

The Studies of Enhanced Fluorescence in the Two Novel Ternary Rare-Earth Complex Systems

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Abstract Two novel ternary rare-earth complexes $\text{SmL}_5 \cdot \text{L}' \cdot (\text{ClO}_4)_2 \cdot 7\text{H}_2\text{O}$ and $\text{EuL}_5 \cdot \text{L}' \cdot (\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (the first ligand $\text{L} = \text{C}_6\text{H}_5\text{COCH}_2\text{SOCH}_2\text{COC}_6\text{H}_5$, the second ligand $\text{L}' = \text{C}_6\text{H}_4\text{OHCOO}^-$) were synthesized and characterized by element analysis, molar conductivity, coordination titration analysis, IR, TG-DSC, ^1H NMR and UV spectra. The detailed luminescence studies on the rare-earth complexes showed that the ternary rare-earth complexes presented stronger fluorescence intensities, longer lifetimes, and higher fluorescence quantum efficiencies than the binary rare-earth materials. After the introduction of the second ligand salicylic acid group, the relative emission intensities and fluorescence lifetimes of the ternary complexes $\text{LnL}_5 \cdot \text{L}' \cdot (\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{Sm}, \text{Eu}; n=7, 6$) enhanced more obviously than the binary complexes $\text{LnL}_5 \cdot (\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$. This indicated that the presence of both organic ligand bis(benzoylmethyl) sulfoxide and the second ligand salicylic acid could sensitize fluorescence intensities of rare-earth ions, and the introduction of salicylic acid group was a benefit for the fluorescence properties of the ternary rare-earth complexes. The fluorescence spectra, fluorescence lifetime and phosphorescence spectra were also discussed.

Keywords Ternary rare-earth complexes · Fluorescence enhancement · Phosphorescence · Fluorescence lifetime

Introduction

In the last decades, many lanthanide complexes were noted for their interesting photophysical properties arising from f–f transitions and were used as candidates for a number of applications, such as electroluminescence devices and photoluminescence devices, and were used as probes and labels in a variety of biological and chemical applications [1–6]. And the usage based on samarium and europium ions were of special interest due to their unique fluorescence properties, such as long fluorescent decay time, narrow emission bands and strong fluorescence electron excited states. Since the f–f transitions were spin-forbidden, the strong fluorescence was attributed to appropriate energy transfer from the photon-excited chromophores (organic ligand) to the rare-earth ions [7]. In rare-earth complexes, the organic ligand had abilities of absorbing and transferring energy [8] efficiently to the rare-earth ions (intra-molecular energy transfer). Consequently the luminescence intensity of rare-earth ions was increased. As a new organic ligand, the sulfoxide ligand had superb coordination ability and their rare-earth complexes had advantage 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 [9, 10]. Thus, as we had noted, a ligand bis(benzoylmethyl) sulfoxide which had two carbonyl groups, large conjugated plane and rigid structure was chosen in the paper.

Many studies showed that the emission intensities and fluorescence lifetimes of ternary rare-earth complexes were enhanced obviously after introducing the second organic ligand [11, 12]. The second organic ligand served as the energy donor and enhanced the fluorescence intensities of binary rare-earth complexes. The effect was called “synergis-

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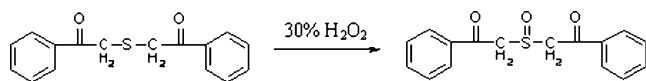


Fig. 1 The synthesis scheme of bis(benzoylmethyl) sulfoxide

tic effect” [13]. Furthermore, the introduction of the second organic ligand would not only reinforce the fluorescence emission intensities, but also fulfilled the coordination numbers of rare-earth complexes. Because of its excellent coordination ability to rare-earth ions and the ability of sensitizing the luminescence of rare-earth ions, salicylic acid had been applied to many ternary rare-earth systems [14, 15]. For this reason, salicylic acid was chosen as the second organic ligand in ternary rare-earth complexes in this paper. Thus, in order to seek new fluorescence materials and study the effects of the second ligand (salicylic acid) on the fluorescence properties of rare-earth complexes, the ternary rare-earth complexes $\text{SmL}_5 \cdot \text{L}' \cdot (\text{ClO}_4)_2 \cdot 7\text{H}_2\text{O}$ and $\text{EuL}_5 \cdot \text{L}' \cdot (\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (the first ligand $\text{L} = \text{C}_6\text{H}_5\text{COCH}_2\text{SOCH}_2\text{COC}_6\text{H}_5$, the second ligand $\text{L}' = \text{C}_6\text{H}_4\text{OHCOO}^-$) had been synthesized by the reaction of bis(benzoylmethyl) sulfoxide and salicylic acid with Sm (III) and Eu (III) respectively and characterized by IR spectra, chemical analysis and elemental analysis. We had also studied the fluorescence properties of the ternary Sm (III), Eu (III) complexes in solid state.

Experiment

Materials

The purity of lanthanide oxide exceeds 99.99%, the rare-earth (III) perchlorates were prepared by dissolving their oxide (99.99%) in HClO_4 (2 mol/L). All other chemicals used were of analytical grade.

Physical measurements

Elemental analysis was carried out on a PE-2400 analyzer. Conductivity measurement was made using a $10^{-3} \text{ mol} \cdot \text{L}^{-1}$ 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

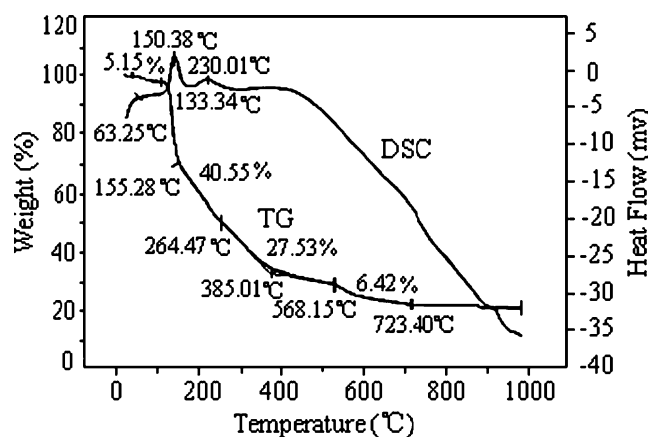


Fig. 2 The TG-DSC curves of $\text{SmL}_5 \cdot \text{L}' \cdot (\text{ClO}_4)_2 \cdot 7\text{H}_2\text{O}$

SDTQ600 differential scanning calorimeter and thermal gravimetric analyzer. The infrared spectra ($\text{IR}, \nu = 4,000\text{--}400 \text{ cm}^{-1}$) were determined by the KBr pressed disc method on a Nicolet NEXUS-670 FT-IR spectrophotometer. The ultraviolet spectra (190–400 nm) of the ligands and the ternary complexes were recorded on a Shimadzu TU-1901 double beam spectrophotometer and DMF was used as a reference and solvent. ^1H NMR spectra were measured on Bruker AC-300 spectrometer in CDCl_3 . 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 ligand

The synthesis scheme was shown in Fig. 1.

Bis(benzoylmethyl) sulfide was dissolved in acetic acid and 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 anhydrous ether until the pH of mixture was 7. Then the white solid was precipitated, filtered and dried in vacuum. Yield: 95%, mp: 110–111 °C. ^1H NMR (CDCl_3 , 300 MHz) δ (ppm): 7.509–8.025 (10H, m, ArH), 4.421–4.820 (4H, s, CH_2). 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%.

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

Complexes	M	Anal.calcd.(found)(%)			λ_m
		C	H	RE	
$\text{SmL}_5 \cdot \text{L}' \cdot (\text{ClO}_4)_2 \cdot 7\text{H}_2\text{O}$	2,042	50.99 (51.11)	4.31 (4.36)	7.25 (7.36)	190.9
$\text{EuL}_5 \cdot \text{L}' \cdot (\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	2,026	51.30 (51.53)	4.20 (4.29)	7.51 (7.50)	196.5

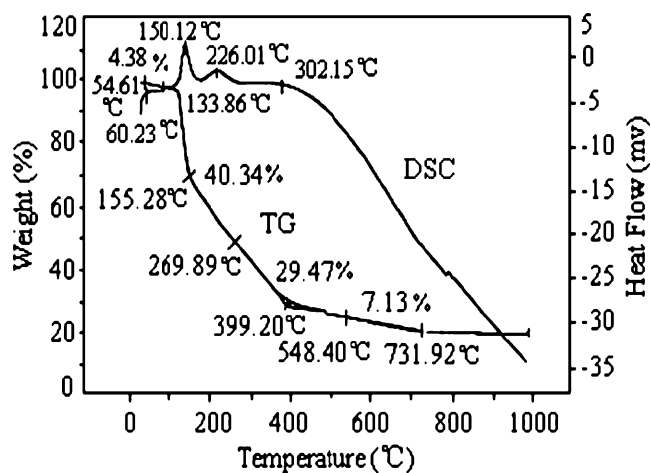


Fig. 3 The TG-DSC curves of $\text{EuL}_5 \cdot \text{L}' \cdot (\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$

Synthesis of the ternary rare-earth complexes

The mixture of 5 mmol bis(benzoylmethyl) sulfoxide and 1 mmol salicylic acid was dissolved in anhydrous ethanol, then the anhydrous ethanol solution (3 ml) of 1 mmol Ln (ClO_4)₃·*n*H₂O (Ln = Sm, Eu) was added dropwise to it. After stirred for 4 h at room temperature, the precipitate was separated from the solution by suction filtration, purified by washing for several times with anhydrous ether, and dried for 24 h in a vacuum (yield >90%).

Results and discussion

Elemental analysis and molar conductivity values were given in Table 1, and the composition of ternary complexes was $\text{SmL}_5 \cdot \text{L}' \cdot (\text{ClO}_4)_2 \cdot 7\text{H}_2\text{O}$ and $\text{EuL}_5 \cdot \text{L}' \cdot (\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (the

first ligand $\text{L} = \text{C}_6\text{H}_5\text{COCH}_2\text{SOCH}_2\text{COC}_6\text{H}_5$, the second ligand $\text{L}' = \text{C}_6\text{H}_4\text{OHCOO}^-$) respectively. The λ_m values of the complexes in DMF were in accordance with the formula as 1:2 electrolytes [16], two ClO_4^- ions were not bonded with rare-earth ions. The complexes were white powder, stable in atmospheric condition and soluble in acetone, DMF and CDCl_3 .

TG-DSC studies

The TG-DSC analysis was carried out up to 1,000 °C in N₂ with heating rate of 10 °C·min⁻¹ and TG-DSC curves of the ternary Sm (III), Eu (III) complexes were depicted in Figs. 2 and 3 respectively. Figures 2 and 3 showed the first weight loss on TG curves from 59.78 °C to 133.34 °C for the ternary Sm (III) complex and from 54.61 °C to 133.86 °C for Eu (III) complex, the percentage of weight loss were 5.15% and 4.38% respectively which was coinciding with the lose numbers of water in ternary complexes. At the same time, there was an endothermic peak at about 60 °C in DSC curves. The comparatively low temperature of water loss showed that they were crystal water. In addition, two obvious weight loss peaks had taken place in TG curves which attributed to the decomposition of three sulfoxide ligands, and two sulfoxide ligands and phenyl group, respectively. Mean-time, two large endothermic bands occurred at about 150 °C and 230 °C on DSC curves. The last weight loss in TG curves was found to coincide with the decomposition of $[(\text{ClO}_4)_2]^{2-}$. The final product was found to be $\text{LnCl}(\text{CO}_3)$ when the temperature was approximately 1,000 °C and the total weight loss of the complexes was close to the calculated values. The results were coinciding with element analysis.

Fig. 4 Infrared absorption spectrum of bis(benzoylmethyl) sulfoxide

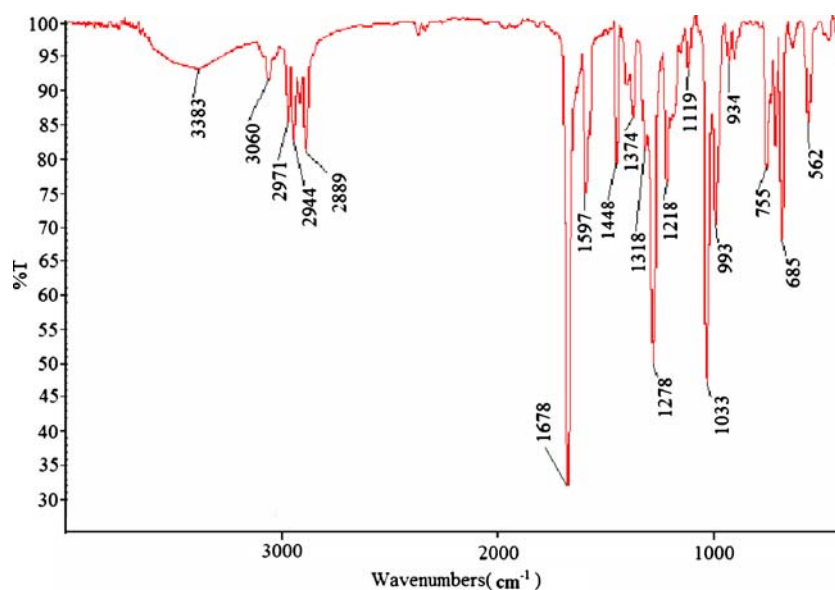
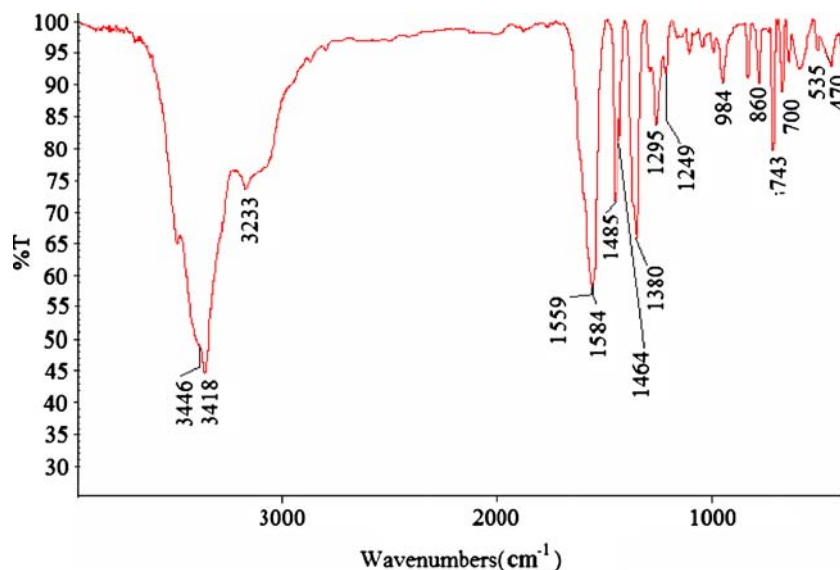


Fig. 5 Infrared absorption spectrum of sodium salicylate



Infrared spectra

The IR spectra of the ligand (bis(benzoylmethyl) sulfoxide, sodium salicylate) and the ternary rare-earth complexes were recorded and the important IR assignments could be seen in the Figs. 4, 5, 6 and Table 2. The spectra of the ternary Sm (III), Eu (III) complexes were similar.

Figure 6 showed the disappearance of the band at the $1,033\text{ cm}^{-1}$ ($\nu_{\text{S=O}}$) and the existence of band at 991 cm^{-1} ($\nu_{\text{S=O}}$), which indicated that rare-earth ions were bonded with oxygen atom in sulfonyl group. The C=O stretching vibration frequency of the ligand appeared at $1,676\text{ cm}^{-1}$ and it was the strongest absorption in Fig. 4. After

coordination, there were no significant shifts, which suggested that the oxygen atom in the carbonyl group was not coordinated with rare-earth ions. The characteristic absorption bands of benzene appeared at approximately $3,060\text{ cm}^{-1}$ ($\nu_{\text{C-H}}$), $1,597\text{ cm}^{-1}$ ($\nu_{\text{C=C}}$), 755 cm^{-1} ($\delta_{\text{C-H}}$) and 685 cm^{-1} ($\delta_{\text{C-H}}$) in the Fig. 4 and they were also found in the spectra of ternary Eu (III) complex.

The $\nu_{\text{as}(\text{COO}^-)}$ and $\nu_{\text{s}(\text{COO}^-)}$ absorption of sodium salicylate occurred at $1,584$ and $1,380\text{ cm}^{-1}$, and the $\Delta\nu$ value was 204 cm^{-1} in the Fig. 5. There were no significant bands between $1,690$ and $1,730\text{ cm}^{-1}$ in the spectra of ternary rare-earth complexes indicated that carboxyl group had taken place deprotonation. The presence of $\nu_{\text{as}(\text{COO}^-)}$

Fig. 6 Infrared absorption spectrum of $\text{EuL}_5\text{L}' \cdot (\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$

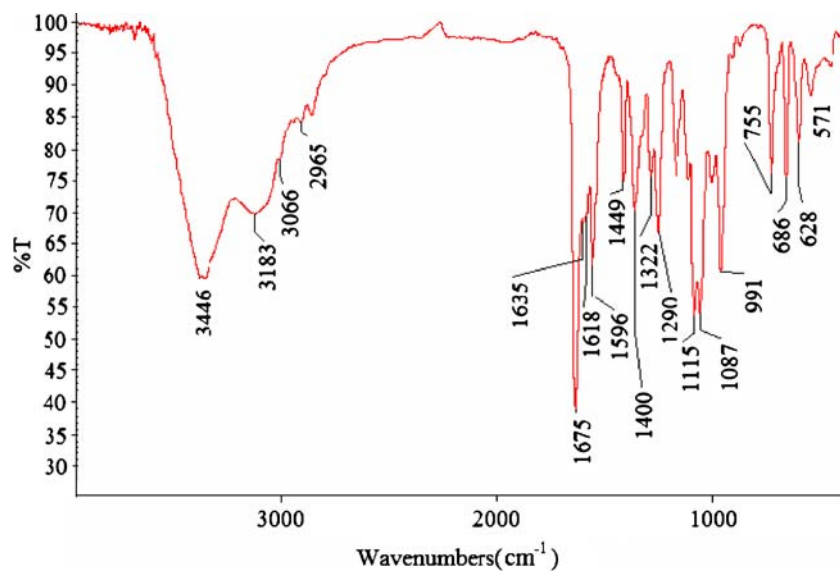


Table 2 Some main IR data of ligands and the ternary rare-earth complexes

Assignment(cm^{-1})	Bis (benzoylmethyl) sulfoxide	Sodium salicylate	Sm (III) complex	Eu (III) complex
$\nu_{\text{O-H}}(\text{H}_2\text{O})$	–	3,446	3,446	3,446
$\nu_{\text{C=C}}(\text{C}_6\text{H}_5)$	1,597	1,599	1,599	1,597
$\nu_{\text{C-H}}(\text{C}_6\text{H}_5)$	3,060	–	3,066	3,066
$\delta_{\text{C-H}}(\text{C}_6\text{H}_5)$	755	–	755	755
	685	–	686	686
$\nu_{\text{S=O}}$	1,033	–	991	991
$\nu_{\text{C=O}}$	1,676	–	1,671	1,675
$\nu_{\text{C-H}}(\text{CH}_2)$	2,971	–	2,965	2,965
$\delta_{\text{C-H}}(\text{CH}_2)$	1,448	–	1,449	1,449
$\nu_{\text{Cl-O}}(\text{ClO}_4^-)$	–	–	1,084	1,087
$\delta(\text{ClO}_4^-)$	–	–	626	628
$\delta_{\text{O-H}}$ (phenolic hydroxyl group)	–	1,483	1,467	1,472
$\nu_{\text{S}}(\text{COO}^-)$	–	1,380	1,400	1,400
$\nu_{\text{as}}(\text{COO}^-)$	–	1,584	1,640	1,635

and $\nu_{\text{S}}(\text{COO}^-)$ absorption bands at 1,635 and 1,400 cm^{-1} in the ternary rare-earth complexes and the $\Delta\nu$ value was 239 cm^{-1} greater than that of sodium salicylate, which could be deduced that carboxyl group was coordinate with rare-earth ions by mono-dentate type [17]. According to the reference [18], the characteristic absorption band of the $\delta_{\text{O-H}}$ (phenolic hydroxyl group) stretching vibration mode appeared at 1,483 cm^{-1} . We could draw the conclusion that rare-earth ions were bonded with oxygen atom in phenolic hydroxyl group when there was an obvious shift of the $\delta_{\text{O-H}}$ stretching frequency towards lower wave number by 11 cm^{-1} in ternary Eu (III) complex. When ClO_4^- was not coordinated, it was Td symmetry and there were two absorption bands. When ClO_4^- was coordinated, it was C_{3v} symmetry and there were five absorptions [19, 20]. In the spectra of the ternary rare-earth complexes, two absorption bands could be seen clearly at approximately 1,087 and 628 cm^{-1} . Therefore, ClO_4^- was Td symmetry. In terms of molar conductivities, it could be suggested that two ClO_4^- were not bonded with rare-earth ions.

UV absorption spectra

The UV absorption spectra of (a) bis(benzoylmethyl) sulfoxide, (b) salicylic acid, (c) the ternary Sm (III) and (d) Eu (III) complexes were recorded in Fig. 7 and DMF was used as a reference and solvent. In Fig. 7 (a) and (b), the major band of π - π^* electronic transition in phenyl group was observed at 266 and 303 nm, respectively. There was

only one absorption band at 266 nm in the absorption spectra of (c) Sm (III) and (d) Eu (III) complex. This resulted a blue-shift of the major π - π^* electronic transition (from 303 nm to 266 nm) for salicylic acid, indicating that the energy of the π^* orbits increased after oxygen atom of salicylic acid coordinated with rare-earth ions.

^1H NMR spectra

The ^1H NMR spectra data of bis(benzoylmethyl) sulfoxide, salicylic acid and the ternary rare-earth complexes could be seen from the Table 3. The ^1H NMR of bis(benzoylmethyl) sulfoxide ligand in CDCl_3 showed two classificatory hydrogen proton resonance peaks which belonged to phenyl and methylene group appeared at δ 7.247–8.015 and δ 4.404–4.801 ppm, and the ratio of resonance peaks area was 10:4. There were multiple hydrogen bonds between hydroxyl and carboxyl group in ligand salicylic acid, so the proton resonance peak of phenolic hydroxyl group was at δ 10.34 ppm which was the average value of carboxyl and phenolic hydroxyl group. The ^1H NMR spectra of the ternary rare-earth complexes were similar. The proton resonance peaks of phenyl and methylene group were very clear, which had shifted at different degree. The reason may be concerned with coordinate effect. The proton resonance peak of carboxyl group disappeared, suggested

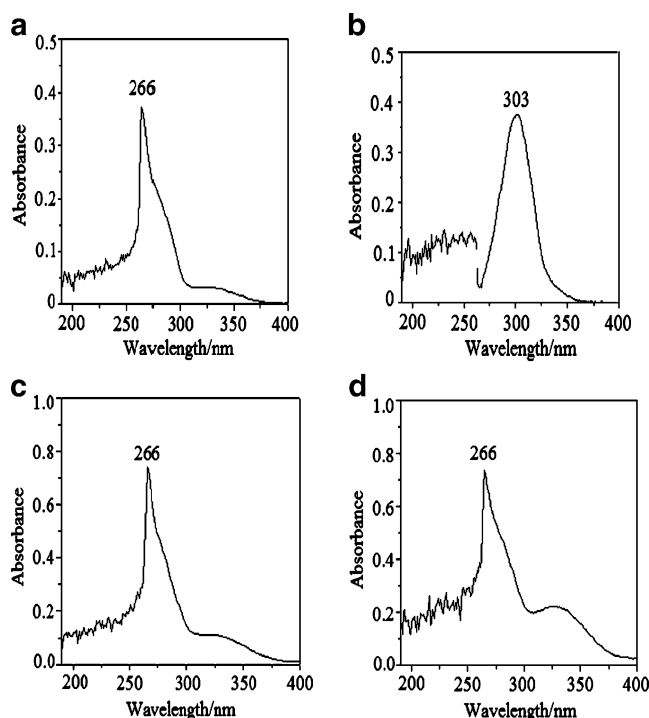


Fig. 7 The UV absorption spectra of **a** bis(benzoylmethyl) sulfoxide, **b** salicylic acid, **c** the ternary Sm (III) and **d** Eu (III) complexes

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

Ligands and complexes	^1H NMR (ppm)			
	-CH ₂ -	-COOH-	-OH-	-C ₆ H ₅ -
L: C ₆ H ₅ COCH ₂ SOCH ₂ COC ₆ H ₅	4.401~4.801(s, 4H)	–	–	7.247~8.015(m, 10H)
L': C ₆ H ₄ OHCOOH	–	10.34 (s, H)	10.34(s, H)	6.913~7.917(m, 4H)
SmL ₅ ·L'·(ClO ₄) ₂ ·7H ₂ O	5.241~5.339(s, 4H)	–	–	7.243~7.766(m, 10H)
EuL ₅ ·L'·(ClO ₄) ₂ ·6H ₂ O	2.787~3.668(s, 4H)	–	–	7.236~8.160 (m, 10H)

that there was coordinated reaction between salicylic acid group and rare-earth ions in the ternary rare-earth complexes. A broad proton resonance peak was found between δ 7.236 and δ 8.160 ppm, which indicated the phenyl group absorption peak of bis(benzoylmethyl) sulfoxide overlapped with that of salicylic acid group.

Luminescence properties

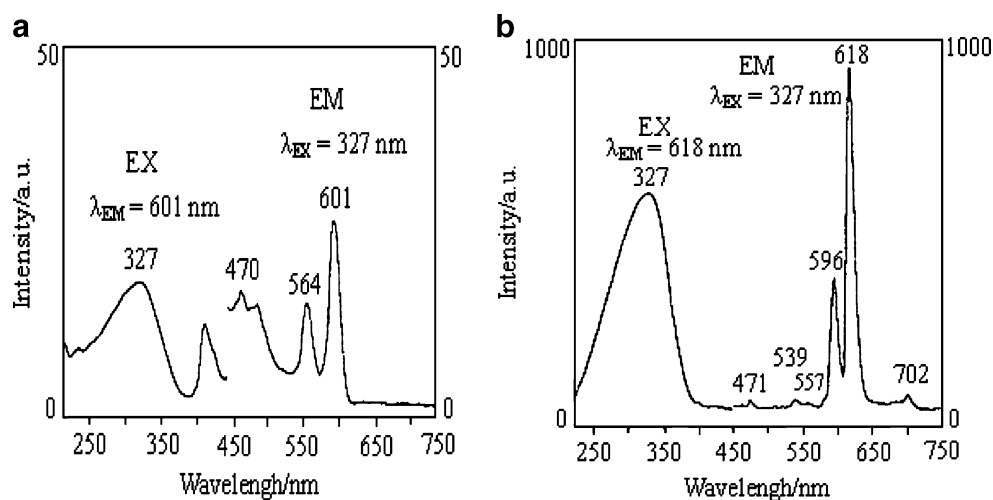
Fluorescence spectra of the ternary rare-earth complexes

The excitation and emission spectra of the ternary Sm (III), Eu (III) complexes in solid state at room temperature were measured. Figure 8a and b showed the excitation and emission spectra of the ternary Sm (III), Eu (III) complexes respectively. The excitation spectra were obtained by monitoring the emission of the Sm (III) complex at 601 nm and Eu (III) complex at 618 nm. Both of the systems had similar excitation spectra which were dominated by a broad band from 250 to 450 nm with the maximum peak at 327 nm. Meantime, in spectra of the ternary Sm (III), Eu (III) complexes, there was a wide excitation band from 200 to 400 nm and the excitation band could overlap effectively with UV absorption spectrum of

the ligand in complexes (Fig. 7c and d). The strong emission intensities between 250 to 350 nm indicated that both ligands were good organic ligand which were beneficial to absorb energy and transfer it to Sm (III), Eu (III) ions, and emitted the characteristic fluorescence of Sm (III), Eu (III) ions [21].

The emission lines of the ternary Sm (III) complex (Fig. 8a) were assigned to $^4\text{G}_{5/2} \rightarrow ^6\text{F}_J$ ($J = 5/2$ and $7/2$) transitions of Sm (III) at 564 and 601 nm, respectively, and the strongest fluorescence emission intensity at 601 nm which was considered to the characteristic emission for the $^4\text{G}_{5/2} \rightarrow ^6\text{F}_{7/2}$ transition of the Sm (III) ion. In Fig. 8b, The emission lines of Eu (III) complex were assigned to the transitions of Eu (III) at 539 ($^5\text{D}_1 \rightarrow ^7\text{F}_0$), 557 ($^5\text{D}_1 \rightarrow ^7\text{F}_1$), 596 ($^5\text{D}_0 \rightarrow ^7\text{F}_1$), 618 ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) and 702 ($^5\text{D}_0 \rightarrow ^7\text{F}_4$) nm. The fluorescence emission spectrum of the ternary Eu (III) complex under the excitation of 327 nm showed the strongest emission peak at 618 nm which corresponded with the characteristic emission for the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of the Eu (III) ion. 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) wasn't locate the centrosymmetric ligand field and gave off the red luminescence. The $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition was magnetic dipole transition,

Fig. 8 Fluorescent excitation and emission Spectra of ternary Sm (III) (a) and Eu (III) (b) complexes



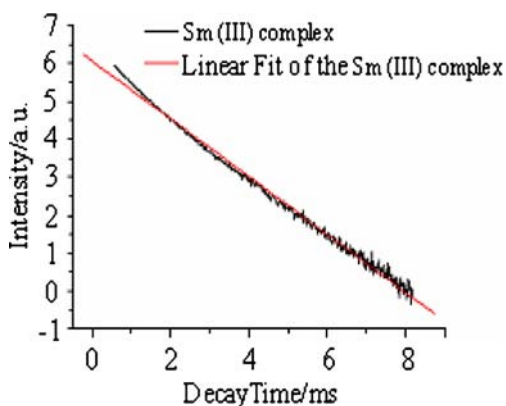


Fig. 9 Linear fit curve of the Sm (III) complex

which became the strongest emission only if Eu (III) ion was in the center of inversion [22]. Furthermore, the intensity ratio of the two transitions ($^5D_0 \rightarrow ^7F_2 / ^5D_0 \rightarrow ^7F_1$) was about 2.58; we could conclude that the Eu (III) was not at the center of an asymmetric coordination field. In order to study the relationship between fluorescence intensity and fluorescence lifetime, the fluorescence decay curves of the ternary Sm (III), Eu (III) complexes were measured. Figures 9 and 10 showed the linear fit curves of the ternary Sm (III), Eu (III) complexes. The fluorescence lifetime values of Sm (III), Eu (III) complexes were calculated by the single exponential mode. From these results, both of the complexes with more preferable fluorescence lifetimes and the fluorescence lifetime of Sm (III) complex (1,763 μ s) was longer than that of Eu (III) complex (1,258 μ s).

The fluorescence properties comparison between the binary and the ternary rare-earth complexes

As we had pointed earlier, the fluorescence properties of rare-earth complexes were related to the second organic ligand significantly. In order to study the effect of the

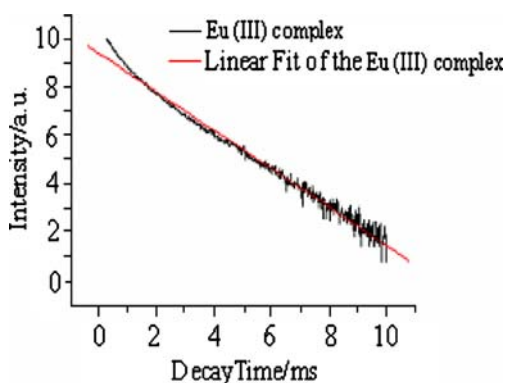


Fig. 10 Linear fit curve of the Eu (III) complex

Table 4 Comparison of fluorescent emission spectra data of binary and ternary complexes

Complexes	λ_{EX} (nm)	λ_{EM} (nm)	I (a.u.)	Energy state transitions
SmL ₅ (ClO ₄) ₃ ·2H ₂ O	338	601	18.63	$^4G_{5/2} \rightarrow ^6H_{7/2}$
SmL ₅ ·L'·(ClO ₄) ₂ ·7H ₂ O	327	601	26.02	$^4G_{5/2} \rightarrow ^6H_{7/2}$
EuL ₅ (ClO ₄) ₃ ·2H ₂ O	332	618	813.4	$^5D_0 \rightarrow ^7F_2$
EuL ₅ ·L'·(ClO ₄) ₂ ·6H ₂ O	327	618	918.6	$^5D_0 \rightarrow ^7F_2$

second ligand (salicylic acid) on the luminescence intensities of the binary rare-earth complexes, the fluorescence spectrum data of the binary rare-earth complexes were measured under similar conditions and listed in Table 4. The characteristic emission lines of complexes were similar. However, the ternary rare-earth complexes present stronger luminescent intensities than the binary rare-earth materials after introduction of the second organic ligand salicylic acid. The strongest characteristic emission intensity of the ternary Sm (III), Eu (III) complexes was 26.02 (a.u.) and 918.6 (a.u.) respectively, which was 1.4 and 1.37 times as great as that of the binary Sm (III), Eu (III) complexes. The reason may be concerned with the intra-molecular energy transfer process between salicylic acid and Sm (III), Eu (III) ions. The salicylic acid with a broad triplet state energy level was thought to be a good synergistic ligand. Furthermore, there was a wide excitation band and the excitation band could overlap effectively with UV absorption spectrum of the ligand in ternary rare-earth complexes. The presence of salicylic acid was benefit to absorb energy effectively and transfer it to Sm (III), Eu (III) ions, emitting the characteristic fluorescence of Sm (III), Eu (III) ions.

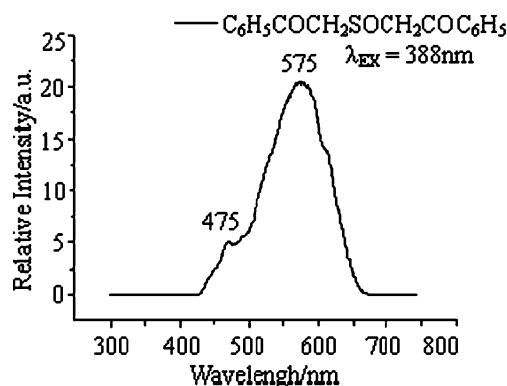


Fig. 11 The phosphorescence spectrum of bis(benzoylmethyl) sulfoxide

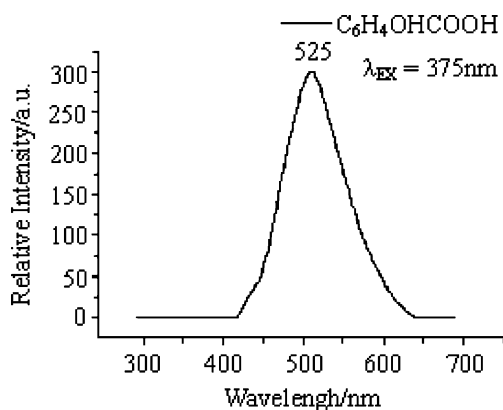


Fig. 12 The phosphorescence spectrum of salicylic acid

Phosphorescence spectra

The phosphorescence spectra of ligands (bis(benzoylmethyl) sulfoxide and salicylic acid) were recorded by F-4500 FL spectrophotometer in solid state and listed in Figs. 11 and 12. According to the energy transfer and intramolecular energy transfer mechanism [23, 24], intramolecular energy transfer efficiency chiefly depended on two energy transfer processes: one was the transitions from the triplet state energy level of ligand to the excited states of the Sm (III) and Eu (III) ion by Dexter's resonant exchange interaction [25], the other was just an inverse energy transfer process by the thermal deactivation mechanism [26]. Based on this theory, we could draw the conclusion that energy difference was of opposite influence on the two energy transfer processes and the optimal value of energy states could be calculated from the spectra. In Fig. 11, two bands could be seen clearly at 575 and 475 nm which corresponded to the triplet state energy level of bis(benzoylmethyl sulfoxide T_1 ($18,349\text{ cm}^{-1}$) and T_2 ($21,053\text{ cm}^{-1}$), respectively. The triplet state energy level T_1 which was appropriately higher than $^4G_{5/2}$ of Sm (III) ion ($17,900\text{ cm}^{-1}$) [27] and 5D_0 of Eu (III) ion ($17,241\text{ cm}^{-1}$) [28] played an important role in transferring energy process from bis(benzoylmethyl sulfoxide to rare-earth ions. Figure 12 showed that the triplet state energy level of the second ligand salicylic acid at 525 nm was close to $19,408\text{ cm}^{-1}$, which was also higher than $^4G_{5/2}$ of Sm (III) ion and 5D_0 of Eu (III) ion. From these different energies, it could be deduced that two ligands could absorb energy effectively and transfer energy to Sm (III), Eu (III) ions, and enhanced the fluorescence emission intensity. The fluorescence intensities of the ternary rare-earth complexes were improved after the introduction of the second ligand salicylic acid. Since salicylic acid group could effectively sensitize the Sm (III) and Eu (III) ions, the ternary rare-

earth complexes had better fluorescence properties than the binary rare-earth complexes as a result.

Conclusion

Two novel ternary Sm (III), Eu (III) complexes had been successfully synthesized and characterized. The composition of the ternary complexes was proved to be $\text{SmL}_5\cdot\text{L}\cdot(\text{ClO}_4)_2\cdot 7\text{H}_2\text{O}$ and $\text{EuL}_5\cdot\text{L}\cdot(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ (the first ligand $\text{L} = \text{C}_6\text{H}_5\text{COCH}_2\text{SOCH}_2\text{COC}_6\text{H}_5$, the second ligand $\text{L} = \text{C}_6\text{H}_4\text{OHCOO}^-$). The photophysical properties of the complexes had been studied with ultraviolet spectra, phosphorescence spectra, excitation and emission spectra, fluorescence lifetimes and phosphorescence spectra. The solid ternary complexes emitted characteristic emission of Sm (III), Eu (III) ions and the fluorescence lifetime of Sm (III) complex ($1,763\text{ }\mu\text{s}$) was longer than that of Eu (III) complex ($1,258\text{ }\mu\text{s}$). The emission intensities and fluorescence lifetimes of ternary Sm (III), Eu (III) complexes enhanced obviously after introducing the second organic ligand salicylic acid. The introduction of the second organic ligand had an effect on the fluorescence intensity of rare-earth organic complexes. Hence, based on the factor, more fluorescence materials could be obtained.

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