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## Two microporous MOFs constructed from different metal clusters SBUs for selective gas adsorption

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**Two microporous MOFs have been constructed from different metal clusters SBUs. Both of them exhibit highly selective CO<sub>2</sub> over CH<sub>4</sub> and N<sub>2</sub> adsorption capacity owing to their abundant active sites.**

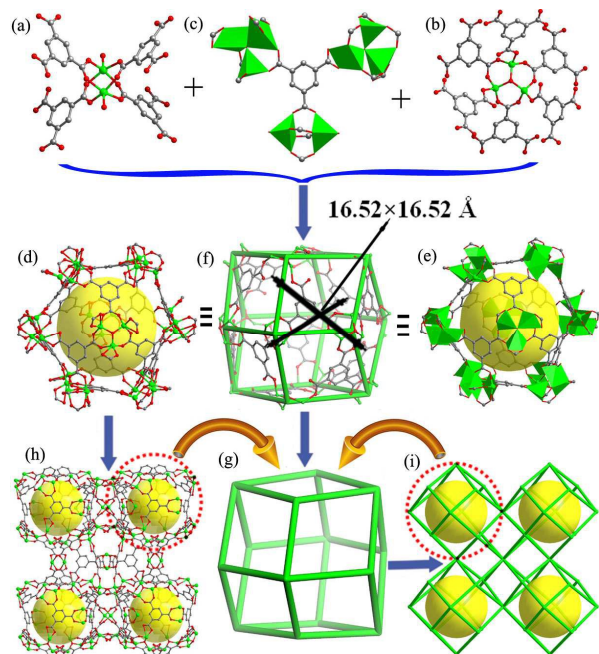
Carbon dioxide (CO<sub>2</sub>) as the primary source of greenhouse gases has always been the focus of international attention.<sup>1</sup> So the exploration of various materials for capture and separation CO<sub>2</sub> are important issues in academic or industrial researches and represent an urgent demand in future energy and environmental technologies fields.<sup>2</sup> Currently, the major research and application concentrate on the traditional activated carbons and zeolites as sorbents, for which they are difficult to tune the pore shape and size or post-modification/decoration in order to meet the capture and selectivity for various gas separations.<sup>3</sup> Porous metal-organic frameworks (PMOFs), as a new type of zeolite analogues and owing to their adjustable and controllable pore structures and functionalities, have become good candidates for selective gas capture and separation.<sup>4-6</sup> Until now, there have some effective strategies been explored for enhancing/improving CO<sub>2</sub> adsorption capacity and selectivity in MOFs, including the control of pore shape and size, the adjustment of pore surface area and volume, the modification/decoration of pore by introducing various active functional sites.<sup>7</sup> Among them, the most promising and achievement strategy is the third one, for example, the generation of coordinatively unsaturated metal centers or open metal sites (OMSs), and the incorporation of specific polar functional groups (-NH<sub>2</sub>, -OH, -CF<sub>3</sub>, uncoordinated nitrogen atoms, flexible C-O-C bonds, etc.) within the porous frameworks which can provide preference interact with CO<sub>2</sub> molecules owing to its large quadrupolar moment.<sup>8,9</sup> Undoubtedly, as much as possible to create high density of OMSs and introduce alkylamines groups in MOFs plays an important role in the selective CO<sub>2</sub> adsorption and separation. In order to achieve this aims, we can construct MOFs using multiple metal clusters subunits (such as the paddle-wheel dimeric copper or zinc clusters, the trimeric clusters, and the tetrameric clusters) as SBUs (secondary building units) which can offer multifarious coordination sites as potential unsaturated metal centers or OMSs by removing coordinated solvent ligands on thermal activation.<sup>8</sup> Moreover, it can often build up anionic frameworks with encapsulation dimethylamine cations guests anchoring onto the surface of MOFs.<sup>10</sup> These OMSs or dimethylamine cations can both greatly increase the interaction between the MOFs and certain particular gas molecules to

manipulate the adsorption selectivity. So the elaboration appropriate ligands to achieve PMOFs containing the above two virtues is undoubtedly hinge. Recently, extensive effort towards utilizing robust 1,3,5-benzenetricarboxylate (H<sub>3</sub>BTC) ligand and its analogues with C<sub>3</sub>-symmetry to assemble classical paddle-wheel dimeric metal clusters as SBUs to target the PMOFs have been demonstrated to be an efficient strategy.<sup>11</sup> By using these tritopic ligands, a series of excellent PMOFs have been synthesized. Inspired by these heuristic/intriguing works, we report herein two PMOFs {[H<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>[Zn<sub>9</sub>O<sub>2</sub>(BTC)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]·3DMA}<sub>n</sub> (**1**), and {[NH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>][Cd(BTC)]·DMA}<sub>n</sub> (**2**) respectively based on distinct metal clusters as SBUs using H<sub>3</sub>BTC ligand. The PMOF **1** contains axis-substituted paddle-wheel dimeric Zn(II)-clusters and μ<sub>3</sub>-oxo centered trimeric Zn(II)-clusters as two distinct SBUs. Noteworthy, the PMOF **1** incorporates twelve open Zn(II) sites in one desolvated polyhedral cage and provides dimethylamine cations at the same time that could facilitate preferential synergistic interactions with CO<sub>2</sub> over CH<sub>4</sub> and N<sub>2</sub> under the same condition. While the PMOF **2** consists of anionic frameworks formed by non-classical paddle-wheel dimeric Cd(II)-clusters which provide abundant dimethylamine cations active sites to perform selective gas adsorption.

The reaction of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O for **2**), H<sub>3</sub>BTC, and H<sub>2</sub>PDA (H<sub>2</sub>PDA = Pyrazine-2,3-dicarboxylic acid) (BTA-AA for **2**, BTA-AA=1H-benzotriazole-1-acetic acid) in DMA at 120 °C for 3 days yielded block-like colorless crystals of **1** (**2**). (For details see ESI) The ligands H<sub>2</sub>PDA and BTA-AA don't appear in the final structures but they play important roles in the syntheses of **1** and **2**. They act as reaction mediation and fine tuning the acid-base reaction conditions to promote the formation of **1** and **2**. Without H<sub>2</sub>PDA and BTA-AA, we only got unknown powder in stead of crystals.

The basic structural unit of **1** contains an anionic [Zn<sub>9</sub>O<sub>2</sub>(BTC)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>] framework based on classical paddle-wheel dimeric {Zn<sub>2</sub>(CO<sub>2</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>} and μ<sub>3</sub>-oxo centered trimeric {Zn<sub>3</sub>O(CO<sub>2</sub>)<sub>6</sub>} clusters as two distinct SBUs (see Fig. 1a-1i). Charge neutrality is achieved by four protonated dimethylamine cations. In comparison, the framework of **1** is similar to a previously reported MOF Zn<sub>9</sub>(BTC)<sub>6</sub>(OH)<sub>2</sub>·2(C<sub>2</sub>H<sub>8</sub>N)·15(DEE) (see ref. 11c). By detailed analysis of this structure, we find that both dangling water ligands can be removed to generate open Zn<sup>2+</sup> sites by degassing and thermal activation process. So in each {Zn<sub>36</sub>O<sub>8</sub>(BTC)<sub>12</sub>} rhombic dodecahedron cage, there will be

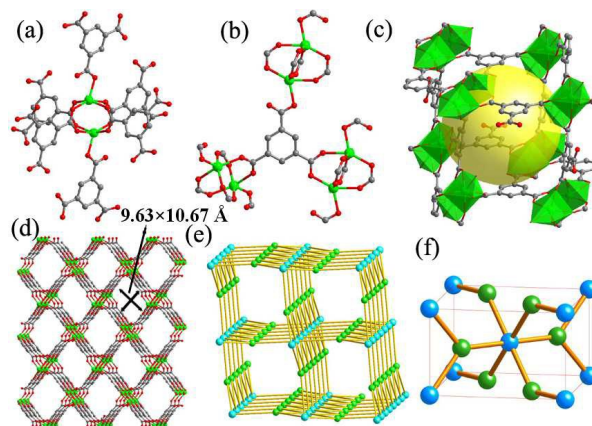
twelve open Zn(II) sites from six dimeric paddle-wheel Zn(II)-clusters SBUs that are activated by thermal liberation of aqua ligands. Such abundant active sites can provide opportunities for probing selective gas adsorption according to references, which caught our attention. Therefore, in this work, we mainly study its selective gas adsorption properties.



**Fig. 1** (a) paddle-wheel dimeric Zn(II)-cluster; (b) trimeric Zn(II)-cluster; (c)  $\text{BTC}^{3-}$  coordination mode; (d) (e) (f) (g)  $\{\text{Zn}_{36}\text{O}_8(\text{BTC})_{12}\}$  rhombic dodecahedron cage; (h) (i) 3D framework and its simplification. (The hydrogen atoms have been omitted for clarity)

The PMOF **2** crystallizes in the monoclinic space group  $P2_1/n$  (For details see Table S1, ESI<sup>†</sup>).<sup>8</sup> The basic structural unit of **2** contains an anionic  $[\text{Cd}(\text{BTC})]$  framework based on non-classical paddle-wheel dimeric Cd(II)-clusters  $\{\text{Cd}_2(\text{CO}_2)_6\}$  as SBUs. Charge neutrality is achieved by one protonated dimethylamine cation. The coordination modes of  $\text{Cd}^{2+}$  centers and  $\text{BTC}^{3-}$  ligands are shown in Fig. 2a-2b. As shown in Fig. 2a, the dimeric Cd(II)-cluster  $\{\text{Cd}_2(\text{CO}_2)_6\}$  exhibits a non-classical paddle-wheel mode with two  $\text{BTC}^{3-}$  molecules appended to its axial directions by two monodentate oxygen. As shown in Fig. 2b, each  $\text{BTC}^{3-}$  ligand bonded to three  $\{\text{Cd}_2(\text{CO}_2)_6\}$  clusters through two different coordinated fashions. On the basis of the above structural feature, eight dimeric paddle-wheel Cd(II)-cluster SBUs are bridged by twelve  $\text{BTC}^{3-}$  ligands to form a  $\{\text{Cd}_{16}(\text{BTC})_{12}\}$  cube cage, in which the eight dimeric cluster SBUs occupy each vertex of the polyhedral cage as shown in Fig. 2c. So the cube cages can be further connected by sharing the paddle-wheel SBUs as vertexes to construct the whole 3D microporous MOF structure with rhombus channels (Fig. 2d). The channels are occupied by several highly disordered dimethylamine cations and solvent DMA molecules. PLATON analysis showed that the effective free volume of **2** is 39.5% of the crystal volume ( $716.5 \text{ \AA}^3$  out of the  $1811.9 \text{ \AA}^3$  unit cell volumes) with dimethylamine cations considered.<sup>12</sup> From the topological point of view, the dimeric cluster SBUs can be abstracted as six-connected nodes, while the  $\text{BTC}^{3-}$  ligands can be

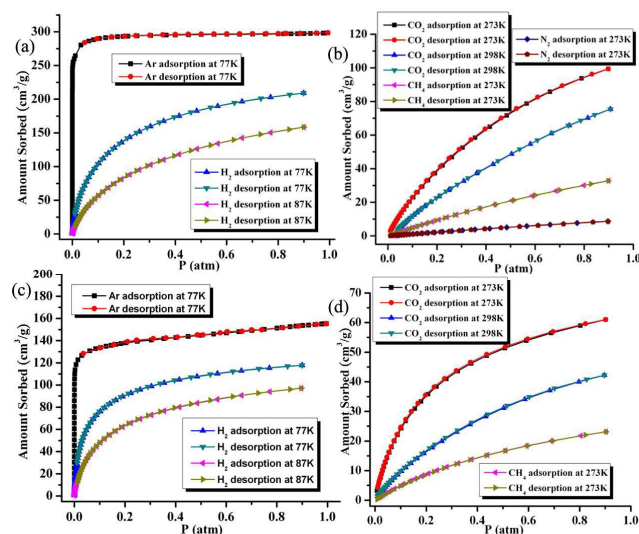
rationalized as three-connected nodes. Based on this simplification, the overall 3D anionic network of **2** can be rationalized as a binodal (3,6)-connected rutile topology with the Schläfli symbol of  $\{4 \cdot 6^2\}_2\{4^2 \cdot 6 \cdot 10 \cdot 8^3\}$  (TD10 = 1180) (Fig. 2e, f).



**Fig. 2** (a) non-classical paddle-wheel dimeric Cd(II)-cluster; (b)  $\text{BTC}^{3-}$  coordination mode; (c)  $\{\text{Cd}_{16}(\text{BTC})_{12}\}$  cube cage; (d) 3D framework; (e) (f) rutile topology (colour code: turquoise, six-connected nodes dimeric cluster, green, three-connected nodes  $\text{BTC}^{3-}$ ). (The hydrogen atoms have been omitted for clarity)

The inherent porosity and potential abundant active sites of the PMOFs **1** and **2** provide opportunities for probing gas adsorption properties. The PXRD patterns indicate that the activated **1a** and **2a** have high crystalline form (Fig. S1). Thermogravimetric (TG) analyses (Fig. S2 and S3) indicate that **1**, **1a** and **2**, **2a** are thermally stable up to  $290 \text{ }^\circ\text{C}$ . Besides, compounds **1** and **2** also exhibit amazing chemical stability. After being immersed in deionized water and organic solvents ( $\text{C}_2\text{H}_5\text{OH}$  and acetone) for 12 hours, they all remain their structural integrity verified by the PXRD patterns, as shown in Fig. S4 and Fig. S5. So, Ar,  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2$  sorption isotherms were carried out to examine their gases loading capacity. Ar sorption measurement for activated **1a** and **2a** were measured at 77 K and 1 atm as shown in Fig. 3a and 3c, respectively. The uptake amount of Ar increases abruptly at the start of the experiment and reaches a plateau about  $298.7 \text{ cm}^3/\text{g}$  (STP) for **1a** and  $205.4 \text{ cm}^3/\text{g}$  (STP) for **2a**, respectively. According to Ar adsorption data, the apparent Brunauer-Emmett-Teller (BET) and Langmuir surface areas are  $844, 1132 \text{ m}^2/\text{g}$  for **1a** and  $406, 539 \text{ m}^2/\text{g}$  for **2a**, respectively. As we can see, the Ar adsorption and desorption are reversible. The median pore size determined by analyzing the Ar isotherm at 77 K is about  $0.58 \text{ nm}$  for **1a** and  $0.54 \text{ nm}$  for **2a** (Fig. S7), and the mainly pores distributions of the two compounds is *ca.*  $4.78\text{--}8.25 \text{ \AA}$  for **1a** and *ca.*  $4.43\text{--}8.65 \text{ \AA}$  for **2a**, respectively. The cage size of **1** measured from the crystal data is *ca.*  $16.52 \times 16.52 \text{ \AA}$  (measured between the two opposite carbon atoms subtract their radius, Fig. 1f). The pore of **2** is measured from the crystal data *ca.*  $9.63 \times 10.67 \text{ \AA}$  (measured between the centers of the two opposite faces deduct their thickness in cube cage, Fig. 2d). In their pores, dimethylamine cations also occupy part of the space. So the gases are not filled the whole cavities and have some weak interactions with the internal surface of the pores.  $\text{H}_2$  sorption isotherms of **1a** and **2a** were also carried out to explore their potential storage application for this attractive energy carrier gas. As shown in Fig. 3a and 3c, the isotherm shows typical type-I behaviours with

good reversibility. The H<sub>2</sub> uptake of **1a** and **2a** reaches *ca.* 209 cm<sup>3</sup>/g (STP) and 118 cm<sup>3</sup>/g (STP) at 77 K and 1 atm, respectively. This storage capacity is comparable with that of many previous MOFs under the same conditions.<sup>13</sup> The H<sub>2</sub> adsorption enthalpies were estimated from the H<sub>2</sub> isotherms at 77 and 87 K by using virial equation.<sup>14</sup> The enthalpies of the adsorption are 7.6–6.2 kJ/mol for **1a** (Fig. S8a) and 8.1–6.5 kJ/mol for **2a** (Fig. S8b), which can compare to the values of many reported MOFs.<sup>13</sup>

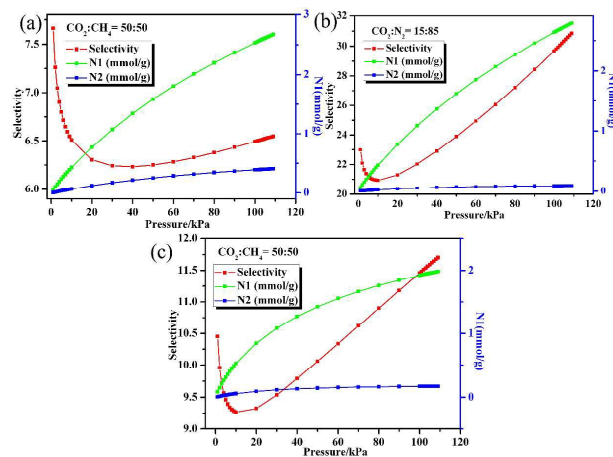


**Fig. 3** (a) (c) Ar/H<sub>2</sub> sorption isotherms for **1a** and **2a**; (b) (d) selective uptake of CO<sub>2</sub> over CH<sub>4</sub> and N<sub>2</sub> for **1a** and **2a**.

The relatively higher H<sub>2</sub> adsorption capacity and the abundant host-guest active sites encourage us to further perform other gases sorption for **1a** and **2a**. We expected that there will be better selectivity of CO<sub>2</sub> over CH<sub>4</sub> and N<sub>2</sub>, owing to the significant quadrupole moment of CO<sub>2</sub> might induce a stronger interaction with the open metal sites and dimethylamine cations dual active sites for **1a** (only dimethylamine cations active sites for **2a**) as revealed in other MOF materials.<sup>8,15,20</sup> So CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> adsorption studies have been systematically carried out at 273 K and 1 atm. Indeed, as the experiment reveal, the compounds **1a** and **2a** both show interesting selective gas adsorption for CO<sub>2</sub> over CH<sub>4</sub> and N<sub>2</sub> at 273 K and 1 atm. As shown in Fig. 3b and 3d, they show comparatively high adsorption amount of CO<sub>2</sub> at 273 K and 1 atm (*ca.* 99 cm<sup>3</sup>/g (STP) for **1a** and 61 cm<sup>3</sup>/g (STP) for **2a**), while only limited amount of CH<sub>4</sub> (*ca.* 32 cm<sup>3</sup>/g (STP) for **1a** and 23 cm<sup>3</sup>/g (STP) for **2a**) in the same condition, respectively. In contrast, they are found almost no N<sub>2</sub> uptake (*ca.* 8 cm<sup>3</sup>/g (STP) for **1a**). The CO<sub>2</sub> uptakes are nearly 3.1 times higher than that of CH<sub>4</sub> for **1a** and 2.7 times for **2a** at 273 K, while 12.4 times higher than that of N<sub>2</sub> for **1a** at 273 K. These selectivities of CO<sub>2</sub> over CH<sub>4</sub> are a little higher than that in the famous MOF-5 and MFI zeolite which the reported values are 2 and 2.5, respectively.<sup>16</sup> Meanwhile, the adsorption amount of CH<sub>4</sub> for **1a** are also a little higher than that of N<sub>2</sub>, which are attributed to the higher polarizability of CH<sub>4</sub> vs. N<sub>2</sub>.<sup>20e,f</sup> Furthermore, by careful analysis the structure of **1**, we find that there also exist the uncoordinated carboxyl groups dangling on the surface of the pores. As references illustrated, as an electron-donating group, the uncoordinated carboxyl group can strengthen the distribution of the electrostatic field in the pores of MOFs to

emphasize the CO<sub>2</sub>–framework interactions, which may also enhance the adsorption selectivity of CO<sub>2</sub>/CH<sub>4</sub> mixture in MOFs.<sup>15,17</sup> The strong interaction between CO<sub>2</sub> and the framework is further confirmed from the isosteric heat of CO<sub>2</sub> adsorption value ( $Q_{st}$ =29–13.6 kJ/mol for **1a** and  $Q_{st}$ =34.7–29.6 kJ/mol for **2a**), as calculated from the adsorption data at 273 and 298 K (Fig. S9).<sup>14</sup> The  $Q_{st}$  of the two compounds can compared to many reported MOFs.<sup>17</sup> These selective adsorptions of CO<sub>2</sub> over CH<sub>4</sub> and N<sub>2</sub> promise their utilization in binary CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> separation or ternary CO<sub>2</sub>/CH<sub>4</sub>/N<sub>2</sub> separation, which may be applied in natural gas purification for energy production and greenhouse gas capturing for environmental protection.

To evaluate the CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> binary mixture selectivities of **1a** and **2a** under mixture gas conditions with single-component isotherms at 273 K, the ideal adsorbed solution theory (IAST)<sup>18</sup> calculation coupled was employed to predict multi-component adsorption behaviors. The predicted adsorption selectivities in **1a** and **2a** for binary CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> (only for **1a**) with mole ratios of 50:50 and 15:85 as a function of total bulk pressure are shown in Fig. 4. The calculated CO<sub>2</sub>/CH<sub>4</sub> selectivities of **1a** and **2a** are 7.7 and 11.7, respectively, which are a little higher than some reported famous MOFs under similar conditions, such as ZIF-100 (5.9),<sup>19a</sup> MOF-177 (4.4),<sup>19b</sup> and CNT@Cu<sub>3</sub>BTC)<sub>2</sub> (5.6).<sup>19c</sup> The initial value of selectivity for CO<sub>2</sub>/N<sub>2</sub> is 23 for **1a** and the selectivity is 30 at 1 bar, respectively. The values are comparable to those high selectivities MOFs functionalized with the OMSs.<sup>10,20</sup>



**Fig. 4** IAST adsorption selectivities of (a) (b) **1a** and (c) **2a**.

In order to explain the selectivity of CO<sub>2</sub> adsorption for **1a** and **2a**, CO<sub>2</sub> binding sites were simulated with grand canonical Monte Carlo (GCMC) using Materials Studio.<sup>9e,15b,21</sup> As shown in Fig. S12 and S13, the most preferential binding sites of the two compounds are different. In **1a**, the CO<sub>2</sub> molecules locate around both of the OMSs hanging on the dimeric Zn(II)-cluster (Fig. S12a) ( $C\cdots Zn = 4.17 \text{ \AA}$ ) and the  $[NH_2(CH_3)_2]^+$  ( $C\cdots N = 4.23 \text{ \AA}$ ) (Fig. S12b), indicating that there are stronger binding interactions for both of them than the other active sites. While in **2a**, the CO<sub>2</sub> molecules locate around the  $[NH_2(CH_3)_2]^+$  ( $C\cdots N = 3.95 \text{ \AA}$ ) which embedded in the small neck (Fig. S13), suggests there is stronger binding interaction between them. These simulated results show good agreement with the experimental values.

In conclusion, two microporous MOFs have been constructed

from different metal clusters SBUs. The PMOF **1** represents a  $\{Zn_{36}O_8(BTC)_{12}\}$  rhombic dodecahedron cages-based 3D microporous structure constructed from classical paddle-wheel dimeric  $\{Zn_2(CO_2)_4(H_2O)_2\}$  and  $\mu_3$ -oxo centered trimeric  $\{Zn_3O(CO_2)_6\}$  clusters as two distinct SBUs, while the PMOF **2** displays a microporous 3D structure built by non-classical paddle-wheel dimeric  $\{Cd_2(CO_2)_6\}$  clusters as SBUs. Moreover, they both exhibit highly selective uptake for  $CO_2$  over  $CH_4$  and  $N_2$  owing to abundant active sites, which provides insight into the potential applications of this material in binary  $CO_2/CH_4$  and  $CO_2/N_2$  separation or ternary  $CO_2/CH_4/N_2$  gas separation.

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## Notes and references

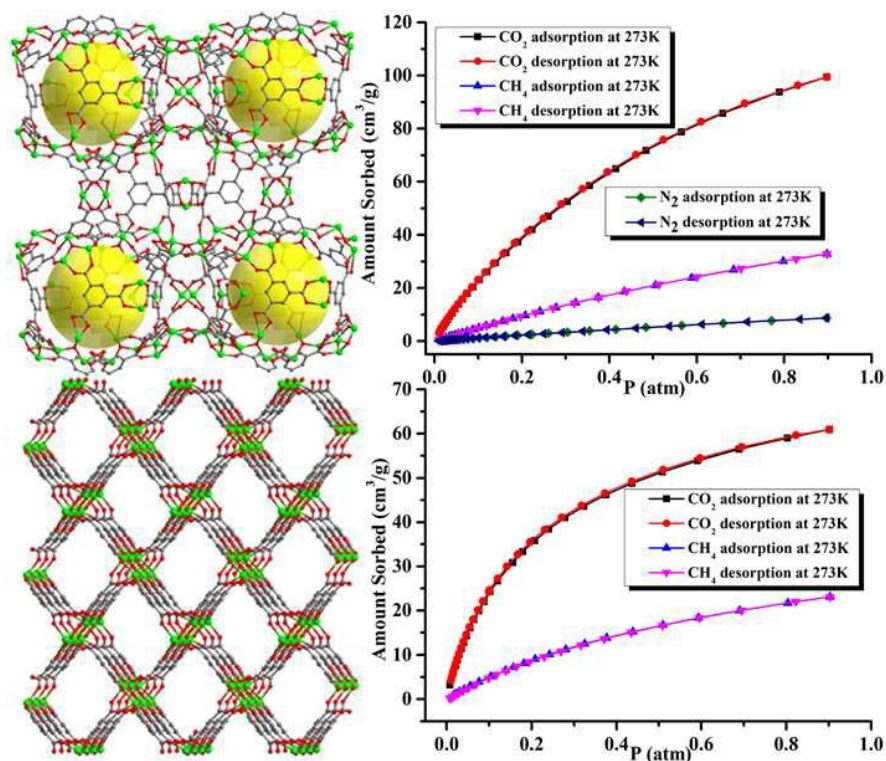
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<sup>c</sup> Electronic Supplementary Information (ESI) available: CCDC1060331 for **1** and 1060332 for **2**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

- J. K. Casper, *Greenhouse Gases: Worldwide Impacts*; Infobase Publishing: New York, 2010.
- (a) L. Y. Kong, Z. H. Zhang, H. F. Zhu, H. Kawaguchi, T. Okamura, M. Doi, Q. Chu, W. Y. Sun and N. Ueyama, *Angew. Chem., Int. Ed.*, 2005, **44**, 4352; (b) D. M. D'Alessandro, B. Smit and J. R. Long, *Angew. Chem., Int. Ed.*, 2010, **49**, 6058; (c) J. R. Li, J. Sculley and H. C. Zhou, *Chem. Rev.*, 2012, **112**, 869; (d) P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, L. Wojtas, M. Eddaoudi, M. J. Zaworotko, *Nature*, 2013, **495**, 80; (e) Z. Zhang, Z. Yao, S. Xiang and B. Chen, *Energy Environ. Sci.*, 2014, **7**, 2868.
- (a) D. W. Beck, *Zeolite Molecular Sieves*, John Wiley & Sons, New York, 1974; (b) S. M. Auerbach, K. A. Carrado and P. K. Dutta, *Handbook of Zeolite Science and Technology*, Marcel Dekker, Inc., New York, 2003; (c) R. R. Xu, W. Q. Pang, J. H. Yu, Q. S. Huo and J. S. Chen, *Chemistry of Zeolites and Related Porous Materials: Synthesis and Structure*, John Wiley & Sons (Asia) Pet Ltd., Singapore, 2007.
- (a) D. J. Tranchemontagne, J. L. Mendoza-Cortes, M. O'Keeffe and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1257; (b) L. J. Murray, M. Dinca and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294; (c) J. R. Li, J. Sculley, H. C. Zhou, *Chem. Rev.*, 2012, **112**, 869; (d) Y. He, W. Zhou, G. Qian, B. Chen, *Chem. Soc. Rev.*, 2014, **43**, 5657.
- (a) S. Xiang, Y. He, Z. Zhang, H. Wu, W. Zhou, R. Krishna, B. Chen, *Nat. Commun.*, 2012, **3**, 954; (b) L. Pan, D. H. Olson, L. R. Ciemnomolnski, R. Heddy and J. Li, *Angew. Chem., Int. Ed.*, 2006, **45**, 616; (c) R. Q. Zou, H. Sakurai, S. Han, R. Q. Zhong and Q. Xu, *J. Am. Chem. Soc.*, 2007, **129**, 8402; (d) D. Wang, T. Zhao, Y. Cao, S. Yao, G. Li, Q. Huo and Y. Liu, *Chem. Commun.*, 2014, **50**, 8648.
- (a) Y. B. Zhang, W. X. Zhang, F. Y. Feng, J. P. Zhang and X. M. Chen, *Angew. Chem., Int. Ed.*, 2009, **48**, 5287; (b) Q. R. Fang, G. S. Zhu, Z. Jin, Y. Y. Ji, J. W. Ye, M. Xue, H. Yang, Y. Wang and S. L. Qiu, *Angew. Chem., Int. Ed.*, 2007, **46**, 6638; (c) Y. Liu, J. F. Eubank, A. J. Cairns, J. Eckert, V. C. Kravtsov, R. Luebke and M. Eddaoudi, *Angew. Chem., Int. Ed.*, 2007, **46**, 3278; (d) T. L. Hu, H. Wang, B. Li, R. Krishna, H. Wu, W. Zhou, Y. Zhao, Y. Han, X. Wang, W. Zhu, Z. Yao, S. Xiang and B. Chen, *Nat. Commun.*, 2015, **6**, 7328.
- (a) D. X. Xue, A. J. Cairns, Y. Belmabkhout, L. Wojtas, Y. Liu, M. H. Alkord and M. Eddaoudi, *J. Am. Chem. Soc.*, 2013, **135**, 7660; (b) Q. Yan, Y. Lin, C. Kong and L. Chen, *Chem. Commun.*, 2013, **49**, 6873; (c) D. D. Zhou, C. T. He, P. Q. Liao, W. Xue, W. X. Zhang, H. L. Zhou, J. P. Zhang and X. M. Chen, *Chem. Commun.*, 2013, **49**, 11728; (d) H. P. Ma, H. Ren, X. Q. Zou, F. X. Sun, Z. J. Yan, K. Cai, D. Y. Wang and G. S. Zhu, *J. Mater. Chem. A*, 2013, **1**, 752; (e) F. Wang, Y. X. Tan, H. Yang, Y. Kang and J. Zhang, *Chem. Commun.*, 2012, **48**, 4842.
- (a) E. D. Bloch, W. L. Queen, R. Krishna, J. M. Zadrozny, C. M. Brown and J. R. Long, *Science*, 2012, **335**, 1606; (b) X. S. Wang, L. Meng, Q. G. Cheng, C. Kim, L. Wojtas, M. Chrzanowski, Y. S. Chen, X. P. Zhang and S. Q. Ma, *J. Am. Chem. Soc.*, 2011, **133**, 16322; (c) Y. W. Li, J. R. Li, L. F. Wang, B. Y. Zhou, Q. Chen and X. H. Bu, *J. Mater. Chem. A*, 2013, **1**, 495.
- (a) M. H. Choi, H. J. Park, D. H. Hong and M. P. Suh, *Chem. Eur. J.*, 2013, **19**, 17432; (b) X. X. Lv, L. J. Li, S. F. Tang, C. Wang and X. B. Zhao, *Chem. Commun.*, 2014, **50**, 6886; (c) L. Hou, W. J. Shi, Y. Y. Wang, Y. Guo, C. Jin and Q. Z. Shi, *Chem. Commun.*, 2011, **47**, 5464; (d) B. S. Zheng, J. F. Bai, J. G. Duan, L. Wojtas and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2011, **133**, 748; (e) J. S. Qin, D. Y. Du, W. L. Li, J. P. Zhang, S. L. Li, Z. M. Su, X. L. Wang, Q. Xu, K. Z. Shao and Y. Q. Lan, *Chem. Sci.*, 2012, **3**, 2114; (f) Y. W. Li, K. H. He and X. H. Bu, *J. Mater. Chem. A*, 2013, **1**, 4186.
- (a) Q. C. Zhang, Y. Liu, X. Bu, T. Wu and P. Y. Feng, *Angew. Chem., Int. Ed.*, 2008, **47**, 113; (b) C. Y. Sun, X. L. Wang, X. Zhang, C. Qin, P. Li, Z. M. Su, D. X. Zhu, G. G. Shan, K. Z. Shao, H. Wu and J. Li, *Nat. Commun.*, 2013, **4**, 2717.
- (a) J. I. Feldblyum, M. Liu, D. W. Gidley and A. J. Matzger, *J. Am. Chem. Soc.*, 2011, **133**, 18257; (b) S. T. Zheng, J. T. Bu, Y. F. Li, T. Wu, F. Zuo, P. Y. Feng and X. Bu, *J. Am. Chem. Soc.*, 2010, **132**, 17062; (c) X. R. Hao, X. L. Wang, K. Z. Shao, G. S. Yang, Z. M. Su and G. Yuan, *CrystEngComm*, 2012, **14**, 5596.
- A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, 2003.
- (a) Y. H. Hu and L. Zhang, *Adv. Mater.*, 2010, **22**, 117; (b) X. Lin, I. Telepeni, A. J. Blake, A. Dailly, C. M. Brown, J. M. Simmons, M. Zoppi, G. S. Walker, K. M. Thomas, T. J. Mays, P. Hubberstey, N. R. Champness and M. Schröder, *J. Am. Chem. Soc.*, 2009, **131**, 2159; (c) A. J. Lan, K. H. Li, H. H. Wu, L. Z. Kong, N. Nijem, D. H. Olson, T. J. Emge, Y. J. Chabal, D. C. Langreth, M. C. Hong and J. Li, *Inorg. Chem.*, 2009, **48**, 7165.
- (a) A. J. Lan, K. H. Li, H. H. Wu, L. Z. Kong, N. Nijem, D. H. Olson, T. J. Emge, Y. J. Chabal, D. C. Langreth, M. C. Hong and J. Li, *Inorg. Chem.*, 2009, **48**, 7165; (b) D. C. Zhong, J. B. Lin, W. G. Lu, L. Jiang and T. B. Lu, *Inorg. Chem.*, 2009, **48**, 8656.
- (a) J. R. Li, Y. Ma, M. C. McCarthy, J. Sculley, J. Yu, H. K. Jeong, P. B. Balbuena and H. C. Zhou, *Coord. Chem. Rev.*, 2011, **255**, 1791; (b) T. Panda, P. Pachfule, Y. F. Chen, J. W. Jiang and R. Banerjee, *Chem. Commun.*, 2011, **47**, 2011.
- (a) Q. Y. Yang, C. L. Zhong, *J. Phys. Chem. B*, 2006, **110**, 17776; (b) R. Babarao, Z. Q. Hu, J. W. Jiang, S. Chempath and S. I. Sandler, *Langmuir*, 2007, **23**, 659.
- (a) J. Liu, P. K. Thallapally, B. P. McGrail, D. R. Brown and J. Liu, *Chem. Soc. Rev.*, 2012, **41**, 2308; (b) W. Mu, D. H. Liu, Q. Y. Yang and C. L. Zhong, *Microporous Mesoporous Mater.*, 2010, **130**, 76.
- A. L. Myers and J. M. Prausnitz, *AIChE J.*, 1965, **11**, 121.
- (a) B. Wang, A. P. Côté, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Nature*, 2008, **453**, 207; (b) D. Saha, Z. B. Bao, F. Jia and S. G. Deng, *Environ. Sci. Technol.*, 2010, **44**, 1820; (c) Z. H. Xiang, X. Peng, X. Cheng, X. J. Li and D. P. Cao, *J. Phys. Chem. C*, 2011, **115**, 19864.
- (a) S. S. Chen, M. Chen, S. Takamizawa, P. Wang, G. C. Lv and W. Y. Sun, *Chem. Commun.*, 2011, **47**, 4902; (b) Y. X. Tan, Y. P. He and J. Zhang, *Inorg. Chem.*, 2011, **50**, 11527; (c) Z. J. Zhang, Z. Li and J. Li, *Langmuir*, 2012, **28**, 12122; (d) L. T. Du, Z. Y. Lu, K. Y. Zheng, J. Y. Wang, X. Zheng, Y. Pan, X. Z. You and J. F. Bai, *J. Am. Chem. Soc.*, 2013, **135**, 562; (e) B. Liu, Y. Li, L. Hou, G. P. Yang, Y. Y. Wang and Q. Z. Shi, *J. Mater. Chem. A*, 2013, **1**, 6535; (f) V. P. Mulgundmath, F. H. Tezel, T. Saatcioglu and T. C. Golden, *Can. J. Chem. Eng.*, 2012, **90**, 730.
- (a) *Accelrys, Materials Studio Getting Started, release 5.0*; Accelrys Software, Inc.: San Diego, CA, 2009; (b) J. B. Lin, J. P. Zhang and X. M. Chen, *J. Am. Chem. Soc.*, 2010, **132**, 6654.

## Graphic Abstract

**Two microporous MOFs constructed from different metal clusters SBUs for selective gas adsorption**Yun-Wu Li,<sup>a,b</sup> Jian Xu,<sup>a</sup> Da-Cheng Li,<sup>b</sup> Jian-Min Dou,<sup>b</sup> Hui Yan,<sup>b</sup> Tong-Liang Hu<sup>\*a</sup> and Xian-He Bu<sup>\*a</sup>

Two microporous MOFs have been constructed from different metal clusters SBUs. Both PMOFs exhibit highly selective uptake for CO<sub>2</sub> over CH<sub>4</sub> and N<sub>2</sub> owing to abundant active sites.