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An Inverted Metal-Organic Framework with Compartmentalized Cavities Constructed by Using an Organic Bridging Unit Derived from the Solid State[**]

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Porous crystalline solids that employ metal-organic components as building blocks, where a rigid, linear organic bridge propagates the coordination geometry of a metal node in one-, two-, or three-dimensions, are attracting much interest.[1–3] Such metal–organic frameworks (MOFs) are designed to exhibit properties that mimic, and improve upon, more conventional porous solids, such as zeolites[4] and mesoporous materials (MCMs).[5] Many porous MOFs, however, have fallen short, in contrast to zeolites and MCMs, as robust porous solids.[2, 6] Interpenetration[6] and framework fragility[2] have hampered progress such that host cavities tend to self-include while guest removal often results in a collapse of host structure. Recently, however, such problems of interpenetration and framework fragility have been largely circumvented by using metal clusters, as secondary building units (SBUs), for host design.[7] SBUs (e.g. metal carboxylates) reduce the likelihood of interpenetration owing to their large sizes which can preclude filling of void spaces,[8] producing stable, porous solids able to support inclusion and catalysis.[1a–c]

Although SBUs have been successfully employed for the construction of MOFs with stable pores, it can be difficult, in contrast to MCMs,[5, 9] to line the interiors of such solids with organic groups since an elaborate covalent synthesis of a linear organic bridge is often required to introduce simple (e.g. -Me) and diverse (e.g. chiral) functional groups. With this in mind, it has occurred to us that one way to circumvent this problem may be to invert the structural role[10] of the SBU and linear organic bridge such that the SBU serves as a linear bridge and the organic ligand serves as a node. In this design, the bonds of the SBU that support the framework are minimized (i.e. two) such that the remaining coordination sites of the SBU may be filled with organic ligands that decorate the interior of the framework. Moreover, such an inverted metal-organic framework (IMOF) would enable the second sphere of a SBU to line the walls of a host, in contrast to a covalent synthesis, supramolecularly[11] where convergent[12] terminal groups may be tailored to define structure and recognition properties of the solid.

Herein, we describe initial results of a strategy for the construction of such a porous IMOF that employs a molecule derived from a template-directed[13] solid-state [2+2] photodimerization[14] as the node (Figure 1). Owing to the presence of divergent and multiple Lewis-base functional groups, we anticipated that the product of this solid-state approach, *rctt*-tetrakis (4-pyridyl)cyclobutane[15] (4,4′-tpcb), upon reaction with the Cu paddle-wheel complex $[Cu_2(O_2CR)_4L_2]$,[16] would serve as a 4-connected node, propagating the dimetal complex, as a linear SBU through axial coordination, within a porous 2D IMOF.[17] Moreover, in contrast to a planar organic node (e.g. 4,4′-bipyridine),[18] the ligand derived from the solid-state synthesis was anticipated to produce cavities with deepened interiors owing to enforced twisting of the

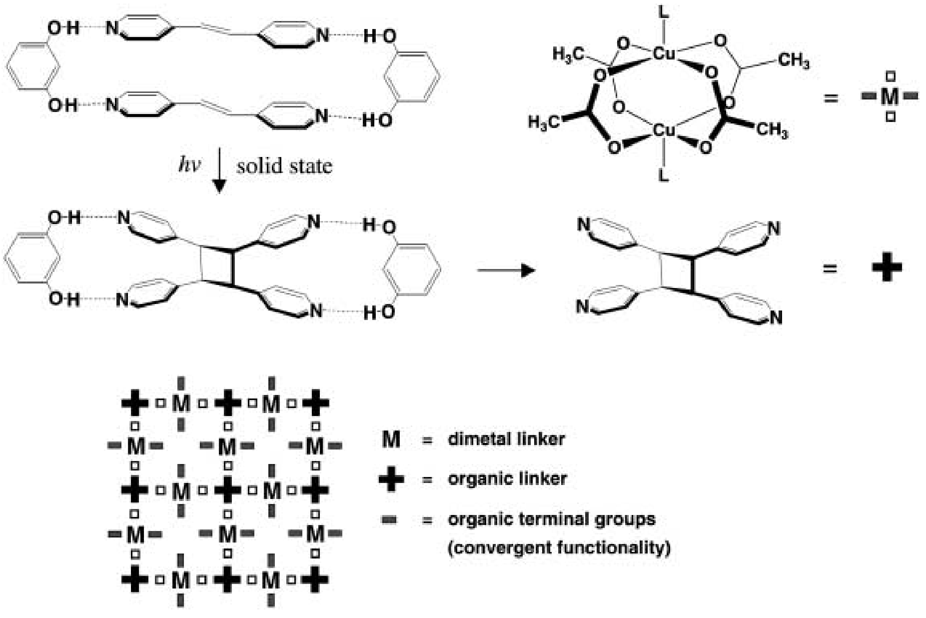

Figure 1. Construction of a porous inverted metal-organic framework (IMOF).

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pyridyl groups with respect to the cyclobutane rings which would orient the pyridyl groups orthogonal to the plane of the 2D framework (Figure 2). That the R groups of the SBU may be readily modified[19] would provide a ready means to decorate the walls of the deepened cavities with organic functional groups.

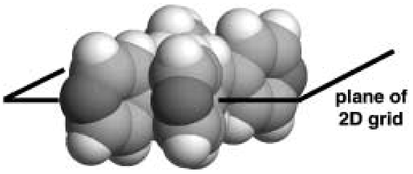

Figure 2. The orientation of the pyridyl groups (space-filling representation) orthogonal to the plane of the 2D framework.

When $[Cu(O_2CCH_3)_2(H_2O)_2]$ (0.06 g) and 4,4′-tpcb (0.025 g) in methanol (15 mL) was layered with benzene (25 mL), green crystals of **1** · 3 benzene grew within approximately three weeks (yield: 75 %). The formulation of **1** · 3 benzene was confirmed by single-crystal X-ray diffraction (Figure 3), X-ray powder diffraction, and thermal analysis.

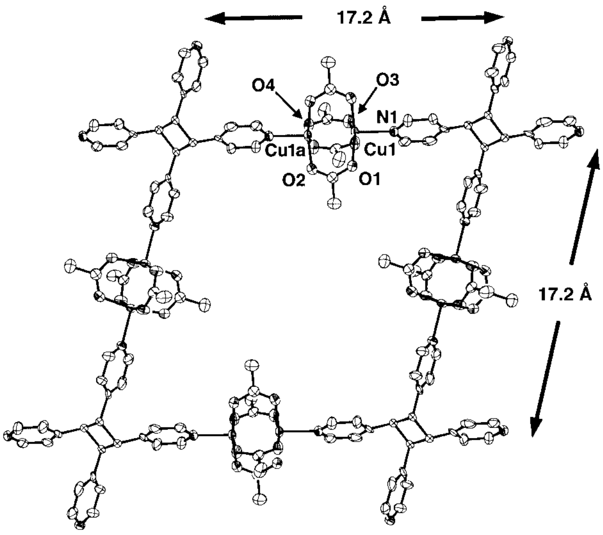

Figure 3. ORTEP perspective of **1**. Selected interatomic distances [Å]: Cu1-N1 2.148(3), Cu1-O1 1.971(3), Cu1-O2 1.980(3), Cu1-O3 1.968(2), Cu1-O4 1.965(2), Cu1 ··· Cu1a 2.600(1).

The components assemble to form a porous 2D IMOF. Each 4,4′-tpcb unit, each of which sits around a crystallographic center of inversion, is surrounded by four paddle-wheel complexes, each of which is bisected by a mirror plane, such that the organic unit serves as a 4-connected vertex. As anticipated, the pyridyl rings are twisted approximately orthogonal with respect to the cyclobutane ring (dihedral angle: 139.8°) such that the pyridyl groups "thicken" the 2D framework.[16, 18] As a consequence of the assembly process, a 2D IMOF with very large rhombic cavities of dimensions of about 17.2 × 17.2 × 5.0 Å and corner angles of about 75° and 105° is formed. Owing to the ability of 4,4′-tpcb to propagate the SBU within a (4,4)-framework, **1** may be regarded a novel inverted analogue of those cavity-containing rhombic- and square-grid frameworks designed by using linear bipyridine groups and transition-metal ions.[17] The cavity of **1** is larger than most metal-(4,4′-bipyridine) rhombic- and square-grid frameworks (dimensions ~12.0 × 12.0 Å)[17] and compares favorably with a metal–bipyridine square grid, $[\{Ni(4,4'\text{-bis}(4\text{-pyridyl})biphenyl)_2(NO_3)_2\}_n]$ (dimensions of about 20.0 × 20.0 Å), with a lengthened linear bridge.[3c]

The cavities of **1**, unlike those metal–bipyridine grids,[17] are decorated with convergent organic functional groups; four methyl groups are directed into the rhombic cavities such that the ligands subdivide each cavity into three compartments (Figure 4). The largest compartment, which defines a large rectangular box of dimensions of about 20.0 × 9.5 × 5.0 Å, runs along the diagonal of the obtuse corner angles and is occupied by one ordered and two disordered benzene guests. The two smaller compartments, which define moderately sized[20] square boxes of dimensions of about 7.0 × 7.0 × 5.0 Å, are located in the remaining corners and are filled by methyl groups, directed above and below each cavity, of adjacent grids. As depicted in Figure 5, the inclusion of the methyl groups (Figure 5 a) results in oblique stacking of the grids (interlayer separation: 5.7 Å) along the crystallographic *c* axis which, in turn, gives rise to a porous 3D MOF with, in a similar way to MCM-41,[5, 9] isolated 1D channels, of dimensions of about 12 × 10 Å (Figure 5 b). The channels are occupied by ordered (one per cavity) and disordered (two per cavity) benzene solvent molecules, which assemble edge-to-face (Figure 5 c), and represent about 40 % of the volume of the unit cell.[21] Thus, the organic functional groups of the SBU accommodate the methyl groups as "pegs" in lining up the layers, preorganizing the grids to form the channels. To our knowledge, such molecular compartmentalization within a MOF has not been realized.[22]

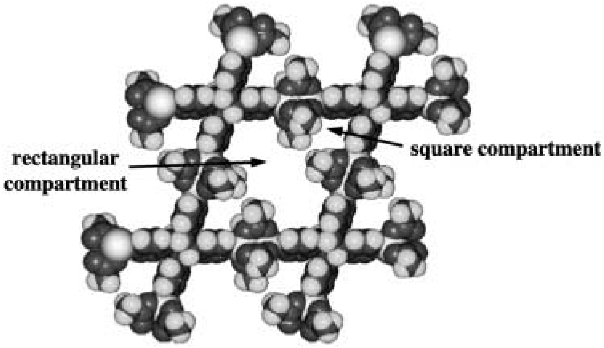

Figure 4. A space-filling view of the rhombic cavity of **1**. The cavity is subdivided by organic functional groups stemming from the SBU to form one rectangular or two square compartments.

Thermogravimetric (TGA) and differential scanning calorimetry (DSC) analysis (see Supporting Information), along with X-ray powder diffraction and optical microscopy, suggest that the structure of **1** is maintained between 27 °C and 180 °C. During this temperature change, the guest is liberated in two mass losses at 27 °C (two guests) and 75 °C (one guest), which may be attributed to the disordered and ordered guests,[3a] respectively, for which DSC and optical microscopy indicate

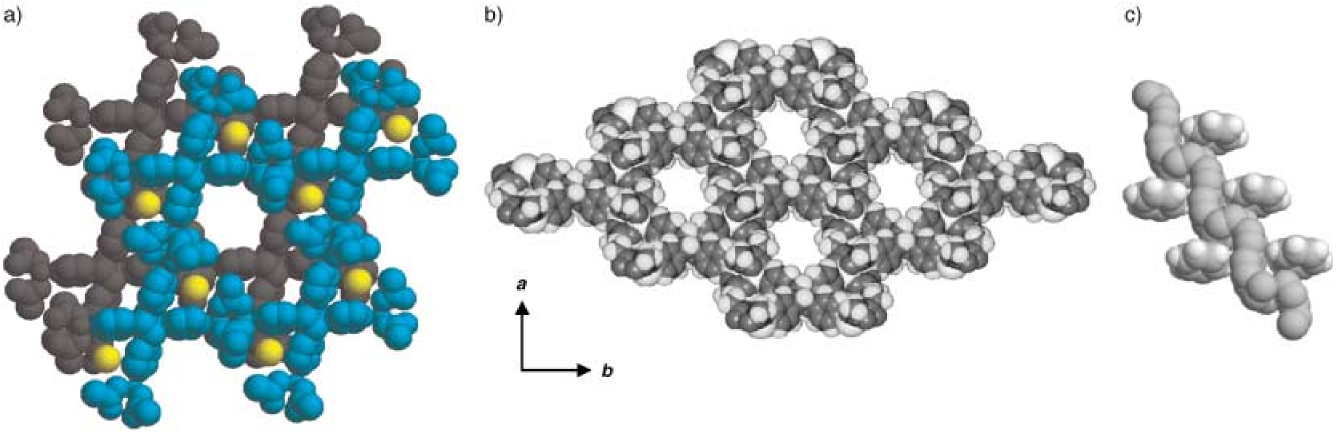

Figure 5. Space-filling views that demonstrate the stacking of the grids of **1** that form 1D channels and enable guest inclusion: a) stacking of two grids showing the inclusion of methyl groups, or "pegs", within the square compartments (hydrogen atoms omitted for clarity; color scheme: two grids have been differentiated using cyan and gray while the yellow spheres represent the included methyl groups), b) the 1D elliptical channels that arise from stacking of the larger compartments, and c) the ordered and disordered benzene guests.

no evidence of a phase change. Moreover, although diffraction-peak broadening is observed with the increase in temperature, single-crystal X-ray analysis performed on a sample after removal of the guest confirms the structure of **1**, the framework being virtually identical to guest-filled **1** save for high thermal motion of the organic components.[23] Indeed, **1** is a rare example of a MOF with single crystals stable to guest removal.[3] Preliminary results reveal that reintroduction of benzene can be achieved by placing **1** in neat benzene and heating the solvent to approximately 70 °C. Notably, guest uptake is accompanied by further diffraction-peak broadening which may be attributed to additional disorder of the organic groups.[24] Heating beyond 180 °C results in decomposition of the solid.

Herein, we have presented a strategy for the construction of porous MOFs that enables the supramolecular decoration of cavities with organic functional groups. Lining of the interior is achieved by using convergent[12] terminal ligands of a linear SBU[7] and a product of a template-directed solid-state organic synthesis.[13] In the present case, the organic functional groups compartmentalize the rhombic cavities of a 2D porous IMOF[22] and preorganize the framework to assemble to form a 3D nanoporous solid. Following these observations, experiments are underway to expand this approach to organic groups of increasing diversity and additional SBUs.[25] That the node has been generated by a template-directed solid-state organic synthesis[13, 14] also suggests that access to MOFs (as in the case of **1**) poorly available,[26, 27] or completely inaccessible, in solution, may now be realized.

Experimental Section

1·3benzene: A solution of $[Cu(O_2CCH_3)_2(H_2O)_2]$ (0.06 g) and 4,4′-tpcb (0.025 g) in methanol (15 mL) was layered with benzene (25 mL) at room temperature. Upon standing, green crystals of **1**·3benzene grew within 3 weeks and were isolated in 75 % yield by way of filtration. IR (KBr pellets): $\tilde{\nu} = 1630$ (s), 1610 (s), 1579 (sh, br), 1428 (s, br), 1346 (m), 1223 (m), 1071 (w), 1022 (m), 835 (m), 682 (m), 527 (m), 565 (m) cm^{-1}. Crystal data for **1**·3benzene: monoclinic, $C2/m$, $a = 14.354(3)$, $b = 27.238(5)$, $c = 8.064(2)$ Å, $\beta = 93.56(3)°$, $V = 3147.0(11)$ Å^3, $2\theta = 45°$, Mo$_{K\alpha}$ radiation ($\lambda = 0.71070$ Å) for $Z = 2$ and $R = 0.037$. Crystal data for the heated sample of **1**: triclinic, space group $P\bar{1}$, $a = 8.002(2)$, $b = 13.956(3)$, $c = 15.409(3)$ Å, $\alpha = 64.33(3)°$, $\beta = 88.01(3)°$, $\gamma = 83.39(3)°$, $V = 1540.3(5)$ Å^3, $2\theta = 40°$, Mo$_{K\alpha}$ radiation ($\lambda = 0.71070$ Å) for $Z = 1$ and $R = 0.128$. The crystal data for **1**·3benzene and the heated sample of **1** were measured on a Nonius Kappa CCD single-crystal X-ray diffractometer at 100 K. After anisotropic refinement of all non-hydrogen atoms, aromatic, methyl, and methine hydrogen atoms were placed in idealized positions and allowed to ride on the atom to which they are attached. The cyclobutane moieties in both **1**·3benzene and the heated sample of **1** were observed to lie disordered across two positions. Correspondingly, ring carbon atoms were refined with fixed site occupancies of 0.50/0.50 and 0.55/0.45, respectively. The disordered guest molecules of **1**·3benzene were disordered in a manner consistent with benzene. The atoms were treated as carbon atoms and refined with isotropic thermal parameters and fixed site occupancies. The mosaic nature of the heated sample of **1** made accurate integration of the reflection data difficult, precluding the possibility of an accurate structure with $2\theta > 40°$. All crystallographic calculations were conducted using SHELXL-97[28] locally implemented on an IBM compatible pentium-based PC. CCDC-172946 (**1**·3benzene) and CCDC-172947 (**1**) contains 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 CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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[23] The rhombic cavity of the heated sample of **1** displays cavity dimensions $\sim 17.1 \times 17.1 \times 5.0$ Å and corner angles of $\sim 72°$ and $108°$. The slight deformation in shape of the cavities results in a lowering in symmetry of the unit cell to the triclinic setting.
[24] The additional peak broadening following reintroduction of the guest precludes a single-crystal structure determination of **1**. Experiments are underway to determine the effect of guest uptake on the structure of **1** and the range of guests that may be included within the framework.
[25] It is possible to decorate the interior of a similar IMOF with olefins (G. S. Papaefstathiou, L. R. MacGillivray, unpublished results).
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Enhanced Luminescence and Photomagnetic Properties of Surface-Modified EuO Nanocrystals**

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Europium(II) oxide (EuO) has localized narrow 4f orbitals that exist as the degeneracy levels between the conduction band (5d orbitals of Eu^{II}) and the valence band (2p orbitals of O^{2-}).[1] The 4f – 5d electron transition and spin configuration of EuO lead to unique optical, magnetic, and electronic properties.[2, 3] In fact, the theoretical quantum-confinement model predicts enhanced luminescence and specific magnetic properties for nanosized Eu^{II} semiconductors.[4, 5] Whereas the preparation of bulk EuO by thermal reduction of Eu_2O_3 above 1000 °C was reported in 1965,[6] EuO nanocrystals were only synthesized and isolated recently. We recently prepared spindle-shaped EuO nanocrystals (average 280 nm in length and 95 nm in width) from Eu metal in liquid ammonia.[7] Here we report on the synthesis of smaller EuO nanocrystals (average diameter: 3.4 nm) by photochemical reduction of

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