

Luminescence comparison of europium complexes with different conjugation length β -diketone in polymer

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Two Eu complexes with different conjugation length β -diketone ligands, Eu(F3PP)₃Phen and Eu(F9PP)₃Phen, have been synthesized and incorporated into poly(methyl methacrylate) (PMMA). Their fluorescent properties have been investigated by fluorescence emission spectra and lifetime measurements. According to the fluorescence emission spectra, the ${}^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ ratio, the Judd-Ofelt parameters Ω_2 , Ω_4 of Eu(F3PP)₃Phen/PMMA and Eu(F9PP)₃Phen/PMMA have been calculated. The influence of the ligands on the luminescence properties of the europium complexes doped PMMA was analyzed also.

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1. Introduction

Lanthanides complexes doped polymer holds considerable potential for applications in photonics, optoelectronics and integrated optics, for it combines the intrinsic luminescent properties of lanthanide ions and the unique physical and chemical properties of polymers [1~4]. From all lanthanides complexes, europium β -diketone complexes are famous for their luminescence properties. As red-emitting material, they have high and sharply spiked fluorescence emission efficiency, long lifetime and good stability [5].

As a polymer material, poly(methyl methacrylate) (PMMA) attracted particular interest for its low optical absorption, simple synthesis and low cost [6]. These characteristics make it suitable as a host material for rare earth ions and organic dye doping.

Because of the optic applications of doped polymers, it is of great interest to study their luminescent properties. In this work, two europium β -diketone complexes with different conjugation length ligands were synthesized and have been incorporated into PMMA. According to their fluorescence spectra, lifetime measurement and Judd-Ofelt analysis, the influence of the ligands on the luminescence properties of the europium complexes doped PMMA was analyzed.

2. Experimental

Two types of β -diketone ligands with different conjugation length were used: *1-(2-furyl)-1-(3-phenanthryl)-1,3-propanedione* (F3PP) and *1-(2-furyl)-1-(9-phenanthryl)-1,3-propanedione* (F9PP). F3PP and F9PP were synthesized according to

modified Claisen condensation methods [7]. *1,10-phenanthroline* (Phen) acts as the second ligand, which can reduce the rate of nonradiative decays and enhance the fluorescence intensity of the complex strongly. The europium ternary complexes, *1,10-phenanthroline-tris[1-(2-furyl)-1-(3-phenanthryl)-1,3-propanedione]-europium*, Eu(F3PP)₃Phen and *1,10-phenanthroline-tris[1-(2-furyl)-1-(9-phenanthryl)-1,3-propanedione]-europium*, Eu(F9PP)₃Phen, were synthesized according to the procedure reported before [8]. Elemental analysis calculated for Eu(F3PP)₃Phen (EuC₃₃H₂₂O₃N₂): C, 61.31%; H, 3.43%; N, 4.33%. Found: C, 61.42%; H, 3.49%; N, 4.30%. Eu(F9PP)₃Phen (EuC₃₃H₂₂O₃N₂): C, 61.31%; H, 3.43%; N, 4.33%. Found: C, 61.40%; H, 3.51%; N, 4.36%. Their molecular structures are shown in Fig. 1 and it can be found that the conjugation length in ligand F3PP is longer than that in ligand F9PP.

Eu complexes doped PMMA were made by bulk polymerization. First, Eu complexes were dissolved in the purified MMA (the concentration of Eu³⁺ is 1000 ppm-wt). Then, 0.01mol/L of 2, 2-Azoisobutyronitrile (AIBN) as an initiator was added to the above solution and mixed in a vessel. To avoid autoacceleration (also referred to as Trommsdor effect) that takes place during the polymerization, prepolymerization of the above solution was carried out in order to get a syrup of partially polymerized MMA. The obtained syrup was injected into a model, and then the thermal polymerization of the filled model was carried out in an oven at 45 °C for 48h under air condition and additionally heated at 90 °C until solidification was fulfilled. The solid samples were cut to 2 mm thickness and polished for fluorescence measurements.

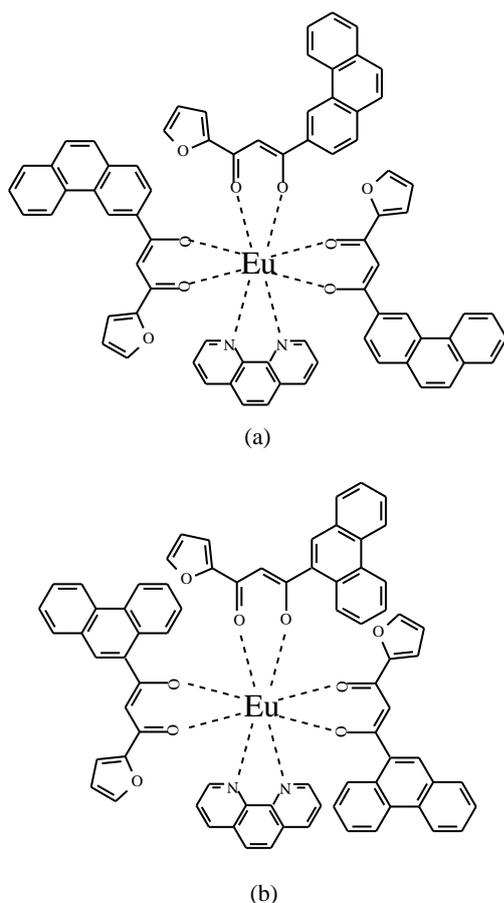


Fig. 1. Chemical structure of Eu(F3PP)₃Phen (a) and Eu(F9PP)₃Phen (b).

Elemental analyses were performed using a Perkin-Elmer 2400CHN elemental analyzer. The fluorescence emission spectra of Eu complexes doped PMMA were recorded on a Shimadzu RF-5301PC spectrofluorophotometer. Lifetime measurements were performed at room temperature. The third harmonic (355 nm) of a Nd:YAG laser was used as a pump source. The emission at the $^5D_0 \rightarrow ^7F_2$ transition of Eu³⁺ was monitored and recorded as a function of time. Data were acquired using a Tektronix TDS 5000 digital oscilloscope and analyzed using a computational program ORIGIN[®]6.1.

3. Results and discussion

3.1 Fluorescence emission spectra

The fluorescence emission spectra of Eu(F3PP)₃Phen/PMMA and Eu(F9PP)₃Phen/PMMA recorded from 500 nm to 750 nm under the excitation at 396 nm are shown in Fig. 2.

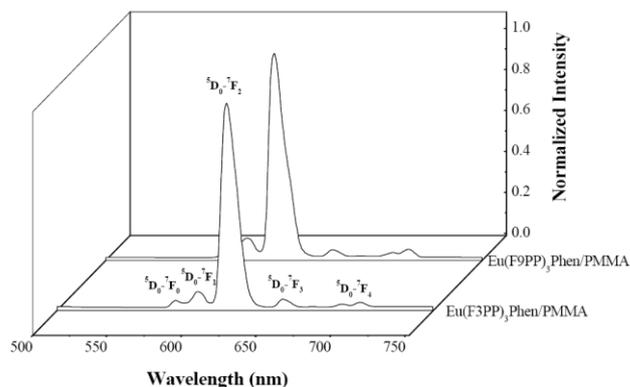


Fig. 2. Fluorescence emission spectra of Eu(F3PP)₃Phen/PMMA and Eu(F9PP)₃Phen/PMMA.

The shape of the fluorescence emission spectra of Eu(F3PP)₃Phen/PMMA and Eu(F9PP)₃Phen/PMMA exhibited very little difference. Emission bands were observed at 579, 590, 612, 651 and 704 nm and were attributed to $f-f$ transitions: $^5D_0 \rightarrow ^7F_0$ (zero-zero band, forbidden transition), $^5D_0 \rightarrow ^7F_1$ (magnetic dipole transition), $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$ and $^5D_0 \rightarrow ^7F_4$ (electric dipole transitions), respectively. The nonexistence of ligand field splitting of $^5D_0 \rightarrow ^7F_0$ transition at 579 nm was due to the fact that 5D_0 and 7F_0 states were no degenerate [9]. From these bands, only the $^5D_0 \rightarrow ^7F_1$ transition occurs through a magnetic dipole mechanism, and thus, its intensity is almost unchanged by the ligand field [10]. The $^5D_0 \rightarrow ^7F_2$ transition, which is the strongest in intensity, is an induced electric dipole transition. It is very sensitive to changes in the environment of the coordination sphere of Eu³⁺. It is well known [11] that the ratio between the intensities of $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ emission bands reflects the site symmetry at which europium is situated, since the $^5D_0 \rightarrow ^7F_2$ band (the hypersensitive one) is strongly dependent on the nearest environment of Eu(III) ion, whereas the $^5D_0 \rightarrow ^7F_1$ one (magnetically allowed transitions), are less environmentally sensitive. The $^5D_0 \rightarrow ^7F_2 / ^5D_0 \rightarrow ^7F_1$ ratio for the Eu(F3PP)₃Phen/PMMA and Eu(F9PP)₃Phen/PMMA are 12.62 and 9.75, respectively. By comparison, the higher value of Eu(F3PP)₃Phen/PMMA indicated that Eu(F3PP)₃Phen is more asymmetric, while Eu(F9PP)₃Phen presents a relative symmetric structure.

3.2 Metastable state lifetime measurement and energy transfer between ligands and Eu ion

The metastable state lifetime of Eu(F3PP)₃Phen/PMMA and Eu(F9PP)₃Phen/PMMA was obtained from the decay curves. The decay curves are shown in Fig. 3.

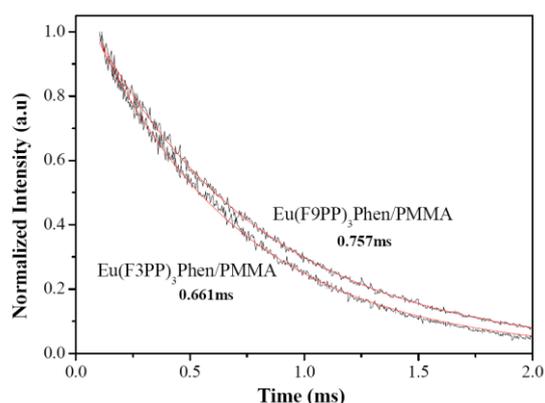


Fig. 3. Decay curves of $\text{Eu}(\text{F3PP})_3\text{Phen/PMMA}$ and $\text{Eu}(\text{F9PP})_3\text{Phen/PMMA}$.

In Fig. 3, the decay curves can be fit with a single exponential, which is indicating that there is only one site symmetry from the Eu^{3+} ion [12]. The lifetime values were 0.661 and 0.757 ms for $\text{Eu}(\text{F3PP})_3\text{Phen/PMMA}$ and $\text{Eu}(\text{F9PP})_3\text{Phen/PMMA}$, respectively, indicating that the lifetime of $\text{Eu}(\text{F9PP})_3\text{Phen/PMMA}$ is longer than for $\text{Eu}(\text{F3PP})_3\text{Phen/PMMA}$. It is possible to relate luminescence lifetimes to the energy gap between the triplet state of the ligand and the acceptor level of the metal ion [13]. Fig. 4 shows the energy level of ligands and the Eu^{3+} ion. As previously observed for other europium systems, it can be deduced that the energy absorbed by the ligand can be transferred via its triplet state to the $^5\text{D}_1$ level of Eu^{3+} . Then, the $^5\text{D}_0$ level is populated through non-radiative relaxation of $^5\text{D}_1$ [14].

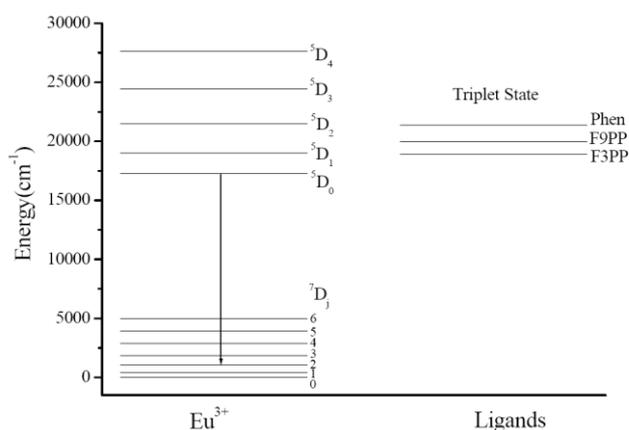


Fig. 4. Energy level diagram of ligands and the Eu^{3+} ion.

The efficiency of the energy transfer from the ligand to the central Eu^{3+} depends on the correlation of the relative positions of the ligand triplet state levels and the Eu^{3+} levels. It has been reported that with the increase of the conjugation length of the ligand, the triplet state level moves to lower energy [15]. If the triplet state level is low, back-transfer from the lanthanide ion to the ligand occurs which reduces the efficiency [16]. According to Fig. 4, the

triplet state levels for F3PP and F9PP are 18900 and 19956 cm^{-1} , respectively [7]. Thus, the longer conjugation length in ligand F3PP makes energy transfer to the Eu^{3+} ion less favorable for it presents a lower triplet state level.

3.3 Judd-Ofelt analysis

The Judd-Ofelt theory provides a very useful method for analyzing the local structure around rare-earth ions. In the case of Eu^{3+} , the pure magnetic dipole transition $^5\text{D}_0 \rightarrow ^7\text{F}_1$ allows the determination of the intensity parameters from the emission spectra. This transition does not depend on the environment and can be used as a reference. Due to selection rules, the $^5\text{D}_0 \rightarrow ^7\text{F}_{2,4,6}$ transitions of Eu^{3+} are allowed by induced electric dipole mechanisms, which depend only on the $U^{(2)}$, $U^{(4)}$ and $U^{(6)}$ reduced matrix elements, respectively. From the fluorescence emission spectra (Fig. 2), the Judd-Ofelt intensity parameters Ω_t ($t=2, 4$ and 6) can be calculated. The equation for the Einstein spontaneous emission coefficient A is given by [17]:

$$A = \frac{4e^2\omega^3}{3hc^3} \frac{1}{2J+1} \chi \sum_t \Omega_t \left\langle ^5\text{D}_0 \left\| U^{(t)} \right\| ^7\text{F}_j \right\rangle^2$$

where h is Planck's constant, ω is the angular frequency of the transition and $\chi = n(n^2+2)^2/9$, a Lorentz local field correction for the index of refraction n of the medium. The reduced matrix elements in the equation were taken from Carnall et al [18]. The obtained values for parameter Ω_2 and Ω_4 of $\text{Eu}(\text{F3PP})_3\text{Phen/PMMA}$ and $\text{Eu}(\text{F9PP})_3\text{Phen/PMMA}$ are listed in Table 1. The Ω_6 intensity parameter was not determined because the $^5\text{D}_0 \rightarrow ^7\text{F}_6$ transition could not be experimentally detected.

Table 1. Ω_2 , Ω_4 parameters of $\text{Eu}(\text{F3PP})_3\text{Phen/PMMA}$ and $\text{Eu}(\text{F9PP})_3\text{Phen/PMMA}$.

| Ω_t | $\text{Eu}(\text{F3PP})_3\text{Phen/PMMA}$ | $\text{Eu}(\text{F9PP})_3\text{Phen/PMMA}$ |
|------------|--|--|
| Ω_2 | $21.3 \times 10^{-20} \text{ cm}^2$ | $19.5 \times 10^{-20} \text{ cm}^2$ |
| Ω_4 | $5.116 \times 10^{-21} \text{ cm}^2$ | $4.221 \times 10^{-21} \text{ cm}^2$ |

According to previous studies, Ω_2 is a useful parameter, because it is sensitive to the local symmetry of the ligand field and bond covalency [19]. The value of Ω_2 increases as the local symmetry of the ligand field decreases and as the bond covalency increases. The relative higher Ω_2 value of $\text{Eu}(\text{F3PP})_3\text{Phen/PMMA}$ in Table 1 indicates that the $\text{Eu}(\text{F3PP})_3\text{Phen}$ is more asymmetric. It can be concluded that the increase of the conjugation length in ligand F3PP also increased the asymmetry of the Eu complex. The Ω_4 parameter has been related together to bulk properties of the lanthanide based

hosts, but there is no theoretical prediction for this sensibility to macroscopic properties [20].

5. Conclusion

In conclusion, two Eu complexes with different conjugation length ligands have been synthesized and incorporated into PMMA. Their luminescence properties have been investigated. It was found that Eu(F3PP)₃Phen/PMMA, which has the longer conjugation length ligands, present a relative higher $^5D_0 \rightarrow ^7F_2/^5D_0 \rightarrow ^7F_1$ ratio (12.62) and larger Ω_2 value ($21.3 \times 10^{-20} \text{ cm}^2$). The longer conjugation length in ligand also makes the triplet state level moves to lower energy level which resulted a relative shorter lifetime for Eu(F3PP)₃Phen/PMMA. The result may be helpful in design lanthanides complexes doped polymer optical materials.

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