J Fluoresc (2012) 22:651–658
DOI 10.1007/s10895-011-1001-5

ORIGINAL PAPER

Syntheses and Fluorescence Properties of Two Novel Lanthanide (III) Perchlorate Complexes with Bis(benzylsulfinyl)methane

Wen-Xian Li · Ying-Jie Li · Wen-Juan Chai · Tie Ren · Yu Liu · Jing Zhang · Bo-Yang Ao

Received: 1 June 2011 / Accepted: 14 October 2011 / Published online: 21 October 2011

Abstract A novel ligand with double sulfinyl groups, bis(benzylsulfinyl)methane, was synthesized by a new method and its two lanthanide (III) complexes were synthesized and characterized by element analysis, molar conductivity, coordination titration analysis, IR, TG-DSC, ^{1}HNMR and UV spectra. The results indicated that the composition of these complexes was $REL_{2.5}(ClO_4)_3 \cdot 3H_2O$ (RE=Tb (III), Dy (III), $L=C_6H_5CH_2SOCH_2SOCH_2C_6H_5$). The FT-IR results revealed that the perchlorate group was bonded with the lanthanide ion by the oxygen atoms, and the coordination was bidentate. The fluorescent spectra illustrated that both the Tb (III) and Dy (III) complexes displayed characteristic fluorescence in solid state, especially for the Tb (III) complex, the peak of $^5D_4 \rightarrow {}^7F_5$ of the Tb (III) ion in 544 nm was stronger than that of others. It indicated that the Tb (III) complex could emit purer green fluorescence. By analysis fluorescence and phosphorescence spectra, it was found that the ligand had the advantage to absorb energy and transfer it to the Tb (III) and Dy (III) ions. The phosphorescence spectra and fluorescence lifetimes of the complexes were also measured.

Keywords Rare earth complexes
Bis(benzylsulfinyl)methane · Fluorescence ·
Phosphorescence

Introduction

In last decades, many rare earth complexes had been given much attention for investigation. An attractive feature of lanthanide complexes was their line-like emission, which resulted in a high color purity of the emitted light [1]. Photoluminescence of lanthanide complexes could be an efficient process. However, direct excitation of lanthanide ions was not efficient enough due to its inherently small absorption cross section. In 1942, Weissman discovered that metal-centered luminescence could be observed for lanthanide complexes with organic ligands [2]. Because of the absorption bands of organic chromophores, much more light could be absorbed by the organic ligands than by the lanthanide ion itself. Subsequently, the excitation energy was transferred from the organic ligands to the lanthanide ion by intramolecular energy transfer.

The structure of the ligands could greatly affect the luminescence of the rare earth ions, therefore, many fluorescent complexes had been synthesized. The major ligands included β-diketon, aromatic carboxylic acid and heterocyclic ligands [3–6]. These complexes had special characteristics, such as extremely narrow emission bands and high internal quantum efficiencies, which were more suitable to be used as the luminescent materials [7]. Consequently, the rare earth complexes were applied to many areas, such as fluorimetric determination, electroluminescent devices and as fluorescence probes and labels in a variety of biological and chemical applications [8–10].

In recent years, W.X. Li etal had found that rare-earth sulphoxide complexes containing an aromatic ring not only had good luminescent properties, but also had good

W.-X. Li (✉) · Y.-J. Li · W.-J. Chai · T. Ren · Y. Liu · J. Zhang · B.-Y. Ao
College of Chemistry and Chemical Engineering,
Inner Mongolia University,
Hohhot 010021, People's Republic of China
e-mail: nmglwx@163.com

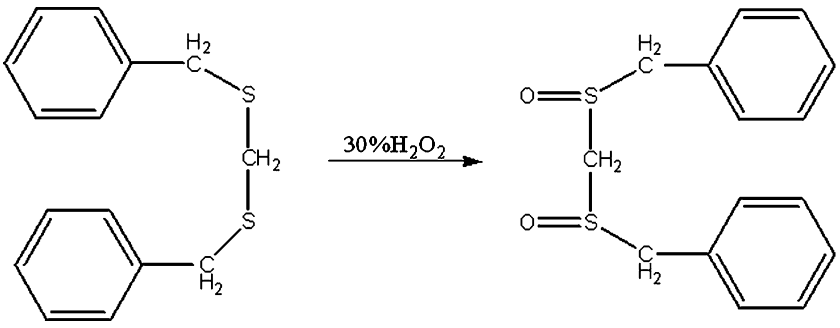


Fig. 1 The synthesis scheme of bis(benzylsulfinyl)methane

solubility and stability. So sulfoxide organic ligands containing aromatic ring were a good class of organic ligands for sensitizing the luminescence of rare-earth ions [11–17]. The object of this study was to seek new fluorescence materials that had strong luminescence, high thermodynamic stability and good solubility. Thus, a novel ligand bis(benzylsulfinyl)methane with two sulfoxide groups had been synthesized, and the corresponding luminescent lanthanide complexes were synthesized and characterized. The luminescence properties of the synthesized complexes had been studied in the solid state.

Experiment

Materials

The purity of lanthanide oxide exceeded 99.99%. The rare earth (III) perchlorates were prepared by dissolving their oxide (99.99%) in $HClO_4$ (2 mol/L). The purity of benzyl mercaptan exceeded 99%. All other chemicals used were of analytical grade.

Physical Measurements

Elemental analysis was carried out on a HANAU analyzer. Conductivity measurement was made using a 10^{-3} mol $\cdot L^{-1}$ solution in DMF on a DDS-11D conductivity meter at room temperature. Rare-earth contents of the complexes were determined by EDTA titration using Xylenol-orange as indicator. The thermal behavior was monitored on SDTQ600 differential scanning calorimeter and thermal gravimetric analyzer. The infrared spectra (IR, ν=4,000–400 cm^{-1}) were determined by the KBr pressed discmethod on a Nicolet NEXUS-670 FT-IR spectrophotometer. The ultraviolet spectra (200–350 nm) of the ligands and the complexes were recorded on a Shimadzu TU-1901 double beam spectrophotometer and DMF was used as a reference and solvent. ^{1}HNMR spectra were measured on Bruker AC-300 spectrometer in DMSO-d_6. Fluorescence excitation and emission spectra were determined on a Hitachi RF-3010 fluorescence photometer with the slit width was 3 nm. The phosphorescence spectra were monitored by F-4500 FL spectrophotometer at room temperature. Fluorescent decay curves were recorded by FLS920 Combined Steady State and Lifetime Spectrometer.

Synthesis of the Ligand

The synthesis scheme was shown in Fig. 1.

Synthesis of the Sulfide

The sulfide was synthesized according to the method of Shriner et al [18].

Sodium hydroxide was dissolved in alcohol. The mechanical stirrer was started and benzyl mercaptan was added in a slow but steady stream. Then dibromomethane was run in drop by drop. The mixture was refluxed, with stirring, on a steam-bath for one and one-half hours. The hot solution was immediately poured on ice powder. A light yellow solid was precipitated, filtered and dried in vacuum. The sulfide was a light yellow crystalline substance which was purified by recrystallization from alcohol. Yield: 60~70%, mp: 46~48. Anal. calcd. For $C_{15}H_{16}S_2$: C, 69.23%; H, 6.154%; found: 69.20 C,%; H, 6.353%.

Table 1 Composition analysis (%) and molar conductivities ($S\bullet cm^2\bullet mol^{-1}$) of the rare earth complexes (25 °C)

Complexes	M	Anal.calcd.(found)(%)			λm(a) ($S\bullet cm^2\bullet mol^{-1}$)
		C	H	RE	
$TbL_{2.5}(ClO_4)_3{\cdot}3H_2O$	1,231.4	36.43(36.25)	3.88(3.71)	13.23(12.91)	148.5
$DyL_{2.5}(ClO_4)_3{\cdot}3H_2O$	1,245.0	35.91(36.14)	3.71(3.70)	13.34(13.05)	150.5

(L=$C_6H_5CH_2SOCH_2SOCH_2C_6H_5$)

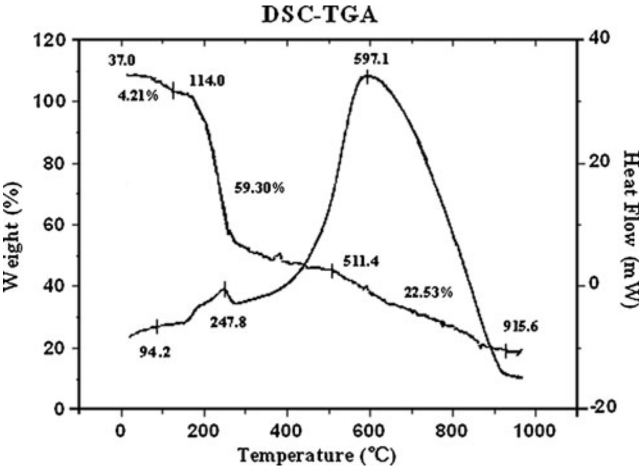


Fig. 2 The TG-DSC curves of $TbL_{2.5}(ClO_4)_3{\cdot}3H_2O$

Synthesis of the Sulfoxide

Bis(benzylthio)methane 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, 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: 80%, mp: 212~214 °C. Anal. calcd. For $C_{15}H_{16}S_2O_2$: C, 61.64%; H, 5.479%; found: C, 61.33%; H, 5.485%.

Preparation of the Complexes

An ether solution containing 3 mmol rare earth perchlorates was added drop by drop in an ether solution containing 5 mmol bis(benzylsulfinyl)methane. After a few minutes a white precipitate 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 drying oven. It looked like white powder (yield>90%).

Results and Discussion

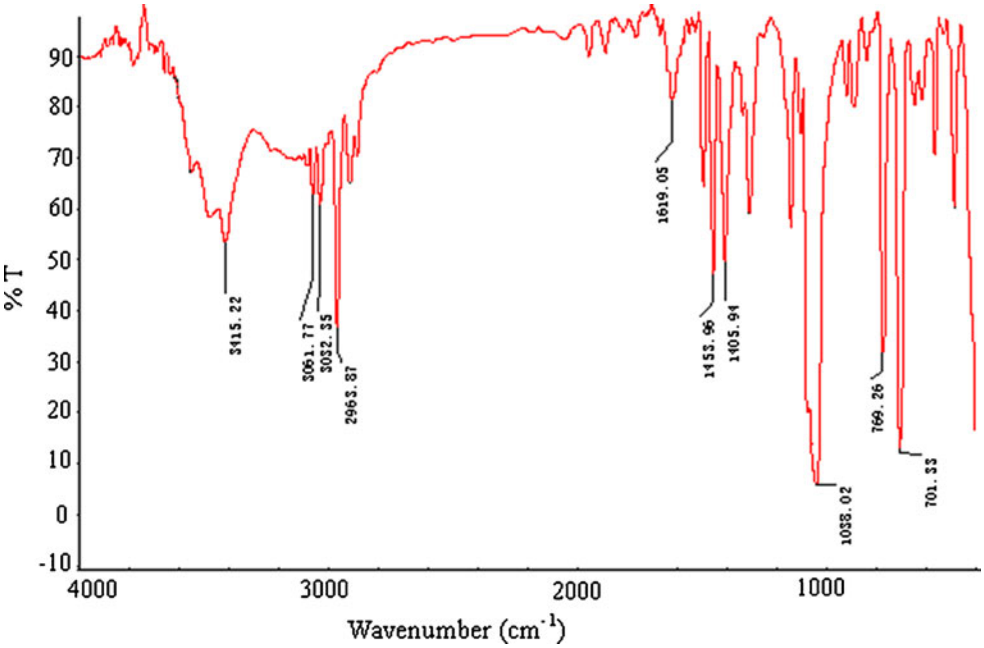
Properties of the Complexes

Analytical data for the complexes, presented in Table 1, conformed to $REL_{2.5}$ $(ClO_4)_2{\cdot}3H_2O$. All the complexes were white powder, stable in atmospheric condition and soluble in DMF and DMSO. The molar conductivity values of the complexes in DMF were in accord with them being formulated as 1:2 electrolytes [19].

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 were similar. The curve of Tb (III) complex was depicted in Fig. 2. The TG curve of Tb (III) complex showed the first mass loss occurred between 37.0~114.0 °C and mass loss percentage was 4.21%. The result was coincided with the release of all the three water content (4.35%) well. At the same time, DSC curve showed small endothermic peak at 94.2 °C when losing water. In addition, there were two exothermic peaks in DSC curve which were attributed to the decomposition of ligands, as well as two obvious weight losses occurring on the TG curve. The final product was found to be Tb_4O_7 (or Dy_2O_3)

Fig. 3 IR absorption spectrum of ligand



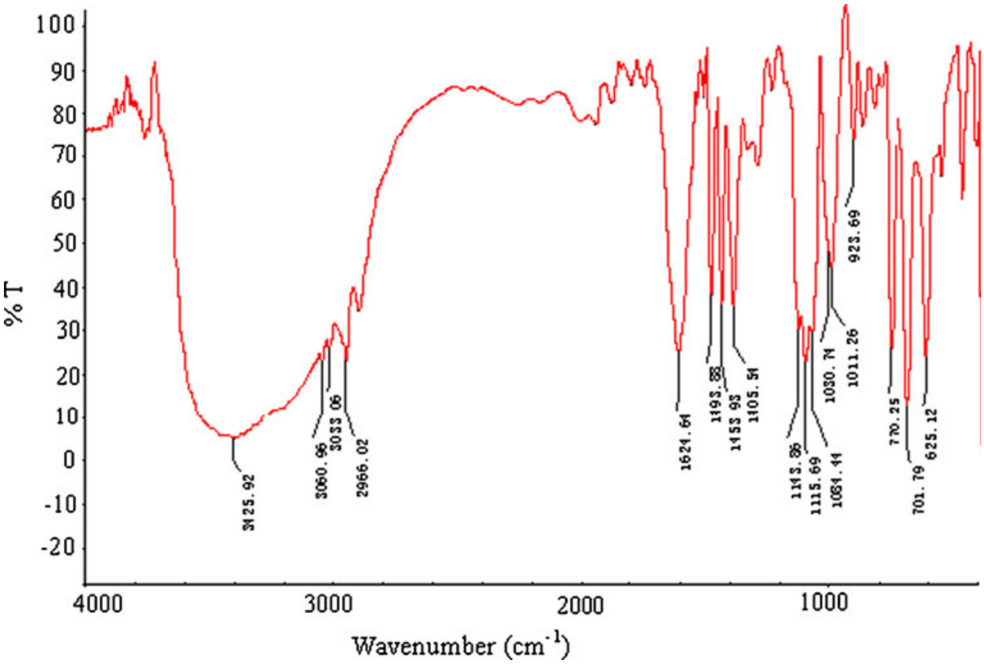


Fig. 4 IR absorption spectrum of $TbL_{2.5}(ClO_4)_2 \cdot 3H_2O$

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 ligands and the complexes could be seen in the Figs. 3 and 4 and Tables 2 and 3.

In the ligand IR spectra, the S=O group stretching modes appeared at 1,038 cm^{-1}. However, the S=O stretching frequency of the two complexes shifted to lower wave number which appeared at 1,011 and 1,008 cm^{-1} respectively, it suggested that rare earth ions bonded with oxygen atom in sulfinyl group.

Table 2 Some main IR data of ligand and the rare earth complexes

Assignment (cm^{-1})	Ligand	Tb	Dy
$\nu_{O\text{-}H}(H_2O)$	–	3,426	3,380
$\nu_{C=C}(C_6H_5)$	1,619	1,625	1,624
$\nu_{C\text{-}H}(C_6H_5)$	3,062	3,061	3,061
$\delta_{C\text{-}H}(C_6H_5)$	769	770	770
	701	702	702
$\nu_{S=O}$	1,038	1,011	1,008
$\nu_{C\text{-}H}$ (C_6H_5-CH_2-SO-)	2,964	2,965	2,965
$\delta_{C\text{-}H}$(C_6H_5-CH_2-SO-)	1,406	1,406	1,406
$\nu_{C\text{-}H}$ (-SO-CH_2-SO-)	3,032	3,033	3,030
$\delta_{C\text{-}H}$ (-SO-CH_2-SO-)	1,454	1,454	1,453

In addition, the IR frequencies of the perchlorate group were listed in Table 3. When the perchlorate group wasn't coordinated, it was Td symmetry. The strong band assigned to the ν_3 mode of its group, which appeared at 1,085~1,090 cm^{-1}. It indicated the presence of ionic perchlorate groups in the complexes. The IR spectra of the complexes showed three strong absorptions about at 1,144, 1,116 and 1,030 cm^{-1}, which were assigned respectively to ν_8, ν_6 and ν_1 vibrations of the coordinating C_{2v} perchlorate group [20]. Therefore, the perchlorate group in these complexes was bonded with the lanthanide ion by the oxygen atoms, and the coordination was bidentate.

UV Spectra

The UV spectra of the ligand and Tb (III) complex were recorded in Fig. 5. In Fig. 5a, the free ligand exhibited one absorption band at 266 nm, which was attributed to $\pi \rightarrow \pi^*$ transition. In Fig. 5b, there was only one band at 267 nm in the absorption spectra of Tb (III) complex which was no significant shift. It indicated that the center cation didn't affect energy of the ligand. The UV absorption of Tb (III)

Table 3 IR absorption bands of the perchlorate group of rare earth complexes (cm^{-1})

Ln	C_{2v}					Td $\nu_3(T_2)$
	$\nu_8(B_2)$	$\nu_6(B_1)$	$\nu_1(A_1)$	$\nu_2(A_1)$	$\nu_7(B_1)$	
Tb	1,144	1,116	1,030	924	625	1,084
Dy	1,147	1,116	1,024	922	627	1,083

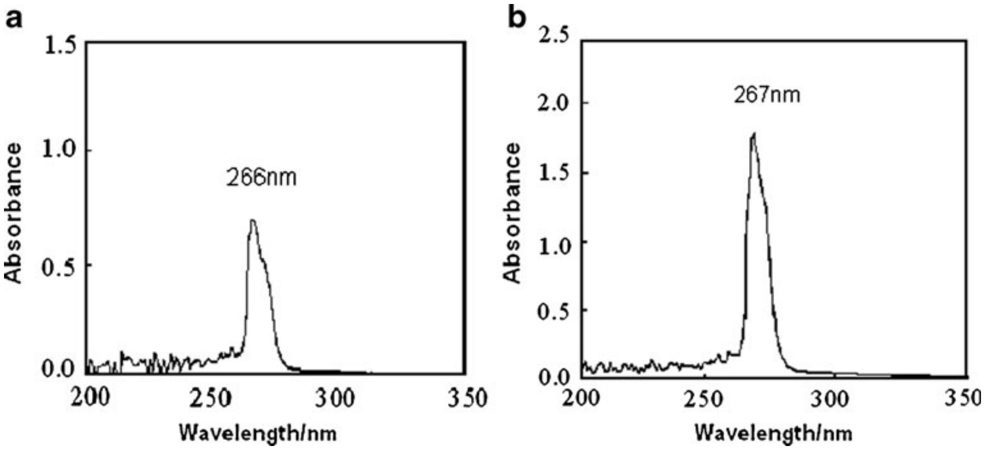


Fig. 5 The UV absorption spectra of **a** bis(benzylsulfinyl) methane, **b** the Tb(III) complex

complex was mainly come from the ligand absorption. Therefore, the ligand transferred energy to Tb (III) ion effectively when complex was formed.

^{1}HNMR Spectra

The ^{1}HNMR spectra data of bis(benzylsulfinyl)methane and its complexes in DMSO-d_6 could be seen from the Table 4. The ^{1}HNMR of the ligand showed the proton resonance of two phenyl group peaks was at δ7.279~7.379 ppm, and the integral intensities showed that it had ten protons. The proton resonance of two methylene group peaks was at δ4.246~4.452 ppm, the integral intensities of peaks showed that it had four protons. There was also one methylene group in the ligand and the proton resonance of its peaks was at δ3.311~4.143 ppm, and the integral intensities showed that it had two protons.

The ^{1}HNMR spectra of the complexes were similar. The proton resonances peaks of phenyl and methylene group were very clear, which shifted to low field at different degree. It resulted from the bond between ligand and 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 Tb (III), Dy (III) complexes were measured in solid state at room temperature. According to the spectra of the complexes that were reported in Fig. 6 and Table 5, we could see that the complexes had excellent luminescent property.

The excitation spectra were obtained by monitoring the emission of the Tb (III) complex at 547 nm and Dy (III) complex at 484 nm, the maximum peak at 378 and 441 nm, respectively. The emission peaks of the Tb (III) complex (Fig. 6a) were assigned to the characteristic $^5D_4 \rightarrow {}^7F_J$ (J= 6, 5, 4, 3) transitions of Tb (III) at 488, 544, 583 and 622 nm. The fluorescence emission spectrum of Tb (III) complex under the excitation of 378 nm showed that the strongest emission peak was at 544 nm which corresponded with the characteristic emission for the $^5D_4 \rightarrow {}^7F_5$ transition of the Tb (III) ion. In Fig. 6b, the emission peaks of the Dy (III) complex were assigned to the characteristic $^4F_{9/2} \rightarrow {}^6H_J$ (J= 15/2 and 13/2) transitions of Dy (III) at 486 and 580 nm, respectively, and the strongest fluorescence emission intensity was at 486 nm, which was considered to the characteristic emission for the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition of the Dy (III) ion. The strongest characteristic emission intensity of the Tb (III), Dy (III) complexes were 8021 (a.u.) and 2089 (a.u.), respectively. Both the two complexes had good luminescence properties, especially the Tb (III) complex, the peak of $^5D_4 \rightarrow {}^7F_5$ of the Tb (III) ion in 544 nm was stronger than others. It indicated that the Tb (III) complex could emit pure green fluorescence. Therefore, Tb (III) complex could be applied to green luminescent materials.

Table 4 Chemical shift data of ^{1}HNMR spectra (1×10^{-6})

Ligand and complexes	^{1}HNMR		
	-CH_2-	-CH_2-(×2)	-C_6H_5-(×2)
$C_6H_5CH_2SOCH_2SOCH_2C_6H_5$	3.311~4.143 (s, 2 H)	4.246~4.452 (s, 4 H)	7.279~7.379 (m, 10 H)
$TbL_{2.5}(ClO_4)_3{\cdot}3H_2O$	3.846~4.176 (s, 2 H)	4.256~4.482 (s, 4 H)	7.316~7.371 (m, 10 H)
$DyL_{2.5}^{-}(ClO_4)_3{\cdot}3H_2O$	3.838~4.153 (s, 2 H)	4.238~4.465 (s, 4 H)	7.298~7.364 (m, 10 H)

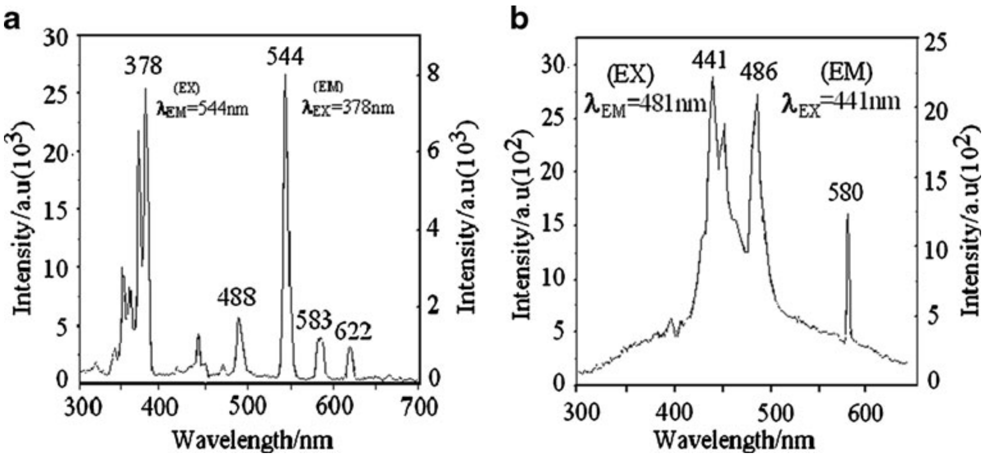


Fig. 6 Fluorescent excitation and emission Spectra of binary Tb(III) (**a**) and Dy(III) (**b**) complexes

The fluorescence decay curves of the Tb (III), Dy (III) complexes were also measured. Figure 7 showed the fluorescence decay curve and linear fit curve of the Tb (III) complex. The fluorescence lifetime values of Tb (III), Dy (III) complex were calculated by the single exponential mode. From the results, the lifetime of the Tb (III) ion was determined to be 760.12 μs, and the lifetime of the Dy (III) ion was determined to be 9.27 μs. This result showed that the lifetime of the Tb (III) ion was longer than that of Dy (III) ion. In the fluorescence spectrum (Fig. 6), the fluorescence intensity of Tb (III) complex was stronger than that of the Dy (III) complex. So we could infer that the life time getting long properly was helpful to increasing the fluorescence intensity in our experimental system.

Phosphorescence Spectra

The phosphorescence spectrum of Gd (III) complex ($GdL_{2.5}(ClO_4)_3 \cdot 3H_2O$) was measured by F-4500 FL spectrophotometer in solid state. The spectrum was listed in Fig. 8. It was known that the energy of the triplet state (T) of the ligand was sensitive to ligand coordination to the metal ion; therefore, the complex of gadolinium was prepared and its phosphorescence spectrum was registered to examine the triplet states of the ligand. According to the intra-molecular energy transfer mechanism [21, 22], intra-molecular energy transfer efficiency chiefly depended on two energy transfer processes: one was the transition from the triplet state energy level of ligand to the excited states of the Tb (III) and Dy (III) ions by Dexter's resonant exchange interaction [23], the other was just an inverse energy transfer process through the thermal deactivation mechanism [24]. Based on the theory, conclusion could be drawn that an optimal value of energy states could be calculated out from the spectra, and energy level difference was an important factor to influence the two energy transfer processes; therefore, an appropriate energy level difference could make the triplet state of ligand energy level and the excited state of rare earth ions energy match able. Otherwise, if the difference of energy level was too large or too small, it would not be conducive to energy transfer. In Fig. 8, two bands could be seen clearly at 519 and 471 nm which corresponded to the triplet state energy level of the ligand of Gd (III) complex T_1 (19,268 cm^{-1}) and T_2 (21,231 cm^{-1}), respectively. The triplet state energy level T_2 was appropriately higher than $^5D_4$ of Tb (III) ion (20,430 cm^{-1}) [25] and $^4F_{9/2}$ of Dy (III) ion (21,100 cm^{-1}) [26]. The energy level difference between T_2 and $^5D_4$ of Tb (III) ion was 801 cm^{-1} and the energy level difference between T_2 and $^4F_{9/2}$ of Dy (III) ion was 131 cm^{-1}. According to the fluorescence spectrum, the strongest characteristic emission intensity of Tb (III) complex was higher than that of the Dy (III) complex, so the triplet state energy level of ligand and the excited state energy of Tb

Table 5 Fluorescent data of Tb (III), Dy(III) complexes in soild at room temperature

Complexes	λ_{EX} (nm)	λ_{EM} (nm)	Intensity (a.u.)	Energy state transitions
$TbL_{2.5}(ClO_4)_3 \cdot 3H_2O$	378	488	1,724	$^5D_4 \rightarrow ^7F_6$
		544	8,021	$^5D_4 \rightarrow ^7F_5$
		583	1,271	$^5D_4 \rightarrow ^7F_4$
		622	995	$^5D_4 \rightarrow ^7F_3$
$DyL_{2.5}(ClO_4)_3 \cdot 3H_2O$	441	486	2,089	$^4F_{9/2} \rightarrow ^6H_{15/2}$
		580	1,231	$^4F_{9/2} \rightarrow ^6H_{13/2}$

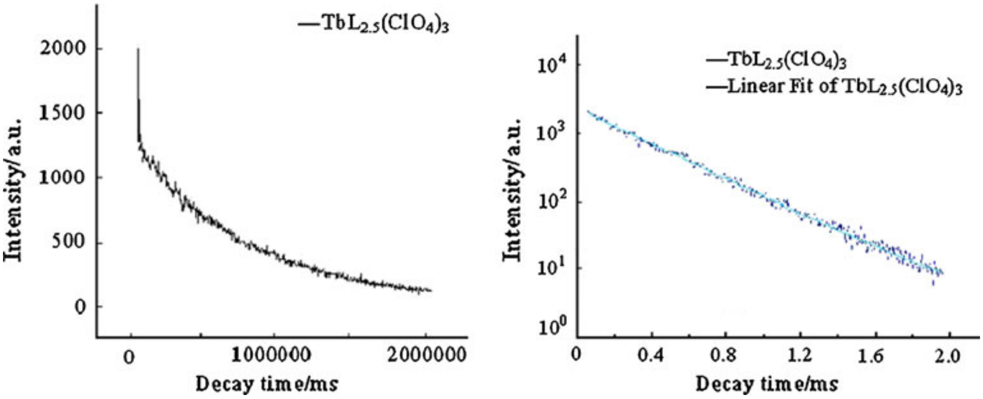


Fig. 7 Fluorescence decay curve and fitted curve of binary Tb(III) complex

(III) ion matched each other very well, and the ligand could absorb and transfer energy effectively to Tb (III) ion as well. Meanwhile, the luminous type of Tb (III) and Dy (III) ions in complexes was the type of L-M.

Conclusion

In this paper, a novel ligand bis(benzylsulfinyl)methane and its two complexes were successfully synthesized and characterized. The composition of the complexes were proved to be $REL_{2.5}(ClO_4)_3 \cdot 3H_2O$ (RE=Tb (III), Dy (III), $L=C_6H_5CH_2SOCH_2SOCH_2C_6H_5$).

The photophysical properties of complexes had been studied with ultraviolet spectra, excitation and emission spectra, fluorescence lifetimes and phosphorescence spectra. Both Tb (III) and Dy (III) complexes had good solubility in DMF and DMSO. In these complexes, the perchlorate group was bonded with the lanthanide ion by the oxygen atom, and the coordination was bidentate. The fluorescence spectra showed that both Tb (III) and Dy (III) complexes displayed characteristic RE (III) ion fluorescence. Therefore, the ligand had a suitable conjugated system to efficiently sensitize RE (III) ion fluorescence. Meantime, the luminous type of Tb (III) and Dy (III) ions in complexes was the type of L-M.

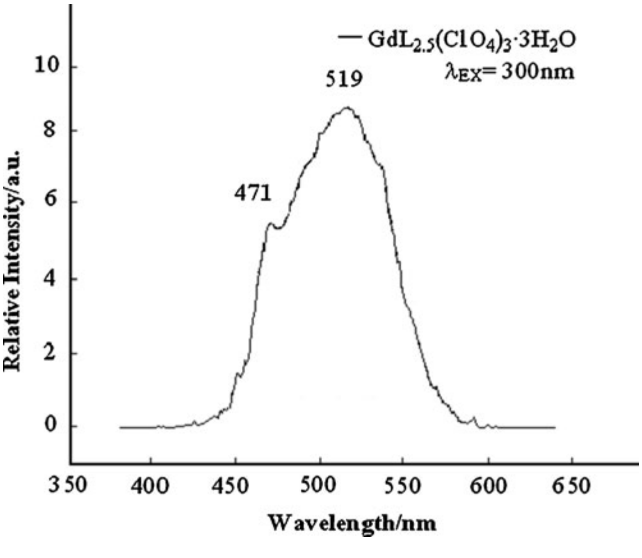


Fig. 8 The phosphorescence spectrum of $GdL_{2.5}(ClO_4)_3 \cdot 3H_2O$

From the experimental results of fluorescence emission, we had known that the peak of $^5D_4 \rightarrow {}^7F_5$ of the Tb (III) ion in 544 nm was stronger than others. It indicated that the Tb (III) complex could emit pure green fluorescence. Therefore, the Tb (III) complex had application potential as green luminescent materials and so on. Hence, based on these factors, more luminescent materials could be obtained in the future.

Acknowledgements This work is supported by the financial supports from the National Natural Science Foundations of China Research project (20861005), Natural Science Foundations of Inner Mongolia Science Foundation (2010 MS 0204) and supported by Inner Mongolia Yili Industrial Group Co. horizontal joint project.

References

1. Binnemans K (2009) Lanthanide-based luminescent hybrid materials. Chem Rev 109:4283–4374
2. Weissman SI (1942) Intramolecular energy transfer the fluorescence of complexes of europium. J Chem Phys 10:214–217
3. Luo YM, Li J, Tang RR, Tang XC (2009) Synthesis, characterization and fluorescence properties of Eu(III) and Tb(III) complexes with novel mono-substituted β-diketon ligands and 1,10-phenanthroline. Spectrochim Acta Part A 72:703–708
4. Xi P, Gu XH, Chen CF, He YX, Huang XA (2007) Synthesis, characterization and fluorescence properties of new highly luminescent organic ligand and complexes of trivalent rare earth. Spectrochim Acta Part A 66:667–671
5. Singh AK, Singh SK, Mishra H, Prakash R, Rai SB (2010) Structural, thermal, and fluorescence properties of Eu $(DBM)_3Phen_X$ complex doped in PMMA. J Phys Chem B 114:13042–13051
6. Song XQ, Zheng JR, Liu WS, Ju ZH (2008) Synthesis, structure and spectroscopic properties of rare earth complexes with a new aryl amide 2,2′-bipydine derivative. Spectrochimica Acta Part A 69:49–55

7. Lv YG, Zhang JC, Cao WL, Fu YL (2009) Enhanced luminescence of novel rare earth complexes Eu(3,5-DNBA)$_3$Phen in nano-TiO$_2$. Spectrochim Acta Part A 72:22–25
8. Wang L, Chen JG, Chen HQ, Zhou CL, Ling B, Fu J (2011) A sensitive fluorimetric method for determination of trace amounts of nitrite based on luminescence energy transfer. J Luminesc 131:83–87
9. Kukhta A, Kolesnik E, Grabchev I, Sali S (2006) Spectral and luminescent properties and electroluminescence of polyvinylcarbazole with 1, 8-naphthalimide in the side chain. J Fluoresc 16:375–378
10. Zamotaiev OM, Postupalenko VY, Shvadchak VV, Pivovarenko VG, Klymchenko AS, Mely Y (2011) Improved hydration-sensitive dual-fluorescence labels for monitoring peptide-nucleic acid interactions. Bioconjugate Chem 22:101–107
11. Shi XY, Li WX, Qin CH, Guo L, Sun XJ, Sun XL, Geng GQ (2008) Synthesis and characterization of quaternary complexes of light rare earth perchlorate with diphenyl sulfoxide, benzoic acid and studies on fluorescence of Eu3+ complex. Chinese J Luminesc 29:772–778
12. Li WX, Guo L, Chen LJ, Shi XY (2008) Synthesis and fluorescence properties of lanthanide (III) perchlorate complexes with bis(benzoylmethyl) sulfoxide. J Fluoresc 18:1043–1049
13. Guo L, Li WX, Shi XY, Sun XJ, Sun XL (2009) Enhanced luminescence of rare-earth Tb (III) by Tm (III) in bis(benzoylmethyl)sulfoxide complexes and intra-molecular energy transfer. J Luminesc 129:639–644
14. Li WX, Zheng YS, Sun XJ, Shi XY, Chai WJ, Ren T (2010) Synthesis and fluorescence properties of lanthanide (III) perchlorate complexes with naphthyl-naphthalinesulphonylpropyl sulfoxide. J Fluoresc 20:235–241
15. Sun XJ, Li WX, Chai WJ, Ren T, Shi XY (2010) The studies of enhanced fluorescence in the two novel ternary rare-earth complex systems. J Fluoresc 20:453–461
16. Li WX, Chai WJ, Sun XJ, Ren T, Shi XY (2010) Synthesis and luminescence properties of two novel lanthanide (III) perchlorate complexes with Bis(benzoylmethyl) sulfoxide and benzoic acid. J Fluoresc 20:873–880
17. Chai WJ, Li WX, Sun XJ, Ren T, Shi XY (2011) Fluorescence enhancement of lanthanide(III) perchlorate by 1,10-phenanthroline in bis(benzoylmethyl) sulfoxide complexes and luminescence mechanism. J Luminesc 131:225–230
18. Shriner RL, Struck HC, Jorison WJ (1930) The preparation and properties of certain sulfoxide and sulfones. Chem Soc 52:2060–2069
19. Greary WJ (1971) The use of conductivity measurements in organic solvents for the characterisation of coordination compounds. Coord Chem Rev 7:81–122
20. Zhang RH, Zhang QW, Kong DL (1991) Studies of DIsulfoxide complexes of lanthanide. J Rare Earths 9:85–89
21. Yan B, Zhang HJ, Wang SB, Ni JZ (1998) Spectroscopic study of luminescence and intramolecular energy transfer of binary andternary rare earth complexes with aromatic carboxylic acids and 1, 10-phenanthroline. Spectro Lett 31:603–608
22. Yan B, Zhang HJ, Wang SB, Ni JZ (1998) Intramolecular energy transfer echanism between ligands internary complexes with aromatic acids and 1, 10-phenanthroline. J Photochem Photobiol A Chem 116:209–214
23. Dexter DL (1953) A theory of sensitized luminescence in solids. J Chem Phys 21:836–841
24. Dean CRS, Shepherd TM (1975) Evaluation of the intramolecular energy transfer rate constants in crystalline Eu(hfaa)$_4$ButNH$_{31}$. J Chem Soc Faraday Trans II 71:146–152
25. Gerisler HF, Hellwege KH (1953) Spectrum and luminescent mechanism of crystal Tb(BrO$_3$)$_3$. Physik 136:293–295
26. Gerisler HF, Hellwege KH (1953) Zeitschrift für Physik A Hadrons and Nuclei 136:293–302