Accepted Manuscript

A charged metal-organic framework for CO_2/CH_4 and CO_2/N_2 separation

Ruiqin Zhong, Zhilong Xu, Wenzhu Bi, Songbai Han, Xiaofeng Yu, Ruqiang Zou

PII: DOI: Dofrance:	S0020-1693(16)00025-6 http://dx.doi.org/10.1016/j.ica.2016.01.014
To appear in:	Inorganica Chimica Acta
Received Date:	7 August 2015
Revised Date:	30 December 2015
Accepted Date:	6 January 2016



Please cite this article as: R. Zhong, Z. Xu, W. Bi, S. Han, X. Yu, R. Zou, A charged metal-organic framework for CO₂/CH₄ and CO₂/N₂ separation, *Inorganica Chimica Acta* (2016), doi: http://dx.doi.org/10.1016/j.ica.2016.01.014

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

A charged metal-organic framework for CO_2/CH_4 and CO_2/N_2 separation

Ruiqin Zhong,^a Zhilong Xu,^b Wenzhu Bi,^b Songbai Han,^c Xiaofeng Yu,^a Ruqiang Zou*,^b

^a State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China; ^b Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China; ^c Neutron Scattering Laboratory, China Institute of Atomic Energy, Beijing 102413, China.

;

Abstract

A microporous metal-organic framework $[InL][(CH_3)_2NH_2].(H_4L= 9-(3,5-dicarboxyphenyl)carbazole-3,6-dicarboxylic acid) (1) was hydrothermally synthesized and structurally characterized by single crystal X-ray diffraction and powder X-ray diffraction. The adsorption behavior of 1 has been investigated with respect to CO₂, CH₄ and N₂, and the separation efficiency has been calculated by the Henry's law analysis of isotherm data. The results indicated that the anionic framework with the inside protonated dimethylamine could enhance its selective adsorption performance for CO₂ through strong adsorbent–adsorbate interaction aroused by a strong electrostatic field and pore size effect.$

Keywords: metal-organic framework; CO₂ separation; gas adsorption; selectivity.

1. Introduction

Metal-organic frameworks (MOFs), consisting of inorganic metal centers connected by organic linkers, are a relatively new family of porous materials that possess fine-tuning structural diversity, and offer great promise for extensively potential applications in many areas, such as gas storage,[1] catalysis,[2] sensing,[3] and magnetism.[4] In recent year, CO_2 capture technologies become more and more significant and continually developed because the removal of CO₂ is not only essential in the fight against climate change, but also greatly beneficial to the promotion of the energy efficiency and conservation in the industrial field.[5] Compared to conventional inorganic porous adsorbents (e.g., activated carbon and zeolites), MOFs have shined brilliantly on the aspect of CO₂ adsorption and separation, owing to their intriguing properties, such as ultra-high surface area, well-ordered pore structures, modifiable pore shapes, pore sizes and chemical environment inside the pores.[6] Many efforts have been made to improve the performance of MOFs for selective CO₂ adsorption and separation, and generally the efficient strategies explored include two aspects. One is to utilize the molecular sieving effect by tuning pore distribution for controllable separation of adsorbates with different of van der Waals diameters.[7] Another is to improve the surface chemistry of pores for the enhanced adsorption interactions. Because of the differences in electronic properties of adsorbate gases such as quadrupolarmoment and polarization, functionalization of pores or open channels,[8] utilization of the Lewis acid sites [9] and framework flexibility [10] could increase the adsorbent-adsorbate interactions. It is worth noting that the MOFs with charged frameworks and counterion species inside of the pores or channels are good candidates to meet both so-called parts, because they not only adjust the pore sizes for better filtering, but also exhibit strong electrostatic interactions with adsorbates in the pores.[11]

In this work, we report a novel charged MOF with N-contained tetracarboxylate ligand (H_4L =9-(3,5-dicarboxyphenyl)carbazole-3,6-dicarboxylic acid) and Indium (III) ions formulated as [InL][(CH₃)₂NH₂] and its selective adsorption and separation

performance for CO₂ over CH₄ and N₂.

2. Experimental section

2.1 General

All chemicals applied in the syntheses were commercial available and used without further purification. ¹HNMR spectra were recorded on a Bruker Advance DMX500 (500 MHz) spectrometer using tetramethysilane (TMS) as an internal standard. Powder X-ray diffraction (PXRD) was performed on a Rigaku Dmax/2400 X-ray diffractometer operating at 40 kV and 100 mA, using Cu-Ka radiation (λ =1.5406 Å). Thermo gravimetric analysis (TGA) was carried out under nitrogen atmosphere on a Q600 SDT TGA-DTA-DSC thermal analyzer from room temperature to 800 °C with a heating rate of 10 °C min⁻¹. Gas adsorption measurements were carried out with QUANTACHROME AUTOSORB-iQ gas adsorption analyzer. The N₂ sorption isotherms for surface area calculation were collected in the pressure range from 0.01 to 0.99 P/P₀ at 77 K in a liquid nitrogen bath. CO₂, CH₄ and N₂ adsorption isotherms were collected in the pressure range from 0.01 to 0.99 P/P₀ at 273K in a circulator with temperature controller with a mixture of 50 v% water and 50 v% ethylene glycol.

2.2. Synthesis of the ligand

Synthesis of the ligand (H₄L) was started with 5-(amino)isophthalic acid (**1'**) and followed the reaction routes shown below. The detailed synthesis procedures are provided in the Supporting Information. ¹H NMR (500 MHz, DMSO- d_6), [ppm]: 13.23-13.25(m, 3H), 8.99(t, 3H), 8.65(t, 1H), 8.36(d, 2H), 8.10-8.12(q, 2H), 7.48-7.50(d, 2H). ¹³C{¹H} NMR (125 MHz, DMSO- d_6), [ppm]: 196.97, 165.68, 143.31, 136.39, 133.63, 131.32, 130.57, 129.55, 127.09, 122.97, 122.82, 109.75. Anal. Calcd for C22H13NO8: C, 63.01; H, 3.12; N, 3.34 %. Found: C, 63.40; H, 3.13; N, 3.62 %.

(Insert Scheme 1)

2.3. Synthesis of $[InL][(CH_3)_2NH_2]$ (1)

A mixture of H₄L (0.012 g, 0.03 mmol), $In(NO_3)_3 \cdot 4.5 H_2O$ (0.015 g, 0.053 mmol) in 10 mL of N,N'-dimethylmethanamide (DMF) and 2 mL of deionized water was placed in a 25 mL Teflon-lined steel autoclave, and the mixture was stirred at room temperature until the solid was completely dissolved. The autoclave was sealed, heated up to 160 °C and kept at this temperature for 4 days. Block-shaped yellow crystals were obtained. The product was filtered out, washed by DMF, soaked in CHCl₃ for 2 days, and then dried under the vacuum. Yield: 29% (based on H4L). IR (cm–1): 3430s, 2918m, 1660m, 1465m, 1393s, 1280m, 1228w, 1099m, 1022m, 812w, 777m, 750w, 719w, 668w, 536w. W:weak, vs=very strong, s=strong, m=medium, sh=shoulder, br=broad. It is noted that the peaks at 3430 and 1469 cm⁻¹ correspond to the stretching vibration of N–H and C–N bonds in DMA⁺, respectively, which further demonstrates its existence inside the framework. [11]

2.4. Single-crystal X-ray crystallography

The crystal data were collected on Agilent SuperNava single-crystal X-ray diffractometer at room temperature with Cu-K α radiation ($\lambda = 1.54$ Å). The structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL [12]. The metal atoms in each complex were located from the E-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses, which were refined with anisotropic thermal parameters on F². The hydrogen atoms of the ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. Solvent molecules in the structure were randomly dispersed, and thus their positions were impossible to refine using conventional discrete-atom models. The crystal and refinement data are collected in Table 1. Selective bond distances and angles are given in Table S1, (Supporting Information).

(Insert Table 1)

3. Results and discussion

3.1. Structural Description

X-Ray crystallographic analysis indicates that 1 crystallizes in an orthogonal $P2_12_12_1$ space group, consisting of anionic [InL] framework and protonated dimethylamine (DMA⁺) in 1:1 stoichiometric ratio. The host framework is composed of an independent In(III) coordinated to a tetragonal L ligand in an asymmetric unit. The L ligand has a disturbed tetrahedronal configuration with the four carboxylate groups on the vertexes and N atom locating in the center (Fig. 1a). Each carboxylate group of L ligand exhibits a unique η^2 coordination mode. The In(III) center adopts an 8-coordinated mode to four carboxylate groups from separate L ligands with the In-O bond lengths falling into the range of 2.227-2.335 Å (Fig. 1b). The anionic framework leads a three-dimensional (3D) network with two types of irregular quadrangular one-dimensional channels with pore size less than 1 nm, respectively. The corresponding protonated DMA⁺ are trapped in the molecular space between two channels (Fig. 1c). Notably, the adjacent carbazole rings of two L ligand lack any π - π stacking interactions. The solvent-accessible volume in 1 is 2916.3 $Å^3$ that constitutes as high as 59.8% volume per unit cell calculated by PLATON routine,[13] indicating its significant porous nature.

To better understand such a complicated structure, the topology of the anion framework of **1** was studied by using Topos 4.0 software.[14] As shown in Fig. 1d, the In(III) center and L ligand are both regarded as four-connected nodes, and therefore **1** leads to a 3D 4-c network with point symbol $\{6^6\}$, which is a classic *unc* topological type based on the search from RCSR database (http://rcsr.net/nets).[14a]

(Insert Fig. 1)

3.2. Thermal stability

The thermal stability of **1** was studied by thermogravimetric analysis (TGA). As shown in Fig. 2, two steps of weight losses were observed in the TGA curve. The first

weight loss step of **1** starts from room temperature and does not end until 120 °C. The corresponding weight loss should be attributed to the loss of guest CHCl₃ molecules after solvent exchanged with DMF. From 120 to 400 °C, the TGA curve of **1** passes through a slight decline, which could be attributed to the partial removal of the decomposed DMA⁺ product with temperature.[11a] The second weight loss step from 400 °C to 800 °C is probably caused by the decomposition of organic ligand.

(Insert Fig. 2)

3.3. Gas adsorption properties

The presence of well-defined channels and the retention of the overall framework structure after removal of the lattice solvent molecules make the complex a potential candidate for gas storage. To account for the porosity of 1, N₂ adsorption measurements were performed at 77 K on the sample that dried under a dynamic vacuum after soaked in $CHCl_3$. Before the gas adsorption, the as-synthesized 1 was soaked in CHCl₃ for 2 days to exchange the nonvolatile DMF solvents included in the channels, and then was further filtered and dried under a dynamic vacuum to remove CHCl₃ molecules. The PXRD patterns of as-synthesized sample and the vacuum-dried sample are in agreement with the simulated pattern based on the crystal structure, indicating that the host framework of **1** remains crystallinity and integrity of the overall framework in both samples (Fig. S4). The observed slight differences in intensity could be due to preferred orientation of the powder samples. Unfortunately, the specific surface area of activated samples of 1 is calculated to be only 20 m^2g^{-1} using the Brunauer-Emmett-Teller (BET) model based on N2 sorption isotherm. The possible reason is that the protonated DMA⁺ cations are highly disordered in the channels and prevent the entrance of N₂ molecules. We further studied the sorption behavior of CO₂, CH_4 and N_2 at 273 K. As shown in Fig. 3, the largest uptake amount of CO_2 is 32.8 cm³ g^{-1} at 1 atm, while those of CH₄ (7.2 cm³ g⁻¹) and N₂ (2.2 cm³ g⁻¹) are quite low under the same conditions.

(Insert Fig. 3)

The selectivities of CO₂ over CH₄ and N₂ at 273 K were further calculated by the Henry's law analysis of isotherm data. For an equimolar binary mixture of CO₂/CH₄ and CO₂/N₂, the separation factor $S_{CO2/CH4}$ and $S_{CO2/N2}$ are 24.97 and 105.09, respectively, which are quite close to those calculated by ideal adsorbed solution theory (IAST) method (Fig. S11). It is known that the kinetic diameters of CH₄ (3.38 Å) and N₂ (3.64 Å) is larger than CO₂ (3.30 Å).[15] Notedly, the pore size suggests that molecular sieve effect could play an important role when considering the selectivity of CO₂ over other gases.[16] In addition, the existence of DMA⁺ enhances the interaction between the host framework and CO₂ molecules. In contrast, the near-linear adsorption isotherms of CH₄ and N₂ are indicative of their low affinity to the charged framework, which can be expected from their relatively low polarizability.

4. Conclusions

In summary, a novel 3D charged metal–organic framework has been synthesized and exhibits selective adsorption ability of CO_2 over CH_4 and N_2 . The anionic framework with the inside DMA⁺ counterion could have the synergistic effect of pore size effect and the enhanced adsorbent–adsorbate interaction aroused by a strong electrostatic field during the CO_2 adsorption. Therefore the charged metal-organic framework can act as an efficient sorbent for selective CO_2 separation from CO_2/CH_4 and CO_2/N_2 mixtures.

Acknowledgements

We gratefully acknowledge the financial supported from the NSFC (No. 21203249 and No. 11375271) and the Science Foundation of China University of Petroleum, Beijing (No. 01JB0229).

Appendix A. Supplementary material

Detailed synthesis procedure of the ligand, crystal structure data, PXRD patterns, N₂ isotherm, selectivity calculation method are provided. Crystallographic data for the structural analysis have been deposited to the Cambridge Crystallographic Data Centre, CCDC No. 1415547 for **1**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] (a) Z. Niu, S. Fang, J. Ma, X. Zhang, P. Cheng, Chem. Commun. 50 (2014) 7797-7799;

(b) N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe, O. M. Yaghi, Science 300 (2003) 1127-1129;

(c) B. Chen, N. W. Ockwig, A. R. Millward, D. S. Contreras, O. M. Yaghi, Angew. Chem. 117 (2005) 4823-4827;

(d) A. G. Wong-Foy, A. Matzger, O. M. Yaghi, J. Am. Chem. Soc. 128 (2006) 3494-3495.

- [2] (a) C. Wu, A. Hu, L. Zhang, W. Lin, J. Am. Chem. Soc. 127 (2005) 8940-8941;
 (b) Y. Liu, X. Xi, C. Ye, T. Gong, Z. Yang, Y. Cui, Angew. Chem. Int. Ed. 53 (2014) 14041-14045;
 - (c) Y. Peng, T. Gong, Y. Cui, Chem. Commun. 49 (2013) 8253-8255;
 - (d) T. Yang, H. Cui, C. Zhang, L. Zhang, C. Su, Inorg. Chem. 52 (2013) 9053-9059;

(e) R. Zhong, R. Zou, T. Nakagawa, M. Janicke, T. A. Semelsberger, A. K. Burrell, R. E. D. Sesto, Inorg. Chem. 51 (2012) 2728-2730.

- [3] (a) R. Zou, R. Zhong, S. Han, H. Xu, A.K. Burrell, N. Henson, J. L. Cape, D.D. Hickmott, T.V. Timofeeva, T. E. Larson, Y. Zhao, J. Am. Chem. Soc. 132 (2010) 17996-17999;
 - (b) Z. Hu, B. J. Deibert, J. Li, Chem. Soc. Rev. 43 (2014) 5815-5840;
 - (c) M. Zhang, G. Feng, Z. Song, Y. Zhou, H. Chao, D. Yuan, T.T.Y. Tan, Z. Guo, Z. Hu, B.Z. Tang, B. Liu, D. Zhao, J. Am. Chem. Soc. 136 (2014) 7241-7244;

(d) J. Sahu, M. Ahmad, P.K. Bharadwaj, Cryst. Growth Des. 13 (2013) 2618-2627;

(e) S. S. Nagarkar, B. Joarder, A.K. Chaudhari, S. Mukherjee, S.K. Ghosh, Angew. Chem. Int. Ed. 125 (2013) 2593-2597.

 [4] (a) P. Mahata, S. Natarajan, P. Panissod, M. J. Drillon, J. Am. Chem. Soc. 131 (2009) 10140-10150;

(b) R. Zhong, R. Zou, M. Du, T. Yamada, G. Maruta, S. Takeda, J. Li, Q. Xu, CrystEngComm 12 (2010) 677-681;

(c) R. Zhong, R. Zou, M. Du, L. Jiang, T. Yamada, G. Maruta, S. Takeda, Q. Xu, CrystEngComm 10 (2008) 605-613;

(d) Y. Li, S. Liu, T. Hu, X. Bu, Dalton Trans. 43 (2014) 11470-11473.

[5] (a) D. M. D'Alessandro, B. Smit, J. R. Long, Angew. Chem. Int. Ed. 49 (2010) 6058-6082;

(b) G. D. Pirngruber, L. Hamon, S. Bourrelly, P. L. Llewellyn, E. Lenoir, V. Guillerm, C. Serre, T. Devic, ChemSusChem 5 (2012) 762-776;

[6] (a) M. Du, M. Chen, X. Yang, J. Wen, X. Wang, S. Fang, C. Liu, J. Mater. Chem. A 2 (2014) 9828-9834;

(b) M. Du, C.P. Li, M. Chen, Z.W.Ge, X. Wang, L. Wang, C.S.Liu, J. Am. Chem. Soc. 136 (2014) 10906-10909;

(d) J. A. Mason, K. Sumida, Z. R. Herm, R. Krishna, J. R. Long, Energy Environ. Sci. 4 (2011) 3030-3040;

(d) S. R. Caskey, A. G. Wong-Foy, A. J. Matzger, J. Am. Chem. Soc. 130 (2008) 10870-10871;

(e) Y. Wang, M. D. LeVan, J. Chem. Eng. Data. 54 (2009) 2839-2844;

(f) T. H. Bae, M. R. Hudson, J. A.Mason, W. L. Queen, J. J. Dutton, K. Sumida, K. J. Micklash, S. S. Kaye, C. M. Brown, J. R. Long, Energy Environ. Sci. 6 (2013) 128-138;

(g) P. D. C. Dietzel, V. Besikiotis, R. J. Blom, Mater. Chem. 19 (2009) 7362-7370;
(h) H. Wu, J. M. Simmons, G. Srinivas, W. Zhou, T. J. Yildirim, Phys. Chem. Lett. 1 (2010) 1946-1951;

(i) L. Valenzano, B. Civalleri, S. Chavan, G. T. Palomino, C. O. Arean, S. J. Bordiga, J. Phys. Chem. C 114 (2010) 11185-11191;

(j) M. C. Das, H. Xu, Z. Wang, G. Srinivas, W. Zhou, Y. Yue, V. N. Nesterov, G. Qian, B. Chen, Chem. Commun. 47 (2011) 11715-11717;

(k) J. Duan, M. Higuchi, S. Horike, M. L. Foo, K. P. Rao, y. Inubushi, T. Fukushima, S. Kitagawa, Adv. Funct. Mater. 23 (2013) 3525-3530;

- (1) J. Duan, M. Higuchi, R. Krishna, T. Kiyonaga, Y. Tsutsumi, Y. Sato, Y. Kubota, M. Takata, S. Kitagawa, Chem. Sci. 5 (2014) 660-666.
- [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, M. J. Zaworotko, Nature 495 (2013) 80-84.
- [8] (a) S. Vaesen, V. Guillerm, Q. Y. Yang, A. D. Wiersum, B. Marszalek, B. Gil, A. Vimont, M. Daturi, T. Devic, P. L. Llewellyn, C. Serre, G. Maurin, G. De Weireld, Chem. Commun. 49 (2013) 10082-10084;
 (b) J. Speneneulos, P. Yudios, C. D. Malliakas, P. N. Trikalitis, Inorg. Chem. 52

(b) I. Spanopoulos, P. Xydias, C. D. Malliakas, P. N. Trikalitis, Inorg. Chem. 52 (2013) 855–862;

(c) P. Li, Y. Zhao, Chem.-Asian J. 8 (2013) 1680-1691;

(d) D. Xue, A. J. Cairns, Y. Belmabkhout, L. Wojtas, Y. Liu, M. H. Alkordi, M.Eddaoudi, J. Am. Chem. Soc. 135 (2013) 7660-7667;

(e) Q. Yan, Y. Lin, P. Wu, L. Zhao, L. Cao, L. Peng, C. Kong, L. Chen, ChemPlusChem, 78 (2013) 86-91.

- [9] (a) H. Xu, Y. B. He, Z. Zhang, S. Xiang, J. Cai, Y. J. Cui, Y. Yang, G. Qian, B. Chen, J. Mater. Chem. A 1 (2013) 77-81;
 (b) A. Demessence, D. M. D'Alessandro, M. L. Foo, J. R. Long, J. Am. Chem. Soc. 131 (2009) 8784-8786
- [10]B. Zornoza, A. Martinez-Joaristi, P. Serra-Crespo, C. Tellez, J. Coronas, J. Gascon, F. Kapteijn, Chem. Commun. 47 (2011) 9522-9524.
- [11] (a) L. Kong , R.Zou , W. Bi , R.Zhong , W. Mu , J. Liu , P. Han, R Zou, J. Mater. Chem. A 2 (2014) 17771-17778;

(b) A. K. Chaudhari, S. Mukherjee, S. S. Nagarkar, B. Joarder, S. K. Ghosh, CrystEngComm, 15 (2013) 9465-9471;

(c) P. He, H. Liu, Y. F. Li, Z. G. Lei, S. P. Huang, P. Wang, H. P. Tian, Mol. Simul. 38 (2012) 72–83;

(d) T. Li, N. L. Rosi, Chem. Commun. 49 (2013) 11385-11387;

- (e) R. Babarao, M. Eddaoudi, J. W. Jiang, Langmuir 26 (2010) 11196-11203.
- [12]G. M. Sheldrick, SHELXTL NT, Program for Solution and Refinement of Crystal Structures, version 5.1, University of Göttingen, Germany, 1997.
- [13] A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2001.
- [14] (a) M. O'Keeffe, M. A. Peskov, S. J. Ramsden, O. M. Yaghi, Acc. Chem. Res. 41 (2008) 1782-1789;

(b) S. R. Batten, N. R. Champness, X.. Chen, J. Garcia-Martinez, S. Kitagawa, L. Öhrström, M. O'Keeffe, M. P. Suh, J. Reedijk, Pure Appl. Chem. 85 (2013) 1715-1724.

[15] (a) D. W. Breck, Zeolite Molecular Sieves: Structure, Chemistry, and Use, Wiley, New York, 1973;

(b) D. M. D'Alessandro, B. Smit, J. R. Long, Angew. Chem. Int. Ed. 49 (2010) 6058-6082.

[16] (a) S. Cavenati , C. A. Grande , A. E. Rodrigues, J. Chem. Eng. Data. 49 (2004) 1095-1101;

(b) 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 495 (2013) 80-84.

Formula	$C_{24}H_{17}InN_2O_8$
Formula weight	576.22
$T(\mathbf{K})$	293(2)
Crystal system	Orthogonal
space group	P212121
<i>a</i> (Å)	12.7580(9)
<i>b</i> (Å)	17.5203(11)
<i>c</i> (Å)	21.8129(11)
$V(\text{\AA}^3)$	4875.7(5)
α (deg)	90
β (deg)	90
γ (deg)	90
Z	4
$\rho (mg/m^3)$	0.785
$\mu (\mathrm{mm}^{-1})$	0.510
F (000)	1152
Range of <i>h</i> , <i>k</i> , <i>l</i>	-10/15,-20/13,-26/20
Total/independent	11239 / 7756
reflections	
Parameters	313
<i>R</i> indices $[I > 2\sigma(I)]$	0.0831, 0.2360
Goodness-of-fit on F^2	1.064
Residuals (e Å ⁻³)	0.889/-1.283
$\mathbf{R}_{1} = \sum F_{o} - F_{c} / F_{o} . \ \mathbf{w} \mathbf{R}_{2} = [\sum_{i=1}^{n} F_{o}] $	$w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o}^{2})^{2}]^{1/2}.$

Table 1. Crystallographic Data and Structural Refinement Summary	for	1.
---	-----	----

Scheme and Figure captions

- Scheme 1 Synthesis of H₄L. Reagents and conditions: (a) SOCl₂, EtOH, 0°C; (b) NaNO₃, HCl, H₂O, KI, 0-5°C; (c) K₂CO₃, Cu, carbazole, 220°C; (d) AlCl₃, CH₃COCl, CH₂Cl₂, 0°C; (e) 1,4-dioxane, NaOH, Br₂, 0°C.
- Fig. 1 Single crystal structure of 1: (a) tetragonal L ligand, (b) four-coordinated In(III) center, (c) the 3D InL⁻ porous anionic framework with DMA⁺ cations, and (d) topological structure. Hydrogen atoms are omitted for clarity.
- TGA curve of the CHCl₃-exchanged sample. Fig. 2
- **Fig. 3** CO_2 , CH_4 and N_2 sorption isotherms of **1** at 273 K.









Highlights:

- A three-dimensional microporous charged metal-organic framework is reported.
- The MOF shows much higher uptake of CO_2 than those of CH_4 and N_2 at 273K and 1 atm.
- The separation factor of CO₂/N₂ and CO₂/CH₄ of 1 could reach 24.97 and 105.09,

ccieron de la constant de

Graphical Abstract

A charged metal-organic framework for CO₂/CH₄ and CO₂/N₂ separation

Ruiqin Zhong, Zhilong Xu, Wenzhu Bi, Xiaofeng Yu, Ruqiang Zou*



A novel three-dimensional charged metal-organic framework has been synthesized, which exhibits high selectivities of CO_2 over CH_4 and N_2 .

DC C