Two Large-Pore Metal–Organic Frameworks Derived from a Single Polytopic Strut

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ABSTRACT: Two noninterpenetrated MOFs with strikingly different structures, NU-108–Cu and NU-108–Zn, were prepared from a single hexa-carboxylated ligand. NU-108–Cu contains paddlewheel-coordinated copper ions as nodes and is based on a 3,24 network associated with an inherently noncatenating rht-topology. Modifications introduced in the hexa-carboxylated struts (uniquely placed phenyl spacers) lead to substantial changes in pore sizes, relative to those found in other MOFs based on 3,24 networks and paddlewheel-coordinated copper ions. NU-108–Zn features a new net based on (3,3,6)-connector and octadehral Zn₄O₆ nodes in which all struts lie in a–b planes.

Metal–organic frameworks (MOFs)¹–³ have attracted tremendous attention over the past decade, in part due to their potential for application to problems ranging from gas storage⁴–⁶ chemical separations⁷–¹¹ chemical sensing¹² catalysis¹³,¹⁴ ion exchange¹⁵,¹⁶ and light harvesting¹⁷,¹⁸ to drug delivery.¹⁹–²¹ Also of substantial interest, however, have been the discovery and/or design and synthesis of MOFs exhibiting topologies previously unknown for porous materials, as well as the extension of known topologies to new organic linkers that may lead to different surface areas, apertures sizes, and/or cavity sizes relative to previously synthesized materials. Such variations can be advantageous, for example, for enhancing gas uptake or improving selectivity in chemical separations.

While many varieties of node/strut coordination have been employed to form equilibrium MOF structures, perhaps the most popular are those involving transition-metal ions or clusters and carboxylate functionalities.²² Owing to their commercial availability and/or typically facile syntheses, candidate linkers containing from two²³ and going as far as twelve²⁴ carboxylate moieties have been employed to form a large number of 3D coordination networks based on a wide variety of topologies. Hexa-carboxylated dendritic ligands (Figure 1A, R₂ absent) have recently attracted significant attention as candidate linkers due, in part, to the modularity of their design. For example, by symmetrically increasing the lengths of the trigonally organized arms (varying R₁ in Figure 1A), and thus the distance from the linker core to each pair of carboxylates, MOF pore volumes can be systematically enlarged (as illustrated, for example, by comparing NOTT-112,²⁵ NOTT-119,²⁶ NOTT-116²⁷/PCN-68,²⁸ PCN-61²⁹/PCN-66,²⁸ and NU-100³⁰/PCN-610³¹ and their component struts).

This strategy recently yielded a MOF, NU-100³⁰ (Figure 1B), having one of the highest³⁰ nitrogen-accessible surface areas yet reported and displaying a record-high value for cryogenic (77 K) excess uptake of molecular hydrogen (i.e., 99.5 mg of H₂ per 1000 mg of MOF). Like the NOTT and PCN examples mentioned above, NU-100 contains Cu²⁺-based paddlewheel nodes and features fused cages/pores of three varieties: cuboctahedral (1), tetrahedral (2), and truncated cubocathedral (pore 3). For NU-100, the pore sizes vary as: 1 < 2 < 3 (Figure 1B).

The structures of NU-100 and related MOFs are describable as 3,24 nets, whose underlying topology is rht.³¹ The rht topology is particularly attractive because it can yield only noncatenated structures. To our knowledge, the first report of a MOF based on a 3,24 net and employing Cu²⁺ paddlewheel coordination was by Eddaoudi and co-workers.³² In contrast to a 1,3,5-substituted phenyl group, however, the trigonal core of their material comprises a Cu₆O₃³⁺ cluster ligated by six water molecules and by half the nitrogen atoms of three tetrazolate fragments. The tetrazolates, in turn, are connected to one isophthalate unit each, to yield an overall hexa-carboxylated building unit.

The guaranteed absence of catenation with the rht topology prompted us to investigate further the effect of linker expansion on pore sizes of MOFs. Although expanding from the core (i.e., lengthening R₂, Figure 1A) has previously proven fruitful, especially for increasing micropore volumes, further application
of the strategy seemed likely to be synthetically laborious. With this in mind, we turned our attention instead to expanding the linker in the R₂ direction (Figure 1A, length of R₂ is increased by a phenyl group) and to comparing the anticipated new compounds to the previously reported hexacarboxylate-containing compounds (Figure 1A, where R₂ is always absent and only R₁ is changed). Herein, we report the synthesis and characterization of a noninterpenetrated material, NU-108-Cu, featuring the previously known (3,24)-connecter rht topology based on Cu²⁺-paddlewheel nodes and containing three types of cages or pores—but now with a much different size distribution. We also report the synthesis and characterization of another noninterpenetrated NU-108-Zn with a new net based on a (3,3,6)-connector, constructed with two equilateral triangle tiles (3,3-connector) from the hexacarboxylated linker L₆⁻ and octahedral (6-connector) Zn₄O nodes.

Synthesis and characterization of the desired hexacarboxylic acid reactant (LH₆ Figure 2) are described in the Supporting Information (SI)). Briefly, however, LH₆ was obtained in quantitative yield via saponification of the corresponding hexaester compound, which, in turn, was obtained in 66%
yield via Sonogashira coupling of 1,3,5-triiodobenzene with an appropriate acetylene-terminated compound.

Reaction of LH₆ (Figure 2) and Cu(NO₃)₂·2.5H₂O in dimethylformamide (DMF)/HBF₄ (100:2.4, v/v) at 80 °C for 20 h afforded teal-colored crystals shaped as truncated cuboctahedra (NU-108-Cu, framework formula [Cu₉(L)·(H₂O)]₉₆ Figure 2A). Solvothermal reaction of LH₆ with Zn(NO₃)₂·6H₂O under the same conditions, except for 48 h, yielded clear hexagon-shaped platelet crystals (NU-108-Zn, framework formula of \([Zn_{6}(O)(L)_{12}]_{96}\) Figure 2 B).

X-ray analysis of a single crystal of NU-108-Cu revealed that this material is characterized by a cubic space group, Fm3m, with an edge length of 63.515(5) Å. Each framework node consists of two copper(II) ions coordinated, in paddlewheel fashion, by one carboxylate from each of four linkers, and axially by water molecules (Figure 3A), which were not well resolved in the X-ray analysis. Each L₆⁻ unit contributes to the formation of three cuboctahedron cages (Figure 3B). NU-108-Cu shows large channels when viewed along the a, b, or c axis (Figure 3C). Gratifyingly, NU-108-Cu displays the rht-topology and 3,24 network observed for the high-porosity materials. Like these compounds, NU-108-Cu contains three types of cages (Figures 4 and 5) that are fused in ways that provide for continuous channels. Also, like the previously described compounds, NU-108-Cu contains twice the number of cage 2 versus cage 1 units but equal numbers of cages 1 and 3.

Each cuboctahedral type-1 cage (Figure 4A) is formed from 24 isophthalate groups from L₆⁻ units and 12 pairs of copper ions (i.e., 24 total). The nodes forming triangular windows in cage 1 are shared with cage 2, while those forming rectangular windows are shared with cage 3 (Figure 4D). As illustrated in Figure 5, type-1 cages are comparatively small for MOFs built supporting the formation of layers 1 and 2, there is a overall structure is three-dimensional: Briefly, for each node possessing three fully coordinated carboxylates along the top of the node and three along the bottom, with each carboxylate lining the channel). Thus, the material is three-dimensionally porous.

While NU-108-Zn evidently lacks a structural precedent, early work by Cha and co-workers should be noted. They used a hexacarboxylated dendritic molecule, 4,4′,4″-tris[N,N-bis(4-carboxyphenyl)amino]triphénylamine, to generate

Figure 4. View of three different cages, 1 (A), 2 (B), 3 (C), and their packing in NU-108-Cu as illustrated by its single-crystal X-ray structure (D). Hydrogens and disordered solvent molecules are omitted for clarity. Carbon, gray; oxygen, red; copper, teal. Purple: representation of the largest spheres that can fit within these cages.
With six octahedral Zn₄O clusters attached, the linker helped define a trigonal prism and ultimately produced a Ni–As type 6,6-network. Additionally, while our study was in progress, a similar ligand to that used for NU-108-Zn, 1,3,5-tris(3,5-bis(4-carboxyphenyl-1-yl)phenyl-1-yl)benzene (R₁ = absent, R₂ = phenyl, Figure 1A), was reported to form a 2-fold interpenetrated MOF, JUC-100, as featuring Zn₄O clusters. Remarkably, in view of the differences in catenation and topology for JUC-100 versus NU-108-Zn, the corresponding linkers differ only in the presence or absence of R₁ acetylene units.

Thermogravimetric analysis (TGA) of NU-108-Cu revealed a 65% mass loss, culminating at about 125 °C and assigned to the loss of solvent molecules (Figure 8). TGA of NU-108-Zn revealed a ca. 55% mass loss, culminating near 150 °C and likewise assigned to the loss of solvent molecules (Figure 8). The phase-purity of the bulk versions of both materials was confirmed by powder X-ray diffraction (PXRD) measurements (Figure 9, panels A and B, respectively), which showed good agreement with simulations based on the corresponding single-crystal structures.

In summary, starting with a single hexa-carboxylated linker, we have obtained a pair of noncatenated MOFs of strikingly different structures. NU-108-Cu contains paddle-wheel-coordinated copper ions as nodes and is based on a 3,24 network associated with an inherently noncatenating rht...
topology. Like NOTT-112, NOTT-119, NOTT-116, PCN-68, PCN-61, PCN-66, and NU-100—
and despite displacement of the carboxylate functionalities away from otherwise terminal benzenes (R2 = phenyl, Figure 1A)—it contains three types of cages. The linker in NU-108-Cu is identical to that in PCN-61, apart from the incorporation of six R2 spacers. The most obvious structural consequences of R2 incorporation are increases in the sizes of all three cages and ballooning of cage 1 to a size much greater than cage 2 and similar to cage 3. When combined with zinc nitrate, the same linker afforded a MOF (NU-108-Zn) featuring a (3,3,6)-connected net with octadehral Zn4O nodes in which all struts lie in α−β planes; nevertheless, NU-108-Zn is characterized by bonding that extends the structure (semi)infinitely in three dimensions, rather than by simple stacking of two-dimensional layers. Both materials initially incorporate substantial amounts of synthesis solvent, as evidenced, in part, by TGA measurements and as expected from the existence of channels in three directions.

Figure 7. Packing of NU-108-Zn viewed along the c axis (A) and the a axis (B) and perspective image showing the channels along the a axis (C). Hydrogens and disordered solvent molecules are omitted for clarity. Carbon, gray; oxygen, red; zinc, yellow.

Figure 8. TGA traces for NU-108-Zn (red, top) and NU-108-Cu (black, bottom) measured using TGA. In each case, the initial large weight loss, culminating at ca. 150 °C, is assigned to removal of free solvent (DMF).

Figure 9. As-synthesized (top) and calculated (bottom) PXRD patterns for NU-108-Cu (A) and NU-108-Zn (B).
Notes
The authors declare no competing financial interest.

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