ChemComm

COMMUNICATION

Counter-cation modulation of hydrogen and methane storage in a sodalite-type porous metal–organic framework†

Yun-Nan Gong, Miao Meng, Di-Chang Zhong, Yong-Liang Huang, Long Jiang and Tong-Bu Lu*

A μ₄-Cl bridged anionic sodalite-type porous metal–organic framework (Et₂NH₂)₃[(Cu₄Cl)₃(TTCA)₈]·26DEF was synthesized, in which Et₂NH₂⁺ can be exchanged by Li⁺ cations. The results of gas measurements indicate that Et₂NH₂⁺ and Li⁺ are beneficial for methane and hydrogen storage, respectively.

In recent years, hydrogen is considered as an ideal clean energy source since no greenhouse gases or other environmentally harmful molecules are emitted during energy extraction from hydrogen. Like hydrogen, methane is also considered as a clean energy gas because the combustion of methane produces the smallest amount of carbon dioxide per unit of heat produced among fossil fuels. However, the design and construction of materials that can effectively store hydrogen and methane remain major challenges.[1]

Metal–organic frameworks (MOFs) are a new class of porous materials that have shown great potential for hydrogen and methane storage.[2] Compared with other solid storage materials, such as carbon nanotubes,[3] activated carbon,[4] and hydrogen clathrates,[5] porous MOFs exhibit a variety of pore surface properties and chemically-tunable structures.[6] Nevertheless, most porous MOF materials still show relatively low hydrogen and methane storage capacity.[7] To enhance hydrogen and methane storage in MOF materials, most research efforts have focused on either (1) increasing the MOF pore volume and surface area to enhance the gas storage capacity or (2) incorporating functional moieties to improve the gas affinity in MOFs. Previous investigations[8] have proved that hydrogen and methane storage can be enhanced significantly by introducing functional moieties into MOF systems. For instance, a Li-doped MOF MIL-53 was reported to exhibit nearly double the hydrogen uptake compared with the undoped MOF.[8b] Similarly, Cao *et al.* also found that a Li-doped MOF can significantly enhance the methane uptake.[8e] Herein, we report a μ₄-Cl bridged anionic sodalite-type porous

MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China. E-mail: lutongbu@mail.sysu.edu.cn; Fax: +86-20-84112921

MOF, (Et₂NH₂)₃[(Cu₄Cl)₃(TTCA)₈]·26DEF (**1**–DEF) (TTCA = triphenylene-2,6,10-tricarboxylate, DEF = *N,N*-diethylformamide), and its gas adsorption properties were investigated.

Solvothermal reaction of triphenylene-2,6,10-tricarboxylic acid (H₃TTCA)[9] with CuCl₂·2H₂O in DEF at 110 °C for 48 h led to the formation of green block-shaped crystals of **1**–DEF. The result of single x-ray structural analysis‡ reveals that **1**–DEF crystallizes in the cubic space groups *Fm*3̄*c*, which adopts square-planar Cu₄(μ₄-Cl) as a secondary building unit (SBU). In **1**, all four Cu atoms in the SBU are five-coordinated with a square-pyramidal geometry (Fig. 1a and 1b), the μ₄-Cl atom lies at a site with 4/*m* imposed symmetry, the TTCA ligand lies about a threefold axis, and the Cu1 atom lies on a mirror plane. Six Cu₄(μ₄-Cl) SBUs and eight TTCA ligands define the faces of a truncated octahedron (Fig. 1c), resulting in a sodalite-type cage with the dimensions of 20.7 × 20.7 × 20.7 Å (based on the distances between Cl atoms). Each cage is surrounded by six neighboring cages to form a three-dimensional (3D) anionic sodalite-type porous metal–organic framework (Fig. 1d), which can be simplified to a 3,8-connected topology
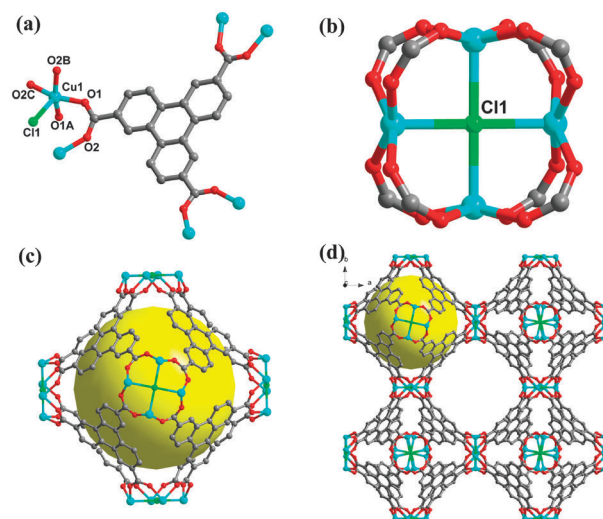

Fig. 1 (a) The coordination environment of Cu1 and the symmetric bridging mode of TTCA³⁻ anions in **1** (symmetry operations: A: *x, y, −z*; B: *x, y* + 1/2, *z*; C: *x, y* + 1/2, *−z*); (b) the μ₄-Cl bridge; (c) the sodalite-type truncated-octahedral unit; (d) the 3D sodalite-type porous metal–organic framework of **1**.

network (Fig. S3, ESI†). Very recently, two similar sodalite-type metal–organic frameworks constructed from the BTC (BTC = 1,3,5-benzenetricarboxylate) ligand were reported.[10] However, the extension from BTC to TTCA leads to a significant increase in pore volume of **1**, so the framework of **1** must have more merits for gas storage. In **1**, the anionic charges are balanced by $Et_2NH_2^+$ cations decomposed from DEF.[10b] The pores of **1**–DEF are filled with disordered DEF molecules, and the solvent-accessible volume calculated using PLATON[11] is 68.9%. Moreover, soaking **1**–DEF in methanol leads to the exchange of DEF guest molecules with methanol to give **1**–MeOH.

The results of thermogravimetric analysis (TGA) indicate that **1**–DEF shows continuous weight loss in the temperature range from 30 to 400 °C, while **1**–MeOH shows plateaus from 60 to 300 °C (Fig. S4, ESI†). The results of variable temperature PXRD measurements of **1**–DEF demonstrate that the framework of **1** is stable up to 300 °C (Fig. S5, ESI†). Furthermore, the $Et_2NH_2^+$ cation in **1**–DEF can be exchanged with the Li^+ cation. Cation exchange was performed by soaking the samples of **1**–DEF in a saturated solution of LiCl in methanol for 7 days to generate **1′·Li**–MeOH. Elemental analysis of bulk Li^+-exchanged samples confirms that no residual N remains in the sample, and the result of ICP-AES measurement indicates that the Li : Cu ratio is approximately 1 : 4 (Table S1, ESI†).[12]

To evaluate the porous features of **1** and **1′·Li**, gas adsorption studies were conducted. N_2 adsorption measurements for **1** and **1′·Li** at 77 K and 1 atm revealed type-I isotherms, which are characteristics of microporous materials (Fig. 2). The Brunauer–Emmett–Teller (BET) surface areas, which were calculated by fitting to the BET equation, were found to be 1680 and 1870 $m^2 g^{-1}$ for **1** and **1′·Li**, respectively. Furthermore, **1** exhibits a micropore volume of 0.639 $cm^3 g^{-1}$, which is slightly less than that of **1′·Li** (0.724 $cm^3 g^{-1}$). These values are significantly higher than those observed for the isoreticular framework reported by Zhang and co-workers.[10b] The CO_2 adsorption isotherm of **1** is measured at 195 K and 1 atm. As shown in Fig. 2, the isotherm shows obvious two-step behavior. The adsorption amounts in the two steps are estimated to be 228 and 351 $cm^3 g^{-1}$ (STP) using the Langmuir equation (Fig. S6, ESI†), which match the calculated pore volume of the one-dimensional (1D) channel (361 $cm^3 g^{-1}$) and the whole

pore system (1D channels and cages, 555 $cm^3 g^{-1}$). This result implies that at low pressure (0–20 kPa), the adsorption should mainly occur in the 1D channels, and the adsorption within the sodalite-type cages is only available at relatively high pressure (20–100 kPa). Interestingly, such stepwise behavior was not observed for N_2 at 77 K, which can be attributed to the small molecular size of N_2 (CO_2 3.4 Å, N_2 3.1 Å).[13]

H_2 adsorption measurements were also conducted for **1** and **1′·Li** at 77 K. As shown in Fig. 3a, the H_2 storage capacities at 1 bar are 0.91 and 1.14 wt% for **1** and **1′·Li**, respectively. As we know, in the low-pressure region ($P < 1$ bar), the amount of H_2 adsorption is mainly controlled by the H_2 affinity towards the framework, which can be quantified by the isosteric heat of adsorption.[14] Virial analysis of the H_2 adsorption isotherms measured at 77 and 87 K (see ESI†) reveals that the adsorption heat of **1′·Li** is 4.74 kJ mol^{-1}, which is higher than that of **1** (3.38 kJ mol^{-1}). This suggests that the Li^+ cation has a crucial effect on the heat of adsorption of H_2, and affords a higher H_2 binding energy compared with that of the $Et_2NH_2^+$ cation. In addition, the H_2 uptakes for **1** and **1′·Li** at 50 bar are 3.29 and 4.75 wt%, respectively. The amount of H_2 adsorption at high-pressure is correlated with the pore volume and surface area,[15] thus the higher H_2 storage capacity of **1′·Li** is mainly due to the higher pore volume and surface areas of **1′·Li**, indicating that
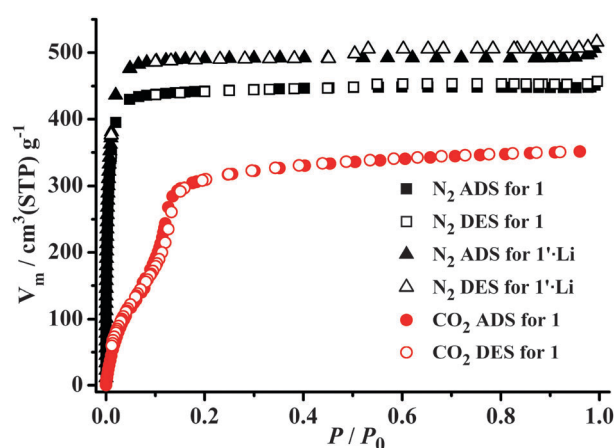

Fig. 2 N_2 adsorption isotherms of **1** and **1′·Li** measured at 77 K, and CO_2 adsorption isotherms of **1** at 195 K.
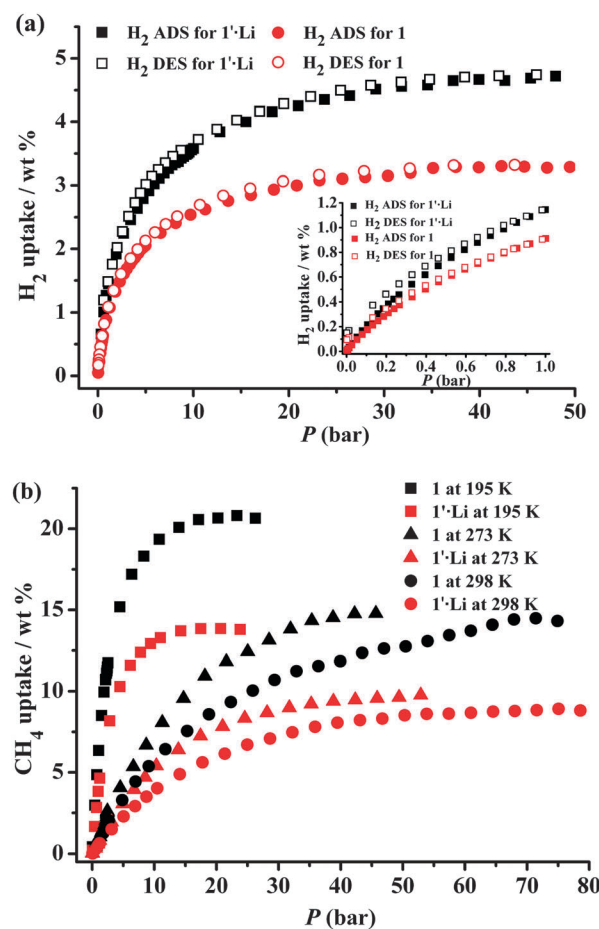

Fig. 3 (a) Low- and high-pressure H_2 adsorption isotherms of **1** and **1′·Li** at 77 K; (b) high-pressure CH_4 adsorption isotherms of **1** and **1′·Li** at various temperatures.

replacing $Et_2NH_2^+$ with smaller Li^+ leads to a higher H_2 storage capacity.

To further evaluate the gas storage capacity of **1** and **1′**·Li, we also measured the methane adsorption of **1** and **1′**·Li at 195, 273 and 298 K (Fig. 3b). For **1**, the amounts of adsorption are 20.81 wt% (201 v/v) at 195 K and 23 bar, followed by 14.78 wt% (143 v/v) at 273 K and 46 bar, and 14.47 wt% (140 v/v) at 298 K and 71 bar, while those for **1′**·Li are 13.84 wt% (134 v/v), 9.76 wt% (94 v/v), and 9.0 wt% (87 v/v) at 195 K/21 bar, 273 K/53 bar, and 298 K/82 bar, respectively (Fig. 3b). These results indicate that **1** displays higher methane storage capacity than that of **1′**·Li at various temperatures, which is different from the trend found in the aforementioned H_2 adsorption study.[16] Virial analysis of the methane adsorption isotherms measured at 273/298 K and 1 atm (see ESI†) reveals that the adsorption heat of **1** is 18.08 kJ mol^{-1}, which is higher than that of **1′**·Li (15.34 kJ mol^{-1}). This suggests that the affinity of $Et_2NH_2^+$ cations towards the methane molecules is stronger than Li^+ cations. At present, we have not fully understood why **1** shows stronger affinity towards methane molecules, probably due to the stronger intermolecular interactions between methane and $Et_2NH_2^+$, as the methane molecule is larger and has more atoms than hydrogen, thus the interactions between methane and $Et_2NH_2^+$ become larger.[17] In addition, in contrast to the methane uptake of some highly porous MOFs at 298 K and 35 bar, such as MOF-200 (41 v/v, BET, 4530 m^2 g^{-1}), MOF-205 (93 v/v, BET, 4460 m^2 g^{-1}) and MOF-210 (53 v/v, BET, 6240 m^2 g^{-1}),[18] **1** (111 v/v at 298 K/35 bar, BET, 1680 m^2 g^{-1}) exhibits a higher methane uptake under the same conditions, indicating that the pore spaces and functional sites of **1** are utilized much more efficiently.

In summary, we have developed a strategy to modulate hydrogen and methane storage by counter-cations exchange. The results demonstrate that the replacement of $Et_2NH_2^+$ with smaller Li^+ leads to an increase in hydrogen uptake due to the increase in pore volume and surface area, as well as the interactions between Li^+ and hydrogen. However, **1** has a higher methane storage compared with **1′**·Li due to the stronger affinity of $Et_2NH_2^+$ cations towards the methane molecules. To our knowledge, counter-cation modulation of hydrogen and methane storage in *one* porous MOF has not been reported so far.

Notes and references

‡ Crystal data for **1**-DEF ($C_{310}H_{394}N_{29}O_{74}Cl_3Cu_{12}$): cubic, space group $Fm\bar{3}c$, $a = b = c = 41.4543(15)$ Å, $V = 71238(4)$ Å^3, $M_r = 6579.51$, $Z = 8$, $\rho_{calcd} = 1.151$ g cm^{-3}, $\mu = 0.791$ mm^{-1}, $T = 173(2)$ K, $R_1 = 0.0353$, w$R_2 = 0.0921$, GOF = 1.068 for 3405 reflections with $I > 2\sigma(I)$. CCDC 900466 (**1**–DEF).

1 S. Q. Ma and H. C. Zhou, *Chem. Commun.*, 2010, **46**, 44.
2 (*a*) M. Dincă, A. Dailly, Y. Liu, C. M. Brown, D. A. Neumann and J. R. Long, *J. Am. Chem. Soc.*, 2006, **128**, 16876; (*b*) M. Dincă and J. R. Long, *J. Am. Chem. Soc.*, 2007, **129**, 11172; (*c*) J. H. Luo, H. W. Xu, Y. Liu, Y. S. Zhao, L. L. Daemen, C. Brown, T. V. Timofeeva, S. Q. Ma and H. C. Zhou, *J. Am. Chem. Soc.*, 2008, **130**, 9626; (*d*) I. Senkovska and S. Kaskel, *Microporous*
Mesoporous Mater., 2008, **112**, 108; (*e*) T. K. Prasad, D. H. Hong and M. P. Suh, *Chem.–Eur. J.*, 2010, **16**, 14043; (*f*) Z. Y. Guo, H. Wu, G. Srinivas, Y. M. Zhou, S. C. Xiang, Z. X. Chen, Y. T. Yang, W. Zhou, M. O'Keeffe and B. L. Chen, *Angew. Chem., Int. Ed.*, 2011, **50**, 3178; (*g*) D. J. Mihalcik, T. Zhang, L. Q. Ma and W. B. Lin, *Inorg. Chem.*, 2012, **51**, 2503; (*h*) S. J. Yang, J. H. Im, H. Nishihara, H. Jung, K. Lee, T. Kyotani and C. R. Park, *J. Phys. Chem. C*, 2012, **116**, 10529.
3 A. D. Leonard, J. L. Hudson, H. Fan, R. Booker, L. J. Simpson, K. J. O'Neill, P. A. Parilla, M. J. Heben, M. Pasquali, C. Kittrell and J. M. Tour, *J. Am. Chem. Soc.*, 2009, **131**, 723.
4 Y. D. Xia, G. S. Walker, D. M. Grant and R. Mokaya, *J. Am. Chem. Soc.*, 2009, **131**, 16493.
5 Y. H. Hu and E. Ruckenstein, *Angew. Chem., Int. Ed.*, 2006, **45**, 2011.
6 (*a*) T. K. Maji, K. Uemura, H. Chang, R. Matsuda and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2004, **43**, 3269; (*b*) L. J. Murray, M. Dincă and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294.
7 (*a*) D. N. Dybtsev, H. Chun, S. H. Yoon, D. Kim and K. Kim, *J. Am. Chem. Soc.*, 2004, **126**, 32; (*b*) D. C. Zhong, J. B. Lin, W. G. Lu, L. Jiang and T. B. Lu, *Inorg. Chem.*, 2009, **48**, 8656; (*c*) M. R. Kishan, J. Tian, P. K. Thallapally, C. A. Fernandez, S. J. Dalgarno, J. E. Warren, B. P. McGrail and J. L. Atwood, *Chem. Commun.*, 2010, **46**, 538; (*d*) S. S. Chen, M. Chen, S. Takamizawa, M. S. Chen, Z. Su and W. Y. Sun, *Chem. Commun.*, 2011, **47**, 752; (*e*) D. C. Zhong, W. X. Zhang, F. L. Cao, L. Jiang and T. B. Lu, *Chem. Commun.*, 2011, **47**, 1204; (*f*) P. Pachfule, R. Das, P. Poddar and R. Banerjee, *Inorg. Chem.*, 2011, **50**, 3855; (*g*) Z. G. Gu, Y. T. Liu, X. J. Hong, Q. G. Zhan, Z. P. Zheng, S. R. Zheng, W. S. Li, S. J. Hu and Y. P. Cai, *Cryst. Growth Des.*, 2012, **12**, 2178.
8 (*a*) S. S. Han and W. A. Goddard, *J. Am. Chem. Soc.*, 2007, **129**, 8422; (*b*) K. L. Mulfort and J. T. Hupp, *J. Am. Chem. Soc.*, 2007, **129**, 9604; (*c*) K. L. Mulfort and J. T. Hupp, *Inorg. Chem.*, 2008, **47**, 7936; (*d*) S. M. Chen, J. Zhang, T. Wu, P. Y. Feng and X. H. Bu, *J. Am. Chem. Soc.*, 2009, **131**, 16027; (*e*) Z. H. Xiang, Z. Hu, D. Q. Cao, W. T. Yang, J. M. Lu, B. Y. Han and W. C. Wang, *Angew. Chem., Int. Ed.*, 2011, **50**, 491.
9 (*a*) J. Y. Choi, J. Kim, H. Furukawa and H. K. Chae, *Chem. Lett.*, 2006, 1054; (*b*) H. Bock, M. Rajaoarivelo, S. Clavaguera and É. Grelet, *Eur. J. Org. Chem.*, 2006, 2889; (*c*) X. S. Wang, S. Q. Ma, D. Q. Yuan, J. W. Yoon, Y. K. Hwang, J. S. Chang, X. Q. Wang, M. R. Jørgensen, Y. S. Chen and H. C. Zhou, *Inorg. Chem.*, 2009, **48**, 7519.
10 (*a*) F. J. Ma, S. X. Liu, C. Y. Sun, D. D. Liang, G. J. Ren, F. Wei, Y. G. Chen and Z. M. Su, *J. Am. Chem. Soc.*, 2011, **133**, 4178; (*b*) Y. X. Tan, Y. P. He and J. Zhang, *Chem. Commun.*, 2011, **47**, 10647.
11 A. L. Spek, *PLATON 99: A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 1999.
12 (*a*) S. H. Yang, S. K. Callear, A. J. Ramirez-Cuesta, W. I. F. David, J. L. Sun, A. J. Blake, N. R. Champness and M. Schröder, *Faraday Discuss.*, 2011, **151**, 19; (*b*) Y. S. Bae, B. G. Hauser, O. K. Farha, J. T. Hupp and R. Q. Snurr, *Microporous Mesoporous Mater.*, 2011, **141**, 231.
13 Y. B. Zhang, W. X. Zhang, F. Y. Feng, J. P. Zhang and X. M. Chen, *Angew. Chem., Int. Ed.*, 2009, **48**, 5287.
14 A. Li, R. F. Lu, Y. Wang, X. Wang, K. L. Han and W. Q. Deng, *Angew. Chem., Int. Ed.*, 2010, **49**, 3330.
15 (*a*) D. Q. Yuan, D. Zhao, D. F. Sun and H. C. Zhou, *Angew. Chem., Int. Ed.*, 2010, **49**, 5357; (*b*) H. Frost, T. Düren and R. Q. Snurr, *J. Phys. Chem. B*, 2006, **110**, 9565.
16 A. W. Thornton, K. M. Nairn, J. M. Hill, A. J. Hill and M. R. Hill, *J. Am. Chem. Soc.*, 2009, **131**, 10662.
17 W. Zhou, H. Wu, M. R. Hartman and T. Yildirim, *J. Phys. Chem. C*, 2007, **111**, 16131.
18 H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. Ö. Yazaydin, R. Q. Snurr, M. O'Keeffe, J. Kim and O. M. Yaghi, *Science*, 2010, **329**, 424.