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A novel ribbon-candy-like supramolecular architecture of cadmium(II)–terephthalate polymer with giant rhombic channels: twofold interpenetration of the 3D $8^2$10-a net

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The hydrothermal reaction of H_2tp (tp = terephthalate), [Ph_3PCH_2Ph]Cl and water with $Cd(O_2CCH_3)_2 \cdot 2H_2O$ gives rise to a novel ribbon-candy-like supramolecular architecture with twofold interpenetration of an unprecedented 3D $8^2$10-a net formed by polymer {[Ph_3PCH_2Ph][Cd(tp)·Cl]·$2H_2O$}$_n$ containing giant rhombic channels, which displays strong fluorescent emission in the solid state.

The design and synthesis of supramolecular architectures analogous to important minerals such as quartz, clays and zeolites using the principles of crystal engineering[1] are of much current interest.[2] In attempts to synthesize zeolite-type coordination frameworks, some organic ligands, for example, 4,4′-bipyridine,[3] pyrazine,[4] 4,4′-trimethylenedipyridine[5] and polyaromatic acids,[6] are usually chosen as rigid 'tectons' to bind metal centers for constructing porous supramolecular architectures. Similarly to the simple rodlike rigid spacer 4,4′-bipyridine, terephthalate[7] is also often chosen as a building block to fabricate square open frameworks. Despite the fact that several interesting examples of porous supramolecular frameworks crystallized from terephthalate ligand with various metal ions have been reported,[7,8] because of the limitation in the length of the tecton and the presence of interpenetrated networks,[3] so far there is still a challenge to obtain materials with large pores within the assembled structure in most cases. It is possible to obtain products with large cavity structure by use of templates to influence the morphology of crystalline deposit. On the other hand, structure-directing effects of templates can be also used to explore and prepare new supramolecular frameworks with interesting topologies.

Recognizing the potential of this approach, we have embarked on a program aimed at using various cations as templating molecules in the assembly of porous supramolecular frameworks. Here, we report an interesting example of ribbon-candy-like supramolecular architecture with twofold interpenetration of 3D $8^2$10-a net formed by the cadmium(II)-terephthalate (tp) polymer, {[Ph_3PCH_2Ph][Cd(tp)·Cl]·$2H_2O$}$_n$ **1**, containing giant rhombic channels displaying strong fluorescent emission, based on the templating effects of the large bulky cation [Ph_3PCH_2Ph]$^+$.

Compound **1** was synthesized by the reaction of $Cd(O_2CCH_3)_2 \cdot 2H_2O$, H_2tp, [Ph_3PCH_2Ph]Cl and H_2O under hydrothermal conditions to give colorless prism-like crystals, which were formulated as {[Ph_3PCH_2Ph][Cd(tp)·Cl]·$2H_2O$}$_n$ on the basis of elemental analysis.† This compound is very stable in air at ambient temperature and is almost insoluble in common solvents such as water, alcohol, acetonitrile, chloroform, acetone and toluene. X-Ray single-crystal analysis‡ revealed that the crystal structure of **1** is a 3D porous framework composed of the well-separated cations, guest aqua molecules and anionic polymer. In the building unit of **1**, the Cd^{II} center lies in a very distorted octahedral coordination sphere, bonding to two bridging μ_2-Cl ligands, and to two pairs of oxygen donors of two chelating carboxylate groups from two separate tp ligands (Fig. 1a); the tp ligand links to two Cd^{II} centers through two chelating carboxylate groups. Due to the structure-directing effects of large bulky cations [Ph_3PCH_2Ph]$^+$ (*ca.* 9.5 Å in diameter), the angle between two adjacent tp ligands coordinated to the same Cd^{II} center is close to 130° [Cd(1a)···Cd(1)···Cd(1c) 129.616°, Fig. 1b], which is clearly different from those of either *ca.* 90 or 180 shown in the most common square networks formed by the rodlike rigid spacer tp ligand.[7,8] In the crystal, these building units are therefore arranged to generate zigzag rhombic open motifs with a giant cavity of *ca.* 33.5 × 22.7 Å, with Cd···Cd separations of 20.210 Å along the rhombic edge of tp–Cd–tp and 3.704 Å along the μ_2-Cl bridge (Fig. 1b), rather than a common small square net motif. Four rhombic open motifs are further polymerized through co-edge and μ_2-Cl bridges to yield an interesting cage subunit (Fig. 2). The cage subunit possesses two rhombic channels which are perpendicular each other but staggered at half-edge positions. Extension of this cage subunit through the symmetry equivalent units gives a 3D porous supramolecular framework having an interesting ribbon-candy-like structure, a topology attributed to the Archimedian 3D net ($8^2$10)-a (Fig. 3a)

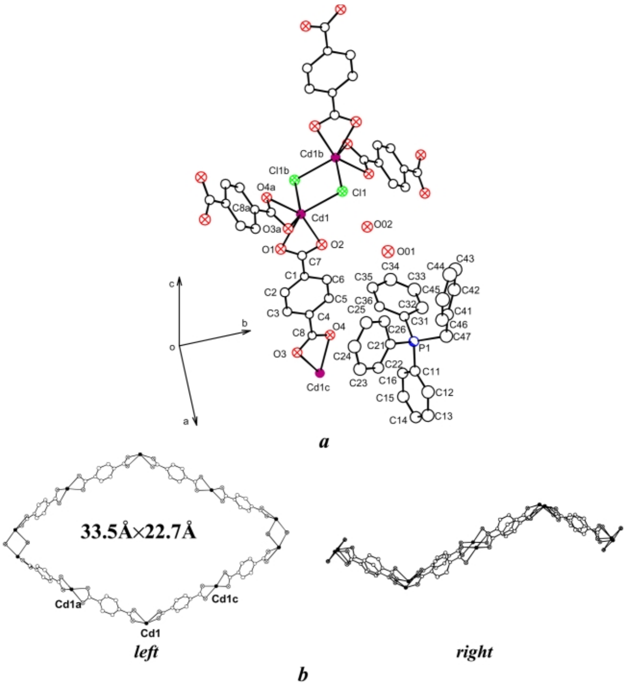

Fig. 1 (*a*) A view of **1** depicting the coordination environment around the Cd(1) center (ellipsoids at 25% probability); the hydrogen atoms are omitted for clarity; (*b*) Top (*left*) and side (*right*) views showing the zigzag rhombic open motif with a giant cavity of *ca.* 33.5 × 22.7 Å in **1**, Hydrogen atoms, part of bridging chlorine atoms and guests are omitted for clarity.

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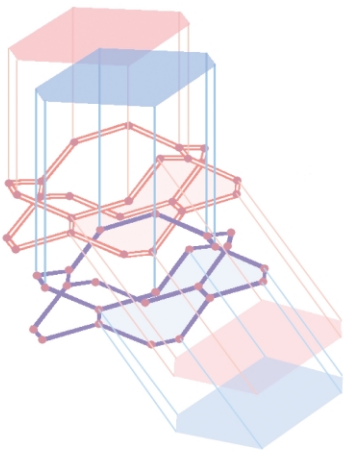

Fig. 2 The cage subunit in **1** and the twofold interpenetrating model for **1**.

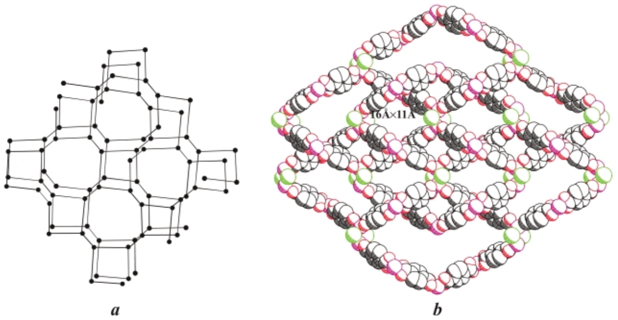

Fig. 3 (*a*) Schematic topology for 8^210-a net of **1**. (*b*) Space-filling view of the twofold interpenetrating 3D supramolecular framework in **1** showing the rhombic channels of *ca.* 16 × 11 Å; guests are omitted for clarity.

classified by Wells[9] and is, to our knowledge, unprecedented in coordination polymer chemistry.

It is notable that the single rhombic channels contains giant cavities of *ca.* 33.5 ×22.7 Å, while the actual crystal structure of compound **1** is a twofold interpenetrating 3D supramolecular framework (Fig. 2) and the resulting cavities in **1** are only *ca.* 16 × 11 Å (Fig. 3b), which are filled by encapsulated guests—aqua molecules and $[Ph_3PCH_2Ph]^+$ counter ions. This is consistent with the fact that crystal structures with such large cavities are stabilized either by inclusion of suitable guests or by interpenetrating lattices.[10]

The TGA trace of **1** shows an obvious weight loss in the range 58–130 °C to give a total weight loss of *ca.* 5.0%, corresponding to the loss of two H_2O molecules per formula unit (calc. 5.13%). Subsequent to this no obvious weight loss occurs up to 300 °C and complete decomposition is observed at *ca.* 610 °C. This suggests that the aqua molecules in **1** are lattice water and the framework of **1** possesses high thermal stability.

The UV–VIS spectrum of **1** in the solid state exhibits only a high-energy absorption at *ca.* 292 nm, which can be assigned to ligand-to-metal charge transfer (LMCT). An intense fluorescent emission of **1** at 474 nm (λ_{exc} = 292 nm) was observed in the solid state at ambient temperature. This suggests that **1** might be an excellent candidate as a photoactive material.

In conclusion, the rational utilization of large bulky templating molecules provides a robust strategy for the design and synthesis of porous supramolecular frameworks with large pores. A novel ribbon-candy-like supramolecular architecture of the polymer $\{[Ph_3PCH_2Ph][Cd(tp)\cdot Cl]\cdot 2H_2O\}_n$ containing giant rhombic channels has been synthesized under hydrothermal conditions based on the templating effects of large bulky cation $[Ph_3PCH_2Ph]^+$. This compound may be an excellent candidate as a photoactive material owing to its fluorescence, thermal stability and insolubility in common polar and non-polar solvents. The open framework structure of this compound may also have potential as a porous material *via* removal of the guest aqua molecules and $[Ph_3PCH_2Ph]^+$ cations. Work on this area is in progress.

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Notes and references

† The hydrothermal reaction of $Cd(O_2CCH_3)_2\cdot 2H_2O$, H_2tp, $[Ph_3PCH_2Ph]Cl$ and H_2O in a molar ratio of 1:1:1:278 was performed in a Teflon-lined stainless steel autoclave under autogenous pressure at 200 °C for 4 days, then the mixture was cooled at a rate of *ca.* 3.5 °C h^{-1}. The resulting colorless prism-like crystals were mechanically separated from the reaction mixture of solid and washed with water and absolute alcohol to give a *ca.* 81.95% yield of **1** based on $Cd(O_2CCH_3)_2\cdot 2H_2O$. Anal. Calc. (found): C, 56.51(56.61); H, 4.31(4.24); P, 4.42(4.40); Cl, 5.05(5.11)%. FTIR(KBr pellet, cm^{-1}): 3462m, 3385m, 3064w, 2920w, 1641w, 1595m, 1552s, 1502m, 1485w, 1465w, 1437m, 1383s, 1311w, 1190w,1163w, 1128w, 1113s, 1086w, 1070w, 1016w, 997m, 845m, 748s, 513m.

‡ *Crystal data* for compound **1**; $C_{33}H_{30}CdClO_6P$, M = 701.39, tetragonal, space group, $P4_2/n$, a = 18.6679(2), b = 18.6679(2), c = 17.8347(2) Å, V = 6215.22(12) Å^3, Z = 8, T = 293(2) K, D_c = 1.499 g cm^{-3}, $F(000)$ = 2848, Mo-Kα radiation (λ = 0.71073 Å), μ = 0.883 mm^{-1}, R_1 = 0.0428, R_w = 0.0988 for 3735 observed reflections from 5529 independent reflections. GOF = 1.152. The data collection was performed on a Siemens SMART-CCD area-detector diffractometer. The structure was solved by direct methods using SHELXS-97[11] and refined by full-matrix least-squares techniques using SHELXL-97.[12] All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms were generated geometrically.

CCDC reference number 168461. See http://www.rsc.org/suppdata/cc/b1/b107592f/ for crystallographic data in CIF or other electronic format.

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