

两种溴代苯甲酸-铽配合物的合成、晶体结构与性质表征

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摘要: 溶液法合成了 2 种配合物 $[\text{Tb}(\text{2-BrBA})_2(\text{CH}_3\text{COO})(\text{2,2'-bipy})]_2$ (**1**) 和 $[\text{Tb}(\text{3-BrBA})_3(\text{2,2'-bipy})]_2 \cdot 2(\text{3-HBrBA}) \cdot 2\text{H}_2\text{O}$ (**2**) ($\text{2-BrBA} = \text{2-bromobenzoate}$, $\text{3-BrBA} = \text{3-bromobenzoate}$, $\text{2,2'-bipy} = \text{2,2'-bipyridine}$), 并用 X-射线单晶衍射方法测定了其晶体结构。配合物 **1** 和 **2** 均属于三斜晶系和 $P\bar{1}$ 空间群。四元混配配合物 **1** 是具有反演中心的二聚体, 其中 Tb^{3+} 离子同时与 2 种不同的羧酸配体配位。4 个 2-BrBA 以双齿桥联的方式把 2 个 Tb^{3+} 离子联结起来, 而乙酸根和 2,2'-bipy 分子则分别以双齿螯合的方式与 Tb^{3+} 离子配位。配合物 **2** 是三元混配配合物, 2 个 Tb^{3+} 离子通过 4 个双齿桥联的 3-BrBA 联结而成具有反演中心的二聚体, 每个 Tb^{3+} 离子还同时与 1 个双齿螯合的 3-BrBA 和 1 个 2,2'-bipy 分子配位。配合物 **1** 和 **2** 在紫外灯照射下能发出强烈的绿光, 而且在它们的荧光光谱中都存在 4 条谱线: 489、545、585 和 621 nm, 分别对应于 Tb^{3+} 离子的 $^5D_4 \rightarrow ^7F_6$ 、 $^5D_4 \rightarrow ^7F_5$ 、 $^5D_4 \rightarrow ^7F_4$ 和 $^5D_4 \rightarrow ^7F_3$ 跃迁。

关键词: 铽配合物; 溴代苯甲酸; 晶体结构; 荧光

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Synthesis, Crystal Structure and Characterization of Two Terbium Complexes with Bromobenzoic Acid

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Abstract: Two complexes of $[\text{Tb}(\text{2-BrBA})_2(\text{CH}_3\text{COO})(\text{2,2'-bipy})]_2$ (**1**) and $[\text{Tb}(\text{3-BrBA})_3(\text{2,2'-bipy})]_2 \cdot 2(\text{3-HBrBA}) \cdot 2\text{H}_2\text{O}$ (**2**) ($\text{2-BrBA} = \text{2-bromobenzoate}$, $\text{3-BrBA} = \text{3-bromobenzoate}$, $\text{2,2'-bipy} = \text{2,2'-bipyridine}$) were synthesized by solvent method and their structures were determined by X-ray single crystal diffraction method. Complexes **1** and **2** both belong to triclinic system and $P\bar{1}$ space group. The complex **1** is a dimer with an inversion center, in which two different carboxylate ligands coordinate to Tb^{3+} ion simultaneously to form quaternary mixed-ligands complex. Four 2-BrBA ligands link the two Tb^{3+} ions by bidentate-bridging mode, two acetate ligands coordinate to two Tb^{3+} ions by bidentate-chelating mode, and two 2,2'-bipy molecules chelate to two Tb^{3+} ion, respectively. The ternary complex **2** is also a dimer with an inversion center, in which the two Tb^{3+} ions are linked by four bidentate-bridging 3-BrBA ligands and each Tb^{3+} ion is further bonded to one bidentate-chelating 3-BrBA ligand and one 2,2'-bipy molecule. The two complexes exhibit strong green fluorescence under ultraviolet light and the fluorescence spectrums of them both have four peaks at 489, 545, 585 and 621 nm corresponding to $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$ and $^5D_4 \rightarrow ^7F_3$ transition emissions of the Tb^{3+} ion, respectively. CCDC: 631975, **1**; 631976, **2**.

Key words: terbium complexes; bromobenzoic acid; crystal structure; fluorescence

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0 Introduction

Most terbium complexes have potential applications in fluorescence materials and electroluminescent devices^[1-4], for emitting intense green fluorescence under ultraviolet light. The luminescence intensity of terbium complexes depends on their ligands, so the selection of a good ligand is very important to design and synthesize a new complex with high quantum yields and thermodynamically stability. Benzoic acid and its derivatives are very popular in the ternary or quaternary complexes of this field, because they are rigid ligands with various coordination modes and can form π - π stacking or hydrogen bonds making the complexes more stable. Furthermore, lanthanide carboxylate complexes with the auxiliary ligand (2,2'-bipyridine or 1,10-phenanthroline) usually have interesting structures, with both high stability and intense fluorescence^[4-10]. It is reported that this type of complexes are usually dimers with an inversion center showing intense fluorescence, in which the center ion often have coordination number of eight or nine and the ligands adopt several coordination modes simultaneously. Although many researches also have been reported about the complexes of fluorobenzoic acid^[5,6] and chlorobenzoic acid^[7] in the literature, reports about the complexes of bromobenzoic acid^[8] or iodobenzoic acid are relatively rare. Our laboratory also has done some work to synthesize a series of complexes of halobenzoic acids with interesting structure^[5,6]. Based on the current situation in this field, we used 2-bromobenzoic acid or 3-bromobenzoic acid and 2,2'-bipyridine as mixed ligands and obtained two terbium complexes, namely $[\text{Tb}(\text{2-BrBA})_2(\text{CH}_3\text{COO})(\text{2,2'-bipy})]_2$ (**1**) and $[\text{Tb}(\text{3-BrBA})_3(\text{2,2'-bipy})]_2 \cdot 2(\text{3-HBrBA}) \cdot 2\text{H}_2\text{O}$ (**2**) (2-BrBA=2-bromobenzoate, 3-BrBA=3-bromobenzoate, 2,2'-bipy=2,2'-bipyridine). In this paper, we report the synthesis, crystal structure, thermal stability and luminescence properties of the two complexes.

1 Experimental

1.1 Reagents and instrumentation

All analytical grade chemicals and solvents were

purchased commercially and used without further purification. $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ was made by the reaction of terbium oxide (99.90%) and hydrochloric acid.

The thermogravimetric analysis was performed on a WCT-1A Thermal Analyzer. The UV spectrum was measured on a TU-1810 Ultraviolet-Visible spectrophotometer. The excitation spectrum and emission spectrum of the solid sample were recorded on an F-4500 Fluorescence Spectrophotometer.

1.2 Synthesis of $[\text{Tb}(\text{2-BrBA})_2(\text{CH}_3\text{COO})(\text{2,2'-bipy})]_2$ (**1**)

1.2 mmol 2-bromobenzoic acid and 0.4 mmol 2,2'-bipy were mixed in 25 mL ethanol, subsequently the mixture was heated with stirring and the pH value was adjusted to be about 5 by 2 mol·L⁻¹ sodium acetate aqueous solution. And then 2 mL ethanol solution of $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ (0.4 mmol) was added into the mixture dropwise. The resulting solution was filtered and the colorless needle-like single crystals suitable for X-ray structural analysis were obtained.

1.3 Synthesis of $[\text{Tb}(\text{3-BrBA})_3(\text{2,2'-bipy})]_2 \cdot 2(\text{3-HBrBA}) \cdot 2\text{H}_2\text{O}$ (**2**)

The synthesis of complex **2** is similar to that of complex **1**, whereas 3-bromobenzoic acid was used instead of 2-bromobenzoic acid and the pH value was adjusted by 2 mol·L⁻¹ NaOH aqueous solution.

1.4 Crystal structure determination of complex

The light single crystals having dimensions of 0.24 mm × 0.20 mm × 0.18 mm for complex **1** and 0.60 mm × 0.20 mm × 0.10 mm for complex **2** were selected for the structural analyses. The data collection was performed at 273(2) K on a Siemens SMART-CCD diffractometer equipped with a graphite monochromatized Mo K α radiation ($\lambda=0.071\,073$ nm). Semi-empirical absorption correction was applied using the SADABS program. The structures were solved by direct methods and refined by full matrix least squares method on F^2 using SHELXS-97 and SHELXL-97 programs, respectively. A summary of the crystallographic data and details of the structure refinements are listed in Table 1. The selected bond lengths and bond angles of complexes **1** and **2** are listed in Table 2 and Table 3, respectively.

CCDC: 631975, **1**; 631976, **2**.

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

Complex	1	2
Empirical formula	C ₅₂ H ₃₈ Br ₄ N ₄ O ₁₂ Tb ₂	C ₇₆ H ₅₄ Br ₃ N ₄ O ₁₈ Tb ₂
Formula weight	1548.32	2268.29
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> / nm	1.026 2(1)	1.182 4(4)
<i>b</i> / nm	1.131 0(2)	1.228 2(4)
<i>c</i> / nm	1.180 1(2)	1.440 6(5)
α / (°)	69.22(1)	104.51(2)
β / (°)	80.33(1)	94.68(2)
γ / (°)	74.43(1)	98.88(2)
Volume / nm ³	1.229 6(3)	1.985 3(1)
<i>Z</i>	1	1
Calculated density / (Mg·m ⁻³)	2.091	1.897
Absorption coefficient / mm ⁻¹	6.172	5.862
<i>F</i> (000)	744	1092
Crystal size / mm	0.24 × 0.20 × 0.18	0.60 × 0.20 × 0.10
θ range for data collection / (°)	1.85 to 28.31	1.74 to 28.32
Limiting indices	$-13 \leq h \leq 13, -15 \leq k \leq 15, -15 \leq l \leq 15$	$-15 \leq h \leq 15, -15 \leq k \leq 16, 19 \leq l \leq 18$
Reflections collected / unique	18 888 / 6 041 ($R_{\text{int}}=0.059$ 3)	25 070 / 9 790 ($R_{\text{int}}=0.033$ 5)
Completeness to $\theta=28.31^\circ$ / %	98.6	97.8
Data / restraints / parameters	6 041 / 0 / 335	9 790 / 2 / 496
Goodness-of-fit on F^2	1.005	1.013
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1=0.035$ 4, $wR_2=0.083$ 6	$R_1=0.043$ 2, $wR_2=0.106$ 8
<i>R</i> indices (all data)	$R_1=0.044$ 4, $wR_2=0.085$ 9	$R_1=0.067$ 0, $wR_2=0.117$ 0
Largest diff. peak and hole / (e·nm ⁻³)	901 and -728	978 and -633

Table 2 Bond lengths (nm) and angles (°) for complex 1

Tb(1)-O(1)	0.231 5(3)	Tb(1)-N(1)	0.253 4(4)	Tb(1)-O(6)	0.256 1(3)
Tb(1)-O(3)	0.233 3(3)	Tb(1)-O(2)#1	0.231 9(3)	Tb(1)-N(2)	0.257 9(3)
Tb(1)-O(5)	0.245 6(3)	Tb(1)-O(4)#1	0.229 6(3)		
O(4)#1-Tb(1)-O(1)	80.47(12)	O(2)#1-Tb(1)-O(6)	133.12(12)	O(3)-Tb(1)-O(5)	145.04(11)
O(1)-Tb(1)-O(2)#1	128.12(11)	O(5)-Tb(1)-O(6)	50.37(11)	O(1)-Tb(1)-O(6)	75.31(12)
O(1)-Tb(1)-O(3)	76.86(12)	O(4)#1-Tb(1)-O(2)#1	73.22(12)	O(3)-Tb(1)-O(6)	143.18(12)
O(4)#1-Tb(1)-O(5)	87.23(13)	O(4)#1-Tb(1)-O(3)	125.67(13)	N(1)-Tb(1)-N(2)	63.93(11)
O(2)#1-Tb(1)-O(5)	97.42(12)	O(2)#1-Tb(1)-O(3)	83.39(12)		
O(4)#1-Tb(1)-O(6)	72.34(13)	O(1)-Tb(1)-O(5)	125.41(11)		

Symmetry transformations used to generate equivalent atoms: #1: $-x+1, -y, -z+1$.

Table 3 Bond lengths (nm) and angles (°) for complex 2

Tb(1)-O(1)	0.243 2(3)	Tb(1)-N(1)	0.258 7(4)	Tb(1)-O(6)#1	0.233 9(3)
Tb(1)-O(3)	0.235 2(3)	Tb(1)-O(2)	0.245 2(3)	Tb(1)-N(2)	0.256 6(4)
Tb(1)-O(5)	0.232 2(3)	Tb(1)-O(4)#1	0.229 0(3)		
O(4)#1-Tb(1)-O(5)	80.29(12)	O(6)#1-Tb(1)-O(2)	76.54(12)	O(3)-Tb(1)-O(1)	81.75(12)

Continued Table 3

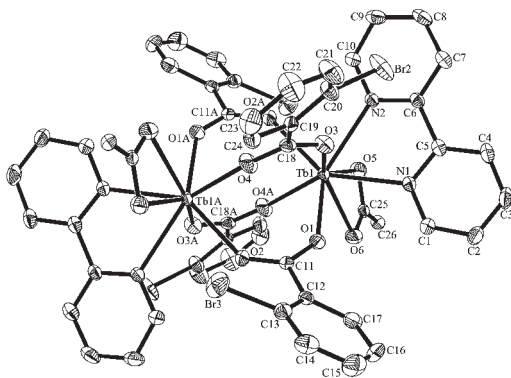
O(5)-Tb(1)-O(6)#1	128.02(12)	O(1)-Tb(1)-O(2)	53.69(12)	(5) O -Tb(1)-O(2)	145.82(12)
O(5)-Tb(1)-O(3)	79.88(12)	O(4)#1-Tb(1)-O(6)#1	76.60(13)	O(3)-Tb(1)-O(2)	133.07(11)
O(4) #1-Tb(1)-O(1)	132.59(12)	O(4) #1-Tb(1)-O(3)	125.79(12)	N(2)-Tb(1)-N(1)	62.58(14)
O(6) #1-Tb(1)-O(1)	73.40(12)	O(6) #1-Tb(1)-O(3)	77.24(13)		
O(4) #1-Tb(1)-O(2)	84.23 (12)	O(5)-Tb(1)-O(1)	146.83(4)		

Symmetry transformations used to generate equivalent atoms: #1: $-x+1, -y, -z+1$.

2 Results and discussion

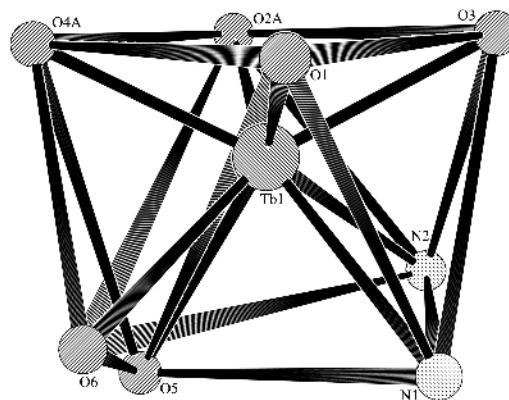
2.1 Crystal structure of $[\text{Tb}(\text{2-BrBA})_2(\text{CH}_3\text{COO})(\text{2,2'-bipy})]_2$ (**1**)

The crystal structure of complex **1** is shown in Fig.1a. The complex **1** is a dimer with an inversion center, in which two different carboxylate ligands coordinate to Tb^{3+} ion simultaneously to form quaternary mixed-ligands complex. The 2-BrBA groups (O1-C11-O2 and O3-C18-O4) link two Tb^{3+} ions in bidentate-bridging mode and the distance of $\text{Tb1} \cdots \text{Tb1A}$ is 0.422 1 nm. While the acetate group (O5-C25-O6) coordinates to Tb^{3+} ion in bidentate-chelating mode and the 2,2'-bipy ligand coordinates to the Tb^{3+} ion in conventional chelating mode with two N atoms forming a five-membered ring. Therefore, each Tb^{3+} ion is coordinated by six O atoms and two N atoms, and the eight atoms form a distorted square-antiprism (Fig.1b). The upper and lower planes of the square-antiprism are structured by O1, O2A, O3, O4A and N1, N2, O5, O6, respectively, with a dihedral angle of 3.8° between them. And the mean deviation from the upper and lower plane is 0.002 27 nm and 0.028 36 nm, respectively.

Fig.1a Molecular structure of complex **1**

The molecular structure of complex **1** is similar

to that of majority ternary complexes containing benzoic acid or its derivatives and 2,2'-bipy or 1,10-phenanthroline^[4,6,9]. However, the complex **1** is different from the complex $[\text{Tb}(\text{2-FBA})_3 \cdot \text{2,2'-bipy}]_2$ (2-FBA=2-Fluorobenzoate)^[5], which contains three independent molecules in the asymmetric unit.

Fig.1b Coordination geometry of Tb^{3+} ion in complex **1**

In complex **1**, the bond lengths of Tb1-O range from 0.229 6 (3) to 0.256 1 (3) nm, and the average bond length is 0.238 0 nm. The bond angles of O-Tb1-O vary in the range of $50.37(11)^\circ \sim 145.04(11)^\circ$. The average bond lengths of Tb1-N is 0.255 7 nm and the bond angle of N-Tb1-N is $63.93(11)^\circ$.

2.2 Crystal structure of $[\text{Tb}(\text{3-BrBA})_3(\text{2,2'-bipy})]_2 \cdot \text{2(3-HBrBA)} \cdot \text{2H}_2\text{O}$ (**2**)

The crystal structure of complex **2** is shown in Fig.2a. The complex **2** is a dimer with an inversion center and the distance of $\text{Tb1} \cdots \text{Tb1A}$ is 0.416 6 nm. The two Tb^{3+} ions are held together by four 3-BrBA ligands in bidentate-bridging mode, with each Tb^{3+} ion further bonding to one 3-BrBA ligand and one 2,2'-bipy molecule. The coordination environment of Tb^{3+} ion can be described as a distorted square-antiprism, in which atoms O3, O4A, O5, O6A and O1, O2, N1, N2 form its two planes. The mean deviation from the

upper and lower plane is 0.001 67 nm and 0.002 72 nm, respectively, and the dihedral angle between the two planes is 2.0° (Fig.2b). The molecule structure of the complex **2** is different from that of complexes $[\text{Eu}(\text{3-ClBA})_3(\text{phen})]_2$ ^[7] and $[\text{Eu}(\text{3-BrBA})_3(\text{H}_2\text{O})(\text{phen})]_2$ ^[8] (3-ClBA=3-chlorobenzoate, 3-BrBA=3-bromobenzoate and phen=1,10-phenanthroline). In $[\text{Eu}(\text{3-ClBA})_3(\text{phen})]_2$, each Eu^{3+} ion is nine-coordinated by one phen molecule, one bidentate 3-ClBA group and four bridging 3-ClBA groups. In $[\text{Eu}(\text{3-BrBA})_3(\text{H}_2\text{O})(\text{phen})]_2$, one phen molecule, one monodentate 3-BrBA group, one water molecule, and four bridging 3-BrBA groups bond the Eu^{3+} ion to form eight-coordinated. Therefore, the molecule structure of the complex is related to the substitute and its position on the benzene ring.

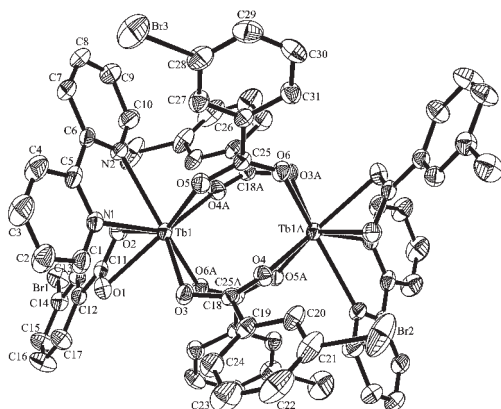


Fig.2a Molecular structure of complex **2**

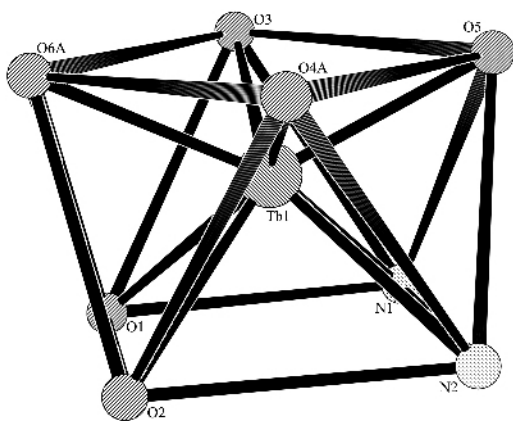


Fig.2b Coordination geometry of Tb^{3+} ion in complex **2**

In complex **2**, the average bond lengths of Tb1-O and Tb1-N are 0.236 5 and 0.257 7 nm, respectively. The bond angles of O-Tb1-O range from $53.69(12)^\circ$ to $146.83(14)^\circ$ and that of N-Tb1-N is $62.58(14)^\circ$. In addition, free 3-HBrBA ligands and water molecules ex-

ist in the crystal lattice of complex **2**. So the hydrogen bonds form among free 3-HBrBA ligands and water molecules: $\text{O7-H7A} \cdots \text{O1W}$ (175.27° , 0.257 2 nm) and $\text{O1W-H1WA} \cdots \text{O8}$ [$-x+1, -y+1, -z+1$] (150.44° , 0.274 1 nm) (Fig.2c).

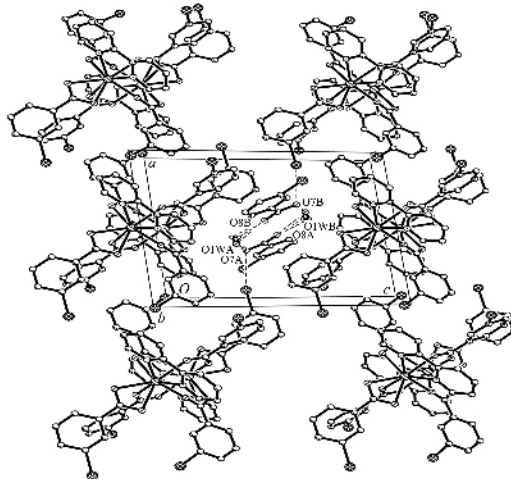


Fig.2c Packing diagram of complex **2** in a cell

2.3 Thermogravimetric analysis

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

The TG-DTA curve exhibits that the complex **1** decomposes step by step. A weight loss of 7.17% at 108°C equivalents to the removal of two acetates (calculated: 7.63%), the second one of about 20.17% at 246°C is ascribed to the release of two 2,2'-bipy molecules (calculated: 20.17%). There is a big exothermic peak at 550°C . The residue Tb_4O_7 was obtained, corresponding to the total loss of 86.92% (calculated: 87.93%).

In the TG-DTA curve of complex **2**, there are two endothermic peaks at 138°C and 207°C , respectively. Besides that, there is also a big exothermic peak at 573°C . The first weight loss of 33.04% responds to the removal of the two water, two 3-HBrBA and two 2,2'-bipy molecules (calculated: 33.08%). Tb_4O_7 was the last residue, paralleling to the total loss of 83.04% (calculated: 83.52%).

2.4 Photophysical properties

The UV spectrum of complexes **1** and **2** ($10^{-4} \text{ mol} \cdot \text{L}^{-1}$, DMF solution) suggests the band of 287.0 nm ($\epsilon=2.232 \times 10^4$) and 285.0 nm ($\epsilon=2.004 \times 10^4$) can be

mostly attributed to $\pi \rightarrow \pi^*$ transition of the ligands, which indicates that the ligand can transfer the absorption energy to the Tb^{3+} ion.

The solid sample of complexes **1** and **2** emit intense green fluorescence under ultraviolet light. Their excitation spectrum was recorded in the range of 200~400 nm, setting 545 nm as the emission wavelength. The emission spectrum of the solid-state was observed

in the range of 450~700 nm under the excitation wavelength of 324 nm for complex **1** and 315 nm for complex **2**, in which there are four main peaks, 489 nm, 545, 585 and 621 nm, corresponding to $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$ and $^5D_4 \rightarrow ^7F_3$ transition emissions of the Tb^{3+} ion, respectively. The most intense emission both appear at 545 nm corresponding to $^5D_4 \rightarrow ^7F_5$ (Fig.3).

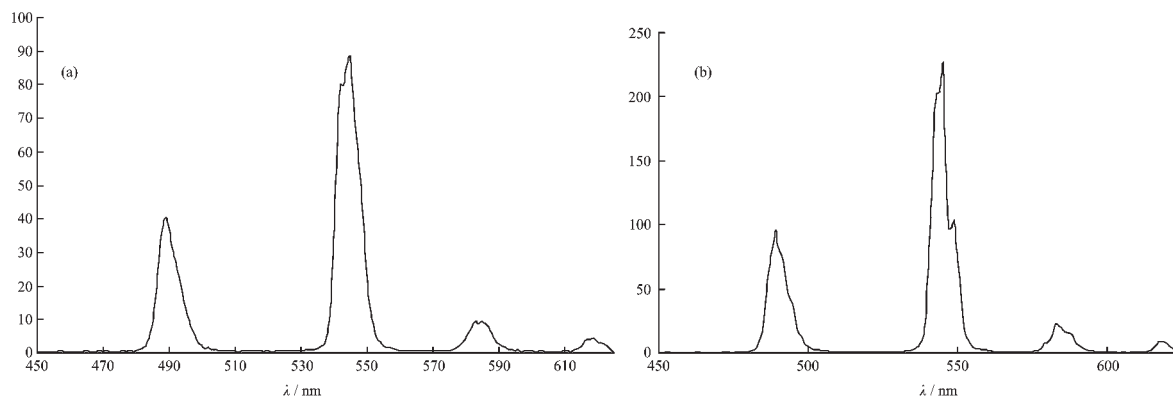


Fig.3 Fluorescence spectral of complex **1** (a) (λ_{ex} =324 nm) and complex **2** (b) (λ_{ex} =315 nm)

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