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Carrier density effect on recombination in PTB7-based solar cell

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Organic solar cells (OSCs) are promising alternatives to the conventional inorganic solar cells due to their low-cost processing and compatibility with flexible substrates. The development of low band-gap polymer, *e.g.*, poly-[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl] [3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3]thiophenediyl]] (PTB7), increases the power conversion efficiency (PCE) in the last decade. Here, we investigated the interrelation between the instantaneous carrier density (n) per donor (D)/acceptor (A) interface area and the carrier density ($n_{\text{collected}}$) collected as photocurrent in PTB7/ C_{70} heterojunction (HJ) device. By means of the time-resolved spectroscopy, we confirmed that the exciton-to-carrier conversion process takes place within ~ 1 ps at the D/A interface of the PTB7/ C_{70} HJ device. We further determined the absolute magnitude of n by combination of the time-resolved and electrochemical spectroscopies. We found that the carrier recombination becomes dominant if n exceeds a critical concentration ($n_c = 0.003$ carriers/nm⁻²). We confirmed that a similar behaviors is observed in the PTB7/[6,6]-phenyl C_{71} -butyric acid methyl ester (PC₇₁BM) bulk heterojunction (BHJ) device. Our quantitative investigation based on the HJ device demonstrates that the fast carrier escape from the D/A interface region is indispensable for high PCE, because the carrier accumulation nonlinearly accelerates the carrier recombination process.

In OSCs, the carriers are produced by the exciton dissociation at the D/A interface in the active layer, reflecting the weak screening effect and/or strong exciton effect (Frenkel exciton)¹. In other words, the carriers are localized at the interface at the initial stage of the photovoltaic process. This makes a sharp contrast with the conventional inorganic solar cells (ISCs): The carriers are produced at every positions of the active layer, reflecting the strong screening effect and/or weak exciton effect (Wannier exciton). Then, the quantitative determination of the branching ratio between the carrier recombination at the interface region and the carrier escape from the region is indispensable for true comprehension of the photovoltaic process of OSCs. The escaped carriers will be collected at the collector electrodes. We propose that we can quantitatively investigate the carrier recombination/escape branching ratio by preparing the instantaneous dense carrier states by photo-excitation with femtosecond light pulses. Especially, in the HJ device, the instantaneous carrier density (n) per D/A interface area can be determined because the interface area is the same as the device area.

BHJ-type OSCs^{2,3}, in which nano-level mixture of electron-donating polymer and electron-accepting fullerene-derivative provides a wide exciton-dissociative region within the active layer, show high PCEs and are promising alternatives to the conventional ISCs. Especially, the development of low band-gap polymer, *e.g.*, PTB7, increases the PCE up to 9%⁴⁻⁶ in the last decade^{7,8}. The increase in PCE stimulates extensive time-resolved spectroscopic investigations of the low-band gap OSCs to reveal the carrier formation process⁹⁻¹². The femtosecond time-resolved spectroscopy is a powerful tool to reveal the carrier

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formation process, because the spectroscopy monitors the relative numbers of the photo-created excitons and carriers in the time domain. Significantly, the spectroscopy decouples the carrier formation and transfer processes, because the former process completes within several ps. Actually, the exciton-to-carrier conversion process in PTB7/PC₇₁BM blend film completes in 0.2–0.5 ps^{9,10}. Recently, a spectroscopic method¹³ was proposed to evaluate the carrier formation efficiency (Φ_{CF}). Φ_{CF} is defined by $n_{\text{formed}}/n_{\text{photon}}$, where n_{formed} (n_{photon}) is the density of the instantaneously formed carriers (absorbed photons) per unit area of the device. n_{formed} includes the weakly-bound state of the carriers. Absolute magnitude of n_{formed} can be estimated by the combination of the time-resolved and electrochemical spectroscopies. Φ_{CF} is the same as the exciton quenching efficiency, if all the quenched excitons are converted to carriers.

In this paper, we investigated the branching ratio between the carrier recombination at the interface region and the carrier escape from the region in the PTB7/C₇₀ HJ device. By means of the time-resolved spectroscopy, we confirmed that the exciton-to-carrier conversion process takes place within ~1 ps at the D/A interface in the PTB7/C₇₀ HJ device. In the PTB7/C₇₀ HJ device, Φ_{CF} (=0.56) is nearly constant against the excitation pulse energy (I_{photon}) per unit area of the device while the internal quantum efficiency (Φ_{IQ}) steeply decreases with increase in I_{photon} beyond 0.8 $\mu\text{J}/\text{cm}^2$. We further determined the interrelation between the instantaneous carrier density (n) per D/A interface area and the carrier density ($n_{\text{collected}}$) collected as photocurrent. We found that the carrier recombination becomes dominant if n exceeds a critical concentration ($n_c = 0.003$ carriers/nm²). A phenomenological rate equation with the carrier recombination term ($-\alpha n^3$) well reproduces the experimental relation between n and $n_{\text{collected}}$. We confirmed that a similar behavior is observed in the PTB7/PC₇₁BM BHJ device even though n_c is considered to be much lower than the value of the HJ device.

Results

Pulse energy dependence of Φ_{IQ} of PTB7-based OSCs. We fabricated the two types of the PTB7-based OSCs: PTB7/C₇₀ HJ solar cell with a structure of indium tin oxide (ITO)/poly-(3,4-ethylenedioxythiophene) (PEDOT): poly-(styrenesulfonate) (PSS) (40 nm)/PTB7 (18 nm)/C₇₀ (25 nm)/bathocuproine (BCP) (5 nm)/MgAg and PTB7/PC₇₁BM BHJ cell with a structure of ITO/PEDOT:PSS (40 nm)/active layer (89 nm)/LiF (1 nm)/Al. We measured current (I)—voltage (V) curves (see Supplementary Fig. S1 online) of the two OSCs. The HJ device exhibits an open circuit voltage (V_{oc}) of 0.68 V, a short circuit current (J_{sc}) of 5.9 mA/cm², a fill factor (FF) of 0.68, and a PCE of 2.7%, while BHJ device exhibits a V_{oc} of 0.74 V, a J_{sc} of 17.7 mA/cm², a FF of 0.65, and a PCE of 8.5%. The FF value (=0.68) of the HJ device is slightly higher than that (=0.65) of the BHJ device. The suppressed FF value of the BHJ device is ascribed to the efficient carrier recombination during the carrier transfer process, reflecting the nano-level mixing of the D and A domains. We measured incident photon-to-current conversion efficiency (IPCE) spectra (see Supplementary Fig. S2 online) of the two OSCs. The IPCE of the HJ device is nearly the half of that of the BHJ device. The suppression is ascribed to the thinner active layer (43 nm) of the HJ device as compared with that (89 nm) of the BHJ device. The thinner active layer is further responsible for the lower PCE and J_{sc} values of the HJ device.

Figure 1a shows I against I_{photon} of femtosecond light pulse at 400 nm in the PTB7-based HJ and BHJ devices. In both the devices, the magnitude of I linearly increases with I_{photon} in the low- I_{photon} region below ~0.2 $\mu\text{J}/\text{cm}^2$. However, I becomes nearly constant (~0.03 mA/cm²) above ~2 $\mu\text{J}/\text{cm}^2$. A similar saturation of I against I_{photon} is observed in P3HT/PCBM BHJ device¹⁴. Figure 1b shows Φ_{IQ} at 400 nm against I_{photon} . The magnitudes of Φ_{IQ} were evaluated from I and I_{photon} with considering the absorption indexes: 0.61 and 0.84 for HJ and BHJ devices, respectively. In the HJ device (open circles), the Φ_{IQ} value (~0.4) in the low- I_{photon} region is nearly the same as the value (=0.59) determined under 400 nm monochromatic radiation of 6.6 mW/cm². The Φ_{IQ} value exponentially decreases with increase in I_{photon} beyond 0.8 $\mu\text{J}/\text{cm}^2$. In the BHJ device (closed circles), the Φ_{IQ} value (~0.6) in the low- I_{photon} region is close to the value (=0.79) determined under 400 nm monochromatic radiation of 6.6 mW/cm². The Φ_{IQ} value exponentially decreases with increase in I_{photon} beyond 0.2 $\mu\text{J}/\text{cm}^2$.

Carrier formation dynamics in PTB7/C₇₀ heterojunction. We investigated ΔOD spectra of PTB7/C₇₀ bilayer, PC₇₁BM neat, and PTB7 neat films at 400 nm (see Supplementary Fig. S3 online). The ΔOD spectra of the PC₇₁BM (PTB7) neat film show a characteristic photoinduced absorption (PIA), which should be ascribed to the acceptor exciton (A^*) [donor exciton (D^*)]. The ΔOD spectra of the PTB7/C₇₀ bilayer film show a broad PIA centered at 1150 nm. In the late stage (>10 ps), the profile of the PIA is essentially unchanged. In addition, the spectral profile is similar to that of the doping-induced spectrum of the PTB7 neat film (see Supplementary Fig. S4 online). Therefore, we ascribed the PIA to the photo-created donor carriers (D^+). In the early state (<10 ps), however, an additional absorption component is observed around 1500 nm. The additional component should be ascribed to the PIAs due to A^* and D^* . We decomposed the ΔOD spectra (ϕ_{exp}) of the PTB7/C₇₀ bilayer film into the components of A^* (ϕ_{A^*}), D^* (ϕ_{D^*}), and D^+ (ϕ_{D^+}). The ΔOD spectra of the PC₇₁BM (PTB7) neat film at 1 ps was regarded as ϕ_{A^*} (ϕ_{D^*}) while the ΔOD spectra of the PTB7/C₇₀ bilayer film at 10 ps was regarded as ϕ_{D^+} . The spectral weights of the respective components were evaluated by least-squares fitting of the observed spectra (ϕ_{exp}) with the linear combination of ϕ_{A^*} , ϕ_{D^*} , and ϕ_{D^+} : $\phi_{\text{cal}} = C_{A^*}\phi_{A^*} + C_{D^*}\phi_{D^*} + C_{D^+}\phi_{D^+}$.

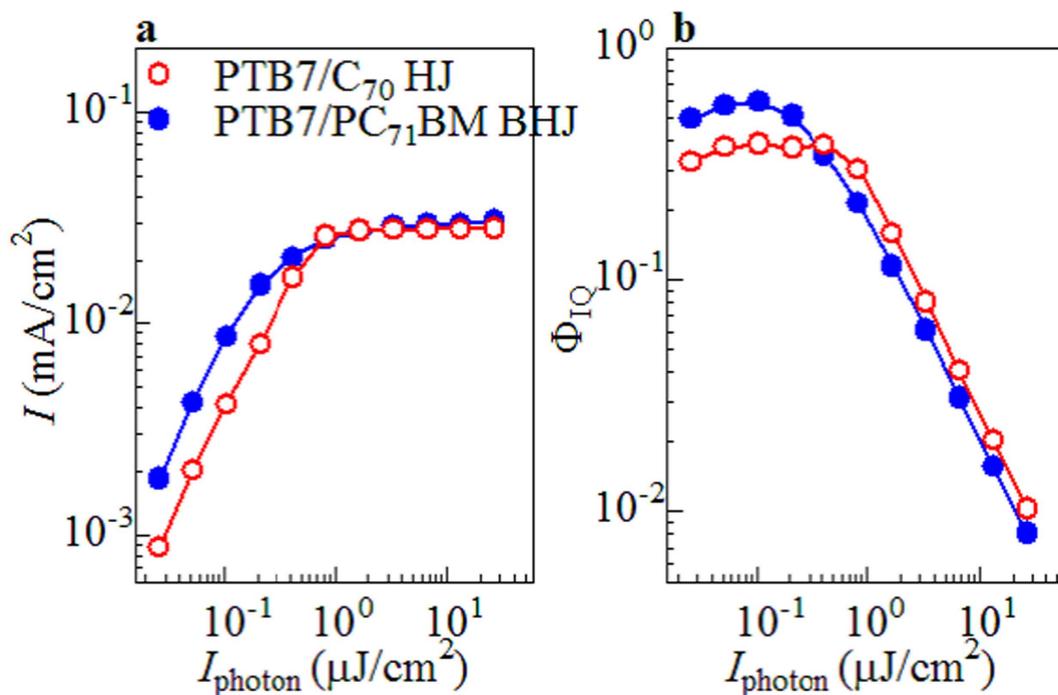


Figure 1. (a) Photocurrent (I) against energy (I_{photon}) of femtosecond light pulse at 400 nm in the PTB7/C₇₀ HJ and PTB7/PC₇₁BM BHJ devices. (b) Φ_{IQ} against I_{photon} . The magnitudes of Φ_{IQ} were estimated with considering the absorption indexes: 0.61 and 0.84 for HJ and BHJ devices, respectively. The curves are merely the guides to the eyes.

The coefficients, C_{A^*} , C_{D^*} and C_{D^+} , were determined so that the evaluation function, $F(C_{A^*}, C_{D^*}, C_{D^+}) = \sum_i (\phi_{\text{exp}} - \phi_{\text{cal}})^2$, becomes the minimum. Figure 2a show an example of the spectral decomposition at 0.9 ps. We clearly observed that the photo-excitation at 400 nm excites D^* in addition to A^* .

Now, let us evaluate the absolute numbers of the acceptor exciton (n_{A^*}), donor exciton (n_{D^*}) and donor carrier (n_{D^+}) per absorbed photon from the ΔOD spectra of the PTB7/C₇₀ bilayer film. For this purpose, we need the spectral intensities, α_{A^*} , α_{D^*} , and α_{D^+} , per unit densities of A^* , D^* , and D^+ . In order to determine α_{A^*} and α_{D^*} , we assumed that one absorbed photon creates one A^* (D^*) in the PC₇₁BM (PTB7) neat film. We determined α_{A^*} (α_{D^*}) with use of the ΔOD spectra of PC₇₁BM (PTB7) neat film (see Supplementary Fig. S3 online): α_{A^*} (α_{D^*}) is evaluated to be 0.002 nm²/photons (0.020 nm²/photons) with considering absorption indexes. Then, n_{A^*} (n_{D^*}) is calculated by $(I_{A^*}/n_{\text{photon}})/\alpha_{A^*}$ [$(I_{D^*}/n_{\text{photon}})/\alpha_{D^*}$], where I_{A^*} (I_{D^*}) and n_{photon} are the intensity of the (A^*) (D^*) component in the PTB7/C₇₀ bilayer film and the absorbed photon number per unit density of the device. The magnitude of α_{D^+} was determined from the electrochemical differential ($\Delta\text{OD}_{\text{EC}}$) spectrum (see Supplementary Fig. S4 online). α_{D^+} is evaluated to be 0.013 nm²/carriers with use of the doped carrier density. Then, n_{D^+} is calculated by $(I_{D^+}/n_{\text{photon}})/\alpha_{D^+}$, where I_{D^+} is the intensity of the D^+ component in the PTB7/C₇₀ bilayer film. The magnitudes of I_{A^*} , I_{D^*} , and I_{D^+} were evaluated by the spectral decomposition of the ΔOD spectra into the A^* , D^* , and D^+ components, as exemplified in Fig. 2a.

Figure 2b shows the absolute numbers of A^* (n_{A^*}), D^* (n_{D^*}) and D^+ (n_{D^+}) per an absorbed photon against the delay time. The n_{A^*} values significantly scatter reflecting the small cross section of A^* ($\alpha_{A^*} = 0.002$ nm²/photons). Nevertheless, we observed steep decreases in n_{A^*} and n_{D^*} with time. The decay times (τ_{decay}) of n_{A^*} and n_{D^*} are roughly evaluated to be 3.1 and 1.6 ps, respectively. On the other hand, n_{D^+} exponentially increases with the rise time (τ_{rise}) of 1.0 ps. The rather slow decay time ($\tau_{\text{decay}} = 3.1$ ps) of A^* suggests that the late decay component (>1 ps) of A^* does not contribute to the carrier formation. Actually, the sum of the initial exciton number, *i.e.*, $n_{A^*} + n_{D^*}$ (~ 0.7 /photon) is slightly larger than the carrier number ($n_{D^+} \sim 0.5$ /photon). Thus, the exciton-to-carrier conversion process in the PTB7/C₇₀ bilayer film takes place at the D/A interface within ~ 1 ps. The carrier formation time (~ 1 ps) in the PTB7/C₇₀ bilayer film is longer than that ($= 0.2\text{--}0.5$ ps) of PTB7/PC₇₁BM blend film¹⁰. The longer conversion time is ascribed to be the longer exciton diffusion to the D/A interface in the HJ device than that in the BHJ device.

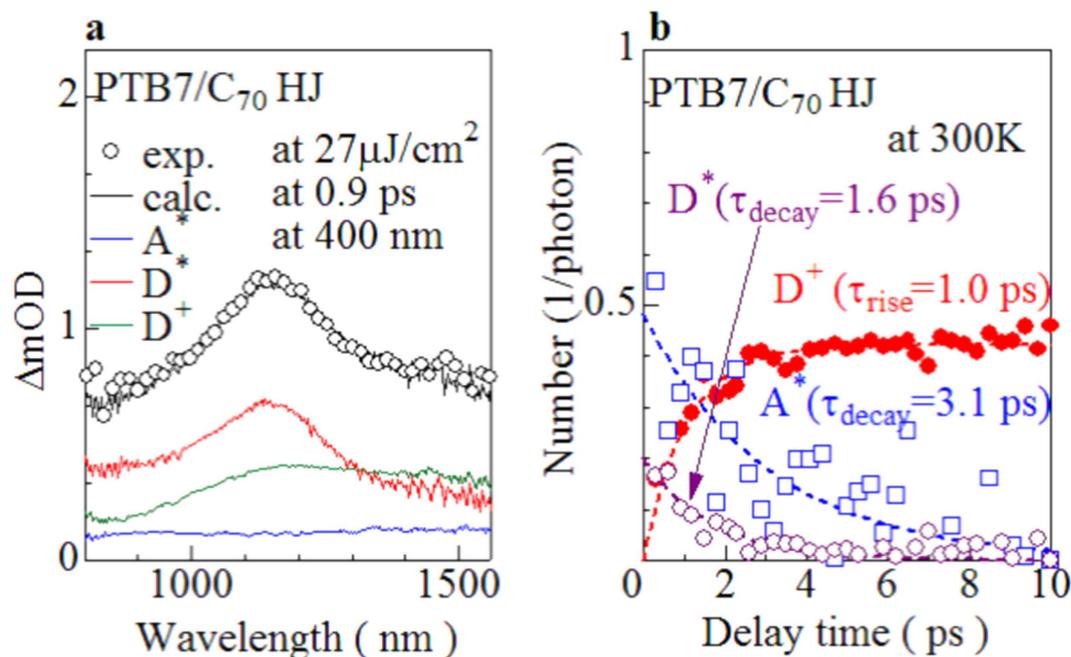


Figure 2. (a) ΔOD spectra (open circles) of PTB7/C₇₀ bilayer film at 0.9 ps and at 400 nm together with the spectral decomposition into acceptor exciton (A*: blue curve), donor exciton (D*: green curve), and donor carrier (D⁺: red curve) components. The ΔOD spectra of the PC₇₁BM neat, PTB7 neat, and PTB7/C₇₀ bilayer films at 1, 1, and 10 ps are regarded as the A*, D*, and D⁺ components, respectively. (b) Absolute number of acceptor exciton (n_{A^*}), donor exciton (n_{D^*}) and donor carrier (n_{D^+}) per an absorbed photon against the delay time. The magnitudes of n_{A^*} , n_{D^*} and n_{D^+} were evaluated by the spectral decomposition of the ΔOD spectra of the PTB7/C₇₀ bilayer film. The solid curves are results of the least-squares fittings with an exponential function.

Pulse energy dependence of Φ_{CF} in PTB7-based OSCs. Next, we investigated pulse energy dependence of the ΔOD spectra at 10 ps of the PTB7/C₇₀ bilayer and PTB7/PC₇₁BM blend films at 400 nm (see Supplementary Fig. S5 online). The magnitude of Φ_{CF} ($=\alpha_{\text{photon}}/\alpha_{D^+}$) can be calculated from the two quantities. α_{photon} ($=I_{D^+}/n_{\text{photon}}$) is the spectral intensities due to D⁺ per unit density of absorbed photons. α_{D^+} is reported to be 0.013 nm²/carriers for PTB7¹³. In the PTB7-based OSCs, the carrier formation time is less than 1 ps. Therefore, we evaluated the α_{D^+} values from the ΔOD spectra at 10 ps of the PTB7/C₇₀ bilayer and PTB7/PC₇₁BM blend films with considering the absorption indexes: 0.37 and 0.60 for the bilayer and blend films, respectively. Thus obtained Φ_{CF} values are plotted in Fig. 3 together with Φ_{IQ} against I_{photon} . We found that Φ_{CF} ($=0.56$) is nearly independent of I_{photon} in the PTB7/C₇₀ bilayer film even though Φ_{CF} at $I_{\text{photon}} < 2 \mu\text{J}/\text{cm}^2$ is difficult to determine. This makes a sharp contrast with a steep decrease in Φ_{IQ} with increase in I_{photon} beyond $0.8 \mu\text{W}/\text{cm}^2$. A similar behavior of Φ_{IQ} and Φ_{CF} is observed in the PTB7/PC₇₁BM BHJ device. In the high- I_{photon} region, most of the carriers recombine and do not contribute to the photocurrent ($\Phi_{IQ} \ll 1$). We note that the carrier recombination process takes several nanoseconds in both the devices (see Supplementary Fig. S6 online). We tentatively evaluate the decay times (τ_{decay}) by least-squares fittings with exponential functions, *i.e.*, $\Delta mOD = A \exp(-t/\tau)$: $\tau_{\text{decay}} = 3.4$ and 5.8 ns for the HJ and BHJ devices, respectively.

Here, we define the instantaneous carrier density (n) per unit area of the D/A interface. In the HJ device, the magnitude of n is the same as n_{D^+} ($=n_{\text{photon}} \times \Phi_{CF}$) because the D/A interface area is the same as the device area. In the BHJ device, however, the magnitude of n is smaller than n_{D^+} because the interface area is much wider than the device area. Under the femtosecond pulse excitation, the carriers are instantaneously produced at the D/A interface before they start migration toward the collector electrodes. Actually, the carriers are generated at the D/A interface within ~ 1 ps. For example, the local carrier density (n) at the interface of the HJ device is ~ 0.1 carriers/nm² at $10 \mu\text{J}/\text{cm}^2$. Under a conventional continuous wave (CW) excitation, however, the carrier migration effectively reduces the n value. For example, the local carrier density at the interface is $\sim 10^{-2}$ carriers/nm² at $100 \text{ mW}/\text{cm}^2$ if the carrier escape time from the interface region is 1 ns. On the other hand, it becomes ~ 1 carriers/nm² at $100 \text{ mW}/\text{cm}^2$ with the carrier lifetime of ~ 1 ms, which is comparable to the value (~ 0.1 carriers/nm²) under the femtosecond pulse excitation at $10 \mu\text{J}/\text{cm}^2$. These arguments indicate that the significant carrier recombination efficiency observed in the high- I_{photon} region should be ascribed to the local dense carriers at the interface. In other words, the carriers at the interface region are amenable to the recombination while the carriers escaped from the region are free from the recombination.

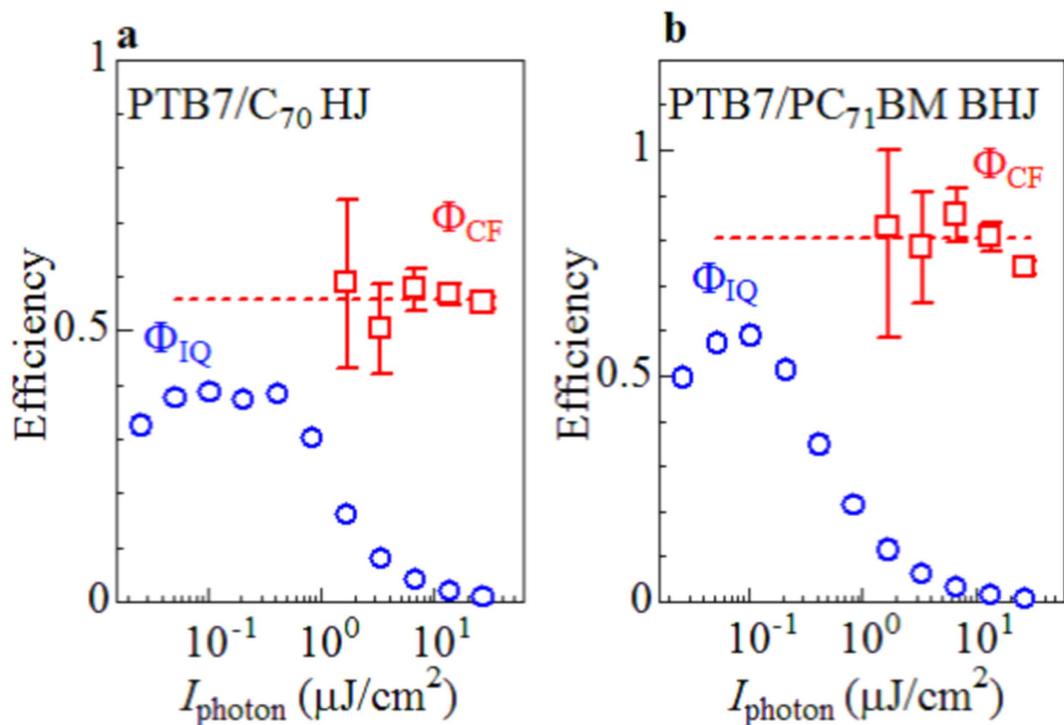


Figure 3. Φ_{CF} and Φ_{IQ} of (a) PTB7/C₇₀ HJ and (b) PTB7/PC₇₁BM BHJ devices against energy (I_{photon}) of femtosecond light pulse at 400 nm. The magnitudes of Φ_{CF} were estimated with considering the absorption indexes: 0.37 and 0.60 for the bilayer and blend films, respectively. The error bars of Φ_{CF} were roughly evaluated from the signal/noise ratio of the femtosecond time-resolved spectra. The magnitudes of Φ_{IQ} were estimated with considering the absorption indexes: 0.61 and 0.84 for HJ and BHJ devices, respectively. The broken lines are merely the guide to the eyes.

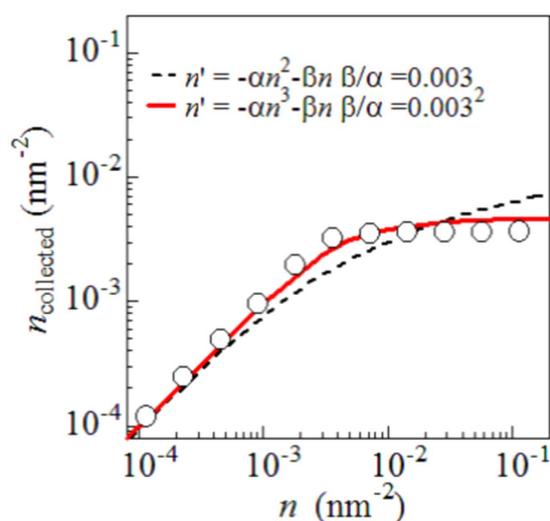


Figure 4. Carrier density ($n_{\text{collected}}$) collected as photocurrent against instantaneous carrier density (n) per unit area of the D/A interface in PTB7/C₇₀ HJ device. The n values were evaluated with assuming constant Φ_{CF} ($=0.56$). The solid and broken curves are drawn by a phenomenological model (see text).

Discussion

Figure 4 shows the carrier density ($n_{\text{collected}}$) collected as photocurrent against n ($=\Phi_{\text{CF}} \times n_{\text{photon}}$) in the HJ device. The n values were evaluated with assuming constant Φ_{CF} ($=0.56$). In the dilute- n region, the photocurrent is proportional to n . In the dense- n region, however, the photocurrent becomes nearly constant. This suggests that there exists a critical carrier density ($n_c = 0.003$ carriers/ nm^2) above which

the carrier recombination becomes dominant. The n_c value ($=0.003$ carriers/nm²) corresponds to the value, in which one carrier exists every 18×18 nm² squares. To quantitatively analyze the carrier recombination kinetics against n , we adopted a phenomenological rate equation: $dn/dt = -\alpha n^N - \beta n$. The first and second terms represent the carrier recombination and the carrier escape from the interface region. The first term at $N=2$ describes the conventional electron–hole recombination process. The ratio between the coefficients, α and β , should be fixed as $\beta/\alpha = n_c^{N-1}$, because the first and the second terms become comparable at $n = n_c$. We assume that all the escaped carriers contribute the photocurrent, *i.e.*, $n_{\text{collected}} = \int \beta n dt$. The solid and broken curves in Fig. 4 are results of the phenomenological model at $N=3$ and 2, respectively. We found that the curve at $N=3$ excellently reproduces the experiment data. The deviation from the conventional n^2 -dependence ($N=2$) is probably ascribed to the electric double layer effect at the interface, which may cause a many-body interaction between the carriers. Here, we note that the recombination/escape branching ratio is determined by the ratio not by the magnitudes of the coefficients, α and β . The magnitude determines only the time scale of the branching kinetics. That is, we have no adjustable parameter in this phenomenological mode.

A similar relation between n and $n_{\text{collected}}$ is observed in the PTB7/PC₇₁BM BHJ device even though we cannot evaluate the magnitude of n . Alternatively, we estimated the critical carrier density ($n_c' = 0.002$ carriers/nm²) per unit area of the device, above which the carrier recombination becomes dominant. We note that n_c (per unit area of the interface) is much smaller than n_c' (per unit area of the device) because the D/A interface area is much wider than that of the device area. That is, n_c of the BHJ device is much lower than n_c ($=0.003$ carriers/nm²) of the HJ device. We ascribe the suppressed n_c of the BHJ device to the unevenness of the D/A interface due to the nano-level mixing of the D and A domains^{15,16}. Hedley *et al.*¹⁵ reported that the domain (100–200 nm) of PTB7/PC₇₁BM blend film consists of small fullerene spheres (20–60 nm) inside the domain. The resultant inhomogeneity of the interface activates only a portion of the interface to dissociate the excitons. Then, the interface inhomogeneity effectively reduces the interface area and increases n (per unit area of the interface). In addition, the inhomogeneity causes the carrier trapping at the interface region. The carrier trapping should enhance the carrier recombination probability. On the other hand, the interface of HJ device, which is prepared by vacuum evaporation process, is considered to be much smoother. Actually, the root-mean-square (RMS) of the PTB7 film is 0.32 nm (see Supplementary Fig. S7 online). Such a smooth interface is free from carrier trapping and is advantageous for the high branching ratio of the carrier escape.

Summary

In summary, we investigated the interrelation between the instantaneous carrier density (n) per D/A interface area and the carrier density ($n_{\text{collected}}$) collected as photocurrent in PTB7/C₇₀ HJ device. By means of the time-resolved spectroscopy, we confirmed that the exciton-to-carrier conversion process takes place within ~ 1 ps at the D/A interface of the PTB7/C₇₀ HJ device. We further determined the absolute magnitude of n by combination of the time-resolved and electrochemical spectroscopies. We found that the carrier recombination becomes dominant if n exceeds a critical concentration ($n_c = 0.003$ carriers/nm²). A phenomenological rate equation with carrier recombination term ($-\alpha n^3$) well reproduces the experimental relation between n and $n_{\text{collected}}$. We confirmed that a similar behavior is observed in the PTB7/PC₇₁BM BHJ devices even though n_c is much lower than the value of the HJ device. Our quantitative investigation based on the HJ device demonstrates that the fast carrier escape from the interface region is indispensable for high PCE, because the carrier accumulation nonlinearly accelerates the carrier recombination process.

Method

Fabrication and characterization of the OSCs. PTB7/C₇₀ HJ solar cell was fabricated with a structure of indium tin oxide (ITO)/poly-(3,4-ethylenedioxythiophene) (PEDOT): poly-(styrenesulfonate) (PSS) (40 nm)/PTB7 (18 nm)/C₇₀ (25 nm)/bathocuproine (BCP) (5 nm)/MgAg. The patterned ITO (conductivity: 10 Ω /sq) glass was pre-cleaned in an ultrasonic bath of acetone and ethanol and then treated in an ultraviolet-ozone chamber. A thin layer of PEDOT:PSS (40 nm) was spin-coated onto the ITO and dried at 110 °C for 10 min on a hot plate in air. A neat PTB7 film was spin-coated from an *o*-dichlorobenzene (*o*-DCB) solution. PTB7 was purchased from Sigma-Aldrich and used as received. The atomic force microscope (AFM) image of the PTB7 film is flat and consists of small grains less than 100 nm. Then, C₇₀ (25 nm) was deposited by vacuum evaporation. Finally, BCP and MgAg were deposited onto the active layer by conventional thermal evaporation at a chamber pressure lower than 5×10^{-4} Pa, which provided the devices with an active area of 2×5 mm².

PTB7/PC₇₁BM BHJ solar cell was fabricated with a structure of ITO/PEDOT:PSS (40 nm)/active layer (140 nm)/LiF (1 nm)/Al. The patterned ITO glass was pre-cleaned in an ultrasonic bath of acetone and ethanol and then treated in an ultraviolet-ozone chamber. A thin layer of PEDOT:PSS (40 nm) was spin-coated onto the ITO and dried in air at 110 °C for 10 min on a hot plate. The substrate was then transferred to an N₂ glove box and dried again at 110 °C for 10 min on a hot plate. An *o*-DCB/1,8-diiodooctane (DIO) solution of PTB7 : PC₇₁BM with a ratio of 2 : 3 by weight (8 : 12 mg/mL) was subsequently spin-coated onto the PEDOT:PSS surface to form an active layer. Finally, LiF (1 nm) and Al (80 nm) were deposited onto the active layer by conventional thermal evaporation at a chamber pressure lower than 5×10^{-4} Pa. The active area of the OSCs is 2×5 mm².

The $J - V$ curves were measured using a voltage—current source/monitor under AM 1.5 solar-simulated light irradiation of 100 mW/cm^2 (Bunkou-keiki, OTENTO-SUN III). The IPCE spectra was measured using a SM-250 system (Bunkou-keiki). The magnitudes of Φ_{IQ} at 400 nm were evaluated from the IPCE spectra with considering the absorption indexes: 0.61 and 0.84 for the HJ and BHJ devices, respectively.

Pulse energy dependence of Φ_{IQ} of the OSCs. The pulse energy dependences of Φ_{IQ} of the OSCs were measured in a N_2 -filled box. For this experiment, the active area of the OSCs is $2 \times 3 \text{ mm}^2$. The excitation light pulse at 400 nm was generated as the second harmonics of a regenerative amplified Ti: sapphire laser in a $\beta\text{-BaB}_2\text{O}_4$ (BBO) crystal. The pulse width and repetition rate were 100 fs and 500 Hz, respectively. The maximum excitation intensity was $27 \mu\text{J/cm}^2$. The photocurrents (I) from the OSCs were measured against the excitation pulse energy (I_{photon}) per unit area of the device. The magnitudes of Φ_{IQ} were evaluated by I and I_{photon} , with considering the absorption indexes: 0.61 and 0.84 for the HJ and BHJ devices, respectively.

Femtosecond time-resolved spectroscopy. The time-resolved spectroscopy was performed in a pump-probe configuration. In order to reduce the irradiation damage, the blend films were placed in N_2 atmosphere. The pump pulse at 400 nm was generated as the second harmonics of a regenerative amplified Ti: sapphire laser in a $\beta\text{-BaB}_2\text{O}_4$ (BBO) crystal. The pulse width, repetition rate, and pulse energy were 100 fs, 1000 Hz, and $27 \mu\text{J/cm}^2$ respectively. The frequency of the pump pulse was decreased by half (500 Hz) to provide “pump-on” and “pump-off” conditions. A white probe pulse, generated by self-phase modulation in a sapphire plate was focused on the sample with the pump pulse. The spot sizes of the pump and probe pulses were 4.0 and 2.1 mm in diameter, respectively. The differential absorption (ΔOD) spectrum is expressed as $-\log(I_{\text{on}}/I_{\text{off}})$, where I_{on} and I_{off} are the transmission spectra under the pump-on and pump-off conditions, respectively.

Films prepared on quartz substrates were used in the time-resolved spectroscopies. PTB7/ C_{70} bilayer film was prepared as follows. First, PTB7 neat film (18 nm) was spin-coated on quartz substrate from an *o*-DCB solution. The spin-coated film was dried in an inert N_2 atmosphere. Then, C_{70} (25 nm) was deposited by vacuum evaporation. PTB7/ $PC_{71}\text{BM}$ blend film was spin-coated on quartz substrate from a mixed solvent of *o*-DCB /DIO (97.5 : 2.5 vol %) of PTB7 : $PC_{71}\text{BM}$ with a ratio of 2 : 3 by weight (8 : 12 mg/mL). PTB7 neat film was spin-coated on quartz substrate from *o*-DCB solution. The spin-coated films were dried in an inert N_2 atmosphere. The thicknesses of the PTB7 and PTB7/ $PC_{71}\text{BM}$ blend films were 100 and 140 nm, respectively.

Pulse energy dependence of Φ_{CF} . The magnitude of Φ_{CF} ($=\alpha_{\text{photon}}/\alpha_{D^+}$) can be calculated from the two quantities. α_{D^+} (α_{photon}) is the spectral intensity due to D^+ per unit density of D^+ (absorbed photons). α_{D^+} is reported to be $0.013 \text{ nm}^2/\text{carriers}$ for PTB7¹³. In the PTB7-based OSCs, the carrier formation time is less than 1 ps. Therefore, we evaluated the α_{D^+} values from the ΔOD spectra at 10 ps of the PTB7/ C_{70} bilayer and PTB7/ $PC_{71}\text{BM}$ blend films with considering the absorption indexes: 0.37 and 0.60 for the bilayer and blend films, respectively.

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Author Contributions

Y.M. planned overall the investigation and wrote the manuscript. T.Y. fabricated and characterized the organic solar cells. He further measured the photon flux dependence of Φ_{IQ} . K.Y. performed femtosecond time-resolved spectroscopies and analyzed the exciton-to-carrier conversion process. He further determined the photon flux dependence of Φ_{CF} .

Additional Information

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