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PAPER

Synthesis, crystal structures, and luminescent properties of Cd(II) coordination polymers assembled from asymmetric semi-rigid V-shaped multicarboxylate ligands†

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A series of seven Cd(II) coordination polymers, namely $[\text{Cd}_3(\text{L}^1)_2(\text{phen})_3]_n \cdot (\text{H}_2\text{O})_{2n}$ (**1**), $[\text{Cd}_3(\text{L}^1)_2(2,2'\text{-bpy})_3(\text{H}_2\text{O})_2]_n \cdot (\text{H}_2\text{O})_{3n}$ (**2**), $[\text{Cd}_3(\text{L}^1)_2(4,4'\text{-bpy})_2]_n \cdot (\text{H}_2\text{O})_{4n}$ (**3**), $[\text{Cd}_3(\text{L}^2)_2(\text{phen})_2]_n$ (**4**), $[\text{Cd}_3(\text{L}^2)_2(2,2'\text{-bpy})_2]_n$ (**5**), $[\text{Cd}_3(\text{L}^3)_2(\text{phen})_2(\text{H}_2\text{O})]_n \cdot (\text{H}_2\text{O})_{2n}$ (**6**), and $[\text{Cd}_3(\text{L}^4)_2(\text{phen})_2(\text{H}_2\text{O})_2]_n \cdot (\text{H}_2\text{O})_{3n}$ (**7**), have been prepared on the basis of four asymmetric semi-rigid V-shaped multicarboxylate ligands including 4-(2-carboxyphenoxy)phthalic acid (H_3L^1), 3-(2-carboxyphenoxy)phthalic acid (H_3L^2), 3-(4-carboxyphenoxy)phthalic acid (H_3L^3), and 4-(4-carboxyphenoxy)phthalic acid (H_3L^4) with the help of 1,10-phenanthroline (phen), 2,2'-bipyridine (2,2'-bpy), or 4,4'-bipyridine (4,4'-bpy) as secondary ligand. Single-crystal X-ray diffraction analysis reveals that compounds **1**, **4**, **5**, and **6** exhibit one-dimensional (1D) double chain structures constructed from trinuclear Cd(II) clusters, which further forms 2D supramolecular architecture *via* intermolecular π - π interaction. Complex **2** possesses a 3D supramolecular network assembled from 2D layered architecture composed of dinuclear cadmium subunits and isolated Cd(II) ions *via* intermolecular π - π interaction. Compound **3** shows a 3D framework structure which is generated from 2D layered motif comprised of trinuclear cadmium subunits pillared by 4,4'-bpy ligands, while the 3D framework of **7** is constructed from two different directional ribbon chains consisting of dinuclear cadmium clusters and isolated Cd(II) ions as node. The different molecular structure for compounds **1**–**3** formed from the same L^1 ligand reveals the spacer effect of secondary ligands on tuning the structure of coordination polymers, while the structural difference among **1**, **4**, **6**, and **7** built from different asymmetric semi-rigid V-shaped multicarboxylate ligand (L^1 , L^2 , L^3 , or L^4) but employing the same secondary ligand of phen reveals the important role of the positions of carboxylic substituents at the asymmetric multicarboxylate ligand in the formation of coordination compounds. Photophysical properties over the series of complexes **1**–**7** have been systematically and comparatively investigated.

Introduction

In the field of supramolecular chemistry and crystal engineering, the design and synthesis of coordination polymers have been emerging as an ongoing field owing to their structural aesthetics and topologies as well as diverse functional properties.^{1–3} Among various kinds of complexes fabricated, those with intriguing fluorescent property attract great attention due to their potential

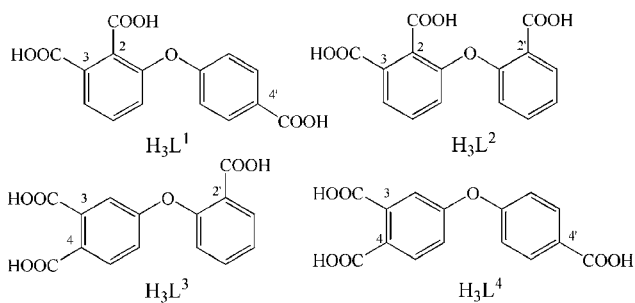
applications in light-emitting diodes (LEDs).⁴ Thus far, significant advance achieved in this field has led to a lot of promising materials through the self-assembly of organic ligands and metal ions.⁵ Nevertheless, it still remains a great and long-term challenge to exactly predict the molecular structure and luminescent properties of coordination polymers because of many subtle factors involved in the crystallization process.

In comparison with the rigid aromatic multicarboxylate ligands such as 1,4-benzenedicarboxylate, 1,3,5-benzenetricarboxylate, and 1,2,4,5-benzenetetracarboxylate with one benzene ring as central molecular framework, the so-called semi-rigid V-shaped multicarboxylate ligands with two benzene rings bridged by a nonmetallic atom (C, O, S, or N atom) as central molecular framework are of increasing flexibility and therefore able to lead to metal complexes with diverse structures because of the free rotation of two benzene rings around the bridged non-metallic atom.^{6,7} By using such semi-rigid V-shaped ligands,

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Scheme 1 Schematic molecular structures of H_3L^1 – H_3L^4 .

different coordination polymers with diverse molecular structures and potential applications in the field of separation, absorption, catalyst, and sensor have been prepared.⁸ It is worth noting that symmetric semi-rigid V-shaped multidentate O-donor ligands with two or four carboxylic substituents attached at the symmetric positions of semi-rigid V-shaped central molecular framework usually generate coordination polymers with discrete metal ions as node, leading to the limitation in tuning the structure and functionality of metal–organic coordination frameworks (MOFs). As a result, effort has been started recently to be devoted to the construction of MOFs using asymmetric semi-rigid V-shaped multidentate O-donor ligands with carboxylic substituents attached at asymmetric positions of central V-shaped molecular framework, resulting in coordination polymers composed of polymeric subunits through tuning the positions of asymmetrically attached carboxylic groups at the central framework.⁹ For the purpose of further clarifying the effect of positions of asymmetrically attached carboxylic groups on the molecular structure and functional properties of MOFs, in the present work four asymmetric semi-rigid V-shaped multicarboxylate ligands H_3L^1 – H_3L^4 , Scheme 1, were selected and employed to assemble a series of seven new coordination complexes including $[Cd_3(L^1)_2(phen)_3]_n \cdot (H_2O)_{2n}$ (**1**), $[Cd_3(L^1)_2(2,2'\text{-bpy})_3(H_2O)_2]_n \cdot (H_2O)_{3n}$ (**2**), $[Cd_3(L^1)_2(4,4'\text{-bpy})_2]_n \cdot (H_2O)_{4n}$ (**3**), $[Cd_3(L^2)_2(phen)_2]_n$ (**4**), $[Cd_3(L^2)_2(2,2'\text{-bpy})_2]_n$ (**5**), $[Cd_3(L^3)_2(phen)_2(H_2O)]_n \cdot (H_2O)_{2n}$ (**6**), and $[Cd_3(L^4)_2(phen)_2(H_2O)_2]_n \cdot (H_2O)_{3n}$ (**7**) with the help of phen, 2,2'-bpy, or 4,4'-bpy as secondary ligand. Their single crystal structures and luminescent properties were also systematically and comparatively investigated.

Experimental

All reagents and solvents employed in the present work were obtained from commercial source and used directly without further purification. The four ligands H_3L^1 – H_3L^4 were synthesized according to the reported procedure.^{9b}

General synthesis procedure for complexes 1–7

In the general synthesis, the target complexes were obtained by using hydrothermal method with the same stoichiometric proportion for the starting materials in the presence of KOH. Teflon-lined stainless steel container (25 mL) was employed as reaction vessel containing all starting materials, which was heated to appropriate temperature and held for 72 h, then cooled

to 50 °C at a descent rate of 10 °C h⁻¹. Finally, the oven was cut off and kept for another 10 h, perfect crystals were isolated.

$[Cd_3(L^1)_2(phen)_3]_n \cdot (H_2O)_{2n}$ (**1**)

The mixture of $Cd(OAc)_2 \cdot 2H_2O$ (0.0533 g, 0.2 mmol), phen (0.0360 g, 0.2 mmol), H_3L^1 (0.0302 g, 0.1 mmol), KOH (0.0168 g, 0.3 mmol), and H_2O (15 mL) was sealed in 25 mL Teflon-lined stainless steel reactor, which was heated to 130 °C. Colourless block-shaped crystals suitable for X-ray diffraction analysis were separated by filtration with the yield of 0.0325 g, 43% (based on L^1 ligand). Anal. calcd for $C_{66}H_{42}Cd_3N_6O_{16}$: C 52.42, H 2.80, N 5.56. Found: C 52.45, H 2.82, N 5.49. IR/cm⁻¹ (KBr): 3064 (m), 1589 (s), 1553 (s), 1406 (s), 1370 (s), 1224 (s), 860 (s), 726 (m).

$[Cd_3(L^1)_2(2,2'\text{-bpy})_3(H_2O)_2]_n \cdot (H_2O)_{3n}$ (**2**)

The mixture of $Cd(OAc)_2 \cdot 2H_2O$ (0.0533 g, 0.2 mmol), 2,2'-bpy (0.0312 g, 0.2 mmol), H_3L^1 (0.0302 g, 0.1 mmol), KOH (0.0168 g, 0.3 mmol), and H_2O (15 mL) H_3L^1 was sealed in 25 mL Teflon-lined stainless steel reactor, which was heated to 150 °C. Colourless block-shaped crystals suitable for X-ray diffraction analysis were separated by filtration with the yield of 0.0366 g, 49% (based on L^1 ligand). Anal. calcd for $C_{60}H_{48}Cd_3N_6O_{19}$: C 48.22, H 3.23, N 5.62. Found: C 48.01, H 3.32, N 5.48. IR/cm⁻¹ (KBr): 3069 (m), 1586 (s), 1553 (s), 1400 (s), 1367 (s), 1223 (s), 870 (m), 733 (m).

$[Cd_3(L^1)_2(4,4'\text{-bpy})_2]_n \cdot (H_2O)_{4n}$ (**3**)

By employing the above-described procedure for preparing **2** with 4,4'-bpy (0.0312 g, 0.2 mmol) instead of 2,2'-bpy (0.0312 g, 0.2 mmol) as starting material, colourless block-shaped crystals suitable for X-ray diffraction analysis were obtained after the reactor was cooled to room temperature from 150 °C with the yield of 0.0369 g, 56% (based on L^1 ligand). Anal. calcd for $C_{50}H_{38}Cd_3N_4O_{18}$: C 45.49, H 2.90, N 4.24. Found: C 45.41, H 2.92, N 4.19. IR/cm⁻¹ (KBr): 3071 (m), 1606 (s), 1540 (m), 1390 (s), 1236 (s), 865 (m), 762 (m).

$[Cd_3(L^2)_2(phen)_2]_n$ (**4**)

Compound **4** was synthesized in a similar manner to **1** by using H_3L^2 (0.0302 g, 0.1 mmol) instead of H_3L^1 as starting material. Colourless blocked crystals suitable for X-ray diffraction analysis were obtained after the reactor was cooled to room temperature from 130 °C with the yield of 0.0473 g, 73% (based on L^2 ligand). Anal. calcd for $C_{54}H_{30}Cd_3N_4O_{14}$: C 50.04, H 2.33, N 4.32. Found: C 50.06, H 2.28, N 4.19. IR/cm⁻¹ (KBr): 3064 (m), 1581 (s), 1552 (s), 1390 (s), 1233 (s), 851 (m), 726 (m).

$[Cd_3(L^2)_2(2,2'\text{-bpy})_2]_n$ (**5**)

By using the same procedure used to prepare **2** with H_3L^2 (0.0302 g, 0.1 mmol) instead of H_3L^1 as starting material, colourless block-shaped crystals suitable for X-ray diffraction analysis were separated by filtration with the yield of 0.0381 g, 61% (based on L^2 ligand). Anal. calcd for $C_{50}H_{30}Cd_3N_4O_{14}$: C 48.03, H 2.29, N 2.21. Found: C 48.11, H 2.39, N 2.29. IR/cm⁻¹

(KBr): 3072 (m), 1591 (s), 1562 (s), 1382 (s), 1233 (s), 857 (m), 761 (m).

$[\text{Cd}_3(\text{L}^3)_2(\text{phen})_2(\text{H}_2\text{O})]_n \cdot (\text{H}_2\text{O})_{2n}$ (6)

By using the same procedure used to prepare **1** with H_3L^3 (0.0302 g, 0.1 mmol) instead of H_3L^1 (0.0302 g, 0.1 mmol) as starting material, colourless blocked crystals suitable for X-ray diffraction analysis were obtained after the reactor was cooled to room temperature with the yield of 0.0324 g, 48% (based on L^3 ligand). Anal. calcd for $\text{C}_{54}\text{H}_{36}\text{Cd}_3\text{N}_4\text{O}_{17}$: C 48.04, H 2.69, N 4.15. Found: C 48.01, H 2.67, N 4.13. IR/ cm^{-1} (KBr): 3057 (m), 1599 (s), 1552 (s), 1387 (s), 1241 (s), 856 (m), 776 (m).

$[\text{Cd}_3(\text{L}^4)_2(\text{phen})_2(\text{H}_2\text{O})_{2n}] \cdot (\text{H}_2\text{O})_{3n}$ (7)

By employing the above-described procedure of **1** with H_3L^4 (0.0302 g, 0.1 mmol) instead of H_3L^1 (0.0302 g, 0.1 mmol) as starting material, colourless blocked crystals suitable for X-ray diffraction analysis were obtained after the reactor was cooled to room temperature with the yield of 0.0454 g, 58% (based on L^4 ligand). Anal. calcd for $\text{C}_{66}\text{H}_{47}\text{Cd}_3\text{N}_6\text{O}_{19}$: C 50.64, H 3.03, N 5.37. Found: C 50.61, H 3.09, N 5.33. IR/ cm^{-1} (KBr): 3071 (m), 1589 (s), 1559 (s), 1384 (s), 1236 (s), 858 (m), 763 (m).

Physical measurements

Elemental analyses were carried out with an Elementary Vario El. The infrared spectroscopy on KBr pellets was performed on a Magna-IR 750 spectrophotometer in the region of 4000–400 cm^{-1} . TGA was performed on a Perkin-Elmer TG-7 analyzer heated from 30–600 °C under nitrogen. The fluorescence spectra were measured on a multifrequency phase and modulation fluorometer.

Table 1 Details of the crystal parameters, data collection and refinement for complexes 1–3

Complex	1	2	3
Formula	$\text{C}_{66}\text{H}_{42}\text{Cd}_3\text{N}_6\text{O}_{16}$	$\text{C}_{60}\text{H}_{48}\text{Cd}_3\text{N}_6\text{O}_{19}$	$\text{C}_{50}\text{H}_{38}\text{Cd}_3\text{N}_4\text{O}_{18}$
FW/g mol ⁻¹	1512.29	1494.24	1320.09
System	Monoclinic	Triclinic	Monoclinic
Space group	<i>C2/c</i>	<i>P</i> $\bar{1}$	<i>C2/c</i>
<i>a</i> /Å	15.159(3)	9.5260(5)	20.8380(15)
<i>b</i> /Å	18.821(3)	15.0310(8)	10.485(2)
<i>c</i> /Å	19.798(3)	22.0200(11)	22.5800(10)
α /°	90	70.5440(10)	90
β /°	92.382(3)	78.3470(10)	102.9680(10)
γ /°	90	84.9060(10)	90
<i>Z</i>	4	2	4
<i>V</i> /Å ³	5643.4(16)	2910.8(3)	4807.6(10)
<i>D</i> _{calcd} /g cm ⁻³	1.780	1.705	1.824
μ /mm ⁻¹	1.202	1.168	1.398
<i>F</i> 000	3008	1492	2616
<i>R</i> _{int} <i>I</i> > 2 θ	0.0521	0.0419	0.0234
<i>R</i> _{w2} <i>I</i> > 2 θ	0.1383	0.1143	0.0619
<i>R</i> _{int} all	0.0609	0.0547	0.0264
<i>R</i> _{w2} all	0.1435	0.1211	0.0635
<i>S</i>	1.064	1.054	1.046

Table 2 Details of the crystal parameters, data collection and refinement for complexes 4–7

Complex	4	5	6	7
Formula	$\text{C}_{54}\text{H}_{30}\text{Cd}_3\text{N}_4\text{O}_{14}$	$\text{C}_{50}\text{H}_{30}\text{Cd}_3\text{N}_4\text{O}_{14}$	$\text{C}_{54}\text{H}_{36}\text{Cd}_3\text{N}_4\text{O}_{17}$	$\text{C}_{66}\text{H}_{47}\text{Cd}_3\text{N}_6\text{O}_{19}$
FW/g mol ⁻¹	1296.02	1247.98	1350.07	1565.30
System	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Cc</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	11.6201(5)	11.2000(9)	14.0039(5)	13.511(3)
<i>b</i> /Å	11.9085(5)	11.5369(9)	28.8677(11)	14.864(3)
<i>c</i> /Å	18.7329(8)	18.3362(14)	13.6293(5)	17.527(3)
α /°	84.387(10)	88.2210(10)	90	66.948(2)
β /°	86.887(10)	81.4750(10)	118.5460(10)	86.831(2)
γ /°	66.265(10)	70.8300(10)	90	67.297(3)
<i>Z</i>	2	2	4	2
<i>V</i> /Å ³	2361.27(2)	2212.8(3)	4840.0(3)	2968.8(1)
<i>D</i> _{calcd} /g cm ⁻³	1.823	1.873	1.853	1.751
μ /mm ⁻¹	1.416	1.506	1.390	1.150
<i>F</i> 000	1276	1228	2672	1562
<i>R</i> _{int} <i>I</i> > 2 θ	0.0305	0.0246	0.0172	0.0439
<i>R</i> _{w2} <i>I</i> > 2 θ	0.0962	0.0607	0.0462	0.1175
<i>R</i> _{int} all	0.0380	0.0300	0.0184	0.0626
<i>R</i> _{w2} all	0.1120	0.0629	0.0555	0.1296
<i>S</i>	1.134	1.047	1.150	1.106

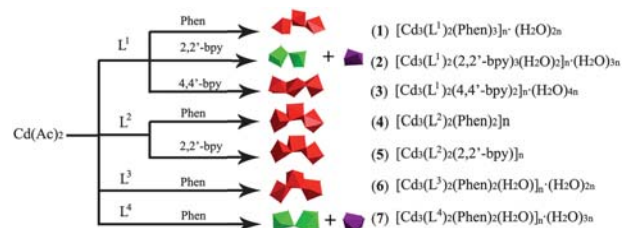
Single-crystal X-ray diffraction determination

Crystal data for all the seven complexes were collected on a Bruker SMART APEXII CCD diffractometer with graphite monochromatic Mo-K α radiation ($\lambda = 0.71073$ Å) using the SMART and SAINT programs at 298 K, and the structures were solved by the direct method (SHELXS-97) and refined by full-matrix least-squares (SHELXL-97) on *F*². Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model. Crystallographic data and other pertinent information for all the complexes are summarized in Table 1 and 2. Selected bond distances and bond angles with their estimated standard deviation are listed in Table S1 (ESI).†

Results and discussion

Preparation of the complexes 1–7

In the present study, complexes 1–7 were prepared from the hydrothermal reaction between corresponding semi-rigid V-shaped multicarboxylate ligand and $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ with the help of assistant ligand including phen, 2,2'-bpy, and 4,4'-bpy ligands, Scheme 2. It was just reported that a similar hydrothermal reaction between $\text{Co}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and semi-rigid



Scheme 2 Schematic synthesis procedure of compounds 1–7.

V-shaped multicarboxylate ligand in the presence of 4,4'-bpy ligand led to the formation of single crystals suitable for X-ray analysis without the necessity using base to adjust the pH value of reaction mixture.^{9b} However, in the present case the reaction between $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and H_3L ($\text{L} = \text{L}^1, \text{L}^2, \text{L}^3, \text{and } \text{L}^4$) with the help of secondary ligand without adding base gave only some white precipitate instead of single crystals of coordination polymers. In good contrast, when solid KOH with the molar ratio of 3 : 1 to the tricarboxylate ligand was added to completely deprotonate the ligand, good single crystals of seven coordination polymers were obtained. In addition, the reaction temperature was also revealed to play an important role in the formation of corresponding complexes as exemplified for the isolation of **2**, **3**, and **5** only at higher temperature of 150 °C but isolation of **1**, **4**, **6**, and **7** at lower temperature of 130 °C.

IR spectra

In the IR spectra of asymmetric semi-rigid V-shaped ligands, the absorption band at 1697, 1694, 1702, and 1670 cm^{-1} for H_3L^1 – H_3L^4 , respectively, is attributed to the asymmetric stretching vibration of uncoordinated carboxylic groups.^{9b} However, this band red-shifts to the range of 1581–1606 cm^{-1} in the spectra of complexes **1**–**7** due to the formation of Cd(II)–O coordination bond of carboxylic oxygen atom in the ligands. This result is in line with that reported for the cobalt analogues.^{9b}

Thermal analysis

The thermal behaviour for compounds **1**–**7** was studied to reveal their thermal stability. TGA experiments were performed on pure single crystal sample of complexes **1**–**7** under N_2 atmosphere with a heating rate of 10 °C min^{-1} in the range of 30–600 °C.

The thermal curves are exhibited in Fig. S1 (ESI).† Complex **1** displays the weight loss by stage owing to the release of water molecules in the range from room temperature to 144 °C (obsd 2.18%, calcd 2.38%). The organic spacers then decomposes from 287–387 °C. For **2**, the TGA curve shows that the water molecules are lost from room temperature to 127 °C, obsd 3.58%, calcd 3.62%. The decomposition temperature of this compound spans the range of 384–485 °C. According to the TGA curve of **3**, the water molecules are lost in the range of 30–243 °C, obsd 5.14%, calcd 5.46%. Both **4** and **5** show similar TGA curve due to their similar molecular architecture with only different secondary ligand. The weight loss is observed owing to the direct decomposition of organic ligands in the range of 330–442 °C for **4** and 334–440 °C for **5**. The release of water molecules is observed in **6** in the range from room temperature to 242 °C (obsd 13.05%, calcd 13.38%). The curve of **7** reveals that the lattice water molecules are lost from room temperature to 214 °C, obsd 3.20%, calcd 3.45%. The residual composition of this complex is then decomposed in the range of 284–481 °C.

Crystal structures of complexes **1**, **4**, **5**, and **6**

The crystal structures of **1**, **4**, **5**, and **6** have been shown in Fig. 1–3, and selected bond lengths and angles compiled in Table S1 (ESI).† Despite the different asymmetric semi-rigid V-shaped ligand or secondary ligand, single-crystal X-ray diffraction

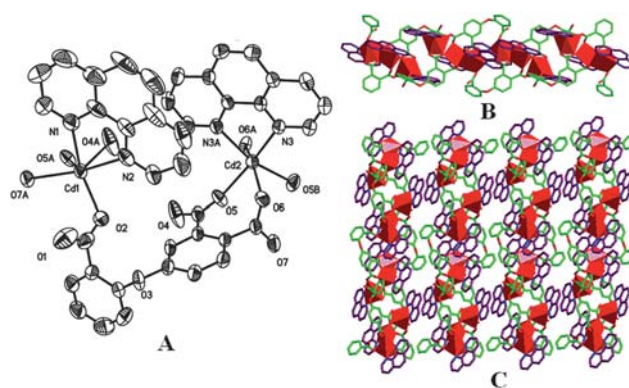


Fig. 1 (A) The ORTEP diagram of coordination environment for Cd(II) atoms in **1** (the 30% probability level), all hydrogen atoms and water molecules have been omitted for clarity. (B) An infinite 1D chain composed of trinuclear subunits. (C) 2D supramolecular network *via* intermolecular π – π interaction.

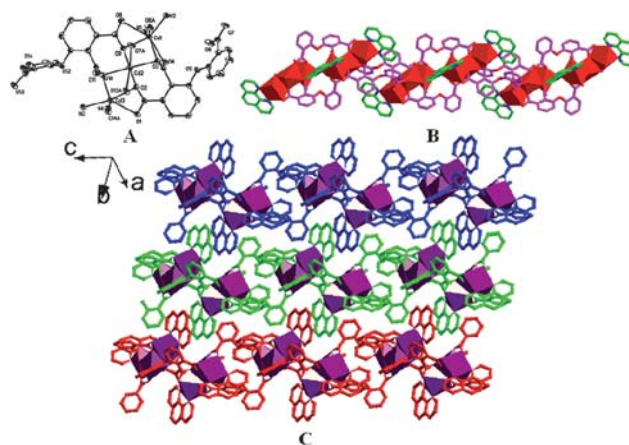


Fig. 2 (A) The ORTEP diagram of coordination sphere for Cd(II) atoms in **4** with the 30% probability level, all hydrogen atoms and water molecules have been omitted for clarity. (B) A infinite 1D molecular structure of **4**. (C) 2D supramolecular network.

analysis reveals that all these four complexes feature a 2D layered supramolecular structure assembled from 1D chain composed of trinuclear subunits *via* intermolecular π – π interaction. As shown in Fig. 1A, compound **1** is composed of two kinds of crystallographically independent Cd(II) ions, of which both Cd1 and Cd2 ions locate in a slightly distorted octahedral coordination sphere formed by two nitrogen atoms from chelating phen ligand and four carboxylic oxygen atoms of L^1 ligand in *cis*-typed conformation with μ_4 -bridging mode binding four Cd(II) ions. The Cd–O and Cd–N bond lengths are in the range of 2.197(5)–2.466(6) and 2.327(5)–2.386(5) Å, respectively. These data are comparable with those of reported compounds containing O–Cd–N segments.¹⁰ As can be seen, the 3- and 4-carboxylic groups in **1** as linkers assemble three Cd(II) ions into trinuclear aggregate, and the 2'-carboxylic group in monodentate mode connects Cd1 ion of the neighbouring trinuclear Cd(II) cluster, forming a 1D infinite chain, Fig. 1B. These chains are further packed into a 2D supramolecular network *via* intermolecular π – π interaction (face–face distance amounting to 3.535(4) Å) between phen

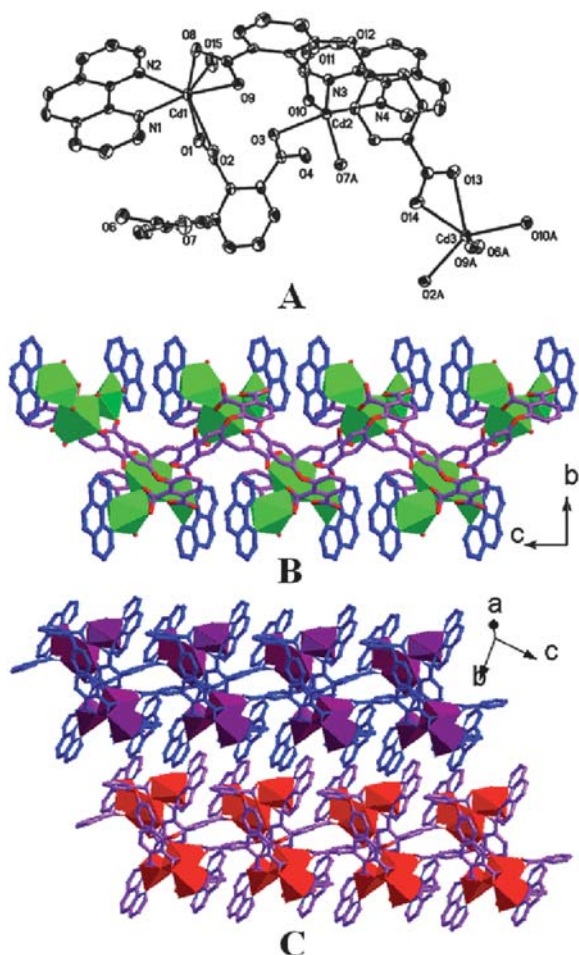


Fig. 3 The coordination geometry of **6** (A), 1D wave ribbon chain along the *c* axis (B), and the 2D supramolecular structures of **6** via intermolecular interactions (C).

ligands of neighbouring chains, Fig. 1C, which consolidates the structure of **1** in cooperation with the coordination interaction.

The detail of molecular structures of isostructural **4** and **5** is elucidated by taking **4** as a typical representative, Fig. 2. Compound **4** is constructed by three kinds of Cd(II) ions, Fig. 2A. Cd1 and Cd3 ions are coordinated by two nitrogen atoms of phen ligand and five oxygen atoms from three L² ligands. Cd2 ion is hexa-coordinated by six oxygen atoms. 2- and 3-carboxylic groups of two kinds of L² ligands with μ_2 - η^2 - η^1 coordination mode bind to three Cd(II) ions, leading to a trinuclear cluster. These trinuclear subunits are further linked by 2'-carboxylic groups from L² ligand, generating a 1D infinitely double chain, Fig. 2B. The neighbouring chains are packed in *a* × *c* plane, giving a 2D supramolecular structure via intermolecular π - π interaction (face-face distance amounting to 3.394(7) and 3.361(3) Å for **4** and **5**, respectively).

In complex **6**, a much wavier chain than in **1**, **4**, and **5** containing two kinds of L³ ligands and three types of Cd(II) ions can be found, Fig. 3A. Cd1 and Cd3 ions are hepta-coordinated. For Cd1 ion, the coordination environment is composed of two nitrogen atoms, four oxygen atoms from two carboxylic groups in μ_2 - η^2 - η^1 mode, and one oxygen atom of water molecules.

Cd2 ion locates in a distorted octahedral coordination geometry completed by four oxygen atoms and two nitrogen atoms of phen ligand. The coordination geometry around Cd3 ion is constructed by seven oxygen atoms of five different carboxylic groups. The Cd1, Cd2, and Cd3 ions are connected by carboxylic groups of L³ ligand to form a trinuclear Cd(II) cluster, which further expands to give a wavy double chain, Fig. 3B. The characteristic wavy chains composed of Cd(II) trimers are further assembled into a 2D supramolecular structure via the π - π interaction (face to face distance amounting to 3.379(3) Å) between the phen ligands of different chains, Fig. 3C. At the end of this paragraph, it is worth noting that the molecular structure of **1**, **4**, **5**, and **6** support the fact that the chelating bidentate ligands phen and 2,2'-bpy favour the formation of 1D coordinative chain by restricting the available metal coordination sites.¹¹

Crystal structure of complex 2

Compound **2** was obtained only by employing 2,2'-bpy instead of phen for preparing **1** as secondary ligand. As can be found in

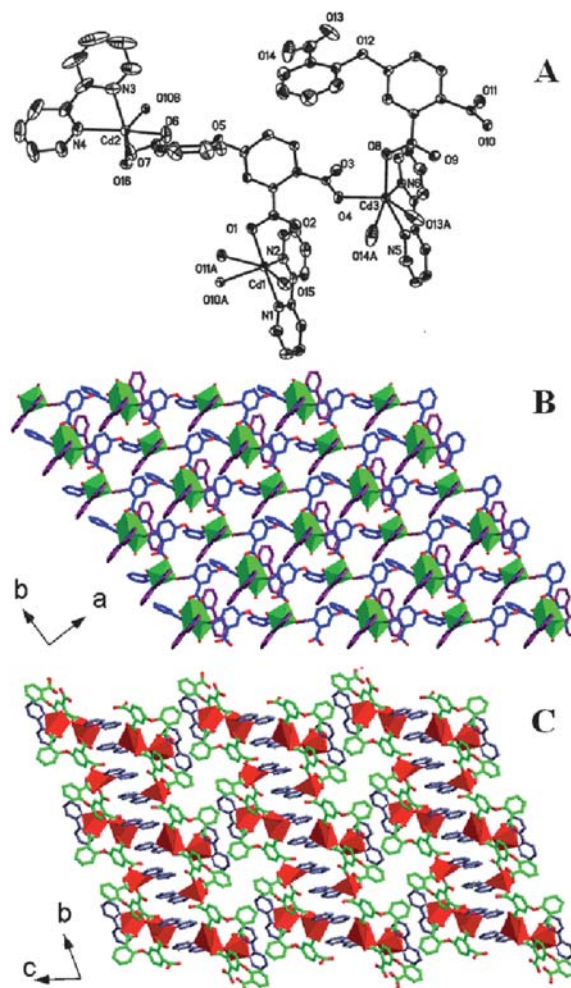


Fig. 4 (A) The ORTEP diagram of coordination geometry for Cd(II) atoms in **2** (the 30% probability level), all hydrogen atoms and water molecules have been omitted for clarity. (B) 2D covalent molecular structure of **2**. (C) 3D supramolecular network via intermolecular π - π interaction.

Fig. 4A, **2** contains three kinds of Cd(II) ions, three kinds of chelating 2,2'-bpy ligand, two types of L¹ ligands, and three coordination water molecule in the asymmetric unit. Cd1 ion is hepta-coordinated by two nitrogen atoms of 2,2'-bpy ligands, four oxygen atoms from two bidentate chelating carboxylic groups, and one oxygen atom of water molecules. Both Cd2 and Cd3 ions possess a distorted octahedral coordination geometry completed by two nitrogen atoms and four oxygen atoms. L¹ ligands of **2** in *trans*-typed conformation with μ_3 - and μ_4 -bridging modes link Cd1 and Cd2 ions into a dinuclear subunit. These dinuclear subunits and isolated Cd3 ions are bridged by L¹ ligands to further generate a 2D covalent network. In the case that L¹ ligand, Cd1 ion, and dinuclear subunit built from Cd2 and Cd3 ions are considered as 3-connected node, the molecular structure of **2** could be classified as a (6,3) herringbone network, Fig. S2 (ESI).† The neighbouring 2D covalent structures further

form a 3D supramolecular framework *via* the π - π interaction (face to face distance amounting to 3.412(3) Å) between 2,2'-bpy ligands. The different structure between **1** and **2** indicates the effect of N-donor size in tuning the structure of coordination polymer.^{8f,12}

Crystal structure of complex 3

Complex **3** was synthesized by introducing rod-like N-donor (4,4'-bpy) secondary ligand instead of the chelating N-donor (phen and 2,2'-bpy ligands), which exhibits a complicated 3D molecular structure as expected. There are two kinds of different Cd(II) ions in **3**, both Cd(II) ions are in octahedral coordination environment, Fig. 5A. However, the octahedral coordination sphere around Cd1 ion is completed by six oxygen atoms from four L¹ ligands in *trans*-typed configuration, and Cd2 ion is hexa-coordinated with the equatorial plane formed by four oxygen atoms and the axis positions occupied by two nitrogen atoms of 4,4'-bpy ligands. One Cd1 ion in the middle position and two Cd2 ions in the terminal positions form a trinuclear cluster, and the coordination polyhedrons of adjacent Cd(II) ions share the same seldge. The neighbouring trinuclear subunits are linked by 4-carboxylic groups in *syn-anti* coordination mode to form an infinite 1D metal chain. The adjacent chains are further connected by the L¹ ligand to form a 2D covalent network, Fig. 5B. Then 4,4'-bpy ligands connect the Cd2 ions of neighbouring 2D layered networks as pillar, forming a 3D molecular structure, Fig. 5C.

Crystal structure of complex 7

In the structure of **7**, there exist three types of Cd(II) ions in Figure 6. Cd1 ion exhibits a hepta-coordinated geometry built from two nitrogen atoms, one oxygen atom from carboxylic group in monodentate mode, and two oxygen atoms from one

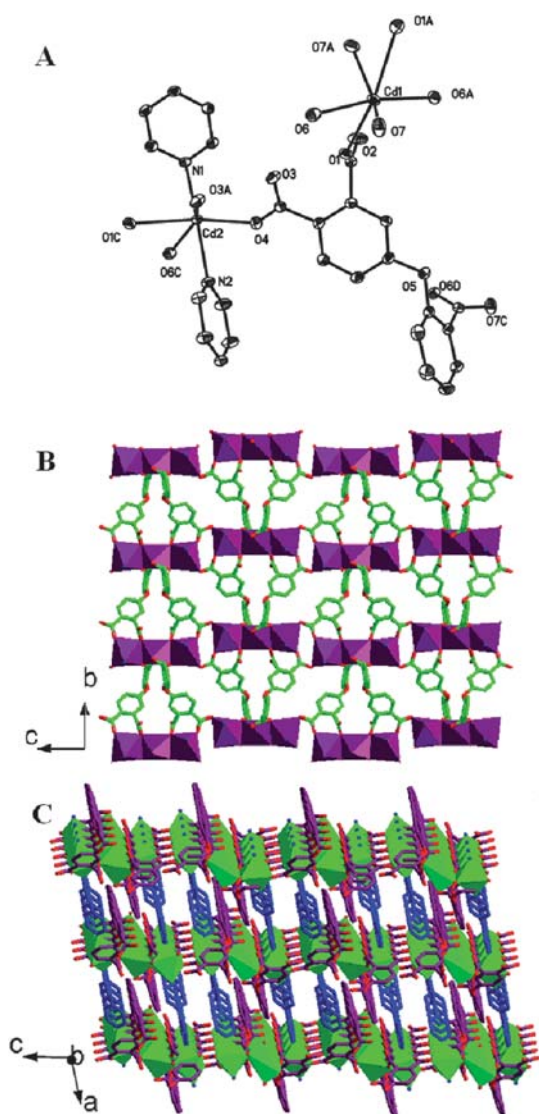


Fig. 5 (A) The ORTEP diagram of coordination geometry for Cd(II) atoms in **3** (the 30% probability level), all hydrogen atoms and water molecules have been omitted for clarity. (B) A 2D covalent molecular structure of **3**. (C) 3D network pillared by 4,4'-bpy ligands.

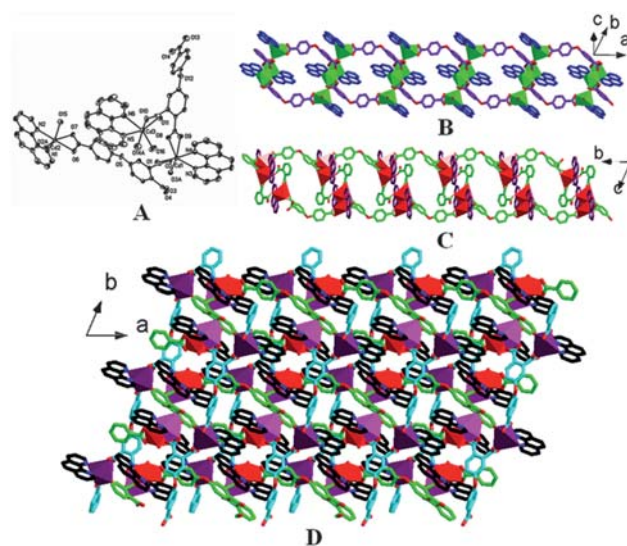


Fig. 6 ORTEP drawing of coordination sphere in the complex **7** (A), an infinite 1D ribbon chain composed of Cd1 and Cd2 ions (B), a infinite 1D ribbon chain composed of Cd1 and Cd3 ions (C), and a 2D molecular structure of **7** (D).

carboxylic group in bidentate chelating mode, and two oxygen atoms from one carboxylic group in μ_2 - η^2 - η^1 coordination mode. Cd2 ion possesses an octahedral coordination sphere formed by two nitrogen atoms of phen ligand, two oxygen atoms from one bidentate chelating carboxylic group, and one oxygen atom of water molecule, and one oxygen atom from one carboxylic group in μ_2 - η^2 - η^1 coordination mode. For Cd3 ion, hepta-coordinated geometry is completed by two nitrogen atoms and five oxygen atoms (four from two bidentate chelating carboxylic groups and one from water molecule). As can be seen, the Cd1 and Cd2 ions share one carboxylic group of the L^4 ligand in μ_2 - η^2 - η^1 coordination mode to form a dinuclear subunit, which is linked by L^4 ligands to generate a 1D ribbon chain along the a axis. The isolated Cd1 and Cd3 ions are assembled into a 1D double chain along the b axis. These two kinds of different directional double chains are compiled through the collective Cd1 ions as node, leading to a 2D covalent framework in $a \times b$ plane. The single crystal structures of **2** and **7** reveal that multicarboxylate ligands with semirigid central framework lead a 2D instead of 1D structure for the resulting complexes in cooperation with the 2,2'-bpy ligand.

Luminescent property of ligands L^1 - L^4 and complexes 1-7

The solid state emission spectra of complexes **1-7** together with the four precursors H_3L^1 - H_3L^4 have been recorded at room temperature and the related data compiled in Table 3. As shown in Fig. S3 (ESI),[†] the solid emission spectra of ligands H_3L^1 - H_3L^4 are very similar with the emission band observed at 395, 397, 399, and 408 nm, respectively, which is assigned to the typical intraligand π - π^* or π - n electronic transition.¹³ The slight difference in the emission peak for H_3L^1 - H_3L^4 is probably due to the slightly different electron-withdrawing effect resulted from different positions of asymmetrically attached carboxylic groups for these four ligands. Formation of Cd(II) complexes with either di- or trinuclear subunits from metal free L^1 - L^4 ligands with the help of secondary ligand does not induce change in the luminescent emission of **1-7** (except **3**) in comparison with corresponding metal free ligand, and the corresponding intraligand emission bands of H_3L^1 - H_3L^4 are in the range of 381-394 nm in the luminescent emission spectra of **1-7** (except **3**), Fig. S4 (ESI).[†] The emission band at 450 nm observed for **3** with a red shift of 55 nm relative to that of metal free ligand is assigned to LMCT on the basis of previous experimental result together with

molecular orbital calculation on the Cd(II) coordination polymers.^{4b,8e,14}

The effect of secondary N-donor ligands and tricarboxylate ligands on the structures of 1-7

As can be seen in Fig. 7, nine types of different coordination modes and two kinds of coordination configurations exist in **1-7** for the four ligands L^1 - L^4 . For the three complexes **1-3** built from L^1 ligand, the difference in their molecular structures reveals the significant spacer effect of secondary N-donor ligands in tuning the molecular structures of coordination polymers as well as the bridging modes and conformations of L^1 ligand, Fig. 7A-7D. In particular, most carboxylate ligands have been revealed to form isostructures of coordination polymers for most transition metals with the help of phen and 2,2'-bpy as secondary ligand due to their similar coordination modes of the later two ligands.¹⁵ However, different framework structure observed between **1** and **2** in the present case clearly indicates the size effect of the secondary N-donor ligand on the complex structure. It is worth noting that the size effect between phen and 2,2'-bpy secondary ligands on tuning the molecular structure of **4** and **5** assembled from L^2 ligand is not observed, indicating that L^1 ligand is more sensitive to the size of secondary ligand during the formation of its coordination polymers than L^2 .

Despite the fact that exact coordination mode and conformation of the four ligands in every complex have been detailed in the above-described molecular structure section, it still appears necessary to reveal and understand the relationship between the coordination mode of carboxylic groups as well as conformation of ligands and the molecular structure of complex for the purpose of rational design and synthesis of functional coordination polymers. In **1-3**, the 4-carboxylic group of L^1 in μ_2 - η^2 - η^1 linking mode as main factor connects the Cd(II) ions into a di- or trinuclear subunit. For **4** and **5**, L^2 ligand exhibits a μ_5 -bridging mode with the 2-, 2'-, and 3-carboxylic groups possessing μ_2 - η^2 - η^1 , μ_2 - η^2 - η^1 , and μ_2 - η^1 - η^1 coordination mode, respectively, inducing the formation of trinuclear subunit in these two complexes. In addition, both *cis*- and *trans*-typed configurations have been observed for symmetric semi-rigid V-shaped ligands.^{7,16} This is also true for the asymmetric L^1 and L^2 ligands in **1** and **4**. As for the other two complexes **6** and **7** assembled from L^3 and L^4 , respectively, also with the same phen secondary ligand,

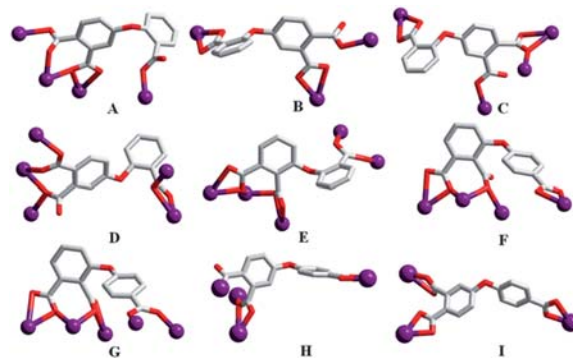


Fig. 7 The coordination modes of the four ligands L^1 - L^4 in **1-7** (A for **1**, B and C for **2**, D for **3**, E for **4** and **5**, F and G for **6**, and H and I for **7**).

Table 3 The data of emissions in solid state of ligands H_3L^1 - H_3L^4 and complexes **1-7**

Compound	λ_{ex}/nm	λ_{em}/nm
L^1	246	395
L^2	246	397
L^3	246	399
L^4	246	408
1	246	394
2	246	389
3	320	450
4	320	381
5	320	383
6	246	390
7	246	391

L³ ligand exhibits a much bender conformation than L¹ and L², resulting in the formation of a much wavier 1D double chain in **6** than in **1** and **4**. This indicates the effect of the positions of three asymmetric carboxylic substituents at the semi-rigid V-shaped central molecular framework on the structure of MOFs. For L⁴ ligand in **7**, the long *trans*-coordination conformation plays an important role in the formation of a 2D covalent network. Comparison in the molecular structure of **7** with **1**, **4**, and **6** also reveals the effect of the asymmetric positions of three carboxylic groups on tuning the structure of coordination polymers.

Conclusion

In summary, four asymmetric semi-rigid V-shaped tricarboxylate ligands have been employed for the first time to construct Cd(II) coordination polymers with di- or trinuclear subunit. Structural investigation reveals that the subunits could be successfully tuned by tuning the positions of asymmetrically attached carboxylic groups at the V-shaped central molecular framework in the tricarboxylate ligand and size of secondary ligand.

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