

## REPORT

## FRAMEWORK CHEMISTRY

# Bottom-up construction of a superstructure in a porous uranium-organic crystal

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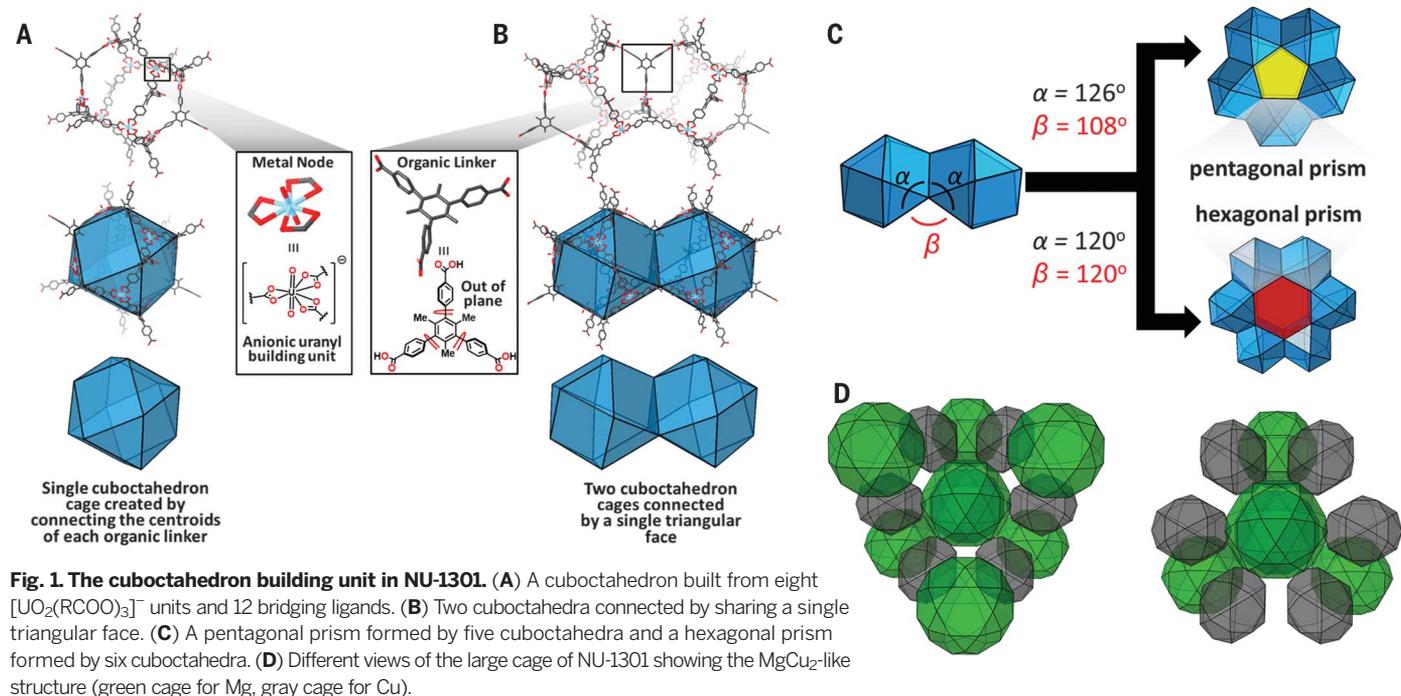
Bottom-up construction of highly intricate structures from simple building blocks remains one of the most difficult challenges in chemistry. We report a structurally complex, mesoporous uranium-based metal-organic framework (MOF) made from simple starting components. The structure comprises 10 uranium nodes and seven tricarboxylate ligands (both crystallographically nonequivalent), resulting in a 173.3-angstrom cubic unit cell enclosing 816 uranium nodes and 816 organic linkers—the largest unit cell found to date for any nonbiological material. The cuboctahedra organize into pentagonal and hexagonal prismatic secondary structures, which then form tetrahedral and diamond quaternary topologies with unprecedented complexity. This packing results in the formation of colossal icosidodecahedral and rectified hexakaidecahedral cavities with internal diameters of 5.0 nanometers and 6.2 nanometers, respectively—ultimately giving rise to the lowest-density MOF reported to date.

The natural and spontaneous assembly of multiple protein chains (each composed of hundreds of amino acids) into giant, precise, complex, and functional secondary, tertiary, and quaternary structures has inspired scientists to study mechanisms of folding and self-

assembly (1–5). Crystal engineering has enabled synthetic chemists to mimic virus-like discrete polyhedral structures with more than 100 components through supramolecular assembly from predesigned units (6, 7). A longstanding challenge, however, is the creation of complex synthetic as-

semblies composed of small and simple building units that combine to form extremely complex superstructures, reminiscent of proteins (8). Here, we describe a hierarchical, mesoporous uranium-based metal-organic framework (MOF), NU-1301, with high structural complexity giving rise to a three-dimensional net, herein named **num** (Northwestern University net) and now added to the Reticular Chemistry Structure Resource (RCSR) database (9). The structure is composed of cuboctahedra that exclusively share triangular faces to form secondary prisms, tertiary cages, and quaternary tetrahedra to yield a channel system with diamond topology. The unit cell of NU-1301 comprises 816 U nodes and 816 organic linkers, therefore giving rise to the largest unit cell reported for any nonbiological structure. Built only from single U atom nodes and a topologically simple tritopic linker (Fig. 1), the net is highly intricate, with 17 topologically distinct nodal vertices and 18 discrete edges. Although composed of U atom nodes, NU-1301 has the lowest framework density (0.124 g/cm<sup>3</sup>; H<sup>+</sup> counterion, see table S3) of any MOF reported to date, owing—at least in part—to the large void space engendered by the colossal cages formed by the packing of secondary prismatic structures. We also show that the pores are accessible and can be used to selectively adsorb organic molecules and biomolecules with different shapes, dimensions, and charges.

To unveil the structure of NU-1301, we focused on creating cuboctahedral structures that pack in space by only sharing triangular faces. Packing regular shapes in space is one of the oldest mathematical problems, and only a few perfect space-filling polyhedra have been proven theoretically (10, 11). A cuboctahedron is a polyhedron with

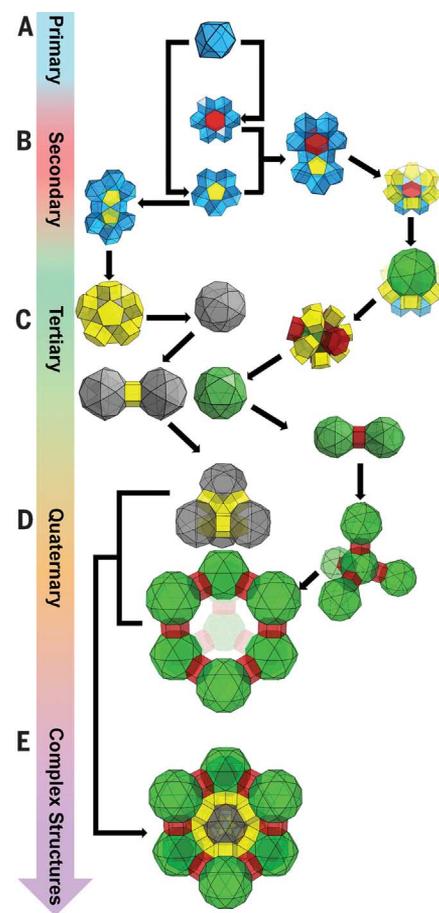


eight triangular faces and six square faces; when packed sharing triangular faces, cuboctahedra yield prismatic structures with empty cages (pores). In our conceptual design, the cuboctahedron vertices are provided by the centers of the tricarboxylate ligands, and the triangular faces correspond to the  $\text{UO}_2$  nodes (centered at each face). The triangular uranium nodes,  $[\text{UO}_2(\text{RCOO})_3]^-$ , are generated in situ and represent the most common geometry among uranium(VI) carboxylate complexes (>570 compounds to date, according to the Cambridge Structural Database) formed by uranyl ( $\text{UO}_2^{2+}$ ) and carboxylate ligands (12). (Fig. 1A). These same triangular nodes,  $[\text{UO}_2(\text{RCOO})_3]^-$ , were used as building blocks to construct NU-1300 by using tetratopic linkers to give a 4,3-connected framework with *tbo* topology (13). We expected that the assembly of  $[\text{UO}_2(\text{RCOO})_3]^-$  nodes and a tritopic linker with three benzoic acid groups orthogonal to the center benzene ring could yield a three-dimensional structure consisting of cuboctahedral cages exclusively sharing triangular faces (Fig. 1B). The regular dihedral angle between triangular and square faces ( $\alpha$ , Fig. 1C) in cuboctahedra is approximately  $125.26^\circ$ ; consequently, the angle left as  $\beta$  when two cuboctahedra pack together by sharing a triangular face is  $109.48^\circ (= 360^\circ - 2\alpha)$ . Symmetry restrictions imposed by this angle of  $109.48^\circ$ , however, forbid the formation of any regular polygons, but with appropriate distortions, the cuboctahedra can pack into secondary structures with either  $C_5$  ( $\alpha = 126^\circ$ ,  $\beta = 108^\circ$ ) or  $C_6$  ( $\alpha = 120^\circ$ ,  $\beta = 120^\circ$ ) rotational symmetry (Fig. 1C). Given that local five-fold rotations are incompatible with periodicity (14), we could predict that the tertiary structure could not be formed solely using pentagonal prisms to achieve long-range translational symmetry (15). Although we could imagine that both secondary pentagonal and hexagonal prisms (Fig. 1C) would form in situ from the simple building blocks used (Fig. 1A), the ratio of pentagonal to hexagonal prisms and the intricate manner in which they would pack were unanticipated (Fig. 1D).

Polyhedral-like yellow crystals of NU-1301 were made by generating the  $[\text{UO}_2(\text{RCOO})_3]^-$  nodes in situ by reacting uranyl nitrate (50.2 mg, 0.1 mmol) and the tritopic linker 5'-(4-carboxyphenyl)-2',4',6'-trimethyl-[1,1':3',1''-terphenyl]-4,4''-dicarboxylic acid (**L**) (48.0 mg, 0.1 mmol) in *N,N*-dimethylformamide (DMF) (5 ml) in the presence of trifluoroacetic acid (80  $\mu\text{l}$ , 1.0 mmol) at  $120^\circ\text{C}$  for 1 day. Single-crystal x-ray diffraction (XRD) was used to clarify the structure of NU-1301, and the initial data collection revealed diffraction from only the U(VI) atoms in the framework. The diffraction pattern observed was indicative of a very large unit cell crystallizing in the cubic *Fd-3m* space group with a unit cell parameter of  $a = 173.26 \text{ \AA}$  and volume of  $5,201,096 \text{ \AA}^3$ . The gigantic unit cell size and

volume of NU-1301 represent the largest unit cell reported to date for a porous crystal—30 times the size of the next largest one (16) and more than 500 times the size of the average unit cell, according to the CoRE (computation-ready, experimental) MOF database (17). For topological density comparison, NU-1301 contains only  $0.00941 \text{ atoms/\AA}^3$ , whereas diamond contains  $0.176 \text{ atoms/\AA}^3$ .

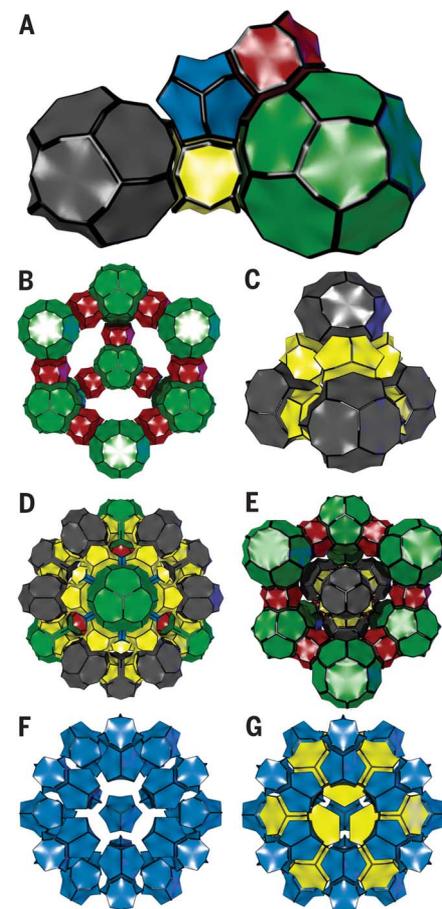
Given the large unit cell and extensive void space of NU-1301, application of conventional small-molecule crystallographic methods was inadequate to achieve a structural solution for the framework. Electron density maps only indicated



**Fig. 2. The arrangement of cuboctahedra into superstructures in NU-1301.**

(A) Cuboctahedron primary structure. (B) Pentagonal and hexagonal prismatic secondary structures. (C) Icosidodecahedron and rectified hexakaidecahedron tertiary structures. (D) Tetrahedron and diamond-topology quaternary structures. (E) Complex structure composed of quaternary structures.

the position of the U atoms, and the organic components were not distinguishable from residual solvent in the pores (fig. S1). What can be discerned, however, is that (i) U atoms are sufficiently far apart to confirm that inorganic MOF nodes are constituted by uranyl ( $\text{UO}_2^{2+}$ ) clusters, and (ii) “neighboring” U atoms form equilateral triangles

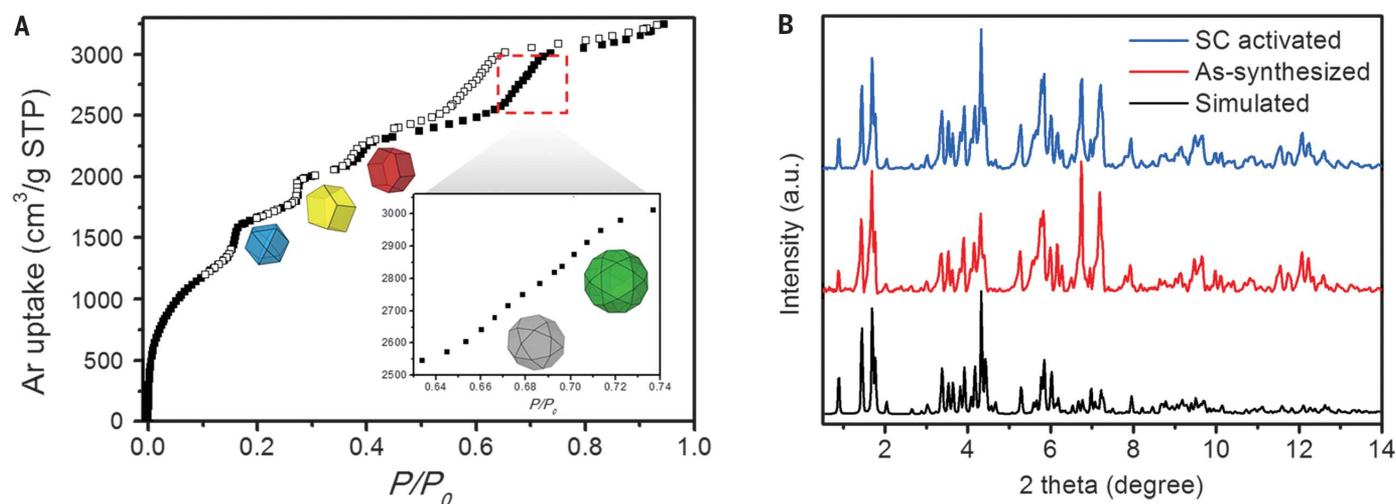


**Fig. 3. The nun of NU-1301 described by tiling using U atoms and ligand vertices.**

(A) The five different cages of NU-1301. (B) The large  $[10^{12}.12^4]$  green tiles, each with four evenly spaced 12-vertex faces, are connected by  $[8^6.12^2]$  red tiles to form a diamondoid superstructure. (C)  $[10^{12}]$  gray tiles are connected by  $[8^5.10^2]$  yellow tiles to form a tetrahedron superstructure. (D) Packing of the gray/yellow tetrahedra with the green/red structure in (A). (E) The gray/yellow tetrahedron at the center of the green/red structure is shown to fill nearly all of the available space. (F) The smallest  $[8^6]$  blue cage is formed by the voids of the superstructure in (E). (G) The blue tiles are arranged around each  $[8^5.10^2]$  yellow tile in a five-fold symmetric pattern.

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**Fig. 4. Porosity and crystallinity measurements of bulk NU-1301.** (A) Ar adsorption/desorption isotherm at 87 K for NU-1301 showing the cages corresponding to the steps in the isotherm. (B) PXRD patterns of the simulated structure (black), as-synthesized NU-1301 (red), and SC-activated NU-1301a (blue).

with sides of 17.5 Å, consistent with U atoms (located at the triangle vertices) bridged by tricarboxylate linkers (L) (whose central ring is located at the triangle centroid). This information can be leveraged to fully elucidate the (3,3)-connected underlying **nun** topological net of NU-1301, which in turn can be used to computationally “synthesize” NU-1301. Indeed, the centroids of the equilateral triangles correspond to the “organic” nodes and were determined using tools available in Materials Studio (18). Once the topological net details were complete, we used the net as a blueprint to construct the porous crystal model of NU-1301 in silico, using a topologically based crystal constructor (ToBaCCo) code (19) to correctly and efficiently place the 816 uranyl nodes and 816 linkers in the unit cell (fig. S2; see detailed simulation method in supplementary materials).

According to the cuboctahedron concept, which considers the organic nodes only as vertices, the structure can be understood as quasi-regular cuboctahedra with diameters of 2.5 nm (Fig. 2A) attached to each of the neighboring cuboctahedra by sharing a triangular face. As predicted, two kinds of secondary assemblies were formed (Fig. 2B): (i) a pentagonal prism (diameter 3.0 nm) assembled by five cuboctahedra, and (ii) a hexagonal prism (diameter 3.6 nm) built from six cuboctahedra (Fig. 2B). The unprecedented complexity of the structure begins with the assembly of secondary prisms into two kinds of tertiary structures (Fig. 2C). One is an icosidodecahedron (diameter 5.0 nm; gray) composed of 20 triangles and 12 pentagons; the other is a rectified hexakaidodecahedron (diameter 6.2 nm; green) composed of 28 triangles, 12 pentagons, and four hexagons. Finally, the tertiary structures are interconnected to form two kinds of quaternary superstructures (Fig. 2D): (i) a tetrahedral structure composed of icosidodecahedra bridged by pentagonal prisms, and (ii) a diamond topology composed of rectified hexakaidodecahedra bridged through hexag-

onal prisms. These two quaternary structures fit together to form a highly complex, ordered, and beautiful structure made from two simple components (Fig. 2E).

The net of NU-1301 (**nun**) can be described in terms of tiling with both U and ligand vertices. In the tiling of **nun**, the ligand vertices are the 3-c vertices and the U atoms are the 2-c vertices. There are five different tiles (Fig. 3A). The largest two tiles have face symbols  $[10^{12}]$  (gray) and  $[10^{12}.12^4]$  (green), which are linked by U vertices making tiles with face symbols  $[8^5.10^2]$  (yellow) and  $[8^6.12^2]$  (red). The green tiles are connected with each other through red tiles in a diamond topology (Fig. 3B), and the gray tiles are linked with neighboring gray tiles by yellow tiles in a tetrahedron topology (Fig. 3C). The green and gray tiles are also bridged via yellow tiles (Fig. 3D). The remaining space is filled by the smallest tile (blue) with face symbol  $[8^6]$ . Note that in the assembled complex structures, the gray and green tiles are spatially arranged in positions similar to those in the simplest and most common binary structure,  $MgCu_2$  (Fig. 3E). Each largest tile (green) is surrounded by 28 blue tiles and 12 yellow tiles (yellow) (Fig. 3, F and G).

Further characterization of NU-1301 using a suite of physical methods confirmed the highly intricate nature of the structure. For example, thermal gravimetric analysis (TGA) revealed that as-synthesized NU-1301 contains a huge amount of solvent with ~65% weight lost from 80° to 120°C, corresponding to both water and DMF (figs. S3 and S4). This large percent weight loss is particularly staggering given that the unit cell of NU-1301 is composed of 816 U atoms. NU-1301 was also found to be thermally stable to temperatures greater than 500°C under both  $N_2$  and air, placing it among the most thermally stable MOFs under these conditions. The porosity of NU-1301 was examined by argon adsorption-desorption experiments performed at 87 K (Fig. 4A) (20). The

Brunauer-Emmett-Teller surface area calculated from the Ar adsorption isotherm following pre-determined consistency criteria (21) was found to be 4750  $m^2 g^{-1}$  (fig. S5A and table S2). The isotherm shape is unique and contains four easily identifiable steps (plus a fifth smaller step) corresponding to the mesoporous cages in the framework. The easily identifiable steps occur at partial pressures of 0.15, 0.27, 0.37, and 0.65, with a fifth step beginning at 0.67. These steps are consistent with the sequential filling of the cuboctahedral cages, pentagonal/hexagonal channels, icosidodecahedral cage, and rectified hexakaidodecahedral cages of NU-1301, respectively (Fig. 4A). The experimental pore volume is 3.9  $cm^3/g$ , meaning that both the surface area and pore volume of NU-1301 are the highest of all actinide-based MOFs described to date (17, 22) and among the highest of all MOFs (23–27). The powder x-ray diffraction (PXRD) patterns of as-synthesized and activated NU-1301 match those predicted for the simulated structure and also confirm the phase purity of the bulk material (Fig. 4B). To observe the low-angle powder diffraction peaks corresponding to the large unit cell, we used a combination of transmission geometry and optimized position of the beam stop. Scanning transmission electron microscopy (STEM) experiments were performed to visualize the cuboctahedral building blocks as well as the high porosity of the sample (fig. S6; see supplementary materials for details).

In addition to the geometric beauty and complexity of self-assembled superstructures (28), porous crystals have captivated the attention of scientists for their potential practical applications. Nanoscale voids inside solid materials that allow guest molecules to be transported, exchanged, and encapsulated (29) create opportunities for storing and sorting on the molecular scale. Owing to the anionic uranyl building units in the structure, NU-1301 can be considered an anionic framework

that should be able to engage in cation exchange with small organic molecules. To confirm the anionic nature of NU-1301, we immersed crystals of the MOF in DMF solutions containing one of two different small organic molecules: methylene blue (cationic) and resorufin sodium salt (anionic). The change in concentration of each compound in solution was monitored by ultraviolet-visible (UV-vis) spectroscopy performed on the supernatant. The cationic dye was adsorbed by NU-1301 while the anionic dye remained in solution (fig. S7), thus confirming the anionic nature of the framework. To test the accessibility of the large pores through the 3.1- and 3.6-nm apertures of the framework, we studied the uptake of two similar-sized proteins, cytochrome c (Cyt-c,  $3.6 \times 2.4 \times 2.2$  nm) and  $\alpha$ -lactalbumin ( $\alpha$ -La,  $4.8 \times 1.8 \times 1.8$  nm) with different isoelectric points (10.3 for Cyt-c, 4.5 for  $\alpha$ -La). Given the isoelectric points, the two proteins should carry different surface charges (positive for Cyt-c, negative for  $\alpha$ -La) in neutral aqueous solution (13). As expected, NU-1301 adsorbed the positively charged Cyt-c but not the negatively charged  $\alpha$ -La (fig. S8) from a neutral aqueous solution. The encapsulation of Cyt-c into the mesoporous structure of NU-1301 was further confirmed by confocal laser scanning microscopy (CLSM) (fig. S9) and scanning electron microscopy with energy-dispersive x-ray spectroscopy (SEM-EDX) (fig. S10).

Inspired by the uptake of both small and large cationic molecules by NU-1301, we used two cationic surfactants, one bearing a hydrophilic tail [8-hydroxy-3,6-dioxaoctyltriethylammonium chloride (HDTEA)] and the other a hydrophobic tail [trimethylnonylammonium bromide (TMNA)], to manipulate the hydrophilicity/lipophilicity of the MOF, leading to complexes HDTEA@NU-1301 and TMNA@NU-1301, respectively (fig. S11). Simple tuning of hydrophilicity/lipophilicity of a MOF by postsynthetic modification is of interest for extraction applications in varying media as well as applications in drug delivery, microfluidics, and sensing (30). The surface wettability of HDTEA@NU-1301 and TMNA@NU-1301 was then characterized using contact-angle measurements (fig. S11, B to E). The contact angles of water and dodecane on HDTEA@NU-1301 were  $9^\circ$  and  $135^\circ$ , respectively, indicating the hydrophilic and lipophobic nature of the modified MOF (fig. S11, B and D). In contrast, TMNA@NU-1301 gave a water con-

tact angle of  $146^\circ$  and a dodecane contact angle of  $11^\circ$ , confirming the hydrophobic and lipophilic nature of the structure (fig. S11, C and E). These results confirm that the hydrophilicity or lipophilicity of the material can be tuned through cation exchange with a suitably charged surfactant containing ethylene glycol or aliphatic groups, respectively. In addition, the porosity of NU-1301 was maintained after cation exchange with HDTEA and TMNA (figs. S12 and S13). To further demonstrate the hydrophilicity/lipophilicity of HDTEA@NU-1301 and TMNA@NU-1301, we added the materials to a mixture containing equal volumes of hexane and water. When HDTEA@NU-1301 or TMNA@NU-1301 was added to the immiscible mixture, the hydrophilic HDTEA@NU-1301 quickly sank to the bottom (polar) phase, while the lipophilic TMNA@NU-1301 collected in the top (non-polar) phase (movies S1 and S2).

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#### SUPPLEMENTARY MATERIALS

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## Bottom-up construction of a superstructure in a porous uranium-organic crystal

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### Intricacy anchored by uranium

Metal-organic frameworks generally have one level of assembly complexity: Organic linkers join inorganic nodes in a repeating lattice. Li *et al.* created a structure composed of cuboctahedra, assembled from uranium cations and organic linkers, that shared triangular faces to form prisms. These structures formed cages, which in turn joined to make tetrahedra that assembled with a diamond-lattice topology. This hierarchical open structure generated a huge unit cell with more than 800 nodes and linkers, containing internal cavities with diameters of 5 and 6 nm.

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