Pore Space Partition by Symmetry–Matching Regulated Ligand Insertion and Dramatic Tuning on Carbon Dioxide Uptake

5 AUTHORS, INCLUDING:

Xiang Zhao
University of California, Riverside
28 PUBLICATIONS **955** CITATIONS

Pingyun Feng
University of California, Riverside
200 PUBLICATIONS **12,348** CITATIONS

Pore Space Partition by Symmetry-Matching Regulated Ligand Insertion and Dramatic Tuning on Carbon Dioxide Uptake

Xiang Zhao,[†] Xianhui Bu,*[,‡] Quan-Guo Zhai,[†] Huy Tran,[‡] and Pingyun Feng*[,†]

[†]Department of Chemistry, University of California, 501 Big Springs Road, Riverside, California 92521, United States and
[‡]Department of Chemistry and Biochemistry, California State University, Long Beach, 1250 Bellflower Boulevard, Long Beach, California 90840, United States

S *Supporting Information*

ABSTRACT: Metal−organic frameworks (MOFs) with the highest CO_2 uptake capacity are usually those equipped with open metal sites. Here we seek alternative strategies and mechanisms for developing high-performance CO_2 adsorbents. We demonstrate that through a ligand insertion pore space partition strategy, we can create crystalline porous materials (CPMs) with superior CO_2 uptake capacity. Specifically, a new material, CPM-33b-Ni without any open metal sites, exhibits the CO_2 uptake capacity comparable to MOF-74 with the same metal (Ni) at 298 K and 1 bar.

Crystalline porous materials have attracted much attention due to their useful porosity and compositional and architectural diversity.[1,2] The relatively simple chemistry allows one to achieve intricate design and precise control over geometry and functionality.[3] It has now become important to realize the fine control over materials properties for specific purposes.[4] Creating CPMs with open metal sites (OMSs) is among the most successful strategies to improve gas sorption properties.[5−7] On the other hand, OMSs could lead to decreased framework rigidity and may also be subject to competitive attacks by species other than desired adsorbates.[8] Therefore, development of alternative strategies for creating high-performance adsorbents is beneficial.[9]

During adsorption, MOFs with a large cavity are expected to promote a greater portion of guest−guest interactions (especially with increasing pressure) among the total combined host−guest and guest−guest interactions. For efficient capture of small gas molecules at ambient conditions, maximizing host−guest interactions by encaging gas molecules in snug pockets of pore space can be a fruitful approach. To put this concept into practice, we have proposed the pore space partition concept and reported several strategies.[10] The essence of these strategies is to anchor a metal ion or cluster at the cage or channel centers and run hooks (functional groups) from the framework to such metal species, thereby partitioning the pore space into multiple domains.

Here, we report a new pore space partition strategy: symmetry-matching regulated ligand insertion (Figure 1a). The strategy entails the insertion of a secondary ligand (L_s) into a primary framework and utilizes the symmetry and size matching between L_s and the geometrical pattern of framework coordination sites and dimension of channels.
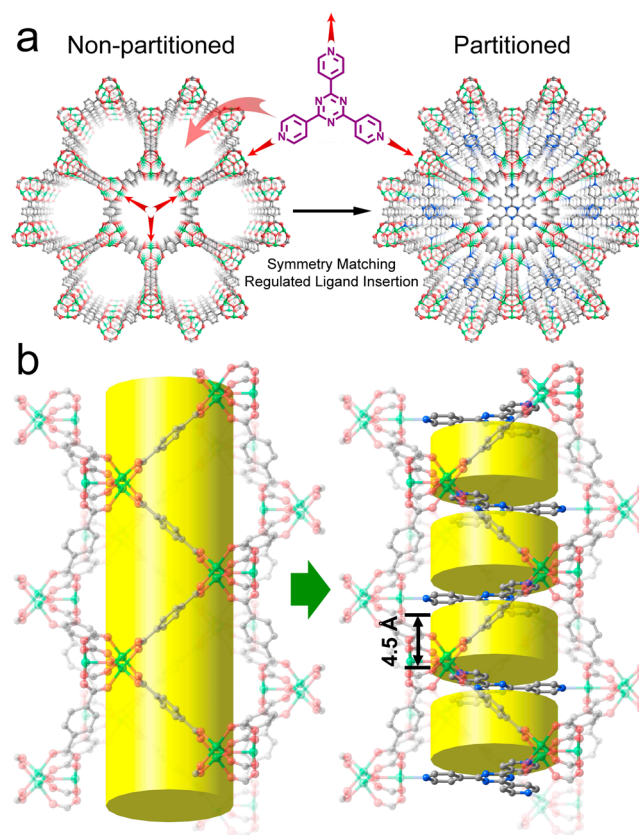

Figure 1. Illustration of pore space partition through symmetry-matching regulated ligand insertion. (a) Viewed along *c* axis and (b) side view of the channels showing the cylindrical channel before and after partition (green: Ni, red: O, blue: N, gray: C).

In this report, MIL-88 type structures were selected as the prototype framework to demonstrate the above strategy. MIL-88, $[M_3O(H_2O)_2X(L)_3]$·guest (M = Fe, Cr; X = F, Cl, acetate; L = fdc, bdc, ndc, bpdc) represents an isoreticular series of MOFs built from metal trimers and linear dicarboxylate ligands.[11−14] Their network topology was assigned as the 6-connected *acs* net and features hexagonal-shaped channels along the *c*-axis, together with trigonal bipyrimidal cages.

Table 1. Crystal Data of CPM-33, 34, 35, and 37

code[a]	formula[b]	a,b (Å)	c (Å)	R (F)
CPM-33a	Ni$_3$OH(bdc)$_3$tpt	16.7775(12)	15.184(3)	0.029
CPM-33b	Ni$_3$OH(dhbdc)$_3$tpt	16.7427(4)	15.3279(8)	0.052
CPM-33c	Ni$_3$OH(NH$_2$bdc)$_3$tpt	16.7446(6)	15.1964(9)	0.055
CPM-33d	Ni$_3$OH(1,4-ndc)$_3$tpt	16.7342(3)	15.2330(5)	0.059
CPM-34	Ni$_3$OH(2,6-ndc)$_3$tpt	16.6706(2)	20.9026(4)	0.036
CPM-35	Ni$_3$OH(bpdc)$_3$tpt	16.6492(15)	25.836(3)	0.036
CPM-37	Ni$_3$OH(bpdc)$_3$tpbtc	20.6087(2)	22.7238(5)	0.1071

[a]The space group of CPM-33d and CPM-34 adopt *P*-3$1c$, while all other compounds adopt *P*6$_3$/*mmc*. [b]bdc = benzene-1,4-dicarboxylate, dhbdc = 2,5-dihydroxybenzene-1,4-dicarboxylate, NH$_2$bdc = 2-aminobenzene-1,4-dicarboxylate, 1,4-ndc = naphthalene-1,4-dicarboxylate, 2,6-ndc = naphthalene-2,6-dicarboxylate, bpdc = biphenyl-4,4′-dicarboxylate, tpt =2,4,6-tri(4-pyridinyl)-1,3,5-triazine, tpbtc = *N,N′,N″*-tri(4-pyridinyl)-1,3,5-benzenetricarboxamide.

In MIL-88, the metals in the trimeric clusters are terminated by pendant ligands (such as water, halide, or acetate) on three axial positions. These pendant groups can be removed or exchanged, leaving potential open metal sites.[15] Furthermore, on each layer along the *ab* plane, three such M−L bonds from three different trimers adopt C$_3$ symmetry and point to the center of hexagonal channel. Such geometric features make it possible to fit in planar tritopic ligands with C$_3$ symmetry, which can occupy all three OMSs simultaneously. In this work, we examined our strategy with select C$_3$ ligands including 2,4,6-tri(4-pyridyl)-1,3,5-triazine (tpt) (Figure 1a).

MIL-88 frameworks are flexible and well known for their giant swelling effect due to the loss or gain of guest species.[11] Such flexibility intrinsic in MIL-88 structural type relaxes the size-matching requirement and makes it easier to select a C$_3$ ligand to fit in the channel. Thus, MIL-88 provides an ideal platform to test our pore space partition strategy.

The synthesis was performed using stoichiometric amount of metal nitrates, dicarboxylic acids, and the neutral tritopic ligands tpt or its extended derivative *N,N′,N″*-tri(4-pyridinyl)-1,3,5-benzene-tricarboxamide (tpbtc) in DMF or DMA. Single crystal X-ray crystallography data confirmed the success of this partitioning strategy. By using different combinations of dicarboxylic acid and tritopic ligands, single crystals of seven isoreticular MOFs were obtained (Table 1). In contrast to the original MIL-88 structures in which the trimers are 6-connected, trimers in CPMs reported here are 9-connected (Figure S3) with their three axial positions occupied by pyridyl groups from tpt or tpbtc ligands.

The immediate result from the partition strategy is the loss of OMSs, which are now occupied by tpt ligand. In addition, the framework is rigidified and no longer breathable. The rigidification leads to well-defined and potentially more stable structures. Such partitioning does not affect the trigonal bipyramidal cage (Figure S2), however, the original large continuous hexagonal channel has now been partitioned by the tpt ligand into infinite number of finite segments. For example, MIL-88b has a continuous cylindrical channel of ∼10.4 Å in diameter, but infinite in length. By partitioning with tpt ligand, the channel in CPM-33a was fragmented into numerous small segments of 4.5 Å in length (Figure 1b) with potential for enhanced confinement effects. The tpt ligand is expected to provide additional sites of adsorption for gas molecules and allows the pore space to be utilized more efficiently for some specific applications.

In addition to the pore space partition, the fine control over pore properties can be accomplished by choosing appropriate ligand combinations. In particular, we were even able to capture

and stabilize the snapshots of two different states during "breathing". CPM-35 and -37 illustrate this success (Figure 2a).
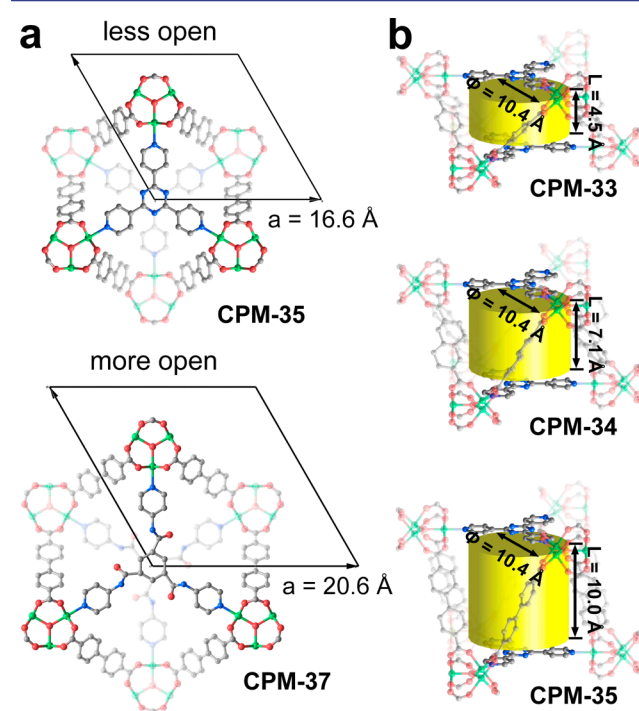

Figure 2. Two methods for the control of pore properties, leading to an entire structural family. (a) By fixing L$_p$ (the primary ligand which is a dicarboxylate here) and tuning L$_s$, the unit cell on the *ab* plane can be accurately defined. CPM-35 and -37 represent the stabilized snapshots of two different states (a more open and a less open state) during framework breathing of MIL-88d. (b) By fixing L$_s$ and tuning L$_p$, the height of cylindrical pores and the density of extra host surface for host−guest interaction can be tuned.

Without the use of our pore partitioning strategy, MIL-88d can expand and shrink with its *a* (or *b*) axis drifting within the range between 10 Å (the collapsed form) and 20 Å (the open form). In comparison, with the support from rigid ligand tpt and tpbtc, CPM-35 and CPM-37 have the *a* (or *b*) axis of 16.6 and 20.6 Å, respectively. These two captured states correspond to a less open form and a more open form during the breathing process of flexible MIL-88d. Clearly, it should be feasible to capture other intermediate breathing states, given proper ligand choice.

The control of pore properties extends beyond the diameter of the cylindrical pore. The height of each segment of cylindrical pore can also be varied by adjusting the length of

the dicarboxylate ligand, as illustrated by CPM-35, -34, and -33 containing bpdc, ndc, and bdc, respectively (Figure 2b). These ligands have quite different lengths, however, they can form the same structure type with almost the same length on the *a* (or *b*) axis (determined by the same tpt ligand) and yet the dramatically different *c* axis (determined by the dicarboxylic acid). Along with this variation in the length of the *c* axis is the increased density of the effective host surface exposed to the adsorbate. For example, CPM-35 provides the extra surface from tpt every 10.0 Å. In contrast, CPM-33 provides the extra surface from tpt every 4.5 Å, which is more than twice denser than in CPM-35.

A series of isoreticular phases with exactly the same backbone with CPM-33a, but with additional -OH, -NH₂ groups and extended aromatic ring attached to the bdc, have also been made (Table 1). Of particular interest is CPM-33b made from H₂dhbdc. In the fully deprotonated −4 form, H₂dhbdc (also denoted as H₂bdc-(OH)₂) was used to build the well-known MOF-74 family,[16,17] which has shown superior gas sorption properties for many gases. However, this ligand is not very commonly seen in other MOF structure types, and its hydroxyl group usually does not undergo deprotonation.[18] In this work, the joint use of L_p and L_s ligands suppressed the formation of MOF-74-Ni and led to the creation of MIL-88-type topology with elegantly partitioned pore space and gas uptake capacity comparable to MOF-74-Ni.

CPM-33a and -33b were selected for gas sorption studies. From N₂ gas sorption (Figure 3a), the surface areas were
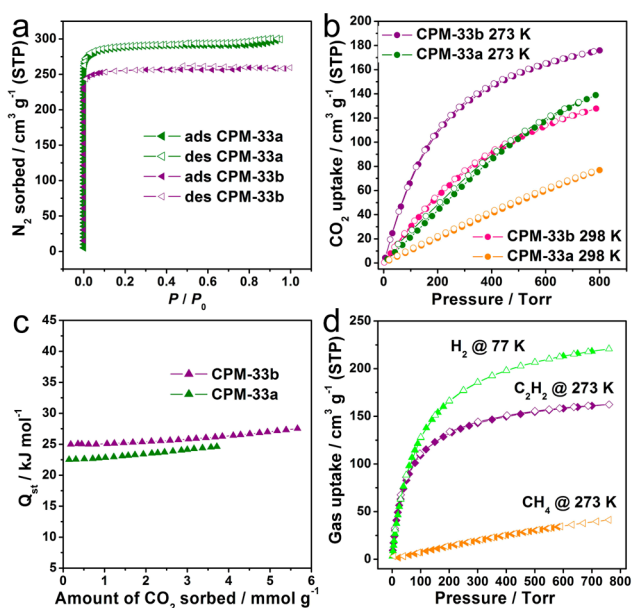

Figure 3. Gas sorption study on compounds CPM-33a and -33b. (a) N₂ sorption isotherm at 77 K. (b) CO₂ sorption at 273 and 298 K, respectively. (c) Isosteric heat plots with low CO₂ loading. (d) H₂, C₂H₂, and CH₄ sorption isotherms for CPM-33b.

estimated to be 966 and 808 m²/g obtained from BET method and 1257 and 1119 m²/g from Langmuir method, respectively. The surface area of CPM-33b is slightly lower than CPM-33a, probably due to the reduced pore space caused by protruding -OH groups on the dhbdc ligand.

For CO₂ (Figure 3b), the uptake of CPM-33a under 1 bar reaches 137.2 cm³/g at 273 K and 73.6 cm³/g at 298 K, respectively. This value is exceptionally high compared to the

value reported for MIL-88 or related structures (Table S1). It should be noted that CPM-33a does not have any exposed metal sites and the pore space partition likely plays a significant role in its high CO₂ uptake.

With two -OH sites on the benzene ring, CPM-33b showed even greater CO₂ uptake capacity. Under 1 bar, CPM-33b can adsorb 173.9 cm³/g at 273 K and 126.4 cm³/g at 298 K. Such uptake values at both temperatures are impressive, and the uptake capacity under ambient condition is comparable to MOF-74-Ni and MOF-74-Zn (Table S2).[5a,6a] To the best of our knowledge, under ambient condition, the gravimetric value of CPM-33b (Ni in this case) is only lower than MOF-74(Mg, Co) (for volumetric uptake capacity, two other MOFs, UTSA-16 and SIFSIX-2-Cu-i, are also higher).[6a,9a,b] This gravimetric value represents the highest CO₂ uptake capacity among MOFs without open metal sites. When converting the sorption amount to the numbers of CO₂ molecules adsorbed in each unit cell, it shows that ∼2 CO₂ molecules are captured at 0.1 bar and ∼12 CO₂ molecules are captured at 1 bar.

With CO₂ sorption isotherms at two different temperatures, the isosteric heat plot for CO₂ sorption is obtained for both compounds (Figure 3c). Without open metal sites, both compounds show a moderate isosteric heat. At zero coverage, the Q_{st} for CPM-33a is estimated to be −22.5 kJ/mol. CPM-33b shows a slightly higher Q_{st} of −25.0 kJ/mol.

The superior sorption performance of CPM-33b for CO₂ prompted us to study the sorption of several fuel molecules such as H₂, C₂H₂, and CH₄ (Figure 3d). Under 1 bar, it can adsorb 220.8 cm³/g H₂ at 77 K. Also its uptake capacity for CH₄ and C₂H₂ reaches 41.3 and 162.5 cm³/g, respectively at 273 K. Its corresponding value at 298 K is 26.5 and 150.7 cm³/g for CH₄ and C₂H₂, respectively (Figures S5 and S6).

In summary, we have introduced a novel symmetry-matching regulated ligand insertion strategy to partition the pore space in CPMs. Through this strategy, fine tailoring of the pore properties can be achieved. By introducing the tripyridyl-type ligand into the synthesis of MIL-88 type structure, a family of Ni-trimer-based MOFs have been obtained. The gas sorption study shows that the CPM-33 family exhibits superior CO₂ uptake capacity. In particular, CPM-33b has the highest gravimetric CO₂ uptake value among MOFs without open metal sites and is comparable to MOF-74-Ni. Importantly, we believe this study reveals a promising family of materials for gas sorption applications. Similar to the MOF-74 platform, which can incorporate different divalent metal ions to allow dramatic tuning of gas sorption properties, the metal trimer based structure platform here bestows even more versatility, because they can potentially incorporate more types of metal ions (even with different charges, Mg, Zn, Co, Ni, Fe, Cr, Sc, V, In, or their mixtures) into the structure. Furthermore, greater flexibility can be achieved not only by tuning metal cations but also by controlling both primary and secondary ligands. This opens up numerous opportunities to tune the functionalities and properties of the materials. As demonstrated here, a small change on the ligand can dramatically improve the CO₂ uptake capacity of the material. Thus, it is expected a great potential can be reached in this family of the materials in properties and applications.

ASSOCIATED CONTENT

S **Supporting Information**

Experimental details, additional figures, and cif file. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors
*xianhui.bu@csulb.edu
*pingyun.feng@ucr.edu

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

REFERENCES

(1) (a) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013**, *341*, 123044. (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. (c) Schoedel, A.; Zaworotko, M. J. *Chem. Sci.* **2014**, *5*, 1269. (d) Zhou, H.-C.; Long, J.; Yaghi, O. M. *Chem. Rev.* **2012**, *112*, 673.

(2) (a) Parnham, E. R.; Morris, R. E. *Acc. Chem. Res.* **2007**, *40*, 1005. (b) Wu, H. H.; Gong, Q. H.; Olson, D. H.; Li, J. *Chem. Rev.* **2012**, *112*, 836. (c) Mohideen, M. I. H.; Xiao, B.; Wheatley, P. S.; McKinlay, A. C.; Li, Y.; Slawin, A. M. Z.; Aldous, D. W.; Cessford, N. F.; Duren, T.; Zhao, X. B.; Gill, R.; Thomas, K. M.; Griffin, J. M.; Ashbrook, S. E.; Morris, R. E. *Nat. Chem.* **2011**, *3*, 304. (d) Takaishi, S.; DeMarco, E. J.; Pellin, M. J.; Farha, O. K.; Hupp, J. T. *Chem. Sci.* **2013**, *4*, 1509.

(3) (a) Perry, J. J.; Perman, J. A.; Zaworotko, M. J. *Chem. Soc. Rev.* **2009**, *38*, 1400. (b) Cohen, S. M. *Chem. Rev.* **2012**, *112*, 970. (c) Farha, O. K.; Yazaydın, A. Ö.; Eryazici, I; Malliakas, C. D.; Hauser, B. G.; Kanatzidis, M. G.; Nguyen, S. T.; Snurr, R. Q.; Hupp, J. T. *Nat. Chem.* **2010**, *2*, 944.

(4) (a) Fei, H.; Shin, J. W.; Meng, Y. S.; Adelhardt, M.; Sutter, J.; Meyer, K.; Cohen, S. M. *J. Am. Chem. Soc.* **2014**, *136*, 4965. (b) Stavila, V.; Talin, A. A.; Allendorf, M. D. *Chem. Soc. Rev.* **2014**, *43*, 5994. (c) Stavila, V.; Bhakta, R. K.; Alam, T. M.; Majzoub, E. H.; Allendorf, M. D. *ACS Nano* **2012**, *6*, 9807. (d) Sun, C.-Y.; Wang, X.-L.; Zhang, X.; Qin, C.; Li, P.; Su, Z.-M.; Zhu, D.-X.; Shan, G. G.; Shao, K. Z.; Wu, H.; Li, J. *Nat. Commun.* **2013**, *4*, 2717. (e) Zhao, X.; Bu, X.; Wu, T.; Zheng, S.-T.; Wang, L.; Feng, P. *Nat. Commun.* **2013**, *4*, 2344.

(5) (a) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Block, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. *Chem. Rev.* **2012**, *112*, 724. (b) Dincă, M.; Dailly, A.; Liu, Y.; Brown, C. M.; Neumann, D. A.; Long, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 16876. (c) Demessence, A.; D'Alessandro, D. M.; Foo, M. L.; Long, J. R. *J. Am. Chem. Soc.* **2009**, *131*, 8784.

(6) (a) Caskey, S. R.; Wong-Foy, A. G.; Matzger, A. J. *J. Am. Chem. Soc.* **2008**, *130*, 10870. (b) Britt, D.; Furukawa, H.; Wang, B.; Glover, T. G.; Yaghi, O. M. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 20637. (c) Yazaydin, A. Ö.; Snurr, R. Q.; Park, T.-H.; Koh, K.; Liu, J.; LeVan, M. D.; Benin, A. I.; Jakubczak, P.; Lanuza, M.; Galloway, D. B.; Low, J. L.; Willis, R. R. *J. Am. Chem. Soc.* **2009**, *131*, 18198.

(7) (a) Li, B. Y.; Zhang, Z. J.; Li, Y.; Yao, K. X.; Zhu, Y. H.; Deng, Z. Y.; Yang, F.; Zhou, X. J.; Li, G. H.; Wu, H. H.; Nijem, N.; Chabal, Y. J.; Shi, Z.; Feng, S. H.; Li, J. *Angew. Chem., Int. Ed.* **2012**, *51*, 1412. (b) Luo, J.; Wang, J.; Li, G.; Huo, Q.; Liu, Y. *Chem. Commun.* **2013**, *49*, 11433. (c) Xiang, S.; Zhou, W.; Gallegos, J. M.; Liu, Y.; Chen, B. *J. Am. Chem. Soc.* **2009**, *131*, 12415.

(8) Kizzie, A. C.; Wong Foy, A. G.; Matzger, A. J. *Langmuir* **2011**, *27*, 6368.

(9) (a) Nugent, P.; Belmabkhout, Y.; Burd, S. D.; Cairns, A. J.; Luebke, R.; Forrest, K.; Pham, T.; Ma, S.; Space, B.; Wojtas, L.; Eddaoudi, M.; Zaworotko, M. J. *Nature* **2013**, *495*, 80. (b) Xiang, S.; He, Y.; Zhang, Z.; Wu, H.; Zhou, W.; Krishna, R.; Chen, B. *Nat. Commun.* **2012**, *3*, 954. (c) Li, J.-R.; Yu, J.; Lu, W.; Sculley, J.; Balbuena, P. B.; Zhou, H.-C. *Nat. Commun.* **2013**, *4*, 1538. (d) McDonald, T. M.; D'Alessandro, D. M.; Krishna, R.; Long, J. R. *Chem. Sci.* **2011**, *2*, 2022. (e) An, J.; Geib, S. J.; Rosi, N. *J. Am. Chem. Soc.* **2009**, *132*, 38. (f) Lin, Q.; Wu, T.; Zheng, S.-T.; Bu, X.; Feng, P. *J. Am. Chem. Soc.* **2012**, *134*, 784. (g) Cui, P.; Ma, Y.-G.; Li, H.-H.; Zhao, B.; Li, J.-R.; Cheng, P.; Balbuena, P. B.; Zhou, H. C. *J. Am. Chem. Soc.* **2012**, *134*, 18892. (h) Wang, F.; Fu, H. R.; Kang, Y.; Zhang, J. *Chem. Commun.* **2014**, *50*, 12065.

(10) (a) Zheng, S.-T.; Bu, J. T.; Li, Y.; Wu, T.; Zuo, F.; Feng, P.; Bu, X. *J. Am. Chem. Soc.* **2010**, *132*, 17062. (b) Bu, F.; Lin, Q.; Zhai, Q.; Wang, L.; Wu, T.; Zheng, S.-T.; Bu, X.; Feng, P. *Angew. Chem., Int. Ed.* **2012**, *51*, 8538. (c) Zheng, S.-T.; Wu, T.; Irfanoglu, B.; Zuo, F.; Feng, P.; Bu, X. *Angew. Chem., Int. Ed.* **2011**, *50*, 8034. (d) Zheng, S.-T.; Wu, T.; Zuo, F.; Chou, C.-T.; Feng, P.; Bu, X. *J. Am. Chem. Soc.* **2012**, *134*, 1934. (e) Zheng, S.-T.; Mao, C.; Wu, T.; Lee, S.; Feng, P.; Bu, X. *J. Am. Chem. Soc.* **2012**, *134*, 11936. (f) Zheng, S.-T.; Zhao, X.; Lau, S.; Fuhr, A.; Feng, P.; Bu, X. *J. Am. Chem. Soc.* **2013**, *135*, 10270.

(11) (a) Serre, C.; Mellot-Draznieks, C.; Surblé, S.; Audebrand, N.; Filinchuk, Y.; Férey, G. *Science* **2007**, *315*, 1828. (b) Serre, C.; Millange, F.; Surble, S.; Férey, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 6286. (c) Mellot-Draznieks, C.; Serre, C.; Surblé, S.; Audebrand, N.; Férey, G. *J. Am. Chem. Soc.* **2005**, *127*, 16273.

(12) (a) Sudik, A. C.; Côté, A. P.; Yaghi, O. M. *Inorg. Chem.* **2005**, *44*, 2998. (b) Ma, S.; Simmons, J. M.; Yuan, D.; Li, J.-R.; Weng, W.; Liu, D.-J.; Zhou, H.-C. *Chem. Commun.* **2009**, 4049.

(13) (a) Ibarra, I. A.; Lin, X.; Yang, S.; Blake, A. J.; Walker, G. S.; Barnett, S. A.; Allan, D. R.; Champness, N. R.; Hubberstey, P.; Schröder, M. *Chem.—Eur. J.* **2010**, *16*, 13671. (b) Dietzel, P. D. C.; Blom, R.; Fjellvåg, H. *Dalton Trans.* **2006**, 2055.

(14) (a) Horcajada, P.; Salles, F.; Wuttke, S.; Devic, T.; Heurtaux, D.; Maurin, G.; Vimont, A.; Daturi, M.; David, O.; Magnier, E.; Stock, N.; Filinchuk, Y.; Popov, D.; Riekel, C.; Férey, G.; Serre, C. *J. Am. Chem. Soc.* **2011**, *133*, 17839−17847. (b) McKinlay, A. C.; Eubank, J. F.; Wuttke, S.; Xiao, B.; Wheadey, P. S.; Bazin, P.; Lavalley, J. C.; Daturi, M.; Vimont, A.; De Weireld, G.; Horcajada, P.; Serre, C.; Morris, R. E. *Chem. Mater.* **2013**, *25*, 1592.

(15) (a) Hwang, K. Y.; Hong, D.-Y.; Chang, J. S.; Jhung, S. H.; Seo1, Y. K.; Kim, J.; Vimont, A.; Daturi, M.; Serre, C.; Férey, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 4144. (b) Mao, C.; Kudla, R. A.; Zuo, F.; Zhao, X.; Mueller, L. J.; Bu, X.; Feng, P. *J. Am. Chem. Soc.* **2014**, *136*, 7579.

(16) (a) Dietzel, P. D. C.; Johnsen, R. E.; Blom, R.; Fjellvag, H. *Chem.—Eur. J.* **2008**, *14*, 2389. (b) Dietzel, P. D. C.; Morita, Y.; Blom, R.; Fjellvag, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 6354. (c) Dietzel, P. D. C.; Panella, B.; Hirscher, M.; Blom, R.; Fjellvag, H. *Chem. Commun.* **2006**, 959.

(17) Deng, H.; Grunder, S.; Cordova, K. E.; Valente, C.; Furukawa, H.; Hmadeh, M.; Gándara, F.; Whalley, A. C.; Liu, Z.; Asahina, S.; Kazumori, H.; O'Keeffe, M.; Terasaki, O.; Stoddart, J. F.; Yaghi, O. M. *Science* **2012**, *336*, 1018.

(18) Furukawa, H.; Gándara, F.; Zhang, Y.-B.; Jiang, J.; Queen, W. L.; Hudson, M. R.; Yaghi, O. M. *J. Am. Chem. Soc.* **2014**, *136*, 4369.