Explaining the Fill-Factor and Photocurrent Losses of Nonfullerene Acceptor-Based Solar Cells by Probing the Long-Range Charge Carrier Diffusion and Drift Lengths

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Organic solar cells (OSC) nowadays match their inorganic competitors in terms of current production but lag behind with regards to their open-circuit voltage loss and fill-factor, with state-of-the-art OSCs rarely displaying fill-factor of 80% and above. The fill-factor of transport-limited solar cells, including organic photovoltaic devices, is affected by material and device-specific parameters, whose combination is represented in terms of the established figures of merit, such as $\alpha$ and $\theta$. Herein, it is demonstrated that these figures of merit are closely related to the long-range carrier drift and diffusion lengths. Further, a simple approach is presented to devise these characteristic lengths using steady-state photocurrent measurements. This yields a straightforward way of determining $\theta$ and $\alpha$ in complete cells and under operating conditions. This approach is applied to a variety of photovoltaic devices—including the high efficiency nonfullerene acceptor blends—and show that the diffusion length of the free carriers provides a good correlation with the fill-factor. It is, finally, concluded that most state-of-the-art organic solar cells exhibit a sufficiently large drift length to guarantee efficient charge extraction at short circuit, but that they still suffer from too small diffusion lengths of photogenerated carriers limiting their fill factor.

1. Introduction

In recent years, the organic semiconductor community has witnessed a rapid increase in the performance of organic solar cells (OSC), with state-of-the-art efficiencies above 18%.[1] Such solar cells based on organic bulk heterojunctions present a radically different approach to photovoltaic operation compared to conventional inorganic $p$-$n$-junctions. Their strong optical absorption, tunable optoelectronic properties, and stability have taken OSC performance to new heights. The emergence of a family of nonfullerene acceptors (NFAs) have delivered a discontinuous advance in cell efficiencies, achieving the efficiency levels of first-generation silicon devices, and with the milestone of 20% now in sight.[1–3] Further technological challenges are related to facilitating the manufacturing process, mainly by increasing the active layer thickness, whilst preserving the device performance.[4–6] To this end, a straightforward and facile quantification of the charge collection performance and losses in transport-limited solar cells is required.[7–9]

To generate an external photocurrent, free charges have to be extracted. This process is diffusive or driven by drift, where extraction (mostly) competes with nongeminate recombination of free charges. A manifestation of this competition is the fill-factor FF. Some attention has been previously focused on correlating the FF with the efficiency of charge collection in organic solar cells based on the competition between the free charge extraction and second-order bimolecular recombination.[10] The bimolecular recombination is described via a recombination coefficient which is based on the Langevin expression multiplied by a reduction factor that takes into account processes that suppress the recombination below the Langevin limit.[11] In this picture, the extraction efficiency, as characterized by the ratio of the extraction to recombination rates,
can be described through simple analytical “figures of merit” (FoM) which take into account relevant device and material specific parameters. Several of such FoMs have been recently introduced which allow to quantify charge collection losses for given device thicknesses, applied voltages and charge transport parameters, based on the competition between extraction and nonemittion recombination.[10,12]

For example, Bartesaghi et al. proposed the parameter \( \theta \),

\[
\theta = \frac{k_{\text{rec}}}{k_{\text{ext}}} = \frac{k_1 G d^4}{\mu_n \mu_p V_{\text{int}}^2} \tag{1}
\]

where \( k_{\text{rec}} \) and \( k_{\text{ext}} \) are the effective recombination and extraction rates, \( k_1 \) is the bimolecular recombination coefficient, \( G \) is the volume generation rate, \( d \) is the active layer thickness, \( \mu_n \) and \( \mu_p \) are the electron and hole mobilities, respectively, and \( V_{\text{int}} \) is the internal voltage, which can be approximated by \( V_{\text{OC}} \) if \( \theta \) is considered at short circuit (SC) conditions.[10] The bias-dependent parameter \( \theta \) has also been defined as the ratio of the charge carrier lifetime and the extraction time in other studies.[13,14] Recently, \( \alpha \), a new field-independent FoM for organic solar cells with transport-limited photocurrent was proposed[12]

\[
\alpha = \frac{q^2 k_1 G d^4}{4 \mu_n \mu_p (k_b T)^2} \tag{2}
\]

Here, \( q \) is the elementary charge, \( k_b \) is the Boltzmann constant, \( T \) is the absolute temperature. In the same paper, an analytical expression for the \( JV \)-curves of organic solar cells was derived bearing a similar functional dependence as the Shockley-equation. It was shown that this equation approaches the traditional Shockley-diode equation for \( \alpha < 1 \), while it provides a good proper description of the \( JV \)-curves of transport-limited solar cells where \( \alpha > 1 \). This highlights the importance of these FoMs and their precise determination.

As seen in Equations (1) and (2), the determination of either \( \theta \) or \( \alpha \) requires performing separate measurements of several device properties, such as the recombination coefficient and the carrier mobilities. Several characterization techniques have been previously employed to investigate charge transport and recombination processes, using electrical or optical probe measurements. For example, the electrical studies have included space charge limited current (SCLC), time-of-flight (TOF), resistant-dependent photovoltage, and field-effect transistor (FET) mobility measurements.[15–18] Unfortunately, the reported values for charge carrier mobilities (or diffusion coefficients) obtained through these different techniques vary significantly since the measurements are often conducted in very different charge carrier density regimes both to one another and with respect to the 1-Sun condition.[19] Similarly, recombinination of free charges in the blend layer and in full devices has been studied by various techniques such as transient absorption (TAS),[20–22] transient photovoltage (TPV),[23,24] bias-assisted and time-delayed charge collection (BACE and TDCF),[25,26] double-injection,[28,29] photoinduced absorption (PIA),[30] though not necessarily at the exact conditions of a functional device at continuous illumination conditions.

In this paper, we demonstrate that the figures of merit \( \theta \) and \( \alpha \) are related to the effective carrier drift and diffusion lengths, respectively and that these parameters can be determined through the measurement of the device photoconductance. We apply this approach to different generations of organic materials, including state-of-the-art nonfullerene acceptor solar cells (Figure 1). This approach renders a simplified quantification of the charge collection performance and losses in transport-limited solar cells.

2. Results and Discussion

2.1. Figures of Merit and Characteristic Carrier Transport Lengths

In the following, we briefly outline the theoretical concept to relate the figures of merit \( \alpha \) and \( \theta \) to the effective carrier transport lengths. Let us first consider the relation between \( \alpha \) and the diffusion length of the photogenerated charges.

We consider \( V_{\text{OC}} \) conditions so that the generation rate \( G \) is equal to the recombination rate \( R = k_1 n p \). Here, \( n \) and \( p \) are the electron and hole density, respectively. We express the recombination rate by the respective carrier lifetimes:

\[
R = \frac{dn}{dt} = - \frac{n}{\tau_n} \Rightarrow k_1 n \tau_n = \tau_n^{-1}.
\]

Similarly, \( k_1 p \tau_p = \tau_p^{-1} \). For an intrinsic semiconductor, the carrier recombination lifetimes are equal: \( \tau_n = \tau_p = \tau. \) Further, we consider balanced carrier mobilities (\( \mu_n = \mu_p = \mu \)). We argue in the Supporting Information that the error associated with this simplification is small as long as the mobility ratio is smaller than 5. Indeed, in this regard many organic solar cells exhibit rather balanced mobilities.[2,31–34] We finally replace the mobility in the FoM \( \alpha \) by the diffusion coefficient using the Einstein relation

\[
\alpha = \frac{q^2 k_1 G d^4}{4 \mu \mu_0 (k_b T)^2} = \frac{d^4}{2 D \tau} = \left( \frac{d}{l_{\text{diff}}} \right)^2 \tag{3}
\]

Here, \( l_{\text{diff}} = \sqrt{D \tau} \) is the diffusion length for the photogenerated charge carriers at \( V_{\text{OC}} \) conditions.

Following the same line of arguments, we can express the FoM \( \theta \) in terms of the carrier drift length, \( l_{\text{dr}} \), via

\[
\theta = \frac{k_1 G}{\mu V_{\text{int}}} = \frac{d^4}{\mu \tau V_{\text{int}}} = \left( \frac{d}{l_{\text{dr}}} \right)^2 \tag{4}
\]

We remind the reader here that the relation between \( k_1 G \) and \( \tau^{-2} \) has been derived under the condition that the generation rate is equal to the recombination rate. Therefore, Equation 4 relates \( \theta \) to the drift length of carriers with a lifetime \( \tau \) corresponding to the \( V_{\text{OC}} \) conditions driven by the internal field present at short circuit (SC) conditions.

2.2. Relation of the Figure of Merits to the Open-Circuit and Short-Circuit Conditions

Let us consider a general picture of the solar cell operation in terms of a typical light \( JV \)-characteristic (Figure 2). Close to \( V_{\text{OC}} \), the electric field is either very small or absent, and diffusion comes forward as the main charge transport mechanism. As such, the value of \( l_{\text{diff}} \) relative to \( d \) plays a major role in charge extraction. This relation is exactly represented by the
FoM $\alpha$. For an ideal device (described by the Shockley–Queisser, SQ, limit), the diffusion length is infinite and $\alpha = 0$. In this regard, value of $\alpha > 0$ describes how strongly real devices deviate from the SQ limit near OC conditions. For reasonably well-performing solar cells, the maximum power point is near $V_{OC}$, and $\alpha$ is a good measure for the FF. Accordingly, we expect a direct relation between the device fill factor and $\frac{l_{dr}}{d}$. At short circuit condition, on the other hand, the carrier transport is dominated by drift, and the internal field across the active layer accounts for the extraction of photogenerated charges. It is only if $l_{dr}$ is significantly larger than the active layer’s width, $d$, that $J_{SC}$ will be equal to the generation current. According to Equation (4), this is the case where $\theta$ approaches zero. A larger value of $\theta$ will go along with inefficient extraction causing a loss of $J_{SC}$. As such, $\theta$ and the related drift length is a good measure for the deviation of the $J_{SC}$ from the ideal case. We remind the reader here that $\theta$ is related to the “hypothetical” drift length of a carrier density at OC but a mobility and electric field at SC. As an increasing internal field will decrease the carrier density (increase the carrier lifetimes), the true drift lengths under short circuit conditions may be even larger and extraction more efficient than predicted by $\theta$.
2.3. Determination of Effective Drift and Diffusion Lengths

As discussed earlier, the knowledge of the carrier drift and diffusion lengths allows to determine the two figures of merit determining the FF- and $J_{SC}$ losses. According to Equations (3) and (4), both transport lengths are related to the lifetime-mobility product $\tau \mu$ in the operating device. This property can be determined from quasi-steady state photoconductance measurements—as part of the impedance spectroscopy—at open circuit conditions (see the Supporting Information)

$$2\tau \mu = \frac{\sigma_{ph}}{J_{ph,sat}} = \frac{d^2}{J_{ph,sat} A} \frac{Y_{ph}}{\sigma_{ph}}$$

(5)

where $\sigma_{ph}$ is the excess photoconductivity due to both types of carriers, $Y_{ph}$ the excess photocurrent density which we take to be the same as the recombination current density $J_{RC}$ at $V_{OC}$. Here, we again assume balanced mobilities ($\mu_+ + \mu_- = 2\mu$). As we outline in the Supporting Information, the error introduced in the determination of $\alpha$ and $\theta$ under this assumption is small as long as the mobility imbalance is not significant.

Photoconductance spectra obtained as part of the impedance measurements of a 100-nm PM6:Y6 solar cell under various light intensities (from 0 to 1.4 Sun-equivalent) at $V_{OC}$ condition are given in Figure 3a. As can be seen, the conductance varies insignificantly in the frequency range 100 Hz to 10 kHz, suggesting that this region is suitable for the determination of the quasi-steady state photoconductivity. Figure 3b plots the dependence of this lower-frequency photoconductance on $V_{OC}$ for the same device at different light intensities. This value is then employed for determination of the lifetime-mobility product to ensure that the further analysis relates to the quasi-steady state condition.$^{[15,36]}$

Now, using Equation (5) we determine $\tau \mu$ in various laboratory photovoltaic devices. To study how strongly these parameters are influenced by the thin film processing methodology and width of the junction, a series of PM6:Y6 devices with different junction thicknesses and different concentrations of the solvent additive was prepared. In addition, to expand on the applicability of the technique, a broader set of systems, exemplifying different generations of organic photovoltaic materials have been investigated (chemical structures given in Figure 1). The performance data for the cells are shown in Table 1. The table reveals a wide spread of the FF even for the same material composition, especially highlighting the difficulty to extract carriers from thick junctions away from the short-circuit condition and upon transition of the dominant carrier transport mechanism from drift to diffusion (compare, e.g., devices 5 and 7 with device 1).

Based on the steady state photoconductance (SSPC) measurements performed at various light intensities, we can compare the illumination intensity dependence of $\tau \mu$ for different types of solar cells, as measured and normalized to the 1 Sun condition. Figure 3c shows this relation for several types of solar cells, including PM6:Y6, PPDT2FB:70%PCBM, and P3HT:1:1C60:PCBM. The same graph including all of the systems considered in Table 1 is given in Figure S2 (Supporting Information). Bearing in mind the photogenerated carrier density dependence on light intensity, it is evident that the obtained plot visualizes the influence of the carrier density on the lifetime-mobility product. Since the carrier density has typically a rather strong influence on the effective carrier lifetime, the weak dependence of $\tau \mu$ on the light intensity in the PM6:Y6 devices points towards a stronger carrier density dependence of mobility $\mu(n)$ in this material, in comparison to the PPDT2FB:70%PCBM and P3HT:1:1C60:PCBM solar cells.$^{[37–39]}$ Alternatively, the recombination behavior at low light intensities may be affected by doping of the active layer, leading to the quasi-first order character.$^{[40,41]}$

The obtained lifetime-mobility products are plotted against the device FF in Figure 3d. Having been employed as one of the initial FoMs to quantify charge collection in photovoltaic devices, the carrier lifetime-mobility product has previously gained much attention.$^{[42–45]}$ At the same time, it has been argued that this parameter is unsuitable for explaining the FF behavior of organic photovoltaic devices as it does not take into account crucial device parameters such as the device thickness and the internal electric field.$^{[9]}$ Figure 3d supports this argument indicating that for transport-limited devices, $\tau \mu$ on its own is not a proper metric for a comparative analysis of charge transport losses and evaluating device performance.

Table 1 tabulates the effective drift and diffusion lengths, defined according to Equations (3) and (4), in complete solar cells under 1-Sun equivalent illumination conditions. Whereas, the drift length at $J_{SC}$ exceeds the active layer thickness for almost all of the tested devices, the effective diffusion length is generally smaller than the active layer thickness and, thus, represents an important factor of loss in carrier extraction when drift is not efficient. As the diffusion length is related to the FoM $\alpha$, this imposes a direct limitation on the FF.

We note, the obtained effective carrier diffusion lengths for the thicker PM6:Y6 devices (over 300 nm) are consistent with our previous report estimating diffusion lengths for...
Figure 3. a) Conductance spectra of 100-nm PM6:Y6 solar cell at various illumination intensities at $V_{OC}$. b) Low-frequency (quasi-steady state) conductance of a 100-nm PM6:Y6 solar cell as a function of $V_{OC}$ at various light intensities. c) Light intensity dependence of the lifetime-mobility product for some of the representative organic solar cells (numbers represent different types of active layers as indicated below). d) Correlation of the fill-factor with the lifetime–mobility product $\tau\mu$ at the 1 Sun-equivalent illumination for the following photovoltaic systems: 1 – PM6:Y6 (100 nm, 0.5%CN); 2 – PM6:Y6 (145 nm, 0.5%CN); 3 – PM6:Y6 (270 nm, 0.5%CN); 4 – PM6:Y6 (285 nm, 0.5%CN); 5 – PM6:Y6 (300 nm, 0.5%CN); 6 – PM6:Y6 (400 nm, 1.5%CN); 7 – PM6:Y6 (550 nm, 0.5%CN); 8 – PM6:Y11 (80 nm); 9 – PM6:N4 (110 nm); 10 – PM6:Y11-N4 (80 nm); 11 – PM6:BTP-eC9 (120 nm); 12 – PPDT2FBT:Y6 (130 nm); 13 – PPDT2FBT:Y6 (120 nm, 1:1); 14 – PPDT2FBT:Y6 (100 nm, 1:2); 15 – PPDT2FBT:[70]PCBM (190 nm); 16 – P3HT: bis[C60]PCBM (150 nm, pristine); 17 – P3HT: bis[C60]PCBM (90 nm, annealed).

Table 1. Device output parameters measured under simulated AM1.5G illumination, compared to the carrier lifetime–mobility product $\tau\mu$, the carrier drift length at the $J_{SC}$ condition $l_{dr}$, and the carrier diffusion length $l_{dif}$ for the studied organic solar cells at the 1 Sun-equivalent illumination.

| Cell number | Active layer | Thickness [nm] | $J_{SC}$ [mA cm$^{-2}$] | $V_{OC}$ [V] | FF [%] | $\tau\mu$ [cm$^2$ V$^{-1}$] | $l_{dr}$ [nm] | $l_{dif}$ [nm] |
|-------------|--------------|----------------|-------------------------|-------------|-------|-----------------|-----------|-----------|
| 1           | PM6:Y6, 0.5% CN | 100            | 25.8                    | 0.826       | 68.9  | 6.50 x 10$^{-10}$ | 530.1     | 41.0      |
| 2           | PM6:Y6, 0.5% CN | 145            | 24.4                    | 0.831       | 67.2  | 1.21 x 10$^{-3}$  | 683.4     | 56.0      |
| 3           | PM6:Y6, 0.5% CN | 270            | 23.7                    | 0.817       | 56.1  | 2.66 x 10$^{-4}$  | 775.6     | 83.0      |
| 4           | PM6:Y6, 0.5% CN | 285            | 25.1                    | 0.815       | 55.0  | 3.07 x 10$^{-5}$  | 856.2     | 89.2      |
| 5           | PM6:Y6, 0.5% CN | 300            | 24.8                    | 0.800       | 57.8  | 3.95 x 10$^{-6}$  | 1025.8    | 101.0     |
| 6           | PM6:Y6,1.5% CN | 400            | 26.3                    | 0.810       | 68.1  | 7.10 x 10$^{-8}$  | 1407.3    | 135.7     |
| 7           | PM6:Y6, 0.5% CN | 550            | 20.9                    | 0.778       | 43.2  | 5.85 x 10$^{-5}$  | 818.3     | 123.0     |
| 8           | PM6:Y11      | 80             | 25.5                    | 0.871       | 53.5  | 2.08 x 10$^{-3}$  | 238.8     | 23.2      |
| 9           | PM6:N4       | 110            | 23.2                    | 0.782       | 64.5  | 6.05 x 10$^{-9}$  | 428.5     | 39.6      |
| 10          | PM6:Y11-N4   | 80             | 16.0                    | 0.858       | 65.4  | 3.45 x 10$^{-10}$ | 360.4     | 29.9      |
| 11          | PM6:BTp-eC9  | 120            | 23.3                    | 0.822       | 72.3  | 1.69 x 10$^{-5}$  | 1152.4    | 66.0      |
| 12          | PPDT2FBT:Y6  | 130            | 22.6                    | 0.676       | 47.0  | 4.17 x 10$^{-10}$ | 212.3     | 32.9      |
| 13          | PPDT2FBT:Y6, 1:1 | 120       | 25.3                    | 0.672       | 53.4  | 5.05 x 10$^{-9}$  | 273.8     | 36.1      |
| 14          | PPDT2FBT:Y6, 1:2 | 80     | 25.9                    | 0.699       | 61.6  | 4.91 x 10$^{-10}$ | 336.4     | 35.6      |
| 15          | PPDT2FBT:[70]PCBM | 190       | 15.9                    | 0.793       | 73.0  | 2.90 x 10$^{-8}$  | 1243.4    | 86.6      |
| 16          | P3HT: bis[C60]PCBM, as-prepared | 150 | 5.3                     | 0.711       | 36.8  | 2.22 x 10$^{-10}$ | 99.7      | 24.0      |
| 17          | P3HT: bis[C60]PCBM, annealed | 90 | 7.5                     | 0.729       | 65.6  | 5.45 x 10$^{-9}$  | 437.4     | 37.5      |
individual carriers based on separate SCLC and PIA measurements (given that $l_{\text{dr}} = \sqrt{l_{\text{u}} \times l_{\text{d}}}$).\cite{41} Moreover, the evaluated lifetime-mobility product for PM6:Y6 is thickness dependent. This insinuates that the mobility and/or the lifetime are also thickness dependent, which agrees with our recent publication on the SCLC measurements of mobilities in PM6:Y6 cells of different active layer thicknesses.\cite{6} Specifically, the reduction in $k_2$ in the PM6:Y6 devices with the progressively increasing active layer thickness agrees with an extended carrier lifetime resulting in higher $l_{\text{dif}}$. This intriguing observation may be assigned to the increased crystallinity and domain size of Y6 upon increasing the junction thickness, which may result in a slow transition from a pure bulk-heterojunction-like morphology to more segregated domains, effectively a combination of a bulk heterojunction and a defined layer structure. For many systems, theoretical and experimental work revealed a strong correlation between the degree of phase separation and the efficiency of CT dissociation, which was attributed to the existence of entropy and a free energy gradient from the intermixed to the phase-separated domains or charge carrier delocalization on aggregates of the pure components.\cite{46–48} It is thought that the energetic cascade between mixed and pure phases drives photogenerated charges to the pure phase, thereby facilitating the spatial separation of charges and reducing CT state recombination losses. This mechanism would explain why phase separated blends often have efficient charge separation and slow charge recombination.

The main concern with using the SSPC measurements to simultaneously determine $l_{\text{up}}$, which represents the $J_{\text{SC}}$ condition, and $l_{\text{dif}}$, which represents the $V_{\text{OC}}$ condition, relates to the carrier density and/or field-dependence of the lifetime-mobility product in organic materials.\cite{19,49,50} Since the measurement is performed at $V_{\text{OC}}$, the derived $l_{\text{dif}}$ is expected to be less contentious than $l_{\text{up}}$, illustrating the advantage of utilizing the diffusion length and $\alpha$ on the other hand, the generalization towards $\theta$ should be possible, when the $\theta$ does not show a strong dependence on carrier density (Figure 3c). An important difference between the definitions of $\alpha$ according to Equation (2) and its definition according to Equation (3) lies in the explicit representation of carrier recombination through the mechanism of bimolecular recombination, hence, $k_2$, in the former expression. Equation (3) does not rely on pinpointing the specific recombination mechanism, instead considering the generalized recombination parameter of the effective lifetime, incorporated into the carrier diffusion length.

2.4. Correlating Transport Lengths with Device Performance

Due to the direct relationship between the fill-factor FoM $\alpha$ and $l_{\text{dif}}/d$ (Equation (3)), the ratio of the effective diffusion length and the active layer thickness can be used on its own for correlating with FF. Figure 4a demonstrates this correlation for a range of organic solar cells with thicknesses ranging from 80 to 550 nm at the 1 Sun-equivalent illumination. The simulated points in the $FF$-$l_{\text{dif}}/d$ plot were obtained via drift-diffusion simulations for the $V_{\text{OC}}$ values of 0.7–0.9 V and at balanced carrier mobilities.\cite{51} The impact of increasing the mobility imbalance on the simulation results may be seen in Figure S3a in the Supporting Information. In addition, Figure 4a shows the analytical $FF$-$l_{\text{dif}}/d$ dependencies, assuming balanced mobilities, according to the following expression\cite{12}

$$FF = \frac{\mu_{\text{OC}} - \ln \left(0.79 + 0.66 \mu_{\text{OC}} \frac{1}{12}\right)}{\mu_{\text{OC}} + 1} \tag{6}$$

where,

$$\mu_{\text{OC}} = -\frac{qV_{\text{OC}}}{(1+\alpha)k_BT} \tag{7}$$

A good overlap of the experimental data both with the analytical expression (Equation (6)) and the simulation results is observed. According to Table 1 and Figure 4a, the $l_{\text{dif}}$ values—at the 1-Sun equivalent condition—for the systems examined in this work are generally smaller than the device thicknesses, with the PM6:BTP-eC9 and PPD2TFBT[70]PCBM systems having the highest relative effective diffusion length and, concomitantly, the highest FF values.\cite{30,52} The presented results in combination with the definition of the FoM $\alpha$, according to Equation (3), show that as $l_{\text{dif}}$ approaches $d$, the value of $\alpha$ gets closer to unity, indicating the transition to a Shockley-type solar cell.\cite{12,13}\ The consideration of $\alpha$ in terms of the relative effective diffusion length allows to formulate an alternative definition of a Shockley-type cell as the cell for which $l_{\text{dif}}/d$ is close to or exceeds unity.

Having been derived from the fill-factor FoM $\theta$ (Equation 4), $l_{\text{dif}}/d$ can be employed for correlating with the FF. On the other hand, we have argued earlier that the parameter $\theta$, and therefore $l_{\text{up}}/d$, is more related to the efficiency of charge extraction at short circuit, $J_{\text{SC}}/J_{\text{G}}$. This is indeed the case. Figure 4b shows the relationship between $J_{\text{SC}}/J_{\text{G}}$ and $l_{\text{up}}/d$ from the simulation of devices as in Figure 4a, with balanced mobilities but all other parameters varying over a wide range.\cite{10} The simulations predict the onset of a significant current loss once the drift length becomes smaller than the device thickness. The very same trend is seen experimentally, with $J_{\text{G}}$ approximated by the saturated photocurrent at the reverse bias $J_{\text{sat}}(\sim 1 \text{ V})$. From these results we learn that the drift length in most systems exceeds the junction thickness; suggesting negligible photocurrent losses at SC conditions. However, there are systems which suffer from such current losses and these are indeed the devices (mostly) with a rather small $l_{\text{up}}$ in relation to device thickness. As evidenced by the simulation results for different carrier mobility ratios, the spread of the experimental points may be related to the imbalanced mobilities, although the influence of such factors as the presence of shunting, field-dependent generation, formation of the space charge region etc., should also not be excluded (see Figure S4 (Supporting Information) and JV-Curves Under Illumination). We note here that a photocurrent loss due to inefficient extraction will always go along with a reduction of the FF and that this FF-loss will set in much earlier than the decrease of $J_{\text{SC}}$. This is the exact reason why the FF deviates from the ideal case already at a $\theta$ of $10^{-4}$ (see Figure S4d in the Supporting Information) corresponding to $d/l_{\text{up}} \approx 0.01$. The direct relationship between the photocurrent loss and $l_{\text{up}}/d$
for a number of photovoltaic systems: 1 – PM6:Y6 (100 nm, 0.5%CN); 2 – PM6:Y6 (145 nm, 0.5%CN); 3 – PM6:Y6 (270 nm, 0.5%CN); 4 – PM6:Y6 (285 nm, 0.5%CN); 5 – PM6:Y6 (300 nm, 0.5%CN); 6 – PM6:Y6 (400 nm, 1.5%CN); 7 – PM6:Y6 (550 nm, 0.5%CN); 8 – PM6:Y6 (110 nm); 9 – PM6:N4 (110 nm); 10 – PM6:Y11-N4 (80 nm); 11 – PM6:BT; eC9 (120 nm); 12 – PPD2TFTBY6 (130 nm); 13 – PPD2TFTBY6 (120 nm, 11); 14 – PPD2TFTBY6 (100 nm, 1,2); 15 – PPD2TFTBY6 (190 nm); 16 – P3HT: bis[C60]PCBM (150 nm, pristine); 17 – P3HT: bis[C60]PCBM (90 nm, annealed). The continuous lines in (a) are obtained using analytical expressions (Equations (9) and (10)) and the dotted line—using Equation S13 in the Supporting Information.

In the Supporting Information (see, respectively, the dashed and dotted lines in Figure 4b). The very good agreement between the experimental data points and the prediction by the Hecht equation is outlined analytically in terms of the effective carrier mobility of \( \mu \) using the steady state photoconductance measurements in a wide range of OPV blends, focusing mainly on nonfullerene acceptor systems. It is shown that these figures of merit are related to the effective drift and diffusion lengths, corresponding to the short-circuit and open-circuit conditions, respectively. Using a simple approach, we show that the drift length in PM6:Y6 and most systems exceeds that of the active layer thickness; thereby not limiting the photocurrent at \( J_{SC} \). On the other hand, the diffusion length in these devices is smaller than the width of the active layer, thereby limiting the FF. However, when \( l_{dd} \) approaches \( d \)—due to high mobility or reduced recombination—the transition to a Shockley-type solar cell occurs and FF around and above 80% can be obtained.

4. Experimental Section

Device Fabrication: A variety of organic photovoltaic (OPV) solar cells employed for the study were fabricated on indium-tin oxide (ITO)-coated pre-etched and pre-cleaned glass substrates. In all OPV devices, a 30-nm-thick poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate) (PEDOT:PSS) film was used as a hole-transporting layer (HTL). Active layer solutions were spin-coated by varying spin speeds and accelerations to obtain the desired thicknesses. The organic donor materials employed in the study include (1) poly[(2,6-(4,8-bis(5-(2-ethylhexyl)-3-fluorothiophen-2-yl)benzo[1,2-b:4,5]dithiophene)-alt-(5,5′-(1′,3′-di-2-thienyl-5′,7′-difluoro-2,3-dihydro-1H-inden-2,1-diyldiene))] (PM6), (2) poly[(2,5-bis(2-hexyldecyloxy)phenylene)-alt-(5,6-difluoro-4,7-di(thieno-2-yl)benzo[c][1,2,5]thiadiazole]) (PPD2TFTBY6), (3) poly(3-hexylythiophene) (P3HT). The organic acceptor materials include both nonfullerene and conventional fullerene electron acceptors: (1) poly[(2,2′-((2,2′-Z)-((12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-1,2,5-thiadiazolo[3,4-e]thieno[2′,3′:4,5′]pyrrolo[3,2-g]thieno[2′,3′:4,5′]thieno[3,2-b]indole-2,10-diyldiene)](1,1′-dihydroidene))dimalonomer(triyne)), (2) poly((2,2′-((2,2′-Z)-((12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-6H-thieno[2′,3′:4,5′]thieno[2′,3′:4,5′]pyrrolo[3,2-g]thieno[2′,3′:4,5′]thieno[3,2-b]indole-2,10-diyldiene)])bis(methanlylidenec))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diyldiene))] (Y6), (3) poly((2,2′-((2,2′-Z)-((12,13-bis(4-ethylcylyl)-3,9-diundecyl-12,13-dihydro-6H-thieno[2′,3′:4,5′]thieno[2′,3′:4,5′]pyrrolo[3,2-g]thieno[2′,3′:4,5′]thieno[3,2-b]indole-2,10-diyldiene)])bis(methanlylidenec))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diyldiene))] (Y11), (4) poly((2,2′-((2,2′-Z)-((12,13-bis(4-ethylcylyl)-3,9-diundecyl-12,13-dihydro-6H-thieno[2′,3′:4,5′]thieno[2′,3′:4,5′]pyrrolo[3,2-g]thieno[2′,3′:4,5′]thieno[3,2-b]indole-2,10-diyldiene)])bis(methanlylidenec))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diyldiene))] (Y11).

3. Conclusion

In summary, we have presented an experimental and analytical framework for the evaluation of the fill-factor figures of merit \( \theta \) and \( \alpha \) using the steady state photoconductance measurements in a wide range of OPV blends, focusing mainly on nonfullerene acceptor systems. It is shown that these figures of merit are related to the effective drift and diffusion lengths, corresponding to the short-circuit and open-circuit conditions, respectively. Using a simple approach, we show that the drift length in PM6:Y6 and most systems exceeds that of the active layer thickness; thereby not limiting the photocurrent at \( J_{SC} \). On the other hand, the diffusion length in these devices is smaller than the width of the active layer, thereby limiting the FF. However, when \( l_{dd} \) approaches \( d \)—due to high mobility or reduced recombination—the transition to a Shockley-type solar cell occurs and FF around and above 80% can be obtained.

The results presented herein point to the possibility of utilizing the photovoltaic characteristics for the characterization of the FF and short-circuit current loss of a wide variety of photovoltaic devices, including state-of-the-art high-performance systems. Specifically, the \( l_{dd}/d \) ratio is shown to provide a good correlation with the device FF, simultaneously allowing to distinguish between the transport-limited and Shockley-type solar cells.
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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data available on request from the authors.

Keywords

diffusion length, drift length, figure of merit, lifetime-mobility product, steady-state photocconductance

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