

Influence of Copolymer Interface Orientation on the Optical Emission of Polymeric Semiconductor Heterojunctions

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We have examined the Coulombic interactions at the interface in a blend of two copolymers with intramolecular charge-transfer character and optimized band offsets for photoinduced charge generation. The combination of both time-resolved measurements of photoluminescence, and quantum-chemical modeling of the heterojunction allows us to show that relative orientation across the heterojunction can lead to either a repulsive barrier (~ 65 meV) or an attractive interaction which can enhance the charge-transfer processes. We conclude that polymer orientation at the heterojunction can be as important as energy-band offsets in determining the dynamics of charge separation and optical emission.

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Efficient optoelectronic devices based on semiconducting polymers as active materials frequently incorporate two polymer components whose interface properties have a crucial impact on device performance. The physics of such polymeric heterojunctions in general is complex, and fundamentally different from that of their inorganic semiconductor counterparts. This is a direct consequence of both strong exciton localization upon excitation, and the quasi-one-dimensional nature of the polymer chain, which makes adequate description through isotropic or uniform models a difficult task. Dissociation of primary photoexcitations in conjugated polymers has been shown to be very efficient at an interface between two polymers with appropriate band-edge offsets [1]. A successful route to controlling these energy levels is the modulation of polymer conjugated backbones with suitable functional building blocks having different electron affinities [2]. However, this also leads to an increased intramolecular charge transfer (ICT) within repeat units of the resulting copolymers. The interactions at the heterojunction between such polymers and the accompanying photophysics should thus be strongly anisotropic. In spite of this, current models of polymeric heterojunctions have so far neglected the effect of ICT and the anisotropic interaction it may induce at the heterojunction. This is mainly because in early examples of conjugated polymers (e.g., poly-*p*-phenylenevinylene, or PPV) the lowest optically excited states were shown to have low charge-transfer character (small electron-hole separation distance) [3]. Interchain charge transfer in PPV-derivative heterojunctions, for example, has previously been described assuming charge excitation of one chain in the presence of a charge of opposite sign on the adjacent chain, leading to only an attractive interaction between the two chains [4].

We demonstrate here for the first time that strong ICT in many conjugated copolymers can lead not only to attrac-

tive interaction but also to a repulsive interaction at heterojunctions. We have investigated the time-resolved photoluminescence of a blend film of two polyfluorene-derivative copolymers. At short (sub-ps) time delays after excitation, excitonic emission from both copolymers in the blend is blueshifted with respect to that of the individual component films. This emission is accompanied by a strong redshifted band that has previously been assigned to an interfacial charge-transfer state (exciplex) formed at heterojunctions [5,6]. We show here that the two contrasting features signify different heterojunction configurations that can lead to either repulsive or attractive interactions. We present quantum-chemical calculations which further illustrate that both features are associated with the charge-rich functional groups.

The two copolymers under investigation are poly(9,9-dioctylfluorene-co-benzothiadiazole) (or F8BT) and poly[9,9-dioctylfluorene-co-bis-*N,N*-(4-butylphenyl)-bis-*N,N*-phenyl-1,4-phenylenediamine] (or PFB). The chemical structures of the two polymers are given in Fig. 1. Samples were prepared by first dissolving the copolymer in chloroform at a concentration of 14 mg/ml. The homopolymer solutions were then spun onto silica substrates to yield films of 170-nm thickness. For blend samples, the homopolymer solutions were mixed together in equal quantities by weight, and then spin coated as before. All fabrication steps were conducted in an N₂ atmosphere. For comparison, blends were prepared in a similar manner but with PFB replaced by poly(9,9-dioctylfluorene), which shows little ICT. All blend films were examined using atomic force microscopy indicating phase separation on a very fine scale (tens of nanometers) in agreement with previous studies [7,8]. The photoluminescence (PL) was time resolved by the up-conversion method using the setup described in detail by Herz and Phillips [9], giving a temporal resolution of 380 fs. Time-integrated PL spectra

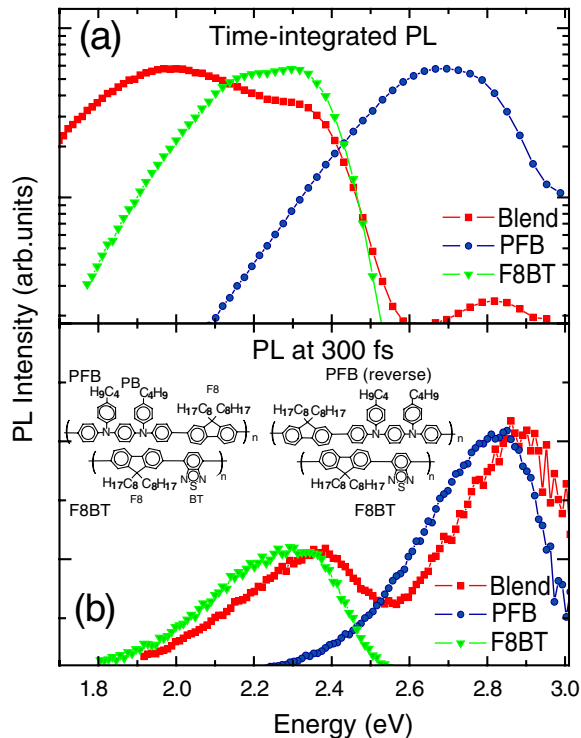


FIG. 1 (color online). (a) Normalized PL intensity for the PFB:F8BT blend and homopolymer films integrated from 0–100 ns (excitation: 3.05 eV, <4 nJ/cm², plotted on the logarithmic scale to show the small feature around 2.8 eV). (b) PL intensity at 300 fs after excitation (excitation: 3.06 eV, ~ 50 nJ/cm²). The homopolymer PFB and F8BT emission are normalized to the respective PFB and F8BT emission band from the blend to display the spectral shift. Inset shows the chemical structures of the PFB and F8BT and the two extreme relative orientations discussed in the text.

were obtained by integrating the first 100 ns of emission detected by a photon counting method. The results showed no dependence on excitation density near the intensities used. The samples were always kept under an inert atmosphere or *in vacuo* (10^{-6} mbar) during measurement.

In Fig. 1(a), we show the time-integrated PL spectra of the blend and of the pure polymers. The pure PFB emits in a broad band with peak intensity at 2.7 eV, and the pure F8BT emits in a band peaking at 2.3 eV. In the blend, the redshifted band around 2.0 eV has been assigned to exciplex emission. In this blend system the exciplex is a relaxed state formed after an initial charge transfer between the two components at their interfaces; thus it shows significant charge-transfer character and low oscillator strength, resulting in a long radiative decay time [5]. The PFB emission from the blend is quenched significantly due to the rapid Förster transfer of excitons from PFB to F8BT, as expected from the good overlap between the F8BT absorption spectrum (not shown) with the PFB emission spectrum. There is also some small residual emission from the blend at energies around 2.8 eV, which can be attributed to recombination involving PFB states. In the time-

integrated spectrum, this small emission peak is blue-shifted with respect to that for pure PFB by about 100 meV. The blueshift observed here could possibly be explained by the PFB excitons in the blend having insufficient time to relax to longer conjugated segments due to rapid Förster transfer to F8BT. However, the spectra measured with high time resolution shown in (b) demonstrate that a blueshift of 65 meV (compared to pure PFB) already occurs even within the 300-fs time window of the excitation pulse. At this short time delay, PFB excitons in the blend are unequivocally emitting at higher energies than PFB excitons in the pure film. Exciplex emission at early time is masked by the much stronger emission from excitons with shorter radiative decay time and thus larger photon emission rate.

We first rule out trivial causes that are not relevant to explain the blueshift in this system. All spectra shown have been corrected for self-absorption. The absorption spectrum (not shown) of the blend film displays no new features and can be modeled sufficiently well by a linear superposition of the spectra of the copolymer components [7]. This eliminates the possibilities of H-like aggregate formation or the breaking of conjugation due to chain entanglements in the blend. Förster transfer between PFB and F8BT rapidly depletes the PFB excited-state population but this results in a reduction of the whole PFB emission rather than a shifting of its spectrum. In addition, we do not observe any significant spectral shifts when blending F8BT with polydioctylfluorene (not shown) indicating that the origin of the blueshift in PFB/F8BT blends is most likely linked to the ICT character of both of its blend components (*vide infra*).

Figure 2 (top) shows the dynamics of the blend emission spectra. Decay curves were taken at 2.25 and 2.7 eV and are shown in Figs. 2(a) and 2(c) together with those for the corresponding pure polymer films. The blend emission at both energies decays faster than that of the pure components as a result of exciton dissociation into charge-transfer or charge-separated states at the interface between the two polymers. In the blend, the PFB emission at 2.7 eV quenches faster than the F8BT emission at 2.25 eV as excitons may also undertake Förster transfer to F8BT. In order to determine the average emission energy we fitted the PL spectra with a Huang-Rhys model [10], assuming a Gaussian density of emitting states with three vibronic replicas for each component. The optimized C-C stretch vibrational energies and Huang-Rhys factors were obtained from fitting the homopolymer spectra. The result for each component (in blend and pure films) is shown in (b) and (d) as a function of time after excitation. The average emission energies for all films shift roughly proportionally to the logarithm of time after excitation in accordance with the dispersive energy relaxation common in conjugated polymers [11,12]. For blend films, the average energies of both PFB and F8BT are initially higher than the corresponding energies for pure films and these energies decrease faster.

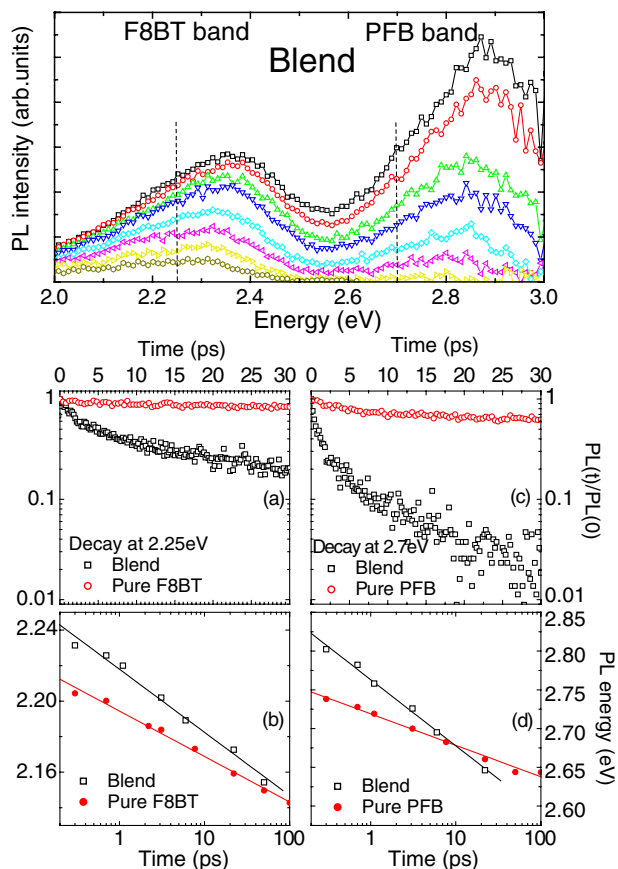


FIG. 2 (color online). (Top) Time-resolved PL of the blend film showing (from the top curve down) the PL dynamics from both PFB and F8BT components measured at 0.1, 0.3, 0.7, 1.1, 3.1, 6, 22, and 50 ps after excitation. The decay dynamics of the blend film at 2.25 eV [2.7] compared with that of the pure F8BT film [pure PFB film] are shown in (a) and (c). The average emission energy from the F8BT and PFB components of the blend film were also extracted and are shown in comparison with their pure-film counterparts in (b) and (d), respectively.

The higher average emission energies apparent at early times, and the faster energy relaxation in the blend, are the signature of a broadening of energy states for excitons in both blend components due to interaction at their hetero-interfaces [12,13]. This broadening can be such that some excitons experience an attractive, and some a repulsive interaction upon photoexcitation at heterojunctions. The blueshifted emission can then be explained, since excitons that experience an attractive interaction may undertake a charge-transfer process even at early times after excitation. As a result, they become quenched by transferring to states with low oscillator strength. In contrast, excitons that experience a repulsive interaction are still emissive and emit at higher energies. From the nanoscale phase segregation in the blend films we expect the presence of numerous molecular heterojunctions with various configurations, the majority of which should support a charge-transfer process upon excitation as there is a favorable energy gain from the band offsets, leaving a minority of hetero-

junctions with repulsive interactions to emit at high energies.

To understand qualitatively how the attractive and repulsive interactions arise, we consider the charge anisotropy along the copolymer chain both in the ground and excited states. PFB exhibits intramolecular charge transfer from the phenylenediamine (PB) group to the dioctylfluorene (F8) group upon photoexcitation as a result of asymmetries in electron affinities between the two groups. Similarly, F8BT has a strong asymmetric charge distribution localized towards the benzothiadiazole (BT) group with respect to the F8. Depending on their relative orientations at the heterojunctions (see Fig. 1), there can be either repulsive or attractive interactions. We simulated the interaction between PFB and F8BT for a variety of geometries. This was carried out by first optimizing, using B3LYP (6-31G basis set) density functional theory [14,15], the ground-state structure of each molecule containing 1–6 repeat units in the case of F8BT and 1–3 repeat units for PFB. The octyl side chains were excluded for both molecules to reduce computation time (these do not contribute significantly to the electronic excitations) [16]. The ground- and excited-state charge distributions were then obtained by combining the semiempirical intermediate neglect of differential overlap Hamiltonian [17,18] with a single configuration interaction technique in the ground-state geometry. We calculated first the change of the charge distribution of PFB upon photoexcitation, and then the associated change in Coulombic interaction with the F8BT ground-state charge distribution. The total interaction energy was determined by pairwise summation between charges on each atom of adjacent polymers for a range of PFB positions relative to the F8BT. One example of a map of the interaction energy is presented in Fig. 3, for the case in which the PFB backbone is slid parallel to the F8BT backbone for a range of x, y displacements. The calculated interaction energies range between -80 and 80 meV. The pattern reveals that strong interactions occur when the functional groups on the two chains are in close proximity to each other, indicating a local interaction between these functional groups. One of the repulsive configurations is displayed at the top of Fig. 3. Here, the F8 units of the PFB upon photoexcitation become partially negative and interact with the partially negative BT groups giving rise to a repulsive interaction. The attractive case is the converse when the PB groups are in close proximity to the BT groups.

The mechanism described here is a first-order effect of the electric field. Generally, the random orientation of polymer chains with respect to the electric field (here locally produced from functional groups) leads to a broadening of the emission spectra rather than a net shift—this situation may be different for small solvent molecules retaining sufficient freedom in the solid state to reorientate in the electric field of the solute molecule [19]. In the PFB/F8BT system, there is a tendency towards charge transfer between the two polymers due to their energy offsets

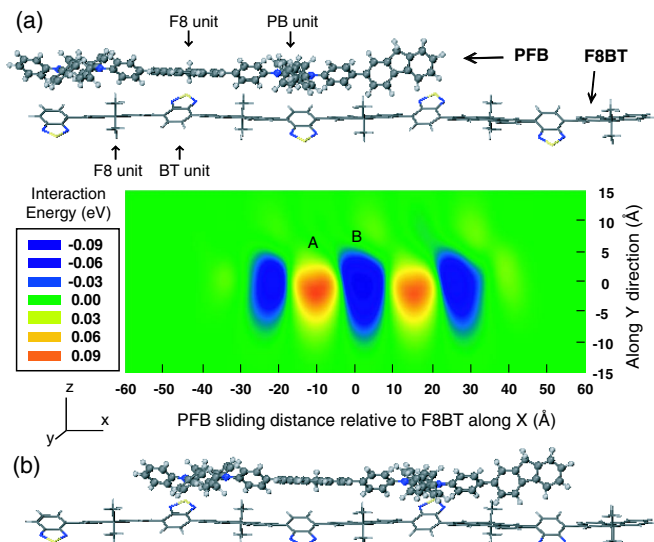


FIG. 3 (color online). At the top the PFB (2 repeat units) and F8BT (5 repeat units) ground-state structures are shown. The planes containing the two structures were slid parallel to each other with the separation distance of 0.45 nm. The contour plot shows, as a function of the position of the two planes, the Coulombic interaction energy between the PFB charge redistribution upon photoexcitation with the F8BT ground-state charge distribution. Positions marked A and B in the contour plot correspond to (a) and (b) arrangements (A: repulsive, B: attractive interaction). F8BT charge redistribution upon excitation interacting with the PFB ground-state charge gives a slightly more complicated pattern (not shown) with smaller interaction energy in the range of -20 to 20 meV.

allowing only those in repulsive orientations, or those far from the interface, to have large oscillator strength. Emission from chains in repulsive configuration leads to the net blueshift observed, whose magnitude depends on the nanoscale blend morphology. Such broadening of energy states is also a common feature in molecularly doped polymers [20] where it is caused by the presence of charged or dipolar species, rather than the functional groups inducing ICT in our system.

While we observe clear spectral shifts in the emission of PFB and F8BT through blending, their absorption is largely unaffected. This observation is in agreement with previous studies revealing the strongly delocalized nature of the absorbing state in π -conjugated systems [21,22]. Photon-echo experiments indicate that absorption is followed by a rapid (≈ 100 fs) conformational relaxation leading to a more localized excited state before emission [21]. Absorption therefore probes an average, charge-neutral environment while the localized emitting state is highly sensitive to local electrostatic interactions.

In summary, we have shown that different chain orientations at the interface between two copolymers with large ICT can give rise to either blueshifted or redshifted emis-

sion. This is the direct result of a strong intramolecular CT character that can have a directionally dependent interaction with the other chains causing either a repulsive or attractive interaction upon photoexcitation. The resulting interaction energies are sufficiently large either to suppress or to supplement the charge-transfer processes. Relative molecular orientation at the heterojunction will therefore have a considerable effect on device efficiencies. In addition, further configurational relaxation into long-lived exciplex states at heterojunctions can be detrimental to device yield unless the state can be efficiently regenerated into excitons or dissociated into free charges [6]. Our results therefore demonstrate that optimization of heterojunction performance requires control over both intermolecular configurational relaxation and relative molecular orientation at the interface.

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