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Four Zn^{II}/Cd^{II} coordination polymers based on 3,3′-(pyridine-3,5-diyl) dibenzoic acid: Syntheses, crystal structures and photoluminescence property

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ABSTRACT

Four new coordination polymers namely, $[Zn(pddb)(H_2O)]_n$ (**1**), $[Zn(pddb)]_n$ (**2**), $\{[Cd_2(pddb)_2]\cdot H_2O\}_n$ (**3**) and $[Cd(pddb)(H_2O)_2]_n$ (**4**), have been solvothermally obtained. Among which, complexes **1** and **3** were prepared in presence of 4-nitrobenzoic acid, and complexes **2** and **4** not, respectively. Complex **1** shows a binodal 3,3-connected wavelike layer structure with the point symbol of $(6^3)_2$. However, **2** performs a binodal 3,6-connected 3D coordination framework with the point symbol of $(4{\cdot}6^2){\cdot}(4^2{\cdot}6^8{\cdot}8^5)$. **3** exhibits a more complicated 3D periodic structure built on an infinite rod-shape secondary blocking units (SBUs), while **4** shows a double-chain structure, extended into 3D supramolecular framework through strong hydrogen bonding interactions. Furthermore, the study about photoluminescence properties of these four complexes and H_2pddb ligand reveals that these diverse structures have significant influence on the photoluminescence signals.

1. Introduction

Recent decades have seen increasing issues upon the design and syntheses of various coordination polymers, not only due to their attracting structures and new fascinating topologies [1–4], but also due to some potential applications, such as gas adsorption [5–7], chemical sensors [8], molecular recognition, photochromism [9], gas separation [10], chemical stability and medical drug [11]. However, how to obtain desired structures with specific properties is still a challenge, because the self-assembly processes can be affected by many factors, for instance, temperature, metal ions, ligands, metal–ligand ratios, solvents, and counterions [12–15]. Among these influential factors, the judicious selections of organic ligands play an indispensable role in the construction and structural diversity of coordination polymers, due to their adjustable flexibility and connectivity information. Recent decade, bifunctional pridine-carboxylate ligands [16–18] have captured the chemistry' s attention, because they possess N– and O– potential electron-donating centers which can exhibit diverse coordination modes with metal centers and various structures. Notably, carboxylate groups on the ligands may facilitate the formation of discrete multinuclear clusters and infinite building blocks by M–COO–M linkage [19]. Lu et al. have reported four metal–organic frameworks by varying water content based on pyridine-3,5-dicarboxylate in which carboxylate groups adopt simple monodentate and chelate coordination moods [20]. Compared with rigid pyridine-3,5-dicarboxylate, H_2pddb (3,3′-(pyridine-3,5-diyl)dibenzoic acid) is a semirigid ligand, owing to the different dihedral angles between two benzene rings and the versatile coordination orientation of two carboxylate groups, which may result into the very distinct structures. Although many transition metal complexes of pyridinedicarboxylates have been previously reported, no Zn^{II}/Cd^{II} complexes based on 3,3′-(pyridine-3,5-diyl)dibenzoic acid have been described [21].

Herein, we utilized H_2pddb and Zn^{II}/Cd^{II} salts under solvothermal condition and successfully synthesized four new distinct frameworks, namely, $[Zn(pddb)(H_2O)]_n$ (**1**), $[Zn(pddb)]_n$ (**2**), $\{[Cd_2(pddb)_2]\cdot H_2O\}_n$ (**3**) and $[Cd(pddb)(H_2O)_2]_n$, (**4**), among which complexes **1** and **3** were obtained in presence of 4-nitrobenzoic acid, while **2** and **4** were not. Further, the photoluminescence studies of these four complexes and H_2pddb were carried out, and the results reveal that the diverse structures had significant effect on the behaviors of photoluminescence.

2. Experimental

2.1. Materials and physical measurements

All reagents and solvents were purchased commercially and used without further purification. The rigid ligand 3,3′-(pyridine-3,5-diyl) dibenzoic acid (H_2pddb) was also purchased. The FT-IR spectra were recorded from KBr pellets in the range of

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400–4000 cm^{-1} on a Bruker Tensor 27 spectrophotometer. Elemental analyses (C, H and N) were carried out on a FLASH EA 1112 elemental analyzer. PXRD Patterns were recorded using Cu Kα1 radiation on a PANalytical X'Pert PRO diffractometer. Thermal analyses were performed on a Netzsch STA 449C thermal analyzer from room temperature at a heating rate of 10 °C min^{-1} in air. The luminescence spectra for the powdered solid samples were measured at room temperature on a Hitachi 850 Fluorescence Spectrophotometer. The excitation slit, as well as the emission slit was 2 nm.

2.2. Preparation of the complexes

2.2.1. Synthesis of $[Zn(pddb)(H_2O)]_n$ (**1**)

A mixture of H_2pddb (0.0128 g, 0.04 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (0.0297 g, 0.1 mmol), 4-nitrobenzoic acid (0.0146 g, 0.10 mmol), water (6 mL), and DMA (1 mL) was heated in 25 mL Teflon-lined stainless steel container at 160 °C for three days, and slowly cooled to room temperature at a rate of 5 °C/h. Then colorless block crystals **1** were obtained with a 75% yield (based on H_2pddb) after being washed several times by water. Elemental analysis: *Anal.* Calc. for $C_{19}H_{13}NO_5Zn$: C, 56.95; H, 3.17; N, 3.50. Found: C, 56.79; H, 3.34; N, 3.33%. IR (KBr, cm^{-1}): 3421 (bw), 3053 (bw), 1612 (w), 1542 (s), 1397 (s), 1277 (w), 1172 (w), 820 (w), 766 (m), 690 (m).

2.2.2. Synthesis of $[Zn(pddb)]_n$ (**2**)

A mixture of H_2pddb (0.0128 g, 0.04 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (0.0297 g, 0.1 mmol), water (6 mL), and DMA (1 mL) was heated in 25 mL Teflon-lined stainless steel container at 160 °C for three days, and slowly cooled to room temperature at a rate of 5 °C/h. Meanwhile, colorless stick crystals were collected, with yield of 60% (based on H_2pddb). Elemental analysis: *Anal.* Calc. for $C_{19}H_{11}NO_4Zn$: C, 59.63; H, 2.90; N, 3.66. Found: C, 59.74; H, 2.82; N, 3.76%. IR (KBr, cm^{-1}): 3049 (w), 2360 (w), 1608 (w), 1540 (s), 1395 (s), 820 (w), 764 (m), 682 (m).

2.2.3. Synthesis of $\{[Cd_2(pddb)_2]\cdot H_2O\}_n$ (**3**)

A mixture of H_2pddb (0.0128 g, 0.04 mmol), CdI_2 (0.0366 g, 0.1 mmol), 4-nitrobenzoic acid (0.0146 g, 0.10 mmol), water (6 mL), and MeCN (2 mL) was heated in 25 mL Teflon-lined stainless steel container at 160 °C for three days, and slowly cooled to room temperature at a rate of 5 °C/h. Thus, colorless block crystals **3** were achieved with a pure yield of 70% (based on H_2pddb). Elemental analysis: *Anal.* Calc. for $C_{38}H_{24}N_2O_9Cd_2$: C, 52.12; H, 2.76; N, 3.19. Found: C, 52.21; H, 2.93; N, 3.02%. IR (KBr, cm^{-1}): 3433 (bw), 3081 (w), 2928 (w), 2484 (w), 2249 (w), 1704 (w), 1604 (m), 1557 (s), 1455 (m), 1395 (s), 1349 (s), 1260 (w), 926 (w), 764 (m), 684 (m).

2.2.4. Synthesis of $[Cd(pddb)(H_2O)_2]_n$ (**4**)

A mixture of H_2pddb (0.0128 g, 0.04 mmol), CdI_2 (0.0366 g, 0.1 mmol), water (6 mL), and MeCN (2 mL) was heated in 25 mL Teflon-lined stainless steel container at 160 °C for three days, and slowly cooled to room temperature at a rate of 5 °C/h. Colorless block crystal **4** were collected, and then filtered to get a yield of 58% (based on H_2pddb). Elemental analysis: *Anal.* Calc. for $C_{19}H_{15}NO_6Cd$: C, 49.00; H, 3.25; N, 3.01. Found: C, 48.82; H, 3.40; N, 3.08%. IR (KBr, cm^{-1}): 3391 (bw), 3080 (w), 2926 (w), 1696 (w), 1605 (m), 1557 (s), 1435 (m), 1351 (s), 1253 (w), 1174 (w), 892 (bw), 765 (m), 688 (m), 567 (w).

2.3. Crystal data collection and refinement

The data of the four polymers were collected on a Rigaku Saturn 724 CCD diffractomer (Mo Kα, $\lambda = 0.71073$ Å) at temperature of 20 ± 1 °C. Absorption corrections were applied by using multi-scan program. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined with a full-matrix least-squares technique based on F^2 with the SHELXL-97 crystallographic software package [22]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of ligands were included in the structure factor calculation at idealized positions by using a riding model and refined isotropically. The hydrogen atoms of coordinating water molecules and solvent water molecules were located from the difference Fourier maps, restrained at fixed positions and refined isotropically. Crystallographic crystal data and structural parameters for **1**–**4** are summarized in Table 1, and selected bond lengths and angles of **1**–**4** are listed in Table S1 in SI (Supporting Information).

3. Results and discussion

3.1. Crystal structures of $[Zn(pddb)(H_2O)]_n$ (**1**)

Single-crystal X-ray analysis reveals that **1** crystallizes in monoclinic space group $P2_1/c$, and exhibits a wavelike layer structure. The asymmetric unit contains one Zn center, one $pddb^{2-}$ ligand and one coordinating water molecule. As shown in Fig. 1a, Zn1 is four-coordinated by three oxygen atoms (O1A, O2, and O4B) from three $pddb^{2-}$ ligands with the Zn—O bond lengths of 1.959–1.978 Å and an oxygen atom (O5) from one water molecule with the Zn—O bond length of 1.978 Å, and the Zn—O distances are in a normal range according to previous reports for Zn^{II} coordination polymers [23–26]. It is worth noting that the nitrogen atoms from $pddb^{2-}$ ligand do not participate in coordination. Furthermore, from the view of $pddb^{2-}$ ligand, two carboxylate groups from the same $pddb^{2-}$ ligand adopt two different coordination modes. One adopts monodentate coordination mode to coordinate with one Zn^{II} ion, and the other adopts μ^2-η^1:η^1 bridging mode with two Zn^{II} ions (Zn⋯Zn = 4.220 Å). If the potential weak Zn—O3 bonds with the bond length of 2.566Å are taken into consideration, the coordination number of Zn center changes to five and the carboxylate group containing O3 adopts bidentate chelating coordination mode to one Zn^{II} ion instead of monodentate mode. Zn^{II} ions link the carboxylate groups from $pddb^{2-}$ ligands to form a wavelike chain by coordinating with O2 and O4 atoms (Fig. 1b), and adjacent chains are linked together to produce a wavelike layer by sharing the O1 atoms from one carboxylate group (Fig. 1c). From the view of topology, if Zn centers are regarded as 3-connected nodes, and $pddb^{2-}$ ligands as 3-connected nodes, the structure of complex **1** is a binodal 3,3-connected wavelike layer with a point symbol of $(6^3)_2$, as depicted in Fig. 1d. Finally, 3D supramolecular structure is packed through two sorts of hydrogen bonding (classical hydrogen bonding: O5⋯N1 = 2.704 Å), as shown in Fig. 1e.

3.2. Crystal structure of $[Zn(pddb)]_n$ (**2**)

When 4-nitrobenzoic acid was absent in the syntheses process of **1**, a structurally different complex **2** was obtained. Single-crystal X-ray analysis reveals that **2** also crystallizes in monoclinic space group $P2_1/c$, but exhibits a distinct 3D framework. The asymmetric unit of **2** contains one Zn center and one $pddb^{2-}$ ligand. As shown in Fig. 2a, Zn centers are in a distorted five-coordinated geometry, which is defined by four oxygen atoms from three different $pddb^{2-}$ ligands with the Zn—O bond lengths of 1.984–2.271 Å and one nitrogen atom from another $pddb^{2-}$ ligand with the Zn—N bond lengths of 2.059Å. The Zn—O/N distances are normal as reported for other Zn^{II} coordination polymers [23–26]. Moreover, different from complex **1**, two carboxylate groups from the same $pddb^{2-}$ ligand adopt two different coordination modes, one of which adopts chelating mode to coordinate with one Zn^{II} ion, and the

Table 1
Crystallographic data and structure refinement details for **1**–**4**.

Complex	**1**	**2**	**3**	**4**
Formula	$C_{19}H_{13}NO_5Zn$	$C_{19}H_{11}NO_4Zn$	$C_{38}H_{24}N_2O_9Cd_2$	$C_{19}H_{15}NO_6Cd$
Formula weight	400.67	382.66	877.39	465.72
T (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a (Å)	15.883(3)	12.409(3)	17.332(4)	17.764(4)
b (Å)	12.631(3)	11.979(2)	17.988(4)	12.648(3)
c (Å)	8.0124(16)	10.352(2)	10.660(2)	8.1797(16)
α (°)	90	90	90	90
β (°)	91.69(3)	107.10(3)	94.12(4)	106.40(3)
γ (°)	90	90	90	90
V (Å^3)	1606.8(6)	1470.9(5)	3315.0(11)	1763.1(6)
Z	4	4	4	4
D_{calc} (g cm^{-3})	1.656	1.728	1.454	1.755
μ (mm^{-1})	1.561	1.696	1.345	1.276
F(000)	816	776	1736	928
Goodness-of-fit on F^2	1.043	1.153	1.168	1.081
R_1 [$I > 2\sigma(I)$][a]	0.0702	0.0684	0.0584	0.0308
wR_2 (all data)[b]	0.1376	0.1713	0.1512	0.0925

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\right]^{1/2}$.

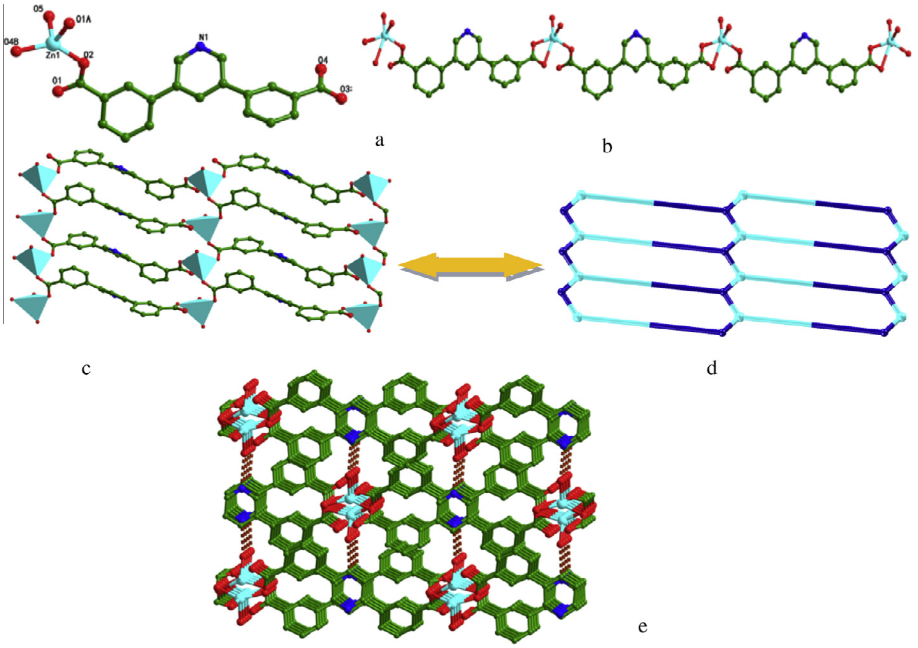


Fig. 1. (a) Coordination environments of the Zn^{II} ions in **1**. Hydrogen atoms and free water molecule are omitted for clarity; (b) the infinite 1D chain formed by Zn^{II} ions and pddb^{2-} ligand. (c) polyhydral view of the 2D layer in **1**; (d) The 3,3-connected topology of the 2D layer viewed by b axis; (e) Perspective view of the supermolecular framework through two kinds of hydrogen-bonding interaction.

other adopts μ^2-η^1:η^1 bridging mode to coordinate with two Zn^{II} ions. As shown in Fig. 2b, two carboxylate groups from pddb^{2-} ligand link three Zn^{II} ions in μ^3-bridging mode to form a sheet structure along *ab* plane. Comparing with that of complex **1**, the architecture of this sheet is composed of infinite linear chains based on a paddle-wheel dinuclear unit [$Zn_2(COO)_2$] with the Zn···Zn distance of 3.917 Å. The sheets are connected together into 3D framework by Zn–N connections (Fig. 2c). A better insight into the present 3D framework can be accessed by the topological method. Each dinuclear [$Zn_2(COO)_2$] unit links six pddb^{2-} ligands and can be simplified as a 6-connected node, and one pddb^{2-} links three dinuclear [$Zn_2(COO)_2$] unit, serving as a 3-connected node, therefore, the structure of complex **2** is a binodal 3,6-connected 3D framework with a point symbol of $(4{\cdot}6^2)(4^2{\cdot}6^8{\cdot}8^5)$, as depicted in Fig. 2d.

3.3. Crystal structure of {[$Cd_2(pddb)_2$]·H_2O}$_n$ (**3**)

Single-crystal X-ray analysis indicates that **3** crystallizes in monoclinic space group *C2/c* and exhibits a complicated 3D periodic framework. The asymmetric unit in complex **3** includes two half of distinct Cd centers, one pddb^{2-} ligand, and one guest water molecule. As shown in Fig. 3a, Cd1 is in a distorted octahedral fashion and surrounded by four oxygen atoms (O2C, O2D, O4E, and O4) from four different pddb^{2-} ligands with Cd1–O distances of 2.289–2.297 Å and two nitrogen atoms (N1A and N1B) from another two pddb^{2-} ligands with Cd–N bond length of 2.362 Å. Unlike Cd1, Cd2 is also in a distorted octahedral fashion but defined by six oxygen atoms (O1, O1d, O3c, O3e, O4a and O4b) from six different pddb^{2-} ligands with the Cd2–O bond lengths of 2.226–2.388 Å. The Cd–O bond lengths are in normal range according to previous reports for

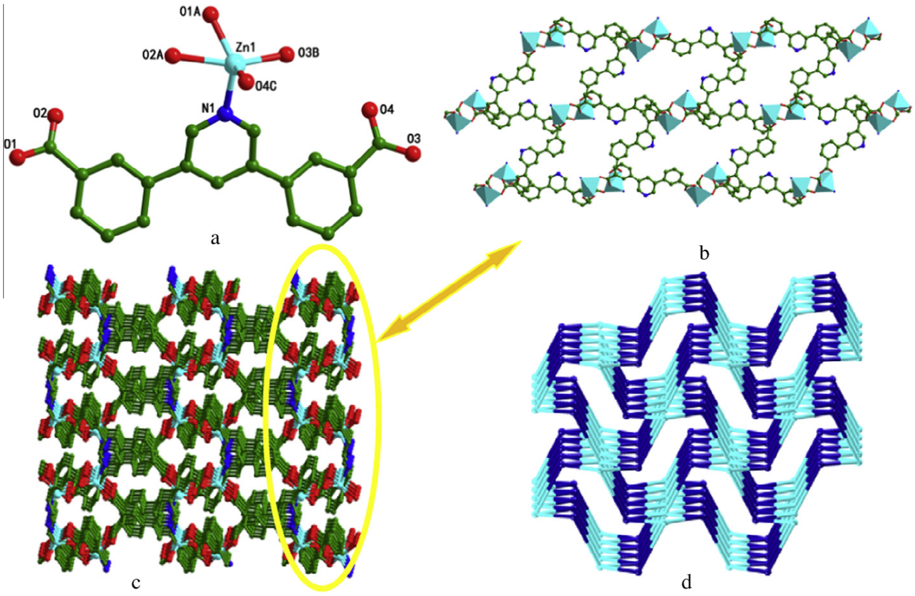


Fig. 2. (a) Coordination environments of the Zn^{II} ions in **2**. (b) Perspective view of the 2D layer in **2**. (c) Perspective view of the 3D framework extended by Zn^{II} coordinating with nitrogen atoms, viewed by the *c* axis. (d) The 3,6-connected topology of the 3D framework. Hydrogen atoms and free water molecule are omitted for clarity.

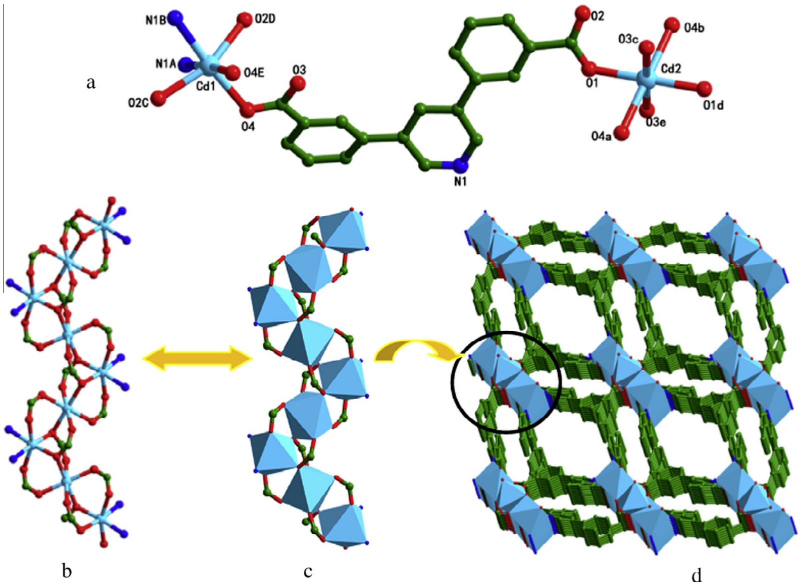
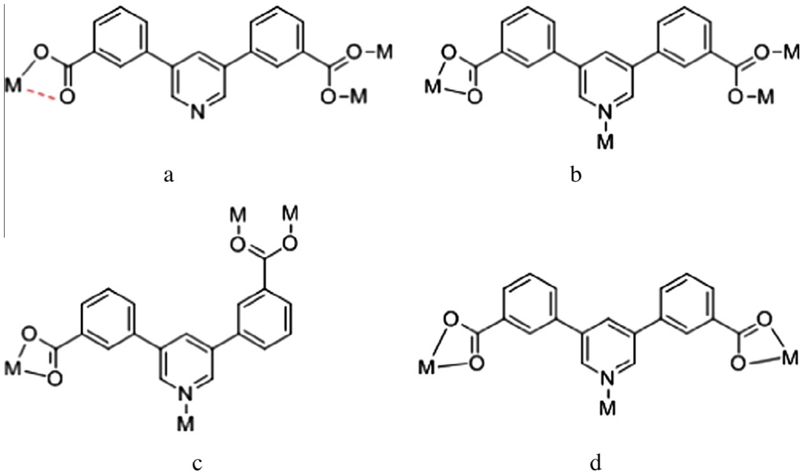


Fig. 3. (a) Coordination environments of the Cd^{II} ions in **3**. (b) The rod SBU unit formed by Cd^{II} ions and carboxylate groups from the $pddb^{2-}$ ligand. (c) polyhydral view of the rod SBU in **3**; (d) Perspective view of the 3D framework formed by the rod SBU linking with four neighbor SBU units by $pddb^{2-}$ ligand. Hydrogen atoms and free water molecule are omitted for clarity.

Cd^{II} coordination polymers [27–29]. As for $pddb^{2-}$ ligand, the two carboxylate groups from the same $pddb^{2-}$ ligand adopt two distinct coordination modes in Scheme 1c. One adopts chelating mode to coordinate with one Cd^{II} ion, and the other adopts μ_3-η^2:η^1 coordination mode to coordinate with three Cd^{II} ions, which favors to the formation of rod secondary building units (SBUs). Along *c* axis, there is a infinite $(Cd1-O-C-O-Cd2)_n$ rod SBU composed by alternative six-coordinated Cd^{II} ions and the carboxylate groups (Fig. 3b and c), according to the previous records [30–32]. The rods connect four neighboring rods by the skeleton of $pddb^{2-}$ along the *ab* plane, resulting in 3D nanovoid framework, in which each cube-type channel of 4.82 × 9.76 $Å^2$ in size is surrounded by four adjacent rectangle-type of 9.76 × 11.21 $Å^2$ in size, as depicted in Fig. 3d. The guest water molecules are located inside the channels, and the valid void occupancy after the removal of uncoordinated solvents is 18%, calculated by the PLATON software.

3.4. Crystal structure of $[Cd(pddb)(H_2O)_2]_n$ (4)

In the absent of 4-nitrobenzoic acid, complex **4** with distinct structure was obtained. Single-crystal X-ray analysis reveals that **4** crystallizes in monoclinic space group *C*2/*c* and exhibits a double-chain structure. The asymmetric unit is composed of one Cd center, half of the $pddb^{2-}$ ligand, and one coordinating water molecule. As shown in Fig. 4a, Cd1 is seven-coordinated by four oxygen atoms (O1B, O2B, O1C, and O2C) from two different $pddb^{2-}$ ligands with Cd–O bond lengths of 2.342–2.495 Å, two oxygen atoms (O3 and O3A) from two water molecules with Cd–O bond lengths of



Scheme 1. The coordination modes of pddb^{2-} in these four complexes: (1a) the coordination modes of pddb^{2-} in complex **1** by introduction of 4-nitrobenzoic acid; (1b) the coordination modes of pddb^{2-} in complex **2** without any other agents; (1c) the coordination modes of pddb^{2-} in complex **3** in the present of 4-nitrobenzoic acid; (1d) the coordination modes of pddb^{2-} in complex **4** without any other agents.

2.347 Å, and one nitrogen atom (N1) from another pddb^{2-} ligand with the Cd—N bond length of 2.276 Å. And the Cd—O/N distances are in normal range according to previous reports for Cd^{II} coordination polymers [27–29]. Different from that in complex **3**, the pddb^{2-} ligand in complex **4** adopts *trans*-conformation and both the carboxylate groups from the same ligands employ bidentate chelating mode to coordinate with one Cd^{II} ion. Therefore, the carboxylate groups from pddb^{2-} ligands link the Cd^{II} ions to form a chain which is extended into double chain by Cd^{II}—N connections (Fig. 4b). Through two sorts of strong hydrogen bonds (O3···O1#4 = 2.819 Å, and O3···O1#5 = 2.739 Å, #4 $-x+1$, $-y+1$, $-z+1$; #5 x, $-y+1$, $z+1/2$), these double chains are extended into 3D supermolecular framework along the *bc* plane, as depicted in Fig. 4c. It is these strong hydrogen bonding interactions that help to further reinforce the 3D supermolecular framework (Fig. 4d).

3.5. PXRD studies and thermal analyses

To confirm the phase purity of these four complexes, the PXRD patterns were recorded and comparable to the corresponding simulated ones calculated from the single-crystal diffraction data (as shown in Fig. S1 (Supporting Information)), indicating a pure phase of each bulky sample. In addition, to estimate thermal stability of these four coordination polymers, thermogravimetric analyses (TGA) were carried out. The curves show that all these complexes are of good thermal stability, which can endure more than 400 °C after losing the coordinated water or the lattice water molecules, as shown in the Fig. S2 (Supporting Information). A slow weight loss of 4.51% in complex **1** from 135 to 210 °C takes place, which is resulted from the loss of coordinating water molecules. A plateau phase occurs until the framework starts to collapse at 427 °C, it is the strong coordination ability between metal ions and pddb^{2-} ligand that stabilizes the structure. For complex **2**, there is no obvious weight loss until the framework begins to decompose at 417 °C. With regard to the complex **3**, the loss weight of 2.86% before 265 °C can be assigned to the loss of the lattice water molecule (Calc., 2.78%), and then the framework begins to decompose at 483 °C. For the complex **4**, the weight loss of 7.3% can be observed in the range of 150–280 °C, which can be seen as the loss of two coordinated water molecules, and the framework can be stable up to 475 °C.

3.6. Photoluminescence properties

Coordination polymers with d^{10} metal centers and conjugated organic linkers are considered as a promising option for

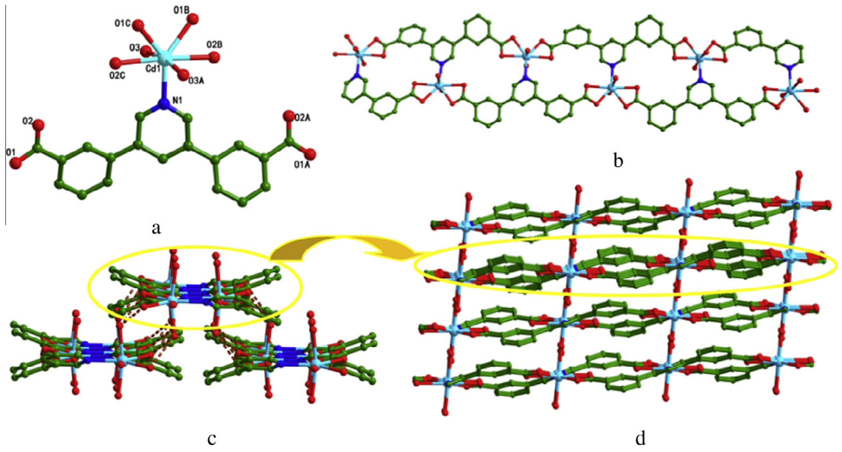


Fig. 4. (a) Coordination environments of the Cd^{II} ions in **4**. (b) The infinite 1D double chain viewed by the *c* axis. (c) The 3D supermolecular frameworks through by two sorts of hydrogen bonding interaction; (d) Perspective view of the supermolecular 3D framework. Hydrogen atoms and free water molecule are omitted for clarity.

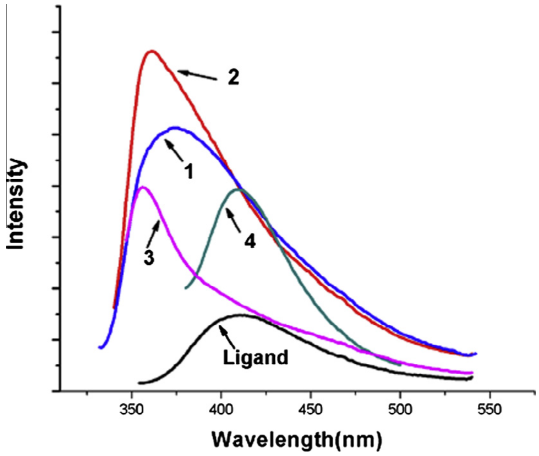


Fig. 5. The florescence curves of these four polymers and H_2pddb.

photoactive materials with potential applications such as chemical sensors and photochemistry [33–35]. With this regard, the solid state photoluminescence properties of these four Zn^{II}/Cd^{II} complexes and H_2pddb ligand have been explored at room temperature (Fig. 5). The free H_2pddb displays intense photoluminescence emissions maximum at λ_{em} = 410 nm upon excitation at 329 nm, which can be ascribed to the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ electronic transitions. Since the Zn^{II}/Cd^{II} ions are difficult to oxidize or reduce, the photoluminescence emission bands of **1** (λ_{em} = 386 nm, λ_{ex} = 331 nm), **2** (λ_{em} = 361 nm, λ_{ex} = 330 nm), **3** (λ_{em} = 356 nm, λ_{ex} = 337 nm), and **4** (λ_{em} = 409 nm, λ_{ex} = 334 nm) are mainly contributed to the interligand or intraligand charge transitions rather than the ligand-to-metal and the metal-to-ligand charge transitions [36–38]. The different hypochromatic shift of emission occurs in complexes **1**–**4**, which is probably due to the different coordination environment around central metal ions, because photoluminescence behavior is closely associated with the local environments around metal ions [39]. The results indicate that the diverse structures have subtle but necessary effect on the photoluminescence signals.

4. Conclusion

Based on a new type of pridine-carboxylate ligand 3,3′-(pyridine-3,5-diyl) dibenzoic acid (H_2pddb), four new coordination polymers have been solvothermally synthesized in the present or absent of 4-nitrobenzoic acid. Complex **1** shows a binodal 3,3-connected wavelike layer structure, and **2** performs a binodal 3,6-connected 3D coordination framework. **3** exhibits a more complicated 3D periodic structure built on an infinite rod-shape secondary blocking units (SBUs), while **4** shows a double-chain structure, extended into 3D supramolecular framework through strong hydrogen bonding interactions. Furthermore, the fluorescence study of these four polymers and H_2pddb ligand indicates that the diverse structures have subtle but necessary effect on the photoluminescence signals.

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Appendix A. Supplementary data

Crystallographic data for the structures in the form of CIF files have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC: 920566–920569 for **1**–**4**, respectively. Copies of these data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; Email: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2013.10.022.

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