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Syntheses, structures and luminescent properties of three cadmium coordination polymers derived from (4-carboxymethoxy-phenyl)-acetate

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ABSTRACT

Three new cadmium(II) coordination polymers $\{[Cd(bipy)(cpa)(H_2O)]\cdot 2H_2O\}_n$ (**1**), $\{[Cd(phen)(cpa)]\cdot 3H_2O\}_n$ (**2**) and $[Cd(cpa)]_n$ (**3**) (bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline, H_2cpa = (4-carboxymethoxy-phenyl)-acetic acid) were synthesized and characterized. The cpa ligands exhibit the versatile coordination modes and play an important role in the construction of their structures. The structures of **1**, **2** and **3** are comprised of one-dimensional chains, infinite molecular ladders and a (4,4)-connected (each Cd(II) links four cpa and each cpa connects four Cd(II)) three-dimensional network, respectively. **1**, **2** and **3** reveal the blue emission maximum at 414, 420 and 458 nm, respectively, in the solid state at room temperature.

1. Introduction

The design and synthesis of metal–organic frameworks have been intensely studied for their potential applications as functional materials for gas storage, separation, microelectronics, nonlinear optics and catalysis, as well as their intriguing variety of topologies [1–7]. Design effective ligands and proper choice of metal centers are the keys to design and construction of novel metal–organic frameworks.

Symmetric organic aromatic polycarboxylate ligands, such as 1,2-benzenedicarboxylate [8–10], 1,3-benzenedicarboxylate [10–12], 1,4-benzenedicarboxylate [10–14], 1,3,5-benzenetricarboxylate [14–16], and 1,2,4,5-benzenetetracarboxylate [9,14,17,18], are good building blocks for the construction of coordination polymers and multidimensional supramolecular networks. However the coordination polymers assembled from asymmetric carboxylate ligands have been less exploited. (4-Carboxymethoxy-phenyl)-acetic acid (H_2cpa) possesses two flexible asymmetric carboxylate groups, one acetate and one oxyacetate, which makes it flexible and can construct versatile coordination polymers with novel structures (Scheme 1). On the other hand, the d^{10} metal coordination polymers have been found to exhibit interesting photoluminescent properties [19–24]. In order to synthesis novel topological frameworks and potential luminescent materials, in the present work, we have synthesized three new cadmium(II) coordination polymers $\{[Cd(bipy)(cpa)(H_2O)]\cdot 2H_2O\}_n$ (**1**), $\{[Cd(phen)(cpa)]\cdot 3H_2O\}_n$ (**2**) and $[Cd(cpa)]_n$ (**3**) (bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline, H_2cpa = (4-carboxymethoxy-phenyl)-acetic acid). Herein we report their syntheses, crystal structures and luminescent properties.

2. Experimental section

2.1. Materials and general methods

All reagents were of analytical grade and used without further purification. (4-Carboxymethoxy-phenyl)-acetic acid (H_2cpa) was synthesized according to literature method [25]. Elemental analyses for C, H and N were performed on a Perkin–Elmer 240C analyser. IR spectra were obtained for KBr pellets on a Nicolet 170SX FT-IR spectrophotometer in the 4000–400 cm^{-1} region. The luminescence measurements were carried out in the solid state at room temperature and the spectra were collected with a PerkinElmer LS50B spectro-fluorimeter.

2.2. Preparation of the complexes

2.2.1. Synthesis of $\{[Cd(bipy)(cpa)(H_2O)]\cdot 2H_2O\}_n$ (1)

A solution of H_2cpa (0.042 g, 0.20 mmol) in 20 mL of H_2O was adjusted to pH 6 with NEt_3. Then, the solution of bipy (0.031 g, 0.20 mmol) and $Cd(NO_3)_2\cdot 4H_2O$ (0.062 g, 0.20 mmol) in 5 mL of EtOH was added. The mixture was stirred for 10 min and filtered. The filtrate was stood on the desk at room temperature. The

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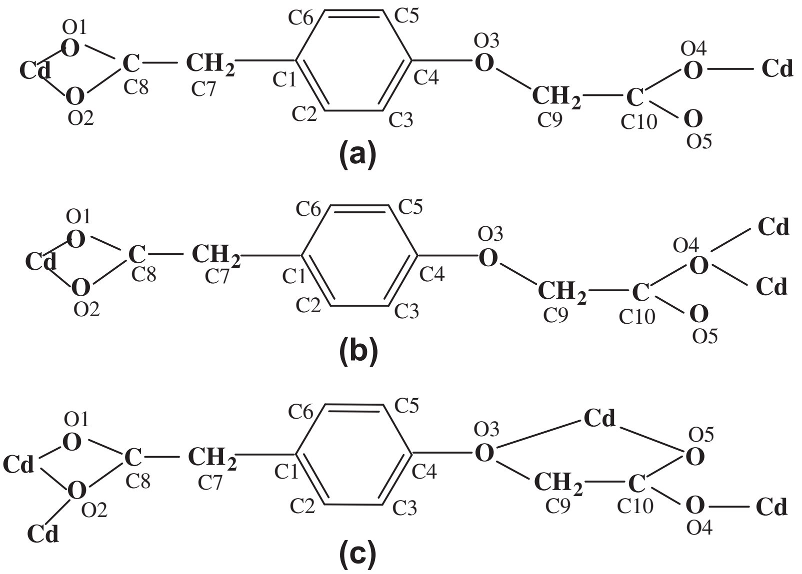

Scheme 1. Three coordination modes of H_2cpa ligand.

colorless single crystals of **1** were obtained after 1 week in 72% yield (0.076 g). Anal. Calc. for $C_{20}H_{22}CdN_2O_8$ (**1**): C, 45.26; H, 4.18; N, 5.28. Found: C, 45.18; H, 4.13; N, 5.21%. IR data (cm^{-1}): 3445s, 1609vs, 1566vs, 1474w, 1439m, 1393s, 1335w, 1246m, 1169w, 1157w, 1061m, 1015w, 806w, 772m, 737w.

2.2.2. {[Cd(phen)(cpa)]·$3H_2O$}$_n$ (**2**)

A solution of H_2cpa (0.021 g, 0.10 mmol) in 15 mL of H_2O was adjusted to pH 6 with NEt_3. Then, the solution of phen (0.018 g, 0.10 mmol) and $Cd(NO_3)_2 \cdot 4H_2O$ (0.031 g, 0.10 mmol) in 5 mL of EtOH was added with stirring. The mixture was added to a 30 mL Teflon-lined stainless autoclave, and was sealed and heated to 110 °C for 24 h and then cooled to room temperature. Yellow block-shaped crystals **2** were collected in 78% yield (0.043 g). Anal. Calc. for $C_{22}H_{22}CdN_2O_8$ (**2**): C, 47.63; H, 4.00; N, 5.05. Found: C, 47.51; H, 3.93; N, 4.99%. IR data (cm^{-1}): 3429s, 1609vs, 1566vs, 1512s, 1423s, 1393m, 1335w, 1242m, 1146w, 1103w, 1061m, 860m, 806w, 783w, 725m.

2.2.3. [Cd(cpa)]$_n$ (**3**)

A solution of H_2cpa (0.042 g, 0.20 mmol) in 10 mL of H_2O was adjusted to pH 7 with NEt_3. Then $Cd(NO_3)_2 \cdot 4H_2O$ (0.062 g, 0.20 mmol) was added with stirring. The mixture was added to a 20 mL Teflon-lined stainless autoclave, and was sealed and heated to 110 °C for 48 h and then cooled to room temperature. Colorless block-shaped crystals **3** were collected in 67% yield (0.043 g). Anal. Calc. for $C_{10}H_8CdO_5$ (**3**): C, 37.47; H, 2.52. Found: C, 37.42; H, 2.47%. IR data (cm^{-1}): 3441w, 1588s, 1509m, 1454m, 1401s, 1338w, 1298m, 1220m, 1184w, 1156w, 1115w, 1053m, 958w, 853w, 820m, 766w, 718w, 651m, 606w, 544m.

2.3. Single-crystal x-ray crystallography

Suitable single crystals of compounds **1**, **2** and **3** were carefully selected under an optical microscope and glued to thin glass fibers. The diffraction data were collected on a Rigaku Mercury CCD diffractometer with graphite monochromated Mo Kα radiation

Table 1
Crystallographic data for **1**, **2** and **3**.

	1	**2**	**3**
Formula	$C_{20}H_{22}CdN_2O_8$	$C_{22}H_{22}CdN_2O_8$	$C_{10}H_8CdO_5$
Fw	530.80	554.82	320.56
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
Temp (K)	293(2)	293(2)	293(2)
a (Å)	6.9411(10)	8.941(3)	10.3920(13)
b (Å)	13.536(2)	11.371(4)	7.1079(8)
c (Å)	22.360(4)	12.541(5)	12.9953(15)
α (°)	90	109.884(7)	90
β (°)	96.869(3)	110.124(7)	102.764(3)
γ (°)	90	95.224(4)	90
V (Å^3)	2085.7(5)	1094.1(7)	936.18(19)
Z	4	2	4
ρ_{calc} (g/cm^3)	1.690	1.684	2.274
μ (mm^{-1})	1.098	1.050	2.334
F(0 0 0)	1072	560	624
Reflections collected	16,876	10,823	8378
Unique reflections	3741 [*R*(int) = 0.0259]	3996 [*R*(int) = 0.0803]	1713 [*R*(int) = 0.0472]
Parameters	293	299	146
Goodness of fit	1.077	1.088	1.015
R_1 [$I > 2\sigma(I)$]	0.0309	0.0835	0.0222
wR_2 (all data)	0.0803	0.2121	0.0558

Table 2
Selected bond lengths (Å) and angles (°) for **1**, **2** and **3**.

1			
Cd(1)–O(1)	2.426(2)	Cd(1)–O(2)	2.369(2)
Cd(1)–O(4A)	2.211(2)	Cd(1)–O(6)	2.338(2)
Cd(1)–N(1)	2.344(2)	Cd(1)–N(2)	2.330(2)
O(1)–Cd(1)–O(2)	54.38(7)	O(4A)–Cd(1)–O(1)	94.74(8)
O(6)–Cd(1)–O(1)	136.43(8)	O(4A)–Cd(1)–O(2)	99.20(8)
O(6)–Cd(1)–O(2)	83.84(8)	O(4A)–Cd(1)–O(6)	78.84(9)
N(1)–Cd(1)–O(1)	87.24(8)	N(1)–Cd(1)–O(2)	88.24(8)
O(4A)–Cd(1)–N(1)	172.03(8)	O(6)–Cd(1)–N(1)	104.98(9)
N(2)–Cd(1)–N(1)	70.39(8)	N(2)–Cd(1)–O(1)	120.03(8)
N(2)–Cd(1)–O(2)	158.51(8)	O(4A)–Cd(1)–N(2)	102.04(9)
N(2)–Cd(1)–O(6)	103.38(9)		
2			
Cd(1)–O(1)	2.388(8)	Cd(1)–O(2)	2.308(8)
Cd(1)–O(4A)	2.260(6)	Cd(1)–O(4B)	2.330(7)
Cd(1)–N(1)	2.383(8)	Cd(1)–N(2)	2.312(9)
O(2)–Cd(1)–O(1)	55.8(3)	O(4A)–Cd(1)–O(1)	103.3(2)
O(4B)–Cd(1)–O(1)	86.3(3)	O(4A)–Cd(1)–O(2)	103.3(2)
O(2)–Cd(1)–O(4B)	140.3(3)	O(4A)–Cd(1)–O(4B)	71.7(3)
N(1)–Cd(1)–O(1)	86.5(3)	N(2)–Cd(1)–O(1)	157.2(3)
O(2)–Cd(1)–N(1)	86.9(3)	O(2)–Cd(1)–N(2)	124.5(3)
O(4A)–Cd(1)–N(1)	168.6(3)	O(4B)–Cd(1)–N(1)	103.7(2)
O(4A)–Cd(1)–N(2)	98.6(3)	N(2)–Cd(1)–O(4B)	94.9(3)
N(2)–Cd(1)–N(1)	71.1(3)		
3			
Cd(1)–O(1)	2.3350(19)	Cd(1)–O(2)	2.3800(18)
Cd(1)–O(2C)	2.2986(18)	Cd(1)–O(5A)	2.2025(18)
Cd(1)–O(3A)	2.5081(16)	Cd(1)–O(4B)	2.2144(17)
O(1)–Cd(1)–O(2)	54.68(6)	O(2C)–Cd(1)–O(1)	124.96(7)
O(5A)–Cd(1)–O(1)	135.49(7)	O(2C)–Cd(1)–O(2)	72.29(7)
O(5A)–Cd(1)–O(2)	166.94(7)	O(5A)–Cd(1)–O(2C)	95.41(7)
O(1)–Cd(1)–O(3A)	87.83(6)	O(2)–Cd(1)–O(3A)	107.81(6)
O(2C)–Cd(1)–O(3A)	95.84(7)	O(5A)–Cd(1)–O(3A)	68.27(6)
O(5A)–Cd(1)–O(4B)	86.32(7)	O(4B)–Cd(1)–O(1)	108.70(7)
O(4B)–Cd(1)–O(2)	97.94(7)	O(4B)–Cd(1)–O(2C)	90.67(7)
O(4B)–Cd(1)–O(3A)	154.22(6)		

Symmetry transformations used to generate equivalent atoms: **1** A $x - 1/2, -y + 1/2, z - 1/2$; **2** A $x - 1, y, z - 1$; B $-x + 1, -y + 1, -z + 2$; **3** A $-x + 1/2, y - 1/2, -z + 1/2$; B $x, y, z + 1$; C $-x, -y, -z + 1$.

(λ = 0.71073 Å). Intensities were collected by the ω scan technique. The structures were solved by direct methods and refined with full-matrix least-squares technique (SHELXTL-97) [26]. The parameters of the crystal data collection and refinement of **1**, **2** and **3** are given in Table 1. Selected bond lengths and bond angles are listed in Table 2.

3. Results and discussion

3.1. Description of the crystal structures

The structure of compound **1** consists of one-dimensional neutral chains. Each Cd(II) ion is six-coordinated by two nitrogen atoms from a bipy and four oxygen atoms from a water molecule and two cpa ligands in a distorted octahedral coordination environment (Fig. 1). The cpa ligand possesses two flexible asymmetric carboxylate groups: one acetate and one oxyacetate. The acetate group shows bidentate mode and the oxyacetate group exhibits monodentate mode (Scheme 1a). Each cpa connects two Cd(II) ions to form a one-dimensional chain with the Cd···Cd distance of 11.308(2) Å.

The bipy rings in one chain are absolutely parallel with two bipy rings ($-x, -y, -z$; $1 - x, -y, -z$) of two adjacent chains. The corresponding perpendicular distances of bipy rings are 3.489 and 3.317 Å, and the centroid-to-centroid distances are 3.931 and 3.714 Å, respectively, exhibiting obvious π–π stacking interactions [27–29]. There are O–H···O hydrogen bonding interaction between the coordination water, lattice water and carboxylate groups of cpa ligands (Table 3). Through these π–π stacking interactions and hydrogen bond interaction complex **1** forms a three dimensional network (Fig. 2).

The structure of **2** is comprised of infinite molecular ladders. Each Cd(II) ion is six-coordinated by two nitrogen atoms from a phen and four oxygen atoms from three cpa ligands in a distorted octahedral geometry (Fig. 3). The acetate group of cpa ligand is bidentate chelating and the oxyacetate group is bidentate bridging (Scheme 1b). The Cd(1)···Cd(1D), Cd(1)···Cd(1B) and Cd(1)···Cd(1C) distances are 3.721(2), 10.651(4) and 12.652(4) Å, respectively (Fig. 3).

The cpa ligand exhibits a tetradentate coordination mode bridging three Cd(II) ions to form a one-dimensional molecular ladder [30–33]. The most interesting feature in such infinite molecular ladder is that the double bridging O(4) atoms are in rails and two cpa are in rungs (Fig. 4). The phen rings of a ladder are absolutely parallel with the phen rings ($-x, -y, 1 - z$) of the adjacent ladder with the perpendicular distance 3.484 Å, and the centroid-to-

Table 3
Hydrogen bonds for 1 (Å and °).

1				
D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
O(6)–H(1W)···O(1)[a]	0.838(18)	1.918(19)	2.751(3)	172(3)
O(6)–H(2W)···O(7)	0.832(17)	2.04(2)	2.828(4)	158(4)
O(7)–H(3W)···O(8)	0.832(17)	2.02(2)	2.819(4)	159(4)
O(7)–H(4W)···O(2)	0.828(17)	2.11(2)	2.837(3)	146(3)
O(8)–H(5W)···O(5)[b]	0.787(17)	2.36(3)	2.818(4)	118(3)
O(8)–H(6W)···O(4)[c]	0.808(17)	2.59(3)	3.004(4)	114(3)
O(8)–H(6W)···O(6)[d]	0.808(17)	2.62(3)	3.247(4)	136(3)

Symmetry transformations used to generate equivalent atoms:
[a] $x - 1, y, z$.
[b] $-x + 3/2, y + 1/2, -z + 1/2$.
[c] $-x + 1/2, y + 1/2, -z + 1/2$.
[d] $-x, -y + 1, -z$.

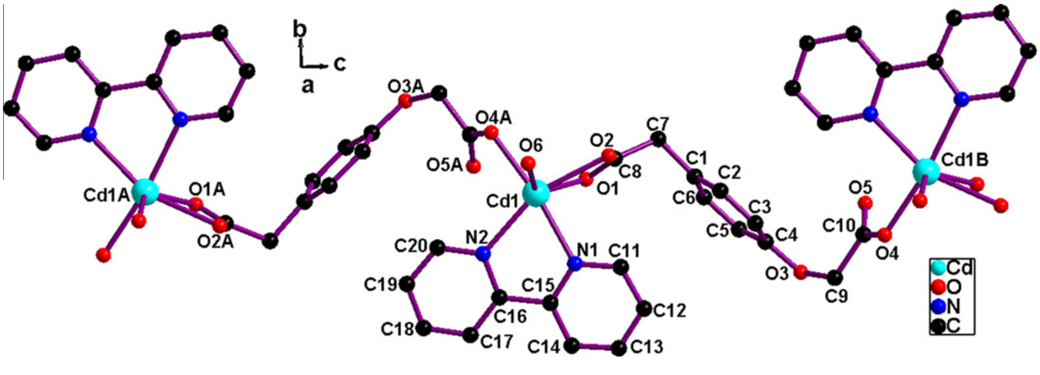

Fig. 1. The coordination environment of the Cd(II) atom in compound **1**.

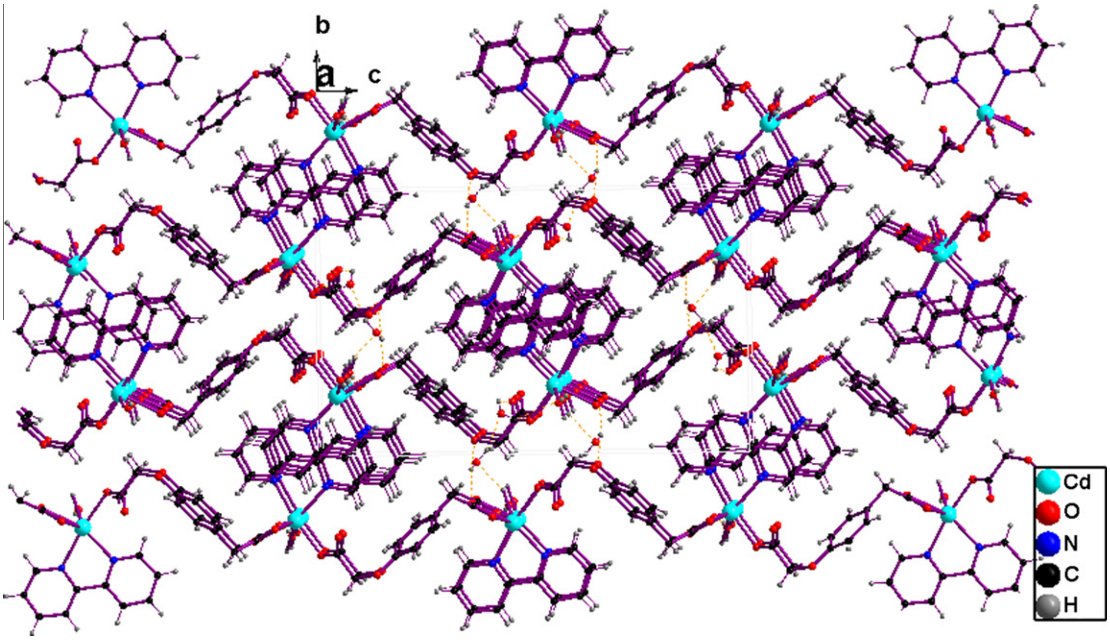

Fig. 2. The packing plot in compound **1**.

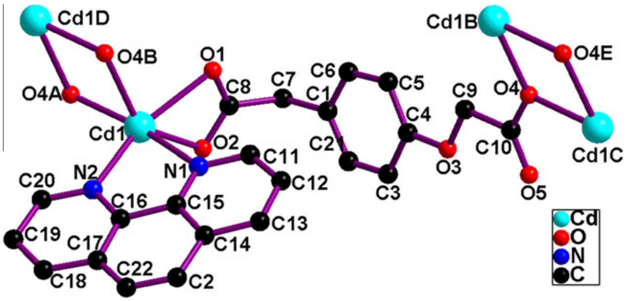

Fig. 3. The coordination environment of the Cd(II) atom in compound **2**.

centroid distance 3.593 Å, exhibiting obvious π–π stacking interactions (Fig. 5) [27–29].

Compound **3** has a novel (4,4)-connected three-dimensional network. There are one independent Cd(II) ion and one independent cpa ligand. Each Cd(II) ion is six-coordinated by six oxygen atoms from four cpa ligands (Cd(II) is 4-connected) in a distorted octahedral coordination environment (Fig. 6). The acetate group is tridentate bridging two Cd(II) ions and the oxyacetate group is tridentate bridging two Cd(II) ions in different mode (Scheme 1c). The cpa ligand exhibits a novel hexadentate coordination mode bridging four Cd(II) ions (The cpa ligand is also 4-connected). The separations of Cd(1)$\cdots$Cd(1C), Cd(1)$\cdots$Cd(1D), Cd(1)$\cdots$Cd(1E), Cd(1C)$\cdots$Cd(1D), Cd(1C)$\cdots$Cd(1E) and Cd(1D)$\cdots$Cd(1E) are 3.779(4), 10.372(1), 12.995(2), 9.902(1), 11.537(2) and 5.260(1) Å, respectively.

Each Cd(II) ion links four cpa ligands and joins ten Cd(II) ions via four cpa ligands (Fig. 7) and further extends to form a novel (4,4)-connected three-dimensional network (Fig. 8).

The structures of **1**, **2** and **3** are comprised of one-dimensional chains, infinite molecular ladders and a (4,4)-connected (Each Cd(II) links four cpa and each cpa connects four Cd(II)) three-dimensional network, respectively. For comparison, some Cd-bipy/phen-polycarboxylate complexes (1,2-bdc = 1,2-benzenedicarboxylate, 1,3-bdc = 1,3-benzenedicarboxylate, 1,4-bdc = 1,4-benzenedicarboxylate, btc = 1,3,5-benzenetricarboxylate and btec = 1,2,4,5-benzenetetracarboxylate) are summarized in Table 4. The different structures are mainly due to the different coordination modes of carboxylate groups of polycarboxylate. Bis-monodentate coordination mode for the biscarboxylate ligand results the dimer [Cd$_2$(phen)$_4$(1,2-bdc)$_2$]·4H$_2$O [34], 1D chain **1** and 1D helical chain [Cd(H$_2$O)(1,2-bdc)(bipy)] [35]. Monodentate and chelating or bis-chelating mode forms 1D chain in [Cd(H$_2$O)(1,4-bdc)(bipy] [38] and [Cd(1,4-bdc)(phen)(H$_2$O)]$_n$ [39]. Chelating and bidentate

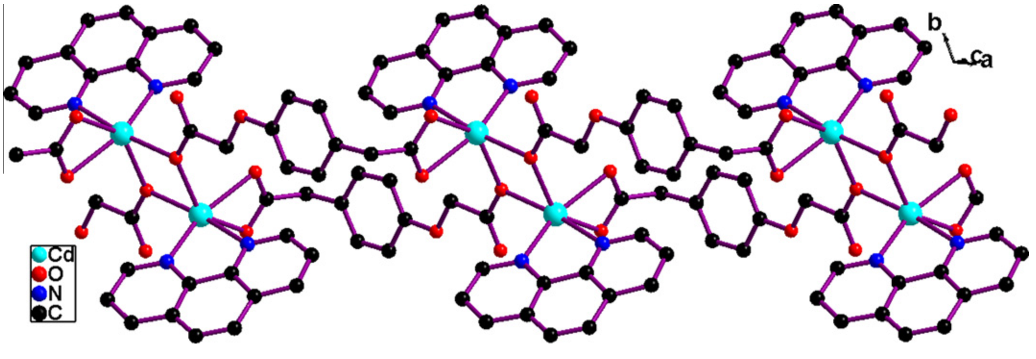

Fig. 4. The one-dimensional molecular ladder in **2**.

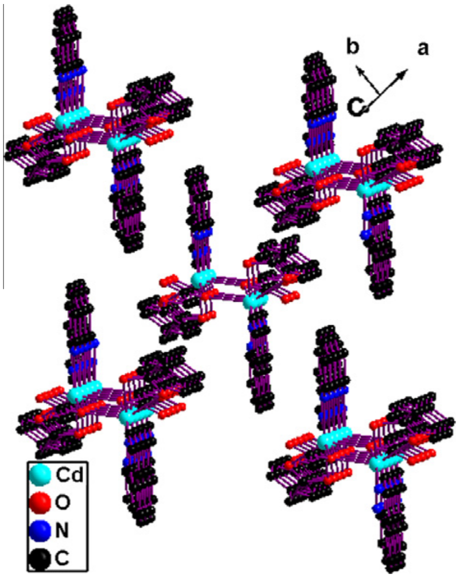

Fig. 5. The packing in compound **2**.

bridging mode for the biscarboxylate ligand constructs 1D molecular ladders in **2**, [Cd (bipy)(1,3-bdc)] and [Cd(phen)(1,3-bdc)] [36]. [Cd(H_2O)(1,3-bdc)] with bis-tridentate bridging mode has a new two-dimensional network [35]. $[Cd_2(bipy)_2(1,3\text{-}bdc)_2]_n$ contains a three-dimensional polymeric channel with tetra –Cd-ip- as building units with versatile monodentate, chelating and tridentate bridging modes [37]. $[Cd_4(btec)_2(phen)_4(H_2O)_4]_n$ possesses an infinite double-chain structure with bis-chelating and bis-monodentate for four carboxylate groups of btec ligand [40]. Cpa shows bidentate and tridentate bridging for two carboxylate groups and ether oxygen monodentate and constructs a novel 3D network for **3**.

3.2. Luminescent properties

The d^{10} metal compounds have exhibited some interesting photoluminescent properties [19–24]. The solid-state luminescent properties of coordination polymers **1**, **2**, **3** and free H_2cpa were investigated at room temperature and their emission spectra are given in Fig. 9. For comparison, the luminescence data of **1–3** and some Cd-bipy/phen polycarboxylate complexes are summarized in Table 4. Because we cannot find one excitation wavelength suitable for the all compounds, we selected maximum excitation wavelengths 350, 330, 380 and 303 nm for **1**, **2**, **3** and H_2cpa, respectively. **1**, **2** and **3** reveal the blue emission maximum at approximately 414, 420 and 458 nm, respectively. Free bipy exhibits the emission at 535 nm. Free phen·H_2O shows the emissions at 365 and 388 nm. The similar luminescence emissions of **1** and **2** are not from bipy and phen. The obvious difference emissions between **3** (458 nm) and **1** (414 nm) or **2** (420 nm) shows that the emissions are not intraligand emission of cpa. Comparably, H_2cpa in the solid state displays a emission band centered at about 336 nm. **1**, **2** and **3** exhibit the obvious red shifts of emission length 78, 84 and 122 nm, respectively. The emissions of **1–3** can be tentatively assigned to the ligand-to-metal charge transfer (LMCT) of cpa [36–42]. [Cd(bipy)(1,3-bdc)] and [Cd(phen)(1,3-bdc)] with different bipy and phen both exhibit intense blue luminescence at 422 and 423 nm, respectively, assigned to the emission of LMCT of 1,3-bdc [36]. The significant blue-shift emission at 405 nm of [Cd(bipy)(1,3-bdc)] can be attributed to the intraligand emission of bipy [36]. The intense luminescence at 435 nm of $Cd_2(bipy)_2(1,3\text{-}bdc)_2]_n$ should be assigned to 1,3-bdc LMCT (not intraligand π–π^* transition stated in [37]). The strong emission at

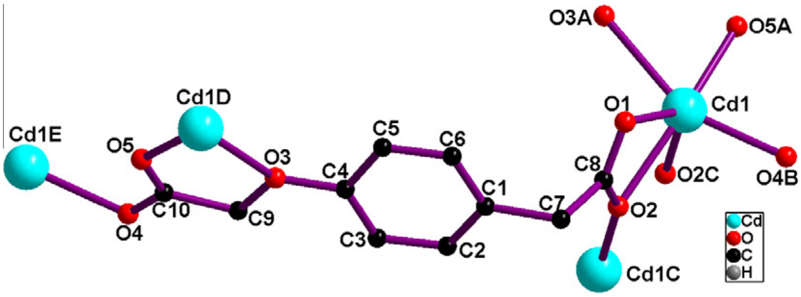

Fig. 6. The coordination environment of the Cd(II) atom in compound **3**.

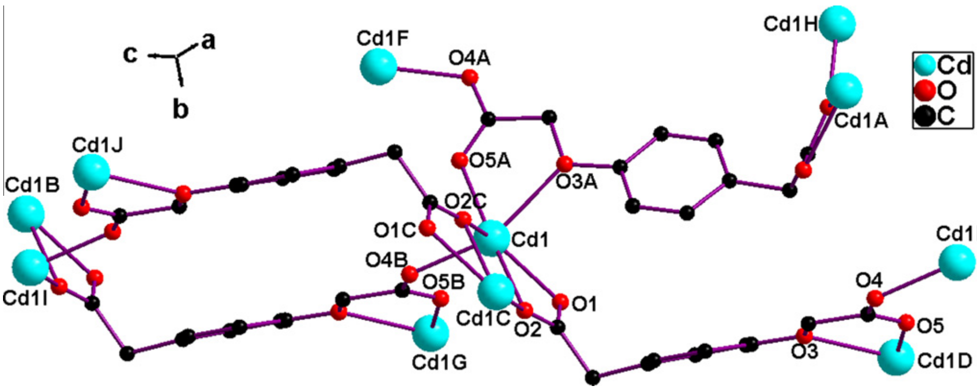

Fig. 7. The linking mode of a Cd(II) atom through four cpa in compound **3**.

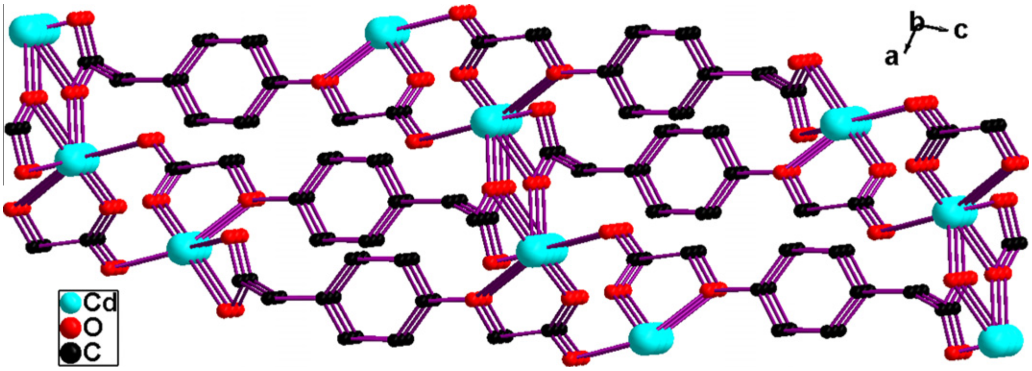

Fig. 8. Three-dimensional network in compound **3**.

Table 4
Summary of Cd-bipy/phen polycarboxylate compounds.

Compound	Structure	Coordination modes of carboxylate groups	Luminescence λ_{em} (nm)	Reference
Bipy			535 nm	[37]
Phen.H_2O			365 and 388 nm	[39]
H_2cpa			336 nm	This work
{[Cd(bipy)(cpa)(H_2O)]·$2H_2O$}$_n$ (**1**)	1D chain	Bis-monodentate	414 nm (cpa LMCT)	This work
{[Cd(phen)(cpa)]·$3H_2O$}$_n$ (**2**)	1D molecular ladder	Chelating, bidentate bridging	420 nm (cpa LMCT)	This work
[Cd(cpa)]$_n$ (**3**)	3D network	Bidentate bridging, tridentate bridging, ether oxygen monodentate	458 nm (cpa LMCT)	This work
[Cd_2(phen)$_4$(1,2-bdc)$_2$]·$4H_2O$	Dimer macrocycle	Bis-monodentate		[34]
[Cd(H_2O)(1,2-bdc)(bipy)]	1D helical chain	Bis-monodentate		[35]
[Cd(H_2O)(1,2-bdc)(phen)]	1D helical ribbon chain	Monodentate, tridentate bridging, bidentate chelating		[35]
[Cd(H_2O)(1,3-bdc)]	2D network	Bis-tridentate bridging		[35]
[Cd (bipy)(1,3-bdc)]	1D molecular ladder	Chelating, bidentate bridging	405 nm (intraligand emission of bipy), 422 nm (1,3-bdc LMCT)	[36]
[Cd(phen)(1,3-bdc)]	1D molecular ladder	Chelating, bidentate bridging	423 nm (1,3-bdc LMCT)	[36]
[Cd_2(bipy)$_2$(1,3-bdc)$_2$]$_n$	3D polymeric channel	Monodentate, chelating, tridentate bridging	435 nm (1,3-bdc LMCT)	[37]
[Cd(H_2O)(1,4-bdc)(bipy)]	1D zigzag chain	Monodentate, chelating	379 nm (intraligand emission of 1,4-bdc)	[38]
[Cd(1,4-bdc)(phen)].H_2O	2D network	Chelating, tridentate brdging		[35]
[Cd(1,4-bdc)(phen)(H_2O)]$_n$	1D chain	Chelating	367, 385 nm (intraligand charge transfer of phen), 404 nm (intraligand fluorescent of phen)	[39]
[Cd_2(Hbtc)$_2$(phen)$_2$]$_{2n}$·nCd(Hbtc)(phen)$_2$	1D chain and a dimer	Chelating, bidentate bridging and uncoordination for chain, bis-monodentate and uncoordination for dimer	380 nm (intraligand charge transfer of phen)	[39]
[Cd_4(btec)$_2$(phen)$_4$(H_2O)$_4$]$_n$	1D double chain	Bis-chelating, bis-monodentate		[40]

379 nm of [Cd(H_2O)(1,4-bdc)(bipy] is attributed to the intraligand emission of 1,4-bdc [38] because the maximum blue-shift of bipy is from 535 nm up to 400 nm [36]. Three emissions maxima at 367, 385 and 404 nm of [Cd(1,4-bdc)(phen)(H_2O)]$_n$ are assigned to intraligand charge transfer or fluorescence of phen [39] (Table 4). There is no defined rule for the luminescent emissions.

4. Conclusion

Three new cadmium(II) coordination polymers {[Cd(bipy)(cpa)(H_2O)]·$2H_2O$}$_n$ (**1**), {[Cd(phen)(cpa)]·$3H_2O$}$_n$ (**2**) and [Cd(cpa)]$_n$ (**3**) were synthesized and characterized. The cpa ligands exhibit versatile coordination modes (Scheme 1): (1) a tridentate bridging two Cd(II) ions in **1** (Scheme 1a); (2) a tetradentate bridging three Cd(II) ions in **2** (Scheme 1b); (3) a novel hexadentate bridging four Cd(II) ions in **3**. The versatile coordination modes of cpa play an important role in the construction of their structures. The structures of **1**, **2** and **3** are comprised of one-dimensional chains, infinite molecular ladders and a (4,4)-connected (Each Cd(II) links four cpa and each cpa connects four Cd(II)) three-dimensional network, respectively. **1**, **2** and **3** reveal the blue emission maximum at 414, 420 and 458 nm, respectively, in the solid state at room

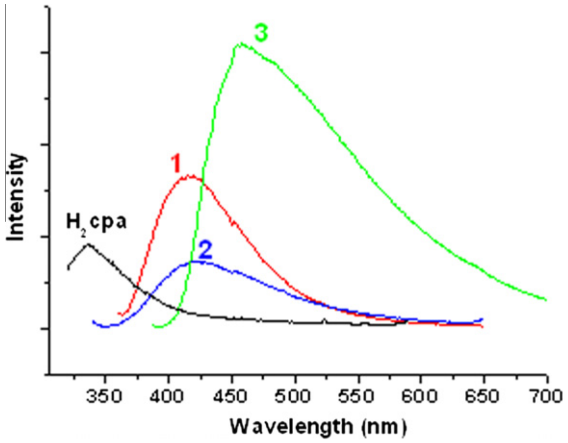

Fig. 9. Solid-state photoluminescent spectra of **1**, **2**, **3** and free H_2cpa at room temperature.

temperature. These three compounds may be excellent candidates for potential photoactive materials.

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Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre with CCDC numbers 796453–796455. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2011.05.038.

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