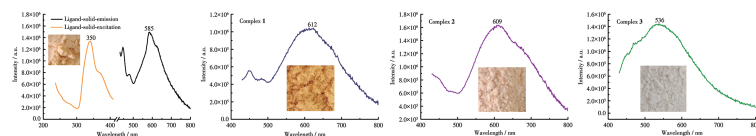


Synthesis, structure and fluorescence
analysis of three Zn(II) complexes based
on (1-methyl-1*H*-benzimidazol-2-yl)
methanol (English)

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Three Zn(II) complexes had good thermal stability, but they had different fluorescence properties. Under 350 nm excitation, complexes **1** and **2** exhibited significant redshifts. However, complex **3** formed by the dehydrogenated ligand exhibited a significant blue shift phenomenon.

基于(1-甲基-1*H*-苯并咪唑-2-基)甲醇构筑的 三个 Zn(II)配合物的合成、晶体结构和荧光分析

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摘要: (1-甲基-1*H*-苯并咪唑-2-基)甲醇(HL)分别与 $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 和 ZnCl_2 在甲醇和乙腈混合溶液中反应,生成了 3 个 Zn(II)配合物 $[\text{Zn}(\text{HL})_2\text{Cl}_2]$ (**1**)、 $[\text{Zn}(\text{HL})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ (**2**) 和 $[\text{Zn}_4(\text{L})_4\text{Cl}_4]$ (**3**)。利用元素分析、IR、热重和单晶 X 射线衍射对它们的结构进行分析,测试结果表明 **1** 和 **2** 是单核配合物,**3** 属于四核配合物。热重分析结果表明,这些配合物具有良好的热稳定性,当温度超过 180 °C 时结构才开始分解。荧光分析表明配合物 **1** 和 **2** 发生了红移现象,当配体失去质子 H 后,配合物 **3** 发生了明显的蓝移现象。配合物 **1**、**2** 和 **3** 的量子产率分别为 1.00%、0.78% 和 2.04%,荧光寿命分别为 2.306 0、2.283 6 和 3.039 9 ns。因此,可以通过使配体失去质子 H 形成多核配合物来增强荧光寿命。

关键词: 配合物; 晶体; 结构; 荧光

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Synthesis, structure and fluorescence analysis of three Zn(II) complexes based on (1-methyl-1*H*-benzimidazol-2-yl) methanol

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Abstract: The (1-methyl-1*H*-benzimidazol-2-yl) methanol (HL) reacted with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and ZnCl_2 in a mixture of methanol and acetonitrile to generate three Zn(II) complexes: $[\text{Zn}(\text{HL})_2\text{Cl}_2]$ (**1**), $[\text{Zn}(\text{HL})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ (**2**), and $[\text{Zn}_4(\text{L})_4\text{Cl}_4]$ (**3**). Their structures were analyzed by elemental analysis, IR, thermogravimetry, and single-crystal X-ray diffraction. The results show that **1** and **2** are mononuclear complexes, and **3** is a tetranuclear complex. The thermogravimetric analysis results show that these complexes had good thermal stability and the structure began to decompose when the temperature exceeded 180 °C. The fluorescence analysis shows that complexes **1** and **2** had a red shift phenomenon, and when the ligand lost proton H, complex **3** had a significant blue shift phenomenon. The quantum yields of complexes **1**, **2**, and **3** were 1.00%, 0.78%, and 2.04%, respectively. And the fluorescence lifetimes were 2.306 0, 2.283 6, and 3.039 9 ns, respectively. Therefore, it is possible to enhance the fluorescence lifetime by causing the ligand to lose proton H and form a polynuclear complex. CCDC: 2183318, **1**; 22500007, **2**; 2183319, **3**.

Keywords: complex; crystal; structure; fluorescence

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0 Introduction

In recent years, the complexes have received continuous attention and research from researchers due to their unique structures (one, two, and three-dimensional) and excellent properties^[1-5]. Thousands of transition metal complexes are successfully designed and synthesized every year. They have been extensively studied in magnetism^[6], fluorescence^[7], biological activity^[8], photocatalytic degradation and conversion^[9], adsorption^[10], and separation^[11]. Among them, the research of fluorescent materials is one of the directions^[12-15]. The fluorescent materials mainly consist of inorganic and organic fluorescent materials. The representatives of inorganic fluorescent materials are transition metal ion (Zn^{2+} , Cd^{2+} , Ag^+) luminescence and transition metal fluorescent materials^[16-19]. Their advantages are strong absorption ability, high conversion rate, narrow band emission of central ions of transition metal complexes conducive to panchromatic display, and stable physical and chemical properties. Therefore, the synthesis of novel fluorescent complexes and their commercial conversion has become a hot topic in recent research. Studies have found that the synthesis of complexes is limited by many factors, such as inorganic ions, solvents, and temperature^[20]. The selection of ligands plays a key role in the synthesis of expected complexes^[21]. Complexes are materials formed by coordination bonds between metals or metal ions and organic ligands. Based on this, abundant electron donor groups on organic ligands play an important role in the construction of complexes. The organic ligand of (1-methyl-1*H*-benzimidazol-2-yl) methanol (HL) contains N and O atoms, which can give lone pair electrons to form complexes.

In this work, the reaction of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, ZnCl_2 , and HL in a mixed solution of methanol and acetonitrile produced three Zn(II) complexes: $[\text{Zn}(\text{HL})_2\text{Cl}_2]$ (**1**), $[\text{Zn}(\text{HL})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ (**2**), and $[\text{Zn}_4(\text{L})_4\text{Cl}_4]$ (**3**). Their structures were analyzed by elemental analysis, IR, thermogravimetry, and single-crystal X-ray diffraction. The thermal stability and fluorescence properties of these complexes were also studied. The results of this study indicate that when organic ligands lose proton H and form polynuclear complexes, the fluores-

cence lifetime and quantum yield of the complexes can be improved.

1 Experimental

All solvents and chemicals were commercial reagents and used without further purification. HL, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, ZnCl_2 , triethylamine, methanol, and acetonitrile were purchased from Saen Chemical Technology (Shanghai) Co., Ltd. The elemental analyses (carbon, hydrogen, and nitrogen) were performed with a Perkin-Elmer 240 elemental analyzer. The IR spectra were measured from KBr pellets on a Nicolet 5DX FT-IR spectrometer. The thermogravimetric analysis (TGA) was performed by Perkinelmer Pyris Diamond TG-DTA. The crystal structure was determined by an Agilent SuperNOVA diffractometer. The fluorescence spectra, quantum yield, and fluorescence lifetime were gained by using FLS 1000 Photoluminescence Spectrometer (Edinburgh Instruments Ltd.). The powder X-ray diffraction (PXRD) analysis was carried out using Rigaku's D/max 2500 X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.156\ 04\ \text{nm}$). The tube voltage was 40 kV, the tube current was 150 mA, a graphite monochromator was used, and 2θ was 3° to 50° .

1.1 Synthesis of complex 1

ZnCl_2 (0.040 8 g, 3 mmol) and HL (0.048 7 g, 3 mmol) were mixed in 5 mL methanol and 5 mL acetonitrile. Next, the mixed solution was subjected to ultrasound for 5 min. The light yellow blocky crystals of **1** were obtained after 12 h of natural volatilization. Yield: 76% (based on HL). Anal. Calcd. for $\text{C}_{18}\text{H}_{20}\text{Cl}_2\text{N}_4\text{O}_2\text{Zn}$ (%): C, 46.89; H, 4.38; N, 12.16. Found(%): C, 46.91; H, 4.35; N, 12.11. IR(cm^{-1}): 3 435s, 3 134s, 1 626s, 1 501w, 1 403s, 1 226m, 1 029s, 865m, 760s, 629m.

1.2 Synthesis of complex 2

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.029 7 g, 1 mmol) and HL (0.016 2 g, 1 mmol) were mixed in 5 mL methanol and 5 mL acetonitrile. Next, the mixed solution was subjected to ultrasound for 10 min. The light yellow blocky crystals of **2** were obtained after 8 h of natural volatilization. Yield: 89% (based on HL). Anal. Calcd. for $\text{C}_{18}\text{H}_{24}\text{N}_6\text{O}_{10}\text{Zn}$ (%): C, 39.29; H, 4.37; N, 15.29. Found (%): C, 39.31; H, 4.41; N, 15.31. IR (cm^{-1}): 3 435m,

3 134s, 1 626s, 1 396s, 1 252w, 1 160w, 1 082s, 937w, 878w, 754s, 616m, 478m.

1.3 Synthesis of complex 3

The synthesis of complex **3** was similar to that of complex **1**, except that an additional 0.1 mL of triethylamine was added to the mixed solution. The colorless blocky crystals of **3** were obtained after 24 h of natural volatilization. Yield: 65% (based on HL). Anal. Calcd. for $C_{36}H_{34}Cl_4N_8O_4Zn_4$ (%): C, 41.30; H, 3.25; N, 10.71. Found(%): C, 41.32; H, 3.27; N, 10.69. IR(cm^{-1}): 3 435m, 3 134s, 1 626s, 1 495w, 1 462w, 1 396s, 1 252w, 1 160w, 1 082s, 937w, 878w, 754s, 616m, 478m.

1.4 Single-crystal X-ray diffraction analysis

Diffraction data for complexes **1**, **2**, and **3** were collected on a Bruker SMART CCD diffractometer (Mo $K\alpha$ radiation and $\lambda=0.071\ 073\ nm$) in Φ and ω scan

modes. The anisotropic displacement parameters were applied to all non-hydrogen atoms in full-matrix least-squares refinements based on F^2 , which were performed by SHELXL-2013. The structure was solved by direct methods and refined using the Olex2 program^[22]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. Crystallographic crystal data and structure processing parameters for complexes **1**, **2**, and **3** are summarized in Table 1. Selected bond lengths and bond angles for complexes **1**, **2**, and **3** are listed in Table 2. Hydrogen bonds for complexes **1**, and **2** are listed in Table 3.

CCDC: 2183318, **1**; 22500007, **2**; 2183319, **3**.

Table 1 Crystal data and structure parameters for complexes **1**, **2**, and **3**

Parameter	1	2	3
Empirical formula	$C_{18}H_{20}Cl_2N_4O_2Zn$	$C_{18}H_{24}N_6O_{10}Zn$	$C_{36}H_{36}Cl_4N_8O_4Zn_4$
Formula weight	460.65	549.80	1 048.01
Temperature / K	293(2)	293(2)	293(2)
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a / nm	0.827 26(11)	1.460 7(2)	1.144 27(6)
b / nm	0.845 00(12)	1.033 5(2)	1.176 76(8)
c / nm	1.419 93(18)	1.613 6(3)	1.884 28(12)
α / ($^\circ$)	79.283(11)		72.927(6)
β / ($^\circ$)	88.432(11)	109.448(18)	73.969(5)
γ / ($^\circ$)	86.764(11)		72.463(5)
Volume / nm ³	0.973 6(2)	2.296 9(8)	2.263 1(3)
Z	2	4	2
D_c / (g·cm ⁻³)	1.571	1.590	1.538
μ / mm ⁻¹	1.557	1.136	2.375
$F(000)$	472	1 136	1 056
Crystal size / mm	0.13×0.12×0.11	0.13×0.11×0.1	0.12×0.1×0.08
2θ range / ($^\circ$)	4.912-59.032	4.602-58.952	2.2-28.1
Index ranges	$-7 \leq h \leq 10$, $-11 \leq k \leq 10$, $-19 \leq l \leq 18$	$-18 \leq h \leq 13$, $-13 \leq k \leq 12$, $-21 \leq l \leq 21$	$-15 \leq h \leq 13$, $-15 \leq k \leq 15$, $-23 \leq l \leq 22$
Reflection collected	7 471	11 349	19 302
Independent reflection	4 511	5 489	10 615
R_{int}	0.049 1	0.053 3	0.033 0
R_σ	0.089 7	0.095 6	0.069 4
Data, restraint, parameter	4 511, 0, 248	5 489, 6, 334	10 615, 0, 525
R indices [$I \geq 2\sigma(I)$]	$R_1=0.070\ 5$, $wR_2=0.186\ 6$	$R_1=0.086\ 0$, $wR_2=0.222\ 2$	$R_1=0.043\ 3$, $wR_2=0.088\ 2$

Continued Table 1

Parameter	1	2	3
Final R indexes (all data)	$R_1=0.095\ 8$, $wR_2=0.208\ 9$	$R_1=0.170\ 4$, $wR_2=0.268\ 8$	$R_1=0.067\ 4$, $wR_2=0.099\ 0$
$(\Delta\rho)_{\max}$, $(\Delta\rho)_{\min}$ / ($\text{e}\cdot\text{nm}^{-3}$)	1 530, -1 210	540, -780	470, -430

Table 2 Selected bond lengths (nm) and bond angles ($^\circ$) for complexes 1, 2, and 3

1					
Zn1—Cl1	0.225 94(13)	Zn1—N1	0.202 9(4)	Zn1—N3	0.203 1(4)
Zn1—Cl2	0.224 82(14)				
Cl2—Zn1—Cl1	107.28(5)	N1—Zn1—N3	111.02(15)	N3—Zn1—Cl2	107.61(12)
N1—Zn1—Cl1	111.33(12)	N3—Zn1—Cl1	107.89(12)	N1—Zn1—Cl2	111.52(12)
2					
Zn1—O3	0.208 4(4)	Zn1—O2	0.234 7(5)	Zn1—O1	0.203 1(5)
Zn1—O4	0.208 5(5)	Zn1—N1	0.230 8(5)	Zn1—N3	0.200 7(5)
O3—Zn1—O4	86.55(19)	N1—Zn1—O3	96.64(19)	N3—Zn1—O4	100.6(2)
O3—Zn1—O1	91.75(19)	N1—Zn1—O4	103.4(2)	N3—Zn1—O1	80.82(18)
O3—Zn1—O2	169.26(18)	N1—Zn1—O1	75.7(2)	N3—Zn1—O2	75.57(19)
O4—Zn1—O1	177.99(17)	N1—Zn1—O2	90.36(19)	N3—Zn1—N1	150.7(2)
O4—Zn1—O2	83.91(19)	N3—Zn1—O3	101.5(2)	O2—Zn1—O1	97.87(19)
3					
Zn1—Cl1	0.228 63(10)	Zn4—O1	0.198 8(2)	Zn2—O1	0.195 0(2)
Zn1—O4	0.196 4(2)	Zn4—O2	0.195 3(2)	Zn2—N3	0.201 2(3)
Zn1—O3	0.199 0(2)	Zn4—N7	0.199 6(2)	Zn3—Cl3	0.224 49(9)
Zn1—N1	0.200 3(3)	Zn2—Cl2	0.225 93(8)	Zn3—O3	0.194 8(2)
Zn4—Cl4	0.226 42(10)	Zn2—O4	0.197 3(2)	Zn3—O2	0.198 3(2)
Zn3—N5	0.200 7(3)				
O4—Zn1—Cl1	105.93(8)	O2—Zn4—Cl4	104.84(8)	O1—Zn2—N3	126.36(11)
O4—Zn1—O3	91.16(9)	O2—Zn4—O1	91.47(9)	N3—Zn2—Cl2	108.85(8)
O4—Zn1—N1	129.13(10)	O2—Zn4—N7	130.23(10)	O3—Zn3—Cl3	107.66(6)
O3—Zn1—Cl1	100.97(7)	N7—Zn4—Cl4	113.75(9)	O3—Zn3—O2	88.70(9)
O3—Zn1—N1	110.62(10)	O4—Zn2—Cl2	108.03(7)	O3—Zn3—N5	129.82(11)
N1—Zn1—Cl1	113.56(8)	O4—Zn2—N3	114.99(10)	O2—Zn3—Cl3	110.45(7)
O1—Zn4—Cl4	102.89(7)	O1—Zn2—Cl2	107.58(6)	O2—Zn3—N5	105.69(10)
O1—Zn4—N7	108.48(10)	O1—Zn2—O4	88.79(9)	N5—Zn3—Cl3	111.22(8)

Table 3 Hydrogen bond parameters for complexes 1 and 2

D—H $\cdots$ A	$d(\text{D—H})$ / nm	$d(\text{H}\cdots\text{A})$ / nm	$d(\text{D}\cdots\text{A})$ / nm	$\angle\text{D—H}\cdots\text{A}$ / ($^\circ$)
1				
O1—H1 $\cdots$ O2	0.082	0.195	0.276 2(5)	168
2				
O3—H3A $\cdots$ O7	0.090	0.193	0.278 9(7)	161
O3—H3B $\cdots$ O6A	0.090	0.183	0.271 4(7)	168
O4—H4A $\cdots$ O10B	0.085	0.203	0.287 3(7)	170
O2—H2 $\cdots$ O8B	0.086(1)	0.186(2)	0.269 6(11)	164(5)

Symmetry codes: A: $-x+1/2$, $y-1/2$, $-z+1/2$; B: $-x+3/2$, $y+1/2$, $-z+1/2$.

2 Results and discussion

2.1 Structure of complexes 1, 2, and 3

X-ray single-crystal diffraction analysis reveals that the molecular structure (Fig. 1) of complex **1** is mainly composed of one Zn(II) ion, two HL molecules, and two Cl[−] anions. The Zn(II) in **1** is coordinated with two N atoms (N1 and N3 are from two HL molecules, respectively) and two Cl[−] anions, respectively. So, the Zn(II) in **1** is tetra-coordinated. For complex **1**, the distances of Zn1—Cl1 and Zn1—Cl2 are 0.225 94(13) and 0.224 82(14) nm, respectively. The distances of Zn1—N1 and Zn1—N3 are 0.202 9(4) and 0.203 1(4) nm, respectively. The bond angles of Cl2—Zn1—Cl1 and N1—Zn1—N3 are 107.28(5)° and 111.02(15)°, respectively. These bond lengths and bond angles are within the range reported in the literature^[23-25]. In addition, there is an intramolecular hydrogen bond of O1—H1···O2 in complex **1**.

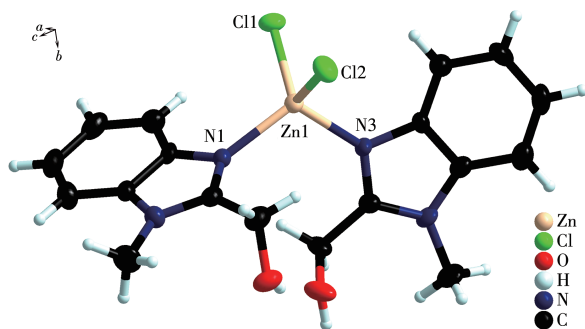


Fig.1 Molecular structure of **1** with thermal ellipsoids at 50% level

The molecular structure (Fig. 2a) of complex **2** shows that it is a material composed of $[\text{Zn}(\text{HL})_2(\text{H}_2\text{O})_2]^{2+}$ cation and NO_3^- anion. It is composed of a Zn(II) ion, two HL molecules, two coordinated water molecules, and two NO_3^- anions. The Zn(II) in **2** is coordinated with two N atoms (N1 and N3 are from two HL molecules, respectively) and four oxygen atoms (O1 and O2 are from two HL molecules; O3 and O4 are from two coordinated water molecules), respectively. Therefore, the Zn(II) in complex **2** is six-coordinated. For complex **2**, the distances of Zn1—N1 and Zn1—N3 are 0.230 8(5) and 0.200 7(5) nm, respectively. The Zn—O distances fall in a range of 0.208 4(4)–0.234 7(5) nm (Zn1—O3 0.208 4(4) nm, Zn1—O2 0.234 7(5) nm, Zn1—O1

0.203 1(5) nm, Zn1—O4 0.208 5(5) nm). The bond angles of N1—Zn1—O1 and O4—Zn1—O1 are 75.7(2)° and 177.99(17)°, respectively. These bond lengths and bond angles are within the range reported in the literature^[23-25]. Due to the hexagonal coordination of Zn(II) in **2**, the NO_3^- with a larger spatial structure can only exist in the form of anions. In addition, due to the presence of two coordinated water molecules in **2**, there are not only intramolecular hydrogen bonds (Fig. 2b), but also intermolecular hydrogen bonds (Fig. 2c). The specific information of these intramolecular hydrogen bonds is listed in Table 3, which includes O3—H3A···O7, O3—H3B···O6A, O4—H4A···O10B, and O2—H2···O8B. The NO_3^- forms hydrogen bonds (Fig. 2c) with water molecules in two adjacent complex **2**, respectively. Therefore, complex **2** forms a 2D structure (Fig. 2d) through these intermolecular hydrogen bonds.

The molecular structure (Fig. 3) of complex **3** shows that it is mainly composed of four Zn(II) ions, four L[−] ions, and four Cl[−] anions. The Zn(II) ions in complex **3** coordinate with three L[−] ions and one Cl[−] ion, respectively. So, the coordination number of Zn(II) ions in complex **3** is four. Due to the similarity in the coordination environment of the four Zn(II) ions in complex **3**, the coordination environment of Zn1 will be discussed here. The Zn1 in complex **3** coordinates with two O atoms (O3 and O4), one N atom (N1), and one Cl[−] anion (Cl1), respectively. The N1, O3, and O4 atoms all come from three different L[−] ions. The distances of Zn1—O3, Zn1—O4, Zn1—N1 and Zn1—Cl1 are 0.199 0(2), 0.196 4(2), 0.200 3(3), and 0.228 63(10) nm, respectively. In the coordination environment of Zn1, the minimum and maximum bond angles are 91.16(9)° (O4—Zn1—O3) and 129.13 (10)° (O4—Zn1—N1). The length of these bond lengths and bond angles are similar to those reported in the literature^[23-25]. It is worth noting that in complex **3**, the hydroxyl groups in HL have lost proton H, which causes O to take the form of $\mu_2-\eta^1:\eta^1$ coordinates with two adjacent Zn(II) ions. In addition, in complex **3** the N atom in L[−] is coordinated with another Zn(II) ion. Therefore, the L[−] in complex **3** takes the form of $\mu_3-\eta^1:\eta^1:\eta^1$ to coordinate with three

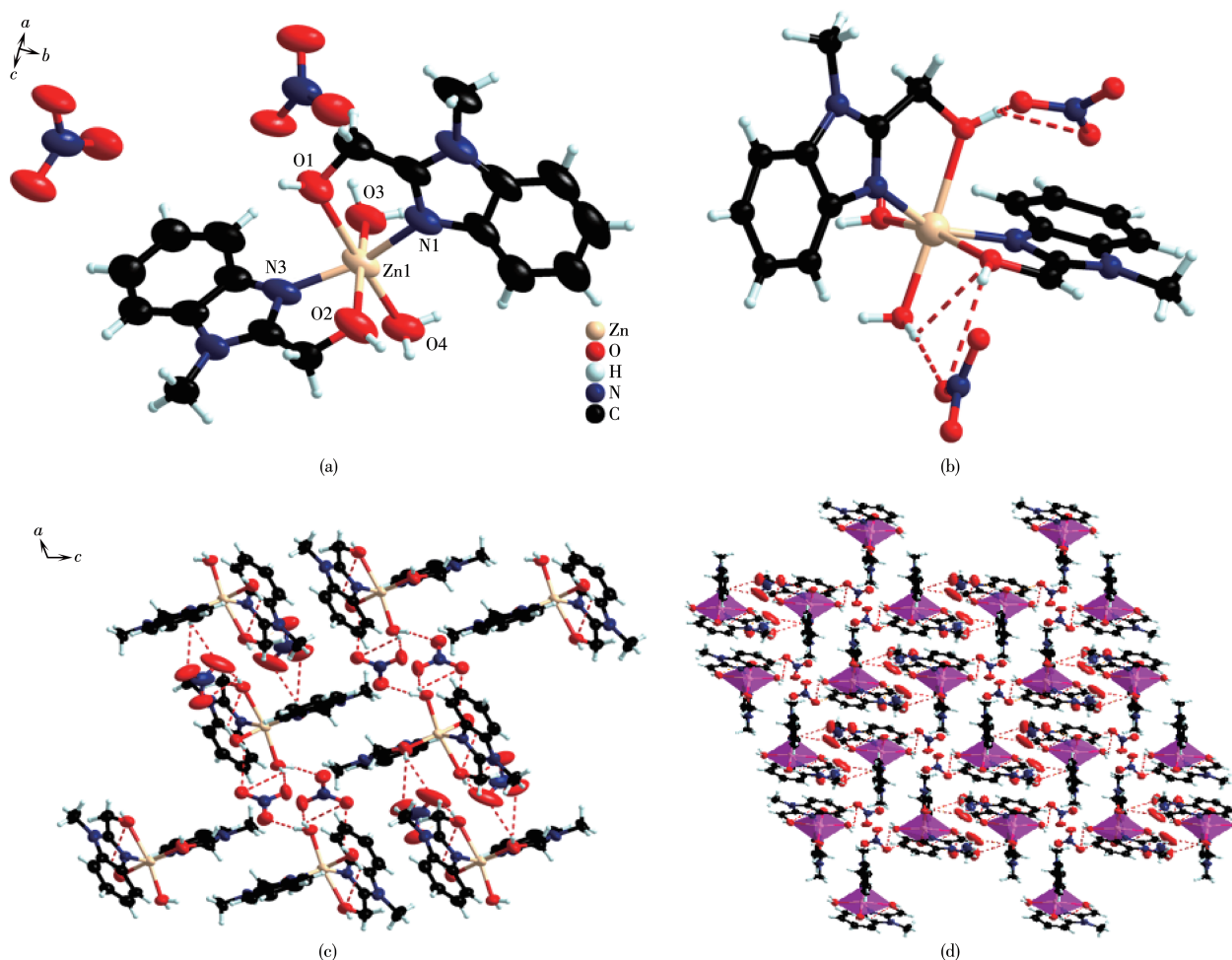


Fig.2 (a) Molecule structure of complex **2** with thermal ellipsoids at 50% level; (b) Intramolecular hydrogen bonds in **2**; (c) Intermolecular hydrogen bonds in **2**; (d) 2D structure formed by hydrogen bonds

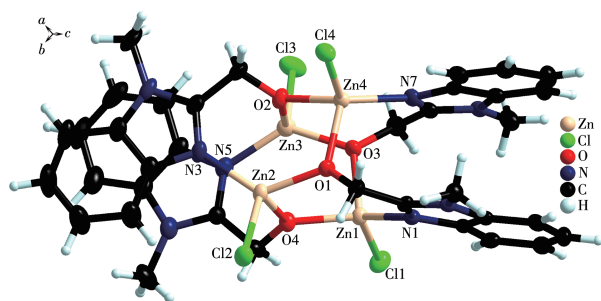


Fig.3 Molecule structure of **3** with thermal ellipsoids at 50% level

different Zn(II) ions.

2.2 PXRD analysis

To check the purity of complexes **1**, **2**, and **3**, the PXRD of the as-synthesized sample was measured at room temperature. The test results (Fig. 4) show that complex **1**, **2**, and **3** exhibited strong diffraction peaks, which were consistent with the theoretical simulation.

The results indicate the good purity of complexes **1**, **2**, and **3** (Fig. 4).

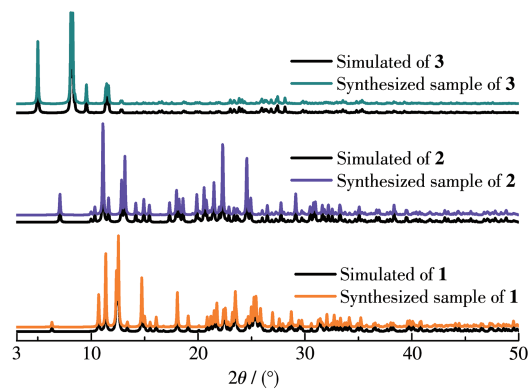


Fig.4 PXRD patterns of complexes **1**, **2**, and **3**

2.3 TGA of complexes 1, 2, and 3

The thermal stability of complexes **1** and **3** was tested in a range of 30–800 $^\circ\text{C}$ under a nitrogen atmosphere at a heating rate of 5 $^\circ\text{C} \cdot \text{min}^{-1}$ for Pyris Dai-

mond TG-DTG Analyzer. However, complex **2** was tested in an air atmosphere. The TGA curves (Fig. 5) of complexes **1**, **2**, and **3** showed that they all had good thermal stability. For complex **1**, in a range of 30–231 °C, the structure of **1** was still very stable. When the temperature exceeded 231 °C, the organic ligand in **1** slowly began to decompose, leaving about 31.7% ZnO. The TGA curve of **2** showed that it could maintain the molecular structure unchanged in a range of 30–114 °C. Complex **2** first lost two coordinated water molecules (Obsd. 5.16%, Calcd. 6.57%) in a range of

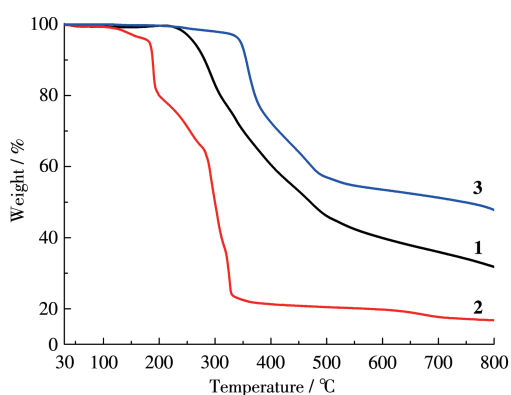


Fig.5 TGA curves of complexes **1**, **2**, and **3**

114–180 °C; further weight loss in a range of 181–280 °C is responsible for all organic components (Obsd. 59.23%, Calcd. 59.22%), with the continuous division of the NO_3^- anion; the last remaining amount of 16.51% might be ZnO (Calcd. 14.87%). For complex **3**, the structure remained unchanged within a range of 30–341 °C. When the heating temperature exceeded 341 °C, the organic ligands in **3** began to decompose, leaving about 47.48% ZnO.

2.4 Fluorescence analysis

Single-crystal X-ray diffraction has shown that the central ions in the structures of complexes **1**, **2**, and **3** are all Zn(II). Their extranuclear electron arrangement is $3d^{10}$. Therefore, it is theoretically known^[26] that complexes **1**, **2**, and **3** should have good fluorescence properties. The fluorescence emission spectra of the ligand and the complex were measured at room temperature (Fig. 6). The results showed that HL was excited by ultraviolet light at 350 nm, and it had a strong emission peak at 585 nm (Fig. 6a). Complexes **1**, **2**, and **3** were also excited using ultraviolet light at 350 nm. The results showed that complexes **1**, **2**, and **3** exhibited

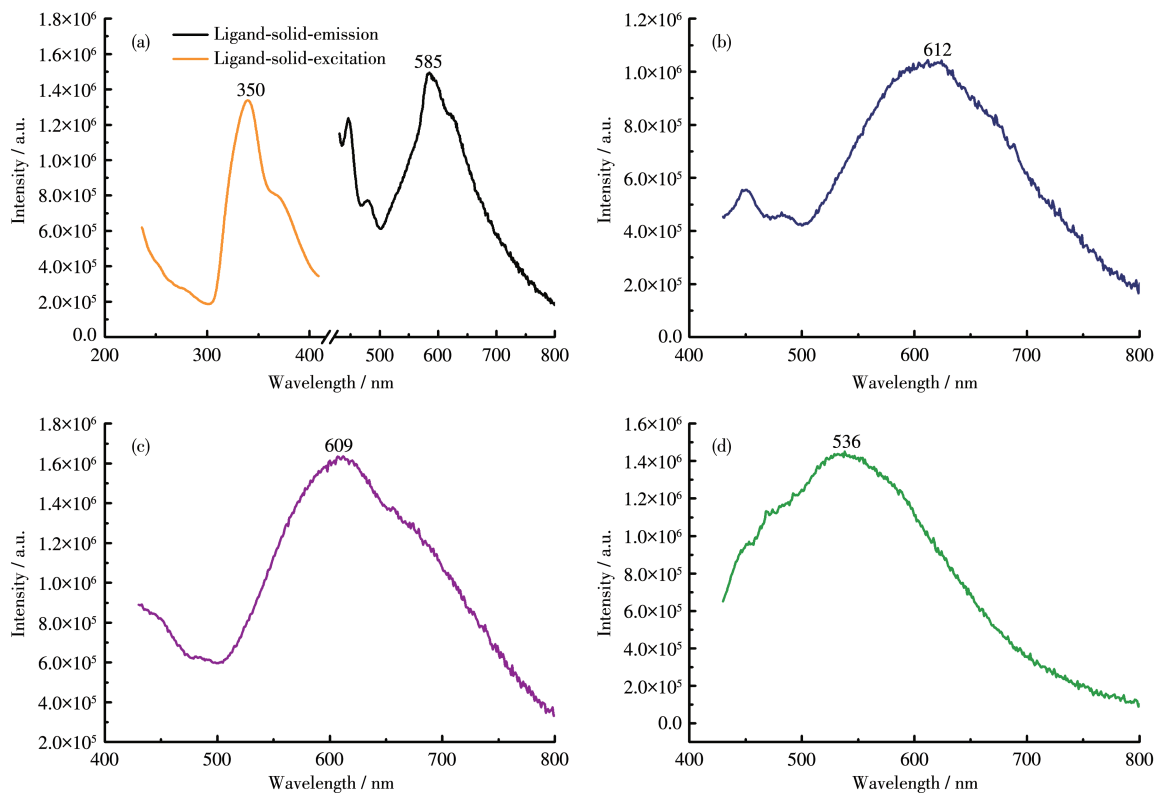


Fig.6 Fluorescence spectra of HL (a), **1** (b), **2** (c), and **3** (d)

strong emission peaks at 612 nm (Fig. 6b), 609 nm (Fig. 6c), and 536 nm (Fig. 6d), respectively. It can be seen that complexes **1** and **2** exhibited significant redshifts of 27 and 24 nm, respectively. This may be caused by intramolecular charge transfer in HL. However, complex **3** exhibited a significant blue shift of 49 nm. This may be caused by the transfer of electrons from ligand (L) to metal. Under the same test conditions, the fluorescence intensity of these complexes was significantly higher than that of HL. The reason may be that the coordination of Zn(II) with HL (or L⁻) can enhance the molecular rigidity of the entire system, reducing the energy consumed by non-radiative transi-

tions. Using 350 nm ultraviolet light to excite the complexes, the quantum yields of complexes **1**, **2**, and **3** were 1.00%, 0.78%, and 2.04%, respectively. Under the same excitation conditions, the fluorescence lifetimes (Fig. 7) of complexes **1**, **2**, and **3** were 2.3060, 2.283 6, and 3.039 9 ns, respectively. It can be seen that the fluorescence lifetime of complex **3** was longer than those of complexes **1** and **2**. This may be because when HL loses proton H, the coordination ability and number of O atoms in L⁻ with Zn(II) are enhanced and increased^[27]. This makes the effect of ligand-to-metal charge transition (LMCT) more obvious, improving the fluorescence lifetime and quantum yield of the complex.

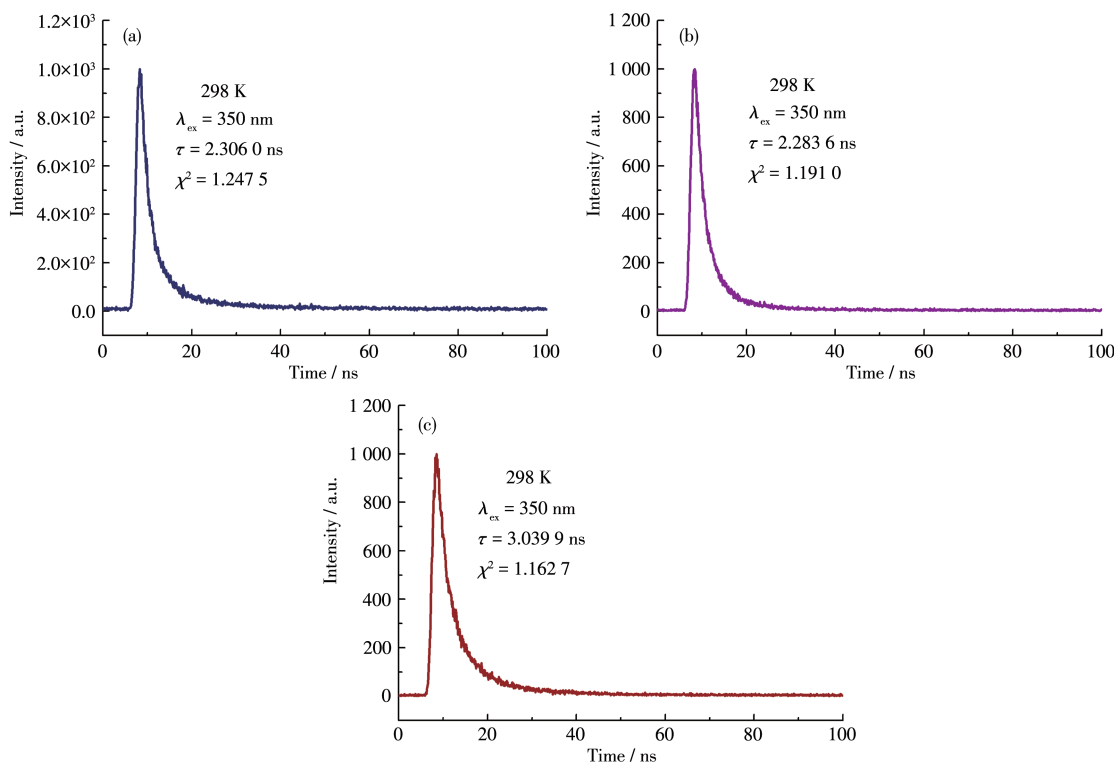


Fig. 7 Fluorescence lifetimes of **1** (a), **2** (b), and **3** (c)

3 Conclusions

In summary, three zinc complexes [Zn(HL)₂Cl₂] (**1**), [Zn(HL)₂(H₂O)₂] (NO₃)₂ (**2**), and [Zn₄(L)₄Cl₄] (**3**), which based on (1-methyl-1*H*-benzimidazol-2-yl) methanol (HL), had been synthesized and characterized by elemental analysis and single-crystal X-ray diffraction analysis. The results show that **1** and **2** are mononuclear complexes, and **3** is a tetranuclear complex. The TGA results showed that these complexes had good

thermal stability and began to decompose when the temperature exceeded 180 °C. The fluorescence analysis showed that complexes **1** and **2** had a significant redshift, while complex **3** had a significant blue shift. This may be because when HL loses proton H, the coordination ability and number of O atoms in L⁻ with Zn(II) are enhanced and increased. This contributes to the occurrence of LMCT and enhances the quantum yield and fluorescence lifetime of the complex.

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