Polyoxometalates

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An Ionothermal Synthetic Approach to Porous Polyoxometalate-Based Metal–Organic Frameworks**

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Porous materials with regular, bulky, accessible cages and channels have aroused great research interest owing to their potential applications in gas storage, separation, ion-exchange, and heterogeneous catalysis.[1,2] Polyoxometalates (POMs), as a unique class of metal oxide clusters, constitute promising building units for targeting multifunctional materials because of their nanosize, adjustable compositions, abundant topologies, and their oxygen-rich surface with strong coordination abilities.[3,4] Despite the unparalleled success in the preparation of microporous/mesoporous compounds by covalently linking simple metal ions and organic ligands, attempts to prepare porous POM-based metal–organic frameworks have met with only limited success.[5] Therefore, the synthesis of such frameworks is one of the most challenging issues in synthetic chemistry.

Normally, porous materials are prepared by conventional solution synthesis and hydro- or solvothermal synthesis. Solvents of these systems have been largely restricted to water and traditional organic solvents, such as methanol, acetonitrile, and acetone. It is undeniable that these solvents have some intrinsic disadvantages: for example, regarding synthesis, their lower boiling points have limited the use of higher temperatures out of safety concerns; furthermore, from the environmental perspective, volatile organic solvents have caused serious health and environmental problems. Therefore, it is very necessary to explore a more effective and environmentally friendly synthetic method to overcome these existing shortcomings. Ionic liquids (ILs), composed of cations and anions, have gained attention owing to their low melting points, high ionic conductivity, non-volatility, non-flammability, high polarity, low toxicity, zero vapor pressure, and relatively low viscosity. Therefore, they may be environmentally friendly alternatives to the traditional solvents. Ionothermal synthesis, with the use of an IL as solvent and structural directing agent, has already been comprehensively discussed in several detailed reviews,[6–9] and has been successfully applied in the synthesis of zeolites[10] or microporous solids.[11] The remarkable work of Pakhomova and others have also proved the feasibility of such ionothermal methods for preparation of non-porous POM-based materials.[12] Inspired by these recent developments, we present herein the extension of the ionothermal method to the realm of POM-based porous frameworks and demonstrate its capacity to produce such crystalline solids. To our knowledge, no reliable design of POM-based porous materials from this approach has yet been reported to date.

In planning the synthesis, we chose a readily available ionic liquid, 1-ethyl-3-methylimidazolium bromide ([Emim]Br) as solvent, the weak coordinating ability of which can facilitate the self-assembly of the polyoxoanions.[9] Meanwhile, to surmount the major obstacle in construction of POM-based solids with extra-large pores, bulky tetrabutylammonium bromide was used. On one hand, it could increase the aperture when it acts as a counterion filling in the cavity;[13] on the other hand, subsequent ion exchange of it with smaller cations would recover the porosity effectively.[14] Indeed, by slightly varying the experimental conditions, three porous POM-based 3D structures have been obtained based on the above design strategy: $(TBA)_2[Cu^{II}(BBTZ)_2(x\text{-}Mo_8O_{26})]$ ($x = \beta$ for **1**, $x = \alpha$ for **2** and **3**) (TBA = tetrabutylammonium cation, BBTZ = 1,4-bis(1,2,4-triazol-1-ylmethyl)-benzene).

Single-crystal X-ray diffraction analysis reveals that the octamolybdate anion in **1** adopts the structural feature of the β-isomer, which consists of eight edge-shared MoO_6 octahedra. Each $[\beta\text{-}Mo_8O_{26}]^{4-}$ unit is covalently linked to two $[Cu^{II}BBTZ_4]$ fragments through terminal oxo groups of octahedral Mo sites with Cu–O distances of 2.302(4) and 2.302(4) Å. Each Cu^{II} cation adopts an octahedral geometry, defined by four N atoms from four BBTZ organic ligands (Cu1–N5 2.022(5), Cu1–N6 2.036(5)), and two O atoms from the $[\beta\text{-}Mo_8O_{26}]^{4-}$ unit. The BBTZ ligands coordinated to the Cu center adopt a U-type configuration, and thus the $Cu^{II}BBTZ_4$ fragment has a windmill-type configuration with the four included angles between the four BBTZ ligands coordinated to the Cu centers of 90° (Supporting Information, Figure S1). The Cu centers of the windmills are extended to a 3D covalent net through the $[\beta\text{-}Mo_8O_{26}]^{4-}$ units and the BBTZ ligands. The structure of **1** is very open, and contains three-directional channel systems. These channels intersect with each other and run along three different directions: 1.20×1.20 nm along the [100] direction, and 1.20×1.37 nm along the [011] and [0–11] directions, as shown in Figure 1a. From the topological view, the 3D architecture of **1** can be

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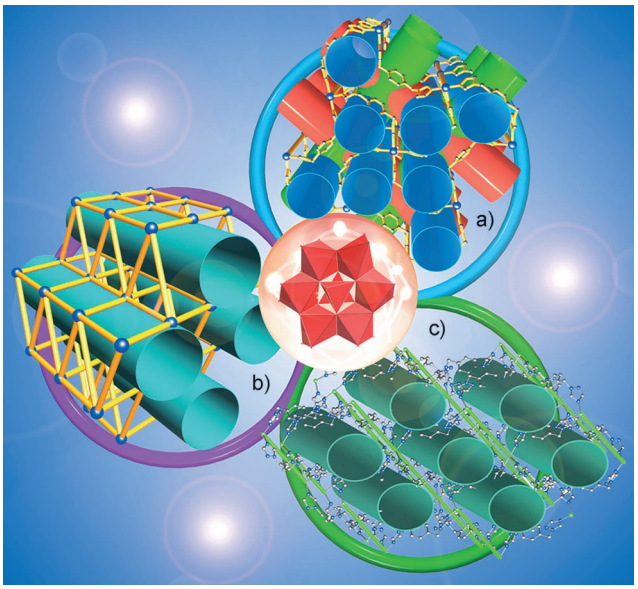

Figure 1. a) A ball-and-stick representation of **1**, highlighting the three directional channels in the 3D framework. The three different colored tubes represent the different channels in **1**. b) A topological representation of **2**. The channels within which are shown in blue tubes. c) Channel and ball-and-stick representations of **3**. In the pictures, the polyanions are shown in sticks.

simplified as the classic α-Po topology (Supporting Information, Figure S1). In contrast to **1**, the octamolybdate anion in **2** adopts the structural feature of the α-isomer, consisting of six MoO_6 octahedra and two MoO_4 tetrahedra. Although the coordination numbers of $[\alpha\text{-}Mo_8O_{26}]^{4-}$ and Cu^{II} centers are the same as compound **1**, the BBTZ ligands coordinated to Cu^{II} center adopt a *z*-type configuration, and thus the $Cu^{II}BBTZ_4$ fragment has a butterfly arrangement, with the four included angles between the four BBTZ coordinated to the Cu centers of 50, 65, 65 and 180° (Supporting Information, Figure S2). The resultant 3D framework contains 1D channels along the [001] direction with window dimensions of 1.6 × 2.4 nm (Figure 1 b). From the topological view, the structure of **2** can be simplified as the **sxd** topology (Supporting Information, Figure S2). The octamolybdate anion in **3**, which is the same as **2**, adopts the structural feature of the α-isomer. Although the BBTZ ligands coordinated to the Cu center adopt the same *z*-type configuration as that in **2**, the $Cu^{II}BBTZ_4$ fragment has a windmill-type configuration with the four included angles between the four BBTZ coordinated to the Cu centers of 62, 118, 62 and 118° (Supporting Information, Figure S3). The resulting 3D framework only contains one-dimensional channels along the [101] direction with an aperture size of 2.40 nm × 1.47 nm (Figure 1 c). From a topological viewpoint, the structure of **3** belongs to the classic α-Po topology (Supporting Information, Figure S3). As described above, the flexible BBTZ ligand and rich isomeric forms of octamolybdate play important roles in the formation of the isomerism. As a result, these three compounds are conformational isomers, as categorized by Moulton and Zaworotko.[15]

The bulky TBA cations are located in the channels of these three compounds, balancing the charges of these frameworks (Supporting Information, Figure S4). PLATON analysis for these structures without the contribution of TBA showed that the effective free volumes of **1**–**3** are 52.9, 51.5, and 49.9 % of the crystal volume, respectively. These values are comparable to that found in some of the most open zeolites, such as faujasite in which the free space is 45–50 % of the crystal volume.[16]

Compound **3** was stable for months under an air atmosphere, and no efflorescence was observed. To examine the thermal stability of these compounds, compound **3** was selected for carrying out thermal gravimetric (TG) and XRPD measurements. The TG curve of **3** (Supporting Information, Figure S5) reveals a weight loss of 21.90 % from 240 to 340 °C, which corresponds to the removal of TBA organic cations. The elimination of TBA cations was confirmed by IR spectroscopy of heated samples (Supporting Information, Figure S6). The second mass loss begins at 340 °C, and is associated with the decomposition of BBTZ organic ligands. As shown in the Supporting Information, Figure S7, the powder X-ray diffraction (PXRD) patterns for samples heated in flowing N_2 from 100 to 400 °C indicate that the structural integrity of the framework remains unchanged until 300 °C. Moreover, the hydrolytic stability of **3** was also investigated. As-synthesized **3** in common organic solvents (methanol, ethanol, acetonitrile, acetone, chloroform, and DMF) was stirred for 10 h at 80 °C and showed no compound dissolution, framework decomposition, or POM leaching, as evidenced by the UV, IR, NMR, and XRD patterns. When it was exposed in deionized water for three months, aliquots of the solution, which were withdrawn periodically, showed no evidence of POM leaching as monitored by UV spectroscopy.

The effective free volumes of these compounds and their high architectural stability prompted us to carry out cation exchange experiments so as to obtain porous materials. Taking compound **3** as an example, the studies reported herein detailed the exchange of bulky TBA cations for d-block transition-metal cations. Co^{II} was used as a suitable probe for exchange experiments when considering its size, stability, and intuition. Fresh crystals of **3** were soaked in acetone containing Co^{2+} ions, and UV spectroscopy was employed to monitor the exchanging process. UV analyses showed no evidence of dissolution of **3** into solution during exchange studies (Supporting Information, Figure S8), and the exchange reached equilibrium when fresh crystals were soaked in acetone containing Co^{2+} ions for 16 h (Figure 2 c). At the end of the exchanged experiments, the crystals changed color from light blue to light purple, whereas the color of the Co^{II} solution became paler, as shown in Figure 2. Subsequent elemental and spectroscopic analyses of fresh crystals of **3** soaked in a solution of Co^{II} ions showed that freshly isolated crystals of **3** can take up 1 mol of Co^{II} per mol of **3**. A PXRD comparison of **3** before and after exchange experiments indicates that the integrity of **3** is retained after Co^{II} uptake (Supporting Information, Figure S9). After 16 h, the disappearance of the characteristic stretching vibrations ascribed to the TBA^+ cations demonstrates the success of cation exchange (Supporting Information, Figure S10).

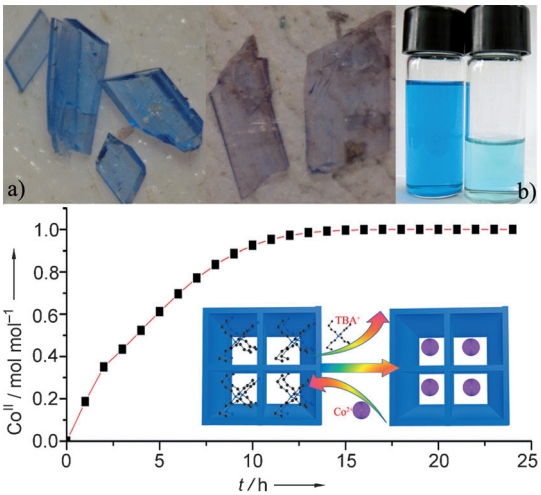

Figure 2. The cation exchange experiment for compound **3**. a) Visual observation of Co^{II} uptake into single crystals of **3**. b) Comparison of the solution before and after cation exchange. c) Plot of uptake of Co^{II} into the channels of **3** over a 24 h period. For **3**, this corresponds to an uptake of 1 mol Co^{II} per mol of **3**. Inset: exchange of Co^{2+} ions with the TBA cations.

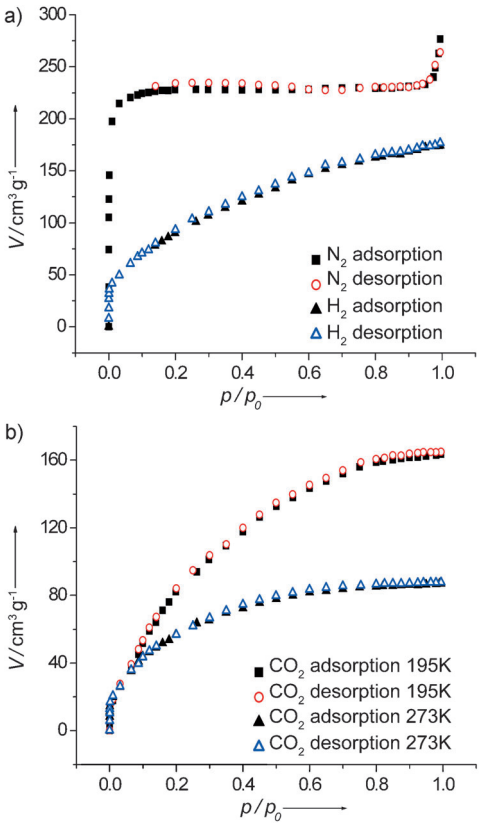

Figure 3. Gas sorption isotherms of activated **3** for a) N_2 and H_2 at 77 K and b) CO_2 at 195 K and 273 K.

Importantly, the ESI-MS mass spectrum analysis shows that the organic TBA cations in the channels went into solution during exchange studies (Supporting Information, Figure S11). Meanwhile, the fact that Co^{II} cations had entered into the channels was verified by the results of EDS (Supporting Information, Figure S12), XPS (Supporting Information, Figure S13), UV spectroscopy, and ICP-AES (atomic emission spectroscopy). According to the quantitative data provided by ICP-AES, XPS, EDS, and TG after exchange (Supporting Information, Figure S14), the final chemical formula of the crystals after the cation exchange experiment for compound **3** is $[Cu^{II}Co^{II}BBTZ_2(Mo_8O_{26})]\cdot n(C_3H_6O)$ (**3a**, $n \approx 8$; for a derivation of the formula, see the Supporting Information). So far we have focused our efforts primarily on Co^{II} uptake; however, analogous exchanges of other 3d transition-metal ions, such as Ni^{II} and Zn^{II}, have also been observed.

A N_2 adsorption measurement was subsequently carried out for the fully activated sample, which was achieved by soaking crystals in acetone containing Co^{2+} ions for 16 h and heating at 150 °C for 8 h in a vacuum, to confirm its porosity. The N_2 sorption isotherm reveals a characteristic type II behavior (Figure 3a). The Langmuir surface area was calculated to be 1024 $m^2 g^{-1}$ (BET, 772 $m^2 g^{-1}$), which is greater than the highest value for classical zeolites (904 $m^2 g^{-1}$ for zeolite Y),[17] and comparable to those of many porous coordination polymers[18] and mesoporous silica materials (BET, 500–1160 $m^2 g^{-1}$).[19] The maximum N_2 uptake of 276 $cm^3 g^{-1}$ (at standard temperature and pressure, STP) was reached at 1 atm. We measured the CO_2 and H_2 gas sorption isotherms of activated **3** to evaluate its permanent porosity. They revealed a reversible type I isotherm and showed no hysteresis upon desorption of gases from the pores. As shown in Figure 3b, the CO_2 sorption isotherms for activated **3** were measured at different temperatures. It exhibits high CO_2 uptake capacity at saturation of 165 $cm^3 g^{-1}$ (7.4 mmol g^{-1}, 231.6 L L^{-1}) at 195 K and 87.7 $cm^3 g^{-1}$ (3.9 mmol g^{-1}, 122.5 L L^{-1}) at 273 K, which is comparable to the highest value of classical zeolite-like MOFs.[20] Surprisingly, although its surface area is below the values reported for ZIF-8 (1630 and 1810 $cm^2 g^{-1}$, respectively),[21] the adsorption isotherm of activated **3** at 77 K reveals that the adsorption amount of H_2 at saturation is about 176 $cm^3 g^{-1}$ (1.55 wt %), which is as high as the reported value of ZIF-8 (145 $cm^3 g^{-1}$). A PXRD comparison of as-synthesized and withdrawn simples after gas adsorption measurements indicates that the main structural features of the porous framework are retained after evacuation (Supporting Information, Figure S15).

The position of the cobalt ion after exchange was optimized at the medium level using the nonlocal PBE[22] functional by the density functional theory (DFT) program DMol3[23] (the optimized structure is shown in the Supporting Information, Figure S16). To explain the high CO_2 uptake of activated **3**, CO_2 adsorption isotherms were simulated with grand canonical Monte Carlo (GCMC).[24] The simulated CO_2 adsorption isotherms for activated **3** at 195 and 273 K matched reasonably well with the experimental isotherms (Supporting Information, Figure S17), suggesting that the samples were well activated. CO_2 binding sites were also obtained from the simulation (Supporting Information, Figure S18). The CO_2 molecule is located inside the channel and forms short contacts with the uncoordinated triazole nitrogen

in the 2-position and terminal oxygen atom of the polyoxoanion (C···N 3.57 Å and C···O 3.35 Å). The results suggest that these favorable interactions play an important role in increasing the gas adsorption ability of activated **3**.

Photocatlytic activity of **3** for H_2 evolution under UV radiation was also investigated. As shown in the Supporting Information, Figure S19, H_2 is continuously produced under UV radiation in this catalytic system. And the average rate of H_2 evolution is 0.78 μmol h^{-1} for **3** as a catalyst. The blank reaction (without **3** as catalyst) was carried out, and it shows that there is no H_2 produced. This result suggests that compound **3** is obviously active for photocatalytic H_2 evolution. Meanwhile, the blank reaction (with $TBA_4Mo_8O_{26}$) was carried out and also shows that there is no H_2 produced. The $[Mo_8O_{26}]^{4-}$ polyoxoanion is photoreduced into $[Mo_8O_{26}]^{5-}$ in the presence of methanol and the methanol itself is oxidized into methanal.[25] The mechanism is outlined in the Supporting Information, Equations (1)–(5).

In conclusion, an ionothermal method has been successfully applied in the synthesis of POM-based porous materials for the first time, and our initial N_2 adsorption and cation exchange results provide an insight into the potential of these porous materials in inclusion chemistry. The intrinsic value of this synthetic approach lies in the ability to offer an environmentally friendly and effective alternative to preparing porous POM-based metal–organic frameworks. Furthermore, the use of bulky template agents could be key for the buildup of macroporous crystalline solids. In view of this potential, further studies will aim to investigate the exchange experiments using smaller inorganic cations, as they are more effective to recover porosity.

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[1] a) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982 – 986; b) X. Zhao, B. Xiao, A. J. Fletcher, K. M. Thomas, D. Bradshaw, M. J. Rosseinsky, *Science* **2004**, *306*, 1012 – 1015; c) R. Kitaura, G. Onoyama, H. Sakamoto, R. Matsuda, S. I. Noro, S. Kitagawa, *Angew. Chem.* **2004**, *116*, 2738 – 2741; *Angew. Chem. Int. Ed.* **2004**, *43*, 2684 – 2687; d) C. D. Wu, A. Hu, L. Zhang, W. J. Lin, *J. Am. Chem. Soc.* **2005**, *127*, 8940 – 8941; e) M. Dincă, J. R. Long, *J. Am. Chem. Soc.* **2005**, *127*, 9376 – 9377; f) H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortés, A. P. Côté, R. E. Taylor, M. O'Keefe, O. M. Yaghi, *Science* **2007**, *316*, 268 – 272; g) J. P. Zhang, X. M. Chen, *J. Am. Chem. Soc.* **2009**, *131*, 5516 – 5521; h) H. Guo, G. Zhu, I. J. Hewitt, S. Qiu, *J. Am. Chem. Soc.* **2009**, *131*, 1646 – 1647.

[2] a) N. W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2005**, *38*, 176 – 182; b) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, *Acc. Chem. Res.* **2005**, *38*, 217 – 225; c) A. K. Cheetham, C. N. R. Rao, R. K. Feller, *Chem. Commun.* **2006**, 4780 – 4795; d) J. J. Perry IV, J. A. Perman, M. J. Zaworotko, *Chem. Soc. Rev.* **2009**, *38*, 1400 – 1417.

[3] a) M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, **1983**; b) P. J. Hagrman, D. Hagrman, J. Zubieta, *Angew. Chem.* **1999**, *111*, 2798 – 2848; *Angew. Chem. Int. Ed.* **1999**, *38*, 2638 – 2684; c) Special Issue on Polyoxometalates (Ed.: C. L. Hill), *Chem. Rev.* **1998**, *1*, 327 – 358; d) D. L. Long, E. Burkholder, L. Cronin, *Chem. Soc. Rev.* **2007**, *36*, 105 – 121; e) J. Hao, Y. Xia, L. Wang, L. Ruhlmann, Y. Zhu, Q. Li, P. Yin, Y. Wei, H. Guo, *Angew. Chem.* **2008**, *120*, 2666 – 2670; *Angew. Chem. Int. Ed.* **2008**, *47*, 2626 – 2630; f) B. S. Bassil, M. H. Dickman, I. RVmer, B. Kammer, U. Kortz, *Angew. Chem.* **2007**, *119*, 6305 – 6308; *Angew. Chem. Int. Ed.* **2007**, *46*, 6192 – 6195; g) S. T. Zheng, J. Zhang, G. Y. Yang, *Angew. Chem.* **2008**, *120*, 3973 – 3977; *Angew. Chem. Int. Ed.* **2008**, *47*, 3909 – 3913; h) S. T. Zheng, J. Zhang, X. X. Li, W. H. Fang, G. Y. Yang, *J. Am. Chem. Soc.* **2010**, *132*, 15102 – 15103; i) J. Zhang, J. Hao, Y. G. Wei, F. P. Xiao, P. C. Yin, L. S. Wang, *J. Am. Chem. Soc.* **2010**, *132*, 14 – 15; j) A. Dolbecq, E. Dumas, C. R. Mayer, P. Mialane, *Chem. Rev.* **2010**, *110*, 6009 – 6048.

[4] a) A. Müller, S. Q. N. Shah, H. Bögge, M. Schmidtmann, *Nature* **1999**, *397*, 48 – 50; b) J. W. Han, C. L. Hill, *J. Am. Chem. Soc.* **2007**, *129*, 15094 – 15095; c) C. Ritchie, C. Streb, J. Thiel, S. G. Mitchell, H. N. Miras, D. L. Long, T. Boyd, R. D. Peacock, T. McGlone, L. Cronin, *Angew. Chem.* **2008**, *120*, 6987 – 6990; *Angew. Chem. Int. Ed.* **2008**, *47*, 6881 – 6884; d) K. Micoine, B. Hasenknopf, S. Thorimbert, E. Lacôte, M. Malacria, *Angew. Chem.* **2009**, *121*, 3518 – 3520; *Angew. Chem. Int. Ed.* **2009**, *48*, 3466 – 3468; e) C. Y. Duan, M. L. Wei, D. Guo, C. He, Q. J. Meng, *J. Am. Chem. Soc.* **2010**, *132*, 3321 – 3330; f) Y. Yan, H. B. Wang, B. Li, G. F. Hou, Z. D. Yin, L. X. Wu, V. W. W. Yam, *Angew. Chem.* **2010**, *122*, 9419 – 9422; *Angew. Chem. Int. Ed.* **2010**, *49*, 9233 – 9236; g) Y. S. Jiang, S. X. Liu, S. J. Li, J. Miao, J. Zhang, L. X. Wu, *Chem. Commun.* **2011**, *47*, 10287 – 10289; h) T. Liu, M. L. K. Langston, D. Li, J. M. Pigga, C. Pichon, A. M. Todea, A. Müller, *Science* **2011**, *331*, 1590 – 1592; i) M. Nyman, *Dalton Trans.* **2011**, *40*, 8049 – 8058.

[5] a) M. I. Khan, E. Yohannes, R. J. Doedens, *Angew. Chem.* **1999**, *111*, 1374 – 1376; *Angew. Chem. Int. Ed.* **1999**, *38*, 1292 – 1294; b) C. D. Wu, C. Z. Lu, H.-H. Zhuang, J. S. Huang, *J. Am. Chem. Soc.* **2002**, *124*, 3836 – 3837; c) A. Tripathi, T. Hughbanks, A. Clearfield, *J. Am. Chem. Soc.* **2003**, *125*, 10528 – 10529; d) H. Y. An, E. B. Wang, D. R. Xiao, Y. G. Li, Z. M. Su, L. Xu, *Angew. Chem.* **2006**, *118*, 918 – 922; *Angew. Chem. Int. Ed.* **2006**, *45*, 904 – 908; e) C. Streb, C. Ritchie, D. L. Long, P. Kögerler, L. Cronin, *Angew. Chem.* **2007**, *119*, 7723 – 7726; *Angew. Chem. Int. Ed.* **2007**, *46*, 7579 – 7582; f) S. G. Mitchell, C. Streb, H. N. Miras, T. Boyd, D. L. Long, L. Cronin, *Nat. Chem.* **2010**, *2*, 308 – 312; g) F. J. Ma, S. X. Liu, C. Y. Sun, D. D. Liang, G. J. Ren, F. Wei, Y. G. Chen, Z. M. Su, *J. Am. Chem. Soc.* **2011**, *133*, 4178 – 4181; h) J. Song, Z. Luo, D. K. Britt, H. Furukawa, O. M. Yaghi, K. I. Hardcastle, C. L. Hill, *J. Am. Chem. Soc.* **2011**, *133*, 16839 – 16846.

[6] E. R. Parnham, R. E. Morris, *Acc. Chem. Res.* **2007**, *40*, 1005 – 1013.

[7] a) E. R. Cooper, C. D. Andrews, P. S. Wheatley, P. B. Webb, P. Wormald, R. E. Morris, *Nature* **2004**, *430*, 1012 – 1016; b) F. H. Aidoudi, D. W. Aldous, R. J. Goff, A. M. Z. Slawin, J. P. Attfield, R. E. Morris, P. Lightfoot, *Nat. Chem.* **2011**, *3*, 801 – 806; c) R. E. Morris, *Chem. Commun.* **2009**, 2990 – 2998.

[8] M. Antonietti, D. Kuang, B. Smarsly, Y. Zhou, *Angew. Chem.* **2004**, *116*, 5096 – 5100; *Angew. Chem. Int. Ed.* **2004**, *43*, 4988 – 4992.

[9] E. Ahmed, M. Ruck, *Angew. Chem.* **2012**, *124*, 314 – 316; *Angew. Chem. Int. Ed.* **2012**, *51*, 308 – 309.

[10] E. J. Fayad, N. Bats, C. E. A. Kirschhock, B. Rebours, A. A. Quoineaud, J. A. Martens, *Angew. Chem.* **2010**, *122*, 4689 – 4692; *Angew. Chem. Int. Ed.* **2010**, *49*, 4585 – 4588.

[11] a) J. R. Li, Z. L. Xie, X. W. He, L. H. Li, X. Y. Huang, *Angew. Chem.* **2011**, *123*, 11597 – 11601; *Angew. Chem. Int. Ed.* **2011**, *50*, 11395 – 11399; b) D. Freudenmann, S. Wolf, M. Wolff, C. Feldmann, *Angew. Chem.* **2011**, *123*, 11244 – 11255; *Angew. Chem. Int. Ed.* **2011**, *50*, 11050 – 11060; c) Z. Ma, J. Yu, S. Dai,

Adv. Mater. **2010**, *22*, 261 – 285; d) R. E. Morris, *Angew. Chem.* **2008**, *120*, 450 – 452; *Angew. Chem. Int. Ed.* **2008**, *47*, 442 – 444; e) P. Kuhn, M. Antonietti, A. Thomas, *Angew. Chem.* **2008**, *120*, 3499 – 3502; *Angew. Chem. Int. Ed.* **2008**, *47*, 3450 – 3453; f) J. Zhang, S. M. Chen, X. H. Bu, *Angew. Chem.* **2008**, *120*, 5514 – 5517; *Angew. Chem. Int. Ed.* **2008**, *47*, 5434 – 5437; g) W. M. Reichert, J. D. Holbrey, K. B. Vigour, T. D. Morgan, G. A. Broker, R. D. Rogers, *Chem. Commun.* **2006**, 4767 – 4779.

[12] a) A. S. Pakhomova, S. V. Krivovichev, *Inorg. Chem. Commun.* **2010**, *13*, 1463 – 1465; b) S. Lin, W. Liu, Y. Li, Q. Wu, E. Wang, Z. Zhang, *Dalton Trans.* **2010**, *39*, 1740 – 1744; c) W. L. Chen, B. W. Chen, H. Q. Tan, Y. G. Li, Y. H. Wang, E. Wang, *J. Solid State Chem.* **2010**, *183*, 310 – 321; d) H. Fu, Y. Li, Y. Lu, W. Chen, Q. Wu, J. Meng, X. Wang, Z. Zhang, E. Wang, *Cryst. Growth Des.* **2011**, *11*, 458 – 465.

[13] a) L. M. Rodriguez-Albelo, A. R. Ruiz-Salvador, A. Sampieri, D. W. Lewis, A. Gòmez, B. Nohra, P. Mialane, J. Marrot, F. Sécheresse, C. Mellot-Draznieks, R. N. Biboum, B. Keita, L. Nadjo, A. Dolbecq, *J. Am. Chem. Soc.* **2009**, *131*, 16078 – 16087; b) B. Nohra, H. E. Moll, L. M. R. Albelo, P. Mialane, J. Marrot, C. Mellot-Draznieks, M. O'Keeffe, R. N. Biboum, J. Lemaire, B. Keita, L. Nadjo, A. Dollbecq, *J. Am. Chem. Soc.* **2011**, *133*, 13363 – 13374.

[14] a) K. Suzuki, Y. Kikukawa, S. Uchida, H. Tokoro, K. Imoto, S. Ohkoshi, N. Mizuno, *Angew. Chem.* **2012**, *124*, 1629 – 1633; *Angew. Chem. Int. Ed.* **2012**, *51*, 1597 – 1601; b) Y. Kikukawa, K. Yamaguchi, M. Hibino, N. Mizuno, *Inorg. Chem.* **2011**, *50*, 12411 – 12413.

[15] B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629 – 1658.

[16] M. J. Bennett, J. V. Smith, *Mater. Res. Bull.* **1968**, *3*, 633 – 642.

[17] A. W. Chester, P. Clement, S. Han, US Pat. Appl. 2000, 6136291A, **2006**.

[18] a) L. Hou, J. P. Zhang, X. M. Chen, S. W. Ng, *Chem. Commun.* **2008**, 4019 – 4021; b) D. Sun, Y. Ke, D. J. Collins, G. A. Lorigan, H. C. Zhou, *Inorg. Chem.* **2007**, *46*, 2725 – 2734; c) X. C. Huang, Y. Y. Lin, J. P. Zhang, X. M. Chen, *Angew. Chem.* **2006**, *118*, 1587 – 1589; *Angew. Chem. Int. Ed.* **2006**, *45*, 1557 – 1559; d) K. Li, J. Lee, D. H. Olson, T. J. Emge, W. Bi, M. J. Eibling, J. Li, *Chem. Commun.* **2008**, 6123 – 6125; e) Q. R. Fang, G. S. Zhu, Z. Jin, Y. Y. Ji, J. W. Ye, M. Xue, H. Yang, Y. Wang, S. L. Qiu, *Angew. Chem.* **2007**, *119*, 6758 – 6762; *Angew. Chem. Int. Ed.* **2007**, *46*, 6638 – 6642.

[19] D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, G. D. Stucky, *J. Am. Chem. Soc.* **1998**, *120*, 6024 – 6036.

[20] J. S. Qin, D. Y. Du, W. L. Li, J. P. Zhang, S. L. Li, Z. M. Su, X. L. Wang, Q. Xu, K. Z. Shao, Y. Q. Lan, *Chem. Sci.* **2012**, *3*, 2114 – 2118.

[21] K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. D. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe, O. M. Yaghi, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 10186 – 10191.

[22] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865 – 3868.

[23] Materials Studio 4.2 Accelrys Inc. San Diego, CA, **2005**.

[24] a) K. S. Walton, R. Q. Snurr, *J. Am. Chem. Soc.* **2007**, *129*, 8552 – 8556; b) Y. S. Bae, A. Ö. Yazaydın, R. Q. Snurr, *Langmuir* **2010**, *26*, 5475 – 5483; c) J. B. Lin, J. P. Zhang, X. M. Chen, *J. Am. Chem. Soc.* **2010**, *132*, 6654 – 6656.

[25] R. Akid, J. R. Darwent, *J. Chem. Soc. Dalton Trans.* **1985**, 395 – 399.

