

Syntheses, Crystal Structures and Properties of Two Coordination Polymers Based on Bisbenzimidazole^①

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ABSTRACT Two novel coordination polymers $\text{Bim}(\text{C}=\text{O})\text{CuI}_2$ (**1**) and $[\text{Bim}(\text{C}=\text{O})\text{CdCl}_2]_2$ (**2**) based on the flexible ligand bis(1*H*-benzo[d]imidazol-2-yl)methane (Bim) were synthesized *via* volatilization method. They crystallize in monoclinic and triclinic crystal systems and adopt space group of $P2_1/c$ and $P\bar{1}$, respectively. The compounds were characterized by elemental analysis, infrared spectroscopy and powder X-ray diffraction analysis. Interestingly, methylene ($-\text{CH}_2-$) in Bim was oxidized to carbonyl ($\text{C}=\text{O}$), which increases its extra-cyclic conjugation effect. For **1** and **2**, their maximum emission wavelength of fluorescence around 440 and 475 nm indicates the potential as promising light-emissive materials. Meaningfully, Co^{2+} ion shows a quenching effect on the fluorescence of compound **1**. Besides, both compounds possess remarkable structure stability.

Keywords: bisbenzimidazole ligand, crystal structure, fluorescence, methylene, carbonyl;

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1 INTRODUCTION

In the history of heterocyclic chemistry^[1-6], benzimidazole and its derivative are widely used in many fields due to its unique properties^[7], such as drug synthesis^[8], coordination chemistry^[9-10], bioinorganic chemistry fields, *etc.* Benzimidazole derivatives could be designed and synthesized as special ligands, and used as monodentate/bidentate ligand due to their unique structures to construct structural diversity metal organic frameworks(MOFs)^[11-15]. Recently, bisbenzimidazole compounds have been perused and attracted widespread attention^[16]. A large number of bisbenzimidazole ligands have been synthesized including rigid^[17] and semi-rigid^[18] structures which break through single coordination method of benzimidazole. Therefore, the structures of the synthesized compounds are even more diverse and interesting, and their properties are more preferable^[19].

In this work, two novel compounds were synthesized *via* volatilization method with bis(1*H*-benzo[d]imidazol-2-yl)methane (Bim), and their structures were determined by single-crystal X-ray diffraction. According to the structure rigidity of compounds, their fluorescence properties were

directly confirmed by photoluminescence spectroscopy measurements. Furthermore, their chemical structure thermal stability and dielectric properties were investigated, indicating their potential as multifunctional materials under a wide temperature range.

2 EXPERIMENTAL

2.1 Materials and instruments

All reagents from commercial sources were used without purification. Thermo-gravimetric analysis (TGA) was showed in the environment of nitrogen at a heating rate of 10 K min^{-1} in the range of 20–800 °C. IR test was recorded by infrared spectrometer (KBr tablet) with wave number 400–4000 cm^{-1} . Powder X-ray diffraction test conditions: tube voltage 40 kV, tube current 10 mA, $\text{CuK}\alpha$ radiation, wavelength 1.5406 Å, test angle range 5–50°, step 0.02° and scanning speed 6 °/min. The sample was ground into powder in an agate mortar and pressed into a tablet press, and a 7mm × 2mm × 0.4mm (length, width, and height) sample was cut and tested using a conductive silver paste fixed on a six-claw electrode. The test frequency range was 500 Hz–1 MHz.

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Fluorescence properties of compounds were also studied at room temperature.

2.2 Single-crystal X-ray diffraction

Crystals of compounds with moderate size and complete appearance were selected for single-crystal X-ray diffraction analysis. Data collections were performed with a multi-scan mode at 296(2) K in the ranges of $2.4^\circ < \theta < 24.9^\circ$ (**1**) and $2.3^\circ < \theta < 26.4^\circ$ (**2**) on a Bruker SMART APEX-II CCD diffractometer equipped with MoK α radiation ($\lambda = 0.71073$ Å). The data sets were corrected by empirical absorption

correction using SADABS. The final refinement gave $R_{(1)} = 0.0498$ and $R_{(2)} = 0.0517$, $wR_{(1)} = 0.0902$ and $wR_{(2)} = 0.0556$, respectively. The crystal structures were solved by direct methods and refined by full-matrix least-squares method on F^2 by means of SHELXL software package. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were located and refined geometrically. Furthermore, calculations of distances and angles between some atoms were performed by DIAMOND or SHELXL. Crystallography data of compound **1** and **2** are listed in Table 1.

Table 1. Crystal Data and Structure Refinement for the Compounds

Compounds	1	2
Empirical formula	C ₁₅ H ₁₀ CuIN ₄ O	C ₁₅ H ₁₀ CdCl ₂ N ₄ O
Formula weight	452.71	445.57
Temperature (K)	296	296
Crystal system	Monoclinic	Triclinic
Space group	<i>P2</i> ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	9.2614(2)	9.2545(12)
<i>b</i> (Å)	17.7440(3)	10.0645(13)
<i>c</i> (Å)	9.6480(2)	10.0645(13)
α (°)	90	93.91
β (°)	113.886(1)	113.604(2)
γ (°)	90	113.604(2)
<i>V</i> (Å ³)	1449.70(5)	757.42(17)
<i>Z</i>	4	2
<i>F</i> (000)	872	436
ρ_{calcd} /g cm ⁻³	2.074	1.954
μ (mm ⁻¹)	3.64	1.80
θ range (°)	2.4 to 24.9	2.3 to 21.6
Collected reflections	3193	5758
Unique reflections	2443	1943
<i>R</i> , <i>wR</i> (<i>I</i> > 2 σ (<i>I</i>))	0.0283 to 0.0681	0.0328 to 0.0504
<i>R</i> , <i>wR</i> (all data)	0.0498 to 0.0902	0.0517 to 0.0556

2.3 Synthesis of the ligand

The synthesis of bis(1*H*-benzo[d]imidazol-2-yl)methane is based on experimental methods reported by previous literature^[20] with a slight modification that malonic acid was replaced by malononitrile (Scheme 1). Malononitrile (3 mmol, 3.380 g), *o*-phenylenediamine (6.6 mmol, 7.1280 g) and hydrochloric acid (4 mol/L, 30 mL) were added to a flask, followed by evacuating and ventilating nitrogen for three times to form an oxygen-free environment. The mixture was heated to 120 °C and kept for 12 h. When the temperature dropped to *ca.* 70 °C, the reaction mixture was poured into ice water (200 mL). After adjusting pH to 10 with NaOH solution, a large amount of white solid was precipitated. Then it was filtered by suction operation, and the filter cake was washed with water for several times. The cake was dried overnight at 60 °C in an oven. Recrystallization from ethanol

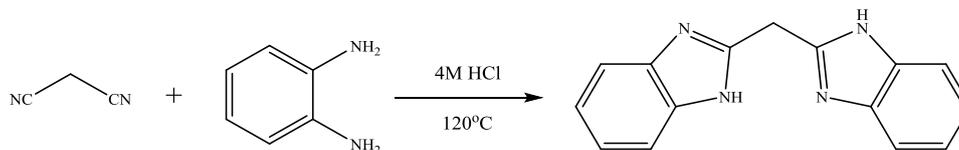
gave a white crystalline powder bis(1*H*-benzo[d]imidazol-2-yl)methane (6.72 g, yield 79%). ESI-MS(*m/z*): [M-H]⁻ 247.6; [M+H]⁺ 248.3. FT-IR (KBr, cm⁻¹): 3434(m), 2767(w), 2627(s), 2549(w), 1614(w), 1463(s, -CH₂-), 1402(s), 1318(s), 1284(m), 1256(m), 1150(w), 1105(w), 982(w), 915(s), 853(s), 736(s), 641(m), 596(w), 506(w).

2.4 Preparation of the compounds

Synthesis of [Bim(C=O)Cu]₂ A mixture of bis(1*H*-benzo[d]imidazol-2-yl)methane (281 mg, 10 mmol), CuI (313 mg, 20 mmol), methanol (10 mL) and water (10 mL) was added to a 50 mL beaker. The mixture was stirred for 10 minutes, and then the insoluble matter was filtered off to give a transparent solution. This resulting solution was placed in shady and dark place to evaporate slowly. Few days later, a slight yellow crystal was obtained with a yield of 48% (based on Cu). Anal. Calcd. for [C₁₅H₁₀ICuN₄O] (%): C, 44.33; H,

2.46; N, 13.80. Found (%): C, 42.67; H, 4.85; N, 14.06. FT-IR (KBr, cm^{-1}): 3443(m), 2745(m), 2633(s), 2555(w), 1952(m), 1745(w, C=O), 1611(s, C=N), 1477(s, C=N),

1382(m), 1293(m), 1215(s), 1019(s), 852(s), 740(s), 617(m), 427(m).

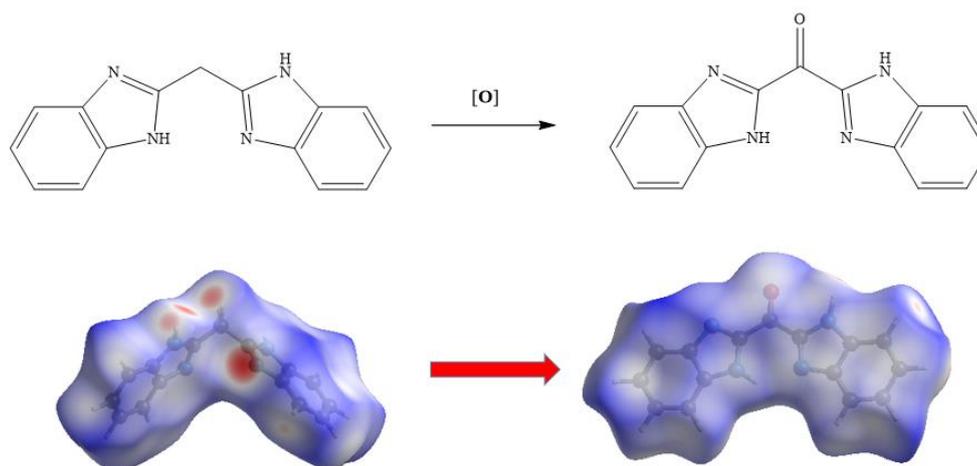


Scheme 1. Synthesis route of bis(1H-benzo[d]imidazol-2-yl)methane

Synthesis of $[\text{Bim}(\text{C}=\text{O})\text{CdCl}_2]_2$ The CuI was replaced by CdCl_2 with other conditions unchanged. Few days later, a slight yellow crystal was obtained with a yield of 53% (based on Cd). Anal. Calcd. for $\text{C}_{15}\text{H}_{10}\text{CdCl}_2\text{N}_4\text{O}$ (%): C, 39.73; H, 2.21; N, 14.13. Found (%): C, 40.50; H, 3.45; N, 14.06. FT-IR (KBr, cm^{-1}): 3501(m), 2725(m), 2643(s), 2547(w), 1952(m), 1746(w, C=O), 1604(s, C=N), 1480(s, C=N), 1379(m), 1300(m), 1215(s), 1021(s), 857(s), 739(s), 615(m), 425(m).

3 RESULTS AND DISCUSSION

According to literature^[21-24], under aerobic conditions, the methylene group is easily oxidized to a carbonyl group. In this way, the central carbon atom is changed from the original sp^3 to the sp^2 hybridization, which increases its out-side-ring conjugation, thus making the compound more stable (Scheme 2).



Scheme 2. Methylene is oxidized to carbonyl and electric cloud density of ligands

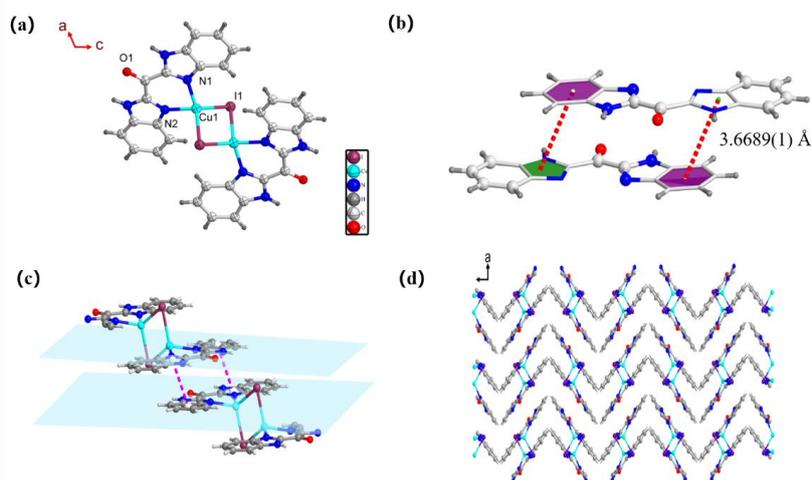
3.1 Description of crystal structure

Structure of compound 1 A transparent single crystal with regular shape and moderate size was selected for single-crystal X-ray diffraction analysis. The results show (Fig. 1) that the structure adopts monoclinic $P2_1/c$ space group. The crystal is a binuclear metal-organic structure. Each copper atom is connected by two bromine and two nitrogen atoms. The iodine atom that bridges with two copper atoms leads to a high symmetry structure. The distances between copper and iodine atoms are 2.7029(19) and 2.5765(17) Å, and those of copper and nitrogen atoms are

2.071(9) and 2.063(10) Å, all within normal ranges^[21, 22]. It can be seen from the packing diagram that the structure presents a zigzag shape through chemical force accumulation (π - π accumulation, *van der Waals* force). Besides, the distance between two centroids is 3.6689(1) Å and the dihedral angle is 0.00°. Interestingly, methylene in the benzimidazole ligand is oxidized to carbonyl group, in which the C-atom converts to sp^2 from the original sp^3 , increasing the extra-cyclic conjugation effect of the ligands. Parts of the major bond lengths and bond angles are listed in Table 2.

Table 2. Parts of Bond Lengths (Å) and Bond Angles (°) for Compound 1

Bond	Dist.	Angle	(°)
Cu(1)–I(1)	2.5748(6)	Cu(1 ¹)–I(1)–Cu(1)	68.584(19)
Cu(1)–N(1)	2.058(3)	I(1 ¹)–Cu(1)–I(1)	111.416(19)
Cu(1)–N(2)	2.054(3)	N(2)–Cu(1)–I(1)	107.68(9)
C(8)–O(1)	1.219(5)	N(1)–Cu(1)–I(1)	110.55(9)

Symmetry code: $i : -x, y+1/2, -z+1/2$ **Fig. 1. Structure of compound 1. (a) Coordination environment. (b) π - π stacking diagram. (c) Schematic diagram of dihedral angle. (d) Stacking diagram**

Structure of compound 2 Compound 2 (Fig. 2) is similar to 1 except that the Cd atom adopts a five-coordination mode to balance the charge. The distances between cadmium and chlorine atoms are 2.6238(15) to 2.4031(12) Å, and the lengths of cadmium and nitrogen

atoms are 2.300(4) to 2.302(4) Å. In π - π stacking, the centroids distance is 3.3730(3) Å and the dihedral angle is 0.000(2)°. Major bond lengths and bond angles are listed in Table 3.

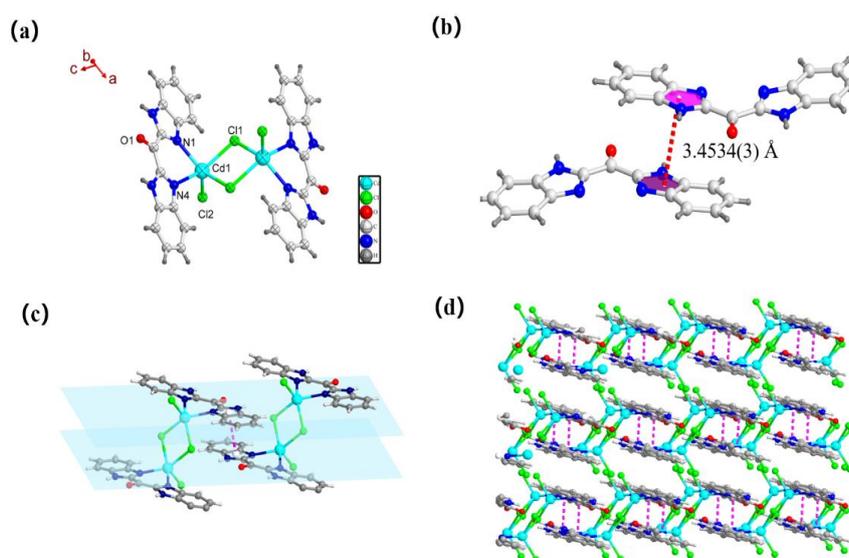
**Fig. 2. Structure of compound 2. (a) Coordination environment. (b) π - π stacking diagram. (c) Schematic diagram of dihedral angle. (d) Stacking diagram**

Table 3. Parts of Bond Lengths (Å) and Bond Angles (°) for Compound 2

Bond	Dist.	Angle	(°)
Cd(1)–Cl(1)	2.6238(15)	Cl(1)–Cd(1)–Cl(1 ⁱ)	79.32(4)
Cd(1)–Cl(2)	2.4031(12)	Cl(1)–Cd(1)–Cl(2)	108.58(5)
Cd(1)–N(1)	2.300(4)	N(4)–Cd(1)–Cl(1)	146.62(10)
Cd(8)–N(4)	2.302(4)	N(1)–Cd(1)–Cl(1)	90.05(11)

Symmetry code : i: -x, -y, -z

3.2 Powder X-ray diffraction

According to powder X-ray diffraction analysis (Fig. 3), the PXRD of two newly prepared compounds is completely

consistent with their calculated peak positions. Therefore, it can be preliminarily determined that two compounds are pure products.

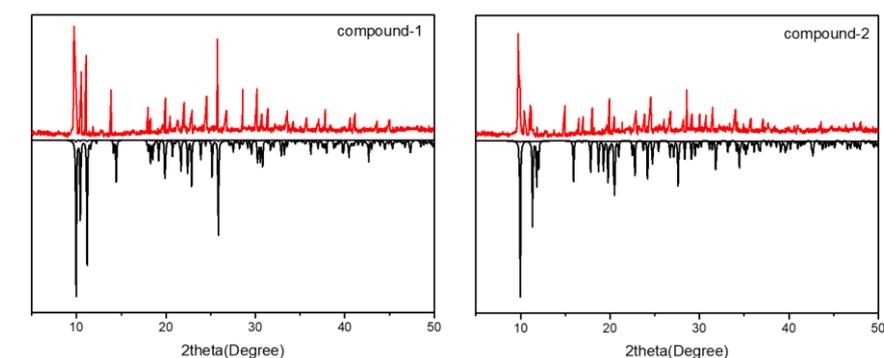


Fig. 3. Powder X-ray diffraction of compounds 1 and 2

3.3 Fluorescent properties

The fluorescence and luminescence properties of the compounds are interesting. According to the principle of fluorescence emission the possible reasons are electronic transitions (including π - π^* and n - π^* transitions) or structural rigidity, non-covalent bonding, large conjugated systems and diamagnetic metals^[25]. When energy provided (ultraviolet light, heat, pressure, *etc.*), it could show strong fluorescence

emission and even aggregation-induce emission (AIE). Recently, cuprous iodide clusters have been used to induce complex luminescence and better results are obtained. The solid-state fluorescent spectrum of compounds 1 and 2 at room temperature reveals maximal emission peaks at 440 and 475 nm (Fig. 4a), suggesting both compounds are potential blue purple luminescent materials.

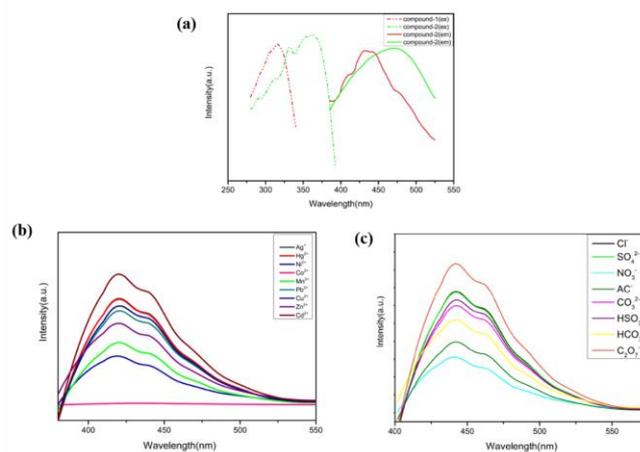


Fig. 4. Fluorescence property. (a) Maximum emission wavelength of compounds 1 and 2. (b) Effect of metal ion on the fluorescence of compound 1. (c) Effect of anion on the fluorescence of compound 1

Through aggregation concentration quenching (ACQ) experiment, the fluorescence of compound **1** is greatly weakened or even disappears with the existence of Co^{2+} (Fig. 4b, 4c). The possible reason is the paramagnetic effect of such ions, which causes the excited electrons to be captured by the metal. To a certain extent, electronic transition is restricted and makes fluorescence quenched.

3.4 Thermal stability analysis

In order to further study the thermal stability of the compounds, thermogravimetric analysis was performed. In the thermogravimetric curve (Fig. 5), compound **1** began to lose weight at *ca* 400 °C, and completely collapsed until 500 °C. Compared to **1**, **2** was completely decomposed until 450 °C. It can be known that both compounds **1** and **2** have better stability.

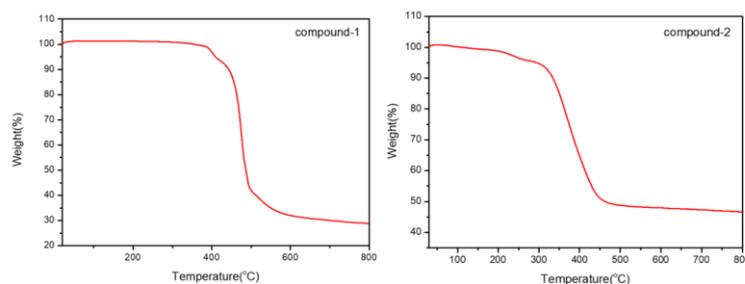


Fig. 5. Thermogravimetric analyses (TGA) of compounds **1** and **2**

3.5 Dielectric properties

Dielectric test (Fig. 6) showed that compounds **1** and **2** are both positive dielectric materials as the dielectric constant

gradually increases with increasing the temperature at different frequencies.

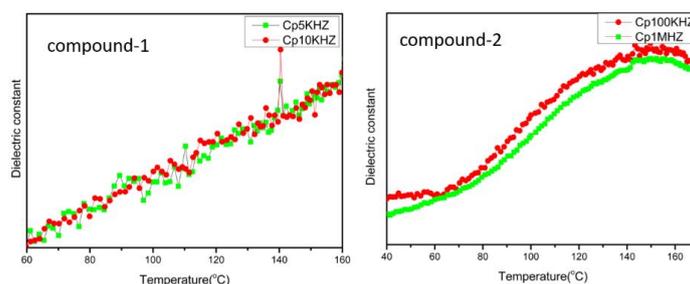


Fig. 6. Dielectric properties of compounds **1** and **2**

4 CONCLUSION

Two novel coordination polymers $[\text{Bim}(\text{C}=\text{O})\text{CuI}]_2$ (**1**) and $[\text{Bim}(\text{C}=\text{O})\text{CdBr}_2]_2$ (**2**) were synthesized *via* volatilization method by using bis(1*H*-benzo[d]imidazol-2-yl)methane (Bim) as the flexible ligand. Interestingly, methylene (CH_2) in Bim was oxidized to carbonyl ($\text{C}=\text{O}$) in air. The

fluorescence emission spectra of **1** and **2** reaches maximum around 440 and 475 nm, which indicate the potential application in LED field. Especially for compound **1**, its fluorescence is quenched when cobalt ion exists in solution. Both two compounds are positive dielectric materials within a wide temperature range for their remarkable thermal stability.

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