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Radiative transition probability of a europium (III) chelating polymer

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A europium (III) chelating polymer has been synthesized. Based on Judd-Ofelt theory, the intensity parameters Ω_2 and Ω_4 have been calculated from the emission spectrum of the chelating polymer. The Ω_2 and Ω_4 parameters have been used to calculate the total radiative transition rate (535.19 s^{-1}) and radiative lifetime (1.868 ms) of the $^5D_0$ exciting state. The stimulated emission cross-sections σ and the fluorescence branch ratios β for the $^5D_0 \rightarrow {}^7F_J$ transitions have been evaluated also. Analysis reveals that the europium (III) chelating polymer is promising for use in optical devices.

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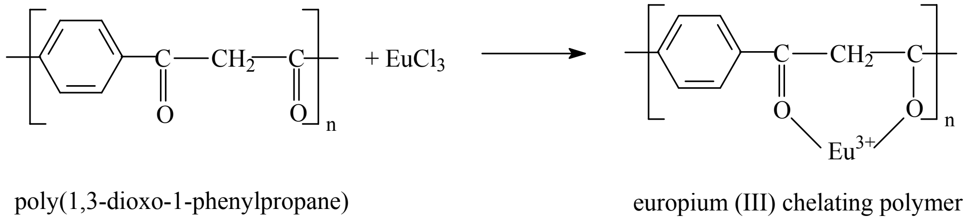
1. Introduction

In recent years, rare earth containing polymers have attracted much attention for their potential applications for fluorescence and laser systems, optical communication devices, such as polymer optical fiber amplifier and integrated waveguide [1~3]. There are two rare earth containing polymer systems: the host-guest systems and the polymeric systems [1]. In a host-guest system, the rare earth complex is dissolved in the polymer matrix or blended with the polymer matrix. Due to its easy preparation and excellent optical properties, the application of rare earth containing polymer host-guest systems in optical devices have been widely investigated [2~6]. However, in a polymeric system, the rare earth metals are directly bonded to the polymer as an integral part of it. The preparation for a rare earth containing polymeric system is relatively complicated and there is little research work for its applications in optical devices.

In this study, a europium (III) chelating polymer has been synthesized, in which the polymer containing *β*-diketone moiety is poly(1,3-dioxo-1-phenylpropane). According to its emission spectrum, the Judd-Ofelt parameters were determined. The calculated Judd-Ofelt parameters were utilized in evaluating the various radiative parameters such as the radiative lifetime of the $^5D_0$ excited state, the stimulated emission cross-sections and the fluorescence branch ratios for the $^5D_0 \rightarrow {}^7F_J$ transitions.

2. Experimental

The europium (III) chelating polymer has been synthesized according to the following procedure. First, a polymer containing *β*-diketone moiety, poly(1,3-dioxo-1-phenylpropane) was prepared by the condensations reaction of *p*-Acetylbenzoic acid and its methyl ester. Then 2.4g $EuCl_3.6H_2O$ was dissolved in 80 ml dimethyl sulfoxide and 3 g poly(1,3-dioxo-1-phenylpropane) was added. The above suspension was stirred at 40 °C for 7 hours and neutralized with piperidine. The resulting precipitate was filtered and dried under vacuum at 50 °C for 10 hours. Fig. 1 showed the reaction and the chemical structures of poly(1,3-dioxo-1-phenylpropane) and its europium (III) chelating polymer.



poly(1,3-dioxo-1-phenylpropane)

europium (III) chelating polymer

Fig. 1. Preparation of europium (III) chelating polymer.

The fluorescence emission spectrum of the europium (III) chelating polymer was recorded on a Shimadzu RF-5301PC spectrofluorophotometer.

3. Results and discussion

3.1 Fluorescence emission spectrum of europium (III) chelating polymer

The fluorescence emission spectrum of europium (III) chelating polymer presented in Fig. 2 was obtained under the excitation at 396 nm.

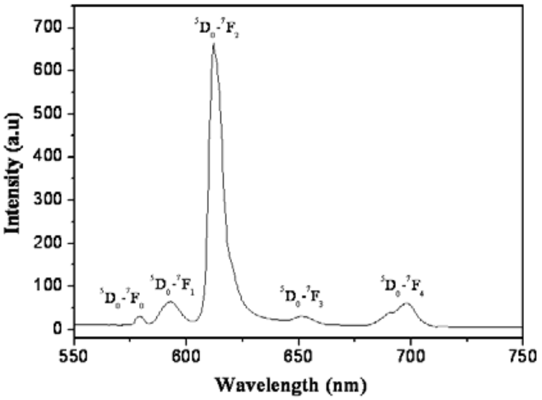


Fig. 2. Fluorescence emission spectrum of europium (III) chelating polymer.

As shown in Fig. 2, the $^5D_0 \rightarrow {}^7F_J$ transition with J=0, 1, 2, 3 and 4 are found at about 580 nm, 592 nm, 612 nm, 651 nm and 701 nm, respectively. The presence of only one $^5D_0 \rightarrow {}^7F_0$ line indicates that the Eu^{3+} ion occupies only a single site and a single chemical environment exists around it. The $^5D_0 \rightarrow {}^7F_1$ transition arises mainly from a magnetic dipole moment and is not strongly dependent on the site symmetry in which the Eu^{3+} ion is situated [7]. The $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ transitions are "forced" electric dipole transitions and may occur only at low symmetry sites [8]. The $^5D_0 \rightarrow {}^7F_2$ named "hypersensitive transition" by Jorgensen and Judd is especially sensitive to environment and increases in intensity with the amount of covalency between Eu^{3+} ion and the surrounding ligand and with decrease of site symmetry [8, 9] The more intense $^5D_0 \rightarrow {}^7F_2$ transition of the europium (III) chelating polymer indicated that Eu^{3+} ion is in a site without a center of inversion.

3.2 Judd-Ofelt intensity parameters of europium (III) chelating polymer

According to Judd-Ofelt theory, the calculated oscillator strength for an induced electric dipole transition from the ground state to an excited state is [10]:

$$f = \frac{8\pi^2 mc\nu}{3h(2J+1)} \frac{(n^2+2)^2}{9n} \sum_{\lambda=2,4,6} \Omega_\lambda \left(\Psi J \left\| U^\lambda \right\| \Psi' J'\right)^2$$

where n is refractive index of the medium, J is the total angular momentum of the ground state, ν is the wave number of the transition, Ω_λ (λ=2, 4, 6) are Judd-Ofelt intensity parameters and $\| U^\lambda \|^2$ (λ=2, 4, 6) are the doubly reduced matrix elements evaluated in the intermediate coupling approximation for a transition $\Psi J \rightarrow \Psi' J'$. The transition intensity f depends on the $\| U^\lambda \|^2$ values between ΨJ and $\Psi' J'$ manifold. Due to selection rules and the unique nature of transition intensities for Eu^{3+} ion, any one of the $\| U^\lambda \|^2$ parameters decide the intensities of the transitions since the remaining two are zero. Thus, Ω_λ (λ=2, 4, 6) parameters can be evaluated independently from the emission transitions of $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_4$ and $^5D_0 \rightarrow {}^7F_6$, respectively [11]. The intensity of the $^5D_0 \rightarrow {}^7F_1$ fluorescent transition is found to be host independent whereas that of the $^5D_0 \rightarrow {}^7F_J$ transition depends on the Ω_λ parameters. This characteristic helps one to evaluate the Ω_λ parameters simply by the ratio of the intensities of the $^5D_0 \rightarrow {}^7F_{2,4,6}$ transitions to the intensity of $^5D_0 \rightarrow {}^7F_1$ transition as follows [10].

$$\int I_J d\nu \Big/ \int I_1 d\nu = A_J / A_1 = \frac{e^2}{S_{md1}} \frac{\nu_J^3}{\nu_1^3} \frac{n\left(n^2+2\right)^2}{9n^3} \sum \Omega_\lambda \left\| U^\lambda \right\|^2$$

where S_{md1} refers to the strength of the magnetic dipole line strength of the $^5D_0 \rightarrow {}^7F_1$ transition in absorption.

The obtained values for parameter Ω_2 and Ω_4 of europium (III) chelating polymer are 13.9×10^{-20} cm^2 and 4.733×10^{-20} cm^2, respectively. Compared with other Eu^{3+} host-guest polymer system, europium (III) chelating polymer show a relative small Ω_2 value [12~14]. It has been well established that the Ω_2 parameter is structure sensitive and depends on the covalency of the rare earth ion sites [5]. It can be found in Fig.1 that the Eu^{3+} ion is coordinated by two oxygen atoms of the polymer ligands. While in Eu^{3+} host-guest polymer system, the Eu^{3+} ion is completely coordinated by the surrounding ligands atoms [12~14]. The decrease of Ω_2 value for europium (III) chelating polymer also indicates a decrease of the covalency between the Eu^{3+} ion and the surrounding ligands. The Ω_4 parameters have been related together to bulk properties of the lanthanide based hosts, but there is no theoretical prediction for this sensibility to macroscopic properties [15]. The Ω_6 intensity parameter was not determined because the $^5D_0 \rightarrow {}^7F_6$ transition could not be experimentally detected. This indicated that the Ω_6 is not important here.

3.3 Radiative transition probability of europium (III) chelating polymer

The electric (A_{ed}) and magnetic (A_{md}) dipole radiative transition probabilities can be evaluated from the following expressions [10]:

$$A_{ed} = \frac{64\pi^4 e^2 v^3}{3h(2J+1)} \frac{n(n^2+2)^2}{9} \sum_{\lambda=2,4,6} \Omega_\lambda \left(\Psi J \left\| U^\lambda \right\| \Psi' J' \right)^2$$

$$A_{md} = \frac{64\pi^4 v^3}{3h(2J+1)} n^3 S_{md}$$

The sum of A_{ed} and A_{md} gives the radiative transition probability (A) for a transition $\Psi J \rightarrow \Psi' J'$ as:

$$A\left(\Psi J, \Psi' J'\right) = A_{ed} + A_{md}$$

The total radiative transition probability (A_T) for an excited state is given as the sum of the $A(\Psi J, \Psi' J')$ terms calculated over all the terminal states.

$$A_T\left(\Psi J\right) = \sum_{\Psi' J'} A\left(\Psi J, \Psi' J'\right)$$

As an excited state ΨJ is relaxed to several lower-lying states $\Psi' J'$, the radiative branching ratio β_R is defined as:

$$\beta_R\left(\Psi J, \Psi' J'\right) = A\left(\Psi J, \Psi' J'\right) / A_T\left(\Psi J\right)$$

The branching ratios can be used to predict the relative intensities of all emission lines originating from a given excited state. The experimental branching ratios can be found from the relative areas of the emission lines.

The rate of depopulation of an excited state is given by the radiative lifetime, $\tau_R(\Psi J)$:

$$\tau_R\left(\Psi J\right) = 1 / A_T\left(\Psi J\right)$$

The stimulated emission cross-section, $\sigma(\lambda_p)(\Psi J, \Psi' J')$, between the states ΨJ and $\Psi' J'$ having a probability of $A(\Psi J, \Psi' J')$ is given by [10]:

$$\delta\left(\lambda_p\right)\left(\Psi J, \Psi' J'\right) = \frac{\lambda_p^4}{8\pi c n^2 \Delta\lambda_{eff}} A\left(\Psi J, \Psi' J'\right)$$

where λ_p is the wavelength of peak emission (in nm) and $\Delta\lambda_{eff}$ is the elective line width of the transition (in nm) found by dividing the integrated area of the emission band by its average height.

The predicted radiative transition probabilities of electric dipole transition A_{ed} and magnetic dipole transition A_{md}, the total transition probability $A_T(^5D_0)$, the fluorescence branching ratio β_R, the stimulated emission cross-section σ and the radiative lifetime τ_R are presented in Table 1.

Table 1. Radiative properties of europium (III) chelating polymer.

ΨJ	$\Psi' J'$	λ(nm)	$\Vert U^2 \Vert^2$	$\Vert U^4 \Vert^2$	$\Vert U^6 \Vert^2$	A_{md} (s^{-1})	A_{ed} (s^{-1})	A (s^{-1})	β (%)	σ (cm^2)
$^5D_0$	$^7F_0$	580	0	0	0	0	0	0	0	0
	$^7F_1$	592	0	0	0	51.90	0	51.90	9.70	0.23×10^{-22}
	$^7F_2$	612	0.0032	0	0	0	417.06	417.06	77.93	2.71×10^{-21}
	$^7F_3$	651	0	0	0	0	0	0	0	0
	$^7F_4$	701	0	0.0023	0	0	66.23	66.23	12.37	1.98×10^{-22}
	$^7F_5$	-	0	0	0	0	-	-	-	-
	$^7F_6$	-	0	0	0.0003	0	-	-	-	-
		A_T ($^5D_0$)=535.19 s^{-1}			τ_R =1.868 ms					

* The $^5D_0 \rightarrow {}^7F_5$ and $^5D_0 \rightarrow {}^7F_6$ transitions could not be experimentally detected.

In Table 1, the transition $^5D_0 \rightarrow {}^7F_2$ showed a β value of 77.93%. It has already established that an emission level with β value near 50% becomes a potential laser emission transition [16]. The most important parameter determining the potential laser performance at room temperature is the stimulated emission cross section σ. The large stimulated emission cross section is an attractive feature for low-threshold, high-gain applications [17]. The stimulated emission cross section at the 612 nm for europium (III) chelating polymer is 2.71×10^{-21} cm^2, which is comparable with those for Er^{3+} doped laser glasses [18].

5. Conclusion

In conclusion, a europium (III) chelating polymer has been synthesized has been synthesized and its radiative properties has been studied. The Judd-Ofelt phenolmenological parameters, Ω_2 and Ω_4 were obtained from the fluorescence emission spectrum are 13.9×10^{-20} cm^2 and 4.733×10^{-20} cm^2, respectively. Radiative properties of europium (III) chelating polymer were investigated also. The high fluorescence branching ratio of $^5D_0\rightarrow{}^7F_2$ transition and large emission cross section showed that europium (III) chelating polymer is a promising material for use in optical devices.

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