

Crystal Structure, Dissolution, and Deposition of a 5 nm Functionalized Metal–Organic Great Rhombicuboctahedron

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Nanosized metal–organic polyhedra (MOPs) are conveniently achieved by linking transition metal ions with either nitrogen or carboxylate donor organic units.^{1–4} Recently, the permanent porosity of MOPs has been demonstrated by measurement of their gas adsorption isotherms, an important step toward their ultimate utility.^{2c,5} Further progress in this area hinges on our ability to functionalize the surface of such particles and to assemble them on substrates.^{4b,6} Here we report the synthesis and X-ray single-crystal structure of a MOP (termed MOP-18) of 5 nm in diameter. MOP-18 is rendered highly soluble in organic solvents by its surface functionalization with dodecoyl groups. We also present evidence of its successful deposition on a graphite substrate.

The synthesis of MOP-18 was accomplished by linking the paddle-wheel unit, a square, with a suitably functionalized dicarboxylate link, which provides the required 120° angles for producing a great rhombicuboctahedron (Figure 1a,b). The same procedure employed to make the nonfunctionalized MOP-1 was followed in the synthesis of MOP-18:³ *N,N*-dimethylformamide (DMF, 10 mL) solutions of 5-dodecoxybenzene-1,3-dicarboxylic acid (5-OC₁₂H₂₅-*m*BDC; 0.147 g, 0.42 mmol) and Cu(CH₃CO₂)₂·H₂O (0.082 g, 0.41 mmol) were mixed to immediately produce blue microcrystalline MOP-18 (95% yield),⁷ which was recrystallized from a hexane/octanol mixture to give prismatic blue crystals that were used for further characterization and experiments. MOP-18 was found to be highly soluble in chloroform, toluene, tetrahydrofuran, ethyl acetate, *N,N*-dimethylacetamide, and hot DMF, but insoluble in dimethyl sulfoxide (DMSO), acetonitrile, methanol, 1-butanol (BuOH), and isoamyl alcohol.^{7,8}

We were successful in obtaining crystals of sufficient quality for single-crystal X-ray diffraction analysis. MOP-18 has a tetragonal unit cell containing four great rhombicuboctahedra with disordered guest molecules. On the basis of further characterization by elemental microanalysis and thermogravimetric analysis (TGA), the crystal formula was formulated as Cu₂₄(5-OC₁₂H₂₅-*m*BDC)₂₄(DMF)₁₂(C₈H₁₇OH)₄(H₂O)₈·(DMF)₂₀(C₈H₁₇OH)₄(H₂O)₈.^{9,10} Indeed the core of MOP-18 is identical to that of original MOP-1, but now the 12 copper paddle-wheel units are joined by 24 functionalized linkers, 5-OC₁₂H₂₅-*m*BDC.^{3,4} Ideally, the paddle-wheel units are expected to have a total of 24 terminal ligands (12 DMF, 4 C₈H₁₇OH, and 8 H₂O); however, only part of them (4 DMF and 4 C₈H₁₇OH) were identified in the electron density maps. The identity of the remaining ligands was found from the X-ray diffraction data, elemental microanalysis (EA), and thermogravimetric analysis (TGA), which gave a conclusion that the other 8 DMF molecules

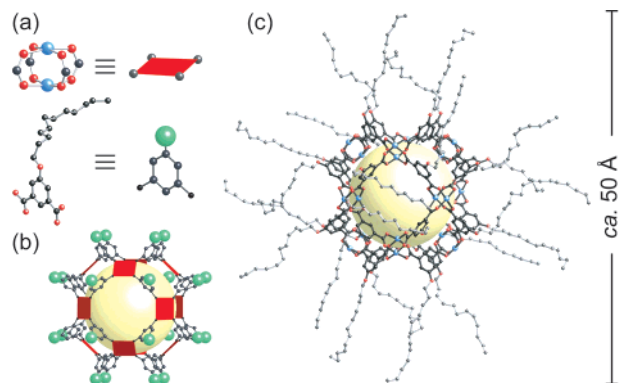


Figure 1. (a) Cu₂(CO₂)₄ paddle-wheel unit and dodecoyl organic link (5-OC₁₂H₂₅-*m*BDC), (b) a great rhombicuboctahedral framework of 13.8 Å diameter void (yellow sphere), and (c) X-ray single-crystal structure of MOP-18. Cu, blue; O, red; C, black; all hydrogen atoms and terminal ligands on the paddle-wheel units are omitted for clarity.

were bound to the copper atoms outside MOP-18 and 8 water molecules were present inside the pore.⁷

In the crystal, the dodecoxy chains showed variable conformations either protruding away from the core or becoming entangled in adjacent similar units on adjacent polyhedra. The non-hydrogen atoms in a rigid part of MOP-18 were refined anisotropically, and most carbon atoms of the dodecoxy chains could not be refined in the same way due to the large thermal motions.⁷ The connectivity of the MOP-18 skeleton was similar to that of MOPs with bent bipyridyl organic links and palladium(II) ions,⁶ but quite different from that with tritopic organic links and platinum(II) ions.^{2a} Although the irregular arrangement of the flexible alkyl chains makes it difficult to define the overall size of the molecule, in its extended state, MOP-18 has a diameter of approximately 50 Å. The center-to-center distance between neighboring polyhedra is 23.935 Å, and the length of the tetrahedral edge is 41.568 and 33.571 Å (Figure 2). Consequently, their overall packing in the crystal is a distorted diamond net. It is interesting to note that the center-to-center distance between neighboring MOPs is almost the same as a diameter of the MOP core (ca. 23 Å).

Considering that dodecoxy chains form lamellar structures along the *ab* plane and that other simple MOPs were packed with *bcc* (MOP-1,^{3,4a} Cu₂₄(5-OH-*m*BDC)₂₄,^{4b} M₂₄(5-*tert*-Bu-*m*BDC)₂₄ (M = Cu and Mo)^{4d}) or *hcp* arrangements (MOP-1,^{4a} Pd₁₂(2,5-bis(4-pyridyl)furan)₂₄,^{9b} MOP-28^{5b}), the diamond packing of MOP-18, being lower in its density than either of *bcc* or *hcp*, may be necessary for the accommodation of the long alkyl chains. Furthermore, as there is more than 30% solvent-accessible volume per unit cell, this space is also regarded as being occupied with guest molecules. The as-synthesized MOP-18 crystals were im-

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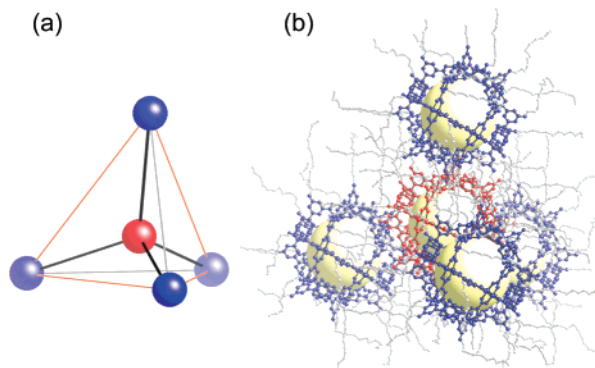


Figure 2. The crystal packing arrangements of MOP-18 are based on the diamond net (a) and are shown here as a large tetrahedron of 5 individual MOP-18 units with the red-colored unit occupying its center (b). The length of orange and gray edge in the tetrahedron is 41.568 and 33.571 Å.

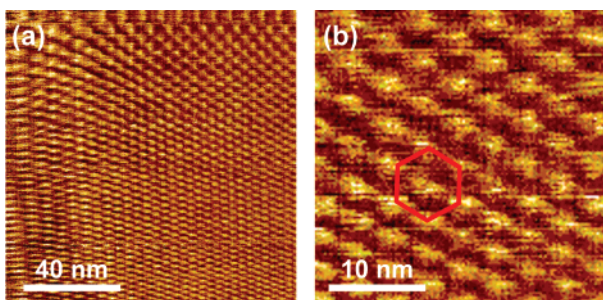


Figure 3. STM image of MOP-18 on graphite substrate (25 °C, ambient pressure): (a) large-scale image showing the long-range ordering, and (b) enlarged image with an overlaying hexagon having a 3.7 nm side.

mersed into DMSO, BuOH, and isoamyl alcohol, and subsequent elemental analysis indicated that most DMF molecules were exchanged—an observation that supports a loose packing of dodecoxy chains in the crystal.¹¹

Because of the solubility of MOP-18 in organic solvents, its assembly could be investigated with scanning tunneling microscopy (STM). The as-synthesized solid of MOP-18 was dissolved in phenyloctane and spread onto a graphite surface. After evaporating most of the phenyloctane, the resultant thin film was examined by STM. The images clearly revealed that MOP-18 formed hexagonal packing with long-range order on a scale of at least 120 nm × 120 nm (Figure 3). Significant drift was observed in all of the STM images, which increased at the end of each image.⁷ This indicates that the STM scanning process is moving the loosely packed MOP-18 polyhedra. This mobility is due to the weak interactions between the self-assembled MOPs. It should be noted that the observation of the self-assembled MOPs on graphite surfaces is unique, although scanning probe microscopy of growing MOP crystals^{4b} and isolated molecules⁶ has been reported.

The distance between two neighboring polyhedra is approximately 3.7 ± 0.6 nm, a value that agrees well with the intermolecular distance of 3.36 nm measured for polyhedra lying in the crystal planes parallel to (001). As the crystal structure has been

established at far lower temperature (−120 °C), it may be natural that the separation in the STM images is slightly wider than those found in the crystal structure arrangement.

Present work in our laboratory is focusing on extending these studies to include assembly of MOP-18 on surfaces in other shapes and dimensionalities.

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Supporting Information Available: Details of synthesis, single-crystal X-ray diffraction data, modeling studies, powder XRD, TGA characterization, and STM observations. This material is available free of charge via Internet at <http://pubs.acs.org>.

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- (7) See Supporting Information for details.
- (8) In contrast to MOP-18, MOP-1 is not soluble in common organic solvents, such as DMF, acetone, tetrahydrofuran, chloroform, and toluene.
- (9) Microanalysis for $\text{Cu}_{24}(5\text{-OC}_{12}\text{H}_{25}\text{-mBDC})_{24}(\text{DMF})_{12}(\text{C}_8\text{H}_{17}\text{OH})_4(\text{H}_2\text{O})_8 \cdot (\text{DMF})_{20}(\text{C}_8\text{H}_{17}\text{OH})_4(\text{H}_2\text{O})_8$: calcd for $\text{C}_{640}\text{H}_{1072}\text{N}_{32}\text{O}_{176}\text{Cu}_{24} = \text{Cu}_{24}(5\text{-OC}_{12}\text{H}_{25}\text{-mBDC})_{24}(\text{DMF})_{32}(\text{C}_8\text{H}_{17}\text{OH})_8(\text{H}_2\text{O})_{16}$. C, 56.70; H, 7.97; N, 3.31%. Found: C, 56.72; H, 7.81; N, 3.42%.
- (10) Single-crystal X-ray diffraction data for MOP-18: $\text{C}_{640}\text{H}_{1072}\text{N}_{32}\text{O}_{176}\text{Cu}_{24}$, $M_r = 13\,556$, tetragonal, space group $I4_1/a$, $a = b = 33.5715(7)$ Å, $c = 68.2468(14)$ Å, $V = 76917(3)$ Å³, $Z = 4$, $d_{\text{calc}} = 1.171$ g cm⁻³, $T = 153(2)$ K, crystal size $0.60 \times 0.24 \times 0.06$ mm, $\lambda = 0.71073$ Å, $2\theta = 46.66^\circ$. Refinement of 1012 parameters and 128 restraints on 27 810 independent reflections out of 274 510 measured reflections ($R_{\text{int}} = 0.0651$) led to $R1 = 0.1178$ ($I > 2\sigma(I)$), 12 244 reflections), $wR2 = 0.3641$ (all data) and $\text{GOF} = 1.066$ with the largest difference peak and hole of 1.212 and -0.670 e⁻/Å³. The diffuse electron density due to the disordered and unidentified moieties was treated with SQUEEZE routine within the PLATON software package. Statistics prior to treatment of data with SQUEEZE were $R1 = 0.1564$ ($I > 2\sigma(I)$), $wR2 = 0.5053$ (all data), and $\text{GOF} = 1.543$.
- (11) **DMF**, $\text{Cu}_{24}(5\text{-OC}_{12}\text{H}_{25}\text{-mBDC})_{24}(\text{DMF})_{25}(\text{H}_2\text{O})_8$: calcd C, 56.21; H, 7.33; N, 2.95%. Found: C, 56.16; H, 7.13; N, 2.95%. **DMSO**, $\text{Cu}_{24}(5\text{-OC}_{12}\text{H}_{25}\text{-mBDC})_{24}(\text{DMF})_1(\text{DMSO})_{27}(\text{H}_2\text{O})_2$: calcd C, 53.28; H, 7.04; N, 0.12%. Found: C, 56.54; H, 7.40; N, 0.09%. **BuOH**, $\text{Cu}_{24}(5\text{-OC}_{12}\text{H}_{25}\text{-mBDC})_{24}(\text{DMF})_2(\text{BuOH})_{22}(\text{H}_2\text{O})_6$: calcd C, 58.56; H, 7.86; N, 0.24%. Found: C, 58.62; H, 7.47; N, 0.24%. **Isoamyl alcohol**, $\text{Cu}_{24}(5\text{-OC}_{12}\text{H}_{25}\text{-mBDC})_{24}(\text{DMF})_1(\text{isoamyl alcohol})_{20}(\text{H}_2\text{O})_8$: calcd C, 59.00; H, 7.94; N, 0.12%. Found C, 59.16; H, 8.11; N, 0.11%.

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