A three-dimensional porous metal–organic framework with the rutile topology constructed from triangular and distorted octahedral building blocks†

Linhua Xie, Shuxia Liu,* Bo Gao, Chundan Zhang, Chunyan Sun, Dehui Li and Zhongmin Su

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The solvothermal reaction of zinc acetate dihydrate with 1,3,5-benzenetricarboxylic acid yields a three-dimensional porous metal–organic framework constructed from triangular and distorted octahedral building blocks, the framework of which can be described as a decorated rutile net.

The design and synthesis of porous metal–organic frameworks (MOFs) is now of great interest due to the significance of discovering new materials.[1] A versatile strategy for constructing porous frameworks is to assemble molecular building blocks with special shapes into extended structures by decoration and expansion of the basic topologies.[2] Indeed, there are many examples of porous MOFs with predetermined topologies that are assembled from required molecular building blocks.[3–6] However, there are still challenges including the ability to design new molecular building blocks that can act as a carrier of the structural and functional information to be expressed in a specific target material.[1a]

Among the most important and frequently encountered mixed connectivity types, the rutile form of TiO_2 is a typical (3,6)-connected net structure. To construct such a decorated net, it seems that assembling triangular building blocks with octahedral building blocks will realize it. However, it has been found that triangular and regular octahedral building blocks will form another more symmetrical net related to the structure of the pyrite form of FeS_2.[5,6] It is theoretically predicted that low-symmetry secondary building units[1b] (SBUs) are required because there are two kinds of Ti–O bond in the rutile structure.[1a] Several compounds with expanded[2b] (increasing the spacing between vertices in a network) rutile nets have been reported, most of which are interpenetrating structures constructed with cyano ligands.[7] However, decorated[2b] (replacing a vertex in a net by a group of vertices) rutile nets are rare in MOFs. To our knowledge, only three interpenetrated decorated rutile nets have been reported hitherto.[8,9] Recently a H-bonded rutile net has been described by Enbo Wang and co-workers.[10] Here we report the synthesis and structure of a three-dimensional (3D) porous metal–organic framework $Zn(BTC)\cdot NH_2(CH_3)_2\cdot DMF$ (**1**) (BTC = 1,3,5-benzenetricarboxylate, DMF = *N,N′*-dimethylformamide) with the decorated rutile topology constructed from triangular and distorted octahedral building blocks. The desorption and adsorption properties of **1** are also presented.

The solvothermal reaction of zinc acetate dihydrate with H_3BTC in *N,N′*-dimethylformamide (DMF) gives block colorless crystals, which are formulated as $Zn(BTC)\cdot NH_2(CH_3)_2\cdot DMF$ established by an X-ray study on a single-crystal.‡ The characteristic bands at around 1700 cm^{-1} attributed to the protonated carboxylic groups are absent from the IR spectrum of **1**, indicating the complete deprotonation of the BTC ligand, which is in accord with the fact that dimethylamine was found to be protonated from the difference Fourier map for overall neutrality. The bulk purity of the product was confirmed by elemental analysis and X-ray powder diffraction measurements in which a number of sharp signals closely match those of a simulated diffractogram based on the single-crystal X-ray data.† It is worth noting that solvent, high temperature and the utilization of acetate as a conjugate base for deprotonation of H_3BTC are key to the formation of **1**. Yaghi and co-workers previously prepared a 1D porous framework $Zn_3(BTC)_2\cdot 12H_2O$ by hydrothermal reactions using zinc acetate dihydrate and H_3BTC,[11] and a 3D porous framework $Zn_2(BTC)(NO_3)\cdot(H_2O)(C_2H_5OH)_5$ with $SrSi_2$ topology using triethylamine as a strong base for the deprotonation of H_3BTC in its room temperature reaction with zinc(II) ethanolic solutions.[12] Many other works on Zn–BTC systems have also been reported.[13]

An X-ray study revealed that **1** has a 3D structure constructed from dimeric zinc carboxylate clusters and BTC linkers (Fig. 1). In the dimeric zinc carboxylate clusters, two zinc centers are related to each other by inversion center symmetry, each of which bonds to four carboxylate O atoms from four different but symmetrically equivalent BTC linkers with distorted tetrahedral geometry . A carboxyl of each BTC linker chelates the two zinc atoms of each cluster in di-monodentate fashion and the other two carboxyls bond to zinc centers in monodentate fashion. The connection of alternating zinc carboxylate clusters and BTC linkers results in an infinite 3D (3,6)-connected net. For perspicuous representation, the clusters are represented by distorted octahedral SBUs and BTC linkers are represented by triangular units (Fig. 2a and b). The framework can be described as a decorated rutile net, in which each SBU connects to six BTC linkers and each BTC linker connects to three SBUs (Fig. 2c), corresponding to the Ti atoms coordinating six O atoms and the O atoms coordinating three Ti atoms respectively in the rutile structure (Fig. 2d). Since the environments of the three carboxyls on each BTC are different in **1**, not all vertices (carboxylate C atoms) of each distorted octahedral SBU are symmetrically equivalent. Consequently **1** crystallized in a lower symmetry space group ($P2_1/n$) compared with rutile ($P4_2/mnm$).

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† Electronic supplementary information (ESI) available: TGA curves, XRPD patterns, IR spectra and additional figures related to the framework. See http://www.rsc.org/suppdata/cc/b5/b501477h/
*liusx@nenu.edu.cn

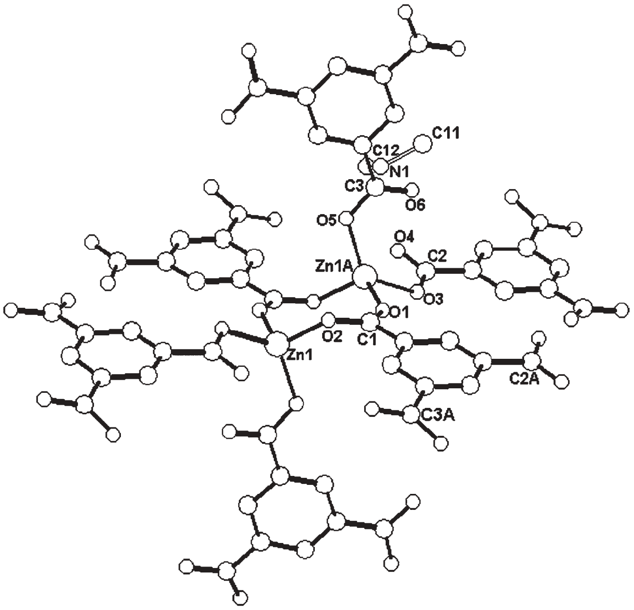

Fig. 1 The building block unit including the asymmetric unit present in **1**. Disordered guest molecules DMF and hydrogen atoms are omitted for clarity. Atoms with additional A label are symmetry related to the atoms labeled without such a subscript.

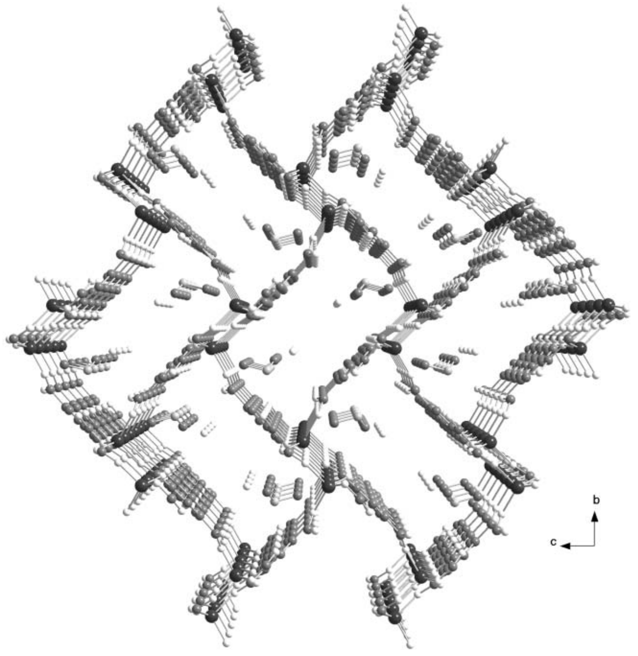

Fig. 3 Perspective view of the framework along the [100] axis. 1D channels are occupied by protonated dimethylamine cations and DMF molecules. For clarity the hydrogen atoms have been omitted and DMF molecules are represented by their O atoms (O_7). Zn—dark grey, O—white, C—medium grey, N—light grey.

Just like many other metal carboxylate frameworks, the decorated rutile framework is also porous. There are rectangular channels along the [100] axis, in which one protonated dimethylamine as counter-cation and one disordered DMF as guest molecule per formula reside (Fig. 3). Hydrogen bonding interactions can be observed between protonated dimethylamine and the framework (N_1–O_4 = 2.705(4) Å), DMF and protonated dimethylamine (O_7–N_1 = 2.747(5) Å). The protonated dimethylamine may be generated during the reaction, as that dimethylamine is often found as a by-product in DMF solvent reactions.[14] Its existence was further confirmed by elemental analysis. The dimension of the channels is estimated to be about 9.0 × 3.1 Å by calculating the distance between the least-square planes through the nearest parallel walls (Fig. S4†).[15] The van der Waals free space of the channels per unit cell (after the counter-cations and DMF molecules have been hypothetically removed) is approximately 861 $Å^3$ corresponding to 52.1% of the volume of the unit cell.[16]

In order to examine the stability of this framework, thermal gravimetric (TG) analyses, desorption and adsorption experiments were carried out. The TG curve shows a weight loss of 18.86% from 110 to 170 °C corresponding to the release of DMF guest

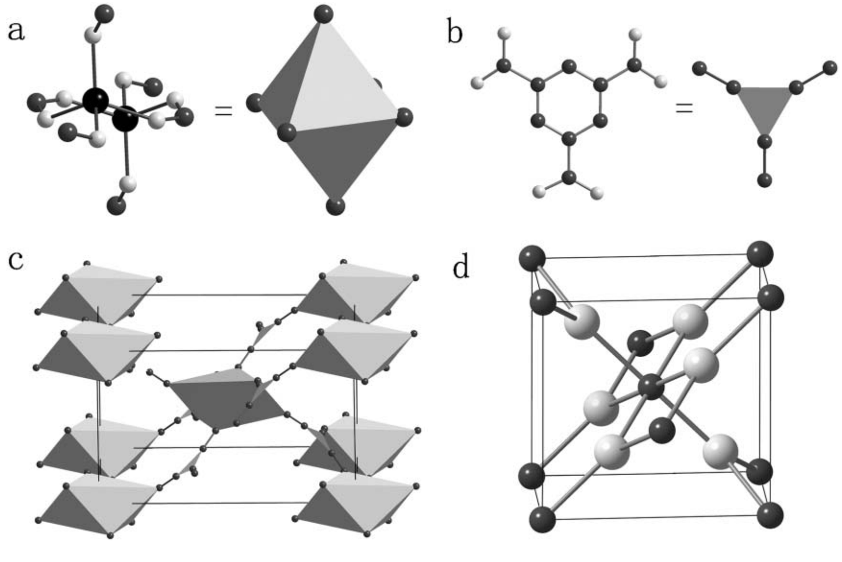

Fig. 2 Simplified views of the (a) distorted octahedral and (b) triangular building blocks in **1**. (c) The topology of the framework of **1** by simplification. Zn—black, O—light grey, C—dark grey. (d) The (3,6)-connected net of rutile (TiO_2). Ti—black, O—light grey.

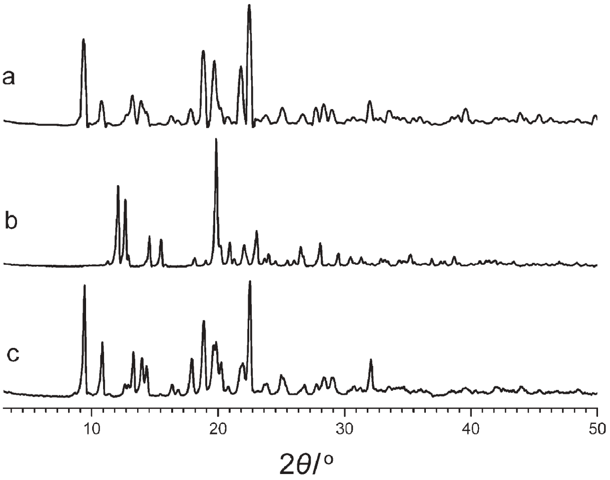

Fig. 4 XRPD patterns of the (a) as-synthesized, (b) evacuated, and (c) DMF reintroduced solids.

molecules (calculated 18.66%). No weight loss was observed between 170 and 270 °C and the framework started to decompose at higher temperatures. These results prove that only the DMF guest molecules can be easily removed. However the van der Waals free space occupied by DMF is still up to 29.8% of the volume of the unit cell. To confirm the porosity, the as-synthesized crystalline solid was placed in a high vacuum oven at 100 °C for 6 h with a 18.69% weight loss to get the evacuated solid. In the X-ray powder diffraction (XRPD) pattern of the evacuated solid, the main sharp diffraction peaks shift remarkably to higher 2θ values compared with those of as-synthesized solid (Fig. 4a and b). This fact may be due to severe deformation of the framework that is still stable and retains high periodicity. The conjecture was further justified by the XRPD pattern of the evacuated solid after soaking in DMF for 24 h, in which the peak positions and their intensities are fully coincident to those observed for the as-synthesized solid (Fig. 4c). The whole cycle can be repeated several times without a significant loss of crystallinity of the material. A detailed study about the deformation of the framework is underway.

In conclusion, we have synthesized a 3D porous metal–organic framework constructed from triangular and distorted octahedral building blocks, the framework of which can be described as an unprecedented non-interpenetrated decorated rutile net. The specifically shaped dimeric zinc carboxylate SBU is expected to be a useful building motif for the design and synthesis of porous MOFs with a specific topology. We are attempting to obtain such a framework with higher porosity by using longer linkers and trivalent metal ions to avoid the need for counter-cations.

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Linhua Xie, Shuxia Liu,* Bo Gao, Chundan Zhang, Chunyan Sun, Dehui Li and Zhongmin Su
Institute of Polyoxometalate Chemistry, Department of Chemistry, Northeast Normal University, Changchun 130024, P. R. China. E-mail: liusx@nenu.edu.cn

Notes and references

‡ A mixture containing $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.26 g, 1 mmol), H_3BTC (0.25 g, 1.2 mmol) dissolved in 10 ml DMF was sealed in a 16 ml Teflon-lined stainless steel container and heated at 140 °C for 2 days. Colorless crystals of **1** were washed by DMF several times and collected by filtration with a yield of 0.32 g (84% based on $Zn(CH_3COO)_2 \cdot 2H_2O$). Anal. calcd. for $ZnC_{14}H_{18}N_2O_7$: C, 42.89; H, 4.59; N, 7.15. Found: C, 43.24; H, 5.13; N, 7.45%. X-Ray data for **1**: $ZnC_{14}H_{18}N_2O_7$, $M = 391.67$, monoclinic, $P2_1/n$ (no. 14), $a = 9.4550(6)$ Å, $b = 16.0074(11)$ Å, $c = 11.0347(7)$ Å, $\beta = 98.4660(10)°$, $V = 1651.90(19)$ Å^3, $T = 188$ K, $Z = 4$, μ(Mo-Kα) = 1.525 mm^{-1}, $d_{calc} = 1.575$ g cm^{-3}, 9962 reflections measured, 3813 unique ($R_{int} = 0.0409$), Siemens SMART CCD diffractometer ($\lambda = 0.71073$ Å). $R_1 = 0.0462$, $wR_2 = 0.1178$ for $I > 2\sigma(I)$, $R_1 = 0.0620$, $wR_2 = 0.1265$ for all data, GOF = 1.058, 227 parameters and 6 restraints. CCDC 258251. See http://www.rsc.org/suppdata/cc/b5/b501477h/ for crystallographic data in CIF or other electronic format.

1 (*a*) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705; (*b*) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keefe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; (*c*) S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; (*d*) C. N. R. Rao, S. Natarajan and R. Vaidhyanathan, *Angew. Chem., Int. Ed.*, 2004, **43**, 1466.
2 (*a*) B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546; (*b*) M. O'Keeffe, M. Eddaoudi, H. Li, T. Reineke and O. M. Yaghi, *J. Solid State Chem.*, 2000, **152**, 3.
3 B. Chen, M. Eddaoudi, T. M. Reineke, J. W. Kampf, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2000, **122**, 11559 (PtS).
4 M. Eddaoudi, J. Kim, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2002, **124**, 376 (NbO).
5 H. K. Chae, J. Kim, O. D. Friedrichs, M. O'Keeffe and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2003, **42**, 3907 (pyrite).
6 H. K. Chae, D. Y. Siberio-Pérez, J. Kim, Y. Go, M. Eddaoudi, A. J. Matzger, M. O'Keeffe and O. M. Yaghi, *Nature*, 2004, **427**, 523 (related to pyrite topology, termed 'qom').
7 (*a*) S. R. Batten, B. F. Hoskins and R. Robson, *J. Chem. Soc., Chem. Commun.*, 1991, 445–447; (*b*) S. R. Batten, B. F. Hoskins, B. Moubaraki, K. S. Murray and R. Robson, *J. Chem. Soc., Dalton Trans.*, 1999, 2977; (*c*) P. Jensen, D. J. Price, S. R. Bateen, B. Moubaraki and K. S. Murray, *Chem. Eur. J.*, 2000, **6**, 3186; (*d*) L. Carlucci, G. Ciani, F. Porta, D. M. Proserpio and L. Santagostini, *Angew. Chem., Int. Ed.*, 2002, **41**, 1907.
8 V. A. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio, *CrystEngComm*, 2004, **6**, 377.
9 (*a*) I. Ino, P. L. Wu, M. Munakata, Y. Maekawa, Y. Suenaga, I. Kuroda-Sowa and Y. Kitamori, *Inorg. Chem.*, 2000, **39**, 2146 (refcode is WEBHEQ cited in ref. 8); (*b*) M. Schwarten, J. Chomic, J. Cernak and D. Babel, *Z. Anorg. Allg. Chem.*, 1996, **622**, 1478 (refcodes are TIYZEG and TIYZIK cited in ref. 8).
10 C. Qin, X. L. Wang, L. Carlucci, M. L. Tong, E. B. Wang, C. W. Hu and L. Xu, *Chem. Commun.*, 2004, 1876.
11 O. M. Yaghi, H. Li and T. L. Groy, *J. Am. Chem. Soc.*, 1996, **118**, 9096.
12 O. M. Yaghi, C. E. Davis, G. Li and H. Li, *J. Am. Chem. Soc.*, 1997, **119**, 2861.
13 (*a*) C. Qin, X. L. Wang, E. B. Wang, C. W. Hu and L. Xu, *Inorg. Chim. Acta*, 2004, **357**, 3683; (*b*) Q. R. Fang, G. S. Zhu, M. H. Xin, D. L. Zhang, X. Shi, G. Wu, G. Tian, L. L. Tang, M. Xue and S. L. Qiu, *Chem. J. Chin. Univ.*, 2004, **25**, 6, 1016.
14 (*a*) S. X. Liu, C. M. Wang, H. J. Zhai and D. H. Li, *J. Mol. Struct.*, 2003, **654**, 215; (*b*) W. Chen, J. Y. Wang, C. Chen, Q. Yue, H. M. Yuan, J. S. Chen and S. N. Wang, *Inorg. Chem.*, 2003, **42**, 944.
15 The channel dimensions were calculated from the distances between walls minus two van der Waals radii for carbon (2 × 1.7 Å).
16 A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 1998.