Nongeminate Recombination in All Polymer Solar Cells with Different Crystallinities

Hyung Do Kim,^{*} Yuya Horiuchi, Shinta Iwasaki, Tomohiro Fukuhara and Hideo Ohkita^{*}

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo, Kyoto 615-8510, Japan

Corresponding Authors Footnote.

Hyung Do Kim

Tel.: +81 75 383 2614

Fax: +81 75 383 2617

Email: hyungdokim@photo.polym.kyoto-u.ac.jp

Hideo Ohkita

Tel.: +81 75 383 2612

Fax: +81 75 383 2617

Email: ohkita@photo.polym.kyoto-u.ac.jp

Abstract

It is one of the most challenging issues facing organic photovoltaic community to realize a high fill factor (FF) even with thick active layers. This is because the thick active layer is beneficial for photon absorption but makes charge collection difficult, which is primarily restricted by nongeminate recombination in solar cells. In this work, we have studied nongeminate recombination in four kinds of polymer solar cells based on blends of donor conjugated polymers with different crystallinities and acceptor conjugated polymers with a naphthalene diimide unit by using transient photovoltage and photocurrent techniques. As a result, we find that nongeminate recombination is considerably suppressed with increasing degree of crystallinity of donor polymers, leading to a high FF of more than 0.6 even with an active layer thickness of 300 nm. The origin of such a phenomenon is further discussed in terms of variations in the states of mixed phases with a cascaded energy structure between crystalline domains and amorphous domains evaluated by conductive atomic force microscopy.

Keywords: all polymer solar cells, thick active layer, fill factor, nongeminate recombination, cascaded energy structure

1. Introduction

All polymer solar cells based on blends of a donor conjugated polymer and an acceptor conjugated polymer have recently attracted tremendous attention because of their outstanding potential merits over conventional fullerene-based polymer solar cells, such as excellent mechanical durability and stretchability as well as tunability of optical bandgap with a high absorption coefficient.^{1–5} The power conversion efficiency (PCE) of these solar cells has experienced a sharp improvement in the past few years and currently exceeded about 16% for single junction solar cells.⁵ This value is higher than that of fullerene-based polymer solar cells or efficient inorganic solar cells.^{6–9}

To further increase device performance for all polymer solar cells toward commercialization, it is of particular importance not only to enhance the light-harvesting efficiency for high photocurrent but also to suppress nongeminate recombination for high voltage and fill factor (FF). It is therefore clearly desirable for them to realize a high FF even with thick active layers that can harvest many more photons from the solar light. In most cases of these devices with a record PCE, however, the optimal thickness of the active layer is typically as thin as about 100 nm. This is because charge carriers formed in thick active layers have to travel a long distance before arriving at each electrode and therefore are more likely to recombine nongeminately, which eventually give rise to decrease in FF. In other words, there is a tradeoff relation between light-harvesting and charge collection efficiencies for all polymer solar cells. Interestingly, some of recent studies have shown a high FF even with thick active layers of more than 300 nm.^{3,4} This is probably ascribed to reduced nongeminate recombination compared with the diffusion-limited Langevin The physical origin behind this phenomenon, however, is as yet not properly recombination. understood.

Herein, we have studied the relationship between crystallinity of donor conjugated polymer and nongeminate recombination in all polymer blend solar cells by measuring transient photovoltage/transient photocurrent (TPV/TPC) of a series of blend films based on donor conjugated polymers with different crystallinities in conjunction with naphthalene diimide based acceptor conjugated polymer (N2200) as shown in Figure 1. In addition, we have measured local current images of regioregular poly(3-hexylthiophene) (P3HT)/N2200 blend films by conductive atomic force microscopy (C-AFM) to discuss how blend morphology impacts on nongeminate recombination and PCE.

2. Results and discussion

2.1. Photovoltaic performance

We have fabricated all polymer blend solar cells using a series of four donor conjugated polymers with different crystallinities in accordance with previous reports:^{10–13} fabrication conditions are summarized in Table S1. Here, we discretionarily classified these polymers into an amorphous polymer PTQ1, less crystalline polymers PBDB-T and J51, and a highly crystalline polymer P3HT on the basis of previously reported data: a coherence length along lamella stacking for the four donor polymers both in neat and in blend films with N2200 measured by X-ray diffraction (Table S2).^{14–20} This was further supported by the photoluminescence quenching efficiency Φ_q measured by selective excitation of donor polymer for all the blends. As shown in Table S3, it was estimated to be about 100, 94, and 86% for PTQ1, J51, and PBDB-T blends, respectively. On the other hand, P3HT blends exhibit Φ_q comparable to or less than about 80% depending on thermal treatments. This finding indicates that the P3HT blends have the highest degree of crystallinity, the J51 and PBDB-T blends have a moderate crystallinity, and the PTQ1 blends exhibit rather amorphous.

Figure 2a shows J-V characteristics of these solar cells, which were measured under AM1.5G simulated solar illumination with 100 mW cm⁻². The photovoltaic parameters of theses solar cells are summarized in Table S4. Figure 2b shows the thickness dependence of FF in these solar cells with different crystallinities. For devices based on the amorphous polymer PTQ1 or less crystalline polymers PBDB-T and J51, FF was sharply decreased with increasing thickness of an active layer. In stark contrast, for devices based on the highly crystalline polymer P3HT, it decreased slightly with increasing their thickness but was still as high as 0.6 even for an active layer thickness of more than 300 nm. This implies that the crystallinity of a donor polymer would lead to a high mobility and/or reduced nongeminate recombination in all polymer devices.

2.2. Charge recombination dynamics

We next study how the crystallinity of donor polymers impacts on charge recombination dynamics by measuring TPV/TPC for these solar cells. TPV measurements allow us to evaluate the lifetime (τ_n) of charge carriers in the device. To be more specific, an extra amount of minority charges generated by a small perturbation of laser pump pulse gives rise to an increase in voltage since the device is held at open circuit. Shortly afterwards, they back to steady state through recombination with majority charges generated by continuous-wave illumination of white light-emitting diode (LED). This transient voltage decay can be treated as a pseudo first-order reaction under above conditions, and thus the lifetime of minority charges $\tau_{\Delta n}$ is given by a single exponential as a function of open-circuit voltage (*V*oc), as follows:

$$\tau_{\Delta n} = \tau_{\Delta n_0} \exp\left(-\frac{qV_{\rm OC}}{vk_{\rm B}T}\right) \tag{1}$$

where $\tau_{\Delta n_0}$ is the lifetime from a linear extrapolation at $V_{OC} = 0$, q is the elementary charge, k_B is the Boltzmann constant, T is the absolute temperature, and v is the ideality factor of charge carrier lifetime. On the other hand, TPC measurements enable us to evaluate total charge carrier density (*n*) in devices in conjunction with TPV measurements. More specifically, the transient voltage is measured through a 50 Ω resistor in which the device is held at short circuit, and therefore can be converted to a transient current using the Ohm's law. The amount of charges generated by the same pulse laser Δq is eventually calculated from the integral of this transient photocurrent over time. The differential capacitance d*C* is defined by

$$dC(V_{\rm OC}) = \frac{\Delta q}{\Delta V_0(V_{\rm OC})}$$
(2)

where ΔV_0 (V_{OC}) is the initial photovoltage increment through TPV measurement based on different background LED intensity. Hence, d*C* is also calculated at various background light intensities. Consequently, *n* is given by

$$n = \frac{1}{qAd} \int_0^{V_{\rm OC}} \mathrm{d}C(V_{\rm OC}) \mathrm{d}V \tag{3}$$

where *A* is the area of the device and *d* is the thickness. Under different bias illumination intensities, *n* exponentially increases with increasing V_{OC} and therefore can be analyzed by

$$n = n_0 \exp\left(\frac{qV_{\rm OC}}{mk_{\rm B}T}\right) \tag{4}$$

where n_0 is the carrier density from a linear extrapolation at $V_{OC} = 0$ and *m* is the ideality factor of charge carrier density. On the basis of these parameters obtained, τ_n is given by

$$\tau_n = \left(\frac{m}{\nu} + 1\right) \tau_{\Delta n} = (\lambda + 1) \tau_{\Delta n} \tag{5}$$

where $\lambda + 1$ represents the reaction order of recombination.^{21,22} Figure 3a shows double logarithmic plots of τ_n against *n* evaluated for four kinds of the polymer solar cells. The bimolecular recombination rate constant (k_{rec}) is given by $k_{rec} = (\tau_n n)^{-1}$. On the other hand, the diffusion-limited Langevin recombination rate constant (k_L) is given by $k_{\rm L} = q\mu/\varepsilon_{\rm r}\varepsilon_0$ where ε_r is the relative dielectric constant of materials, which is assumed to be 3 for all the blend films, ε_0 is the vacuum permittivity, and μ is charge carrier mobility, which is employed as the slower one of electron and hole mobilities (Table S5).^{11,23} Note that the electron and hole mobilities were estimated by space-charge-limited current (SCLC) method for an (ITO/ZnO/blend/PFN-Br/Al) electron-only device and for a hole-only device (ITO/PEDOT:PSS/blend/Au), respectively. The recombination reduction factor (ζ) is defined by $\zeta = k_{rec}/k_{L}$.^{21,24,25} Figure 3b shows the dependence of ζ on *n* for all polymer solar cells. As shown in the figure, ζ was estimated to be on the order of 0.1 for the devices based on the amorphous PTQ1 or less crystalline polymers such as PBDB-T and J51. Among them, ζ of PTQ1/N2200 devices was as large as 0.67. On the other hand, it was estimated to be on the order of 0.001 for the devices using highly crystalline P3HT. This finding indicates that nongeminate recombination is remarkably suppressed in P3HT/N2200 devices, but rather is close to the Langevin recombination in PTQ1/N2200 devices. In other words, nongeminate recombination is closely related to the crystallinity of donor polymers.

2.3. P3HT/N2200 blend systems

For an in-depth understanding of the origin of suppressed nongeminate recombination in P3HT/N2200 blend systems, we systematically consider three control blends fabricated with/without typical thermal annealing treatments (Table S1). Figure 4 shows absorption spectra of P3HT and N2200 obtained by spectral resolution of each P3HT/N2200 blend film: each absorption was normalized at 556 nm for P3HT region and at 710 nm for N2200 region for comparison. On the basis of H-aggregate model,^{26,27} we estimated the fraction of crystalline P3HT and the exciton bandwidth *W*, which are measures of P3HT crystallinity. As summarized in Figure S4 and Table S6, the fraction of crystalline P3HT increased from 56 (as-cast film) to 57% while *W* decreased from 0.146 (as-cast film) to 0.131 eV with increasing annealing temperature. On the other hand, negligible change in the peak wavelength of N2200 was observed without regard to the annealing temperatures. This suggests that annealing processes for the control blend films have limited impact on the crystallinity of P3HT and have negligible effect on the crystallinity of N2200.

We fabricated three kinds of P3HT/N2200 devices using the active layers described above and measured J-V characteristics as displayed in Figure S1. The resulting photovoltaic parameters of these solar cells are summarized in Table S7. With increasing annealing temperature, as summarized in Table S7, short-circuit current density (J_{SC}) increased while the photoluminescence quenching efficiency Φ_q decreased (Table S3). As described later, the increase in J_{SC} is probably due to enhanced charge collection by thermal annealing and the decrease in Φ_q is attributed to grown each domain by thermal annealing. On the other hand, V_{OC} exhibited a slight decrease in comparison with that of devices without annealing, which is possibly related to changes in energy level of charge transfer (CT) state and/or differences in voltage loss caused by charge recombination. Although it was expected that FF would increase with increasing annealing temperatures for donor polymers, no variation in FF was observed for the devices with typical annealing treatments. This is probably because the crystallinity of P3HT was subtly increased even after thermal annealing.

Firstly, we evaluated μ by the SCLC measurement for the electron- and hole-only devices using a series of three P3HT/N2200 blend films. As summarized in Table S8, μ was improved both for electrons and holes with increasing annealing temperature. This is probably because of a subtle increase in crystallinity of P3HT and/or changes in molecular packing and orientation of N2200. Such an increase in mobility, however, is not consistent with no improvement in FF in P3HT/N2200 devices. Hence, we next measured TPV/TPC of these solar cells to consider charge recombination dynamics. Figure 5a shows log–log plots of τ_n against *n* for the devices with the different annealing treatments. On the basis of these values together with slower μ , we examined the dependence of ζ on *n* for these devices. As shown in Figure 5b, ζ was evaluated to be 0.05 and 0.07 for the devices without the thermal treatments and with annealing at 90 °C for 10 min, respectively, whereas it was evaluated to be 0.12 for the devices with annealing at 190 °C for 10 min. In other words, there is no distinct differences in nongeminate recombination between them independently of the thermal treatments. This is probably because thermal annealing has limited and negligible impacts on the crystallinity of P3HT and N2200, respectively, as described before.

2.4. Blend morphology for P3HT/N2200

To address the effects of morphological changes on nongeminate recombination for P3HT/N2200 blends, we measured C-AFM images of P3HT/N2200 blend films with the

different thermal annealing. Note that the thickness of all the samples was adjusted to be about 60 nm to prevent the thickness dependence of current density. Figures 6a-c show C-AFM hole current images $(3 \times 3 \ \mu m^2)$ for these blend films. Conductive hot spots locally found increased with increasing thermal annealing temperature in the control blend films, which is well consistent with improved μ as mentioned before. This is attributed to slightly ordered P3HT chains induced by the thermal treatments. In addition, Figure S2 shows histograms of hole currents for these samples as well as the neat films. As shown in the figure, P3HT neat films exhibit a wide distribution in the hole currents from 50 to 350 pA. Here, the lower limit value of the hole current about 50 pA for this neat film was used as a criterion in separating three kinds of phases, which include a donor-rich phase, an acceptor-rich phase, and a mixed disordered phase. To be more specific, the region with more than 50 pA was assigned to donor-rich phases, a nonconductive region with less than 0.6 pA, which is the higher limit value of N2200 neat films, was assigned to acceptor-rich phases, and the other one was assigned to mixed disordered phases. As shown in Figures 6d-f, we obtained three-phase images on the basis of the above analysis. Figure 7 shows the fraction of each phase composition in the blend films with the different annealing treatments. We found that each donor-rich and acceptor-rich domain occupied about 15% in the as-cast blend films while the phase composition increased to 32% for donor-rich and to 22% for acceptor-rich domains in the blend films annealed at 190 °C for 10 min. As a result, the fraction of mixed phases decreased from about 70% in the as-cast blend films to 46% in the blend films heated at 190 °C for 10 min, which is consistent with Φ_q shown in Table S3.

2.5. Origin of reduced nongeminate recombination

We finally discuss the origin of reduced nongeminate recombination in terms of blend

morphology and crystallinity of donor polymers. Among the all polymer solar cells we studied, only high crystalline donor polymers i.e, P3HT give rise to suppress nongeminate recombination as described before. On the other hand, however, there is no clear correlation between the charge recombination dynamics and blend morphology or crystallinity in P3HT/N2200 blends with typical annealing treatments. More specifically, ζ for the control blends was evaluated to be more or less the same (0.05 - 0.12) under typical thermal annealing conditions even though its blend morphology was clearly dependent on the thermal annealing conditions: as the annealing temperature was increased from 90 to 190 °C each rich phase increased but instead the mixed phase decreased in comparison with the as-cast film. However, the crystallization of P3HT was improved subtly but rather remained almost the same under typical annealing conditions. This is consistent with more or less the same ζ for the control blends mentioned above. On the other hand, ζ for the optimized blends was evaluated to be as low as 0.008, which is one to two orders of magnitude smaller than those of the control blends, suggesting that nongeminate recombination is more suppressed in the optimized blends than in the control blends. To clarify the origin of this large difference, we have estimated the P3HT crystallinity for the optimized blends on the basis of the same analysis described above (Figure S4 and Table S6). As a result, the fraction of crystalline P3HT increased from 56 to 60% and W decreased from 0.146 to 0.108 eV for the optimized blends, suggesting that they have more ordered crystalline structures compared with the control blends. We therefore focus on the optimized blends to understand the origin of reduced nongeminate recombination in more detail.

Figures 8a and 8b show C-AFM hole current and phase separation images $(3 \times 3 \ \mu m^2)$ for the optimized blend films. As shown in the figure, they exhibit a fibrillar-like structure of P3HT as well as a finer intermixed morphology. The fraction of mixed phases for the optimized blend films was estimated to be about 72% on the basis of the same analysis described in the previous section, which is comparable to that of as-cast films. In addition, Figure 8c shows an enlarged image of phase separation, which corresponds to square box shown in the inset image. As shown in the figure, there are many narrow mixed phases with a width of less than 20 nm as shown by the arrows. Here, we focus not on the absolute value but rather on the relative one because the lateral resolution of this measurement is not high considering a cantilever tip radius of curvature (<10 nm). This implies that there are two distinct features compared with the control blends. The first one is that there is a higher crystallinity of P3HT in comparison with the control blends, which is in good agreement with absorption spectra of P3HT component (Figures S3 and S4). A recent study has shown that the highest occupied molecular orbital (HOMO) level of P3HT crystalline is about 150 meV shallower than that of P3HT amorphous due to a difference in the effective conjugation length between them.²⁸ Moreover, the P3HT fibrillar-like nanostructures have the HOMO level, which is shallower by 100 meV than that of P3HT crystalline aggregates as previously reported.²⁹ This facilitates the formation of mixed phases with a cascaded energy structure in the HOMO levels between crystalline domains and amorphous domains at donor/acceptor interfaces with a sufficient energy offset as shown in Figure 9. The second one is that the mixed phases are likely to be formed in the immediate vicinity of donor-rich and acceptor-rich domains, which is beneficial for a spatial separation of charge carriers. Such a morphology with cascaded energy landscape at the donor/acceptor interface is a primary factor to reduce nongeminate recombination in this blend system. This is in line with previous studies for polymer/small molecular blend systems in which one or both of donor and acceptor materials have a high crystallinity as previously reported.^{30–33}

In addition to the above factors, there are other possible parameters, inclusive of the domain purity and the charge dissociation efficiency from CT states, which have a critical effect on nongeminate recombination in polymer solar cells.^{25,34–37} In general, the donor

polymers with a high crystallinity facilitate the formation of their pure domains in the blend films. Taking into account X-ray diffraction reported previously and absorption data (Figure S4 and Table S6), we can conjecture that the optimized blends with fibrillar-like nanostructures of P3HT observed by C-AFM have more ordered crystalline structures in comparison with the control blends, which enable us to obtain the purest P3HT domains in the blend films. Such a pure domain has more number of charge states, which gives rise to increase entropy effect in the free energy. This entropy effect would result in a decrease in Coulomb attraction energy, and hence play a crucial role in the suppressed nongeminate recombination.^{38,39} The charge dissociation from CT states is also one other possible factor affecting nongeminate recombination.³⁷ In many cases, the blends based on a highly crystalline polymers are likely to form the delocalized CT states at the donor/acceptor interface, and thus may enhance the charge dissociation efficiency. In this study, however, there is no clear correlation between them because the highest FF was found for the lowest EQE device as shown in Figure S5. This suggests that charge dissociation from CT states has little effects on nongeminate recombination in our blend system. A further study is required to gain in-depth understanding of the relationship between nongeminate recombination and charge dissociation from CT states.

In summary, the optimized blends have a proper morphology with not too much growth in donor and acceptor domains as well as a higher crystallinity of P3HT. Such a blend results in a cascaded energy structure with a sufficient energy offset where electrons and holes at the donor/acceptor interfaces are likely to move from mixed disordered phases to more stable crystalline phases. This gives rise to a spatial separation of charge carriers in which they are unlikely to be encountered each other, eventually leading to suppressed nongeminate recombination. In contrast, the control blends have morphologies that donor and acceptor domains are not mixed well as a result of the growth of each domain via the thermal

treatments, which is not beneficial for charge generation. In particular, they exhibit a moderate crystallinity of P3HT even after the thermal annealing, which is not enough to form a proper cascaded energy structure in HOMO levels between crystalline domains and amorphous domains. This makes it difficult to take place a spatial separation of charge carriers and hence accelerate nongeminate recombination.

3. Conclusions

Nongeminate recombination was systematically studied for a series of four solar cells based on blends of donor conjugated polymers with different crystallinities and N2200 acceptor conjugated polymer by TPV/TPC techniques together with C-AFM measurements. By measuring the thickness dependence of device performance, we found that the devices based on highly crystalline polymer P3HT show little dependence of the thickness up to 300 nm on FF compared with the other devices based on amorphous polymer PTQ1 and less crystalline polymers PBDB-T and J51. This is because nongeminate recombination is substantially reduced by two orders of magnitude in P3HT/N2200 blend systems than in the other counterparts. On the other hand, little change in FF was observed for P3HT/N2200 control devices with typical annealing treatments. By analyzing TPV/TPC data, we found that there are no distinct changes in nongeminate recombination. In other words, no clear correlation between charge recombination dynamics and blend morphology or crystallinity was observed for P3HT/N2200 control blends independently of the annealing treatments. On the other hand, reduced recombination was observed for the optimized devices. We therefore further investigated blend morphology in the optimized and control devices by C-AFM measurements. As a result, with increasing annealing temperature for the control blends, the phase fraction of mixed phases decreased from ~70 to ~50% due to the growth of each rich domain, which is not suitable for charge generation. Particularly, as the annealing temperature increased, the crystallinity of P3HT was subtly increased but not enough to build a cascaded energy structure in HOMO levels between crystalline domains and amorphous domains at donor/acceptor interface, leading to accelerate nongeminate recombination. On the other hand, the optimized blends have a finer intermixed morphology with a moderate growth of donor and acceptor domains in which the mixed phases would be formed nearby donor-rich and acceptor-rich domains. In addition, they show highly crystalline fibrils of P3HT, which facilitates the formation of mixed phases with sufficient energetic offsets between the crystalline phase and the amorphous phase. Such conditions enable charge carriers at the donor/acceptor interfaces to move from mixed disordered phases to more stable crystalline phases, resulting in a spatially separation of charge carriers, and thus suppresses nongeminate recombination in the devices. In summary, for achieving a high FF even with thick active layers in all polymer blend systems, it is of key importance to obtain an intimately mixed blend morphology with a sufficient energetic offset between the crystalline phase and the amorphous phase which can be incurred by highly crystalline of donor polymers. This will attract more interest in photovoltaic community and furthermore would pave the way towards commercially viable all polymer solar cells with high PCE as well as excellent mechanical durability.

4. Experimental Section

Materials

All of the polymers were employed without further purification as follows: Poly(3-hexylthiophene-2,5-diyl)-regioregular (P3HT, Sigma–Aldrich, regioregularity >90%, and $M_n = 23,600$, poly[2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diyl-*alt*-thiophene-2,5-diyl] (PTQ1, Ossila, $M_{\rm n}$ 61,571, PDI and 2.44), = = poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(2-ethylhexyl)thiophene))-a1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)] (PBDB-T, Solarmer Materials, Inc.), poly{2,6-bis(trimethyltin)-4,8-bis[5-(2-ethylhexyl)thiophen-2-yl]benzo[1,2-b:4,5-b']dithiophe ne-alt-4,7-bis(5-bromothiophen-2-yl)-2-(2-butyloctyl)-5,6-difluoro-2H-benzo[d][1,2,3]triazol e} (J51, Sigma–Aldrich, $M_{\rm n}$ = 22,100. and PDI = 2.6), poly{[*N*,*N*'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-*alt*-5,5'-(2, $M_{
m n}$ 2'-bithiophene) (N2200. Osilla. =31.000. and PDI = 4.26). 2,9-bis[3-(dimethyloxidoamino)propyl]anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10 (2H,9H)-tetrone (PDINO Solarmer Materials, and Inc.). poly[(9,9-bis(3-(N,N-dimethyl)-N-ethylammonium)-propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctyl fluorene)]dibromide (PFN-Br and Solarmer Materials. Inc.). and poly(3,4-ethylenedioxythiophene) with poly(4-styrenesulfonate) (PEDOT:PSS and H. C. Starck Clevios PH500).

Device Fabrication

All polymer solar cells based on active layers of PTQ1/N2200, J51/N2200, and P3HT/N2200 were fabricated with a conventional device structure, which is indium–tin-oxide (ITO)-coated glass substrate/PEDOT:PSS/active layer/buffer layer/metal cathode. In particular, to control the crystallization of P3HT and mixed-phase states, P3HT/N2200 devices were intentionally fabricated with two deposition methods, which are described in detail below. On the other hand, PBDB-T/N2200 solar cells were fabricated with an inverted device structure, which is ITO-coated glass substrate/ZnO/active layer/MoO₃/Ag. For the devices with a normal layered structure, a hole-transporting buffer layer (~40 nm) of PEDOT:PSS was spin-coated

onto the cleaned ITO-coated glass substrates at 3000 rpm for 99 s, and then dried on a hot plate at 140 °C for 10 min. In contrast, for the devices with an inverted layered structure, an electron-transporting buffer layer (~20 nm) of zinc oxide (ZnO) was deposited on the cleaned ITO-coated glass substrates by spin-coating at 1200 rpm for 20 s from a solution of ZnO nanoparticles prepared by the method reported previously.^{S1} Prior to deposition of active layers, these substrates were transferred into an inert glove box under a nitrogen atmosphere (H₂O and O₂ < 1 ppm). The blend active layers were prepared atop ITO/PEDOT:PSS or ITO/ZnO substrates according to each fabrication condition (Table S1). For J51/N2200 blend devices, PDINO buffer layer (~10 nm) was spin-coated at 3000 rpm for 30 s from a methanol solution (1.0 mg mL⁻¹). Finally, metal electrode was thermally evaporated under vacuum at 2.5×10^{-4} Pa in accordance with each device (Table S1). The devices were encapsulated in the glovebox using a UV curable epoxy (Ossila) for the *J–V* and TPV/TPC measurements to prevent device degradation caused by air exposure.

Measurements

Absorption and PL Spectroscopy: The absorption spectra were measured with a spectrophotometer (Hitachi, U-4100). The photoluminescence spectra were measured with a fluorophotometer (Horiba Jobin Yvon, NanoLog). The samples were excited at 500 nm and 700 nm for selective excitation of donor and acceptor, respectively.

Macroscopic J–V Measurements: The macroscopic mobility measurements were performed in a nitrogen-filled chamber. On the basis of the Mott–Gurney equation, it was evaluated from J-V curves in the SCLC region for hole-only devices with a layered structure of ITO/PEDOT:PSS/active layer/Au and electron-only devices with a layered structure of ITO/ZnO/active layer/PFN-Br/Al. The J-V characteristics for solar cells were measured using a DC voltage and current source/monitor (Keithley, 2611B) in a dark and under AM1.5G simulated solar illumination at 100 mW cm⁻². The light intensity was corrected with a calibrated Si photodiode (Bunko-Keiki, BS-520).

TPV/TPC Measurements: TPV/TPC measurements were performed for the polymer solar cells under bias white light illumination from a white LED with diverse 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) with a repetition rate of 100 Hz and a pulse width of <1.8 ns. The transient photovoltage generated by the laser pulse was monitored with a 200-MHz digital oscilloscope (Tektronix, TDS2022B). For TPV measurements, the input impedance of the oscilloscope was set to 1 M Ω to keep the device at open circuit. For TPC measurements, the input impedance of the oscilloscope was set to 50 Ω to hold the device at short circuit. The transient photovoltage was measured through the 50 Ω resistor, which can be converted to transient current on the basis of Ohm's law.

C-AFM Measurement: C-AFM measurements were performed with a layered structure of ITO/PEDOT:PSS/Active layer/Au using a microscope (Shimadzu, SPM-9700) in contact mode with an Au-coated silicon probe (Nanosensors, PPP-CONTAu, a tip radius of curvature <10 nm, and a spring constant of 0.2 N m⁻¹) under the room light in ambient atmosphere. The surface topography and corresponding current images were simultaneously obtained with operating at a constant sample bias of -1.5 V (reverse bias). Note that the room light has little effects on the generation of hole currents. In addition, the hole currents of P3HT are not linearly dependent on the portion of P3HT because there is a variation in its hole currents in accordance with the degree of crystallization and/or domain purity.

Supporting information

This material is available free of charge via the Internet at http://pubs.acs.org.

Acknowledgments

This study was supported by the Advanced Low Carbon Technology Research and Development Program (ALCA) of Japan Science and Technology Agency (JST) (Grant No. JPMJAL1404), the JST Mirai Program (Grant No. JPMJMI20E2), and KAKENHI from Japan Society for the Promotion of Science (JSPS) (Grant Nos. 19K22217 and 21H04692).

REFERENCES

(1) Lee, C.; Lee, S.; Kim, G.-U.; Lee, W.; Kim, B. J. Recent Advances, Design Guidelines, and Prospects of All-Polymer Solar Cells. *Chem. Rev.* **2019**, *119*, 8028–8086.

(2) Benten, H.; Mori, D.; Ohkita, H.; Ito, S. Recent Research Progress of Polymer Donor/ Polymer Acceptor Blend Solar Cells. *J. Mater. Chem. A* **2016**, *4*, 5340–5365.

(3) Liu, X.; Li, X.; Zheng, N.; Gu, C.; Wang, L.; Fang, J.; Yang, C. Insight into the Efficiency and Stability of All-Polymer Solar Cells Based on Two 2D-Conjugated Polymer Donors: Achieving High Fill Factor of 78%. *ACS Appl. Mater. Interfaces* **2019**, *11*, 43433–43440.

(4) Jia, T.; Zhang, J.; Zhong, W.; Liang, Y.; Zhang, K.; Dong, S.; Ying, L.; Liu, F.; Wang, X.;
Huang, F.; Cao, Y. 14.4% Efficiency All-Polymer Solar Cell with Broad Absorption and Low
Energy Loss Enabled by a Novel Polymer Acceptor. *Nano Energy* 2020, 72, No. 104718.

(5) Liu, T.; Yang, T.; Ma, R.; Zhan, L.; Luo, Z.; Zhang, G.; Li, Y.; Gao, K.; Xiao, Y.; Yu, J.;
Zou, X.; Sun, H.; Zhang, M.; Peña, T. A. D.; Xing, Z.; Liu, H.; Li, X.; Li, G.; Huang, J.; Duan,
C.; Wong, K. S.; Lu, X.; Guo, X.; Gao, F.; Chen, H.; Huang, F.; Li, Y.; Li, Y.; Cao, Y.; Tang,

B.; Yan, H. 16% Efficiency All-Polymer Organic Solar Cells Enabled by a Finely Tuned Morphology via the Design of Ternary Blend. *Joule* **2021**, *5*, 914–930.

(6) Green, M. A.; Dunlop, E.; Hohl-Ebinger, J.; Yoshita, M.; Kopidakis, N.; Hao, X. Solar Cell Efficiency Tables (version 57). *Prog. Photovolt. Res. Appl.* **2021**, *29*, 3–15.

(7) Kini, G. P.; Jeon, S. J.; Moon, D. K. Design Principles and Synergistic Effects of Chlorination on a Conjugated Backbone for Efficient Organic Photovoltaics: A Critical Review. *Adv. Mater.* **2020**, *32*, No. 1906175.

(8) Ramanujam, J.; Bishop, D. M.; Todorov, T. K.; Gunawan, O.; Rathc, J.; Nekovei, R.; Artegiani, E.; Romeo, A. Flexible CIGS, CdTe and a-Si:H based Thin Film Solar Cells: A Review. *Prog. Mater. Sci.* **2020**, *110*, No. 100619.

(9) Gao, F.; Zhao, Y.; Zhang, X.; You, J. Recent Progresses on Defect Passivation toward Efficient Perovskite Solar Cells. *Adv. Energy Mater.* **2020**, *10*, No. 1902650.

(10) Schubert, M.; Dolfen, D.; Frisch, J.; Roland, S.; Steyrleuthner, R.; Stiller, B.; Chen, Z.; Scherf, U.; Koch, N.; Facchetti, A.; NeherL, D. Influence of Aggregation on the Performance of All-Polymer Solar Cells Containing Low-Bandgap Naphthalenediimide Copolymers. *Adv. Energy Mater.* **2012**, *2*, 369–380.

(11) Mori, D.; Benten, H.; Okada, I.; Ohkita, H.; Ito, S. Low-Bandgap Donor/Acceptor Polymer Blend Solar Cells with Efficiency Exceeding 4%. *Adv. Energy Mater.* **2014**, *4*, No. 1301006.

(12) Gao, L. Zhang, Z.-G.; Xue, L.; Min, J.; Zhang, J.; Wei, Z.; Li, Y. All-Polymer Solar Cells Based on Absorption-Complementary Polymer Donor and Acceptor with High Power Conversion Efficiency of 8.27%. *Adv. Mater.* **2016**, *28*, 1884–1890.

(13) Liu, X.; Zou, Y.; Wang, H.-Q.; Wang, L.; Fang, J.; Yang, C. High-Performance All-Polymer Solar Cells with a High Fill Factor and a Broad Tolerance to the Donor/Acceptor Ratio. *ACS. Appl. Mater. Interfaces* **2018**, *10*, 38302–38309.

(14) Xia,Y.; Musumeci, C.; Bergqvist, J.; Ma, W.; Gao, F.; Tang, Z.; Bai, S.; Jin, Y.; Zhu, C.; Kroon, R.; Wang, C.; Andersson, M. R.; Hou, L.; Inganäs, O.; Wang, E. Inverted All-Polymer Solar Cells based on a Quinoxaline–Thiophene/Naphthalene-Diimide Polymer Blend Improved by Annealing. *J. Mater. Chem. A* **2016**, *4*, 3835–3843.

(15) Gao, L.; Zhang, Z.-G.; Bin, H.; Xue, L.; Yang, Y.; Wang, C.; Liu, F.; Russell, T. P.; Li, Y. High-Efficiency Nonfullerene Polymer Solar Cells with Medium Bandgap Polymer Donor and Narrow Bandgap Organic Semiconductor Acceptor. *Adv. Mater.* **2016**, *28*, 8288–8295

(16) Zhang, Q.; Chen, Z.; Ma, W.; Xie, Z.; Liu, J.; Yu, X.; Han, Y. Efficient Nonhalogenated Solvent-Processed Ternary All-Polymer Solar Cells with a Favorable Morphology Enabled by Two Well- Compatible Donors. *ACS Appl. Mater. Interfaces* **2019**, *11*, 32200–32208.

(17) Li, W.; Yan, D.; Liu, F.; Russell, T.; Zhan, C.; Yao, J. High-Efficiency Quaternary Polymer Solar Cells Enabled with Binary Fullerene Additives to Reduce Nonfullerene Acceptor Optical Band Gap and Improve Carriers Transport. *Sci. China Chem.* **2018**, *61*, 1609–1618.

(18) Zhang, N.; Xu, Y.; Zhou, X.; Zhang, W.; Zhou, K.; Yu, L.; Ma, W.; Xu, X. Synergistic Effects of Copolymerization and Fluorination on Acceptor Polymers for Efficient and Stable All-Polymer Solar Cells. *J. Mater. Chem. C* **2019**, *7*, 14130–14140.

(19) Schubert, M.; Collins, B. A.; Mangold, H.; Howard, I. A.; Schindler, W.; Vandewal, K.;
Roland, S.; Behrends, J.; Kraffert, F.; Steyrleuthner, R.; Chen, Z.; Fostiropoulos, K.; Bittl, R.;
Salleo, A.; Facchetti, A.; Laquai, F.; Ade, H. W.; Neher, D. Correlated Donor/Acceptor Crystal
Orientation Controls Photocurrent Generation in All-Polymer Solar Cells. *Adv. Funct. Mater.* **2014**, *24*, 4068–4081.

(20) Pavlopoulou, E.; Kim, C. S.; Lee, S. S.; Chen, Z.; Facchetti, A.; Toney, M. F.; Loo, Y.-L.
Tuning the Morphology of All-Polymer OPVs through Altering Polymer–Solvent Interactions. *Chem. Mater.* 2014, 26, 5020–5027.

(21) Maurano, A.; Shuttle, C. G.; Hamilton, R.; Ballantyne, A. M.; Nelson, J.; Zhang, W.; Heeney, M.; Durrant, J. R. Transient Optoelectronic Analysis of Charge Carrier Losses in a Selenophene/Fullerene Blend Solar Cell. *J. Phys. Chem. C* **2011**, *115*, 5947–5957.

(22) Kirchartz, T.; Nelson, J. Meaning of Reaction Orders in Polymer: Fullerene Solar Cells.*Phys. Rev. B* 2012, *86*, No. 165201.

(23) Zhang, X.; Zuo, X.; Xie, S.; Yuan, J.; Zhou, H.; Zhang, Y. Understanding Charge Transport and Recombination Losses in High Performance Polymer Solar Cells with Non-Fullerene Acceptors. *J. Mater. Chem. A* **2017**, *5*, 17230–17239

(24) Juška, G.; Arlauskas, K.; Stuchlik, J.; Österbacka, R. Non-Langevin Bimolecular Recombination in Low-Mobility Materials. *J. Non-Cryst. Solids* **2006**, 352, 1167–1171.

(25) Fukuhara, T.; Tamai, Y.; Ohkita, H. Nongeminate Charge Recombination in Organic Photovoltaics. *Sustain. Energy Fuels* **2020**, *4*, 4321–4351.

(26) Spano, F. C. Modeling Disorder in Polymer Aggregates: The Optical Spectroscopy of Regioregular Poly(3-hexylthiophene) Thin Films. *J. Chem. Phys.* **2005**, *122*, No. 234701.

(27) Spano, F. C. Absorption in Regio-Regular Poly(3-Hexyl)Thiophene Thin Films: Fermi Resonances, Interband Coupling and Disorder. *Chem. Phys.* **2006**, *325*, 22–35.

(28) Sweetnam, S.; Graham, K. R.; Ndjawa, G. O. N.; Heumüller, T.; Bartelt, J. A.; Burke, T. M.; Li, W.; You, W.; Amassian, A.; McGehee, M. D. Characterization of the Polymer Energy Landscape in Polymer:Fullerene Bulk Heterojunctions with Pure and Mixed Phases. *J. Am. Chem. Soc.* 2014, *136*, 14078–14088.

(29) Marchesi, L. F.; Pereira, E. C. The Influence of The Drying Process on Electrochemical Properties of P3HT/PCBM (1.00/0.25 wt%) Electrodes. *Synth. Met.* **2014**, *194*, 82–87.

(30) Jamieson, F. C.; Domingo, E. B.; McCarthy-Ward, T.; Heeney, M.; Stingelin, N.; Durrant, J. R. Fullerene Crystallisation as a Key Driver of Charge Separation in Polymer/Fullerene Bulk Heterojunction Solar Cells. *Chem. Sci.* **2012**, *3*, 485–492.

(31) Groves, C. Suppression of Geminate Charge Recombination in Organic Photovoltaic Devices with a Cascaded Energy Heterojunction. *Energy Environ. Sci.* **2013**, *6*, 1546–1551.

(32) Burke, T. M.; McGehee. M. D. How High Local Charge Carrier Mobility and an Energy Cascade in a Three-Phase Bulk Heterojunction Enable >90% Quantum Efficiency. *Adv. Mater.* **2014**, *26*, 1923–1928.

(33) Wang, Z.; Zhu, X.; Zhang, J.; Lu, K.; Fang, J.; Zhang, Y.; Wang, Z.; Zhu, L.; Ma, W.; Shuai, Z.; Wei, Z. From Alloy-Like to Cascade Blended Structure: Designing High-Performance All-Small-Molecule Ternary Solar Cells. *J. Am. Chem. Soc.* **2018**, *140*, 1549–1556.

(34) Heiber, M. C.; Baumbach, C.; Dyakonov, V.; Deibel, C. Encounter-Limited Charge-Carrier Recombination in Phase-Separated Organic Semiconductor Blends. *Phys. Rev. Lett.* **2015**, *114*, No. 136602.

(35) Venkatesan, S.; Chen, J.; Ngo, E. C.; Dubey, A.; Khatiwada, D.; Zhang, C.; Qiao, Q. Critical Role of Domain Crystallinity, Domain Purity and Domain Interface Sharpness for Reduced Bimolecular Recombination in Polymer Solar Cells. *Nano Energy* **2015**, *12*, 457–467.

(36) Gehrig, D. W.; Howard, I. A.; Sweetnam, S.; Burke, T. M.; McGehee, M. D.; Laquai, F. The Impact of Donor–Acceptor Phase Separation on the Charge Carrier Dynamics in pBTTT:PCBM Photovoltaic Blends. *Macromol. Rapid Commun.* **2015**, *36*, 1054–1060.

(37) Göhler, C.; Wagenpfahl, A.; Deibel, C. Nongeminate Recombination in Organic Solar Cells. *Adv. Electron. Mater.* **2018**, *4*, No. 1700505.

(38) Clarke, T. M.; Durrant, J. R. Charge Photogeneration in Organic Solar Cells. *Chem. Rev.***2010**, *110*, 6736–6767.

(39) Hood, S. N.; Kassal, I. Entropy and Disorder Enable Charge Separation in Organic Solar Cells. *J. Phys. Chem. Lett.* **2016**, *7*, 4495–4500.

Figures and Figure Captions



Figure 1. Chemical structures of materials employed in this study: a) P3HT, b) PTQ1, c) PBDB-T, d) J51, and e) N2200.



Figure 2. a) *J*–*V* characteristics (solid lines) and b) thickness dependence of FF (symbols) of all polymer solar cells based on blends of donor conjugated polymers with different crystallinities and N2200 acceptor conjugated polymers: red (P3HT), blue (PTQ1), green (PBDB-T), and orange (J51).



Figure 3. a) Double logarithmic plots of τ_n against *n* and b) the dependence of ζ on *n* for all polymer solar cells using different donor conjugated polymers: red diamonds (P3HT), blue circles (PTQ1), green triangles (PBDB-T), and orange squares (J51). Closed symbols indicate τ_n and ζ under 1 sun illumination condition.



Figure 4. Absorption spectra of a) P3HT and b) N2200 obtained by spectral resolution of each P3HT/N2200 blend film with different annealing treatments: blue (as cast), green (90 °C for 10 min), and red (190 °C for 10 min).



Figure 5. a) Double logarithmic plots of τ_n against *n* and b) the dependence of ζ on *n* for P3HT/N2200 devices with the different annealing treatments: blue circles (as cast), green triangles (90 °C for 10 min), and red squares (190 °C for 10 min). Closed symbols indicate τ_n and ζ under 1 sun illumination condition.



Figure 6. a-c) C-AFM current images and d-f) phase separation of P3HT/N2200 blend films with the different annealing treatments: the left column (as cast), the center column (90 °C for 10 min), and the right column (190 °C for 10 min). The scale bars correspond to 1 μ m in length.



Figure 7. Fraction of each phase in P3HT/N2200 blend films with the different annealing treatments: red bar (donor-rich component), green bar (mixed component), and blue bar (acceptor-rich component).



Figure 8. a) C-AFM current images, b) phase separation images, and c) an enlarged image of phase separation for the optimized P3HT/N2200 blend films. The scale bars correspond to 1 μ m (a and b) and 200 nm (c) in length. The arrows indicate the width of mixed phases existing between P3HT-rich domain and N2200-rich domain.



Figure 9. Schematic illumination of blend morphology at donor/acceptor interfaces with a cascaded energy structure between crystalline domains and amorphous domains.

TOC GRAPHICS

