

# ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

# Polyhedral Metal-Organic Framework Based on Supramolecular Building Blocks Strategy Exhibiting High Performance for Carbon Dioxide Capture and Separation of Light Hydrocarbon

Dongmei Wang, Bing Liu, Shuo Yao, Tao Wang, Guanghua Li, Qisheng Huo, and Yunling Liu\*

Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

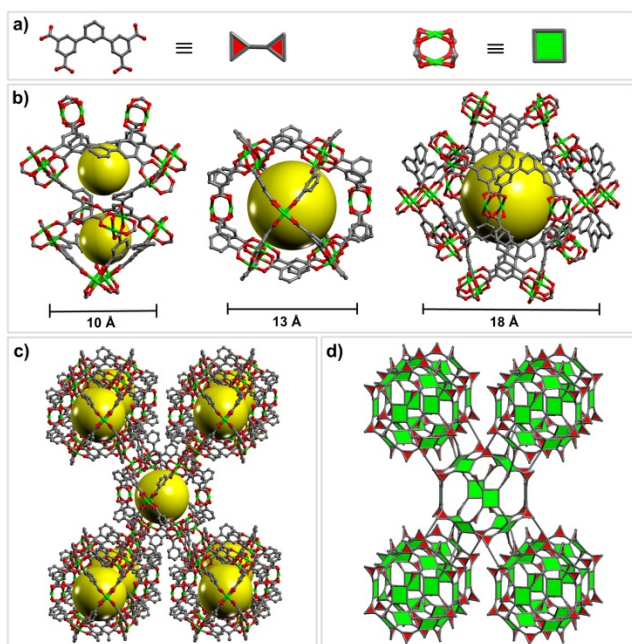
By using supramolecular building blocks (SBBs) strategy, a polyhedron-based metal-organic framework (PMOF), which features three types of cages with multiple sizes and shapes, has been synthesized. It exhibits high performance for CO<sub>2</sub> capture (170 cm<sup>3</sup> g<sup>-1</sup> at 273 K under 1 bar) and selectivity of CO<sub>2</sub>/CH<sub>4</sub> (9.4) and C<sub>3</sub>H<sub>8</sub>/CH<sub>4</sub> (271.5).

Porous metal-organic frameworks (MOFs) as a burgeoning class of adsorbent materials have drawn considerable attention because of their large surface area, tunable pore size and shape, functional pore surface and high stability, etc.<sup>1</sup> However, metal-organic polyhedral (MOP) based MOFs are different from traditional MOFs, which both have cages carrying large voids and open-channel-type pores. In the polyhedron-based MOFs (PMOFs), individual cages with large voids are interconnected through relatively small windows. Due to sieving effect, the sizes of windows can make the suitable gas molecules go through the pores/cages while the others are blocked outside. A large number of reported PMOFs exhibit high H<sub>2</sub> storage and CO<sub>2</sub> capture, excellent catalysis, drug delivery, rapid and selective adsorption of dyes.<sup>2</sup>

Up to now, several synthetic strategies have been developed sequentially to construct PMOFs. The supramolecular building blocks (SBBs) approach has recently been verified a powerful strategy for the design and construction of PMOFs. In general, PMOFs can be assembled by numerous types of SBBs.<sup>3</sup> For example, tetrahedral,<sup>4</sup> cubic,<sup>5</sup> octahedral,<sup>6</sup> cuboctahedral,<sup>7</sup> rhombic dodecahedral,<sup>8</sup> and tri-capped trigonal prism SBBs.<sup>9</sup> In the most of PMOFs, the metal often exists in the form of paddlewheel or trinuclear cluster which offers great stability and high-density open metal sites (OMSs) after de-solvent.<sup>10</sup> Meanwhile, the surface area of the cavities and the sizes of the windows can be tuned by changing the length of the linker. With the largely reported PMOFs, paddlewheel as molecule building blocks (MBBs) offering a platform to construct MOPs has been extensively and elaborately studied.<sup>11</sup> Herein, by using SBBs strategy, we successfully synthesized a novel PMOF with three types of MOPs based on a less explored bent tetracarboxylate ligand<sup>12</sup> [H<sub>3</sub>O][Cu<sub>6</sub>(tpta)<sub>3</sub>(DMA)<sub>4</sub>(COO)]·12H<sub>2</sub>O·7DMA (**JLU-Liu22**)

(H<sub>4</sub>tpta = [1,1':3',1''-terphenyl]-3,3'',5,5''-tetracarboxylic acid). To our knowledge, the linker is vital to the construction of the stable framework with large surface area. Blindly extending the length of the ligands often results in the framework either collapse upon guest molecules removal or self-interpenetrate.<sup>13</sup> Therefore, selecting an optimal ligand is the prerequisite to build target product. Herein, we select the C<sub>2</sub>-symmetric bent ligand H<sub>4</sub>tpta with appropriate length 7.1 Å (the terminal benzenes center distance) as the optimum linker to ensure the fabricating of MOPs with large surface area and avoid interpenetrating. The H<sub>4</sub>tpta ligand with 120° angle from the terminal isophthalate moieties built by Cu paddlewheel afford the platform to fabricate the well-known MOP-1.<sup>3b,7a,14</sup> Fascinatingly, the expected PMOF material **JLU-Liu22** based on anionic skeleton with high-density OMSs and large pore volume exhibits high performance for CO<sub>2</sub> capture and natural gas (NG) purification. The selectivity of CO<sub>2</sub>/CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>/CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub>/CH<sub>4</sub> were appraised by the ideal adsorbed solution theory (IAST).

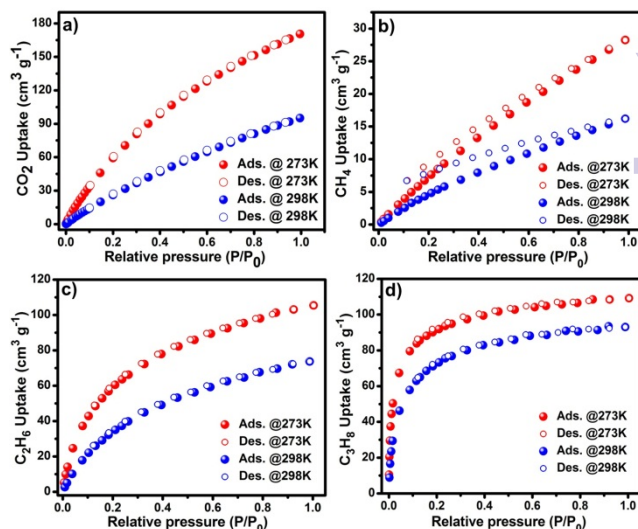
In the structure of **JLU-Liu22**, the PMOF is assembled by binary MBBs: the typical Cu paddlewheel with square geometry and the organic MBBs simplified a pairs of triangle geometry (Fig. 1a). The HCOO<sup>-</sup> bridging linker instead of two solvent molecules located in the center of two paddlewheels. **JLU-Liu22** features three types of cages with different sizes and shapes (10, 13, and 18 Å, respectively): small cage consisted of 12 Cu paddlewheel MBBs and 6 tpta<sup>4-</sup> linkers to construct a truncated tetrahedron (T-T<sub>d</sub>) configuration, medium cage with cuboctahedron (cuo) geometry, constructed by 12 Cu paddlewheel MBBs and 24 tpta<sup>4-</sup> linkers; and large cage outlined in truncated octahedron (T-O<sub>h</sub>) built from 24 Cu paddlewheel MBBs and 16 tpta<sup>4-</sup> linkers (Fig. 1b, S1 ESI†). The three types of polyhedron packing arrangement results in a novel (3,4)-connected network with multiple pore system, such as a 1D square channel with an approximate diameter of 6.8 × 6.8 Å<sup>2</sup> along the *c* axis (regardless of the van der Waals radii) (Fig. 1c, d, S2, ESI†). From another viewpoints of topology, the Cu paddlewheel MBBs and tpta<sup>4-</sup> ligands both regarded as 4-c nodes, **JLU-Liu22** adopts a new topology with a Schläfli symbol of {4.6<sup>2</sup>.8<sup>3</sup>}{4.6<sup>4</sup>.8}{4.6<sup>5</sup>}<sub>4</sub>, which is different from PCN-306 based on the same H<sub>4</sub>tpta ligand and Cu(II) paddlewheel (Fig. S3, ESI†).<sup>12a</sup>



**Fig. 1** Description of the structure of **JLU-Liu22**: a) binary MBBs; b) three types of cages with different size (diagonal Cu-Cu distance, regardless of Van der Waals radii); c) ball and stick model of the 3D framework; d) polyhedral view of the net. Colour scheme: carbon = gray, oxygen = red, copper = green. Guest molecules and H atoms have been omitted for clarity.

The total accessible volume after removal of the guest and coordinated solvent molecules is 66.5% calculated by PLATON. **JLU-Liu22** exhibits good thermal stability, which can be stable up to 300 °C (Fig. S8, ESI†). N<sub>2</sub> sorption experiment for desolvated **JLU-Liu22** shows a reversible type-I isotherm characteristic of microporous material (Fig. S9, ESI†). The Brunauer-Emmett-Teller (BET) surface area for **JLU-Liu22** is calculated to be 1487 m<sup>2</sup> g<sup>-1</sup>. On the basis of the N<sub>2</sub> sorption isotherm, the micropore volume is 0.77 cm<sup>3</sup> g<sup>-1</sup>, which is close to the theoretical value of 0.83 cm<sup>3</sup> g<sup>-1</sup>.

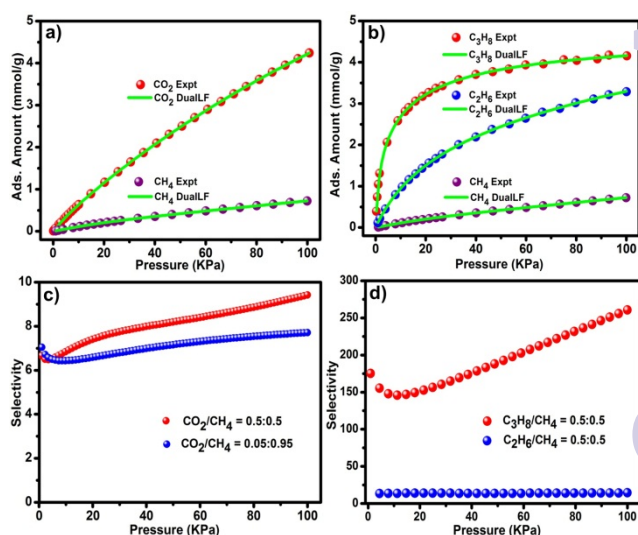
High-porosity together with multiple-pore system and high-density OMSs (1.0 per nm<sup>3</sup>) in this PMOF inspired us to investigate its gas uptake capacity. As shown in Fig. 2, the amount of CO<sub>2</sub> uptake for **JLU-Liu22** is 170 (33.4 wt%) and 95 (18.5 wt%) cm<sup>3</sup> g<sup>-1</sup> at 273 and 298 K under 1 bar, respectively, which overpasses many reported MOFs based on bent tetracarboxylate ligands (Table S1 ESI†), and exceeds NTU-111 with high-density Lewis basic sites (LBSs) and PCN-88 with predesigned single-molecule-traps (SMT).<sup>2j,15</sup> To date, although large numbers of PMOFs with good H<sub>2</sub> storage and CO<sub>2</sub> capture performance have been reported, only a few exhibit high performance for adsorption and separation of light hydrocarbon.<sup>16</sup> Nevertheless, **JLU-Liu22** exhibits notable adsorption capacities to C<sub>2</sub>H<sub>6</sub> (105 and 74 cm<sup>3</sup> g<sup>-1</sup>) and C<sub>3</sub>H<sub>8</sub> (109 and 93 cm<sup>3</sup> g<sup>-1</sup>), which overpass the values of BIF-24.<sup>17</sup> It adsorbs a little amount of CH<sub>4</sub> (28 and 16 cm<sup>3</sup> g<sup>-1</sup>). To evaluate the affinity of the **JLU-Liu22** for gas molecules, the isosteric heats ( $Q_{st}$ ) for small gases (CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>) were calculated based on the adsorption isotherms at 273 and 298 K (Fig. S11-S18, ESI†). At zero-coverage, the  $Q_{st}$  value of CH<sub>4</sub> is 11 kJ mol<sup>-1</sup>, whereas the  $Q_{st}$



**Fig. 2** a) CO<sub>2</sub>; b) CH<sub>4</sub>; c) C<sub>2</sub>H<sub>6</sub> and d) C<sub>3</sub>H<sub>8</sub> gas sorption isotherms for **JLU-Liu22** at 273 K (red) and 298 K (blue) under 1 bar.

values of CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> are 30, 30.5 and 30.3 kJ mol<sup>-1</sup> respectively. The lower  $Q_{st}$  of CH<sub>4</sub> can be attributed to the lower Van der Waals interactions with the framework, together with the ionic skeleton of **JLU-Liu22** possesses worst interactions with the hardest polarized CH<sub>4</sub> molecule. The results show that it may be an ideal material for highly selective separation for CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>8</sub> over CH<sub>4</sub>.

To imitate the separation behavior of **JLU-Liu22** under a more real-world setting, the gas selectivity of CO<sub>2</sub>/CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>/CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub>/CH<sub>4</sub> in a binary mixture were calculated via IAST based on the experimental single-component isotherms fitted by the dual site Langmuir Freundlich (DSLFF) model at 298 K under 1 bar (Fig. 3). The selectivity of CO<sub>2</sub>/CH<sub>4</sub> (50% and 50%, 5% and 95%) is 9.4 and 7.7, which can be classified as the top rank of the MOFs materials,<sup>18</sup> and comparable to the attractive Mg-MOF-74 with open Mg sites (selectivity of CO<sub>2</sub>/CH<sub>4</sub> is 11.5 under the same conditions).<sup>19</sup>



**Fig. 3** CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> adsorption isotherms at 298 K along with the dual-site Langmuir Freundlich (DSLFF) fits (a, b); CO<sub>2</sub>/CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>/CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub>/CH<sub>4</sub> adsorption selectivity are predicted by IAST at 298 K and 1 bar for **JLU-Liu22** (c, d).

Furthermore, the selectivities of C<sub>2</sub>H<sub>6</sub>/CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub>/CH<sub>4</sub> are 14.4 and 271.5, respectively. It is highlighted that the high selectivity of C<sub>3</sub>H<sub>8</sub>/CH<sub>4</sub> is much higher than many reported MOFs, such as JLU-Liu5,<sup>18</sup> UTSA-35a.<sup>20</sup> The PMOF **JLU-Liu22** exhibiting great separation for CH<sub>4</sub> can be attributed to many reasons: i) ionic framework and OMSs can enhance framework-CO<sub>2</sub> interactions through charge-induced forces due to its greater quadrupole moment and polarizability compared with CH<sub>4</sub>; ii) CH<sub>4</sub> is the smallest molecule and therefore has the weakest interactions with adsorbent; iii) the uptake capacity of hydrocarbons increases with polarizability (CH<sub>4</sub> = 25 × 10<sup>-25</sup>, C<sub>2</sub>H<sub>6</sub> = 44 × 10<sup>-25</sup>, C<sub>3</sub>H<sub>8</sub> = 63 × 10<sup>-25</sup> cm<sup>3</sup>), due to increasing charge-induced dipole interactions with the OMSs.

In summary, based on the powerful SBB strategy, we have successfully constructed a novel PMOF **JLU-Liu22** with well-known MOP-1 fabricated by Cu-paddlewheel and bent tetracarboxylate ligand. It features three types of cages: cuo, T-T<sub>d</sub>, and T-O<sub>h</sub>. **JLU-Liu22** with the ionic skeleton exhibits high CO<sub>2</sub> capture as well as highly selective separation of CO<sub>2</sub> and light hydrocarbons (C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>) over CH<sub>4</sub>. Subsequently, these emerging and promising porous PMOFs materials will be candidate for the application in the field of industrially important gas capture and separation in the near future.

This work was supported by the National Natural Science Foundation of China (Nos. 21373095, 21371067 and 21171064).

## Notes and references

<sup>30</sup> State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China. Fax: +86-431-85168624; Tel: +86-431-85168614; E-mail: yunling@jlu.edu.cn

† Electronic Supplementary Information (ESI) available: [materials and methods, crystal data and structure refinement, structure information, XRD, TGA, gases adsorption properties of **JLU-Liu22**. CCDC 1410333]. See DOI: 10.1039/b000000x/

- (a) H.-C. Zhou, J. R. Long and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 673-674; (b) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724-781; (c) J. A. Mason, M. Veenstra and J. R. Long, *Chem. Sci.*, 2014, **5**, 32-51; (d) O. K. Farha, A. Özgür Yazaydin, I. Eryazici, C. D. Malliakas, B. G. Hauser, M. G. Kanatzidis, S. T. Nguyen, R. Q. Snurr and J. T. Hupp, *Nat Chem.*, 2010, **2**, 944-948; (e) S. Kitagawa, R. Kitaura and S.-i. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334-2375; (f) W. Lu, Z. Wei, Z.-Y. Gu, T.-F. Liu, J. Park, J. Park, J. Tian, M. Zhang, Q. Zhang, T. Gentle III, M. Bosch and H.-C. Zhou, *Chem. Soc. Rev.*, 2014, **43**, 5561-5593; (g) S.-T. Zheng, X. Zhao, S. Lau, A. Fuhr, P. Feng and X. Bu, *J. Am. Chem. Soc.*, 2013, **135**, 10270-10273.
- (a) Q.-F. Sun, J. Iwasa, D. Ogawa, Y. Ishido, S. Sato, T. Ozeki, Y. Sei, K. Yamaguchi and M. Fujita, *Science*, 2010, **328**, 1144-1147; (b) U. Stoeck, S. Krause, V. Bon, I. Senkowska and S. Kaskel, *Chem. Commun.*, 2012, **48**, 10841-10843; (c) Y. Yan, S. Yang, A. J. Blake and M. Schröder, *Acc. Chem. Res.*, 2014, **47**, 296-307; (d) D. Yuan, D. Zhao, D. Sun and H.-C. Zhou, *Angew. Chem., Int. Ed.*, 2010, **49**, 5357-5361; (e) B. Li, Z. Zhang, Y. Li, K. Yao, Y. Zhu, Z. Deng, F. Yang, X. Zhou, G. Li, H. Wu, N. Nijem, Y. J. Chabal, Z. Lai, Y. Han, Z. Shi, S. Feng and J. Li, *Angew. Chem. Int. Ed.*, 2012, **51**, 1412-1415; (f) H.-N. Wang, X. Meng, G.-S. Yang, X.-L. Wang, K.-Z. Shao, Z.-M. Su and C.-G. Wang, *Chem. Commun.*, 2011, **47**, 7128-7130; (g) L. Meng, Q. Cheng, C. Kim, W.-Y. Gao, L. Wojtas, Y.-S. Chen, M. J. Zaworotko, X. P. Zhang and S. Ma, *Angew. Chem., Int. Ed.*, 2012, **51**, 10082-10085; (h) J. Park, J.-R. Li, Y.-P. Chen, J. Yu, A. A. Yakovenko, Z. U. Wang, L.-B. Sun, P. B. Balbuena and H.-C. Zhou, *Chem. Commun.*, 2012, **48**, 9995-9997; (i) Z. Zhu, Y.-L. Bai, I. Zhang, D. Sun, J. Fang and S. Zhu, *Chem. Commun.*, 2014, **50**, 14674-14677; (j) J.-R. Li, J. Yu, W. Lu, L.-B. Sun, J. Sculley, P. B. Balbuena and H.-C. Zhou, *Nat Commun.*, 2013, **4**, 1538-1545.
- (a) J. J. Perry IV, J. A. Perman and M. J. Zaworotko, *Chem. Soc. Rev.*, 2009, **38**, 1400-1417; (b) V. Guillerm, D. Kim, J. F. Eubank, R. Luebke, X. Liu, K. Adil, M. S. Lah and M. Eddaoudi, *Chem. Soc. Rev.*, 2014, **43**, 6141-6172; (c) R. Chakrabarty, P. S. Mukherjee and P. J. Stang, *Chem. Rev.*, 2011, **111**, 6810-6918; (d) T. R. Cook, Y.-R. Zheng and P. J. Stang, *Chem. Rev.*, 2013, **113**, 734-777; (e) F. Chevreau, T. Devic, F. Salles, G. Maurin, N. Stock and C. Serre, *Angew. Chem., Int. Ed.*, 2013, **52**, 5056-5060; (f) K. Liu, B. Li, Y. L. X. Li, F. Yang, G. Zeng, Y. Peng, Z. Zhang, G. Li, Z. Shi, S. Feng and D. Song, *Chem. Commun.*, 2014, **50**, 5031-5033.
- (a) A. C. Sudik, A. R. Millward, N. W. Ockwig, A. P. Côté, J. Kirsh and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 7110-7118; (b) G. Férey, C. Serre, C. Mellot-Draznicks, F. Millange, S. Surlé, J. Dutour and I. Margiolaki, *Angew. Chem., Int. Ed.*, 2004, **43**, 6296-6301.
- Y. Liu, V. Kravtsov, R. D. Walsh, P. Poddar, H. Srikanth and M. Eddaoudi, *Chem. Commun.*, 2004, 2806-2807.
- (a) Z. Ni, A. Yassar, T. Antoun and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 12752-12753; (b) Y. Liu, V. Ch. Kravtsov, D. V. Beauchamp, J. F. Eubank and M. Eddaoudi, *J. Am. Chem. Soc.*, 2005, **127**, 7266-7267; (c) J.-R. Li, D. J. Timmons and H.-C. Zhou, *J. Am. Chem. Soc.*, 2009, **131**, 6368-6369.
- (a) M. Eddaoudi, J. Kim, J. B. Wachter, H. K. Chae, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2001, **123**, 4368-4369; (b) Perry, V. C. Kravtsov, G. J. McManus and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2007, **129**, 10076-10077.
- J. Park, S. Hong, D. Moon, M. Park, K. Lee, S. Kang, Y. Zou, R. John, G. H. Kim and M. S. Lah, *Inorg. Chem.*, 2007, **46**, 10208-10213.
- V. Guillerm, J. Weseliński-Lukasz, Y. Belmabkhout, A. J. Cairns, V. D'Elia, Wojtas-Lukasz, K. Adil and M. Eddaoudi, *Nature Chem.*, 2014, **6**, 673-680.
- (a) F. Nouar, J. F. Eubank, T. Bousquet, L. Wojtas, M. J. Zaworotko and M. Eddaoudi, *J. Am. Chem. Soc.*, 2008, **130**, 1833-1835; (b) S. Hong, M. Oh, M. Park, J. W. Yoon, J.-S. Chang and M. S. Lah, *Chem. Commun.*, 2009, **36**, 5397-5399.
- M. Eddaoudi, J. Kim, D. Vodak, A. Sudik, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 4900-4904.
- (a) Y. Liu, J.-R. Li, W. M. Verdegall, T.-F. Liu and H.-C. Zhou, *Chem. Eur. J.*, 2013, **19**, 5637-5643; (b) L. Zhang, L. Liu, C. Huang, X. Han, L. a. Guo, H. Xu, H. Hou and Y. Fan, *Cryst. Growth Des.*, 2015, **15**, 3426-3434.
- P. Zhang, B. Li, Y. Zhao, X. Meng and T. Zhang, *Chem. Commun.*, 2011, **47**, 7722-7724.
- B. Moulton, J. J. Lu, A. Mondal and M. J. Zaworotko, *Chem. Commun.*, 2001, 863-864.
- P.-Z. Li, X.-J. Wang, K. Zhang, A. Nalaparaju, R. Zou, R. Zou, J. Jiang and Y. Zhao, *Chem. Commun.*, 2014, **50**, 4683-4685.
- Y. He, R. Krishna and B. Chen, *Energy Environ. Sci.*, 2012, **5**, 9107-9120.
- H.-X. Zhang, H.-R. Fu, H.-Y. Li, J. Zhang and X. Bu, *Chem. - Eur. J.*, 2013, **19**, 11527-11530.
- D. Wang, T. Zhao, Y. Cao, S. Yao, G. Li, Q. Huo and Y. Liu, *Chem. Commun.*, 2014, **50**, 8648-8650.
- (a) S. R. Caskey, A. G. Wong-Foy and A. J. Matzger, *J. Am. Chem. Soc.*, 2008, **130**, 10870-10871; (b) Z. Bao, L. Yu, Q. Ren, X. Lu, S. Deng, *J. Colloid Interface Sci.*, 2011, **353**, 549-556.
- (a) Y. He, Z. Zhang, S. Xiang, F. R. Fronczek, R. Krishna and B. Chen, *Chem. Commun.*, 2012, **48**, 6493-6495; (b) Y. He, S. Xiang, Z. Zhang, S. Xiong, F. R. Fronczek, R. Krishna, M. O'Keeffe and B. Chen, *Chem. Commun.*, 2012, **48**, 10856-10858.
- J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477-1504.