Carbon Dioxide Fixation

Anionic Metal–Organic Framework for Selective Dye Removal and CO$_2$ Fixation

Sanjay Kumar,[a,b] Gaurav Verma,[a] Wen-Yang Gao,[a] Zheng Niu,[a] Lukasz Wojtas,[a] and Shengqian Ma*[a]

Abstract: A microporous Zn-based anionic metal–organic framework (MOF) was synthesized with triangular 4,4′,4′′-(pyridine-2,4,6-triyl)tribenzoic acid. The anionic MOF material featuring open channels proved to be a good capturing agent for the cationic dye methylene blue. In addition, the Zn-MOF demonstrated excellent catalytic activity for CO$_2$ fixation by cycloaddition reaction with epoxides for the generation of cyclic carbonates.

Introduction

The brighter side of the discovery of synthetic dyes by W. H. Perkin in 1956 is plagued by a darker side linked to toxicity and environment pollution. Nearly 40000 dyes are currently listed in the color index, which consists of over 7000 chemical scaffolds.[1] The effluent of several industries, namely, the textile, printing, leather, paper, pharmaceutical, and food industries, contains dyes that contribute to toxicity in the environment and that endanger aquatic life.[2] Furthermore, dye wastes are toxic, carcinogenic, and mutagenic and thus also affect humans and other terrestrial animals.[3,4] There have been consistent efforts to develop techniques for dye removal to decrease their adverse effects on the biosphere. As a result, a plethora of methods including chemical oxidation,[5] photolytic degradation,[6] biological treatment,[7] and adsorption have been reported in the literature for removal of dye wastes.[8,9]

Among them, the adsorption of dyes is one of the most effective strategies for the removal of these toxic materials from the environment owing to low cost and operational simplicity.[8,10] On these lines, a variety of adsorbent materials have been developed, including agricultural waste products, activated carbon, zeolites, metal–organic frameworks (MOFs), and porous organic polymers. Among the porous materials, MOFs have been receiving considerable attention owing to their excellent properties, which include high surface areas and tailor-made structures and pore sizes, and their applications in gas adsorption, sensors, and catalysis.[11–15] Until now, however, only a few MOFs have been examined for the adsorption and separation of dyes.[16] Most porous materials used for dye separation operate on a size-exclusion basis, but the separation of dyes of similar sizes is typically difficult.[16] Therefore, the development of materials for the efficient adsorption or separation of dyes of similar sizes is timely and highly desirable.

In addition, industries that use dyes, including the textile industry, are not only adding dye effluents to the environment, but they also have a large water footprint and contribute to CO$_2$ emissions. Current technologies available to curb this menace are either corrosive or energy intensive.[17] Adsorptive technologies that exploit the physisorption of CO$_2$ into porous materials, especially MOFs, have gained momentum as a result of the facile regeneration process.[12,18] Keeping these points in mind, we synthesized a zinc-based metal–organic framework with 4,4′,4′′-(pyridine-2,4,6-triyl)tribenzoic acid (H$_3$L) and explored its use in dye adsorption and CO$_2$ fixation.

Results and Discussion

The zinc-based anionic microporous metal–organic framework (Zn-MOF) with the triangular ligand 4,4′,4′′-(pyridine-2,4,6-triyl)tribenzoic acid (H$_3$L) was synthesized by using the solvothermal technique and was characterized by a variety of techniques, including single-crystal X-ray diffraction (SCXRD), powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), and Fourier-transform infrared (FTIR) spectroscopy to establish the structure of the MOF (Figure 1). As revealed by SCXRD, there are two kinds of Zn^{II} ions in the structure: hexacoordinated Zn^{II} and tetracoordinated Zn^{II}. The adjacent Zn^{II} ions are connected through a carbonyl O atom of the ligand or formic acid thus to form a chain structure. The ligands connect each chain and construct a 3D framework with chiral square channels. The framework structure is similar to a reported one.[19] The dimensions of the channel are 9.053 × 9.053 Å, which enables entrance of the dye molecules. PXRD studies were performed to verify the phase purity of the MOF. The diffraction pattern of the fresh sample is consistent with the calculated one (Figure S2, Supporting Information). TGA of the synthesized MOF shows initial loss of solvent and decomposition after 400 °C, which is indicative of the high thermal stability of the frame-

[a] Department of Chemistry, University of South Florida,
4202 E. Fowler Avenue, Tampa, Florida 33620, USA
E-mail: sqma@usf.edu
http://sqma.myweb.usf.edu/
[b] Department of Chemistry, Multani Mal Modi College,
Patiala 147001, Punjab, India
Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/ejic.201600218.

ChemPubSoc
Europe

EurJIC
European Journal
of Inorganic Chemistry

Communication

work (Figure S3). Furthermore, the synthesized MOF was evaluated in terms of its capacity for dye uptake. The Zn-MOF exhibits highly selective uptake and release of the cationic dye methylene blue through an ion-exchange process, and the MOF can effectively separate this dye from another dye with a similar size, that is, methyl orange.
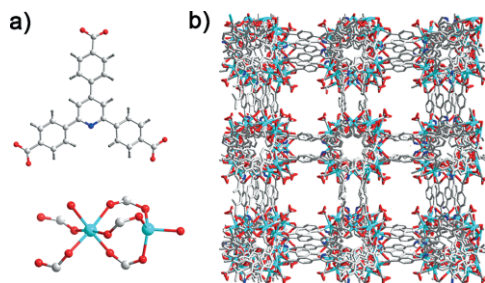

Figure 1. (a) 4,4′,4′′-(Pyridine-2,4,6-triyl)tribenzoic acid (H$_3$L) and secondary building unit. (b) 3D packing of Zn-MOF.

Dye Adsorption and Separation

As evident from structural studies of the crystals, pores available in the framework can be promising for the adsorption of dye molecules. For the synthesized MOF, we studied dyes of similar sizes with different charges, namely, methylene blue, a cationic dye, and methyl orange, an anionic dye. We started the experiment with the adsorption of methylene blue (MB) on the Zn-MOF: typically, freshly prepared crystalline MOF (10 mg) was added to a 10 mL solution of the dye, and absorption of the dye solution was monitored by UV/Vis spectroscopy. The intensity of the MB solution decreased gradually as a function of time (Figure 2, a). The dark blue color of the solution started to vanish and changed to almost colorless. These results demonstrated that the dye molecules could be adsorbed by the MOF, which highlights that the open channels of the Zn-MOF were accessible to the dye molecules. We consider that the adsorption can be attributed to the anionic framework, which captures the cationic dye molecule by exchanging the [(CH$_3$)$_2$NH$_2$]$^+$ counterion generated in situ in the framework. To support this view, we used methyl orange (MO) as a control for dye adsorption. Despite the fact that its size is similar to that of methylene blue, methyl orange was not adsorbed by the Zn-MOF (Figure 2, b), which supports our assumption of adsorption of the cationic dye in the framework with charge selectivity. To further support this selectivity, we ran the adsorption experiment by using a mixture of MB and MO with the Zn-MOF. The green color of the mixed dye solution, resulting from a combination of the blue color of MB and the orange color of MO, gradually changed to orange color, which indicated that MB was selectively taken up by the MOF, whereas MO remained in the solution (Figure 3). Further, to confirm the exchange mechanism of the dye molecule with the [(CH$_3$)$_2$NH$_2$]$^+$ cation of the framework molecule, we performed a dye-release experiment in pure DMF and in NaCl-containing DMF solution. After the adsorption of MB onto the framework, the blue-colored crystals of the MOF were thoroughly washed with DMF, and then these crystals were separately treated with pure DMF and a NaCl-containing solution of
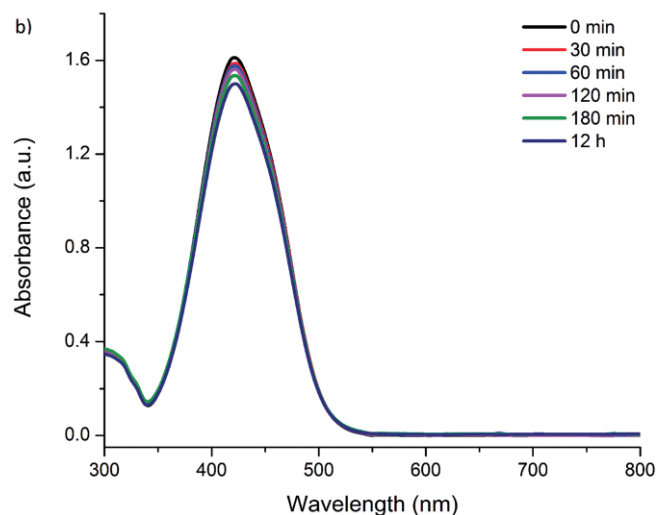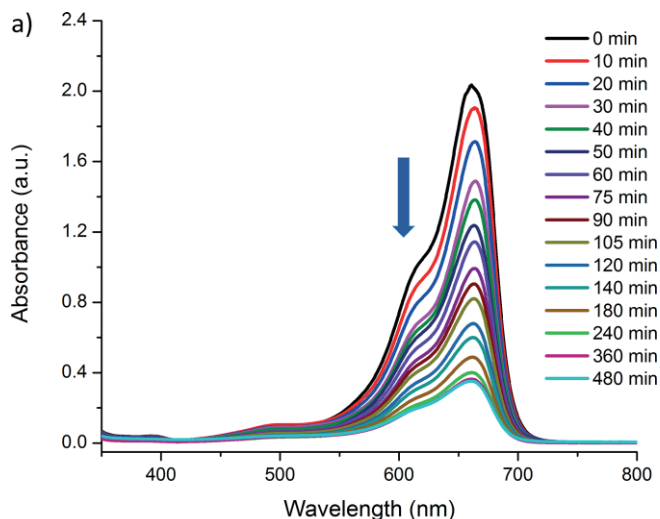

Figure 2. Absorption spectra of (a) methylene blue and (b) methyl orange with Zn-MOF.
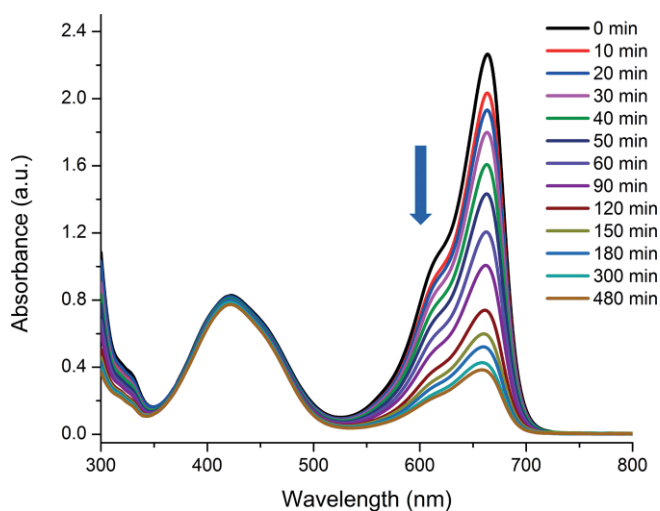

Figure 3. Absorption spectra for a mixture of methylene blue and methyl orange with Zn-MOF.

ChemPubSoc
Europe

EurJIC
European Journal
of Inorganic Chemistry

Communication

DMF. It was observed that negligible dye release occurred in pure DMF, whereas in NaCl, the solution started to turn blue and the intensity of the color increased as time progressed, which indicated release of the dye molecule in the solution, as monitored by UV/Vis spectroscopy (Figure 4). The results implied that only the cationic guest could enter the Zn-MOF, whereas the negatively charged dye molecule could not be adsorbed by the anionic framework (Figure 5). The maximum MB adsorption uptake was determined to be 410 mg g^{-1}.
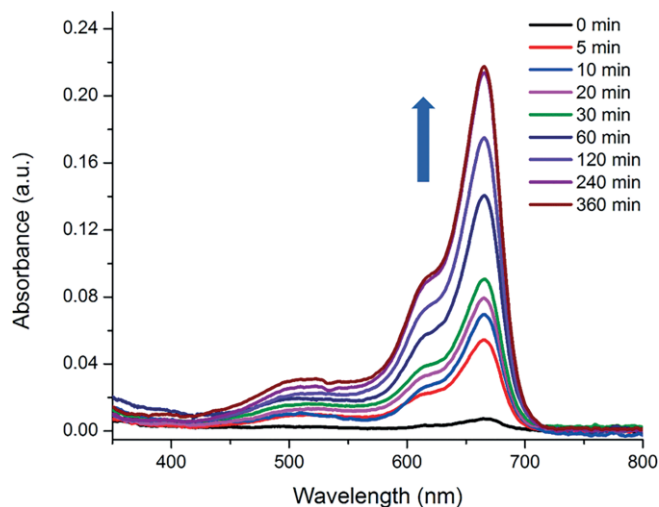

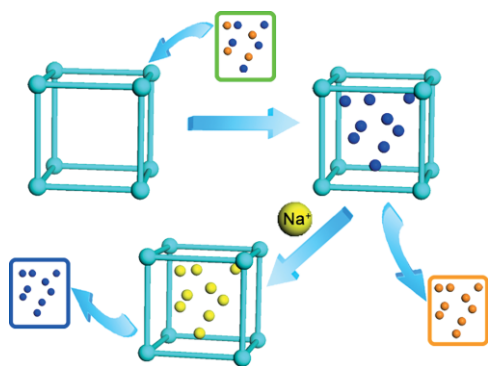Figure 4. Absorption spectra for release of methylene blue.

Figure 5. Graphical representation of dye adsorption and release.

Cycloaddition of CO$_2$ with Epoxides

Metal–organic frameworks, having the advantages of structural tunability, active metal sites, and accessible pore volumes,[11] have emerged as efficient and selective heterogeneous catalysts.[14,15] Though several MOFs have been developed and evaluated for their use as Lewis acid catalysts for the chemical conversion of CO$_2$ into value-added chemicals, synthetic conditions involving pressures greater than 3 MPa and temperatures above 100 °C limit their large-scale and industrial use.[20] Herein, we employed the Zn-MOF for the catalytic addition of CO$_2$ to epoxides to generate cyclic carbonates. To evaluate the generality of the reaction, different substituted epoxides were used, and reactions were performed at room temperature under atmos-

pheric pressure. The results of these catalytic reactions are summarized in Table 1. It is clear that the Zn-MOF showed high catalytic efficiency for the cycloaddition of propylene oxide to form propylene carbonate in 92.1 % yield over 48 h. This efficacy is comparable to that of MMCF and MMPF reported previously by our group.[21] High catalytic activity was also observed for the catalytic conversion of other epoxides into their corresponding carbonates in quantitative yields (Table 1) at ambient temperature over 48 h. The decrease in the yield with an increase in the size of the epoxide can be attributed to the limited diffusion of larger epoxide molecules in the channels of the MOF.

Table 1. Zn-MOF-catalyzed addition of CO$_2$ and epoxides.

Entry	Epoxide	Product[a]	Yield (%)
1			92.1
2			88.6
3			78.4
4			69.7
5			39.2

[a] Reaction conditions: epoxide (25 mmol), Zn-MOF (20 mg), nBu$_4$NBr (0.58 g), r.t., CO$_2$ (101.3 kPa), 48 h.

A tentative mechanism for the cycloaddition of CO$_2$ and epoxides to form cyclic carbonates was proposed on the basis of some reports available in the literature.[22] The Zn-MOF can help to accelerate the cycloaddition process in a dual manner. First, a Lewis acidic site in the framework interacts with the epoxide through the oxygen atom of the epoxide, which activates the epoxy ring; second, being anionic, the framework interacts with the ammonium ion, which increases the availability of the Br$^-$ ion. Attack of the Br$^-$ ion leads to ring opening, and the oxygen anion of the opened epoxy ring then combines with CO$_2$ to form an alkyl carbonate anion. In the final step, ring closing leads to the generation of the cyclic carbonate.

Conclusions

In summary, a new Zn-based anionic metal–organic framework was synthesized under solvothermal conditions. The MOF exhibited highly selective adsorption and separation of the cationic dye methylene blue from its anionic counterpart methyl

orange on the basis of a charge-exclusion effect. Further, the use of the Zn-MOF as a heterogeneous catalyst for the cycloaddition of CO_2 with epoxides to give cyclic carbonates under ambient conditions was very successful and provided the targeted products in good to excellent yields.

Experimental Section

General: All reagents and solvents were purchased from commercial sources and were used as received, whereas 4,4′,4″-(pyridine-2,4,6-triyl)tribenzoic acid was synthesized according to the literature.[23]

Synthesis of Zn-MOF: A 20 mL scintillation vial was charged with H_3L (0.04 g, mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (0.16 g, mmol), HBF_4 (0.1 mL), and DMF (5.0 mL), and the mixture was sonicated for 10 min. The mixture was then heated in the sealed vial at 120 °C for 24 h to produce rodlike crystals. The crude product was washed with DMF to give pure Zn-MOF (43 % yield, based on H_3L). IR: $\tilde{v}$ = 2981 (w, br.), 1588 (m), 1538 (m), 1381 (s), 1181 (m), 1107 (w), 1055 (m), 1015 (s) 854 (s), 778 (s), 812 (m), 702 cm^{-1} (m).

Dye Adsorption: In a typical experiment, a fresh crystalline sample of Zn-MOF (10 mg) was put in the dye solution (10 mL, 200 ppm). The adsorption spectra of the dye treated with the Zn-MOF were recorded by using a UV/Vis spectrometer. The maximum adsorption capacity of MB was investigated by adding the as-synthesized Zn-MOF (35 mg) into of a 10 mmol L^{-1} DMF solution (20 mL) at room temperature. Similarly, the maximum uptake was determined by using UV/Vis spectroscopy.

Dye Release: Dye-release experiments were performed in pure DMF and NaCl (50 mg) containing DMF solution, respectively. UV/Vis spectra were used to measure the release ability of the Zn-MOF.

Cycloaddition of CO_2 with Epoxides: In a typical reaction, a Schlenk tube was charged with propylene oxide (25 mmol), Zn-MOF (20 mg), and nBu$_4$NBr (0.58 g), and the mixture was purged with CO_2 (101.3 kPa) with stirring under solvent-free conditions at room temperature for 48 h. The progress of the reaction was monitored by NMR spectroscopy/GC. A similar synthetic procedure was followed for the other epoxides. All products were identified by comparison with authentic samples.

[1] A. Demirbas, *J. Hazard. Mater.* **2009**, *167*, 1–9.
[2] M. S. Tsuboy, J. P. F. Angeli, M. S. Mantovani, S. Knasmüller, G. A. Umbuzeiro, L. R. Ribeiro, *Toxicol. in vitro* **2007**, *21*, 1650–1655.
[3] K. Golka, S. Kopps, Z. W. Myslak, *Toxicol. Lett.* **2004**, *151*, 203–210.
[4] K. T. Chung, *J. Environ. Sci. Health, Part C: Environ. Carcinog. Ecotoxicol. Rev.* **2000**, *18*, 51–74.
[5] W. Chen, W. Lu, Y. Yao, M. Xu, *Environ. Sci. Technol.* **2007**, *41*, 6240–6245.

[6] a) J. J. Du, Y. P. Yuan, J. X. Sun, F. M. Peng, X. Jiang, L. G. Qiu, A. J. Xie, Y. H. Shen, J. F. Zhu, *J. Hazard. Mater.* **2011**, *190*, 945–951; b) Q. Chen, Q. Wu, *J. Hazard. Mater.* **2015**, *283*, 193–201.
[7] S. Zhang, M. Zeng, J. Li, J. Li, J. Xu, X. Wang, *J. Mater. Chem. A* **2014**, *2*, 4391–4397.
[8] a) Z. Hasan, S. H. Jhung, *J. Hazard. Mater.* **2015**, *283*, 329–339; b) E. Haque, J. W. Jun, S. H. Jhung, *J. Hazard. Mater.* **2011**, *185*, 507–511.
[9] a) J. Lu, J. X. Lin, X. L. Zhao, R. Cao, *Chem. Commun.* **2012**, *48*, 669–671; b) Z. Yang, S. Gao, H. Li, R. Cao, *J. Colloid Interface Sci.* **2012**, *375*, 172–179; c) M. Cao, J. Lin, J. Lü, Y. You, T. Liu, R. Cao, *J. Hazard. Mater.* **2011**, *186*, 948–951.
[10] a) R. L. Liu, Y. Liu, X. Y. Zhou, Z. Q. Zhang, J. Zhang, F. Q. Dang, *Bioresour. Technol.* **2014**, *154*, 138–147; b) H. Jiang, P. Chen, S. Luo, X. Tu, Q. Cao, M. Shu, *Appl. Surf. Sci.* **2013**, *284*, 942–949.
[11] a) B. Li, M. Chrzanowski, Y. Zhang, S. Ma, *Coord. Chem. Rev.* **2016**, *307*, 106–129; b) N. C. Burtch, K. S. Walton, *Acc. Chem. Res.* **2015**, *48*, 2850–2857; c) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705; d) M. O'Keeffe, *Chem. Soc. Rev.* **2009**, *38*, 1215; e) S. Qiu, M. Xue, G. Zhu, *Chem. Soc. Rev.* **2014**, *43*, 6116–6140.
[12] a) S. Ma, H.-C. Zhou, *Chem. Commun.* **2010**, *46*, 44–53; b) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae, J. R. Long, *Chem. Rev.* **2012**, *112*, 724–781; c) M. P. Suh, H. J. Park, T. K. Prasad, D.-W. Lim, *Chem. Rev.* **2012**, *112*, 782–835; d) Y. He, W. Zhou, G. Qian, B. Chen, *Chem. Soc. Rev.* **2014**, *43*, 5657–5678.
[13] a) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne, J. T. Hupp, *Chem. Rev.* **2012**, *112*, 1105–1125; b) M. D. Allendorf, C. A. Bauer, R. K. Bhakta, R. J. T. Houk, *Chem. Soc. Rev.* **2009**, *38*, 1330–1352.
[14] a) B. Li, K. Leng, Y. Zhang, J. J. Dynes, J. Wang, Y. Hu, D. Ma, Z. Shi, L. Zhu, D. Zhang, Y. Sun, M. Chrzanowski, S. Ma, *J. Am. Chem. Soc.* **2015**, *137*, 4243–4248; b) Y. Zhang, B. Li, S. Ma, *Chem. Commun.* **2014**, *50*, 8507–8510.
[15] a) J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, C.-Y. Su, *Chem. Soc. Rev.* **2014**, *43*, 6011–6061; b) M. Yoon, R. Srirambalaji, K. Kim, *Chem. Rev.* **2012**, *112*, 1196–1231; c) J. Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, *Chem. Soc. Rev.* **2009**, *38*, 1450–1459; d) L. Ma, C. Abney, W. Lin, *Chem. Soc. Rev.* **2009**, *38*, 1248–1256.
[16] a) X. Lian, B. Yan, *RSC Adv.* **2016**, *6*, 11570–11576; b) X. Zhao, X. Bu, T. Wu, S. T. Zheng, L. Wang, P. Feng, *Nat. Commun.* **2013**, *4*, 2344–2348; c) X. Zhang, Y. Gao, H. Liu, Z. Liu, *CrystEngComm* **2015**, *17*, 6037–6043; d) X. L. Hu, F. H. Liu, H. N. Wang, C. Qin, C. Y. Sun, Z. M. Su, F. C. Liu, *J. Mater. Chem. A* **2014**, *2*, 14827–14834; e) A. X. Yan, S. Yao, Y. G. Li, Z. M. Zhang, Y. Lu, W. L. Chen, E. B. Wang, *Chem. Eur. J.* **2014**, *20*, 6927–6933; f) Y. Q. Lan, H. L. Jiang, S. L. Li, Q. Xu, *Adv. Mater.* **2011**, *23*, 5015–5020; g) H. L. Jiang, Y. Tatsu, Z. H. Lu, Q. Xu, *J. Am. Chem. Soc.* **2010**, *132*, 5586–5587; h) S. Han, Y. Wei, C. Valente, I. Lagzi, J. J. Gassensmith, A. Coskun, J. F. Stoddart, B. A. Grzybowski, *J. Am. Chem. Soc.* **2010**, *132*, 16358–16361; i) F.-Y. Yi, W. Zhu, S. Dang, J.-P. Li, D. Wu, Y.-h. Lib, Z.-M. Sun, *Chem. Commun.* **2015**, *51*, 3336–3339; j) F.-Y. Yi, J.-P. Li, D. Wu, Z.-M. Sun, *Chem. Eur. J.* **2015**, *21*, 11475–11482.
[17] a) J. Johnson, *Chem. Eng. News* **2004**, *82*, 36–37; b) C. Wang, H. Luo, D. Jiang, H. Li, S. Dai, *Angew. Chem. Int. Ed.* **2010**, *49*, 5978–5981; *Angew. Chem.* **2010**, *122*, 6114–6117.
[18] a) C. Song, Y. He, B. Li, Y. Ling, H. Wang, Y. Feng, R. Krishna, B. Chen, *Chem. Commun.* **2014**, *50*, 12105–12108; b) A. M. Fracaroli, H. Furukawa, M. Suzuki, M. Dodd, S. Okajima, F. Gándara, J. A. Reimer, O. M. Yaghi, *J. Am. Chem. Soc.* **2014**, *136*, 8863–8866; c) K. Liu, B. Li, Y. Li, X. Li, F. Yang, G. Zeng, Y. Peng, Z. Zhang, G. Li, Z. Shi, S. Feng, D. Song, *Chem. Commun.* **2014**, *50*, 5031–5033; d) D. M. D'Alessandro, B. Smit, J. R. Long, *Angew. Chem. Int. Ed.* **2010**, *49*, 6058–6082; *Angew. Chem.* **2010**, *122*, 6194–6219; e) J.-R. Li, Y. Ma, M. C. McCarthy, J. Sculley, J. Yu, H.-K. Jeong, P. B. Balbuena, H.-C. Zhou, *Coord. Chem. Rev.* **2011**, *255*, 1791–1823; f) Y.-S. Bae, R. Q. Snurr, *Angew. Chem. Int. Ed.* **2011**, *50*, 11586–11596; *Angew. Chem.* **2011**, *123*, 11790–11801; g) G. Férey, C. Serre, T. Devic, G. Maurin, H. Jobic, P. L. Llewellyn, G. D. Weireld, A. Vimont, M. Daturif, J.-S. Chang, *Chem. Soc. Rev.* **2011**, *40*, 550–562; h) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae, J. R. Long, *Chem. Rev.* **2012**, *112*, 724–781; i) J. Liu, P. K. Thallapally, B. P. McGrail, D. R. Brown, J. Liu, *Chem. Soc. Rev.* **2012**, *41*, 2308–2322.
[19] D. Sun, Y. Ke, D. J. Collins, G. A. Lorigan, H. C. Zhou, *Inorg. Chem.* **2007**, *46*, 2725–2734.

[20] a) T. Yano, H. Matsui, T. Koike, H. Ishiguro, H. Fujihara, M. Yoshihara, T. Maeshima, *Chem. Commun.* **1997**, 1129–1130; b) Y. Xie, T.-T. Wang, X.-H. Liu, K. Zou, W.-Q. Deng, *Nat. Commun.* **2013**, *4*, 1960–1966; c) R. Srivastava, D. Srinivas, P. Ratnasamy, *J. Catal.* **2005**, *233*, 1–15; d) J. Chun, S. Kang, N. Kang, S. M. Lee, H. J. Kim, S. U. Son, *J. Mater. Chem. A* **2013**, *1*, 5517–5523.

[21] a) W.-Y. Gao, Y. Chen, Y. Niu, K. Williams, L. Cash, P. J. Perez, L. Wojtas, J. Cai, Y.-S. Chen, S. Ma, *Angew. Chem. Int. Ed.* **2014**, *53*, 2615–2619; *Angew. Chem.* **2014**, *126*, 2653–2657; b) W.-Y. Gao, L. Wojtas, S. Ma, *Chem. Commun.* **2014**, *50*, 5316–5318.

[22] M. H. Beyzavi, C. J. Stephenson, Y. Liu, O. Karagiaridi, J. T. Hupp, O. K. Farha, *Front. Energy Res.* **2015**, *2*, 63.

[23] Q. Yao, A. B. Gómez, J. Su, V. Pascanu, Y. Yun, H. Zheng, H. Chen, L. Liu, H. N. Abdelhamid, B. Martín-Matute, X. Zou, *Chem. Mater.* **2015**, *27*, 5332–5339.