

# A robust microporous metal–organic framework constructed from a flexible organic linker for highly selective sorption of methanol over ethanol and water†

Qian Huang,<sup>a</sup> Jianfeng Cai,<sup>a</sup> Hui Wu,<sup>cd</sup> Yabing He,<sup>b</sup> Banglin Chen<sup>\*ab</sup> and Guodong Qian<sup>\*a</sup>

Received 2nd November 2011, Accepted 30th March 2012

DOI: 10.1039/c2jm15604k

A microporous metal–organic framework MOF **1** [Zn(L)<sub>2</sub>(methanol)<sub>2</sub>] (H<sub>2</sub>L = (1*R*,3*S*)-1,2,2-trimethyl-3-(pyridin-4-ylcarbonyl)cyclopentanecarboxylic acid) constructed from a flexible Zn<sup>2+</sup> node and a flexible organic linker L was obtained by solvothermal reaction of diamond topology, and exhibits highly selective sorption of methanol over ethanol and water.

## 1. Introduction

It took almost one decade to realize a few porous coordination polymers (PCPs) and/or metal–organic frameworks (MOFs) whose gas/vapor sorption isotherms were established during the 1990s.<sup>1</sup> This is mainly because “Nature abhors the vacuum”, thus the as-synthesized coordination polymers are easily collapsed to form condensed ones once the solvent molecules have been removed during thermal and/or vacuum activation. The establishment of permanent porosities in many porous MOFs during the 2000s has indicated that the rigid metal-containing clusters (typically termed as secondary building units (SBUs)) and highly conjugated rigid organic linkers have played crucial roles to stabilize the framework structures and thus to sustain the permanent porosities. Since then, tremendous research has been carried out to incorporate suitable rigid SBUs and organic linkers for the construction of porous MOFs and thus for their important applications in gas storage,<sup>2</sup> separation,<sup>3–23</sup> heterogeneous catalysis,<sup>24</sup> sensing<sup>3c</sup> and drug delivery.<sup>25</sup> Among the diverse porous MOFs, those with small pores of less than 4 Å are particularly useful for gas/vapor separation. In this regard, framework interpenetration has been demonstrated as

a very powerful methodology to tune the small pores within porous MOFs to direct their highly selective gas/vapor separation.<sup>4</sup> However, framework interpenetration is typically not the default choice when we assemble rigid SBUs and organic linkers into their framework structures, mainly because the spatial arrangements of these SBUs and organic linkers have enabled them to construct porous MOFs with moderate pore spaces which cannot provide enough empty space to hold the second framework. Although framework interpenetration does occur in some cases, most of such interpenetrated frameworks tend to have condensed structures because of multiple framework interpenetration. The importance of porous MOFs with small pores has motivated the community to explore more methodologies to synthesize such porous MOFs with small pores for their highly selective gas/vapor separation. One of the questions posted to the community might be: whether or not the isolated single metal nodes and flexible less conjugated organic linkers will also have the capacity to construct porous MOFs with small pores and thus to direct their highly selective gas/vapor separation. We define such less conjugated organic linkers as flexible ones because they can easily have conformational changes, leading to contracted and expanded pores of the synthesized porous MOFs under thermal/vacuum activation (generally termed as framework flexible dynamics).<sup>3b</sup> During our research on chiral organic linkers for the construction of nonlinear optical metal–organic frameworks (chiral space groups are the pre-requisite for nonlinear optical properties), we developed a new flexible organic linker (1*R*,3*S*)-1,2,2-trimethyl-3-(pyridin-4-ylcarbonyl)cyclopentanecarboxylate (L) to have both pyridyl and carboxylate groups for their coordination with metal ions/clusters to form MOFs. We accidentally realized a rare example of porous MOF **1** [Zn(L)<sub>2</sub>(methanol)<sub>2</sub>] built from an isolated single Zn<sup>2+</sup> as the node and L as the organic linker of the heavily distorted diamond *dia* topology for highly selective sorption of methanol over ethanol and water at room temperature.

<sup>a</sup>State Key Laboratory of Silicon Materials, Cyrus Tang Center for Sensor Materials and Applications, Department of Materials Science & Engineering, Zhejiang University, Hangzhou 310027, China. E-mail: gdqian@zju.edu.cn

<sup>b</sup>Department of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas 78249-0698, USA. E-mail: banglin.chen@utsa.edu; Fax: (+1) 210-458-7428

<sup>c</sup>NIST Center for Neutron Research, Gaithersburg, Maryland 20899-6102, USA

<sup>d</sup>Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742, USA

† Electronic supplementary information (ESI) available. CCDC reference numbers 826452 and 870505 (guest free MOF). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2jm15604k

## 2. Experimental section

### 2.1 Materials and methods

All the chemicals were commercially available and used without further purification. Infrared spectra (IR) were recorded on a Thermo Fisher Nicolet iS10 spectrometer using KBr pellets. Elemental analyses for C, H, and N were performed on an EA1112 microelemental analyzer. Powder X-ray diffraction (PXRD) patterns were collected in the  $2\theta = 5\text{--}60^\circ$  range on an X'Pert PRO diffractometer with Cu-K $\alpha$  ( $\lambda = 1.5420 \text{ \AA}$ ) radiation at room temperature. Thermogravimetric analyses (TGA) were carried out on a TA Instruments SDT Q600 with a heating rate of  $10^\circ \text{C min}^{-1}$  in  $\text{N}_2$  atmosphere. Luminescence spectra for the solid samples were recorded with a Hitachi F4500 fluorescence spectrometer. The photomultiplier tube voltage was 700 V and the scan speed was  $240 \text{ nm min}^{-1}$ . The slit widths were both 2.5 nm for excitation and emission spectra.

### 2.2 Synthesis of H<sub>2</sub>L

To a suspension of  $\text{PCl}_5$  (8.32 g, 40 mmol) in petroleum ether at  $0^\circ \text{C}$  was added D-camphoric acid (4.74 g, 20 mmol) in portions at  $0^\circ \text{C}$  for 5 h. The solvent was evaporated under reduced pressure to give the crude product as a pale yellow oil (**2**).<sup>27</sup> A suspension of 3-pyridinamine (7.52 g, 80 mmol) in  $\text{CH}_2\text{Cl}_2$  at  $0^\circ \text{C}$  was added in portions. The solution was allowed to stir at  $0^\circ \text{C}$  for 5 h and then warmed to room temperature and allowed to stir overnight. Then the precipitate was filtered off, the solvent in filtrate was removed *in vacuo* and the residue was purified by silica gel column chromatography using ethyl acetate as the eluent to afford a pure white solid (**3**).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.24(s, 1H), 8.21(s, 1H), 7.27(t, 1H), 7.15(t, 1H), 2.82(t, 1H), 2.03(m, 1H), 1.93(m, 1H), 1.90(m, 2H), 1.16(s, 3H), 1.04(s, 3H), 0.944(s, 3H). A mixture of **3** and triethylamine was stirred at  $50^\circ \text{C}$  for 24 h. The precipitate was filtered off and the solvent was removed *in vacuo* to give the product (1*R*,3*S*)-1,2,2-trimethyl-3-(pyridin-4-ylcarbamoyl)cyclopentanecarboxylic acid ( $\text{H}_2\text{L}$ ) as a white solid (80% yield).  $^1\text{H NMR}$  (DMSO):  $\delta$  10.06(s, 1H), 8.41(d, 2H), 7.59(d, 2H), 2.92(t, 1H), 2.46(m, 1H), 2.04(m, 1H), 1.76(m, 1H), 1.42(m, 1H), 1.19(s, 6H), 0.78(s, 3H).  $^{13}\text{C NMR}$  (DMSO): 179.748, 173.589, 144.045, 141.305, 136.551, 126.424, 123.842, 56.709, 55.074, 46.361, 34.115, 24.501, 23.606, 22.856, 21.841. MS (ESI), exact mass calcd for  $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_3$  [ $\text{M} + \text{H}$ ]<sup>+</sup>, 277.2. Found 277.1; [ $\text{M} - \text{H}$ ]<sup>-</sup>, 275.2, Found 275.0. HRMS (ESI); exact mass calcd for  $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_3$  [ $\text{M} + \text{H}$ ]<sup>+</sup>, 277.1547. Found: 277.1540.

### 2.3 Synthesis of MOF **1**

A mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.119 g, 0.4 mmol),  $\text{H}_2\text{L}$  (0.0552 g, 0.2 mmol), methanol (3 mL) and water (0.5 mL) was sealed into a 20 mL Teflon cup. The vessel was heated at  $100^\circ \text{C}$  for 2 days. After the mixture was slowly cooled to room temperature, colorless block crystals were obtained in 60% yield. Elemental analysis (%). Calcd for  $\text{C}_{32}\text{H}_{46}\text{N}_4\text{O}_8\text{Zn}$ : C, 56.51; H, 6.82; N, 8.24. Found: C, 56.60; H, 6.32; N, 8.11. IR (KBr,  $\text{cm}^{-1}$ ): 3413(s), 2964(s), 1671(s), 1610(w), 1584(s), 1540(s), 1479(w), 1429(s), 1396(w), 1358(s), 1328(w), 1305(w), 1275(s), 1197(s), 1175(s), 1130(s), 1040(s), 821(s), 699(s), 647(w).

### 2.4 Single-crystal X-ray crystallography

Crystal structure analyses: Diffraction data were collected on an Oxford Xcalibur Gemini Ultra diffractometer with an Atlas detector using graphite monochromatic Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 293 K. The structures of MOF **1** was solved by direct methods and refined with full-matrix least-squares on  $F^2$  with the SHELXL-97 program package. Crystal data for MOF **1**: molecular formula:  $\text{C}_{32}\text{H}_{46}\text{N}_4\text{O}_8\text{Zn}$ , formula weight: 680.10, tetragonal,  $P4_32_12$ ,  $a = 14.3035(3) \text{ \AA}$ ,  $b = 14.3035(3) \text{ \AA}$ ,  $c = 15.9627(6) \text{ \AA}$ ,  $V = 3265.8(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $T = 293(2)$ , crystal size =  $0.32 \times 0.29 \times 0.21 \text{ mm}^3$ ,  $D_c = 1.383 \text{ g cm}^{-3}$ ,  $F(000) = 438$ , 14844 reflections collected, 2989 independent reflections ( $R_{\text{int}} = 0.0543$ ) which were used in all the calculations. After the refinement cycles, reliability factors were  $R_1 = 0.0616$ ,  $wR_2 = 0.1256$  for [ $I > 2\sigma(I)$ ], and  $R_1 = 0.0648$ ,  $wR_2 = 0.1270$  for all 2989 data. CCDC 867452 and 870505.

## 3. Results and discussion

### 3.1 Synthesis

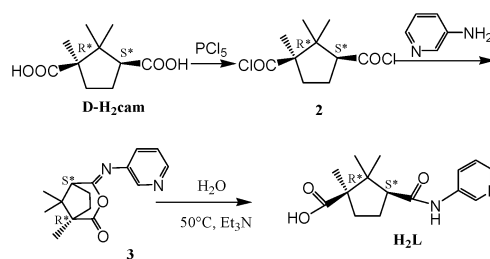
The free organic linker  $\text{H}_2\text{L}$  can be straightforwardly synthesized from the precursor D-camphoric acid in three steps as shown in Scheme 1. The as-synthesized MOF **1** can be readily obtained by solvothermal reaction of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and L in a methanol/water mixture at  $100^\circ \text{C}$  for 48 h as colourless crystals. It was formulated as  $[\text{Zn}(\text{L})_2(\text{MeOH})_2]$  by elemental analysis and single-crystal X-ray diffraction studies, and the phase purity of the bulk material was independently confirmed by powder X-ray diffraction (PXRD).

### 3.2 Crystal structure descriptions

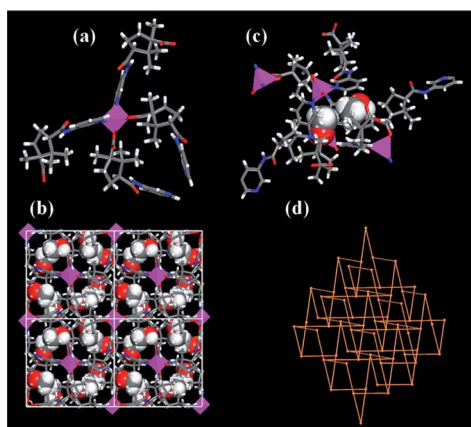
The X-ray single crystal structure of MOF **1** features a three-dimensional framework structure in which each  $\text{Zn}^{2+}$  is tetrahedrally coordinated by four organic linker L whose pyridyl nitrogen and carboxylate oxygen are involved in the coordination (Fig. 1a). The overall structure is a three-dimensional framework exhibiting irregular cages of  $3.82 \times 7.12 \text{ \AA}$  (Fig. 1b) which can hold two methanol molecules per cage (Fig. 1c). The framework topology can be considered as a highly distorted diamond one. The void space accounts approximately 15.3% of the whole crystal volume calculated by PLATON analysis.

### 3.3 Thermal properties and powder X-ray diffraction studies

To investigate the thermal stability of the framework of **1**, thermogravimetric analyses (TGA) were carried out. As shown



Scheme 1 Synthesis of the organic linker  $\text{H}_2\text{L}$ .



**Fig. 1** Single-crystal X-ray structure of **1**, showing (a) the isolated single  $\text{Zn}^{2+}$  is coordinated by two pyridyl nitrogen and two carboxylate oxygen atoms from four organic linkers **L**, (b) the resulting three-dimensional framework exhibiting irregular cages of about  $3.82 \times 7.12 \text{ \AA}$  viewed along the  $c$  axis, (c) each cage can hold two methanol molecules and (d) the highly distorted diamond topology (color scheme: C, gray; H, white; O, red; Zn, pink).

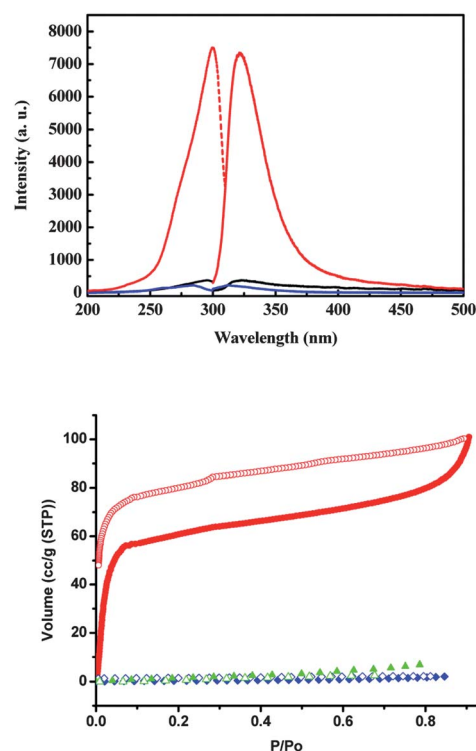
in Fig. S1,† TGA analysis indicates that methanol molecules can be readily released in the temperature range of  $25\text{--}160 \text{ }^\circ\text{C}$  to form guest-free phase MOF **1a**, which is stable up to  $260 \text{ }^\circ\text{C}$ .

Rietveld structural refinement indicates that the activated MOF **1a** keeps the basic framework structure with slight shrinking from the original unit cell volume of  $3265.8 \text{ \AA}^3$  in MOF **1** to  $3232.9 \text{ \AA}^3$  in MOF **1a**, and all the methanol molecules have been completely removed from the pores during the activation. Once the methanol is re-adsorbed into the activated MOF **1a**, the structure is recovered into the original MOF **1** (see ESI† for the details). These studies indicate that the framework is robust and the adsorption of MOF **1a** for methanol is reversible. A small amount of secondary impurity phase(s) was observed after activation (see ESI†), however, the impurity phase has little effect on the structure restoration from MOF **1a** to MOF **1** after re-adsorption of methanol and on the solvent selectivity of this new MOF material.

### 3.4 Luminescent and adsorption properties

Upon excitation at  $276 \text{ nm}$ , MOF **1** exhibits intensive blue luminescence centered at  $\lambda_{\text{max}}$  of  $321 \text{ nm}$  (Fig. 2(upper), red) which is significantly stronger than the free organic linker  $\text{H}_2\text{L}$  in the solid state (black) and in dilute solution of ethanol (blue). Such luminescence enhancement might be due to the coordination of the organic linker **L** to the  $\text{Zn}^{2+}$ , which increases the rigidity of the ligand and thus reduces the loss of energy by radiationless decay.

The most important and interesting feature of MOF **1** is the highly selective sorption of methanol over ethanol and water. As shown in Fig. 2(bottom), the activated MOF **1a** (the as-synthesized MOF **1** was thermally activated at  $120 \text{ }^\circ\text{C}$  under high vacuum overnight to generate activated MOF **1a**) takes up significantly different saturated amounts of methanol, ethanol and water of  $101$ ,  $2$  and  $7 \text{ cm}^3 \text{ g}^{-1}$ , respectively, at  $298 \text{ K}$ . This is really remarkable, highlighting this new MOF as a potentially



**Fig. 2** The excitation (dashed line) and PL spectra (solid line) of MOF **1** (red), **L** in solid state (black) and in ethanol solution ( $10^{-4} \text{ mol l}^{-1}$ ) (blue) (upper), and vapor sorption isotherms of the MOF **1a** for methanol (red), ethanol (blue) and water (green) (bottom; solid symbols: sorption; empty symbols: desorption) at  $298 \text{ K}$ .

useful microporous material for the separation of methanol over ethanol and water. Separation of methanol over water might be of more practical importance among these two potential applications, and can be utilized to generate high purity methanol by releasing the adsorbed methanol molecules from MOF materials. Such highly exclusive sorption of methanol over ethanol and water might be attributed to matching of methanol molecules into the small cages within MOF **1a** which has enhanced the much stronger interactions between host porous **1a** and guest methanol molecules.

The robustness of this framework constructed from a flexible single metal ion node and flexible organic linker is very unusual. It highlights the potential to make use of these flexible building blocks to construct robust porous MOF materials with small pores and thus for their highly selective gas/vapor separation. Robust MOFs are those whose structures remain the same after thermal/vacuum activation (generally can be established by single and/or powder X-ray diffraction studies) and the activated ones can take up gas/vapor molecules.

It needs to be mentioned that most of the MOFs generated from flexible units are easily collapsed and thus non-porous as exemplified in one of the first such MOFs,  $\text{Cu}(\text{I})[4,4',4'',4''']\text{-tetracyanotetraphenylmethane} \cdot \text{BF}_4 \cdot x\text{C}_6\text{H}_5\text{NO}_2$ .<sup>1b</sup> The very few examples of robust MOFs from such flexible metal ion nodes and organic linkers are  $[\text{CuSiF}_6(4,4'\text{-bipyridine})_2] \cdot 8\text{H}_2\text{O}$  (single  $\text{Cu}^{2+}$  as the flexible node with rigid organic linker 4,4'-Bipy)<sup>1f</sup> and  $\text{CuG}(4,4'\text{-bipyridine})_{0.5}$  ( $\text{G} = \text{glutarate}$ ; rigid paddle-wheel

$\text{Cu}_2(\text{COO})_4$  node with rigid organic linker 4,4'-Bipy and flexible organic linker glutarate).<sup>26</sup> Close structure examination indicates that the multiple hydrogen bonding and van der Waals interactions among the organic linkers have played important roles in stabilizing the framework. This accidental discovery in this reported MOF might motivate more comprehensive research endeavors on the construction of robust porous MOFs from a variety of flexible metal ion nodes and organic linkers, and then on their applications for highly selective gas/vapor separation in the near future.

## Acknowledgements

We are grateful for financial support for this work from PCSIRT, the National Natural Science Foundation of China (Nos. 50625206, 50928201, 50972127 and 51010002). This work was also partially supported by an Award AX-1730 from Welch Foundation (BC).

## Notes and references

- (a) B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1989, **111**, 5962; (b) B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546; (c) M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka and S. Kitagawa, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1725; (d) H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276; (e) S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148; (f) S.-I. Noro, S. Kitagawa, M. Kondo and K. Seki, *Angew. Chem., Int. Ed.*, 2000, **39**, 2082.
- (a) S. Ma and H.-C. Zhou, *Chem. Commun.*, 2010, **46**, 44; (b) X. Lin, N. R. Champness and M. Schröder, *Top. Curr. Chem.*, 2010, **293**, 35; (c) W. Zhou, *Chem. Rec.*, 2010, **10**, 200; (d) S. Xiang, W. Zhou, J. M. Gallegos, Y. Liu and B. Chen, *J. Am. Chem. Soc.*, 2009, **131**, 12415; (e) S. Xiang, W. Zhou, Z. Zhang, M. A. Green, Y. Liu and B. Chen, *Angew. Chem., Int. Ed.*, 2010, **49**, 4615; (f) Z. Guo, H. Wu, S. Gadipelli, T. Liao, Y. Zhou, S. Xiang, Z. Chen, Y. Yang, W. Zhou, M. O'Keeffe and B. Chen, *Angew. Chem., Int. Ed.*, 2011, **50**, 3178.
- (a) J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.*, 2011, DOI: 10.1021/cr200190s; (b) J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477; (c) B. Chen, S. Xiang and G. Qian, *Acc. Chem. Res.*, 2010, **43**, 1115; (d) Z. Zhang, S. Xiang and B. Chen, *CrystEngComm*, 2011, **13**, 5983; (e) H.-L. Jiang and Q. Xu, *Chem. Commun.*, 2011, **47**, 3351; (f) L. J. Murray, M. Dincă and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294; (g) D. M. D'Alessandro, B. Smit and J. R. Long, *Angew. Chem., Int. Ed.*, 2010, **49**, 6058; (h) S. Kitagawa, R. Kitaura and S.-I. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; (i) R. E. Morris and P. S. Wheatley, *Angew. Chem., Int. Ed.*, 2008, **47**, 4966; (j) M. C. Das, S. Xiang, Z. Zhang and B. Chen, *Angew. Chem., Int. Ed.*, 2011, **50**, 10510.
- (a) B. Chen, C. Liang, J. Yang, D. S. Contreras, Y. L. Clancy, E. B. Lobkovsky, O. M. Yaghi and S. Dai, *Angew. Chem., Int. Ed.*, 2006, **45**, 1390; (b) B. Chen, Y. Ji, M. Xue, F. R. Fronczek, E. J. Hurtado, J. U. Mondal, C. Liang and S. Dai, *Inorg. Chem.*, 2008, **47**, 5543; (c) B. Chen, S. Ma, E. J. Hurtado, E. B. Lobkovsky, C. Liang, H. Zhu and S. Dai, *Inorg. Chem.*, 2007, **46**, 8705; (d) B. Chen, S. Ma, E. J. Hurtado, E. B. Lobkovsky and H.-C. Zhou, *Inorg. Chem.*, 2007, **46**, 8490; (e) B. Chen, S. Ma, F. Zapata, F. R. Fronczek, E. B. Lobkovsky and H.-C. Zhou, *Inorg. Chem.*, 2007, **46**, 1233; (f) Z. Chen, S. Xiang, H. D. Arman, P. Li, D. Zhao and B. Chen, *Eur. J. Inorg. Chem.*, 2010, 3745; (g) Z. Chen, S. Xiang, H. D. Arman, J. U. Mondal, P. Li, D. Zhao and B. Chen, *Inorg. Chem.*, 2011, **50**, 3442; (h) M. C. Das, H. Xu, S. Xiang, Z. Zhang, H. D. Arman, G. Qian and B. Chen, *Chem.-Eur. J.*, 2011, **17**, 7817; (i) M. C. Das, H. Xu, Z. Wang, G. Srinivas, W. Zhou, Y. Yue, V. N. Nesterov, G. Qian and B. Chen, *Chem. Commun.*, 2011, **47**, 11715; (j) S. Xiang, Z. Zhang, C.-G. Zhao, K. Hong, X. Zhao, D.-L. Ding, M.-H. Xie, C.-D. Wu, R. Gill, K. M. Thomas and B. Chen, *Nat. Commun.*, 2011, **2**, 204; (k) Y. He, S. Xiang and B. Chen, *J. Am. Chem. Soc.*, 2011, **133**, 14570; (l) Y. He, Z. Zhang, S. Xiang, F. R. Fronczek, R. Krishna and B. Chen, *Chem.-Eur. J.*, 2012, **18**, 613; (m) Y. He, Z. Zhang, S. Xiang, H. Wu, F. R. Fronczek, W. Zhou, R. Krishna, M. O'Keeffe and B. Chen, *Chem.-Eur. J.*, 2012, **18**, 1901.
- (a) L. Pan, D. H. Olson, L. R. Ciemniolowski, R. Heddy and J. Li, *Angew. Chem., Int. Ed.*, 2006, **45**, 616; (b) L. Pan, B. Parker, X. Huang, D. H. Olson, J. Lee and J. Li, *J. Am. Chem. Soc.*, 2006, **128**, 4180; (c) K. Li, D. H. Olson, J. Seidel, T. J. Emge, H. Gong, H. Zeng and J. Li, *J. Am. Chem. Soc.*, 2009, **131**, 10368.
- (a) S. Ma, D. Sun, X.-S. Wang and H.-C. Zhou, *Angew. Chem., Int. Ed.*, 2007, **46**, 2458; (b) S. Ma, D. Sun, D. Yuan, X.-S. Wang and H.-C. Zhou, *J. Am. Chem. Soc.*, 2009, **131**, 6445.
- (a) R. Vaidyanathan, S. S. Iremonger, G. K. H. Shimizu, P. G. Boyd, S. Alavi and T. K. Woo, *Science*, 2010, **330**, 650; (b) R. Vaidyanathan, S. S. Iremonger, K. W. Dawson and G. K. H. Shimizu, *Chem. Commun.*, 2009, 5230.
- D. Britt, D. Tranchemontagne and O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**, 11623.
- C. Y. Lee, Y.-S. Bae, N. C. Jeong, O. K. Farha, A. A. Sarjeant, C. L. Stern, P. Nickias, R. Q. Snurr, J. T. Hupp and S. T. Nguyen, *J. Am. Chem. Soc.*, 2011, **133**, 5228.
- Z. R. Herm, J. A. Swisher, B. Smit, R. Krishna and J. R. Long, *J. Am. Chem. Soc.*, 2011, **133**, 5664.
- (a) Y.-S. Bae and R. Q. Snurr, *Angew. Chem., Int. Ed.*, 2011, **50**, DOI: 10.1002/anie.201101891; (b) A. Ö. Yazaydin, R. Q. Snurr, T.-H. Park, K. Koh, J. Liu, M. D. LeVan, A. I. Benin, P. Jakubczak, M. Lanuza, D. B. Galloway, J. J. Low and R. R. Willis, *J. Am. Chem. Soc.*, 2009, **131**, 18198.
- (a) J. An, S. J. Geib and N. L. Rosi, *J. Am. Chem. Soc.*, 2010, **132**, 38; (b) J. An and N. L. Rosi, *J. Am. Chem. Soc.*, 2010, **132**, 5578.
- R. Krishna and J. R. Long, *J. Phys. Chem. C*, 2011, **115**, 12941.
- E. Barea, G. Tagliabue, W.-G. Wang, M. Pérez-Mendoza, L. Mendez-Liñan, F. J. López-Garzon, S. Galli, N. Masciocchi and J. A. R. Navarro, *Chem. Eur. J.*, 2010, **16**, 931.
- (a) J.-P. Zhang and X.-M. Chen, *J. Am. Chem. Soc.*, 2008, **130**, 6010; (b) J.-P. Zhang and X.-M. Chen, *J. Am. Chem. Soc.*, 2009, **131**, 5516.
- (a) S. Chen, J. Zhang, T. Wu, P. Feng and X. Bu, *J. Am. Chem. Soc.*, 2009, **131**, 16027; (b) S.-T. Zheng, J. T. Bu, Y. Li, T. Wu, F. Zuo, P. Feng and X. Bu, *J. Am. Chem. Soc.*, 2010, **132**, 17062.
- (a) K. A. Cychoz, R. Ahmad and A. J. Matzger, *Chem. Sci.*, 2010, **1**, 293; (b) R. Ahmad, A. G. Wong-Foy and A. J. Matzger, *Langmuir*, 2009, **25**, 11977.
- (a) T. Panda, P. Pachfule and R. Banerjee, *Chem. Commun.*, 2011, **47**, 7674; (b) T. Panda, P. Pachfule, Y. Chen, J. Jiang and R. Banerjee, *Chem. Commun.*, 2011, **47**, 2011.
- (a) S. Horike, S. Shimomura and S. Kitagawa, *Nat. Chem.*, 2009, **1**, 695; (b) J. Seo, R. Matsuda, H. Sakamoto, C. Bonneau and S. Kitagawa, *J. Am. Chem. Soc.*, 2009, **131**, 12792; (c) J.-R. Li, Y. Tao, Q. Yu, X.-H. Bu, H. Sakamoto and S. Kitagawa, *Chem.-Eur. J.*, 2008, **14**, 2771.
- (a) L. Hamon, P. L. Llewellyn, T. Devic, A. Ghoufi, G. Clet, V. Guillerm, G. D. Pirngruber, G. Maurin, C. Serre, G. Driver, W. v. Beek, E. Jolimaître, A. Vimont, M. Daturi and G. Férey, *J. Am. Chem. Soc.*, 2009, **131**, 17490; (b) P. L. Llewellyn, P. Horcajada, G. Maurin, T. Devic, N. Rosenbach, S. Bourrelly, C. Serre, D. Vincent, S. Loera-Serna, Y. Filinchuk and G. Férey, *J. Am. Chem. Soc.*, 2009, **131**, 13002.
- Y.-X. Tan, Y.-P. He and J. Zhang, *Chem. Commun.*, 2011, **47**, 10647.
- Q.-K. Liu, J.-P. Ma and Y.-B. Dong, *J. Am. Chem. Soc.*, 2010, **132**, 7005.
- (a) M.-S. Chen, M. Chen, S. Takamizawa, T.-A. Okamura, J. Fana and W.-Y. Sun, *Chem. Commun.*, 2011, **47**, 3787; (b) S.-S. Chen, M. Chen, S. Takamizawa, P. Wang, G.-C. Lv and W.-Y. Sun, *Chem. Commun.*, 2011, **47**, 4902.
- (a) L. Ma, C. Abney and W. Lin, *Chem. Soc. Rev.*, 2009, **38**, 1248; (b) G. Nickerl, A. Henschel, R. Grünker, K. Gedrich and S. Kaskel, *Chem. Ing. Tech.*, 2011, **83**, 90–103.
- P. Horcajada, C. Serre, G. Maurin, N. A. Ramsahye, F. Balas, M. Vallet-Regí, M. Sebban, F. Taulelle and G. Férey, *J. Am. Chem. Soc.*, 2008, **130**, 6774–6780.
- B. Rather and M. J. Zaworotko, *Chem. Commun.*, 2003, 830.
- M. G. Moloney, D. R. Paul, R. M. Thompson and E. Wright, *Tetrahedron: Asymmetry*, 1996, **7**, 2551.