Influence of photon excess energy on charge carrier dynamics in a polymer-fullerene solar cell

Published in:
Advanced Energy Materials

DOI:
10.1002/aenm.201200030

Published: 01/01/2012

Document Version
Accepted manuscript including changes made at the peer-review stage

Please check the document version of this publication:

• A submitted manuscript is the author's 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.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

Citation for published version (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Download date: 11. Dec. 2018
Influence of Photon Excess Energy on Charge Carrier Dynamics in a Polymer-Fullerene Solar Cell

Tom G. J. van der Hofstad, Daniele Di Nuzzo, Mauricio van den Berg, René A. J. Janssen, and Stefan C. J. Meskers*

An important question in research on polymer solar cells is the mechanism of free charge carrier generation. In organic bulk heterojunction solar cells, photoinduced electron transfer between the donor and acceptor molecules leads to population of a charge transfer (CT) state at the donor-acceptor interface. The residual electrostatic binding energy between electron and hole in the CT state may be considerable; experimental studies indicate a binding energy of 0.1–0.2 eV which is much higher than the thermal energy ($k_B T = 0.025$ eV). Given the low dielectric constant of organic materials ($\varepsilon_r = 3–4$) charges need to be separated over a large distance (10–15 nm) before their electrostatic interaction energy becomes comparable to $k_B T$. Even though the lifetime of the CT state can be as short as only a few nanoseconds,[5,6] the efficiency of free charge carrier generation can be very high. In optimized polymer solar cells, charge carrier generation occurs with an efficiency close to unity.[7,8] The mechanism by which the large energy barrier for charge separation from the CT state is overcome within the short lifetime is not known. Several explanations have been proposed, but no consensus on this issue has yet been reached.[9,10]

One particular explanation for the efficient charge generation involves the excess energy liberated in the photoinduced electron transfer step leading to the formation of the CT state.[11–13] In polymer-methanofullerene solar cells containing poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PC$_{60}$BM), there is a large difference in energy between the lowest singlet excited states $S_1$ on P3HT (1.9 eV) and on PC$_{60}$BM (1.7 eV) relative to the CT state (1.1 eV).[14,15] Photoinduced electron transfer from the $S_1$ state on PC$_{60}$BM or from the higher lying $S_1$ state on P3HT, leads to formation of a “hot” CT state and the 0.6 eV energy dissipated in the electron transfer step may still be available to drive apart the positive and negative charge in the CT state to yield a charge separated state. For this mechanism to be efficient, charge separation needs to be much faster than vibrational relaxation within the manifold of CT states. This mechanism is illustrated in Figure 1.

It has been shown that the CT state in the P3HT:PC$_{60}$BM junction can be populated directly from the ground state by illumination with 1.2–1.6 eV photons.[14,16,17] This opens the possibility to generate “cold” CT states with much less excess energy and to test the abovementioned hypothesis on the importance of the excess energy for charge separation.

By comparing the internal quantum efficiency and the open circuit voltage ($V_{oc}$) for P3HT:PC$_{60}$BM solar cells upon excitation of the lowest excited singlet state of P3HT and under direct excitation of the CT state, Lee et al. conclude that the influence of excess energy liberated in the electron transfer process is negligible for the formation of free charges.[17]

Here we investigate the influence of excess energy on the charge recombination process and on the presence of long-lived, photo-generated charge carriers in P3HT:PC$_{60}$BM photovoltaic cells employing the charge extraction by linear increasing voltage (CELIV) method.[18–20] In the photo-CELIV experiment, a short light pulse is used to generate carriers (Figure 2) and by applying a voltage ramp at a variable delay after the excitation pulse, charge carriers are extracted. During illumination, a compensating bias voltage $V_{bias}$ comparable in magnitude to $V_{oc}$ is applied to minimize extraction of charge carriers due to built-in electric fields in the cell. During the ramp, the applied bias is lowered to extract long-lived charge carriers by $\Delta V = 2.0$ V, starting from $V_{bias}$ and reaching a reverse bias voltage $V_{cell}$ of approximately $-1.5$ V.

Results from photo-CELIV measurements for as-cast P3HT:PC$_{60}$BM solar cells are shown in Figure 3. In as-cast P3HT:PC$_{60}$BM films the mixing of the donor and acceptor is relatively intimate and large semi-crystalline domains of P3HT and PC$_{60}$BM have not yet been formed.[21] Figure 3a shows results for direct excitation of the CT state in P3HT:PC$_{60}$BM using 1.55 eV excitation. An average number density of light induced extractable charge carriers, $n_{avg}$, is determined by integrating the photoinduced excess current during the extraction pulse over time and dividing by the volume of the bulk heterojunction. $n_{avg}$ is plotted as a function of delay time.
time-integrated photocurrent as a function of fluence. For the low fluences used in the CELIV experiment, the number of extracted carriers varies linearly with fluence. This excludes two-photon absorption by either P3HT or PC60BM as excitation mechanism in the charge generation process. Moreover, insertion of additional low-pass cut-off filter to eliminate any high energy photons with energy >1.59 eV did not result in any detectable change in the signal for either spontaneous photocurrent or delayed extraction current.

The dynamics of the charge carriers created by sub-gap excitation can be compared to the case of above-gap excitation, where 2.14 eV photons are used. The results are shown in Figure 3b,d. Also for excitation with 2.14 eV photons we observe a power-law type decay for the extractable charge carriers, with an exponent that is very similar to the case of sub-gap excitation via the CT transition.

In order to compare carrier dynamics for direct and indirect population of the CT states more quantitatively, we have determined the fraction of the total number of extractable carriers which can still be extracted after a delay time ($\tau_{\text{delay}}$, Figure 2). To obtain this surviving fraction, first the total number of extractable photogenerated carriers was determined by integrating the photocurrent upon application of a constant $V_{\text{bias}} = -2$ V, bias during pulsed illumination. Dividing the number of charge carriers after a delay time by this total number of extractable carriers then yields the fraction. For the two photon energies between illumination pulse and the onset of the charge extraction ramp. As can be seen, 5 µs after the light pulse the cell holds around $10^{15}$ extractable carriers per cm$^3$. With increasing delay time, $n_{\text{avg}}$ decays following a power-law. Upon lowering the fluence $I$ of the laser pulse used to illuminate the cell, fewer photoinduced charge carriers can be extracted. Figure 3a shows results for three difference fluencies by attenuating the primary beam with fluence $I_0 = 4$ mJ cm$^{-2}$ per pulse.

The range of fluences used for each measurement was chosen such that the deviations in linearity of the magnitude of the spontaneous photocurrent with light intensity under short circuit condition were less than <5%. To illustrate the linearity, we show in the inset of Figure 3c the dependence of the spontaneous, 

![Image](https://www.materialsviews.com/images/2012/figure2.png)

**Figure 2.** a) Schematic diagram of the photo-CELIV method showing timing of the laser pulse and voltage ramp. $V_{\text{bias}}$ indicates the compensating bias that is applied to the solar cell and $V_{\text{coll}}$ indicates the minimum of the voltage ramp. b) The electrical circuit used to determine the current and voltage of the solar cell.

![Image](https://www.materialsviews.com/images/2012/figure3.png)

**Figure 3.** Extracted photoinduced charge carriers in an as-cast P3HT:PC60BM bulk heterojunction cell as function of delay time between pulsed illumination and bias ramp. a) The average number density of extracted charges ($n_{\text{avg}}$) upon excitation via the charge transfer transition at 1.55 eV and $V_{\text{bias}} = 0.52$ V. b) $n_{\text{avg}}$ upon excitation of the polymer $S_1 \rightarrow S_0$ transition at 2.14 eV and $V_{\text{bias}} = 0.44$ V. In the inset, the black squares show $n_{\text{avg}}$ at constant zero applied bias and the circles $n_{\text{avg}}$ at a constant applied bias of $-2$ V. c,d) Fraction of the total number of extractable carriers at constant $-2$ V bias that can still be extracted after a delay for 1.55 and 2.14 eV, respectively, plotted versus delay time.
used, 1.55 eV (Figure 3c) and 2.14 eV (Figure 3d), and a delay of 5 μs we find a fraction of extractable carriers of 0.12. The similarity in the fraction for sub-gap and above-gap excitation shows that the excess energy liberated during photoinduced electron transfer from the excited singlet state has a negligible influence on the recombination dynamics of the charge carriers. By comparing the fraction determined for different excitation fluences, we observe that for long delay times, the probability for survival of charge carriers becomes higher at lower light intensity (Figure 3c). This provides direct evidence for bimolecular recombination kinetics of the long-lived carriers, implying that a significant fraction of the directly created CT states has dissociated into free carriers. The observation of bimolecular recombination of photogenerated charges in P3HT:PC$_{60}$BM films is consistent with previous reports.\(^{[22-25]}\)

We note that the intensity of the 1.55 eV beam is $10^2$ higher than for the 2.14 eV light. Lee et al. report that the absorption at 1.55 and 2.14 eV differs by $10^2$. Hence, the density of primary photoexcitations should be similar for the two different excitation beams. The experimental observation of a similar density and fraction of extracted carriers for the two excitation photon energies, indicates that the charge carrier dynamics for the sub-gap and above-gap excitation are very similar.

The fraction of charges extractable after a delay determined from the experiments contains information on the efficiency of charge generation. To explain this we write the overall efficiency of charge collection $\eta$ in a solar cell as the product of efficiencies for absorption ($\eta_{\text{abs}}$), diffusion of excitations to the donor-acceptor interface followed by formation of a CT state ($\eta_{\text{CT}}$), dissociation of the CT state into free carriers ($\eta_{\text{dis}}$), and collection of the charges ($\eta_{\text{coll}}$): $\eta = \eta_{\text{abs}} \eta_{\text{CT}} \eta_{\text{dis}} \eta_{\text{coll}}$. We assume that $\eta_{\text{abs}}$ and $\eta_{\text{CT}}$ are independent of electric bias ($V_{\text{bias}}$) and charge carrier density ($\rho$), but that $\eta_{\text{dis}}$ may depend on photon energy ($\nu$), the magnitude of $V_{\text{bias}}$ at which the device is held during the delay $\Delta t$, and the voltage $V_{\text{coll}}$ used for collecting the charges, hence, $\eta_{\text{dis}} = \eta_{\text{dis}}(\nu, V_{\text{bias}}, \Delta t, V_{\text{coll}})$. Further, $\eta_{\text{coll}}$ will depend on $\rho$ (in case of bimolecular recombination) and $V_{\text{coll}}$ such that $\eta_{\text{coll}} = \eta_{\text{coll}}(\rho, V_{\text{coll}})$. The ratio $f$ of the number of charges extracted using the $V_{\text{coll}}$ (-2 V) pulse after a delay $\Delta t$, at which the cell was kept at $V_{\text{bias}}$ and the number of charges extracted under constant $V_{\text{coll}}$ (-2 V) bias can then be expressed as:

$$f = \frac{\eta_{\text{dis}}(h\nu, V_{\text{bias}}, \Delta t, V_{\text{coll}}) \eta_{\text{coll}}(\rho, V_{\text{coll}})}{\eta_{\text{dis}}(h\nu, V_{\text{coll}}, 0, V_{\text{coll}}) \eta_{\text{coll}}(\rho', V_{\text{coll}})}$$  \hspace{1cm} (1)

In Equation (1) the term $\eta_{\text{dis}}(h\nu, V_{\text{coll}}, 0, V_{\text{coll}})$ in the denominator signifies that $V_{\text{bias}} = V_{\text{coll}}$ and $\Delta t = 0$ under constant collection bias. From Equation (1) the ratio of the fractions of extractable carriers after a delay $\Delta t$ for sub-gap ($h\nu_{\text{sg}}$) and above-gap ($h\nu_{\text{ag}}$) excitation equals:

$$\frac{f(h\nu_{\text{sg}}, \Delta t)}{f(h\nu_{\text{ag}}, \Delta t)} = \frac{\eta_{\text{dis}}(h\nu_{\text{sg}}, V_{\text{bias}}, \Delta t, V_{\text{coll}}) \eta_{\text{coll}}(\rho, V_{\text{coll}})}{\eta_{\text{dis}}(h\nu_{\text{ag}}, V_{\text{coll}}, 0, V_{\text{coll}}) \eta_{\text{coll}}(\rho', V_{\text{coll}})} \times \frac{\eta_{\text{dis}}(h\nu_{\text{ag}}, V_{\text{coll}}, 0, V_{\text{coll}})}{\eta_{\text{dis}}(h\nu_{\text{sg}}, V_{\text{bias}}, \Delta t, V_{\text{coll}})}$$  \hspace{1cm} (2)

In Equation (2) we assume that $\eta_{\text{coll}}$ is independent of the small difference between the charge carrier densities $\rho_{\text{sg}}$ and $\rho_{\text{ag}}$ that exist for above-gap excitation and sub-gap excitation. Figures 3a and 3b confirm that the carrier density and dynamics in the two CELIV experiments with $h\nu_{\text{ag}} = 1.55$ eV and $h\nu_{\text{sg}} = 2.14$ eV are virtually identical. At sufficiently negative $V_{\text{coll}}$ it can be expected that virtually all interfacial CT states will dissociate into free carriers, independent of how they were generated. In that case the rightmost term in Equation (2) cancels and we find that:

$$\frac{f(h\nu_{\text{sg}}, \Delta t)}{f(h\nu_{\text{ag}}, \Delta t)} = \frac{\eta_{\text{dis}}(h\nu_{\text{sg}}, V_{\text{bias}}, \Delta t, V_{\text{coll}})}{\eta_{\text{dis}}(h\nu_{\text{ag}}, V_{\text{coll}}, 0, V_{\text{coll}})}$$  \hspace{1cm} (3)

Equation (3) suggests that the ratio of the fractions reflects the dissociation ratio for sub-gap and above-gap excitation. Figure 3c,d show that $f(h\nu_{\text{sg}}, \Delta t) = f(h\nu_{\text{ag}}, \Delta t)$ and, hence, we find that $\eta_{\text{dis}}(h\nu_{\text{sg}}, V_{\text{bias}}, \Delta t, V_{\text{coll}}) = \eta_{\text{dis}}(h\nu_{\text{ag}}, V_{\text{bias}}, \Delta t, V_{\text{coll}})$.

To find support for this conclusion, we performed external quantum efficiency (EQE) measurements as function of photon energy and applied bias voltage (Figure 4). As expected, the EQE...
has three main spectral components. Below 1.65 eV, the contribution of the CT absorption is visible. Above 1.7 eV, charge generation via the $S_1 \rightarrow S_0$ transition for PCBM and P3HT can be seen. When normalizing the EQE to unity at 2.53 eV excitation, we notice that the applied bias, ranging from $V_{bias}=V_{oc}$ to $-2$ V, has no significant effect on the EQE under direct excitation of the CT transition. This implies that the electric field $V_{bias}$ does not change the ratio between charge formation for above-gap and sub-gap excitation. In the EQE experiment a special condition of Equation (3) occurs, namely $\Delta t=0$ and $V_{bias}=V_{cell}$. As the ratio of the EQE for above-gap and sub-gap excitation is found to be independent of $V_{bias}$, it follows that the relation between excitation photon energy and dissociation of charges from the interface must be such that: $\eta_{avg}(hv_{ag})=\eta_{avg}(hv_{sg})$. This conclusion is the same as the one inferred from the CELIV experiments.

We note that for excitation photon energies of 2.0 eV there is a relatively small variation of normalized EQE with applied bias. We tentatively attribute this to a variation in the collection efficiency. Near 2.0 eV crystalline domains of P3HT can be selectively excited and these ordered domains hole transport is expected to be faster than in the disordered phase. This interpretation is supported by EQE measurements on thermally annealed cells (Figure 4b). After annealing, most of the P3HT will be in the crystalline phase and transport limitations should be lifted. Indeed the measurements now show a complete independence of the normalized EQE value with respect to applied bias.

From the similarity of the fraction of carriers extractable after a delay for sub-gap and above-gap excitation we conclude, making use of Equation (3), that the efficiency of dissociation of the CT state under open circuit conditions is virtually independent of the excitation photon energy used. The hypothesis mentioned in the introduction that “cold” CT states lacking excess energy can only give rise to strongly bound geminate charge pairs has to be dismissed for P3HT:PC$_{60}$BM films.

Photo-CELIV characterization of thermally annealed P3HT:PC$_{60}$BM cells are shown in Figure 5. Thermal annealing results in a considerably enhanced performance of the solar cell as a result of more coarse phase separation and enhanced crystallinity of both P3HT and PC$_{60}$BM. Comparing the photono-CELIV results at 1.55 and 2.14 eV excitation, we find that also for annealed cells, the excess energy dissipated in the carrier generation process has negligible influence on the fraction of long-lived charge carriers. In contrast to the as-cast heterojunctions, charge carrier dynamics in annealed P3HT:PC$_{60}$BM films results in an approximately exponential decay of the number of extractable carriers with delay time. The decay rate is virtually independent of the excitation fluence. This rapid, monomolecular decay may be rationalized by rapid diffusion of carriers during the delay followed by recombination at the electrodes. The occurrence of this particular lifetime limiting process in annealed cells, is consistent with the known fact that thermal annealing significantly improves the transport properties, and that bimolecular recombination in thermally annealed P3HT:PC$_{60}$BM films is significantly suppressed as compared to as-cast films. In as-cast films, diffusion to the contacts would be slower, resulting in carrier lifetimes limited by bimolecular recombination.

In conclusion, photo-CELIV measurements provide a means to compare the recombination dynamics in polymer solar cells. In combination with EQE measurements, we find that excess energy liberated in photocarrier generation by photons with energy far above the energy of the CT state, has no significant effect on the charge generation and recombination process. This indicates that in P3HT:PC$_{60}$BM blends a large excess energy in the electron transfer step, is not a strict requirement for free carrier generation.
Experimental Section

Photovoltaic devices were made by spin coating poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) (Clevios P, VP AI4083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates (14 Ω per square) (Nanaro Substrates). The photoactive layer was deposited by spin casting in air at 1000 rpm, using a 1:1 (v/v) chloroform: chlorobenzene solution containing 15 mg mL\(^{-1}\) P3HT (Rieke, M\(_{w}\) < 50 kg mol\(^{-1}\), 98% regioregular) and 15 mg mL\(^{-1}\) [6,6]-phenyl-C\(_{61}\)-butyric acid methyl ester PC\(_{60}\)BM (Solenne). The metal electrode, consisting of LiF (1 nm) and Al (100 nm), was deposited by vacuum evaporation at \(\sim 3 \times 10^{-7}\) mbar. Thermal annealing of cells was done at 120 °C for 15 min after deposition of the top metal contact. The active area of the cells was 0.091 cm\(^2\) and the thickness of the active layer was 200 nm. Under \(1\) sun white light illumination (tungsten-halogen lamp with a Schott GG385 UV filter and a Hoya LB120 daylight filter at 100 mW cm\(^{-2}\)) the pristine devices showed a short circuit current (\(I_{SC}\)) of 5.8 mA cm\(^{-2}\), a fill factor (FF) of 0.51, and an open circuit voltage (\(V_{oc}\)) of 0.58 V, resulting in a maximum power point (MPP) of 1.7 mW cm\(^{-2}\).

After thermal annealing, the \(J_{SC}\) increased to 7.2 mA cm\(^{-2}\) and the \(V_{oc}\) decreased to 0.51 V, resulting in an MPP of 2.5 mW cm\(^{-2}\).

To excite into the S\(_1\) state of P3HT, the second harmonic of the output of an amplified Ti:sapphire laser was used (photon energy 1.55 eV, pulse duration 10\(^{-12}\) fs, fluence 4 J m\(^{-2}\) per pulse, spot size 0.07 cm\(^2\)).

To excite into the S\(_1\) state of P3HT, the second harmonic of the output of an optical parametric amplifier (OPA) pumped by the Ti:sapphire laser was used (photon energy 2.14 eV, fluence 1.6 J m\(^{-2}\) per pulse and spot size 0.03 cm\(^2\)).

The fluence was varied using neutral density filters. Voltage ramps were generated using an Agilent 33250A arbitrary wave generator. A compensating voltage (\(V_{comp}\), see Figure 2) was applied to minimize charge extraction before the start of the voltage ramp. The length \(t\) of the voltage ramp was 12.5 μs. The extraction voltage \(V_{extr}\) equals: \(V_{extr} = AV = V_{comp} - 2.0 V = -1.5 V\). A 50 Ω probe resistor was used to record the transient photocurrent through the solar cell using an oscilloscope. The number of photogenerated charge carriers extracted was calculated by integrating the difference between the extraction currents upon application of the voltage ramp in dark and after pulsed illumination. Transient currents were determined averaging over 10\(^3\) laser pulses and the statistical error of measurement was estimated by triplicating each transient current experiment.

EQE measurements were done in a homebuilt set-up, with the devices kept in a nitrogen filled box with a quartz window and illuminated through an aperture of 2 mm. Mechanically modulated (Stanford Research, SR 540) monochromatic (Oriel, Cornerstone 130) 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 a representative illumination intensity for 1 sun conditions. 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.

Acknowledgements

The work of D.D.N. forms part of the research program of the Dutch Polymer Institute (DPI, project #631).

Received: January 10, 2012
Revised: March 19, 2012
Published online: