

## 镝与二甘醇酸的配位聚合物的水热合成、晶体结构及荧光性质

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**摘要:**  $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$  与二甘醇酸( $\text{H}_2\text{dga}$ )在水热条件下反应得到配位聚合物  $\{[\text{Dy}_2(\text{dga})_3(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}\}_n$ , 用 X-射线衍射单晶结构分析方法确定了其晶体结构。该配合物的晶体属于正交晶系,  $C222_1$  空间群。在配合物中,  $\text{Dy}^{3+}$  离子存在两种类型的配位环境。九配位的  $\text{Dy1}$  离子与 3 个二甘醇酸根的 6 个羧基氧原子和 3 个醚氧原子配位, 其配位多面体可描述为一个扭曲的单帽四方反棱柱; 八配位的  $\text{Dy2}$  离子周围的 8 个配位氧原子形成一个扭曲的四方反棱柱配位多面体, 其中 4 个氧原子来自 4 个二甘醇酸根, 另外 4 个氧原子由 4 个配位水分子提供。二甘醇酸配体的 2 个羧基和其醚氧原子同时与  $\text{Dy}^{3+}$  离子配位而形成 2D 网状结构。该配合物在室温下的固体荧光光谱显示了中心  $\text{Dy}^{3+}$  离子的特征荧光, 位于 483 nm 和 574 nm 的发射峰分别对应于  $\text{Dy}^{3+}$  离子的  $^4F_{9/2} \rightarrow ^6H_{15/2}$  和  $^4F_{9/2} \rightarrow ^6H_{13/2}$  跃迁。

**关键词:** 镝; 二甘醇酸; 配位聚合物; 晶体结构; 荧光

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### Hydrothermal Synthesis, Crystal Structure and Fluorescence Property of Dysprosium Coordination Polymer with Diglycolic Acid

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**Abstract:** A new lanthanide coordination polymer  $\{[\text{Dy}_2(\text{dga})_3(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}\}_n$  was prepared by hydrothermal method with  $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$  and diglycolic acid ( $\text{H}_2\text{dga}$ ), and structurally characterized by single-crystal X-ray diffraction technique. The complex crystallizes in Orthorhombic system,  $C222_1$  space group with  $a=1.773\ 5(11)$  nm,  $b=0.875\ 2(6)$  nm,  $c=1.504\ 3(9)$  nm,  $V=2.335\ 0(3)$  nm<sup>3</sup>,  $D_c=2.359$  Mg·m<sup>-3</sup>,  $Z=4$ ,  $\mu=6.447$  mm<sup>-1</sup>,  $F(000)=1\ 584.0$ ,  $R=0.050\ 7$ ,  $wR=0.121\ 6$ . In the complex, there are two types of coordination environments for  $\text{Dy}^{3+}$  ion. One  $\text{Dy1}$  ion is nine-coordinated by three diglycolato groups via six carboxyl oxygen atoms and three ether oxygen atoms. The  $\text{Dy1}$  ion is in a distorted monocapped square-antiprism coordination geometry. Whereas the other  $\text{Dy2}$  ion is eight-coordinated and the coordination sphere around each  $\text{Dy2}$  ion consists of four carboxyl oxygen atoms from four diglycolato ligands and four oxygen atoms from four coordinated water molecules. The coordination polyhedron of  $\text{Dy2}$  ion can be described as a distorted square-antiprism. Eight- and nine-coordinate  $\text{Dy}^{3+}$  ions are linked by diglycolato ligands to form a 2D network structure. The fluorescence spectral of the complex in solid state at room temperature shows that the diglycolic acid is suitable for the sensitization on the luminescence of  $\text{Dy}^{3+}$  ion. CCDC: 660435.

**Key word:** dysprosium; diglycolic acid; coordination polymer; crystal structure; fluorescence

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Coordination polymers constructed by polycarboxylates and lanthanide ions have been an attractive area of research due to their fascinating crystal structure and potential applications in optoelectronic devices, luminescent probes, magnetism materials, superconductors and catalysts<sup>[1-4]</sup>. Polycarboxylate ligands are mainly divided into two kinds, namely, rigid ligands and flexible ligands. Rigid ligands, such as aromatic polycarboxylic acids<sup>[3,5-9]</sup> are usually used, for they can bridge the center ions and can form the  $\pi$ - $\pi$  stacking to increase the stability of the structure. However, the flexible ligands are running in the configuration of coordination polymers, which may lead to intriguing structures<sup>[2,4,10-20]</sup>.

Diglycolic acid is a flexible ligand with four carboxyl oxygen atoms and one ether oxygen atom. There are some reports about its coordination complexes with transition metal ions<sup>[12-16]</sup> or lanthanide metal ions<sup>[17-20]</sup>. However, dysprosium complex with diglycolic acid has not been reported. Furthermore, dysprosium is one of the rare earth elements with luminescence properties<sup>[8,9]</sup>. Therefore, we used diglycolic acid as ligand and prepared a dysprosium complex by hydrothermal method, namely,  $\{[\text{Dy}_2(\text{dga})_3(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}\}_n$  ( $\text{H}_2\text{dga}$  = diglycolic acid), which shows 2D network structure, good fluorescence property and thermal stability.

## 1 Experimental

All reagents purchased were of analytical grade and used without further purification, except that the hydrated dysprosium chloride was prepared by reaction of  $\text{Dy}_2\text{O}_3$  and hydrochloric acid.

### 1.1 Synthesis of $\{[\text{Dy}_2(\text{dga})_3(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}\}_n$

The complex was prepared from the reaction

mixture of  $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$  (0.113 0 g, 0.3 mmol), diglycolic acid (0.080 5 g, 0.6 mmol), sodium hydroxide (2 mol  $\cdot$  L<sup>-1</sup>, 0.5 mL) and water (10 mL) in a 25 mL Teflon-lined stainless steel autoclave, under autogenous pressure at 180 °C for 5 days, and then cooled to room temperature at a rate of 10 °C  $\cdot$  h<sup>-1</sup>. Finally, colorless single crystals suitable for X-ray diffraction were obtained.

### 1.2 Physical measurements

The TG-DTA analysis experiment was carried out on a WCT-1A Thermal Analyzer. The fluorescence spectral of the solid sample was performed on an F-4500 FL Spectrophotometer at room temperature.

### 1.3 X-ray crystallographic studies

A single crystal of the complex with dimensions of 0.24 mm  $\times$  0.20 mm  $\times$  0.16 mm was selected for X-ray diffraction. Data were collected at 273(2) K on a Bruker Smart 1000 CCD diffractometer equipped with a graphite monochromatized Mo  $K\alpha$  radiation ( $\lambda=0.071\ 073$  nm). A total of 6 670 reflections were collected in the range of  $2.60^\circ < \theta < 28.28^\circ$ , of which 2 830 independent ones ( $R_{\text{int}}=0.075\ 1$ ) were used. Semi-empirical absorption corrections were applied using the SADABS program. The structure was solved by direct method. The coordinates of all non-hydrogen atoms and the anisotropic thermal parameters were refined by full-matrix least-squares method. The hydrogen atoms were placed in calculated positions. All calculations were carried out on a computer by using the SHELXTL crystallographic software package. The crystallographic data and structure refinement data of the complex are summarized in Table 1.

CCDC: 660435.

Table 1 Crystal data and structure refinement for the title complex

Empirical formula	$\text{C}_{12}\text{H}_{24}\text{Dy}_2\text{O}_{21}$	$D_c / (\text{Mg} \cdot \text{m}^{-3})$	2.359
Formula weight	829.31	$\mu / \text{mm}^{-1}$	6.447
Crystal size / mm	$0.24 \times 0.20 \times 0.16$	$F(000)$	1 584
Temperature / K	293(2)	$\theta / (^\circ)$	2.60~28.28
Wavelength / nm	0.071 073	Limiting indices	$-11 \leq h \leq 23, -11 \leq k \leq 11, -10 \leq l \leq 19$
Crystal system	Orthorhombic	Reflections collected / unique	6 670 / 2 830
Space group	$C22_1$	Data / restraints / parameters	2 830 / 6 / 163
$a / \text{nm}$	1.773 5(11)	Goodness-of-fit on $F^2$	1.106
$b / \text{nm}$	0.875 2(6)	Final $R$ indices $[I > 2\sigma(I)]$	$R_1=0.050\ 7, wR_2=0.121\ 6$

Continued Table 1				
$c$ / nm	1.504 3(9)	$R$ indices (all data)	$R_1$ =0.052 5, $wR_2$ =0.123 1	
$V$ / nm <sup>3</sup>	2.355 0(3)	Largest diff. peak and hole / (e·nm <sup>-3</sup> )	3 591 and −4 862	
$Z$	4			

2 Results and discussion

2.1 Crystal structure of  $[\{\text{Dy}_2(\text{dga})_3(\text{H}_2\text{O})_4\} \cdot 2\text{H}_2\text{O}]_n$

There are two unique Dy(III) ions in the asymmetric unit of the title complex, as shown in Fig.1. The bond lengths and bond angles are listed in Table 2. Obviously, the center Dy<sup>3+</sup> ion has two types of coordination environments. One Dy1 ion is coordinated to nine atoms: six carboxyl oxygen atoms (O1, O1A, O4, O4A, O7 and O7A) (A:  $x, -y+2, -z$ ) and three ether oxygen

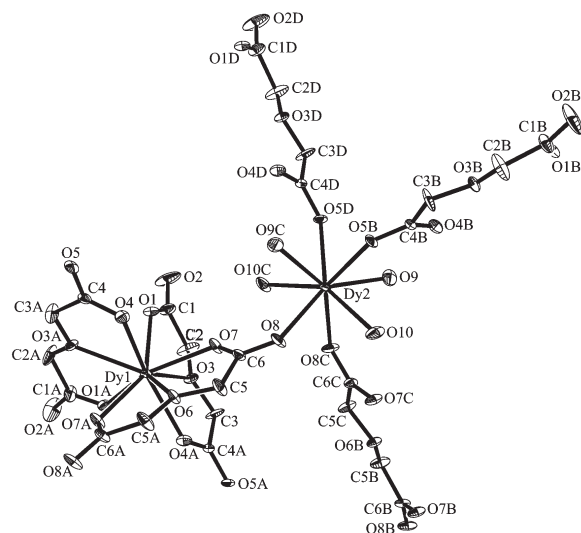
atoms (O3, O3A and O6) (A:  $x, -y+2, -z$ ) from three diglycolato ligands. The nine coordinated atoms around Dy1 ion form a distorted monocapped square-antiprism coordination polyhedron (Fig.2a), the upper and lower planes of which are structured by atoms O1, O1A, O4A, O7 and O4, O6, O7A, O3A (A:  $x, -y+2, -z$ ), respectively, the mean deviation from the upper and lower planes is 0.017 88 nm and 0.027 62 nm, respectively, and the dihedral angle between the two planes is 1.9°. The capping vertex of the polyhedron is occupied by atom O3. The Dy1-O (carboxyl) bond

Table 2 Bond lengths (nm) and angles (°) for the title complex

Dy(1)-O(3)#1	0.244 9(4)	Dy(1)-O(3)	0.244 9(4)	Dy(1)-O(6)	0.248 4(6)
Dy(2)-O(5)#2	0.233 5(6)	Dy(2)-O(5)#3	0.233 5(6)	Dy(2)-O(10)	0.235 1(6)
Dy(2)-O(10)#4	0.235 1(6)	Dy(2)-O(8)#4	0.237 1(6)	Dy(2)-O(8)	0.237 1(6)
Dy(2)-O(9)	0.248 0(8)	Dy(2)-O(9)#4	0.248 0(8)		
O(7)-Dy(1)-O(7)#1	127.6(3)	O(7)-Dy(1)-O(1)	78.6(2)	O(7)#1-Dy(1)-O(1)	146.0(3)
O(7)-Dy(1)-O(1)#1	146.0(3)	O(7)#1-Dy(1)-O(1)#1	78.6(2)	O(1)-Dy(1)-O(1)#1	88.6(3)
O(7)-Dy(1)-O(4)#1	83.8(2)	O(7)#1-Dy(1)-O(4)#1	81.1(2)	O(1)-Dy(1)-O(4)#1	127.7(2)
O(1)#1-Dy(1)-O(4)#1	79.4(2)	O(7)-Dy(1)-O(4)	81.1(2)	O(7)#1-Dy(1)-O(4)	83.8(2)
O(1)-Dy(1)-O(4)	79.4(2)	O(1)#1-Dy(1)-O(4)	127.7(2)	O(4)#1-Dy(1)-O(4)	145.2(3)
O(7)-Dy(1)-O(3)#1	137.9(3)	O(7)#1-Dy(1)-O(3)#1	73.4(3)	O(1)-Dy(1)-O(3)#1	72.7(2)
O(1)#1-Dy(1)-O(3)#1	63.7(2)	O(4)#1-Dy(1)-O(3)#1	138.3(2)	O(4)-Dy(1)-O(3)#1	64.1(2)
O(7)-Dy(1)-O(3)	73.4(3)	O(7)#1-Dy(1)-O(3)	137.9(3)	O(1)-Dy(1)-O(3)	63.7(2)
O(1)#1-Dy(1)-O(3)	72.7(2)	O(4)#1-Dy(1)-O(3)	64.1(2)	O(4)-Dy(1)-O(3)	138.3(2)
O(3)#1-Dy(1)-O(3)	117.7(2)	O(7)-Dy(1)-O(6)	63.80(15)	O(7)#1-Dy(1)-O(6)	63.80(15)
O(1)-Dy(1)-O(6)	135.69(14)	O(1)#1-Dy(1)-O(6)	135.69(14)	O(4)#1-Dy(1)-O(6)	72.62(14)
O(4)-Dy(1)-O(6)	72.62(14)	O(3)#1-Dy(1)-O(6)	121.13(10)	O(3)-Dy(1)-O(6)	121.13(10)
O(5)#2-Dy(2)-O(5)#3	76.7(3)	O(5)#2-Dy(2)-O(10)	141.9(2)	O(5)#3-Dy(2)-O(10)	70.5(2)
O(5)#2-Dy(2)-O(10)#4	70.5(2)	O(5)#3-Dy(2)-O(10)#4	141.9(3)	O(10)-Dy(2)-O(10)#4	146.4(3)
O(5)#2-Dy(2)-O(8)#4	117.4(2)	O(5)#3-Dy(2)-O(8)#4	139.8(2)	O(10)-Dy(2)-O(8)#4	79.1(2)
O(10)#4-Dy(2)-O(8)#4	74.8(3)	O(5)#2-Dy(2)-O(8)	139.8(2)	O(5)#3-Dy(2)-O(8)	117.4(2)
O(10)-Dy(2)-O(8)	74.8(3)	O(10)#4-Dy(2)-O(8)	79.1(2)	O(8)#4-Dy(2)-O(8)	77.4(4)
O(5)#2-Dy(2)-O(9)	72.1(2)	O(5)#3-Dy(2)-O(9)	78.2(2)	O(10)-Dy(2)-O(9)	82.4(3)
O(10)#4-Dy(2)-O(9)	108.7(3)	O(8)#4-Dy(2)-O(9)	72.1(3)	O(8)-Dy(2)-O(9)	144.8(3)
O(5)#2-Dy(2)-O(9)#4	78.2(2)	O(5)#3-Dy(2)-O(9)#4	72.1(2)	O(10)-Dy(2)-O(9)#4	108.7(3)
O(10)#4-Dy(2)-O(9)#4	82.4(3)	O(8)#4-Dy(2)-O(9)#4	144.8(3)	O(8)-Dy(2)-O(9)#4	72.1(3)
O(9)-Dy(2)-O(9)#4	141.9(3)				

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

distances range in 0.235 4(6)~0.238 6(7) nm with the average bond distance of 0.236 7 nm, The Dy1-O (ether) bond distances vary in the range of 0.244 9 (4) ~ 0.248 4(6) nm with the average bond distance of 0.246 7 nm. Whereas the other Dy2 ion is eight-coordinated by four carboxyl oxygen atoms (O5B, O5D, O8 and O8C) (B:  $x, -y+1, -z$ ; C:  $-x+1, y, z+1/2$ ; D:  $-x+1, -y+1, z+1/2$ ) from four diglycolato ligands and four oxygen atoms (O9, O9C, O10 and O10C) (C:  $-x+1, y, z+1/2$ ) from four water molecules. The eight oxygen atoms form a distorted square-antiprism coordination polyhedron around the Dy2 ion (Fig.2b), in which four oxygen atoms (O5B, O10, O8, O9C) (B:  $x, -y+1, -z$ ; C:  $-x+1, y, -z+1/2$ ) form the upper plane and the others (O5D, O9, O8C, O10C) (C:  $-x+1, y, z+1/2$ ; D:  $-x+1, -y+1, z+1/2$ ) form the bottom plane, respectively, and the mean deviation from the upper and lower planes is 0.009 18 nm and 0.009 18 nm, respectively. The dihedral angle between the two planes is  $0.7^\circ$ . The bond distances of Dy2-O (carboxyl) are in the range of 0.233 5(6)~0.237 1(6) nm with the average bond distance of 0.235 3 nm, the bond distances of Dy2-O(water) are in the range of 0.235 1(6)~0.248 0(8) nm with the average bond distance of 0.241 6 nm. The distance between the neighboring Dy1 and Dy2 ions is 0.609 0 nm.

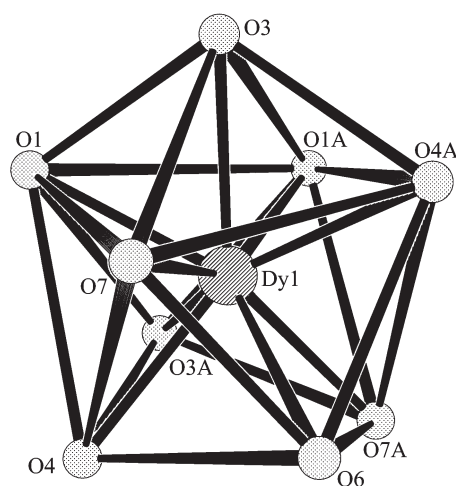


Thermal ellipsoids are shown at 30% probability

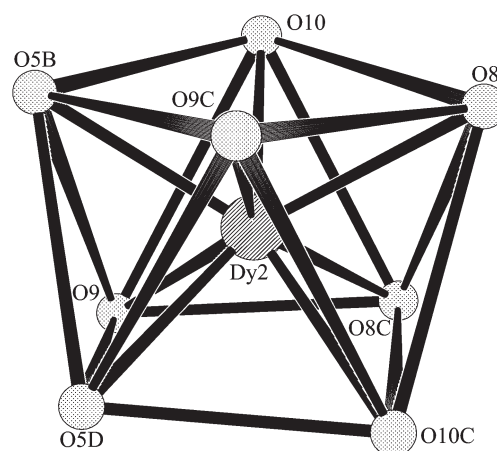
Hydrogen atoms and lattice water molecules are omitted for clarity

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

Fig.1 Asymmetric unit of the title complex



(a) Dy1 ion



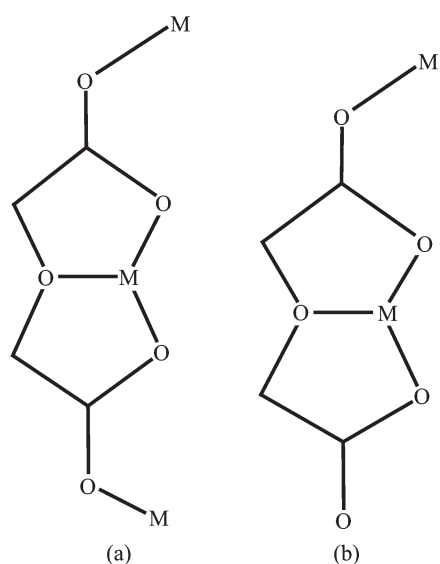
(b) Dy2 ion

Symmetry code: A:  $x, -y+2, -z$ ; B:  $x, -y+1, -z$ ; C:  $-x+1, y, -z+1/2$ ; D:  $-x+1, -y+1, z+1/2$

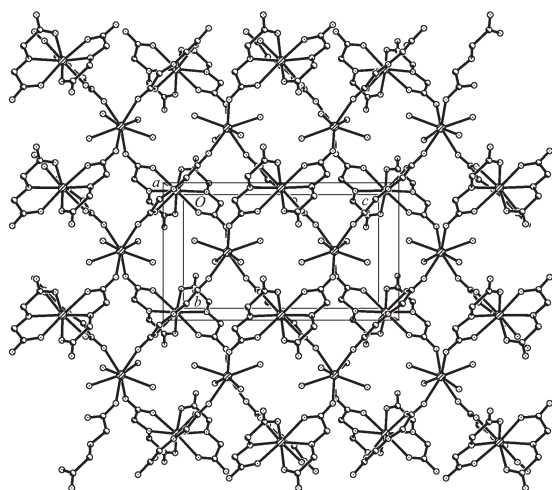
Fig.2 Coordination geometry of  $\text{Dy}^{3+}$  ion in the title complex

In the title complex, diglycolato ligands exhibit two coordination modes: (1) The two carboxyl groups of diglycolato ligand act as bidentate bridging coordination modes toward three  $\text{Dy}^{3+}$  ions (Scheme 1a); (2) The two carboxyl groups of diglycolato ligand act as monodentate and bidentate bridging coordination modes, respectively, toward two  $\text{Dy}^{3+}$  ions (Scheme 1b). The ether oxygen atoms of diglycolato ligands also coordinate  $\text{Dy}^{3+}$  ions simultaneously. So,  $\text{Dy}^{3+}$  ions are linked by diglycolato ligands to form a 2D network structure (Fig.3), in which, each four neighboring  $\text{Dy}^{3+}$  ions construct quadrangle with the size of 0.609 0 nm  $\times$  0.616 6 nm based on the  $\text{Dy} \cdots \text{Dy}$  separation.

The title complex different from reported



Scheme 1 Coordination modes of the diglycolato ligands in the title complex



All hydrogen atoms and lattice water molecules are omitted for clarity

Fig. 3 Diagram of the 2D network structure

dysprosium-cuprum complex with oxydiacetate,  $[\{Cu_3Dy_2(oda)_6(H_2O)_6\} \cdot 12H_2O]_n$  (oda = Oxydiacetate)<sup>[21]</sup>, which crystallizes in hexagonal crystal system,  $P6/mcc$  space group. The latter complex is built up from two small and simple building blocks,  $DyO_9$  and  $CuO_6$ , which come together to form a 3D framework of close-packed channels. However, the  $Dy^{3+}$  ion in the complex coordinates to two inner carboxyl oxygen atoms and to a ether oxygen atom of three oda ligands to form a nine-coordinated polyhedron, this is identical to the coordination environment of Dy1 in the title complex.

## 2.2 Thermogravimetric analysis

The TG-DTA analysis was performed in air atmosphere with a heating rate of  $10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$  in the temperature range from 20 to  $1\ 000\text{ }^\circ\text{C}$ .

In the DTA curve, there appears a small endothermic peak at  $166.0\text{ }^\circ\text{C}$  and a big exothermic peak at  $440.0\text{ }^\circ\text{C}$  with a shoulder peak at  $410.0\text{ }^\circ\text{C}$ . In the TG curve, the first weight loss of 12.98% is attributing to the removal of two crystal water molecules and four coordinated water molecules (calculated, 13.02%). And then the complex begins to decompose.  $Dy_2O_3$  was the last residue, corresponding to the total loss of 54.98% (calculated, 55.02%).

## 2.3 Fluorescence property

The excitation spectral of the complex was recorded in the range of 200~400 nm, setting 484 nm as the emission wavelength. And the emission spectral of the solid-state was observed from 400 to 700 nm under the strongest excitation wavelength of 326 nm (Fig.4). The emission spectral is similar to that of other dysprosium complexes<sup>[8,9]</sup>, showing the luminescent properties of the  $Dy^{3+}$  ion. In the emission spectral, there are two peaks at 483 and 574 nm, corresponding to  $^4F_{9/2} \rightarrow ^6H_{15/2}$  and  $^4F_{9/2} \rightarrow ^6H_{13/2}$  transition emissions of  $Dy^{3+}$  ion, respectively.

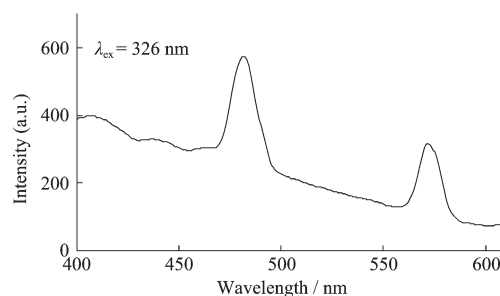


Fig. 4 Fluorescence spectral of the title complex

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