

- [6] Crystal data for **1**·hexane: colorless crystal, $0.18 \times 0.23 \times 0.38$ mm, triclinic, PI , $a = 10.7828(3)$, $b = 13.1998(5)$, $c = 16.1826(7)$ Å, $\alpha = 105.724(2)$, $\beta = 103.774(2)$, $\gamma = 92.199(3)^\circ$, $V = 2140.2(7)$ Å³, $Z = 1$, $\rho_{\text{calcd}} = 1.098$ g cm⁻³, $\mu = 0.120$ mm⁻¹, $2\theta_{\text{max}} = 56.5^\circ$. A total of 10232 ($R_{\text{int}} = 0.053$) unique reflections were collected (Enraf Nonius CCD, MoK α radiation ($\lambda_0 = 0.71073$ Å), $T = 123$ K) and used in least-squares refinement on F^2 , 469 refined parameters, GOF = 1.030 (based on F^2), $R1 = 0.073$, $\omega R2 = 0.169$ ($I > 2\sigma(I)$), $R1 = 0.134$, $\omega R2 = 0.198$ (all data), residual electron density $-0.366/0.525$ e Å⁻³. The hydrogen atoms were placed in calculated positions using a riding model. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-157276. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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- [13] Typical elemental analyses calcd for **1** C₇₂H₉₈Li₁₀N₄O₈Si₄ (%): C 65.06, H 7.43, N 4.21 (**1**·hexane C₇₈H₁₁₂Li₁₀N₄O₈Si₄: C 66.19, H 7.98, N 3.96); found: C 62.98, H 7.74, N 4.44.

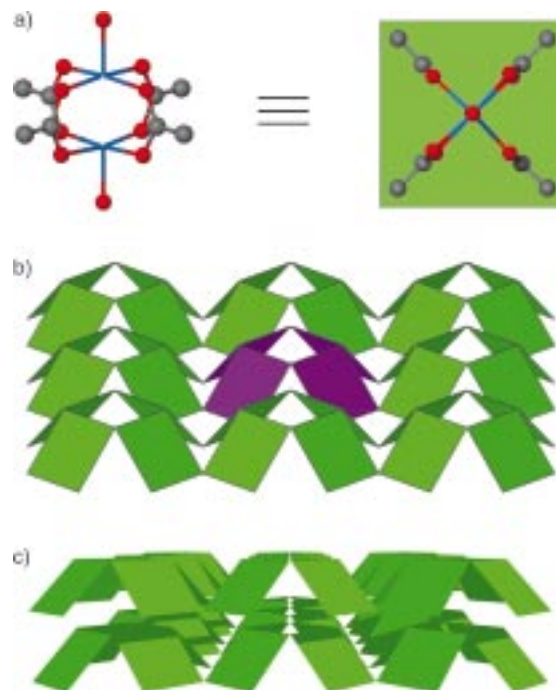
Self-Assembly of Nanometer-Scale Secondary Building Units into an Undulating Two-Dimensional Network with Two Types of Hydrophobic Cavity**

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By using some of the recently enunciated principles of crystal engineering^[1–3] and self-assembly it has become possible to design and construct new classes of crystalline compounds from molecular components that possess useful

physical properties including bulk magnetism,^[4] nonlinear optical properties,^[5] and porosity.^[6–9] Open-framework structures can be assembled by using metals or metal clusters as nodes and multifunctional organic ligands to link these nodes. This approach has afforded structures that exhibit high surface areas, affinity for a wide range of organic guest molecules,^[10] and some show potential for catalysis.^[9] Herein we illustrate how the use of metal-organic secondary building units (SBUs) that are linked by angular ligands can generate nanoscale SBUs (nSBUs) with curvature.

The use of carboxylate-bridged metal clusters as metal-organic SBUs to build extended self-assembled structures has been delineated by Yaghi et al.^[8] Scheme 1 a illustrates such a



Scheme 1. Schematic illustrations of a) the square SBU (green) based on metal ions bridged by carboxylate anions, b) how the square SBUs can self-assemble at their vertices to generate nanosized bowls (purple) which in turn form curved sheets, and c) how the curved sheets pack because of shape considerations.

cluster—in this case two metal ions are bridged by four carboxylate anions and each metal is bonded to one axial pyridine ligand. When viewed along the axial direction the extension of the carboxylate ligands forms a “square SBU”. Such clusters are ubiquitous in the Cambridge Structural Database,^[11] but most contain monofunctional carboxylates and, therefore, they will not generate extended structures. However, the use of bifunctional carboxylate ligands such as 1,4-benzenedicarboxylate allows the formation of self-assembled infinite structures that contain channels capable of incorporating a variety of guest molecules.^[12–15] 1,3-Benzenedicarboxylate is suitable for the linking of square SBUs at 120° and Scheme 1 b shows one of the ways in which square SBUs can pack when there is a 120° angle at their vertices: a two-dimensional (2D) infinite metal-organic framework resembling a layer of upended bowls. In such a structure one bowl

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may be regarded as a “nanometer-scale SBU” (nSBU) which consists of four metal cluster SBUs.

The compounds $\{[M_2(1,3\text{-bdc})_2(\text{py})_2]_4\}_n$ (**1**) (1,3-bdc = 1,3-benzenedicarboxylate, py = pyridine, $M = \text{Zn}$, **1a**, Cu , **1b**) demonstrate that four square SBUs can indeed combine to form one bowl-shaped nSBU ($[M_2(1,3\text{-bdc})_2(\text{py})_2]_4$), which in turn self-assembles with other nSBUs to form the undulating sheet structure depicted in Scheme 1b. Each bowl has an outer diameter of 0.94 nm; a depth (as measured by the perpendicular distance from the center of the base to midpoint of a line joining the top hydrogen atoms on opposite bdc moieties) of 0.84 nm and a solvent-accessible volume of 0.518 nm^3 .^[16] The bowls are occupied by disordered benzene or pyridine guests and by the bottom of a bowl from the adjacent sheet. The layers therefore pack as illustrated in Scheme 1c, giving rise to a channel between adjacent bowls. The channels are hour-glass-shaped with a cavity of maximum dimensions of about $0.90 \times 0.90 \times 0.65 \text{ nm}$ and are occupied by benzene or pyridine guest molecules (in one unit cell the solvent-accessible volume is 0.28 nm^3 ^[16]). Between these cavities the channel narrows to an opening of about $0.15 \times 0.15 \text{ nm}$ which restricts the movement of the guest molecules through the channel. The distance between guest molecules is 0.81 nm. Figure 1a presents the coordination networks, and Figure 1b illustrates the networks in stick representation and the guest molecules in the channel in space-filling mode (the guests in the bowls have been omitted for clarity). The profile of the hour-glass channel is shown in Figure 1c. The total volume of both types of cavity represents about 23 % of the volume of the unit cell.^[17] Single crystals maintained at room temperature under vacuum overnight gave identical thermogravimetry MS curves to those obtained directly from solution, indicating that **1** is stable at ambient temperatures. However, thermogravimetry data also indicates that crystals of **1** are not stable to loss of guest because the pyridine ligands must be removed from the metal cluster to facilitate free release of guest molecules.

In summary, **1a** and **1b** exhibit an infinite 2D structure formed by the self-assembly of nSBUs that are formed by four square carboxylate-bridged di-metal(II) SBUs. Compounds **1a** and **1b** are curved as a result of the 120° angle subtended by the bdc ligands and that they may be considered to be supramolecular isomers^[18] of discrete polyhedra based upon molecular squares. The shape and chemical nature of the bowls in **1** resembles calixarenes and we are investigating the ability to incorporate guest molecules that are known to form complexes with calixarenes.^[19]

Experimental Section

$\{[\text{Zn}_2(1,3\text{-bdc})_2(\text{py})_2]_4\}_n$ (**1a**): A methanolic solution (20 mL) of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol, 0.297 g) and benzene-1,3-dicarboxylic acid (1 mmol, 0.166 g) in the presence of pyridine (0.5 mL) and benzene (1 mL) was refluxed for about 30 mins. Slow cooling at room temperature afforded colorless crystalline plates of **1a**.

$\{[\text{Cu}_2(1,3\text{-bdc})_2(\text{py})_2]_4\}_n$ (**1b**): An ethanolic (10 mL) solution containing lutidine (0.90 mmol, 0.1 mL) was layered onto $\text{CuNO}_3 \cdot 2.5\text{H}_2\text{O}$ (0.231 g, 1.0 mmol) and benzene-1,3-dicarboxylic acid (0.360 g, 2.2 mmol) in DMF (10 mL). Slow diffusion over several days yielded blue platelike crystals of **1b**. Single crystals of **1a** and **1b** were subjected to thermogravimetry–mass spectrometry (TG-MS) analysis on a TA Instruments 2950 TGA with N_2 as

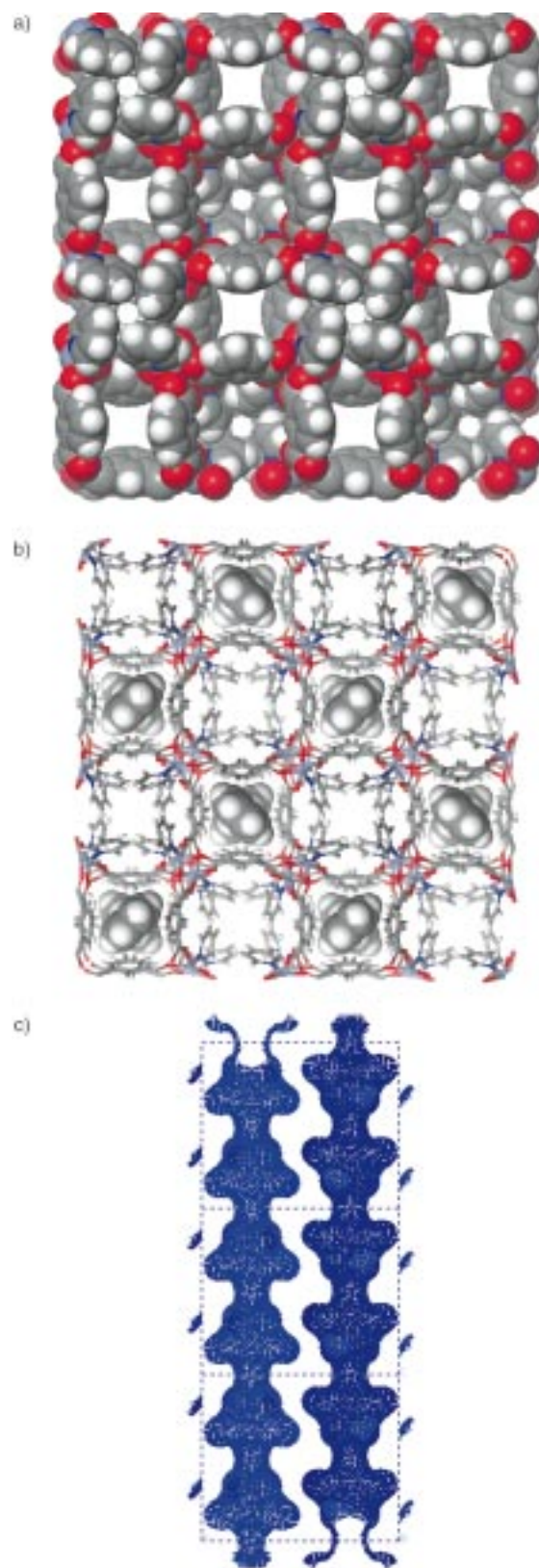


Figure 1. a) Space-filling diagram of the crystal structure of $\{[M_2(1,3\text{-bdc})_2(\text{py})_2]_4\}_n$. Guest molecules have been omitted for clarity. b) Structure of $\{[M_2(1,3\text{-bdc})_2(\text{py})_2]_4\}_n$ viewed along [001]. The guest molecules occupying the hour-glass channels are shown with van der Waals radii. Each bowl is also occupied by a benzene or pyridine guest, which has been omitted for clarity. c) Profile of the hour-glass shaped channels between adjacent bowls. The shaded area is the empty volume; guest molecules are located in the widest areas of the channels.

purge gas. 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 ($M^+ = 78$) and pyridine ($M^+ = 79$). Further heating leads to decomposition above 400 °C. The IR spectrum shows two strong peaks at 1635 cm^{-1} and 1446 cm^{-1} ; the difference between these peaks is 189 cm^{-1} as would be expected for bridging bidentate carboxylates.^[20]

Crystal data for **1a**: Tetragonal, $P4/ncc$, $a = 19.0356(9)$, $c = 16.253(1)$ Å, $V = 5889.3(6)$ Å³, $Z = 8$ (for $[\text{Zn}_2(1,3\text{-bdc})_2(\text{py})_2]$), $\rho_{\text{calc}} = 1.744$ g cm^{-3} , $\mu = 1.69$ mm⁻¹, $F(000) = 3168$, $2\theta_{\text{max}} = 50.1^\circ$. Crystal data for **1b**: Tetragonal, $P4/ncc$, $a = 18.7912(8)$, $c = 16.8886(10)$ Å, $V = 5963.5(8)$ Å³, $Z = 8$ (for $[\text{Cu}_2(1,3\text{-bdc})_2(\text{py})_2]$), $\rho_{\text{calc}} = 1.507$ g cm^{-3} , $\mu = 1.48$ mm⁻¹, $F(000) = 2750$, $2\theta_{\text{max}} = 56.54^\circ$. The data for **1a** and **1b** were collected at -100 °C on a Bruker SMART APEX diffractometer using $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å) and were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 .^[21] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on the pyridine and bdc ligands were placed in geometrically calculated positions and refined with temperature factors 1.2 times those of their parent atoms. The guest molecules inside the bowl-shaped cavity were disordered in such a manner that they could not be readily resolved. Guest molecules in the hour-glass-shaped channels were better resolved, but it is not possible to differentiate between benzene and pyridine molecules in these channels. Guest atoms were therefore treated as carbon atoms and refined with fixed isotropic thermal parameters and variable site occupancy. Final residuals for **1a** were $R1 = 0.0372$ and $wR2 = 0.0958$ for 1782 reflections with $I > 2\sigma(I)$, and $R1 = 0.0591$, $wR2 = 0.1028$ for all 2625 data (181 parameters). Values for **1b** were $R1 = 0.0407$ and $wR2 = 0.1063$ for 2289 reflections with $I > 2\sigma(I)$, and $R1 = 0.0680$, $wR2 = 0.1139$ for all 3632 data. Residual electron density was 0.82 and -0.58 e Å⁻³ for **1a** and 0.96 and -0.87 e Å⁻³ for **1b**. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-152547 and CCDC-162957. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Polygons and Faceted Polyhedra and Nanoporous Networks**

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Design principles that are based upon the concepts of crystal engineering and self-assembly have recently afforded new classes of crystalline solids that possess important physical properties such as bulk magnetism^[1, 2] or porosity.^[3–5] Furthermore, given that these structures are designed from first principles, they offer chemists an inherent ability to control the chemical nature of the molecular components and therefore influence the bulk physical properties of the material. Similar principles of self-assembly have been applied toward the design and isolation of nanosized spheroid architectures that are based upon regular (Platonic) and semiregular (Archimedean) polyhedral solids.^[6–13] However, there exist other well-documented examples of uniform polyhedra^[14, 15] that to our knowledge remain unexplored at the molecular level. In particular, there are nine polyhedra that are closely related to Platonic and Archimedean solids but differ in that they can be designed and built through linking of the vertices of polygons rather than the edges of polygons. Such structures are termed *faceted polyhedra*^[16] (Figure 1a) since they necessarily contain both open and closed faces. Of particular interest in the context of this study are those polyhedra that are sustained by triangles, squares, or combinations thereof.

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