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ARTICLE TYPE

# Six Zn(II) and Cd(II) Coordination Polymers Assembled from a Similar Binuclear Building Unit: Tunable Structures and Luminescent Properties

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Six Zn(II) and Cd(II) coordination polymers were constructed by treating a 2-substituted 8-hydroxyquinolate ligand containing pyridyl group with zinc or cadmium salts, and characterized by a variety of techniques. Interestingly, based on a similar binuclear Zn(II) or Cd(II) building unit, the 10 supramolecular structures of the six coordination polymers (**1-6**) exhibit an unprecedented structural diversification due to the different choices of metal salts. **1** and **2** represent a novel 2D framework containing 1D infinite right- and left-handed helical chains. **4** and **5** are 2D coordination frameworks based on binuclear Cd(II) building units. For **3** and **6**, the L ligands can bridge binuclear building units forming a 1D infinite chain. Interestingly, the adjacent Cd<sub>2</sub>O<sub>2</sub> planes of 1D chain in **6** are in parallel with 15 each other, while the dihedral angle between two Zn<sub>2</sub>O<sub>2</sub> planes in **3** is 83.43°. Photoluminescent properties revealed that six coordination polymers exhibit redshifted emission maximum compared with free ligand HL, which can be ascribed to the increased conformational rigidity and the fabrication of coplanar binuclear building units M<sub>2</sub>L<sub>2</sub> in **1-6**. Coordination polymers **1-6** also display distinct fluorescent lifetimes and quantum yields because of their different metal centers and supramolecular structures.

## 20 Introduction

The chemistry of metal quinolates has attracted a lot of attention since the first report on the use of aluminum tris-8-hydroxyquinoline (AlQ<sub>3</sub>) as an emissive material in organic light-emitting diodes (OLEDs).<sup>1</sup> 8-Hydroxyquinoline can bridge the 25 gaps between the neutral 2,2'-bipyridine (bipy) and the dianionic catecholate because it possesses one pyridine donor of bipy and one phenolate unit of catecholate.<sup>2</sup> Hence 8-hydroxyquinoline and its derivatives are versatile organic ligands towards a wide range of metal ions, including main group, transition and rare 30 earth metal ions, resulting in some materials with promising photoluminescent properties.<sup>3</sup> Numerous reports have demonstrated that luminescent properties of 8-hydroxyquinolate-based complexes are not only related to the composition of the materials, but also are heavily dependent on 35 the molecular and supramolecular structure fabricated via the intermolecular noncovalent interactions;<sup>4</sup> it is thus very important to control the three-dimensional structure and intermolecular packing at the molecular level.<sup>5</sup> To overcome the limitations of the MQ<sub>n</sub>-type mononuclear complexes, Lewiński and our groups 40 recently have synthesized a series of multinuclear Zn(II) and Cd(II) involving 8-hydroxyquinolate ligands to obtain improved and controllable photoluminescence features.<sup>6,7</sup> However, the chemistry of coordination polymers based on 8-hydroxyquinolate ligands still remains surprisingly poorly 45 explored.<sup>8</sup>

As a result of the structural richness and promising applications

in chemical sensors, light-emitting devices, and biomedicine, luminescent coordination polymers (CPs) have attracted great interest for chemists.<sup>9,10</sup> Luminescent CPs distinguish themselves 50 from other inorganic and organic luminescent materials because of their potentially collaborative multifunctionalities. The metal centers, organic moieties, metal-organic charge transfer, and guest molecules within porous CPs all can potentially generate luminescence.<sup>11-13</sup> The photophysical properties such as 55 maximum emission wavelength and lifetime of organic linkers in solid CPs are often different from those of the free molecules.<sup>14</sup> This is because the incorporation of metal ion can effectively increase the conformational rigidity of organic linkers, which may reduce the nonradiative decay rate and lead to increased 60 fluorescence intensity, lifetimes, and quantum efficiencies.<sup>15</sup> However, the basic studies for luminescent CPs often focus on temperature- and excitation wavelength-dependence luminescence. Some in-depth studies on the other important luminescent properties, particularly quantum yield and lifetime, 65 also should be carried out in the future.<sup>16</sup> In addition, intramolecular or intermolecular interactions in solid CPs also play the important roles in the luminescence properties of the resulting CPs.<sup>17</sup>

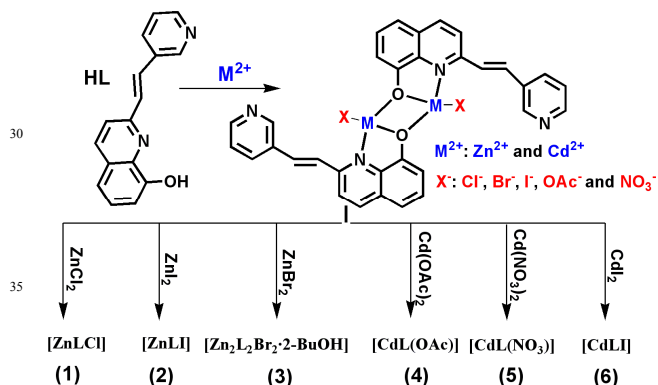
According to our previous reports, multinuclear 8- 70 hydroxyquinolate-based complexes can be synthesized from 2-substituted 8-hydroxyquinolate ligands under solvothermal conditions.<sup>7</sup> In this work, to construct coordination polymers based on binuclear M(II) building units, 8-hydroxyquinolate ligand HL involving pyridyl group was prepared. Our goal is to

achieve control over the molecular or supramolecular structures and thereby the physical properties of the new coordination polymers. Using this strategy, six novel coordination polymers **1-6** were synthesized and characterized by a variety of techniques, including microanalysis, IR, and powder and single-crystal X-ray diffraction. Interestingly, although coordination polymers **1-6** possess similar binuclear building unit ( $M_2L_2$ ), their polymeric skeletons exhibit a structural diversification due to the different choices of metal salts. As a result, the six Zn(II) and Cd(II) polymers exhibit disparate fluorescent properties (emission wavelength, lifetime and quantum yield) due to their different metal center and supramolecular structures.

## Results and discussion

### Synthetic Chemistry

Ligand (*E*)-2-[2-(3-pyridyl)ethenyl]-8-hydroxyquinolin (HL) was prepared in two steps according to our previous reports.<sup>18</sup> Reaction of HL with  $ZnX_2$  ( $X = Cl^-, Br^-$  and  $I^-$ , 0.1 mmol) or  $CdX_2$  ( $OAc^-$ ,  $NO_3^-$  and  $I^-$ , 0.1 mmol) in a mixed solvent of DMF, MeOH (or 2-BuOH), and  $H_2O$  by heating at 65 °C afforded coordination polymers [ZnLCl] (**1**), [ZnLI] (**2**), [Zn<sub>2</sub>L<sub>2</sub>Br<sub>2</sub>·2-BuOH] (**3**), [CdL(OAc)] (**4**), [CdL(NO<sub>3</sub>)] (**5**), and [CdLI] (**6**) in good yields. In the solid state, the formulations were supported by the results of microanalysis, IR spectroscopy, and single-crystal X-ray diffraction. It is notable that an anion-dependent self-assembly behavior was observed in **1-6**.



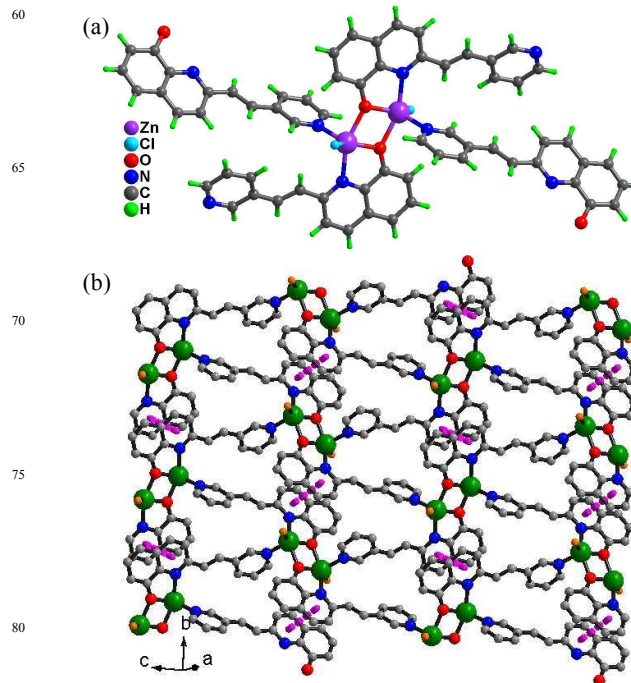
**Scheme 1** Synthesis of coordination polymers **1-6** with a similar binuclear building unit.

### Structural description

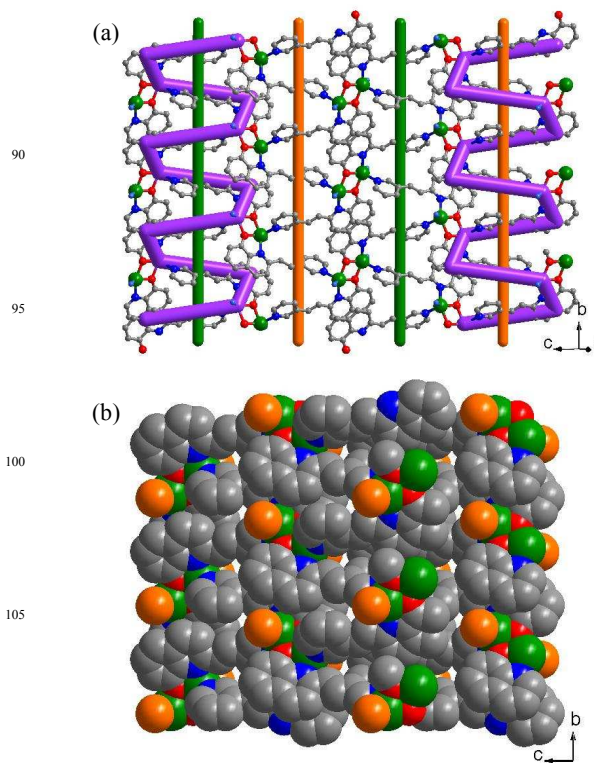
[ZnLCl] (**1**) and [ZnLI] (**2**). Complex **1** crystallizes in the monoclinic  $P2_1/n$  space group with  $Z = 4$ . In the asymmetric unit, there are one crystallographically unique Zn(II) atom, two L ligands and one coordinated chlorine anion. As shown in Fig. 1a, the basic building unit is a binuclear Zn unit with the Zn–Zn distance of 3.3277(12) Å, which are bridged by two phenolate oxygen atoms of two ligands L. The Zn(II) center is five-coordinated to two nitrogen atoms from two ligands L, two phenolate oxygen atoms and one coordinated chlorine anion, forming a distorted trigonal bipyramidal geometry. The bond lengths and angles around Zn(II) are 2.084(5)–2.206(5) Å for Zn–N, 1.983(4)–2.173(4) Å for Zn–O, 2.213(3) Å for Zn–Cl, 73.70(19)–170.99(11)° for O–Zn–O, 78.49(12)–154.19(11)° for

O–Zn–N, and 93.66(12)–112.22(14)° for N–Zn–N, respectively.

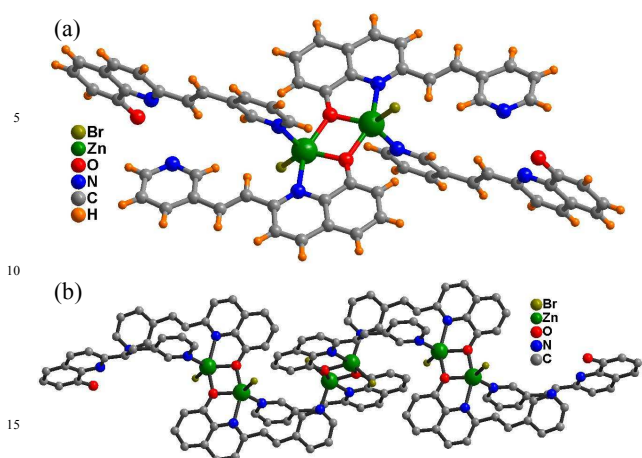
In the *bc* plane, each binuclear Zn(II) unit is linked to four adjacent binuclear zinc units through the chelating NO donors and pyridyl groups of ligands L to generate a 2D supramolecular structure.



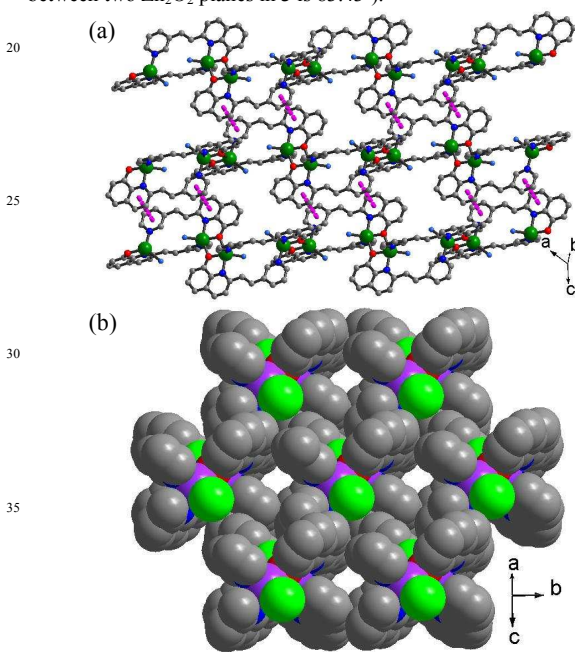
**Fig. 1** (a) View of the coordination geometry of Zn(II) atoms in **1**; (b) 2D supramolecular structure of **1** mediated by coordination bonds and  $\pi$ - $\pi$  stacking interactions.



**Fig. 2** (a) 2D layer structure of **1** containing *meso*-helical chains (*P+M*) in the *bc* plane; (b) View of 3D supramolecular structure in **1**.



**Fig. 3** (a) View of the coordination geometry of Zn(II) atoms in **3**; (b) The binuclear units are linked into 1D infinite chain (The dihedral angle between two  $Zn_2O_2$  planes in **3** is  $83.43^\circ$ ).

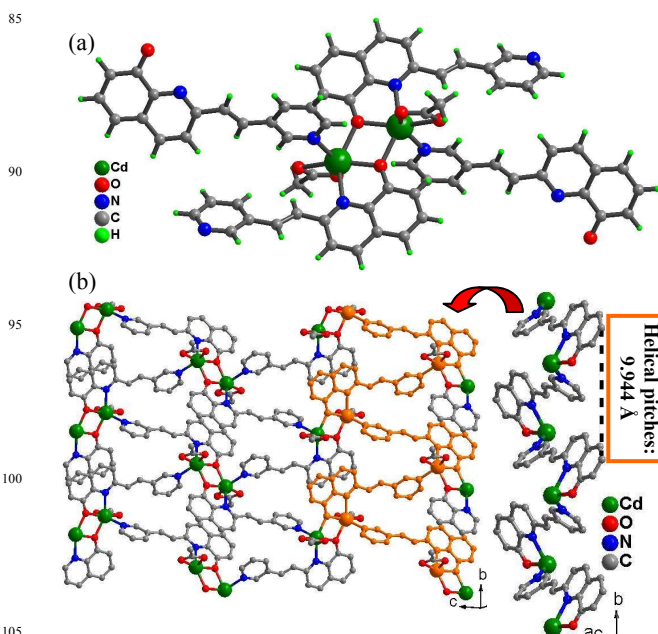


**Fig. 4** (a) The  $\pi\cdots\pi$  stacking interactions between the quinoline and pyridyl rings of adjacent ligands in **3**; (b) View of 3D supramolecular structure in **3**.

Additionally, the intermolecular  $\pi\cdots\pi$  interactions between the quinoline rings of adjacent ligands (interligand distance of ca.  $3.591 \text{ \AA}$ ) also play an important role in the fabrication of the 2D structure (Fig. 1b). It is notable that a kind of *meso*-helical chains ( $P+M$ ) constructed via the metal-ligand coordination interactions are observed in the solid state of this compound (Fig. 2a). These *meso*-helical chains with a pitch of  $9.670(5) \text{ \AA}$  are alternately arranged along  $b$  axis, which is identical to the  $b$  axis length. The 2D layers are further stacked into 3D supramolecular structure (Fig. 2b) via  $C-H\cdots Cl$  hydrogen bond ( $C-H\cdots Cl$ :  $3.738(7) \text{ \AA}$ ) between the C-H group of quinoline ring and coordinated chlorine atom, and  $C-H\cdots\pi$  interaction between the C-H group of pyridyl ring and phenolate ring (Fig. S2). The structure of complex **2** is isostructural to complex **1** (Fig. S3 and 4). The main distinction is that the coordinated chloride ions were replaced

with bromide anions. Although the frameworks are intact, the supramolecular polymer undergoes a anion-responsive structural change. In particular, the pitches of *meso*-helices increase from  $9.670(5) \text{ \AA}$  in **1** to  $10.1689(11) \text{ \AA}$  in **2** to accommodate larger anions.

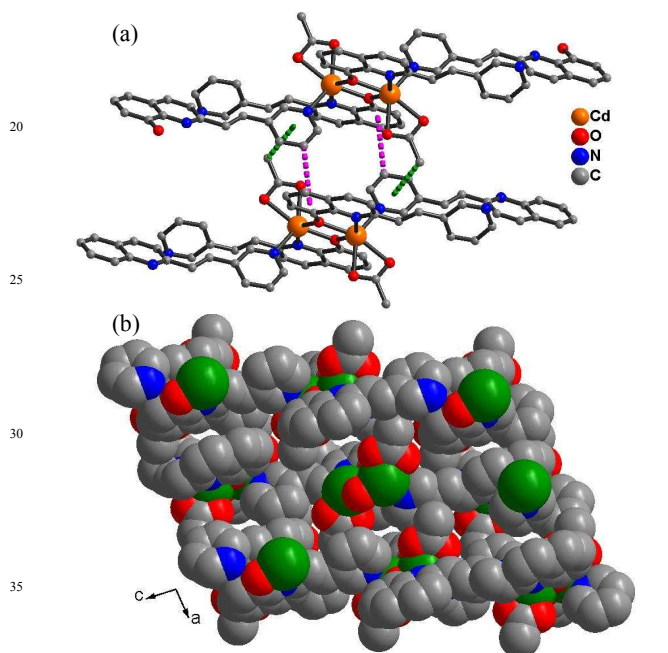
$[Zn_2L_2Br_2\cdot 2-BuOH]$  (**3**). Single-crystal structure analysis reveals that **3** crystallizes in the monoclinic space group  $C2/c$ , with one half of a formula unit in the asymmetric unit, that is, one Zn(II) atom, one ligand L, one coordinated bromine atom, and one half of a 2-BuOH molecule. Similar to compound **1**, compound **3** is built around a binuclear Zn(II) unit with the Zn–Zn distance of  $3.2659(5) \text{ \AA}$ . The two Zn(II) ions in **3** are bridged by phenolate oxygen atoms of two ligands. The Zn(II) center is five-coordinated by one coordinated bromine atom, two phenolate oxygen atoms and two nitrogen atoms from three ligands L displaying a distorted trigonal bipyramidal geometry. Each L ligand uses one bidentate NO donor site to bind one binuclear Zn(II) unit and uses pyridyl nitrogen atom to bind the other binuclear Zn(II) unit. Both two quinoline rings are practically coplanar with the basal  $Zn_2O_2$  plane (dihedral angles:  $7.36^\circ$ ). Adjacent binuclear units are thus linked by L ligands to form a 1D infinite chain as shown in Fig. 3b. Through  $\pi\cdots\pi$  stacking interactions with a face-to-face distance of  $3.573(3) \text{ \AA}$  between the quinoline and pyridyl rings of adjacent ligands (Fig. 4a), the 1D infinite chains in **3** are linked into 3D porous structure (Fig. 4b).



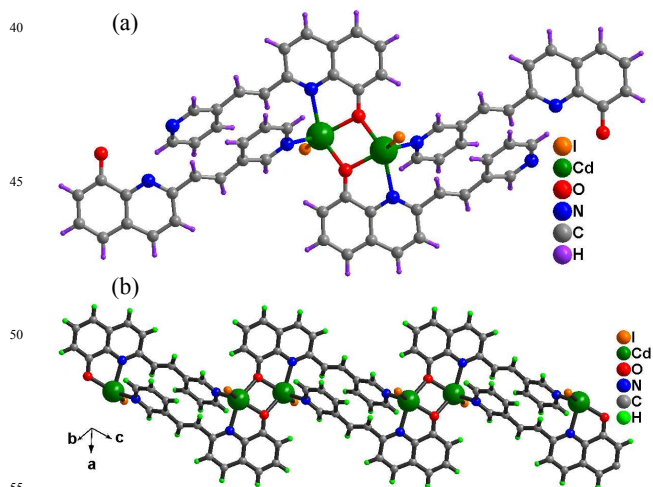
**Fig. 5** (a) View of the coordination geometry of Zn(II) atoms in **4**; (b) A kind of *meso*-helical chain ( $P+M$ ) in **4** are alternately arranged in the  $bc$  plane.

$[CdL(OAc)]$  (**4**) and  $[CdL(NO_3)]$  (**5**). A single-crystal X-ray diffraction study shows that coordination polymer **4** is a 2D network structure, with one crystallographically independent Cd(II) ion, one L ligand and one coordinated  $OAc^-$  anion in the asymmetric unit. The binuclear building unit contains two Cd(II) atoms, four L ligands, and two coordinated acetate anions. Both of Cd(II) centers adopt a distorted octahedral geometry with the equatorial plane occupied by one phenolate oxygen atom, one

pyridyl nitrogen atom and acetate anion, and the apical position by quinoline nitrogen and oxygen atoms (Fig. 5a). In the *bc* plane, each binuclear Cd(II) unit is linked to four adjacent binuclear Cd(II) units through the chelating NO donors and pyridyl groups of ligands L to form a 2D structure (Fig. 5b). These 2D layers are further linked by the C–H $\cdots$  $\pi$  (C(14)–H(14A) $\cdots$  $\pi$ : between C–H group of pyridine and phenolato ring of adjacent ligand, 3.636(3) Å; C(18)–H(18A) $\cdots$  $\pi$ : between C–H group of acetate ion and pyridyl ring of adjacent ligand, 3.574(4) Å) interactions (Fig. 6a) along the *a* axis to form a 3D framework structure (Fig. 6b). Similar to **1**, a kind of *meso*-helical chain (*P+M*) are alternately arranged in the *bc* plane (Fig. 5b). The helical pitch of 9.9439(11) Å in **4** is longer than that of **1**. The structure of complex **5** is identical to complex **4**. The main distinction is that the coordinated acetate ion were replaced with nitrate anion.

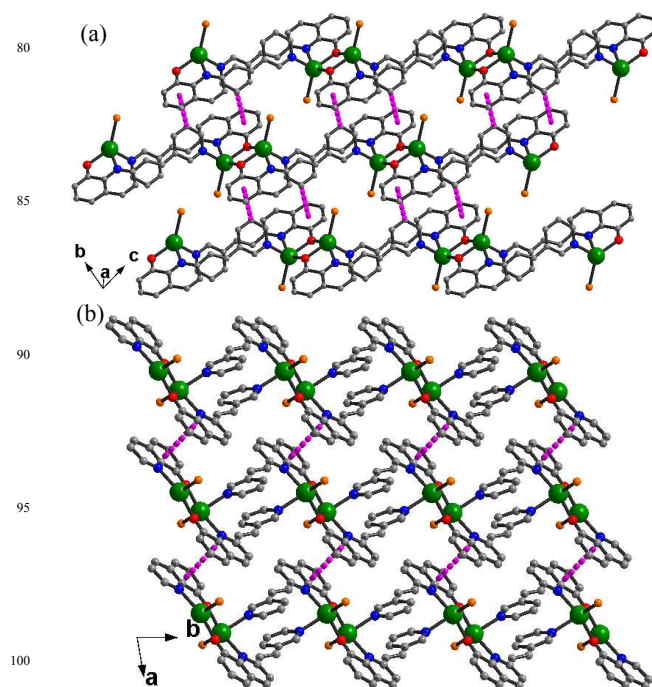


**Fig. 6** (a) Two different C–H $\cdots$  $\pi$  interactions in adjacent binuclear units of **4**; (b) View of 3D supramolecular structure in **4**.



**Fig. 7** (a) View of the coordination geometry of Zn(II) atoms in **6**; (b) The binuclear Cd(II) units in parallel are linked into 1D infinite chain.

[CdLI] (**6**). The crystal structure determination reveals that complex **6** crystallizes in the triclinic crystal system of *P*-1. The local coordination geometry around the binuclear Cd unit is depicted in Fig. 7a. The Cd1 atom coordinates to two oxygen and two nitrogen atoms from three ligands L, and one iodide anion. The binuclear zinc unit of **6** shows an obvious difference in comparison with those of complexes **1–5**. Both two quinoline rings in **6** are nonplanar with the basal Cd<sub>2</sub>O<sub>2</sub> plane (dihedral angles: 25.66°). Each L ligand links two binuclear Cd units, acting as a linker to form a 1D infinite chain (Fig. 7b). Interestingly, the adjacent Cd<sub>2</sub>O<sub>2</sub> planes of 1D chain in **6** are in parallel with each other, while the dihedral angle between two Zn<sub>2</sub>O<sub>2</sub> planes in **3** is 83.43° (Fig S5). As shown in Fig. 8a, through C–H $\cdots$  $\pi$  interactions between C–H group of pyridine and phenolato ring of adjacent ligand (3.417(5) Å), the neighbouring 1D chains in **6** are linked into 2D layers in the *bc* plane (Fig. 8a). In **6**, each phenolate ring is parallel to the one in the reverse side of the neighboring unit in the *ab* plane (Fig. 8b), and  $\pi$  $\cdots$  $\pi$  interaction exists between them with a face-to-face distance of 3.536(2) Å. The 2D layers are further assembled into a 3D supramolecular network (Fig. S10) via  $\pi$  $\cdots$  $\pi$  interactions.



**Fig. 8** (a) The neighbouring 1D chains in **6** are linked into 2D layers in the *bc* plane; (b) The 2D supramolecular structure of **6** in the *ab* plane mediated by  $\pi$  $\cdots$  $\pi$  stacking interactions.

### Photophysical properties

To check the phase purity of the products, powder X-ray diffraction (PXRD) experiments have been carried out for these coordination polymers (Fig. 9). The experimental PXRD patterns are in good agreement with the simulated patterns. The results indicate that the crystal structures are truly representative of the bulk crystal products. The observed differences in intensity could be due to preferred orientation of the powder samples.

Luminescent complexes are of great interest owing to their various applications in chemical sensors, photochemistry, and light-emitting diodes (LEDs).<sup>9,10</sup> Therefore, it is important to

investigate the photophysical properties of coordination polymers in view of potential applications. The photoluminescent behaviors of coordination polymers **1-6** and free ligand HL are studied in the solid state at room temperature. As shown in Fig. S11, the free HL ligand displays an intense emission between 400 and 600 nm ( $\lambda_{\text{max}} = 465$  nm upon excitation at 360 nm), which originated from charge transfer of the internal HL ligand. Under the same excitation condition, coordination polymers **1-6** exhibit strong emission peak at 562, 569, 559, 562, 562, 559 nm (Fig. 10), respectively. In comparison to the emission spectrum of the corresponding ligand HL, the red shift of emission bands of compounds **1-6** can be ascribed to the following two reasons<sup>19</sup>: the coordination of metal ions effectively enhances the mobility of the electron transfer in backbone and reduces the loss of energy via vibration motions. On the other hand, two ligands L are practically coplanar with the basal  $\text{Zn}_2\text{O}_2$  plane in the binuclear units of **1-6**, which increases the conjugation of L ligand, thus reducing the energy gap between the  $\pi$  and  $\pi^*$  molecular orbital of the ligand.

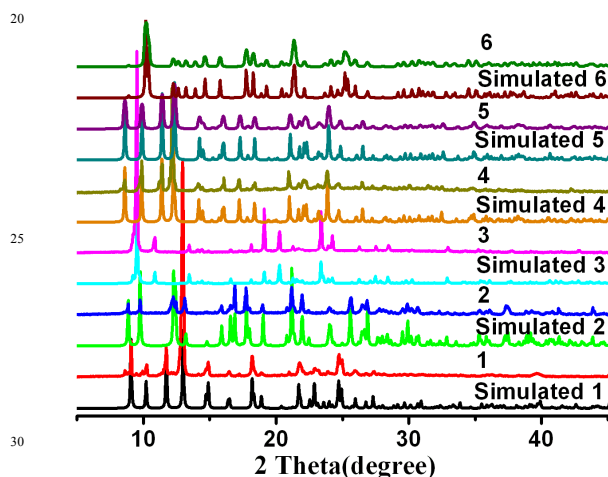


Fig. 9 PXRD patterns of coordination polymers **1-6**.

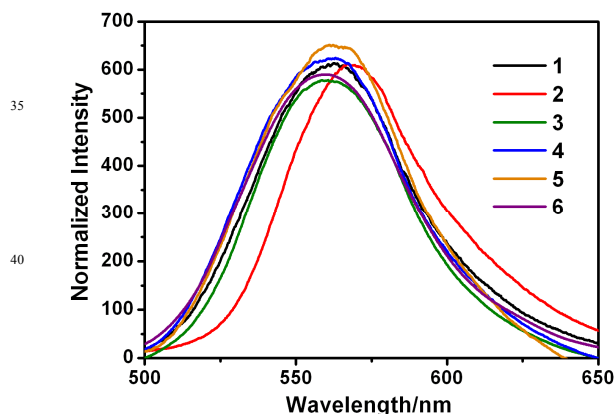


Fig. 10 Emission spectra of coordination polymers **1-6** in the solid state.

Furthermore, the emission decay lifetimes (Fig. S12) and quantum yields of **1-6** were monitored at room temperature in the solid state. The results are summarized in Table 2. The average lifetime (Figure S14-18) was determined by allowing  $\alpha_i$  and  $\tau_i$  to vary, and then convoluting eq 1 with the instrument response function. The data was successfully modeled using double exponentials, and the average lifetime was determined using eq 2.

In both equations  $t$  is time,  $\tau$  is lifetime, and  $\alpha$  is a pre-exponential factor.<sup>20</sup> The shorter fluorescence lifetime of coordination polymers **2, 5** and **6** (**2**, 0.30 ns; **5**, 0.22 ns; **6**, 0.31 ns) may arise from a combined contribution from a competitive non-radiative decay process in the metal complexes (such as the incompletely hindered electron transfer), different metal centers and distinct supramolecular structures in comparison with polymers **1, 3** and **4** (**1**, 0.93 ns; **3**, 0.52 ns; **4**, 0.86 ns). However, the luminescent properties of **1-6** are comparable with those found in 8-hydroxyquinolate-based multinuclear complexes.<sup>7</sup> In addition, the intrinsic porosity of these coordination polymers potentially enables the adsorption of guest molecules and therefore tunes the luminescent properties via host-guest interactions.<sup>10</sup>

$$(1) I(t) = \sum_{i=1}^n \alpha_i \exp(-t/\tau_i) \quad (2) \tau_{\text{avg}} = \frac{\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2}$$

Table 1. Detailed parameters extracted from photoluminescent properties of **1-6**.

Compound	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{em}}$ (nm)	$\tau_{\text{avg}}$ (ns)	$\Phi$
<b>1</b>	400	562	0.93	0.16
<b>2</b>	400	569	0.30	0.04
<b>3</b>	400	559	0.52	0.08
<b>4</b>	400	562	0.86	0.11
<b>5</b>	400	562	0.22	0.07
<b>6</b>	400	559	0.31	0.05

$\lambda_{\text{ex}}$ : Excitation wavelength;  $\lambda_{\text{em}}$ : Emission wavelength;  $\tau_{\text{avg}}$ : Average fluorescence lifetimes;  $\Phi$ : quantum yield.

## Experimental Section

### Chemicals, reagents, and analyses

All of the chemicals are commercial available, and used without further purification. Elemental analyses were performed with an EA1110 CHNS-0 CE elemental analyzer. The IR (KBr pellet) spectrum was recorded (400-4000 $\text{cm}^{-1}$  region) on a Nicolet Magna 750 FT-IR spectrometer. Powder X-ray diffraction (PXRD) data were collected on a DMAX2500 diffractometer using  $\text{Cu K}\alpha$  radiation. The calculated PXRD patterns were produced using the SHELXTL-XPOW program and single crystal reflection data. All fluorescence measurements were carried out on a LS 50B Luminescence Spectrometer (Perkin Elmer, Inc., USA). The room-temperature (RT) lifetime measurements were determined on a FLS920 time-resolved and steady-state fluorescence spectrometer (Edinburgh Instruments).

### Synthesis

(*E*)-2-[2-(3-pyridyl)ethenyl]-8-hydroxyquinolin (HL) was synthesized in two steps according to our previous report.<sup>18</sup>

Synthesis of coordination polymers **1-6**: A mixture of  $\text{ZnX}_2$  ( $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ , 0.1 mmol) or  $\text{CdX}_2$  ( $\text{OAc}^-$ ,  $\text{NO}_3^-$  and  $\text{I}^-$ , 0.1 mmol), HL (12.4 mg, 0.05 mmol),  $\text{H}_2\text{O}$  (0.2 mL), DMF (0.2 mL) and MeOH (or 2-BuOH, 2 mL) in a capped vial was heated at 80 °C for one day. Yellow blocklike crystals of **1-6** suitable for single-crystal X-ray diffraction were collected, washed with ether and dried in air. Yield: **1**, 13.8 mg, 80%; **2**, 16.4 mg, 75%; **3**, 17.5 mg, 82%; **4**, 16.6 mg, 79%; **5**, 17.1 mg, 81%; **6**, 18.5 mg, 76%.

Elemental Analysis data and IR of **1**: Anal (%). Calcd for  $[\text{ZnLCl}] \text{C}_{16}\text{H}_{11}\text{ClN}_2\text{O}_2\text{Zn}$ : C, 55.20; H, 3.18; N, 8.05. Found: C, 55.08; H,

Table 2. Crystal data and structure refinement for 1-6.

Complex	1	2	3	4	5	6
formula	C <sub>16</sub> H <sub>11</sub> ClN <sub>2</sub> OZn	C <sub>16</sub> H <sub>11</sub> IN <sub>2</sub> OZn	C <sub>36</sub> H <sub>32</sub> Br <sub>2</sub> N <sub>4</sub> O <sub>3</sub> Zn <sub>2</sub>	C <sub>18</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> Cd	C <sub>16</sub> H <sub>11</sub> N <sub>3</sub> O <sub>4</sub> Cd	C <sub>16</sub> H <sub>11</sub> CdIN <sub>2</sub> O
fw	348.09	439.54	849.14	418.71	421.68	486.57
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>C</i> <sub>2</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> -1
<i>a</i> (Å)	7.767(4)	7.4490(8)	23.908(4)	8.0700(9)	8.036(17)	8.8073(6)
<i>b</i> (Å)	9.670(5)	10.1689(11)	11.2970(17)	9.9439(11)	9.919(2)	9.0322(6)
<i>c</i> (Å)	19.707(10)	20.082(2)	16.294(2)	20.676(2)	21.302(4)	10.2851(7)
<i>α</i> (deg)	90	90	90	90	90	77.7640(10)
<i>β</i> (deg)	98.545(10)	96.345(2)	130.487(2)	96.206(2)	105.484(7)	79.3150(10)
<i>γ</i> (deg)	90	90	90	90	90	78.0290(10)
<i>V</i> (Å <sup>3</sup> )	1463.7(13)	1511.9(3)	3347.0(9)	1649.5(3)	1636.4(6)	773.59(9)
<i>Z</i>	4	4	4	4	4	2
<i>D</i> <sub>c</sub> (g cm <sup>-3</sup> )	1.580	1.931	1.685	1.686	1.712	2.089
<i>F</i> (000)	704	848	1680	832	832	460
reflns/unique	9994/2561	12827/3460	14309/3832	26848/3871	10993/2856	4015/2691
<i>R</i> <sub>int</sub>	0.0436	0.0339	0.0376	0.0439	0.0230	0.0100
data/restraints/ params	2561/184/190	3460/0/190	3832/1/202	3871/0/217	2856/0/197	2691/0/190
GOF on <i>F</i> <sup>2</sup>	1.056	1.059	1.018	1.087	1.106	1.084
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.0600, 0.1823	0.0392, 0.1095	0.0358, 0.0872	0.0259, 0.0607	0.0283, 0.0705	0.0259, 0.0627
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0858, 0.2075	0.0568, 0.1193	0.0575, 0.0983	0.0359, 0.0648	0.0318, 0.0727	0.0278, 0.0643
largest diff. peak and hole (e Å <sup>-3</sup> )	2.379, -0.845	1.103, -0.884	0.584, -0.466	0.617, -0.461	0.741, -0.843	1.344, -1.453

3.29; N, 7.94. FTIR (KBr pellet): 3442.69(s), 2069.50(w), 1612.76(m), 1554.94(m), 1504.24(w), 1436.56(m), 1375.29(w), 1340.53(m), 1283.32(w), 1114.19(s), 970.54(w), 829.80(w), 750.38(w), 622.39(w), 545.25(w).

Elemental Analysis data and IR of **2**: Anal (%). Calcd for [ZnLI] C<sub>16</sub>H<sub>11</sub>IN<sub>2</sub>OZn: C, 43.72; H, 2.52; N, 6.37. Found: C, 43.58; H, 2.70; N, 6.21. FTIR (KBr pellet): 3445.29(m), 3038.53(w), 1947.61(w), 1598.65(s), 1578.62(w), 1553.49(s), 1504.66(s), 1487.11(w), 1452.61(s), 1437.23(s), 1422.90(s), 1375.69(s), 1338.09(s), 1320.35(m), 1284.02(s), 1230.26(w), 1214.84(w), 1190.27(w), 1152.30(w), 1123.70(w), 1105.75(s), 1059.61(m), 1033.86(w), 958.46(s), 883.32(m), 828.97(s), 809.76(m), 792.65(w), 763.19(s), 737.70(s), 699.09(m), 686.77(w), 655.28(w), 616.36(w), 568.34(w), 514.50(w), 488.08(w), 473.77(w).

Elemental Analysis data and IR of **3**: Anal (%). Calcd for [Zn<sub>2</sub>L<sub>2</sub>Br<sub>2</sub>·2-BuOH] C<sub>36</sub>H<sub>32</sub>Br<sub>2</sub>N<sub>4</sub>O<sub>3</sub>Zn<sub>2</sub>: C, 50.32; H, 3.75; N, 6.52. Found: C, 50.14; H, 3.92; N, 6.37. FTIR (KBr pellet): FTIR (KBr pellet): 3439.14(s), 3058.95(w), 2955.43(w), 2923.00(w), 2066.69(w), 1632.02(s), 1597.79(s), 1575.50(w), 1551.07(s),

1499.34(m), 1449.07(s), 1429.12(s), 1377.61(s), 1340.42(s), 1329.06(m), 1289.51(w), 1276.03(m), 1191.27(w), 1127.78(w), 1099.48(s), 1061.41(w), 1027.03(w), 959.98(m), 910.49(w), 885.60(w), 837.93(s), 812.59(w), 794.47(w), 766.00(m), 738.09(m), 702.77(w), 688.09(w), 650.98(w), 613.09(w), 575.57(w), 513.78(w), 478.59(w).

Elemental Analysis data and IR of **4**: Anal (%). Calcd for [CdL(OAc)] C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>Cd: C, 51.63; H, 3.37; N, 6.69. Found: C, 51.49; H, 3.52; N, 6.48. FTIR (KBr pellet): 3426.24(w), 3095.74(w), 3013.47(w), 2928.55(w), 1947.99(w), 1594.18(m), 1550.82(s), 1506.04(w), 1437.73(s), 1420.78(s), 1370.86(m), 1343.24(s), 1314.25(w), 1286.90(s), 1231.41(w), 1214.96(w), 1184.93(w), 1124.71(w), 1107.48(s), 1054.03(w), 1029.04(w), 1015.29(w), 973.00(s), 933.22(w), 882.89(m), 830.72(s), 810.33(s), 750.94(s), 735.47(s), 704.99(s), 690.29(w), 675.90(s), 650.40(w), 619.57(w), 597.42(w), 569.92(m), 505.37(w), 485.37(w).

Elemental Analysis data and IR of **5**: Anal (%). Calcd for [CdL(NO<sub>3</sub>)] C<sub>16</sub>H<sub>11</sub>N<sub>3</sub>O<sub>4</sub>Cd: C, 45.57; H, 2.63; N, 9.96. Found: C, 45.50; H, 2.85; N, 9.86. FTIR (KBr pellet): 3428.50(m),

3028.91(w), 2928.63(w), 1948.13(w), 1594.52(w), 1549.88(s),  
1506.48(w), 1481.61(w), 1442.49(s), 1371.34(m), 1343.80(s),  
1314.49(w), 1284.15(s), 1184.87(w), 1106.37(s), 1053.18(w),  
971.27(s), 933.14(w), 881.51(m), 830.91(s), 809.18(w), 737.38(s),  
703.98(w), 676.74(w), 649.69(w), 619.81(w), 579.02(w),  
569.80(w), 505.86(w), 481.98(w).

Elemental Analysis data and IR of **6**: Anal (%). Calcd for [CdLI]  
C<sub>16</sub>H<sub>11</sub>CdIN<sub>2</sub>O: C, 39.49; H, 2.28; N, 5.76. Found: C, 39.32; H,  
2.35; N, 5.66. FTIR (KBr pellet): 3443.38(s), 2352.74(w),  
2068.79(w), 1594.32(m), 1548.08(w), 1503.82(s), 1436.06(s),  
1419.71(s), 1369.83(w), 1338.11(s), 1313.64(s), 1280.53(m),  
1119.47(m), 1103.18(m), 953.13(w), 869.32(w), 828.19(m),  
812.89(w), 760.60(w), 736.27(w), 693.50(w), 633.28(w).

### X-ray crystallography

Single-crystal XRD data for compounds **1-6** were all collected on  
a Bruker APEX area-detector X-ray diffractometer with MoK $\alpha$   
radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The empirical absorption correction  
was applied by using the SADABS program (G. M. Sheldrick,  
SADABS, program for empirical absorption correction of area  
detector data; University of Göttingen, Göttingen, Germany,  
1996). The structure was solved using direct method, and refined  
by full-matrix least-squares on  $F^2$  (G. M. Sheldrick, SHELXTL97,  
program for crystal structure refinement, University of Göttingen,  
Germany, 1997). Crystal data and details of the data collection  
are given in Table 2, whereas the selected bond distances and  
angles are presented in Table S1-6. The CCDC numbers of 1-6  
are 1024557-1024562, respectively.

### Conclusion

In summary, six coordination polymers with different structures  
are prepared under solvothermal conditions, using Zn(II) or Cd(II)  
salts and one pyridyl-based quinolate ligand synthesized from  
the cheap commercial available 8-hydroxyquinoline. In the solid  
state, single-crystal X-ray diffraction reveals that coordination  
polymers **1-6** possess a similar binuclear M(II) building units. Six  
compounds **1-6** feature four kinds of supramolecular networks  
controlled by some non-covalent interactions, such as  $\pi \cdots \pi$   
stacking, C-H $\cdots\pi$ , hydrogen bonding and halogen-related  
interactions. The fluorescent properties of compounds HL, and **1-6**  
were investigated in the solid state at room temperature.  
Coordination polymers **1-6** exhibit remarkable red shift in  
comparison with the free ligand HL. The six Zn(II) and Cd(II)  
coordination polymers display disparate photophysical properties  
(emission bands, fluorescent lifetimes and quantum yields) due to  
their different metal centers and supramolecular structures. These  
results further enrich our knowledge of structural topologies for  
coordination networks, and they also provide a synthetic strategy  
to tune the structures and properties for the design of novel  
functional coordination polymers.

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### Notes and references

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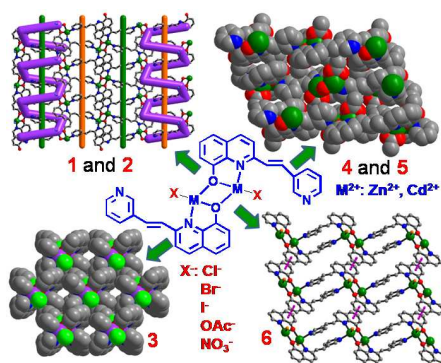
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Six coordination polymers with different structures have been prepared. The tunable structures and photoluminescent properties were observed due to their different metal centers and supramolecular structures.