

Efficient Charge Generation and Collection in Amorphous Polymer-Based Solar Cells

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ABSTRACT

The charge generation and recombination dynamics in amorphous blend films of poly[2,7-(9,9-dioctylfluorene)-*alt*-5,5-(5',8'-di-2-thienyl-2',3'-diphenylquinoxaline)] (N-P7) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) were comprehensively studied in order to address the origin of the relatively high performance for amorphous polymer-based solar cells. Upon photoexcitation, N-P7 singlet excitons are promptly converted to the interfacial charge transfer (CT) state, which is a coulombically bound pair of the N-P7 polaron and PCBM radical anion, with 100% efficiency in a picosecond. More than half of the N-P7 polarons in the CT state are dissociated into free carriers and the rest of them recombine to the ground state in a nanosecond. The dissociation efficiency η_{CD} is estimated to be 0.65 under the open-circuit condition and is slightly enhanced up to 0.7 – 0.8 under the short-circuit condition. Such highly efficient dissociation is well explained by considering charge delocalization. The charge collection efficiency η_{CC} is as high as >0.9 in the thin device but decreases to <0.8 in the thick device, suggesting that bimolecular recombination loss is not negligible in the thick device. Furthermore, the origin of the efficient device performance is discussed in terms of the field dependence and the charge delocalization.

Keywords: Charge Transfer State, Charge Delocalization, Fluorene-Based Copolymer, Fullerene, Polymer Solar Cells

1. Introduction

Polymer/fullerene solar cells have made remarkable progress in recent years.¹⁻⁴ Currently, the power conversion efficiency (PCE) has exceeded 10%.⁵ This is due largely to intensive developments in various conjugated polymers. There are two synthetic strategies for the developments of conjugated polymers for improving the device performance of polymer solar cells. One is to expand the light-harvesting wavelength region in order to increase the short-circuit current density (J_{SC}).⁶⁻¹² The other is to increase the ionization potential of donor polymers in order to obtain a larger open-circuit voltage (V_{OC}).¹³⁻¹⁶ As such, various fluorene-based copolymers have been developed because their optoelectronic properties can be finely tuned by chemical modifications and copolymerization with various units.¹⁷⁻²⁰ Some amorphous fluorene-based copolymers have ionization potentials larger than a benchmark polymer of crystalline regioregular poly(3-hexylthiophene) (RR-P3HT), which exhibits a modest V_{OC} of ~0.6 V. For example, a polymer solar cell based on a blend of an amorphous fluorene-based copolymer of poly[2,7-(9,9-dioctylfluorene)-*alt*-5,5-(5',8'-di-2-thienyl-2',3'-diphenylquinoxaline)] (N-P7) and a C₇₀ fullerene derivative ([70]PCBM) shows a larger V_{OC} of 0.99 V and a comparable J_{SC} of 10 mA cm⁻², and hence a higher PCE of 5.5%^{13,14} than those of the polymer solar cells based on RR-P3HT and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM).^{12,21,22}

The photovoltaic performance is critically dependent on whether conjugated polymers employed are crystalline or amorphous. For example, the device performance is much higher for crystalline blends of RR-P3HT and PCBM than for amorphous blends of regiorandom P3HT (RRa-P3HT) and PCBM. Our recent studies have shown that the charge dissociation efficiency is more than 0.9 for RR-P3HT/PCBM but is as low as 0.3 for RRa-P3HT/PCBM.²³ Furthermore, crystalline conjugated polymers generally exhibit high charge mobility, which is beneficial for

the efficient charge collection. As such, various crystalline conjugated polymers have been intensively developed to improve the device performance of polymer solar cells recently.^{4,24–26} On the other hand, as mentioned above, several amorphous polymers also exhibit relatively efficient photovoltaic performance.^{6,13–15,27} However, the photovoltaic conversion mechanism in blend films of such efficient amorphous polymers and PCBM is not fully understood.

Herein, we study the charge generation, recombination, and collection dynamics in N-P7/PCBM amorphous blends by transient absorption and device characteristics measurements, and thereby evaluate all the photovoltaic efficiencies of the exciton diffusion to a donor/acceptor interface, the charge transfer at the interface, the charge dissociation into free carriers at the interface, and the charge collection to electrodes quantitatively. As a result, we found that the geminate recombination is one of the primary loss processes in the device performance and the bimolecular recombination is additional loss process in the thick device. Furthermore, we discuss the charge dissociation efficiency in terms of the field dependence and the charge delocalization on the basis of the Onsager–Braun model.²⁸

2. Experimental

For the device fabrication, indium/tin oxide (ITO)-coated glass substrates (10 Ω per square) were washed by ultrasonication in toluene, acetone, and ethanol for 15 min, dried with N₂, and then cleaned with a UV–O₃ cleaner (Nippon Laser & Electronics NL-UV253S) for 30 min. A thin layer (~40 nm) of poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS; H. C. Starck, PH500) was spin-coated on the cleaned substrates at a spin rate of 3000 rpm, and the layer was dried at 140 °C for 10 min in air. The solution of PEDOT:PSS was filtered using a 0.45- μ m PTFE syringe filter prior to the spin coating. Blend layers of N-P7/PCBM (1:4 by

weight) were spin-coated from chlorobenzene solution. The N-P7 ($M_n = 15600$, $M_w/M_n = 2.03$) was synthesized according to a previously reported method^{13,14} and [60]PCBM (99.9%) was purchased from Frontier Carbon, both of which were used without further purification. The thicknesses of active layers were estimated by AFM measurement (Shimadzu, SPM-9600) for blend films fabricated by the similar method on bare glass substrates. Finally, Al (70 nm) was thermally deposited on top of the active layer at 2.5×10^{-4} Pa.

For spectroscopic measurements, blend films of N-P7 and PCBM were fabricated by spin-coating on a bare glass substrate. An UV–visible–Near-IR spectrophotometer (Hitachi, U-4100) and a spectrofluorometer (Horiba, NanoLog) were used for the absorption and fluorescence measurements, respectively. For the fluorescence lifetime measurement, a spectrofluorometer (Horiba, FluoroCube) equipped with a TCSPC unit (Horiba, FluoroHub) and a liquid-nitrogen-cooled photomultiplier tube (Hamamatsu Photonics, R5509-73) were used. For transient absorption measurements, blend films of N-P7 and PCBM were fabricated by spin-coating on a glass substrate. The transient absorption measurements were performed for these sample films over the time range from picosecond to microsecond in nitrogen atmosphere. The apparatus employed here has been described elsewhere.^{12,23} For the white bias light source, a 150W-Xe lamp (Kenko Tokina, XEF-152S) was used.

3. Results

---<< Figure 1 >>---

---<< Table 1 >>---

Figure 1a shows the J – V characteristics of N-P7/PCBM solar cells in the dark and under the simulated solar illumination at 100 mW cm^{-2} . The short-circuit current density (J_{SC}) increased with increasing thickness of the active layer: 5.1 (90 nm), 6.3 (140 nm), and 7.3 mA cm^{-2} (220 nm). This is ascribed to the increase in the photon absorption efficiency as will be described below. Note that these J_{SC} are smaller than previously reported values^{13,14} because [60]PCBM is employed instead of [70]PCBM for simplicity in the transient absorption analysis. The open-circuit voltage (V_{OC}) also increased slightly with increasing thickness of the active layer, which is ascribed to the increase in J_{SC} (see the Supporting Information). The fill factor (FF) decreased with increasing thickness of the active layer, suggesting poorer charge collection in thicker devices. These device parameters are summarized in **Table 1**. As shown in Figure 1b, the EQE spectra of the N-P7/PCBM solar cells were dependent on the thickness of the active layer. The hole mobility and surface topography of these devices were independent of the film thickness (see the Supporting Information), indicating that phase-separated structures are independent of the film thickness. Rather, as shown in Figure 1c, a similar thickness dependence was observed for the absorption spectra of these device measured by reflection mode at an incident angle of 5° normal to the substrate. Here, the photon absorption efficiency $\eta_{\text{A}}(\lambda)$ is defined as $\eta_{\text{A}}(\lambda) = 1 - R(\lambda)$ where $R(\lambda)$ is the reflectance of the device at a wavelength λ . Thus, the thickness dependence is probably due to the optical interference in the solar cells. The absorption band at around 400 – 500 nm is ascribed to N-P7 because PCBM has no distinct absorption band in the visible region, suggesting that the photon absorption is mainly due to N-P7. As shown in the figure, the EQE and photon absorption efficiency η_{A} at 400 nm are estimated to be 0.25 and 0.35 (90 nm), 0.50 and 0.80 (140 nm), and 0.50 and 0.85 (220 nm), respectively. The slight difference between the EQE and η_{A} spectra is probably due to the different incident angles. We note that the absorption spectrum of an N-P7 neat film is the same as that of N-P7 in a toluene

solution (see the Supporting Information). Furthermore, the device performance is higher for the device without thermal annealing as reported previously.^{13,14} These are indicative of amorphous nature of N-P7.

---<< Figure 2 >>---

Figure 2a shows the photoluminescence (PL) spectra of N-P7 and PCBM neat films and N-P7/PCBM blend films. As shown in the figure, N-P7 and PCBM neat films exhibited fluorescence bands at 680 and 720 nm, respectively. These two PL bands were completely quenched in N-P7/PCBM blend films independently of the film thickness. Instead, a red-shifted PL band was observed at around 850 – 950 nm, which is similar to the emission from interfacial charge transfer (CT) state reported previously for blend films of fluorene-based copolymer and PCBM.^{29,30} As shown in Figure 2b, the red-shifted PL band decayed with a lifetime of 2.2 ns, which is again comparable to that of the CT emission reported previously.²⁹ We therefore ascribe the PL band at 950 nm to interfacial CT state formed at N-P7/PCBM heterojunction.

---<< Figure 3 >>---

Figure 3 shows the normalized transient absorption spectra of N-P7/PCBM blend films. Only the absorption spectrum at <0.1 ps was different from the other spectra after a few picoseconds; there was a spectral difference over 900 to 1300 nm. At this wavelength region, the absorption band of N-P7 singlet exciton was observed for N-P7 neat films as shown by the broken line in this figure. We therefore ascribe the short-lived absorption observed over 900 to 1300 nm at <0.1 ps to the N-P7 singlet exciton. The large absorption band at around 850 nm decayed in a

few nanoseconds and was still observed on a time scale of microseconds even in an oxygen atmosphere. We therefore ascribe the large absorption at around 850 nm to the N-P7 polaron, which is consistent with a previous report:³¹ the N-P7 polaron exhibits an absorption peak with a molar absorption coefficient of $\varepsilon_{\text{N-P7}^+} = 40000 \text{ M}^{-1} \text{ cm}^{-1}$ at 850 nm.

---<< Figure 4 >>---

To analyze the charge generation dynamics, we resolved the transient absorption spectra into N-P7 singlet exciton and charged species (N-P7 polaron and PCBM radical anion) by spectral simulation. As shown in **Figure 4a**, the transient absorption spectrum at <0.1 ps can be well reproduced by the sum of the absorption spectrum of N-P7 singlet exciton and that of the charged species. Figure 4b shows the time evolution of N-P7 singlet exciton and polaron in N-P7/PCBM blend films. It is noteworthy that 80% of N-P7 polarons were promptly generated at <0.1 ps. The remaining N-P7 polarons were generated with a time constant of 0.3 ps and N-P7 singlet excitons decayed exponentially with the same time constant. This agreement suggests rapid generation of N-P7 polarons from singlet excitons, which is consistent with the efficient fluorescence quenching.

---<< Figure 5 >>---

Figure 5 shows the time evolution of transient signals at 900 nm (N-P7 polaron) observed for N-P7/PCBM blend films on a time scale of nanoseconds. At laser intensities below $4 \mu\text{J cm}^{-2}$, the decay dynamics were independent of the excitation intensity, suggesting monomolecular recombination. Note that the charge carrier density under the lowest excitation is in the order of

10^{16} cm^{-3} , which corresponds to a typical carrier density under the device operating conditions. The polaron decay was in good agreement with the photobleaching recovery (see the Supporting Information), suggesting the recombination to the ground state. Therefore, the decay dynamics is ascribed to the monomolecular recombination to the ground state. Indeed, the decay dynamics can be well fitted by a single exponential function with a constant fraction: $\Delta OD = A \exp(-t/\tau_m) + B$. From the fitting, the decay constant and the constant fraction are evaluated to be $\tau_m = 2.2 \text{ ns}$ and $A : B = 35 : 65$, respectively, independently of the film thickness. This is in good agreement with the lifetime of the CT emission observed for this blend film mentioned above. We therefore ascribe the decay fraction in the polaron band on a time scale of nanoseconds to the interfacial CT state, which is the coulombically bound pair of N-P7 polaron and PCBM radical anion at the heterojunction.

---<< Figure 6 >>---

We move onto the transient absorption on a time scale of nano- to microseconds under illumination of continuous white light to discuss the bimolecular recombination of dissociated charges under the device operating condition. Under the white bias light of 100 mW cm^{-2} (1 sun), the steady-state density of charge carriers n_{bias} is as high as in the order of 10^{16} cm^{-3} ,^{32,33} which is much larger than the transient density of charge carriers induced by weak laser pulses $\Delta n(t)$. Thus, the decay dynamics of the laser-induced carrier density $\Delta n(t)$ is followed by a pseudo-first-order kinetics. **Figure 6** shows the decay dynamics of N-P7 polarons in N-P7/PCBM blends under the continuous white bias light. The laser-induced charge carrier density $\Delta n(t)$ was estimated as described in the Supporting Information. The decay dynamics was well fitted by a single exponential function with a lifetime of $3.4 \text{ } \mu\text{s}$ under a weak laser excitation

whereas it was not followed by an exponential function under a strong excitation. Details will be discussed in the following section.

4. Discussion

We discuss here the efficiency of each photovoltaic conversion process after the photon absorption individually: the efficiency of the exciton diffusion to a donor/acceptor interface η_{ED} , the efficiency of the charge transfer at the donor/acceptor interface η_{CT} , the efficiency of the charge dissociation into free carriers at the donor/acceptor interface η_{CD} , and the efficiency of the charge collection to each electrode η_{CC} .

First, we focus on the charge generation in N-P7/PCBM blends. As shown in Figure 4, 80% of charge carriers are formed within an excitation pulse duration (0.1 ps) and the other 20% are formed with a time constant of 0.3 ps. Such a rapid charge generation has been observed for other amorphous blend films.^{25,34} As reported previously, fluorene-based copolymers form amorphous films, in which PCBM molecules are dispersed in polymer domains as minority component.^{35,36} On the basis of the static quenching analysis, the quenching radius of PCBM molecules R_q is estimated to be as short as ~ 2 nm (see the Supporting Information), which is a typical reaction radius for electron transfer in organic materials.³⁷ This finding shows that 80% of N-P7 singlet excitons are located within ~ 2 nm from PCBM molecules in the blend films, suggesting homogeneous dispersion of PCBM molecules. More importantly, the charge generation is much more rapid than the lifetime of the singlet exciton that was estimated by the fluorescence lifetime measurement of N-P7 neat films (1.9 ns). Therefore, we can safely conclude that the exciton diffusion efficiency η_{ED} to and the charge transfer efficiency η_{CT} at a donor/acceptor interface are unity in N-P7/PCBM blend films.

We move onto the charge recombination dynamics on a time scale of sub-nanoseconds. It is of importance to analyze the recombination dynamics to assign the charge separated state because there is no spectral difference between a pair of polymer polaron and PCBM radical anion coulombically bound at the heterojunction (interfacial CT state) and dissociated polymer polaron and PCBM radical anion in amorphous polymer/PCBM blends as reported previously.^{25,34,38} As mentioned before, the decay dynamics of N-P7 polaron is in good agreement with the recovery dynamics of the photobleaching and independent of the excitation intensity, suggesting the monomolecular recombination to the ground state. Furthermore, this decay constant $\tau_m = 2.2$ ns is also in good agreement with the lifetime of the interfacial CT state emission at 950 nm observed for the same blend films as shown in the Figure 2 (2.2 ns). We therefore ascribe the polaron band at around 850 nm to N-P7 polaron that is coulombically bound with PCBM radical anion to form the interfacial CT state. From the fitting parameters, the charge dissociation efficiency η_{CD} under the open-circuit condition is estimated to be 0.65, and the charge dissociation and recombination rates at the zero-field are estimated to be $k_{dis} = 2.9 \times 10^8$ s⁻¹ and $k_{rec} = 1.6 \times 10^8$ s⁻¹, respectively. It is noteworthy that these rate constants are independent of the film thickness. This charge dissociation efficiency ($\eta_{CD} = 0.65$) is larger than that for amorphous RRa-P3HT/PCBM (0.31),²⁵ is comparable to that for amorphous PCPDTBT/PCBM (0.70),³⁴ but is lower than that for crystalline RR-P3HT/PCBM blend films (0.80 – 0.90).²⁵

---<< Figure 7 >>---

Next, we discuss the charge collection efficiency η_{CC} on the basis of the lifetime of dissociated charge carriers under the white bias illumination. The charge carrier density was reported to be typically of the order of $\sim 10^{16}$ cm⁻³ at 1 sun ($n_{bias} = 3 \times 10^{16}$ cm⁻³ for RR-P3HT/PCBM, $n_{bias} = 2$

$\times 10^{16} \text{ cm}^{-3}$ for Si-PCPDTBT/PCBM, and $n_{\text{bias}} = 5 \times 10^{16} \text{ cm}^{-3}$ for PCDTBT/PCBM blend films).^{32,33} As shown in Figure 6, weakly laser-induced charge carriers ($\Delta n(t) < 10^{16} \text{ cm}^{-3}$) decay exponentially with a lifetime of $\tau_c = 3.4 \text{ }\mu\text{s}$ under the white bias illumination at 1 sun. Consequently, the pseudo-first-order lifetime can be considered as the charge carrier lifetime at $n \approx 10^{16} \text{ cm}^{-3}$ under the device operating condition. The charge collection efficiency can be estimated with the charge carrier lifetime $\tau_c = 3.4 \text{ }\mu\text{s}$ by the Hecht equation

$$\eta_{\text{CC}} = \frac{\mu \tau_c V_b}{dd_c} \left\{ 1 - \exp \left[- \frac{dd_c}{\mu \tau_c V_b} \right] \right\} \quad (1)$$

where d is the thickness of the active layer, d_c is the average collection length ($= d/2$), V_b is the internal bias voltage at the short circuit ($\sim V_{\text{OC}}$), and μ is the charge mobility.³⁹⁻⁴² **Figure 7** shows the voltage dependence of the charge collection efficiency η_{CC} calculated by eq 1. Note that the charge carrier lifetime τ_c is set as a constant value because the carrier density dependence of τ_c is negligibly small ($\tau_c = 5 \text{ }\mu\text{s}$ at 0.1 sun, see the Supporting Information), and μ is set to the hole mobility ($\mu = 2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), which is slower than the electron mobility ($\sim 5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$),^{43,44} because the charge collection is limited by the slower charge. As shown in the figure, η_{CC} remains high with increasing applied voltage and then steeply drops at $\sim V_{\text{OC}}$ for the thin devices ($d = 90$ and 140 nm) whereas it gradually drops with increasing applied voltage for the thick device ($d = 220 \text{ nm}$). As a result, $\eta_{\text{CC}}(0)$ was estimated to be 0.96 ($d = 90 \text{ nm}$), 0.90 ($d = 140 \text{ nm}$), and 0.79 ($d = 220 \text{ nm}$) under the short-circuit condition. For comparison, $\eta_{\text{CC}}(0)$ of RR-P3HT/PCBM solar cells is as high as 0.96 even for $d = 200 \text{ nm}$ because of a long charge carrier lifetime of $\tau_c = 20 \text{ }\mu\text{s}$ due to the reduced bimolecular recombination³⁴ (see the Supporting Information). The difference in the charge carrier lifetime is ascribed to the formation of the interfacial CT state in amorphous N-P7/PCBM blends as reported previously.³⁴ We therefore conclude that the primary origin of the lower η_{CC} in N-P7/PCBM thick devices is the shorter

charge carrier lifetime τ_c because the charge mobility in N-P7/PCBM is similar to that in P3HT/PCBM blends.

---<< Figure 8 >>---

---<< Table 2 >>---

We further discuss the voltage-dependent charge dissociation efficiency $\eta_{CD}(V)$ on the basis of the voltage-dependent charge collection efficiency $\eta_{CC}(V)$ and the voltage-dependent current density in the dark $J_d(V)$ and under the illumination $J(V)$. The overall voltage-dependent photoinduced current $J_{ph}(V)$ is described as follows:

$$J_{ph}(V) = J_d(V) - J(V) = q\phi[\eta_A\eta_{ED}\eta_{CT}\eta_{CD}(V)\eta_{CC}(V)] \quad (2)$$

where $J(V)$ and $J_d(V)$ are the current density of the solar cell at voltage V under illumination and in the dark, respectively, q is the elementary charge, ϕ is the incident photon flux on the device, and $\eta_{CD}(V)$ and $\eta_{CC}(V)$ is the voltage-dependent CT state dissociation and charge collection efficiency, respectively. On the other hand, the EQE and IQE are defined by the product of these efficiencies under the short-circuit condition:

$$\text{EQE} = \eta_A \eta_{ED} \eta_{CT} \eta_{CD}(0) \eta_{CC}(0) = \eta_A \text{IQE} \quad (3)$$

Thus, the voltage dependence of the CT state dissociation efficiency $\eta_{CD}(V)$ is given by eq 4 because $\eta_{ED} = \eta_{CT} = 1$ as mentioned above.

$$\eta_{CD}(V) = \text{IQE} \frac{1}{\eta_{CC}(V)} \frac{J_{ph}(V)}{J_{ph}(0)} \quad (4)$$

Here, the IQE is estimated as an open parameter so that the extrapolated value of $\eta_{CD}(V)$ to $V \rightarrow V_{OC}$ coincides with $\eta_{CD} = 0.65$ that was evaluated from the transient analysis. Note that these IQE values are roughly equal to EQE/η_A at 400 nm (see the Supporting Information). As shown

in Figure 7, η_{CD} is dependent on the applied voltage for the thin devices ($d = 90$ and 140 nm) whereas η_{CD} is independent of the applied voltage for the thick device ($d = 220$ nm). Note that these IQE values are roughly equal to $\text{EQE}/\eta_{\text{A}}$ at 400 nm (see the Supporting Information). Interestingly, plots of $\eta_{\text{CD}}(V)$ against the electric field strength $|F|$ follows a unique master curve for all the N-P7/PCBM devices as shown in **Figure 8**, suggesting that the voltage dependence of $\eta_{\text{CD}}(V)$ is due to the electric field strength $|F|$ in the device. The electric field in the thin devices is as strong as several MV m^{-1} under the short-circuit conditions, and hence assist the dissociation from the CT state to give η_{CD} higher than that under the open-circuit condition. Such field-assisted charge dissociation has been reported previously.^{28,45} We therefore conclude that the dissociation from the interfacial CT state in the thin devices is enhanced by the electric field under the short-circuit condition. As summarized in **Table 2**, the products of each efficiency $\Pi\eta_i$ are close to the corresponding EQE observed, suggesting that each efficiency evaluated from the transient absorption study is closely related to the device performance. On the basis of these analyses, we conclude that the geminate recombination is the primary loss process in all the devices though the CT dissociation is slightly assisted by the electric field in the thin devices, and that the bimolecular recombination is additional loss process in the thick device.

Finally, we discuss the efficient charge dissociation shown in Figure 8. The charge dissociation efficiency is estimated by eqs 5–7 based on the Onsager–Braun model.²⁸

$$\eta_{\text{CD}} = \frac{k_{\text{dis}}(F)}{k_{\text{dis}}(F) + k_{\text{rec}}} \quad (5)$$

$$k_{\text{dis}}(F) = \frac{3q\mu}{4\pi\epsilon\epsilon_0 r_{\text{eh}}^3} \exp\left(-\frac{E_{\text{b}}}{k_{\text{B}}T}\right) \frac{J_1\left(2\sqrt{-2b(F)}\right)}{\sqrt{-2b(F)}} \quad (6)$$

$$b(F) = \frac{e^3 F}{8\pi\epsilon\epsilon_0 (k_{\text{B}}T)^2} \quad (7)$$

where μ is the charge mobility, q is the elementary charge, $\epsilon\epsilon_0$ is the permittivity of the active layer, r_{eh} is the initial electron–hole separation distance, E_{b} is the Coulombic binding energy ($= e^2/(4\pi\epsilon\epsilon_0 r_{\text{eh}})$), k_{B} is the Boltzmann constant, and J_1 is the Bessel function of the first kind of order one. Here, k_{rec} is set to $k_{\text{rec}} = 1.6 \times 10^8 \text{ s}^{-1}$, which is evaluated by the spectroscopic analysis as mentioned above, and μ is set to $\mu = 5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is an electron mobility reported for PCBM films,^{43,44} assuming that the charge dissociation is controlled by the faster charge. As shown by the broken lines in the figure, the efficient charge dissociation can be roughly reproduced with $r_{\text{eh}} = 3.5 \text{ nm}$ although it cannot be reproduced with $r_{\text{eh}} = 1 \text{ nm}$ that is a typical separation distance of contact ion pairs. Note that it would be reproduced with $r_{\text{eh}} = 2.5 \text{ nm}$ if the mobility is set to $\mu = 1 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ reported as a local charge mobility.^{46,47} In any case, such long electron–hole distance suggests the charge delocalization in the interfacial CT state. This is in good agreement with the correlation between singlet exciton size and charge dissociation efficiency as we have reported.³⁴ Furthermore, efficient charge dissociation has been explained by Monte Carlo simulation considering a charge delocalization along conjugated polymer chains.⁴⁸ Therefore, these findings suggest that the charge delocalization play important roles on efficient charge dissociation in amorphous polymer solar cells.

5. Conclusion

The charge generation and recombination dynamics were studied for N-P7/PCBM amorphous blend films. Upon the photoexcitation, N-P7 singlet excitons rapidly decay and N-P7 polarons are promptly generated with 100% efficiency in a picosecond. Thus, the exciton diffusion and charge transfer efficiencies are estimated to be $\eta_{\text{ED}} = 1$ and $\eta_{\text{CT}} = 1$, respectively. This is because PCBM molecules are homogeneously dispersed in amorphous polymer films. The N-P7

polarons observed on a time scale of sub-nanoseconds are ascribed to the interfacial CT state, which is a coulombically bound pair of N-P7 polaron and PCBM radical anion, because the monomolecular decay constant is consistent with the lifetime of the CT emission. In nanoseconds, the majority of N-P7 polarons in the CT state are dissociated into free carriers and the rest of them recombine to the ground state. The dissociation efficiency η_{CD} is estimated to be 0.65 under the open-circuit condition and is slightly enhanced to 0.7 – 0.8 under the short-circuit condition. This dissociation efficiency is comparable to that of amorphous PCPDTBT/PCBM solar cells but lower than that of crystalline RR-P3HT/PCBM solar cells. This finding suggests that the charge dissociation efficiency in blends of amorphous polymer and PCBM is limited by the formation of the interfacial CT state as reported previously. Nonetheless, the charge dissociation efficiency is still high for the contact ion pair. The relatively high charge dissociation efficiency can be well reproduced by the Onsager–Braun model considering charge delocalization. This result suggests that the charge delocalization play important roles on efficient charge dissociation in amorphous polymer solar cells. The charge collection efficiency η_{CC} is as high as 0.96 in the N-P7/PCBM thin devices. However, it drops to 0.79 for the N-P7/PCBM thick device ($d = 220$ nm) whereas it is still as high as 0.96 for P3HT/PCBM solar cells ($d = 220$ nm). This finding suggests that the bimolecular recombination loss is not negligible in the thick amorphous device because the charge carrier lifetime in N-P7/PCBM (3.4 μ s) is shorter than that in P3HT/PCBM (20 μ s). In conclusion, the relatively high performance of amorphous N-P7/PCBM solar cells is primarily due to the efficient charge dissociation, which is slightly assisted by the internal field and primarily enhanced by the charge delocalization, although there is still room to improve the limited dissociation efficiency and the short charge carrier lifetime.

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Supporting Information Available: Chemical Structures of materials, measurements on hole mobility, AFM images, diode parameters of N-P7/PCBM blend films, and more detailed information on transient absorption and charge carrier lifetime measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

REFERENCES

- (1) Brabec, C. J.; Gowrisanker, S.; Halls, J. J. M.; Laird, D.; Jia, S.; Williams, S. P. Polymer-Fullerene Bulk-Heterojunction Solar Cells. *Adv. Mater.* **2010**, *22*, 3839–3856.
- (2) Heeger, A. J. Semiconducting Polymers: the Third Generation. *Chem. Soc. Rev.* **2010**, *39*, 2354–2371.
- (3) Ohkita, H.; Ito, S. Transient Absorption Spectroscopy of Polymer-Based Thin-Film Solar Cells. *Polymer* **2011**, *52*, 4397–4417.
- (4) Beaujuge, P. M.; Fréchet, J. M. J. Molecular Design and Ordering Effects in π -Functional Materials for Transistor and Solar Cell Applications. *J. Am. Chem. Soc.* **2011**, *133*, 20009–20029.
- (5) Green, M. A.; Emery, K.; Hishikawa, Y.; Warta, W.; Dunlop, E. D. Solar Cell Efficiency Tables (version 40). *Prog. Photovolt. Res. Appl.* **2012**, *20*, 606–614.
- (6) Peet, J.; Kim, J. Y.; Coates, N. E.; Ma, W. L.; Moses, D.; Heeger, A. J.; Bazan, G. C. Efficiency Enhancement in Low-Bandgap Polymer Solar Cells by Processing with Alkane Dithiols. *Nat. Mater.* **2007**, *6*, 497–500.
- (7) Bundgaard, E.; Krebs, F. C. Low Band Gap Polymers for Organic Photovoltaics. *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 954–985.
- (8) Liang, Y.; Yu, L. Development of Semiconducting Polymers for Solar Energy Harvesting. *Polym. Rev.* **2010**, *50*, 454–473.
- (9) Honda, S.; Nogami, T.; Ohkita, H.; Benten, H.; Ito, S. Improvement of the Light-Harvesting Efficiency in Polymer/Fullerene Bulk Heterojunction Solar Cells by Interfacial Dye Modification. *ACS Appl. Mater. Interfaces* **2009**, *1*, 804–810.

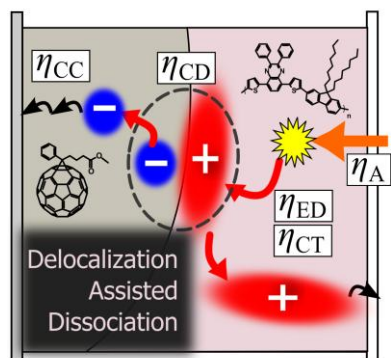
- (10) Honda, S.; Ohkita, H.; Benten, H.; Ito, S. Multi-Colored Dye Sensitization of Polymer/Fullerene Bulk Heterojunction Solar Cells. *Chem. Commun.* **2010**, *46*, 6596–6598.
- (11) Honda, S.; Ohkita, H.; Benten, H.; Ito, S. Selective Dye Loading at the Heterojunction in Polymer/Fullerene Solar Cells. *Adv. Energy Mater.* **2011**, *1*, 588–598.
- (12) Honda, S.; Yokoya, S.; Ohkita, H.; Benten, H.; Ito, S. Light-Harvesting Mechanism in Polymer/Fullerene/Dye Ternary Blends Studied by Transient Absorption Spectroscopy. *J. Phys. Chem. C* **2011**, 11306–11317.
- (13) Kitazawa, D.; Watanabe, N.; Yamamoto, S.; Tsukamoto, J. Quinoxaline-Based π -Conjugated Donor Polymer for Highly Efficient Organic Thin-Film Solar Cells. *Appl. Phys. Lett.* **2009**, *95*, 053701.
- (14) Kitazawa, D.; Watanabe, N.; Yamamoto, S.; Tsukamoto, J. Quinoxaline-Based Donor Polymers for Organic Solar Cells *J. Photopolym. Sci. Technol.* **2010**, *23*, 293–296.
- (15) Park, S. H.; Roy, A.; Beaupré, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J. Bulk Heterojunction Solar Cells with Internal Quantum Efficiency Approaching 100%. *Nat. Photonics* **2009**, *3*, 297–303.
- (16) Yuan, J.; Zhai, Z.; Dong, H.; Li, J.; Jiang, Z.; Li, Y.; Ma, W. Efficient Polymer Solar Cells with a High Open Circuit Voltage of 1 Volt. *Adv. Funct. Mater.* **2012**, DOI: 10.1002/adfm.201201535.
- (17) Svensson, M.; Zhang, F.; Veenstra, S. C.; Verhees, W. J. H.; Hummelen, J. C.; Kroon, J. M.; Inganäs, O.; Andersson, M. R. High-Performance Polymer Solar Cells of an Alternating Polyfluorene Copolymer and a Fullerene Derivative. *Adv. Mater.* **2003**, *15*, 988–991.

- (18) Inganäs, O.; Zhang, F.; Andersson, M. R. Alternating Polyfluorenes Collect Solar Light in Polymer Photovoltaics. *Acc. Chem. Res.* **2009**, *42*, 1731–1739.
- (19) Chen, J.; Cao, Y. Development of Novel Conjugated Donor Polymers for High-Efficiency Bulk-Heterojunction Photovoltaic Devices. *Acc. Chem. Res.* **2009**, *42*, 1709–1718.
- (20) Zhou, E.; Cong, J.; Tajima, K.; Hashimoto, K. Synthesis and Photovoltaic Properties of Donor–Acceptor Copolymers Based on 5,8-Dithien-2-yl-2,3-diphenylquinoxaline. *Chem. Mater.* **2010**, *22*, 4890–4895.
- (21) Moulé, A. J.; Meerholz, K. Controlling Morphology in Polymer–Fullerene Mixtures. *Adv. Mater.* **2008**, *20*, 240–245.
- (22) Jo, J.; Kim, S.-S.; Na, S.-I.; Yu, B.-K.; Kim, D.-Y. Time-Dependent Morphology Evolution by Annealing Processes on Polymer:Fullerene Blend Solar Cells. *Adv. Funct. Mater.* **2009**, *19*, 866–874.
- (23) Guo, J.; Ohkita, H.; Benten, H.; Ito, S. Charge Generation and Recombination Dynamics in Poly(3-hexylthiophene)/Fullerene Blend Films with Different Regioregularities and Morphologies. *J. Am. Chem. Soc.* **2010**, *132*, 6154–6164.
- (24) Wang, C.; Dong, H.; Hu, W.; Liu, Y.; Zhu, D. Semiconducting π -Conjugated Systems in Field-Effect Transistors: A Material Odyssey of Organic Electronics. *Chem. Rev.* **2012**, *112*, 2208–2267.
- (25) Liang, Y.; Xu, Z.; Xia, J.; Tsai, S.-T.; Wu, Y.; Li, G.; Ray, C.; Yu, L. For the Bright Future—Bulk Heterojunction Polymer Solar Cells with Power Conversion Efficiency of 7.4%. *Adv. Mater.* **2010**, *22*, E135–138.

- (26) Osaka, I.; Saito, M.; Mori, H.; Koganezawa, T.; Takimiya, K. Drastic Change of Molecular Orientation in a Thiazolothiazole Copolymer by Molecular-Weight Control and Blending with PC₆₁BM Leads to High Efficiencies in Solar Cells. *Adv. Mater.* **2011**, 425–430.
- (27) Wang, E.; Hou, L.; Wang, Z.; Hellström, S.; Zhang, F.; Inganäs, O.; Andersson, M. R. An Easily Synthesized Blue Polymer for High-Performance Polymer Solar Cells. *Adv. Mater.* **2010**, 22, 5240–5244.
- (28) Braun, C. C. L. Electric Field Assisted Dissociation of Charge Transfer States as a Mechanism of Photocarrier Production. *J. Chem. Phys.* **1984**, 80, 4157–4161.
- (29) Veldman, D.; İpek, Ö.; Meskers, S. C. J.; Sweelssen, J.; Koetse, M. M.; Veenstra, S. C.; Kroon, J. M.; van Bavel, S. S.; Loos, J.; Janssen, R. A. J. Compositional and Electric Field Dependence of the Dissociation of Charge Transfer Excitons in Alternating Polyfluorene Copolymer/Fullerene Blends. *J. Am. Chem. Soc.* **2008**, 130, 7721–7735.
- (30) Veldman, D.; Meskers, S. C. J.; Janssen, R. A. J. The Energy of Charge-Transfer States in Electron Donor-Acceptor Blends: Insight into the Energy Losses in Organic Solar Cells. *Adv. Funct. Mater.* **2009**, 19, 1939–1948.
- (31) Yamamoto, S.; Ohkita, H.; Benten, H.; Ito, S. Formation Mechanism of Fullerene Cation in Bulk Heterojunction Polymer Solar Cells. *Adv. Funct. Mater.* **2012**, 22, 3075–3082.
- (32) Maurano, A.; Hamilton, R.; Shuttle, C. G.; Ballantyne, A. M.; Nelson, J.; Zhang, W.; McCulloch, I.; Azimi, H.; Morana, M.; Brabec, C. J. *et al.* Recombination Dynamics as a Key Determinant of Open Circuit Voltage in Organic Bulk Heterojunction Solar Cells: A Comparison of Four Different Donor Polymers. *Adv. Mater.* **2010**, 22, 4987–4992.

- (33) Credgington, D.; Durrant, J. R. Insights from Transient Optoelectronic Analyses on the Open-Circuit Voltage of Organic Solar Cells. *J. Phys. Chem. Lett.* **2012**, *11*, 1465–1478.
- (34) Yamamoto, S.; Ohkita, H.; Benten, H.; Ito, S. Role of Interfacial Charge Transfer State in Charge Generation and Recombination in Low-Bandgap Polymer Solar Cell. *J. Phys. Chem. C* **2012**, *116*, 14804–14810.
- (35) Li, Y.; Ding, J.; Day, M.; Tao, Y.; Lu, J.; D'iorio, M. Synthesis and Properties of Random and Alternating Fluorene/Carbazole Copolymers for Use in Blue Light-Emitting Devices. *Chem. Mater.* **2004**, *16*, 2165–2173.
- (36) Keivanidis, P. E.; Howard, I. A.; Friend, R. H. Intermolecular Interactions of Perylene diimides in Photovoltaic Blends of Fluorene Copolymers: Disorder Effects on Photophysical Properties, Film Morphology and Device Efficiency. *Adv. Funct. Mater.* **2008**, *18*, 3189–3202.
- (37) Miller, J. R.; Peeples, J.; Schmitt, M. J.; Closs, G. L. Long-Distance Fluorescence Quenching by Electron Transfer in Rigid Solutions. *J. Am. Chem. Soc.* **1982**, *104*, 6488–6493.
- (38) Etzold, F.; Howard, I. A.; Forler, N.; Cho, D. M.; Meister, M.; Mangold, H.; Shu, J.; Hansen, M. R.; Mullen, K.; Laquai, F. The Effect of Solvent Additives on Morphology and Excited State Dynamics in PCPDTBT:PCBM Photovoltaic Blends. *J. Am. Chem. Soc.* **2012**, *134*, 10569–10583.
- (39) Hecht, K. Zum Mechanismus des Lichtelektrischen Primärstromes in Isolierenden Kristallen. *Z. Phys.* **1932**, *77*, 235–245.
- (40) Street, R. A. *Hydrogenated Amorphous Silicon (Cambridge solid state science series)*; Cambridge University Press: Cambridge, U.K., 2005.

- (41) Cowan, S. R.; Roy, A.; Heeger, A. J. Recombination in Polymer-Fullerene Bulk Heterojunction Solar Cells. *Phys. Rev. B* **2010**, *82*, 245207.
- (42) Baumann, A.; Lorrmann, J.; Rauh, D.; Deibel, C.; Dyakonov, V. A New Approach for Probing the Mobility and Lifetime of Photogenerated Charge Carriers in Organic Solar Cells Under Real Operating Conditions. *Adv. Mater.* **2012**, *24*, 4381–4386.
- (43) Mihailetschi, V. D.; van Duren, J. K. J.; Blom, P. W. M.; Hummelen, J. C.; Janssen, R. a. J.; Kroon, J. M.; Rispen, M. T.; Verhees, W. J. H.; Wienk, M. M. Electron Transport in a Methanofullerene *Adv. Funct. Mater.* **2003**, *13*, 43–46.
- (44) Tuladhar, S. M. M.; Poplavskyy, D.; Choulis, S. A. a.; Durrant, J. R. R.; Bradley, D. D. C. D. C.; Nelson, J. Ambipolar Charge Transport in Films of Methanofullerene and Poly (phenylenevinylene)/Methanofullerene Blends. *Adv. Funct. Mater.* **2005**, *15*, 1171–1182.
- (45) Nenashev, A.; Baranovskii, S.; Wiemer, M.; Jansson, F.; Österbacka, R.; Dvurechenskii, A.; Gebhard, F. Theory of Exciton Dissociation at the Interface between a Conjugated Polymer and an Electron Acceptor. *Phys. Rev. B* **2011**, *84*, 035210.
- (46) Savenije, T.; Kroeze, J.; Wienk, M.; Kroon, J.; Warman, Mobility and Decay Kinetics of Charge Carriers in Photoexcited PCBM/PPV Blends. *J. Phys. Rev. B* **2004**, *69*, 155205.
- (47) de Haas, M. P.; Warman, J. M.; Anthopoulos, T. D.; de Leeuw, D. M. The Mobility and Decay Kinetics of Charge Carriers in Pulse-Ionized Microcrystalline PCBM Powder. *Adv. Funct. Mater.* **2006**, *16*, 2274–2280.
- (48) Deibel, C.; Strobel, T.; Dyakonov, V. Origin of the Efficient Polaron-Pair Dissociation in Polymer-Fullerene Blends. *Phys. Rev. Lett.* **2009**, *103*, 036402.



FIGURES

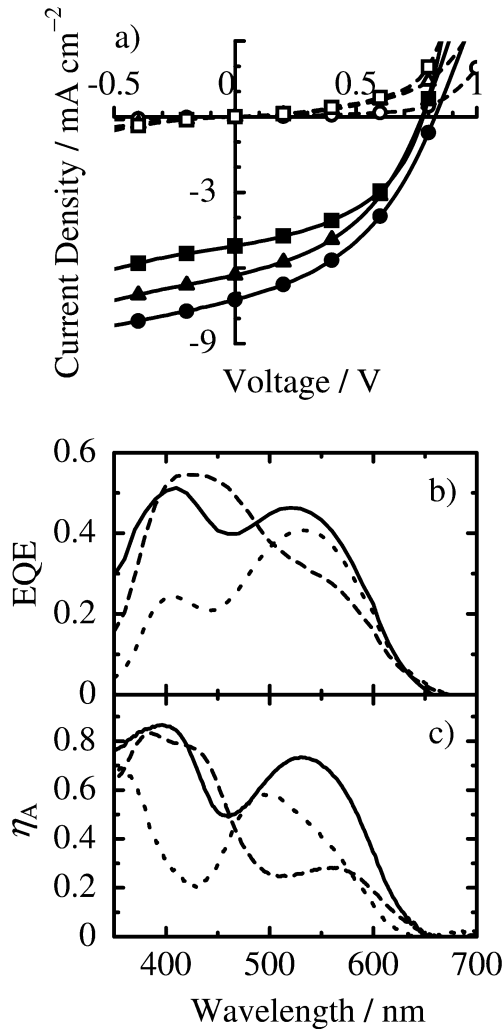


Figure 1. a) J - V characteristics of N-P7/PCBM solar cells with active layer of 90 (squares), 140 (triangles), and 220 nm (circles) thick. The solid and broken lines represent J - V characteristics under AM1.5G simulated solar illumination at 100 mW cm^{-2} and in the dark, respectively. b) EQE spectra of N-P7/PCBM solar cells with active layer of 90 (dotted line), 140 (broken line), and 220 nm (solid line) thick. c) Absorption spectra measured by reflection mode of ITO|PEDOT:PSS (40 nm)|N-P7/PCBM|Al (70 nm) devices with an active layer of 90 (dotted line), 140 (broken line), and 220 nm (solid line) in thick.

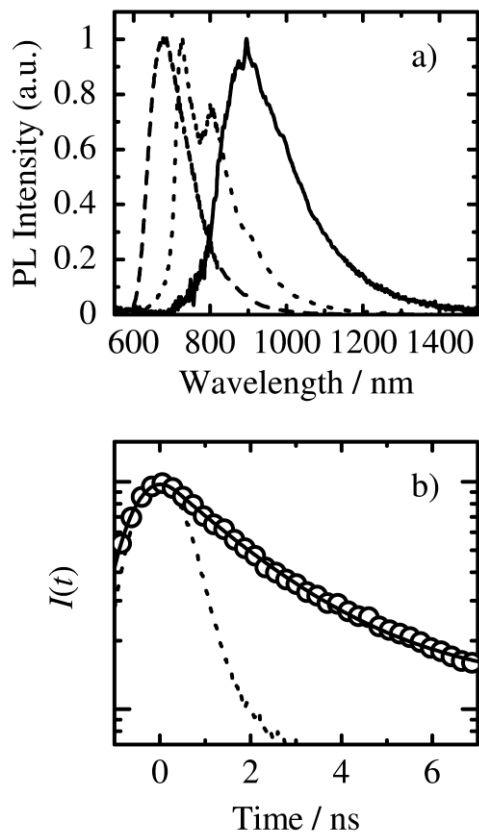


Figure 2. a) Fluorescence spectra of N-P7 neat films (broken line), PCBM neat films (dotted line) and an N-P7/PCBM blend film (solid line) on excitation at 407 nm. b) The emission decay kinetics monitored at 950 nm on excitation at 407 nm (open circles). The solid and dotted line shows the fitting line with the time constant of $\tau = 2.2$ ns and instrumental response function, respectively.

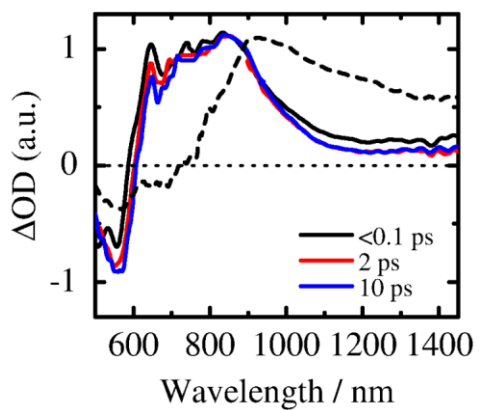


Figure 3. Normalized transient absorption spectra of N-P7/PCBM blend films. The excitation intensity was set at $3 \mu\text{J cm}^{-2}$ at 400 nm. The delay times are <0.1 ps (black), 2 ps (red), and 10 ps (blue). The broken line shows the transient spectra of the N-P7 neat film at <0.1 ps. The dotted line shows the baseline.

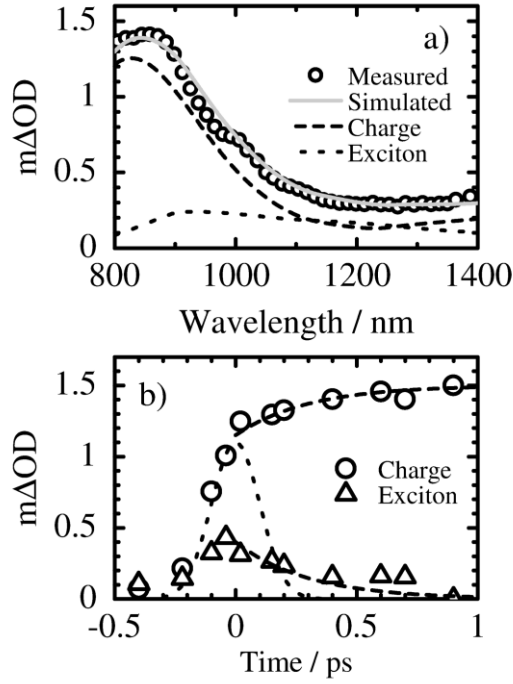


Figure 4. a) Transient absorption spectrum at 0.2 ps of the N-P7/PCBM blend film (open circles). The gray solid line shows the spectrum simulated by the sum of the absorption spectrum at <0.1 ps of N-P7 neat films (N-P7 singlet exciton, dotted line) and the absorption spectrum at 10 ps of the blend film (N-P7 polaron and PCBM radical anion, broken line). b) The time evolution of N-P7 singlet exciton (triangles) and charge carriers (circles) in the N-P7/PCBM blend film. The broken lines show the fitting lines by exponential functions: $A[1 - \exp(-t/\tau_r)] + B$ for the rise and $C \exp(-t/\tau_d)$ for the decay kinetics with $\tau_r = \tau_d = 0.3$ ps and $A : B = 20 : 80$. The dotted line shows the instrument response function.

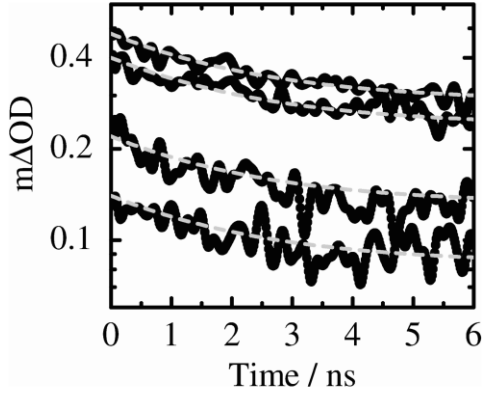


Figure 5. Semi-log plots of the transient decay of N-P7 polaron in an N-P7/PCBM blend film probed at 900 nm. The laser intensities at 400 nm are 1, 2, 3, and 4 $\mu\text{J cm}^{-2}$ from bottom to top. The broken lines show the fitting by an exponential function with a constant fraction: $\Delta\text{OD} = A \exp(-t/\tau_m) + B$ with $\tau_m = 2.2$ ns and $A : B = 35 : 65$.

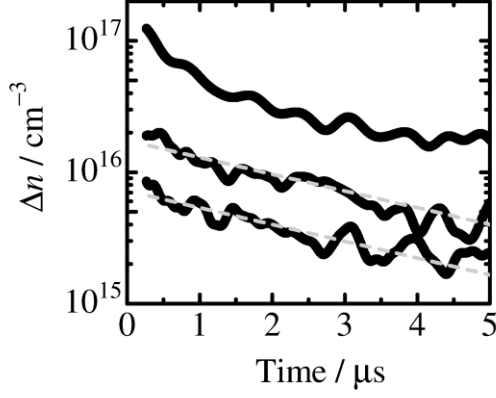


Figure 6. Time evolution of the charge carrier density in N-P7/PCBM blend films under illumination of continuous white light of 100 mW cm^{-2} . The laser intensities at 400 nm are 0.25, 0.5, and $7.5 \text{ } \mu\text{J cm}^{-2}$ from bottom to top. The gray broken lines show the fitting curves by an exponential function: $\Delta n(t) = \Delta n_0 \exp(-t/\tau)$ with $\tau = 3.4 \text{ } \mu\text{s}$. The Δn_0 of upper and lower gray lines are $\Delta n_0 = 1.7 \times 10^{16} \text{ cm}^{-3}$ and $7.5 \times 10^{15} \text{ cm}^{-3}$, respectively.

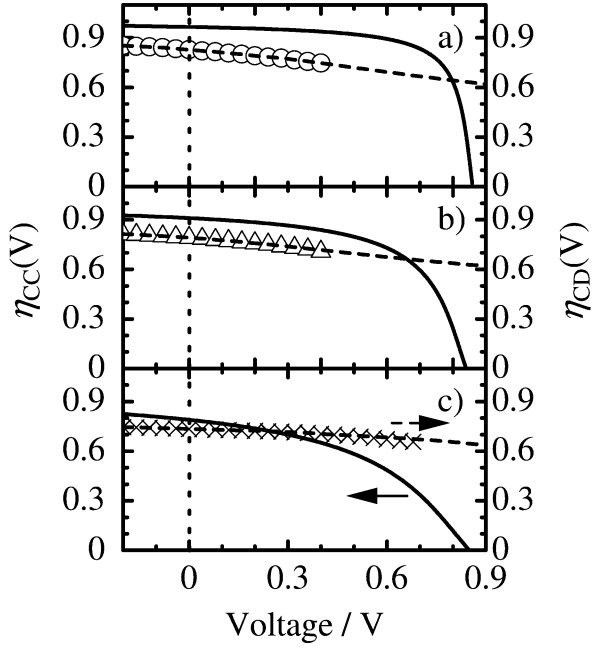


Figure 7. Charge collection efficiency $\eta_{cc}(V)$ (solid lines) and charge dissociation efficiency $\eta_{cd}(V)$ (symbols) of N-P7/PCBM solar cells devices with an active layer of (a) 90, (b) 140, and (c) 220 nm in thick plotted against the applied voltage. The broken lines show the extrapolations of $\eta_{cd}(V)$ to the open-circuit voltage.

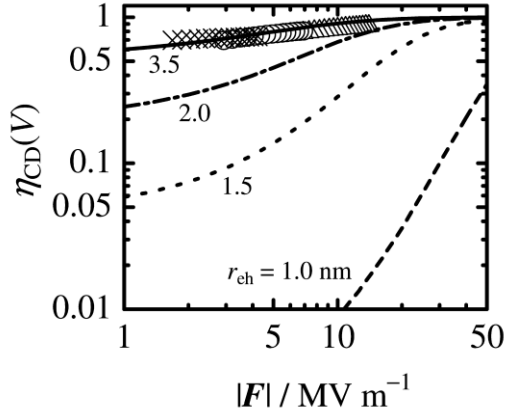


Figure 8. Dependence of the charge dissociation efficiency $\eta_{\text{CD}}(V)$ on the electric field strength $|F|$. The open triangles, open circles, and crosses show $\eta_{\text{CD}}(V)$ of the devices with an active layer of 90, 140, and 220 nm in thickness, respectively. The broken lines show the charge dissociation efficiency estimated by the Onsager–Braun model with a charge pair distance of $r_{\text{ch}} = 1.0$ (broken line), 1.5 (dotted line), 2.0 (dashed-dotted line), and 3.5 nm (solid line). The other fixed parameters are $\mu = 5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $k_{\text{rec}} = 1.6 \times 10^8 \text{ s}^{-1}$, $\varepsilon = 3.7$, and $T = 300 \text{ K}$.

TABLES

Table 1. The device parameters of N-P7/PCBM solar cells.

thickness / nm	$J_{SC} / \text{mA cm}^{-2}$	V_{OC} / V	FF	PCE / %
90	5.1	0.77	0.47	1.8
140	6.3	0.78	0.42	2.1
220	7.3	0.83	0.41	2.5

Table 2. The photovoltaic conversion efficiency of N-P7/PCBM blends under the short-circuit condition.

Thickne ss / nm	η_A	η_{ED}	η_{CT}	η_{CD}	η_{CC}	$\Pi\eta_i^a$	EQE
90	0.35	1	1	0.80	0.96	0.27	0.25
140	0.80	1	1	0.75	0.90	0.54	0.53
220	0.85	1	1	0.70	0.79	0.47	0.50

^a $\Pi\eta_i = \eta_A \eta_{ED} \eta_{CT} \eta_{CD} \eta_{CC}$