Inorganic Chemistry

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Novel Microporous Metal–Organic Framework Exhibiting High Acetylene and Methane Storage Capacities

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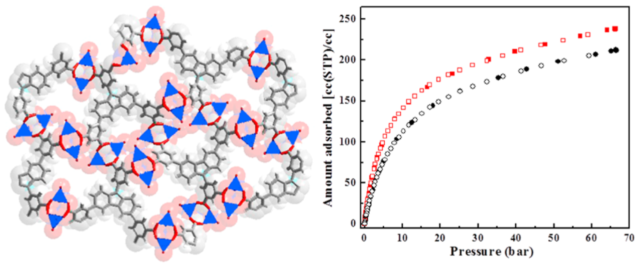
Supporting Information

ABSTRACT: A new organic hexacarboxylic acid, 5,5′,5″-(9*H*-carbazole-3,6,9-triyl)triisophthalic acid (H_6CTIA), was developed to construct its first microporous metal–organic framework (MOF), $Cu_6(CTIA)_2$ (ZJU-70). With open metal sites and suitable pore sizes, this MOF exhibits high acetylene and methane storage capacities at room temperature.



INTRODUCTION

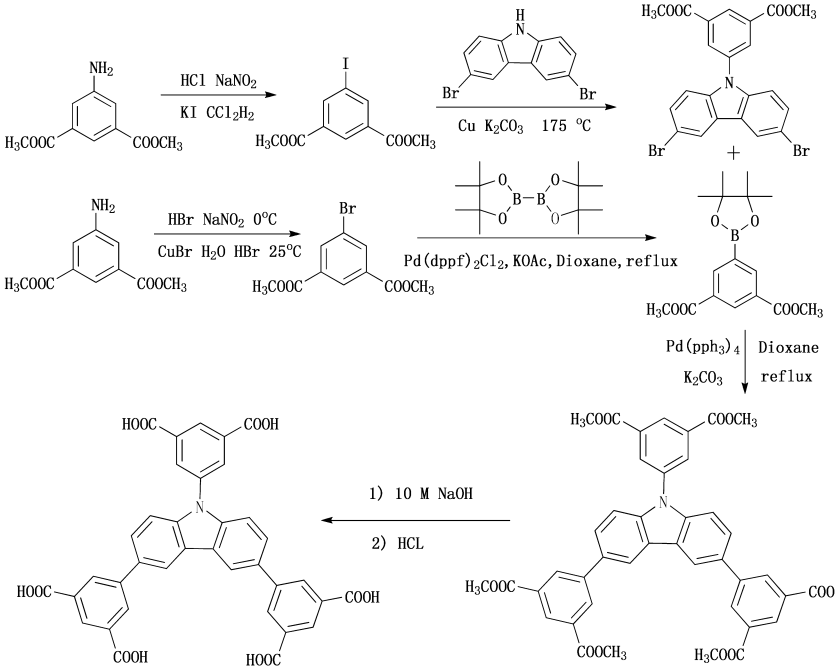
Methane and acetylene are promising fuel alternatives for future vehicle and residential usage. Realization of suitable materials for large amounts of methane and acetylene storage at room temperature can significantly promote the eventual wide applications of these two gas resources for our daily life.[1,2] Microporous metal–organic frameworks (MOFs) are very attractive for such an important application because of their tunable pore spaces and immobilized functional sites for the recognition of molecules.[3−16]

In the pursuit of MOFs for large amounts of gas storage, deliberate synthesis and choice of organic linkers are very important, which have been clearly demonstrated by a series of MOFs containing *meta*-benzenedicarboxylate units.[14−16] These organic units not only enforce the generation of open metal sites on the paddle-wheel $Cu_2(COO)_4$ copper sites, but also systematically tune the pores to efficiently make use of the pore spaces. Self-assembly of the organic linker H_6BHB (H_6BHB = 3,3′,3″,5,5′,5″-benzene-1,3,5-triylhexabenzoic acid) and the paddle-wheel $Cu_2(COO)_4$ SBU generates UTSA-20, which has a high density of open copper sites and high methane storage capacities.[15b] Hupp's group uses a series of hexacarboxylic acid linkers to construct isoreticular MOFs NU-111,[15c] NU-125,[15d] NU-138,[15e] NU-139,[15e] and NU-140[15e] with varying pore sizes. Among them, NU-125, with suitable pore apertures, exhibits a high volumetric working capacity of 183 cc(STP)/cc. During our extensive studies on diverse organic ligands for their assembly of porous multifunctional MOFs, a new hexacarboxylic acid, 5,5′,5″-(9*H*-carbazole-3,6,9-triyl)-triisophthalic acid (H_6CTIA), which can construct the MOF material with a high density of open metal sites, was designed and synthesized. This new organic linker can be considered as an H_6BHB analogue in which the central benzene ring in H_6BHB was replaced by the carbazole moiety in H_6CTIA. The H_6CTIA linker, which is less symmetric, can result in noninterpenetrated frameworks. At the same time, it offers an approach to bring in a new connection manner of building units, and the obtained MOFs can possess new topologies and interesting properties. Herein we report the first example of porous MOFs from this new hexacarboxylate linker, $Cu_6(CTIA)_2$ (ZJU-70; ZJU = Zhejiang University). As expected, the resulting MOF ZJU-70 does have open copper metal sites and suitable pore sizes once it was suitably activated. As a result, the activated ZJU-70a exhibits high acetylene (191 $cm^3\ g^{-1}$ at 298 K and 1 bar) and methane (178 cm^3 (STP) cm^{-3} at 35 bar and 211 cm^3 (STP) cm^{-3} at 65 bar) uptake at room temperature.

Received: January 26, 2015
Published: April 15, 2015

DOI: 10.1021/acs.inorgchem.5b00194

Scheme 1. Synthetic Route to the Organic Linker Used To Construct ZJU-70



EXPERIMENTAL SECTION

Materials, Measurements, and X-ray Collection and Structure Determination. ^1H NMR spectra, elemental analyses, powder X-ray diffraction (PXRD) studies, thermogravimetric analyses (TGA), gas sorption isotherms, and single X-ray crystallographic measurements were carried out through the commercially available instruments. The details can be found in the Supporting Information. High-pressure CH_4 sorption isotherms were measured using a computer-controlled Sieverts-type apparatus.[17]

Isosteric Heat of Adsorption. The binding energies of CH_4 and C_2H_2 in ZJU-70a are reflected in the isosteric heat of adsorption, Q_{st}, defined as

$$Q_{st} = RT^2\left(\frac{\partial \ln p}{\partial T}\right)_q \qquad (1)$$

These values were determined using the pure component isotherm fits.

Synthesis of the Organic Linker H_6CTIA. H_6CTIA was synthesized via Suzuki coupling followed by hydrolysis and acidification as shown in Scheme 1.

5-Aminoisophthalic acid dimethyl ester (50g) was added into 15% hydrobromic acid (900 mL) and cooled to 0 °C. Sodium nitrite solution (2.5 M, 120 mL) was added gradually under fast stirring to produce the solution of diazonium bromide. The resulting solution was introduced to a solution containing CuBr (49 g) and 15% hydrobromic acid (450 mL) at a temperature below 0 °C. After all the reactants had been added, the resulting solution was left overnight with stirring at room temperature. The solution was filtrated, and the filter cake was dissolved in CCl_2H_2, dried with $MgSO_4$, filtered, and concentrated in a vacuum to get the crude product. It was purified by column chromatography (silica gel, ethyl acetate/petroleum ether, 1:8 v/v) to obtain dimethyl 5-bromobenzene-1,3-dicarboxylate as a white powder. Yield: 85%. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.95 (s, 6 H), 8.35 (d, 2 H), 8.61 (s, 1 H) ppm.

Dimethyl (5-pinacolboryl)isopthalate was synthesized by stirring the mixture of dimethyl 5-bromobenzene-1,3-dicarboxylate (5.4 g), bis(pinacolato)diborane (6.0 g), potassium acetate (5.6 g), Pd-$(dppf)_2Cl_2$ (0.2 g), and dried 1,4-dioxane (50 mL) at 70 °C for 24 h and afterward extracted with ethyl acetate (20 mL). The organic layer was dried with anhydrous $MgSO_4$, and the solvent was removed in a vacuum to get the crude product. It was purified by column chromatography (silica gel, ethyl acetate/petroleum ether, 1:8 v/v). Yield: 66%. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.37 (m, 12 H), 3.95 (s, 6 H), 8.64 (d, 2 H), 8.76 (s, 1 H) ppm.

5-Aminoisophthalic acid dimethyl ester (24g) was added into hydrochloric acid (6 M, 270 mL) and cooled to 0 °C. Sodium nitrite solution (1.7 M, 70 mL) was added gradually to produce a solution of diazonium chloride. The resulting solution was introduced to a solution containing 25.2 g of KI and 240 mL of H_2O under stirring at a temperature below 0 °C. After the addition was completed, 480 mL of CCl_2H_2 was added, and the reaction mixture was kept stirring under room temperature overnight. The organic layer was separated and washed three times with water, dried with $MgSO_4$, filtered, and concentrated in a vacuum. The crude product was purified by column chromatography (silica gel, ethyl acetate/petroleum ether, 1:15 v/v) to obtain dimethyl 5-iodoisophthalate. Yield: 85%. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.95 (s, 6 H), 8.52 (d, 2 H), 8.61 (s, 1 H) ppm.

Dimethyl 5-(3,6-dibromo-9*H*-carbazol-9-yl)isophthalate was synthesized by stirring a mixture of 3,6-dibromo-9*H*-carbazole (3 g), dimethyl 5-iodoisophthalate (4.43 g), potassium carbonate (1.55 g), and copper powder (7.38g) at 175 °C for 24 h and afterward extracted with dichloromethane (100 mL). The organic layer was dried with anhydrous $MgSO_4$, and the solvent was removed in a vacuum. The crude product was purified by column chromatography (silica gel, dichloromethane/petroleum ether, 1:1 v/v). Yield: 60%. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.95 (s, 6 H), 7.22 (d, 2 H), 7.51 (d, 2 H), 8.20 (s, 2 H), 8.37 (s, 2 H), 8.79 (s, 1 H) ppm.

Dimethyl 5-(3,6-dibromo-9*H*-carbazol-9-yl)isophthalate (3 g), dimethyl (5-pinacolboryl)isopthalate (5.57 g), and K_2CO_3 (8 g) were added to 1,4-dioxane (100 mL), and the mixture was deaerated under Ar for 15 min. $Pd(PPh_3)_4$ (0.47g) was added to the reaction mixture with stirring, and the mixture heated to 80 °C for 3 days under Ar. Afterward it was extracted with trichloromethane (150 mL). The organic layer was separated and dried with anhydrous $MgSO_4$, and the solvent was removed in a vacuum. The crude product was purified by column chromatography to obtain hexamethyl 5,5′,5″-(9*H*-carbazole-3,6,9-triyl)triisophthalate. Yield: 56.2%. ^1H NMR (500 MHz, $CDCl_3$): δ = 4.00 (s, 18 H), 7.28 (d, 1 H), 7.44 (d, 1 H), 7.54 (d, 1 H), 7.75 (d, 1 H), 8.35 (d, 2 H), 8.44 (s, 2 H), 8.51 (s, 2 H), 8,56 (s, 2 H), 8.66 (s, 1 H), 8.72 (s, 1 H), 8.81 (s, 1 H) ppm.

Hexamethyl 5,5′,5″-(9*H*-carbazole-3,6,9-triyl)triisophthalate (5 g) was then suspended in a mixture of 1,4-dioxane (40 mL), to which 150 mL of NaOH (15.5 g) aqueous solution was added. The mixture was

DOI: 10.1021/acs.inorgchem.5b00194
Inorg. Chem. 2015, 54, 4377−4381

stirred under reflux overnight. Dilute HCl was added to the remaining aqueous solution until the solution was at pH = 2. The solid was collected by filtration, washed with water, and dried to give 5,5′,5″-(9*H*-carbazole-3,6,9-triyl)triisophthalic acid (H_6CTIA) (96.7% yield). ^1H NMR (500 MHz, DMSO): δ = 7.59 (d, 2 H), 7.91 (d, 2 H), 8.42 (s, 2 H), 8.49 (s, 2 H), 8.61 (s, 4 H), 8.64 (s, 1 H), 9.04 (s, 2 H), 13.47 (s, 6 H) ppm.

Synthesis of ZJU-70. A mixture of H_6CTIA (2 mg, 0.003 mmol) and $Cu(NO_3)_2 \cdot 2.5H_2O$ (2.916 mg, 0.012 mmol) was dissolved in DMF/EtCN/H_2O (2.6 mL, 10:1:2, v/v) in a screw-capped vial. After HNO_3 (140 μL) (69%, aq) was added to the mixture, the vial was capped and placed in an oven at 80 °C for 72 h. The resulting blue ellipsoidal-shaped single crystals were washed with DMF several times to give ZJU-70. Anal. Calcd for $[Cu_6(C_{72}H_{30}N_2O_{24})(H_2O)_6](C_3H_7NO)_{12}(H_2O)_9(C_2H_3N)_5$ ($C_{118}H_{159}N_{19}O_{51}Cu_6$): C, 46.61; H, 5.28; N, 8.75. Found: C, 46.64; H, 5.26; N, 8.69.

■ RESULTS AND DISCUSSION

The organic ligand H_6CTIA was readily synthesized via a Pd-catalyzed Suzuki coupling reaction. The solvothermal reaction of the linker H_6CTIA with $Cu(NO_3)_2$ in DMF/EtCN/H_2O in the presence of a small amount of nitric acid at 80 °C for 72 h yielded small ellipsoidal-shaped blue crystals of ZJU-70. The structure was examined by single-crystal and powder X-ray diffraction studies (Figure S1) and thermogravimetric analysis (Figure S2).

ZJU-70 adopts a three-dimensional (3D) framework that crystallizes in the orthorhombic space group $Cmc2_1$. As expected, the structure of ZJU-70 is constructed by three isophthalate groups in H_6CTIA linked through $Cu_2(COO)_4$ SBUs (Figure 1a) to form a 3D porous framework (Figure 1c and d). The overall topology is a (4, 6)-connected binodal $(4^26^4)_3(4^66^48^5)_2$ net if the organic ligand and the $Cu_2(COO)_4$ are taken as 6- and 4-connected nodes, respectively (Figure 1b). ZJU-70 exhibits two different types of irregular pores along the *a*-axes in the range 4.4 to 9.6 Å, taking into account the van der Waals radii (Figure 1c). The pores are filled with terminal water molecules and free solvent molecules. Once the terminal water and free guest molecules were removed after thermal activation, the open copper sites can be generated (Figure 1d). The void space accounts for approximately 62.5% of the whole crystal volume (17 006 $Å^3$ out of the 27 228 $Å^3$ per unit cell volume) by PLATON analysis.[18]

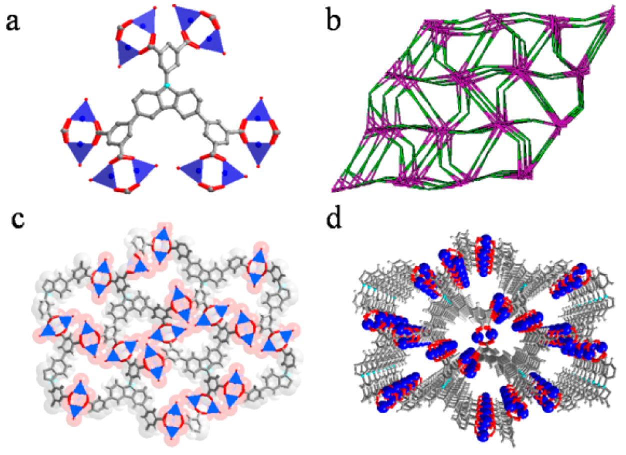


Figure 1. X-ray single-crystal structure of ZJU-70 showing (a) each hexacarboxylate ligand connects with six $Cu_2(COO)_4$ clusters; (b) the channel along the *a*-axis and (4,6)-connected topology with a Schläfli symbol of $(4^26^4)_3(4^66^48^5)_2$; (c) the structure viewed along the *a*-axis showing the irregular pore diameter in the range 4.4 to 9.6 Å; (d) the structure viewed along the *a*-axis displaying an open Cu^{2+} site.

The activated ZJU-70a shows a type I sorption isotherm and takes up a 461 cm^3/g amount of N_2 at 77 K and 1 bar (Figure 2). The Brunauer−Emmett−Teller (BET) and Langmuir surface areas of ZJU-70a are 1791 and 1999 m^2/g, respectively. Its pore volume is 0.676 cm^3/g. The calculated BET from its X-ray single-crystal structure is 2509 m^2/g, which is higher than the experimentally measured one, indicating a certain degree of framework deformation during the activation. The PXRD pattern of activated sample after the gas sorption measurements shows that the MOF still retains its crystallinity (Figure S1). The pore size distribution basically corresponds to the pore sizes from single-crystal X-ray diffraction (Figure S3). The moderately high porosity and the high density of open copper sites of ZJU-70a prompted us to check its possible application for acetylene and methane storage.

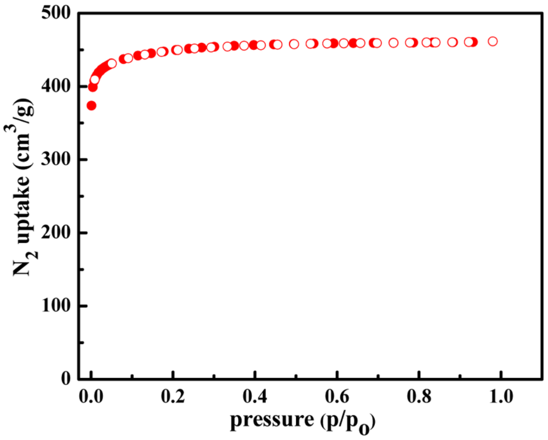


Figure 2. N_2 sorption isotherm of ZJU-70a at 77 K.

The interesting structure characteristics of ZJU-70a and open Cu^{II} sites of the MOF motivated us to carry out their gas storage application. As show in Figure 3a, ZJU-70a exhibits quite high acetylene uptakes. The C_2H_2 uptakes are 235 cm^3 g^{-1} at 273 K and 1 bar and 191 cm^3 g^{-1} at 298 and 1 bar. Its gravimetric C_2H_2 uptake at room temperature and 1 bar is among the very best MOFs for acetylene storage.[4d,19] The molecular dimensions[20] and kinetic diameter[21] of acetylene are 3.32 × 3.34 × 5.7 $Å^3$ and 3.3 Å, which are in conformity with the pore sizes of ZJU-70a. So we speculate that both the suitable pore sizes/curvatures and high density of open copper sites within ZJU-70a play important roles for the high storage of acetylene. As shown in the Figure 3a inset, the corresponding adsorption enthalpy for C_2H_2 is around 17.2 kJ/mol at zero coverage, slighter lower than those reported.[4d,22] When the adsorption step occurs, the adsorption enthalpies of C_2H_2 increase to 22.4 kJ/mol, then decline.

Methane adsorption isotherms for ZJU-70a were carried out using a high-pressure volumetric Sievert apparatus[17] up to 65 bar. The excess methane isotherms for ZJU-70a are shown in Figure.S4. Given the fact that the total volumetric methane storage might be even more important than the total gravimetric one in order to fully utilize the space, we estimated the total volumetric methane storage capacities as well. Figure 3b shows the total volumetric methane uptake isotherms at 273 and 298 K. Under 65 bar, the total volumetric uptakes of ZJU-

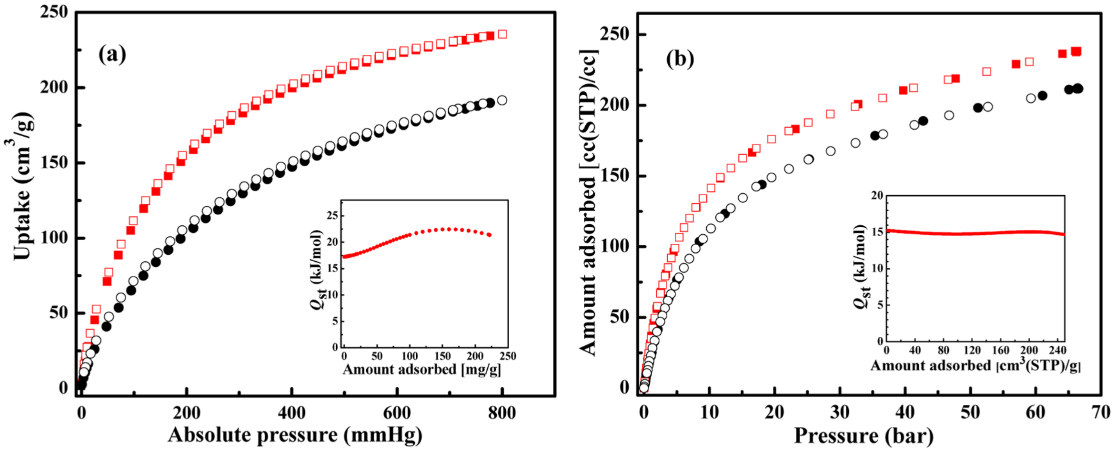


Figure 3. Gas sorption isotherms of ZJU-70a for (a) C_2H_2 at 273 and 298 K and (b) high-pressure CH_4 at 273 and 298 K. Inset: Isosteric heats of adsorption of C_2H_2 and CH_4 calculated using the virial method. Solid symbols: adsorption, open symbols: desorption.

70a for methane can reach 238 and 211 cm^3 (STP) cm^{-3} at 273 and 298 K, respectively, featuring ZJU-70a as one of the very few MOF materials with high methane storage.[1c] Its methane storage capacity of 178 cm^3 (STP) cm^{-3} at 298 K and 35 bar is also comparable to those found in the reported MOFs ZJU-25,[23] ZJU-35,[24] NOTT-102,[25] and IRMOF-6.[26] We speculate that both the suitable pore spaces and high density of open copper sites within ZJU-70a make the contribution to the high methane storage. Considering 5 and 65 bar as the specific lower and upper pressure limit, respectively, the methane working amount of ZJU-70a is 135 cm^3 (STP) cm^{-3} (from 65 to 5 bar), which is moderately high. The initial Q_{st} of CH_4 adsorption is 15.2 kJ mol^{-1}, as shown in the inset of Figure 3b. The Q_{st} of CH_4 adsorption does not change significantly with the CH_4 loading.

■ CONCLUSIONS

In conclusion, we have developed a novel aromatic hexacarboxylic acid and constructed its first 3D microporous metal−organic framework. ZJU-70a exhibits moderately high storage capacities for both acetylene and methane. Given the fact that this organic linker is unique, it will be more extensively explored with other types of metal ions/clusters for the construction of a variety of MOFs; thus a number of new MOF materials will be emerging for their diverse usages.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis of the organic linker H_6CTIA, TGA and high-pressure excess CH_4 sorption isotherm, and single X-ray crystallographic data (CCDC 1026814) given in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grants 51272231 and 51229201), Program for Innovative Research Team in University of Ministry of Education of China (IRT13R54), Grant AX-1730 from the Welch Foundation (B.C.), and the Zhejiang Provincial Natural Science Foundation of China (No. LZ15E020001).

■ REFERENCES

(1) (a) Liu, K.; Li, B.; Li, Y.; Li, X.; Yang, F.; Zeng, G.; Peng, Y.; Zhang, Z.; Li, G.; Shi, Z.; Feng, S.; Song, D. *Chem. Commun.* **2014**, *50*, 5031−5033. (b) Asadi, T.; Ehsani, M. R.; Ribeiro, A. M.; Loureiro, J. M.; Rodrigues, A. E. *Chem. Eng. Technol.* **2013**, *36*, 1231−1239. (c) He, Y.; Zhou, W.; Qian, G.; Chen, B. *Chem. Soc. Rev.* **2014**, *43*, 5657−5678.

(2) (a) Samsonenko, D. G.; Kim, H.; Sun, Y.; Kim, G. H.; Lee, H. S.; Kim, K. *Chem.—Asian J.* **2007**, *2*, 484−488. (b) Li, J. R.; Tao, Y.; Yu, Q.; Bu, X. H.; Sakamoto, H.; Kitagawa, S. *Chem.—Eur. J.* **2008**, *14*, 2771−2776. (c) Zhang, Z.; Xiang, S.; Chen, B. *CrystEngComm* **2011**, *13*, 5983−5992. (d) Hou, X.; He, P.; Li, H.; Wang, X. *J. Phys. Chem. C* **2013**, *117*, 2824−2834.

(3) (a) Suh, M. P.; Park, H. J.; Prasad, T. K.; Lim, D. *Chem. Rev.* **2012**, *112*, 782−835. (b) Sumida, K.; Rogow, D.; Mason, J.; McDonald, T.; Bloch, E.; Herm, Z.; Bae, T.; Long, J. R. *Chem. Rev.* **2012**, *112*, 724−781. (c) He, Y.; Zhou, W.; Krishna, R.; Chen, B. *Chem. Commun.* **2012**, *48*, 11813−11831. (d) Cai, J.; Rao, X.; He, Y.; Yu, J.; Wu, C.; Zhou, W.; Yildirim, T.; Chen, B.; Qian, G. *Chem. Commun.* **2014**, *50*, 1552−1554. (e) Liao, P.; Zhou, D.; Zhu, A.; Jiang, L.; Lin, R.; Zhang, J.; Chen, X. *J. Am. Chem. Soc.* **2012**, *134*, 17380−17383. (f) Gándara, F.; Furukawa, H.; Lee, S.; Yaghi, O. M. *J. Am. Chem. Soc.* **2014**, *136*, 5271−5274. (g) 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*, 8489−8492. (h) Ma, S. Q.; Zhou, H. C. *Chem. Commun.* **2010**, *46*, 44−53. (i) Gao, W.; Wojtas, L.; Ma, S. Q. *Chem. Commun.* **2014**, *50*, 5316−5318. (j) Liu, J.; Thallapally, P. K.; McGrail, B. P.; Brown, D. R.; Liu, J. *Chem. Soc. Rev.* **2012**, *41*, 2308−2322. (k) Lu, W.; Wei, Z.; Gu, Z.; Liu, T.; Park, J.; Park, J.; Tian, J.; Zhang, M.; Zhang, Q.; Gentle, T., III; Bosch, M.; Zhou, H. *Chem. Soc. Rev.* **2014**, *43*, 5561−5593.

(4) (a) Li, J.; Sculley, J.; Zhou, H. *Chem. Rev.* **2012**, *112*, 869−932. (b) Lan, Y.; Jiang, H.; Li, S.; Xu, Q. *Adv. Mater.* **2011**, *23*, 5015−5020. (c) He, Y.; Tan, Y.; Zhang, J. *Chem. Commun.* **2013**, *49*, 11323−11325. (d) He, Y.; Krishna, R.; Chen, B. *Energy Environ. Sci.* **2012**, *5*,

9107–9120. (e) Li, B.; Wen, H. M.; Zhou, W.; Chen, B. *J. Phys. Chem. Lett.* **2014**, *5*, 3468–3479.

(5) (a) Lee, J.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. *Chem. Soc. Rev.* **2009**, *38*, 1450–1459. (b) Liu, J.; Chen, L.; Cui, H.; Zhang, J.; Zhang, L.; Su, C. Y. *Chem. Soc. Rev.* **2014**, *43*, 6011–6061. (c) Jiang, H. L.; Feng, D.; Liu, T. F.; Li, J. R.; Zhou, H. C. *J. Am. Chem. Soc.* **2012**, *134*, 14690–14693. (d) Hu, Y.; Verdegaal, W. M.; Yu, S. H.; Jiang, H. L. *ChemSusChem* **2014**, *7*, 734–737.

(6) (a) Cui, Y.; Yue, Y.; Qian, G.; Chen, B. *Chem. Rev.* **2012**, *112*, 1126–1162. (b) Chen, B.; Xiang, S.; Qian, G. *Acc. Chem. Res.* **2010**, *43*, 1115–1124. (c) Kang, Y.; Wang, F.; Zhang, J.; Bu, X. *J. Am. Chem. Soc.* **2012**, *134*, 17881–17884.

(7) (a) Della Rocca, J.; Liu, D.; Lin, W. *Acc. Chem. Res.* **2011**, *44*, 957–968. (b) Horcajada, P.; Gref, R.; Baati, T.; Allan, P. K.; Maurin, G.; Couvreur, P.; Férey, G.; Morris, R. E.; Serre, C. *Chem. Rev.* **2012**, *112*, 1232–1268.

(8) (a) Li, L.; Tang, S.; Wang, C.; Lv, X.; Jiang, M.; Wu, H.; Zhao, X. *Chem. Commun.* **2014**, *50*, 2304–2307. (b) Li, L.; Bell, J. G.; Tang, S.; Lv, X.; Wang, C.; Xing, Y.; Zhao, X.; Thomas, K. M. *Chem. Mater.* **2014**, *26*, 4679–4695.

(9) (a) Pang, J.; Jiang, F.; Wu, M.; Yuan, D. Q.; Zhou, K.; Qian, J.; Su, K.; Hong, M. *Chem. Commun.* **2014**, *50*, 2834–2836. (b) Wen, H. M.; Li, B.; Yuan, D. Q.; Wang, H.; Yildirim, T.; Zhou, W.; Chen, B. *J. Mater. Chem. A* **2014**, *2*, 11516–11522. (c) Qian, J.; Jiang, F.; Zhang, L.; Su, K.; Pan, J.; Li, Q.; Yuan, D.; Hong, M. *Chem. Commun.* **2014**, *50*, 1678–1681.

(10) (a) Gómez-Gualdrón, D. A.; Gutov, O. V.; Krungleviciute, V.; Borah, B.; Mondloch, J. E.; Hupp, J. T.; Yildirim, T.; Farha, O. K.; Snurr, R. Q. *Chem. Mater.* **2014**, *26*, 5632–5639. (b) Barin, G.; Krungleviciute, V.; Gutov, O.; Hupp, J. T.; Yildirim, T.; Farha, O. K. *Inorg. Chem.* **2014**, *53*, 6914–6919.

(11) (a) Caskey, S. R.; Wong-Foy, A. G.; Matzger, A. J. *J. Am. Chem. Soc.* **2008**, *130*, 10870–10871. (b) Liu, B.; Wong-Foy, A. G.; Matzger, A. J. *Chem. Commun.* **2013**, *49*, 1419–1421.

(12) Mason, J. A.; Veenstrab, M.; Long, J. R. *Chem. Sci.* **2014**, *5*, 32–51.

(13) (a) Wilmer, C. E.; Farha, O. K.; Yildirim, T.; Eryazici, I.; Krungleviciute, V.; Sarjeant, A. A.; Snurr, R. Q.; Hupp, J. T. *Energy Environ. Sci.* **2013**, *6*, 1158–1163. (b) Liu, D.; Wu, H.; Wang, S.; Xie, Z.; Li, J.; Lin, W. *Chem. Sci.* **2012**, *3*, 3032–3037. (c) Kennedy, R. D.; Krungleviciute, V.; Clingerman, D. J.; Mondloch, J. E.; Peng, Y.; Wilmer, C. E.; Sarjeant, A. A.; Snurr, R. Q.; Hupp, J. T.; Yildirim, T.; Farha, O. K.; Mirkin, C. A. *Chem. Mater.* **2013**, *25*, 3539–3543.

(14) Nouar, F.; Eubank, J. F.; Bousquet, T.; Wojtas, L.; Zaworotko, M. J.; Eddaoudi, M. *J. Am. Chem. Soc.* **2008**, *130*, 1833–1835.

(15) (a) He, Y.; Li, B.; O'Keeffe, M.; Chen, B. *Chem. Soc. Rev.* **2014**, *43*, 5618–5656. (b) Guo, Z.; Wu, H.; Srinivas, G.; Zhou, Y.; Xiang, S.; Chen, Z.; Yang, Y.; Zhou, W.; O'Keeffe, M.; Chen, B. *Angew. Chem., Int. Ed.* **2011**, *50*, 3178–3181. (c) Farha, O. K.; Wilmer, C. E.; Eryazici, I.; Hauser, B. G.; Parilla, P. A.; O' Neill, K.; Sarjeant, A. A.; Nguyen, S. T.; Snurr, R. Q.; Hupp, J. T. *J. Am. Chem. Soc.* **2012**, *134*, 9860–9863. (d) Wilmer, C. E.; Farha, O. K.; Yildirim, T.; Eryazici, I.; Krungleviciute, V.; Sarjeant, A. A.; Snurr, R. Q.; Hupp, J. T. *Energy Environ. Sci.* **2013**, *6*, 1158–1163. (e) Barin, G.; Krungleviciute, V.; Gomez-Gualdron, D. A.; Sarjeant, A. A.; Snurr, R. Q.; Hupp, J. T.; Yildirim, T.; Farha, O. K. *Chem. Mater.* **2014**, *26*, 1912–1917.

(16) Yuan, D.; Zhao, D.; Sun, D.; Zhou, H. *Angew. Chem., Int. Ed.* **2010**, *49*, 5357–5361.

(17) Zhou, W.; Wu, H.; Hartman, M. R.; Yildirim, T. *J. Phys. Chem. C* **2007**, *111*, 16131–16137.

(18) Spek, L. *PLATON*; The University of Utrecht: Utrecht, The Netherlands, 1999.

(19) Xiang, S.; Zhou, W.; Gallegos, J. M.; Liu, Y.; Chen, B. *J. Am. Chem. Soc.* **2009**, *131*, 12415–12419.

(20) Reid, C. R.; Thomas, K. M. *J. Phys. Chem. B* **2001**, *105*, 10619–10629.

(21) Uchida, S.; Kawahara, R.; Ogasawara, Y.; Mizuno, N. *Dalton Trans.* **2013**, *42*, 16209–16215.

(22) Xu, H.; He, Y.; Zhang, Z.; Xiang, S.; Cai, J.; Cui, Y.; Yang, Y.; Qian, G.; Chen, B. *J. Mater. Chem. A* **2013**, *1*, 77–81.

(23) Duan, X.; Yu, J.; Cai, J.; He, Y.; Wu, C.; Zhou, W.; Yildirim, T.; Zhang, Z.; Xiang, S.; O'Keeffe, M.; Chen, B.; Qian, G. *Chem. Commun.* **2013**, *49*, 2043–2045.

(24) Kong, G. Q.; Han, Z. D.; He, Y.; Ou, S.; Zhou, W.; Yildirim, T.; Krishna, R.; Zou, C.; Chen, B.; Wu, C. D. *Chem.—Eur. J.* **2013**, *19*, 14886–14894.

(25) He, Y.; Zhou, W.; Yildirim, T.; Chen, B. *Energy Environ. Sci.* **2013**, *6*, 2735–2744.

(26) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469–472.