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Luminescence analysis of Eu complexes containing diphenanthryl β-diketone ligands doped silicone rubber

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Abstract Two Eu complexes containing symmetrical and asymmetrical diphenanthryl β-diketone ligands have been incorporated into silicone rubber. Their luminescence properties have been investigated by luminescence spectra and lifetime measurements. According to the fluorescence emission spectrum, the Judd–Ofelt parameters Ω_2, Ω_4 of europium complexes doped silicone rubber have been calculated and the influence of ligand's symmetry on the luminescence properties of Eu complex doped silicone rubber was discussed.

Introduction

Due to the extreme narrow-width emission band and good stability, europium β-diketone complexes have attracted considerable interest for the design of laser materials [1–3]. The luminescence of europium ion stems from the intra-4*f* transitions, which in principle are forbidden transitions, resulting in relatively low emission efficiency. An efficient way to increase the luminescence efficiency is to modify the complexes with different kinds of ligands that have broad and intense absorption bands [4–6].

Polymer materials have excellent properties such as simple processing steps, low cost and compatible with silicon substrate. According to these advantages, polymers are promised host candidates for applications in photonics, optoelectronics, and integrated optics [1–3]. The growing importance of polymer materials in integrated optic technology makes it interesting to study the incorporation of lanthanides complexes in a polymer.

As polymer hosts, silicone based polymers possess a unique set of properties such as excellent thermal stability and mechanical properties, highly transparent in the ultraviolet, visible, and selected bands of the near-IR spectra, etc. These characteristics make them highly suitable for optical applications [7].

In this work, two europium ternary complexes containing diphenanthryl β-diketone ligands have been incorporated into a silicone based polymer, methyl vinyl silicone rubber (Si–R). According to the luminescence spectra, lifetime measurement and Judd–Ofelt analysis, the influence of ligand's symmetry on the luminescence properties of Eu complex doped silicone rubber was discussed.

Experimental

Materials and samples preparation

Two types of diphenanthryl β-diketone ligands were used: symmetrical and asymmetrical. The europium (III) ternary complexes, 1,10-phenanthroline-tris[1,3-di(9-phenanthryl)-propane-1,3–dione]-europium (Eu complex 1) and 1,10-phenanthroline-tris[3-(3-phenanthryl)-1-(9-phenanthryl) propane-1,3–dione]-europium (Eu complex 2), were

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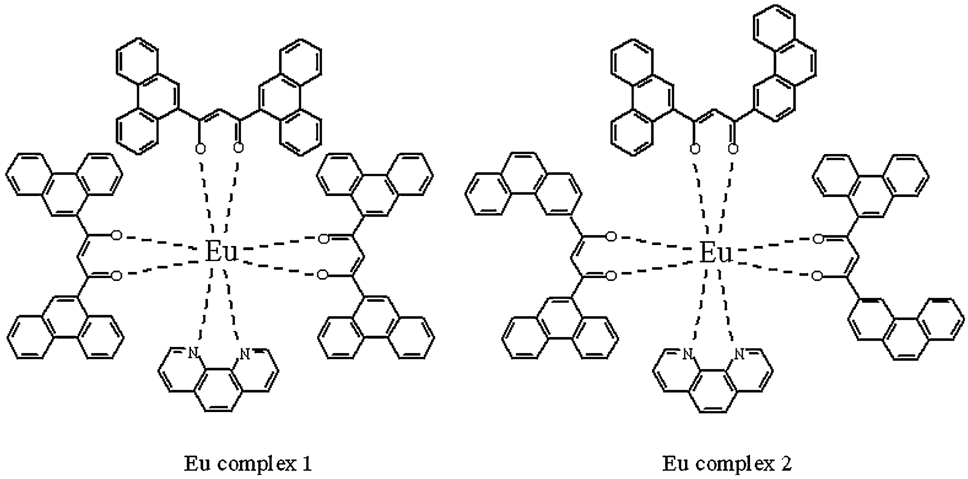

Eu complex 1

Eu complex 2

Fig. 1 Chemical structure of Eu complexes

synthesized according to the procedure reported before [8]. Their molecular structures are shown in Fig. 1. The central Eu^{3+} ion is bound to three diphenanthryl *β*-diketone ligands. The second ligand is phenanthroline, which can form stable five membered ring complexes by the coordination of the two nitrogens with europium ion.

Methyl vinyl silicone rubber (brand 110) was supplied by Dongjue Silicone Group Company Limited. Eu complexes doped silicone rubber fluorescence material was prepared by mixing 100 g of the silicone rubber, 2 g of 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane (DHBP) and 5 g of Eu complexes in a Haake rheomix 600 mixer at 50 °C and at 80 rpm for 15 min. Then, the achieved compound was put into a mould of 10 mm thickness and vulcanized under the pressure of 20 MPa for 20 min at 180 °C to obtain the cured Eu complexes doped silicone rubber material.

Characterizations

The luminescence spectra of Eu complexes doped silicone rubber were recorded on a Shimadzu RF-5301PC spectrofluorophotometer. The measurement of the fluorescence decay curves was 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 Eu^{3+} 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.

Results and discussion

Luminescence spectra of Eu complexes doped silicone rubber

The luminescence spectra of Eu complexes doped-silicone rubber were recorded form 500 to 750 nm under the excitation at 396 nm (see Fig. 2).

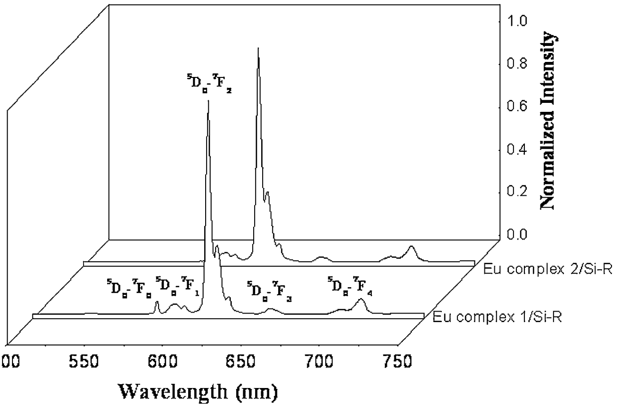

Fig. 2 Luminescence spectra of Eu complexes doped silicone rubber

The luminescence spectra of both Eu complexes doped silicone rubber show the narrow Eu^{3+} emission bands that correspond to the $^5D_0 \rightarrow {}^7F_J$ transitions (see Fig. 2). The radiative transitions within the $[Xe]4f^6$ configuration of Eu^{3+} are parity forbidden and consist mainly of weak magnetic dipole (MD) and induced electric dipole (ED) transitions. The emission bands of Eu^{3+} remain narrow even in an organic polymer matrix due to the fact that the partially filled 4*f* orbitals are shielded from the environment by the filled 5*s* and 5*p* orbitals. The $^7F_0$ state is nondegenerate, and therefore the $^5D_0 \rightarrow {}^7F_0$ emission band does not exhibit ligand field splitting. The single peak at 579 nm in the emission spectra therefore indicates that there is only one luminescent Eu^{3+} species in polymer matrix for each Eu complex. The $^5D_0 \rightarrow {}^7F_1$ emission around 592 nm is a pure MD transition. The strongest emission is observed around 612 nm corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition. The intensities of some ED transitions are extremely sensitive to the nature and symmetry of the coordinating environment, and the $^5D_0 \rightarrow {}^7F_2$ transition is an example of such a hypersensitive transition. The spectra show splitting of the $^5D_0 \rightarrow {}^7F_1$ and the $^5D_0 \rightarrow {}^7F_2$ emission bands caused by the ligand field.

It is well known that the probabilities of MD transitions are independent of the chemical environment of the ion, in contrast to those of the ED transitions. Thus, the intensity of the MD $^5D_0 \rightarrow {}^7F_1$ transition is independent of the coordination sphere and the $^5D_0 \rightarrow {}^7F_2$ transition is a hypersensitive transition, the intensity ratio of the $^5D_0 \rightarrow {}^7F_2$ transition and the $^5D_0 \rightarrow {}^7F_1$ transition ($I_{^7F_2}/I_{^7F_1}$) is a good measure of the nature and symmetry of the first coordination sphere [9, 10]. According to the luminescence spectra, the calculated $I_{^7F_2}/I_{^7F_1}$ values for Eu complex 1/Si–R and Eu complex 2/Si–R are 11.08 and 12.58, respectively. The higher $I_{^7F_2}/I_{^7F_1}$ value of Eu complex 2/Si–R indicated that the Eu complex 2 is more asymmetric, while Eu complex 1 presents a relative symmetric structure. It is obvious according to their chemical structure showed in Fig. 1.

Luminescence lifetimes of Eu complexes doped silicone rubber

The luminescence lifetimes of Eu complexes doped silicone rubber were measured from the decay curves and the results are shown in Fig. 3.

In a semi-logarithmic plot, a single-exponential decay function results in a straight line, this is also indicating that there is only one site symmetry from the Eu^{3+} ion [11]. The lifetime values were 0.561 and 0.598 ms for Eu complex 1/Si–R and Eu complex 2/Si–R, respectively, indicating that the lifetime of Eu complex 2/Si–R is longer than for Eu complex 1/Si–R. 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 [12]. Therefore, the shorter luminescence lifetime of Eu complex 1/Si–R suggest that the energy gap between the symmetrical diphenanthryl β-diketone ligand triplet state and the $^5D_0$ state of Eu^{3+} is smaller than that of Eu complex 2, which results a more efficient energy transfer.

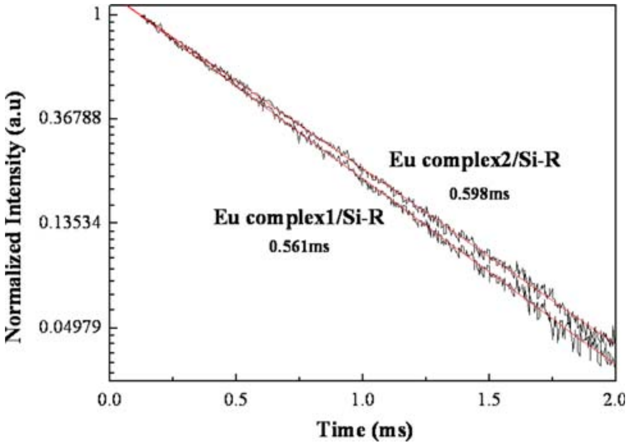

Fig. 3 Decay curve of Eu complexes doped silicone rubber

Judd–Ofelt analysis of Eu complexes doped silicone rubber

The Judd–Ofelt theory provides a very useful method for analyzing the local structure around rare-earth ions. According to the Judd–Ofelt theory, the $^5D_0 \rightarrow {}^7F_{2,4,6}$ transitions of Eu^{3+} are allowed by induced electric dipole. The electric dipole radiative transition probability A_{ed} between initial J manifold $\Psi J$to terminal manifold $\Psi' J'$ can be calculated by [13, 14]

$$\begin{aligned} A_{ed} = A[(S,L)J;(S',L')J'] &= \frac{64\pi^4 e^2 v^3}{3h(2J+1)} \frac{n(n^2+2)^2}{9} S_{ed} \\ &= \frac{64\pi^4 e^2 v^3}{3h(2J+1)} \frac{n(n^2+2)^2}{9} \sum_{t=2,4,6} \Omega_t \left\langle \Psi J \middle\| U^{(t)} \middle\| \Psi' J' \right\rangle^2 \end{aligned}$$

where h is Plank's constant, m is the mass of the electron, c is the velocity of light, n is the refractive index of the medium, v is the wavenumber of the transition, J is the quantum number of angular momentum of the initial state and J' is that of the final state. The $\left\| U^{(t)} \right\|^2$ are the squared reduced matrix elements of the rank $t = 2, 4, 6$ and the values for the Eu^{3+} ion are given in Table 1 [15]. The three coefficients $\Omega_2, \Omega_4, \Omega_6$ contain implicitly the odd-symmetry crystal field terms, radial integrals and perturbation denominators.

The $^5D_0 \rightarrow {}^7F_1$ of Eu^{3+} ion is a magnetic dipole transition which is independent of the environment and can be used as a reference. The spontaneous emission probability of magnetic dipole transition A_{md} is [16]:

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

S_{md} refers to the strength of the magnetic dipole line strength of the $^5D_0 \rightarrow {}^7F_1$ transition, which is a constant and independent of the medium.

The spontaneous emission probability of an electric dipole transition A_{ed} depends on $\left\| U^{(t)} \right\|^2$. The Ω_t can be determined from the ratios of intensities of $^5D_0 \rightarrow {}^7F_{2,4,6}$ transitions to the intensity of $^5D_0 \rightarrow {}^7F_1$ transition as follows:

$$\frac{\int I_J(v)dv}{\int I_{md}(v)dv} = \frac{A_J}{A_{md}} = \frac{e^2}{S_{md}} \frac{v_J^3}{v_{md}^3} \frac{(n^2+2)^2}{9n^2} \Omega_t \left\langle \Psi J \middle\| U^{(t)} \middle\| \Psi' J' \right\rangle^2$$

The obtained values for parameter Ω_2 and Ω_4 of Eu complexes doped silicone rubber were presented in Table 2.

Table 1 Squared reduced matrix elements for Eu^{3+} ion

Transition	$\left\| U^{(2)} \right\|^2$	$\left\| U^{(4)} \right\|^2$	$\left\| U^{(6)} \right\|^2$
$^5D_0 \rightarrow {}^7F_2$	0.0032	0	0
$^5D_0 \rightarrow {}^7F_4$	0	0.0023	0
$^5D_0 \rightarrow {}^7F_6$	0	0	0.0002

Table 2 Ω_2, Ω_4 parameters of Eu complexes doped silicone rubber

	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)
Eu complex 1/Si–R	19.6	2.102
Eu complex 2/Si–R	21.8	1.923

The Ω_6 intensity parameter was not determined because the $^5D_0 \rightarrow {}^7F_6$ transition could not be experimentally detected. As a matter of fact, the parameter Ω_6 can be negligible compared with Ω_2 and Ω_4, because $\left\|U^{(6)}\right\|^2$ is comparatively small.

The parameter Ω_2 is associated to the covalence and the symmetry of the ligand field in the rare-earth site [17]. Compared with Eu^{3+} doped inorganic system, Eu complexes doped silicone rubber shows a relative larger Ω_2 value [16, 18]. The large Ω_2 value indicates the presence of covalent bonding between the Eu^{3+} ion and the surrounding ligands [19]. The much stronger hypersensitive transition $^5D_0 \rightarrow {}^7F_2$ of both Eu complexes doped silicone rubber accounts for such a Ω_2 value. The higher Ω_2 value of Eu complex 2/Si–R also indicates that Eu complex 2 is more asymmetric than that of Eu complex 1. 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 [20].

Conclusion

In conclusion, two Eu complexes containing symmetrical and asymmetrical diphenanthryl *β*-diketone ligands have been incorporated into silicone rubber and their luminescence properties have been studied. It was found that the symmetry of the ligand has a significant effect on the luminescence properties. Compared with symmetrical Eu complex 1/Si–R, the asymmetrical Eu complex 2/Si-R presented a higher $I_{^7F_2}/I_{^7F_1}$ value (12.58), a longer luminescence lifetime (0.598 ms) and a higher Ω_2 value (21.8×10^{-20} cm^2). The result may be helpful in design rare-earth doped polymer optical materials.

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