

Synthesis and Luminescence Properties of Two Novel Lanthanide (III) Perchlorate Complexes with Bis(benzoylmethyl) Sulfoxide and Benzoic Acid

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Abstract Two novel ternary rare earth complexes of Tb(III) and Dy(III) perchlorates with bis(benzoylmethyl) sulfoxide (L) and benzoic acid (L') had been synthesized and characterized by elemental analysis, coordination titration analysis, molar conductivity, IR, TG-DSC, ¹HNMR and UV spectra. The results indicated that the composition of these complexes was $REL_5L'(ClO_4)_2 \cdot nH_2O$ (RE= Tb(III), Dy(III); $L=C_6H_5COCH_2SOCH_2COC_6H_5$, $L'=C_6H_5COO$; $n=6,8$). The fluorescence spectra illustrated that the ternary rare earth complexes presented stronger fluorescence intensities, longer lifetimes and higher fluorescence quantum efficiencies than the binary rare earth complexes $REL_5 \cdot (ClO_4)_3 \cdot 2H_2O$. After the introduction of the second ligand benzoic acid group, the relative fluorescence emission intensities and fluorescence lifetimes of the ternary complexes $REL_5L'(ClO_4)_2 \cdot nH_2O$ (RE= Tb(III), Dy(III)) enhanced more obviously than the binary complexes. This indicated that the presence of both organic ligands bis(benzoylmethyl) sulfoxide and the second ligand benzoic acid could sensitize fluorescence intensities of rare earth ions, and the introduction of benzoic acid group was resulted in the enhancement of the fluorescence properties of the ternary rare earth complexes. The phosphorescence spectra were also discussed.

Keywords Rare earth complexes · Bis(benzoylmethyl) sulfoxide · Benzoic acid · Fluorescence · Phosphorescent spectrum

Introduction

The study of the coordination compounds of the trivalent rare earth ions (RE^{3+}) continued to be an active research area, which was attributed to the specific fluorescent and magnetic properties of rare earth ions and their applications as electroluminescent (EL) devices, optical signal amplifiers, and luminescent probes in biological systems [1–3]. Among these compounds, the fluorescent rare earth complexes were of special interest because these complexes could show narrow emission bands, a large Stokes' shift, long luminescence decay times and especially the possibility of obtaining improved efficiency over the more conventional materials [4]. 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 [5–8]. Thus, as we had noted, a ligand bis(benzoylmethyl) sulfoxide which had two carbonyl groups, large conjugated plane and rigid structure was chosen for this study.

Previous studies showed that the emission intensities and fluorescence lifetimes of ternary rare earth complexes were enhanced by the use of the secondary ligand beside ligand sensitization [9, 10]. The second organic ligand served as the energy donor and enhanced the fluorescence intensities of binary rare earth complexes. The effect was called “synergistic effect” [11]. Furthermore, the introduction of the second organic ligand did not only reinforce the fluorescence emission intensities, but also completed the coordination numbers of rare earth complexes. Because of its excellent coordination ability to rare earth ions and the ability of sensitizing the lumines-

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

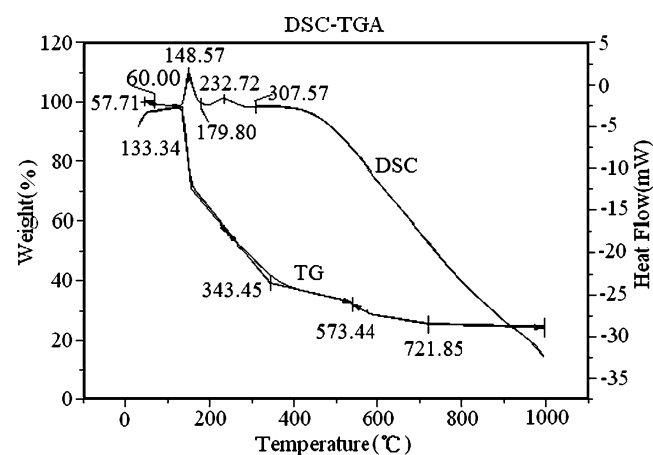
Complexes	M	Anal.calcd.(found)(%)			$\lambda_m(a)$ ($S \cdot cm^2 \cdot mol^{-1}$)
		C	H	RE	
TbL ₅ L'·(ClO ₄) ₂ ·6H ₂ O	2017.05	51.25 (51.76)	4.181 (4.31)	7.76 (7.88)	194.0
DyL ₅ L'·(ClO ₄) ₂ ·8H ₂ O	2056.62	50.96 (50.76)	4.42 (4.42)	7.86 (7.90)	191.7

cence of rare earth ions, aromatic carboxylic acid had been applied to many ternary rare earth systems [12, 13]. For this reason, benzoic acid was chosen as the second organic ligand in ternary rare earth complexes in this paper. Thus, in order to obtain new fluorescence materials which had strong luminescence, high thermodynamic stability and good solubility and study the effects of the second ligand (benzoic acid) on the fluorescence properties of rare earth complexes, the ternary rare earth complexes REL₅L'(ClO₄)₂·nH₂O (RE= Tb(III), Dy(III); L=C₆H₅COCH₂SOCH₂COC₆H₅, L'=C₆H₅COO⁻; n=6,8) had been synthesized by the reaction of bis(benzoylmethyl) sulfoxide and benzoic acid with Tb(III) and Dy(III) respectively and characterized by elemental analysis, IR, TG-DSC, ¹HNMR and UV spectra. We had also studied the fluorescence properties of the ternary Tb(III), Dy(III) complexes in solid state.

Experiment

Materials

Bis(benzoylmethyl) sulfoxide [7] was prepared according to the literature method. The purity of lanthanide oxide exceeds 99.99%, the rare earth (III) perchlorates were prepared by dissolving their oxide (99.99%) in HClO₄ (2 mol/L). Other chemicals were obtained from commercial sources and used without further purification.

**Fig. 1** The TG-DSC curves of TbL₅L'·(ClO₄)₂·6H₂O

Physical measurements

Elemental analysis was carried out on a PE-2400 analyzer. Conductivity measurement was made using a 10^{-3} mol·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 an indicator. The thermal behavior was monitored on SDTQ600 differential scanning calorimeter and thermal gravimetric analyzer. The infrared spectra (IR, $\nu=4,000$ – 400 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. ¹HNMR spectra were measured on Bruker AC-300 spectrometer in CDCl₃. 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 ternary rare earth complexes

The mixture of 5 mmol bis(benzoylmethyl) sulfoxide and 1 mmol benzoic acid was dissolved in anhydrous ethanol,

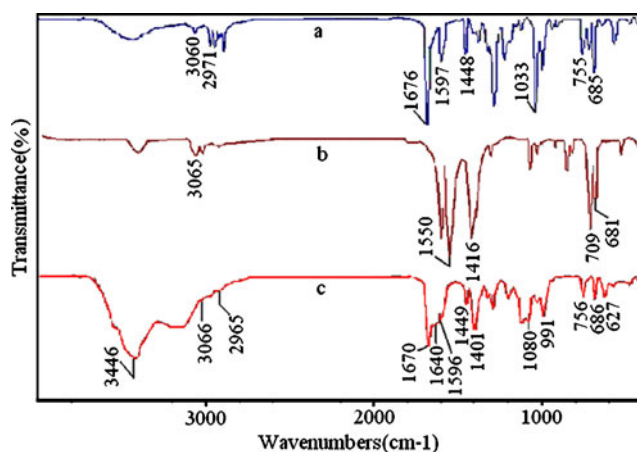
**Fig. 2** IR absorption spectra of the Tb(III) complex and the ligands. **a** ligand L, **b** benzoic acid, **c** the ternary Tb(III) complex

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

Assignment (cm ⁻¹)	Bis(benzoylmethyl) sulfoxide	Sodium benzoate	Tb (III) complex	Dy (III) complex
$\nu_{\text{O-H}}(\text{H}_2\text{O})$	–	–	3446	3446
$\nu_{\text{C=C}}(\text{C}_6\text{H}_5)$	1597	–	1596	1598
$\nu_{\text{C-H}}(\text{C}_6\text{H}_5)$	3060	3066	3066	3066
$\delta_{\text{C-H}}(\text{C}_6\text{H}_5)$	755	709	756	756
	685	681	686	686
$\nu_{\text{S=O}}$	1033	–	991	991
$\nu_{\text{C=O}}$	1676	–	1670	1674
$\nu_{\text{C-H}}(\text{CH}_2)$	2971	–	2965	2966
$\delta_{\text{C-H}}(\text{CH}_2)$	1448	–	1449	1449
$\nu_{\text{Cl-O}}(\text{ClO}_4^-)$	–	–	1080	1088
$\delta(\text{ClO}_4^-)$	–	–	627	625
$\nu_{\text{S}}(\text{COO}^-)$	–	1416	1401	1401
$\nu_{\text{as}}(\text{COO}^-)$	–	1550	1640	1635

then the 3 ml anhydrous ethanol solution including 1 mmol $\text{RE}(\text{ClO}_4)_3 \cdot n\text{H}_2\text{O}$ (RE= Tb(III), Dy(III)) was added to it. After stirring 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

Properties of the complexes

Analytical data for the complexes, presented in Table 1, conformed to $\text{REL}_5\text{L}'(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$. All the complexes

Fig. 3 The UV absorption spectra of **a** bis(benzoylmethyl) sulfoxide, **b** benzoic acid, **c** the ternary Tb(III) complex

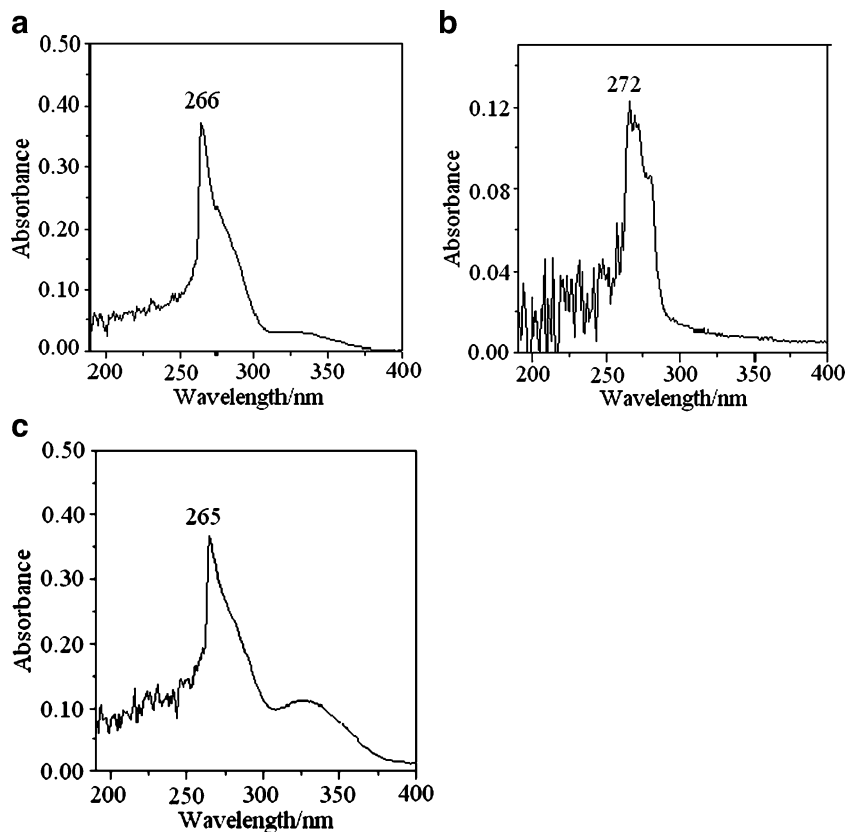


Table 3 Chemical shift data of ^1H NMR spectra (1×10^{-6})

Ligands and complexes	^1H NMR (ppm)		
	$-\text{CH}_2-$	$-\text{COOH}-$	$-\text{C}_6\text{H}_5-$
L : $\text{C}_6\text{H}_5\text{COCH}_2\text{SOCH}_2\text{COC}_6\text{H}_5$	4.401~4.801(s, 4H)	–	7.247~8.015(m, 10H)
L' : $\text{C}_6\text{H}_5\text{COOH}$	–	12.400 (s, H)	7.259~8.152 (m, 5H)
$\text{TbL}_5\text{L}'(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	4.333~5.165 (s, 4H)	–	7.231~7.249(m, 10H)
$\text{DyL}_5\text{L}'(\text{ClO}_4)_2 \cdot 8\text{H}_2\text{O}$	3.952~4.746 (s, 4H)	–	7.265~7.303 (m, 10H)

were white powder like, stable in atmospheric condition and soluble in acetone, DMF and DMSO. The molar conductivity values of the complexes in DMF were in accord with them being formulated as 1:2 electrolytes [14].

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} . The TG-DSC curves of rare earth (III) complexes were similar. The curve of Tb(III) complex was depicted in Fig. 1. The TG curve of Tb(III) complex showed the first mass loss occurred between $57.71\text{ °C} \sim 133.34\text{ °C}$ and mass loss percentage was 4.91%. The result was coincided with the release of all the six water content (5.31%) well. At the same time, DSC curve showed small endothermic peak at 60 °C when losing water. In addition, there were two exothermic peaks in DSC curve which were attributed to the decomposition of the five ligands L and benzene ring of benzoic acid, as well as two obvious weight losses occurred on the TG curve. The final products were proved to be Tb_4O_7 (or Dy_2O_3) when the temperature reached near 1,000 °C, and the total weight loss of the complexes was found to be close to the calculated values. The results were 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 Fig. 2 and Table 2.

In the first ligand L IR spectrum (Fig. 2a), the S=O group stretching modes appeared at $1,033\text{ cm}^{-1}$. However, the S=O stretching frequency of the complexes shifted to a lower wave number by 42 cm^{-1} , it suggested that rare earth ions were bonded with oxygen atom in sulfinyl group. The C=O stretching frequency of the ligand appeared a strong peak at $1,676\text{ cm}^{-1}$. In ternary Tb(III) complex (Fig. 2c), there was no significant shift for $\nu_{\text{C=O}}$, which suggested that the oxygen atoms in carbonyl group were not coordinated with rare earth ions. The $\nu_{\text{as}(\text{COO}^-)}$ and $\nu_{\text{s}(\text{COO}^-)}$ absorption of sodium benzoate occurred at $1,550\text{ cm}^{-1}$ and $1,416\text{ cm}^{-1}$, and the $\Delta\nu$ value was 134 cm^{-1} in the Fig. 2b. There were no significant bands between $1,690$ and $1,730\text{ cm}^{-1}$ in the spectra of ternary rare earth complexes, which indicated carboxyl group had taken place deprotonation. The presence of $\nu_{\text{as}(\text{COO}^-)}$ and $\nu_{\text{s}(\text{COO}^-)}$ absorption bands were at $1,635 \sim 1,640\text{ cm}^{-1}$ and $1,401\text{ cm}^{-1}$ in the ternary rare earth complexes and the $\Delta\nu$ value was $234 \sim 239\text{ cm}^{-1}$ greater than that of sodium benzoate, which could be deduced that carboxyl group was coordinated with rare earth ions by mono-dentate type [15].

Fig. 4 Fluorescent excitation and emission Spectra of ternary Tb(III) **a** and Dy(III) **b** complexes

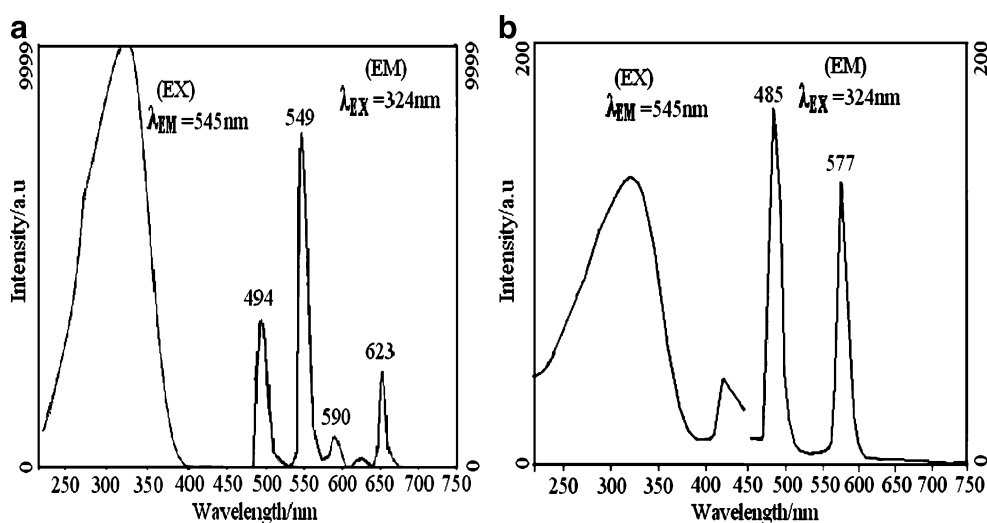


Table 4 Comparison of solid fluorescent data of Tb(III), Dy(III) binary and ternary complexes at room temperature

Complexes	λ_{EX} (nm)	λ_{EM} (nm)	Intensity (a.u.)	Energy state transitions
TbL ₅ (ClO ₄) ₃ ·2H ₂ O	325	493.4	2613	⁵ D ₄ → ⁷ F ₆
		547.8	5724	⁵ D ₄ → ⁷ F ₅
TbL ₅ ·L'·(ClO ₄) ₂ ·6H ₂ O	324	493.8	3531	⁵ D ₄ → ⁷ F ₆
		547.8	7980	⁵ D ₄ → ⁷ F ₅
DyL ₅ (ClO ₄) ₃ ·2H ₂ O	326	485.4	143.4	⁴ F _{9/2} → ⁶ H _{15/2}
		577.0	100.9	⁴ F _{9/2} → ⁶ H _{13/2}
DyL ₅ ·L'·(ClO ₄) ₂ ·8H ₂ O	321	485.8	169.0	⁴ F _{9/2} → ⁶ H _{15/2}
		577.0	134.2	⁴ F _{9/2} → ⁶ H _{13/2}

Additionally, there were two peaks about 1,080~1,088 cm⁻¹ and 627~625 cm⁻¹, both of them were attributed to the ClO₄⁻ group in complexes. According to literature, when ClO₄⁻ was not coordinated, it was Td symmetry and there were two absorptions. When ClO₄⁻ was coordinated, it was C_{3v} symmetry and there were five absorptions [16, 17]. In the IR spectra of these complexes, two absorptions could be seen clearly. So ClO₄⁻ was Td symmetry. In terms with the molar conductivities, it could be induced that two ClO₄⁻ were not coordinated with RE(III).

UV spectra

The UV spectra of the ligands and Tb(III) complex were shown in Fig. 3. In Fig. 3(a) and (b), the major band of π - π^* electronic transition in phenyl group was observed at 266 and 272 nm, respectively. There was only one absorption band at 265 nm in the absorption spectra of Tb(III) complex. This resulted a blue-shift of the major π - π^* electronic transition (from 272 nm to 265 nm) for benzoic acid, indicating that the energy of the π^* orbits increased after oxygen atom of benzoic acid coordinated with rare earth ions.

¹H NMR spectra

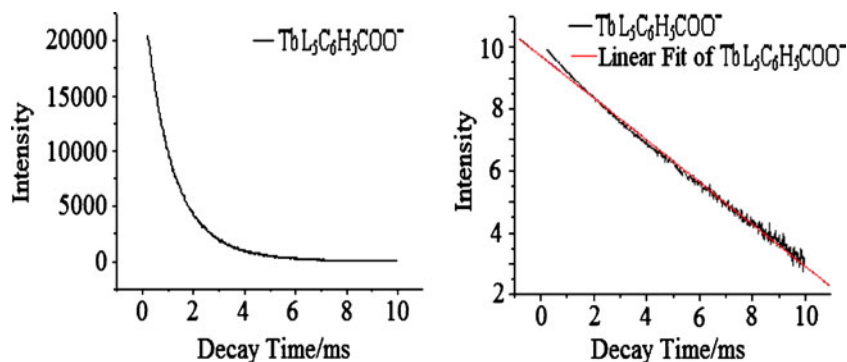
The ¹H NMR spectra data of bis(benzoylmethyl) sulfoxide, benzoic acid and the ternary rare earth complexes could be

seen from the Table 3. The ¹H NMR of bis(benzoylmethyl) sulfoxide ligand in CDCl₃ 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 also two classificatory hydrogen proton resonance peaks of benzoic acid which belonged to phenyl and carboxyl group appeared at δ 7.259–8.152 and δ 12.400 ppm. 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 that there was coordinated reaction between benzoic acid group and rare earth ions in the ternary rare earth complexes. A broad proton resonance peak was found between δ 7.231 and δ 7.303 ppm, which indicated the phenyl group absorption peak of bis(benzoylmethyl) sulfoxide overlapped with that of benzoic acid group.

Fluorescence spectra

Fluorescence spectra of the ternary rare earth complexes

The excitation spectra and emission spectra of Tb(III) and Dy(III) complexes were measured in solid state at room temperature. According to the spectra of complexes that

Fig. 5 Fluorescence decay curve and fitted curve of ternary Tb(III) complex

were reported in Fig. 4 and Table 4, we could see that the complexes had excellent fluorescence 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. 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 324 and 321 nm, respectively. Meantime, in spectra of the ternary Tb(III) and Dy(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. 4a). The strong emission intensities between 250 to 350 nm indicated that both of the two ligands were good organic ligand which were beneficial to absorb energy and transfer it to Tb(III), Dy(III) ions, and emitted the characteristic fluorescence of Tb(III), Dy(III) ions.

The emission lines of the ternary Dy(III) complex (Fig. 4b) were assigned to the characteristic ${}^4F_{9/2} \rightarrow {}^6H_J$ ($J = 15/2$ and $13/2$) transitions of Dy(III) at 485 and 577 nm, respectively, and the strongest fluorescence emission intensity at 485 nm which was considered to be the characteristic emission for the ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition of the Dy(III) ion. In Fig. 4a, the emission lines of Tb(III) complex were assigned to the characteristic ${}^5D_4 \rightarrow {}^7F_J$ ($J = 6, 5, 4, 3$) transitions of Tb(III) at 494, 548, 590 and 623 nm. The fluorescence emission spectrum of the ternary Tb(III) complex under the excitation of 324 nm showed the strongest emission peak at 548 nm which corresponded with the characteristic emission for the ${}^5D_4 \rightarrow {}^7F_5$ transition of the Tb(III) ion. In order to study the relationship between fluorescence intensity and fluorescence lifetime, the fluorescence decay curves of the ternary Tb(III), Dy(III) complexes were measured. Figure 5 showed the fluorescence decay curve and linear fit curve of the ternary Tb(III) complex. The fluorescence lifetime values of Tb(III), Dy(III) complexes were calculated by the single exponential mode. From these results, both of the complexes with more preferable fluorescence lifetime and the fluorescence

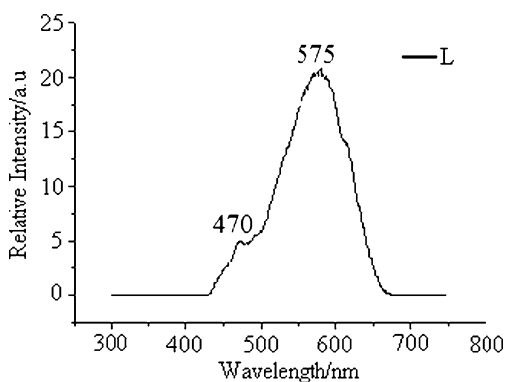


Fig. 6 The phosphorescence spectrum of bis(benzoylmethyl) sulfonide

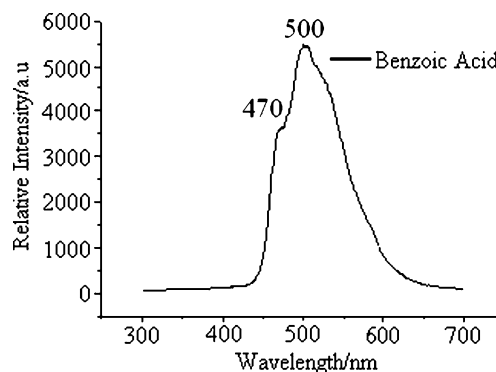


Fig. 7 The phosphorescence spectrum of benzoic acid

lifetime of Tb(III) complex (1,468 μ s) was longer than that of Dy(III) complex (1,378 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 second ligand (benzoic acid) on the fluorescence 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 presented stronger luminescent intensities than the binary rare earth materials after introduction of the second organic ligand benzoic acid. The strongest characteristic emission intensity of the ternary Tb(III), Dy(III) complexes was 7980 (a.u.) and 169 (a.u.) respectively, which was 1.4 and 1.2 times as

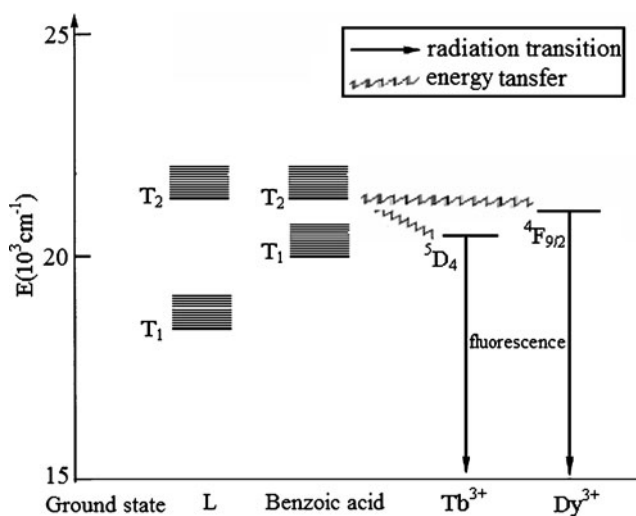


Fig. 8 Intra-molecular energy transfer mechanism

great as that of the binary Tb(III), Dy(III) complexes. The reason may be concerned with the intra-molecular energy transfer process between benzoic acid and Tb(III), Dy(III) ion. The benzoic 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 benzoic acid was benefit to absorb energy effectively and transfer it to Tb(III), Dy(III) ions, emitting the characteristic fluorescence of Tb(III), Dy(III) ions.

Phosphorescence spectra

The phosphorescence spectra of ligands (bis(benzoylmethyl) sulfoxide and benzoic acid) were recorded by F-4500 FL spectrophotometer in solid state and listed in Figs. 6 and 7. According to the intra-molecular energy transfer mechanism [18, 19], intra-molecular 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 Tb(III) and Dy(III) ions by Dexter's resonant exchange interaction [20], the other was just an inverse energy transfer process by the thermal deactivation mechanism [21]. Based on this theory, we could draw the conclusion that energy level 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. 6, two bands could be seen clearly at 575 and 470 nm which corresponded to the triplet state energy level of bis(benzoylmethyl) sulfoxide T_1 ($18,349\text{ cm}^{-1}$) and T_2 ($21,276\text{ cm}^{-1}$), respectively. The triplet state energy level T_2 which was appropriately higher than 5D_4 of Tb(III) ion ($20,430\text{ cm}^{-1}$) [22] and $^4F_{9/2}$ of Dy(III) ion ($21,100\text{ cm}^{-1}$) [23] played an important role in transferring energy process from bis(benzoylmethyl) sulfoxide to rare earth ions.

In Fig. 7, two bands also could be seen at 500 and 470 nm which corresponded to the triplet state energy level of benzoic acid T_1 ($20,000\text{ cm}^{-1}$) and T_2 ($21,276\text{ cm}^{-1}$), respectively. The triplet state energy level T_2 of the second ligand benzoic acid was also higher than 5D_4 of Tb(III) ion and $^4F_{9/2}$ of Dy(III) ion. From these different energies, it could be deduced that two ligands could absorb energy effectively and transfer energy to Tb(III), Dy(III) ions, and enhanced the fluorescence emission intensity. On the other hand, the triplet state energy level T_2 of benzoic acid was the same as that of the ligand L ($21,276\text{ cm}^{-1}$), indicating that the triplet state energy level of the two ligands matched well each other. They could transfer the energy to rare earth ions available together. At the same time, the relative emission intensity of the second ligand benzoic acid was higher than that of the first ligand L in the phosphorescence spectra. The intra-molecular energy transfer mechanism

was shown in Fig. 8. So benzoic acid could absorb and transfer energy to rare earth ions more effectively and this ligand was thought to be a good synergistic ligand. The fluorescence intensities of the ternary rare earth complexes were improved after the introduction of the second ligand benzoic acid. Since benzoic acid could effectively sensitize the Tb(III) and Dy(III) ions, the ternary rare earth complexes had better fluorescence properties than the binary rare earth complexes as a result.

Conclusion

Two novel ternary Tb(III), Dy(III) complexes had been successfully synthesized and characterized. The composition of the ternary complexes was proved to be REL_5L' (ClO_4) $_2 \cdot nH_2O$ ($RE = Tb(III), Dy(III)$; $L = C_6H_5COCH_2SOCH_2COC_6H_5$, $L' = C_6H_5COO^-$; $n = 6, 8$). The photophysical properties of them had been studied with ultraviolet spectra, excitation and emission spectra, fluorescence lifetimes and phosphorescence spectra. The solid ternary complexes emitted characteristic emission of Tb(III), Dy(III) ions, and the fluorescence lifetime of Tb(III) complex ($1,468\text{ }\mu s$) was longer than that of Dy(III) complex ($1,378\text{ }\mu s$). The emission intensities and fluorescence lifetimes of ternary Tb(III), Dy(III) complexes enhanced obviously after introducing the second organic ligand benzoic acid. The introduction of the second organic ligand could influence the fluorescence intensity of rare earth organic complexes.

The triplet state energy level of the two ligands matched well each other. In the phosphorescence spectra, the relative emission intensity of the second ligand benzoic acid was higher than that of the first ligand L. So benzoic acid could absorb and transfer energy to rare earth ions more effectively and this ligand was thought to be a good synergistic ligand. Furthermore, it could sensitize luminescence of rare earth ions. Therefore, considering this factor, more fluorescence materials could be obtained.

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