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A Large-Surface-Area Boracite-Network-Topology Porous MOF Constructed from a Conjugated Ligand Exhibiting a High Hydrogen Uptake Capacity

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A new porous metal−organic framework, PCN-20 with a twisted boracite net topology, was constructed based on a highly conjugated planar tricarboxylate ligand; PCN-20 possesses a large Langmuir surface area of over 4200 m^2/g as well as demonstrates a high hydrogen uptake capacity of 6.2 wt % at 77 K and 50 bar.

In light of the high surface areas as well as uniform yet tunable pore sizes together with well-defined adsorbate interaction sites, porous metal−organic frameworks (MOFs)[1] have been actively studied as one of the most promising candidates to approach the U.S. Department of Energy (DOE) targets[2] for on-board hydrogen storage application.[3] In particular, the construction of isoreticular MOFs under the concept of “reticular synthesis”[4] allows systematic assessment of ligand functionalization on hydrogen uptake, and this has been well illustrated in α-Po-[5] and NbO[6]-type porous MOFs.

Recently, we have been particularly interested in the construction of porous MOFs with boracite network topology based on trigonal-planar carboxylate ligands and copper paddlewheel secondary building units (SBUs).[7] Our

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(1) (a) Kitagawa, S.; Kitaura, R.; Noro, S.-i. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334. (b) Férey, G. *Chem. Soc. Rev.* **2008**, *37*, 191. (c) Suh, M. P.; Cheon, Y. E.; Lee, E. Y. *Coord. Chem. Rev.* **2008**, *252*, 1007. (d) Ma, S.; Wang, X.-S.; Collier, C. D.; Manis, E. S.; Zhou, H.-C. *Inorg. Chem.* **2007**, *46*, 8499. (e) Ma, S.; Wang, X.-S.; Yuan, D.; Zhou, H.-C. *Angew. Chem., Int. Ed.* **2008**, *47*, 4130. (f) Ma, S.; Sun, D.; Forster, P. M.; Yuan, D.; Zhuang, W.; Chen, Y.-S.; Parise, J. B.; Zhou, H.-C. *Inorg. Chem.* **2009**, *48*, 4616. (g) Ma, S.; Simmons, J. M.; Yuan, D.; Li, J.-R.; Weng, W.; Liu, D.-J.; Zhou, H.-C. *Chem. Commun.* **2009**, 4049. (h) Li, J.-R.; Kuppler, R. J.; Zhou, H.-C. *Chem. Soc. Rev.* **2009**, *38*, 1477.

(2) U.S Department of Energy. Targets for on-board hydrogen storage systems: The current R&D focus is on 2015 targets with the potential to meet ultimate targets.

(3) (a) Rowsell, J. L. C.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4670. (b) Ma, S.; Zhou, H.-C. *J. Am. Chem. Soc.* **2006**, *128*, 11734. (c) Wong-Foy, A. G.; Matzger, A. J.; Yaghi, O. M. *J. Am. Chem. Soc.* **2006**, *128*, 3494. (d) Rowsell, J. L. C.; Yaghi, O. M. *J. Am. Chem. Soc.* **2006**, *128*, 1304. (e) Dinc, M.; Dailly, A.; Liu, Y.; Brown, C. M.; Neumann, D. A.; Long, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 16876. (f) Latroche, M.; Surblé, S.; Serre, C.; Mellot-Draznieks, C.; Llewellyn, P. L.; Lee, J.-H.; Chang, J.-S.; Jhung, S. H.; Férey, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 8227. (g) Dinc, M.; Han, W. S.; Liu, Y.; Dailly, A.; Brown, C. M.; Long, J. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 1419. (h) Kaye, S. S.; Dailly, A.; Yaghi, O. M.; Long, J. R. *J. Am. Chem. Soc.* **2007**, *129*, 14176. (I) Collins, D. J.; Zhou, H.-C. *J. Mater. Chem.* **2007**, *17*, 3154. (j) Dinc, M.; Long, J. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 6766. (k) Thomas, K. M. *Dalton Trans.* **2009**, 1487. (l) Zhao, D.; Yuan, D.; Zhou, H.-C. *Energy Environ. Sci.* **2008**, *1*, 222. (m) Murray, L. J.; Dinc, M.; Long, J. R. *Chem. Soc. Rev.* **2009**, *38*, 1294. (n) Ma, S.; Yuan, D.; Chang, J.-S.; Zhou, H.-C. *Inorg. Chem.* **2009**, *48*, 5398.

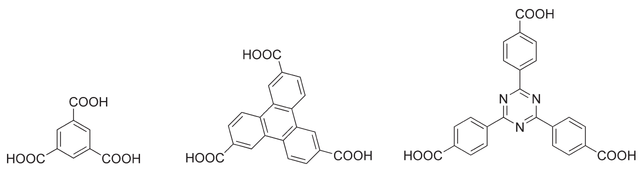
(4) (a) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O’Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319. (b) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705.

(5) (a) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O’Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469. (b) Choi, E.-Y.; Park, K.; Yang, C.-M.; Kim, H.; Son, J.-H.; Lee, S. W.; Lee, Y. H.; Min, D.; Kwon, Y.-U. *Chem.—Eur. J.* **2004**, *10*, 5535. (c) Dybtsev, D. N.; Chun, H.; Kim, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 5033. (d) Chun, H.; Dybtsev, D. N.; Kim, H.; Kim, K. *Chem.—Eur. J.* **2005**, *11*, 3521. (e) Xue, M.; Liu, Y.; Schaffino, R. M.; Xiang, S.; Zhao, X.; Zhu, G.-S.; Qiu, S.-L.; Chen, B. *Inorg. Chem.* **2009**, *48*, 4649.

(6) (a) Chen, B.; Ockwig, N. W.; Millward, A. R.; Contreras, D. S.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4745. (b) Lin, X.; Jia, J.; Zhao, X.; Thomas, K. M.; Blake, A. J.; Walker, G. S.; Champness, N. R.; Hubberstey, P.; Schröder, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 7358. (c) Wang, X.-S.; Ma, S.; Forster, P. M.; Yuan, D.; Eckert, J.; Lopez, J. J.; Murphy, B. J.; Parise, J. B.; Zhou, H.-C. *Angew. Chem., Int. Ed.* **2008**, *47*, 7263. (d) Ma, S.; Sun, D.; Simmons, J. M.; Collier, C. D.; Yuan, D.; Zhou, H.-C. *J. Am. Chem. Soc.* **2008**, *130*, 1012. (e) Wang, X.-S.; Ma, S.; Rauch, K.; Simmons, J. M.; Yuan, D.; Wang, X.; Yildirim, T.; Cole, W. C.; Lόpez, J. J.; Meijere, A.; Zhou, H.-C. *Chem. Mater.* **2008**, *20*, 3145. (f) Lin, X.; Telepeni, I.; Blake, A. J.; Dailly, A.; Brown, C. M.; Simmons, J. M.; Zoppi, M.; Walker, G. S.; Thomas, K. M.; Mays, T. J.; Hubberstey, P.; Champness, N. R.; Schröder, M. *J. Am. Chem. Soc.* **2009**, *131*, 2159. (g) Ma, S.; Sun, D.; Simmons, J. M.; Yuan, D.; Zhou, H.-C. *Inorg. Chem.* **2009**, *48*, 5263.

(7) (a) Sun, D.; Ma, S.; Ke, Y.; Collins, D. J.; Zhou, H.-C. *J. Am. Chem. Soc.* **2006**, *128*, 3896. (b) Wang, X.-S.; Ma, S.; Sun, D.; Parkin, S.; Zhou, H.-C. *J. Am. Chem. Soc.* **2006**, *128*, 16474. (c) Ma, S.; Sun, D.; Ambrogio, M.; Fillinger, J. A.; Parkin, S.; Zhou, H.-C. *J. Am. Chem. Soc.* **2007**, *129*, 1858. (d) Ma, S.; Eckert, J.; Forster, P. M.; Yoon, J.; Hwang, Y. K.; Chang, J.-S.; Collier, C. D.; Parise, J. B.; Zhou, H.-C. *J. Am. Chem. Soc.* **2008**, *130*, 15896.

Scheme 1. Planar Tricarboxylate Ligands: (a) H_3BTC; (b) H_3TTCA; (c) H_3TATB



utilization of the planar H_3TATB (TATB = 4,4′,4″-*s*-triazine-2,4,6-triyltribenzoate) ligand (Scheme 1c) to assembly with in situ generated copper paddlewheel SBU led to the formation of a porous MOF, PCN-6′ (PCN represents porous coordination network),[7a] which is isostructural with Cu-BTC (also known as HKUST-1) of twisted boracite topology.[8] Our studies revealed that the extension from BTC to TATB led to the enlargement of square channel size from 8.0 Å in Cu-BTC to 15.16 Å in PCN-6′ together with a higher Langmuir surface area of 2700 m^2/g for PCN-6′ compared to 1800 m^2/g for Cu-BTC. Despite the significant increase of the surface area, ligand extension did not result in sufficient enhancement of the hydrogen uptake in PCN-6′. This can be ascribed to many unused voids resulting from the large pore sizes of PCN-6′, as evidenced by our inelastic neutron scattering studies.[7d] Herein, we designed a new trigonal-planar ligand, triphenylene-2,6,10-tricarboxylic acid (H_3TTCA; Scheme 1b).[9] We expect that the smaller size of TTCA compared to TATB will shrink the pore size, and the highly conjugated fused triphenylene ring can provide more hydrogen adsorption sites, as predicted from recent theoretical calculations,[10] thus leading to a high hydrogen uptake capacity. Under solvothermal conditions, the reaction of $Cu(NO_3)_2 \cdot 2.5H_2O$ and H_3TTCA in dimethylformamide at 65 °C afforded dark-blue MOF crystals denoted as PCN-20.

Single-crystal X-ray studies[11] conducted using synchrotron microcrystal diffraction at the Advanced Photon Source, Argonne National Laboratory, revealed that PCN-20 crystallizes in the cubic space group *F*432. This is different from Cu-BTC and PCN-6′, both of which crystallize in the cubic space group $Fm\bar{3}m$,[7,8] and can be attributed to the lack of a mirror plane to the carboxylate groups in the TTCA ligand. PCN-20 also adopts a dicopper paddlewheel motif as its SBU, and the copper atoms become coordinatively unsaturated upon axial aqua ligand removal. In PCN-20, there are three types of cages. The first type is an octahedral cage, which is formed by six copper paddlewheel SBUs occupying the vertices and four ligands occupying four faces of the octahedral cages, and has triangle windows of 11.89 Å (Cu—Cu distance along the edge; Figure 1a). The second type is the cuboctahedral cage, where the paddlewheel SBUs occupy the 12 vertices of a cuboctahedron (Figure 1b), while 24 TTCA ligands using two carboxylate groups span all 24 edges. The square faces are 11.89 × 11.89 Å, and the triangle faces are also 11.89 Å in dimension. The third one is also a cuboctahedral cage, but it is different from the second one. In the third cage, the paddlewheel SBUs occupy 12 vertices, but unlike the second cage, only eight ligands occupy eight faces of a cuboctahedron (Figure 1c). Each square face is connected to another square face of a neighboring cuboctahedron, and each triangle face is connected to another triangle face of a neighboring octahedron. Every cuboctahedron connects six others in three orthogonal directions to form a three-dimensional framework with a twisted boracite net topology (Figure S2 in the Supporting Information). Viewed from the [0 0 1] direction, the size of the square channel is 11.89 Å

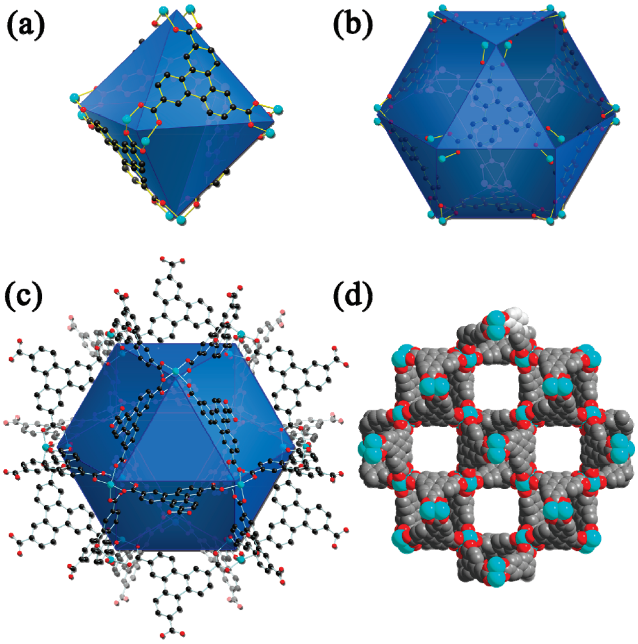


Figure 1. (a) Octahedral cage in PCN-20. (b) Cuboctahedral cage with alignment of the unsaturated metal centers (UMCs) in PCN-20. (c) Cuboctahedral cage with open metal sites aligned orthogonally in PCN-20. (d) Square channels viewed from the [0 0 1] direction (hydrogen atoms were omitted for clarity). Color scheme: Cu, aqua; C, black; N, blue; O, red.

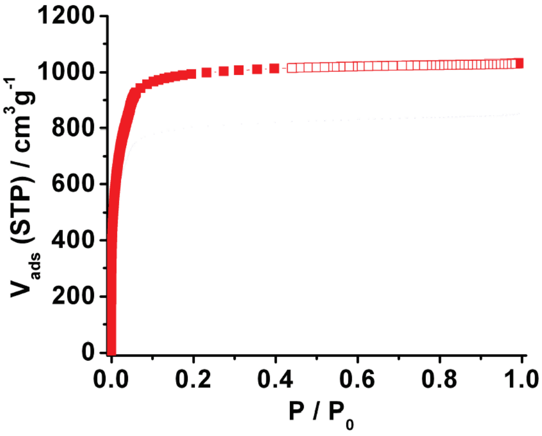


Figure 2. N_2 sorption isotherms for PCN-20 (filled and open symbols represent adsorption and desorption data, respectively).

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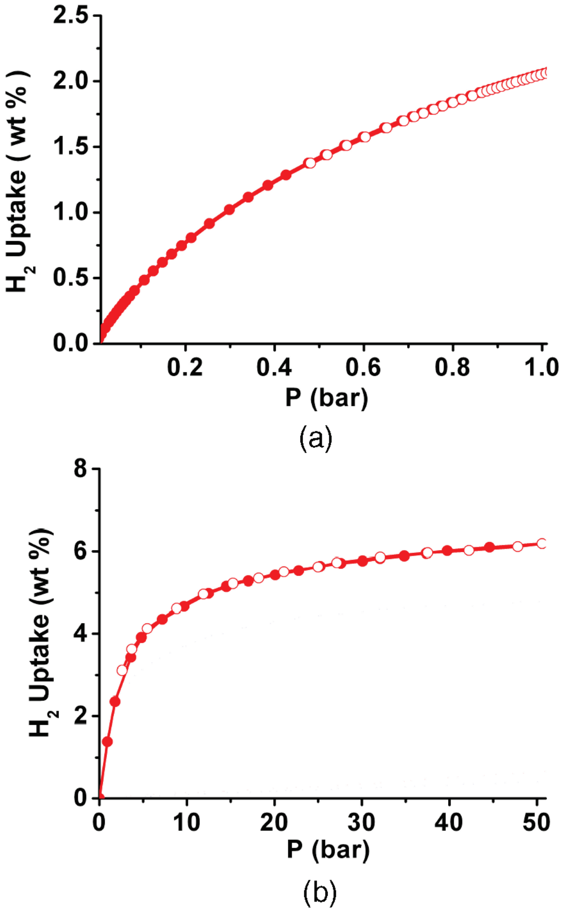
(8) Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148.

(9) (a) Bock, H.; Rajaoarivelo, M.; Clavaguera, S.; Grelet, É. *Eur. J. Org. Chem.* **2006**, 2889. (b) Choi, J. Y.; Kim, J.; Furukawa, H.; Chae, H. K *Chem. Lett.* **2006**, *35*, 1054.

(10) (a) Sagara, T.; Klassen, J.; Ortony, J.; Ganz, E. *J. Chem. Phys.* **2005**, *123*, 014701. (b) Han, S. S.; Deng, W.-Q.; Goddard, W. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 6289.

(11) Crystal data for PCN-20: $C_{84}H_{48}Cu_6O_{30}$, M_r = 1918.46; blue block, T = 20(2) K, cubic, space group *F*432, a = 37.230(9) Å, V = 51604(22) $Å^3$, Z = 16, d_{calcd} = 0.466 g/cm^3; R1 [$I > 2\sigma(I)$] = 0.0666, wR2 (all data) = 0.1641, GOF = 1.083. CCDC-685824 (PCN-20) contains the supplementary crystallographic data for this Communication. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, U.K.; fax (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).



(a)

(b)

Figure 3. H_2 sorption isotherms of PCN-20 at 77 K: (a) low pressure; (b) high pressure (filled and open symbols represent adsorption and desorption data, respectively).

along the edge (Cu−Cu distance; Figure 1d), which is significantly smaller than that of PCN-6′ of 15.16 Å.

To investigate its sorption properties, a freshly prepared PCN-20 sample was fully activated according to the procedures reported in our previous work.[7] The N_2 sorption isotherms, as shown in Figure 2, reveal that PCN-20 exhibits typical type I sorption behavior without hysteresis, a characteristic of microporous materials. Derived from the N_2 adsorption data, the Langmuir surface area of PCN-20 is 4237 m^2/g, corresponding to a Brunauer−Emmett−Teller surface area of 3525 m^2/g and a pore volume of 1.59 mL/g. The Langmuir surface area of PCN-20 is much higher than those of Cu-BTC and PCN-6′, confirming the theoretical prediction that fused aromatic rings favor high surface area in porous MOFs.[10]

To evaluate the hydrogen storage performance of PCN-20, hydrogen sorption isotherms were measured at 77 K under both low and high pressures. As shown in Figure 3a, PCN-20 can adsorb 2.1 wt % (excess) hydrogen at 1 bar and 77 K. With the pressure increased to 50 bar (Figure 3b), its excess gravimetric hydrogen uptake capacity can reach as high as 6.2 wt %, which is among the highest for reported porous MOFs.[3] This value is much higher than those of Cu-BTC (3.4 wt %) and PCN-6′ (4.0 wt %)[7d] under the same conditions and can be ascribed to its much larger surface area, resulting from the highly conjugated fused triphenylene ring.

In summary, a porous MOF, PCN-20 with a twisted boracite topology, was constructed based on a designed planar TTCA ligand. The highly conjugated fused triphenylene ring of the TTCA ligand renders PCN-20 with an exceptionally large surface area of 4237 m^2/g as well as affords its high hydrogen uptake capacity of 6.2 wt % with full reversibility at 77 K and 50 bar, promising it as a potential candidate for hydrogen storage application.

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Supporting Information Available: Experimental procedures for the synthesis of PCN-20, PXRD patterns of PCN-20, image of a twisted boracite topology, TGA plot of PCN-20, and an X-ray crystallographic file of PCN-20 in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.