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A Shockley-Type Polymer: Fullerene Solar Cell

Ardalan Armin,* Zhiming Chen, Yaocheng Jin, Kai Zhang, Fei Huang,* and Safa Shoaee*

Charge extraction rate in solar cells made of blends of electron donating/accepting organic semiconductors is typically slow due to their low charge carrier mobility. This sets a limit on the active layer thickness and has hindered the industrialization of organic solar cells (OSCs). Herein, charge transport and recombination properties of an efficient polymer (NT812):fullerene blend are investigated. This system delivers power conversion efficiency of >9% even when the junction thickness is as large as 800 nm. Experimental results indicate that this material system exhibits exceptionally low bimolecular recombination constant, 800 times smaller than the diffusion-controlled electron and hole encounter rate. Comparing theoretical results based on a recently introduced modified Shockley model for fill factor, and experiments, clarifies that charge collection is nearly ideal in these solar cells even when the thickness is several hundreds of nanometers. This is the first realization of high-efficiency Shockley-type organic solar cells with junction thicknesses suitable for scaling up.

1. Introduction

Donor:acceptor bulk heterojunction (BHJ) solar cells are the mainstream of organic photovoltaic devices such as organic solar cells (OSC) and photodetectors. The power conversion efficiency of polymer OSCs has recently approached\[1,2] and even exceeded\[3,4] 10% in single junctions, and the most recent reports claim even efficiencies greater than 13%.\[5\] However, there has been a little success in scaling up the fabrication of these devices from laboratory to industrial scales. One of the obstacles in this regard is the thickness of the active layer; high throughput deposition techniques are more applicable when the junction thickness is at least several hundreds of nanometers. Such thicknesses are larger than the typical thicknesses of most laboratory-scale organic solar cells—often limited to less than 100 nm. The reason behind the use of thin junctions is the inefficient charge collection in these solar cells which becomes worse as the junction thickness increases. To the first order, the inefficient charge collection is due to the lower effective internal electric field and longer charge carrier travel distance in thick junctions.\[6,7\] Other effects such as formation of space charges of slower carriers,\[8,9\] surface photogeneration,\[9,10\] and doping-induced field screening\[28\] are other factors that also play a role in limiting the charge collection efficiency in the thick junctions. The inherent limitation of OSCs on the active layer thickness is a disadvantage that must be overcome for large-scale production purposes and to further increase their power conversion efficiency (PCE).\[11\]

In order to achieve a high charge collection efficiency in thick junction devices, researchers have tried or proposed different directions, including increasing the electron and hole mobilities,\[11–13\] reducing the bimolecular recombination,\[11,14,15\] and extrinsic doping.\[16\] While there has been modest success in increasing the charge carrier mobility of organic polymers and small molecules over the past decade, the charge carrier mobilities in organic donor:acceptor blends are still limited to values much less than 1 cm² V⁻¹ s⁻¹. In particular, even if the hole mobility can exhibit mobilities as large as 0.1 cm² V⁻¹ s⁻¹, the electron mobility would not exceed 0.003 cm² V⁻¹ s⁻¹ when fullerenes are used as electron acceptor. As long as such imbalance mobility exists, further unidirectional increase of donor hole mobility is not beneficial, but even destructive for the performance of the thick junction organic solar cells as shown before.\[9,10\] Development of nonfullerene acceptors is a promising ongoing effort; however, as far as charge transport is concerned, it seems to be very unlikely that the electron mobility of the nonfullerene acceptors can exceed the hole mobility of the best current donors due to the disordered nature of organic semiconductors.

Given the limitation in increasing charge carrier mobility—resulting in limited charge extraction rate—reducing the bimolecular recombination is an alternative approach to deliver high charge collection efficiency, fill factor (FF), and ultimately highly efficient solar cells with thicker junctions.\[8,15,17\] Annealed poly(3-n-hexylthiophene): phenyl-C61-butyric acid methyl ester (P3HT:PC61BM) has shown...
reduced recombination\[7,18,19\] with respect to the diffusion-controlled rate given by Langevin equation. However, these devices have never exhibited high efficiencies due to limitations such as large bandgap and moderate quantum efficiency. We have recently reported on reduced recombination in a donor:acceptor system that can deliver high FF and power conversion efficiencies up to 9% in junctions as thick as 300 nm.\[15\] Despite previous reports on moderate suppression of bimolecular recombination in few polymer:fullerene systems,\[14,20\] possibly this was the first report on the real benefit of reduced recombination in a high-efficiency system; delivering compelling efficiencies. The authors tentatively attributed this reduced bimolecular recombination to the fast dissociation of the charge transfer (CT) states relative to their decay to the ground state, as also suggested by Burke et al.\[17\] This proposal for the mechanism behind reduced bimolecular recombination is inline with the model suggested by Hilczer and Tachiya in 2010 for the bulk recombination in which the carriers recombine at a finite rate and a nonzero distance\[21\] and a seminal work by Koster and Blom.\[22\] In addition, Schwarz et al. have shown that in the same donor:acceptor system for which Armin et al.\[19\] identified significantly reduced recombination, when the intersystem crossing of the triplet CT states to the triplet excitons is turned off, the system behaves more efficiently due to significantly suppressed bimolecular recombination rates.\[24\] as proposed by Rao et al.\[25\] For the future of organic solar cells, it is indeed very important to identify the pathways that lead to reduce bimolecular recombination through material design. However, this has never been systematically achieved and is still an outlook for the organic electronic community. A recent study suggests that simultaneous suppression of back electron transfer from triplet CT states to triplet excitons and decay of singlet CT states is a necessity to achieve reduced bimolecular recombination.\[25\] Identification of more material systems with reduced bimolecular recombination characteristic is indeed a key to understanding the exact mechanisms behind this phenomenon and developing material design rules for high-efficiency solar cells.

Theoretical and experimental investigations have been carried out in order to determine the minimum required mobility and reduction factor of bimolecular recombination for organic solar cells to operate with minimum charge collection loss at a given thickness.\[16,7,26,27\] The mobility and carrier lifetime product have been extensively used as a “figure of merit” (FoM) to quantify the quality of the charge collection in (organic) solar cells. While this product reflects the charge collection efficiency at a certain condition, it cannot be considered as a device-material FoM. This is because the carrier lifetime of one type of carrier is dependent on the density of its counterpart and thereby on the light intensity. This has been addressed by introduction of a material FoM that is the product of slower carrier mobility and bimolecular recombination reduction factor.\[7,28\] However, this FoM is not a device FoM and does not account for the active layer thickness and light intensity regime and does not yield the fill factor. Recently, a modified Shockley equation was introduced by Neher et al.\[26\] based on their previous efforts to correlate the FF with transport and recombination properties.\[26\] Although this model does not take into account for the role of space charge effects as shown later\[29\] and the carrier distribution profile,\[9,10\] it can explain the FF of organic solar cells under operational conditions by introducing a FoM that contains material, device, and illumination conditions at the same time. The work of Neher et al.\[20\] shows that depending on parameters such as thickness of the photoactive layer, light intensity, electron and hole mobilities, and bimolecular recombination rate constant, the operation of the organic solar cells can either be transport limited or Shockley type, in which the device is not affected by charge collection loss. Indeed, it is desirable to have organic solar cells operating in the Shockley-type regime but at active layer thicknesses on the order of several hundreds of nanometer, as preferred for scaling up to large areas.

Recently, a novel naphtho[1,2-c:5,6-c’][Bis[1,2,5]-Thiadiazole]-based polymer (NT812) has been introduced with power conversion efficiencies as high as 10% in junctions with thickness of several hundreds of nanometer—very exceptional results for OSCs.\[4\] Herein, we examined the charge transport properties and the recombination rate constant of blends of NT812 with phenyl-C71-butyric acid methyl ester (PC71BM). We show that the electron and hole mobility in the optimized blend are very typical of BHJ solar cells; however, the bimolecular recombination rate constant is 800 times smaller than the diffusion-controlled rate given by Langevin equation. This is exceptional for any high-efficiency donor:acceptor solar cell reported so far, which has resulted in high efficiencies in thick junctions. We employed the modified Shockley model presented by Neher et al.\[26\] and show that this model can explain the thickness-, blend ratio-, and light intensity-dependent fill factor. In addition, we show that Neher’s model is more effective where the solar cells are less transport limited. Our results exemplify the applicability of the modified Shockley model to predict the FF of organic solar cells and also an exceptional model system for strongly reduced bimolecular recombination. NT812:PC71BM is the first reported OSC that can operate as a Shockley-type solar cell, i.e., not limited by charge collection losses. Understanding such systems can guide the community toward intelligent design of donor:acceptor systems with larger reduction factors, less dependent on charge carrier mobilities, and more affordable large thicknesses—a prerequisite for scaling up and industrialization of organic solar cells.

2. Material System

Blends of the donor polymer (NT812) and the electron acceptor (PC71BM) are used in this study. The synthesis of NT812 has been previously reported.\[4\] The molecular structures of these organic semiconductors are shown in Figure 1a. Conventional solar cell architectures have been used in which electrons are extracted through a silver electrode on the top of the NT812:PC71BM photovoltaic layer, while the holes are extracted through the indium tin oxide (ITO) electrode modified by PEDOT:PSS. Figure 1b shows the current density–voltage (J–V) curves of NT812:PC71BM (optimized blend ratio 1:1.5 by weight) with different active layer thicknesses. As shown in the figure, a FF = 0.71 and PCE = (10.2 ± 0.2)% are achieved in 300 nm
3. Charge Transport Properties

To investigate charge transport properties of BHJ solar cells, electron and hole mobilities ($\mu_n$ and $\mu_p$) and equilibrium charge carrier concentration are required to be quantified. We performed double injection transient measurement and resistance-dependent photovoltage (RPV) to selectively quantify faster and slower carrier mobilities.$^{[29]}$ The former method is a useful technique only when a system exhibits reduced recombination, otherwise no features in the transients will be observed. The RPV method also allows for quantification of slower and faster carrier mobilities at operational device conditions, although it is subject to a relatively large uncertainty in the evaluation of the transient times. We used both of these techniques to more confidently evaluate the slower and faster carrier mobilities.

Figure 2a shows drift-diffusion simulation results of double injection transient for a solar cell with reduced recombination. Under forward bias, the injection current rises with time when the bimolecular recombination is reduced compared to Langevin rate (this will be discussed in the next section in more detail). It has been shown that slower and faster carrier transit times can be detected from these transients for materials with low equilibrium charge carrier density such as NT812:PC71BM (see Figure S1 in the Supporting Information).$^{[7]}$ The arrival time of the slower and faster carriers on the electrodes may be seen as “kinks” in the transients. These features might not be directly observable especially due to the dispersive charge transport. The time derivative of the injection current can more clearly show the transit time as shown in Figure 2a. Figure 2b shows double injection transient currents for an 800 nm NT812:PC71BM solar cell at different applied voltages. While the arrival times are barely detectable in this figure, the time derivatives in Figure 2c show the transit times. The faster carrier transit time cannot be detected for 2 V and 2.5 V transients due to the resolution limit of the experiment.

For RPV measurements, two different active layer thicknesses of 300 and 800 nm were examined in order to verify the independence of mobilities on the thickness through morphological effects and/or field-dependent mobility. RPV transients are shown in Figure 2d,e. The slower and faster carrier transient times and their uncertainty range are specified with the dashed boxes. In RPV, the transit times are essentially the saturation points in the rise of the photovoltage as the load resistance increases. Due to the dispersive nature of charge transport, and also charge trapping—especially in case of thick samples—the features are broader than expected for a nondispersive case. As such, like many other techniques, RPV can provide an estimation of the mobilities.

Mobility results from RPV and double injection (DI) transients versus electric field are plotted and shown in Figure 2f. The open symbols correspond to the RPV results for two different thicknesses (and hence different electric field, tested at short circuit condition) and the solid symbols show the mobility results of DI transients. Overall, within the uncertainty of the RPV measurement, there is a good agreement between the two techniques and no significant thickness and electric field-dependent mobility is observed.

The average faster carrier mobility of $\approx 2 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ corresponds to typical electron mobility for efficient blends with sufficient fullerene loading.$^{[29,30]}$ Therefore, we attribute the average slower carrier mobility of $\approx 5 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ to the hole mobility through NT812’s percolations. It should be noted that the assignment of faster and slower mobilities to electron and holes does not influence the analysis of our results throughout this study.

Electron and hole mobilities of the order of $10^{-3}$ and $10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ are very typical for organic semiconductors.
and not considered as high values. Therefore, charge extraction rate is not anticipated to be extraordinary in this system, in particular for the thicker junctions. Calculation of the charges accumulated on the electrodes per transit time of the slower carriers for a 300 nm thick film, suggests a current of $\frac{CV_{Bl}}{t_{tr}} \approx 3.7 \text{ mA cm}^{-2}$ (assuming dielectric constant of $\approx 4$ (as measured charge extraction using linearly increasing voltage in the dark (dark-CELIV)—see Figure S1 in the Supporting Information) and $V_{Bl} \approx V_{OC}$ at short circuit condition). This would mean that bimolecular recombination becomes effective when the current is greater than 3.7 mA cm$^{-2}$—a threshold limit far below the short circuit current of our high-efficiency devices. As such, one arrives at the presumption that bimolecular recombination must be suppressed such that the devices can afford carrier densities larger than $CV_{Bl}$. This scenario implies that while the charge extraction rate is typically slow in the thick junctions, the bimolecular recombination rate is also slow so that an efficient charge collection efficiency can be achieved.

Figure 2. a) Modeled injection current for a solar cell with reduced recombination using drift diffusion simulation. The dashed line is the derivative of the current and clearly shows the arrival time of the slower and faster carriers on the electrodes. b) Experimental double injection currents of a NT812:PC71BM (1:1.5) solar cell with thickness of 800 nm at different voltages. c) The derivative of the current transients. The transit times and their uncertainty range are shown with boxes. d) Resistance-dependent photovoltage (RPV) transients for NT812:PC71BM solar cells with active layer thickness of 300 and 800 nm. e) The slower and faster carrier transit times are specified within their uncertainties with boxes. The measurements are performed at quasi-short circuit condition, i.e., no additional voltage is applied to the devices. f) Faster and slower carrier mobility as a function of electric field (combined RPV and double injection results).
4. Reduced Bimolecular Recombination Rate Constant

In order to investigate bimolecular recombination in NT812:PC71BM, we performed double injection current experiment on our operational solar cells in the dark, both in steady state and transient modes. The transient double injection current is a unique experiment allowing for precise determination of the recombination rate constant.\(^\text{[7,11]}\) For a low-conductivity semiconductor under forward bias \(V\), with encounter-limited recombination (diffusion controlled), the double injection current is given by (see the Experimental Section)

\[
J_{\text{SCLC}} = \frac{9}{8} \varepsilon \varepsilon_0 (\mu_p + \mu_e) \frac{V^2}{d} \quad \text{(diffusion controlled recombination)} \quad (1)
\]

where \(\varepsilon\) is the dielectric constant of the semiconductor (for NT812:PC71BM \(\varepsilon \approx 4\); see Figure S1 in the Supporting Information). If the bimolecular recombination rate constant \(\beta\) is suppressed with respect to the Langevin recombination rate constant, \(\beta = \frac{[\mu_p + \mu_e] \varepsilon \varepsilon_0}{d^2}\) (see the Experimental Section), the double injection current will be higher than Equation (1) and given by

\[
J_{\text{DI}} = \frac{3}{2} \varepsilon \varepsilon_0 (\pi \mu_p \mu_e) \frac{V^2}{d} \quad \text{(reduced recombination)} \quad (2)
\]

where \(\gamma = \beta / \beta\).

Figure 3a shows voltage-dependent current injection. Using the quantified electron and hole mobilities from RPV experiment as shown in Figure 2, Equation (2) is fitted to the experimental data and best fitting is obtained for \(\gamma = 800\), which is considerably larger than that previously obtained for high-efficiency solar cells based on a liquid crystalline donor material.\(^\text{[15]}\) This strongly reduced recombination rate constant will have a great influence on reducing the charge collection losses in the thick junctions by allowing a larger free carrier concentration and by lowering the onset of recombination. Figure 3b shows injection current transient at a forward bias voltage of 1.5 V. At \(t = 0\), when a voltage pulse in forward bias is applied to the device, there is a sharp RC-decay (at time scales \(< 300\) ns, not shown in the figure) charging the electrodes that we have minimized through using small load resistor, and device area and afterward the current starts to flow through the film.

The injected current is initially composed of two independent space charge currents of electrons and holes that are being injected from each electrode inward—as per Equation (1)—independent of the recombination rate. The difference between cases with different recombination rates becomes distinct as the two space charge limited electron and hole (SCL) currents meet in space. In the case of diffusion limited recombination, there will be no rise to the current and the two SCL currents recombine, and therefore the total current will be the sum of the two SCL currents. When the recombination is suppressed, the carrier density increases due to the coexistence of electrons and holes in the film (often called plasma formation) until the current reaches \(J_{\text{DI}}\) as given by Equation (2). As such, by experimentally measuring the ratio between the saturated injection current at longer timescales (\(J_{\text{sat}} = J_{\text{DI}}\)) and its initial value (\(J_{\text{sat}} = J_{\text{SCLC}}\)), one can quantify the reduction factor, independent of the film thickness, by dividing Equation (2) with Equation (1)

\[
\gamma = \frac{9}{16\pi} \frac{(\mu_p + \mu_e)^2 J_{\text{sat}}}{\mu_p \mu_e J_{\text{t=0}}} \quad (3)
\]

Employing our mobility values in Equation (3) together with the ratio of the saturation and initial injected currents \((\approx 25)\), we further confirm \(\gamma = 800\).

5. Figure of Merit for Thick Junction NT812:PC71BM Solar Cells

We now turn our attention to modeling NT812:PC71BM solar cells and correlating the charge transport properties and the recombination reduction factor to the device performance. This is of particular importance at this time; new device models have been proposed to explain the \(J-V\) characteristics of organic solar cells and predict their performance once all the other
parameters are known. Whether or not such models can successfully explain the behavior of systems with strongly reduced recombination has not been investigated yet.

It has been previously established that the onset of bimolecular recombination can be delayed in systems with nonunity reduction factor $\gamma$—conventionally referred to as non-Langevin type system—by a factor of $\gamma^{1/2}$ at short circuit condition.\textsuperscript{[28]} This implies that such systems can be bimolecular-recombination-free at short circuit condition when their short circuit current is smaller than $I_{SC,\text{lower}}^{1/2}$ (where $I_{SC,\text{lower}}$ is the space charge limited current of the slower carriers).\textsuperscript{[32]} As such, $\mu_y^{1/2}$ has been considered as an FoM to explain the performance of organic solar cells. For the FF to be modeled, the field dependence of the charge collection must be considered. This resulted in investigating the competition between charge extraction and recombination from which other figures of merit have been introduced.\textsuperscript{[6,26]} These FoMs are in accordance with $\mu_y^{1/2}$ but applicable in a broader voltage range and able to explain the $J-V$ characteristics. In this regard, Neher et al. have introduced a modified Shockley equation\textsuperscript{[26]} to explain the $J-V$ characteristics of disordered solar cells. In this model, the current is written as

$$J(V) = eG\left\{\exp\left[\frac{e}{k_B T} (V - V_{oc})\right]^{-1}\right\}$$

(4)

in which $V$ is the applied voltage, $G$ is the charge generation rate in the volume, $k_B$ is the Boltzmann constant, and $\alpha$ is the FoM for the operation of the solar cell

$$\alpha = \frac{e^2 B G \gamma}{4 \mu_s \mu_y (k_B T)}$$

(5)

It has been shown that Equations (4) yield same results as one would obtain from drift-diffusion simulations but they have an analytical form which is an advantage.\textsuperscript{[26]} The authors correlated FF with $\alpha$ such that one can predict the FF for given mobility values and recombination rate constant at a given active layer thickness, light intensity, and temperature.

Figure 4a shows the FF from the $J-V$ curve of Equation (4) as a function of $\alpha$ (the dashed line) together with the experimental data points of blends of NT812:PC71BM (1:1.5 by weight) at different light intensities corresponding to modulation of $G$ and thereby $\alpha$. There is a good agreement between the experiments and the modified Shockley model confirming the validity of the recombination reduction factor, which was experimentally quantified using steady-state and transient double injection. Figure 4b shows the same plot; however, with experimental data points acquired from devices with different thickness, thereby modulating $\alpha$ by using NT812:PC71BM devices with blend ratios of 1:3.5, 1:3, and 3:1 (see the Supporting Information for transport and recombination measurement of the 1.3 and 3:1 blends). It is important to note that some of these devices have $\alpha < 1$, which implies they are not transport limited and can be considered as Shockley-type solar cells even though the thickness is still above 100 nm. This is important, for an organic solar cell to be bimolecular-recombination-free, and should be considered as a model system for future material design. Although organic solar cells use disordered semiconductors with low charge carrier mobilities and very short charge carrier diffusion length, our data suggest that they can perform in a similar way as their inorganic counterparts in terms of charge collection efficiency with recombination-free FF. Furthermore, these results confirm the capability of the model proposed by Neher et al. to predict the performance of organic solar cells with both small and large recombination reduction.

**Figure 4.** Comparison of experimental FF of NT812:PC71BM solar cells and prediction of modified Shockley model. a) Experimental FF versus figure of merit $\alpha$ and the calculated values using the modified Shockley equation. Different experimental data points are obtain through varying $\alpha$ via changing the light intensity on a device with active thickness of 300 nm. b) FF of 1:1.5, 1:3, and 3:1 blends as a function of the figure of merit $\alpha$, which is experimentally varied through changing the active layer thickness. c) FF of same devices as a function of active layer thickness with the values calculated using the modified Shockley model. The Dashed black line corresponds to the model acquired with the mobility and reduction factor values relevant to the 1:1.5 and 1:3 devices. The solid line corresponds to the model obtained from the mobility and reduction factor values of 3:1 device. The agreement between experimental and theoretical values is more acceptable where the charge collection is less transport limited (smaller $\alpha$).
factors as obtained from 1:1.5 ($\gamma = 800$), 1:3 ($\gamma = 800$), and 3:1 ($\gamma = 2$) devices (see Figure S2 in the Supporting Information for mobility and double injection data). We note that the model becomes less accurate with increasing thickness. This may originate from the fact that the model does not take into account the photogeneration profile in the film and considers a uniform generation profile which is a less acceptable approximation for a thick film. Nevertheless, the simplicity of the analytical equation is beneficial for an analysis to be done with reasonable precision.

Figure 4c demonstrates the modeled FF as function of active layer thickness for the same devices as Figure 4b. The figure also shows the fittings with relevant mobility and recombination factors that match well with the experiment data and also the theoretical values for each case, had the recombination been diffusion limited. There is a considerable difference in the FF of systems with reduced and nonreduced recombination rates as exemplified by the 1:1.5 and 3:1 blends. The dotted line in Figure 4c shows the calculated FF for a hypothetical system with both electron and hole mobility of 0.1 cm$^2$ V$^{-1}$ s$^{-1}$—a very optimistic value which has not yet been observed in organic solar cells—however, with diffusion controlled recombination. The data show that in thick junction, even an optimistic mobility of 0.1 cm$^2$ V$^{-1}$ s$^{-1}$ cannot increase the charge collection efficiency any further when the recombination is not reduced. Therefore, the FF data shown in Figure 4c demonstrate the importance of the requirement of reduced bimolecular recombination (and not merely increasing charge carrier mobility) as an achievable optimization pathway for the future of organic solar cells. In particular, the figure clearly demonstrates the possibility of realizing transport loss-free organic solar cells with high FFs and PCEs at large thicknesses with ordinarily low charge carrier mobility materials.

6. Conclusions

In summary, we showed that blends of NT812 polymer with PC71BM exhibit strongly reduced bimolecular recombination; as low as 800 times smaller than the diffusion-limited encounter rate of the electrons and holes. Having bimolecular recombination strongly suppressed, charge collection efficiency in this system is very efficient even when the junction thickness is increased to several hundreds of nanometer. We employed a recently proposed modified Shockley model to calculate the fill factor of NT812:PC71BM solar cells. The model explains the FF of these systems at various light intensities and different thicknesses. The results show the ability of this recent analytical proposal in predicting the current–voltage characteristics of organic solar cells at illumination condition. Furthermore, the results indicate that NT812:PC71BM devices with thicknesses as large as 300 nm can exhibit Shockley-type behavior, i.e., the charge collection at various voltages is unaffected by bimolecular recombination, which is unexpected for organic solar cells. This system is a promising candidate for scaling up to large areas as it can deliver high efficiencies and charge collection at thicknesses on the order of several hundreds of nanometer. Given the limitations in increasing the electron and hole mobility of organic semiconductors further from the current values, reducing bimolecular recombination rate constant is an effective and practical approach to achieve highly efficient charge collection in organic solar cells, as shown in this work. The exact reason behind strongly reduced recombination is an ongoing research subject of organic optoelectronics community for which NT812:PC71BM system can be used as an important model system.

7. Experimental Section

Double injection: The equilibrium charge carrier density (doping level) in this system is much smaller than the amount of charges accumulated on the electrodes at operational condition as confirmed by charge extraction by linearly increasing voltage performed in dark condition, [8] Dark-CELIV (see Figure S1 in the Supporting Information). As such, the theory of charge injection into insulators [33, 34] applies when these diodes are in forward bias configuration. It can be assumed that a semiconductor (with low equilibrium carrier density) is sandwiched between an anode and a cathode in a forward bias condition. The total injected current can be written in simple general form of

$$J_{Di} = \frac{9}{8} \varepsilon_{0} \varepsilon_{r} \mu_{\text{eff}} V^{2} \frac{\partial J}{\partial t}$$

where effective mobility, $\mu_{\text{eff}}$, is

$$\mu_{\text{eff}} = \mu_{e} \nu_{e} \nu_{p} / 3 \left[ \frac{2}{3} \left( \nu_{e} + \nu_{p} \right) \right]$$

as calculated by Parmenter and Ruppel. [35] The dimensionless mobility is defined as

$$\nu_{i} = \frac{\mu_{i}}{\mu_{e}} \quad i = n \text{ or } p$$

with the definition of “recombination mobility”

$$\mu_{e} = \frac{\varepsilon_{0} \left( \nu \sigma_{e} \right)}{2 \varepsilon_{0}}$$

where $\beta = \frac{\mu_{e} + \mu_{p}}{\varepsilon_{0}}$ is the Langevin recombination rate constant, $\gamma$ is the recombination reduction factor, and $\nu$ is the relative velocity of the carriers that scales with the sum of the electron and hole mobilities. Equations (6) and (7) fully describe current injection into insulators for various cases, including one-carrier injection (when the contacts are only able to inject/extract one type of carrier) or double-injection (where both species can be injected) in both cases of small and large recombination rates. When the bimolecular recombination is diffusion controlled, i.e., $\gamma = 1$, the absorption cross-section is given by the Coulomb radius of the charge carriers and $\mu_{e}$ has its largest value for given electron and hole mobility ($\beta = \beta_{c}$). As such $0 < \nu < \approx 1$ for which it can be assumed that the relation $\left( \nu_{i} = 1 \right) = 1 / \nu_{i}$ holds and Equation (6) simplify to the well-known form of

$$J_{SCLC} = \frac{9}{8} \varepsilon_{0} \left( \mu_{e} + \mu_{p} \right) V^{2} \frac{\partial J}{\partial t} = J_{n}^{SCL} + J_{p}^{SCL}$$

a generalized form of the Mort–Gurney law for two-carrier injection. This simply implies that in the case of diffusion-controlled recombination, the total injected current can be written as the sum of SCL currents. In the context of inorganic semiconductors where the large dielectric constant often results in low recombination cross-section, Parmenter and Ruppel assumed that recombination mobility $\mu_{e}$ is lower than expected from the diffusion-controlled rate with a reduction factor $\gamma > 1$, such that $\mu_{e}$ is much lower than typical charge carrier mobilities.
of those semiconductors, and therefore it can be concluded that \( \gamma \gg 1 \). Under such conditions Equation (7) can be simplified to the well-known Parmenter-Ruppel equation\(^\text{[35]} \) for plasma injection by using Stirling’s formula and substituting it in Equation (6) yields the double injection current in case of reduced recombination

\[
J_{D2} = \frac{q}{\epsilon_0} \left( \frac{2}{3} \left( \frac{\mu_0 + \mu_p}{\mu_0 \mu_p} \right) \right)^{\frac{3}{2}} \left( \frac{4}{\nu} \right)^{\frac{1}{2}} \left( \frac{4}{\nu} \right)^{\frac{1}{2}}
\]

Equation (11) allows for injected current to be much larger than that of a system with diffusion controlled recombination (Equation (10)). This is the logic behind performing injection current measurements in the dark; in order to quantify the bimolecular reduction factor \( \gamma \) by comparing the actual injection current in a given system with the predicted current for diffusion-controlled case. Recent works of Murthy et al.\(^\text{[20]} \), Heiber et al.\(^\text{[21]} \), Armin et al.\(^\text{[15]} \) and Burke et al.\(^\text{[16]} \) together with a seminal publication by Koster et al.\(^\text{[22]} \) collectively indicate that the mechanism of reduced bimolecular recombination in BHJ system is not necessarily same as the reduction in the encounter rate as appeared in Equation (11). Instead, they suggest that the reduced recombination must be due to the suppressed decay of CT states to the ground state. This will not quantitatively change the above double injection scenario so that one can still imagine that in a system with suppressed recombination due to the high ionization probability of the CT states, the encounter cross-section of free charges is effectively reduced, and Equation (11) is valid.

**Solar-Cell Fabrication and Characterization:** Patterned ITO–glass substrates were precleaned successively with detergent, acetone, DI water, and IPA and dried in oven at 70 °C for 8 h. The dried substrates were treated by oxygen plasma at room temperature for 20 min and then coated with PEDOT:PSS by spin-coating (3000 rpm for 30 s, thickness of \( 40 \) nm) and then were baked at 150 °C for 15 min in air. The active layer (NT812 with \( M_0 = 35 \times 1000 \) and polydispersity index, PDI = 2) was deposited in a glove box by spin-coating hot (70 °C) CB:DCB = 3:1 solution containing the polymer and PC71BM at a weight ratio of 1:1.5 at 1100 rpm for 60 s. The active-layer thickness was controlled by changing the concentration of the solution; for example, a 10 mg mL\(^{-1} \) solution (based on polymer concentration) typically gave an active layer of 300–350 nm thickness. Thermal annealing of the blend films was carried out by placing them on a hot plate at 100 °C for 15 min in a nitrogen atmosphere. A 5 nm PFN–Br layer was then spin-coated from methanol solution onto the active layer. The thin films were transferred into a vacuum evaporator connected to the glove box, and Ag (100 nm) was deposited sequentially through a shadow mask under a pressure of \( 1 \times 10^{-7} \) mbar, with an active area of the cells of 0.04 cm\(^2 \).

**Steady State and Transient Double Injection:** Double injection current–voltage curves were recorded in the dark using a Keithley 2400 Source Measure Unit. The double injection current transients were measured using an Agilent 33250A arbitrary waveform generator synchronized by a Stanford Research Systems DG535 delay generated. The signal was recorded using a digital storage oscilloscope (LeCroy WaveRunner A6200) via a LabVIEW code.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

charge transport, non-Langevin recombination, organic solar cells, thick junctions

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