

1,3-金刚烷二乙酸配体构筑的两个镉配合物的合成、表征及晶体结构

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摘要: 合成了 2 个一维 Cd(II)配合物 $[\text{CdL}(2,2'\text{-bipy})]_n \cdot n\text{H}_2\text{O}$ (**1**)和 $[\text{CdL}(2,2'\text{-bipy})(\text{H}_2\text{O})]_n \cdot 4n\text{H}_2\text{O}$ (**2**)(H_2L 为 1,3 金刚烷二乙酸),并经 X-射线单晶衍射方法测定了它们的晶体结构。在配合物 **1** 中,中心金属 Cd(II)为七配位的单帽三棱柱结构,而在配合物 **2** 中, Cd(II)为七配位的五角双锥结构。1,3 金刚烷二乙酸根作为桥联配体连接中心金属 Cd(II)离子形成一维链,同时通过氢键和 π - π 堆积作用形成三维超分子结构。研究了配合物 **1** 的荧光光谱。

关键词: Cd(II)配合物; 1,3-金刚烷二乙酸; 晶体结构; 荧光性质

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Syntheses, Characterizations and Crystal Structures of Two Cadmium(II) Coordination Polymers Constructed by 1,3-Adamantanediacyetic Acid

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Abstract: Two new one-dimensional coordination polymers, $[\text{CdL}(2,2'\text{-bipy})]_n \cdot n\text{H}_2\text{O}$ (**1**) and $[\text{CdL}(2,2'\text{-bipy})(\text{H}_2\text{O})]_n \cdot 4n\text{H}_2\text{O}$ (**2**) (H_2L =1,3-adamantanediacyetic acid, 2,2'-bipy=2,2'-bipyridine), have been synthesized and characterized by single-crystal X-ray diffraction. Complex **1** belongs to triclinic system, space group $P\bar{1}$ with $a=1.037\ 2(1)$ nm, $b=1.043\ 2(1)$ nm, $c=1.090\ 7(1)$ nm, $\alpha=90.616(4)^\circ$, $\beta=92.526(4)^\circ$, $\gamma=108.756(4)^\circ$, $V=1.116\ 0(1)$ nm³, $Z=2$, $M_r=536.88$, $F(000)=548$, $D_c=1.598\ \text{g}\cdot\text{cm}^{-3}$, $\mu=1.017\ \text{mm}^{-1}$, the final $R=0.022\ 0$ and $wR=0.054\ 9$ for 4 834 observed reflections ($I>2\sigma(I)$). Complex **2** belongs to monoclinic system, space group $P2_1/n$ with $a=1.366\ 3(1)$ nm, $b=1.413\ 2(1)$ nm, $c=1.510\ 2(1)$ nm, $\beta=114.611(2)^\circ$, $V=2.651\ 1(1)$ nm³, $Z=4$, $M_r=608.95$, $F(000)=1\ 256$, $D_c=1.526\ \text{g}\cdot\text{cm}^{-3}$, $\mu=0.877\ \text{mm}^{-1}$, the final $R=0.030\ 1$ and $wR=0.071\ 2$ for 4 592 observed reflections ($I>2\sigma(I)$). The cadmium ion is seven-coordinated in a distorted monocapped triangular prismatic arrangement for **1** and in a distorted pentagonal-bipyramidal arrangement for **2**, and 1,3-adamantanediacyetic acids act as the bridge to link the cadmiums to 1D chains. Non-covalent interactions, such as hydrogen-bonding and aromatic π - π interactions, lead the complexes to supramolecular architectures. The luminescent property for **1** has also been studied. CCDC: 747686, **1**; 747687, **2**.

Key words: Cd(II) complex; 1,3-adamantanediacyetic acid; crystal structure; luminescent property

Studies of the coordination chemistry of cadmium (II) with carboxylate ligands have aroused more interest in the last decade in view of their interesting structural

and photoluminescent properties^[1-4]. Many cadmium-carboxylate polymers with 1D helix structure^[5], 2D honeycomb-like structure^[6,7] and 3D open framework

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structure^[8,9] have been reported. In order to obtain the complexes with novel structures it is necessary to select suitable multidentate bridging ligand. 1,3-adamantanediadic acid (H_2L) would similarly be expected to be useful ligand, considering that it also have rich coordination mode. However, few metal complexes with 1,3-adamantanediadic acid (H_2L) reported in the literature^[10-12]. Herein, we select 1,3-adamantanediadic acid as the bridging ligand and 2,2'-bipyridine as a terminal ligand to generate two new cadmium coordination polymers, $[CdL(2,2'-bipy)]_n \cdot nH_2O$ (**1**) and $[CdL(2,2'-bipy)(H_2O)]_n \cdot 4nH_2O$ (**2**), which were obtained by using hydrothermal technique and characterized by single crystal X-ray diffraction.

1 Experimental

1.1 Materials and measurement

All solvents and chemicals were of analytical grade and used without further purification. Elemental analyses were carried out using a Perkin-Elmer 2400 II elemental analyzer. The diffraction data were collected on a Bruker SMART APEX II CCD diffractometer. IR spectra were measured in KBr pellets on a Nicolet 5DX FTIR spectrometer. The thermogravimetric measurements were performed on preweighed samples in an oxygen stream using a Netzsch STA449C apparatus with a heating rate of $10\text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$. The excitation and luminescence spectra were performed on a HITACHI-F-2500 fluorescence spectrometer in solid state at room temperature.

1.2 Syntheses of the complexes $[CdL(2,2'-bipy)]_n \cdot nH_2O$ (**1**) and $[CdL(2,2'-bipy)(H_2O)]_n \cdot 4nH_2O$ (**2**)

A mixture of H_2L (0.126 g, 0.5 mmol), $Cd(Ac)_2 \cdot$

$2H_2O$ (0.133 g, 0.5 mmol), 2,2'-bipyridine (0.039 g, 0.25 mmol) and Na_2CO_3 (0.053 g, 0.5 mmol) were dissolved in 18 mL distilled water. The solution was heated to 433 K for 72 h and then cooled to room temperature over 3 d. Colorless block crystals of **1** were isolated from the solution (yield 32%). Anal. Calcd. (%) for $C_{24}H_{28}CdN_2O_5$: C, 53.69; H, 5.26; N, 5.22. Found (%): C, 53.60; H, 5.28; N, 5.26. IR (KBr, cm^{-1}): 3 457m, 2 889s, 2 844s, 1 542s, 1 478m, 1 414s, 1 358m, 1 312m, 1 243m, 1 151m, 1 014m, 761s, 733m.

After evaporating above filtration at room temperature for a week, colorless crystals of **2** were obtained (yield 32%). Anal. Calcd. (%) for $C_{24}H_{36}CdN_2O_9$: C, 47.34; H, 5.96; N, 4.60. Found (%): C, 47.22; H, 5.68; N, 4.56. IR (KBr, cm^{-1}): 3 386s, 3 286s, 2 898s, 2 840m, 1 555s, 1 478m, 1 439s, 1 409s, 1 357m, 1 151m, 1 023m, 766s, 675m.

1.3 X-ray crystallography

Single crystals of complexes **1** and **2** were mounted on a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromatic $Mo\ K\alpha$ radiation ($\lambda=0.071073\text{ nm}$) for data collection at 296(2) K. The data intensity was corrected by Lorentz-polarization factor and empirical absorption on the SADABS program^[13]. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with the SHELX-97 program package^[14]. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to carbon were located by geometrical calculations, while those to oxygen were located from difference Fourier maps. The crystallographic data are summarized in Table 1 and the selected bond lengths and bond angles are given in Table 2.

CCDC: 747686, **1**; 747687, **2**.

Table 1 Crystal data and structure refinement for **1** and **2**

Compound	1	2
Empirical formula	$C_{24}H_{28}CdN_2O_5$	$C_{24}H_{36}CdN_2O_9$
Formula weight	536.88	608.95
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a / nm	1.037 2(1)	1.366 3(1)
b / nm	1.0432(1)	1.4132(1)
c / nm	1.0907(1)	1.5102(1)

Continued Table 1

$\alpha / (^{\circ})$	90.616(4)	
$\beta / (^{\circ})$	92.526(4)	114.611(2)
$\gamma / (^{\circ})$	108.756(4)	
V / nm^3	1.116 0(1)	2.651 1(1)
Z	2	4
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.598	1.526
μ / mm^{-1}	1.017	0.877
$F(000)$	548	1256
Crystal color	Colorless	Colorless
Crystal dimension / mm	0.45×0.18×0.11	0.46×0.19×0.06
$\theta_{\min} \theta_{\max} / (^{\circ})$	1.87~27.68	2.07~26.49
Reflections collected	17 739	22 316
Unique reflections (R_{int})	5 135 (0.019 4)	5 489 (0.034 1)
Data with $I > 2\sigma(I)$	4 834	4 592
Parameters refined	295	355
R, wR ($I > 2\sigma(I)$)	0.022 0, 0.054 9	0.030 1, 0.071 2
R, wR (all reflections)	0.024 1, 0.056 3	0.039 7, 0.075 0
Goodness-of-fit (on F^2)	1.036	1.037
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}} / (\text{e} \cdot \text{nm}^{-3})$	0.451, -0.414	0.869, -0.529
$(\Delta/\sigma)_{\text{max}}$	0.001	0.000

Table 2 Selected bond lengths (nm) and angles ($^{\circ}$)

Complex 1					
Cd(1)-O(2)	0.232 3(2)	Cd(1)-N(1)	0.236 7(2)	Cd(1)-O(4)	0.237 9(2)
Cd(1)-N(2)	0.239 1(2)	Cd(1)-O(3)#1	0.239 6(2)	Cd(1)-O(1)	0.241 7(2)
Cd(1)-O(3)	0.243 2(2)				
O(2)-Cd(1)-N(1)	140.32(6)	O(2)-Cd(1)-O(4)	135.22(6)	N(1)-Cd(1)-O(4)	84.19(6)
O(2)-Cd(1)-N(2)	93.34(6)	N(1)-Cd(1)-N(2)	68.81(6)	O(4)-Cd(1)-N(2)	102.43(6)
O(2)-Cd(1)-O(3)#1	81.54(5)	N(1)-Cd(1)-O(3)#1	79.82(6)	O(4)-Cd(1)-O(3)#1	120.73(5)
N(2)-Cd(1)-O(3)#1	123.01(6)	O(2)-Cd(1)-O(1)	54.19(6)	N(1)-Cd(1)-O(1)	150.98(7)
O(4)-Cd(1)-O(1)	84.52(6)	N(2)-Cd(1)-O(1)	87.74(7)	O(3)#1-Cd(1)-O(1)	128.64(6)
O(2)-Cd(1)-O(3)	109.14(6)	N(1)-Cd(1)-O(3)	98.17(6)	O(4)#1-Cd(1)-O(3)	53.84(5)
N(2)-Cd(1)-O(3)	155.02(6)	O(3)#1-Cd(1)-O(3)	72.59(5)	O(1)-Cd(1)-O(3)	96.53(6)
Complex 2					
Cd(1)-O(1)	0.229 9(2)	Cd(1)-O(1W)	0.230 5(2)	Cd(1)-N(1)	0.234 2(2)
Cd(1)-N(2)	0.235 3(2)	Cd(1)-O(3)#1	0.237 0(2)	Cd(1)-O(4)#1	0.251 1(2)
Cd(1)-O(2)	0.254 6(2)				
O(1)-Cd(1)-O(1W)	102.05(7)	O(1)-Cd(1)-N(1)	97.93(7)	O(1W)-Cd(1)-N(1)	159.23(7)
O(1)-Cd(1)-N(2)	132.45(7)	O(1W)-Cd(1)-N(2)	92.11(7)	N(1)-Cd(1)-N(2)	69.95(8)
O(1)-Cd(1)-O(3)#1	84.09(6)	O(1W)-Cd(1)-O(3)#1	103.99(7)	N(1)-Cd(1)-O(3)#1	83.58(7)
N(2)-Cd(1)-O(3)#1	136.17(7)	O(1)-Cd(1)-O(4)#1	135.55(6)	O(1W)-Cd(1)-O(4)#1	81.62(7)
N(1)-Cd(1)-O(4)#1	88.14(7)	N(2)-Cd(1)-O(4)#1	91.05(7)	O(3)#1-Cd(1)-O(4)#1	52.72(6)
O(1)-Cd(1)-O(2)	53.17(6)	O(1W)-Cd(1)-O(2)	95.03(7)	N(1)-Cd(1)-O(2)	92.36(7)
N(2)-Cd(1)-O(2)	80.78(7)	O(3)#1-Cd(1)-O(2)	136.18(6)	O(4)#1-Cd(1)-O(2)	171.08(6)

Symmetry codes: **1**: #1 $-x+1, -y+2, -z+1$; **2**: #1: $x-1/2, -y+1/2, z-1/2$.

Table 3 Hydrogen bond lengths and angles

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle(\text{DHA}) / (^\circ)$
Complex 1				
O(1W)-H(1WA)···O(1)#4	0.086(2)	0.282(5)	0.331(4)	118(4)
O(1W)-H(1WB)···O(1)#5	0.087(2)	0.202(2)	0.286(3)	161(5)
O(1W)-H(1WB)···O(1W)#6	0.087(2)	0.294(4)	0.340(6)	115(4)
O(1W)-H(1WA)···O(4)#4	0.086(2)	0.231(3)	0.311(4)	155(4)
Complex 2				
O(5W)-H(5WA)···O(3)#1	0.083(2)	0.186(2)	0.268 9(3)	176(4)
O(2W)-H(2WA)···O(4)#1	0.084(2)	0.197(3)	0.278 6(3)	161(5)
O(1W)-H(1WA)···O(5W)#3	0.082(2)	0.198(2)	0.279 6(3)	173(3)
O(1W)-H(1WB)···O(1)#3	0.085(2)	0.187(2)	0.270 6(3)	168(3)
O(5W)-H(5WB)···O(2W)#2	0.081(2)	0.206(2)	0.287 1(4)	174(4)
O(4W)-H(4WA)···O(2)	0.084(2)	0.195(2)	0.277 3(3)	166(4)
O(2W)-H(2WB)···O(3W)	0.084(2)	0.221(4)	0.287 9(4)	137(5)
O(4W)-H(4WB)···O(5W)#3	0.083(2)	0.206(2)	0.288 5(4)	173(4)
O(3W)-H(3WB)···O(4W)#4	0.084(2)	0.194(2)	0.276 8(4)	170(5)

Symmetry codes: 1: #4: $-x+2, -y+2, -z+1$; #5: $x+1, y+1, z$; #6: $-x+3, -y+3, -z+1$; 2: #1: $x-1/2, -y+1/2, z-1/2$; #2: $x+1/2, -y+1/2, z+1/2$; #3: $-x+1, -y+1, -z$; #4: $x-1/2, -y+3/2, z-1/2$.

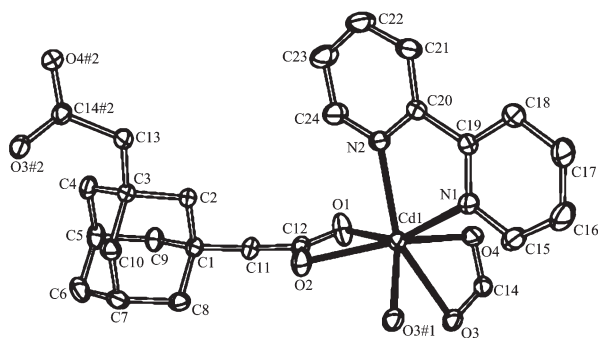
2 Results and discussion

2.1 Molecular structures

2.1.1 Crystal structure of complex 1

The molecular structure and atomic labeling scheme is shown in Fig.1. The crystal structure of complex 1 is composed of a one-dimensional double chain $[\text{CdL}(\text{2,2'}\text{-bipy})]_n$ and lattice water molecules. Each Cd(II) ion is seven-coordinated and exhibits a distorted monocapped triangular prismatic coordination geometry formed by five oxygen atoms from three carboxylate groups of three L^{2-} ligands (Cd-O 0.232 3(2)

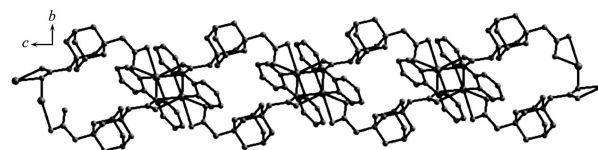
~ 0.243 2(2) nm, O-Cd-O $54.19(6)^\circ \sim 135.22(6)^\circ$), and two nitrogen atoms of 2,2'-bipyridine ligand (Cd-N 0.236 7(2), 0.239 1(2) nm, N(1)-Cd(1)-N(2) $68.81(6)^\circ$). Each L^{2-} ligand acts as a tetradentate linker (Fig.2), and carboxylate groups connecting Cd(II) ions through its chelating and chelating-bridging modes. Two Cd(II) are joined by two chelating-bridging carboxyl groups to form dinuclear Cd(II) centers with $\text{Cd}\cdots\text{Cd}$ distance of 0.389 1(3) nm. Thus, the L^{2-} ligands join the metal centers in a head-to-tail fashion into a 1D double chain structure with a cavity.



Symmetry codes: #1: $-x+1, -y+2, -z+1$; #2: $x, y, z-1$

Lattice water molecule and hydrogen atoms were omitted for clarity

Fig.1 ORTEP view of complex 1 with 30% probability displacement ellipsoids, showing the atom-labeling scheme



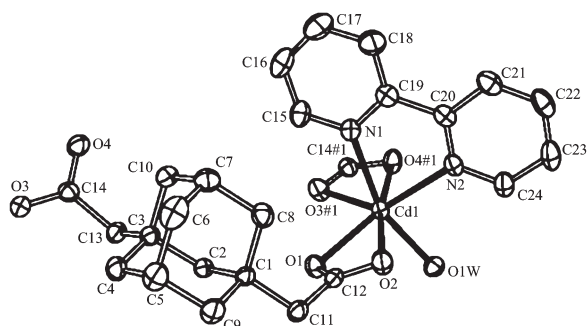
Hydrogen atoms are omitted for clarity

Fig.2 View of one-dimensional double chain along the c axis in 1

Hydrogen-bonding interactions are usually important in the syntheses of supramolecular architectures^[15,16]. There are persistent intermolecular hydrogen bonds involving lattice water molecules and corresponding carboxylate oxygen atoms in the neighboring chains. The $\text{O-H}\cdots\text{O}$ hydrogen bonds link the neighboring chains to yield 2D layer.

2.1.2 Crystal structure of complex **2**

The molecular structure and atomic labeling scheme is shown in Fig.3. The Cd(II) ion also seven-coordinated by two nitrogen atoms of 2,2'-bipy ligand (Cd-N 0.234 2(2)~0.235 3(2) nm, N(1)-Cd(1)-N(2) 69.95(8)°) and four carboxyl oxygen atoms of two L²⁻ ligands (Cd-O 0.229 9(2)~0.254 6(2) nm, O-Cd-O 52.72(6)°~171.08(6)°, and one water molecule (Cd(1)-O(1W) 0.230 5(2) nm). As shown in Fig.4, L²⁻ ligand acts as bridge ligand to link two Cd(II) ions to generated a one-dimensional wave chain structure propagating along the *b* axis, with the Cd···Cd separation of 1.028 (1) nm. The guest water molecules locate on two sides of the chain. The hydrogen bonds between the lattice water molecules and carboxyl oxygen atoms (O···O=0.268 9(3)~0.288 5(4) nm) link adjacent chains to a 2D layer structure. Offset-panel π - π stacking interactions are observed between pyridine ring N(2)-C(20)-C(21)-C(22)-C(23)-C(24) and its adjacent centrosymmetric ring (symmetry code: $-x, 1-y, 1-z$; centroid-to-centroid



Symmetry codes: #1: $x-1/2, -y+1/2, z-1/2$

Lattice water molecules and hydrogen atoms were omitted for clarity

Fig.3 ORTEP view of complex **2** with 30% probability displacement ellipsoids, showing the atom-labeling scheme

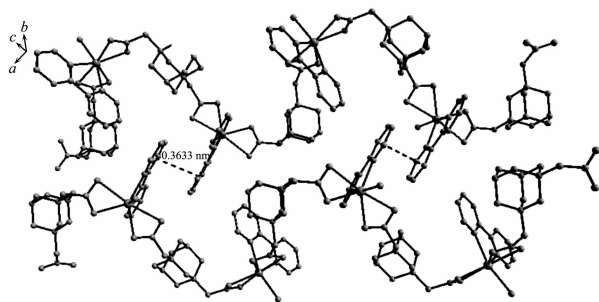


Fig.4 Packing diagram of the compound **2** showing the extensive π - π stacking interactions

distance 0.363 3 nm and plane-to-plane distance 0.326 9 nm). Thus, hydrogen-bonding interactions between adjacent chains together with π - π stacking interactions extend the complex into a three-dimensional supramolecular architecture (Fig.4).

2.2 Thermal property

The samples of complexes **1** and **2** were heated at a rate of 10 °C·min⁻¹ under O₂ atmosphere. As shown in Fig.5, the TG curve of **1** shows two weight loss steps. The first step of a loss of 3.3% in the range of 78~116 °C attributes to the loss of lattice water molecule (calcd. 3.4%). The second weight loss of 74.3% from 257 to 486 °C corresponds to the burning of the coordinated organic ligands. The final solid product may be CdO (calcd. 23.9%). Decomposition of **2** begins from 33 °C, the first weight loss of 14.3% from 33 to 82 °C corresponds to the loss of four lattice water molecules (calcd. 14.0%), then the weight loss of 3.2% in the range of 164~211 °C attributes to the removal of the coordinated water molecule. A rapid and significant weight loss of 61.1% occurs in the range of 302~530 °C corresponds to loss of L²⁻ and 2,2'-bipy ligands. It also gives the final solid product CdO (calcd. 21.1%).

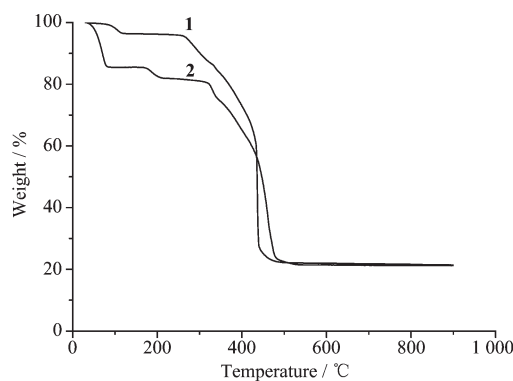


Fig.5 TG diagram for complexes **1** and **2** (under oxygen atmosphere)

2.3 Luminescent property

Metal-organic polymeric complexes with a d¹⁰ closed-shell electronic configuration have been found to exhibit fluorescent properties^[17-19]. Here, the solid-state luminescent property of complex **1** was investigated at room temperature, and the emission spectra are given in Fig.6. Complex **1** exhibits an intense photoluminescence, and the maximum emission wavelength is at 420

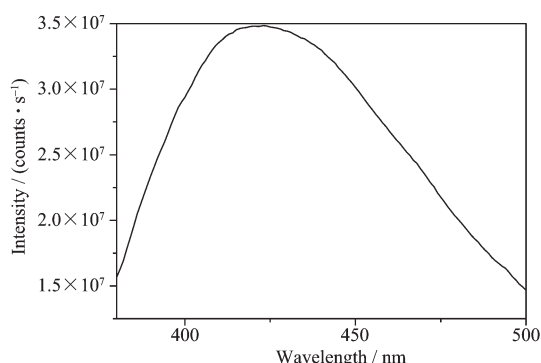


Fig.6 Solid-state luminescent emission spectra of complex **1** at room temperature

nm ($\lambda_{\text{ex}}=360$ nm). At room temperature, the free ligand H_2L shows no detectable luminescence and the free 2,2'-bipy ligand displays fluorescent properties in the solid state at room temperature with the emission maxima being located at 540 nm^[20]. Therefore, the emission band of **1** may be mainly ascribed to π - π electronic transition of the ligand^[21,22].

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