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The photoluminescence and gas sorption properties of three Cd(μ) MOFs based on 1,3,5-benzenetribenzoate with $-NH_2$ or -OH groups⁺

The functionalization and modification of the ligand 1,3,5-tris(4-carboxyphenyl)benzene (H₃BTB) have been realized with amine (NH₂-H₃BTB) and hydroxy (HO-H₃BTB) groups. Three new Cd(\parallel) compounds

based on R-H₃BTB ligands (R = $-NH_2$ and -OH) have been synthesized and structurally characterized.

Compounds 1 and 2 show pillared-layer frameworks and display strong fluorescence emission ability.

Compound 3 features a 3D porous framework with trinuclear Cd units linked by the NH₂-BTB ligand. The

activated framework of $\mathbf{3}$ has good gas storage and separation properties for CO₂ and hydrocarbons.

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Introduction

Coordination polymers or metal–organic frameworks (MOFs) are a class of crystalline materials, which have been synthesized through the assembly between metals and various organic ligands.¹ The architectures and functions of these materials can be tailored easily by choosing different metal ions and organic linkers with various function, size and shape. Because of these outstanding characteristics, such materials have potential applications in gas sorption and separation,² luminescence,³ host–guest chemistry,⁴ photo-, electro-, and magnetic materials.^{5–7}

The functionalization and modification of the ligands to construct new metal-organic frameworks are fascinating. It is possible to construct MOFs with immobilized functional groups such as $-NH_2$, -OH, -COOH, or halogen within the organic linkers. The presence of such immobilized functional groups on the porous surface, not only facilitates direct interaction with the gas substrate, fluorescence and other physical properties, but also supplies additional coordinate sites.⁸ In both theoretical and experimental aspects, the functional groups have effects on the pore nature and the host-guest interactions.⁹ The most used organic ligands on the synthesis of MOFs are those carboxylate linkers, especially the aromatic carboxylates. Numerous carboxylato-containing MOFs have been reported in recent years. As is well known, 1,3,5-benzenetribenzoic acid (H₃BTB) has been extensively used for the construction of MOFs. It created the famous MOF-177,¹⁰ UMCM-1, UMCM-2,¹¹ and DUT-6.¹² For example, the combination of H₃BTB and Zn(II) generated MOF-177 with a BET surface area of 4500 m² g⁻¹. Thus, the functionalization of H₃BTB is an attractive target for modifying the properties of these highly porous MOFs. Through the pre-synthetic modification strategy, Cohen and co-workers successfully synthesized an –OMe functionalized MOF-177 by using a H₃BTB–[OMe]₃ ligand.¹³ Such a simple idea may be known by everybody, however, there are no other reports about the modification of this ligand up to now.

In this work, we use the functional groups $-NH_2$ and -OH to embellish the H₃BTB ligand, aiming to prepare new functional MOFs (Scheme 1). Three new Cd(II) compounds based on R-H₃BTB ligands (R = $-NH_2$ and -OH), namely [Cd₂(NH₂-BTB)₂(bpy)] [NH₂(CH₃)₂]₂·DMF·5H₂O (1; NH₂-H₃BTB = 1,3,5-(tri-benzoic acid)aniline; bpy = 4,4'-bipyridine; DMF = *N*,*N*-dimethylformamide), [Cd₂(HO-BTB)₂(bpy)][NH₂(CH₃)₂]₂. DMF·6H₂O (2; HO-H₃BTB = 1,3,5-(tri-benzoic acid) phenol)



Scheme 1 Structures of the $R-H_3BTB(R = NH_2 \text{ or OH})$ ligands.



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and $[Cd_3(NH_2-BTB)_2(H_2O)_2]\cdot 3DMA \cdot 5H_2O$ (3; DMA = *N*,*N*-dimethylacetamide) are successfully synthesized and structurally characterized. Furthermore, compounds **1** and **2** display a strong fluorescence emission ability, and compound **3** adsorbs selectively CO_2 , H_2 or CH_4 over N_2 .

Experimental section

Materials and instrumentation

All reagents were purchased commercially and used without further purification. All Powder X-ray diffraction (PXRD) analyses were recorded on a MiniFlex-II diffractometer with Cu Kα radiation ($\lambda = 1.54056$ Å) with a step size of 0.05°. The thermal stability studies were carried out on a NETSCHZ STA-449C thermoanalyzer with a heating rate of 10 °C min⁻¹ under an air atmosphere. Gas adsorption measurement was performed in the ASAP (Accelerated Surface Area and Porosimetry) 2020 System.

The synthesis of $[Cd_2(NH_2-BTB)_2(bpy)][NH_2(CH_3)_2]_2$. DMF·5H₂O (1). A solution of NH₂-H₃BTB (0.020 g, 0.045 mmol), bpy (0.010 g, 0.60 mmol) and Cd(NO₃)₂·6H₂O (0.060 g, 0.20 mmol) in DMF-H₂O (5:3, v/v; 8 mL), to which was 3 drops of HBF₄ using a syringe, was sealed in a 23 mL Teflon-lined autoclave, kept at 80 °C for 3 days and then cooled to room temperature. The obtained crystals were washed with DMF and H₂O, then dried at room temperature in air (yield: 15.6 mg, 53% based on NH₂-H₃BTB). Elemental analysis (wt%) for 1: calcd C 49.3, N 6.31, H 4.24; found C 51.4, N 6.38, H 4.04.

The synthesis of $[Cd_2(HO-BTB)_2(bpy)][NH_2(CH_3)_2]_2$. DMF-6H₂O (2). The mixture of HO-H₃BTB (0.020 g, 0.045 mmol), bpy (0.010 g, 0.60 mmol) and Cd(NO₃)_2·6H₂O (0.060 g, 0.20 mmol) in DMF-ethanol-H₂O (4:2:2, v/v/v; 8 mL), to which was added 4 drops of HBF₄ or 3 drops of formic acid using a syringe, was sealed in a 23 mL Teflon-lined autoclave, kept at 80 °C for 3 days, and then cooled to room temperature. The obtained crystals were washed with DMF and H_2O , then dried at room temperature in air (yield: 13.5 mg, 45% based on HO- H_3BTB). Elemental analysis (wt%) for 2: calcd C 54.58, N 4.94, H 4.61; found C 55.98, N 5.28, H 4.79.

The synthesis of $[Cd_3(NH_2-BTB)_2(H_2O)_2]\cdot 3DMA\cdot 5H_2O$ (3). The mixture of $Cd(NO_3)_2\cdot 6H_2O$ (0.060 g, 0.20 mmol), NH_2 - H_3BTB (0.045 g, 0.10 mmol) and $DMA-H_2O$ (2 : 2, v/v; 8 mL) was sealed in a 23 mL Teflon-lined autoclave, heated to 120 °C for 8 hours, and then cooled to room-temperature. Colorless crystals of 3 were obtained (yield: 87.5 mg, 75% based on NH_2 - H_3BTB). Elemental analysis (wt%) for 3: calcd C 48.65, N 4.65, H 4.0; found C 51.05, N 5.08, H 4.33.

X-ray diffraction analysis

Suitable single crystals of 1–3 were carefully selected under an optical microscope and glued to thin glass fibers. Whereafter, single-crystal X-ray diffraction analyses were performed on a computer-controlled XCalibur E CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda_{MO-K\alpha} = 0.71073$ Å) at T = 293 K. The structures were solved using the direct method and refined by full-matrix least-squares methods on F^2 by using the SHELX-97 program package.¹⁴ Non-hydrogen atoms were refined anisotropically. The SQUEEZE option of PLATON¹⁵ was used to eliminate the contribution of the disordered guest molecules to the reflection intensities. CCDC numbers 966925–966927 (1–3) contain the supplementary crystallographic data for this paper. The crystallographic data for compounds 1–3 are listed in Table 1.

Results and discussion

The structures of 1–3 were characterized by single-crystal X-ray diffraction. All compounds are stable in air and insoluble in

Compound reference	1	2	3
Chemical formula	$C_{64}H_{40}Cd_2N_4O_{12}$	$C_{64}H_{28}Cd_2N_2O_{14}$	$C_{54}H_{32}Cd_3N_2O_{14}$
Formula mass	1281.80	1273.71	1270.05
Crystal system	Monoclinic	Monoclinic	Triclinic
a/Å	17.1902(10)	17.0229(8)	9.3028(5)
b/Å	29.7214(18)	29.8118(10)	14.9043(7)
c/Å	16.0823(6)	16.1301(6)	15.2092(7)
$\alpha/^{\circ}$	90.00	90.00	70.594(4)
$\beta/^{\circ}$	98.722(5)	99.179(4)	83.472(4)
γ/°	90.00	90.00	84.978(4)
Unit cell volume/Å ³	8121.7(7)	8080.9(6)	1973.29(17)
Temperature/K	293(2)	293(2)	293(2)
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
No. of formula units per unit cell, Z	4	4	1
No. of reflections measured	28 028	31 346	8068
No. of independent reflections	14 303	14244	8068
R _{int}	0.0501	0.0393	0.0460
Final R_1 values $(I > 2\sigma(I))$	0.0775	0.0680	0.0485
Final $wR(F^2)$ values $(I > 2\sigma(I))$	0.2213	0.1879	0.1317
Final R_1 values (all data)	0.1077	0.0986	0.0515
Final $wR(F^2)$ values (all data)	0.2501	0.2046	0.1342
Goodness of fit on F^2	1.051	1.064	1.063

Paper

common solvents, such as methanol, ethanol, *n*-propanol, isopropanol, acetone, acetonitrile, dichloromethane (CH_2Cl_2) or DMF. The results of the powder X-ray diffraction (PXRD) measurements indicate that the peaks displayed in the measured PXRD patterns closely match those in the simulated patterns generated from single-crystal diffraction data, demonstrating the phase purity of **1–3**.

Single crystal X-ray analysis revealed that compounds 1-2 are isostructural and crystallize in the same space group $P2_1/c$. Here, only the structure of 1 is described in detail. Each independent crystallographic unit of 1 contains two independent Cd(II) centers, two NH₂-BTB³⁻ linkers and one bpy ligand. As illustrated in Fig. 1a, the coordination environments of Cd1 and Cd2 are similar to each other. the Cd1 atom is seven-coordinated by six carboxylate oxygen atoms (O1, O2, O3B, O4B, O11A, O12A) from three NH₂-BTB³⁻ and one nitrogen atom from a μ_2 -bpy ligand (Fig. 1a). the Cd–N distances (2.3492(1)– 2.3541(1) Å) are close to those in the previously reported MOFs.¹⁶ Each NH₂-BTB links three Cd(II) ions through its three carboxyl groups, and each Cd(II) ion is bound by three NH₂-BTB ligands. Thus, the linkage between the Cd(II) ions and the NH2-BTB ligands leads to the formation of a honeycomb-like layer. The layers are further pillared by the bpy ligands to form a 3D anionic framework with large inner spaces (Fig. 1b). However, these free spaces are occupied by two other interpenetrating frameworks, so the whole framework of 1 is a 3-fold interpenetrating framework (Fig. 1c). After the interpenetration, there are still free spaces to locate the guest solvent molecules and dimethylamine cations (Fig. 1d). The free solvent-accessible volume is about 40.7%, estimated by using the PLATON program.

Compound 3 features a 3D porous framework with trinuclear Cd units linked by the NH2-BTB ligand. The asymmetry unit of 3 contains one and a half $Cd(\pi)$ ions, one NH_2 -BTB³⁻ anion and one coordinate H₂O molecule. As shown in Fig. 2a, the secondary building unit (SBU) is a trinuclear Cd unit with central symmetry, Two Cd(2) are centrosymmetric around Cd(1). The Cd(2) center adopts a distorted triangular prism geometry, which is coordinated to five oxygen atoms from three individual NH₂-BTB ligands, and one N atom from the NH₂-BTB ligand. The Cd(1) center is coordinated to six oxygen atoms from four individual NH2-BTB ligands and two H2O molecules, forming an octahedral coordination geometry. Without considering the Cd-N bonds, the NH₂-BTB ligands link the Cd centers into a double-layer through the Cd-O coordination (Fig. 2b). Furthermore, the adjacent doublelayers are linked each other to form the final 3D framework through the Cd-N bonds (Fig. 2c). The resulting 3D architecture is a non-interpenetrating framework with large channels (Fig. 2d). The window size of each channel is $14.2 \times 11.1 \text{ Å}^2$ (measured by the atom-atom distances). The coordinated H₂O molecules sit in the channels. The total solvent-accessible volume for 3 was estimated to be 50% by the PIATON software.

The thermal behaviours of 1-3 were investigated on polycrystalline samples by thermogravimetric analyses (TGA). The TG trace for **1** reveals that the guest water solvents are



Fig. 1 (a) The coordination environment in 1 with the hydrogen atoms and lattice water molecules omitted for clarity. (b) The pillared-layer framework in 1. (c) The topological structure of three-fold interpenetrated frameworks. (d) The resulting 3D architecture with the rhombohedral channels along the *a* axis. Color code for (a,b): Cd, green; C, black; N, blue; O, red. Symmetry codes: (A) 1 - x, 2 - y, -z; (B) 1 - x, -0.5 + y, 1.5 - z; (C) 2 - x, -0.5 + y, 0.5 - z; (D) x, 1.5 - y, -1.5 + z.

gradually removed in proceeding from 30 to 145 °C. The weight loss of 18.82% from 145 to 340 °C corresponds to the removal of the DMF molecules and dimethylamine cations



Fig. 2 (a) The coordination environment in **3**; (b) the double-layer in **3**; (c) the double-layers connect to a 3D framework through the Cd–N bonds. (d) the 3D structure of **3**. Color for (a,b,c): Cd, green; C, black; N, blue; O, red. Symmetry codes: (A) -1 + x, 1 + y, z; (B) -1 + x, y, 1 + z; (C) -1 - x, 1 - y, 2 - z; (D) -x, -y, 2 - z; (E) 1 - x, -y, 2 - z; (F) -x, 1 - y, 1 - z; (G) -x, 1 - y, 2 - z; (H) -1 + x, y, z.

(cacld 17.79%). Above 350 °C, the weight loss is due to the decomposition of the organic ligands, accompanying the collapse of the whole framework. The TG curve of 2 reveals that the main weight loss of about 21.38% occurs between room temperature and 320 °C, which corresponds to the loss of free



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Fig. 3 The emission spectra of 1, 2 and the free ligands in the solid state at room temperature.

water, DMF molecules and dimethylamine cations (calcd 21.25%). For 3, the weight loss of about 25.23% below 200 °C corresponds to the release of the free water, DMA molecules and coordinated water (cacld 26.25%).

The solid-state emission spectra of compounds 1 and 2 as well as the free ligands have been measured at room temperature (Fig. 3). Upon excitation at 350 nm, the NH₂-H₃BTB and HO-H₃BTB ligands exhibit main emission bands at 478 nm and 447 nm, respectively. For 1 and 2, their corresponding emission bands were observed at 450 and 448 nm. The free bpy displayed a weak emission peak at 390 nm upon excitation at 318 nm.¹⁷ There are no peaks in the range of 350 to 400 nm in above profiles, thus, the luminescent emission of bpy is negligible. So the peaks for 1 and 2 should be attributed to the charge transfer $(\pi \rightarrow \pi^* \& n \rightarrow \pi^*)$ of the internal ligands. However, no enhancement in the fluorescence intensity is realised. Compared with the emission of the free ligand, the slight blue shift of the emission of 2 can be ascribed to the weak $\pi^*-\pi$ transitions of the NH₂-BTB ligands, admixing with the influence of the coordination effect between the ligands and metal ions.

For the gas sorption studies, the sample of **3** was exchanged by acetone and further activated by heating at 200 °C for 10 hours under vacuum. The PXRD pattern of this activated sample reveals that the framework of **3** is retained upon evacuation (Fig. S4 in the ESI†). Unfortunately, the desolvated framework of **3** did not show N₂ adsorption at 77 K. But CO₂ and H₂ can be adsorbed under different conditions. The CO₂ uptake value is 43.4 cm³ g⁻¹ STP at 273 K and 1 atm (Fig. 4a). Although the CO₂ adsorption capacity of **3** is lower than that of some other reported MOFs,¹⁸ it shows an excellent ideal CO₂/N₂ adsorption selectivity of 75 at STP (calculated by weight percentage), because N₂ was hardly adsorbed under the same conditions (0.58 cm³ g⁻¹) (Fig. 4a).¹⁹ The H₂ uptake value is 78.5 cm³ g⁻¹ (0.70 wt%) at 77 K and 1 atm, a value equalling that of the most favorable zeolite ZSM-5 (0.7 wt%).



Fig. 4 The gas sorption isotherms of 3. (a) The CO₂ and N₂ sorption isotherms at 273 K and H₂ sorption isotherms at 77 K; (b) the C₂H₄, C₂H₆, C₃H₈ and CH₄ sorption isotherms at 273 K; (c) the C₂H₄, C₂H₆, C₃H₈ and CH₄ sorption isotherms at 293 K.

In addition to the N₂, H₂ and CO₂ uptakes, some hydrocarbon (CH₄, C₂H₄, C₂H₆, and C₃H₈) sorption measurements of 3 have been performed at 273 K and 293 K, respectively (Fig. 4b–c). The uptake amounts of CH₄, C₂H₄, C₂H₆ and C₃H₈ are 20.2 cm³ g⁻¹, 53.2 cm³ g⁻¹, 49.3 cm³ g⁻¹ and 44.9 cm³ g⁻¹, respectively. The results explain that a molecule sieving effect does not exist. Noteworthy, the CH₄ uptake value of 3 is higher than those of CuBTC, PCN-16, NOTT-101/102 and MgMOF-74 at 273 K and 1 bar.²⁰ To evaluate the gas separation ability of compound **3**, we calculated the C₃H₈/CH₄, C₂H₆/CH₄ and C₂H₄/CH₄ adsorption selectivity by Henry's law. The selectivities for C₃H₈, C₂H₆ and C₂H₄ over CH₄, calculated based on the equation $S_{ij} = \text{KH}(i)/\text{KH}(\text{CH}_4)$, are 16.7, 32.7 and 23.2 at 273 K (82.6, 22.2 and 13.2 at 298 K), respectively. These results indicate that the hierarchy of the adsorption capacity is commonly CH₄ < C₂H₄ < C₂H₆ < C₃H₈.²¹

Conclusions

In conclusion, we have successfully synthesis three new MOFs with $Cd(\pi)$ and the H_3BTB ligand modified by an amino group or a hydroxyl group. Compounds 1 and 2 display a strong fluorescence emission ability. The desolvated 3 can selectively adsorb CO_2 and H_2 over N_2 , as well as C_3H_8 and C_2H_6 over CH_4 .

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Notes and references

- (a) S. Kitagawa, R. Kitaura and S. I. Noro, Angew. Chem., Int. Ed., 2004, 43, 2334; (b) G. Férey, Chem. Soc. Rev., 2008, 37, 191; (c) S. Yang, X. Lin, A. J. Blake, G. Walker, P. Hubberstey, N. R. Champness and M. Schroder, Nat. Chem., 2009, 1, 487; (d) H. L. Jiang, Y. Tatsu, Z. H. Lu and Q. Xu, J. Am. Chem. Soc., 2010, 132, 5586.
- (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; (b) J. R. Li, J. Sculley and H. C. Zhou,
 Chem. Rev., 2012, **112**, 869; (c) H. H. Wu, Q. Gong,
 D. H. Olson and J. Li, *Chem. Rev.*, 2012, **112**, 836.
- 3 (a) Y. J. Cui, Y. F. Yue, G. D. Qian and B. L. Chen, *Chem. Rev.*, 2012, **112**, 1126; (b) B. C. Tzeng, S. L. Wei and T. Y. Chang, *Chem.-Eur. J.*, 2012, **18**, 16443.
- 4 (a) N. Yanai, T. Uemura, M. Inoue, R. Matsuda, T. Fukushima, M. Tsujimoto, S. Isoda and Kitagawa, *J. Am. Chem. Soc.*, 2012, 134, 4501; (b) D. N. Dybtsev, H. Chun and K. Kim, *Angew. Chem., Int. Ed.*, 2004, 38, 503; (c) P. Y. Wu, C. He, J. Wang, X. J. Peng, X. Z. Li, Y. L. An and C. Y. Duan, *J. Am. Chem. Soc.*, 2012, 134, 1499; (d) Q. K. Liu, J. P. Ma and Y. B. Dong, *J. Am. Chem. Soc.*, 2010, 132, 7005; (e) F. C. Pigge, *CrystEngComm*, 2011, 13, 1733.
- 5 (a) F. Schröder, D. Esken, M. Cokoja, E. V. Berg,
 O. I. Lebedev, G. V. Tendeloo, B. Walaszek, G. Buntkowsky,
 H. H. Limbach, B. Chaudret and R. A. Fischer, *J. Am. Chem. Soc.*, 2008, 130, 6119; (b) Z. L. Fang, R. M. Yu, X. Y. Wu,

J.-S. Huang and C. Z. Lu, *Cryst. Growth Des.*, 2011, **11**, 2546; (c) L.-F. Ma, M.-L. Han, J.-H. Qin, L.-Y. Wang and M. Du, *Inorg. Chem.*, 2012, **51**, 9431; (d) D.-S. Li, J. Zhao, Y.-P. Wu, B. Liu, L. Bai, K. Zou and M. Du, *Inorg. Chem.*, 2013, **52**, 8091.

- 6 (a) P. Falcaro and D. S. Furukawa, Angew. Chem., Int. Ed., 2012, 51, 8431; (b) A. Morozan and F. Jaouen, Energy Environ. Sci., 2012, 5, 9269; (c) L. M. Li, H. F. Wang and X. P. Yan, Electrophoresis, 2012, 33, 2896; (d) P. Pachfule, V. M. Dhavale, S. Kandambeth, S. Kurungot and R. Banerjee, Chem.-Eur. J., 2013, 19, 974; (e) J. Gómez-Herrero and F. Zamora, Adv. Mater., 2011, 23, 5311.
- 7 (a) X.-M. Zhang, Z. M. Hao, W. X. Zhang and X. M. Chen, Angew. Chem., Int. Ed., 2007, 46, 3456; (b) M. Kurmoo, Chem. Soc. Rev., 2009, 38, 1353–1379; (c) J. Rocha, L. D. Carlos, F. A. A. Paz and D. Ananias, Chem. Soc. Rev., 2011, 40, 926–940; (d) E. Pardo, C. Train, G. Gontard, K. Boubekeur, O. Fabelo, H. Liu, B. Dkhil, F. Lloret, K. Nakagawa, H. Tokoro, S. I. Ohkoshi and M. Verdaguer, J. Am. Chem. Soc., 2011, 133, 15328; (e) Z. G. Xie, C. Wang, K. E. deKrafft and W. B. Lin, J. Am. Chem. Soc., 2011, 133, 2056.
- 8 (a) S. M. Cohen, Chem. Rev., 2012, 112, 970; (b) M. Kim, J. A. Boissonnault, P. V. Dau and S. M. Cohen, Angew. Chem., Int. Ed., 2011, 50, 12193; (c) R. K. Deshpande, J. L. Minnaar and S. G. Telfer, Angew. Chem., Int. Ed., 2010, 49, 4598; (d) H. L. Jiang, D. Feng, T. F. Liu, J. R. Li and H. C. Zhou, J. Am. Chem. Soc., 2012, 134, 14690; (e) Z. Wang and S. M. Cohen, J. Am. Chem. Soc., 2007, 129, 12368.
- 9 (a) T. Devic, P. Horcajada, C. Serre, F. Salles, G. Maurin, B. Moulin, D. Heurtaux, G. Clet, A. Vimont, J.-M. Grenéche, B. LeOuay, F. Moreau, E. Magnier, Y. Filinchuk, J. Marrot, J.-C. Lavalley, M. Daturi and G. Férey, J. Am. Chem. Soc., 2010, 132, 1127; (b) V. Colombo, C. Montoro, A. Maspero, G. Palmisano, N. Masciocchi, S. Galli, E. Barea and J. A. R. Navarro, J. Am. Chem. Soc., 2012, 134, 12830; (c) A. Torrisi, R. G. Bell and C. Mellot-Draznieks, Microporous Mesoporous Mater., 2013, 168, 225; (d) A. Torrisi, C. Mellot-Draznieks and R. G. Bell, J. Chem. Phys., 2009, 130, 194703; (e) A. Torrisi, C. Mellot-Draznieks and R. G. Bell, J. Chem. Phys., 2010, 132, 44705.
- 10 (a) H. K. Chae, D. Y. Siberio-Perez, J. Kim, Y. B. Go, M. Eddaoudi, A. J. Matzger, M. O'Keeffe and O. M. Yaghi, *Nature*, 2004, 427, 523; (b) R. C. Stephen, W. F. G. Antek and A. J. Matzger, *Inorg. Chem.*, 2008, 47, 7751; (c) A. R. Millward and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, 127, 17998; (d) D. f. Sun, S. q. Ma, Y. x. Ke, D. J. Collins and H. C. Zhou, *J. Am. Chem. Soc.*, 2006, 128, 3896.
- 11 (a) K. Koh, A. G. Wong-Foy and A. J. Matzger, Angew. Chem., Int. Ed., 2008, 47, 677; (b) K. Koh, A. G. Wong-Foy and A. J. Matzger, J. Am. Chem. Soc., 2009, 131, 4184; (c) K. K. Tanabe, C. A. Allen and S. M. Cohen, Angew. Chem., Int. Ed., 2010, 49, 9730; (d) M. Padmanaban,

P. Müller, C. Lieder, K. Gedrich, R. Grünker, V. Bon, I. Senkovska, S. Baumgärtner, S. Opelt, S. Paasch, E. Brunner, F. Glorius, E. Klemm and S. Kaskel, *Chem. Commun.*, 2011, 47, 12089.

- 12 (a) N. Klein, I. Senkovska, K. Gedrich, U. Stoeck, A. Henschel, U. Mueller and S. Kaskel, Angew. Chem., 2009, 121, 10139, (Angew. Chem., Int. Ed., 2009, 48, 9954); (b) K. Koh, A. G. Wong-Foy and A. J. Matzger, Angew. Chem., 2008, 120, 689, (Angew. Chem., Int. Ed., 2008, 47, 677); (c) K. Koh, A. G. Wong-Foy and A. J. Matzger, J. Am. Chem. Soc., 2009, 131, 4184.
- 13 P. V. Dau, K. K. Tanabe and S. M. Cohen, *Chem. Commun.*, 2012, **48**, 9370.
- 14 (a) G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112; (b) G. M. Sheldrick, SHELXL-97 Program for Crystal Structure Solution and Refinement, University of Göttingen, Göttingen, Germany, 1997.
- 15 L. Spek, *PLATON*, The University of Utrecht, Utrecht, The Netherlands, 1999.
- 16 C. J. Adams, M. F. Haddow, M. Lusi and A. Guy Orpen, CrystEngComm, 2011, 13, 4324.
- 17 (a) J. J. Wang, C.-S. Liu, T. L. Hu, Z. Chang, C. Y. Li, L. F. Yan, P. Q. Chen, X. H. Bu, Q. Wu, L. J. Zhao, Z. Wang and X. Z. Zhang, *CrystEngComm*, 2008, **10**, 681; (b) C. S. Liu, J. J. Wang, Z. Chang, L. F. Yan and X. H. Bu, *CrystEngComm*, 2010, **12**, 1833.
- 18 (a) K. Sumida, S. Horike, S. S. Kaye, Z. R. Herm,
 W. L. Queen, C. M. Brown, F. Grandjean, G. J. Long,
 A. Dailly and J. R. Long, *Chem. Sci.*, 2010, 1, 184; (b) J.-R. Li,
 Y. G. Ma, M. C. McCarthy, J. Sculley, J. M. Yu, H.-K. Jeong,
 P. B. Balbuena and H.-C. Zhou, *Coord. Chem. Rev.*, 2011,
 255, 1791; (c) H. Yang, F. Wang, Y. Kang, T. H. Li and
 J. Zhang, *Dalton Trans.*, 2012, 41, 2873.
- 19 (a) K. Sumida, S. Horike, S. S. Kaye, Z. R. Herm,
 W. L. Queen, C. M. Brown, F. Grandjean, G. J. Long,
 A. Dailly and J. R. Long, *Chem. Sci.*, 2010, 1, 184;
 (b) Y. X. Tan, Y. P. He and J. Zhang, *Cryst. Growth Des.*, 2012, 12, 2468.
- 20 (a) Y. B. He, R. Krishna and B. L. Chen, Energy Environ. Sci., 2012, 5, 9107; (b) P. D. C. Dietzel, R. Blom and H. Fjellvåg, Eur. J. Inorg. Chem., 2008, 3624; (c) P. D. C. Dietzel, Y. Morita, R. Blom and H. Fjellvåg, Angew. Chem., Int. Ed., 2005, 44, 6354; (d) D. Sun, S. Ma, J. M. Simmons, J.-R. Li, D. Yuan and H.-C. Zhou, Chem. Commun., 2010, 46, 1329; (e) X. Lin, J. Jia, X. Zhao, Κ. М. Thomas, A. J. Blake, G. S. Walker, N. R. Champness, P. Hubberstey and M. Schröder, Angew. Chem., Int. Ed., 2006, 45, 7358.
- 21 (a) M. C. Das, H. Xu, S. Xiang, Z. Zhang, H. D. Arman, G. Qian and B. L. Chen, *Chem.-Eur. J.*, 2011, 17, 7817;
 (b) H. Xu, J. f. Cai, S. c. Xiang, Z. j. Zhang, C. d. Wu, X. t. Rao, Y. j. Cui, Y. Yang, R. Krishna, B. L. Chen and G. Qian, *J. Mater. Chem. A*, 2013, 1, 9916.