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Preparation and Fluorescent Property of $Eu(TTA)_3Phen$ Incorporated in Polycarbonate Resin

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ABSTRACT: Rare earth complex $Eu(TTA)_3Phen$ was synthesized with a new method. The product was characterized by element analysis, IR, UV, TGA and fluorescence spectra. The strong fluorescence and high thermal stability of $Eu(TTA)_3Phen$ were used for modification of resin. $Eu(TTA)_3Phen$-PC composite was prepared at 220 °C for 30 min under stirring. The fluorescence spectra showed that the prepared $Eu(TTA)_3Phen$-PC composite materials retained the fluorescent characteristic and strong red fluorescence emission of Eu^{3+} complex and its fluorescence intensity was found to be increased with increase in the mass fraction of $Eu(TTA)_3Phen$ in PC resin.
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KEY WORDS Eu Complex / 2-Thenoyltrifluoroacetone / Composite Material / Polycarbonate Resin / Fluorescence /

The rare earth organic complexes can be used both in electric luminescent (EL) and photoluminescent (PL) devices.[1] They become the research topics of inorganic, organic and bio-luminescence. Among them, particularly europium β-diketonates complexes have been intensively studied with respect to application for luminescence owing to their inherent extremely sharp emission bands, potentially high internal quantum efficiency and chemical stability.[2] 2-Thenoyltrifluoroacetone belongs to β-diketonate compounds, it can coordinate with Eu^{3+}, and obtains red electroluminescent and photoluminescent materials (about 610 nm).[3] There were fewer reports that the rare earth complexes were used for modification of polycarbonate (PC) resin.[4] New rare earth complex $Eu(TTA)_3$-Phen was synthesized in ethanol and water, and 8-hydroxyquinoline as acidity inhibitor was used in the synthesis. Because of its high thermal stability, it was used to the polymerization of resin in order to bring into the fluorescence in resin. Therefore, the polycarbonate resin composite was prepared, and its excitation and emission spectra was studied. The results showed that the $Eu(TTA)_3Phen$-PC resin composite material retained the fluorescence characteristics and strong red emission of Eu^{3+}.

EXPERIMENTAL

Eu_2O_3 (99.95%) was purchased from Shanghai Yuelong Metal Cooperation; 2-thenoyltrifluoroacetone was purchased from Fluka Cooperation. All other chemicals were AR reagent grade.

C, H, N were determined by Carbo-Eroa 1106 elemental analyzer. Eu^{3+} ion was analyzed by complexometric titration with EDTA. The mole conductivity was determined by DDS-11A Conductivity Instrument. The preparation of the composite material was carried out by Germany HAAKE RHEO MIXING 600.

The Preparation of $Eu(TTA)_3Phen$

The preparation method see ref.[5] 5 mL 6 mol L^{-1} HNO_3 was added to 0.3 mmol Eu_2O_3, dried at 70–80 °C, solved in 10 mL ethanol; 1.2 mmol 8-hydroxyquinoline, 0.6 mmol 1,10-phenanthroline and 7 mmol 2-thenoyltrifluoroacetone (HTTA) were added to the mixed solution of 2 mL water and 10 mL ethanol. The above two solutions were mixed and laid aside. And then pale yellow product was obtained after 2–3 d. Yield: 73.3%.

The Preparation of $Eu(TTA)_3Phen$-PC Resin Composite Material

0.0%, 0.02%, 0.06%, 0.1%, 0.6%, 1.0% (mass fraction) $Eu(TTA)_3Phen$ were mixed with PC resin in polymerization. Then polycarbonate resin composites were prepared at 220 °C for 30 min under stirring, then cooled to room temperature.

RESULTS AND DISCUSSION

Composition and Mole Conductivity of $Eu(TTA)_3Phen$

The Elemental analytical data are reported as follows: Eu 15.20% (15.22%); C 43.36% (43.29%); H 2.23% (2.32%); N 3.04% (2.83%). Calculated values are given in parentheses. The mole conductivity val-

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ues is 51 $S \cdot cm^2/mol$, which suggests that the complex is non-electrolyte.[6] These values indicate the formula of the complex is $Eu(TTA)_3Phen$. The complex is slightly soluble in methanol, ethanol and tetrahydrofuran, and soluble in N,N-Dimethylformamide (DMF) and Dimethyl sulfoxide (DMSO), but insoluble in ether and methyl-cyanide.

IR Spectra

IR spectra were recorded on USA Nicolet FT-IR670 Nexus Spectrometer (KBr discs). The characteristic ring stretching vibration band of free phenanthroline shifted from 1561 cm^{-1}, 855 cm^{-1} and 740 cm^{-1} to 1540 cm^{-1}, 844 cm^{-1}, 724 cm^{-1}, likely when coordinated. The absorption peak at about 462 cm^{-1} can be assigned to Eu–O vibration absorption band.[7] In the free HTTA,[8] there are two anti-symmetric stretch vibration peaks, one is $\nu_{C=O}$ (1661 cm^{-1}) near the thienyl, another is $\nu_{C=O}$ (1642 cm^{-1}) near the strong electronegativity trifluoro-base. The $\nu_{C=O}$ obviously shifts to 1625 cm^{-1} and 1601 cm^{-1}, which results from the coordination of TTA with Eu(III). It means that the resonance structures of C–O–Eu and C=O···Eu bonds reduce C=O bond after C=O coordinated Eu, resulting in the bonds constant decreases and C=O shifts to lower frequency. These IR data are close to the relevant literature report. The IR data list in Table I.[9]

It was known that the composition and structure of $Eu(TTA)_3Phen$ is as Figure 1.

UV Spectrum

UV Spectrum was determined on 760 CRT bi-light beam UV-visible spectrograph. The ligands and complex were dissolved in DMSO and UV-visible absorption spectrum was determined in 200–500 nm. It was found they have strong absorption under UV excitation, and the UV absorption peak (310 nm) of the complex is near that of HTTA (326 nm) and is also near the largest fluorescence excitation band (344 nm) of complex. It means that the characteristic fluorescence of complex results from the energy transmission among the molecule, which mainly TTA^- absorbed energy.

Fluorescent Spectra

The fluorescent spectra of $Eu(TTA)_3Phen$ was measured on LS50 Fluorescence spectrum. Figure 2a is the emitting spectrum of $Eu(TTA)_3Phen$ (λ_{em} = 612 nm); There are two exciting bands, 306 and 390 nm respectively (Figure 2b). Then the characteristic fluorescent spectrum of Eu^{3+} was obtained. They belong to 4f electron transmission $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3, 4) of Eu^{3+}. The emission peaks lie in 579, 611, 710 nm.

The strongest emission is attributed to the $^5D_0 \rightarrow {}^7F_2$ (about 614.2 nm) transition of Eu^{3+}. The coordination with Eu(III) exhibited intense red light. The measurement results indicate that the triple state energy of HTTA transmits to Eu^{3+} by energy transmission among the molecule, when HTTA has the largest absorption peak in 310 nm. The colour purity of the complex in 614 nm is 96.44%.

Table I. The IR data in $Eu(TTA)_3Phen$ (cm^{-1})

$\nu_{sC=O}$	$\nu_{asC=C}$	$\nu_{sC=C}$	$\nu_{as(CF_3)}$	$\nu_{s(CF_3)}$
1625	1508	1188	1357	1309
1601		1143		

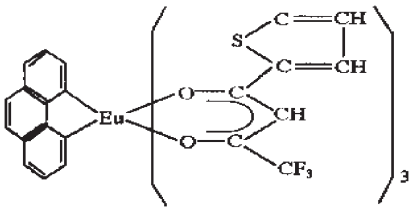
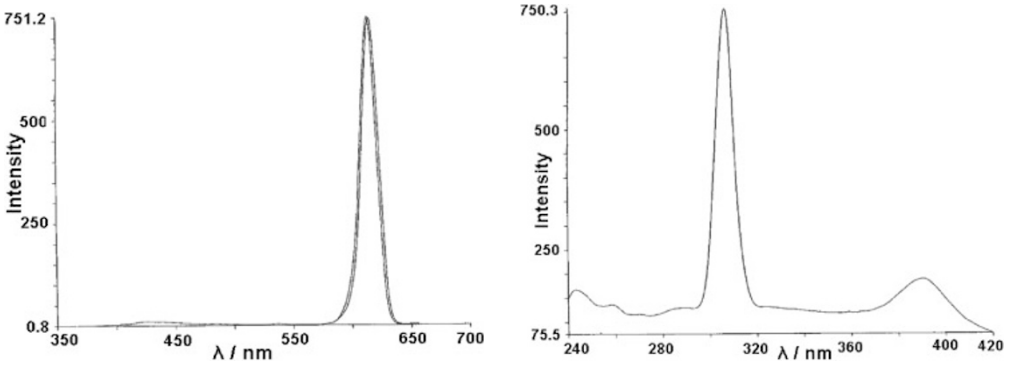


Figure 1. The Structure of $Eu(TTA)_3Phen$.



(a) (b)

Figure 2. The Emitting spectrum (a) and the Exiting spectrum (b) of $Eu(TTA)_3Phen$.

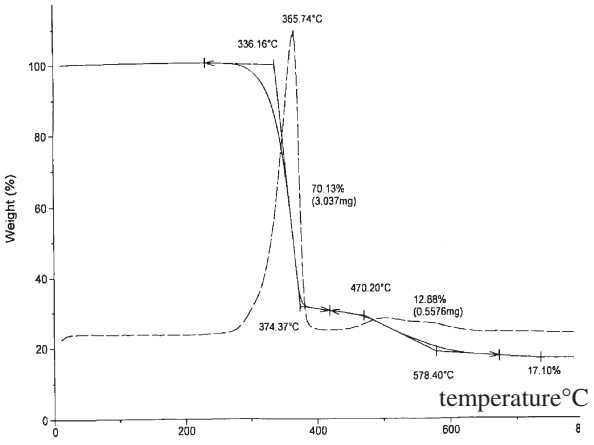


Figure 3. The TGA spectrum of Eu(TTA)$_3$Phen.

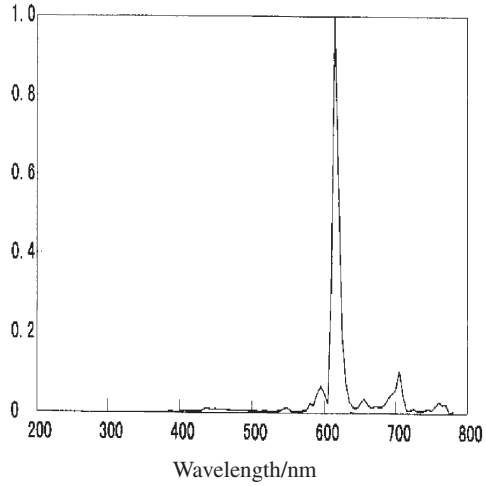


Figure 4. The Emitting spectrum of Eu(TTA)$_3$Phen-PC composite material.

Table II. The relationship of mass fraction of Eu(TTA)$_3$Phen composite material with fluorescence lightness (in PC)

Mass fraction of Eu(TTA)$_3$Phen	Eu(TTA)$_3$Phen	0.0%	0.02%	0.06%	0.1%	0.6%	1.0%
Fluorescence lightness	33.3	0.7	2.1	2.7	2.7	3.1	3.9
Radiation lightness	0.128	0.005	0.011	0.013	0.014	0.018	0.034
Color purity	0.9644	0.3506	0.5284	0.5952	0.7156	0.7190	0.8601

TGA Analysis

The thermal analysis was carried out between room temperature and 800 °C in the N_2 atmosphere on TG 2050 Thermal Gravimetric Analyzer. The thermal decomposition of Eu(TTA)$_3$Phen proceeded in 2 stages. The first stage is 336.16–374.37 °C, and the second stage is 470.20–578.40 °C. The first stage results from decomposition of ligands TTA, phen. The decomposition reaction is as follows:

$$\text{Eu(TTA)}_3\text{Phen} \xrightarrow{336.16\text{–}578.40\,^\circ\text{C}} \text{Eu}_2\text{O}_3$$

The thermal analytical information shows the coordination compound decomposes before its melting. The amount of residue is 17.62%, calculated values is 17.10%. It favours the preparation of composite material, because the decomposition temperature of Eu(TTA)$_3$Phen is 336 °C. The TGA spectrum sees Figure 3.

Fluorescent Spectra of Eu(TTA)$_3$Phen-PC Composite Material

The characteristic fluorescent spectrum of Eu^{3+} was obtained in the Eu(TTA)$_3$Phen-PC composite material ($\lambda_{em} = 612$ nm). It means that this kind of composite material keeps the fluorescent nature of Eu(TTA)$_3$Phen.

Figure 4 is the emission spectrum of composite material, in which its mass fraction is 1% ($\lambda_{em} = 615$ nm). Although the ratio added complex is very low, the composite materials still show high emission efficiency. The strong orange colour fluorescence was seen by the naked eyes. Therefore, it is a good photo luminescent material.

Table II is the relationship of mass fraction of Eu(TTA)$_3$Phen composite material versus fluorescence lightness ($\lambda_{em} = 612$ nm) in the room temperature. The results show that the more the amount of Eu(TTA)$_3$Phen is, the stronger its fluorescence lightness, the higher radiation lightness, and better colour purity. This study provides a kind of way to choose good material of organic electro-luminescent and photo luminescent material.

The luminescent nature of Eu(TTA)$_3$Phen-PC composite material was compared with that of Eu(TTA)$_3$Phen-PMMA composite material. The luminescent nature of Eu(TTA)$_3$Phen-PMMA composite material sees Table III. In the same content of Eu(TTA)$_3$Phen, the fluorescence lightness and radiation lightness of Eu(TTA)$_3$Phen-PC is obviously superior than those of Eu(TTA)$_3$Phen-PMMA composite material.[10] All kinds of index improve 50–100%. The improvement reasons of the luminescent intense in the composite material lie in: one is that the rare earth complex in the resin is bound by the polymer molecular link

Table III. The relationship of mass fraction of $Eu(TTA)_3Phen$ composite material with fluorescence lightness (in PMMA)

Mass fraction of $Eu(TTA)_3Phen$	$Eu(TTA)_3Phen$	0.0%	0.02%	0.06%	0.1%	0.6%	1.0%
Fluorescence lightness	33.3	0.6	0.8	1.5	1.6	2.5	3.2
Radiation lightness	0.128	0.005	0.005	0.007	0.008	0.010	0.013
Color purity	0.9644	0.1987	0.3402	0.5579	0.6912	0.8824	0.8795

net, resulting in that the molecule movement is limited, bond vibration is weakened, therefore reduce activation way by non-radiation, improve fluorescence lightness. Another reason is that the chemical environment of the rare earth complex in the resin changed. Environment pattern symmetric around the rare earth ion in the transparent resin becomes lower, resulting in fluorescence intensity improvement.

CONCLUSION

A ternary solid complex of rare earth nitrate with 1, 10-phenanthroline, and 2-thenoyltrifluoroacetone has been synthesized at the ordinary condition. The results based on elemental analysis and other effective methods show that the resultant complex agrees with the formula $Eu(TTA)_3Phen$, which shows non-electrolyte. The fluorescent spectra show that $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} complex. $Eu(TTA)_3Phen$ was used for modification of polycarbonate resin. The fluorescence intensity was found to be increased with increase in the mass fraction of $Eu(TTA)_3Phen$ in PC resin, but not linear relation.

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