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Metal-organic networks based upon dicarboxylato ligands

Zhenqiang Wang  
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Metal-Organic Networks Based Upon Dicarboxylato Ligands

by

Zhenqiang Wang

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science
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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 thesis is primarily concerned with developing an in-depth understanding of the basic principles that govern the supramolecular behaviors of metal-organic networks 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. Conformational analysis of these structural models suggests the geometric foundations for the existence of superstructural diversity. Controlled crystallization experiments further reveal the synthetic factors that might determine the formation of supramolecular isomers.

Careful selection of more labile organic components, on the other hand, leads to
flexible metal-organic networks exhibiting dynamic characteristics that have not been observed in their rigid counterparts. The guest-dependent closing/opening 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.
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-packing 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—rhombs, 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\(^4\)
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.\(^5\)

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 Ce⁺) 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.\textsuperscript{14-18} 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.\textsuperscript{19-20} Two main tenets, \textit{molecular recognition} and \textit{supramolecular function}, lie at the center of understanding the concepts of supramolecular chemistry.\textsuperscript{21} 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.\textsuperscript{20} 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) \textit{supermolecules}, well-defined, discrete \textit{oligomolecular} species that result from the intermolecular association of a few components; 2) \textit{supramolecular assemblies}, \textit{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, \textit{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. 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.25-30 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, \(^{31}\) whereas the unusual associations of pairs of guests within the cylindrical capsule lead to the discovery of “social isomerism”. \(^{32}\) Nevertheless, since only relatively weak intermolecular interactions, i.e., hydrogen bonds, are involved, the formation and disassociation of the

Figure 1.1. Rebek’s molecular capsules: the “softball” (left) and the cylinder (right).
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.33,34 In particular, a M₆L₄ type octahedral cage (Figure 1.2)

![Figure 1.2. Fujita’s octahedral M₆L₄ cage (left) and Raymond’s tetrahedral M₆L₆ cage (right).](image)

has been shown to possess a cavity large enough to accommodate up to four guest species, which can be used as ideal molecular chambers for mediating chemical reactions such as Diels-Alder reaction, [2+2] cycloaddition, and Wacker oxidation.35,36 Most recently, it was
demonstrated that an aqueous solution of the octahedral M₆L₄ 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.³⁷

Raymond’s group uses an alternative strategy, namely, bidentate chelating ligands and octahedral transition metal units, to direct the assembly of a M₄L₆ type anionic tetrahedral cage (Figure 1.2) and other related molecular containers.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 Δ or Λ 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.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, ⁴² the term “crystal engineering” was initially introduced by Pepinsky in 1955 in an effort to solve the “phase problem” in crystallography.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\(\cdots\)X and C-H\(\cdots\)\(\pi\) 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 \textit{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.\(^{56}\) 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</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>Hemoglobin</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 Networks

1.4.1 History and Scope

Metal-organic networks, also known as metal-organic frameworks, represent a new class of compounds consisting 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 metal-organic networks that have been structurally characterized appeared in 1943, although similar studies can be traced back to 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 networks was not prospering until the late 1980’s when Robson initiated the now famous “node-and-spacer” approach to incorporate both transition metal ions of well-defined coordination geometries and rod-
like organic ligands in the design of framework materials. Subsequently, the work by Zaworotko, \textsuperscript{56, 59-61} Yaghi, \textsuperscript{62-65} and others\textsuperscript{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).

![Figure 1.3 Number of citations containing the key word “coordination polymers” in titles or abstracts in the past 16 years (source: SciFinder Scholar, 07/15/2006).](image)

In Robson’s original node-and-spacer approach, the nets were usually constructed from organic-based linear spacers and metal-cation nodes, which 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.\textsuperscript{71} Figure 1.4 illustrates some representative examples of organic ligands with linear/angular, trigonal, and tetrahedral shapes.

1.4.2 Design Principles
Metal-organic networks exemplify how crystal engineering has become a paradigm for the design of new supramolecular materials. Since the structures are 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 metal-organic networks. 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 investigations on the geometric basis of...
crystal chemistry.\textsuperscript{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.\textsuperscript{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.

![Figure 1.5](image1.png)

**Figure 1.5** “Node-and-spacer” representations of metal-organic networks: 

- a) 0D nanoball
- b) 1D zigzag chain
- c) 1D helix
- d) 1D ladder
- e) 2D bilayers
- f) 2D square grid
- g) 2D honeycomb
- h) 3D (10,3)-\textit{a} net
- i) 3D diamondoid net
- j) 3D primitive cubic net
- k) 3D NbO net

![Figure 1.6](image2.png)

**Figure 1.6** “Vertex-linked Polygons or Polyhedra” (VLPP) representations of metal-organic networks: 

- a) 0D nanoball
- b) 3D (10,3)-\textit{a} net
- c) 3D diamondoid net
- d) 3D primitive cubic net
- e) 3D NbO net
Another approach, also based upon geometric principles, takes into account the specific shapes of the building blocks and represents nets as being sustained by vertex-linked polygons or polyhedra (VLPP). 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 more fundamentally reveals the geometrical relationship between various building units.

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. For example, the planar square grid (Figure 1.5f) can be represented as \((4, 4)\) and the symbol \((10, 3)\) implies a 3-connected net based upon 10-membered rings (Figure 1.5h).

Although Wells notation is still widely accepted in the literature, it also has some limitations because of its over-simplification. For example, the above mentioned symbol \((10, 3)\) in fact represents at least seven different 3D nets that are topologically related but distinct. Therefore a more informative system based upon Schláfli symbols, namely, vertex symbols, has been proposed by O’Keeffe. 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 \(10_2 \cdot 10_3 \cdot 10_3\) 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 \((10, 3) - b\), respectively. Note that sometimes the subscripts are omitted and the short vertex symbols in these two examples can then both be written as \(10^3\).

However, it should be pointed out even O’Keeffe’s vertex symbol is not entirely satisfying, as exemplified by the case of 4-connected diamond and lonsdaleite (hexagonal diamond) nets. Although belonging to two distinct nets that exhibit significantly different connectivities, these two nets display identical vertex symbols (\(6_2 \cdot 6_2 \cdot 6_2 \cdot 6_2 \cdot 6_2 \cdot 6_2\) for both). It thus follows that a more rigorous way of describing detail topological information of nets is necessary and a practical solution 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>
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<th>(k)</th>
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<th>3</th>
<th>4</th>
<th>5</th>
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<th>7</th>
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<td>42</td>
<td>64</td>
<td>92</td>
<td>124</td>
<td>162</td>
<td>204</td>
<td>252</td>
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<td>Lonsdaleite</td>
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<td>44</td>
<td>67</td>
<td>96</td>
<td>130</td>
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<td>6</td>
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</tr>
</tbody>
</table>
Chapter 2

Metal-Organic Networks Based Upon Rigid Angular Dicarboxylates

2.1 Introduction

2.1.1 Secondary Building Units (SBUs)

Crystal engineering, and in particular, design strategy based upon geometric principles, provides a successful approach to the synthesis of metal-organic networks. Enormous progress has been made in the past decades, giving rise to a large number of aesthetically pleasing and potentially functional coordination polymers. 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).

Figure 2.1 Metal-organic networks based upon 4, 4’-bipyridine and mono-metal centers: a) 1D chain; b) 1D ladder; c) 2D square grid; d) 3D diamondoid net.
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 from 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 (Figure 2.2). Expansion of SBUs by multifunctional ligands, such as 1, 4-benzenedicarboxylate and 1, 3, 5-benzenetricarboxylate, allows for the construction of neutral open frameworks of high structural stability.

Figure 2.2 Four commonly encountered secondary building units (SBUs) in metal-organic networks.
In this thesis, we focus upon exploiting SBU I and II, both of which have a general formula of M₂(RCOO)₄ (axial ligands omitted). SBU I, a paddle-wheel dimetal tetracarboxylate, has been well known for decades because of its ubiquity and easy accessibility. It is perhaps the most frequently used SBU 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. SBU II, on the other hand, is far less common than I and remains largely unexploited in the crystal engineering of metal-organic networks. Nevertheless, I and II are related in that both can be simplified as 4-connected nodes according to node-and-spacer approach while they are characterized by their distinct shapes from VLPP perspective (Figure 2.4).

Figure 2.3 Distribution of the paddle-wheel SBUs I deposited in the Cambridge Structural Database (CSD) among various transition metal ions.

Figure 2.4 Interpretations of SBU I and II from both node-and-spacer and VLPP perspectives.
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. Zaworotko first recognized superstructural diversity in metal-organic networks in 1997 where 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.\textsuperscript{60} He subsequently defined supramolecular isomerism as “the existence of more than one type of network superstructure for the same molecular building blocks”\textsuperscript{56}. 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.

Previous work from our group, which focuses upon Cu(II)/Zn(II)-based paddle-wheel SBUs I and angular spacer 1,3-benzenedicarboxylate (BDC), has afforded 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

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.
isolated: 0D nanoballs (A), 2D tetragonal sheets (B) and Kagomé lattices (C), and 3D USF-1 net (D) and CdSO₄ net (E) (more supramolecular isomers are expected: see the discussions in section 2.2.3).

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

The fact that 1, 3-benzenedicarboxylate (BDC) is a rigid and angular bridging 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

![Figure 2.6 Four possible configurations associated with BDC-linked SBU I: four downs (“4D”), two adjacent downs (“1, 2-D”), two opposite downs (“1, 3-D”), and three downs (“3D”).](image-url)
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(NO₃)₂ and H₂BDC under appropriate conditions.⁷⁵ As revealed by Figure 2.7a, 12 SBU’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: $(3\cdot3\cdot4\cdot4)_1$), 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 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 \([\text{Cu}_2(5\text{-MeO-BDC})_2(\text{MeOH})_6(\text{H}_2\text{O})_{1.83-x}]_{12}\), \(\mathbf{1}\), 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 H$_2$O) molecules.\textsuperscript{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 \(\mathbf{1}\) 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 *hexagonal packing of parallel cylinders (rods).*\(^7\) In effect, compound 1 has exemplified the principles of suprasupramolecular chemistry.\(^22\-23\)

---

**Figure 2.8** Crystal structure and crystal packing of 1: a) illustration of the methoxy moieties that bridge adjacent nanoballs in blue; b) 1D chain of nanoballs sustained by double cross-links; c) hexagonal packing of nanoball chains represented as green cylinders (rods).
2.2.2 Two-Dimensional Tetragonal Sheets and Kagomé Lattices

Tetragonal sheet $B^{76}$ and Kagomé lattice $C^{83}$ 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 2.9). Both $B$ and $C$ exhibit the undulating nature as a result of the $120^\circ$ angle subtended by 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 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 2.9b, d), then the
dihedral angles can be written as either $\angle DD$ (same as $\angleUU$) 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
2.9b and 2.9d 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 \(\text{Cu(NO}_3\text{)}_2\cdot2.5\text{H}_2\text{O}\) 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, \([\text{[Cu}_2(5\text{-MeO-BDC})_2(\text{MeOH})_2](\text{guest})_x]\infty\), was obtained from a methanol solution of \(\text{Cu(NO}_3\text{)}_2\cdot2.5\text{H}_2\text{O}\) 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 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 2.10). The interlayer distances for 2, 3 and C are 11.6Å, 10.4 Å, and 9.9 Å, respectively (Table 2.1), underlining the different sizes of the substituted groups at the 5- position of BDCs.

Table 2.1 Comparison of chemical and structural information for compound 2, 3 and their parent compound.

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>L (axial ligand of SBU)</th>
<th>Space Group</th>
<th>Packing Sequence</th>
<th>Interlayer Distance (Å)</th>
</tr>
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<tbody>
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<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-3C1</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;85 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.

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 2.11, 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 ligands 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 their different torsion angles. 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 $6_2\cdot6_2\cdot6_2\cdot12\cdot6_3\cdot6_3$ and $6\cdot6\cdot6\cdot6\cdot6\cdot6^*$, for D and E, respectively. While CdSO$_4$ 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.\footnote{86-90}

Figure 2.11 Crystal structures of USF-1 D (a) and CdSO$_4$ 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 2.12–2.15).

![Figure 2.12 Ball-and-stick and schematic representations of hypothetical structure H1. Blue box illustrates the “1, 3-D” configuration of SBUs in the structure.](image)

Structures H1 and H2 are both three-dimensional architectures. The inherent topology of H1 is related to that of the sodalite net seen in zeolites.⁸¹,⁹² Note that the 1, 3-alternative configuration of SBUs has in effect rendered each node a pseudo-S₄ symmetry.
(since the SBU only has $D_{2h}$ symmetry), resulting in a tetrahedral framework (Figure 2.12). $H_2$ 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 2.13).93 Table 2.2 shows a short summary of the crystallographic data for $H_1$ and $H_2$.

![Figure 2.13 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.](image)

<table>
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<tr>
<th>Compound</th>
<th>Space Group</th>
<th>a/Å</th>
<th>b/Å</th>
<th>c/Å</th>
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<th>β/°</th>
<th>γ/°</th>
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<td>90</td>
<td>90</td>
<td>18280.8</td>
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<tr>
<td>$H_2$</td>
<td>P4$_2$/nnm</td>
<td>18.6273</td>
<td>18.6273</td>
<td>26.3430</td>
<td>90</td>
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<td>90</td>
<td>9140.4</td>
</tr>
</tbody>
</table>

Structures $H_3$ and $H_4$ illustrates 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 H3 exhibit a much more undulating nature than those of C (Figure 2.14). 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 2.15).

Figure 2.14 Perspective and side views of hypothetical structure 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 2.15 Perspective and side views of hypothetical structure 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 Network from SBU I and 1, 3-Adamantanedicarboxylate

Similar to BDC, a ligand that subtends an angle of 120°, 1, 3-adamantane-dicarboxylate (ADC) represents another rigid and angular dicarboxylato ligand that can be employed in the construction of novel metal-organic networks. 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 2.16a).

Accordingly one would expect different types of structures can be assembled from ADC and SBU I.

Indeed, single crystals of \{[Zn₂(ADC)₂(Pyridine)₂](MeOH)₂\}₅, 4, were attained by layering a methanolic solution of H₂ADC and pyridine onto a methanolic solution of

Figure 2.16 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).
Zn(NO\textsubscript{3})\textsubscript{2}•6H\textsubscript{2}O that contains nitrobenzene as the template. As illustrated in Figure 2.16, the square SBUs I are double-linked by ADC motifs resulting in 1D architecture of molecular ladder topology (Figure 2.16\textit{b}). 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 π•••π interactions (\(d_{\text{centroid-centroid}} = 4.3\text{ Å}\)). 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 π•••π interaction (Figure 2.16\textit{c}). 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 2.16\textit{d}).

![Figure 2.17 A predicted cylindrical structure (H5) based upon ADC and SBU I.](image)

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 metal-organic networks; c) In principle, other supramolecular isomers of 4 might as well be possible. In fact, a cylindrical structure H5, 1D analogue of 2D tetragonal sheets B, has been proposed (Figure 2.17).

2.4 Metal-organic Networks 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 metal-organic networks 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 determine 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 metal-organic networks, 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 Zn(NO₃)₂•6H₂O 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 2.18a). 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 2.18b).
When replacing benzene with toluene and leaving everything else in the reaction mixture unchanged, colorless crystals of a new form, compound 6 of formula \( \text{[Zn}_2\text{(BDC)}_2(4-\text{PhPy})_4\text{(Toluene)}_2]_\infty \) 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 2.19a). 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 2.19b).

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 close. Retrospectively, therefore, benzene

\[ a \] 

\[ b \] 

Figure 2.19 2D layer structure (a) and its packing (b) in compound 6. Toluene guests are shown in a space-filling mode. Blue box illustrates the divergent fashion in which BDCs link SBUs II.
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 2.20 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 2.20a) 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 2.20b). These complementary hydrogen bonds thus assemble 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 2.20c).

8, \{[\text{Zn}_2(5\text{-OH-BDC})_2(\text{isoquinoline})_3](\text{Benzene})_{1.5}\}_\infty, was isolated when replacing 3,5-lutidine with isoquinoline and the resulting compound bears a close resemblance to 6,

Figure 2.21 2D layer structure (a) and the crystal packing (b) of compound 8.
i.e., a 2D planar sheet. 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 the 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 (Figure2.21a).

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 Experimental

2.5.1 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.

\textit{Synthesis of }[\text{Cu}_2(5-\text{MeO-BDC})_2(\text{MeOH})_x(\text{H}_2\text{O}_{1.83-x})]_{12}, \textbf{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(NO_3)_2•2.5H_2O (23 mg, 0.099 mmol). Typical yield of the reaction is \textit{ca.} 18mg for each vial.

\textit{Synthesis of }[[\text{Cu}_2(5-\text{MeO-BDC})_2(4-\text{MeO-Pyridine})_2](\text{guest})_x]_{\infty}, \textbf{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(NO$_3$)$_2$$\cdot$2.5H$_2$O (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 $\{[Cu_2(5-Br-BDC)_2(MeOH)_2](guest)_x\}_\infty$, 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(NO$_3$)$_2$$\cdot$2.5H$_2$O (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 $\{[Zn_2(ADC)_2(Pyridine)_2](MeOH)_2\}_\infty$, 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 Zu(NO$_3$)$_2$$\cdot$6H$_2$O (149 mg, 0.500 mmol). Colorless crystals appeared at the interlayer boundary after 7 days.

**Synthesis of $\{[Zn_2(BDC)_2(4-PhPy)_4](Benzene)\}_\infty$, 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(NO$_3$)$_2$$\cdot$6H$_2$O (60 mg, 0.20 mmol). Colorless crystals appeared after 7 days.
Synthesis of $\left[\text{Zn}_2(\text{BDC})_2(\text{4-PhPy})_4\right]_2(\text{Toluene})_2\infty$, 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 $\text{Zn(NO}_3)_2\cdot6\text{H}_2\text{O}$ (60 mg, 0.20 mmol). Colorless prism crystals appeared within 3 days.

Synthesis of $\left[\text{Zn}_2(\text{5-OH-BDC})_2(\text{3,5-lutidine})_2\right]_2(\text{Benzene})_2\infty$, 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 $\text{Zn(NO}_3)_2\cdot6\text{H}_2\text{O}$ (297 mg, 1.00 mmol). Colorless needle crystals appeared after 24 hours.

Synthesis of $\left[\text{Zn}_2(\text{5-OH-BDC})_2(\text{isoquinoline})_3\right]_2(\text{Benzene})_{1.5}\infty$, 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 $\text{Zn(NO}_3)_2\cdot6\text{H}_2\text{O}$ (297 mg, 1.00 mmol). Colorless block crystals appeared after 24 hours.

2.5.2 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 ($\lambda = 0.7107$ 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
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 2.3 Crystallographic data for compounds 1–8.

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* The poor quality of X-ray diffraction data for 2 and 4 and their structural refinements only result in reliable structural models and respective cell parameters.
### Compound

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<td>93.4 %</td>
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<td>1.000 and 0.527</td>
<td>1.000 and 0.790</td>
<td>1.000 and 0.846</td>
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<td>3468 / 3 / 337</td>
<td>9024 / 0 / 496</td>
<td>10625 / 0 / 606</td>
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<td>wR² = 0.0932</td>
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<td>R₁ = 0.0570</td>
</tr>
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<td>wR² = 0.4181</td>
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<td>wR² = 0.1002</td>
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<td>Large diff. peak and hole, e·Å⁻³</td>
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<td>2.188 and -1.100</td>
<td>0.821 and -0.446</td>
<td>0.436 and -0.347</td>
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### Other Characterizations

Low resolution X-ray Powder Diffraction (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 and Powder Cell for Windows Version 2.4 (programmed by W. Kraus and G. Nolze, BAM Berlin, © 2000).

Figure 2.22 Experimental and simulated XPD pattern of I.
Chapter 3

Metal-Organic Networks Based upon a More Flexible Dicarboxylate

3.1 Introduction

3.1.1 Rigidity vs. Flexibility

Metal-organic networks, 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. One of the most representative examples, MOF-5, is a highly porous cubic open framework with remarkable thermal stability, which is assembled from SBU III (see Figure 2.2) and 1, 4-benzenedicarboxylate, a rigid and linear building block. 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 metal-organic networks that are integrated with more flexible structural elements.\textsuperscript{94-101} 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.\textsuperscript{102} An elegant example of dynamic metal-organic networks, 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).\textsuperscript{103}

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

In principle, the resilience of metal-organic networks 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 metal-organic networks 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 metal-organic frameworks 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, 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, provides an ideal platform because a systematic analysis of structural parameters can be conveniently realized with the aid of appropriate softwares.

In particular, we are concerned with two prototypal ligands, namely, 4, 4’-bipyridine (4, 4’-bipy) and benzoates/benzoic acids (molecules that contain at least one carboxyl group attached to a benzene ring), since they represent two of the most widely used ligand systems. 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).

In particular, we are concerned with two prototypal ligands, namely, 4, 4’-bipyridine (4, 4’-bipy) and benzoates/benzoic acids (molecules that contain at least one carboxyl group attached to a benzene ring), since they represent two of the most widely used ligand systems. We define torsion angle of 4, 4’-bipy as the dihedral angle between the
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.

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 increase the 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 Networks from Tetrafluoro-1, 3-benzenedicarboxylate (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 metal-organic network 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 systematically investigated a particular compound, namely, tetrafluoro-1, 3-benzenedicarboxylate (TFBDC), a fluorinated version of BDC, to explore its use in the context of metal-organic networks.

The solid state structure of H₂TFBDC reveals that of 1D zigzag chain motifs which are sustained by an array of carboxylic dimers (Figure 3.5). 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
$\pi$•••$\pi$ 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 are identified in those structures.

Figure 3.5 1D zigzag chain structures of the ligand H$_2$TFBDC ($a$) and compound 9 ($b$).
3.2.2 Guest-Dependent Opening/Closing 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, \{Cu₂(TFBDC)₂(quinoline)₂\}_∞, was acquired as green single-crystalline materials from an ethanol solution of Cu(NO₃)₂•2.5H₂O and TFBDC using quinoline as the base and relatively large aromatic molecules (such as toluene and xylenes) as the template. X-ray 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_{centroid-centroid} = 3.665Å) and they therefore engage in fairly strong π-π interactions. Such a short contact,

![Crystal structure and crystal packing of compound 10a.](image)

Figure 3.6 Crystal structure (a) and crystal packing (b) of compound 10a.
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.
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).

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 p-dichlorobenzene instead of toluene or xylenes as the template,
we obtained compound 10b, {{Cu2(TFBDC)2(quinoline)2}(p-dichlorobenzene)0.5}∞, as the
major product. Single-crystal X-ray diffraction suggests that 10b retains a very similar

![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.](image)
2D architecture as 10a, i.e., a distorted tetragonal sheet. In contrast to 10a, however, guest molecules p-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, p-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 2.4Å (6.793Å vs. 4.390Å)! Within the open cavities, each of the crystallographically disordered p-dichlorobenzene molecules is sandwiched by two TFBDCs and the centroid-centroid distance from p-dichlorobenzene to each of the TFBDC rings is 3.397Å, exactly half of the value 6.793Å, indicating perfectly parallel \(\pi\)-\(\pi\) interactions between these aromatic systems. It is perhaps of interest to compare the centroid-centroid distances of the closed cavities in 10b (4.390Å) with those in 10a (3.665Å) and presumably such a discrepancy can be attributed to the structural distortion of 10b which is induced by the presence of p-dichlorobenzene.

The structural deformations caused by p-dichlorobenzene can be further exemplified by the subtle changes of intra-layer and inter-layer interactions among quinolines. Whereas quinolines within each layer still participate in C-H\(\cdots\)\(\pi\) 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 \(\pi\cdots\pi\) (\(d\text{centroid-centroid} = 3.355\)Å and 3.341Å) and C-H\(\cdots\)\(\pi\) bonding (\(D = 3.765\)Å), in contrast to the solo appearance of C-H\(\cdots\)\(\pi\) 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 isolated as single-crystalline product when using chlorobenzene as the crystallization template. This new compound, namely, 10c, with a formula of {[Cu$_2$(TFBDC)$_2$(quinoline)$_2$](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 ($d_{\text{centroid-centroid}} = 4.149\text{Å}$ and $4.652\text{Å}$; 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 in an array of C-H•••π interactions ($D = 3.977\text{Å}$). 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 $\pi\cdots\pi$ stacking ($d_{\text{centroid-centroid}} = 3.927\,\text{Å}$) and C-H$\cdots\pi$ bonding ($D = 3.576\,\text{Å}$ and $3.977\,\text{Å}$), the entrapped chlorobenzene molecules are sandwiched by TFBDC rings from adjacent layers through two-fold $\pi\cdots\pi$ interactions ($d_{\text{centroid-centroid}} = 3.998\,\text{Å}$). Nevertheless, only half of these inter-layer cavities are occupied by chlorobenzene molecules and the other half remain guest-free (Figure 3.9b). Calculations$^{105}$ further suggest a volume of ca. $130\,\text{Å}^3$ for the first type of cavities, in good accordance with the molecular volume of chlorobenzene ($98.5\,\text{Å}^3$),$^{106}$ and a near-zero volume for the second type. One would probably be amazed by the extremely high local molar concentration (ca. $12.8\,\text{M}$) 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

Figure 3.9 The open (a) and closed (b) inter-layer cavities in 10c.
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 room temperature.

Compounds 10a–c therefore represent a prototypal example of metal-organic networks 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 compounds that are based upon the ligand BDC. In contrast to other highly rigid compounds, 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 applications of separation, molecular sensing and storage.

Until now, nevertheless, the following questions concerning the host-guest relationships and the diversity of molecular recognitions remain unanswered: 1) why would 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 \( p \)-dichlorobenzene, the limited space enclosed by each of the inter-layer cavities has eliminated the inclusion of slightly larger \( p \)-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 play a central role in the case of dichlorobenzene while thermodynamic factors are 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 metal-organic networks. 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 un-substituted counterparts.

Since both intra-layer and inter-layer cavities are amenable to investigation in these structures, it is perhaps appropriate to further evaluate the feasibility of using a similar strategy to transform the nature of inter-layer cavities. Quinoline, a relatively large

![Figure 3.10 Three axial ligands of SBU I used for the functionalization of inter-layer cavities.](image)

Figure 3.10 Three axial ligands of SBU I used for the functionalization of inter-layer cavities.
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 molecule), might as well be suited to direct the formation of various inter-layer cavities (Figure 3.10).

Indeed, green crystals of 11, \{[Cu₂(TFBDC)₂(EtOH)₂](EtOH)₂(benzene)\}_∞, precipitate from an ethanol solution containing Cu(NO₃)₂•6H₂O, TFBDC, benzene and 2,6-lutidine. Structural analysis 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 π•••π stacking (Figure 3.11a; \(d_{\text{centroid-centroid}} = 3.481\,\text{Å} \) 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 surfaces of the 2D network. 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 ($d_{\text{oxygen}} = 2.609\text{Å}, 2.817\text{Å}; 2.633\text{Å},$ and $2.980\text{Å}$) are also well within the anticipated range for this type of interactions.

![Figure 3.12 Two hydrogen-bonding motifs occurred between ethanol guests and the frameworks in 11.](image)

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 $\{[\text{Cu}_2(\text{TFBDC})_2(\text{2-picoline})_2(\text{EtOH})_1.3(\text{HFB})]\}_\infty$. 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 $4.281\text{Å}$, in good consistence with those of its analog 10c ($d_{\text{centroid-centroid}} = 4.149\text{Å}$ and $4.652\text{Å}$) but slightly larger than those in 10a ($d_{\text{centroid-centroid}} = 3.665\text{Å}$). 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

![Diagram of crystal structure and packing](image)

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.

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 \((d_{\text{centroid-centroid}} = 3.632\text{Å})\).

In short, in addition to the use of fluorinated ligands as flexible structural ingredients, we have illustrated another compelling strategy that can be employed to manipulate supramolecular structures and functions, i.e., systematically fine-tuning the chemical nature of the surfaces of 2D metal-organic networks. 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 Experimental

3.3.1 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 $[\text{Cu}_2(\text{TFBDC})_2(\text{Pyridine})_4]_{\infty}$, 9*

Compound 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 $[\text{Cu}_2(\text{TFBDC})_2(\text{Quinoline})_2]_{\infty}$, 10a*

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

Compound 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)
mmol) onto 3.5 mL of an ethanol/p-dichlorobenzene solution (2.5:1, v/v) containing Cu(NO$_3$)$_2$$\cdot$2.5H$_2$O (23 mg, 0.10 mmol). Green block crystals formed at the interlayer boundary within 24 hours.

_Synthesis of $\{[\text{Cu}_2(\text{TFBDC})_2(\text{quinoline})_2](\text{chlorobenzene})_{0.5}\}_\infty$, 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$$\cdot$2.5H$_2$O (23 mg, 0.10 mmol). Green block crystals formed at the interlayer boundary within 24 hours.

_Synthesis of $\{[\text{Cu}_2(\text{TFBDC})_2(EtOH)_2](EtOH)_2(benzene)\}_\infty$, 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$$\cdot$2.5H$_2$O (23 mg, 0.10 mmol). Green block crystals formed at the interlayer boundary within 24 hours.

_Synthesis of $\{[\text{Cu}_2(\text{TFBDC})_2(2\text{-picoline})_2](EtOH)_{1.3}(\text{HFB})\}_\infty$, 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$$\cdot$2.5H$_2$O (23 mg, 0.10 mmol). Green block crystals formed at the interlayer boundary within 24 hours.

3.3.2 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 SHELXL 5.1 program package.

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>9</th>
<th>10a</th>
<th>10b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>C18H10CuF4N2O4</td>
<td>C34H14Cu2F8N2O8</td>
<td>C37H16ClCu2F8N2O8</td>
</tr>
<tr>
<td>Formula weight</td>
<td>457.82</td>
<td>857.55</td>
<td>931.05</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>100(2)</td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
<td>Pbea</td>
<td>P-1</td>
</tr>
<tr>
<td>a, Å</td>
<td>19.275(3)</td>
<td>12.2599(9)</td>
<td>11.2399(9)</td>
</tr>
<tr>
<td>b, Å</td>
<td>11.4617(16)</td>
<td>12.1377(9)</td>
<td>12.9837(11)</td>
</tr>
<tr>
<td>c, Å</td>
<td>17.162(2)</td>
<td>21.1716(16)</td>
<td>13.4073(11)</td>
</tr>
<tr>
<td>α, deg</td>
<td>90</td>
<td>90</td>
<td>89.5790(10)</td>
</tr>
<tr>
<td>β, deg</td>
<td>115.903(2)</td>
<td>90</td>
<td>67.1740(10)</td>
</tr>
<tr>
<td>γ, deg</td>
<td>90</td>
<td>90</td>
<td>79.6010(10)</td>
</tr>
<tr>
<td>V, Å³</td>
<td>3410.5(8)</td>
<td>3150.5(4)</td>
<td>1769.5(3)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>(\rho_{\text{calcld}}, \ g/\text{cm}^3)</td>
<td>1.783</td>
<td>1.808</td>
<td>1.747</td>
</tr>
<tr>
<td>(\mu, \ \text{mm}^{-1})</td>
<td>1.353</td>
<td>1.456</td>
<td>1.377</td>
</tr>
<tr>
<td>F(000)</td>
<td>1832</td>
<td>1704</td>
<td>926</td>
</tr>
<tr>
<td>Crystal size, mm</td>
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<td>0.10 x 0.10 x 0.05</td>
<td>0.30 x 0.05 x 0.05</td>
</tr>
<tr>
<td>θ range for data collection, deg</td>
<td>2.13 to 28.27</td>
<td>1.92 to 28.30</td>
<td>1.60 to 28.26</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-24&lt;(h)&lt;20</td>
<td>-15&lt;(h)&lt;9</td>
<td>-16&lt;(h)&lt;14</td>
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<tr>
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<td>-11&lt;(k)&lt;15</td>
<td>-14&lt;(k)&lt;15</td>
<td>-16&lt;(k)&lt;17</td>
</tr>
<tr>
<td></td>
<td>-22&lt;(l)&lt;22</td>
<td>-27&lt;(l)&lt;28</td>
<td>-17&lt;(l)&lt;17</td>
</tr>
<tr>
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<td>18652</td>
<td>15388</td>
</tr>
<tr>
<td>Unique reflections</td>
<td>3941</td>
<td>3743</td>
<td>7977</td>
</tr>
<tr>
<td>R(int)</td>
<td>0.0543</td>
<td>0.0559</td>
<td>0.0327</td>
</tr>
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<td>Completeness to θ</td>
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<td>95.5 %</td>
<td>91.1 %</td>
</tr>
<tr>
<td>Absorption correction</td>
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<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>1.000 and 0.857</td>
<td>1.000 and 0.808</td>
<td>1.000 and 0.920</td>
</tr>
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<td>Data/ restraints/ parameters</td>
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<td>3743 / 0 / 244</td>
<td>7977 / 0 / 550</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>1.061</td>
<td>1.089</td>
<td>1.026</td>
</tr>
<tr>
<td>Compound</td>
<td>10c</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>----------</td>
<td>-----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>C37H16Cl0.50Cu2F8N2O8</td>
<td>C30H30Cu2F8O12</td>
<td>C31H21.50Cu2F8.50N2O9.25</td>
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<tr>
<td>Formula weight</td>
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<td>858.58</td>
</tr>
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<td>Temperature, K</td>
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<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
<td>P21/n</td>
<td>P21/n</td>
</tr>
<tr>
<td>a, Å</td>
<td>11.3895(11)</td>
<td>13.2869(10)</td>
<td>13.0006(14)</td>
</tr>
<tr>
<td>β, Å</td>
<td>12.7032(12)</td>
<td>13.5884(11)</td>
<td>12.9131(13)</td>
</tr>
<tr>
<td>c, Å</td>
<td>13.2957(13)</td>
<td>19.2207(15)</td>
<td>20.042(2)</td>
</tr>
<tr>
<td>α, deg</td>
<td>89.200(2)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β, deg</td>
<td>69.464(2)</td>
<td>103.6920(10)</td>
<td>103.889(2)</td>
</tr>
<tr>
<td>γ, deg</td>
<td>78.878(2)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V, Å³</td>
<td>1764.6(3)</td>
<td>3371.6(5)</td>
<td>3266.2(6)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>ρcalcd, g·cm⁻³</td>
<td>1.719</td>
<td>1.697</td>
<td>1.746</td>
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<tr>
<td>μ, mm⁻¹</td>
<td>1.343</td>
<td>1.367</td>
<td>1.409</td>
</tr>
<tr>
<td>F(000)</td>
<td>909</td>
<td>1744</td>
<td>1720</td>
</tr>
<tr>
<td>Crystal size, mm</td>
<td>0.50 x 0.40 x 0.20</td>
<td>0.10 x 0.10 x 0.02</td>
<td>0.20 x 0.10 x 0.04</td>
</tr>
<tr>
<td>θ range for data collection, deg</td>
<td>1.64 to 28.27</td>
<td>1.69 to 28.26</td>
<td>1.70 to 27.50</td>
</tr>
<tr>
<td>Limiting indices</td>
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<td>-15&lt;=h&lt;=17</td>
<td>-16&lt;=h&lt;=16</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>15312</td>
<td>20876</td>
<td>19720</td>
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<td>Unique reflections</td>
<td>7939</td>
<td>7877</td>
<td>7389</td>
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<td>R(int)</td>
<td>0.0416</td>
<td>0.0581</td>
<td>0.0940</td>
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<tr>
<td>Completeness to θ</td>
<td>90.7 %</td>
<td>94.3 %</td>
<td>98.6 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>1.00 and 0.824</td>
<td>1.00 and 0.842</td>
<td>?</td>
</tr>
<tr>
<td>Data/ restraints/ parameters</td>
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<td>7877 / 0 / 483</td>
<td>7389 / 1 / 451</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.036</td>
<td>1.024</td>
<td>0.923</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0. 0539</td>
<td>R1 = 0. 0532</td>
<td>R1 = 0. 0565</td>
</tr>
<tr>
<td>wR2 = 0. 1258</td>
<td>wR2 = 0. 1148</td>
<td>wR2 = 0. 1152</td>
<td></td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0. 0740</td>
<td>R1 = 0. 0865</td>
<td>R1 = 0. 1124</td>
</tr>
<tr>
<td>wR2 = 0. 1370</td>
<td>wR2 = 0. 1286</td>
<td>wR2 = 0. 1271</td>
<td></td>
</tr>
<tr>
<td>Large diff. peak and hole, e·Å⁻³</td>
<td>0.997 and -0.494</td>
<td>0.980 and -0.826</td>
<td>0.669 and -0.661</td>
</tr>
</tbody>
</table>
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 2θ 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.
Chapter 4

Conclusions and Future Directions

4.1 Summary and Conclusions

The research presented in this thesis is primarily concerned with developing an in-depth understanding of the basic principles that govern the supramolecular behaviors of metal-organic networks and gaining an experimental control over the structure and function of these new classes of hybrid materials. In particular, this work has contributed to the rationalization of supramolecular isomerism, a phenomenon referred to the existence of more than one type of superstructure from the same set of molecular building blocks, and the functionalization of prototypal metal-organic materials. To summarize, we have illustrated the following aspects:

i) Under various conditions, the self-assembly of rigid and angular ligand 1, 3-benzenedicarboxylate (BDC) and Cu(II)/Zn(II)-based paddle-wheel secondary building units (SBUs), a dimetal tetracarboxylate, which can be viewed as a molecular square, generates a wide array of metal-organic networks 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.
In addition, the employment of two geometric principles, namely, node-and-spacer and VLPP approaches, and the use of rigorous topological descriptions, such as vertex symbols and coordination sequences, have significantly facilitated the recognition, interpretation, and prediction of complicated metal-organic network structures.

ii) Other angular ligands, such as 1, 3-adamantane dicarboxylate (ADC), also self-assemble with paddle-wheel square SBUs to give rise to some novel structures including 1D ladder topology. These results, along with those already mentioned in i), highlight the myriad possibilities of linking square building units.\textsuperscript{107} 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.\textsuperscript{72-73,79,108} 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 2.12 for an example of tetrahedral frameworks illustrated in a square fashion), and \textit{vice versa}. If taking into account the numerous examples of tetrahedron-based zeolite nets, \textsuperscript{81} 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.\textsuperscript{109} 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 \textit{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) The introduction of fluorine atoms to BDC moieties has been shown to lead 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 networks 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 hasn’t been observed in the original un-fluorinated 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 of adjusting 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.

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

4.2 Future Directions

Although it was deliberately intended that a focus on design and structural aspects would be placed upon the main body of this thesis, as is limited by the scope of this document, it is the function of solids that should be driving the field of crystal engineering and metal-organic networks into its next level of advancements. Specifically, interfacing with other cutting-edge areas, such as materials science, bio-sciences and nanotechnology, is rapidly becoming and will continue to be a main theme in the coming decades.

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{110} 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.
References


2. A Oxford English Dictionary (online version, [http://www.oed.com/](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).


60. Hennigar, T. L.; MacQuarrie, D. C.; Losier, P.; Rogers, R. D.; Zaworotko, M. J. 


92. Vertex symbol for the sodalite net: 4•4•6•6•6•6.

93. Vertex symbol for the PtS net: (4•4•8•8•8•8)( 4•4•8•8•8•8).


104. ConQuest Version 1.8, Copyright CCDC, 2006.


