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Energy Transfer in a Blend of Electroluminescent Conjugated Polymers

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The energy transfer in a blend of electroluminescent conjugated polymers, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and conjugated−nonconjugated multiblock copolymers (CNMBC), was investigated. Energy transfer from CNMBC to MEH-PPV leads to the enhanced emission of MEH-PPV. Fluorescence decays also support this energy-transfer process, which is faster than radiative and nonradiative decays. PL and EL quantum efficiencies of the blended polymer were enhanced as the relative content of CNMBC was increased, and surprisingly, 500 times improved EL efficiency was observed for some blend ratios. These results provide further insight into the photophysics of conjugated polymers and the improvement of the electroluminescence quantum efficiency using the blended polymer systems.

Introduction

Conjugated polymers have attracted much research interest in science and technology in the past few decades as semiconductors and electroactive materials for diverse applications such as batteries, molecular electronic devices, and light-emitting diodes (LEDs), etc.[1−7] Especially, the electroluminescence has emerged as a promising application of polymeric LEDs in semiconducting polymers.[4−7] Thus the photophysics and photochemistry of conjugated polymers have been investigated in many research groups because they can provide a synthetic approach to a deeper understanding of the electroluminescence of conjugated polymers.[8−11]

Poly(1,4-phenylenevinylene) (PPV) and its derivatives are promising new materials for polymeric LEDs because of their good physical, chemical and optical properties compared with other conjugated polymers.[4−7] Substitution on the phenylene ring of the monomer with different types of substituents shows a significant difference in the electronic structure of the corresponding polymers and affects the electrical properties of the polymer, and thus the color tuning of the electroluminescence is also feasible.[12−14]

Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) has been a subject of intense investigation because it can be dissolved in many organic solvents which allows MEH-PPV to be easily processed into various types.[12,15] It is well-known that this polymer shows yellowish-red light when it is processed into electroluminescence devices, and the different quantum efficiencies were obtained by changing the work function of the electrode.[16,17] Recently, conjugated−nonconjugated multiblock copolymers (CNMBC) were reported for blue-light-emitting diodes, which can be synthesized by using a Wittig reaction between the appropriate aldehyde and triphenylphosphonium halide.[18−21] They can be dissolved in various organic solvents and thus effectively blended with MEH-PPV.

Previously, we reported the electroluminescence of the blended polymer system of MEH-PPV and conjugated−nonconjugated multiblock copolymer, poly[1,3-propanedioxy-1,4-phenylene-1,2-ethenylene(2,5-bis(trimethylsilyl)-1,4-phenylene)-1,2-ethenylene-1,4-phenylene] (DSiPV), whose synthesis was reported by our group.[20,22] The electroluminescence quantum efficiency of this

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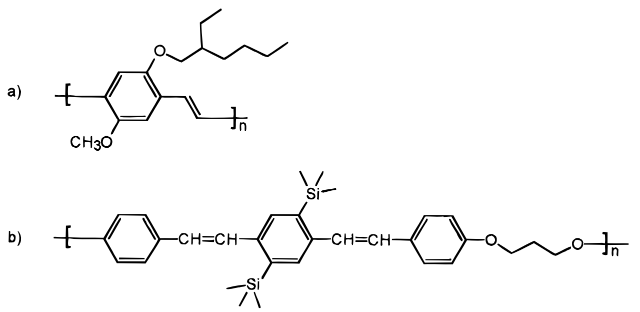

Figure 1. Structures of (a) MEH-PPV and (b) DSiPV.

blended polymer system can be improved as high as 2 orders of magnitude. In this report, we present the photochemical studies of these blended polymers with various weight fractions, which were investigated by the steady-state and time-resolved fluorescence spectroscopies. The energy-transfer process from DSiPV to MEH-PPV was observed, and thus the emission of MEH-PPV was exclusively observed when the blended polymer film was photoexcited by light whose energy was corresponding to the absorption of DSiPV. Moreover, the relative PL quantum efficiency increased as the weight ratio of DSiPV in the blended polymer increased.

Experimental Section

MEH-PPV and DSiPV were synthesized according to the previously reported methods,[22,23] and their structures are shown in Figure 1. These polymers are soluble in common organic solvents such as methylene chloride, tetrahydrofuran (THF), and 1,2-dichloroethane, etc. Both polymers were dissolved in 1,2-dichloroethane changing their weight ratios and spin-coated on a fused silica. AFM (atomic force microscopy) and SEM images showed no indication of phase separation or layer formation due to the immiscibility of two polymers. The optical density of the polymer coating was controlled by the spinning rate. All the photophysical measurements were performed at room temperature. The absorption spectra of the coated films were recorded by a Shimadzu UV-3100S spectrophotometer. Steady-state PL spectra of the films were taken by pumping with the third-harmonic output (355 nm) from a Q-switched Nd:YAG laser of 8 ns pulse duration and 488 nm cw from argon ion laser. The fluorescence signal was dispersed by a monochromator, and detected by using a Boxcar averager and a photon counter, respectively. We measured the relative PL quantum efficiency by comparing the integration of the emission spectrum of the blended polymer samples with that of MEH-PPV under the identical experimental condition. The solution PL spectra of the blended polymers were also obtained using a Perkin-Elmer LS-50 luminescence spectrometer. All of the EL measurements were performed according to the previously reported methods.[17,22] EL devices were composed of aluminum rectifying contact on the polymers which have been spin-cast onto ITO glass as a hole-injecting contact. The electron-injecting aluminum contact was deposited by vacuum evaporation at pressures below 10^{-6} Torr.

Fluorescence decay was recorded by the time-correlated single-photon counting method. The light source was a cavity-dumped dye laser synchronously pumped by a mode-locked argon ion laser. The cavity-dumped dye laser has 1 ps pulse width and the average power of ca. 50 mW at a 3.8 MHz dumping rate. It was tunable over the range 560−620 nm using rhodamine 6G for a gain dye and DODCI for a saturable absorber. The dye laser pulse was frequency-doubled by a β-BBO crystal (290 nm) to excite the samples. The fluorescence decay profiles were collected at the wavelength of interest using a microchannel plate PMT (Hamamatsu R2809U) and then fit to exponential decay functions using the previously described deconvolution technique to obtain a best fit. This allows a time resolution of about 20 ps.[24]

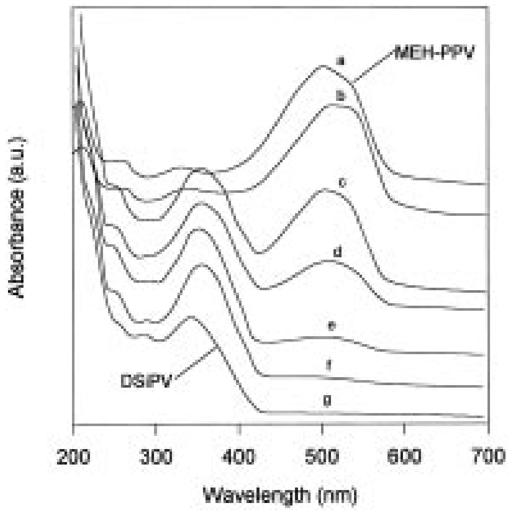

Figure 2. Optical absorption spectra of (a) MEH-PPV, (b) 9:1, (c) 6:4, (d) 3:7, (e) 1:9, (f) 1:15 (MEH-PPV:DSiPV) blended polymers, and (g) DSiPV thin films.

Results and Discussion

Figure 2 shows the absorption spectra of DSiPV, MEH-PPV, and the blended polymers with various weight fractions. The broad absorption resulted from MEH-PPV appeared around 420−580 nm, which is due to $\pi-\pi^*$ transitions of polyconjugated systems. DSiPV film showed a broad absorption, which is also attributable to $\pi-\pi^*$ transitions, around 300−420 nm. Blended polymer films showed the absorption peaks corresponding to both MEH-PPV and DSiPV films, and their intensities were varied depending on the weight fractions of the two polymers.

The emission spectra of the thin film polymers, which were normalized by the optical density at the excitation wavelength (355 nm), are shown in Figure 3. The emission of the DSiPV film appeared in the range 400−550 nm (spectrum f in Figure 3), whereas that of the MEH-PPV film was weakly observed in the range 530−650 nm (spectrum a in Figure 3). Interestingly, when the blended polymers were excited by 355 nm pulses, they showed strong emissions at about 560 nm which corresponds to yellowish-red light of MEH-PPV emission, whereas DSiPV emission in the blue region was weakly or not observed depending on its weight fraction. These emissions are much stronger than that of MEH-PPV homopolymer, and as the relative weight of DSiPV to MEH-PPV was increased, the emission intensities of the blended polymer films were increased. These results suggest that the energy-transfer process from the photoexcited DSiPV to MEH-PPV results in an enhancement of the yellowish-red emission originated from MEH-PPV. This energy-transfer process is probably more efficient than the fluorescence decay of DSiPV. Above the optimum ratio between MEH-PPV

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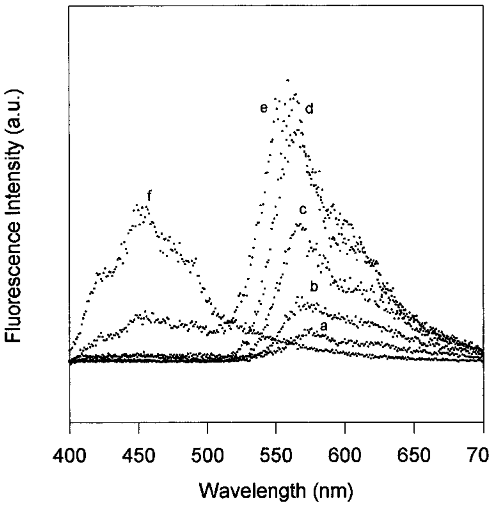

Figure 3. Photoluminescence spectra of (a) MEH-PPV, (b) 6:4, (c) 3:7, (d) 1:9, (e) 1:15 (MEH-PPV:DSiPV) blended polymers, and (f) DSiPV thin films. All PL spectra were recorded with an excitation at 355 nm.

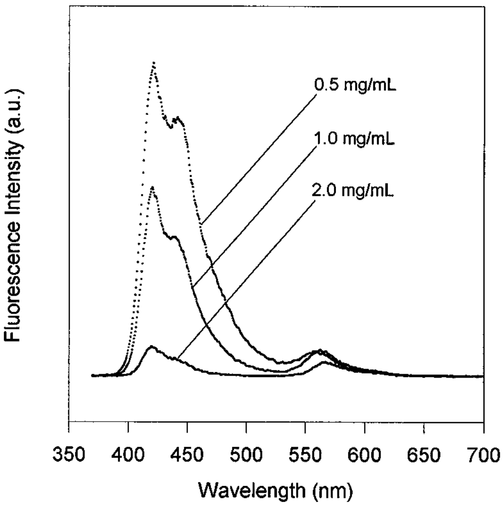

Figure 4. Photoluminescence spectra of 6:4 (MEH-PPV: DSiPV) blended polymer solution in 1,2-dichloroethane. Their concentrations are 2.0, 1.0, and 0.5 mg/mL.

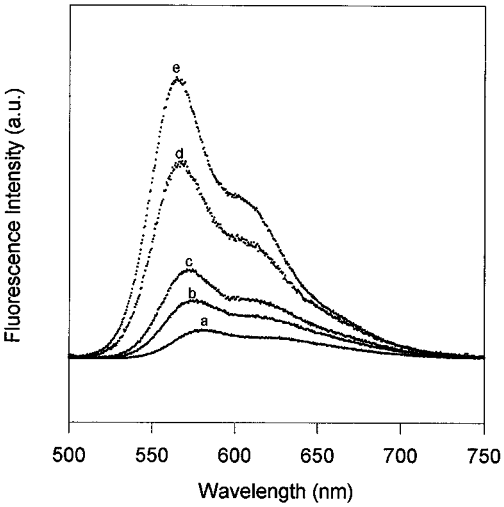

Figure 5. Photoluminescence spectra of (a) MEH-PPV, (b) 6:4, (c) 3:7, (d) 1:9, and (e) 1:15 (MEH-PPV:DSiPV) blended polymer thin films. All PL spectra were recorded with an excitation at 488 nm.

and DSiPV (spectrum e in Figure 3), the energy transfer becomes saturated, which results in the appearance of DSiPV emission in the blue region.

To obtain useful structural information from energy transfer, the measured efficiency must be related to the distance R between the two chromophores. According to Forster theory,[25,26] the energy transfer rate is

$$k = (1/\tau)(R_0/R)^6$$

where τ is the fluorescence lifetime of the donor in the absence of the acceptor. The inverse sixth power comes from the square of the dipole−dipole coupling, which depends on R^{-3}. R_0 is called the characteristic transfer distance, which is related to the spectral overlap between donor emission and acceptor absorption, and a complex geometric factor. The spectral overlap between DSiPV emission in the 400−550 nm region and MEH-PPV absorption in 420−580 nm region is large enough for the efficient energy transfer.

We also recorded the solution PL spectra (Figure 4) of the 6:4 (MEH-PPV:DSiPV) blended polymer at various concentrations to confirm the energy transfer between the two polymers. Generally, since the energy transfer rate is inversely proportional to the sixth power of the intermolecular distance, the energy transfer in solution is hardly observed. We observed much weaker emission from MEH-PPV in solution relative to that in the solid state. Moreover, as the concentration of the blended polymer solution is decreased, the DSiPV emission is strongly increased, whereas the emission from MEH-PPV is nearly unchanged and weak. These results indicate that the energy transfer from DSiPV to MEH-PPV does not occur in solution.

We recorded the PL spectra (Figure 5) of the blended polymer films with an excitation of 488 nm cw to examine the blending ratio dependence on the MEH-PPV emission intensity. MEH-PPV strongly absorbs the light at 488 nm, but DSiPV does not (Figure 2). The emission profile is very similar to the previously reported one.[15] It has been also reported that the emission intensity is enhanced as the emitting chromophore is diluted by other inert polymers in solid state.[27] The emission intensity was increased as MEH-PPV was diluted by DSiPV, which is consistent with the previous results.[27,28] It can be explained by the fact that the nonradiative decays, especially intermolecular quenching, are reduced by the dilution, which was also observed when the blended polymers were excited by 355 nm pulses. Therefore, we can conclude that the radiative decay of MEH-PPV through energy transfer and internal excitation is increased as MEH-PPV is diluted. This can be confirmed by the fluorescence decay results.

Figure 6 shows the picosecond time-resolved fluorescence decay profiles of MEH-PPV and the blended polymers (Figure 6A), and DSiPV and 1:15 (MEH-PPV: DSiPV) blended polymer (Figure 6B), pumped by 290 nm pulses at room temperature. The decay dynamics were monitored at 560 nm which corresponds to the MEH-PPV emission. The best fit was obtained using

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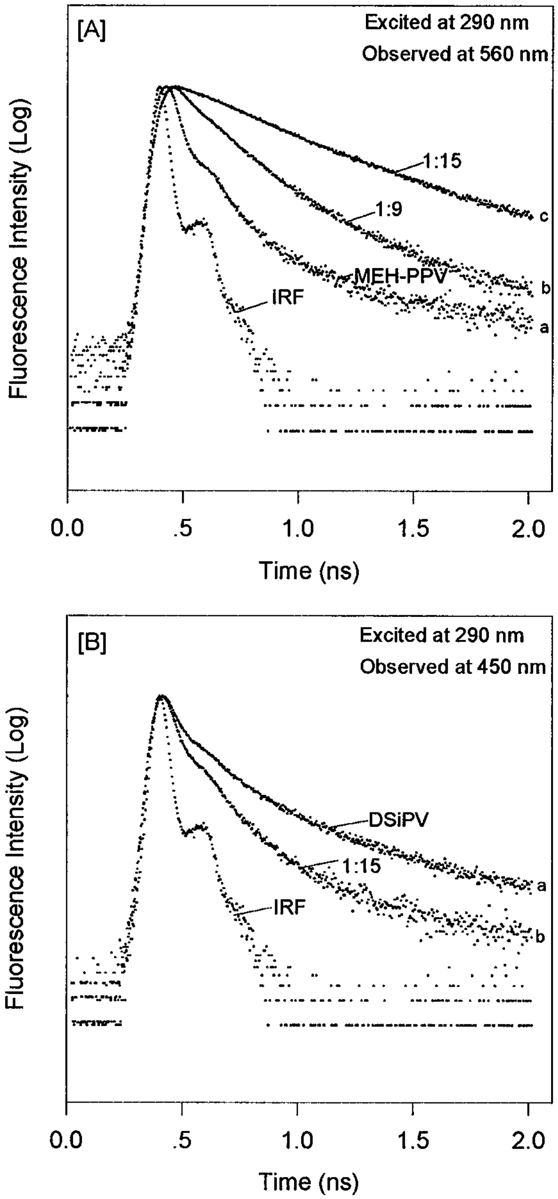

Figure 6. (A) Time-resolved PL decays of (a) MEH-PPV, (b) 1:9, and (c) 1:15 (MEH-PPV:DSiPV) blended polymer thin films observed at 560 nm. (B) Time-resolved PL decays of (a) DSiPV and (b) 1:15 (MEH-PPV:DSiPV) blended polymer thin films observed at 450 nm. The instrumental response function (IRF) of TCSPC is shown in the short time region.

two lifetime components of 20 and 100 ps for MEH-PPV and three lifetime components of 20 ps rise and the other two decay terms for the blended polymers. The two decay lifetimes were in the ranges of 50 and 200 ps for 1:9 weight ratio of MEH-PPV and DSiPV blended polymer and 200 and 500 ps for the 1:15 blended polymer, respectively. The amplitude of the rise component was increased as the weight fraction of DSiPV was increased. This behavior can be explained in terms of the enhanced energy transfer between the two polymers and the reduced intermolecular quenching as the DSiPV weight ratio is increased, which results in an increase in the emission intensity. The fluorescence decays were also monitored at 450 nm which corresponds to the DSiPV emission (Figure 6B). The 1:15 (MEH-PPV:DSiPV) blended polymer shows a faster PL decay than DSiPV due to the energy transfer in the blended polymer. The best fit was acquired by using 30 and 100 ps lifetimes of biexponential decays with different amplitude ratios for both polymers. The short decay may be contributed by the intrinsic decay and energy-transfer process, and consequently the amplitude of the short decay was increased in the blended polymer. To summarize the above explanation, the schematic diagram of kinetic pathways for deactivation of excited donor, DSiPV, through the energy transfer to MEH-PPV is presented in Figure 7.

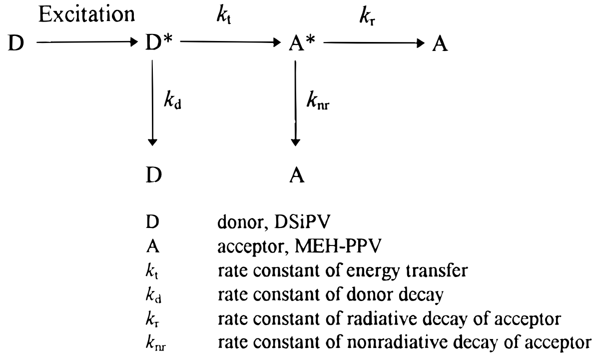

Figure 7. Schematic diagram for luminescence dynamics in our blended polymer system

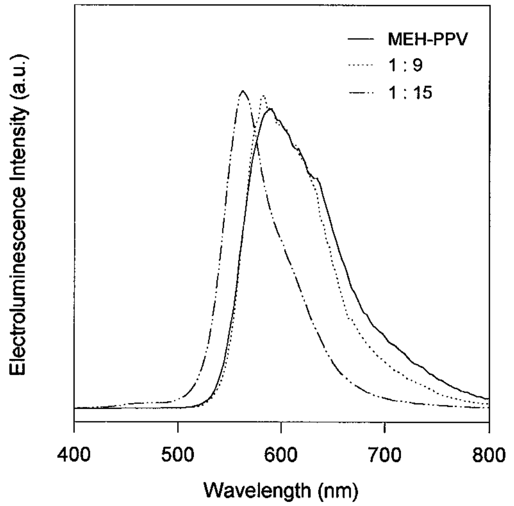

Figure 8. Electroluminescence spectra of MEH-PPV, 1:9, and 1:15 (MEH-PPV:DSiPV) blended polymers.

Figure 8 shows the electroluminescence spectra of MEH-PPV and blended polymers. We have found good device-to-device reproducibility. The emission peak of MEH-PPV occurs at around 600 nm and those of the blended polymers range from 560 to 580 nm depending on blending ratios, whereas the emission of DSiPV did not appear. The EL spectra of the blended polymers are similar to the PL spectra of the same blended polymers, which indicates that the same excitation processes are involved in both cases. The blue-shift of the blended polymers probably results from the chain conformation or aggregation of MEH-PPV in DSiPV.[29]

The relative quantum efficiencies of MEH-PPV and blended polymer devices are listed in Table 1. The relative PL and EL quantum efficiencies of blended polymers increase with increasing DSiPV content, and surprisingly the EL quantum efficiency of 1:15 (MEH-PPV:DSiPV) blended polymer is about 500 times higher than that of MEH-PPV. The previous reports showed

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Table 1. Photoluminescence and Electroluminescence Quantum Efficiencies of MEH-PPV, DSiPV, and Blended Polymers

	relative PL quantum efficiency			
polymers	excited by 355 nm pulses	excited by 488 nm cw	operation electric field (10^8 V/m)	relative EL quantum efficiency
MEH-PPV	1	1	0.52	1
9:1[a]		1.2	1.1	2.0
6:4[a]	1.6	2.0	1.7	11
3:7[a]	3.1	2.8	2.1	19
1:9[a]	5.0	5.7	2.6	17
1:15[a]	7.0	7.6	4.4	480
DSiPV	3.8		4.5	44

[a] The ratios are the weight ratios between MEH-PPV and DSiPV.

that the absolute EL efficiency of MEH-PPV under the same electrode configuration as our experimental conditions was about 8 × 10^{-3}%.[17] So we could deduce that the enhanced EL efficiency of the 1:15 blended polymer would be about 4.0%. Similar results were also reported by Yu et al. in the blended polymer of MEH-PPV and poly(3-hexylthiophene) (PHT).[30] Energy transfer or charge transfer also exists in MEH-PPV and PHT, and several explanations are possible to understand the enhancement of EL quantum efficiency in this type of blended polymer system. But the detailed mechanism about the enhancement of EL quantum efficiency was not fully understood, and more information on the electronic structure of DSiPV and MEH-PPV is necessary for understanding the behavior of these polymeric LED devices. Anyway, the blended polymer system in which the energy transfer is possible, can be a candidate for a high-efficiency electroluminescence device.

Conclusions

These preliminary observations of the photophysics of the blended polymers, consisting of DSiPV and MEH-PPV, suggest that the excitons in DSiPV produced upon photoexcitation rapidly transfer to MEH-PPV. The energy-transfer process enhances not only the PL quantum efficiency of the blended polymers but also the EL quantum efficiency.

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