Fluorescence enhancement of europium complex co-doped with terbium complex in a poly(methyl methacrylate) matrix

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Abstract

The enhanced fluorescence of Eu(DBM)3Phen(DBM: dibenzoylmethide; Phen: phenanthroline) by Tb(DBM)3Phen in a poly(methyl methacrylate) (PMMA) has been studied. A combinatorial methodology was adopted to allow rapid optimization of the fluorescence enhancement conditions of thin-film samples in arrays of microwells. Based on Eu(DBM)3Phen doped PMMA, three material libraries were generated in order to compare the effects of species identity and Tb(DBM)3Phen content to the effect of other complexes containing enhancing ions (La3+, Gd3+, Dy3+, Y3+, Ce3+) on the luminescence efficiency of the Eu3+ complex in PMMA. The fluorescence enhancement of Eu(DBM)3Phen in PMMA is considered to originate from intramolecular and intermolecular energy transfer processes. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

Rare-earth complexes such as europium and samarium are attractive because of their large toke shifts, narrow emission bandwidths and long emission lifetimes, which make them suitable candidates for applications as light-emitting diode (LED) [1], laser materials [2], optical signal amplification [3], and fluoroimmunoassay [4,5]. The growing importance of polymer thin-films in integrated optic technology makes it interesting to study the incorporation of rare-earth complexes in a polymer [6]. Rare-earth complexes doped polymers are important because they possess the properties of the complexes while they can be processed from solution and are mechanically flexible (e.g., the stable transparent mixtures could be easily spin-coated and thermally converted to uniform films).

Luminescence from trivalent lanthanide ions arises from electronic transitions between the 4f orbitals. These transitions are forbidden on symmetry grounds, leading to poor absorption cross sections and relatively long-lived excited states [7]. An approach to increase the luminescent efficiency is to modify the complexes with different kinds of ligands characterized by broad and intense absorption bands [8,9]. The fluorescent lanthanides Eu3+, Sm3+, Tb3+ and Dy3+, in this case can accept energy from the ligand in close proximity, provided that the excited state of the donor is above the emitting level of the ions. It has also been found that an efficient energy transfer takes place between the complexes of different rare-earth ions under conditions that ensure close proximity between the acceptor and the donor complexes. The non-fluorescent β-diketone complexes of yttrium, lanthanum, lutetium and gadolinium, and sometimes terbium, can donate energy...
that they have absorbed to the analogous fluorescent complexes of europium. Within the donating complex, the rare-earth ion cannot accept energy from the level of the ligand, but the energy is transferred to the respective fluorescent complex, provided that the complexes are in close proximity, e.g., in an aqueous suspensions, co-precipitates, and LB films, containing a large excess of the donating complex [10–12]. This phenomenon was called co-fluorescence, or enhanced luminescence [13–15].

In our previous work, we have investigated the enhancing efficiency of the La$^{3+}$ complex to Eu$^{3+}$ complex in PMMA using a combinatorial method, and concluded that at the content of 5 wt% Eu(DBM)$_3$Phen, the maximum luminescence observed for the Eu-complex in the presence of the La-complex is as much as 20 times that observed without the co-dopant [16]. Moreover, Ci and Lan showed that the closer the ionic radius of the enhancing ion was to that of the luminescence ion, the greater the enhancement of the luminescence intensity [17]. Because the radius of Tb$^{3+}$ is closer to that of Eu$^{3+}$ than La$^{3+}$, in this paper, the fluorescence enhancement phenomenon based on Eu(DBM)$_3$Phen co-doped with a Tb$^{3+}$ complex in PMMA is studied using the combinatorial method. In the first round screen, different kinds of enhancing ion complexes and contents were synthesized to compare the enhancing efficiency of Tb$^{3+}$ complex with other ion (La$^{3+}$, Gd$^{3+}$, Dy$^{3+}$, Y$^{3+}$, Ce$^{3+}$) complexes in PMMA. In the second round screen, another library with different contents of Tb(DBM)$_3$Phen was synthesized to identify the best fluorescence enhancement ratio of Tb(DBM)$_3$Phen to Eu(DBM)$_3$Phen. Then, six scale-up samples were synthesized to confirm the results from the combinatorial libraries and to study the fluorescence enhancement mechanism.

2. Experimental

Rare-earth complexes (Re(DBM)$_3$Phen, Re$^{3+}$ = Eu$^{3+}$, Tb$^{3+}$, La$^{3+}$, Gd$^{3+}$, Dy$^{3+}$, Y$^{3+}$, Ce$^{3+}$) were synthesized according to the procedure reported in literature [18].

The final products were recrystallized in acetone/petroleum ether (2:1). Poly(methyl methacrylate)(PMMA, Mw ~ 350000) were purchased from Acros Chemical company and used as-received. The rare-earth complexes and PMMA were dissolved in cyclopentanone solvent with a concentration of 5 g/L, respectively.

Then the solutions were deposited into the wells on a fluorophlogopite substrate using a micro-liter pipette. The as-deposited libraries were evaporated in air at room temperature. The instrument for spectrum measurement of material chips is an example of a multiple-parallel luminescence measurement system that has been successfully used to measure the luminescence property and represents a valid alternative to single luminescence measurement apparatus [16,19].

To confirm the results of combinatorial method and study the fluorescence enhancing mechanism, individual films were prepared at spin speed of 2500 revolution per minute (rpm). The photoluminescence measurement was performed on a FLUOROLOG-3-TAU steady-state/lifetime spectrofluorometer.

3. Results

Before beginning carefully quantitative measurement of the fluorescence efficiencies of Tb$^{3+}$/Eu$^{3+}$ complex co-doped PMMA system, we used the first material library to compare quickly the enhancing efficiency of Tb$^{3+}$ complex with those of other enhancing ions (La$^{3+}$, Gd$^{3+}$, Dy$^{3+}$, Y$^{3+}$, Ce$^{3+}$) complexes to Eu$^{3+}$ complex in PMMA. The PMMA solution was pipetted into an array of 6 $\times$ 6 wells. Varying amounts of each complex were then pipetted across each row of the array. Fig. 1(a) shows the photoluminescent photograph of the library with different kinds and contents of enhancing ion complexes in PMMA matrix under 365 nm UV excitation, and the PL intensity of Eu$^{3+}$ dependence on enhancing ions content in PMMA matrix. $X$ is defined as the weight ratio of the rare-earth complexes to PMMA for the rest of this paper unless other specified.

![Fig. 1. (a) The digital photograph of the emission from a series of Re/(Eu) library of six rare-earth ion complexes sensitized Eu$^{3+}$ complex in PMMA matrix. (b) The normalized PL intensity of the Eu(DBM)$_3$Phen at 614 nm as a function of the enhancing ions content in PMMA matrix. $X$ is defined as the weight ratio of the rare-earth complexes to PMMA for the rest of this paper unless other specified.](image-url)
$X$ is defined as the weight ratio of the rare-earth ion complexes to PMMA for the rest of this paper unless otherwise specified.

To quantitatively determine the enhancing efficiency of the Tb$^{3+}$ complex to Eu$^{3+}$ complex, a series of distinct content of Tb$^{3+}$/Eu$^{3+}$ complex co-doped PMMA was pipetted into the second material library. The photo-luminescence photograph of the second material library with different contents of Tb$^{3+}$ and Eu$^{3+}$ complex in PMMA matrix under 365 nm UV excitation is shown in Fig. 2(a) and the relationships between the corresponding fluorescence enhancement factors $F$, a factor of luminescence enhancement expressing the efficiency of energy transfer [20] and the Tb$^{3+}$ complex content are plotted in Fig. 2(b). $F$ is a ratio of the luminescence intensity of the film that contains Tb(DBM)$_3$Phen to that which does not in this paper.

To confirm the results, individual scale-up films were fabricated with selected composition of Eu$_{0.05}$:Tb$_X$ ($X = 0, 0.1, 0.2, 0.4, 0.6$ and $0.8$) identical to those of the samples in the library. The relationship between the fluorescence enhancement factor of the scale-up films and the content of Tb(DBM)$_3$Phen is shown in Fig. 3.

In order to investigate the influence of PMMA matrix on the fluorescence enhancement effect, the third material library was made with the same kinds and contents of enhancing ion complexes as the first library shown in Fig. 4(a) and (b) without PMMA.
4. Discussion

From Fig. 1, for La(DBM)₃Phen, the luminescence intensity of Eu³⁺ at 614 nm increases as the content of various enhancing ion complex increases and when \( X = 0.4 \), the fluorescence intensity reaches the maximal value, a further increase of the content of enhancing ion complex decreases the luminescence intensity. The luminescence intensity increases with the increase of the content of Tb³⁺ and Gd³⁺ complex in the same content range of Eu(DBM)₃Phen; the addition of Y³⁺ and Dy³⁺ complex has no influence on the luminescence intensity; finally, the luminescence intensity of Eu³⁺ decreases with the increase of the content of Ce³⁺ complex because Eu³⁺ has the tendency to divalent due to the formation of complexes containing Ce⁴⁺–Eu³⁺ [21,22]. Among these enhancing ion complexes, it can be clearly seen that five ions are arranged in the order of their enhancement factors, terbium, gadolinium, Lanthanum > yttrium, dysprosium > cerium for Eu(DBM)₃Phen system and that Tb³⁺ complex causes the greatest fluorescence enhancement. This is the same as the conclusion reported earlier by Zhong et al. [12] and Ci et al. [15]. This result tells us that the closer the sizes of rare-earth ions in donor and acceptor complexes are, the more effective the energy transfer.

As seen from values of \( F \) in Fig. 2, the lower content of Eu(DBM)₃Phen exists in the film, the higher efficiency of luminescence enhancement (\( F_{\text{max}} = 27 \)). It indicates that the efficiency of energy transfer is dependent on the content of Eu(DBM)₃Phen and Tb(DBM)₃Phen in the sample. The value of \( F \) increased as the content of enhancing ion complex increasing because the more Tb(DBM)₃Phen molecules surround Eu(DBM)₃Phen molecular, the more effective the energy transfer.

The tendency of the scale-up sample of the fluorescence enhancement factor as the function of Tb(DBM)₃Phen content is fairly consistent with that from the small samples in the library. Therefore, it is feasible to study the fluorescence enhancement in rare-earth complex doped PMMA using combinatorial methods.

The curves in Fig. 4 clearly show that there is almost no luminescence enhancement without the PMMA and the addition of enhancing ion complexes results in only a decrease of the PL intensity. Compared with Fig. 1, it is concluded that the fluorescence enhancement effect exists in PMMA and cannot be observed without PMMA.

Why did the fluorescence enhancing effect occur in PMMA? In the rare-earth complexes, it is possible for the Re³⁺ ions to form aggregates in a special environment. It has been reported that the co-fluorescence effect is caused through the intermolecular energy transfer between the two complex types [23]. Considering the Foster [24] and Dexter's theories, energy can be transferred to molecules in short distance through an intermolecular energy transfer. The efficiency of the intermolecular energy transfer is dependent on proximity of donor to acceptor. It has been reported that the fluorescence intensity for Eu³⁺ fluorescence is highest when the Eu(dnm)₃Phen content in CN–PPP is \( \approx 5–10 \) wt%. At higher concentrations, the fluorescence intensity is reduced by concentration quenching due to the formation of aggregation [1]. Ci and Lan [17] studied the fluorescence of Sm(TTA)₃Phen/Gd(TTA)₃Phen in Triton X-100 micelle. They suggested that a close proximity of donor to acceptor is achieved in the micelle medium due to its hydrophobic inner space, which results in an efficient energy transfer from Gd(TTA)₃Phen to Sm(TTA)₃Phen. In this work, when the higher content (10–80 wt%) of enhancing ion complex is doped into PMMA, we suggested the PMMA enwraps the rare-earth complexes and keeps the donors and acceptors close [16]. The aggregate particles composed of two kinds of complexes are created in PMMA matrix, which is a phase rich in rare-earth complexes at a suitable content for energy transfer between them within the matrix. At the same content of Eu(DBM)₃Phen, the fluorescence intensity of Eu(DBM)₃Phen increases with the content of Tb(DBM)₃Phen increases with the content of Eu(DBM)₃Phen and Tb(DBM)₃Phen complexes, the energy absorbed by its chelate molecules can not be dissipated through those energy levels, but is transferred to the nearby molecules Eu(DBM)₃Phen; the enhancing ions (Tb³⁺) used have not suitable excited 4f or 4d levels for the excited triplet levels of the DBM, and the energy absorbed by its chelate molecules can be dissipated through those energy levels, a large part of the energy transferred to the nearby molecules Eu(DBM)₃Phen.

After DBM absorbing light energy, Tb³⁺ can be excited to the \( ^{3}D_{4} \) level by intramolecular energy transfer from a part of the energy of DBM absorbed in the complex and the transitions from the \( ^{3}D_{4} \) level of Tb³⁺ to the \( ^{5}P_{0} \) and \( ^{5}F_{5} \) levels occur, responding to the intrinsic emissions of Tb³⁺ at 490 and 545 nm, respectively. The dependence of the fluorescence intensity of Tb(DBM)₃Phen(a) and Eu(DBM)₃Phen(b) on the content of Tb(DBM)₃Phen content is shown in Fig. 5.

From Fig. 5, after continuously adding Tb(DBM)₃Phen to Eu(DBM)₃Phen complex, the fluorescence of Tb³⁺ complex is gradually weaken (Fig. 5(a)) and that of Eu³⁺ is gradually enhanced (Fig. 5(b)). This indicates that there is the intermolecular energy transfer between Tb(DBM)₃Phen and Eu(DBM)₃Phen complexes, the energy absorbed by the complex can be transferred to \( ^{5}D_{0} \) of Eu³⁺ in Eu(DBM)₃Phen, and then enhances the fluorescent intensity of Eu(DBM)₃Phen.

The dependence of luminescence intensity of Eu³⁺ on the content of Tb³⁺ complex is relevant to a triplet–triplet intermolecular energy transfer from DBM in Tb(DBM)₃Phen to that in Eu(DBM)₃Phen in PMMA [19]. Besides, an important factor that accounts for the fluorescence enhancing of Eu³⁺ luminescence is the energy transfer...
between Eu$^{3+}$ and Tb$^{3+}$. As schematically shown in Fig. 6, the resonance energy level of Eu$^{3+}$ ($^5D_4$, 17 500 cm$^{-1}$) is lower than that of Tb$^{3+}$ ($^5D_4$, 20 400 cm$^{-1}$). It is possible that the Eu$^{3+}$ in the mixed complex diverts a large portion of the energy from the $^5D_4$ level of the Tb$^{3+}$, thus promoting the luminescence enhancing of the Eu$^{3+}$, which does not exist in the other ions (La$^{3+}$, Gd$^{3+}$) doped PMMA films. The model for energy transfer processes is established in Fig. 6 based on Refs. [25,26].

5. Conclusion

It was found that the fluorescence of Eu(DBM)$_3$Phen can be enhanced by Tb(DBM)$_3$Phen addition in PMMA. This is a new co-fluorescence system. This system is studied in detail using a combinatorial method. The results in the first material library show that the Tb$^{3+}$ complex has the highest enhancing efficiency among the ions tested. The results in the second material library indicate that the lower the content of Eu(DBM)$_3$Phen that exists in the film, the higher the efficiency luminescence enhancement that will be obtained in the presence of Tb(DBM)$_3$Phen ($F_{max} = 27$). The intramolecular and intermolecular energy transfer processes between Tb(DBM)$_3$Phen and Eu(DBM)$_3$Phen in PMMA are responsible for the co-fluorescence effect. The fluorescence enhancement of Eu(DBM)$_3$Phen by Tb(DBM)$_3$Phen in PMMA occurs because the PMMA keeps the donors and acceptors close, which results in the effective intermolecular energy transfer and consequently, the high enhancing efficiency.

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References