Communication

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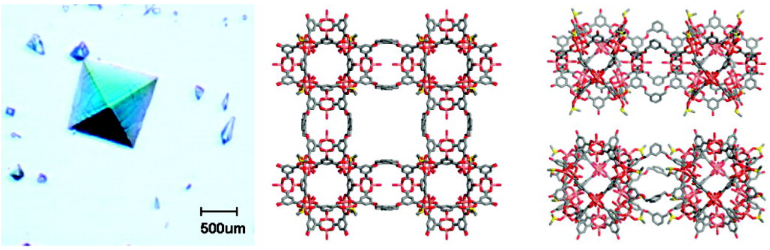

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# Bottom up Synthesis That Does Not Start at the Bottom: Quadruple Covalent Cross-Linking of Nanoscale Faceted Polyhedra

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Coordination polymers[1] exemplify how crystal engineering holds great promise for control of the arrangement of atoms in space. Robson[2] exploited the "node and spacer" approach described by Wells[3] for the characterization of inorganic compounds in terms of their topology by utilizing metal ions to serve as nodes and polytopic rigid organic molecules as linear spacers for the generation of infinite architectures. The "node and spacer" method has also been used extensively for construction of discrete stuctures.[4] A paradigm shift occurred when carboxylato secondary building units (SBUs) were used in lieu of single metal ion nodes to build nanoporous structures through self-assembly.[5]

Carboxylato SBUs can also afford discrete polyhedra,[6] which we have termed nanoballs.[6a] For example, dicopper tetracarboxylate "paddlewheel" SBUs afford faceted polyhedra of formulas $[Cu_2(bdc)_2L_2]_{12}$ (L = solvent or nitrogen base such as pyridine; bdc = 1,3-benzenedicarboxylate). The bdc naturally subtends the 120° angle needed to generate the *small rhombihexahedron* (Figure 1a). Such nanoballs possess $O_h$ symmetry and consist of 12 square SBUs that generate 8 triangular (Figure 1b) and 6 square open "windows". The bdc ligand can be functionalized at the 5-position for decoration of the outer surface of the nanoball. Therefore, it occurred to us that nanoballs could serve as nanoscale nodes[7] in suprasupermolecular[8] nets since the $O_h$ symmetry of the nanoballs could facilitate 4-connected nets (diamondoid), 6-connected nets (octahedral or tetragonal nets), or 8-connected nodes (bcc nets). Indeed, 5-$SO_3$-bdc ligands afford bcc nets.[9]

In this contribution we realize covalent cross-linking of nanoballs through all 24 bdc ligands. Whereas double or sextuple connections are unlikely because of the orientation of the decoration sites, triple cross-links (i.e., eight nearest neighbors, a "bcc net") or quadruple cross-links (i.e., six nearest neighbors, "octahedral net" or "tetragonal net") are feasible for flexible cross-links. Quadruple cross-linking can afford connectivity via the six square open windows to sustain an "octahedral net" node ($O_h$ symmetry) or through four square SBUs and two square open windows (Figure 1c) to facilitate a "tetragonal net" node ($D_{4h}$ symmetry). A logical choice for generating such structures would be two $H_2$bdc moieties linked through their 5-positions, and we report herein the coordination chemistry of a tetracarboxylic acid with a flexible aryloxy group, $\mathbf{H_4L}$ (Figure 2).[11]

Crystals[12] of [**1**], $[Cu_{24}(L)_{12}(H_2O)_{16}(DMSO)_8]_n$, covalently cross-linked nanoballs, were obtained via self-assembly of Cu(II) cations and **L** in DMSO/*o*-dichlorobenzene (2:1) heated in a sealed scintillation vial.[13] Each node in the resulting primitive cubic network is a nanoball with a diameter of 2.73 nm and a molecular volume of ca. 10.7 $nm^3$. Figure 3 illustrates how [**1**] adopts the "tetragonal net" node in which four SBUs and two square windows generate six nearest neighbors (Figure 4).[14] The flexibility of **L** allows for multiple conformations and there are two crystallographically independent ligands. **LA** (*a*-, *b*-axes) adopts a syn conformation and forms a cylinder with dimensions 7.24 Å (Cu to Cu from SBU) × 10.54 Å (centroid−centroid of the bridging aryloxy group). The benzene ring of the aryloxy group is disordered over two positions with equal probability. **LB** (*c*-axis) resides on a 2-fold axis and adopts an anti-conformation. The cylinder formed from these four ligands is 5.86 Å (oxygen atoms that start the bridge) × 17.88 Å. The void created by the cylinders along the *a*- and *b*-axes is filled with axially coordinated ligands of the SBU, whereas the cylinder along the *c*-axis formed by the meeting of square windows, generates a persistent void that becomes a channel along the *c*-axis. As seen in Figure 3 the net contains large square cavities with a length of ca. 18.3 Å (as measured centroid to centroid of the aryloxy benzene moieties) and a diagonal of ca. 25.0 Å. A similar centroid−centroid measurement along the *c*-axis affords a distance of 13.56 Å.

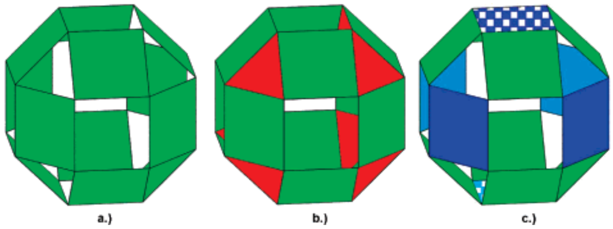

***Figure 1.*** (a) Schematic of *small rhombihexahedron*. Connection through the 6 square windows seen here would result in octahedral connectivity. (b) Red triangles indicate the 8 triangular windows (1 hidden) necessary for bcc connectivity. (c) The 6 blue tiles demonstrate tetragonal connectivity; solid blue tiles are SBUs (closed faces) while the checkered patterns (top and bottom) represent open windows.

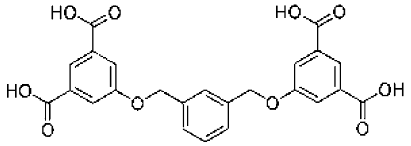

***Figure 2.*** 1,3-bis(5-methoxy-1,3-benzene dicarboxylic acid)benzene, $\mathbf{H_4L}$.

[**1**] exhibits 2-fold interpenetration[15] and nearly all of the 1.8 × 1.8 × 1.4 nm cavity is filled with a nanoball from the second framework (see Supporting Information). However the channels formed via the open windows of the nanoball nodes and the cross-linking cylinders along the *c*-axis persist. The smallest cross section in this channel corresponds to the oxygen−oxygen distance between solvent axial ligands on two SBU moieties across from one another and when taking van der Waals radii into consideration the effective

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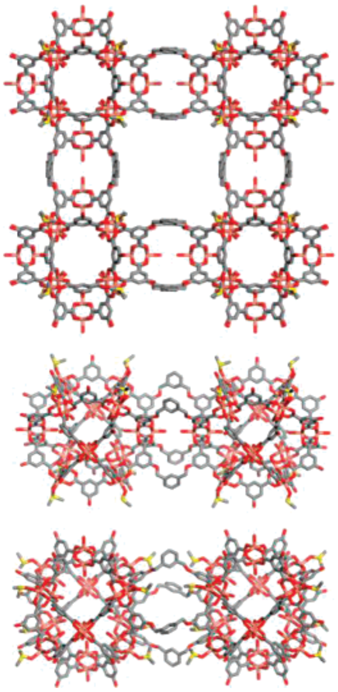

***Figure 3.*** (Top) ab plane of [**1**]. Hydrogen atoms and some axially coordinated solvent molecules have been deleted for clarity. (Middle) Nanoball cross-linking observed along *a*, *b* axes. The ligands adopt a syn conformation. (Bottom) Nanoball cross-linking observed along *c*-axis. Here the ligands adopt an anti conformation.

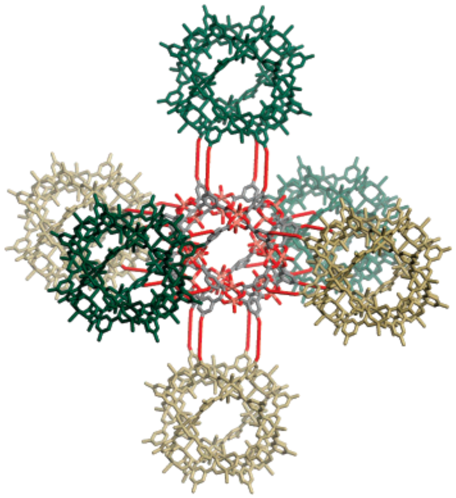

***Figure 4.*** Red lines illustrate the cross-linking observed in [**1**]. Nanoball nodes are colored alternating green and gold for improved clarity and visualization.

diameter for these channels is reduced to 5.962 Å, or roughly 0.6 nm. Whereas interpenetration reduces free volume it does not necessarily mitigate against surface area. Ongoing investigations are addressing the properties of [**1**], generation of a non-interpenetrated version of [**1**], and routes to the "octahedral net" and "bcc net" supramolecular isomers of [**1**].

In summary, we present herein a conceptual "bottom-up" design principle focused upon the use of nanoscale building blocks, that is, nanoballs, rather than SBUs as our targets for nodes to be used in the generation of 3D nets.

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**Supporting Information Available:** Additional structure figures, thermal gravimetric analysis plot, powder X-ray diffraction (PXRD) data, and crystallographic data (CIF) for [**1**]. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Crystal data for [**1**], $[Cu_{24}(L)_{12}(H_2O)_{16}(DMSO)_8]_n$ green prisms: tetragonal, space group $I422$, $a = b = 28.885(4)$ Å, $c = 28.305(6)$ Å, $V = 23616(7)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.194$ mg/m$^3$, $T = 100(2)$ K, $\mu = 1.167$mm$^{-1}$, 8752 reflections measured, 2505 independent reflections $[I > 2\sigma(I)]$, $R1_{final} = 0.1032$ $wR2_{final} = 0.2570$, Mo K$\alpha$ $\lambda = 0.71073$ Å, crystal size: $0.10 \times 0.08 \times 0.07$ mm$^3$.

(13) In a typical reaction, 1,3-bis(5-methoxy-1,3-benzene dicarboxylic acid)-benzene (0.101mmol, 47mg) was dissolved along with copper(II)nitrate hemipentahydrate (0.202 mmol, 47 mg) in a mixture of DMSO and *o*-dichlorobenzene (2:1, 3 mL). Upon addition of pyridine (0.6 mmol, 49 $\mu$L) a bright blue solution resulted which was subsequently heated in an oven at 115° C for 24 h after which a deep-green solution was generated. This solution was allowed to sit in a capped vial at room temperature for several weeks upon which small green prismatic single crystals of x-ray diffraction quality were produced.

(14) (a) **Topology and Coordination Sequence.** Node 1 (**LA**): Schläfli vertex symbol, 4.6(4).8; long topological (O'Keeffe) vertex symbol, 4(3).8-(6).6.6.6.6; coordination sequence, 4, 9, 20, 37, 64, 88, 124, 161, 214, 263. Node 2 (**LB**): Schläfli vertex symbol, 4(2).6(2).8(2); long topological (O'Keeffe) vertex symbol, 4.4.6(2).6(2).8(5).8(5); coordination sequence, 4, 10, 24, 36, 60, 86, 120, 168, 208, 244. Node 3 (Cu1−Cu2 paddle-wheel): Schläfli vertex symbol, 4(6); long topological (O'Keeffe) vertex symbol, 4.4.4.4.4.4; coordination sequence, 4, 9, 20, 40, 68, 92, 116, 184, 216, 232. Node 4 (Cu3−Cu4 paddlewheel): Schläfli vertex symbol, 4.6-(2).8(3); long topological (O'Keeffe) vertex symbol, 4.8(5).6(2).6(2).8-(2).8(2); coordination sequence, 4, 11, 22, 40, 60, 91, 126, 164, 210, 264. (b) Vertex symbols were determined using **OLEX**: Dolomanov, O. V.; Blake, A. J.; Champness, N. R.; Schröder, M. *J. Appl. Cryst.* **2003**, *36* (5), 1283−1284.

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