle-wheel SBUs I and bridging ligand L2a. In contrast to those seen in 16a–c, L2a exists as the cis isomer, although the two
phenyl groups are not in the same plane. There are three crystallographically independent motifs of them and three different torsion angles that are defined by the phenyl rings with respect to the diimide rings: 61.6°, 66.9°, and 67.1°. The 2D bi-layer architecture can perhaps be described as an alternative way of linking molecular squares (also see section 4.2.1), which is topologically related to the tetragonal sheets. As a result of the bi-layer arrangement, large free space is present on both sides of the layer, which is nevertheless mitigated by interdigitation that occurs between adjacent layers (Figure 5.11c).

It should be pointed out that, contrary to 16a~c, where solvent molecules (DMF/MeOH/H2O) serve as the axial ligands of SBUs I, the bulky isoquinoline molecules instead are coordinating to SBU I in 17. Such a seemingly subtle difference might in fact play a critical role in favoring the cis conformation of L2a and thus the formation of a bi-layer topology. Unfortunately, repeated X-ray single-crystal diffraction experiments on different samples from the same reaction conditions suggest that compound 17 is perhaps simply a side product of the reaction and the bulk sample contains a large portion of compound 16c.

5.4 Summary

This Chapter is focused upon the discussions of the following topics:

1) Scaled-up metal-organic frameworks (SUMOFs) are extended versions of MOFs based upon existing (or unprecedented) prototypal metal-organic structures. Expansion of either organic linkers or inorganic nodes can equally lead to new SUMOFs that might possess giant pores or extremely high surface areas.
2) *Imide reactions* afford a series of BDC analogues that are ideally suitable for the design of SUMOFs.

3) The imide-type carboxylato ligands are also accessible from *solid state synthesis*, especially with the aid of solvent-drop grinding technique.

5.5 Experimental

5.5.1 Syntheses

The materials in the synthesis were used as received from reliable commercial sources (Sigma-Aldrich, Fischer Scientific, and City Chemical); solvent methanol was purified and dried according to standard methods.

*Synthesis of N-(3, 5-dicarboxylphenyl)-1, 8-naphthalimide (L1a)*\(^{303}\)

A mixture of 1, 8-naphthalic anhydride (700 mg, 3.53 mmol) and 5-aminoisophthalic acid (1.270 g, 7.060 mmol) in dry DMF (20 mL) is heated to 100°C and stirred vigorously for 24 h. After cooled to room temperature, the mixture is poured into water and filtered. The filter is then rinsed with MeOH and CH\(_2\)Cl\(_2\), respectively, and dried in the air. The crude product is recrystallized from a DMSO/MeOH mixture solvent, giving rise to yellowish powder (yield: 1.082 g, 84.9%).

*Synthesis of N-(3, 5-dicarboxylphenyl)-3-nitro-1, 8-naphthalimide (L1b)*

A mixture of 3-nitro-1, 8-naphthalic anhydride (858 mg, 3.53 mmol) and 5-aminoisophthalic acid (1.270 g, 7.060 mmol) in dry DMF (20 mL) is heated to 100°C and stirred vigorously for 24 h. After cooled to room temperature, the clear solution with a dark brown color is poured into ca. 70 mL of water and reddish powder precipitates out.
The mixture is then filtered and dried in the oven. The crude product is recrystallized from a DMF/H₂O mixture solvent.

*Synthesis of N-(3, 5-dicarboxyphenyl)-4-sulfo-1, 8-naphthalimide, potassium salt (L1c).*

A mixture of 4-sulfo-1, 8-naphthalic anhydride (1.240 g, 3.53 mmol) and 5-aminoisophthalic acid (1.270 g, 7.060 mmol) in dry DMF (20 mL) is heated to 100°C and stirred vigorously for 24 h. After cooled to room temperature, the mixture is poured into MeOH and filtered. The filter is then rinsed with MeOH and CH₂Cl₂, respectively, and dried in the air. The crude product is recrystallized from hot water (yield: 0.990g, 58.5%).

*Synthesis of N,N'-di(3-carboxyphenyl)-1,4,5,8-naphthalenetetracarboxylic diimde (L2a).*

A mixture of 1, 4, 5, 8-naphthalenetetracarboxylic dianhydride (947 mg, 3.53 mmol) and 3-aminobenzoic acid (967 g, 7.060 mmol) in dry DMF (20 mL) is heated to 100°C and stirred vigorously for 36 h. After cooled to room temperature, the mixture is poured into H₂O and filtered. The filter is then rinsed with MeOH and CH₂Cl₂, respectively, and dried in the air. The crude product is recrystallized from a DMF/MeOH mixture solvent (yield:1.237g, 69.2%).

Solid state syntheses 1 (dry grinding): A mixture of 1, 4, 5, 8-naphthalenetetracarboxylic dianhydride (13 mg, 0.050 mmol) and 3-aminobenzoic acid (14 mg, 0.10 mmol) is ground for 4 min and the mixture is placed in the oven and heated for ca. 14 h before cooled to room temperature. Single crystals of the pyridine solvate of L2a are grown from a pyridine solution of the product via slow evaporation.

Solid state syntheses 2 (DMF grinding): A mixture of 1, 4, 5, 8-naphthalenetetracarboxylic dianhydride (98 mg, 0.36 mmol), 3-aminobenzoic acid (102 mg, 0.72 mmol) and DMF (20 μL, 0.26 mmol) is ground for 4 min and the mixture is placed in the
oven and heated for ca. 14 h before cooled to room temperature. Single crystals of the
dioxane solvate of the co-crystal AH6•AM1 are grown from a dioxane solution of the
DMF grind via slow evaporation.

*Synthesis of N, N'-di(3-carboxylphenyl)-1,2,4,5-benzenetetracarboxylic diimde (L2b).*

A mixture of 1, 4, 5, 8-benzenetetracarboxylic dianhydride (770 mg, 3.53 mmol)
and 3-aminobenzoic acid (967 g, 7.060 mmol) in dry DMF (20 mL) is heated to 100°C
and stirred vigorously for 24 h. After cooled to room temperature, the mixture is placed
in an ice bath for overnight and yellow crystalline powder precipitates. The product is
collected by filtration and the filter is then rinsed with MeOH and CH2Cl2, respectively,
and dried in the air (yield: 800 mg, 49.7%).

*Synthesis of N, N'-di(3, 5-dicarboxylphenyl)-1,4,5,8-naphthalenetetracarboxylic diimde
(L3a).*

A mixture of 1, 4, 5, 8-naphthalenetetracarboxylic dianhydride (947 mg, 3.53 mmol)
and 5-aminoisophthalic acid (1.270 g, 7.060 mmol) in dry DMF (20 mL) is heated to
100°C and stirred vigorously for 36 h. After cooled to room temperature, the mixture is
poured into H2O and filtered. The filter is then rinsed with MeOH and CH2Cl2,
respectively, and dried in the air. The crude product is recrystallized from a DMF/MeOH
mixture solvent.

*Synthesis of N, N'-di(3, 5-dicarboxylphenyl)-1,2,4,5-benzenetetracarboxylic diimde (L3b).*

A mixture of 1, 4, 5, 8-benzenetetracarboxylic dianhydride (770 mg, 3.53 mmol)
and 5-aminoisophthalic acid (1.270 g, 7.060 mmol) in dry DMF (20 mL) is heated to
100°C and stirred vigorously for 48 h. After cooled to room temperature, the mixture is
placed in an ice bath for overnight and yellow crystalline powder precipitates. The
product is collected by filtration and the filter is then rinsed with MeOH and CH₂Cl₂, respectively, and dried in the air.

*Synthesis of 1,3-bis(N-trimellitoyl)benzene (L₄).*

A flask is charged with 1, 3-phenylenediamine (216 mg, 2.00 mmol), trimellitic anhydride (960 mg, 5.00 mmol), and glacial acid (10 mL). The mixture is refluxed for 15 h. The mixture is filtered and rinsed with enough MeOH to give rise to bright yellow powder (yield: 318 mg, 34.8%).

*Synthesis of [Zn₂(L₁a)₂(DMF)₃]•(guest)ₓ (15).*

Yellowish crystals of compound 15 are isolated by heating a mixture of Zn(NO₃)•6H₂O (8 mg, 0.025 mmol), L₁a (9 mg, 0.025 mmol), DMF (1.5 mL) and benzene (0.5 mL) at 85°C for 48 h (yield: 13 mg)

*Synthesis of [Zn₂(L₂a)₂(MeOH/H₂O)₂]•(guest)ₓ (16a).*

A typical reaction involves layering a methanolic solution (3 mL) of Zn(NO₃)•6H₂O (15 mg, 0.050 mmol) onto a DMF (4 mL) solution of L₂a (10 mg, 0.020 mmol), and 2, 6-lutidine (7 μL, 0.06 mmol). Yellowish crystals appear within 24 h. Yield: 10 mg.

*Synthesis of [Zn₂(L₂a)₂(DMF)₂]•(guest)ₓ (16b).*

A typical reaction involves layering a methanolic solution (3 mL) of Zn(NO₃)•6H₂O (15 mg, 0.050 mmol) onto a DMF (3 mL) solution of L₂a (10 mg, 0.020 mmol), chlorobenzene (1 mL) and 2, 6-lutidine (7 μL, 0.06 mmol). Yellowish crystals appear within 24 h. Yield: 9.2 mg.

*Synthesis of [Zn₂(L₂a)₂(DMF)₂]•(guest)ₓ (16c).*

A typical reaction involves layering a methanolic solution (3 mL) of Zn(NO₃)•6H₂O (15 mg, 0.050 mmol) onto a DMF (3 mL) solution of L₂a (10 mg, 0.020 mmol), o-
xylene (1 mL) and 2, 6-lutidine (7µL, 0.06 mmol). Yellowish crystals appear within 24 h. Yield: 9.4 mg.

_Synthesis of [Zn₂(L²a)₂(isoquinoline)₂]·(guest)ₓ (17)._ 

Single crystals of compound 17 are obtained by layering a methanolic solution (3 mL) of Zn(NO₃)·6H₂O (15 mg, 0.050 mmol) onto a DMF (3 mL) solution of L²a (10 mg, 0.020 mmol), o-xylene (1 mL) and isoquinoline (7µL, 0.06 mmol). Yellowish crystals appear within 24 h.

5.5.2 Characterizations

_Crystal Structure Determination_

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 Moka radiation (λ = 0.7107 Å). The data were corrected for Lorentz and polarization effects and for absorption using the SADABS program. The structures were solved using direct methods and refined by full-matrix least-squares on |F|^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions and refined with temperature factors 1.2 times those of their bonded atoms. All crystallographic calculations were conducted with the SHELXTL 5.1 program package.
Table 5.2 Crystallographic data for compounds 16a–b.

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<tr>
<th>Compound</th>
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<th>16b</th>
</tr>
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<tbody>
<tr>
<td>Chemical formula</td>
<td>C_{29}H_{6}N_{2}O_{29.5}Zn</td>
<td>C_{66}H_{38}N_{6}O_{24}Zn_{2}</td>
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<tr>
<td>Formula weight</td>
<td>919.73</td>
<td>1429.76</td>
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<td>Temperature, K</td>
<td>100(2) K</td>
<td>100(2) K</td>
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<td>Triclinic</td>
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<tr>
<td>Space group</td>
<td>C2/m</td>
<td>P-1</td>
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<tr>
<td>a, Å</td>
<td>11.745(3)</td>
<td>9.043(3)</td>
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<td>b, Å</td>
<td>24.471(6)</td>
<td>13.640(5)</td>
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<td>c, Å</td>
<td>17.395(4)</td>
<td>14.068(5)</td>
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<td>α, deg</td>
<td>90</td>
<td>85.029(7)</td>
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<td>β, deg</td>
<td>108.864(4)</td>
<td>75.164(6)</td>
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<td>γ, deg</td>
<td>90</td>
<td>89.353(7)</td>
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<td>4731.1(19)</td>
<td>1670.9(10)</td>
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<td>Z</td>
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<td>1</td>
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<td>F(000)</td>
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<td>728</td>
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<td>Crystal size, mm</td>
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<td>1.24 to 18.03°</td>
<td>1.50 to 22.52°</td>
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<td>Limiting indices</td>
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<td>h≤9, -9≤k≤12, -12≤l≤15</td>
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<td>Reflections collected</td>
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<td>5416</td>
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<td>Unique reflections</td>
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<td>R(int)</td>
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<td>0.0815</td>
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<td>Completeness to θ</td>
<td>99.5 %</td>
<td>94.7 %</td>
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<td>Absorption correction</td>
<td>SADABS</td>
<td>SADABS</td>
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<td>Max. and min. transmission</td>
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<td>1.000 and 0.096</td>
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<td>Data/ restraints/ parameters</td>
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<td>4150 / 0 / 420</td>
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<td>Goodness-of-fit on F²</td>
<td>1.467</td>
<td>0.927</td>
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<td>Final R indices [I&gt;2σ(I)]</td>
<td>R1 = 0.1430, wR2 = 0.3520</td>
<td>R1 = 0.1171, wR2 = 0.2828</td>
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<tr>
<td>R indices (all data)</td>
<td>R1 = 0.1784, wR2 = 0.3791</td>
<td>R1 = 0.2260, wR2 = 0.3336</td>
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<td>Large diff. peak and hole, e·Å⁻³</td>
<td>0.804 and -0.648</td>
<td>1.258 and -0.726</td>
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Table 5.3 Cell parameters of compounds 15, 16c, and 17.

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<th>Compound</th>
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<th>b, Å</th>
<th>c, Å</th>
<th>α, deg</th>
<th>β, deg</th>
<th>γ, deg</th>
<th>Space group</th>
<th>V, Å³</th>
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<tr>
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<td>90</td>
<td>90</td>
<td>P2₁2₂₁</td>
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</tr>
<tr>
<td>16c</td>
<td>8.8884</td>
<td>14.083</td>
<td>14.099</td>
<td>92.213</td>
<td>92.167</td>
<td>104.677</td>
<td>P-1</td>
<td>1703.86</td>
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<tr>
<td>17</td>
<td>27.882</td>
<td>22.844</td>
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<td>90</td>
<td>90.533</td>
<td>90</td>
<td>C2/c</td>
<td>15649.8</td>
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</table>

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Other Characterizations

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. Infrared spectra were recorded on a Nicolet Avatar 320 FT-IR spectrometer. Thermogravimetric analysis was performed under nitrogen on TA Instruments TGA 2950 Hi-Res. The simulated XRPD patterns were produced using and Powder Cell for Windows Version 2.4 (programmed by W. Kraus and G. Nolze, BAM Berlin, © 2000). Mass spectra were obtained from Agilent Technologies LC/MSD VL (with electrospray ionization). Samples for NMR experiments were dissolved in DMSO-d₆. ¹H-NMR spectra and ¹³C-NMR spectra were recorded on an Oxford NMR AS 400 (400 MHz).

Figure 5.12 Mass spectra of L1a.
Figure 5.13 Mass spectra of L2a.

Figure 5.14 Mass spectra of L3a.

Figure 5.15 $^1$H-NMR (left) and $^{13}$C-NMR (right) of L1a.
Figure 5.16 $^1$H-NMR (left) and $^{13}$C-NMR (right) of L1b.

Figure 5.17 $^1$H-NMR (left) and $^{13}$C-NMR (right) of L1c.

Figure 5.18 $^1$H-NMR (left) and $^{13}$C-NMR (right) of L2a.
Figure 5.19 $^1$H-NMR (left) and $^{13}$C-NMR (right) of L3a.

Figure 5.20 $^1$H-NMR (left) and $^{13}$C-NMR (right) of L3b.

Figure 5.21 $^1$H-NMR (left) and $^{13}$C-NMR (right) of L4.
Figure 5.22 XPD of compound 15.

Figure 5.23 TGA trace of compound 16a.
Figure 5.24 FT-IR of compound 16a.

Figure 5.25 XPD of compound 16a.
Chapter 6
Conclusions and Future Directions

Even the longest voyage begins with the first step.
Lao-tse 64, about 400 B.C.

6.1 Summary and Conclusions

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

i) Under various conditions, self-assembly of rigid and angular ligand 1,3-benzenedicarboxylate (BDC) and square paddle-wheel secondary building units (SBUs) generates a wide array of MOFs ranging from 0D nanoballs, 2D tetragonal sheets and Kagomé lattices, to 3D CdSO₄ net and an unprecedented “USF-1” net. The remarkable diversity of the resulting superstructures from such simple structural ingredients can be rationalized on the bases of angularity and distortion of the molecular building blocks. A detail conformation and configuration analysis not only reveals the fundamental geometric relationships among the existing supramolecular isomers, but also predicts a number of other interesting structures that are in principle possible to be isolated.

ii) Other angular ligands, such as 1,3-adamantanedicarboxylate (ADC) and the BDC analogue L2a, also self-assemble with paddle-wheel square SBUs to give rise to
some novel structures including 1D ladder topology and a 2D bi-layer structure. These results, along with those reported elsewhere, highlight the myriad possibilities of linking square building units. It is quite obvious that structures based upon square building units can always be simplified as 4-connected nets, which are probably among the best-understood classes of topologies. From a topological point of view, square and tetrahedral nodes are in fact interchangeable in the sense that each square-based net can be equally represented as a tetrahedron-based net by adjusting the shape of linkers (see Figure 2.14 for an example of tetrahedral frameworks illustrated in a square fashion), and vice versa. If taking into account the numerous examples of tetrahedron-based zeolite nets, it is perhaps appropriate to regard the design principles we delineate in this work concerning the use of square SBUs as a potential alternative to zeolite-like metal-organic frameworks (ZMOFs), a recently developed area pioneered by Eddaoudi. We believe the key to the success relies upon the rational selection of suitable spacers that can link square building blocks in a desired manner.

iii) The assembly of BDC and its hydroxyl derivative with another dimetal tetracarboxylate, a pseudo-square SBU, also results in a series of supramolecular isomers such as 1D ladders and 2D sheets. Our controlled experiments demonstrate the subtle influences of both templates and axial ligands of SBUs on the resulting superstructures. These results unambiguously indicate that it is in principle possible to experimentally control supramolecular isomerism.

From an added perspective, if one considers supramolecular isomerism in a broader sense, the 1D ladders and 2D sheets based upon pseudo-square SBUs can also be regarded as supramolecular isomers of those structures mentioned in i) since they all
contain the same framework compositions. It thus further complicates the situation of superstructural diversity because not only the contributions from organic ligands (e.g., their angularity and conformation) but also those from metal ions (e.g., various factors that determine the formation of a certain chromophore) need to be taken into consideration. Nevertheless, the presence of an overwhelming amount of superstructures from a limited number of easily accessible building blocks might as well be considered as an opportunity from a materials point of view, as is exactly the case for the four different forms of carbons.

iv) Although a large portion of this dissertation is devoted to establish a general formulation for design and analysis of MOFs, it should not be forgotten that it is the practical utility of MOFs that should ultimately drive this area to its next level of development. In this context, recent progress on heterogeneous catalysis and gas storage highlights the future direction of MOF chemistry.

v) The introduction of fluorine atoms to BDC moieties is shown to have led to a dramatic increase of flexibility of the molecule and the incorporation of tetrafluoro-1, 3-benzenedicarboxylate (TFBDC) with paddle-wheel square SBUs results in a wide array of 2D metal-organic frameworks that are based upon a distorted tetragonal sheet topology. The flexibility on the molecular level is thus translated into the supramolecular level as these 2D networks manifest guest-dependent closing/opening of intra- and inter-layer cavities, a unique aspect that has not been observed in the original compounds. It therefore represents an effective approach toward functionalized metal-organic networks.

By systematically modifying the chemical nature of ligands on the axial site of paddle-wheel SBUs, we have further shown our capability to adjust the environments on
the outer surfaces of the 2D frameworks, which in turn results in a better control over the size, shape and hydrophobicity of the inter-layer cavities. In particular, a small variation on the size of the axial ligands (i.e., from quinoline to 2-picoline) has transformed the inter-layer free space from discrete cavities to 1D continuous channels that can be utilized by a much higher amount of guest species.

 vi) It remains our major argument that discovery and recognition of novel three-periodic metal-organic nets is a nontrivial exercise. Rigorous topological analysis on complicated MOFs has been repeatedly emphasized, with a focus on establishing reliable structural descriptions and standard references for relevant comparison. On the other hand, the concepts of vertex linked polygons and polyhedra (VLPP) and ternary nets underscore the importance of geometrical information in the context of structural and functional design. Overall, we have exemplified the fundamental principles of “metal-organic structural chemistry”.

 vii) Scaled-up metal-organic frameworks (SUMOFs) are potentially accessible with the aid of existing prototypal structures and a systematic study on ligand design.

 In short, the main effort of this work is devoted to illuminating basic principles of supramolecular chemistry and crystal engineering in the context of designing metal-organic frameworks, which are applicable to a much broader range of functional supramolecular materials.

 4.2 Future Directions

 It is the author’s belief that the ultimate goal of this field is to “make molecules at will”. Even though our understanding on the supramolecular and suprasupramolecular
level remains relatively limited, as compared to that on the molecular level,\textsuperscript{310} it is only a matter of time that such a dream will be realized, especially with the view of increasing progress that have been made in gaining better controls on metal-organic systems, as unambiguously demonstrated by this thesis. As part of efforts that are aimed at this ambition, we propose the following initiatives, among others, to highlight the future direction of our research:

1) Stronger tools for structural determination of molecules, including effective techniques for routine elucidation of structures of polycrystalline and amorphous solids;

2) A thorough understanding of hierarchies of weak intermolecular forces and the roles they play in the supramolecular entities;

3) Controlling supramolecular structure by manipulating molecular structures

4) A direct correlation of structure and function of molecules.

Finally, to quote Feynman, “what would the properties of materials be if we could really arrange the atoms the way we want them? …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.”\textsuperscript{311}
References


2. A Oxford English Dictionary (online version, http://www.oed.com/) definition of “crystal”: *A form in which the molecules of many simple elements and their natural compounds regularly aggregate by the operation of molecular affinity: it has a definite internal structure, with the external form of a solid enclosed by a number of symmetrically arranged plane faces, and varying in simplicity from a cube to much more complex geometrical bodies.*


4. Haüy, R. J. *Essai d'une théorie sur la structure des cristaux*; Paris, **1784**.

5. Numbers of entries contained in the major primary crystallographic databases: i) 348,481, Cambridge Structural Database of organic and metal-organic structures (CSD, v5.27, including a Jan 2006 update); ii) 89,366, Inorganic Crystal Structure Database (ICSD, as of Dec 2005); iii) 35,701, Protein Data Bank (PDB, as of Mar 21, 2006); iv) 3,647, Biological Macromolecule Crystallization Database (BMCD, v2.00); v) 3,000, Nucleic Acid Database (NDB, as of Mar 14, 2006).


110. Pores will be classified, depending on their width, as micropores (<2 nm), mesopores (2-50 nm), and macropores (>50 nm); see: IUPAC Manual of Symbols and Terminology, Appendix 2, Pt. 1, Colloid and Surface Chemistry. *Pure Appl. Chem.* **1972**, *31*, 578.


120. Chester, A. W., Clement, P.; Han, S. *Faujasite zeolitic materials. US patent 6,136,291A* (24 October **2000**).


<table>
<thead>
<tr>
<th>Number</th>
<th>Author(s)</th>
<th>Journal</th>
<th>Volume</th>
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<td>134</td>
<td>Lin, X.; Blake, A. J.; Wilson, C.; Sun, X. Z.; Champness, N. R.; George,</td>
<td>J. Am. Chem. Soc.</td>
<td>2006</td>
<td>128, 10745-10753</td>
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<td>M. W.; Hubberstey, P.; Mokaya, R.; Schroeder, M.</td>
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<td>T. C.; Suzuki, M.</td>
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<td>Taulelle, F.; Bourrely, S.; Llewellyn, P. L.; Latroche, M.</td>
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228. The Department of Energy, in its Year 2010 guidelines, has set performance targets for on-board automobile storage systems to have densities of


237. Vertex symbol for the sodalite net: 4•4•6•6•6•6.
Vertex symbol for the PtS net: \((4\cdot4\cdot8\cdot8\cdot8\cdot8)(4\cdot4\cdot8\cdot8\cdot8\cdot8)\).


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273. All the topological calculations in this dissertation are performed using the program OLEX (v2.55, Release 10.09.2004): Dolomanov, O. V; Blake, A. J.; Champness, N. R.; Schröder, M. J. Appl. Cryst. 2003, 36, 1283-1284. The crystallographic cif. files that contain the structural information of analyzed compounds are used and they are typically edited wherever appropriate using the program Materials Studio (v2.2, Copyright©2002, Accelrys Software Inc.) prior to the calculations.


293. McManus, G.; Zaworotko, M. J. *unpublished results*.


About the Author

Zhenqiang Wang (nickname Rick) was born in Xining, Guangdong province, China, in 1977. He received a B.S. degree in chemistry from Peking University in 2000. In August 2002, Zhenqiang 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 American Association for the Advancement of Science. In addition to coauthoring 3 publications in chemical journals, he is also contributed to one manuscript that has been submitted, and is currently preparing for several other manuscripts. He has made a number of oral presentations at local, regional, and national conferences, including Annual Raymond N. Castle Student Research Conference, Florida Annual Meeting and Exposition of the American Chemical Society (FAME), Southeast Regional Meeting of the American Chemical Society (SERMACS), and American Chemical Society National Meeting (ACS).