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# Effects of the size of aromatic chelate ligands and d<sup>10</sup> metal ions on the structures of dicarboxylate complexes: From dinuclear molecule to helical chains and 2D network

Zhong-Xi Han<sup>a</sup>, Ji-Jiang Wang<sup>a,b</sup>, Huai-Ming Hu<sup>a,\*</sup>, Xiao-Li Chen<sup>a,b</sup>, Qing-Ran Wu<sup>a</sup>, Dong-Sheng Li<sup>b</sup>, Qi-Zhen Shi<sup>a</sup>

<sup>a</sup> Department of Chemistry, Shaanxi Key Laboratory of Physico-inorganic Chemistry, Northwest University, Xi'an 710069, China <sup>b</sup> Department of Chemistry and Chemical Engineering, Shaanxi Key Laboratory of Chemical Reaction Engineering, Yanan University, Yan'an 716000, China

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# ABSTRACT

Four new mixed-ligand complexes, namely  $[Zn_2(pam)_2(2,2'-bpy)_2]$  (1),  $[Cd(pam)(2,2'-bpy)_2]_n$  (2),  $[Zn(pam)(phen)]_n$  (3) and  $[Cd (pam)(phen)]_n \cdot 0.5n CH_3CH_2OH \cdot 0.5nH_2O$  (4)  $(H_2pam = pamoic acid, 2,2'-bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline) have been synthesized under hydro(solvo)thermal conditions. Complex 1 possesses a discrete dinuclear metallamacrocyclic structure. Complex 2 is a 1D homochiral helical coordination polymer that is built from achiral components, whereas 3 displays a 1D helical chain structure. 4 is an unusual 2D double-layered structure generated by <math>\pi \cdots \pi$  interactions of two 2D networks. The structural differences of these complexes are mainly due to the differences of the size of the rigid aromatic chelate ligands and d<sup>10</sup> metal ions. It appears that the chelate ligands and metal ions of the larger size favor the formation of high-dimensional structures, whereas those of the smaller size favor the formation of low-dimensional structures in the present system. The photoluminescence and thermal stability of these complexes were investigated.

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# 1. Introduction

The construction of coordination polymers has attracted considerable attention in recent years due to their interesting properties and promising applications in the areas of catalysis, gas storage, magnetism and optics [1]. Polynuclear d<sup>10</sup> metal (Cu<sup>l</sup>, Ag<sup>l</sup>, Au<sup>l</sup>, Zn<sup>II</sup> or Cd<sup>II</sup>) complexes have been found to exhibit intriguing structures and photoluminescent properties [2]. A series of d<sup>10</sup> metal organic frameworks have been described recently [3]. However, to the best of our knowledge, the studies on the effects of the size of the rigid aromatic chelate ligands and d<sup>10</sup> metal ions on framework formation of their complexes have rarely been reported [4].

It is well known that the final framework of coordination compounds depends both on the coordination geometry of the metal ions and on the properties of the organic ligands. When long/flexible/V-shaped bridging dicarboxylate ligands are used to connect metal ions, their versatile coordination modes may lead to new architectures with fantastic structures and desirable properties [4,5].

Pamoic acid (H<sub>2</sub>pam) is a multifunctional ligand containing both carboxylic and phenoxy groups, which can potentially afford various coordination modes and diverse metal-organic framework (MOF) architectures. Meanwhile, it also possesses both rigidity and flexibility, since the naphthyl rings can freely rotate around the methylene ( $-CH_2-$ ) groups according to the small change in the coordination environment in order to minimize steric hindrance. In addition, pamoic acid (H<sub>2</sub>pam) is a very cheap industrial precursor and used as a counter ion to obtain long-acting pharmaceutical formulations of certain basic drugs [6]. As far as we know, H<sub>2</sub>pam metal complexes have scarcely been studied previously.

The judicious selection of auxiliary ligands has a significant effect on the formation and structure of final metal complexes. Aromatic chelate ligands, such as 1,10-phenanthroline (phen) and 2,2'-bipyridine (2,2'-bpy) are important in maintaining the dimensionality of the coordination polymers and may provide potential supramolecular recognition sites for  $\pi$ - $\pi$  aromatic stacking interactions to form interesting supramolecular structures such as double-stranded helices and molecular zippers [5b,7].

With the aim of understanding the coordination chemistry of  $H_2pam$  and studying the influence of the size of aromatic chelate ligands and  $d^{10}$  metal ions on the framework structures of their complexes, we are currently interested in the structures of metal pamoate complexes with the mixed ligand. Herein, we report four interesting  $d^{10}$  metal complexes, namely  $[Zn_2(pam)_2(2,2'-bpy)_2]$ 

<sup>\*</sup> Corresponding author. Tel./fax: +86 29 88303331.

E-mail address: Chemhu1@nwu.edu.cn (H.-M. Hu).

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(1),  $[Cd(pam)(2,2'-bpy)_2]_n$  (2),  $[Zn(pam)(phen)]_n$  (3) and  $[Cd(pam)(phen)]_n \cdot 0.5nCH_3CH_2OH \cdot 0.5nH_2O$  (4). All four pamoate complexes contain  $pam^{2-}$  spacers and auxiliary ligands (2,2'-bpy/ phen), and display very different structures, ranging from dinuclear molecule to helical chains and 2D Network.

## 2. Experimental section

# 2.1. Materials and methods

The reagents and solvents employed were commercially available and used as received without further purification. Elemental analyses (C, H, N) were determined with a Vario EL III elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm<sup>-1</sup> on a Bruker EQUINOX-55 spectrometer. Thermogravimetric analyses (TGA) were performed under nitrogen with a heating rate of 10 °C · min<sup>-1</sup> using a METTLER TGA851 thermogravimetric analyzer. Fluorescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer at room temperature.

# 2.2. Synthesis

# 2.2.1. Synthesis of [Zn<sub>2</sub>(pam)<sub>2</sub> (2,2'-bpy)<sub>2</sub>](**1**)

A mixture of  $Zn(OAc)_2 \cdot 2H_2O$  (0.10 mmol),  $H_2pam$  (0.10 mmol), NaOH (0.20 mmol) and 2,2'-bpy (0.10 mmol) in 6 mL water-ethanol (1:5) was stirred for 30 min in air, then sealed in a 15 mL Telfon-lined stainless steel container, which was heated to 160 °C for 72 h. After cooling to room temperature at a rate of 2 °C per hour, yellow crystals were obtained in ca. 52% yield. Anal. found (calcd) for  $C_{66}H_{44}Zn_2N_4O_{12}$ : C, 65.15 (65.14); H, 3.60 (3.62), N, 4.61 (4.63); FT-IR (KBr, cm<sup>-1</sup>): 3410(m), 1639(m), 1604(w), 1574(w), 1507(m), 1447(m), 1393(m), 1335(w), 1244(w), 811(m), 763(m), 735(m), 653(w), 630(m), 551(w), 516(m), 486(w), 433(w), 411(w).

#### 2.2.2. Synthesis of $[Cd(pam)(2,2'-bpy)_2]_n(2)$

The preparation of **2** was similar to that of **1** except that  $Cd(NO_3)_2 \cdot 4H_2O(0.10 \text{ mmol})$  was used instead of  $Zn(OAc)_2 \cdot 2H_2O$ . Pale-yellow crystals were obtained in ca. 60% yield. Anal. found (calcd) for  $C_{43}H_{30}CdN_4O_6$ : C, 63.64(63.62); H 3.73(3.70); N, 6.88(6.90); FT-IR (KBr, cm<sup>-1</sup>): 3410(m), 1635(m), 1597(w), 1508(w), 1443(m), 1387(m), 1244(w), 856(m), 736(m), 647(w), 597(w), 550(w), 483(w).

#### 2.2.3. Synthesis of $[Zn(pam)(phen)]_n(3)$

A mixture of  $Zn(OAc)_2 \cdot 2H_2O(0.1 \text{ mmol})$ ,  $H_2pam(0.10 \text{ mmol})$ , NaOH (0.20 mmol) and phen  $\cdot H_2O(0.10 \text{ mmol})$  in 6 mL water–ethanol (1:5) was stirred for 30 min in air, then sealed in a 15 mL Telfon-lined stainless steel container, which was heated to 160 °C for 72 h. After cooling to room temperature at a rate of 2 °C per hour, pale-yellow large block crystals were obtained in ca. 60% yield. Anal. found (calcd) for  $C_{35}H_{22}N_2O_6$  Zn: C, 64.48 (66.46); H, 3.46 (3.48); N, 4.45 (4.43); FT-IR (KBr, cm<sup>-1</sup>): 3425(m), 1638(s), 1581(s), 1550(s), 1509(s), 1452(s), 1407(s), 1344(s), 1322(s), 854(m), 767(m), 645(w), 594(w), 551(w), 479(w).

#### 2.2.4. Synthesis of $[Cd(pam)(phen)]_n \cdot 0.5nCH_3 CH_2 OH \cdot 0.5nH_2O(4)$

The preparation of **4** was similar to that of **3** except that  $Cd(OAc)_2 \cdot 2H_2O$  (0.10 mmol) was used instead of  $Zn(OAc)_2 \cdot 2H_2O$ . Colorless crystals were obtained in ca. 65% yield. Anal. found (calcd) for  $C_{36}H_{26}CdN_2O_7$ : C, 60.74(60.76); H, 3.68(3.66); N, 3.96(3.94); FT-IR (KBr, cm<sup>-1</sup>): 3422(m), 1637(m), 1548(m), 1512(m), 1456(m), 1369(w), 1236(w), 808(m), 766(m), 746(w), 723(m), 549(m), 520(w), 486(w), 435(w).

#### 2.3. X-ray crystallography

Intensity data were collected on a Bruker Smart APEX II CCD diffractometer with graphite-monochromated Mo–K<sub>α</sub> radiation ( $\lambda = 0.71073$  Å) at room temperature. Empirical absorption corrections were applied by using the SADABS program. The structures were solved by direct methods and refined by the full-matrix least-squares based on  $F^2$  using SHELXTL-97 program [8]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms of organic ligands were generated geometrically. Crystal data and structural refinement parameters for **1–4** are summarized in Table 1 and selected bond distances and bond angles are listed in Table S1, Supplementary Material.

#### 3. Results and discussion

#### 3.1. Crystal structures

#### 3.1.1. Crystal structure of $[Zn_2 (pam)_2 (2,2'-bpy)_2]$ (1)

Complex 1 is a dinuclear metallamacrocyclic complex containing cavity without guest molecule. As shown in Fig. 1a, there are one Zn<sup>II</sup> ion, one pam<sup>2–</sup> anion and one 2,2'-bpy ligand in the asymmetric unit. Each Zn<sup>II</sup> ion is coordinated to three oxygen atoms of two pam<sup>2-</sup> ligands and two nitrogen atoms of a 2,2'-bpy ligand, and is located in a slightly distorted square-pyramidal geometry. However, the distance of 2.510(3) Å between Zn1 and O2 of carboxylate group of pam<sup>2-</sup> ligand suggests a nonnegligible interaction between them. Thus, the Zn<sup>II</sup> ion can be regarded as a distorted octahedron. The average Zn-N bond length is 2.066(3) Å and Zn-O bond lengths are in the range 1.983(3)-2.276(2) Å. Zn1 and Zn1A are bridged by two  $pam^{2-}$  ligands with a distance 10.513(2) Å. Each pam<sup>2-</sup> ligand in **1** adopts a *trans* conformation and serves as a monodentate-bidentate bridging ligand, linking two Zn<sup>II</sup> ions (see Scheme 1a). It is interesting that the adjacent metallamacrocycle are stacked through significant C-H  $\cdots \pi$ interactions between the naphthyl rings and pyridyl rings from adjacent metallamacrocycle with the edge-to-face separation of 3.4–3.7 Å, resulting in 1D supramolecular double-chain structures containing micropores (Fig. 1b). Although the area is ca. 10.513 Å  $\times$  10.687 Å [based on Zn1–Zn1A and C12–C12A distances] in each micropore structure, the real volume of the cavity is further reduced due to the significant offset stacking of adjacent metallamacrocycles.

# 3.1.2. Crystal structure of $[Cd (pam)(2,2'-bpy)_2]_n(2)$

Unexpectedly, when Zn<sup>II</sup> ion is replaced by Cd<sup>II</sup> ion, a d<sup>10</sup> metal ion with larger radius, structurally different 1D helical coordination polymer is formed in 2 under similar reaction conditions for the preparation of **1**. X-ray crystallography shows **2** is a 1D homochiral helical coordination polymer that is built from achiral components. As illustrated in Fig. 2a, there are one Cd<sup>II</sup> ion, one pam<sup>2–</sup> anion, two 2,2'-bpy ligands in the asymmetric unit. The coordination polyhedron around each Cd<sup>II</sup> ion is a square antiprism with four oxygen atoms of two chelating pam<sup>2-</sup> ligands and four nitrogen atoms of two chelating 2,2'-bpy ligands. The average Cd-N bond distance (2.428(7) Å) is similar to those of other Cd<sup>II</sup> coordination polymers with mixed ligands, such as 1D polymer  $[Cd(bpea)(phen)_2]$ (bpea = biphenylethene-4,4'-dicarboxylate) (2.477(3) Å) [9]. The Cd–O bond distances range from 2.308(7) to 2.760(6) Å, which are also comparable to those in the literatures [10]. The two carboxylate groups of  $pam^{2-}$  ligand in **2** adopt a *trans* conformation and exhibit another kind of chelating bis(bidentate) bridging with Cd<sup>II</sup> atoms, as shown in Scheme 1b. [Cd(2,2' $bpy_{2}^{2+}$  molecular corners are bridged by  $pam^{2-}$  ligands to form infinite helical chain running along a axis (Fig. 2b). The helix is gen-

#### Table 1

Crystal data and structural refinement parameters for complexes 1-4

Complex	1	2	3	4
Empirical formula	C <sub>66</sub> H <sub>44</sub> N <sub>4</sub> O <sub>12</sub> Zn <sub>2</sub>	C43H30CdN4O6	C <sub>35</sub> H <sub>22</sub> N <sub>2</sub> O <sub>6</sub> Zn	C <sub>36</sub> H <sub>26</sub> CdN <sub>2</sub> O <sub>7</sub>
Formula weight	1215.79	811.11	631.92	710.99
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_{1}2_{1}2_{1}$	$P2_1/c$	P2/n
a/Å	12.4791(7)	9.3119(6)	13.6026(17)	11.6092(7)
b/Å	12.3400(7)	14.1906(9)	11.8085(15)	15.6578(10)
c/Å	17.9739(10)	26.0335(17)	18.570(2)	18.8917(14)
α/°	90	90	90	90
β/°	105.932(1)	90	107.245(2)	107.8080(10)
v/°	90	90	90	90
V/Å <sup>3</sup>	2661.5(3)	3440.1(4)	2848.8(6)	3269.5(4)
Z	2	4	4	4
$\rho_{\text{calc}} (\text{g cm}^{-3})$	1.517	1.566	1.473	1.444
$\mu (mm^{-1})$	0.975	0.694	0.914	0.719
F(000)	1248	1648	1296	1440
$\lambda (Mo-K\alpha)/Å$	0.71073	0.71073	0.71073	0.71073
Reflections collected	13204	17532	13791	16297
Unique reflections	4718	6080	5059	5824
Parameters	382	490	399	419
S on F <sup>2</sup>	1.028	0.957	1.015	1.046
$R_1, wR_2 [I > 2\sigma(I)]$	0.0397, 0.0872	0.0532, 0.1076	0.0390, 0.1165	0.0463, 0.1280
$R_1, wR_2$ (all data)	0.0707, 0.0988	0.1148, 0.1329	0.0555, 0.1278	0.0766, 0.1410
$\Delta  ho_{ m min \ and \ max}$ (e Å <sup>-3</sup> )	0.227 and -0.290	0.368 and -0.395	0.457 and -0.327	0.898 and -0.417



**Fig. 1.** (a) A perspective view of dinuclear metallamacrocycle in 1. (b) The 1D double-chain structures viewed along the b axis in 1. All hydrogen atoms have been omitted for clarity.

erated around the  $2_1$  screw axis with an exceptionally long pitch of 26.034(2) Å, equal to the length of the *c* axis. Notably, each pair of nearly perpendicular 2,2'-bpy ligands bonded to the Cd<sup>II</sup> atom point away from the helical axis; this steric orientation may lead to the generation of **2**.

In complex **2**, the neighboring chains are linked to each other via  $\pi \cdots \pi$  interactions between pyridyl and adjacent naphthyl rings (the nearest carbon to carbon separation of 3.3 Å) to lead to a 3D supramolecular framework containing 1D chiral channels (Fig. 2c). Although the area is 7.991 Å × 14.493 Å (based on Cd–Cd) in each channel structure, the real volume of the cavity is fur-



**Scheme 1.** The coordination modes of pam<sup>2–</sup> ligand in **1–4**.

ther reduced due to the significant offset stacking of adjacent helical chains.

# 3.1.3. Crystal structure of $[Zn(pam)(phen)]_n$ (3)

To further examine the influence of the auxiliary ligands on the structure of **1**, a larger size aromatic chelate ligand phen is used instead of 2,2'-bpy. Consequently, **3**, which feature a 1D helical chain polymer, was obtained. As shown in Fig. 3a, there are one  $Zn^{II}$  ion, one pam<sup>2–</sup> anion and one phen molecule in the asymmetric unit. The  $Zn^{II}$  ion is in a distorted square pyramidal geometry coordinated by two nitrogen atoms from a chelate phen, two oxygen atoms from the chelating carboxylate group of a pam<sup>2–</sup> ligand. An oxygen atom from the monodentate carboxylate group of an other pam<sup>2–</sup> ligand occupies the remaining site. Similar to **1**, the



**Fig. 2.** (a) Coordination environment of the Cd<sup>II</sup> ion in **2**. (b) The 1D helical structure in **2**. (c) The 3D chiral network viewed along *a* axis in **2**. All hydrogen atoms have been omitted for clarity.

distance of 2.602(3) Å between Zn1 and O2 of a carboxylate group of pam<sup>2–</sup> ligand suggests a nonnegligible interaction between them. Thus, the Zn<sup>II</sup> ion can be regarded as a distorted octahedron. The bond lengths of Zn–O and Zn–N are similar to those in other zinc carboxylate coordination polymers [4]. Unlike those in complexes **1** and **2**, each pam<sup>2–</sup> ligand in **3** adopts *cis* conformation and bridges two Zn<sup>II</sup> atoms in monodentate and chelating bidentate mode (Scheme 1c) to form a 1D infinite helical chain as shown in Fig. 3b. Interestingly, the adjacent chains are linked to each other via C–H ···  $\pi$  interactions between phen molecules and adjacent naphthyl rings (the carbon to carbon separation of 3.4–3.6 Å) to lead to a 1D supramolecular double-chain structures viewed along the *b* axis (Fig. 3c).

# 3.1.4. Crystal structure of $[Cd(pam)(phen)]_n \cdot 0.5nCH_3CH_2$ OH $\cdot 0.5nH_2O$ (**4**)

Similar to **3**, using phen in place of 2,2'-bpy of **2** under the same reaction conditions, **4** is achieved. Complex **4** features an unusual 2D double-layered structure generated by  $\pi \cdots \pi$  interactions. As shown in Fig. 4a, there are one Cd<sup>II</sup> ion, two half pam<sup>2–</sup> anions, one half water and one half ethanol molecules in the asymmetric unit. Each Cd<sup>II</sup> ion is coordinated to five oxygen atoms of three pam<sup>2–</sup> ligands and two nitrogen atoms of one phen molecule to furnish a distorted capped-octahedral geometry. The Cd–N bond distances (2.320(1) and 2.352(1) Å) are similar to those of other Cd<sup>II</sup> coordination polymers with mixed ligands, such as 1D polymer [Cd(mpa)(phen)]<sub>n</sub> and [Cd<sub>2</sub>(mpa)<sub>2</sub>(2,2'-bpy)<sub>2</sub>]<sub>n</sub> (mpa = *m*-phthalate) [4]. The Cd–O bond lengths fall in the range 2.250(1)–2.763(2) Å, which are also comparable to those in the literatures [10]. There are two types of coordination modes for the bridging pam<sup>2–</sup> ligands in a *trans* conformation in **4**, namely bis (chelating



**Fig. 3.** (a) Coordination environments of the  $Zn^{II}$  ion in **3.** (b) The 1D helical chain structures in **3.** (c) The 1D double-chain structures viewed along the *b* axis in **3.** All hydrogen atoms have been omitted for clarity.

bidentate) (Scheme 1b) and bis(chelating/bridging bidentate) (Scheme 1d). The dinuclear species  $[Cd_2(pam)_2(phen)_2]$ , which has a Cd–Cd distance of 3.867(2) Å, can be regarded as a secondary building unit (SBU). These SBUs are linked by  $pam^{2-}$  ligands into 2D networks with phen ligands attached to one side of the networks (Fig. 4b), and the adjacent two 2D networks in face-to-face manner are further packed into a double-layered structure by weak  $\pi \cdots \pi$  interactions between phen molecules (the nearest distance 3.718 Å) (Fig. 4c). Although the area of the 2D networks is 11.609 Å × 15.031 Å (based on Cd–Cd) in each channel structure, the real volume of the cavity is further reduced due to the significant offset stacking of adjacent two 2D networks. Calculations using PLATON [11] revealed that the free volume of channels constitute about 22% of the crystal volume and are filled with CH<sub>3</sub>CH<sub>2</sub>OH and H<sub>2</sub>O solvent molecules.

In a comparison of the structures of **1–4**, it is found that coordination geometry of the central metal ions and the sizes of the auxiliary ligands have significant effects on the formation and structures of the resulting complexes. As demonstrated by a comparison of complexes **1/3** and **2/4**, the high coordination number of the metal ion is an important factor for the formation of a high-dimensional structure. In addition, different aromatic chelates also have a significant effect on the structures, as evidenced by the fact that the structures of **1/2** are significantly different from that of **3/4**.



**Fig. 4**. (a) Coordination environments of the Cd<sup>II</sup> ion in **4**. (b) The 2D network viewed along the *b* axis in **4**. (c) Double-layered structure generated by π ··· π interactions in **4**. Carbon atoms of phen in (b) are omitted for clarity.

Furthermore, the comparison of **1–4** with 1D polymer [M(mpa) (phen)]<sub>n</sub>, [M<sub>2</sub>(mpa)<sub>2</sub>(2,2'-bpy)<sub>2</sub>]<sub>n</sub> (M = Zn or Cd and mpa = *m*-phthalate) [4], [Cu<sub>2</sub>(mpa)<sub>2</sub>(phen)<sub>2</sub>(H<sub>2</sub>O)]<sub>n</sub> and [Cu(mpa)(2,2'-bpy)(H<sub>2</sub>O)]<sub>n</sub> · 2nH<sub>2</sub>O [5b] shows that the higher flexibility and greater lengths of dicarboxylate ligands may play a key role in determining the structures of the complexes.

#### 3.2. Thermal analyses studies

To study the thermal stabilities of these complexes, thermogravimetric analyses (TGA) of complexes **1–4** were performed (Fig. S2, Supplementary Material, shows the TG curves for **1–4**). In TG analysis of **1**, there is no weight loss until 294 °C. A continuous weight loss can be detected from 294 to 498 °C attributed to the complete decomposition of pam<sup>2–</sup> and 2,2'-bpy (Calcd.: 89.25%; Found: 87.85%). Polymer **2** is very stable. There is no weight loss until 318 °C. The weight reduces to 85.96% (Calcd.: 86.15%) at 645 °C, which is presumed to be the complete decomposition of pam<sup>2–</sup> and 2,2'-bpy. TG analyses of polymer **3** shows that there is a continuously two-step weight loss in the range of 252– 650 °C, corresponding to the decomposition of pam<sup>2–</sup> and phen (Calcd.: 92.51%; Found: 86.90%). Polymer **4** lost  $CH_3CH_2OH$  and  $H_2O$  solvent molecules below 140 °C. The TG curve of the dehydrated product shows no weight loss up to 267 °C, followed by a continuously two-step weight loss of 82.02% from 267 to 634 °C (Cald: 82.22%). The TGA result of **4** indicates that the 2D net does not decompose and is stable below 267 °C. The TGA results of **1– 4** show that they are stable below 250 °C, which indicate their good thermal stability.

### 3.3. Luminescent properties

The solid-state photoluminescent spectra of complexes **1–4** are depicted in Fig. 5. Complex **1** exhibits two intense emission peaks at ca. 461 and 528 nm upon excitation at 340 nm. The emission peak is located at 528 nm, which means a red shift of ca. 51 nm relative to that of free H<sub>2</sub>pam ligand ( $\lambda_{max} = 477$  nm) (Fig. S1, Supplementary Material, shows solid state emission spectrum of free H<sub>2</sub>pam). We tentatively assign it to the intraligand ( $\pi$ – $\pi$ <sup>\*</sup>) fluorescence since a weak similar emission with  $\lambda_{max}$ at 477 nm is also observed for free ligand. The peak at 461 nm would be distributed to the intraligand emission from 2,2'-bpy ligand [4,12]. Complex **2** 



**Fig. 5.** The emission spectra of **1–4** in the solid state at room temperature upon excitation at 340 nm.

also exhibits an intense emission peak upon excitation at 340 nm. The emission peak is located at 523 nm for 2, and compared with  $H_2$  pam ligand a clearly red shift occurs in **2**, which might also be attributed to the intraligand  $(\pi - \pi)$  fluorescence [13]. Interestingly, complex 3 exhibits an intense blue radiation emission upon excitation at 340 nm. The emission peak is located at 437 nm for 3, which means a blue shift of ca. 40 nm relative to that of free H<sub>2</sub>pam ligand  $(\lambda_{\text{max}} = 477 \text{ nm})$ . As known, the intraligand emissions for the same ligand can be tuned by its conformations [14]. The blue shift of **3** indicates that pam<sup>2-</sup> ligands display an uncommon *cis* conformation (Scheme 1c), while pam<sup>2-</sup> ligands of **1**, **2** and **4** adopt *trans* conformation (Scheme 1a, b, d), which confirm by X-ray crystal structures. Complex 4 also exhibits two intense emission peaks at ca. 460 and 523 nm upon excitation at 340 nm. Similar to 1, the peak at 523 nm would be also assigned to the intraligand ( $\pi$ - $\pi^*$ ) fluorescence from pam<sup>2–</sup>, while the peak at 460 nm might be attributed to the emission of ligand-to-metal charge transfer (LMCT) [4]. In a comparison of the emission spectra of **1–4**, it is found that **2** exhibits a greatly enhanced emission compared to those of 1,3 and 4. The enhancement of 2 is probably related to its helical structure [15]. The results suggest that 2 may be good green-light-emitted materials.

# 4. Conclusions

In summary, four new d<sup>10</sup> metal complexes with different structures have been synthesized under hydro(solvo)thermal conditions. Complex 1,  $[Zn_2(pam)_2(2,2'-bpy)_2]$ , possesses a discrete dinuclear metallamacrocyclic structure. Complex 2.  $[Cd(pam)(2,2'-bpy)_2]_n$ , is a 1D homochiral helical coordination polymer that is built from achiral components. Complex 3,  $[Zn(pam)(phen)]_n$ , displays a 1D helical chain structure. Complex **4**,  $[Cd(pam)(phen)]_n \cdot 0.5nCH_3CH_2OH \cdot 0.5nH_2O$ , exhibits an unusual 2D double-layered structure generated by  $\pi \cdots \pi$  interactions of two 2D networks. The structural differences of these complexes are mainly due to the differences of the size of the rigid aromatic chelate ligands and d<sup>10</sup> metal ions. It appears that the chelate ligands and metal ions of the larger size favor the formation of high-dimensional structures, whereas those of the smaller size favor the formation of low-dimensional structures in the present system.

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# Appendix A. Supplementary data

CCDC Nos. 620299, 620300, 620301 and 620302 for **1**, **2**, **3** and **4** contain the supplementary crystallographic data. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: (internat) +44 1223 336 033; E-mail: <u>deposit@ccdc.cam.ac.uk</u>]. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2008.04.010.

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