Preparation and luminescence of rare earth complex

Eu(DBM)$_3$(TPPO)

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Abstract. Using Eu$_2$O$_3$ as source of europium, anhydrous ethanol as solvent system, methylene
benzoyl(DBM) as first ligands, triphenyl phosphine (TPPO) as second ligands, the europium(III)
ternary rare earth complex Eu(DBM)$_3$TPPO has been successfully prepared. The samples were
characterized by fluorescence spectrum(FS), Fourier transform infrared spectroscopy(FT-IR),
thermogravimetry differential scanning calorimetry(TG-DS) and scanning electron microscope(SEM).
The influence of TPPO on luminescence intensity, color temperature, color coordinates, morphology
and thermal stability of the samples were analyzed. The results showed that the addition of second
ligand could enhance the luminescence intensity of Eu(DBM)$_3$TPPO. Eu(DBM)$_3$TPPO can emit
strong red fluorescence when excited by 395nm ultraviolet light. The color coordinate of
Eu(DBM)$_3$(TPPO) is (0.63, 0.36). The Eu(DBM)$_3$TPPO is a kind of red luminous material with
wide application prospect.

1. Introduction

The complex of europium has a half-peak width (about 10nm), a characteristic emission peak of about
612nm, and a pure red light (color coordinate 0.66, 0.33) [1], which is an important red LED material.
Europium complexes have broad application prospects in fluorescent anti-counterfeiting field, fluorescent
probe field [2], biomedical field [3] and optical field [4]. Therefore, it is of great value and significance to
study europium complexes, especially europium ternary complexes. At present, the preparation methods of
europium ternary complexes mainly include sol-gel method [5], hydrothermal method [6] and precipitation
method [7]. The sedimentation method has the advantages of simple experimental process and convenient
operation.

2. Experimental details

2.1 preparation of rare earth complexes

The purity of Eu$_2$O$_3$ purchased from Aladdin reagent company is 99.9%. Other chemical reagents are
analytically pure. Typical experimental process, weigh a certain amount of Eu$_2$O$_3$ and dissolve it in
concentrated hydrochloric acid, the white crystal, EuCl$_3$· 6H$_2$O, was obtained by evaporation under heating
and stirring. EuCl$_3$· 6H$_2$O was dissolved in ethanol with the first ligand DBM and the second ligand
TPPO(molar ratio 1:3:2). And the pH was adjusted to 6~7 by ammonia reagent. After heating and stirring for
1 h, the precipitation was allowed to stand still, filtered, washed with ethanol for 3 times and dried to obtain
the complexes of rare-earth europium.

2.2 reagents and instruments

The fluorescence quantum efficiency of Eu(DBM)$_3$(TPPO) was measured by Quantaurus-QY absolute quantum efficiency measuring instrument of Hamamatsu photonics trading (China) co. LTD. The fluorescence spectra of Eu(DBM)$_3$(TPPO) was determined by flouroSENS type steady state fluorescence spectrometer (FS) of Gilden. The infrared spectra of Eu(DBM)$_3$(TPPO) was determined by the Nicolet5700 Fourier transform infrared spectrometer of Thermo colliers. Eu(DBM)$_3$(TPPO) sample was measured by the American TA-SDTQ600 thermal analyzer. The morphology of Eu(DBM)$_3$(TPPO) was characterized by Hitachi S-3400N scanning electron microscope of Hitachi Company. The content of europium was determined by EDTA method.

3. Results and discussion

3.1 Infrared spectral analysis of Eu(DBM)$_3$(TPPO)

Figure 1 shows infrared spectra of ligands and ternary complexes. As can be seen from figure 1, the characteristic absorption peak of infrared spectrum of complexes and characteristic absorption peak of ligands are obviously different. After the formation of complexes, the P=O absorption peak of TPPO moves from 1190 cm$^{-1}$ to 1160 cm$^{-1}$, indicating that TPPO uses its O atom to coordinate with Eu to form the Eu-O(TPPO) bond. The Eu-O absorption peak of complex was 541 cm$^{-1}$. The significant reduction of wave number of carbonyl and unsaturated carbon-carbon bonds in complexes reflect the average of single and double bonds on the chelating ring. According to the literature, the metal and the complexes form the coordination structure of the six-membered cycle-ring, the carboxyl oxygen atoms of the free ligand DBM and the oxygen atoms of TPPO participate in the coordination.

![Figure 1 FT-IR spectra of Eu(DBM)$_3$(TPPO).](image)

3.2 Excitation spectral analysis of Eu(DBM)$_3$(TPPO)

Figure 2 shows the excitation spectra of Eu(DBM)$_3$(TPPO). It can be seen from figure 2 that the excitation spectra of Eu(DBM)$_3$(TPPO) is strongly excited between 390-410nm and the maximum excitation wavelength is 396nm.
Figure 2: Excitation spectra of Eu(DBM)$_3$(TPPO)

3.3 Emission spectral analysis of Eu(DBM)$_3$(TPPO)
Figure 3 is emission spectrogram of Eu(DBM)$_3$(TPPO) measured with the excitation wavelength of 395nm. As can be seen from figure 3, the $^5$D$_0 \rightarrow ^7$F$_2$ transition with the strongest emission wavelength of 612nm is the electric dipole transition of Eu$^{3+}$, with sharp peak shape, half peak width of 11nm and good monochromatic property. By comparing the emission spectrum of the complex Eu(DBM)$_3$(TPPO) with that of the ligand DBM, it can be seen that the ligand DBM has strong emission between 500-550nm, while the complex Eu(DBM)$_3$(TPPO) has no emission between 500-550nm, which indicates that after the formation of the Eu(DBM)$_3$(TPPO) complex, DBM transfers energy to Eu$^{3+}$ central ion effectively.

Figure 3: Emission spectra of Eu(DBM)$_3$(TPPO)

3.4 Color coordinates and color temperature of Eu(DBM)$_3$(TPPO)
Figure 4 is color coordinate diagram of Eu(DBM)$_3$(TPPO). It can be seen from figure 4 that the color coordinate of Eu(DBM)$_3$(TPPO) is (0.63, 0.36). This further indicates that Eu(III) ions coordinate with ligand DBM and ligand TPPO successfully.
3.5 SEM image analysis of Eu(DBM)$_3$(TPPO)

Figure 5 is a scanning electron microscope image of complex Eu(DBM)$_3$(TPPO). It can be seen from figure 5 that the particles of Eu(DBM)$_3$(TPPO) are irregular flakes with uneven distribution. The average grain size is about 50-80 microns.

3.6 TG-DSC analysis of Eu(DBM)$_3$(TPPO)

The TG-DSC curve of Eu(DBM)$_3$(TPPO) is shown in figure 6. According to the TG curve in figure 6, from room temperature 25°C to 300°C, the complexes have a loss of weight of about 4%, and there is a strong endothermic peak around 175°C on the DSC curve, which should be the removal of endothermic absorption of the complexes adsorbed solvents. The sample began to decompose when the temperature was greater than 300°C, and the surface sample has good thermal stability. From 300°C to 600°C, the total weight loss was about 68% and the exothermic peaks were obvious at 454°C, 514°C and 577°C, indicating that the decomposition process of the complex was carried out step by step. At about 600°C, the complex has been decomposed, and the total weight loss is about 72%. The remaining 28% should be Eu$_2$O$_3$. This is consistent with the theoretical weight remaining from the thermal decomposition of Eu(DBM)$_3$(TPPO), which also indicates that the coordination of ligand and europium is successful.

4. Conclusions

In ethanol solvent, Eu$_2$O$_3$ as europium source, DBM as the first ligand, TPPO as the second ligand, we use precipitation method to synthesize red europium (III) ternary rare earth complexes Eu(DBM)$_3$(TPPO). Eu(DBM)$_3$(TPPO) complex has good luminescence and thermal stability, and can emit pure red light.
Eu(DBM)$_3$TPPO is a kind of red luminescent material with broad application prospects.

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