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## Significant Positional Isomeric Effect on Structural Assemblies of Zn(II) and Cd(II) Coordination Polymers Based on Bromoisophthalic Acids and Various Dipyridyl-Type Coligands

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**ABSTRACT:** Seven Zn(II) and Cd(II) coordination polymers, formulated as  $\{[\text{Zn}_2(\text{5-Br-ip})_2(\text{bpy})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}\}_n$  (**1**),  $\{[\text{Zn}(\text{5-Br-ip})(\text{bpa})(\text{H}_2\text{O})]\}_n$  (**2**),  $\{[\text{Cd}(\text{5-Br-ip})(\text{bpp})(\text{H}_2\text{O})]\}_n$  (**3**),  $\{[\text{Zn}(\text{5-Br-ip})(\text{bpe})]\}_n$  (**4**),  $\{[\text{Zn}_2(\text{4-Br-ip})_2(\text{bpy})]\cdot \text{H}_2\text{O}\}_n$  (**5**),  $\{[\text{Zn}(\text{4-Br-ip})(\text{bpa})(\text{H}_2\text{O})]\}_n$  (**6**), and  $\{[\text{Cd}(\text{4-Br-ip})(\text{bpp})]\}_n$  (**7**), were prepared by hydrothermal reactions based on 4-bromo- or 5-bromoisophthalic acid (4-Br-H<sub>2</sub>ip or 5-Br-H<sub>2</sub>ip) and different dipyridyl-type coligands 4,4'-bipyridyl (bpy), 1,2-bi(4-pyridyl)ethane (bpa), 1,3-di(4-pyridyl)propane (bpp), and 1,2-di(4-pyridyl)ethene (bpe). All complexes **1**–**7** were characterized by elemental analysis, IR spectra, and X-ray single-crystal diffraction. Complex **1** is a 2D (6,3) coordination network and further assembled into a 3D framework via  $\pi-\pi$  stacking interactions. Complex **2** shows a 1D coordination array and further forms a 2D supramolecular network via H-bonding interactions. Complex **3** has a 2-fold interpenetrating 3D diamond framework. Complex **4** is a 3-fold interpenetrating 3D network with CdSO<sub>4</sub> topology, constructed from alternately left- and right-handed helical arrays. Complex **5** has a 3D (3,4)-connected network with  $(4\cdot 8^2)(4\cdot 8^2\cdot 10^3)$  topology. Complex **6** features a 1D coordination chain and further forms a 2D helical supramolecular pattern by H-bonding. Complex **7** exhibits a (3,5)-connected 2D layer with the Schläfli symbol of  $(4^2\cdot 6)(4^2\cdot 6^7\cdot 8)$ . The results reveal that the diverse coordination networks of **1**–**7** can be adjusted by the different dispositions of the -Br substituent of isophthalate building blocks, as well as the metal ions and the dipyridyl coligands. Moreover, the luminescent properties of the complexes have been investigated.

### Introduction

The design and synthesis of coordination polymers are of great interest, owing to their elegant framework topologies as well as their tremendous potential applications in nonlinear optics, catalysis, luminescence, gas sorption, and magnetism.<sup>1–3</sup> Studies in this field have been focused on the design and construction of new coordination frameworks as well as the elucidation of their structure–function relationship.<sup>4,5</sup> However, it is still a big challenge to rationally and predictably prepare the desired crystalline products. The resulting structures will be determined by several factors, including the coordination geometry of metal ions, the structural characteristics of ligands, the solvent system, the counteranions, and so on. In this regard, the selection of suitable spacer ligands is extremely important to control and adjust the topology of coordination frameworks.<sup>6,7</sup> Among various organic ligands, multicarboxylates have attracted considerable attention due to their various coordination modes.<sup>8</sup> So far, a large number of metal–carboxylate coordination complexes have been reported. However, a systematic study of the positional isomeric effect of multicarboxylates on the structural assemblies with d<sup>10</sup> metal ions is relatively rare.

On the other hand, rodlike N,N'-donor building blocks, such as the conventionally employed 4,4'-bipyridine, have been extensively studied in coordination chemistry. Furthermore, the recent results show that the modified 4,4'-bipyridine derivatives, such as bpa, bpe, and bpp, which have different

spacers between the two 4-pyridyl groups, can cause distinct spatial effect and, thus, result in unexpected architectures and/or interesting properties. The use of these auxiliary ligands may also contribute to an understanding of the processes for assembly and recognition.<sup>9,10</sup>

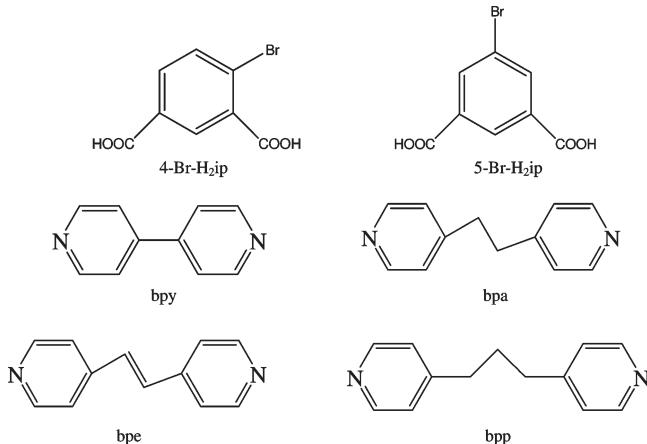
To evaluate the effect of positional isomeric ligands on forming the coordination frameworks, we have selected 4-bromoisophthalic acid (4-Br-H<sub>2</sub>ip) and 5-bromoisophthalic acid (5-Br-H<sub>2</sub>ip) as the tectons in this work (see Scheme 1). These two polycarboxyl ligands are closely related and only differentiated by the positions of the -Br substituent, which may afford different supramolecular assemblies in view of their isomeric effect. Here, we present the syntheses and crystal structures of seven Zn(II) and Cd(II) coordination polymers with such two isomeric tectons and various dipyridyl ligands, including  $\{[\text{Zn}_2(\text{5-Br-ip})_2(\text{bpy})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}\}_n$  (**1**),  $\{[\text{Zn}(\text{5-Br-ip})(\text{bpa})(\text{H}_2\text{O})]\}_n$  (**2**),  $\{[\text{Cd}(\text{5-Br-ip})(\text{bpp})(\text{H}_2\text{O})]\}_n$  (**3**),  $\{[\text{Zn}(\text{5-Br-ip})(\text{bpe})]\}_n$  (**4**),  $\{[\text{Zn}_2(\text{4-Br-ip})_2(\text{bpy})]\cdot \text{H}_2\text{O}\}_n$  (**5**),  $\{[\text{Zn}(\text{4-Br-ip})(\text{bpa})(\text{H}_2\text{O})]\}_n$  (**6**), and  $\{[\text{Cd}(\text{4-Br-ip})(\text{bpp})]\}_n$  (**7**). In addition, their solid-state luminescent properties have also been investigated and analyzed.

### Results and Discussion

**Description of Crystal Structures.**  $\{[\text{Zn}_2(\text{5-Br-ip})_2(\text{bpy})\cdot (\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}\}_n$  (**1**). The asymmetric unit of **1** contains two Zn(II) centers, two 5-Br-ip anions, one bpy, one water ligand, and two lattice water molecules. As shown in Figure 1a, each Zn(II) center is coordinated by two carboxylate oxygen atoms from two 5-Br-ip, one water ligand, and one nitrogen

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**Scheme 1. Structures of Dicarboxylic Acids and Dipyriddy Coligands Used in This Work**

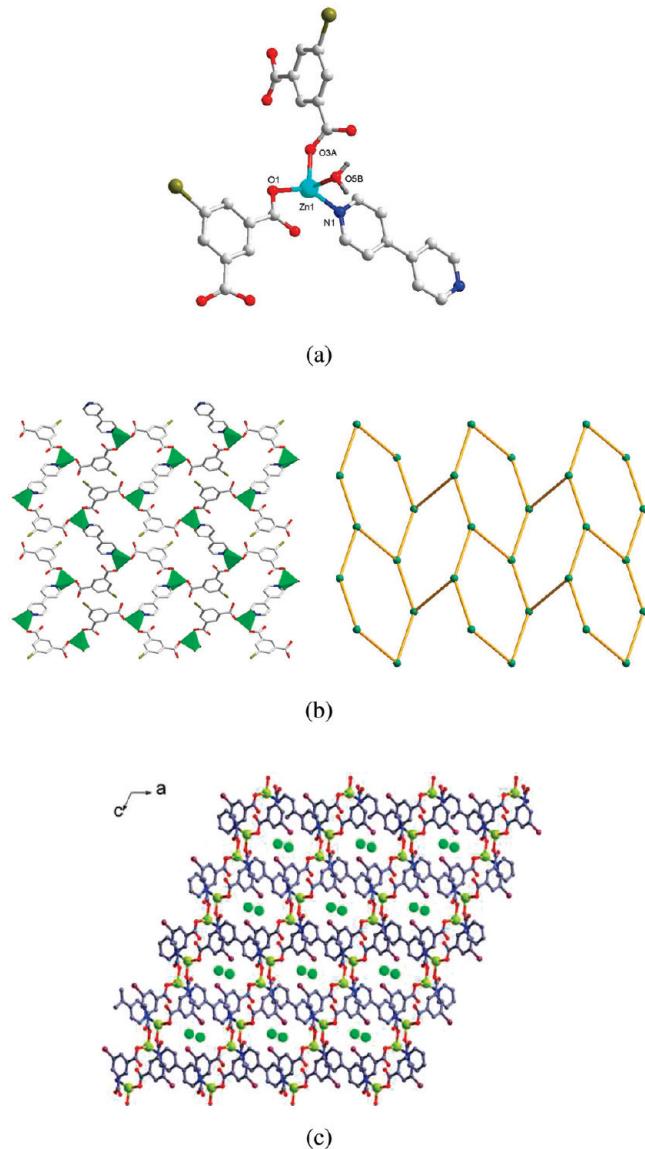


atom from bpy to result in a  $\text{ZnO}_3\text{N}$  tetrahedral geometry. The  $\text{Zn}-\text{N}$  bond distance is  $2.029(2)$  Å, and the  $\text{Zn}-\text{O}$  bond lengths are in the range  $1.9573(18)$ – $2.159(2)$  Å. The adjacent  $\text{Zn}(\text{II})$  ions are bridged by the 5-Br-ip ligands to form a 1D chain, and such 1D chains are further connected by the bpy spacers via  $\text{Zn}-\text{N}$  coordination bonds, leading to the formation of a 2D (6,3) network (see Figure 1b). Such 2D layers are parallel along the *b* axis with some offset, and the plane-to-plane distance between the adjacent 5-Br-ip ligands is  $3.256$  Å, suggesting the existence of interlayer  $\pi-\pi$  interactions. Thus, the 2D layers are assembled into a 3D supramolecular network (see Figure 1c), which shows channels along the *b* axis that are occupied by the lattice water molecules. The effective free volume of **1** is  $178.3$  Å<sup>3</sup> (6.4% of the unit cell volume), as calculated by PLATON.

$\{[\text{Zn}(5\text{-Br-ip})(\text{bpa})(\text{H}_2\text{O})]\}_n \cdot (2)$ . In this structure, the  $\text{Zn}(\text{II})$  ions are bridged by the 5-Br-ip ligands to form 1D chains, which are further connected by the  $\text{O}_5\text{-H}_1\text{W}\cdots\text{N}_2$  hydrogen bonds to afford a 2D supramolecular layer (see Figure 2a and Table S2, Supporting Information). The adjacent 2D networks are parallel and arranged in an ABAB stacking sequence (see Figure 2b). This structure has been reported recently.<sup>11</sup>

$\{[\text{Cd}(5\text{-Br-ip})(\text{bpp})(\text{H}_2\text{O})]\}_n \cdot (3)$ . As shown in Figure 3a, the structure of **3** consists of one Cd(II) ion, one 5-Br-ip anion, one bpp ligand, and one coordinated water molecule. Each Cd(II) center is coordinated by three carboxylate oxygen atoms from two 5-Br-ip anions, one water molecule, and two nitrogen atoms from two bpp ligands, showing a distorted octahedral sphere. The  $\text{Cd}-\text{O}$  bond lengths are in the range  $2.218(3)$ – $2.639(6)$  Å, and the  $\text{Cd}-\text{N}$  bond distances are  $2.375(3)$  and  $2.284(3)$  Å, respectively. The  $\text{Cd}-\text{O}(\text{carboxylate})$  and  $\text{Cd}-\text{N}$  bond parameters are in agreement with those Cd(II) complexes containing carboxylate and bpp.<sup>12</sup> As depicted in Figure 3b, the Cd(II) ions are linked by the 5-Br-ip ligands to form a 1D zigzag chain. Furthermore, these 1D arrays are connected by the exobidentate bpp bridges to form a 2-fold interpenetrating 3D framework with the diamondoid-like topology (see Figure 3c and d).

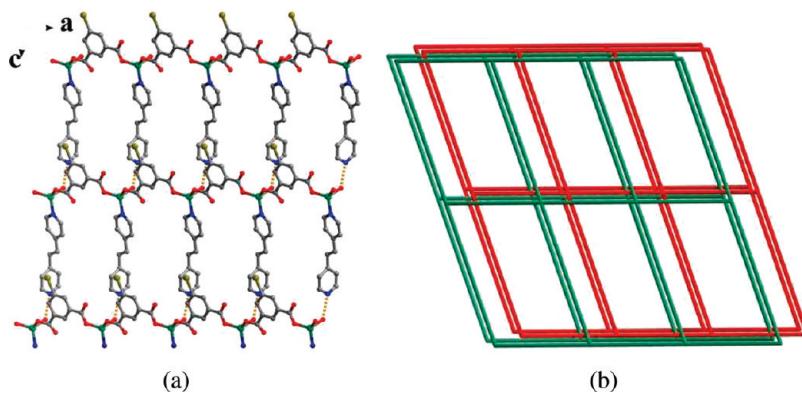
$\{[\text{Zn}(5\text{-Br-ip})(\text{bpe})]\}_n \cdot (4)$ . The asymmetric unit of **4** contains one Zn(II) center, one 5-Br-ip anion, and one bpe. As shown in Figure 4a, the Zn(II) center is coordinated by two oxygen atoms from two 5-Br-ip ligands and two nitrogen atoms from two bpe to form a  $\text{ZnO}_2\text{N}_2$  tetrahedral geometry. The  $\text{Zn}-\text{O}$  ( $1.954$  Å) and  $\text{Zn}-\text{N}$  ( $2.064(3)$  Å) bond lengths



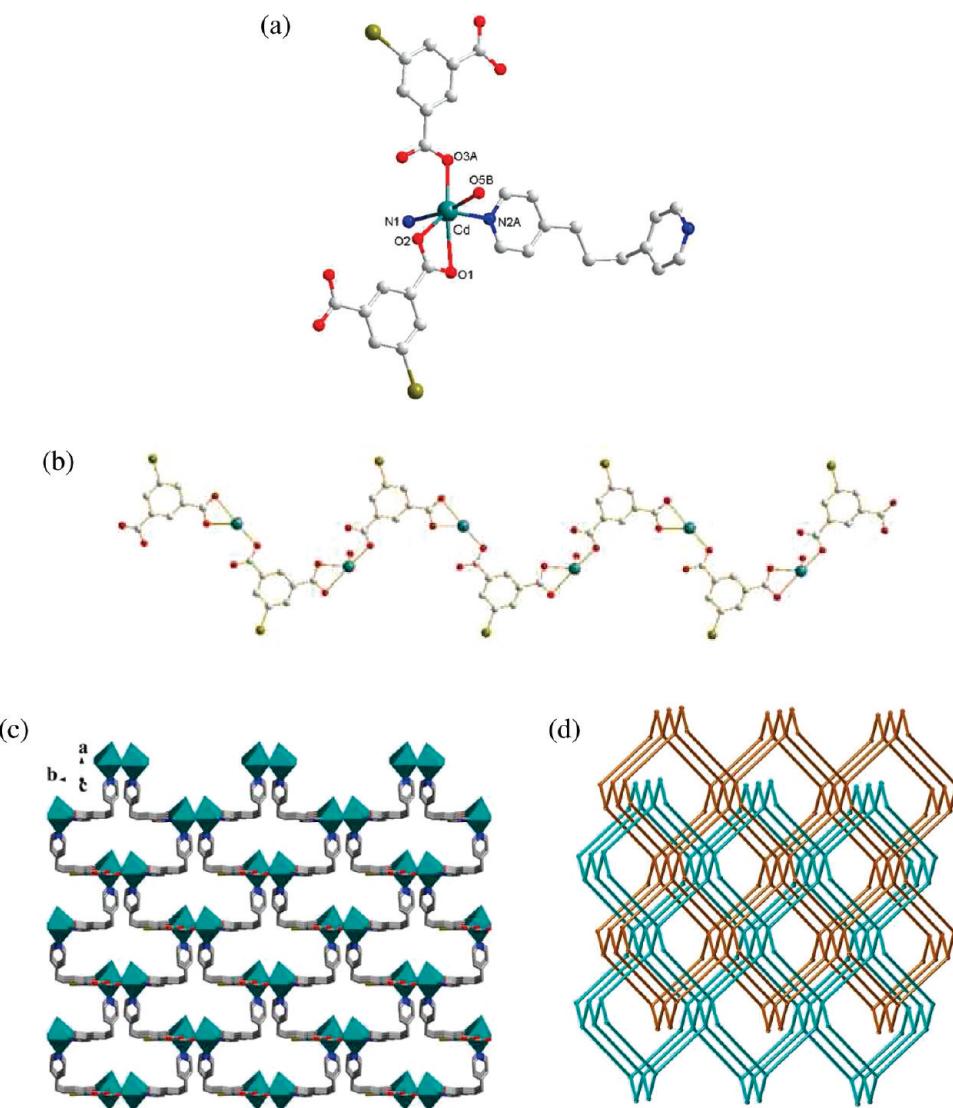
**Figure 1.** Views of **1**. (a) Coordination environment of  $\text{Zn}(\text{II})$ . (b) Perspective view of the 2D coordination network. (c) 3D supramolecular framework with lattice water guests (green balls) located in the channels.

are also similar to those observed in other tetrahedral zinc(II) complexes.<sup>13</sup> Each 5-Br-ip ligand connects the adjacent  $\text{Zn}(\text{II})$  ions to form left-handed and right-handed helical arrays (Figure 4b). The bpe ligands further link the 1D arrays to form a 3D network composed of alternate  $(\text{Zn}-5\text{-Br-ip}-\text{Zn}-5\text{-Br-ip}-\text{Zn}-\text{bpe}-\text{Zn}-\text{bpe})_n$  helices (see Figure 4c and d). Topologically, the coordination architecture of **4** can be simplified as a  $\text{CdSO}_4$  network. The large cavities allow three such 3D networks to weave into a 3-fold interpenetrating structure (see Figure 4e).

$\{[\text{Zn}_2(4\text{-Br-ip})_2(\text{bpy})]\cdot \text{H}_2\text{O}\}_n \cdot (5)$ . The asymmetric unit of **5** consists of one Zn(II) ion, one 4-Br-ip anion, one-half bpy, and one-half lattice water molecule. Each Zn(II) center is coordinated by three carboxylate oxygen atoms from three 4-Br-ip ligands and one pyridyl nitrogen donor from bpy to constitute a tetrahedral geometry (see Figure 5a). The  $\text{Zn}-\text{N}$  bond length is  $2.033(3)$  Å, and the  $\text{Zn}-\text{O}$  bond distances are in the range  $1.928(3)$ – $1.997(3)$  Å. The Zn(II) ions are bridged by the 4-Br-ip ligands to give rise to a 2D network with  $4\cdot 8^2$



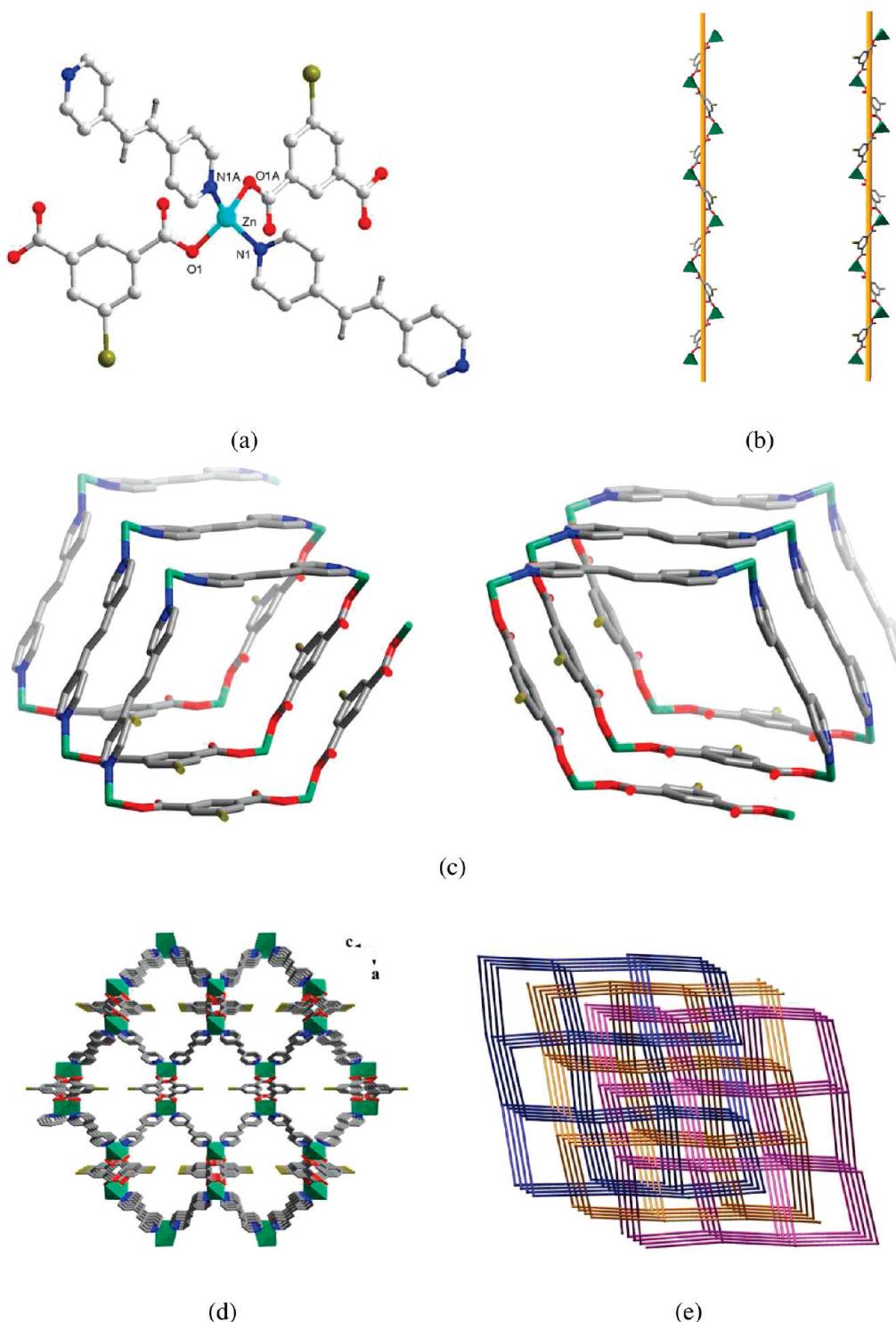
**Figure 2.** Views of **2**. (a) Perspective view of the 2D network. Interchain H-bonds are represented as dashed lines. (b) ABAB parallel stacking of the 2D layers.



**Figure 3.** Views of **3**. (a) Coordination environment of Cd(II). (b) 1D chain (the bpp ligands are omitted for clarity). (c) 3D coordination network. (d) Schematic representation of the 2-fold interpenetrating diamond framework.

topology (see Figure 5b and c). The 2D layers are further extended by the bpp ligands to construct a 3D pillar-layered framework. From the viewpoint of network topology, the overall 3D structure can be regarded as a (3,4)-connected network (see Figure 5d) with the Schläfli symbol  $(4 \cdot 8^2)(4 \cdot 8^2 \cdot 10^3)$ .

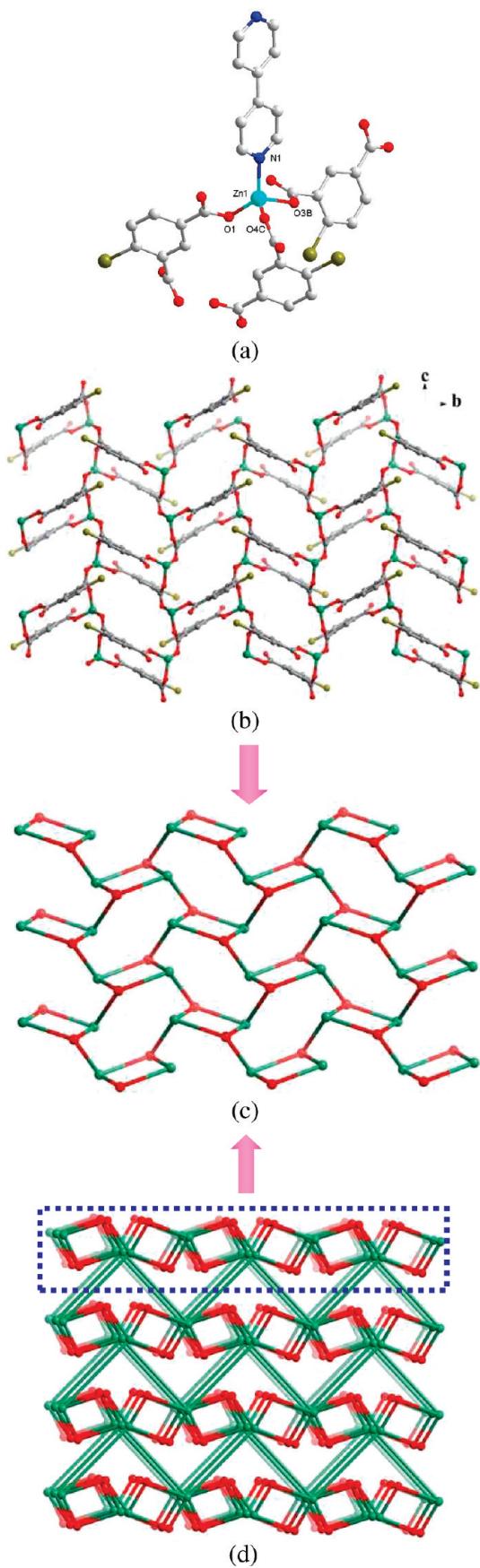
$\{[\text{Zn}(\text{4-Br-ip})(\text{bpa})(\text{H}_2\text{O})]\}_n \cdot (\textbf{6})$ . The asymmetric unit of **6** contains one Zn(II) center, one 4-Br-ip anion, one bpa, and one coordinated water molecule. As shown in Figure 6a, the Zn(II) center is coordinated by three oxygen atoms from two carboxylate groups and one water molecule, as well as one



**Figure 4.** Views of **4**. (a) Coordination environment of Zn(II). (b) View of the left- and right-handed infinite Zn–5-Br-ip helical chains. (c) View of the left- and right-handed infinite Zn–5-Br-ip–bpe helical chains. (d) View of the 3D network along the *b* axis. (e) Schematic representation of the 3-fold interpenetrating architecture.

nitrogen atom from bpa to form a  $\text{ZnO}_3\text{N}$  tetrahedral geometry. The  $\text{Zn}-\text{N}$  bond distance is  $2.016(2)$  Å, which is similar to those for other tetrahedral zinc(II) complexes of bpa.<sup>12</sup> The  $\text{Zn}-\text{O}$  bond lengths are in the range  $1.933(2)$ – $2.001(2)$  Å, also being within the range reported for tetrahedral zinc(II)-carboxylate complexes.<sup>14</sup> In this case, each 4-Br-ip connects the adjacent Zn(II) ions to form a 1D chain structure. The 1D chains are further connected via the  $\text{O}1-\text{H}1\text{W}\cdots\text{N}2$  H-bonds to form a 2D supramolecular

network (see Figure 6b and Table S2, Supporting Information), in which the adjacent channels show alternating chirality. When both coordination bonds and H-bonds are considered, the 4-Br-ip and bpa ligands serve as the bridging spacers, which connect the zinc(II) ions to form left-handed and right-handed 1-D chains (see Figure 6c). Further, two such 2D networks are entangled to generate a 2-fold interpenetrating structure, as depicted in Figure 6d.

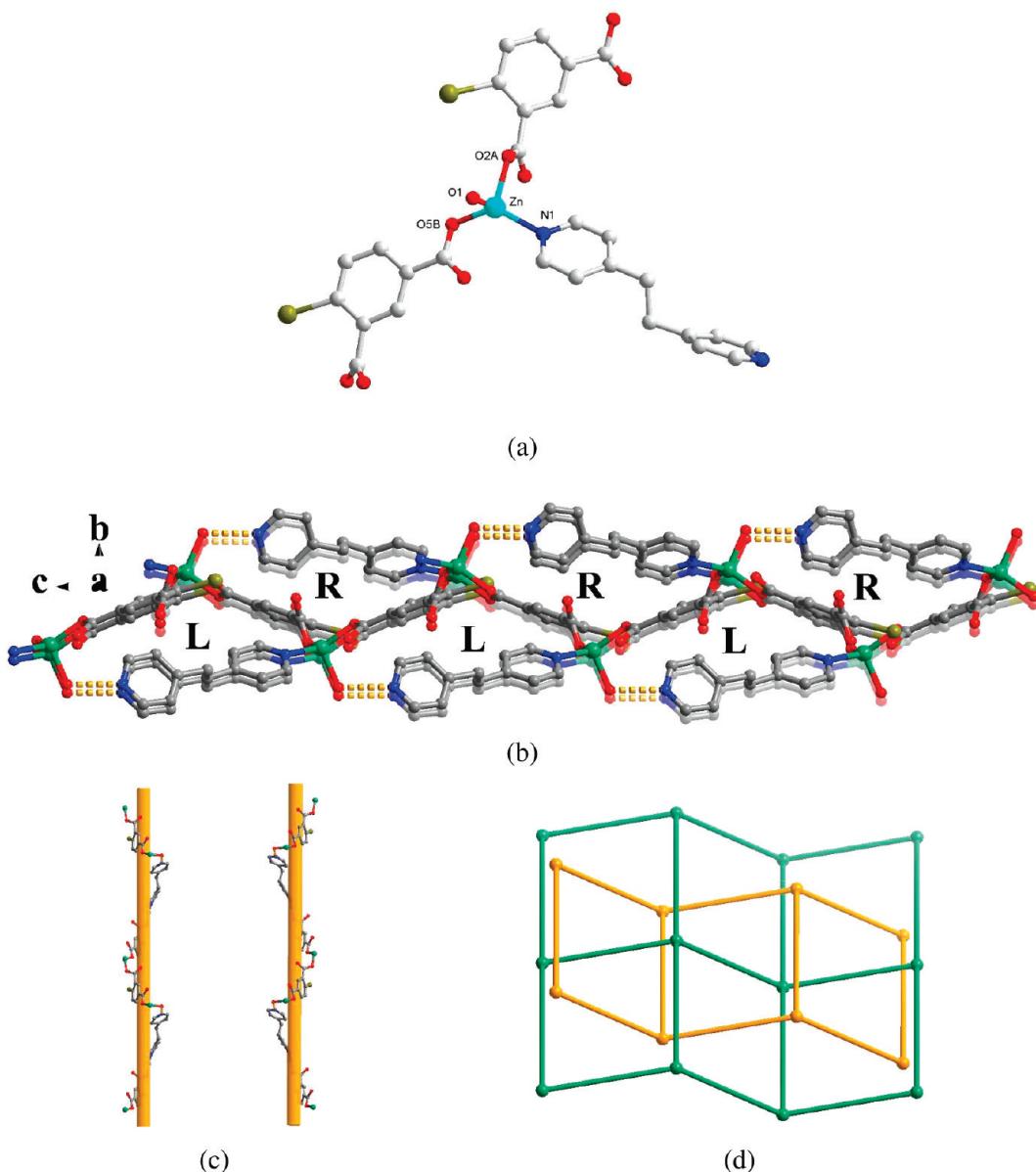


**Figure 5.** Views of **5**. (a) Coordination environment of Zn(II). (b and c) Perspective views of the 2D network. (d) Schematic description of the (3,4)-connected ( $4 \cdot 8^2$ ) ( $4 \cdot 8^2 \cdot 10^3$ ) topology.

$\{[\text{Cd}(\text{4-Br-ip})(\text{bpp})]\}_n$  (**7**). The fundamental building unit (see Figure 7a) consists of one crystallographically independent Cd(II) ion, one 4-Br-ip anion, and one bpp ligand. The Cd(II) center is six-coordinated by four carboxylate O atoms from three 4-Br-ip anions and two pyridyl N donors from two bpp ligands, taking a slightly distorted octahedral geometry. The Cd–O bond lengths are in the range 2.277(6)–2.508(6) Å, and the Cd–N bond distances are 2.312(6) and 2.430(7) Å, being in agreement with those of Cd(II) complexes with carboxylate and bpp.<sup>12</sup> The 4-Br-ip ligands link the Cd(II) ions to form a 1D chain with the adjacent Cd···Cd distance of 4.068 Å (see Figure 7b). Such 1D chains are further extended through the bpp ligands to result in a 2D layer, which can be classified as a (3,5)-connected network with  $(4^2 \cdot 6)$  ( $4^2 \cdot 6^7 \cdot 8$ ) topology (see Figures 7c and d).

**Synthetic Chemistry and Structural Diversity.** 4-Br-H<sub>2</sub>ip and 5-Br-H<sub>2</sub>ip are a pair of Br-substituted isomers of isophthalic acid, which differ in the position of the -Br moiety at the substituted benzene ring. However, such a subtle difference may significantly influence the resulting metal–organic frameworks, although -Br will not be involved in metal coordination. In the present study, four new Zn(II) and Cd(II) coordination polymers have been prepared from 5-Br-H<sub>2</sub>ip in combination with different dipyridyl-type coligands under similar conditions. However, when 4-Br-H<sub>2</sub>ip was used, only three complexes were structurally determined, showing completely different coordination architectures from those of the corresponding species with 5-Br-H<sub>2</sub>ip. As for the assembly of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ , 4-Br-H<sub>2</sub>ip, and bpe, no single crystal product suitable for X-ray diffraction analysis can be obtained. We have also tried to prepare the Cd(II) analogues of complexes **1**, **2**, **4**, **5**, and **6**, and also, only polycrystalline powders can be obtained using the similar synthetic methods. With regard to the bpy-bridged complexes **1** and **5**, along with the variation of dicarboxylate building blocks (from 5-Br-ip to 4-Br-ip), their net patterns are changed from a 2D (6,3) layer to a 3D (3,4)-connected network with  $(4 \cdot 8^2)(4 \cdot 8^2 \cdot 10^3)$  topology. Similarly, with regard to the bpa-bridged complexes **2** and **6**, their network arrays are changed from a 2D (4,4) supramolecular layer for 5-Br-ip to a 2D helical supramolecular framework for 4-Br-ip. And also for bpp, a 2-fold interpenetrated diamondoid-like network and a (3,5)-connected 2D layer with the Schläfli symbol of  $(4^2 \cdot 6)(4^2 \cdot 6^7 \cdot 8)$  are obtained for **3** and **7**, respectively. Compounds **1**–**7** are air stable, insoluble in common organic solvents, and can retain their crystalline integrity at ambient temperature for a long time. The synthetic route and structural diversity of the complexes are shown in Scheme 2. The results undoubtedly discover the positional isomeric effect of dicarboxylate bridging ligands in molecular tectonics of coordination networks, which, as expected, are also dependent on the metal ions and dipyridyl coligands.

The coordination modes of 4-Br-ip and 5-Br-ip in this work are summarized in Scheme 3. For complexes **1**, **5** and **3**, **7**, the 4-Br-ip and 5-Br-ip ligands display diverse bridging fashions. In **1**, each 5-Br-ip ligand adopts the bis-monodentate coordination mode (Scheme 3a) while, in **5**, the carboxylate groups of 4-Br-ip take the bis-monodentate bridging and monodentate modes, respectively (Scheme 3c). In **3**, the carboxylate groups of 5-Br-ip take the chelating and monodentate modes, respectively (Scheme 3b), while, in **7**, the two carboxylate groups in 4-Br-ip take the chelating and bis-monodentate bridging coordinating modes, respectively (Scheme 3e). The choice of different Br-substituted isomers



**Figure 6.** Views of **6**. (a) Coordination environment of Zn(II). (b) Projection along the *a* axis of the 2D supramolecular network. (c) View of left- and right-handed helical chains. (d) Schematic representation of the interpenetrating structure, in which the balls represent the zinc(II) nodes.

of isophthalic acid is clearly critical to determine the binding fashions of carboxylates. In **2** and **6**, although the 4-Br-ip and 5-Br-ip ligands display similar coordination modes, significant structural difference are still observed and may be ascribed to the positional isomeric effect.

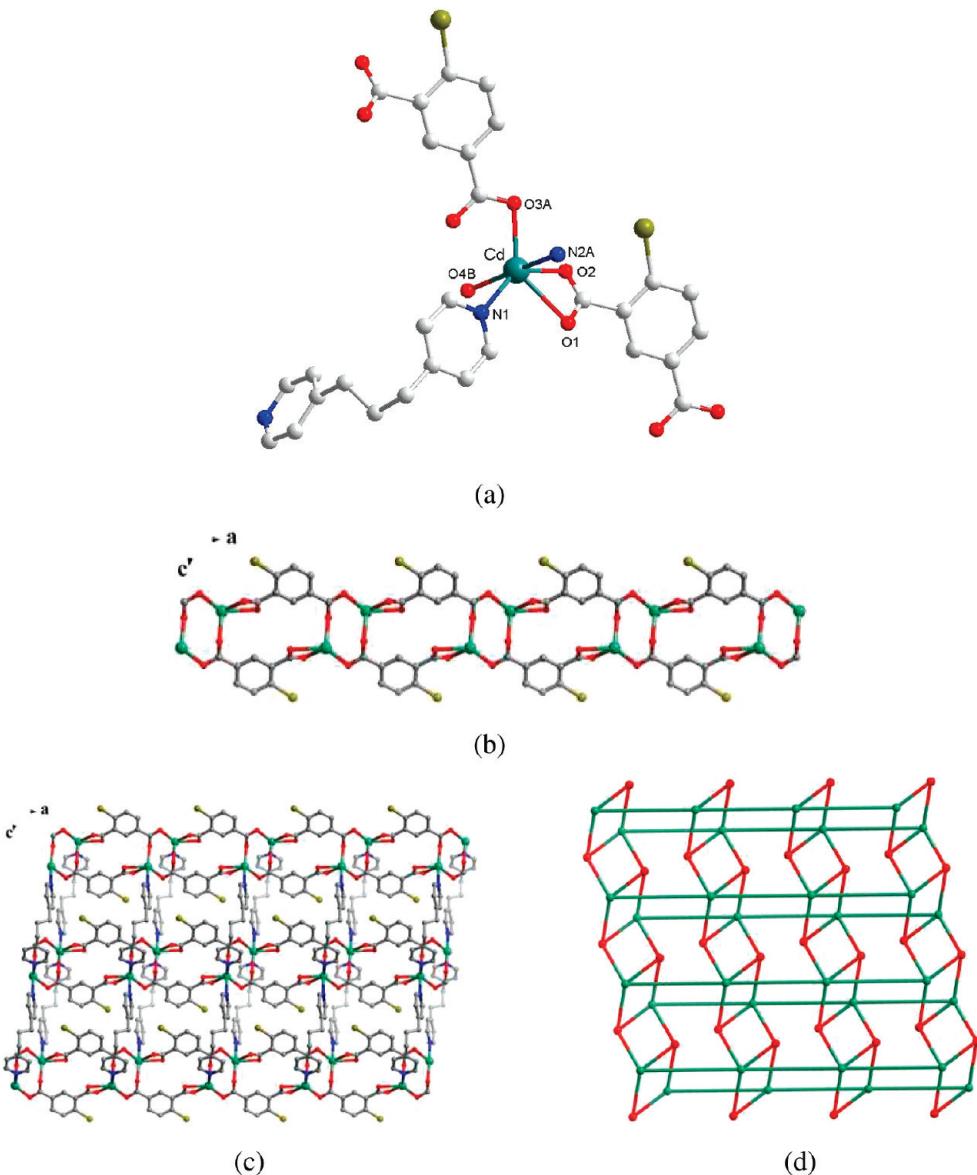
It is plausible that the presence of the electron withdrawing -Br groups encourages greater Lewis acidity of Zn(II) and Cd(II) centers in **1–7**. The different dispositions of the -Br substituent of the isophthalate may also result in their different Lewis acidity. Moreover, the adjacent -Br substituent in 4-Br-H<sub>2</sub>ip may have greater steric hindrance to cause the two carboxylates to vary more greatly from planarity with respect to the aromatic ring, which may change the coordination modes of carboxylate groups. Thus, the structural diversity is attributed to both the electronic effect and the steric hindrance effect of Br-H<sub>2</sub>ip isomers used in the assembled process.

**Luminescent Properties.** Solid state luminescent properties of Zn(II) or Cd(II) complexes have been attracting more

interest because of their potential applications in chemical sensors, photochemistry, and electroluminescent display.<sup>15,16</sup> Here, emission bands are observed at 445 nm ( $\lambda_{\text{ex}} = 375$  nm) for **1**, 416 nm ( $\lambda_{\text{ex}} = 300$  nm) for **2**, 427 nm ( $\lambda_{\text{ex}} = 320$  nm) for **3**, 410 nm ( $\lambda_{\text{ex}} = 300$  nm) for **4**, 525 nm ( $\lambda_{\text{ex}} = 320$  nm) for **5**, 453 nm ( $\lambda_{\text{ex}} = 290$  nm) for **6**, and 455 nm ( $\lambda_{\text{ex}} = 400$  nm) for **7**, respectively (see Figures S1 and S2), which should be assigned to the intraligand fluorescent emissions.<sup>17</sup>

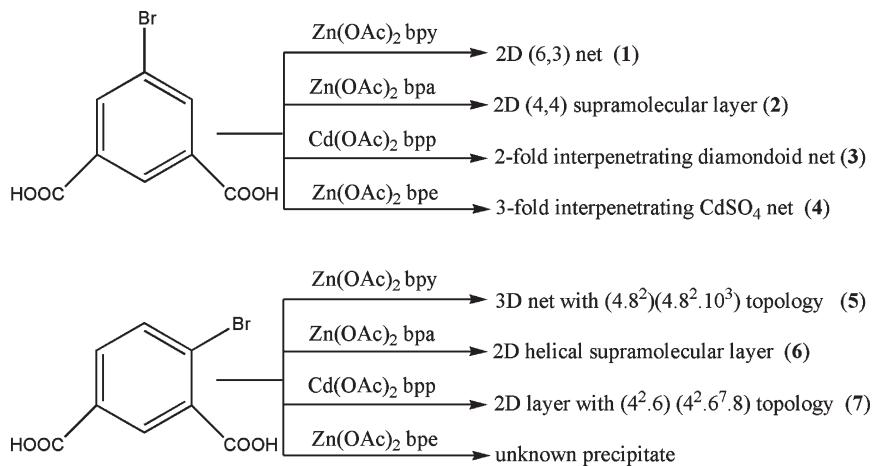
## Conclusions

Seven new coordination polymers have been successfully isolated under hydrothermal conditions by reactions of 4-Br-H<sub>2</sub>ip or 5-Br-H<sub>2</sub>ip and Zn(II) or Cd(II) salt, together with different dipyridyl auxiliary ligands. Our present discovery indicates that the differently oriented -Br atoms in the dicarboxyl isomers play a significant role in molecular tectonics of the metal–organic frameworks. The successful synthesis of



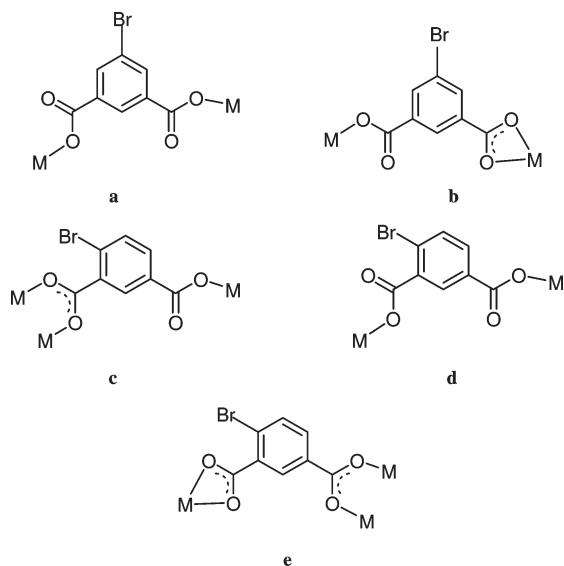
**Figure 7.** Views of 7. (a) Coordination environment of Cd(II). (b) 1D coordination chain (bpp ligands are omitted for clarity). (c) 2D layer. (d) Perspective view of the (3,5)-connected network topology.

**Scheme 2. Synthetic Route and Structural Diversity of Complexes 1–7**



these complexes will provide some useful information on the selection of suitable organic building blocks for controllable

design and synthesis of desired crystalline solids with predictable structures and properties.

**Scheme 3. Coordination Modes of 4-Br-H<sub>2</sub>ip and 5-Br-H<sub>2</sub>ip in 1–7****Experimental Section**

**Materials and Physical Measurements.** All reagents used in syntheses were of analytical grade. Elemental analyses for carbon, hydrogen, and nitrogen were performed on a Vario EL III elemental analyzer. The infrared spectra (4000–400 cm<sup>-1</sup>) were recorded by using KBr pellet on an Avatar 360 E.S.P. IR spectrometer. Fluorescent spectroscopy of the solid samples was performed on an Hitachi F-4500 analyzer at room temperature.

**Preparation of 1–7.**  $\{[\text{Zn}_2(5\text{-Br-ip})_2(\text{bpy})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}\}_n$  (**1**). A mixture of 5-Br-H<sub>2</sub>ip (0.2 mmol, 49 mg), bpy (0.1 mmol, 17.9 mg), Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.2 mmol, 44.0 mg), KOH (0.20 mmol, 11.2 mg), and distilled water (15 mL) was placed in a Teflon-lined stainless steel vessel, heated to 150 °C for 3 days, and then cooled to room temperature over 24 h. Colorless block crystals of **1** were obtained in 32% yield (based on Zn). Elem anal. Calcd for C<sub>26</sub>H<sub>20</sub>Br<sub>2</sub>Zn<sub>2</sub>N<sub>2</sub>O<sub>11</sub>: C, 37.76; H, 2.44; N, 3.39. Found: C, 37.80; H, 2.40; N, 3.42. IR (cm<sup>-1</sup>): 3437 m, 3068 m, 1618 m, 1550 s, 1446 m, 1360 s, 1224 m, 1119 m, 1031 m, 810 m, 776 m, 645 m.

$\{[\text{Zn}(5\text{-Br-ip})(\text{bpa})(\text{H}_2\text{O})]\}_n$  (**2**). **2** was synthesized in a similar way to that for **1**, except that bpy was replaced by bpa. Yield: 41% (based on Zn). Elem anal. Calcd for C<sub>20</sub>H<sub>17</sub>BrZn·N<sub>2</sub>O<sub>5</sub>: C, 47.04; H, 3.35; N, 5.49. Found: C, 47.12; H, 3.30; N, 5.53. IR (cm<sup>-1</sup>): 3410 m, 2972 m, 1633 m, 1433 m, 1367 s, 1336 m, 1007 m, 815 m, 772 m, 725 m, 651 m.

**Table 1. Crystallographic Data for Complexes 1, 3, and 4**

	<b>1</b>	<b>3</b>	<b>4</b>
formula	C <sub>26</sub> H <sub>20</sub> Br <sub>2</sub> Zn <sub>2</sub> N <sub>2</sub> O <sub>11</sub>	C <sub>21</sub> H <sub>19</sub> BrCdN <sub>2</sub> O <sub>5</sub>	C <sub>20</sub> H <sub>13</sub> BrZnN <sub>2</sub> O <sub>4</sub>
fw	827.00	571.69	490.60
crystal system	monoclinic	monoclinic	orthorhombic
space group	C2/c	C2/c	Pnna
unit cell dimensions (Å, deg)	a = 20.5194(19) b = 8.6326(8) c = 17.3333(16) β = 115.0090(10)	a = 14.3379(15) b = 18.9193(19) c = 16.5885(17) β = 100.7390(10)	a = 7.9942(11) b = 17.413(3) c = 14.575(2) β = 90
V (Å <sup>3</sup> )	2782.5(4)	4421.0(8)	2028.9(5)
Z	4	8	4
F(000)	1632	2096	976
D <sub>c</sub> (g cm <sup>-3</sup> )	1.974	1.718	1.606
data/restraints/parameters	2587/0/195	4121/3/271	1895/0/129
hkl range	-24 ≤ h ≤ 24 -10 ≤ k ≤ 10 -20 ≤ l ≤ 20	-17 ≤ h ≤ 17 -22 ≤ k ≤ 22 -19 ≤ l ≤ 20	-9 ≤ h ≤ 9 -20 ≤ k ≤ 21 -13 ≤ l ≤ 17
reflections collected/unique	10312/2587	16341/4121	9059/1895
R <sub>int</sub>	0.0175	0.0462	0.0380
GOF	1.036	1.002	1.026
R <sub>1</sub> , wR <sub>2</sub> [I > 2σ(I)]	0.0261, 0.0607	0.0355, 0.0673	0.0315, 0.0649
R <sub>1</sub> , wR <sub>2</sub> (all data)	0.0304, 0.0629	0.0655, 0.0780	0.0583, 0.0752

**Table 2. Crystallographic Data for Complexes 5–7**

	<b>5</b>	<b>6</b>	<b>7</b>
formula	C <sub>26</sub> H <sub>16</sub> Br <sub>2</sub> Zn <sub>2</sub> N <sub>2</sub> O <sub>9</sub>	C <sub>20</sub> H <sub>17</sub> BrZnN <sub>2</sub> O <sub>5</sub>	C <sub>21</sub> H <sub>17</sub> BrCdN <sub>2</sub> O <sub>4</sub>
fw	790.97	510.64	553.68
crystal system	monoclinic	monoclinic	monoclinic
space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /n	P2 <sub>1</sub> /n
unit cell dimensions (Å, deg)	a = 10.0154(16) b = 14.546(2) c = 9.2314(15) β = 97.496(2)	a = 10.997(6) b = 14.578(8) c = 12.963(7) β = 105.993(6)	a = 10.173(2) b = 17.211(3) c = 11.681(2) β = 99.371(2)
V (Å <sup>3</sup> )	1333.3(4)	1997.7(19)	2017.8(7)
Z	2	4	4
F(000)	776	1024	1088
D <sub>c</sub> (g cm <sup>-3</sup> )	1.970	1.698	1.823
data/restraints/parameters	2381/0/190	3691/0/262	3739/0/262
hkl range	-11 ≤ h ≤ 12 -17 ≤ k ≤ 17 -10 ≤ l ≤ 11	-13 ≤ h ≤ 11 -17 ≤ k ≤ 17 -15 ≤ l ≤ 15	-12 ≤ h ≤ 12 -20 ≤ k ≤ 20 -14 ≤ l ≤ 14
reflections collected/unique	9302/2381	11051/3691	14116/3739
R <sub>int</sub>	0.0318	0.0329	0.0416
GOF	1.038	1.045	1.105
R <sub>1</sub> , wR <sub>2</sub> [I > 2σ(I)]	0.0406, 0.1053	0.0309, 0.0698	0.0566, 0.1532
R <sub>1</sub> , wR <sub>2</sub> (all data)	0.0500, 0.1116	0.0458, 0.0749	0.0829, 0.1728

$\{[\text{Cd}(\text{5-Br-ip})(\text{bpp})(\text{H}_2\text{O})]\}_n$  (**3**). **3** was synthesized in a similar way to that for **1**, except that bpy and  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  were replaced by bpp and  $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ . Yield: 43% (based on Cd). Elem anal. Calcd for  $\text{C}_{21}\text{H}_{19}\text{BrCdN}_2\text{O}_5$ : C, 44.12; H, 3.35; N, 4.90. Found: C, 44.15; H, 3.30; N, 4.94. IR ( $\text{cm}^{-1}$ ): 3427 m, 2943 m, 1612 m, 1559 m, 1352 s, 1226 m, 1068 m, 819 m, 772 m, 733 m.

$\{[\text{Zn}(\text{5-Br-ip})(\text{bpe})]\}_n$  (**4**). **4** was synthesized in a similar way to that for **1**, except that bpy was replaced by bpe. Yield: 52% (based on Zn). Elem anal. Calcd for  $\text{C}_{20}\text{H}_{13}\text{BrZnN}_2\text{O}_4$ : C, 48.96; H, 2.67; N, 5.71. Found: C, 48.90; H, 2.71; N, 5.75. IR ( $\text{cm}^{-1}$ ): 3434 m, 2972 m, 1611 m, 1561 m, 1361 s, 1208 m, 1025 m, 833 m, 775 m, 735 m.

$\{[\text{Zn}(\text{4-Br-ip})_2(\text{bpy})]\cdot\text{H}_2\text{O}\}_n$  (**5**). **5** was synthesized in a similar way to that for **1**, except that 5-Br-H<sub>2</sub>ip was replaced by 4-Br-H<sub>2</sub>ip. Yield: 28% (based on Zn). Elem anal. Calcd for  $\text{C}_{26}\text{H}_{16}\text{Br}_2\text{Zn}_2\text{N}_2\text{O}_9$ : C, 39.49; H, 2.04; N, 3.54. Found: C, 39.45; H, 2.10; N, 3.60. IR ( $\text{cm}^{-1}$ ): 3315 m, 3074 m, 1617 m, 1552 s, 1435 m, 1375 s, 1224 m, 1110 m, 1073 m, 827 m, 774 m, 645 m.

$\{[\text{Zn}(\text{4-Br-ip})(\text{bpa})(\text{H}_2\text{O})]\}_n$  (**6**). **6** was synthesized in a similar way to that for **2**, except that 5-Br-H<sub>2</sub>ip was replaced by 4-Br-H<sub>2</sub>ip. Yield: 38% (based on Zn). Elem anal. Calcd for  $\text{C}_{20}\text{H}_{17}\text{BrZnN}_2\text{O}_5$ : C, 47.04; H, 3.35; N, 5.49. Found: C, 47.10; H, 3.31; N, 5.45. IR ( $\text{cm}^{-1}$ ): 3408 m, 2972 m, 1639 m, 1427 m, 1355 s, 1328 m, 1026 m, 831 m, 779 m, 738 m, 661 m.

$\{[\text{Cd}(\text{4-Br-ip})(\text{bpp})]\}_n$  (**7**). **7** was synthesized in a similar way to that for **3**, except that 5-Br-H<sub>2</sub>ip was replaced by 4-Br-H<sub>2</sub>ip. Yield: 49% (based on Cd). Elem anal. Calcd for  $\text{C}_{21}\text{H}_{17}\text{Br}\cdot\text{CdN}_2\text{O}_4$ : C, 45.56; H, 3.09; N, 5.06. Found: C, 45.51; H, 3.12; N, 5.10. IR ( $\text{cm}^{-1}$ ): 3410 m, 2951 m, 1590 m, 1560 m, 1384 s, 1215 m, 1028 m, 810 m, 778 m, 734 m.

**X-ray Crystallography.** Single crystal X-ray diffraction analyses of **1–7** were carried out on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) by using a  $\varphi/\omega$  scan technique at room temperature. The structures were solved via direct methods and successive Fourier difference synthesis (SHELXS-97),<sup>18</sup> and refined by the full-matrix least-squares method on  $F^2$  with anisotropic thermal parameters for all non-H atoms (SHELXL-97).<sup>19</sup> The empirical absorption corrections were applied by the SADABS program.<sup>20</sup> The H-atoms of carbon were assigned with common isotropic displacement factors and included in the final refinement by the use of geometrical restraints. H-atoms of water molecules were first located by the Fourier maps and then refined by the riding mode. The crystallographic data for complexes **1–7** are listed in Tables 1 and 2, respectively. CCDC reference numbers are as follows: 776696 (**1**), 776697 (**3**), 776698 (**4**), 776699 (**5**), 776700 (**6**), 776701 (**7**).

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**Supporting Information Available:** Crystallographic data in CIF format for complexes **1** and **3–7**, selected bond lengths and angles for complexes **1–7**, H-bonding geometries for complexes **2**, **3**, and **6**, and solid-state emission spectra of complexes **1–7** at room temperature. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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