Effect of regioregularity on recombination dynamics in inverted bulk heterojunction organic solar cells

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Abstract
The effect of polymer regioregularity on the charge transport properties and bimolecular recombination rates of polymer-based solar cells is studied in detail using transient photovoltaic techniques. We compare organic solar cells fabricated with an ITO/ZnO/PEIE/P3HT:PCBM/MoO\textsubscript{3}/Ag structure using either 100\% regioregular poly(3-hexylthiophene) (DF-P3HT) yielding an average power conversion efficiency (PCE) of 3.8 ± 0.3\% or 92\% regioregular P3HT (rr-P3HT) that yields an average PCE of 3.28 ± 0.4\%. Transient photocurrent measurements reveal the presence of less mobile photoinduced charges in rr-P3HT:PCBM cells when compared to DF-P3HT:PCBM solar cells. Transient photovoltage measurements are used to establish the relationship between regioregularity and bimolecular recombination rate constant ($k$) finding that under 1 Sun, devices with high regioregularity have a longer $\tau$ despite having a higher $k$. The high value of $k$ for the DF-P3HT:PCBM system as compared to the rr-P3HT:PCBM system is attributed to enhanced mobility and better charge transport of mobile charges in the DF-P3HT:PCBM system, consistent with enhanced fibrillar order in DF-P3HT films observed with transmission electron microscopy. We also note a slight decrease in cell open circuit voltage with increase in polymer regioregularity, which is due to the increase in $k$. Other recombination mechanisms such as trap-assisted recombination are found to be important in the lower regioregular P3HT device compounded by the reduced mobility and poor inter-chain ordering.

Keywords: organic solar cells, bimolecular recombination, defects, transient photovoltage

\textsuperscript{\dag}Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

1. Introduction

Fullerene-based bulk heterojunction (BHJ) solar cells have reached efficiencies of over 10\% in recent years [1–3]. Understanding of loss mechanisms involved inside BHJ solar cells is important for enabling efficiency improvements. The loss mechanisms involved in a BHJ organic solar cell include geminate recombination, bimolecular recombination, trap-assisted recombination, surface/interface recombination along with losses due to current leakage and shunts [4–8]. Even though development and use of novel, low band-gap donor polymers in BHJ solar cells has enabled this technology to...
reach efficiencies beyond 10%; poly(3-hexylthiophene): [6,6]-phenyl C61 butyric acid methyl ester (P3HT:PCBM) remains a material system of prominent interest among the researchers because of its simple synthesis route and easy availability [9]. For P3HT:PCBM (chemical structure in figure 1(a)) BHJ solar cells it is found that losses associated with disorder affects charge transport inside the device and is more pronounced near the short circuit condition of the cell [10, 11]. On the other hand, bimolecular recombination which is also found to be a major loss mechanism is more prominent near the open circuit condition of the cell [11–13], strongly influencing device performance at the maximum power point. Since both these recombination processes are pivotal in determining the overall performance of the cell, it is important to separately study these recombination mechanisms and understand how they vary with material properties.

Transient photocurrent (TPC) experiments are well-suited to study the charge carrier dynamics inside a device at short circuit. In a TPC experiment the device is illuminated with a square light pulse with pulse width long enough for the device to reach steady state conditions. Examining the turn on and turn off response time of the device to the square pulse of different intensity gives information regarding the transport and collections properties occurring inside the device [10, 14]. To quantitatively determine the bimolecular recombination rate constant, the charge density (n) and carrier lifetime (τ) inside the device under operating conditions have to be obtained. There are a few techniques that have been employed to this end including time-of-flight [15], transient photovoltage (TPV) [13, 16], transient absorption spectroscopy (TAS) [17–19], charge extraction [13] and photocell (PEIE) [20]. Among the techniques mentioned above, TPV involves not only simple instrumentation, but can also be used on devices with standard film thicknesses and under standard operating conditions. Maurano et al showed that the values of n and τ derived from TPV are in good agreement with the values obtained from other measurement techniques [21]. The schematic representation of a typical TPV setup is shown in the figure 1(c).

It has been shown that the performance of P3HT-based BHJ solar cells depends on the polymer regioregularity (RR) established mainly by connecting steady-state solar cell characteristics with structural characterizations [22–25]. The degree of RR is defined as the percentage of alkylthiophene monomers forming head-to-tail (H–T) coupling instead of the less favorable head-to-head or tail-to-tail configurations. The H–T coupling facilitates a low energy planar configuration of the backbone and the formation of crystalline lamellae. Higher RR additionally promotes interchain order resulting in improved optical [26, 27] and electrical properties [22, 28, 29]. Even though detailed studies have been made on the effect of RR on the optoelectronic properties, charge transport and device performance [22, 23, 30], the influence of RR on the recombination dynamics inside the BHJ solar cells has not been explored in great detail [13, 17, 21]. In this paper, we probe the recombination mechanisms of P3HT:PCBM devices fabricated using 100% regioregular P3HT (DF-P3HT) and commercially available 92% regioregular P3HT (rr-P3HT).

We firstly establish a connection between the charge transport properties and bulk morphology of P3HT:PCBM blends using TPC studies. Secondly, employing TPV studies the bimolecular recombination rate of the blend is linked to the RR of the donor polymer, the background photoinduced carrier density and the recombination lifetime. This study provides fresh insight into the device physics of P3HT-based solar cells, in particular elucidating the role of P3HT RR on TPC and photovoltage profiles.

2. Experimental section

Solvents and materials were obtained from Sigma Aldrich and were used as received unless otherwise mentioned. Inverted solar cells were fabricated with the following architecture: ITO/ZnO/PEIE/P3HT:PCBM/MoO3/Ag. ITO-coated glass substrates were procured from Lumetec (sheet resistance 15 Ω sq−1) and were cleaned by ultra-sonicating in acetone and IPA consecutively, each for 10 min. Cleaned ITO substrates were then treated with air-oxygen plasma at an RF power 18 W for 10 min. A zinc oxide (ZnO) precursor solution was prepared from 0.1 M concentrated zinc acetate in 2-methoxyethanol solution. After spin-coating a thin film of the ZnO precursor film it was converted to ZnO by annealing at 200 °C in air for 10 min. Subsequently a thin layer of polyethyleneamine (PEIE) from a 0.4 wt% solution in a 2-methoxyethanol was coated and cured at 110 °C for 10 min in air. The substrates were then transferred into an N2-filled glove box (GB) for the spin coating of the active layer. Two polymer blend solutions were prepared: one with commercially available rr-P3HT (Rieke Metals 4002) with weight average molecular weight (MW) and dispersity of 51 kDa and 2.4, respectively, and the other with the DF-P3HT custom synthesized as per the procedure described in the supporting information [16, 21, 30, 31]. PC61BM was purchased from Nano C (Westwood, MA) and used as the acceptor in both cases. P3HT and PCBM with a weight ratio of 1:1 was dissolved in 1,2 dichlorobenzene (anhydrous 99%) at a concentration of 40 mg ml−1. The blend solution was spin-coated over the ZnO/PEIE-coated ITO substrates with the spin-coating parameters optimized to achieve the best performance in both the DF and rr-P3HT:PCBM devices. We found rr-P3HT:PCBM and DF-P3HT:PCBM cells performed best with an active layer thickness of ca. 130 nm and ca. 230 nm, respectively. The substrates were annealed at 150 °C for 10 min before deposition of the top electrodes. Please note that pre-annealing was performed rather than post-annealing since post-annealing is detrimental to the performance of inverted devices used here, with pre-annealing instead optimizing the performance of inverted cells [32, 33]. A hole extraction layer of MoO3 (15 nm) and silver top electrode (100 nm) were thermally evaporated at a pressure of 7 × 10−7 mbar inside a vacuum chamber that was integrated within the GB. The devices were encapsulated inside the GB with the Devcon 2-Ton Epoxy resin and a glass cover slide and taken out for characterization.

Dark and light current–voltage (J–V) characteristics of the solar cells were measured with a Keithley 2635 source meter.
A Photo Emission Tech model SS50AAA solar simulator was used to generate simulated sunlight (100 mW cm\(^{-2}\) AM1.5G) with the intensity of the solar simulator calibrated with reference silicon solar cell with KG3 filter (PV Measurements). External quantum efficiency (EQE) was measured by dispersing light from a tungsten halogen lamp (Newport 250 W QTH) through a monochromator (Oriel Cornerstone 130). The intensity of the light used in the EQE measurement was typically <1 mW cm\(^{-2}\), with the spot size employed smaller than the active area of the device. The spectral mismatch between solar simulator lamp and AM1.5G spectrum with respect to the P3HT:PCBM cell response was found to be ca. 0.99.

TPC measurements were performed by illuminating cells with a 200 \(\mu\)s square pulse from a Kingbright L-7104VGC-H green led (525 nm wavelength) driven by a function generator (Agilent 33522A). The rise time and fall time of the green LED is measured to be less than 50 ns with a Thorlabs DET10A/M Si photodetector. The TPC response was recorded on an Agilent Technologies InfiniiVision DSO-X 3032A digital oscilloscope (DOSC) using 50 \(\Omega\) oscilloscope termination [14]. Care has been taken to ensure that the TPC characteristics are not limited by the RC time constant of the circuit. The TPC curves were collected at different green light intensity (from 34.6 mW cm\(^{-2}\) to 2.7 mW cm\(^{-2}\)) excitation with and without the presence of 35 mW cm\(^{-2}\) DC background light. TPV measurements were performed by illuminating devices with a constant (DC background light) intensity high-power warm white LED (Thorlabs MWWHL3) with a small light perturbation that was provided by the same Kingbright green LED driven again by the Agilent 33522A function generator. A pulse width of 500 ns was used for the perturbation and the transient response of the cell recorded with the DOSC using 1 M\(\Omega\) input impedance. The intensity of the background white LED was changed to achieve different \(V_{OC}\) conditions of the device.

Transmission electron microscopy (TEM) measurements were performed at the Monash Centre for Electron Microscopy with a JEOL JEM 2100F FEGTEM operated at 200 kV in bright-field mode using a small (20 \(\mu\)m) objective aperture to enhance mass-thickness contrast.

3. Result and discussion

3.1. Device characterization and morphology

Average power conversion efficiencies of 3.28 ± 0.4% and 3.8 ± 0.3% were achieved for the rr-P3HT:PCBM and DF-P3HT:PCBM solar cells, respectively, averaged over 16 cells each (see figure 2(a) for average current voltage characteristics under simulated sunlight). The best rr-P3HT:PCBM cell showed an efficiency of 3.6% while the best DF-P3HT:PCBM cell achieved an efficiency of 4.1%. The solar cell parameters of the best devices and average PCE are summarized in the table 1. The device performance is influenced by other polymer characterization parameters like RR weight averaged MW and dispersity, \(D\). An increase in the MW of P3HT in particular has been found to hinder the fill-factor and carrier mobility of P3HT-based solar cells, resulting in a decreased performance of cells fabricated with high MW P3HT [34, 35]. In contrast, we observe the performance enhancement in the DF-P3HT based device which have high MW (MW = 88 kDa) than rr-P3HT (MW = 51 kDa) devices. And since these batches of P3HT have similar dispersity, we attribute the improvement in cell performance to the higher RR rather than differences in MW or dispersity. The increase in the efficiency of the DF-P3HT cell is largely the result of the increase in short-circuit current (\(J_{SC}\) and FF with cell \(V_{OC}\) dropping slightly with respect to the rr-P3HT-based cell. The increase in \(J_{SC}\) is also reflected in the increase in EQE over the 500nm to 620 nm wavelength range (see figure 2(b)), whereas improved
FF is attributed to better charge transport which will be discussed further in detail in the TPC analysis section. The integrated current values from the EQE spectrum for rr-P3HT and DF-P3HT devices are 7.5 mA cm\(^{-2}\) and 9 mA cm\(^{-2}\), respectively. We attribute this discrepancy to the small active area of the solar cells 0.045 cm\(^2\) [36]. A related study describing the effect of DF-P3HT on device performance has recently reported by us with structural, optical and steady-state results presented [37]. In particular it was shown that the increase in the performance of the DF-P3HT when compared to the commercially available rr-P3HT is connected with an improvement in interchain ordering [38, 39] and improved morphology. This is further supported by TEM images shown in figure 3. The images of the DF-P3HT:PCBM films show distinct fibrillar features extending up to hundreds of nanometers in length in contrast to the more nodular morphology (highlighted in the inset figure) of the rr-P3HT:PCBM blend. Such extended fibrils should support higher charge carrier mobilities and efficient charge collection. While the above and our previous study have examined the link between RR optical properties and molecular order, we further establish the link between RR and device performance through in-depth analysis of transient device behavior.

### 3.2. Transient photocurrent (TPC)

Figure 4 shows the TPC response of the rr-P3HT and DF-P3HT devices at short circuit condition to a 200 \(\mu\)s square pulse from a green LED with no background illumination. The raw data of the TPC response at different green LED light intensities is shown in the supporting information figure S1 (stacks.iop.org/JPhysD/51/015501/mmedia). Using 200 \(\mu\)s pulse width instead of using a short pulse excitation (few nano second using laser) [20] allows the device to reach the steady state condition. This permits us to examine the turn-on and turn-off dynamics of the devices under test. Additionally, exploring the turn-on and turn-off dynamics as a function of pulse intensity provides information regarding charge density dependent transport processes including trapping and detrapping effects [14, 40]. For systems with fast charge-pair dissociation and charge density independent transport, the time taken for the TPC curve to reach the steady state primarily depends on the charge carrier mobility with the shape of the curve independent of light intensity [10]. From the normalized TPC plots in figures 4(a) and (b) one can clearly observe that the rr-P3HT:PCBM device requires a longer time to reach steady state especially at lower light intensities. The rise time which is defined as the time take for the square response to go from 10% to 90% of its steady-state value is found to be 9.1 \(\mu\)s for the rr-P3HT cell at 2.7 mW cm\(^{-2}\) decreasing to 1.5 \(\mu\)s at 34.6 mW cm\(^{-2}\). On the other hand, for the DF-P3HT:PCBM devices the rise time is independent of the intensity of the green LED with rise time <3 \(\mu\)s for all curves. Examining the turn-off dynamics of the photocurrent curves, the initial fast decay of the curve is due to the collection of free charge carriers, while the delayed dynamics after the turn-off is attributed to the detrapping of trapped charges [14]. From figure 4(c) it is evident that rr-P3HT devices have long decay dynamics which are intensity dependent, whereas for DF-P3HT devices all the photocurrent decay overlaps with each other independent of the intensity. The monotonic rise of the transient peak with increase in the light intensity is indicated with an arrow. From these observations it is found that the rr-P3HT:PCBM device has poorer charge transport properties compared to the DF-P3HT:PCBM device at short circuit. This is in agreement with the mobility value reported by us where DF-P3HT:PCBM cells have ca. 3 times better hole mobility than rr-P3HT:PCBM solar cells [37]. The poor charge transport property in rr-P3HT:PCBM cells is primarily attributed to the presence of shallow traps. It is noteworthy that the rr-P3HT:PCBM device also has slower
transport kinetics with a thinner active layer thickness than the DF-P3HT:PCBM device.

We also examine the TPC response of the device in the presence of constant background DC light (35 mW cm$^{-2}$), see figure S1 in the supporting information. With background illumination the rise time of the rr-P3HT device reduces to ~5 µs for a pulse intensity of 2.7 mW cm$^{-2}$ and shows faster turn-off dynamics. This observation is attributed to the partial filling of shallow traps in the rr-P3HT:PCBM device with background illumination which quickens the rise and fall dynamics of the TPC curve [14, 36]. In contrast there is no change in the rise time for the DF-P3HT:PCBM cell with background illumination. Hence from the TPC experiment, it can be concluded that there are more traps present in the rr-P3HT device which hinder the charge transport property inside the blend when compared to the DF-P3HT device.

3.3. Bimolecular recombination

TPV measurements combined with differential charging measurements are used to measure the charge carrier lifetime ($\tau$) and the carrier density ($n$) of the devices held at open circuit under different light intensities [16, 41]. The intensity of the DC background illumination modifies the $V_{OC}$ and charge density in the device with the small perturbation provided by the pulsed LED inducing a small increase in carrier density, $\Delta n$. Since at open circuit no carriers can escape the device, they must recombine inside the device. From the decay profile of the open-circuit voltage signal that results the lifetime $\tau_{\Delta n}$ of the transient charges can be determined by fitting with a monoexponential curve. The raw data of the TPV curves at different background intensities and the exponential fits are shown in the supporting information (figure S2). The small perturbed charge carrier lifetime $\tau_{\Delta n}$ has an exponential relationship with the applied bias, as described in the equation below:

$$\tau_{\Delta n} = \tau_{\Delta n_0} \exp(-\beta V_{OC})$$

(1)

where $\beta$ is the rate at which the charge carriers decay with respect to the voltage. A plot of $\tau_{\Delta n}$ as a function of the bias intensity is shown in figure 5(a). The decay constant $\beta$ signifies the rate of charge carrier decay with respect to the $V_{OC}$ under different background light intensities. The $\beta$ values obtained for the rr-P3HT and DF-P3HT:PCBM cells are 20.2 V$^{-1}$ and 16.4 V$^{-1}$, respectively. From the $\beta$ values it is evident that the DF-P3HT:PCBM cell has a slower rate of decay when compared to the rr-P3HT:PCBM cell. The values that we obtain here match well with the values reported earlier for P3HT:PCBM cells [16, 21]. At one Sun, the $\tau_{\Delta n}$ values for the rr-P3HT and DF-P3HT cells are 2.6 µs and 4.0 µs, respectively, indicating that the DF-P3HT:PCBM cell has longer lived charges when compared to rr-P3HT:PCBM.

Figure 3. Bright field TEM images of rr-P3HT:PCBM (a) and (c) and DF-P3HT:PCBM (b) and (d) films. Inset in (c) is the zoom image of image (c) to highlight the nodular region of P3HT.
The charge carrier density, \( n \), which was present in the system before perturbation was calculated using the differential charging method as described by Shuttle et al \[16\].

The \( n \) inside the solar cells are calculated using the relation 
\[
\frac{d}{dt} \int_n \frac{1}{C} \, dV = \frac{\Delta Q}{\Delta V},
\]
where \( A \) is the active area of the device, \( e \) and \( d \) are the electronic charge and thickness of the PV active layer, respectively. The differential capacitance \( C \) is calculated by \( \frac{\Delta Q}{\Delta V} \); \( \Delta Q \) is obtained by integrating the short-circuit photocurrent curve with respect to time (see figure S2(c)). The pulse width of the LED used is same as that of TPV measurements, i.e., 500 ns. Since the charge generated because of the 500 ns LED is very short, the recombination at the short circuit is not observed (the shape of the all traces remain the same at different background light intensities; see figure S2(d)). \( \Delta V_o \) is the initial rise of the TPV pulse. The exponential increase of total \( n \) in the cells as a function of light bias is shown in the figure 5(b). The equation used for the fitting is 
\[
n = n_0 \exp(\gamma V_{oc}),
\]
where \( n_0 \) is the charge carrier density in the dark, and \( \gamma \) is the rate of increase of \( n \) upon white light bias voltage or quasi-Fermi level splitting. From the fits to the data, \( \gamma \) is found to take values of 7.3 \( V^{-1} \) and 8.8 \( V^{-1} \) for the rr-P3HT:PCBM and DF-P3HT:PCBM cells, respectively. The values of \( \gamma \) obtained here match well with previous reported values for P3HT:PCBM devices \[16\]. In an ideal semiconductor which has well defined energy levels (valence and conduction band edges) the parameter \( \gamma \) is expected to be 19 \( V^{-1} \) (\( \approx e/2K_BT \)) \[21\]. From figure 5(b) it is observed that the charge carrier concentration inside the devices increases exponentially with the white light bias. The value of \( \gamma \) determined for the P3HT:PCBM solar cell deviates from that of an ideal semiconductor suggesting the presence of an exponential density of states that extends into the bandgap of the polymer. This has also been observed in other organic systems and is consistent with TAS and modeling studies on the P3HT:PCBM system \[12, 21, 40\]. These tail states lead to the formation of energetic disorder, which increases the recombination inside the active layer and hinders charge transport \[21, 40\]. It is to be noted that the \( \gamma \) value is lower in rr-P3HT:PCBM cells, suggesting a higher density of tail states than DF-P3HT:PCBM cells, in agreement with the TPC measurements. The lifetime \( \tau_{\Delta n} \) is plotted against the total charge carrier density \( n \) in the cells in figure 5(c) exhibiting a power law dependence:
\[
\tau_{\Delta n} \propto n^{-\lambda}.\tag{3}
\]
The parameter \( \lambda \) can also be obtained by dividing the decay time constant \( \beta \) with the rate at which \( n \) decays with respect to time, that is, \( \lambda = \beta/\gamma \). The value of \( \lambda \) is determined to be 2.8 and 1.9 for rr-P3HT:PCBM and DF-P3HT:PCBM devices, respectively matching the range of previously reported values for P3HT:PCBM cells \[16, 40\]. The power law parameter \( \lambda \)
provides information regarding the order of recombination in the bulk donor acceptor medium, where \((\lambda + 1)\) corresponds to the recombination order inside the BHJ solar cells [12, 16, 42, 43]; a \(\lambda\) value of ca. 2 suggests that charge carrier recombination inside the device has a third order dependence on charge carrier density present inside the device. This high dependence of decay dynamics with \(n\) has been observed before by Shuttle et al in the P3HT:PCBM system. Shuttle et al explained this high dependence of TPV decay on \(n\) at \(V_{OC}\) condition in terms of bimolecular recombination combined with a density-dependent recombination rate [12, 16]. A \(\lambda\) value greater than 2 is often observed in organic solar cells and commonly attributed to the presence of an exponential tail in the density of states [44]. However, the spatial distribution of charge carriers due to presence of Gaussian distribution of midgap trap states can also contribute to values of \(\lambda\) larger than expected [45]. Especially for active layer thickness \(\sim 100\) nm, unintentional background doping of the polymer active layer can result in a non-uniform spatial distribution of carriers in the active material [45]. Since the \(\lambda\) values obtained here are very similar to the previously reported values for P3HT:PCBM cells, we are confident that bimolecular recombination is the dominant recombination process in these devices at open circuit condition. The difference in the \(\lambda\) value however between rr-P3HT and DF-P3HT based cells could be because of the difference in the active layer thickness and/or presence of localized states in the exponential tail in the rr-P3HT:PCBM cells since \(\lambda\) value is higher than DF-P3HT:PCBM cells [45, 46].

The total charge carrier lifetime \(\tau\) in the device is obtained using the simple relation \(\tau = \frac{1}{k(n) \cdot n}\). The rate of bimolecular recombination, \(k\), as a function of the charge carrier density, \(n\), is shown in figure 5(d). It is observed that \(k\) is higher in DF-P3HT:PCBM cells than in rr-P3HT:PCBM for all values of \(n\). This is expected because in DF-P3HT:PCBM cells, the energy of the charge transfer states is lower as reported elsewhere [37], and the increase in the polymer crystallinity promotes a higher mobility of free charges [37]. These two phenomena make the mobile charge encounter the opposite charges and recombine bimolecularly before they are collected at the electrodes. This high bimolecular recombination in DF-P3HT cells causes the cell voltage to decrease [12, 46, 49]. We have also calculated \(k\)
for other thickness P3HT:PCBM BHJ solar cells (see figure S3 in the supporting information) and found that at any given thickness DF-P3HT:PCBM cells have higher $k$ as compared to rr-P3HT devices. Previous studies on different regioregular P3HT BHJ solar cells also observed a decrease in the $V_{OC}$ with increase in RR, but failed to explain the reason behind it [22, 50]. We explain the lower $V_{OC}$ in DF or high RR P3HT:PCBM cells as the result of a higher bimolecular recombination that occurs near open circuit conditions and reduced $E_{CT}$ state. Although the $V_{OC}$ of the cell is slightly hindered by the increase in bimolecular recombination in the DF-P3HT BHJ devices, because of the better interchain ordering, optical and charge transport properties. These devices have better $J_{SC}$ and FF than devices with rr-P3HT which provides an overall increase in device performance.

To validate that bimolecular recombination is dominant in the open-circuit condition of these devices, we use equation (5) to calculated the bimolecular recombination flux at $V_{OC}$ condition of the device [12],

$$J_{BI} = -k \times n \times p \times d \times e,$$

where, $k$ is the bimolecular recombination coefficient, $n$ and $p$ are the electron and hole charge carrier density, $d$ is the thickness of the active-layer and $e$ is the electronic charge. At one Sun condition, we obtained $J_{BI}$ of 10.2 mA cm$^{-2}$ and 11.1 mA cm$^{-2}$ for rr-P3HT:PCBM and DF-P3HT:PCBM cells, respectively. This is in good agreement with the $J_{SC}$ obtained at short-circuit condition proving that bimolecular recombination is dominant at open-circuit condition and validating our results [51]. The minor mismatch of $J_{BI}$ and $J_{SC}$ could be due to the spectral mismatch of the LED used for TPV study and the simulator lamp, and/or a small error in the active-layer thickness.

4. Conclusions

In conclusion, the application of TPC and photovoltage techniques have been used to explain the improvement of efficiency in P3HT:PCBM solar cells with increased P3HT RR. The TPC response of different RR devices indicate the presence of a higher trap density in rr-P3HT devices when compared to DF-P3HT devices. The higher trap density in rr-P3HT device hinders the charge transport properties and is one of the major reasons causing decrease in the performance (in terms of $J_{SC}$ and FF) of these cells when compared to high regioregular or DF-P3HT devices. The DF-P3HT based films are also found to be more ordered from TEM analysis. From TPV measurements we have obtained the bimolecular rate constant $k$, with a value of $k$ 1.17 times higher for the DF-P3HT:PCBM cell compared to the rr-P3HT:PCBM cell at one Sun. This increase in $k$ in the DF device is attributed to improved charge transport inside the device, which in turn increases the probability of free charges meeting the opposite charge and recombining bimolecularly before they are collected at the electrodes at/near open circuit condition. Overall, the improved carrier transport in the DF-P3HT:PCBM cell leads to a superior PCE compared to the rr-P3HT:PCBM cell despite the slight decrease in cell $V_{OC}$ for the DF-P3HT:PCBM cell which is attributed to high bimolecular recombination and less $E_{CT}$.

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Supplementary material

See supplementary material for raw data of transient photocurrent, transient photovoltage, neat polymer film TEM images and DF-P3HT synthesis details.

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