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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 pump–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 2×10^{-4} cm²/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.^{4,6} 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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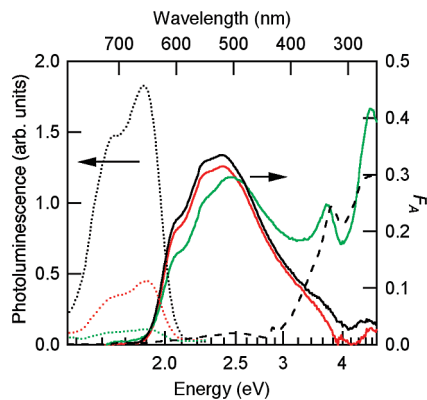


Figure 1. Optical attenuation (full lines, right vertical axis) and photoluminescence (dotted lines, left vertical axis) spectra of P3HT (black) and blends with 5% (red) and 50% (green) PCBM. F_A is the fraction of photons absorbed. The absorption spectrum of PCBM in chloroform solution is also shown for comparison (dashed black curve).

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 charge 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.

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 $^\circ\text{C}$. 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 N_2 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 $\text{TA} = -\Delta T/T = -(T_{\text{on}} - T_{\text{off}})/T_{\text{off}}$, where T_{on} denotes the probe transmission with pump on, and T_{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.^{23,24} 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

parametric amplification seeded by white light was used to produce the 500 nm pump pulse (<100 fs, TOPAS-800-fs, Coherent) and 600–1800 nm probe pulses (<100 fs, Opera, Coherent). The duration of the pump and probe pulses results in a time-resolution of ~ 200 fs. Using a home-built 1 kHz Ti:Sapphire multipass amplifier, pump pulses at 530 nm (30 fs) were produced with a noncollinear optical parametric amplifier (NOPA), while probe pulses at 3100 nm (~ 70 fs) were obtained with a 3-stage IR OPO.²⁴ Unless otherwise specified, the fluence of the pump beam was taken to be 0.7 $\mu\text{J}/\text{cm}^2$, which was found to be sufficiently low so that the magnitude of the TA scaled linearly with the fluence and the time-dependence was independent of fluence. The maximum possible delay was 1 ns when probing in the 600–1800 nm range or 100 ps in the case of the 3100 nm probe. The polarization vectors of the pump and probe light were parallel to each other.

Transmission (I_T) and reflection (I_R) spectra of the P3HT film and blends with PCBM were recorded with a Perkin-Elmer Lambda 900 spectrophotometer equipped with an integrating sphere. The attenuation spectra, which represent the fraction of photons absorbed by the sample, were obtained according to

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

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.

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.²⁵ 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/PCBM¹⁹ 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,²⁶ MDMO-PPV/PCBM,²⁷ and P3HT/F8BT.²⁸ 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.

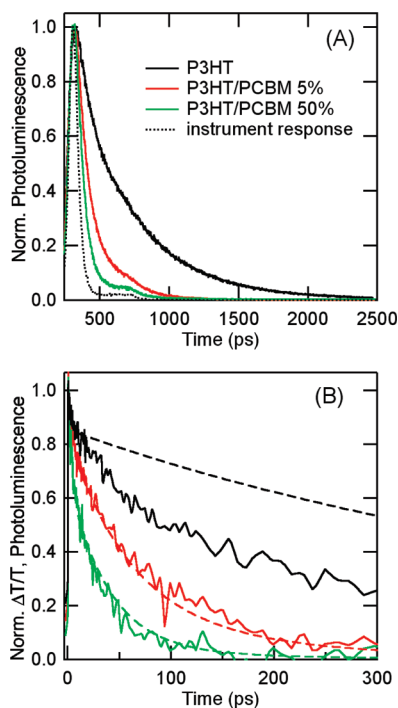


Figure 2. (A) Time-resolved PL measured at 650 nm following excitation at 404 nm. (B) Comparison between fits to PL decays (dashed lines) and TA transients at a probe of 0.9 eV (full lines) following 500 nm excitation. For neat P3HT (black) the PL decay is significantly slower than the TA signal. For blends with 5% (red) or 50% (green) PCBM the decay kinetics of PL and TA are similar.

TABLE 1: Decay Times ($1/e$) of Photoluminescence, τ_{PL} , at 650 nm and Transient Absorption, τ_{TA} , at a Probe Photon Energy of 0.9 eV^a

	P3HT	P3HT/PCBM 5%	P3HT/PCBM 50%
τ_{PL}	660 ps	70 ps	40 ps
τ_{TA}	200 ps	60 ps	20 ps
QY_{PL}	1	0.20	0.07

^a Also shown are the relative quantum yields for photoluminescence, QY_{PL} .

It is important to bear in mind that the quantum yield of PL excitons in regioregular P3HT is only of the order of 1%.^{6,22} This small quantum yield is the consequence of interchain interactions that result in a forbidden character of the lowest optical transition.²⁹ Consequently, the fluorescence cannot be considered representative for exciton dynamics, since the majority of excitons undergo nonradiative decay. Therefore, detection methods such as TA, which are sensitive to the total exciton population, are more adequate to study the behavior of excitons. As will be discussed in Section 3.3, TA can selectively monitor excitons at a probe photon energy of 0.9 eV. Figure 2B shows TA transients obtained by photoexcitation at 2.5 eV and probing at 0.9 eV, together with the fits to the PL decays in Figure 2B. The transients were normalized at 10 ps, i.e., the time resolution of the PL measurements. Clearly, the TA and PL decays are different for the neat P3HT film. From Figure 2B it is evident that the small fraction of fluorescent excitons has a much longer lifetime than the majority of nonfluorescent excitons that are probed by TA. It is evident that the PL decay is not a good probe of the fate of the majority of excitons. The PL and TA transients for the 5% and 50% P3HT/PCBM blends show similar kinetics. Apparently, upon addition of PCBM 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

$$k = \frac{1}{\tau} - \frac{1}{\tau_0} = 4\pi R D_E N \quad (2)$$

where τ_0 is the exciton lifetime in neat P3HT, τ 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 $R D_E = 2 \times 10^{-11} \text{ cm}^3/\text{s}$. Taking the reaction radius equal to half the intrinsic persistence length of P3HT, 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 $\tau_{\text{TA}} = 200 \text{ ps}$ from Table 1 give a diffusion length $\Lambda_E = \sqrt{D_E \tau_{\text{TA}}} = 2 \text{ nm}$ 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 Λ_E are significantly smaller than those obtained for fluorescent excitons from PL quenching measurements ($D_E > 5 \times 10^{-4} \text{ cm}^2/\text{s}$,³² $D_E = 1.8 \times 10^{-3} \text{ cm}^2/\text{s}$,³³ $\Lambda_E = 6.5\text{--}8.5 \text{ nm}$ ³⁴). 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 τ_{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.²⁰

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 $6 \mu\text{J}/\text{cm}^2$ or higher the initial amplitude of the normalized TA transients decreases and the decay becomes

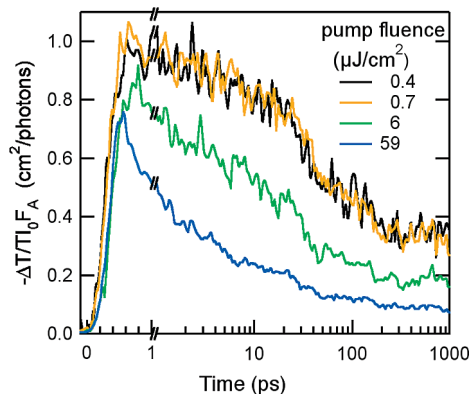


Figure 3. Effect of pump fluence at 500 nm on TA transients for neat P3HT at a probe energy of 1.25 eV. The transients have been normalized to the number of absorbed photons per unit area. The horizontal scale is linear until 1 ps and logarithmic from then to 1 ns.

faster, reflecting decay of excitons and/or charges by mutual interactions. Note, that second-order decay is already observed at pump fluence values used for previous ultrafast pump–probe experiments on P3HT and blends with PCBM.^{4,6,10,12,13,15} Transients recorded at different fluences for the blend films and at different wavelengths showed similar behavior to that described above for the pure polymer.

The reduction of the initial amplitude of the normalized TA signal for higher pump fluence implies that excitons and/or charges interact on a time scale less than the time-resolution of ~ 200 fs, i.e., before motion of the species is significant. The amplitude reduction is clear already at $6 \mu\text{J}/\text{cm}^2$ and is absent at $0.7 \mu\text{J}/\text{cm}^2$. For the close-to-homogeneous distribution of photoexcitations across the film thickness, these fluence values correspond to a mean separation between excitations of 8 and 17 nm, respectively. These minimum and maximum values of the interaction distance correspond with 20–40 repeat units along the polymer backbone or interchain distances and largely exceed the typical persistence length of P3HT, which is about 1 nm.³⁰ The large interaction distance agrees very well with the range of 3–20 nm reported previously for exciton-hole quenching in P3HT.³⁶ Note, that the interaction distance for exciton–exciton or exciton charge annihilation processes can largely exceed the spatial extent of the species, since the electronic coupling for annihilation via a Förster-like mechanism is determined by a Coulombic interaction and does not require spatial overlap of wave functions.

In order to avoid higher order effects in the experiments described below, a pump fluence of $0.7 \mu\text{J}/\text{cm}^2$ was used.

3.3. Assignment of Transient Absorption Due to Excitons and Charges. Transient spectra for different delay times after photoexcitation 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 photobleaching (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

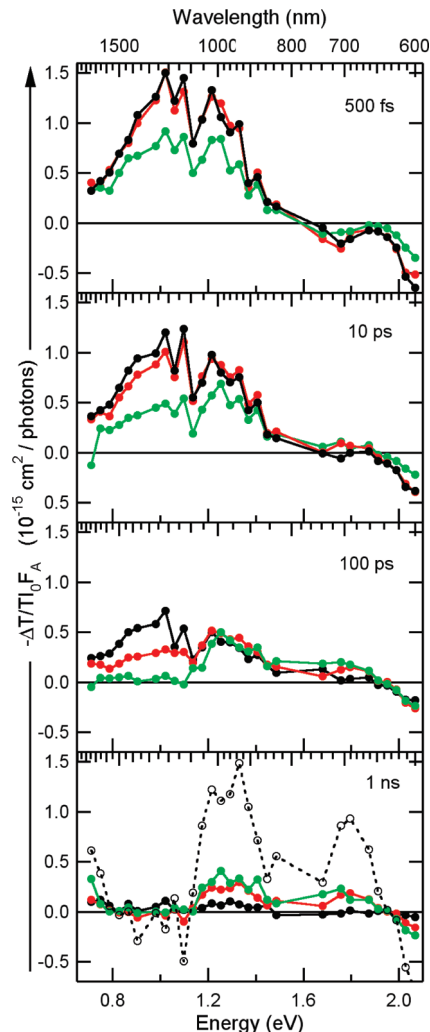


Figure 4. Transient absorption for neat P3HT (black) and blends with 5% (red) and 50% (green) PCBM following excitation at 500 nm. The TA data are normalized by the number of absorbed pump photons per unit area. The open circles in the lowest panel correspond to data for the 5% blend scaled by a factor 5.

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

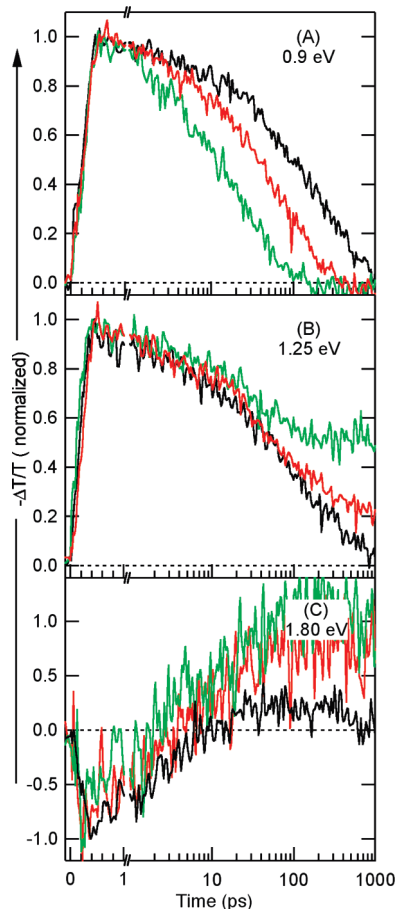


Figure 5. TA decay profiles obtained at 0.9, 1.25, and 1.80 eV probe photon energy for neat P3HT (black) and blends with 5% (red) or 50% (green) PCBM. Excitation was at 500 nm. The transients have been normalized to illustrate the different decay kinetics. Note, that the horizontal scale is linear until 1 ps and logarithmic from then to 1 ns.

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.^{6,38} 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.^{6,39} 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

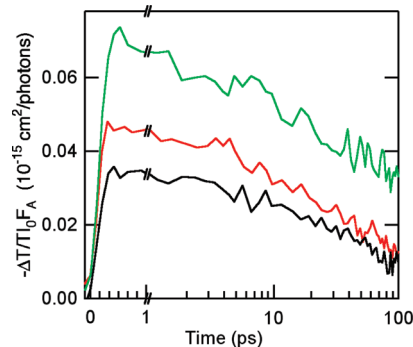
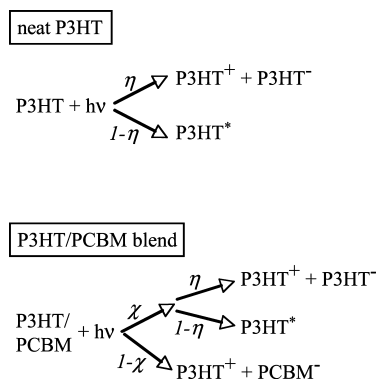


Figure 6. TA transients measured at 0.4 eV probe after 530 nm excitation for P3HT (black) and blends with 5% (red) or 50% (green) PCBM. The horizontal scale is linear until 1 ps and logarithmic from then to 100 ps.

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,⁴⁰ 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, $1 - \eta$. In 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 $(1 - \chi)$ 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 $(1 - \eta)$ and in the blend to $\chi(1 - \eta)$. 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

SCHEME 1: Nature and Yields of Transient Species Produced upon Photoexcitation of Neat P3HT and a Blend with PCBM as Electron Acceptor

TABLE 2: Initial Quantum Yields of Charges and Excitons

	P3HT ⁺	P3HT ⁻	P3HT*	PCBM ⁻
neat P3HT	0.15	0.15	0.85	—
P3HT/PCBM 50%	0.5	0.1	0.5	0.4

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,⁴¹ 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 $Y_{\text{blend}}(\text{P3HT}^+) = \eta\chi + (1 - \chi) = 0.5$, $Y_{\text{blend}}(\text{P3HT}^-) = \eta\chi = 0.1$, $Y_{\text{blend}}(\text{P3HT}^*) = \chi(1 - \eta) = 0.5$, and $Y_{\text{blend}}(\text{PCBM}^-) = 1 - \chi = 0.4$. These values are summarized in Table 2. It can be seen in the lower panel of Figure 4 that after 1 ns the yield of charges in the 5% blend is similar to that for the 50% blend.

Note, that the current method to determine the yield of charges and excitons differs from that in ref 6. In the present work the absorption cross sections at 0.4 eV for positive and negative charges are taken similar on basis of theoretical results,⁴¹ rather than making the assumption that the absorption strengths of charges and excitons are the same. The benefit of the current approach is that it is not necessary to measure the entire absorption band in the infrared.

The yield of charges for neat P3HT is much higher than usually found for other conjugated polymers, in agreement with previous results.⁶ Note that the yield after 20 ns, as found previously from microwave conductivity measurements,⁹ is much lower due to charge recombination. As a result of the presence of 50% PCBM approximately half of the absorbed photons directly produce charges, while the other half yields excitons in P3HT. The fraction, F , of excitons that can give rise to delayed charge formation by diffusion to an interface with PCBM, followed by electron transfer can be obtained from

the $1/e$ decay times, τ_{TA} , in Table 1. This gives for the 50% blend $F = 1 - \tau_{\text{TA}}(\text{blend})/\tau_{\text{TA}}(\text{P3HT}) = 0.9$. Hence, a fraction of 0.45 of the absorbed photons can give rise to delayed charge formation. Despite the large fraction of charges that could be generated from the diffusing excitons, no further rise but a decay of the TA at 0.4 eV is observed in Figure 6. As discussed in the previous section, delayed charge formation may be compensated by geminate recombination or transfer or free electrons from P3HT to PCBM.

When adding the fraction of 0.45 absorbed photons that could give rise to delayed formation of charges to the 0.5 initially generated, results in a total quantum yield of 0.95 charge pairs per absorbed photon. This value is slightly higher than the internal quantum efficiency of 0.8 for a photovoltaic device based on a P3HT/PCBM blend,²¹ which implies that almost all charges produced on a sub-nanosecond time scale can be extracted from the device before they recombine. In an actual device, the internal electric field may facilitate escape of charges from recombination.

The lower panel in Figure 4 shows that at 1 ns after excitation, very few species are left for neat P3HT, while a significant proportion of charges survive in the blends. Interestingly, the charge yields at 1 ns are quite similar in the 5% and the 50% blends. Hence, the initial photoexcitations are efficiently quenched by PCBM even at low concentration.

4. Conclusions

For P3HT or other materials with low fluorescence quantum yield, TA appears to be a more adequate tool to study exciton dynamics, as it is sensitive to the majority of excitons and not only to the small fraction that decays by fluorescence. The fraction ($\sim 1\%$) 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 2×10^{-4} cm²/s, which is about an order of magnitude smaller than literature values for fluorescent excitons.

For a pump laser fluence above 0.7 $\mu\text{J}/\text{cm}^2$ 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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