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# Field-Independent Charge Photogeneration in PCPDTBT/PC$_{70}$BM Solar Cells

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ABSTRACT Transient absorption spectroscopy has been used to investigate charge photogeneration in organic solar cells based upon PCPDTBT/PC$_{70}$BM (poly-[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]-dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)]/[6,6]-phenyl-C$_{71}$-butyric acid methyl ester) photoactive layers as a function of externally applied bias. We find that the yield of dissociated polarons is independent of applied bias in these devices.

SECTION Kinetics, Spectroscopy
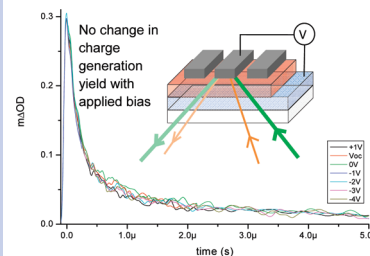
Organic photovoltaic (OPV) devices are attracting extensive interest as a potentially lower cost alternative to inorganic solar cells. Particular attention is being placed on OPV devices employing blends of semiconducting polymers and fullerenes as the photoactive layer.[1−4] Solar energy conversion in such devices is based upon the separation of photogenerated excited states (or excitons) at the polymer/fullerene interface, yielding dissociated electrons and holes. A key consideration for this charge photogeneration process is that the initially generated electron and hole pairs may form Coulombically bound charge-transfer (CT) states at the polymer/fullerene interface. Geminate recombination of these CT states has been suggested to be a key loss pathway limiting the efficiency of organic solar cells,[5] specifically limiting the device short-circuit current (J_{SC}) and fill factor (FF). In this regard, it has widely suggested that macroscopic electric fields, present in such organic solar cells due charge accumulation on the device electrodes, may be a key factor in enabling dissociation of the CT states, thereby reducing geminate recombination losses. Such electric field dependence has typically been discussed in the context of Onsager−Braun theory.[6] As the magnitude of these electric fields is dependent upon device voltage, electric-field-dependent charge generation has been suggested to be a key factor determining the shape of current/voltage curve, and particularly the FF, of such devices.[7−9]

Most experimental studies of the electric field dependence of charge photogeneration have relied upon analysis of the overall device current/voltage behavior. More direct studies of charge photogeneration as a function of applied field have been relatively limited to date but include photoluminescence (PL) studies,[10,11] electroluminescence (EL),[12,13] photocurrent measurements[14,15] and transient absorption spectroscopy (TAS).[7,16] In particular, several previous studies have interpreted changes in the photoluminescence of interfacial CT states (sometimes called exciplex emission) observed under strong reverse bias conditions in terms of electric-field-dependent

dissociation of these CT states,[10] a conclusion recently supported by a transient absorption study by Marsh et al.[7] This conclusion however contrasts with our own transient photoinduced absorption study of the yield of long-lived, dissociated polarons in P3HT/PC$_{60}$BM based solar cells, where we observed, for applied voltages between 0 and 1 V forward bias, that the yield of dissociated polarons was not strongly dependent upon applied bias.[16] Supporting this conclusion, we have employed a range of transient optoelectronic measurements to provide evidence that the shape of the current/voltage curve of P3HT/PC$_{60}$BM solar cells, and in particular the device FF, originates not from electric field dependence of charge photogeneration (and the associated geminate recombination losses) but rather from the charge density dependence of nongeminate recombination of dissociated charges.[17] As such, there remains significant controversy over the electric field dependence of charge photogeneration in bulk heterojunction solar cells.

Particularly promising device efficiencies, up to 5.5 %,[18] have been achieved for organic solar cells employing the donor polymer poly[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]-dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)] (C-PCPDTBT) blended with the acceptor [6,6]-phenyl-C$_{71}$-butyric acid methyl ester (PC$_{70}$BM) by the use of the processing agent, octanedithiol (ODT). In this paper, we employ transient absorption spectroscopy to probe the electric field dependence of charge photogeneration for organic solar cells based upon C-PCPDTBT/PC$_{70}$BM blends with and without ODT, as well as devices employing the silicon bridged derivative of the donor polymer (Si-PCPDTBT). The structures of these materials are shown in Figure 1a. In particular, and with regard to the differing experimental results discussed
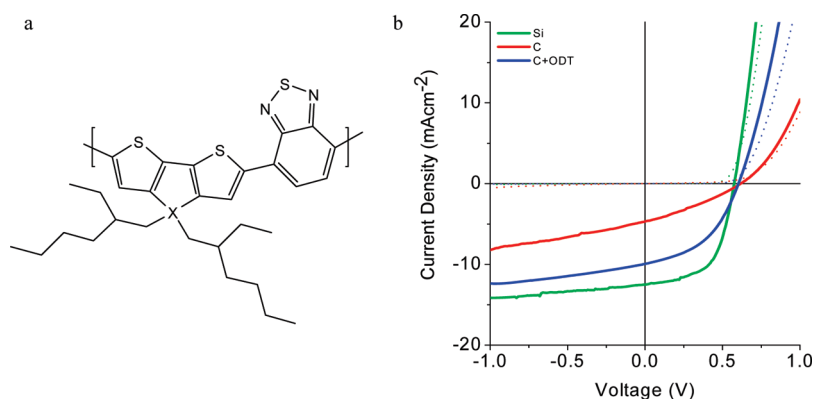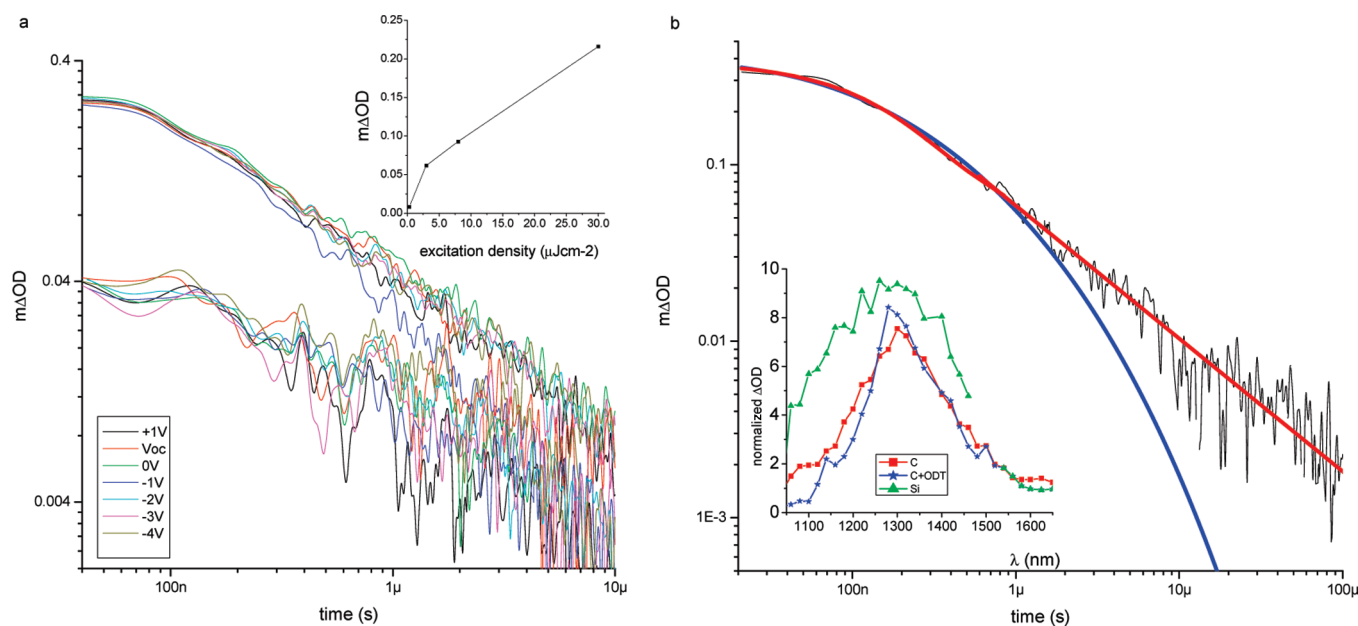
Figure 1. (a) Structure of one monomer unit of PCPDTBT, where X is either C or Si. (b) $J-V$ curves for C-PCPDTBT/PC$_{70}$BM and C-PCPDTBT/PC$_{70}$BM with ODT and Si-PCPDTBT/PC$_{70}$BM blends between -1 and $+1$ V at 1 sun light intensity. Power conversion efficiencies are 0.9% for C-PCPDTBT, 2.8% for C-PCPDTBT + ODT, and 4.9% for Si-PCPDTBT.

Figure 2. (a) Photoinduced absorption transients measured at 1310 nm for C-PCPDTBT/PC$_{70}$BM with ODT solar cells, with excitation densities at 8 μJcm^{-2}, lower transients at 85 μJcm^{-2}, and upper transients between 20 ns and 10 μs, with applied biases ranging between V_{oc} and -4 V. The inset is the ΔOD signal as a function of the laser excitation density, showing an almost linear dependence of the charge generation with fluence. (b) A typical decay from (a) is overlaid with bimolecular (power law, red) and monomolecular (stretched exponential, blue) fits to this decay. It is apparent that only the nongeminate (power law) analysis fits the experimental data. The inset is the transient spectrum of all three blends at 1 μs indicating that the polymer polarons are observed between 1280 and 1330 nm.

above for P3HT/PC$_{60}$BM based devices, we investigate whether we observe any electric field dependence of charge photogeneration in these PCPDTBT based devices and whether such dependencies can explain differences in the current/voltage performance of these devices.

Figure 1b shows the $J-V$ characteristics of C-PCPDTBT/PC$_{70}$BM (1:2 wt %) and C-PCPDTBT/PC$_{70}$BM (1:2 wt %) with ODT and Si-PCPDTBT/PC$_{70}$BM (1:2 wt %) devices between -1 and $+1$ V at 1 sun light intensity. These results are typical of those reported previously for these blend compositions.[18,19] The shape of the $J-V$ curves should be highlighted as only a small chemical modification in the active layer leads to considerable differences in the J_{sc} and FF of these devices.

The gradient of the current/voltage curve near short circuit has previously been suggested to be associated with electric-field-dependent charge photogeneration.[9,20] This gradient is observed to be largest for C-PCPDTBT/PC$_{70}$BM blends without ODT, yielding a device FF of only 33%, being smaller for the C-PCPDTBT/PC$_{70}$BM+ODT blend (FF of 45%) and Si-PCPDTBT/PC$_{70}$BM blend (FF of 58%). The increase in J_{sc} and FF correlates with an increase in power conversion efficiency from 0.9 to 4.9%.

Transient absorption spectroscopy was employed, as previously, to monitor the photoinduced absorption of photogenerated polarons in these devices on the nanosecond to millisecond time scales. Typical data are shown in Figure 2.

Transient spectra recorded as a function of wavelength at a time delay of 1 μs for the corresponding films of the three different blends all exhibited a well-defined polymer polaron absorption band between 1200 and 1400 nm, as shown in the inset in Figure 2b, consistent with our previous observations.[21] For device studies, a 1310 nm laser diode was employed to monitor this photoinduced absorption in reflection mode, as previously,[16] except that an alternative detector was employed to improve the instrument response to ~50 ns.

Figure 2a shows typical absorption transients measured at 1310 nm for a C-PCPDTBT/PC$_{70}$BM + ODT device measured as a function of applied electric bias for two different excitation densities, ~8 and ~80 μJ cm^{-2}. It is apparent that all of these transients exhibit straight line decays on this log/log plot, corresponding to a power law decay of ΔOD $\propto t^{-\alpha}$, with plateaus at early times. As we have discussed extensively previously, and confirmed by numerical modeling, such power law kinetics are characteristic of diffusion-limited non-geminate recombination of dissociated charge carriers, where polaron transport is mediated by trapped states. Such non-geminate recombination kinetics can be readily distinguished from the geminate recombination in such blend films, with the latter exhibiting exponential decay dynamics characteristic of such monomolecular processes on the picoseconds to nanosecond time scales, as we and others have shown previously.[22−25]

Figure 2b shows a comparison of bimolecular (power law) and monomolecular (stretched exponential) fits to these decays, confirming that these decay dynamics exhibit a power law rather than exponential dynamics and are therefore indicative of nongeminate recombination. The exponent α of the power law decays for C-PCPDTBT/PC$_{70}$BM was found to be ~0.75, consistent with our previous studies of analogous films and indicative of an overall reaction order of 2.3 with respect to charge density, consistent with nongeminate (bimolecular) recombination in the presence of energetic disorder. It is apparent that the magnitude of the transient signal increases approximately linearly with excitation density (10-fold, with the 10-fold increase in excitation density), confirming that the transient signal is not saturated, as further indicated by the approximately linear dependence of charge generation with excitation density in the inset of Figure 2a. The plateau of the transient decays at early times is again typical of nongeminate recombination processes,[16] with the plateau time corresponding to the onset of nongeminate recombination. As expected, this plateau onset is later at lower excitation densities, consistent with the slower nongeminate recombination losses expected at a lower charge carrier density. We note that our initial transient absorption signal size at 8 μJ cm^{-2} (ΔOD = 4 × 10^{-5}) is almost 2 orders of magnitude smaller than that reported recently in an analogous study of P3HT/PC$_{60}$BM devices,[7] indicative of the low excitation conditions used in our study. We further note that carrier sweep out by the device electrodes may also contribute to the later time decay data, as we have discussed previously.[16] A more detailed analysis of this issue will be presented elsewhere.

The analysis above confirms that the transient absorption signals observed in Figure 2a correspond to the photoinduced
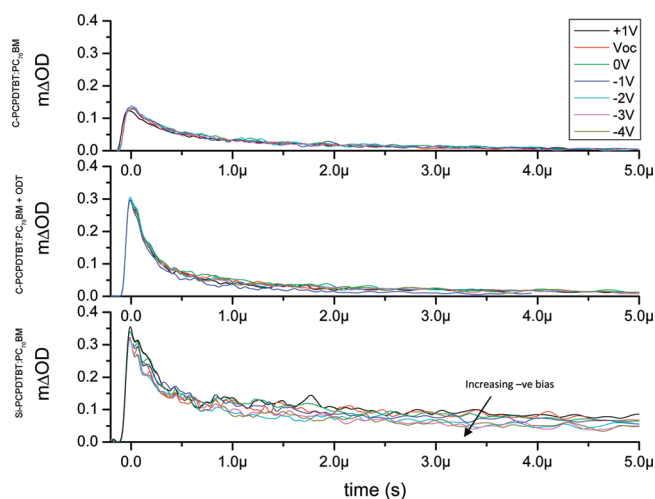
Figure 3. Photoinduced absorption transients measured for all three blend devices at an excitation density of 85 μJ cm^{-2} in reflection mode with varying applied biases between +1 and −4 V. (top) C-PCPDTBT/PC$_{70}$BM; (middle) C-PCPDTBT/PC$_{70}$BM+ODT; (bottom) Si-PCPDTBT/PC$_{70}$BM.

absorption of dissociated polarons and that the decay dynamics that we observe correspond to nongeminate recombination. The excitation density comparison confirms that these signals are not saturated and therefore that the initial signal magnitude, corresponding to the polaron absorption prior to the onset of nongeminate recombination, is a direct assay of the yield of dissociated polarons following photoexcitation. We turn now to considering the effect of bias potential upon this charge photogeneration yield. It is already apparent from the data in Figure 2a that the amplitude of the polaron absorption signal observed for C-PCPDTBT + ODT devices is not significantly dependent upon applied bias for a bias ranging from +1 V forward bias to −4 V reverse bias, corresponding to electric fields ranging from ~0 to ~5 × 10^5 V cm^{-1}. This dependence (or lack of it) upon bias voltage is addressed in more detail in Figure 3, where we plot data on linear axes and include data for devices employing all three different photoactive layers. It is apparent that for all three devices, the magnitude of the initial transient absorption signal, assigned to the yield of dissociated polarons, is, within the limits of our signal-to-noise (~±10%), independent of applied bias. Similar bias-independent data were obtained for several different cells of each type and for a range of excitation densities, and all showed negligible reverse bias dependence on charge photogeneration. We therefore conclude that for all of the device types studied herein, charge photogeneration, which we define herein as the yield of dissociated polarons per absorbed photon, is independent of applied bias.

It is also apparent from Figure 3 that the initial magnitude of the transient absorption signals, corresponding to the yield of dissociated polarons, correlates with short-circuit photocurrent density (J_{SC}). Both the initial ΔOD signal and J_{SC} increase in the order C < C + ODT < Si. This correlation is in agreement with previous studies[21] and provides further confirmation that our ΔOD assay is an effective measure of the efficiency of charge photogeneration in these devices.

The lower charge photogeneration observed for the C-PCPDTBT device is assigned to geminate recombination of interface CT states on the picosecond/nanosecond time scales, as we have discussed previously.[20,26] We emphasis, however, that while we observe the yield of charge photogeneration, and therefore geminate recombination, to vary between devices, for all three devices, we observe no influence of device electric field, indicating that geminate recombination losses in these devices are independent of electric field, at least within our experimental error ($\pm 10\%$).

We note that the conclusions that we report herein are distinct from those drawn by Marsh et al. from analogous studies of P3HT/PC$_{60}$BM based solar cells.[7] In this regard, it is important to appreciate that the experiments reported herein, and by Marsh et al., are "large perturbation" experiments, where the optical excitation generates a significantly greater polaron density ($\sim 10^{17}-10^{18}$ cm^{-3}) than that present in the device under cw solar irradiation ($10^{16}-10^{17}$ cm^{-3} under one sun irradiation[27]). As such, significant caution should be used in relating such measurements directly to device performance. In particular, it is difficult to use such data to analyze any potential electric-field-dependent transition between geminate and nongeminate recombination losses under device operation (as proposed by Marsh et al.) due to the strong nonlinear dependence of nongeminate recombination upon polaron density. Instead, quantification of nongeminate losses requires small perturbation measurements, such as transient photovoltage analyses, as we have reported elsewhere.[27] Rather, the focus of the analysis reported herein is on the initial yield of dissociated charges, expected to be less strongly dependent upon charge carrier density, consistent with approximately linear excitation density dependence reported herein.

In conclusion, we find that charge photogeneration in all of the devices studied herein is independent of the electric field (to within $\pm 10\%$), at least over the range of bias conditions studied herein. As such, differences in the fill factors and photoshunt resistances observed between these devices cannot be assigned to differences in their electric field dependence of charge photogeneration or the competing geminate recombination. Analysis of alternative explanations of these differences in the fill factor are ongoing, including consideration of differences in nongeminate recombination kinetics, and will be reported elsewhere.

EXPERIMENTAL SECTION

Encapsulated devices were supplied and fabricated at Konarka Technologies, as described previously.[28] PEDOT/PSS was deposited on ITO glass, followed by the active layer blend (1:2), before aluminum was deposited and the devices were sealed. The active layer thickness was 90 ± 20 nm. Similar bias-independent transient absorption data were also obtained for devices fabricated in house. Device efficiencies and $J-V$ curves were measured using a Keithley 238 source measure unit. Illumination was provided using a 300 W xenon arc lamp solar simulator (Oriel Instruments) and calibrated using a silicon photodiode with appropriate long-pass filters. Transient absorption decays were measured in reflection mode, reflecting off of the aluminum electrode, following optical excitation at 532 nm with a Nd:YAG laser (Quantel, Big Sky Laser) at intensities between 5 and 80 μJ cm^{-2} and a pulse repetition frequency of 4 Hz (we note that at 532 nm, the film is OD ≈ 0.1, such that $\sim 10\%$ of the incident excitation intensity is absorbed by the film). A laser diode at 1310 nm, 10 mW (Thorlabs TCLDM9), and controlled externally (Thorlabs ITC502) was used as the probe source. The reflected probe beams were monitored using an InGaAs (Hamamatsu G8370-82) photodiode (instrument response ≈ 50 ns), and the signal was amplified (Costronics Electronics) and collected with a digital oscilloscope (Tektronics, TDS220) using data acquisition software (Costronics Electronics). External bias was applied with a power supply (TTi PL303-P).

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