Absolute photoluminescence quantum yield enhancement of poly(2-methoxy 5-[2’-ethylhexyloxy]-p-phenylenevinylene)

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In the last 15 years the fast growing field of organic light emitting diodes (OLEDs) has led to the synthesis of numerous new luminescent polymers. An important class of these polymers consists of poly(p-phenylenevinylene) (PPV) and its derivatives such as poly(2-methoxy 5-[2’-ethylhexyloxy]-p-phenylenevinylene) (MEH-PPV) (Fig. 1). Their stability, solution processability, and electrical and optical properties have led to their investigation for use in a wide variety of applications. A fundamental understanding of the excited state processes in these quasi-one-dimensional materials is a key component in the optimization and development of new and more efficient OLEDs.

In this letter a twofold absolute photoluminescence (PL) quantum yield (PLQY) enhancement of MEH-PPV is demonstrated by simple preparation of films where the polymer is blended with the small organic molecule 7,8,10-triphenylfluoranthenone (3PF). The photophysical properties of this particular energy transfer process was carried out using steady state absorption/luminescence spectroscopy and optically detected magnetic resonance techniques. The enhanced PLQY is attributed to direct sensitization of the intrachain emitting state of MEH-PPV by energy transfer from 3PF. © 2006 American Institute of Physics.

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In this letter a twofold absolute photoluminescence (PL) quantum yield (PLQY) enhancement of MEH-PPV is demonstrated by simple preparation of films where the polymer is blended with the small organic molecule 7,8,10-triphenylfluoranthenone (3PF). Figure 1 shows the normalized absorption and emission spectra of pristine MEH-PPV and the blended films excited between 3PF and MEH-PPV. Figure 3 shows the emission spectra of pristine MEH-PPV and the blended films excited at 375 and 500 nm, where 3PF and MEH-PPV, respectively, preferentially absorb the incident light. Due to the good overlap between the 3PF emission and MEH-PPV absorption (Fig. 2) and the potentially close contact between the dopant and the polymer in the solid film, the energy transfer process is very efficient for this system. In fact, when exciting at 375 nm, where 95% of the incident light is absorbed by 3PF only, the emission is due only to MEH-PPV, whereas the strong solid state fluorescence of 3PF is totally quenched (Fig. 3).

FIG. 1. Structural formulas of MEH-PPV and 3PF.
An interesting feature emerges when comparing the shapes of the emission bands of the pristine and blended materials. The slight increase in vibronic structure and the width decrease suggest that in the blended films the polymer chains interact more weakly than in the pristine films. This effect can be attributed to 3PF molecules that intercalate between adjacent polymer chains, reducing intermolecular interactions and inhibiting the formation of interchain excitations. As noted elsewhere, these interchain species are characterized by an extended delocalization of the electronic wave function among two or more chains that often give rise to a decrease in vibrational resolution and an increase in the bandwidth of the emission. In comparing the absolute PLQY of the blends with that of the pristine material, two important and unusual photophysical phenomena were found: (i) an enhancement of the PLQY in the blended films and (ii) a much higher PLQY when exciting the 3PF at 365 nm than when exciting the MEH-PPV band at 488 nm.

To the best of our knowledge the few examples of efficiency enhancement reported in the literature are all related to the electroluminescence quantum efficiency in blended polymer light emitting diodes. In these cases the phenomenon is mainly attributed to changes in the film morphology induced by the interactions between the two materials that form the blend.

The phenomenon that we report in this letter is related to the change in the PLQY of the material and not to changes in the devices’ efficiency, thus differing from the previous papers for reasons described below. The PLQY enhancement of the blended film (PLQY=9%) relative to that of the pristine material (PLQY=7.5%), when both are excited at 488 nm, is due to the presence of 3PF. The latter prevents the formation of low fluorescence interchain species. The dramatic enhancement in the PLQY of the blended films excited at 365 nm (PLQY=18%) is, to our knowledge, the first observation of this phenomenon; it is suspected to be due to direct sensitization from 3PF to the intrachain MEH-PPV excitation.

Theoretically, in a simple dyad system, where only one acceptor’s excited state has the right energy to be involved in the energy transfer process, this phenomenon should not be observed, even if the energy transfer efficiency is η=1. In fact, when the energy transfer involves the same acceptor’s excited state that can be populated by direct absorption of light, the PLQY of the system is the product of the efficiencies of energy transfer and radiative emission, so it can only be, at best, the same PLQY obtained when exciting the fluorophore directly. A different scenario, however, can occur when the acceptor’s emitting state is not the one that is directly populated by absorption. In this case direct sensitization on this emitting excited state (process KD*A* in Fig. 4) avoids possible internal relaxation from the upper state to the ground state (process KX*A), resulting in a strong enhancement of the overall PLQY. To explain the unusual behavior we found for the blended film excited at the 3PF absorption band we propose a kinetic scheme where the donor (D) is the 3PF molecule and the acceptor (A) is the MEH-PPV polymer. Considering the shape comparison between emission bands of pristine and blended films, it is reasonable to conclude that the MEH-PPV chains in the blended films are more separated than those in the pristine material. As a result, the equilibrium between the strongly emitting intrachain excited states and the weakly emitting interchain excited states (invoked to explain the photophysical properties of PPV derivatives) is eliminated.

Irradiating the blended films at 365 nm, the 3PF excited state is mainly populated and two different paths are possible.
possible: energy transfer to one of the excited states centered on MEH-PPV (X\(^\ast\), A\(^\ast\)) or normal radiative and nonradiative decays from the excited 3PF (D\(^\ast\)) state to the ground state. As previously mentioned, no 3PF luminescence was observed in the blended films, indicating that the sensitization process is highly efficient. This unusual behavior can be explained by considering that through sensitization the excited state A\(^\ast\) is populated directly (process K\(_{D\ast A\ast}^\ast\)), without passing through X\(^\ast\) and thus not losing in this way the fraction of the excited states that decays nonradiatively to the ground state through the process K\(_{X\ast A\ast}^\ast\). This more efficient sensitization mechanism is supported by the PL excitation spectrum, which is shown in Fig. 5. In fact, with a film that absorbs the same quantity of light in the PPV band as in the 3PF band, the excitation spectrum is more intense in the 3PF absorption band than in the PPV. This proves that the number of emitted photons resulting from absorption by 3PF is higher than that band than in the PPV. This proves that the number of emitted photons resulting from absorption by 3PF is higher than that.

In conclusion, we have demonstrated that blending of MEH-PPV with 3PF can result in a twofold increase in the PLQY of MEH-PPV, without a noticeable change in its emission color. Thus, the efficiency of solution-processed MEH-PPV-based OLEDs can be improved by doping the MEH-PPV with 3PF. We concluded that this enhanced PLQY is due to direct sensitization of the intrachain emitting state in MEH-PPV by energy transfer from 3PF.

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