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Long-Range Energy Migration in Photoexcited Polymers

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ABSTRACT: Excitation migration dynamics and the energy-transfer process in a donor−acceptor pair system on photoexcitation have been investigated by using static and time-resolved photoluminescence (PL) measurements. The PL spectrum of poly(*N*-vinylcarbazole) (PVK) was fully superposed on the electronic absorption spectrum of poly(9,9′-di-*n*-hexyl-2,7-fluorenylvinylene) (PDHFV) to fulfill a requirement for an efficient Förster-type energy transfer. In the PL spectrum of a blended PVK film with 0.5 wt % PDHFV on photoexcitation at 340 nm, the PL emission of PDHFV, which exhibits little absorbance at the excitation wavelength, prevailed over the PL emission of PVK. The PL spectrum of a bilayered structure with a PVK layer thickness of 4 μm and a PDHFV layer thickness of 80 nm, which was prepared by spin-casting PDHFV solution in trichloroethylene on a PVK film, also showed the PL emission of PDHFV on photoexcitation of the PVK layer at 340 nm without a trace of the PL emission of PVK. Excitation energy migration through a PVK bulk was observed up to a PVK thickness of 23 μm. A time-correlated single-photon counting (TCSPC) study deduced an energy migration velocity of 3.5×10^6 cm/s and a dwell time between each hopping of 85 fs, respectively, in the PVK bulk of the bilayered structures with a PDHFV layer thickness of 10 or 80 nm.

Introduction

Polymer-based light-emitting diodes (LEDs) for full-color displays have been a target to be developed since electroluminescence (EL) from a conjugated polymer was first reported.[1] High quantum efficiency of LEDs was achieved by balanced charge injections from respective electrodes.[2,3] The charge injections are controlled by setting the difference in the energy levels between the work functions of the electrodes and the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO) of the polymers.[4] The recombination site of the two opposite charges for formation of an exciton is determined by the charge mobilities in the system.[5] Light-emitting polymers mostly exhibit either hole or electron transporting capabilities, and consequently, excitons are formed close to either the anode or the cathode when a single emitting layer is sandwiched between the electrodes. When a charge transporting layer which also works as an opposite charge blocking layer is inserted in the emitting system, the EL quantum efficiency of an LED is significantly enhanced.[6]

A blend of two polymers with different band gaps generally emits light from a fluorophore of the polymer with the narrower band gap on photoexcitation of a chromophore of the polymer with the wider band gap.[7,8] Energy transfer from the chromophore with the wider band gap to that with the narrower one occurs within the Förster distance of about 100 Å,[9] and the PL efficiency of the polymer with the narrower band gap in a polymer blend is often observed to be higher on the indirect photoexcitation than on the direct photoexcitation.[10] The energy-transfer efficiency is high when the PL spectrum of the chromophore with a wide band gap overlaps with the electronic absorption spectrum of the chromophore with a narrow one.[11]

The present work attempts to deduce the range of energy transfer between two chromophores with different band gaps, the excitation energy migration velocity, and the dwell time of the excitation on each hopping in the polymer bulk. The energy transfer between a donor and an acceptor in a bilayered structure was examined by changing thickness of each layer. A static and time-resolved PL spectroscopy was employed to characterize the PL emission of the bilayered structure.

Experimental Section

Poly(*N*-vinylcarbazole) (PVK) and poly(methyl methacrylate) (PMMA) were supplied by Aldrich. PVK had a molecular weight (M_w) of 10^6 g/mol and was purified by dissolving and precipitating three times using THF and methanol as the solvent and the precipitant, respectively, but PMMA (intrinsic viscosity of 0.2) was used as received. Poly(9,9′-di-*n*-hexyl-2,7-fluorenylvinylene) (PDHFV) was synthesized by employing a Heck reaction with 2,7-dibromo-9,9′-di-*n*-hexylfluorene and 2,7-divinyl-9,9′-di-*n*-hexylfluorene as the alternating copolymer units and palladium(II) acetate as a catalyst as described elsewhere.[12] Polymer blend films were made by spin-casting the blend solution of 2 wt % in chlorobenzene which was filtered with a 0.2 μm filter. The bilayered structures were obtained by spin-casting the PDHFV solution in trichloroethylene, nonsolvent for PVK, on PVK films. The thickness of each layer was controlled by the solution concentration and the spinning rate.

UV−vis absorption spectra were recorded with a HP 8452A diode array spectrophotometer. The PL spectra were recorded with an ISS PL-1 fluorometer. A time-correlated single-photon counting (TCSPC) technique was used for the time-resolved PL measurement. A detailed description of an experimental setup for TCSPC can be found elsewhere.[13] The excitation

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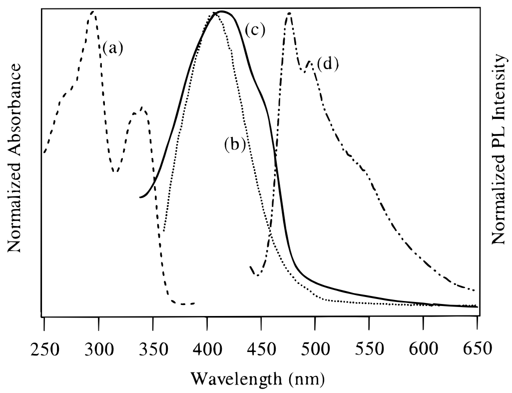

Figure 1. Absorption and emission characteristics of PVK and PDHFV: (a) PVK absorption, (b) PVK emission, (c) PDHFV absorption, and (d) PDHFV emission.

source is a cavity-dumped dye laser pumped by the frequency-doubled output (532 nm) of a picosecond Nd:YAG laser. The dye laser output is 5 ps of pulse width and 50 mW at 580 nm of the average power with a 3.8 MHz repetition rate. The laser pulse was frequency-doubled by using a β-BBO crystal to generate the optical pulse at 290 nm. The emission was collimated by using a 8 cm focal length fused silica lens at the right angle geometry to the excitation laser beam and focused onto a Jobin-Yvon HR320 monochromator by using a 20 cm focal length lens. The light signal was detected by using a microchannel plate photomultiplier tube (MCP-PMT; Hamamatsu R2809U). The signal from the PMT was amplified by a wide-band amplifier (Philips Scientific), sent to a Quad constant fraction discriminator (Tennelec), a time-to-amplitude converter (TAC; Tennelec), a multichannel analyzer (Tennelec/Nucleus), and finally stored in a computer.

Results and Discussion

Figure 1 shows the normalized absorption and PL spectra of PVK and PDHFV. PVK shows two electronic absorption maxima at 295 and 340 nm while PDHFV has the featureless absorption spectrum with the maximum at 420 nm. The PL emission on photoexcitation of PVK at 340 nm resulted from a radiative singlet decay of the low-energy excimer.[14] The PL spectrum of a PDHFV film on photoexcitation at 420 nm exhibits the emission maximum at 475 nm with a vibronic structure and a full width at half-maximum (fwhm) of 60 nm, revealing a random conformational arrangement of the polymer molecules for a narrow spectrum.[15] It is apparent that the dimeric fluorene rearrangement to form an excimer is unfavorable in the PDHFV bulk in contrast with poly(dialkylfluorene) in which the singlet excimer emission at 550 nm is dominated.[16] A complete superposition of the absorption spectrum of PDHFV on the PL spectrum of PVK predicts an efficient Förster-type energy transfer from PVK to PDHFV.[11]

It has been observed that the blends of PVK with fluorene-based light-emitting polymers revealed phase separation with various domain sizes but efficient energy transfer from PVK excitations to PDHFV by showing only the PL spectrum of the latter on photoexcitation of PVK at 340 nm.[17] Some excimers generated at the center of the PVK domains with radii larger than 500 nm might be too far away from PDHFV to transfer energy by the Förster-type mechanism. However, the energy transfer was completed in the phase-separated blend system probably by the Huber-type mechanism.[18] The energy-transfer process between the chromophores in these two polymers was considered as a long-range interaction.

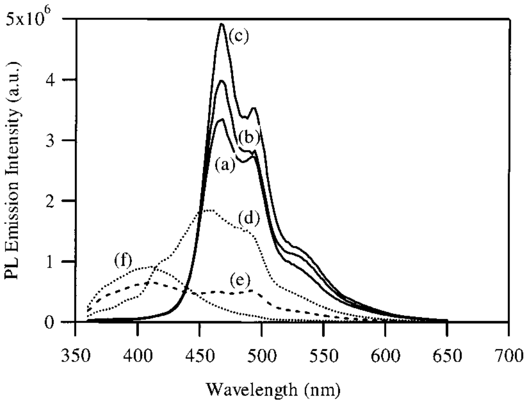

Figure 2. PL spectra of PVK/PDHFV bilayer structures with fixed PDHFV thickness of 80 nm with a variation of PVK thickness of (a) 350, (b) 800, (c) 2700, (d) 9000, (e) 23 000 nm, and (f) PVK-only film.

Figure 2 shows that the energy transfer from PVK to PDHFV in the bilayered structures was carried out in a much longer range than the Förster critical distance. When PVK films with various thicknesses were covered by a PDHFV film with a fixed thickness of 80 nm by spin-coating, the excitations generated in the PVK layer with a thickness of up to 2700 nm on photoexcitation at 340 nm completely transferred the energy to PDHFV, and no trace of the PVK excimer emission at 410 nm was observed. The normalized PL spectrum of a bilayered structure with a PVK thickness of 2700 nm or less was identical to that of the PDHFV-only film excited at 420 nm (Figure 1d). The PL intensity of the bilayered structures was much higher than that of the PDHFV-only film. There was no enhancement in the secondary PL emission at 550 nm although the PDHFV layer was 80 nm thick in the bilayered structures. When the PVK layer thickness was 9000 nm, the PL spectrum was blue-shifted with a decrease in its intensity, and the PVK excimer emission was observed as a shoulder at 410 nm. The PL peak intensity at 475 nm further decreased and became almost the same as that at 410 nm for the bilayered structure with a PVK thickness of 23 000 nm. This proves that the excitations migrated in the range of up to 23 μm in the PVK bulk while part of the PVK excitations formed excimers for radiative emission.

Up to 99% of the excitation light with a wavelength of 340 nm was absorbed by the PVK film of 400 nm thick in the present work. The PL intensity of PDHFV (the acceptor) at 475 nm on photoexcitation of PVK (the donor) at 340 nm increased rapidly with the increases in the PVK thickness up to 1300 nm, and the high intensity was sustained over a donor thickness of 4 μm without a trace of the PVK excimer emission at 410 nm as shown in Figure 3. This implies that few excimers were formed in the PVK bulk with the thickness of up to 4 μm. The excimer emission of PVK in the bilayered structure was finally observed when the PVK thickness was increased to 6 μm, which suggests that some of excitations failed to migrate to the distance over 6 μm but formed excimers for the radiative decay. This indicates that the energy migration range is long but finite. The highest excimer emission intensity at 410 nm was observed for the PVK layer thickness of 9 μm, and the intensity decreased with a further increase in the PVK thickness. It is noteworthy that the excitations in the donor could migrate to the acceptor through the

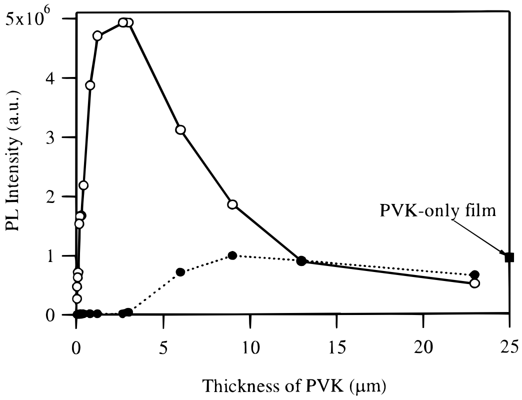

Figure 3. PL emission intensity at 475 nm (○) and 410 nm (●) vs thickness of PVK layer (thickness of acceptor: 80 nm).

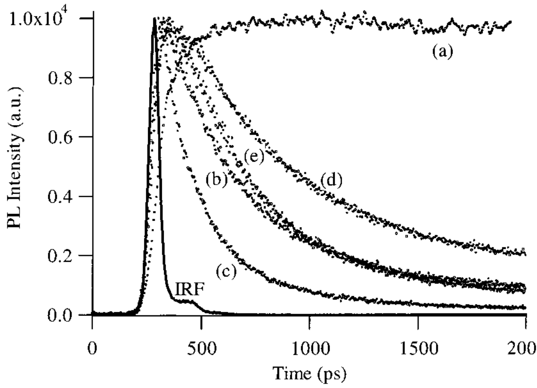

Figure 4. TCSPC data of PVK/PDHFV layer emitted at 410 nm (light through PVK). PVK/PDHFV: (a) PVK-only, (b) 650/10, (c) 650/80, (d) 2500/10, and (e) 5000/80 nm/nm.

Table 1. Rise and Decay Times of PL of Bilayered Structures at a Given Wavelength

PVK (nm)	PDHFV (nm)	excitation side	detection (nm)	rise time (ps)	decay time (ps)
2500		PVK	410	~400	11000
650	10	PVK	410	45	470
650	80	PVK	410	25	225
2500	10	PVK	410	65	885
5000	80	PVK	410	65	525
650	10	PDHFV	410	55	600
650	80	PDHFV	410	25	235
2500	10	PDHFV	410	200	~2200
5000	80	PDHFV	410	50	400
	80	PDHFV	470	10	50
650	80	PDHFV	470	60	800
650	10	PVK	470	430	1440
650	80	PVK	470	135	850
2500	10	PVK	470	480	1660
2500	80	PVK	470	190	950
5000	80	PVK	470	260	1180

23 μm thick PVK bulk as revealed by the observation of the emission band at 475 nm from the acceptor layer.

It is likely that the excitations or the excimers generated in PVK had a long lifetime and migrated to a long distance of 23 μm to transfer the energy. Since excimers have no ground state,[19] excimeric migration in PVK was infeasible. It is apparent that the excitations rather than the singlet excitons in PVK migrated toward PDHFV in the bilayered structure since no emission of singlet excitons was observed from excited PVK. However, there is no evidence that the excitations in PVK transferred the energy directly to PDHFV. The direct energy transfer may be unfavorable since there is little spectral overlap between the PL spectrum of PVK singlet excitons and the absorption spectrum of PDHFV. Thus, we can expect that PVK excimers should be formed at the PVK−PDHFV interface prior to the energy transfer to PDHFV. The increase in the PL intensity of PDHFV at 475 nm with a PVK film thicker than the full absorption thickness of 400 nm on static photoexcitation might be attributed to the increased number of the excitations that were formed indirectly in the PVK bulk beyond 400 nm due to the migration.

PVK with the glass transition temperature (T_g) of 200 °C might have a fixed number of excimer-forming sites distributed in the polymer bulk at room temperature.[20,21] Photoexcitation of a PVK-only film at 340 nm generated a substantial amount of excimers and showed a strong PL emission. In a bilayered structure, however, the excitation migration toward the acceptor layer prevailed over the excimer formation in the PVK bulk. The migrating excitations might experience different molecular arrangements near the PVK−PDHFV interface from those in the PVK bulk, and the microscopic structural difference would hinder the continuous migration through the interface. The different molecular arrangements would act as efficient excimer formation sites so that the energy of PVK excitations was effectively transferred to PDHFV through the Förster-type mechanism after the excimer formation.

To clarify the energy transfer dynamics in the bilayered polymer films, we performed a time-resolved PL study. The time-resolved PL decay profiles of the bilayered structure at 410 nm on photoexcitation at 290 nm are shown in Figure 4. The results of temporal profile analyses are listed in Table 1. The temporal profile of the excimer emission in a PVK-only film at 410 nm showed a rise time of around 400 ps. It is worthwhile to note that the constant PL intensity of the PVK-only film at 410 nm was sustained for a long time, and the decay time of 11 ns was deduced. If there was no other nonradiative decay channel faster than the excitation lifetime (11 ns), the PVK excitations in dynamic equilibrium with excimers would roam in the PVK bulk. The excimer formation rate might depend on both the number of excimer forming sites and the relaxation time of the excitations to an energy level for the excimer formation. The excimer formation and the radiative excimer emission rates should be in equilibrium in order to exhibit the constant PL intensity at 410 nm for a long time. This implies that the lifetime of the PVK excitations is much longer than the lifetime of the PVK excimers. The overall PL decay dynamics in the PVK-only film represents the decay of the singlet excitations.

In the case of bilayered structures, the PL decay profiles on photoexcitation at 290 nm exhibited a completely different feature (Figure 4b−e) compared with that of the PVK-only film (Figure 4a). The excimer PL decay profiles of all the bilayered structures at 410 nm exhibited much shorter lifetimes than that of the PVK-only film. The rise and decay times of a bilayered structure with the PVK/PDHFV thickness ratio of 650/10 were 45 and 470 ps, respectively. As the thickness of PDHFV increased to 650/80, the rise and decay times reduced to 25 and 225 ps, respectively, and the time constants increased to 65 and 885 ps, respectively, with an increase in the PVK layer thickness to 2500/10. It appeared that the rise and decay times of the PVK excimer emission became longer for thicker donor layers and thinner acceptor layers. The rise and decay times

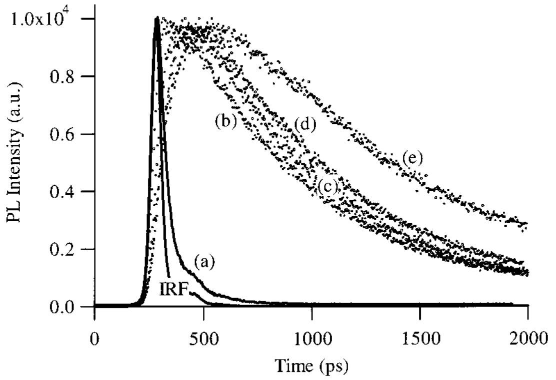

Figure 5. TCSPC data of PVK/PDHFV layer emitted at 475 nm (light through PVK). PVK/PDHFV: (a) PDHFV-only, (b) 650/80 (light through PDHFV), (c) 650/80, (d) 2500/80, and (e) 5000/80 nm/nm.

seemed to be dependent on both the migration distance of excitations in the donor bulk and the acceptor capacity.

When the incident excitation beam at 290 nm impinged through the PDHFV layer to photoexcite PVK, the rise and decay times exhibited a similar trend to those on the direct excitation of the PVK layer as shown in Table 1. The rise times were in the same range as those of the excimer PL for the bilayered structure photoexcited through PVK except for the bilayered structure of the PVK/PDHFV ratio of 2500/10 where the rise and the decay times were 200 and >2200 ps, respectively, much longer than the rest of them. It seems that only a small portion of donor excitations formed close to the interface transferred energy to the acceptor by the cascade energy transfer in the early stage while the rest of the excitations migrated away from the interface and roamed in the PVK bulk until relaxing enough to form excimers. This observation is compatible with the notion that the excimers were formed after the excitation relaxation to a suitable energy level.

The PL temporal profiles of the bilayered structures at 475 nm are shown in Figure 5 and Table 1. The rise and decay times of the PL emission from the PDHFV-only film excited at 305 nm were 10 and 50 ps, respectively. The PL intensity of the PDHFV-only film at 475 nm was very weak on photoexcitation at 305 nm compared with the intensity of the excimer emission of PVK at 410 nm. When the excitation beam of 290 nm penetrated through the acceptor in the bilayered film with a thickness ratio of 650/80, the rise and decay times at 475 nm were 60 and 800 ps, respectively. This result suggests that it took approximately 50 ps for the donor excitations to transfer the energy to the acceptors. The transfer time was probably the time for the relaxation of the excitations to form excimers near the interface. It is apparent that the excitation energy failed to be transferred directly to the acceptors. It probably took some time for the excitations to relax to a suitable energy level to form excimers.

When the excitation beam of 290 nm was illuminated at the donor side, the rise and decay times of the PL emission of the bilayered structure at 475 nm with the PVK/PDHFV ratio of 650/10 were 430 and 1440 ps, respectively. The rise and decay times decreased to 135 and 850 ps, respectively, for the bilayered structure with the ratio of 650/80. It was observed that the acceptor capacity of the 10 nm thick layer was insufficient to receive the excimer energy as fast as the 80 nm thick layer did. The excimer sites were saturated near the interface, and the excitations roamed around until the excimers transferred the energy to PDHFV. It again proved that the lifetime of excitations was long.

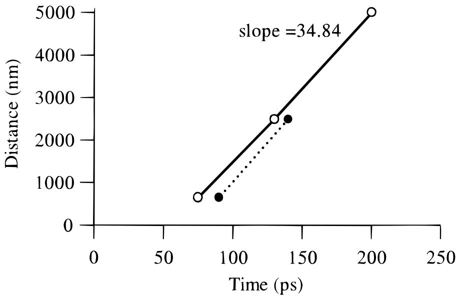

Figure 6. Plot of the migration distance vs the rise time of the intensity at 475 nm (thickness of acceptor: (○) = 80 nm, (●) = 10 nm).

The PVK layer thickness as a function of the migration distance was plotted against the rise time of the acceptor PL emission as shown in Figure 6. The migration velocity of 3.5×10^6 cm/s was deduced from the slope regardless of the acceptor thickness. The intercept of the slope to the abscissa could be equivalent to the time required for an excimer formation of PVK at the interface and subsequent energy transfer from the donors to the acceptors as revealed by the rise time in the acceptor PL emission excited through the acceptor layer. The volume and the lattice constant of a single repeating unit of PVK are calculated as $2.67 \times 10^{-8}\ \mu\text{m}^3$ and $2.99 \times 10^{-3}\ \mu\text{m}$, respectively, based on the PVK density of 1.2 g/cm^3 and the molecular weight of the repeating unit of 193 g/mol. Since a PVK film was photoexcited on the surface away from the interface, the saturated excitations propagated one-dimensionally toward the acceptor layer. The excitation migration velocity of 3.5×10^6 cm/s corresponds to the dwell time between each hopping of 85 fs if we assume that the excitation hopping occurs through the nearest neighbors of a simple cubic lattice and the 12 next-nearest-neighbor sites at the face diagonals. This time constant would be a lower limit of the dwell time in PVK. An upper limit of the excitation hopping time of 250 fs was observed in the time-resolved PL study of a poly(*p*-phenylenevinylene) (PPV) film with the excess energy of ca. 400 meV above the absorption edge.[22] A fast decay dynamics with the time constant for the exciton transport was also observed to be 120 fs in polybithiophene with the excess energy of 200 meV.[23] Since the initial excess energy of PVK excitations in our study can be estimated to be about 800 meV, the excitation migration time in PVK bulk is expected to be shorter than 100 fs.

Conclusion

PDHFV with an alternating structure of fluorene and vinylene units showed the absorption maximum at 420 nm and the PL emission peak at 475 nm with a vibronic shoulder at 490 nm and a weak secondary emission at 550 nm. The excimer emission spectrum of PVK was fully superposed on the electronic absorption spectrum of PDHFV for an efficient Förster-type energy transfer. The energy transfer from photoexcited PVK to PDHFV was very efficient and suppressed the excimer emission of PVK in the polymer blend with a PDHFV concentration of 0.5 wt %. The energy transfer in a bilayered structure with PVK and PDHFV reveals that the migration distance of PVK excitations for a complete suppression of the excimer emission by PDHFV with a thickness of 80 nm was 4 μm. Moreover, the energy could be transferred partially to the PDHFV layer up to 23 μm away from the initial photoexcitation spot, a very long migration distance. The PL intensity of a bilayered structure with the emission maximum at 475 nm kept increasing with an increase in the donor thickness beyond the 99% absorption thickness of 400 nm. The strongest PL intensity at 475 nm was observed in the bilayered structure with the donor thickness of 4 μm. A time-resolved PL study on the bilayered structure reveals that the decay time of PVK excitations of 11 ns decreases with a decrease in the PVK layer thickness as well as an increase in the PDHFV layer thickness. The migration velocity of the PVK excitations was deduced as 3.5×10^6 cm/s regardless of the layer thickness of the donor or the acceptor. The lower limit of the dwell time was calculated to be 85 fs between each hopping. However, the initial emission time at 475 nm after the cascade energy transfer from PVK to PDHFV was shortened by the decrease in the PVK/PDHFV thickness ratio.

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