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Ligand-controlled assembly of Cd(II) coordination polymers based on mixed ligands of naphthalene-dicarboxylate and dipyrido[3,2-d:2′,3′-f]quinoxaline: From 0D+1D cocrystal, 2D rectangular network (4,4), to 3D PtS-type architecture

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ABSTRACT

Three novel Cd(II) coordination polymers, namely, [Cd(Dpq)(1,8-NDC)$(H_2O)_2$][Cd(Dpq)(1,8-NDC)]$\cdot 2H_2O$ (**1**), [Cd(Dpq)(1,4-NDC)(H_2O)] (**2**), and [Cd(Dpq)(2,6-NDC)] (**3**) have been obtained from hydrothermal reactions of cadmium(II) nitrate with the mixed ligands dipyrido [3,2-d:2′,3′-f]quinoxaline (Dpq) and three structurally related naphthalene-dicarboxylate ligands [1,8-naphthalene-dicarboxylic acid (1,8-H_2NDC), 1,4-naphthalene-dicarboxylic acid (1,4-H_2NDC), and 2,6-naphthalene-dicarboxylic acid (2,6-H_2NDC)]. Single-crystal X-ray diffraction analysis reveals that the three polymers exhibit novel structures due to different naphthalene-dicarboxylic acid. Compound **1** is a novel cocrystal of left- and right-handed helical chains and binuclear complexes and ultimately packed into a 3D supramolecular structure through hydrogen bonds and π–π stacking interactions. Compound **2** shows a 2D rectangular network (4,4) bridged by 1,4-NDC with two kinds of coordination modes and ultimately packed into a 3D supramolecular structure through inter-layer π–π stacking interactions. Compound **3** is a new 3D coordination polymer with distorted PtS-type network. In addition, the title compounds exhibit blue/green emission in solid state at room temperature.

1. Introduction

The rational design and synthesis of novel functional coordination compounds is the current interest in the field of supramolecular chemistry and crystal engineering, stemming from their potential applications as functional materials along with their intriguing variety of architectures [1–5]. However, one of the obvious challenges to chemists is the rational and controllable preparation of the target metal organic frameworks in this area [6], the formation of which is greatly affected by the ligand nature [7], counterions [8], template [9,10], and other factors. As an important family of multidentate O-donor ligands, organic aromatic polycarboxylate anions as bridging ligand seem to be excellent building block with charge, versatile coordination modes as well as the remarkable rigidity and stability, and they can be regarded not only as hydrogen bond acceptors but also as hydrogen bond donors, depending on the number of deprotonated carboxylic groups for constructing high-dimensional networks with interesting properties [11]. On the other hand, 2,2′-bipyridyl-like (bpy-like) chelating ligands have been extensively employed in the preparation of metal–organic complexes as they may provide potential supramolecular recognition sites for π–π aromatic stacking interactions to form interesting supramolecular structures [12].

On the basis of the aforementioned points, we chose three structurally related naphthalene-dicarboxylate ligands [1,8-naphthalene-dicarboxylate acid (1,8-NDC), 1,4-naphthalene-dicarboxylate acid (1,4-NDC), 2,6-naphthalene-dicarboxylate acid (2,6-NDC)] and dipyrido[3,2-d:2′,3′-f]quinoxaline (Dpq) as the mixed ligands because of their remarkable advantages: (i) Naphthalene-dicarboxylate ligands, a preferred multifunctional oxygen-donor connector with diverse chelating and bridging modes for constructing coordination complex, has been recently utilized to generate a variety of coordination polymers [13–16]. (ii) Comparing to benzene-dicarboxylate ligands, naphthalene-dicarboxylate ligands has the larger aromatic-ring system and may provide potential supramolecular recognition sites for π–π aromatic stacking interactions and the steric hindrance may yield novel coordination polymer networks [17–19]. (iii) The carboxylate groups for generating metal oxygen cluster as the secondary building units (SBUs) and the variety of length and angle of carboxylate groups for producing higher dimensionality coordination polymers give the good opportunity to yield novel metal–organic frameworks [20,21]. (iv) Compared to 2,2′-bipyridine and

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1,10-phenathroline, Dpq has larger aromatic-ring system and may provide potential supramolecular recognition sites for π–π aromatic stacking interactions [22–24].

In this paper, we report the syntheses, crystal structures and characterization of three novel Cd(II) coordination polymers: a novel cocrystal of left- and right-handed helical chains and binuclear complexes [Cd(Dpq)(1,8-NDC)(H_2O)$_2$][Cd(Dpq)(1,8-NDC)]·$2H_2O$ (**1**), 2D rectangular Network (4,4) [Cd(Dpq)(1,4-NDC)(H_2O)] (**2**), and 3D PtS-type coordination polymer [Cd(Dpq)(2,6-NDC)] (**3**) through changing the naphthalene-dicarboxylate bridging ligands.

2. Experimental section

2.1. *Materials and instrumentation*

All chemicals purchased were of reagent grade and used without further purification. Dpq was synthesized by the method of the literature [25] and characterized by ^{1}HNMR spectrometer analyses and FT-IR spectra. ^{1}HNMR analyses were performed on a Varian Mercury Vx300 spectrometer Analyzer and FT-IR spectra (KBr pellets) were taken on a Magna FT-IR 560 spectrometer. Fluorescence spectra were performed on an F-4500 fluorescence/phosphorescence spectrophotometer at room temperature and elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C analyzer. Thermogravimetric data for the title compounds were collected on a Pyris Diamond thermal analyzer.

2.2. *Synthesis*

2.2.1. *[Cd(Dpq)(1,8-NDC)(H₂O)₂][Cd(Dpq)(1,8-NDC)]·2H₂O* (**1**)

A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.1 mmol), Dpq (0.1 mmol), 1,8-NDC (0.1 mmol), NaOH (0.2 mmol), H_2O (12 mL), stirred for 20 min, was sealed to a Teflon-lined stainless steel autoclave (25 mL) and kept at 170 °C for 3 days. After the mixture was slowly cooled to room temperature, yellow block crystals suitable for X-ray diffraction of **1** were isolated by mechanical separation from a white amorphous solid in 38% yield (based on Cd^{II} salt). The compound was washed several times with distilled water and acetone. The same methods of purification and isolation were adopted for **2** and **3**. Anal. Calc. for $C_{52}H_{36}Cd_2N_8O_{12}$: C 52.45, H 3.03, N 9.41%. Found: 52.49, H 3.05, N 9.42%. IR (KBr, cm^{-1}): 3377(s), 1616(m), 1558(s), 1548(s), 1500(m), 1487(m), 1473(m), 1433(m), 1402(s), 1388(s), 1352(s), 1213(m), 1172(w), 1122(w), 1082(w), 1020(w), 839(w), 812(m), 773(s), 738(s), 702(w), 638(w).

2.2.2. *[Cd(Dpq)(1,4-NDC)(H₂O)]* (**2**)

Similar procedures were performed to obtain yellow crystals of complex **2**, except that 1,4-NDC was used instead of 1,8-NDC. Yield: ~45%. Anal. Calc. for $C_{26}H_{15}CdN_4O_5$: C 54.18, H 2.60, N 9.73%. Found: C 54.22, H 2.59, N 9.72%; IR (KBr, cm^{-1}): 3406(s), 1602(s), 1581(s), 1558(s), 1510(w), 1477(w), 1458(w), 1436(w), 1406(s), 1392(s), 1352(s), 1309(m), 1259(m), 1207(w), 1159(w), 1124(w), 1082(m), 1028(w), 873(w), 794(s), 736(s), 705(w), 642(w), 563(w).

2.2.3. *[Cd(Dpq)(2,6-NDC)]* (**3**)

Similar procedures were performed to obtain yellow crystals of complex **3**, except that 2,6-NDC was used instead of 1,8-NDC. Yield: ~28%. Anal. Calc. for $C_{26}H_{14}CdN_4O_4$: C 55.83, H 2.51, N 10.02%. Found: C 55.85, H 2.53, N 10.04%; IR (KBr, cm^{-1}): 1627(s), 1568(s), 1490(w), 1471(w), 1406(m), 1386(s), 1355(s), 1334(m), 1309(w), 1253(w), 1236(w), 1213(w), 1188(w), 1089(m), 937(w), 873(w), 779(s), 738(s), 700(w), 636(w), 563(w).

Table 1
Crystal data and structure refinement for complexes **1–3**.

Complex	**1**	**2**	**3**
Formula	$C_{52}H_{36}Cd_2N_8O_{12}$	$C_{26}H_{15}CdN_4O_5$	$C_{26}H_{14}CdN_4O_4$
Formula wt.	1189.69	575.82	558.81
Cryst. syst.	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$C2/c$
a (Å)	9.2357(7)	22.4719(13)	20.8064(17)
b (Å)	10.8172(8)	12.3127(5)	13.7609(17)
c (Å)	47.004(3)	19.3004(10)	7.3544(7)
β (deg)	99.907(2)	120.5070(10)	101.562(2)
V (Å^3)	4625.9(6)	4601.0(4)	2062.9(4)
Z	4	4	4
D (g cm^{-3})	1.708	1.663	1.799
μ (mm^{-1})	0.997	0.996	1.104
$F(000)$	2384	2296	1112
θ_{max} (deg)	1.76–26.00	1.96–26.00	1.79–26.00
Index ranges	$-8 \leqslant h \leqslant 11$	$-27 \leqslant h \leqslant 26$	$-25 \leqslant h \leqslant 23$
	$-13 \leqslant k \leqslant 13$	$-14 \leqslant k \leqslant 15$	$-16 \leqslant k \leqslant 9$
	$-55 \leqslant l \leqslant 57$	$-12 \leqslant l \leqslant 23$	$-9 \leqslant l \leqslant 8$
Reflections collected	24 972	12 505	5561
Unique reflections	9073	4506	2024
R_{int}	0.0511	0.0343	0.0407
R_1[a] $[I>2\sigma(I)]$	0.0432	0.0465	0.0321
wR_2[b] (all data)	0.0873	0.1429	0.0700
GOF	0.998	1.092	1.042
$\Delta\rho_{max}$ (e Å^{-3})	0.564	1.829	0.464
$\Delta\rho_{min}$ (e Å^{-3})	−0.613	−0.606	−0.373

[a] $R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$.
[b] $wR_2 = \Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2]^{1/2}$.

2.3. *X-ray crystallographic measurements*

All diffraction data were collected using a Bruker P4 diffractometer (Mo-$K\alpha$ radiation, graphite monochromator, $\lambda = 0.71073$ Å). The structures were solved by direct methods with *SHELXS*-97 and Fourier techniques and refined by the full-matrix least-squares method on F^2 with *SHELXL*-97 [26,27]. All nonhydrogen atoms were refined anisotropically, and hydrogen atoms of the ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. H atoms of water molecules were located in different Fourier synthesis maps. In complex **2**, one of the 1,4-NDC ligands is disordered and the C19, C20, C21, C22 positions were refined with half-occupancy. All the crystal data and structure refinement details for the three compounds are given in Table 1. The data of relevant bond distances and angles are listed in Table S1, and the details about π–π stacking interactions hydrogen-bonding geometries are summarized in Tables S2 and S3. Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC reference numbers 686266–686268 for compounds **1–3**, respectively.

3. Results and discussion

3.1. *Description of crystal structure*

Single-crystal X-ray analysis shows that compound **1** is a 3D supramolecular network derived from 1D left- and right-handed helical chains linked by binuclear cadmium complexes. The coordination environment of Cd(II) is shown in Fig. 1. There are two crystallographically independent Cd(II) atoms. The Cd1 atom is six coordinated by two nitrogen atoms of Dpq [Cd–N 2.327(3), 2.368(3) Å], four carboxylate oxygen atoms with the Cd–O distances ranging from 2.272(3) to 2.340(3) Å. Two such cadmium atoms are connected by bridging ligands 1,8-NDC1 to

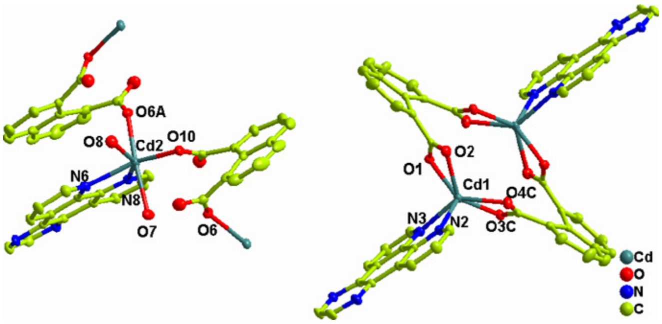


Fig. 1. Coordination environment of **1** with 30% probability thermal ellipsoids.

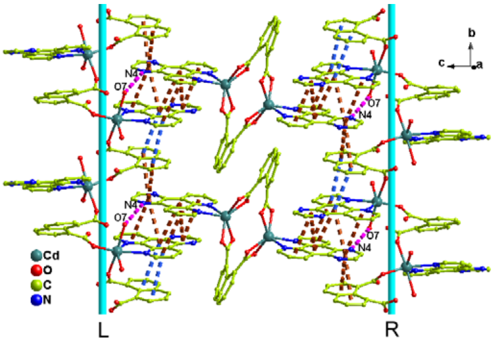


Fig. 2. The 2D supramolecular network of **1** constructed by 1D left- and right-handed helical chains and binuclear complexes through hydrogen bonds and π–π interactions.

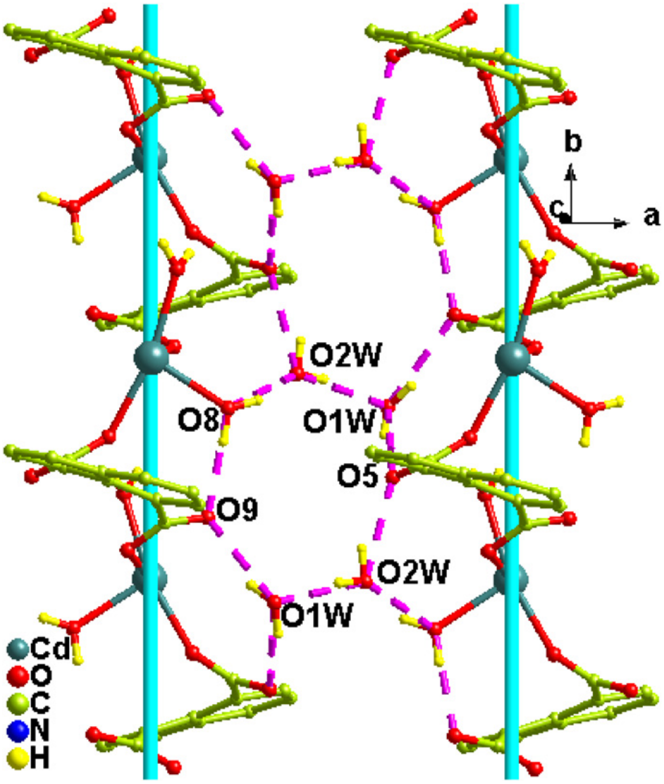


Fig. 3. The 2D supramolecular network of **1** constructed by 1D single handed helical chains through hydrogen bond interactions (Dpq ligands are omitted for clarity).

form a bimetallic SBU with the Cd$\cdots$Cd distance of 4.725 Å, in which 1,8-NDC1 ligand adopts a chelating bis-bidentate coordination mode (Scheme 2a left). Each Cd2 atom is coordinated by two nitrogen atoms of Dpq [Cd–N 2.376(3), 2.379(3) Å], two carboxylate oxygen atoms [Cd–O 2.239(3), 2.310(3) Å], two water molecules [Cd–O 2.341(3), 2.369(3) Å], showing a distorted octahedral coordination geometry. Adjacent cadmium atoms are connected by bridging ligands 1,8-NDC2 to form 1D helical chain along [010] direction with the Cd$\cdots$Cd distance of 5.943 Å, in which 1,8-NDC2 ligand adopts a bis-monodentate coordination mode (Scheme 2a right). The bond angles of the Cd1 atom with nitrogen and oxygen atoms vary from 56.99(10)° to 136.67(11)° and the bond angles of Cd2 atom vary from 70.04(11)° to 167.51(10)°, indicating the Cd1 octahedron is slightly more distorted than Cd2 octahedron, which may be caused by the steric effect and the difference of coordination environment around cadmium.

It is worth mentioning that adjacent 1D helical chains are linked by adjacent binuclear cadmium complexes through inter-molecular π–π interactions, giving rise to a 2D wave-like supramolecular network stabilized by O–H$\cdots$N hydrogen bonds interactions between the coordinated water molecules from helical chains and the N atoms of Dpq ligands from binuclear cadmium complexes [O7–H7B$\cdots$N4, 2.967(5) Å, 161°, Figs. 2 and S1–S2]. The Cg–Cg (distance between ring centroids) distances between adjacent aromatic rings of Dpq ligands from helical chains and binuclear cadmium complexes are from 3.600(2) to 3.863(2) Å, and the dihedral angels are in the range of 6.98–8.88°. The Cg–Cg distances between adjacent aromatic rings of 1,8-NDC2 from helical chains and Dpq ligands from binuclear motifs are from 3.700(3) to 3.751(2) Å and the dihedral angels are in the range of 4.00–2.40°. Each helical chain of 2D wave-like supramolecular network is stabilized by the intra-chains π–π interactions between Dpq and 1,8-NDC2 ligands [Cg–Cg 3.658(3)–3.683(3) Å, the dihedral angels 2.21–4.03°] and the intra-chain O–H$\cdots$O hydrogen bonds interactions between the coordinated water molecules and the carboxylate oxygen atoms [O7–H7A$\cdots$O6, 2.762(4) Å, 157°]. In addition, there are novel co-edge seven-member ring O–H$\cdots$O hydrogen bonds units associated with the coordinated water molecules and carboxylate oxygen atoms of 1D helical chains and lattice water molecules between the same single-stranded helical chains [O1W$\cdots$O5 2.846(5) Å, 153°; O2W$\cdots$O1W 2.807(4) Å, 165°; O8$\cdots$O2W 2.655(4) Å, 148°; O8$\cdots$O9 2.838(5) Å, 176°; O1W$\cdots$O9 2.950(4) Å, 157°; O2W$\cdots$O5 2.793(5) Å, 150°], which extend the 2D layer into 3D supramolecular network (Figs. 3, S1–S2 and Tables S2–S3).

There are some examples of metal–organic coordination compounds with left- and right-handed helical chains such as [Co(1,3-BDC)(Dpdq)H_2O]·(H_2O) (Dpdq = 2,3-di-2-pyridylquinoxaline) [28] and [Co_2(phen)$_2$(1,4-chdc)$_2$(H_2O)$_2$] (chdc = cyclohexanedicarboxylate, phen = 1,10-phenanthroline) [29]. However, most of these helices coordination polymers are alternately linked only via hydrogen bonds [30], π–π stacking interactions [12] or covalence bond [31–34] into high dimensional network. Interestingly, the left- and right-handed helical chains are linked via binuclear complexes in compound **1**. Another interesting structural feature is that compound **1** is a novel 0D+1D co-crystal of binuclear complexes and the left- and right-handed helical chains. Gao and coworkers have been obtained an interesting co-crystal of binuclear motifs [Zn_2(bta)$_2$(NH_3)$_2$] and 1D zigzag chains [Zn(bta)(NH_3)$_2$]$_n$ (bta = bis(5-tetrazolyl)amine) [35]. Mohanta et al. has been reported some novel 0D+0D co-crystals with heteropolynuclear or mixed valence state complexes [36–38]. They are all structurally different from that of **1**.

The X-ray structural analysis of **2** reveals that a 2D coordination polymer of (4,4) rectangular grid is constructed by binuclear cadmium units and 1,4-NDC linkers. Two Cd(II) centers in the unit have an inversion center as illustrated in Fig. 4. Each Cd(II) in the dinuclear motif is six-coordinate: two oxygen atoms from two carboxylate groups (bridging monodentate fashion) of different 1,4-NDC [Cd–O 2.309(3), 2.330(4) Å], one oxygen atom from carboxylate group (monodentate fashion) of another 1,4-NDC [Cd–O 2.234(4) Å] one oxygen atom [Cd–O5 2.359(4)] of coordination water molecule, and two nitrogen atoms from a chelating Dpq ligand [Cd–N 2.315(4), 2.338(4) Å]. In the coordination octahedron, the bond angles of the cadmium atom with nitrogen and oxygen vary from 71.31(15)° to 169.24(14)°, indicating the octahedron is slightly distorted.

In the 2D polymer skeleton (Fig. 5), two Cd(II) centers were linked by two O(3) atoms with μ_2-bridges fashion forming a bimetallic SBU [$Cd_2N_4O_6$], with a Cd⋯Cd separation of 3.712 Å. Adjacent bimetallic SBUs are extended into 2D grid (9.650 × 12.313 Å, based on the distances between the cores of SBUs) by 1,4-NDC adopted two kinds of coordination modes [bridging bis-monodentate 1,4-NDC1 (Scheme 1b left) and bi-monodentate 1,4-NDC2 (Scheme 1b right)], and the 2D grid are stabilized by intra-layer π–π stacking interactions between the aromatic rings of Dpq and 1,4-NDC1 ligands [Cg–Cg 3.663(3)–3.770(4) Å, and the dihedral angles 2.33°–7.97°] (Fig. S3) and intra-layer O–H⋯O hydrogen bonds interactions between the coordinated water molecules and the carboxylate oxygen atoms [O5–H5A⋯O2, 2.629(7) Å, 159°; O(5)–H(5B)⋯O(4), 2.814(9) Å, 152°]. The 2D networks are ultimately packed into a 3D supramolecular structure through inter-layer π–π stacking interactions between the pyrazine and coordinated pridine rings of Dpq ligands from different layers [Cg–Cg 3.577(3) Å, and the dihedral angles 4.62°] (Fig. 6). The distance between the binuclear cores of inter-layers is 12.812 Å.

Coordination polymers with (4,4) net based on binuclear SBUs have been prepared by many chemists [39,40]. Chen and our group also have obtained three rhombic grids [22,23]. However, compound **2** is a rectangular grid which is mainly attributed to the difference of coordination mode of 1,4-NDC pillars. On the other hand, 1,4-NDC2 ligand is disordered but 1,4-NDC1 is not, which may be attributed to the π–π stacking interactions between the aromatic rings of Dpq ligands and 1,4-NDC1.

Single-crystal X-ray analysis shows that compound **3** is a 3D coordination polymer with a cooperite PtS topology. Each cadmium atom is six-coordinated by four oxygen atoms of carboxyl groups from four different 2,6-NDC ligands (Cd–O bond distances are ranging from 2.204(2) to 2.357(2) Å), and two nitrogen atoms from a chelating Dpq ligand [Cd–N 2.402(3) Å] exhibiting a slightly distorted octahedronal geometry (the bond

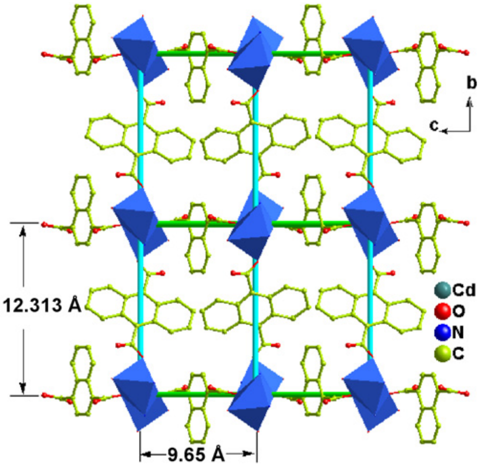
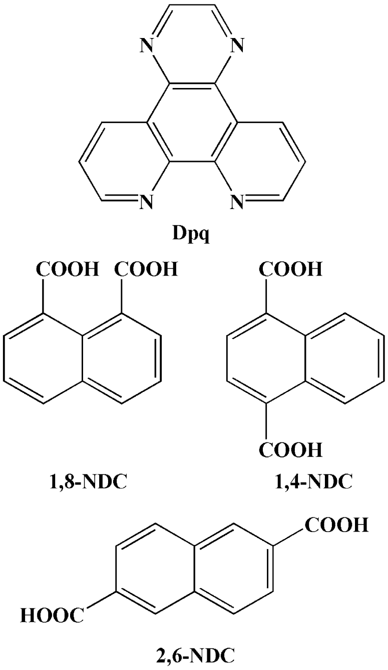


Fig. 5. The 2D coordinated network of **2** (Dpq ligands are omitted for clarity).



Scheme 1. Ligands used in the paper.

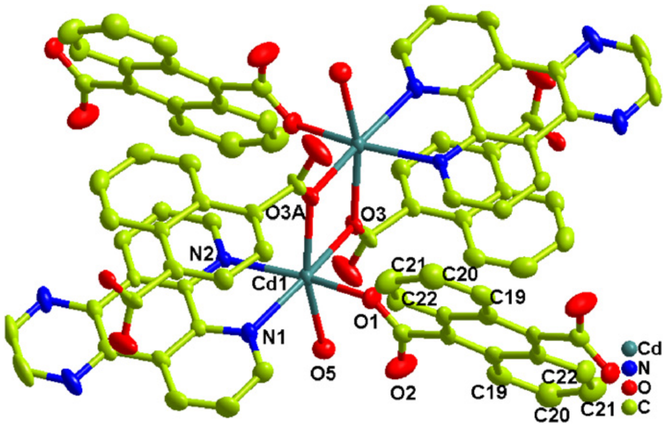


Fig. 4. Coordination environment of **2** with 30% probability thermal ellipsoids.

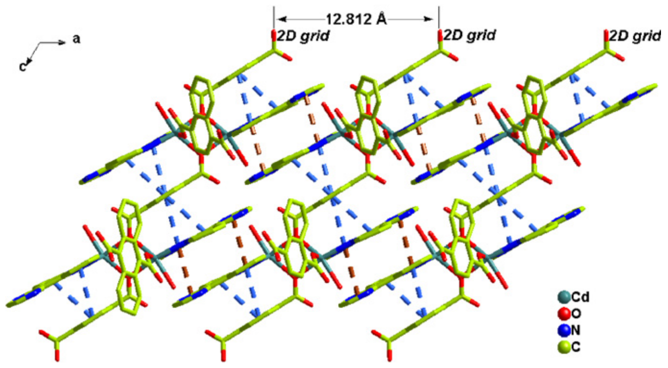


Fig. 6. The 3D supramolecular network of **2** through inter-molecular π–π interactions.

angles of the cadmium atom with nitrogen and oxygen vary from 69.10(12)° to 164.59(11)°) (Fig. 7). Two carboxyl groups of 2,6-NDC ligand adopt bridging bis-bidentate coordination modes (Scheme 1c). This bridge of the carboxyl pattern results in infinite Cd–O–C rods SBUs running along the [001] direction, with a Cd⋯Cd distance of 4.411 Å (Fig. 8c). The rods are linked by the 2,6-NDC arms that connect each rod to four neighboring rods in the directions of [110] and [1$\bar{1}$0], and extended into 3D structure (Fig. 8b) (Scheme 2).

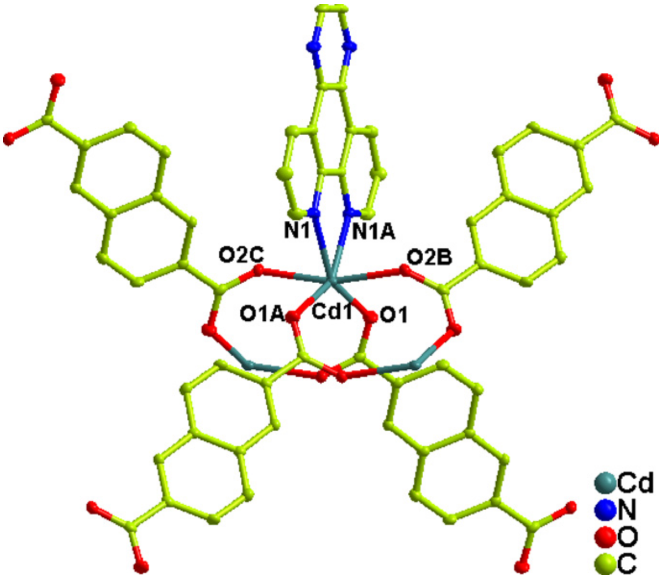


Fig. 7. Coordination environment of **3** with 30% probability thermal ellipsoids.

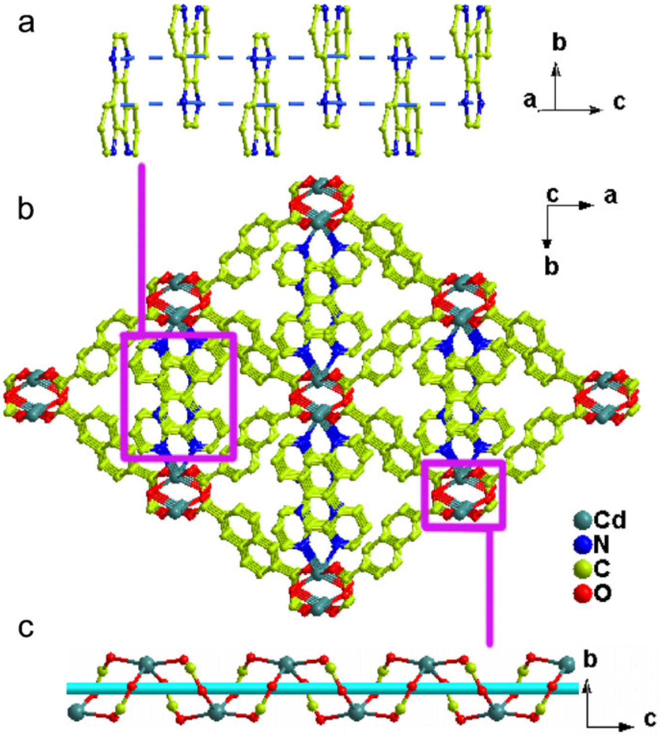
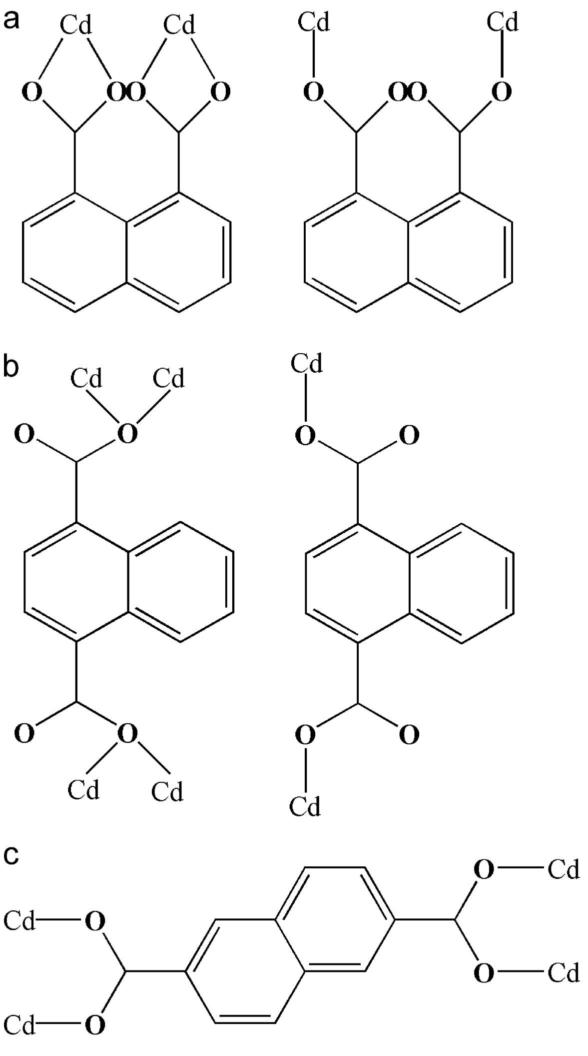


Fig. 8. Views of the three structural motifs in **3**: (a) the unusual 1D supramolecular Dpq arrays through π–π interactions; (b) view of the 3D network; and (c) infinite rod-like building block.

To best understand the framework topology, it is necessary to simplify the building blocks from which the 3D coordination polymer of **3** is built. Considering each six-coordinated Cd atom as a tetrahedral node, and every 2,6-NDC ligand as square planar node, the whole structure of **3** can be considered to be a cooperite PtS network (Fig. 9). Although there are some examples of coordination polymers with the noninterpenetrated [41–45], 2-fold or 3-fold interpenetrated PtS type frameworks [46–49], to the best of our knowledge, compound **3** is new 3D coordination polymer with distorted PtS network topology constructed from bpy-like chelating ligands and naphthalene-dicarboxylate ligands. Long ligands usually lead to large voids and may further result in interpenetration and entangle structures [50]. In addition, the unusual 1D supramolecular Dpq arrays extended in a parallel fashion at both sides of a Cd–O–C rod through π–π interactions between the pyrazine and pridine/phenyl rings of Dpq ligands from different rods (Cg–Cg 3.611 (2)–3.680(2) Å, the dihedral angles 1.28–1.74°) may prohibit the interpenetration of 3D framework by steric hindrance (Fig. 8a).

Compared with the title compounds, the effects of the organic-acid ligands with different length and angles on the coordination polymer structures have been clearly demonstrated. The carboxyl groups in a parallel fashion of 1,8-NDC adopt two coordination



Scheme 2. Coordination modes of the NDC ligands in **1–3**.

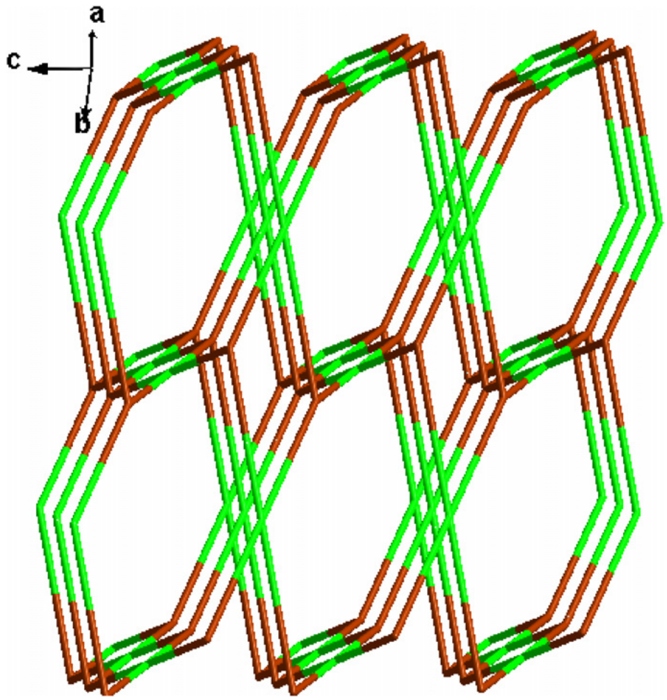


Fig. 9. PtS topology of **3** (every Cd atom as tetrahedral node in brown and every 2, 6-NDC as square planar node in green).

modes to form the binuclear units and the left- and right-handed helical chain in **1** simultaneously. It has been noted that employment of flexible or V-shaped *exo*-bidentate organic bridges can improve the helicity of the polymeric chains [12], and the phthalate-like ligands usually lead to form binuclear complex [51]. Therefore, 1,8-NDC may be an excellent ligand in construction of novel supramolecular structures with helical chains and binuclear complexes simultaneously. The linear 1,4-NDC also adopts two coordination modes to form a binuclear metal cluster, leading to formation of a 2D rectangular grid in **2**. Interestingly, the long and linear naphthalene-dicarboxylate ligand 2,6-NDC in **3** only adopts one coordination mode to form a distorted PtS-type network. On the other hand, the π–π aromatic stacking interactions of naphthalene-dicarboxylate ligands play some roles in constructing **1** and **2**. The Dpq and the 1,8-NDC2 ligands are extended in a parallel fashion at both sides of a helical chain (Fig. 2a), which further enhances the aromatic stacking interactions, and results in the formation of supramolecular structures **1**. The π–π aromatic stacking interactions between Dpq and 1,4-NDC2 stabilized the 1,4-NDC2 (Fig. S3), leading to the formation of supramolecular structures **2**. Therefore, an appropriate combination of the naphthalene-dicarboxylate and aromatic chelating ligands is a valuable approach in construction of coordination polymers.

3.2. *IR spectra*

The main features in the IR spectra of the title compounds concern the carboxylate groups and the ligand Dpq. The bands at about 780 and 738 cm^{-1} may be attributed to the $\nu_{\text{C–N}}$ stretching of the pyrazinyl ring or pyridyl ring [23]. No strong absorption peaks around 1700 cm^{-1} for carboxylate groups were observed, indicating that all carboxyl groups of organic moieties in **1**, **2**, and **3** are deprotonated [52]. For complex **1**, the strong broad bond at around 3377 cm^{-1} was assigned to the ν(O–H) vibrations of coordinated and lattice water molecules. The asymmetric and symmetric vibrations of carboxylate groups appeared at 1617, 1548, and 1388 cm^{-1}, respectively. The Δ values, which represents the separation between ν_{asym}(–COO) and ν_{sym}(–COO) suggest there are different coordination modes of the carboxylate groups. For complex **2**, the ν(O–H) vibrations of coordinating water molecules appeared at around 3406 cm^{-1}, carboxylate group bands appeared at 1602, 1477, and 1392 cm^{-1} for the asymmetric and symmetric vibrations, respectively. The Δ is 210 and 85 cm^{-1}, which is in agreement with the results of the crystal analysis. For complex **3**, its characteristic bands of the carboxylate groups are shown at 1627 cm^{-1} for asymmetric vibrations and at 1386 cm^{-1} for symmetric vibrations. The Δ value is 241 cm^{-1} indicates that the carboxylate groups adopt bridging bis-bidentate coordination modes [53,54].

3.3. *TG analyses*

The TG curve of **1** exhibits three weight loss stages in a range of 25–535 °C as shown in Fig. S4. The first weight loss of 6.12% around 25–143 °C corresponds to the release of the coordinated and lattice water (calcd 6.05%). The second and the third weight losses in a range of 250–515 °C were attributed to the decomposition of the framework to form CdO as a final product (observed 21.66, calcd 21.58%). For **2**, the weight loss occurring between 25 and 166 °C may suggest the loss of the coordinated water molecules (calcd 3.13, found 3.20%). The second and the third weight losses in 300–480 °C come from the decomposition of the framework and the remaining weight corresponds to CdO (observed 22.32, calcd 22.29%). In comparison with **1** and **2**, complex **3** is slightly more stable up to 400 °C, where the decomposition of the framework starts a rapid and significant weight loss of 77.02% in the temperature range of 400–520 °C, and the resulting residue is CdO (observed 23.12, calcd 22.98%). By comparison of the title compounds, the different decomposing temperature for the frameworks may be due to the difference of their structural dimensionality.

3.4. *Photoluminescence analyses*

The photoluminescent properties of the title compounds (Fig. 10) and NDC ligands (Fig. S5) in the solid state are investigated at room temperature. As shown in Fig. 10, compound **1** exhibits a blue/green photoluminescence with an emission maximum at ca. 461 nm upon excitation at 396 nm. Comparing with the emission of the free ligand 1,8-H_2NDC ($\lambda_{\text{ex}} = 385$ nm, $\lambda_{\text{em}} = 450$ nm) and Dpq ($\lambda_{\text{ex}} = 360$ nm, $\lambda_{\text{em}} = 436$ nm), red shift of

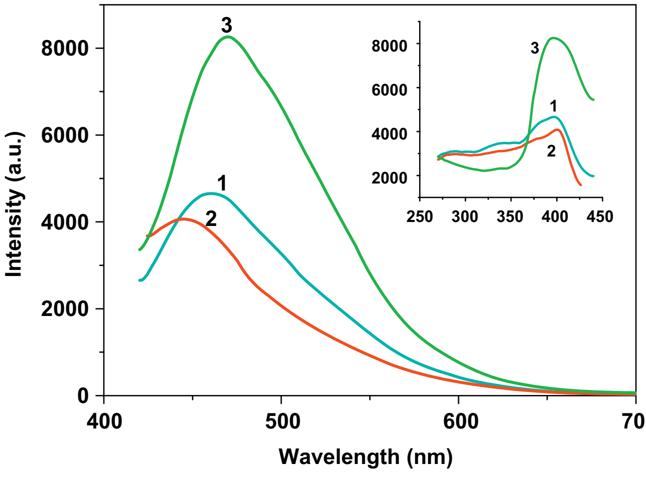


Fig. 10. Emission and excitation spectra (inset) of **1–3**.

ca. 11 nm and ca. 25 nm have been observed, respectively [23], upon the coordination of the 1,8-NDC and Dpq to Cd(II). The main emission band of **1** may be assigned to $\pi^* \rightarrow \pi$ transition of coordinated 1,8-NDC and Dpq ligands [17,55,56]. The red-shift emission peak probably is related to the intra-ligand fluorescent emission [57,58]. Interestingly, the main emission band of **2** with a peak at ca. 445 nm ($\lambda_{ex} = 400$ nm), is obviously different from that of **1**. Comparing with the emission of the free ligands, a blue shift of ca. 45 nm for 1,4-H_2NDC ($\lambda_{ex} = 344$ nm, $\lambda_{em} = 490$ nm) and a red shift of ca. 9 nm for Dpq have been observed, respectively. However, it would be also probably assigned to $\pi^* \rightarrow \pi$ transition of coordinated Dpq ligands [17,55,56]. Compound **3** shows an emission with a maximum at ca. 469 nm upon excitation at 395 nm (for 2,6-H_2NDC $\lambda_{ex} = 332$ nm, $\lambda_{em} = 461$ nm), but the fluorescent intensity of **3** is much higher than that of **1** and **2**. The emission peak position of **3** is similar to the emission bands of **1** and **2** that also can be attributed to intra-ligand fluorescent emission [17,55–58]. The different emission positions and intensities of **1–3** may be due to the significant difference of their topological structures because the fluorescence behavior is closely associated with the metal ions and the ligands coordinated around them [59,60]. Comparing with the excitation of ligands, the significant difference of the peak locations of the title complexes also can be related to the coordination of ligands to metal ions [61].

4. Conclusions

Three novel Cd(II) coordination compounds have been synthesized under hydrothermal conditions exhibiting a systematic variation in architecture by the employment of three structurally related naphthalene-dicarboxylate ligands, and representing examples of structural changes from the 0D+1D cocrystal to 3D coordination polymeric network. Comparing the structures of the title compounds, we found that the introduction of naphthalene-dicarboxylate ligands with different coordination modes, the length, and angle may have significant effects on the formation and dimension of the resulting structure, which may provide a promising pathway for crystal engineering.

Supporting information available

X-ray crystallographic information files (CIF) for **1–3**, selected bond distances and angles, TG spectra. These materials are available free of charge via the Internet at http://pubs.acs.org.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at 10.1016/j.jssc.2008.11.019.

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