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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)]$\cdot$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)(H$_2$O)$_2$][Cd(Dpq)(1,8-NDC)]$\cdot$2H$_2$O* (**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)(H$_2$O)]* (**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	$-8 \leqslant h \leqslant 11$ $-13 \leqslant k \leqslant 13$ $-55 \leqslant l \leqslant 57$	$-27 \leqslant h \leqslant 26$ $-14 \leqslant k \leqslant 15$ $-12 \leqslant l \leqslant 23$	$-25 \leqslant h \leqslant 23$ $-16 \leqslant k \leqslant 9$ $-9 \leqslant l \leqslant 8$
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