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Structural diversity in metal-organic nanoscale supramolecular architectures

Heba, Abourahma

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Structural Diversity in Metal-Organic Nanoscale Supramolecular Architectures

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy
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To Lamees for her never ending encouragement and support and for her positive attitude in life
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<thead>
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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>4-pic = 4-picoline</td>
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</tr>
<tr>
<td>5-NO2-bdc = 5-Nitrobenzene-1,3-dicarboxylate</td>
<td></td>
</tr>
<tr>
<td>5-NO2-H2bdc = 5-Nitroisophthalic acid</td>
<td></td>
</tr>
<tr>
<td>5-OEt-bdc = 5-Ethoxybenzene-1,3-dicarboxylate</td>
<td></td>
</tr>
<tr>
<td>5-OEt-H2bdc = 5-Ethoxyisophthalic acid</td>
<td></td>
</tr>
<tr>
<td>5-OH-bdc = 5-Hydroxybenzene-1,3-dicarboxylate</td>
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<td>5-OH-H2bdc = 5-Hydroxyisophthalic acid</td>
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<td>5-OPr-bdc = 5-Propoxybenzene-1,3-dicarboxylate</td>
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<td></td>
</tr>
<tr>
<td>5-ph-bdc = 5-Phenylbenzene-1,3-dicarboxylate</td>
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</tr>
<tr>
<td>5-ph-H2bdc = 5-Phenylisophthalic acid</td>
<td></td>
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<tr>
<td>AFM = Atomic force microscopy</td>
<td></td>
</tr>
<tr>
<td>Bdc = Benzene-1,3-dicarboxylate</td>
<td></td>
</tr>
<tr>
<td>CSD = Cambridge structural database</td>
<td></td>
</tr>
<tr>
<td>DMF = Dimethylformamide</td>
<td></td>
</tr>
<tr>
<td>DMSO = Dimethylsulfoxide</td>
<td></td>
</tr>
<tr>
<td>ES FT-ICR = Electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry</td>
<td></td>
</tr>
</tbody>
</table>
ES-MS = Electrospray mass spectrometry
Et = Ethyl
EtOAc = Ethylacetate
EtOH = Ethanol
H$_2$bdc = Isophthalic acid
H$_3$TMA = Trimesic acid
MeCN = Acetonitrile
MeOH = Methanol
NMR = Nuclear magnetic resonance
nSBU = Nanoscale secondary building unit
pdc = 1-Methylpyrole-2,4-dicarboxylate
Ph = Phenyl
py = pyridine
SBU = Secondary building unit
TGA = Thermal gravitational analysis
TG-MS = Thermal gravitational-mass spectrometry
THF = Tetrahydrofuran
TLC = Thin layer chromatography
XPD = X-ray powder diffraction
Supramolecular synthesis has gained much attention in recent years. Such an approach to synthesis represents an attractive alternative to traditional, multi-step synthesis, especially for making complex, nanoscopic structures. Of particular interest, in the context of this work, is the use of metal-organic interactions to direct the self-assembly of nanoscopic architectures. These interactions are highly directional, relatively “strong” (compared to other supramolecular interactions) and kinetically labile, which allows for “self-correction” and in turn the production, often in high yield, of defect-free products. This also means that a number of related, yet structurally diverse products (supramolecular isomers) could be isolated.

The work presented herein demonstrates the supramolecular synthesis of related, yet structurally diverse family of metal-organic nanoscale supramolecular architectures that are based on the ubiquitous paddle-wheel dimetal tetracarboxylate secondary building unit (SBU) and angular dicarboxylate ligands. It also demonstrates that the SBU self-assembles into clusters of four (tetragonal) and three (trigonal) nanoscale secondary building units (nSBU), which further self-assemble into nanoscale structures that include discrete (0D) faceted polyhedra, tetragonal 2D sheets and another 2D sheet that conforms
to the so-called Kagomé lattice. In addition, the work herein demonstrates that synthesis under thermodynamic equilibrium conditions facilitates “self-correction” so that the most stable thermodynamic product is obtained. Synthesis, characterization and crystal structure analysis of these structures is presented herein.
Chapter 1

INTRODUCTION

1.1 Supramolecular Chemistry

Supramolecular chemistry, which has its roots in biological systems, was defined by Lehn as the chemistry beyond the molecule. The concepts of supramolecular chemistry are derived from biology and rely on the phenomena of molecular recognition and self-assembly: molecules recognize complementary sites (functionality, geometry, size, etc.) on other molecules and associate into larger entities, supermolecules, via weaker, non-covalent interactions such as hydrogen bonding and π-π stacking interactions. The phenomenon of molecular association has been long recognized and the term “Übermoleküle” i.e. supermolecule was introduced as early as 1930s to describe highly organized assemblies that result from the association of units. The application of the concepts of supramolecular chemistry to synthesis, however, is a recent phenomenon. Such an approach to synthesis presents an attractive alternative to traditional, multi-step synthesis. The latter, although very useful for the synthesis of relatively small organic molecules, is intrinsically limited, especially for the synthesis of complex nanoscale architectures. In addition to being time consuming and overall low yielding, defected products are difficult to fix because of the kinetic inertness of the
covalent bond. Supramolecular synthesis, on the other hand, can be accomplished in a one-pot reaction. Upon combining the appropriate building blocks, they spontaneously self-assemble into a well-defined supramolecular architecture under thermodynamic equilibration. In addition, since supramolecular interactions are specific and kinetically labile, defect-free products are obtained in a single step, often in high yield. Consequently, there has been a wide shift towards the use of this synthetic approach to building nanoscale architectures over the last decade as it offers the possibility of preparing compounds with complexity nearing those of biological systems. Various supramolecular interactions have been exploited including hydrogen bonding, coordinate covalent bonds, electrostatic and charge transfer interactions and aromatic π-stacking interactions. The directionality and reliability of the hydrogen bond and the coordinate covalent bond resulted in the two being perhaps the most widely used interactions in supramolecular synthesis.

1.2 Crystal Engineering

Crystal engineering is the application of the supramolecular concepts of self-assembly to the design and synthesis of functional solids. The term “crystal engineering” was first introduced in 1955 by Pipensky. Schmidt’s work in topochemistry then showed that crystals can be thought of as supramolecular assemblies that result from a series of molecular recognition events and self-assembly. The work of Etter and Desiraju in the 1980s, which focused on using the Cambridge Structural Database (CSD) to analyze, interpret and design non-covalent bonding patterns, specifically hydrogen bonding in organic solids, developed the field further. Desiraju later introduced
the concept of “supramolecular synthon”,\textsuperscript{15} which resulted in the wide spread of supramolecular synthesis via hydrogen bonding interactions. Although the beginnings of crystal engineering were mainly concerned with organic molecules, the field today encompasses additionally organometallics\textsuperscript{20} and coordination compounds.\textsuperscript{6,7}

Self-assembly via coordination, or “metal-directed”\textsuperscript{6} self-assembly provides a highly attractive supramolecular synthetic approach. The coordination bond is a relatively strong bond (10-30 kcal/mol) compared to other non-covalent interactions (0.7-10 kcal/mol) and in turn is kinetically stable. Yet, it is thermodynamically labile, which facilitates “self-correction”.\textsuperscript{6,7} A bond that forms incorrectly can dissociate and re-associate correctly leading to a defect-free product. In addition, incorporation of transition metals into the supramolecular structure may have important implications for the chemical reactivity or physical properties of the superstructure such as color, Lewis acidity, magnetism, redox activity and luminescence.\textsuperscript{21} Furthermore, the wide range of available transition metals with various geometries can be “mixed-and-matched” with a variety of coordinating ligands to tailor-make products with specific shapes, sizes and properties. Since coordination compounds necessarily consist of at least two components, they are inherently modular.\textsuperscript{22} Modularity leads to structural diversity since the same type of network can be obtained for a number of different metals and organic ligands. Consequently, supramolecular synthesis via the modular approach is powerful as it facilitates fine-tuning of structural and functional features by careful selection the molecular building blocks.

The concept of spontaneous self-assembly of molecular components into a desired superstructure is highly appealing; however, it must be acknowledged that a number of
factors influence the self-assembly process and ultimately product formation. These include solvent effect, concentration, pH, possible formation of kinetic products, and the presence of sterically or electronically demanding functional groups on the substrates.\(^7\) This can be viewed as an opportunity to generate a number of related, yet structurally diverse networks from the same set of building blocks by controlling the factors that affect the reaction. Zaworotko \textit{et al.} has coined the term “supramolecular isomerism” to describe structurally related supermolecules that result from different arrangement of the same molecular components in the solid state.\(^{10,12,23}\)

1.3 Supramolecular Isomerism

Just as atoms can combine in different ways on the molecular level and give rise to molecular isomerism, molecular components of a modular system can combine in different ways to give rise to supramolecular isomerism. Structural diversity, be it by varying the molecular components or varying the architecture or topology (architectural isomerism)\(^{24}\) of the superstructure, results in diversity in the bulk physical properties such as magnetism, optical activity, polarity, porosity and robustness. For example, 3D structures would be expected to be zeolite-like structures and have rigidity and porosity,\(^{25-27}\) whereas 2D structures are expected to behave as clay-mimics intercalating guest molecules between their layers.\(^{12,28}\) 1D structures would be expected to have variability in close-packing in the context of how close the chains pack with respect to one another,\(^{29}\) whereas for 0D (discrete) structures one would expect monodispersity and solubility. Of course, the number of supramolecular isomers possible from a set of building blocks is limited by the number of rational superstructures that can be generated.
from the molecular components present in a network. We can classify supramolecular isomerism, just as one would for molecular isomerism, into the four following categories.

1.3.1 Structural Isomerism

![Scheme 1.1 Schematic illustration of supramolecular superstructures obtained to date from the a T-shape node and a linear spacer](image)

(a) 1D ladder, (b) 2D brick wall, (c) 2D herringbone, (d) 3D Lincoln Logs, (e) another 3D framework, (f) 2D bilayer

This type of isomerism arises when the molecular components of a system arrange in a number of different ways in the solid state. Scheme 1.1 illustrates the diversity in the supramolecular superstructures obtained to date from the combination of a T-shape node, which could be a mer-substituted octahedral metal or a trisubstituted square planar metal moiety, and a linear spacer: (a) ladder, (b) brick wall, (c) herringbone, (d) 3D frame of “Lincoln Logs”, (e) another 3D frame and (f) 2D bilayer. Three of the isomers, the ladder, the bilayer, and the 3D frame have
been observed for the asymmetric unit resulting from Co(NO₃)₂ as the metal and bipy as the linear ligand, whereas the other three have been seen in similar compounds that utilize bipy or an extended analogue as the linear spacer. It is apparent from the schematic that these structures would have dramatically different chemical and physical properties.

1.3.2 Conformational Isomerism

This type of isomerism is possible, when the organic ligand is flexible. Such isomerism is observed, for example, in the crystal structures obtained from 1,2-bis(pyridyl)ethane (bipy-eta), which can adopt two conformations: gauche or anti. This can lead to subtle changes in the crystal structure. For example, when Co(NO₃)₂ and bipy-eta are crystallized from chloroform, bipy-eta adopts the anti conformation and a ladder structure containing six chloroform molecules per cavity results. However, when a different crystallization solvent is used, such as MeCN or dioxane, a bilayer architecture is obtained where both conformations are observed: two anti- and one gauche-spacer ligand per metal. Conformational polymorphism is a closely related subject. 5-Methyl-2-[(2-nitrophenylamino)]-3-thiophenecarbonitrile is known to crystallize in at least six polymorphic phases that differ in the angle between the thiophene moiety and the o-nitroaniline fragment, which varies from 21.7° to 104.7°. This is a dramatic illustration of how the conformational flexibility can influence crystal packing in organic compounds.
1.3.3 Catenane Isomerism

This type of isomerism is often observed in crystal structures of supermolecules that have large cavities. In the desire of the structure to close-pack and avoid open cavities, independent frameworks generally interpenetrate one another. In the context of coordination polymers, Batten and Robson have published a thorough review on the subject.\textsuperscript{47} It is becoming obvious that one can control the generation of either the open framework or the interpenetrated isomer by the use of appropriate template molecules. For example, the diamondoid network based on Cd(CN)\textsubscript{2}\textsuperscript{48} and square grids based on M(bipy)\textsubscript{2}X\textsubscript{2} have been prepared as both catenated and open framework\textsuperscript{49} forms upon use of appropriate templates. In the context of organic molecules, trimesic acid, H\textsubscript{3}TMA, is perhaps the prototypical example. Pure H\textsubscript{3}TMA\textsuperscript{50} is known to self-assemble via H-bonding into 2D honeycomb grid with cavities of ca. 1.4 nm in diameter. Three phases of H\textsubscript{3}TMA have been characterized to date: two interpenetrated and one open framework. In one of the interpenetrated structures, the honeycomb grid is puckered and interpenetrated by two other independent networks (3-fold interpenetration).\textsuperscript{50,51} There still exist small cavities that host guest molecules. In the other interpenetrated form of H\textsubscript{3}TMA the sheets are flat and contain 1D channels. The open framework structure of H\textsubscript{3}TMA is obtained when it is crystallized in the presence of a long chain alkane.\textsuperscript{51,52}

1.3.4 Optical Isomerism

Chirality in crystals can result by one of at least four ways:\textsuperscript{10} (1) crystallization of achiral building blocks into a chiral space group, (2) building a chiral framework from
achiral building blocks, (3) presence of chiral guest molecules in an achiral host framework built from achiral building blocks, (4) an achiral framework built from achiral building blocks and hosts achiral guest molecules. This type of supramolecular isomerism is highly relevant to spontaneous resolution of chiral solids.53-59

1.4 Coordination Polymers

Coordination polymers represent an ideal example where the supramolecular concepts of self-assembly have been applied to crystal engineering. For the design and synthesis of coordination polymers, the “Wellsian” approach60 is widely practiced. Wells, whose work focused on inorganic networks,61 defined crystal structures in terms of their topology by reducing them to a series of points (nodes) of certain geometry (tetrahedral, trigonal planar, etc.) that are connected to a fixed number of other points. The resulting structures, which can also be calculated mathematically, can either be 1-, 2- or 3-D periodic nets. Robson and co-workers62 later expanded Wells’ work on inorganic network structures into the realm of metal-organic coordination polymers, which facilitated the rapid development of the field. The “node and spacer” approach has been exceptionally successful in producing predictable network architectures. The “node” is typically a transition metal, whereas the “spacer” is typically an organic ligand that propagates the node. Scheme 1.2 illustrates some of the simplest architectures that can be generated using commonly available metal moieties and linear organic spacer ligands.
A number of features are apparent from the scheme: the structures are all modular consisting of at least two components; the dimensionality of the resulting superstructure is dependent on dimensionality of the node; the structures inherently contain voids which leads to porosity. In principle, these network structures can be regarded as blueprint for the construction of networks from a diverse range of chemical components, provided the components are predisposed to self-assembly. Examples of coordination polymers are presented below.

### 1.4.1 Examples of 3D Structures

The two most common types of 3D structures are the diamondoid and octahedral networks, both of which have precedence in nature. The former is generated from
tetrahedral nodes, whereas the latter is generated from octahedral nodes. The diamondoid networks reported by Robson in the 1990s, \(^{63-66}\) based on a tetrahedral metal node (Zn or Cd) and a linear spacer (CN\(^-\) ligand), are the prototypical examples of metal-organic diamondoid networks. Both structures are 2-fold interpenetrated, but the Cd(CN)\(_2\) structure was also obtained as non-interpenetrated open framework in the presence of CCl\(_4\), which fits snugly inside the cavity preventing interpenetration.\(^{67}\) The two Cd(CN)\(_2\) networks could be considered catenated and non-catenated supramolecular isomers of each other. Following Robson’s report, a number of modular diamondoid networks were reported with interpenetration (2-, 3-, 4-, 5-, 7-, or 9-fold) being observed in all cases.\(^{68-71}\) Octahedral networks have been known and studied for a long time and are exemplified by iron cyano compounds. X-ray studies\(^{72}\) of Berlin Green [Fe\(^{III}\)Fe\(^{II}\)(CN)\(_6\)], Prussian blue, [KFe\(^{II}\)Fe\(^{III}\)(CN)\(_6\)] and Turnbull’s Blue, [K\(_2\)Fe\(^{II}\)-Fe\(^{II}\)(CN)\(_6\)] revealed that the metal acts as an octahedral node that is linked by the linear CN\(^-\) ligand. These three networks are isostructural differing only in the amount of K\(^+\) included in the structure and the oxidation state of the iron ion. The first synthetic metal-organic octahedral networks were reported in 1995. Ionic\(^{73}\) and neutral\(^{74}\) examples of the octahedral network were reported with different metal ions and different length organic spacer. Octahedral networks, which are less common relative to their diamondoid counterparts, have great potential as porous materials.\(^{25}\) This is highlighted by a recent report of an octahedral network, Zn\(_4\)O(BDC)\(_3\),\(^{75}\) which has an unprecedented porosity in a crystalline solid and remarkable stability to loss of guest even when heated to temperatures above 300 °C. A number of other types of 3D networks that do not have precedence in nature have also been prepared. One strategy to obtain such 3D structures is by “pillaring” 2D structures.
Effectively, in this synthetic strategy a vertical linker is used to connect 2D sheets together resulting in 3D frameworks.\textsuperscript{24,76-80} Another strategy is to cross-link infinite 1D chains via metal-metal bonds into 3D “Lincoln Log” structures. Examples of the latter exhibit 3-fold interpenetration, yet they are open enough to facilitate ion exchange of loosely bound nitrate anions.\textsuperscript{38,39}

1.4.2 Examples of 2D Structures

The most common topology of 2D structures is the square grid. This topology has been reported for a variety of metals and linear bifunctional ligands. The first reported 2D grids were based on cyano ligands.\textsuperscript{81-84} Today, a wide range of spacer ligands with variable lengths such as pyrazines,\textsuperscript{85-87} bipyridine\textsuperscript{32,74,88-92} and extended bipyridines\textsuperscript{90,93} have been used to generate square grids with different size cavities. Square grids are clay mimics and are capable of intercalating guest molecules between the grids, but additionally they can intercalate guest molecules in the square cavities present in the plane of the grid.\textsuperscript{10,94} Other possible 2D structures are illustrated in scheme 1.3, all of which are based on a T-shaped node: a) brick wall, b) herringbone, c) bilayer, d) long and short brick, and e) basket weave.
It is interesting to note that three of the topologies illustrated in scheme 1.3(a-c) have already been obtained synthetically and perhaps it is only a matter of time before the remaining two are obtained. The honeycomb topology is another example of a 2D net that is commonly observed in organic structures, but rarely observed in coordination polymers. This is because of the wide availability of trigonal organic nodes such as trimesic acid (benzene-1,3,5-tricarboxylic acid), and the rarity of trigonal and trigonal bipyramidal metal geometries. One example of a honeycomb coordination polymer is the crystal structure of $[\text{Cu(pyrazine)}_{1.5}]\text{BF}_4$\textsuperscript{95} which is based on trigonal Cu(t). More honeycomb coordination polymers should be expected in the future as a large number of organic ligands with trigonal geometry have been reported in recent literature.\textsuperscript{6,96-102}
1.4.3 **Examples of 1D Structures**

These can be obtained from any metal geometry, but require a ditopic coordinating ligand. Scheme 1.4 illustrates two possible examples of 1D coordination polymers, the zigzag chain and the helix. The zigzag chain is widely encountered, whereas the helix remains rare for coordination polymers. The helix is particularly interesting because of its inherent chirality. Another example of a 1D structure is the ladder motif (scheme 1.1(a)), which can be obtained from a T-shaped node and a linear spacer. The ladder is fundamentally different from the chain and the helix in that it contains cavities that can host guest molecules.

![Scheme 1.4 1D structures based on a 90° angular node and a linear spacer](image)

(a) zigzag chain, (b) helix. The two structures could be considered supramolecular isomers

1.4.4 **Examples of 0D (Discrete) Structures**

Although clearly not infinite polymers, it is appropriate to include 0D structures in this discussion because of their conceptual relevance to the “Wellsian”\(^{60,103}\) approach. Recent years have witnessed increased number of reports of discrete 0D structures
(metallocycles) with shapes that approximate regular polygons such as triangles, squares, pentagons and hexagons and more complex polyhedra (regular Platonic and semi-regular Archimedean). Polyhedral structures are known in naturally occurring systems such as zeolites (Linde A is based on the edge-skeleton of fused truncated octahedral)\textsuperscript{104} and in biological self-assembled systems such as mammalian picornaoviruses\textsuperscript{105-109} and proteins.\textsuperscript{110} Three general design strategies have been outlined in the literature for the synthesis of 0D structures these include the “molecular library model”,\textsuperscript{96} the “symmetry interaction model” and the “weak-link model”.\textsuperscript{111}

The “molecular library model” presents a reliable system for predetermining the shape of the resulting discrete polygon or polyhedron by geometrical consideration of the molecular building blocks. For example, to construct a molecular triangle one could combine three linear spacers with three complementary, angular, ditopic ligand ($\theta = 60^\circ$). A molecular square could be assembled in a number of different ways: from the self-assembly of two complementary angular ditopic ligands ($\theta = 90^\circ$) in 1:1 ratio, or from the self-assembly of angular ditopic ligands ($\theta = 90^\circ$) with complementary linear spacers in 1:4 ratio. The same strategy could be applied to making the more complex polyhedra, but obviously in this case tritopic ligands must be employed. For example, a dodecahedron (a Platonic solid) could be prepared from the self-assembly of twenty angular tritopic ligands ($\theta = 109.5^\circ$) with thirty linear spacers. The geometry of the metal node is controlled by using chelating ligands or “directing ligands”, which block some sites on the metal and make available ones that lead to the desired geometry. This approach was first applied by Verkade,\textsuperscript{112} then elaborated by Fujita,\textsuperscript{102} and finally systematized by Stang.\textsuperscript{96,113} It is a powerful approach because of its modularity, which
facilitates the generation of the same architecture from a variety of building blocks that have the appropriate geometries, in addition to facilitating the generation of a number of architectures from one building block upon combining it with different complementary ones. For example, the same angular ditopic ligand ($\theta = 120^\circ$), could be used to generate a rhomboid, a pentagon and a hexagon upon combining it with complementary angular ditopic ligands with angles of 60°, 120° and 180°, respectively.

The “symmetry interaction model” employs multibranched chelating ligands and transition metals that are ligated by weakly coordinating ligands. The inherent symmetry of the coordination sites drives the formation of a desired supramolecular shape. This strategy is widely used by Saalfrank,\textsuperscript{114} Lehn\textsuperscript{115,116} and Raymond\textsuperscript{97,117} who reported a number of elegant structures including tetrahedra, cylinders, prisms and helicates via this method.

The “weak-link model”\textsuperscript{111} employs as starting materials flexible ligands and transition metal complexes that are free of blocking ligands. The formation of the desired product is preceded by the formation of an intermediate metal complex which is ligated by hemilabile ligands. As the ligands leading to the final product are introduced, they replace the weak hemilabile ligands resulting in the formation of the desired product.

It is interesting to note that a number of discrete structures reported to date are highly complex and nanometric, \textit{i.e.} have dimensions in the nanometer region. Such structures with high complexity would have not been readily feasible via traditional synthetic approaches. Few examples of such structures will be presented for illustrative purposes.
1.4.4.1 Polygons

The simplest of the polygons is the triangle. There are relatively few examples of molecular triangles in the literature. Fujita et al.\textsuperscript{118} reported molecular triangles made with capped Pd corners and linear organic spacers with variable lengths. Studies showed that this triangle is in equilibrium with the corresponding molecular square. Chan et al.\textsuperscript{118} reported luminescent molecular triangles that are obtained by combining wide angle molecular ligands ($\theta=150^\circ$) with angular ditopic metal nodes ($\theta=90^\circ$). Cotton et al.\textsuperscript{119} recently reported an example of a molecular triangle that is based on capped diruthenium tetracarboxylate building units.

Molecular squares are the most widely studied molecular polygons. The groups of Fujita,\textsuperscript{118} Stang\textsuperscript{96,120} and Hupp\textsuperscript{121-123} have contributed considerably in this area and a number of review articles have appeared concerning the subject. The molecular square is enthalpically favored as it is not strained and consequently some of the reported molecular triangles are found in equilibrium with their square counterparts. Molecular squares are generally prepared from a ditopic angular ligand ($\theta=90^\circ$), typically a metal complex, and a linear spacer. It is therefore not surprising that the square planar Pd and Pt metals are the most exploited in making molecular squares. Cotton et al.\textsuperscript{119} also reported a molecular square isomer of the triangle based on diruthenium tetracarboxylates. Molecular squares could be considered supramolecular isomers of the infinite 1D zigzag chain and helix obtained from a 90° angle node and a linear spacer.

Few examples of molecular pentagons\textsuperscript{124-126} and hexagons\textsuperscript{124,126-129} have been reported to date.
1.4.4.2 Polyhedra

The regular Platonic and semi-regular Archimedean polyhedra have been widely studied in recent years and a number of review articles describing molecular versions of such polyhedra have appeared in the literature. Figure 1.1 illustrates the five Platonic and thirteen Archimedean polyhedra. In both types of polyhedra, a convex structure results from molecular polygons sharing edges. In Platonic solids, only one type of polygon exists in each polyhedron. For example, the cube results from the edge-sharing of squares whereas the tetrahedron results from the edge-sharing of triangles. The Archimedean solids, on the other hand, result from more than one type of polygon sharing edges to yield the convex solid. All of the Archimedean solids are derived from the Platonic solids by truncation or twisting.

![Polyhedra Diagram](image)

**Figure 1.1** Platonic (regular) and Archimedean (semi regular) solids
Molecular versions of such polyhedra have been made via self-assembly of molecular components using non-covalent interactions including hydrogen bonding and metal-organic covalent bonding. Atwood et al\textsuperscript{131} reported the synthesis and crystal structure of a neutral nanometric spheroid that conforms to a snub cube, an Archimedean solid, and results from the self-assembly of six calix[4]resorcinarenes and eight water molecules via 60 H-bonding interactions. Stang et al\textsuperscript{132} reported the synthesis of the wire-frame of a dodecahedron, a Platonic solid, via 60 metal-ligand interactions of 50 components: 20 angular tritopic ligands of tri(4’-pyridyl)methanol and 30 linear ditopic ligands of bis[4,4’-(\textit{trans}-Pt(PR\textsubscript{3})\textsubscript{2}OTf)]arene (R = Et, Ph and arene = benzene, biphenyl). The estimated diameters of the two derivatives of the dodecahedron are 5.5 and 7.5 nm, respectively. Fujita et al\textsuperscript{98} reported the self-assembly of 18 Pd(II) ions and 6 triangular ligands (1,3,5-tris(3,5-pyrimidyl)benzene) into a nanoscale tetrahedral capsule all the faces of which are closed. A common feature to all these nanometric-sized, highly complex structures is that they result from the self-assembly of simple starting materials that are an order of magnitude smaller.

1.5 Nanochemistry and Nanotechnology

Nanotechnology is a multidisciplinary field that encompasses chemistry, physics, biology and engineering. It is concerned with entities with dimensions in the 1-100 nm regions. This field has gained lots of attention in recent years for what it promises in revolutionizing many existing industries. Miniaturization is a key feature for this modern technology. A top-down approach that allows the manipulation of matter at a small level using methods such as photo- and electron-beam lithography is used, largely, by
However, this approach has its intrinsic limitations. An alternative and promising approach is the “bottom-up” approach utilized by chemists. The unique ability of chemists to manipulate molecules via synthesis puts them in an ideal position to develop bottom-up strategies to building nanoscale molecules. This is a challenging task, but success has already been reported. A number of fascinating organic, metal-organic and inorganic structures, discrete and infinite, have been reported to date.

### 1.6 Characterization of Nanoscale Architectures

With the advances made in the design and synthesis of nanoscale architectures, the formation of such structures has become more manageable. The biggest challenge, however, remains in the characterization of such structures, particularly the discrete self-assembled structures. Multinuclear NMR spectroscopy can provide useful data for monitoring the formation of the final product by monitoring the chemical shifts characteristic of metal-ligand interactions. However, it fails to provide adequate data in the case of highly symmetrical structures. In addition, if the superstructure is based on paramagnetic metals such as d⁹ Cu(II), this technique becomes obsolete. Mass spectrometry has become a widely used tool for the characterization of such systems. Electrospray mass spectrometry (ES-MS) in particular, with its soft ionization conditions results in highly charged systems that allow for the determination of m/z ratio with an isotopic distribution patterns. However, the high dilution conditions typically required for ES-MS coupled with the lability of the metal-ligand bond can affect the thermodynamic equilibrium and result in the formation of entropically favored smaller
assemblies. X-ray crystallography presents an ideal characterization technique; however, since most of the large self-assembled structures are spheroids, they do not pack efficiently in the crystal lattice making it difficult to grow single crystals suitable for this technique and hindering taking full advantage of it. Moreover, the cavities in these structures and the interstitial space between the spheroids are typically filled with solvent and/or counter ions, making the handling of the crystals difficult and the refinement of the structure challenging because of disordered or non-located solvent and counterions.

1.6 Scope and Focus

1.6.1 Scope

We have focused our research efforts on the paddlewheel dimetal tetracarboxylate cluster $[M_2(RCO_2)_4(L)_2]$ illustrated in Figure 1.2. The cluster results from four $\mu_2$-bridging carboxylate moieties to two Cu(II) ions in the equatorial position. In addition, each Cu(II) ion is coordinated by one apical ligand. The chemical and structural features of this moiety have been widely studied and are well-established.

![Figure 1.2 Paddlewheel dimetal tetracarboxylate](image)

*Figure 1.2 Paddlewheel dimetal tetracarboxylate is a 4-connected node (molecular square) and a linear spacer*
A search using the Cambridge Structural Database (CSD)\textsuperscript{19} of deposited structures based on the paddlewheel up to January 2004 returned 1116 hits, involving 21 transition metals. Scheme 1.1 demonstrates the relative use of d-block transition metals in the dimetal tetracarboxylate cluster. Cu(II) is the most widely used transition metal representing 43\% (483 hits) of the structures in the CSD, followed by Rh representing 22\% (240 hits), then Ru representing 10\% (111 hits). 40\% of the structures have oxygen coordinating ligands in the apical position whereas 36\% have nitrogen coordinating ligands in the apical position.

**Scheme 1.5** Pie chart illustrating relative use of transition metals in the paddlewheel cluster

A survey of bond distances for all paddlewheel structures of all transition metals returned a wide range of values. For the bond distances to be more meaningful and as the research in this dissertation will focus on Cu(II), a survey of bond distances of paddlewheel structures based on Cu(II) only was conducted. For structures with oxygen
coordinating ligands in the apical position, the bond distance for the four basal Cu-O bonds ranged between 2.290 and 1.890 Å with an average of 1.968(29) Å. The apical Cu-O bond distance ranged between 2.283 and 1.932 Å with an average of 2.146(43) Å, whereas Cu-Cu bond distances ranged between 3.256 and 2.575 Å with an average of 2.640(82) Å. For structures with nitrogen coordinating ligands in the apical position, the bond distance for the four basal Cu-O bonds ranged between 2.351 and 1.880 Å with an average of 1.974(38) Å. The apical Cu-N bond distance ranged between 2.360 and 2.005 Å with an average of 2.174(54) Å, whereas Cu-Cu bond distances ranged between 3.261 and 2.585 Å with an average of 2.702(128) Å. On average, bond distances in structures with nitrogen coordinating ligands in the apical position are longer, but within the standard deviation range for oxygen-coordinated structures. Data of average bond distance of all structures (includes O-coordinating, N-coordinating and a mixture of O- and N-coordinating ligands), which are summarized in Table 1.1., reveal that there is no statistical difference between the two types of structures. As can be seen from the table, bond distances of the four oxygen atoms of the carboxylate functionalities coordinated in the basal plane range between 2.080 to 1.866 Å with an average of 1.968(15) Å. The copper distance to the apical ligand is longer with a range of 2.570 to 2.092 Å and an average of 2.179(64) Å. This defines a square pyramidal geometry for the Cu(II) ions in the paddlewheel. The Cu-Cu separation ranges from 2.951 to 2.533 Å with an average of 2.646(50) Å.
Table 1.1 Bond distance data of surveyed paddlewheel moieties based on Cu(II) from the CSD

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<tbody>
<tr>
<td><strong>Max</strong></td>
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<td>2.067</td>
<td>2.130</td>
<td>2.080</td>
<td>2.570</td>
<td>2.951</td>
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<tr>
<td><strong>Min</strong></td>
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<td>1.912</td>
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<td>2.092</td>
<td>2.553</td>
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<tr>
<td><strong>Average</strong></td>
<td>1.968(15)</td>
<td>1.968(17)</td>
<td>1.970(17)</td>
<td>1.970(18)</td>
<td>2.179(64)</td>
<td>2.646(50)</td>
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1.6.2 The Paddlewheel: a Secondary Building Unit (SBU)

The use of the dimetal tetracarboxylate as a secondary building unit (SBU) for larger networks is a recent phenomenon. This is evident by the fact that 81% of the paddlewheel structures deposited in the database are discrete structures. Furthermore, of small number of polymeric structures reported (18%), 86% were reported after 1980.

The term “SBU” is derived from the nomenclature of minerals and zeolites. SBUs are finite topological component units that comprise the zeolite framework. Yaghi et al introduced the term in the context of extended metal-organic frameworks as they used the paddlewheel to generate porous, zeolite-like structures. The term is widely used now to describe the dimetal tetracarboxylate moiety.

The appeal of the dimetal tetracarboxylate moiety as an SBU is due to a number of attractive features: 1) its chemical and structural features are widely studied and well-established; 2) it is known for a wide range of metals including catalytically (e.g. Rh$^{2+}$) and magnetically (e.g. Cu$^{2+}$) active ones; 3) it is a large, rigid, well-defined structure, which means using it as a node with a rigid spacer will ensure a rigid, stable superstructure, with potentially large pores; 4) it is neutral, which eliminates counter ions that typically occupy space in the crystal structure; 5) it is robust and readily accessible; 6) it is modular, which means it can be produced from different combination...
of carboxylate moieties and metal ions; 7) it is versatile as it can be utilized as a 4connected node, or as a linear spacer along the M-M bond (Fig 1.2).

In this context, the use of polycarboxylate ligands has been shown to facilitate the utility of the SBU as a 4-connected node where the carboxylate ligands coordinate in the equatorial positions and extend in four directions. A view down the four-fold axis of the SBU moiety reveals that it also resembles a molecular square and that binding of the carboxylates in the equatorial positions would result in linking “molecular squares” at the vertexes.\textsuperscript{144,163-166,180} The nature of the polycarboxylate ligand, specifically the angle at which the carboxylate moieties are predisposed, controls the angle at which the molecular squares are connected. Linear dicarboxylates, such as benzene-1,4-dicarboxylate, link the SBUs at angle of 180°, whereas angular dicarboxylates, such as benzene-1,3-dicarboxylate where the two carboxylates are predisposed at an angle of 120°, link the SBUs at the same angle. The topology of the resulting structure is directly influenced by the choice of the polycarboxylate ligand. The use of aromatic polycarboxylates affords structures with high degree of rigidity and stability, and in the case that the structure possesses large pores, exchange or removal of guest molecules can be facilitated without destroying the framework. This has been demonstrated in extended metal-organic framework (MOF) reported by Yaghi \textit{et al}, where a porous extended network was evacuated from coordinated and guest molecules without collapse of the network. Furthermore, due to the large size of the pores in the structure, it exhibits high degree of porosity that exceeds that of known zeolites.\textsuperscript{181} Flexible polycarboxylates have also been shown to afford extended structures with a great degree of structural diversity due to the rotational flexibility of the organic ligands.\textsuperscript{162}
The SBU could also be employed as a linear spacer with an organic ligand acting as the node to generate extended networks. Structures generated via such strategy where the roles of the metal and organic ligand have been reversed compared to traditional coordination polymers have been termed “inverted” metal-organic frameworks. Using the SBU as a linear spacer is attractive, because not only does it provide a rigid, relatively long spacer, but it can also facilitate decorating the walls of the resulting extended structure with the functionalities present on the bridging carboxylate ligands. A number of examples have demonstrated the successful use of the SBU as a linear spacer in infinite structures.

1.6.3 Focus

The focus of this dissertation is on employing the dicopper (II) tetracarboxylate paddlewheel as a molecular square and connecting it at the vertexes with angular aryl dicarboxylate ligands. We primarily focused on benzene-1,3-dicarboxylate (bdc) and its derivatives to link the SBUs. The angular bdc has the two carboxylate moieties rigidly predisposed at 120°, which facilitates bridging the SBUs at the same angle. Figure 1.3 illustrates the linking of SBUs at the angle subtended by bdc. Additionally, we employed the wider angle ligand 1-methylpyrrole-2,4-dicarboxylate (pdc) which has its carboxylates predisposed at an angle of 157°. This ligand would link the SBUs in the same manner, but at the wider angle of the ligand.
Confining the SBU into an extended structure is expected to have geometric consequences on the bridging angular dicarboxylate ligand. Figure 1.4 illustrates two possible modes of distortion in the bridging ligand that would be expected in order to accommodate the geometry of the resulting structure.

The carboxylate functionalities could twist out of plane with respect to one another by an angle $\theta$, or they could bend towards each other from the plane of the benzene ring by an angle $\varphi$ while staying coplanar. Such distortion would help relieve the strain resulting from confining the paddlewheels into an extended structure. It is possible, of course, to have a combination of the two distortions. A published CSD
search of 42 discrete dicopper(II) tetraarylcarboxylate revealed that the phenyl ring twists from the plane of the Cu$_2$O$_4$ on average by an angle $\theta$ of 18(20)$^\circ$ with a range of 0 to 88.96$^\circ$ and bends out of plane by an angle $\phi$ on average by 5(4)$^\circ$ with a range of 0.18 to 17.98$^\circ$.\textsuperscript{189} Although the size of the sample of structures is small, it can serve as a reference point to determine the relative distortion of the bridging ligands in the structures presented in this work.

Herein we will describe the synthesis and structural analysis of a diverse family of related structures, discrete and infinite that result from linking molecular square dicopper tetracarboxylates at the vertexes by angular aryl dicarboxylates. We will demonstrate that it is possible to build nanoscale, complex structures, with drastically different and interesting properties from simple, commercially available starting materials in single step reactions. We will also demonstrate that the modularity of these systems is powerful as large diversity can be obtained by simple modification of reaction conditions. Finally, we will demonstrate that reactions conducted under thermodynamic equilibrium conditions can result in a number of other chromophores, which would not be possible under solvothermal conditions that yield interesting nanoscale structures.
Chapter 2

0D nanostructures- nanoballs

2.1 Preface

Polyhedral structures are known in naturally occurring systems such as zeolites (Linde A is based on the edge-skeleton of fused truncated octahedra\textsuperscript{104}) and in biological self-assembled systems such as mammalian picornaoviruses\textsuperscript{105-109} and proteins\textsuperscript{110}. The regular Platonic and semi-regular Archimedean polyhedra have been widely studied in recent years and a number of seminal papers describing molecular versions of such polyhedra have appeared in the literature.\textsuperscript{130,132,190} The design principles behind the development and isolation of these classes of compounds are based upon the concepts of self-assembly of geometrically suitable molecular components. In the context of metal-organic compounds, two general design principles have been implemented to generate molecular versions of these solids. One strategy involves the use of linear bifunctional rod-like ligands to connect molecular vertices with the appropriate geometry to generate the desired polyhedral shape.\textsuperscript{6,96} For example, a molecular version of the dodecahedron has been prepared from the reaction of a linear spacer with tetrahedral node.\textsuperscript{132} This design strategy, which has been widely used by Stang, generates the wire-frame or the edge-skeleton of the targeted polyhedron and in turn all the faces of the convex structure.
are open windows. The second design strategy, which has been extensively used by Fujita, is “molecular paneling”.\textsuperscript{191} This approach is based on connecting molecular moieties that have the shape of regular polygons at their edges. This design approach results in convex structures, all the faces of which are closed.

Other examples of uniform polyhedra such as prisms and antiprisms, polyhedra with star faces and vertices, and polyhedra with both concave and convex faces, have remained unexplored synthetically until recently.\textsuperscript{144,180,192} The latter group (one containing concave and convex faces) is known as \textit{faceted} polyhedra.

There are nine uniform \textit{faceted} polyhedra that are closely related to the Platonic and Archimedean solids but differ in the fact that their convex faces are constructed by connecting regular polygons at the vertices. This results in both open (concave) and closed (convex) faces, hence the name \textit{faceted}. Figure 2.1 depicts all nine faceted
polyhedra, which can be divided into four groups based on their constituent polygons: triangles only (a-c), squares only (d-f), pentagons only (g), mixed polygons (squares and triangles (h) and pentagons and triangles (i)). Since we targeted the molecular square SBU as a building block, the square-only faceted polyhedra are relevant. These three polyhedra differ by the angle at which the squares are connected: the *cubohemiocatohedron* (d) has the squares connected at 90° angle, the *small rhombiexahedron* (e) has the squares connected at 120° angle, and the *small rhombidodecahedron* (f) has the squares connected at 144° angle. Since our dicarboxylate linker, bdc, has its carboxylate moieties predisposed at an angle of 120°, the generation of the *small rhombiexahedron* should be feasible.

Herein we discuss the synthesis, characterization and structural analysis of three examples of the *small rhombiexahedron* obtained from the reaction of bdc and its derivatives with Cu(NO$_3$)$_2$.

### 2.2 Results and Discussion

The slow diffusion of a methanolic solution of Cu(NO$_3$)$_2$·2.5H$_2$O into a methanolic solution of H$_2$bdc and pyridine containing nitrobenzene template molecules yielded blue-green crystals, compound 1, within hours. Single crystal X-ray data revealed that 1 is the spherical structure shown in Figure 2.2. There are two crystallographically independent copper ions in the crystal structure of 1 that sit on a 4-fold rotation axis; *i.e.* all coordinated oxygen atoms of the bridging bdc ligands are equivalent (d$_{Cu1...O1} = 1.9592(53)$ Å; d$_{Cu2...O2} = 1.9522(53)$ Å). The apically coordinated ligand is highly disordered and has been modeled as a single oxygen atom, but could be
methanol, water or pyridine ($d_{\text{Cu1...O11}} = 2.1644(105) \ \text{Å}; d_{\text{Cu2...O21}} = 2.1646(129) \ \text{Å}$). This defines a square pyramidal geometry around the copper ions. The two copper ions are separated by 2.6039(25) Å. All bond distances are in agreement with those calculated from the CSD search (section 1.7.1). Examining the bdc ligand to determine if it is distorted as it confines the SBUs into this spherical structure reveals that the twist angle $\theta$ by which the two carboxylates twist out of plane with respect to each other is $9.65^\circ$ and the bend angle $\phi$, by which the two carboxylates bend towards each other, is $5.34^\circ$. This is comparable to $\theta$ and $\phi$ observed in discrete SBUs ($\theta_{\text{avg}} = 18(20)^\circ, \phi_{\text{avg}} = 5(4)^\circ$).189

The structure consists of 24 bdc moieties, 12 Cu$_2$ dimers, and 24 apical ligands coordinated to the Cu(II) ions; i.e. the structure results from the self-assembly of 72 components in a single step into the spherical entity depicted in Figure 2.2. Representing the structure schematically by replacing each SBU with a square reveals that the squares connect at the vertices into a spherical structure that conforms to the shape of the small rhombiheXahedron. The structure has 12 square faces, 6 square windows, 8 triangular windows and a hollow cavity. Each square face contains in its center a Cu$_2$ dimer with one Cu(II) ion lying on the exterior of the sphere and one on the interior of the sphere. In turn, two types of apical ligands exist, exterior and interior.
Compound 1 has an effective exterior diameter of 2.89 nm, as measured from opposite H-atoms of the 5-position of opposite bdc ligands, and a molecular volume including the solvent sphere of 10,615 Å³. The diameter of the internal cavity of 1 measured from opposite copper ions is 16.02 Å. To calculate the effective volume available for guest molecules, however, one must take into account the volume occupied by the internal axial coordinating ligands. Due to the high disorder of the coordinating apical ligands (over two positions and/or by rotation), location of all atoms of the coordinated ligand was problematic. As a result, the internal diameter could only be calculated based on located and refined coordinated oxygen atom of the ligand. The effective diameter measured from opposite coordinated oxygen atoms is 8.89 Å, which results in a cavity volume of ca. 367 Å³. To put this in context, a C₆₀ molecule has a diameter of 7 Å and an effective volume of ca. 326 Å³. In other words, the cavity in compound 1 is big enough to encapsulate a C₆₀ molecule. The calculated solvent accessible volume in 1 is 4251.8 Å³, which corresponds to 20.0% of the structure. This

![Figure 2.2 Crystal structure and schematic representation of compound 1*](image)

*Crystal structure presented in stick mode. Coordinated apical ligands are presented as single oxygen atoms. Non-ordinated guest molecules are removed for clarity.
would be increased to 11791.9 Å³ (55.5%) upon removal of guest. Each sphere of 1 has 14 closest neighbors: eight of the closest neighbors are 23.98 Å away, as measured by centroid to centroid separation, whereas the other six are 27.69 Å away. This results in body-centered cubic (bcc) packing as shown in Figure 2.3. For the nanometric size of compound 1 and its spherical shape, it is termed nanoball.  

![Figure 2.3 Crystal structure packing and schematic representation for compound 1](image)

*Non-coordinated guest molecules have been removed for clarity. Coordinated apical ligands are presented as single oxygen atoms; remaining atoms were removed for clarity*

Microcrystals of 1 can also be obtained quantitatively by direct mixing of the reactants and allowing the solution to stand. The crystals are stable in solution, but lose crystallinity when removed from the mother liquor. The nanoball is sparingly soluble in organic solvents such as THF, EtOAc, DMSO, DMF and MeOH, which facilitated its characterization by mass spectrometry. Electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ES FT-ICR) of 1 confirmed the persistence of the nanoball structure in solution as a span of m/z values corresponding to isotope clusters of the +3 cationic species, \([\text{Cu}_{24}(\text{bdc})_{24}(\text{MeOH})_{m}(\text{H}_2\text{O})_{n}(\text{Li})_3]^{+3}\), were detected (M⁺=...
2094.67 m/z (calc’d 2091.56) for m=24, n=0). The MS spectrum of nanoball 1 can be found in Appendix 1.

Zaworotko et al reported two other phases of this nanoball, a triclinic and a monoclinic phase, in addition to another nanoball structural isomer that differs in the connectivity of the SBUs.144 Yaghi et al also reported the same nanoball structure, which was obtained via hydrothermal synthesis, and described it as a cuboctahedron.193

A derivative of parent nanoball 1 was obtained from the reaction of a derivative of bdc, namely 5-OH-bdc with Cu(NO₃)₂.180 An alternative synthetic approach to slow diffusion of methanolic solutions of the starting materials was needed to produce X-ray quality single crystals of this nanoball. Since the targeted product is a spherical structure with 24 OH-groups decorating the surface, slow diffusion of methanolic solutions of the starting materials did not produce crystals or precipitate. The limited solubility of the starting materials to polar solvents, however, restricted the choice of solvent. As a result, the reaction was performed in methanol and diethyl ether was allowed to slowly diffuse into the reaction mix to aid crystallization. Small crystals, unsuitable for X-ray crystallography formed via this method. Consequently, a different synthetic approach was implemented that ultimately led to the formation of single crystals suitable for X-ray crystallography, efficiently and reproducibly. Equimolar amounts of Cu(NO₃)₂·2.5H₂O and 5-OH-H₂bdc were mixed in methanol to yield a blue solution. Upon addition of 2 equivalents of 2,6-lutidine, an immediate color change (from blue to deep blue-green) was observed. Addition of diethyl ether resulted in a precipitate, which upon recrystallization from hot DMSO yielded crystals suitable for X-ray crystallography within hours. Contrary to the synthesis of nanoball 1, the use of template molecules did
not appear to have an effect on the formation of nanoball 2. Performing the reaction in methanol in the presence or absence of nitrobenzene following the procedure outlined above produced the same result, as confirmed by X-ray crystallography. Performing the reaction directly in DMSO also yields the desired product; however, crystals form after 10-14 days in a small amount.

![Figure 2.4 Crystal structure of compound 2\(^*\)](image)

\(^*\) Crystal structure of 2 presented in stick mode (a) and space-filling mode (b). Coordinated apical ligands are presented as single oxygen atoms with the remaining atoms removed for clarity. Non-coordinated guest molecules were removed for clarity.

Figure 2.4 depicts the crystal structure of nanoball 2. There are four crystallographically independent copper ions in the structure each set of two comprising an SBU (d\(_{\text{Cu1-Cu2}}\) = 2.654(5), d\(_{\text{Cu3-Cu4}}\) = 2.641(3) Å). The average Cu-O distance for the four oxygen atoms of the four \(\mu_2\) 5-OH-bdc ligands coordinated in the basal positions is 1.953(10) Å. The apical position is coordinated by DMSO (d\(_{\text{Cu3-O}}\) = 2.121(6) Å), MeOH (d\(_{\text{Cu2-O}}\) = 2.09(3) Å) or H\(_2\)O (d\(_{\text{Cu1-O}}\) = 2.06(3), d\(_{\text{Cu4-O}}\) = 2.138(16) Å). Of the 12 exterior copper ions four are coordinated by MeOH molecules and eight are coordinated by DMSO molecules. All the interior copper ions are coordinated by water molecules.
A close look at the 5-OH-bdc ligands to determine whether they are distorted reveals that two types are present: ones that constitute the square windows and ones that constitute the triangular windows. The 5-OH-bdc ligands constituting the square windows have their carboxylate moieties twisted from planarity with respect to one another by $\theta = 8.61^\circ$, whereas the ones constituting the triangular windows have their carboxylate moieties twisted by $5.71^\circ$. The bend angle $\varphi$ was found to be $4.89^\circ$ and $5.13^\circ$ for the ligands in the square and triangular windows, respectively. The average twist and bend angles observed in this nanoball is smaller than that observed in compound 1 (9.65 and 5.33°, respectively). This nanoball is not perfectly spherical as evident by two measured lengths for the diameter. The external and internal diameters measured from two opposite copper ions gave two values each: 21.229, 21.239Å and 15.947, 15.931Å, respectively.

The effective external diameter of nanoball 2 measured from opposite hydroxyl group oxygen atoms is 2.99 nm. A single molecule of 2 occupies a volume of 17,422 Å$^3$ (including the solvent sphere) and has a molecular weight of 7.43 kDa. The average internal diameter of nanoball 2 (measured from opposite copper ions) is 15.94 Å. However, taking into account the volume occupied by the coordinated axial ligands results in an effective diameter of 9.02 Å measured between opposite coordinated oxygen. This affords a cavity with a volume of 384 Å$^3$ (slightly bigger than that of nanoball 1, 339 Å$^3$). The solvent accessible volume per one nanoball of 2 is 8241 Å$^3$, which corresponds to 47.3% of the structure. This could be increased to 25,611 Å$^3$ (73.5%) upon removal of guest molecules. Disordered solvent molecules occupy the cavity of the nanoball and the interstitial space between the nanoballs, which pack in a
body-centered cubic fashion as illustrated in Figure 2.5. It is important to note that not all solvent and/or guest molecules were located in the crystal structure, which is reflected in the high value of the calculated solvent accessible volume and the low density of the structure ($\rho = 0.708 \text{ g/cm}^3$).

Crystals of 2 persist in solution indefinitely; however, they are highly deliquescent, turning into liquid, briefly upon exposure to the atmosphere. It is possible that this is due to excess DMSO on the surface of the crystals, since rinsing with an abundance of ether or placing the crystals under vacuum overnight allows the isolation of microcrystals of nanoball 2.

![Figure 2.5 Perspective view of the bcc packing in the crystal structure of 2*](image)

*Apical coordinating ligands are presented as single oxygen atoms with the remaining atoms removed for clarity. Non-coordinated guest molecules were removed for clarity.

The stability of nanoball 2 to acidic and basic conditions was evaluated, qualitatively. The blue methanolic solution of nanoball 2 was found to change color and produce a white precipitate in strongly acidic (pH $\leq 3$) and strongly basic (pH $\geq 9$) media, suggesting the deformation of the nanoball.
Nanoball 2 is readily soluble in polar protic solvents (MeOH, EtOH, i-PrOH), and sparingly soluble in hot DMF and hot acetonitrile. The persistence of the ball structure in methanol solution was confirmed by ES FT-ICR mass spectrometry, where a span of \( m/z \) values corresponding to isotope clusters of the +4 cationic species, \([Cu_{24}(5-OH-bdc)_{24}(MeOH)_m(H_2O)_n(Li)_4]^{+4}\), was detected in the spectrum \((M^+ = 1670.35 \text{ } m/z \text{ (calc'd } 1661.20) \text{ for } m=24, n=0)\). The mass spectrum of 2 can be found in Appendix 2.

The enhanced solubility of compound 2 in MeOH facilitated microcrystals growth on the surface of mica and glass via evaporation from methanol solution and study of its surface properties by atomic force microscopy (AFM). AFM has become one of the most widely used tools for studying crystal growth and behavior on surfaces.\(^{194-199}\) For example, AFM has been used for the study of size control of nanocrystals on Langmuir-Blodgett films,\(^{194}\) protein crystal growth,\(^{195}\) molecular and nanotribology,\(^{196}\) statistical analysis of 2-D crystal sizes,\(^{197}\) dopant effects on crystal growth,\(^{198}\) and annealing effect on crystallization.\(^{199}\) AFM studies revealed that microcrystals of nanoball 2 have uniform dimensions and that they are stable even after mild heating. The images obtained on a mica surface, without thermal treatment, show increasing density of microcrystals with increasing concentration (Figure 2.6). The microcrystals have an average size of 1.3 (±0.4) nm, average height of 140 (±30) nm and roughness (RMS) of 56 nm. In the case of films prepared on glass, it was found that thermal treatment (at 37 °C and 75 °C for 24hrs) was necessary to remove a contaminant film formed by residual solvent. Annealing at 37 °C and 75 °C resulted in microcrystals having RMS of 236 and 261 nm, respectively. Image analysis shows that the average crystal size of 1.4 (±0.4) nm is the same for both temperatures; height of crystals was found randomly distributed
around 500 nm for the sample annealed at 37 °C, whereas the sample annealed at 75 °C, showed a clear statistical distribution of heights at 300, 600 and 900 nm.

Synthesis of a second derivative of the parent nanoball was feasible from the reaction of another derivative of bdc, namely 5-NO₂-bdc with Cu(NO₃)₂. The slow diffusion of a methanolic solution of pyridine into a methanolic solution containing Cu(NO₃)₂·2.5H₂O, 5-NO₂-H₂bdc and nitrobenzene template molecules yielded blue-green cubic crystals suitable for X-ray crystallography.

Figure 2.6 Microcrystals of 2 annealed for 24 hrs on mica

![Figure 2.6](image)

Figure 2.7 Crystal structure of compound 3*

*Crystal structure of 3 presented in stick mode (a) and space filling mode (b). Coordinated apical ligands are presented as single atoms in the space filling mode with the remaining of the atoms removed for clarity. Non-coordinated guest molecules were removed for clarity.
The crystal structure of compound 3 is depicted in Figure 2.7. There are 12 crystallographically independent copper ions in the crystal structure of 3 each having a square pyramidal geometry. The basal plane is defined by four oxygen atoms of the four \( \mu_2 \) 5-NO\(_2\)-bdc moieties (\( \text{d}_{\text{Cu-O(avg.)}} = 1.9428(124), 1.9549(124), 1.9632(90), 1.9713(87) \) Å) and the apical position is occupied by coordinating pyridine (\( \text{d}_{\text{Cu5-N}} = 2.097(7), \text{d}_{\text{Cu7-N}} = 2.102(6), \text{d}_{\text{Cu9-N}} = 2.089(8), \text{d}_{\text{Cu11-N}} = 2.103(8) \) Å), water (\( \text{d}_{\text{Cu4-O}} = 2.150(8) \) Å) or methanol (\( \text{d}_{\text{Cu1-O}} = 2.150(8), \text{d}_{\text{Cu2-O}} = 2.154(8), \text{d}_{\text{Cu4-O}} = 2.150(8), \text{d}_{\text{Cu6-O}} = 2.164(8), \text{d}_{\text{Cu8-O}} = 2.168(8), \text{d}_{\text{Cu10-O}} = 2.159(9), \text{d}_{\text{Cu12-O}} = 2.165(8) \) Å). The Cu-Cu distance is in the range of 2.6265(18) and 2.6583(18) Å with an average of 2.6480(120) Å. All bond distances are in agreement with the average bond distances calculated from the CSD search.

Of the 12 exterior copper ions of nanoball 3, two are coordinated by MeOH molecules, two by water molecules and eight by pyridine molecules. All interior copper ions are coordinated by disordered methanol molecules. Nanoball 3 is not perfectly spherical as the diameter of the equators differed. The external diameter measured from opposite copper ions ranged between 21.180 and 21.385 Å with an average of 21.298(83) Å. The internal diameter measured from opposite copper ions ranged between 15.896 and 16.105 Å with an average of 16.003(89) Å. In order to determine the effective volume of the cavity available to guest molecules, one must take into account the volume occupied by internal coordinating axial ligands. The effective shortest diameter measured from opposite coordinated oxygen atoms is 8.80 Å, which affords a cavity with a volume of 357 Å\(^3\) (compared to 339 and 384 Å\(^3\) for nanoballs 1 and 2, respectively). The average effective external diameter measured from opposite nitro groups is 3.13 nm.
A single molecule of 3 occupies a volume of 12,645 Å³ (including the solvent sphere) and has a molecular weight of 7.76 kDa (excluding guest molecules).

![Figure 2.8](image)  

**Figure 2.8** Nanoball 3 encapsulates guest molecules in the triangular and square windows*  

* The wire-frame of the nanoball is presented in stick mode and colored yellow for clarity. Guest molecules are presented in space filling mode.

Guest molecules are encapsulated in the square and triangular windows of the ball, but not in the internal cavity. Figure 2.8 illustrates the host-guest inclusion complex that results from nanoball 3. Three types of square windows were identified. (a) One square window hosts pyridine and a nitrobenzene molecule that interact with each other by face-to-face π-π stacking interactions (d_{centroid...centroid} = 3.682 Å). This is within the acceptable range of 3.4-3.8 Å for centroid-centroid distances of aromatic rings involved in face-to-face π-π stacking interactions.²⁰⁰,²⁰¹ Additionally, the pyridine molecule interacts with one of the 5-NO₂-bdc ligands constituting the wall of the square window (d_{centroid...centroid} = 3.449 Å). Figure 2.9(a) illustrates these interactions. (b) The second type of square window hosts two anti-paralleled nitrobenzene molecules that do not interact with each other, but each interacts with one of the 5-NO₂-bdc ligands constituting
the walls of the window (d_{centroid...centroid} = 3.757, 3.904 Å). Figure 2.9(b) illustrates these interactions. (c) The third type of square window hosts disordered water and methanol molecules (Figure 2.9(c)). The guest methanol molecules appear to be involved in H-bonding interactions.

![Figure 2.9](image)

**Figure 2.9** Host-guest interactions in the square windows of compound 3*.

*Three types of square windows identified: (a) nitrobenzene and pyridine guest molecules interact with each other by face-to-face π-π stacking interactions. (b) Two nitrobenzene guest molecules interact with the walls of the square window by face-to-face π-π stacking interactions. (c) Guest water and methanol molecules in the third type of square window. Guest molecules are presented in space-filling mode whereas the windows are presented in stick mode. Apical coordinated ligands are presented as single atoms with the remaining atoms removed for clarity.

Four types of triangular windows were identified. (a) One type of triangular window hosts two nitrobenzene molecules that interact with each other by CH-π interactions (d_{CH...π} = 2.568 Å). Additionally, the nitrobenzene molecule parallel to the wall interacts with the 5-NO2-bdc constituent of the wall by face-to-face π-π stacking interactions (d_{centroid...centroid} = 3.568 Å). These interactions are illustrated in Figure 2.10(a). (b) The second type of triangular window hosts a methanol and water molecule that sit inside the cavity in addition to a nitrobenzene molecule that sits above the cavity with the nitro group pointing in so that it interacts with the water molecule by weak hydrogen bonding (d_{O...O} = 3.138 Å). This is illustrated in Figure 2.10(b). (c) The third type of window hosts one water molecule, as illustrated in Figure 2.10(c). The shortest
O…O contact between the guest water molecule and the coordinated methanol ligands is 3.630 Å. (d) The fourth type of triangular window hosts disordered water molecules, as illustrated in Figure 2.10(d).

![Image of host-guest interactions](Figure 2.10 Host-guest interactions in the triangular windows of compound 3)

Different values for the bending and twisting angles of the 5-NO\textsubscript{2}-bdc ligands in nanoball 3 were determined depending on whether they are in the square or triangular window, but in general ranged between 4.13° and 6.08° with an average of 5.31° for \( \phi \) and 2.92° and 16.0° with an average of 11.2° for \( \theta \). In general, these distortions appear to be influenced by \( \pi-\pi \) interactions with guest molecules present in the windows.

In addition to guest molecules occupying the windows of the nanoball, guest nitrobenzene, pyridine and methanol were located in the interstitial space between the nanoballs as illustrated in Figure 2.11.
The solvent accessible volume per a single nanoball of 3 is 932.3 Å³, which corresponds to 7.4% of the structure (compared to 20.0% and 47.3% for 1 and 2, respectively). This could be increased to 6586 Å³ (52.1%) upon removal of guest molecules. Each nanoball is surrounded by twelve (8+4) closest neighbors with distances in the range of 24.204-26.384 Å for the former and 28.017 Å for the latter. As a result, the geometry around each nanoball can be described as a distorted cuboctahedron, which results in a packing arrangement similar to cubic closest-packing (ccp).

It is worth noting that our laboratory has generated eight other variants of nanoball 3 that differ in the identity of the coordinating apical ligands, and exhibit similar inclusion properties.

The three nanoball structures have a number salient features that are worth highlighting. (1) They are nanometric in size. The exterior diameters of nanoballs 1, 2 and 3 are ca. 2.89, 2.99 and 3.13 nm, respectively. (2) The use of substituted bdc results

**Figure 2.11** Aromatic guest molecules occupy the interstitial space between nanoballs of compound 3

* Guest molecules that occupy the interstitial space between the nanoballs is presented in space filling mode and color coded for clarity. The nanoballs are presented in stick mode. Guest molecules that sit in the windows have been removed for clarity. Methanol molecules have been removed.
in highly decorated nanoballs with 24 functional groups on the surface. This enhances the solubility of the nanoballs in addition to introducing a handle on the molecule that facilitates further derivatization. (3) They contain 24 copper ions that can be utilized, for instance, for catalysis, redox or magnetism. The modular nature of the structures makes it feasible to exchange the copper ions with different transition metals for which the SBU molecular square is known. In turn, a number of different properties can be incorporated just by varying the metal ion. (4) They are porous containing a hollow core in addition to square and triangular windows. Compound 3 clearly demonstrates the ability of the nanoball to encapsulate guest molecules in its triangular and square windows via supramolecular interactions. The shape and size of windows results in different host/guest and guest/guest interactions. Similar properties are expected for the other two nanoballs; however, crystal structure data for 1 and 2 did not allow analysis of their inclusion properties. The effective internal cavity of the nanoball is ca. 0.37 nm\(^3\), which is large enough to encapsulate a C\(_{60}\) molecule. Characteristic features of nanoballs 1-3 are summarized in Table 2.1.

<table>
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<th>Compound</th>
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<td>7,760</td>
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<td>Volume (nm(^3))</td>
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<td>Effective cavity volume (nm(^3))</td>
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<td>0.357</td>
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<td>% Porosity (maximum)</td>
<td>20.0 (55.5)</td>
<td>47.3 (73.5)</td>
<td>7.40 (52.1)</td>
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</tbody>
</table>

* The molecular weight is based on the formula [Cu\(_2\)(5-R-bdc)\(_2\)(L)\(_3\)]\(_{12}\) and excludes guest and uncoordinated solvent molecules. The % porosity is calculated per a single molecule. Maximum porosity represents the maximum porosity possible upon removal of guest and solvent molecules.

The triangular and square windows of nanoballs 1-3 are curved due to the angularity of the bridging bdc ligands. The dimensions of the windows are nanometric.
The sides of the triangular and square windows are all equal in compound 1 measuring 10.613 and 8.613 Å at the wide and narrow ends, respectively. The angles around the copper corners of the triangles and squares are perfect 60.00° and 90.00°, respectively. The windows in compound 2 are slightly distorted and smaller compared to compound 1. The sides of the square windows are not all equal with lengths of 10.636 and 10.606 Å at the wide end and 8.003 and 7.955 Å at the narrow end. The triangular window is an isosceles triangle with side lengths equal to those of the square window. The angles also deviate from those observed in compound 1. The angles of the squares are 89.56° and 90.143°, whereas the angles of the triangle are 59.91° and 60.18°. The distortion is further pronounced in compound 3 where all the sides of the triangles and squares are variable in length (10.699-10.588 Å for the wide end and 8.055-7.876 Å for the narrow end). The angles also vary ranging between 60.323-59.825° for the triangles and 91.25-88.88° for the squares. These nanometric triangular and square windows, which can be viewed as trigonal and tetragonal clusters of SBUs, could be considered the secondary building units comprising the nanoball structures (Figure 2.12) and hence have been termed nSBUs. In other words, we can consider the nanoballs the result of self-assembly of trigonal and tetragonal nSBUs at the vertices. This will become more relevant in the next two chapters.
Characterization of the nanoball structures is complicated. X-ray crystallography is the best tool for definite structural determination, but even then due to the large number of atoms, high disorder of solvent, guest and coordinated ligands it is difficult to locate atoms of guest and solvent molecules, as was the case in compounds 1 and 2. In addition, due to the high porosity of the structures, there is low electron density and in turn poor diffraction which complicates data collection. Consequently, definite determination of guest molecules and thorough structural analysis of host-guest interactions could not be performed. X-ray powder diffraction (XPD) typically represents a good tool to confirm that the bulk sample has the same crystal structure as the single crystal from which data was collected. However, the nanoballs were found to produce poor XPD patterns, making it difficult to ascertain the identity of the bulk powder. A typical XPD spectrum obtained of a nanoball structure showed broad, indefinite peaks suggesting no long-range order in the crystals. Furthermore, since these nanoballs were prepared from Cu(II), a d⁹ paramagnetic metal, NMR could not be utilized.
2.3 Conclusions

We have demonstrated herein a design strategy to generate a molecular version of the faceted polyhedron the small rhombihexahedron that involves linking molecular squares (SBU) at the vertexes at the required angle of 120° using the angular ligand bdc. This design strategy is different from ones previously implemented to generate metal-organic Platonic and Archimedean polyhedra, which involved edge-sharing of polygons\textsuperscript{98,131,143,191} that generates a closed-face polyhedron, or the use of nodes and spacers with the appropriate geometries\textsuperscript{190} and resulted in the wire-frame of the polyhedron.

Compounds 1-3 are synthesized from simple reactions of bdc and its derivatives with Cu(II) under thermodynamic equilibrium conditions. These compounds are spherical and nanometric in size and hence are termed nanoballs. The average diameter of compounds 1-3 is 3.05 nm and the average molecular weight is > 6500 Da.

The nanoballs are porous materials with an internal cavity and open square and triangular window. It was demonstrated with compound 3 that they are able to encapsulate guest molecules in their windows \textit{via} supramolecular interactions and display rich host-guest chemistry. These triangular and square windows, which have sides measuring 1.06 and 0.80 nm at the wide and narrow ends, respectively, could be viewed as the “SBUs” that constitute the nanoballs and hence are termed nSBUs. The nanoballs could be envisioned as building blocks of even larger superstructures. Zaworotko \textit{et al} have already demonstrated\textsuperscript{192} that it is indeed possible to use the nanoballs as nodes for larger structures, suprasupermolecules.\textsuperscript{203,204} With their large windows and cavity and their exhibited inclusion properties, the nanoballs could be envisioned as carriers for
other molecules such as pharmaceuticals, and hence can have potential application as drug delivery systems.

2.4 Experimental

**General methods:** All materials were used as received; solvents were purified and dried according to standard methods. Mass spectroscopic data were obtained on a 9.4 Tesla FT-ICR mass spectrometer by the National High Magnetic Field Laboratory at Florida State University. TGA data were obtained on a TA instruments 2950 TGA at high resolution with N₂ as purge gas.

**Synthesis of [Cu₂(bdc)₂(MeOH)₂]₁₂, (1):** A methanolic solution (5 mL) of H₂bdc (0.066 g, 0.40 mmol) and 2,6-dimethylpyridine (0.12 mL, 1.0 mmol) was layered on top of a methanolic solution (5 mL) of Cu(NO₃)₂·2.5H₂O (0.093 g, 0.41 mmol) containing nitrobenzene (3 mL). Upon slow diffusion of the two solutions, blue-green square crystals of 1 formed.

**Synthesis of [Cu₁₂(5-OH-bdc)₁₂(DMSO)₄(MeOH)₂(H₂O)₆]₂, (2):** To a methanolic solution (100 mL) of 5-OH-H₂bdc (5.092 g, 28.0 mmol) and Cu(NO₃)₂·2.5H₂O (6.390 g, 27.5 mmol) was added 6.40 mL (54.9 mmol) of 2,6-dimethylpyridine and the solution was stirred for 15 minutes. Upon addition of 150 mL of diethyl ether, a precipitate formed, which was filtered and air dried over night. Crystallization of a sample of the crude (60.0 mg) from DMSO (14 mL) afforded greenish-blue plates, which were identified by X-ray crystallography as the title compound. The crystals were isolated by
pipetting into a clean vial and placing under vacuum over night to yield 28.5 mg, (50 % yield by weight). Direct filtering of the crystals failed to isolate the product in a solid form, rather the product turned liquid. Rinsing with ether helped maintain the crystallinity of the product; however, a large portion of the sample was lost.

**Synthesis of [Cu12(5-NO2-bdc)12(MeOH)7(Py)4(H2O)]2, (3):** Slow diffusion of a methanolic solution (10 mL) of Cu(NO3)2·2.5H2O (124 mg, 0.533 mmol) into a methanolic solution (10 mL) of 5-NO2-H2bdc containing pyridine (0.080 mL, 0.989 mmol), naphthalene (25 mg, 0.195 mmol) and nitrobenzene (3 mL) yielded large square green blue crystals within months. Single crystal X-ray crystallography confirmed the identity of the crystals as the title compound. Yield could not be determined as the crystals dissolved and new crystals formed (see compound 14, Chapter 4).

**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 MoKα radiation (λ = 0.7107 Å). The data were corrected for Lorentz and polarization effects and for absorption using the SADABS program. The structures were solved using direct methods and refined by full-matrix least-squares on |F|^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions and refined with temperature factors 1.2 times those of their bonded atoms. All crystallographic calculations were conducted with the SHELXTL 5.1 program package. Crystallographic data for compounds 1-3 are presented in Table 2.2.
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<td>0.1531, 0.4259</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1, wR2</td>
<td>0.1069, 0.2953</td>
<td>0.2128, 0.4702</td>
</tr>
<tr>
<td>Largest diff. peak and hole (e.Å$^{-3}$)</td>
<td>0.831 and -0.438</td>
<td>1.051 and -0.592</td>
<td>0.960 and -0.625</td>
</tr>
</tbody>
</table>
Chapter 3
TETRAGONAL 2D SHEETS

3.1 Preface

The last chapter demonstrated that trigonal and tetragonal nSBUs self-assemble into discrete nanoscale spherical structures (nanoballs) that conform to the shape of the faceted polyhedron, the small rhombihexahedron. It is possible, however, to obtain other structures that are based on one type of nSBU exclusively. In this chapter we will present examples of 2D infinite structures that are based on tetragonal nSBUs only (Fig 3.1). Since the molecular square SBUs are linked at the angle of 120° subtended by the carboxylate moieties of the bridging bdc ligand, the resulting nSBUs possess curvature and torsional flexibility. It was demonstrated in the previous chapter that these nSBUs exhibit inclusion properties and can host molecules via supramolecular interactions. It occurred to us that the shape and chemical nature of the tetragonal nSBU resembles that of a calix[4]arene molecule and that square nSBUs therefore might be subject to atropisomerism.\textsuperscript{205}
3.1.1 **Square Grids**

$4^4$ square grids are the most common topology of 2D structures. Square grids are clay mimics and hence are capable of intercalating guest molecules between the grids, and additionally they can intercalate guest molecules in the square cavities present in the plane of the grid. The first reported 2D grids were based on cyano ligands; since then a wide range of N-bound spacer ligands such as pyrazines, bipyridine and extended bipyridines have been used to generate square grids with different size cavities. Despite great success in enlarging the size of the cavity by using longer spacers, interpenetration remains a problem that precludes space and diminishes the potential of the square grids as porous host materials. In addition, since the framework of the grid is charged, counter ions typically occupy the cavities of the grid, preventing porosity. Attempts to remove or exchange ions from the cavities have almost consistently, with few exceptions, resulted in collapse of the framework.

The use of the SBU as a node for constructing square grids presents an excellent alternative. Instead of one metal ion serving as a node in the framework (as in

![Figure 3.1 Tetragonal 2D sheets sustained by tetragonal nSBU building blocks](image)
metal-bipyridine compounds) the SBU moiety serves as a rigid node. Linking the SBU nodes with rigid spacers (terephthalate) has been shown to afford robust, stable superstructures with necessarily larger pores than possible with traditional M-N bonds. Furthermore, since the SBU is neutral, counter ions that typically occupy space in the crystal structure are eliminated. Such structures have been shown to be highly porous and capable of sorption of large volumes of gas. The use of flexible dicarboxylate has also been shown to generate extended porous structures with large degree of diversity due to the rotational flexibility about single C-C bonds.

The angular bdc, being a ditopic ligand, is also able to link the SBUs in 2D infinite sheets and form 4\(^4\) square grid-like structures. The angularity of the bdc ligand, however, is expected to affect the planarity of the resulting 2D sheets and generate undulating ones in order to relieve the strain within the plane of the grid. In addition, the cavities of the grid, which are the cavities of the nSBUs, would be expected to be bowl-shaped.

### 3.1.2 Calixarenes and Metallacalixarenes

Calixarenes are macrocyclic compounds prepared by the condensation of \(n\) molecules of formaldehyde and \(n\) molecules of phenol, which results in \(n\) phenyl rings bridged by \(n\) methylene groups. The size of the resulting macrocycle is specified in its name by inserting the number \(n\) in brackets between calix and arene. Thus a cyclic tetramer is designated calix[4]arene. Calixarenes are known to complex small guest molecules in their bowl-shaped cavity and hence they represent a large and continually growing area of research in the context of supramolecular chemistry.
Atropisomerism\textsuperscript{220} is a phenomenon that arises when rotation around a covalent bond is impeded enough as to allow for the isolation of different isomers. This phenomenon has been observed in a variety of systems including porphyrins, biaryls and calixarenes. There are four possible atropisomers of calix[4]arenes\textsuperscript{221-225} that were designated by Gutsche and coworkers\textsuperscript{211} as the cone, partial cone, 1,2-alternate and 1,3-alternate, all illustrated in Figure 3.2.\textsuperscript{226,227-229} The nomenclature refers to the orientation of the arene rings with respect to one another. In the cone conformation, all arenes point up and form a cone-like structure, whereas in the partial cone three arenes point up and one points down. Similar behavior has been observed for larger calixarenes.\textsuperscript{230} Due to the curvature of the tetragonal nSBU imparted by the angularity of the bdc ligands, it can be regarded as being a metal-organic calix, or a “metalla[4]calix”, where the CH\textsubscript{2} bridging groups have been replaced by the SBU. Metallicalixarenes\textsuperscript{231-237} are metal-organic analogous of the organic calixarenes that result from the assembly of metal nodes and organic spacers. Examples based on Pt(II) and Pd(II) complexes of 2-hydroxypyrimidine have been shown to resemble calix[4]arenes in their shape, conformation and chemical properties.\textsuperscript{233}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{atropisomers.png}
\caption{Atropisomers of a calix[4]arene}
\end{figure}

This chapter will demonstrate that tetragonal nSBUs do indeed exhibit atropisomerism in the solid state. We will present seven structures with the general formula \{[Cu\textsubscript{2}(aryldicarboxylate)\textsubscript{2}L\textsubscript{2}]\textsubscript{4}\}_n (aryldicarboxylate= bdc, 5-OEt-bdc, 5-OPr-bdc,
pdc; L= pyridine, 4-picoline) that are based on the self-assembly of tetragonal nSBUs.

We will demonstrate that atropisomerism has a profound effect on the polymeric structures in terms of crystal structure, porosity and inclusion properties.

### 3.2 Results and Discussion

In this study, we employed bdc and two of its derivatives, 5-OEt-bdc and 5-OPr-bdc, all of which have the carboxylate moieties predisposed at 120°. In addition, we used the wider angle dicarboxylate ligand pdc (1-methylpyrrole-2,4-dicarboxylate), which has the two carboxylate moieties predisposed at an angle of 157°. The ligands are illustrated in Figure 3.3.

![Figure 3.3 Angular aryl dicarboxylates employed for making tetragonal 2D sheets](image)

The slow diffusion of an ethanolic solution of H₂bdc and pyridine into an ethanolic solution of Cu(NO₃)₂·2.5H₂O containing benzene template molecules afforded blue green crystals of 4a, \{[Cu₂(bdc)₂(py)₂]₄\}_n. The crystal structure of 4a is depicted in Figure 3.4 and reveals that it is a 4⁴ undulating grid that results from the self-assembly of tetragonal nSBUs at the vertices. There is one crystallographically independent copper ion having a square pyramidal geometry (d_{Cu1-Cu1} = 2.6676(7) Å). The basal plane is
defined by four oxygen atoms of the four bdc moieties (d$_{Cu-O}$= 1.9959(20), 1.9500(20), 1.9417(19), 2.0063(20) Å) and the apical position is occupied by a pyridine coordinating ligand (d$_{Cu-N}$= 2.1582(23) Å). All bond distances are within agreement with the average bond distances calculated from the CSD search (section 1.7.1). The carboxylate moieties of the bdc ligand are twisted out of plane with respect to each other (θ = 12°). This is larger than the twisting observed in the carboxylate moieties of bdc in the nanoball structure, compound 1 (θ = 9.65°). The carboxylate moieties of the bdc ligand also bend towards each other from the plane of the benzene ring by an angle φ= 4.36° resulting in an undulated sheet. A closer look at the tetragonal nSBUs in 4a reveals that they adopt two conformations in an alternating fashion: the cone and 1,3-alternate conformations. Each cone has a diameter of 15.13 Å (measured from opposite copper ions) and a depth of 10.01 Å (measured from the center of the bottom of the bowl to the midpoint of a line joining the top hydrogen atoms on opposite bdc moieties). Each type of nSBU contains highly disordered guest benzene molecules. The undulating sheets stack eclipsed (interlayer separation of 8.44 Å) so that the cones stack inside one another and the 1,3-alternate nSBUs define hourglass shaped channels that run parallel to [001]. The solvent accessible volume in the unit cell of 4a is only 0.5%, and would be increased to 27.5% upon removal of guest molecules.$^{238}$
Compound 4b, \([\mathrm{Cu}_2(\mathrm{bdc})_2(\mathrm{py})_2)_4]_n\), was obtained from an ethanolic solution containing H_2bdc, pyridine, Cu(NO_3)_2·2.5H_2O and nitrobenzene. There are two crystallographically independent copper ions in the crystal structure of 4b (d_{Cu1-Cu1} = 2.6373(15), d_{Cu2-Cu2} = 2.6351(17) Å). The geometry around each copper is square pyramidal. The basal plane is defined by four oxygen atoms of the four bdc moieties (d_{Cu1-O} = 1.957(5), 1.961(5), 1.964(4), 1.988(5); d_{Cu2-O} = 1.954(4), 1.954(5), 1.976(5), 1.977(5) Å) and the apical position is occupied by a pyridine coordinating ligand (d_{Cu1-N} = 2.152(6); d_{Cu2-N} = 2.137(6) Å). All bond distances are in agreement with the average bond distances calculated from the CSD search. Crystal structure of 4b (Fig 3.5) reveals that it is another undulating 2D sheet structure. A closer look at the nSBU constituents of 4b reveals that they adopt the partial cone conformation. The partial cone is defined by one of the bdc ligands in the tetragonal nSBU lying in a plane almost perpendicular to the plane defined by the other three bdc ligands (dihedral angle = 97.0°). The partial cone has a diameter of 14.08 Å (measured from opposite copper ions) and a depth of 10.53 Å.
(measured from the center of bottom of the bowl to the line joining the top hydrogen atoms of opposite bdc moieties that are in the same plane). In order for the SBUs to afford this partial cone conformation, the bdc ligands are more significantly distorted compared to the previous structures. The carboxylate moieties of the bdc ligands that lie in plane in the partial cone are twisted out of plane with respect to one another by \( \theta = 5 \) and 44°, while the carboxylate moieties of the fourth bdc ligand pointing down are twisted by \( \theta = 19^\circ \). The bdc ligands bend by an angle \( \phi \) that ranges between 2.61-4.48°. Each partial cone in 4b contains a disordered nitrobenzene molecule (Fig 3.6).

![Figure 3.5 Crystal structure of 4b*](image)

(a) (b)

\(^*\) (a) Top-view illustrating the partial cone nSBU hosting disordered nitrobenzene guest molecules. (b) Side-view of 4b which packs in an AAA fashion

The nitrobenzene molecules appear to be involved in \( \pi-\pi \) stacking interactions with the walls of the cavity, however, centroid-centroid distances could not be calculated due to the high disorder of the nitrobenzene molecules. Within the sheet, the nitrobenzene guest molecules arrange in such a way that their dipole moments cancel. The sheets stack eclipsed so that the partial cones sit inside one another with an interlayer separation of ca. 9.40 Å. Disordered ethanol molecules are intercalated between the layers. There is no
solvent accessible area in the unit cell of $4b$; however, upon removal of guest the accessible area would be 12.0%.\textsuperscript{238} Since the framework in $4b$ has an identical chemical formula to $4a$, it can be considered a supramolecular isomer.

![Figure 3.6 Nitrobenzene guest molecules occupy the cavities in compound $4b$](image)

Compound $5$, $\{[\text{Cu}_2(\text{bdc})_2(\text{4-pic})_2]_4\}_n$, was obtained by the slow diffusion of a methanolic solution of $\text{H}_2\text{bdc}$ and 4-picoline into a methanolic solution of $\text{Cu(NO}_3\text{)}_2\cdot 2.5\text{H}_2\text{O}$ containing $o$-dichlorobenzene. There are two crystallographically independent copper ions in the SBU. The basal plane is occupied by four oxygen atoms of the bdc moieties ($d_{\text{Cu1-O}} = 1.958(3), 1.966(3), 1.972(3), 1.996(4)$; $d_{\text{Cu2-O}} = 1.965(4), 1.966(4), 1.974(4), 2.005(4)$ Å), whereas the apical position is occupied by a coordinated picoline molecule ($d_{\text{Cu1-N}} = 2.154(4), d_{\text{Cu2-N}} = 2.145(4)$ Å). The copper ions in the SBU are separated by 2.6682(6) Å. The bond distances are comparable to those of $4a$ and $4b$ and in agreement of those calculated from the CSD search. The crystal structure of compound $5$ is shown in Figure 3.7 and reveals that it is also a 2D $4^4$ corrugated grid structure.
A closer look at the crystal structure reveals that the tetragonal nSBUs adopt the 1,2-alternate conformation. In order for the SBUs to afford this conformation of the tetragonal nSBU, the bdc ligands are distorted with the two carboxylate ligands of the bdc moieties twisting out of plane by $\theta = 47^\circ$. This is the greatest distortion observed in the bdc ligands for all the structures discussed so far. The bend angle, however, is minimal ranging between 0.30 and 0.83 $^\circ$. 2D grids of 5 propagate in the bc-plane and stack along the a-axis in an ABAB fashion with an interlayer separation of 9.81 Å. The effective dimensions of the grids measure 1.2 x 1.0 nm$^2$ (distance from Cu-Cu mid point of opposite SBU units in the nSBU taking into account the van der Waals radii of copper). Each nSBU contains a guest molecule of o-dichlorobenzene, which interacts with three of the bdc moieties that constitute the walls of the cavity via CH…π interactions ($d_{CH...centroid} = 2.686, 2.921, 3.424$ Å), as can be seen in Figure 3.8. There is no solvent accessible area in the unit cell of 5, but upon removal of guest the potential solvent accessible area is 25.9%.238

Figure 3.7 Crystal structure of compound 5

(a) Top-view of the 4th grid in 5. The 1,2-alternate nSBU constituent on the 2D sheet is highlighted for clarity. Guest o-dichlorobenzene guest molecules occupy the nSBU. (b) Side-view illustrating the stacking of the sheets in an ABAB fashion.
Structures 4a, 4b and 5 collectively exhibit all four atropisomers of the nSBU likely to be generated by the angularity that results from bdc serving as a bridging ligand. Figure 3.9 illustrates the nSBU constituents of polymeric structures 4a, 4b and 5.

The cone isomer (a) has C$_{4v}$ symmetry where all four dicarboxylate ligands orient in the same direction (the 5-position pointing towards the viewer). The partial cone (b) has C$_{s}$ symmetry with three dicarboxylate ligands oriented up and one down. The 1,2-alternate isomer (c) also exhibits C$_{s}$ symmetry with two adjacent dicarboxylate ligands oriented up and two down. Finally, the 1,3-alternate isomer (d) exhibits C$_{2}$ symmetry.
with opposite dicarboxylate ligands oriented in the same direction. We have reported a set of isostructural analogues based on Zn(II)\textsuperscript{166} that exhibit the same atropisomerism phenomenon.\textsuperscript{239}

When derivatives of bdc were investigated, namely 5-OEt-bdc, and 5-OPr-bdc, two isostructural compounds were obtained: \([\text{Cu}_2(5-\text{OEt-}\text{bdc})_2(\text{py})_2]_n\), \(6\), and \([\text{Cu}_2(5-\text{OPr-}\text{bdc})_2(\text{py})_2]_n\), \(7\). Crystal structure of \(6\) is depicted in Figure 3.10.

There is one crystallographically independent copper ion in the SBU having a square pyramidal geometry. The basal plane is defined by four oxygen atoms of the four bdc moieties (d\text{Cu}\text{-O}= 1.938(5), 1.939(5), 1.987(5), 2.016(5) Å) and the apical position is occupied by a pyridine coordinating ligand (d\text{Cu}\text{-N}= 2.146(7) Å). The two copper ions of the SBU are separated by 2.6662(19) Å. All bond distances are in agreement with the average bond distances calculated from the CSD search. As can be seen from the crystal structure of \(6\) (Fig. 3.10), the structure is related to \(4a\) consisting of undulating sheets that result from the self-assembly of alternating cone and 1,3-alternate nSBUs. The structure
is different, however, in the fact that only one type of cavity is present, which results from the cone nSBUs. Each cone hosts four water molecules. The hour-glass shaped channels present in 4a, which result from the 1,3-alternate nSBUs, are occupied by the ethyl chain substituents. This is reflected in the solvent-accessible volume in the unit cell of 6, which was calculated to be 1%, but would be increased only to 9.7% upon removal of solvent molecules compared to an increase to 27.5 % for 4a.\textsuperscript{238} The cone nSBUs have the same outer diameter as those of 4a (0.94 nm), however, they are obviously deeper due to the alkyl chain substituents and measure 1.30 nm from the center of the base to the midpoint of a line joining opposite terminal hydrogen atoms of the ethyl substituents. Distortion in the bdc ligand is also observed in this structure where the carboxylate moieties twist out of plane with respect to each other by an angle $\theta = 16$ and 20°, which is greater than that observed in 4a ($\theta = 12^\circ$) and any of the nanoball structures, which also contain tetragonal nSBUs in the cone conformation. The carboxylate moieties of 5-OEt-bdc are also bent by an angle $\phi = 4.37^\circ$, which is comparable to that observed in 4a. The undulating sheets in 6 stack eclipsed so that each cone contains disordered solvent molecules and the bottom of a cone from the adjacent sheet. The interlayer separation is 8.68 Å.

Compound 6 formed reproducibly from a variety of different solvents (MeOH, EtOH, DMSO), in the presence of different bases (pyridine, 2,6-lutidine), in the absence of template molecules and in the presence of a variety of them (nitrobenzene, benzene, $o$-dichlorobenzene, naphthalene). It is therefore not unreasonable to assume that the alkyl chain substituent plays a template role that directs the formation of this structure exclusively.
The crystal structure of compound 7 reveals that it is also a 2D corrugated sheet that results from the self-assembly cone and 1,3-alternate nSBUs. The sheets stack eclipsed so that the cones sit inside one another and the 1,3-alternate nSBUs define hourglass shaped channels. These channels are occupied by the alkyl chain substituents of the bdc ligands. Structure 7 could not be refined below R_f = 0.2925 due to the high thermal motion and/or disorder and consequently could not be thoroughly analyzed. 7, as in the case of 6, was isolated in the absence of template molecules as well as in the presence of various ones including nitrobenzene, benzene, o-dichlorobenzene and naphthalene. It was also isolated from a variety of solvents including MeOH, EtOH or DMSO and in the presence of different bases, including pyridine or 2,6-lutidine.

When the wider angle ligand pdc was employed, two related structures were obtained under different reaction conditions. The reaction of H_2pdc, pyridine and Cu(NO_3)_2·2.5H_2O in methanol yielded blue green crystals of 8, \{[Cu_2(pdc)_2(py)_2]_4\}_n, overnight whereas crystals of 9, \{[Cu_2(pdc)_2(4-pic)_2]_4\}_n, were obtained by the slow diffusion of a methanolic solution of H_2pdc and 4-picoline into a methanolic solution of Cu(NO_3)_2·2.5H_2O containing nitrobenzene.

Crystal structure of 8, which is illustrated in Figure 3.11, reveals that it is a 4^4 square grid. There is one crystallographically independent copper ion in the SBU having a square pyramidal geometry.
The basal plane is defined by four oxygen atoms of the four pdc moieties \( (d_{\text{Cu-O}} = 1.953(4), 1.971(4), 1.971(4), 1.9781(4) \text{ Å}) \) and the apical position is occupied by a pyridine coordinating ligand \( (d_{\text{Cu-N}} = 2.164(6) \text{ Å}) \). The two copper ions of the SBU are separated by 2.6688(16) Å. There is no significant effect on bond distances with the use of the wider angle dicarboxylate, pdc. All bond distances are in agreement with those of structures based on bdc and with the average bond distances calculated from the CSD search. The effective dimensions of the grid measure 10.98 x 12.17 Å (distance from Cu-Cu mid point of opposite SBU units in the nSBU taking into account the van der Waals radii for copper). The grids stack slipped in an ABCABC fashion with an interlayer separation of 6.499 Å. This staggered stacking facilitates the inclusion of the coordinated pyridine molecules from one grid in the cavities of the neighboring grids where they interact with the pdc ligands constituting the walls of the grid by face-to-face π-π stacking interactions \( (d_{\text{centroid…centroid}} = 3.592 \text{ Å}) \). This is within the acceptable range of 3.4-3.8 Å for centroid-centroid distances of aromatic rings involved in face-to-face π-π stacking interactions. \(^{200}\) Guest methanol molecules are intercalated between the grids in

\[ \text{Figure 3.11 Crystal structure of compound 8}\]^{*}

\(^{*}\) (a) Top-view illustrating the square grid. Coordinated pyridine molecules are presented as single nitrogen atoms with the remaining atoms deleted for clarity (b) Sheets of 8 stack in an ABC-fashion. The layers have been color coded for clarity.
There is no solvent accessible volume in the structure of 8, but upon removal of guest 7.1% volume is available for guest molecules.238 A closer look at the tetragonal nSBU in the structure of 8 reveals that it is in the 1,2-alternate conformation. To adopt this conformation, the carboxylate moieties of the pdc ligand twist out of plane with respect to one another by an angle $\theta = 24^\circ$, which is much smaller than that observed for the bdc ligand in the tetragonal nSBU adopting the 1,2-alternate ($\theta = 47^\circ$). This is not surprising, however, as this ligand has a wider angle and in turn is more flexible. The bend angle, on the other hand ($\varphi = 4.7^\circ$), is much greater than that in 5 ($\varphi = 0.31-0.83^\circ$).

Compound 9 has the same crystal structure as that of 8, shown in Figure 3.11. There is one crystallographically independent copper ion having a square pyramidal geometry ($d_{\text{Cu1-Cu1}} = 2.6598(15)$ Å, slightly shorter than that observed in 8, 2.6688(16) Å). The basal plane is defined by four oxygen atoms of the four pdc moieties ($d_{\text{Cu-O}} = 1.957(4), 1.962(4), 1.966(4), 1.9781(4)$ Å) and the apical position is occupied by a pyridine coordinating ligand ($d_{\text{Cu-N}} = 2.153(5)$ Å). All bond distances are in agreement with the average bond distances calculated from the CSD search. The effective dimensions of the grids measure 10.80 x 11.84 Å (distance from Cu-Cu mid point of opposite SBU units in the nSBU taking into account the van der Waals radii for copper). As in 8, the grids stack parallel and slipped in one direction so that every fourth layer repeats, i.e. ABCABC packing (Fig. 3.11), with an interlayer separation of 6.940 Å. This is slightly longer than the interlayer separation in 8 (6.499 Å), as 4-picoline is slightly longer than pyridine. This packing arrangement facilitates the inclusion of the coordinated picoline ligands into the cavities of neighboring grids (Fig 3.12) where they interact with the pdc ligands constituting the walls of the cavity by face-to-face $\pi-\pi$
stacking interactions ($d_{\text{centroid}...\text{centroid}} = 3.632 \text{ Å}$). This is within the acceptable range of 3.4-3.8 Å for centroid-centroid distances of aromatic rings involved in face-to-face π-π stacking interactions. Disordered water molecules are intercalated between the grids. There is no solvent accessible volume in the crystal structure of 9, but upon removal of guest there would be 5.2% solvent accessible volume.\textsuperscript{238} Nitrobenzene was not used in the synthesis of 8, but was used in the synthesis of 9. Since the same coordination polymer forms in both cases, and nitrobenzene is not incorporated in the structure of 9, it is reasonable to assume that additional template molecules are not necessary to direct the formation of this atropisomer of pdc and that coordinated pyridine ligands play a templating role. This distortion in the bridging pdc ligand in this structure is comparable to that in 8.

The use of the wider angle dicarboxylate pdc results in the 1,2-alternate nSBU atropisomer only (Figure 3.13). Examination of the SBU moieties in the nSBUs of structures 8 and 9 revealed that the “trans” carboxylate moieties are planar ($\theta = 0^\circ$), which could account for the formation of this nSBU exclusively. The larger angle at

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.12.png}
\caption{Packing of square grids in 9 facilitates π-π stacking interactions\textsuperscript{*}}
\end{figure}

\textsuperscript{*}Perspective view of two stacked grids in stick mode (a) and space-filling mode (b). Packing of the sheets facilitates π-π stacking interactions between coordinated pyridine molecules and pdc ligand constituting the wall of the cavity (c).
which the two carboxylates are predisposed results in flexibility and in turn allows for planarity in the SBU moiety.

![Tetragonal nSBU constituent](image)

**Figure 3.13** Tetragonal nSBU constituent of compounds 8 and 9

### 3.3 Conclusions

We have demonstrated herein that tetragonal nSBUs can self-assemble exclusively into 2D structures. The torsional flexibility in the tetragonal nSBU results in greater degree of structural diversity in the solid state, where extended structures with the same topology (4$^+$) differ due to atropisomrism in their nSBU constituents. The shape, chemical nature and conformational flexibility of the tetragonal nSBUs make them reasonable analogues of calix[4]arenes. They can be considered metallacalix[4]arenes where the bridging CH$_2$ groups are replaced by the SBU moiety. Indeed, all four atropisomers that are known to exist for calixarenes were observed in the tetragonal nSBU components of the coordination polymers presented herein. In particular, the types of cavities present and the relative solvent or guest accessible volumes change quite dramatically depending upon which atropisomer is present in the structures. Template molecules appear to have an effect on which atropisomer is formed. In the absence of substituents on the bdc ligand, all atropisomers are observed and their formation is dependent on what template molecules are used. The cone/1,3-alternate atropisomers...
form in the presence of benzene, the partial cone forms in the presence of nitrobenzene, whereas the 1,2-alternate forms in the presence of o-dichlorobenzene. Guest molecules interact with the walls of the nSBUs via aromatic stacking interactions. In order to accommodate the formation of the different atropisomers, the bdc ligands are distorted by the carboxylate moieties twisting out of plane. The most twisting occurs in the case of the 1,2-alternate nSBUs, in which the carboxylates are out of the plane by an angle of 47°. However, this nSBU exhibits the least distortion in terms of bending. When substituents are present on the bdc ligand, they appear to play a templating effect as the presence of a variety of templates or their absence does not appear to have an effect on the resulting structure. The wider angle dicarboxylate pdc yielded one atropisomer, namely the 1,2-alternate. Some of these 2D structures, namely 8 and 9, are well suited for pillaring, a commonly used strategy for the generation of 3D porous materials.

Future studies will be directed towards the preparation of discrete molecular versions of the nSBUs, which would serve as even more direct analogues of calix[4]arenes. We shall also focus upon the inherent modularity of the nSBU and seek to customize it so that, depending on which variable is changed, one might control size, shape and chemical nature of the nSBU and the cavities and channels thereby formed.

3.4 Experimental

**General methods:** All materials were used as received; solvents were purified and dried according to standard methods. TLC plates were visualized using a short wave (254 nm) UV lamp. $^1$H and $^{13}$C NMR spectra were obtained from DMSO-$d_6$ solutions on a Bruker instrument operating at 250 and 62.5 MHz, respectively. TGA data were obtained on a
TA instruments 2950 TGA at high resolution with N$_2$ as purge gas. Formulations of the coordination polymers are based upon nSBUs rather than empirical units. 1-Methylpyrrole-2,4-dicarboxylic acid was provided by G. J. Bodwell at Memorial University of Newfoundland. It was synthesized according to the literature procedure$^{243}$ and published elsewhere.$^{164}$

**Synthesis of alkoxy dimethyl isophthalate esters:** Established literature procedures$^{244}$ were followed except for using acetone as the solvent instead of DMF.

**Saponification of alkoxy dimethyl isophthalate esters:** A sample of the ester was heated at 50 °C in methanol/20%NaOH (aq.) until TLC indicated the completion of the reaction (ca. 45 min). The reaction mixture was then cooled in an ice bath and concentrated HCl was added dropwise until the solution is acidic (pH 3-4). Cooling the solution to 4 °C over night yielded a white, crystalline product.

**Synthesis of 5-ethoxybenzene-1,3-dicarboxylic acid (5-OEt-1,3-H$_2$bdic):** Dimethyl 5-hydroxyisophthalate (5.01 g, 24.1 mmol) was dissolved in acetone (100 mL) and treated with potassium carbonate (10.9 g, 10 equiv) and ethyl iodide (2.10 mL, 1.1 equiv) according to the literature procedure to yield 5.48 g of the yellowish ester product. The ester was then saponified according to the general procedure to yield the title compound in quantitative yield (4.77 g). $^1$H NMR: δ = 7.95 (s, 1H, CH arom), 7.55 (s, 2H, CH arom.), 4.09 (q, 2H, CH$_2$), 1.29 (t, 3H, CH$_3$); $^{13}$C NMR: δ = 166.84 (CO$_2$H), 159.00 (C-O), 132.94 (C-CO$_2$H), 122.48 (CH), 119.31 (CH), 64.12 (OCH$_2$), 14.86 (CH$_3$).
Synthesis of 5-propoxybenzene-1,3-dicarboxylic acid (5-OPr-1,3-H$_2$bdcc): Dimethyl 5-hydroxyisophthalate (5.11 g, 24.1 mmol) was dissolved in acetone (100 mL) and treated with potassium carbonate (11.4 g, 3.5 equiv) and propyl iodide (2.60 mL, 1.1 equiv) according to the literature procedure to yield 4.51 g of an oily yellow residue, TLC of which (Silica, EtOAc/ Hex 3:2) indicated the presence of starting material. The crude product was chromatographed (Silica, gradient elution EtOAc/ Hex) to yield an off-white solid (1.29 g), which upon saponification according to the general procedure yielded 0.512 g (44 %) of the title compound. $^1$H NMR: $\delta$ = 7.95 (s, 1H, CH arom), 7.55 (s, 2H, CH arom.), 4.09 (q, 2H, CH$_2$), 1.29 (t, 3H, CH$_3$); $^{13}$C NMR: $\delta$ = 166.84 (CO$_2$H), 159.00 (C-O), 132.94 (C-CO$_2$H), 122.48 (CH), 119.31 (CH), 64.12 (OCH$_2$), 14.86 (CH$_3$).

Synthesis of $\{[\text{Cu}_2(\text{bdcc})_2(\text{py})_2\text{Guest}]_n\}$_4 (4a): Blue-green crystals of 4a were obtained from slow diffusion of an ethanolic solution (4 mL) of 1,3-H$_2$bdcc (166 mg, 0.999 mmol) and pyridine (0.240 mL, 2.97 mmol) into an aqueous solution (4 mL) of Cu(NO$_3$)$_2$·2.5H$_2$O (233 mg, 1.00 mmol). Crystals form within days in 40% yield. The crystals are thermally stable to above 150 °C after which the TG curve shows a mass loss of about 33% between 180 and 300 °C, which is consistent with and corresponds to the loss of benzene and pyridine (determined by TG-MS). Further heating leads to decomposition above 400 °C. The most intense peaks observed in the X-ray powder diffraction (XPD) patterns from the bulk sample are consistent with those calculated from single crystal diffraction data.
Synthesis of \([\text{Cu}_2(\text{bdc})_2(\text{py})_2]_4\cdot4\text{Nitrobenzene}\cdot2\text{EtOH}\)\(_n\) (4b): Blue-green crystals of 4b were obtained upon standing of an ethanolic solution of 1,3-H\(_2\)bdc (254 mg, 1.53 mmol), pyridine (0.38 mL, 4.70 mmol), Cu(NO\(_3\))\(_2\)\(\cdot\)2.5H\(_2\)O (346 mg, 1.49 mmol) and nitrobenzene (3 mL) at room temperature for 3-6 months in 7.5% yield. The crystals are thermally stable to ca 100 °C after which the TG curve shows a weight loss of 40% between 110 and 200 °C and second weight loss of 37% between 280 and 400 °C. Further heating results in decomposition of the sample.

Synthesis of \([\text{Cu}_2(\text{bdc})_2(4\text{-pic})_2]_4\cdot4\text{o-Dichlorobenzene}\cdot8\text{MeOH}\)\(_n\) (5): Blue-green crystals of 5 were obtained from the slow diffusion of a methanolic solution (7 mL) of 1,3-H\(_2\)bdc (166 mg, 0.999 mmol) and 4-picoline (0.30 mL, 3.1 mmol) into a methanolic solution (7 mL) of Cu(NO\(_3\))\(_2\)\(\cdot\)2.5H\(_2\)O (233 mg, 1.00 mmol) containing 5 mL of o-dichlorobenzene. Crystals formed after 3-5 months in 50% yield. The crystals are thermally stable to above 200 °C after which the TG curve shows a weight loss of 58% between 250 and 300 °C and second weight loss of 16% between 350 and 400 °C. Further heating of the sample results in decomposition.

Synthesis of \([\text{Cu}_2(5\text{-OEt-bdc})_2(\text{py})_2]_4\cdot8\text{H}_2\text{O}\)\(_n\) (6): Blue-green crystals of 6 were obtained within days from the slow diffusion of a methanolic solution (5 mL) of 5-OEt-1,3-H\(_2\)bdc (87.8 mg, 0.424 mmol) and 2,6-dimethylpyridine (0.10 mL, 0.85 mmol) into a solution of Cu(NO\(_3\))\(_2\)\(\cdot\)2.5H\(_2\)O (98.6 mg, 0.424 mmol) in 5 mL of methanol containing template molecules (nitrobenzene, benzene, naphthalene, o-dichlorobenzene or none). TG
analysis shows removal of guest molecules at 88 °C followed by removal of coordinating pyridine molecules at 223 °C then decomposition above 305 °C.

**Synthesis of \{[\text{Cu}_2(5\text{-OPr-bdc})_2(\text{py})_2]_4\text{•Guest}\}_n (7):** Blue-green crystals of 7 were obtained within days from the slow diffusion of a methanolic solution (5 mL) of 5-OPr-1,3-H_2bdc (113 mg, 0.511 mmol) and pyridine (0.20 mL, 2.5 mmol) into a methanolic solution of Cu(NO_3)_2\cdot2.5H_2O (117 mg, 0.503 mmol) in 5 mL of methanol that contains template molecules (3 mL) (nitrobenzene, benzene, o-dichlorobenzene, naphthalene or none) in 18.0% yield. TG analysis reveals loss of guest molecules below 200 °C followed by a weight loss of 80.1% between 280 and 350 °C. Further heating of the sample resulted in decomposition.

**Synthesis of \{[\text{Cu}_2(pdc)_2(\text{py})_2]_4\text{•4MeOH}\}_n (8):** To a methanolic solution (5 mL) containing N-Me 2,4-H_2pdc (111 mg, 0.656 mmol) and pyridine (ca. 0.30 mL, 2.6 mmol) was added Cu(NO_3)_2\cdot2.5H_2O (145 mg, 0.623 mmol) in methanol (5 mL). An immediate color change occurred and blue-green crystals formed overnight in 19.2% yield. TG analysis reveals loss of guest/solvent below 200 °C after followed by a mass loss of about 65% between 235 and 300 °C. Further heating resulted in decomposition of the sample. The most intense peaks observed in the X-ray powder diffraction (XPD) patterns from the bulk sample are consistent with those calculated from single crystal diffraction data.
Synthesis of \([\{\text{Cu}_2(\text{pdc})_2(4\text{-pic})_2\}_4\cdot4\text{H}_2\text{O}\}]_n\) (9): Blue-green crystals of 9 were obtained by slow diffusion of a methanolic solution (10 mL) containing N-Me 2,4-H$_2$pd (96 mg, 0.57 mmol) and 4-picoline (0.17 mL, 1.7 mmol) into a methanolic solution (10 mL) of Cu(NO$_3$)$_2$·2.5H$_2$O (131 mg, 0.563 mmol) containing nitrobenzene (3 mL). Crystals formed within days in 36.4 % yield. TG analysis shows loss of guest between 100 and 190 °C followed by a mass loss of 64% between 235 and 300 °C. Further heating resulted in decomposition of the sample. The most intense peaks observed in the X-ray powder diffraction (XPD) patterns from the bulk sample are consistent with those calculated from single crystal diffraction data.

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 Mo$_{ka}$ radiation (λ = 0.7107 Å). The data were corrected for Lorentz and polarization effects and for absorption using the SADABS program. The structures were solved using direct methods and refined by full-matrix least-squares on |F|$^2$. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions and refined with temperature factors 1.2 times those of their bonded atoms. All crystallographic calculations were conducted with the SHELXTL 5.1 program package. Crystallographic data for compounds 4a-9 are presented in Table 3.1.
Table 3.1 Crystallographic data for compounds 4a-9

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Chapter 4

2D Kagomé Lattices: Nanoscale Molecular Magnets

4.1 Preface

The last decade has witnessed tremendous advances in our understanding of and ability to manipulate molecular and supramolecular assemblies. New paradigms for the design and synthesis of a new generation of porous and magnetic materials now exist. Such advances are a consequence of the fundamental understanding of intermolecular interactions and of structure and cooperativity in many aspects of molecular science. Thus, the prospects for design, control and manipulation of molecular materials, particularly in areas related to non-covalent bonding, self-assembly and nanoscale structures are now truly exceptional.

Crystal engineering concepts can be applied to the design of novel framework topologies and nanostructures that are based upon simple geometric principles. The last two chapters discussed examples of discrete nanoballs that result from the self-assembly of trigonal and tetragonal nSBUs (Chapter 2), and of infinite 2D nanostructures that result from the self assembly of tetragonal nSBUs only (Chapter 3). This chapter will present examples of infinite 2D networks that result from the self-assembly of trigonal nSBUs only (Figure 4.1).
4.1.1 Molecular Magnetism

Geometric frustration of magnetic materials has been theoretically predicted to lead to a variety of novel magnetic ground states.\textsuperscript{245} A triangular lattice represents an example of geometrically frustrated topology. Many such lattices are possible, but most attention has been directed at the 2D triangle, 2D Kagomé, 3D Face centered cubic (FCC), and 3D pyrochlore lattices (Figure 4.2).

In addition to the clear division of the four lattices based on dimensionality, they can be further subdivided based on the connectivity of their constituent triangles: the FCC and triangle lattices result from edge-sharing of triangles, whereas the Kagomé and
the pyrochlore lattices result from vertex-sharing of triangles. The Kagomé lattice has gained most attention out of the four lattices because of its inherent manifestation of spin active sites into a high degree of spin frustration.

Molecular magnetism is a field that has been developing independently of metallic and oxide magnets, and has the potential to make significant contributions in the area of material science. Molecular magnets\textsuperscript{246-250} are materials in which molecules are the spin carriers or facilitate communication between spin carriers. One advantage of molecular magnets is that the spatial arrangement of the spin carriers is not limited to the traditional metallic lattices, and that two-dimensional networks are easily accessible. It therefore seems appropriate to target frustrated lattices by synthesizing molecular materials from magnetic components.

4.1.2 Examples of Molecular Kagomé Lattices

Few examples of molecular Kagomé lattices have been reported to date.\textsuperscript{165,209,251-254} For the most part, experimental studies have focused on inorganic materials. An example of such material is SrCr$_9$xGa$_3$xO$_{19}$, which has been shown to have spin-liquid type behavior by neutron scattering.\textsuperscript{255} In this compound the Cr ions occupy the lattice points. One disadvantage of metallic Kagomé compounds, however, is that ordering of the spins can be accommodated by interconnectivity of the layers thereby diminishing spin frustration within the layers.\textsuperscript{256}

An example an organic Kagomé lattice is a compound based on the radical cation $m$-N-methylypyridinium $\alpha$-nitronyl nitroxide that has been shown to exhibit antiferromagnetic behavior at very low temperatures.\textsuperscript{251,257}
In the context of metal-organic structures, three examples of a Kagomé lattice have been reported to date. Zaworotko et al\textsuperscript{165,258} reported the synthesis and characterization of a Kagomé lattice that results from self-assembly of trigonal nSBUs at the vertexes into 2D sheets with trigonal and hexagonal cavities. The crystal structure of this compound is shown in Figure 4.3.

![Figure 4.3](image_url)

*Figure 4.3 Crystal structure of a 2D structure that exhibits the Kagomé lattice topology*

(a) crystal structure of a compound reported by Zaworotko et al\textsuperscript{165} having that Kagomé topology, (b) Schematic representation of a Kagomé lattice demonstrating the spin frustration

The lattice is sustained by Cu\textsubscript{2} dimers that occupy the lattice points and are bridged by bdc ligands. The copper ions are coordinated by pyridine in the apical positions. The trigonal nSBU constituents of the lattice have dimensions of 8.2 Å thereby generating hexagonal cavities with an effective diameter of 9.1 Å. The sheets stack eclipsed in an AAA fashion generating hexagonal channels with the same dimensions as the hexagons. Highly disordered solvent molecules occupy the trigonal and hexagonal cavities. Magnetic studies of this compound revealed that it does exhibit ferromagnetic behavior even at 300 K.\textsuperscript{165,259}
Yaghi et al.\textsuperscript{209} reported a relevant Kagomé lattice that results from the self-assembly of trigonal nSBUs based on the wider-angle ligand 2,5-thiophenedicarboxylate. This compound has the same 2D sheet structure as that described for the structure above. The resulting hexagonal cavities, however, are obviously larger having an effective diameter of 12.3 Å. The sheets stack staggered in an ABCABC fashion decreasing the size of the channels that would result from the hexagonal cavities.

Domasevitch et al.\textsuperscript{254} recently reported a 3D structure that results from the pillaring of 2D Kagomé lattices. Three examples of this structure based on Co, Zn and Cd were reported. The lattice is sustained by the metal ion sitting at the lattice points and bridged by the flexible organic ligand 3,3’,5,5’-tetramethyl-4,4’-bipyrazolyl to yield a 2D sheet with trigonal and hexagonal cavities in the plane of the 2D sheet. The hexagonal cavity has an effective diameter of \textit{ca.} 8 Å. The 2D sheets are pillared into the third dimension by dithionate ligands. These compounds were prepared for the objective of using them as zeolite-like, porous materials.

4.1.3 \textit{Modification of Molecular Kagomé Lattice}

Figure 4.4 depicts a schematic presentation of the Kagomé lattice reported by Zaworotko \textit{et al.}\textsuperscript{165} The SBUs are represented by green squares the center of each is occupied by a Cu\textsubscript{2} dimer, which is coordinated by axial ligands (red and blue balls). The SBUs are bridged by bdc ligands (yellow balls). It is clear from the schematic that the structure is modular; hence, it should be feasible to modify it by varying its molecular components.
This could be accomplished in one of four ways. (1) The metal component could be exchanged, especially since the SBU is known for a large number of transition metals. This would be expected to not only alter the magnetic properties in the structure, but also incorporate new properties such as luminescence and catalysis depending on the metal used. (2) The bridging ligand could be either modified or replaced. Modifying the ligand by introducing substituents with different electronic and steric properties is expected to alter the magnetic properties and interlayer separation in the structure. Electron donating or withdrawing substituents introduced onto the bdc ring are expected to enhance or reduce the magnetic properties, respectively, by altering the intradimer coupling. The use of a wider angle bridging ligand has already been shown to alter the packing in the lattice. (3) The apical coordinating ligands could be varied, which is expected to alter the interlayer separation depending on the bulkiness of the ligand, in addition to affecting the magnetic properties of the lattice. It has already been demonstrated that varying the apical ligand has a measurable effect on the magnetism on
the dicopper tetracarboxylate SBU.$^{250}$ (4) Guest molecules with different properties (chirality, luminescence, magnetism, etc) could be incorporated in the cavities. This is expected to have a significant effect on the bulk physical properties.

This chapter will demonstrate that it is indeed feasible to modify the Kagomé lattice. We will present five new structures with the general formula $\{[\text{Cu}_2(5-R-\text{bdc})_2\text{L}_2]_3\}_n$ ($R = \text{H, Ph, NO}_2$; $\text{L} = \text{MeOH, H}_2\text{O, pyridine, 4-picoline}$) that sustain the Kagomé topology and examine the effect of modifying the axial ligand and the bdc ligand on the packing, interlayer separation and porosity of the structures.

### 4.2 Results and Discussion

For this study, we employed bdc and two of its derivatives: 5-ph-bdc and 5-NO$_2$-bdc (Fig 4.5).

![Figure 4.5 bdc ligands employed for making Kagomé lattices](image)

Compound $\textbf{10}$, $\{[\text{Cu}_2(\text{bdc})_2\text{L}_2]_3\}_n$, ($\text{L} = \text{MeOH and/or 4-picoline}$) was obtained by the slow diffusion of a methanolic solution of Cu(NO$_3$)$_2$·2.5H$_2$O into a methanolic solution of H$_2$bdc and 4-picoline in the presence of nitrobenzene template molecules. The crystal structure of $\textbf{10}$, which is shown in Figure 4.6, can be described as bowl-
shaped trigonal nSBUs self-assembled at the vertexes into a 2D Kagomé lattice. The Cu$_2$ dimers of the SBU sit on the lattice points and are bridged by the bdc ligands, which results in trigonal and hexagonal cavities within the layer. There is one crystallographically independent copper ion having a square pyramidal geometry. The basal plane is defined by four oxygen atoms of the four µ$_2$ bdc moieties (d$_{Cu-O}$ = 1.953(8), 1.954(8), 1.961(8), 1.962(8) Å) and the apical position is occupied by disordered MeOH and/or 4-picoline ligands (statistical probability of MeOH to 4-picoline in the crystal structure is 8:2; d$_{Cu-O}$ = 2.166(12), d$_{Cu-N}$ = 2.16(3) Å). The two copper ions of the SBU are separated by 2.637(3) Å. All bond distances are in agreement with the average bond distances calculated from the CSD search (section 1.7.1). The apical coordinating ligands point towards the trigonal cavities, whereas the 5-position of the bdc ligands points, in an alternating up and down fashion, towards the hexagonal cavity. This structure could be considered a supramolecular isomer of that published by Zaworotko et al as it has the same chemical formula $\{[\text{Cu}_2(\text{bdc})_2(L_2)]_3\}_n$, (L = pyridine for published structure, 4-picoline/methanol for 10).
As the paddlewheels are confined in a trigonal cluster the bdc ligand distorts to accommodate this arrangement. The carboxylate moieties of the bdc are twisted out of plane with respect to each other by an angle $\theta = 14.0^\circ$, compared to the twisting of the carboxylates in the tetragonal nSBu of 4a of $12.0^\circ$ and the nanoball in compound 1 ($\theta = 9.65^\circ$). The carboxylate functionalities are also bent towards each other from the plane of the benzene ring by an angle $\varphi = 5.38^\circ$, which is slightly greater than that seen in the tetragonal nSBu of 4a ($\varphi = 4.33^\circ$) and more comparable to the nanoball structures ($\varphi_{\text{avg.}} = 5.22^\circ$). The trigonal nSBU could be described as a curved equilateral triangle with sides measuring 10.623 and 7.977 Å, at the wide and narrow ends, respectively (measured from neighboring copper ions). The angles around the copper corners are perfect $60.00^\circ$. The dimensions of the nSBU are comparable to the trigonal nSBU constituents of compound 1. Figure 4.7 depicts the trigonal nSBU in 10.

![Figure 4.7 Trigonal nSBU constituent of compound 10*](image)

* Coordinated apical ligands are presented as a single nitrogen atom with the remaining atoms removed for clarity. Disordered guest molecule in the cavity has been removed for clarity

The layers are undulating due to the curvature of the trigonal nSBU bowls imparted by the angularity of the bdc ligand and stack in an ABCABC fashion along the
c-axis with an interlayer separation of 8.739 Å, contrary to the reported structure which stacks in an AAA eclipsed fashion with an interlayer separation of 9.916 Å. It is likely that the slipped stacking of the sheets reduces steric interactions between the coordinated 4-picoline ligands and results in shorter interlayer separation. Despite this staggered stacking, the structure is porous. The calculated solvent accessible volume in the unit cell of 10 was found to be 28.5%, and would be increased to 41.0%, upon removal of guest. Highly disordered guest molecules occupy the trigonal and hexagonal cavities.

Kagomé lattice 11, \{[\text{Cu}_2(5\text{-ph-bdc})_2(\text{py})_2]_3\}_n, was obtained by the slow diffusion of an ethanolic solution of Cu(NO_3)_2·2.5H_2O into an ethanolic solution of 5-ph-H_2bdc and pyridine in the absence of template molecules. Blue-green crystals of 11 form exclusively within hours. Figure 4.8 illustrates the crystal structure of 11.

![Figure 4.8 Crystal structure of compound 11](image)

Figure 4.8 Crystal structure of compound 11

* (a) top view of 11 in space filling mode, (b) side view of 11 illustrating the AAA stacking. Coordinated pyridine molecules in (b) are shown as a single nitrogen atom with the remaining atoms deleted for clarity. Guest molecules were removed for clarity.

The sheet structure in 11 is consistent with that described above for 10 and results from the assembly of trigonal nSBUs at the vertexes. There is one crystallographically independent copper ion having a square pyramidal geometry (d_{Cu1-Cu1} = 2.656(2) Å). The
basal plane is defined by four oxygen atoms of the four $\mu_2$ bdc moieties ($d_{Cu-O}$ = 1.965(7), 1.963(7), 1.976(7), 1.977(8) Å) and the apical position is occupied by a disordered coordinating pyridine ligand ($d_{Cu-N}$ = 2.151(3) Å). All bond distances are in agreement with the average bond distances calculated from the CSD search. The trigonal nSBU (Fig 4.9) can be described as a curved equilateral triangle with the sides measuring 10.677 and 8.100 Å at the wide and narrow ends, respectively (measured from neighboring copper ions). The angles of the triangle are perfect 60.00°. In order for the SBUs to accommodate this trigonal arrangement, the 5-ph-bdc moieties are distorted with the two carboxylate functionalities twisting out of plane with respect to each other ($\theta = 19.0^\circ$) and bending towards each other from the plane of the benzene ring by $\phi = 6.18^\circ$. This distortion is much more pronounced here than in 10 ($\theta = 14.0^\circ$ and $\phi = 5.38^\circ$).

Figure 4.9 Trigonal nSBU constituent of compound 11

*(a) Trigonal nSBU constituent of 11 is an equilateral triangle with sides measuring 10.677 and 8.100 Å, at the wide and narrow ends, respectively. (b) Stacking trigonal nSBUs are involved in CH...π interactions (2.949 Å) between the coordinated pyridine and the Ph-substituents of the 5-Ph-bdc. Guest molecules were removed for clarity*
A disordered ethanol molecule occupies the cavity of the trigonal nSBU. The phenyl substituents on the bdc ligands are orthogonal to the plane of the benzene ring and point away from the trigonal cavity and towards the hexagonal cavity that is generated as the nSBUs assemble into a 2D sheet, occupying part of it. The layers stack eclipsed (AAA packing) with the bottom of the bowls in one sheet sitting inside the bowls of adjacent sheets. This facilitates CH-π interactions between the coordinated pyridine ligands (bottom of one bowl) with the ph-substituents on the bdc rings of another bowl (d_{CH- centroid} 2.949 Å), as seen in Figure 4.9. The interlayer separation in 11 is 9.968 Å. This is consistent with the interlayer separation of the prototype Kagomé (9.916 Å) which also has pyridine as the apical coordinating ligand. The eclipsed stacking results in hexagonal channels that run along the c-axis. Since the ph-substituents occupy part of the hexagonal cavity, an hour-glass shaped cavity results with an effective diameter of 10.738 Å calculated based on the shortest contact from the center of the hexagon. This corresponds to a spherical area with a volume of 648 Å³. This is substantially larger than the spherical cavity of the nanoball structures (average cavity volume = 369 Å³). The calculated solvent accessible volume in the unit cell of 11 was found to be 20.1%, and would be increased only to 27.4% upon removal of guest (compared to 41% for 10). This is not surprising since the bulky phenyl substituents occupy part of the space in the channels. Microcrystals of 11 can also be obtained by direct mixing of the reactants and allowing the solution to stand. The powder diffraction pattern obtained from the powder sample is consistent with the one calculated from single crystal data.

When crystals of 11 are removed from the mother liquor and exposed to the atmosphere, they are found to undergo a transformation into a new compound, 12, while
maintaining crystallinity, as confirmed by single crystal X-ray. Crystal structure of compound 12, \([\text{Cu}_2(5-\text{Ph}-\text{bdc})_2(\text{py})(\text{H}_2\text{O})]_n\), is illustrated in Figure 4.10 and reveals that one of the apical coordinating pyridine ligands is displaced by a coordinating water molecule. This is a single-crystal-to-single-crystal transformation, a phenomenon few examples of which have been reported to date.\(^{162,207,260-262}\)

There are two crystallographically independent copper ions in the crystal structure of 12 resulting in an unsymmetrical SBU. Both copper ions have a square pyramidal geometry with the basal plane defined by four oxygen atoms of the four \(\mu_2\) 5-Ph-bdc moieties (\(d_{\text{Cu1-O}} = 1.954(6), 1.956(6), 1.966(6), 1.971(6)\); \(d_{\text{Cu2-O}} = 1.960(6), 1.963(6), 1.970(6), 1.970(6)\) Å). The apical position is occupied by a disordered coordinating pyridine ligand for one of the copper ions (\(d_{\text{Cu1-N}} = 2.151(3)\) Å), whereas the other copper ion is coordinated by a water molecule (\(d_{\text{Cu2-O}} = 2.172(6)\) Å). The two copper ions of the SBU are separated by 2.635(12) Å. The bond distances are in agreement with the

![Figure 4.10 Crystal structure of compound 12](image)
average bond distances calculated from the CSD search. The trigonal nSBU constituent of 12 (Fig 4.11) is also a curved equilateral triangle with the sides measuring 10.615 and 7.935 Å at the wide and narrow ends, respectively (measured from neighboring copper ions), which is comparable to the dimensions of the nSBU in 11 (10.677 and 8.100 Å). The angles of the triangle are perfect 60.00°. The 5-ph-bdc moieties are distorted, as in 11, to accommodate this trigonal arrangement. The two carboxylate functionalities are twisted out of plane with respect to each other (θ = 20.6°) and bent towards each other from the plane of the benzene ring by φ = 6.00°.

![Figure 4.11 Trigonal nSBU moiety in compound 12*](image)

*(a) Trigonal nSBU constituent of 12 is an equilateral triangle with sides measuring 10.615 and 7.935 Å, at the wide and narrow ends, respectively. Coordinated water molecules are presented as single oxygen atoms. Guest molecules were removed for clarity

The nSBUs assemble at the vertexes into a 2D undulating sheet generating hexagonal cavities. The sheets stack eclipsed. A closer look at the stacking reveals that 12 packs in such a way that generates a bilayer structure: the coordinated pyridines in neighboring layers point towards each other and the coordinated water molecules in neighboring layers point towards each other. This creates two distinct regions between
the layers: a hydrophobic region containing coordinated pyridines and a hydrophilic region containing coordinated water molecules (Figure 4.12). Consequently, two interlayer separations exist: 9.406 Å for the hydrophobic region and 6.905 Å, for the hydrophilic region and the packing could be described as AA’AA’.

![Figure 4.12 Bilayer packing of compound 12*](image)

*Two distinct layers with different interlayer separations are observed in 12. Coordinated pyridine and water ligands are presented in space filling mode.

Such packing results in distinct interactions within each region. In the hydrophilic region, guest water molecules are present. For each nSBU, there are three water molecules each of which hydrogen bonds to two of the coordinated water molecules in a bifurcated fashion ($d_{O\ldots O} = 2.908$, 2.913 Å). These nSBU bowls sit inside neighboring bowls in such a way that they are in close proximity to the coordinated water molecules of the neighboring bowl. No H-bonding interactions were found, however. In the hydrophobic region, the coordinated pyridine ligands of each nSBU interact with one another via CH-$\pi$ interactions so that each pyridine acts as a donor once and as an
acceptor once ($d_{CH...π} = 2.548 \text{ Å}$). These nSBU bowls sit inside neighboring bowls so that the coordinated pyridines are in close proximity to the Ph-substituents. van der Waals interactions stabilize this packing arrangement. Figure 4.13 illustrates the interactions for the nSBUs present in each of the two regions.

The eclipsed stacking generates hour-glass channels from the hexagonal cavities that run along the c-axis. The effective diameter of the channel calculated from the shortest contact to the center of the hexagon is 8.136 Å, significantly shorter than that of 11 (10.738 Å). This corresponds to a smaller spherical area with a volume of 282 Å$^3$, which is reflected in the calculated solvent accessible volume in the unit cell of 9.27% (compared to a volume of 648 Å$^3$ and calculated solvent accessible area of 20.1% in 11). The accessible volume would be increased to 12.6% upon removal of guest molecules (compared to 27% in 11).
The transformation of 11 into 12 happens for a crystalline sample, as well as a powder sample. The powder diffraction pattern of a freshly-collected sample of 11 was consistent with that calculated from single crystal data of 11, however, upon leaving the sample to stand in a closed vial and taking an XPD of the same powder sample after 35 days produces a pattern that is consistent with that calculated from single crystal data of 12. Compound 12 is thermally stable to temperatures in excess of 300 °C and decomposes after losing guest molecules at 174 °C and at 286 °C.

The other derivative of bdc, namely 5-NO2-bdc produced two Kagomé lattices under different reaction conditions. The slow diffusion of a methanolic solution of pyridine into a methanolic solution of Cu(NO3)2·2.5H2O and 5-NO2-H2bdc containing hexamethylbenzene (HMB) and nitrobenzene afforded compound 13, \([\text{Cu}_2(5-\text{NO}_2-\text{bdc})_2(\text{MeOH})_2]_n\). The crystal structure of 13 is illustrated in Figure 4.14.

There are two crystallographically independent copper ions in the crystal structure of 13, each comprising an SBU. The geometry around each copper ion is square
pyramidal ($d_{\text{Cu1-Cu1}} = 2.6312(18)$, $d_{\text{Cu2-Cu2}} = 2.6231(13)$ Å). The basal plane is defined by four oxygen atoms of the four 5-NO$_2$-bdc moieties ($d_{\text{Cu1-O}} = 1.954(7)$, $1.956(6)$, $1.964(5)$, $1.979(6)$; $d_{\text{Cu2-O}} = 1.943(7)$, $1.943(7)$, $1.966(7)$, $1.966(7)$ Å) and the apical position is occupied by a coordinating methanol molecule ($d_{\text{Cu1-O}} = 2.145(7)$; $d_{\text{Cu2-O}} = 2.147(1)$ Å). The bond distances are in agreement with the other Kagomé structures and the average bond distances calculated from the CSD search.

The trigonal nSBU constituent of 13 consists of three centrosymmetric SBUs two of which are equivalent, as illustrated in Figure 4.15. The 5-NO$_2$-bdc ligand bridging the two equivalent SBU moieties is different from the other two 5-NO$_2$-bdc ligands. The nSBU could be described as a curved isosceles triangle with sides measuring 10.526 and 10.468 Å at the wide ends and 7.699 and 7.772 Å at the narrow ends. The angles of the triangle are 59.64° and 60.18°. These dimensions are consistent with those in compound 3, NO$_2$-nanoball.

![Figure 4.15 Trigonal nSBU constituent of compound 13](image)

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*The nSBU resembles an isosceles triangle with sides equal to 10.526 and 10.468 Å at the wide end and 7.699 and 7.772 Å at the narrow end. The angles of the triangle measure 59.64° and 60.18°. Hexamethylbenzene and methanol are present in the cavity. Coordinated methanol is represented as a single atom with the remaining atoms removed for clarity.*
The 5-NO₂-bdc ligands are distorted to accommodate this trigonal arrangement. The twist angle \( \theta \) in the two equivalent 5-NO₂-bdc ligands is comparable to that in compounds 11 and 12 measuring 21.9°, but much smaller in the third 5-NO₂-bdc bridging ligand measuring 5.5°, only. The bending angle \( \phi \) in the two equivalent bridging ligands is also comparable to 11 and 12 measuring 5.65°, whereas in the third ligand the bending is more pronounced with a bend angle \( \phi \) of 7.47°. A closer look at the crystal structure reveals that this bending is due to a strong \( \pi-\pi \) stacking interaction (d\( _{\text{centroid}} \)…\( _{\text{centroid}} \) 3.356 Å) between the 5-NO₂-bdc ligand and a HMB guest molecule that is present in the cavity (Fig. 4.15). Each trigonal nSBU also hosts a disordered methanol molecule. The other two 5-NO₂-bdc ligands are involved in \( \pi-\pi \) stacking interactions with guest nitrobenzene molecules. The trigonal nSBU bowls assemble at the vertexes into an undulated 2D sheet generating hexagonal cavities. The nitro substituents of the bdc point towards the hexagonal cavities, whereas the coordinated methanol molecules point towards the trigonal cavities. The hexagonal cavities are occupied by two disordered nitrobenzene molecules, which are involved in \( \pi-\pi \) stacking interaction with the two equivalent 5-NO₂-bdc ligands (d\( _{\text{centroid}} \)…\( _{\text{centroid}} \)=3.870 Å). Figure 4.16 illustrates one hexagon in the 2D sheet of 13.
The effective diameter of the hexagon based on the closest contact to the center of the hexagon is 8.450 Å, comparable to that in structure 12 (8.136 Å) and NO$_2$-nanoball compound 3 (8.80 Å). The undulating sheets stack staggered in an ABAB fashion with an interlayer separation of 10.328 Å. Figure 4.17 demonstrates that viewing the stacked sheets at a slight incline down the a-axis reveals the presence of large channels.

Figure 4.16 Perspective view of a hexagon extracted from the crystal structure of 13$^*$

$^*$HMB and nitrobenzene are presented in space filling mode. Coordinated methanol molecules are presented as single oxygen atom with remaining atoms removed for clarity

Figure 4.17 Large channels in crystal structure of compound 13$^*$

$^*$View down the a-axis at an incline reveals large channels in the structure. Coordinated methanol is presented as single oxygen atom with the remaining atoms removed for clarity. Guest molecules were removed for clarity.
This is reflected in the calculated accessible volume which was found to be 17.1%, and would be increased to 52.0% upon removal of guest molecules.

It is worth noting that the reaction that yields compound 13 yields another product (blue crystals), which were found to change quantitatively while in solution within a period of ca. 10 days into crystals of 13. This other product (compound 15) will be discussed in detail in Chapter 5.

Another Kagomé structure based on 5-NO2-bdc was obtained, interestingly from the same reaction vial as that affording nanoball 3. Compound 14, \([\text{Cu}_2(5\text{-NO}_2\text{-bdc})_2(H_2O)_2]_n\), forms upon leaving the reaction vial over a period of two weeks where the nanoball crystals dissolved and new hexagonal blue-green crystals form. The identity of the crystals was confirmed as Kagomé lattice by single crystal X-ray crystallography. The crystal structure of 14 is depicted in Figure 4.18.

![Figure 4.18](image)

(a) Top view in space filling mode illustrating the Kagomé lattice. (b) Side view illustrating the ABC packing. The layers have been colored for clarity. Coordinated water molecules are presented as single oxygen atom with the hydrogen atoms removed for clarity. Guest molecules have been removed for clarity.

There is one crystallographically independent copper ion in the crystal structure of 14 having a square pyramidal geometry. The basal plane is defined by four oxygen
atoms of the four μ₂ 5-NO₂-bdc moieties (d₂Cu-O= 1.947(5), 1.948(5), 1.962(5), 1.964(5) Å) and the apical position is occupied by a water molecule (dCu-O= 2.153(5) Å). The two copper ions of the SBU are separated by 2.6490(17) Å. Bond distances are comparable to those of the other four structures reported herein and in agreement with the average bond distances calculated from the CSD search. The apical coordinating ligands point towards the trigonal cavities, whereas the nitro substituents on the bdc ligands point, in an alternating up and down fashion, towards the hexagonal cavity. The 5-NO₂-bdc ligands are distorted to accommodate this trigonal arrangement of the paddlewheels. The carboxylate moieties of the 5-NO₂-bdc are twisted out of plane with respects to each other by an angle θ= 10.2°. The carboxylate functionalities are also bent towards each other from the plane of the benzene ring by an angle ϕ= 5.18°, which is comparable to the bend angle in the nanoball structures (ϕavg. = 5.22°) and compound 10 (ϕ= 5.38°). The trigonal nSBU could be described as a curved equilateral triangle with sides measuring 10.554 and 7.773 Å, at the wide and narrow ends, respectively (measured from neighboring copper ions). The angles around the copper ion corners are perfect 60.00°. Figure 4.19 depicts the trigonal nSBU in 14. Disordered methanol molecules occupy the trigonal nSBU.
The trigonal nSBUs assemble at the vertexes into an undulating 2D sheet generating hexagonal cavities. The hexagonal cavities are occupied by two disordered nitrobenzene molecules in addition to a methanol molecule. The diameter of the hexagonal cavity measured based on the closest contact to the center of the hexagon is 10.492 Å, which is larger than that of compound 13 based on NO₂-bdc (8.450 Å) and comparable to that of 11 based on 5-Ph-bdc (10.738 Å).

The sheets in 14 stack staggered in an ABCABC fashion along the c-axis with an interlayer separation of 10.437 Å (corresponds to 1/3 translation along the c-axis). This packing style eliminates hexagonal channels in the structure that would arise from the hexagonal cavities; however, channels are present in the structure as can be seen in Figure 4.20, when the structure is viewed at an incline down the c-axis. This is reflected in the calculated solvent accessible volume of 14 which was found to be 9.06%, and
would be increased to 60.2% upon removal of guest molecules (highest of all the structures described herein).

![Crystal structure of compound 14 reveals large channels](image)

**Figure 4.20** Crystal structure of compound 14 reveals large channels*

* Crystal structure of 14 is presented in stick mode with coordinated water molecules presented as single oxygen atoms. Guest molecules have been removed for clarity

Even though there is no structural diversity within the sheet structure of the 5 Kagomé compounds presented herein, they are significantly different in their packing style, interlayer separations, and porosity. From the results presented herein, it appears that the electronic properties of the substituent of the bdc ligand influence the packing style: electron donating groups (e.g. Ph in 11 and 12) result in eclipsed AAA-type packing whereas electron withdrawing groups (e.g. NO₂ in 13 and 14) result in staggered ABAB or ABCABC-type packing. This is further supported by eight other Kagomé structures generated by our group that will be the subject of a future publication. The three packing styles are illustrated in scheme 4.1.
The eclipsed stacking results in hexagonal channels that run through the structure. If bulky substituents are present on the bdc moiety, they occupy the hexagonal channels minimizing their accessible volume. This is reflected in the calculated solvent accessible volumes of compounds 11 and 12 (Ph substituent), which have significantly lower volumes than the other structures. Staggered stacking precludes the presence of channels that would result from the hexagonal cavities; however, another type of channels is present and attributes to the large calculated solvent accessible volume in compounds 10, 13 and 14.

The size of the substituent on the bdc ligand does not affect the interlayer separation. This is not surprising since the substituents point towards the hexagonal channels and occupy the space therein.

Guest/solvent molecules present in the structure interact with the framework resulting in greater distortion in the bdc moieties, as seen in compound 13. The strong \( \pi-\pi \) interactions between the HMB and 5-NO\(_2\)-bdc increase the bend angle \( \phi \) and thus distort the resulting hexagonal cavity.
4.3 Conclusions

We presented herein 5 new compounds that have a topology that has been much sought after by material scientists and physicists, namely the Kagomé lattice. These structures result from the self-assembly of trigonal nSBU bowls into sheet structures. The sheet in each compound is sustained by Cu(II) dimers that are linked by 5-R-bdc ligands (R= H, Ph, NO₂) thereby generating trigonal and hexagonal cavities within the layer. Although there is no diversity in the sheet of these structures, there are dramatic differences in terms of the interlayer separation, the packing style and porosity. It can be concluded from the structures presented herein that the electronic and steric properties of the bdc moiety affect the packing style and porosity, respectively. All five Kagomé lattices presented have significant volumes accessible to guest molecules. The bend angles in the bdc moieties appear to be strongly influenced by guest molecules, which interact with the walls of the trigonal nSBU by supramolecular interactions.

With the potential magnetic properties of these compounds and their demonstrated porosity, they represent good candidates for multifunctional metamaterials. It is worth emphasizing that such dramatic changes were effected by simple modification of the reactants. A study of the effect of these modifications on the magnetic properties is currently underway.
4.4 Experimental

**General methods:** All materials were used as received; solvents were purified and dried according to standard methods. TGA data were obtained on a TA instruments 2950 TGA at high resolution with N₂ as purge gas.

**Synthesis of \( \{[\text{Cu}_2(\text{bdc})_2(\text{4-picoline})_2]\}_n \) (10):** The slow diffusion of a methanolic solution (7 mL) of H₂bdc (166 mg, 1.0 mmol) and 4-picoline (0.3 mL, mmol) into a methanolic solution of Cu(NO₃)₂·2.5H₂O (232 mg, 1.0 mmol) containing naphthalene guest molecules (256 mg, 2.0 mmol) yielded hexagonal blue green crystals. The most intense peaks observed in the XPD pattern from the bulk sample are consistent with those calculated from single crystal diffraction data.

**Synthesis of \( \{[\text{Cu}_2(\text{5-Ph-bdc})_2(\text{pyridine})_2]\}_n \) (11):** To a sample of 5-ph-H₂bdc (59 mg, 0.24 mmol) in ethanol (10 mL) was added pyridine (60 µL, 0.74 mmol). The solution was heated and stirred to maximize dissolution then filtered and layered on top of an ethanolic solution (5mL) of Cu(NO₃)₂·2.5H₂O (57 mg, 0.24 mmol). Blue-green crystals of the title compound form within hours at the interface (45.4% yield). The title compound can also be obtained in 43.0 % yield by direct mixing of the ingredients in ethanol, as confirmed by XPD. TG analysis reveals that 11 is thermally stable to ca. 315°C and loses guest and solvent molecules at 174.0°C in 6.78% and at 286.2°C in 8.9%. The most intense peaks observed in the XPD pattern from the bulk sample are consistent with those calculated from single crystal diffraction data.
**Synthesis of \([\text{Cu}_2(5-\text{Ph-bdc})_2(\text{H}_2\text{O})(\text{pyridine})]_3\) \((12)\):** Crystals of \(12\) were obtained from \(11\) by removing from the mother liquor and allowing the sample to stand under ambient conditions. \(12\) can be obtained *quantitatively* from a sample of \(11\) upon standing, as confirmed by XPD which shows a pattern consistent with that calculated from single crystal X-ray data.

**Synthesis of \([\text{Cu}_2(5-\text{NO}_2\text{-bdc})_2(\text{MeOH})_2]_3\) \((13)\):** Slow diffusion of a methanolic solution (5 mL) of pyridine into a methanolic solution (10 mL) of Cu(NO₃)₂·2.5H₂O (239 mg, 1.03 mmol) and 5-NO₂-H₂bdc (200 mg, 0.947 mmol) containing hexamethylbenzene (33 mg, 0.20 mmol) and nitrobenzene (1 mL) yielded, within 24 hrs, two types of crystals: blue (15) and blue-green (13) hexagons. Upon allowing the solution to stand for a period of ca. 10 days, 15 disappeared and only 13 prevailed. Single crystal X-ray crystallography of blue green crystals confirmed their identity as the title compound. The most intense peaks observed in the XPD pattern from the bulk sample are consistent with those calculated from single crystal diffraction data. %yield = 63.0% based on Cu(II).

**Synthesis of \([\text{Cu}_2(5-\text{NO}_2\text{-bdc})_2(\text{H}_2\text{O})_2]_3\) \((14)\):** Slow diffusion of a methanolic solution (10 mL) of Cu(NO₃)₂·2.5H₂O (124 mg, 0.533 mmol) into a methanolic solution (10 mL) of 5-NO₂-H₂bdc containing pyridine (0.080 mL, 0.989 mmol), naphthalene (25 mg, 0.195 mmol) and nitrobenzene (3 mL) yielded large square green blue crystals within months. Single crystal X-ray crystallography determined the identity of the crystals as compound 3 (see chapter 2). Upon reexamining the reaction vial after a period of three weeks, the
large square crystals disappeared and small hexagonal blue green crystals appeared. X-ray crystallography determined the identity of the crystals as the title compound.

**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 MoKα radiation (λ = 0.7107 Å). The data were corrected for Lorentz and polarization effects and for absorption using the SADABS program. The structures were solved using direct methods and refined by full-matrix least-squares on |F|^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions and refined with temperature factors 1.2 times those of their bonded atoms. All crystallographic calculations were conducted with the SHELXTL 5.1 program package. Crystallographic data for compounds 10-14 is presented in Table 4.1.
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Chapter 5
ADDITIONAL RELATED CHROMOPHORES

5.1 Preface

5.1.1 Self-assembly Under Thermodynamic Equilibrium Conditions

A characteristic feature of a thermodynamic self-assembly process is that all reaction steps are under equilibrium. This means that all reaction steps are reversible and the proportion of each product obtained is dependent on its relative thermodynamic stability. This reversibility is due to the lability of the coordination bond, which can dissociate and re-associate until the most stable thermodynamic product is obtained. The slow diffusion technique typically employed in the synthesis of the metal-organic structures reported in the previous chapters is a thermodynamic equilibrium process where the reactants interact at a gradient of different concentrations as they slowly diffuse into one another. As the conditions vary, a number of different chromophores are possible. In addition to the binuclear SBU chromophore forming, mononuclear chromophores are also possible.
5.1.2 CSD Survey of Cu(II)

Copper(II) has been extensively studied and is known to exist in a number of different geometries. It can be tetrahedral, square pyramidal, trigonal bipyramidal or octahedral. A CSD\textsuperscript{19} search of copper compounds containing two carboxylate ligands returned 978 hits. Only 21\% of the structures (201 hits) have the carboxylate moieties bound in a monodentate fashion, while the remaining structures have the carboxylates chelating to the metal center. Of those 201 structures, 38 (19\%) have the carboxylates syn around the metal center. The coordination number around the Cu(II) ion varies between four (93 structures), five (53 structures), and six (55 structures) with one example of a 2-coordinated Cu(II) ion (Ref code PANFOZ). The Cu-O bond distance ranges between 1.821 and 2.451 Å with an average of 1.966(70) Å. Figure 5.1 illustrates some of the simple geometries possible for Cu(II).

![Figure 5.1 Some of the possible chromophores of Cu(II)](image)
5.1.3 Supramolecular Isomers

Isophthalic acid is an angular ligand with the two functionalities predisposed at an angle of 120°. As it is possible for the building blocks to arrange into more than possible way in the solid state, a number of supramolecular isomers are possible. Figure 5.2 illustrates three possible supramolecular isomers that can be generated from the same set of 120° angular node and linear spacer: (a) hexagon, (b) helix and (c) zigzag chain. The hexagon represents a discrete planar species few examples of which have been reported to date. A number of hexagons based on isophthalic acid and its derivatives have been reported to date. Hamilton et al. utilized the supramolecular hydrogen bonding interactions of the carboxylic acid functionality to assemble a supramolecular hexagon, whereas Moore et al. assembled a molecular hexagon from functionalized isophthalic acids through acetylene bonds making polyphenyleneacetylenes. Other examples of metal-organic supramolecular hexagons have been reported by Lehn, Stang, Newkome, and Lin. Lehn used a flexible polydentate ligand, but directed the formation of the hexagon by using a template anion that fits inside the cavity. All the others used an angular bifunctional ligand that has the functionalities predisposed at an angle of 120°. In all cases, the reported hexagons are charged species. The zigzag polymer has been widely encountered, whereas the helix remains quite rare in the context of coordination polymers. Additional supramolecular isomers from the angular ligand and linear spacer are also possible and include larger ring systems (non-planar), catenane supramolecular isomers, and other discrete polyhedra.
5.1.4 *Isophthalic Acids*

Isophthalic acid\textsuperscript{268} is known to exist in the solid state as a zigzag chain sustained by the centrosymmetric carboxylic acid dimer. As isophthalic acid represents an angular ligand with the two carboxylic acid moieties predisposed at an angle of 120°, other possible supramolecular isomers include a helix and a discrete hexagon. Strategies of directing the formation of the discrete self-assembled hexagon over the zigzag chain have been investigated for isophthalic acid. Hamilton et al\textsuperscript{129} demonstrated that placing a bulky substituent on the 5-position of the isophthalic moiety disrupts the packing of the chains and results in the formation of a self-assembled hexagon. The group reported the synthesis and crystal structure of a discrete hexagon based on the self-assembly of 5-OC\textsubscript{10}H\textsubscript{21}-H\textsubscript{2}bdc. The planar hexagons are sustained by the 12 hydrogen bonding interactions (six centrosymmetric carboxylic acid dimers), and have an effective diameter of 1.2 nm (measured from opposite phthaloyl hydrogen atoms). The hexagons stack on top of one another creating channels. The long alkyl chains extend above and below the
plane of the hexagon in an alternating fashion. This elegant strategy of directing the formation of the discrete macrocycle over the infinite chain by adding bulky substituents was first employed by Whitesides et al.,\textsuperscript{269} who controlled the formation of a rosette structure over a crinkled tape in the cyanuric/melamine acid systems by adding bulky substituents that sterically hinder the formation of the tape and favor the formation of the discrete structure.

Vittal \textit{et al}.\textsuperscript{244, 270} has also done some extensive studies on the effect of alkyl chain substituents on the aggregation of isophthalic acids in the solid state. The studies revealed that the length of the alkyl chain has a significant effect on the resulting crystal structure. 5-OR-H\textsubscript{2}bdc were found to self-assemble via hydrogen bonding into zigzag chains that pack into lamella-type structures when the alkyl chain, R, consists of 12 carbons or more. When the alkyl chain consists of 6-10 carbons, the isophthalic acids were found to self-assemble into discrete hexagons, where the alkyl groups extend above and below the plane of the rings. As in the structure reported by Hamilton \textit{et al},\textsuperscript{129} the hexagons stack on top of one another generating channels. The cavities of the hexagons are filled by part of the alkyl chains (3-4 carbon atoms) of neighboring hexagons.

Crystal structures of other simple isophthalic acid derivatives that have been reported in the CSD include 5-nitro-, 5-sulfo- and 5-hydroxyisophthalic acids. 5-nitroisophthalic acid (5-NO\textsubscript{2}-H\textsubscript{2}bdc) is known to self-assemble via hydrogen bonding into 1D chain structures. Two phases of 5-NO\textsubscript{2}-H\textsubscript{2}bdc have been reported to date, a hydrated and a non-hydrated phase. In the former, 1D linear chains result from the catemar synthon in which a water molecule bridges two carboxylic acid moieties. Thus the chains arrange in pairs that are sustained by bridging water molecules with the nitro substituents
in one chain aligned on the same side, but opposite to that of the other chain of the pair. This could be described as a tape structure. The tapes close-pack into corrugated sheets that stack on top of one another. In the other phase of 5-NO₂-H₂bdc, zigzag chains sustained by the centrosymmetric carboxylic acid dimer form.

A CSD search of isophthalates coordinated to transition metals returned 17 hits (search excluded structures that included the SBU chromophore). 10 of the structures are based on bdc, 6 on 5-OH-bdc and 1 on 5-SO₃-bdc. All structures, with the exception of one, are polymeric.

5.2 Results and Discussion

5.2.1 Compound 15

The slow diffusion of a methanolic solution of pyridine into a methanolic solution of Cu(NO₃)₂·2.5H₂O and 5-NO₂-H₂bdc containing HMB and nitrobenzene resulted in two types of crystals: blue and blue green hexagonal plates. The latter was identified as compound 13 (discussed in Chapter 4), which is based on the dimetal tetracarboxylate SBU. The crystal structure of the blue hexagonal plates, compound 15, is shown in Figure 5.3. The structure is a 1D tape that results from two 1D linear chains sustained by 5-NO₂-bdc ligands coordinated to copper ions in a monodentate fashion. The chains arrange in such a way so that the nitro substituents of one chain are aligned in the same direction and opposite to that of the other chain in the tape.
The Cu(II) ions have a square pyramidal geometry where the basal plane is defined by two anti monodentate carboxylate ligands (d$_{\text{Cu-O1}}$ 1.9736(13) Å, d$_{\text{Cu-O2}}$ 2.0264(17) Å) and two orthogonal pyridine ligands (d$_{\text{Cu-N1}}$ 1.9969(17) Å, d$_{\text{Cu-N2}}$ 2.0204(17) Å) and the apical position is occupied by a carboxylate oxygen atom from the 5-NO$_2$-bdc moiety in the opposite chain of the tape (d$_{\text{Cu-O3}}$ 2.2550(14) Å). This tape structure is similar to that of the hydrated form of the parent 5-NO$_2$-H$_2$bdc. The tape structure is reinforced by CH–π interactions (d$_{\text{CH…centroid}}$ 2.905 Å) between the coordinated pyridine ligands (Fig 5.4a). The tapes stack in such a way as to facilitate π–π stacking interactions between the 5-NO$_2$-bdc moieties of the stacked tapes (d$_{\text{centroid…centroid}}$ 3.766 Å) (Fig 5.4b). It is worth noting that we have previously reported an analogous structure based on bdc that has the same chromophore. The bond distances and interactions in that structures are consistent with the one reported herein.$^{271}$
Interestingly, when crystals of 15 are left in contact with the mother liquor, they turn into blue green crystals of 13, the Kagomé structure, as confirmed by unit cell determination and XPD of the bulk sample. Closer examination of the chromophore in 15 reveals that this is not so surprising. The chromophore, illustrated in Fig 5.5, is bis(µ₂-carboxylato)copper(II) in which two Cu ions are bridged by two carboxylate moieties and each is coordinated by a monodentate carboxylate with the carbonyl oxygen of each available for further binding to the metal centers. Figure 5.5 illustrates how the tetrakis(µ₂-carboxylato)dicopper SBU can form when the two carbonyl oxygen atoms rotate and displace two of the coordinated pyridine ligands. In other words, bis(µ₂-carboxylato)copper(II) could be considered a precursor to the tetrakis(µ₂-carboxylato)dicopper(II), SBU. A CSD search to determine the abundance of this chromophore revealed that it is known for a wide number of transitions metals (209 hits), but in general, it appears to form when the dicarboxylate used is bulky (e.g. 2,2-dimethylpropanoate), or a chelating ligand is employed (e.g. ethylenediamine, N,N,N’,N’-
tetraethylethenediamine). Only four structures were reported for Cu(II) (JOZMAM, JEKLUG, PRTDCU, QEDQAR). The transformation of 15 into the 2D Kagomé structure suggests that the paddlewheel chromophore is the more stable thermodynamic one.

![Diagram of compound 15](image)

**Figure 5.5** Possible rearrangement in chromophore of compound 15

*Bis(μ₂-carboxylato)copper(II) chromophore can rearrange to yield the tetrakis(μ₂-carboxylato)dicopper(II) chromophore, SBU

5.2.2 Compounds 16a and 16b

When 5-NO₂-H₂bdc is reacted with Cu(NO₃)₂·2.5H₂O in the presence of a non-coordinating amine, 2,6-lutidine, a different chromophore is obtained. Figure 5.6 illustrates the square pyramidal Cu(II) chromophore observed in compounds 16a and 16b. In order to determine how well-known this chromophore is, a CSD search was performed. A search for a five-coordinate copper with two monodentate carboxylates returned 53 hits. 40 of those have the carboxylate moieties planar with syn and anti conformation around the metal center. Only 6 of the hits had the carboxylates in an anti conformation, with the rest adopting a syn conformation. Surveying the bond distances in these structures revealed that the four bonds in the basal plane are shorter than the one
in the apical plane. This is in accordance with the Jahn-Teller distortion exhibited by the d⁹ electron configuration of Cu(II) ion. The average bond distances in the basal plane were found to be \(d_{Cu-O1} 1.952(21) \text{ Å}, \ d_{Cu-O2} 1.957(17) \text{ Å}, \ d_{Cu-L1} 2.039(78) \text{ Å}, \ d_{Cu-L2} 2.014(35) \text{ Å}, \ d_{Cu-L3} 2.275(119) \text{ Å}\) for the \textit{anti} structures, and \(d_{Cu-O1} 1.952(22) \text{ Å}, \ d_{Cu-O2} 1.955(27) \text{ Å}, \ d_{Cu-L1} 2.029(75) \text{ Å}, \ d_{Cu-L2} 2.058(106) \text{ Å}, \ d_{Cu-L3} 2.201(112) \text{ Å}\) for the \textit{syn} structures. No significant difference in bond distances to copper of the basal ligands exists between the \textit{syn} and \textit{anti} conformations, but the apical ligand distance is significantly longer in the \textit{anti} structures (2.275 Å compared to 2.201 Å).

The reaction of 5-NO₂-H₂bdc with Cu(NO₃)₂·2.5H₂O and 2,6-lutidine in methanol yields a precipitate, crystallization of which from DMSO yields pale blue square plates, \textbf{16a}. X-ray crystal data of \textbf{16a} revealed that it is an infinite 1D zigzag chain, crystal structure of which is illustrated in Figure 5.7a. There are two crystallographically independent copper ions in the structure. The basal plane of each is occupied by two \textit{syn}-monodentate 5-NO₂-bdc ligands (\(d_{Cu1-O1} 1.962(3), \ d_{Cu1-O2} 1.959(3) \text{ Å}; \ d_{Cu2-O1} 1.954(3), \ d_{Cu2-O2} 1.954(3) \text{ Å} \)), one DMSO molecule (\(d_{Cu1-O} 1.966(3); \ d_{Cu2-O} 1.993(3) \text{ Å} \)) and one water molecule (\(d_{Cu1-O} 1.962(3); \ d_{Cu2-O} 1.977(3) \text{ Å} \)), but the apical position is occupied by
water on one copper center \( (d_{Cu1-O} \ 2.227(3) \ \text{Å}) \) and DMSO on the other \( (d_{Cu2-O} \ 2.216(3) \ \text{Å}) \). The bond distances are all in agreement with the bond distances determined from the CSD survey. The chains extend along the a-axis and associate in pairs that stack along the b-axis. The stacked chains are sustained by \( \pi-\pi \) stacking interactions between the aromatic 5-NO\(_2\)-bdc moieties \( (d_{\text{centroid...centroid}} \ 3.700\text{Å}) \) and hydrogen bonding interactions between the coordinated ligands. Figure 5.7b demonstrates the aromatic stacking and H-bonding interactions.

Each chromophore is involved in four hydrogen bonding interactions between the equatorially coordinated water molecule in one chain and the carbonyl oxygen atoms of the 5-NO\(_2\)-bdc moieties of the neighboring chain \( (d_{O...O} \ 2.666 \text{ and } 2.679 \ \text{Å}) \). This gives a total of four hydrogen bonding interactions per chromophore (Figure 5.8), which enhances the stability of the chromophore.
Upon leaving crystals of 16a in the mother liquor for a period of few weeks, they disappear and new darker blue, hexagonal crystals appear, 16b. X-ray crystal data of 16b revealed that the new compound is a discrete hexagonal structure based on the same chromophore as in 16a. There are two crystallographically independent copper ions in the structure of the hexagon. The basal plane of each is occupied by two syn-monodentate 5-NO2-bdc ligands ($d_{\text{Cu1-O1}}$ 1.965, $d_{\text{Cu1-O2}}$ 1.909 Å; $d_{\text{Cu2-O1}}$ 1.936, $d_{\text{Cu2-O2}}$ 1.936 Å), one DMSO molecule ($d_{\text{Cu1-O}}$ 1.955; $d_{\text{Cu2-O}}$ 1.783 Å) and one water molecule ($d_{\text{Cu1-O}}$ 1.964; $d_{\text{Cu2-O}}$ 1.966 Å), but the apical position is occupied by methanol on one copper center ($d_{\text{Cu1-O}}$ 2.239 Å) and water on the other ($d_{\text{Cu2-O}}$ 2.298 Å). All bond distances in 16b are in agreement with those of the zigzag chain and the CSD survey, except for the distance of the coordinated DMSO on Cu2 ($d_{\text{Cu2-O}}$ 1.783 Å), which is significantly shorter than expected (shortest bond distance from CSD search is 1.952 Å).

Figure 5.9 illustrates the crystal structure of 16b, which results from the self-assembly of thirty molecular components: six 5-NO2-bdc moieties, six Cu(II) ions and eighteen coordinated solvent molecules. The hexagons are neutral and planar. The effective outer diameter of the hexagon measured from opposite nitro groups is 3.14 nm. The distance from the center of the hexagon to the closest contact, coordinated solvent
molecule, is 0.58 nm, which affords an internal cavity with an effective diameter of ca. 0.8 nm. This is 0.3 nm longer than the hexagon resulting from the self-assembly of the alkyloxyisophthalic acid derivative reported by Hamilton et al.\textsuperscript{129} (effective inner diameter of hexagon measured from opposite phthaloyl 2-H sites is 1.5 nm, compared to 1.2 nm for the hexagons formed by H\textsubscript{2}bdc-5-OC\textsubscript{10}H\textsubscript{21}.

![Figure 5.9 Crystal structure of compound 16b*](image)

\textsuperscript{*}(a) Top view of hexagon 16b in space-filling mode. (b) Side view illustrating the planarity of 16b. Coordinated ligands are presented as single oxygen atoms with the remaining atoms removed for clarity. Guest MeOH molecules have been removed for clarity

Molecules of 16b pack into sheets with unusually large voids between the hexagons (Figure 5.9a). The separation between two neighboring hexagons within a sheet is 3.5 nm (measured from centroid to centroid). As the sheets pack, they stagger so that every fourth layer repeats, \textit{i.e.} ABCABC packing (Figure 5.10b,c), creating hourglass shaped channels along [001] with an effective diameter equal to that of the hexagon (0.8 nm). This packing arrangement is contrary to eclipsed stacking of the other
self-assembled hexagons based on derivatives of H₂bdc, but can be explained upon examining the stacked hexagons more closely.

A closer look at the packing interactions in the crystal structure of 16b reveals that each apically coordinated water molecule is involved in hydrogen bonding interactions (dO…O 2.637 Å) with two carbonyl oxygen atoms of 5-NO₂-bdc moieties in the adjacent sheet (Figure 5.11).

**Figure 5.10** Crystal structure packing in 16b

**Figure 5.11** Hydrogen bonding interactions between stacking hexagons of 16b
This results in 4 hydrogen bonding interactions per chromophore and a total of 24 hydrogen bonding interactions for each hexagon, all of which contribute significantly to the stability of this packing arrangement. The hydrogen bonding pattern observed in the hexagons, 16b, is the same as that observed in the supramolecular isomeric chain 16a (Fig 5.8), but the interactions are slightly stronger (dO…O 2.637 Å vs. 2.673 Å for the hexagon and chain, respectively). The stacked sheets of hexagons are also involved in π-π stacking interactions between the aromatic rings of 5-NO2-bdc resulting in an inter-layer separation is 3.34 Å.\textsuperscript{201}

It would be expected from the crystal structure that 16b would be porous. The calculated solvent accessible void is \textit{ca}. 10% of the total volume; however, this would be increased to 57% upon removal of guest and replacing the coordinated DMSO and MeOH molecules with water molecules.

16b is readily soluble in MeOH and sparingly soluble in hot DMSO and DMF. The enhanced solubility in methanol facilitated its characterization by electrospray mass spectroscopy, which indicated that 16b exists in solution with 4 coordinated DMSO molecules and 14 coordinated MeOH molecules (M\textsuperscript{+} = 2396 m/z). The mass spectrum of 16b can be found in Appendix 3.

The conversion of 16a into 16b upon leaving is solution for an extended period of time suggested that 16a is the kinetic product, while 16b is the thermodynamic product. To confirm this, the crude precipitate obtained from the initial reaction was heated in DMSO (\textit{ca.} 110 °C) for 24 hours and the solution was allowed to stand. The most intense peaks observed in the X-ray powder diffraction (XPD) patterns from the bulk sample were consistent with those calculated from single crystal diffraction data confirming that
the hexagon 16b forms exclusively under thermodynamic conditions. Thermal stability
data shows that 16b is stable up to 220 °C and loses guest and coordinated solvent in
9.1% at 48.2 °C (calc. 7.5%), and 31% at 91.0 °C (calc. 28.5%).

5.3 Conclusions

The results presented herein demonstrate that under thermodynamic equilibrium a
number of chromophores are possible leading to a number of different products. The
chromophore based on bis(µ2-carboxylato)copper(II) can be considered a precursor to the
SBU, tetrakis(µ2-carboxylato)dicopper(II). The lability of the ligands facilitates the re-
arraignment of the chromophore into the desired, thermodynamically stable SBU. When
a non-coordinated amine is used (2,6-lutidine), a square pyramidal chromophore
sustained by two syn monodentate carboxylate moieties and three coordinated solvent
molecules results. The ability of the coordinated solvent ligands to participate in
hydrogen bonding, more specifically 4 hydrogen bonding interactions per chromophore,
tremendously enhances its stability. Consequently, the chromophore remains intact even
when the kinetic 1D zigzag chain re-arranges into its supramolecular isomeric hexagon.

We have further demonstrated supramolecular isomerism by presenting two
structures that are based on the same building units, yet they are dramatically different
from one another. The 1D zigzag chain, 16a, is the kinetic product forming first and then
converting into the hexagon supramolecular isomer 16b, which is the thermodynamic
product. Hexagon 16b exhibits an unusual packing arrangement where large voids are
present within the sheets of hexagons (separation of 3.5 nm between centers of
neighboring hexagons). Strong interlayer interactions between the sheets, hydrogen
bonding interactions (24 per hexagon) and π-π stacking interactions, tremendously stabilize this packing arrangement.

Future work with the hexagon could involve using as it a building block for even larger structures. For example, one could use linear ditopic ligands such as pyrazine, or bipyridine to stack the hexagons into nanotubes.

5.4 Experimental

General methods: All materials were used as received; solvents were purified and dried according to standard methods. TGA data were obtained on a TA instruments 2950 TGA at high resolution with N₂ as purge gas.

Synthesis of \{\text{Cu}(5-\text{NO}_2\text{-bdc})(\text{py})_2\}_n \text{ (15)}: \) Slow diffusion of a methanolic solution (5 mL) of pyridine into a methanolic solution (10 mL) of Cu(NO₃)₂·2.5H₂O (239 mg, 1.03 mmol) and 5-NO₂-H₂bdc (200 mg, 0.947 mmol) containing hexamethylbenzene (33 mg, 0.20 mmol) and nitrobenzene (1 mL) yielded, within 24 hrs, two types of crystals: blue (15) and blue-green (13) hexagons. No yield was determined as crystals of 15 turned into 13 upon standing in the mother liquor.

Synthesis of \{\text{Cu}(5-\text{NO}_2\text{-bdc})(\text{DMSO})_{1.5}(\text{H}_2\text{O})_2(\text{MeOH})_{0.5}\}_n \text{ (16)}: \) To a methanolic solution of 5-nitroisophthalic acid (250 mg, 1.184 mmol) and copper nitrate (276 mg, 1.184 mmol) was added 2,6-lutidine (254 mg, 2.368 mmol). The resulting blue precipitate (371 mg) was recrystallized from DMSO to afford 16a and 16b. Alternatively, 16b was exclusively obtained by heating a solution of the crude precipitate (197 mg) in
DMSO (15 ml) for 24 hours and allowing the solution to sit for 3 weeks to yield 128.3 mg (ca. 27%) of deep blue precipitate. Most intense peaks in the XPD are consistent with those calculated from the single crystal data. TG analysis showed that crystals of 16b are thermally stable to 220°C and lose guest and solvent molecules at 48.2°C in 9.1% (calc. 7.5%), and at 91.0°C in 31% (calc. 28.5%).

**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 MoKα radiation (λ = 0.7107 Å). The data were corrected for Lorentz and polarization effects and for absorption using the SADABS program. The structures were solved using direct methods and refined by full-matrix least-squares on |F|^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions and refined with temperature factors 1.2 times those of their bonded atoms. All crystallographic calculations were conducted with the SHELXTL 5.1 program package. Crystal structure data of compounds 15, 16a and 16b are presented in Table 5.1.
Table 5.1 Crystallographic data for compounds 15, 16a, 16b

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Chapter 6

GENERAL CONCLUSIONS AND FUTURE DIRECTIONS

6.1 Summary

This dissertation presented a series of related, yet structurally diverse supramolecular architectures that are obtained from simple starting materials in single step reactions under thermodynamic equilibrium conditions. The modular nature of the systems presented herein contributes greatly to the structural diversity observed. The lability of the metal-ligand coordinate covalent bond that directs the formation of these structures facilitated the formation and isolation of a number of possible products. In more than one case we presented examples where the kinetic product converts into the thermodynamic product under thermodynamic equilibrium.

We presented a new design strategy by which molecular squares, SBUs, are linked at the vertices to generate two nanoscale SBUs: a tetragonal (collection of four squares) and trigonal (collection of three squares) nSBUs. We demonstrated that these nSBUs self-assemble to generate architectures with different dimensionality, complexity and topology. Self-assembly of both types of nSBUs results in discrete spherical structures that conform to the shape of a faceted polyhedron, the small rhombihexahedron, which we termed nanoballs. The nanoballs have the general formula
[Cu$_2$(5-R-bdc)$_2$(L)$_2$]$_{12}$ and are distinguished by a number of features including their high molecular weight, large molecular volume and diameter and high porosity. The nanoballs exhibit inclusion properties in their windows, which are reminiscent of host-guest interactions in calixarenes.

Self-assembly of the tetragonal nSBUs only results in tetragonal 2D sheets, 4$^4$ grids, which have the general formula \{[Cu$_2$(5-R-bdc)$_2$(L)$_2$]$^4$\}$_n$, when bdc and its derivatives are employed and \{[Cu$_2$($\text{pdc}$)$_2$(L)$_2$]$^4$\}$_n$, when the wider angle pdc is employed. Further structural diversity in the solid state in this series of structures is observed due to atropisomerism of the nSBU that arises from its conformational flexibility. The diversity is underlined by the presence of different shape and size cavities, different inclusion properties and by different solvent accessible volumes in the structures. This further strengthens the similarity of the nSBU to a calixarene.

Self-assembly of the trigonal nSBUs only results in trigonal 2D sheets with the general formula \{[Cu$_2$(5-R-bdc)$_2$(L)$_2$]$^3$\}$_n$. The topology of this series of structures is of one that has been much sought after by material scientists and physicists, the Kagomé lattice. Although there is no structural diversity within the sheet of the structures that belong to this series, there is diversity in the packing of the sheets, in the interlayer separation and in the porosity. The differences between the Kagomé structures were effected by varying the molecular components of the system.

Molecular formulas for compounds belonging to the three structure topologies summarized above have been presented throughout this work in such a way as to
emphasize their close relationship. All three topologies have the same basic formula and hence could be viewed as structural supramolecular isomers of one another.

Performing the synthesis under thermodynamic equilibrium conditions facilitated the generation and isolation of other chromophores that ultimately resulted in related nanostructures. Two such chromophores were presented, one is bis(μ₂-carboxylato)copper(II), which is a kinetic product that arranges in solution into tetrakis(μ₂-carboxylato)dicopper(II), the SBU, to ultimately generate an SBU-based Kagomé product. The other chromophore is [Cu(5-NO₂-bdc)(DMSO)₁.₅(MeOH)₀.₅(H₂O)], which forms a polymeric chain in which it is highly stabilized by strong H-bonding interactions. As a result, the chromophore stays intact as the polymer rearranges into a more thermodynamically stable product, a discrete nanoscale hexagon, which is one of the largest metal-organic molecular hexagons isolated and characterized by single crystal X-ray crystallography.

6.2 Conclusions

Angular dicarboxylate ligands can bridge the SBU, which represents a molecular square, at the vertexes into related discrete and infinite structures that are porous. The distortion in the bridging ligand as it confines the SBUs into these structures is influenced by guest molecules. Strong intramolecular interactions result in greater distortion in the aryl ligand. The size of the building blocks facilitates the generation of nanoscale materials in single step reactions. Performing the reactions under thermodynamic equilibrium conditions is advantageous as it allows for the isolation of related products that otherwise would not be possible. The self-assembly process is influenced by a
number of factors including template molecules, solvent and concentration. Varying the reaction conditions can result in a number of related, yet structurally diverse supramolecular architectures. This diversity can arise from conformational flexibility, guest/host interactions and packing of molecules in the crystal lattice. The diversity is exemplified by different topologies which effect significantly different properties. Careful analysis of supramolecular interactions in the crystal structures and understanding the subtle molecular interactions can help better design experiments that would generate desired products reproducibly.

6.3 Future Directions

A thorough and systematic evaluation of the effect of reaction conditions on the resulting supramolecular structure could be conducted. The effect of the bdc ligand, coordinating base and solvent could be evaluated. The steric and electronic properties of the bdc ligand are expected to affect the resulting supramolecular isomer. It is likely that a trend as that seen for isophthalic acid, in terms of the effect of bulky substituents on the resulting supramolecular structure, would be seen in these systems. Bulky substituents are expected to preclude the formation of the $4^4$ tetragonal sheets as they are sterically demanding and the crystal structure cannot accommodate them. They would not hinder the formation of the nanoball, however, as they would be decorating the surface and not interacting with each other, and they would not hinder the formation of the Kagomé lattice as they would extend into the large, available hexagonal channels, as seen from the results presented herein.
As for the effect of the base, whether the base can coordinate or not can affect the resulting chromophore. Other bases with electron donating or withdrawing substituents or branched or long alky chains could be evaluated as they may lead to the formation of other interesting chromophores.

Different solvents also need to be evaluated as in conjugation with the employed base they can lead to different products, as illustrated in the mononuclear chromophore presented in chapter 5, if they able to coordinate to the metal site and/or have hydrogen bonding capabilities.

Synthesis of other derivatives of the small rhombihexahedron could be targeted by using other derivatives of bdc. Bdc ligands with different steric and electronic properties are expected to have direct effect on the bulk physical properties of the nanoballs in terms of solubility, stability, etc. Furthermore, these substituents are expected to have an effect on the trigonal and tetragonal windows and in turn on their inclusion properties. For example, the use of a bdc substituted with bulky aryl groups would alter the shape and electronic nature of the windows. The depth of the window would be greater and its hydrophobicity would be enhanced. This could alter the selectivity of the windows to guest molecules. A systematic evaluation of the selectivity of the windows to different guest molecules could be conducted to determine how the shape, size or chemical nature affects the inclusion properties.

The synthesis of other faceted polyhedra could also be targeted, specifically ones based on molecular squares only: the cubohemioctahedron and the small rhombidodecahedron. Judicial control over the angle at which the squares are connected would control the formation of these polyhedra. To generate the cubohemioctahedron,
one needs to link the molecular squares at 90° angle. Obviously, such an angle is not readily obtained for organic molecules; however, it is reasonable to assume that the use of ligands with slightly bigger or smaller angles could yield the desired product as these ligands could sustain some distortion from their ideal angle. A possible dicarboxylate ligand that subtends such angles is \(N\)-methylpyrrole-3,4-dicarboxylate (72°). To generate the small rhombidodecahedron, one needs to link the molecular squares at a wider angle (144°). This could be effected by using the dicarboxylate ligand \(N\)-methylpyrrole-2,4-dicarboxylate, which subtends an angle of ca. 157°, yet it is flexible to accommodate the formation of the desired product. Another ligand that could be used is the commercially available thiophene-2,5-dicarboxylate. This ligand subtends an angle of 145° and would also be suitable for the generation of the small rhombidodecahedron.

The nanoballs could also be used as building blocks for even larger structures. The nanoballs could serve as nodes for extended networks. This has already been demonstrated with a derivative of bdc.\(^{192}\) The nanoballs have two possible branching points: the 5-position of the bdc ligand, or the coordinated apical ligand. Compound 2, for example, is decorated with 24 OH-functionalities that are suitable for derivatizing the nanoball further either by forming covalent bonds or supramolecular interactions with hydrogen-bond acceptors. The use of labile apical ligands could facilitate their displacement with other polytopic coordinating ligands to generate extended structures.

The nanoballs could also serve as a core for dendritic structures. The high multiplicity on the surface of the balls makes them prime candidates for such purpose. Such structures could be prepared in one of two ways: using a pre-made nanoball and reacting it further with dendritic wedges (via covalent or supramolecular interactions) or
using branched bdc ligands to self-assemble in situ into the dendritic product. The use of very highly branched dendrons, however, could sterically hinder the self-assembly process.

The former strategy requires evaluating the stability of the nanoballs to various reaction conditions such as solvent effect, pH, temperature, etc. The preliminary results presented herein suggest that it would feasible to subject the nanoballs to further reactions.

The Kagomé structures are suitable for generating multifunctional metamaterials since they are lamellar and contain large hexagonal cavities. Guest molecules with different properties could be incorporated in the channels or between the layers and this would be expected to have a significant effect on the bulk physical properties of these materials. Magnetic studies need to be conducted to evaluate the effect of the substituents of the bdc on the magnetism.
References


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186. Papaefstathiou, G. S.; MacGillivray, L. R. *Angew. Chem., Int. Ed.*, **2002**, 41,


238. Spek, A. L. *PLATON*, Utrecht University, The Netherlands, **2000**.


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Appendixes
Appendix 1. Mass spectrum for compound 1
Appendix 2. Mass spectrum for compound 2
Appendix 3. Mass spectrum for compound 16b
ABOUT THE AUTHOR

Heba Abourahma received her Bachelor’s degree with honours in chemistry from Saint Mary’s University in Halifax, Nova Scotia in 1997. It was there where she had her first research experience and first publication. She earned her Master’s degree from the University of Ottawa in 1999 after working in the area of carbohydrate synthesis. While pursuing her Ph.D. at the University of South Florida, the author held a visiting assistant professor position at Eckerd College where she taught general, organic and inorganic chemistry, in addition to holding a senior instructor position at the University of South Florida.

Heba has received honors and awards throughout her academic training including three Natural Sciences and Engineering Research Counsel of Canada (NSERC) awards, academic and industrial, teaching awards and outstanding graduate student conference presentation awards. She has published a number of publications and presented contributed talks at regional, national and international conferences.