Assembly of CdI_2-type coordination networks from triangular ligand and octahedral metal center: topological analysis and potential framework porosity

Sheng-Run Zheng,[a] Qing-Yuan Yang,[a] Yong-Ru Liu,[a] Jian-Yong Zhang,[a] Ye-Xiang Tong,[a] Cun-Yuan Zhao[a] and Cheng-Yong Su*[ab]

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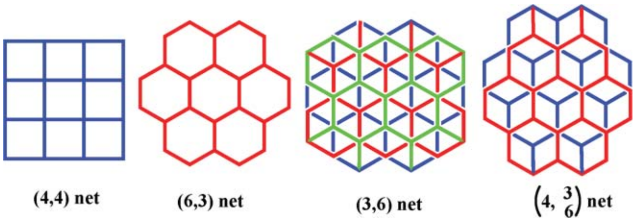
Reaction of a rigid triangular ligand 2,4,6-tris[4-(1*H*-imidazole-1-yl)phenyl]-1,3,5-triazine (TIPT) with Cd^{2+} ions afforded rare non-interpenetrating CdI_2-type networks which display high thermostability and potential porosity; the topological character of the CdI_2-type networks have been analyzed in comparison with three common uniform (4,4), (6,3) and (3,6) plane nets.

The construction of metal–organic frameworks (MOFs) represents a fast growing area in coordination chemistry and supramolecular chemistry due to their variety of architectures and structural topologies, as well as their potential applications in molecular selection, ion exchange, adsorption, fluorescence, and magnetic properties.[1] Various two-dimensional (2D) networks, such as molecular grids, brick-walls, herringbones and honeycombs, have been studied widely.[2] One of the targets in construction of these 2D networks is to create large voids by using long organic connectors. However, when the single network becomes loose, interpenetration usually occurs to achieve close packing. This often causes disappearance of the intended voids. Therefore, design of networks retaining permanent porosity without interpenetration remains a challenge. To prevent interpenetration, strategies such as using bulky building blocks, or using suitable guest molecules which can occupy the voids, have been proven successful.[3] Alternatively, it is also possible to seek for a topology which can avoid interpenetrating by its inherent structural nature.

Scheme 1 illustrates three regular (4,4), (6,3) and (3,6) plane nets which represent the most common topologies observed in 2D coordination networks.[4] Wells long ago summarized that, besides these three uniform plane nets, there are eight nonuniform plane nets corresponding to the Archimedean solids (all nodes are connected in the same manner but have two or more types of polygons) and an additional eight dual nets corresponding to the Catalan solids (all nodes are surrounded by congruent polygons but have two or more types of nodes).[5] However, these net topologies have drawn only little attention so far in construction of 2D coordination networks. The CdI_2-type net is one of the Catalan nets which is known in inorganic compounds such as metal alkoxides and hydroxides.[6] The topological character of the CdI_2 net is that it only contains congruent quadrangles similar to the (4,4) net, but there are two types of nodes in 2 : 1 ratio: the former is 3-connecting as in a (6,3) net while the latter is 6-connecting as in a (3,6) net. Therefore, the net topology can be represented by Wells notation $(4,{}^{3}_{6})$. As depicted in Scheme 1, the CdI_2 net can be regarded to form by offset overlap of two (6,3) nets, while the (3,6) net formed by offset overlap of three (6,3) nets. Therefore, the CdI_2 net may be considered as an intermediate net between the (6,3) and (3,6) net. Since the (6,3) net is usually loose and apt to interpenetrate but the (3,6) net is more dense and disfavors interpenetration, the intermediate CdI_2 net may take advantages of both to lead to coordination networks possessing voids but avoiding interpenetration.

In this paper we describe two CdI_2 topological MOFs, namely, $\{[Cd(TIPT)_2](OTs)_2{\cdot}H_2O\}_n$ **1** and $\{[Cd(TIPT)_2](OTf)_2{\cdot}3.5DMF{\cdot}2.5H_2O\}_n$ **2** (TIPT = 2,4,6-tris[4-(1*H*-imidazole-1-yl)phenyl]-1,3,5-triazine, OTs = p-$CH_3C_6H_5SO_3^-$, OTf = $CF_3SO_3^-$). The use of the rigid triangular TIPT ligand and the octahedral Cd^{2+} ion afforded non-interpenetrating CdI_2 networks in which the ligands were arranged non-coplanar to create large voids above each ligand.

The ligand TIPT was synthesized from cyclization of 4-imidazol-1-ylbenzonitrile. Reaction of the ligand with $Cd(OTs)_2$ and $Cd(OTf)_2$ resulted in complexes **1** and **2** as shown in Scheme 2.† A single-crystal X-ray diffraction study unambiguously revealed the same topological networks for the two complexes **1** and **2**.‡ As shown in Fig. 1(a), each Cd^{2+} ion is six-coordinated with six imidazole nitrogen donors from six different TIPT ligands, while each TIPT ligand binds three Cd^{2+} ions to give rise to the 2D network. Complex **1** crystallizes in the $P\bar{3}c1$ space group. The asymmetric unit contains one ligand, two Cd^{2+} ions of which one is located on a 3-fold axis and the other on a site with crystallographically imposed $\bar{3}$ symmetry, and two OTs^- anions and two water molecules with 1/3 and 1/6 site occupancy,



Scheme 1 Comparison between three regular nets and the CdI_2-type net.

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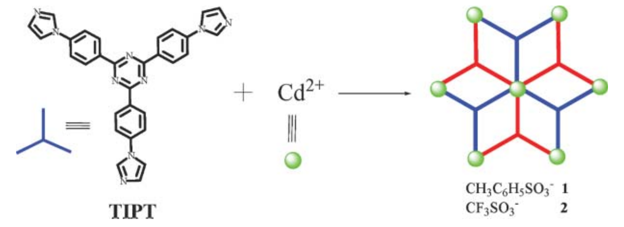
[a] *MOE Laboratory of Bioinorganic and Synthetic Chemistry, State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou, 510275, China. E-mail: cesscy@mail.sysu.edu.cn; Fax: (+86) 20-8411-5178*
[b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, 200032, China*



Scheme 2 Molecular structure of the ligand and formation of complexes.

respectively. In complex **2**, which crystallizes in the $P2_1/c$ space group, the asymmetric unit consists of two ligands, one Cd^{2+} ion, two OTf^- anions of which one is disordered over three positions, 3.5 DMF molecules and 2.5 water molecules which are distributed fractionally over several positions. Therefore, the metal-to-ligand ratio of both coordination networks is 1 : 2. In both structures the Cd^{2+} ion is in an octahedral geometry with the Cd–N bond distances falling in the range 2.346(5)–2.366(5) in **1** and 2.342(5)–2.377(5) Å in **2**, respectively.

A topological analysis of the cationic networks in **1** and **2** revealed the CdI_2-type net as shown in Fig. 1(b). If the TIPT ligand is simplified as a 3-connecting node,[4a] a 2D binodal net is obvious. The 6-connecting nodes are Cd^{2+} ions (vertex symbol $4^6 6^6 8^3$). There are twice as many 3-connecting nodes (vertex symbol of 4^3) than 6-connecting nodes (Fig. 1(b)). Therefore, the short Schläfli vertex notation of the net can be represented as $(4^6 6^6 8^3)(4^3)_2$, which is characteristic of CdI_2-type networks. For an easier comparison with three uniform (4,4), (6,3) and (3,6) nets, the Wells notation $(4,{}^{3}_{6})$ may be more convenient.

Although assembly of CdI_2-type networks can be simply speculated to be achievable by using a trigonal tris-monodentate ligand in combination with a six-coordinate metal center, an important aspect of our networks is the 6-connecting planar node. This is difficult to achieve in coordination networks, which explains why there are few examples in spite of various known coordination polymers assembled from trigonal ligands.[7] In the present cases, the trigonal ligand has a significant 'kink' in the coordinating arms with the imidazole N donors making an angle with respect to the central four-ring base, which just matches the geometrical requirement of the octahedral metal centers. As described above, the CdI_2 network can be regarded to form from two (6,3) networks. It is clear from Fig. 1(c) that the TIPT ligands are arranged around the Cd^{2+} ion in two directions. If we define a plane across all Cd^{2+} ions, half of the ligands are located above the plane while the remainder are below. In each side, the (6,3) network is formed by using three connections of the Cd^{2+} ion. Two such (6,3) networks were joined together by Cd^{2+} ions to give rise to a CdI_2 network. Therefore, the ligands in this CdI_2 network are actually non-coplanar, but are arranged alternately up and down to form a concavo-convex 2D layer.

So far, few MOFs were reported to display CdI_2 net topology except for some cyanide complexes.[8] One similar example, although the network topology was not stated by the author, can be found from a Co_6-carboxylate cluster based network,[9a] in which the hexanuclear cluster can be regarded as the 6-connecting node. Another example was derived from a (4,4) coordination network,[9b] where the hydrogen bond was considered as connections. To the best of our knowledge, the present structures represent the simplest, yet well connected, CdI_2 topological coordination network. An interesting characteristic of this type of network is its reluctance to interpenetrate. The intrinsic factor that prevents interpenetration in CdI_2 nets may be the presence of two types of nodes which makes the two nets misfit with each other for interpenetration.

The concavo-convex feature of the 2D layer could render potential porosity to the cationic framework (Fig. 2(a)). The TIPT ligand is bulky and rigid, but its imidazole arms twist to match the octahedral geometry of the Cd^{2+}, thus forming a bowl-shaped void above each TIPT ligand as shown in Fig. 2(b). Such bowl-shaped voids exist in both sides of the network. In addition, the four-ring base of the TIPT ligand strongly favors $\pi\cdots\pi$ interaction in crystal packing. Therefore, every two neighbouring layers are stacked in parallel directed by the $\pi\cdots\pi$ interactions (3.6 Å) with two adjacent bowls face-to-face coupled to form a large capsule. The size of such capsules can be estimated by Cd···Cd distances (19 × 19 × 19 Å) and separation of two triazine rings (11 Å). Solvent molecules and anions are encapsulated inside the capsule as shown in Fig. 2(c)–(e). There are spacious windows which allow small guest molecules to permeate between the capsules. If only the present anions are retained, complex **1** has a potential solvent area volume of 1860 $Å^3$ (14%) while for complex **2** this is 3017.7 $Å^3$ (33.6%) estimated by PLATON.[10] Considering the coordination framework alone, the solvent accessible voids rise to 6705 $Å^3$ (50.7%) for **1** and 8993 $Å^3$ (51.6%) for **2**. This means that such CdI_2 networks could be expected to afford significant potential framework porosity

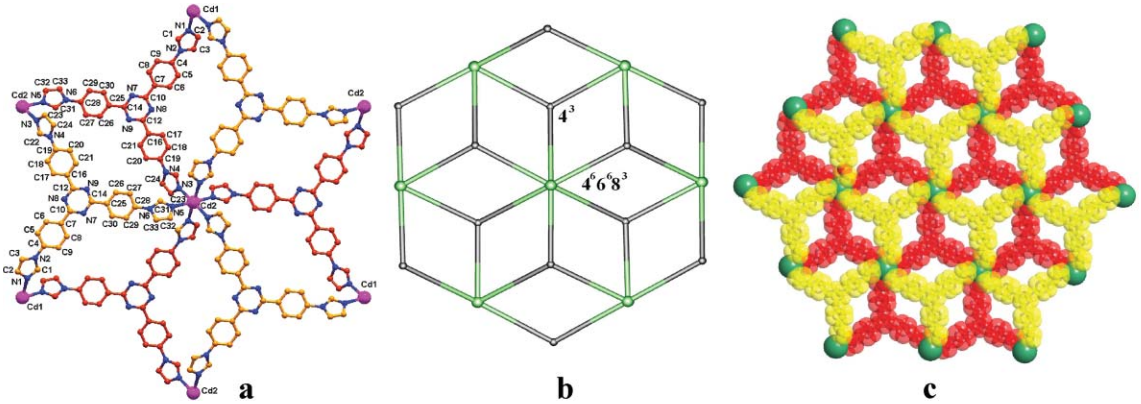


Fig. 1 (a) Molecular structure in **1** showing atomic labeling and 6-connecting Cd^{2+} coordination geometry, (b) net topology of **1** and **2** with the two vertex symbols indicated, and (c) space-filling view of the CdI_2 network showing the up (yellow) and down (red) arrangement of the 3-connecting ligands.

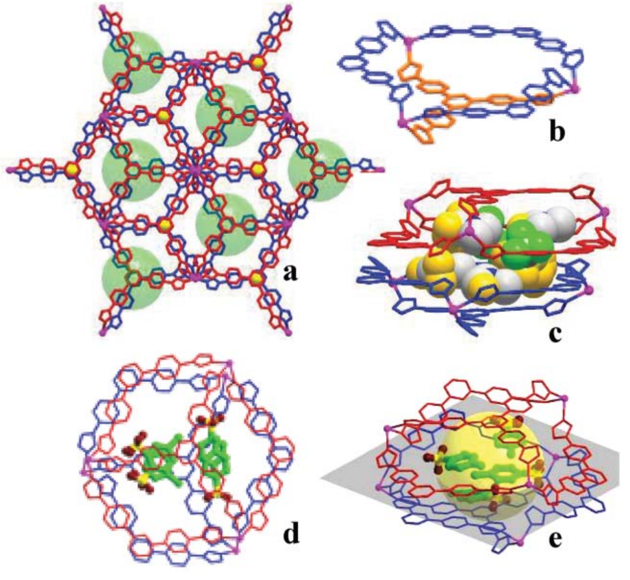


Fig. 2 (a) Parallel packing of two adjacent 2D layers directed by π⋯π interactions (highlighted in yellow) providing capsule-like voids (shown by green balls), (b) bowl-shaped void in network, (c) capsule formed by two face-to-face bowls encapsulating solvents and anions in **2**, (d) top view and (e) side view of the capsule in **1** encapsulating four OTs^- anions.

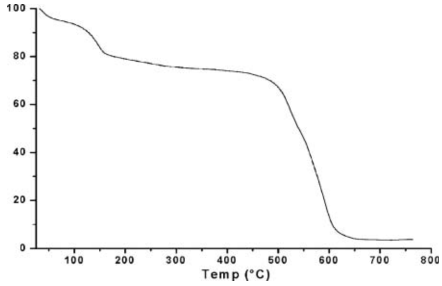


Fig. 3 TGA curve for complex **2**.

providing the networks are neutral or the counter anions are small. Unfortunately, in the present complexes the large voids are occupied by solvents and anions to diminish the porosity. However, construction of CdI_2 topological networks by using octahedral metal centers and bulky triangular ligands as demonstrated in this work implies a possible strategy to fabricate genuine porous coordination polymers.[11]

Thermogravimetric analyses (TGA) of complex **2** shows weight losses in the temperature range 25–150 °C as seen from Fig. 3, corresponding to release of solvent molecules. A major weight loss occurs in the range 450–650 °C, suggesting decomposition of the coordination framework. Due to easy escape of the solvated molecules, the crystals of both complexes **1** and **2** effloresce rapidly when isolated from the mother-liquor. This caused a difficulty to check how the crystal packing is retained upon heating by XRD measurement. However, the TGA results suggest that the coordination framework remains undecomposed up to 450 °C, and a large amount of solvated molecules hosted inside the network voids can be released by heating.

In summary, two CdI_2 networks have been assembled from Cd^{2+} ions and a triangular rigid TIPT ligand. The topological relationship between the CdI_2 net and three uniform 2D nets has been analyzed. Interpenetration which usually takes place in (4,4) and (6,3) networks with long ligands may be prevented in CdI_2 networks. Therefore, construction of 2D coordination networks of CdI_2 topology by using octahedral metal ions and bulky triangular ligands may offer good chances to achieve good framework porosity.

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Notes and references

† *Preparation* of **1**: A solution of $Cd(OTs)_2{\cdot}6H_2O$ (5 mg, 0.01 mmol) in MeOH (5 mL) was layered onto a solution of TIPT (5 mg, 0.01 mmol) in DMF (5 mL) in a test tube. Colorless crystals were formed after several days. Yield: 40%. IR (KBr, cm^{-1}): $\nu(OTs^-)$ 1186, 1059, 654; $\nu(H_2O)$ 3432. **2**: Prepared in a similar way to **1** by using $Cd(OTf)_2{\cdot}6H_2O$ and EtOH. Yield: 35%. IR (KBr, cm^{-1}): $\nu(OTf^-)$ 1260, 1117, 1059, 641; $\nu(H_2O)$ 3397.

‡ *Crystal data*: for **1**: $C_{67}H_{51}CdN_{18}O_{3.67}S$, $M_r = 1311.38$, hexagonal, space group $P\bar{3}c1$, $a = 32.5392(6)$, $c = 14.4167(12)$ Å, $V = 13219.3(12)$ Å^3, $Z = 6$, $D_c = 0.988$ g cm^{-3}, μ(Mo-Kα) = 2.576 mm^{-1}, $T = 150$ (2) K, 6824 unique reflections out of 28640 with $I > 2\sigma(I)$ ($R_{int} = 0.0764$), final $R1 = 0.0850$, $wR2 = 0.1855$. For **2**: $C_{145}H_{143}Cd_2F_{12}N_{43}O_{24}S_4$, $M_r = 3453.06$, monoclinic, space group $P2_1/c$, $a = 18.5838(3)$, $b = 33.2158(5)$, $c = 14.8187(3)$ Å, $\beta = 100.552(2)°$, $V = 8992.5(3)$ Å^3, $Z = 2$, $D_c = 1.275$ g cm^{-3}, μ(Cu-Kα) = 3.041 mm^{-1}, $T = 150$ (2) K, 13296 unique reflections out of 36947 with $I > 2\sigma(I)$ ($R_{int} = 0.0312$), final $R1 = 0.11734$, $wR2 = 0.2419$. CCDC 654162 and 654163. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b711457e.

1 (*a*) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; (*b*) O. R. Evans and W.-B. Lin, *Acc. Chem. Res.*, 2002, **35**, 511; (*c*) S. M. Kil and P. S. Myunghyun, *J. Am. Chem. Soc.*, 2000, **122**, 6834; (*d*) M. Fujita, H. Oka, K. Yamaguchi and K. Ogura, *Nature*, 1995, **378**, 469; (*e*) C.-L. Chen, B.-S. Kang and C.-Y. Su, *Aust. J. Chem.*, 2006, **59**, 3.

2 (*a*) G.. S. Hanan, D. Volkmer, U. S. Schubert, J. M. Lehn, G. Baum and D. Fenske, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1842; (*b*) K. Biradha, Y. Hongo and M. Fujita, *Angew. Chem., Int. Ed.*, 2002, **41**, 3395; (*c*) K. E. Holmes, P. F. Kelly and M. R. J. Elsegood, *Dalton Trans.*, 2004, 3488; (*d*) C.-W. Liu, B. J. Liaw, L. S. Liou and J.-C. Wang, *Chem. Commun.*, 2005, 1983; (*e*) J. J. M. Amoore, C. A. Black, L. R. Hanton and M. D. Spicer, *Cryst. Growth Des.*, 2005, **5**, 1255.

3 (*a*) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469; (*b*) J.-H. Fournier, T. Maris and J. D. Wuest, *J. Org. Chem.*, 2004, **69**, 1762; (*c*) G. J. E. Davidson and S. J. Loeb, *Angew. Chem., Int. Ed.*, 2003, **42**, 74; (*d*) M. P. Suh, H. J. Choi, S. M. So and B. M. Kim, *Inorg. Chem.*, 2003, **42**, 676.

4 (*a*) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460; (*b*) L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.*, 2003, **246**, 247.

5 A. F. Wells, *Three-dimensional Nets and Polyhedra*, John Wiley & Sons, Inc., New York, 1977, p. 183.

6 (*a*) C. G. Subhash, A. M. Michael, Y. C. Michael and E. B. William, *J. Am. Chem. Soc.*, 1991, **113**, 1844; (*b*) M. P. Annika, L. G.. Westin and K. Mikael, *Chem.–Eur. J.*, 2001, **7**, 3439; (*c*) D. Thomas, E. Michel, M. L. Yves, C. Enric, A.-S. Pascale, F. Marc and B. Patrick, *J. Am. Chem. Soc.*, 2003, **125**, 3295.

7 (*a*) S. R. Batten, B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1995, **117**, 5385; (*b*) S. R. Batten, B. F. Hoskins and R. Robson, *Angew. Chem., Int. Ed.*, 2003, **34**, 820.

8 (*a*) V. Niel, A. Galet, A. B. Gaspar, M. C. Muñoz and J. A. Real, *Chem. Commun.*, 2003, 1248; (*b*) B. Yan, C. S. Day and A. Lachgar, *Chem. Commun.*, 2004, 2390.

9 (*a*) J.-H. He, Y.-T. Zhang, Q.-H. Pan, J.-H. Yu, H. Ding and R.-R. Xu, *Microporous Mesoporous Mater.*, 2006, **90**, 145; (*b*) M. Du, Z.-H. Zhang, L.-F. Tang, X.-G. Wang, X.-J. Zhao and S. R. Batten, *Chem.–Eur. J.*, 2007, **13**, 2578.

10 A. L. Spek, PLATON, *J. Appl. Crystallogr.*, 2003, **36**, 7.

11 (*a*) S. Kitagawa, R. Kitaura and S.-I. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; (*b*) L. J. Barbour, *Chem. Commun.*, 2006, 1163.