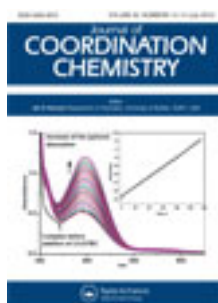


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### Three Mn(II) complexes with 1,3-bis(4-pyridyl)propane and their supramolecular nets

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## Three Mn(II) complexes with 1,3-bis(4-pyridyl)propane and their supramolecular nets

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Three complexes,  $[\text{Mn}(\text{bpp})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 1.5\text{H}_2\text{O}$  (**1**),  $[\text{Mn}(\text{bpp})_3\text{Br}_2] \cdot 2\text{H}_2\text{O}$  (**2**), and  $[\text{Mn}(\text{bpp})_2(\text{H}_2\text{O})_2](\text{ClO}_4) \cdot \text{I} \cdot \text{H}_2\text{O} \cdot \text{bpp}$  (**3**) (bpp = 1,3-bis(4-pyridyl)propane), were synthesized and structurally characterized by single-crystal X-ray diffraction. Complex **1** is mononuclear where M(II) is coordinated to a monodentate TT-bpp, three monodentate TG-bpp, and two water molecules. Complex **2** possesses a single-stranded helical chain formed from  $\text{MnN}_4\text{Br}_2$  octahedra by a single TT-bpp, with pendant monodentate TG-bpp ligands. Complex **3** consists of a ribbon-type double-stranded chain formed from  $\text{MnN}_4\text{O}_2$  octahedra by double TG-bpp ligands. 2-D supramolecular architectures of **1–3** are formed by hydrogen bonds. The fluorescence of the three complexes comes from the  $\pi^*-\pi$  transition of the ligand.

*Keywords:* Manganese complex; 1,3-Bis(4-pyridyl)propane; Crystal structure; Fluorescence

### 1. Introduction

Numerous metal–organic frameworks (MOFs) have been reported because of their interesting architectures and potential application in ion-exchange, catalysis, luminescence, and gas storage [1–10]. The basic building blocks containing metal ions and ligands assemble leading to 1-, 2-, and 3-D structures, which are commonly known as coordination polymers or MOFs. 1-D coordination polymer is the simplest topological type of coordination array and is considered to be the least interesting structurally. Coordination polymers of various structural motifs of 1-D such as linear, zigzag, helical, ladder, and ribbon are known [10–20]. Noncovalent interactions between 1-D infinite chains can lead to formation of supramolecular architectures. Self-assembly of supramolecular complexes results from noncovalent interactions and can result in formation of more structural motifs. The flexible 1,3-bis(4-pyridyl)propane (bpp) can assume different conformations (TT, TG, GG, and GG') owing to the relative orientations of three methylene groups between two pyridine rings that display quite different N-to-N distances [21, 22]. A flexible ligand that adopts a variety of conformations can lead to unexpected and interesting supramolecular structures. Many examples of polymeric species containing bpp ligand have been reported in

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recent years, including complicated polycatenated networks and self-penetrating 3-D structures [21–33]. Furthermore, the formation and structural features of complexes containing bpp are related to the counteranions, the solvents, and synthetic methods. Using bpp as ligand, the three simple complexes were obtained. Reaction of  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  with bpp afforded a mononuclear molecule (0-D)  $[\text{Mn}(\text{bpp})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 1.5\text{H}_2\text{O}$  (**1**); upon adding KBr or KI into the reaction system,  $[\text{Mn}(\text{bpp})_3\text{Br}_2] \cdot 2\text{H}_2\text{O}$  (**2**) and  $[\text{Mn}(\text{bpp})_2(\text{H}_2\text{O})_2](\text{ClO}_4) \cdot \text{I} \cdot \text{H}_2\text{O} \cdot \text{bpp}$  (**3**) were obtained. They exhibit two distinct motifs, single-stranded helical chain (**2**) and ribbon-type double-stranded chain (**3**), due to the different role of halides ( $\text{Br}^-$  and  $\text{I}^-$ ).  $\text{Br}^-$  and  $\text{I}^-$  play important roles in the self-assembly of supramolecular architectures. Herein, we report the syntheses, structures, and luminescent properties of **1–3**. Packing of simple structures (0-D and 1-D) result in interesting supramolecular architectures.

## 2. Experimental

### 2.1. Materials and physical measurement

All analytical grade reagents and solvents were commercially available and used without purification. Elemental analyses (C, H, and N) were determined on an Elementar Vario EL elemental analyzer. Infrared (IR) spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer using KBr pellets from  $400\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$ . Excitation and emission spectra of the solid samples were recorded on an F-4500 Fluorescence Spectrophotometer at room temperature. Thermogravimetric (TG) analyses were carried out on a WCT-1 A Thermal Analyzer at a heating rate of  $10^\circ\text{C min}^{-1}$  from room temperature to  $1000^\circ\text{C}$  in air.

### 2.2. Synthesis of 1–3

Preparation of  $[\text{Mn}(\text{bpp})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 1.5\text{H}_2\text{O}$  (**1**):  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.0724 g, 0.2 mmol) and bpp (0.0784 g, 0.4 mmol) were dissolved in 20 mL ethanol–water (1 : 1) solution. After stirring for 2 h, the mixture was filtered. Light-pink block-shaped single crystals were obtained from the filtrate after a few days. Yield: 64% (based on Mn). Anal. Calcd (Found) for  $\text{C}_{52}\text{H}_{62}\text{Cl}_2\text{MnN}_8\text{O}_{11.50}$  (1108.94) (%): C, 56.32 (56.17); H, 5.48 (5.28); N, 10.10 (10.01). Selected IR (KBr pellet,  $\nu/\text{cm}^{-1}$ ): 3055 br, w; 1952w, 1615vs, 1557m, 1454m, 1426s, 1228m, 1127w, 1100vs, 1014s, 838m, 807m, 759w, 623m, 574m, 517s.

Preparation of  $[\text{Mn}(\text{bpp})_3\text{Br}_2] \cdot 2\text{H}_2\text{O}$  (**2**): **2** was prepared as described for **1** except that KBr (0.0476 g, 0.4 mmol) was added. Yield: 61% (based on Mn). Anal. Calcd (Found) for  $\text{C}_{39}\text{H}_{46}\text{Br}_2\text{MnN}_6\text{O}_2$  (845.58) (%): C, 55.40 (55.05); H, 5.48 (5.44); N, 9.94 (10.10). Selected IR (KBr pellet,  $\nu/\text{cm}^{-1}$ ): 3055 br, w; 1952w, 1615vs, 1558m, 1505m, 1455s, 1427m, 1228m, 1086vs, 1014s, 886m, 836m, 807w, 623m, 584m, 516s.

Preparation of  $[\text{Mn}(\text{bpp})_2(\text{H}_2\text{O})_2](\text{ClO}_4) \cdot \text{I} \cdot \text{H}_2\text{O} \cdot \text{bpp}$  (**3**): **3** was prepared as described for **1** except that KI (0.0664 g, 0.4 mmol) was added. Yield: 58% (based on Mn). Anal. Calcd (Found) for  $\text{C}_{39}\text{H}_{48}\text{ClIMnN}_6\text{O}_7$  (930.12) (%): C, 50.36 (50.16); H, 5.20 (5.01); N, 9.03 (9.43). Selected IR (KBr pellet,  $\nu/\text{cm}^{-1}$ ): 3055br, w; 1951w, 1609vs, 1557s, 1504m, 1452m, 1425vs, 1226m, 1087vs, 1013vs, 838s, 806s, 758m, 624m, 573m, 515s.

Table 1. Crystal data and structure refinement for 1–3.

Complex	1	2	3
Empirical formula	C <sub>52</sub> H <sub>62</sub> Cl <sub>2</sub> MnN <sub>8</sub> O <sub>11.50</sub>	C <sub>39</sub> H <sub>46</sub> Br <sub>2</sub> MnN <sub>6</sub> O <sub>2</sub>	C <sub>39</sub> H <sub>48</sub> ClMnN <sub>6</sub> O <sub>7</sub>
Formula weight	1108.94	845.58	930.12
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>Pbca</i>	<i>C2/c</i>	<i>P2(1)</i>
Unit cell dimensions (Å, °)			
<i>a</i>	19.0938(2)	31.7502(5)	11.1368(11)
<i>b</i>	15.9423(2)	16.4836(3)	17.2650(16)
<i>c</i>	37.4688(4)	17.7820(3)	11.9320(13)
$\beta$	90.00	121.7610(10)	111.7800(10)
Volume (Å <sup>3</sup> ), <i>Z</i>	11405.5(2),8	7912.7(2),8	2130.5(4),2
Calculated density (Mg m <sup>-3</sup> )	1.292	1.420	1.450
Absorption coefficient (mm <sup>-1</sup> )	0.389	2.394	1.150
<i>F</i> (000)	4648	3464	950
Crystal size (mm <sup>3</sup> )	0.35 × 0.20 × 0.18	0.18 × 0.14 × 0.10	0.20 × 0.16 × 0.18
$\theta$ range for data collection (°)	1.75–27.98	2.23–27.97	2.30–25.02
Limiting indices	–21 ≤ <i>h</i> ≤ 25; –20 ≤ <i>k</i> ≤ 20; –49 ≤ <i>l</i> ≤ 42	–41 ≤ <i>h</i> ≤ 41; –21 ≤ <i>k</i> ≤ 20; –23 ≤ <i>l</i> ≤ 23	–13 ≤ <i>h</i> ≤ 13; –20 ≤ <i>k</i> ≤ 20; –12 ≤ <i>l</i> ≤ 14
Reflections collected	80,659	48,491	10,872
Independent reflections	13,564 [ <i>R</i> (int) = 0.0594]	9467 [ <i>R</i> (int) = 0.0335]	7186 [ <i>R</i> (int) = 0.0311]
Data/restraints/parameters	13,564/0/676	9467/0/452	7186/1/491
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.047	1.020	1.027
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0651, <i>wR</i> <sub>2</sub> = 0.1780	<i>R</i> <sub>1</sub> = 0.0471, <i>wR</i> <sub>2</sub> = 0.1133	<i>R</i> <sub>1</sub> = 0.0655, <i>wR</i> <sub>2</sub> = 0.1850
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1351, <i>wR</i> <sub>2</sub> = 0.2172	<i>R</i> <sub>1</sub> = 0.0911, <i>wR</i> <sub>2</sub> = 0.1332	<i>R</i> <sub>1</sub> = 0.0767, <i>wR</i> <sub>2</sub> = 0.1964
Largest difference peak and hole (e Å <sup>-3</sup> )	0.728 and –0.508	0.934 and –0.634	1.568 and –1.094

### 2.3. X-ray crystal structure determination

X-ray single-crystal data collection for 1–3 was performed on a Bruker Smart Apex II CCD diffractometer equipped with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 293(2) K. Semiempirical absorption corrections were applied on the complexes using SADABS. The structures were solved by direct methods and refined by full-matrix least-squares method on *F*<sup>2</sup> using SHELXS-97 and SHELX-97 [34, 35]. All non-hydrogen atoms in the complexes were refined anisotropically. Hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement. Summary of the crystallographic data and details of the structure refinements are listed in table 1. Selected bond lengths and angles of 1–3 are listed in table 2.

## 3. Results and discussion

### 3.1. Structural description of 1–3

[Mn(bpp)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> · 1.5H<sub>2</sub>O (1) consists of mononuclear cationic [Mn(bpp)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>, perchlorates, and free water. Mn(II) is attached to four monodentate bpp and two water molecules forming MnN<sub>4</sub>O<sub>2</sub> in a distorted octahedral

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

<b>Complex 1</b>			
Mn(1)–N(1)	2.280(3)	Mn(1)–N(7)	2.265(3)
Mn(1)–N(3)	2.292(3)	Mn(1)–O(1)	2.179(2)
Mn(1)–N(5)	2.284(3)	Mn(1)–O(2)	2.189(2)
N(7)–Mn(1)–N(5)	89.76(10)	N(7)–Mn(1)–N(1)	91.14(10)
N(1)–Mn(1)–N(3)	90.20(10)	N(1)–Mn(1)–N(5)	176.94(10)
N(5)–Mn(1)–N(3)	89.04(10)		
<b>Complex 2</b>			
Mn(1)–N(1)	2.296(3)	Mn(2)–N(4)	2.300(3)
Mn(1)–N(3)	2.296(3)	Mn(2)–N(5)	2.298(3)
Mn(1)–N(1)#1	2.296(3)	Mn(2)–N(4)#2	2.300(3)
Mn(1)–N(3)#1	2.296(3)	Mn(2)–N(5)#2	2.298(3)
Mn(1)–Br(1)	2.7013(4)	Mn(2)–Br(2)	2.7043(4)
Mn(1)–Br(1)#1	2.7013(4)	Mn(2)–Br(2)#2	2.7043(4)
N(3)–Mn(1)–N(3)#1	92.66(14)	N(5)#2–Mn(2)–N(5)	90.04(13)
N(3)–Mn(1)–N(1)	177.7(1)	N(5)#2–Mn(2)–N(4)#2	89.04(10)
N(3)#1–Mn(1)–N(1)	88.76(10)	N(5)–Mn(2)–N(4)#2	178.35(9)
N(3)–Mn(1)–N(1)#1	88.76(10)	N(5)#2–Mn(1)–N(4)	178.35(9)
N(1)–Mn(1)–N(1)#1	89.88(14)	N(5)–Mn(2)–N(4)	89.04(10)
N(3)#1–Mn(1)–N(1)#1	177.7(1)	N(4)#2–Mn(1)–N(4)	91.93(14)
<b>Complex 3</b>			
Mn(1)–O(1)	2.206(5)	Mn(1)–N(2)	2.297(5)
Mn(1)–O(2)	2.163(5)	Mn(1)–N(3)	2.311(5)
Mn(1)–N(1)	2.329(5)	Mn(1)–N(4)	2.312(5)
N(2)–Mn(1)–N(1)	93.25(19)	N(2)–Mn(1)–N(3)	89.11(19)
N(2)–Mn(1)–N(4)	176.3(2)	N(3)–Mn(1)–N(4)	90.90(19)
N(4)–Mn(1)–N(1)	86.74(18)		

Symmetry transformations used to generate equivalent atoms for **2**: #1:  $-1-x, y, 1.5-z$ ; #2:  $1-x, y, 0.5-z$ .

environment (figure 1a). The bpp ligands in **1** adopt the TT and TG conformations with dihedral angles between two pyridine rings of 78.0° for N1/N2, 92.6° for N3/N4, 68.6° for N5/N6, and 61.0° for N7/N8. The Mn–N and Mn–O bond distances are 2.189(2)–2.292(3) Å and 2.179(2)–2.189(2) Å, respectively. Although mononuclear Mn(II) complexes have been reported, such as Mn(2,2'-bpy)<sub>2</sub>(HFGA) (H<sub>2</sub>HFGA = hexafluoroglutaric acid and 2,2'-bpy = 2,2'-bipyridine) [36] and [Mn(bipy)<sub>5</sub>(H<sub>2</sub>O)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>·2(abz)<sub>2</sub>(H<sub>2</sub>O) (bipy = 4,4'-bipyridine, abz = 3-aminobenzoate) [37], the mononuclear bpp-complex has not been found and monodentate coordination of bpp is seldom seen. The crystal packing structure of **1** shows a 2-D supramolecular network (figure 1b). The ClO<sub>4</sub><sup>-</sup> anions, free water (O3w), and noncoordinated nitrogen atoms of bpp play an important role in sustaining the supramolecular architecture through hydrogen bonds (table S1). Free water O3w is a double hydrogen-bond donor and double acceptor showing a [2 + 2] H-bonding pattern and approximately tetrahedral arrangement. The O···O and O···N distances range from 2.682(4) to 2.722(4) Å and 2.736(4) to 2.844(4) Å, respectively. The ClO<sub>4</sub><sup>-</sup> is an acceptor to form O···H–C hydrogen bonds; the O···C distances range from 3.204(4) to 3.374(4) Å.

[Mn(bpp)<sub>3</sub>·Br<sub>2</sub>]·2H<sub>2</sub>O (**2**) is constructed from helical chains by a single bpp (figure 2a). The asymmetric unit contains one Mn(II), three bpp, two Br<sup>-</sup>, and two free water molecules. There are two crystallographically different Mn(II) ions in **2**. Both Mn(1) and Mn(2) adopt similar octahedral coordination environments, but the bond lengths and bond angles are slightly different. Each Mn(II) is coordinated by four nitrogen atoms from four bpp and two Br<sup>-</sup> ions. The Mn–N and Mn–Br bond distances

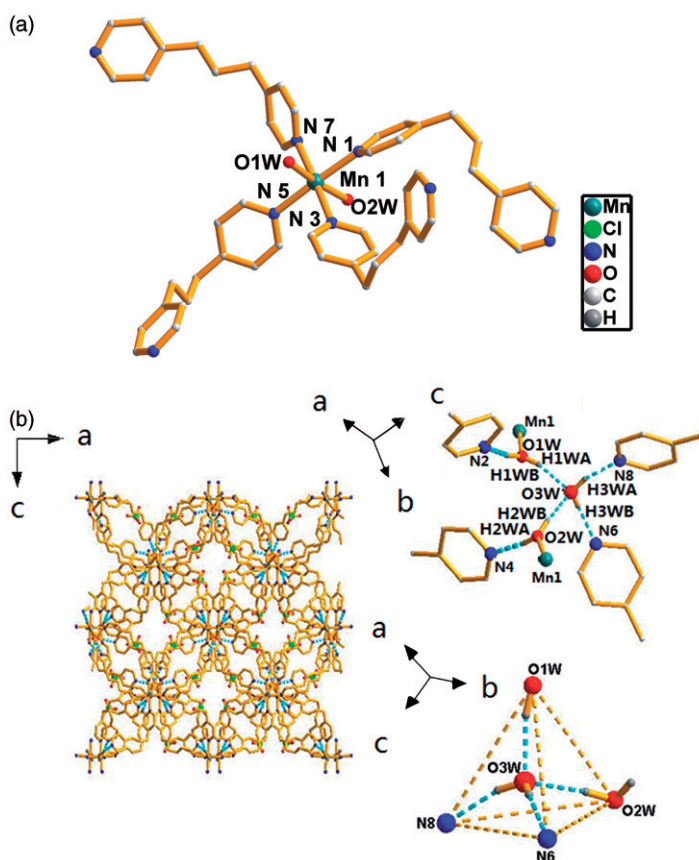


Figure 1. View of the structure of **1**: (a) molecular structure. All hydrogen atoms, free  $\text{ClO}_4^-$ , and water are omitted for clarity; (b) 2-D supramolecular network (left) and hydrogen bonds showing O3w in a tetrahedral configuration (right). Free  $\text{ClO}_4^-$  ions are omitted.

range from 2.296(3) to 2.300(3) Å and 2.7013(4) to 2.7043(4) Å, respectively. The bpp ligands are bidentate TT-bpp and monodentate TG-bpp conformations, with dihedral angles between two pyridines of 71.2° and 24.1°, respectively. Thus each bidentate TT-bpp links two Mn(II) ions, giving a Mn-bpp 1-D chain, while monodentate TG-bpp are terminal ligands on both sides of the chain. The Mn1...Mn2 distance is 13.957(5) Å and the angle Mn...Mn...Mn is 79.14(6)°. An interesting feature is that the Mn-bpp chain is a chiral single-stranded helical structure along the *c*-axis. Each turn of the helix contains two bpp and two Mn(II) with a pitch of 17.782 Å. The crystal is a racemic mixture of right- and left-handed helices. Adjacent right- and left-handed chains in **2** lead to a double helices motif. Mn-Br...H-C interactions (Br...C, 3.755–3.761 Å) are observed with Br...H distances of 2.825 and 2.832 Å within the range 2.77–3.10 Å [38]. Thus, the crystal packing of **2** shows a 2-D supramolecular network, wherein the helices are arranged in AAA parallel fashion and held together by Br...H-C supramolecular interactions (figure 2b). The water molecules are hydrogen-bonded to the chain through O-H...Br and O-H...N hydrogen bonds. The hydrogen-bond distances of O...Br and O...N are 3.514(2) and 3.566(2), and 2.933 (2) and 3.002(2) Å, respectively (table S2).



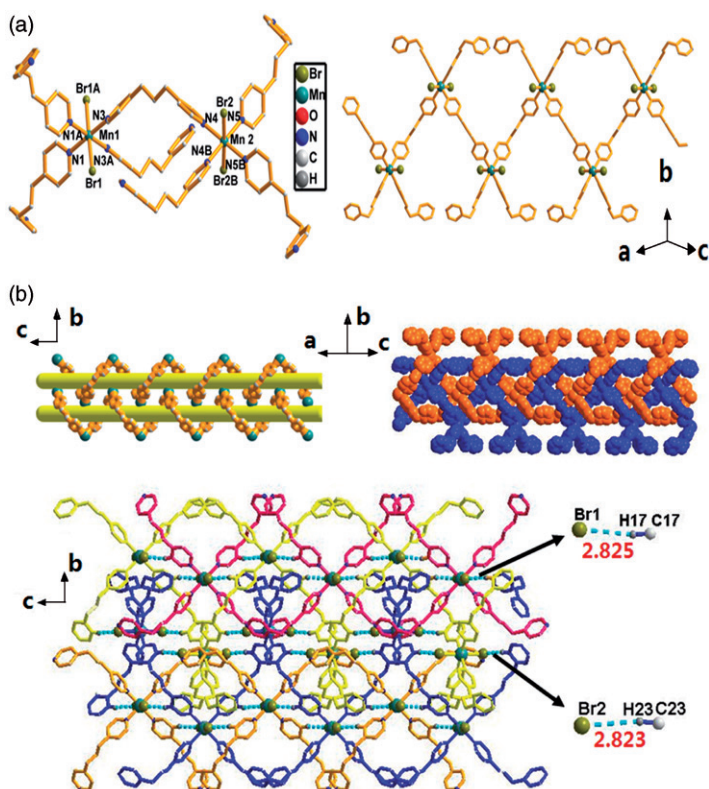


Figure 2. View of the structure of **2**: (a) the coordination environment of Mn(II) (left) and 1-D chain (right). All hydrogen atoms and free water molecules are omitted for clarity. Symmetry code A:  $1-x, y, 1.5-z$ ; B:  $1-x, y, 0.5-z$ ; (b) packing of adjacent helices showing the presence of the left- and right-handed helices (the pendant monodentate bpp ligands are omitted for clarity) (top left), hugging a double helices motif (top right), and 2-D supramolecular network by Br $\cdots$ H-C hydrogen bonds (bottom).

Coordination polymers of various helical motifs by different ligands are known, such as  $[M(L)(Phen)(H_2O)]_n \cdot nH_2O$  ( $M = Ni, Co, Zn$ ) by rigid 2-methylquinoline-3,4-dicarboxylate as connectors [39], cyanide-bridged complex  $\{[Ni(tren)][Ni(CN)_4]\}_n$  ( $tren = \text{tris}(2\text{-aminoethyl})\text{amine}$ ) [40], 2-methyl-imidazole-4,5-dicarboxylate (HMIDC)-bridged complex  $[Mn(HMIDC)(H_2O)_2] \cdot H_2O$  [41],  $N^2, N^6$ -bis((pyridin-2-yl)methyl)pyridine-2,6-dicarboxamide (L)-bridged complexes  $[AgL]_n \cdot nAsF_6$  and  $[AgL]_n \cdot nSbF_6$  [42], and 2,6-bis((pyridine-4-carboxamido)pyridine (L)-bridged complex  $[Mn(L)_3(SCN)_2]_n$  [43]. However, **2** is constructed from helical chain by flexible *N*-ligand bpp.

$[Mn(bpp)_2(H_2O)_2](ClO_4) \cdot I \cdot H_2O \cdot bpp$  (**3**) crystallizes in monoclinic, chiral space group  $P2_1(1)$ . The structure of **3** is a ribbon-type double-stranded chain (figure 3a). The asymmetric unit contains  $[Mn(bpp)_2(H_2O)_2]^{2+}$ ,  $ClO_4^-$ ,  $I^-$ , and free bpp and water;  $ClO_4^-$  and  $I^-$  anions are not bound to the metal. Mn(II) is six-coordinate by four bpp ligands and two water molecules in an octahedral coordination environment. The Mn-N and Mn-O bond distances are 2.297(5)–2.329(5) Å and 2.163(5)–2.206(5) Å, respectively. The bound bpp in **3** adopts TG conformation with dihedral angles between the pyridine rings of 65.2° for N3/N4A and 112.7° for N1A/N2, while noncoordinated bpp adopts GG' conformation. Two neighboring Mn(II) centers are linked by double TG-bpp

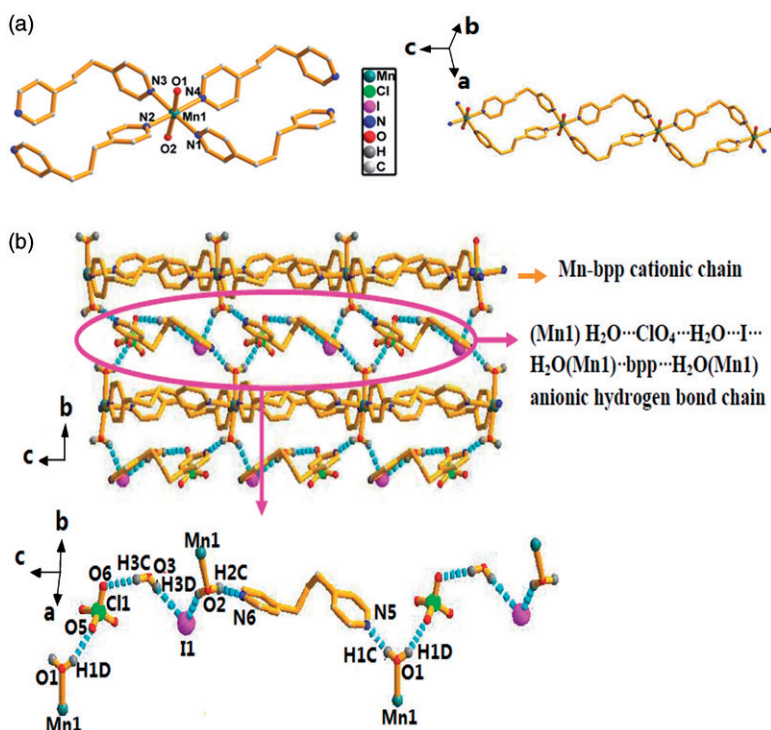


Figure 3. View of the structure of **3**: (a) the coordination environment of Mn(II) (left) and the ribbon-type double-stranded chain (right). All hydrogen atoms and free water and bpp molecules are omitted for clarity; (b) 2-D supramolecular network showing the 1-D anionic hydrogen bond chain (bottom).

ligands, generating bimetallic  $[\text{Mn}_2(\text{bpp})_2]$  loops. Neighboring loops share Mn(II) centers to produce a 1-D cationic ribbon chain. The  $\text{Mn} \cdots \text{Mn}$  distance is 11.932(5) Å and the  $\text{Mn} \cdots \text{Mn} \cdots \text{Mn}$  angle is  $180^\circ$ . Although **3** and the reported  $[\text{Mn}(\text{3-PIP})(1,3\text{-bdc})]_n$  (3-PIP = 2-(3-pyridyl)-imidazo[4,5,f]1,10-phenanthroline and 1,3-H<sub>2</sub>bdc = enzene-1,3-dicarboxylic acid) [44] and  $[\text{Mn}(\text{L})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  (HL = 3,5-bis(pyridin-4-ylmethyl)aminobenzoic acid) [45] have similar 1-D coordination polymers by double ligands, they have remarkable compositional and structural differences. The interesting crystal packing structure of **3** is that the linear cationic chains are arranged along the *c*-axis, where  $\text{ClO}_4^-$  and  $\text{I}^-$  occupy positions between cationic chains and provide the appropriate charge balance. A 1-D anionic hydrogen-bond chain,  $(\text{Mn1}) \text{H}_2\text{O} \cdots \text{ClO}_4^- \cdots \text{H}_2\text{O} \cdots \text{I}^- \cdots \text{H}_2\text{O}(\text{Mn1}) \cdots \text{bpp} \cdots \text{H}_2\text{O}(\text{Mn1})$  is formed by hydrogen bonds among free water (O3),  $\text{ClO}_4^-$ ,  $\text{I}^-$ , free bpp(N5/N6), and coordinated water (O1 and O2) (table S3). These cationic ribbons are linked by anionic hydrogen-bond chains forming extended 2-D supramolecular layers, with guest molecules intercalated and supported with hydrogen bonds (figure 3b).

### 3.2. Photoluminescence properties

Fluorescence spectra of the three complexes and free bpp in the solid state were recorded at room temperature upon excitation at 365 nm (figure 4). The complexes and



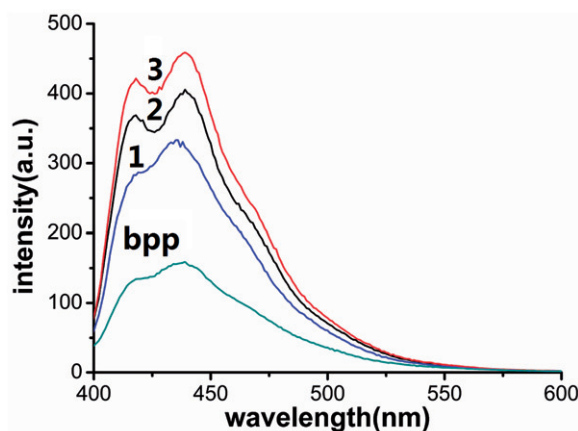


Figure 4. The emission spectra of complexes and bpp ligand in solid state ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ).

bpp have similar emission spectra. The emission spectrum of bpp shows a broad band and splits at 417 and 438 nm. The three complexes display similar spectra to that of bpp, a broad emission band around 436 nm for **1**, 439 nm for **2**, and **3**, with split peak at 417 nm. The fluorescence of **1–3** comes from the intraligand  $\pi^*-\pi$  transition of bpp [25].

### 3.3. Thermogravimetric analysis

TGA-DTA analyses of **1–3** were studied from room temperature to 1000°C (figure S1). The first weight losses start at 116°C for **1**, 116°C for **2**, and 109°C for **3**, from loss of free water; corresponding weight losses are 2.64% (Calcd 2.43%) for **1**, 4.77% (Calcd 4.26%) for **2**, and 1.99% (Calcd 1.90%) for **3**. Upon further heating the dehydrated compounds decompose in the temperature range 216–558°C for **1**, 232–620°C for **2**, and 210–552°C for **3**. The total weight losses are 91.58% for **1**, 87.89% for **2**, and 88.25% for **3**.

## 4. Conclusion

Reaction of  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  with bpp afforded a discrete zero-dimensional complex  $[\text{Mn}(\text{bpp})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 1.5\text{H}_2\text{O}$  (**1**). Introduction of halides ( $\text{Br}^-$  and  $\text{I}^-$ ) into the reaction system leads to single-stranded helical chain  $[\text{Mn}(\text{bpp})_3\text{Br}_2] \cdot 2\text{H}_2\text{O}$  (**2**) and a ribbon-type double-stranded chain  $[\text{Mn}(\text{bpp})_2(\text{H}_2\text{O})_2](\text{ClO}_4) \cdot \text{I} \cdot \text{H}_2\text{O} \cdot \text{bpp}$  (**3**). They exhibit distinct structures based on octahedral Mn(II) centers and different conformations of bpp. These 0-D or 1-D structures stack into different supramolecular architectures *via* intermolecular packing forces. The results indicate that  $\text{Br}^-$  and  $\text{I}^-$  play different templating roles in crystallization of these materials, possibly arising from the greater steric effect and less donating ability of  $\text{I}^-$  than that of  $\text{Br}^-$ . Furthermore,  $\text{Br}^-$  and  $\text{I}^-$  anions play important roles in the self-assembly of the supramolecular structures. The fluorescence of the complexes comes from the  $\pi^*-\pi$  transition of the ligand.

## Supplementary material

The crystallographic data of **1** (CCDC-861930), **2** (CCDC-856199), and **3** (CCDC-861931) can be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44(0)1223-336033; E-mail: deposit@ccdc.cam.ac.uk; <http://www.ccdc.cam.ac.uk/deposit>

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