

Reduced Bimolecular Recombination in Polymer Solar Cells

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Polymer solar cells with a thick active layer can generate large photocurrent because they absorb many more photons. In most cases, however, the active layer is as thin as ~100 nm under the optimized condition. In this work, we have studied bimolecular charge recombination in highly efficient polymer solar cells with a thick active layer by transient photovoltage and photocurrent measurements. As a result, we found that the bimolecular recombination rate is smaller by three orders of magnitude than that predicted from the diffusion-limited Langevin recombination. We therefore conclude that such reduced bimolecular recombination enables efficient charge collection even in the solar cell with a thick active layer.

Keywords: polymer solar cell, bimolecular recombination, Langevin recombination, transient photovoltage, transient photocurrent

1. Introduction

Polymer solar cells have been attracting much attention as next-generation solar cells because of easy production of lightweight and flexible devices. The power conversion efficiency (PCE) has increased in the last decade and exceeded 10% recently [1–4]. However, it is still lower than that of inorganic solar cells and hence should be improved furthermore. Of particular importance is to harvest as many photons from the sun light as possible.

The thick photoactive layer is desirable for harvesting many more photons. In most polymer solar cells, however, the active layer is typically as thin as $\sim 100 \text{ nm} [5-7]$. This is because charge carriers are likely to recombine bimolecularly before being collected into the electrodes in polymer solar cells with a thick active layer. In other words, there is a tradeoff relation between photon absorption and charge collection efficiencies. For further improvement, this trade-off relation should be Indeed, a recent study has shown overcome. that the active layer should be as thick as ~ 300 nm to improve PCE up to 15% [8].

Recently, several polymer solar cells have been reported to exhibit high PCEs even with a thick active layer. For example, a benchmark polymer solar cell based on blends of poly(3-hexylthiophene) (P3HT) and a fullerene derivative (PC₆₁BM) exhibit a PCE of 4.4% with a high fill factor (FF) of 0.67 even for the 210-nm thick active layer [9]. For another example, polymer solar cells based on blends of a diketopyrrolopyrrole (DPP)based polymer (DT-PDPP2T-TT) and a fullerene derivative (PC₇₁BM) exhibit a PCE of 6.3% with a high FF of 0.61 even for the 300-nm thick active layer [10].

Herein, we have studied bimolecular recombination in P3HT/PC₆₁BM and DT-PDPP2T-TT/PC71BM solar cells by transient photovoltage (TPV) and transient photocurrent (TPC) measurements. The TPV and TPC measurements can evaluate charge carrier lifetime and charge carrier density. respectively, in solar cells under operating condition [11,12]. We discuss the charge carrier dynamics in two polymer solar cells by comparing the bimolecular recombination rate with the diffusion-limited Langevin recombination rate.

2. Experimental

2.1. Device fabrication

Figure 1 shows the chemical structures of materials employed in this study. The devices were fabricated as follows. Indium-tin-oxide (ITO) substrates were cleaned by ultrasonication in toluene, acetone, and ethanol each for 15 min, dried with N_2 gas flow, and cleaned with a UV-ozone cleaner. A transparent conductive layer of poly(3,4-ethylenedioxythiophene):poly(4-

styrenesulfonate) (PEDOT:PSS; H. C. Starck, PH500) was spin-coated on the ITO substrate, which was annealed at 140 °C for 10 min in air. Subsequently, a photoactive layer was spincoated from a mixed solvent of chloroform and 1,2-dichlorobenzene (1 : 1 by volume) with DT-PDPP2T-TT (1-Material) and PC71BM (Frontier Carbon, E110) (1 : 3 by weight) or from a chlorobenzene solution of P3HT (Aldrich) and PC₆₁BM (Frontier Carbon, E100H) (1 : 1 by weight). Finally, a metal electrode of LiF (1 nm)/Al (70 nm) and Ca(10 nm)/Al(70 nm) was thermally deposited on top of the active layer of P3HT/PC61BM and DT-PDPP2T-TT/PC₇₁BM, respectively under vacuum at 4×10^{-4} Pa.



Fig. 1. Chemical structures of materials employed in this study: a) P3HT, b) DT-PDP2T-TT, c) $PC_{61}BM$, and d) $PC_{71}BM$.

2.2. TPV/TPC measurements

For the solar cells fabricated, TPV/TPC measurements were performed under bias white light illumination from a 500-W Xenon lamp (Tonika, XEF-152S) with various intensities from ~ 0.1 to 1 sun. A small perturbation pump pulse at 532 nm was provided from an Nd:YAG laser (Elforlight, SPOT-10-200-532): the repetition rate was 100 Hz and the pulse width was <1.8 ns. The transient voltage generated by the laser pulse was monitored with a 500-MHz digital oscilloscope (Tektronix, TDS3052B). For TPV measurements, the input impedance of the oscilloscope was set to 1 M Ω to hold the device at open-circuit. The transient signal obtained was amplified by a factor of 100 with an amplifier (FEMTO, HVA-10M-60-F). For TPC measurements, the transient voltage was measured through a 50 Ω resistor, which can be converted to transient current on the basis of the Ohm's law.

3. Results and Discussion

3.1. TPV analysis

Figure 2 shows transient photovoltage observed for P3HT/PC₆₁BM solar cells under 1 sun bias illumination. As shown in the figure, the initial transient voltage increase ΔV was as small as ~1.3 mV, which is much smaller than the open-circuit voltage (V_{OC}) of the device (The device parameters of the solar cells are summarized in Table 1). Under such conditions, the number of charges additionally



Fig. 2. Transient photovoltage decay of $P3HT/PC_{61}BM$ solar cells under 1 sun bias illumination.

Table 1. Device parameters of the solar cells.

Blends	$J_{\rm SC}$ / mA cm ⁻²	$V_{\rm OC}$ / V	FF	PCE / %	Thickness / nm
P3HT/PC ₆₁ BM	7.12	0.628	0.568	2.54	130
DT-PDPP2T-TT/PC71BM	9.77	0.733	0.614	4.39	75

generated by the laser pulse is much smaller than that of charges stationary generated by the bias illumination. Thus, the minority charges additionally generated should recombine by pseudo-first-order reaction with the majority charges stationary generated. In other words, the transient photovoltage can be analyzed by a single exponential equation (1)

$$\Delta V = \Delta V_0 \exp\left(-\frac{t}{\tau_{\Delta n}}\right) \tag{1}$$

where ΔV_0 is the initial photovoltage increment and $\tau_{\Delta n}$ is the lifetime of additionally generated charges. Figure 3 shows semilogarithmic plots of the $\tau_{\Delta n}$ against $V_{\rm OC}$ under various bias illumination intensities. As shown in the figure, $\tau_{\Delta n}$ decreases exponentially with increasing $V_{\rm OC}$ and hence can be analyzed by a single exponential equation (2)

$$\tau_{\Delta n} = \tau_{\Delta n_0} \exp\left(-\frac{qV_{\rm OC}}{\nu k_{\rm B}T}\right) \tag{2}$$



Fig. 3. Semi-logarithmic plots of the lifetimes of additional charges in $P3HT/PC_{61}BM$ (circles) and DT-PDPP2T-TT/PC₇₁BM (squares) solar cells against different open-circuit voltages. The closed plots are the lifetime under 1 sun bias illumination. The solid lines represent fitting lines by using equation (2).

where $\tau_{\Delta n_0}$ is the extrapolated lifetime at $V_{\rm OC} = 0$, q is the elementary charge, $k_{\rm B}$ is the Boltzmann constant, T is the absolute temperature, and v is the ideality factor of charge carrier lifetime.

3.2. TPC analysis

Figure 4 shows transient photocurrent observed for P3HT/PC₆₁BM solar cells under short-circuit condition at 1 sun bias illumination. As shown in the figure, the transient photocurrent decayed exponentially with a time constant of $0.5 \,\mu s$, which is much faster than the lifetime of additional charge carriers observed under the open-circuit condition in TPV measurements. Such rapid charge decay is ascribed to efficient charge collection to the electrode. Thus, the amount of photogenerated charges Δq can be evaluated from the integral of the TPC decay signals over the time. Here, the differential capacitance (dC) is defined as follows:

$$dC(V_{\rm OC}) = \frac{\Delta q}{\Delta V_0(V_{\rm OC})} \tag{3}$$

where $\Delta V_0(V_{OC})$ is the initial amplitude of TPV transients measured under the same bias



Fig. 4. Transient photocurrent decay of $P3HT/PC_{61}BM$ solar cells under 1 sun bias illumination.



Fig. 5. Semi-logarithmic plots of the charge carrier density in P3HT/PC₆₁BM (circles) and DT-PDPP2T-TT/PC₇₁BM (squares) solar cells against different open-circuit voltages. The closed plots are the charge carrier density under 1 sun bias illumination. The solid lines represent fitting lines by using equation (5).

illumination intensity. Consequently, the charge carrier density is given by equation (4)

$$n = \frac{1}{qAd} \int_0^{V_{\rm OC}} \mathrm{d}C(V_{\rm OC}) \mathrm{d}V \tag{4}$$

where d and A are the thickness and the area of the device, respectively. Figure 5 shows semi-logarithmic plots of the carrier density n against V_{OC} under various bias illumination intensities. As shown in the figure, the carrier density exponentially increases with increasing V_{OC} and hence can be analyzed by a single exponential equation (5)

$$n = n_0 \exp\left(\frac{qV_{\rm OC}}{mk_{\rm B}T}\right) \tag{5}$$

where n_0 is the extrapolated carrier density at $V_{\rm OC} = 0$ and *m* is the ideality factor of charge carrier density. The charge carrier lifetime can be evaluated from the values of *v* obtained from equation (2) and *m* from equation (5) as described later.

3.3. Charge carrier lifetime

As reported previously [12], the charge carrier lifetime (τ_n) in solar cells is related to the lifetime of TPV transient $(\tau_{\Delta n})$ as follows:

$$\tau_n = (\lambda + 1)\tau_{\Delta n} \tag{6}$$

where $\lambda + 1$ corresponds to the overall reaction order defined by equation (7) [13].

$$\lambda = \frac{m}{\nu} \tag{7}$$

Figure 6 shows the charge carrier lifetimes plotted against the charge carrier density. Under 1 sun condition, the charge carrier lifetime in P3HT/PC₆₁BM solar cells is evaluated to be 16.3 μ s, which is in good agreement with that reported previously [14]. On the other hand, the charge carrier lifetime in DT-PDPP2T-TT/PC₇₁BM solar cells is evaluated to be 2.6 μ s. This is shorter than that in P3HT/PC₆₁BM solar cells.



Fig. 6. Log-log plots of charge carrier lifetimes of $P3HT/PC_{61}BM$ (circles) and DT-PDPP2T-TT/PC₇₁BM (squares) solar cells against the charge carrier density. The closed plots are the charge carrier lifetime under 1 sun bias illumination.

3.4. Bimolecular recombination

Here, we discuss bimolecular recombination rate on the basis of the carrier lifetime evaluated by the TPV/TPC measurements. The bimolecular recombination rate k_{rec} is given by equation (8).

$$\frac{dn}{dt} = -k_{\rm rec} n^2 \tag{8}$$

The charge carrier lifetime τ_n is defined as the reciprocal of the first-order rate constant, and thus k_{rec} is given by equation (9).

$$k_{\rm rec} = \frac{1}{\tau_n n} \tag{9}$$

On the other hand, the diffusion-limited Langevin recombination rate $k_{\rm L}$ is given by equation (10)

$$k_{\rm L} = \frac{q\mu}{\varepsilon\varepsilon_0} \tag{10}$$

where μ is the slowest charge carrier mobility [15], ε is the dielectric constant, and ε_0 is the vacuum permittivity. The slowest charge carrier mobility is reported to be 2.4×10^{-4} cm² V⁻¹ s⁻¹ for P3HT/PC₆₁BM [16] and 7.6 × 10⁻³ cm² V⁻¹ s⁻¹ for DT-PDPP2T-TT/PC₇₁BM blend films [17]. The dielectric constant is assumed to be 3.5. Here, the recombination reduction factor ζ is defined as a ratio of $k_{\rm rec}$ to $k_{\rm L}$.

$$\zeta = \frac{k_{\rm rec}}{k_{\rm L}} \tag{11}$$

As summarized in Table 2. the recombination reduction factor of P3HT/PC₆₁BM solar cells is of the order of 10^{-2} - 10^{-3} , which is in good agreement with the previous report [14]. The ζ of DT-PDPP2T-TT/PC₇₁BM solar cells is of the same order. This finding suggests that bimolecular recombination is as well suppressed as in $P3HT/PC_{61}BM$ solar cells, which enables efficient charge collection even for the 300-nm thick active layer.

Finally, we briefly discuss the origin of the reduced bimolecular recombination although it has not been fully understood. As reported previously [18–20], one possible mechanism is non-diffusion-limited recombination due to high charge dissociation efficiency at a donor/acceptor interface. In such cases, charge carriers encountered at the interface are



Fig. 7. Schematic illustration of a) blend morphology and b) cascaded energy levels with three phases: crystalline polymer phase, polymer/fullerene mixed phase, and fullerene aggregate phase.

not likely to recombine but rather to split back into free carriers again. As a result, bimolecular recombination is effectively This is consistent with efficient suppressed. device performance of the two polymer solar The other mechanism is due to cells. cascaded energy structures both in the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels as shown in Figure 7 [21]. In such energy diagram, hole carriers are likely to transfer from disordered mixed phases to more stable polymer crystalline domains and electron carriers are likely to transfer from disordered mixed phases to more stable fullerene aggregate domains. As a result, most of free carriers are located at polymer crystalline domains and fullerene aggregate domains, which are effectively separated by mixed disordered domains, and hence are

Table 2	Rimolecular	recombination	rates and	recombination	reduction	factors
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Blends	$k_{\rm rec}$ / cm ³ s ⁻¹	$k_{\rm L}$ / cm ³ s ⁻¹	ζ
P3HT/PC ₆₁ BM	1.1×10^{-12}	1.3×10^{-10}	8.7×10^{-3}
DT-PDPP2T-TT/PC71BM	1.7×10^{-11}	4.0×10^{-9}	4.2×10^{-3}

unlikely to be encountered. Indeed, both P3HT and DT-PDPP2T-TT are highly crystalline polymers and $PC_{61}BM$ and $PC_{71}BM$ are likely to form aggregated clusters in blend films.

4. Conclusion

We studied the charge carrier dynamics in P3HT/PC61BM and DT-PDPP2T-TT/PC71BM solar cells by transient photovoltage and photocurrent measurements. As a result, we found that the bimolecular recombination in the solar cells is slower by three orders of magnitude than that predicted from the diffusion-limited Langevin recombination. We therefore conclude that such reduced bimolecular recombination enables efficient charge collection even in the solar cell with a thick active layer. One possible mechanism is non-diffusion-limited recombination due to high charge dissociation efficiency at a donor/acceptor interface. Another one is due to cascaded energy structures in the HOMO and LUMO levels at a donor/acceptor interface. which would suppress interface recombination effectively.

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