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### Synthesis, crystal structures and photoluminescence of three new Mn(II) coordination polymers assembled from 2,4'-diphenic acid

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## Synthesis, crystal structures and photoluminescence of three new Mn(II) coordination polymers assembled from 2,4'-diphenic acid

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Three new metal coordination polymers,  $[\text{Mn}(\text{Hdpa})_2(4,4'\text{-bipy})_2]_n$  (**1**),  $[\text{Mn}(\text{dpa})(1,10\text{-phen})(\text{H}_2\text{O})]_n$  (**2**), and  $[\text{Mn}(\text{dpa})(2,2'\text{-bipy})]_n$  (**3**) ( $\text{H}_2\text{dpa} = 2,4'$ -biphenyl-dicarboxylic acid,  $4,4'$ -bipy =  $4,4'$ -bipyridine,  $1,10\text{-phen} = 1,10$ -phenanthroline, and  $2,2'\text{-bipy} = 2,2'$ -bipyridine), have been synthesized and characterized by elemental analysis, IR, and X-ray diffraction. Single-crystal X-ray analyses reveal that  $2,4'$ -diphenic acid is a bridging ligand, exhibiting three coordination modes to link metal ions:  $\mu_1\text{-}\eta^1:\eta^1/\mu_0\text{-}\eta^0:\eta^0$ ;  $\mu_2\text{-}\eta^2:\eta^0/\mu_1\text{-}\eta^1:\eta^0$ ; and  $\mu_2\text{-}\eta^1:\eta^1/\mu_2\text{-}\eta^1:\eta^1$ . Intermolecular hydrogen bonds in **1** lead to a zigzag chain. In **2**, the 2-D supramolecular arrays extended along *b*-axis through  $\pi\text{-}\pi$  interactions between  $1,10\text{-phen}$ . The dinuclear paddle-wheel second building units (SBUs) constructed by four  $\text{dpa}^{2-}$  ligands in **3** are linked by  $\text{dpa}^{2-}$  into double-strand chains. The fluorescence of  $\text{H}_2\text{dpa}$  and **1–3** are also determined.

**Keywords:** Diphenic acid; Coordination polymer; Crystal structure; Fluorescent property

### 1. Introduction

Rational design and syntheses of metal–organic frameworks (MOFs) are of current interest in chemical research and materials science, stemming from their potential applications in magnetism, nonlinear optics, gas absorption, and luminescence [1–9]. The most common strategy used to obtain coordination polymers is to employ appropriate bridging ligands capable of binding to several metal centers through direct bond formation. An important family of multidentate O- or N-donor ligands has been extensively employed in the construction of extended structures. In the development of synthetic strategies and functional materials, the combination of dicarboxylate ligands and neutral N-donor ligands (such as  $4,4'$ -bipy,  $1,10\text{-phen}$ , and  $2,2'$ -bipy) afford knowledge about assembly with metal ions that can be adjusted through changing the types of organic ligands [10, 11]. Diphenic acid ( $\text{H}_2\text{dpa}$ ) as O-donor ligand has received much attention in the design of coordination polymers because the two functional groups may have different coordination modes and the carboxylate can adopt versatile

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coordination conformations allowing the generation of metal–oxygen chains or clusters [12–15].

We selected 2,4'-biphenyl-dicarboxylic acid which is relatively unexplored although it has great potential for coordinative interactions and bidentate aromatic nitrogen donors, and synthesized three new Mn(II) coordination polymers:  $[\text{Mn}(\text{Hdpa})_2(4,4'\text{-bipy})_2]_n$  (**1**),  $[\text{Mn}(\text{dpa})(\text{phen})(\text{H}_2\text{O})]_n$  (**2**), and  $[\text{Mn}(\text{dpa})(2,2'\text{-bipy})]_n$  (**3**).

## 2. Experimental

### 2.1. General materials and method

All reagents and solvents were commercially available and used as received without purification. The elemental analysis was carried out on a Carlo Erba 1106 fully-automatic trace organic elemental analyzer. FT-IR spectra were recorded with a Bruker Equinox 55 FT-IR spectrometer as dry KBr pellets from 400 to 4000  $\text{cm}^{-1}$ .

### 2.2. Preparation of compounds

**2.2.1.  $[\text{Mn}(\text{Hdpa})_2(4,4'\text{-bipy})_2]_n$  (**1**).** A mixture of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (0.099 g, 0.5 mmol),  $\text{H}_2\text{dpa}$  (0.121 g, 0.5 mmol),  $\text{NaOH}$  (0.04 g, 1 mol), 4,4'-bipy (0.156 g, 1 mmol) and distilled water (18 mL) was placed in a 25 mL stainless steel reactor with a Teflon liner, heated to 160°C for 96 h, and then cooled to room temperature. The resulting reaction products were yellow block crystals that were washed with alcohol to give pure samples (Yield: 63% based on Mn). Elemental Anal. Calcd (%) for  $\text{C}_{48}\text{H}_{32}\text{MnN}_4\text{O}_8$ : C, 68.01; H, 3.80; N, 6.61. Found: C, 67.86; H, 3.84; N, 6.57. IR: 3235 br, 3124 w, 1612 s, 1573 s, 1486 w, 1244 w, 1107 m, 970 w, 830 m, 771 w, 627 w.

**2.2.2.  $[\text{Mn}(\text{dpa})(\text{phen})(\text{H}_2\text{O})]_n$  (**2**).** Compound **2** can be obtained following the same synthetic procedure as that for **1** except for the use of 1,10-phen instead of 4,4'-bipy. Yellow block crystals of **2** were obtained with 70% yield based on Mn. Elemental Anal. Calcd (%) for  $\text{C}_{26}\text{H}_{18}\text{MnN}_2\text{O}_5$ : C, 63.29; H, 3.68; N, 5.68. Found: C, 62.96; H, 3.75; N, 5.61. IR: 3298 m, 3060 br, 1607 s, 1580 s, 1572 s, 1482 s, 1367 w, 1305 w, 1268 w, 1171 m, 1136 w, 1220 w, 950 w, 864 s, 781 s, 748 s, 720 m, 684 w, 634 w, 548 w, 509 w.

**2.2.3.  $[\text{Mn}(\text{dpa})(2,2'\text{-bipy})]_n$  (**3**).** Compound **3** was prepared in a similar manner as to compound **1** except for the use of 2,2'-bipy instead of 4,4'-bipy. Yellow block crystals of **3** were obtained with 71% yield based on Mn. Elemental Anal. Calcd (%) for  $\text{C}_{24}\text{H}_{16}\text{MnN}_2\text{O}_4$ : C, 63.87; H, 3.57; N, 6.21. Found: C, 62.14; H, 3.68; N, 6.19. IR: 3018 br, 1615 s, 1560 s, 1430 m, 1273 m, 1052 m, 941 s, 867 m, 741 s, 656 m, 608 m.

### 2.3. X-ray crystallography

The diffraction intensities for **1–3** were collected on a Bruker Smart 1000 CCD area-detector diffractometer with a Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) by using a  $\omega$ -scan

Table 1. Crystallographic data and structure refinement summary for 1–3.

Empirical formula	C <sub>48</sub> H <sub>32</sub> MnN <sub>4</sub> O <sub>8</sub>	C <sub>26</sub> H <sub>18</sub> MnN <sub>2</sub> O <sub>5</sub>	C <sub>24</sub> H <sub>16</sub> MnN <sub>2</sub> O <sub>4</sub>
Formula weight	847.72	493.37	491.13
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>P</i> <i>na</i> 2 <sub>1</sub>	<i>P</i> 2(1)/ <i>c</i>
Unit cell dimensions (Å, °)			
<i>a</i>	19.181(5)	20.528(5)	9.496(5)
<i>b</i>	7.665(5)	10.547(5)	10.535(5)
<i>c</i>	28.319(5)	20.633(5)	21.023(5)
Volume (Å <sup>3</sup> ), <i>Z</i>	3994(3), 4	4467(3), 4	2098.8(16), 4
Calculated density (mg/m <sup>3</sup> )	1.410	1.467	1.428
<i>F</i> (000)	1748	2024	924
$\theta$ range for data collection (°)	2.53–28.09	2.17–25.35	2.16–27.49
Limiting indices	–25 ≤ <i>h</i> ≤ 19; –10 ≤ <i>k</i> ≤ 9; –35 ≤ <i>l</i> ≤ 37	–26 ≤ <i>h</i> ≤ 26; –13 ≤ <i>k</i> ≤ 13; –26 ≤ <i>l</i> ≤ 18	–11 ≤ <i>h</i> ≤ 12; –13 ≤ <i>k</i> ≤ 10; –26 ≤ <i>l</i> ≤ 27
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.990	0.989	1.016
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0398, <i>wR</i> <sub>2</sub> = 0.0925	<i>R</i> <sub>1</sub> = 0.0371, <i>wR</i> <sub>2</sub> = 0.0759	<i>R</i> <sub>1</sub> = 0.0315, <i>wR</i> <sub>2</sub> = 0.0801
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0484, <i>wR</i> <sub>2</sub> = 0.0976	<i>R</i> <sub>1</sub> = 0.0533, <i>wR</i> <sub>2</sub> = 0.0831	<i>R</i> <sub>1</sub> = 0.0381, <i>wR</i> <sub>2</sub> = 0.041
Largest difference peak and hole (e Å <sup>–3</sup> )	0.539 and –0.402	0.358 and –0.257	0.375 and –0.295

$$w = 1/[\sigma^2(F_o)^2 + (AP)^2 + BP], \quad wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2} \quad \text{with } P = (F_o^2 + 2F_c^2)/3.$$

mode. An empirical absorption correction was applied using the SADABS programs [16]. All the structures were obtained by direct methods and refined by full-matrix least-squares methods on *F*<sup>2</sup> using the program SHEXL 97 [17]. All non-hydrogen atoms were refined anisotropically. The hydrogens were located by geometrical calculations, and their positions and thermal parameters were fixed during the structure refinement. The crystallographic data and experimental details of structural analyses for manganese coordination polymers are summarized in table 1. The selected bond parameters are listed in table 2.

### 3. Results and discussion

#### 3.1. Structure description

**3.1.1. [Mn(Hdpa)<sub>2</sub>(4,4'-bipy)<sub>2</sub>]<sub>n</sub> (1).** The X-ray crystallographic study reveals that **1** crystallizes in the monoclinic system, *C*2/*c* space group. Each independent Mn(II) is located at an inversion center and coordinated by two pyridine nitrogens [Mn–N = 2.242(19) Å] and four carboxylate oxygens [Mn(1)–O(3) = 2.147(17) Å and Mn(1)–O(4) = 2.297(19) Å] to furnish an octahedral geometry (figure 1a). Only one of the carboxylate groups of Hdpa is deprotonated which is similar to the structures of [Cu(bipy)<sub>2</sub>(2,2'-Hdpa)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] and [Ni(bipy)<sub>2</sub>(2,2'-Hdpa)(H<sub>2</sub>O)<sub>2</sub>] [18], and Hdpa<sup>–</sup> is a μ<sub>1</sub>-ligand with one carboxylate chelating one Mn(II) (μ<sub>1</sub>-η<sup>1</sup>:η<sup>1</sup>/μ<sub>0</sub>-η<sup>0</sup>:η<sup>0</sup> as shown in

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

<b>Compound 1</b>			
Mn(1)–O(3)#1	2.147(17)	Mn(1)–N(1)#1	2.242(19)
Mn(1)–O(4)#1	2.297(19)		
O(3)#1–Mn(1)–O(4)#1	57.94(6)	O(3)#1–Mn(1)–N(1)#1	93.97(7)
O(3)#1–Mn(1)–O(3A)	114.43(11)	O(4)#1–Mn(1)–O(4A)	128.88(11)
O(3A)–Mn(1)–N(1)#1	135.02(7)	O(4A)–Mn(1)–N(1)#1	87.62(7)
<b>Compound 2</b>			
Mn(1)–O(1)	2.200(2)	Mn(1)–O(3)#1	2.126(3)
Mn(1)–O(5)#1	2.199(2)	Mn(1)–N(1)#1	2.274(3)
Mn(1)–N(2)#1	2.254(3)	Mn(1)–O(1w)#1	2.278(3)
O(3)#1–Mn(1)–O(1)	100.33(11)	O(3)#1–Mn(1)–O(5)#1	90.21(11)
O(1)–Mn(1)–O(5)#1	76.62(8)	O(3)#1–Mn(1)–N(2)#1	91.68(12)
O(1)–Mn(1)–N(2)#1	167.89(10)	O(5)#1–Mn(1)–N(2)#1	105.18(10)
O(3)#1–Mn(1)–N(1)#1	164.55(11)	O(1)–Mn(1)–N(1)#1	94.71(10)
N(1)#1–Mn(1)–N(2)#1	73.21(11)	O(5)#1–Mn(1)–O(1w)	165.00(9)
<b>Compound 3</b>			
Mn(1)–O(1)#1	2.143(13)	Mn(1)–O(2)#1	2.170(13)
Mn(1)–O(3)#2	2.179(15)	Mn(1)–O(4)#2	2.153(15)
Mn(1)–N(1)#2	2.319(15)	Mn(1)–N(2)#2	2.310(17)
O(1A)#3–Mn(1)–O(4)#2	85.99(6)	O(1)#1–Mn(1)–O(2A)#3	146.54(5)
O(2)#1–Mn(1)–O(4)#2	81.71(6)	O(1)#1–Mn(1)–O(3)#2	82.09(6)
O(3)#2–Mn(1)–O(4A)#3	146.20(6)	O(2)#1–Mn(1)–O(2A)#3	91.09(6)
O(1)#1–Mn(1)–N(2A)#2	123.60(5)	O(4)#2–Mn(1)–N(1)#2	132.02(6)
O(2)#1–Mn(1)–N(2)#2	86.82(5)	O(3)#2–Mn(1)–N(2A)#2	86.82(5)
N(1)#2–Mn(1)–N(2)#2	69.44(6)		

Symmetry code for compounds: (1) #1:  $-x, y, 0.5 - z$ ; (2) #1:  $x, 1 + y, z$ ; (3) #1:  $2 - x, -y, -z$ ; #2:  $2 - x, -y, -z$ ; #3:  $-1 + x, y, z$ .

scheme 1a). The dihedral angles between two phenyl rings in Hdpa<sup>−</sup> and two pyridine rings in 4,4'-bipy are observed at 57.93° and 30.54°, respectively.

The intermolecular hydrogen bond between the O–H group from Hdpa<sup>−</sup> and the nitrogen of 4,4'-bipy, with a D···A distance of 2.663(4) Å (symmetry code:  $x, -1 - y, 1/2 + z$ ) and an angle of 173(4)°, indicates that there is a strong hydrogen bonding in the compound. Through hydrogen bonds, the molecules form zigzag chains along the  $z$ -axis (figure 1b).

**3.1.2. [Mn(dpa)(phen)(H<sub>2</sub>O)]<sub>n</sub> (2).** The crystallographic analysis reveals that [Mn(dpa)(phen)(H<sub>2</sub>O)]<sub>n</sub> crystallizes in the orthorhombic system, space group *Pna*2<sub>1</sub>. The coordination environment around the Mn(II) centers is represented in figure 2(a). The central Mn1 ion is six-coordinate with an octahedral geometry in which the equatorial positions are defined by two carboxyl oxygens [Mn(1)–O(1) = 2.200(2) Å and Mn(1)–O(3) = 2.126(3) Å] and two nitrogens from 1,10-phen [Mn(1)–N(1) = 2.274(3) Å and Mn(1)–N(2) = 2.254(3) Å], and the axial positions are occupied by one carboxyl oxygen [Mn(1)–O(5) = 2.199(2) Å] and one coordinated water [Mn(1)–O(1w) = 2.278(3) Å] with an O–Mn–O angle of 165.00(9)°. Mn(1) is displaced 0.143 Å out of the plane defined by four equatorial atoms. Dpa<sup>2−</sup> is a  $\mu_3$ -ligand ( $\mu_2$ - $\eta^2$ : $\eta^0$  and  $\mu_2$ - $\eta^1$ : $\eta^1$  shown in scheme 1b) with one carboxylate bridging two Mn(II) atoms in monodentate-bridging, and the other carboxylate bridges another Mn(II) through a

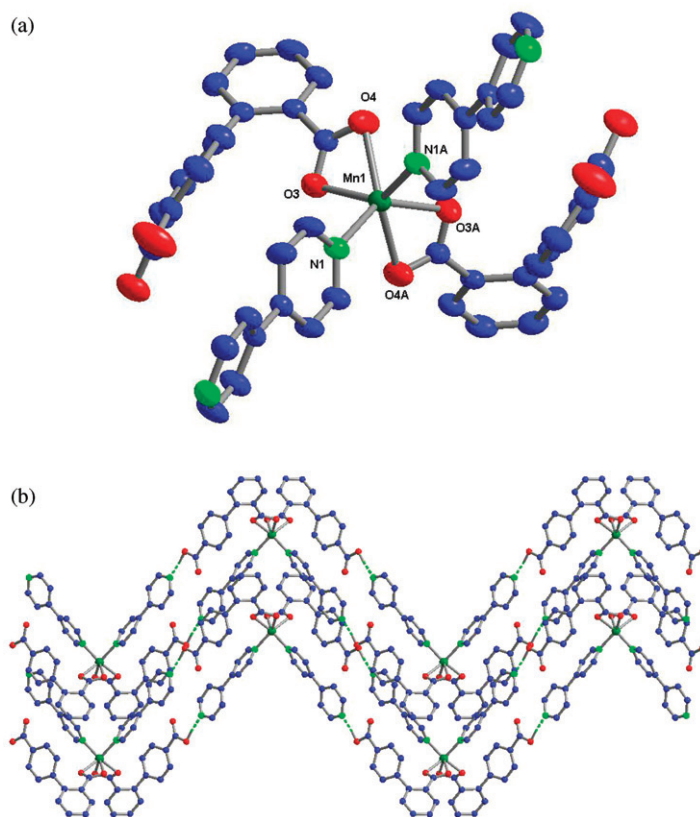
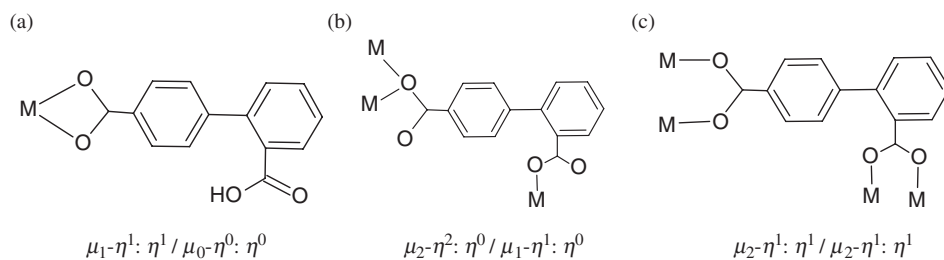


Figure 1. (a) The structure of **1** with ellipsoids at 50% probability (all hydrogens are omitted for clarity) and (b) 1-D supramolecular network formed through hydrogen bonding interactions viewed along the *a*-axis.



Scheme 1. Coordination modes of ligands in **1–3**.

monodentate mode which lead to dinuclear Mn(II) units. Each pair of Mn(II) atoms is linked by two  $\text{dpa}^{2-}$  anions with an Mn $\cdots$ Mn separation of 3.471 Å. The organic ligands link inorganic Mn(II) nodes to form a 1-D chain (figure 2b). The dihedral angle between two phenyl rings in  $\text{dpa}^{2-}$  is 39.06°.

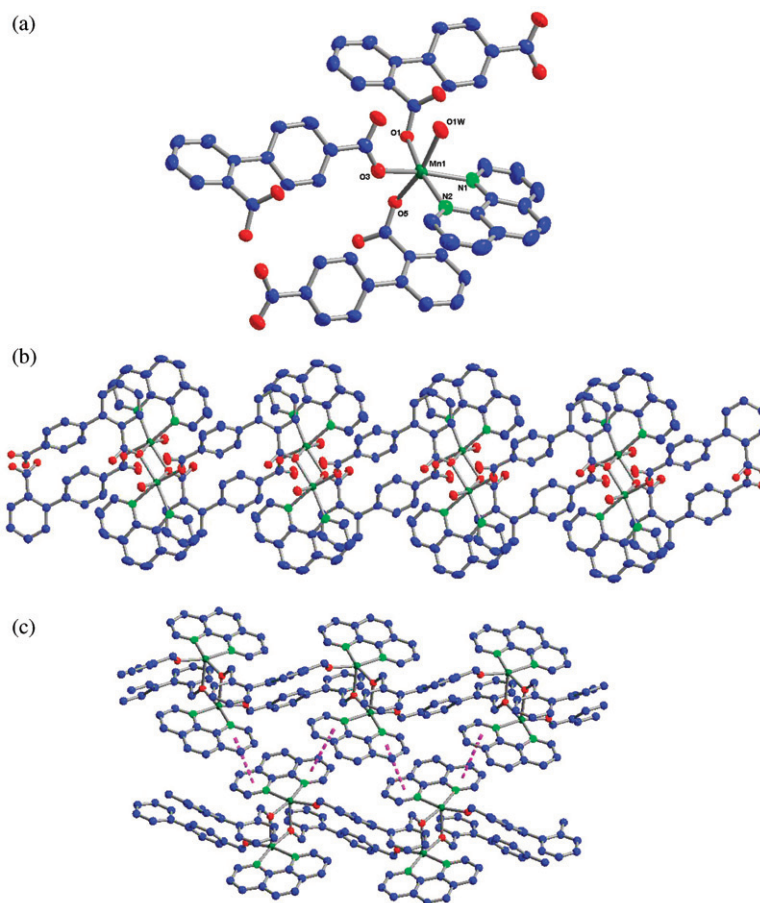


Figure 2. (a) Molecular structure and atomic labels of the non-hydrogen atoms for **2** with ellipsoids at 50% probability; (b) 1-D chain structure of **2** (Hydrogens are omitted for clarity) and (c) The 2-D supramolecular architecture formed through  $\pi$ - $\pi$  interaction in **2**.

Intermolecular  $\pi$ - $\pi$  stacking further assembles the 1-D chains to form a 2-D supramolecular framework. The interplanar angle between neighboring 1,10-phen groups is  $13.58^\circ$  and the corresponding centroid-to-centroid distances are *ca* 3.75 and 3.81 Å, indicating the presence of face-to-face  $\pi$ - $\pi$  stacking interactions that further stabilize the crystal structure (figure 2c).

**3.1.3. [Mn(dpa)(2,2'-bipy)]<sub>n</sub> (3).** The single-crystal X-ray diffraction analysis reveals that **3** consists of dinuclear Mn(II) units (figure 3a), each of which is symmetrically bridged by four carboxylate groups. Neighboring dinuclear units are interlinked *via* two diphenate ligands to form 1-D strands that can be described as double zigzag chains along the *b*-axis (figure 3b). It is interesting to note that four  $\mu_4$ -carboxylate groups bridge the dinuclear Mn(II) centers in *syn-syn* coordination which leads to a paddle-wheel secondary building unit (SBU). The Mn···Mn separation within the SBU is 3.462 Å. As shown in figure 3a, each Mn(II) center exhibits octahedral geometry,

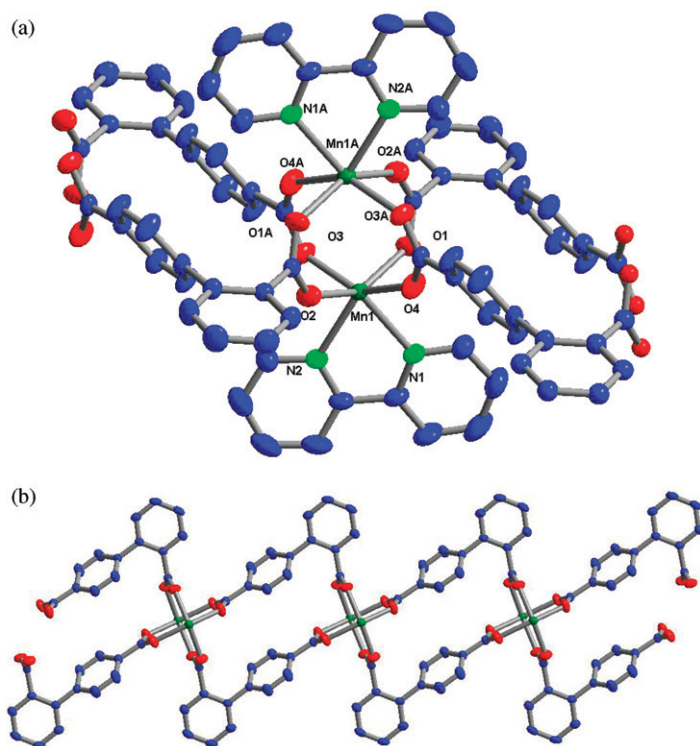


Figure 3. (a) Local coordination geometry of central Mn(II) with thermal ellipsoids drawn at 50% probability (all hydrogens are omitted for clarity) and (b) 1-D chain structure of **3** viewed along the *b*-axis. Hydrogens and 2,2'-bipy molecules are omitted for clarity.

coordinated by four carboxylate oxygens [Mn–O, ranging from 2.143(13) to 2.179(13) Å] and two nitrogens from 2,2'-bipy [Mn–N, 2.310(17) Å and 2.319(15) Å]. The carboxylate groups are twisted with respect to the corresponding linking phenyl rings with dihedral angles of 0.73° and 33.52° ( $\mu_2\text{-}\eta^1:\eta^1/\mu_2\text{-}\eta^1:\eta^1$  as shown in scheme 1c), and two phenyl rings about the central bond have a dihedral angle 56.87°.

Contrasting **1–3**, this research demonstrates that the assembly of 2,4'-dpa and N-donor ligands not only can afford novel molecular structures but also can induce 2,4'-dpa to adopt different conformations in the presence of different nitrogen donors.

### 3.2. Photoluminescent properties

The emission spectra of the free H<sub>2</sub>dpa and three Mn(II) compounds at room temperature are depicted in figure 4. H<sub>2</sub>dpa exhibits a broad weak fluorescent emission centered at 354 nm with an excitation maximum at 278 nm, which can be attributed to a  $\pi^*\text{-}\pi$  transition of the  $\pi$ -electrons of the aromatic rings. Intense luminescence emission bands are observed at 372 nm ( $\lambda_{\text{ex}} = 315$  nm) for **1**, 378 nm ( $\lambda_{\text{ex}} = 322$  nm) for **2**, and 396 nm ( $\lambda_{\text{ex}} = 324$  nm) for **3**, all of which could be assigned to the ligand-to-metal charge-transfer (LMCT) [19–22].



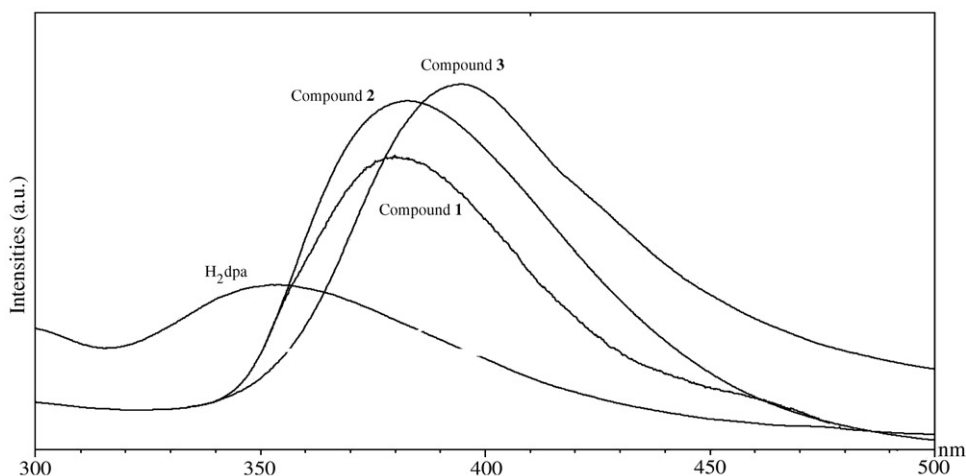


Figure 4. Fluorescent emission spectra of  $H_2dpa$  and **1–3** in the solid state at room temperature.

#### 4. Conclusion

In this article, we prepared three manganese(II) complexes with different structural motifs based on 2,4'-dpa and nitrogen-donor ligands. Single-crystal X-ray analyses reveal that  $Hdpa^-$  is a  $\mu_1$ -ligand with one carboxylate group bidentate chelating one Mn(II) in a 0-D structure in **1**. Compound **2** consists of dinuclear Mn units, and the neighboring dinuclear units are interlinked *via* two diphenate ligands to form 1-D strands that can be described as double zigzag chains along the *b*-axis. In **3**, four  $\mu_4$ -carboxylate groups bridge the dinuclear Mn(II) centers in *syn-syn* coordination mode giving a paddle-wheel SBU. The preparation of these complexes provides a valuable approach for the construction of many other MOFs from anionic and neutral ligands. Moreover, the fluorescence of **1–3** in the solid state at room temperature shows that emissions arise from LMCT, indicating that they may have potential applications as optical materials.

#### Supplementary material

Crystallographic information of the three compounds has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC [Mn( $Hdpa$ )<sub>2</sub>(4,4'-bipy)<sub>2</sub>]<sub>n</sub> (741085), CCDC [Mn(dpa)(phen)(H<sub>2</sub>O)]<sub>n</sub> (741086) and CCDC [Mn(dpa)(2,2'-bipy)]<sub>n</sub> (741087). The copies of the data may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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