

基于 8-羟基喹啉与 d^{10} 金属原位合成的双核配合物的合成、晶体结构及其光致发光性质

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摘要: 利用 8-羟基喹啉原位反应, 通过溶剂热方法制备出 3 种新颖的 d^{10} 配合物 $[M_2(HL)_3]NO_3 \cdot H_2O$ ($M = Cd$ (**1**), Zn (**2**, **3**)), H_2L 为 1,1-(7,7'-二-(8-羟基喹啉))。单晶结构表明, 3 种配合物有着相同的带正电荷的结构单元 $[M_2(HL)_3]^+$, 但由于客体分子所处空间位置的不同表现为不同的空间结构, 配合物 **1** 和 **3** 结晶于六方晶系($P6_3/m$), 配合物 **2** 结晶于三方晶系($R\bar{3}$)。中心金属离子以六配位的模式与来自 HL^- 配体上的 3 个氧原子和 3 个氮原子形成一个轻微扭曲的八面体几何构型。存在于 HL^- 配体与客体分子(NO_3^- , H_2O)间大量的弱作用力在结构空间堆积上起到了重要的作用。3 种配合物均具有良好的热稳定性和绿色荧光发射性质。同时, 通过从配合物 **1** 中提取出原位生成的配体 H_2L , 首次报道了其蓝色荧光发射性质。

关键词: d^{10} 配合物; 原位反应; 晶体结构; 弱作用; 荧光性质

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Syntheses, Crystal Structures and Luminescent Properties of Dinuclear d^{10} Complexes Based on a Ligand Formed *in Situ* by 8-Hydroxyquinoline

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Abstract: Three novel d^{10} complexes $[M_2(HL)_3]NO_3 \cdot H_2O$ ($M = Cd$ (**1**), Zn (**2**, **3**), $H_2L = 7,7'$ -(ethane-1,1-diyl)diquinolin-8-ol) have been synthesized under solvothermal conditions. Single crystal X-ray diffraction analysis reveals that the complexes have the same coordination positive charged unit, $[M_2(HL)_3]^+$, but different lattice structures due to the different places of the guest molecules. Complexes **1** and **3** crystallize in hexagonal system ($P6_3/m$) and complex **2** crystallizes in trigonal system ($R\bar{3}$). The metal ions are six-coordinated with three oxygen atoms and three nitrogen atoms of three HL^- ligands, presenting a slightly distorted octahedron geometry. There are abundant weak interactions between HL^- ligands and guest molecule (NO_3^- and H_2O), which play a vital role in the form of the crystal packing. These complexes show good thermal stabilities and exhibit green fluorescence. Further, the fluorescence of ligand H_2L extracted from the complex **1** has also been studied firstly and blue light emission of it was observed. CCDC: 1842916, **1**; 1842917, **2**; 1842918, **3**.

Keywords: d^{10} complexes; *in situ* reaction; crystal structures; weak interaction; luminescent properties

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In situ ligand synthesis involved in the research of coordination complexes is a special method to design and synthesis of intriguing organic ligands and coordinated structures with good potential applications, such as magnetism, luminescence and gas sorption^[1-4]. In recent years, a large number of *in situ* synthetic ligands have been discovered such as 5-substituted 1*H*-tetrazoles, [2+2] cycloaddition, [3+3] cycloaddition^[5-9]. Among such enormous cases, the *in situ* reaction for 8-hydroxyquinoline, which has been few reported yet^[10-12], gave out an excellent ligand, 7,7'-(ethane-1,1-diyl)diquinolin-8-ol) (H_2L), with rich binding sites and transformable dihedral angle for two quinoline rings. Up to now, the *in situ* synthetic ligands H_2L have mostly emerged in the structures involving heterometallic multinuclear units, such as transition metal ions (3*d*)-lanthanide ions (4*f*)^[11], alkaline metal ions (3*s*)-3*d*^[13]. Because of the flexibility and symmetry of the quinoline rings which like a pair of oar in H_2L ligand, homometallic multinuclear units could be constructed. Recently, we have reported a green *in situ* synthetic method for this H_2L ligand in a homometallic dinuclear Zn(II) complex^[14], which structure are documented at the same time^[12].

The research on the influence factor in constructing coordination structures is one of the most attractive areas throughout the development of chemistry. The guest molecules including solvents molecules and/or counter ions could affect dramatically the lattice structures^[15-16]. Furthermore, plenty of noncovalent interactions such as hydrogen bonds and/or π - π stacking between H_2L ligands could make coordination complexes stable and diverse spatial structures, which is worth to explore the relationship between structures and properties^[17-18].

Herein, we report three novel d^{10} zinc and cadmium coordination complexes based on H_2L ligand formed by 8-hydroxyquinoline *in situ*, $[M_2(HL)_3]NO_3 \cdot H_2O$ ($M=Cd$ (**1**), Zn (**2**, **3**)). Complexes **1~3** contain trilobed wheel-like positive charged dinuclear units $[M_2(HL)_3]^+$ which are rare in the structure of complexes^[19-21], composed of three partial deprotonated HL^- ligands and two metal ions. Meanwhile, it is interesting that the guest molecules, one NO_3^- counterion

and one free water molecule, are crystallized in different places for the complexes and make the lattice structures different through different noncovalent interactions. It is intriguing for us to explore the influence between space structure and properties. Further, the thermal stabilities and the luminescent properties of complexes and the *in situ* synthetic ligands have been studied. The fluorescence of complex **1~3** show green emission, which are obviously bathochromic shift comparing to that of organic ligands H_2L which are firstly extracted from complexes.

1 Experimental

1.1 Materials and physical measurements

All reagents and solvents were commercially available and used as received without further purification. Power X-ray diffraction (PXRD) data for microcrystalline samples of **1~3** were recorded at 293 K on a Bruker D8 Advance X-ray powder diffractometer with $Cu K\alpha$ radiation ($\lambda=0.154\ 184\ nm$) at 40 kV and 40 mA. The scans were run from 5° to 50° . Simulated PXRD patterns of **1~3** were generated by Mercury software. Infrared spectra were recorded in KBr tablets in the range of $4\ 000\sim400\ cm^{-1}$ on a Nicolet FT-IR-170SX spectrophotometer. Thermogravimetric analysis (TGA) was performed on a NETZSCH TG209F3 thermogravimetric analyzer at a heating rate of $10\ ^\circ C \cdot min^{-1}$ in N_2 atmosphere. The emission and excitation spectra of solid samples of **1~3** were measured on a Hitachi F-4600 Spectrophotometer at room temperature with a xenon arc lamp as the light source.

1.2 Syntheses of the complexes **1~3** and ligand

1.2.1 Synthesis of $[Cd_2(HL)_3]NO_3 \cdot H_2O$ (**1**)

Complex **1** was successfully synthesized by solvothermal reaction. A mixture of $Cd(NO_3)_2 \cdot 6H_2O$ (151.7 mg, 0.5 mmol), 8-hydroxyquinoline (72.5 mg, 0.5 mmol) and $0.25\ mol \cdot L^{-1}$ NaOH (1 mL) in C_2H_5OH/H_2O (4 and 8 mL, respectively) solution was heated in a stainless-steel reactor with a Teflon liner (23 mL) at $160\ ^\circ C$ for 72 h and cooled to ambient temperature for 48 h. Brown polyhedral crystals were obtained in 62.8% yield based on 8-hydroxyquinoline ligand. Elemental analysis Calcd. for $C_{60}H_{47}N_7O_{10}Cd_2(\%)$: C, 57.61; H, 3.79; N, 7.84. Found(%): C, 57.31; H, 3.80; N, 7.23.

1.2.2 Synthesis of $[Zn_2(HL)_3]NO_3 \cdot H_2O$ (**2**)

Complex **2** was obtained by a similar method as described for **1** using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (152.5 mg, 0.5 mmol) in place of $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and without NaOH in the system. Yellow block crystals were obtained in 58.9% yield based on 8-hydroxyquinoline ligand. Elemental analysis Calcd. for $\text{C}_{60}\text{H}_{47}\text{N}_7\text{O}_{10}\text{Zn}_2$ (%): C, 62.29; H, 4.10; N, 8.48. Found(%): C, 62.38; H, 4.21; N, 8.27.

1.2.3 Synthesis of $[\text{Zn}_2(\text{HL})_3]\text{NO}_3 \cdot \text{H}_2\text{O}$ (**3**)

Complex **3** was synthesized by a mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (151.5 mg, 0.5 mmol), 8-hydroxyquinoline (73.5 mg, 0.5 mmol) in $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ (8 and 2 mL, respectively) solution was heated in a stainless-steel reactor with a Teflon liner (23 mL) at 120 °C for 72 h and cooled to ambient temperature for 18 h. Yellow block crystals were obtained in 49% yield based on 8-hydroxyquinoline ligand. Elemental analysis Calcd. for $\text{C}_{60}\text{H}_{47}\text{N}_7\text{O}_{10}\text{Zn}_2$ (%): C, 62.29; H, 4.10; N, 8.48. Found(%): C, 62.22; H, 4.16; N, 8.34.

1.2.4 H_2L ligand extraction

H_2L ligand has been extracted by dissolving the crystals of complex **1** (12.6 mg) in 15 mL CH_2Cl_2 , and gradually add Na_2S aqueous solution. After centrifugation and filtration. The mother liquid was moved to a

clean small beaker, with the volatilization of solvent, the brownish yellow precipitate was collected, (7.3 mg, Yield: 76.1%). The FT-IR spectra, ^1H NMR, and mass spectra of ligand H_2L are shown in Fig.S4~S6.

1.3 X-ray crystallography

The single-crystal diffraction data of complexes **1~3** were collected on Oxford Diffraction Xcalibur Nova with Cu $K\alpha$ radiation ($\lambda=0.154\ 184\ \text{nm}$) at 150(2) K. The absorption corrections were applied by SADABS^[22]. The structure were solved by direct method, and all non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques using SHELXTL^[23]. Hydrogen atoms connected to carbon atoms were idealized positions and riding model was used for their refinement. Further details of the crystal data and structure refinements for complexes **1~3** are summarized in Table 1. The bond lengths, angles and Hydrogen bonds are represented in Table S1 and S2, respectively. The presence of $-\text{CH}-\text{CH}_3$ in H_2L ligand have been confirmed by single crystal X-ray diffraction data and FT-IR spectra analysis (Fig.S3) with the characteristic peaking at $2\ 972\ \text{cm}^{-1}$ (ν_{as}), $2\ 929\ \text{cm}^{-1}$ (ν_{s}), $2\ 893\ \text{cm}^{-1}$ (ν) and $1\ 247\ \text{cm}^{-1}$ (δ_{s}).

CCDC: 1842916, **1**; 1842917, **2**; 1842918, **3**.

Table 1 Crystal data and structure refinements for **1~3**

	1	2	3
Empirical formula	$\text{Cd}_2\text{C}_{60}\text{H}_{47}\text{N}_7\text{O}_{10}$	$\text{Zn}_2\text{C}_{60}\text{H}_{47}\text{N}_7\text{O}_{10}$	$\text{Zn}_2\text{C}_{60}\text{H}_{47}\text{N}_7\text{O}_{10}$
Formula weight	1 250.84	1 156.78	1 156.78
Crystal system	Hexagonal	Trigonal	Hexagonal
Space group	$P6_3/m$	$R\bar{3}$	$P6_3/m$
a / nm	1.438 69(3)	1.529 01(2)	1.413 26(2)
b / nm	1.438 69(3)	1.529 01(2)	1.413 26(2)
c / nm	1.500 57(5)	3.898 94(6)	1.487 18(3)
V / nm^3	2.689 81(14)	7.894 0(2)	2.572 40(9)
Z	2	6	2
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.544	1.460	1.493
μ / mm^{-1}	6.891	1.692	1.730
Reflection collected	5 234	6 390	5 147
Independent reflection	1 618($R_{\text{int}}=0.038\ 2$)	3 347($R_{\text{int}}=0.017\ 2$)	1 547($R_{\text{int}}=0.031\ 6$)
S	1.079	1.048	1.107
$R_1^a, wR_2^b [I>2\sigma(I)]$	0.028 6, 0.076 4	0.040 5, 0.109 6	0.031 2, 0.082 3
R_1^a, wR_2^b (all data)	0.030 7, 0.078 1	0.042 5, 0.111 5	0.033 1, 0.083 8

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

2 Results and discussion

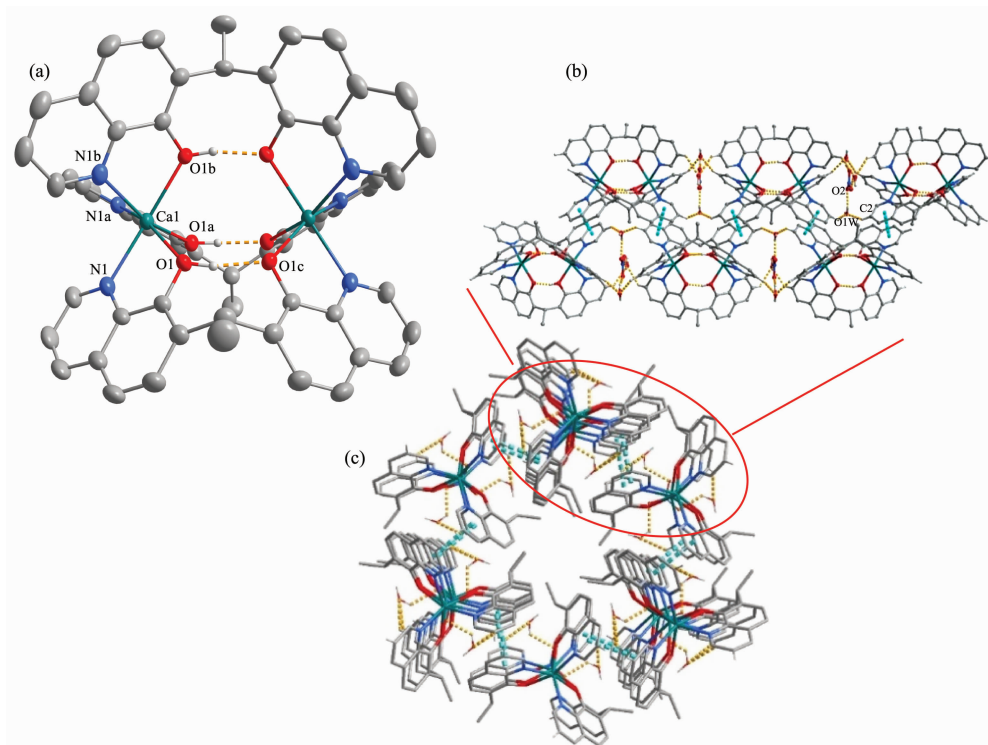
2.1 Synthesis

As mentioned above, synthesis is the heart of chemistry. The development of green synthetic methods is of great benefit to the environment and chemistry. While building the complexes, we found that NaN_3 , a toxic substance for living beings used in the previous literatures, was not necessary in the *in situ* synthesis of 8-hydroxyquinoline and can be replaced by other bases, such as NaOH , Na_2CO_3 and NaHCO_3 , even without any additional base. However, the environment of *in situ* synthesis should not be acid because no crystals could be obtained when tiny Lewis acids are mixed in the system. Furthermore, for zinc complexes, different temperatures could affect the crystallization of structures. To improve the product yields of complex **3**, different ratio for the ethanol and H_2O are explored and show that the volume ratio of ethanol/ H_2O , equal to 8:2, is the best ratio. For cadmium complex, higher temperatures could improve the

yields, and unfortunately could not play a part in the formation of another structure which has not been obtained yet even. This moderate *in situ* reaction conditions give suggestive and significant ways to explore greener synthetic methods.

2.2 Structural description

Single-crystal structure analysis reveals that the structures of complex **1** and **3** crystallize in the same space group $P6_3/m$, and the 6_3 screw axis is along c axis. Therefore, we just describe the structure of complex **1** in detail. The asymmetric unit of **1** consists of one third of crystallographic independent Cd^{2+} cation, half of a HL^- ligand, one-sixth of lattice water molecule and NO_3^- . As shown in Fig.1a, Cd^{2+} ion is surrounded by three oxygen atoms and three nitrogen atoms from 8-quinolinol units of HL^- ligands in a distort octahedral geometry. Two Cd^{2+} cations are connected by three HL^- ligands to form a trilobed wheel-like positive charged cadmium dinuclear unit $[\text{Cd}_2(\text{HL})_3]^+$ ($\text{Cd}-\text{O}$ 0.231 32(16) nm, $\text{Cd}-\text{N}$ 0.230 0(2) nm). The partially deprotonated HL^- ligand exhibit a particular intramolecular hydrogen



Symmetry codes: a: $1-x+y, 1-x, 0.5-z$; b: $1-y, x-y, 0.5-z$; c: $x, y, 0.5-z$; d: $1-y, x-y, z$; e: $1-x+y, 1-x, z$

Fig.1 (a) Coordination structure for the $[\text{Cd}_2(\text{HL})_3]^+$ unit in **1** with thermal ellipsoids shown at 50% probability; (b) View of 1D supramolecular chain; (c) View along c axis of 3D supramolecular framework extended by the intermolecular hydrogen bonding and π - π stacking interactions

bond (O(1)⋯O(1c) 0.243 9(3) nm), which play an important role in structural stability and charge balance. Meanwhile, the configuration of HL^- ligand is V-shaped with the dihedral angle of $61.56(14)^\circ$, which differ from the dihedral angle of $56.05(2)^\circ$, 89.6° and 83.1° in literature^[11,13]. As shown in Fig.1b, the C2 atoms in 8-quinolinol rings are connected by the weak hydrogen bonds with the free water molecules O1w (C(2)⋯O(1W) 0.309 2(9) nm), resulting in the formation of 1D supramolecular chains. Furthermore, intermolecular hydrogen bonding interactions between O1w atoms and the O2 atoms from NO_3^- (O(1W)⋯O(2) 0.256 1(12) nm), and π - π stacking interactions between the pyridine rings (Cg4⋯Cg4a 0.346 8(2) nm; Cg4 is the centroid of the N1-C1-C2-C3-C4-C9 ring; Symmetry codes: a: $y, -x+y, -z$) expand the structure into 3D supramolecular network (Fig.1c).

For complex **2**, the coordination unit $[\text{M}_2(\text{HL})_3]^+$ is similar to that of **1**, but the lattice structures are different. Complex **2** crystallizes in a space group $R\bar{3}$. The rotation axis is the link of N atoms in nitrate ions along c axis too. As shown in Fig.2a, weak hydrogen bonds between the C5, C3, C12 from HL^- ligands and O3 atoms from NO_3^- ions extend the $[\text{Zn}_2(\text{HL})_3]^+$ units into 2D supramolecular layers (C(5)⋯O(3g) 0.342 0(4) nm, C(3)⋯O(3g) 0.357 3(4) nm, C(12)⋯O(3d) 0.369 7(4) nm). Further, another hydrogen bonding interactions (C(10)⋯O(3) 0.334 8(4) nm) connect the layers into 3D supramolecular network (Fig.2b). The aqua molecules are disorderly situated in the relative hydrophobic environment. Comparing to the two kinds of lattice structures, different interactions between guest molecules (NO_3^- groups and aqua molecules) and $[\text{M}_2(\text{HL})_3]^+$ units are the key role.

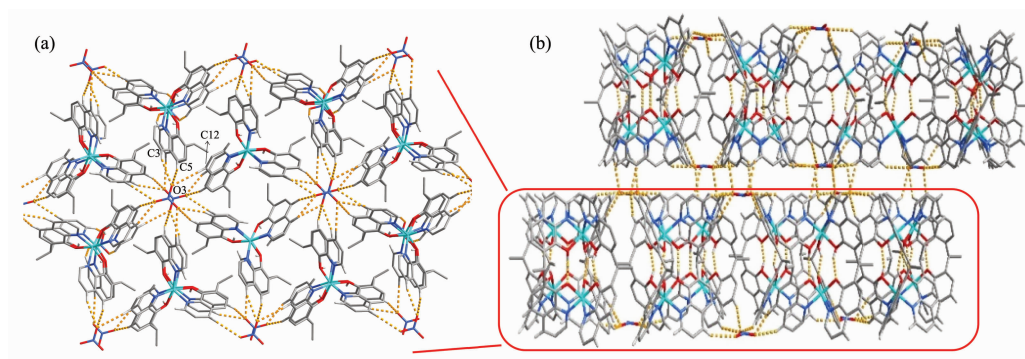


Fig.2 (a) View along c axis of 2D supramolecular layer; (b) 3D supramolecular network connected via weak hydrogen bonds between H atoms of carbon and O atoms of NO_3^- ions

2.3 Thermogravimetric analysis

The thermal stabilities of complexes **1** and **2** were determined by TG in the temperature range of 30~800 $^\circ\text{C}$ under nitrogen gas (Fig.3). The pure phase of complexes **1~3** were confirmed by the PXRD (Fig. S1 and S2). Complex **1** gradually lost a weight of 1.81% from room temperature to 310 $^\circ\text{C}$, releasing one lattice water (Calcd. 1.44%). Meanwhile, complex **2** gradually lost one lattice water (Calcd. 1.56%, Obsd. 1.89%), from room temperature to 350 $^\circ\text{C}$. And then for both complexes, a large sudden weight loss occurred. It indicates the cation units in the structures are both highly thermal stable, but complex **2** have a better thermal stability, due to the difference in space

stack interactions caused by different locations of guest molecules H_2O and NO_3^- . Interestingly, the weight loss of the two complexes is obviously different. In **1**, the weight loss should correspond to the decomposi-

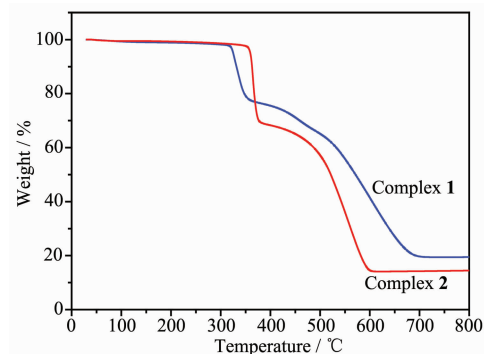


Fig.3 TG curves of complexes **1** and **2**

tion of one HL^- ligand (Calcd. 25.2%); while in **2**, that might be due to the loss of one HL^- ligand and one NO_3^- counter ion (Calcd. 32.6%). From structural analysis, nitrate groups in **2** form hydrogen bonds to the cation units $[\text{M}_2(\text{HL})_3]^+$ much more than those groups in **1**. Therefore, while the HL^- ligand break away from the structure, the NO_3^- group in **2** might be more fragile.

2.4 Luminescent properties

Although there are several structures about the in situ synthetic ligand H_2L , it is not reported about the luminescent properties of the ligand. As the molecular structure of ligand H_2L contains two 8-hydroxyquinoline units which connected by an ethyl group, it is possible to exhibit aggregation-induced emission (AIE) effect^[24], so we extracted it from the complex **1** and explored its fluorescence properties. The solid-state fluorescence shows that the emission peak is 484 nm, excited at 367 nm (Fig.4a). While dissolved in acetone, and deionized water is added dropwise to the solution, unfortunately, the results show the ligand H_2L has no AIE characteristics. The solid-state luminescent prop-

erties of the as-synthesized samples **1~3** are also investigated at room temperature (Fig.4b). The fluorescence of complexes **1** and **3** showed green emission peaks at 518 nm ($\lambda_{\text{ex}}=430$ nm) and 503 nm ($\lambda_{\text{ex}}=375$ nm), respectively. However, the fluorescence of complex **2** exhibited a yellow-green emission peaks at 551 nm ($\lambda_{\text{ex}}=425$ nm), which had a similar curve and showed an obvious bathochromic-shifted emission by 48 nm comparing to the fluorescence of complex **3**. The result might be related to the different lattice structures of two complexes, which composed of different noncovalent interactions of guest molecules H_2O and NO_3^- . This observation is meaningful in deeply understanding the relationship between structure and fluorescence performance. Furthermore, the lifetimes for complexes **1** and **2** were *ca.* 7.8 and 2.83 ns, respectively^[25-26]. The short lifetime suggests that luminescence should be attributed to the intraligands fluorescent emission rather than the LMCT (ligand-to-metal charge transfer) (Fig.S8 and S9), the difference of lifetime may be the result of different noncovalent interactions.

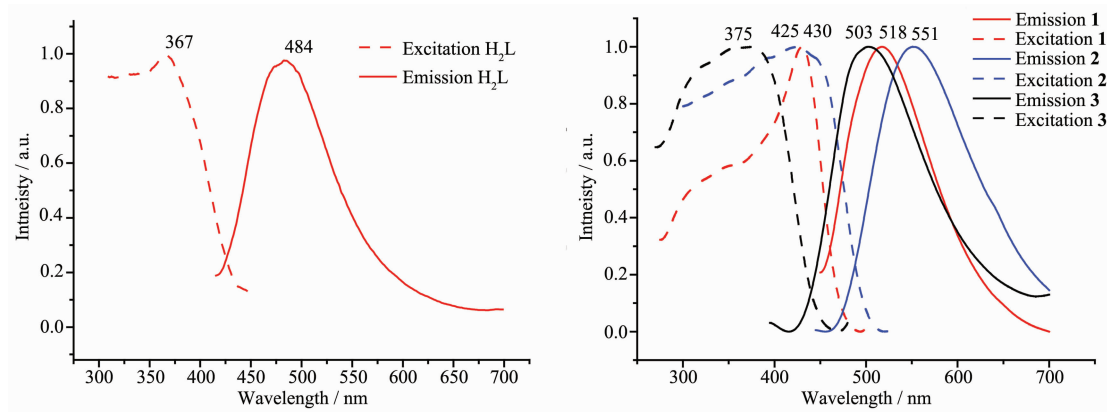


Fig.4 Luminescent spectra of H_2L ligand and complexes **1~3**

3 Conclusions

In summary, we have synthesized and characterized three novel d^{10} zinc and cadmium complexes **1~3**, and the ligand H_2L has been extracted in the first time from complex **1**. Complexes **1~3** contain novel positively charged dinuclear unit, $[\text{M}_2(\text{HL})_3]^+$, which is unique in the structure of complexes and exhibit green light emissions. H_2L ligand show a blue

light emission. Different locations of guest molecules in structures result in different noncovalent interactions between guest molecules and positively charged dinuclear units, and the obvious bathochromic-shifted emission in three complexes. It is meaningful in deeply understanding the relationship between lattice structures and fluorescence performance.

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