



A series of Cd(II) complexes with π - π stacking and hydrogen bonding interactions: Structural diversities by varying the ligands

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ABSTRACT

Seven new Cd(II) complexes consisting of different phenanthroline derivatives and organic acid ligands, formulated as $[\text{Cd}(\text{PIP})_2(\text{dnba})_2]$ (**1**), $[\text{Cd}(\text{PIP})(\text{ox})] \cdot \text{H}_2\text{O}$ (**2**), $[\text{Cd}(\text{PIP})(1,4\text{-bdc})(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$ (**3**), $[\text{Cd}(3\text{-PIP})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ (**4**), $[\text{Cd}_2(3\text{-PIP})_4(4,4'\text{-bpdC})(\text{H}_2\text{O})_2] \cdot 5\text{H}_2\text{O}$ (**5**), $[\text{Cd}(3\text{-PIP})(\text{nip})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (**6**), $[\text{Cd}_2(\text{TIP})_4(4,4'\text{-bpdC})(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (**7**) (PIP=2-phenylimidazo[4,5-*f*]1,10-phenanthroline, 3-PIP=2-(3-pyridyl)imidazo[4,5-*f*]1,10-phenanthroline, TIP=2-(2-thienyl)imidazo[4,5-*f*]1,10-phenanthroline, Hdnba=3,5-dinitrobenzoic acid, H₂ox=oxalic acid, 1,4-H₂bdc=benzene-1,4-dicarboxylic acid, 4,4'-H₂bpdC=biphenyl-4,4'-dicarboxylic acid, H₂nip=5-nitroisophthalic acid) have been synthesized under hydrothermal conditions. Complexes **1** and **4** possess mononuclear structures; complexes **5** and **7** are isostructural and have dinuclear structures; complexes **2** and **3** feature 1D chain structures; complex **6** contains 1D double chain, which are further extended to a 3D supramolecular structure by π - π stacking and hydrogen bonding interactions. The N-donor ligands with extended π -system and organic acid ligands play a crucial role in the formation of the final supramolecular frameworks. Moreover, thermal properties and fluorescence of **1–7** are also investigated.

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1. Introduction

The design and construction of discrete and polymeric metal-organic complexes with coordination bonds and noncovalent intermolecular forces have attracted great attention in recent years [1–7]. To date, much researches have focused on controlling motifs of metal-organic complexes through coordination bonds, whereas relatively less attention has been given to noncovalent interactions [6–9]. In general, it has been recognized that noncovalent intermolecular forces such as hydrogen bonding interactions, being reasonably strong and highly directional, can be used as structure-directing tools in generating many molecular solids with novel properties [10–14]. The π - π stacking interaction is also an important and powerful noncovalent intermolecular interaction for directing the supramolecular architectures [15,16]. A successful strategy in constructing such solid materials is to employ appropriate versatile functional ligands which have strong coordination ability as well as providing the hydrogen bond acceptors/donors and π -conjugated system for extending their networks [16–18].

As is known, the 1,10-phenanthroline (phen) ligand has been widely used to construct supramolecular architectures [19,20]. As important phen derivatives, to our knowledge, 2-phenylimidazo[4,5-*f*]1,10-phenanthroline (PIP), 2-(3-pyridyl)imidazo[4,5-*f*]1,10-phenanthroline (3-PIP), 2-(2-thienyl)imidazo[4,5-*f*]1,10-phenanthroline (TIP) are less investigated [7,21–24]. Compared with phen, these ligands

contain both an extended π -system and an imidazole ring, capable of acting as hydrogen bond acceptors/donors or of forming coordination interactions to some metal ions, as well as extending the π -system themselves [25]. Therefore, these ligands as good candidates have attracted our interest for construction of metal-organic supramolecular architectures. On the other hand, polycarboxylate ligands, such as benzenedicarboxylates have been extensively employed to construct coordination polymers exhibiting a wide range of structural diversities and potential applications as functional materials [26–28].

In this paper, we report the syntheses, structures and properties of seven new Cd(II) complexes, namely, $[\text{Cd}(\text{PIP})_2(\text{dnba})_2]$ (**1**), $[\text{Cd}(\text{PIP})(\text{ox})] \cdot \text{H}_2\text{O}$ (**2**), $[\text{Cd}(\text{PIP})(1,4\text{-bdc})(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$ (**3**), $[\text{Cd}(3\text{-PIP})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ (**4**), $[\text{Cd}_2(3\text{-PIP})_4(4,4'\text{-bpdC})(\text{H}_2\text{O})_2] \cdot 5\text{H}_2\text{O}$ (**5**), $[\text{Cd}(3\text{-PIP})(\text{nip})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (**6**), $[\text{Cd}_2(\text{TIP})_4(4,4'\text{-bpdC})(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (**7**). All structures are extended into three dimensional (3D) supramolecular frameworks by strong π - π stacking and hydrogen bonding interactions. On the basis of synthesis and structural characterization, the role of intermolecular forces in the creation of molecular architectures is discussed. The thermal stabilities and luminescent properties of complexes **1–7** have been reported (Scheme 1).

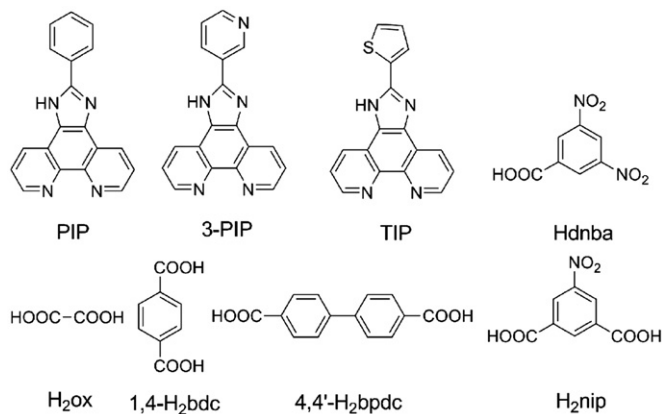
2. Experimental section

2.1. General materials and methods

Solvents and starting materials for synthesis were commercially available and used as received. The N-donor ligands PIP, 3-PIP and

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Scheme 1. Structures of the PIP, 3-PIP, TIP ligands and organic acid ligands appeared in complexes 1–7.

TIP were synthesized by the methods of the literature [29] and characterized by FT-IR spectra and ^1H NMR. FT-IR spectra (KBr pellets) were taken on a Magna FT-IR 560 spectrometer. Thermogravimetric data for complexes 1–7 were performed using a Pyris Diamond thermal analyzer. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C analyzer. Fluorescence spectra were recorded at room temperature on a Hitachi F-4500 fluorescence/phosphorescence spectrophotometer.

2.2. Synthesis

2.2.1. $[\text{Cd}(\text{PIP})_2(\text{dnba})_2] \cdot (\mathbf{1})$

A mixture of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.031 g, 0.1 mmol), PIP (0.015 g, 0.05 mmol), Hdnba (0.0212 g, 0.1 mmol), NaOH (0.2 mmol), and H_2O (8 mL) was stirred for 20 min and sealed in a 25 mL Teflon-lined stainless-steel container. The container was heated to 170 °C and held at this temperature for 4 days. It was then cooled to room temperature at a rate of 5 °C h^{-1} . Yellow block crystals suitable for X-ray diffraction of complex 1 were isolated by mechanical separation from amorphous solid in 25% yield (based on Cd(II) salt). Anal. Calcd for $\text{C}_{52}\text{H}_{30}\text{CdN}_{12}\text{O}_{12}$: C 55.35, H 2.66, N 14.90%. Found: C 55.31, H 2.69, N 14.87%. IR (KBr, cm^{-1}): 3095 (w), 2970(w), 2855(w), 2360(w), 1615(s), 1538(s), 1346(s), 1079(m), 818(s), 733(s).

2.2.2. $[\text{Cd}(\text{PIP})(\text{ox})] \cdot \text{H}_2\text{O} (\mathbf{2})$

The synthetic procedure for 2 is the same as that for 1 except that H_2ox (0.0126 g, 0.1 mmol) was used instead of Hdnba. Yellow block crystals suitable for X-ray diffraction of complex 2 were isolated by mechanical separation from amorphous solid in 40% yield (based on Cd(II) salt). Anal. Calcd for $\text{C}_{21}\text{H}_{13}\text{CdN}_4\text{O}_5$: C 49.05, H 2.53, N 10.90%. Found: C 49.02, H 2.54, N 10.87%. IR (KBr, cm^{-1}): 3486(m), 3065(w), 2843(w), 2360(w), 1652(s), 1592(s), 1463(s), 1308(s), 1079(m), 795(s), 733(s).

2.2.3. $[\text{Cd}(\text{PIP})(1,4\text{-bdc})(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O} (\mathbf{3})$

The synthetic procedure for 3 is the same as that for 1 except that 1,4- H_2bdc (0.0166 g, 0.1 mmol) was used instead of Hdnba. Yellow block crystals suitable for X-ray diffraction of complex 3 were isolated by mechanical separation from amorphous solid in 23% yield (based on Cd(II) salt). Anal. Calcd for $\text{C}_{27}\text{H}_{26}\text{CdN}_4\text{O}_9$: C 48.87, H 3.92, N 8.45%. Found: C 48.81, H 3.95, N 8.41%. IR (KBr, cm^{-1}): 3456(w), 3062(w), 2361(w), 1581(s), 1477(m), 1446(m), 1392(m), 1342(s), 1288(m), 1234(m), 1172(w), 1072(w), 948(m), 844(m), 802(m), 753(s), 698(m).

2.2.4. $[\text{Cd}(3\text{-PIP})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O} (\mathbf{4})$

The synthetic procedure for 4 is the same as that for 1 except that 3-PIP (0.015 g, 0.05 mmol) was used instead of PIP, and Hdnba (0.021 g, 0.1 mmol) was not used. Yellow block crystals suitable for X-ray diffraction of complex 4 were isolated by mechanical separation from amorphous solid in 28% yield (based on Cd(II) salt). Anal. Calcd for $\text{C}_{36}\text{H}_{34}\text{CdN}_{10}\text{O}_6$: C 53.00, H 4.17, N 17.18%. Found: C 53.06, H 4.21, N 17.14%. IR (KBr, cm^{-1}): 3326(w), 3060(w), 2360(m), 1608(w), 1581(s), 1477(m), 1386(s), 1338(m), 1213(s), 1128(m), 1080(s), 823(m), 732(m).

2.2.5. $[\text{Cd}_2(3\text{-PIP})_4(4,4'\text{-bpdc})(\text{H}_2\text{O})_2] \cdot 5\text{H}_2\text{O} (\mathbf{5})$

The synthetic procedure for 5 is the same as that for 1 except that 3-PIP (0.015 g, 0.05 mmol) and 4,4'- H_2bpdc (0.0246 g, 0.1 mmol) were used instead of PIP and Hdnba. Yellow block crystals suitable for X-ray diffraction of complex 5 were isolated by mechanical separation from amorphous solid in 25% yield (based on Cd(II) salt). Anal. Calcd for $\text{C}_{86}\text{H}_{62}\text{Cd}_2\text{N}_{20}\text{O}_{11}$: C 58.10, H 3.49, N 15.76%. Found: C 58.03, H 3.52, N 15.74%. IR (KBr, cm^{-1}): 3425(w), 3062(w), 2362(m), 1570(s), 1460(m), 1386(s), 1070(m), 947(m), 821(w), 731(m).

2.2.6. $[\text{Cd}(3\text{-PIP})(\text{nip})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O} (\mathbf{6})$

The synthetic procedure for 6 is the same as that for 1 except that 3-PIP (0.015 g, 0.05 mmol) and H_2nip (0.0211 g, 0.1 mmol) were used instead of PIP and Hdnba. Yellow block crystals suitable for X-ray diffraction of complex 6 were isolated by mechanical separation from amorphous solid in 45% yield (based on Cd(II) salt). Anal. Calcd for $\text{C}_{26}\text{H}_{18}\text{CdN}_6\text{O}_8$: C 47.64, H 2.75, N 12.83%. Found: C 47.58, H 2.78, N 12.85%. IR (KBr, cm^{-1}): 3334(m), 3080(w), 2367(w), 1600(s), 1562(m), 1523(m), 1446(m), 1353(s), 1194(m), 1079(m), 962(m), 825(m), 718(s), 633(m).

2.2.7. $[\text{Cd}_2(\text{TIP})_4(4,4'\text{-bpdc})(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O} (\mathbf{7})$

The synthetic procedure for 7 is the same as that for 1 except that TIP (0.015 g, 0.05 mmol) and 4,4'- H_2bpdc (0.0246 g, 0.1 mmol) were used instead of PIP and Hdnba. Yellow block crystals suitable for X-ray diffraction of complex 7 were isolated by mechanical separation from amorphous solid in 30% yield (based on Cd(II) salt). Anal. Calcd for $\text{C}_{82}\text{H}_{58}\text{Cd}_2\text{N}_{16}\text{O}_9\text{S}_4$: C 55.77, H 3.29, N 12.69%. Found: C 55.73, H 3.32, N 12.63%. IR (KBr, cm^{-1}): 3356(w), 3040(w), 2365(w), 1605(m), 1578(s), 1523(m), 1378(s), 1059(m), 1000(m), 833(s), 773(s), 730(s), 698(s), 676(s).

2.3. X-ray crystallographic study

A Bruker Apex CCD diffractometer (MoK α radiation, graphite monochromator, $\lambda=0.71073$ Å) was used to collect data. The structures were solved by direct methods with SHELXS-97 and Fourier techniques and refined by the full-matrix least-squares method on F^2 with SHELXL-97 [30,31]. All non-hydrogen atoms were refined anisotropically, the H-atoms from nitrogen atom of imidazole ring in PIP, 3-PIP, or TIP were located in different Fourier synthesis maps, and other hydrogen atoms of the ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The H-atoms of water molecules have not been localized. All the crystal data and structure refinement details for the seven complexes are given in Table 1. The data of relevant bond distances and angles are listed in Table S1. Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC reference numbers 784,899, 784,900, 784,901, 784,902, 784,903, 784,904, and 784,905 for complexes 1, 2, 3, 4, 5, 6, and 7, respectively.

Table 1
Crystal data and structure refinement parameters for complexes **1–7**.

Complex	1	2	3	4	5	6	7
Formula	C ₅₂ H ₃₀ CdN ₁₂ O ₁₂	C ₂₁ H ₁₃ CdN ₄ O ₅	C ₂₇ H ₂₆ CdN ₄ O ₉	C ₃₆ H ₃₄ CdN ₁₀ O ₆	C ₈₆ H ₆₂ Cd ₂ N ₂₀ O ₁₁	C ₂₆ H ₁₈ CdN ₆ O ₈	C ₈₂ H ₅₈ Cd ₂ N ₁₆ O ₉ S ₄
<i>F_w</i>	1127.28	513.75	662.93	815.13	1776.38	654.86	1764.48
Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Tetragonal	Triclinic	Tetragonal
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> –1	<i>Pbcn</i>	<i>I</i> 4 ₁ / <i>a</i>	<i>P</i> –1	<i>I</i> 4 ₁ / <i>a</i>
<i>a</i> (Å)	14.0642(10)	8.9750(9)	9.4948(15)	13.805(5)	20.627(2)	9.002(5)	20.587(5)
<i>b</i> (Å)	22.4799(15)	17.6523(17)	10.7833(17)	9.278(5)	20.627(2)	11.139(5)	20.587(5)
<i>c</i> (Å)	15.6391(10)	12.6855(12)	13.591(2)	25.858(5)	35.584(5)	12.831(5)	34.824(5)
α (deg)	90	90	93.820(2)	90.000(5)	90	69.824(5)	90.000(5)
β (deg)	102.1330(10)	99.6480(10)	102.414(2)	90.000(5)	90	83.066(5)	90.000(5)
γ (deg)	90	90	104.722(2)	90.000(5)	90	85.805(5)	90.000(5)
<i>V</i> (Å ³)	4834.0(6)	1981.3(3)	1303.5(3)	3312(2)	15140(3)	1198.1(10)	14759(5)
<i>Z</i>	4	4	2	4	8	2	8
<i>D_c</i> (g cm ^{–3})	1.549	1.722	1.689	1.635	1.559	1.815	1.588
μ (mm ^{–1})	0.531	1.145	0.902	0.725	0.641	0.979	0.763
<i>F</i> (000)	2280	1020	672	1664	7214	656	7152
Tot. data	26,348	9887	11,306	31,413	38,506	6169	52,395
Uniq. data	9462	3477	5140	4123	6686	4202	6537
<i>R</i> _{int}	0.0381	0.0348	0.0693	0.0289	0.1253	0.0308	0.0742
<i>R</i> ₁ ^a / <i>wR</i> ₂ ^b	0.0403/0.0982	0.0318/0.0652	0.0480/0.0942	0.0311/0.0879	0.0539/0.1199	0.0433/0.0790	0.0340/0.0737
GO _F on <i>F</i> ²	0.980	1.025	0.881	1.059	1.000	1.010	1.079

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|.$$

$$^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)] \}^{1/2}.$$

3. Results and discussion

3.1. Description of crystal structures for **1–7**

3.1.1. [Cd(PIP)₂(dnba)₂] (**1**)

The crystal structure of **1** consists of a discrete mononuclear [Cd(PIP)₂(dnba)₂]. As shown in Fig. 1a, each Cd(II) atom is six-coordinated and adopts a distorted octahedral arrangement, being ligated by four nitrogen atoms from two chelating PIP ligands with bond distances of 2.325(3)–2.429(3) Å, and two oxygen atoms of two dnba ligands (Cd1–O1 = 2.298(3), Cd1–O3 = 2.298(3) Å). The N1, N5, N6, and O3 atoms comprise the equatorial plane, whereas the N2 and O1 atoms are located in the axial positions. The adjacent discrete mononuclears are arranged into a 1D supramolecular architecture by intermolecular π – π stacking interactions (3.679, 3.771 and 3.878 Å) and one kind of hydrogen bonding interactions between the N atom of imidazole group and carboxylate oxygen atom [N(3)–H(1)···O(4) 2.8081 Å, 168° and N(7)–H(7A)···O(2) 2.7323 Å, 164°] (Fig. 1b, Fig. S1a, S1b). The adjacent 1D supramolecular chains are further connected by another kind of hydrogen bonding interactions between the C atom of pyridine group and carboxylate oxygen atom [C(14)–H(14A)···O(7) 3.2743 Å, 131°, and C(43)–H(43A)···O(8) 3.4429 Å, 166°] to form a 2D supramolecular network (Fig. 1c, Fig. S1c). The adjacent 2D supramolecular layers are further connected by intermolecular π – π stacking interactions (3.954 Å) to form a 3D supramolecular network (Fig. 1d, Fig. S1d).

3.1.2. [Cd(PIP)(ox)]·H₂O (**2**)

The structure of **2** is a 1D zigzag chain. The asymmetric unit of **2** is composed of one Cd atom, one PIP ligand, one ox ligand and one uncoordinated water molecule (Fig. 2a). Each Cd(II) atom displays a distorted octahedral coordination geometry, which is coordinated by four oxygen atoms from two ox ligands and two nitrogen atoms from one chelating PIP ligand. The Cd–O bond lengths are in the range of 2.238(2)–2.317(2) Å, and the Cd–N bond lengths are in the range of 2.296(3)–2.312(3) Å. Each Cd atom is linked to adjacent Cd atoms through the bridging bis-chelating ox ligands, forming a

unique zigzag chain structure (Fig. 2b), where the Cd–Cd–Cd angle, defined by the orientation of the ox ligands in the chain, is 100.016(6)°. The PIP ligands in **2** are arranged in a parallel fashion at both sides of the chain, leading to a structure suitable to form π – π stacking interactions. The 1D zigzag chains are further extended into a 3D supramolecular architecture by intermolecular π – π stacking (3.800 Å) and hydrogen bonding interactions between the N atom of imidazole group and carboxylate oxygen atom [N(4)–H(4A)···O(3) 2.767 Å, 168°] (Fig. 2c, Fig. S2a, S2b). The results indicate that the weak noncovalent interactions are important in the formation of the final supramolecular structure of **2**.

3.1.3. [Cd(PIP)(1,4-bdc)(H₂O)]·4H₂O (**3**)

The structure of **3** is also a 1D zigzag chain. The asymmetric unit of **3** is composed of one Cd atom, one PIP ligand, one 1,4-bdc ligand, one coordinated water molecule and four uncoordinated water molecules (Fig. 3a). Each Cd(II) atom is coordinated by four carboxylic oxygen atoms from two different 1,4-bdc ligands and one oxygen atom from one coordinated water molecule, and two nitrogen atoms from one chelating PIP ligands, thereby forming a seven-coordinated structure with a N₂O₅ donor set. The Cd–O bond lengths are in the range 2.238(4)–2.527(4) Å, and the Cd–N bond lengths are in the range 2.335(4)–2.405(4) Å. Each Cd atom is linked to adjacent Cd atoms through the bridging bis-chelating 1,4-bdc ligands, forming a unique zigzag chain structure (Fig. 3b), where the Cd–Cd–Cd angle, defined by the orientation of the 1,4-bdc ligands in the chain, is 95.588(4)°. The PIP ligands in **3** are arranged in a parallel fashion at both sides of the chain, leading to a structure suitable to form π – π stacking interactions. The adjacent 1D zigzag chains are further extended into a 2D supramolecular architecture by intermolecular π – π stacking interactions (3.705 Å) and two kinds of hydrogen bonding interactions between the N atom of imidazole group and carboxylate oxygen atom [N(4)–H(4A)···O(4) 2.8644 Å, 149°], and between the oxygen atom of coordinated water and carboxylate oxygen atom [O(5)–H(5A)···O(2) 2.7251 Å, 157°] (Fig. 3c, Fig. S3a). The adjacent 2D supramolecular architectures are further connected by intermolecular π – π stacking interactions (3.921 Å) to form a 3D supramolecular network (Fig. 3d, Fig. S3b).

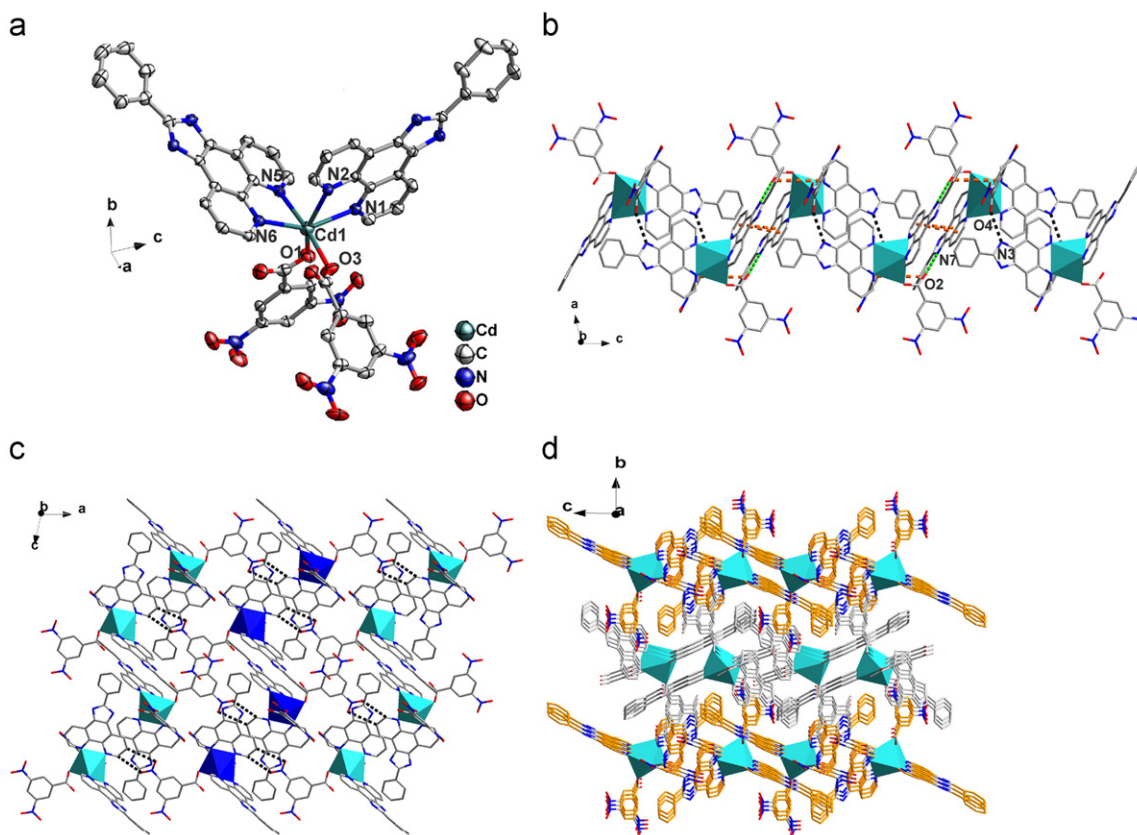


Fig. 1. View of (a) the coordination environment for Cd(II) atom in **1** (thermal ellipsoids are at the 30% probability level); (b) the 1D chain of **1** formed through intermolecular π - π stacking and hydrogen bonding interactions; (c) the 2D layer of **1** formed between 1D chains by hydrogen bonding interactions; and (d) the 3D structure of **1** formed through π - π stacking interactions between different supramolecular layers.

3.1.4. $[Cd(3\text{-PIP})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ (**4**)

The crystal structure of **4** consists of a discrete mononuclear $[Cd(3\text{-PIP})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$. As shown in Fig. 4a, each Cd(II) atom is six-coordinated and adopts a distorted octahedral arrangement, being ligated by four nitrogen atoms from two chelating 3-PIP ligands with bond distances of 2.3653–2.3712 Å, and two oxygen atoms from two coordinated water molecules with bond distances of 2.2188(15) Å. Moreover, there are four uncoordinated water molecules in **4**. The adjacent discrete mononuclears are arranged into a 2D supramolecular architecture by intermolecular π - π stacking interactions (3.536, 3.574, 3.591, and 3.682 Å) and hydrogen bonding interactions between the N atom of imidazole group and oxygen atom of coordinated water molecules [N(3)–H(3B)⋯O(1) 2.6477 Å, 160°] (Fig. 4b, Fig. S4a). The adjacent 2D supramolecular architectures are further connected by intermolecular π - π stacking interactions (3.644 Å) to form a 3D supramolecular network (Fig. 4c, Fig. S4b).

3.1.5. $[Cd_2(3\text{-PIP})_4(4,4'\text{-bpdC})(\text{H}_2\text{O})_2] \cdot 5\text{H}_2\text{O}$ (**5**)

The crystal structure of **5** consists of a discrete dinuclear $[Cd_2(3\text{-PIP})_4(4,4'\text{-bpdC})(\text{H}_2\text{O})_2] \cdot 5\text{H}_2\text{O}$. As shown in Fig. 5a, each Cd(II) atom is six-coordinated and adopts a distorted octahedral arrangement, being ligated by four nitrogen atoms from two chelating 3-PIP ligands with bond distances of 2.337(5)–2.376(5) Å, and two oxygen atoms from 4,4'-bpdC and one water molecule, respectively, [Cd1–O1 = 2.226(4), Cd1–O5 = 2.320(4) Å]. Moreover, there are five uncoordinated water molecules in **5**. The adjacent discrete dinuclears (Fig. 5a) are arranged into a 3D supramolecular architecture by intermolecular π - π stacking interactions (3.609, 3.617, 3.656,

3.666, 3.743, and 3.941 Å) and hydrogen bonding interactions between the N atom of imidazole group and oxygen atom of coordinated water molecules [N(3)–H(3 A)⋯O(5) 2.6978 Å, 156°] (Fig. 5b, Fig. S5a, S5b).

3.1.6. $[Cd(3\text{-PIP})(\text{nip})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (**6**)

The structure of **6** is a 1D double chain structure. The asymmetric unit of **6** is composed of one Cd atom, one 3-PIP ligand, one nip ligand, one coordinated water molecule and one uncoordinated water molecule (Fig. 6a). Each Cd(II) atom displays a distorted octahedral coordination geometry, which is coordinated by two carboxylic oxygen atoms from two different nip ligands and one oxygen atom from one coordinated water molecule, two chelating nitrogen atoms of the 3-PIP ligand and one nitrogen atom from 3-pyridyl group of another 3-PIP ligand. The O2 atom from the nip ligand has a weak bonding interaction with the Cd(II) atom (Cd(1)–O(2) = 2.613(5) Å), which is longer than ones found in other complexes [32], indicative of weak interactions between the oxygen atom and the Cd(II) center. The Cd–O bond lengths are in the range 2.286(6)–2.541(5) Å, and the Cd–N bond lengths are in the range 2.357(5)–2.419(5) Å. It was noted that the coordination environment of the Cd(II) atom in **6** is clearly different from complexes **4** and **5**, the N atom from individual 3-pyridyl group of 3-PIP act as the bridging site. Each Cd atom is linked to adjacent Cd atoms through the bridging 3-PIP ligands, forming a unique linear chain structure. The adjacent two linear chains are further connected into a double chain structure through the bridging bis-monodentate nip ligands (Fig. 6b). The adjacent 1D double chains are further arranged into a 2D supramolecular architecture by intermolecular π - π

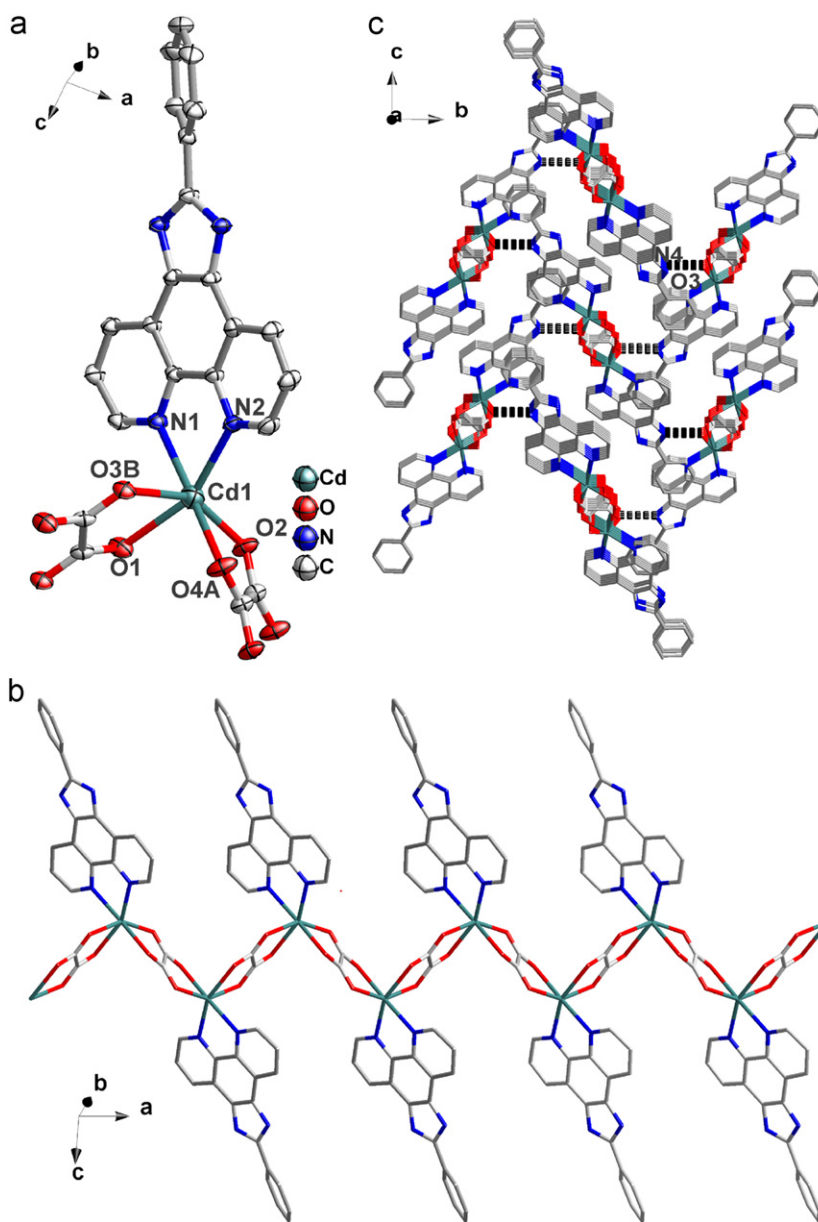


Fig. 2. View of (a) the coordination environment for Cd(II) atom in **2** (thermal ellipsoids are at the 30% probability level); (b) the 1D zigzag chain in **2**; and (c) the 3D supramolecular structure of **2** formed through π - π stacking and hydrogen bonding interactions.

stacking interactions (3.817 Å) and one kind of hydrogen bonding interactions between the oxygen atom of coordinated water molecule and carboxylate oxygen atom [O(3)-H(3C)⋯O(5) 2.7716 Å, 172°] (Fig. 6c, Fig. S6a). The adjacent 2D supramolecular architectures are further connected by intermolecular π - π stacking interactions (3.674 Å) and another kind of hydrogen bonding interactions between the N atom of imidazole group and carboxylate oxygen atom [N(5)-H(5A)⋯O(4) 2.7340 Å, 161°] to form a 3D supramolecular network (Fig. 6d, Fig. S6b).

3.1.7. $[Cd_2(TIP)_4(4,4'-bpdc)(H_2O)_2] \cdot 3H_2O$ (**7**)

Complexes **7** and **5** are isostructural, which has similar neutral coordination environment to that of **5**, also shows distorted octahedral geometry (Fig. 7). Compared with **5**, the arranged fashion of the thienyl group of TIP ligands in **7** is different, leading to a structure suitable to form π - π interactions. Thus, the face-to-

face distances between the paired TIP rings are 3.868 and 3.902 Å (Fig. S7b). In fact, π - π stacking interactions play an important role in the formation and stabilization of the supramolecular structure [16].

3.2. Effect of the N-donor ligands and organic carboxylate anions on the structures of the complexes

In this paper, the structural differences of **1-7** indicate that both phen derivatives and organic carboxylate anions play an important role in the formation of such coordination architectures. Comparing complexes **1-3** obtained from the same PIP and Cd(NO₃)₂ under the same conditions, in **1**, pair of crossed PIP ligands coordinate to one Cd(II) atom, and dnba carboxylate anions exhibit monodentate coordination mode. The existence of the substituted -NO₂ groups increases the steric hindrance of the dnba ligand, resulting in the mononuclear structure of **1**. In **2** and **3**, only one PIP ligand coordinates

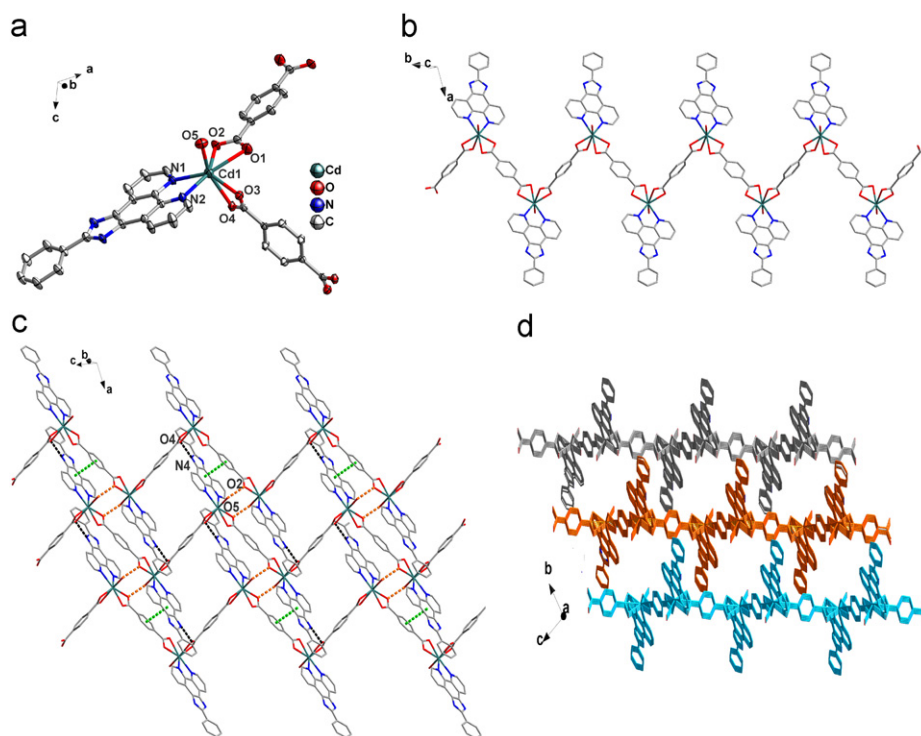


Fig. 3. View of (a) the coordination environment for Cd(II) atom in **3** (thermal ellipsoids are at the 30% probability level); (b) the 1D zigzag chain in **3**; (c) the 2D supramolecular structure of **3** formed between 1D chains by π - π stacking and hydrogen bonding interactions; and (d) the 3D structure of **3** formed through π - π stacking interactions between different supramolecular layers.

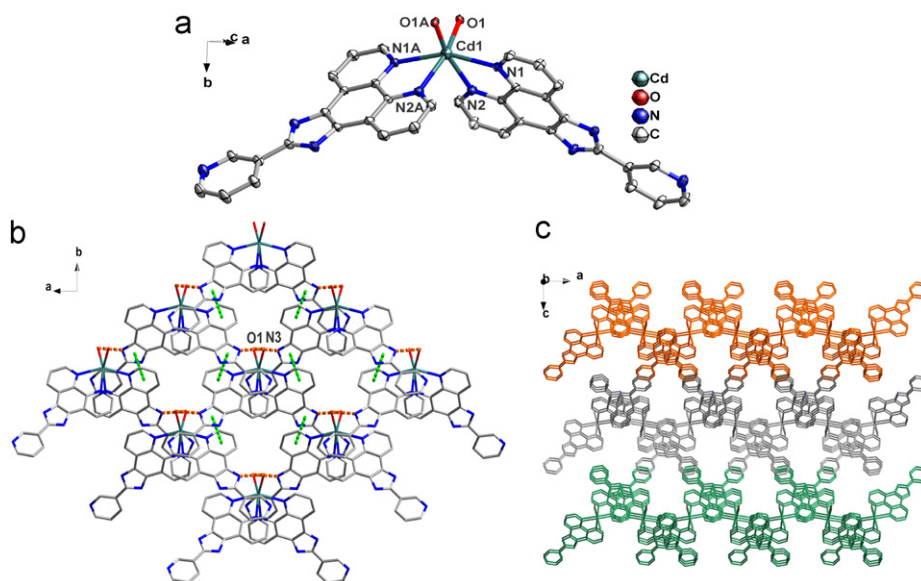


Fig. 4. View of (a) the coordination environment for Cd(II) atom in **4** (thermal ellipsoids are at the 30% probability level); (b) the 2D supramolecular structure of **4** formed through π - π stacking and hydrogen bonding interactions; and (c) the 3D structure of **4** formed through π - π stacking interactions between different supramolecular layers.

to one Cd(II) atom, the ox and 1,4-bdc carboxylate anions adopt bridging bis-chelating coordination mode and serve as a μ_2 bridge, resulting in 1D zigzag chains in **2** and **3**. The structural differences in **1–3** show the influence of the number of the carboxylate groups. Complexes **4–6** based on the same 3-PIP and Cd(NO₃)₂ also demonstrate the influence of the carboxylate anions on their structures. In **4**, the two water molecules and pair of crossed 3-PIP ligands all

coordinate to one Cd(II) atom, resulting in the mononuclear structure of **4**. In **5**, pair of crossed 3-PIP ligands coordinate to one Cd(II) atom, one 4,4'-bpdccarboxylate anion bridges two Cd(II) centers to form a very stable dinuclear structure. Clearly, the longer linear 4,4'-bpdccarboxylate ligand helps the formation of the discrete dinuclear complex **5**. Compared with PIP ligand in complexes **1–3**, 3-PIP ligand in complexes **4–6** has one extra coordination site, i.e. the nitrogen atom of

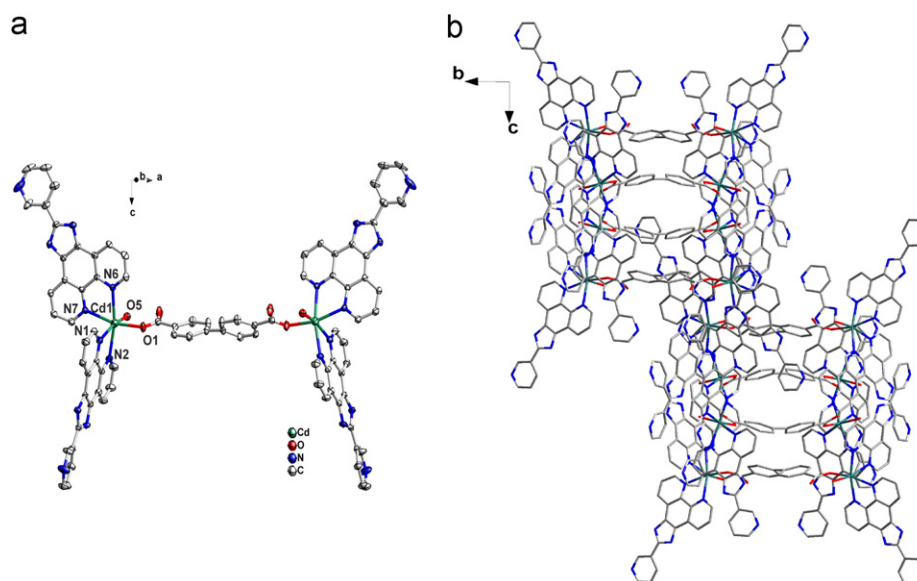


Fig. 5. View of (a) the dinuclear compound **5** (thermal ellipsoids are at the 30% probability level); (b) the 3D supramolecular framework of **5** formed through π - π stacking and hydrogen bonding interactions.

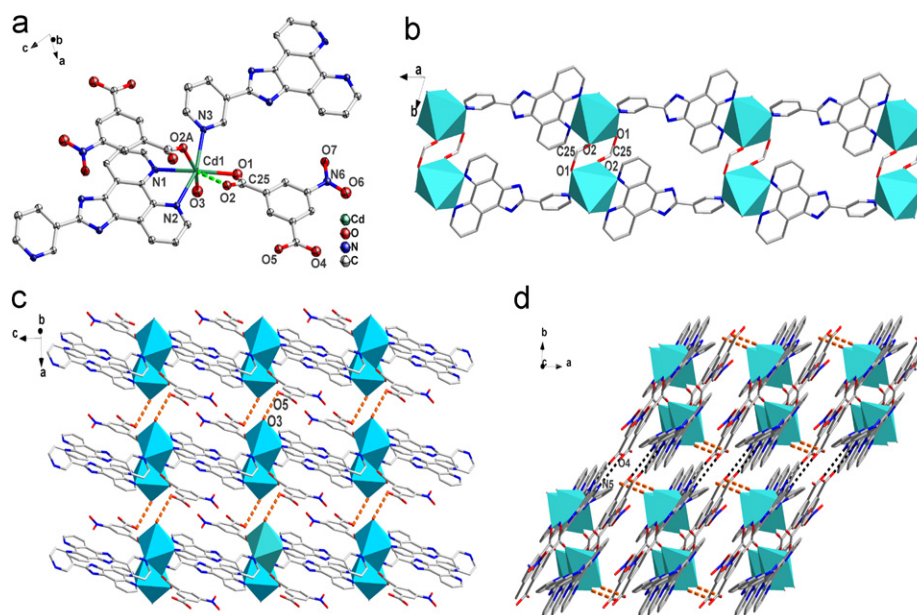


Fig. 6. View of (a) the coordination environment for Cd(II) atom in **6** (thermal ellipsoids are at the 30% probability level); (b) the double chain structure in **6** based on the dinuclear unit; (c) the 2D supramolecular structure of **6** formed between 1D chains by π - π stacking and hydrogen bonding interactions; and (d) the 3D structure of **6** formed through π - π stacking and hydrogen bonding interactions between different supramolecular layers.

pyridyl group of 3-PIP ligand, which could coordinate to the Cd atom as the bridging site. Fortunately, we obtained complex **6** with 1D double chain structure. In **6**, it is noted that the coordination environment of the Cd(II) atom is clearly different from that of complexes **4** and **5**, the N atom from individual 3-pyridyl group of 3-PIP act as the bridging site. Each Cd atom is linked to adjacent Cd atoms through the bridging 3-PIP ligands, forming a unique linear chain structure. The adjacent two linear chains are further extended into a double chain structure through the bridging bis-monodentate nip ligands.

The supramolecular structures constructed by π - π stacking and hydrogen bonding interactions can be modified by varying the

neutral N-donor chelating ligands. Although complexes **1** and **4** show similar mononuclear structures, the π - π interactions of the neutral ligands in them are slightly different. In **1**, the mononuclear structures connect with adjacent mononuclear structures through four types of π - π interactions and C-H...O and N-H...O hydrogen bonds to form a 3D supramolecular structure. However, in **4**, the mononuclear structures interact through five types of π - π interaction and N-H...O hydrogen bond to form a 3D supramolecular structure. Complexes **7** and **5** are isostructural. In **5**, the dinuclear structures interact through six types of π - π interaction and N-H...O hydrogen bonding interaction to form a 3D supramolecular structure. However, in **7**, the dinuclear structures

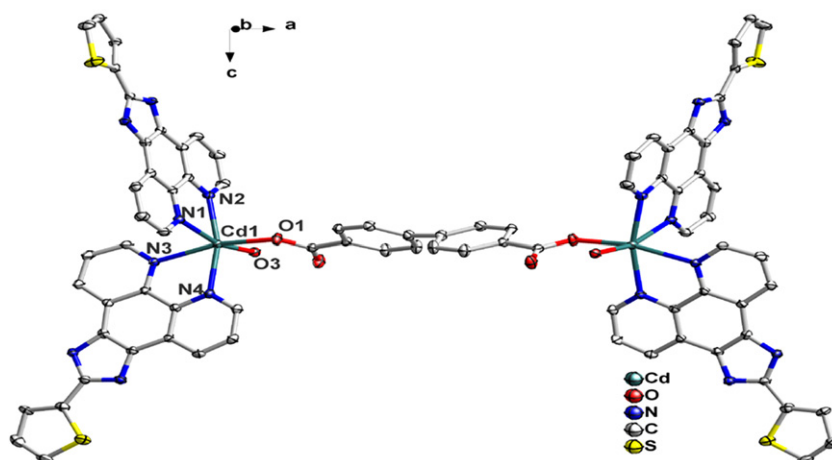


Fig. 7. View of the dinuclear compound **7** (thermal ellipsoids are at the 30% probability level).

interact by eight types of π - π interaction and N-H...O hydrogen bond to form a 3D supramolecular structure. Compared with **5**, there exist π - π interactions between TIP ligands in **7** with face-to-face distances of 3.868 and 3.902 Å. In contrast **2**, **3**, and **6**, in **2**, the zigzag chains are further stacked via one type of π - π interaction and N-H...O hydrogen bond to form a 3D supramolecular structure. However, in **3** and **6**, the chain structures are linked by two types of π - π interaction and two types of hydrogen bonds to form a 3D supramolecular structure. It is noteworthy that the structure of **3** is entirely different from that of the related structure [Cd(BDC)(phen)₂(C₂H₅OH)(H₂O)], where the two Cd(II) atoms are only bridged by BDC ligands to form a 1D zigzag chain [32]. The N-donor ligands with extended π -system play crucial role in the formation and stabilization of the final supramolecular frameworks.

3.3. Thermogravimetric analyses

Thermogravimetric analyses (TGA) are performed to gauge the thermal stabilities of these complexes as shown in Fig. S8. For **1**, there is only one-step weight loss. TGA shows complex **1** is stable below 350 °C. The successive mass loss from 350 to 713 °C may be attributed to the gradual elimination of the organic ligands. The remaining weight of 10.3% corresponds to the final product CdO (calcd, 11.4%). For **2**–**7**, there are two separate weight loss steps, respectively. For **2**, the first weight loss of 3.2% occurs at about 87 °C, which is attributed to the evacuation of crystallized water molecules (calcd, 3.5%). The second gradual elimination of the organic ligands between 344 and 820 °C corresponds to the loss of 69.56%. The remaining weight of 26.24% corresponds to the percentage (calcd, 25.00%) of the Cd and O components, indicating that the final product is CdO. The TG curve of complex **6** was similar to that of complex **2**, but the first weight loss of 5.3% is attributed to the evacuation of crystallized water molecules and coordinated water molecules (calcd, 5.5%). The remaining weight of 20.69% corresponds to the final product CdO (calcd, 19.16%). The TG curves of complexes **3**–**5** and **7** indicate that the framework of these compounds all began to collapse from 360 °C. In complex **3**, the mass loss region from 100 to 155 °C is due to dehydration of the crystallized water molecules and coordinated water molecules (obsd 14.00%, calcd 13.58% for **3**). The successive mass loss from 360 to 436 °C may be attributed to the rapid weight loss of the organic ligands. A residue of CdO remained (obsd 20.17%, calcd 19.37%). The resulting residue of compounds **4** and **5** remain as CdO (obsd 15.50%, calcd 15.75% for **4**; obsd 7.49%, calcd 7.23% for **5**) after the complete decomposition of the organic ligands. In compound **7**,

a rapid weight loss from 360 to 530 °C corresponds to the organic ligands and the remaining residue is CdO (obsd 7.49%, calcd 7.28%).

3.4. Luminescent properties of **1**–**7**

The solid-state luminescence properties of complexes **1**–**7** are measured at room temperature (Fig. 8). The emission of ligand PIP occurs at 444 nm upon excitation at 280 nm. Complexes **2** and **3** exhibit intense fluorescent emission bands with maximum at 474 and 510 nm, respectively, upon excitation at 300 nm, displaying some shifts relative to that of free PIP ligand. Therefore, the emission of complexes **2** and **3** may be attributed to ligand-to-metal charge transfer (LMCT) based on PIP ligand. The emission profile of **1** is very weak compared with that of **2** and **3**, which may be attributed to the significant difference of their structures. The emission for complexes **4**–**6** exhibit intense fluorescent emission bands with maximum at 494, 533, and 510 nm, respectively, upon excitation at 300 nm, while the free ligand 3-PIP shows luminescence in the solid state at $\lambda_{\text{max}}=424$ nm upon excitation at $\lambda_{\text{ex}}=260$ nm under the same experimental conditions. Complex **7** exhibits intense luminescent emission at $\lambda_{\text{max}}=551$ nm upon excitation at $\lambda_{\text{ex}}=310$ nm, while the free ligand TIP shows luminescence in the solid state at $\lambda_{\text{max}}=443$ nm upon excitation at $\lambda_{\text{ex}}=293$ nm under the same experimental conditions. Compared with that of the free ligand 3-PIP, the emission profiles of **4**–**6** are red-shifted, which may be due to the increase of conjugation upon metal coordination and originate from the ligand-to-metal charge-transfer (LMCT) [33].

4. Conclusions

Seven new supramolecular architectures have been successfully isolated under hydrothermal conditions by reactions of different phen derivatives and Cd(II) salts together with organic carboxylate anions auxiliary ligands. The influence of the N-donor ligands and organic carboxylate anions on the structures of the complexes has been studied. Complexes **1** and **4** have mononuclear structures, while complexes **5** and **7** have dinuclear structures; complexes **2** and **3** feature chain structures; complex **6** contains double chain structure. The structural difference of **1**–**7** indicates that phen derivatives and organic carboxylate anions play an important role in the formation of final architectures. Complexes **1**–**7** are further extended to a 3D structure by π - π stacking and hydrogen bonding interactions. As important phen derivatives, the key role of PIP,

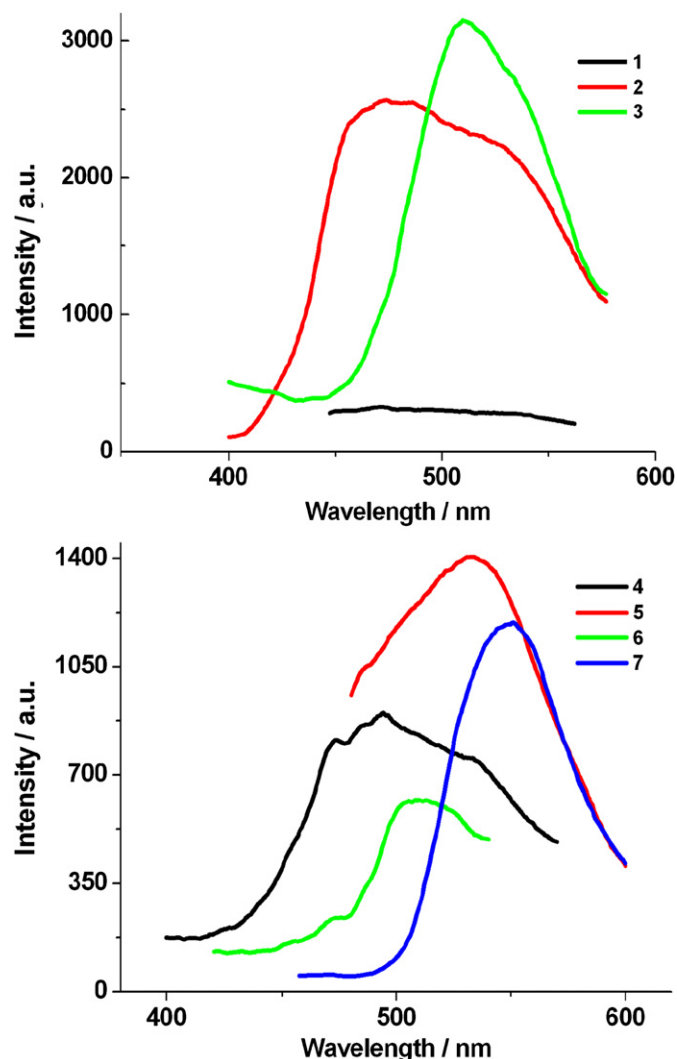


Fig. 8. Emission spectra of complexes 1–7.

3-PIP, and TIP, which are N-donor chelating ligands with extended π -systems, in the construction of metal–organic supramolecular architectures are demonstrated.

Supporting information available

X-ray crystallographic information files (CIF) for 1–7, selected bond distances and angles, TG curves, together with intermolecular π – π and H-bonding interactions for 1–7 are available free of charge via the Internet at <http://pubs.acs.org>.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jssc.2010.11.016](https://doi.org/10.1016/j.jssc.2010.11.016).

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