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Inter- and intra-molecular energy transfer during sensitization of $Eu(DBM)_3Phen$ luminescence by $Tb(DBM)_3Phen$ in PMMA

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Abstract

A series of $Eu(DBM)_3Phen$ and $Tb(DBM)_3Phen$ co-doped poly(methyl methacrylate) (Eu_xTb_y-PMMA, subscript x and y denote molar ratio of the ion to repeating unit of PMMA in each sample) were prepared with different Eu/Tb contents. During luminescence measurement of these samples, it was found that for $Eu_{0.010}Tb_0$-PMMA the maximum excitation was found to be at 363 nm, and for $Eu_0Tb_{0.010}$-PMMA the maximum excitation at 274 nm. This difference reveals that there is different intra-molecular energy transfer mechanism for these two complexes, which contain the same ligands but different central ions. For $Eu_{0.0050}Tb_y$-PMMA ($y = 0$, 5.0×10^{-6}, 3.0×10^{-5}, 5.0×10^{-5}, 3.0×10^{-4}, 4.0×10^{-4}, 1.0×10^{-3}, 4.0×10^{-3}, 1.0×10^{-2}, 2.0×10^{-2}, 4.0×10^{-2}, 6.0×10^{-2} and 8.0×10^{-2}, respectively), enhanced luminescence of Eu^{3+} at 612 nm for ${}^5D_0 \rightarrow {}^7F_2$ was observed at the concentration of Tb^{3+} higher than 0.0048 mol/L. At this Tb^{3+} content, the minimum intensity of the luminescence of $Eu(DBM)_3Phen$ was observed, which comes from the balance between absorption consumption of ligands in $Tb(DBM)_3Phen$ and sensitizing in luminescence of Eu^{3+} by Tb^{3+}. $Eu_xTb_{0.010}$-PMMA ($x = 0$, 5.0×10^{-3}, 8.0×10^{-3}, 9.0×10^{-3}, 0.013, 0.020, 0.030, 0.040 and 0.060) showed a gradually increasing emission of Eu^{3+} at 535 nm along with decreasing of Tb^{3+} emission at 546 nm, which resulted from a fast intra-molecular energy transfer from ${}^5D_1$ to ${}^5D_0$ of Eu^{3+} and an inter-molecular energy transfer from the triplet state of DBM in $Tb(DBM)_3Phen$ to ${}^5D_1$ of Eu^{3+}, and the latter energy transfer process is directly dependent on the distance between two kinds of ions. Based on observation above, it was realized that there will be a critical distance between two kinds of complexes in each Eu_xTb_y-PMMA sample, which determines the minimum concentration of $Tb(DBM)_3Phen$ for the sensitization in luminescence of the sample. To give a vivid picture for this complex system, a model for the sensitization of Eu_xTb_y-PMMA was established in terms of Perrin formulation. The radius of the quenching sphere, which corresponds to the critical distance between Eu^{3+} and Tb^{3+}, was found to be 1.633 nm for the sensitization in Eu_xTb_y-PMMA.

Keywords: Energy transfer; Luminescence; Quenching sphere; Lanthanide complexes; Sensitization

1. Introduction

Lanthanide organic complexes have received great interest due to their intense emission peaks (half-maximum width <10 nm) in the visible and near-infrared region under UV excitation. As light-conversion units, these complexes were used in a variety of areas such as fluoroimmunoassays [1,2], energy harvesting devices [3], optical signal amplification [4,5], etc. Generally, in these complexes, emission intensity is strongly dependent on efficiency of ligand absorption, efficiency of ligand-to-metal energy transfer [6] and efficiency of metal emission.

The main problem in these applications is the concentration quenching when the complexes concentration reaches a high critical value. One of methods to resolve this problem is co-doping other lanthanide ions that can considerably enhance photoluminescent intensity (co-luminescence effect or sensitization) and have been widely observed in various systems [7–11]. It is believed that there exists an energy transfer among different lanthanide ions in these co-doped materials [12,13]. Energy transfer from Tb^{3+} to Eu^{3+} has been used in various matrices [12–15], in which Eu^{3+} was used as an acceptor and Tb^{3+} as a donor.

It has been known that spectroscopy of lanthanide molecules incorporated in different matrices often shows marked different characters [14–17]. All the while, the incorporation of lanthanide complexes in polymer matrix has attracted much attention, because such a composite possesses advantages of the lumi-

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nescence characteristics of lanthanide ions and the excellent mechanical properties of plastics such as light weight, good transparency, impact resistance, low temperature processability and so on. Poly(methyl methacrylate) (PMMA) has often been used as a polymer matrix for lanthanide complexes. A systematical study on the co-photoluminescent effect caused by co-doped of $Tb(DBM)_3Phen$ and $Eu(DBM)_3Phen$ in PMMA has been performed by the combinatorial method in our previous work, in which large collections of compounds are synthesized and screened in a materials library simultaneously for a particular physical or chemical property [18,19]. However, mechanism of inter- and intra-molecular energy transfer still needs more work. In this paper, detailed study on absorption and luminescence spectra of $Eu(DBM)_3Phen$ and $Tb(DBM)_3Phen$ co-doped PMMA is presented to reveal the mechanism of the energy transfer between complexes. Under this circumstance, a series of $Eu(DBM)_3Phen$ and $Tb(DBM)_3Phen$ co-doped PMMA were prepared with different Eu/Tb contents, and quantitative analysis on their absorption and luminescence was carried out. A quenching sphere model was established, from which some critical properties of the co-doped PMMA can be obtained.

2. Experimental

Lanthanide complexes ($Ln(DBM)_3Phen, Ln^{3+} = Eu^{3+}, Tb^{3+}$) were synthesized according to the procedure reported before [20]; their molecular structure is shown in the inset of Fig. 1. The central ion (Ln^{3+}) is bound to three ligands of dibenzoylmethide (DBM) ions. 1,10-Phenanthroline (Phen) acts as a synergic shielding ligand, which can reduce the rate of non-radiative decays and enhance the luminescence intensity of the complex strongly [21]. The final products were recrystallized in acetone/petroleum ether (2:1). Narrow dispersed PMMA ($M_w \sim 350{,}000$) was purchased from Acros Chemical company and used as received.

As followed-up work of the combinatorial study reported [19], two series of film samples were made. For the first series, when the concentration of $Tb(DBM)_3Phen$ is low, $Tb(DBM)_3Phen$ was dissolved in tetrahydrofuran (THF) with a concentration of 0.004 g/ml, and $Eu(DBM)_3Phen$ and PMMA were dissolved in THF with the concentration of 0.004 g/ml and 0.08 g/ml, respectively. And then different doses of $Tb(DBM)_3Phen$ solution (0, 0.0005, 0.003, 0.005, 0.05,0.03,0.04,0.01 and 0.4 ml) were added to 0.5 ml solution co-doped with $Eu(DBM)_3Phen$ and PMMA and then the solution was diluted to 1 ml. Subsequently, the solution was spin-coated on clean glass slides and finally dried at 50 °C under vacuum for 2 days. Film samples are defined as Eu_xTb_y-PMMA, in which subscript x and y denotes molar ratio of each ion to repeating unit of PMMA in each sample. Corresponding samples are $Eu_{0.0050}Tb_y$-PMMA ($y = 0, 5.0 \times 10^{-6}, 3.0 \times 10^{-5}, 5.0 \times 10^{-5}, 3.0 \times 10^{-4}, 4.0 \times 10^{-4}, 1.0 \times 10^{-3}$ and 4.0×10^{-3}, respectively). When the concentration of $Tb(DBM)_3Phen$ is high, film samples $Eu_{0.0050}Tb_y$-PMMA ($y = 1.0 \times 10^{-2}, 2.0 \times 10^{-2}, 4.0 \times 10^{-2}, 6.0 \times 10^{-2}$ and 8.0×10^{-2}, respectively) and $Eu_{0.010}Tb_0$-PMMA were made as the second series of film samples. For the second series of film samples, $Tb(DBM)_3Phen$ and PMMA were dissolved in THF with the concentration of 0.004 g/ml and 0.04 g/ml, respectively, and then different doses of $Eu(DBM)_3Phen$ (0, 0.0020, 0.0033, 0.0037, 0.0053, 0.0082, 0.0120, 0.0160, 0.0240 g) were added to 1 ml solution above-mentioned. Corresponding sample are $Eu_xTb_{0.010}$-PMMA ($x = 0, 5.0 \times 10^{-3}, 8.0 \times 10^{-3}, 9.0 \times 10^{-3}$, 0.013, 0.020, 0.030,0.040 and 0.060). All the film samples were prepared at the spin speed of 2500 revolution per minute (rpm) and the film thickness is about 20 nm.

Photoluminescence was measured on the RF-5301PC, and absorption spectra of dibenzoylmethane (HDBM), Phen and two complexes in solution of methyl methacrylate (MMA) were obtained on a UV-VIS photometer (SHIMADZU UV-2401PC).

3. Results and discussion

3.1. Intra-molecular energy transfer within each complex

Absorption spectra of HDBM, Phen and two complexes in solution of methyl methacrylate (MMA) are shown in Fig. 1. All the concentrations were about 10 ppm. It can be seen that for HDBM, there is a strong absorption band from 250 nm to 380 nm, for Phen, the characteristic absorption is about 290 nm and the intensity is weak, but for both of complexes there is a strong absorption band from 300 nm to 400 nm, and the absorption of Phen is also shown and the peak is more weak. The little red shift from the absorption peak of HDBM to that of the complex shows the formation of the coordinating bond between ligands and central ions [22]. It is worth to note that the absorption of $Tb(DBM)_3Phen$ shows similar absorption band to that of $Eu(DBM)_3Phen$ for their close structures.

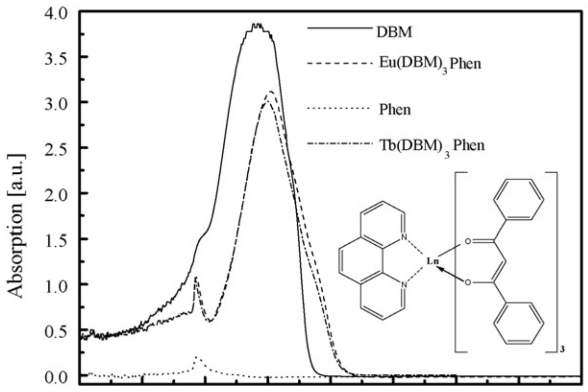

Fig. 1. Absorptions of HDBM, Phen and two complexes in solution of MMA. Inset is the chemical structure of $Ln(DBM)_3Phen$.

The emission spectrum of $Eu_{0.010}Tb_0$-PMMA was recorded from 550 nm to 720 nm under excitation at 363 nm as shown in Fig. 2(a). It can be seen that five emission peaks are centered at 579, 592, 612, 652, 704 nm, and can be assigned to the $^5D_0 \to {}^7F_0, {}^5D_0 \to {}^7F_1, {}^5D_0 \to {}^7F_2, {}^5D_0 \to {}^7F_3, {}^5D_0 \to {}^7F_4$, respectively. The presence of only one $^5D_0 \to {}^7F_0$ line indicates that Eu^{3+} ion exists in a single chemical environment

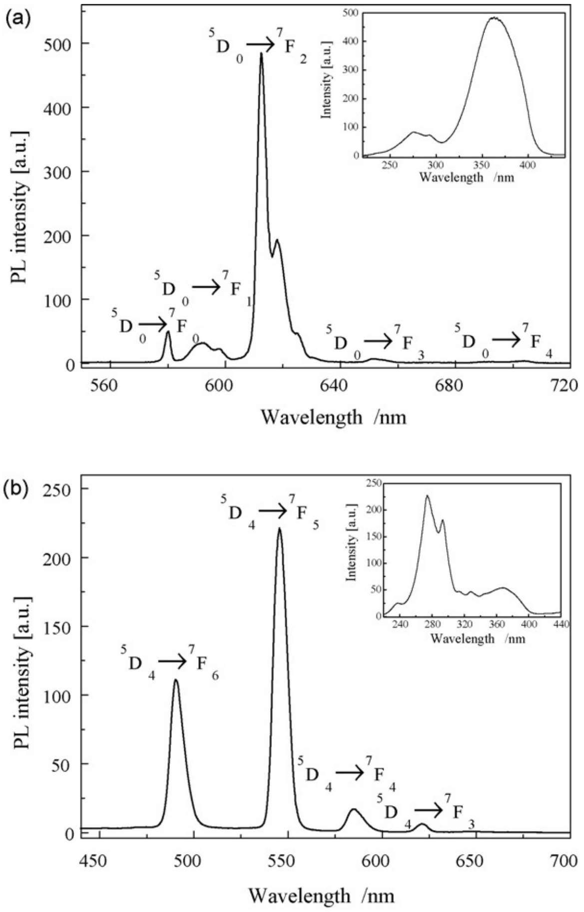

Fig. 2. Emission spectra of $Eu_{0.010}Tb_0$-doped PMMA (a) ($\lambda_{ex}=363$ nm) and $Eu_0Tb_{0.010}$-doped PMMA (b) ($\lambda_{ex}=274$ nm) and their respective excitation spectra shown in the insets of (a) ($\lambda_{em}=612$ nm) and (b) ($\lambda_{em}=546$ nm).

[23]. The much stronger intensity of $^5D_0\rightarrow{}^7F_2$ than those of other transitions indicates that Eu^{3+} ion is in a single site without a center of inversion [24]. There are four emission peaks in the luminescence spectrum of $Eu_0Tb_{0.010}$-PMMA as shown in Fig. 2(b), which are centered at 489, 546, 584, 620 nm, and can be attributed to the $^5D_4\rightarrow{}^7F_6$, $^5D_4\rightarrow{}^7F_5$, $^5D_4\rightarrow{}^7F_4$, $^5D_4\rightarrow{}^7F_3$, respectively. The strongest peak is located at 546 nm. The exciting and emitting slit pairs of the spectrofluorometer for $Eu_{0.010}Tb_0$-PMMA and $Eu_0Tb_{0.010}$-PMMA were 3 and 1.5 nm, respectively. Seen from Fig. 2, it can be found that the intensity of $Eu_{0.010}Tb_0$-PMMA luminescence is much stronger than that of $Eu_0Tb_{0.010}$-PMMA in comparison Fig. 2(a) with Fig. 2(b). This result shows that the luminescence yield of the former is larger than that of the latter, which reveals that there is a difference in energy transfer processes within two complexes.

On the other hand, their excitation spectra are, respectively, shown in the inset of Fig. 2(a) monitored at 612 nm and the inset of Fig. 2(b) monitored at 546 nm. The excitation spectra from 220 nm to 440 nm, the bands of $^7F_j\rightarrow{}^5D_i$ transitions are too weak to present in it. Only a broad strong UV band is observed in the excitation spectra of the co-doped samples, corresponding to transitions populating ligand-centered excited states [25–27]. Furthermore, the relative intensity of the broad UV band to the intrinsic Eu^{3+} and Tb^{3+} lines hidden in fact shows the so-called "antenna" role played by the β-diketone molecules.

For $Eu(DBM)_3Phen$ the ligand DBM absorbs the energy from excitation at 363 nm, and is excited to its singlet state. For the characteristic emission of $Eu(DBM)_3Phen$ in PMMA, according to the Dexter's theory [28], the excited singlet state of DBM undergoes a nonradiative transition to the triplet state of Phen, whose energy level is 22,075 cm^{-1} (453 nm), and to the triplet state of DBM, whose energy level is 20,520 cm^{-1} (487 nm)[29]. At last, the energy transfers to Eu^{3+} via a state that is any state with energy higher than the $^5D_0$ state, possibly $^5D_1$ of Eu^{3+}[30]. $^5D_1$ state can directly decay by intra- molecular quenching to the excited state $^5D_0$. Subsequently, Eu^{3+}undergoes radiative transitions from $^5D_0$ to ^7F_j, which are characteristic emissions of Eu^{3+}.

From Fig. 2 it can be found that the excitation spectra of $Tb(DBM)_3Phen$ and $Eu(DBM)_3Phen$ are totally different although they have the same ligands and the absorption spectra. For $Eu(DBM)_3Phen$ the maximal excitation peak is at around 363 nm primarily attributing to the absorption of DBM. But for $Tb(DBM)_3Phen$, the maximal excitation peak is at about 274 nm mostly belonging to the absorption of Phen. It has been known that the triplet state energy level of DBM is 20,520 cm^{-1}(487 nm), which is much closer to the resonance energy level of Tb^{3+}($^5D_4$, 20,400 cm^{-1}, 490 nm). Under this circumstance, the excited singlet state of Phen prefers transfer to the triplet state of Phen with energy level about 22,075 cm^{-1}(453 nm) [31] other than the triplet state of DBM (487 nm). As a result, most of energy is directly transferred to $^5D_4$ of Tb^{3+} from the triplet state of Phen and only a little energy is diverted to the triplet state of DBM. In succession, Tb^{3+}undergoes radiative transitions from $^5D_4$ to ^7F_j, which are characteristic emissions of Tb^{3+}. It is interesting to note at this moment that most energy absorbed by DBM in $Tb(DBM)_3Phen$ does not be used in luminescence of Tb^{3+} by comparing absorption (Fig. 1) and excitation (Fig. 2) spectra of $Tb(DBM)_3Phen$. When these two complexes were co-doped into PMMA, intermolecular energy transfer would be included, which could result in co-luminescence or sensitization.

3.2. *Inter-molecular energy transfer between complexes*

In our previous work [19], which was concerned with co-doping two kinds of lanthanide complexes in PMMA, it has been found that under irradiation of light at 365 nm $Tb(DBM)_3$ Phen and $Eu(DBM)_3Phen$ co-doped PMMA showed a stronger luminescence of Eu^{3+} than that of $Eu(DBM)_3Phen$ doped PMMA, showing evidently enhancement by $Tb(DBM)_3Phen$. To quantitatively investigate the enhancement, relation between the luminescence intensity of $Eu(DBM)_3Phen$ and Tb^{3+} concentration was investigated with samples of $Eu_{0.0050}$ Tb_x-PMMA ($x=0$, 5.0×10^{-6}, 3.0×10^{-5}, 5.0×10^{-5}, 3.0×10^{-4}, 4.0×10^{-4}, 1.0×10^{-3}, 4.0×10^{-3}, 1.0×10^{-2}, 2.0×10^{-2}, 4.0×10^{-2}, 6.0×10^{-2} and 8.0×10^{-2}) and the result is shown in Fig. 3. It can be seen that there is the lowest point on the curve in Fig. 3 for $^5D_0\rightarrow{}^7F_2$ transition of Eu^{3+} at the

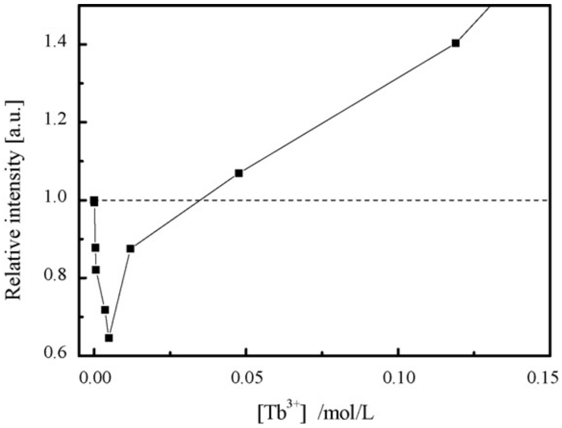

Fig. 3. Relationship between the relative photoluminescent intensity of $Eu_{0.0050}Tb_x$-PMMA and the content of $Tb(DBM)_3Phen$ under excitation at 365 nm. The relative intensity is the ratio of luminescence intensity at x to that at $x = 0$, which was integrated from 603 nm to 638 nm.

concentration of Tb^{3+} about 0.0048 mol/L, which is resulted from two competing factors: one is absorption of ligands of $Tb(DBM)_3Phen$, and another is sensitization from $Tb(DBM)_3$ Phen. Within lower concentration range of $Tb(DBM)_3Phen$, sensitization in the luminescence of $Eu(DBM)_3Phen$ did not occur because the distance between two kinds of complexes is too far from each other. However, small amount of $Tb(DBM)_3$ Phen still consumed part of exciting light. When concentration of $Tb(DBM)_3$ Phen was high, the content of Tb^{3+} is over 0.0048 mol/L, the second factor played a more important role and sensitization could be observed. Especially when the content of Tb^{3+} was more than 0.034 mol/L, the luminescence intensity of Eu^{3+} with $Tb^{3+}$was stronger than that of Eu^{3+} without Tb^{3+}, which resulted in enhancement of luminescence of Eu^{3+}. Obviously, relative concentration, which determines the average distance between two kinds of complexes, is a key factor during the enhancement because the enhancement is strongly dependent on inter-molecular energy transfer processes according to Forster [32] and Dexter's theories.

In order to further demonstrate this sensitization another series of scale-up films were fabricated with the composition of $Eu_xTb_{0.010}$-PMMA ($x = 0$, 5.0×10^{-3}, 8.0×10^{-3}, 9.0×10^{-3}, 0.013,0.020, 0.030,0.040 and 0.060), in which Tb^{3+} concentration was kept at 0.058 mol/L, which is above the critical concentration for sensitization. Within this concentration range emission of $^5D_1 \rightarrow {}^7F_1$ transition of Eu^{3+} at 535 nm and emission of $^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+} at 546 nm were observed under excitation of light at 365 nm as shown in Fig. 4. With increase of Eu^{3+} concentration the emission at 546 nm decreased and the emission at 535 nm increased gradually, showing inter-molecular energy transfer taken place and resulting in the sensitization of $Tb^{3+}$to Eu^{3+} as shown in Fig. 3. It is worth to point out that this result was obtained by exciting at 365 nm that is not the maximal excitation peak for $Tb(DBM)_3Phen$ as discussed above concerning intra-molecular energy transfer. This reveals that Eu^{3+} in the co-doped system diverts a large portion of the energy from the triplet state of DBM in $Tb(DBM)_3Phen$, which promoted the luminescence quenching of the Tb^{3+} and the luminescence enhancement of Eu^{3+}, although the luminescence is not strong under excitation at 365 nm.

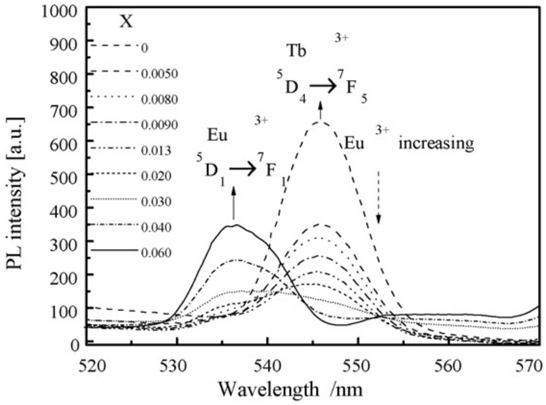

Fig. 4. Luminescence emission of Eu^{3+} at 535 nm and Tb^{3+} at 546 nm in $Eu_xTb_{0.010}$-PMMA under excitation at 365 nm using 3–3 nm excitation-emission slit pairs.

These change trends can be seen more clearly in Fig. 5, in which luminescence of two ions are opposed to each other and complementary to each other. Different from the emission of Eu^{3+} at 535 nm the emission at 612 nm for $^5D_0 \rightarrow {}^7F_2$ hypersensitive transition of Eu^{3+} shows a maximum at Eu^{3+}concentration of 0.35 mol/L under excitation at 365 nm as shown in Fig. 5. This is caused by the difference in lifetime of two excited states. It has been known that the lifetime for $^5D_0$ state is about 0.77 μs and the lifetime of $^5D_1$ is more short than this [30]. Under this circumstance, self-quenching would take place and result in decrease of luminescence at 612 nm when Eu^{3+} concentration is high enough. On the other hand, because short lifetime will have a high self-quenching concentration the emission for $^5D_1 \rightarrow {}^1F_1$ of Eu^{3+} at 535 nm increases with increase of Eu^{3+} concentration within the given concentration range as shown in Fig. 5. From the analysis above it is known that luminescence intensity of Eu^{3+} in Eu_xTb_y-PMMA samples is related with energy transfer process between the resonance energy levels of the respective

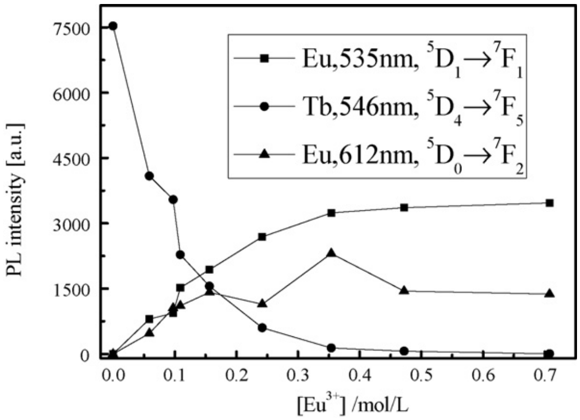

Fig. 5. Relationship between photoluminescent intensity of Eu^{3+} at 535 nm, Tb^{3+} at 546 nm and Eu^{3+} at 612 nm (using 1.5–1.5 nm excitation–emission slit pairs) and the content of $Tb(DBM)_3Phen$ in $Eu_xTb_{0.010}$-PMMA under excitation at 365 nm.

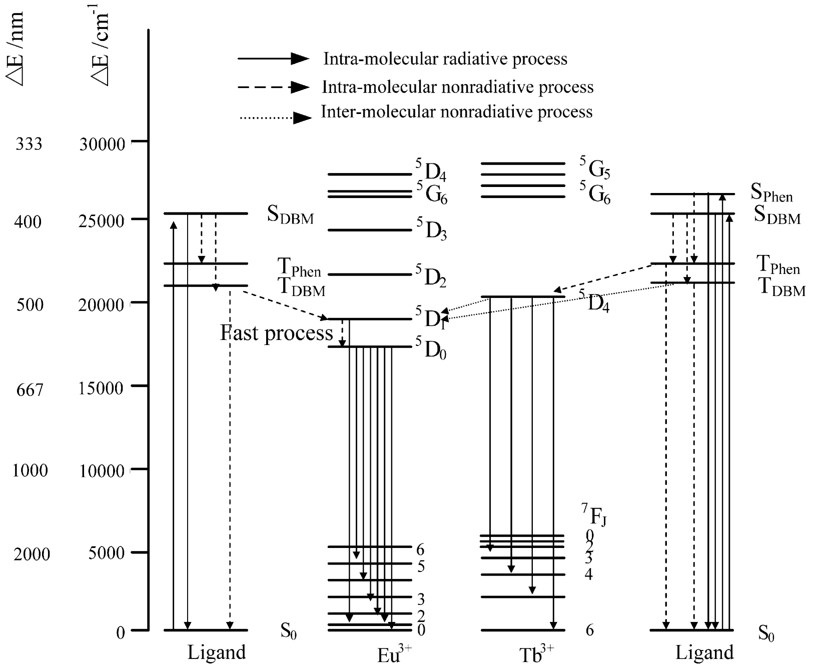

Fig. 6. Schematic energy decay pathways for relaxation and energy transfer process of Eu(DBM)$_3$Phen, Tb(DBM)$_3$Phen and Eu$_x$Tb$_y$-PMMA.

lanthanide ions as schematically shown as in Fig. 6, including both of intra-molecular and inter-molecular energy transfers.

3.3. *Quantitative model for luminescence enhancement of Eu$_x$Tb$_y$-PMMA*

Obviously, the luminescence enhancement in Eu$_x$Tb$_y$-PMMA is also strongly dependent on the distance between two kinds of complexes. According to the quenching sphere of action model [33,34], there exists:

$$\ln \frac{I_0}{I} = VN[\mathrm{Eu}^{3+}] \quad (1)$$

when taking $^5D_4 \to {}^7F_5$ (at 546 nm) and $^5D_1 \to {}^7F_1$ (at 535 nm) as the dominant group into consideration, where I_0 is the integrated intensity at 546 nm of the sample with $[\mathrm{Eu}^{3+}] = 0$, I is integrated intensity at 546 nm for the samples containing Eu^{3+} ions, V is the volume of the active sphere of quenching (in L), N is Avogadro's number, and [Eu^3+] is the concentration of Eu^{3+} ions in mol/L and when calculating the concentration of ions, the volume of the complex is neglected. In this way, subsequent treatment [Eu^{3+}] and [Tb^{3+}] presents each complex concentration, respectively.

According to Eq. (1), a plot of $\ln(I_0/I)$ versus [Eu^{3+}] yields NV, and V may be directly evaluated. The data in Fig. 4 were fitted by the least-square method and a linear line was obtained with $r = 0.998$ as shown as in Fig. 7. From Fig. 7 and Eq. (1), the volume of the active sphere of quenching V may be obtained as about $(1.824 \pm 0.044) \times 10^{-23}$ L, and the radius R of the quenching sphere can be calculated as about (1.633 ± 0.013)nm, which is consistent with the distance of dipole–dipole interaction [13,28,32].

In terms of this model, Eu$_x$Tb$_y$-PMMA sample can be represented as spheres shown in Fig. 8. When two complexes are within the sphere as shown as in Fig. 8(a), the sensitization would take place, otherwise, when two complexes are separated with a distance larger than (1.633 ± 0.013)nm as shown as in Fig. 8(b), which is out of the distance for the dipole-dipole interaction and no quenching and sensitization will happen. Using statistic average it is easy to obtain that each quenching sphere may have a Tb^{3+} and a Eu^{3+} when both of [Tb^{3+}] and [Eu^{3+}] are about 0.091 mol/L.

As mentioned above, it is clearly seen that adding Tb(DBM)$_3$Phen to Eu(DBM)$_3$Phen is an efficient method to enhance luminescence intensity of a co-doped system. Based on this realization, we can avoid the concentration quenching of Eu(DBM)$_3$Phen and enhance its luminescence by adding sensitization complexes. Adding less Eu(DBM)$_3$Phen can get brighter

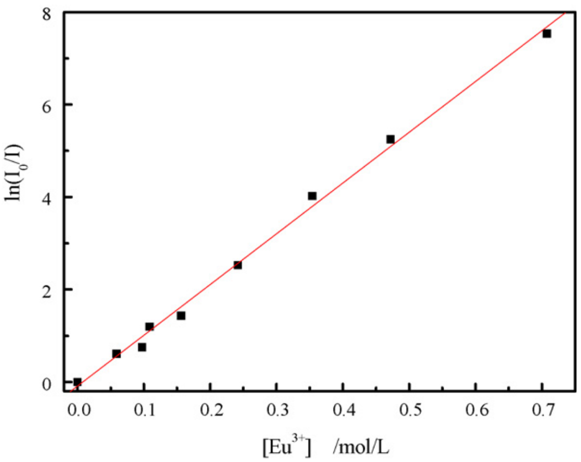

Fig. 7. Linear plot of $\ln(I_0/I)$ vs. [Eu^{3+}] for Eu$_x$Tb$_{0.010}$-PMMA.

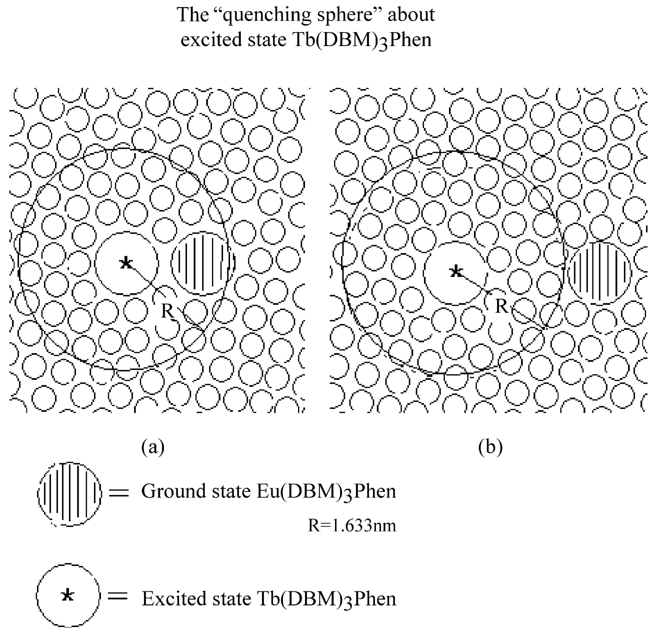

Fig. 8. Two-dimensional representation of the Perrin formulation of a "quenching sphere" containing $Tb(DBM)_3Phen$, $Eu(DBM)_3Phen$ and polymer chains. (a) $Tb(DBM)_3Phen$ and $Eu(DBM)_3Phen$ is close to each other and the distance of them is shorter than 1.633 nm. (b) $Tb(DBM)_3Phen$ and $Eu(DBM)_3Phen$ is far from each other and the distance of them is longer than 1.633 nm.

luminescence with the large quantities of $Tb(DBM)_3Phen$. Brighter polymer luminophor can be obtained, adding more than 0.034 mol/L $Tb(DBM)_3Phen$, when the concentration of $Eu(DBM)_3Phen$ is about 0.35 mol/L.

4. Conclusion

$Tb(DBM)_3Phen$ and $Eu(DBM)_3Phen$ were co-doped into PMMA matrix that is amorphous. Enhancement in luminescence of Eu^{3+} was found at 0.0048 mol/L of Tb^{3+} concentration in $Eu_{0.0050}$ Tb_x-PMMA sample. Over this concentration of Tb^{3+} luminescence of Eu^{3+} was found increasing with decrease of luminescence of Tb^{3+}. These phenomena revealed that there is inter-molecular energy transfer process in $Tb(DBM)_3Phen$ and $Eu(DBM)_3Phen$ co-doped polymers. Based on detailed analysis of these phenomena, a quenching spherical model was proposed in terms of Perrin formulation, from which an effective quenching radius was obtained as (1.633 ± 0.013)nm. Within such a distance dipole–dipole interaction could take place, resulting in inter-molecular energy transfer between two kinds of complexes.

Acknowledgements

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