

Synthesis and Fluorescence Properties of Lanthanide (III) Perchlorate Complexes with Naphthyl-Naphthalinesulphonylpropyl Sulfoxide

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Abstract A ligand with double sulfinyl groups, naphthyl-naphthalinesulphonylpropyl sulfoxide (dinaphthyl disulfoxide, L), was 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-DTA, ¹H NMR and UV spectra. The composition of these complexes, were RE₂(ClO₄)₆(L)₅·nH₂O (RE=La, Nd, Eu, Tb, Yb, n=2~6, L=C₁₀H₇SOC₃H₆SOC₁₀H₇). The fluorescent spectra illustrated that the Eu (III) complex had an excellent luminescence. It was supposed that the ligand was benefited for transferring the energy from ligand to the excitation state energy level (⁵D₀) of Eu (III). The Tb (III) complex displayed weak luminescence, which attributed to low energy transferring efficiency between the average triplet state energy level of ligand and the excited state (⁵D₄) of Tb (III). So the Eu (III) complex displayed a good antenna effect for luminescence. The phosphorescence spectra and the relationship between fluorescence lifetime and fluorescence intensity were also discussed.

Keywords Rare earth complexes · Fluorescence · Phosphorescence · Fluorescence lifetime · Naphthyl-naphthalinesulphonylpropyl sulfoxide

Introduction

Luminescent rare-earth complexes are interesting materials not only due to their academic importance but essentially due to a variety of potential technological applications, such as fluorescence materials [1, 2], electroluminescence devices [3–6] fluorescence probes and labels in a variety of biological systems [5–7].

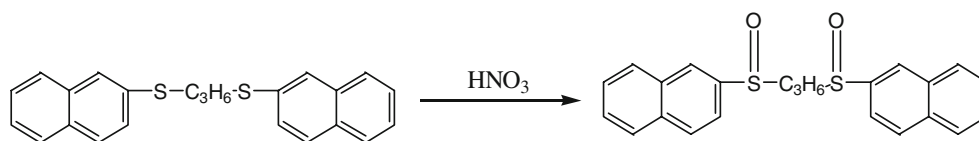
The intra-configuration 4f–4f transitions in rare earth ions are forbidden (Laporte rule), so the absorption and emission spectra of the RE (III) ions show weak intensity. However, the population of the excited states of the RE (III) ions may be increased by coordination to organic ligands, which act as sensitizers [8]. The ligands that present this property were called by Lehn [9] as “antennas”. In RE (III)-complexes, the organic ligand could absorb and transfer energy to the metal ion (intra-molecular energy transfer) efficiently, which increased their luminescence intensity.

Based on the different ligands and the central RE (III), many fluorescent complexes were synthesized. The main ligands included aromatic carboxylic acid, 1, 10-phenanthroline (phen), pyridine and β-diketon, etc. [10]. As a new organic ligand, the sulfoxide ligand had the ability of excellent coordination. After the Eu (III) and Tb (III) complexes were formed, they had the ability of good solubility, high stability and strong luminescence intensities. In the past several decades, many sulfoxide complexes had been synthesized and intensively studied due to their special fluorescence properties [11–14]. The RE (III)-sulfoxide complexes had become one important luminescence material, which had a promising future. In this paper, a ligand named naphthyl-naphthalinesulphonylpropyl sulfoxide and its several RE (III) complexes were synthesized and characterized. At the same time, the luminescence properties of Eu (III) and Tb (III) complexes were studied in solid state.

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Fig. 1 The synthesis route of the ligand



Experiment

Reagents and apparatus

The purity of lanthanide oxide exceeds 99.99%, the rare earth perchlorates were prepared by dissolving the oxide (99.99%) in HClO_4 (2 mol/L). All the other chemicals were of analytical reagent grade. Carbon, hydrogen analysis were determined by PE-2400 elemental analysis instrument. Rare earth contents of the complexes were determined by EDTA titration using Xylenol-orange as an indicator. Conductivity measurements was made using a $10^{-3} \text{ mol} \cdot \text{L}^{-1}$ 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 $400\sim 4000 \text{ cm}^{-1}$ 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 and solvent. ^1H NMR spectra were measured by Bruker AC-300 instrument in DMSO-d_6 . The fluorescence spectra were determined by SHIMADZU RF-5301PC fluorescence photometer. The phosphorescence spectrum was 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.

Dinaphthyl disulfide was synthesized according to the method of ref. [15]. Sodium was dissolved in alcohol. Then 2-naphthalenethiol and 1, 3-dibromopropane was added dropwise respectively. The mixture was stirred continuously and refluxed by steam distillation for 2 h. 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: 93%. mp: 96–98 °C. Anal. calcd. For $\text{C}_{10}\text{H}_7\text{SC}_3\text{H}_6\text{SC}_{10}\text{H}_7$: C, 76.66%; H, 5.25%; found: C, 76.54%; H, 5.21%.

16 mmol dinaphthyl disulfide was dissolved in 100 ml benzene, then the mixed solution of 6 ml concentrated HNO_3 and 2 ml water was added in it at once. The mixture was stirred continuously at room temperature for 6 h. After the reaction had stopped, the mixture was washed with sodium carbonate solution (5%) until the pH of mixture was 7. Benzene was removed with reduced pressure distillation. Then a white solid was precipitated, filtered and dried in vacuum. Yield: 45%. mp: 125–127 °C. Anal. calcd. For $\text{C}_{10}\text{H}_7\text{SOC}_3\text{H}_6\text{SOC}_{10}\text{H}_7$: C, 70.41%; H, 5.10%; Found: C, 70.26%; H, 5.21%.

Preparation of the complexes

An anhydrous ethanol solution containing 1 mmol of rare earth perchlorates was added dropwise in an anhydrous ethanol solution of L (5 mmol) with stirring. After a few minutes a white precipitate was formed. The mixture was stirred for 0.5 h and precipitate was filtered. The products were washed with ether for several times, and then dried in vacuum to give the complexes as a white powder. (yield > 90%)

Results and discussion

Elemental analysis and molar conductivity values were given in Table 1, and the composition of these complexes were $\text{RE}_2(\text{ClO}_4)_6 \cdot (\text{L})_5 \cdot n\text{H}_2\text{O}$ (RE=La, Nd, Eu, Tb, Yb, $n=2\sim 6$, $\text{L}=\text{C}_{10}\text{H}_7\text{SOC}_3\text{H}_6\text{SOC}_{10}\text{H}_7$). The λ_m values of the complexes in DMSO were in accordance with the formula as 1:2 electrolytes [16].

Table 1 Elemental analyses and molar conductivity values for the complexes

Complexes	M	Anal. calcd. (found) (%)			λ_m (a)
		C	H	RE	
$\text{La}_2(\text{ClO}_4)_6 \cdot (\text{L})_5 \cdot 2\text{H}_2\text{O}$	2871	48.07(48.22)	3.62(3.72)	9.46(9.67)	168.2
$\text{Nd}_2(\text{ClO}_4)_6 \cdot (\text{L})_5 \cdot 6\text{H}_2\text{O}$	2953	46.73(46.73)	3.96(3.79)	9.43(9.77)	169.0
$\text{Eu}_2(\text{ClO}_4)_6 \cdot (\text{L})_5 \cdot 2\text{H}_2\text{O}$	2897	47.63(48.03)	3.59(3.50)	10.49(10.62)	167.0
$\text{Tb}_2(\text{ClO}_4)_6 \cdot (\text{L})_5 \cdot 2\text{H}_2\text{O}$	2911	47.40(48.00)	3.57(3.48)	10.92(11.1)	164.0
$\text{Yb}_2(\text{ClO}_4)_6 \cdot (\text{L})_5 \cdot 4\text{H}_2\text{O}$	2975	46.61(46.39)	3.63(3.60)	11.63(11.60)	160.0

$a = \text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$

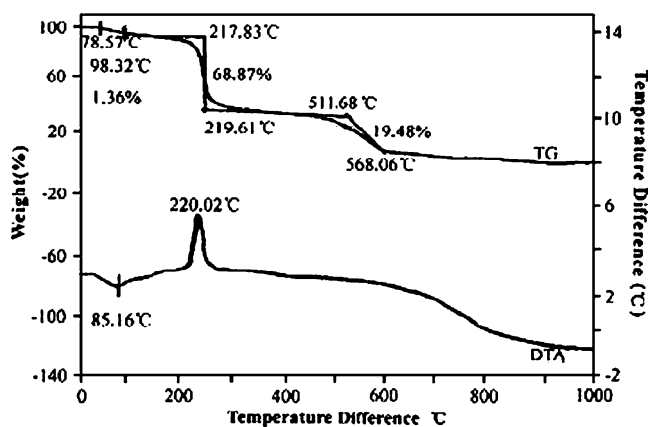


Fig. 2 TG-DTA curves of $\text{La}_2(\text{ClO}_4)_6(\text{L})_5 \cdot 2\text{H}_2\text{O}$

General property

All the complexes were white powder, stable in atmospheric condition and soluble in acetone, DMF and DMSO.

TG-DTA studies

The TG-DTA analysis was carried out up to 1000 °C in N_2 at heating rate of 10 °C min^{-1} . All the TG-DTA curves of RE (III) complexes were similar. The curves of La (III) complex were depicted in Fig. 2. The TG curve of complex showed a first mass loss between 78.57 °C and 98.32 °C with 1.36%, which was coincide with the release of all the two water content (1.25%) very well. The relatively low temperature of water loss showed that they were crystal water. At the same time, DTA curves showed small endothermic peak at 85.16 °C when losing water. In

addition, there were two exothermic peaks in DTA curve which attributed to the decomposition of ligand, and two obvious weight losses occurring on the TG curve. The final product was found to be RE_2O_3 (RE_4O_7 for Tb) when the temperature was near 1000 °C, and the total weight loss of the complexes was found to be close to the calculated value. The results were coinciding with element analysis.

Infrared spectra

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

In the IR spectra of complexes, some absorption bands had obviously shifted compared with IR spectrum of the ligand. It showed that rare earth ions were bonded with the ligands. In the ligand IR spectrum, the S=O group stretching mode appeared at 1033 cm^{-1} . A shift of the S=O stretching frequency towards low wave number by 48~50 cm^{-1} in complexes, it suggested that rare earth ions were bonded with oxygen atom in sulfinyl group. In the IR spectrum of the ligand, the absorptions of naphthyl group appeared at 3052 cm^{-1} ($\nu_{\text{C-H}}$), 818 cm^{-1} ($\delta_{\text{C-H}}$), 746 cm^{-1} ($\delta_{\text{C-H}}$), they had no significant shift, which indicated that naphthyl group was not coordinated. Moreover, there were three additional peaks at about 1095~1115 cm^{-1} , 1021~1040 cm^{-1} and 622~629 cm^{-1} , all of them attributed to ClO_4^- group. When ClO_4^- was not coordinated, it was Td symmetry and there were two absorptions. When ClO_4^- was coordinated, it was C_{3v} symmetry and there were five absorptions [17, 18]. In the IR spectra of the complexes, three absorption bands could be seen clearly. So four ClO_4^-

Fig. 3 IR absorption spectrum of ligand

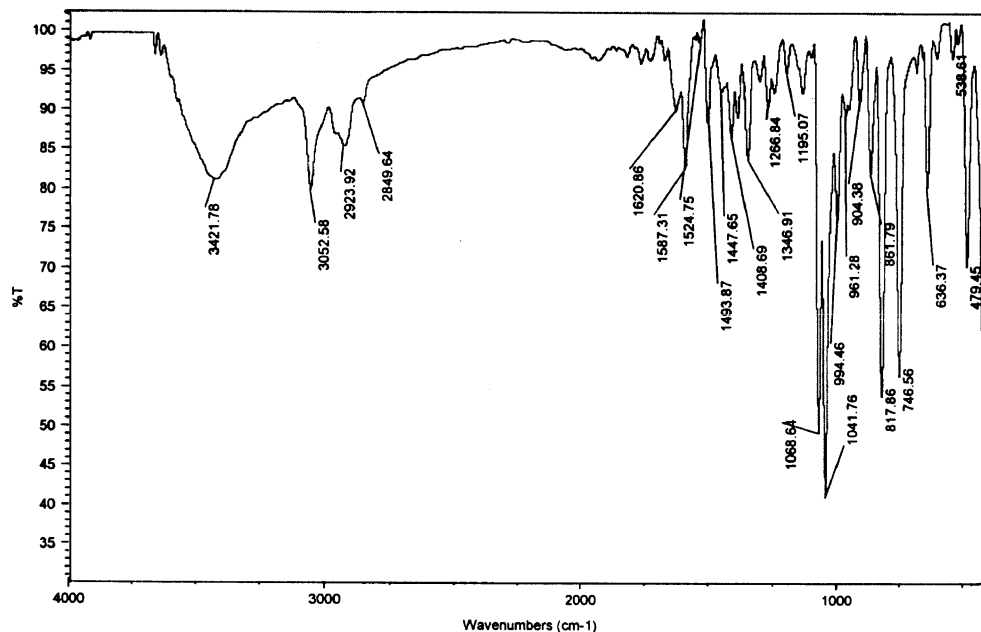
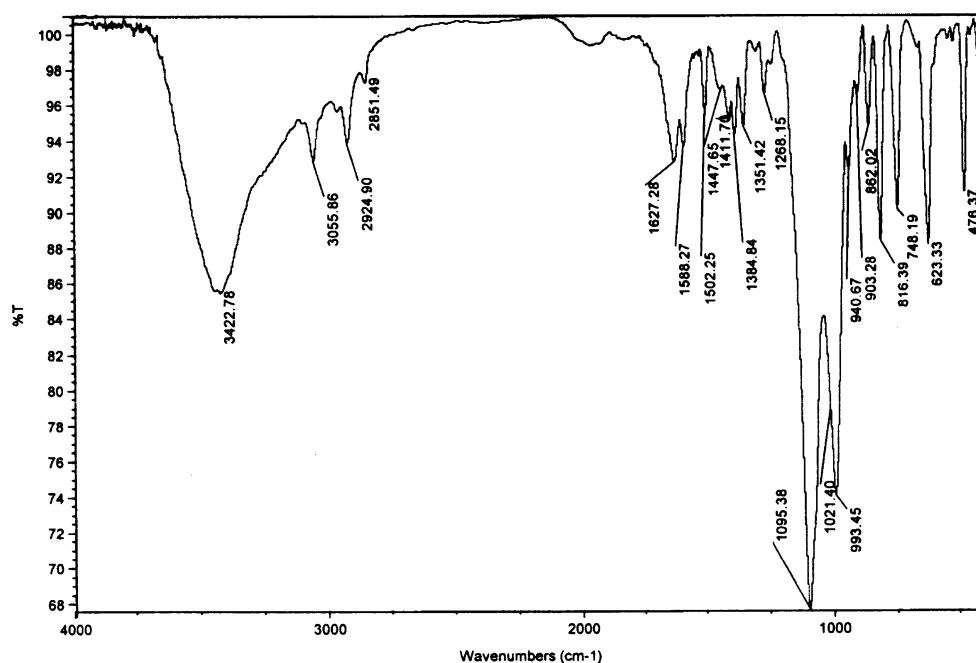


Fig. 4 IR absorption spectrum of $\text{Eu}_2(\text{ClO}_4)_6 \cdot (\text{L})_5 \cdot 2\text{H}_2\text{O}$



were not all with the T_d symmetry and some of them should have C_{3v} symmetry. In terms with the molar conductivities, it could be induced that four ClO_4^- were bonded with RE (III) through oxygen atom respectively.

UV spectra

The UV spectra of the ligand and Eu (III) complex were recorded on a Shimadzu UV-265 spectrophotometer and DMSO was used as a reference and solvent, and the data were listed in Figs. 5 and 6. The free ligand exhibited one absorption band at 261.1 nm, which attributed to $\pi \rightarrow \pi^*$ transition. In UV spectrum of the complex, a shifting of wide band was seen from 261.1 nm to 282.6 nm and the width of semi-peak of band located from 270.0 nm to 310.5 nm, which indicated that complex was formed. At the

same time the conjugated system was increased after coordinating with the RE (III) ions [19].

^1H NMR spectra

The ^1H NMR spectra data of the ligand and its complexes in DMSO-d_6 could be seen from the Table 3. The ^1H NMR of the ligand showed the proton resonance of two naphthyl groups was multiple peaks at $\delta 8.15\text{--}7.59$ ppm, and the integral intensities showed that it had fourteen protons. The proton resonance of three methylene group peaks was at

Table 2 Some main IR data of ligand and the complexes

Assignment (cm^{-1})	Ligand	La	Nd	Eu	Tb	Yb
$\nu_{\text{O-H}}(\text{H}_2\text{O})$		3442	3443	3422	3422	3446
$\nu_{\text{C-H}}(\text{C}_{10}\text{H}_7)$	3052	3053	3053	3055	3054	3049
$\delta_{\text{C-H}}(\text{C}_{10}\text{H}_7)$	818	815	816	816	816	816
	746	748	747	748	747	748
$\nu_{\text{S=O}}$	1041	993	993	993	991	993
$\nu_{\text{C-H}}(\text{CH}_2)$	2924	2926	2918	2924	2923	2927
$\delta_{\text{C-H}}(\text{CH}_2)$	1447	1447	1442	1447	1440	1447
$\nu_{\text{Cl-O}}(\text{ClO}_4^-)$	—	1115	1115	1095	1095	1115
	—	1031	1026	1021	1040	1036
$\delta(\text{ClO}_4^-)$	—	629	629	623	622	629

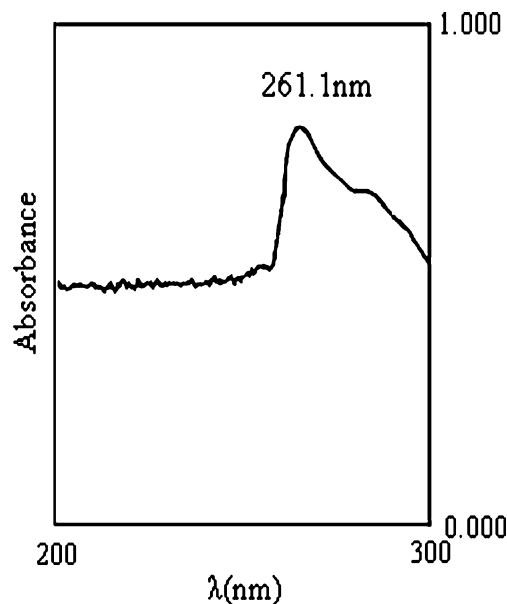


Fig. 5 UV absorption spectrum of ligand

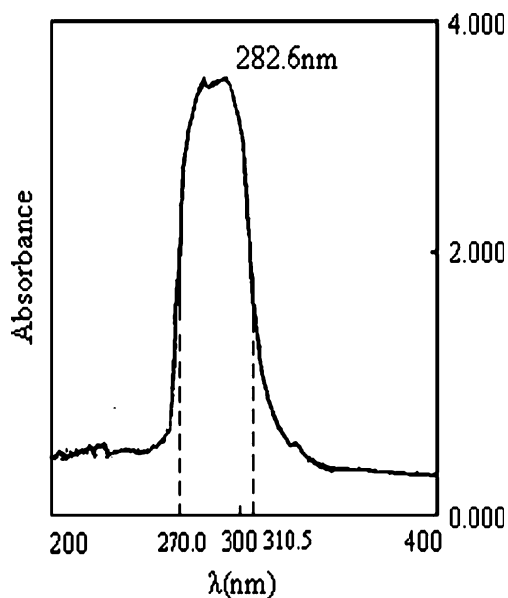


Fig. 6 UV absorption spectrum of $\text{Eu}_2(\text{ClO}_4)_6(\text{L})_5 \cdot 2\text{H}_2\text{O}$

δ 1.75–1.73 ppm and δ 3.02–2.92 ppm, the integral intensities of peaks showed that it had six protons respectively. The ^1H NMR spectra of the complexes were similar. The proton resonance peaks of naphthyl and methylene group were very clear, which shifted to low field at different degree. At the same time, methylene group resonances peaks had been split in the complexes. The result indicated that the sulfinyl group's oxygen of ligand coordinated with RE (III) ions, which produced the remove shielded effect and led to the proton resonance peaks shifting to lower field.

Fluorescence spectra

The excitation spectra and emission spectra of Eu (III), Tb (III) complexes in solid state were measured at room temperature. From the Fig. 7, Eu (III) complex displayed more effective luminescence than the Tb (III) complex did.

In the spectrum of Eu (III) complex (Fig. 7a), there was a wide excitation band from 200~400 nm and the excitation band could overlap effectively with UV absorption spectrum

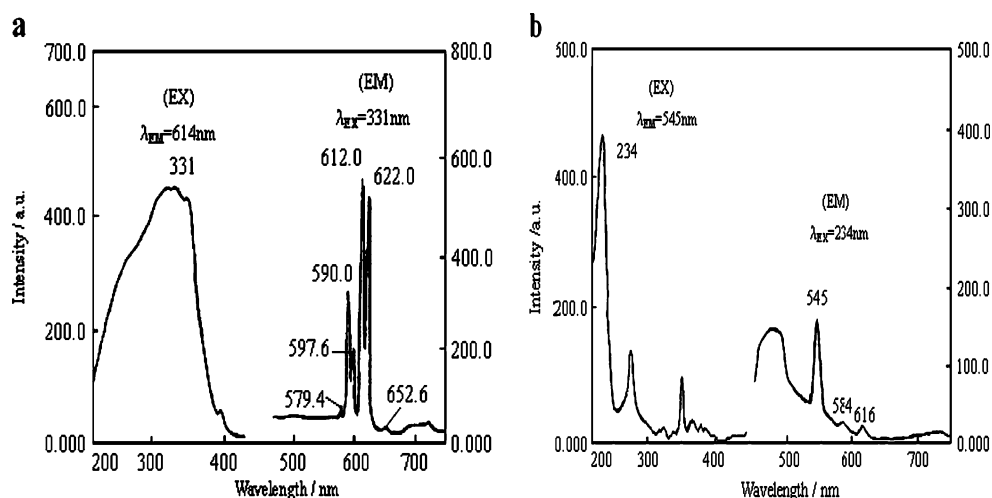
of the ligand in complex (Fig. 6). The strong emission intensities indicated that the ligand was a good organic ligand, which could absorb and transfer energy to Eu (III) ion, emitting the characteristic fluorescence. Besides, there were a series of sharp excitation bands in the spectrum of Tb (III) complex (Fig. 7b), which couldn't superposition with UV absorption band of the ligand or transferred energy from ligand to Tb (III) ions, displayed weaker fluorescence intensities than Eu (III) complex.

For Eu (III) complex, the fluorescence emission spectrum showed seven peaks under the excitation of 331 nm: 579.4 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_0$), 590.0 nm and 597.6 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_1$), 612.0 nm and 622.0 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) corresponded with the characteristic emission for the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J=0-4$) transition of the Eu (III) ion. The red luminescence, the emission intensity of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition was the strongest. The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition was electric dipole transition, which could be detected as a relatively strong peak when Eu (III) did not lie in centrosymmetric ligand field. The $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition was a magnetic dipole transition, which became the strongest emission only when Eu (III) ion was in the center of inversion [20]. Also the intensity ratio of the two lines ($^5\text{D}_0 \rightarrow ^7\text{F}_2$ / $^5\text{D}_0 \rightarrow ^7\text{F}_1$) was about 1.73, which indicated that the Eu (III) ion was not at the center of an asymmetric coordination field. At the same time, the peaks of $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ had been split, which showed that the symmetry of the complex was lower. For Tb (III) complex, the fluorescence emission spectrum illustrated that the three peaks under the excitation of 234 nm: 545.0 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_5$), 583.6 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_4$) and 616.2 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_3$), which attributed to the characteristic emission for the $^5\text{D}_4 \rightarrow ^7\text{F}_J$ ($J=3-5$) transition of the Tb (III) ion. The $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition exhibited fairly fluorescence emission. Comparing with the two complexes, the Eu (III) complex displayed more effective luminescence than the Tb (III) complex did. Eu (III) complex showed a good antenna effect, it meant that the triplet state energy level of the ligand matched with the $^5\text{D}_0$ excited state energy level of Eu (III), but Tb (III) did not. Because the $^5\text{D}_4$ excited state energy level of terbium ion was higher than the triplet energy level of the ligand, So the ligand could not transfer

Table 3 Chemical shift data of ^1H NMR spectra (1×10^{-6})

Ligand and complexes	^1H NMR (ppm)		
	CH_2	$-\text{CH}_2-(\times 2)$	$-\text{C}_{10}\text{H}_7(\times 2)$
$\text{C}_{10}\text{H}_7\text{SOCH}_2\text{CH}_2\text{CH}_2\text{SOC}_{10}\text{H}_7(\text{L})$	1.75~1.73 (s,2H)	3.02~2.92(s, 6H)	8.15~7.59 (m, 14H)
$\text{La}_2(\text{ClO}_4)_6(\text{L})_5 \cdot 2\text{H}_2\text{O}$	1.81~1.71 (m,2H)	3.20~3.11, 3.01~2.87 (m, 2H), (m, 2H)	8.15~7.59(m, 14H)
$\text{Nd}_2(\text{ClO}_4)_6(\text{L})_5 \cdot 6\text{H}_2\text{O}$	1.78~1.73 (m,2H)	3.20~3.10,3.01~2.92 (m, 2H), (m, 2H)	8.14~7.58 (m, 14H)
$\text{Yb}_2(\text{ClO}_4)_6(\text{L})_5 \cdot 4\text{H}_2\text{O}$	1.79~1.74(m,2H)	3.20~3.10, 3.01~2.89 (m, 2H), (m, 2H)	8.16~7.59 (m, 14H)

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



the energy efficiently. As a result, more energy could transfer efficiently from the ligand to the Eu (III), which made the Eu (III) complex exhibits the stronger characteristic fluorescence. However, Tb (III) was different from Eu (III), because the symmetry of the Tb (III) complex was very low and the forbidden of f-f electric dipole transition had been released at a certain degree. Under this case Tb (III) oneself absorbed UV energy and emitted fluorescence. In order to study the relationship between fluorescence intensity and fluorescence lifetime, the fluorescence decay curves of Eu (III) and Tb (III) complexes were measured. Figure 8 showed the fitted curve of Eu (III) complex. The lifetime values of Eu (III), Tb (III) complexes were calculated by the single exponential mode. From these results, the fluorescence lifetime of Eu (III) complex (1,576 μ s) was longer than that of Tb (III) complex (13 μ s).

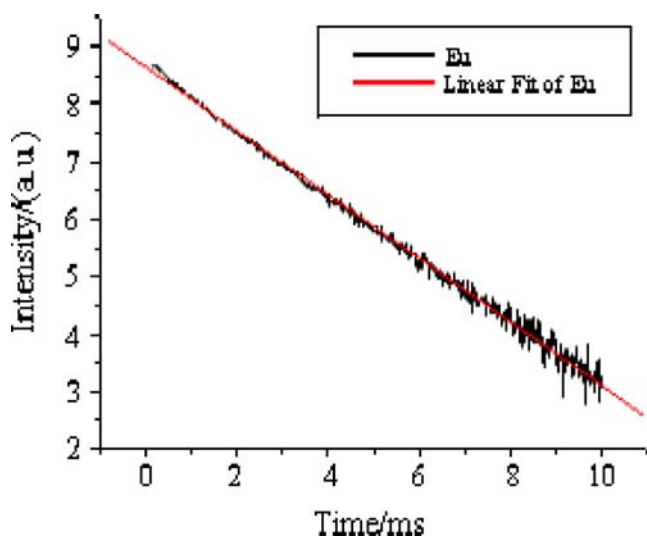


Fig. 8 Fit curve of $\text{Eu}^{3+} {}^5\text{D}_0$ level in Eu (III) complex

Phosphorescence properties of ligand

The phosphorescence spectrum of ligand was measured by SPEX1934D phosphorescence photometer in solid state. According to the phosphorescence spectrum (Fig. 9), the energy transfer and intramolecular energy mechanism [21, 22], intramolecular energy transfer efficiency chiefly depended on two energy transfer processes: one of them was led from the triplet level state of ligands to the emissive energy state of the Eu (III) and Tb (III) ion by Dexter's resonant exchange interaction [23], the other side was just an inverse energy transfer by the thermal deactivation mechanism [24]. Based on this theory, the conclusion could be drawn that energy differences was of opposite influence on the two energy transfer processes, an optimal value could be calculated. The peak at 515 nm showed that the triplet state energy level of the ligand was approximately $19,417 \text{ cm}^{-1}$, which was higher than ${}^5\text{D}_0$ of Eu (III) ion ($17,241 \text{ cm}^{-1}$) [25] and lower than ${}^5\text{D}_4$ of Tb (III) ion

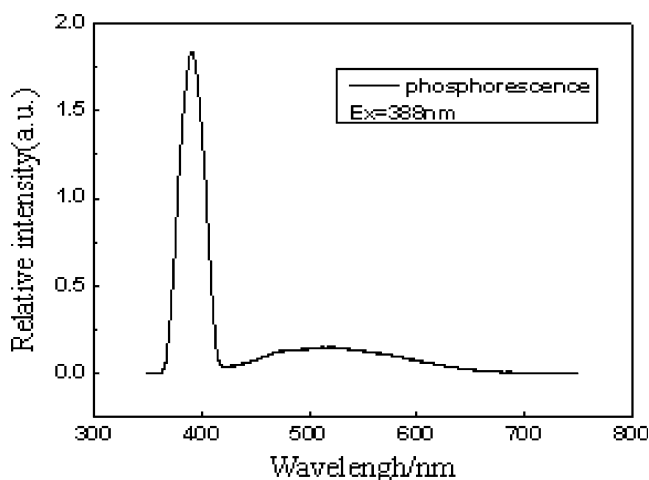


Fig. 9 Phosphorescence properties of ligand

(20,430 cm^{-1}) [26]. From these different energies, it could be seen that ligand could effectively sensitize the Eu (III) ion, but could not sensitize the Tb (III).

Conclusion

The novel ligand (naphthyl- naphthalinesulphonylpropyl sulfoxide) and its complexes were synthesized and characterized. Composition of these complexes were proved to be $\text{RE}_2(\text{ClO}_4)_6 \cdot (\text{L})_5 \cdot n\text{H}_2\text{O}$ ($\text{RE}=\text{La(III), Nd(III), Eu(III), Tb(III), Yb(III)}$, $n=2\sim 6$, $\text{L}=\text{C}_{10}\text{H}_7\text{SOC}_3\text{H}_6\text{SOC}_{10}\text{H}_7$). The photophysical properties of the complexes had been studied with ultraviolet spectra, phosphorescence spectra, excitation and emission spectra, fluorescence lifetimes and phosphorescence spectra. The ligand had a suitable conjugated system to sensitize Eu (III) ion fluorescence efficiently. The fluorescence spectra showed that Eu (III) complex displayed characteristic Eu (III) ion fluorescence. Meanwhile, Eu (III) complex exhibited stronger fluorescence than Tb (III) complex.

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