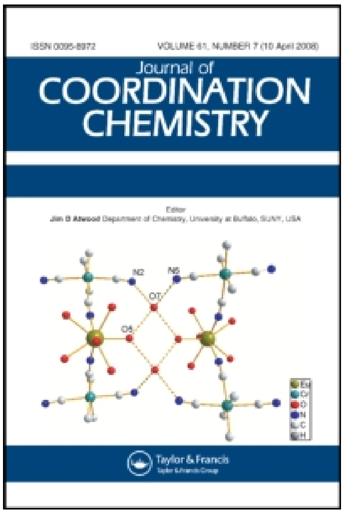

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Synthesis, structures and properties of two carboxylate-bridged coordination polymers with linear and ladder chain motifs

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Two cadmium(II) compounds, $[Cd(nip)(phen)_2]_n$ (**1**) and $[Cd_2(nip)_2(phen)_2]_n$ (**2**) [nip = 5-nitroisophthalate, phen = 1,10-phenanthroline], have been synthesized under hydro (or solvo) thermal conditions and characterized by single-crystal X-ray diffraction. Compound **1** exhibits a 1-D linear chain structure adopting the coordination mode in which one Cd is coordinated to two phen ligands. The formation of **1** was favored by selecting $Cd(phen)_2(NO_3)_2$ as metal source in ethanol-water. Compound **2** displays a 1-D ladder-like chain structure featuring di-cadmium units. Both **1** and **2** are further assembled into 3-D supramolecular frameworks through interchain hydrogen bonding.

Keywords: Carboxylic acid; Chain structures; Metal source; Solvent; Photoluminescence

1. Introduction

Metal-organic frameworks (MOFs) have drawn an ever-increasing level of attention because of structural diversity [1], useful properties and promising applications as functional materials [2]. Final architectures of MOFs depend on the building modules (organic ligands, metal ions, their counter ions and solvent molecules) and their compatibilities. Among MOFs with 1-D to 3-D architectures, the 1-D frameworks have the most basic structural motif which can be viewed as metal ion coordinated with two ligands, and metal ions and organic ligands alternate "infinitely" [3]. The linear [4a], zigzag [4b], helical [4c], double chains [4d], ladder [4e] and railroad [4f] motifs are typical for 1-D MOFs. Moreover, the 1-D motifs can be found in some 2-D or 3-D architectures [5], and some 1-D structures transform into 2-D layers as well as 3-D structures under appropriate experimental conditions [6]. Thus, the 1-D framework is important in understanding coordination polymers.

In this article, we report two new 1-D compounds of Cd^{2+}, $[Cd(nip)(phen)_2]_n$ (**1**) and $[Cd_2(nip)_2(phen)_2]_n$ (**2**) [nip = 5-nitroisophthalate, phen = 1,10-phenanthroline]. Recent studies have shown that 5-nitroisophthalate (nip or NIPH) is a versatile bridging ligand with two carboxylate groups and one nitro group [7–10]. The carboxylate groups in nip

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can bind and bridge metals in diverse coordination modes and the nitro group can serve as hydrogen bond acceptor in formation of polymeric networks. All these characteristics of nip are important in constructing MOFs. Employing 1,10-phenanthroline or 2,2′-bipyridine as auxiliary ligands, several compounds with nip have been reported for Co^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+} [7] and lanthanide ions Pr^{3+}, Ho^{3+}, Er^{3+} [8], but no compounds of Cd^{2+}. Utilizing the hydro (or solvo) thermal technique, we synthesized two new Cd^{2+} compounds, $[Cd(nip)(phen)_2]_n$ (**1**) and $[Cd_2(nip)_2(phen)_2]_n$ (**2**). Single-crystal X-ray diffraction analyses show the two coordination polymers are based on different 1-D chain motifs (linear chain in **1**; ladder chain in **2**), in which Cd centers chelated by phen are linked by nip bridges. **1** and **2** have also been characterized by powder X-ray diffraction, IR spectroscopy and elemental analysis. Compound **2** exhibits fluorescence at room temperature in the solid state.

2. Experimental

2.1. *Materials and measurements*

$Cd(phen)_2(NO_3)_2$ was synthesized by the literature method [11]. All other reagents were obtained from commercial sources and used without further purification.

Elemental analyses were performed with a Perkin-Elmer 2400 CHN elemental analyzer. Inductively coupled plasma (ICP) analyses were conducted on a Perkin-Elmer Optima 3300DV ICP spectrometer. Powder X-ray diffraction (XRD) data were obtained using a SHIMADZU XRD-6000 diffractometer with Cu-Kα radiation ($\lambda = 1.5418$ Å), with the step size and count time of 0.04° and 4s, respectively. FT-IR spectra were recorded on a Nicolet Impact 410 spectrometer between 400–4000 cm^{-1} using KBr pellets. Photoluminescence spectrum was collected on a Shimadzu RF-5301PC spectrophotometer.

2.2. *Synthesis*

2.2.1. $[Cd(nip)(phen)_2]_n$ (1). A mixture of 5-nitroisophthalic acid (0.053 g, 0.25 mmol), NaOH (0.020 g, 0.50 mmol) and $Cd(phen)_2(NO_3)_2$ (0.150 g, 0.25 mmol) in 5 mL of distilled water and 1 mL of absolute ethanol was stirred for 50 min and sealed in a Teflon-lined stainless steel autoclave (filled to ~30% volume capacity). The resulting mixture was heated at 120°C for 72 h under autogenous pressure. Colorless block crystals of **1** were isolated after the reaction system was cooled gradually, and washed with distilled water (yield = 79.4% based on Cd). Anal. Calcd for $C_{32}H_{19}CdN_5O_6$: C, 56.36; H, 2.81; Cd, 16.48; N, 10.27. Found: C, 56.13; H, 2.63; Cd, 16.13; N, 10.16%.

2.2.2. $[Cd_2(nip)_2(phen)_2]_n$ (2). A mixture of 5-nitroisophthalic acid (0.106 g, 0.50 mmol) and NaOH (0.010 g, 0.25 mmol) in 6 mL of distilled water was stirred for 45 min, then $Cd(NO_3)_2 \cdot 4H_2O$ (0.077 g, 0.25 mmol) and phen · H_2O (0.050 g, 0.25 mmol) was added to the mixture. The resulting mixture was sealed in a Teflon-lined stainless steel autoclave (filled to ~30% volume capacity) and heated at 120°C for 120 h under autogenous pressure. Colorless block crystals of **2** were isolated after the reaction

Table 1. Crystallographic data for **1** and **2**.

	1	**2**
Empirical formula	$C_{32}H_{19}CdN_5O_6$	$C_{40}H_{22}Cd_2N_6O_{12}$
Formula weight	681.92	1003.44
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2(1)/c$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	9.433(2)	10.206(3)
b	25.245(6)	14.423(5)
c	14.080(3)	14.435(5)
α	90	67.528(12)
β	97.096(9)	78.542(9)
γ	90	69.747(10)
Volume (Å^3)	3327.3(13)	1836.8(10)
Z	4	2
Calculated density (Mg m^{-3})	1.361	1.814
$F(000)$	1368	992
Data/restraints/parameters	5840/0/397	8252/0/541
Goodness-of-fit on F^2	1.068	1.054
Final R indices $[I > 2(I)]$[a]	$R_1 = 0.1176$, $wR_2 = 0.3353$	$R_1 = 0.0944$, $wR_2 = 0.2579$

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

system was cooled gradually and then washed with distilled water (yield = 86.6% based on Cd). Anal. Calcd for $C_{40}H_{22}Cd_2N_6O_{12}$: C, 47.88; H, 2.21; Cd, 22.40; N, 8.38. Found: C, 47.67; H, 2.16; Cd, 22.33; N, 8.25%.

2.3. *X-ray crystallography*

Data collection (single crystal with dimensions of $0.38 \times 0.22 \times 0.15\,mm^3$ for **1** and $0.29 \times 0.28 \times 0.21\,mm^3$ for **2**) were performed at 293(2) K on a Rigaku R-AXIS RAPID diffractometer equipped with Mo-Kα radiation ($\lambda = 0.71073$ Å) in the ω scanning mode. The structures were solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL-97 [12]. All non-hydrogen atoms were refined anisotropically. The H atoms were located based on the riding model. Crystallographic data, selected bond lengths and angles, and hydrogen bond parameters for **1** and **2** are presented in tables 1, 2 and 3, respectively.

3. Results and discussion

3.1. *Structure of $[Cd(nip)(phen)_2]_n$ (1)*

Single-crystal X-ray structural analysis showed that **1** is a 1-D polymeric coordination chain with one Cd(II), one bis-monodentate nip, and two chelating phen ligands in a crystallographic unit. Each Cd(II) is coordinated to four N atoms (N2, N3, N4, N5) from two phen, and two O atoms (O1, O3) from two different nip to give a distorted octahedral geometry (figure 1). The adjacent Cd(II) atoms are bridged by nip with a long pitch of 9.433 Å and exhibit a linear chain along a with Cd···Cd···Cd angles of 180° (figure 2), and the phenyl rings of nip are nearly parallel with each other.

Table 2. Selected bond lengths (Å), angles (°) and hydrogen bond parameters for **1**.

Cd(1)–O(1)	2.293(9)	Cd(1)–O(3)	2.296(8)
Cd(1)–N(2)	2.381(8)	Cd(1)–N(3)	2.435(10)
Cd(1)–N(4)	2.391(9)	Cd(1)–N(5)	2.345(9)
O(1)–Cd(1)–O(3)	93.9(3)	O(1)–Cd(1)–N(2)	100.0(3)
O(1)–Cd(1)–N(3)	87.0(3)	O(1)–Cd(1)–N(4)	167.2(4)
O(1)–Cd(1)–N(5)	96.8(3)	O(3)–Cd(1)–N(2)	82.0(3)
O(3)–Cd(1)–N(3)	151.4(3)	O(3)–Cd(1)–N(4)	94.7(3)
O(3)–Cd(1)–N(5)	122.0(3)	N(2)–Cd(1)–N(3)	69.8(3)
N(2)–Cd(1)–N(4)	90.7(3)	N(5)–Cd(1)–N(2)	149.7(3)
N(4)–Cd(1)–N(3)	90.0(3)	N(5)–Cd(1)–N(3)	86.2(3)
N(5)–Cd(1)–N(4)	70.6(3)		
D–H···A	d(H···A)	d(D···A)	∠(DHA)
C(28)–H(28)···O(5)#1	2.63	3.517(19)	159.5
C(22)–H(22)···O(3)#2	2.57	3.486(18)	169.0
C(9)–H(9)···O(3)	2.45	3.064(15)	123.2
C(30)–H(30)···O(2)	2.63	3.491(18)	154.0

Symmetry transformations used to generate equivalent atoms: #1: $-x$, $0.5+y$, $1.5-z$; #2: x, $1.5-y$, $0.5+z$.

Table 3. Selected bond lengths (Å), angles (°) and hydrogen bond parameters for **2**.

Cd(1)–O(1)	2.362(8)	Cd(1)–O(2)	2.421(8)
Cd(1)–O(4)	2.267(8)	Cd(1)–O(6)	2.314(8)
Cd(1)–N(3)	2.348(10)	Cd(1)–N(4)	2.331(9)
Cd(2)–O(3)	2.349(8)	Cd(2)–O(5)	2.288(8)
Cd(2)–O(7)	2.527(9)	Cd(2)–O(8)	2.272(8)
Cd(2)–N(5)	2.359(10)	Cd(2)–N(6)	2.300(9)
O(1)–Cd(1)–O(2)	55.0(3)	O(4)–Cd(1)–O(1)	83.4(3)
O(6)–Cd(1)–O(1)	98.7(3)	N(3)–Cd(1)–O(1)	103.9(3)
N(4)–Cd(1)–O(1)	140.9(3)	O(4)–Cd(1)–O(2)	138.1(3)
O(6)–Cd(1)–O(2)	94.5(3)	N(3)–Cd(1)–O(2)	98.8(4)
N(4)–Cd(1)–O(2)	86.6(3)	O(4)–Cd(1)–O(6)	96.1(3)
O(4)–Cd(1)–N(3)	86.1(4)	O(4)–Cd(1)–N(4)	133.5(3)
O(6)–Cd(1)–N(3)	157.5(3)	O(6)–Cd(1)–N(4)	90.7(3)
N(4)–Cd(1)–N(3)	72.1(4)	O(5)–Cd(2)–O(3)	98.5(3)
O(3)–Cd(2)–O(7)	92.8(3)	O(8)–Cd(2)–O(3)	96.4(3)
O(3)–Cd(2)–N(5)	149.0(3)	N(6)–Cd(2)–O(3)	85.1(3)
O(5)–Cd(2)–O(7)	138.5(3)	O(8)–Cd(2)–O(5)	84.9(3)
O(5)–Cd(2)–N(5)	84.6(4)	O(5)–Cd(2)–N(6)	134.9(3)
O(8)–Cd(2)–O(7)	54.1(3)	N(5)–Cd(2)–O(7)	105.2(3)
N(6)–Cd(2)–O(7)	85.6(3)	O(8)–Cd(2)–N(5)	114.6(3)
O(8)–Cd(2)–N(6)	139.7(3)	N(6)–Cd(2)–N(5)	71.6(3)
D–H···A	d(H···A)	d(D···A)	∠(DHA)
C(24)–H(24)···O(2)#1	2.48	3.299(17)	147.0
C(36)–H(36)···O(10)#2	2.35	2.879(17)	115.5
C(33)–H(33)···O(11)#3	2.67	3.399(18)	135.4
C(21)–H(21)···O(12)#4	2.80	3.57(2)	141.1

Symmetry transformations used to generate equivalent atoms: #1: $-1-x$, $1-y$, $1-z$; #2: $-1+x$, $1+y$, z; #3: x,$1+y$, z; #4: x,$1+y$, $-1+z$.

The nip bridges two Cd(II) in *bis*-monodentate fashion, so the Cd–O bonds have liberty to rotate to some extent and do not show distortion, similar to the linking mode of Cd(bqdc)(phen)$_2\cdot$2H$_2$O (bqdc = bi-phenyldicarboxylate) [14a]. The two phen groups chelate to Cd(II) with a dihedral angle of 79.8° in **1**.

Hydrogen-bonding interactions play an important role in constructing the supramolecular structure of **1**. Each chain connects to four adjacent chains by two

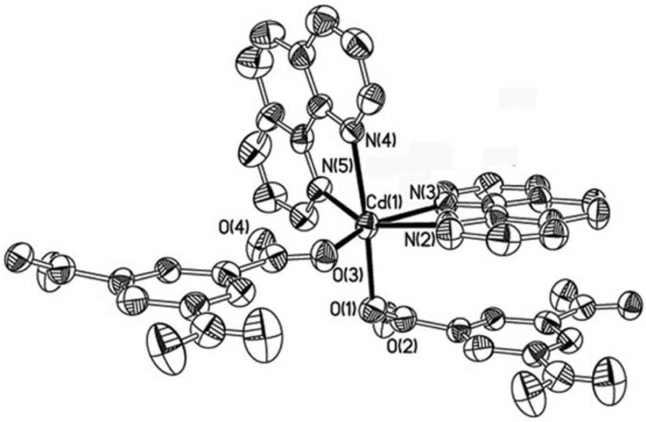

Figure 1. Coordination around Cd in **1** (ellipsoids at 50% probability), the H atoms are omitted for clarity.

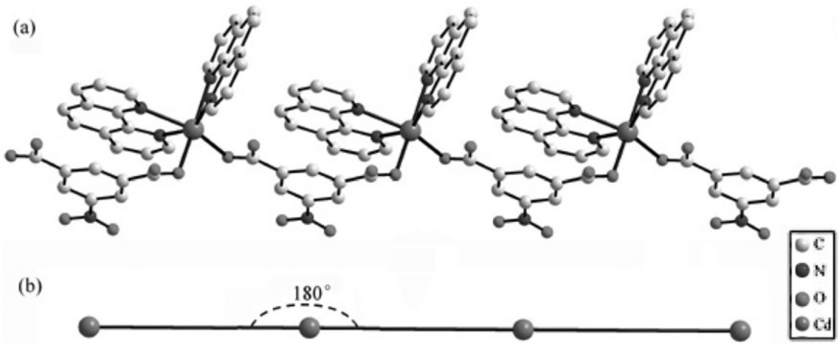

Figure 2. (a) The 1-D linear chain in **1**; (b) The Cd atoms in single chain with Cd ··· Cd ··· Cd angles of 180°.

kinds of C–H ··· O hydrogen bonds involving C–H groups (C22–H22, C28–H28) from phen between the coordinated carboxylate oxygen (O3) and uncoordinated nitro oxygen (O5), respectively. A 3-D supramolecular framework is constructed by these hydrogen bonds (figure 3). In addition, two hydrogen bonds (C9–H9 ··· O3, C30–H30 ··· O2) between C–H groups and O atoms of carboxylate groups exist within the chain (table 2).

The Cd in **1** is coordinated with two phen ligands, which is rare; commonly, to avoid severe steric hindrance resulting from the bulky phen group, compounds containing phen ligands possess either two capping phen in clusters [13] or one chelating phen in 1-D to 3-D structures [14]. There are distinct differences between **1** and $Cd(bpdc)(phen)_2 \cdot 2H_2O$ [14a] and $Cd(BDC)(phen)_2 \cdot (C_2H_5OH)(H_2O)$ (BDC = benzene-1,3-dicarboxylate) [14b] with two phen ligands coordinated to one metal center. For **1**, a 120° angular ligand (nip) bridges two metals to form a 1-D chain with Cd ··· Cd ··· Cd angles of 180°. For $Cd(bpdc)(phen)_2 \cdot 2H_2O$ [14a] and $Cd(BDC)(phen)_2 \cdot (C_2H_5OH)(H_2O)$ [14b], linear ligands (BDC and bpdc) construct a 1-D zigzag chain. Compound **1** exhibits its own structural characteristics compared to the related compounds containing the nip and chelating bipyridyl-like

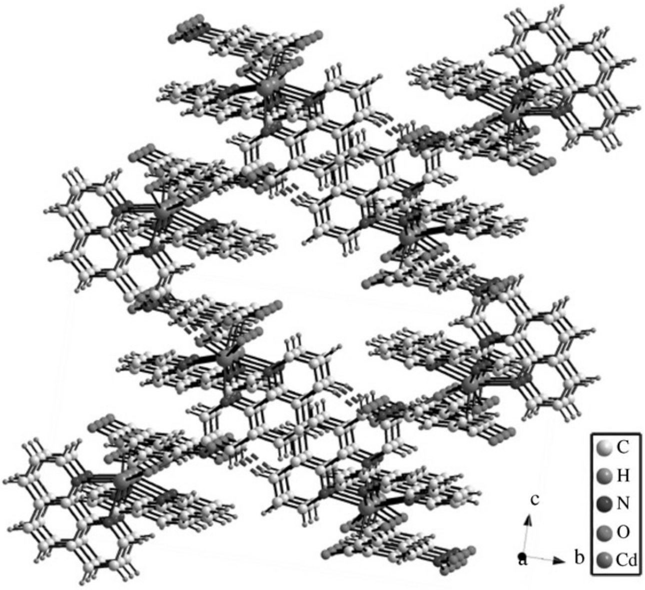

Figure 3. The 3D supramolecular structure connected by C–H $\cdots$ O hydrogen bonds in **1**.

ligands (phen or 2,2′-bpy). For instance, compounds [Cu(nip)(phen)]$_n$ [7c] and [Zn(nip)(phen)]$_n$ [7d] are composed of single helical chains and zigzag chains, respectively. While [$Ni_2(C_8H_3NO_6)_2(C_{12}H_8N_2)_2(H_2O)$] ($C_8H_3NO_6$ = nip, $C_{12}H_8N_2$ = phen) [7a] is a dinuclear cluster, lanthanide (Pr, Ho and Er) compounds usually exhibit 2-D structures or show the high coordination numbers of lanthanide ions compared to Cd in **1** [8]. Thus, the linear chain of **1** enriches the topology of compounds containing nip ligands.

3.2. *Structure of [Cd$_2$(nip)$_2$(phen)$_2$]$_n$ (2)*

X-ray crystallography reveals that **2** is a 1-D polymeric ladder. In the asymmetric unit of **2**, there are two Cd(II)'s, two bridging and chelating bis-bidentate nip ligands, and two chelating phen ligands. Cd1 adopts a distorted octahedral geometry by coordinating two N atoms (N3, N4) from one phen, and four O atoms (O1, O2, O4, O6) from three different nip's (figure 4). The coordination environment of Cd2 is the same as that of Cd1. Selected bond lengths and angles, listed in table 3, are in close agreement with bond parameters previously reported for cadmium coordination polymers containing carboxylate and phen [15]. The two crystallographically independent Cd(II) atoms are bridged by two carboxylate groups of nip to generate the 8-membered ring (Cd $\cdots$ Cd distance is 4.101 Å) and the 16-membered ring (Cd $\cdots$ Cd distance is 8.011 Å) alternately through a mutual C–O–Cd border, resulting in the formation of a 1-D ladder (figure 5). The crystallographically equivalent phen ligand is extended in a parallel fashion at a face-to-face distance of 9.98 Å or 9.45 Å, while two different phen ligands locate at one side of the chain with a dihedral angle of 17.6°. Since all the phen ligands are orientated in one direction of the chain, the

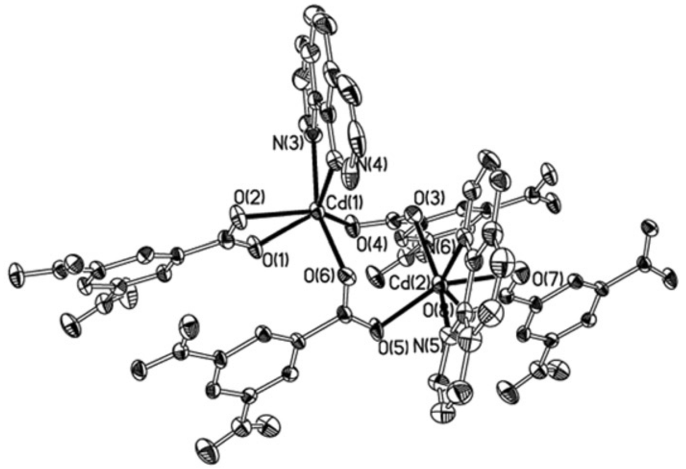

Figure 4. Coordination around Cd in **2** (ellipsoids at 50% probability), the H atoms are omitted for clarity.

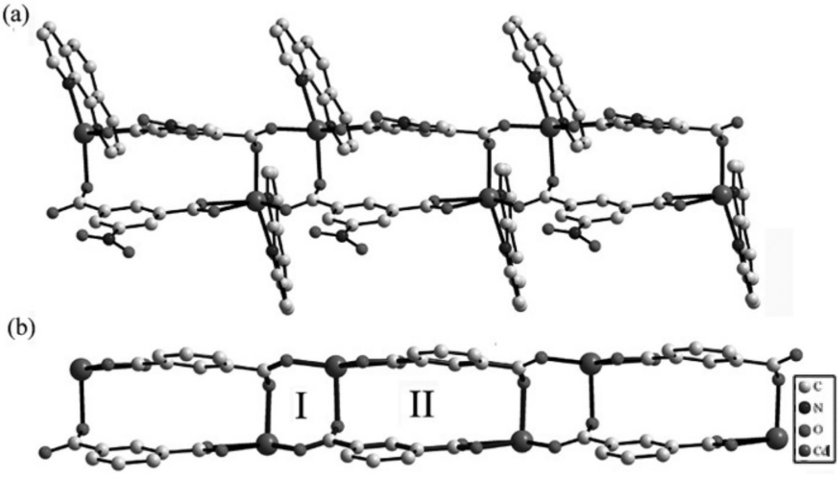

Figure 5. (a) The 1-D ladder in **2**; (b) A view of **2** showing how the 8-member and 16-member rings (marked with I and II) contribute to the construction of the infinite chain.

adjacent chains interact strongly through π–π stacking between the lateral phen ligands (phen: formed by C17 to C28, N3 and N4) at an offset face-to-face distance of ca 3.25 Å. The C–H groups (C24–H24, C36–H36, C33–H33 and C21–H21) of phen ligands form four C–H $\cdots$ O hydrogen bonds with coordinated carboxylate oxygen (O2) and uncoordinated nitro oxygens (O10, O11 and O12). Just as **1**, the non-coordinated nitro group in nip ligand plays an important role as hydrogen acceptor. As a result, a 3-D supramolecular framework is formed by hydrogen bonds among 1-D ladders in **2** (figure 6).

The 1-D chain structure composed of an 8-member ring and 16-member ring alternately can be observed in $[\{Co(dpe)(NO_2\text{-}BDC)\}\ 0.5(dpe)]_n \cdot nH_2O$ [10b], $[Co_2(nip)_2(phen)_2]_n$ [7b], $\{[Er(5\text{-}nip)_{1.5}(2,2'\text{-}bpy)](H_2O)\}_n$ [8b] and [Ln(5-nip)(phen)

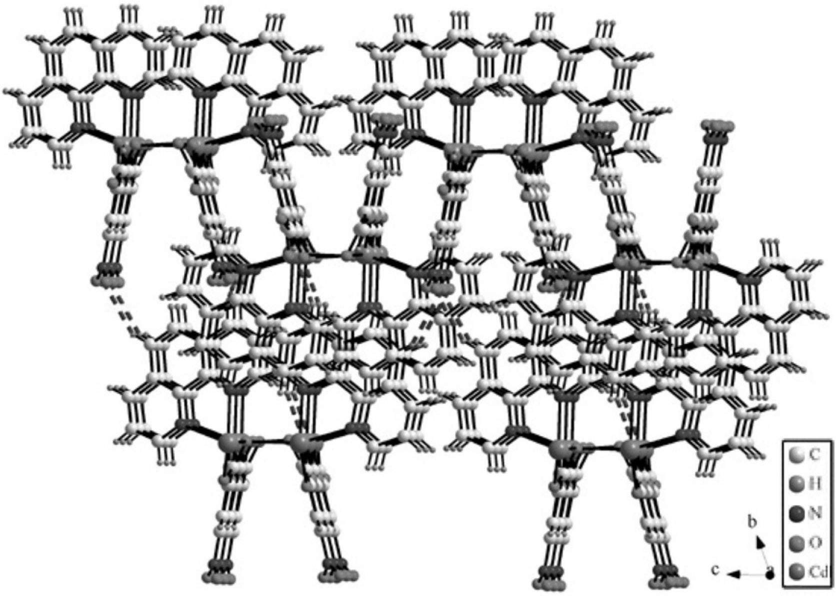

Figure 6. The 3-D supramolecular structure connected by C–H $\cdots$ O hydrogen bonds in **2**.

$(NO_3)(DMF)]_n$ (Ln = Pr or Ho) [8a]. Due to different metal ions, auxiliary ligands and solvent molecules, the differences between those compounds and **2** are obvious. For example, the 1-D ladder $[Co_2(NO_2–BDC)_2]$ of $[\{Co(dpe)(NO_2–BDC)\}\ 0.5(dpe)]_n \cdot nH_2O$ connect by bpe ligands to form a 2-D bilayer. Differences in M $\cdots$ M distances also exist between Cd–, Co– and Ln– (Ln = Pr or Ho) compounds.

3.3. *Synthesis*

Compound **1** has two phen ligands chelated to Cd. According to the literature [14], this is due to use of $Cd(phen)_2(NO_3)_2$ as metal source. In our system, we selected $Cd(NO_3)_2 \cdot 4H_2O$ and obtained the product (Sample a) with the same structure to **1** confirmed by powder XRD. We have tried $Cd(phen)_2(NO_3)_2$ and $Cd(NO_3)_2 \cdot 4H_2O$ in pure water (Samples b, c) or absolute ethanol (Samples d, e) system. The results showed that the water system formed product with the same structure as **1**, whereas the ethanol system formed $Cd(phen)_2(NO_3)_2$ (figure 7). We found that addition of ethanol favored formation of **1** and $Cd(phen)_2(NO_3)_2$ is suitable for the high quality crystals, although the simple metal salt $Cd(NO_3)_2 \cdot 4H_2O$ and pure water could also lead to formation of **1**. The different reaction conditions for **1**, including variations of the metal source and solvent, are summarized in table 4.

3.4. *Spectral characterization*

The powder X-ray diffraction patterns of compounds **1** and **2** with the pattern simulated on the basis of single crystal structure correspond well, indicating the as-synthesized samples **1** and **2** are pure. In **2**, the difference in reflection intensities

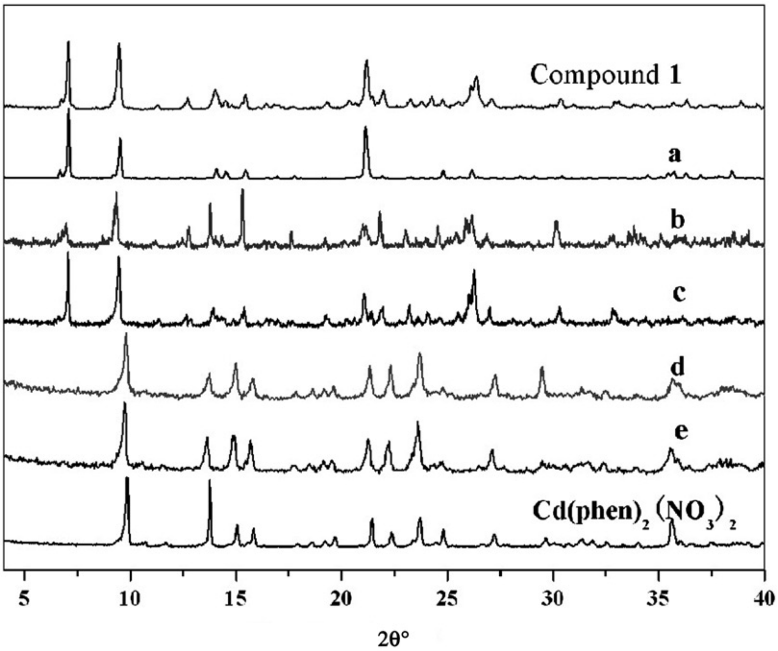

Figure 7. XRD patterns of **1a** to **e** and $Cd(phen)_2(NO_3)_2$.

between the simulated and experimental patterns was due to the variation in crystal orientation of the powder sample.

Spectra of **1** and **2** contain characteristic bands from 1620–1340 cm^{-1} for asymmetric and symmetric vibrations of the carboxylate groups. The large bands above 3050 cm^{-1} are due to the C–H stretching vibrations. The characteristic C–H out-of-plane bending vibrations of phen are observed at about 848 cm^{-1} and 727 cm^{-1} for **1**, 845 cm^{-1} and 729 cm^{-1} for **2**, respectively [16], lower wavenumber than free phen, 864 cm^{-1} and 739 cm^{-1}, proving bidentate coordination of phen [17]. Characteristic bands are alike in **1** and **2**, indicating that these compounds are similar.

3.5. *Fluorescent properties*

The emission spectrum of **2** (figure 8) at room temperature in the solid state has bands at 360, 420, 448 and 465 nm ($\lambda_{exc.} = 300$ nm). The emission bands for free phen · H_2O are at 365 and 388 nm ($\lambda_{exc.} = 310$ nm), attributed to the $\pi^* \rightarrow \pi$ transition [11]. The emission band for **2** at 360 nm is probably due to intraligand charge transfer of coordinated phen, similar to the emission of free phen · H_2O. Free H_2nip does not emit luminescence in the range 400–800 nm [10c]. The strong electron-withdrawing group (–NO_2) of H_2nip also results in fluorescence quenching, so the carboxylate ligand almost has no contribution to the fluorescent emission of **2**. Thus, the bands at 420, 448 and 465 nm of **2** may be assigned as intraligand fluorescent emission of coordinated phen ligands due to the planar configuration of excimeric phen molecules maintained by cadmium. The enhancement of the luminescence of **2** compared to that of the free

Table 4. Synthesis conditions varied with metal sources and solvents of **1**.

	Metal source	Ligand	Solvent (mL)		Form of final product	Phase confirmed by XRD
			C_2H_5OH	H_2O		
1	$Cd(phen)_2(NO_3)_2$	nip	1	5	Colorless block crystals	**1**
a	$Cd(NO_3)_2 \cdot 4H_2O$	Phen + nip	1	5	Colorless block crystals with flaw	**1**
b	$Cd(phen)_2(NO_3)_2$	nip	0	6	Minor crystals and white powder	**1**
c	$Cd(NO_3)_2 \cdot 4H_2O$	Phen + nip	0	6	Irregular block crystals	**1**
d	$Cd(phen)_2(NO_3)_2$	nip	6	0	Opaque rod crystals	$Cd(phen)_2(NO_3)_2$
e	$Cd(NO_3)_2 \cdot 4H_2O$	Phen + nip	6	0	Opaque rod crystals	$Cd(phen)_2(NO_3)_2$

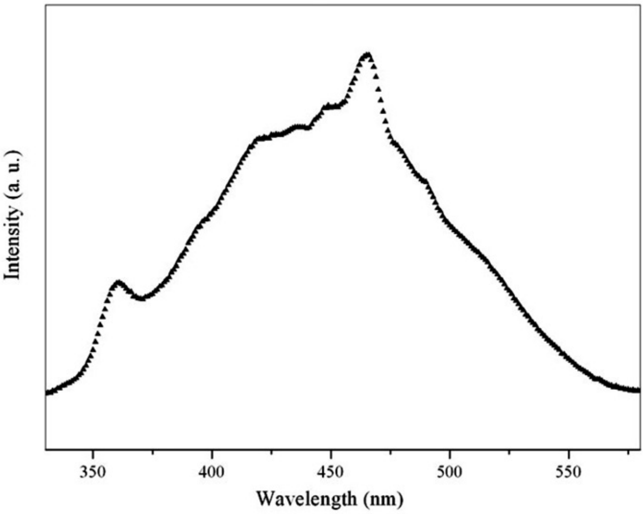

Figure 8. Solid-state fluorescent emission spectrum of **2** at room temperature.

phen ligand may be attributed to chelating phen to the metal ion and the strong π–π stacking between the phen ligands of adjacent chains, which effectively increases the rigidity of the ligand and reduces the loss of energy by radiationless decay of the intraligand emission excited state. The luminescence of **2** indicates that it may be good candidate for photoactive materials.

4. Conclusions

Two new cadmium(II) coordination polymers based on nip and phen have been hydro (or solvo) thermally synthesized and characterized. For **1**, the adjacent Cd(II) atoms are bridged by nip to form a linear chain. While for **2**, two crystallographically independent Cd(II) atoms are bridged by nip to construct a di-cadmium carboxylate moiety, resulting in a ladder with two different rings packed alternately. The nitro group as a hydrogen bond acceptor plays an important role in formation of **1** and **2**. The 3-D supramolecular frameworks are constructed through hydrogen bonding in both compounds.

Supplementary materials

Crystallographic data for **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 654626, 654627, respectively. Copies of this data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223–336–033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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