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Charge Transfer Channels in Formation of Exciplex in Polymer Blends *

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The strong dependence of photoluminescence of charge transfer excited states or exciplex in a blend film of poly(9,9'-dioctylfluorene-co-benzothiadiazole) (F8BT) and poly(9,9'-dioctylfluorene-co-bis-N,N'-(4-butylphenyl)-bis-N,N'-phenyl-l,4– phenylenediamine) (PFB) on the excitation wavelengths and morphology is investigated. The experimental results reveal that electron transfer in the LUMOs from PFB to F8BT is more efficient than hole transfer in the HOMOs from PFB to F8BT for the formation of exciplex at the interfacial junctions between these two types of molecules in the blend film. Furthermore, energy transfer from the blue-emitting PFB to the green-emitting F8BT at the interfaces introduces an additional two-step channel and thus enhances the formation of an exciplex. This is important for understanding of charge generation and separation in organic bulk heterojunctions and for design of optoelectronic devices.

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Polymeric bulk heterojunctions are usually employed in the development of organic optoelectronic devices due to the more efficient charge transport by the larger interfaces.[1] They are usually composed of two different polymeric semiconductors for electron- and hole-transport. The interactions between these polymers in the heterojunction lead to the formation of an exciplex or charge-transfer excited states through coulomb interactions between the donor and the acceptor polymers, and is generally identified by red-shifted and long-lived photoluminescence under optical excitation of the blend film.[2,3] Exciplex has been proved to influence significantly the performance of light-emitting or photovoltaic diodes.[4,5] Therefore, understanding and possible control of the formation of exciplexes are important in the development of new optoelectronic devices.

Poly(9,9'-dioctylfluorene-co-benzothiadiazole) (F8BT) and poly(9,9'-dioctyl- fluorene-co-bis-N,N'-(4-butylphenyl)-bis-N,N'- phenyl-l,4 – phenylenediamine) (PFB) are two typical copolymers of polyfluorene for optoelectronic devices, which show high performance in photo-induced charge generation and temperature stability.[6,7] They may be used to fabricate bulk heterojunction structures potentially important for the development of efficient solar cells.[8] Photophysics has been studied systematically on the exciplex formed in the blend film of these two polymers.[9] In this Letter, we investigate the possible channels that are involved in the formation of an exciplex in this blend film by analyzing the dependence of exciplex emission on excitation wavelengths and morphology of the solid film.

The chemical structures of F8BT and PFB are shown in Fig. 1. In the experiment, these two materials are dissolved in p-xylene at a concentration of 15 mg/ml, respectively, before they are mixed together with different volume ratios. Then, the blend solutions are spin-coated onto the glass substrate at a speed of 2000 rpm, producing solid films with a thickness of about 100 nm.

The absorption spectra of the blend film were measured using the UV-VIS spectrometer (Shimadzu UV-3150) and the PL spectra measurement using the FLS920 time-correlated single-photon counting (TCSPC) system from Edinburg Instrument. Different excitation wavelengths were provided by a xenon lamp after a monochromator. The morphology properties of the films were obtained by the tapping-mode atomic force microscopy (AFM) (Veeco Multimode).

The absorption (ABS, red curves) and photoluminescence (PL, black curves) spectra of F8BT (solid curves) and PFB (dashed curves) are shown in Fig. 2. The absorption and PL spectra of F8BT are peaked at about 462 and 540 nm, respectively, and those of PFB at 380 and 465 nm, respectively. The overlap between the absorption spectrum of F8BT and the PL spectrum of PFB implies possible energy transfer from PFB to F8BT when the excitation wavelength is within the PFB absorption spectrum.

Figure 3 compares the absorption spectra of F8BT, PFB and the blend film. Clearly, PFB has a peak absorption at 380 nm, whereas F8BT has a minimum absorption at this wavelength. In this case, the excitation of F8BT mainly results from energy transfer from PFB to F8BT, which takes place only in a limited range close to the interface between the two molecular phases. F8BT has the peak absorption at about

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462 nm and can be excited most strongly, however, PFB has almost no absorption at this wavelength. Therefore, using different excitation wavelengths is an effective approach to resolve the roles that energy transfer plays in the formation of an exciplex. Four excitation wavelengths of 320, 380, 400, 450 nm have been chosen in the experiment, as indicated by the arrows in Fig. 3.

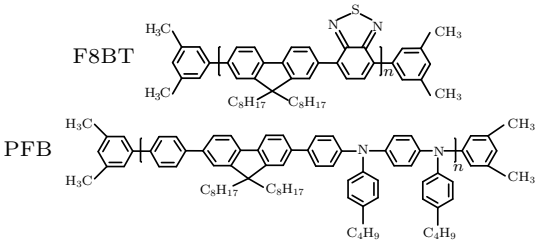

Fig. 1. The chemical structures of F8BT and PFB.

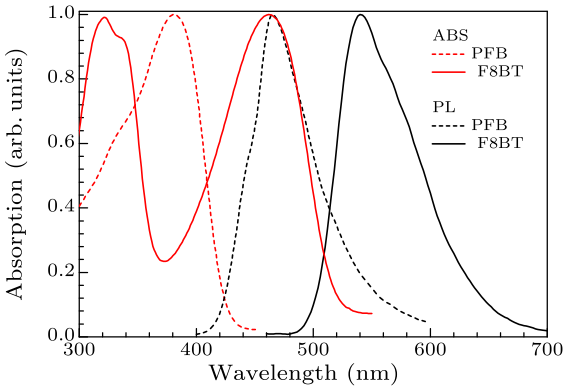

Fig. 2. The absorption (ABS) and the photoluminescence (PL) spectra of F8BT and PFB.

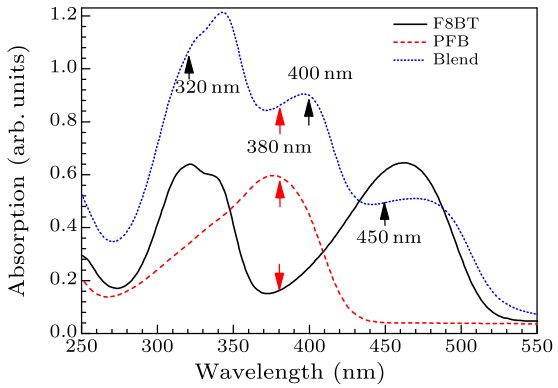

Fig. 3. The absorption spectra of F8BT (black), PFB (red) and the blend film (blue).

Figures 4(a)–4(d) show the PL spectra of F8BT:PFB blend films with a composite weight ratio of 1:1, 3:1, 1:3, 1:6, respectively. All of these spectra in Fig. 4 have been normalized to the same intensity at about 540 nm, which is the peak wavelength of the PL spectrum of F8BT. This intends to resolving more clearly the contribution from the exciplex emission to the PL spectrum. The exciplex is as generally identified as a red-shifted emission at about 620 nm in the blends of these two polymers.[7] For each composite ratio, we have measured the PL spectrum at different excitation wavelengths: 320, 380, 400 and 450 nm. It is clear that, with changing the excitation wavelength, the contribution of the exciplex emission to the PL spectrum is modulated strongly. However, the excitation at 380 nm induces the strongest exciplex emission, whereas the 450 nm excitation produces the weakest exciplex emission, with respect to the intensity at 540 nm for all these different composite ratios. It is clear that excitation at 380 nm actually excites mainly the PFB molecules. This leads to the direct electron transfer in the LUMOs from the excited PFB to the ground-state F8BT. Furthermore, as has been discussed above, excitation of F8BT at 380 nm is mainly through energy transfer, however, no energy transfer takes place at an excitation wavelength of 450 nm. Therefore, excitation at 380 nm has also excited efficiently the F8BT molecules that are located at the heterointerfaces, which may contribute to the exciplex formation through hole transfers in the HOMOs from the ground-state PFB to the excited F8BT. This kind of hole transfer may take place between PFB and F8BT molecules that have been related to each other through energy transfer. It should be noted that both the energy transfer distance and the exciton diffusion length are approximately 10 nm.[10,11] Although it is not quite clear if the two-step or indirect charge transfer process is more efficient than the direct charge transfer, the energy transfer process through dipole-dipole coupling or Förster resonance energy transfer within a spatial range of about 10 nm may correlate the PFB donor and the F8BT acceptor by making the excitons willing to go to the interface, thus opening up new channels for charge transfer and favoring the formation of exciplex.[12,13] This indicates that energy transfer might play an important role in formation of exciplexes.

Figures 4(a)–4(d) also imply that the exciplex emission depends strongly on the composite ratios between the two polymers. Figure 5(a) shows the dependence of the PL spectrum of the blend film on the composite ratios, where the PL spectra have been normalized to the peak intensity of the F8BT intrinsic emission at about 540 nm. A excitation wavelength at 380 nm has been employed for the measurements in Fig. 5(a). Clearly, as the composite ratio of F8BT:PFB is changed from 4:1 to 1:6, the contribution of the exciplex emission to the PL spectrum increases monotonically. However, when the ratio is changed to 1:7, the exciplex emission begins to reduce with respect to the F8BT emission at about 540 nm. This indicates that the composite ratio of 1:6 corresponds to the largest contribution of the exciplex emission to the PL spectrum with respect to the F8BT intrinsic emission. For the completion of char-

acterization of the exciplex, the decay dynamics of the PL intensity at 620 nm of the blend film with different composite ratios are presented in Fig. 5(b), which were measured using the time-correlated single-photon counting system from Edinburgh Instrument Ltd. and a pulsed laser at 405 nm is used as the excitation. The lifetime of exciplex emission is measured to be about 20 ns. Figure 5(b) confirms again that for a composite ratio of 1:6 the exciplex emission (longer-lifetime component) contributes mostly to the PL spectrum with respect to the F8BT intrinsic emission at 540 nm when compared with those for composite ratios of 1:2, 1:3, 1:4 and 1:7. Furthermore, microscopic investigation has found that different composite ratios induce difference morphologies of these blend films. This also leads to different shapes and different total areas of the interfaces between the two phases in the blend film. Therefore, investigation of the dependence of exciplex emission on morphology of the blend film is also an effective approach to understand the mechanisms for the formation of exciplexes and how these mechanisms are influenced by energy transfer.

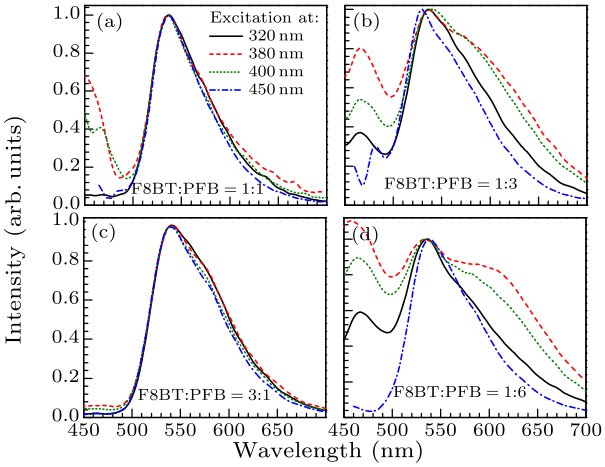

Fig. 4. The PL spectra of F8BT:PFB blend films with a composite ratios (w/w) of 1:1 (a), 1:3 (b), 3:1 (c), 1:6 (d), respectively, at different excitation wavelengths.

Figures 6(a) and 6(b) show the atomic force microscopic (AFM) images of the F8BT:PFB blend films prepared using composite ratios of 1:1 and 1:6, respectively. The brighter phase in the AFM images can be identified as F8BT-rich phase and the darker one is PFB-rich phase. For a composite ratio of 1:1, the F8BT-rich phase is about 60 nm higher than the PFB-rich phase. Clearly, with reducing the composite ratio of F8BT:PFB from 1:1 to 1:6, the F8BT-rich phase reduces significantly from 730 to 230 nm in the mean diameter, leading to the decrease in the height to 40 nm and increase in the total area of F8BT phase. Thus, with reducing the composite ratio of F8BT:PFB, the size of F8BT phase is reduced and the total interfacial area is increased, which favors the formation of the exciplex.

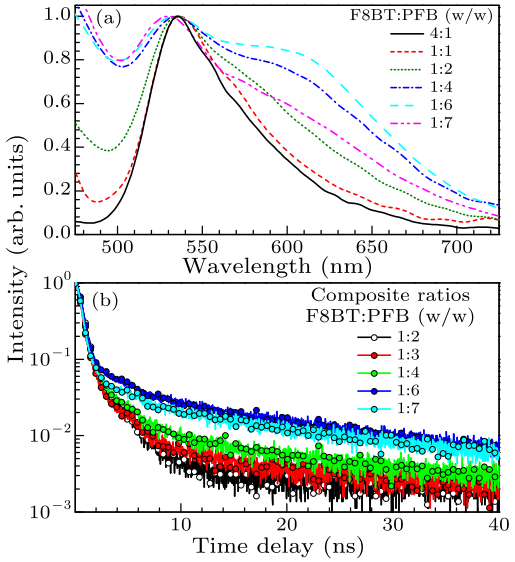

Fig. 5. (a) The PL spectra of F8BT:PFB blend films with different composition ratios at an excitation wavelength of 380 nm. (b) The decay dynamics of the emission at 620 nm from the blend films with different composite ratios.

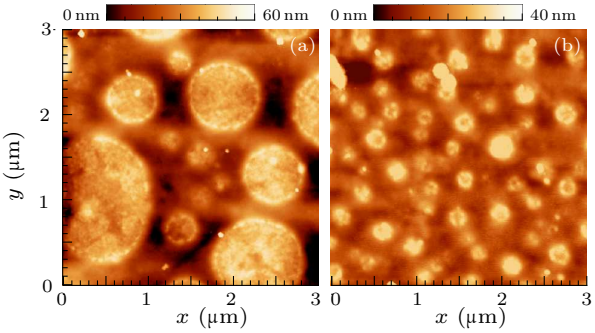

Fig. 6. The AFM images of F8BT:PFB blends prepared in p-xylene with the composite ratios of (a) 1:1 and (b) 1:6.

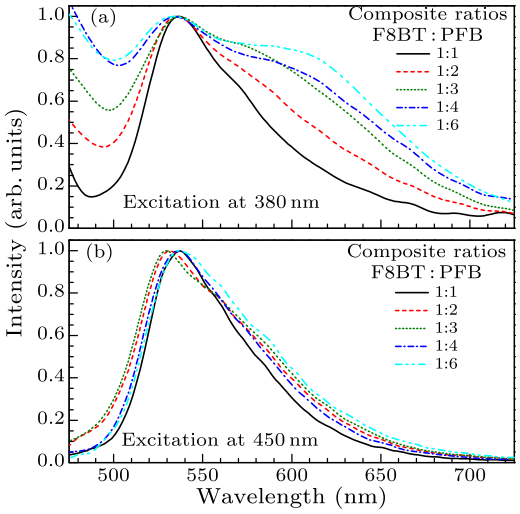

Fig. 7. The PL spectra of F8BT:PFB blends with different composite ratios and the excitation wavelengths at (a) 380 nm and (b) 450 nm.

Figure 7 compares the PL spectra of the blend films with different composite ratios (1:1, 1:2, 1:3,

1:4 and 1:6) at excitation wavelengths of 380 nm (Fig. 7(a)) and 450 nm (Fig. 7(b)), where all spectra have been normalized to the same intensity at 540 nm. Figure 7(a) shows that for the excitation at 380 nm, there is a dramatic increase in the exciplex emission at about 620 nm with respect to the PL intensity at 540 nm, as the composite ratio is changed from 1:1 to 1:6. This means that larger amount of F8BT (larger F8BT-rich phase) and smaller interfacial area lead to the relatively weaker exciplex emission for a composite ratio of 1:1 than for 1:6. Therefore, we expect a larger probability of the formation of exciplexes at a composite ratio of 1:6 than 1:1. This should also work for an excitation wavelength of 450 nm. However, using an excitation wavelength of 450 nm, there is a very small increase in the relative PL intensity at the exciplex emission spectrum around 620 nm, as shown in Fig. 7(b), which results mainly from the increase in the interfacial area. The only difference between the experimental conditions in Figs. 7(a) and 7(b) is such that excitation at 380 nm excites both PFB and F8BT molecules and F8BT is mainly excited by energy transfer, whereas excitation at 450 nm only excites F8BT molecules without any energy transfer process. Thus, the formation of an exciplex through selective excitation of F8BT molecules is not as efficient as that through excitation of PFB. Therefore, we can conclude that the direct electron transfer in LUMOs from PFB to F8BT plays a major role in the excitation of an exciplex and the energy transfer process taking place simultaneously also makes important contributions through subsequent hole transfer process. However, the pure hole transfer in LUMOs from F8BT to PFB after the selective excitation of F8BT is much less efficient.

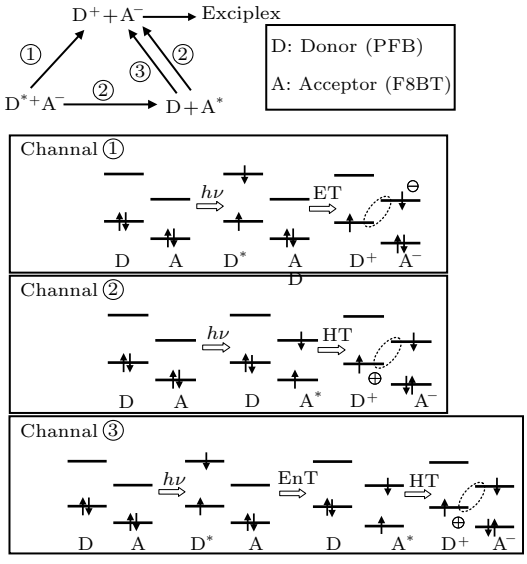

Fig. 8. The possible channels for the formation of an exciplex. ET, HT and EnT denote electron transfer, hole transfer and energy transfer, respectively.

According to the above experimental studies, we summarize the possible channels shown in Fig. 8 for the formation of an exciplex. Using an excitation wavelength of 380 nm, there are three possible channels for the generation of an exciplex, namely, channels 1, 2 and 3. However, using an excitation wavelength of 450 nm, only channel 2 supports the formation of an exciplex. In channel 1, electron transfer takes place directly after the donor (PFB) is excited at 380 nm, producing an exciplex. In channel 2, the direct hole transfer process takes place between the ground-state PFB and excited F8BT, enabling exciplex formation. In channel 3, PFB is excited first before the energy transfer process from the donor to the acceptor (F8BT), then the hole transfer between ground-state PFB and excited F8BT enables exciplex formation. Furthermore, the energy transfer process through dipole-dipole coupling or Förster resonance energy transfer within a spatial range of about 10 nm may correlate the PFB donor and the F8BT acceptor by making the excitons willing to go to the interface and thus introducing more channels for charge transfer and favoring exciplex formation.

In conclusion, the dependence of the spectroscopic properties of exciplex emission in polymer blends of F8BT:PFB on excitation wavelengths and morphology is investigated experimentally. Multiple channels have been analyzed for exciplex excitation. Using excitation wavelengths within the PFB absorption band is much more efficient for the generation of exciplex at the heterointerfaces than the selective excitation of F8BT. Energy transfer is supposed to have played important roles in exciplex formation, since more charge transfer channels are induced and the exciton motion to the interface might be enhanced by energy transfer.

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