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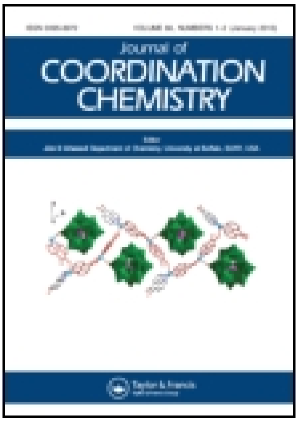

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Topological diversification of two new Cd(II) photoluminescent coordination polymers via auxiliary N-donor ligands

Guilan Xu [a] & Feng Guo [a]

[a] Key Laboratory of Coordination Chemistry and Functional Materials in Universities of Shandong , Dezhou University , Shandong , P.R. China

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Topological diversification of two new Cd(II) photoluminescent coordination polymers via auxiliary N-donor ligands

GUILAN XU and FENG GUO*

Key Laboratory of Coordination Chemistry and Functional Materials in Universities of Shandong, Dezhou University, Shandong, P.R. China

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Two new cadmium(II) coordination polymers, $[Cd_2(nda)_2(L_1)]_n$ (**1**) and $[Cd(nda)(L_2)_{0.5}]_n$ (**2**), were hydrothermally synthesized with 1,4-naphthalenedicarboxylic acid (H_2nda) and auxiliary N-donor coligands [$L_1 = $ 1,5-bis(2-methyl-imidazol-1-yl)pentane and $L_2 = $ 4,4′-bis(2-methyl-imidazol-1-ylmethyl) biphenyl]. Single-crystal X-ray diffraction analyses showed that the topological networks are different when the N-donor ligands are changed. Compound **1** showed a $(4^{16}.6^5)$ topology and **2** showed a twofold interpenetrating pcu topology.

Keywords: Coordination polymer; Crystal structure; Luminescence

1. Introduction

Construction of coordination polymers (CPs) based on metal ions and organic ligands has attracted attention for potential applications in gas storage, molecular magnetism, and luminescence and also for intriguing structural topologies [1–9]. To construct novel CPs, a number of N-donor bridging ligands have been employed to construct new CPs. N-donor ligands provide cooperative coordination with carboxylates to meet the coordination geometry requirements of metal ions in the assembly process [10–14]. Flexible bidentate ligands with imidazole nitrogen donors are useful organic building blocks for new CPs with versatile topologies [15–17]. Rigid aromatic dicarboxylates have been applied because of their diverse coordination modes [18–23], including connecting metal ions to form metal clusters as secondary building units (SBUs). The success of the strategy of using SBUs for construction of CPs has been shown by Yaghi, Kitagawa, and others [24, 25]. In SBUs, the paddle-wheel structural unit is very well known and used to construct many CPs. Less reported is the use of paddle-wheel structural units to construct Cd(II) CPs [26, 27].

In light of this, we have used two different imidazole ligands and a rigid carboxylate ligand together with the strategy of the paddle-wheel structural unit to synthesize $Cd_2(nda)_2(L_1)]_n$ (**1**) and $[Cd(nda)(L_2)_{0.5}]_n$ (**2**). The luminescent properties of **1** and **2** are also presented.

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*Corresponding author. Email: guofeng1510@yeah.net

2. Experimental

2.1. *General materials and methods*

All reagents and solvents were commercially available and used as received. Elemental analyses were carried out on a Carlo Erba 1106 full-automatic trace organic elemental analyzer. FT-IR spectra were recorded with a Bruker Equinox 55 FT-IR spectrometer with dry KBr pellets from 400–4000 cm^{-1}. Solid-state fluorescence spectra were recorded at room temperature on a Hitachi F-4600 equipped with a xenon lamp and a quartz carrier. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 diffractometer operated at 40 kV and 40 mA using Cu-Kα radiation ($\lambda = 0.15418$ nm).

2.2. *Synthesis*

2.2.1. Synthesis of $[Cd_2(nda)_2(L_1)]_n$ (1). **1** was hydrothermally synthesized by reaction of $Cd(OAc)_2 \cdot 4H_2O$ (0.308 g, 1 mM), H_2nda (0.216 g, 1 mM), L_1 (0.232 g, 1 mM), NaOH (0.08 g, 2 mM), and deionized water (18 mL) in a sealed 25 mL Teflon-lined stainless steel vessel at 160 °C for 96 h. After cooling to room temperature, colorless block-shaped crystals were obtained and washed several times with absolute alcohol (Yield: 41% based on Cd). Anal. Calcd for $C_{37}H_{32}Cd_2N_4O_8$: C, 50.19; N, 6.33; H, 3.64. Found: C, 50.15; N, 6.36; H, 3.63. IR/cm^{-1} (KBr): 1626 s, 1551 m, 1413 m, 1357 m, 1272 m, 1149 m, 1076 m, 999 m, 835 m, 793 m, 686 m, 560 m.

2.2.2. Synthesis of $[Cd(nda)(bib)_{0.5}]_n$ (2). The preparation of **2** was similar to that of **1** except that L_2 (0.342 g, 1 mM) was used in place of L_1. Colorless crystals of **2** were obtained in 46% yield based on Cd. Anal. Calcd for $C_{23}H_{17}CdN_2O_4$: C, 55.49; N, 5.63; H, 3.44. Found: C, 55.53; N,5.60; H, 3.46. IR/cm^{-1} (KBr): 1604 s, 1551 m, 1429 m, 1391 m, 1220 m, 1137 m, 1088 m, 934 m, 854 m, 727 m, 664 m.

2.3. *X-ray crystallography*

Single-crystal X-ray diffraction analyses of **1** and **2** were carried out on a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å) in ω-scan mode. Empirical absorption corrections were applied using the SADABS programs [28]. All the structures were solved by direct methods and refined by full-matrix least squares on F^2 using SHEXL 97 [29]. All non-hydrogen atoms were refined anisotropically. Hydrogens were located by geometric calculations, and their positions and thermal parameters were fixed during the structure refinement. The crystallographic data and refinement parameters for **1** and **2** are summarized in table 1. Selected bond and angle parameters are listed in table 2.

3. Results and discussion

3.1. *Structure description*

3.1.1. $[Cd_2(nda)_2(L_1)]_n$ (1). Single-crystal X-ray structural analysis of **1** revealed that the asymmetric unit consists of two crystallographically unique Cd(II) ions, each exhibiting identical coordination environments with four carboxylate oxygens from four nda^{2-} [Cd–O, ranging from 2.201 to 2.290 Å] and one nitrogen of L_1 [Cd(1)–N(1) = 2.213(3) Å and Cd(2)–N(4) = 2.269(3) Å], in tetragonal pyramidal geometries (figure 1(a)). The bond

Table 1. Crystallographic data and structure refinement parameters for **1** and **2**.

Empirical formula	$C_{37}H_{32}Cd_2N_4O_8$	$C_{23}H_{17}CdN_2O_4$
Formula weight	885.47	497.79
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
Unit cell dimensions	$a = 16.290(3)$ Å	$a = 17.3010(12)$ Å
	$b = 15.036(3)$ Å	$b = 14.396(2)$ Å
	$c = 16.412(3)$ Å	$c = 20.5570(15)$ Å
	$\beta = 119.2790(19)°$	$\beta = 110.393(3)°$
Volume (Å^3)	3506.3(10)	4799.1(9)
Z	4	8
Calculated density (mg m^{-3})	1.677	1.378
Independent reflections ($I > 2\sigma(I)$)	7976	5469
$F(000)$	1768	1992
θ range for data collection	1.43–27.48	1.94–27.47
Goodness of fit on F^2	1.034	1.090
R_1^{a}, wR_2^{b} [$I > 2\sigma$(I)]	$R_1 = 0.0341$	$R_1 = 0.0385$
	$wR_2 = 0.0806$	$wR_2 = 0.1128$
R_1^{a}, wR_2^{b} (all data)	$R_1 = 0.0435$	$R_1 = 0.0472$
	$wR_2 = 0.0864$	$wR_2 = 0.1201$
Largest diff. peak and hole (e Å^{-3})	1.303 and −0.819	1.067 and −0.756

$^{a}R = \Sigma(||F_0| - |F_C||)/\Sigma|F_0|$.
$^{b}wR = [\Sigma w(|F_0|^2 - |F_C|^2)^2/\Sigma w(F_0{}^2)]^{1/2}$.

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

Compound **1**			
Cd(1)–O(8)	2.164(3)	Cd(2)–O(1)	2.235(3)
Cd(1)–N(1)	2.214(3)	Cd(2)–O(5)	2.257(2)
Cd(1)–O(6)^{i}	2.242(2)	Cd(2)–N(4)^{iii}	2.270(3)
Cd(1)–O(4)^{ii}	2.248(3)	Cd(2)–O(3)^{ii}	2.200(3)
Cd(1)–O(2)	2.290(3)	Cd(2)–O(7)	2.219(3)
O(8)–Cd(1)–N(1)	117.62(18)	O(4)^{ii}–Cd(1)–O(2)	84.51(15)
O(8)–Cd(1)–O(6)^{i}	90.54(17)	O(3)^{ii}–Cd(2)–O(7)	142.63(16)
N(1)–Cd(1)–O(6)^{i}	121.67(11)	O(3)^{ii}–Cd(2)–O(1)	94.64(15)
O(8)–Cd(1)–O(4)^{ii}	137.43(16)	O(7)–Cd(2)–O(1)	82.76(14)
N(1)–Cd(1)–O(4)^{ii}	99.86(12)	O(3)^{ii}–Cd(2)–O(5)	91.84(11)
O(6)^{i}–Cd(1)–O(4)^{ii}	85.90(11)	O(7)–Cd(2)–O(5)	125.08(15)
O(1)–Cd(2)–O(5)	87.45(11)	O(7)–Cd(2)–N(4)^{iii}	84.45(14)
O(3)^{ii}–Cd(2)–N(4)^{iii}	97.19(13)	O(1)–Cd(2)–N(4)^{iii}	166.92(14)
Compound **2**			
Cd(1)–N(1)	2.199(3)	Cd(1)–O(2)^{i}	2.225(3)
Cd(1)–O(3)^{ii}	2.217(3)	Cd(1)–O(1)	2.214(3)
Cd(1)–O(4)^{iii}	2.239(3)		
N(1)–Cd(1)–Cd(1)^{i}	170.05(10)	O(3)^{ii}–Cd(1)–O(4)^{iii}	90.97(14)
N(1)–Cd(1)–O(3)^{ii}	108.26(13)	O(3)^{ii}–Cd(1)–O(2)^{i}	150.36(15)
N(1)–Cd(1)–O(4)^{iii}	93.90(13)	O(2)^{i}–Cd(1)–O(4)^{iii}	83.57(16)
N(1)–Cd(1)–O(2)^{i}	101.19(14)	O(1)–Cd(1)–O(3)^{ii}	88.54(15)
N(1)–Cd(1)–O(1)	105.08(14)	O(1)–Cd(1)–O(4)^{iii}	160.16(15)
O(3)^{ii}–Cd(1)–Cd(1)^{i}	77.74(9)	O(1)–Cd(1)–O(2)^{i}	87.08(16)

Symmetry codes for **1**: (i) $x, -y+3/2, z-1/2$; (ii) $-x+2, y+1/2, -z+3/2$; (iii) $x-1, y, z$; for **2**: (i) $-x, y, -z+3/2$; (ii) $-x+1/2, y+1/2, -z+3/2$; (iii) $x-1/2, y+1/2, z$.

distances are in the expected range for such complexes [30, 31]. The two unique Cd ions are bridged by three *syn–syn* carboxylates to form a paddle-wheel $[Cd_2(CO_2)_3]$ motif with Cd···Cd distance of 3.639 Å. The $[Cd_2(CO_2)_3]$ motifs are further connected to five

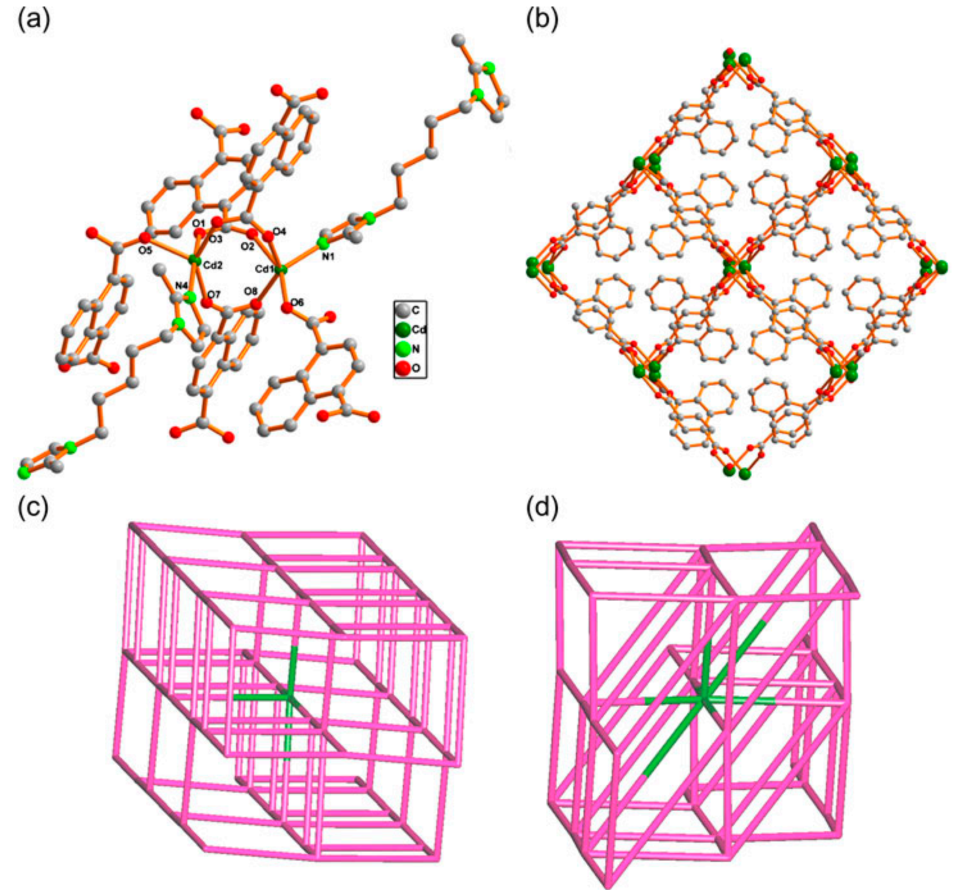

Figure 1. (a) The coordination environment of Cd(II) in **1**, (b) the 3-D network formed by nda^{2-}, (c) the nov topology for **1** formed by nda^{2-}, and (d) the seven-connected topological network for **1**.

equivalent neighbors through nda^{2-} to form a five-connected nov ($4^4.6^6$) topology (figure 1(b) and 1(c)). The size of the large rhombic windows is 9.874 × 11.806 Å. The five-connected nodes are further cross-linked by L_1 leading to a seven-connected net with ($4^{16}.6^5$) topology (figure 1(d)).

3.1.2. $[Cd(nda)(L_2)_{0.5}]_n$ (2). In the asymmetric unit of **2**, there is one crystallographically independent Cd(II), one nda^{2-}, and one L_2. Each Cd(II) is five-coordinate with four carboxylate oxygens from four nda^{2-} (Cd–O bond lengths varying from 2.217 (3) to 2.239 Å) and one nitrogen from one L_2 (Cd(1)–N(1) = 2.199(3) Å) in a tetragonal pyramidal geometry (figure 2(a)). Two crystallographically equivalent Cd are bridged by two pairs of nda^{2-} carboxylates to form a dinuclear cadmium unit with a Cd···Cd distance of **3.173** Å [*au: should this number be 3.713* Å]. The $Cd_2(CO_2)_4$ moieties are linked by four *syn–syn* nda^{2-} to four adjacent $Cd_2(CO_2)_4$ clusters, thus generating a 2-D (4,4) layer (figure 2(b)). The fifth Cd coordination site, which is not involved in $Cd_2(CO_2)_4$ clusters,

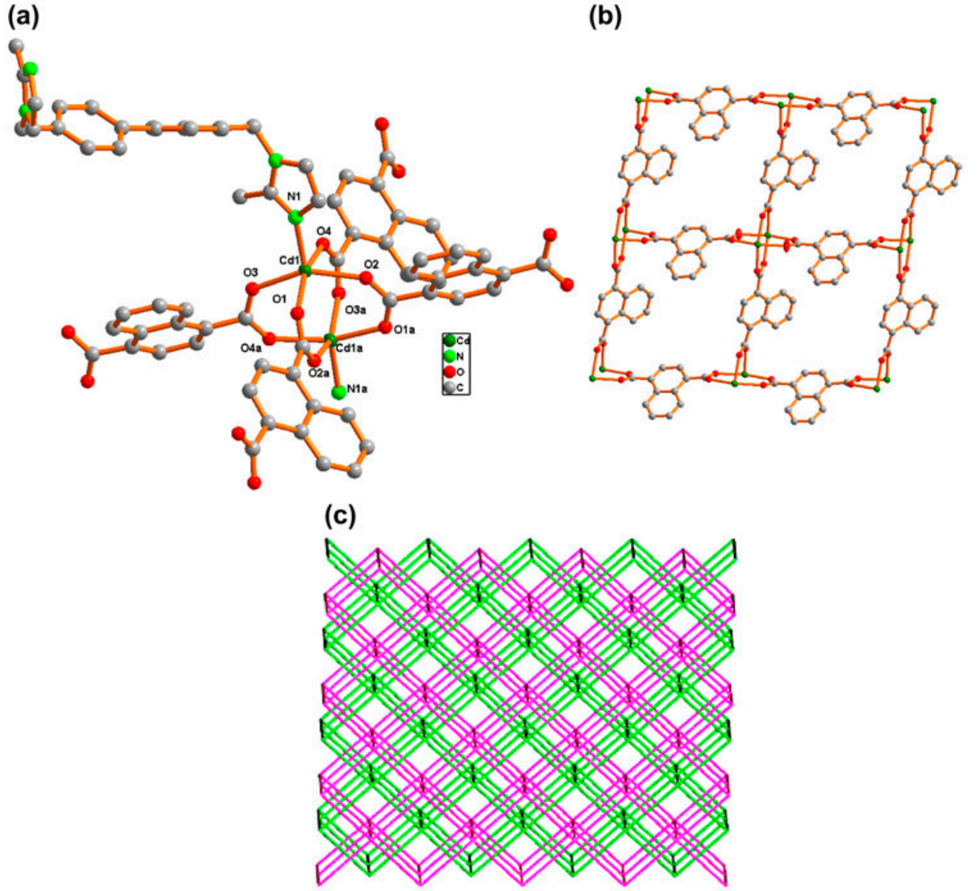

Figure 2. (a) The coordination environment of Cd(II) in **2**, (b) the 2-D network formed by nda^{2-}, and (c) the two fold interpenetrating pcu topology for **2**.

is occupied by N of L_2, which further connects adjacent 2-D layers into a 3-D network. From a topological point of view, if the $[Cd_2(CO_2)_4]$ unit can be treated as a six-connected node, and nda^{2-} and L_2 as linkers, the 3-D structure can be classified as a pcu net (α-Po topology), with large rhombic windows (11.254 × 11.254 Å). Due to the large void space in the 3-D framework, the potential voids in **2** are filled via mutual interpenetration of two identical 3-D nets, which directly leads to a twofold interpenetrated network (figure 2(c)).

1 and **2** adopt different topological nets, which can be the result of different lengths of N-donor ligands. In **1** and **2**, the Cd–Cd distance is comparable with those observed in other dinuclear Cd(II) complexes [30–32], in particular $[Cd(Dpq)(1,4\text{-NDC})(H_2O)]$ (3.712 Å) and $[Cd_2(NDC)_2(L)_2(H_2O)]\cdot 0.5DMF$ (3.640 Å) (Dpq = [3,2-d:2′,3′-*f*]quinoxaline, 1,4-NDC = 1,4-naphthalene-dicarboxylic acid, and L = pyrazino[2,3-*f*][1,10]phenanthroline) [33, 34]. In the latter two complexes, the Cd(II) ions have a coordination number six, different from **1** and **2**.

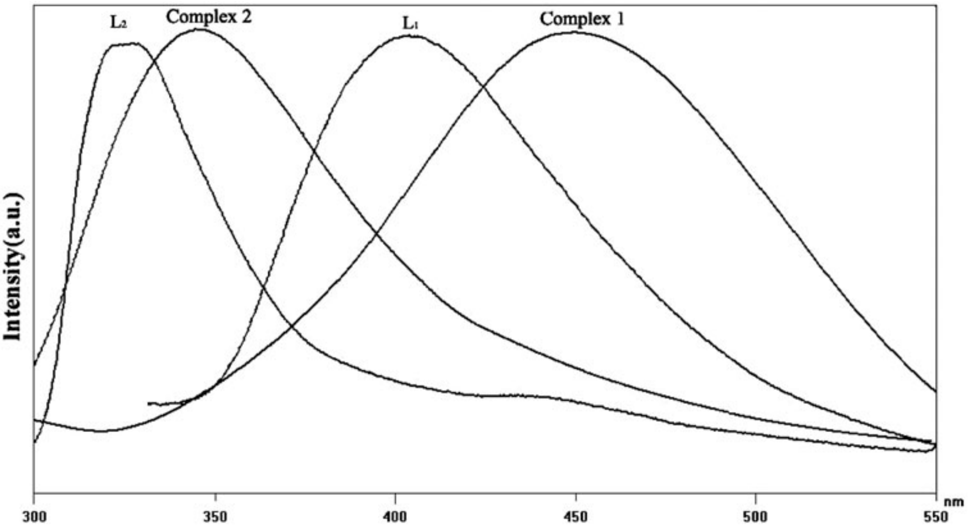

Figure 3. Fluorescent emission spectra for L_1, L_2, **1**, and **2** in the solid state at room temperature.

3.2. *XRPD and luminescent properties*

The simulated and experimental PXRD patterns of **1** and **2** are shown in figure S1. The peak positions are in agreement with each other, indicating the phase purity of products.

The photoluminescent properties of **1** and **2** were investigated at room temperature. As shown in figure 3, **1** and **2** have an emission maximum at 346 nm ($\lambda_{ex} = 304$ nm) and 451 nm ($\lambda_{ex} = 376$ nm), respectively. The emission maxima for 1,4-nda, L_1, and L_2 are at 490 nm ($\lambda_{ex} = 344$ nm) [33], 403 ($\lambda_{ex} = 322$ nm), and 332 nm ($\lambda_{ex} = 284$ nm), respectively. The emissions of **1** and **2** are tentatively assigned to an intraligand transition due to their similarity to the emission spectra of ligands. Cd(II) is difficult to oxidize or to reduce [35, 36].

4. Conclusions

We have described two new Cd(II) CPs based on the rigid dicarboxylate nda^{2-} and two different N-donors. Complexes **1** and **2** display different topological nets due to different N-donor ligands. Both **1** and **2** contain dinuclear Cd(II) units and nda^{2-} connects these dinuclear Cd(II) units to form a five-connected 3-D framework for **1** and a four-connected 2-D framework for **2**. L_1 and L_2 join these five-connected nodes and four-connected nodes to form a seven-connected 3-D framework for **1** and six-connected pcu net for **2**. Both **1** and **2** exhibit emission in the solid state at room temperature.

Supplementary materials

Experimental and simulated PXRD patterns for **1** and **2**. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC reference numbers 891574 and 891575. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk or the Cambridge Crystallographic Data Center, 12 Union

Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk).

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