An unprecedented nanoporous and fluorescent supramolecular framework with an SrAl$_2$ topology controllably synthesized from a flexible ditopic acid†

Su-Na Wang,[a] Yong Yang,[a] Junfeng Bai,*[a] Yi-Zhi Li,[a] Manfred Scheer,[b] Yi Pan*[a] and Xiao-Zeng You[a]

A novel supramolecular framework was obtained from the ligand H$_2$BDOA (benzene-1,3-dioxyacetic acid) that exhibited an SrAl$_2$ topology with 1.7 × 1.7 nm channels formed by strong hydrogen bonds and demonstrated an interesting crystal-to-crystal transformation property.

Recent years have witnessed the rapid development of nanoporous molecular solids, including metal–organic and pure organic frameworks, not only for their potential applications but also for their fascinating architectures and topologies.[1,2] Compared to less exploited hydrogen-bonded nanoporous frameworks,[3] the design of coordination driven assemblies has been intensively and, to some extent, successfully investigated.[4,5] Prominently, the construction of open metal–organic frameworks (MOFs) based on inorganic rod-shaped secondary building units (SBUs) has been explored and summarized in detail.[6] Could we introduce such great concepts into hydrogen-bonded nanoporous MOFs?

Along with our recent work on the construction of coordination and supramolecular open MOFs of flexible ligands,[7] herein, by the controlled deprotonation of a flexible ditopic acid, benzene-1,3-dioxyacetic acid (H$_2$BDOA), we have successfully synthesized a supramolecular open framework, [Ca(HBDOA)$_2$(H$_2$O)$_2$]·4H$_2$O (1), with an SrAl$_2$ topology. In addition, it exhibits an interesting crystal-to-crystal transformation and luminescent properties.

The reaction of H$_2$BDOA with anhydrous CaCl$_2$ in a 2 : 1 ratio under mild conditions lead to complex 1.‡[8] X-Ray crystallographic analysis indicates that, in the complex, the metal center Ca(II) is coordinated by eight oxygen atoms, of which two are monodentate oxygen atoms from different HBDOA⁻ ligands, four are chelating oxygen atoms from two ligands and two are oxygen atoms from two water molecules (Fig. S1†).§ The whole coordination geometry can be viewed as a distorted trigonal dodecahedron, and the Ca–O bond distances range from 2.370(4) to 2.517(3) Å. The H$_2$BDOA ligand is incompletely deprotonated and bound to two metal centers through the deprotonated carboxylate group with a μ$_2$-η^2:η^1-bridging coordination mode. The ligands bridge the metal centers in such a way that one-dimensional Ca–O–C rods are constructed from edge-shared eight-coordinated Ca(II) centers

[a]State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, P. R. China. E-mail: bjunfeng@nju.edu.cn; Fax: + 86 25-8331-4502
[b]Institut für Anorganische Chemie der Universität Regensburg, 93040 Regensburg, Germany
† Electronic supplementary information (ESI) available: Asymmetric unit, other supplementary figures, TGA and XRPD of 1. See DOI: 10.1039/b710389a

parallel to the c-axis (Fig. 1, Fig. S2†). Ca(II) ions are doubly-bridged by two carboxylate oxygen atoms (μ^2-O2), and two neighboring metal centers are separated by a distance of 3.937(2) Å and a Ca1–O2–Ca1^i (symmetry codes: i, 1 − x, 2 − y, 1 − z) angle of 107.6°, respectively. The resulting three-dimensional arrangement is quite intriguing, with the formation of an open framework through the anticipated hydrogen bonding interactions between the coordinated water molecules and the coordinated, as well as the protonated, carboxyl groups of H$_2$BDOA, which connect each rod to four neighboring rods in the a- and b-directions, generating one-dimensional rhombic channels of 17.003(5) × 17.003(5) Å along the c-direction, based on the metal separations, without considering the van der Waals radius (Fig. S3†). Due to the presence of a large number of solvent molecules within the channel, no interpenetration occurred. To the best our knowledge, this may represent one of the largest nanotubes constructed by hydrogen bonding interactions.

To fully appreciate the structure and its topology, it is helpful to connect all the points-of-extension (the carboxylate C atoms) to give a tetrahedral net with the C atoms at the vertices. Further examination shows that the Ca–O–C rods become square ribbons, corresponding to the infinite rod-like SBUs, and the hydrogen bonding interactions between them represent the lines that connect these SBUs together (Fig. 2). Alternatively, the whole net shows that neighboring parallel ladders are linked to each other. This topology is identical to that of the Al net in SrAl$_2$, which was also characterised by Wells[9] as a 4^{2}6^{3}8-b net and referred to by Smith[10] as the ABW tetrahedral net in Li-A(BW) zeolite. Except for the MOFs of discrete SBUs based on clusters, the less explored MOFs concerned with rod-shaped SBUs can also have stable
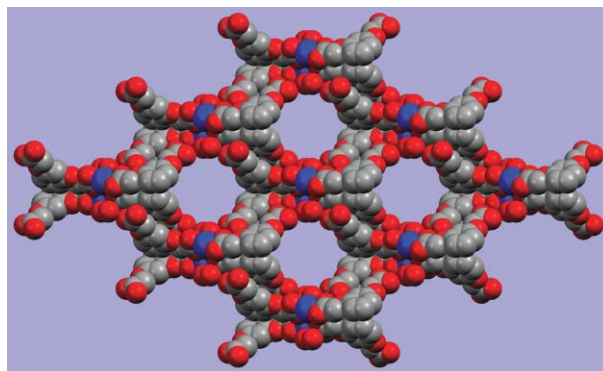

Fig. 1 Space-filling illustration of the hydrogen-bonded network of complex 1 with 1.7 nm-wide rhombic channels.
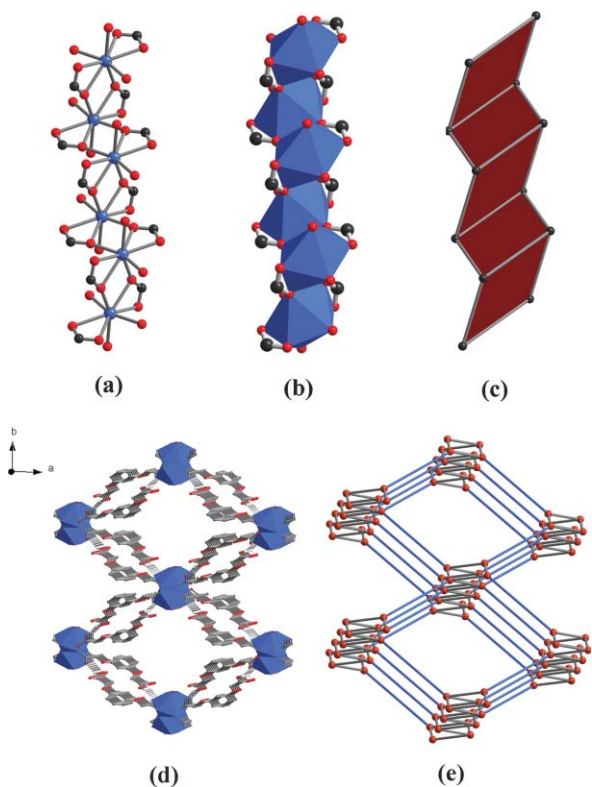
Fig. 2 (a) The rod-shaped SBUs of complex **1** (red, O; blue, Ca; black, C); (b) a polyhedron representation of the SBUs; (c) a zigzag ladder representation of the SBUs by connecting the carboxylate carbon atoms; (d) the hydrogen-bonded framework of complex **1**, shown in a polyhedron representation; (e) the SrAl₂ net of complex **1** formed by connecting the carboxylate carbon atoms, the long blue rods showing the hydrogen bonds between the ligands.
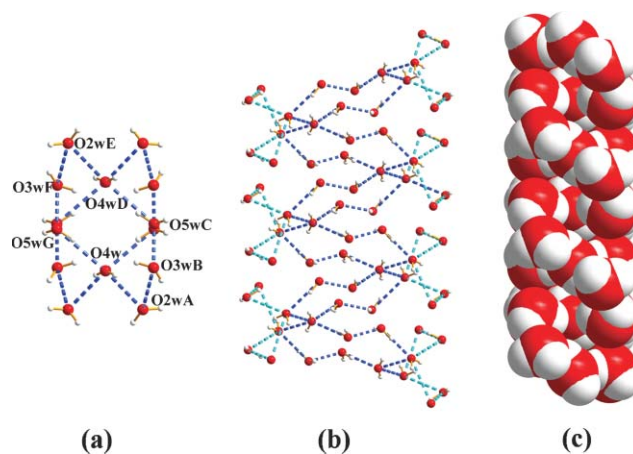

Fig. 3 (a) Hydrogen-bonding interactions between the solvent molecules; (b) corner-sharing water clusters and hydrogen-bonding interactions within, as well as interactions with, the framework; (c) space-filling view of the one-dimensional nanosized water column in the channel along the *b*-axis. Symmetry codes to generate atoms: A, $\frac{1}{2} + x$, $\frac{1}{2} - y$, $-\frac{1}{2} + z$; B, $\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$; C, $\frac{1}{2} + x$, $- y$, $\frac{1}{2} + z$; D, $2 - x$, $1 - y$, $1 - z$; E, $- x$, $\frac{1}{2} + y$, $- z$; F, $- x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$; G, $- x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$; H, $- x$, $\frac{1}{2} - y$, $1 - z$.

architectures and permanent porosity[6] that never interpenetrate due to the intrinsic packing arrangement of such rods in the crystal structure. Statistically, among the large numbers of MOFs, only several decades of compounds have been reported with this topology,[11] and to the best of our knowledge, such a topology based on hydrogen bonding interactions may be unprecedented.

A large number of disordered solvent molecules are trapped in the channels, and these show an interesting arrangement (Fig. 3, Fig. S4†). The guest water molecules O2w, O3w, O4w and O5w are situated at special sites that form a centrosymmetric cyclic cluster with a distorted chair conformation. Each water molecule in the cluster is involved in two kinds of hydrogen bonds with adjacent water molecules. The water octamers are self-assembled along the channels to form a large nanometer-sized water column[12] by sharing O4w molecules. Additionally, the fully occupied sites of O2w atoms are also tied with the coordinated aqua molecules O1w and O5, which can form another kind of cyclic hydrogen bond $R_4^4(10)$[13] with a much distorted chair arrangement, connecting the water columns with the host framework. The total potential solvent column in the unit cell is 914.7 Å³, about 30.2% of the whole unit cell calculated by PLATON.[14]

The stability of the whole framework was further investigated by thermogravimetric analysis (TGA) and powder X-ray diffraction (XPRD) (Fig. S5 and Fig. S6†). The weight loss of 11.21% in the range 40–150 °C corresponds to the loss of the solvent water molecules (4H₂O in per unit, calc. 12.03%), and the whole structure began to decompose at 250 °C. XPRD measurements under different conditions were performed. After heating the sample at 100 °C for 2 h under reduced pressure, the peaks changed to a large extent, indicating a probable crystal-to-crystal transformation after removing some of the solvent molecules. Unfortunately, due to the poor diffraction properties of the heated crystals, no structure could be identified.

The luminescent properties of alkaline earth metal complexes have not been well-studied to date,[15] and only inorganic materials containing calcium and barium atoms have been reported.[16] It is interesting that both the as-synthesized and dehydrated sample of complex **1** showed strong luminescent properties at room temperature (Fig. S7†). Compared with the ligand, which has no luminescence, the greatly enhanced photoluminescence intensities may be attributable to the coordination of the metal centers.[15] Interestingly, the dehydrated sample showed stronger intensities, which may indicate that the crystal structure becomes more condensed after the loss of the solvent molecules,[17] and thus may reduce, to some extent, the loss of energy by radiationless decay.

In conclusion, we have reported an unprecedented nanoporous and fluorescent supramolecular open framework with an SrAl₂ topology, controllably synthesized from a flexible ditopic acid. A rare nanosized water column was trapped within the channels. The complex shows an interesting guest-induced crystal-to-crystal transformation, and both as-synthesized and dehydrated samples demonstrate different photoluminescent properties. Further investigations are ongoing.

Notes and references

1 (a) O. M. Yaghi, H. Li, C. Davis, D. Richardson and T. L. Groy, *Acc. Chem. Res.*, 1998, **31**, 474–484; (b) C. Janiak, *Dalton Trans.*, 2003, **17**, 2781–2804.
2 (a) G. S. Papaefstathiou and L. R. MacGillivray, *Coord. Chem. Rev.*, 2003, **246**, 169–184; (b) D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior and M. J. Rosseinsky, *Acc. Chem. Res.*, 2005, **38**, 273–282; (c) S. Kitagawa, S. Noro and T. Nakamura, *Chem. Commun.*, 2006, **7**, 701–707.
3 (a) I. Goldberg, *Chem. Commun.*, 2005, 1243–1254 and references therein; (b) S. Varughese and V. R. Pedireddi, *Chem. Commun.*, 2005, 1824–1826; (c) D. S. Li, Y. Y. Wang, X. J. Luan, P. Liu, C. H. Zhou, H. R. Ma and Q. H. Shi, *Eur. J. Inorg. Chem.*, 2005, 2678–2684; (d) M. Dan, A. K. Cheetham and C. N. R. Rao, *Inorg. Chem.*, 2006, **45**, 8227–8238.
4 (a) G. Ferey, M. Latroche, C. Serre, F. Millange, T. Loiseau and A. Percheron-Guegan, *Chem. Commun.*, 2003, 2976–2977; (b) S. Kitagawa, R. Kitaura and S. I. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334–2375; (c) C. N. R. Rao, S. Natarajan and R. Vaidhyanathan, *Angew. Chem., Int. Ed.*, 2004, **43**, 1466–1496.
5 (a) D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior and M. J. Rosseinsky, *Acc. Chem. Res.*, 2005, **38**, 273–282; (b) J. L. C. Rowsell and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2005, **44**, 4670–4679; (c) S. S. Kaye and J. R. Long, *J. Am. Chem. Soc.*, 2005, **127**, 6506–6507; (d) C. D. Wu and W. B. Lin, *Angew. Chem., Int. Ed.*, 2005, **44**, 1958–1961; (e) J. L. C. Rowsell and O. M. Yaghi, *J. Am. Chem. Soc.*, 2006, **128**, 1304–1315; (f) M. Dinca, A. F. Yu and J. R. Long, *J. Am. Chem. Soc.*, 2006, **128**, 8904–8913.
6 (a) C. Serre, F. Millange, C. Thouvenot, M. Noguès, G. Marsolier, D. Louër and G. Férey, *J. Am. Chem. Soc.*, 2002, **124**, 13519–13526; (b) K. Barthelet, J. Marrot, G. Férey and D. Riou, *Chem. Commun.*, 2002, 520–521; (c) J. H. He, J. H. Yu, Y. T. Zhang, Q. H. Pan and R. R. Xu, *Inorg. Chem.*, 2005, **44**, 9279–9282; (d) N. L. Rosi, J. Kim, M. Eddaoudi, B. L. Chen, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 1504–1518; (e) Y. G. Huang, B. L. Wu, D. Q. Yuan, Y. Q. Xu, F. L. Jiang and M. C. Hong, *Inorg. Chem.*, 2007, **46**, 1171–1176.
7 (a) G. Q. Jiang, Y. Z. Li, W. J. Hua, Y. Song, J. F. Bai, S. H. Li, M. Scheer and X. Z. You, *CrystEngComm*, 2006, **8**, 384–387; (b) G. Q. Jiang, J. F. Bai, H. Xing, Y. Z. Li and X. Z. You, *Cryst. Growth Des.*, 2006, **6**, 1264–1266; (c) S. N. Wang, H. Xing, Y. Z. Li, J. Bai, Y. Pan, M. Scheer and X. Z. You, *Eur. J. Inorg. Chem.*, 2006, 3041–3054; (d) S. N. Wang, J. F. Bai, Y. Z. Li, Y. Pan, M. Scheer and X. Z. You, *CrystEngComm*, 2007, 228–235; (e) S. N. Wang, J. F. Bai, H. Xing, Y. Z. Li, Y. Song, Y. Pan, M. Scheer and X. Z. You, *Cryst. Growth Des.*, 2007, **7**, 747–754; (f) S. N. Wang, H. Xing, J. F. Bai, Y. Z. Li, Y. Pan, M. Scheer and X. Z. You, *Chem. Commun.*, 2007, 2293–2295.
8 One Ca–BDOA complex was reported previously: S. Gao, L. H. Huo, J. W. Liu and S. W. Ng, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2005, **61**, m407–m409.
9 A. F. Wells, *Structural Inorganic Chemistry*, Clarendon–Oxford University Press, New York, 4th edn, 1975.
10 J. V. Smith, *Chem. Rev.*, 1988, **88**, 149–182.
11 (a) P. Y. Feng, X. H. Bu, S. H. Tolbert and G. D. Stucky, *J. Am. Chem. Soc.*, 1997, **119**, 2497–2504; (b) N. L. Rosi, M. Eddaoudi, J. Kim, M. O'Keeffe and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2002, **41**, 284–287; (c) Z. R. Qu, Z. Zhao, X. S. Wang, Y. H. Li, Y. M. Song, Y. J. Liu, Q. Ye, R. G. Xiong, B. F. Abrahams, Z. L. Xue and X. Z. You, *Inorg. Chem.*, 2003, **42**, 7710–7712; (d) N. W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2005, **38**, 176–182; (e) Q. R. Fang, G. S. Zhu, M. Xue, J. Y. Sun and S. L. Qiu, *Dalton Trans.*, 2006, 2399–2402; (f) X. M. Zhang, J. J. Hou, W. X. Zhang and X. M. Chen, *Inorg. Chem.*, 2006, **45**, 8120–8125.
12 J. W. Ko, K. S. Min and M. P. Suh, *Inorg. Chem.*, 2002, **41**, 2151–2157.
13 C. E. Margaret, *Acc. Chem. Res.*, 1990, **23**, 120–126.
14 A. L. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, C34.
15 (a) L. Prodi, F. Bolletta, N. Zaccheroni, C. I. F. Watt and N. Mooney, *Chem.–Eur. J.*, 1998, **4**, 1090–1094; (b) H. F. Zhu, Z. H. Zhang, W. Y. Sun, T.-a. Okamura and N. Ueyama, *Cryst. Growth Des.*, 2005, **5**, 177–182.
16 (a) F. S. Kao and T. M. Chen, *J. Solid State Chem.*, 2000, **155**, 441–446; (b) M.-S. Zhang, J. Yu, J. Chu, Q. Chen and W. Chen, *J. Mater. Process. Technol.*, 2003, **137**, 78–81.
17 (a) H. J. Choi, T. S. Lee and M. P. Suh, *Angew. Chem., Int. Ed.*, 1999, **38**, 1405–1408; (b) C. Serre, F. Millange, C. Thouvenot, M. Noguès, G. Marsolier, D. Louër and G. Férey, *J. Am. Chem. Soc.*, 2002, **124**, 13519–13526; (c) K. Biradha and M. Fujita, *Angew. Chem., Int. Ed.*, 2002, **41**, 3392–3395; (d) O. Saied, T. Maris and J. D. Wuest, *J. Am. Chem. Soc.*, 2003, **125**, 14956–14957; (e) R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, T. C. Kobayashi, S. Horike and M. Takata, *J. Am. Chem. Soc.*, 2004, **126**, 14063–14070; (f) C. L. Chen, A. M. Goforth, M. D. Smith, C. Y. Su and H. C. zur Loye, *Inorg. Chem.*, 2005, **44**, 8762–8769.