

Coordination assemblies of the Cd^{II}–BDC/bpt mixed-ligand system: positional isomeric effect, structural diversification and luminescent properties†

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To further systematically investigate the influence of the positional isomeric ligands on the structures and properties of transition metal complexes, we synthesized six Cd(II) complexes with three positional isomeric dipyridyl ligands (4,4'-bpt, 3,4'-bpt and 3,3'-bpt) and three positional isomeric phenyl dicarboxylate anions (*p*-BDC, *m*-BDC and *o*-BDC), namely, [Cd₃(*p*-BDC)₃(4,4'-bpt)₂(H₂O)₅]·H₂O (**1**), [Cd(*p*-HBDC)(*p*-BDC)_{0.5}(3,4'-bpt)] (**2**), [Cd₄(*p*-BDC)₄(3,3'-bpt)₄]·9H₂O (**3**), [Cd(*m*-BDC)(3,3'-bpt)(H₂O)]·2H₂O (**4**), [Cd(*o*-BDC)(3,3'-bpt)(H₂O)]·(3,3'-bpt)·4H₂O (**5**), [Cd(*o*-BDC)(3,4'-bpt)(H₂O)]·H₂O (**6**). Structural analysis reveals that **1** is composed of a three dimensional (3D) 4-connected net giving an interesting 3-fold interpenetrating architecture. **2** and **3** possess a similar two dimensional (2D) layer structures. **4** presents an infinite one dimensional (1D) tubular-like chain. **5** displays a 2D honeycomb structure consisting of a 1D metal–organic helical chain. **6** exhibits a 2D wave-like layer structure with a (4⁴)-*sql* network. Structural diversities indicate that the nature of isomeric benzene–dicarboxylates and bpt ligands plays crucial roles in modulating structures of these complexes. Intermolecular forces have important effects on the formation and strengthening of the supra-molecular architecture in these complexes. Moreover, the luminescent properties of them have been briefly investigated.

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Introduction

The design and synthesis of coordination polymers, especially Metal–Organic Frameworks (MOFs), have achieved considerable interest in the realm of supra-molecular chemistry and crystal engineering, not only owing to their tremendous potential applications as functional materials,^{1–4} but also because of their intriguing variety of architectures and topologies.^{5–9} Consequently, a series of studies in this field have mainly focused on the design and preparation, as well as the structure–property relationships. At present, significant progress has been achieved.¹⁰ Nevertheless, it is still a great challenge to predict and control the synthesis of final products

at this stage. The following factors, such as the coordination geometry of the nature of organic ligands, the coordination geometry of metal ions, metal–ligand ratio, and the pH value of the solution, *etc.*, which may influence the self-assembly of coordination polymeric frameworks with unique structures and functions.^{11,12}

Among the reported studies, much effort has been focused on the rational design and controlled synthesis of coordination polymers using multidentate ligands such as polycarboxylate and *N*-heterocyclic ligands.¹³ The *N*-heterocyclic ligands are good molecular building blocks and co-ligands for constructing MOFs with interesting structures and properties, which have been widely reported by Yaghi, Snurr, Chen, Du *etc.*^{14,15} Moreover, the introduction of additional polycarboxylate ligands to such synthetic systems can modify the structures and physical properties of the final materials.^{16–18} Recently, we have reported a series of Zn^{II}/Co^{II} coordination polymers with fascinating structures and networks based on the mixed-ligand systems of three positional isomeric *N*-heterocyclic-like ligands: 1*H*-3,5-bis(4-pyridyl)-1,2,4-triazole (4,4'-bpt), 1*H*-3-(3-pyridyl)-5-(4-pyridyl)-1,2,4-triazole (3,4'-bpt), 1*H*-3,5-bis(3-pyridyl)-1,2,4-triazole (3,3'-bpt) (Scheme 1) and three positional isomeric phenyl dicarboxylate anions: 1,2-benzenedicarboxylate anion (*o*-BDC), 1,3-benzenedicarboxylate anion (*m*-BDC), 1,4-benzenedicarboxylate anion (*p*-BDC).¹⁹ The

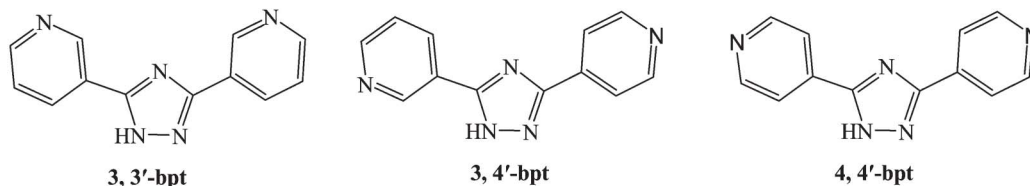
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† Electronic supplementary information (ESI) available: Selected bond distances and angles for the complexes 1–6 (Table S1), selected geometrical parameters of hydrogen bonds in the complexes 2, 3, 5, 6 (Table S2), packing diagrams of 4, 5, and 6 (Fig. S1–S3) and measured and calculated powder X-ray diffraction (PXRD) pattern of all complexes (Fig. S4–S9). CCDC 862815–862820. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ce26905a



Scheme 1 Positional isomeric bridging ligands (3,3'-bpt, 3,4'-bpt, and 4,4'-bpt) used in this work.

phenyl dicarboxylate isomers with different orientation disposition of the carboxylate groups behave as linear (*p*-BDC) or angular (*m*-BDC and *o*-BDC) building blocks, which are further extended *via* the isomeric bpt connectors in different directions. A series of systematic and interesting coordination architectures could be readily produced. However, an investigation for understanding the relationship between the structural diversification and the positional isomeric effect is still challenging.

As an extension of this work, herein, we have successfully synthesized six new Cd(II) complexes: $[\text{Cd}_3(\text{p-BDC})_3(4,4'\text{-bpt})_2(\text{H}_2\text{O})_5]\cdot\text{H}_2\text{O}$ (**1**), $[\text{Cd}(\text{p-HBDC})(\text{p-BDC})_{0.5}(3,4'\text{-bpt})]$ (**2**), $[\text{Cd}_4(\text{p-BDC})_4(3,3'\text{-bpt})_4]\cdot 9\text{H}_2\text{O}$ (**3**), $[\text{Cd}(\text{m-BDC})(3,3'\text{-bpt})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$ (**4**), $[\text{Cd}(\text{o-BDC})(3,3'\text{-bpt})(\text{H}_2\text{O})]\cdot (3,3'\text{-bpt})\cdot 4\text{H}_2\text{O}$ (**5**), $[\text{Cd}(\text{o-BDC})(3,4'\text{-bpt})(\text{H}_2\text{O})]\cdot \text{H}_2\text{O}$ (**6**). The positional isomeric effects of the bpt bridges and carboxylate ligands on framework formation of the coordination complexes were further elucidated. Moreover, the luminescent properties of these compounds have been investigated in detail.

Experimental section

Materials and physical measurements

With the exception of the ligands of 4,4'-bpt, 3,4'-bpt and 3,3'-bpt, which were prepared according to the literature procedure,²⁰ all reagents and solvents for synthesis and analysis were commercially available and used as received. IR spectra were taken on a Perkin-Elmer spectrum One FT-IR spectrometer in the 4000–400 cm^{-1} region with KBr pellets. Elemental analyses for C, H and N were carried out on a Model 2400 II, Perkin-Elmer elemental analyzer. Powder X-ray diffraction (XRD) intensities were measured on a Rigaku D/max diffractometer (Cu $K\alpha$, $\lambda = 1.54056 \text{ \AA}$). The single-crystalline powder samples were prepared by crushing the crystals and scanned from 2–50° with a step of 5° min^{-1} . Calculated patterns of the complexes were generated with PowderCell. Steady state fluorescence measurements were performed using an FL3-P-TCSPEC Fluorescence spectrofluorometer at ambient temperature in the solid-state. TG-DTA tests were performed on a Perkin-Elmer thermal analyzer from room temperature to 800 °C under N_2 atmosphere at a heating rate of 5 °C min^{-1} .

Preparation

$[\text{Cd}_3(\text{p-BDC})_3(4,4'\text{-bpt})_2(\text{H}_2\text{O})_5]\cdot\text{H}_2\text{O}$ (**1**). A mixture containing $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ (154 mg, 0.5 mmol), 4,4'-bpt (112 mg, 0.5

mmol), *p*-H₂BDC (83 mg, 0.5 mmol), NaOH (40 mg, 1 mmol), water (10 mL) and ethanol (3 mL) was sealed in a Teflon-lined stainless steel vessel (23 mL), which was heated at 140 °C for 3 days and then cooled to room temperature at a rate of 5 °C h^{-1} . Colorless block crystals of **1** were obtained and picked out, washed with distilled water and dried in air. Yield: 47% (based on Cd(II)). Anal. calcd. (%) for $\text{C}_{48}\text{H}_{38}\text{Cd}_3\text{N}_{10}\text{O}_{18}$: C, 41.74; H, 2.75; N, 10.14. Found: C, 41.70; H, 2.42; N, 10.28. IR (KBr, cm^{-1}): 3406 (m), 1615 (m), 1568 (vs), 1397 (s), 1145 (w), 1011 (w), 993 (w), 841 (m), 744 (s).

$[\text{Cd}(\text{p-HBDC})(\text{p-BDC})_{0.5}(3,4'\text{-bpt})]$ (**2**). The same synthetic procedure as that for **1** was used except that 4,4'-bpt and the solvent was replaced by 3,4'-bpt and water (12 mL), giving colorless block X-ray-quality crystals of **2** in a 40% yield (based on Cd(II)). Anal. calcd. (%) for $\text{C}_{24}\text{H}_{15}\text{CdN}_5\text{O}_6$: C, 49.41; H, 2.57; N, 12.01. Found: C, 49.23; H, 2.48; N, 12.05. IR (KBr, cm^{-1}): 3067 (m), 1717 (m), 1598 (s), 1557 (vs), 1401 (vs), 1245 (m), 1178 (w), 1150 (w), 1103 (w), 1000 (w), 848 (s), 754 (s), 698 (m).

$[\text{Cd}_4(\text{p-BDC})_4(3,3'\text{-bpt})_4]\cdot 9\text{H}_2\text{O}$ (**3**). The same synthetic procedure as that for **2** was used except that 3,4'-bpt was replaced by 3,3'-bpt, giving colorless block X-ray-quality crystals of **3** in a 68% yield (based on Cd(II)). Anal. calcd. (%) for $\text{C}_{80}\text{H}_{70}\text{Cd}_4\text{N}_{20}\text{O}_{25}$: C, 44.42; H, 3.24; N, 12.96. Found: C, 44.51; H, 3.49; N, 13.05. IR (KBr, cm^{-1}): 3419 (m), 1551 (vs), 1392 (vs), 1188 (w), 1147 (m), 1124 (w), 1045 (w), 987 (m), 844 (s), 749 (s), 693 (m).

$[\text{Cd}(\text{m-BDC})(3,3'\text{-bpt})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$ (**4**). The procedure is similar to the synthesis of **1** by using $\text{CdCl}_2\cdot 2.5\text{H}_2\text{O}$ (114 mg, 0.5 mmol), *m*-H₂BDC (83 mg, 0.5 mmol) and 3,3'-bpt (112 mg, 0.5 mmol), NaOH (40 mg, 1 mmol), water (10 mL) and ethanol (3 mL). Colorless block X-ray-quality crystals of **4** were obtained. Yield: 30% (based on Cd(II)). Anal. calcd. (%) for $\text{C}_{20}\text{H}_{18}\text{CdN}_5\text{O}_7$: C, 43.42; H, 3.26; N, 12.66. Found: C, 43.21; H, 3.49; N, 12.69. IR (KBr, cm^{-1}): 3395 (m), 1612 (vs), 1567 (s), 1385 (s), 1351 (vs), 1149 (w), 1083 (w), 1053 (w), 993 (w), 834 (w), 751 (s), 725 (s), 625 (m).

$[\text{Cd}(\text{o-BDC})(3,3'\text{-bpt})(\text{H}_2\text{O})]\cdot (3,3'\text{-bpt})\cdot 4\text{H}_2\text{O}$ (**5**). The procedure is similar to the synthesis of **1** by using CdCO_3 (86 mg, 0.5 mmol), *o*-H₂BDC (83 mg, 0.5 mmol), 3,3'-bpt (112 mg, 0.5 mmol) and water (12 mL) to provide colorless block X-ray-quality crystals of **5**. Yield: 48% (based on Cd(II)). Anal. calcd. (%) for $\text{C}_{32}\text{H}_{32}\text{CdN}_{10}\text{O}_9$: C, 47.27; H, 3.91; N, 17.23. Found: C, 47.32; H, 4.00; N, 17.29. IR (KBr, cm^{-1}): 3378 (m), 1552 (vs), 1407 (s), 1290 (w), 1148 (m), 1085 (w), 1051 (w), 987 (m), 837 (w), 750 (m), 700 (m).

$[\text{Cd}(\text{o-BDC})(3,4'\text{-bpt})(\text{H}_2\text{O})]\cdot \text{H}_2\text{O}$ (**6**). The procedure is similar to the synthesis of **1** by using $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ (154 mg, 0.5 mmol), *o*-H₂BDC (83 mg, 0.5 mmol), 3,4'-bpt (112 mg, 0.5

mmol), Na₂CO₃ (40 mg, 0.5 mmol), water (10 mL) and ethanol (3 mL). Colorless needle-like X-ray-quality crystals of **6** were obtained. Yield: 60% (based on Cd(II)). Anal. calcd. (%) for C₂₀H₁₅CdN₅O₆: C, 44.96; H, 2.81; N, 13.11. Found: C, 45.04; H, 2.76; N, 13.17. IR (KBr, cm⁻¹): 3516 (m), 1552 (vs), 1413 (s), 1149 (w), 1089 (w), 980 (w), 842 (m), 749 (m), 701 (m), 655 (w).

Crystal structure determination

X-ray single-crystal diffraction data for **1–6** were collected with a Bruker SMART CCD instrument by using graphite monochromatic Mo K α radiation ($\lambda = 0.71073$ Å). The data were collected at 293(2) K, and there was no evidence of crystal decay during data collection. A semiempirical absorption correction was applied using SADABS, and the program SAINT was used for integration of the diffraction profiles.²¹ The structure was solved by direct methods with the program SHELXS-97²² and refined by full-matrix least-squares methods on all F^2 data with SHELXL-97.²³ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms of water molecules were located in a difference Fourier map and refined isotropically in the final refinement cycles. Other hydrogen atoms were placed in calculated positions and refined by using a riding model. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. Further crystallographic data and structural refinement details are summarized in Table 1, and selected bond lengths and bond angles are given in Table S1, ESI†. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center. CCDC reference numbers: 862815–862820 (**1–6**).

Results and discussion

Description of the crystal structures

[Cd₃(*p*-BDC)₃(4,4'-bpt)₂(H₂O)₅]·H₂O (**1**). Single crystal X-ray diffraction analysis reveals that the asymmetric unit of **1**

contains three crystallographically independent Cd atoms, three *p*-BDC ligands, two 4,4'-bpt ligands, five aqua ligands and one lattice water molecule. As illustrated in Fig. 1a, Cd1 and Cd3 are both coordinated by two N atoms from two 4,4'-bpt ligands, and five O atoms from two *p*-BDC ligands and an aqua ligand, to yield a distorted pentagonal bipyramid geometry. While Cd2 adopts a distorted trigonal bipyramid geometry coordinated by five O donors from two *p*-BDC ligands and three aqua ligands. Both carboxylic groups of the *p*-BDC ligands exhibit two types of coordinate modes, as shown in Scheme 2. One is bidentate and chelates to Cd1 or Cd3. The other one is unidentate, which binds to Cd2. Based on these connection modes, adjacent Cd(II) atoms are connected by *p*-BDC ligands to form a Cd(*p*-BDC)_n chain. Such chains are arranged in an interdigitated mode to form supra-molecular layers (Fig. 1b), which are further connected by 4,4'-bpt bridging ligands to generate a novel 3D open framework, as shown in Fig. 1c.

Better insight into this framework can be achieved by topology analysis. On the basis of the connectivity of Cd1 and Cd3 atoms, both of them are viewed to be 4-connected nodes, the *p*-BDC ligands and 4,4'-bpt ligands are considered as linkers, then the 3D structure can be classified as a 4-connected network with (4²·6³·7) topology.^{24a,b} Because of the large void space in the 3D framework, three identical 3D frameworks mutually interpenetrate each other to generate an interesting 3-fold interpenetrating architecture, leaving a small space for the inclusion of solvent molecules (Fig. 1d). This is a new example of a 3-fold interpenetrating framework, which is different from the previous example of reported frameworks showing 3-fold interpenetrating structure.^{24c,d}

[Cd(*p*-HBDC)(*p*-BDC)_{0.5}(3,4'-bpt)] (**2**). When the positional isomeric 3,4'-bpt ligand was used instead of the 4,4'-bpt ligand, a structurally different 2D framework is formed in **2**. As shown in Fig. 2a, the asymmetric unit of **2** consists of one independent Cd(II) atom, one 3,4'-bpt ligand, one protonated *p*-HBDC ligand and a half of *p*-BDC ligand. The Cd(II) ions

Table 1 Crystal data and structure refinement summary for complexes **1–6**

Complex	1	2	3	4	5	6
Empirical formula	C ₄₈ H ₃₈ Cd ₃ N ₁₀ O ₁₈	C ₂₄ H ₁₆ CdN ₅ O ₆	C ₈₀ H ₇₀ Cd ₄ N ₂₀ O ₂₅	C ₂₀ H ₁₉ CdN ₅ O ₇	C ₃₂ H ₃₂ CdN ₁₀ O ₉	C ₂₀ H ₁₅ CdN ₅ O ₆
Formula weight	1380.12	582.83	2161.20	553.80	813.09	533.78
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 1	<i>P</i> 1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	11.175(2)	9.985 (2)	14.495(3)	9.5869(5)	16.931(3)	7.0410(14)
<i>b</i> (Å)	11.499(2)	10.440(2)	16.313(3)	9.7706(6)	9.908(2)	23.337(5)
<i>c</i> (Å)	22.243(4)	11.511(2)	19.838(4)	13.3468(6)	21.471(4)	13.814(4)
α (°)	83.95(3)	93.48(3)	90	75.481(4)	90	90
β (°)	83.06(3)	97.29(3)	107.07(3)	81.145(4)	108.61(3)	116.54(2)
γ (°)	76.05(3)	100.15(3)	90	63.890(5)	90	90
Volume (Å ³)	2745.0(9)	1167.4(4)	4484.1(16)	1085.39(10)	3413.5(12)	2030.7(8)
<i>Z</i>	2	2	2	2	4	4
<i>F</i> (000)	2310	516	3780	556	2870	1064
Reflections collected	7609	4898	6394	3798	4480	2812
Independent reflections	9516 (<i>R</i> _{int} = 0.046)	5217 (<i>R</i> _{int} = 0.018)	7875 (<i>R</i> _{int} = 0.060)	4257 (<i>R</i> _{int} = 0.033)	6148 (<i>R</i> _{int} = 0.069)	3587 (<i>R</i> _{int} = 0.079)
Data/restraints/parameters	9516/33/721	5217/0/337	7875/38/595	4257/10/316	6148/95/469	3579/0/289
Goodness-of-fit on F^2	1.002	1.076	1.181	1.037	0.984	1.282
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.1036 <i>wR</i> ₂ = 0.2605	<i>R</i> ₁ = 0.0318 <i>wR</i> ₂ = 0.0904	<i>R</i> ₁ = 0.0671 <i>wR</i> ₂ = 0.1539	<i>R</i> ₁ = 0.0313 <i>wR</i> ₂ = 0.0763	<i>R</i> ₁ = 0.0685 <i>wR</i> ₂ = 0.1417	<i>R</i> ₁ = 0.1260 <i>wR</i> ₂ = 0.2899
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1225 <i>wR</i> ₂ = 0.2745	<i>R</i> ₁ = 0.0358 <i>wR</i> ₂ = 0.0923	<i>R</i> ₁ = 0.0899 <i>wR</i> ₂ = 0.1631	<i>R</i> ₁ = 0.0372 <i>wR</i> ₂ = 0.0807	<i>R</i> ₁ = 0.1039 <i>wR</i> ₂ = 0.1594	<i>R</i> ₁ = 0.1529 <i>wR</i> ₂ = 0.3007

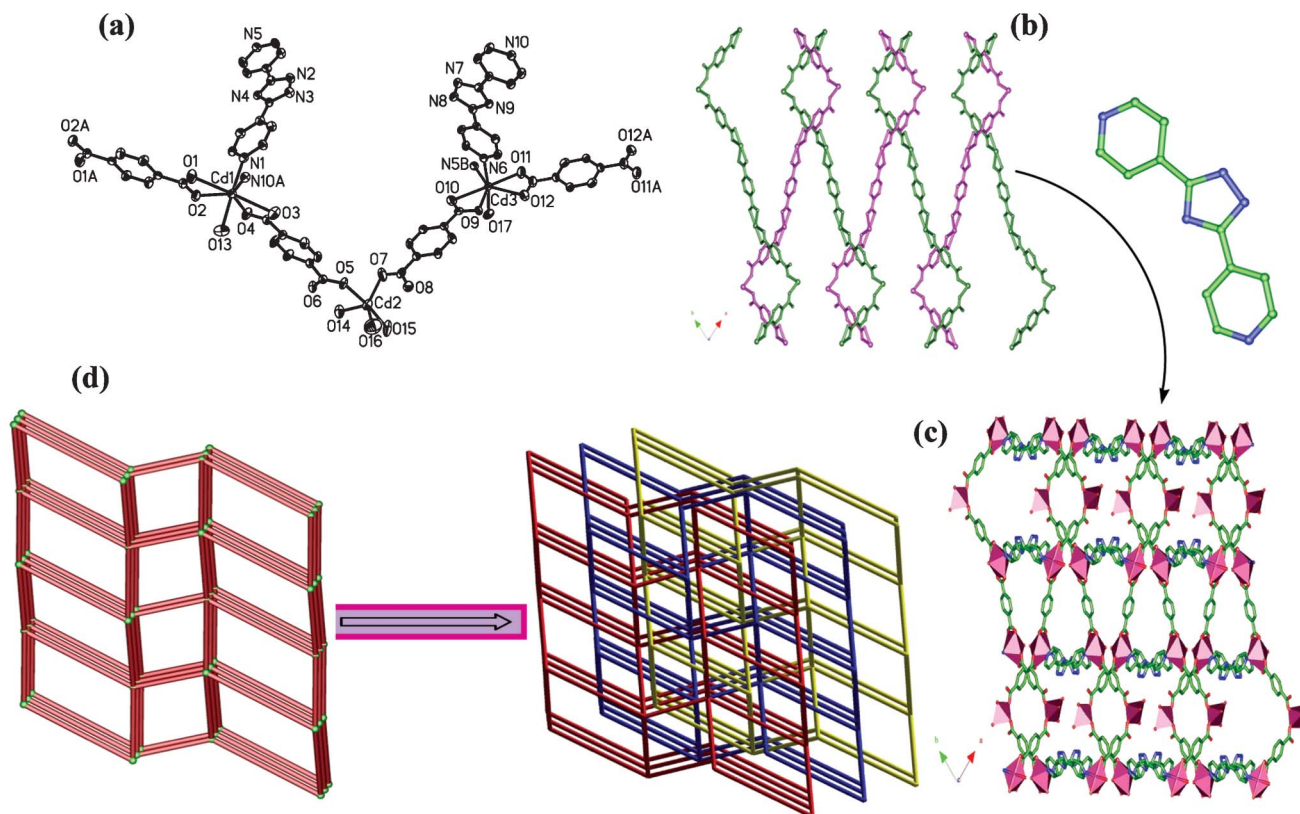
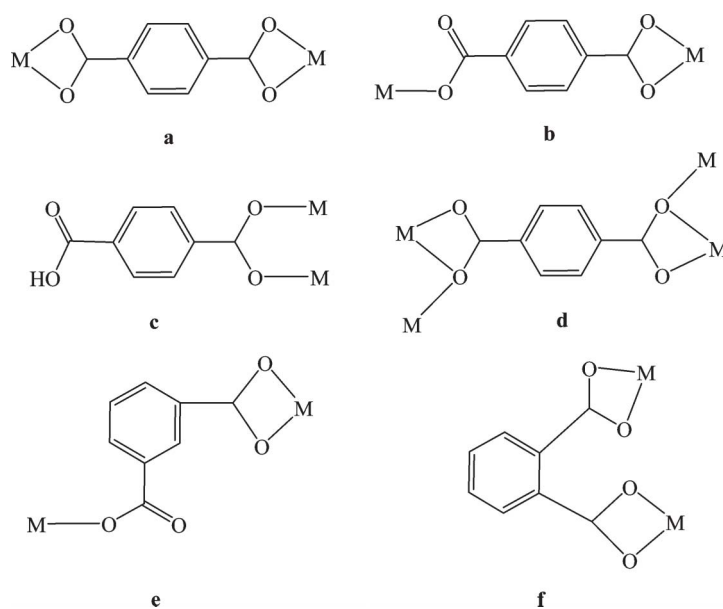


Fig. 1 (a) ORTEP view of **1** showing the coordination environment of the Cd(II) atoms. (b) View of the 1D [Cd(*p*-BDC)]_n chain. (c) The 3D network. (d) Schematic representation of the 3-fold interpenetrating architecture.

exhibit a distorted octahedral geometry, which is provided by four equatorial O atoms from three *p*-BDC ligands, and two apical N atoms from two 3,4'-bpt ligands. The protonated

p-HBDC ligands bridge the adjacent Cd(II) atoms in bridging bidentate mode to give a [Cd(CO₂)₂Cd] dimeric unit with the Cd...Cd distance of 3.993(9) Å. While the adjacent dimeric



Scheme 2 The coordination modes of positional isomeric *p*-BDC, *m*-BDC and *o*-BDC ligands.

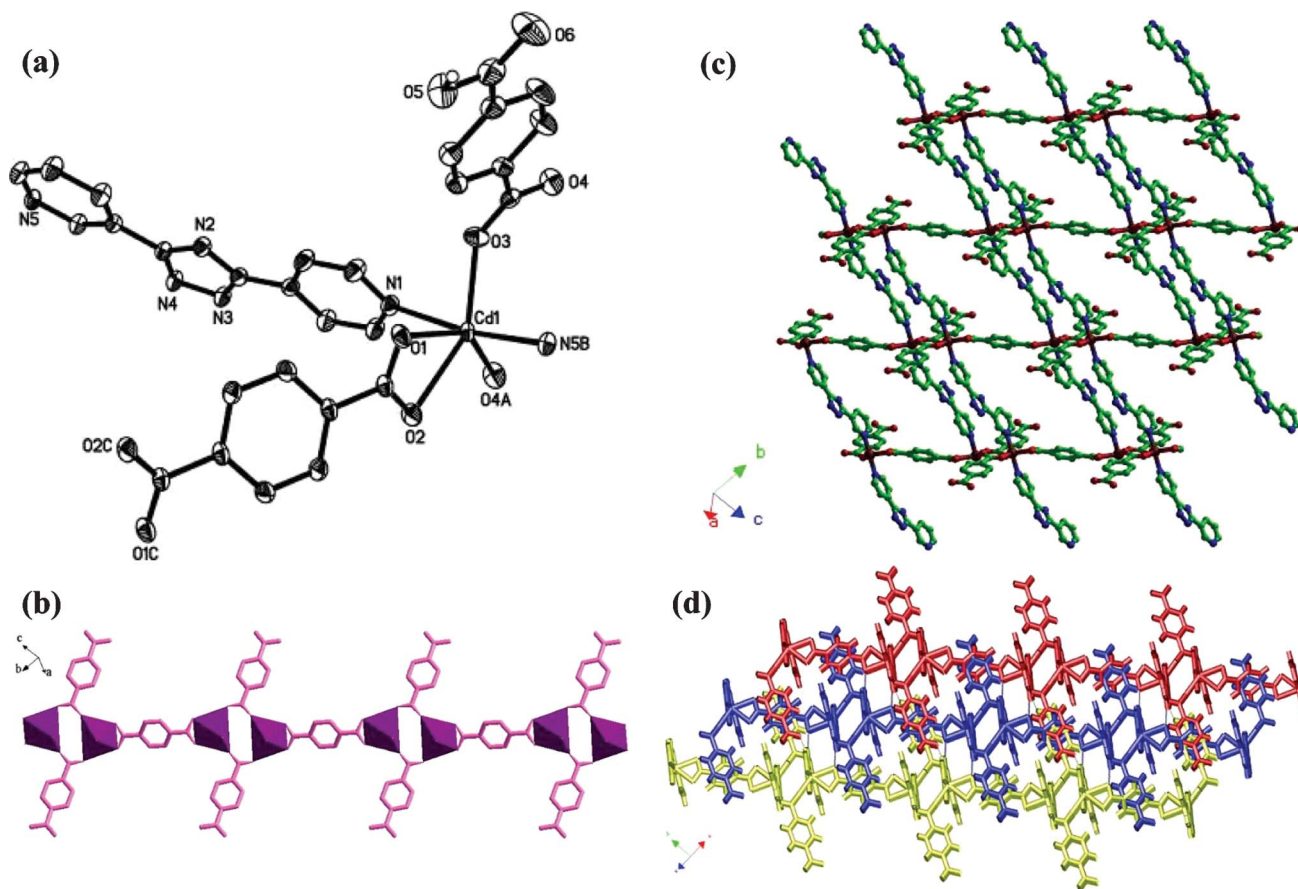


Fig. 2 (a) ORTEP view of **2** showing the coordination environments of the Cd(II) atoms. (b) View of the 1D $[[\text{Cd}(\text{p-BDC})]_n$ chain. (c) The layer architecture. (d) The overall 3D network in the ab plane.

units are linked through the *p*-BDC ligands in bidentate chelating mode, resulting in 1D chains along the *c* axis (Fig. 2b), which are further linked by 3,4'-bpt ligands to generate a 2D layered motif (Fig. 2c). The adjacent 2D layered structures are stacked *via* the hydrogen bonding interactions (Table S2 in ESI†) between the triazole N atoms of the 3,4'-bpt ligands and the coordinated carboxylate O atoms to afford a 3D supra-molecular network (Fig. 2d).

[Cd₄(*p*-BDC)₄(3,3'-bpt)₄·9H₂O (3). When the 3,4'-bpt was replaced by 3,3'-bpt, a new complex **3** was obtained with a 2D (4,5)-connected architecture. As illustrated in Fig. 3a, the asymmetric unit of **3** is composed of two Cd(II) atoms, two *p*-BDC ligands, and two 3,3'-bpt ligands, and four and a half lattice water molecules. Both crystallographically independent Cd(II) ions adopt a similar pentagonal bipyramid geometry, linking to three *p*-BDC ligands at the equatorial plane as well as two 3,3'-bpt ligands located at the apical positions. The Cd1 and Cd2 ions are bridged by μ_2 -bridging O1 and O3B (symmetry codes: B: $x, -y + 1/2, z + 1/2$) to form a binuclear Cd(II) unit with a Cd...Cd distance of 3.9207 Å. As to the *p*-BDC ligands, they present two kinds of coordination features in **3**: one *p*-BDC ligand adopts a μ_2 bridge with chelating mode coordinating to Cd(II) ions, while the other exhibits a chelating-bridging mode coordinating to four other adjacent

Cd(II) ions, which are further stabilized through pairs of 3,3'-bpt ligands (*via syn-syn* mode, as shown in Scheme 3), affording an interesting S-shaped chain along the *c* direction (see Fig. 3b). Adjacent chains are further connected through *p*-BDC ligands to generate a novel 2D layer (Fig. 3c).

From a topological view, the μ_4 -bridging *p*-BDC ligands can be viewed as a 4-connected node, the Cd(II) center is considered as a 5-connected single node, the bpt ligands and μ_2 -bridging *p*-BDC ligands can be viewed as linkers. Then the whole framework of complex **3** can be simplified as a binodal (4,5)-connected framework with $(3^2 \cdot 4^2 \cdot 5^2)(3^2 \cdot 4^3 \cdot 5^4 \cdot 6)$ topology (Fig. 3d). Additionally, the 2D layered structures in a ABAB packing pattern are arranged into a 3D supra-molecular framework by weak $\pi \cdots \pi$ interactions occurring between the adjacent layers. Furthermore, the crystal structure of complex **3** is further stabilized through the hydrogen bonding interactions among the lattice water molecules, coordinated carboxylate O atoms and the triazole N atoms of the 3,4'-bpt ligands (Fig. 3e).

[Cd(*m*-BDC)(3,3'-bpt)(H₂O)]·2H₂O (4). Complex **4** has a 1D infinite tubular-like structure, and the asymmetric unit consists of one Cd(II) ion, one 3,3'-bpt ligand, one *m*-BDC ligand, one aqua ligand, and two lattice water molecules. As shown in Fig. 4a, the Cd(II) center exhibits a distorted

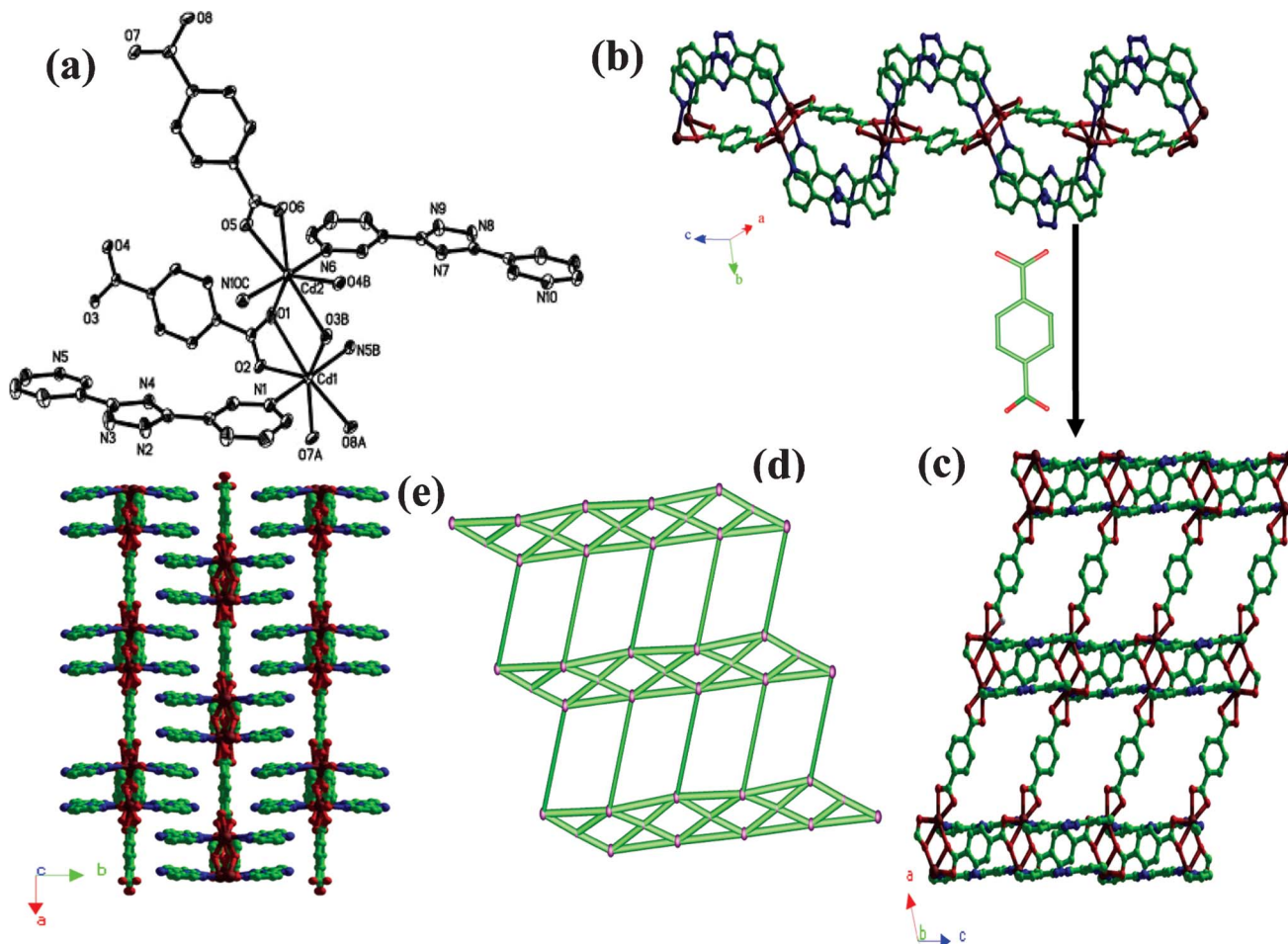
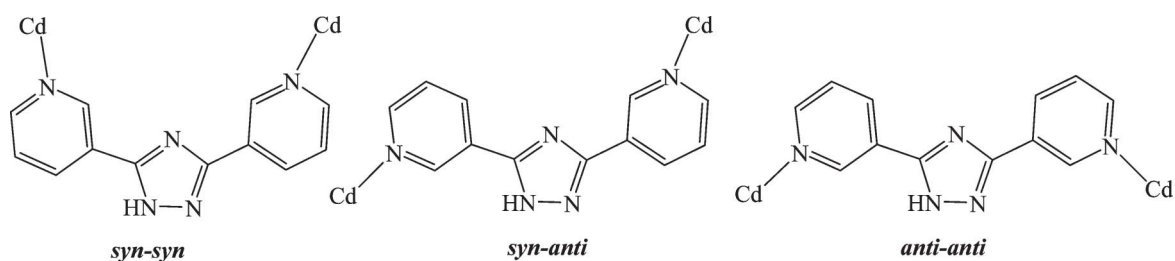


Fig. 3 (a) ORTEP view of **3** showing the coordination environment of the Cd(II) atoms. (b) View of the 1D S-shape chain of $[\text{Cd}_2(p\text{-BDC})(3,3'\text{-bpt})_2]_n$. (c) The 2D layer formed by the $[\text{Cd}_2(p\text{-BDC})(3,3'\text{-bpt})_2]_n$ chain and the *p*-BDC connector. (d) Schematic view of the (4,5)-connected network of **3**. (e) The 3D supra-molecular network showing the interlayer aromatic stacking interaction.

octahedral geometry that is defined by four O atoms from one aqua ligand and two different *m*-BDC ligands with dicarboxylate groups adopting bidentate chelating and monodentate coordination mode and two N atoms from two 3,3'-bpt ligands. Two independent 3,3'-bpt ligands present *syn-syn* mode connect Cd(II) cations giving closed $[\text{Cd}(\text{bpt})_2\text{Cd}]$ loops with the Cd...Cd distance of 8.519(2) Å, which are infinitely extended by *m*-BDC ligands to afford a 1D metal-organic tubular framework (Fig. 4b).

Although the structure of **4** has definite tubular-like geometry, the topological type is in fact that of a ladder-like network (Fig. 4c). Analysis of the crystal packing reveals that the *m*-BDC ligands have weak $\pi\cdots\pi$ stacking contacts, occurring between the benzene rings. As a result, the 1D chains in an parallel arrangement are further extended *via* the weak $\pi\cdots\pi$ stacking interactions to form 2D supramolecular layers. Furthermore, $\pi\cdots\pi$ stacking interactions are also observed between the neighboring 3,3'-bpt segments in the



Scheme 3 Coordination modes of 3,3'-bpt ligands used in the construction of coordination polymer frameworks.

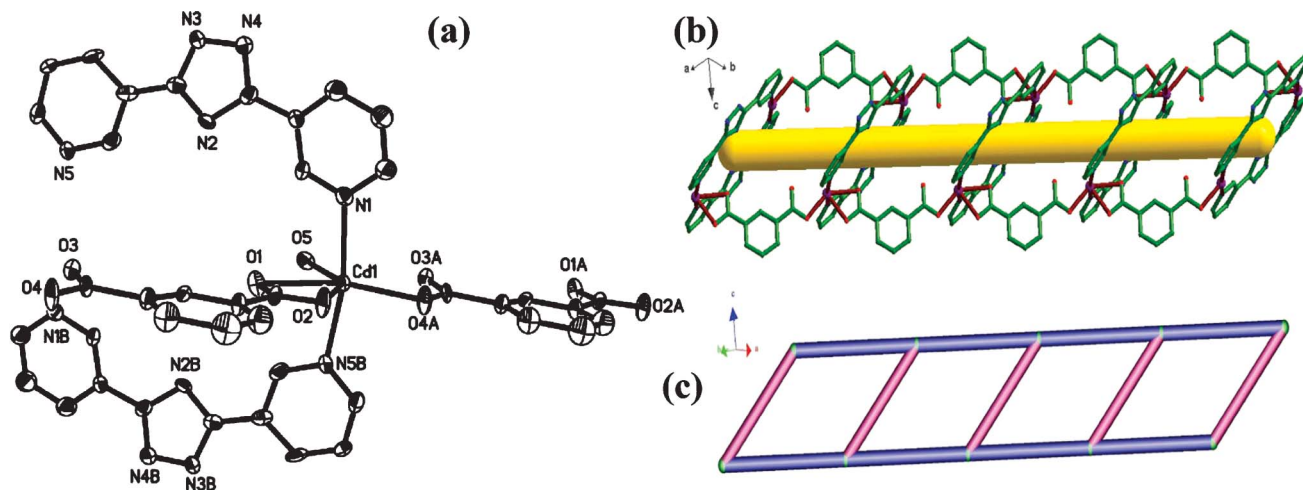


Fig. 4 (a) ORTEP view of **4** showing the coordination environments of the Cd(II) atoms. (b) View of the 1D tubular-like structure. (c) The ladder-like network.

adjacent layers, giving a 3D supra-molecular architecture (Fig. S1 in ESI†). In addition, the lattice water molecules are located at the interspace between such parallel 3D networks, with no significant secondary interaction being observed.

[Cd(*o*-BDC)(3,3'-bpt)(H₂O)]·(3,3'-bpt)·4H₂O (5**).** Complex **5** crystallizes in the monoclinic space group $P2_1/n$ and it has a 2D infinite honeycomb-like structure. The asymmetric unit consists of one Cd ion, one *o*-BDC ligand, one 3,3'-bpt ligand, one aqua ligand, four lattice water molecules, and one uncoordinated 3,3'-bpt ligand. As illustrated in Fig. 5a, the Cd(II) center exhibits a distorted pentagonal bipyramid, surrounded by five O atoms from one aqua ligand and two different *o*-BDC ligands, and two N atoms from two 3,3'-bpt ligands. In **5**, the dicarboxylate groups of the *o*-BDC ligand

present a bidentate chelating mode coordinating to the adjacent Cd(II) cations giving 1D metal-organic helical chains with a Cd...Cd distance of 6.366(1) Å (Fig. 5b). The helical chains wind around the 2_1 screw axis with a pitch of 9.908(2) Å, which are arranged in an alternately parallel mode, and further connected through the 3,3'-bpt ligands (*via syn-syn* mode, as shown in Scheme 3) along the *c* axis to create a 2D infinite honeycomb-like architecture (see Fig. 5c). Hydrogen bonds exist among the nitrogen atoms of coordinated 3,3'-bpt ligands, free 3,3'-bpt ligands, oxygen atoms of *o*-BDC ligands, coordinated water molecules and lattice water molecules. These intermolecular hydrogen bonding interactions further connect the neighboring honeycomb-like layers to give a 3D supra-molecular architecture. Otherwise, weak $\pi\cdots\pi$ interac-

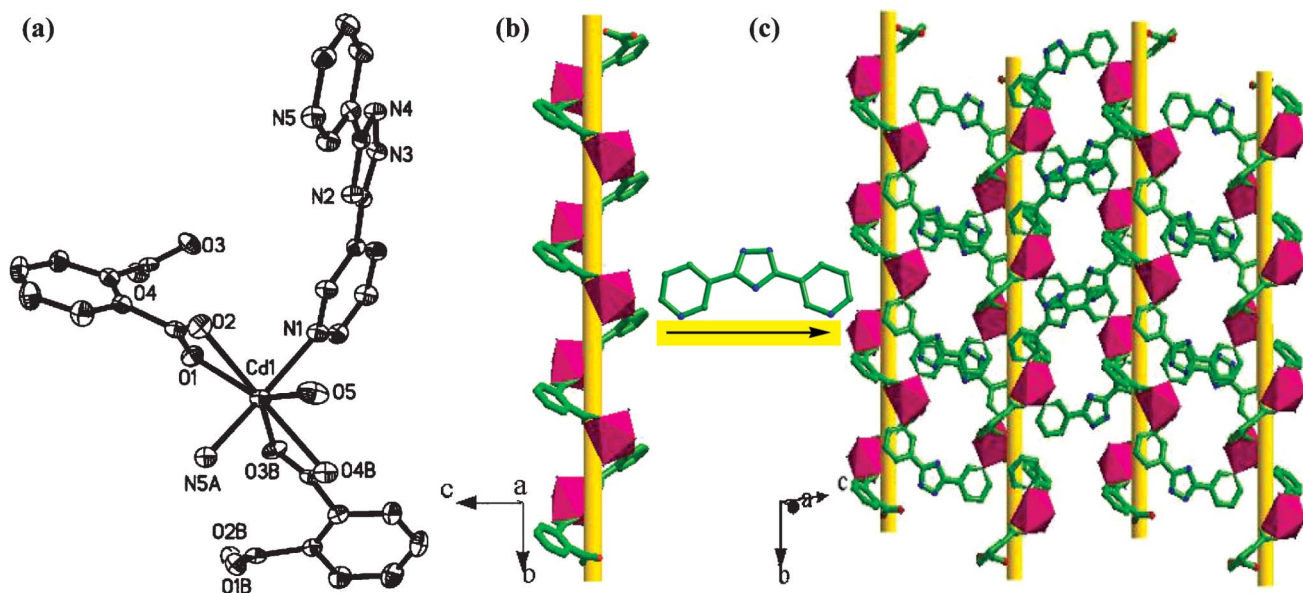


Fig. 5 (a) ORTEP view of **5** showing the coordination environments of the Cd(II) atoms. (b) Perspective view of the 1D helical chain along the *b* axis. (c) The 2D honeycomb-like structure in **5** viewed in the *bc* plane.

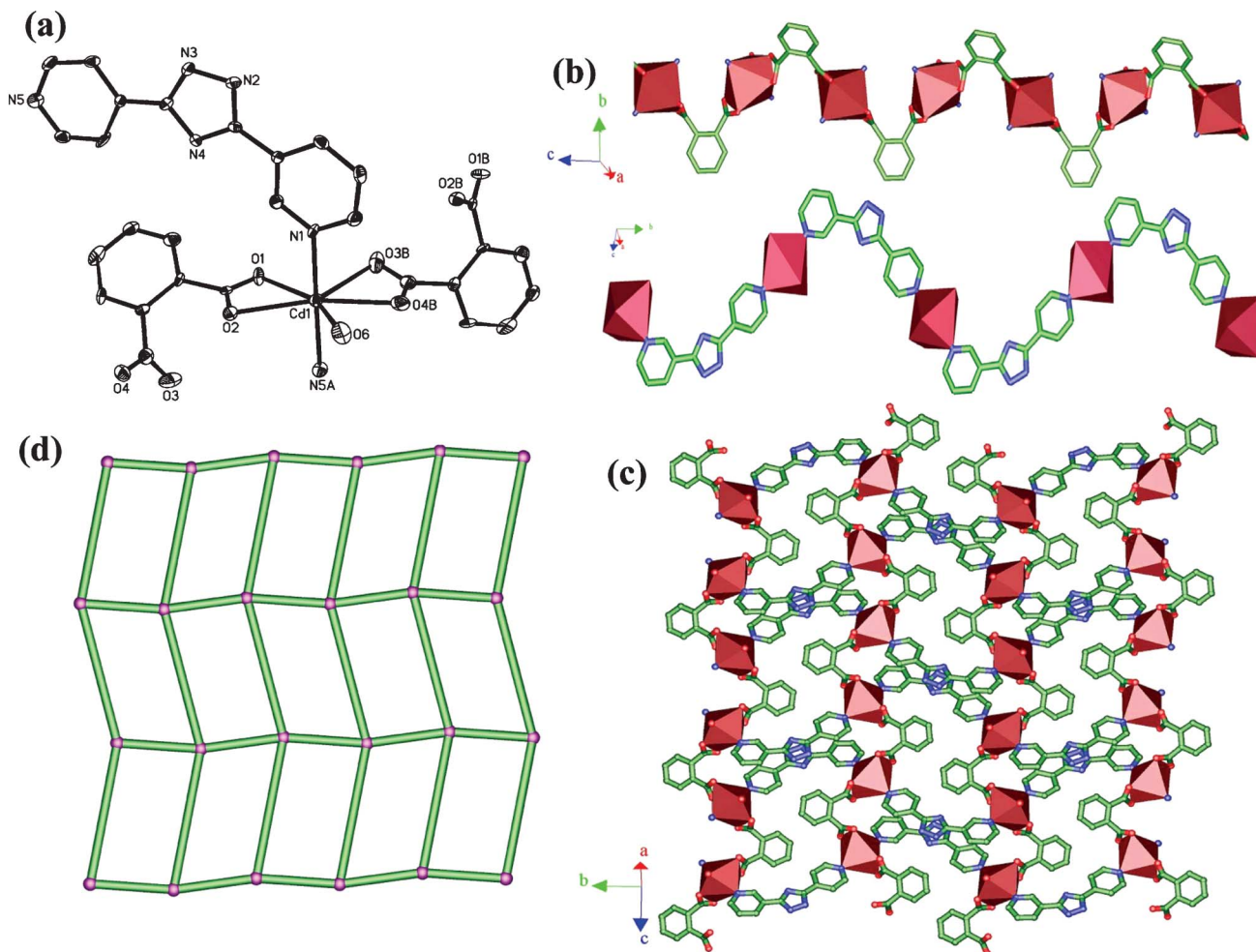


Fig. 6 (a) ORTEP view of **6** showing the coordination environment of the Cd(II) atoms. (b) The 1D infinite $[\text{Cd}(\text{o-BDC})]_n$ chain and zigzag chain. (c) The 2D network of **6** formed by the $[\text{Cd}(\text{o-BDC})]_n$ chains and Cd-bpt zigzag chains. (d) 2D layered structure displays $(4^4)\text{-sql}$ network in **6**.

tions occur between the adjacent layers that further stabilize the 3D structure (Fig. S2 in ESI†).

$[\text{Cd}(\text{o-BDC})(3,4'\text{-bpt})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (6**).** Different to **5**, complex **6** shows a network featuring 2D 4^4 grid-like layers. The fundamental building unit contains one independent Cd(II) center, one *o*-BDC ligand, one 3,4'-bpt ligand, one aqua ligand and one lattice water molecule. Each Cd(II) ion is seven-coordinate by five O atoms from two *o*-BDC ligands and one aqua ligand in the equatorial plane, as well as two N atoms from two 3,4'-bpt ligands at the axial sites, showing a distorted pentagonal bipyramid geometry (see Fig. 6a). The adjacent Cd(II) centers are linked by the carboxylic groups of a *o*-BDC ligand with a bidentate chelating mode to form infinite $[\text{Cd}(\text{o-BDC})]_n$ chains ($\text{Cd}\cdots\text{Cd} = 6.943(1) \text{ \AA}$) running along the crystallographic *c* axis; the neighbouring Cd(II) centers are also bridged by bent 3,4'-bpt ligands to generate zigzag chains running along the *b* axis with the $\text{Cd}\cdots\text{Cd}$ separation of $12.052(2) \text{ \AA}$ (see Fig. 6b). The two types of chains share Cd atoms and give rise to a 2D wave-like layer structure (see Fig. 6c), which can be best described as a $(4^4)\text{-sql}$ network (see Fig. 6d). Furthermore, these parallel layers are linked by

hydrogen bonding interactions among the triazole N atoms, coordinated water molecules and lattice water molecules, to generate a 3D supra-molecular architecture. Additionally, the 3D structure is further stabilized with the presence of significant interlayer aromatic stacking between the pyridyl rings of the 3,4'-bpt ligands (Fig. S3 in ESI†).

Comparison of the structures of coordination polymers

The structures described above show that the simultaneous use of the conformational phenyl dicarboxylate isomers with differently oriented carboxyl groups and triazole containing dipyridine isomers with differently oriented pyridyl groups to react with Cd(II) ions affords diverse architectures (1D, 2D, and 3D). In all complexes, the metal centers normally adopt the pentagonal bipyramid coordination except the Cd2 ion in **1** and Cd1 in **2** and **4** with a tetrahedral, octahedral geometry, respectively. The structural diversity of these complexes can be discussed below.

First of all, phenyl dicarboxylate ligands play a dominating effect on constructing the polymer structures. These dicarboxylate isomers exhibit several coordination patterns (see

Scheme 2), in which the carboxylate groups can adopt the bridging, unidentate and chelating modes, respectively. Thus, the *p*-BDC, *m*-BDC and *o*-BDC linkers with two separated carboxylate groups can be apart considered as linear or bent building blocks. For *p*-BDC-containing MOFs **1–3**, four coordination modes of *p*-BDC are observed and, interestingly, three different types of frameworks are generated. Secondly, the differently oriented pyridyl N atoms in these triazole-containing bpt isomers, which has a bent backbone, may play significant roles in the formation of different topological structures. For example, 1D chains formed in the presence of BDC ligands are uniformly observed in **1**, **2**, **5**, **6**, and the extension of such chains *via* the isomeric bpt connectors leads to the formation of four types of coordination networks. Furthermore, the N atoms of the triazole ring can provide potential coordination or hydrogen bonding sites that will influence the final coordination architectures. Thirdly, the connectivity of polymeric frameworks is strongly related to the metal centers. Comparing with the complexes containing Zn(II)/Co(II) ions that we have reported before,¹⁹ the ionic radius of Cd(II) is longer than Zn(II) and Co(II) which means the Cd(II) center can adopt higher coordination numbers leading to a distinct polymeric framework. In this work, the Cd(II) center adopts a seven-coordinated mode expect six-coordinated complexes **2** and **4**. The structural diversity of coordination polymers is perhaps due to the use of different metal ions, and rational assembly of the metal centers plays crucial roles in the formation of target coordination polymeric frameworks. Additionally, intermolecular interactions are also important to construct these overall supra-molecular structures, in which significant $\pi\cdots\pi$ stacking and/or H-bonding contacts are observed.

Powder X-ray diffraction and thermal stability analyses

In order to check the phase purity of these complexes, powder X-ray diffraction (XRD) patterns of **1–6** have been checked at room temperature. For compounds **1–6**, the measured XRD patterns closely match the patterns simulated from the respective single-crystal diffraction data for the six complexes, indicative of pure products. The dissimilarities in intensity may be attributed to the preferred orientation of the crystalline powder samples (Fig. S4–S9 in ESI†).

To further estimate the thermal stability of these complexes, their thermal behaviors were studied by thermogravimetric analyses (TGA) (see Fig. 7). For complex **1**, the first weight loss occurred from 91 °C to 198 °C and corresponded to the release of the lattice water and coordinated water molecules. The weight loss was 7.22% (calcd. 7.85%). The residual framework starts to decompose beyond 301 °C with a series of complicated weight losses and does not stop until heating ends. For complex **2**, it was stable up to 355 °C and then began to decompose. In the case of complex **3**, there was a weight loss of 7.22% below 175 °C, which is attributed to the release of lattice water molecules (calcd. 7.50%), and then the decomposition of the framework occurred at about 348 °C. Complex **4** showed a weight loss of 3.11% occurring in the range of 62–166 °C corresponding to the release of one lattice water molecule (calcd. 3.2%), and then the framework started to collapse accompanied by the decomposition of the residual

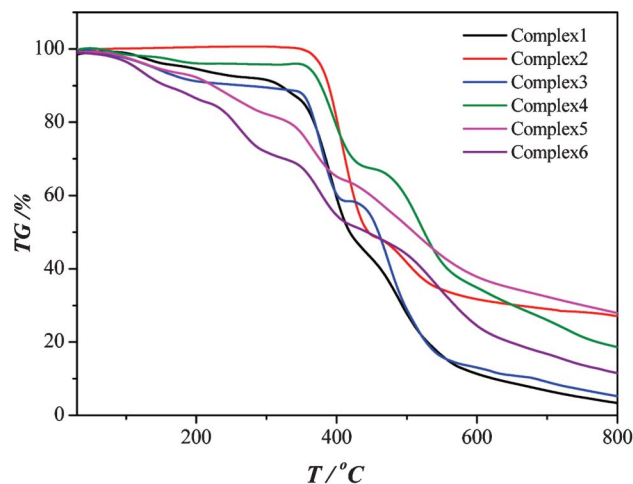


Fig. 7 TGA curves for complexes **1–6**.

of lattice water molecule and the organic components at about 349 °C. The TGA curves of **5** and **6** are similar, suggesting that a series of consecutive steps of weight loss does not stop until heating ends.

Luminescent properties

The compounds constructed by d^{10} metal centers and conjugated organic linkers are promising candidates for photoactive materials with potential applications such as chemical sensors and photochemistry.²⁵ These crystalline solids usually display regulable photoluminescence properties.^{26,27} As is well-known, Cd(II) complexes as d^{10} transition metal complexes exhibit interesting luminescence properties. Thus, the syntheses of Cd(II) complexes can be an efficient method for obtaining new types of luminescent materials.^{28–32} Hence, the solid state photoluminescent behaviors of **1–6** (Fig. 8) as well as the free ligands were investigated in the solid state at room temperature. The photoluminescence of the free ligands agrees well with our previously reported studies.^{19a} On

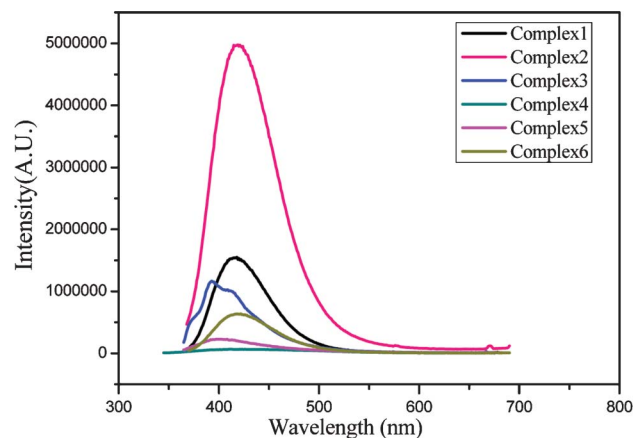


Fig. 8 Photoluminescence properties of complexes **1–6** in solid state at room temperature.

complexation of these ligands with Cd(II) atoms, strong luminescence was observable in the solid state. For **1–6**, their emission spectra also display similar shoulder peaks at *ca.* 415 nm ($\lambda_{\text{ex}} \approx 350$ nm). The enhancements of luminescence, may be attributed to the chelating and/or bridging effects of the ligands to the metal centers, which effectively increases the rigidity of the ligands and reduces the loss of energy *via* radiation less pathway.³³ In addition, the small blue shift of the emission band observed in **1–6**, compared with that of the bpt ligands, are due to the increase of conjugation upon metal coordination. The fluorescent emission of **1–6** can be tentatively assigned to the intraligand $n-\pi^*$ and $\pi^*-\pi$ transitions. Similar emission has also been observed in other polynuclear d¹⁰ metal polymers.^{28–32,34} These results indicate that the structures of the complexes can strongly affect their fluorescent properties.

Conclusions and perspectives

In summary, the solvothermal reactions of cadmium salts with mixed-ligand systems of three positional isomeric phenyl dicarboxylate anions (*p*-BDC, *m*-BDC and *o*-BDC) and three positional isomeric dipyridyl bridging ligands (4,4'-bpt, 3,4'-bpt and 3,3'-bpt) afford a new family of Cd(II) MOFs, which are described well and present diverse architectures. The structural diversities indicate that the phenyl dicarboxylate isomers with different orientation disposition of the carboxylate groups play dominating roles in modulating the formation of structures of these crystalline materials; that is, the BDC ligands display more diverse coordinate modes and they behave as linear (*p*-BDC) or angular (*m*-BDC and *o*-BDC) building blocks, which are further extended *via* the isomeric bpt ligand connectors in different directions, resulting in diverse and more interesting coordination architectures than before. These experimental results further reveal the isomeric effect of the mixed bridging ligands in the self-assembly process of the metal–organic frameworks. Accordingly, on one hand, this work will further enrich the crystal engineering strategy and offer the possibility of controlling the formation of the desired network structures. On the other hand, it will provide new perspectives for the design and preparation of novel coordination networks with mixed bpt isomers and other aromatic multicarboxylate isomers as spacers, and further efforts on this perspective are under way.

Acknowledgements

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