

Synthesis and fluorescent properties in complexes of Eu(III), Tb(III), and Sm(III) with β -diketone and 2,2'-bipyridine

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Abstract

Three new rare earth ternary complexes, RE(PB)₃bpy (RE=Sm³⁺, Eu³⁺, and Tb³⁺), were synthesized by the reaction of 1-(*p*-phenylethynyl-phenyl)-1,3-butanedione (HPB) and 2,2'-bipyridine (bpy) with rare earth chloride RECl₃, respectively, in alcohol solution. The compositions were characterized by means of infrared (IR) spectra, chemical analysis, elemental analysis, and thermodynamic analysis. Luminescent properties of the three complexes were studied. At room temperature, under UV light excitation, the Sm³⁺, Eu³⁺, and Tb³⁺ complexes exhibit characteristic emission of the central ions. The fluorescence spectra show that the fluorescence emission intensity of Eu³⁺ complex is the strongest. The narrow strongest emission band of Eu³⁺ complex is considered to be a valuable material with bright red fluorescence.

Keywords: β -diketone; 2,2'-bipyridine; lanthanide complex; luminescent property

1 Introduction

The spectroscopic and magnetic properties of rare earth ions have made them one of the essential components in the preparation of new materials and ideal probes in studies of biological system [1]. Considerable attention has been paid to the luminescent rare earth complexes because these functional complexes have great potential applications as labels and sensors for natural science, medical science, and biochemistry [2–6]. Much work has been done to design and synthesize lanthanide chelates with good luminescence property. Generally, fluorescent enhancement can be achieved through ligand sensitization [7]. Different kinds of ligands have been used for this purpose, such as aromatic carboxylic acids [8–9]; especially, β -diketones have been intensively studied due to their strong coordination capability to the rare earth ions and enhanced luminescence of rare earth complexes by providing some proper conjugate absorption groups suitable for energy transfer. Studies show that rare earth luminescence enhancement can be facilitated in complexes by adding aromatic rings possessing a nitrogen atom, such as 1,10-phenanthroline or pyridine [10]. Our group has designed and synthesized some rare earth ternary complexes with 1,10-phenanthroline and β -diketone [11–17].

Three novel rare earth ternary complexes with 2,2'-bipyridine and β -diketone were designed and prepared in this work. The luminescent properties of the three complexes in solid state were investigated in detail.

2 Experimental

Microanalyses for C and H were conducted on a vario micro cube elemental analyzer. Sm, Eu, and Tb content was determined by EDTA titration after the Sm³⁺, Eu³⁺, and Tb³⁺ in the complexes were dissociated with 10% hydrochloric acid. Infrared (IR) spectra were recorded on an IRPrestige-21 Fourier transform spectrophotometer by dispersing samples in KBr pellets. Thermodynamic analysis was carried out on a NETZSCH STA 409 PC/PG thermal analyzer. Luminescent spectra were recorded on a Cary-eclipse spectrophotometer. The β -diketone ligand (HPB) was prepared in a similar way as described in Ref. [17].

2.1 Synthesis of Sm(PB)₃bpy

Samarium chloride (0.1824 g, 0.50 mmol) in anhydrous ethanol (12 ml) was added dropwise to a stirred solution of HPB (0.3934 g, 1.50 mmol) and bpy (0.0711 g, 0.50 mmol) in anhydrous ethanol (20 ml) at 50 °C; then, the pH of the

reaction mixture was adjusted to about 6.5 with aqua ammonia (1:1). The resulting solution was stirred at 50°C for another 5 h and left still at room temperature overnight and then it was filtered. The filter cake was washed with ethanol (95 vol.%) and dried in vacuum. Finally, the product (0.291 g, 54.9 wt.%) that was light yellow powder was obtained. After the elemental analysis of $\text{Sm}(\text{C}_{18}\text{H}_{13}\text{O}_2)_3(\text{C}_{10}\text{H}_8\text{N}_2)$ (wt.%), we obtained C: 71.62 (70.49), H: 4.25 (4.34), N: 2.37 (2.57), and Sm: 13.86 (13.79). The values in brackets are the calculated ones.

2.2 Synthesis of $\text{Eu}(\text{PB})_3\text{bpy}$

$\text{Eu}(\text{PB})_3\text{bpy}$ was prepared from HPB (0.3934 g, 1.50 mmol), bpy (0.0711 g, 0.50 mmol), and europium chloride (0.1832 g, 0.50 mmol) by the same method as described above. The yield was 0.284 g (52.7%) as light yellow powder. The results of the elemental analysis and calculation of $\text{Eu}(\text{C}_{18}\text{H}_{13}\text{O}_2)_3(\text{C}_{10}\text{H}_8\text{N}_2)$ (wt.%) were C: 70.49 (70.39), H: 4.37 (4.34), N: 2.16 (2.56), and Eu: 14.14 (13.92). The values in brackets are the calculated ones.

2.3 Synthesis of $\text{Tb}(\text{PB})_3\text{bpy}$

$\text{Tb}(\text{PB})_3\text{bpy}$ was prepared from HPB (0.3934 g, 1.50 mmol), bpy (0.0711 g, 0.50 mmol), and terbium chloride (0.1867 g, 0.50 mmol) by the same method as described above. The yield was 0.281 g (51.7%) as light yellow powder. The results of the elemental analysis and calculation of $\text{Tb}(\text{C}_{18}\text{H}_{13}\text{O}_2)_3(\text{C}_{10}\text{H}_8\text{N}_2)$ (wt.%) were C: 69.71 (69.94), H: 4.64 (4.31), N: 2.02 (2.55), and Tb: 14.62 (14.46). The values in brackets are the calculated ones.

3 Results and discussion

3.1 Structure analysis of rare earth complexes

The composition and structure of the rare earth complexes are confirmed by IR spectra, elemental analysis, and thermodynamic analysis.

The IR spectra of all three complexes are similar, indicating that they are structurally alike. Table 1 summarizes the characteristic bands observed for the ligands and their rare earth complexes. C=O vibration in the complexes shifts

Table 1 Main IR spectra data of ligands and complexes (cm^{-1})

Compounds	$\sigma_{\text{O-H}}$	$\sigma_{\text{C=O}}$	$\sigma_{\text{C=N}}$
$\text{Sm}(\text{PB})_3\text{bpy}$	—	1535.3	1502.6
$\text{Eu}(\text{PB})_3\text{bpy}$	—	1535.2	1498.6
$\text{Tb}(\text{PB})_3\text{bpy}$	—	1510.2	1508.6
HPB	3450.6	1604.8	—
bpy	—	—	1454.3

to lower wave number and C=N vibration in the complexes shifts to higher wave number. $\sigma_{\text{C=O}}$ changes from 1604.8 cm^{-1} in HPB to 1535.3 cm^{-1} in coordinated $\text{Sm}(\text{PB})_3\text{bpy}$, 1535.2 cm^{-1} in coordinated $\text{Eu}(\text{PB})_3\text{bpy}$, and 1510.2 cm^{-1} in coordinated $\text{Tb}(\text{PB})_3\text{bpy}$, respectively. $\sigma_{\text{C=N}}$ changes from 1454.3 cm^{-1} in bpy to 1502.6 cm^{-1} in coordinated $\text{Sm}(\text{PB})_3\text{bpy}$, 1498.6 cm^{-1} in coordinated $\text{Eu}(\text{PB})_3\text{bpy}$, and 1508.6 cm^{-1} in coordinated $\text{Tb}(\text{PB})_3\text{bpy}$, respectively. These results establish that the Sm(III), Eu(III), and Tb(III) ions are coordinated to the ligands. The enolic O-H stretching absorption is observed as a broad band at 3450.6 cm^{-1} in HPB and disappears in the complexes. The typical OH absorption at 3200–3500 cm^{-1} is not observed in the complexes, implying that there are no coordinated H_2O molecules in the complexes, which matches well with the result of the elemental analyses.

Thermal properties were evaluated by means of DTA and TG in air. The results are presented in Figs. 1–3.

Figs. 1–3 show that the three rare earth complexes display similar decomposition. The TG diagram shows that the mass loss of $\text{Sm}(\text{PB})_3\text{bpy}$, $\text{Eu}(\text{PB})_3\text{bpy}$, and $\text{Tb}(\text{PB})_3\text{bpy}$ is 80.5%, 88.1%, and 85.2% respectively, which is in good agreement with the calculated mass loss. The calculated

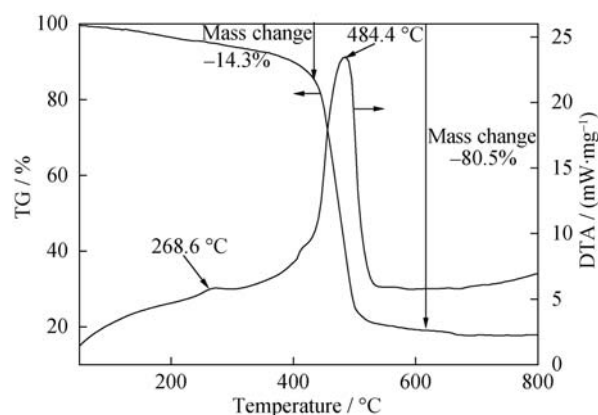


Fig. 1 TG-DTA spectrum of $\text{Sm}(\text{PB})_3\text{bpy}$

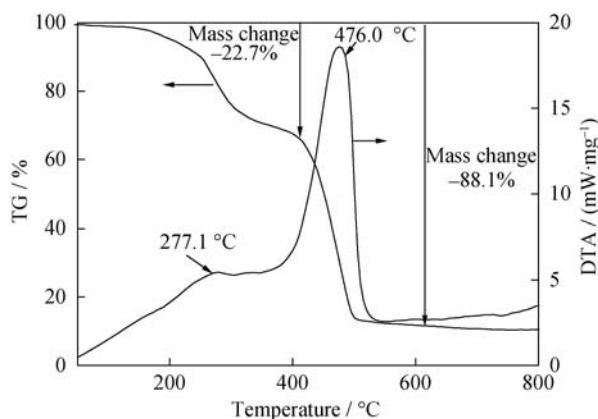


Fig. 2 TG-DTA spectrum of $\text{Eu}(\text{PB})_3\text{bpy}$

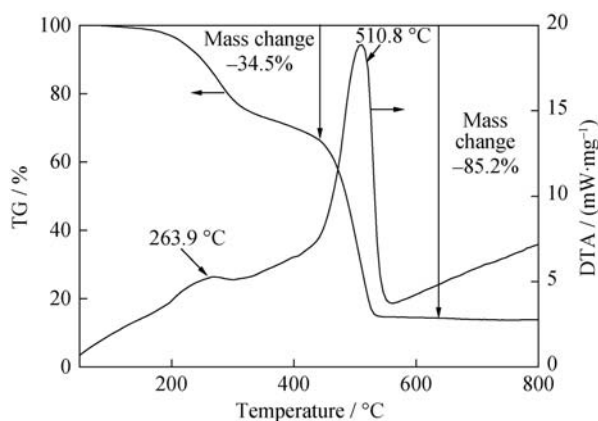


Fig. 3 TG-DTA spectrum of Tb(PB)₃bpy

mass loss of Sm(PB)₃bpy, Eu(PB)₃bpy, and Tb(PB)₃bpy is 84.0%, 83.9%, and 83.4% respectively, when the complex is completely decomposed into rare earth oxide.

From the analyses (IR spectra, chemical analysis, elemental analysis, and thermodynamic analysis) above, we can conclude the composition and molecular structure of the complexes as shown in Fig. 4.

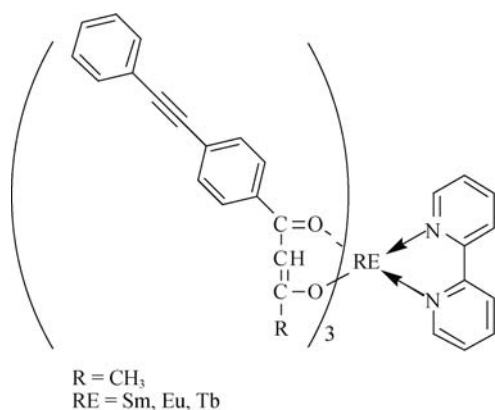


Fig. 4 Molecular structures of compounds

3.2 Luminescence studies

The luminescent properties of the rare earth complexes were investigated. The fluorescence data for each of the complexes were measured at room temperature in the solid state. The results are presented in Table 2 and Figs. 5~7.

Table 2 Main fluorescent spectra data of Sm(PB)₃bpy, Eu(PB)₃bpy, and Tb(PB)₃bpy

Complexes	λ_{ex} / nm	λ_{em} / nm	Emission intensity / a.u.	Transition
Sm(PB) ₃ bpy	312	563	50	$^4G_{5/2} \rightarrow ^6H_{5/2}$
		601	127	$^4G_{5/2} \rightarrow ^6H_{7/2}$
		643	191	$^4G_{5/2} \rightarrow ^6H_{9/2}$
Eu(PB) ₃ bpy	363	613	707	$^5D_0 \rightarrow ^7F_2$
Tb(PB) ₃ bpy	471	542	11	$^5D_4 \rightarrow ^7F_5$

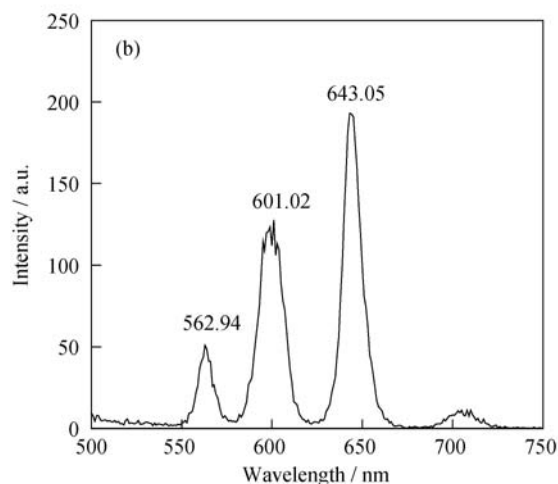
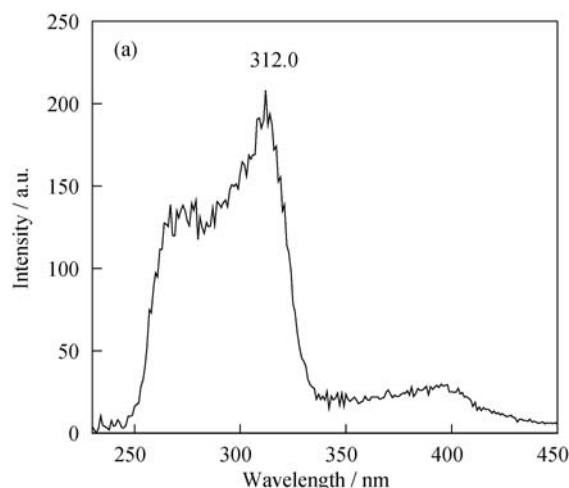


Fig. 5 Emission spectrum (a) and excitation spectrum (b) of Sm(PB)₃bpy

The maximum excitation wavelengths (λ_{ex}) of the Sm³⁺, Eu³⁺, and Tb³⁺ complexes are 312, 363, and 471 nm, respectively.

The emission spectrum of Sm(PB)₃bpy, excited at 312 nm, exhibits the characteristic emissions of Sm³⁺. As shown in Fig. 5, emission peaks at 563, 601, and 643 nm correspond to the $^4G_{5/2} \rightarrow ^6H_{5/2}$, $^4G_{5/2} \rightarrow ^6H_{7/2}$, and $^4G_{5/2} \rightarrow ^6H_{9/2}$ transitions respectively.

The emission spectrum of Eu(PB)₃bpy, excited at 363 nm, exhibits the characteristic emissions of Eu³⁺. The band at 579 nm is assigned to the $^5D_0 \rightarrow ^7F_0$ transition and 593 nm is assigned to the $^5D_0 \rightarrow ^7F_1$ transition, while the peaks at 613, 653, and 701 nm correspond to the $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$, and $^5D_0 \rightarrow ^7F_4$ transitions, respectively.

The emission spectrum for Tb(PB)₃bpy was excited at 471 nm, exhibiting the characteristic emission of Tb³⁺ at 542 nm, which corresponds to $^5D_4 \rightarrow ^7F_5$ transition.

As can be seen in Table 2 and Figs. 5~7, the fluorescent intensities observed from Sm(PB)₃bpy and Tb(PB)₃bpy

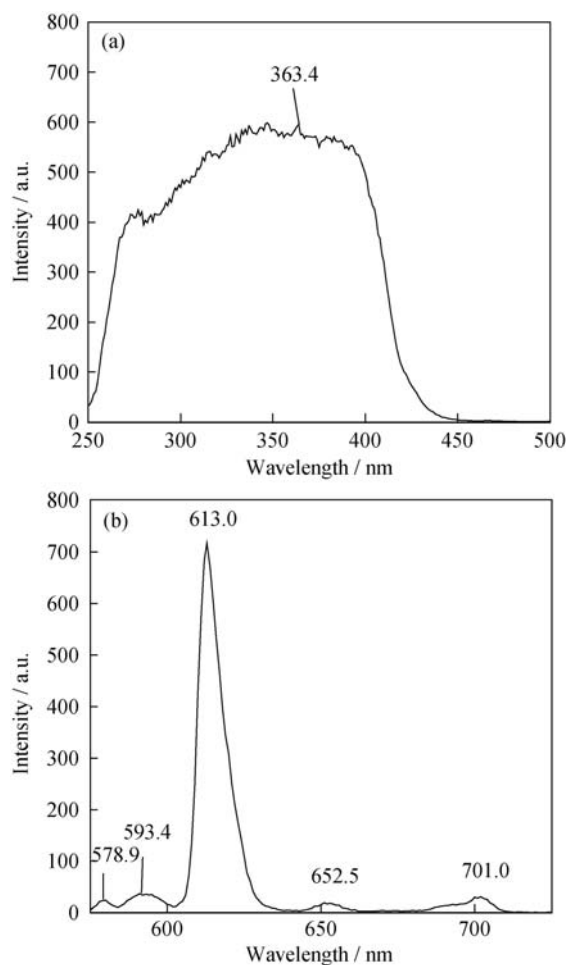


Fig. 6 Emission spectrum (a) and excitation spectrum (b) of $\text{Eu}(\text{PB})_3\text{bpy}$

are weak, while very strong fluorescence is observed from the $\text{Eu}(\text{PB})_3\text{bpy}$ at 613 nm. One factor that can contribute to the observed emission intensity is the energy gap between the two energy states involved. Since the luminescent intensity of the Eu^{3+} complex at 613 nm is much stronger than other complexes we have studied, it can be inferred that the energy difference between the ligand triplet states and the emitting energy state of Eu^{3+} is more favorable for energy transfer from the ligand to the Eu^{3+} than to the Sm^{3+} and Tb^{3+} .

4 Conclusion

We have successfully synthesized three novel rare earth ternary complexes: $\text{Sm}(\text{PB})_3\text{bpy}$, $\text{Eu}(\text{PB})_3\text{bpy}$, and $\text{Tb}(\text{PB})_3\text{bpy}$. Differences in the IR spectra of the free ligands and the complexes indicate that coordination of each of the three rare earth ions to the ligands occurs at the oxygen atoms of the carbonyl and enol groups and the nitrogen atom of the 2,2'-bipyridine. Each of the complexes exhibits the

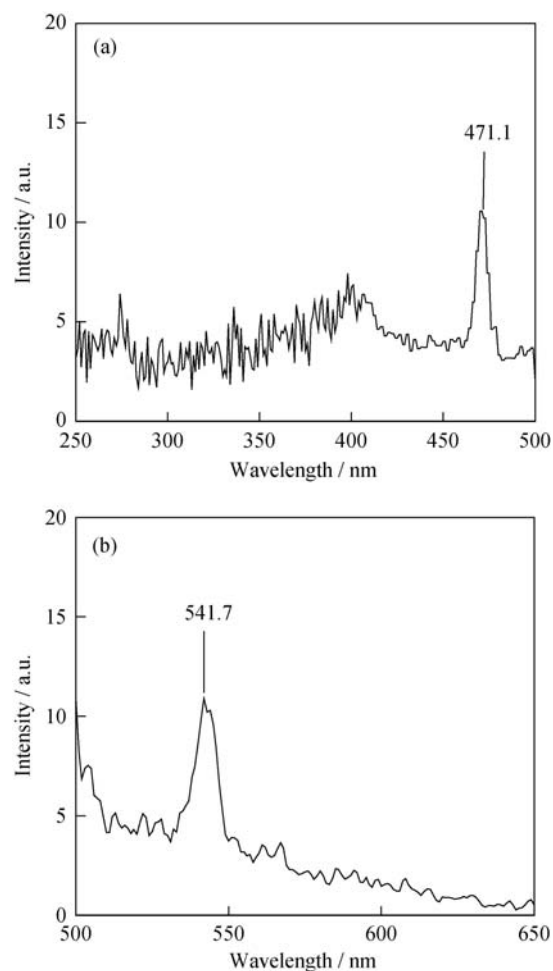


Fig. 7 Emission spectrum (a) and excitation spectrum (b) of $\text{Tb}(\text{PB})_3\text{bpy}$

characteristic emission of the central ion. The narrow and strong luminescence of the Eu^{3+} complex at 613 nm could be considered as a candidate material for applications in organic light-emitting devices.

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