Comparing the Device Physics, Dynamics and Morphology of Polymer Solar Cells Employing Conventional PCBM and Non-Fullerene Polymer Acceptor N2200

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Abstract

Current all polymer solar cells still suffer from low fill factors (FF) and short-circuit current density (J_{sc}) compared with the conventional polymer/fullerene system. Herein in this work, devices using PTP8 as the electron donor and [70]PCBM as well as widely used polymer N2200 as the electron acceptor were systematically studied and compared. The major loss mechanisms in the all polymer solar cells were investigated to understand their relatively lower performance than the PTP8/fullerene system. By performing in-depth analysis on ultrafast transient transmission spectroscopy results, we estimated that in PTP8/N2200 device nearly half of the charges recombine geminately, which is confirmed as the major factor hindering the

device performance of all polymer solar cells compared with polymer/fullerene system. Through thorough morphology analysis, the low charge generation efficiency is attributed to the reduced crystallinity of N2200 in the blend film and the unfavorable face-to-edge orientation at the donor/acceptor heterojunction. Coupling these results with knowledge from efficient polymer/fullerene systems, the future design of new polymers can devote to increase the attraction between the π face of donor and acceptor, leading to enhanced face-to-face orientation at the heterojunction, while maintaining a high π - π stacking order for each polymer.

1. Introduction

Polymer solar cells (PSCs) have demonstrated steady growth in efficiencies over the past several years, with record efficiencies for single-junction devices reaching 12%.¹ Nearly all efficient PSCs utilize hetero-junction consisting of a conjugated polymer as the electron donor and a fullerene derivative as the electron acceptor.² However, purifying fullerene derivatives normally requires specialized equipment such as high-performance liquid chromatography which limits their scalability and raises the cost.³ Moreover, most fullerene derivatives have weak absorption in visible and near-infrared regions, resulting in inefficient utilization of solar radiation.⁴ In comparison, polymer acceptors can have advantages like tunable chemical and electronic properties as well as enhanced absorption and thermal stability. Solution-processed bulk hetero-junction (BHJ) polymer-polymer (all-polymer) solar cells⁵ have proven to be a viable alternative to the polymer/fullerene system, with

reported power conversion efficiencies (PCE) now exceeding 8%.⁶ However, the optimized PCE is still significantly lower than that of the polymer/fullerene and polymer/molecules systems. There have only been a few investigations to study the fundamental processes that govern the device performance of all-polymer solar cells,⁷ while the loss mechanisms in this system are of particular interest as many all-polymer systems suffer from low fill factors (FF) and short-circuit currents (J_{sc}).^{5a-5c, 6d, 7a, 8} Previous studies on polymer/fullerene solar cells have shown that the current-voltage (J - V) characteristics of organic photovoltaic (OPV) depend strongly on the exciton generation, dissociation and charge transport processes within the BHJ blend film.⁹ The efficiency of charge generation will be first affected by geminate recombination.¹⁰ Then subsequently the non-geminate recombination will compete with the transport of free charge carriers in the active film.¹¹ Geminate recombination occurs in electron-hole pair that originated from a single absorption event while non-geminate recombination is a bimolecular processes.¹² If either recombination process plays an important role,¹⁰⁻¹² the resultant losses can significantly limit photovoltaic parameters like J_{sc} and FF .

We adopted in this work a wide-spread polymer electron acceptor poly{[N,N'-bis(2-octyldodecyl)-1,4,5,8-naphthalenedicarboximide-2,6-diyl]-alt-5,5'-(2,2'-bithio-phenylene)} (P(NDI2OD-T2), Polyera ActivInk N2200), which exhibits several favorable properties for solar cell application: ¹³ highly ordered solid state structure with field-effect electron mobility up to $0.85 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; and a narrower optical band gap ($\sim 1.45 \text{ eV}$) compared to fullerene derivatives ($\sim 2.0 \text{ eV}$).

Nevertheless, BHJ all-polymer solar cells using PTP8 and N2200 in our previous work has demonstrated a PCE of 4.3 %, ¹⁴ significantly lower than the PCE of 6.2% for PTP8/[70]PCBM devices,¹⁵ mainly due to the relatively lower FF and J_{sc} . Previous reports have ascribed the performance difference to low electron mobility, limited exciton diffusion length and unfavorable nano-scale morphology in all-polymer solar cells.^{4d, 6, 8} The revealed mechanisms, however, are far from clear. Furthermore, a systematic comparison between polymer/fullerene and polymer/polymer system is urgently needed to obtain deeper understanding of the limitation for current all-polymer solar cells, leading to new insight into the future material design and device fabrication. Therefore, we performed in-depth comparison between PTP8/[70]PCBM and PTP8/N2200 based polymer solar cells. In particular, we investigate (1) charge generation and transport; (2) geminate and non-geminate recombination process, and (3) nano-scale film morphology difference in the two BHJ blend films.

2. Experimental

Characterization: UV-vis-NIR spectra were recorded on a Perkin Elmer model Lambda 750. DSC (Model Q-20) with about 3-5 mg samples at a rate of 10 °C / min in the temperature range of 30 to 350 °C. Tapping-mode AFM images were obtained with a Veeco Multimode V instrument, TEM images were performed on Tecnai G2 F20 S-Twin Transmission Electron Microscope. GIWAXS measurements were performed at the Stanford Synchrotron Radiation Lightsource (SSRL) on Beamline

11-3, with a MAR345 image plate area detector, at 12.7 keV incident photon energy, and at incident angles of 0.12°. The crystal correlation lengths (CCL) were estimated by the following equation: $CCL = \frac{2\pi}{FWHM}$, Where FWHM is the full-width-at-half-maximum of the fitted Gaussian.

Solar Cells Device Fabrication and Characterization: Solution-processed solar cells devices with conventional architecture of ITO/PEDOT:PSS/active layer/LiF(0.6 nm)/Al (80 nm) were fabricated. The ITO-coated glass substrates were firstly treated with UV/ozone for 20 min, PEDOT:PSS (Clevios PH or Al 4083) layer was deposited and dried at 150 °C in ambient atmosphere for 10 mins. Active layers were spun at a spin rate of 1500 rpm from PTP8/[70]PCBM (w/w=1/0.8, 14.4 mg/mL, chloroform+1.5% DIO, thickness: 95 nm) and PTP8/N2200 solutions (w/w=1/0.5, 12 mg/mL, chloroform+0.5% DIO, thickness: 85 nm), the thickness was measured by profilometer, cathodes were deposited by sequential thermal evaporation of 0.6 nm of LiF followed by 80 nm of aluminum. The device area was 7.25 mm². The current density-voltage characteristics of the photovoltaic cells were measured using a Keithely 2400 (I–V) digital source meter under simulated AM 1.5G solar irradiation at 100 mW/cm² (Newport, Class AAA solar simulator, 94023A-U). The light intensity was calibrated by a certified Oriel Reference Cell (91150V) and verified with a NREL calibrated Hamamatsu S1787-04 diode. The external quantum efficiency (EQE) was performed using a certified IPCE instrument (Zolix Instruments, Inc, SolarCellScan100).

EL measurements: an Oriel optical light guide was located close to the biased cell and connected to the entrance slit of the spectrometer. A Newton electron-multiplying CCD (charge-coupled device) Si array detector cooled to $-60\text{ }^{\circ}\text{C}$ in conjunction with a Shamrock sr 303i spectrograph from Andor Technology served as the emission-detection system. The system was wavelength-calibrated by an argon lamp to a resolution better than 0.5 nm . The transmission of the entire fiber-monochromator-CDD system was further radiometrically calibrated by an Optronic OL245M standard spectral irradiance lamp. The CCD detector is ‘back illuminated’, which increases the sensitivity but unfortunately also gives rise to some interference effects at wavelengths between 850 and 1000 nm .

Transient Transmission Spectroscopy (TAS) measurements: The TAS measurements were performed in an optical cryostat under vacuum at room temperature. For transient absorption spectroscopy, the laser source was a Ti:Sapphire amplifier laser whose center wavelength is 800 nm , the pulse width and the repetition rate are 120 fs and 1 kHz respectively. The pump pulses used in our measurement is 400 nm , which were obtained through doubling the amplifier’s fundamental output with a beta barium borate (BBO) crystal. The pump beam was modulated by a mechanical chopper at the frequency of $\sim 325\text{ Hz}$ and focused on the sample with a spot diameter of $\sim 3\text{ mm}$. We focused the fundamental 800 nm light onto a sapphire plate to generate the supercontinuum white light, which passed through the different color filters with a 10 nm bandwidth, serving as the probe pulses in the range of $500\text{--}1000\text{ nm}$. The pump and probe beam were spatially overlapped on the

sample, and the probe light has much smaller energy density than the pump beam. The transmitted probe beam was detected by a silicon photodiode connected to a lock-in amplifier.

GIWAXS measurements: The 2d-GIWAXS patterns were obtained at the Stanford Synchrotron Radiation Lightsource (SSRL) beamline 11-3 with an X-ray wavelength of 0.9752 Å, at a 40 cm sample to detector distance at an incidence angle of 0.12°. Samples were probed with an exposure time of 20 s while under a helium environment to minimize beam damage and reduce diffuse scattering. The measurements were calibrated using a LaB6 standard.

3. Results and Discussion

2.1. Molecular Structure and Solar Cell Performance

The chemical structures and energy levels of PTP8 and [70]PCBM/N2200 are shown in Figure 1. The energy levels of PTP8/[70]PCBM and PTP8/N2200 can both form a type II band structure, allowing exciton dissociation at the donor/acceptor interface. The film absorption spectra of the adopted polymers are shown in Figure S1a. The donor polymer PTP8 with a wide optical bandgap of 1.78 eV exhibits good absorption in the visible region, ending at ~700 nm. The absorption of pristine N2200 is stronger and broader (optical band-gap of 1.46 eV) compared with fullerene acceptors, showing an absorption edge at ~850 nm (Figure S1b), which is complementary to the absorption of PTP8. It is worth noting that the vibronic peak of PTP8 in PTP8/N2200 blend film is enhanced compared to that in PTP8/[70]PCBM

film, suggesting enhanced solid state order of PTP8 in the all-polymer blend, as shown in Figure S1b.

Figure 1. Chemical structures of donor PTP8 as well as acceptor [70]PCBM and P(NDI2OD-T2); the energy levels of these materials; schematic illustrations of solar cell device configuration and *J*-*V* curves of optimized PTP8/[70]PCBM and PTP8/N2200 solar cell devices measured under AM 1.5 G solar illumination (100 mW/cm²)

The conventional device architecture of ITO/PEDOT:PSS/Active layer/LiF/Al (Figure 1) was adopted.[14-15] As show in Figure 1 and Table 1, the optimized PTP8/N2200 BHJ device exhibits a V_{oc} of 0.98 V, which is slightly higher than the 0.96 V of PTP8/[70]PCBM system. However, both the J_{sc} and FF are notably decreased (8.4 mA/cm² vs 11.0 mA/cm², 0.53 vs 0.59 V), resulting in a decrease of PCE from 6.2% for PTP8/[70]PCBM to 4.4% for PTP8/N2200. The result seems contradictory to the merit of all polymer solar cells since N2200 has stronger absorption than that of fullerene derivatives. We thus explored a few major loss mechanisms in the optimized PTP8/[70]PCBM and PTP8/N2200 solar cells to

interpret the PCE reduction.

Table 1. Characteristics of optimized solar cells of PTP8 with [70]PCBM or N2200 as the acceptor

	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE ^{a)} (%)	E_{loss} ^{b)} (eV)	μ_h ^{c)} (cm ² V ⁻¹ s ⁻¹)	μ_e ^{c)} (cm ² V ⁻¹ s ⁻¹)
PTP8/[70]PCBM	10.5 ± 0.5	0.95 ± 0.01	0.59 ± 0.02	6.0 ± 0.2	0.78	3.0 *10 ⁻⁴	2.8*10 ⁻⁴
PTP8/N2200	8.4 ± 0.4	0.97 ± 0.01	0.52 ± 0.02	4.1 ± 0.2	0.53	5.6 *10 ⁻⁵	3.0*10 ⁻⁵

^{a)} The a values were obtained from at least 6 devices.; ^{b)} $E_{loss} = E_g - eV_{oc}$, E_g was calculated from the onset of EQE curves; ^{c)} The values were obtained from SCLC method.

2.2 V_{oc} Loss

Although in our case the V_{oc} of all polymer solar cell is slightly higher than that of corresponding polymer/fullerene devices, it is still of general interest to study the V_{oc} loss mechanisms in all polymer solar cells and investigate their possible potential in realizing high V_{oc} devices. The V_{oc} loss, also known as energy loss (E_{loss}), was generally defined by $E_{loss} = E_g - eV_{oc}$.¹⁶ E_g was the bandgap of the donor or acceptor material whichever has a smaller bandgap, generally calculated from the onset of the corresponding devices EQE curves.¹⁶⁻¹⁷ In this work, we calculated $E_g = 1.74$ eV for PTP8/[70]PCBM blend and $E_g = 1.50$ eV for PTP8/N2200 blend. While similar V_{oc} values were obtained for both devices, the E_{loss} is notably decreased (0.53 eV vs 0.78 eV) for all polymer solar cells (**Table 1**), largely due to the smaller E_g resulting from the narrower bandgap of polymer acceptor N2200. It is well known that for most polymer/fullerene solar cell devices, the eV_{oc} is usually significantly lower than the energy of absorbed photons, resulting in a large E_{loss} of more than 0.7 eV.¹⁷ In

comparison, the quite low E_{loss} of 0.53 eV in our case is among the lowest values for PSCs. More investigations were subsequently carried out to study the details of E_{loss} in both systems. As shown in Figure 2a, in polymer solar cells, the energy loss is determined by the loss from excitons (singlet state, S1) to charge transfer states (CTs) as well as the loss between CTs and the final V_{oc} . As electrons and holes transport in the active layer, they may recombine through available states. For the bulk heterojunction structure, the lowest energetic state that allows for recombination is the

Figure 2. a) Schematic diagram of the energy levels of both PTP8/[70]PCBM and PTP8/N2200 solar cell devices to illustrate voltage losses incurred from photon absorption to V_{oc} ; b) The electroluminescence (EL) spectra of neat PTP8, neat N2200, PTP8/[70]PCBM and PTP8/N2200 blend films.

CT state. Thus to locate the position of CTs is important for understanding the V_{oc} loss. Electroluminescence (EL) is an easy way to detect the presence as well as the position of CT states.¹⁸ However, note that the position of the EL maximum can be influenced by the reorganization energy of the CT state and might additionally by the red-shift due to inhomogeneous broadening. From the EL spectra measured for the blends shown in **Figure 2b**, we can observe the emission peak (or bump) around 1000 nm together with those of pristine PTP8 (770 nm) and N2200 (866 nm), which is

assigned to the EL of CTs. The CTs emission peak of PTP8/PCBM is quite close to that of PTP8/N2200, with only a slight red-shift. The resemblance of CT position indicates similar value of V_{oc} for both system, which is in accordance with the small difference (-0.02V) of their V_{oc} for the corresponding devices (Figure 2a). It is not surprising the position of CTs is similar since the energy levels of PCBM and N2200 are relatively close, as shown in Figure 1. Thus in our all-polymer solar cells, there is no extra V_{oc} loss compared with polymer/PCBM system, since no apparent shift of CTs is observed. On the contrary, the energy loss is largely reduced as a benefit of using N2200 acceptor with a narrower band-gap. However, it is worth noting that large photon energy loss may assist charge separation as it usually provides higher driving force to separate CTs pairs and help to get higher IQE and EQE.

1. Photo-Current Loss

To investigate the possible loss of photo-current in all-polymer system, the external quantum efficiency (EQE) and the absorption (extracted from reflection spectrum (R) by $100\% - R$) of optimized PTP8/[70]PCBM and PTP8/N2200 devices have been measured, as shown in Figure 3a and Figure S1b. We can observe that the maximum value of EQE for PTP8/N2200 only reaches ~40%, significantly lower compared to the value of ~60% for PTP8/[70]PCBM device. The J_{sc} calculated by integrating the EQE curve is 10.5 mA/cm^2 and 8.3 mA/cm^2 for PTP8/PCBM and PTP8/N2200, respectively, which is within 5% error compared to the corresponding J_{sc} obtained from the J - V curves. To further consider the effect of absorption on the EQE result, the internal quantum efficiency (IQE) of both systems was also measured.

Figure 3. a) EQE and IQE curves of the optimized PTP8/[70]PCBM and PTP8/N2200 solar cells; b) J_{sc} as a function of light intensity; c) characteristics of photocurrent density (J_{ph}) versus effective voltage (V_{eff}), insert shows the corresponding dark $J-V$ characteristics.

The IQE of a solar cell is defined as the percentage of absorbed photons that are successfully converted to current. The IQE of the optimized devices have been calculated using EQE result shown in Figure 3a and the absorption spectra shown in Figure S1b,[19] with the resultant IQE shown in Figure 3a. Firstly, we can see that the

absolute absorption of all-polymer devices is broader and stronger than that of polymer/fullerene ones. Consequently, the difference between their IQE values is more pronounced than that of EQE. Thus the photon conversion efficiency of PTP8/[70]PCBM is much higher than that of PTP8/N2200. Meanwhile, the average IQE value in the region between 700 and 850 nm for PTP8/N2200 is only ~25 %, which is only about half of the value for the visible region (~50 %). Since the IQE value in the long wavelength region is contributed from the polymer acceptor N2200 only, the strong polymer absorption and low IQE value indicate extremely low conversion efficiency for the photons absorbed by the polymer acceptor. Thus serious photo-current loss exists in our all-polymer system, which may be the major factor limiting its device performance. To resolve the current loss mechanism, we carried out detailed investigation on carrier generation, transport and recombination, since they are important in determining the solar cell device performance.²⁰

2.4 Carrier Generation, Transport and Recombination

The carrier mobility was firstly studied by using the space charge limited current (SCLC) method, which is an important factor for solar cell device performance. In addition, both the electron and hole mobility are crucial to achieve efficient and balanced carrier transport. To compare the charge transport properties of PTP8/[70]PCBM and PTP8/N2200 blends, hole only and electron-only diodes were fabricated and measured (see Supporting Information).²¹ As shown in Figure S2 and Table 1, the hole and electron mobilities of the optimized PTP8/[70]PCBM blend are $3.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $2.8 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, which are about one order

larger than those of the optimal PTP8/N2200 blend. Nonetheless, both systems have relatively balanced hole/electron transport. The superior electron transport in PTP8/PCBM blend film can be attributed to the high electron mobility and unique three-dimensional electron transport pathways of fullerenes.²² The higher carrier mobility in PTP8/PCBM system may be one of the factors for its relatively higher FF than that of the all-polymer devices.

The dependence of J_{sc} on light intensity was measured to examine if non-geminate recombination might significantly limit the carrier transport and J_{sc} . In J_{sc} -light intensity measurements, the J_{sc} should follow a power law relationship as $J \sim I^\alpha$ where $\alpha < 1.0$ is indicative of the extent of bimolecular recombination in the film.²³ As shown in Figure 3b, for the optimized device, J_{sc} scales almost linearly with light intensity ($\alpha=0.99$ for PTP8/[70]PCBM and $\alpha=0.95$ for PTP8/N2200). The relatively lower values of FF and α in all-polymer system indicate less efficient carrier transport and increased bimolecular recombination,^{4d} which, however, seems not like a determining factor for its low J_{sc} . Additionally, as shown in Figure S3, the V_{oc} of optimal PTP8/N2200 devices exhibits a logarithmic dependence on light intensity with a slope of 1.05 kTq^{-1} compared to that of 1.01 kTq^{-1} in PTP8/PCBM system. A system with purely bimolecular recombination may appear to have a slope $>1.0 \text{ kT/q}$.^{24b} Thus, the slightly increased slope in PTP8/N2200 is again suggesting increased bimolecular recombination. To further understand the whole charge extraction process, as shown in Figure 3c, the dependence of the photocurrent density (J_{ph}) on the effective voltage (V_{eff}) were recorded under illumination at 100 mWcm^{-2} .

J_{ph} is equal to $J_L - J_D$, where J_L and J_D are the measured current under illumination and in dark, respectively. V_{eff} is equal to $V_0 - V_a$ where V_0 is the voltage when J_{ph} is zero and V_a is the applied voltage.²⁵ At low effective voltage below 0.5 V, the J_{ph} of PTP8/[70]PCBM increases drastically and reaches a plateau at higher voltage, suggesting that free carriers are swept out efficiently. In comparison, the J_{ph} of PTP8/N2200 increases with a slower rate, indicating less efficient carrier transport. More importantly, the J_{ph} of the latter is significantly smaller than that of the former at all applied voltage, which is in accordance with its lower IQE value. Considering that the all-polymer film has even better absorption, its smaller J_{ph} suggests that the carrier generation process for all-polymer system must be much less efficient than that of polymer/fullerene system.

2.5 Ultrafast Transient Transmission Spectroscopy

To further probe the charge generation dynamics in the blend films, photoluminescence (PL) measurements was performed at first to assess the exciton quenching efficiency in PTP8/N2200 and PTP8/[70]PCBM, as shown in Figure S4. We can observe that the PL in both systems is quenched efficiently while the quench efficiency of PTP8/PCBM is slightly higher than that of PTP8/N2200 blend (see insert), which implies that exciton diffusion to the donor/acceptor heterojunction and subsequent charge-transfer events are efficient in both systems. Subsequently, we performed the ultrafast transient transmission (TA) spectroscopy measurement.²⁶ Figure 4 show the transient differential transmission ($\Delta T/T$) spectra of the neat and blend films at different time delays after the pump pulse excitation at 400 nm. For the

Figure 4. The transient absorption spectrum of the neat PTP8 (a), neat N2200 (b), neat [70]PCBM (c), PTP8/N2200 blend (d) and PTP8/[70]PCBM (e) blend films at different time delays with the excitation wavelength of 400 nm and intensity of $70 \mu\text{J cm}^{-2}$; (f) steady-state photoinduced absorption spectrum of neat and blend films.

neat N2200 film (Figure 4b), we observe the transient photoinduced bleaching (PB) signals in the range of 600-750 nm, which can be attributed to the ground state bleaching, and the photoinduced absorption (PA) signals around 500 nm and 850 nm, which arise from the absorption of the excitons. These transient signals decay very quickly and greatly diminish at the time delay $\Delta t = 100$ ps. However, we note a weak but long-lived positive component beyond 500 ps in the range of 650-850 nm, which may be due to the HOMO depletion as a result of the formation of triplet excitons via

intersystem crossing.²⁷ For the neat PTP8 film (see Figure 4a), we can identify two pronounced transient PB peaks centered around 650 nm and 550 nm, which coincide with the polymer's two static absorption peaks (Figure S1a). The recovery of the transient PB signal represents the recombination process of the excitons generated in the PTP8, which occurs at the time scale of 100 ps. For the PTP8/N2200 blend film, the overall transient PB signals at 650 nm are contributed from both PTP8 and N2200. However, the PB signals at 750 nm arise only from N2200 because of the negligible transient signal in the neat PTP8 film probed at this wavelength, thus allowing us to separate the two contributions to the 650-nm PB signals at the peak position ($\Delta t \approx 1$ ps) in the blend film. We estimate only ~15% spectra weight contributed from the N2200 at 650 nm in the blend film. In addition, the decay of this PB signal from the N2200 can be compensated by the hole transfer from the N2200 to PTP8. Therefore, the fast decay of the transient PB signal in the blend film is mainly caused by the geminate recombination of excitons generated in the PTP8 domain. Figure 5b shows the dynamics of transient PB signal from the PTP8 at 650 nm after deducting the contribution from the N2200 (the middle curve). The PB signal at 650 nm arising from the PTP8 can be divided into two parts: 1) the rapid decay within 50 ps, and 2) the slow decay after 50 ps. The rapid decay is due to the direct recombination of photoexcited excitons within the PTP8, and also the recombination of coulombically attracted electrons and holes that can't escape the interface in time. Both recombination processes belong to the geminate recombination. The slow decay part after 50 ps corresponds to the free charge recombination process corresponding to the

non-geminate recombination. The non-geminate recombination time is on the order of nanosecond. This thus means that the contribution of the non-geminate recombination to the decay of the PB signal is negligible within 50 ps. Hence, the decay within 50 ps is the consequence of the geminate recombination. From the decay of the PB signal of slightly more than 50% within 50 ps, we then have determined that nearly 50% charges recombine geminately. The remaining excitons are dissociated at the interface and successfully generate long-lived charge carriers, manifested as the slow decay of the PB signal after 50 ps. In this evaluation, we assume that the amplitude of the PB signal is proportional to the number of PTP8 excitons (holes in the HOMO of PTP8).²⁸ We also observe the long-lived PA signals around 900 nm originated from the absorption of hole polaron in PTP8 formed after the charge transfer, which is consistent with the results of the continuous wave pump probe measurements (Figure 4f).

Figure 5. The transient signal dynamics of the neat PTP8 film and PTP8/[70]PCBM blend film (a), the neat PTP8 film and PTP8/N2200 blend film (b) probed at 650 nm under excitation intensity $70 \mu\text{J cm}^{-2}$ with the wavelength of 400 nm. The middle line is the dynamic process of the transient

signal caused by the PTP8 exciton in the blend film.

Compared to the neat PTP8 film, the transient PB signals of the neat [70]PCBM film probed at 650 nm are much weaker (see Figure 4c). Thus the transient PB signals at 650 nm in the blend film are dominated by the contributions from the PTP8 component, as shown in Figure 5a, there is hardly any change of the 650-nm PB signal at the time scale of 100 ps for the PTP8/[70]PCBM blend film, indicating the efficient electron transfer from PTP8 to PC₇₁BM and negligible geminate recombination of the PTP8 excitons. If the fast decay of the PB signal within 2 ps is considered as the contribution of the geminate recombination, the geminate recombination ratio is calculated to be only 6.7%, as shown in Figure S5. This suggests that nearly all of the PTP8 excitons can dissociate to yield electron transfer from the PTP8 to [70]PCBM through the interface. The slow decay process after 100 ps can be attributed to the weak bimolecular recombination. We note from **Figure 5** that the bimolecular recombination is similar for both PTP8/[70]PCBM blend and PTP8/N2200 blend. Nevertheless, the much more efficient electron transfer in the PTP8/[70]PCBM blend film can restrain the geminate recombination of the PTP8 excitons and facilitate the charge carrier generation.^{4b} Therefore, the better carrier generation in PTP8/[70]PCBM solar cell may be the prominent factor for its significantly higher J_{ph} than that of the PTP8/N2200 all-polymer solar cell.

In order to evaluate the impact of bimolecular recombination and possible exciton-exciton annihilation on the overall charge generation and collection, we performed the pump fluence dependence of PB dynamics at 650 nm for both

PTP8/N2200 and PTP8/PCBM blend films (Figure S6). For different pump fluence in PTP8/N2200, the PB signals at delay time longer than 100 ps display a similar slow recovery. However, at short time scale within 50 ps, we note a slower decay at smaller pump fluence and the decay rate becomes unchanged below $14 \mu\text{J cm}^{-2}$. This indicates that the exciton-exciton annihilation may play a role for high pump fluence. For the pump fluence of $7 \mu\text{J cm}^{-2}$ which yields a carrier density comparable to that under one solar illumination, we determine a geminate recombination ratio of $\sim 50.3\%$ (See Figure S7). Thus, we may conclude that more than half of excitons are geminately recombined in PBPT/N2200 for the application relevant situation. As a comparison, the PB signals at 650 nm in PTP8/PCBM also show slower decay at short time scale within 50 ps, because of reduced exciton-exciton recombination, with decreasing pump fluence. Consequently, for pump fluence below $7 \mu\text{J cm}^{-2}$, the PB signal at time scale within 150 ps even exhibits a small increase, which is possibly due to the contribution from the hole transfer from [70]PCBM to PTP8 and the recovery of absorption signal from [70]PCBM. This result corroborates efficient charge transfer in PTP8/PCBM with electron transfer efficiency nearly to 100%. In addition, the PB recovery at long time scale in PTP8/PCBM becomes somewhat faster with increasing pump fluence, indicating bimolecular annihilation is stronger for high pump fluence. For pump fluence below $7 \mu\text{J cm}^{-2}$, the charge annihilation induced PB recovery is very slow, similar to that in PTP8/N2200.

2.6 Morphological Characterization

Previous works¹⁻² have demonstrated that the exciton dissociation and charge

transport process is strongly affected by the polymer/PCBM blend morphology. Therefore, a thorough morphological study may be helpful to understand the less efficient carrier generation and transport process in all-polymer solar cells. The morphology of optimal PTP8/[70]PCBM and PTP8/N2200 blend films were first examined by atomic force microscopy (AFM) (Figure 6a-6b). By adopting alkyl aromatic side-chains to both D/A co-monomers in donor polymer PTP8, the increased side-chain rigidity and bulkiness can prevent the intercalation of fullerenes at a

Figure 6. AFM and TEM images of PTP8/[70]PCBM (a,c) and PTP8/N2200 (b, d) blend films.

molecular level.¹⁵ The enhanced packing and reduced π - π stacking distance further promote the polymer: fullerene demixing, leading to a rougher surface (RMS 3.6 nm) and larger domain size. In contrast, the PTP8/N2200 blend films exhibit smooth surface, with a moderate RMS of 1.8 nm. In order to gain insight into the phase

separation, we also investigated the film morphology by using transmission electron microscopy (TEM), as shown in Figure 6c-6d. For PTP8/[70]PCBM, the donor polymer exhibits an ideal nanofiber structure, which is beneficial for carrier transport. In addition, the diameter of the polymer fiber can be estimated to be around 10 nm, which can assure efficient exciton dissociation. In contrast, the blend film of PTP8/N2200 shows quite different blend morphology, without any apparent polymer fiber structure. Coupling the AFM and TEM results, the well mixed all-polymer blend morphology may interpret the relatively lower carrier mobility but cannot fully account for the inefficient carrier generation efficiency.

Figure 7. DSC curves with a heating rate of 10 °C/min under an inert atmosphere (N₂).

It has been reported that organic blend may form interesting morphology like alloy,^[27] which may in turn dramatically affect the properties of the blend film. In order to thoroughly study the phase separation morphology in all-polymer blends, we performed differential scanning calorimetry (DSC) measurements to detect possible

thermal transitions in both neat and bulk films.²⁷ Herein, we performed DSC measurements on the powder samples, as the second scans shown in **Figure 7**, [70]PCBM exhibits a cold crystallization temperature of 193 °C²⁹ and a melting temperature of 320 °C. N2200 exhibits a sharp DSC peak at 320 °C and a subsequent peak at 300 °C upon cooling. However, no transition peak can be observed when heating or cooling PTP8, implying no significant endothermic transitions or a nontrivial thermal relaxation process.³⁰ When blending PTP8 with [70]PCBM, we observe no thermal transition peak of [70]PCBM during the heating cycle of PTP8/[70]PCBM blend, indicating strong interaction between polymer and fullerene. In contrast, endothermic transitions of N2200 can be observed in the PTP8/N2200 blend, suggesting the component in the all-polymer blend can still retain their individual phases and properties. This simple mixing can avoid the effect of more complex factors on the carrier dynamics in all-polymer blend. Thus we conducted X-ray diffraction to further probe the fine morphology structures of PTP8/N2200, hoping to finally reveal the reason for low carrier generation efficiency.

2.7 Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) Measurements

We performed grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements to investigate the microscopic structures of the films.³¹ Two-dimensional (2-d) scattering images of PTP8 and N2200 neat polymer films are shown in Figure 8a. In both films, a diffraction spot corresponding to the π - π stacking structure appears along the q_z axis (out-of-plane direction) at $q = 1.72 \text{ \AA}^{-1}$ and $q = 1.60 \text{ \AA}^{-1}$, which corresponds to a stacking distance of 3.61 Å and 3.93 Å, respectively,

suggesting a preference for face-on orientation. When blending PTP8 with electron acceptor [70]PCBM, we can still observe its π -stacking diffraction peak (Figure S8), suggesting that PTP8 partially retains its packing orientation in the blend film. Meanwhile, we observe a broad diffraction ring around $q = 1.50 \text{ \AA}^{-1}$ for PCBM. For N2200, the strong π -stacking diffraction peak of neat N2200 is convoluted in the blend with the PTP8 π -stacking diffraction peak, while the alkyl-stacking peaks of N2200 and π -stacking peaks of PTP8 are clearly observable for the blend film. The

Figure 8. a) Two-dimensional GIWAXS image of the neat polymer and blend films; insets: close-up of the lamellar (100), diffraction region; b) Pole figures extracted from the (010) and c) (100) diffraction for the neat polymer and blend film, definitions of the polar angle (χ) range corresponding to the edge-on and face-on crystallites are shown.

weak π -stacking and strong lamellar packing of N2200 may be attributed to several reasons, including polymer miscibility, D/A ratio, and processing solvent, etc.³² More precisely, the crystal correlation lengths (CCL)³³ were calculated from the (010) peak in the out-of-plane direction (Table 2), showing the following results: 3.6 nm for neat PTP8 film, 4.5 nm for neat N2200 film, 4.1 nm for PTP8 in PTP8/[70]PCBM blend film and 4.3 nm for PTP8 in PTP8/N2200 blend film. These results indicate that PTP8 can develop a certain degree of π -stacked crystallites in both neat and blend films, which is useful for charge transport. N2200 mostly shows alkyl-stacked crystallites in the in-plane direction in the blend film. Considering the fraction of N2200 is relatively low in the all-polymer blend, we have directly compared the diffraction peak intensities of the blends with those of the pure films to gain insight into the change of packing orientation upon blending. Pristine N2200 is a semi-crystalline material,¹³ with both well-ordered crystallites and disordered fractions. The ordered regions usually demonstrate better charge transport, larger exciton and charge delocalization than the amorphous regions.^{32a} Therefore, the reduced π stacking of N2200 in the all-polymer blend may thus hinder the exciton dissociation and subsequent charge transport.

We also carried out an in-depth pole figure analysis on the 2-d GIWAXS patterns to probe the molecular orientation (Figure S8).³¹ The microscopic structure of the donor and acceptor at the heterojunction can affect the generation and dissociation of excitons.³⁴ Thus the relative backbone orientation of the donor/acceptor may also play an important role. For the neat film, the integrated intensities of (010) peak along the

polar angle χ (as marked area in **Figure 8a**) in the range of 0–45° and 135–180° (A_{xy}) denote the contribution of π -stacking edge-on crystallites, while those in the range of 45–85° and 95–135° (A_z) correspond to the fractions of face-on crystallites. For the blend film, the (100) peak with higher intensity was used for calculation. The integral with polar angle χ in the ranges of 0–45° as well as 135–180° (A_{xy}) and 45–135° (A_z) denote the contribution of lamellar face-on and edge-on crystallites, respectively.³⁵

Figure 8b-8c show the pole figures extracted from the π -stacking diffraction (010) and lamellar diffraction (100), respectively. As shown in **Table 2**, it is interesting to note that the ratio of face-on/edge-on crystallites for the neat polymer films is 2.70 and 2.84 for PTP8 and N2200 respectively, confirming that there is a large population of polymer crystallites with the face-on orientation in neat films. In contrast, the portion of face-on oriented crystallites was about 70% and 65% in PTP8/[70]PCBM and PTP8/N2200 blend film, respectively, indicating that edge-on and face-on crystallites co-exist in the blend film with a very close ratio of 2.3 and 1.9. Therefore, it is evident that at the bulk-heterojunction in the all polymer blend, the donor and

Table 2. Characteristics of in-plane (100) peak and out-of-plane (010) peak from GIWAXS measurements.

	Lamellar distance (Å)	π -stacking distance (Å)	CCL alkyl-stacking (nm)	CCL π -stacking (nm)	Face on /Edge-on crystallites (ratio)
PTP8	26.5	3.61	17.5	3.6	80%/20% (4.0)
N2200	24.4	3.93	26.2	4.5	90%/10% (9.0)
PTP8/[70]PCBM	26.6	3.61	20.5	4.1	70%/30% (2.3)
PTP8/N2200	25.5	3.61	17.9	4.3	65%/35% (1.9)

acceptor will very likely adapt different packing orientation. These results indicate that the proper packing orientation and degree of crystallinity in polymer may be helpful to efficiently dissociate electron-hole pairs into free charge carriers. For very anisotropic all-polymer system, to well control the orientation and crystallinity of both donor and acceptor crystals at the BHJ blend is a challenging task.³⁶ However, fullerenes are spherically symmetric materials which can have close contact with the donor molecules in arbitrary directions to achieve efficient charge transfer. Meanwhile, fullerene derivatives tend to form highly crystalline domains with large charge delocalization which will lower the Coulomb barrier and hence improve exciton dissociation.^{32c} Fullerene crystallization was also reported to increase its electron affinity and generate energetic driving force to spatially separate electrons and hole.^{34b} In addition, fullerene derivatives exhibit unique three-dimensional electron transport and high mobility of roughly around $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in most BHJ blend film, which is critical for the weakly attracted electrons to escape from the heterojunction. In comparison, the reduced π - π stacking of N2200 and unfavorable orientation in the all polymer blend leads to limited charge delocalization, inefficient carrier transport³⁷ and larger potential barrier, resulting in apparent disadvantage for

Figure 9. Schematic illustrations of PTP8/[70]PCBM (left) and PTP8/N2200 blend films in the PSCs.

charge separation and transport. As shown in **Figure 9**, we propose a schematic illustrations for the BHJ blend morphology of the two compared systems. In conventional PTP8/[70]PCBM cells, PTP8 crystallites are mixed with PCBM with random orientations. The heterojunctions between crystalline polymer and fullerene phase exhibit efficient charge separation without the need for preferential packing orientation. In contrast, in the PTP8/N2200 cell, the N2200 show weak π -stacking order than PTP8, the unfavorable crystal orientation and low degree of π -stacking in polymer acceptor domains may greatly hinder the electron-hole pairs dissociation into free charge carriers, resulting in inefficient separation of geminate pairs as well as increased bimolecular recombination of free carriers. This model is in good agreement with the morphology characterization as well as lower J_{sc} and FF of the all polymer devices compared with the polymer/fullerene ones.

4. Conclusion

In summary, we have investigated the major loss mechanisms in all polymer solar cells based on PTP8 and the mostly used polymer donor N2200, by performing in-depth comparisons between PTP8/PCBM and PTP8/N2200 blends, in terms of charge generation, transportation and recombination, as well as the bulk-heterojunction morphology. Apparently, the all polymer blend exhibits lower V_{oc} loss, which can theoretically further improve the device performance. However, from ultrafast transient transmission spectroscopy analysis, we can estimated that in

PTP8/N2200 device almost half of the charges recombine geminately, which is confirmed as the major factor hindering the device PCE of the current all polymer solar cells compared with polymer/fullerene system. Through thorough GIWAXS analysis, the low charge generation efficiency is attributed to the unfavorable morphology in the all-polymer blend compared with the polymer/fullerene system.³² Coupling these results with knowledge from efficient polymer/fullerene systems, the future design of new polymers can aim to increase the attraction between the π face of donor and acceptor, leading to improved crystallinity at the heterojunction and well controlled packing orientation in the all-polymer system.

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Graphical Abstract: