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FULL PAPER

Does Excess Energy Assist Photogeneration in an Organic Low-Bandgap Solar Cell?

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The field dependence of the photocurrent in a bilayer assembly is measured with the aim to clarify the role of excess photon energy in an organic solar cell comprising a polymeric donor and an acceptor. Upon optical excitation of the donor an electron is transferred to the acceptor forming a Coulomb-bound electron–hole pair. Since the subsequent escape is a field assisted process it follows that photogeneration saturates at higher electric fields, the saturation field being a measure of the separation of the electron–hole pair. Using the low bandgap polymers, PCDTBT and PCPDTBT, as donors and C_{60} as acceptor in a bilayer assembly it is found that the saturation field decreases when the photon energy is roughly 0.5 eV above the S_1–S_0 0–0 transition of the donor. This translates into an increase of the size of the electron-hole-pair up to about 13 nm which is close to the Coulomb capture radius. This increase correlates with the onset of higher electronic states that have a highly delocalized character, as confirmed by quantum-chemical calculations. This demonstrates that accessing higher electronic states does favor photogeneration yet excess vibrational energy plays no role. Experiments on intrinsic photogeneration in donor photodiodes without acceptors support this reasoning.

1. Introduction

In an organic photovoltaic cell (OPV) the conversion of an optically excited state to a pair of charge carriers is thought to be a multistep process. An electron of the optically excited donor is first transferred to an acceptor with lower lying LUMO (lowest unoccupied molecular orbital) thereby forming a Coulomb-bound electron–hole pair.[1–9] That pair has to escape from the mutual Coulomb potential. While this notion is by now firmly established, the mechanism by which the pair is liberated is heavily debated. It is obvious that in an OPV cell with high quantum efficiency the initial pair must be fairly expanded so that the Coulomb binding energy is small. How can this be accomplished? One possibility is that the excess energy that is dissipated when the excited electron of the donor is transferred to the acceptor is at least partially converted to kinetic energy. This would help generating a weakly bound electron–hole pair. If so, a large energy difference between the LUMOs of donor and acceptor would be of advantage. On the other hand, any energy dissipating process lowers the power efficiency of the cell. Therefore, an optimization of the energy difference between donor and acceptor LUMO is required. Indeed, experimental results seem to corroborate this notion.[10,11] The question is, though, how conclusive this reasoning is.

At this stage it is helpful to recall how the photogeneration of charge carriers in molecular crystals occurs. It had been firmly established that within the spectral regime of the first singlet transition (S_1–S_0) photogeneration is of extrinsic origin, caused by either exciton dissociation at an electrode or at sensitizing impurities. The pioneering work of Chance and Braun[12] and Geacintov and Pope[13] showed that—except for some dissociation of charge–transfer states—intrinsic photogeneration is due to autoionization of higher electronic states of the crystal. Remarkably, for molecular crystals such as anthracene, the photogeneration yield is constant within the spectral range of the S_2–S_0 transition. It does not increase until the S_3–S_0 transition is reached and it saturates again at higher photon energies. This is a clear indication that excess energy of the autoionizing state is helpful, yet that it is the *electronic* excess energy of S_2 and S_3 excitations relative to S_1 exciton that matters rather than any *vibrational* energy coupled to an S_1 exciton. From an analysis of the temperature and field dependence of the photocarrier yield one learns that the autoionization process generates an electron–hole pair with an intrapair separation r_0 = 3–5 nm depending on the kind of electronic excitation. That pair can either fully dissociate in the course on an Onsager-type diffusive random walk

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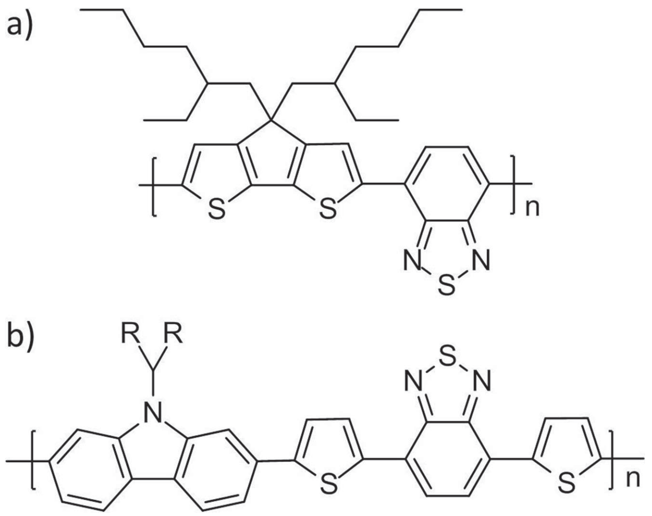

Figure 1. Chemical structures of a) PCPDTBT and b) PCDTBT. R=C_8H_{17}.

or recombine geminately. Photoionization in conjugated polymers is consistent with this notion. In films of MEH-PPV[14,15] and MeLPPP[16] onset of intrinsic photogeneration is coincident with the origin of the S_2–S_0 transition, i.e., energetically above the estimated electrical gap. Confirmed by quantum chemical calculations[14] this proves that it is the spatial extension of the wavefunction of the excited state that determines the yield of dissociation of an excited state.

From this perspective we shall address the question regarding the importance of the excess photon energy on photogeneration in a donor–acceptor OPV cell. Employing ultrafast pump–probe spectroscopy on OPV cell with CuPc as electron donor and C_{60}/C_{70} as an acceptor Jailaubekov et al.[17] showed that within an photon energy range of 1.85–2.10 eV excess vibrational energy has little effect on the yield of formation of primary electron–hole pairs. On the other hand, Grancini et al.[18] studied the evolution of electron–hole pairs in a high efficiency OPV cell with PCPDTBT–PCBM as a donor–acceptor pair (see **Figure 1** for the chemical structure of PCPDTBT. PCBM is a fullerene-derivative). They found that the appearance time of the electron–hole pair decreases from 50 to 20 fs when increasing the photon energy from 1.65 to 2.55 eV and attributed this to hot exciton dissociation. Quantum-chemical calculations indicate that in this spectral range there are several excited states that differ regarding the degree of mixing of exciton and CT states. At first sight one would conjecture that the dissociation yield of those different precursor states is also different. However, this notion has been challenged recently. Vandewal et al.[19] found that it does not matter if the primary photons excite the donor, the acceptor or a charge–transfer state. Obviously, there is need for further clarifying work.

In this work we study the field dependence of photogeneration in bilayers of PCPDTBT and PCDTBT with C_{60} as an electron acceptor. The reason for choosing bilayers is that in bilayers the liberated electrons and holes are confined to the acceptor and donor compartments of the diode. Therefore, bimolecular recombination is greatly reduced and the field dependence of the photocurrent under reverse bias is predominately controlled by the charge generation process, i.e., the dissociation of the initially generated electron–hole pair. The yield of pair dissociation saturates at higher fields with the saturation field being determined by the balance between the Coulomb binding energy of the electron–hole pair and the gain of the electrostatic potential due to the applied field. The larger the electron–hole separation of the pair is the lower will be the saturation field that compensates the Coulomb energy. From previous work we know that the saturation field decreases as a function of the effective conjugation length of the polymer chain.[7] This is a plausible result because a large effective conjugation length should facilitate the formation of more loosely bound electron–hole pairs that are easier to completely dissociate. It is straightforward to investigate whether or not an excess energy of the primary excitation has an effect on the size of the dissociating electron–hole pair, monitored via a change of the saturation field as a function of photon energy. Our results will substantiate the notion that excess energy does assist the dissociation of geminately bound electron–hole pair. Importantly, it is the extra electronic rather than vibrational energy associated with a vibronic Franck–Condon state that matters. To substantiate this conclusion we also studied intrinsic photogeneration in single layer PCPDTBT diodes. We find that in PCPDTBT intrinsic photodissociation—albeit inefficient—also increases with excess photon energy. This confirms the conclusion derived from classic molecular crystal work that indicates that it is the extent of the wavefunction function of the donor phase that determines the size of a geminate electron–hole pair and, concomitantly, its subsequent dissociation.

2. Experimental and Theoretical Methods

The low bandgap polymer PCDTBT was synthesized according to the procedure described by Leclerc and co-workers[20] while PCPDTBT was purchased from Sigma-Aldrich. For photocurrent measurements on bilayer assemblies we prepared solar cells. For this, we used patterned ITO substrates that were additionally structured with photoresist in a way to allow for the application homogeneous electric fields up to 1 MV cm^{-1} without risking spurious breakdown effects near the electrode edges.[7] In order to reduce the dark current in the device a 15 nm thick MoO_3 layer (Sigma-Aldrich) was vapor deposited on top of the patterned ITO using a shadow-mask. Afterward, the donor polymer PCPDTBT or PCDTBT is spin-coated from chlorobenzene solution to yield films with a typical thickness of 30 nm. Subsequently, a 30 nm thick layer of C_{60} (American Dye Source Inc.) as acceptor was vapor deposited. Aluminum was vapor deposited as top electrode. The entire device fabrication was done in a glovebox filled with nitrogen atmosphere.

Current–voltage characteristics of the bilayer devices were measured under vacuum at room temperature under variable monochromatic illumination from a 450 W Xenon lamp within a photon energy range between 1.5 to 3.5 eV using a Keithley source–measure unit. The internal electric field was calculated as $F = -(V - V_{oc})/d$ where V is the applied external voltage, V_{oc} is the open circuit voltage determined for each excitation wavelength, and d is the thickness of the polymer-acceptor bilayer. Exemplary current–voltage curves are shown in the Supporting Information.

Finally, the present experimental analyses are corroborated by accurate ab initio Green's function many-body perturbation

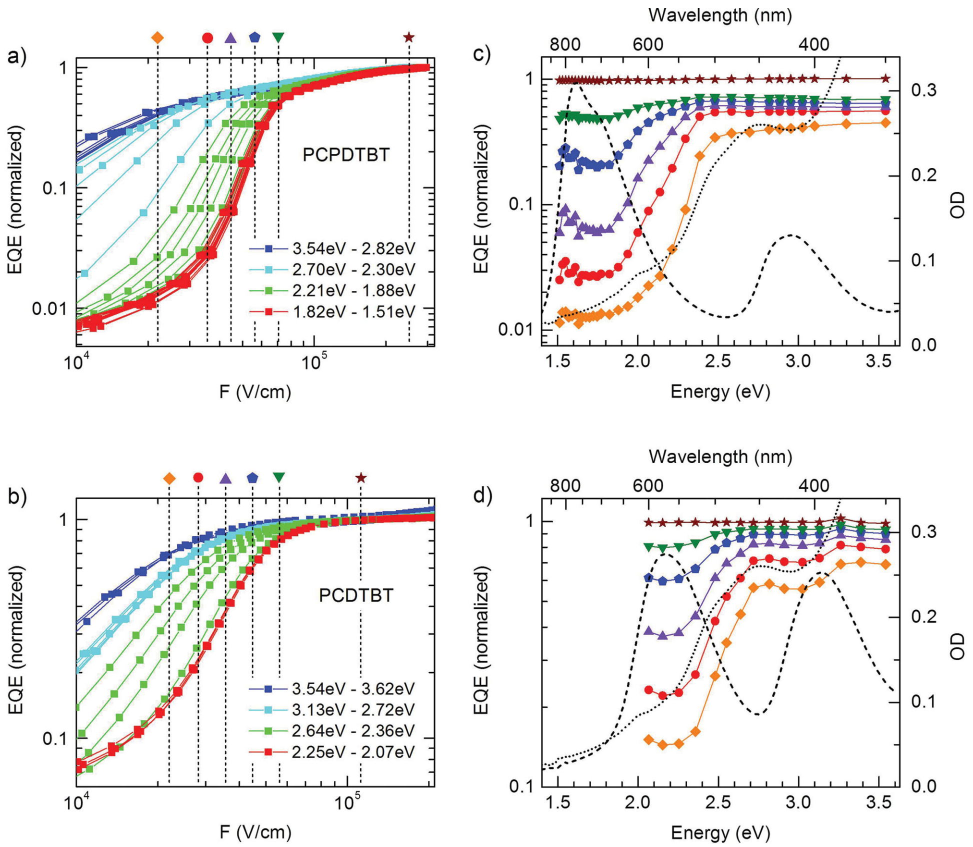

Figure 2. External quantum efficiency (EQE) of the donor–acceptor solar cell, normalized to unity at the saturation field, for a) PCPDTBT and b) PCDTBT parametric in photon energy. On the right side the normalized EQE is shown for a specific field as a function of photon energy (cut through the EQE-curves on the left side, tagged by the dashed line). This is done for several field strengths for c) PCPDTBT and d) PCDTBT. The symbols on the top axis in (a,b) indicate the specific field strength for the corresponding normalized EQE curves in (c,d). On the right ordinate in (c), the optical density of C_{60} (30 nm) (dotted line) and PCPDTBT (30 nm) (dashed line) or PCDTBT (30 nm) (dashed line) are shown.

theory calculations within the framework of the so-called GW and Bethe–Salpeter formalisms,[21] focusing on hot excitations for a model PCBM/PCDTBT complex. The present GW/BSE approach has been recently shown by several groups to describe both localized (Frenkel) and charge–transfer (CT) excitations in excellent agreement with available experimental data or high-level multideterminantal quantum chemistry calculations.[22–25] Our calculations are performed with a large triple-zeta and double-polarization (Gaussian) TZ2P basis using a resolution-of-the-identity approach for the description of the Coulomb integrals and follow a recent study of the low lying excitations in PCBM-polymer complexes where a close agreement between the present Bethe–Salpeter calculations and optimized range-separated hybrids (BNL) TDDFT calculations was observed.[26]

3. Results

The essential information on the role of the photon energy in the photodissociation process in a bilayer diode with PCDTBT and PCPDTBT as donor materials will be inferred from the dependence of the stationary photocurrent as a function of the electric field acting on the geminate electron–hole pair excited and on the photon energy. Since in our diodes the parasitic dark currents are less than 1% of the total current, the latter is identified with the photocurrent. To calculate the field dependence of the yield of photogeneration one has to correct the applied electric field for the built-in field V_{oc}/d where V_{oc} is the open-circuit voltage. V_{oc} is the voltage at which the dissociation and recombination of electron–hole pairs generated at the donor–acceptor interface under zero field electric are exactly balanced thus resulting in a net current of zero. The concentration of those electron–hole pairs depends on their generation rate, i.e., on the light intensity, the optical density of the absorber, and the emission spectrum of the light source, yielding a logarithmic dependence of V_{oc} on the electron–hole pair generation rate.[27,28] For this reason we consider in the following V_{oc} as an experimentally determined input parameter for the individual current–voltage curves parametric in photon quantum energy under reverse bias condition. In the absence of bimolecular recombination the photocurrent then reflects photogeneration in the bilayers as a function of the internal electric field $F = -(V - V_{oc})/d$, and photon energy. The external quantum efficiencies (EQE), i.e., the photocurrent $j(F)$ normalized to the incident light intensity, for a PCPDTBT and a PCDTBT cell with C_{60} as an acceptor as a function of electric field are shown in **Figure 2**a,b. The related dependencies of the EQE as a function of photon energy for different fields are shown in Figure 2c,d in which the separate optical densities of the donor layers and the C_{60} layer are included. It turns out that EQE characteristics shift to lower values of the electric field with increasing photon energy and feature a saturation effect. It translates into an increase of EQE in the low photon energy range upon raising the electric field. In the case of PCDTBT the increase of EQE with photon energy matches more or less the increase of the OD of the C_{60} layer while for PCPDTBT that increase occurs at lower photon energies already. This is consistent with the bathochromic shift of the absorption spectrum. It is remarkable that—depending on photon energy—EQE(F) can saturate at electric fields F below the build-in field V_{oc}/d which is on the order of 10^5 V cm^{-1} for donor–acceptor thickness of 60 nm and a typical V_{oc} of 0.5–0.8 eV. The saturation field F_{sat} can operationally be determined from the intersection of the tangents to the photocurrent below and above saturation. A plot of the saturation field with photon energy is shown in **Figure 3**. From Figures 2 and 3 it is evident that the field dependence reduces with increasing photon energy.

Complementary to experiments on bilayers we also measured the photocurrent normalized to the number of absorbed photons, i.e. the internal quantum efficiency generation (IQE), in single layer PCPDTBT and PCDTBT diodes, without the C_{60} electron acceptor (**Figure 4**a,b). As expected, the photocurrent is typically two orders of magnitude lower than in bilayers and no saturation is observed at fields up to 8×10^5 V cm^{-1} (**Figure 5**). Obviously, in single layer devices the dissociating electron–hole pairs are more strongly Coulombic bound than those in bilayers diodes but, importantly, at a given electric field the yield also increases with photon energy in a similar fashion as we found with bilayers (Figure 2). For reference, the EQE and donor absorption of the cells presented in Figure 4 are shown in the Supporting Information.

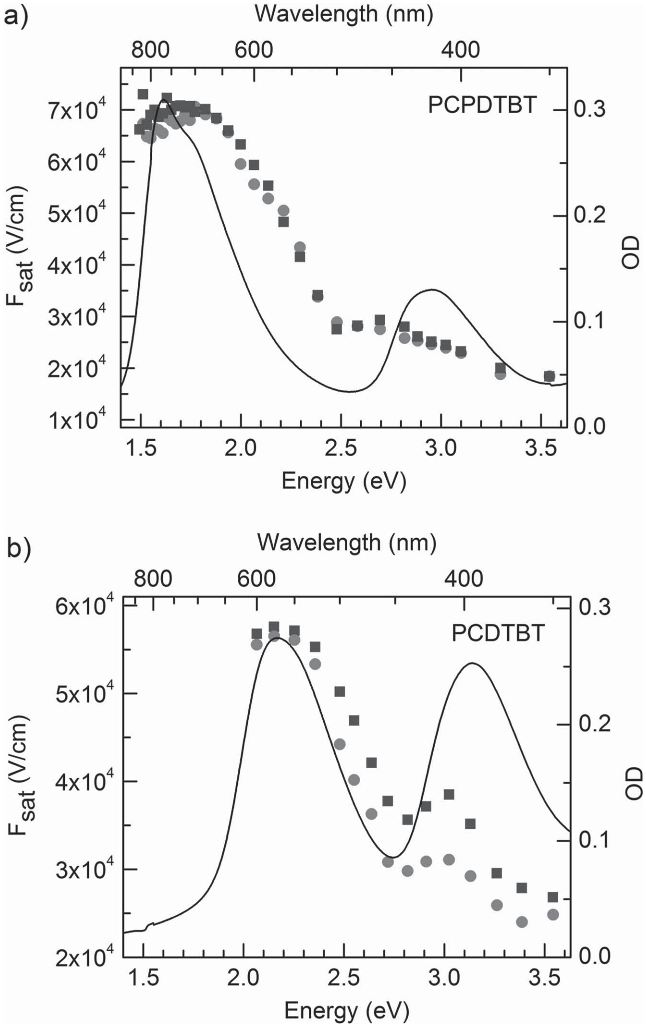

Figure 3. Saturation field F_{sat} as a function of photon energy in donor–acceptor solar cells with C_{60} as acceptor for a) PCPDTBT and b) PCDTBT. Data are shown for several solar cells. The black line indicates the donor absorption.

4. Discussion

4.1. Donor–Acceptor Bilayers: Experiment

In both, single layer cells as well as in donor–acceptor bilayers the photocurrent originates from the dissociation of geminate electron–hole pairs against their Coulomb binding energy. In bilayers, the energetic off-set between the LUMOs and HOMOs of donor and acceptor assists the dissociation process, while in a single layer diode this additional contribution is absent. As a result, the yield of intrinsic photogeneration in a single layer diode is much lower than in a bilayer diode and is often controlled by sensitization due to inadvertent impurities or by exciton-induced charge injection from the electrodes. A measure of how strong or weak an electron–hole pair is Coulomb bound is the electric field strength F_{sat}, at which a photocurrent saturates. Photocurrent saturation occurs when the Coulomb energy of the dissociating electron–hole pair

$$\mathrm{eV}_{\mathrm{Coulomb}} = \frac{e^2}{4\pi\epsilon_0\epsilon_r}\cdot\frac{1}{r_0} \tag{1}$$

with an initial intrapair separation r_0 is compensated by the applied potential $eF_{sat}\cdot r_0$, i.e.,

$$r_0 = \sqrt{\frac{e}{4\pi\epsilon_0\epsilon_r}\cdot\frac{1}{F_{\mathrm{sat}}}} \tag{2}$$

The saturation field is, thus, a measure of the "size" of the electron–hole pair if the simple picture of point-like charges is adopted. This electron–hole separation can be inferred from the data in Figure 3 using Equation (2) (**Figure 6**). Previous experiments on photogeneration in bilayer diodes with conjugated poly-phenylene-type donor polymers with different conjugation length and C_{60} as acceptor indicated that the saturation field scales inversely with the effective conjugation length of the donor polymer, i.e., the more extended the π-electron distribution of the polymer is, the larger is the dissociation yield.[7] However, there is always a finite, non-negligible saturation field even though in some cases it can become comparable to the built-in field under short circuit condition of the diode. Therefore, the generation of free charge carriers is always funneled from precursor geminate pairs. The crucial parameter that

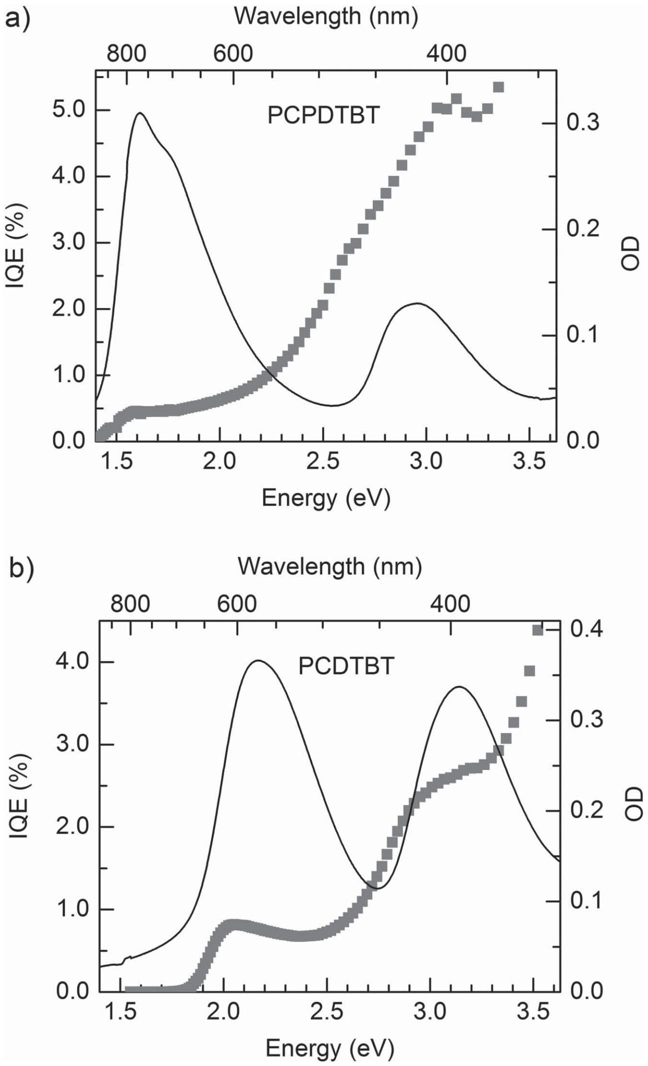

Figure 4. IQE for solar cells without acceptor in the structure a) ITO/MoO_3/30 nm PCPDTBT/Al and b) ITO/MoO_3/40 nm PCDTBT/Al. On the right axis the measured optical density of the polymer used is shown. The IQE was calculated by correcting the EQE for the optical density of the polymer layer and for the transmission of the glass, ITO and MoO_3 layers.

determines F_{sat} is the delocalisation of the charges constituting the geminate pair.

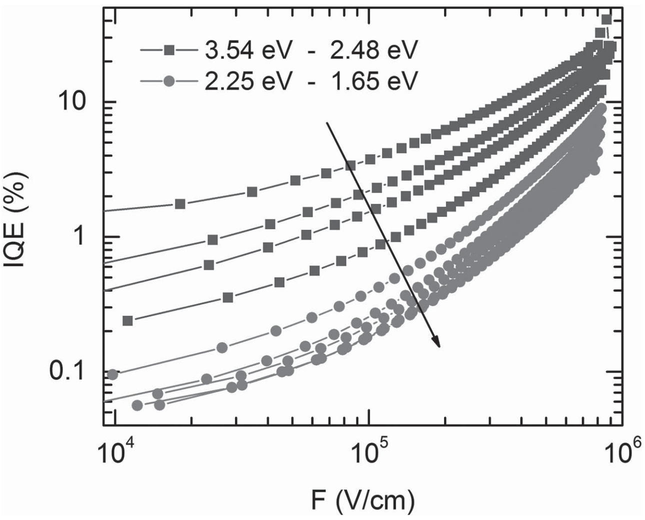

Figure 5. Internal quantum efficiency (IQE) of a monolayer solar cell for a ITO/MoO_3/30 nm PCPDTBT/Al cell as a function of electric field for different photon energies. The arrow indicates decreasing excitation energy.

Figure 3 shows that for diodes with C_{60} acceptor there is a striking correlation between the dependence of the field dependence F_{sat} and the donor absorption spectra. F_{sat} is constant within a photon energy range of 0.4 eV above the S_1–S_0 0–0 transition and decreases with increasing photon energies featuring an intermediate shoulder that correlates with the plateau in the absorption spectrum. It is caused by the superposition of the minimum of the donor spectrum and the onset of the second electronic transition of C_{60}. Although the point charge concept, on which Equation (2) is based on, is certainly only a crude approximation of the separation, r_0, of the electron on C_{60} and the delocalized hole on a conjugated polymer, the decrease of F_{sat} that occurs upon raising the photon energy demonstrates that the electron–hole pairs generated at higher quantum energy are more expanded. When using Equation (2) we end up with a value of 8 nm within a spectral range up to about 0.5 eV above the $S_1 \leftarrow S_0$ 0–0 transition and this increases to 13 nm at $h\nu = 3.5$ eV (Figure 6).

This may be compared to the field dependence of the dissociation yield in the series of polyphenylenes with different conjugation length reported earlier.[7] In that work, we found that the saturation field reduces with increasing conjugation length, that is, when going from the highly disordered DOOPPP to the well-ordered MeLPPP. This translates into an r_0 ranging from 2 nm for DOOPPP—which appears to be a realistic value for a tightly bound electron–hole pair in a donor–acceptor couple—to values up to 9 nm for MeLPPP, clearly reflecting a larger delocalization for this more conjugated polymer. The reduction of F_{sat} with increasing conjugation length also seems to suggest that the increase of the dissociation yield is not associated with entropy effects. The work by Gregg shows that entropy effects can be important in three-dimensional systems in contrast to one-dimensional systems.[29] This is at variance with the observation that F_{sat} reduces when the polymer acquires a more one-dimensional character—as is the case when elongating the conjugated π-system from DOOPPP to MeLPPP. By the same token, more delocalized, and thus more one-dimensional character associated with transitions contribution to the second absorption band, such as the $S_3 \leftarrow S_0$ transition shown in **Figure 7**, implies that entropy effects do not play a significant role here.

Obviously, excess photon energy facilitates photodissociation but the fact that r_0 stays constant within a spectral window of 0.4–0.5 eV above the S_1–S_0 0–0 transition proves that excess vibrational energy has virtually no effect. This is consistent with classic work on crystalline anthracene which shows that the yield increases only when a higher electronic state is reached while it remains constant within the spectral range of the Franck–Condon vibrational progression built on an electronic 0–0 transition.[12] This is a plausible result because the formation of an electron–hole pair from a neutral exciton can be considered as an autoionization process that depends on the

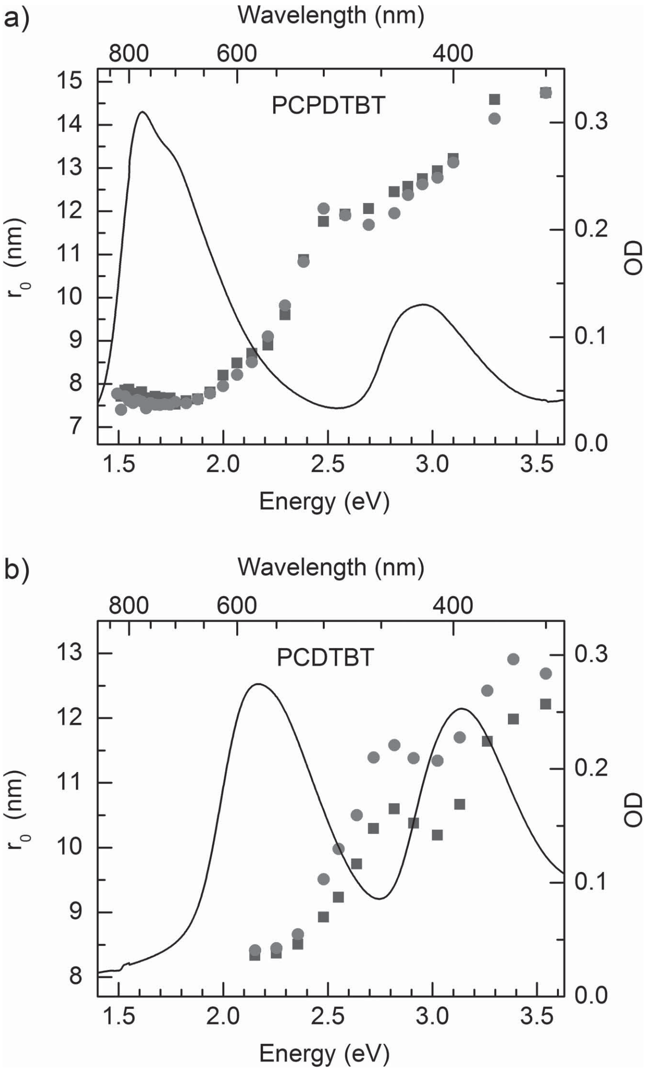

Figure 6. Thermalization radii calculated out of the saturation field F_{sat} as a function of photon energy in donor–acceptor solar cells with C_{60} as acceptor for a) PCPDTBT and b) PCDTBT. Circles and squares indicate different solar cells of the same type. The black line indicates the donor absorption.

wavefunction overlap between initial and final state. It should be indeed independent of an additional vibrational excitation of a chromophore. The observed decrease of F_{sat} and the concomitant increase of the size of the electron–hole pair is therefore a signature of the involvement of higher electronic states.

The conclusion that excess vibrational energy has no effect on photodissociation is consistent with work of Jailaubekov et al.[17] on solar cells with CuPc as electron donor and C_{60}/C_{70}, yet it is in disagreement with the works of Arkhipov et al.[30] who suggest local heating due to vibrational cooling of a higher Franck–Condon state as the origin for increased photogeneration at higher photon energies. At first glance the conclusion that excess photon energy can enhance the dissociation yield is at variance with the work of Vandewal et al.[19] These authors found that the efficiency of charge collection in a chemically very similar PBDTTBT-PCBM solar diode is the same if one excites the charge–transfer transition, the S_1–S_0 0–0 transition or a state at 2.0 eV which is 0.4 eV above the S_1–S_0 0–0 transition. However, based upon our experiments there is no contradiction because the increase of the photocarrier yield starts not until the next higher electronic state. Moreover, the effect of an electronic excess energy on efficiency of photodissociation tends to saturate already at electric fields close to or above the built-in field.

It is important to be aware of the low magnitude of the saturation field for these low-bandgap polymers. If such a device is measured under short-circuit condition, i.e., at the built-in field, the resulting internal quantum efficiency should be nearly flat with photon energy, such as the curves indicated by green triangles in Figure 2c,d.[31] In contrast, in spectroscopic measurements, a film is always measured without a field being present, so that the resulting photogeneration will have a strong dependence on the photon energy such as the curves measured at very low fields that are indicated by the orange diamonds in Figure 2c,d.

4.2. Donor–Acceptor Bilayers: Theory

To explore why a higher electronic state of the donor should assist the separation of the electron–hole pair, we consider quantum chemical calculations. Density functional theory (DFT)/Zerner intermediate neglect of differential overlap (ZINDO) calculations by Granchini at al.[18] have indeed shown that in PCPDTBT there is a S_2–S_0 0–0 transition at 1.88 eV and a S_4–S_0 0–0 transition at 2.32 eV, in addition to the calculated S_1–S_0 0–0 transition at 1.65 eV (which, by the way, is in excellent agreement with experiment). Both transitions overlap with the vibronic Franck Condon progression built on the S_1–S_0 transition.[18] Those transitions carry oscillator strengths of roughly 10% of the S_1–S_0 0–0 transition. Spectroscopic pump–probe experiments by Grancini et al. further demonstrated that the appearance time for the electron–hole pairs formed from precursor neutral excitons decreases from 48 to 38 fs and 22 fs upon raising the photon energy from 1.75 to 1.94 eV and 2.41 eV. They suggest that this is a signature of increasing coupling strength between excitonic states and ionized states that increases the rate of electron transfer to the acceptor. This is associated with an enhanced delocalization of the excited state that controls also the escape of the hole from the sibling charge on the C_{60} acceptor.

In order to support the present experimental findings, and to complement the DFT/ZINDO study by Grancini et al.[18] of the PCPDTBT case,[18] we further perform accurate many-body Green's function Bethe–Salpeter (BSE) calculations of the optical (excitonic) properties of a short PCDTBT polymer taken to be isolated or facing a PCBM acceptor (Figure 7). Due to the cost of these techniques, the PCDTBT polymer we study is composed of 2 monomers, for a total length of about 4.2 nm. Such a simple geometry does not allow discussing the full delocalization of the hole over several polymer units, but it already provides an extremely clear signature of the delocalization for hot donor excitations. However, when comparing experimental and calculated spectra one has to take into account that the calculations pertain to a short oligomer in vacuum. Therefore, the energy scale is shifted to higher values since transition energies increase with decreasing oligomer length.

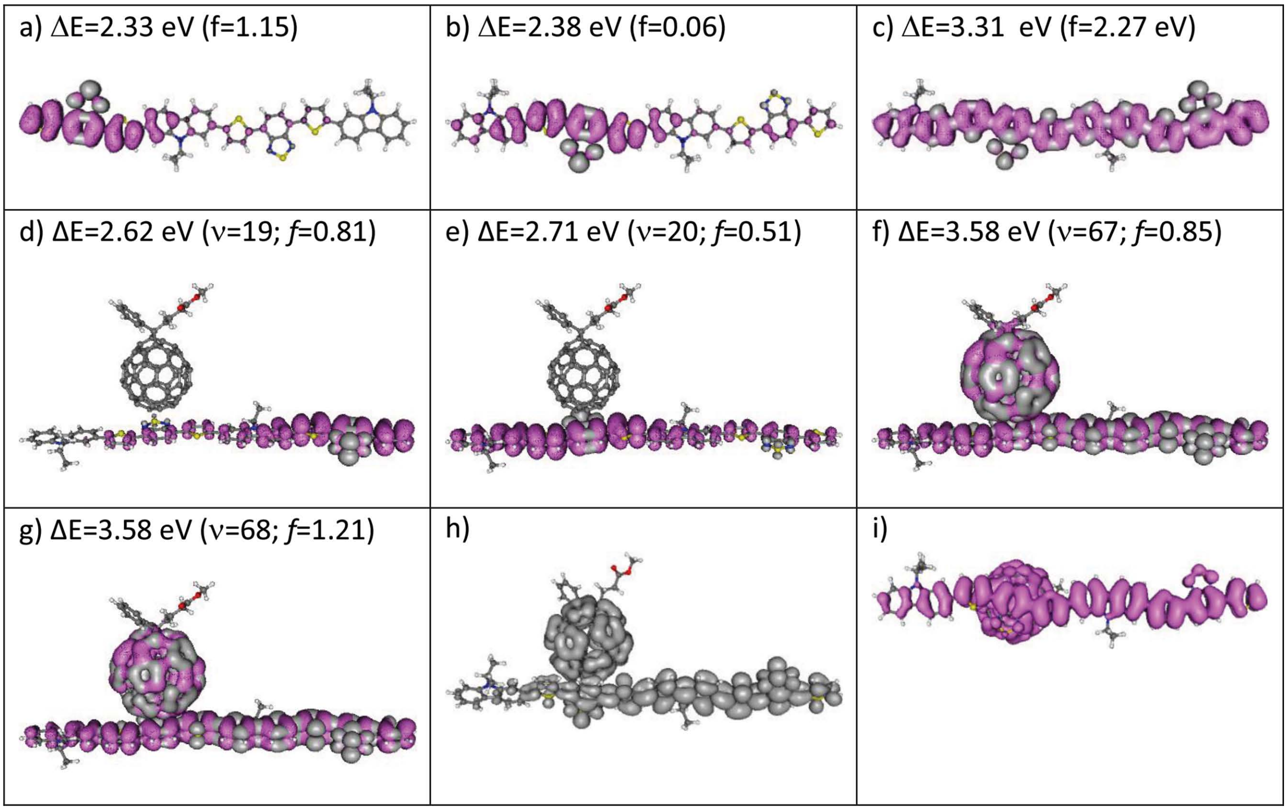

Figure 7. Representation for selected excitations in the PCDTBT polymer and PCDTBT/PCBM complex of the electron-averaged hole density (purple wireframe) and the hole-averaged electron density (solid gray) calculated from the corresponding Bethe–Salpeter electron–hole $\psi^{\mathrm{BSE}}_{0\to N}(r_e,r_h)$ excitonic states. a–c) Lowest lying (S_N–S_0) transitions (N = 1, 2) and first dipole-allowed "hot" (S_3–S_0) transition on the isolated polymer. d,e) Lowest lying (S_N–S_0) transitions (N = 1, 2) on the PCDTBT/PCBM complex. f,g) Lowest "hot" dipole allowed excitations with large weight on both the polymer and PCBM. h,i) Electron-only and hole-only distribution for the state represented in (f). For the hole density in (i), we have rotated the complex to better see the polymer. We provide above each picture the absolute excitation energy (ΔE) and oscillator strength f. For the complex, the absolute (ν) index transition is provided (the lowest $\nu = 1$ transition is a pure Frenkel PCBM transition). Isodensity contours have been taken at 1% of the maximum hole or electron density value in all cases.

We present in Figure 7a,b the energy, oscillator strength and excitonic wavefunctions corresponding to the lowest two polymer (S_N–S_0) transitions (N = 1, 2) showing some degree of localization on the benzothiadiazole units.[32] The first higher lying transition with significant oscillator strength is the (S_3–S_0) transition calculated to be at 3.3 eV (Figure 7c). In the absence of environmental (bulk) screening and Stokes shift, it is located about 1 eV above the lowest (S_1–S_0) transition, which compares favorably with the corresponding energy difference measured in solution (≈0.93 eV). The same behavior can be observed in the case of the PCDTBT/PCBM complex. The wavefunction for the lowest lying (S_N–S_0) transitions (N = 1, 2) is represented in Figure 7d,e showing clear similarities with the lowest lying excitations on the corresponding isolated polymer. The next excitations of the complexes exhibiting both a large oscillator strength and a large weight on the polymer are represented in Figure 7f,g. As for the isolated polymer chain, these are again located about 0.8–1.0 eV above the (S_1–S_0) transition. Comparing the complex with the isolated polymer case, we see that hot excitations located at about the same energy above the (S_1–S_0) transition start delocalizing not only over the entire polymer chain but also on the neighboring fullerene as a signature of excess kinetic energy. An analysis of the electron-only (Figure 7h) and hole-only (Figure 7i) distribution for these hot excitations on the complex clearly indicates that these are not charge–transfer states, but really states with the hole (the electron) completely delocalized over the two neighboring molecules. It is worth stressing that these optically accessible excited states are quasidegenerate in energy with a number of charge–transfer states with enhanced electron–hole radii,[26] so that charge separation at higher excitation energy could be favored either through an indirect pathway (i.e., involving a nonadiabatic coupling between the polymer S_3 and hot CT states) or a direct pathway (i.e., through wavefunction mixing in the much higher density of states of a realistic donor–acceptor interface, not captured by the calculations reported here for simple complexes). Obviously, delocalization of the higher excited donor excitations has a great impact on the size of the geminate pair that can subsequently fully dissociate but also the acceptor plays a major role because the strength of coupling depends on both partners.

4.3. Comparison to Single Layer Diodes

Figure 4 shows that there is also photodissociation in single layer PCPDTBT and PCDTBT diodes but it is roughly two orders of magnitude less efficient than in bilayers. This disparity is even greater in single layer diodes with MEH-PPV and MeLPPP[14–16] that are homo-polymers with unpolar repeat units as compared to donor–acceptor type copolymers. It is straightforward to associate this quantitative difference with the polarity of the donor that affects the size of the geminate electron–hole pair and, consequently, its Coulomb binding energy. In the case of single layer PCPDTBT and PCDTBT diodes, the saturation field of the photocurrent is beyond 10^6 V cm^{-1} (Figure 5). At higher field strength, the photocurrent cannot be measured reliably. Therefore, we can only give an upper limit for r_0. According to Equation (2), $F_{sat} > 10^6$ V cm^{-1} translates into $r_0 = 2$ nm, i.e., a factor of at least 4 lower than the electron–hole pair size in the donor–acceptor assembly. A more concise estimate would require a theory for photodissociation. Fitting the current field characteristic using an Onsager[33] or Onsager–Braun[34] formalism turns out to be unsuccessful. The reason is that those theories are premised on a point charge approximation that is inappropriate for conjugated polymers in which the excited state is more delocalized.[35] Nevertheless, 2 nm appears to be a realistic value for a strongly allowed S_1 state with partial charge character. Recall, on the other hand, that in typical π-conjugated homo-polymers the mean electron–hole separation is around 1 nm.[36]

When raising the photon energy from 1.8 to 3.5 eV the IQE increases by a factor of 30, equivalent to an increase of r_0 by almost by a factor of 2. Importantly, the IQE starts increasing not until an excess energy of about 0.5 eV above the $S_1 \leftarrow S_0$ 0–0 transition is supplied. This is in analogy with the constant saturation field in the bilayers and consistent with the notion that it is the electronic rather than vibronic excess energy that matters. It is also consistent with the spectral dependence of photoconduction in MEH-PPV and MeLPPP.[14–16]

5. Conclusions

Upon photoexciting PCDTBT or PCPDTBT a geminate electron–hole pair is generated that is only weakly Coulomb bound as evidenced by the low saturation field strength of the photocarrier yield. In fact, the electric field that exists in the bilayer due the built-in voltage is already sufficient to liberate the pair from its weak Coulomb potential. We find that dissociation is further facilitated by exciting the donor chromophore into a higher electronic state whose wavefunction is more extended. For the efficiency of the solar cell this has little influence because the intrapair electron separation is already on the order of 10 nm. Therefore, the electric field needed for complete dissociation is comparable to or lower than the built-in electric field. The generated electron–hole pair is therefore essentially free. In this case photodissociation becomes indistinguishable from direct optical excitation from a delocalized to a decoupled charge pair state, even more so if the photon energy is about 1 eV above the S_1–S_0 0–0 transition.[37] Nevertheless, photodissociation is, in its nature, not an instantaneous but a sequential process. This is not only borne out by the field dependent photocurrent measurements shown here, but it has also been demonstrated by the experiments by Grancini et al.[18] They show that upon excitation of the donor material electron–hole pairs are generated from precursor excitons at a rate of order of 2×10^{13} s^{-1}. This is also consistent with ultrafast pump–probe measurements by Herrmann et al.[5] on P3HT/C$_{60}$ bilayer cells structures that unambiguously show the instantaneous appearance of absorption from neutral excitations, while the signature from electron–hole pairs appears only subsequently with a rise time of 120 fs.[5]

We finally comment on the character of “hot” exciton dissociation. The underlying idea concerning hot dissociation is that an excited electron is kicked further away from the donor as the initial photon quantum energy increases. This would imply a larger electron–hole pair separation and a reduced rate for geminate recombination. The present results modify this concept. They demonstrate that it is the spatial extension of the initial excited state wavefunction that is important. After exciting a higher-lying state, the hole and electron are momentarily in a more delocalized and, consequently, in a high mobility state and are therefore able to further escape from each other in the course of a ballistic process rather than a thermalization process.[38] Obviously, the chains themselves should be fairly ordered. Recent spectroscopic work on PCPDTBT in solution shows that there is a transition from a disordered to a more ordered phase and, importantly, the absorption spectra of PCPDTBT films are identical with those of the ordered aggregates.[39]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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