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Analysis of Recombination Losses in a Pentacene/C_{60} Organic Bilayer Solar Cell

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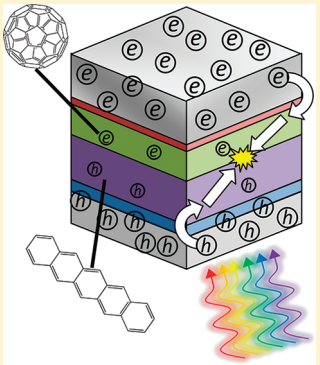
Supporting Information

ABSTRACT: Transient photovoltage and charge extraction analyses are used to quantify the rate of nongeminate recombination loss within a pentacene/C_{60} bilayer solar cell across the power-generating quadrant of the device. Employing these data, a simple model of cell function, based on field-independent generation and a charge-dependent nongeminate loss current without the use of any adjustable fitting parameters, is shown to be in good agreement with the experimental current/voltage behavior of the device both in the dark and under illumination.

SECTION: Energy Conversion and Storage



Small-molecule-based organic photovoltaics (OPVs) are attracting significant interest for low-cost solar energy conversion.[1] Vacuum-deposited multijunction devices have now demonstrated power conversion efficiencies of >8%.[2] Such devices are based on the formation of an interface between electron-donating and electron-accepting organic materials, either as a flat bilayer interface or within a mixed phase (often called a bulk heterojunction, BHJ). A key challenge is to understand the underlying physical processes that allow, or limit, the operation of such devices and thereby to enable their continued improvement. Models of bilayer device performance are typically based on an equivalent circuit model incorporating either a fixed diode-like term and a voltage-dependent (and therefore implicitly field-dependent) photocurrent term[3−5] or a fixed photocurrent term coupled with a variable diode-like term.[6,7] Good evidence exists that a field-dependent dissociation term is required to understand the behavior of organic photodetectors,[4] but it is less clear whether it is required to understand the behavior of organic solar cells, which operate within a different voltage regime.

In this Letter, we provide experimental evidence that an alternative device model, based upon electric-field-independent charge generation and charge-density-dependent recombination losses, can be employed to successfully recreate the current/voltage behavior of a pentacene/C_{60} organic bilayer solar cell without the use of any fitting parameters. The experimental approach employed herein builds upon our recent studies of solution-processed BHJ organic solar cells.[8−10] It is based on the use of transient photovoltage (TPV) and charge extraction (CE) measurements to determine charge carrier lifetimes and charge densities in such devices under a range of device operating conditions. These measurements have allowed us to quantify the magnitude of nongeminate recombination losses within a variety of BHJ cells under different operating conditions and thereby allowed us to quantify the impact of these loss processes on the device open-circuit voltage and fill factor. Herein, we present an example of such a transient optoelectronic analysis of the charge carrier densities and lifetimes for thermally evaporated pentacene/C_{60} bilayer solar cells.

Planar evaporated cells, for which pentacene/C_{60} is a prototypical materials system,[11] are of particular interest due to the control that may be exercised over their fabrication,[1,6,12] rendering them suitable as a basis for efficient multijunction architectures.[1,2] This class of crystalline organic solar cells typically exhibit lower energetic disorder than BHJs, allowing for significantly higher polaron mobilities than are achievable in typical polymer/fullerene blend systems.[13] Compared to their BHJ counterparts, their lower interfacial area might be expected to slow nongeminate recombination losses (i.e., the recombination of dissociated carriers across the heterointerface). In addition, the alignment of the interface relative to any macroscopic electric field is favorable for field-assisted dissociation of bound geminate

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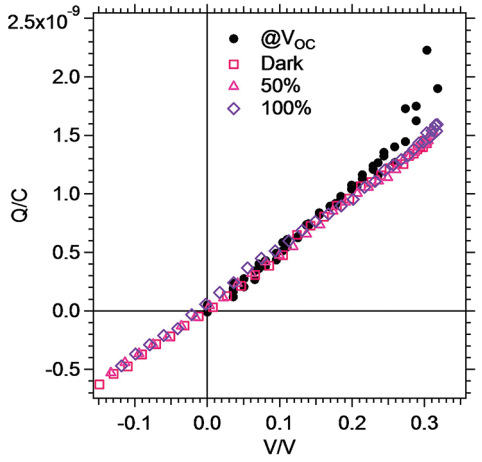

Figure 1. Total extracted charge (Q) as a function of applied bias (V) and/or light intensity for a pentacene/C_{60} bilayer solar cell, measured relative to dark, short-circuit conditions. The data at applied bias has been corrected for the external series resistance of 110 Ω (~60 Ω measured intrinsic resistance plus 50 Ω measurement load).

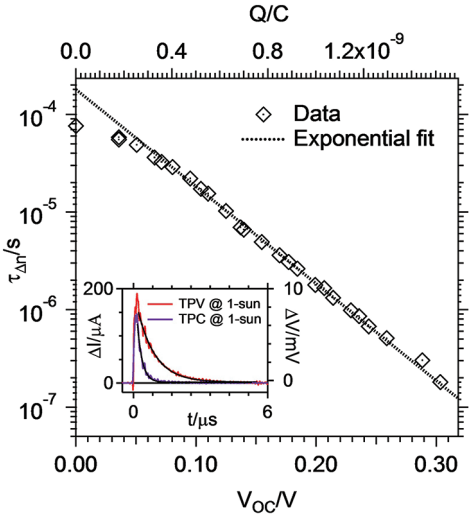

Figure 2. Small-perturbation charge carrier decay time $\tau_{\Delta n}$ measured from photovoltage transients versus V_{OC} and Q for a pentacene/C_{60} solar cell held at open circuit, as a function of bias light intensity. The inset compares TPC (short circuit, left axis) and TPV (open circuit, right axis) transients under 1 sun background illumination for this device.

pairs. As such, it might also be expected that geminate, rather than nongeminate, losses play a significant role in cell performance.

Pentacene/C_{60} bilayer cells were fabricated with the following structure: ITO/PEDOT/PSS (40 nm)/pentacene (30 nm)/C_{60} (40 nm)/bathocuproine (BCP) (10 nm)/Ca (20 nm)/Al (100 nm), with active area 4.5 mm^2. Except for PEDOT/PSS, all layers were deposited via thermal evaporation under high vacuum (~10^{-6} mbar), with thicknesses estimated using a quartz crystal microbalance. Current/voltage analyses under simulated AM1.5 sunlight (see Supporting Information and Figure 4 below) yielded device efficiencies of ~1%, similar to those reported previously for analogous devices.[6,11,14] The short-circuit current (J_{SC}) was observed to increase linearly with light intensity (LI), such that $J_{SC} \propto LI^{0.97}$, indicative of negligible nonlinear (e.g., nongeminate) losses at short circuit.

Charge extraction[8,15] measurements were conducted as a function of both applied bias and light intensity, as shown in Figure 1. The total extracted charge Q (relative to dark, short-circuit conditions) followed a linear dependence on cell voltage V, given by $Q = CV$, with $C \approx 5$ nF and with C only very weakly dependent on illumination intensity. C is approximately equal to the geometric capacitance of the cell electrodes C_0, estimated as $C_0 = 4.9$ nF from measurements of the extracted charge under reverse bias in the dark, when the injected charge is expected to be relatively small. The amount of charge present within the photoactive layer must therefore be small compared to the capacitative charge residing on the device electrodes and, as such, appears similar to previous reports of CE measurements on blended small-molecule cells.[16] The bulk charge appears only to contribute significantly at the highest illumination intensities ($V_{OC} > 0.25$ V, LI > 200% sun), which we will not consider here. We note that this behavior differs from that which we have previously reported for a range of polymer−fullerene BHJ devices, in which the charge density was observed to increase exponentially with applied bias and to be dependent on light intensity, consistent with most of the charge residing in the photoactive layer of such devices.[8,10,17]

Transient photovoltage measurements of the charge carrier lifetime were conducted on the same cell under open-circuit conditions and are shown in Figure 2. These TPV transients record the small-perturbation decay dynamics of dissociated charges within the cell, corresponding to nongeminate decay pathways (we note that geminate recombination of bound polaron pairs will not be observed in such measurements as these charge-neutral species do not give rise to electrical signals unless the polarons dissociate). These transients show an exponential dependence of the small-perturbation carrier lifetime $\tau_{\Delta n}$ on the open-circuit voltage of the form $\tau_{\Delta n} = \tau_{\Delta n_0} e^{-\beta V_{OC}}$, giving an overall exponential dependence of this lifetime on the cell charge. This is in contrast with the observation that, for many BHJ cells, the relationship between the carrier lifetime and charge density is a power law. This difference in behavior is consistent with the dominance of the (linear) electrode capacitance in these bilayer cells over the (often exponential) chemical capacitance of the active layer for many BHJ devices.[10,17,18]

Typical transient photocurrent and photovoltage transients, both measured under 1 sun illumination, are shown in Figure 2 (inset), exhibiting time constants of 2×10^{-7} and 8×10^{-7} s, respectively. The faster time constant for the transient photocurrent relative to the small perturbation photovoltage transient shows that extraction to short circuit is efficient at 1 sun for applied biases within the power-generating quadrant. The relatively small (~5% at V_{OC}) loss of charge to recombination during extraction has been corrected for at all points by iteratively estimating the instantaneous loss currents as the cell discharges. At illumination intensities of 2 suns and above, recombination and extraction begin to compete strongly toward V_{OC} and at forward bias, and our iterative correction may no longer give a good estimate of the true charge. We therefore do not consider higher illumination intensities here.

We now employ these data in a simple device model analogous to that previously employed by us for solution-processed BHJ devices.[8,10,17,18] The model is based on assuming that the overall device current J is given by

$$J = J_{gen} - J_{loss}$$

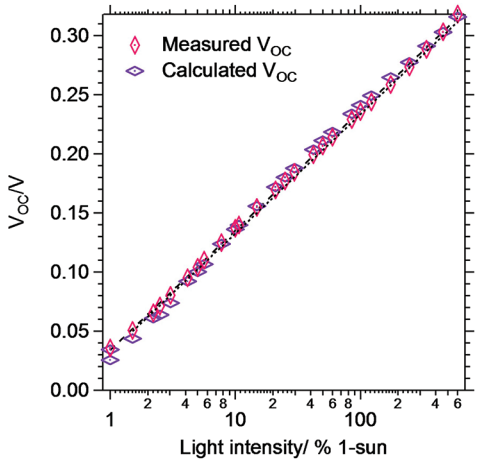

Figure 3. Comparison of measured V_{OC} versus the V_{OC} calculated from eq 2 using our simple device model, as a function of light intensity. Dashed lines show fits to the data, which yield predicted light ideality factor = 1.67 and measured ideality factor = 1.69.

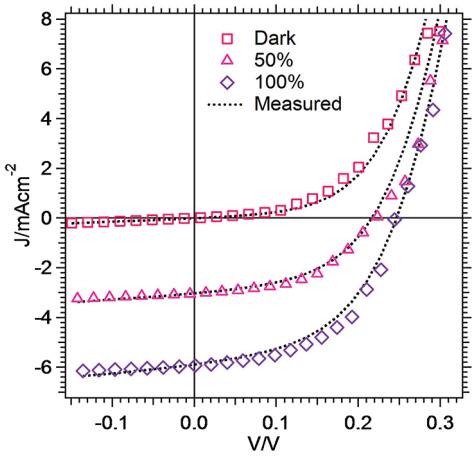

Figure 4. Measured $J(V)$ versus that calculated from eq 1 at three light intensities. The voltage drop across the additional 50 Ω load resistance used for the CE measurements has been accounted for.

where J_{gen} is a voltage-independent charge photogeneration flux and J_{loss} is the charge-dependent charge carrier loss flux, as determined from the transient measurements above by using

$$J_{loss}(Q) = \frac{1}{A}\frac{Q}{\tau} = \frac{e^{\beta Q/C}}{A\tau_{\Delta n_0}\left(1 + \frac{\beta Q}{C}\right)} + \frac{V}{R_P A} \qquad (1)$$

where A is the device area, Q, C, and β have been defined above, and the bulk carrier lifetime τ is determined directly from the small-perturbation recombination lifetime $\tau_{\Delta n}$, as detailed in the Supporting Information. The first term represents the loss current of the device charge (stored primarily on the device electrodes), corresponding to the photovoltage decay transients. The second term accounts for the a small dark leakage apparent in the $J(V)$ curves shown in Figure 4, corresponding to a 16 kΩ parallel or "shunt" resistance. We measure this from the gradient of the dark $J(V)$ curve at 0 V and assume it to be fixed under all other conditions. This leakage resistance most probably results from pinholes or spikes connecting the device electrodes. The presence of this leakage pathway can also be observed from the flattening of the voltage dependence of the charge carrier lifetime at low cell voltages, where at low charge densities, this leakage pathway becomes the dominating process limiting charge carrier lifetime.

For the charge generation term J_{gen}, corresponding to the generation of dissociated charge carriers, we assume $J_{gen} = J_{SC}$. This assumption is consistent with our observation that the photocurrent time constant < transient photovoltage time constant, which indicates that nongeminate charge recombination losses are negligible at short circuit, and with the observed linearity of J_{SC} with light intensity. We note that our analysis furthermore assumes J_{gen} to be independent of cell voltage, which we discuss further below.

This simple model can be employed to determine the cell open-circuit voltage as a function of light intensity. To make a prediction of the open-circuit voltage under the assumption of voltage-independent photogeneration and efficient extraction at short circuit, we simply set $J = J_{gen} - J_{loss} = 0$, which yields an expression for V_{OC} given by

$$V_{OC} = \frac{1}{\beta}\ln\left(\frac{\left(J_{SC} - \frac{V}{R_P A}\right)A\tau_{\Delta n_0}\left(1 + \frac{\beta Q}{C}\right)}{Q}\right) \qquad (2)$$

Figure 3 compares the measured V_{OC} to that predicted by eq 2 as a function of light intensity. It is striking that there is an excellent agreement between the cell voltage and that predicted from our analysis. In addition, we recreate the measured ideality factor of the device very accurately. This agreement indicates that the nonideality of V_{OC} versus light intensity for this device is derived directly from the exponential dependence of charge carrier decay time on device voltage/charge, as measured in our TPV analysis.

We may go further and track the loss current as a function of applied cell voltage under constant illumination intensity, as described by Shuttle et al.[8] Again, we assume a voltage-independent generation current equal to J_{SC} at each light intensity. To this, we add the calculated loss current and the small dark leakage current (eq 1). The resulting predicted $J(V)$ behavior is shown in Figure 4 and compared to the measured curves. In addition to reproducing the measured variation of V_{OC} with light intensity, we also reproduce here the decrease in fill factor with increasing light intensity. In this system, we note that this trend of fill factor is primarily the result of the external series resistance of the cell[19,20] (see Supporting Information) and not large variations in carrier density with illumination.[8,9] It should be emphasized that no additional fitting parameters are required for this calculation; the recombination flux at each voltage and light intensity is calculated directly from the measured carrier lifetime and total extractable charge.

We therefore conclude that our simple device model is in remarkably good agreement with the experimentally observed photovoltaic device performance. Our model is based on an assumption of field-independent charge generation and on the use of TPV to quantify nongeminate recombination losses in the device as a function of cell voltage/charge. Our conclusion that we are able to equate the losses at open circuit to those across the $J(V)$ curve demonstrates that even in a bilayer cell, where

macroscopic electric fields might be expected to play a part in carrier generation, no such dependence is required to successfully recreate the light-intensity-dependent behavior of the cell, at least within the experimental errors inherent in our data; by varying the assumed generation rate and comparing the quality of our predicted to our measured variation of V_{OC} with light intensity, we estimate that we would be insensitive to changes in generation between open and short circuit of less than ~10% in our analyses. The presence of such additional loss pathways might, in particular, explain the slight underprediction of the slope of the illuminated $J(V)$ curves at short circuit, leading to a slight overprediction of fill factor for these curves.

We note that we have only applied our analysis to a limited potential range, corresponding to voltages close to the power-generating quadrant of device operation. Our analysis becomes increasingly uncertain when predicting the behavior of the cell in strong forward bias due primarily to increasingly large losses during extraction and the uncertainty in correcting for these. As such, this limited potential range corresponds to only modest device electric fields, consistent with our observation that we can recreate the device photovoltaic properties without inclusion of any electric field dependence of charge separation.

Our studies do not allow us to directly determine the mechanism of nongeminate charge carrier decay monitored by our TPV transients because TPV alone does not provide this information.[21] However, it is striking that the charge carrier decay lifetime varies exponentially with cell open-circuit voltage (Figure 2). We note that the charge density in the active layer of the device is also expected to increase exponentially with Fermi level splitting and therefore cell voltage (although, as mentioned, we are not able to observe this charge directly as the total amount of this photoactive layer charge is small relative to the electrode charge for these devices). As such, our observation of the carrier lifetime decreasing exponentially with voltage is consistent with the dominant loss pathway being associated with nongeminate recombination losses of photoactive layer charge carriers. The most obvious nongeminate recombination pathway for these devices would be charge carrier recombination across the organic pentacene/C_{60} interface, although other pathways cannot be ruled out. In this interpretation, the TPV decays analyzed herein are assigned to recombination of the active layer charge that is in rapid equilibrium with a larger reservoir of slowly recombining electrode charge. We note that this interpretation is analogous to that which we have previously described for BHJ cells, in which a large reservoir of slowly recombining trapped charge is assumed to maintain equilibrium with a smaller subpopulation of mobile carriers. Both device families can therefore be understood within the same model, despite the differences in the detailed nature of the particular charge reservoirs and actively recombining populations.

The success of our simple model in recreating the device photovoltaic performance indicates that even though the bilayer geometry has a lower interfacial area than BHJ devices, nongeminate recombination is still the key pathway limiting cell voltage and fill factor. We also conclude that any field dependence of geminate losses within the power-generating quadrant is weak, we estimate <10%, which may reflect the low voltages achievable with this materials combination. We are therefore in agreement with previous models of bilayer cells that consider a roughly fixed photogeneration flux in combination with a quantification of the diode-like behavior of the cells.[7] In particular, reduction of the reverse saturation current J_0 in these models corresponds, in our analysis, to a reduction in the nongeminate recombination rate and therefore leads to an improvement in cell performance, as has been widely reported.[3,7,22] In addition, because the cell analysis is not complicated by significant light-dependent effects, we conclude that the shape of the $J(V)$ curve as a function of light intensity is a simple convolution of a charge- and, therefore, voltage-dependent nongeminate loss pathway with a fixed series resistance and a fixed shunt pathway.

In summary, we have demonstrated that transient photovoltage and charge extraction are effective techniques for analyzing the charge carrier decay dynamics of a bilayer pentacene/C_{60} OPV device. The data obtained are indicative of the device fill factor and open-circuit voltage being primarily determined not by electric-field-dependent charge separation but rather by nongeminate recombination losses.

■ ASSOCIATED CONTENT

Supporting Information. Figures summarizing the full $J(V)$ curves, J_{SC} versus illumination intensity, and J_{loss} versus cell voltage after series resistance correction, in addition to the derivation of the relationship between the carrier lifetime and measured small-perturbation lifetime for a cell with linear $Q(V)$. This material is available free of charge via the Internet at http://pubs.acs.org.

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