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## ARTICLE

## High and selective CO<sub>2</sub> uptake in a nitrogen-rich pillar-layered metal organic framework

Chao Chen\*, Minfeng Jia, Gang Wang, Xiaoli Li and Shimin Li

A nitrogen-rich pillar-layered metal organic framework, Co(Imda)(4,4'-bpy), comprised of cobalt (II) clusters interconnected by imidazole-4,5-dicarboxylic acid and 4, 4'-bipyridyl groups was synthesized, and characterized by powder X-ray powder diffraction, N<sub>2</sub> adsorption-desorption measurement, thermogravimetric analysis, and scanning electron microscopy. This material was firstly investigated for CO<sub>2</sub> capture. It exhibited several outstanding attributes as a CO<sub>2</sub> adsorbent: high CO<sub>2</sub> uptake (135 mg/g at 298 K, 1 bar), good separation selectivity against N<sub>2</sub> (CO<sub>2</sub>/N<sub>2</sub> selectivity of ca. 18 at 298 K, 1 bar), fast adsorption kinetics (saturation within 10 min), easy regeneration (298 K, argon purge) and excellent stability in moisture and during consecutive adsorption-desorption cycles.

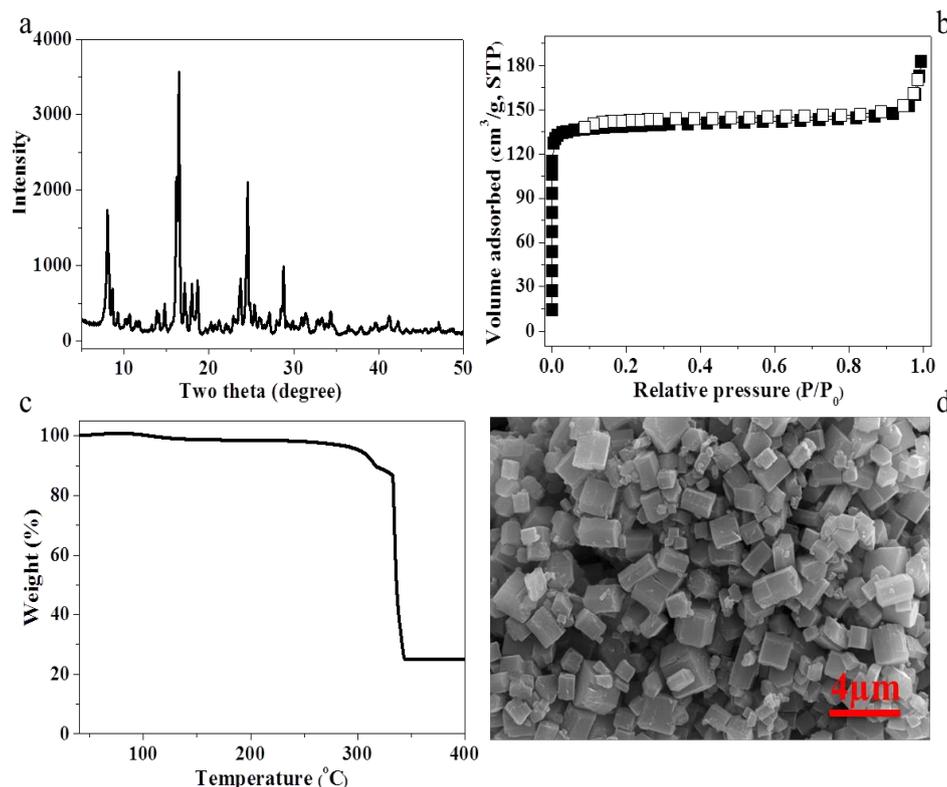
The gradually rising level of CO<sub>2</sub> concentration in the atmosphere, largely caused from the combustion of fossil fuels, has raised serious public concerns about global warming. Carbon capture and sequestration scheme is one approach that holds high promise for reducing CO<sub>2</sub> emissions in short term.<sup>1</sup> At present, large-scale CO<sub>2</sub> capture and separation processes operating in power plants around the world are employing liquid phase amine absorption technology.<sup>2</sup> On the other hand, CO<sub>2</sub> adsorption and separation processes based on solid sorbents have also been actively investigated, which are considered to be more efficient for CO<sub>2</sub> capture owing to their lower regeneration energy cost involved and good cyclic performances.<sup>3</sup> Over the last decade, diverse metal organic frameworks (MOFs) in which metal ions or clusters are interconnected by organic linkers forming crystalline structures with well-ordered micropores have been prepared by solvothermal methods, and increasingly investigated as CO<sub>2</sub> adsorbents.<sup>4</sup> Their excellent structural and chemical properties, such as large surface areas and pore volumes, tunable pore sizes, coordinatively unsaturated metal sites, and surface properties easily adjustable by post-synthetic functionalization seem to make them highly promising as CO<sub>2</sub> adsorbents.<sup>5,6</sup>

Pillar-layered MOFs are consisted of two-dimensional layers (formed by metal ions and organic linkers) that have ligating sites available for linkage with pillars (different organic species) to form three dimensional porous structures, and have been under growing attention recently due to the fact that the two different types of ligand employed allow higher flexibility to tune their structural and chemical properties than for common MOFs that are synthesized from a single ligand species only. So far, only limited groups have considered CO<sub>2</sub> capture by the pillar-layered MOF materials.<sup>7-12</sup> Nugent et al. reported a high gravimetric CO<sub>2</sub> uptake by SIFSIX-2-

Cu-i at 298K and 1 bar (238 mg/g),<sup>7</sup> which is among the highest capture capacities reported yet among MOFs. Gao et al. synthesized a porous metal-triazolate framework, MTAF-3, which shows remarkable enhancement of CO<sub>2</sub> uptake capacity compared to the parent MOF-508 through changing the pillar ligand, 4,4'-bipyridine in MOF-508 with 4,4'-(2H-1,2,3-triazole-2,4-diyl)dipyridine.<sup>9</sup>

In this work, a nitrogen-rich pillar-layered cobalt(II) metal organic framework, Co(Imda)(4, 4'-bpy), was firstly investigated for CO<sub>2</sub> capture. The material is a three dimensional non-interpenetrated microporous MOF structure, in which the layers based on imidazole-4,5-dicarboxylic acid (Imda) and the cobalt cluster are pillared by 4, 4'-bipyridyl (4, 4'-bpy). The CO<sub>2</sub> capture performance of this material was evaluated in terms of its adsorption capacity and selectivity (towards N<sub>2</sub>), adsorption kinetics, regeneration, and stability in the adsorption-desorption cycles.

The XRD diffraction pattern of Co(Imda) (4, 4'-bpy) (Fig. 1a) was in agreement with the one reported by Li et al.<sup>13</sup> A comparison of XRD patterns of Co(Imda) (4, 4'-bpy) with cobalt oxide and cobalt hydroxide (Fig.S1) indicate that the MOF product is 100% pure. N<sub>2</sub> adsorption-desorption isotherms (Fig. 1b) showed a reversible type I isotherm, which indicated the microporous structure of this material. In the region P/P<sub>0</sub> > 0.9, the isotherm began to increase sharply, indicating the presence of some textural mesopores caused by inter-particle voids.<sup>14</sup> The BET surface area was estimated to be 572 m<sup>2</sup>/g based on the N<sub>2</sub> adsorption-desorption measurement. The TGA curve (Fig. 1c) indicated that the structural decomposition took place above ca. 250 °C, where the structure begins collapse and the coordinated ligands start to be released. SEM picture showed that the material exhibited particle morphology of hexagonal prism, with particles of ca. 0.5 to 3 μm in size (Fig. 1d).



**Fig. 1** (a) XRD pattern; (b)  $N_2$  adsorption–desorption isotherms; (c) TGA profile; and (d) SEM image of Co(Imda) (4, 4'-bpy).

The Static  $CO_2$  adsorption by Co(Imda) (4, 4'-bpy) was examined at ambient conditions. Fig. 2a shows the corresponding  $CO_2$  adsorption isotherm. At 298 K, 1 bar, Co(Imda) (4, 4'-bpy) exhibited a high  $CO_2$  adsorption capacity of 135 mg/g, surpassing the values reported by other pillar-layered MOFs except SIFSIX-2-Cu-i (Table 1). In addition, the adsorbed  $CO_2$  amount increased rapidly at a lower pressure range near 0.15 bar and a  $CO_2$  adsorption capacity of ca. 76 mg/g was achieved, which accounts for nearly 56% of the total capacity established at 1 bar, which would be useful in a post-combustion  $CO_2$  capture system. In a post-combustion  $CO_2$  capture system, a high concentration of  $N_2$  (ca. 70%) exists in the flue gas, so high  $CO_2$  selectivity from the  $CO_2/N_2$  mixture is desirable. Thus,  $N_2$  adsorption isotherm was independently measured at 298 K (Fig. 2a). Based on the amounts of respective gas adsorbed (mg/g) at 1 bar, the  $CO_2/N_2$  selectivity was estimated to be ca. 18, which is significantly higher than those of prototypical activated carbons,<sup>15</sup> MOFs,<sup>16,17</sup> and comparable to those reported for ZIFs.<sup>18</sup> We also calculated the  $CO_2/N_2$  adsorption selectivity using the Ideal Adsorbed Solution Theory (IAST) for  $CO_2:N_2$  mixture in the ratio of 0.15:0.85 (Fig. S2).<sup>19,20</sup> The IAST  $CO_2/N_2$  selectivity at 1 bar was calculated to be 64.1 at 298K. We attribute the high and selective  $CO_2$  uptake in Co(Imda) (4, 4'-bpy) to the combined effects of its microporosity, and strong quadrupolar interactions of  $CO_2$  with nitrogen atoms present in the organic linkers (Fig. 2b).<sup>18</sup>

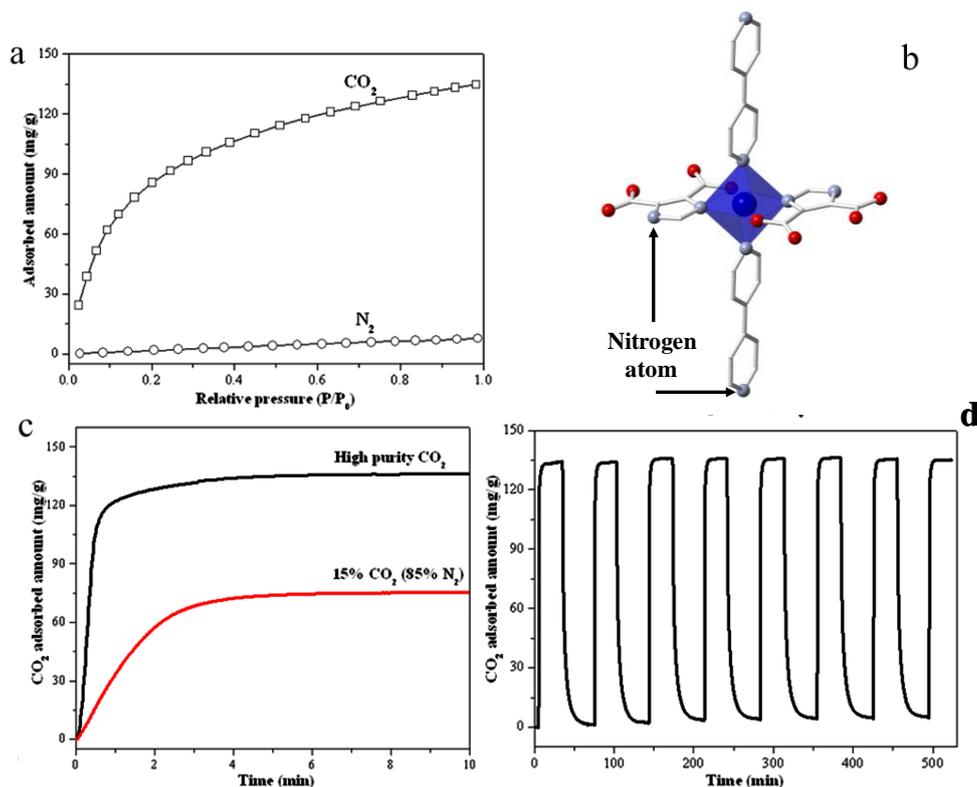
The  $CO_2$  adsorption kinetics of Co(Imda) (4, 4'-bpy) at 298 K was examined by TGA. As shown in Fig. 2c, the sample showed fast  $CO_2$  adsorption kinetics with practical  $CO_2$  adsorption equilibrium achieved within 10 min in both high purity  $CO_2$  and 15%  $CO_2$  (85%  $N_2$ ) condition; lower concentration of  $CO_2$  in the feed gas mixture led to slower adsorption kinetics. This is an advantage over other

$CO_2$  adsorbents that require a long time to reach adsorption equilibrium, such as polyethylenimine-impregnated mesoporous silica that requires more than 1 h for its adsorption equilibrium.<sup>21</sup> To save energy in adsorbent regeneration, adsorbed  $CO_2$  should be desorbed easily from the adsorbent during a multi-cycle operation. As shown in Fig. 2d,  $CO_2$  could be easily desorbed at 298 K with only an argon gas purge in a TGA measurement. Furthermore, it showed a stable adsorption-desorption performance in 8 consecutive runs without noticeable deterioration of  $CO_2$  capture capacities. It is also worth mentioning that this material is stable in moisture condition as can be expected from its hydrothermal synthesis, which makes it a good candidate material in practical applications.

**Table 1** A comparison of  $CO_2$  capture capacities by reported pillar MOFs.

Sample	Temp. (K)	$CO_2$ uptake <sup>a</sup> (mg/g)	Reference
Co(Imda) (4, 4'-bpy)	298	135	This work
SIFSIX-2-Cu-i	298	238	[7]
SIFSIX-3-Zn	298	112	[7]
UTSA-15a	296	61	[8]
MTAF-3	273	100	[9]
SNU-M11	298	92	[10]
MOFOUR-1-Ni	298	108	[11]
Cu(TCMBT)(bpp)( $\mu_3$ -OH)	298	88	[12]

<sup>a</sup>  $CO_2$  uptake measured at 1 bar.



**Fig. 2** (a) CO<sub>2</sub> and N<sub>2</sub> adsorption isotherms of Co(Imda) (4, 4'-bpy) at 298 K; (b) A single unit of coordinated molecular building blocks of Co(Imda) (4, 4'-bpy): blue, red and grey balls represent Cobalt, Oxygen, and Nitrogen atoms; (c) CO<sub>2</sub> adsorption profile of Co(Imda) (4, 4'-bpy) at 298 K by TGA, and (d) cyclic CO<sub>2</sub> adsorption-desorption runs (high purity CO<sub>2</sub>) of Co(Imda) (4, 4'-bpy).

In summary, a nitrogen-rich pillar-layered metal organic framework, Co(Imda)(4, 4'-bpy), exhibited an excellent CO<sub>2</sub> capture performance, including high CO<sub>2</sub> uptake, good CO<sub>2</sub> selectivity against N<sub>2</sub>, fast CO<sub>2</sub> adsorption kinetics, easy regeneration, and excellent stability in moisture and during consecutive adsorption-desorption cycles. These outstanding attributes make it a promising candidate for post combustion CO<sub>2</sub> capture.

### Acknowledgements

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### Notes and references

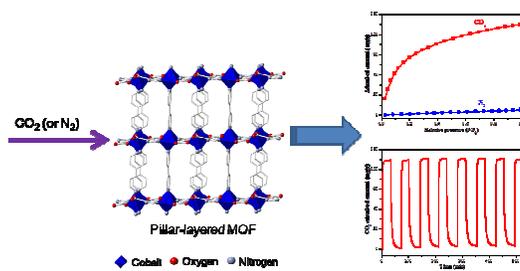
College of Chemistry and Chemical Engineering, Xinyang Normal University, Xinyang 464000, Henan Province, China  
Tel: +86 376 6393906

E-mail: chencao@xynu.edu.cn

† Electronic supplementary information (ESI) available: Experimental details, such as material synthesis and characterization, CO<sub>2</sub> or N<sub>2</sub> adsorption-desorption measurements, CO<sub>2</sub>/N<sub>2</sub> selectivity calculation. A comparison of XRD patterns of Co(Imda) (4, 4'-bpy) with CoO and Co(OH)<sub>2</sub> was shown in Fig.S1; CO<sub>2</sub> and N<sub>2</sub> adsorption isotherms fitted by dual-site Langmuir model and single-site Langmuir model respectively for IAST CO<sub>2</sub>/N<sub>2</sub> selectivity calculation of Co(Imda) (4, 4'-bpy) was shown in Fig. S2.

- 1 J. D. Figueroa, T. Fout, S. Plasynski, H. McIlvried and R. D. Srivastava, *Int. J. Greenhouse Gas Control*, 2008, **2**, 9.
- 2 G. T. Rochelle, *Science*, 2009, **325**, 1652.
- 3 G. P. Hao, W. C. Li and A. H. Lu, *J. Mater. Chem.* 2011, **21**, 6447.
- 4 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.
- 5 Q. M. Wang, D. Shen, M. Bulow, M. L. Lau, S. Deng, F. R. Fitch, N. O. Lemcoff and J. Semancin, *Micropor. Mesopor. Mater.*, 2002, **55**, 217.
- 6 A. R. Millward and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 17998.
- 7 P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, L. Wojtas, M. Eddaoudi and M. J. Zaworotko, *Nature*, 2013, **495**, 80.
- 8 Z. Chen, S. Xiang, H. D. Arman, J. U. Mondal, P. Li, D. Zhao, B. Chen, *Inorg. Chem.*, 2011, **50**, 3442.
- 9 W. Y. Gao, W. Yan, R. Cai, K. Williams, A. Salas, L. Wojtas, X. Shi and S. Ma, *Chem. Commun.*, 2012, **48**, 8898.
- 10 H. S. Choi and M. P. Suh, *Angew. Chem. Int. Ed.*, 2009, **48**, 6865.
- 11 M. H. Mohamed, S. K. Elsaïdi, L. Wojtas, T. Pham, K. A. Forrest, B. Tudor, B. Space and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2012, **134**, 19556.

- 12 Z. Lu, H. Xing, R. Sun, J. Bai, B. Zheng and Y. Li, *Cryst. Growth Des.*, 2012, **12**, 1081.
- 13 C. J. Li, S. Hu, W. Li, C. K. Lam, Y. Z. Zheng and M. L. Tong, *Eur. J. Inorg. Chem.*, 2006, 1931.
- 14 W. Zhang, T. R. Pauly and T. J. Pinnavaia, *Chem. Mater.*, 1997, **9**, 2491.
- 15 S. Sircar, T. C. Golden and M. B. Rao, *Carbon* 1996;34:1-12.
- 16 S. Surblé F. Millange, C. Serre, T. Düren, M. Latroche, S. Bourrelly, P. L. Llewellyn and G. Férey, *J. Am. Chem. Soc.*, 2006, **128**, 14889.
- 17 L. Bastin, P. S. B árcia, E. J. Hurtado, J. A. C. Silva, A. E. Rodrigues and B. Chen, *J. Phys. Chem. C*, 2008, **112**, 1575.
- 18 B. Wang, A. P. Côté, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Nature*, 2008, **453**, 207.
- 19 H. A. Patel, D. Ko and C. T. Yavuz, *Chem. Mater.*, 2014, **26**, 6729.
- 20 H. A. Patel, S. H. Je, J. Park, D. P. Chen, Y. Jung, C. T. Yavuz and A. Coskun, *Nat. Commun.*, 2013, **4**:1357, doi:10.1038/ncomms2359.
- 21 C. Chen, S. T. Yang, W. S. Ahn and R. Ryoo, *Chem. Commun.*, 2009, 3627.



**A pillar-layered cobalt(II) MOF exhibits high  $\text{CO}_2$  uptake and  $\text{CO}_2/\text{N}_2$  selectivity, fast adsorption kinetics, easy regeneration and excellent stability.**