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Chains, ladders and sheets of d¹⁰ metal–organic polymers generated from the flexible bipyridyl ligands

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Abstract

By use of the three-layer diffusion method, reactions of flexible bipyridyl ligands (4,4'-bpp or 3,3'-bpp) with M(II) salts (M = Zn, Cd) and multi-carboxylate ligands resulted in the formation of four interesting d^{10} metal–organic coordination polymers: $[Zn(\mu-4,4'-bpp)Br_2]_n$ (1), $[Zn(\mu-4,4'-bpp)(1,2-bdc)]_n \cdot nH_2O$ (2), $[Zn(\mu-3,3'-bpp)(1,3-bdc)]_n \cdot nCH_3OH \cdot 2nH_2O$ (3) and $[Cd(\mu-3,3'-bpp)(C_4H_2O_4)]_n \cdot 3nH_2O$ (4) (4,4'-bpp = 2,2'-bis(4-pyridylmethyleneoxy)-1,1'-biphenylene; 3,3'-bpp = 2,2 '-bis(3-pyridylmethyleneoxy)-1,1'-biphenylene; bdc=benzenedicarboxylate, C₄H₄O₄ = fumaric acid). Complex 1 has a 2D sheet structure consisting of two unusual zigzag Zn(II) chains which are nearly perpendicular to each other. Complex 2 is comprised of two-leg ladders, in which [Zn(4,4'-bpp)] chains serve as the side rails and 1,2-bdc ligands serve as the cross rungs. In complex 3, every two 1,3-bdc ligands connect the neighbouring Zn(II)-3,3'-bpp dimetallic rings in η^1 coordination modes into an interesting chain structure. Complex 4 consists of an anionic macrocycle-containing cadmium dicarboxylate sheets that are separated by 3,3'-bpp. These d¹⁰ metal complexes exhibit high thermal stabilities and strong luminescence efficiencies.

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Keywords: Flexible bipyridyl; d¹⁰ Metal; Multi-carboxylate; Crystal structure; Coordination polymer; Optical properties

1. Introduction

The design of metal-organic coordination frameworks has undergone explosive growth over the past decade because of their intriguing structures and, more importantly, their potential applications as functional materials [1-4]. Recently, optically active 1,1-bi-2-naphthol (BINOL) has been widely used as a starting material and an auxiliary in asymmetric synthesis or chiral recognition owing to its axial chirality and configurational stability. Based on BINOL-derived ligands, Lin and co-workers have recently prepared a series of well-documented single-, double-, triple- and quadruple-stranded as well as circular and cylin-

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drical complexes [5–7]. With the aim of introducing valuable functional chiral spacers into pyridine-donor ligands, the two flexible bipyridyl ligands 2,2'-bis(4-pyr-idylmethyleneoxy)-1,1'-biphenylene (4,4'-bpp) and 2,2'-bis(3-pyridylmethyleneoxy)-1,1'-biphenylene (3,3'-bpp) have been designed and synthesized by bringing monopyridine functional groups and a dipyridyl connector into the reaction system (Scheme 1).

In constructing coordination polymers, 4,4'-bpp or 3,3'bpp can be recognized as a useful starting material, since their configurations can be greatly altered along the 1,1'bond to meet the considerable requirements for the construction of metal–organic frameworks. Moreover, due to the flexibility and conformational freedom of 4,4'-bpp or 3,3'-bpp, they promise great possibilities for generating an infinite variety of aesthetic frameworks with useful properties [8–10]. Recently, we have studied the above

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Scheme 1. Structure of 4,4'-bpp and 3,3'-bpp ligands.

{M-bpp} systems with the introduction of multi-carboxylate ligands. With various flexible coordination modes for carboxylate group ligands, dicarboxylate ligands can bridge two or more different metal centers and produce neutral architectures. These additional ligands could exhibit a variety of bridging abilities and have a strong tendency to form multidimensional structures, which would be markedly different from those of M-(4,4'-bpp) and M-(3,3'-bpp) complexes [11–17]. The combination of bipyridyl and dicarboxylate with d¹⁰-metal ions could produce some unique frameworks with beautiful aesthetics and useful properties.

Herein, we report the syntheses, crystal structures, thermal stability and the fluorescence properties of four new complexes: $[Zn(\mu-4,4'-bpp)Br_2]_n$ (1), $[Zn(\mu-4,4'-bpp)(1,2-$ (2), $[Zn(\mu-3,3'-bpp)(1,3-bdc)]_n \cdot nCH_3O$ bdc]_n · nH_2O $H \cdot 2nH_2O$ (3) and $[Cd(\mu - 3, 3' - bpp)(C_4H_2O_4)]_n \cdot 3nH_2O$ (4) (bdc = benzenedicarboxylate, $C_4H_4O_4$ = fumaric acid). The research results reported here are of interest with respect to the following aspects: (1) the introduction of multi-carboxylate ligands to {M-bpp} systems via the three-layer diffusion method plays an important role in the formation of fascinating metal-organic frameworks, which is significant for further exploring coordination polymer chemistry; (2) complexes 1-4 with flexible bipyridyl ligands present novel and unprecedented topologies such as perpendicularly linked chains, two-leg ladders and macroanionic sheets structures; (3) combination of d¹⁰ center metals with the conjugated aromatic or pyridine rings from both ligands provides fluorescent materials; (4) complexes such as 1 and 3, owing to absence of inversion centers, could function for a second harmonic generation (SHG) response.

2. Experimental

2.1. General

2,2'-Biphenol and 4-picolyl chloride hydrochloride were purchased from Acros Ltd. Company and were used without further purification, the other reagents were commercially available and were used as purchased. The 4,4'-bpp and 3,3'-bpp ligands were prepared according to the literature methods [9]. The NMR spectra were recorded on a Varian Inova-500 spectrophotometer at room temperature. The mass spectra were measured on a Fisons VG platform. The IR spectra as KBr discs were recorded on a Magna 750 FT-IR spectrophotometer. C, H and N analyses were determined on an Elemental Vario ELIII elemental analyzer. Fluorescent spectra were measured on an Edinburgh Instruments analyzer model FL920. Thermal analyses were performed using a Thermal Analyst 2100 TA Instrument and a SDT 2960 Simultaneous TGA-DTA Instrument.

2.2. Synthesis of complexes

2.2.1. Synthesis of $[Zn(\mu-4,4'-bpp)Br_2]_n$ (1)

A solution of $ZnBr_2 \cdot 4H_2O$ (0.029 g, 0.10 mmol) in H_2O (5 mL) was carefully covered by a buffer layer, prepared by mixing MeOH and water (in a 1:1 ratio). Then a solution of 4,4'-bpp (0.036 g, 0.10 mmol) in MeOH (5 mL) was slowly added above the buffer layer. Over a period of four weeks, light yellow block crystals formed on the buffer layer. Yield: 0.040 g (68%). Elementary *Anal.* Calc. for $C_{24}H_{20}Br_2N_2O_2Zn$ (593.61): C, 48.56; H, 3.40; N, 4.72. Found: C, 48.51; H, 3.43; N, 4.68%. IR (KBr, cm⁻¹): 3430 (vw), 2923 (w), 1623 (s), 1596 (w), 1505 (s), 1483 (s), 1444 (s), 1328 (m), 1269 (s), 1234 (s), 1147 (s), 1054 (m), 1029 (s), 862 (w), 751 (s), 707 (s), 492 (vw).

2.2.2. Synthesis of $[Zn(\mu-4,4'-bpp)(1,2-bdc)]_n \cdot nH_2O(2)$

A solution of $\text{ZnBr}_2 \cdot 4\text{H}_2\text{O}$ (0.029 g, 0.10 mmol), NaOH (0.008 g, 0.20 mmol) and 1, 2-H₂bdc (0.017 g, 0.10 mmol) in H₂O (5 mL) was carefully covered by a buffer layer (MeOH:H₂O = 1:1). Then a solution of 4,4'-bpp (0.036 g, 0.10 mmol) in MeOH (5 mL) was slowly added above the buffer layer. Over a period of four weeks, light yellow block crystals of **2** formed at the buffer layer Yield: 0.051 g (83%). Elementary *Anal.* Calc. for C₃₂H₂₆N₂O₇Zn (615.93): C, 62.40; H, 4.25; N, 4.55. Found: C, 62.15; H, 4.61; N, 4.50%. IR (KBr, cm⁻¹): 3435 (w), 3038 (w), 2853 (w), 1621 (w), 1595 (m), 1479 (m), 1432 (s), 1290 (w), 1231 (s), 1162 (m), 1118 (w), 1029 (m), 812 (w), 751 (s), 726 (s), 643 (w), 494 (w).

2.2.3. Synthesis of $[Zn(\mu-3,3'-bpp)(1,3-$

bdc)]_n · nCH₃OH · 2nH₂O (**3**)

A solution of $\text{ZnBr}_2 \cdot 4\text{H}_2\text{O}$ (0.029 g, 0.10 mmol), NaOH (0.008 g, 0.20 mmol) and 1,3-H₂bdc (0.017 g, 0.10 mmol) in H₂O (5 mL) was carefully covered by buffer layer (MeOH:H₂O = 1:1). Then a solution of 3,3'-bpp (0.036 g, 0.10 mmol) in MeOH (5 mL) was slowly added above the buffer layer. Light yellow block crystals were produced at the buffer layer after a few weeks. Yield: 0.048 g (72%). Elementary *Anal.* Calc. for C₃₃H₃₂N₂O₉Zn (666.01): C, 59.51; H, 4.84; N, 4.21. Found: C, 59.43; H, 4.88; N, 4.16%. IR (KBr, cm⁻¹): 3065 (vw), 2927 (w), 1594 (m), 1500 (s), 1481 (s), 1444 (s), 1432 (s), 1284 (m), 1252 (s), 1227 (s), 1194 (m), 1161 (w), 1107 (s), 1050 (m), 1019 (s), 966 (vw), 871 (w), 751 (s), 701 (s), 669 (w), 616 (vw).

2.2.4. Synthesis of $[Cd(\mu-3,3'-bpp)(C_4H_2O_4)]_n \cdot 3nH_2O(4)$

A solution of $CdBr_2 \cdot 4H_2O$ (0.034 g, 0.10 mmol) and fumaric acid (0.012 g, 0.10 mmol) in H_2O (5 mL) was care-

fully covered by a buffer layer (MeOH:H₂O = 1:1). Then a solution of 3,3'-bpp (0.036 g, 0.10 mmol) in MeOH (5 mL) was slowly added above the buffer layer. Light yellow block crystals of **4** were obtained at the buffer layer after a few weeks. Yield: 0.048 g (75%). Elementary *Anal.* Calc. for C₂₈H₂₈CdN₂O₉ (648.95): C, 51.82; H, 4.35; N, 4.32. Found: C, 52.21; H, 3.99; N, 4.30%. IR (KBr, cm⁻¹): 3109 (vw), 2922 (w), 2165 (w), 1618 (w), 1595 (m), 1583 (m), 1500 (w), 1489 (m), 1453 (s), 1438 (s), 1286 (w), 1271 (s), 1241 (s), 1191 (m), 1161 (w), 1128 (s), 1049 (m), 1031 (m), 937 (vw), 911 (vw), 866 (w), 783 (m), 685 (s), 648 (w) 615 (vw), 544 (vw), 486 (vw), 454 (vw).

2.3. X-ray crystallography

Single crystals of these complexes with appropriate dimensions were mounted on a glass fiber and used for data collection. Data were collected at 293(2) K on a Siemens Smart CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Empirical absence of the centers of symmetries meets the essential requirement of a SHG response. Absorption corrections were applied by using the SADABS program for the Siemens area detector. The structures were solved with direct methods and all calculations were performed using the SHELXTL package [18]. The structures displacement parameters were calculated for all non-hydrogen atoms. The positions of H atoms were generated geometrically and treated as riding on their parent atoms. Details of the crystal data are listed

Table 1				
Crystallographic	data	for	complexes	1–4

in Table 1. Selected bond lengths and angles are listed in Table 2.

3. Results and discussion

3.1. Description of crystal structures

3.1.1. $[Zn(\mu-4,4'-bpp)Br_2]_n$ (1)

Single crystal X-ray diffraction analysis reveals that complex 1 is a chain structure and crystallizes in the orthorhombic space group C222. As depicted in Fig. 1a, complex 1 contains two independent Zn(II) centers. Each Zn(II) center has a slightly distorted tetrahedral geometry and is coordinated by two terminal bromide anions (Zn(1)– Br(1) 2.360(5) Å, Br(1)–Zn(1)–Br(1A) 117.84(3)°; and Zn(2)–Br(2) 2.348(8) Å, Br(2)–Zn(2)–Br(2A) 115.14(5)°). The remaining two coordinative sites of the Zn(II) center in each line are occupied by two nitrogen atoms from different 4,4'-bpp ligands. The bond distances between the Zn(II) center and the nitrogen donor are Zn(1)–N(1) 2.044(3), Zn(2)–N(2) 2.061(4) Å.

Because of steric exclusion, the pyridyl rings of two independent 4,4'-bpp ligands are highly twisted, the dihedral angles between the two pyridyl rings are 68.5° and 21.0° . The dihedral angles between the two phenyl rings in two 4,4'-bpp ligands are 127.6° and 71.5° . The Zn(II) centers are linked by the twisted 4,4'-bpp ligands into a zigzag chain structure. It is noteworthy that the two chains in 1 are nearly perpendicular to each other, as shown in

Complexes	1	2	3	4
Formula	$C_{24}H_{20}Br_2N_2O_2Zn$	C ₃₂ H ₂₆ N ₂ O ₇ Zn	$C_{33}H_{32}N_2O_9Zn$	C28H28CdN2O9
Formula weight	593.61	615.93	666.01	648.95
Crystal size (mm)	$0.45 \times 0.28 \times 0.22$	$0.38 \times 0.26 \times 0.20$	$0.52 \times 0.48 \times 0.40$	$0.32 \times 0.24 \times 0.41$
Crystal system	orthorhombic	triclinic	triclinic	monoclinic
Space group	C222	$P\overline{1}$	$P\overline{1}$	C2
<i>a</i> (Å)	12.631	10.234(3)	10.132(3)	12.9512(10)
b (Å)	14.540	11.079(3)	11.409(3)	31.835(2)
c (Å)	25.6933(10)	12.982(4)	14.038(4)	8.6952(7)
α (°)	90	90.652(2)	86.80(1)	90
β (°)	90	107.426(2)	73.84(1)	100.022(2)
γ (°)	90	102.549(4)	73.69(1)	90
$V(\text{\AA}^3)$	4718.76(18)	1366.1(7)	1495.4(7)	3530.3(5)
Ζ	8	2	2	4
$D_{\rm calc} ({\rm Mg}{\rm m}^{-3})$	1.671	1.502	1.479	1.210
$\mu (\mathrm{mm}^{-1})$	2.460	0.953	0.882	0.663
<i>F</i> (000)	2352	640	692	1296
$T(\mathbf{K})$	173(2)	173(2)	173(2)	173(2)
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073
Reflections collected	16959	11240	11674	3805
Unique reflections	5341	6661	6767	1695
Parameters	141	379	414	199
Goodness-of-fit (S) of F^2	1.042	1.046	1.062	1.165
$R_1, wR_2 [I > 2\sigma(I)]^{\mathrm{a}}$	0.0373, 0.0794	0.0353, 0.1008	0.0422, 0.1019	0.0608, 0.1686
R_1 , wR_2 (all data) ^b	0.0443, 0.0824	0.0399, 0.1029	0.0471, 0.1052	0.0731, 0.1819
Maximum and minimum Δho (e ${ m \AA}^{-3}$)	0.0818 and -0.855	0.687 and -0.704	0.968 and -0.641	0.843 and -0.686

^a
$$R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|.$$

^b
$$wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}, w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}, P = (2F_c^2 + F_o^2)/3.$$

Compound 1							
Zn1–Br1	2.360(5)	Zn1–N1	2.044(3)	Zn2–N2	2.061(4)	N2–Zn2–Br2A	107.17(1)
N1–Zn1–N1A	96.10(2)	N1–Zn1–Br1	112.65(1)	Zn2–Br2A	2.348(8)	N2–Zn1–Br2	113.28(1)
N1A–Zn1–Br1	107.76(1)	N1–Zn1–Br1A	107.76(1)	N2–Zn1–N2A	99.7(3)	Br2A–Zn2–Br	115.14(5)
N1A–Zn1–Br1A	112.65(1)	Br1–Zn1–Br1A	117.84(3)	N2A-Zn2-Br2A	113.28(1)	2 N2A–Zn2–Br2	107.17(1)
Compound 2							
Zn1–O1	1.9246(1)	Zn1–O3B	1.953(1)	Zn1–N2A	2.049(2)	Zn1–N1	2.0751(2)
O1–Zn1–O3B	111.45(6)	O3B-Zn1-N2	104.18(6)	O3B-Zn1-N1	96.90(6)	N2A-Zn(1)-N1	104.91(6)
O1–Zn1–N2A	132.34(6)	O1–Zn1–N1	101.20(6)				
Compound 3							
Zn1–O1	1.974(2)	Zn1-N2A	2.019(2)	Zn1–O3B	1.983(2)	Zn1–N1	2.053(2)
O1–Zn1–O3B	98.00(7)	O1–Zn1–N1	111.19(8)	O3B1-Zn1-N2A	116.61(7)	N2A-Zn1-N1	109.62(8)
O1–Zn1–N2A	110.60(7)	O3B–Zn1–N1	111.36(7)				
Compound 4							
Cd–N1A	2.302(8)	Cd-O1	2.416(9)	Cd–O1B	2.324(9)	Cd–O2	2.486(8)
N1A-Cd-N1	178.8(4)	Cd–O3	2.418(1)	Cd–O4	2.362(9)	N1-Cd-O2	89.6(2)
N1A-Cd-O1B	89.9(2)	N1-Cd-O3	90.57(2)	N1A-Cd-O1	89.42(2)	O1B-Cd-O2	125.5(3)
N1-Cd-O1B	89.85(2)	O1B-Cd-O3	92.6(3)	N1-Cd-O1	89.42(2)	O4–Cd–O2	87.2(4)
N1A-Cd-O4	90.43(2)	O4–Cd–O3	54.6(4)	O1B-Cd-O1	72.4(3)	O1-Cd-O2	53.1(3)
N1-Cd-O4	90.43(2)	O1–Cd–O3	165.1(3)	O4CdO1	140.3(3)	O3–Cd–O2	141.9(4)
		N1A-Cd-O2	89.6(2)	N1A-Cd-O3	90.57(2)	O1B-Cd-O4	147.3(3)

Table 2 Selected bond lengths (Å) and angles (°) for 1–4

Symmetry codes: For 1 A: -x + 1/2, -y + 1/2, B: -x, -y + 1, z, C: -x + 1, -y + 1, z. For 2 A: x - 1, y, z, B: -x + 1, -y + 2, -z + 1. For 3 A: -x, -y + 2, -z + 1, B: x - 1, y, z. For 4 A: x, -y, z, B: -x, -y, -z + 1, C: x, -y, -z + 2.



Fig. 1a. View of the coordination environment of the Zn(II) center in **1** (A: -x + 1/2, -y + 1/2, z; B: -x, -y + 1, z; C: -x + 1, -y + 1; D: x - 1/2, y - 1/2, z).

Fig. 1b. The $Zn \cdots Zn$ separation in both chains is of the same distance, 9.630 Å, while the two nearest Zn(II) centers are at a distance of 11.728 Å. No guest molecules are observed within the distorted rings owing to the high distortion and flexibility of 4,4'-bpp.

3.1.2. $[Zn(\mu-4,4'-bpp)(1,2-bdc)]_n \cdot nH_2O(2)$

The structure of **2** comprises a two-leg ladder running along the [001] direction. An ORTEP view of complex **2** is shown in Fig. 2a. The Zn(II) ion adopts a distorted tetrahedral coordination geometry and is coordinated by two nitrogen atoms from different 4,4'-bpp ligands (Zn(1)– N(2A) 2.0438(15), Zn(1)–N(1) 2.0751(15) Å) and two carboxyl groups from two different 1,2-bdc ligands (Zn(1)–



Fig. 1b. View of the vertical polymer chains in 1.

O(1) 1.9246(13), Zn(1)–O(3B) 1.9534(13) Å, O(1)–Zn(1)–O(3B) 111.45(6)°).

The legs of such a ladder are made up of $[Zn(4,4'-bpp)]_n$ chains, in which Zn(II) ions are bridged by 4,4'-bpp ligands and each ligand acts as an *exo*-bidentate ligand. In the legs, two phenyl rings and two pyridyl rings of each 4,4'-bpp ligand are twisted more evidently than those in **1**. The dihedral angles between them are 111.5° and 51.3°, respectively. The cross rungs of the ladder are made up of 1,2-bdc ligands, where each of the carboxyl groups in a monodentate coordination mode bridges two Zn(II) ions on either side of the ladder. Interestingly, the dihedral angles between the phenyl rings and their corresponding carboxylates are 94.2° and 99.0°, respectively, indicating that the



Fig. 2a. View of the coordination environment of the Zn(II) center in 2 (A: x - 1, y, z; B: -x + 1, -y + 2, -z + 1).

carboxylates are approximately perpendicular, respectively, to phenyl rings. In addition, the $Zn \cdots Zn$ separation among the legs of the ladder is 10.233 Å and the $Zn \cdots Zn$ separation in the cross rungs is 5.153 Å, as shown in Fig. 2b.

3.1.3. $[Zn(\mu-3,3'-bpp)(1,3-bdc)]_n \cdot nCH_3OH \cdot 2nH_2O(3)$

The structure of **3** consists of neutral 1D chains through the connection of [Zn(3,3'-bpp)] units and 1,3-bdc bridging ligands (Fig. 3a). The central Zn(II) ion is coordinated tetrahedrally by two monodentate carboxylate oxygen atoms from two different 1,3-bdc ligands and two nitrogen atoms from two 3,3'-bpp ligands. The Zn–O bond lengths are 1.9721(17) and 1.9836(16) Å, in good agreement with those bond lengths found in other extended structures con-



Fig. 2b. View of two-leg ladder structure in 2.



Fig. 3a. View of the coordination environment of the Zn(II) center in 3 (A: -x, -y + 2, -z + 1; B: x - 1, y, z).

structed from 1,3-bdc and Zn(II) ions, and the Zn–N bond distances are typical, with values of 2.019(0) and 2.052(7) Å. The angles O(1)–Zn(1)–O(3B) of 98.00(7)° and O(3B)–Zn(1)–N(2A) of 116.61(7)° indicate a slight distortion compared with the ideal value of 109°28′. The dihedral angle of the two pyridyl rings attaching to the Zn(II) ion is 83.2°, i.e. they are approximately perpendicular to each other. The 3,3′-bpp ligand acts as *exo*-bidentate, and its pyridyl rings are twisted out of the plane of the linking phenyl rings by 69.0° and 73.7°, while the two phenyl rings of 3,3′-bpp themselves have a drastic twisting with the dihedral angle between them being 25.6°. The combination of these twistings allows 3,3′-bpp to link two Zn(II) ions into a dimetallic ring with the Zn···Zn separation being 8.139 Å.

In addition, both carboxyl groups of the 1,3-bdc ligand link the metal Zn(II) ion in a monodentate fashion and they are deprotonated which is consistent with the IR data (no absorption peaks in the 1715–1680 cm⁻¹ region). The Zn...Zn distance separated by 1,3-bdc is 10.132 Å. The dihedral angles between the phenyl rings and their corresponding carboxylates are 33.7° and 49.7°, indicating a slight twist between them. Thus, every two 1,3-bdc ligands, acting in the monodentate mode, connect the neighbouring



Fig. 3b. View of 1D polymeric chain with dimetallic rings of 3.

dimetallic rings formed by the 3,3'-bpp ligand and Zn(II) centers into an interesting 1D chain structure as shown in Fig. 3b.

3.1.4. $[Cd(\mu-3,3'-bpp)(C_4H_2O_4)]_n \cdot 3nH_2O(4)$

Complex 4 consists of anionic macrocyclic cadmium dicarboxylate sheets which are separated by 3.3'-bpp. The local coordination environment around the Cd(II) center in 4 can be described as a greatly distorted pentagonal bipyramid, as shown in Fig. 4a. Two nitrogen donors from two 3.3'-bpp ligands take up two vertexes of the coordination polyhedron to stop the layer from developing into a 3D framework (Cd-N(1) 2.302(8), Cd-N(1A) 2.302(8) Å, N(1)-Cd-N(1A) 178.8(4)°). The equatorial plane of the coordination polyhedron is composed of five oxygen atoms belonging to three fumarate ligands. Two of the three fumarate units bind the Cd(II) ions through a chelating interaction, while the remaining one exhibits a chelating/bridging bis-bidentate mode. All of five the Cd-O bond lengths are in the range of the documented Cd-O(carboxy) distances (2.324(9)-2.486(8) Å). The oxygen atom O(1), which participates in the chelate-bridged interaction, bridges two Cd(II) atoms to form Cd_2O_2 dimers (Cd. · · Cd, 3.825 Å) through the monodentate interaction, and exhibits the shortest coordination distance (Cd–O(1), 2.324(9) Å). The above binuclear Cd₂O₂ subunit is connected to four neighbouring subunits forming a network which is topologically equivalent to a (4,4) network. Thus, the binuclear subunits are inter-connected through fumarate ligands, which bridge the Cd₂O₂ to generate a parallegram-like sheet with dimensions of 16.809×14.288 Å, as measured from the centers of the binuclear subunits (Fig. 4b).

Moreover, every two 3,3'-bpp ligands, both in *exo*bidentate modes, are attached to the hybrid through the Cd–N bonds to form a hybrid layer as shown in Fig. 4c. It is noteworthy that 3,3'-bpp, twisted due to the steric exclusion requirement, links two Cd(II) centers into a big



Fig. 4a. View of **4** showing the coordination environment around the Cd(II) center (A: x, -y, z, B: -x, -y, -z + 1, C: x, -y, -z + 2).



Fig. 4b. View of 2D structure of the macroanionic cadmium maleic sheets in **4**.



Fig. 4c. View of the hybrid layer of 4.

dimetallic ring, where the dihedral angles between the two phenyl rings and the two pyridyl rings of the 3,3'bpp ligand are 75.3° and 3.1°, respectively. Thus, the metal-metal layers are planar with two N atoms from the 3,3'-bpp ligand pointing above and below the plane. The layers are linked by strong π - π interactions, and the adjacent layers stacking mode can be described as the ABAB type in a staggered arrangement, as shown in Fig. 4d.

3.2. TGA results

To study the stability of the polymers, the thermogravimetric analyses (TGA) for these complexes were performed on polycrystalline samples under a nitrogen atmosphere. The TG curves showed neither weight loss nor structural change up to about 260 °C, demonstrating that the frameworks of 1–4 were retained up to these high temperatures. Immediately above this point, the samples began to lose ligands, the whole frameworks collapsed in a continuous fashion and finally decomposed into unidentified products.

3.3. Luminescence properties

Luminescent polynuclear d^{10} metal complexes (such as Zn(II) and Cd(II)) are of great interest because of their



Fig. 4d. View of the layers constructed of the ... ABAB... type for 4.

potential application in chemical optical sensors, photosensitization and electroluminescent devices. Here, the photoluminescence of these complexes was examined and the solid-state emission spectra are shown in Fig. 5. Complex 1 exhibits a broad emission band with the maximum intensity at 502 nm upon excitation at 370 nm, while complexes 2 and 3 produce an intense pure blue sharp emission with the maximum at ca. 441 nm and a broad emission band with the maximum intensity at 457 nm, respectively, with excitation at 370 nm. For complex 4, two broad emissions at 490 and 526 nm can be observed. For contrast, the free 4.4'-bpp and 3.3'-bpp molecules display the luminescence at around 480 nm in the solid state. Generally, the intraligand fluorescence emission wavelength is determined by the energy gap between the π and π^* molecular orbitals of the free ligand, which is simply related to the extent of π conjugation in the system. As for the metal complexes, the red or blue shifted emissions of complexes 1-4 compared to their free ligands are not only assigned to the



Fig. 5. The emission spectra of 1-4 in the solid state at room temperature.

intramolecular π - π^* and n- π^* transitions of the ligands, but are also attributable to ligand-to-metal charge transfers (LMCT) [19].

In comparison with complex 1, a blue-shift of 61 nm has been observed in complex 2, partially due to the replacement of the Br^- anion by the ligand 1,3-bdc. Although complexes 2 and 3 have different structural motifs, both complexes demonstrate some similar photoluminescence behaviours. The blue-shifted emissions of 2 and 3 may originate from their larger conjugated systems for the two types of ligands as well as their similar distorted tetrahedral coordination geometries of d¹⁰ metal centers, where each of the Zn(II) ions is coordinated by two pyridyl N atoms and two carboxylate O atoms.

Complexes such as 1 and 3 do not have a center of symmetry, which meets the essential requirement of a SHG response. Thus, Kurtz powder SHG measurements on the acentric 1 and 3 were performed, and very weak SHG emissions were observed for both complexes. The weak SHG efficiency may be due to the following fact: the acentricities of 1 and 3 are caused by their twist of the bpp ligands and the arrangements of the individual chains result in a partial cancellation of the effective dipolar moments [20,21].

4. Conclusions

In summary, a series of novel coordination polymers with interesting structural motifs have been synthesized from the flexible bipyridyl ligands (4,4'-bpp or 3,3'-bpp) and d^{10} metal ions (Zn²⁺ or Cd²⁺) as well as carboxylate ligands by the three-layer diffusion method. Complex 1 is a chain structure containing two unusual nearly vertical zigzag Zn(II) chains, and 2 comprises a two-leg ladder, where the legs and cross rungs are made of $[Zn(4,4'-bpp)]_n$ chains and bdc ligands, respectively. In 3, every two 1,3bdc ligands connect the neighbouring dimetallic rings into an interesting 1D structure, while the 2D structure in 4 consists of macroanionic cadmium fumarate sheets separated by 3,3'-bpp ligands. Moreover, TGA measurements exhibit that complexes 1-4 have very similar thermal stability, and studies on the luminescent emissions of these obtained compounds reveal that the d¹⁰ metal ions cause red or blue shifts of the emissions, assigned to intramolecular $\pi - \pi^*$ and $n-\pi^*$ transitions of the ligands.

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Appendix A. Supplementary material

CCDC 268340, 268341, 292808 and 292809 contain the supplementary crystallographic data for 1, 2, 3 and 4.

These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.07.048.

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