

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

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Supporting Information

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 paddlewheelcoordinated copper ions. NU-108-Zn features a new net



based on (3,3,6)-connecter and octadehral Zn_4O nodes in which all struts lie in a-b planes.

etal–organic frameworks $(MOFs)^{1-3}$ have attracted I tremendous attention over the past decade, in part due to their potential for application to problems ranging from gas storage,^{4–6} chemical separations,^{7–11} chemical sensing,¹² catalysis,^{13,14} ion exchange,^{15,16} and light harvesting^{17,18} 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-61,²⁸ PCN-66,²⁸ and NU-100²⁹/PCN-610²⁸ and their component struts).

This strategy recently yielded a MOF, NU-100²⁹ (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 H_2 per 1000 mg of MOF). Like the NOTT and PCN examples mentioned above, NU-100 contains Cu^{II}-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 stuructures 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 Cu^{II}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 Cu₃O³⁺ 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 R₁, Figure 1A) has previously proven fruitful, especially for increasing micropore volumes, further application

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Figure 1. Schematic representation of hexacarboxylic acid ligand that can be extended in either or both $R1/R_2$ directions (A). An example of the use of the deprotonated form of one these ligands to form a highly porous MOF, NU-100,²⁹ featuring fused cages of three distinct sizes and shapes (see text) (B). NU-100 reprinted with permission from *Nature* (http://www.nature.com), ref 29. Copyright 2010 Nature Publishing Group.



Figure 2. Schematic representation of ligand LH₆ and photographic images of NU-108-Cu (A) and NU-108-Zn (B) MOFs.



Figure 3. L^{6-} linker connecting with Cu_{2}^{II} paddleweheel units (A). View of single linker with three cuboctahedron cages around it (B). Packing of **NU-108-Cu** in a 2 × 2 × 2 unit cell in the X-ray crystal structure looking down the *a*-axis (C). Hydrogens and disordered solvent molecules are omitted for clarity. Carbon, gray; oxygen, red; copper, teal.

of the strategy seemed likely to be synthetically laborious. With this in mind, we turned our attention instead to expanding the linker in the R_2 direction (Figure 1A, length of R_2 is increased by a phenyl group) and to comparing the anticipated new compounds to the previously reported hexacarboxylatecontaining compounds (Figure 1A, where R_2 is always absent and only R_1 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 Cu^{II}-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)-connecter, constructed with two equilateral triangle tiles (3,3-connecter) from the hexacarboxylated linker L^{6-} and octahedral (6-connecter) Zn₄O nodes.

Synthesis and characterization of the desired hexacarboxylic acid reactant (LH_6 , Figure 2) are described in the Supporting Information (SI)). Briefly, however, LH_6 was obtained in quantitative yield via saponification of the corresponding hexaester compound, which, in turn, was obtained in 66%

yield via Sonagashira 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 $[Cu_3(L)-(H_2O)_3]_n$, 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 $[Zn_4(O)(L)_6]_n$, Figure 2 B).

X-ray analysis of a single crystal of \overline{NU} -108- \mathbb{Cu}^{33} revealed that this material is characterized by a cubic space group, $Fm3\overline{m}$, 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 \mathbf{L}^{6-} 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*-topology³¹ 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



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.

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 3 and 1.

Each cuboctahedral type-1 cage (Figure 4A) is formed from 24 isophthalate groups from L^{6-} 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 from hexatopic struts lacking R_2 units, e.g. NOTT-112,²⁵ NOTT-119,²⁶ NOTT-116²⁷/PCN-68,²⁸ PCN-61,²⁸ PCN-66,²⁸ and NU-100²⁹/ PCN-610.²⁸ (Type-1 cages are of identical size for these six materials, with each cage capable of accommodating a sphere of diameter ~1.3 nm) Inclusion of R_2 = phenyl in the linker (as in NU-108-Cu) causes the sphere associated with cage 1 to balloon to 2.7 nm (Figure 5C). (Calculations are based on the van der Waals surface of the

framework interior and were done using Gelb and Gubbins' method;³⁴ Figure S11 of the SI).

Cage 2 of NU-108-Cu (Figure 4B) defines a truncated tetrahedron, is formed from isophthalate groups from four L^{6-} linkers and 12 pairs of copper ions (i.e., 24 total), and can accommodate a sphere of diameter 1.9 nm. For comparison, cage 2 units in PCN-61²⁸ and NU-100²⁹ can accommodate spheres of diameter 1.2 and 1.5 nm, respectively (Figure 5).

As expected, cage 3 of NU-108-Cu (Figure 4C) is describable as a truncated cuboctahedron and is formed by 24 Cu^{II}₂ paddlewheel nodes and portions of eight distinct L⁶⁻ units. Inclusion of R₂ spacers in the linker also substantially increases the size of cage 3. Thus, the version of cage 3 in PCN-61 (R₂ absent) can accommodate a sphere of diameter 1.9 nm, while the version in NU-108-Cu (R₂ = phenyl) can accommodate one of diameter 2.8 nm (Figure 5).

X-ray analysis of a single crystal of NU-108-Zn³⁵ revealed that this MOF has the trigonal space group $R3\overline{c}$ with unit-cell lengths of a = b = 24.5270(10) and c = 71.355(4) Å. The framework nodes of NU-108-Zn are octahedral and consist of Zn₄O⁶⁻ clusters (Figure 6A and B) coordinated by six carboxylates derived from each of six distinct L⁶⁻ units (Figure 6C). $Zn_4O(COO)_6$ is a commonly encountered node in MOF chemistry, appearing, for example, in MOF- 5^{36} and other IRMOFs,²³ MOF- $177,^{37}$ UMCM- $1,^{38}$ UMCM- $2,^{39}$ and MOF- $210,^{30}$ The unit cell of NU-108-Zn comprises six Zn₄O clusters and six L^{6-} linkers. NU-108-Zn displays a topology based on (3,3,6)-connected vertices and, to our knowledge, not previously encountered in coordination chemistry (see the SI for more details of tiling and their symbols). The MOF can be viewed as being constructed from octahedral (6-connecter) Zn₄O nodes (Figure 6C) and overlapping pairs of triangular tiles (3,3-connecter) from the hexacarboxylated linkers. Looking down the c axis, three carboxylates from L^{6-} form an equilateral triangle (light purple in Figure 6D) that is located below the central phenyl group of the linker. The other three carboxylates define a second equilateral triangle (purple in Figure 6D) that is positioned above the central phenyl. Expressed another way, but again viewing the structure along the c axis, each tilted-octahedral node can be viewed as possessing three fully coordinated carboxylates along the top of the node and three along the bottom, with each carboxylate originating from a different linker. Thus, each node serves to support the formation of an upper and a lower 2D layer of linkers normal to the c axis (Figure 7A). Nevertheless, the overall structure is three-dimensional: Briefly, for each node supporting the formation of layers 1 and 2, there is a corresponding node supporting the formation of layers 2 and 3, and so on for additional nodes. Layers that are proximal to each other in the *c* direction are maximally displaced from each other in the *a* and *b* directions (Figure 7A). Consequently, the channels formed in the c direction are much smaller than anticipated, for example, from viewing only Figure 6E. Finally, viewing NU-108-Zn along the a or b axis reveals, in each case, the presence of two rectangular channels (Figure 7B and C). The larger of the two has cross-sectional dimensions of 1 nm \times 1.1 nm (after accounting for the van der Waals radii of atoms lining the channel). Thus, the material is three-dimensionally porous.

While **NU-108-Zn** evidently lacks a structural precedent, early work by Chae and co-workers should be noted.⁴⁰ They used a hexacarboxylated dendritic molecule, 4,4',4''-tris(*N*,*N*bis(4-carboxylphenyl)amino)triphenylamine, to generate



Figure 5. Comparison of relative sizes of cages 1, 2, and 3 within PCN-61²⁸(A), NU-100²⁹ (B), and NU-108-Cu (C) in terms of the largest sphere that can fit within each cage. The smallest sphere has a diameter of 1.2 nm, while the largest has a diameter of 2.8 nm.



Figure 6. Drawing of $Zn_4(O)(CO_2)_6$ (A). Representation (in yellow) of $Zn_4(O)(CO_2)_6$ as an octahedral node (B). View along the *c* axis of L⁶⁻ linked to six nodes. Black lines drawn from carboxylate corners form two equilateral triangles (C). Three carboxylates attach to nodes sited largely above the plane defined by the central phenyl group of the linker (purple), and three attach to nodes sited largely below (light purple) (D). View of packing of a single layer of the MOF formed by octahedrally coordinated Zn₄O nodes and by linkers (represented by parallel pairs of triangles) viewed along the c axis (E). Hydrogens and disordered solvent molecules are omitted for clarity. Carbon, gray; oxygen, red; zinc, yellow.

MODF-1.40 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, 1,3,5tris(3,5-bis(4-carboxyphenyl-1-yl)phenyl-1-yl)benzene (R_1 = absent, R_2 = phenyl, Figure 1A), was reported to form a 2fold interpenetrated MOF, JUC-100,41 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 singlecrystal structures.

In summary, starting with a single hexa-carboxylated linker, we have obtained a pair of noncatenatenated MOFs of strikingly different structures. NU-108-Cu contains paddlewheel-coordinated copper ions as nodes and is based on a 3,24 network associated with an inherently noncatenating rht



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).

topology. Like NOTT-112,²⁵ NOTT-119,²⁶ NOTT-116²⁷/ PCN-68,²⁸ PCN-61,²⁸ PCN-66,²⁸ and NU-100²⁹/PCN-610 and despite displacement of the carboxylate functionalities away from otherwise terminal benzenes (R_2 = 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 R_2 spacers. The most obvious structural consequences of R_2 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 a-b 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.

ASSOCIATED CONTENT

S Supporting Information

General procedures, materials, instrumentation, synthesis and characterization (¹H and ¹³C NMR) of LH₆ ligand, synthesis and X-ray crystallographic information files (CIF) for NU-108-Cu and NU-108-Zn MOFs, and theoretical pore size distribution for NU-108-Cu. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

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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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(33) Crystal data for **NU-108-Cu**: $C_{24}H_{12}CuO_4$, $M_r = 427.88$, cubic, space group is $Fm\overline{3}m$, a = 63.515(5) Å, b = 63.515(5) Å, c = 63.515(5) Å, $a = 90.00^{\circ}$, $\beta = 90.00^{\circ}$, $\gamma = 90.00^{\circ}$, V = 256229(61) Å³, Z = 96, T = 225.0 K, d = 0.266 mg/m³, absorption coefficient = 0.332 mm⁻¹, reflections collected = 2600, independent reflections = 2600 [R(int) = 0.0000], data/restraints/parameters = 2600/163/145, final R_1 (wR_2) = 0.0727 (0.1895) with $I > 2\sigma(I)$.

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(35) Crystal data for **NU-108-Zn**: $C_{144}H_{72}O_{26}Zn_8$, $M_r = 2740.98$, trigonal, space group is $R\overline{3}c$, a = 24.5270(10) Å, b = 24.5270(10) Å, c = 71.355(4) Å, $\alpha = 90.00^{\circ}$, $\beta = 90.00^{\circ}$, $\gamma = 120.00^{\circ}$, V = 37174(4) Å³, Z = 3, T = 225.0 K, d = 0.367 mg/m³, absorption coefficient = 0.575 mm⁻¹, reflections collected = 42268, independent reflections = 4828 [R(int) = 0.1192], data/restraints/parameters = 4828/0/200, final R_1 (wR_2) = 0.0695 (0.1834) with $I > \sigma 2(I)$.

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