Effect of 2-D Delocalization on Charge Transport and Recombination in Bulk-Heterojunction Solar Cells

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Abstract—Charge-carrier transport and recombination in thermally treated and untreated films of poly(3-hexylthiophene) (P3HT) and 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methanofullerene (PCBM) bulk-heterojunction solar cells (BHSCs) have been measured using various electrooptical techniques. The formation of lamellar structure in P3HT has a large effect on the efficiency, carrier transport, and recombination of photogenerated charge carriers. Treated P3HT/PCBM solar cells show greatly reduced carrier recombination compared to what is typically expected in low-mobility materials and electric-field-independent carrier generation. In untreated films, the recombination is close to Langevin-type with electric-field-dependent quantum efficiency, consistent with the typically observed Onsager-type generation. Furthermore, we observe an increased effective capacitance in treated films, consistent with increased charge screening. The importance of the interface between the lamellar structured P3HT and PCBM is evident from optical spectroscopies showing that 2-D polarons are directly generated using sub-gap excitation. We conclude that the formation of lamellar structures in the polymer donor, and subsequent, delocalization of the charges is favorable for making efficient BHSCs.

Index Terms—Organic compounds, photovoltaic cell materials, photovoltaic cells, physics.

I. INTRODUCTION

BULK-HETEROJUNCTION solar cells (BHSCs) have achieved power-conversion efficiencies up to 7.8%, as recently reported by Solarmer, Inc., and continue to attract great interest in both the academic society and in industry as a potential low-cost alternative to traditional inorganic photovoltaics [1], [2]. The first-generation BHSC was typically made from derivatives of poly(p-phenylene vinylene), mainly the poly [2-methoxy-5-(3,7-dimethyloctyloxy)-phenylene vinylene] (MDMO-PPV) mixed with 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methanofullerene (PCBM) and showed efficiencies typically around 2.5% [3], [4]. In 2004, higher efficiencies closer to 5% in cells made from regioregular (RR) poly (3-hexylthiophene)(P3HT)/PCBM system was reported by several groups [5]–[8]. RR-P3HT has reported mobilities as high as 0.1 cm^2/Vs obtained using FETs [9], [10] and the reason for the dramatic increase in carrier mobility is due to the increased interchain coupling found in self-assembled films showing 2-D lamellar structures [11]–[13], giving rise to delocalized polarons (DPs) over adjacent chains [13]–[16]. Chang *et al.* suggested a simplified chain-folding scheme showing that P3HT forms nanoribbon-type structures [17]. These nanoribbons consists of 3–4 lamellae stacked on top of each other. The width of the ribbons are typically 15–20 nm, independent on the used molecular weight, suggesting multiple folding of the polymer chains into the ribbons. The nanoribbons are also responsible for the observed photophysical properties of P3HT, namely weakly interacting H-aggregates [18] and DPs.

Numerous publications have shown that the power-conversion efficiency of BHSC is closely related with the fabrication techniques [5]–[8]. In RR-P3HT, this is expected to be especially important due to the relatively strong interchain coupling observed compared to amorphous polymers. For instance, Yang *et al.* reported that thermal annealing induces crystallization and demixing of P3HT and PCBM in such a way that the efficiency is doubled [7]; while Kim *et al.* reported a strong regioregularity effect on the absorption, transport, and efficiency properties in solar cells made from these films [19]. The most important factor for the increased efficiency is the increased crystallinity in both P3HT and PCBM [7], [20]. The observation of phase separation on the length scale of exciton diffusion allows for efficient quenching of the exciton at interfaces between P3HT and PCBM rich domains [7], [20]. Even though the nanoribbons (in pure P3HT) forms mainly in the plane of the film, the formed lamellaes in the blends can be seen to extend vertically in the films giving rise to fast hole transport through the device.

Besides the need for extending the absorption to better match the solar irradiance spectrum, the way to overcome the main loss mechanism, namely efficient carrier generation and extraction in polymeric solar cells, is still not very clear. The carrier generation in homogeneous polymeric semiconductors is

of Onsager-type, which means that the generation is governed by the Brownian motion of the geminate pair within their mutual Coulomb potential. The criterion for this process is that the hopping distance is much shorter than the Coulomb radius $r_c = e^2/4\pi\varepsilon\varepsilon_0 kT$, where e is the electron charge, $\varepsilon(\varepsilon_0)$ is the relative (absolute) dielectric permittivity, k is the Boltzmann constant, and T is the temperature. If a geminate pair can separate this distance, the probability for escaping the geminate recombination is exactly one half and the carriers become free to participate in the transport. When an electric field is applied, the maximum Coulomb potential will be lowered, thus leading to a decreased Coulomb radius, and consequently, the carrier generation will show a strong field dependence. The Onsager process has typically a very strong temperature dependence. However, in organics, the process is almost temperature independent, which was explained as being due to excess photon energy forming a local heat bath assisting the separation process [21].

The time-reversal process to the Onsager generation is Langevin recombination [22]. In Langevin recombination, also expected for all low-mobility materials where the carrier hopping distance (or mean-free path) is much lower than the Coulomb radius, the rate-limiting step is *finding* the opposite charge carrier, independent of the subsequent recombination mechanism. The recombination rate is then proportional to both carrier densities as follows:

$$R = \beta_L np \tag{1}$$

where $n(p)$ is the density of electrons(holes) and the proportionality constant defined by the carrier mobilites as

$$\beta_L = \frac{e}{\epsilon\epsilon_0}(\mu_n + \mu_p) \tag{2}$$

where $\mu_n(\mu_p)$ is the electron(hole) mobility [23].

To achieve current densities of the same order as in crystalline solar cells, the concentration of photogenerated charge carriers (n_{ph}) must be much higher for BHSCs because the mobilities are much lower. High carrier concentration shortens the lifetime of the charge carriers due to second-order recombination. The lifetime can be defined as $\tau(t) = [\beta n_{ph}(t)]^{-1}$, where β is the bimolecular recombination coefficient. Consequently, the effect is that the lower $\mu\tau$-product shortens the drift distance.

Time of flight (TOF) is typically used to measure the charge-carrier mobility in low-conductivity semiconductors [25]. Usually, one uses current-mode TOF at low light intensities (number of generated charges much less than what can be stored on the electrodes, $Q_{gen} \ll CU$, where C is the geometrical capacitance and U the applied voltage), so that the electric field is uniform throughout the sample. At high laser intensities, this technique can be used to directly measure the bimolecular recombination coefficient in low-mobility materials [24], [25].

In this technique, the number of photogenerated charge carriers is increased as much as possible to create a space-charge-limited current (SCLC) transient. If the recombination is of Langevin-type, then the recombination will limit the transient so that exactly CU can be extracted and space-charge-perturbed current transients are observed [26]. If on the other hand,

carrier recombination is much slower compared to Langevin ($\beta/\beta_L \ll 1$), a carrier reservoir will be formed where the electric field is zero. As a result, the reservoir will be emptied with a constant SCLC. When the carrier reservoir is emptied, i.e., when the electric field is nonzero throughout the whole sample, then the current drops, with the appearance of the reservoir extraction time, from which we can directly calculate the bimolecular recombination coefficient [24].

In 2005, we used this technique and found that in good solar cells made from P3HT/PCBM blends, the carrier recombination was greatly reduced. The effective recombination coefficient normalized with the Langevin coefficient was as low, as $\beta/\beta_L = 10^{-4}$ [27]. The same effect was later on verified using other experimental techniques, such as double-injection transients [28]–[30], current–voltage characteristics [31], carrier extraction in a linearly increasing voltage (CELIV) [32], [33], transient photovoltage measurements [34], [35], as well as in dynamic admittance studies [36].

The mechanism for the reduced recombination has been heavily debated. Arkhipov *et al.* suggested a mechanism resting on the notion of dipole formation between fullerenes and parallel chains of P3HT [37]. The model predicts an increased carrier-generation probability due to an effective energy barrier for geminate pair recombination at the interface. For recombination, the same model can also be applied. To reach the chain nearest the interface, the hole on the next-to-nearest polymer chain has to overcome an extra energy barrier, thus leading to a reduced probability for carrier recombination. Indeed, Osikowicz *et al.* have measured a dipole layer being formed at P3HT/C60 interfaces [38].

Koster *et al.* suggested a model based on Langevin recombination limited by the mobility of the slowest charge carrier when being separated in different phases [31]. However, this model fails to account for the fact that in annealed samples, where the mobilities are almost balanced, the greatest reduction in the recombination is observed. Shuttle *et al.* [34], Juška *et al.* [30], and Deibel *et al.* [33] all found evidence for a strong density dependence of the recombination. Shuttle ascribed this as the bimolecular recombination coefficient having a linear carrier-density dependence ($\beta \propto n$); while Juška and Deibel pointed toward the possibility of having trimolecular recombination, i.e., Auger-type recombination.

The effect of anisotropy in the mobilities has been considered by Groves and Greenham in simulations, where they found the recombination to be reduced by approximately a factor of 20–50 [39]. However, they noted that the anomalously low effective recombination observed in annealed P3HT/PCBM cannot be explained by their model, but suggested deep trapping to be the reason for the observed behavior. Juška *et al.* could not find any evidence for trapping in annealed P3HT/PCBM solar cells [40]. Deibel *et al.* suggested a model for the reduced recombination due to the discrepancy between the local product of np being different from the macroscopically averaged (extracted) charge density. They could calculate the measured temperature dependence of the recombination and suggested that the reduction can be decomposed into two parts, namely a static part and a dynamic part [41]. The dynamic part is suggested

due to the local mismatch of the concentration of electron and holes. However, Deibel's model cannot explain the formation of a charge plasma, as suggested in double-injection-transient experiments [29]. The static part is a constant and could be due to geometrical factors. Szmytkowski derived a temperature-independent reduction factor based on interface recombination taking the image force into account [42], [43]. The interface recombination will be smaller than bulk recombination due to the difference in the static dielectric constants with a factor

$$\xi = \left| \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right| \qquad (3)$$

where $\varepsilon_1(\varepsilon_2)$ is the lower(higher) dielectric constant [42].

The effect of lamellar formation in P3HT has been included in a 2-D Langevin model suggested by Juška et $al.$ [44]. In this model, the recombination rate will have a density dependence of $n^{2.5}$ in agreement with the transient absorption data [45]. The 2-D recombination is then reduced compared to the 3-D Langevin recombination as follows:

$$\frac{\beta_{2D}}{\beta_{3D}} = \frac{3\sqrt{\pi}}{4} \frac{e(\mu_n + \mu_p)}{\varepsilon \varepsilon_0} (ln)^{3/2} = 6 \times 10^{-3} \qquad (4)$$

given the lamellar separation being $l = 1.6$ nm and at a charge density of $n = 10^{16}$ cm^3. The model agrees very well both qualitatively as well as quantitatively with observed transient and steady-state behavior [44]. The implication is that the recombination is limited by the 2-D character of the formed lamellar structure of the P3HT.

In this paper, we focus on the differences between treated and untreated samples of P3HT/PCBM solar cells. The cells are made with explicit reference for making the difference between the nanomorphology as large as possible. We show that the lamellar formation in P3HT are extremely important for the reduction in the recombination coefficient pointing to the fact that 2-D delocalization of charge carriers in the polymer phase is favorable for making efficient solar cells.

II. EXPERIMENTAL

The solar cell fabrication was done at Konarka and two identical samples were made, one heat treated and one untreated (hereafter refereed to as treated and untreated, respectively). The RR-P3HT and PCBM were dissolved in chloroform solution with 1:2 (RR-P3HT:PCBM) weight ratio. Using chloroform as solvent results in the highest difference between thermally treated and untreated devices. The sandwich-type samples were prepared on an indium tin oxide (ITO) substrate coated with a thin poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) film. The RR-P3HT/PCBM solution was deposited using doctor blading. As the top electrode, a thin lithium fluoride film followed by a semitransparent aluminum film was evaporated. Finally, the devices were sealed with the top cover glass to protect them from atmosphere and degradation. The treated samples were annealed at $110\,^{\circ}$C, according to the recipe in [46]. All samples were sealed in nitrogen atmosphere. The sample thickness d of the untreated film was 270 nm, while the treated sample had a thickness of 284 nm and 1.4 μm with typical contact areas of 10.5–16.5 mm^2. The built-in voltage

was 0.59 and 0.62 V, fill factor 0.625 and 0.424, and short circuit current -1.49 and -0.2 mA for the treated and untreated samples, respectively.

For measurements of the capacitance C and bulk conductivity σ, we used CELIV and an 1-MHz capacitance bridge. The linear increasing voltage pulse (increase rate $A = dU/dt$, where U is the voltage) in the reverse direction was applied over the electrodes, i.e., "+" on Al and "−" on ITO, unless otherwise stated. Standard TOF (with voltages applied in reverse bias) and dark injection transients were used to clarify the electrical and transport characteristics, as well as the quantum efficiencies [25]. The voltages used in the graphs are applied voltages, not corrected for unless otherwise stated. TOF at high laser intensities was used to clarify the recombination coefficients [27]. External quantum efficiency (EQE) as a function of wavelength was measured using standard procedures at Konarka. For the quantum-efficiency measurements, we use the 532 nm output from a Quantel Nd:Yag 5 ns laser to ensure strongly absorbed light at low enough intensity. The experimental conditions are also carefully checked to ensure complete collection, i.e., the sample thickness being less than the carrier drift distance $d < \mu\tau E$, where E is the electric field.

For the photoinduced absorption (PIA) measurements, P3HT and PCBM were acquired from Plextronics (OS2100) and Nano-C, respectively. Three treated samples were prepared in a glove box by spin-coating from anhydrous dichlorobenzene solutions: neat P3HT, P3HT:PCBM 4:1, and P3HT:PCBM 1:1. Film thicknesses were estimated [using atomic force microscopy (AFM)] to be 475, 300, and 80 nm, respectively. The PIA spectra were measured using standard measurement techniques [58] using a liquid-nitrogen-cooled cryostat (Janis Research VPF-475), a tungsten lamp, a monochromator (Acton Research Corporation 300i), and a lock-in amplifier (Stanford Research Systems SR830 DSP). Pump light was provided by an Argon ion laser (Coherent INNOVA 90C) for 514 nm excitation with an intensity of 600 mW/cm^2, or a diode laser (Power Technology PMT45(785-50)G3) for 785 nm excitation with an intensity of 180 mW/cm^2.

III. RESULTS AND DISCUSSION

A. External Quantum Efficiency

To demonstrate the difference in the efficiency between treated and untreated devices, we have measured the EQE as a function of wavelength, which is shown in Fig. 1. The EQE in the treated devices resembles the typical shape for RR-P3HT/PCBM BHSC, whereas the maximum value of the EQE at strongly absorbed light is approximately five times larger than in untreated films. Furthermore, we see that the carrier generation is pronounced toward the low-energy side, in good agreement with the appearance of weakly interacting H-aggregates in ordered RR-P3HT domains [18]. We have also measured the EQE under white light illumination (dc background light). The EQE spectrum of the treated devices basically remained unchanged (amplitude and shape), while the amplitude in the untreated device was significantly reduced. This also suggests stronger carrier recombination in untreated films.
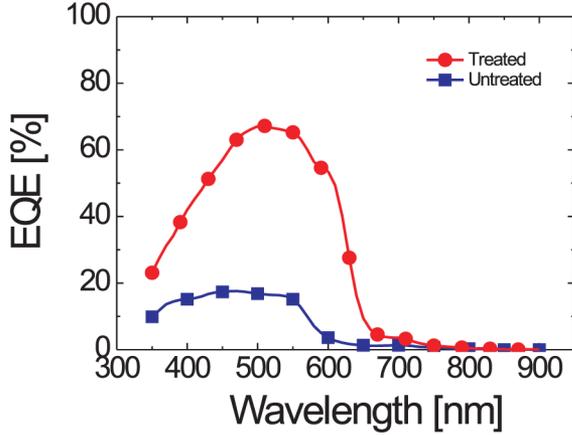
Fig. 1.   EQE as a function of wavelength.

Fig. 3.   Extracted charge normalized to CU and the extraction time shown as a function of light intensity in the treated and untreated devices. Note the increase in the extraction time at the same time $Q_{\rm ext}/CU > 1$ indicated by the vertical dashed line.
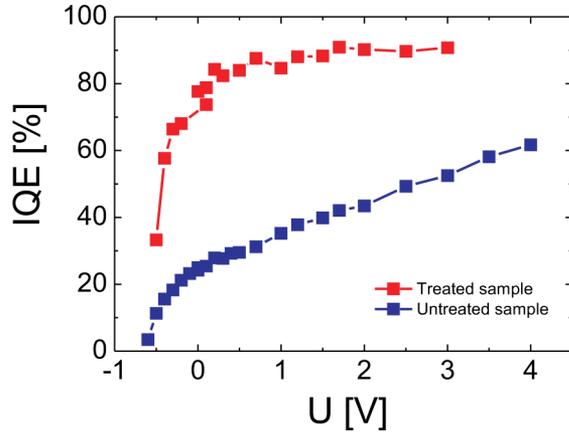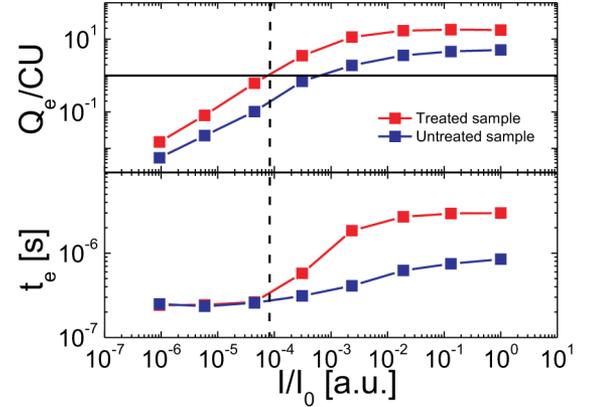

Fig. 2.   Internal quantum efficiency under pulsed excitation as a function of applied voltage in reverse bias, showing the field-independent quantum efficiency in the treated sample.

B.   Time of Flight

In order to estimate the difference between the charge-carrier generation, transport, and recombination, we have used TOF. The faster carrier mobility in treated films $\mu \approx 10^{-2}$ cm^2/Vs and the mobility in untreated films $\mu \approx 10^{-3}$ cm^2/Vs. We have also measured the internal quantum efficiency under pulsed excitation as a function of applied electric field, the so called Hecht curve in both the treated and untreated films (see Fig. 2). Since the drift distance is larger than the interelectrode distance, the extracted charge is directly related to the generation efficiency. In the untreated samples, the extracted charge shows a strong electric field dependence, without reaching saturation similar to what has been observed in MDMO-PPV-based devices [4]. Hence, the electric-field-dependent generation demonstrates that the charge-carrier generation process originates from Coulombically bound charge pairs. However, for the treated solar cell, the quantum efficiency rapidly increases with applied electric field, and finally, saturates to a value close to 90%, leading to a conclusion that the charge-carrier photogeneration efficiency is close to unity.

We have also used the TOF technique at high light intensities to directly clarify the recombination coefficient in both types of films. The extracted charge Q_e normalized to CU and extraction time t_e as a function of light intensity are shown in Fig. 3. At low light intensities, the extracted charge follows a linear dependence in both films. At the highest intensities (hundreds of millijoules per square centimeter), the extracted charge saturates due to bimolecular carrier recombination. For the untreated films, the extracted charge exceeds the CU value about five times, which is possible even in the case of Langevin-type recombination [24]. In the treated films, the maximum extracted charge exceeds the CU value with as much as 20 times. Moreover, the appearance of the reservoir extraction time [27], seen as a tenfold increase in the extraction time t_e (shown in Fig. 3), is observed in the treated samples at the same time the extracted charge starts to increase ($Q_e/CU > 1$). Using the absolute values of the extracted charge and the extraction time at highest intensities, we can directly calculate the normalized recombination coefficient $\beta/\beta_L = 10^{-4}$ in treated films.

C.   Dark Injection

We have measured the steady-state current–voltage characteristics, as shown in Fig. 4. The experimentally measured (bipolar) current (data points) is compared with the calculated unipolar SCLC (straight lines). The mobility of faster carriers (obtained from both integral and differential TOF techniques) is used to calculate the SCLC current. The experimentally measured current values differ by orders of magnitude at the same electric field in treated and untreated films, as seen in Fig. 4. The current value exceeds the SCLC in the treated films, whereas in the untreated films, the current approaches SCLC at high applied voltages. The high current density in the treated films confirm that the electron and hole injection are not limited by the contacts, but by the carrier recombination in the bulk of the film [47].

The reason for such a high current levels in treated devices is the formation of a charge plasma within the bulk due to
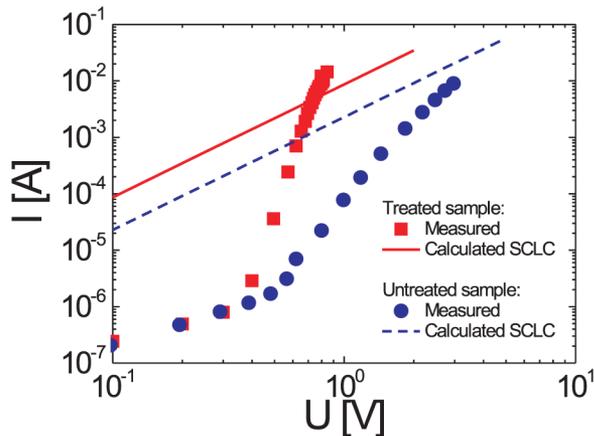
Fig. 4. Steady-state current–voltage characteristics in treated and untreated devices. The points are experimentally measured data and the lines are calculated SCLC value using the carrier mobility obtained using TOF.
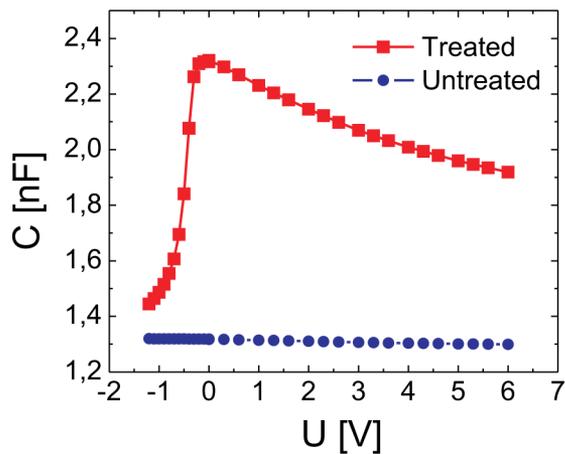

Fig. 5. Capacitance of the treated and untreated sample at 10 MHz.

reduced recombination. Hence, the size of the interpenetrating network must be smaller than the Debye screening length so that the charge neutrality is preserved [48]. We note that when Langevin-type carrier recombination is active, the maximum current density will be given by the (bipolar) SCLC value. The need for effective charge screening is therefore a must for observing such a high charge density. In the next section, we will see that the demixing causes better screening observed as an increase in the capacitance.

D. Current-Voltage Spectroscopy

The measured capacitance (using CELIV and a 1-MHz capacitance bridge) as a function of applied bias is shown in Fig. 5 for the treated and untreated device. Obviously, annealing significantly increases the capacitance. This can be explained as due to the demixing, it not only forms an increased concentration of lamellar structures in the polymer, but also larger phase of fullerenes. The increased capacitance leads to better charge screening with an enhanced carrier generation and re-

duced recombination as a consequence. The observed increase of the capacitance in the treated devices clearly has an positive effect on the screening of the charge carriers at the interface, as also discussed by Sliaužys *et al.* [32] and Lungenschmied *et al.* [36].

E. Optical Spectroscopy

The previous subchapters have shown that upon forming lamellar structure in the polymer phase, we will see greatly reduced recombination accompanied by increased screening, as observed in the capacitance spectrum. The interface between P3HT and PCBM turns out to be very important, as suggested by Arkhipov *et al.* [37]. However, interaction between the PCBM and P3HT should also be revealed by spectroscopic techniques. Photothermal deflection spectroscopy (PDS) and Fourier-transform photocurrent spectroscopy (FTPS) are sensitive methods used to study low-level absorptions and photocurrents [49]. For P3HT:PCBM 1:1 blends, a significant increase in the absorption coefficient compared to the neat P3HT and PCBM is observed even down to 1 eV [50], [51], indicative of interaction between the two materials causing subgap states to be formed.

There is experimental evidence for subgap states that are formed at the donor–acceptor interfaces due to a wave function overlap between the polymer and the fullerene, also called charge-transfer (CT) states [52]–[55]. Two routes for populating the CT states have been reported. The first is relaxation from singlet states formed via either above-bandgap excitation or injection from contacts [52], [56]. Here, the charge pair migrates to a donor–acceptor interface and minimizes its energy by populating the CT state at the interface. Tvingstedt *et al.* [52] measured the redshift of the electroluminescence of the donors when blended with PCBM. This redshift is assigned to luminescence from a CT state that is formed when the donor and acceptor are mixed. Photoluminescence measurements have also shown the appearance of a new, low-energy luminescence peak upon blending donor polymers with PCBM [54]. This new luminescence peak cannot be ascribed to either the donor or the acceptor molecule. The second route for populating a CT state is by direct optical excitation already in the ground state of the blend, at the donor–acceptor interfaces and can be directly excited using sub-gap light [55], [57]. It has also been shown that annealing a P3HT/PCBM blend reduces the photoluminescence from the CT state [52], [54]. Furthermore, regiorandom-P3HT/PCBM blends show a much higher luminescence intensity from the CT band than the blend with RR-P3HT [54].

We have prepared three treated samples by spin coating from dichlorobenzene solutions: neat P3HT, P3HT:PCBM 4:1, and P3HT:PCBM 1:1. Steady-state PIA spectra for each of these samples were measured at 80 K using both above-bandgap (514 nm, upper panel in Fig. 6) and sub-gap (785 nm, lower panel in Fig. 6) excitation light. The results are presented in Fig. 6. In the pure P3HT, we only observe signs of triplet excitons without any sign of charge carriers. Also, we cannot generate any kind of photoexcitations in the neat P3HT material using
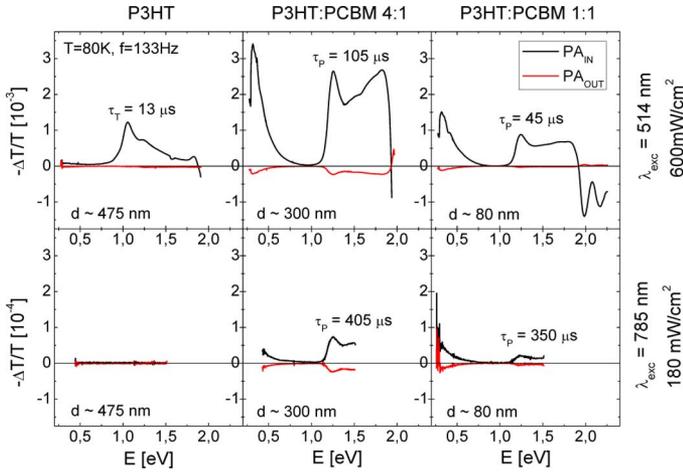
Fig. 6. PIA spectra measured at 80 K in three samples of treated films of (left) P3HT, (middle) 4:1 P3HT:PCBM, and (right) 1:1 P3HT:PCBM. In the upper panel, the spectra are recorded using above-gap excitation (514 nm) and the lower panel using sub-gap excitation (754 nm).

sub-gap light, as also expected, since there is no absorption in P3HT above 700 nm.

However, things becomes completely different in the blended films. Using above-gap excitation, we observe the expected signatures of photogenerated 2-D polarons [13], [14]. What is interesting is that when using sub-gap light, we are also *directly* generating 2-D polarons in the blends. This indicates that a ground-state charge-transfer state is formed that can be optically excited even with sub-gap light. Furthermore, the charge is immediately *delocalized* along the stacking direction in the polymer, giving rise to the characteristic absorption bands of the 2-D DP. We note that the spectral shapes for the above- and below-gap excitation are essentially identical.

From our PIA data, we can estimate the lifetimes of the photoexcitations. This is done by comparing the in-phase and quadrature components of the PIA spectra [58]. The polarons generated using sub-gap light have significantly longer lifetimes than the polarons generated using above-gap light have (405 μs versus 105 μs for the 4:1 blend, and 350 μs versus 45 μs for the 1:1 blend). The reason for this could be that the subgap-generated polarons are residing in the tail of the density of states, and are thus restricted in their movements (i.e., less mobile). At present, we are making more detailed studies on the optical properties of the observed sub-gap excitation light, but it is clear that it can be very detrimental to PIA dynamics due to the constant carrier background that the probe creates.

IV. Summary

In conclusion, we have measured charge-carrier transport and recombination in treated and untreated P3HT/PCBM BHSCs using various electrooptical techniques. We have demonstrated that the formation of lamellar structure in P3HT has a large effect on the efficiency, carrier transport, and recombination of photogenerated charge carriers. The quantum efficiency was found to be electric field dependent in untreated films, consistent with the Onsager-type electric-field-assisted charge-carrier

generation in these films. In treated films with greatly reduced carrier recombination (compared to Langevin-type), the quantum efficiency becomes electric field independent, as expected. Furthermore, we observe an increased effective capacitance in treated films, which is consistent with better charge screening and absence of Langevin recombination. The importance of the interface between a lamellar structure (P3HT) and PCBM is evidenced from the PIA data, where we show that 2-D polarons are directly generated using sub-gap excitation. We conclude that the formation of lamellar structure in the polymer donor, and subsequent, delocalization of the charges is favorable for making efficient BHSCs.

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