Charge Pair Dissociation and Recombination Dynamics in a P3HT-$PC_{60}BM$ Bulk Heterojunction

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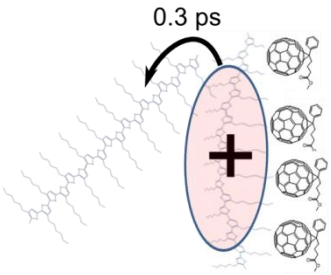
Abstract

The mechanism by which Coulombically bound charge pairs dissociate into free carriers in photovoltaic donor-acceptor blends is of great interest. Here we use polarization sensitive transient absorption (TA) to study the diffusion of photogenerated holes in a polythiophene (P3HT) - fullerene ($PC_{60}BM$) blend. We observe an initial anisotropy value of 0.4 for the absorption of photogenerated holes, indicating that holes generated on a 100 fs timescale are localized on the same polymer chain as their precursor excitons. Depolarization dynamics indicate fast initial hole motion on a 0.3-ps timescale and slower migration up to 100 ps. Charge pair recombination is found to occur on a much longer timescale of 10-1000 ns via a purely bimolecular process independent of excess energy. Our results show that nearly all charge pairs get separated by at least 7 nm in the absence of an external field, and indicate that high charge mobility is crucial for charge separation.



TOC Image

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Bulk heterojunctions formed by blending a conjugated polymer with an electron acceptor (usually a fullerene derivative) have attracted much attention due to their potential applications in organic photovoltaic (OPV) devices. The mechanism of photocurrent generation in OPV is still a matter of debate. There is considerable experimental evidence that charge separation proceeds through an intermediate state consisting of a Coulombically bound charge pair [1-15]. This charge pair may dissociate and produce spatially separated carriers, or it may recombine. An alternative proposed mechanism for charge generation is that free charges are generated directly from an initially delocalized precursor [16, 17]. Several studies have indicated that in some blends, excess energy transferred to the electron acceptor helps charge pair dissociation [6, 7, 14]. However, in efficient OPV blends the excess energy of neutral excited states with respect to the thermalized charge pairs does not appear to be important [1-5, 7]. Instead, it has been suggested that very high mobility of the photogenerated electrons and holes [2, 3, 5-7, 18-21] or dipole moments of charge transfer (CT) complexes at the interface [20, 22, 23] helps charge pairs to overcome the Coulomb attraction and separate.

In this letter we use polarized transient absorption (TA) dynamics to monitor the motion of holes in the conjugated polymer poly-(3-hexylthiophene) (P3HT) which are generated by electron transfer to the functionalized fullerene, phenyl-C60-butyric methyl ester (PCBM). We provide strong evidence that dissociation of Coulombically bound charge pairs is driven by high initial hole mobility rather than thermalization energy.

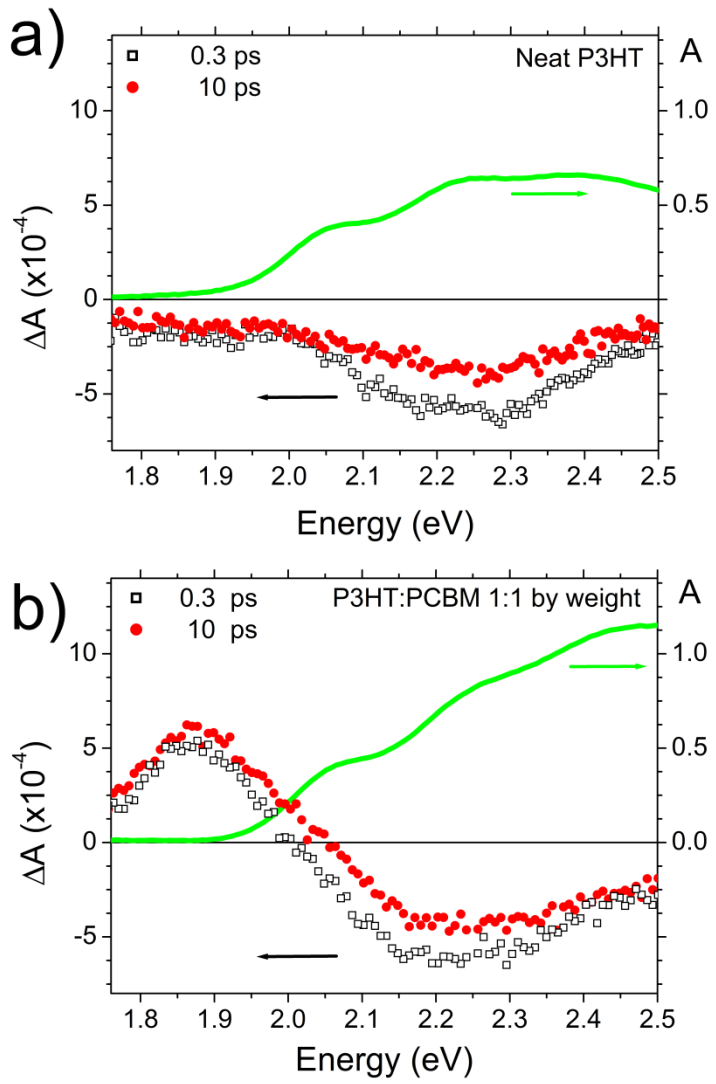

Figure 1 - Differential absorbance ΔA spectra at two different time delays (symbols) following 3.11 eV excitation for both a neat (a) P3HT film and (b) a P3HT:PCBM 1:1 by weight blend. Solid lines are ground state absorption spectra for the respective films.

Fig 1 shows TA spectra measured at 0.3 ps and 10 ps after excitation. A negative ΔA signal is observed at photon energies > 2eV which we assign to ground state bleaching. Between 2 eV and 1.76 eV where ground state absorption is very small, a negative ΔA signal in neat P3HT is observed and assigned to stimulated emission, whereas in the blend with PCBM we observe a positive signal signifying photo-induced absorption. We attribute this to absorption by photo-

generated charges. This is in agreement with previous studies which found that photo-induced absorption in this spectral region is dominated by hole absorption in polythiophene [8, 24-26]. Electron absorption on the C60 fullerene has been shown to consist of a sharp absorption feature in the near-infrared, so does not contribute to our measurements in the 1.76-2.5 eV region [27].

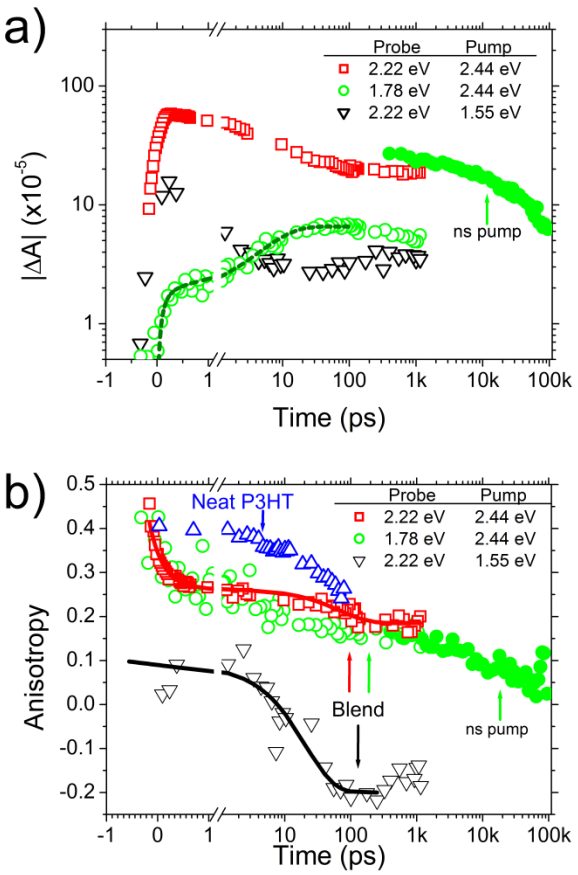

Figure 2- a) Magic angle TA kinetics of a P3HT:PCBM 1:1 blend measured with different pump and probe photon energies displayed as absolute values of ΔA signal. Absorbed photon densities were measured as ~ $1x10^{18}$ cm^{-3} for 2.44 eV excitation and estimated from signal strength as ~ $2x10^{17}$ cm^{-3} for 1.55 eV excitation. For the nanosecond pump data shown, the pump was 2.33 eV, the probe was 1.78 eV and the absorbed photon density was measured as ~$3x10^{18}$ cm^{-3}. The dashed line is a bi-exponential fit to the rise of the signal at 1.78 eV as described in the text. (b)

Polarization anisotropy of the signals shown in (a), solid lines are fits to exponential functions described in text. Polarization anisotropy data for a neat P3HT film pumped at 2.44 eV and probed at 2.22 eV is included for comparison. The time axis is linear to1 ps and logarithmic at longer times.

Fig 2a shows TA kinetics of a 1:1 P3HT:PCBM blend excited and probed at several different photon energies. Absorption at 2.44 eV excites predominantly P3HT chromophores. Absorption at 1.55 eV excites interfacial charge transfer (CT) complexes which have weak but non-zero ground state absorption and are formed by partial electron transfer from the ground state of the donor to the acceptor[28, 29]. We note that electron transfer from the neutral excited state of the donor to acceptor does not require the formation of a CT complex. Therefore, a bound charge pair generated following electron transfer from the donor may differ from a directly excited CT complex.

TA signals measured with probe polarizations parallel (ΔA_{para}) and perpendicular (ΔA_{perp}) to the excitation polarization were used to reconstruct "magic angle" transients using $\Delta A_{magic} = (\Delta A_{para} + 2\Delta A_{perp})/3$ which show only the population dynamics independent of polarization of probe light. The polaron absorption at 1.78 eV grows over time, and can be described by a two exponential rise. The fit indicates that 27 % of the total charge population grows in with a time constant of 0.11 ps, with the remainder of the charges generated with a time constant of 7 ps. This is consistent with previous studies of P3HT-PCBM 1:1 blends in which a significant proportion of charge pairs are generated on a sub 1-ps timescale by very fast electron transfer to PCBM [16, 26, 30, 31]. The TA kinetics at 2.22 eV (corresponding to the ground state bleach of P3HT) measured after excitation at 2.44 eV show an instantaneous rise, followed by a partial decay within 100 ps. This can be explained by the growth of an overlapping charge absorption signal

which has opposite sign to the bleach. Strong polaron absorption overlapping the bleach has been observed in neat P3HT by Österbacka et al [32]. Following excitation of interfacial CT complexes at 1.55 eV, we observe a partial decay on a 10 ps timescale which can also be explained by the growth of overlapping charge absorption as CT excitons dissociate into charge pairs. No ground state recovery is observed from 0.1 to 1 ns which indicates that charge pair recombination is negligible on this time scale for both excitation energies. We therefore attribute the small decay of the signal at 1.78 eV on a 0.1 to 1 ns timescale to changes in the charge absorption spectrum in P3HT as photo-generated holes diffuse in the blend.

To investigate the motion of the photo-generated charges, we calculate the time dependent polarization anisotropy *r* of TA signals defined by

$$r = \frac{\Delta A_{para} - \Delta A_{perp}}{\Delta A_{para} + 2\Delta A_{perp}} \qquad (1)$$

For a random distribution of rod-like transition dipoles in a 3D sample excited by a linearly polarized pump, a value of $r = 0.4$ indicates that the orientation of transition dipoles seen by the probe is parallel to the orientation of the initially excited dipoles, a value of $r = -0.2$ indicates that the dipoles being probed are perpendicular to the initially excited dipoles, whilst $r = 0$ indicates that transition dipoles have become uncorrelated. The dipoles may become uncorrelated through motion of excitations, dynamic localization or rotational diffusion (the latter does not occur in a solid film). This makes polarization anisotropy a useful tool to assess the motion of charges and excitons.

Polarization anisotropy is shown in Fig 2b. The initial anisotropy of both ground state bleach and photo-generated hole absorption in P3HT following 2.44 eV excitation is $r \approx 0.4$. This indicates that the holes generated on a 100 fs timescale by electron transfer from photo-excited

P3HT to PCBM are localized on the same polymer segment as their precursor P3HT excitons. Fitting a bi-exponential function to the 2.44 eV pump 2.22 eV probe anisotropy signal (shown by open squares) indicates that 36% of the anisotropy decays with a time constant of 0.3 ps, 19% decays with a time constant of 68 ps, and the long lived anisotropy of about 0.2 is preserved up to 1 ns. As mentioned previously, the signal measured at 2.22 eV is dominated by ground state bleach, but there is also overlapping hole ESA at this energy, and overlapping signals can make the interpretation of polarization anisotropy results problematic [33]. However, from Fig. 1 we see that there is no ground state absorption at 1.78 eV, and thus the signal at 1.78 eV has no contribution from bleach and is purely due to hole ESA. The depolarization dynamics exhibited at 1.78 eV are the same as those exhibited at 2.22 eV indicating that the anisotropy at both energies are associated with the same species, and that the anisotropy values obtained at 2.22 eV are unaffected by the presence of overlapping signals. Extending measurements at 1.78 eV to longer time with a nanosecond pump laser we observe full depolarization after 100 ns. The initial anisotropy value of 0.4 and the final value of 0 give further indication that this measurement is free from artifacts.

The depolarization observed in the blend is significantly faster than the depolarization of the ground state bleaching in neat P3HT film which is also shown in Fig. 2b and associated with migration of neutral excitations. On the basis of this difference we attribute the rapid depolarization in the blend to the migration of photo-generated holes. The percentage (36%) of depolarization which is fitted with a time constant of 0.3 ps and the percentage of charge pairs generated on a 100 fs timescale (27%) are similar, which indicates that the majority of photo-generated holes migrate on a 0.3 ps timescale. Comparing the ground state absorption spectra of the blend and of the neat P3HT film shown in Fig.1, we see that the optical density of both is

similar in the 1.8-2.2 eV region, however at 2.44 eV it is 40 % greater than that in the neat film. P3HT absorption in the 1.8 eV-2.2 eV region is largely due to crystalline regions, whereas at higher energies disordered chains dominate [34]. Thus this difference at 2.44 eV is mainly due to absorption by disordered P3HT chains, as PCBM has very weak absorption at this energy. This indicates that the addition of fullerene increases the number of disordered P3HT chromophores by ~ 40% which are likely to be located in close proximity to fullerene molecules. Upon excitation these disordered P3HT chromophores donate electrons to PCBM very quickly which agrees with ~ 30% of charges generated on a 100 fs timescale. In contrast, excitations on ordered P3HT chromophores are further away from PCBM molecules and thus undergo much slower electron transfer on a picosecond timescale. Therefore, we attribute the rapid depolarization in the blend to the initial hopping of photo-generated holes in disordered P3HT chains near the interface with the fullerene.

The anisotropy following 1.55 eV excitation starts at $r \approx 0.1$ then changes sign to give a value of $r = -0.2$ between 100-300 ps. An anisotropy of -0.2 indicates that the transition dipole of the bleached ground state absorption (GSA) observed at 100-300 ps is perpendicular to the absorption dipole of the ground state interfacial CT complex. This is expected as the absorption dipole of the ground state CT complex is orientated from P3HT to the fullerene and the transition dipole of the bleached GSA is along the P3HT chain. The initial value of $r = 0.1$ indicates that the transition dipole orientations of the CT excitation and of the initial GSA are weakly correlated, which can be explained by the mixed nature of the CT absorption transition which has contributions from delocalized neutral excitations of P3HT and PCBM and from the pure CT transition. The change in anisotropy from 0.1 to -0.2 can be fitted with a time constant of $\tau = 20$ ps which we attribute to the splitting of the CT exciton into a charge pair where the hole is

localized on one polymer chain and the corresponding dipole of the bleached GSA is along the polymer chain. Partial depolarization is observed between 100 and 1000 ps which we attribute to charge pair dissociation and subsequent hole motion. Slower dissociation of CT states compared to bound pairs generated by electron transfer can be explained by higher binding energy of CT states. This is expected because the CT states have a transition dipole associated with ground state absorption which require non-zero overlap of the ground state and excited state wave-functions. Thus the effective distance between charge pairs in the CT state will be small.

Grancini *et al.* have reported polarized TA measurements probed at 1.94 eV with sub micrometer resolution in a P3HT:PCBM blend [35]. At the border between P3HT rich and PCBM rich domains they observed an initial positive anisotropy of ~0.2 which changed sign to -0.2 in 10 ps and remained fairly constant for 200 ps. These results are somewhat different from those reported in this letter, which may be due to the use of higher excitation photon energy and (deduced from the signal strengths) higher excitation densities than in the results we report here.

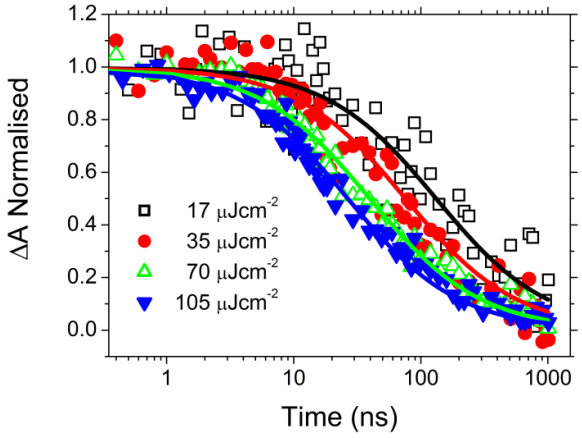

Figure 3 - Symbols are magic angle TA kinetics probed at 2.22 eV following excitation at 2.33 eV. Solid lines are fits to Eqn. (2) which give $\gamma = 3.8 \pm 0.1 \times 10^{-12}$ $cm^3 s^{-1}$. Excitation densities are shown in the inset.

In order to distinguish whether the holes we are observing are spatially separated from electrons or trapped in charge pairs we carried out TA measurements for a range of excitation densities over a broad timescale, the results are shown in Fig. 3. These traces can be fitted very well with equation (2) which describes a purely bimolecular process with a function *G*(t) describing the generation of charges. This indicates that charge recombination is non-geminate. The bimolecular recombination rate constant of $\gamma = 3.8 \pm 0.1 \times 10^{-12}$ cm^3s^{-1} is in excellent agreement with the previously published value [36].

$$\frac{dn}{dt} = G(t)n(0) - \gamma n(t)^2 \qquad (2)$$

For charges to show purely non-geminate recombination at a particular excitation density, the electron-hole separation in each geminate pair has to be larger than the mean distance between geminate pairs. This is because non-geminate recombination requires that a hole is just as likely to recombine with an electron generated from any another charge pair as it is to recombine with its geminate partner, and therefore must travel far enough to encounter other electrons. The lowest incident pulse density at which non-geminate recombination is observed of 17 μJcm^{-2} gives an initial exciton density of $n(0) = 3 \times 10^{18}$ cm^{-3}. Assuming that each exciton splits into a geminate pair we can estimate the mean distance between pairs to be $n(0)^{-1/3} = 7$ nm. This value is a lower bound for the separation distance of a geminate pair and is good agreement with separation distances obtained in a P3HT:PCBM blend using direct measurements of ultrafast charge mobility and Monte Carlo simulations for zero electric field [21].

The fact that no ground state recovery is observed up to 1 ns in Fig. 2a indicates that charge pair recombination is negligible on this timescale even following the direct excitation of

interfacial CT complexes. We note that we have no external field to assist dissociation, in contrast to previous studies which arrived at a similar conclusion[1-5, 7].These results are summarized in the scheme provided in Fig 4.

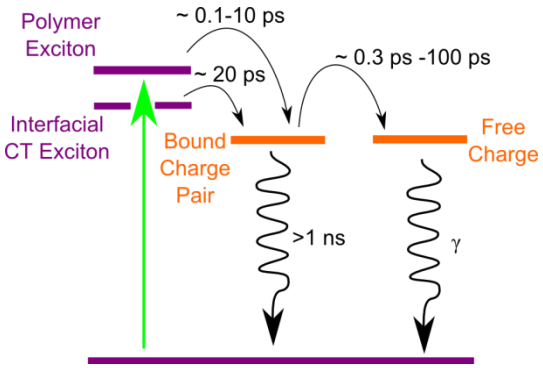

Figure 4 – Schematic of photoinduced processes in P3HT:PCBM blend studied in this work.

To achieve the 7 nm separation distance, charges have to make many sequential hops along and between chains, and the time for this separation according to depolarization dynamics in Fig 2 extends beyond 1 ns. The excess thermal energy released by relaxation of higher CT states can help fast hole motion in the first picosecond but would have no effect on the longer time scale. Direct excitation of CT complexes with 1.55 eV without excess energy also gives efficient charge separation. For the charge separation rate to be faster than geminate recombination there must be a driving force for charge pair dissociation other than excess energy, and/or charges should be sufficiently mobile to overcome Coulombic attraction [2, 3, 5-7, 18-21]. From the results presented here, it is not possible to specify if there is any driving force for dissociation but theoretical arguments have been put forward for interfacial dipoles [20, 22, 23] and structural disorder of the polymer [37] providing a potential energy gradient away from the interface.

Our results pertain only to the dynamics of hole polarons in this blend. Electron dynamics in P3HT-PCBM blends have been studied by Pensack and Asbury using ultrafast solvatochromism assisted vibrational spectroscopy [3]. They found that electron transport from the interface to the

bulk occurred on a broad timescale from 10 ps to several nanoseconds. These results and the observations we report in this letter suggest that charge pair dissociation is driven by fast motion of both types of carriers in P3HT:PCBM blends.

In summary we found that Coulombically bound charge pairs are generated via two processes- electron transfer by P3HT excitons to PCBM on a timescale of 0.1 to 10 ps, and by splitting of directly generated interfacial CT states on a 20 ps timescale. The excess vibrational energy received by the electron following charge transfer has no measurable effect on the recombination kinetics. Charge pairs dissociate with near 100 % efficiency aided by fast hole motion away from the donor-acceptor interface.

Experimental Methods

P3HT with a regio-regularity of 98.5 % and a number averaged molecular weight of 76000 $gmol^{-1}$ was obtained from Merck. $PC_{60}BM$ was obtained from Solenne. Materials were dissolved in chlorobenzene with a 1:1 P3HT:PCBM mass ratio. Solutions were spin coated onto quartz discs and then thermally annealed at 140 ^{o}C for 20 minutes, all in the nitrogen environment of a glove box. They were then transferred to a high vacuum ($5x10^{-5}$ mbar) for transient absorption measurements.

Polarization sensitive TA measurements in the time range of < 1 ns were performed using light pulses with a pulse duration of ~100 fs generated in an optical parametric amplifier pumped by an amplified femtosecond laser at 5 kHz. Probe pulses were delayed using a motorized translation stage, which allowed us to scan through time. Probe polarization was set 45^{o} relative to that of the pump before focusing onto the sample. After the sample, a Glan polarizer was used to split the probe light into two components with polarizations parallel and

perpendicular to that of the pump and each was detected using a silicon photodiode. A beam chopper was used to modulate the repetition rate of the pump pulses at 2.5 kHz and the pump induced changes were measured with lock-in amplifiers. The pump area at $1/e^2$ of peak intensity was $5x10^{-3}$ cm^2 and that of the probe was $1x10^{-3}$ cm^2, both were measured with a Coherent beam-profiler.

For TA measurements in 0.5 – 1000 ns range, the apparatus was identical to the system described above, except that pump pulses of 0.5 ns duration were generated by an actively Q-switched laser and electronic delay between pump and probe pulses was introduced by a Stanford Systems delay generator.

For spectrally resolved TA measurements, the apparatus was as described for polarization sensitive TA, but with white-light probe generated by focusing the 800 nm output of the amplified femtosecond laser onto a rotating CaF disc. This was then focused onto the sample by parabolic mirrors, before being spectrally separated by a prism and collected on a photodiode array. Differential absorption was calculated using a home-made computer program which separated photodiode spectra with and without pump based on an electronic trigger.

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