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# Syntheses, Structures, and Characterizations of a Series of Polymers Constructed by Two V-Shape Dipyridine-Containing Ligands

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**ABSTRACT:** Two flexible V-shape ligands, namely, 1,3-bis(pyridine-4-ylmethoxy)benzene (4-bpmb) and 1,3-bis(pyridine-2-ylmethoxy)benzene (2-bpmb), have been synthesized and employed for constructing eight novel coordination polymers, {[Zn(4-bpmb)(H<sub>2</sub>O)(NO<sub>3</sub>)<sub>2</sub>]·(4-bpmb)}<sub>n</sub> (1), {[Cd(4-bpmb)(H<sub>2</sub>O)(NO<sub>3</sub>)<sub>2</sub>]·(4-bpmb)}<sub>n</sub> (2), {[Hg(4-bpmb)(H<sub>2</sub>O)(NO<sub>3</sub>)<sub>2</sub>]·(4-bpmb)]<sub>n</sub> (3), {[Zn<sub>4</sub>(2-bpmb)<sub>4</sub>Cl<sub>8</sub>]·C<sub>5</sub>H<sub>5</sub>N]<sub>n</sub> (4), {[Hg(2-bpmb)Cl<sub>2</sub>]·2H<sub>2</sub>O]<sub>n</sub> (5), [Cu<sub>4</sub>( $\mu$ -CH<sub>3</sub>COO)<sub>8</sub>(2-bpmb)<sub>2</sub>]<sub>n</sub> (6), [Ag(2-bpmb)(NO<sub>3</sub>)]<sub>n</sub> (7), {[Cu(2-bpmb)(H<sub>2</sub>O)<sub>2</sub>]·(NO<sub>3</sub>)<sub>2</sub>]<sub>n</sub> (8). These complexes were characterized by elemental analyses and IR spectra and structurally determined by powder and single crystal X-ray diffraction analyses. The photoluminescence properties of complexes 1–3 are studied. The results revealed that the 4-bpmb ligands react with II B group transitional metallic nitrates to give three isostructural 1D wavelike chains (complexes 1–3), which are further decorated by equimolar 4-bpmb molecules to form the wavelike double-stranded chain structures *via* hydrogen bonds. In the packing model of complex 3, a 2D layer network is observed considering the interaction between mercury atoms and nitrate anions from the adjacent chains. The 2-bpmb ligands reacting with the corresponding transition metal salts generate three 1D helical chains, as expected (complexes 4–6). Complex 7 has a 2D layer structure produced by nitrate anions bridging with 1D opposite homohanded helical chains. Complex 8 displays a straight chain due to the coordination of two O atoms of each 2-bpmb ligand with copper cations.

## Introduction

The well-designed inorganic-organic hybrid compounds with intriguing architectures and wide potential applications have received intense attention in recent years.<sup>1-4</sup> Many rational construction strategies have been brought forward and proved to be significant in the design of the supramolecular structures,<sup>5</sup> but it is very difficult to master the thorough principles of assembling well-defined molecular architectures. The structures of polymeric species are determined by several factors, such as the coordination environment of the metal, the type of the ligands, the nature of the anions, the reaction conditions, and noncovalent interactions such as hydrogen bonds and  $\pi - \pi$  interactions that can help to stabilize certain architectures.<sup>6–9</sup> Among those, the selection of proper ligands as building blocks and metal ions with different coordination geometries or radii is very important in constructing the coordination frameworks. To date, many pyridyl-containing bidentate organic ligands<sup>10–14</sup> have been extensively investigated due to their strong coordination ability in the design and functional characteristics of coordination networks. The organic bipyridyl ligands containing benzene spacer tend to constitute attractive high-dimensional polymers, such as parasubstituted bispyridylbenzene $^{15-17}$  and meta-substituted bispyridylbenzene.<sup>18–20</sup> Steel and Mirkin have reported some silver(I) complexes with zigzag chains<sup>21</sup> that are obtained by reacting 1,4-bis(2-pyridylmethoxy)benzene with various silver

salts. Gao and co-workers have investigated the coordination of four flexible bipyridyl ligands with silver salts and obtained several helical complexes.<sup>22</sup> In view of these research results, the flexible ligands with bispyridylbenzene structure may contribute to the construction of helical chains.

It has been regarded as one of the efficient routes to react flexible meta-substituted bipyridylbenzene ligands with transitional metals in constructing helical structures. Nevertheless, it should be noted that the different substitution sites of pyridine rings in this kind of ligands will influence the distortion of whole molecules and further result in the generation of different structures.<sup>23</sup> Based on this consideration, we designed and synthesized two flexible meta-substituted V-shape ligands consisting of a benzene backbone and two appended pyridines with different substitution sites, 1,3-bis(pyridine-4ylmethoxy)benzene (4-bpmb) and 1,3-bis(pyridine-2-ylmethoxy)benzene (2-bpmb), in hopes of investigating their differences in constructing metal-organic frameworks (Scheme 1). Herein, we use 4-bpmb ligand to react with Zn(II), Cd(II), and Hg(II) nitrates in an equimolar ratio, which lead to three new complexes, { $[Zn(4-bpmb)(H_2O)(NO_3)_2] \cdot (4-bpmb)$ }<sub>n</sub>(1),  $\{ [Cd(4-bpmb)(H_2O)(NO_3)_2] \cdot (4-bpmb) \}_n$  (2), and  $\{ [Hg(4$ bpmb)(H<sub>2</sub>O)(NO<sub>3</sub>)<sub>2</sub>]·(4-bpmb)}<sub>n</sub>(3). They result in similar wavelike structures, as we expected, and double-stranded chains, which were unexpected. On the other hand, in the hope of obtaining the helical structures and probing the influence of different metal salts and the flexibility of such ligands on the helical structures, we react the 2-bpmb ligand with ZnCl<sub>2</sub>, HgCl<sub>2</sub>, Cu(CH<sub>3</sub>COO)<sub>2</sub>, AgNO<sub>3</sub>, and  $Cu(NO_3)_2$  to produce five new complexes, {[Zn<sub>4</sub>(2-bpmb)<sub>4</sub>- $Cl_8] \cdot C_5H_5N_n$  (4), {[Hg(2-bpmb)Cl\_2] \cdot 2H\_2O\_n (5), [Cu<sub>4</sub>( $\mu$ - $CH_3COO_{8}(2-bpmb)_{2}_{n}$  (6),  $[Ag(2-bpmb)(NO_3)]_{n}$  (7), {[Cu- $(2-bpmb)(H_2O)_2$   $(NO_3)_2$  (8). Consequently, the complexes

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Scheme 1. Different Coordination Frameworks of 4-bpmb and 2bpmb Ligands



**4**, **5**, **6**, and **7** show diverse helical structures, but complex **8** exhibits a straight chain because the oxygen atoms of the 2-bpmb ligand also take part in the coordination with the metal atoms, which leads to the fact that the flexible ligand changes to a rigid one.

#### **Experimental Section**

All chemicals are used as commercially received without further purification. Elemental analyses were performed on a CARLO ERBA 1106 analyzer. Infrared (IR) spectra were recorded on a Bruker Equinox 55 FT-IR spectrometer using KBr pellets. <sup>1</sup>H NMR spectra were performed on a Bruker AV 300 MHz spectrometer. Thermogravimetric measurements were done on a Perkin-Elmer TGA 7 analyzer in N<sub>2</sub> atmosphere at a heating rate of 10 °C·min<sup>-1</sup>. The luminescence spectra for the solid samples were recorded at room temperature on a Perkin-Elmer LS 55 luminance meter.

Synthesis of 4-bpmb and 2-bpmb. A mixture of 1,3-dihydroxybenzene (resorcinol) (1.1 g, 10 mmol), 4-chloromethylpyridine hydrochloride or 2-chloromethylpyridine hydrochloride (3.28 g, 20 mmol), and NaOH (1.6 g, 40 mmol) in acetonitrile (50 mL) was refluxed under nitrogen with stirring for 24 h. After cooling to room temperature, the reactant was filtered, and the residue was washed with acetonitrile several times. The mixed filtrate was evaporated under reduced pressure, and the red residue was dissolved in dichloromethane and then washed twice with water and once with brine. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. After the removal of the solvent under reduced pressure, the residue was purified by chromatography on silica gel to give a colorless solid substance: 4-bpmb Yield: 2.10 g (72% based on resorcinol). Elemental analysis: Calcd for C<sub>18</sub>H<sub>16</sub>O<sub>2</sub>N<sub>2</sub>: C, 73.95; H, 5.52; N, 9.58%. Found: C, 73.77; H, 5.49; N, 9.52%. IR (KBr, <sup>1</sup>): 3025 (m), 2907 (w), 1596 (s), 1562 (s), 1495 (s), 1449 (s), 1416 cm<sup>-</sup> (s), 1385 (s), 1271 (s), 1186 (s), 1160 (s), 1059 (s), 1044 (s), 829 (s), 794 (s), 755 (s), 682 (m), 481 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 5.08 (4H, s, CH<sub>2</sub>), 6.58 (1H, s), 6.60 (2H, d), 7.21 (1H, t), 7.30 (4H, d), 8.62 (4H, d). 2-bpmb Yield: 2.57 g (88% based on resorcinol). Elemental analysis: Calcd for  $C_{18}H_{16}O_{2}N_{2}$ : C, 73.95; H, 5.52; N, 9.58%. Found: C, 73.78; H, 5.50; N, 9.53%. IR (KBr, cm<sup>-1</sup>): 3062 (w), 3015 (w), 2918 (w), 1594 (s), 1574 (m), 1493 (s), 1433 (s), 1377 (m), 1271 (m), 1188 (s), 1161 (s), 1043 (m), 840 (m), 747 (s), 681 (m). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 5.21 (4H, s, CH<sub>2</sub>), 6.62 (1H, s), 6.69 (2H, d), 7.24 (1H, t), 7.28 (2H, t), 7.53 (2H, d), 7.72 (2H, t), 8.62 (2H, d).

Synthesis of {[Zn(4-bpmb)(H<sub>2</sub>O)(NO<sub>3</sub>)<sub>2</sub>]·(4-bpmb)}<sub>*n*</sub> (1). Complex 1 was synthesized by reaction between a solution of 4-bpmb ligand (0.0292 g, 0.10 mmol) in MeOH (5 mL) and a solution of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.0297 g, 0.1 mmol) in water (5 mL). The mixture was heated to 40 °C and stirred for about 1 h. After filtration, colorless block crystals suitable for X-ray diffraction were obtained by slow evaporation at room temperature for several days in 40% yield. Elemental analysis: Calcd for  $C_{36}H_{34}ZnN_6O_{11}$ : C, 54.59; H, 4.33; N, 10.61%. Found: C, 54.41; H, 4.29; N, 10.59%. IR (KBr, cm<sup>-1</sup>): 3413 (w), 2865 (w), 1596 (s), 1497 (m), 1461 (s), 1294 (s), 1187 (m), 1041 (m), 822 (m), 769 (m), 684 (m), 492 (m).

Synthesis of { $[Cd(4-bpmb)(H_2O)(NO_3)_2] \cdot (4-bpmb)$ }<sub>n</sub> (2). The procedure is similar to the synthesis of 1 except that  $Cd(NO_3)_2 \cdot$ 

 $4H_2O(0.0308 \text{ g}, 0.1 \text{ mmol})$  was used instead of  $Zn(NO_3)_2 \cdot 6H_2O$  in 47% yield. Elemental analysis: Calcd for  $C_{36}H_{34}CdN_6O_{11}$ : C, 51.53; H, 4.08; N, 10.02%. Found: C, 51.35; H, 4.05; N, 10.03%. IR (KBr, cm<sup>-1</sup>): 3413 (w), 2923 (s), 1596 (s), 1496 (s), 1424 (s), 1291 (s), 1185 (s), 1072 (s), 1039 (s), 804 (s), 770 (s), 686 (m), 490 (s).

**Synthesis of** {[**Hg**(**4-bpmb**)(**H**<sub>2</sub>**O**)(**NO**<sub>3</sub>)<sub>2</sub>·(**4-bpmb**)}<sub>*n*</sub> (3). The procedure is similar to the synthesis of **1** except that Hg(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O (0.0343 g, 0.1 mmol) was used instead of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in 39% yield. Elemental analysis: Calcd for C<sub>36</sub>H<sub>34</sub>HgN<sub>6</sub>O<sub>11</sub>: C, 46.63; H, 3.70; N, 9.06%. Found: C, 46.56; H, 3.68; N, 9.03%. IR (KBr, cm<sup>-1</sup>): 3426 (m), 3030 (w), 2904 (w), 1599 (s), 1498 (m), 1416 (m), 1385 (m), 1298 (m), 1186 (m), 1053 (m), 951 (m), 794 (m), 760 (w), 484 (m).

Synthesis of { $[Zn_4(2-bpmb)_4Cl_8] \cdot C_5H_5N$ }<sub>*n*</sub>(4). Complex 4 was synthesized by reaction between a solution of 2-bpmb ligand (0.0292 g, 0.1 mmol) in MeOH (5 mL) and a solution of ZnCl<sub>2</sub> (0.0136 g, 0.1 mmol) in water (5 mL). Then pyridine (1 mL) was added to the mixture. The mixture was heated to 40 °C and stirred for about 1 h. After filtration, colorless crystals suitable for X-ray diffraction were obtained by slow evaporation for several days in 37% yield. Elemental analysis: Calcd for C<sub>77</sub>H<sub>68</sub>Cl<sub>8</sub>N<sub>9</sub>O<sub>8</sub>Zn<sub>4</sub>: C, 51.59; H, 3.82; N, 7.03%. Found: C, 51.47; H, 3.79; N, 7.01%. IR (KBr, cm<sup>-1</sup>): 3435 (w), 3031 (w), 2907 (w), 1612 (s), 1493 (s), 1390 (s), 1263 (m), 1181 (s), 1026 (s), 784 (m), 757 (s), 651 (m), 420 (w).

**Synthesis of** {[**Hg**(2-bpmb)**Cl**<sub>2</sub>]·2**H**<sub>2</sub>**O**}<sub>*n*</sub> (5). Complex 5 was synthesized by reaction between a solution of 2-bpmb ligand (0.0292 g, 0.10 mmol) in MeOH (5 mL) and a solution of HgCl<sub>2</sub> (0.0272 g, 0.1 mmol) in water (5 mL). The mixture was heated to 40 °C and stirred for about 1 h. After filtration, colorless block crystals suitable for X-ray diffraction were obtained by slow evaporation at room temperature for several days in 45% yield. Elemental analysis: Calcd for  $C_{18}H_{20}Cl_2N_2O_4Hg$ : C, 36.04; H, 3.36; N, 4.67%. Found: C, 35.95; H, 3.33; N, 4.64%. IR (KBr, cm<sup>-1</sup>): 3428 (w), 3082 (w), 2873 (w), 1599 (m), 1492 (m), 1443 (w), 1380 (w), 1264 (w), 1153 (m), 1039 (m), 838 (w), 758 (m), 684 (w).

Synthesis of  $[Cu_4(\mu$ -CH<sub>3</sub>COO)<sub>8</sub>(2-bpmb)<sub>2</sub>]<sub>n</sub> (6). The procedure is similar to the synthesis of complex 5 except that Cu(OAc)<sub>2</sub> (0.0200 g, 0.1 mmol) was used instead of HgCl<sub>2</sub> and green block crystals suitable for X-ray diffraction were obtained in 50% yield. Elemental analysis: Calcd for C<sub>52</sub>H<sub>56</sub>Cu<sub>4</sub>N<sub>4</sub>O<sub>20</sub>: C, 47.63; H, 4.30; N, 4.27%. Found: C, 47.52; H, 4.28; N, 4.24%. IR (KBr, cm<sup>-1</sup>): 3446 (w), 3073 (w), 2933 (w), 1626 (m), 1492 (s), 1433 (s), 1269 (w), 1160 (m), 1051 (m), 944 (w), 835 (m), 772 (m), 681 (m), 455 (m).

**Synthesis of**  $[Ag(2-bpmb)(NO_3)]_n$  (7). The procedure is similar to the synthesis of complex 5 except that AgNO<sub>3</sub> (0.0170 g, 0.1 mmol) was used instead of HgCl<sub>2</sub> in 50% yield. Elemental analysis: Calcd for C<sub>18</sub>H<sub>16</sub>AgN<sub>3</sub>O<sub>5</sub>: C, 46.77; H, 3.49; N, 9.09%. Found: C, 46.65; H, 3.48; N, 9.04%. IR (KBr, cm<sup>-1</sup>): 3413 (w), 3079 (w), 2939 (w), 1601 (s), 1494 (s), 1344 (s), 1173 (s), 1017 (m), 921 (m), 823 (s), 768 (s), 684 (m), 627 (m), 413 (w).

**Synthesis of {**[ $\hat{Cu}(2-bpmb)(H_2O)_2$ ]·( $NO_3)_2$ }<sub>*n*</sub>(8). The procedure is similar to the synthesis of complex **5** except that  $Cu(NO_3)_2 \cdot 3H_2O$  (0.0242 g, 0.1 mmol) was used instead of HgCl<sub>2</sub> and blue block crystals suitable for X-ray diffraction were obtained in 55% yield. Elemental analysis: Calcd for  $C_{18}H_{20}CuN_4O_{10}$ : C, 41.90; H, 3.91; N, 10.86%. Found: C, 41.79; H, 3.89; N, 10.81%. IR (KBr, cm<sup>-1</sup>): 3068 (s), 1600 (s), 1572 (s), 1499 (s), 1424 (s), 1384 (s), 1315 (s), 1284 (s), 1176 (s), 1039 (s), 961 (m), 856 (m), 773 (s), 726 (m), 689 (m), 439 (m).

X-ray Crystallography. The X-ray diffraction measurements for complexes 1-8 were carried out on a Rigaku R-AXIS RAPID imaging plate diffractometer with graphite-monochromated Mo  $K\alpha$  ( $\lambda = 0.71073$  Å) at 293 K. Empirical absorption corrections based on equivalent reflections were applied. The structures of 1-8were solved by direct methods using SHELXS 97. All nonhydrogen atoms were refined anisotropically by the full-matrix least-squares method on  $F^2$ . H atoms bound to C atoms were placed in calculated positions and treated as riding on their parent with C-H = 0.93 Å(aromatic) or 0.97 Å (methylene) and with  $U_{iso}$  (H) = 1.2 $U_{eq}$  (C). Water H atoms were initially located in a difference Fourier map, but they were treated as riding on their parent atoms with O-H =0.85 Å and with  $U_{iso}$  (H) = 1.5 $U_{eq}$  (O). The nitrate anions in complexes 1, 3, and 8, the pyridine molecule in complex 4, and the water molecules in complex 5 are disordered. The crystal parameters, data collection, and refinement results for complexes 1-8

		Tab	le 1. Crystal Data and S	Structure Refinement Para	meters for Complexes 1–8	8		
	1	2	3	4	ъ	9	7	8
empirical formula	C <sub>36</sub> H <sub>34</sub> ZnN <sub>6</sub> O <sub>11</sub>	C <sub>36</sub> H <sub>34</sub> CdN <sub>6</sub> O <sub>11</sub>	$\mathrm{C}_{36}\mathrm{H}_{34}\mathrm{HgN}_{6}\mathrm{O}_{11}$	$\mathrm{C_{77}H_{68}Cl_8N_9O_8Zn_4}$	$C_{18}H_{20}Cl_2N_2O_4Hg$	C <sub>52</sub> H <sub>56</sub> Cu <sub>4</sub> N <sub>4</sub> O <sub>20</sub>	$C_{18}H_{16}AgN_3O_5$	$C_{18}H_{20}CuN_4O_{10}$
formula weight	792.08	839.09	927.28	1792.48	599.85	1311.17	462.21	515.92
temperature	293(2) K	293(2) K	293(2) K	293(2) K	293(2) K	293(2) K	293(2) K	293(2) K
wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
crystal system	orthorhombic	orthorhombic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	Pnma	Pmma	Pnma	P2(1)/c	P21/c	P21/n	P21/n	P21/n
a (Å)	28.2850(15)	28.506(2)	28.494(6)	8.7756(18)	13.040(3)	14.714(3)	14.774(3)	10.098(2)
$b(\mathbf{A})$	17.141(5)	17.416(4)	17.351(4)	16.381(3)	8.8214(18)	7.9808(16)	8.0109(16)	17.660(4)
c (Å)	7.163(8)	7.062(8)	7.1330(14)	14.364(3)	16.590(3)	25.341(5)	15.737(3)	11.824(2)
a (deg)	60	90	06	06	06	06	90	90
$\beta$ (deg)	06	90	90	93.67(3)	102.43(3)	104.63(3)	109.92(3)	102.86(3)
$\gamma$ (deg)	06	90	90	06	06	60	90	90
$V(Å^3)$	3473(4)	3506 (4)	3526.6(12)	2060.6(7)	1863.6(6)	2879.3(10)	1751.1(6)	2055.5(7)
Z	4	4	4	1	4	2	4	4
$\rho_{\rm calcd}~({\rm g/cm^3})$	1.515	1.590	1.746	1.444	2.138	1.512	1.753	1.667
$\mu \ (mm^{-1})$	0.780	0.695	4.436	1.467	8.574	1.534	1.187	1.129
F(000)	1640	1712	1840	913	1152	1344	928	1060
reflections collected	25356	24630	21980	19851	13327	20768	16385	19672
unique reflections	3171	3179	3198	4715	3237	6211	4009	4665
parameters	269	259	284	253	244	365	244	307
goodness-of-fit	1.050	1.033	1.044	1.047	0.787	1.073	1.034	1.045
$\mathbf{RI}\left[I > 2\sigma(I)\right]$	0.0639	0.0386	0.0254	0.0461	0.0503	0.0430	0.0340	0.0690
wR <sub>2</sub>	0.1281	0.0809	0.0510	0.1206	0.1303	0.1235	0.0797	0.1691
R (int)	0.1115	0.0628	0.0387	0.0748	0.0682	0.0556	0.0426	0.1241
largest diff peak	0.362	0.669	0.930	0.436	1.007	0.399	0.855	0.802
hole $(e \cdot \dot{A}^{-3})$	-0.429	-0.482	-0.438	-0.345	-1.343	-0.476	-0.733	-0.717



Figure 1. (a) Coordination environment of Zn(II) in complex 1 with the ellipsoids drawn at the 50% probability level; all hydrogen atoms are omitted for clarity with the exception of hydrogen atoms of water molecules. (b) A wavelike double-strand chain diagram of complexes 1-3 along the crystallographical *b*-axis. (c) M–O weak interaction among neighboring chains existing in complexes 1 and 2. (d) The 2D layer structure connected by Hg–O interaction among neighboring chains in complex 3. (e) The different coordination environments of metal atoms in complexes 1-3.

are summarized in Table 1. Selected bond lengths and angles are listed in Table S2 (see the Supporting Information).

### **Results and Discussion**

Crystal Structure Description. Complexes 1-3. For further understanding of the supramolecular architecture construction, we studied the role of the same subgroup metal cations in the assembly of complexes based on the 4-bpmb ligand. Thus, we obtained three new isostructural complexes 1-3 by the reaction of three metallic nitrates,  $Zn(NO_3)_2$ ,  $Cd(NO_3)_2$ , and  $Hg(NO_3)_2$ , with 4-bpmb ligands under the same reaction conditions, and the structure of complex 1 is used as an example of the three isostructural complexes for a detailed description. To the best of our knowledge, the crystalline isostructural phenomena are common, but the isostructural complexes based on the whole group metal cations of Zn, Cd, and Hg are rarely discussed to date. In complex 1 the Zn(II) ions are bridged by cis-4-bpmb molecules [Zn-N = 2.115(4) Å] and each ligated by one water molecule [Zn-O = 2.037(5) A] and two nitrate anions [Zn-O = 2.005(7), 2.375(7) Å] to give a 1:1 ligand/metal infinite polymeric chain  $[Zn \cdots Zn = 17.141 \text{ Å}]$  (Figure 1a). Within the ligand, the arrangement of two pyridines is symmetric, and the average planes of these pyridine rings are inclined at an angle of 23.2° to that of the linking benzene ring, while the mean planes of two pyridine rings are inclined to each another at an angle of 4.1°. In particular, in complex 1 there exists equimolar ligands that do not coordinate to the

metal atoms but locate in parallel with the coordinated ligands, in which two terminal N atoms of each ligand connect with hydrogen atoms of coordinated water molecules by N····H-O hydrogen-bonding interactions. The distance of 3.901 Å between the pyridine rings of the two parallel 4-bpmb ligands indicates weak aromatic  $\pi$ - $\pi$  stacking interactions. Consequently, the metal atoms are linked by the exobidentate ligands to generate a one-dimensional wavelike double-stranded chain (Figure 1b).

It should be noted that M-O weak interactions between metal cations and nitrate anions from the neighboring chains linked the 1D polymeric chains into a 2D layered architecture (Figure 1c). But with the enlargement of the metal cations' diameters, such weak M-O interactions become real coordination interactions in complex 3 (Figure 1d). In addition, we found the coordination numbers of metal atoms increase from 6 to 8 in response to the enlargement of the metal cations' diameters ( $Zn^{2+}$ : 0.74 Å;  $Cd^{2+}$ : 0.95 Å;  $Hg^{2+}$ : 1.02 Å). X-ray crystallographical analyses revealed that complex 1 has one six-coordinated Zn(II) atom in a distorted octahedral environment but seven-coordinated Cd(II) in a distorted monocapped octahedral environment for complex 2 and eight-coordinated Hg(II) in a distorted dicapped octahedral environment for complex 3 (Figure 1e), which are caused by one multidentate coordinated nitrate anion adopting several different coordination modes (monodentate mode in complex 1, bidentate mode in complex 2, tridentate mode in complex 3). That is to say, the larger the



Figure 2. (a) Coordination environment of Zn(II) in 4 with the ellipsoids drawn at the 50% probability level; all hydrogen atoms are omitted for clarity. (b) The 1D helical chain structures in complex 4. (c) View of complex 4 along the *b*-axis. (d) Packing diagram of complex 4 via  $C-H\cdots Cl$  hydrogen bonding interactions.

diameter of the metal cation is, the stronger the covelation ability of the metal cation is. As a result, the instances of intermolecular interaction have been shortened with the enlargement of metal cations' diameters, which is testified by the  $\pi$ - $\pi$  packing distances 3.901, 3.872, and 3.647 Å (complexes 1-3) between the pyridine rings of two parallel ligands, as well as the distances 3.226 Å (Zn-O), 2.907 Å (Cd-O), and 2.840 Å (Hg-O) between metal cations and nitrate anions from the neighboring 1D chain.

**Complexes 4–7.** Single-crystal X-ray structural analyses revealed that complexes 4-7 all exhibited helical chain structures, as we have expected. Different from the single helical chains in complexes 4-6, the helical chains in complex 7 are further bridged by the nitrate anions to form a 2D layered structure. Selected bond distances and angles for complexes 4-7 are given in Table S2.

The helical chain structure of complex **4** crystallizes in the P2(1)/c space group. As shown in Figure 2a, each Zn(II) atom is four-coordinated by two Cl atoms and two N atoms from different 2-bpmb ligands with a distorted tetrahedral geometry. The Zn–Cl bond lengths are in the range 2.223(1)–2.245(1) Å, and Zn–N bond lengths are in the range 2.044(3)–2.066(3) Å, which are both typical values for Zn–N<sub>py</sub> coordination distances.<sup>21</sup> The Cl(1)–Zn–Cl(2) bond angle (113.47°) and the N(1)–Zn–N(2) bond angle (115.42°) are nearly equal to the ideal angle of 120° to minimize the steric hindrance. The ligand with two terminal pyridine units is oriented in a divergent fashion, in which one pyridyl ring is nearly parallel to the corresponding linking phenyl rings and the other one is distorted drastically to reach the trans conformation with the dihedral angles between them being 3.67° (0.15) and 70.07° (0.18), respectively. With this coordination mode, the Zn(II) atoms are bridged by the flexible ligands to furnish a helical chain running along a crystallographical *b*-axis with a pitch of 16.381 Å, which is equal to the b dimension of the unit cell, corresponding to the next-nearest  $Zn \cdots Zn$  distance along the chain. Interestingly, the structure features left-hand and right-hand helical chains that are alternately arranged along the crystallographical c-axis (Figure 2b). The benzene rings of 2-bpmb ligands are located next to the helical axis to form a very narrow helical tube  $1.5 \times 7.0$  Å (Figure 2c). The driving force of the alternate left-hand and right-hand arrangement is likely to be C-H···Cl interactions, with the distances ranging from 2.813 to 2.915 Å, which bridge the adjacent helical chains into the 3D network structure (Figure 2d).

In complex 5, we reacted  $HgCl_2$  with the 2-bpmb ligand to generate a 1D helical chain instead of  $ZnCl_2$ . The 2-bpmb ligands serve as bidentate bridges to link Hg(II) cations into an infinite helical chain along the *b*-axis with two terminal pyridine units oriented in a convergent fashion that is different from that of complex 4 (Figure 3a). It is worthy to note that the two pyridine rings are drastically distorted



**Figure 3.** (a) Coordination environment of Hg(II) in 5 with the ellipsoids drawn at the 50% probability level; all hydrogen atoms are omitted for clarity. (b) The 1D helical chain structures in complex 5. (c) View of complex 5 along the *b*-axis. (d) Packing diagram of complex 5 via  $C-H\cdots Cl$  hydrogen bonding interactions.

from each other, with the dihedral angles being  $56.3(5)^\circ$ , and that the dihedral angles between the two pyridine rings and the benzene ring are  $84.8(4)^{\circ}$  and  $53.6(4)^{\circ}$ , respectively. The pitch (8.82 Å) is much shorter than that of complex 4(Figure 3b). It is probably the drastic distortion of the two pyridine rings that leads to the formation of the helical chain and the decrease of the pitch. The benzene moieties of the V-shape 2-bpmb ligand point away from the helical axis to produce a hollow cylinder with the dimensions  $2.4 \times 4.6$  Å, which is larger than those of complex 4 (Figure 3c). Like complex 4, the structure features left-hand and right-hand helical chains which arrange alternately along the crystallographical c-axis in complex 5.  $C-H\cdots$ Cl (2.85 Å) hydrogen bonding interactions serve as driving forces, which bridge the adjacent helical chains into the 3D network structure (Figure 3d).

The acetate salt was employed to react with 2-bpmb ligand to give a 1D helical chain structure of complex **6**. In this structure, each ligand with two pyridine units oriented in a divergent fashion links two Cu(II) acetate dimeric units to form an infinite helical chain running along a crystallographical *c*-axis direction with a long pitch of 25.89 Å [Cu(1)– N(2) = 2.236 Å, Cu(2)–N(1) = 2.225 Å], in which the Cu–Cu bond length is 2.636 Å, the Cu–O bond lengths are ranging from 1.96(7) Å to 1.98(7) Å, and the O–Cu–O bond angles are ranging from 86.88° to 90.96° (Figure 4a). Within the ligands, the mean planes of the pyridine rings are inclined highly to that of the benzene ring at angles of  $85.25^{\circ}$  (0.12) and  $75.55^{\circ}$  (0.14), which results in the 2-bpmb ligands being extended like a "S" and occupying the latent part of the axis but not winding along the axis (Figure 4b). Compared with the metal chloride salts in complexes **4** and **5**, the Cu(II) acetate dimeric units in **6** own stronger rigidity and larger volume. The above-mentioned reasons lead to no helical tube in the helical chain (Figure 4c). The weak hydrogen-bonding interactions of one pyridine C–H group and a carboxylate O atom (O···H 2.626, 2.703 Å) from the adjacent chain allow pairing of two opposite single-strand helical chains to generate a double-strand zipperlike helical chain (Figure 4d).

The nitrate salt with various coordination fashions was used in complex 7, which resulted in comparatively higher dimensional structure. As shown in Figure 5a, each silver atom locates at a distorted tetrahedral environment with two nitrogen atoms from different ligands [Ag-N = 2.22-2.23 Å] and oxygen atoms from different nitrate anions [Ag-O = 2.59-2.70 Å]. The 2-bpmb ligands with two terminal pyridines in a divergent fashion connect adjacent Ag atoms to produce the infinite helical chains, which characterize left-hand and right-hand alternate arrangements (Figure 5b). Two pyridyl rings twist drastically to the corresponding linking benzene rings just like a circle, with the dihedral angles between them being 84.9° (0.1) and 81.0° (0.1), respectively. So the dimension of the helical tube



**Figure 4.** (a) A helical chain in **6** with the ellipsoids drawn at the 50% probability level; all hydrogen atoms are omitted for clarity. (b) The 1D helical chain structures in complex **6**. (c) View of complex **6** along the helical axis. (d) Views showing the alternate packing of the right-hand and left-hand helical chains.

is about 2.0 × 3.0 Å (Figure 5c). The pitch (8.011 Å) is shorter than those of complexes 4 and 6, nearly equal to that of complex 5. Each monohand helical chain is linked to two opposite-hand helical chains by two different nitrate anions in  $\mu_2$  modes and generates a 2D layer structure with a Ag···Ag distance of 6.30 Å (Figure 5d).

Complex 8. Different from above complexes, in which the ligands act as bidentate ligands to coordinate with metal cations through nitrogen atoms only, in complex 8 the nitrogen atoms and oxygen atoms of each ligand all joined in the coordination with Cu atoms (Figure 6a). Thus, we obtained a straight-like chain unexpectedly. X-ray diffraction analysis reveals that Cu(II) atoms adopt a distorted octahedral arrangement and are coordinated in the basal plane by a N2O2 donor set, in which two N atoms come from two pyridine rings and two O atoms are from two water molecules, with the elongated axial site occupied by two OLigand donors. Selected bond distances and angles for complex 8 are given in Table S2. The ligand is arranged in a syn conformation with both pyridine rings oriented on the same side of the benzene ring. The mean planes of the pyridine rings are inclined to that of the benzene ring at angles of 40.58° (0.12) and 39.25° (0.12), but the two pyridines are almost parallel to each other at an angle of 1.47° (0.21). In complex 8, each ligand coordinates to the metal atoms  $[N(1)-Cu-N(2) = 174.78^{\circ}]$  to form a 1D straightlike polymeric chain along the *b*-axis with a Cu···Cu distance of 8.86 Å (Figure 6b). Acting as counterions, the nitrates disordered over two orientations do not coordinate with metals but bond with coordinated water molecules through hydrogen bonds to connect the adjacent 1D straightlike chains into a 3D net structure (Figure 6c).

Effects of the 2-bpmb Ligand's Conformation and Anions on the Structures of Complexes 4-8. An investigation of the structures reveals that the 2-bpmb ligand with two terminal pyridines oriented in the *trans* conformation tends to form helical polymeric chainlike complexes 4, 6, and 7. In complex 5, the ligands serve as *cis* linkers and also bridge the Hg(II) cations into the helical chains resulted from the relatively drastic distortion of the pyridine rings and the benzene ring. The arrangement of the ligand in complex 8 is identical with complex 5 in a convergent fashion, but it does not result in the formation of a helical chain. Study of the coordinated anions around the metal center may explain the differences among these complexes. For complexes 4 and 5, the large volume of the coordinated Cl<sup>-</sup> anions is the key factor that prevents further coordination of the metal center with the O atoms of the ligands. The dimeric acetate copper leaves the copper atom only one coordination site in complex 6. In complex 7, the nitrate anions serve as tridentate linkers to bridge Ag atoms from adjacent chains to fulfill the coordination of Ag atoms. In contrast to complex 7, the



**Figure 5.** (a) Coordination environment of Ag(I) in 7 with the ellipsoids drawn at the 50% probability level; all hydrogen atoms are omitted for clarity. (b) View of the two types of helical chains arranged along the *b*-axis. (c) View of the helical channel in complex 7. (d) Packing diagram of complex 7: green color indicates the left-hand helical chains, and violet color indicates the right-hand helical chains.

charge-balanced nitrate anions do not take part in coordination with metal atoms in complex  $\mathbf{8}$ , and the copper atom is coordinated to two water molecules which are smaller than Cl<sup>-</sup> anions, leading to the formation of the tetracoordinate mode of the 2-bpmb ligand.

**Thermogravimetric Analysis.** For complexes 1–3, the first weight losses of 17.85%, 16.87%, and 15.26% are attributed to the release of one H<sub>2</sub>O molecule and two nitrate anions from room temperature to 272, 288, and 190 °C, respectively (calcd 17.93%, 16.93%, 15.39%). After that, the complexes begin to decompose and are stable up to 603, 581, and 622 °C, corresponding to the loss of two ligands per formula unit. In complexes 4 and 5, the first weight losses of 4.37% and 5.87% take place at 162-237 °C and 143-229 °C, corresponding to the dissociation of free pyridine and a water molecule, respectively (calcd 4.43% and 6.00%). The second weight loss occurs between 230 and 290 °C and are assigned to the release of Cl<sup>-</sup>. And consecutive decompositions indicate the total destruction of the framework. In complex 6, the release of four acecate anions takes place from room temperature to 218 °C (obsd 35.95% calcd. 36.03%) and the removal of the ligands occurs under higher temperature. In the temperature range 202-241 °C, complex 7 begins to lose the nitrate anion (obsd 13.36%, calcd 13.44%). The weight loss of ligands (63.15%) is observed from 241 to 565 °C (calcd 63.28%). For complex 8, the first weight loss (7.05%) occurs at 90-180 °C, corresponding to the release of two

 $H_2O$  molecules (calcd 6.92%). The next weight loss of 23.95% is assigned to the loss of two nitrate anions from 180 to 233 °C (calcd 24.03%). The framework collapses above 233 °C, with an observed weight loss of 56.57% (calcd 56.69%).

Photoluminescent Properties. We investigated the luminescence properties of coordination complexes in view of their potential applications as light-emitting diodes (LEDs).<sup>24</sup> The 2-bpmb ligand exhibits much weaker emission centered at 420 nm than 4-bpmb, and no clear fluorescent emission was observed for complexes 4-8. Hence, we focus on studying the luminescence properties of complexes 1-3. The solidstate fluorescent analyses of complexes 1, 2, and 3 show similar fluorescent properties with the same excitation wavelength of 370 nm. It can be tentatively assigned to the intraligand fluorescenct emission, since a similar emission can be observed for the free 4-bpmb ligand. As shown in Figure 7, the 4-bpmb ligand has an emission band with the maximum intensity at 424 nm, while the maxima emission peaks of complexes 1-3 are slightly red shifted to 433.5 nm for complex 1, 432 nm for complex 2 and 430 nm for complex 3, which is ascribed to the metal ion bridged to ligands. In contrast to the case of the ligand, it is found that the emissions of 1-3 are remarkably enhanced. The phenomena may be attributed to the increase of the ligands conformational rigidity due to the coordination with Zn(II) and Cd(II) and Hg(II) ions.





Figure 6. (a) Coordination environment of Cu(II) in complex 8 with the ellipsoids drawn at the 50% probability level; all hydrogen atoms are omitted for clarity with the exception of hydrogen atoms of water molecules. (b) The 1D straight-like chain structure along the *b*-axis in complex 8. (c)  $C-H\cdots O$  hydrogen bonding interactions link the 3D network structure (dark yellow bonds represent the 1D straight-like chain structure viewed along the *b*-axis).



Figure 7. Photoluminescence emission spectra of the 4-bpmb ligand and complexes 1-3.

# Conclusions

We have synthesized two flexible V-shape bidentate ligands, 1,3-bis(pyridine-4-ylmethoxy)benzene (4-bpmb) and 1,3-bis(pyridine-2-ylmethoxy)benzene (2-bpmb), and reacted them with transitional metal salts to obtain wavelike and helical chains. The assembly of 4-bpmb ligand with the same subgroup metal salts, zinc, cadium, and mercury nitrate, resulted in three isologous wavelike double-stranded chains,  $\{[Zn(4-bpmb)(H_2O)(NO_3)_2] \cdot (4-bpmb)\}_n(1)$ ,  $\{[Cd(4-bpmb)-(H_2O)(NO_3)_2] \cdot (4-bpmb)\}_n(2)$ , and  $\{[Hg(4-bpmb)(H_2O)(NO_3)_2] \cdot (4-bpmb)\}_n(3)$ , which further testifies that the same subgroup metals tend to construct similar structural topologies. Because of the differences among the diameters of metal ions in three isologues, the distances of the adjacent chains and that of two stacking pyridines in one crystal unit are shortened with the enlargement of the atomic diameters. We constructed four helical complexes **4**–**7** based on a flexible 2-bpmb ligand. Unexpectedly, complex **8** exhibits a straightlike chain, in which the 2-bpmb ligands adopt a tetradentate bridging coordination mode and the charge-balanced nitrate anions do not join in coordination. In summary, this research shows that assembly of flexible V-shape dipyridine phenyl ligands and metal cations could generate unique structural motifs, which cannot be obtained by using normal rigid ligands, and the counteranions play important roles in the construction of the metal–organic framework.

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Supporting Information Available: Hydrogen-bonding data, selected bond lengths and angles, IR spectroscopic data, TGA trace, powder XRD data, checkcif report; and X-ray crystallographic information files (CIF) for complexes 1–8. This material is available free of charge via the Internet at http://pubs.acs.org.

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