

# Solvent as structure directing agent for the synthesis of novel coordination frameworks using a tripodal flexible ligand†

Sujit K. Ghosh<sup>a</sup> and Susumu Kitagawa<sup>\*abc</sup>

Received 23rd July 2008, Accepted 24th September 2008

First published as an Advance Article on the web 15th October 2008

DOI: 10.1039/b812645c

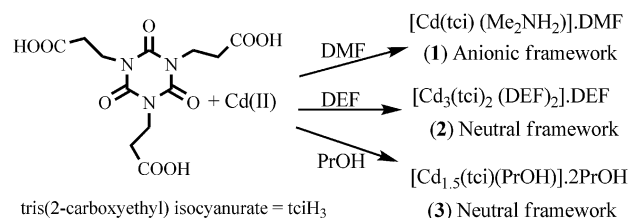
Three novel three-dimensional (3D) coordination polymers have been synthesized by the self-assembly of a flexible tricarboxylate ligand and Cd(II) metal ion in dimethylformamide (DMF), diethylformamide (DEF) and isopropanol (PrOH), where changes of solvent with different size and shape lead to the formation of solvent templated neutral and anionic frameworks with different pore sizes and shapes as shown by X-ray crystallography.

The design and synthesis of new porous coordination polymers (PCPs) have attracted considerable attention due to their potential applications in molecular sieves, gas storage and heterogeneous catalysis as functional porous solid materials.<sup>1–5</sup> For successful performance of porous functions, structural variations with different pore size and shape are essential. It is well-known that during the self assembly process, structure directing agents are crucial for the synthesis of 3D porous structures, which was mostly used for the zeolite synthesis.<sup>6</sup> For the synthesis of porous coordination frameworks this method is also equally useful, where slight changes of the size of guest molecules leads to the formation of completely different structures. Solvent molecules as guests sometime behave like structure directing agents during the self assembly process and generate new structures in different solvents.

In addition to the size of the guest molecules, the nature of ligands may have a profound effect on the framework synthesis. To make porous frameworks by the self-assembly process flexible ligands are much more sensitive to other factors than the rigid ligands, which arises from their easily possible conformational changes, such as, if the ligand is not flexible then it may not be very effective for producing different structures by changing the guest, but for the flexible ligands it is most likely that changes of the guest will generate frameworks with a different pore size, shape and even connectivity. We report herein, the syntheses and structures of three coordination frameworks [Cd(*tc*)(Me<sub>2</sub>NH<sub>2</sub>)]·DMF (1), [Cd<sub>3</sub>(*tc*)<sub>2</sub>(DEF)<sub>2</sub>]·DEF (2), and [Cd<sub>1.5</sub>(*tc*)(PrOH)]·2PrOH (3) using a flexible tricarboxylate ligand tris(2-carboxyethyl) isocyanurate and Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O in DMF/DEF/PrOH as solvents (Scheme 1). Only changing the solvents leads to formation of three different types of structures. The

framework of compound 1 is anionic, which is neutralized by a dimethyl ammonium cation generated from the DMF, whereas those of compounds 2 and 3 are neutral.

Compound 1 was synthesized from *tc*H<sub>3</sub> and Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O in DMF solvent by a solvothermal technique.† X-Ray structural analysis revealed† that 1 crystallizes in monoclinic space group *P*2<sub>1</sub>/*c*.§ The asymmetric unit of 1 consists of one *tc*<sup>3-</sup> unit, one Cd(II), one dimethyl ammonium cation, and one free DMF molecule. All three carboxylate groups of the tripodal ligand are deprotonated and to make the framework neutral one DMF molecule has been cleaved to a dimethyl ammonium cation. Each metal ion exhibits seven-coordination, bonding from three bidentate carboxylate units of three different ligands and seventh coordination is occupied by the bridging carboxylate O of another metal center (Fig 1). All three carboxylate groups of the *tc*<sup>3-</sup> unit are making bidentate chelating bonds with Cd(II), where one of them is forming a bridge with another Cd(II) to extend the framework. This bridging bond is extending the metal centres to make a metal-carboxylate chain along the *c*-axis. Three



Scheme 1

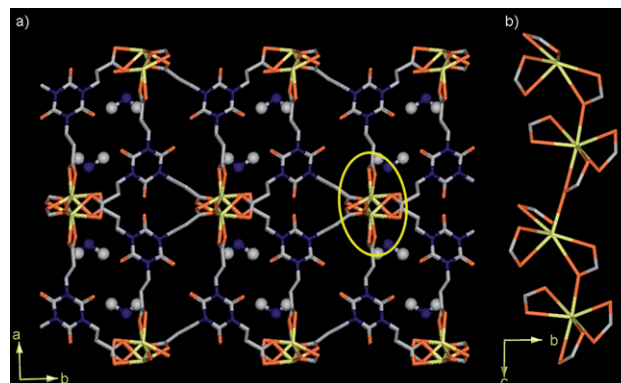


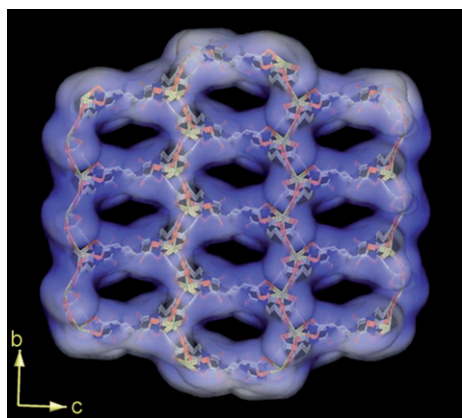
Fig. 1 (a) Perspective view of the 3D framework of 1 along the *c*-axis. (b) Coordination environment (yellow circle of Fig. 1a) of the carboxylate chain along the *a*-axis. (Colour code; carbon: gray, nitrogen: blue, oxygen: orange, cadmium: yellow). The dimethyl ammonium cations are shown in ball and stick mode, the others are shown in stick mode.

<sup>a</sup>Department of Synthetic Chemistry and Biological Chemistry, Kyoto University, Katsura, Nishikyo-ku, Kyoto, 615-8510, Japan. E-mail: kitagawa@sbchem.kyoto-u.ac.jp

<sup>b</sup>Kitagawa Integrated Pore Project, ERATO, JST, Kyoto Research Park, Bldg#3, Shimogyo-ku, Kyoto, 600-8815, Japan

<sup>c</sup>Institute for Integrated Cell-Material Sciences (iCeMS), Kyoto University, 69 Konoe-cho, Yoshida, Sakyo-ku, Kyoto, 606-8501, Japan

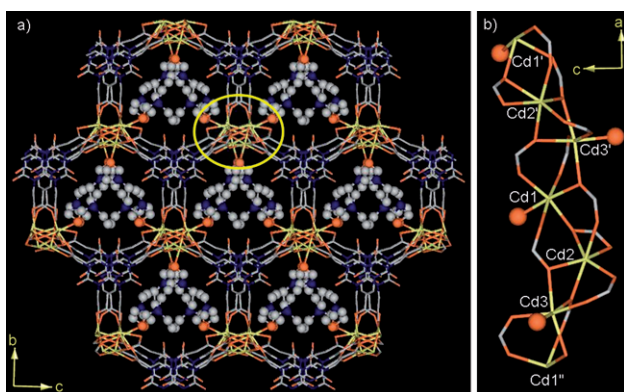
† CCDC reference numbers 694561–694562 and 695570. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b812645c



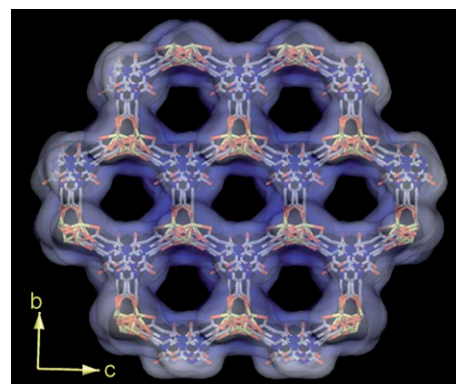
**Fig. 2** Perspective view of the 3D framework of showing channels **1** along the *a*-axis. The DMF guest and the dimethyl ammonium cations are deleted for clarity.

arms of the ligand are bridged with three such metal-carboxylate chains and this continuous network forms the assembled 3D structure. The resultant three-dimensional framework contains one-dimensional channels along the *a*-axis. The cavities of the framework are occupied by DMF and dimethyl ammonium cations, with the channels dimensions  $\sim 7 \times 3 \text{ \AA}^2$  (the channel size is measured by considering the van der Waals radii for constituting atoms). After omitting the DMF and dimethyl ammonium cations, PLATON<sup>7</sup> analysis revealed that the 3D porous structure was composed of large voids of  $1039.4 \text{ \AA}^3$  that represent 43.2% per unit cell volume (Fig 2).

Compound **2** was synthesized in a similar procedure as compound **1**, but here DEF is used as solvent instead of DMF.<sup>‡</sup> Single crystal X-ray crystallographic analysis revealed<sup>†</sup> that the compound crystallized in orthorhombic space group *Pna*2<sub>1</sub>.<sup>§</sup> The asymmetric unit contains three crystallographically independent Cd<sup>2+</sup> ions, each in a slightly distorted octahedral geometry. Two fully deprotonated tricarboxylate ligands in the asymmetric unit make the framework neutral. Other than the metal ions and ligands, two DEF molecules are coordinated to two different metal ions and a third DEF remains uncoordinated. The linear trinuclear metal ions are bridged by the



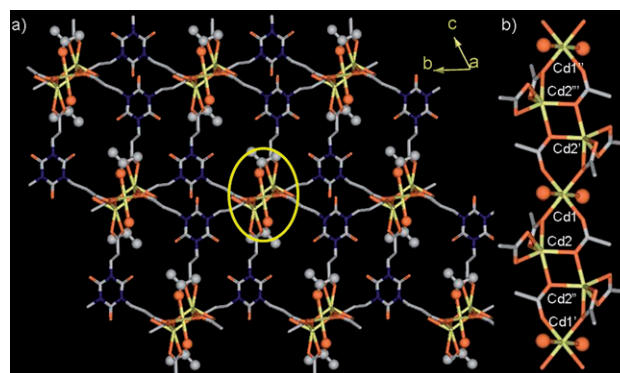
**Fig. 3** (a) Perspective view of the 3D framework of **2** along the *a*-axis. (b) Coordination environment (yellow circle of Fig. 3a) of the carboxylate chain along the *b*-axis. (Colour codes as in Fig 1). Coordinated DEF molecules inside the channels are shown in ball and stick mode, the others are shown in stick mode.



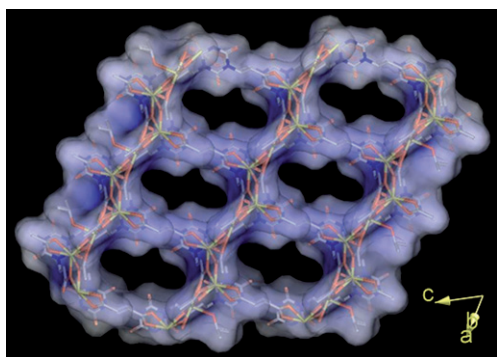
**Fig. 4** Perspective view of the 3D framework of **2** showing the channels along the *a*-axis. DMF molecules are deleted for clarity.

carboxylate groups and further connected by both sides to other similar trinuclear units by carboxylate bridges to extend the metal-carboxylate chain along the *a*-axis. All three metal centres (Cd1–Cd3) are hexacoordinated with a O<sub>6</sub> donor set. Cd1 is coordinated from five carboxylate oxygens from the five different *tc*i units (three monodentate carboxylate O atoms, two  $\mu_2$ -O) and one O atom from DEF. Cd2 is coordinated by one bidentate, two  $\mu_2$ -O, and two monodentate O atoms from five different *tc*i units. Cd3 is also coordinated from five different *tc*i units by three  $\mu_2$ -O, two monodentate carboxylate O atoms and sixth coordination is occupied by the oxygen atom of DEF (Fig 3). The three carboxylate groups of the tripodal ligand are connected to the three different metal-carboxylate chains to make a porous 3D structure. The resultant three-dimensional framework makes one-dimensional channels along the *a*-axis with a channel diameter of  $\sim 6.5 \text{ \AA}$  (the channel size is measured by considering van der Waals radii for constituting atoms). The cavities of the framework are occupied by the coordinated and free DEF molecules. After omitting the DEF molecules from the channels, PLATON<sup>7</sup> analysis revealed a large void volume of  $2336.2 \text{ \AA}^3$  that represents 46.1% per unit cell volume (Fig 4).

Compound **3** was synthesized in isopropanol solvent following the above procedures.<sup>‡</sup> The X-ray structural analysis of **3** reveals<sup>†</sup> that the compound crystallized in triclinic space group *P*-1 Cd1 lies on.



**Fig. 5** (a) Perspective view of the 3D framework of **3** along the *a*-axis. (b) Coordination environment (yellow circle of Fig. 5a) of the carboxylate chain. (Colour codes as in Fig 1). Coordinated PrOH molecules inside the channels are shown in ball and stick mode, the others are shown in stick mode.

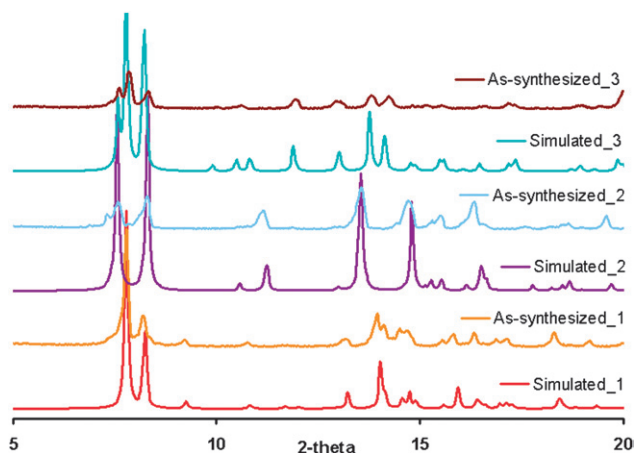


**Fig. 6** Perspective view of the 3D framework of **3** showing the channels. PrOH solvent molecules are deleted for clarity.

The asymmetric unit contains two crystallographically different Cd<sup>2+</sup> ions, one in a special position (Cd1) with a half occupancy and lying on an inversion centre, whereas the other one with a full occupancy in normal position (Cd2). The fully deprotonated tricarboxylate ligand *tc* makes the framework neutral. Two kinds of three isopropanol solvent molecules are present, one of them is coordinated to the Cd1 and other two are free. Both metal centres (Cd1 and Cd2) are hexacoordinated with the O<sub>6</sub> donor set. Cd1 is coordinated from two monodentate, two μ<sub>2</sub>-O from four different ligands and two O atoms from two solvent molecules. Cd2 is coordinated from two bidentate carboxylate groups and two μ<sub>2</sub>-O atoms (which is forming a bridge between other Cd2 centres) from three different ligands. Dinuclear Cd2 units are bridging on both sides to the Cd1 by carboxylate oxygen atoms making carboxylate chains along the *a* axis. All carboxylate groups attached to one metal-carboxylate chain come from different ligands and two other carboxylate groups of these tripodal ligands are coordinated to the other two metal-carboxylate chains, making a 3D framework (Fig 5). The resultant 3D framework makes 1D channels with channel dimensions ~9 × 3 Å<sup>2</sup> (the channel size is measured by considering van der Waals radii for constituting atoms). After omitting the solvent molecules, PLATON<sup>7</sup> analysis revealed that the 3D framework structure was composed of large voids of 698.6 Å<sup>3</sup> which represent 49.9% per unit cell volume (Fig 6).

It is interesting to note that just by using different solvents under the same reaction conditions three different compounds have been synthesized with the same ligand and metal ion. As we discussed above, the structures of all three compounds are different due to the template effect of the solvents. Most interestingly, compound **1** has an anionic framework but compounds **2** and **3** have neutral frameworks, although all three frameworks are constructed by metal-carboxylate chains connected by the tripodal arms of the ligand. Due mainly to the flexible nature of the ligand, it is possible to change the reaction products largely by a slight variation of the reaction components. Ligand flexibility has also been used to synthesise different frameworks of lanthanide metal ions, where by using structure directing agent we succeeded to synthesise a 2D framework but without such effect under the same reaction conditions it forms 3D frameworks.<sup>4</sup> As in the current compounds, in the lanthanide compounds also the coordination behaviour of the *tc* ligand is very similar.

The powder X-ray diffraction (PXRD) patterns of all three compounds **1**, **2** and **3** have been matched with the simulated patterns (Fig 7). Thermogravimetric and PXRD analysis revealed that



**Fig. 7** PXRD analysis of the as-synthesised compounds **1**, **2** and **3** with their simulated patterns.

desolvated materials can not maintain the frameworks after removal of the guest molecules.

In conclusion, we have presented the synthesis and structural characterization of three novel coordination frameworks of Cd(II), by simply changing the solvent in the reaction system. The resulting compounds give anionic/neutral frameworks with a different pore size and shape templated by the solvent guest molecules, which show that solvents may play a crucial role in the synthesis of various kinds of frameworks.

## Notes and references

‡ Synthesis of **1**: A single crystal of **1** was prepared by reacting 0.5 mmol of *tc*H<sub>3</sub> (172 mg) with 0.75 mmol of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (231 mg) in 8 mL of dimethylformamide by a solvothermal technique, in a Teflon-lined autoclave. The autoclave was heated under an autogenous pressure to 120 °C for 2 d and then cooled to rt for 24 h period. Upon cooling to rt, the desired product appeared as colorless crystals in ~60% yield. Synthesis of **2** and **3**: Compounds **2** and **3** were synthesized using the same method as for compound **1** but here DEF/isopropanol has been used as solvent instead of DMF. Yield, respectively, ~55% and ~60%.

§ Data were collected on a Rigaku Mercury CCD diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å). All structures were solved by direct methods using SHELXTL<sup>8</sup> and refined on *F*<sup>2</sup> by a full-matrix least-square technique using the SHELXL-97<sup>9</sup> program package. Crystal data for **1**: Formula C<sub>17</sub>H<sub>27</sub>N<sub>5</sub>O<sub>10</sub>Cd, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 12.375 (3) Å, *b* = 23.376 (5) Å, *c* = 8.5893 (17) Å,  $\beta$  = 104.46 (3)°, *V* = 2406.0(9) Å<sup>3</sup>, *Z* = 4, *T* = 293 (2) K, *R* = 0.0999, *wR*<sub>2</sub> = 0.2861, GOF = 1.077. Crystal data for **2**: Formula C<sub>39</sub>H<sub>57</sub>N<sub>9</sub>O<sub>21</sub>Cd<sub>3</sub>, orthorhombic, space group *P*na2<sub>1</sub>, *a* = 17.640 (2) Å, *b* = 13.380(3) Å, *c* = 21.460(4) Å, *V* = 5065.1 (16) Å<sup>3</sup>, *Z* = 4, *T* = 293(2) K, *R* = 0.0606, *wR*<sub>2</sub> = 0.1703, GOF = 1.062. Crystal data for **3**: Formula C<sub>21</sub>H<sub>36</sub>N<sub>3</sub>O<sub>12</sub>Cd<sub>1.5</sub>, triclinic, space group *P*-1, *a* = 9.550 (2) Å, *b* = 13.300(5) Å, *c* = 13.377(4) Å,  $\alpha$  = 61.820 (5)°,  $\beta$  = 69.880 (7)°,  $\gamma$  = 76.100 (5)°, *V* = 1400.1 (7) Å<sup>3</sup>, *Z* = 2, *T* = 293(2) K, *R* = 0.0814, *wR*<sub>2</sub> = 0.2548, GOF = 1.163. For all three compounds free solvent molecules could not be determined properly, owing to disorder, and so those are not included in the final refinements. The contributions of the DMF molecule, non-coordinated DEF molecule and two non-coordinated isopropanol molecules, respectively, for compound **1**, **2** and **3** were removed using the PLATON SQUEEZE process.

1 R. J. Robson, *J. Chem. Soc., Dalton Trans.*, 2000, 3735; G. Férey, C. Mellot-Draznieks, C. Serre and F. Millange, *Acc. Chem. Res.*, 2005, **38**, 217; S. Kitagawa, R. Kitaura and I. S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; O. M. Yaghi, M. O'Keeffe,

- N. W. Ockwig, H. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705; G. S. Papaefstathiou and L. R. MacGillivray, *Coord. Chem. Rev.*, 2003, **246**, 169; D. Bradshaw, E. J. Claridge, E. J. Cussen, T. J. Prior and M. J. Rosseinsky, *Acc. Chem. Res.*, 2005, **38**, 273; C. N. R. Rao, S. Natarajan and R. Vaidhyanaathan, *Angew. Chem., Int. Ed.*, 2004, **43**, 1466; O. R. Evans and W. Lin, *Acc. Chem. Res.*, 2002, **35**, 511; B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.
- 2 M. Dincă, A. F. Yu and J. R. Long, *J. Am. Chem. Soc.*, 2006, **128**, 8904; X. Lin, A. J. Blake, C. Wilson, X. Z. Sun, N. R. Champness, M. W. George, P. Hubberstey, R. Mokaya and M. Schröder, *J. Am. Chem. Soc.*, 2006, **128**, 10745; F. Nouar, J. F. Eubank, T. Bousquet, L. Wojtas, M. J. Zaworotko and M. Eddaoudi, *J. Am. Chem. Soc.*, 2008, **130**, 1833; S.-Q. Ma, D.-F. Sun, M. Ambrogio, J. A. Fillinger, S. Parkin and H.-C. Zhou, *J. Am. Chem. Soc.*, 2007, **129**, 1858; S. R. Halper, L. Do, J. R. Stork and S. M. Cohen, *J. Am. Chem. Soc.*, 2006, **128**, 15255; J. -P. Zhang, Y. -Y. Lin, W. -X. Zhang and X. -M. Chen, *J. Am. Chem. Soc.*, 2005, **127**, 14162.
- 3 B. L. Chen, C. D. Liang, J. Yang, D. S. Contreras, Y. L. Clancy, E. B. Lobkovsky, O. M. Yaghi and S. Dai, *Angew. Chem., Int. Ed.*, 2006, **45**, 1390; L. Pan, B. Parker, X.-Y. Huang, D. L. Olson, J. Y. Lee and J. Li, *J. Am. Chem. Soc.*, 2006, **128**, 4180.
- 4 S. K. Ghosh, J. -P. Zhang and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2007, **46**, 7965; S. K. Ghosh, S. Bureekaew and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2008, **47**, 3403.
- 5 S. Horike, D. Tanaka, K. Nakagawa and S. Kitagawa, *Chem. Commun.*, 2007, 3395; T. K. Maji, G. Mostafa, R. Matsuda and S. Kitagawa, *J. Am. Chem. Soc.*, 2005, **127**, 17152.
- 6 C. Y. Cundy and P. A. Cox, *Microporous Mesoporous Mater.*, 2005, **82**, 1.
- 7 A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, C34.
- 8 G. M. Sheldrick, *SHELX-97, Program for crystal structure solution*, University of Göttingen, Germany, 1997.
- 9 G. M. Sheldrick, *SHELX-97, Program for crystal structure refinement*, University of Göttingen, Germany, 1997.