A two-fold interpenetrated (3,6)-connected metal–organic framework with rutile topology showing a large solvent cavity†‡

Xiaokai Song,§[ab] Yang Zou,§¶[b] Xinfang Liu,[ab] Minhak Oh[a] and
Myoung Soo Lah*[a]

Received (in Montpellier, France) 13th April 2010, Accepted 18th June 2010
DOI: 10.1039/c0nj00272k

A two-fold interpenetrated metal–organic framework (MOF), [$(Zn_4O)_2L_4(DMF)_2(H_2O)_3$], was prepared using the tritopic ligand 4,4′,4′′-[1,3,5-benzenetriyltris(carbonylimino)]trisbenzoic acid (H_3L) and zinc nitrate. The MOF, based on the hexatopic tetranuclear $Zn_4O(COO)_6$ secondary building unit, has a (3,6)-connected network with an rtl topology and a large solvent cavity.

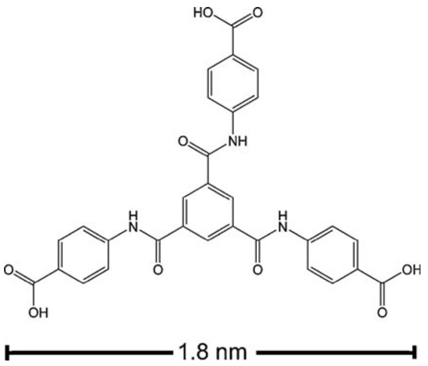
Metal–organic frameworks (MOFs) with large inner cavities[1] have attracted considerable interest because of their potential applications in gas storage, separation and heterogeneous catalysis.[2] The utilities of such architectures largely depend on the size, shape and properties of the cavity. One way to increase the cavity of a MOF is to extend the size of the ligand sustaining the framework.[3] In addition, appropriately selected metal ions can reduce the degree of interpenetration, which contributes negatively to the porosity of the open framework.[4]

Gaining an understanding of network topology is an important and essential aspect in the design and analysis of MOFs. MOFs with various network topologies can be designed and prepared using a simple node-and-linker approach.[5] Nodes of 3-, 4- and 6-connectivity are of most relevance, and a variety of such uninodal network topologies have been achieved so far. However, there is a disappointing lack of systematic investigations on higher-dimensional networks with mixed connectivity, such as (3,6)-, (4,6)- and (4,8)-connected frameworks,[6] which are considered more difficult to achieve.

As one of the most efficient synthetic routes, a controlled approach based on secondary building units (SBUs) was developed by Yaghi and co-workers with the use of the tetranuclear zinc cluster $Zn_4O(COO)_2$ as a uninodal octahedral hexatopic node.[7] There has also been increasing interest in the use of three-connected centers as basic structural units for the construction of open-framework materials.[8] It was found that rigid symmetric trinodal building blocks combined with octahedral building blocks, such as the tetranuclear $Zn_4O(COO)_6$ zinc cluster, led to the highest symmetry (3,6)-connected net of **pyr** topology.[9] However, combinations of lower symmetry building blocks, either lower symmetric trinodal organic ligands and/or distorted octahedral building blocks, have led to (3,6)-connected MOFs with **rtl** topologies.[10] To our knowledge, no MOFs of **rtl** topology constructed from the octahedral hexatopic $Zn_4O(COO)_6$ SBU have been reported.

Here, we describe the synthesis and structure of a (3,6)-connected MOF with the ligand 4,4′,4′′-[1,3,5-benzenetriyltris(carbonylimino)]trisbenzoic acid (H_3L) as a nanometre-sized trigonal tritopic node (Scheme 1) and tetranuclear $Zn_4O(CO_2)_6$ cluster as a six-connected octahedral hexatopic node. The amide groups in the ligand increase the size of the trinodal ligand, which could potentially generate a large inner cavity in a MOF, and also increase the flexibility of the ligand, which could lead to a (3,6)-connected network with reduced symmetry rather than a highest possible symmetric network of **pyr** topology, which could be obtained with rigid C_3 symmetry trinodal ligands.[9a]

A solvothermal reaction of the ligand with zinc nitrate in *N*,*N*-dimethylformamide (DMF) led to a colorless block crystalline product, **1**. The X-ray structure of a single crystal of **1** is shown in Fig. 1.‡ The asymmetric unit is composed of four L^{3-} ligands, two Zn_4O clusters and five solvent molecules, two DMF and three water molecules. Ligand L^{3-} acts as an organic trinodal building block (Fig. 1a) and six carboxylates from six ligands bridge zinc ions to form a tetranuclear Zn cluster, $Zn_4O(COO)_6$, as an SBU that serves as an octahedral



Scheme 1 A nano-sized potential C_3 symmetry triscarboxylic ligand, where the amide residues are drawn in a less symmetric orientation.

---

[a] *Interdisciplinary School of Green Energy, Ulsan National Institute of Science & Technology, Ulsan, 689-798, Korea. E-mail: mslah@unist.ac.kr; Fax: +82 522172019; Tel: +82 522172931*
[b] *Department of Chemistry and Applied Chemistry, Hanyang University, Ansan, Kyunggi-do, 426-791, Korea*

† This article is part of a themed issue on Coordination polymers: structure and function.

‡ Electronic supplementary information (ESI) available: Experimental procedure, crystallographic details, tables of selected angles, and an X-ray crystallographic file in CIF format of **1**, and PXRD. CCDC reference number 772289. For ESI and crystallographic data in CIF or other electronic format see 10.1039/c0nj00272k

§ These authors contributed equally to this article.

¶ Present address: Department of Chemistry, Zhejiang Sci-Tech University, HangZhou, 310018, China.

hexatopic node (Fig. 1b). The combination of the octahedral hexanodes and the trigonal trinodes gives rise to a 3-D network having a binodal (3,6)-connected network topology (Fig. 1c). The 3-D network is doubly-interpenetrated to generate curved 3-D channels (Fig. 2 and S1‡). Although the highest possible symmetry of the ligand is C_3, all of the ligands in network **1** are in a conformation with reduced symmetry, as shown in Scheme 1 and Fig. 1a, where the two carbonyl groups of the amide residues are placed on the same side. The trigonal angles of the ligands deviate from the ideal 120°, the smallest angles being in the range 86.8–97.3°, the medium angles 114.0–117.0° and the largest angles 146.0–157.5° (see Table S2‡).‖ The overall conformations of the four ligands in the asymmetric unit vary depending on the environment in the framework. The twisting angles of the benzoate groups *vs.* the central benzene ring range from 25.4 to 131.8° (see Table S3‡). Various coordination geometries of the zinc centers, the ordinary tetrahedral geometry with three carboxylate oxygen atoms and one oxo oxygen atom, the trigonal pyramidal geometry, and the octahedral geometry with one and two additional donor atoms from the solvent molecules, respectively, were observed in the tetranuclear hexatopic $Zn_4O(COO)_6$ clusters. The overall geometries of the two hexatopic $Zn_4O(COO)_6$ clusters in **1** are close to that of an octahedral hexatopic node. The angles measured from the C atom of the carboxylic group in a ligand to the central oxo-anion and to another C atom of a neighboring carboxylic group in the other ligand around the $Zn_4O(COO)_6$ clusters are in the range of a slightly distorted octahedral geometry (see Table S4‡). From a topological point of view, the single (3,6)-connected net can be viewed as an **rtl** net (Fig. 1c).[11] Although assembling trigonal building blocks with octahedral building blocks can lead to a framework of **pyr** topology as the highest possible symmetry network, a framework of an **rtl** topology was obtained as the next-highest possible symmetry network. Ligand L^{3-} is a trinodal SBU, but in the reduced symmetry environment seen here leads to a network with an **rtl** topology rather than a **pyr** topology.

The trinodal units (representing the central benzene ring of L^{3-}) of the two discrete networks in the single-crystal structure are displaced from each other by 9.2 Å. The rings of one network are penetrated by links of the other so that they are interpenetrated. The two intertwined networks (Fig. 2) hold each other solely through van der Waals interactions, even though the amide groups of the ligand in one network could be involved with amide groups in the other network through hydrogen bonding interactions. The two-fold interpenetrated **rtl** network belongs to Class IIa, with the two nets related by a center of inversion.[11b] This is the first case of a two-fold interpenetrated **rtl** network of Class IIa; all other known examples are of Class Ia, with the two nets being related by a translation.[10a] The solvent cavity, calculated by the Platon program, is 71.1% of the total crystal volume,[12] a value seldom observed for interpenetrating networks, which generally incorporate either a very small or no free solvent cavity.[13]

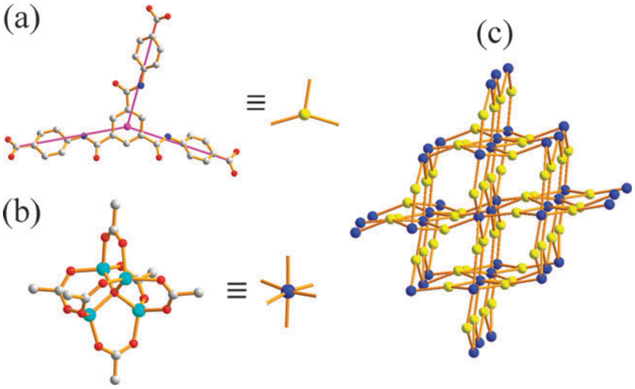


Fig. 1 The crystal structure of **1** is composed of (a) ligand L^{3-} as a trigonal trinode and (b) tetranuclear zinc cluster $Zn_4O(COO)_6$ as an octahedral hexanode, which assemble into (c) a network of **rtl** topology. All hydrogen atoms are omitted in (a) and (b) for clarity. Color codes: zinc, cyan; carbon, gray; nitrogen, blue; oxygen, red.

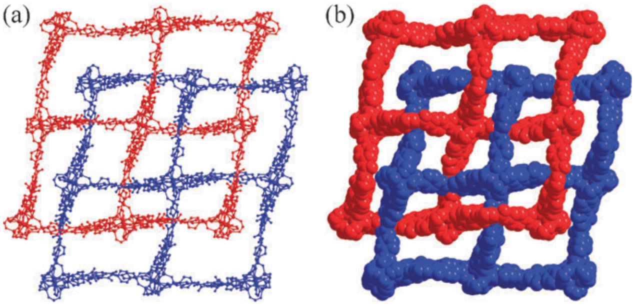


Fig. 2 (a) A two-fold interpenetration in the 3-D porous network of **1** in a ball-and-stick model viewed along the crystallographic *a*-axis, where solvent molecules are omitted for clarity. The two individual nets are indicated by different colors (blue and red). (b) A space-filling view of (a) showing the 3-D solvent cavity.

The use of long linkers in the design of MOFs, on the one hand, can increase the framework size, which may help to increase their porosity. On the other hand, it also increases the chance of interpenetration, which is considered to be a major impediment in the achievement of porous crystalline structures with large solvent cavities. In other words, the smaller the degree of interpenetration in a MOF, the greater the chance of a large available cavity occurring in it. According to Yaghi *et al.*'s work,[14] control of interpenetration can be achieved by modulation of the size of both linker and node. As shown in Fig. 3, the diameter of the ring of one net (blue) that another net (red) has interpenetrated is about 14 Å. By way of contrast, the diameter of the octahedral tetranuclear zinc cluster $[Zn_4O(COO)_6]$ is 7.2 Å, which is too large to allow a third network to fit in the space remaining after the formation of two interpenetrating networks. This results in only two-fold interpenetration and a large solvent cavity.

The powder X-ray diffraction (PXRD) pattern of the bulk crystalline sample is different from the simulated pattern of the single-crystal structure of **1** (Fig. S2).‡ However, the morphologies of the crystals in a batch from a microscope study looked the same as each other and the unit cell parameters of more than 10 different crystals in the same batch were the same as those of the single crystal used for the structure determination carried out in this study, which shows that the loss of a small amount of guest solvent molecules from the solvent cavity led to the structural transformation of **1** to a

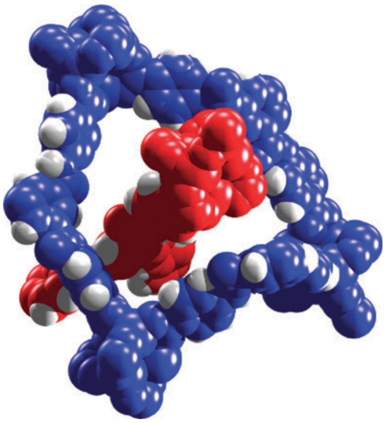


Fig. 3 A space-filling representation of the region that highlights the interwoven nature of the 3-D network. Hydrogen atoms are shown in white. The other atoms of the two different networks are shown in different colors (blue and red, respectively).

structure that has yet to be identified. The PXRD of activated sample **1a**[‡] indicates a complete loss of crystallinity. Not surprisingly, considering the huge solvent cavity volume, the flexibility of the ligands in the framework and the complete loss of crystallinity upon activation, **1a** did not show any significant gas sorption properties for various gas molecules, such as N_2, H_2, CO_2 or CH_4, which suggests that **1** collapses its porosity when the guest solvent molecules in the cavity have been removed.

In summary, when a distorted trigonal ligand with flexible amide groups as a three-connected node was combined with the $Zn_4O(COO)_6$ cluster (an octahedral hexatopic SBU), a (3,6)-connected network with an **rtl** topology was obtained. Ligand L^{3-} in a reduced symmetry conformation might be responsible for the formation of a MOF with an **rtl** topology rather than a **pyr** topology. This MOF has an extremely large solvent cavity that is due to the nanometre-sized trigonal linking ligand and the limited degree of interpenetration. This might offer a new way to explore the synthesis of MOFs with large porosities.

This work was supported by NRF-2009-0052888, WCU program (R31-2008-000-20012-0) and the 2010 Research Fund of UNIST. The authors acknowledge PAL for beam line use (2010-1063-04).

Experimental

Preparation of 4,4′,4′′-[1,3,5-benzenetriyltris(carbonylimino)]-trisbenzoic acid ($H_3L\cdot3H_2O$)

3.98 g (15.0 mmol) of 1,3,5-benzenetricarboxylic acid chloride was added to a solution of 6.18 g (45.1 mmol) of 4-aminobenzoic acid and 3.62 mL (26.0 mmol) of triethylamine in 80 mL of *N*,*N*-dimethylacetamide (DMA). The mixture was stirred for 16 h at room temperature. After 300 mL of water had been added to the DMA solution, the resulting precipitate was collected by filtration, followed by washing with acetone, a large amount of water and methanol. The product was then air-dried. Yield = 8.41 g, 90.2%. Elemental analysis: calc. for $H_3L\cdot3H_2O$ ($C_{30}H_{21}N_3O_9\cdot3H_2O$): C, 57.97; H, 4.38; N, 6.76%. Found: C, 58.21; H, 4.07; N, 6.72%. IR (KBr, cm^{-1}): 3322, 3189, 3070, 2656, 2548, 1697, 1600, 1531, 1407, 1320, 1249, 1173, 1116, 1014, 954, 853. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.78 (s, 3H, –COOH), 10.89 (s, 3H, –CONH), 8.75 (s, 3H, Ar-$\underline{H}$), 7.97 (s, 12H, Ar-$\underline{H}$); ^{13}C-NMR (150 MHz, DMSO-d_6): δ 167.5, 165.3, 143.4, 135.7, 130.8, 130.7, 126.5, 120.1.

Preparation of $[(Zn_4O)_2L_4(DMF)_2(H_2O)_3]\cdot25H_2O$ (1a)

A sample of 61.6 mg (0.206 mmol) of $Zn(NO_3)_2\cdot6H_2O$ was added to 5 mL of a DMF solution containing 28.4 mg (0.0457 mmol) of $H_3L\cdot3H_2O$. The solution was sealed in a Pyrex tube and heated at 95 °C for 1 d. After cooling to room temperature, colorless block crystals of **1** were filtered and washed with DMF. An activated sample, **1a**, was prepared by soaking **1** in fresh DMF for several days, before drying under a dynamic vacuum at 120 °C overnight and then by exposure to air (yield: 33 mg, 83%). Elemental analysis: calc. for $[(Zn_4O)_2(C_{30}H_{18}N_3O_9)_4(C_3H_7NO)_2(H_2O)_3]\cdot25H_2O$ (**1a**): C, 43.69; H, 4.13; N, 5.66. Found: C, 43.52; H, 3.71; N, 5.71%. IR (KBr, cm^{-1}): 3286 (m), 3080 (m), 2996 (m), 1660 (s), 1605 (vs), 1563 (m), 1525 (vs), 1403 (s), 1316 (m), 1253 (s), 1178 (w), 1107 (w), 1014 (w), 956 (w), 861 (w), 782 (w), 732 (w), 698 (w).

Crystal data for 1

M = 3013.10, monoclinic, space group $P2_1/c$, a = 36.130(7), b = 27.033(5), c = 34.291(7) Å, β = 108.81(3)°, V = 31 704(11) Å^3, T = 100(2) K, Z = 4, μ (synchrotron, λ = 0.75000 Å) = 0.632 mm^{-1}, 149 700 reflections were collected, 40 052 were unique [R_{int} = 0.0811]. $R1$ (w$R2$) = 0.0846 (0.2347) for 20 269 reflections [$I > 2\sigma(I)$], $R1$ (w$R2$) = 0.1247 (0.2602) for all reflections.

Notes and references

[‖] The trigonal angle was measured from the C atom of the carboxylic group to the dummy atom, the center of the central phenyl ring of the ligand, to another C atom of a neighboring carboxylic group in the ligand, as shown in Fig. 1a.

1 (*a*) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; (*b*) G. Férey, C. Mellot-Draznieks, C. Serre and F. Millange, *Acc. Chem. Res.*, 2005, **38**, 217; (*c*) D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior and M. J. Rosseinsky, *Acc. Chem. Res.*, 2005, **38**, 273; (*d*) N. W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2005, **38**, 176; (*e*) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705.

2 (*a*) L. J. Murray, M. Dincă and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294; (*b*) J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477; (*c*) J. Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450; (*d*) L. Ma, C. Abney and W. Lin, *Chem. Soc. Rev.*, 2009, **38**, 1248; (*e*) A. U. Czaja, N. Trukhanb and U. Müller, *Chem. Soc. Rev.*, 2009, **38**, 1284.

3 (*a*) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469; (*b*) D. Sun, Y. Ke, T. M. Mattox, S. Parkin and H.-C. Zhou, *Inorg. Chem.*, 2006, **45**, 7566; (*c*) X. Lin, I. Telepeni, A. J. Blake, A. Dailly, C. Brown, J. Simmons, M. Zoppi, G. S. Walker, K. M. Thomas, T. J. Mays, P. Hubberstey, N. R. Champness and M. Schröder, *J. Am. Chem. Soc.*, 2009, **131**, 2159; (*d*) S. Hong, M. Oh, M. Park, J. W. Yoon, J.-S. Chang and M. S. Lah, *Chem. Commun.*, 2009, 5397; (*e*) Y. Yan, I. Telepeni, S. Yang, X. Lin, W. Kockelmann, A. Dailly, A. J. Blake, W. Lewis, G. S. Walker,

D. R. Allan, S. A. Barnett, N. R. Champness and M. Schröder, *J. Am. Chem. Soc.*, 2010, **132**, 4092.
4 S. L. James, *Chem. Soc. Rev.*, 2003, **32**, 276.
5 (*a*) A. F. Wells, *Three-Dimensional Nets and Polyhedra*, Wiley-Interscience, New York, 1977; (*b*) M. O'Keeffe, M. Eddaoudi, H. Li, T. Reineke and O. M. Yaghi, *J. Solid State Chem.*, 2000, **152**, 3; (*c*) M. O'Keeffe, M. A. Peskov, S. J. Ramsden and O. M. Yaghi, *Acc. Chem. Res.*, 2008, **41**, 1782.
6 (*a*) M. Du, Z.-H. Zhang, L.-F. Tang, X.-G. Wang, X.-J. Zhao and S. R. Batten, *Chem.–Eur. J.*, 2007, **13**, 2578; (*b*) L. Zhang, Z.-J. Li, Q.-P. Lin, J. Zhang, P.-X. Yin, Y.-Y. Qin, J.-K. Cheng and Y.-G. Yao, *CrystEngComm*, 2009, **11**, 1934; (*c*) R. Natarajan, G. Savitha, P. Dominiak, K. Wozniak and J. N. Moorthy, *Angew. Chem., Int. Ed.*, 2005, **44**, 2115; (*d*) H. Chun, D. Kim, D. N. Dybtsev and K. Kim, *Angew. Chem., Int. Ed.*, 2004, **43**, 971; (*e*) R.-Q. Zou, R.-Q. Zhong, M. Du, T. Kiyobayashi and Q. Xu, *Chem. Commun.*, 2007, 2467; (*f*) Y.-Q. Lan, S.-L. Li, Y.-G. Li, Z.-M. Su, K.-Z. Shao and X.-L. Wang, *CrystEngComm*, 2008, **10**, 1129.
7 (*a*) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; (*b*) H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276; (*c*) J. L. C. Rowsell, E. C. Spencer, J. Eckert, J. A. K. Howard and O. M. Yaghi, *Science*, 2005, **309**, 1350.
8 (*a*) K. Biradha and M. Fujita, *Angew. Chem., Int. Ed.*, 2002, **41**, 3392; (*b*) G. J. Halder, M. Neville and C. J. Kepert, *CrystEngComm*, 2005, **7**, 266; (*c*) B. F. Abrahams, S. R. Batten, J. Grannas, H. Hamit, B. F. Hoskins and R. Robson, *Angew. Chem., Int. Ed.*, 1999, **38**, 1475; (*d*) T. Kawamichi, T. Haneda, M. Kawano and M. Fujita, *Nature*, 2009, **461**, 633; (*e*) X.-S. Wang, S. Ma, D. Yuan, J. W. Yoon, Y. K. Hwang, J.-S. Chang, X. Wang, M. R. Jørgensen, Y.-S. Chen and H.-C. Zhou, *Inorg. Chem.*, 2009, **48**, 7519; (*f*) S. Ma, D. Sun, M. Ambrogio, J. A. Fillinger, S. Parkin and H.-C. Zhou, *J. Am. Chem. Soc.*, 2007, **129**, 1858.
9 (*a*) H. K. Chae, D. Y. Siberio-Pérez, J. Kim, Y. Ko, M. Eddaoudi, A. J. Matzger, M. O'Keeffe and O. M. Yaghi, *Nature*, 2004, **427**, 523; (*b*) H. K. Chae, J. Kim, O. D. Friedrichs, M. O'Keeffe and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2003, **42**, 3907; (*c*) E. Y. Lee, S. Y. Jang and M. P. Suh, *J. Am. Chem. Soc.*, 2005, **127**, 6374.
10 (*a*) V. A. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio, *CrystEngComm*, 2004, **6**, 378; (*b*) X. Zhao, G. Zhu, Q. Fang, Y. Wang, F. Sun and S. Qiu, *Cryst. Growth Des.*, 2009, **9**, 737; (*c*) L. Xie, S. Liu, B. Gao, C. Zhang, C. Sun, D. Li and Z. Su, *Chem. Commun.*, 2005, 2402; (*d*) C. Qin, X.-L. Wang, E.-B. Wang and Z.-M. Su, *Inorg. Chem.*, 2005, **44**, 7122; (*e*) M.-X. Jiang, C.-H. Zhan, Y.-L. Feng and Y.-Z. Lan, *Cryst. Growth Des.*, 2010, **10**, 92; (*f*) F. Luo, Y.-X. Che and J.-M. Zheng, *Eur. J. Inorg. Chem.*, 2007, 3906.
11 (*a*) V. A. Blatov, M. O'Keeffe and D. M. Proserpio, *CrystEngComm*, 2010, **12**, 44; (*b*) V. A. Blatov, A. P. Shevchenko and V. N. Serezhkin, *J. Appl. Crystallogr.*, 2000, **33**, 1193.
12 P. van der Sluis and A. L. Spek, Platon program, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, 194.
13 (*a*) M. P. Suh, H. J. Choi, S. M. So and B. M. Kim, *Inorg. Chem.*, 2003, **42**, 676; (*b*) B. Chen, S. Ma, F. Zapata, F. R. Fronczek, E. B. Lobkovsky and H.-C. Zhou, *Inorg. Chem.*, 2007, **46**, 1233.
14 T. M. Reineke, M. Eddaoudi, D. Moler, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2000, **122**, 4843.