Communication

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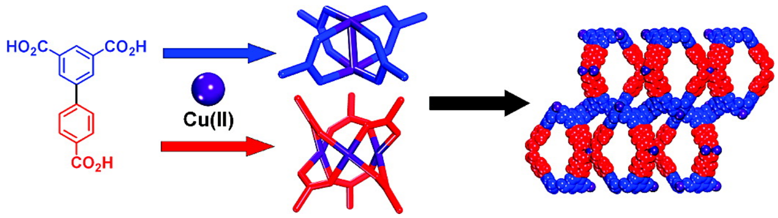

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Porous Crystal Derived from a Tricarboxylate Linker with Two Distinct Binding Motifs

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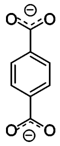
Although remarkable advances in the understanding of structure−property relationships of porous coordination polymers have taken place over the past decade,[1] there remains a pressing need to design higher performance materials. However, it is just a matter of time before commercial applications in gas storage, catalysis, and separations are realized because the combination of high surface area, tunable functionality, and defined pore structure are unrivaled by other classes of materials.[2] The fevered pitch of research in this area has centered around high-symmetry structures mainly for aesthetic reasons, although the resultant simplification in predicting connectivity is much heralded.[3] The first materials that showcased the potential of metal-carboxylates as network building nodes, MOF-5[4] and HKUST-1,[5] are derived from highly symmetrical organic linkers (**1** and **2**, respectively) bound to high-symmetry metal clusters. MOF-177,[6] the material exhibiting the highest gravimetric levels of physisorbed hydrogen reported to date,[7] derives from a carboxylate linker (**3**) that has idealized D_{3h} symmetry. On the other hand, the use of organic linkers in which the coordinating functionalities are not symmetry equivalent (termed “unsymmetrically substituted”) may allow the formation of coordination polymers with geometries and properties previously unseen. Few examples of such linkers have been reported in the literature,[8,9] and unsymmetrical linkers with identical coordinating functionality have not yet been reported for carboxylates, the most important class of linkers.[10] Although the increased topological complexity introduced by less symmetrical linkers may frustrate attempts at prediction, there is an opportunity to drive new modes of network assembly required to satisfy the constraints imposed by unique linker geometries. These reasons make it appealing to explore the use of unsymmetrically substituted linkers to generate novel porous coordination polymers.



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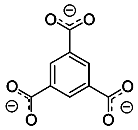

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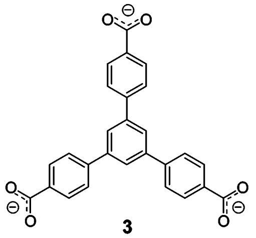

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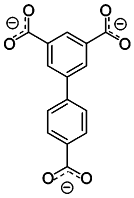

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Herein we report the use of biphenyl-3,4′,5-tricarboxylate (**4**) with Cu(II) to generate a highly porous crystalline material containing both the common binuclear Cu(II) paddlewheel cluster, $[Cu_2(O_2CR)_4]$, and the exotic trinuclear Cu(II) cluster, $[Cu_3(O_2CR)_6]$. This material, termed UMCM-150 (University of Michigan crystalline material), shows relatively high excess gravimetric and volumetric H_2 uptake.

Aquamarine hexagonal plates of UMCM-150 were synthesized by the solvothermal reaction of H_3-**4** with $Cu(NO_3)_2 \cdot 2.5H_2O$ in DMF/dioxane/H_2O 4:1:1 at 100 °C for 4 h in 78% yield. Multiple solvent exchanges followed by evacuation at 100 °C for 4 h led to a change in color of the material to deep purple. The evacuated material was formulated as $Cu_3(C_{15}H_7O_6)_2$ by elemental analysis, and this assignment is corroborated by X-ray crystallography (vide infra). No significant change in the PXRD pattern was observed after solvent removal (see Supporting Information).

The structure of UMCM-150 was solved by single-crystal X-ray diffraction in the space group *P*63*/mmc*.[11] Views of the crystal lattice along the *a* and *c* axes are provided in Figure 1a and 1b. The carboxylates on the 3- and 5-positions (isophthalate ring) of the linker each form Cu paddlewheel clusters with three neighboring molecules and this is a ubiquitous motif in network solids derived form Cu carboxylate clusters. Notably, the carboxylate on the 4′-position (carboxyphenyl ring) assembles into a $Cu_3(O_2CR)_6$ cluster (Figure 1c), which is unknown in coordination polymers despite the hundreds of examples reported.[12] UMCM-150 derives from a [3,4,6]-connected net consisting of three types of cagelike structures. One type of cage possesses a hexagonal bipyramidal shape with an aperture (accounting for the van der Waals radii) of approximately 5.2 Å × 5.8 Å (Figure 1d). The walls of the cages are formed by the faces of six linker molecules. Trinuclear Cu clusters are located in the apical positions, whereas Cu paddlewheels occupy the equatorial positions. The second type of cage possesses a trigonal bipyramidal shape with a larger aperture of 10.2 Å × 13.7 Å. In the apical positions, small cylindrical pores about 4.2 Å in diameter resulting from the assembly of three linker molecules by three paddlewheels are observed; Cu_3 clusters are located in the equatorial positions and linker molecules occupy the faces (Figure 1e). The third type of cage possesses all three different apertures observed in the other two types of cages (Figure 1f). Each apical position of the cage is formed from three paddlewheels and three linker molecules pointing outward, while three Cu_3 clusters are located in the equatorial positions. The edges of twelve linker molecules form the cage walls. Notably, for the first two types of cages only aromatic groups face toward the inside, whereas the axial coordination sites of the Cu paddelwheels are directed inward in the third type of cage.

The N_2 adsorption isotherm of UMCM-150 (see Supporting Information) reveals type I behavior with no hysteresis upon desorption. From these data, a total pore volume of 1.0 cm^3/g was determined, and the apparent surface area was calculated using the Langmuir method to be 3100 m^2/g (2300 m^2/g BET), thus confirming the permanent porosity of UMCM-150. Ar adsorption (see Supporting Information) yields the following pore distribution diameters: 6.5−8 Å, 10.5−12 Å, and 12.5−13 Å. These pore sizes are consistent with the three types of cages observed in the crystal structure.

The H_2 sorption isotherm recorded at 77 K shows type I behavior with no hysteresis and no noticeable change in properties upon

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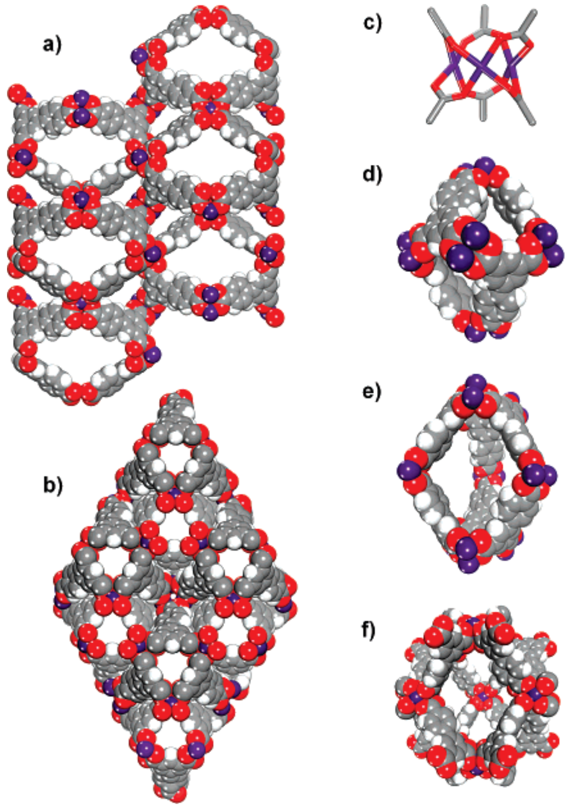

Figure 1. (a) View along the *a*-axis of a 2 × 2 × 1 array of unit cells of the crystal structure of UMCM-150. C atoms (dark gray), H atoms (white), O atoms (red), Cu atoms (purple). Guest molecules are omitted for clarity. (b) View along the *c*-axis. (c) Detail of a $Cu_3(O_2CR)_6$ cluster. (d) Hexagonal bipyramidal cage formed by six molecules of **4** linked by eight Cu clusters. (e) Trigonal bipyramidal cage formed by six molecules of **4** linked by nine Cu clusters. (f) Cage formed by twelve molecules of **4** linked by nine Cu clusters.

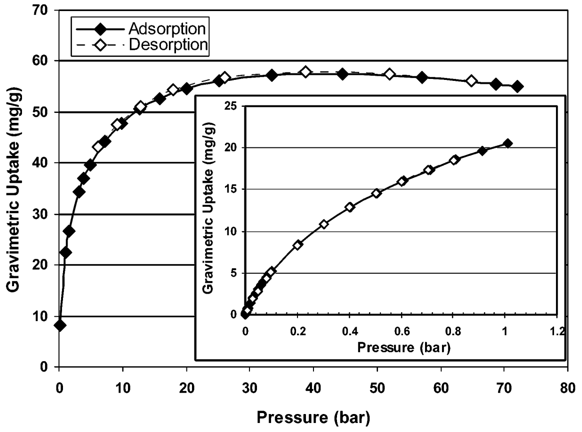

Figure 2. Hydrogen sorption isotherm at 77 K for UMCM-150. Inset: isotherm from 0 to 1 bar.

repeated cycling. UMCM-150 showed an excess gravimetric H_2 uptake of 2.1 wt % at 1 bar (Figure 2), a number that lies in the upper range of physisorptive materials. Heat of adsorption measurements (Supporting Information) show an affinity of 7.3 kJ/mol at low coverage which is above MOF-5 and HKUST-1.[13] However, this affinity rapidly drops to a level below that of HKUST-1, but still above MOF-5. The good uptake at 1 bar can therefore be ascribed to a combination of good affinity sites and high surface area. In a previous study we conducted, it was found that HKUST-1 and MOF-74, which show a similarly steep rise in the low-pressure region, suffered from poor capacity.[7] Gratifyingly, high-pressure studies on UMCM-150 revealed 5.7 wt % at 45 bar (Figure 2). From the crystallographic density of the fully evacuated material (0.636 g/cm^3), an upper limit on the excess volumetric uptake could be estimated as 36 g/L. These values are among the highest reported for a copper-based coordination polymer.

In conclusion, we have demonstrated that a linker with carboxylate groups distributed in an unsymmetrical fashion leads to a coordination polymer possessing rare trinuclear Cu(II) clusters. Lifting the constraint of symmetry equivalent functional groups offers entry into a variety of new linker types and represents a starting point toward a new generation of high performance coordination polymers.

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Supporting Information Available: Synthetic procedures, crystallographic data, powder X-ray diffraction data, thermogravimetric analysis, N_2 and Ar sorption isotherms, pore size distribution and heat of adsorption data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) An apparent exception are the networks derived from monosubstituted terephthalic acids or substituted biphenyl-4,4′-dicarboxylic acids. These are, however, isostructural with the terephthalic acid parent compound, MOF-5, and therefore express apparent higher symmetry in the crystal due to disorder.

(11) X-ray crystal data for UMCM-150: $C_{30}H_{14}Cu_3O_{15}$, hexagonal, space group *P63/mmc* (no. 194); $a = b = 18.3532(11)$ Å, $c = 40.667(3)$ Å, $V = 11862.9(14)$ Å^3, $Z = 6$, $T = 298(2)$ K, $\rho_{calcd} = 0.663$ g/cm^3, $F(000) = 2358$, total reflections = 44060, independent reflections = 3899, $R_1 = 0.0907$, $wR_2 = 0.2162$, ($R_1 = 0.1402$, $wR_2 = 0.3205$ before SQUEEZE), GOF = 0.830, residuals based on $[I > 2\sigma\Delta I(I)]$.

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