

High photoluminescence efficiency in polymer containing rare earth

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Three novel kinds of polymers containing rare earth europium have been synthesized and the integrating sphere technique was employed to measure the absolute photoluminescence (PL) efficiency. The PL efficiencies were found to be up to about 40%, which indicates the potential usage in organic light emitting devices (OLED). The energy transfer from ligand to Eu ions and the $^5D_0 \rightarrow ^7F_2$ transition of Eu^{3+} were analyzed under the PL process.

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Organic electroluminescent (EL) devices were firstly demonstrated in the 1960s, but great interest was not shown until 1987 that Tang and Vanslyke succeeded in developing an effective device using tris(8-hydroxyquinoline) aluminum (Alq_3) as the emitter^[1-4]. Since then, different kinds of organic dyes, chelate metal complex and polymers were synthesized to fabricate higher efficiency devices. Polymers containing rare earth have been used to fabricate the full-color devices because the very sharp emission lines are seen from intra-atomic transitions by rare earth ion. Europium^[5] and terbium^[6] ions have been used as emitting centers for narrow red and green light respectively in EL devices. The synthesis of high quantum yield polymers containing rare earth is a key work for successful EL devices. Therefore, the understanding of luminescence properties of organic materials is essential to direct tailor-made design and performance control of the device. One of the important parameters of material employed in EL devices is photoluminescence (PL) efficiency. EL efficiency of organic EL device can be estimated according to^[7]

$$\phi_{\text{EL}} = \chi \phi_{\text{PL}} \eta_r \eta_e, \quad (1)$$

where ϕ_{PL} is the PL efficiency of the material, η_e is the fraction of emitted photons that are coupled out of the device, and η_r is the fraction of injected charge carriers that form excitons, χ is the fraction of charge carrier recombinations in the host resulting in singlet excitons, which is presumed to be 25% from spin statistics for fluorescent material. EL is the result of radiative decay

of singlet excitons, so the theoretical extremum of the EL efficiency can be assumed as 25% of the PL efficiency. For this consideration, the measurement of PL efficiency is helpful to estimating the EL efficiency of device and to synthesizing new material by adding appropriate complex.

In this paper, we measured the PL efficiencies of three novel kinds of polymers (P1, P2, and P3) containing rare earth europium with integrating sphere technique. The molecular structures of three materials (with the purity of 51.5%) are shown in Fig. 1. Quartz glass was selected as the substrate which was cleaned by successive scrubbing in acetone. The films were prepared by spin-coating from their chloroform solutions at 5-mg/ml concentration. The thickness of the film was about 100 nm. All measurements were performed at room temperature.

Figure 2 shows the PL spectra of three samples recorded with a spectrophotometer (Hitachi 850). There is a very narrow band emission around 612 nm from the $^5D_0 \rightarrow ^7F_2$ transition of Eu^{3+} with the 260-nm excitation. It means that the PL of the three samples comes mainly from the emission of Eu^{3+} .

PL of organic materials is originated from the radiative transition of the singlet excitons. Nonradiative processes such as inter-chain energy transfer and quenching of excitons are other approaches to exciton decay, which will reduce the PL efficiency. The competition between radiative and nonradiative processes in the transition of excited molecules determines the efficiency of radiative transition, which can be given by

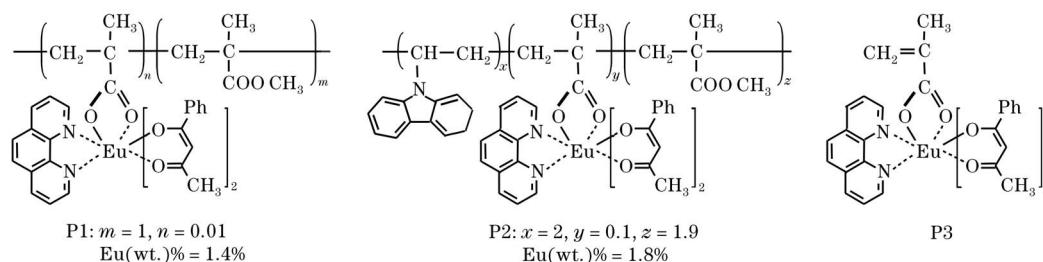


Fig. 1. Molecular structures of the materials. P1: PMMA-co-Eu(BA)₂(MAA)phen; P2: PVK-co-MMA-co-Eu(BA)₂(MAA)phen; P3: Oligo(Eu(BA)₂(MAA)phen).

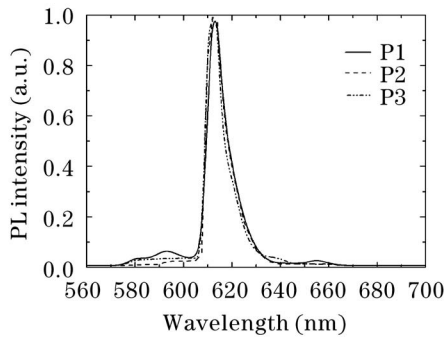


Fig. 2. Photoluminescence spectra of samples.

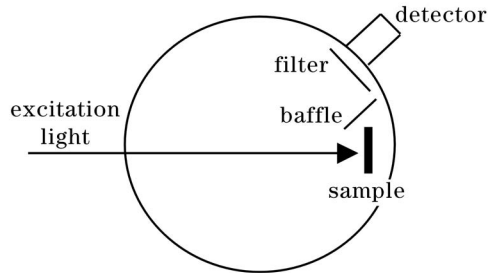


Fig. 3. Experimental setup for integrating sphere measurement.

$$\eta = \frac{1/\tau_R}{(1/\tau_R + 1/\tau_{NR})} = \left(1 + \frac{\tau_R}{\tau_{NR}}\right)^{-1}, \quad (2)$$

where τ_R and τ_{NR} are the lifetimes of radiative and non-radiative processes, respectively.

We measured the absolute PL quantum efficiencies of samples using integrating sphere technique^[8]. A 20-cm-diameter integrating sphere which was coated inside with diffusely reflecting materials MgO_2 was used to collect the emitted light. The flux received at an exit aperture is proportional to the total amount of light produced inside the sphere. Figure 3 shows the experimental setup of the measurement.

The samples on quartz substrates were mounted near the wall of the integrating sphere. The excitation light at 260 nm from deuterium lamp was normally incident onto the sample through a small aperture in the sphere wall, the typical excitation power is 0.07 mW with a beam diameter of about 2 mm. A suitable filter was placed in front of the detector to absorb the excitation light. A diffusely reflecting baffle was positioned between the sample and the exit aperture in order to prevent the exciting or emitting light from reaching the detector directly. The normal reflectance and transmittance of each sample were measured at the wavelength $\lambda = 612$ nm. Suppose R is the reflectance, T is the transmittance, and X_{light} is the signal measured with excitation light incident on the sphere with no sample and filter, X_{sample} and X_{sphere} are the signals measured with the sample and filter in place, with the excitation light on the sample and sphere wall, respectively. Then the PL efficiency neglecting the spectral variation of the system response can be expressed as

$$x = \frac{X_{sample} - (R + T)X_{sphere}}{(1 - R - T)X_{light}}, \quad (3)$$

and the calibration factor for spectral response is

$$y = \int \frac{S_{sphere}(\lambda)L(\lambda)G(\lambda)F(\lambda)}{S_{lamp}(\lambda)} d\lambda \times \left(\frac{S_{sphere}(\lambda_{ex})G(\lambda_{ex})}{S_{lamp}(\lambda_{ex})} \int L(\lambda) d\lambda \right)^{-1}, \quad (4)$$

where S_{lamp} is the spectrum of the lamp, S_{sphere} is the reflectance of the sphere surface, $L(\lambda)$ is the emission spectrum, $G(\lambda)$ is the quantum efficiency of the photodiode, $F(\lambda)$ is the transmission of the filter, and λ_{ex} is the excitation wavelength. The absolute PL efficiency is calculated to be

$$\eta = x/y. \quad (5)$$

The results obtained for the samples are listed in Table 1.

From Table 1, the PL efficiencies of three samples are about 40%, which means the energy transfer of PL is effective. The process of PL can be described as Fig. 4.

Absorption of excitation energy by the singlet ground state S_0 of the ligand BA (benzoylacetonate) results in an singlet excited state S_1 via transition of $\pi \rightarrow \pi^*$, the energy can be transferred by a nonradiative intersystem crossing to the ligand triplet T_1 , then through the nonradiative process to the vibration energy level 5D_0 of Eu^{3+} ion, and finally it forms the radiative transition back to 7F_2 , which leads to the Eu^{3+} characteristic fluorescence at $\lambda = 612$ nm.

In conclusion, the absolute PL quantum efficiencies of three novel kinds of polymers which containing rare earth metal europium were measured. It was found that the three materials have PL spectra with Eu^{3+} characteristic emission and the PL efficiencies are about 40% under the 260-nm excitation by the energy transfer from ligand BA to Eu^{3+} ion.

Table 1. PL Efficiencies and Errors of the Materials

Material	PL Efficiency (%)	Error (%)
P1	44.16	± 2
P2	40.38	± 2
P3	40.17	± 2

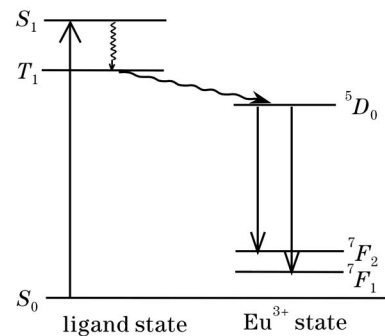


Fig. 4. Energy level diagram for the system energy transfer.

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