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Photogeneration and Ultrafast Dynamics of Excitons and Charges in P3HT/PCBM Blends

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The photogeneration quantum yield and dynamics of charge carriers and excitons in thin films of neat regioregular poly(3-hexylthiophene) (P3HT) and blends with [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) were studied with ultrafast optical pulse—probe spectroscopy. In neat P3HT the quantum yield for direct photogeneration of charge carriers amounts to 0.15 per absorbed photon. The remaining fraction of absorbed photons leads to formation of excitons. Recombination of charges reduces the quantum yield to about 25% of its initial value on a time scale of 100 ps followed by decay to a no longer observable yield after 1 ns. Addition of 50% PCBM by weight leads to ultrafast (<200 fs) formation of charge pairs with a total quantum yield of 0.5. The presence of 50% PCBM causes exciton decay to be about an order of magnitude faster than in neat P3HT, which is expected to be at least in part due to interfacial exciton dissociation into charge carriers. The yield of charges in the blend has decayed to about half its initial value after 100 ps, while no further decay is observed within 1 ns. The small fraction (~1%) of excitons in neat P3HT that is probed by photoluminescence measurements has a lifetime of 660 ps, which significantly exceeds the 200 ps lifetime of nonfluorescent excitons that are probed by transient absorption measurements. The nonfluorescent excitons have a diffusion coefficient of about $2 \times 10^{-4}$ cm$^2$/s, which is an order of magnitude smaller than reported values for fluorescent excitons. The interaction radius for second-order decay of photoexcitations is as large as 8–17 nm, in agreement with an earlier result in the literature.

1. Introduction

Conjugated polymers are of great promise for application as light-absorbing and charge-transporting components in cheap and mechanically flexible photovoltaics.1,2 In a polymer-based photovoltaic device light absorption by the polymer usually results predominantly in formation of Coulombically bound electron−hole pairs in the form of excitons and to some extent into direct generation of free charge carriers.3−7 The excitons must dissociate into free charges that can contribute to the photocurrent. To realize this, the polymer is brought into contact with an electron-accepting material. In its most simple configuration the photovoltaic device consists of a bilayer of the light-absorbing conjugated polymer and an electron-accepting layer. Excitons must then diffuse through the polymer layer to reach the interface with the electron acceptor, where they can dissociate into free charges. To absorb most of the incident sunlight the polymer layer thickness needs to be about 100 nm, which largely exceeds the exciton diffusion length. Hence, in the above-mentioned bilayer configuration most excitons cannot reach the interface with the electron acceptor, which severely limits the device efficiency. To overcome this, the polymer and electron acceptor can be blended to form a bulk-heterojunction.1,2 To date, some of the best efficiencies (near 5%) have been reported for devices based on a thin blend film of the conjugated polymer regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) as electron acceptor.8 Owing to the promising prospects for use of this blend in a photovoltaic cell, the nature and dynamics of photoexcitations in P3HT and blend films with PCBM have been subject of several time-resolved spectroscopic studies.4,6,9−17 Despite these efforts, there is still much debate about the nature of primary photoexcitations in P3HT and blend films with PCBM. There is a consensus that the primary photoexcitations in P3HT solutions are intrachain singlet excitons.16 Photoexcitation of regioregular P3HT in a thin film leads to significant generation of free charge carriers in addition to excitons.4,6,10−13,15 An initial quantum yield for photogeneration of charges as high as 30% has been reported for regioregular P3HT.6 This value is much higher than for other conjugated polymers.16 The high charge-carrier yield in regioregular P3HT has been attributed to strong coupling between neighboring polymer chains, resulting from the microcrystalline lamellar stacking.18 The presence of PCBM in a P3HT/PCBM blend film gives rise to photoluminescence (PL) quenching19 and formation of long-lived free charges,20 which can be extracted from a photovoltaic device with an internal quantum efficiency as high as ~0.8.21 Since the PL quantum yield in P3HT is of the order of only 1%,6,22 the PL cannot be considered as representative for the majority of excitons that undergo nonradiative decay. Owing to the small PL quantum yield and the high initial yield of charges in photoexcited P3HT, it cannot be inferred that charge generation in a P3HT/PCBM blend occurs via the conventional pathway of exciton diffusion followed by dissociation into charges at an interface with PCBM.

The aim of this study is to examine the nature and dynamics of the primary photoexcitations and the role of PCBM in charge separation and collection in P3HT/PCBM blends. Using ultrafast
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2. Experimental Methods

Electronic grade regioregular P3HT (90–93% regioregularity) was purchased from Rieke Metals and was used as received. PCBM was acquired from Solenne (99.5% purity). Solutions of P3HT, as well as of blends with 5% or 50% PCBM by weight, containing 8 mg/mL polymer were prepared by dissolving the compounds in 1,2-dichlorobenzene (Sigma-Aldrich, anhydrous, 99%). Solutions were filtered using 0.45 µm PTFE filters to remove any insoluble aggregates. Films were spin-coated on quartz substrates and annealed for 30 min at 150 °C. The thickness of the samples was ∼30 nm, as measured with a step-profilometer (Dektak 8, Veeco). The sample preparation, post treatments, and optical measurements were performed in an inert N2 atmosphere.

Ultrafast measurements of transient changes of the optical transmission of the samples were carried out using a pump wavelength of 500 nm (2.5 eV) in combination with probe pulses in the range 600–1800 nm (0.7–2.1 eV) or using pump pulses at 530 nm (2.3 eV) with probe pulses at 3100 nm (0.4 eV). The measured fractional transmission signals, called transient absorption in the following, are given by \( \Delta T / T = -I_{\text{on}} / I_{\text{off}} \), where \( I_{\text{on}} \) denotes the probe transmission with pump on, and \( I_{\text{off}} \) the probe transmission with pump off. With this definition, an increase in absorption yields a positive TA signal, while bleach and emission yield negative TA signals. The laser systems have been described elsewhere. Briefly, a Ti:Sapphire regeneratively amplified laser system (Mira-Legend USP, Coherent) running at 1 kHz was used to generate 60 fs pulses at 795 nm with an energy of 2.5 mJ/pulse. Optic pump–probe transient absorption (TA) spectroscopy, it is demonstrated that charges are generated by (1) photoexcitation of P3HT and ultrafast (<200 fs) electron transfer to PCBM in the vicinity, (2) direct photogeneration of electron–hole pairs within P3HT followed by electron transfer to PCBM, and (3) exciton diffusion from P3HT to an interface with PCBM followed by electron transfer to PCBM. Photoexcitation of a neat P3HT film results in an initial quantum yield of 0.15 charges pairs per absorbed photon. In a blend containing 50% PCBM by weight, the yield of charge pairs increases to 0.5 within the time-resolution of the measurements (∼200 fs). Diffusion-controlled exciton quenching at the P3HT/PCBM interface occurs on a longer time scale of ∼20 ps, bringing the internal quantum efficiency for charge generation to the value of 0.95.

3. Results and Discussion

3.1. Optical Absorption and Emission. Figure 1 shows the optical attenuation spectra of the neat P3HT film and the blends containing 5% or 50% PCBM weight fraction. The spectra exhibit the characteristic π→π* band due to electronic transitions in P3HT. The shoulder near 2 eV is due to interchain excitons, resulting from π-stacking of the polymer chains in lamellar aggregates. The absorption of the 50% blend at higher photon energy is due to PCBM, as is evident from comparison with the absorption spectrum of PCBM in chloroform solution.

It can be seen in Figure 1 that the PL yield decreases with the PCBM content. The PL yield is already quenched by a factor of 5 when adding 5% PCBM and is further quenched by an additional factor of 3 in the 50% blend. The degree of PL quenching is consistent with previous studies on P3HT/PCBM and is generally ascribed to exciton quenching at the polymer/acceptor interface. This conclusion was also reached for various other systems including P3HT/nc-ZnO, MDMO-PPV/PCBM, and P3HT/F8BT. Exciton quenching is also manifest in a reduction of the PL lifetimes when PCBM is present, see Figure 2A. Despite the dispersive character of the PL decays, they could be satisfactorily fitted by a sum of two exponentials convoluted with the instrument response function. Taking this form to describe the PL decay does not imply the presence of two types of excitons, but is only used to remove effects of the instrument response time, which makes comparison of PL and TA data possible. The PL decay times are presented in Table 1 in terms of the 1/e decay times obtained after this process.

Figure 1. Optical attenuation (full lines, right vertical axis) and photoluminescence (dotted lines, left vertical axis) spectra of P3HT (black) and blends with 5% (red) and 50% (green) PCBM. \( F_A \) is the fraction of photons absorbed.

\[
F_A = 1 - \left( \frac{I_T + I_R}{I_0} \right)
\]

where \( I_0 \) is the incident light fluence. Attenuation spectra were recorded before and after completing the pump–probe laser measurements to ensure that there was no sample degradation.

Photoluminescence spectra and decay kinetics were recorded by time-correlated single-photon counting (LifeSpec-ps, Edinburgh Instruments). Samples were excited with a pulsed diode at 404 nm. The decay transients were deconvoluted with the instrument response function, resulting in a time resolution of 10 ps.
650 nm and Transient Absorption, exciton quenching by the acceptor becomes the dominant decay process, leading to the same decay kinetics for fluorescent and nonfluorescent excitons.

The change in TA lifetime when PCBM is present is related to the rate of exciton diffusion and quenching. Albeit that exciton diffusion is likely to be dispersive, an insight into exciton diffusion and quenching can be obtained by assuming a normal diffusion-controlled quenching rate, \( k \), so that

\[
k = \frac{1}{\tau} = \frac{1}{\tau_0} = 4\pi RD_eN
\]

where \( \tau_0 \) is the exciton lifetime in neat P3HT, \( \tau \) is the lifetime in the blend with PCBM, \( R \) is the radius for quenching of an exciton by a PCBM molecule, \( D_e \) is the exciton diffusion coefficient, and \( N \) is the number density of PCBM molecules. Using the TA exciton lifetimes for neat P3HT and the 5% blend from Table 1, it is found that \( RD_e = 2 \times 10^{-11} \text{ cm}^2/\text{s} \). Taking the reaction radius equal to half the intrinsic persistence length of P3HT, \( \text{i.e., } R = 1 \text{ nm} \), \( 30 \) yields for the exciton diffusion coefficient \( D_e = 2 \times 10^{-4} \text{ cm}^2/\text{s} \). This value and \( \tau_{TA} = 200 \text{ ps} \) from Table 1 give a diffusion length \( \Lambda_e = \sqrt{D_e\tau_{TA}} = 2 \text{ nm} \) for the nonfluorescent excitons in neat P3HT, which is close to that reported previously.\(^{31} \) It is interesting to note that the above values for \( D_e \) and \( \Lambda_e \) are significantly smaller than those obtained for fluorescent excitons from PL quenching measurements (\( D_e > 5 \times 10^{-3} \text{ cm}^2/\text{s} \),\(^{32} \) \( D_e = 1.8 \times 10^{-3} \text{ cm}^2/\text{s} \),\(^{33} \) \( \Lambda_e = 6.5-8.5 \text{ nm} \)). To some extent this can be due to the fact that PCBM molecules in the 5% blend are partly clustered, which leads to a smaller effective number density. Hence, in the present work the number density, \( N \), in eq 3 might be overestimated.

However, diffusion of fluorescent excitons is likely to be more efficient than for those decaying nonradiatively, since the Förster rate for exciton transfer increases with the dipole oscillator strength for decay to the ground state.\(^{35} \)

The exciton quenching rate obtained from eq 2 with the \( \tau_{TA} \) values in Table 1 for the 50% blend is approximately four times higher than for the 5% blend. This is much smaller than the 10-fold difference in PCBM content. The sublinear scaling of the quenching rate with the PCBM content can be attributed to formation of PCBM clusters in the 50% blend, which leads to a smaller interfacial area between P3HT and PCBM.\(^{30} \)

**3.2. Effects of Photoexcitation Density.** At higher pump laser fluence, excitons and charge carriers are generated in closer proximity and it becomes more likely that they encounter each other during their lifetime. In that case the transient species can undergo second-order decay by mutual interactions, such as exciton–exciton or exciton–charge annihilation.\(^{36,37} \) To get insight into the importance of second-order decay, the dependence of the TA transients on pump fluence was studied at different probe wavelengths. Owing to the thinness of the films used, approximately one-third of the incident pump photons (500 nm, 2.5 eV) are absorbed, see Figure 1. This results in a rather homogeneous excitation density in the film.

A representative example of the fluence dependence of the TA transients for neat P3HT at a probe photon energy of 1.25 eV is given in Figure 3. As will be discussed below, the TA at this probe energy is due to both excitons and charges. The transients have been normalized to the number of photons absorbed per unit area, \( I_0 F_A \), with \( I_0 \) the incident fluence and \( F_A \) the fraction of absorbed photons. For the two lowest values of the pump fluence the TA transients are identical and second-order decay processes are insignificant. However, for a pump fluence of 6 µJ/cm² or higher the initial amplitude of the normalized TA transients decreases and the decay becomes...
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3.3. Assignment of Transient Absorption Due to Excitons and Charges. Transient spectra for different delay times after photocexcitation at 500 nm are shown in Figure 4, for neat P3HT and the films containing 5% or 50% PCBM by weight fraction. At short delay times, 500 fs, the films exhibit very similar spectral features. The transient spectra show a broad photoinduced absorption that extends from 0.8 to 1.4 eV. A negative signal is observed in the 1.6–1.8 eV range, which coincides with the photoluminescence of P3HT (see Figure 1) and may therefore be identified as stimulated emission (SE). At probe energies above 1.9 eV, the photo-bleaching (PB) of the ground-state absorption can be observed. Interestingly, for the 50% blend the TA at 0.8–1.4 eV is quenched by approximately a factor two on an ultrafast time scale within 500 fs.

At 10 ps after the pump pulse, a faster TA decay is already evident on the low-energy side of the main absorption feature for the samples containing PCBM. After 100 ps the absorption below 1.1 eV has vanished for the 50% blend. At 1 ns after excitation, the TA for neat P3HT has completely decayed at all probe energies, while a broad absorption extending from 1.1 to 1.9 eV is apparent for the blends. In addition, there is a small absorption below 0.8 eV. The expected effect of adding PCBM is to quench the excitons and enhance the charge yield and lifetime by separation of the electron and hole. On the basis of this reasoning, it is concluded that the TA in the region 0.8–1.1 eV is due to excitons only. At higher probe energies the TA at short times is due to both excitons and charges, while at longer times after decay of excitons, the remaining charges in the blends give rise to a TA band in the range 1.1–1.9 eV and below 0.8 eV.

The assignments of TA to excitons and charges are reinforced when considering TA transients at different probe energies, examples of which are shown in Figure 5. The decay of the TA due to excitons at 0.9 eV (Figure 5A) becomes faster as the PCBM content increases, as expected. This directly reflects exciton quenching by PCBM with 1/e decay times listed in Table 1. At 1.25 eV (Figure 5B) the initial decay is similar for all samples and starts to differ only after a few tens of picoseconds when a long-lived component associated with the presence of

Figure 3. Effect of pump fluence at 500 nm on TA transients for neat P3HT at a probe energy of 1.25 eV. The transients have been normalized to the number of absorbed photons per unit area. The horizontal scale is linear until 1 ps and logarithmic from then to 1 ns.

Figure 4. Transient absorption for neat P3HT (black) and blends with 5% (red) and 50% (green) PCBM following excitation at 500 nm. The TA data are normalized by the number of absorbed pump photons per unit area. The open circles in the lowest panel correspond to data for the 5% blend scaled by a factor 5.
6. Recombination of charges reduces the quantum yield to about indicating that charges are immediately generated, see Figure 6. A fast rising signal is observed for neat P3HT, energy of 0.4 eV, for which it is commonly accepted that only additional measurements were performed with a probe photon changes as a function of time and wavelength. SE and (electro)absorption, the relative importance of which early times). In actuality, this can be due to the summation of amount of charges if only one wavelength is probed (by fortuitous selection of a wavelength which has zero signal at of the TA. This may be misinterpreted as a growing in of the to charges becomes dominant, which appears as an in-growth As the excitons decay during time, the (electro)absorption due to charges is evident only for the blends, while the TA for neat P3HT has vanished after 1 ns. The initial decay at 1.25 eV is the same for all samples and equal to that for excitons in neat P3HT probed at 0.9 eV (Figure 5A). At 1.25 eV both excitons and charges contribute to the TA and apparently the faster decay of excitons in the blends is compensated by an increased number of charges. At times longer than 100 ps the charges are dominant. The absorption due to charges is broad and extends to the absorption onset. This is due to the overlap of the absorption by charges with the photoinduced electroabsorption, which is related to the Stark shift of the absorption onset due to the presence of charges. At 1.8 eV (Figure 5C) the initial signal is negative due to a dominant role of SE from excitons. As the excitons decay during time, the (electro)absorption due to charges becomes dominant, which appears as an in-growth of the TA. This may be misinterpreted as a growing in of the amount of charges if only one wavelength is probed (by fortuitous selection of a wavelength which has zero signal at early times). In actuality, this can be due to the summation of SE and (electro)absorption, the relative importance of which changes as a function of time and wavelength.

In order to elucidate the kinetics of charge carrier generation, additional measurements were performed with a probe photon energy of 0.4 eV, for which it is commonly accepted that only charges absorb. A fast rising signal is observed for neat P3HT, indicating that charges are immediately generated, see Figure 6. Recombination of charges reduces the quantum yield to about 25% of its initial value on a time scale of 100 ps followed by decay to a no longer observable yield after 1 ns, see Figures 6 and 5B, respectively. On addition of PCBM, an increase of the initial yield of charges is observed, with no in-growth observed within the time resolution (<150 fs). This ultrafast increase in the charge population correlates with the immediate reduction of the TA associated with excitons when adding 50% PCBM, see upper panel in Figure 4. It can be concluded that there is an ultrafast reaction of part of the photogenerated excitons with PCBM.

The yield of charges in the blend has decays to about half its initial value within 100 ps, while no further decay is observed on a time scale of 1 ns, see Figures 6 and 5B, respectively. This does not necessarily mean that excitons do not diffuse to an interface with PCBM to undergo delayed separation into charges. The TA signal due to delayed charge formation may be compensated by geminate recombination, transfer of free electrons from P3HT to PCBM, and/or depolarization of the diffusing charges. In order to investigate the effects of depolarization in the TA signals at 0.4 eV, additional measurements (data not shown) were performed where the polarization vector of the probe light was taken perpendicular to that of the pump. In this situation, a similar decay to that measured in the parallel pump and probe configuration was observed, which indicates that polarization memory decay cannot account for the decay of the signal related to charges.

3.4. Yields of Excitons and Charges. The PCBM anion (PCBM−) absorbs only weakly at 1.2 eV, and therefore, the TA is determined by excitons and positive and negative excess charges in P3HT. Because PCBM scavenges negative charges, the charge balance in the polymer is broken for the blends and positive and negative charge carriers should be counted separately. The initial quantum yield of charges and excitons per absorbed photon can be determined from the TA signals due to these species at 0.4 and 0.9 eV, respectively, by considering the relevant processes depicted in Scheme 1. Photoexcitation of neat P3HT leads to formation of positive and negative charges with quantum yield, η, and to excitons with yield, 1 − η. If a blend with PCBM a fraction, χ, of the photons is absorbed sufficiently far away from an interface with PCBM to yield charges and excitons in P3HT with quantum yields identical to those for neat P3HT. The remaining fraction (1 − χ) of photons is absorbed sufficiently close to an interface with PCBM to give rise to formation of P3HT+ and PCBM− within the time-resolution of ~200 fs. Hence, the amplitude of the TA due to excitons in neat P3HT is proportional to (1 − η) and in the blend to χ(1 − η). At 500 fs the TA near 0.9 eV due to excitons only. In the 50% blend it has an amplitude ~0.6 times that for
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SCHEME 1: Nature and Yields of Transient Species Produced upon Photoexcitation of Neat P3HT and a Blend with PCBM as Electron Acceptor

![Diagram of Scheme 1]

TABLE 2: Initial Quantum Yields of Charges and Excitons

<table>
<thead>
<tr>
<th></th>
<th>P3HT⁺</th>
<th>P3HT⁻</th>
<th>P3HT*</th>
<th>PCBM⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>neat P3HT</td>
<td>0.15</td>
<td>0.15</td>
<td>0.85</td>
<td>–</td>
</tr>
<tr>
<td>P3HT/PCBM 50%</td>
<td>0.5</td>
<td>0.1</td>
<td>0.5</td>
<td>0.4</td>
</tr>
</tbody>
</table>

neat P3HT, see upper panel of Figure 4. Hence, the fraction of photoexcitations that is not immediately affected by PCBM is \( \chi = 0.6 \).

Assuming the absorption cross section for positive and negative charges in P3HT to be identical, as indicated by theoretical studies, it is likely that the initial yield of charges can be estimated from the effect of PCBM on the TA amplitudes at 0.4 eV where only charges absorb. In neat P3HT the TA amplitude due to positive and negative charges is proportional to \( Q_{\text{P3HT}} = 2\eta \). In the blend with PCBM both positive and negative charges generated within the neat polymer domains and only positive charges generated at the PCBM interfaces contribute with an extent proportional to \( Q_{\text{blend}} = 2\eta\chi + (1 - \chi) \). Figure 6 shows that the initial amplitude of the TA for the 50% blend is approximately twice that for neat P3HT. Hence \( Q_{\text{blend}} = 2Q_{\text{P3HT}} \), which yields \( \eta = 0.15 \). Thus, the initial quantum yield of charges in neat P3HT is \( Y_{\text{neat}}(\text{P3HT}^+) = Y_{\text{neat}}(\text{P3HT}^-) = 0.15 \) and the exciton yield is \( Y_{\text{neat}}(\text{P3HT}^*) = 0.85 \). Following Scheme 1 the initial quantum yields for the 50% blend are found to be \( Y_{\text{blend}}(\text{P3HT}^+) = \eta\chi + (1 - \chi) = 0.5 \), \( Y_{\text{blend}}(\text{P3HT}^-) = \eta\chi = 0.1 \), \( Y_{\text{blend}}(\text{P3HT}^*) = (1 - \eta) = 0.5 \), and \( Y_{\text{blend}}(\text{PCBM}^-) = 1 \).

4. Conclusions

For P3HT or other materials with low fluorescence quantum yield, TA appears to be a more adequate tool to study excitation dynamics, as it is sensitive to the majority of excitons and not only to the small fraction that decays by fluorescence. The fraction (~1%) of excitons in P3HT that is probed by PL measurements has a lifetime of 660 ps, which significantly exceeds the 200 ps lifetime of nonfluorescent excitons that are probed by transient absorption measurements. The nonfluorescent excitons have a diffusion coefficient of about \( 2 \times 10^{-4} \) cm²/s, which is about an order of magnitude smaller than the literature values for fluorescent excitons.

For a pump laser fluence above 0.7 \( \mu \text{J/cm}^2 \) the TA signals are strongly affected by second-order decay processes. It could be inferred that photoexcitations interact at distances of \( 8-17 \) nm.

By selectively probing the TA due to excitons and charges at 0.9 and 0.4 eV, respectively, the quantum yields for photogeneration of these species could be determined. In neat P3HT the quantum yield for direct photogeneration of charge carriers amounts to 0.15 per absorbed photon. The remaining fraction of absorbed photons leads to formation of excitons. Addition of 50% PCBM by weight, leads to ultrafast formation of charge pairs with a total quantum yield of 0.5. The presence of 50% PCBM causes exciton decay to become about an order of magnitude faster than for neat P3HT, which is expected to be at least in part due to interfacial exciton dissociation into charge carriers. It was found that addition of 5% PCBM is already sufficient to yield a large amount of long-lived charges, similar to that of the 50% blend at 1 ns after excitation. The higher percentages used in optimized devices is mainly necessary to create paths for the negative charges to percolate to the cathode.

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