

Crystal Engineering of the Coordination Architecture of Metal Polycarboxylate Complexes by Hydrothermal Synthesis: Assembly and Characterization of Four Novel Cadmium Polycarboxylate Coordination Polymers Based on Mixed Ligands

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Four novel compounds, $[\text{Cd}(\text{tp})(\text{bpp})]_n$ (**1**), $[\text{Cd}(\text{tp})(\text{bpy})]_n$ (**2**), $[\{\text{Cd}_4(\text{bpa})_4(\text{bpy})_6\}(\text{bpy})_{0.5}\cdot 7\text{H}_2\text{O}]_n$ (**3**) and $[\text{Cd}_2\{\text{Htp}(\text{tp})_{1.5}\}(\text{bpe})]_n$ (**4**) [tp = terephthalate, bpp = 1,3-bis(4-pyridyl)propane, bpy = 4,4'-bipyridine, bpa = 4,4'-biphenyldicarboxylate, bpe = 1,2-bis(4-pyridyl)ethane], of cadmium(II) polycarboxylate coordination polymers based on mixed ligands were obtained by a hydrothermal method. Complex **1** ($\text{C}_{21}\text{H}_{18}\text{CdN}_2\text{O}_4$) crystallizes in the orthorhombic *Pbca* space group [$a = 11.9401(0)$ Å, $b = 16.8148(3)$ Å, $c = 20.2743(3)$ Å, and $Z = 8$]. Complex **2** ($\text{C}_{18}\text{H}_{12}\text{CdN}_2\text{O}_4$) belongs to the monoclinic *C2/m* space group [$a = 20.299(3)$ Å, $b = 10.720(1)$ Å, $c = 11.764(2)$ Å, $\beta = 110.944(2)^\circ$, and $Z = 6$]. Complex **3** ($\text{C}_{121}\text{H}_{98}\text{Cd}_4\text{N}_{13}\text{O}_{23}$) belongs to the monoclinic *P2₁/c* space group [$a = 23.2208(0)$ Å, $b = 11.8103(1)$ Å, $c = 45.4670(6)$ Å, $\beta = 104.516(1)^\circ$, and $Z = 4$]. Complex **4** ($\text{C}_{32}\text{H}_{23}\text{Cd}_2\text{N}_2\text{O}_{10}$) belongs to the monoclinic *P2₁/n* space group [$a = 6.9896(1)$

Å, $b = 22.6294(1)$ Å, $c = 19.7738(3)$ Å, $\beta = 99.380(1)^\circ$, and $Z = 4$]. The Cd^{II} centers in the four compounds are bridged by mixed polycarboxylate ligands with bpy and related species to form the twofold parallel interpenetration topology of an undulating 2D 4^4 net for **1**, a twofold interpenetration topology of a 3D α -Po net for **2**, a fourfold interpenetration topology of a 3D 5-connected borazone 4^66^4 net for **3** and an interesting 3D spiral pipe-like structure with a bolt for **4**. These four compounds exhibit strong fluorescent emissions at 549 and 582 nm ($\lambda_{\text{ex}} = 532$ nm) for **1**, 493 nm ($\lambda_{\text{ex}} = 360$ nm) for **2**, 413 and 424 nm ($\lambda_{\text{ex}} = 315$ nm) for **3** and 350 nm ($\lambda_{\text{ex}} = 220$ nm) for **4** in the solid state at room temperature. These are novel structural topologies and could be significant in the field of photoactive materials.

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Introduction

There has been an enormous growth in the crystal engineering of coordination-polymeric solids in recent decades owing to their intriguing applications, including catalysis, nonlinear optics, sensors, magnetism and molecular recognition.^[1–10] Although a number of new coordination-polymeric solids with beautiful architectures and interesting topologies based on the assembly of bridging ligands and metal centers using the principles of crystal engineering have been reported,^[11–31] a rational synthesis strategy to manipulate the assembly of donor and acceptor building blocks to generate desired supramolecular architectures is

still one of the great challenges in this areas. For the design of coordination-polymeric solids that mimic mineral architectures such as quartz, clays and zeolites, an effective strategy is the choice of rigid “tecton” ligands containing O- or N-donors to bind metal centers as building blocks of the extended framework used to construct novel supramolecular architectures.^[32,33] Polycarboxylates are often employed as bridging ligands to construct porous coordination polymers due to their versatile coordination modes and high structural stability.^[7,8,26,34–53] These polymeric solids can be essentially regarded as a class of metal polycarboxylate salts. Hence, the structures of the resulting compounds are influenced by the degree of deprotonation, the coordination modes and capabilities, the sizes and shape of the polycarboxylic acids, as well as by the coordination sphere of the metal centers. Thus, it is possible to synthesise polymeric frameworks with interesting topologies through the appropriate choice of ligand, and tailoring and manipulation of the reaction conditions, including pH, temperature, stoichiometry, and the addition of templates or structure-directing agents.^[26,33–46] In order to resolve the poor solubility of

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reactants and products, the hydrothermal reaction technique offers a powerful synthetic route to prepare polymeric solids with better crystallinity^[7,54] than traditional solution techniques such as evaporation, diffusion and cooling etc. In most cases, water is not only a solvent but also acts as a competing ligand in these hydrothermal reactions. An interesting phenomenon can be observed whereby many coordination polymers constructed from polycarboxylate ligands usually contain water molecules as terminal or bridging ligands in the coordination sphere of the metal, thus increasing the variety of the assembled structural topology of the polymers. It is therefore possible to obtain metal polycarboxylates with novel coordination architectures of diverse sizes and shapes by use of other suitable compounds with different steric demands and ligating capabilities as the competing bridging ligand to substitute the water ligands mentioned above. Taking account of the potential of these approaches, we have embarked on a program aimed at using mixed ligands containing O- and N-donors to prepare coordination-polymeric solids that mimic mineral architectures. Herein, we report four interesting examples of coordination polymeric architectures based upon mixed bridging ligands: $[\text{Cd}(\text{tp})(\text{bpp})]_n$ (**1**), $[\text{Cd}(\text{tp})(\text{bpy})]_n$ (**2**), $[\{\text{Cd}_4(\text{bpa})_4(\text{bpy})_6\} \cdot (\text{bpy})_{0.5} \cdot 7\text{H}_2\text{O}]_n$ (**3**), and $[\text{Cd}_2\{(\text{Htp})(\text{tp})_{1.5}\}(\text{bpe})]_n$ (**4**) [tp = terephthalate, bpp = 1,3-bis(4-pyridyl)propane, bpy = 4,4'-bipyridine, bpa = 4,4'-biphenyldicarboxylate, bpe = 1,2-bis(4-pyridyl)ethane]. X-ray single-crystal analyses show that these four polymers possess novel structural topologies, namely the twofold parallel interpenetration topology of an undulating 2D 4^4 net for **1**, the twofold interpenetration topology of a 3D α -Po net for **2**, the fourfold interpenetration topology of a 3D 5-connected borazone $4^6 6^4$ net for **3** and an interesting 3D spiral pipe-like structure with a bolt for **4**. The compounds display strong fluorescent emissions at 549 and 582 nm (λ_{ex} = 532 nm) for **1**, 493 nm (λ_{ex} = 360 nm) for **2**, 413 and 424 nm (λ_{ex} = 315 nm) for **3** and 350 nm (λ_{ex} = 220 nm) for **4** in the solid state at room temperature, implying that they may be excellent candidates for potential photoactive materials.

Results and Discussion

Synthesis and Characterization

The four coordination polymers were obtained in a similar way. The appropriate acidity or basicity of the reactants for deprotonation of polycarboxylates is very important for preparing these four compounds, as is the case for some other metal polycarboxylate coordination polymers reported in our earlier studies.^[26] These four compounds were also prepared at different pHs: compound **1** at pH 5.5, compound **2** at pH 9.1, compound **3** at pH 8.0 and compound **4** at pH 5.6. We tried to prepare these four compounds at different pHs but without success. Besides the pH, a suitable steric geometry of the reactants is also very important for fabrication of the resulting coordination architectures. As described in the Exp. Sect., although the synthesis conditions are very similar, only a small difference in the steric

demands of the reactants, for example between bpp and bpe , results in the different coordination architectures of compounds **1** and **4**. In addition, the synthesis of compounds **1** and **4** cannot be performed in the absence of $(\text{Ph}_3\text{PCH}_2\text{Ph})\text{Cl}$, while another supramolecular isomer of compound **2**, reported by Chen,^[21] was obtained when the synthesis of compound **2** was carried out in the absence of hexamethylenetetraamine, even though neither $(\text{Ph}_3\text{PCH}_2\text{Ph})\text{Cl}$ nor hexamethylenetetraamine are found as ligands or guests in the resulting coordination polymers. This suggests that both $(\text{Ph}_3\text{PCH}_2\text{Ph})\text{Cl}$ and hexamethylenetetraamine play a template or structure-directing role in the construction of the resulting coordination architectures.

The elemental analysis data for the four compounds are in good agreement with the formulas $[\text{Cd}(\text{tp})(\text{bpp})]_n$ (**1**), $[\text{Cd}(\text{tp})(\text{bpy})]_n$ (**2**), $[\{\text{Cd}_4(\text{bpa})_4(\text{bpy})_6\} \cdot (\text{bpy})_{0.5} \cdot 7\text{H}_2\text{O}]_n$ (**3**) and $[\text{Cd}_2\{(\text{Htp})(\text{tp})_{1.5}\}(\text{bpe})]_n$ (**4**). The IR spectra of these compounds show the characteristic bands of the dicarboxylate groups in the usual region^[55] at $1400\text{--}1375\text{ cm}^{-1}$ for the symmetric vibration and at $1610\text{--}1539\text{ cm}^{-1}$ for the asymmetric vibration, as well as the bands of the bpp ligand at 2953, 2939, 2860, 1616, 1504 and 1429 cm^{-1} for **1**, the bands of the bpy ligand at 1491 cm^{-1} for **2**, the bands of the bpy or bpa ligand at 1585, 1489, 3082 and 3055 cm^{-1} for **3**, and the bands of the bpe ligand at 1504, 1551, 1574, 3051 and 2929 cm^{-1} for **4**. The splitting of $\nu_{\text{asym}}(\text{CO}_2)$ in both **2** and **4** confirms that the carboxylate groups have a variety of coordination fashions. Moreover, for **4**, the peak at 1705 cm^{-1} suggests the presence of a protonated carboxylate group. These proposals are consistent with the crystal structures. The TGA traces for **1**, **2** and **4** show that the decomposition of the three compounds occurs at ca. $297\text{--}524\text{ }^\circ\text{C}$, $373\text{--}587\text{ }^\circ\text{C}$ and $210\text{--}600\text{ }^\circ\text{C}$, respectively. The TGA trace for **3** shows an obvious weight loss starting at about $50\text{ }^\circ\text{C}$ up to $100\text{ }^\circ\text{C}$ to give a total weight loss of ca. 5.4%, corresponding to the loss of seven water molecules per formula unit (calcd. 4.9%). Subsequent to this no obvious weight loss occurs for **3** up to $186.9\text{ }^\circ\text{C}$, followed by an obvious weight loss up to $271.9\text{ }^\circ\text{C}$ to give a total weight loss of ca. 2.9% corresponding to the loss of 0.5 bpy molecules per formula unit (calcd. 3.1%). Complete decomposition of **3** occurs at $271.9\text{ }^\circ\text{C}$ and finishes at ca. $511\text{ }^\circ\text{C}$. This is consistent with the structure of **3** and suggests that the framework of **3** possesses a similar thermal stability to the above three compounds.

Crystal Structures

X-ray single-crystal analysis revealed that the crystal structure of **1** is a twofold parallel interpenetration topology of a 2D 4^4 network polymer. As shown in Figure 1, the fundamental building unit of **1** is composed of a six-coordinate Cd^{II} center, a tp ligand and a bpp ligand, in which each Cd center is coordinated in a distorted tetrahedral geometry to two tp ligands and two bpp ligands through two chelating carboxylate groups (O1 , O2 and O3a , O4a) [$\text{Cd}\text{--}\text{O}$: $2.254(3)\text{--}2.444(3)\text{ \AA}$] and two nitrogen donors (N1 , N2b) [$\text{Cd}\text{--}\text{N}$: $2.295(3)\text{ \AA}$]. Each tp and bpp ligand is

bridged to two different Cd centers, which provides the 4-linking nodes resulting in an interesting square-grid motif with a window of about $11.9 \times 11.1 \text{ \AA}$ (Figure 1). No guest molecules are found in this square grid. The square-grid motifs are linked to each other to form a typical 2D 4^4 network.^[8,14,32,56] Neither tp ligands nor bpp ligands bridging to the same Cd center are coplanar; the N–Cd–N bond angle is $98.57(12)^\circ$, while the angle between two adjacent tp ligands chelated to the same Cd center is 132.5° . This 2D 4^4 network is interesting as the 4-linking nodes

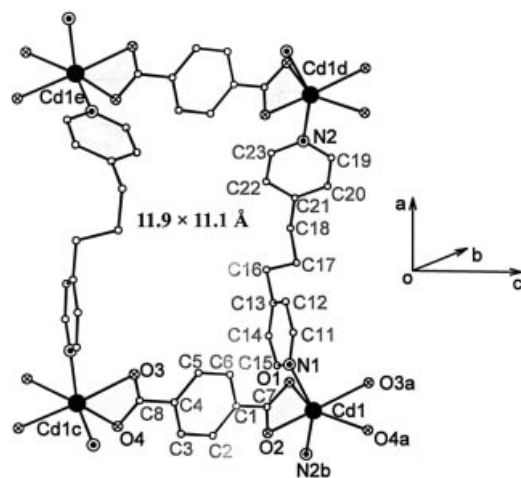


Figure 1. A drawing of **1** depicting the coordination environment around the Cd^{II} center to form a typical 4^4 net with a $11.9 \times 11.1 \text{ \AA}$ window; the hydrogen atoms are omitted for clarity: (a) $x, -y + 1/2, z + 1/2$; (b) $x - 1, y, z$; (c) $x, -y + 1/2, z - 1/2$; (d) $x + 1, y, z$; (e) $x + 1, -y + 1/2, z - 1/2$

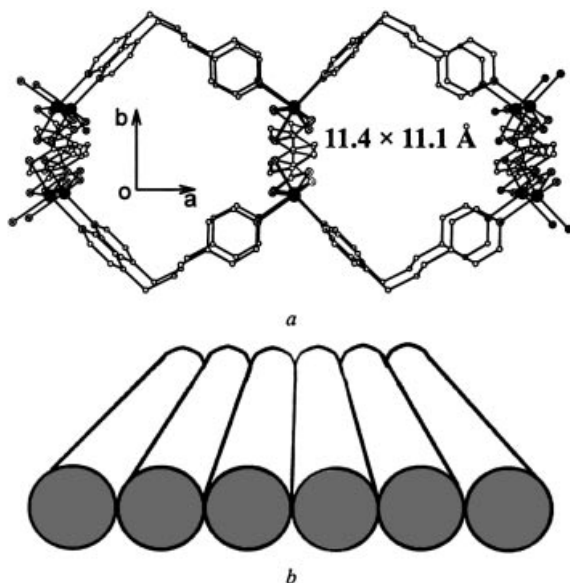


Figure 2. (a) A view of a single 4^4 net along the ab plane in **1** showing an interesting pipe-comb-like 2D layer structure with an $11.4 \times 11.1 \text{ \AA}$ channel; the hydrogen atoms are omitted for clarity; (b) schematic diagram showing a pipe-comb-like 2D layer motif based upon **1**

come from a tetrahedral geometry rather than from a pseudo-octahedral geometry; 4-linking nodes of tetrahedral geometry usually result in adamantoid networks. Due to the N–Cd–N bond angle of $98.57(12)^\circ$ and the flexibility of the bpp ligands, an interesting pipe-comb-like 2D layer structure with a channel of about $11.4 \times 11.1 \text{ \AA}$ occurs in this single 4^4 network along the ab plane (Figure 2). Moreover, the 4-linking nodes allow the 2D 4^4 network to have the undulating nature of the square grid polycatenated by another independent, symmetry-related 4^4 network, thus showing a twofold parallel interpenetration topology (Figure 3). This interpenetration means that the effective voids in the crystal structure of **1** actually have a volume of only $58.1 \text{ \AA}^3$, which is 1.4% of the unit-cell volume, even though the single 4^4 network contains a big window and channel as described above.

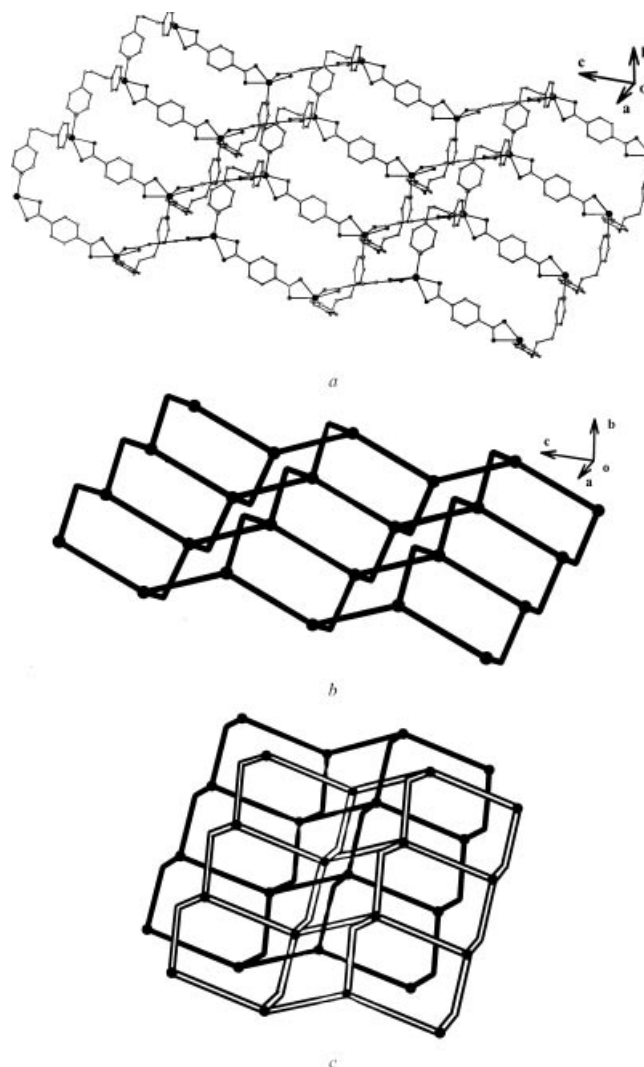


Figure 3. (a) The undulating nature of a single 4^4 net in **1**; the hydrogen atoms are omitted for clarity; (b) schematic diagram of **1**; (c) the twofold parallel interpenetration topology of **1**

The crystal structure of **2** consists of two independent six-coordinate Cd^{II} centers (Cd1, Cd2) that are bridged by

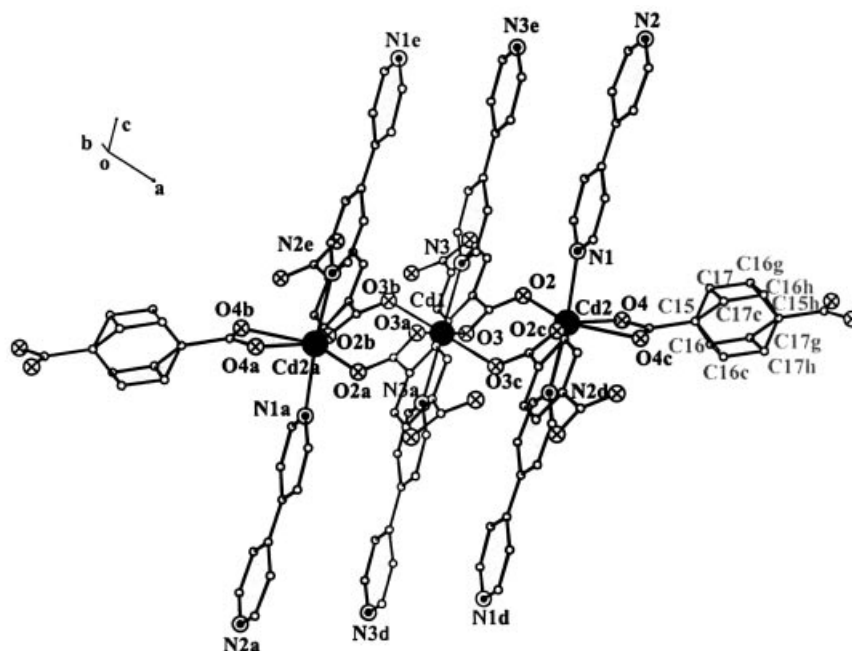


Figure 4. The coordination environment around the Cd^{II} centers in **2**; the hydrogen atoms are omitted for clarity: (a) $-x, -y, -z$; (b) $-x, y, -z$; (c) $x, -y, z$; (d) $x, y, z - 1$; (e) $-x, -y, -z + 1$; (g) $-x + 1, y, -z + 1$; (h) $-x + 1, -y, -z + 1$

two bis-bidentate tp ligands, the distance between the two metal centers ($\text{Cd1} \cdots \text{Cd2}$) being 4.099 Å (Figure 4). The Cd1 center is in a distorted octahedral coordination sphere completed by two nitrogen atoms (N3, N3a) [Cd1-N : 2.342(12) Å] of two bpy ligands as the apices and four oxygen atoms (O3, O3a, O3b and O3c) [Cd1-O : 2.304(9) Å] in the equatorial positions; these oxygen atoms come from four bis-bidentate carboxylate groups of four different tp ligands. The Cd2 center also lies in a distorted octahedral coordination sphere, and is coordinated by two nitrogen atoms (N1, N2d) [Cd2-N : 2.338(14)–2.366(12) Å] of the other two bpy ligands as the apices and four oxygen atoms

[Cd2-O : 2.231(8)–2.399(10) Å] in the equatorial positions, two (O2, O2c) of which are from two bridging bis-bidentate carboxylate groups of two different tp ligands, and the other two (O4, O4c) belong to a chelating carboxylate group of a tp ligand, whose aromatic ring shows positional disorder over two sites (C15, C16, C17g, C15h, C16h, C17c and C15, C16c, C17h, C15h, C16g, C17; see Figure 4). These two Cd^{II} centers (Cd1, Cd2) as well as Cd2a, an equivalent atom related to the Cd2 center, are bridged to construct a linear trinuclear $\{\text{Cd}_3\text{O}_{12}\text{N}_6\}$ cluster. In this way, the trinuclear $\{\text{Cd}_3\text{O}_{12}\text{N}_6\}$ clusters are interconnected through tp ligands to yield an interesting rectangular sheet

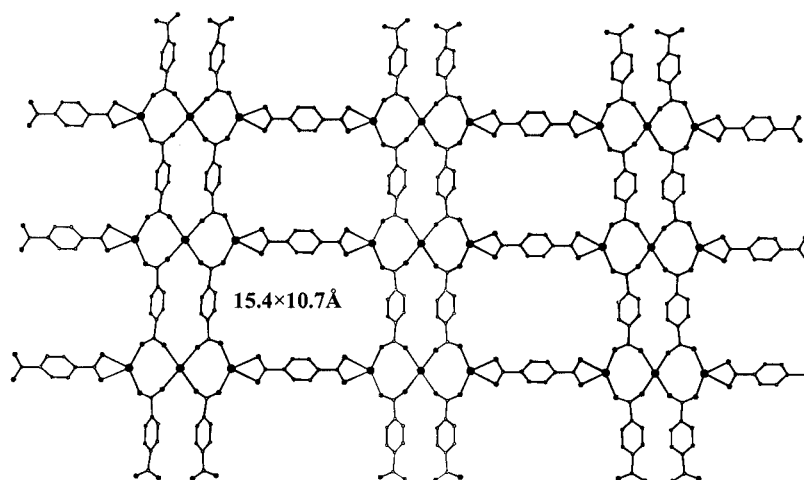


Figure 5. A view of the 2D rectangular $\{\text{Cd}(\text{tp})\}$ sheet subunit with a window of 15.4×10.7 Å in **2**; the hydrogen atoms are omitted for clarity

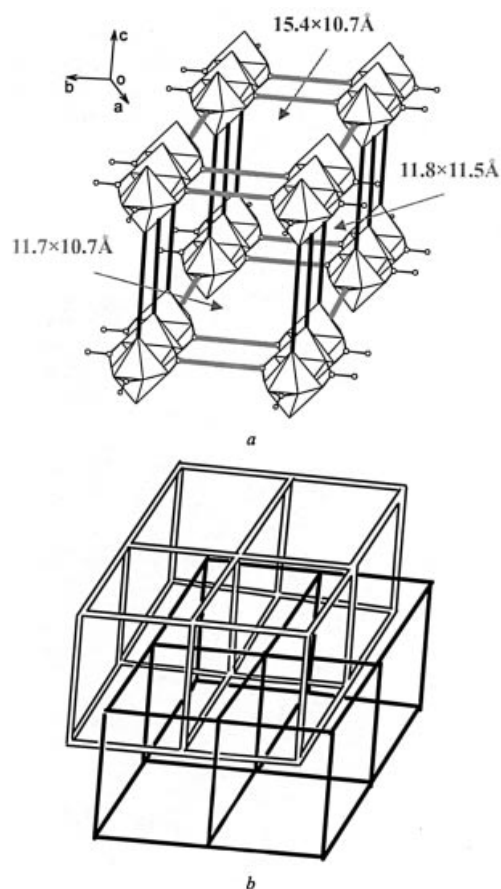


Figure 6. (a) A view depicting a 3D α -Po net topology in **2** assembled by the rectangular sheet subunits and bpy pillars (gray lines indicate the tp struts, black lines represent bpy struts); (b) the twofold interpenetration topology of **2**

with a window of $15.4 \times 10.7 \text{ \AA}$ (Figure 5), which is different from similar reported structures.^[21] The rectangular sheets are further pillared by bpy ligands to form a box-like 3D supramolecular architecture, a topology attributed to the α -Po net (Figure 6a), and the whole crystal structure of **2** exhibits twofold interpenetration (Figure 6b).

The crystal structure of **3** is a 3D porous framework composed of a well-separated host polymer, guest bpy molecules and lattice water molecules. There are four independent seven-coordinate Cd^{II} centers in the building unit of **3**, and the coordination sphere of each seven-coordinate Cd^{II} center is equivalent (Figure 7). In the host polymer, each seven-coordinate Cd^{II} center lies in a distorted pentagonal bipyramidal sphere, completed by two pairs of oxygen donors of two chelating carboxylate groups from two separate bpa ligands and three nitrogen donors from three different bpy ligands, in which two bpa and a bpy ligands are in the equatorial positions with the other two bpy ligands as the apices (Figure 7). Every bpa and bpy ligand links to two Cd^{II} centers through two chelating carboxylate groups and two nitrogen donors, respectively. Due to the angles between two adjacent bpa ligands and between bpa and bpy ligands coordinated to the same Cd^{II} center in the equatorial plane (130.5° and 112.6° , respectively), the Cd^{II} center and the bridging ligands actually form a slightly distorted trigonal-bipyramidal subunit, which has seldom been observed in metal-organic polymers.^[32] In the crystal, these subunits are arranged to generate a honeycomb-like 3D supramolecular architecture, an unprecedented 5-connected borazone $4^6 6^4$ net topology,^[57,58] with giant hexagonal channels about $30.5 \times 24.8 \text{ \AA}$ across (Figure 8). To the best of our knowledge, this structural topology is still very rare

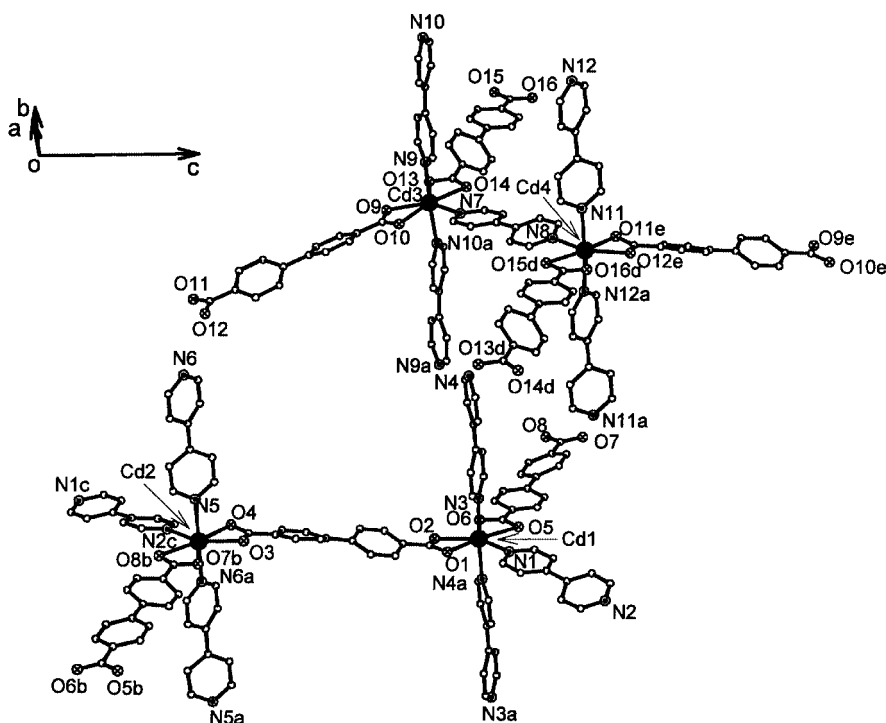


Figure 7. A view of **3** depicting the coordination environment around the Cd^{II} centers; hydrogen atoms, guest bpy and water molecules are omitted for clarity: (a) $x, y - 1, z$; (b) $x - 1, -y - 3/2, z - 1/2$; (c) $x, -y - 3/2, z - 1/2$; (d) $x - 1, y, z$; (e) $x, -y + 1/2, z + 1/2$

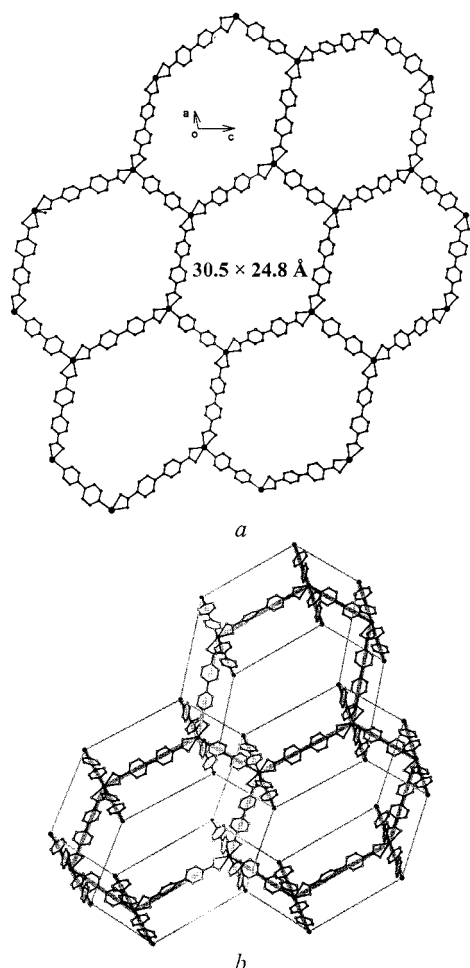


Figure 8. (a) A projective view along the *b* axis showing the honeycomb-like channels with a giant hexagonal cavity of about $30.5 \times 24.8 \text{ \AA}$ in **3**; the hydrogen atoms and guests are omitted for clarity; (b) schematic topology of the 5-connected borazone 4^66^4 net of **3**

in coordination polymer chemistry.^[32,58] Each hexagonal channel has a giant cavity of about $30.5 \times 24.8 \text{ \AA}$, while the actual crystal structure of compound **3** is a fourfold interpenetrating 3D supramolecular architecture (Figure 9). The resulting effective cavities, after removal of encapsulated guests – aqua and bpy molecules – in **3** has a volume of about $2609 \text{ \AA}^3$, which is only 22% of the unit-cell volume.

The local coordination environment around the Cd^{II} centers in **4** is depicted in Figure 10. The two crystallographically distinct Cd^{II} centers (Cd1 , Cd2) are each coordinated in a distorted octahedral sphere by five oxygen donors (O1 , O21 , O22 , O24b and O12a for Cd1 ; O2 , O11 , O22 , O23d and O24d for Cd2) and one nitrogen donor (N1 for Cd1 ; N2c for Cd2), in which the oxygen donors are from the carboxylate groups of four different tp ligands and the nitrogen donor is from a separate bpe ligand. Four different tp ligands bridge two Cd^{II} centers alternately in three different coordination fashions – chelating/bridging bis-bidentate, bis-bidentate and bidentate to form Cd-tp chains along the *a* axis (Figure 11a). Extension of these Cd-tp chains along the *ac* plane therefore gives a novel 2D abatis-like sheet (see b in Figure 11). These adjacent 2D abatis-like

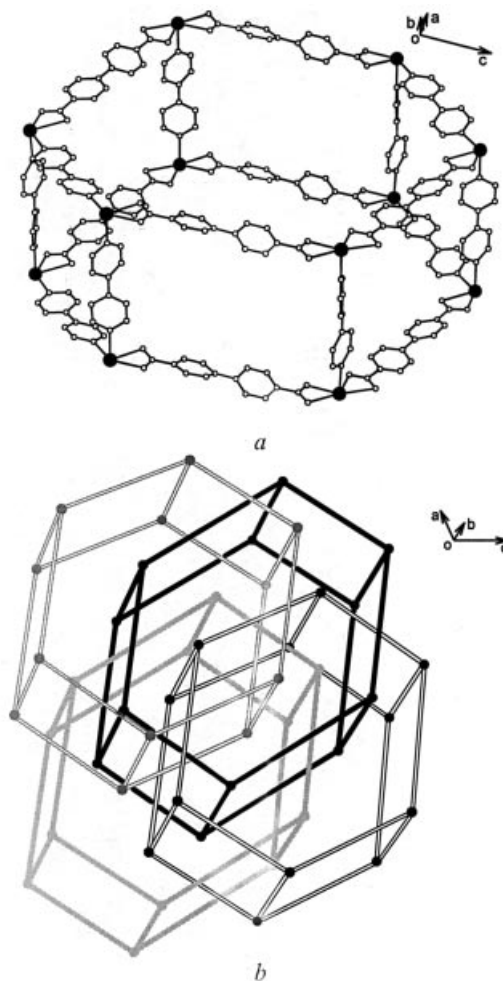


Figure 9. (a) A single hexagonal unit of the 3D honeycomb-like architecture in **3**; (b) the fourfold interpenetrating model of **3**

sheets are further crosslinked in a staggered fashion through bridging bpe ligands to generate an interesting 3D spiral pipe-like structure with a bolt (Figure 12). Although there is no interpenetration or incorporated guest molecule in **4**, the actual crystal structure has an effective void of an only $107 \text{ \AA}^3$, which is 3.5% of the unit cell volume, due to the bolt described above.

Fluorescent Properties

To study the fluorescent properties of these four polymeric solids, the emission spectra of **1–4** were recorded for a polycrystalline sample of each of these materials in the solid state at ambient temperature. Intense fluorescent emissions at 549 and 582 nm ($\lambda_{\text{exc}} = 532 \text{ nm}$) for **1**, 493 nm ($\lambda_{\text{exc}} = 360 \text{ nm}$) for **2**, 413 and 424 nm ($\lambda_{\text{exc}} = 315 \text{ nm}$) for **3** and 350 nm ($\lambda_{\text{exc}} = 220 \text{ nm}$) for **4**, were observed, which can be assigned to ligand-to-metal charge transfer (LMCT) transitions. It is noticeable that compound **2** exhibits a quenching of the fluorescence with $\tau = 5.44 \text{ ns}$. This suggests that **2** may be an excellent candidate for potential photoactive material.

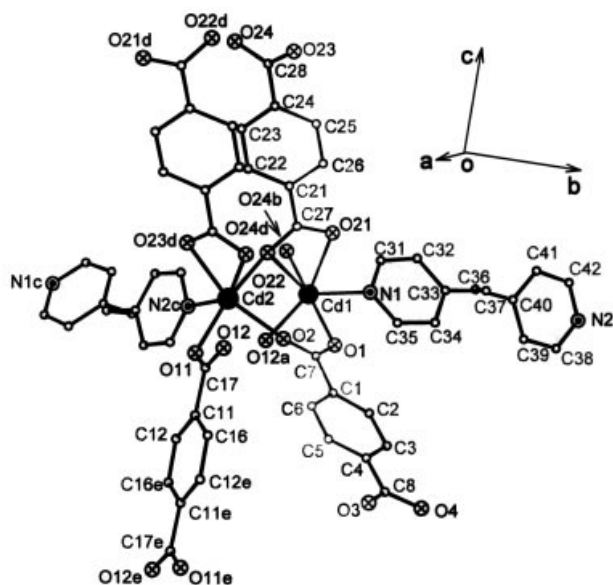


Figure 10. The local coordination of Cd^{II} centers in **4**; the hydrogen atoms are omitted for clarity: (a) $x - 1, y, z$; (b) $-x, -y, -z + 2$; (c) $-x - 3/2, y - 1/2, -z + 3/2$; (d) $-x + 1, -y, -z + 2$; (e) $-x + 1, -y, -z + 1$

Experimental Section

General Remarks: All the syntheses were performed in Parr Teflon-lined stainless steel autoclaves under autogenous pressure. Chemicals were purchased commercially and used as received without further purification. Infrared spectra were recorded on a Magna 750 spectrometer as KBr pellets. The C, H, O and N elemental microanalyses were carried out with a Vario EL III elemental analyzer. Fluorescent data were collected on an Edinburgh FL-FS920 TCSPC system at the Spectroscopy Lab of Fuzhou University, and TGA (thermal gravimetric analysis) was performed under nitrogen with a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ using a TA5200/MDSC2910 system at the Thermal Analysis Lab of Huaqiao University. The pore-volume analysis was performed with the PLATON software package.^[59]

[Cd(tp)(bpp)]_n (1): Compound **1** was synthesized hydrothermally from the reaction of cadmium acetate dihydrate (1.5 mmol), H_2tp (1 mmol), bpp (1.075 mmol), $(\text{Ph}_3\text{PCH}_2\text{Ph})\text{Cl}$ (1 mmol) and water (5 mL) in a molar ratio of 3:2:2.15:1:556 at $200\text{ }^{\circ}\text{C}$ for 4 days. The mixture was then cooled at a rate of about $3.5\text{ }^{\circ}\text{C}\cdot\text{h}^{-1}$ to give a 32% yield of **1** (228.8 mg), based on Cd, as colorless block crystals, which were collected by hand and washed with water and absolute alcohol. $\text{C}_{21}\text{H}_{18}\text{CdN}_2\text{O}_4$ (474.77): calcd. C 53.12, H 3.82, N 5.90, O 13.48; found C 53.39, H 3.32, N 5.43, O 13.67. IR (KBr pellet): $\tilde{\nu} = 3401\text{ cm}^{-1}$ (w, br), 3064 (vw), 2953 (w), 2939 (w), 2860 (w),

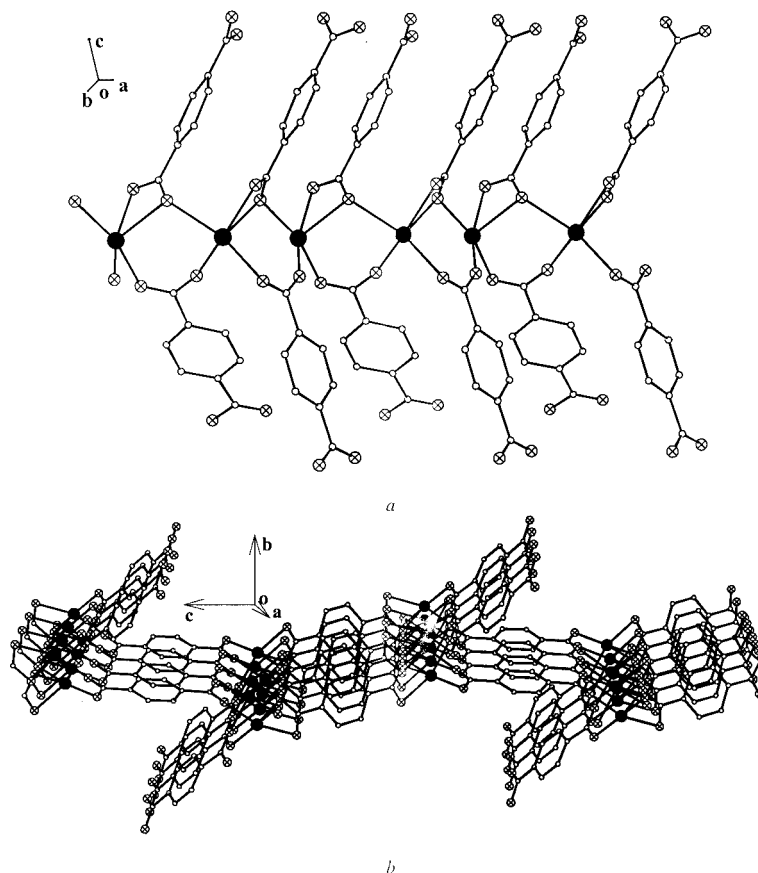


Figure 11. A view showing (a) the Cd-tp chains in **4** extended along the ac plane to generate (b) a novel 2D abatis-like sheet subunit; the hydrogen atoms are omitted for clarity.

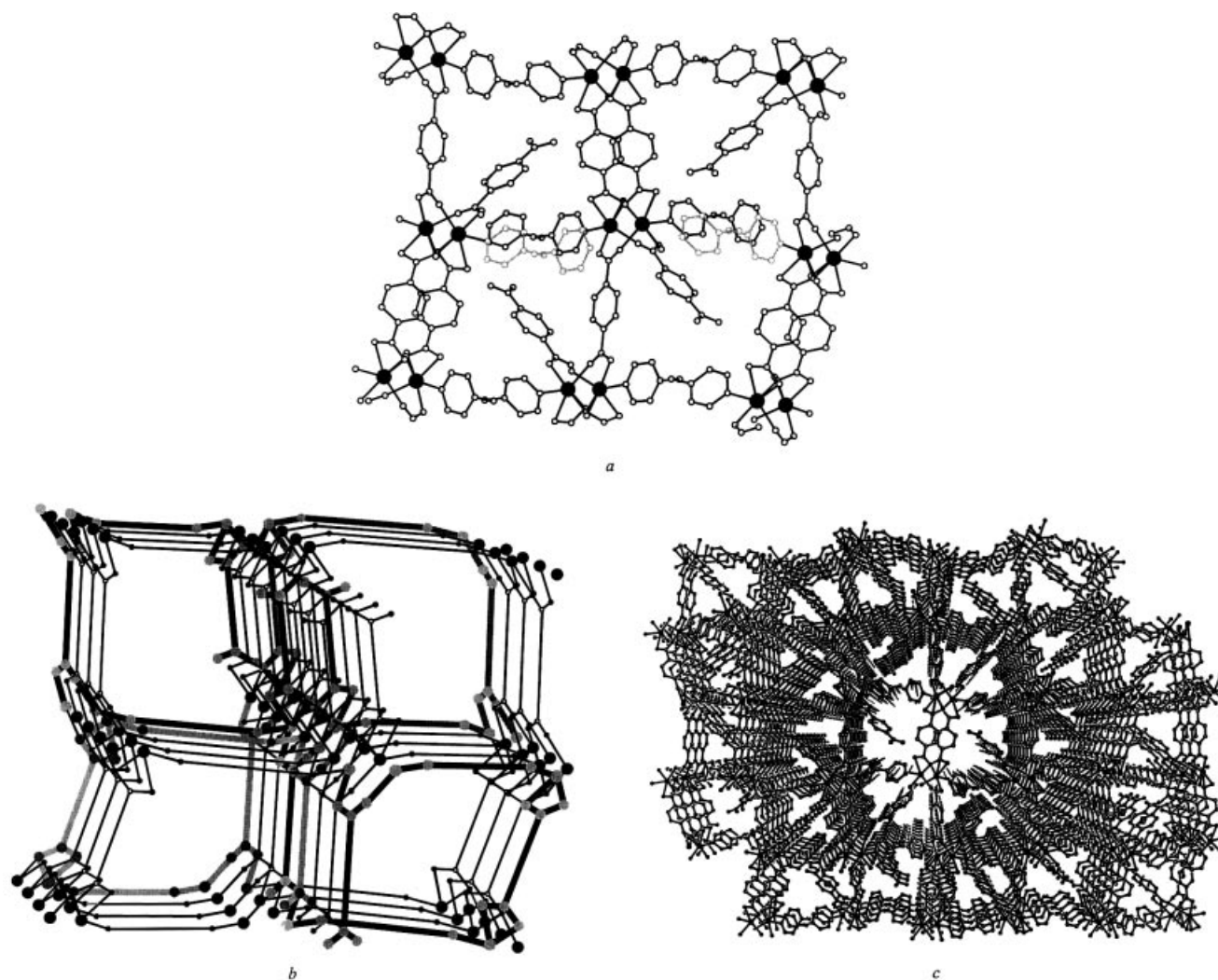


Figure 12. (a) An interesting 3D spiral pipe-like structure with a bolt in **4** constructed by 2D abatis-like sheet subunits with bpe bridging ligands; (b) 3D spiral pipe-like structure motif based on **4**, the bolts are omitted for clarity; (c) perspective view of the 3D architecture in **4** along the *a* axis

Table 1. Crystal parameters, data collections and structure refinements for **1–4**

Compound	1	2	3	4
Formula	C ₂₁ H ₁₈ CdN ₂ O ₄	C ₁₈ H ₁₂ CdN ₂ O ₄	C ₁₂₁ H ₉₈ Cd ₄ N ₁₃ O ₂₃	C ₃₂ H ₂₃ Cd ₂ N ₂ O ₁₀
Molecular mass	474.77	432.69	2551.72	820.32
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	<i>Pbca</i>	<i>C2/m</i>	<i>P2₁/c</i>	<i>P2₁/n</i>
<i>a</i> (Å)	11.9401(0)	20.299(3)	23.2208(0)	6.9896(1)
<i>b</i> (Å)	16.8148(3)	10.720(1)	11.8103(1)	22.6294(1)
<i>c</i> (Å)	20.2743(3)	11.764(2)	45.4670(6)	19.7738(3)
<i>a</i> (°)	90	90	90	90
<i>β</i> (°)	90	110.944(2)	104.516(1)	99.380(1)
<i>γ</i> (°)	90	90	90	90
<i>V</i> (Å ³)	4070.48(9)	2390.6(6)	12071.0(2)	3085.81(7)
<i>Z</i>	8	6	4	4
ρ_{calc} (g·cm ⁻³)	1.549	1.803	1.404	1.766
<i>T</i> (K)	293(2)	293(2)	293(2)	293(2)
μ (cm ⁻¹)	1.101	1.396	0.768	1.440
λ (Mo- <i>Kα</i>) (Å)	0.71073	0.71073	0.71073	0.71073
Collected reflections	14577	3808	35409	10386
Independent reflections	3600	2227	21219	5360
Observed reflections	2581 (>2 σI)	1215 (>2 σI)	13274 (>2 σI)	4468 (>2 σI)
<i>R</i> _{int}	0.0354	0.0554	0.0400	0.0232
<i>R</i> ^[a]	0.0306	0.0720	0.0725	0.0352
<i>R</i> _w ^[b] [<i>c</i>]	0.0710	0.1604	0.2014	0.0875

[a] $R = (F_o - F_c)/F_o$. [b] $R_w = \{w[(F_o^2 - F_c^2)/w[(F_o^2)^2]]^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.

1957 (vw), 1709 (w), 1616 (vs), 1556 (vs), 1504 (s), 1429 (s), 1385 (vs), 1296 (m), 1225 (m), 1182 (w), 1074 (w,sh), 1026 (w,sh), 889 (w), 839 (s), 810 (m), 777 (w), 752 (vs), 729 (m), 613 (m), 577 (m), 528 (w), 511 (w), 480 (m), 451 (w).

[Cd(tp)(bpy)]_n (2): Similar to the preparation of **1**, the hydrothermal reaction of cadmium acetate dihydrate (1.5 mmol), H₂tp (1 mmol), bpy (1 mmol), hexamethylenetetraamine (1 mmol) and water (5 mL) in a molar ratio of 3:2:2:2:556 was performed at 200 °C for 4 days, then the reactant was cooled to a rate of about 3.5 °C·h⁻¹ to give about a 10% yield of **2** (64.8 mg), based on Cd, as brown block crystals, which were separated by hand from the reaction mixture and washed with water and absolute alcohol. The sample was allowed to dry in air and was found to be indefinitely stable. C₁₈H₁₂CdN₂O₄ (432.69): calcd. C 49.96, H 2.80, N 6.47, O 14.79; found C 49.77, H 2.41, N 6.31, O 14.48. IR (KBr pellet): $\tilde{\nu}$ = 3419 cm⁻¹ (w, br), 3055 (w), 1603 (m), 1566 (vs), 1491 (w), 1400 (s), 1375 (s), 1221 (m), 1076 (m), 1043 (w), 1014 (m), 887 (vw), 823 (m), 806 (m), 744 (m), 727 (w), 631 (m), 509 (w).

[{Cd₄(bpa)₄(bpy)₆·(bpy)_{0.5}·7H₂O}]_n (3): Similar to the synthesis of **1**, the hydrothermal reaction of cadmium acetate dihydrate (1.5 mmol), H₂bpa (1 mmol), bpy·2H₂O (1 mmol), NaOC₂H₅ (4 mmol) and H₂O (5 mL) in a molar ratio of 3:2:2:8:556 was performed at 200 °C for 4 days, then the reactant was cooled to a rate

Table 2. Selected bond lengths (Å) for **1–4**

Compound 1 ^[a]			
Cd(1)–O(1)	2.444(3)	Cd(1)–O(4a)	2.254(3)
Cd(1)–O(2)	2.271(3)	Cd(1)–N(1)	2.295(3)
Cd(1)–O(3a)	2.392(3)	Cd(1)–N(2b)	2.295(3)
Compound 2 ^[b]			
Cd(1)–O(3)	2.304(9)	Cd(2)–O(4)	2.399(10)
Cd(1)–N(3)	2.342(12)	Cd(2)–N(1)	2.366(12)
Cd(2)–O(2)	2.231(8)	Cd(2)–N(2d)	2.338(14)
Compound 3 ^[c]			
Cd(1)–O(1)	2.549(2)	Cd(3)–O(9)	2.335(3)
Cd(1)–O(2)	2.337(3)	Cd(3)–O(10)	2.551(3)
Cd(1)–O(5)	2.617(3)	Cd(3)–O(13)	2.323(3)
Cd(1)–O(6)	2.288(3)	Cd(3)–O(14)	2.488(3)
Cd(1)–N(1)	2.367(3)	Cd(3)–N(7)	2.380(3)
Cd(1)–N(3)	2.378(3)	Cd(3)–N(9)	2.378(3)
Cd(1)–N(4a)	2.351(3)	Cd(3)–N(10a)	2.378(3)
Cd(2)–O(3)	2.338(3)	Cd(4)–O(11e)	2.473(3)
Cd(2)–O(4)	2.580(3)	Cd(4)–O(12e)	2.363(3)
Cd(2)–O(7b)	2.342(3)	Cd(4)–O(15d)	2.589(3)
Cd(2)–O(8b)	2.528(3)	Cd(4)–O(16d)	2.268(3)
Cd(2)–N(2c)	2.364(3)	Cd(4)–N(8)	2.361(3)
Cd(2)–N(5)	2.360(3)	Cd(4)–N(11)	2.371(3)
Cd(2)–N(6a)	2.392(4)	Cd(4)–N(12a)	2.377(3)
Compound 4 ^[d]			
Cd(1)–O(1)	2.262(3)	Cd(2)–O(2)	2.177(4)
Cd(1)–O(12a)	2.192(3)	Cd(2)–O(11)	2.214(3)
Cd(1)–O(21)	2.415(3)	Cd(2)–O(22)	2.464(3)
Cd(1)–O(22)	2.395(3)	Cd(2)–O(23d)	2.304(3)
Cd(1)–O(24b)	2.453(3)	Cd(2)–O(24d)	2.449(3)
Cd(1)–N(1)	2.282(4)	Cd(2)–N(2c)	2.278(4)

^[a] a: $x, -y + 1/2, z + 1/2$; b: $x - 1, y, z$. ^[b] d: $x, y, z - 1$. ^[c] a: $x, y - 1, z$; b: $x - 1, -y - 3/2, z - 1/2$; c: $x, -y - 3/2, z - 1/2$; d: $x - 1, y, z$; e: $x, -y + 1/2, z + 1/2$. ^[d] a: $x - 1, y, z$; b: $-x, -y, -z + 2$; c: $-x - 3/2, y - 1/2, -z + 3/2$; d: $-x + 1, -y, -z + 2$.

Table 3. Selected bond angles (°) for **1–4**^[a]

Compound 1			
O(4a)–Cd(1)–O(2)	113.25(12)	N(1)–Cd(1)–O(3a)	83.77(12)
O(4a)–Cd(1)–N(1)	138.51(12)	N(2b)–Cd(1)–O(3a)	105.46(15)
O(2)–Cd(1)–N(1)	105.72(12)	O(4a)–Cd(1)–O(1)	103.29(11)
O(4a)–Cd(1)–N(2b)	94.13(13)	O(2)–Cd(1)–O(1)	55.33(10)
O(2)–Cd(1)–N(2b)	91.62(11)	N(1)–Cd(1)–O(1)	87.10(11)
N(1)–Cd(1)–N(2b)	98.57(12)	N(2b)–Cd(1)–O(1)	146.54(11)
O(4a)–Cd(1)–O(3a)	54.75(12)	O(3a)–Cd(1)–O(1)	107.94(14)
O(2)–Cd(1)–O(3a)	159.19(15)		
Compound 2			
O(3a)–Cd(1)–O(3)	180.0(5)	O(2c)–Cd(2)–O(2)	128.7(6)
O(3a)–Cd(1)–O(3b)	104.0(5)	O(2c)–Cd(2)–N(2d)	94.1(3)
O(3)–Cd(1)–O(3b)	76.0(5)	O(2)–Cd(2)–N(2d)	94.1(3)
O(3a)–Cd(1)–O(3c)	76.0(5)	O(2c)–Cd(2)–N(1)	83.4(3)
O(3)–Cd(1)–O(3c)	104.0(5)	O(2)–Cd(2)–N(1)	83.4(3)
O(3b)–Cd(1)–O(3c)	180.0(5)	N(2d)–Cd(2)–N(1)	173.9(4)
O(3a)–Cd(1)–N(3a)	96.7(3)	O(2c)–Cd(2)–O(4)	140.2(4)
O(3)–Cd(1)–N(3a)	83.3(3)	O(2)–Cd(2)–O(4)	89.5(4)
O(3b)–Cd(1)–N(3a)	96.7(3)	N(2d)–Cd(2)–O(4)	93.9(4)
O(3c)–Cd(1)–N(3a)	83.3(3)	N(1)–Cd(2)–O(4)	91.6(4)
O(3a)–Cd(1)–N(3)	83.3(3)	O(2c)–Cd(2)–O(4c)	89.5(4)
O(3)–Cd(1)–N(3)	96.7(3)	O(2)–Cd(2)–O(4c)	140.2(4)
O(3b)–Cd(1)–N(3)	83.3(3)	N(2d)–Cd(2)–O(4c)	93.9(4)
O(3c)–Cd(1)–N(3)	96.7(3)	N(1)–Cd(2)–O(4c)	91.6(4)
N(3a)–Cd(1)–N(3)	180.0(6)	O(4)–Cd(2)–O(4c)	51.0(5)
Compound 3			
O(6)–Cd(1)–O(2)	87.46(9)	O(13)–Cd(3)–O(9)	87.89(11)
O(6)–Cd(1)–N(4a)	89.55(10)	O(13)–Cd(3)–N(9)	86.18(11)
O(2)–Cd(1)–N(4a)	93.17(10)	O(9)–Cd(3)–N(9)	96.95(12)
O(6)–Cd(1)–N(1)	136.80(9)	O(13)–Cd(3)–N(7)	135.75(10)
O(2)–Cd(1)–N(1)	135.72(9)	O(9)–Cd(3)–N(7)	136.32(10)
N(4a)–Cd(1)–N(1)	89.24(11)	N(9)–Cd(3)–N(7)	89.23(11)
O(6)–Cd(1)–N(3)	91.98(10)	O(13)–Cd(3)–N(10a)	95.33(12)
O(2)–Cd(1)–N(3)	90.43(11)	O(9)–Cd(3)–N(10a)	88.05(12)
N(4a)–Cd(1)–N(3)	176.15(11)	N(9)–Cd(3)–N(10a)	174.83(12)
N(1)–Cd(1)–N(3)	87.22(11)	N(7)–Cd(3)–N(10a)	86.24(12)
O(6)–Cd(1)–O(1)	140.18(9)	O(13)–Cd(3)–O(14)	52.55(11)
O(2)–Cd(1)–O(1)	53.06(9)	O(9)–Cd(3)–O(14)	139.60(11)
N(4a)–Cd(1)–O(1)	96.79(9)	O(9)–Cd(3)–O(10)	53.37(10)
N(1)–Cd(1)–O(1)	82.74(9)	N(9)–Cd(3)–O(10)	94.09(10)
N(3)–Cd(1)–O(1)	84.28(9)	N(7)–Cd(3)–O(10)	83.14(10)
O(6)–Cd(1)–O(5)	52.50(10)	N(10a)–Cd(3)–O(10)	87.84(10)
O(2)–Cd(1)–O(5)	139.87(10)	O(14)–Cd(3)–O(10)	166.15(11)
N(4a)–Cd(1)–O(5)	84.88(11)	O(13)–Cd(3)–C(55)	27.19(13)
N(1)–Cd(1)–O(5)	84.39(9)	O(9)–Cd(3)–C(55)	114.91(13)
N(3)–Cd(1)–O(5)	93.26(11)	N(9)–Cd(3)–C(55)	86.27(13)
O(1)–Cd(1)–O(5)	167.00(10)	N(7)–Cd(3)–C(55)	108.61(13)
O(3)–Cd(2)–O(7b)	88.11(11)	N(10a)–Cd(3)–C(55)	92.82(13)
O(3)–Cd(2)–N(5)	93.18(12)	O(14)–Cd(3)–C(55)	25.41(13)
O(7b)–Cd(2)–N(5)	96.02(13)	O(10)–Cd(3)–C(55)	168.25(13)
O(3)–Cd(2)–N(2c)	136.74(10)	O(16d)–Cd(4)–N(8)	136.92(10)
O(7b)–Cd(2)–N(2c)	134.84(10)	O(16d)–Cd(4)–O(12e)	83.70(11)
N(5)–Cd(2)–N(2c)	87.84(12)	N(8)–Cd(4)–O(12e)	139.16(11)
O(3)–Cd(2)–N(6a)	87.89(12)	O(16d)–Cd(4)–N(11)	91.96(12)
O(7b)–Cd(2)–N(6a)	90.19(13)	N(8)–Cd(4)–N(11)	87.73(12)
N(5)–Cd(2)–N(6a)	173.72(13)	O(12e)–Cd(4)–N(11)	96.31(13)
N(2c)–Cd(2)–N(6a)	87.15(13)	O(16d)–Cd(4)–N(12a)	91.54(12)
O(3)–Cd(2)–O(8b)	140.35(10)	N(8)–Cd(4)–N(12a)	86.32(12)
O(7b)–Cd(2)–O(8b)	52.31(10)	O(12e)–Cd(4)–N(12a)	89.02(13)
N(5)–Cd(2)–O(8b)	89.43(12)	N(11)–Cd(4)–N(12a)	173.92(13)
N(2c)–Cd(2)–O(8b)	82.87(10)	O(16d)–Cd(4)–O(11e)	136.69(11)
N(6a)–Cd(2)–O(8b)	93.69(12)	N(8)–Cd(4)–O(11e)	86.23(10)
O(3)–Cd(2)–O(4)	51.92(11)	O(12e)–Cd(4)–O(11e)	53.00(12)
O(7b)–Cd(2)–O(4)	139.79(11)	N(11)–Cd(4)–O(11e)	93.65(11)
N(5)–Cd(2)–O(4)	90.99(11)	N(12a)–Cd(4)–O(11e)	87.21(10)
N(2c)–Cd(2)–O(4)	84.83(10)	O(16d)–Cd(4)–O(15d)	52.81(11)
N(6a)–Cd(2)–O(4)	84.80(11)	N(8)–Cd(4)–O(15d)	84.23(10)
O(8b)–Cd(2)–O(4)	167.66(10)	O(12e)–Cd(4)–O(15d)	136.51(11)
N(9)–Cd(3)–O(14)	89.06(12)	N(11)–Cd(4)–O(15d)	86.33(11)

Table 3. (Continued)

N(7)–Cd(3)–O(14)	83.42(10)	N(12a)–Cd(4)–O(15d)	91.83(10)
N(10a)–Cd(3)–O(14)	87.95(13)	O(11e)–Cd(4)–O(15d)	170.45(11)
O(13)–Cd(3)–O(10)	141.07(11)		
Compound 4			
O(12a)–Cd(1)–O(1)	87.38(15)	O(2)–Cd(2)–O(23d)	157.81(18)
O(12a)–Cd(1)–N(1)	113.42(15)	O(11)–Cd(2)–O(23d)	100.56(14)
O(1)–Cd(1)–N(1)	88.13(14)	N(2c)–Cd(2)–O(23d)	92.27(13)
O(12a)–Cd(1)–O(22)	105.45(13)	O(2)–Cd(2)–O(24d)	103.33(17)
O(1)–Cd(1)–O(22)	103.42(13)	O(11)–Cd(2)–O(24d)	100.92(13)
N(1)–Cd(1)–O(22)	139.91(12)	N(2c)–Cd(2)–O(24d)	146.80(12)
O(12a)–Cd(1)–O(21)	159.46(13)	O(23d)–Cd(2)–O(24d)	55.29(10)
O(1)–Cd(1)–O(21)	100.01(13)	O(2)–Cd(2)–O(22)	82.37(14)
N(1)–Cd(1)–O(21)	86.14(12)	O(11)–Cd(2)–O(22)	165.52(13)
O(22)–Cd(1)–O(21)	54.28(10)	N(2c)–Cd(2)–O(22)	80.89(12)
O(12a)–Cd(1)–O(24b)	85.80(12)	O(23d)–Cd(2)–O(22)	91.86(11)
O(1)–Cd(1)–O(24b)	165.57(13)	O(24d)–Cd(2)–O(22)	92.24(10)
N(1)–Cd(1)–O(24b)	82.95(12)	O(2)–Cd(2)–C(28d)	131.05(18)
O(22)–Cd(1)–O(24b)	90.66(10)	O(11)–Cd(2)–C(28d)	103.75(14)
O(21)–Cd(1)–O(24b)	90.72(11)	N(2c)–Cd(2)–C(28d)	118.83(14)
O(2)–Cd(2)–O(11)	88.69(17)	O(23d)–Cd(2)–C(28d)	27.13(12)
O(2)–Cd(2)–N(2c)	107.81(18)	O(24d)–Cd(2)–C(28d)	28.25(11)
O(11)–Cd(2)–N(2c)	91.12(14)	O(22)–Cd(2)–C(28d)	90.70(11)

[a] See footnotes to Table 2 for symmetry operations for each compound.

of about 3.5 °C·h^{−1}. The resulting primrose needle crystals were separated by hand from the reaction mixture and washed with water and absolute alcohol to give about a 39% yield of **1** (373.0 mg) based on Cd. C₁₂₁H₉₈Cd₄N₁₃O₂₃ (2551.7): calcd. C 56.95, H 3.87, N 7.14, O 14.42; found C 56.92, H 2.97, N 7.17, O 14.18. FT-IR (KBr pellet): $\tilde{\nu}$ = 3390 cm^{−1} (s), 3082 (w), 3055 (w), 1942 (w), 1585 (s), 1539 (s), 1489 (m), 1385 (s), 1219 (s), 1176 (w), 1105 (w), 1074 (m), 1043 (w), 1005 (s), 833 (s), 806 (s), 775 (s), 764 (s), 729 (w), 702 (w), 677 (m), 629(s), 567 (w), 492 (m).

[Cd₂{(Htp)(tp)_{1.5}(bpe)}_n (**4**): Similar to the synthesis of **1**, the hydrothermal reaction of cadmium acetate dihydrate (1.5 mmol), H₂tp (1 mmol), bpe (1 mmol), (Ph₃PCH₂Ph)Cl (0.5 mmol) and water (5 mL) in a molar ratio of 3:2:2:1:556 was performed at 200 °C for 4 days, then the reactant was cooled at a rate of about 3.5 °C·h^{−1}. The resulting colorless crystals were separated by hand from the reaction mixture and then washed with water and absolute alcohol to give about a 37% yield of **4** (227.2 mg) based on Cd. C₃₂H₂₃Cd₂N₂O₁₀ (820.32): calcd. C 46.85, H 2.83, N 3.41, O 19.50; found C 46.78, H 2.12, N 3.51, O 19.72. IR (KBr pellet): $\tilde{\nu}$ = 3051 cm^{−1} (vw), 2929 (vw), 2617 (vw), 2480 (vw), 1954 (vw), 1705 (s), 1610 (vs), 1574 (vs), 1551 (vs), 1504 (s), 1394 (vs), 1313 (m), 1242 (s), 1111 (m), 1072 (m), 1016 (m), 881 (w), 831 (m), 777 (m), 735 (s), 677 (w), 633(w), 544 (m), 513 (m), 445 (w).

Crystallographic Studies: Intensity data for the four compounds were collected at 293(2) K on a Siemens Smart CCD area-detector diffractometer with Mo-K α radiation (λ = 0.71073 Å) and a graphite monochromator using the ω -scan mode. Data reductions and absorption corrections were performed with the SMART and SADABS software packages, respectively. The structures were solved by direct methods using SHELXS-97^[60] and were refined by full-matrix least-squares methods using SHELXL-97.^[61] Anisotropic displacement parameters were refined for all non-hydrogen atoms except for the disordered benzene ring of tp molecules. No attempt was made to locate the hydrogen atoms of water and disordered atoms; the other hydrogen atoms were added in the riding model and not refined. Final R = (F_o − F_c)/ F_o , R_w = $\{w[(F_o^2 - F_c^2)]/w$

$[(F_o^2)^2]\}^{1/2}$, with $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ [where $P = (F_o^2 + 2F_c^2)/3$]. The structure reliability factors for **2** and **3** were not satisfactory (R = 0.0720 and 0.0725, respectively), probably as a result of the presence of disordered tp molecules and guest water and not refined. The crystallographic data are summarized in Table 1, and selected bond lengths and bond angles of the three compounds are listed in Tables 2 and 3, respectively.

CCDC-224384 to -224387 (for compounds **1–4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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