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Enhanced luminescence of rare-earth complexes $Tb_{1-x}Eu_x(m-NBA)_3$ Phen in ZnS

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Abstract

Rare-earth ternary complexes $Tb_{1-x}Eu_x(m-NBA)_3Phen (X=1, 0.25, 0.5, 0.75, 1.0)$ were synthesized and characterized by IR, DTA–TG, UV, fluorescent spectra and elemental analysis. It was found that luminescence of Eu^{3+} complex was enhanced by doped with Tb^{3+} . It is proved by TG curve that the complexes are stable, ranging from ambient temperature to 360 °C in air. The organic–inorganic combined structural device was fabricated, and the electroluminescence intensity of the combined structural device was improved compared with the device of the purely organic components.

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1. Introduction

Rare-earth metal complexes are suitable to be used as the emission materials because of their special characteristics, such as extremely narrow emission bands and high internal quantum efficiencies [1–4]. And considerable studies have been focused on the design and assembly of lanthanide complexes with organic ligands such as β -diketone, cryptands, calixarenes, etc. Therefore, many rare-earth complexes have been synthesized and used as photoluminescence emitters and electroluminescence devices [5–8]. It has been reported that introduction of Tb³⁺ into europium complex can ensure brighter red light under particular conditions [9,10]. Because the energy transfer from Tb³⁺ to Eu³⁺ can be effective, introduction of Tb³⁺ can enhance europium emission. However, little attention has been paid to rare-earth ternary complexes with Eu³⁺ (or Tb³⁺), *m*-NBA (*m*-nitrobenzoic acid) and 1,10-phen (1,10-phenanthroline).

In this paper, rare-earth (Eu³⁺ and Eu³⁺/Tb³⁺) ternary complexes with *m*-NBA and 1,10-phen, $Tb_{1-x}Eu_x(m-NBA)_3$ Phen (*X*=0, 0.25, 0.5, 0.75, 1.0) were synthesized, and the

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organic–inorganic combined structural device (ITO/PVK: Eu complexes/ZnS/Al) was fabricated. It may be an effective method to improve the electroluminescence intensity of lan-thanide complex by using inorganic semiconductor materials.

2. Experiments details

2.1. Sample preparation

One millimole mixture of EuCl₃·6H₂O and TbCl₃·6H₂O (mole ratios of the Eu³⁺ to Tb³⁺ are 1.0:0, 0.75:0.25, 0.5:0.5, 0.25:0.75 and 0:1.0, respectively), and 3 mmol of *m*-NBA were dissolved in ethanol. The pH value of the mixture was adjusted to 6–7 by adding 3 mmol ammonia. Then 1,10-phenanthroline in ethanol solution was added to the reaction mixture, the molar ratio of 1,10-phenanthroline to RE³⁺ ion was 1:1. The precipitate was filtered, washed with water and ethanol, dried at room temperature, and then stored in a silica-gel drier. The structure of ternary complexes is shown in Fig. 1.

2.2. Electroluminescence device preparation

In order to improve the performance of ternary complexes thin film, $Tb_{1-x}Eu_x(m-NBA)_3$ Phen was doped into PVK at dif-

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Fig. 1. Chemical structure of ternary complexes.

ferent weight ratio. ZnS thin film was prepared by electron beam evaporation at the growth rate of 0.5 Å/S under high vacuum of 2×10^{-6} Torr. The top Al electrode was prepared by thermal evaporation about 100 nm. Two kinds of structural devices were fabricated and signed symbols A and B, respectively [11–15]:

- Device A: ITO/PVK: $Tb_{1-x}Eu_x(m-NBA)_3Phen (60 nm)/ZnS(30 nm)/Al$
- Device B: ITO/PVK: Tb_{1-x}Eu_x(m-NBA)₃Phen(60 nm)/BCP (10 nm)/Alq₃(8 nm)/Al

2.3. Measurements

DTA–TG curves were obtained with a TGA-DTA 1700-Perkin-Elmer. Infrared spectra were recorded in the range of $4000-400 \text{ cm}^{-1}$ by a prostige-21IR spectrophotometer in KBr flake. Elemental analyses were carried out by the Perkin-Elmer 240 °C analytical instrument. UV–vis spectra were performed on a UV-2501PCS double spectrophotometer. The excitation and emission spectra measurements were performed on a Shimadzu 5301 spectrofluorophotometer equipped with a 150 W xenon lamp as the excitation source. Lifetimes were measured with a Spex 1934D phosphorimeter using a 450-W flash lamp as the excitation source (pulse width = 3 µs). The EL spectra were measured by SPEX Fluorolog-3 spectrometer at room temperature. The luminance was measured by PR-650 spectra-scan spectrometer. The current–voltage characteristics of the devices were analyzed using Keithley Source Meter 2410.

Table 1 DTA–TG peaks of complexes



Fig. 2. DTA-TG plots of complex Tb_{0.5}Eu_{0.5}(*m*-NBA)₃Phen.

3. Results and discussion

3.1. DTA-TG analysis

DTA-TG plots of Tb_{0.5}Eu_{0.5}(m-NBA)₃Phen are shown in Fig. 2. Different content of doped ion showed similar curve patterns. For DTA plots of Tb_{0.5}Eu_{0.5}(m-NBA)₃Phen, exothermic peak at 435.8 and 497.3 °C, the gross weight loss is 67.5%. Tb_{1-x}Eu_x(m-NBA)₃Phen decompose in two steps, ranging from 360 to 600 °C, TG curves prove that the complexes are stable. Table 1 shows the complexes contents (RE₂O₃%) are not significantly different from the results of calculation, according to the formula.

3.2. IR spectra analysis and composition of the complexes

FTIR absorption spectra of ligands and complexes are shown in Fig. 3. It is noted that similar results are obtained from Eu³⁺ and Eu³⁺/Tb³⁺ complexes. The band in the spectra of complexes at about 525 cm⁻¹ which cannot be observed in the ligands reveals the presence of $O \rightarrow RE$. The band at wavenumber 1560 cm⁻¹ is due to stretching vibration of N=C, while at 721 cm⁻¹ is corresponding to r_{C-H} vibration of 1,10-phenanthroline. In addition, typical asymmetric vibration of $V_{C=O}$ group bands is detected at about 1608 and 1531 cm⁻¹. The IR spectra of doped complexes are similar to that of the pure complexes [16,17]. The compositions of the complexes were confirmed by elemental analysis. Elemental analysis data of europium (terbium) complex and Tb_{1-x}Eu_x(m-

Sample Tb(<i>m</i> -NBA) ₃ Phen	Decompose temperature				Gross	RE2O3%
	T_{m1} (°C) v	weight loss (%)	$T_{\rm m2}$ (°C) v	weight loss (%)	Weight loss (%)	
	366.6	19.6	518.1	42.3	61.9	21.4 (21.9)
Eu(m-NBA) ₃ Phen	383.7	21.2	510.3	43.5	64.7	20.7 (20.8)
Tb _{0.5} Eu _{0.5} (m-NBA) ₃ Phen	435.8	23.3	497.3	44.2	67.5	20.6 (20.9)



Fig. 3. (a) Infrared spectra of ligands and complexes in the range of $4000-400 \text{ cm}^{-1}$. (b) Infrared spectra of ligands and complexes in the range of $2300-400 \text{ cm}^{-1}$.

NBA)₃Phen (X = 0.5, which is selected randomly) were listed in Table 2.

3.3. UV absorption spectra and fluorescence properties

The UV absorption spectra of the complexes are shown in Fig. 4, it can be seen that the absorption bands of $Tb_{1-x}Eu_x(m-NBA)_3$ Phen do not show significant difference in comparison with the pure complexes except that the absorption peaks shifted slightly to a longer wavelength. They all exhibit domain absorption peaks in the ultraviolet region (200–400 nm), and the maximum absorption peaks are located at 292 and 272 nm, respectively.

Table 2 Elemental analysis



Fig. 4. UV spectra of ternary complexes: (a) $Tb(m-NBA)_3Phen$, (b) $Eu(m-NBA)_3Phen$ and (c) $Tb_{0.5}Eu_{0.5}(m-NBA)_3Phen$.



Fig. 5. Typical excitation spectrum of complex Tb_{0.5}Eu_{0.5}(*m*-NBA)₃Phen.

Excited state manifold diagram of lanthanide ternary complexes is shown in Figs. 5 and 6. The excitation and emission spectra of all complexes with different content of doped ion showed the similar profile. For Tb_{0.5}Eu_{0.5}(*m*-NBA)₃Phen, the excitation spectrum consists of a broad band, ranging from 230 to 320 nm ($\lambda_{max} = 298$ nm). Fig. 6 shows the emission spectra of Tb_{0.5}Eu_{0.5}(*m*-NBA)₃Phen, the spectra are typical of Eu³⁺(III) centered transitions from the ⁵D₀ levels to the lower ⁷F₀₋₄ levels. As expected, the main emissions occurred to be the ⁵D₀ \rightarrow ⁷F₂ transition, the ligands (and Tb³⁺) absorb the energy and the energy was transferred to Eu(III) ions, then the Eu(III) emits

Complex	Eu (Tb) (%)	Analytically found (calculated) (%)			
		С	Н	Ν	
Eu(<i>m</i> -NBA) ₃ Phen	18.11 (18.28)	47.70 (47.63)	2.26 (2.41)	8.65 (8.42)	
Tb(<i>m</i> -NBA) ₃ Phen	18.63 (18.96)	46.98 (47.23)	2.13 (2.38)	8.42 (8.35)	
Tb _{0.5} Eu _{0.5} (<i>m</i> -NBA) ₃ Phen	18.32 (18.58)	47.12 (47.31)	2.20 (2.39)	8.28 (8.36)	



Fig. 6. Typical emission spectrum of complex Tb_{0.5}Eu_{0.5}(m-NBA)₃Phen.

typically red luminescence. Fluorescence emission intensity of the complexes is enhanced with an addition of Tb^{3+} ion. For $Tb_{1-x}Eu_x(m-NBA)_3$ Phen complex, different mole fraction of Tb^{3+} have different influences on the emissions intensity of doped complexes. The optimum mole fraction of doped Tb^{3+} is 0.5, which exhibited optimal photoluminescence emission at 614 and 699 nm. However, at higher Tb^{3+} content, the emission intensity was reduced. A very weak emission from Tb^{3+} (in complex $Tb(m-NBA)_3$ Phen) is observed at 545 nm. And the complex of $Tb_{0.5}Eu_{0.5}(m-NBA)_3$ Phen shows the longest lifetime in Table 3 (about 1026 µs).

3.4. Electroluminescence properties

Fig. 7 shows EL emission spectra of $Tb_{0.5}Eu_{0.5}(m-NBA)_3$ Phen at a driving voltage of 12 V. In general, BCP thin film acts as a hole blocking layer and Alq₃ thin film acted as an electron-transporting layer for the device B. In the device A, semiconductor ZnS thin film acts as electron function (transporting, acceleration) layer and hole blocking layer according to its electronic characteristics and energy level instead of BCP and Alq₃ thin films in the device B, the intensity of the red emission at 614 nm in device A is stronger than device B. In both structural devices, the characteristic emissions of europium ions at 594, 614, 655 and 690 nm are obtained. These emission peaks are ascribed to four energy level transitions of ${}^5D_0 - {}^7F_J$ (J = 1-4) of europium ion (Eu³⁺), respectively. The luminescence intensity of ${}^5D_0 - {}^7F_2$ is the strongest.



Fig. 7. EL spectra of complex $Tb_{0.5}Eu_{0.5}(m-NBA)_3$ Phen in different devices A and B (at a driving voltage of 12 V).



Fig. 8. Current-voltage curves for the two types of structure devices.

There is a new route for the excitation of lanthanide ions based on the organic–inorganic combined structural device: electrons directly impact excitation the lanthanide ions through resonant energy transfer. It is found that the combined structural device may be an effective way to improve the electroluminescence intensity of lanthanide ions. As shown in Fig. 8, the electron current and hole current for two types of structural devices are studied, the electron current in the combined device is much larger than in the pure organic structural device due to the drastically different electron mobility. Another important reason is the influence of the electric field strength in the PVK layer on

Table	3
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Emission peak positions and relative intensity of the complexes

Eu:Tb Sample ($Tb_{1-x}Eu_x(m-NBA)_3Phen$)	λ_{ex} (nm)	λ_{em} (nm)	Relative intensities (a.u.)	Lifetimes (µs)
0.0:1.0	351	545	360	372
0.25:0.75	352	613	760	845
0.5:0.5	352	613	1898	1026
0.75:0.25	352	613	1350	965
1.0:0.0	352	613	850	665

hole current. The electric field strength of the PVK layer in the combined structural device is larger than that in the pure organic structural device under the same driving voltage. So, the hole current in the combined structural device is larger than that in the pure organic structural device.

4. Conclusion

Following conclusions can be drawn from this work:

The complexes of $\text{Tb}_{1-x}\text{Eu}_x(m\text{-NBA})_3\text{Phen show good luminescence characteristics based on the 4f electronic transitions of Eu³⁺ ions. It is proved by TG curve that the complexes are stable, ranging from ambient temperature to 360 °C in air. Their PL and EL properties were systematically studied by using these complexes as emissive materials. PL spectra indicate that the Tb³⁺ emission is almost quenched and the Eu³⁺ emission is enhanced by co-doping the complexes. The Tb³⁺ ion acts as an energy transfer bridge that helps energy transfer from PVK to Eu³⁺. The electroluminescence intensity of the combined structural device was improved compared with the device of the purely organic components.$

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