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# Synthesis, Structure, and Luminescent Property of One Zinc (II) Coordination Polymer Constructed From 1H-Benzoimidazole

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A new metal-organic coordination polymer $[Zn(bm)(AcO)]_n$ (**1**), where Hbm is 1H-benzoimidazole), has been prepared and structurally characterized by IR, elemental analysis and single-crystal X-ray diffraction. Single-crystal X-ray analysis shows that it crystallizes in the monoclinic space group of $P2_1/c$ with $a = 10.8231(5)$ Å, $b = 9.8329(4)$ Å, $c = 8.8665(4)$ Å, $\beta = 99.298(4)°$, $V = 931.20(7)$ Å$^3$, and $Z = 4$. The *bm* ligand bridges two adjacent Zn(II) with its two nitrogen atoms to form a one-dimensional chain, which further constructed 2D network through a bridge bidentate $AcO^-$ ligand. Furthermore, luminescent property of **1** was investigated.

**Keywords:** 1H-benzoimidazole, coordination polymer, crystal structure, luminescent property

## Introduction

Metal-organic frameworks (MOFs) have raised an upsurge of interest in the fields of crystal engineering and functional materials, due to their intriguing structural features as well as desired properties, including sensor technology,[1–3] separation processes,[4–6] gas storage,[7–11] luminescence,[12,13] ion exchange,[14,15] magnetism,[16–20] and catalytic materials.[21–23] Studies in this field have been focused on the design and construction of new metal-organic frameworks and the relationships between their structures and properties. Although big progress has been achieved, it remains difficult to predict the exact structures and compositions of the final products built by coordination bonds and/or hydrogen bonds in crystal engineering.[24] It is known that several factors, such as the presence of auxiliary ligands, the coordination nature of the metal ions, and the stoichiometries of components and reaction environments, may be crucial for the rational design of the metal-organic frameworks.[25–27] Therefore, systematic research on this topic is still important for understanding the roles of these factors in the formation of metal-organic coordination polymers. In the past years, analogue of 1H-benzoimidazole such as 5,6-dimethyl-1H-benzoimidazole,[28] 5-chloro-1H-benzoimidazole,[28] 5-nitro-1H-benzoimidazole (Hnbm),[29] 2-nitro-1H-imidazole (Hnm),[28,29] 5-methyl-1H-benzoimidazole (Hmbm),[29] 5-bromo-1H-benzoimidazole,[29] 1H-benzoimidazole,[28,30] and tris((benzimidazol-2-yl)methyl)amine[31] have been used to construct novel metal-organic frameworks with transition metal ions. In this study, we constructed a new zinc(II) coordination polymer $[Zn(bm)(AcO)]_n$ (**1**) under solvothermal conditions. In addition, luminescent property of **1** was measured and discussed.

## Experimental

### *Materials and Measurements*

All solvent and chemicals were commercial reagents and were used without further purification. The elemental analysis was performed on a PE 1700 CHN auto elemental analyzer. The crystal structure was determined by Agilent G8910A CCD diffractometer and SHELX crystallographic software of molecular structure. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm$^{-1}$ on a Bio-Rad FTS-7 spectrometer. Luminescence spectrum was obtained with a RF-5301PC fluorescence spectrometer.

### *Synthesis of $[Zn(bm)(AcO)]_n$ (1)*

The ligand (2-amino-2-(1H-benzo[d]imidazol-2-yl)ethanol (HL)) was prepared with benzene-1,2-diamine and L-serine according to a literature procedure.[32] The Hbm ligand was

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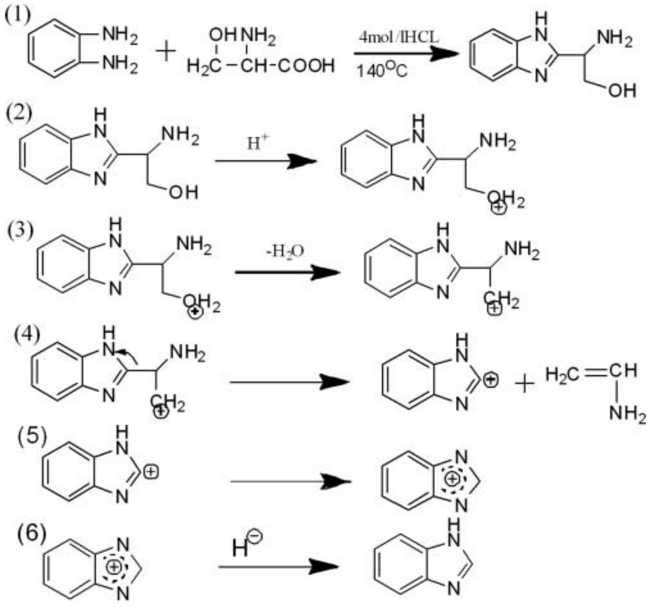

**Sch 1.** Formation mechanism of Hbm.

attained through an *in situ* reaction (The formation mechanism of Hbm see Scheme 1).

The mixture of $Zn(AcO)_2{\cdot}2H_2O$ (0.220 g, 1 mmol), Hbm (0.118 g, 1 mmol) was dissolved in 10 ml methanol. The pH was adjusted to 7.5 by addition triethylamine. Consequently, the resulting mixture was transferred to a 25 mL Teflon-lined stainless steel vessel, which was sealed and heated at 140°C for 120 h, and then the reaction system was cooled to room temperature. Block, colorless crystals of **1** were collected by filtration and washed with methanol several times with a yield of 70%. Anal. Calcd. for $C_9H_8N_2O_2Zn$ (%): C, 44.71; H, 3.31; N, 11.59; Found: (%): C,44.66; H,3.35; N, 11.67.

**Table 1.** Crystallographic data for complex **1**

| Complex | **1<** |
|---|---|
| Formula | $C_9H_8N_2O_2Zn$ |
| $M_r$ | 241.56 |
| Crystal size (mm) | 0.25 × 0.18 × 0.13 |
| $T$ (K) | 293 (2) |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| $a$ (Å) | 10.8231 (5) |
| $b$ (Å) | 9.8329 (4) |
| $c$ (Å) | 8.8665 (4) |
| $\beta$ (°) | 99.298 (4) |
| $V$ (Å$^3$) | 931.20 (7) |
| $F$(000) | 488 |
| $Z$ | 4 |
| $D_c$ (g cm$^{-3}$) | 1.732 |
| $\mu$ (mm$^{-1}$) | 2.609 |
| $\theta$ range (°) | 3.12–25.10 |
| Ref. meas. / indep. | 5627, 1665 |
| Obs. ref.[$I > 2\sigma(I)$] | 1273 |
| $R_{int}$ | 0.0487 |
| $R_1$ [$I \geq 2\sigma(I)$] [a] | 0.0407 |
| ω$R_2$(all data)[b] | 0.0927 |
| Goof | 1 |
| $\Delta\rho$(max, min) (e Å$^{-3}$) | 0.938, –0.611 |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma w(|F_o{}^2| - |F_c{}^2|)^2/\Sigma w(|F_o{}^2|)^2]^{1/2}$.

**Table 2.** Metal–ligand bond lengths (Å) and angles (°) in complex **1**

| | |
|---|---|
| O1-Zn1$^{i}$ | 1.983(3) |
| O2-Zn1 | 2.005(3) |
| N1-Zn1 | 1.979(3) |
| N2-Zn1$^{ii}$ | 1.985(3) |
| Zn1-O1$^{iii}$ | 1.983(3) |
| Zn1-N2$^{iv}$ | 1.985(3) |
| C7-N1-Zn1 | 125.8(3) |
| C1-N1-Zn1 | 129.2(3) |
| C9-O2-Zn1 | 133.4(3) |
| C7-N2-Zn1$^{i}$ | 126.8(3) |
| C6-N2-Zn1$^{i}$ | 128.4(3) |
| C9-O1-Zn1$^{ii}$ | 110.5(3) |
| N1-Zn1-O1$^{iii}$ | 111.79(14) |
| N1-Zn1-N2$^{iv}$ | 118.29(14) |
| O1$^{iii}$-Zn1-N2$^{iv}$ | 114.42(13) |
| N1-Zn1-O2 | 102.61(13) |
| O1$^{iii}$-Zn1-O2 | 102.79(13) |
| N2$^{iv}$-Zn1-O2 | 104.56(13) |

Symmetry codes: (i) $x, -y+1/2, z-1/2$; (ii) $-x+1, y+1/2, -z+3/2$; (iii) $x, -y+1/2, z+1/2$; (iv) $-x+1, y-1/2, -z+3/2$.

### *Crystal Structure Determination*

A Block, colorless crystal of complex **1** having approximate dimensions 0.25 × 0.18 × 0.13 mm was selected and mounted on a glass fiber. All measurements were made on a Agilent G8910A CCD diffractometer with a graphite-monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å) by using the $\omega$-$\theta$ scan mode in the range of $3.12 \leq \theta \leq 25.10°$ at 298 K. Raw frame data was integrated with the SAINT program.[33] The structure was solved by direct methods with SHELXS-97 and refined by full-matrix least-squares on $F^2$ using SHELXL-97.[33] The empirical absorption correction was applied with the program SADABS.[33] All non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were set in the calculated positions and refined by a riding model. The crystallographic details are provided in Table 1, while the selected bond distances and angles are listed in Table 2. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center. CCDC reference number for **1** is 979343.

## Results and Discussion

### *Crystal Structure Description*

The molecular structure of complex **1** is illustrated in Figure 1. Each Zn(II) atom is four-coordinated by two nitrogen atoms of two bm bridging ligands, and two oxygen atoms from two acetato ligands, forming a distorted tetrahedron

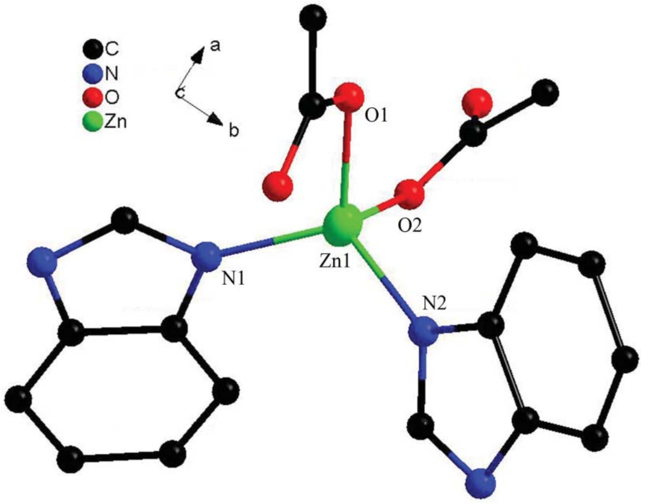

**Fig. 1.** The structure of **1**, all hydrogen atoms were omitted.

geometry. The structure of **1** is similarly adopted by $[Zn_2(nbm)_2(nm)_2]_n$ and $[Zn_2(mbm)_2(nm)_2]_n$[29] and $\{[Zn_2(nm)_2(bm)_2]\cdot(H_2O)\}_n$.[28] The bond lengths of Zn1—O1$^i$ [1.983(3) Å, symmetry: (i): *x*, 0.5 − *y*, −0.5 + *z*], Zn1— O2 [2.005(3) Å], Zn1—N1 [1.979(3) Å], Zn1—N2$^{ii}$ [1.985(3) Å, symmetry: (ii): − *x*, 1 − *y*, − *z*] are comparable to the ones found in $\{[Zn_2(ipa)(bm)_2]\cdot(H_2O)\}_n$ (Hipa is isophthalic acid).[34]

Each bm ligand coordinates to two Zn (II) atoms through its two aromatic N atoms and acts as a bridging bidentate ligand to form an infinite 1-D chain structure (Figure 2). The Zn···Zn separation across the bridging bm is 5.923 Å. Which is among the range that observed in $\{[Zn_2(nm)_2(bm)_2]\cdot(H_2O)\}_n$ (Zn···Zn distance is 5.796–5.974 Å).[28] The 1-D chain further constructs a 2-D network though the acetato ligand. The acetato ligand also coordinates to the two Zn atoms in a bidentate fashion. The Zn···Zn separation across the bridging acetato ligand is 4.455 Å, which is longer than that observed in other acetato ligand polymers[35] (Zn···Zn distance is 2.900(1)-4.162(1) Å). Herein, the coordination mode of carboxyl group is *syn-anti*-bidentate.[36] The C9-O (O atoms of carboxyl group) distances are almost equaled (C9-O1, 1.267(5) Å; C9—O2, 1.248(5) Å), in accordance with the bidentate coordination mode of carboxyl groups but that is different from the monodentate coordination mode.[37]

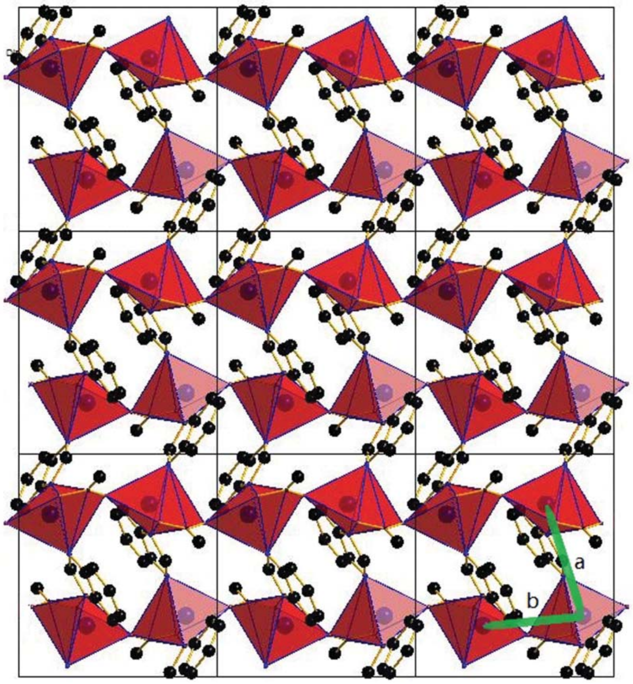

**Fig. 2.** 2-D network of **1**, all hydrogen atoms were omitted. a = 5.923 Å, b = 4.455 Å.

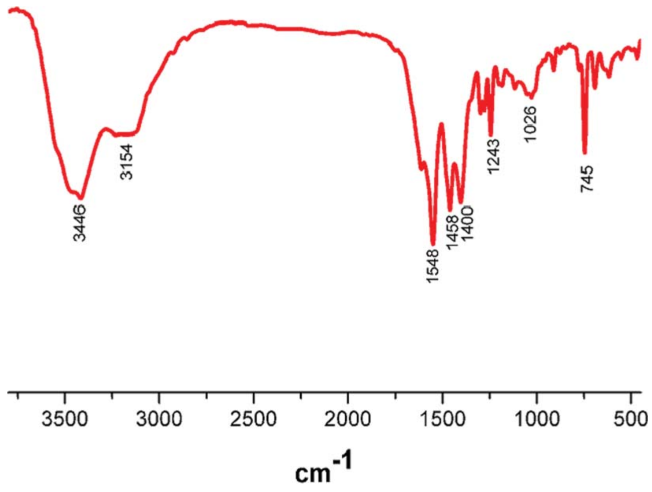

**Fig. 3.** IR spectra of **1**.

## *IR Spectrum of 1*

The IR spectral data of the compound **1** is shown in Figure 3. There are indications that broad bands in the range of 3154 cm$^{-1}$ can be assigned to weak hydrogen bond (C8–H8C···O1$^i$, 3.372 Å, symmetry code: (i) *x*, 0.5 - *y*, 0.5 + *z*). The bands of 1458 and 1400 cm$^{-1}$ are assigned to $\nu_s COO^-$ and $\nu_{as} COO^-$, respectively which indicate bidentate coordination mode.[38,39] The bands at 1243 cm$^{-1}$ may be assigned to the *ν*(C-N) stretching frequencies. The strong peak of 1548 cm$^{-1}$ for **1** may be attributed to the C = N stretching vibration of the imidazole ring of the bm ligand. The IR attribution is consistent with the crystal structure determination.

## *Luminescent Property of 1*

Coordination polymers based on d$^{10}$ metal centers and organic ligands are promising candidates for photoactive materials with potential applications.[40] In this study, luminescent property of compound **1** and the free ligand has been investigated in DMF solvent that concentrations are $4 \times 10^{-6}$ and $6 \times 10^{-5}$ mol·L$^{-1}$, respectively. As is shown in Figure 4, excitation at 280 nm leads to luminescent with emission maxima at 299 nm for free ligand, 309 nm for **1**. The similarity between emission spectra of the polymer and free ligand, excluding emission intensity, implies that the luminescent signal transduction mechanism should be ascribed to the intra-ligand *π*-*π** and *n*-*π** luminescent emission.[41] On the other hand, slight red shifts of 10 nm and

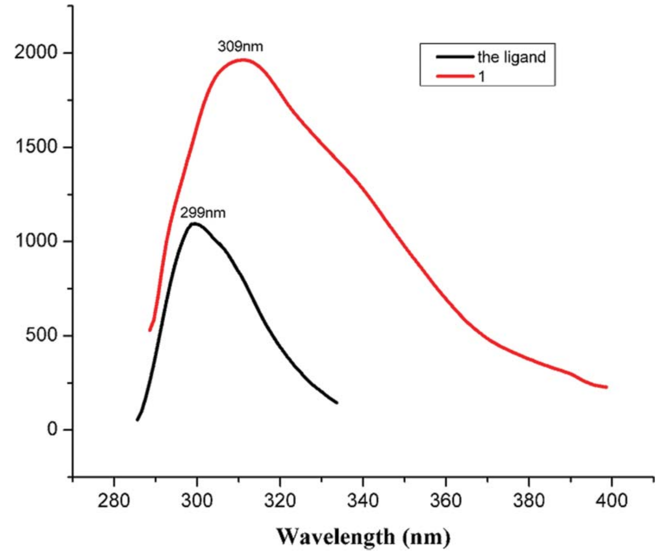

**Fig. 4.** Luminescent emission spectra of **1** and Hbm ligand at room temperature.

significant enhancement of the emission peak for **1** in contrast to the free ligand is considered to originate from metal–ligand coordination.[41,42] The result indicates that the complex **1** may be a potential candidate of luminescent materials.

## Conclusion

Using 1H-benzoimidazole (Hbm), one new zinc(II) coordination polymer has been synthesized. The compound shows a 1D chain structure though the bm ligand, which then further forms 2-D framework though the acetato ligand. The elemental analysis, IR data, and luminescent property are consistent with the X-ray analysis results. The excellent luminescent property indicates that the complex may be a potential candidate of luminescent materials.

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## Supplementary material

Crystallographic data (excluding structure factors) for the structure in this study have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 979343. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: 44 1223 336033, E-mail: deposit@ccdc.cam.ac.uk].

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