UvA-DARE (Digital Academic Repository)

Enhanced CO₂ sorption and selectivity by functionalization of a NbO-type metal-organic framework with polarized benzothiadiazole moieties

Song, C.; He, Y.; Li, B.; Ling, Y.; Wang, H.; Feng, Y.; Krishna, R.; Chen, B.

DOI

[10.1039/c4cc05833j](https://doi.org/10.1039/c4cc05833j)

Publication date

2014

Document Version

Final published version

Published in

Chemical Communications

[Link to publication](#)

Citation for published version (APA):

Song, C., He, Y., Li, B., Ling, Y., Wang, H., Feng, Y., Krishna, R., & Chen, B. (2014). Enhanced CO₂ sorption and selectivity by functionalization of a NbO-type metal-organic framework with polarized benzothiadiazole moieties. *Chemical Communications*, 50(81), 12105-12108. <https://doi.org/10.1039/c4cc05833j>

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

UvA-DARE is a service provided by the library of the University of Amsterdam (<https://dare.uva.nl>)

Cite this: *Chem. Commun.*, 2014, 50, 12105

Received 28th July 2014,
Accepted 20th August 2014

DOI: 10.1039/c4cc05833j

www.rsc.org/chemcomm

Enhanced CO₂ sorption and selectivity by functionalization of a NbO-type metal–organic framework with polarized benzothiadiazole moieties†

Chengling Song,^a Yabing He,^{*a} Bin Li,^b Yajing Ling,^a Hailong Wang,^b Yunlong Feng,^a Rajamani Krishna^c and Banglin Chen^{*b}

A new NbO-type metal–organic framework ZJNU-40 incorporating highly polarized benzothiadiazole moieties exhibits a high CO₂ uptake of 108 cm³ g^{−1} at 296 K and 1 atm, as well as good adsorption selectivities of CO₂ over CH₄ and N₂ at room temperature, which is superior to that of the analogous MOF NOTT-101.

The escalating level of atmospheric CO₂ is a subject of widespread public concern associated with global warming and climate change, and consequently, there remains an urgent need to selectively capture and sequester CO₂ to reduce its greenhouse effect in the atmosphere. Most of the CO₂ capture processes make use of liquid amine-based absorbents to chemically adsorb CO₂; however, they suffer from the drawbacks of the corrosive nature of the solvents and high energy demand for solvent regeneration. In contrast, using porous materials to capture CO₂ appears to be an energy-efficient alternative approach due to their low energy requirements, thus stimulating extensive efforts to find suitable adsorbents for removing CO₂. In this regard, metal–organic frameworks (MOFs), an emerging class of porous materials, have shown charming properties with respect to CO₂ storage and separation because their chemically adjustable organic and inorganic moieties can be carefully pre-designed to direct the molecular recognition of CO₂.¹ In fact, several MOFs with large CO₂ storage capacity and high selectivity have been recently reported.²

Of various porous MOFs, the NbO-type MOF-505 series constructed from dicopper paddlewheels and diisophthalates has attracted tremendous attention because this class of MOF materials exhibit excellent gas sorption properties due to their

high surface area, tunable pore size and open copper sites suitable for gas adsorption. Some of them exhibited high adsorption capacity for H₂ and CH₄.³ To improve the ability of NbO-type MOFs for CO₂ capture and separation, great efforts have been devoted to tune the pore size/shape and/or engineer surface chemistry. It has been reported that the inclusion of some active binding sites into the framework such as NO₂, amide, imide, and oxalamide is capable of increasing CO₂ binding affinity.⁴ Since benzothiadiazole containing two nitrogen and one sulfur atoms is a polar, fused heterocyclic building block with the molecular dipole of 4.8 Debye estimated by Chemical 3D software, we plan to incorporate such a highly polarized benzothiadiazole unit as a spacer between two isophthalate moieties to develop a new tetracarboxylic acid (H₄L, Scheme 1), and with which to target the corresponding NbO-type MOF designated as ZJNU-40. With a moderate surface area of 2209 m² g^{−1}, open metal sites (OMSS) of 1.52 nm^{−3}, accessible donor sites, two types of nanoscopic cages, and a polarized cage surface within the framework, the activated ZJNU-40a exhibits high CO₂ uptake capacity, as well as good adsorption selectivity of CO₂ over CH₄ and N₂, which is superior to that of the analogous MOF NOTT-101 constructed from 1,4-benzenediisophthalate ligands of the same length as H₄L.

The organic linker H₄L, 5,5′-benzo[*c*][1,2,5]thiadiazole-4,7-diyl-diisophthalic acid, was readily synthesized by a Suzuki cross-coupling of 4,7-dibromobenzo[*c*][1,2,5]thiadiazole and dimethyl (5-pinacolboron)isophthalate followed by hydrolysis and acidification. ZJNU-40 was obtained as blue rhombic crystals *via* a solvothermal reaction of the organic ligand and Cu(NO₃)₂·3H₂O in a mixed solvent of *N,N*-diethylformamide (DEF) and H₂O

Scheme 1 The organic building block H₄L used to construct the MOF ZJNU-40, with the local molecular dipole moment, highlighted in red, perpendicular to the molecular long axis.

^a College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua 321004, China. E-mail: heyabing@zjnu.cn

^b Department of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas 78249-0698, USA. E-mail: banglin.chen@utsa.edu

^c Van't Hoff Institute for Molecular Sciences, University of Amsterdam Science Park 904, 1098 XH Amsterdam, The Netherlands

† Electronic supplementary information (ESI) available: Synthesis and characterization, PXRD, TGA, sorption isotherms, IAST and breakthrough calculations. CCDC 1014276. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc05833j

Fig. 1 Single-crystal X-ray structure of **ZJNU-40**. (a) Each organic linker connects with four dicopper paddlewheel $\text{Cu}_2(\text{COO})_4$ units; (b) two types of nanocages; (c) CPK representation of a 3D open framework viewed along the *c* direction.

under acidic conditions. The crystal structure was characterized by single-crystal X-ray diffraction studies, and the phase purity of the bulk material was verified by powder X-ray diffraction (PXRD, Fig. S1, ESI†). Based on the single-crystal X-ray diffraction structure determination, thermogravimetric analysis (TGA, Fig. S2, ESI†) and microanalysis, **ZJNU-40** can be formulated as $[\text{Cu}_2\text{L}(\text{H}_2\text{O})_2] \cdot 4\text{DEF} \cdot 6\text{H}_2\text{O}$.

Single-crystal X-ray diffraction analysis revealed that **ZJNU-40** is isoreticular to **NOTT-101**. As expected, a pair of copper centers are linked by four bridging carboxylates to form a paddlewheel secondary building unit (SBU) serving as a 4-connected square-planar node, which is bridged by the 4-connected rectangular organic building blocks to form a three-dimensional (3D) noninterpenetrated 4,4-connected NbO-type network (Fig. 1). Alternatively, if the bridging organic linker is considered as having two 3-coordinated (3-c) branch points, then in combination with the 4-coordinated dicopper paddlewheels, the derived net is the one with the RCSR symbol fof^5 . Interestingly, the central benzothiadiazole sites remain unbound, and thus provide additional gas binding sites. If the centers of dicopper paddlewheel SBUs are taken as vertices of polyhedra, the framework of **ZJNU-40** contains two distinct types of nanoscopic cages shown in Fig. 1b. The small octahedral cage consists of 12 ligands and 6 paddlewheel SBUs, and the diameter is about 12 Å, taking into account the van der Waals radii of the atoms; while the large cuboctahedral cage is constructed from 6 ligands and 12 paddlewheel SBUs with dimensions of *ca.* 9×18 Å. It is worth noting that the two cages are densely decorated with a big molecular dipole of benzothiadiazole functionalities.

The permanent porosity was unambiguously established by the N_2 sorption isotherm at 77 K. Prior to gas sorption analysis, the as-prepared **ZJNU-40** was solvent-exchanged with dry acetone and then evacuated at 373 K under dynamic vacuum, generating the activated **ZJNU-40a**. The integrity of the framework was confirmed by powder X-ray diffraction (Fig. S1, ESI†). The nitrogen sorption isotherms at 77 K reveal a typical reversible type-I sorption behavior (Fig. S3, ESI†), characteristic of microporous materials. Based on the N_2 sorption isotherms, Brunauer–Emmett–Teller

Fig. 2 CO_2 , CH_4 , and N_2 sorption isotherms of **ZJNU-40a** (red) and **NOTT-101** (blue) at 296 K. The solid and open symbols represent adsorption and desorption, respectively.

(BET) and Langmuir surface areas were estimated to be 2209, and $2328 \text{ m}^2 \text{ g}^{-1}$, respectively (Fig. S4, ESI†). The pore volume calculated from the maximum amount of N_2 adsorbed is $0.88 \text{ cm}^3 \text{ g}^{-1}$. These values are lower than those of **NOTT-101**³ due to the presence of the thiadiazole moieties pointing to the pore, but are comparable to those of some copper-based NbO-type frameworks such as **NOTT-105**,^{3a} **NOTT-125a**,^{4c} **PCN-16**,⁶ **NU-135**,⁷ **UTSA-80**,⁸ **SNU-50**,^{4c} **NJU-Bai14**^{4a} and **HNUST-2**⁹ (Table S2, ESI†).

Establishment of permanent porosity prompts us to examine its utility as an adsorbent for CO_2 capture and separation. Accordingly, CO_2 , CH_4 and N_2 sorption isotherms were collected up to 1 atm at two different temperatures of 273 K and 296 K. As shown in Fig. 2, the isotherms are completely reversible and show no hysteresis. At 1 atm, **ZJNU-40a** exhibited a CO_2 uptake of 170 and $108 \text{ cm}^3 (\text{STP}) \text{ g}^{-1}$ at 273 and 296 K, respectively, corresponding to about 40 and 26 CO_2 molecules per unit cell. Remarkably, this gravimetric CO_2 adsorption capacity at room temperature is significantly higher than that of **NOTT-101** ($83 \text{ cm}^3 \text{ g}^{-1}$), and is among the highest reported for isoreticular Cu-based NbO-type MOFs (Table S2, ESI†): **MOF-505**^{2a} ($73 \text{ cm}^3 \text{ g}^{-1}$), **NOTT-101** ($83 \text{ cm}^3 \text{ g}^{-1}$), **NOTT-102** ($72 \text{ cm}^3 \text{ g}^{-1}$), **UTSA-40**¹⁰ ($73 \text{ cm}^3 \text{ g}^{-1}$), **NU-135**⁷ ($79 \text{ cm}^3 \text{ g}^{-1}$), **SNU-50**^{4c} ($80 \text{ cm}^3 \text{ g}^{-1}$), **NOTT-125**^{4e} ($93 \text{ cm}^3 \text{ g}^{-1}$), **HNUST-1**^{4b} ($93 \text{ cm}^3 \text{ g}^{-1}$), **NJU-Bai14**^{4a} ($100 \text{ cm}^3 \text{ g}^{-1}$), and **$\text{Cu}_2(\text{dbip})$** ¹¹ ($122 \text{ cm}^3 \text{ g}^{-1}$). In sharp contrast to CO_2 , **ZJNU-40a** can adsorb only limited amounts of CH_4 and N_2 , indicating that **ZJNU-40a** has potential application in the separation of CO_2 – CH_4 and CO_2 – N_2 mixtures.

Ideal Adsorbed Solution Theory (IAST) was used to calculate the adsorption selectivities and CO_2 uptake of **ZJNU-40** and **NOTT-101** for the following binary gas mixtures: 50/50 CO_2/CH_4 , 5/95 CO_2/CH_4 , and 15/85 CO_2/N_2 . These mixtures mimic biogas treatment, natural gas upgrading, and post-combustion capture applications, respectively. Fig. S8 (ESI†) presents the values of the adsorption selectivity for these gas mixtures maintained under isothermal conditions at 296 K in **ZJNU-40a** and **NOTT-101**. It can be seen that **ZJNU-40a** has much higher selectivity towards CO_2 for all three mixture compositions. Fig. S9 (ESI†) presents IAST calculations for CO_2 uptake from 50/50 CO_2/CH_4 , 5/95 CO_2/CH_4 , and 15/85 CO_2/N_2 gas mixtures maintained under isothermal conditions at 296 K in **ZJNU-40a**, and **NOTT-101**.

Fig. 3 50/50 CO₂/CH₄ mixture breakthrough characteristics as a function of the dimensionless time in an adsorber packed with (a) **ZJNU-40a**, and (b) **NOTT-101** and maintained under isothermal conditions at 296 K. In these calculations the total pressure is maintained at 200 kPa.

Again, **ZJNU-40a** has a much higher CO₂ uptake in all three cases. The combination of higher CO₂ uptake capacity and higher adsorption selectivity of CO₂ over CH₄ and N₂ will lead to a better separation performance of **ZJNU-40a**.

To further compare the separation performance of **ZJNU-40a** and **NOTT-101**, we perform transient breakthrough simulations using the methodology described in the literature.¹² The details are provided in ESI† Fig. 3 compares 50/50 CO₂/CH₄ mixture breakthrough characteristics as a function of the dimensionless time in an adsorber packed with **ZJNU-40a** and **NOTT-101** and maintained at 296 K and a total pressure of 200 kPa. The breakthrough of CO₂ occurs at a later time with **ZJNU-40a**, indicating that this material has a better separation performance. Furthermore, based on the material balance on the fixed bed adsorber, the productivities of methane with a purity of 99.95%+ are calculated to be 2.84 mol per kg of **ZJNU-40a**, and 1.78 mol per kg of **NOTT-101** (Fig. S11 and 12, ESI†). This implies that **ZJNU-40a** has a 50% higher productivity than **NOTT-101**. Likewise, when separation of 5/95 CO₂/CH₄ mixtures at 296 K and a total pressure of 200 kPa is considered, the productivities of methane with a purity of 99.95%+ are calculated to be 5.80 mol per kg of **ZJNU-40a**, and 3.62 mol per kg of **NOTT-101** (Fig. S13 and 14, ESI†). These productivity values are higher than the corresponding ones for 50/50 CO₂/CH₄ mixtures because a lower amount of CO₂ needs to be captured. For 5/95 CO₂/CH₄ mixtures, **ZJNU-40a** has a 60% higher productivity than **NOTT-101**. As for the separation of 15/85 CO₂/N₂ gas mixtures at 296 K and a total pressure of 100 kPa, the productivities of N₂ with a purity of 99.95%+ can be determined to be 3.29 mol per kg of **ZJNU-40a**, and 2.08 mol per kg of **NOTT-101** (Fig. S15 and 16, ESI†). Taken together, these breakthrough calculations clearly demonstrate that **ZJNU-40a** has a better separation performance than **NOTT-101**.

To understand the gas-framework interaction, the coverage dependent adsorption enthalpies were calculated using the Clausius–Clapeyron equation by fitting the adsorption isotherms taken at 273 and 296 K to the Langmuir expression. As expected (Fig. S17, ESI†), **ZJNU-40a** exhibits a higher CO₂ binding affinity than CH₄ and N₂ throughout the adsorption process. **ZJNU-40a** has a slightly lower isosteric heat of CO₂ adsorption than **NOTT-101**, indicating that the binding sites can play even more important roles than the interaction strengths in enhancing carbon dioxide uptake and thus gas separation selectivities.^{1c} Such phenomena are

even more clearly demonstrated in unique UTSA-16 because of its extraordinarily high carbon dioxide capture and separation.^{2c} The introduction of the heterocyclic functional sites and the smaller pore sizes within **ZJNU-40a** have played the most important roles for its better performance than **NOTT-101** for carbon dioxide capture and separation.

In summary, we have synthesized a new NbO-type MOF, **ZJNU-40**, by utilizing a unique tetracarboxylate containing benzothiadiazole as a polarized functional site. With moderately high BET surface area, two types of nanoscopic cages, open metal sites, accessible donor sites, and smaller pore spaces within the framework, the activated **ZJNU-40a** exhibits higher CO₂ uptake capacity as well as better adsorption selectivity of CO₂ over CH₄ and N₂, and thus better CO₂ capture performance than the isorecticular **NOTT-101**. This work demonstrated that incorporation of a polarized heteroaromatic ring into the framework provides a promising route to improve CO₂ gas sorption and selectivity and thus to produce materials with enhanced CO₂ separation performance.

This work was supported by the National Natural Science Foundation of China (No. 21301156), Open Research Fund of Top Key Discipline of Chemistry in Zhejiang Provincial Colleges and Key Laboratory of the Ministry of Education for Advanced Catalysis Materials (ZJHX201313), and Grant AX-1730 from the Welch Foundation (B.C.).

Notes and references

- (a) 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; (b) J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.*, 2012, **112**, 869–932; (c) Z. Zhang, Z.-Z. Yao, S. Xiang and B. Chen, *Energy Environ. Sci.*, 2014, **7**, 2868–2899; (d) J.-P. Zhang and X.-M. Chen, *J. Am. Chem. Soc.*, 2009, **131**, 5516–5521; (e) R.-J. Li, M. Li, X.-P. Zhou, D. Li and M. O’Keeffe, *Chem. Commun.*, 2014, **50**, 4047–4049; (f) Y.-X. Tan, Y.-P. He and J. Zhang, *Chem. Commun.*, 2011, **47**, 10647–10649; (g) D.-S. Zhang, Z. Chang, Y.-F. Li, Z.-Y. Jiang, Z.-H. Xuan, Y.-H. Zhang, J.-R. Li, Q. Chen, T.-L. Hu and X.-H. Bu, *Sci. Rep.*, 2013, **3**, 3312; (h) Y.-L. Huang, Y.-N. Gong, L. Jiang and T.-B. Lu, *Chem. Commun.*, 2013, **49**, 1753–1755.
- (a) A. R. Millward and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 17998–17999; (b) S. R. Caskey, A. G. Wong-Foy and A. J. Matzger, *J. Am. Chem. Soc.*, 2008, **130**, 10870–10871; (c) S. Xiang, Y. He, Z. Zhang, H. Wu, W. Zhou, R. Krishna and B. Chen, *Nat. Commun.*, 2012, **3**, 954; (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 and M. J. Zaworotko, *Nature*, 2013, **495**, 80–84.
- (a) 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**, 2159–2171; (b) Y. He, W. Zhou, T. Yildirim and B. Chen, *Energy Environ. Sci.*, 2013, **6**, 2735–2744.
- (a) M. Zhang, Q. Wang, Z. Lu, H. Liu, W. Liu and J. Bai, *CrystEngComm*, 2014, **16**, 6287–6290; (b) B. Zheng, H. Liu, Z. Wang, X. Yu, P. Yia and J. Bai, *CrystEngComm*, 2013, **15**, 3517–3520; (c) T. K. Prasad, D. H. Hong and M. P. Suh, *Chem. – Eur. J.*, 2010, **16**, 14043–14050; (d) Z. Wang, B. Zheng, H. Liu, X. Lin, X. Yu, P. Yi and R. Yun, *Cryst. Growth Des.*, 2013, **13**, 5001–5006; (e) N. H. Alsmail, M. Suyetin, Y. Yan, R. Cabot, C. P. Krap, J. Lü, T. L. Easun, E. Bichoutskaia, W. Lewis, A. J. Blake and M. Schröder, *Chem. – Eur. J.*, 2014, **20**, 7317–7324.
- (a) M. Li, D. Li, M. O’Keeffe and O. M. Yaghi, *Chem. Rev.*, 2014, **114**, 1343–1370; (b) R.-J. Li, M. Li, X.-P. Zhou, S. W. Ng, M. O’Keeffe and D. Li, *CrystEngComm*, 2014, **16**, 6291–6295.
- D. Sun, S. Ma, J. M. Simmons, J.-R. Li, D. Yuan and H.-C. Zhou, *Chem. Commun.*, 2010, **46**, 1329–1331.
- R. D. Kennedy, V. Krungleviciute, D. J. Clingerman, J. E. Mondloch, Y. Peng, C. E. Wilmer, A. A. Sarjeant, R. Q. Snurr, J. T. Hupp,

- T. Yildirim, O. K. Farha and C. A. Mirkin, *Chem. Mater.*, 2013, **25**, 3539–3543.
- 8 H.-M. Wen, B. Li, D. Yuan, H. Wang, T. Yildirim, W. Zhou and B. Chen, *J. Mater. Chem. A*, 2014, **2**, 11516–11522.
- 9 Z. Wang, B. Zheng, H. Liu, P. Yi, X. Li, X. Yu and R. Yun, *Dalton Trans.*, 2013, **42**, 11304–11311.
- 10 Y. He, S. Xiang, Z. Zhang, S. Xiong, C. Wu, W. Zhou, T. Yildirim, R. Krishna and B. Chen, *J. Mater. Chem. A*, 2013, **1**, 2543–2551.
- 11 Z. Liang, J. Du, L. Sun, J. Xu, Y. Mu, Y. Li, J. Yu and R. Xu, *Inorg. Chem.*, 2013, **52**, 10720–10722.
- 12 R. Krishna and J. R. Long, *J. Phys. Chem. C*, 2011, **115**, 12941–12950.