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Preparation of Eu(Avobenzone)$_3$TPPO by precipitation method and its luminescence performance

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Abstract. Using Eu_2O_3 as raw material, anhydrous ethanol as solvent system, 1-(4-Methoxyphenyl) -3-(4-tert-butylphenyl)-1,3-propanedione (Avobenzone) as first ligands and triphenylphosphane oxide (TPPO) as second ligands, the rare earth complex Eu(Avobenzone)$_3$TPPO has been successfully prepared by precipitation method. The Eu(Avobenzone)$_3$TPPO were characterized by fluorescence spectrum analysis (FS), Fourier transform infrared spectroscopy(FT-IR) and color coordinate calculation. The thermal stability of Eu(Avobenzone)$_3$TPPO was studied by thermogravimetry differential scanning calorimetry (TG-DSC). The results showed that Eu(Avobenzone)$_3$TPPO emitted strong red characteristic fluorescence, the optimal excitation wavelength was 397nm, the characteristic emission wavelength was 612 nm, and the color coordinates were (0.66, 0.34). Eu(Avobenzone)$_3$TPPO decomposes at about 200℃, it shows good thermal stability.

1. Introduction

Because the luminescence of rare earth ions has characteristics of long fluorescent life and high color purity[1], it has been widely used in the field of rare earth luminescent materials. In 1942, Weissman[2] first discovered that there was a stable conversion efficiency from covalent europium ions to ionic compounds. The fluorescence properties of rare earth ions could be enhanced by means of intra-molecular energy transfer, it also known as the 'antenna effect'. Since then, the studies on organic complexes of europium have developed rapidly. Trivalent europium ternary organic complexes showed high purity, stable chemical properties and good luminescence performance. Trivalent europium ternary organic complexes are widely used in fluorescent probes [3], biomedicine [4], optics and other fields. Therefore, the study of europium ternary complexes has important research value and significance.

2. Experimental details

2.1 Preparation of Eu(Avobenzone)$_3$TPPO

The following are the reagents used in the experiment. Eu_2O_3(purity99%), 1-(4-Methoxyphenyl) -3-(4-tert-butylphenyl)-1,3-propanedione, triphenylphosphane oxide, hydrochloric acid, anhydrous ethanol and sodium hydroxide were all analytically pure. The following are specific steps used in the experiment. 0.3519g Eu_2O_3 was dissolved in 20ml hydrochloric acid to obtain $EuCl_3$ solution, and $EuCl_3$ solution was evaporated to obtain $EuCl_3$. $EuCl_3$ was dissolved in 10ml anhydrous ethanol to form solution A. Avobenzone of 0.9312g was weighed and dissolved in 10ml anhydrous ethanol to obtain solution B. TPPO of 0.2783g

was weighed and dissolved in 10ml anhydrous ethanol to obtain solution C. Mix solution B and C, then add the mixture into solution A drop by drop, and react at 60℃ for 30min at a constant temperature. Adjusting the pH to 6.5-7 with 1mol/L NaOH ethanol solution. The reaction solution was incubated at 60℃ for 2h and centrifuged to obtain pale yellow precipitation. The product was washed with anhydrous ethanol and dried in an oven at 60℃.

2.2 Experimental instruments and testing methods

The luminescence performance of Eu(Avobenzone)$_3$TPPO sample was characterized by sens9000/9003 model fluorescence spectrometer (Beijing Zhuoli Hanguang Instrument Co. Ltd.). The infrared spectra of Eu(Avobenzone)$_3$TPPO sample was determined by Nicolet 5700 Fourier of the US Thermo Corporation, it using the KBr pressing plate method. Eu(Avobenzone)$_3$TPPO sample was measured by the American TA-SDTQ600 thermal analyzer, the temperature range of the TG-DSC is from 20℃ to 600℃ and the heating rate is 10℃/min.

3. Results and discussion

3.1 Fluorescence spectrum analysis

Figure.1 is the excitation spectrum of Eu(Avobenzone)$_3$TPPO. It can be seen from Figure.1 that the excitation band of Eu(Avobenzone)$_3$TPPO is located at 300-600nm, and the optimal excitation wavelength is 397nm[5].

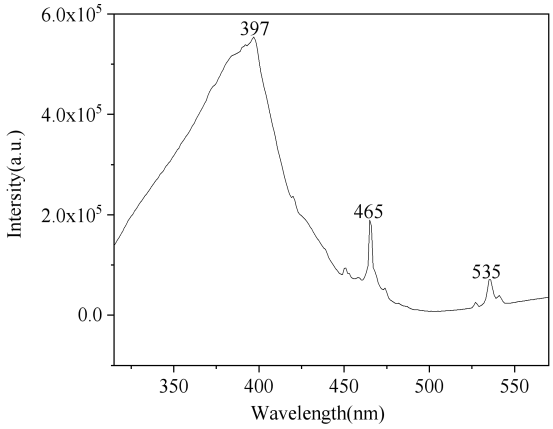

Figure.1 Excitation spectra of Eu(Avobenzone)$_3$TPPO

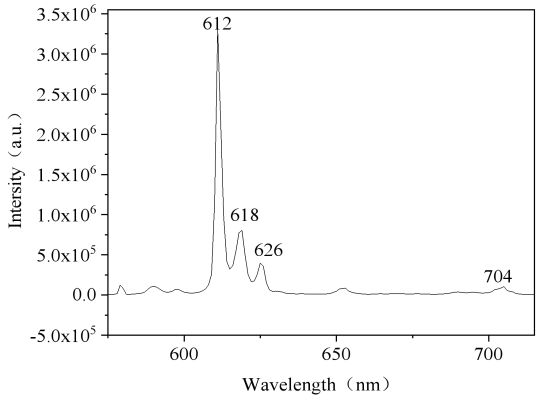

Figure.2 Emission spectra of Eu(Avobenzone)$_3$TPPO

Figure.2 is the emission spectrum of Eu(Avobenzone)$_3$TPPO. It can be seen from figure.2 that the excitation

band of Eu(Avobenzone)$_3$TPPO is at 500~720nm, and 612nm is the characteristic emission wavelength. The characteristic emission peaks of Eu(III) ions are respectively located at 612, 618, 626 and 704nm, the $^5D_0$-$^7F_1$,$^5D_0$-$^7F_2$,$^5D_0$-$^7F_3$ and$^5D_0$-$^7F_4$ energy level transitions of Eu(III) ions are correspond to these characteristic emission peaks [6-7]. The strongest energy level transitions of $^5D_0$-$^7F_1$ are electric dipole moment transitions, which is the red strongest characteristic luminescence of central ion Eu(III).

According to the fluorescence emission data of complexes and ligands, CIE 1931 was used to calculate the CIE color coordinates of complexes and ligands. The color coordinate data were shown in table 1. According to the data in table 1, the color coordinate diagram drawn is shown in Figure.3. The ligand Avobenzone is in the green light zone, TPPO is in the yellow light zone, and Eu(Avobenzone)$_3$TPPO is in the red light zone. They have different color regions, so the ligand can be coordinated successfully on Eu^{3+}.

Table 1 color coordinates and color temperature data of complexes

category	Nomenclature	X coordinate	Y coordinate	Color temperature
First ligands	Avobenzone	0.36	0.59	5129K
Second ligands	TPPO	0.46	0.51	3313K
Complexes	Eu(Avobenzone)$_3$TPPO	0.66	0.34	12899K

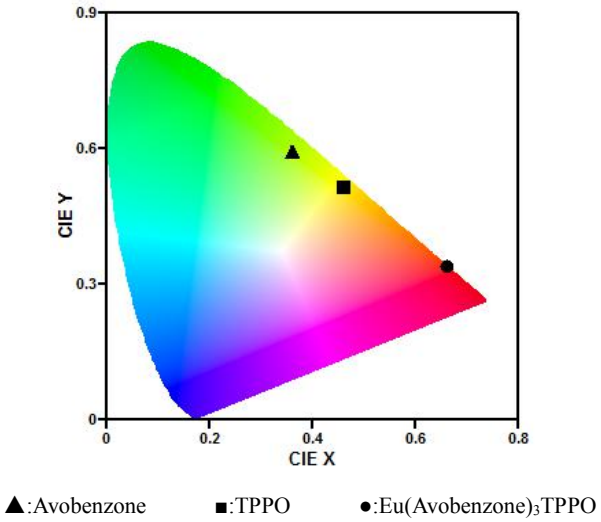

Figure.3 Color coordinate complexes and ligand

3.2 Infrared spectral analysis

Figure.4 is the infrared spectrum of Eu(Avobenzone)$_3$TPPO. As can be seen from figure.4, the absorption peak of Eu(Avobenzone)$_3$TPPO at 3451cm^{-1} corresponds to the first ligand Avobenzone. Compared with the second ligand TPPO, the stretching vibration peak of the C=O bond in the activity moves from the original 1493cm^{-1} to 1431cm^{-1}, this situation is due to the Eu-O coordination bond formed by Eu(III) ions and ligand TPPO, which results in the decrease of P=O bond force constant and the absorption peak of Eu(Avobenzone)$_3$TPPO moves towards the short-wave number[8-9]. Thus, the coordination between TPPO and Eu(III) ion is successful.

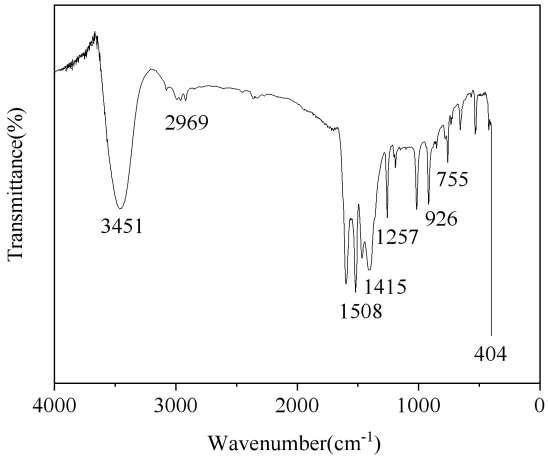

Figure.4 Infrared spectra of Eu(Avobenzone)$_3$TPPO

3.3 Thermogravimetric analysis

TG-DSC curve of Eu(Avobenzone)$_3$TPPO is shown in figure.5. As can be seen from figure.5, on the TG curve, the complexes has a loss of weight of about 8.7% in the range of 30℃~300℃, and on the DSC curve, there is a small endothermic peak at 241℃, which should be the removal and endothermic absorption of the complexes adsorbed water and other substances. As can be seen from the TG curve, the complexes began to decompose at 300℃, with a loss of weight of about 85.8% in the range of 300℃~600℃, while there was a small endothermic peak at 349℃ and a strong exothermic peak at 484℃ on the DSC curve, indicating that the decomposition process of the complexes was carried out step by step. At about 600℃, the complexes have been decomposed, and the rest should be Eu_2O_3, indicating the successful coordination between the partial distributor and europium. Moreover, there is basically no decomposition before 280℃, which indicates that Eu(Avobenzone)$_3$TPPO has a good thermal stability and meets temperature requirements for a lot of luminescent materials [10].

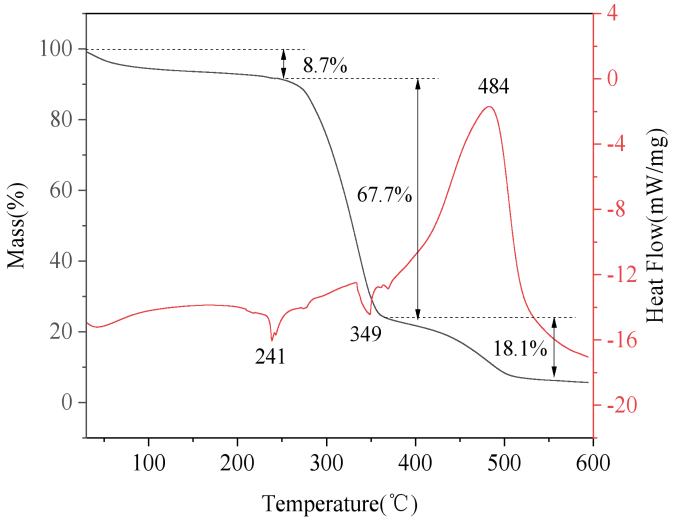

Figure.5 Eu(Avobenzone)$_3$TPPO thermogravimetric- ifferential scanning heat maps

4. Conclusions

The ternary complex Eu(Avobenzone)$_3$TPPO was prepared with Eu_2O_3 as europium source, 1-(4-Methoxyphenyl)-3-(4-tert-butylphenyl)-1,3-propanedione (Avobenzone) and triphenylphosphane oxide (TPPO) as preparation systems. Eu(Avobenzone)$_3$TPPO has good thermal stability and can emit characteristic red fluorescence. The strongest fluorescence emission peak is 612 nm, and the color coordinates are (0.66, 0.34). Eu(Avobenzone)$_3$TPPO is a kind of red fluorescent material with high luminous quantum efficiency of organic compounds and good stability of inorganic compounds.

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