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Combinatorial Study of Cofluorescence of Rare Earth Organic Complexes Doped in the Poly(Methyl Methacrylate) Matrix

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The luminescence enhancement effect of different kinds and contents of rare earth complexe ($RE(DBM)_3Phen$, $RE = Dy$, La, Gd, Sm, Y; DBM = dibenzoylmethane; $Phen$ = 1,10-phenanthroline) sensitized $Eu(DBM)_3Phen$ doped in poly(methyl methacrylate) (PMMA) matrix was investigated using the combinatorial method. The efficiency of the luminescence enhancement increases with a decrease in the weight percentage of the $Eu(DBM)_3Phen$ and an increase in the molecular weight of the PMMA in the systems. Among these sensitization ion complexes, $La(DBM)_3Phen$ shows the highest sensitization efficiency. At the optimal content of 5 wt % $Eu(DBM)_3Phen$ and 350 000 g/mol weight average molecular weight ($\overline{M}_w$) of PMMA, the maximum sensitization efficiency of $La(DBM)_3Phen$ is ∼20 times. We believe that the PMMA with high molecular weight enwraps the rare earth complexes and keeps the donors and acceptors close, which results in the effective intermolecular energy transfer and, consequently, the high sensitization efficiency.

Introduction

Luminescent rare earth organic complexes are of both fundamental and technical interest due to their characteristic luminescence properties, such as extremely sharp emission bands, long lifetime, and potential high internal quantum efficiency. Used as light-conversion materials, these complexes have been widely applied in a variety of areas, such as fluoroimmunoassays,[1,2] electroluminescence devices,[3,4] and polymer optical fibers.[5,6]

The luminescence of rare earth ions stems from the intra-4f transitions, which in principle are forbidden transitions, resulting in relatively low emission efficiency. An effective approach to increase the luminescent efficiency is to modify the complexes with different kinds of ligands that have broad and intense absorption bands[7,8] so that the absorbed photon energy has a large chance to transfer to the higher energy levels of rare earth ions. Another way is to mix the complexes with different sensitization ions.[9,10] It was reported that adding certain nonfluorescing lanthanide ions, such as La^{3+}, Gd^{3+}, Tb^{3+}, and Y^{3+}, could significantly enhance the photoluminescence of the chelates of Eu^{3+}, Tb^{3+}, and Sm^{3+}. This type of fluorescence enhancement is actually an intrinsic fluorescence phenomenon referred to as the "cofluorescence" effect[11−15] which can be found in coprecipitates, chelate suspensions, and LB films.[16−18]

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. Dibenzoylmethane (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.[19] In addition to that, DBM also shows excellent solubility in a polymer host.[20] To provide an insulating layer around the lanthanide complex and to reduce the probability of radiationless energy transfer from the complex to the solvent, Phen was incorporated as the synergistic agent.[21]

Under the above considerations, a systematical study of the cofluorescence effect of $RE(DBM)_3Phen$ ($RE = Dy$, La, Gd, Sm, Y) on the $Eu(DBM)_3Phen$ doped in PMMA is necessary to identify the best sensitization conditions. However, such a systematic search involves a lot of time-consuming synthesis and characterization efforts using the traditional one-at-a-time approach. 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. The purpose of this research is to screen "leads" for a polymer optical fiber application. In the first-round screen, a library with different kinds of sensitization ion complexes and contents was synthesized to determine the best sensitization ion complex. In the second-round screen, another library of different complex contents was synthesized

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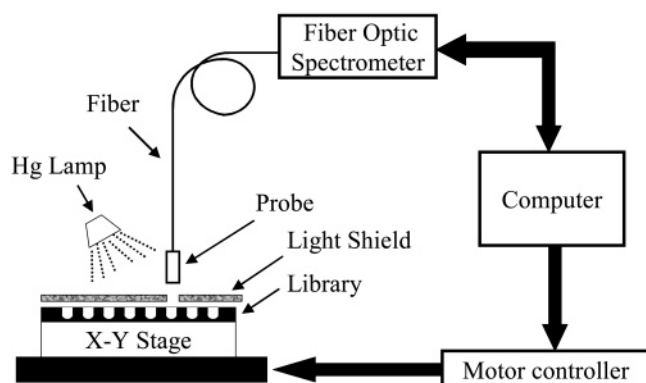
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Figure 1. Schematic diagram of the scanning spectroscopy system.

Figure 2. Photoluminescent photograph of the library of the five rare earth complexes sensitized Eu(DBM)$_3$Phen in a PMMA matrix under the illumination of 365-nm ultraviolet light. All of the subscripts in the Figure are defined as the weight ratio of the rare earth complexes to the PMMA unless other specified.

Figure 3. The PL intensity as a function of the sensitization ion content.

to identify the best sensitization composition. Then six scale-up samples were synthesized to confirm the results from the combinatorial libraries. Meanwhile, the effect of the PMMA molecular weight was also studied.

Experimental Section

Rare earth complexes (RE(DBM)$_3$Phen, RE = Eu, Dy, La, Gd, Sm, Y) were synthesized according to the procedure reported in the literature,[22] and the final products were recrystallized in acetone/petroleum ether (2:1).

The synthesized rare earth complexes (RE(DBM)$_3$Phen) and PMMA were dissolved in cyclopentanone solvent with a ratio of 5 g/L. The libraries were synthesized by dispensing the solutions into the microwells drilled on a fluorophlogopite substrate with different doses according to the library design using a microliter pipet ($\sim$0.1 to 2.5 μL), and the solutions were mixed there naturally. When the solvent in the as-prepared libraries was evaporated in air at room temperature, thin films were formed in the microwells.

The photoluminescence of the libraries was first examined using UV photography under 365-nm illumination, and then the emission spectra of the samples in the libraries were measured using a homemade scanning spectroscopy system, as shown in Figure 1. The system consists of a 4-W Hg lamp, a portable fiber spectrometer (Ocean Optics, Inc., model SD2000), and an X–Y stage. The spectrometer is equipped with a 25/200-μm slit, a 600-grooves/mm grating blazed at 400 nm, and a 2048-element linear silicon CCD-array detector. It covers the spectral range from 200 to 850 nm with efficiency >30%. The library was fixed on the moving table of the X–Y stage, and the emission spectra from the microwells were measured when the fiber-optic probe was focused on the bottom of the reactor. To avoid the interference between wells, a light shield was used. The whole measurement was controlled automatically using a computer running software developed in our group.

Results and Discussion

Figure 2 shows the photoluminescent (PL) photograph of the library with different kinds and contents of sensitization ion complexes that sensitized the Eu(DBM)$_3$Phen in the PMMA matrix under 365-nm UV excitation (all of the subscripts in the Figure are defined as the weight ratio of the rare earth complexes to PMMA unless other specified). The red PL intensity integrated from 603 to 638 nm as
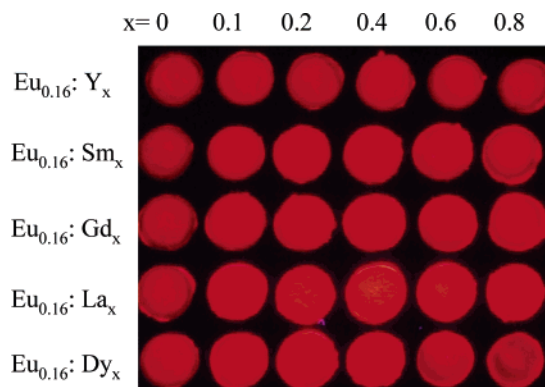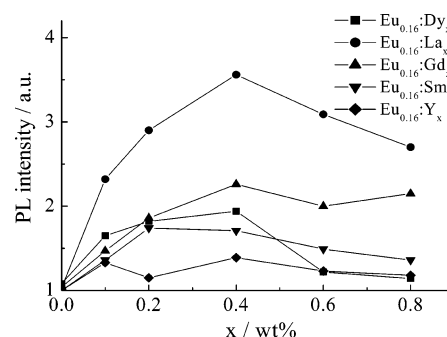
functions of the content of different sensitization ion complexes is presented in Figure 3. From the curves, we found that the luminescence intensity of PMMA–Eu-(DBM)$_3$Phen increases with the content of sensitization ion complexes and reaches a maximum, indicating an efficient energy transfer from sensitization ion complexes to Eu-(DBM)$_3$Phen in the PMMA matrix. A further increase in the content decreases the luminescence intensity, which is an indication of the concentration's quenching. Among these sensitization ions, La(DBM)$_3$Phen exhibits the highest sensitization efficiency.

The PL photograph of the library of La(DBM)$_3$Phen sensitized Eu(DBM)$_3$Phen in the PMMA matrix with different contents of La(DBM)$_3$Phen and Eu(DBM)$_3$Phen is shown in Figure 4, and the corresponding PL intensities are plotted in Figure 5. It can be seen that the luminescence intensity decreases with a decrease in the Eu(DBM)$_3$Phen content in the PMMA matrix, but the sensitization efficiency of La(DBM)$_3$Phen increases remarkably. At a Eu(DBM)$_3$Phen content of 5 wt %, the maximum sensitization efficiency of La(DBM)$_3$Phen is more than 20 times.

To confirm these results, six scale-up samples (20-nm thickness films on glass) with composition of Eu$_{0.05}$/La$_x$ (x = 0, 0.1, 0.2, 0.4, 0.6, and 0.8) were fabricated. Their PL intensity is shown in Figure 6. The tendency of the intensity as a function of La(DBM)$_3$Phen content is fairly consistent with that from the small samples in the library.

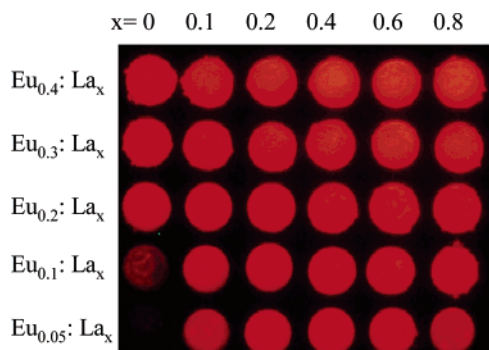The influence of the PMMA matrix on the luminescence properties was also investigated. A library with the same

Figure 4. Photoluminescence photograph of the library with different contents of La(DBM)$_3$Phen and Eu(DBM)$_3$Phen in the PMMA matrix under illumination of 365-nm ultraviolet light.
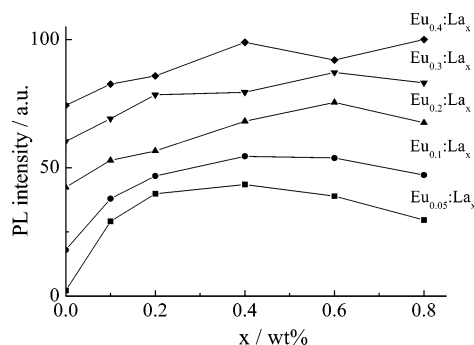

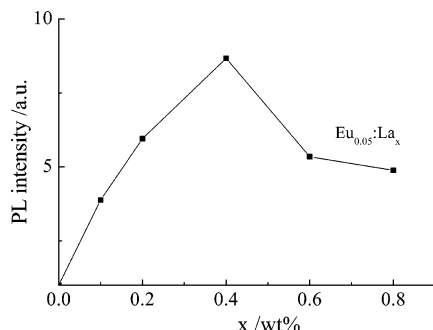**Figure 5.** PL intensity as a function of the content of La-(DBM)$_3$Phen and Eu(DBM)$_3$Phen.

Figure 6. PL intensity of the scaleup films as a function of the content of La(DBM)$_3$Phen.
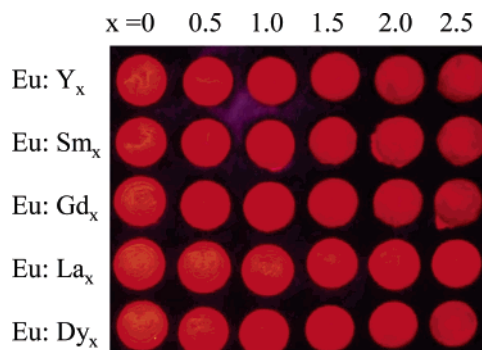

Figure 7. Photoluminescence photograph of the library of the five rare earth ion complexes sensitized Eu(DBM)$_3$Phen without the PMMA matrix under the illumination of 365-nm ultraviolet light. *x* is the weight ratio of the sensitization ion complexe to Eu-(DBM)$_3$Phen.
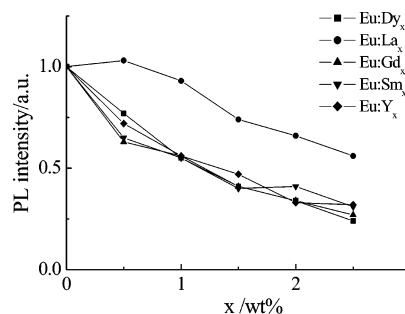

Figure 8. PL intensity as a function of the sensitization ion contents. *x* is defined as the weight ratio of the sensitization ion complexe to Eu(DBM)$_3$Phen.
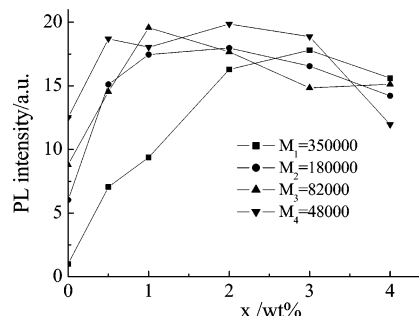

Figure 9. PL intensity as a function of the content of La-(DBM)$_3$Phen for different molecular weights of PMMA. *x* is the weight ratio of La(DBM)$_3$Phen in Eu(DBM)$_3$Phen/La(DBM)$_3$Phen/PMMA of *x*:0.25:5.

kinds and contents of sensitization ion complexes as the library shown in Figure 2, but without PMMA, was made. Figure 7 is the PL photograph of the library, and the corresponding PL intensity is presented in Figure 8. The curves in Figure 8 clearly show that there is almost no luminescence enhancement without the PMMA, and the addition of sensitization ion complexes results in only a monotone decrease of the PL intensity. We also studied the effect of PMMA molecular weight on the luminescence. As shown in Figure 9, the relationship between the PL intensity and the molecular weight of PMMA unambiguously reveals that the sensitization efficiency of La(DBM)$_3$Phen increases with an increase in the molecular weight of the PMMA matrix.

The characteristic emission of Eu(DBM)$_3$Phen in PMMA can be explained according to the Dexter's theory.[23] The excited singlet state of DBM ligand undergoes a nonradiative transition to the triplet state, whose energy level is 24 000cm^{-1}. This is close to the excited-state energy level of Eu^{3+} (17 300

cm^{-1} for the $^5D_0$ level), and therefore, an efficient intramolecular energy transfer can take place from the lowest triplet state of DBM to the coordinating Eu(DBM)$_3$Phen, which in turn undergoes a multiphoton relaxation and subsequent emission in the visible region.[24]

However, the intramolecular energy transfer cannot explain the intensity changes of Eu(DBM)$_3$Phen with the addition of RE(DBM)$_3$Phen (RE = Dy, La, Gd, Sm, Y) in the PMMA matrix. The above studies reveal that the enhancement of the fluorescence intensity of Eu(DBM)$_3$Phen by RE-(DBM)$_3$Phen can take place only in the presence of PMMA, and the enhancement is stronger in higher molecular weight PMMA. These results indicate that an effective energy transfer from donor (RE(DBM)$_3$Phen) to acceptor (Eu-(DBM)$_3$Phen) can be achieved only in the PMMA matrix. Liu[25] and Bermudez[26] suggested that there might exist a

chemical interaction between RE^{3+} and PMMA, and the evidence is that a new peak will be observed in the IR spectra. However, with our system, we have not found any new peaks or peak shift in the IR spectra (not shown), indicating that the energy could not transfer through this mechanism.

It is well-known that the efficiency of the intermolecular energy transfer is strongly dependent on the distance between the donor and acceptor.[27] Ci et al. studied the fluorescence of $Sm(TTA)_3Phen/Gd(TTA)_3Phen$ in Triton X-100 micelle. They suggested that a close approach or contact 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 $Sm(TTA)_3Phen$.[28] According to this point of view, it is suggested that for the present system, the PMMA molecule, due to its long chain, has the capability to enwrap the rare earth complexes and keeps the acceptors and donors close. In such a case, energy can be transferred efficiently from $RE(DBM)_3Phen$ to $Eu(DBM)_3Phen$, resulting in the enhancement of intrinsic Eu^{3+} emission of a $Eu(DBM)_3Phen$. Meanwhile, the PMMA can also protect and stabilize both the lowest triplet state of the donor and the lowest singlet state of the acceptor. This assumption can explain why the fluorescence enhancement takes place only in the presence of PMMA and the PL intensity increases with the increase of the molecular weight of PMMA: because the increase in the length of the chain would enhance the enwrapping capability of PMMA and subsequently the efficiency of the intermolecular energy transfer. However, further studies on the structure and sensitization mechanism are in progress.

Conclusion

In summary, the luminescence of the rare earth ion complex ($RE(DBM)_3Phen$, RE = Dy, La, Gd, Sm, Y) sensitized $Eu(DBM)_3Phen$ in PMMA matrix was systematically studied using the combinatorial method. The La-$(DBM)_3Phen$ shows the highest sensitization efficiency among these sensitization ion complexes. Decreasing the weight percentage of the $Eu(DBM)_3Phen$ or increasing the molecular weight of the PMMA in the systems enhances the luminescent intensity. At the content of 5 wt % Eu-$(DBM)_3Phen$ and 350000 g/mol weight average molecular weight ($\overline{M}_w$) of PMMA, the maximum sensitization efficiency of $La(DBM)_3Phen$ is ~20 times.

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