

Synthesis and Characterization of Eu³⁺ + 2-thenoyltrifluoroacetone + triphenylphosphine Oxide Ternary Complex

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Abstract. Rare earth europium ion (Eu³⁺) can emit red characteristic fluorescence under UV excitation and is preferred for the preparation of red phosphors for near-UV white LEDs. In this paper, the effects of solvent, reflux time and preparation method on the preparation of europium ternary complexes were studied with europium ion as the central coordination ion, 2-thenoyltrifluoroacetone as the first ligand and triphenylphosphine oxide as the second ligand. The results showed that the better reaction solvent was anhydrous ethanol and the better reflux time was 8 hours. Both the common synthesis method and the solvothermal method could successfully synthesize the europium ternary complex, and the solvothermal method has a higher yield. The europium ternary complex was characterized by inductively coupled plasma emission spectroscopy, element analysis and infrared spectroscopy, and it was proved that the europium complex could emit a strong characteristic red fluorescence of europium with the structure of Eu(TTA)₃(TPPO)₂ in 1:3:2 coordination ratio.

1 Introduction

White light emitting diode (WLED) is an emerging solid-state cold light source. Compared with the long-developed incandescent lamp and fluorescent lamps, it has the advantages of environmental protection, no radiation, high brightness, low power consumption, small mass, small size, good directionality, compact structure, long service life and fast response time, etc [1].

Among the many technologies for realizing white LEDs, fluorescent conversion white LEDs are the most promising. Among them, the near-ultraviolet (UV) white LEDs, which obtain white light by UV chip excitation of red, green and blue mixed phosphors, are attracting attention by the advantages of their luminescence independent of the chip output light, high white light color rendering index, small color temperature drift and stable color [2, 3]. The excitation spectrum of white phosphors for near-UV white LEDs must match the chip emission spectrum. Rare earth fluorescent materials can be excited by UV light in the emission spectrum band of the chip and can be prepared to emit different colors of fluorescence in the visible region by selecting different kinds of rare earth ions [4-6]. Under the excitation of UV, rare earth europium ions (Eu³⁺) can emit red fluorescence, which can be used to make red phosphor to prepare near-UV white LEDs [7-10]. Rich rare earth resources are stored in the vast territory of our country, which provides unique conditions for the development of white LEDs in China.

In this experiment, we prepared europium ternary complexes with trivalent rare earth europium ion (Eu³⁺) as the central coordination ion, 2-thenoyltrifluoroacetone (TTA) as the first ligand and triphenylphosphine oxide (TPPO) as the second ligand under different conditions by changing the solvent type, reflux time and preparation method. The optimal conditions for this preparation reaction were derived from the thin layer chromatography (TLC) performance, yield and other factors.

2 Materials and Methods

2.1 Reagents and instruments

The experimental reagents in this experiment are shown in Table 1, and the instruments are shown in Table 2.

Table 1. Experimental reagents

Reagent	Specification	Manufacturer
Anhydrous europium chloride	Analytical pure	Shanghai Macklin biochemical technology Co., Ltd
2-thenoyltrifluoroacetone	Analytical pure	Shanghai Macklin biochemical technology Co., Ltd
Triphenylphosphine oxide	Analytical pure	Shanghai Macklin biochemical technology Co., Ltd
Anhydrous ethanol	Analytical pure	Shanghai

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		Lingfeng chemical reagent Co., Ltd
Methanol	Analytical pure	Shanghai Lingfeng chemical reagent Co., Ltd
Dichloromethane	Analytical pure	Shanghai Lingfeng chemical reagent Co., Ltd
Sodium hydroxide	Analytical pure	Chengdu Kelong chemical Co., Ltd
Hydrochloric acid	36%	Hangzhou Shuanglin chemical reagent Co., Ltd

Table 2. Experimental instruments

Instrument	Model	Manufacturer
Electronic balance	FA 2004B	Shanghai Jingmi scientific instrument Co., Ltd
Collector type constant temperature heating magnetic stirrer	DF-101S	Henan Yuhua instrument Co., Ltd
Triple-use UV lamp	ZF-2	Shanghai Anting electronic instrument factory
Circulating water type multi-purpose vacuum pump	SHZ-D(III)	Henan Yuhua instrument Co., Ltd
Electric heating constant temperature blast drying oven	DHG-9140A	Henan Yuhua instrument Co., Ltd
Vacuum drying oven	DZF-6020	Henan Yuhua instrument Co., Ltd
Polytetrafluoroethylene lined hydrothermal reactor	KH-25	Shanghai Yushen instrument Co., Ltd

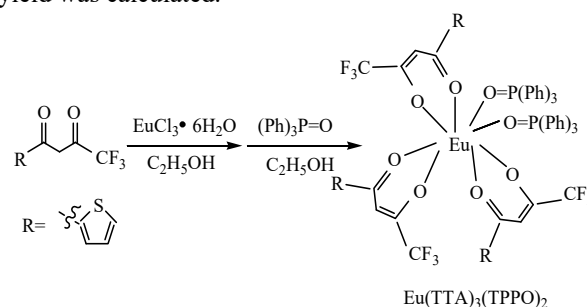
2.2 Preparation of europium ternary complexes

2.2.1 Common synthesis method

A typical common synthesis process was as follows:

The first step was to prepare a mixed solution. Anhydrous europium chloride (EuCl_3 , 1.5 mmol, 0.387 g), TTA (4.5 mmol, 1.000 g) and TPPO (3 mmol, 0.835 g) were weighed in 1:3:2 mol ratio, and dissolved in 30, 60 and 60 mL of anhydrous ethanol respectively in sequence with ultrasonic shaking for use. The ethanol solution of TTA was first added to a 250mL three-necked flask, and after magnetic stirring at 55 °C for 10 minutes, the ethanol solution of EuCl_3 was added dropwise. The pH of the solution was adjusted to 5.5 with hydrochloric acid and NaOH in ethanol. After stirring at a constant temperature of 55 °C for 30 minutes, the ethanol solution of TPPO was added dropwise, and then the pH value of the solution was adjusted to 7.0 with the ethanol solution of NaOH.

The second step was to synthesis and purification. The reaction was kept at 80 °C and refluxed for 8 hours at atmospheric pressure, the product obtained from the reaction was filtered under reduced pressure, and the precipitate was washed twice with distilled water and anhydrous ethanol in turn, then dried in vacuum at 65 °C. The product was purified by recrystallization with anhydrous ethanol to obtain an orange solid powder, that is, europium ternary complex. The reaction equation is shown in Fig. 1. The product mass was weighed and the yield was calculated.

**Fig. 1.** Synthesis of europium ternary complex

The reaction process was followed by thin-layer chromatography.

2.2.2 Solvothermal synthesis method

As the first step of 2.2.1 common synthesis method, an ethanol solution of a homogeneous mixture of EuCl_3 , TTA and TPPO with pH 7.0 was obtained.

Then the mixed solution was transferred to a reactor lined with polytetrafluoroethylene, and reacted at 80 °C for 8 hours. After cooling, the product was taken out, and filtered under reduced pressure. The orange precipitate was washed twice with distilled water and anhydrous ethanol. The solid was purified by recrystallization with ethanol, dried at constant temperature, and the product was obtained. The mass was weighed and the yield was calculated.

3 Results and Discussion

3.1 Effect of solvent

We prepared europium ternary complexes by the 2.2.1 common synthesis method, in which the solvents were ethanol and methanol, respectively, to study the effect of different solvents on the reaction. The reaction process was followed by TLC, and the developing solvent was a 1:1 mixture of cyclohexane and ethyl acetate reagent.

After the TLC was finished developing, we put the thin-layer plate under a triple-use UV lamp to observe the reaction of the raw materials on the plate. It was found that if the reaction was carried out with methanol as the solvent, the red spot of the product europium ternary complex on the thin layer plate was lighter, while the red spot was more obvious when ethanol was used as the reaction solvent. So we chose ethanol as the solvent for the reaction.

3.2 Effect of reflux time

We still prepared europium ternary complexes by the common synthesis method, and the samples were analyzed by thin layer chromatography after reflux for 2 hours, 4 hours, 6 hours, 7 hours and 8 hours respectively to study the effect of different reflux time on the reaction.

The results of the spots on the thin-layer plate showed that the concentrations of TTA and TPPO in the reaction solution decreased gradually with the increase of reflux time, and the spots of TTA and TPPO were almost invisible at the time of 8 hours. At the same time, the red spot of europium complex became more and more obvious, which indicated that the reaction was basically completed after 8 hours of reflux time. So we chose the reflux time to be 8 hours.

3.3 Effect of preparation method

The europium ternary complexes prepared by the common synthesis method and the solvothermal method were both orange-red powders, and both could produce red fluorescence when irradiated under the triple-use UV lamp. The yield of common synthesis method was 34.92%, and that of solvothermal method was 55.66%. Compared with the two, the yield of the solvothermal method was higher.

Fig. 2 shows the color of the solid powder of europium ternary complex under the triple-use UV lamp, with strong red fluorescence, indicating that the europium complex strengthened the fluorescence intensity of europium ion.

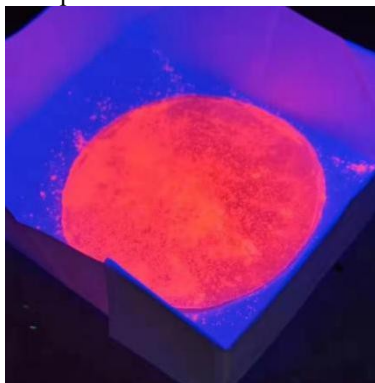


Fig. 2. Europium ternary complex powder under triple-use UV lamp irradiation

3.4 Result of inductively coupled plasma emission spectroscopy (ICP) characterization

Table 3 shows the result of the ICP determination of the elements Eu and P for europium ternary complex.

As can be seen from the table, in the 0.0071 g europium complex sample, 0.8157 mg of Eu element was measured. According to our predicted product formula $\text{Eu}(\text{TTA})_3(\text{TPPO})_2$, the theoretical mass of Eu is 0.7872 mg. The ratio of the two was 1.0362, which was close to 1. ICP measured 0.3054 mg of P element, while the theoretical mass is 0.3211 mg, and the ratio of the two is 0.9511, which is also close to 1. This indicated

that the final product we synthesized was indeed the product we expected, $\text{Eu}(\text{TTA})_3(\text{TPPO})_2$.

Table 3. ICP determination result of europium ternary complex

Sample mass (mg)	Theoretical value (mg)		ICP determination value (mg)	
	Eu	P	Eu	P
7.1	0.7872	0.3211	0.8157	0.3054

3.5 Result of element analysis

Table 4 shows the result of characterization by element analysis of C, H, N, and O for europium ternary complex.

It can be seen from the table that calculated with the formula $\text{Eu}(\text{TTA})_3(\text{TPPO})_2$, the theoretical percentage of C element is 52.38% and the actual measured percentage was 51.23%, the theoretical percentage of H element is 2.84% and the actual measured percentage was 2.56%, the theoretical percentage of N element is 0 and the actual measured percentage was 0.06%, the theoretical percentage of O element is 9.31% and the actual measured percentage was 9.64%. The actual measured values of C, H, N and O were close to the theoretical values. Combining the measurement results of Eu and P by ICP in 3.4, we can confirm that the molecular formula of the europium complex we synthesized was indeed $\text{Eu}(\text{TTA})_3(\text{TPPO})_2$.

Table 4. Determination result of element analysis of C, H, N, O in Europium ternary complex

Element	Theoretical percentage (%)	Percentage determined by element analysis (%)
C	52.38	51.23
H	2.84	2.56
N	0	0.06
O	9.31	9.64

3.6 Result of infrared spectrum characterization

Fig. 3 is the infrared spectra of europium ternary complex. It can be seen from Figure 3 that after the reaction, the two stretching vibration peaks of C=O groups in the ligand TTA molecule appeared near 1610 cm^{-1} and 1521 cm^{-1} , with a low frequency shift relative to 1656 cm^{-1} and 1642 cm^{-1} of the free ligand TAA before the reaction, indicating that the coordination of the rare earth metal Eu and the carbonyl group resulted in a shortening of the bond length and thus a red shift. The P=O stretching vibration peak was also shifted from 1188 cm^{-1} in the free ligand TPPO to around 1171 cm^{-1} .

In addition, an Eu-O peak appeared around 540 cm^{-1} . And there was a relatively weak -OH antisymmetric stretching absorption peak around 3560 cm^{-1} , which was significantly different from that of the free ligand TTA at 3420 cm^{-1} , and it was the contribution of the enol hydroxyl group in TTA. These results indicate that rare earth ion had been coordinated with the ligands TTA and TPPO via oxygen atoms.

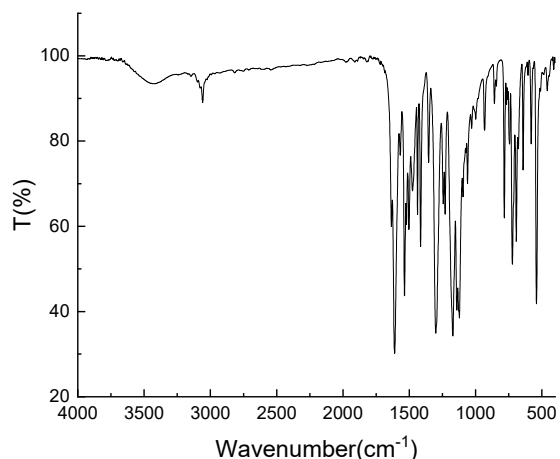


Fig. 3. Infrared spectra of europium ternary complex

4 Conclusion

(1) We used anhydrous europium chloride, 2-thenoyl trifluoroacetone, and triphenyl phosphine oxide as raw materials, and explored the effects of solvent, reflux time and preparation method on the synthesis of europium ternary complexes. The experimental results show that the reaction solvent was anhydrous ethanol, and the products could be successfully synthesized by both the common synthesis method and the solvothermal method under the condition of refluxing for 8 hours. The product can emit the characteristic red fluorescence of europium strongly, and the synthesis yield was higher by the solvothermal method.

(2) We characterized the products prepared under optimal synthesis conditions by ICP, elemental analysis, and infrared spectroscopy. The characterization results show that after the reaction, the rare earth Eu ions had indeed coordinated with the ligands TTA and TPPO via O atoms, and the molecular formula of the obtained product europium complex was indeed $\text{Eu}(\text{TTA})_3(\text{TPPO})_2$.

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