

# Synthesis and Fluorescence Properties of Lanthanide (III) Perchlorate Complexes with Bis(benzoylmethyl) Sulfoxide

Wen-Xian Li · Lei Guo · Li-Juan Chen · Xiao-Yan Shi

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**Abstract** A ligand with two carbonyl groups and one sulfinyl group has been synthesized by a new method and its several lanthanide (III) complexes were synthesized and characterized by element analysis, molar conductivity, coordination titration analysis, IR, TG-DSC,  $^1\text{H}$  NMR and UV spectra. The results indicated that the composition of these complexes is  $\text{RE}_5(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$  (RE=La(III), Pr(III), Eu(III), Tb(III), Yb(III),  $\text{L}=\text{C}_6\text{H}_5\text{COCH}_2\text{SOCH}_2\text{COC}_6\text{H}_5$ ). The fluorescent spectra illustrate that both the Tb (III) and Eu (III) complexes display characteristic metal-centered fluorescence in solid state, indicating the ligand favors energy transfer to the excitation state energy level of them. However, the Tb (III) complex displays more effective luminescence than the Eu (III) complex, which is attributed to especial effectively in transferring energy from the average triplet energy level of the ligands (T) onto the excited state ( $^5\text{D}_4$ ) of Tb (III) than that ( $^5\text{D}_0$ ) of Eu (III), showing a good antenna effect for Tb (III) luminescence. The phosphorescence spectra and the relationship between fluorescence lifetimes and fluorescence intensities were also discussed.

**Keywords** Rare earth complexes · Fluorescence · Phosphorescence · Fluorescence lifetime · Bis(benzoylmethyl) sulfoxide

## Introduction

In the last decades many rare earth complexes have attracted much attention due to their long fluorescence

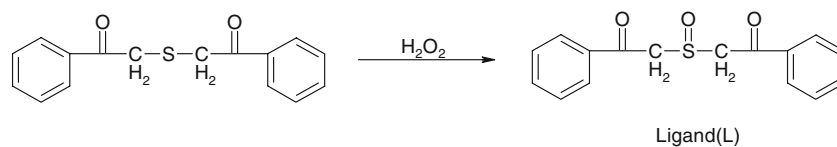
lifetimes and strong fluorescence emissions. These complexes have been used in many areas, such as fluorescence materials [1–3], electroluminescence devices [4–7] and as fluorescence probes and labels in a variety of biological systems [8–11]. Among these studies, the luminescence properties of rare earth complexes are of special interest because these complexes could show narrow emission bands, a large Stokes' shift and long luminescence decay time.

The intra-configuration 4f–4f transitions in rare earth ions are parity forbidden (Laporte rule), consequently the absorption and emission spectra of the RE (III) ions show weak intensity. However, the population of the excited states of the RE (III) ions may be increased by coordination to organic ligands, which act as sensitizers [12]. The ligands that present this property were called by Lehn [13] as “antennas”. In RE (III)-complex, the organic ligand absorbs and transfers energy efficiently to the metal ion (intra-molecular energy transfer) and consequently increases its luminescence intensity.

So based on the different ligands and the central RE (III), many fluorescent complexes have been synthesized. The main ligands include aromatic carboxylic acid, 1, 10-phenanthroline (phen), pyridine and  $\beta$ -diketon [14–16]. Because of good coordination abilities and solubilities, many sulfoxide complexes were intensely studied in the past several decades [17, 18]. Then they also become one important group for strong sensitized luminescence of RE (III) ions. So we synthesized a novel ligand bis(benzoylmethyl) sulfoxide with two carbonyl groups, which has large conjugated plane and rigid structure. In this paper, the highly luminescent complexes were synthesized and characterized. At the same time, we studied the luminescence properties of the complexes in the solid state.

W.-X. Li (✉) · L. Guo · L.-J. Chen · X.-Y. Shi  
College of Chemistry and Chemical Engineering,  
Inner Mongolia University,  
Hohhot 010021, People's Republic of China  
e-mail: ndleiguo@163.com

**Fig. 1** The synthesis route of the ligand



## Experimental

### Reagents and apparatus

The purity of lanthanide oxide exceeds 99.99%, the rare earth perchlorates were prepared by dissolving the oxide (99.99%) in  $\text{HClO}_4$  (2 mol/l). All other chemicals were of analytical reagent grade. Carbon, hydrogen analyses were determined by PE-2400 elemental analyses instrument. Rare earth contents of the complexes were determined by EDTA titration using Xylenol-orange as an indicator. Conductivity measurements were made using a  $10^{-3}$  mol  $\text{l}^{-1}$  solution in acetone on a DDS-11D conductivity meter at room temperature. The thermal behavior was monitored on SDTQ600 differential scanning calorimeter and thermal-gravimetric analyzer. IR spectra were recorded on KBr disk using NEXUS-670 FT spectrometer in  $400\text{--}4,000\text{ cm}^{-1}$  region. The ultraviolet spectra (190–400 nm) of the ligand and its complexes were recorded on a Shimadzu UV-265 spectrophotometer and DMSO was used as a reference solvent (concentrations:  $5 \times 10^{-5}$  mol/l).  $^1\text{H}$  NMR spectra were measured by BrukerAC-300 instrument in  $\text{DMSO-d}_6$ . The fluorescence spectra were determined by Hitachi F-3010 fluorescence photometer. The phosphorescence spectra were measured by SPEX1934D phosphorescence photometer at room temperature. Fluorescent decay curves were determined by FLS920 Combined Steady State and Lifetime Spectrometer.

### Synthesis of the ligand

The synthesis route of the ligand was expressed in Fig. 1.

Bis(benzoylmethyl) sulfide was synthesized according to the method of Shriner et al. [19].

$\alpha$ -Bromoacetophenone was dissolved in alcohol. Then the sodium sulfide which had been dissolved in distilled water was added. The mixture was stirred continuously at room temperature for two hours. The solution was poured directly on cracked ice. A white solid was precipitated, filtered and dried in vacuum. The sulfide was a white crystalline substance which was purified by recrystallization from alcohol. Yield: 60–70%. mp: 73–74 °C, anal. calcd. For  $\text{C}_{16}\text{H}_{14}\text{SO}_2$ : C, 71.1%; H, 5.19%; found: C, 70.45%; H, 5.15%.

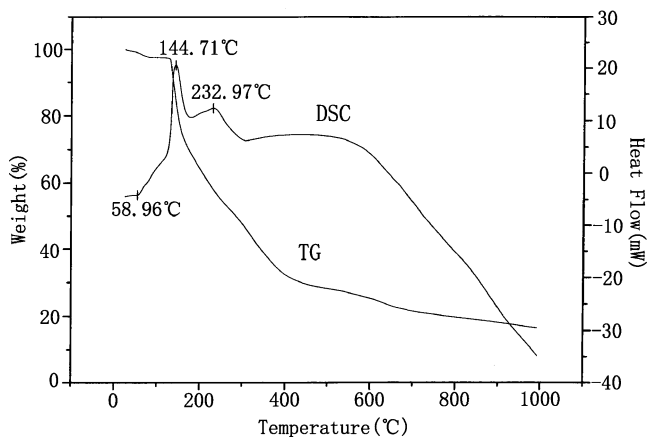
Bis(benzoylmethyl) sulfoxide was dissolved in acetic acid, then 30% hydrogen peroxide was added to it at once. The mixture was stirred continuously at room temperature for 24 h. After the reaction stopped, the mixture was extracted with ether until the pH of mixture was 7. Then a white solid was precipitated, filtered and dried in vacuum. Yield: 95%. mp: 110–111 °C. Anal. calcd. For  $\text{C}_{16}\text{H}_{14}\text{SO}_3$ : C, 67.1%; H, 4.90%; found: C, 66.6%; H, 4.68%.

### Preparation of the complexes

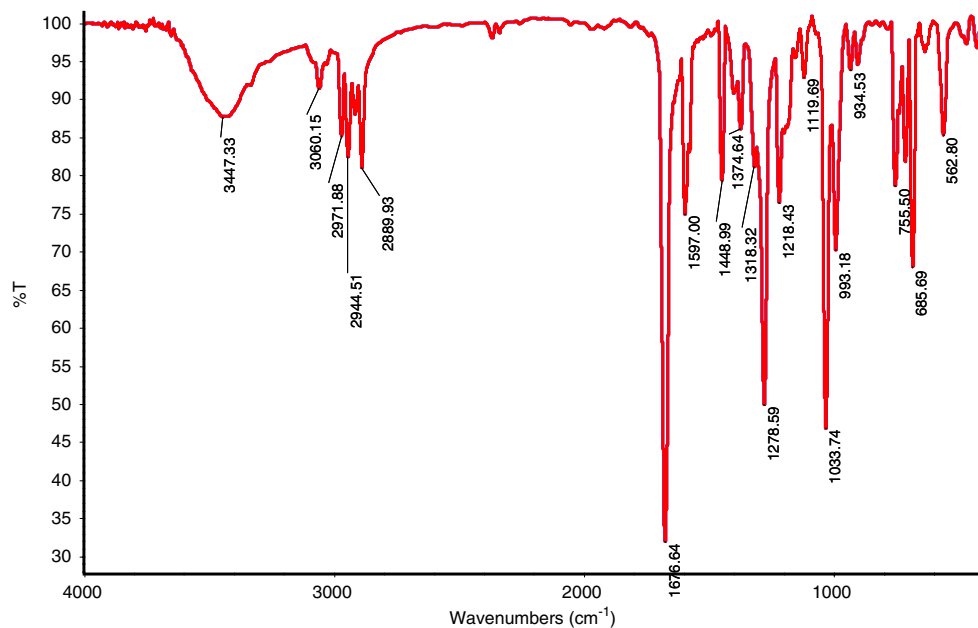
To a solution of L (5 mmol) in anhydrous ethanol, an anhydrous ethanol solution containing 1mmol of rare earth perchlorates was added dropwise with stirring. After a few minutes a white precipitate formed. The mixture was stirred for 0.5 h and precipitate was filtered. The products were

**Table 1** Elemental analyses and molar conductivity values for the complexes

Complexes	<i>M</i>	Anal. calcd.(found)(%)			$\lambda_m$ ( $\text{Scm}^2$ $\text{mol}^{-1}$ )
		C	H	RE	
$\text{LaL}_5(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$	1,921.4	49.96 (49.77)	3.96 (3.94)	7.23 (7.43)	160.3
$\text{PrL}_5(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$	1,923.4	49.91 (49.57)	3.95 (3.70)	7.33 (7.15)	156.4
$\text{EuL}_5(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$	1,934.5	49.63 (49.85)	3.93 (3.71)	7.86 (7.45)	150.9
$\text{TbL}_5(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$	1,941.4	49.45 (49.60)	3.91 (3.71)	8.19 (8.34)	155.4
$\text{YbL}_5(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$	1,955.5	49.09 (48.77)	3.89 (3.70)	8.85 (8.49)	164.0



**Fig. 2** TG-DSC curves of  $\text{PrL}_5(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$

**Fig. 3** IR absorption spectrum of ligand

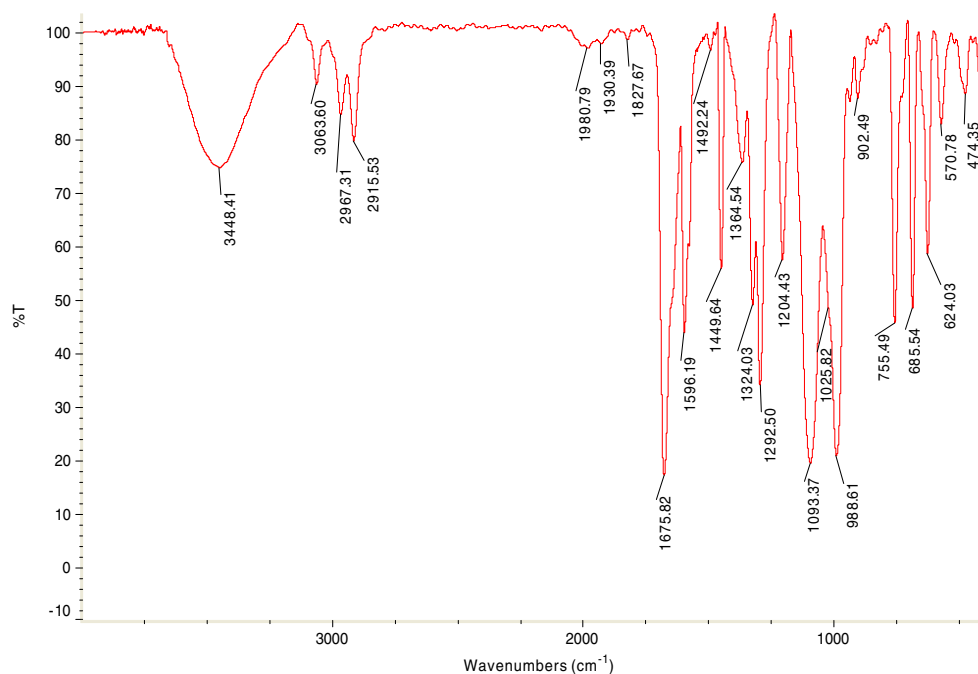
washed with ether for several times, and then dried in vacuum to give the complexes as a white powder. (yield > 90%)

## Results and discussion

Analytical data for the complexes, presented in Table 1, conform to  $REL_5(ClO_4)_3 \cdot 3H_2O$ . All the complexes are white powder like, stable in atmospheric condition and soluble in acetone, DMF and DMSO. The molar conductivity values of the complexes in acetone are in accord with them being formulated as 1:1 electrolytes [20].

## TG-DSC studies

The TG-DSC analyses were carried out up to 1,000 °C in  $N_2$  at a heating rate of 10 °C  $min^{-1}$ . All the TG-DSC curves of rare earth (III) complexes are similar. The curve of Pr (III) complex is depicted in Fig. 2. The TG curve of complex shows a first mass loss between 57.96 and 77.02 °C with 2.73%, respectively, which corresponds very well to release of all the three water content (2.81%). The relatively low temperature of water loss shows that they are crystal water [21]. At the same time, DSC curve show small endothermic peak at 58.96 °C when losing water. In addition, there are

**Fig. 4** IR absorption spectrum of  $PrL_5(ClO_4)_3 \cdot 3H_2O$ 

**Table 2** Some main IR data of ligand and its complexes

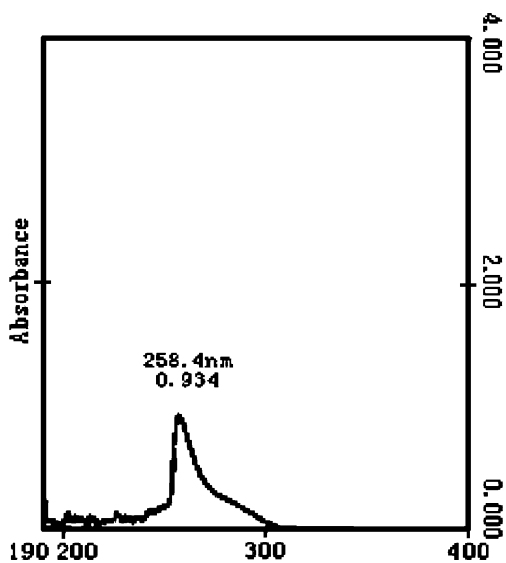
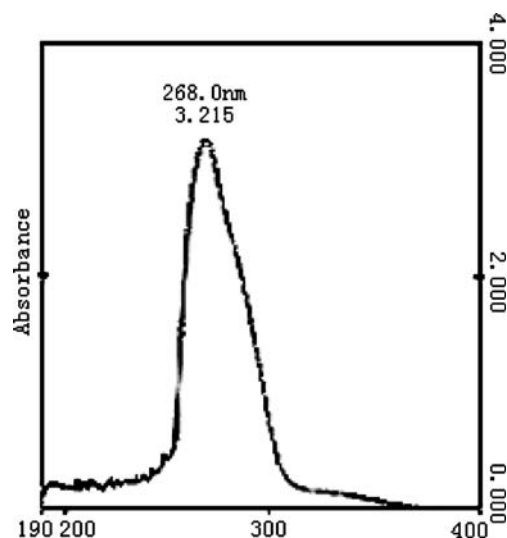
Assignment (cm <sup>-1</sup> )	Ligand	La	Pr	Eu	Tb	Yb
$\nu_{\text{O-H}}(\text{H}_2\text{O})$		3,444	3,448	3,444	3,447	3,446
$\nu_{\text{C=C}}(\text{C}_6\text{H}_5)$	1,597	1,595	1,596	1,596	1,596	1,596
$\nu_{\text{C-H}}(\text{C}_6\text{H}_5)$	3,060	3,063	3,063	3,063	3,063	3,063
$\delta_{\text{C-H}}(\text{C}_6\text{H}_5)$	755	755	755	755	755	755
	685	684	685	685	685	685
$\nu_{\text{S=O}}$	1,033	988	988	989	988	989
$\nu_{\text{C=O}}$	1,676	1,676	1,675	1,675	1,675	1,676
$\nu_{\text{C-H}}(\text{CH}_2)$	2,971	2,969	2,967	2,967	2,967	2,968
$\delta_{\text{C-H}}(\text{CH}_2)$	1448	1,448	1,449	1,449	1,449	1,449
$\nu_{\text{Cl-O}}(\text{ClO}_4^-)$	–	1,094	1,092	1,094	1,094	1,094
	–	1,020	1,025	1,025	1,020	1,020
$\delta(\text{ClO}_4^-)$	–	622	624	623	624	623
	–	476	474	475	476	475

two exothermic peaks in DSC curve which are attributed to the decomposition of five ligands, as well as two obvious weight losses occurring on the TG curve. The final product was found to be  $\text{RE}_2\text{O}_3$  ( $\text{RE}_4\text{O}_7$  for Tb) [22] when the temperature was near 1,000 °C, and the total weight loss of the complexes was found to be close to the calculated values. The results are consistent with element analyses.

#### Infrared spectra

The most important IR assignments in the spectra of the ligand and the complexes can be seen in the Figs. 3 and 4 and Table 2.

In the IR spectra of complexes, compared with IR spectrum of the ligand, some absorption bands have

**Fig. 5** UV Spectrum of  $\text{C}_6\text{H}_5\text{COCH}_2\text{SOCH}_2\text{COC}_6\text{H}_5$ **Fig. 6** UV Spectrum of  $\text{TbL}_5(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ 

shifted. It is showed that rare earth ions are bonded with the ligand.

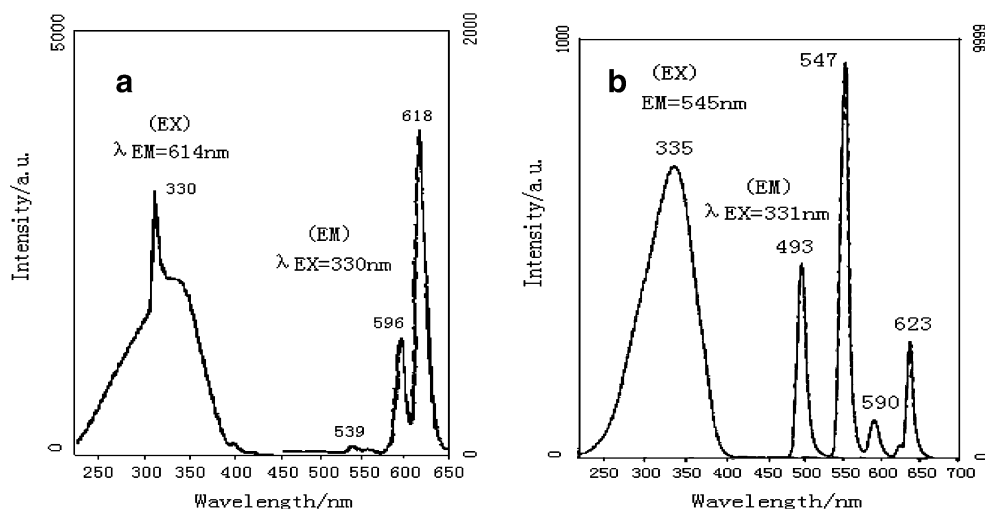
In the ligand IR spectra, the S=O group stretching modes appears at 1,033  $\text{cm}^{-1}$ . However, the S=O stretching frequency of the complexes shift to a lower wave number by 44–45  $\text{cm}^{-1}$ , it suggests that rare earth ions are bonded with oxygen atom in sulfinyl group. The C=O stretching frequency of the ligand appears at 1,676  $\text{cm}^{-1}$  as the strongest absorption in IR spectra. After coordination, there is no significant shift, which suggests that the oxygen atoms in carbonyl group are not coordinated to rare earth ions.

In the IR spectrum of the ligand the absorptions of phenyl group appear at 3,060  $\text{cm}^{-1}$  ( $\nu_{\text{C-H}}$ ), 1,597  $\text{cm}^{-1}$  ( $\nu_{\text{C=C}}$ ), 755  $\text{cm}^{-1}$  ( $\delta_{\text{C-H}}$ ), 685  $\text{cm}^{-1}$  ( $\delta_{\text{C-H}}$ ). These absorption bands have no significant shift in the complexes indicates that phenyl is not coordinated. In addition, there are four additional peaks about 1,092–1,094, 1,020–1,025, 622–624 and 474–476  $\text{cm}^{-1}$ , both of them are attributed to the  $\text{ClO}_4^-$  group. When  $\text{ClO}_4^-$  isn't coordinated, it is Td symmetry and there are two absorptions. When  $\text{ClO}_4^-$  is coordinated, it is  $\text{C}_{3v}$  symmetry and there are five absorptions [23, 24]. In the IR spectra of the complexes, four absorptions can be seen clearly. So  $\text{ClO}_4^-$  isn't all with

**Table 3** Chemical shift data of  $^1\text{H}$ NMR Spectra ( $1 \times 10^{-6}$ )

Ligand and complexes	$^1\text{H}$ NMR (ppm)	
	$-\text{CH}_2-(\times 2)$	$-\text{C}_6\text{H}_5(\times 2)$
$\text{C}_6\text{H}_5\text{COCH}_2\text{SOCH}_2\text{COC}_6\text{H}_5(\text{L})$	4.421~4.820 (s, 4 H)	7.509~8.025 (m, 10 H)
$\text{LaL}_5(\text{ClO}_4)_3 \cdot 3 \text{H}_2\text{O}$	4.816(s, 4 H)	7.560~8.039(m, 10 H)
$\text{PrL}_5(\text{ClO}_4)_3 \cdot 3 \text{H}_2\text{O}$	4.818 (s,4 H)	7.561~8.042 (m, 10 H)
$\text{EuL}_5(\text{ClO}_4)_3 \cdot 3 \text{H}_2\text{O}$	4.823 (s, 4 H)	7.564~8.045(m,10 H)
$\text{TbL}_5(\text{ClO}_4)_3 \cdot 3 \text{H}_2\text{O}$	4.818 (s,4 H)	7.584~8.040 (m,10 H)
$\text{YbL}_5(\text{ClO}_4)_3 \cdot 3 \text{H}_2\text{O}$	4.821(s, 4 H)	7.563~8.044 (m,10 H)

**Fig. 7** Excitation and emission spectra of the Eu(III) complex (a) and the Tb(III) complex (b) in solid state at room temperature



the Td symmetry and some of them should have  $C_{3v}$  symmetry. In terms with the molar conductivities, it can be induced that two  $ClO_4^-$  are bonded with RE (III) through oxygen atom respectively.

#### UV spectra

The UV spectra of the ligand and Tb (III) complex can be seen in Figs. 5 and 6. The free ligand exhibits one absorption band at 258.4 nm, which is attributed to  $\pi \rightarrow \pi^*$  transition. In the spectra of the complexes the band is shifted to 267–270 nm. This indicates that complexes are formed and the conjugated system is increased after coordinating with the RE (III) ions [25].

#### $^1H$ NMR spectra

The  $^1H$  NMR spectra data of the ligand and its complexes can be seen from the Table 3. The  $^1H$  NMR of the ligand in DMSO- $d_6$  shows the proton of two phenyl group's

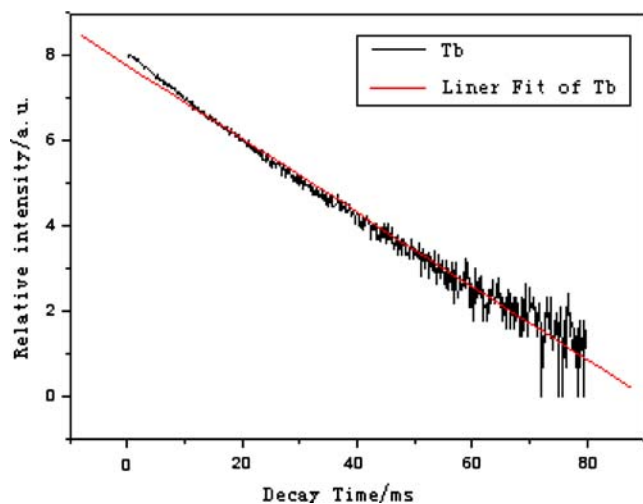
resonances is multiple peaks at  $\delta$  7.509–8.025 ppm, and integral intensity shows it has ten protons; The proton of two methylene group's resonances peak is at  $\delta$  4.421–4.820 ppm, and integral intensity shows it has four protons.

The  $^1H$  NMR spectra of the complexes are similar. The protons of phenyl and methylene group resonances peaks are all clear, and all shift to a lower field at different degrees. The result indicated the sulfinyl group's oxygen of ligand coordinated with rare earth ions, which produced the remove shielded effect, it led to the proton resonances peaks shifting to a lower field.

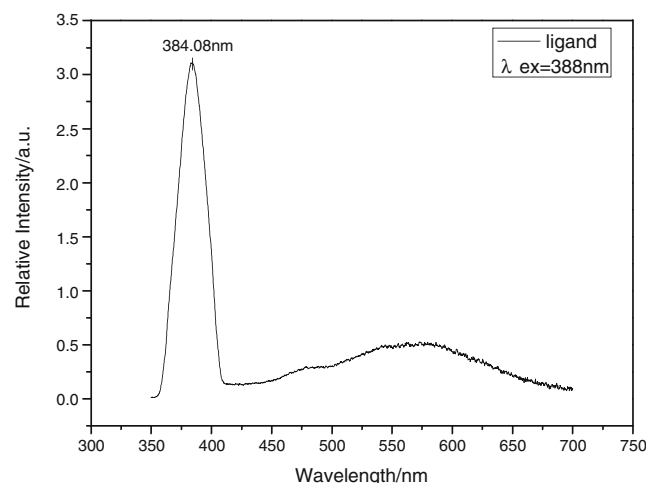
#### Fluorescence spectra

The excitation spectra and emission spectra of Eu(III), Tb (III) complexes in solid state at room temperature are measured. According to the spectra of complexes that are reported in Fig. 7, we can see that the complex has excellent luminescent property.

In the spectra of Tb(III) and Eu(III) complexes (Fig. 7), the wide excitation band, from about 250–450 nm, and the



**Fig. 8** Fluorescence fitted curve of  $Tb^{3+}$  complex



**Fig. 9** Phosphorescence spectrum of ligand

strong emission intensities indicate that the ligand is a good organic ligand to absorb energy and transfer them to RE (III) ion, emitting the characteristic fluorescence of them.

For Eu(III) complex, the emission spectra show three emission peaks under the excitation of 330 nm: 539 nm ( $^5D_1-^7F_0$ ), 596 nm ( $^5D_0-^7F_1$ ), 618 nm ( $^5D_0-^7F_2$ ), corresponded with the characteristic emission for the  $^5D_0-^7F_J$  transition ( $J=0-4$ ) of the Eu(III) ion. Among the red luminescence intensity of  $^5D_0-^7F_2$  transition is the strongest. The  $^5D_0-^7F_2$  transition is an electric dipole transition; it can be detected as a relatively strong peak when Eu (III) does not lie in centrosymmetric ligand field. The  $^5D_1$  transition is a magnetic dipole transition, and its fluorescence intensity becomes the most intensive only when Eu (III) ion is the center of inversion [26]. Also, the intensity ratio of the two lines ( $^5D_0 \rightarrow ^7F_2 / ^5D_0 \rightarrow ^7F_1$ ) is about 2.79, which indicates that the RE (III) ion is not at the center of an asymmetric coordination field. For Tb (III) complex, the emission spectra show four emission peaks under the excitation of 331 nm: 493 nm ( $^5D_4-^7F_6$ ), 547 nm ( $^5D_4-^7F_5$ ), 590 nm ( $^5D_4-^7F_4$ ), 623 nm ( $^5D_4-^7F_3$ ), attributed to be the characteristic emission for the  $^5D_4-^7F_J$  transition ( $J=6-3$ ) of the Tb(III) ion. Among the  $^5D_4-^7F_5$  transition exhibits the strongest green emission, and  $^5D_4-^7F_6$  transition shows the second strongest emission. Both of two complexes show a good antenna effect for Eu(III), Tb(III) luminescence, it means the triplet energy level of the ligand matched as well with the 4f ( $^5D_0$ ) excited state energy level of Eu(III) and the 4f ( $^5D_4$ ) excited state energy level of Tb (III). Because the  $^5D_4$  excited state energy level of terbium ion is higher than the  $^5D_0$  excited state energy level of the europium ion. This effect results in the more energy transfer efficiency from the ligand to the terbium ion, and the stronger fluorescent intensity of the terbium complex. In order to study the relationship between fluorescence intensity and fluorescence lifetime, we measured the fluorescence decay curve of Eu (III) and Tb (III) complexes. Figure 8 shows the fitted curve of Tb (III) complex. The lifetime values of Eu(III), Tb(III) complexes are calculated by the single exponential mode. From the results, the fluorescence lifetime of Tb (III) complex (1,159  $\mu$ s) is longer than that of Eu (III) complex (1,107  $\mu$ s).

#### Phosphorescence properties of ligand

The phosphorescence spectrum of ligand was measured by SPEX1934D phosphorescence photometer in the solid state at room temperature (Fig. 9). According to the energy transfer and intramolecular energy mechanism [27, 28], intramolecular energy transfer efficiency depends chiefly on two energy transfer processes: the first one leads from the triplet level of ligands to the emissive energy level of the  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ion by Dexter's resonant exchange

interaction [29]; the second one is just an inverse energy transfer by a thermal deactivation mechanism [30]. Established on this theory, the conclusion can be drawn that energy differences is of opposite influence on the two energy transfer processes and an optimal value can be assumed to exist. The peak at 475 nm shows ligand's triplet state energy level is approximately  $21,053 \text{ cm}^{-1}$ . It is higher than  $^5D_4$  of Tb (III) ion ( $20430 \text{ cm}^{-1}$ ) [31] and  $^5D_0$  of Eu (III) ion ( $1,7241 \text{ cm}^{-1}$ ) [32]. From these energy differences, it can be seen that ligand can sensitize the two lanthanide ions effectively.

#### Conclusion

The novel ligand and its complexes were synthesized and characterized. Composition of these complexes are revealed to be  $\text{REL}_5(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$  (RE=La(III), Pr(III), Eu(III), Tb (III), Yb(III), L= $\text{C}_6\text{H}_5\text{COCH}_2\text{SOCH}_2\text{COC}_6\text{H}_5$ ). The photo-physical properties of them have been studied with ultraviolet spectra, phosphorescence spectra, excitation and emission, and fluorescence lifetimes. As we expected, the ligand has a suitable conjugated system to efficiently sensitize RE (III) ion fluorescence. The fluorescence spectra show that both Eu (III) and Tb (III) complexes display characteristic RE (III) ion fluorescence. Meanwhile, Tb (III) complex exhibits stronger fluorescence than of Eu (III) complex.

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