A New Microporous Metal-Organic Framework for Highly Selective C₂H₂/CH₄ and C₂H₂/CO₂ Separation at Room Temperature

Xing Duan,*^{,a} Tifeng Xia,^b Zhenguo Ji,^a Yuanjing Cui,^b Yu Yang,^b and Guodong Qian^{*,b}

^a College of Materials & Environmental Engineering, Hangzhou Dianzi University, Hangzhou, Zhejiang 310027, China

^b State Key Laboratory of Silicon Materials, Cyrus Tang Center for Sensor Materials and Applications, School of Materials Science & Engineering, Zhejiang University, Hangzhou, Zhejiang 310027, China

We have successfully designed and synthesized a new tetracarboxylic linker, which constructed its first three-dimensional microporous metal-organic framework (MOF), $[Cu_2(DDPD)(H_2O)_2] \cdot G_x$ (**ZJU-13**, H₄DDPD= 5,5'-(2,6-dihydroxynaphthalene-1,5-diyl)diisophthalic acid, ZJU=Zhejiang University, G=guest molecules) via solvothermal reaction. Due to open Cu²⁺ sites and optimized pore size, the activated **ZJU-13a** displays high separation selectivity for C₂H₂/CH₄ of 74 and C₂H₂/CO₂ of 12.5 at low pressure by using Ideal Adsorbed Solution Theory (IAST) simulation at room temperature.

Keywords metal-organic frameworks, micro-porous materials, selective separation, open metal sites, optimizedpore size

Introduction

Acetylene is one of greatly important raw materials in the field of petrochemical and industry, for example, high-purity acetylene flame is often used for cutting and welding of metal materials. Obtaining high purity of acetylene is the precondition of making effective use of this hydrocarbon. Therefore, the separation and purification of acetylene are the extremely essential process in the industry.^[1-7] The traditional cryogenic distillation method has been extensively applied to separate acetylene from other gas molecules, for example carbon dioxide and methane. Whereas due to the similarity of molecule dimensional size, kinetic diameter and volatility for C₂H₂, CO₂, and CH₄, such separation process is rather energy-consuming and ineffective. So, the design and exploitation of economic efficient separation methods are the pursuing goal for numerous researchers. Taking advantage of high surface area of the adsorbent for cost- and energy-effective separation of acetylene is considered to be one of the promising separation technology.^[8,9] Some conventional porous carbon materials and molecular sieve have been utilized in the separation of acetylene, but their pore space cannot be effectively controlled, the separation performance is not ideal. So, it is necessary to seek the porous materials with high separation selectivity for acetylene.

Metal organic frameworks (MOFs), as a novel family of inorgainc-organic hybrid porous materials, have exhibited excellent potential in the application of gas storage and separation.^[10-42] MOFs constituted from metal ions/clusters and organic bridging linkers are a kind of crystalline porous materials with periodic infinite network structure. Due to their inherent characteristics, MOFs have many advantages compared to conventional porous materials: (1) the synthesis of MOFs is mostly by a one-step method which is simple and facile; (2) the shape and size of channel/pore/cage can be controlled for the requirement of practical application by choosing appropriate metal ions/secondary building units (SBUs) or organic linkers, to achieve better effect of gas screening and storage; (3) the surface of channel/pore/cage can be decorated by synthesis or postsynthesis, such as immobilizing open metal sites (OMSs) and/or organic-functional groups (-NH₂, -OH, -SO₃H, -COOH), to reach the purpose of selective recognition of different guest molecules.^[25-48] Zaworotko and co-workers^[43,44] reported two MOFs materials with different pore size, SIFSIX-2-Cu $(13.05 \times 13.05 \text{ Å}^2)$ and SIFSIX-2-Cu-I (5.15×5.15 Å²). IAST (Ideal Adsorbed Solution Theory) simulation and breakthrough tests exhibited the selectivity of SIFSIX-2-Cu-I for CO₂/CH₄ and CO_2/N_2 to be 7-10 times higher than that of SIFSIX-2-Cu. Chen and co-workers^[45] decorated -OH

^{*} E-mail: star19871127@hdu.edu.cn

Received January 12, 2017; accepted March 30, 2017; published online XXXX, 2017.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cjoc.201700040 or from the author.

groups on the pore surfaces of MOFs to obtain their high separation selectivity of C_2H_2/CH_4 and CO_2/CH_4 at room temperature. It is an effective method to promote gas separation selectivity by utilizing both the immobilized functional sites within pore surface of MOFs and size-exclusive effects. MOFs comprised of tetracarboxylic acid linkers and Cu²⁺ paddle-wheel cluster (Cu₂(COO)₄) with NbO-type topology are considered to be one of the most competitive porous materials because of their high gas storage and selective separation performance. Herein, we introduced dihydroxynaphthalene into ligand to develop a new tetracarboxylic organic linker H_4DDPD ($H_4DDPD = 5,5'-(2,6-dihydroxynaph$ thalene-1,5-diyl)diisophthalic acid, Scheme 1) and its first 3D microporous MOF, $[Cu_2(DDPD)(H_2O)_2] \cdot G_x$ (**ZJU-13**, $H_4DDPD = 5,5'-(2,6-dihydroxynaphthalene-$ 1,5-diyl) diisophthalic acid, ZJU=Zhejiang University, G=guest molecules). With open Cu^{2+} sites and optimized pore size, ZJU-13a exhibited high separation selectivity of 74 and 12.5 for C₂H₂/CH₄ and C₂H₂/CO₂ at room temperature, respectively.

Scheme 1 The organic linker H_4DDPD for the construction of ZJU-13



Experimental

Materials and methods

All solvents and reagents were obtained from commercial sources, and were used without further purification. ¹H NMR spectra were collected on a Bruker Advance DMX 500 MHz spectrometer in CDCl₃ and DMSO solution using tetramethylsilane (TMS, δ 0) as an internal standard at room temperature. The X-ray powder diffraction (PXRD) experiment was carried out on a PANalyticalX'Pert Pro X-ray diffractometer with Cu-K α (λ = 1.542 Å) at room temperature and the data were collected in the $2\theta = 3^{\circ} - 50^{\circ}$ range. Thermogravimetric analyses (TGA) were recorded on a Netszch TGA 209 F3 thermogravimeter under N₂ atmosphere heated from room temperature to 900 °C at the heating rate of 5 K•min⁻¹. Elemental analyses (C, H, and N) were performed on an EA1112 micro elemental analyzer.

Synthesis of ZJU-13

In a 20 mL glass vial, the organic linker H₄DDPD (10 mg, 0.0204 mmol) was dissolved in 7.5 mL of *N*,*N*-dimethyl formamide (DMF) and 2.5 mL of ethanol. Then Cu(NO₃)₂•2.5H₂O (20 mg, 0.086 mmol) and 5 mL of H₂O were added into the vial, then 250 μ L of HNO₃

(65%, aq.) was added. The vial was capped and placed in a precise oven at 80 °C for 3 d. The resulting blue rhombic shaped crystals were washed with DMF to afford **ZJU-13**. Elemental analysis: calcd for $[Cu_2-(C_{26}H_{12}O_{10})(H_2O)_2] \cdot (DMF)_5 \cdot (H_2O)_2(C_{41}H_{55}Cu_2N_5O_{19},$ %): C 46.9, H 5.30, N 6.68; found C 46.8, H 5.423, N 6.79.

Gas sorption measurements

A Micromeritics ASAP 2020 surface area analyzer was used to measure the BET surface and gas sorption isotherms of C_2H_2 , CO_2 and CH_4 . Prior to the measurement, to have the guest-free framework, the fresh as-synthesized sample was washed with DMF several times, then guest-exchanged with anhydrous acetone at least 10 times, then filtered. Afterwards, the sample was vacuumed at 273 K for 24 h and at 298 K for 12 h and then at 353 K until the outgas rate was 5 μ mHg•min⁻¹. An activated sample of **ZJU-13** (100 mg) was used for the gas adsorption measurements. The N₂ adsorption measurement was kept at 77 K with liquid nitrogen. The C₂H₂, CO₂ and CH₄ adsorption measurements were performed at 273 K with an ice-water bath and at 298 K with a water bath.

Results and Discussion

1,5-Dibromo-2,6-dimethoxynaphthalene was obtained via Williamson etherification and addition reaction. Dimethyl (5-pinacolboryl)isophthalate was synthesized by substitution reaction using Pd(dppf)₂Cl₂ as catalyst and KOAc as bases at 65 °C. 1,5-Dibromo-2,6-dimethoxynaphthalene and dimethyl (5-pinacolboryl) isophthalate yielded tetramethyl 5,5'-(2,6-dimethoxynaphthalene-1,5-diyl)diisophthalate via Suzuki cross-coupling reaction taking advantage of the Pd(PPh₃)₄-catalysis, then demethylation, hydrolysis and acidification reaction to give 5,5'-(2,6-dihydroxynaphthalene-1,5-diyl) diisophthalic acid (H₄DDPD) (Scheme S1). All chemical structures of above-mentioned reaction products were confirmed by the ¹H NMR spectra.

A single blue rhombic shaped crystal of ZJU-13 was obtained by the solvothermal reaction of H₄DDPD and Cu(NO₃)₂•2.5H₂O in a mixture solvent of DMF/EtOH/ H₂O with the addition of a small amount of HNO₃ at 80 °C for 72 h. The crystal structure was determined by the single-crystal X-ray diffraction (SCXRD) analysis which exhibited ZJU-13 crystallizes in the trigonal space group R-3m. Crystallographic data, data collection parameters, and refinement are summarized in Table S1. As shown in the Figure 1a, ZJU-13 reveals two types of cage along the c axis of about 7.2 Å and 6×20 Å² in diameter with -OH functional groups pointing to the cages of the framework, taking into account the van der Waals radii. The sizes of window openings are about 3 Å along c axis and 2 Å and 2.8 \times 5.6 Å² along a, b axis (Figures 1b and 1c). Due to the introduction of the naphthalene and -OH functional groups, the sizes of the cages and window openings are smaller than those of NOTT-101. The phase purity of bulk crystal material is confirmed by the good agreement with PXRD (powder X-ray diffraction) of as-synthesized crystal material and simulated one (Figure S1). TGA (thermogravimetric analysis) exhibits a weight loss of 39.1% from room temperature to 250 °C, corresponding to the solvent molecules (five DMF and two H₂O molecules) and two coordinated water molecules (Figure S2). The void volume of **ZJU-13** is 64.7% (7752 Å³ out of 11965 Å³) by the PLATON software.^[49]



Figure 1 X-ray single crystal structure of **ZJU-13**, indicating (a) two types of cage along the *c* axes of about 7.2 Å and 6×20 Å² in diameter; (b) the structure viewed along the *a* axes indicating the window openings of about 2 Å and 2.6×5.8 Å², respectively; (c) the structure viewed along the *c* axes showing the window openings of about 3 Å.

The fresh as-synthesized sample of **ZJU-13** was washed with DMF and guest-exchanged with dry-acetone and vacuumed at 80 °C for 2 h to obtain the activated **ZJU-13a**. The N₂ sorption-desorption isotherm at 77 K was measured by utilizing Micromeritics ASAP 2020 surface area analyzer. The result shows that **ZJU-13a** displays a typical reversible Type-I sorption behavior with the saturation uptake of 277.1 cm³•g⁻¹ (Figure 2). The Brunauer-Emmett-Teller (BET) and Langmuir surface areas are 1056 m²•g⁻¹ and 1075 m²•g⁻¹ by BET equation and Langmuir equation calculation, respectively (Figure S3). **ZJU-13a** has a pore volume of 0.427 cm³•g⁻¹.

The permanent porosity, optimized pore size and





open Cu²⁺ sites encourage us to study its potential application to selective gas separation. As shown in Figure 3, all of the adsorption isotherms are reversible. **ZJU-13a** can take up C₂H₂ of 153 cm³•g⁻¹ at 273 K and 115 cm³•g⁻¹ at 298 K, which is further higher than that of CO₂ (122 cm³•g⁻¹ at 273 K and 70 cm³•g⁻¹ at 298 K) and CH₄ (31 cm³•g⁻¹ at 273 K and 20 cm³•g⁻¹ at 298 K). The uptake amount of C₂H₂ at room temperature in **ZJU-13a** is higher than those of some well-known MOFs such as ZJU-26a (84 cm³•g⁻¹),^[29] UTSA-50 (91 cm³•g⁻¹),^[4] MOF-5 (26 cm³•g⁻¹),^[27] UTSA-33a (84 cm³•g⁻¹),^[50] Cu₂(NDC)₂(DABCO) (97 cm³•g⁻¹),^[51] and Zn₂(NDC)₂(DABCO) (106 cm³•g⁻¹),^[51] which is attributed to the open Cu²⁺ sites and optimized pore sizes resulting in the efficient sorption of acetylene molecules in **ZJU-13a** micropores.



Figure 3 C_2H_2 (black), CO_2 (red) and CH_4 (blue) adsorption isotherms of **ZJU-13a** at 273 K and 298 K. Solid symbols: adsorption, open symbols: desorption.

The adsorption enthalpies of **ZJU-13a** for C_2H_2 , CO_2 , and CH_4 are calculated by the virial expression. The adsorption data were fitted by the following equation:

$$\ln\left(p\right) = \ln\left(N\right) + \left(\frac{1}{T}\right) \sum_{i=0}^{m} a_i \times N^i + \sum_{j=0}^{n} b_j \times N^j \tag{1}$$

The isosteric heat of adsorption, $Q_{\rm st}$, is defined as

3

follows:

$$Q_{\rm st} = -R \sum_{i=0}^{m} a_i N^i \tag{2}$$

where *N* is the adsorption capacity of adsorbate, *p* is the pressure, *R* is the Planck constant of 8.314 mol⁻¹•K⁻¹, *T* is the temperature, a_i , b_i are the virial coefficients.

The isosteric heats of adsorption for C_2H_2 , CO_2 , and CH_4 49.7 kJ•mol⁻¹, 33 kJ•mol⁻¹, and 20 kJ•mol⁻¹, respectively (Figure 4). The adsorption enthalpy for C_2H_2 (49.7 kJ•mol⁻¹) in **ZJU-13a** is far greater than those of most MOFs materials and is comparable to those of MMOF-74 (M=Fe, Mg, Co) and UTSA-60 with open metal sites,^[52] which further indicates the open Cu²⁺ sites and optimized pore size can improve the affinity between framework and acetylene molecules.



Figure 4 The isosteric heats of adsorption with error bars of C_2H_2 , CO_2 and CH_4 on ZJU-13a.

Such large differences of adsorption capacities and adsorption enthalpies for C₂H₂, CO₂, and CH₄ enable us to calculate the separation selectivity for C₂H₂/CH₄ and C₂H₂/CO₂ by using Ideal Adsorbed Solution Theory (IAST). The mixture adsorption isotherms and separation selectivity at different temperature and pressures for C_2H_2/CH_4 (50 : 50) and C_2H_2/CO_2 (50 : 50) are shown in Figure 5 and Figure S4. The IAST calculation displays that the separation selectivities of C_2H_2/CH_4 are estimated to be 170 and 74 at 1 kPa at 273 K and 298 K and then rapidly dropdown to 68-80 and 20-25, respectively, which are higher than those of MFM-202a^[38] and the crystal without -OH residues (Figure S5). To the best of our knowledge, the C₂H₂/CH₄ separation selectivity at room temperature is one of the highest of reported MOFs materials at present.^[6,29,36,38,50,55-56] The separation selectivities of ZJU-13a are calculated to be 17 and 12.5 for C_2H_2/CO_2 at very low pressure at 273 K and 298 K, then both reduce to 4-5. Such good separation selectivities for C₂H₂/CH₄ and C₂H₂/CO₂ indicate open metal sites and optimized pore size can improve the interaction with the framework and the acetylene molecules. This work demonstrats ZJU-13a is a prospective microporous MOF material for selective gas



Figure 5 The adsorption selectivities predicted by IAST of ZJU-13a for C_2H_2/CH_4 and C_2H_2/CO_2 at 273 K and 298 K, respectively.

separation in the near future.

Conclusions

In conclusion, we have successfully prepared a novel microporous MOF Cu₂DDPD (**ZJU-13a**) with optimized pore sizes and open Cu²⁺ sites. These features enable the activated **ZJU-13a** to exhibit high separation selectivity for C₂H₂/CH₄ of 74 and C₂H₂/CO₂ of 12.5 at 1 kPa at room temperature and the values in the plateau regions are 20–5 and 4–5, respectively. It is expected that this microporous MOFs material will have the application potential for selective gas separation in industry in the future.

Acknowledgement

The authors gratefully acknowledge financial support from National Natural Science Foundation of China (Nos. 51602087, 51472217and 51432001) and Zhejiang Provincial Natural Science Foundation (No. LZ15E020001).

References

[1] Molero, H.; Bartlett, B. F.; Tysoe, W. T. J. Catal. 1999, 181, 49.

[2] Fu, H.-R.; Kang, Y.; Zhang, J. Inorg. Chem. 2014, 53, 4209.

- [3] Procopio, E. Q.; Linares, F.; Montoro, C.; Colombo, V.; Maspero, A.; Barea, E.; Navarro, J. A. R. Angew. Chem., Int. Ed. 2010, 49, 7308.
- [4] Xu, H.; He, Y.; Zhang, Z.; Xiang, S.; Cai, J.; Cui, Y.; Yang, Y.; Qian, G; Chen, B. J. Mater. Chem. A 2013, 1, 77.
- [5] Peng, Y.; Srinivas, G.; Wilmer, C. E.; Eryazici, I.; Snurr, R. Q.; Hupp, J. T.; Yildirim, T.; Farha, O. K. *Chem. Commun.* 2013, 49, 2992.
- [6] Liu, K.; Ma, D.; Li, B.; Li, Y.; Yao, K.; Zhang, Z.; Han, Y.; Shi, Z. J. Mater. Chem. A 2014, 2, 15823.
- [7] Song, C.; Ling, Y.; Feng, Y.; Zhou, W.; Yildirim, T.; He, Y. Chem. Commun. 2015, 51, 8508.
- [8] Zhang, Z.; Xiang, S.; Chen, B. CrystEngComm2011, 13, 5983.
- [9] Su, Z.; Fan, J.; Okamura, T.-A.; Sun, W. Chin. J. Chem. 2012, 30, 2016.
- [10] Matsuda, R.; Kitaura, R.; Kitagawa, S.; Kubota, Y.; Belosludov, R. V.; Kobayashi, T. C.; Sakamoto, H.; Chiba, T.; Takata, M.; Kawazoe, Y.; Mita, Y. *Nature* 2005, *436*, 238.
- [11] Sato, H.; Kosaka, W.; Matsuda, R.; Hori, A.; Hijikata, Y.; Belosludov, R. V.; Sakaki, S.; Takata, M.; Kitagawa, S. Science 2014, 343, 167.
- [12] He, Y.; Zhou, W.; Qian, G.; Chen, B. Chem. Soc. Rev. 2014, 43, 5657.
- [13] He, Y.; Zhou, W.; Yildirim, T.; Chen, B. *Energy Environ. Sci.* **2013**, *6*, 2735.
- [14] Zhang, Z.; Yao, Z.-Z.; Xiang, S.; Chen, B. Energy Environ. Sci. 2014, 7, 2868.
- [15] Wang, P.; Kang, M.; Sun, S.; Liu, Q.; Zhang, Z.; Fang, S. Chin. J. Chem. 2014, 32, 838.
- [16] Zhang, E.; Jia, Q.; Zhang, J.; Ji, Z. Chin. J. Chem. 2016, 34, 191.
- [17] Li, L.; Cao, X.; Huang, R. Chin. J. Chem. 2016, 34, 143.
- [18] Pei, X.; Chen, Y.; Li, S.; Zhang, S.; Feng, X.; Zhou, J.; Wang, B. *Chin. J. Chem.* **2016**, *34*, 157.
- [19] Zhang, E.; Zhang, L.; Tan, Z.; Ji, Z.; Li, Q. Chin. J. Chem. 2016, 34, 233.
- [20] Gui, B.; Meng, X.; Xu, H.; Wang, C. Chin. J. Chem. 2016, 34, 186.
- [21] Li, Y.; Zhang, W.; Liu, Z.; Xie, Z. Acta Chim. Sinica 2015, 73, 641.
- [22] Xu, G; Gang, F.; Dong, T.; Fu, Y.; Du, Z. Chin. J. Org. Chem. 2016, 36, 1513.
- [23] Huang, G.; Chen, Y.; Jiang, H. Acta Chim. Sinica 2016, 74, 113.
- [24] Pang, J.; Jiang, F.; Wu, M.; Liu, C.; Su, K.; Lu, W.; Yuan, D.; Hong, M. Nat. Commun. 2015, 6, 7575.
- [25] Zhang, M.; Li, B.; Li, Y.; Wang, Q.; Zhang, W.; Chen, B.; Li, S.; Pan, Y.; You, X.; Bai, J. Chem. Commun. 2016, 52, 7241.
- [26] Song, C.; Jiao, J.; Lin, Q.; Liu, H.; He, Y. Dalton Trans. 2016, 45, 4563.
- [27] Makal, T. A.; Li, J. R.; Lu, W.; Zhou, H. C. Chem. Soc. Rev. 2012, 41, 7761.
- [28] Xiang, S.; Zhou, W.; Zhang, Z.; Green, M. A.; Liu, Y.; Chen, B. Angew. Chem., Int. Ed. 2010, 49, 4615.
- [29] Duan, X.; Cai, J.; Yu, J.; Wu, C.; Cui, Y.; Yang, Y.; Qian, G. Microporous Mesoporous Mater. 2013, 181, 99.
- [30] Duan, X.; Wang, H.; Cui, Y.; Yang, Y.; Wang, Z.; Chen, B.; Qian, G. RSC Adv. 2015, 5, 84446.
- [31] Cai, J.; Wang, H.; Wang, H.; Duan, X.; Wang, Z.; Cui, Y.; Yang, Y.; Chen, B.; Qian, G. RSC Adv. 2015, 5, 77417.

- [32] Cai, J.; Lin, Y.; Yu, J.; Wu, C.; Chen, L.; Cui, Y.; Yang, Y.; Chen, B.; Qian, G. RSC Adv. 2014, 4, 49457.
- [33] Rao, X.; Cai, J.; Yu, J.; He, Y.; Wu, C.; Zhou, W.; Yildirim, T.; Chen, B.; Qian, G. Chem. Commun. 2013, 49, 6719.
- [34] Hu, Y.; Xiang, S.; Zhang, W.; Zhang, Z.; Wang, L.; Bai, J.; Chen, B. Chem. Commun. 2009, 7551.
- [35] Xiang, S.; Zhou, W.; Gallegos, J. M.; Liu, Y.; Chen, B. J. Am. Chem. Soc. 2009, 131, 12415.
- [36] Colombo, V.; Montoro, C.; Maspero, A.; Palmisano, G.; Masciocchi, N.; Galli, S.; Barea, E.; Navarro, J. A. R. J. Am. Chem. Soc. 2012, 134, 12830.
- [37] Yang, S.; Ramirez-Cuesta, A. J.; Newby, R.; Garcia-Sakai, V.; Manuel, P.; Callear, S. K.; Campbell, S. I.; Tang, C. C.; Schröder, M. *Nat. Chem.* 2015, 7, 121.
- [38] Gao, S.; Morris, C. G.; Lu, Z.; Yan, Y.; Godfrey, H. G. W.; Murray, C.; Tang, C. C.; Thomas, K. M.; Yang, S.; Schröder, M. *Chem. Mater.* **2016**, *28*, 2331.
- [39] Duan, X.; Wu, C.; Xiang, S.; Zhou, W.; Yildirim, T.; Cui, Y.; Yang, Y.; Chen, B.; Qian, G. Inorg. Chem. 2015, 54, 4377.
- [40] Herm, Z. R.; Bloch, E. D.; Long, J. R. Chem. Mater. 2014, 26, 323.
- [41] Jiao, J.; Dou, L.; Liu, H.; Chen, F.; Bai, D.; Feng, Y.; Xiong, S.; Chen, D. L.; He, Y. Dalton Trans. 2016, 45, 13373.
- [42] Xia, T.; Cai, J.; Wang, H.; Duan, X.; Cui, Y.; Yang, Y.; Qian, G. Microporous Mesoporous Mater. 2015, 215, 109.
- [43] Burd, S. D.; Ma, S.; Perman, J. A.; Sikora, B. J.; Snurr, R. Q.; Thallapally, P. K.; Tian, J.; Wojtas, L.; Zaworotko, M. J. J. Am. Chem. Soc. 2012, 134, 3663.
- [44] Nugent, P.; Belmabkhout, Y.; Burd, S. D.; Cairns, A. J.; Luebke, R.; Forrest, K.; Pham, T.; Ma, S.; Space, B.; Wojtas, L.; Eddaoudi, M.; Zaworotko, M. J. *Nature* 2013, 495, 80.
- [45] Chen, Z.; Xiang, S.; Arman, H. D.; Mondal, J. U.; Li, P.; Zhao, D.; Chen, B. *Inorg. Chem.* 2011, 50, 3442.
- [46] Li, P.; He, Y.; Zhao, Y.; Weng, L.; Wang, H.; Krishna, R.; Wu, H.; Zhou, W.; O'Keeffe, M.; Han, Y.; Chen, B. *Angew. Chem.*, *Int. Ed.* 2015, 54, 574.
- [47] Du, L.; Lu, Z.; Xu, L.; Ma, M.; Zhang, J. Eur. J. Inorg. Chem. 2016, 29, 4727.
- [48] Roztocki, K.; Senkovska, I.; Kaskel, S.; Matoga, D. Eur. J. Inorg. Chem. 2016, 27, 4450.
- [49] Spek, L. PLATON, The University of Utrecht, Utrecht, The Netherlands, 1999.
- [50] He, Y.; Zhang, Z.; Xiang, S.; Fronczek, F. R.; Krishna, R.; Chen, B. *Chem. Eur. J.* 2012, *18*, 613.
- [51] Tanaka, D.; Higuchi, M.; Horike, S.; Matsuda, R.; Kinoshita, Y.; Yanai, N.; Kitagawa, S. Chem. Asian J. 2008, 3, 1343.
- [52] Wen, H. M.; Li, B.; Wang, H.; Wu, C.; Alfooty, K.; Krishna, R.; Chen, B. Chem. Commun. 2015, 51, 5610.
- [53] Duan, J.; Jin, W.; Krishna, R. Inorg. Chem. 2015, 54, 4279.
- [54] Liu, K.; Li, B.; Li, Y.; Li, X.; Yang, F.; Zeng, G.; Peng, Y.; Zhang, Z.; Li, G.; Shi, Z.; Feng, S.; Song, D. Chem. Commun. 2014, 50, 5031.
- [55] He, Y.; Krishna, R.; Chen, B. Energy Environ. Sci. 2012, 5, 9107.
- [56] Duan, X.; Wang, H.; Ji, Z.; Cui, Y.; Yang, Y.; Qian, G. J. Solid State Chem. 2016, 241, 152.

(Pan, B.; Fan, Y.)