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Design, Synthesis and Structural Diversity in Coordination Polymers

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Summary: The fundamental precept of crystal engineering is that all the information necessary for the design of a network is already stored in the molecular building blocks used. Coordination polymers represent an example of how crystal engineering has become a paradigm for the synthesis of new architectures and compositions. We report herein ten structures that are supramolecular isomers of one another. The structures are prepared from the same building blocks under mild reaction conditions. The modularity of coordination polymers imparts structural diversity that otherwise would not be possible.

Keywords: coordination polymers; dimetal tetracarboxylate; isomerism; SBU; supramolecular

Introduction

Supramolecular chemistry was defined by Lehn as the chemistry beyond the molecule.[1,2] The concepts of supramolecular chemistry are derived from nature 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 interactions. It should be stressed that supramolecular approaches to synthesis provide an alternate paradigm to sequential multi-step synthesis that is particularly attractive since it can be accomplished in a single step, often in high yield. In short, one can design a supermolecule with predictable architecture by selecting the appropriate set of building blocks that have complementary sites.

Crystal engineering[3-8] is inherently linked to supramolecular chemistry. Schmidt demonstrated in his early work that crystals can be thought of as the sum of a series of molecular recognition events and self-assembly, rather than the need to “avoid a vacuum”.[3] The field of crystal

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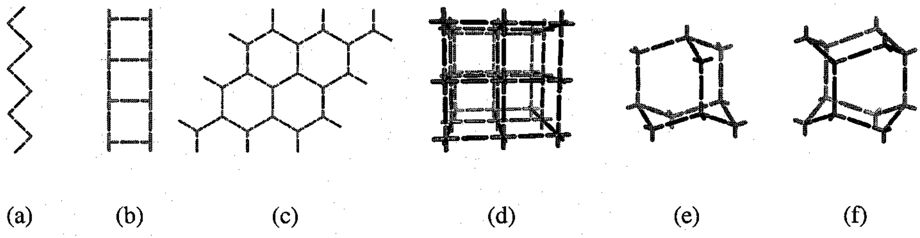
engineering developed further in the 1980s with the work of Etter[9-11] and Desiraju,[8,12] who concentrated upon applying the Cambridge Structural Database[13] (CSD) to the analysis, interpretation and design of non-covalent bonding patterns in organic solids.

In this contribution we focus upon how coordination polymers exemplify how crystal engineering has become a paradigm for the design of new supramolecular architectures. The work of Wells[14,15] serves as an excellent starting point concerning how one can define crystal structures in terms of their topology by reducing them to a series of points (nodes) of a 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 discrete (0D) polyhedra or infinite (1-, 2-, or 3-D) periodic nets. Robson and co-workers[16] delineated the "Wellsian" work on inorganic network structures into the realm of metal-organic coordination polymers, in turn facilitating the rapid development of the field. In this context, the "node and spacer" approach has been remarkably successful for producing predictable network architectures. The metal typically acts as the "node" and an organic ligand acts as the "spacer" that propagates this node. Scheme 1 illustrates some of the simplest architectures that can be generated using commonly available metal moieties and linear organic "spacer" ligands. It is obvious from the scheme that each network consists of at least two components; i.e. the structure is modular.[17] In principle, these network structures can be regarded as blueprints for the construction of networks from a diverse range of chemical components, provided the components are predisposed to self-assembly. The modular approach is powerful because it facilitates fine-



Scheme 1. A schematic representation of some of the simple 1D, 2D and 3D network architectures that have been structurally characterized for metal-organic polymers: (a) zigzag chain; (b) ladder; (c) honeycomb; (d) octahedral; (e) cubic diamondoid; (f) hexagonal diamondoid.

tuning of the structural and functional features. In addition, since, in principle, it is possible for a given set of building blocks to arrange into more than one possible superstructure the phenomenon of supramolecular isomerism may arise.[18] This concept is illustrated by structures (e) and (f) in scheme 1, which represent cubic and hexagonal diamondoid structures, respectively. It is important to note that, although supramolecular isomerism affords structural diversity, it is limited by the number of possible architectures that can be generated *rationally* from the molecular components present in a network.

The architecture alone often affords information that allows the chemist to predict some of the bulk properties. For example, most of the structures in scheme 1 inherently generate cavities that are based upon the size and length of the spacer ligand. The 3D architectures (d)-(f) represent in some ways the ultimate challenge in terms of crystal engineering since they lead directly to crystal structure prediction. It should therefore be unsurprising that diamondoid[17] and octahedral[19-21] frameworks have attracted considerable attention. In general, for 3D architectures one would expect rigidity to be coupled with porosity (zeolite-like properties).[17,21-23] For 2D architectures, one would expect inherent ability to intercalate guest (clay-like properties).[5,24-27] In the case of 1D structures one would normally expect close-packing variability in the context of how adjacent networks pack with respect to one another.[28-33] It should be noted that the construction of networks from single component systems is also an active area of research, but that the two approaches are conceptually different.

In this contribution we explore further the field of coordination polymers by highlighting examples of 2D and 3D coordination polymers that exhibit supramolecular isomerism. The molecular components that we targeted to build our coordination polymers are the metal cluster dizinc tetracarboxylate and the angular ligand benzene-1,3-dicarboxylate (bdc), both illustrated in

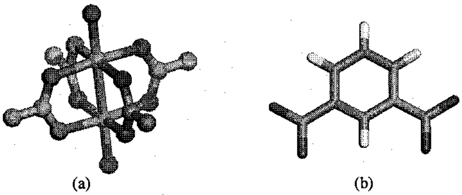

(a) (b)

Figure 1. (a) The dimetal tetracarboxylate cluster can be considered a molecular square when viewed down the four-fold axis, (b) The angular bdc ligand.

Figure 1. All structures reported herein have the same empirical chemical formula, $Zn_2(bdc)_2(L)_2$ (L= coordinated base), yet they have dramatically different architectures. The dimetal tetracarboxylate[34] secondary building unit (SBU)[35] is a ubiquitous metal cluster that is present in the CSD[13] for over 1000 structures involving 21 transition metals. However, SBUs based on Zn(II) remain rare as evident by the presence only 10 structures in the CSD.[36-42] Furthermore, only one of these structures utilizes the Zn(II) SBU as a building block in a coordination polymer.[42] The use of such SBUs as building blocks for the generation of discrete and infinite networks is a relatively recent phenomenon. Nevertheless, it is already clear that its structural and functional versatility makes it a particularly attractive molecular building block: the metal can be varied with resulting property changes; the carboxylate moiety has many permutations; the axial ligand can be varied almost at will. Two approaches to the use of this SBU have thus far been delineated: as a linear spacer when coordination occurs at the axial positions,[43-47] or as a molecular square linked at the vertices (as suggested when viewing the SBU down the four-fold axis in Fig. 1).[42,48] To most effectively utilize the SBU as a molecular square building block simple polycarboxylate ligands can be exploited. Benzene-1,4-dicarboxylate[49] (a linear dicarboxylate), benzene-1,3-dicarboxylate[42,48,50-52] (an angular dicarboxylate) and benzene-1,3,5-tricarboxylate[53] (a three-directional carboxylate) have all afforded self-assembled structures with rational, if not predictable, topologies.

We have focused our efforts on the angular ligand bdc, which has the two carboxylate moieties that are predisposed rigidly at 120°, and we have demonstrated that it can facilitate the assembly of square SBUs into square (a cluster of four SBUs) or triangular (a cluster of three SBUs) nanoscale SBUs, nSBUs.[42] These nSBUs can further assemble into discrete faceted polyhedra[48,50] or infinite networks. The former contains both types of nSBUs (square and triangular), whereas two types of the latter result: one that contain square nSBUs only,[42] and one that contain triangular nSBUs only.[52] We have reported these findings for structures based on the SBU derived from Cu(II). In this contribution we demonstrate that structures previously reported for Cu(II) are also accessible when using Zn(II).

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 N_2 as purge gas. XRPD data were obtained on a Rigaku MiniFlex$^+$ Diffractometer. Formulations of the coordination polymers are based upon nSBUs rather than embirical units.

Synthesis of $\{[Zn_2(bdc)_2(pyridine)_2]_4$•Benzene $\}_n$ (1)

Colorless crystals of **1** were obtained from slow diffusion via layering an ethanolic solution (10.0mL) of 1,3-H_2bdc (82mg, 0.49mmol) and zinc nitrate hexahydrate (150mg, 0.50mmol) through an ethanolic layer (10.0mL) onto an ethanolic solution (10.0mL) of pyridine (0.12mL, 1.5mmol) and benzene (2.0mL). Crystals formed within days in 3.5% yield. 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 $\{[Zn_2(bdc)_2(2\text{-picoline})_2]_4$•2Nitrobenzene $\}_n$ (2)

Colorless crystals of **2** were obtained from slow diffusion via layering a methanolic solution (10.0mL) of 1,3-H_2bdc (84mg, 0.50mmol) and zinc nitrate hexahydrate (150mg, 0.50mmol) through a methanolic layer (10.0mL) onto a methanolic solution (10.0mL) of 2-picoline (0.15mL, 1.5mmol) and nitrobenzene (2.0mL). Crystals formed within days in 14% yield. The crystals are thermally stable upto 120 °C after which the TG curve shows a mass loss of about 39% between 140 and 240 °C, which is consistent with and corresponds to the loss of guest and axial ligands. Further heating leads to decomposition of the structure above 300 °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 $\{[Zn_2(bdc)_2(4\text{-picoline})_2]_4$•*o*-Dichlorobenzene $\}_n$ (3a)

Colorless crystals of **3a** were obtained from slow diffusion via layering a methanolic solution (20.0mL) of 1,3-H_2bdc (166mg, 0.999mmol) and zinc nitrate hexahydrate (297mg, 0.998mmol) through a methanolic layer (10.0mL) onto a methanolic solution (10.0mL) of 4-picoline (0.30mL, 3.1mmol) and *o*-dichlorobenzene (2.0mL). Crystals formed within days in 6.1% yield. The crystals are thermally stable upto 190 °C after which the TG curve shows a mass loss of about 40% between 220 and 320 °C, which is consistent with and corresponds to the loss of guest and axial ligands. Further heating leads to decomposition of the structure above 380 °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 $\{[Zn_2(bdc)_2(4\text{-picoline})_2]_4{\bullet}\text{Nitrobenzene}\}_n$ (3b)

Colorless crystals of **3b** were obtained from slow diffusion via layering a methanolic solution (20.0mL) of 1,3-H_2bdc (166mg, 0.999mmol) and zinc nitrate hexahydrate (297mg, 0.998mmol) through a methanolic layer (10.0mL) onto a methanolic solution (10.0mL) of 4-picoline (0.30mL, 3.1mmol) and nitrobenzene (2.0mL). Crystals formed within days in 28% yield. 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 $\{[Zn_2(bdc)_2(3,5\text{-lutidine})_2]_4{\bullet}o\text{-Dichlorobenzene}\}_n$ (3c)

Colorless crystals of **3c** were obtained from slow diffusion via layering a methanolic solution (10.0mL) of 1,3-H_2bdc (84mg, 0.50mmol) and zinc nitrate hexahydrate (150mg, 0.50mmol) through a methanolic layer (10.0mL) onto a methanolic solution (10.0mL) of 3,5-lutidine (0.17mL, 1.5mmol) and *o*-dichlorobenzene (2.0mL). Crystals formed within days in 32% yield. 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 $\{[Zn_2(bdc)_2(3,5\text{-lutidine})_2]_4{\bullet}\text{Benzene}\}_n$ (3d)

Colorless crystals of **3d** were obtained from slow diffusion via layering a methanolic solution (10.0mL) of 1,3-H_2bdc (84mg, 0.50mmol) and zinc nitrate hexahydrate (150mg, 0.50mmol) through a methanolic layer (10.0mL) onto a methanolic solution (10.0mL) of 3,5-lutidine (0.17mL, 1.5mmol) and benzene (2.0mL). Crystals formed within days in 47% yield. 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 {$[Zn_2(bdc)_2(4\text{-methoxypyridine})_2]_4$•Benzene }$_n$ (3e)

Colorless crystals of **3e** were obtained from slow diffusion via layering an ethanolic solution (10.0mL) of 1,3-H_2bdc (82mg, 0.49mmol) and zinc nitrate hexahydrate (150mg, 0.50mmol) through an ethanolic layer (10.0mL) onto an ethanolic solution (10.0mL) of 4-methoxypyridine (0.15mL, 1.5mmol) and benzene (2.0mL). Crystals formed within days in 19% yield. The crystals are thermally stable upto 180 °C after which the TG curve shows multiple mass losses, which are consistent with and corresponds to the loss of guest and axial ligands. Further heating leads to decomposition of the structure above 300 °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 {$[Zn_2(bdc)_2(\text{isoquinoline})_2]_4$•*o*-Dichlorobenzene }$_n$ (3f)

Colorless crystals of **3f** were obtained from slow diffusion via layering a methanolic solution (10.0mL) of 1,3-H_2bdc (84mg, 0.50mmol) and zinc nitrate hexahydrate (150mg, 0.50mmol) through a methanolic layer (10.0mL) onto a methanolic solution (10.0mL) of isoquinoline (0.18mL, 1.5mmol) and *o*-dichlorobenzene (2.0mL). Crystals formed within days in 38% yield. 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 {$[Zn_2(bdc)_2(4\text{-methoxypyridine})_2]_4$•guest}$_n$ (4)

Colorless crystals of **4** were obtained from slow diffusion via layering a methanolic solution (10.0mL) of 1,3-H_2bdc (82mg, 0.49mmol) and zinc nitrate hexahydrate (150mg, 0.50mmol) through a methanolic layer (10.0mL) onto a nitrobenzene solution (10.0mL) of 4-methoxypyridine (0.15mL, 1.5mmol). Crystals formed within days in 1.4% yield. 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 {$[Zn_2(bdc)_2(\text{quinoline})_2]_4$•Nitrobenzene }$_n$ (5)

Colorless crystals of **5** were obtained from slow diffusion via layering a methanolic solution (20.0mL) of 1,3-H_2bdc (166mg, 0.999mmol) and zinc nitrate hexahydrate (297mg, 0.998mmol) through a methanolic layer (10.0mL) onto a methanolic solution (10.0mL) of quinoline (0.24mL, 2.0mmol) and nitrobenzene (2.0mL). Crystals formed within days in 13% yield. The crystals are thermally stable upto 190 °C after which the TG curve shows multiple mass losses, which are consistent with and corresponds to the loss of guest and axial ligands. Further heating leads to decomposition of the structure above 300 °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.

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 $Mo_{K\alpha}$ radiation (λ = 0.7107 Å). The data were corrected for Lorentz and polarization effects and for absorption using the SADABS program. The structures were solved using direct methods and refined by full-matrix least-squares on $|F|^2$. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions and refined with temperature factors 1.2 times those of their bonded atoms. All crystallographic calculations were conducted with the SHELXTL 5.1 program package. Table 1 provides crystallographic data for compounds **1-5**. CCDC-# 206112 - 206120 and 202849 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Table 1. Crystallographic data for structures **1-5**.

Compound	**1**	**2**	**3a**	**3b**	**3c**
Formula	$C_{32}H_{20}Zn_2N_2O_8$	$C_{40}H_{32}Zn_2N_4O_{12}$	$C_{34}H_{26}Zn_2N_2O_8Cl_2$	$C_{34}H_{27}Zn_2N_3O_{10}$	$C_{36}H_{30}Zn_2N_2O_8Cl_2$
MW	691.24	891.44	792.21	768.33	820.26
Color, habit	Colorless, column	Colorless, column	Colorless, column	Colorless, column	Colorless, column
Crystal system	Tetragonal	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group, Z	P4/ncc, 8	Pbcm, 4	C2/c, 4	C2/c, 4	C2/c, 4
a (Å)	19.0707 (7)	10.5778 (10)	19.2652 (15)	19.796 (2)	18.8097 (17)
b (Å)	19.0707 (7)	19.6493 (18)	12.9285 (10)	12.2755 (15)	13.1619 (12)
c (Å)	16.2329 (11)	19.1872 (18)	14.4703 (11)	14.8457 (18)	14.3915 (13)
α (°)	90°	90°	90°	90°	90°
β (°)	90°	90°	115.3510 (10)°	116.064 (2)°	109.109 (2)°

γ (°)	90°	90°	90°	90°	90°
V	5903.8 (5)	3988.0 (6)	3257.0 (4)	3240.7 (7)	3366.6 (5)
Temp (K)	100 (2)	100 (2)	100 (2)	100 (2)	100 (2)
M (mm^{-1})	1.68	1.271	1.693	1.544	1.641
Theta range	1.51 – 28.28°	1.93 – 28.26°	1.96 - 28.26°	2.02 – 28.25°	1.93 – 28.24°
Reflections collected	33447	24385	13748	9716	6391
Independent refelections (R_{int})	3612 (0.0765)	4931 (0.0388)	7080 (0.0237)	5974 (0.0257)	3302 (0.0226)
R (F), R_w(F)	0.0534, 0.1311	0.0557, 0.1475	0.0338, 0.0849	0.0359, 0.0931	0.0322, 0.0817

Compound	**3d**	**3e**	**3f**	**4**	**5**
Formula	$C_{36}H_{32}Zn_2N_2O_8$	$C_{34}H_{28}Zn_2N_2O_{10}$	$C_{40}H_{26}Zn_2N_2O_8Cl_2$	$C_{29}H_{26}Zn_2N_2O_{11}$	$C_{34}H_{22}Zn_2N_2O_8$
MW	751.38	755.32	864.27	709.26	717.28
Color, habit	Colorless, column	Colorless, column	Colorless, column	Colorless, hexagonal	Colorless, column
Crystal system	Monoclinic	Monoclinic	Monoclinic	Trigonal	Rhombohedral
Space group, Z	C2/c, 4	C2/c, 4	C2/c, 4	P-3m1	R-3c
a (Å)	19.206 (2)	19.291 (7)	20.416 (3)	18.9565(8)	30.2394 (11)
b (Å)	13.0543 (16)	13.439 (5)	13.2052 (18)	18.9565(8)	30.2394 (11)
c (Å)	14.339 (18)	13.864 (5)	13.8901 (19)	11.1246(9)	18.2791 (13)
α (°)	90°	90°	90°	90	90°
β (°)	109.542 (2)°	114.797 (6)°	109.447 (2)°	90	90°
γ (°)	90°	90°	90°	120	120°
V	3386.8 (7)	3263 (2)	3530.4 (8)	3462.0(3)	14475.4 (13)
Temp (K)	100 (2)	100 (2)	100 (2)	100(2)	100 (2)
M (mm^{-1})	1.471	1.532	1.569	1.080	1.545
Theta range	1.92 – 28.34°	1.91 – 23.27°	1.87 – 28.25°	1.83 – 28.33 °	2.33 – 28.28°
Reflections collected	10274	6724	10475	21996	28023
Independent refelections (R_{int})	3963 (0.0538)	2354 (0.0567)	4104 (0.0534)	3028 (0.0396)	3916 (0.0489)
R (F), R_w(F)	0.0442, 0.0954	0.0867, 0.1727	0.0859, 0.1993	0.0796, 0.2729	0.0437, 0.1149

Results and Discussion

Three supramolecular isomers based on dizinc tetracarboxylate SBU and bdc have been obtained: (a) 2D sheet structures based on square nSBUs only, $\{[Zn_2(bdc)_2(L)_2]_4\}_n$, (b) 2D sheet structure based on triangular nSBUs only, $\{[Zn_2(bdc)_2(L)_2]_3\}_n$ (Kagomé lattice), (c) 3D structure with a $6^5.8$ topology, $\{[Zn_2(bdc)_2(L)_2]\}_n$. Figure 2 illustrates the schematic for the three polymeric networks. The geometry around the zinc ion in all structures is that of a square pyramid. The basal positions are occupied by carboxylate moieties and the apical positions are occupied by the base used. Bond distances and angles in the Zn SBU are consistent with those reported in the literature.[36-42] Structures **1-5** are discussed in detail below.

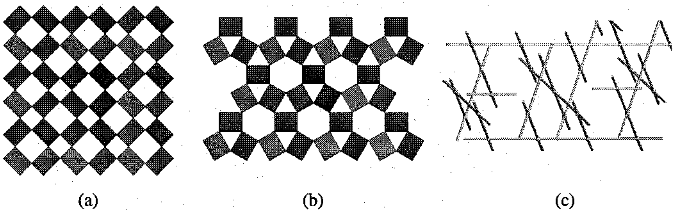


Figure 2. Schematic representaion of the three network topologies of structures 1-5. (a) 2D tetragonal network (1-3), (b) 2D trigonal network (4), (c) 3D $6^5.8$ network (5).

(a) 2D sheet structures based on square nSBUs only

Compounds **1-3** are supramolecular isomeric 2D sheet structures that result from the self-assembly of square nSBUs only. In this series of compounds four SBUs are linked in an angular fashion by bdc ligands and the resulting nSBU therefore possess curvature and, in principle, torsional flexibility. Close examination of the square nSBU reveals that it resembles a calix[4]arene in its shape and ability to adopt different conformations. Calixarenes have been isolated in different conformations (atropisomers)[54-58] that have been designated by Gutsche and coworkers[59] as the cone, partial cone, 1,2-alternate and 1,3-alternate. The nomenclature refers to the orientation of the arene rings with respect to one another. We have previously observed the square nSBU in the cone and 1,3-alternate conformations.[42] Structures **1-3** are polymeric structures based on the metal-organic calix-like monomeric nSBUs shown in Figure 3.

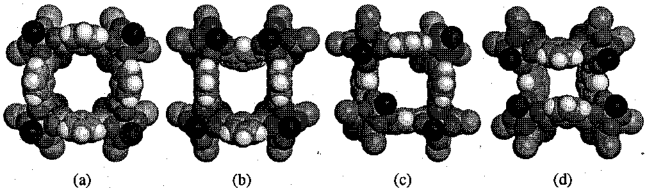


Figure 3. Monomeric nSBU constituents of polymeric structures 1-3. (a) Cone, (b) partial cone, (c) 1,2-alterante, (d) 1,3-alternate.

Compound **1**, $\{[Zn_2(bdc)_2(py)_2]_4\}_n$, contains two atropisomeric nSBUs, namely the cone and the 1,3-alternate (Figure 4). The nSBUs self-assemble, alternating between the cone and the 1,3-alternate conformations and thereby yield an undulating sheet structure. Each cone has an outer diameter of 0.94 nm and a depth of 0.84 nm (measured from the center of the base to the midpoint of a line joining the top hydrogen atoms on opposite bdc moieties). When the sheets stack, they eclipse one another so that the cones sit inside one another and the 1,3-alternate nSBUs define hour-glass-shaped channels. Disordered guest molecules occupy both types of cavities. The potential solvent accessible-volume in one unit cell is 5.5%, but would be increased to 18.1% upon removal of guest molecules.[60] We have previously reported an isostructural Cu(II) version[42] where Cu(II) nSBUs self-assemble into undulating sheets containing both conformers of the nSBU.

Compound **2**, $\{[Zn_2(bdc)_2(2\text{-}pic)_2]_4\}_n$, results from the self-assembly of partial cone nSBUs into an undulating sheet structure (Figure 4). The partial cone is the result of a bdc ligand lying in a plane almost perpendicular to the plane defined by the three others. The outer diameter of the partial cone (measured from opposite bdc ligands that lie in one plane) is 0.96 nm and the depth is 0.47 nm (measured from the centers of the lines joining the top and bottom hydrogen atoms of opposite bdc moieties that are in the same plane). Each partial cone in **2** hosts two disordered nitrobenzene molecules. The sheets stack eclipsed so that the partial cones sit inside one another with interlayer separation of *ca.* 1.06 nm. The unit cell contains no residual solvent accessible area; however, the potential solvent area, upon removal of guest, is 35.2%.[60]

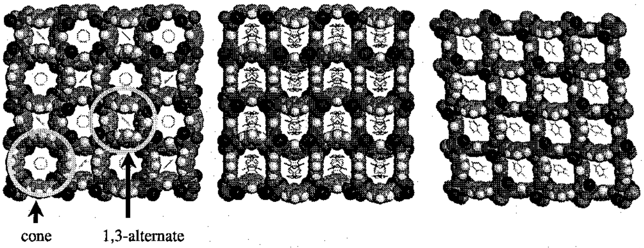


Figure 4. Crsytal structures of 1 (left), 2 (middle) and 3a (right), shown in space filling mode. The view illustrates the resulting 2D sheets hosting guest molecules (shown in line mode). The cavities contain disordered guest molecules in 1 and 2 (nitrobenzene) and ordered dichlorobenzene in 3a. Note that the aromatic rings of the axial ligands have been removed for clarity.

In compounds **3a-f**, $\{[Zn_2(bdc)_2(L)_2]_4\}_n$, (L = 4-picoline for **3a** and **3b**; 3,5-lutidine for **3c** and **3d**; 4-methoxypyridine for **3e** and isoquinoline for **3f**), the nSBU adopts the 1,2-alternate conformation and hosts guest molecules (*o*-dichlorobenzene for **3a**, **3c** and **3f** (solvent molecules are disordered for **3c** and **3f**); nitrobenzene for **3b**; and benzene for **3d** and **3e**) in the resulting cavity. The nSBUs self-assemble into 2D corrugated square grids that propagate in the YZ-plane (Figure 4) and stack along the X-axis in an ABCD fashion with an interlayer separations ranging between 0.87 and 0.96 nm. The effective dimensions of the grids range between 1.1 x 1.1 and 1.2 x 0.95 nm (distance from Zn-Zn mid point of opposite SBU units in the nSBU taking into account the van der Waals radii of zinc). The unit cell of all structures contains no residual solvent accessible area except for **3e** (2.1%); however, the average potential solvent accessible area for all structures upon removal of guest is 25.1%.[60]

1, **2** and **3a-f** therefore, collectively, exhibit all four atropisomers of the nSBU likely to be generated due to the angularity of the bridging bdc ligand. The curvature of the cone nSBU affects the "trans" carboxylate moieties in the basal position of the SBUs, which twist slightly from planarity (dihedral angle between planes of trans carboxylates $\theta = 7.74°$). On the other hand, since in the partial cone and the 1,2-alternate nSBUs the bdc ligand is rotated, all "trans" carboxylates are planar ($\theta = 0°$), except for **3a** and **3b**, where the dihedral angle is 23.3° and 23.7°, respectively.

(b) 2D structure based on triangular nSBUs only (Kagomé lattice)

Compound **4**, $\{[Zn_2(bdc)_2(4\text{-methoxypyridine})_2]_3\}_n$, results from the self-assembly of triangular nSBUs only into a 2D sheet structure. The resulting structure has a topology that is an example of a Kagomé lattice.[61] A Kagomé lattice is a spin-frustrated lattice where spins are located on the vertices of triangles. There are few examples of molecular Kagome lattices[62-64] and we have recently reported the first example of a nanoscale Kagome lattice based on Cu(II) SBU.[52] Zn(II) produces the same topology where Zn_2 dimers are positioned at the lattice points and are bridged by the bdc ligands, thereby generating large hexagonal cavities within the layer. The bowl-shaped nSBUs pack eclipsing one another thereby generating hexagonal channels with effective diameter of 0.93 nm. The potential solvent accessible area in the unit cell is 31.6%, which can be increased further to 46.3 % upon removal of guest molecules.[60] The resulting 2D sheet is undulated due to the curvature of the nSBU imparted by the angularity of the bdc ligand. It is important to note that this lattice would not have magnetic properties since Zn(II) is a d^{10} ion.

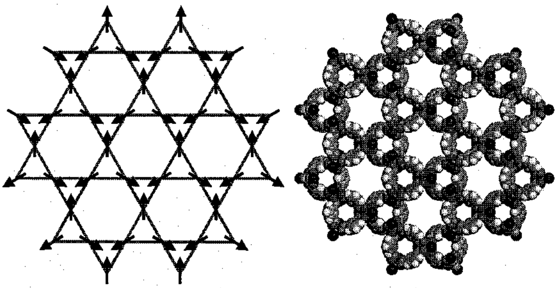


Figure 5. Schematic representaion (left) and crystal structure (right) of the Kagome lattice 4 .

(c) 3D structure with $6^5.8$ topology $\{[Zn_2(bdc)_2(quinoline)_2]_n\}$

We have analyzed the above two supramolecular isomers as molecular squares connected at the vertices. Although we can do the same for this isomer, little will be gained for our understanding of it in terms of topology. To derive the schematic illustrated in Fig 2c, we treated the dimetal cluster as a single node located between the two metal ions, and connecting the nodes according to the connectivity defined by the bdc bridging ligands. This yields a $6^5.8$ 3D network that is sustained by distorted square planar nodes. The distortion is the result of treating the angular bdc ligand as a linear connection. Although the schematic can be modified to illustrate this it provides no significant insight into the structure or properties, and the simplified illustration therefore seems appropriate. **5** does not possess notable pores or cavities (effective diameter is ca. 0.25 nm) and contains no residual solvent accessible area; however, the potential solvent-accessible area upon removal of guest is 17.3%.[60]

Conclusions

In this contributiuon, we have presented examples of coordination polymers that illustrate the type of control and structural diversity that is possible in such compounds. It should be noted that the three different architectures reported herein are dramatically different event though they are prepared from the same set of building blocks. Furthermore, the reaction conditions used are mild and utilize commercially available starting materials. It is simply fine-tuning of the reaction conditions that effects changes in the architecture of the resulting supramolecular structure and in turn the chemical and physical properties such as porosity, guest-encapsulation, *etc.* We have also demonstrated that metals can be interchanged without affecting the structural possibilities. This is particularly important in the context of the development of functional coordination polymers in which the properties arise directly from the presence of transtion metals (e.g. magnetism, luminescence, catalysis). Future work will attempt to exapnd the range of structures and compositions even further.

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