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.3–5 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.5–8 Semi-conducting 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, Morte-ani 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.16–18 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.46 More recently, it was demonstrated that polaronic relaxation of such directly photo-generated CT states brings about CT localisation.11

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 C68-
butyric acid methyl ester).99 BTT-DPP/PCBM has no offset or
‘driving force’ for charge separation -0.05eV, calculated by
ΔE_{CSeff} ≈ SE - (IP_D - EA_L).99 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 poly-
mer DPP-TT-T (structure shown in Figure 1a).8 This poly-
mer blended with PCBM has ΔE_{CSeff} -0.15eV. It exhibits rela-
tively efficient photocurrent generation, consistent with the
larger energy offset favoring efficient charge dissociation, in
agreement with our previous studies.9,14

We employed transient absorption spectroscopy on the
nano- to microsecond timescales to estimate the yield of
photogenerated charges as a function of excitation wave-
lengths 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 (ΔOD≈t^{-α}).14 The power exponent α
was used for the pump-push photocurrent spectroscopy and
TAS. Details of polymer synthesis are included in the sup-
porting information (SI).

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 sup-
porting 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.

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 wave-
length and thus constructed a transient-absorption ex-
citation 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 pho-
ton 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 inter-
ference 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 densi-
ties.99,21 We note that for wavelengths >650 nm, PCBM ab-
sorption in the BTT-DPP/PCBM blend is negligible (<0.3%,
inset Figure 1b). Therefore, the observed excitation wave-
length dependence of charge photogeneration and photocur-
rent 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 genera-
tion for this blend.

Figure 2. The TES (red open circles) of a BTT-DPP/PCBM
blend was recorded at the polymer polaron band (150 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: pho-
toluminescence 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 ef-
ciciency of charge generation can depend upon the energy of
the photoexcited polymer excitons, so that excitons generat-
ed 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 photolu-
minescence quenching experiments as shown in the inset of
Figure 2 indicate that quenching of the BTT-DPP singlet ex-
citons is independent of excitation wavelength, which sug-
gests that the efficiency of free charge generation is not de-
termined 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 exper-
iment, a BTT-DPP/PCBM PV device is first exposed to a visi-
ble-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 polaron,
as the neutral polymer chains are transparent in this spectral
region whilst polymer polaron typically exhibit a strong
absorption at this wavelength.14 The IR ‘push’ pulse provides
these hole polaron 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 $\delta J$, making the experiment selective solely to the ratio of bound/free polaron states generated by the pump pulse.

![Figure 3](Image)

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. 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-

![Figure 4](Image)

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. 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. 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. This suggests that charge dissociation in both of these blends is not a thermally activated pro-
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.\textsuperscript{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 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.\textsuperscript{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 \(-0.2 \text{ eV}\) 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.\textsuperscript{19} 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, \(^{1}H\) 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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