

Helical Ribbons of Cadmium(II) and Zinc(II) Dicarboxylates with Bipyridyl-Like Chelates – Syntheses, Crystal Structures and Photoluminescence

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Four mixed-ligand complexes of $[M(\text{mpa})(\text{phen})]_n$ [$M = \text{Cd}$ (**1**) or Zn (**2**) and $\text{mpa} = m$ -phthalate and $\text{phen} = 1,10$ -phenanthroline] and $[M_2(\text{mpa})_2(2,2'\text{-bpy})_2]_n$ [$M = \text{Zn}$ (**3**) or Cd (**4**) and $2,2'\text{-bpy} = 2,2'$ -bipyridine] have been synthesized and their crystal structures have been established by single-crystal X-ray diffraction. They all consist of one-dimensional ribbons featuring dinuclear units. Both **1** and **2** crystallize isomorphously in the monoclinic space group $P2_1/c$ and feature

helical chains. While **3** and **4** crystallize in the triclinic space group $P\bar{1}$. The one-dimensional ribbons are assembled into three-dimensional networks by π - π stacking interactions. They all show strong blue photoluminescence and are stable in air up to ca. 402, 371, 365 and 370 °C, respectively.

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Introduction

The construction of supramolecular architectures is currently of great interest owing to their intriguing network topologies and potential functions such as adsorption, ion exchange, shape-selective catalysis, non-linear and magnetic materials.^[1–3] The strategies for design and tailor-making of such supramolecular architectures with dicarboxylate spacers such as terephthalate, malate, oxalate, 4,4'-oxybis(benzoic acid) are currently interesting. Recently, we and others have reported some interesting polymeric architectures containing linear, nonlinear flexible and V-shaped dicarboxylates together with bipyridyl-like ligands.^[4–11] Chelating bipyridyl-like ligands such as 1,10-phenanthroline and 2,2'-bipyridine are important in maintaining the one dimensionality of the coordination polymers and may provide potential supramolecular recognition sites for π - π aromatic stacking interactions to form interesting supramolecular structures such as double-stranded helices and molecular zippers.^[7,8]

On the other hand, polynuclear d^{10} metal complexes are very attractive in that they not only exhibit intriguing structures but also photoluminescent properties.^[12–17] As a sequel to our previous reports on a series of d^{10} complexes, which show strong luminescent properties,^[4,5,14–16] we now describe four one-dimensional coordination polymers $[M(\text{mpa})(\text{phen})]_n$ [$M = \text{Cd}$ (**1**) or Zn (**2**); $\text{mpa} = m$ -phthalate and $\text{phen} = 1,10$ -phenanthroline] and $[M_2(\text{mpa})_2(2,2'$ -

$\text{bpy})_2]_n$ [$M = \text{Zn}$ (**3**) or Cd (**4**) and $2,2'\text{-bpy} = 2,2'$ -bipyridine], which exhibit different structures compared to the related Cu^{II} complexes,^[7,8] all of which show blue luminescence.

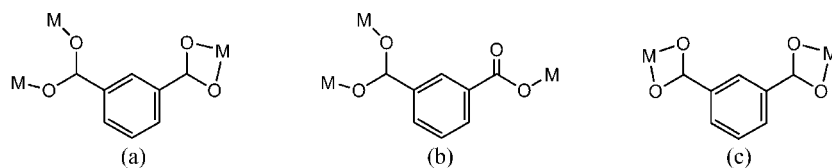
Results and Discussion

Characterization

The IR spectrum of **1** shows characteristic bands of the dicarboxylate groups in the usual region at 1564 and 1515 cm^{-1} for the asymmetric stretching and at 1400 cm^{-1} for the symmetric stretching. The separations (Δ) between $\nu_{\text{asym}}(\text{CO}_2)$ and $\nu_{\text{sym}}(\text{CO}_2)$ are at 164 and 115 cm^{-1} , which are attributed to the existence of both bridging and chelate modes of the carboxylate groups, respectively (Scheme 1, a).^[18] For **2**, the bands are at 1614 and 1558 cm^{-1} for the asymmetric stretching and at 1397 cm^{-1} for the symmetric stretching; the Δ values are at 217 and 161 cm^{-1} , and are attributable to the co-existence of the monodentate and bridging modes (Scheme 1, b). For **3**, the bands of the dicarboxylate units are shown at 1562 and 1532 cm^{-1} for the asymmetric stretching and at 1431 cm^{-1} for the symmetric stretching; the Δ values are at 131 and 101 cm^{-1} , which are attributed to co-existence of the bridging and chelate modes (Scheme 1a, c). Whereas for **4**, the characteristic bands and Δ values are very similar to those found for **1**, indicating that the carboxylate groups exhibit both a bridging and chelate mode. The IR spectra indicate that the mpa carboxylate groups function in different coordination modes, consistent with the crystal structures of **1**, **2**, **3** and **4**.

Thermogravimetric analysis (TGA) was performed on polycrystalline samples in air. There was no decomposition

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Scheme 1. Coordination modes of mpa: (a) chelate-bidentate, (b) monodentate-bidentate and (c) chelating bis(bidentate)

up to ca. 402, 371, 365 and 370 °C for **1**, **2**, **3** and **4**, respectively, suggesting that the products are more stable than the related ones synthesized by the conventional solution method, at room temperature.^[17]

Crystal Structures

Complexes **1**, **2**, **3** and **4** all consist of one-dimensional ribbons. Both **1** and **2** crystallize isomorphously in the monoclinic space group $P2_1/c$, while **3** and **4** crystallize in the triclinic space group $P\bar{1}$ (see Tables 1 and 2).

In the crystal structure of **1**, there is one Cd^{II} atom, one mpa ligand and one phen ligand in each independent crystallographic unit. As shown in Figure 1, each Cd^{II} atom in **1** is primarily coordinated by two nitrogen atoms [$\text{Cd1-N1} = 2.395(4)$, $\text{Cd1-N2} = 2.377(5)$ Å, $\text{N2-Cd1-N1} = 70.5(2)^\circ$] of a chelating phen ligand, two oxygen atoms of two μ -carboxylate ends of two mpa ligands [$\text{Cd1-O2A} = 2.255(4)$, $\text{Cd1-O1B} = 2.301(4)$ Å, $\text{O2A-Cd1-O1B} = 99.7(2)^\circ$] and two oxygen atoms of one chelating carboxylate end of one mpa ligand [$\text{Cd1-O4} =$

$2.453(4)$, $\text{Cd1-O3} = 2.331(4)$ Å, $\text{O3-Cd1-O4} = 55.2(1)^\circ$] to furnish a highly distorted octahedral geometry. Two Cd^{II} atoms related by a twofold axis are bridged by a pair of the mpa μ -carboxylate ends into a dinuclear unit [$\text{Cd1}\cdots\text{Cd1A} = 3.99$ Å]. A face-to-face distance of 3.51 Å between a pair of phen ligands coordinated to the two Cd^{II} atoms is observed, showing significant intramolecular π - π interactions.

In fact, the V-shaped mpa ligand acts in the chelate-bidentate coordination mode (see Scheme 1, a) to link the adjacent Cd^{II} atoms into one-dimensional helical ribbons with a pitch of 9.55 Å running along the c axis (Figure 2, a). Pairs of phen ligands are alternately attached to both sides of the ribbon; the adjacent zigzag ribbons are packed through intercalation of the lateral phen ligands (face-to-face distance 3.32 Å), in the zipper-like fashion, into two-dimensional networks parallel to the bc plane. Adjacent ribbons also have strong intermolecular π - π interactions^[19–23] between the mpa phenyl rings in an offset fashion with a face-to-face distance of ca. 3.38 Å, which

Table 1. Crystallographic data for **1–4**

	1	2	3	4
Empirical formula	$\text{C}_{20}\text{H}_{12}\text{CdN}_2\text{O}_4$	$\text{C}_{20}\text{H}_{12}\text{N}_2\text{O}_4\text{Zn}$	$\text{C}_{36}\text{H}_{24}\text{N}_4\text{O}_8\text{Zn}_2$	$\text{C}_{36}\text{H}_{24}\text{Cd}_2\text{N}_4\text{O}_8$
Formula mass	456.72	409.69	771.33	865.39
Temperature [K]	293	293	293	228
Crystal color and form	colorless prisms	pale-yellow blocks	pale-yellow blocks	colorless blocks
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$ (no. 13)	$P2_1/c$ (no. 13)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a [Å]	8.391(6)	8.730(4)	9.44(1)	9.425(2)
b [Å]	10.681(8)	10.34(1)	11.40(1)	10.267(2)
c [Å]	19.10(2)	18.57(2)	16.98(1)	18.649(4)
α [°]			100.07(1)	74.03(3)
β [°]	100.73(2)	99.65(2)	94.02(1)	85.93(3)
γ [°]			110.50(1)	64.15(3)
Volume [Å ³]	1682(2)	1652(2)	1670(2)	1558.8(6)
Z	4	4	2	2
$D_{\text{calcd.}}$ [Mg/m ³]	1.803	1.647	1.534	1.844
Absorption coefficient [mm ⁻¹]	1.329	1.517	1.496	1.428
$F(000)$	904	832	784	856
Crystal size [mm]	$0.30 \times 0.25 \times 0.20$	$0.35 \times 0.33 \times 0.27$	$0.50 \times 0.40 \times 0.35$	$0.52 \times 0.48 \times 0.42$
θ_{max} [°]	26.0	28.0	26.0	28.31
Reflections collected	3554	2938	6572	10180
Independent reflections	3321	2685	6553	7385
Number of parameters	245	245	452	452
Goodness-of-fit on F^2	1.053	1.060	1.038	1.179
Final R indices [$I \geq 2\sigma(I)$] ^[a] ^[b]	$R_1 = 0.0455$, $wR_2 = 0.1226$	$R_1 = 0.0538$, $wR_2 = 0.1370$	$R_1 = 0.0651$, $wR_2 = 0.1537$	$R_1 = 0.0342$, $wR_2 = 0.0827$
R indices (all data) ^[a] ^[b]	$R_1 = 0.0621$, $wR_2 = 0.1331$	$R_1 = 0.0707$, $wR_2 = 0.1491$	$R_1 = 0.1247$, $wR_2 = 0.1837$	$R_1 = 0.0392$, $wR_2 = 0.0939$
Largest peak and hole [e ⁻ Å ⁻³]	0.947 and -0.849	0.631 and -0.836	0.502 and -0.845	0.882 and -0.623

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

Table 2. Selected bond lengths [Å] and angles [°]; symmetry codes: (A) $x, -y, z + 1/2$, (B) $-x, -y, -z$, for **1** and **2**, (A) $-x, -y, -z + 1$, (B) $x, y + 1, z$, for **3**, (A) $-x, -y + 2, -z + 1$, (B) $x + 1, y - 1, z + 1$, for **4**

1			
Cd(1)–O(3)	2.331(4)	Cd(1)–O(4)	2.453(4)
Cd(1)–O(2A)	2.255(4)	Cd(1)–N(1)	2.395(4)
Cd(1)–O(1B)	2.301(4)	Cd(1)–N(2)	2.377(5)
O(2A)–Cd(1)–O(1B)	99.7(2)	O(3)–Cd(1)–N(2)	137.4(1)
O(2A)–Cd(1)–O(3)	100.6(2)	O(2A)–Cd(1)–N(1)	169.7(2)
O(1B)–Cd(1)–O(3)	94.7(1)	O(1B)–Cd(1)–N(1)	79.2(2)
O(2A)–Cd(1)–N(2)	101.4(2)	O(3)–Cd(1)–N(1)	89.7(2)
O(1B)–Cd(1)–N(2)	116.9(2)	N(2)–Cd(1)–N(1)	70.5(2)
O(2A)–Cd(1)–O(4)	99.2(2)	O(1B)–Cd(1)–O(4)	146.9(1)
O(3)–Cd(1)–O(4)	55.2(1)	N(2)–Cd(1)–O(4)	85.4(1)
N(1)–Cd(1)–O(4)	86.7(2)		
2			
Zn(1)–O(3)	2.026(3)	Zn(1)–N(2)	2.175(4)
Zn(1)–O(1B)	2.033(4)	Zn(1)–N(1)	2.218(4)
Zn(1)–O(2A)	2.045(3)		
O(3)–Zn(1)–O(1B)	97.4(2)	O(2A)–Zn(1)–N(2)	92.9(2)
O(3)–Zn(1)–O(2A)	101.8(2)	O(3)–Zn(1)–N(1)	92.5(2)
O(1B)–Zn(1)–O(2A)	96.2(2)	O(1B)–Zn(1)–N(1)	83.4(2)
O(3)–Zn(1)–N(2)	131.4(2)	O(2A)–Zn(1)–N(1)	165.6(1)
O(1B)–Zn(1)–N(2)	127.0(2)	N(2)–Zn(1)–N(1)	76.2(2)
3			
Zn(1)–O(1)	2.454(5)	Zn(2)–O(7)	2.066(4)
Zn(1)–O(2)	2.085(4)	Zn(2)–O(8)	2.391(5)
Zn(1)–O(6)	2.095(5)	Zn(2)–O(4B)	2.012(5)
Zn(1)–O(5A)	2.039(4)	Zn(2)–O(3B)	2.469(5)
Zn(1)–N(1)	2.165(5)	Zn(2)–N(3)	2.165(6)
Zn(1)–N(2)	2.198(6)	Zn(2)–N(4)	2.086(5)
O(5A)–Zn(1)–O(2)	103.8(2)	O(4B)–Zn(2)–O(7)	101.0(2)
O(5A)–Zn(1)–O(6)	105.5(2)	O(4B)–Zn(2)–N(4)	152.3(2)
O(2)–Zn(1)–O(6)	93.6(2)	O(7)–Zn(2)–N(4)	106.4(2)
O(5A)–Zn(1)–N(1)	103.5(2)	O(4B)–Zn(2)–N(3)	98.3(2)
O(2)–Zn(1)–N(1)	151.1(2)	O(7)–Zn(2)–N(3)	105.9(2)
O(6)–Zn(1)–N(1)	88.6(2)	N(4)–Zn(2)–N(3)	77.7(2)
O(5A)–Zn(1)–N(2)	85.9(2)	O(4B)–Zn(2)–O(8)	98.4(2)
O(2)–Zn(1)–N(2)	96.9(2)	O(7)–Zn(2)–O(8)	59.7(2)
O(6)–Zn(1)–N(2)	162.3(2)	N(4)–Zn(2)–O(8)	92.4(2)
N(1)–Zn(1)–N(2)	75.5(2)	N(3)–Zn(2)–O(8)	159.8(2)
O(5A)–Zn(1)–O(1)	158.6(2)	O(4B)–Zn(2)–O(3B)	57.9(2)
O(2)–Zn(1)–O(1)	58.2(2)	O(7)–Zn(2)–O(3B)	151.0(2)
O(6)–Zn(1)–O(1)	88.3(2)	N(4)–Zn(2)–O(3B)	95.1(2)
N(1)–Zn(1)–O(1)	93.1(2)	N(3)–Zn(2)–O(3B)	97.4(2)
N(2)–Zn(1)–O(1)	85.1(2)	O(8)–Zn(2)–O(3B)	101.0(2)
4			
Cd(1)–O(1)	2.281(3)	Cd(2)–O(7)	2.245(2)
Cd(1)–O(2)	2.524(3)	Cd(2)–O(8)	2.559(3)
Cd(1)–O(6)	2.246(2)	Cd(2)–O(4B)	2.247(3)
Cd(1)–O(5A)	2.252(3)	Cd(2)–O(3A)	2.285(3)
Cd(1)–N(1)	2.379(3)	Cd(2)–N(3)	2.325(3)
Cd(1)–N(2)	2.333(3)	Cd(2)–N(4)	2.332(3)
O(5A)–Cd(1)–O(2)	87.3(1)	O(4B)–Cd(2)–O(7)	90.7(1)
O(5A)–Cd(1)–O(6)	117.1(1)	O(4B)–Cd(2)–N(4)	93.9(1)
O(2)–Cd(1)–O(6)	138.58(9)	O(7)–Cd(2)–N(4)	105.9(1)
O(5A)–Cd(1)–N(1)	84.6(1)	O(4B)–Cd(2)–N(3)	88.6(1)
O(2)–Cd(1)–N(1)	131.56(9)	O(7)–Cd(2)–N(3)	176.65(9)
O(6)–Cd(1)–N(1)	86.1(1)	N(4)–Cd(2)–N(3)	70.89(9)
O(5A)–Cd(1)–N(2)	133.8(1)	O(4B)–Cd(2)–O(8)	140.0(1)
O(2)–Cd(1)–N(2)	83.13(9)	O(7)–Cd(2)–O(8)	54.40(8)
O(6)–Cd(1)–N(2)	99.00(9)	N(4)–Cd(2)–O(8)	79.96(9)
N(1)–Cd(1)–N(2)	69.27(9)	N(3)–Cd(2)–O(8)	125.06(8)
O(5A)–Cd(1)–O(1)	100.2(1)	O(4B)–Cd(2)–O(3A)	123.2(1)
O(2)–Cd(1)–O(1)	54.08(8)	O(7)–Cd(2)–O(3A)	94.6(1)
O(6)–Cd(1)–O(1)	87.3(1)	N(4)–Cd(2)–O(3A)	137.5(1)
N(1)–Cd(1)–O(1)	173.14(9)	N(3)–Cd(2)–O(3A)	88.6(1)
N(2)–Cd(1)–O(1)	109.9(1)	O(8)–Cd(2)–O(3A)	82.64(9)

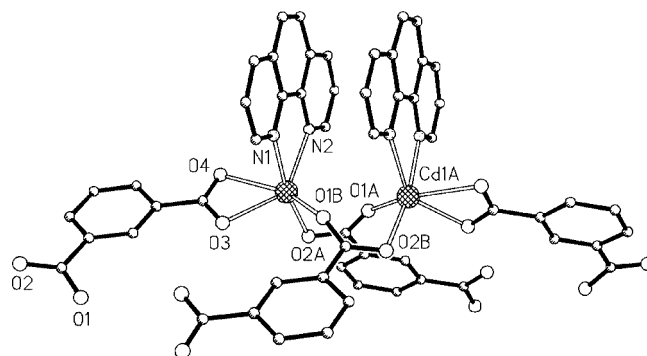


Figure 1. Perspective view of the coordination environments of the metal atoms with atomic labels in **1**

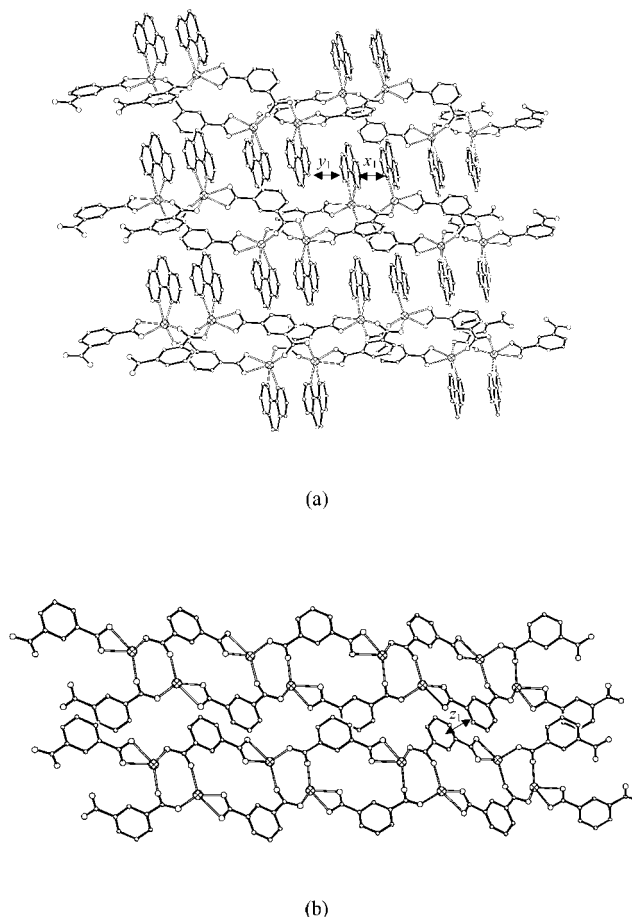


Figure 2. Perspective views of the two-dimensional networks parallel to the bc plane (a) and the ac plane (b) in **1**; the arrow in (b) highlights the intermolecular π – π interaction between the mpa phenyl rings; the face-to-face distances for the π – π interactions are $x_1 = 3.51$ Å, $y_1 = 3.32$ Å and $z_1 = 3.38$ Å

also extend the ribbons into two-dimensional networks (Figure 2, b) in another direction parallel to the ab plane. Therefore, these ribbons are in fact stacked through two different kinds of aromatic π – π stacking interactions, between phen ligands and mpa ligands, into a three-dimensional architecture in the lattice.

In the crystal structure of **2**, each Zn^{II} atom is primarily coordinated by two nitrogen atoms [$\text{Zn}–\text{N} = 2.175(4)$ or

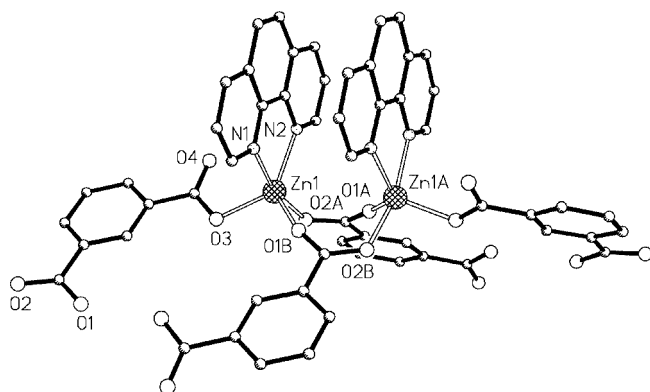
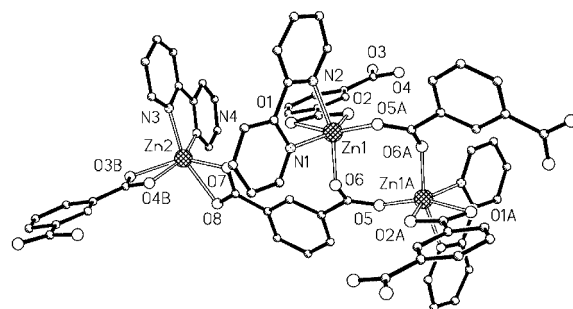


Figure 3. Perspective view of the coordination environments of the metal atoms with atomic labels in **2**

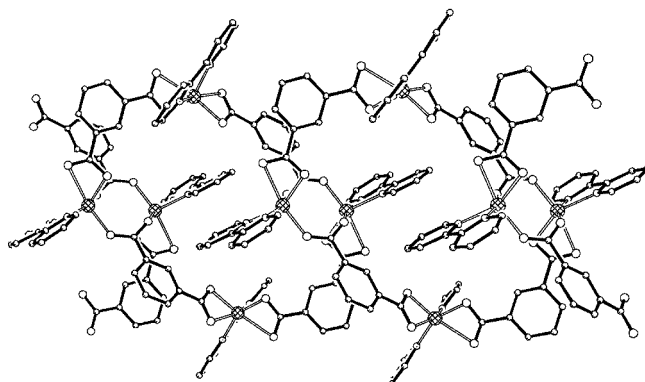
2.218(4) Å] from a chelating phen ligand and three oxygen atoms [Zn–O = 2.026(3)–2.045(3) Å] from two μ -carboxylate ends and one monodentate carboxylate end of three mpa ligands in a distorted trigonal arrangement, in which the N1 and O2A atoms occupy the axial positions and the pendant carboxy O4 atom has no significant interaction with Zn1 [Zn1...O4 = 2.675(4) Å] (Figure 3). The intradimeric Zn...Zn distance (3.933 Å) and the face-to-face distance (3.52 Å) between the two phen ligands are similar to those found in **1**.

All the mpa ligands in **2** exhibit the monodentate-bidentate coordination mode (Scheme 1, b), and the pitch of the helical ribbon is 9.29 Å, being shorter than that in **1**. These differences may be attributed to the radius of the Cd^{II} atom being larger than that of the Zn^{II} atom, resulting in different coordination environments. On the other hand, adjacent ribbons in **2** are packed in a highly similar fashion to **1** through the π – π stacking interactions between the lateral phen ligands with face-to-face distances of ca. 3.29 Å and between the mpa phenyl rings with face-to-face distances of ca. 3.35 Å, into a three-dimensional network in the solid.

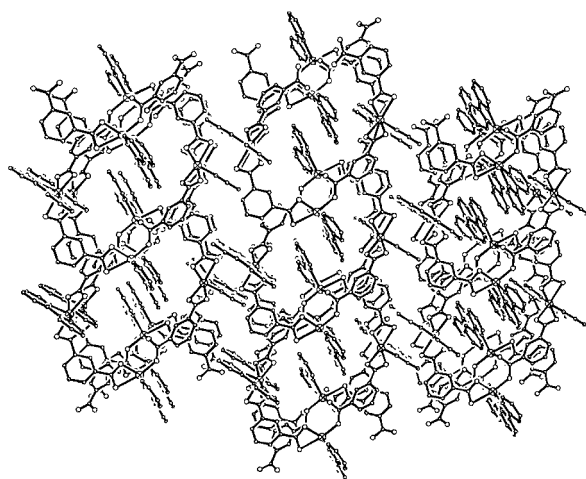
When 2,2'-bpy, an aromatic chelate ligand of smaller size, was used instead of phen, different ribbons were formed in **3** and **4** under similar reaction conditions. As illustrated in Figure 4 (a), there are two different metal coordination environments in **3**. Zn1 is coordinated by two oxygen atoms of one chelating carboxylate end of one mpa ligand [Zn1–O1 = 2.454(5), Zn1–O2 = 2.085(4) Å, O1–Zn1–O2 = 58.2(2)°], two oxygen atoms of two μ -carboxylate ends of two mpa ligands [Zn1–O5A = 2.039(4), Zn1–O6 = 2.095(5) Å, O5A–Zn1–O6 = 105.5(2)°] and two nitrogen atoms of a chelate 2,2'-bpy ligand [Zn1–N1 = 2.165(5), Zn1–N2 = 2.198(6) Å, N1–Zn1–N2 = 75.5(2)°] to furnish a highly distorted octahedral environment, whereas Zn2 is ligated by four oxygen atoms of two chelating carboxylate ends of two mpa ligands [Zn2–O = 2.012(5)–2.469(5) Å, O3B–Zn2–O4B = 57.9(2), O7–Zn2–O8 = 59.7(2)°] and two nitrogen atoms of a chelate 2,2'-bpy ligand [Zn2–N4 = 2.086(5), Zn2–N3 = 2.165(6) Å, N3–Zn2–N4 = 77.7(2)°] to complete a highly distorted octahedral geometry.



(a)



(b)



(c)

Figure 4. Perspective views of the coordination environments of the metal atoms with atomic labels (a), the one-dimensional ribbon running along the *b* axis (b) and the three-dimensional network (c) in **3**

The Zn1 atom in **3** is bridged by two μ -carboxylate ends to a crystallographically equivalent Zn^{II} atom to generate a dinuclear unit [Zn1...Zn1A = 4.324 Å] (Figure 4, a). The distance of Zn1...Zn1A is longer than in **2**, which may be attributed to the different coordination geometry and the orientation of the two 2,2'-bpy ligands around the two Zn^{II} atoms. The dinuclear units are interconnected to the mononuclear Zn2 sites, furnishing one-dimensional ribbons

along the *b* axis, which exhibit large rings each comprising four bridging V-shaped mpa ligands, two dinuclear units and two mononuclear units. The ribbon is decorated by 2,2'-bpy ligands in four different orientations (Figure 4, b). In fact, the V-shaped mpa ligands in **3** exhibit two different modes, chelate-bidentate (Scheme 1, a) and chelating bis(bidentate) (Scheme 1, c). The bridging bidentate ends of the chelate-bidentate mpa ligands contribute to the formation of the dinuclear units, whereas the chelate ends are connected to both the mono- and dinuclear Zn^{II} sites. The 2,2'-bpy ligands are orientated outwards of the ribbon and thus play an important role in packing adjacent ribbon chains into three-dimensional networks (Figure 4, c) through π - π stacking interactions (face-to-face distance ca. 3.56 or 3.62 Å). It should be pointed out that the π - π stacking interactions for mpa ligands in **3** are insignificant compared to those of **1** and **2**.

In the crystal structure of **4**, there are two Cd^{II} atoms, two mpa ligands and two phen ligands in each independent crystallographic unit. Cd1 is coordinated by two oxygen atoms from one chelating carboxylate end of one mpa ligand [Cd1–O1 = 2.281(3), Cd1–O2 = 2.524(3) Å, O1–Cd1–O2 = 54.08(8)°], two oxygen atoms of two μ -carboxylate ends of two mpa ligands [Cd1–O5A = 2.252(3), Cd1–O6 = 2.246(2) Å, O5A–Cd1–O6 = 117.1(1)°] and two nitrogen atoms of a chelate 2,2'-bpy ligand [Cd1–N1 = 2.379(3), Cd1–N2 = 2.333(3) Å, N1–Cd1–N2 = 69.27(9)°] to furnish a highly distorted octahedral coordination. Similarly to Cd1, Cd2 is also coordinated in a highly distorted octahedral geometry (see Table 2). The two crystallographically independent Cd^{II} atoms are each bridged by two μ -carboxylate ends to its crystallographically equivalent Cd^{II} atom to generate a dinuclear unit (Figure 5, a). Such dinuclear units are further extended by the bridging mpa ligands into one-dimensional helical ribbons with a pitch of 9.71 Å running along the (1 $\bar{1}$ 1) direction, which are decorated by 2,2'-bpy ligands at both sides. Since the pair of 2,2'-bpy ligands are orientated in opposite directions of the dinuclear unit, the geometry of the unit is hence different, concomitant with larger intradinuclear metal–metal distances (Cd1...Cd1A = 4.364 Å, Cd2...Cd2A = 4.181 Å) compared to that in **1**. These geometric differences may be attributed to the significant intramolecular π - π stacking interactions in **1**. The V-shaped mpa ligands in **4** exhibit uniquely the chelate-bidentate coordination mode (Scheme 1, a). Adjacent ribbons are intercalated in a zipper fashion into two-dimensional layers through the π - π stacking interactions between the 2,2'-bpy ligands with face-to-face distances of ca. 3.47–3.64 Å (Figure 5, b), and the layers are further packed into a three-dimensional network by van der Waals interactions. Similar to **3**, there are no significant π - π stacking interactions from the mpa ligands.

In our previous reports, we have shown that appropriate combinations of nonlinear flexible/V-shaped dicarboxylates with chelating phen can furnish interesting one-dimensional supramolecular structures such as molecular zippers as well as single- and double-stranded helices.^[7,8] In particular, a

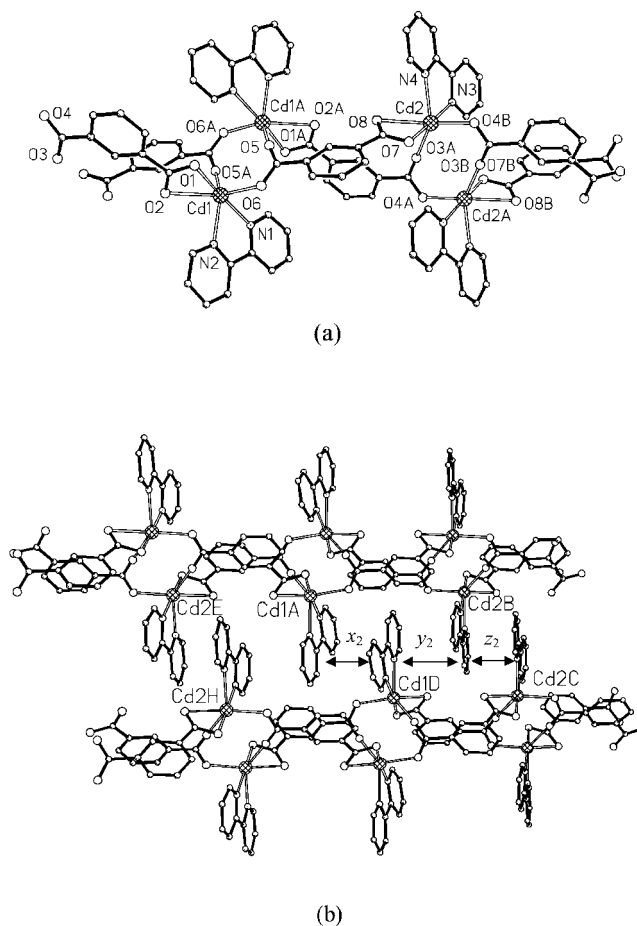


Figure 5. Perspective views of the coordination environments of the metal atoms (a) and the two-dimensional ribbons (b) in **4**; the face-to-face distances for the π - π interactions are x_2 = 3.48 Å, y_2 = 3.64 Å and z_2 = 3.47 Å

combination of V-shaped mpa ligands with chelating phen and 2,2'-bpy ligands along with the Cu^{II} ions generated single-stranded helical chains, namely [Cu₂(mpa)₂(phen)₂·(H₂O)]_n and [Cu(mpa)(2,2'-bpy)]_n·2nH₂O.^[7] In contrast, using Cd^{II} or Zn^{II} atoms in place of Cu^{II} atoms under similar reaction conditions, the one-dimensional ribbons of **1–4** comprising dinuclear units were isolated. These observations may be attributed to the fact that the Cu^{II} has a greater tendency towards square-planar coordination tendency than the Cd^{II} and Zn^{II} atoms and the fact that Cd^{II} and Zn^{II} atoms have a tendency to form dinuclear structural units in the presence of the aromatic chelates. Actually, in [Cu₂(mpa)₂(phen)(H₂O)]_n and [Cu(mpa)(2,2'-bpy)]_n·2nH₂O as well as other related coordination polymers,^[7] the one-dimensional chains are based on mononuclear structural units featuring primarily a square-planar geometry, compared to those in **1**, **2**, **3** and **4**. Therefore the dinuclear structural units in **1**, **2**, **3** and **4** represent new examples of building blocks among the dicarboxylate-bridged one-dimensional coordination polymers. On the other hand, different aromatic chelates also have a significant effect on the structures, as evidenced by the fact that the structure of **3** is significantly different from that of **1** and **2**.

Photoluminescence

The solid-state photoluminescent spectra of **1**, **2**, **3** and **4** at room temperature are depicted in Figure 6. Complexes **1** and **2** both exhibit intense blue photoluminescence with an emission maximum at ca. 423 and 420 nm upon excitation at 317 and 334 nm, respectively. According to the previous observations,^[4,16,24–29] these emission bands would be assigned to the emission of ligand-to-metal charge transfer (LMCT). Whereas there are two intense emission maxima at ca. 397 and 413 nm for **3**, and ca. 405 and 422 nm for **4** upon excitation at ca. 347 and 355 nm, respectively. The peaks at 413 and 422 nm would be assigned to the emission of LMCT,^[4,5,26,28,29] while the peaks at 397 and 405 nm would be distributed to the intraligand emission from the 2,2'-bpy ligand.^[5,30] It is known that the free 2,2'-bpy molecule displays a weak luminescence at ca. 530 nm in the

solid state at room temperature. The enhancement and significant blue-shift (up to 400 nm)^[30] of the luminescence of the 2,2'-bpy ligand compared to that of the free 2,2'-bpy molecule may therefore be attributed to the chelating of the 2,2'-bpy ligand to the metal ion, which effectively increases the rigidity of the ligand and reduces the loss of energy by radiationless decay of the intraligand emission excited state.^[24]

Conclusion

We have synthesized four stable one-dimensional ribbon-like coordination polymers under hydrothermal conditions, which show new dinuclear structural units as building blocks among the dicarboxylate-bridged one-dimensional coordination polymers as well as interesting photoluminescent properties. Compared to our previous one-dimensional copper(II) analogues, it has been found that different coordinations may have a very significant effect on the structures of the one-dimensional chains. Different combinations of nonlinear flexible/V-shaped dicarboxylates with chelating phen and 2,2'-bpy ligands in the presence of different metal ions, such as Cu, Cd and Zn, can furnish different one-dimensional supramolecular structures, such as molecular zippers, single- and double-stranded helices,^[7,8] as well as helical ribbons.

Experimental Section

General Remarks: All chemicals were commercially available and used as received without further purification. The C, H and N microanalyses were carried out with a Perkin–Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{−1} with a Nicolet 5DX spectrometer. All the excitation and emission spectra were measured with an Aminco Bowman Series 2 with a xenon arc lamp as the excitation light source for the solid-state samples. Thermogravimetric analysis (TGA) data were collected with a Perkin–Elmer TGS-2 analyzer in air at a heating rate of 10 °C min^{−1}.

Preparation of [Cd(mpa)(phen)]_n (1**):** A mixture of Cd(NO₃)₂·9H₂O (1.0 mmol), H₂mpa (0.5 mmol), phen (1.0 mmol), NaOH (1.0 mmol) and water (10 mL) was stirred in air for 15 min, then transferred and sealed in a 23-mL Teflon-lined reactor, which was heated at 160 °C for 5 d and then cooled to room temperature at a rate of 5 °C h^{−1}. Colorless prisms were obtained, washed with deionized water and absolute ethanol (yield > 40% based on Cd). C₂₀H₁₂CdN₂O₄ (456.72): calcd. C 52.59, H 2.65, N 6.13; found C 52.70, H 2.59, N 6.20. IR (KBr, cm^{−1}): $\tilde{\nu}$ = 3417 s, 3169 s, 1979 w, 1615 s, 1564 s, 1515 m, 1481 w, 1400 s, 1145 m, 1102 m, 1049 w, 909 w, 859 s, 825 w, 783 m, 729 s and 635 m. TGA analysis of **1** shows a weight loss starting at ca. 402 °C.

Preparation of [Zn(mpa)(phen)]_n (2**):** Complex **2** was prepared as for **1**. Pale yellow blocks of **2** were obtained, washed with deionized water and absolute ethanol (yield > 60% based on Zn). C₂₀H₁₂N₂O₄Zn (409.69): calcd. C 58.63, H 2.95, N 6.84; found C 58.58, H 2.88, N 6.90. IR (KBr, cm^{−1}): $\tilde{\nu}$ = 3433 s, 3334 m, 3193 m, 3000 w, 1614 s, 1558 m, 1515 m, 1453 m, 1397 s, 1271 w, 1168 m, 1098 w, 850 s, 782 m, 744 w, 723 s, 592 m and 528 w. Decomposition of the polymeric framework of **2** began at ca. 371 °C.

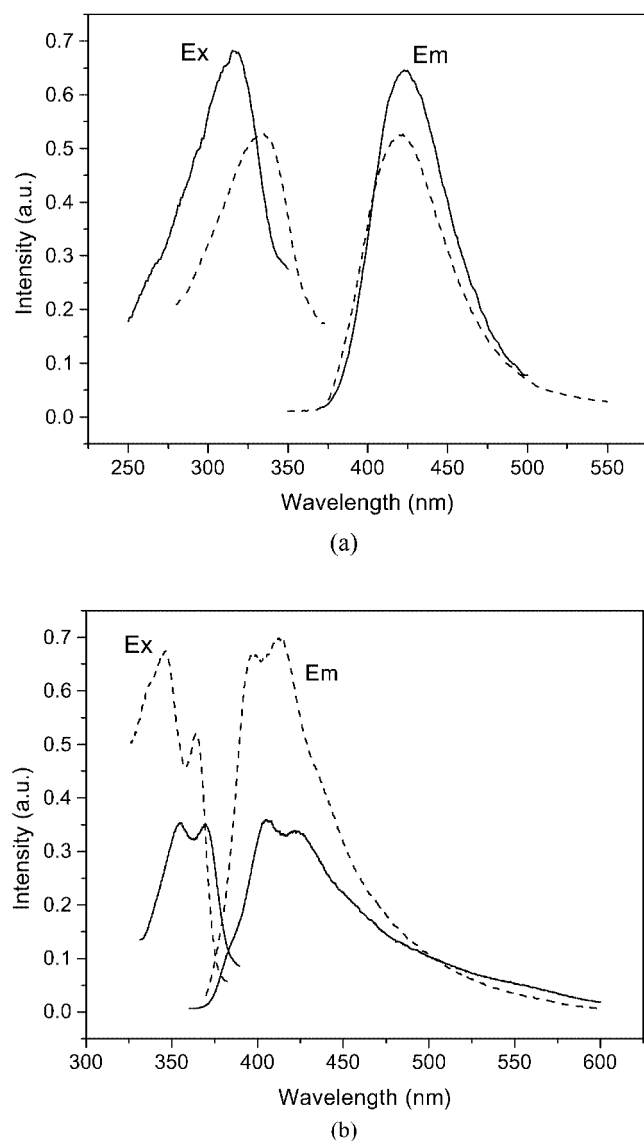


Figure 6. The excitation and emission spectra of **1–4** in the solid state at room temperature; the solid lines represent **1** and the dash-dot ones represent **2** in (a); the solid lines represent **4** and the dash-dot ones represent **3** in (b)

Preparation of $[\text{Zn}_2(\text{mpa})_2(2,2'\text{-bpy})_2]_n$ (3): A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ (1.0 mmol), H_2mpa (0.5 mmol), $2,2'\text{-bpy}$ (1.0 mmol), NaOH (1.0 mmol) and water (10 mL) was stirred in air for 15 min, then transferred and sealed in a 23-mL Teflon-lined reactor, which was heated at 160 °C for 5 d and then cooled to room temperature at a rate of 5 °C h⁻¹. Colorless prisms were obtained, washed with deionized water and absolute ethanol (yield > 35% based on Zn). $\text{C}_{36}\text{H}_{24}\text{N}_4\text{O}_8\text{Zn}_2$ (771.33): calcd. C 56.05, H 3.14, N 7.26; found C 56.11, H 3.01, N 7.33. IR (KBr, cm⁻¹): $\tilde{\nu}$ = 3424 s, 3108 s, 3069 s, 1902 w, 1943 w, 1612 s, 1562 s, 1532 s, 1431 s, 1383 s, 1159 m, 1074 m, 1020 m, 934 w, 849 m, 827 m, 750 m, 658 s, and 583 m. TGA analysis of **3** shows a weight loss starting at ca. 365 °C.

Preparation of $[\text{Cd}_2(\text{mpa})_2(2,2'\text{-bpy})_2]_n$ (4): Complex **4** was prepared as for **3**. Colorless blocks of **4** were obtained, washed with deionized water and absolute ethanol (yield > 50% based on Zn). $\text{C}_{36}\text{H}_{24}\text{Cd}_2\text{N}_4\text{O}_8$ (856.39): calcd. C 49.96, H 2.80, N 6.47; found C 49.88, H 2.85, N 6.54. IR (KBr, cm⁻¹): $\tilde{\nu}$ = 3414 s, 3109 m, 3050 m, 1602 s, 1552 s, 1474 m, 1436 s, 1381 s, 1314 m, 1247 w, 1154 m, 1078 m, 1016 s, 908 w, 827 m, 727 m, 717 s, and 652 w. Decomposition of the polymeric framework of **4** began at ca. 370 °C.

X-ray Crystallographic Study: A summary of the crystal data for **1**, **2**, **3** and **4** is given in Table 1. Selected bond lengths and angles are listed in Table 2. Drawings were produced with SHELXTL. The intensity data of **1**, **2** and **3** were collected with a Siemens R3m diffractometer using the ω -scan technique with graphite-monochromated Mo- K_α (λ = 0.71073 Å) radiation at room temperature and the intensity data of **4** were collected with a Bruker Apex CCD diffractometer with the graphite-monochromated Mo- K_α (λ = 0.71073 Å) radiation at 228 K in the ω -2 θ scan mode. Lorentz-polarization and absorption corrections were applied.^[31] The structures were solved with direct methods and refined with a full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs,^[32,33] respectively. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically (C–H 0.96 Å); the aqua hydrogen atoms were located from difference maps and refined with isotropic temperature factors. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.^[34] CCDC-212917 (**1**), -212918 (**2**), -212919 (**3**), -212920 (**4**) contain the supplementary crystallographic data for this paper. 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: deposit@ccdc.cam.ac.uk].

Acknowledgments

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