Combinatorial method for the study of new co-fluorescence enhancement system

Hongfang Jiu a, Jianjun Ding b, Jun Bao b, Qijin Zhang a,∗, Chen Gao b

a Structure Research Laboratory and Department of Polymer Science and Engineering, University of Science and Technology of China, Road 96, East Campus, Hefei 230026, PR China
b National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230026, PR China

Received 7 November 2004; accepted 30 November 2004

Abstract

The new co-fluorescence enhancement system was found in polymer matrix and studied with a combinatorial approach based on Re(DBM)3 phen (Re3+: T b3+, L a3+, G d3+, Y 3+; dbm: dibenzoylmethane; phen: phenanthroline) and Sm3+ complex co-doped poly(methyl methacrylate)(PMMA). We have presents a new methodology for the rapid optimization of the luminescence conditions of thin-film sample in arrays of microwells. Two libraries were generated in order to study the effect of the species and content of enhancing ions on the luminescence enhancing efficiency, respectively. At the optimal content of 20 wt.% Sm(DBM)3 phen, the maximum sensitization efficiency of Tb(DBM)3 phen is about nine times. The intramolecular and intermolecular energy transfer processes in rare-earth complex-doped PMMA are discussed. The energy transfer processes make the co-fluorescence effect come true. Although, the methodology described here was implemented for optimization of co-fluorescence conditions, it is can be further implemented for a variety of applications in which optimization of parameters can be studied in situ using spectroscopic tool.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Co-fluorescence; Combinatorial method; Samarium complex-doped PMMA

1. Introduction

Rare-earth complexes such as europium and samarium are of both fundamental and technological interest because of their large stoke shifts, narrow emission bandwidths and long emission lifetimes. Due to these characteristics, they are suitable candidates for applications as light-emitting diode (LED) [1], laser materials [2], optical signal amplification [3] and fluoroimmunoassay [4,5].

One of the major activities in many studies has been the fluorescence enhancement of the lanthanides, since the lanthanides have low absorptivities and poor quantum yields [6]. Fluorescence enhancement has generally been achieved through ligand sensitization [7,8]. Another method to increase the fluorescence of the lanthanide complex is through the use of certain ions such as La3+, Gd3+, Tb3+ and Y3+. In the presence of these ions, the fluorescence of Tb3+, Eu3+ and Sm3+ in their respective complexes can be enhanced [9,10].

This type of fluorescence enhancement is actually an intrinsic fluorescence phenomenon referring as the “co-fluorescence” effect [11–13], which can be found in the co-precipitates, chelate suspensions and LB films [14–16].

As a polymer material, poly(methyl methacrylate) (PMMA) has attracted a lot of interest for its low optical absorption, simple synthesis and low cost. These characteristics make it suitable for host material of luminescent rare-earth complexes. Dibenzoylemethane (DBM) is a kind of high absorbing chelating reagent because of the existence of β-diketones. In rare-earth complexes, DBM can absorb the photon and transfer the energy to the central metal ion effectively and give rise to very strong luminescence [17].

In addition to that, DBM also shows excellent solubility in polymer host. In order to provide an insulating layer around...
the lanthanide complex and reduce the probability of radiationless energy transfer from the complex to the solvent, phen was incorporated as the synergistic agent [18].

Taking the above considerations, it is necessary to study the co-fluorescence phenomenon in Re(DBM)₃ phen (Re = Tb, La, Gd, Y) and Sm(DBM)₃ phen co-doped PMMA. It is well-known that in the co-fluorescence systems parameters such as the species and content of enhancing ions can significantly influence the fluorescence enhancing efficiency. Optimization of sensitization conditions are often very time-consuming, an issue that research on new luminescence measurement is carried out becomes important. In this paper, the combinatorial method, by which large collections of compounds are synthesized and screened in a materials library simultaneously for a particular physical or chemical property, is adopted. In the first round screen, a library with different kinds and contents of sensitization ion complexes was synthesized to determine the best sensitization ion complex. In the second round screen, another library with different complexes contents was synthesized to identify the best sensitization composition. Then six scale-up samples were synthesized to confirm the results from the combinatorial libraries.

2. Experimental

2.1. Material library preparation

Rare-earth complexes (Re(DBM)₃ phen, Re³⁺ = Sm³⁺, Tb³⁺, La³⁺, Gd³⁺, Y³⁺) were synthesized according to the procedure reported in literature [19]. The final products were recrystallized in acetone/petroleum ether (2:1). Poly(methyl methacrylate) (PMMA, Mₜ ≈ 350,000) 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 (0.1–2.5 µL). The diameter of the well is 1.5 mm. The as-deposited libraries were evaporated in air at room temperature.

2.2. Material library fluorescence characteristics

The novel instrument in Fig. 1 is an example of a multiple-parallel luminescence measurement apparatus that we have successfully used to measure the luminescence property and represents a valid alternative to single luminescence measurement apparatus [20]. After the solutions had dried, the material chip was illuminated with UV lamp and the emission spectra were detected using an SD2000 Ocean Optical fiber spectrometer. The spectrophotometer was equipped with a 200 µm slit, covering the spectral range from 250 to 800 nm. Emission light in each microwell of the material chip was collected when the common end of the fiber-optic probe was positioned on the top of the well at an angle 90° to the normal to the surface. The second arm of the probe was coupled to the portable spectrophotometer through an in-line optical filter holder.

For fluorescence analysis of Re/polymer, each microwell array was arranged on an X-Y translation stage and the common end of the fiber optical probe was held stationary to measure emission spectra. The size of the excitation beam was depending on the probe-microwell distance.

2.3. Scale-up sample preparation

To confirm the results of combinatorial method, 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 spectrophotometer.

3. Results and discussion

3.1. Sensitization ion species

Before beginning careful quantitative measurement of the fluorescence efficiencies of Re/polymer blends, we used the first material chip to quickly determine the sensitized effectiveness of the different enhancing ions (Tb³⁺, La³⁺, Gd³⁺, Y³⁺) complex for Sm³⁺ complex. The PMMA solution was pipetted into an array of 4 × 6 wells. Varying amounts of each complex were then pipetted across each row of the array. The PL intensity dependence of Sm³⁺ on each enhancing ion content in PMMA matrix under 365 nm UV excitation is illustrated in Fig. 2, in which the intensity is normalized with the intensity in the absence of enhancing ions. x is the defined as the weight ratio of sensitization ions complexes compared to PMMA in this paper.
As seen in Fig. 2, for Tb(DBM)₃phen at the same content, the luminescent intensity of Sm³⁺ at 648 nm increases as the content of various sensitization ions increasing and when 20 wt.%, the fluorescence intensity reaches the maximum value, a plateau is obtained when the Tb(DBM)₃phen content is greater than 20 wt.%; for Gd(DBM)₃phen and La(DBM)₃phen in the same content range, the luminescent intensity of Sm³⁺ at 648 nm increases with the increase of the content of Gd³⁺ and La³⁺ complex and reach a maximum at the Gd³⁺ and La³⁺ complex content of 20 wt.%, a further increase of the content of sensitization ions complex decreases the luminescent intensity; finally, the fluorescence intensity of Sm³⁺ decreases with the increase of the content of Y³⁺ complex. Among these sensitization ions, it is can be clearly seen that four ions are arranged in the order of their enhancement factors, terbium, gadolinium, lanthanum (R > 1), yttrium (R < 1) for Sm(DBM)₃phen system and that Tb³⁺ complex causes the highest sensitization effectiveness.

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 is. This is the same as the conclusion reported earlier by Ci and Lan [13] and Zhong et al. [16].

In the Ln–organic complexes, it is possible for the Ln³⁺ ions to form aggregates. Actually, the rare-earth complex stoichiometry of 1:3:1–2 (Ln/β-diketone:synergistic ligand) has been verified for co-fluorescence aggregates [14,21]. It has been reported that the co-fluorescence effect is caused only by the intermolecular energy transfer between the two chelate types [22]. Considering the Foster [23] 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 close approach or contact of donor to acceptor. For Sm(DBM)₃phen and Re(DBM)₃phen co-doped PMMA, the content of the enhancing ions in Re(DBM)₃phen doped PMMA is also high enough to create the aggregate particles inside which the efficient energy transfer is possible. The enhancing ions (Tb³⁺, La³⁺, Gd³⁺) used have not suitable excited 4f or 4d levels for the excited triplet levels of the DBM and the energy absorbed by its complex molecules can not be effectively dissipated through those energy levels but is transferred to the nearby molecules Sm(DBM)₃phen in the aggregated particles. Thus, the luminescence of Sm³⁺ is enhanced through an intermolecular energy transfer process. The detailed study of the mechanism is in process.

3.2. Sensitization ion concentration

To quantitatively determine the sensitized effectiveness of the Tb complex for Sm complex, a series of distinct content of Tb/Sm complex co-doped PMMA system were pipetted into the second material library. The relationships between the fluorescence intensity enhancement factors F of Sm³⁺, a factor of luminescence enhancement expressing the efficiency of energy transfer [13] and the Tb concentration in the second material chip are plotted in Fig. 3.

To confirm the results, individual scale-up films (20 nm thickness films on glass) were fabricated with the selected composition of Sm₀.₀₅:Tbₓ (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)₃phen is shown in Fig. 4. The tendency 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 a combinatorial method.

As seen from values of F, the lower content of Sm(DBM)₃phen exists in the film, the higher efficiency of luminescence enhancement (F=9) is. It indicates that the efficiency of energy transfer is dependent on the content of Sm(DBM)₃phen and Tb(DBM)₃phen in the sample. The dependence of luminescent intensity of Sm³⁺ on the content of Tb³⁺ is relevant both to the attractions between the lanthanide ions themselves and to the difference of the resonance energy levels of the respective lanthanide ions. [10] In the
Ln–organic complexes, it is possible for the Ln$^{3+}$ ions to form aggregates, regarded as multiplets, which appear as a result of dipole–dipole attractions between different quadruplets with asymmetric distribution of charges [24]. The attraction results in an enhanced electrostatic attraction between them [25]. This, in turn, could markedly increase the attractions between the lanthanide ions. Energy transfer between the lanthanide ions themselves is a nonradiative process, which partially contributes to the fluorescence enhancing of the Sm$^{3+}$ ions. Another factor that accounts for the fluorescence enhancing of Sm$^{3+}$ luminescence is the energy transfer between Sm$^{3+}$ and Tb$^{3+}$. As schematically shown in Fig. 5, the resonance energy level of Sm$^{3+}$ ($4\text{G}_{5/2}$) is lower than that of Tb$^{3+}$ ($5\text{D}_{4}$). It is possible that the presence of Sm$^{3+}$ in the mixed complex diverts a large portion of the energy from the $5\text{D}_{4}$ level of the Tb$^{3+}$, thus, promoting the luminescence enhancing of the Sm$^{3+}$, 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. 5 based on refs. [26,27].

4. Conclusion

The luminescent of rare-earth ions complexes (Re(DBM)$_3$phen, Re$^{3+}$ = Tb$^{3+}$, La$^{3+}$, Gd$^{3+}$, Y$^{3+}$) sensitized the Sm$^{3+}$ complex in PMMA matrix was found and studied using a combinatorial method. The luminescence of the Sm$^{3+}$ complex doped PMMA changed significantly with the species and the content of the enhancing ion. The first material library results show that the Tb$^{3+}$ complex has the highest enhancing efficiency among these enhancing ions. The second material library results demonstrate that the lower concentration of Sm(DBM)$_3$phen exists in the film, the higher efficiency of luminescence enhancement is ($F = 9$). The intramolecular energy transfer and intermolecular energy transfer processes in aggregates of Sm(DBM)$_3$phen and Re(DBM)$_3$phen co-doped PMMA films make the co-fluorescence effect come true. In conclusion, the results clearly illustrate that a multi-parallel approach is a valid possibility for luminescence measurement and represents a valid tool to rapidly optimize the luminescence condition.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 50025309 and No. 90201016), which the author gratefully acknowledges.

References


