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A Route to Metal–Organic Frameworks through Framework Templating

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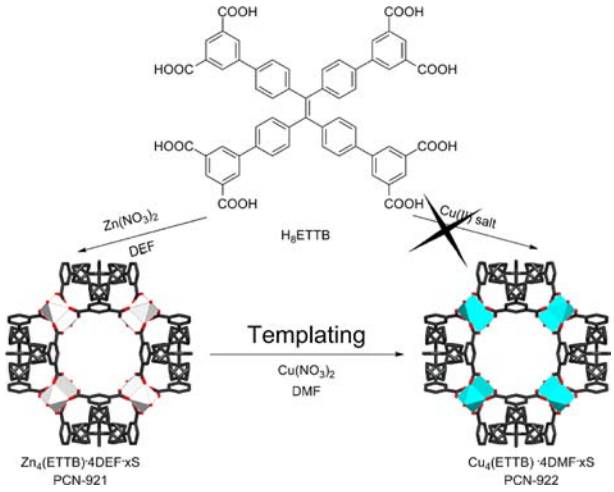
Supporting Information

ABSTRACT: A microporous metal–organic framework (MOF), PCN-922 [Cu_4(ETTB)], containing a dendritic octatopic organic linker and a Cu_2-paddlewheel structural motif, has been synthesized by using a Zn_2-paddlewheel-based MOF as a template to prearrange the linkers for the Cu_2-based MOF target. PCN-922 shows permanent porosity and excellent gas adsorption capacity.

Metal–organic frameworks (MOFs) are a new class of porous materials and have been intensively studied during the last decades.[1] Owing to their high specific surface areas, diverse structures, tunable pore sizes, and functionalities, MOFs have great application potential in gas storage and separation,[2] chemical sensing,[3] catalysis,[4] and drug delivery.[5]

MOFs are composed of organic linkers and metal or metal-containing structural units, often called secondary building units (SBUs). To construct highly porous MOFs for applications, especially for gas storage, using dendritic ligands was demonstrated to be a direct and effective method.[6] Thus, the acid of an octatopic carboxylate ligand, 4′,4‴,4⁗,4⁗′,4⁗′′-ethene-1,1,2,2-tetrayltetrakis{([1,1′-biphenyl]-3,5-dicarboxylate)} (H_8ETTB), has been designed and synthesized (Scheme 1). We are particularly interested in a Cu_2-paddlewheel motif as a SBU because it is superior to a Zn_2-paddlewheel motif in stability.[7] Moreover, after removal of the terminally coordinated solvent molecules, the unsaturated Cu centers have been demonstrated to enhance gas adsorption capacity because of their reported interaction with gas molecules.[8]

Scheme 1. Synthesis of PCN-922 Using PCN-921 as a Template



However, sometimes it is nontrivial to obtain single crystals of Cu-based MOFs, especially with extensive linkers, for structure determination.[6b,9] Direct synthesis of a Cu-based MOF from solvothermal reactions between a copper(II) salt and H_8ETTB only yielded powders under various reaction conditions including different solvents, reaction temperatures, metal salts, and pH values (Table S1 in the Supporting Information, SI). In contrast to the labile Zn–O, the more inert Cu–O coordination bond may hamper defect repair during crystal growth. On the other hand, thanks to the d^{10} configuration of the Zn^{II} ion, the labile Zn–O coordination bond may facilitate ligand exchange and defect repair during crystal growth, assisting the access of single crystals for X-ray diffraction (XRD) and structure determination.[10] Meanwhile, both the Zn_2- and Cu_2-paddlewheel SBUs, which possess very similar coordination environments and geometric parameters, are quite common in MOFs.[9b,11] It has been demonstrated that a Zn_2-paddlewheel in a MOF can be substituted by a Cu_2 paddlewheel.[12] Preparing new metal–organic polyhedra by a ligand-substitution strategy has also been reported.[13] With these considerations in mind, we set out to produce the Cu-based MOF using a Zn-based MOF as a template to prearrange the linkers.

The first step is to synthesize the MOF template containing the Zn_2-paddlewheel structural motif. As expected, the reaction between H_8ETTB and $Zn(NO_3)_2·6H_2O$ in *N*,*N*-diethylformamide (DEF) in the presence of HBF_4 produced a Zn-based MOF, Zn_4(ETTB)·4DEF·*x*S (S represents noncoordinated solvent molecules), designated PCN-921 (PCN stands for porous coordination network). A single-crystal XRD[14] study reveals that PCN-921 is a porous 3D framework composed of ETTB linkers and Zn_2 paddlewheels as desired. Subsequently, the colorless crystals of PCN-921 were immersed in a *N*,*N*-dimethylformamide (DMF) solution of $Cu(NO_3)_2$ at room temperature for 4 days (Scheme 1) to ensure complete metal replacement and permanent porosity (vide infra). The crystals became green in color, and X-ray photoelectron spectroscopy studies on a thoroughly washed and grinded MOF sample clearly indicate that no significant amount of zinc was left in the framework (Figure S11 in the SI). The resultant Cu-based MOF, Cu_4(ETTB)·4DMF·*x*S (PCN-922), was obtained as green crystal. Single-crystal XRD studies have revealed that

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PCN-921 and PCN-922 are isostructural with only a slight difference in cell parameters. In the following, only the structure of PCN-922 will be illustrated in detail.

PCN-922 crystallizes in space group $I4/mmm$ with $a = b = 18.583(16)$ Å and $c = 35.68(3)$ Å. In the structure of PCN-922, the bond angle (107.96°) between the two single bonds at each end sp^2 carbon atom of the central ethylene fragment highly deviates from the ideal value (120°). The six carbon atoms at the center of the linker are coplanar; the dihedral angle between the benzene ring of one isophthalic moiety and the *central* plane is 90°. Each carboxylate group of an ETTB ligand connects one Cu_2-paddlewheel so that each ETTB ligand, in a rectangular prismatic arrangement, connects eight Cu_2 SBUs, leading to a highly porous 3D network. The framework contains two types of microporous cages with different sizes. The small one (14 Å in diameter) is composed of 8 Cu_2 SBUs and 8 ETTB linkers (Figure 1a), while the large one (18 Å) is formed by 8 Cu_2

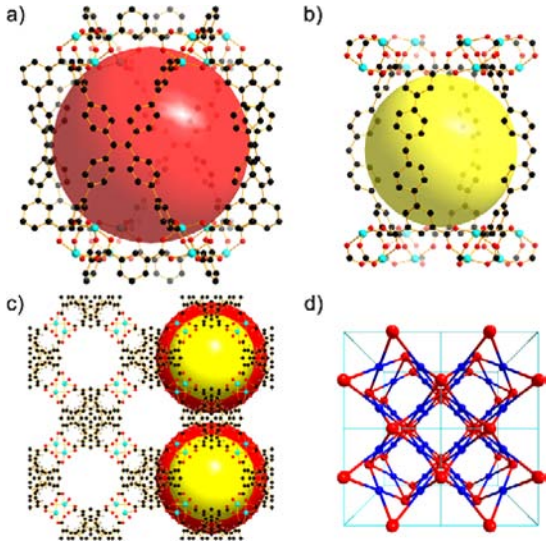

Figure 1. (a) Large cage. (b) Small cage. (c) View of the structure of PCN-222 along the *c* axis. (d) Topological view of PCN-922 (hydrogen atoms and disordered structural components are omitted for clarity).

SBUs and 12 ETTB linkers (Figure 1b). The two types of cages alternate in a 1:1 ratio, forming 1D channels of 9 Å running along the *c* axis of the framework (Figure 1c). If the paddlewheel SBU and ETTB linkers are viewed as 4- and 8-connected nodes, respectively, the framework can be simplified as a 4,8-*c* 2-nodal net with *scu* topology, which is the same as that of other reported MOFs assembled with octatopic linkers and 4-connected SBUs (Figure 1d).[6]

In the frameworks, both Zn^{II} and Cu^{II} ions adopt distorted square-pyramidal geometry, with each metal atom sitting above the square base of the pyramid (Figure 2). The distances between the metals and bases are 0.386 Å for Zn and 0.184 Å for Cu, respectively, indicating that the coordination environment of Zn^{II} undergoes more severe distortion than that of Cu^{II}. Meanwhile, after removal of the apical solvent molecule, the Zn^{II} ion prefers a tetrahedral to a square-planar ligand field.[10b] Therefore, Zn_2-paddlewheel SBUs, upon removal of coordinated solvates, often collapse. On the basis of a simple angular overlap model (AOM), we can estimate the preference energy in terms of e_σ (based on an ideal overlap between the d_{z^2} orbital and a σ-donor ligand) and e_π (based on an ideal overlap

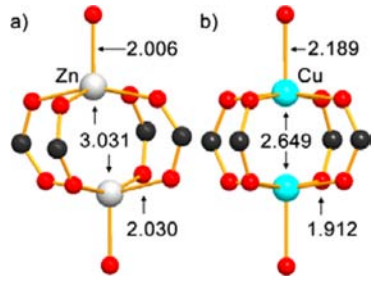

Figure 2. (a) Zn_2- and (b) Cu_2-paddlewheel SBUs in PCN-921 and PCN-922, respectively.

between a d_{xz} or d_{yz} orbital and a p π-donor ligand), respectively.[10b] On the basis of the orbital diagrams constructed from the AOM, the net stabilization energy for Cu^{II} in a square-pyramidal coordination environment is $3e_\sigma$, and that for a square-planar or tetrahedral coordination environment is $3e_\sigma$ or $({}^4/_3e_\sigma + {}^8/_9e_\pi)$, respectively (Figures S13–S15 in the SI). Thus, the Cu_2 paddlewheel is more stable than the Zn_2 one in a square-pyramidal coordination environment, shifting the metathesis equilibrium toward the Cu-based MOF. Furthermore, because e_σ is often much larger than $2e_\pi$, four-coordinated Cu^{II} is more stable in square-planar than in tetrahedral structures, which is why the Cu_2 paddlewheel can survive the activation process.

Calculations using the *CALCSOLV* routine in *PLATON* software were performed to evaluate the porosities of PCN-921 and PCN-922.[15] The results indicate that the solvent-accessible volumes of fully desolvated MOFs (1.8 Å probe radius) are 66.0% for PCN-921 and 66.2% for PCN-922, respectively. To confirm the porosities, both samples were degassed under dynamic vacuum at 85 °C for 10 h each after solvent exchange with methanol and dichloromethane. After activation, the colorless PCN-921 became yellow, possibly a sign of crystal decomposition. Indeed, it showed no N_2 adsorption as expected. Upon activation, the color of PCN-922 changed from green to deep blue, indicating the generation of open metal sites in Cu-based MOFs.[6b,16] PCN-922 showed a type I isotherm for N_2 sorption at 77 K and 1 bar, revealing the microporous nature of the framework, consistent with the observed porosity from the crystal structure (Figure 3a). Langmuir and Brunauer–Emmett–Teller surface areas are 2615 and 2006 $m^2\ g^{-1}$, respectively.[15] The total pore volume is 0.94 $cm^3\ g^{-1}$, approaching the value (0.99 $cm^3\ g^{-1}$) calculated from the crystal structure using the *PLATON* routine.

The microporosity, high density of open metal sites, and robustness of PCN-922 encouraged us to investigate its gas adsorption capacity. It exhibited very high hydrogen and CO_2 uptake capacities under low pressure. Hydrogen uptake of PCN-922 can reach 2.3 wt % at 77 K and 1 bar (Figure 3b). PCN-922 also exhibited high CO_2 uptake (142.97 and 80.78 $cm^3\ g^{-1}$ at 273 and 298 K, respectively; Figure 3c).[2b,d] Meanwhile, the CH_4 sorption isotherms indicate that PCN-922 has adsorption capacities of 29.3 and 20.56 $cm^3\ g^{-1}$ at 273 and 298 K, respectively (Figure 3d).

In summary, a robust and porous MOF, PCN-922, which could not be assembled directly from copper(II) salts and an octatopic ligand ETTB by conventional one-step synthesis, has been successfully synthesized with a framework-templating strategy by using a Zn-based MOF as a template to prearrange the linkers in place. PCN-922 has high gas uptakes and may be used for carbon capture and hydrogen/methane storage.

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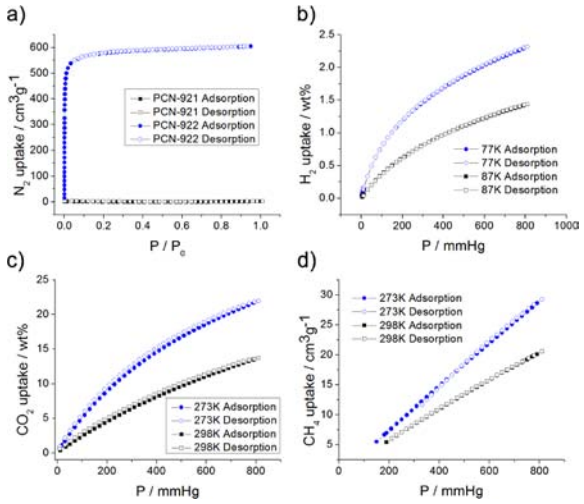

Figure 3. (a) N_2 sorption isotherms for PCN-921 and PCN-922 at 77 K. (b) H_2 sorption isotherms for PCN-922 at 77 and 87 K. (c) CO_2 sorption isotherms for PCN922 at 273 and 298 K. (d) CH_4 sorption isotherms for PCN922 at 273 and 298 K.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data for PCN-921 and PCN-922 in CIF format as well as other experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705. (b) Ferey, G.; Serre, C. *Chem. Soc. Rev.* **2009**, *38*, 1380. (c) Long, J. R.; Yaghi, O. M. *Chem. Soc. Rev.* **2009**, *38*, 1213. (d) Zhou, H.-C.; Long, J. R.; Yaghi, O. M. *Chem. Rev.* **2012**, 673.

(2) (a) Ma, S.; Zhou, H.-C. *Chem. Commun.* **2010**, *46*, 44. (b) Suh, M. P.; Park, H. J.; Prasad, T. K.; Lim, D.-W. *Chem. Rev.* **2012**, *112*, 782. (c) Li, J.-R.; Sculley, J.; Zhou, H.-C. *Chem. Rev.* **2012**, *112*, 869. (d) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. *Chem. Rev.* **2012**, *112*, 724.

(3) (a) Chen, B.; Xiang, S.; Qian, G. *Acc. Chem. Res.* **2010**, *43*, 1115. (b) Jiang, H.-L.; Tatsu, Y.; Lu, Z.-H.; Xu, Q. *J. Am. Chem. Soc.* **2010**, *132*, 5586. (c) Kreno, L. E.; Leong, K.; Farha, O. K.; Allendorf, M.; Van Duyne, R. P.; Hupp, J. T. *Chem. Rev.* **2012**, *112*, 1105. (d) Takashima, Y.; Martínez, V. M.; Furukawa, S.; Kondo, M.; Shimomura, S.; Uehara, H.; Nakahama, M.; Sugimoto, K.; Kitagawa, S. *Nat. Commun.* **2011**, *2*, 168.

(4) (a) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982. (b) Farrusseng, D.; Aguado, S.; Pinel, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 7502. (c) Ma, L.; Abney, C.; Lin, W. *Chem. Soc. Rev.* **2009**, *38*, 1248. (d) Corma, A.; García, H.; Llabrés i Xamena, F. X. *Chem. Rev.* **2010**, *110*, 4606. (e) Jiang, H.-L.; Xu, Q. *Chem. Commun.* **2011**, *47*, 3351.

(5) (a) An, J.; Geib, S. J.; Rosi, N. L. *J. Am. Chem. Soc.* **2009**, *131*, 8376. (b) Della Rocca, J.; Liu, D.; Lin, W. *Acc. Chem. Res.* **2011**, *44*, 957. (c) Horcajada, P.; Gref, R.; Baati, T.; Allan, P. K.; Maurin, G.; Couvreur, P.; Férey, G.; Morris, R. E.; Serre, C. *Chem. Rev.* **2012**, *112*, 1232.

(6) (a) Zhuang, W.; Yuan, D.; Liu, D.; Zhong, C.; Li, J.-R.; Zhou, H.-C. *Chem. Mater.* **2011**, *24*, 18. (b) Lu, W.; Yuan, D.; Makal, T. A.; Li, J.-R.; Zhou, H.-C. *Angew. Chem., Int. Ed.* **2012**, *51*, 1580. (c) Tan, C.; Yang, S.; Champness, N. R.; Lin, X.; Blake, A. J.; Lewis, W.; Schroder, M. *Chem. Commun.* **2011**, *47*, 4487. (d) Blatov, V. A. *IUCr CompComm Newsletter* **2006**, *7*, 4.

(7) Cychosz, K. A.; Matzger, A. J. *Langmuir* **2010**, *26*, 17198.

(8) (a) Collins, D. J.; Zhou, H.-C. *J. Mater. Chem.* **2007**, *17*, 3154. (b) Dincă, M.; Long, J. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 6766. (c) Rowsell, J. L. C.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4670. (d) Vitillo, J. G.; Regli, L.; Chavan, S.; Ricchiardi, G.; Spoto, G.; Dietzel, P. D. C.; Bordiga, S.; Zecchina, A. *J. Am. Chem. Soc.* **2008**, *130*, 8386. (e) Gedrich, K.; Senkovska, I.; Klein, N.; Stoeck, U.; Henschel, A.; Lohe, M. R.; Baburin, I. A.; Mueller, U.; Kaskel, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 8489.

(9) (a) Yuan, D.; Zhao, D.; Sun, D.; Zhou, H.-C. *Angew. Chem., Int. Ed.* **2010**, *49*, 5357. (b) Zhao, D.; Yuan, D.; Sun, D.; Zhou, H.-C. *J. Am. Chem. Soc.* **2009**, *131*, 9186.

(10) (a) Haque, E.; Jeong, J. H.; Jhung, S. H. *CrystEngComm* **2010**, *12*, 2749. (b) Miessler, G. L. T.; Donald, A. *Inorganic Chemistry*; Pearson Education, Inc.: Upper Saddle River, NJ, 2004.

(11) (a) Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148. (b) Feldblyum, J. I.; Liu, M.; Gidley, D. W.; Matzger, A. J. *J. Am. Chem. Soc.* **2011**, *133*, 18257.

(12) (a) Dincă, M.; Long, J. R. *J. Am. Chem. Soc.* **2007**, *129*, 11172. (b) Mi, L.; Hou, H.; Song, Z.; Han, H.; Xu, H.; Fan, Y.; Ng, S.-W. *Cryst. Growth Des.* **2007**, *7*, 2553. (c) Mi, L.; Hou, H.; Song, Z.; Han, H.; Fan, Y. *Chem.—Eur. J.* **2008**, *14*, 1814. (d) Das, S.; Kim, H.; Kim, K. *J. Am. Chem. Soc.* **2009**, *131*, 3814. (e) Tian, J.; Saraf, L. V.; Schwenzer, B.; Taylor, S. M.; Brechin, E. K.; Liu, J.; Dalgarno, S. J.; Thallapally, P. K. *J. Am. Chem. Soc.* **2012**, *134*, 9581. (f) Yao, Q.; Sun, J.; Li, K.; Su, J.; Peskov, M. V.; Zou, X. *Dalton Trans.* **2012**, *41*, 3953. (g) Wang, X.; Li, P.-Z.; Liu, L.; Zhang, Q.; Borah, P.; Wong, J. D.; Chan, X. X.; Rakesh, G.; Li, Y.; Zhao, Y. *Chem. Commun.* **2012**, *48*, 10286. (h) Song, X.; Kim, T. K.; Kim, H.; Kim, D.; Jeong, S.; Moon, H. R.; Lah, M. S. *Chem. Mater.* **2012**, *24*, 3065.

(13) Li, J.-R.; Zhou, H.-C. *Nat. Chem.* **2010**, *2*, 893.

(14) Sheldrick, G. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

(15) (a) Langmuir, I. *J. Am. Chem. Soc.* **1916**, *38*, 2221. (b) Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309.

(16) Britt, D.; Tranchemontagne, D.; Yaghi, O. M. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 11623.