



Cite this: *Chem. Commun.*, 2017, 53, 3224

Received 15th January 2017,  
Accepted 23rd February 2017

DOI: 10.1039/c7cc00363c

rsc.li/chemcomm

# Robust high-connected rare-earth MOFs as efficient heterogeneous catalysts for CO<sub>2</sub> conversion†

Na Wei,<sup>a</sup> Rong-Xia Zuo,<sup>a</sup> Yu-Yang Zhang,<sup>a</sup> Zheng-Bo Han<sup>\*a</sup> and Xue-Jun Gu<sup>\*b</sup>

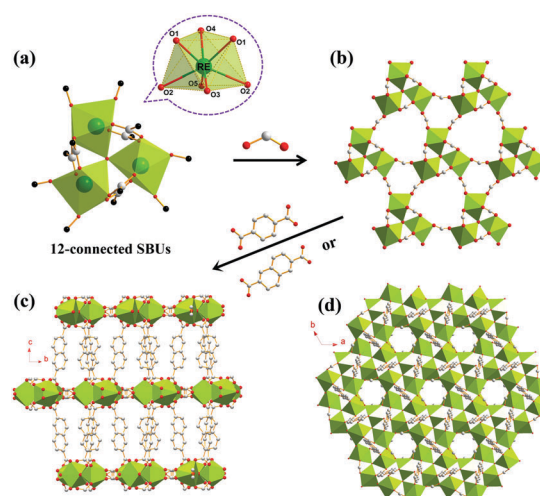
**Two series of chemically and thermally stable rare-earth MOFs were constructed using trinuclear [M<sub>3</sub>(μ<sub>3</sub>-OH)(COO)<sub>6</sub>] SBUs and linear dicarboxylate linkers, which feature three-dimensional 12-connected frameworks with an hcp topology. These materials contain a large density of Lewis acidic sites, leading to high catalytic activity towards the cycloaddition of CO<sub>2</sub> and epoxides under mild conditions.**

Over the past two decades, metal-organic frameworks (MOFs) have been studied extensively due to their intriguing architecture and potential applications in multiple areas, such as gas separation and storage,<sup>1</sup> small-molecule separation,<sup>2</sup> chemical sensing<sup>3</sup> and catalysis.<sup>4</sup> Because of the highly designable nature of MOFs, their multiple structures, dimensionality and chemical properties can be realized *via* the scientific selection and assembly of secondary building units (SBUs): multifunctional organic linkers and metal ions (clusters) with various shapes and extension nodes.<sup>5</sup> However, reversible coordination bonding of metal ions and organic ligands generally results in the poor stability of the MOF materials,<sup>6</sup> which is commonly identified as the major shortcoming for their practical applications in most research areas. Therefore, construction of MOFs with improved stability has become a significant goal for a lot of researchers.

The trinuclear [M<sub>3</sub>(μ<sub>3</sub>-O/μ<sub>3</sub>-OH)(COO)<sub>6</sub>] cluster, as a classical shape changeable trigonal-prismatic SBU, facilitates construction of a plethora of polyhedral nets and highly porous materials.<sup>7</sup> Due to its flexibility, MOFs assembled by [M<sub>3</sub>(μ<sub>3</sub>-O/μ<sub>3</sub>-OH)(COO)<sub>6</sub>] SBUs and linear dicarboxylate linkers exhibit various topologies, as exemplified by 6-connected MIL-88 (acs network),<sup>8</sup> MIL-101 (mtn network),<sup>9</sup> MCF-35 (flu-e network),<sup>10</sup> the predicted MIL-hypo-2/constructed nickel-complex (reo-e network),<sup>11</sup> *etc.* High-connected

MOFs usually exhibit enhanced stability towards harsh chemical conditions or elevated temperatures.<sup>7</sup> So increasing the connectivity of known SBUs is of great interest. In the trinuclear [M<sub>3</sub>(μ<sub>3</sub>-O/μ<sub>3</sub>-OH)(COO)<sub>6</sub>] family, the reported highest connectivity is the 9-connected MCF-19 (ncb network);<sup>12</sup> however, no other higher connected network has been reported so far.

Herein, two series of 12-connected rare-earth (RE = Y, Tb and Er) MOFs incorporating [RE<sub>3</sub>(μ<sub>3</sub>-OH)(COO)<sub>6</sub>] SBUs (Fig. 1a) and linear dicarboxylates were synthesized with the formulae [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>][RE<sub>3</sub>(μ<sub>3</sub>-OH)(BDC)<sub>3</sub>(HCOO)<sub>3</sub>] (**RE-BDC**) and [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>][RE<sub>3</sub>(μ<sub>3</sub>-OH)(NDC)<sub>3</sub>(HCOO)<sub>3</sub>] (**RE-NDC**) (H<sub>2</sub>BDC = 1,4-benzenedicarboxylic acid and H<sub>2</sub>NDC = 2,6-naphthalenedicarboxylic acid) (Fig. S1, ESI†). These materials show very high thermal and chemical stability in common organic solvents and water with pH values ranging from 2 to 12. Owing to the high-density of Lewis acidic sites, all these complexes exhibit high catalytic activity towards the cycloaddition of CO<sub>2</sub> and epoxides under mild conditions.



**Fig. 1** (a) 12-Connected trinuclear [RE<sub>3</sub>(μ<sub>3</sub>-OH)(COO)<sub>6</sub>] SBUs. Inset: The coordination environment of each RE(III) ion. (b) 2D layer formed by [RE<sub>3</sub>(μ<sub>3</sub>-OH)(COO)<sub>6</sub>] SBUs and HCOO<sup>-</sup>. Views of the structure of **RE-NDC** along the *a*-axis (c) and the *c*-axis (d).

<sup>a</sup> College of Chemistry, Liaoning University, Shenyang 110036, P. R. China. E-mail: ceshzb@lnu.edu.cn

<sup>b</sup> Institute of Rare and Scattered Elements, College of Chemistry, Liaoning University, Shenyang 110036, P. R. China. E-mail: sheshen311@126.com

† Electronic supplementary information (ESI) available: Experimental details of synthesis and catalysis, and additional characterization studies. CCDC 1525133 and 1525134. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7cc00363c

The reaction of  $\text{RE}(\text{NO}_3)_3$  ( $\text{RE} = \text{Y}, \text{Tb}$  and  $\text{Er}$ ) with  $\text{H}_2\text{BDC}/\text{H}_2\text{NDC}$  in a mixture of DMF and  $\text{H}_2\text{O}$  in the presence of nitric acid and 2-fluorobenzoic acid at  $105^\circ\text{C}$  affords crystals of **RE-BDC/RE-NDC**. Single-crystal X-ray crystallography showed that **RE-BDC** and **RE-NDC** crystallize in the hexagonal space group  $P6_3/m$ . Each  $\text{RE}(\text{III})$  ( $\text{Y}, \text{Tb}$  and  $\text{Er}$ ) center is seven-coordinated by four dicarboxylates, one  $\mu_3\text{-OH}$  and two  $\text{HCOO}^-$  in a triangular capping-square coordination environment (Fig. 1a). Besides the linear dicarboxylate linkers, the  $\text{HCOO}^-$  sites of these clusters also act as  $\mu_2$ -bridging ligands to furnish  $[\text{RE}_3(\mu_3\text{-OH})(\text{COO})_6]$  SBUs as 12-connected nodes. Due to their higher coordinate numbers, the  $\text{RE}(\text{III})$  ions provide more extension points than the hexa-coordinated transition metal centers. Along the  $a$ -axis, the 12-connected  $[\text{RE}_3(\mu_3\text{-OH})(\text{COO})_6]$  SBUs are connected by six coordinated  $\text{HCOO}^-$  sites, extending into a 2D layer (Fig. 1b), and the ratio between the dicarboxylates and coordinated  $\text{HCOO}^-$  was determined using  $^1\text{H-NMR}$  integral results (Fig. S2, ESI $^\dagger$ ). The 2D layers are further connected together through BDC or NDC linkers along the  $c$ -axis direction, resulting in a 3D framework (Fig. 1c and d) with an unusual uninodal 12-connected hcp topology (Fig. S3, ESI $^\dagger$ ). The vertex symbol for this net is  $3^{24}\cdot 4^{33}\cdot 5^9$ , as analyzed using the TOPOS program. PLATON $^{13}$  analysis reveals that the frameworks of **RE-BDC** and **RE-NDC** are composed of voids of  $518.2 \text{ \AA}^3$  and  $546.6 \text{ \AA}^3$ , respectively.

Generally, MOFs sustained by high connectivity SBUs tend to exhibit higher thermal and chemical stability. The trigonal prismatic  $[\text{M}_3(\mu_3\text{-O})(\text{COO})_6]$  SBUs as multi-connected nodes are notable for their historical constructions of many MOFs, and most of the resulting complexes tend to exhibit excellent chemical stability. $^{9,12,14}$  So, it is suspected that the 12-connected  $[\text{RE}_3(\mu_3\text{-OH})(\text{COO})_6]$  clusters maybe endow these RE-based MOFs with excellent chemical stability. To verify this, the chemical stabilities of **Er-BDC** and **Er-NDC** were checked using powder X-ray diffraction (PXRD) studies. The results show that the experimental PXRD patterns are consistent with the simulated ones upon soaking in various organic solvents for 48 h (Fig. S4 and S5a, ESI $^\dagger$ ), even in aqueous solutions with  $\text{pH} = 2$  (0.01 M HCl) and 12 (0.01 M NaOH) for 12 h (Fig. 2 and Fig. S5b, S6, ESI $^\dagger$ ), indicating that no framework collapse or phase transition occurs during the chemical stability tests. However, when crystal samples are soaked in 0.1 M HCl and 0.1 M NaOH solution, observable changes in color, morphology and transparency occur in several minutes. Similarly, Y- and Tb-complexes also show super stability toward aqueous solutions with  $\text{pH} = 2$  and 12 (Fig. S7, ESI $^\dagger$ ). **RE-BDC** and **RE-NDC** also display high thermal stability. Thermogravimetric analysis (TGA) curves (Fig. S8, ESI $^\dagger$ ) show that these complexes present no obvious weight loss below  $300^\circ\text{C}$  (ca. 3.4% weight loss assigned to the removal of dimethylammonium cations). Variable-temperature PXRD patterns demonstrated that these complexes maintain their crystalline form with the environmental temperature ranging from ambient temperature to  $300^\circ\text{C}$  (Fig. S9, ESI $^\dagger$ ), and then obvious changes in diffraction patterns are observed as the temperature was increased up to  $350^\circ\text{C}$ . It is confirmed that **Er-BDC** and **Er-NDC** retain their structural stability until the environmental temperature exceeds  $300^\circ\text{C}$ , which are superior to 6-connected MIL-88 MOFs; the latter

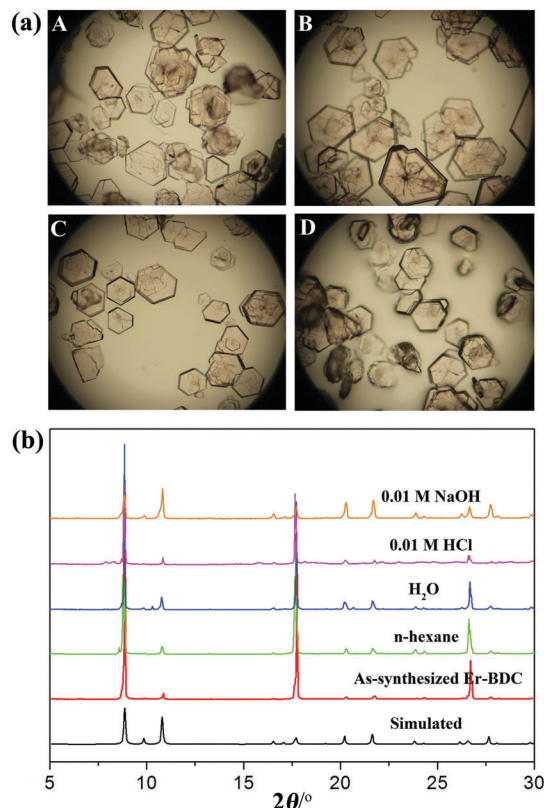
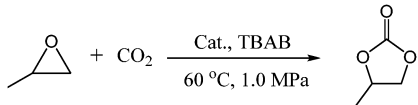


Fig. 2 (a) Pictures of **Er-BDC** under an optical microscope: as-synthesized (A) and after soaking in  $n$ -hexane (B), 0.01 M HCl (C) and 0.01 M NaOH (D). (b) PXRD patterns of **Er-BDC** and the samples treated with  $n$ -hexane,  $\text{H}_2\text{O}$ , 0.01 M HCl and 0.01 M NaOH.

present a similar structure but with lower connectivity. $^8$  For instance, when MIL-88B(V) $^{15}$  was heated to  $200^\circ\text{C}$ , the PXRD patterns exhibited a large variation in the position of the peaks, indicating that the crystalline phase has changed.

**RE-BDC** and **RE-NDC** are potential Lewis acidic catalysts owing to the high concentration of the Lewis acidic seven-coordinated  $\text{RE}(\text{III})$  ions in their structures. To determine this point, pyridine adsorption experiments were carried out on **Y-BDC** and **Y-NDC** at room temperature. The pyridine adsorption Fourier-transform infrared (Py-IR) spectra show peaks at  $1448 \text{ cm}^{-1}$  and  $1605 \text{ cm}^{-1}$  typical for pyridine adsorbed on Lewis acid sites, confirming the Lewis acidity of **Y-BDC** and **Y-NDC** (Fig. S10, ESI $^\dagger$ ). $^{16}$  The combination of Lewis acidity and excellent stability of these complexes inspired us to investigate their heterogeneous Lewis acidic catalytic activities towards the cycloaddition of  $\text{CO}_2$  and epoxides.

Recently, the cycloaddition of  $\text{CO}_2$  and epoxides as one of the most powerful and attractive strategies for  $\text{CO}_2$  chemical fixation has attracted more attention from researchers. $^{17}$  In this reaction, the valuable chemical products, cyclic carbonates, can be converted from  $\text{CO}_2$  as a cheap C-1 source. $^{18}$  So, the cycloaddition of  $\text{CO}_2$  and propylene oxide (PO) acts as a typical reaction to study the catalytic activity of **RE-BDC** and **RE-NDC**. The reactions were carried out in an autoclave reactor using the epoxides (28.6 mmol) and  $\text{CO}_2$  under 1 MPa pressure at  $60^\circ\text{C}$  in the presence of 0.05 mmol **RE-BDC** as a catalyst and 0.3 mmol

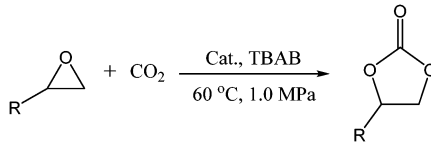
**Table 1** Cycloaddition of CO<sub>2</sub> and propylene oxide catalyzed by a variety of catalysts


Entry	Catalyst	Conversion <sup>a</sup> (%)	TON <sup>b</sup>
1	Y-BDC, TBAB	95	543
2	Er-BDC, TBAB	91	521
3	Tb-BDC, TBAB	89	509
4	Y-NDC, TBAB	94	538
5	Er-NDC, TBAB	90	515
6	Tb-NDC, TBAB	87	498
7	TBAB	30	29
8 <sup>c</sup>	Y(NO <sub>3</sub> ) <sub>3</sub> , TBAB	90	—
9 <sup>d</sup>	Y <sub>2</sub> O <sub>3</sub> , TBAB	12	—

Reaction conditions: propylene oxide (28.6 mmol), catalyst (0.05 mmol, corresponding to the RE<sub>3</sub> cluster), TBAB (0.3 mmol) under CO<sub>2</sub> (1.0 MPa), 60 °C and 12 hours. <sup>a</sup> The conversions were determined by GC. <sup>b</sup> TON is the turnover number (product (mmol)/catalyst (mmol)). <sup>c</sup> Y(NO<sub>3</sub>)<sub>3</sub> (0.15 mmol), TBAB (0.3 mmol), CO<sub>2</sub> (1.0 MPa), 60 °C, 10 h. <sup>d</sup> Y<sub>2</sub>O<sub>3</sub> (0.075 mmol), TBAB (0.3 mmol), CO<sub>2</sub> (1.0 MPa), 60 °C, 12 h.

TBAB (tetrabutylammonium bromide) as a co-catalyst. The conversions of the PO were confirmed by gas chromatography (GC) analyses and the results are summarized in Table 1. After 12 hours, the conversion of PO catalyzed by **Y-BDC** reaches 95%, demonstrating the highest catalytic activity of **Y-BDC** with a TON value of 543 followed by **Er-BDC** and **Tb-BDC** with values of 521 and 509, respectively. The different atomic radii of the central RE atoms (Y < Er < Tb) may contribute to the diversity of their catalytic capacities.<sup>19</sup> Under the same conditions, the **RE-NDC** series exhibit high activities toward the cycloaddition of CO<sub>2</sub> and PO (Table 1, entries 4–6), in which **Y-NDC** also gives the highest conversion (94%) of PO. Compared with other benchmark MOF catalysts (Table S3, ESI<sup>†</sup>), **Y-BDC** and **Y-NDC** also exhibit good catalytic activity towards the cycloaddition of CO<sub>2</sub> with PO. We also tested simple Y(NO<sub>3</sub>)<sub>3</sub> (0.15 mmol) as a homogeneous catalyst for the cycloaddition of CO<sub>2</sub> with PO. The result shows that the Y(NO<sub>3</sub>)<sub>3</sub>/TBAB system displays powerful catalytic activity under the same conditions (Table 1, entry 8). Y<sub>2</sub>O<sub>3</sub>, because of its insolubility in the reaction system, was also studied as a heterogeneous catalyst for this reaction under similar conditions (Table 1, entry 9). The low catalytic activity of Y<sub>2</sub>O<sub>3</sub> indicated that the high accessibility of the Lewis acidic Y(III) sites is indispensable for epoxide activation as the first reaction step.

In consideration of the higher activities of Y-based complexes, we chose **Y-BDC** and **Y-NDC** to investigate the cycloaddition of CO<sub>2</sub> and other epoxides. After 12 hours, **Y-BDC** and **Y-NDC** (0.05 mmol, 0.17 mol%) both afforded high conversions of epoxybutane (88% and 86%), allyl glycidyl ether (85% and 83%) and butyl glycidyl ether (80% and 82%, Table 2), outperforming some MOF-based catalysts. For instance, {Cu(Hip)<sub>2</sub>(Bpy)}<sub>n</sub> reported by Park *et al.* gave an allyl glycidyl ether conversion of 89.2% using an approximately tenfold amount of the catalyst (1.6 mol%) at 80 °C under 1.2 MPa CO<sub>2</sub> pressure.<sup>20</sup> Another Y-based catalyst, gea-MOF-1,<sup>21</sup> demonstrates catalytic activity for the cycloaddition of propylene oxide/epoxybutane and CO<sub>2</sub> with yields of 88% and 94% under

**Table 2** Cycloaddition of CO<sub>2</sub> and various epoxides catalyzed by **Y-BDC** and **Y-NDC**


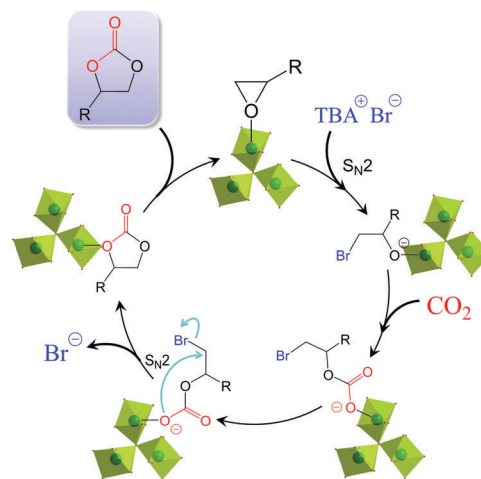
Entry	Epoxides	<b>Y-BDC</b>		<b>Y-NDC</b>	
		Conversion <sup>a</sup> (%)	TON <sup>b</sup>	Conversion (%)	TON
1		88	503	86	492
2		85	486	83	475
3		80	458	82	469
4		72	412	70	400

Reaction conditions: epoxides (28.6 mmol), catalyst (0.05 mmol, corresponding to the Y<sub>3</sub> cluster), TBAB (0.3 mmol) under CO<sub>2</sub> (1.0 MPa), 60 °C and 12 hours. <sup>a</sup> The yields were determined by GC. <sup>b</sup> TON is the turnover number (product (mmol)/catalyst (mmol)).

relatively harsh conditions (120 °C and 2 MPa CO<sub>2</sub> pressure). The comparatively lower conversions of styrene oxide (72% and 70%) are attributable to the low reactivity at its β-carbon center (Table 2, entry 4).<sup>20</sup>

A tentative mechanism for the cycloaddition of CO<sub>2</sub> and epoxide into cyclic carbonate is proposed to be the Lewis acid catalysis.<sup>22</sup> As illustrated in Fig. 3, epoxides first bind to the Lewis acidic RE sites through the O atoms to activate the epoxy ring. Then, TBAB attacks the less-hindered C atoms of the epoxide using its Br<sup>−</sup> as nucleophiles to open the epoxy ring. Subsequently, the opened epoxy ring interacts with CO<sub>2</sub> forming an alkylcarbonate anion, which is converted into the corresponding

relatively harsh conditions (120 °C and 2 MPa CO<sub>2</sub> pressure). The comparatively lower conversions of styrene oxide (72% and 70%) are attributable to the low reactivity at its β-carbon center (Table 2, entry 4).<sup>20</sup>

**Fig. 3** Proposed catalytic mechanism for the cycloaddition of CO<sub>2</sub> and epoxide into cyclic carbonate over **RE-BDC** and **RE-NDC**.



cyclic carbonate through the final ring-closing step, and TBAB is recycled simultaneously. In view of the small window size of the 12-connected framework (*ca.* 1.7 Å<sup>2</sup>), the substrates can't enter the pore, and the reactions almost occur on the external surface of the catalysts.

Leaching tests were performed to test the heterogeneous nature of the catalysts **Y-BDC** and **Y-NDC**. The results show that the transformation of the PO dramatically decreases after the removal of catalysts at 6 h (Fig. S11, ESI†). In addition, inductively coupled plasma (ICP) analyses also excluded the leaching of Y, confirming the stability and insolubility of the catalysts in this reaction system. The recyclability and reusability of the catalysts for the cycloaddition of CO<sub>2</sub> and PO were further investigated. After 5 runs of reactions, the complexes still retain equivalent catalytic activity to the original ones (Fig. S12, ESI†), which can be isolated from the reaction suspensions by simple filtration. The PXRD patterns of recycled **Y-BDC** and **Y-NDC** after 5 cycles are comparable to those of the fresh ones (Fig. S13, ESI†), indicating the stability of the catalysts. Thus, the remarkably highly efficient catalytic activities towards cycloaddition of CO<sub>2</sub> and epoxides confirm that both **Y-BDC** and **Y-NDC** present significant advantages for chemical fixation of CO<sub>2</sub> and preparation of cyclic carbonates.

In conclusion, we have successfully synthesized two series of trinuclear RE cluster-based MOFs, **RE-BDC** and **RE-NDC** (RE = Y, Tb, and Er), with a 12-connected hcp topology. These constructed MOFs exhibit remarkable thermal stability in a wide temperature range and chemical stability in water and common organic solvents. In particular, **RE-BDC** and **RE-NDC** contain a high density of accessible Lewis acidic RE(III) sites, which have been demonstrated to be highly efficient heterogeneous catalysts for CO<sub>2</sub> chemical fixation. We hope that this work will open a new way to constructing novel and stable MOFs.

This work was granted financial support from the National Natural Science Foundation of China (Grant 21671090 and 21271096).

## 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) L. J. Murray, M. Dincà and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294–1314; (c) S. T. Meek, J. A. Greathouse and M. D. Allendorf, *Adv. Mater.*, 2011, **23**, 249–267.
- (a) Q. Zhang, J. Yu, J. Cai, R. Song, Y. Cui, Y. Yang, B. Chen and G. Qian, *Chem. Commun.*, 2014, **50**, 14455–14458; (b) X. Zhao, X. Bu, T. Wu, S.-T. Zheng, L. Wang and P. Feng, *Nat. Commun.*, 2013, **4**, 2344; (c) J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.*, 2011, **112**, 869–932.
- (a) Y. Cui, Y. Yue, G. Qian and B. Chen, *Chem. Rev.*, 2011, **112**, 1126–1162; (b) Z. Hu, B. J. Deibert and J. Li, *Chem. Soc. Rev.*, 2014, **43**, 5815–5840.
- (a) J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang and C.-Y. Su, *Chem. Soc. Rev.*, 2014, **43**, 6011–6061; (b) L. Ma, C. Abney and W. Lin, *Chem. Soc. Rev.*, 2009, **38**, 1248–1256; (c) J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450–1459.
- (a) W. Lu, Z. Wei, Z.-Y. Gu, T.-F. Liu, J. Park, J. Park, J. Tian, M. Zhang, Q. Zhang, T. Gentle III, M. Bosch and H.-C. Zhou, *Chem. Soc. Rev.*, 2014, **43**, 5561–5593; (b) D. J. Tranchemontagne, J. L. Mendoza-Cortés, M. O'Keeffe and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1257–1283; (c) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705–714; (d) S. Qiu and G. Zhu, *Coord. Chem. Rev.*, 2009, **253**, 2891–2911.
- (a) J. Canivet, A. Fateeva, Y. Guo, B. Coasne and D. Farrusseng, *Chem. Soc. Rev.*, 2014, **43**, 5594–5617; (b) J. Gascon and F. Kapteijn, *Angew. Chem., Int. Ed.*, 2010, **49**, 1530–1532; (c) S. Keskin, T. M. van Heest and D. S. Sholl, *ChemSusChem*, 2010, **3**, 879–891.
- A. Schoedel and M. J. Zaworotko, *Chem. Sci.*, 2014, **5**, 1269–1282.
- C. Serre, C. Mellot-Draznieks, S. Surblé, N. Audebrand, Y. Filinchuk and G. Férey, *Science*, 2007, **315**, 1828–1831.
- G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040–2042.
- Y.-S. Wei, J.-Q. Shen, P.-Q. Liao, W. Xue, J.-P. Zhang and X.-M. Chen, *Dalton Trans.*, 2016, **45**, 4269–4273.
- (a) C. Mellot-Draznieks, J. Dutour and G. Férey, *Z. Anorg. Allg. Chem.*, 2004, **630**, 2599–2604; (b) G. Ren, S. Liu, F. Wei, F. Ma, Q. Tang and S. Li, *Dalton Trans.*, 2012, **41**, 11562–11564.
- Y.-B. Zhang, W.-X. Zhang, F.-Y. Feng, J.-P. Zhang and X.-M. Chen, *Angew. Chem., Int. Ed.*, 2009, **48**, 5287–5290.
- A. L. Spek, *PLATON*, A. M. C. T. Utrecht University, Utrecht. The Netherlands, 1998.
- D. Feng, T.-F. Liu, J. Su, M. Bosch, Z. Wei, W. Wan, D. Yuan, Y.-P. Chen, X. Wang, K. Wang, X. Lian, Z.-Y. Gu, J. Park, X. Zou and H.-C. Zhou, *Nat. Commun.*, 2015, **6**, 5979.
- F. Carson, J. Su, A. E. Platero-Prats, W. Wan, Y. Yun, L. Samain and X. Zou, *Cryst. Growth Des.*, 2013, **13**, 5036–5044.
- S. A. Bagshaw and R. P. Cooney, *Chem. Mater.*, 1993, **5**, 1101–1109.
- M. H. Beyzavi, C. J. Stephenson, Y. Liu, O. Karagiari, J. T. Hupp and O. K. Farha, *Front. Energy Res.*, 2015, **2**, 63.
- (a) M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann and F. E. Kühn, *Angew. Chem., Int. Ed.*, 2011, **50**, 8510–8537; (b) I. Omae, *Coord. Chem. Rev.*, 2012, **256**, 1384–1405.
- (a) R. F. D'Vries, M. Iglesias, N. Snejko, S. Alvarez-García, E. Gutierrez-Puebla and M. A. Monge, *J. Mater. Chem.*, 2012, **22**, 1191–1198; (b) N. C. Jeong, J. S. Lee, E. L. Tae, Y. J. Lee and K. B. Yoon, *Angew. Chem., Int. Ed.*, 2008, **47**, 10128–10132.
- A. C. Kathalikkattil, D.-W. Kim, J. Tharun, H.-G. Soek, R. Roshan and D.-W. Park, *Green Chem.*, 2014, **16**, 1607–1616.
- V. Guillerme, L. J. Weseliński, Y. Belmabkhout, A. J. Cairns, V. D'Elia, L. Wojtas, K. Adil and M. Eddaoudi, *Nat. Chem.*, 2014, **6**, 673–680.
- (a) L. Liu, S.-M. Wang, Z.-B. Han, M. Ding, D.-Q. Yuan and H.-L. Jiang, *Inorg. Chem.*, 2016, **55**, 3558–3565; (b) Z.-R. Jiang, H. Wang, Y. Hu, J. Lu and H.-L. Jiang, *ChemSusChem*, 2015, **8**, 878–885.