**Structural Diversification and Photocatalytic Properties of Three Cd(II)
Coordination Polymers Decorated with Different Auxiliary Ligands**

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Abstract

Three cadmium coordination polymers, $[\text{Cd}(\text{bismip})]_n$ (**1**), $\{[\text{Cd}(\text{bismip})(\text{phen})]\cdot\text{H}_2\text{O}\}_n$ (**2**) and $\{[\text{Cd}_2(\text{bismip})_2(4,4'\text{-bipy})]\cdot 2\text{H}_2\text{O}\}_n$ (**3**) (H_2bismip = 5-(1H-benzoimidazol-2-ylsulfanylmethyl)-isophthalic acid, phen = 1,10-phenanthroline, 4,4'-bipy = 4,4'-bipyridine) have been prepared under solvothermal conditions. In **1**, the $[\text{Cd}_4(\text{bismip})_3]$ units are jointed by bismip ligands to afford a three-dimensional (3D) architecture. Complex **2** exhibits a 3D supramolecular framework based on the interconnection of 1D chains through hydrogen bonding interactions and π - π packing interactions. **3** is a two-fold interpenetrating 3D architecture with a $(4\cdot 8^2)(4^2\cdot 8^4)$ Schläfli symbol in which 2D layers are interlinked by 4,4'-bipy ligands. The diverse structures of compounds **1** – **3** indicate that the auxiliary ligands have significant effects on the final structures. The photoluminescent properties and photocatalytic properties of these coordination polymers in the solid state were also investigated. Remarkably, **3** shows the wide gap semiconductor nature and exhibit excellent photocatalytic performance.

Keywords: Coordination polymer; Cadmium; Crystal structure; Photocatalytic properties

1. Introduction

In decade years, there have been existed keen interests in the research on coordination polymers (Cps) since their potential applications in a wide area such as photoluminescence, magnetism, catalysis, nonlinear optics, drug delivery, gas adsorption and separation [1-13]. Among numerous strategies for constructing these infinite networks, the most effective way is to choose suitable multidentate organic ligand as blocks to participate in the self-assembly of the transition metal salts [14-16]. Large amounts of novel crystalline materials with excellent properties have been synthesized by solvothermal method, diffusion method, gel-diffusion method, volatilization method, surfactant-thermal method, *etc* [17-24]. Previous studies demonstrated that N- and O-donor multidentate ligands were extremely outstanding organic building components for the

formation of Cps [25-33]. The various coordination groups in these ligands provide the feasibility to the construction of Cps with diverse structures and properties. Usually, the flexibility plays very important roles to tune the structural architectures and functionalities of coordination polymers because the free swing groups of ligands can coordinate metal ions with versatile coordination modes. Furthermore, the additions of other ancillary ligands also do great influence on the conformation of the final coordination polymers [34-37].

Nowadays, with the development of modern industry especially the dyeing industry, the problem about the treatment of wastewater containing toxic organic has gained increasing concerns throughout the world. The photocatalyst based on Cps was widely researched because their convenience and recyclable approach in degrading dye effluents [38-41]. However, investigating an efficient and stable photocatalyst remains a great challenge. Recently, we focused on the exploration of the Cps based on H₂bismip (5-(1H-benzimidazol-2-ylsulfanylmethyl)-isophthalic acid) for their photodegradation of organic pollutants in wastewater. On the one hand, the flexible benzimidazol-2-ylsulfanylmethyl group has more rotation freedom to adjust the coordination angle and can meet the coordination geometries of metal ions in the assembly process. On the other hand, due to the specific angles of meta-carboxylate groups in the rigid plane, H₂bismip can act as an aromatic multicarboxylate ligand to connect metal ions in diverse coordination modes to exhibit unexpected properties. In our previous work, we successfully prepared four Zn^{II} polymers based on H₂bismip with diverse architectures and topologies [41]. The results showed the coordination polymers could combine the advantages both of the flexible multicarboxylate and the rigidity of auxiliary ligands to show good photodegradation capabilities to methyl orange. To the further investigation, here we selected Cd^{II} as metal ion to obtain [Cd(bismip)]_n (**1**), {[Cd(bismip)(phen)]·H₂O}_n (**2**) and {[Cd₂(bismip)₂(4,4'-bipy)]·2H₂O}_n (**3**) in the present of phen and 4,4'-bipy, respectively. Herein, we report the syntheses, crystal structures, thermal, photoluminescent properties and photocatalytic properties of **1** – **3**.

(Scheme 1 here)

2. Experimental

2.1. Materials and methods

The ligand H₂bismip was prepared according to the literature method [42]. Other chemicals and reagents were obtained from commercial sources and used as received. Elemental analyses were

performed on a PE 2400II elemental analyzer. The FT-IR spectra were recorded on a Nicolet 380 spectrometer with pressed KBr pellets (4000-400 cm^{-1}). The powder X-ray diffraction (PXRD) measurements were carried out on a Rigaku D/max-2200/PC system. Thermal gravimetric analysis (TGA) was performed on a NETZSCH STA 449F3C analyzer in N_2 with heating rates of 10 $^{\circ}\text{C min}^{-1}$. The fluorescent spectra were recorded on a Hitach F-4600 fluorescence spectrometer with polycrystalline sample.

2.2. Preparation of **1** – **3**

2.2.1. Synthesis of $[\text{Cd}(\text{bismip})]_n$ (**1**)

To a solution of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (30 mg, 0.1 mmol) in H_2O (2 mL) was added a solution containing H_2bismip (33 mg, 0.1 mmol) in DMF (2 mL). The mixture was sealed in a glass tube container and heated at 110 $^{\circ}\text{C}$ for 1 days. After cooling to room temperature at the rate of 5 $^{\circ}\text{C h}^{-1}$, colorless block crystals were obtained. Yield: 21 mg (48% based on Cd). Anal. Calcd. for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_4\text{SCd}$: C, 43.60; H, 2.74; N, 6.36%. Found: C, 43.02; H, 2.56; N, 6.63%. IR (cm^{-1} , KBr): 3414s, 3150s, 1608s, 1552m, 1367s, 1242m, 1104w, 1011m, 929w, 761s, 619w, 495m.

2.2.2. Synthesis of $\{[\text{Cd}(\text{bismip})(\text{phen})] \cdot \text{H}_2\text{O}\}_n$ (**2**)

Compound **2** was obtained as colorless blocks in a manner similar to that described for **1**, using $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (30 mg, 0.1 mmol) in 2 mL of H_2O and H_2bismip (33 mg, 0.1 mmol) and phen (20 mg, 0.1 mmol) in DMF (2 mL). Yield: 33 mg (52% based on Cd). Anal. Calcd. for $\text{C}_{28}\text{H}_{20}\text{N}_4\text{O}_5\text{SCd}$: C, 52.80; H, 3.16; N, 8.80%. Found: C, 51.95; H, 3.01; N, 8.96%. IR (KBr, cm^{-1}): 3414s, 3157s, 1614s, 1549s, 1415s, 1375s, 1222m, 1140m, 1098w, 929w, 852m, 778s, 731s, 630m, 488m.

2.2.3. Synthesis of $\{[\text{Cd}_2(\text{bismip})_2(4,4'\text{-bipy})] \cdot 2\text{H}_2\text{O}\}_n$ (**3**)

Compound **3** was prepared as colorless blocks in a manner similar to that described for **1**, using $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (30 mg, 0.1 mmol) in 2 mL of H_2O and H_2bismip (33 mg, 0.1 mmol) and 4,4'-bipy (16 mg, 0.1 mmol) in DMF (2 mL). Yield: 30 mg (55% based on Cd). Anal. Calcd. for $\text{C}_{21}\text{H}_{17}\text{N}_3\text{O}_6\text{SCd}$: C, 45.71; H, 3.11; N, 7.61%. Found: C, 45.82; H, 2.86; N, 6.76%. IR (cm^{-1} , KBr): 3414s, 3070s, 2975m, 1611s, 1550s, 1415s, 1375s, 1221m, 1070m, 997w, 812m, 778m, 738s, 625m, 481m.

2.3. Crystallographic studies

Data for **1** – **3** were collected on a Bruker APEX II diffractometer with graphite-monochromated

Mo- $K\alpha$ radiation ($\lambda = 0.071073$ nm) by using the Φ/ω scan technique. The data were corrected for Lorentz and polarization effects with the SMART suite of programs and for absorption effects with SADABS [43]. All these structures were solved by the direct method and refined by full-matrix least-squares fitting on F^2 by SHELXTL-14 program [44, 45]. The O, S, N and C atoms in **1** were split into two sites with an occupancy ratio of 0.5/0.5 for O1/O1A, O2/O2A, S1/S1A, N1/N1A, N2/N2A, C1-C7/C1A-C7A, C10/C10A, C11/C11A and C13/C13A. All non-hydrogen atoms refined anisotropically. All the hydrogen atoms were put on calculated positions or located from the Fourier maps and refined isotropically with the isotropic vibration parameters related to the non-H atom to which they are bonded. The crystallographic and refinement details are listed in are presented in Table 1 and selected bond lengths and angles are given in Tables 2.

2.4. Photocatalytic activity study

The photocatalytic activities of the solid samples **1** – **3** were evaluated by the degradation of MB in aqueous solution. 80 mL of a methylene blue (MB) aqueous solution with a concentration of 0.01 g L^{-1} were mixed with 40 mg of the catalysts, respectively. A high pressure mercury lamp (500 W) was used as the UV light source. During the degradation reaction, the mixture was stirred continuously with a magnetic stirrer. At regular time intervals, 3 mL solution was sampled and filtered. The UV-vis absorption spectra of the MB aqueous solutions were obtained on an Agilent Cary-300 spectrophotometer.

3. Results and Discussion

3.1. Synthesis, spectroscopic characterization and thermal analysis

Colorless blocks of complex **1** was prepared based on the reaction between $\text{Cd}(\text{NO}_3)_2$ and H_2bismip in the mixed system of DMF/ H_2O solvent under solvothermal condition. Furthermore, complexes **2** and **3** were obtained from the analogous synthetic procedure in the presence of phen and 4,4'-bipy, respectively. An exploration of the synthesis of **1** – **3** in the solvent mixtures reveals that **1** – **3** was only formed in the case where the ratio of H_2O and DMF is 1 to 1. In addition, attempts to prepare crystalline complex by using MeOH, EtOH, or CH_3CN instead of DMF were not successful. It is inferred that some DMF molecules can play as lewis base to self-adjust the pH in the system to meet the requirements of the deprotonation of H_2bismip and benefits the

self-assembly between bismip²⁻ anions and Cd cations. However, the temperature, reaction time, and mole ratio does little effect on the formation of the final products except of the yields. Compounds **1–3** are air-stable and insoluble in common organic solvents. In the IR spectra of complexes **1–3**, the bands observed at 1608 and 1367 cm⁻¹ for complex **1**, 1614 and 1375 cm⁻¹ for complex **2** and 1611 and 1375 cm⁻¹ for complex **3** are assigned to the asymmetric and symmetric stretching vibrations of $\nu_{C=O}$ of the coordinated carboxylic groups [46]. The strong peaks ranging from 778 cm⁻¹ to 731 cm⁻¹ mean the existence of benzimidazole groups. The identities of **1–3** were further confirmed by single-crystal X-ray diffraction analyses.

Thermogravimetric analysis (TGA) of **1** (Fig. S2, ESI†) shows there is almost no weight loss below 200 °C which can be attributed to no lattice water molecules. The removal of organic components occurred in the range of 200 °C - 530 °C. The remaining residue corresponding to the CdO (obsd. 29.77%, cald. 29.10%). For **2** and **3**, the first weight loss of 2.80% and 6.78% from 25 °C - 150 °C correspond to the losses of the water solvent molecules in **2** (calculated 2.83%) and **3** (calculated 6.53%). The second steps from 250 °C - 550 °C can be attributed to the release of the organic ligands. The remaining weights correspond to CdO residue (obsd. 20.72%, cald. 20.16%; obsd. 23.68%, cald. 23.37%). **1**, **2** and **3** began to release organic ligands above 200 °C which suggest that **1–3** have a high thermal stability in a nitrogen atmosphere. As shown in Fig. S3, ESI†, the powder patterns of **1 – 3** match well with those simulated from the single crystal diffraction data, indicating that the compounds exist as a single phase.

(Table 1 here)

(Table 2 here)

3.2. Description of the structures

3.2.1. Crystal structure of **1**. X-ray structural analysis revealed that complex **1** crystallizes in orthorhombic crystal system with $I2_12_12_1$ space group. The asymmetric unit contains a [Cd(bismip)] molecule (Fig. 1a). Each Cd atom is in a distorted octahedral geometry by four carboxylic O atoms of two bismip ligands and two N atoms from two benzimidazole groups. The Cd–O bond distance are 2.293(6) Å and 2.387(8) Å which are similar with that of [Cd₂(D-cam)₂(dmbl)₄]_n (D-H₂cam = D-(+)-camphoric acid, dmbl = 5,6-dimethylbenzimidazole) [47], while the Cd–N bond length 2.296(16) Å is closed to that in [Cd(tpcb)_{0.5}(1,3-BDC)]_n

(H₃NTC = 5-nitrobenzene- 1,2,3-tricarboxylic acid, bimbh = 1,6-bis(imidazol-1-yl)-hexane) [48]. In compound **1**, each four Cd atoms are bridged by three equivalent bismip ligands through carboxylic O atoms and benzimidazole N atoms to afford a [Cd₄(bismip)₃] cluster. The tetranuclear cluster can be viewed as the basic subunit, which is connected to each other, giving rise to a 2D grid net extending in the *bc* plane (Fig. 1b). Thus, these nearby layers are interconnected by the bismip ligands to generate a 3D network (Fig. 1c).

(Fig. 1. here)

3.2.2. Crystal structure of **2**. Single crystal analysis revealed **2** crystallizes in the monoclinic space group *C2/c*. The asymmetric unit consists of a [Cd(bismip)(phen)] molecule and one solvent water molecule. As shown in Fig. 2a, each Cd atom is connected with four carboxylic O atoms of three different bismip ligands and two pyridine N atoms of a phen molecule, generating a distorted octahedral coordination geometry. The Cd–O bond distance ranging from 2.231(4) Å to 2.386(4) Å is shorter than that of {[Cd(dpq)(L₂)]_n} (H₂L₂ = 2,5-(s-acetic acid) dimercapto-1,3,4-thiadiazole) [49], while the Zn–N bond length (2.345(4) Å and 2.331(4) Å) is comparable to that of {[Cd₂(dpstc)(phen)₄(H₂O)₂]·6H₂O}_n (H₄dpstc = 3,3',4,4'-diphenylsulfonetetracarboxylic acid) [50]. Each two Cd atoms are bridged by two carboxylate groups with $\mu_1-\eta_1:\eta_1$ bridging mode to obtain a [Cd₂(μ -O₂C)₂] unit. The adjacent units are connected by two bismip ligands forming a wave-like chain running along *c* axis (Fig. 2b). The inter-linkage of chains by π - π packing interactions among the aromatic rings of phen resulted in a two dimensional layer extending in the *ac* plane (Fig. 2c). Furthermore, the organic-inorganic hybrid layers are hold together by extensive hydrogen bonding interactions [N(2) - H(2) ... O(3)] leading to a 3D supramolecular structure. (Fig. 2d).

(Fig. 2. here)

3.2.3. Crystal structure of **3**. X-ray structural analysis revealed that complex **3** crystallizes in monoclinic crystal system with *P2/c* space group. As shown in Fig. 3a, its asymmetric unit contains half a [Cd₂(bismip)₂(4,4'-bipy)] molecule and two solvent water molecules. There are two types of crystallographic independent Cd atoms existed in **3**. For Cd1, it is six-coordinated by four O atoms of two independent bismip ligands and two N atoms from two individual 4,4'-bipy

ligands. Cd²⁺ atom is also located in an octahedral coordination environment, linked by four O atoms of two different bismip ligands and two N atoms from other two bismip ligands. The Cd–O/N bond lengths are in the range of 2.271 (2) Å–2.443(4) Å, which are close to those in $\{[\text{Cd}_3\text{L}_2(4,4'\text{-bipy})_3(\text{H}_2\text{O})]\cdot 2.5\text{H}_2\text{O}\}_n$ ($\text{H}_3\text{L} = 5\text{-(4-carboxybenzyloxy) isophthalic acid}$, 4,4'-bipy = 4,4'-bipyridine) [51]. Each two equivalent Cd atoms are jointed to each other by two independent bismip ligands generating an infinite chain extending *b* axis (Fig. 3b). Then, these chains are interlinked by sharing $[\text{CdO}_4]$ dimers, thus leading to a 2D network in the *ac* plane (Fig. 3c). The 2D network is further connected to its adjacent ones by bidentate bridging 4,4'-bipy ligands in a criss-cross fashion to perform a 3D framework. Although the single 3D architecture of **3** contains large channels, its void space is mainly minimized by the interpenetration of other one equivalent network, leaving only small voids to hold solvent water molecules. This structure can also be regarded as a two-fold interpenetrating 3D framework when the bismip ligands and Cd atoms are considered as 3- and 4-connecting nodes, respectively.

The 3D framework compound **1** is remarkably different from $\{[\text{Zn}(\text{bismip})]\cdot 2\text{H}_2\text{O}\}_n$ which has a 2D binodal (3,6)-connected kgd network [41]. The 1D chain compound **2** may be compared with the $\{\text{Zn}_2(\text{bismip})_2(\text{phen})\}_n$, however, the latter is a binodal 3D (3,4)-connected network with the Schläfli symbol of $(8^3)(8^6)$ [41]. Compound **3** and $\{[\text{Zn}_2(\text{bismip})_2(4,4'\text{-bipy})]\cdot 2\text{H}_2\text{O}\}_n$ [41] both exhibit two-fold interpenetrating 3D architecture with a $(4\cdot 8^2)(4^2\cdot 8^4)$ Schläfli symbol while the coordination modes of H_2bismip are remarkably different (scheme 1). In compounds **1** – **3**, the carboxy groups in bismip ligands coordinate to the Cd ions in bis-monodentate and bidentate chelate fashion. Most notably, the imidazole N is not deprotonated in compound **2**.

(Fig. 3. here)

3.3. Luminescent properties of **1** – **3**.

The study of the metal organic coordination polymers containing with d^{10} electron configuration metal ions becomes a trend because of their potential applications in the field of photoactive materials for light emitting diodes (LEDs), chemical sensors and electrochemical displays [52–54]. Thus, the solid state emission properties of complexes **1** – **3** were investigated at room temperature. As shown in Fig. 4, the emission bands for **1** – **3** appear similar, and their emission maxima were located at 430 nm ($\lambda_{\text{ex}} = 332$ nm), 470 nm ($\lambda_{\text{ex}} = 363$ nm) and 513 nm ($\lambda_{\text{ex}} = 340$ nm). The emissions of **1** – **3** are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge

transfer (LMCT) in nature since Cd^{II} ion is difficult to oxidize or reduce due to its d^{10} configuration. The close resemblance to the emission bands of auxiliary ligands suggests that this may be tentatively attributed to the π - π^* intraligand fluorescence [55-57].

(Fig. 4. here)

3.4 UV-vis absorption spectra of **1** – **3**.

As the metal-organic frameworks can behave as semiconductors if exposed to the light [58, 59], thus, the optical properties of **1** – **3** were investigated using UV-vis diffuse reflectance spectra at room temperature (Fig. S4, ESI†).

The absorption (α/S) data were calculated from the reflectance using the Kubelka–Munk function [60]:

$$\alpha/S = \frac{(1 - R)^2}{2R}$$

where α represents the absorption, S is the scattering coefficient, and R is the reflectance at a given energy. The energy band gaps (E_{onset}) obtained by extrapolation of the linear portion of the absorption edges were estimated to be 3.74 eV (**1**), 3.44 eV (**2**), and 2.81 eV (**3**), respectively (Fig. 5) which indicated that **1**–**3** are potential wide gap semiconductor materials such as photocatalysts.

(Fig. 5. here)

3.5 Photocatalytic Properties of **1** – **3**.

Photocatalysts based on Cps have received much more attention due to their potential applications in purifying polluted water by thoroughly decomposing organic compounds [61, 62]. Herein, methyl blue (MB), as a main dye contaminant in textile industry, was selected for studying the activities of photocatalysts under UV irradiation. The absorption peaks of MB decreased obviously along with the prolonging of reaction time which suggested compounds **1** – **3** possess good photocatalytic activities (Fig. S5, ESI†). However, **3** showed the best degradation capability for MB among the three compounds. Their photocatalytic activities are mainly related with the complex structures, such as the numbers of the coordinated water molecules, the coordination environments of the central metals, the extent of the conjugation and the sizes of the metal–oxygen clusters [63]. In addition, the concentrations of MB (C) versus irradiation time (t) of compounds **1** – **3** are plotted in Fig. 6. It can be seen that the photocatalytic activities increase

from 54% (without any catalyst) to 72% for **1**, 85% for **2**, and 92% for **3** after 3 h of irradiation. The degradation rate agrees with $3 > 2 > 1$, which is perfectly consistent with the theoretical results. In addition, the stabilities of compounds **1** – **3** were studied using powder PXRD patterns during the course of the photocatalytic reactions (Fig. S3, ESI†). The PXRD patterns are nearly identical to those of the original compounds, which indicate that compounds **1** – **3** are stable during photocatalytic reactions.

(Fig. 6. here)

4. Conclusion

We have successfully synthesized three novel Cd(II) coordination polymers based on a benzimidazole-substituted dicarboxylic ligand under hydrothermal condition. For **1**, bismip ligands play as multiconnectors to link Cd ions into a 3D network. **2** exhibits a 1D chain because the chelate phen ligands limit the dimensionality comparing with **1**. On contrast, **3** is a 3D (3,4)-connected framework bridged by bis-monodentate 4,4'-bipy ligands. The results indicate that the auxiliary ligands do great effect on the geometrical configurations and structural motifs of the coordination polymers. Further investigations indicate that **1**–**3** have good photoluminescence and photocatalytic properties. Among the three coordination polymers, compound **3** exhibits excellent photocatalytic activities for the degradation of MB. Further work to explore new transition metal dicarboxylates with fascinating structures and interesting properties based on benzimidazole-substituted dicarboxylic ligands is going on in our laboratory.

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Captions for Schemes and Figures

Table 1 Crystal data and structure refinements for compounds **1** – **3**

Compound	1	2	3
Formula ^a	C ₁₆ H ₁₂ N ₂ O ₄ SCd	C ₂₈ H ₂₀ N ₄ O ₅ SCd	C ₂₁ H ₁₇ N ₃ O ₆ SCd
Formula weight	440.74	636.94	551.86
T (K)	291(2)	291(2)	291(2)
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	<i>I</i> 2 ₁ 2 ₁ 2 ₁	<i>C</i> 2/ <i>c</i>	<i>P</i> 2/ <i>c</i>
<i>a</i> /Å	14.328(4)	26.981(18)	13.854(3)
<i>b</i> /Å	9.957(3)	10.137 (7)	10.832(3)
<i>c</i> /Å	14.914(4)	18.901(13)	18.731(3)
α /°	90.00	90.00	90.00
β /°	90.00	100.74(2)	130.62(10)
γ /°	90.00	90.00	90.00
<i>V</i> /Å ³	2127.7(10)	5078.9(6)	2133.5(9)
<i>Z</i>	4	8	4
<i>D</i> _c /g·cm ⁻³	1.376	1.666	1.718
μ /mm ⁻¹	1.142	0.990	1.166
<i>F</i> (000)	872	2560	1104
<i>R</i> _{int}	0.069	0.04	0.062
Goodness-of-fit on <i>F</i> ²	1.171	1.005	1.082
Total	6394	17887	22309
unique data	1877	4445	9927
<i>R</i> ₁ , [<i>I</i> > 2σ (<i>I</i>)] ^b	0.0671	0.0412	0.0461
<i>wR</i> ₂ [<i>I</i> > 2σ (<i>I</i>)] ^b	0.1632	0.1200	0.1221
<i>R</i> ₁ , (all data) ^b	0.0696	0.0575	0.0514
<i>wR</i> ₂ (all data) ^b	0.1643	0.1362	0.1282
(Δρ) _{max} /e·Å ⁻³	1.50	0.66	1.86
(Δρ) _{min} /e·Å ⁻³	-1.95	-0.64	-1.66

^a Including solvent molecules. ^b $R_1 = \Sigma (|F_0| - |F_C|) / \Sigma |F_0|$, $wR_2 = [\Sigma w (|F_0| - |F_C|)^2 / \Sigma w F_0^2]^{1/2}$.

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

Cd(1)-N(1)	2.296(16)	O(1A)-Cd(1)-O(1B)	127.28(3)
Cd(1)-O(1A)	2.294(8)	O(1A)-Cd(1)-O(2B)	93.00(4)
Cd(1)-O(2A)	2.387(8)	O(1A)-Cd(1)-N(1C)	100.49(5)
Cd(1)-O(1B)	2.294(8)	O(1B)-Cd(1)-O(2A)	93.00(4)
Cd(1)-O(2B)	2.387(8)	O(2A)-Cd(1)-O(2B)	107.31(3)
Cd(1)-N(1C)	2.296(16)	O(2A)-Cd(1)-N(1C)	151.91(5)
O(1A)-Cd(1)-N(1)	114.23(5)	O(1B)-Cd(1)-O(2B)	54.65(4)
O(2A)-Cd(1)-N(1)	84.74(5)	O(1B)-Cd(1)-N(1C)	114.23(5)
O(1B)-Cd(1)-N(1)	100.49(5)	O(2B)-Cd(1)-N(1C)	84.74(5)
O(2B)-Cd(1)-N(1)	151.91(5)	O(1A)-Cd(1)-O(2A)	54.65(4)
N(1)-Cd(1)-N(1C)	96.32(6)		

Complex 2

Cd(1)-O(1)	2.231(4)	N(4)-Cd(1)-N(3)	71.26(17)
Cd(1)-N(3)	2.345(4)	O(1)-Cd(1)-O(4B)	102.28(16)
Cd(1)-N(4)	2.331(4)	O(2A)-Cd(1)-O(4B)	89.03(15)
Cd(1)-O(2A)	2.258(4)	N(4)-Cd(1)-O(4B)	90.02(16)
Cd(1)-O(3B)	2.386(4)	N(3)-Cd(1)-O(4B)	138.56(14)
Cd(1)-O(4B)	2.353(4)	O(1)-Cd(1)-O(3B)	85.73(14)
O(1)-Cd(1)-O(2A)	103.68(18)	O(2A)-Cd(1)-O(3B)	143.33(14)
O(1)-Cd(1)-N(4)	167.28(16)	N(4)-Cd(1)-O(3B)	99.10(14)
O(2A)-Cd(1)-N(4)	79.49(18)	N(3)-Cd(1)-O(3B)	91.56(13)
O(1)-Cd(1)-N(3)	96.98(16)	N(4B)-Cd(1)-O(3B)	54.30(12)
O(2A)-Cd(1)-N(3)	121.53(17)		

Complex 3

Cd(1)-O(1)	2.382(3)	O(1A)-Cd(1)-O(2A)	55.68(11)
Cd(1)-O(2)	2.313(3)	N(3A)-Cd(1)-O(1)	144.39(12)
Cd(1)-N(3)	2.297(3)	O(1)-Cd(1)-N(3)	94.72(12)
Cd(1)-O(1A)	2.382(3)	O(2)-Cd(1)-O(1)	55.68(11)
Cd(1)-O(2A)	2.313(3)	O(2A)-Cd(1)-O(1)	89.99(13)
Cd(1)-N(3A)	2.297(3)	O(1A)-Cd(1)-O(1)	92.4(2)
Cd(2)-N(1)	2.278(3)	O(4C)-Cd(2)-O(4B)	127.40(13)
Cd(2)-O(3B)	2.443(4)	O(4B)-Cd(2)-N(1D)	92.89(10)
Cd(2)-O(4B)	2.271(2)	O(4C)-Cd(2)-N(1D)	124.02(11)
Cd(2)-O(3C)	2.443(4)	N(1)-Cd(2)-N(4B)	124.02(10)
Cd(2)-O(4C)	2.271(2)	N(1)-Cd(2)-N(4C)	92.89(10)
Cd(2)-N(1D)	2.278(3)	N(1D)-Cd(2)-N(1)	93.01(17)
N(3)-Cd(1)-N(3A)	99.42(16)	O(4B)-Cd(2)-O(3B)	54.39(11)
O(2)-Cd(1)-N(3A)	89.45(11)	O(4C)-Cd(2)-O(3B)	92.64(13)
O(2)-Cd(1)-N(3)	122.57(12)	N(1D)-Cd(2)-O(3B)	142.58(13)
O(2A)-Cd(1)-N(3A)	122.57(12)	N(1)-Cd(2)-O(3B)	92.22(13)
N(3)-Cd(1)-O(2A)	89.45(11)	O(4B)-Cd(2)-O(3C)	92.64(13)
O(2A)-Cd(1)-O(2)	131.75(16)	O(4C)-Cd(2)-O(3C)	54.39(11)
N(3A)-Cd(1)-O(1A)	94.72(12)	N(1D)-Cd(2)-O(3C)	92.22(13)

N(3)-Cd(1)-O(1A)	144.39(12)	N(1)-Cd(2)-O(3C)	142.58(13)
O(2)-Cd(1)-O(1A)	89.88(13)	O(3B)-Cd(2)-O(3C)	105.5(2)

Symmetry codes for **1**: (A) $-x + 2, -y + 3/2, z$; (B) $x - 1/2, y - 1/2, z - 1/2$; (C) $-x + 3/2, y, -z + 1$; for **2**: (A) $-x + 2, y, -z + 3/2$; (B) $x, -y, z - 1/2$; for **3**: (A) $-x + 2, y, -z + 3/2$; (B) $-x + 1, -y, -z + 1$; (C) $x, -y, z + 1/2$; (D) $-x + 1, y, -z + 3/2$.

Scheme 1 The coordination modes of H_2bismip in $\{[\text{Zn}(\text{bismip})]\cdot 2\text{H}_2\text{O}\}_n$ (a), $\{\text{Zn}_2(\text{bismip})_2(\text{phen})\}_n$ (b), $\{[\text{Zn}_2(\text{bismip})_2(4,4'\text{-bipy})]\cdot 2\text{H}_2\text{O}\}_n$ (b), compound **1** (d), compound **2** (c) and compound **3** (d).

Fig. 1. (a) ORTEP drawing of **1** (30% probability ellipsoids). Hydrogen atoms are omitted for

clarity. Symmetry codes for the generated atoms: (A) $-x + 2, -y + 3/2, z$; (B) $-x + 2, y - 1/2, -z + 3/2$; (C) $x - 1/2, y - 1/2, z - 1/2$; (D) $-x + 3/2, y, -z + 1$; (E) $x, -y + 1, -z + 3/2$; (F) $-x + 3/2, -y + 1, z - 1/2$; (G) $x - 1/2, -y + 3/2, -z + 1$. (b) View of the 2D layer of **1**. (c) View of the 3D structure of **1**.

Fig. 2. (a) ORTEP drawing of **2** (30% probability ellipsoids). Hydrogen atoms and lattice water molecules are omitted for clarity. Symmetry codes for the generated atoms: (A) $-x + 2, y, -z + 3/2$; (B) $x, -y, z - 1/2$. (b) View of the 1D [Cd(bismip)(phen)]_n chain in **2**. (c) View of the 2D layer. (d) View of the 3D framework of **2**.

Fig. 3. (a) ORTEP drawing of **3** (30% probability ellipsoids). Hydrogen atoms and lattice water molecules are omitted for clarity. Symmetry codes for the generated atoms: (A) $-x + 2, y, -z + 3/2$; (B) $-x + 1, -y, -z + 1$; (C) $x, -y, 1/2 + z$; (D) $-x + 1, y, -z + 3/2$, (E) $-x + 2, -y + 2, -z + 1$; (F) $x, -y + 2, z + 1/2$. (b) View of the 1D $[\text{Cd}(\text{bismip})]_n$ chain in **3**. (c) View of the 2D layer of **3**. (d) View of the topological net of **3**. The cyan and red balls represent the 3-connecting bismip ligands and the 4-connecting Cd atoms.

Fig. 4. Solid state emission spectra of compounds **1** – **3** at room temperature.

Fig. 5. Solid-state optical diffuse-reflection spectra of **1** – **3** derived from diffuse reflectance data at ambient temperature.

Fig. 6. Curves of photodegradation of MB by **1** – **3** and without catalyst under UV light.

Graphic Abstract

Three cadmium coordination polymers with different architectures based on 5-(1H-benzoimidazol-2-ylsulfanylmethyl)-isophthalic acid have been prepared. Their photoluminescent properties were also investigated.

Structural Diversification and Photocatalytic Properties of Three Cd(II) Coordination

Polymers Decorated with Different Auxiliary Ligands

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