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Three new d¹⁰ coordination polymers based on 2-(2-pyridyl)benzimidazole ligand: Synthesis, structures and properties

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ABSTRACT

Three coordination polymers containing 2-(2-pyridyl)benzimidazole (PyHBIm) ligand, namely { $[Zn_3(PyBIm)_3 (PyHBIm)_2(tma)(H_2O)]^{+}H_2O\}_n$ (1), $[Zn(PyHBIm)(oba)]_n$ (2), $[Cd(PyHBIm)(oba)]_n$ (3), (tma = trimesate, oba = 4,4'-oxybis-(benzoate)), have been prepared through hydrothermal reaction. Compound 1 exhibits onedimensional (1D) helical structure. However, compounds 2 and 3 display 1D *meso*-helical structure. These 1D structures are further assembled into three-dimensional (3D) networks through aromatic π - π stacking interactions and hydrogen bonding interactions. Moreover they all exhibit strong photoluminescence at room temperature and may be good candidates for potential luminescence materials.

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Over the past few decades, much effort has been paid to the study of metal coordination polymers due to their fascinating structures as well as potential applications, such as molecular based magnet, catalysis, luminescence, ion exchange and adsorption [1–6]. So far, large numbers of coordination polymers with interesting compositions and topologies have been prepared. Among these, the construction of helical structures has always been a popular subject because helicity plays a critical role in biology systems [7,8] and advance materials such as optical devices and asymmetric catalysis [9-12]. One of the best approaches toward the helical coordination polymer networks involves the use of one or more flexible or V-shaped bidentate bridging ligands [13-16] and chelate end-blocking ligands such as 2,2'-bipyridyl and 1,10-phenanthroline [17–20]. However, 2-(2-pyridyl)benzimidazole (PyHBIm), as a chelate ligand, is rarely investigated, which has multiple coordination modes in forming metal coordination polymers. It can not only be chelate endblocking ligand but also can be bridging ligand when it is deprotonated. As we know, an odd carboxylate anion ligand and divalent metal ions cannot reach charge balance, which will require the PyHBIm ligand to deprotonate to make the coordination polymer reach charge balance. Therefore, trimesate (tma) is used for our synthetic strategy. With these background in mind, three new one-dimensional metal-organic coordination polymers, $\{[Zn_3(PyBIm)_3(PyHBIm)_2(tma)(H_2O)] \cdot H_2O\}_n$ (**1**), $[Zn(PyHBIm)(oba)]_n$ (**2**), $[Cd(PyHBIm)(oba)]_n$ (**3**) (oba=4,4'oxybis-(benzoate)), have been prepared through hydrothermal reaction. They exhibit two different kinds of helical structures. Compound 1 exhibits 1D helical structure that is further assembled into 3D networks

through aromatic π - π stacking interactions and hydrogen bonding interactions. When another carboxylate ligand is used in the place of tma under the same condition, compounds **2** and **3** have been obtained which display 1D *meso*-helical structures that are also further assembled into 3D networks through aromatic π - π stacking interactions and hydrogen bonding interactions. Compared with helical structure, *meso*-helical structure is more special and coordination polymers with this kind of structure have been rarely reported [21–24]. In compounds **2** and **3**, the PyHBIm ligand is neutral with one kind of coordination mode. However, it is partly deprotonated with three kinds of coordination modes in compound **1**, which is, to our knowledge, the first example that three kinds of coordination modes of PyHBIm ligand exist in one compound. Moreover, compounds **1–3** exhibit strong photoluminescence at room temperature and may be good candidates for potential luminescence materials.

X-ray diffraction analysis reveals that **1** exhibit 1D helical structure with space group *P*. There are three zinc atoms, one tma ligand, one coordinated water, one free water, three anionic PyBIm ligands and two neutral PyHBIm ligands in the asymmetry unit (Fig. 1). The Zn1 atom is coordinated by two nitrogen atoms of one PyBIm ligand (Zn(1)-N(5) 2.023(6), Zn(1)-N(4) 2.176(6) Å), two nitrogen atoms of one PyHBIm ligand (Zn(1)-N(1) 2.113(6), Zn(1)-N(3) 2.271(6) Å) and two oxygen atoms from one tma ligand (Zn(1)-O(1) 2.212(5), Zn(1)-O(2) 2.241 (4) Å), showing a distorted octahedral geometry. The Zn2 atom is coordinated by four nitrogen atoms from two different PyBIm ligands (Zn(2)-N(10) 2.043(5), Zn(2)-N(7) 2.043(5), Zn(2)-N(12) 2.156(5), Zn (2)-N(9) 2.187(5) Å) and two oxygen atoms from one tma ligand (Zn (2)-O(3) 2.224(4), Zn(2)-O(4) 2.291(4) Å), showing a distorted octahedral geometry. The structure shows a distorted trigonal bipyramidal configuration with five coordinations to the Zn3 atom. And it is

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Fig. 1. The coordination environment of the Zn(II) atoms in compound 1.

coordinated by one nitrogen atom from one PyBIm ligand (Zn(3)-N(11))2.043(5) Å), two nitrogen atoms from one PyHBIm ligand (Zn(3)-N(13) 2.175(5), Zn(3)-N(15) 2.186(6) Å), one oxygen atom from one tma ligand (Zn(3)-O(5)#1 2.101(4) Å) and one oxygen atom from water (Zn (3)-O(7) 2.008(4) Å). The selected bond lengths and angles for 1 are listed in Table S1. The neighboring Zn2 and Zn3 atoms are bridged by interval PyBIm and tma ligands which form a 1D helical chain running along b axis (Fig. 2a). The pitch of the helix is 13.53 Å. There are three kinds of hydrogen bonds between the adjacent chains. The first is connecting oxygen atoms of coordinated water molecules with uncoordinated nitrogen atoms (O7-H7WA···N8). The second is between uncoordinated nitrogen atoms and carboxylate oxygens (N14-H14A···O3). These two kinds of hydrogen bonds direct the 1D chain to form a 2D structure (Fig. S1). The third is connecting nitrogen atoms and carboxylate oxygens (N2-H2A···O2) (Fig. 2b), allowing the 2D structure to form a 2D bilayer structure (Fig. S2). Otherwise, there are three kinds of coordination modes of PyHBIm ligands in the asymmetry unit, as illustrated in Scheme 1. Notably, to our knowledge, it has never been reported that three kinds of coordination modes of PyHBIm ligands exist in one compound until now. One PyBIm group bridging Zn2 and Zn3 by the third coordination mode (Scheme 1c), which is an important factor in forming the 1D chain structure. Two PyBIm ligands connect Zn2 and Zn3 in two different chelate coordination modes (Scheme 1a and b) from the opposite sides of the helix chain, which allow the helixs to pack into a 2D layer network through strong π - π stacking interactions with face to face distance of 3.706(2) Å (Fig. 2c). Such grid layers are further extended into the final 3D supramolecular network *via* π - π stacking interactions (Fig. 2d).

When the oba ligand is used in the place of tma under the same condition, compounds **2** and **3** have been obtained through hydrothermal reaction. X-ray diffraction analysis reveals that **2** and **3** are isomorphous,



Fig. 2. The views of helical chain (a), π-π stacking interactions and hydrogen bonding interactions (b), 2D layers along the *ab* plane (c) and 3D networks (d) in 1.



Scheme 1. Coordination Modes of 2-(2-pyridyl)benzimidazole (PyHBIm) in Compound 1.

so that only the structure of **2** is described here. Compound **2** contains 1D meso-helical chain constructed by oba ligands and zinc ions. In 2, the asymmetric unit consists of one Zn atom, one oba ligand and one PyHBIm ligand, as shown in Fig. 3. The zinc(II) atom is coordinated by four oxygen atoms from two oba ligands (Zn(1)-O(1) 2.126(5), Zn(1)-O(2) 2.147(5), Zn(1)-O(5)#1 2.150(4), Zn(1)-O(4)#1 2.232(5) Å) and two nitrogen atoms from PyHBIm ligand (Zn(1)-N(1) 2.236(7), Zn(1)-N(2) 2.035(6) Å), showing a distorted octahedral geometry. The selected bond lengths and angles for 2 and 3 are listed in Table S1. The neighboring zinc atoms are bridged by long flexible spacers in a chelate coordination mode to form a meso-helical chain running along a axis (Fig. 4a). The pitch of the helix is 25.28 Å. The two benzene rings of oba ligand are severely bent which is an important factor in forming the meso-helical structure. All PyHBIm groups bristle out from the two sides of the helix which play a critical role in packing into a higher network through π - π stacking interactions. The adjacent meso-helical chains are intercalated into two-dimensional (2D) grid layers parallel to the *ab* plane (Fig. 4c) through hydrogen bonding interactions (N3-H3A···O5) and strong aromatic π - π stacking interactions between PyHBIm ligands with face to face distance of 3.669(2) Å (Fig. 4b). Such grid layers are further extended into the final 3D supramolecular network via π - π stacking interactions of PyHBIm rings from different layers (Fig. 4d).

Thermal analyses for compounds **1–3** are performed in the N_2 atmosphere between 20 and 1000 °C. The results show that these complexes have similar stability in the range of 100–500 °C. Compound **1** is stable up to near 320 °C, and then begins to decompose (Fig. S3). Compound **1** gets weight loss of 20.13% in the temperature range 100–500 °C which corresponds to the releases of two water molecules and

one tma group (calculated: 17.45%). The DSC curve shows a sharp exothermic peak at near 350 °C. Compounds 2 and 3 are stable up to near 410 °C and 385 °C respectively, and then start to decompose (Figs. S4 and S5). Compounds 1-3 exhibit strong photoluminescence in the solid state at room temperature. The emission spectra are shown in Fig. 5. Excitation of solid sample of **1** at $\lambda = 300$ nm produces an intense luminescence with a peak maximum at 440 nm. Excitation of solid sample of **2** at $\lambda = 260$ nm produces an intense luminescence with a peak maximum at 416 nm. Excitation of solid sample of **3** at $\lambda = 280$ nm produces an intense luminescence with a peak maximum at 422 nm. And the peaks of **2** and **3** are stronger and sharper than that of **1**. We have analyzed the photoluminescence properties of the free PyHBIm molecule which displays a weak luminescence at ca. 370 nm in the solid state at room temperature. It has been reported that organic compound oba does not emit any luminescence in the range of 400-800 nm [17]. These emission bands might be assigned to the emission of metal-toligand charge transfer (MLCT) [25,26].

Three new metal-organic coordination polymers containing 2-(2pyridyl)benzimidazole have been successfully synthesized by hydrothermal reaction. They exhibit two different kinds of 1D helical structures. Compound **1** exhibits 1D helical structure. However, compounds **2** and **3** display 1D *meso*-helical structure. These 1D structures are further assembled into three-dimensional (3D) networks through aromatic π - π stacking interactions and hydrogen bonding interactions. In compounds **2** and **3**, the PyHBIm ligand is neutral with one kind of coordination mode, whereas it is partly deprotonated with three kinds of coordination modes in compound **1**, which owing to the change of carboxylate ligands between them. And, to our knowledge, there is no previous example that



Fig. 3. The coordination environment of the Zn(II) atom in compound 2.



Fig. 4. The views of meso-helical chain (a), π-π stacking interactions and hydrogen bonding interactions (b), 2D layers along *ab* plane (c) and 3D networks (d) in 2 and 3.

three kinds of coordination modes of PyHBIm ligand exist in one compound. In summary, the carboxylates and the deprotonated or neutral PyHBIm ligands dominate the coordination structures. Meanwhile, the intermolecular π – π stacking interactions and hydrogen bonding interactions have a significant influence on the supramolecular structures. Moreover, compounds **1–3** exhibit acceptable thermal stability and strong photoluminescence at room temperature.

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Synthesis of { $[Zn_3(PyBIm)_3(PyHBIm)_2(tma)(H_2O)]$ • H_2O }_n (1): A solution of $Zn(OAc)_2$ • $2H_2O$ (0.220 g, 1.0 mmol), PyHBIm (0.195 g, 1.0 mmol), tma (0.042 g, 0.20 mmol), NaOH (0.040 g, 1.0 mmol) and H_2O (15 mL) was stirred under ambient conditions, then sealed in a Teflon-lined steel autoclave, heated at 160 °C for 5 days, and cooled to room temperature at a rate of 5 K/h. The resulting product was recovered by filtration, washed with distilled water and dried in air (70% yield). Anal. Calcd (%) for C₆₉H₄₆N₁₅O₈Zn₃: C, 58.89; H, 3.15; N, 14.93. Found: C, 58.76; H, 3.05; N,



Fig. 5. Solid-state emission spectra of 1-3 at room temperature.

14.78. IR (KBr pellet, cm-1): 3423 w, 3054 w, 1607 s, 1559 m, 1445 s, 1421 s, 1364 s, 1150 w, 1049 w, 1008 w, 796 w, 741 s, 643 w.

Synthesis of $[Zn(PyHBIm)(oba)]_n$ (2): A solution of $Zn(OAc)_2$ •2H₂O (0.220 g, 1.0 mmol), PyHBIm (0.195 g, 1.0 mmol), oba (0.256 g, 1.0 mmol), NaOH (0.04 g, 1.0 mmol) and H₂O (15 mL) was stirred under ambient conditions, then sealed in a Teflon-lined steel autoclave, heated at 160 °C for 5 days, and cooled to room temperature at a rate of 5 K/h. The resulting product was recovered by filtration, washed with distilled water and dried in air (75% yield). *Anal.* Calcd (%) for C₂₆H₁₆N₃O₅Zn: C, 60.54; H, 3.13; N, 8.15. Found: C, 60.12; H, 3.05; N, 7.96. IR (KBr pellet, cm⁻¹): 3435 s, 1599 s, 1545 m, 1498w, 1392 s, 1232 m, 1156 w, 1096 w, 928 w, 877 w, 787 w, 744 m, 661 w.

Synthesis of $[Cd(PyHBIm)(oba)]_n$ (**3**): Compound **3** was synthesized in a procedure analogous to that of **2** except that the $Zn(OAc)_2 \cdot 2H_2O$ was replaced by $Cd(OAc)_2 \cdot 2H_2O$. The resulting product was recovered by filtration, washed with distilled water and dried in air (75% yield). *Anal.* Calcd (%) for $C_{26}H_{16}N_3O_5Cd$: C, 55.48; H, 2.87; N, 7.47. Found: C, 55.16; H, 2.61; N, 7.21. IR (KBr pellet, cm⁻¹): 3415 s, 1596 s, 1546 m, 1497 w, 1395 s, 1230 m, 1158 w, 1096 w, 977 w, 878 w, 776 w, 737 m, 657 w.

Crystal data for **1**: { $[Zn_3(PyBIm)_3(PyHBIm)_2(tma)(H_2O)]$ • H_2O }_n, T = 293(2) K, M = 1410.33, Triclinic, space group $P\bar{1}$, a = 11.930(17) Å, b = 13.534(19) Å, c = 21.013(3) Å, $\alpha = 90.597(2)^\circ$, $\beta = 100.438(2)^\circ$, $\gamma = 112.774(2)^\circ$. V = 3064.3(8) Å³, Z = 2, $R_1 = 0.0624$, $wR_2 = 0.1280$, GOF = 0.998.

Crystal data for **2**: $[Zn(PyHBIm)(oba)]_n$, T = 293(2) K, M = 516.8, Monoclinic, space group $P2_1/n$, a = 7.4391(12) Å, b = 18.537(3) Å, c = 16.235(3) Å, $\alpha = 90^{\circ}$, $\beta = 99.742(2)^{\circ}$, $\gamma = 90^{\circ}$. V = 2206.6(6) Å³, Z = 4, $R_1 = 0.0738$, $wR_2 = 0.1711$, GOF = 1.037.

Crystal data for **3**: $[Cd(PyHBIm)(oba)]_n$, T = 293(2) K, M = 563.8, Monoclinic, space group $P2_1/n$, a = 7.4964(11) Å, b = 18.366(3) Å, c = 16.569(2) Å, $\alpha = 90^{\circ}$, $\beta = 97.785(2)^{\circ}$, $\gamma = 90^{\circ}$. V = 2260.1(6) Å³, Z = 4, $R_1 = 0.0672$, $wR_2 = 0.1886$, GOF = 1.022.

Suitable single crystals of **1–3** were carefully selected under an optical microscope and glued to thin glass fibers. The diffraction data were collected on a Siemens SMART CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 298 K. An empirical absorption correction was applied using the SADABS program. The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 by using the SHELX-97 program package [27]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of PyHBIm were generated geometrically, and no attempts were made to locate the hydrogen atoms of water.

Appendix A. Supplementary material

CCDC-755562, 755564 and 755565 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc. cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche. 2010.07.029.

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