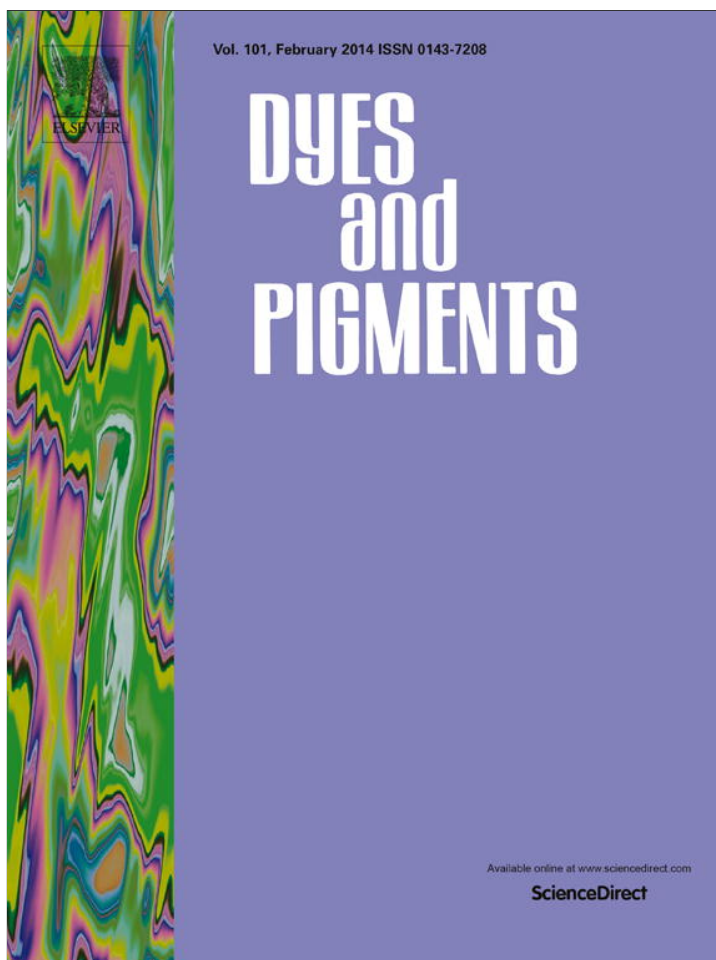


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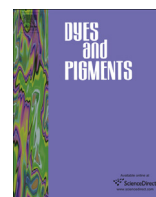
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Three novel transition metal coordination polymers based on (2,3-f)-pyrazino(1,10)phenanthroline-2,3-dicarboxylic acid sodium salt: Hydrothermal syntheses, structures, and properties



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ABSTRACT

Three novel transition metal coordination polymers including $[\text{Cd}_2(\text{Na}_2\text{PPDA})_2\text{Cl}_4]_n$ (**I**), $[\text{Zn}(\text{Na}_2\text{PPDA})(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}]_n$ (**II**) and $[\text{Ni}(\text{Na}_2\text{PPDA})(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}]_n$ (**III**) were prepared under hydrothermal conditions based on (2,3-f)-pyrazino(1,10)phenanthroline-2,3-dicarboxylic acid sodium salt (Na_2PPDA) and characterized by elemental analysis, infrared spectrometry and single crystal X-ray diffraction. The outstanding structural feature of **I** is that four cadmium atoms are linked into a zigzag-shaped polymeric chain in the sequence of $\text{Cd}-(\text{Cl})_2-\text{Cd}-(\text{Cl})_2-\text{Cd}-(\text{Cl})_2-\text{Cd}$ by three μ_2 -Cl bridges. Findings indicate that **I** displays a three-dimensional (3D) network constructed via hydrogen bonds and $\text{C}-\text{H} \cdots \pi$ interactions. Both coordination polymers of **II** and **III** present isomorphous and isostructural characters, in which the adjacent metal centers in the same chain connected up and down through hydrogen bonds (generated through μ_2 - ClO_4 anions) to construct the left- and right-handed helical chains which are further interconnected by hydrogen bonds, thereby affording a two-dimensional (2D) layer. Moreover, thermogravimetric (TG) analyses, the magnetic and luminescent properties of as-synthesized coordination polymers were also investigated.

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1. Introduction

Recently, metal–organic frameworks (MOFs) are currently one of the most intensively studied in the inorganic and material science not only because of their intriguing variety of architectures and topologies, but also because of their potential applications in ion exchange, catalysis, magnetism and gas storage [1–10]. Specifically, there is an increasing trend in the exploration and discovery of functional luminescent MOFs. A variety of luminescent MOFs have been prepared using transition metal ions, and the Cu, Ag, Zn and Cd involved MOFs are the most commonly reported because the d^{10} metal ions not only possess various coordination numbers and geometries, but also exhibit luminescent properties when bound to functional ligands [11–16]. Selection of suitable ligands with fixed geometry and variable coordination modes is very important for the design and synthesis of luminescent MOFs with interesting geometric configurations. As an important member in the family of multidentate O/N donor ligands, [2,3-f]pyrazino [1,10]

phenanthroline 2,3 dicarboxylic acid (H_2PPDA) possesses unique structural features that inspired our research interest. Firstly, its multidentate coordination N/O donors can adopt a variety of coordination modes with metal atoms and is therefore able to provide diversified structural motifs; thus, H_2PPDA may be an excellent candidate for the construction of multidimensional coordination polymers. Secondly, owing to the presence of two carboxylate groups and conjugated larger π systems, which are beneficial to the formation of π – π stacking, allowing H_2PPDA ligand possesses the recognition information for the fabrication of interesting supramolecular structures. Thirdly, the conjugated larger π systems and N-containing aromatic rings are currently of interest in the development of fluorescent materials and as model compounds for luminescence and optical switching devices [17,18]. Moreover, H_2PPDA can be partially or completely deprotonated to generate HPPDA^- and HPPDA^{2-} when the pH value is carefully controlled, which provides H_2PPDA with various acidity-dependant coordination modes; not to mention that H_2PPDA in the synthetic system acts not only as a necessary coordination ligand but also as a pH value adjuster of the reaction mixture. However, only a few H_2PPDA metal complexes have been reported up to date [6,19]. To the best of our knowledge, the structures and properties of metal–organic

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coordination polymers with transition metals assembled from H₂PPDA ligand have not been investigated systematically, especially, compounds assembled by Na₂PPDA ligand have not been reported hereunto. In this work, we report the syntheses, structures and properties of three novel transition metal coordination polymers based on Na₂PPDA ligand, namely, [Cd₂(Na₂PPDA)₂Cl₄]_n (**I**), [Zn(Na₂PPDA)(ClO₄)₂·4H₂O]_n (**II**) and [Ni(Na₂PPDA)(ClO₄)₂·4H₂O]_n (**III**). The typical coordination modes of Na₂PPDA in the coordination polymers (mode a for (**I**) and mode b for (**II**) and (**III**)) are summarized in Scheme 1.

2. Experimental

2.1. Materials and measurements

All starting chemicals were of analytical grade and were used without further purification. Elemental analysis was performed with a Perkin–Elmer 240C elemental analyzer. Fourier transform infrared (FT-IR) were recorded with an AVATAR 360 FT-IR spectrometer (KBr pellets, in the region of 4000–400 cm⁻¹). The crystal structure was determined with a Bruker Smart CCD X-ray single-crystal diffractometer. Fluorescent data were collected with an F-7000 FL spectrophotometer at room temperature. Thermogravimetric (TG) analysis was conducted with a Perkin–Elmer TGA7 system under flowing N₂ stream (flow rate 40 mL/min) from room temperature to 1000 °C at a heating rate of 10 K/min. Magnetic susceptibility measurement was carried out by using a Quantum Design MPMS-5 magnetometer in the temperature range of 2.0–300.0 K.

2.2. Synthesis of the coordination polymers **I**, **II** and **III**

2.2.1. Synthesis of coordination polymer **I**

I was synthesized from the reaction mixture of Na₂PPDA and CdCl₂·2.5H₂O in molar ratio of 1:7 in 10 mL methanol. The mixture was homogenized by stirring for 30 min, then transferred into 20 mL Teflon-lined stainless steel autoclave under autogenous pressure at 110 °C for 4 days. After cooling the reaction system to room temperature at a rate of 5 °C/h, clear block crystals were isolated. Calcd. for the coordination polymer C₃₂H₁₂O₈N₈Cl₄Na₄Cd₂ (%): C, 35.10; H, 1.10; N, 10.23%. Found: C, 35.08; H, 1.07; N, 10.21%. selected IR (KBr): 3461(br), 3086(m), 2955(m), 1742(s), 1614(w), 1577(m), 1543(w), 1517(s), 1490(w), 1449(w), 1399(w), 1383(w), 1273(m), 1240(w), 1206(s), 1162(s), 1139(m), 1096(m), 1081(w), 1047(m), 949(m), 911(w), 845(m), 826(w), 798(m), 765(s), 739(m), 710(m), 639(w), 547(w), 522(w), 439(w), 421(m), 374(w).

2.2.2. Synthesis of coordination polymer **II**

II was synthesized from the reaction mixture of Na₂PPDA and Zn(ClO₄)₂·6H₂O in molar ratio of 1:7 in 10 mL methanol. The mixture was homogenized by stirring for 30 min, then transferred into 20 mL Teflon-lined stainless steel autoclave under autogenous pressure at 110 °C for 4 days. After cooling the reaction system to

room temperature at a rate of 5 °C/h, the resulting green solution was filtered to remove any suspended residue and kept at room temperature for slow evaporation. After two weeks, clear block crystals of **II** formed. They were collected by filtration and dried in air. Calcd. for the coordination polymer C₁₆H₁₄O₁₆N₄Cl₂Na₂Zn (%), mass fraction, the same hereafter): C, 27.43; H, 2.01; N, 8.00%. Found: C, 27.41; H, 1.97; N, 7.97%. selected IR (KBr): 3561(br), 2016(w), 1730(w), 1638(s), 1620(s), 1145(s), 1115(s), 1089(s), 627(s), 482(m), 402(m), 941(m), 2027(w), 1521(w), 1460(w), 1441(w), 1356(w), 1278(w), 1243(w), 799(w), 736(w), 515(w), 475(w).

2.2.3. Synthesis of coordination polymer **III**

III was prepared in the same way as that of **II**, except that using Ni(ClO₄)₂·6H₂O instead of Zn(ClO₄)₂·6H₂O. After slow evaporation, green crystals of **III** were obtained and collected by filtration and dried in air. Calcd. for the coordination polymer C₁₆H₁₄O₁₆N₄Cl₂Na₂Ni (%): C, 27.70; H, 2.03; N, 8.07%. Found: C, 27.62; H, 1.97; N, 8.01%. selected IR (KBr): 3413(br), 2026(w), 1732(w), 1638(s), 1619(s), 1145(s), 1115(s), 1089(s), 628(s), 482(m), 402(m), 2027(w), 1733(w), 1518(w), 1442(w), 1400(w), 1356(w), 1239(w), 1206(w), 738(w), 515(w), 475(w).

3. Results and discussion

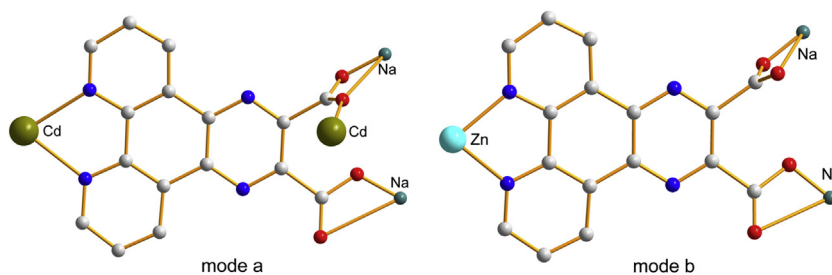
3.1. X-ray crystallographic determination

Single-crystal X-ray diffraction measurements of coordination polymers **I**, **II** and **III** were carried out on a Bruker Smart CCD X-ray single-crystal diffractometer. Reflection data were measured at 296(2) K using graphite monochromated MoK α -radiation ($\lambda = 0.71073\text{\AA}$) and ω -scan technique. All independent reflections were collected in a range of 2.07–25.00, 1.74 to 25.00 and 1.73 to 25.00 for **I**, **II** and **III**, respectively, and determined in the subsequent refinement. SADABS Multi-scan empirical absorption corrections were applied to the data processing. The crystal structures were solved by direct methods and Fourier synthesis. Positional and thermal parameters were refined by the full-matrix least-squares method on F^2 using the SHELXTL software package. Isotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. The crystallographic data, selected bond lengths and angles for coordination polymers **I**, **II** and **III** are listed in Tables 1–3, respectively.

3.2. X-ray structures of the coordination polymers **I**, **II** and **III**

3.2.1. Structure analysis of [Cd₂(Na₂PPDA)₂Cl₄]_n (**I**)

Single-crystal X-ray structural analysis shows that the asymmetrical unit in **I** contains three coordinated Na₂PPDA ligands, four Cl atoms and two Cd atoms, as illustrated in Fig. 1. Both Cd1 and Cd2



Scheme 1. Coordination modes of Na₂PPDA ligand in coordination polymers **I**–**III**.

Table 1
Summary of crystallographic data for I–III.

Data	I	II	III
Empirical formula	C ₃₂ H ₁₂ O ₈ N ₈ Cl ₄ Na ₄ Cd ₂	C ₁₆ H ₁₄ O ₁₆ N ₄ Cl ₂ Na ₂ Zn	C ₁₆ H ₁₄ O ₁₆ N ₄ Cl ₂ Na ₂ Ni
Formula weight	1095.06	700.56	693.9
Temperature/K	296(2)		
Wavelength/Å	0.71073		
Crystal system	Triclinic	Monoclinic,	Monoclinic,
Space group	<i>P</i> -1	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>n</i>
<i>a</i> /Å	10.0086(6)	8.128(6)	8.1808(6)
<i>b</i> /Å	14.0943(8)	13.349(9)	13.4902(9)
<i>c</i> /Å	14.2981(8)	23.496(16)	23.6221(17)
α (°)	82.1220(10)	90	90
β (°)	80.2830(10)	95.285(11)	95.3350(10)
γ (°)	86.0980(10)	90	90
<i>Z</i>	2	4	4
Density(calculated)	1.842 Mg/m ³	1.833 Mg/m ³	1.776 Mg/m ³
<i>F</i> (000)	1064	1408	1400
Crystal size/mm ³	0.52 × 0.48 × 0.39	0.51 × 0.28 × 0.12	0.64 × 0.57 × 0.05
Range for data collection/(°)	2.07 to 25.00	1.74 to 25.00	1.73 to 25.00
Limiting indices	−11 ≤ <i>h</i> ≤ 11, −9 ≤ <i>k</i> ≤ 16, −17 ≤ <i>l</i> ≤ 16	−9 ≤ <i>h</i> ≤ 9, −13 ≤ <i>k</i> ≤ 15, −27 ≤ <i>l</i> ≤ 25	−9 ≤ <i>h</i> ≤ 9, −16 ≤ <i>k</i> ≤ 14, −24 ≤ <i>l</i> ≤ 28
Reflections collected/unique	68,291/5558 [<i>R</i> _(int) = 0.0138]	44,029/4169 [<i>R</i> _(int) = 0.0275]	45,648/4144 [<i>R</i> _(int) = 0.0299]
Refinement method	Full-matrix least-squares on <i>F</i> ²		
Data/restraints/parameters	6870/0/523	4467/0/370	4572/0/370
Goodness-of-fit on <i>F</i> ²	1.057	1.096	1.103
Volume/Å ³	1967.2(2)	2539.3	2595.66
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0470, <i>wR</i> ₂ = 0.1278	<i>R</i> ₁ = 0.0645, <i>wR</i> ₂ = 0.1989	<i>R</i> ₁ = 0.0635, <i>wR</i> ₂ = 0.1753
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0523, <i>wR</i> ₂ = 0.1314	<i>R</i> ₁ = 0.0745, <i>wR</i> ₂ = 0.2092	<i>R</i> ₁ = 0.0778, <i>wR</i> ₂ = 0.1853
Largest diff. peak and hole/(e·Å ^{−3})	1.407 and −0.988	1.324 and −0.976	1.219 and −0.874

atoms adopt slightly distorted octahedral configurations. Cd1 is coordinated by four μ_2 -Cl atoms and two N atoms from a chelating Na₂PPDA ligand, while Cd2 is coordinated by two μ_2 -Cl and one terminal Cl atoms, two N atoms from one chelating Na₂PPDA ligand, one O atom from another chelating Na₂PPDA ligand. The Cd–N bond distances ranging from 2.338(4) to 2.408(4) Å. The Cd–Cl bond distances of 2.449(1)–2.743(1) Å are in common values, which are obviously longer than those of Cd–N bonds, owing to the differences of N and Cl atom radii. In terms of the framework of coordination polymer **I**, the particular structural feature is that four cadmium atoms are linked by six μ_2 -Cl bridges into a polymeric chain in the sequence of Cd2–(Cl)₂–Cd1–(Cl)₂–Cd1a–(Cl)₂–Cd2a (Cd4Cl6 unit), with corresponding distances of Cd2…Cd1, Cd2…Cd1a and Cd1a…Cd2a being 3.791 Å, 3.878 Å and 3.791 Å, respectively, as shown in Fig. 2. Within the binuclear rhombic polymeric unit, each Cd2Cl2 subunit is nearly coplanar; however, the adjacent Cd2Cl2 planes are twisted to each other with the dihedral angle of about 76.52°. As a result, each Cd4Cl6 unit is blocked by terminal coordinating Na₂PPDA molecules to form an infinite zigzag-shaped chain, as shown in Fig. 3(a). To the best of our knowledge, there are only few reported tetranuclear cadmium compounds connected by bridging μ_2 -Cl atoms and coordinated carboxyl O atoms from H₂PPDA ligands [11–16]. It's noteworthy that there exists a Cd2–(Na₂PPDA)₂ ring-shaped motif acting as the linkage between the adjacent Cd4Cl6 units, in which the intramolecular π – π interactions between the parallel benzene rings of Na₂PPDA are observed (the centroid–centroid distance of Na₂PPDA benzene rings is about 3.564 Å. These interactions take effect on the stabilization of **I**. Another special structural feature of **I** is that both carboxylic groups of each H₂PPDA ligand chelate to one Na atom, respectively, thereby the prolongation of carboxyl-ends are prohibited resulting the dimensionality reduction of the as-synthesized coordination polymer in covalently fashion. In this case, the carboxyl-ends-occupied Na₂PPDA ligands coordinate Cd atoms only through the phenanthroline motif in an N,N-chelating fashion which is none reported hitherto. Findings indicate that

1D zigzag-shaped chains based on Cd4Cl6 units are further linked into 2D layers through hydrogen bonds (such as C2–H2A…Cl3: 2.746 Å, 168.1°, see Fig. 3(b)) and C–H… π interactions (i.e. C13–H13… π : 3.749 Å, 94.4°; C31–H31… π : 3.888 Å, 90.3°, see Fig. 3(c)) in different directions. The adjacent 2D layers extending in different directions are interconnected into 3D network through weak interactions above-mentioned in clinker-built fashion (as shown in Fig. 3(d)). It should be mentioned that Chen and co-workers reported the Cd(II) based on coordination polymer similar to **I**, containing the esterified (CH₃)₂–PPDA ligands instead of Na₂PPDA ligands [5].

3.2.2. Structure analysis of [Zn(Na₂PPDA)(ClO₄)₂·4H₂O]_n (**II**) and [Ni(Na₂PPDA)(ClO₄)₂·4H₂O]_n (**III**)

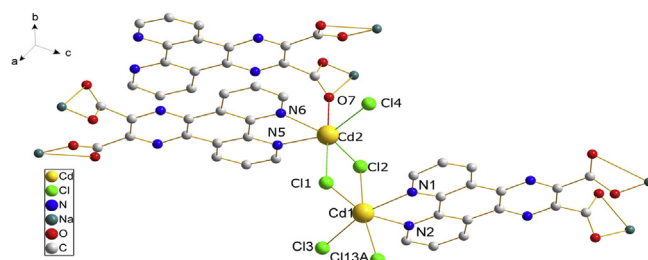
X-ray single-crystal diffraction reveals that coordination polymers **II** and **III** are isomorphous and isostructural. Thus, only the structure of **II** is described here in detail as a typical example. The Zn(II) center binds to four water molecules and two nitrogen atoms from one Na₂PPDA ligand, as illustrated in Fig. 4. The whole geometry of the center can be best described as a distorted octahedral geometry. The Zn–Ow bond lengths are in the range of 2.057(4)–2.105(4) Å. Obviously, the Zn–N bond lengths of 2.100(4) and 2.110(4) Å are longer than those of Zn–Ow. Besides, the Ow–Zn–Ow angles lie in the range of 83.21(16)–168.47(15)°, which agree well with those previously reported zinc complexes [20,21]. Moreover, in the discrete unit, there exist two dissociative ClO₄[−] anions which connect the adjacent metal centers up and down through hydrogen bonds (i.e. O1W–H1WA…O11: 2.940(8) Å, 166.4° and O4W–H4WB…O10: 2.686(6) Å, 173.6°, see Table 3 and Fig. 5(a)) in μ_2 -ClO₄[−] fashion to construct the left- and right-handed helical chains with a pitch of 13.349 Å, as illustrated in Fig. 5(b). Both two types of helical chains prolongate in the sequence of (…Cd… μ_2 -ClO₄[−]…Cd… μ_2 -ClO₄[−]…)∞ (dashed means hydrogen bonds). The adjacent left- and right-handed helical chains are further interconnected by hydrogen bonds (i.e. O1W–H1WB…O7: 2.706(8) Å, 144.4°; O4W–H4WA…O5: 2.726(8) Å, 174.0°) generated

Table 2
Selected bond lengths(Å) and bond angles(°)for I–III.

Bond lengths				
I				
Cd1–N1	2.338(4)	Cd2–N4	2.409(4)	
Cd1–N2	2.376(4)	Cd2–Cl4	2.4490(14)	
Cd1–Cl3	2.5283(12)	Cd2–Cl2	2.5453(12)	
Cd1–Cl1	2.5648(13)	Cd2–O7	2.592(4)	
Cd1–Cl2	2.6812(13)	Cd2–Cl1	2.6721(14)	
Cd1–Cl3	2.7431(14)	Cl1–Na1	3.218(8)	
Cd2–N3	2.368(4)	Cl3–Cd1	2.7431(14)	
II				
Zn1–O2W	2.057(4)	Zn1–O1W	2.105(4)	
Zn1–O4W	2.071(4)	Zn1–N1	2.100(4)	
Zn1–O3W	2.088(4)	Zn1–N2	2.110(4)	
III				
Ni1–O4W	2.049(4)	Ni1–O3W	2.069(4)	
Ni1–O1W	2.058(4)	Ni1–N2	2.074(4)	
Ni1–N1	2.065(4)	Ni1–O2W	2.077(4)	
I				
N1–Cd1–N2	70.48(14)	N3–Cd2–N4	68.96(13)	
N1–Cd1–Cl3	162.63(11)	N3–Cd2–Cl4	155.19(11)	
N2–Cd1–Cl3	95.14(10)	N4–Cd2–Cl4	93.82(10)	
N1–Cd1–Cl1	92.43(10)	N3–Cd2–Cl2	90.59(10)	
N2–Cd1–Cl1	159.71(11)	N4–Cd2–Cl2	159.33(10)	
Cl3–Cd1–Cl1	103.38(5)	Cl4–Cd2–Cl1	106.55(5)	
N1–Cd1–Cl2	86.88(11)	N3–Cd2–O7	76.92(15)	
N2–Cd1–Cl2	81.65(11)	N4–Cd2–O7	95.24(13)	
Cl3–Cd1–Cl2	100.98(4)	Cl4–Cd2–O7	87.47(11)	
Cl1–Cd1–Cl1	86.70(4)	Cl2–Cd2–O7	82.47(10)	
N1–Cd1–Cl3	85.07(11)	N3–Cd2–Cl1	96.63(12)	
N2–Cd1–Cl3	90.49(11)	N4–Cd2–Cl1	91.99(10)	
Cl3–Cd1–Cl3	85.37(4)	Cl4–Cd2–Cl3	101.88(5)	
Cl1–Cd1–Cl3	99.09(4)	Cl2–Cd2–Cl1	87.29(4)	
Cl2–Cd1–Cl3	170.27(4)	O7–Cd2–Cl1	67.79(11)	
II				
O2W–Zn1–O4W	89.58(17)	O3W–Zn1–O1W	87.03(17)	
O2W–Zn1–O3W	93.53(19)	N1–Zn1–O1W	94.37(17)	
O4W–Zn1–O3W	84.45(19)	O2W–Zn1–N2	93.04(16)	
O2W–Zn1–N1	170.70(15)	O4W–Zn1–N2	97.39(17)	
O4W–Zn1–N1	94.14(18)	O3W–Zn1–N2	173.19(18)	
O3W–Zn1–N1	95.31(19)	N1–Zn1–N2	78.03(15)	
O2W–Zn1–O1W	83.21(16)	O1W–Zn1–N2	91.98(16)	
O4W–Zn1–O1W	168.47(15)			
III				
O4W–Ni1–O1W	89.50(16)	N1–Ni1–N2	79.77(15)	
O4W–Ni1–N1	93.63(17)	O3W–Ni1–N2	91.39(15)	
O1W–Ni1–N1	172.29(15)	O4W–Ni1–O2W	85.79(18)	
O4W–Ni1–O3W	171.39(15)	O1W–Ni1–O2W	91.66(18)	
O1W–Ni1–O3W	84.28(16)	N1–Ni1–O2W	95.59(17)	
N1–Ni1–O3W	93.28(17)	O3W–Ni1–O2W	88.44(16)	
O4W–Ni1–N2	94.87(17)	N2–Ni1–O2W	175.33(17)	
O1W–Ni1–N2	92.96(16)			

Table 3
Hydrogen bond geometry (Å) in I–III.

I				
D–H...A	d(D–H)	d(H...A)	d(D...A)	∠(DHA)
C2–H2A...Cl3	0.93	2.75	3.661(7)	168.1
II				
O1W–H1WA...O11	0.85	2.11	2.940(8)	166.4
O1W–H1WB...O7	0.85	1.97	2.706(8)	144.4
O2W–H2WA...O4	0.85	2.00	2.847(5)	173.0
O2W–H2WB...O8	0.85	1.87	2.713(7)	171.4
O4W–H4WA...O5	0.85	1.88	2.726(8)	174.0
O4W–H4WB...O10	0.85	1.84	2.686(6)	173.6
III				
O1W–H1WA...O7	0.85	1.90	2.736(7)	168.2
O1W–H1WB...O4	0.85	2.02	2.868(5)	176.1
O3W–H3WA...O8	0.85	1.96	2.742(8)	153.2
O3W–H3WB...O9	0.85	2.16	2.940(7)	153.1
O4W–H4WA...O5	0.85	1.93	2.765(7)	168.7
O4W–H4WB...O12	0.85	1.87	2.718(6)	172.5

**Fig. 1.** Coordination environment of I; the asymmetric unit and the related coordination atoms are labeled; hydrogen atoms are omitted for clarity.

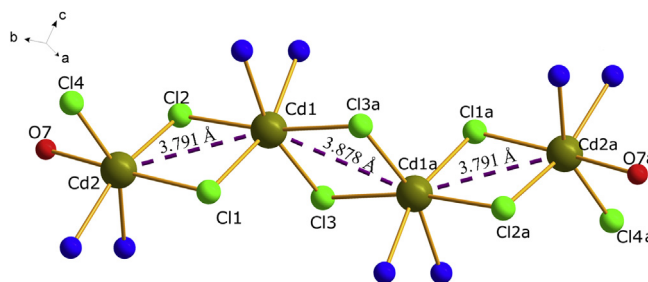
by μ_2 -ClO₄ anions to give rise to a 2D layer network, where the 16-membered closed rings (denoted as Cd₂(μ_2 -ClO₄)₂, see Fig. 5(a)) are formed acting as the linkers between two adjacent helical chains. Furthermore, the left-handed helical chains are reciprocally parallel and the distance between two adjacent chains is 24.144(2) Å, the same cases are observed in the right-handed helical chains. Interestingly, two types of helical chains are alternately arranged in the 2D layer. Owing to the similar cases to I, both carboxylic groups of each H₂PPDA ligand chelate to one Na atom, respectively, thereby the prolongation of carboxyl-ends are prohibited resulting the dimensionality reduction of the coordination polymer II and III.

3.3. Thermal analysis

The TG curve of coordination polymer I is shown in Fig. 6, which indicate that I decomposes in three steps. Coordination polymer I has weight losses of 5.47%, 15.47% and 56.66% in temperature ranges of 41–95 °C, 326–530 °C and 530–1000 °C, respectively (relevant calculated weight losses are 5.34%, 16.02% and 55.52%). The final mass remnant of 11.12% is indicative of deposition of Na₂O (theoretical loss is 11.31%). Besides, the coordination polymer III decomposes in two steps, as illustrated in Fig. 6. III loses 9.18% and 70.84% of weight in the temperature ranges of 27–137 °C and 137–326 °C, respectively (relevant calculated weight losses are 9.22% and 71.08%). The decomposition product may be identified as NiO and Na₂O. The observed weight (19.76 wt%) is in good agreement with the calculated value (19.70%).

3.4. Luminescent properties

The luminescent properties of d¹⁰ metal (e.g. Cu⁺, Zn²⁺ and Cd²⁺) coordination polymers have been attracting intensive research interest, owing to their potential applications in the fields of chemical sensors, photochemistry, electroluminescent and catalysis etc. [22,23]. As shown in Fig. 7, the solid-state luminescence properties of the as-synthesized coordination polymers I, II and III were investigated at room temperature. I, II and III all exhibit characteristic luminescent peaks in the visible region at the excitation of 400, 463 and 401 nm for I, II and III, respectively,

**Fig. 2.** The tetranuclear Cd cluster connected by μ_2 -Cl bridges in I.

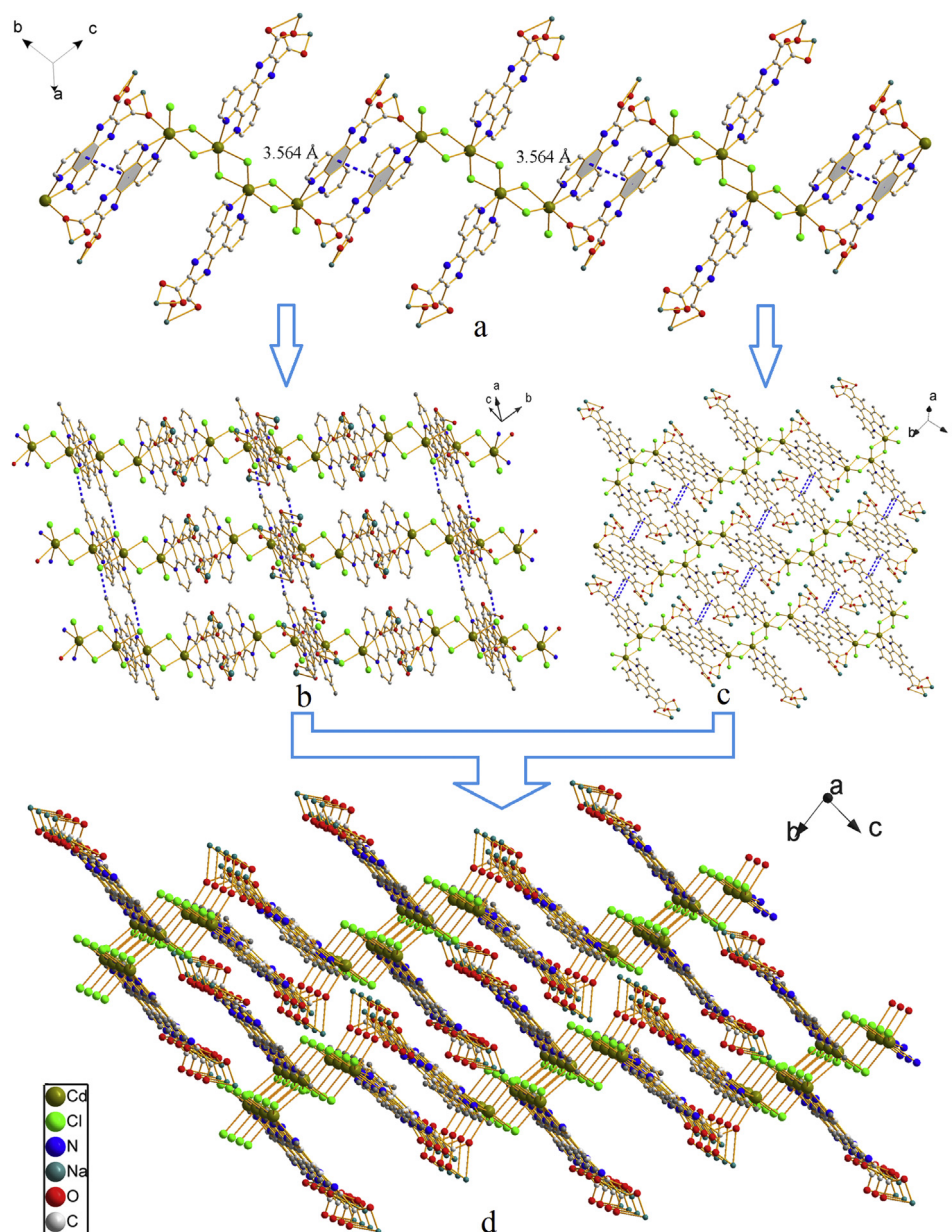


Fig. 3. (a) Diagram showing the 1D infinite zigzag-shaped chain in **I**. (b) and (c) Diagram showing the 2D layers connected through hydrogen bonds and C–H... π interactions between 1D chains in different directions. (d) 3D network viewed along *a* axis overlaid via 2D layers (hydrogen atoms are omitted for clarity).

which display corresponding broad green luminescent emission bands at ~470, 697 and 618 nm. The comparison among three metal polymers indicate polymer **I** with 3D structure shows much shorter maximum emission wavelength than other two polymers.

Therefore, the maximum emission bands for those polymers should be correlated with the structure of metal polymers. While in a 3D structure like polymer **I**, the aggregation of the ligands are dramatically confined, the aggregation of ligand in polymer **II** and **III** become more likely. As a result, the aggregation of the ligand leads to a red shift in the maximum emission band. It can be understood that the emission peaks mainly originate from intraligand $\pi-\pi^*$ transition of Na_2PPDA ligand and the ligand to ligand charge transfer (LLCT) from Cl^- to Na_2PPDA . In comparison to the reported emission peak at 428 nm ($\lambda_{\text{ex}} = 390$ nm) of free H_2PPDA [6], the maximum of the emission bands of **I**, **II** and **III** present significant red shifts. This phenomenon may be ascribed to the structural character of carboxyl-ends-occupied (Na_2PPDA) of H_2PPDA , which modifies the rigidity and the steric effect of the ligand resulting the radiation decay of intraligand emission excited state for luminescent properties are closely related to the metal ions and the coordination environment of certain ligands [5].

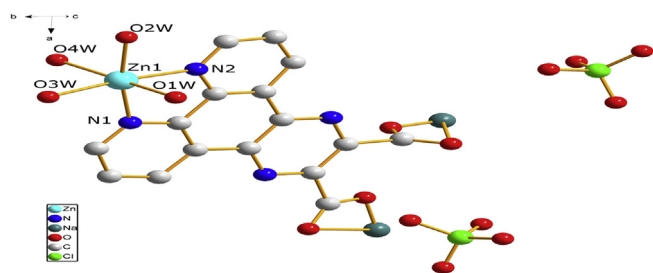


Fig. 4. Coordination environment of **II**; the asymmetric unit and the related coordination atoms are labeled; hydrogen atoms are omitted for clarity.

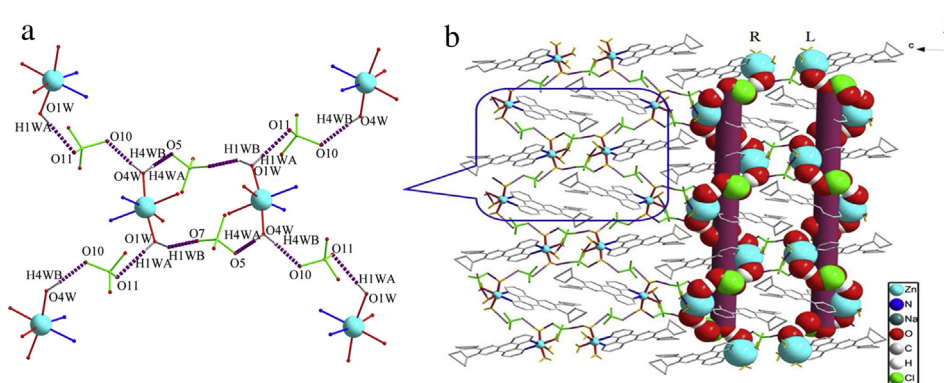


Fig. 5. (a) Hydrogen-bonding interactions in and between the helical chains in **II** viewed along *a* axis. (b) Space-filling diagrams of the right-handed (R) and left-handed (L) helices in the 2D layer in **II**.

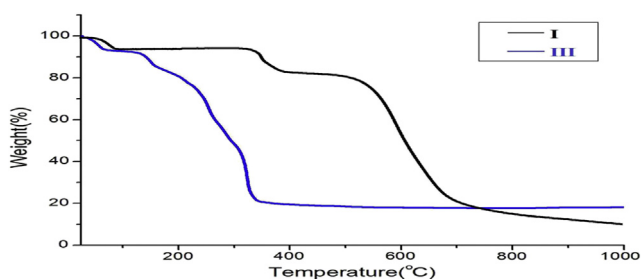


Fig. 6. TG curves of coordination polymers **I** and **III**.

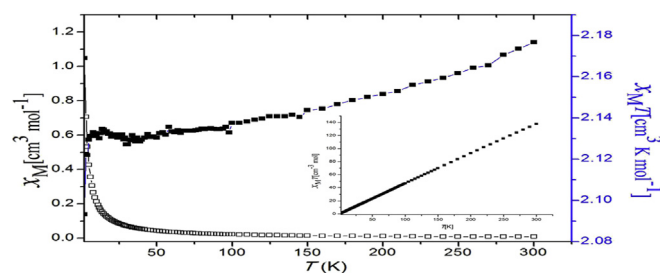


Fig. 8. Thermal variation of χ_M and $\chi_M T$ for **III**. Insert: Plot of thermal variation of χ_M^{-1} for **III**.

3.5. Magnetic properties

The magnetic property of **III** was investigated in the temperature range of 2.0–300.0 K, as shown in Fig. 8. The $\chi_M T$ value at 300 K is 2.177 cm³ K mol⁻¹ (4.173 μ_B), which is higher than the expected value (1 cm³ K mol⁻¹, 2.828 μ_B) of isolated spin-only Ni(II) ion ($s = 1$, $g = 2$). As T is lowered, $\chi_M T$ decreases continuously to a value of 1.048 cm³ K mol⁻¹ at 2.0 K. Consequently, this behavior indicates a dominant antiferromagnetic interaction between the Ni(II) ions in the structures. The shortest Ni⋯Ni distance across the ClO₄⁻ bridge in **III** is 6.404 Å. Therefore, the antiferromagnetic interaction between Ni(II) centers is expected to be through the ClO₄⁻ bridge. The $1/\chi_M$ versus T plot of **III** is in correspondence with the Curie–Weiss law in the range of 2.0–300.0 K with $C = 2.164$ cm³ K mol⁻¹ and $\theta = 0.670$ K [24,25].

4. Conclusion

We report here three novel coordination polymers including [Cd₂(Na₂PPDA)₂Cl₄]_n (**I**), [Zn(Na₂PPDA)(ClO₄)₂·4H₂O]_n (**II**) and [Ni(Na₂PPDA)(ClO₄)₂·4H₂O]_n (**III**) generated from a rigid N-containing dicarboxylic acid ligand (Na₂PPDA) under hydrothermal conditions. Structural characterization results of as-synthesized coordination polymers demonstrate that the Na₂PPDA ligand affords different coordination modes in these polymers thereby resulting in different interesting topological frameworks. Coordination polymer **I** is identified as coordination mode a, which presents infinite zigzag-shaped chains and thereafter extends into 2D and 3D architectures *via* hydrogen bonds and π – π interactions, whereas isomorphous and isostructural **II** and **III**, are identified as coordination mode b, give rise to 2D layer through hydrogen bonds.

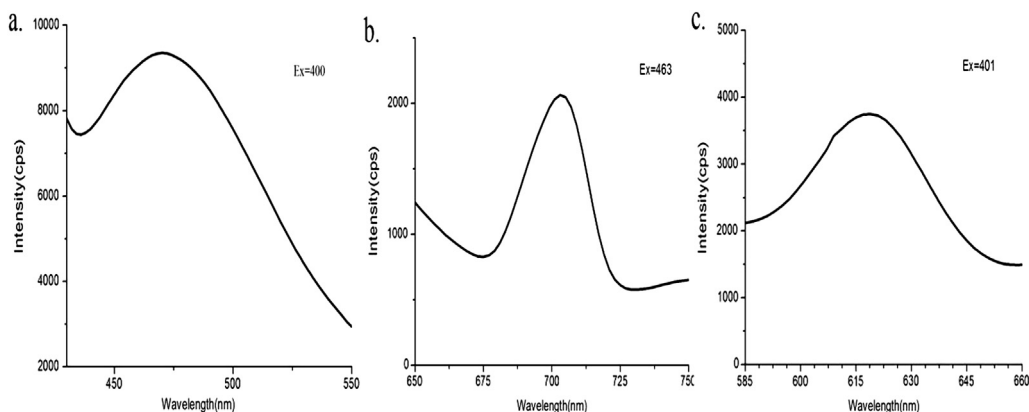


Fig. 7. Solid-state emission and excitation spectra of **I–III** (denoted as a, b and c) recorded at room temperature.

The thermogravimetric analysis of coordination polymers **I**, **III** and the photoluminescent properties of **I–III** were discussed. The emission spectra demonstrate that these coordination polymers may be potential candidates for efficient luminescent materials in the visible and near-infrared regions. Particularly, antiferromagnetic interaction can be deduced by the Weiss constant and the decrease in χ_{MT} for **I**.

Acknowledgments

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Appendix A. Supplementary material

CCDC 920558, 933561 and 918560 contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac>.

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