

## Different Dimensional and Structural Variations in Coordination Compounds of Cadmium, Manganese and Nickel Constructed from the Ligand 2,2'-Bipyridine-3,3',6,6'-tetracarboxylic Acid (H<sub>4</sub>bptc)

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The reactions of hydrated CdCl<sub>2</sub>, MnCl<sub>2</sub>, and NiCl<sub>2</sub> with 2,2'-bipyridine-3,3',6,6'-tetracarboxylic acid (H<sub>4</sub>bptc) afforded the mononuclear [Cd<sup>II</sup>(H<sub>2</sub>bptc)(H<sub>2</sub>O)<sub>3</sub>]-H<sub>2</sub>O (**1**), linear {[Cd(H<sub>2</sub>bptc)(H<sub>2</sub>O)]·3H<sub>2</sub>O}<sub>n</sub> (**2**), 3-D hetero-bimetallic [NaCd(Hbptc)(H<sub>2</sub>O)] (**3**), layer [Mn(H<sub>2</sub>bptc)(H<sub>2</sub>O)]<sub>n</sub> (**4**) and a dinuclear compound [Ni<sub>2</sub>(H<sub>2</sub>bptc)(H<sub>2</sub>O)<sub>2</sub>]-6H<sub>2</sub>O (**5**). These compounds have been characterized by elemental analysis, IR, and their structures have been determined by X-ray crystallography. The thermal stabilities of **1-3** were measured by thermogravimetric analysis (TGA) and their solid state luminescence properties together with the free ligand H<sub>4</sub>bptc were investigated at room temperature.

**Key Words** : Bipyridinetetracarboxylic acid, Cd(II) complex, Crystal structures, Luminescence

### Introduction

The rational design and synthesis of inorganic-organic hybrid materials consisting of N-/O-donor ligands and transition metal ions are one of the most attracted areas in material science not only for their interesting properties such as host-guest chemistry, catalysis and magnetic behavior, but also for their structural diversity of the architectures.<sup>1-3</sup> To establish these classes of materials, many factors including solvent, temperature, different kinds of bases, pH value of solution, and the coordination preference of the metal ions should be considered.<sup>4-8</sup> However, the selected ligand is one of most important factors, since its functionality, flexibility, symmetry and the non-covalent forces such as hydrogen-bonding and  $\pi$ - $\pi$  stacking could significantly influence the self-assembly of metal-organic frameworks (MOFs).<sup>9</sup> Multi-carboxylate ligands have been proved to be excellent candidates to construct this class of functional materials owing to their diversified coordination modes.<sup>10,11</sup> So far, the coordination chemistry of bipyridinedicarboxylate and phenanthrolinedicarboxylate ligands have been extensively investigated.<sup>12-15</sup> Compared with bipyridinedicarboxylate, the coordination chemistry of bipyridinetetracarboxylate ligands is much less common. Until now, a series of bipyridinetetracarboxylate ligands including 4,4'-bipyridine-2,2',6,6'-tetracarboxylic acid,<sup>16</sup> 2,2'-bipyridine-5,5',6,6'-tetracarboxylic acid,<sup>17</sup> and 2,2'-bipyridine-4,4',6,6'-tetracarboxylic acid have been synthesized.<sup>18</sup> Recently, Pruchnik has reported a new synthetic route to obtain 2,2'-bipyridine-3,3',6,6'-tetracarboxylic acid ligand (H<sub>4</sub>bptc) *via* the oxidation of 2,9-dimethyl-1,10-phenanthroline with KMnO<sub>4</sub> in water basic condition.<sup>19</sup> Subsequently, Twaróg reported a novel C-C

bond cleavage of H<sub>4</sub>bptc that was catalyzed by the starting rhenium salt under the solvothermal reaction.<sup>20</sup> The reactions of H<sub>4</sub>bptc with lanthanide(III) ions afforded four isostructural complexes [Ln<sub>2</sub>(Hbptc)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sub>n</sub>·2nH<sub>2</sub>O (Ln = Sm, Eu, Gd, and Tb).<sup>21</sup> However, the coordination chemistry of H<sub>4</sub>bptc deserves more attention. It could be anticipated that H<sub>4</sub>bptc could exhibit rich coordination modes, since there are four carboxylic acids and two pyridine rings that will provide numerous coordinating sites and flexible connection modes. Herein, we intend to further investigate the coordination chemistry mainly based on the following considerations: (i) the coordination sites of N and O donors in this ligand are less steric; (ii) weak supra-molecular interactions such as H-bonding and  $\pi$ - $\pi$  stacking are readily formed; (iii) the deprotonated H<sub>3</sub>bptc<sup>-</sup>, H<sub>2</sub>bptc<sup>2-</sup>, and Hbptc<sup>3-</sup> species could be readily formed to balance the charge; (iv) two pyridyl rings can rotate around the C-C single bond, which could increase the potential possibility to form helical or chiral structure.

Also, there has been growing interest in the photochemistry of luminescent Cd<sup>II</sup> coordination complexes.<sup>22</sup> Herein, the reactions of H<sub>4</sub>bptc with hydrated Cd<sup>II</sup>, Mn<sup>II</sup> and Ni<sup>II</sup> salts have been conducted at different reaction conditions. Five new coordination compounds have been obtained and their crystal structures were determined by X-ray crystallography. These Cd<sup>II</sup> complexes were characterized by elemental analysis, IR, TGA, and their solid state photoluminescence properties were measured at room temperature.

### Experimental Section

**Materials and Physical Measurements.** 2,2'-Bipyridine-

3,3',6,6'-tetracarboxylic acid ( $H_4bptc$ ) was synthesized according to the reference's procedures.<sup>19</sup> Hydrated metal salts  $CdCl_2$ ,  $NiCl_2$  and  $MnCl_2$ , and the bases  $NH_4OH$ , and  $NaOH$  were purchased from Aldrich and used as received. All solvents were purified prior to use following standard methods. IR spectra were obtained in the  $4000-400\text{ cm}^{-1}$  range as KBr discs with a Nicolet 360 FTIR spectrophotometer. Elemental analysis was performed with an Elementar Vario EL Analyzer. Thermogravimetric analysis experiments were carried out with a Perkin-Elmer TGA7 thermogravimetric analyzer with the heating rate of  $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$  from 30 to  $600\text{ }^\circ\text{C}$  in a nitrogen atmosphere. Fluorescence spectra of compounds **1-3** and  $H_4bptc$  were recorded with an F-2500 FL Spectrophotometer analyzer at room temperature.

**X-ray Crystallography.** Intensity data were collected on an Oxford CCD diffractometer using graphite-monochromated  $MoK_\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ) for compounds **1-5**. Details of the intensity data collection and crystal data are given in Table S1. Absorption corrections were done by the multi-scan method. Their structures were resolved by the heavy-atom Patterson method or direct method and refined by full-matrix least-squares using SHELX-97 and expanded using Fourier techniques.<sup>23,24</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms except partial H atoms on the aqua and lattice water molecules were generated by the program SHELXL-97. The positions of hydrogen atoms were calculated on the basis of riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of final R indices. All calculations were performed using the teXsan crystallographic software.<sup>25</sup> Crystallographic data for the structures reported here have been deposited with CCDC (Deposition No. CCDC-924614 (**1**); CCDC-924615 (**2**); CCDC-924617 (**3**); CCDC-924618 (**4**); CCDC-924619 (**5**)). These data can be obtained free of charge *via* <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

**[Cd<sup>II</sup>(H<sub>2</sub>bptc)(H<sub>2</sub>O)<sub>3</sub>]·H<sub>2</sub>O (**1**):**  $H_4bptc$  (33.0 mg, 0.1 mmol) and  $CdCl_2\cdot 2H_2O$  (21.9 mg, 0.1 mmol) were added into a mixed solvent of  $H_2O/EtOH$  (30 mL, v:v = 1:1) and the mixture was stirred at room temperature for 1 h. A colorless clear solution was obtained. The colorless block crystals suitable for X-ray crystallography were obtained after standing at room temperature for 2 weeks. Yield: 48% (24.7 mg). Selected IR (KBr,  $\text{cm}^{-1}$ ): 3312, 2954, 2917 (s), 2849 (s), 1641 (s), 1546 (s), 1523 (s), 1463, 1444, 1398 (s), 1357, 1249, 1141, 1097, 983, 833, 719, 687. Anal. Calcd for  $C_{14}H_{14}CdN_2O_{12}$ : C, 32.67; H, 2.74; N, 5.44. Found: C, 32.58; H, 2.82; N, 5.40.

**[Cd(H<sub>2</sub>bptc)(H<sub>2</sub>O)<sub>2</sub>]·3H<sub>2</sub>O (**2**):**  $NH_4OH$  (0.1 mol/L, 2 mL) was added into a suspension of  $H_4bptc$  (33.0 mg, 0.1 mmol) in water (10 mL) and a colorless solution was obtained.  $CdCl_2\cdot 2H_2O$  (31.0 mg, 0.14 mmol) in EtOH was slowly added into the solution and the solution was stirred at room temperature for 1 h (if the white precipitates were generated, they should be removed by filtration immediate-

ly). Standing the solution at room temperature for 1 week, colorless block crystals suitable for X-ray crystallography were obtained with yield 56% (29.8 mg). Selected IR (KBr,  $\text{cm}^{-1}$ ): 1733, 1716, 1697, 1652, 1635, 1615 (s), 1575. (s), 1557 (s), 1506, 1488, 1472, 1457, 1404 (s), 1363 (s), 1270, 1232, 1194, 1127, 1082, 853, 803, 766, 717. Anal. Calcd for  $C_{14}H_{16}CdN_2O_{13}$ : C, 31.57; H, 3.03; N, 5.26. Found: C, 31.60; H, 3.10; N, 5.33.

**[NaCd(Hbptc)(H<sub>2</sub>O)] (**3**):**  $NaOH$  (8.0 mg, 0.2 mmol) was added into a suspension of  $H_4bptc$  (33.0 mg, 0.1 mmol) in water (10 mL) and a colorless solution was obtained.  $CdCl_2\cdot 2H_2O$  (31.0 mg, 0.14 mmol) in EtOH was slowly added into the solution and the solution was stirred at room temperature for 1 h. Standing the solution at room temperature for 1 week, colorless block crystals suitable for X-ray crystallography were obtained with yield 42% (20.3 mg). Selected IR (KBr,  $\text{cm}^{-1}$ ): 1698, 1606 (s), 1557 (s), 1467, 1413 (s), 1377, 1299, 1268 (s), 1223 (s), 1191, 1080, 877, 858, 799 (s), 761 (s), 747, 693. Anal. Calcd for  $C_{14}H_7CdN_2NaO_9$ : C, 34.84; H, 1.46; N, 5.80. Found: C, 34.82; H, 1.50; N, 5.76.

**[Mn(H<sub>2</sub>bptc)(H<sub>2</sub>O)]<sub>n</sub> (**4**):** A mixture of  $MnCl_2\cdot 4H_2O$  (27.7 mg, 0.14 mmol) and  $H_4bptc$  (33.0 mg, 0.1 mmol) in a mixed solvent EtOH/ $H_2O$  (15 mL, v:v = 2:1) was stirred for 5 min, sealed in a  $23\text{ cm}^3$  Parr bomb, and heated to  $140\text{ }^\circ\text{C}$  for 3 days, and then cooled to room temperature at the rate of  $0.1\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ . Colorless crystals of **4** were obtained with yield 52% (20.2 mg) based on  $H_4bptc$ . Selected IR (KBr,  $\text{cm}^{-1}$ ): 1700 (s), 1636, 1594, 1558, 1463, 1407, 1374, 1302, 1268, 1231, 1194, 1125, 1082, 896, 880, 801, 792, 763, 747, 717. Anal. Calcd for  $C_{14}H_8MnN_2O_9$ : C, 41.71; H, 2.00; N, 6.95. Found: C, 41.69; H, 2.10; N, 6.87.

**[Ni<sub>2</sub>(H<sub>2</sub>bptc)(H<sub>2</sub>O)<sub>2</sub>]·6H<sub>2</sub>O (**5**):** A mixture of  $NiCl_2\cdot 6H_2O$  (33.2 mg, 0.14 mmol) and  $H_4bptc$  (33.0 mg, 0.1 mmol) in a mixed solvent EtOH/ $H_2O$  (15 mL, v:v = 2:1) was stirred for 5 min, sealed in a  $23\text{ cm}^3$  Parr bomb, and heated to  $140\text{ }^\circ\text{C}$  for 3 days, and then cooled to room temperature at the rate of  $0.1\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ . Green block crystals of **5** were obtained with yield 60% (28.7 mg). Selected IR (KBr,  $\text{cm}^{-1}$ ): 1721, 1630, 1588, 1572, 1479, 1452, 1374, 1251, 1182, 1088, 1073, 810, 796, 735, 708. Anal. Calc. for  $C_{28}H_{32}N_4Ni_2O_{26}$ : C, 35.11; H, 3.37; N, 5.85. Found: C, 35.20; H, 3.50; N, 5.79.

## Results and Discussions

The reactions of  $H_4bptc$  with hydrated  $CdCl_2$  in neutral environment or in the presence of  $NH_4OH$  or  $NaOH$  afforded the discrete  $[Cd^{II}(H_2bptc)(H_2O)_3]\cdot H_2O$  (**1**), linear  $\{[Cd(H_2bptc)(H_2O)_2]\cdot 3H_2O\}_n$  (**2**), and 3-D heteronuclear  $[NaCd(Hbptc)(H_2O)]_n$  (**3**), respectively. The solvothermal reactions of  $H_4bptc$  with hydrated  $MnCl_2$  and  $NiCl_2$  afforded layer  $[Mn^{II}(H_2bptc)(H_2O)]_n$  (**4**) and dinuclear compound  $[Ni_2(H_2bptc)(H_2O)_2]\cdot 6H_2O$  (**5**), respectively. Compound **5** is isotopic to its  $Fe^{II}$  and  $Co^{II}$  analogues.<sup>19</sup> The ligand  $H_4bptc$  in these compounds exhibits different deprotonated forms of  $H_2bptc^{2-}$ ,  $Hbptc^{3-}$ , and  $bptc^{4-}$  bearing formally -2, -3, and -4 charges, respectively. IR spectra of these compounds reveal

the presence of H-bonding interactions. The broad  $\nu(\text{O-H})$  stretching bands of the coordinated aqua ligands, lattice water molecules and carboxylic acid groups are observed in the range of  $3400\text{--}3100\text{ cm}^{-1}$ . Due to the coexistence of carboxylic groups and bipyridine groups, the combined vibration modes of carboxylic groups and pyridine ring deformation appear and it is difficult to distinguish the contribution of carboxylic species from that of bipyridine groups. In general, the carboxylic groups are expected to give rather intense bands from asymmetric stretching vibration in the range of  $1630\text{--}1500\text{ cm}^{-1}$  and symmetric stretching vibration in the range of  $1460\text{--}1350\text{ cm}^{-1}$ .<sup>26,27</sup> As a result, the strong absorption bands at in the range of  $1630\text{--}1546\text{ cm}^{-1}$  in compounds **1-5** can be assigned to the asymmetric stretching vibration  $\nu_{\text{as}}(\text{COO})$  of carboxylic groups.

The crystal structure of **1** is shown in Figure 1. The  $\text{Cd}^{\text{II}}$  atom is seven-coordinated in a pentagonal bipyramid by two carboxylate O atoms and two N atoms from a  $\text{H}_2\text{bptc}^{2-}$  ligand, and three water O atoms. Selected bond parameters are summarized in Table S2. The ligand is dianionic *due* to the deprotonation of 6,6'-carboxylic acid groups. The dihedral angle between the two pyridyl rings is  $34.1(1)^\circ$ . The angles between the pyridyl rings and carboxylate COO planes for 3,3'-carboxylic groups are  $27.2(1)$  and  $35.3(1)^\circ$ , respectively while those for 6,6'-carboxylic groups are  $9.4$  and  $11.4(1)^\circ$ , respectively. These values are considerably different from those of free ligand  $\text{H}_4\text{bptc}$ ,<sup>19</sup> possibly *due* to the coordination of 6,6'-carboxylate groups of  $\text{H}_2\text{bptc}^{2-}$  with metal atom and formation of strong intermolecular hydrogen bonds with coordinated water molecules (Figure S1). The O5 and O7 donors are located in the axial positions, while the N1, N2, O2, O3, and O6 donors are in the equatorial plane. The deviation of equatorial angles of N1-Cd-N2, N1-Cd-O5, N2-Cd-O2, O2-Cd-O6, and O3-Cd-O6 from the theoretical average angle of  $72^\circ$  can be explained by the narrow bite angle resulting from the coordination of rigid tetradentate ligands. The bond lengths of Cd-N1 and Cd-N2 are  $2.363(4)$  and  $2.408(4)\text{ \AA}$ , respectively. The equatorial Cd-O2 and Cd-O3 bond lengths are  $2.431(3)$  and  $2.349(3)\text{ \AA}$ , respectively which are slightly longer than that of Cd-O6 ( $2.295(4)\text{ \AA}$ ). The axial Cd-O5 and Cd-O7 bond lengths are  $2.347(4)$  and  $2.296(4)\text{ \AA}$ , respectively. These bond para-

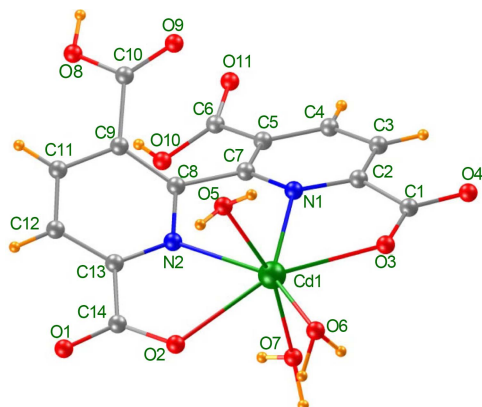


Figure 1. Perspective view of **1**.

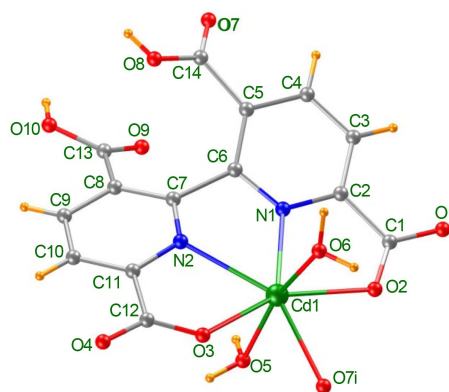


Figure 2. The structure fragment for **2** (symmetry code  $i: x-1, y, z$ ).

eters are comparable to the related cadmium-based complexes.<sup>28,29</sup> Extensive H-bonding interactions among carboxylate groups, aqua ligands and lattice water molecules are found (Table S3).

The structural fragment of **2** is shown in Figure 2. The asymmetric unit of **2** is composed of one Cd atom, one  $\text{H}_2\text{bptc}^{2-}$  ligand, two coordinated water molecules, and three lattice water molecules. The  $\text{Cd}^{\text{II}}$  atom is seven-coordinated in a pentagonal bipyramid by three carboxyl O atoms and two N atoms from two symmetry-related  $\text{H}_2\text{bptc}^{2-}$  ligands (O2, O3, O7', N1 and N2; symmetry code  $i: x-1, y, z$ ) and two aqua O atoms (O5 and O6). Similar to **1**, the ligand is dianionic *due* to the deprotonation of 6,6'-carboxylic acid groups. The two pyridyl rings are twisted with respect to each other with a dihedral angle of  $31.1(1)^\circ$ . The dihedral angles of 3,3',6,6'-carboxylate groups with respect to the attached pyridyl groups are  $29.8(1)$ ,  $30.9(1)$ ,  $9.8(1)$ , and  $11.9(1)^\circ$ , respectively. The equatorial positions are occupied by N1, N2, O2, O3 and O7' donors, while the axial positions are occupied by two aqua ligands (O5 and O6). The two Cd-N distances are  $2.366(7)$  and  $2.405(6)\text{ \AA}$ , respectively and the Cd-O distances are in the range of  $2.298(5)\text{--}2.372(6)\text{ \AA}$ , which are similar to those related  $\text{Cd}^{\text{II}}$  complexes.<sup>28,29</sup> The equatorial angles also deviate from the theoretical average angle of  $72^\circ$ . The bridging behavior of carboxyl O7' atom leads to a 1-D linear chain along  $a$  axis (Figure 3). In the extended structure, the nearest Cd $\cdots$ Cd separation is  $9.215(6)\text{ \AA}$ .

There are three lattice water molecules in each asymmetric unit and they are clustered by the H-bonding interactions, which are indicated by the shorter O $\cdots$ O separation (O11 $\cdots$ O12 =  $3.276\text{ \AA}$ ).

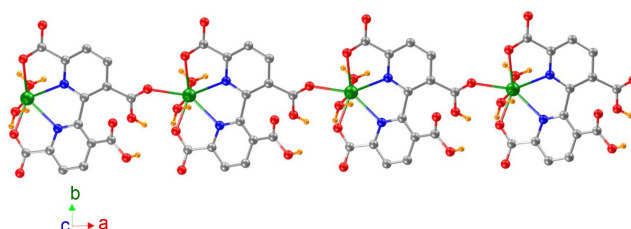
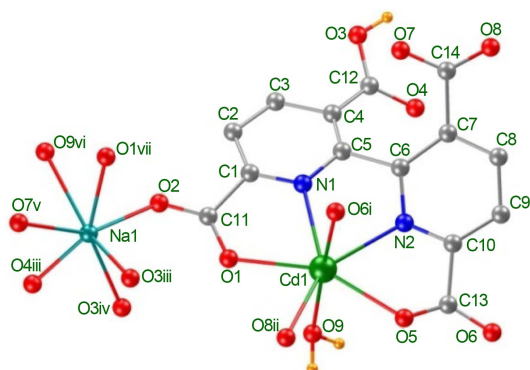
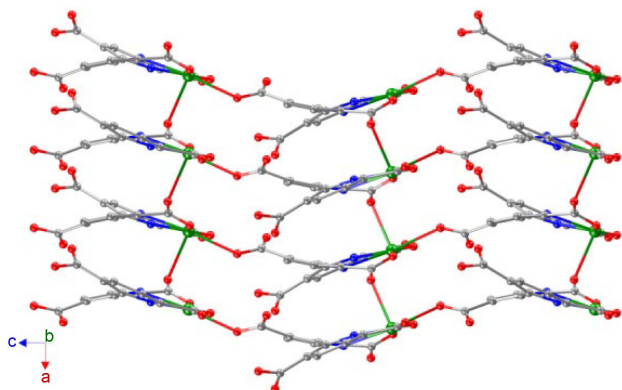


Figure 3. The 1-D linear chain in **2** along  $a$  axis.

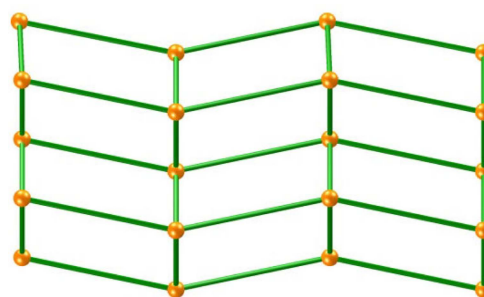


**Figure 4.** The structural fragment of  $\text{NaCd}(\text{Hbptc})(\text{H}_2\text{O})$  (**3**).

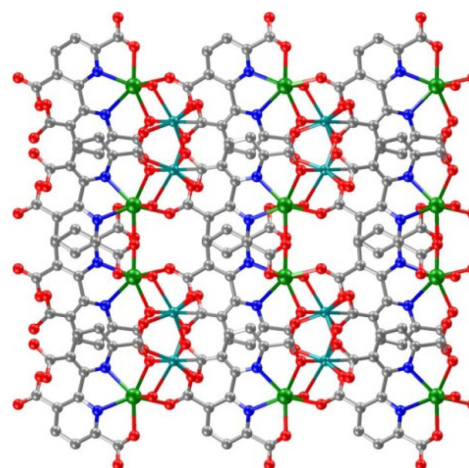
The structural fragment of **3** is shown in Figure 4. The asymmetric unit consists of one  $\text{Hbptc}^{3-}$  ligand, one  $\text{Cd}^{\text{II}}$  ion, one aqua ligand, and one  $\text{Na}^+$  ion. Selected bond parameters are summarized in Table S5. The Cd1 is seven-coordinated in a pentagonal bipyramid by four carboxylate O atoms and two N atoms from three symmetry-related  $\text{Hbptc}^{3-}$  (O1, O5, O6<sup>i</sup>, O8<sup>ii</sup>, N1 and N2 symmetry code (i):  $x-1/2, -y+2$ ; (ii):  $-x+1/2, y, z-1/2$ ), and an aqua O atom (O9). The  $\text{Na}^+$  is also seven-coordinated by seven O donors. The dihedral angle of two pyridyl rings is  $31.2(1)^\circ$  and the dihedral angles of 3,3',6,6'-four carboxylate groups with respect to the attached pyridyl rings are  $33.1(1)$ ,  $24.0(1)$ ,  $11.8(1)$ , and  $32.8(1)^\circ$ , respectively. The four carboxylate groups bond to the Cd ions in the different coordination modes. The 3-carboxylic acid (O4-C12-O3) bonds to a  $\text{Na}^+$  ion via  $\mu_1-\eta^1$ :  $\eta^0$  monodentate mode, while 3'-carboxylate group (O7-C14-O8) bridges a  $\text{Cd}^{2+}$  and a  $\text{Na}^+$  with  $\mu_2-\eta^1$ :  $\eta^1$  *syn-syn* bridging mode. The 6-carboxylate (O1-C11-O2) bridges a  $\text{Cd}^{2+}$  and a  $\text{Na}^+$  with  $\mu_2-\eta^2$ :  $\eta^0$  bridging mode and 6'-carboxylate (O5-C13-O6) bridges two  $\text{Cd}^{2+}$  ions in  $\mu_2-\eta^1$ :  $\eta^1$  *syn-anti* bridging mode. Along *ac* plane, the bridging behaviors of two carboxylate groups initially lead to a 2-D layer structure (Figure 5). These adjacent layers stack in an  $\cdots AAA \cdots$  sequence along the *b* axis. If the metal centers are taken as nodes and the  $\text{Hbptc}^{3-}$  ligands are taken as linkers of a topological network, a  $4^4$  grid topological architecture is generated, as shown in Figure 6. The adjacent layers are



**Figure 5.** The layer structure in **3** along *ac* plane.



**Figure 6.** Topological view of the layer structure of **3**.



**Figure 7.** Perspective view of **3** showing the adjacent layers are connected by the  $\text{Na}^+$ .

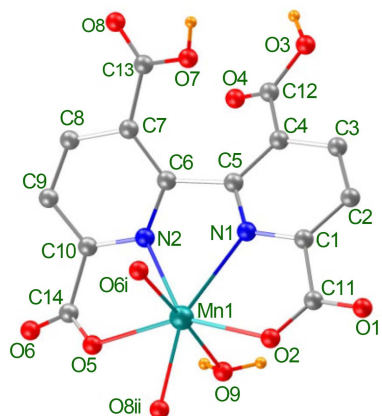
further linked by  $\text{Na}^+$  ions via the coordination of seven O donors to give an extended 3-D network (Figure 7). There are extensive H-bonding interactions between coordinated aqua ligands with carboxylate groups (Table S6).

The two Cd-N bond lengths are 2.405(12) and 2.419(13) Å, respectively. The Cd-O bond distances are in the range of 2.300(11)-2.401(11) Å, which are comparable to those in complexes **1** and **2**, and are also similar to those in related  $\text{Cd}^{\text{II}}$  compounds.<sup>28,29</sup> The Na-O bond distances are in the range of 2.299(13)-2.576(15) Å, which are similar to related ionic Na-O bond distance in the range of 2.25-2.78 Å.<sup>31</sup> The  $\pi-\pi$  interactions of aromatic rings are found with the centroid-to-centroid distance of 3.686(6) Å.

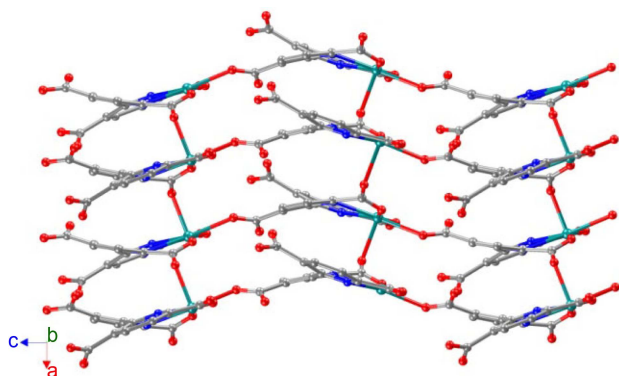
The structural fragment of compound **4** is shown in Figure 8. Each  $\text{Mn}^{\text{II}}$  atom is seven-coordinated in a pentagonal bipyramid by four carboxyl O atoms, one aqua O atom and two N atoms. Two of these O donors (O6<sup>i</sup> and O8<sup>ii</sup>) originate from two symmetry-related structural units (Symmetry codes (i)  $x-1/2, -y+2, z$ ; (ii)  $-x+1/2, y, z-1/2$ ). The ligand is dianionic due to the deprotonation of 6,6'-carboxylic acid groups. The structure of **5** reveals that the dihedral angle between two pyridyl rings is  $30.9(1)^\circ$ . The dihedral angles of 3,3'-carboxylic groups with respect to the attached pyridyl rings are  $31.9(1)$  and  $21.9(1)^\circ$ , respectively, while those for 6,6'-carboxylic groups are  $10.8(1)$  and  $33.4(1)^\circ$ , respectively.

The O6 and O9 donors are located in the axial positions,





**Figure 8.** Structural fragment of **4** showing the coordination geometry of Mn ion (symmetry code *i*:  $x-1/2, -y+2, z$ ; *ii*:  $-x+1/2, y, z-1/2$ ).

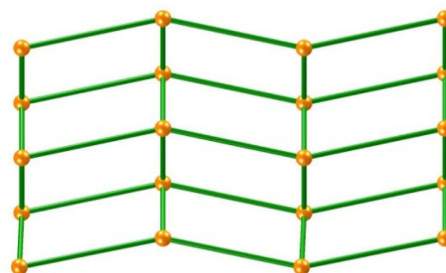


**Figure 9.** The packing diagram of **4** along *ac* plane.

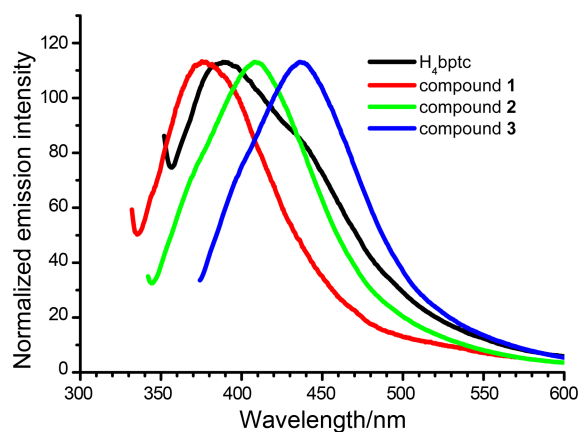
and the N1, N2, O2, O5, and O8 donors are in the equatorial plane. The equatorial angles of N1-Mn-N2, N2-Mn-O5, N1-Mn-O2, O8-Mn-O5, and O2-Mn-O8 deviate from the theoretical average angle of  $72^\circ$ . The bond lengths of Mn-N1 and Mn-N2 are 2.366(7) and 2.375(8) Å, respectively. The Mn-O bond lengths are in the range of 2.175(6)-2.335(6) Å, which are similar to those in the related manganese-based complexes.<sup>32</sup>

The bridging behaviors of two carboxylic acid groups result in an approximately square-grid structure, which is further edge-shared with its equivalent to form an undulated 2-D layer sustained by coordination bonds parallel to the *ac* plane (Figure 9). If the metal centers are taken as nodes and  $H_2bptc^{2-}$  are taken as linkers of a topological network, a  $4^4$  grid topological architecture is generated, as shown in Figure 10. In each layer, there are extensive  $\pi$ - $\pi$  interactions between pyridine rings with an average centroid-to-centroid distance of 3.678(7) Å. Moreover, the layer structures are further linked to each other to form a 3-D supra-molecular network, mainly by virtue of three pairs of O-H $\cdots$ O hydrogen bonds (Table S7).

The crystal structure of **5** is shown in Figure S3, which is isostructural to its  $Fe^{II}$  and  $Co^{II}$  analogues. In each asymmetric unit, there are two  $Ni^{II}$  ions and two  $H_2bptc^{2-}$  ligands, four aqua ligands, and six lattice water molecules. These



**Figure 10.** Topological view of **4**.



**Figure 11.** Solid-state emission spectra of free ligand  $H_4bptc$  and compounds **1-3**.

water molecules and carboxylate groups are seriously disorder, which result in the larger *R* value. Thus, the bond parameters around the metal centers are not available. However, the structure clearly exhibits the octahedral coordination geometry around the metal center.

In the above structures, the ligand's conformations vary on the basis of its coordination with different metal ions. We considered that conformational changes occur in this ligand to allow the metal-ligand distance to optimize. The two pyridine rings are rotatable around central C-C bond; thus, a limited range of metal-donor atom distances can be optimally accommodated within this ligand. The coordination preference and ionic size may have profound effects on the ligand conformation, which may be mostly responsible for structural diversity of these compounds. Extensive weak interactions such as H-bonding and  $\pi$ - $\pi$  stacking among the aromatic rings are found in these compounds, which are commonly encountered in the metal compounds bearing pyridine multi-carboxylate ligands. Usually, these interactions may be regarded as the stabilizing factor for the whole framework.<sup>33</sup>

**Thermal Stability of the Compounds 1-3.** The thermal behaviors of three cadmium complexes **1-3** were studied by thermogravimetric analysis (TGA) under a  $N_2$  atmosphere with a heating rate of  $10^\circ C/min$  (Figure S4). Compounds **1** and **2** lost their water molecules in the range of  $25-145^\circ C$ , with the weight loss of 13.14% and 16.05%, respectively, corresponding to the loss of the lattice and coordinated water

molecules per formula unit (calc. 13.98% and 16.89%, respectively). The dehydration process is followed by a plateau of stability from 145–298 °C, and then the compounds decompose rapidly with a two-step weight loss. The TGA curve of **3** shows a weight loss from room temperature to 92 °C, corresponding to the loss of one coordinated water molecule (observed 3.90%, calculated 3.72%). The dehydrated solid shows no further weight loss until 259 °C and then further heating leads to the final decomposition of the compound **3**.

**Fluorescence Properties.** The luminescent properties of complexes with  $d^{10}$  metal centers are of great interest for their potential applications in photochemistry, chemical sensors, and electroluminescent display.<sup>34</sup> The luminescence properties of compounds **1–3**, as well as the free H<sub>4</sub>bptc ligand, were investigated in the solid state at room temperature. As shown in Figure 11, intense emission bands were observed at  $\lambda_{em} = 388$  nm upon the excitation at  $\lambda_{ex} = 342$  nm for H<sub>4</sub>bptc, while compounds **1**, **2**, and **3** show the emission maximums at  $\lambda_{em} = 376$ , 408, and 437 nm upon the excitation at  $\lambda_{ex} = 322$ , 364, 332 nm, respectively.

The observed emission bands of **1–3** may result from intraligand  $\pi \rightarrow \pi^*$  transition between the  $\pi$ -bonding orbital (HOMO) and  $\pi^*$ -antibonding orbital (LUMO) of H<sub>4</sub>bptc ligand due to their resemblance to the emission of H<sub>4</sub>bptc ligand, rather than metal-to-ligand charge transfer (MLCT) or ligand-to-metal charge transfer (LMCT) in nature. Compared with H<sub>4</sub>bptc, the blue/red-shifts of these compounds may be assigned to the ligand chelating or bridging effect due to the coordination of Cd<sup>II</sup> center, changing the rigidity and conjugation of H<sub>4</sub>bptc.<sup>34</sup> The emission of Cd<sup>II</sup>-containing polymers may be complicated in mechanism since there are so many contributive interactions in this system. In these complexes, the two pyridyl rings form different dihedral angles. The smaller dihedral angle favors an orbital conjugation between two cycles. Moreover, the cooperative effect of the weak interactions such as H-bonding interaction and  $\pi$ - $\pi$  stacking could also influence the observed emission spectra, since these classes of weak interactions may play an essential role to decrease the HOMO-LUMO energy gap of ligand.<sup>35</sup> The strong fluorescence emissions of these compounds make them potentially useful candidates for hybrid photoactive materials.

### Conclusion

Three cadmium(II) compounds, a manganese(II), and a nickel(II) compounds have been obtained from the reactions of H<sub>4</sub>bptc with hydrated salts in mild conditions. The different deprotonated forms of Hbptc<sup>3-</sup>, H<sub>2</sub>bptc<sup>2-</sup>, and bptc<sup>4-</sup> are found in these compounds. The two pyridyl rings could rotate around the central C-C bond to form the different dihedral angles. The luminescence properties of Cd(II) compounds bearing H<sub>4</sub>bptc could be readily tuned by the subtle alteration of coordination environments of metal center. The stronger fluorescence emissions also indicate that these compounds are potential candidates for hybrid photoactive materials.

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