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Synthesis and emission analysis of novel rare earth complex $Eu(TTA)_3(2NH_2\text{-Phen})$

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Abstract: The rare earth ternary complex of Eu^{3+} with thenoyltrifluoroacetone, and 4, 7-$2NH_2$ phenanthroline was synthesized and well characterized by UV, fluorescent, IR spectrometry and X-ray diffractometry (XRD) as well as elemental analysis. The results show that the complex of Eu(III) emits strong red luminescence when excited by UV light, and $Eu(TTA)_3(2NH_2\text{-Phen})$ has the higher sensitized luminescent efficiency and longer lifetime than $Eu(TTA)_3(Phen)$. In device of ITO/PVK/$Eu(TTA)_3(2NH_2\text{-Phen})$/Al, the spectra of $Eu(TTA)_3(2NH_2\text{-Phen})$ with different ratios for spin-cast film were monitored. The main emitting peak at 614 nm can be attributed to the transition of $^5D_0\rightarrow{}^7F_2$ of Eu^{3+} and this process results in the enhancement of red emission from electroluminescence device. The effect and mechanism of the ligands on the luminescence properties of europium complex were discussed. The results show that the luminescence intensity of the title complexes greatly increases in comparison with that of their corresponding complexes, revealing that the second ligands form very good synergistic effect with the first ligands. The title complexes possess excellent thermal stability properties, and are hopefully developed into fine PL and EL red materials.
Key words: synthesis; ternary complex; luminescence; electroluminescence

1 Introduction

In recent years, rare earth complex fluorescence materials have generated much research interest in many fields such as materials science, chemistry, biological technology and information technology. Luminescent phosphors have attracted more attention in the development of different luminescent display systems[1−4]. Many rare earth complexes have been developed as the emitters in organic photo-luminescence and electroluminescence devices[5−9]. As some lanthanide ions, e.g. Eu^{3+} and Tb^{3+}, possess good luminescence characteristics (high color purity) based on the transitions between the 4f energy levels, many compounds activated with Eu^{3+} and Tb^{3+} have been studied for practical application as laser materials. Many research groups have extensively studied various Eu(III) complexes for the purpose of achieving desirable luminescent properties[10−15]. However, the quantum efficiency of most of these lanthanide complexes is still low. This may be mostly due to inefficiency of the energy transfer, particularly, triplet–triplet transfer in these lanthanide complexes. One of the most important problems in this field is a selection of suitable ligands, which would provide high efficiency of emission of the metal ions

In this work, we have successfully synthesized complex $Eu(TTA)_3(2NH_2\text{-Phen})$ with remarkably sharp red emission bands. In PVK/$Eu(TTA)_3(2NH_2\text{-Phen})$ blend, the red emission of europium complex was enhanced and PVK emission was quenched. The results show that the complex of Eu (III) emits strong red luminescence when excited by UV light. The present

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study may be important and helpful for the development of red color rare earth display applications.

2 Experimental

2.1 Sample preparation

$EuCL_3·6H_2O$ (1 mmol) and HTTA (3 mmol) were dissolved in 50 mL ethanol. pH value of the mixture was adjusted to 6−7 using triethylamine. Then, 4, 7-$2NH_2$ phenanthroline in ethanol solution was added to the reaction mixture, and the molar ratio of $2NH_2$-Phen to Eu^{3+} 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[16].

2.2 Measurements

Elemental analyses were performed on a Perkin-Elmer 240 C analytical instrument. X-ray diffraction (XRD) analysis was carried out by D/MAX2500VB2+/PC(Cu K_α(λ=1.540 56 Å), V=40 kV, I=200.0 mA, λ=1.540 56 Å). Infrared spectra were recorded in the range of 4 000−400 cm^{-1} by a prostige-21IR spectrophotometer in KBr flake. UV-Vis spectra were performed on a UV−2501PCS double spectrophotometer. The excitation and emission spectra were recorded on a Shimadzu 5301 spectrofluorophotometer equipped with a 150 W xenon lamp as the excitation source. Spectra were recorded using monochromator with slit widths of 1.5 nm on both excitation and emission sides. 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 on a fluorolog-3 spectrophotometer (American SPEX Company). The luminance was measured by PR−650 spectra-scan spectrometer.

3 Results and discussion

3.1 IR spectrum analysis and XRD analysis

Infrared spectrum of $Eu(TTA)_3(2NH_2\text{-Phen})$ is shown in Fig1. Bands at 1 539, 2 438 and 730 cm^{-1} are corresponded to stretching vibration of —N═C, —N═O vibration, and r_{C-H} vibration of 4,7-$2NH_2$ phenanthroline, respectively. In addition, typical asymmetric vibration of the carbonyl group in HTTA is detected at about 1 605 and 1 549 cm^{-1}. The peak at about 520 cm^{-1} reveals the presence of O→RE, which cannot be observed in the ligands. The elemental analysis data and the structure of the europium complex are shown in Table 1 and Fig.2. We conducted an investigation into samples by XRD. From the obtained grain size and complex XRD microstructural parameter, we found some patterns according to Scherrer formula: $D=0.89\lambda/(\beta\cos\theta)$, for complex, grain size D=60.2 Å.

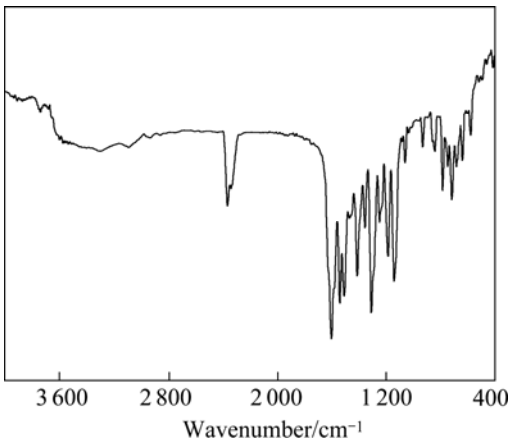

Fig.1 Infrared spectrum of complex $Eu(TTA)_3(2NH_2\text{-Phen})$

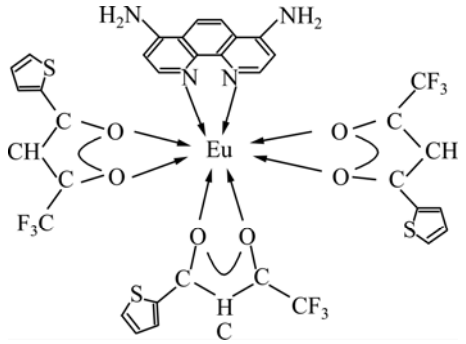

Fig.2 Structure of complex $Eu(TTA)_3(2NH_2\text{-Phen})$

Table 1 Results of analytical data of complex (mass fraction, %)

Complex	Eu	C	H	N
$Eu(TTA)_3$-($2NH_2$-Phen)	14.78 (14.81)*	42.13 (42.11)*	2.12 (2.14)*	5.43 (5.46)*

* Calculated data

3.2 UV absorption spectrum and fluorescence properties

UV spectrum of the complex $Eu(TTA)_3(2NH_2\text{-Phen})$ is shown in Fig.3. The complex exhibits absorption in the ultraviolet region with the maximal absorption of $Eu(TTA)_3(2NH_2\text{-Phen})$ at 275, 296 and 353 nm.

Fluorescence emission spectrum of the $Eu(TTA)_3(2NH_2\text{-Phen})$ complex is shown in Fig.4 (λ_{ex}=332 nm). Five typical Eu^{3+} luminescence peaks appear at 583.0, 593.5, 614.0, 656.0 and 707.5 nm, which are due to $^5D_0\rightarrow{}^7F_0$, $^5D_0\rightarrow{}^7F_1$, $^5D_0\rightarrow{}^7F_2$, $^5D_0\rightarrow{}^7F_3$ and $^5D_0\rightarrow{}^7F_4$, respectively. As shown in Fig.4, the relative intensity of $^5D_0\rightarrow{}^7F_2$ is stronger than other luminescence emissions. Moreover, the emission peak positions of $Eu(TTA)_3(2NH_2\text{-Phen})$ indicate that there is a typical Eu^{3+} luminescence emission. In Table 2, the complex $Eu(TTA)_3(2NH_2\text{-Phen})$ also shows longer

lifetime (about 982 μs) than $Eu(TTA)_3(Phen)$ (about 756 μs).

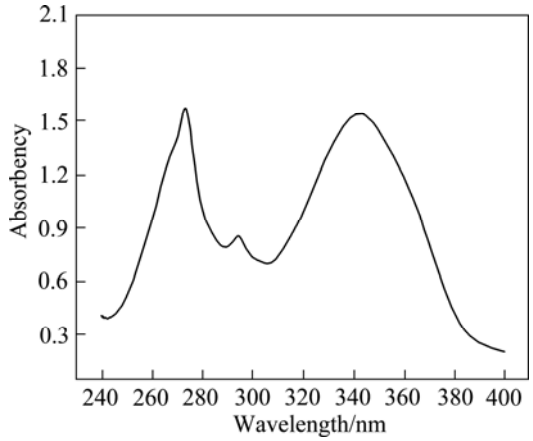

Fig.3 UV spectrum of complex $Eu(TTA)_3(2NH_2\text{-}Phen)$

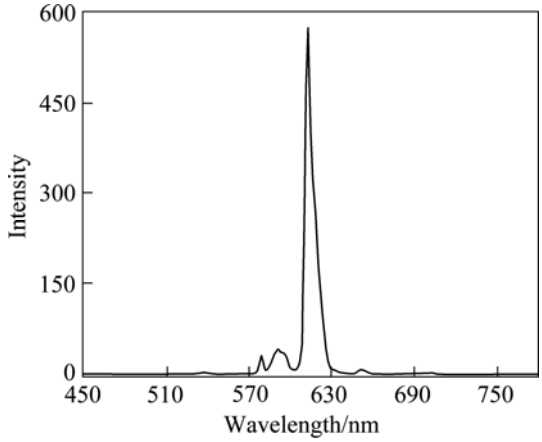

Fig.4 Typical emission spectrum of complex $Eu(TTA)_3(2NH_2\text{-}Phen)$ excited at 332 nm

Table 2 Luminescence properties of rare earth complex

Complex	λ_{ex}/nm	λ_{em}/nm	Relative intensity	Lifetime/μs
$Eu(TTA)_3(Phen)$	336	613	912	756
$Eu(TTA)_3(2NH_2\text{-}Phen)$	332	613	1 105	982

3.3 Electroluminescence

The device structure of the complex $Eu(TTA)_3(2NH_2\text{-}Phen)$ was fabricated according to Refs.[17−18]. Poly(N-vinylcar-bazole) (PVK) was dissolved in 10 mg/mL chloroform. In order to improve the performance of $Eu(TTA)_3(2NH_2\text{-}Phen)$ thin film, $Eu(TTA)_3(2NH_2\text{-}Phen)$ was doped into PVK at mass ratio of 1:3. The PVK: $Eu(TTA)_3(2NH_2\text{-}Phen)$ thin film was fabricated on the top of cleaned ITO coated glass substrate by spin-coating method. 2, 9-dimethyl-4, 7-diphenyl-1, 10-phenanthroline (BCP) and aluminum quinoline (Alq_3) films were fabricated by thermal evaporation at a rate of about 0.3 Å /s under high vacuum of 266.644 μPa.

Fig.5 shows the electroluminescent spectrum of the complex $Eu(TTA)_3(2NH_2\text{-}Phen)$ at a driving voltage of 13 V. The dependence of electroluminescence intensity on the driving voltage is obtained by using the time-base spectra. In the structural device, electro-luminescence intensity sharply increases when the driving voltage goes beyond 15 V. Furthermore, the enhancement of red emission in device of ITO/PVK/$Eu(TTA)_3(2NH_2\text{-}Phen)$/Al is most likely due to the energy transfer enhancement from PVK and ligand to Eu^{3+}. This process results in the enhancement of red emission from electro-luminescent device, which is made from metal complexes.

Fig.6 shows the power—voltage curves for the complex $Eu(TTA)_3(2NH_2\text{-}Phen)$ structure devices at various driving voltages. The electron current in the $Eu(TTA)_3(2NH_2\text{-}Phen)$ device sharply increases when the driving voltage goes beyond 12 V. It is found that the $Eu(TTA)_3(2NH_2\text{-}Phen)$ structural device effectively improves the electro-luminescence intensity of lanthanide ions.

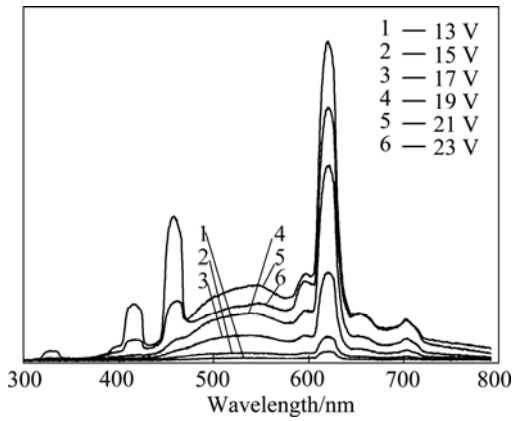

Fig.5 EL spectra of complex $Eu(TTA)_3(2NH_2\text{-}Phen)$ at various driving voltages

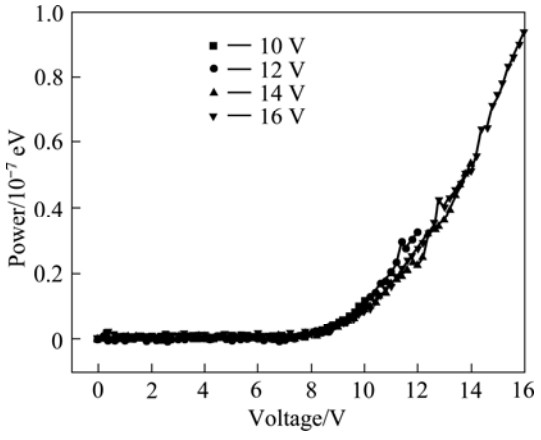

Fig.6 Power — voltage curves for complex $Eu(TTA)_3(2NH_2\text{-}Phen)$ at various driving voltages

4 Conclusions

1) By using a chemical coprecipitation method, the novel ternary complex $Eu(TTA)_3(2NH_2\text{-}Phen)$ was successfully synthesized and characterized for photoluminescence and electro-luminescence properties.

2) $Eu(TTA)_3(2NH_2\text{-}Phen)$ has higher sensitized luminescent efficiency and longer lifetime than $Eu(TTA)_3(Phen)$.

3) In PVK/$Eu(TTA)_3(2NH_2\text{-}Phen)$ blend, the red emission of europium complex is enhanced and PVK emission is quenched. Results show that the complex of Eu (III) emits strong red luminescence when excited by UV light.

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