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Citation for published version (APA):

Di Nuzzo, D., Koster, L. J. A., Gevaerts, V., Meskers, S. C. J., & Janssen, R. A. J. (2014). The role of photon energy in free charge generation in bulk heterojunction solar cells. *Advanced Energy Materials*, 4(18), 1400416-1/10. [1400416]. <https://doi.org/10.1002/aenm.201400416>

DOI:

[10.1002/aenm.201400416](https://doi.org/10.1002/aenm.201400416)

Document status and date:

Published: 01/01/2014

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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- The final published version features the final layout of the paper including the volume, issue and page numbers.

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The Role of Photon Energy in Free Charge Generation in Bulk Heterojunction Solar Cells

Daniele Di Nuzzo, L. Jan Anton Koster, Veronique S. Gevaerts, Stefan C. J. Meskers, and René A. J. Janssen*

To determine the role of photon energy on charge generation in bulk heterojunction solar cells, the bias voltage dependence of photocurrent for excitation with photon energies below and above the optical band gap is investigated in two structurally related polymer solar cells. Charges generated in (poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (C-PCPDTBT):[6,6]-phenyl-C61-butyric acid methyl ester (PCBM) solar cells via excitation of the low-energy charge transfer (CT) state, situated below the optical band gap, need more voltage to be extracted than charges generated with excitation above the optical band gap. This indicates a lower effective binding energy of the photogenerated electrons and holes when the excitation is above the optical band gap than when excitation is to the bottom of the CT state. In blends of PCBM with the silicon-analogue, poly[(4,4-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl] (Si-PCPDTBT), there is no effect of the photon energy on the electric field dependence of the dissociation efficiency of the CT state. C-PCPDTBT and Si-PCPDTBT have very similar electronic properties, but their blends with PCBM differ in the nanoscale phase separation. The morphology is coarser and more crystalline in Si-PCPDTBT:PCBM blends. The results demonstrate that the nanomorphological properties of the bulk heterojunction are important for determining the effective binding energy in the generation of free charges at the heterojunction.

1. Introduction

The dissociation of a charge transfer (CT) state at an organic donor-acceptor (D-A) interface into a charge separated (CS) state where electrons and holes are free to move is a critical

process in the operational mechanism of organic solar cells. At present the mechanistic details of the charge separation process are only partly understood. Due to the low dielectric constant, the electron and hole in the D^+-A^- CT state can be expected to be bound by Coulomb interactions across the heterojunction interface,^[1-4] typically by few hundreds of millielectronvolts, exceeding the thermal energy at room temperature by roughly a factor 10. At first glance, this makes dissociation of CT states into the free charges (CS) improbable. Yet an increasing number of organic solar cells exhibit internal quantum efficiencies for charge generation up to unity,^[5-7] implying very efficient dissociation of the interfacial D^+-A^- CT state or bypassing its formation via a “hot” process. **Figure 1** summarizes some of the critical processes in the charge generation and recombination in organic solar cells.

Under standard illumination conditions, photogenerated charges in an organic solar cell are dominantly created via excitation above the optical band gap, i.e., with photon energies $h\nu > E_{S1}$, where E_{S1} is the energy of the lowest excited

singlet state in the D-A blend ($E_{S1} = \min(E_{S1}(D), E_{S1}(A))$). For efficient organic solar cells, the energy of the CT state (E_{CT}) is preferably close to E_{S1} to prevent losing photon energy, yet $E_{S1} - E_{CT}$ has to be large enough to enable quantitative forward electron transfer. In addition, also direct excitation of the CT state can produce free charges.^[8,9] The low absorption coefficient of the interfacial CT state makes this sub optical band gap excitation ($E_{CT} < h\nu < E_{S1}$) of negligible importance for the power conversion efficiency of organic solar cells. Nevertheless the dissociation from the CT state into free charges is not only of scientific interest but also of profound importance for the overall performance if illumination with light $h\nu > E_{S1}$ produces fully relaxed CT states, before free charges are created. At present a strongly debated question is whether the excess energy (E_e), defined as the difference between the energy of the absorbed photons ($h\nu$) and the energy of the bottom of the CT band (E_{CT}), $E_e = h\nu - E_{CT}$, assists in the formation of free charges. CT excitons for which $E_e > 0$ are often indicated as “hot” CT excitons. Because hot CT excitons possess more delocalized wave functions, they are easier to dissociate. Evidence of a correlation between available excess energy and charge generation efficiency has been recently reported in literature.^[10-15]

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DOI: 10.1002/aenm.201400416

Figure 1. State diagram of a donor-acceptor organic solar cell and relevant photophysical processes. Direct excitation of the donor (D) or acceptor (A) can result in a relaxed interfacial D⁺-A⁻ charge transfer (CT) state or, avoiding relaxation, produce a charge separated state (CS) with free electrons and holes directly. Alternatively, the CT state can be excited and then lead to charge separation. Loss processes that can occur from the CT state are charge recombination to the ground state (GS) or formation of a triplet state (T₁). The diagram shows triplet formation for the donor only, but depending on its energy level it may also occur for the acceptor. The absorption coefficient for direct CT excitation is orders of magnitude less than for excitation of the two S₁ states, making direct absorption to the CT state less important for the solar cell performance.

On the other hand, it has also been demonstrated in various polymer-fullerene blends that the availability of photon excess energy does not influence the efficiency of CT state dissociation into free charges.^[16–21] Clearly, a better understanding of the mechanism of free charge generation at donor-acceptor heterojunctions is needed. Such an improved understanding is essential for further optimizing device performance. The need of excess energy for efficient CT dissociation would impose a limit to the maximum attainable open-circuit voltage (V_{oc}), since the latter scales with the energy of the CT state.^[8,22,23] In this respect it is important to understand that the energy difference between E_{S_1} and E_{CT} represents, in principle, an undesired energy loss, but if excess energy is important for achieving quantitative charge separation, this energy loss could enhance photocurrent.

Apart from the relative positioning of energy levels such as shown in Figure 1, the kinetics of the various processes is also important. Starting from the energetically relaxed CT state, the ratio of the rates for radiative and non-radiative charge recombination vs that of charge separation is crucial for the amount of free charges formed. Likewise, for hot CT states vibrational relaxation within the CT manifold competes with the dissociation of the hot CT state. It is well established that the nanoscale morphology of the blends plays a role in the kinetics of charge separation and recombination.^[24–26] In intimately, almost molecularly mixed, donor-acceptor blends charges have higher chance of recombining. In contrast, the presence of nanocrystalline fullerene domains has been found to enhance the dissociation of charge transfer states into free charge carriers.^[24,25] Several recent studies also suggest that the delocalization of electron and hole wave functions is beneficial for the efficiency of CT dissociation, because delocalized charges

result in a lower net binding energy at the interface.^[14,15,27–29] Molecular structures favoring such delocalization are therefore the best suited to obtain efficient CT dissociation. Finally, Monte Carlo simulations demonstrate that electron and holes may escape efficiently from their Coulomb interaction by using the static energetic disorder that is associated with organic semiconductors.^[30–33]

To investigate the role of excess energy in the photogeneration of charges in polymer:fullerene solar cells experimentally, it is possible to compare the electric field dependence of the external quantum efficiency (EQE) for a wide range of photon energies, corresponding to excitation to the bottom of the CT state ($CT \leftarrow S_0$) and above the optical band gap ($S_1 \leftarrow S_0$ and $S_n \leftarrow S_0$). For relaxed CT states the presence of an electric field can reduce the barrier for dissociation into free charges, while for higher excited CT states the electric field should have a lesser role. Hence, comparing the bias voltage dependence of charge generation for excitation at different photon energies $h\nu \geq E_{CT}$ can provide useful insight into the role of the excess energy.

In this paper we are specifically interested in the effect of the nanomorphology in free charge generation in relation to excess energy. We compare a blend of (poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b'']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (C-PCPDTBT) with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) to a blend of poly[(4,4-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl] (Si-PCPDTBT) with PCBM (Figure 2a). The only difference in chemical structure between the two small band gap polymers, C-PCPDTBT and Si-PCPDTBT, is the bridging atom in the CPDT unit, which is either a carbon or a silicon atom. This small structural change has a

Figure 2. a) Chemical structure of C-PCPDTBT, Si-PCPDTBT, and PCBM. b) Absorption spectra of C-PCPDTBT:PCBM and Si-PCPDTBT:PCBM films.

minimal effect on the molecular electronic structure and the absorption spectra of blend films with PCBM cover the same spectral range (Figure 2b), yet it induces a rather large difference in the nanoscale morphology in blends of these polymers with PCBM.^[34] As a result, Si-PCPDTBT:PCBM solar cells show a considerably higher power conversion efficiency compared to C-PCPDTBT:PCBM cells.^[34] We will show that the electric field dependence of charge separation in C-PCPDTBT:PCBM solar cells depends to a small, but distinct, extent on the photon energy for $E_{CT} < h\nu < E_{S1}$, but that it is independent of photon energy for $h\nu \geq E_{S1}$. For Si-PCPDTBT:PCBM cells, in contrast, charge generation is independent of the electric field for all photon energies. The results indicate that for above band gap excitations excess energy plays no role in free charge generation, even in relatively poor photovoltaic blends. Furthermore, in blends with optimized nanoscale morphology exciting the CT state band results in the same charge generation efficiency as when above-gap excitations are used.

2. Results and Discussion

2.1. Bias Dependent Current Density and External Quantum Efficiency

Figure 3 shows the J - V characteristics under 100 mW cm⁻² white light illumination (corresponding to ≈ 1 sun) of solar cells based on C-PCPDTBT:PCBM and Si-PCPDTBT:PCBM blends. Both blends were spin cast from a chlorobenzene solution containing the polymer and fullerene in a weight ratio of 1:2 without any co-solvents. Comparing C-PCPDTBT to Si-PCPDTBT, the fill factor (FF) and short-circuit current (J_{sc}) improve considerably, going from 0.39 to 0.62 and from 7 to 12 mA cm⁻² respectively, resulting in power conversion efficiencies increasing from close to 2% to about 4%, consistent with previous observations.^[34–36] We note that the optimized polymer–fullerene weight ratio varies somewhat with the exact polymer, but the performance does not change significantly for weight ratios between 1:2 and 1:3.^[34–36]

Figure 4a shows the normalized EQE of a C-PCPDTBT:PCBM solar cell for photon energies ranging from 1.24 to 3.1 eV, measured for applied bias voltages between -3 and $+0.65$ V. For this cell $V = +0.65$ V corresponds to a value slightly lower than V_{oc} under ≈ 1 sun illumination. The EQE was measured with modulated monochromatic light using sensitive lock-in detection. To create conditions representative for ≈ 1 sun operational illumination intensity, the measurements were performed with a constant background illumination (see Experimental Section). The curves in Figure 4a are all normalized to the maximum EQE, which always occurs at the same photon energy (1.75 eV) and coincides with the maximum of optical absorption of the blend. Figure 4a shows only a small selection of the complete set of measurements, namely the normalized EQE spectra recorded at $+0.65$, 0 , and -3 V. The maximum of the un-normalized EQE

Figure 3. J - V characteristics under white light (100 mW cm⁻²) for C-PCPDTBT:PCBM (empty circles) and Si-PCPDTBT:PCBM (full circles) solar cells. The solid line represents the numerical simulation of the illumination J - V curve of the C-PCPDTBT:PCBM solar cell.

Figure 4. a) Semi-logarithmic plot of the normalized EQE spectra of a C-PCPDTBT:PCBM solar cell at three different applied voltage biases. The inset shows the normalized EQEs for low photon energies. The blue curve represents the normalized electroluminescence (EL) from the same device obtained when biasing the device at +3 V forward bias. The vertical dashed line at 1.45 eV is a guide to the eye to differentiate between the $CT \leftarrow S_0$ and $S_1 \leftarrow S_0$ absorption bands. b) EQE recorded at different photon energies ranging from 1.31 to 3.02 eV (see legend) as function of applied bias, normalized to the EQE at $h\nu = 1.75$ eV.

increased from 9% at 0.65 V to 53% at -3 V, passing 28% at short circuit (0 V).

The normalized EQE spectra are shown in a semi-logarithmic plot to better visualize the different absorption bands. The low energy absorption is attributed to the $CT \leftarrow S_0$ transition.^[22,37] The $S_1 \leftarrow S_0$ of C-PCPDTBT transitions give rise to the absorption band with onset at ≈ 1.45 eV, as measured on thin films. The contribution of the absorption by C-PCPDTBT to the EQE extends to the UV. The PCBM contribution likely starts at the onset of absorption (1.75 eV), but it only becomes appreciable at 2.5 eV where the absorption coefficient of PCBM is much larger than at the onset. The EQE for excitations via the C-PCPDTBT and PCBM absorption bands is between 10 and 100 times higher than for direct excitation to the CT state.

Figure 4a shows no significant change in spectral shape of the EQE with applied bias for photon energies above ≈ 1.45 eV that correspond to excitations above the optical band gap. This observation rules out any effect of the excess energy for above optical band gap excitation in this blend, in accordance with

previous observations. In contrast, for photon energies below 1.45 eV, i.e., sub-optical band gap excitation, the normalized EQEs reveal a small, but distinct, monotonic increase going to higher reverse bias. The inset in Figure 4a illustrates that the increase is higher at the lower photon energies. Figure 4b depicts the EQE recorded at different photon energies normalized with respect to the EQE at $h\nu = 1.75$ eV and plotted as function of applied voltage bias. The change in the normalized EQE at $h\nu = 1.31$ eV amounts to $\approx 30\%$ going from 0.65 to -3 V bias. Above the optical band gap the change in normalized EQE with applied bias is negligible. At $h\nu = 3.02$ eV the normalized EQE shows a sharp, small decrease at $V = 0.65$ V, i.e., very close to V_{oc} where the absolute value of the EQE becomes very small. Therefore, we did not further consider this feature.

Figure 4a also shows the electroluminescence spectrum of the same device measured by applying a forward bias of $V = +3$ V. The electroluminescent emission can be attributed to the radiative recombination of the CT state,^[38] which is formed by recombination of injected electrons and holes that meet at the heterojunction. The photon energy of maximum electroluminescence intensity is an estimate for a lower bound for the energy of the bottom of the CT band: $E_{CT} = 1.18$ eV. We note, however, that energetic disorder in these bulk heterojunctions creates a distribution in E_{CT} . Taking $E_{CT} = 1.18$ eV and $V_{oc} = 0.70$ V, we find that $E_{CT} - qV_{oc} = 0.48$ eV, in excellent agreement with general relation $E_{CT} = qV_{oc} - 0.47$ eV found previously.^[22]

Figure 5a shows the corresponding EQE measurements for a Si-PCPDTBT:PCBM solar cell at $V = +0.5$, 0, and -2.2 V, normalized at the maximum of polymer absorption ($h\nu = 1.77$ eV). In this solar cell $V_{oc} = 0.56$ V. At $V = +0.5$ V the EQE signal became undetectable for photon energies below 1.25 eV. The maximum of the EQE has an absolute value of 29% at $V = +0.5$ V, increases to 50% at short circuit, and to 58% at -2.2 V. The assignment of the EQE bands to $CT \leftarrow S_0$ and $S_1 \leftarrow S_0$ excitations is indicated in Figure 5a and does not differ significantly from the assignment for C-PCPDTBT:PCBM (Figure 4a). Given the very similar chemical structure of the two polymers, the optical properties are rather similar. The Si-PCPDTBT:PCBM did not show any detectable electroluminescence from the CT state, in accordance with previous results.^[34] To estimate a lower bound for the energy of the CT state in the Si-PCPDTBT:PCBM we use the linear relation between E_{CT} and V_{oc} and consider that $E_{CT} \approx 0.56 + 0.47 = 1.03$ eV in Si-PCPDTBT:PCBM.

Figure 5a reveals that for the Si-PCPDTBT:PCBM solar cell there is no measurable change in the shape of the EQE in the bias range $-2.2 < V < 0$ V. A change in spectral shape of the EQE is only observed in the bias range $0 < V < +0.5$ V, at photon energies between 2.5 and 3 eV, and below 1.5 eV. In these two regions of the EQE spectrum more bias is required to extract charges compared to those created by exciting between 1.5 and 2.5 eV. The inset in Figure 5a shows the normalized spectra at three different biases in the low energy region below 1.4 eV. The normalized spectra recorded at -2.2 and 0 V are virtually identical. The normalized EQE recorded at +0.5 V deviates from the other two spectra.

The behavior of the EQE as function of bias at low photon energy is shown in Figure 5b. Here the EQE recorded for different photon energies and normalized to the values at

Figure 5. a) Semi-logarithmic plot of the normalized EQE spectra of a Si-PCPDTBT:PCBM solar cell at three different applied voltage biases. The inset shows the normalized EQEs in the low energy band. The vertical dashed line is a guide to discriminate between the $CT \leftarrow S_0$ and $S_1 \leftarrow S_0$ absorption bands. b) EQE recorded at different photon energies ranging from 1.31 to 3.02 eV (see legend) as function of applied bias, normalized to the EQE at $h\nu = 1.77$ eV.

$h\nu = 1.77$ eV is shown as function of applied voltage bias. Between -2.2 and $+0.3$ V the normalized EQE values are essentially constant with bias. The normalized EQE reduces substantially only above 0.4 V. Apart from the fact that the photocurrent is approaching zero for bias >0.4 V, which reduces the accuracy of the measurement, the explanation for this might be found in the fact that the Si-PCPDTBT polymer is known to aggregate more strongly than C-PCPDTBT.^[34] The spectral response related to Si-PCPDTBT falls in the ≈ 1.6 – 2.1 eV region. Regions in the bulk with lower degree of order could be present. In these regions the transport of photogenerated charges is expected to be more problematic and therefore more field dependent than in the more ordered domains. We tentatively attribute the stronger field dependence observed between 2.5 and 3 eV to lower collection efficiency of charges created in less ordered regions of the bulk. We previously observed a similar behavior on the EQE spectral dependence on bias of P3HT:PCBM solar

cells.^[18] An alternative explanation is the generation of bound electron-hole pairs in the PCBM domains.

Summarizing, the spectral shape of the EQE changes with applied bias for C-PCPDTBT:PCBM solar cells in the low energy part of the spectrum, corresponding to direct absorption to the CT state. Charges created via excitations in this part of the spectrum require more bias voltage to be dissociated compared to charges created via excitations of C-PCPDTBT or PCBM. Compared to C-PCPDTBT:PCBM cells, the bias voltage dependence of the EQE spectral shape is much smaller in Si-PCPDTBT:PCBM solar cells. A barely detectable change of the low energy part of the spectrum appears only for bias voltages between short circuit and open circuit. Si-PCPDTBT:PCBM devices do not give any measurable electroluminescence in forward bias. For C-PCPDTBT:PCBM devices, instead, a clear CT electroluminescence is observed.

2.2. Transmission Electron Microscopy (TEM)

Bright field TEM images on bulk heterojunction thin films consisting of C-PCPDTBT or Si-PCPDTBT mixed with PCBM are shown in **Figure 6**. The films were spin coated from chlorobenzene solutions under the conditions as the active layers in the solar cells devices. Consistent with previous reports,^[34,39] we find a very finely dispersed blend for C-PCPDTBT:PCBM, with the TEM images showing barely any contrast. The images of Si-PCPDTBT:PCBM blends show instead a clear contrast, which is attributed to phase separation between PCBM richer domains (darker regions) and Si-PCPDTBT domains.^[34] The phase separation appears to be in the order of a few tens of nanometers. The polymer domains show a fibril-like structure, indicating aggregation. Enhanced polymer aggregation in Si-PCPDTBT:PCBM is also indicated by the presence of an additional ring in the electron diffraction image (inset of Figure 6b), which is not visible in the C-PCPDTBT:PCBM case (inset in Figure 6a). The additional diffraction ring indicates a stacking distance of 0.36 nm, which is in the typical range of distances for π - π stacking between polymer chains.^[34]

Additionally we observe the formation of 20 – 30 nm size lamellar crystals in the Si-PCPDTBT:PCBM blend (Figure 6c), showing an average d -spacing of 1.7 nm. This value is in good correspondence with the observed 2θ of around 5° observed in grazing incidence $CuK\alpha$ ($\lambda = 1.5418$ Å) X-ray diffraction measurements on similar Si-PCPDTBT:PCBM blends compositions by Morana et al., corresponding to $d = 1.77$ nm.^[34] These semicrystalline structures can be attributed to Si-PCPDTBT π -stacked chains forming lamellae, separated from each other by the side chains. Similar structures have been observed previously with TEM in P3HT domains inside P3HT:PCBM blends.^[40]

2.3. Modeling of Photocurrents in C-CPDTBT:PCBM

We now attempt to quantify the bias-dependence of the photocurrent in terms of a binding energy and an electron-hole separation. We make the assumption that the transport properties of free carriers are independent of the energy of the primary photoexcitations from which they are generated. With this assumption, the comparison of the bias dependence of extracting charges

Figure 6. Bright field TEM images and electron diffraction patterns (inset) of the active layers containing a) C-PCPDTBT:[60]PCBM and b) Si-PCPDTBT:[60]PCBM. (1:2 weight ratios). c) High magnification bright field TEM image of the active layer with Si-PCPDTBT:PCBM.

generated with different photon energies reduces to a comparison of the bias dependence of the separation of the CT state into free charges at the donor-acceptor heterojunction. At this point one might argue that with different photon energies free charges are generated which have different CT states as precursors.

To investigate the nature of the CT states as precursor states to free charges, we analyzed the results by means of numerical simulations. We use numerical one-dimensional drift-diffusion simulations to reproduce the dependence of the EQE on the applied bias at each photon energy $h\nu$. In the numerical simulations, the field dependence of charge generation is treated using the Onsager-Braun model for the dissociation of the CT state,^[41–43] as proposed by Blom et al.^[44] In the Onsager-Braun model the field dependent rate of CT state dissociation k_d is described as:

$$k_d(E, T) = k_r \frac{3}{4\pi R_{cc}^3} e^{-E_B/k_B T} \frac{J_1(2\sqrt{-2b(E, T)})}{\sqrt{-2b(E, T)}} \quad (1)$$

where R_{cc} is the electron-hole separation distance in the CT state (i.e., with the electron on the fullerene acceptor and the

hole on the polymer donor) and E_B is the binding energy, expressed as $E_B = q^2/4\pi\epsilon_0\epsilon_r R_{cc}$, with ϵ_r the dielectric constant of the medium. J_1 is the Bessel function of order 1 and b is given by $b(E, T) = q^3 E/8\pi\epsilon_0\epsilon_r k_B^2 T^2$. The recombination rate constant is modeled via the Langevin equation as $k_r = q\langle\mu\rangle/\epsilon_0\epsilon_r$, with $\langle\mu\rangle$ the average charge mobility of the electrons and holes. In the model, the field and temperature dependent probability $P(E, T)$ of CT state dissociation is calculated as $P(E, T) = k_d(E, T)/[k_d(E, T) + k_r]$, where $k_d(E, T)$ is the rate of dissociation into free charges and k_r is the rate of CT state recombination. To account for disorder in the blend, a distribution of CT states having different separation distances was incorporated into the numerical simulations. To this purpose a normalized distribution function $f(R_{cc}, \gamma)$ was used as proposed by Blom et al.^[44]

$$f(R_{cc}, \gamma) = \frac{4}{R_{cc}^3 \sqrt{\pi}} \gamma^2 e^{-\gamma^2/R_{cc}^2} \quad (2)$$

$f(R_{cc}, \gamma)$ reaches its maximum at R_{cc} , and the average electron-hole distance can be calculated as:

$$d = \int_0^\infty \gamma \cdot f(R_{cc}, \gamma) d\gamma = \frac{2R_{cc}}{\sqrt{\pi}} \quad (3)$$

The dissociation probability P is calculated as the integrated probability over the distribution of separation distances, so that:

$$P(E, T) = \int_0^\infty p(E, T, \gamma) f(R_{cc}, \gamma) d\gamma \quad (4)$$

where $p(E, T, \gamma)$ is the dissociation probability at a specific distance γ . The procedure used for the numerical simulations has been described in detail by Koster et al.^[45] (see also Experimental Section).

We emphasize that the Onsager-Braun model might not correctly describe all the microscopic physical details of the complex kinetics of the CT dissociation process.^[33,46] The Onsager-Braun model assumes an equilibrium between CT state and free carriers, which does not exist for not-relaxed CT states that may be involved in the charge generation. Further one often finds that fitted rates for CT recombination (k_r) are in the microsecond domain, which is long compared to the fluorescence lifetime of the CT states, which is rather in the nanosecond domain. However, presently, better models are not available. We use the model to parameterize the experimental data in terms of an effective electron-hole separation distance and an effective binding energy, without implying exactness of the values obtained. We simulate the photocurrent recorded at different photon energies as function of the bias voltage and we fit the results to the experimental data using R_{cc} as fit parameter. The correlation between R_{cc} and the energy of the exciting photons can then be evaluated. This analysis was possible for the C-PCPDTBT:PCBM cells. For the Si-PCPDTBT:PCBM cells the change in dependence on field at different photon energies was too minute to obtain meaningful information.

As starting point, we simulated the J - V characteristics of the C-PCPDTBT:PCBM cell under constant white light illumination (Figure 3). The best fit was obtained using $R_{cc} = 1.9$ nm

Table 1. Parameters used in the numerical simulations.

Parameter ^{a)}	Description	Value
T	Temperature	295 K
L	Thickness of the active layer	80 nm
N_C	DOS of conduction and valence band	$2.5 \times 10^{25} \text{ m}^{-3}$
μ_n	Electron mobility	$7 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$
μ_p	Hole mobility	$1.5 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$
g_{max}	Maximum charge generation rate	$11.6 \times 10^{27} \text{ m}^{-3} \text{ s}^{-1}$
k_f	CT recombination rate	$6.25 \times 10^6 \text{ s}^{-1}$
ϵ_r	Relative dielectric constant	3
R	Langevin recombination pre-factor	0.25
R_{cc}	Electron-hole separation in CT	1.9 nm

^{a)}To fit the IQE vs voltage bias at different excitation photon energies only R_{cc} was varied.

as separation distance of the electron and hole in the CT state (solid line in Figure 3), corresponding to an average distance of about 2.1 nm Equation (3). The relevant parameters used in the simulation are shown in Table 1 and are similar to the parameters used by Lenes et al.^[47]

The EQE of a solar cell is given by $\text{EQE}(h\nu) = \eta_{\text{abs}}(h\nu) \cdot \text{IQE}(h\nu)$, where $\eta_{\text{abs}}(h\nu)$ is the efficiency of photon absorption at a given wavelength and IQE is the internal quantum efficiency. In our modeling, $\eta_{\text{abs}}(h\nu)$ is considered independent of applied bias. Conceptually, the IQE can be considered as being determined by three consecutive processes: photoinduced charge transfer to produce a CT state, dissociation of the CT state into free charges, and the transport and collection of free charges. Transport and collection are in competition with recombination, which may reduce the IQE. For the present discussion we assume that all absorbed photons create relaxed or hot CT states that may be dissociated or recombine. For C-PCPDTBT:PCBM blends this assumption is justified by the virtually complete quenching of the polymer photoluminescence together with the appearance of CT photoluminescence. In the Onsager-Braun model, the IQE approaches unity in the limit of high reverse bias. We therefore normalized the simulated photocurrent to the saturation value at high reverse voltage, obtaining the simulated IQE of the solar cell as function of bias. We fitted the simulated IQE vs bias to the experimental EQE vs bias data divided by η_{abs} defined above, which in this case is an additional free fitting parameter. To fit the field dependence at different excitation photon energies, only η_{abs} and R_{cc} were changed. All the other parameters were kept fixed in the simulations to the values in Table 1, corresponding to the assumption that the transport of charges is independent of the properties of the intermediate CT state from which they were generated. Hence we interpret differences in the field dependence of the photocurrent for different photon energies as being solely caused by differences in dissociation efficiency of CT states.

The results of the simulations on a reduced set of photon energies are shown in Figure 7. The data are plotted versus effective voltage bias V_{eff} , which corresponds to the absolute values of the difference between the applied voltage and the voltage at which $J_{\text{photo}}(V) = 0$, where J_{photo} is the photocurrent

Figure 7. IQE at as function of the effective voltage bias of a C-PCPDTBT:PCBM solar cell (circles) for selected photon energies and simulated IQE (lines). The experimental data have been fitted, changing only the separation distance (R_{cc}) of electron and hole in the geminate pair. The legend lists the photon energies $h\nu$ and the corresponding fitted R_{cc} .

density. For each photon energy, the IQE vs V_{eff} curve can be reproduced by changing only R_{cc} . The curve recorded at 1.24 eV was fitted using $R_{\text{cc}} = 1.47$ nm. Increasing the photon energy results in an increase of R_{cc} , reaching values of around 1.9 nm at ≈ 1.7 eV. For higher photon energies, the R_{cc} needed to fit the curves does not change sensibly. R_{cc} is 1.98 nm for excitations at 3.02 eV. R_{cc} values of ≈ 1.9 nm for above band gap excitations are in agreement with the value of 1.9 nm used to fit the white light J - V curve. This is not surprising, since the main part of the current under white light illumination is generated via above band gap excitations.

Figure 8 shows the R_{cc} values obtained for several of the used photon energies as function of the excess photon energy $E_e = h\nu - E_{\text{CT}}$ (with $E_{\text{CT}} = 1.18$ eV). Two regions can be discerned. First R_{cc} rises steeply with increasing photon excess energy. Then it reaches a value of ≈ 1.9 nm at around $E_e = 0.5$ eV and does not increase sensibly for higher excess energies. As stated above, R_{cc} is used as measure of the effective binding energy E_B of the CT pair, which is calculated as:

$$E_B = \int_0^\infty \frac{q^2}{4\pi\epsilon_0\epsilon_r\gamma} \cdot f(R_{\text{cc}}, \gamma) d\gamma = \frac{q^2}{2\pi\sqrt{\pi}\epsilon_0\epsilon_r R_{\text{cc}}} \quad (5)$$

where we use $\epsilon_r = 3$. The values of E_B as function of excess energy are also shown in Figure 8. The estimated binding energy amounts to ≈ 0.39 eV for the lowest excited CT states and decreases to a stable value of ≈ 0.28 eV for photons carrying more excess energy. The saturation value of R_{cc} and E_B is reached at a photon energy of ≈ 1.7 eV, that is for excitations in the C-PCPDTBT absorption band.

The results suggest that in C-PCPDTBT:PCBM blends free charges are generated via intermediate CT states which have different effective binding energy depending on the energy of the exciting photon. In particular, photo-excitations above the

Figure 8. Values of R_{cc} (full symbols) obtained from the simulations plotted versus the available excess energy E_e for C-PCPDTBT:PCBM blends. The photon energy $h\nu$ is also shown on the top axis. The corresponding effective binding energies E_b of the CT pairs calculated using $E_b = q^2 / 2\pi\sqrt{\epsilon_0\epsilon_r R_{cc}} - 2\pi\sqrt{\epsilon_0\epsilon_r R_{cc}}$ Equation (5) and $\epsilon_r = 3$ are shown (empty symbols).

optical band gap result in free charge generation via intermediate CT states with effective binding energy lower than for CT states populated through optical excitation in the tail of the CT absorption band, the difference reaching about 0.1 eV. CT states populated with higher photon energy are the most relevant precursors to free charges in the solar cell under standard white light illumination (≈ 1 sun), because the absorption coefficient is above the optical band gap.

Our analysis cannot provide an exact insight into the microscopic nature of the difference in photocurrent generation at low and high photon energies. A possible interpretation could be that higher photon energies give access to CT states that are less bound because of more delocalized electron and hole wave functions, consistent with the findings of Refs. [14,15] and [29]. An alternative explanation is consistent with recent results that consider the importance of energetic disorder in the dissociation of CT states. Monte Carlo simulations indicate that CT dissociation in bulk heterojunctions can proceed via states which are in the low energy tail of a disorder-broadened density of states (DOS).^[33] Depending on the initial energies of the electron and hole, the energy the charges can gain by further relaxation in the DOS may, or may not, be small as compared to the Coulomb barrier to be overcome. In the former case the electron and hole have high probability for dissociation into free charges at low electric fields. In the latter case, which is likely to coincide with excitation in the lower energy part of the CT band, the simulations showed lower probability of CT dissociation and a stronger dependence on electric field.

3. Conclusion

We measured the electrical field dependence of the EQE spectra of C-PCPDTBT:PCBM and Si-PCPDTBT:PCBM solar cells to investigate the influence of the photon energy ($h\nu$)

on the process of charge generation in organic solar cells. In C-PCPDTBT:PCBM blends we find that the extraction of charges generated with sub band gap excitations in the CT band have a stronger dependence on applied voltage bias than the extraction of charges generated with above band gap excitations. We attribute the increased field-dependence of the EQE spectra to a bias dependence of the dissociation of the interfacial CT state. We analyzed the measured photocurrents in terms of the Onsager-Braun model for field dependent CT state dissociation and parameterized the differences in an effective binding energy of the corresponding CT state that acts as precursor of free charges. In C-PCPDTBT:PCBM solar cells we find that the effective binding energy of the charge transfer state precursor of free charges decreases with increasing photon excess energy for photon energies below the optical band gap. For excitations above the optical band gap the effective binding energy is lower than for sub band gap excitations and is practically independent on the amount of available excess energy. Under white illumination the vast majority of extracted charges are generated via above band gap excitations. Therefore our results suggest that, in solar cells working under standard conditions, the relevant intermediate states in charge generation are a reduced set of CT states with energies higher than the completely relaxed state at the bottom of the CT band. The microscopic nature of the different CT states that might be involved in charge generation when sub band gap or above band gap excitations are used is beyond the reach of our analysis. As a consequence we presently cannot unravel the exact mechanism of CT dissociation in the studied blend. Possible interpretations are CT dissociation via states with different degree of delocalization^[14,15,29] or dissociation assisted by energetic disorder.^[33]

For Si-PCPDTBT:PCBM solar cells the excess energy does not enhance the CT dissociation efficiency, if not at very small effective fields corresponding to $\approx V_{oc}$ conditions. This suggests that relaxed CT states have the same dissociation efficiency as higher energy CT states. The difference we observed between C-PCPDTBT and Si-PCPDTBT based blends correlates with a difference in nanomorphology. In C-PCPDTBT:PCBM blends the donor and acceptor are very finely mixed. In contrast, Si-PCPDTBT:PCBM blends show enhanced phase separation and semicrystalline polymer domains with sizes in the order of 20–30 nm. Hence an alternative explanation is that, due to larger domains of the Si-PCPDTBT:PCBM blend, the exciton excess energy is lost before it reaches the interface. This explanation, however, is less likely to hold for direct excitation of the CT state which only occurs at the donor-acceptor interface. The results confirm that CT dissociation is favored by donor-acceptor nanomorphologies with separated and ordered phases.^[24,25] Large and ordered domains can be expected to result in enhanced delocalization of the electron and hole wave functions, which would in turn reduce the effective binding energy of the CT pairs.^[48] Moreover, Si-PCPDTBT:PCBM blends exhibit less geminate recombination to the ground state and to the triplet state of the polymer compared to C-PCPDTBT:PCBM,^[49] supporting the idea of enhanced CT dissociation efficiency. The independence of charge generation on excess energy in Si-PCPDTBT:PCBM can therefore be explained in terms of the enhanced CT dissociation efficiency: in this blend all the CT states, including the ones created at the bottom

of the CT band dissociate with the same (high) efficiency in presence of moderate electric fields. Consistently with our suggestions, in systems showing similar phase-separated nanomorphologies comparable to that of Si-PCPDTBT:PCBM, such as P3HT:PCBM or MDMO-PPV:PCBM, other authors have also concluded that excess energy is not a necessary requirement for CT dissociation.^[16,17]

In conclusion, we suggest that to achieve high charge generation efficiency large energy offsets between the donor and acceptor materials in the bulk heterojunction are probably not really mandatory. Rather, the morphological properties of the donor-acceptor blend should be tuned to optimize the efficiency of CT dissociation.

4. Experimental Section

Solar Cell Fabrication: Photovoltaic devices were made by spin coating poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) (Clevios P, VP Al4083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates (14 Ω per square) (Naranjo Substrates). The photoactive layer was deposited by spin casting in air at 1500 rpm, using a chlorobenzene solution containing 10 mg mL⁻¹ C-PCPDTBT (M_w = 55.7 kg mol⁻¹, PD = 2.28, Konarka) or Si-PCPDTBT (M_w = 52.8 kg mol⁻¹, PD = 2.85, Konarka), blended with 20 mg mL⁻¹ [6,6]-phenyl-C₆₁-butyric acid methyl ester [60]PCBM (Solenne). The metal electrode, consisting of LiF (1 nm) and Al (100 nm), was deposited by vacuum evaporation at $\approx 3 \times 10^{-7}$ mbar. The active area of the cells was 0.091 cm² and the thickness of the active layer was ≈ 80 nm for both C-PCPDTBT and Si-PCPDTBT cells.

J-V and EQE Measurements: J-V curves were recorded using a Keithley 2400 source meter. White light 100 mW cm⁻² illumination was provided by a tungsten-halogen lamp corrected with a Schott GG385 UV filter and a Hoya LB120 daylight filter. Under these conditions C-PCPDTBT based devices showed a short-circuit current (J_{sc}) of 7.0 mA cm⁻², a fill factor (FF) of 0.39 and an open-circuit voltage (V_{oc}) of 0.69 V, resulting in a maximum power point (MPP) of 1.91 mW cm⁻². Si-PCPDTBT based devices showed a short-circuit current (J_{sc}) of 12 mA cm⁻², a fill factor (FF) of 0.62 and an open-circuit voltage (V_{oc}) of 0.56 V, resulting in a maximum power point (MPP) of 4.20 mW cm⁻². EQE measurements were performed with the devices kept in a nitrogen-filled sealed box with a quartz window and illuminated through an aperture of 2 mm. Mechanically modulated (Stanford Research, SR 540) monochromatic (Ortel, Cornerstone 130 Monochromator) light from a 50 W tungsten halogen lamp (Osram 64610) was used as probe light, in combination with continuous bias light from a solid state laser (B&W Tek Inc. 532 nm) to create representative illumination intensity for 1 sun conditions, which were set matching J_{sc} with the J_{sc} obtained under 100 mW cm⁻² white light. The response was recorded as the voltage over a 50 Ω resistance, using a lock-in amplifier (Stanford Research Systems SR830). Variable voltage bias over the cell was applied by the lock-in-amplifier. The measurement in the low energy EQE band was also repeated placing a low-pass cutoff filter ($h\nu > 1.59$ eV) in front of the device, to rule out contributions from higher energy stray photons coming out of the monochromator.

TEM: TEM was performed on a Tecnai G² Sphera TEM (FEI) operated at 200 kV. Bright field TEM images were acquired under slight defocusing conditions (see also Ref. [34]) The thin films were prepared under the same processing conditions as for the active layer of the solar cells.

Photoluminescence and Electroluminescence: To measure steady state electro-luminescence the solar cell was driven in forward bias (+3 V) in a nitrogen-filled sealed box with a quartz window. The experiment was performed at room temperature using an Edinburgh Instruments FLSP920 double-monochromator luminescence spectrometer equipped with a nitrogen-cooled near-IR sensitive photomultiplier (Hamamatsu). The luminescence signal was corrected for the spectral response of the monochromators and photomultiplier.

Drift-Diffusion Simulations: A detailed description of the model and the algorithm implemented can be found in ref. [45]. In the present work constant electron and hole mobilities were used. No electron and hole traps were included. The Onsager-Braun field dependence of charge generation was implemented with the distribution of electron-hole separation distances in the CT state given by Equation (2). The generation rate was assumed to be constant in space through the active layer. Ohmic collecting electrodes were used in the simulation.

Acknowledgements

The authors thank Dominique Wehenkel and Martijn Kemerink for useful discussions. The work of D.D.N. and V.S.G. formed part of the research program of the Dutch Polymer Institute (DPI, projects 631 and 660). L.J.A.K. acknowledges support by a grant from STW/NWO (VENI 11166). The research leading to these results has received funding from the Ministry of Education, Culture and Science (Gravity program 024.001.035) and was part of the Solliance Organic Photovoltaics Programme.

Received: March 8, 2014

Revised: July 6, 2014

Published online: August 4, 2014

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