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On the Energetic Dependence of Charge Separation in Low Bandgap Polymer/Fullerene Blends

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Supporting Information Placeholder

ABSTRACT: The energetic driving force required to drive charge separation across donor/acceptor heterojunctions is a key consideration for organic optoelectronic devices. Herein, we report a series of transient absorption and photocurrent experiments as a function of excitation wavelength and temperature for two low bandgap polymer/fullerene blends to study the mechanism of charge separation at the donor-acceptor interface. For the blend which exhibits the smallest donor/acceptor LUMO energy level offset the photocurrent quantum yield falls as the photon excitation energy is reduced towards the bandgap, but the yield of bound, interfacial charge transfer states rises. This interplay between bound and free charge generation as a function of initial exciton energy provides key evidence for the role of excess energy in driving charge separation of direct relevance to the development of low bandgap polymers for enhanced solar light harvesting.

Charge separation and recombination at organic donor/acceptor (D/A) heterojunctions is a key factor in the successful design of organic optoelectronic devices, including light emitting diodes and solar cells.[1-3] Minimizing the energy offset required to drive charge separation at this interface is a key consideration for optimizing the thermodynamic efficiency of such devices, including in particular the utilization of new donor polymers with lower optical bandgaps, and therefore improved harvesting of solar irradiation.[4-6] Semiconducting organic materials typically have dielectric constants of ~3. These low dielectric constants cannot screen the electrostatic interactions between opposing charges across the D/A interface, which can result in the formation of interfacial bound electron-hole (e-h) pairs. Often referred as charge transfer (CT) states, these e-h pairs have binding energies approximately one order of magnitude higher than kT.[7] Understanding what determines whether these interfacial states dissociate to form free charges is a key unresolved challenge for such organic optoelectronic devices.

Most models of charge photogeneration in organic materials derive from the Onsager theory for charge separation, which predicts the escape probability of photogenerated coulombically-bound electron-hole pairs from the laws of Brownian motion. [7-8] Building upon Onsager theory, Morteani et al. and Peumans and Forrest proposed that excess energy is an important factor in overcoming the electrostatic e-h attraction of the bound charges.[9,10] Two types of CT states were identified; relaxed CT states that predominantly recombine to ground state and "hot" CT states with enough excess energy to drive efficient charge dissociation. We note that these 'hot' CT states may correspond to different electronic states, and/or states with higher degrees of delocalisation.[11-13] The importance of excess energy was later supported by Ohkita et al. who showed, in a study of a series of polythiophene polymer/fullerene blends, that whilst the exciton separation was efficient for all the blends studied, the yield of dissociated charges correlated with the magnitude of the energy offset driving charge separation. This was assigned to 'hot' CT states being required to drive charge dissociation.[14,15] However, experimental evidence against the importance of large excess energy for charge separation has also been provided.[16-18] For example, Lee et al. used direct photocurrent spectroscopy to compare the device photocurrents in polymer/PCBM blends with a rather large energy offset for below and above band gap excitations, and concluded that charge generation in polymer/fullerene blends does not require large excess energy, but rather that the directly photogenerated CT state could undergo charge dissociation.[16] More recently, it was demonstrated that polaronic relaxation of such directly photo-generated CT states brings about CT localisation.[13]

In this letter, we report a study of charge photogeneration as a function of excitation wavelength in two low bandgap polymer/fullerene bulk heterojunctions with relatively small material energy offsets. Our studies employ both transient optical studies of polaron yields and innovative pump – push studies of CT state dissociation to show that, for systems with low driving energy for charge separation, the amount of excess energy injected onto the CT state determines the final yield of free charges.

Figure 1a displays the chemical structure of the BTT-DPP polymer used in this study, a small bandgap polymer with a

high hole mobility but exhibiting relatively inefficient charge generation from polymer excitons when blended with the widely used fullerene acceptor PCBM ([6,6]-phenyl C61-butyric acid methyl ester).[19] BTT-DPP/PCBM has no offset or 'driving force' for charge separation ~0.0eV, calculated by $\Delta E_{CSeff} = SE - (IP_D - EA_A)$.[20] This D/A pair was chosen because of its low ΔE_{CSeff} and poor charge generation properties, which make it a good candidate to investigate any possible excitation wavelength dependence of charge generation. A reference blend employed an analogous small bandgap polymer DPP-TT-T (structure shown in Figure 1a).[6] This polymer blended with PCBM has ΔE_{CSeff} ~0.15eV. It exhibits relatively efficient photocurrent generation, consistent with the larger energy offset favoring efficient charge dissociation, in agreement with our previous studies.[13,14]
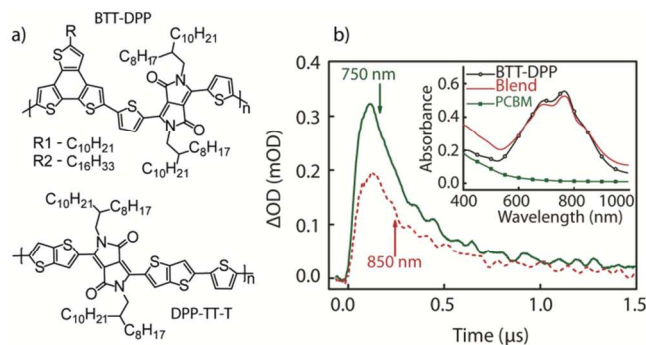

Figure 1. a) Chemical structures of BTT-DPP and DPP-TT-T. Two different batches of BTT-DPP with different sidechains were used for the pump-push photocurrent spectroscopy and TAS. Details of polymer synthesis are included in the supporting information (SI). b) Transient absorption decays at 750 and 850nm. Inset: steady-state absorption spectra of thin films of BTT-DPP, PCBM, and 1:1 BTT-DPP/ PCBM blend.

We employed transient absorption spectroscopy on the nano- to microsecond timescales to estimate the yield of photogenerated charges as a function of excitation wavelengths and temperature.[15,21] For the BTT-DPP/PCBM blend we first identified the maximum absorption of the positive polymer polaron to be at 1200 nm (Figure S3 in the SI). The decay dynamics of this polaron absorption signal fitted well to a single power law ($\Delta OD \approx t^{-\alpha}$) decay, characteristic of diffusion limited non-geminate recombination of trapped dissociated polarons.[14] We did not observe change in the exponent alpha with excitation wavelength. The negative PCBM polaron absorbs at 1050 nm with a low extinction coefficient. Therefore, the amplitude of the 1200 nm band reflects the photoinduced polaron concentration in the studied blends.

To explore the effect of excitation photon energy on charge separation, we recorded the amplitude of the transient absorption signal at 0.2μs as a function of excitation wavelength and thus constructed a transient-absorption excitation spectrum (TES). Displayed in Figure 2, the TES of the BTT-DPP/PCBM blend reveals that the quantum yield of charges depends on the wavelength of the excitation pulses. Notably, as the excitation wavelength is extended beyond 750 nm, the yield of photogenerated charges per absorbed photon is reduced. This is also visible in Figure 1b, in which the ΔOD transient for 750 and 850 nm excitation is plotted. This TES was compared to the photocurrent internal quantum efficiency of a corresponding BTT-DPP/PCBM photovoltaic

(PV) device (determined without correcting for optical interference effects). A good match between the TES and IQE spectrum is observed, consistent with our previous studies showing a close correlation between our transient absorption assay of charge generation and device photocurrent densities.[19,22] We note that for wavelengths >650 nm, PCBM absorption in the BTT-DPP/PCBM blend is negligible (<0.3%, inset Figure 1b). Therefore, the observed excitation wavelength dependence of charge photogeneration and photocurrent IQE between 650 and 900 nm can be assigned to the excitation of polymer excitons with different initial energies. In contrast to the BTT-DPP/PCBM blend, the control TES data with DPP-TT-T/PCBM blend showed no dependence upon excitation wavelength (Figure S4), consistent with the larger ΔE_{CSeff} for this blend enabling efficient charge generation for this blend.
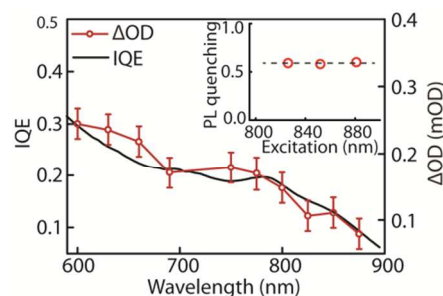

Figure 2. The TES (red open circles) of a BTT-DPP/PCBM blend was recorded at the polymer polaron band (1150 nm) at a 0.2 μs time delay. Error bars are one standard deviation combined with scaling uncertainty. Both the TES and the IQE of the corresponding device (black line) show similar increase in charge yields with excitation wavelength. Inset: photoluminescence quenching of the BTT-DPP/PCBM blend plotted as a function of excitation wavelength.

The TES and IQE data on Figure 2 demonstrate that the efficiency of charge generation can depend upon the energy of the photoexcited polymer excitons, so that excitons generated at the band edge yield fewer charges than excitons above the band edge. This property of the BTT-DPP/PCBM blend could derive from an excitation wavelength dependence of the exciton quenching. However, the results from photoluminescence quenching experiments as shown in the inset of Figure 2 indicate that quenching of the BTT-DPP singlet excitons is independent of excitation wavelength, which suggests that the efficiency of free charge generation is not determined by the exciton dissociation yields in this system.

To elucidate further the dynamics of charge separation and bound CT state formation we applied a novel ultrafast pump-push photocurrent technique, Figure S6.[13,23] In the experiment, a BTT-DPP/PCBM PV device is first exposed to a visible-light 200 fs pump pulse. After a certain delay time, a 2200 nm 250 fs IR 'push' pulse illuminates the PV device. This 2200 nm pulse is selectively absorbed by the hole polarons, as the neutral polymer chains are transparent in this spectral region whilst polymer polarons typically exhibit a strong absorption at this wavelength.[24] The IR 'push' pulse provides these hole polarons with excess energy, bringing them to an otherwise energetically-inaccessible 'hot' state. Therefore, bound charge pairs generated at the organic interface by the visible pump pulse can potentially be converted to free charge carriers with the help of the excess energy provided

by the push pulse. In the experiment, we detect the effect of the push pulse by monitoring the relative increase of the photocurrent output ($\delta J/J$) of the PV device. We note that free positive polarons contribute to the photocurrent J without the push pulse and thus do not affect the experimentally observable δJ, making the experiment selective solely to the ratio of bound/free polaron states generated by the pump pulse.
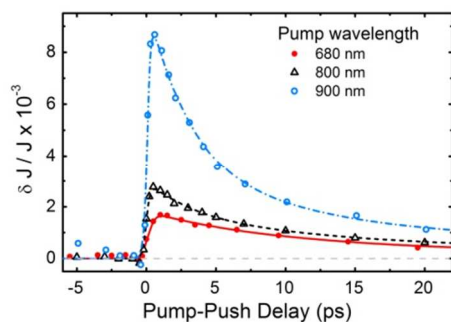

Figure 3. Results of pump-push photocurrent ($\delta J/J$) measurements on BTT-DPP/PCBM devices at different excitation wavelengths. Lines are exponential fits convoluted with the 200 fs response function.

Figure 3 shows the change in the photocurrent due to the 'push' pulse as a function of pump-push delay for the BTT-DPP/PCBM PV device excited at different pump wavelengths. In all experiments, when the 'push' pulse arrives before the 'pump', the effect on photocurrent $\delta J/J$ is negligible since there are very few charges in the cell to be influenced by the IR photons. When the 'push' arrives after the 'pump', the $\delta J/J$ increases for all the PV devices. This is a direct evidence of the existence of bound charge pairs at the D/A interface. The sharp increase in signal is dominated by a prompt component demonstrating that the majority of bound polarons are generated on an ultrafast timescale. Interestingly, as the energy of the pump photon decreases from 1.80 eV (680 nm) to 1.38 eV (900 nm) the amplitude of the $\delta J/J$ response increases dramatically. This provides direct evidence that the amount of bound charges is increasing (at least 2 times) with the decreasing amount of excess energy initially put into the exciton. This result is in qualitative and quantitative agreement with IQE and TES spectra. More importantly, the increase of the yield of bound charges with the pump wavelength indicates that the variations in the IQE and charge yields do not originate from inefficient exciton dissociation but rather from increased charge trapping in bound, relaxed interfacial CT states which are unable to dissociate efficiently. Another conclusion that may be drawn from the pump-push photocurrent experiments is based on the observation that bound states are formed very fast, within ~1ps after excitation. The absence of a growing component in the transients signifies that charge separation is not preceded by an extensive exciton migration and occurs locally.[25] However, much slower diffusion limited processes may also be present for a sub-ensemble of excitonic states due to possible different morphology configurations in the blends but not resolved in our experiment.

It is important to consider the role of inhomogeneity in the donor polymer. Though the absorption spectrum in Figure 1 shows evidence for vibronic structure, this is not partic-

ularly well developed and the long wavelength tail of the absorption is relatively shallow, both indications that there is a distribution of local π-π^* polymer band gaps associated with different local chain configurations. Thus, the local driving energy for charge separation will vary (being larger for larger bandgap regions of the polymer). Therefore, excitation of different colours in IQE, TES, or pump-push photocurrent experiments both controls the excess energy above the vibrationally-relaxed exciton and also can target different sub-ensembles of heterojunctions with a different electronic structure.
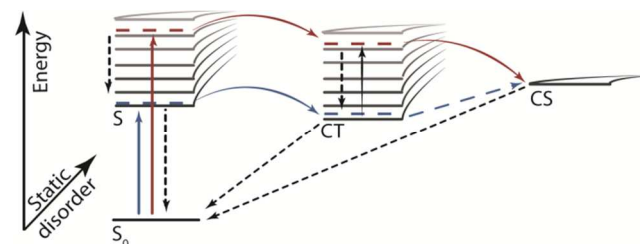

Figure 4. An energy level diagram depicting two charge separation processes initiated by light excitations with photons of high (red arrows) and low (blue arrows) energy.

To explain the observed excitation-wavelength dependent charge generation in the BTT-DPP blend we propose a qualitative model of charge generation as illustrated in Figure 4.[1,2] In this model, photon-to-charge conversion is realized by evolution through three state manifolds - singlet excitons (S), CT states and separated charges (CS). We assume that possible variations in the local morphologies create also a distribution of the manifold energies, which also causes the broadening of the absorption spectrum. During the charge separation, electron transfer from the polymer to the fullerene competes successfully with other non-radiative reaction pathways for exciton relaxation, such as thermal relaxation or internal conversion of the excitons to the bottom of the exciton band.[26-28] In this case, all photogenerated excitons, irrespective of their energy, can dissociate at the D/A interface and translate their excess energy to the CT state. This ultrafast reaction therefore generates different vibrational or electronic CT states with different excess energies. Both relatively "hot" CT states and relatively relaxed CT states will be populated depending on the energy of the exciting photons and on the local morphology/energy-level structure. However, the efficiency of dissociation of these CT states into free charges is dependent upon the amount of excess energy of the initially generated CT states.

The model presented in Figure 4 illustrates the concept that relaxed CT states and 'hot' CT states with insufficient high driving energy are not able to undergo efficient charge dissociation. This concept is consistent with these interfacial CT states exhibiting a significant coulomb binding energy and the proposal that efficient charge dissociation proceeds only from unrelaxed or 'hot' CT states. In order to test this issue further, we undertook additional tests on the charge photogeneration properties of the BTT-DPP and DPP-TT-T blends as a function of temperature. The results for both polymer/PCBM blends (Figure S5) showed temperature independent charge generation between 110 and 300K in agreement with previous studies of charge separation in polymer/fullerene blends.[29,30] This suggests that charge dissociation in both of these blends is not a thermally activated pro-

cess. Another conclusion, coming from the absence of temperature dependence data is strong trapping of charges in the relaxed CT state.

Previous studies of charge photogeneration as a function of excitation wavelength in polymer/fullerene blends have typically compared the response of blends to photoexcitations at or below the polymer bandgap.[12,16,18] Such studies have focused on blends such as P3HT:PCBM where bandgap excitation results in efficient charge generation, and have observed that photoexcitation below this bandgap into a weak absorption tail assigned to direct excitation of CT states can also result in efficient charge generation. In the present study, we took a different approach, employing a low bandgap polymer where the small LUMO level offset results in bandgap excitation generating only a relatively low yield of charges. This allows us to investigate whether above bandgap photoexcitation into strongly allowed optical transitions of the polymer results in enhanced charge generation. Our study therefore avoids the difficulties associated with interpretation of data from excitation of very low oscillator strength optical transitions and is moreover of direct relevance to technology drives to utilize lower bandgap polymers to enhance solar light absorption.[4-6]

In summary, we have performed a detailed study of the mechanism of charge photogeneration in a model organic D/A system with a relatively small driving force for charge separation. The charge photogeneration behavior of the blend film is found to be strongly dependent upon the photon energy used to generate the polymer excitons. Specifically, increasing this photon energy by ~0.2 eV above the optical band gap was observed to double the quantum yield of dissociated charges and the device photocurrent IQE, correlated with a substantial decrease in the yield of relaxed, bound interfacial charge transfer states. These data strongly support a model where charge dissociation is dependent upon the excess energy of initially generated 'hot' CT states overcoming their coulomb attraction. The particular mechanism of this dissociation probably involves relatively high level of delocalisation of 'hot' CT states.[13] These results thus provide new insight into the energy offsets required to drive charge dissociation at organic donor/acceptor interfaces which comprise the ultimate limits to the efficiencies achievable with organic photovoltaic heterojunctions.

ASSOCIATED CONTENT

Supporting Information. Synthesis of monomers and the BTT-DPP copolymer, 1H NMR and TGA analysis. Details of film and device preparation, transient absorption and pump-push photocurrent spectroscopy, temperature dependent and fluorescence measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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