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Supramolecular assembly of a series of new coordination polymers based on 4,4'-(carbonylimino)dibenzoic acid: Syntheses, structures and photoluminescence investigation

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ABSTRACT

Assembly reactions of acylamide-containing dicarboxylate ligand 4,4'-(carbonylimino)dibenzoic acid (H₂L) with corresponding divalent metal ions resulted in the formation of seven new coordination polymers, namely Cd(L)(H₂O) (1), Zn(L)(H₂O) (2), Zn₅(L)₂(OH)₆ (3), [Ni(L)(H₂O)₂]·H₂O (4), [Cd(L)(py)(H₂O)]·(DMF)·(C₆H₅Cl) (5), [Cd(L)(py)₂]·2CH₃OH (6) and [Mn (HL)₂(py)₂]·2DMF (7). In complex 1, the double chains composed Cd^{II} and L²⁻ are connected by interlayer Cd–O bonds to form a three-dimensional architecture. Complex 2 exhibits a three-dimensional supramolecular architecture extended by hydrogen bonds involving O–H···O and N–H···O types. Complex 3 displays a three-dimensional framework consisting of zinc-hydroxide layers and L²⁻ pillars. Complex 4 is also a supramolecular three-dimensional network generated from linkage of Ni–O chains via versatile hydrogen bonds. Complex 5 exhibits an interdigitated network in which the cavities are occupied by guest DMF and C₆H₅Cl molecules. In complex 6, two-dimensional square-grid network was generated by linkage of Cd₂ units with L²⁻ ligands. Mono-depronated ligand presents in complex 7. The adjacent [Mn(py)(HL)] chains are arranged parallel to each other by forming hydrogen bonding between the acylamide groups and guest DMF molecules. The stability properties of 2, 3, 4, 6 and 7 have been presented. In addition, photoluminescence properties of complexs 2, 3, 5 and 6 are investigated.

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1. Introduction

The exploration of coordination bond in the construction of coordination polymers (CP) has resulted in a wide range of multi-dimensional solid-state architectures [1]. Applications including heterogeneous catalysis, photochemistry, magnetism, gas storage and separation based on coordination polymers have been well documented [2]. In a parallel development, the highly directional bonds such as hydrogen bonding and π - π stacking are frequently used as cohesive forces in the crystal engineering [3]. The combination of coordination bonds, hydrogen bonding and/or other weak interactions has been recognized as a very powerful and versatile strategy in supramolecular assembly and material chemistry [4].

Our conceived strategy in the present study is to investigate the assembly of coordination polymers based on bicarboxylate ligand

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functionalized with acylamide unit: 4,4'-(carbonylimino)dibenzoic acid (H₂L). There are multiple reasons for exploring H₂L: (1) It contains two carboxylate groups, therefore, versatile coordination modes could be adopted in the formation of new complexes with fascinating properties [5]; (2) the presence of an acylamide group, -CONH, may be expected to have a particularly potent as structure-determining unit in the formation of hydrogen bonds among themselves and/or interacting with the guest molecules incorporated into the coordination architectures, which might turn out to be significant structure-controlling factors [6]. In addition, the relatively free rotatable capability of C-N bond of acylamide group and C-C bond between phenyl ring and carboxylate group make this ligand a flexible skeleton. In this article, we present the isolation and structural characterization of seven new coordination polymers: $Cd(L)(H_2O)$ (1), $Zn(L)(H_2O)$ (2), $Zn_5(L)_2(OH)_6$ (3), $[Ni(L)(H_2O)_2] \cdot H_2O$ (4), $[Cd(L)(py)_2(H_2O)] \cdot (DMF) \cdot (C_6H_5C1)$ (5), $[Cd(L)(py)_2] \cdot 2CH_3OH$ (6) and $[Mn(HL)_2(py)_2] \cdot 2DMF$ (7) (py = pyridine, DMF = dimethylformamide, C_6H_5Cl = chlorobenzene). The crystallographic data of 1-7 are summarized in Table 1. In addition, thermal stability and luminescent properties of the new complexes were also investigated.





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Table 1	
Crystal data and structure refinement for complexes	1-7.

Complex	1	2	3	4	5	6	7
Empirical formula	C ₁₅ H ₁₁ NO ₆ Cd	C ₁₅ H ₁₁ NO ₆ Zn	C15H12NO8Zn2.5	C ₁₅ H ₁₅ NO ₈ Ni	C34H33ClN4O7Cd	C ₂₆ H ₂₅ N ₃ O ₇ Cd	$C_{23}H_{22}N_3O_6Mn_{0.5}$
Formula weight	413.65	366.62	497.68	395.99	757.49	603.89	463.91
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	Рс	C2/c	Сс	C2/c	$P2_1/c$	ΡĪ
a (Å)	16.0892(4)	14.6567(8)	34.634(2)	6.9058(8)	34.952(1)	12.9342(4)	8.5227(3)
b (Å)	11.7307(3)	5.4421(3)	5.5604(4)	35.957(4)	6.1056(2)	20.3616(6)	8.6792(4)
<i>c</i> (Å)	7.2224(2)	8.7148 (5)	16.399(1)	6.0158(7)	33.918(1)	10.5043(3)	15.6198(6)
α (°)	90	90	90	90	90	90	99.603(1)
β (°)	97.841(1)	93.383(1)	100.453(2)	95.749(4)	114.634(1)	112.552(1)	105.233(1)
γ (°)	90	90	90	90	90	90	96.321(1)
V (Å ³)	1350.39(6)	693.91(7)	3105.7(4)	1486.2(3)	6579.3(4)	2554.9(1)	1084.70(8)
Ζ	4	2	8	4	8	4	2
$ ho_{ m calc}(m mgcm^{-3})$	2.035	1.755	2.116	1.770	1.529	1.570	1.420
μ (mm ⁻¹)	1.651	1.803	3.892	1.354	0.800	0.905	0.376
F(000)	816	372	1960	816	3088	1224	481
θ (°)	3.09-25.01	1.39-25.50	2.39-25.01	2.27-25.00	1.32-25.01	1.70-25.01	1.38-25.00
R _{int}	0.0182	0.0218	0.0396	0.0308	0.0258	0.0240	0.0207
Final R indices	$R_1 = 0.0163$,	$R_1 = 0.0339$,	$R_1 = 0.0503$,	$R_1 = 0.0329$,	$R_1 = 0.0898,$	$R_1 = 0.0443$,	$R_1 = 0.0596$
$[I > 2\sigma(I)]$	$wR_2 = 0.0404$	$wR_2 = 0.0892$	$wR_2 = 0.1296$	$wR_2 = 0.0850$	$wR_2 = 0.2118$	$wR_2 = 0.1008$	$wR_2 = 0.1472$
R indices (all data)	$R_1 = 0.0172$,	$R_1 = 0.0341$,	$R_1 = 0.0619$,	$R_1 = 0.0351$,	$R_1 = 0.0913$,	$R_1 = 0.0458$,	$R_1 = 0.0666$,
	$wR_2 = 0.0409$	$wR_2 = 0.0895$	$wR_2 = 0.1422$	$wR_2 = 0.0867$	$wR_2 = 0.2126$	$wR_2 = 0.1016$	$wR_2 = 0.1527$

2. Experimental

2.1. Materials and general methods

All reagents and solvents employed were commercially available and used without further purification. NMR spectra were obtained using a Bruker Avance II 300 M instrument. Elemental analyses were determined on an Elementar Vario ELIII analyzer. The FT-IR spectra were recorded in the range 500–4000 cm⁻¹ using KBr pellets on a Nicolet NEXUS 670 spectrophotometer. Thermogravimetric analyses (TGA) were performed on a Mettler Toledo TGA/SDTA851 instrument by heating from 25 to 800 °C under flowing N₂ atmosphere at a heating rate of 10 °C/min. Powder Xray diffraction (PXRD) patterns were recorded on recorded using a Rigaku (D/Max-Ultima IV) diffractometer equipped with Cu Ka radiation, with a step size and a scan speed of 0.02° and 5° min⁻¹, respectively. Simulated PXRD patterns were calculated with the Mercury program using the single-crystal data [7]. Solid-state photoluminescent spectra of complexes 2, 3, 5 and 6 were measured at room temperature using a Varian Cary Eclipse fluorescence spectrometer.

2.2. Synthesis of H_2L and complexes 1–7

H₂L was synthesized according to the literature method [8].

2.2.1. Synthesis of $Cd(L)(H_2O)(1)$

A mixture of Cd(NO₃)₂·4H₂O (0.043 g, 0.14 mmol) and H₂L (0.01 g, 0.035 mmol) in 5 mL DMF/H₂O (1:1, v:v) was sealed in a Teflon-lined stainless autoclave and heated at 100 °C under autogeneous pressure for 24 h, and then cooled to room temperature (cooling rate: 0.1 °C/min). Colorless plate-like crystals of **1** were obtained.

For complex **1**, the synthesis was found to be fully reproducible. However, the yield was very low and the resulting crystals were always accompanied by powders of un-determined composition. So it is hard to carry out other characterizations.

2.2.2. Synthesis of $Zn(L)(H_2O)(2)$

When the synthetic procedure for **1** was repeated with $Zn(NO_3)_2 \cdot 6H_2O$ (0.015 g, 0.053 mmol) instead of $Cd(NO_3)_2 \cdot 4H_2O$ in 2.5 mL DMF/H₂O (3:2, v:v). Colorless plate-like crystals of **2** were

obtained (yield: 30%, based on H_2L). Anal. Found: C, 49.00; H, 3.039; N, 3.829%. Calc. for $C_{15}H_{11}O_6NZn$: C, 49.14; H, 3.025; N, 3.821%. IR (KBr, cm⁻¹): 3360w, 3120w, 1670m, 1600m, 1530vs, 1420s, 1320w, 1250w, 1180w, 787m, 764w, 661w.

2.2.3. Synthesis of $Zn_5(L)_2(OH)_6$ (3)

A mixture of Zn(NO₃)₂·6H₂O (0.044 g, 0.15 mmol) and H₂L (0.014 g, 0.05 mmol) in 2 mL DMA/H₂O (3:1, v:v) was sealed in a Teflon-lined stainless autoclave and heated at 150 °C under autogeneous pressure for 30 h, and then cooled to room temperature. Colorless prismatic crystals were obtained (yield: 46%, based on H₂L). IR (KBr, cm⁻¹): 3500w, 3380w, 1660m, 1600s, 1550vs, 1400vs, 1320m, 1250m, 1180w, 1010w, 856w, 779m, 731w.

2.2.4. Synthesis of $[Ni(L)(H_2O)_2] \cdot H_2O(4)$

A mixture of Ni(NO₃)₂·6H₂O (0.0204 g, 0.07 mmol) and H₂L (0.010 g, 0.035 mmol) in 2 mL DMA/H₂O (1:3, v:v) was sealed in a Teflon-lined stainless autoclave and subjected to solvothermal condition at 150 °C for 30 h, and then cooled to room temperature. Green prismatic crystals were obtained (yield: 87%, based on H₂L). *Anal.* Found: C, 45.24; H, 3.76; N, 3.54%. Calc. for C₁₅H₁₅O₈NNi: C, 45.50; H, 3.82; N, 3.54%. IR (KBr, cm⁻¹): 3410w, 3020s, 1660vs, 1600s, 1510w, 1430m, 1380w, 1320w, 1250m, 1180w, 1110w, 1010w, 783m, 735w, 509m.

2.2.5. Synthesis of $[Cd(L)(py)_2H_2O]$ ·DMF· (C_6H_5Cl) (5)

A mixture of Cd(NO₃)₂·4H₂O (0.03 g, 0.1 mmol) and H₂L (0.014 g, 0.05 mmol) was dissolved in a 5 mL vial containing DMF (0.5 mL) and H₂O (0.5 mL). Slow diffusion of pyridine/C₆H₅Cl (1:10, v:v) into the mixture resulted in the formation of **5** after 14 days (yield: 53%, based on H₂L). IR (KBr, cm⁻¹): 3276m, 2930w, 2360w, 1660s, 1600s, 1490s, 1390vs, 1320s, 1260m, 1180m, 1100w, 1010w, 860m, 785m, 737w, 695w, 652w.

2.2.6. Synthesis of [Cd(L)(py)₂]·2CH₃OH (**6**)

A procedure similar to that for **5** was carried out to prepare **6**, except that $C_6H_5Cl(5 \text{ mL})$ was replaced by $CH_3OH(5 \text{ mL})$. Colorless block crystals of **6** were obtained (yield: 63%, based on H_2L). IR (KBr, cm⁻¹): 3280m, 3070w, 1940w, 1660s, 1600vs, 1520s, 1390vs, 1320s, 1253m, 1170w, 1010w, 864w, 787w, 700s.

2.2.7. Synthesis of $[Mn (HL)_2(py)_2] \cdot 2DMF(7)$

A procedure similar to that for **5** was repeated to prepare **7**, except that $Cd(NO_3)_2 \cdot 4H_2O$ was replaced by $MnCl_2 \cdot 4H_2O$ (0.014 g, 0.07 mmol). After 30 days, colorless block crystals of **7** were obtained (yield: 45%, based on H₂L). IR (KBr, cm⁻¹): 3290w, 1650vs, 1540vs, 1400s, 1330m, 1180w, 1100w, 1010w, 856w, 783w, 733w.

2.3. X-ray crystallography

Single-crystal X-ray diffraction data were collected on a Bruker SMART Apex II diffractometer equipped with graphite-monochromatic Mo K α radiation (λ = 0.71073 Å). Crystals were coated with paratone oil and the diffraction data were collected at 173 or 123 K cooled in a nitrogen stream. Frames were collected with 0.6° intervals in φ and ω for 30 s per frame such that a hemisphere of data was collected. Raw data collection and refinement were done using SMART [9]. Data reduction was performed using SAINT+ 10]. Absorption corrections were applied using the SADABS program 11]. The structures were solved by direct method and refined by full-matrix least-squares on F^2 with anisotropic displacement using SHELX-97 [12]. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All the hydrogen atoms attached to carbon atoms were placed in calculated positions and refined using the riding model.

3. Results and discussion

3.1. Crystal structures

3.1.1. Crystal structure of $Cd(L)(H_2O)$ (1)

Single-crystal X-ray diffraction analysis revealed that complex **1** crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit contains one Cd^{II} atom, one L²⁻ ligand and an agua ligand.

The coordination environment around Cd^{II} can be described as a slightly distorted [CdO₆] octahedron involving five carboxylate oxygen atoms from four L^{2-} ligands and an aqua ligand (O1w). The relevant Cd–O (carboxylate oxygen: O1, O2, O4, O5) bond distances range from 2.127(1) to 2.380(1) Å, whereas the Cd-O1w bond distance is 2.279(2) Å (Fig. 1a). Two Cd^{II} atoms are linked by two μ_3 -0,0,0' carboxylate groups from two L²⁻ to form a dinuclear cadmium unit with a Cd · · Cd separation of 3.528 Å, which are further connected by μ_2 -0,0' carboxylate units with bond type Cd1–O5 2.380(1) Å to generate an infinite double chain along the c direction (Fig. 1a). There are two kinds of carboxylate coordination modes exist in **1**, namely μ_3 -0,0,0' and μ_2 -0,0', the latter one further connected the chains into a three-dimensional (3D) network via bond type Cd1-O4, 2.127(1) Å (Fig. 1b). From a topological point of view, the dinuclear cadmium SBU in complex 1 can be regarded as a 6-connected node with a point symbol of $\{4^2.6^{10}.8^3\}$, and L^{2-} acting as a 3-connected node with a point symbol of $\{4.6^2\}$. Therefore, the whole structure thus can be represented as a $\{4.6^2\}\{4^2.6^{10}.8^3\}$ network topology (Fig. S14).

3.1.2. Crystal structure of $Zn(L)(H_2O)$ (2)

When the synthetic procedure for **1** was repeated with $Zn(NO_3)_2 \cdot 6H_2O$ instead of $Cd(NO_3)_2 \cdot 4H_2O$, a quite different structure of complex **2** was obtained. The asymmetric unit of **2** is composed of one Zn^{II} atom, one L^{2-} and an aqua ligand. The Zn^{II} atom is in a distorted tetrahedral geometry, being coordinated by one aqua ligand (Zn-O1w = 1.980(3)Å), three carboxylate oxygen atoms from three L^{2-} ligands (Zn-O = 1.931(3)-1.985(3)Å). Further expansion of the structure through the bis(monodentate)/monodentate carboxylates create a layer (Fig. 2a). Notably the aqua ligand plays a key role in the structure of **2**: (1) the tetrahedral coordination environment of Zn^{II} and L^{2-} is reinforced by intermolecular hydrogen bonding between the aqua ligand and the carboxylate



Fig. 1. (a) Portion of the infinite chain of Cd(L)(H₂O) (1) viewed along the *c* direction; (b) Schematic showing of the 3D structure of 1 viewed along the *a* direction constructed from linkage of chains via bond type Cd1–O4.

ylate group with the aqua ligand serving as donors and the carboxylate oxygen atoms as acceptors $[O1w-H1wb\cdots O1 (x + 1, -y + 1, z + 1/2), O1w\cdots O1 = 2.689 Å, H1wb\cdots O1 = 1.85 Å, O1w-H1wb\cdots O1 = 167.9^{\circ}];$ (2) the layers are further connected by hydrogen bonding with the aqua ligand serving as donors and the carboxylate oxygen as acceptors into a 3D architecture $[O1w-H1wa\cdots O1 (x + 1, y - 1, z + 1), O1w\cdots O1 = 2.655 Å, H1wa\cdots O1 = 1.799 Å, O1w-H1wa\cdots O1 = 158.9^{\circ}]$ (Fig. 2b).

3.1.3. Crystal structure of $Zn_{2.5}(L)(OH)_3$ (3)

Single-crystal diffraction study revealed that complex 3 crystallizes in monoclinic space group C_2/c . There are two and a half crystallographic independent Zn^{II} atoms, one L^{2-} and three hydroxyl groups. In **3**, Zn1 atom adopts a distorted triangular bipyramid geometry, being surrounded by two hydroxyl groups [Zn-O (O8, O7c = 2.066(3)-2.073(3)Å] at the apical positions and two hydroxyl oxygen atoms [Zn–O (O6, O7b) = 2.018(4)–2.029(6) Å] and one carboxylate oxygen atom at the basal positions [Zn-O (O1a) = 1.987(4) Å]; Zn2 is six-coordinated with a distorted octahedral geometry, and the metal center is surrounded by four hydroxyl oxygen atoms [Zn–O (O6, O7, O8, O9) = 1.984(4)– 2.4512(7) Å] and two carboxylate oxygen atoms from two individual L^{2-} ligands [Zn-O (05, O2d) = 2.062(4)-2.219(4) Å]. Zn3 lies in a 2-fold axis and adopts a slightly distorted triangular bipyramid geometry, coordinated by two carboxylate oxygen atoms [Zn-O (04, 04e) = 2.231(4)Å] from two L²⁻ ligands at the apical positions and three hydroxyl oxygen atoms [Zn-O (O8, O8e, O9b) = 1.928(6)-1.952(4)Å] at the basal positions.

A prominent structural feature of **3** is the zinc-hydroxide layers generated from connection of Zn^{II} via μ_3/μ_4 hydroxyl oxygen atoms. Each Zn1 atom is connected to six other Zn atoms (three Zn2, two Zn1, and one Zn3) via hydroxyl groups, while each Zn2 atom is joined with seven other Zn atoms (three Zn1, two Zn3, and two Zn2) via hydroxyl groups. In addition, each Zn3 atom is linked to total six Zn atoms (four Zn2 and two Zn1) through the hydroxyl groups, leading to the formation of 2D zinc-hydroxide layers with Zn₃(OH)₃, Zn₄(OH)₅, Zn₂(OH)₂ circular units (Fig. 3b), which are quite different from those in the other coordination polymers incorporating Cd-hydroxide or Fe-hydroxide layers [13]. Adjacent layers are further pillared by L^{2–} ligands functioning in the μ_2 -0,0' coordination mode to generate a 3D network.

3.1.4. Crystal structure of $[Ni(L)(H_2O)_2] \cdot H_2O$ (4)

X-ray crystallography reveals that **4** crystallizes in the monoclinic space group *Cc*. The asymmetric unit consists of one Ni^{II} atom, one L²⁻, two aqua ligands and one guest water molecule. In **4**, each Ni^{II} ion is six-coordinated in a octahedral geometry involving two carboxylate oxygen atoms from two different L²⁻ ligands [Ni–O (O2, O3a) = 1.967(7)–1.977(7) Å] and four aqua ligands [Ni–O (O1w, O2w) = 2.082(9)–2.115(9) Å] (Fig. 4a). In the two carboxylate units of L²⁻, only one carboxylate of L²⁻ adopts a *syn–syn* bidentate coordination mode. The Ni^{II} atoms are linked by aqua ligands, together with the *syn–syn* bidentate carboxylate group, to generate a 1D chain extending along the *a* direction (Ni…Ni = 3.009 Å). The most interesting feature of **4** arises from the supramolecular level involving the uncoordinated carboxylate



Fig. 2. (a) Ball-and stick showing of the layer structure of complex Zn(L)(H₂O) (**2**); (b) Three-dimensional architecture of **2** viewed the *c* direction. Hydrogen bonds are represented by broken lines.



Fig. 3. (a) Local coordination environments of the Zn1, Zn2, Zn3 center in Zn₅(L)₂(OH)₆ (3) (hydrogen atoms were omitted for clarity); (b) View of 2D zinc-hydroxide layers of 3; (c) View of the 3D coordination network of 3.

unit, aqua ligand and guest water molecule. As shown in Fig. 4b, the infinite Ni(II) chains are interconnected by $O1w-H\cdots O5$, $O2w-H\cdots O4$ hydrogen bonds to form a 2D layer structure along the *b* axis. It is noteworthy that O3w plays a dual role serving as a hydrogen bonding donor as well as an acceptor to construct a 3D structure by forming four hydrogen bonds $O1w-H\cdots O3w$, $O2w-H\cdots O3w$, $O3w-H\cdots O4$, $O3w-H\cdots O5$ (the distances are in the range of 2.64–2.66 Å) to generate a hybrid 3D structure (Fig. 4c).

3.1.5. Crystal structure of $[Cd(L)(py)_2H_2O]$ ·DMF·(C₆H₅Cl) (**5**)

Complex **5** crystallizes in the monoclinic space group C2/c. Its asymmetric unit contains one Cd^{II} atom, one L^{2-} , two coordinated

pyridine molecules, one aqua ligand, one guest DMF molecule, and one C_6H_5Cl molecule. Each Cd^{II} atom adopts a pentagonal bipyramid geometry being coordinated by two pyridine molecules at the axial positions (Cd–N = 2.334(7)–2.371(7) Å) and four oxygen atoms from the chelating carboxylates of two L^{2-} (Cd–O = 2.345(6)–2.475(6) Å) and one aqua ligand in the equatorial plane (Cd–O (aqua) = 2.334(6) Å) (Fig. 5a). Linkage of L^{2-} and Cd^{II} gives rise to the 1D chain. Each aqua ligand (O1w) from one chain forms three different hydrogen bonds (O1W–H···O2, O1W–H···O4, O1W–H···O2) with two carboxylate oxygen atoms (O2 and O4) from another chain to generate a layer (Fig. 5a). The layers are further mutually interdigitated to create a stable 3D assembled framework, with the cavities occupied by guest DMF and C_6H_5Cl arranged alternatively (Fig. 5b).



(b)



Fig. 4. (a) Local coordination environment of the Ni^{II} center in [Ni(L)(H₂O)₂]·H₂O (4); (b) Two-dimensional layer of 4 connected by hydrogen bonds; (c) Three-dimensional hydrogen-bonded network of 4.

Note that the 3D framework is reinforced by π - π stacking between adjacent pyridine rings (centroid-to-centroid distance between adjacent pyridine rings is 3.774 Å). It should be pointed out that hydrogen bonds exist between the skeleton and the guest DMF molecules (N1-H···O6_{DMF} is about 2.869 Å). Another interesting feature is the π - π stacking interactions between pairs of C₆H₅Cl guest molecules existing in the structure (centroid-to-centroid distance between C₆H₅Cl is 3.845 Å).

3.1.6. Crystal structure of $[Cd(L)(py)_2] \cdot 2CH_3OH(\mathbf{6})$

Two-dimensional square-grid structure was generated from linkage of Cd_2 units ($Cd \cdots Cd$ separation of 3.936 Å) with

 L^{2-} ligands in complex **6**. The asymmetric unit contains one Cd^{II} atom, one L^{2-} , two coordinated pyridine molecules and two guest CH₃OH molecules. It is worth to note that the seven-coordinated Cd^{II} atom shows a pentagonal–bipyramidal coordination geometry. The metal center was coordinated by five carboxylate oxygen atoms in the equatorial plane (Cd–O = 2.325(2)–2.639(3) Å) and two pyridine nitrogen atoms (Cd–N = 2.287(8)–2.295(8) Å) locating at the apical position (Fig. 6a). Each binuclear motif is further linked to four identical motifs through four L^{2-} ligands, leading to a 2D coordination layer (Fig. 6b). Taking the binuclear motifs as 4-connecting nodes and the ligands as linkers, the layer can be considered to be a (4,4) net. The dimensions of the rhombic windows of





Fig. 5. (a) Local coordination environments of the Cd^{II} center in $[Cd(L)(py)(H_2O)] \cdot (DMF) \cdot (C_6H_5CI)$ (5) (hydrogen atoms were omitted for clarity); (b) Two-dimensional hydrogen-bond layer of 5; (c) View of three-dimensional assembled structure, with the cavities are occupied by guest DMF and C_6H_5CI molecules.

the layer are about 17.91×16.46 Å which is large enough to accommodate the guest molecule (the shortest Cd···Cd distance spanned by the two independent L^{2–} ligands). The moderate strong hydrogen bonding interactions can be found between the guest molecules CH₃OH and the acylamide group of about 2.8 Å.

3.1.7. Crystal structure of [Mn_{0.5}(HL)(py)]·DMF (7)

Determination of the structure of complex **7** by single-crystal Xray diffraction analysis indicates that **7** crystallizes in the triclinic space group $P\bar{1}$. Its asymmetric unit contains a divalent Mn atom lying on a crystallographic inversion center, one mono-deprontated HL⁻ anion, one pyridine ligand and one guest DMF molecule of crystallization. Operation of the inversion center at the metal center revealed that the Mn^{II} center is in an octahedral geometry, being coordinated by two pyridine molecules (Mn– N = 2.257(1) Å) and four carboxylate oxygen atoms (Mn– O = 2.142(2)–2.156(1) Å) from four different HL⁻ ligands (Fig. 7a). It is noteworthy that one carboxyl group of H₂L is not ionized and therefore giving rise to HL⁻ instead of L^{2–}. Ligands HL⁻ in bis(mondentate) coordination mode connect the Mn^{II} atoms to form a linear [Mn(py)(HL)] chain with Mn···Mn contact distance of about 16.139 Å. Moreover, the [Mn(py)(HL)] chains are reinforced by intermolecular hydrogen bonding between carboxylic acid group and carboxylate unit $(d(D \cdot \cdot A) = 2.469$ Å, $d(H \cdot \cdot A)$ 1.652 Å). Adjacent chains are arranged parallel to each other by forming hydrogen bonding (acylamide) N–H···O(DMF) about 3.035 Å to create a 2D assembled sheet, with DMF guest molecules hosted inside via hydrogen bonding between the acylamide group of HL and carbonyl group of DMF molecules $d(D \cdot \cdot A) = 3.035$ Å, $d(H \cdot \cdot A)$ 2.259 Å (Fig. 7b).

The preparation of coordination polymers is a complicated process and can be influenced by many factors such as molar ratio, solvents employed, reaction temperature, pH etc. Subtle change in the reaction conditions may result in complete different structure. For instance, reaction of $H_2L Zn(NO_3)_2 \cdot 6H_2O$ in DMF at 80 °C gave rise to NJU-Bai1 exhibiting a 2-fold interpenetrated pcu-type network. Its structure is quite different from that of **1** obtained in DMF–H₂O system at 100 °C [8]. Also, complexes **1** and **2** in this report showed entirely different structures under similar reaction conditions with different metal ions.



Fig. 6. (a) Local coordination environments of the Cd^{II} center in [Cd(L)(py)₂]·2CH₃OH (6) (hydrogen molecules were omitted for clarity); (b) Two-dimensional (4,4) network based on the binuclear Cd₂ units.

3.2. Thermal stability analysis and powder X-ray diffraction (PXRD) analysis

Thermogravimetric analyses (TGA-DSC) are performed on crystalline samples to examine the thermal stability.

TGA data for the crystalline sample **2** indicates a 4.3% weight loss during 18-187 °C, corresponding to the loss of one coordinated water molecule (calcd, 4.9%). No further weight loss is observed from 187 to 425 °C. The decomposition begins at 425 °C accompanied by a large exothermic peak (Fig. S1). For the crystalline sample 3, the weight loss of 5.2% at 17–346 °C corresponds to the loss of three OH groups (calcd, 5.8%). Decomposition of the framework begins at 425 °C and the final residue is ZnO (observed 49.3%, calcd, 48.9%) (Fig. S2). From the TGA of complex 4, the weight loss of 9.0% during 185-220 °C corresponds to the loss of two coordinated water molecules (calcd, 9.1%). Then decomposition occurred with a large exothermic peak within the temperature range of 405-450 °C to give NiO as the final product (observed 38.5%, calcd, 37.9%) (Fig. S3). The TGA curve of 5 exhibits a large weight loss (43.7%) at 25-252 °C, corresponding to the loss of all the coordinated water and pyridine molecules, the guest C₆H₅Cl and DMF in the structure (calcd, 44.5%). Decomposition began at temperature of 397 °C. The final residue is CdO (observed 17.5%; calcd, 16.9%) (Fig. S4). As to 6, one guest CH₃OH molecule was lost before TGA test. The TGA curves shows the first weight loss of 5.2% in the range of 25-85 °C, corresponding to the loss of the other methanol (calcd, 5.5%). The loss of two coordinated pyridine molecules was found in the range of 85–280 °C (observed 26.9%; calcd, 25.6%). When the temperature is higher than 400 °C, the framework began to collapse to give CdO as the final residue (observed 21.3%; calcd, 20.7%) (Fig. S5). The TGA of **7** shows the first weight loss of 16.7% (calcd, 15.9%) around 186 °C, corresponding to the loss of guest DMF molecule. The second weight loss of 18.0% (calcd, 17.1%) around 397 °C corresponds to the loss of two coordinated py molecules. When the temperature is higher than 400 °C, the remaining HL⁻ units were removed (observed 31.2%; calcd, 30.6%) and the collapse of the framework began. The final residue is MnO (observed 23.7%; calcd, 23.0%) (Fig. S6).

PXRD analyses are carried out to check the structural identity. For **2–7**, the measured PXRD pattern closely matches the one simulated from single-crystal diffraction data, indicating the phase purity (Figs. S7–S12).

3.3. Luminescent properties of 2, 3, 5 and 6

Luminescent properties of d¹⁰ metal-containing complexes have attracted much attention due to their potential applications in electroluminescent display, chemical sensors, and photochemistry. Therefore, in this work, the luminescent properties of complexes **2**, **3**, **5** and **6** as well as the free H₂L ligand were investigated in the solid state at room temperature (Fig. 8). The main emission peaks of the free H₂L at 437 nm (λ_{ex} = 348 nm)



Fig. 7. (a) Local coordination environments of the Mn^{II} center in [Mn (HL)₂(py)₂]·2DMF (**7**); (b) View of two-dimensional assembled layer along the *a* axis.



Fig. 8. Solid-state emission spectra for 2, 3, 5 and 6.

may be ascribed to the $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transitions (Fig. S13). Complexes **2**, **3**, **5** and **6** show emission peaks at 445 nm ($\lambda_{ex} = 348$ nm), 452 nm ($\lambda_{ex} = 342$ nm), 447 nm ($\lambda_{ex} = 320$ nm) and 443 nm ($\lambda_{ex} = 334$ nm), respectively (Fig. S14). The emission peaks of **2**, **3**, **5** and **6** are close to that of the free H₂L, so the emission peaks of the four complexes can probably be attributed to the intraligand fluorescent emission. The enhancement of luminescence for the four complexes compared with the free H_2L under the same conditions may mainly originate from the coordination interactions between the metal atom and the ligand, which enhanced its conformational rigidity and then decreased the nonradiative energy loss [14]. It is noteworthy that a similar emission band at about 450 nm has also been observed previously in other H_2L -based Zn-containing coordination polymers.

Besides, in comparison with the free ligand, red-shifts of about 8, 15, 10, 6 nm are found for **2**, **3**, **5** and **6**, respectively. These results suggest that **2**, **3**, **5** and **6** may be good candidates for potential hybrid inorganic–organic photoactive materials.

4. Conclusions

In summary, the combination of coordination bond, hydrogen bond and π - π stacking leads to a series of coordination polymers showing interesting solid-state structures. Complexes **1** and **3** show 3D dense architecture built by coordination bond only, while complexes **2**, **5**, **6** and **7** are constructed by coordination bond, π - π stacking together with hydrogen bonding into 3D supramolecular frameworks. Weak interactions play an important role in constructing above complexes. In addition, the luminescent emission intensities of complexes **2**, **3**, **5** and **6** are much stronger than that of the ligand, so they may be suitable candidates for fluorescent materials. Our continue research will further expand to other reaction systems to obtain new coordination polymers with fascinating structures and potential applications.

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Appendix A. Supplementary data

CCDC 892604–892610 contains the supplementary crystallographic data for complexes **1–7**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB 21 EZ, UK; fax: (+44) 1223-336-033; or e-mail: 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.2013.03.029.

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