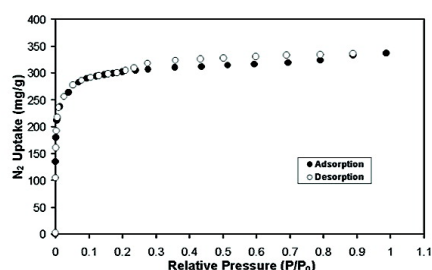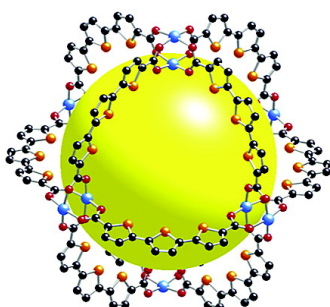Communication

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Porous Metal−Organic Truncated Octahedron Constructed from Paddle-Wheel Squares and Terthiophene Links

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A number of designed 3-D discrete molecular shapes have been assembled by joining metal ions with organic linkers.[1] Success of such syntheses is critically dependent on identifying chemical units with specific geometry that would assemble into a target structure. In this context, for a square unit, there are *only* three truncated 3-D discrete shapes that can be assembled in which all squares and all links are equivalent: octahedron, cuboctahedron, and icosidodecahedron.[2] This report concerns the truncated octahedron for which two construction strategies have been previously implemented wherein either alternative faces, **a**, or all faces, **b**, of the octahedron are built from triangular organic linkers, and vertices from protected squares (Pd^{2+}, Pt^{2+}, Mo_2^{4+}), **a**, or unprotected squares, **b**.[3,4] Here, we report the construction of a truncated octahedron of the third type, **c**, from $Cu_2(CO_2)_4$ building blocks, in which the carboxylate carbon atoms define a *rigid* square, **d**, and 2,2′:5′,2″-terthiophene-5,5″-dicarboxylate (TTDC) having a linking angle very close to *90°* when in the *cis,cis* conformation, **e**.[5] We further show that molecular structures of this kind can be designed to have truly porous architectures and remarkable capacity for adsorption of gases, as evidenced by this compound's Type I gas sorption isotherm.

To prepare truncated octahedron, **c**, we used reactions known to produce the $Cu_2(CO_2)_4$ paddle-wheel unit. These were uncovered in an earlier study involving the use of such units with 1,3-benzenedicarboxylate to produce a 25 Å-sized truncated cuboctahedron, metal−organic polyhedron-1 (MOP-1).[6] Reaction of equimolar amounts of $Cu(NO_3)_2 \cdot 2.5H_2O$ and H_2TTDC at 85 °C for 24 h in a mixture of NMP (2-methyl-1-pyrrolidinone) and DMA (*N,N*-dimethylacetamide) gives green crystals of $[Cu_{12}(TTDC)_{12}(NMP)_6(H_2O)_6] \cdot 13NMP \cdot DMA \cdot H_2O$ (termed MOP-28).[7]

The structure of MOP-28 was determined by single-crystal X-ray diffraction studies.[8] Each MOP-28 molecule is composed of 6 $Cu_2(CO_2)_4$ paddle-wheel building blocks and 12 *cis,cis*-terthiophene linking units (Figure 1a−c). Each paddle-wheel unit (square) has two terminal ligands: one water pointing toward and one NMP pointing away from the center of the truncated octahedral cage (Figure 1a). The asymmetric unit of MOP-28 contains two crystallographically independent TTDC linkers for which the linking angles are 93.8(6) and 86.6(4)°.[9] Both angles deviate slightly from 90° in opposite directions to provide the required 90° angle. It is noteworthy that the *cis,cis* conformation of terthiophene units also results in a unique sulfur-rich interior of the truncated octahedron.

The internal cavity of MOP-28, illustrated by the yellow sphere (Figure 1b), has a diameter of 16.0 Å (without terminal ligands).[10] The overall diameter of MOP-28 is 27.0 Å (without terminal ligands), which is similar to that of the truncated cuboctahedron MOP-1.[6,10] Since MOP-28 only has half the number of $Cu_2(CO_2)_4$ paddle-wheel building blocks as MOP-1, larger openings within

Chart 1. Truncated Octahedral Shapes Built from Square Units
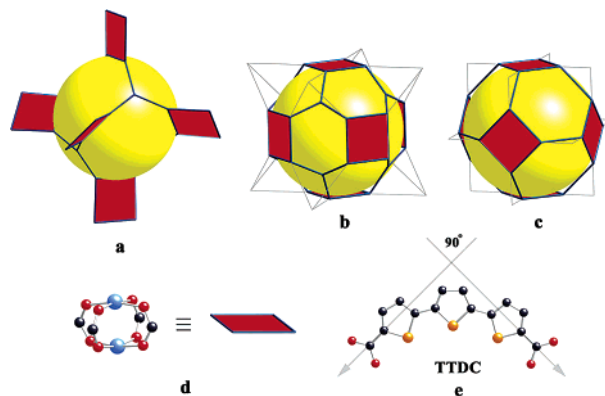
MOP-28 truncated octahedron are observed. The diameter size of the eight triangular apertures in MOP-28 is 9.0 Å, whereas those of the triangular and square apertures in MOP-1 are 3.8 and 7.0 Å, respectively.[10] We note that, due to the highly porous nature of MOP-28 (solvent accessible area accounts for 68.4% of the crystal volume), attempts to model the free guest molecules using the X-ray single-crystal data were unsuccessful.[11] Nevertheless, we undertook a study to examine the mobility of the guests and the likelihood of using the open space for gas sorption.

As-synthesized MOP-28 was solvent-exchanged with THF, and both the as-synthesized and the THF-exchanged samples were analyzed by thermal gravimetry. For the as-synthesized sample, a gradual weight loss of 20.2% (50−180 °C) and a sharp weight loss of 10.9% (180−200 °C) were observed, corresponding to the escape of free guests (13 NMP, 1 DMA, and 1 H_2O; calcd 20.3%) and terminal ligands (6 NMP and 6 H_2O; calcd 10.2%).[9] For the THF-exchanged sample, a sharp weight loss (<50 °C) and, more significantly, a plateau region in the temperature range of 80−200 °C indicate that the molecular architecture of MOP-28 is stable up to 200 °C in the absence of guests. The vast openness of the structure and the consequent facile loss of THF alter the crystallinity of the sample and give slightly shifted powder X-ray diffraction lines with reduced intensities.[9] It is not unreasonable to attribute these differences to distortions in the positions of MOP-28 truncated octahedral units with respect to each other upon guest evacuation, thereby resulting in a random arrangement of those units in the solid. However, on the molecular level, MOP-28 structure and its porosity are maintained as unequivocally proven by gas sorption.

Nitrogen sorption isotherm measurements (Figure 2) were performed on an evacuated sample of the THF-exchanged MOP-28 solid. Indeed, it shows a Type I gas sorption behavior indicative of a microporous material. The reproducibility of the isotherm was confirmed by repeating the adsorption−desorption cycle three times. Significantly, all gas molecules can be removed, as observed from the desorption branch of the plot. A small H4-type hysteresis loop

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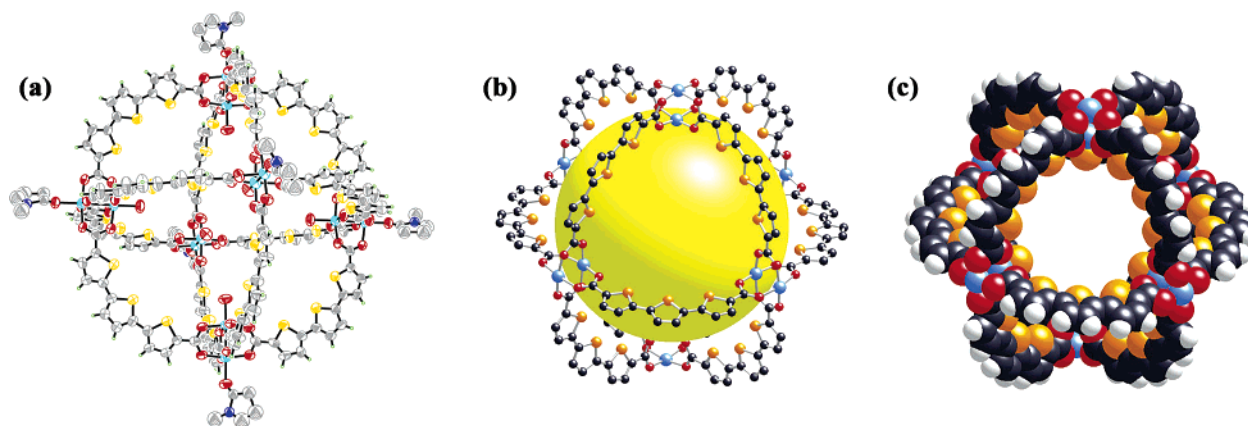[‡] Université Paris 7.

Figure 1. The crystal structure of MOP-28. (a) An ORTEP diagram of a truncated octahedral molecule of MOP-28. Thermal ellipsoids are drawn at 35% probability level (Cu, turquoise; O, red; C, gray; S, yellow; N, blue; H, green). For the purpose of clarity, the disordered coordinating NMP is only shown at one site. (b) A ball-and-stick model of a MOP-28 molecule viewed approximately down the 3-fold axis, showing the internal cavity (yellow sphere) of 16.0 Å in diameter. (c) A space-filling model of a MOP-28 molecule viewed down the 3-fold axis, showing the large triangular apertures of 9.0 Å in diameter. (For b−c: Cu, blue; O, red; C, black; S, orange; H, light gray. All terminal ligands have been omitted.)
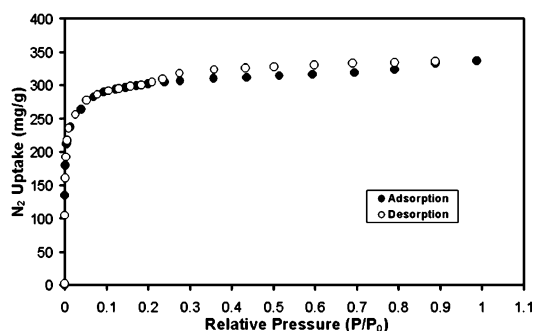

Figure 2. Nitrogen sorption isotherm (77 K) for MOP-28.

is also observed in the isotherm. Given the location of the lower closure point of the loop ($P/P_0 = 0.21$), the hysteresis must be attributed to causes other than capillary condensation of N_2 in large pores.[9] From the adsorption branch of the isotherm, Langmuir surface area of 1100 m^2/g, BET surface area of 914 m^2/g, and pore volume of 0.39 cm^3/g (Dubinin−Radushkevitch model) have been obtained. The amount of N_2 adsorbed in the pores (337 mg/g) corresponds to 57 N_2 molecules per truncated octahedron. It is remarkable that MOP-28, being a solid composed of discrete molecules, exhibits porosity similar to that of extended metal−organic frameworks.[12] To our knowledge, MOP-28 is the most porous *molecular* structure and stands among the first to be characterized by gas sorption.[13]

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Supporting Information Available: Syntheses of TTDC acid and MOP-28, crystallographic data of MOP-28 (including CIF), analysis of the linking angles, PXRD patterns, TGA traces, and details of sorption experiment of MOP-28. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) For recent reviews, see: (a) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 369−378. (b) Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972−983. (c) Cotton, F. A.; Lin, C.; Murillo, C. A. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4810−4813. (d) Fiedler, D.; Leung, D. H.; Bergman, R. G.; Raymond, K. N. *Acc. Chem. Res.* **2005**, *38*, 349−358. (e) MacGillivray, L. R.; Atwood, J. L. *J. Solid State Chem.* **2000**, *152*, 199−210. (f) Moulton, B.; Zaworotko, M. J. *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 117−123.

(2) Eddaoudi, M.; Kim, J.; Vodak, D.; Sudik, A.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4900−4904.

(3) For the constructions based on **a**: (a) Fujita, M.; Oguro, D.; Miyazawa, M.; Oka, H.; Yamaguchi, K.; Ogura, K. *Nature* **1995**, *378*, 469−471. (b) Stang, P. J.; Olenyuk, B.; Muddiman, D. C.; Smith, R. D. *Organometallics* **1997**, *16*, 3094−3096. (c) Cotton, F. A.; Daniels, L. M.; Lin, C.; Murillo, C. A. *J. Chem. Soc., Chem. Commun.* **1999**, 841−842.

(4) For the constructions based on **b**: (a) Chand, D. K.; Biradha, K.; Fujita, M.; Sakamoto, S.; Yamaguchi, K. *J. Chem. Soc., Chem. Commun.* **2002**, 2486−2487. (b) Hong, M.; Zhao, Y.; Su, W.; Cao, R.; Fujita, M.; Zhou, Z.; Chan, A. S. C. *J. Am. Chem. Soc.* **2000**, *122*, 4819−4820.

(5) Two similar octahedral assemblies based on relatively flexible single ion vertices were reported recently: (a) Natarajan, R.; Savitha, G.; Moorthy, J. N. *Cryst. Growth Des.* **2005**, *5*, 69−72. (b) Liu, Y.; Kravtsov, V. C.; Beauchamp, D. A.; Eubank, J. F.; Eddaoudi, M. *J. Am. Chem. Soc.* **2005**, *127*, 7266−7267.

(6) Eddaoudi, M.; Kim, J.; Wachter, J. B.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2001**, *123*, 4368−4369.

(7) The yield of MOP-28 is 24%. Elemental microanalysis for MOP-28: Cu$_{12}$-(TTDC)$_{12}$(NMP)$_6$(H$_2$O)$_6$·(NMP)$_{13}$(DMA)(H$_2$O), calcd C 46.67, H 3.90, N 4.08, S 16.80; found C 46.59, H 3.61, N 4.07, S 16.80. See Supporting Information for details of synthesis.

(8) Single-crystal X-ray diffraction data for MOP-28: Cu$_{12}$(TTDC)$_{12}$(NMP)$_6$-(H$_2$O)$_6$·G, C$_{198}$H$_{72}$N$_6$O$_{60}$S$_{36}$Cu$_{12}$, M_r = 5411.73, rhombohedral (hexagonal obverse setting), space group $R\bar{3}$, $a = b$ = 29.457(5) Å, c = 54.236(20) Å, V = 40756(18) Å^3, Z = 3, ρ_{calc} = 0.661 g/cm^3, T = 258(2) K, crystal size 0.36 × 0.30 × 0.24 mm, λ = 0.71073 Å, 2θ = 41.62°. Refinement of 454 parameters and 6 restraints on 9472 independent reflections out of 51 351 measured reflections (R_{int} = 0.0651) led to $R1$ = 0.0430 ($I > 2\sigma(I)$, 5577 reflections), $wR2$ = 0.0986 (all data) and S = 1.004 with the largest difference peak and hole of 0.188 and −0.225 e$^-$/Å^3. The terminal ligands coordinating to copper atoms were resolved, but the highly disordered guest molecules could not be modeled properly. Instead, the diffuse electron density peaks were treated with SQUEEZE routine within the PLATON software package. Statistics prior to treatment of data with SQUEEZE were $R1$ = 0.1410 ($I > 2\sigma(I)$), $wR2$ = 0.4395 (all data) and S = 1.583.

(9) See Supporting Information for details.

(10) All measurements of distances were performed using Cerius^2 software; van der Waals radii were taken into consideration in all cases (Cu, 1.40; C, 1.70; H, 1.20; O, 1.52; S, 1.80; N, 1.55 Å). The yellow sphere represents the size of the largest molecule that may occupy the pore without contacting the van der Waals internal surface of MOP-28.

(11) Calculation of the total potential solvent area volume was performed using the CALC SOLV routine within the PLATON software package with a probe radius of 1.20 Å.

(12) (a) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469−472. (b) Chae, H.; Siberio-Perez, D.; Kim, J.; Go Y.; Eddaoudi, M.; Matzger, A.; O'Keeffe, M.; Yaghi, O. M. *Nature* **2004**, *427*, 523−527.

(13) (a) Dinolfo, P. H.; Hupp, J. T. *Chem. Mater.* **2001**, *13*, 3113−3125. (b) Chatterjee, B.; Noveron, J. C.; Resendiz, M. J. E.; Liu J.; Yamamoto, T.; Parker, D.; Cinke, M.; Nguyen, C. V.; Arif, A. M.; Stang, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 10645−10656. (c) Sudik, A. C.; Millward, A. R.; Ockwig, N. W.; Côté, A. P.; Kim, J.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 7110−7118. (d) Barrer, R. M.; Shanson, V. H. *J. Chem. Soc., Chem. Commun.* **1976**, 333−334.

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