

## Effect of Imbalanced Charge Transport on the Interplay of Surface and Bulk Recombination in Organic Solar Cells

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Surface recombination has a major impact on the open-circuit voltage ( $V_{OC}$ ) of organic photovoltaics. Here, we study how this loss mechanism is influenced by imbalanced charge transport in the photoactive layer. As a model system, we use organic solar cells with a 2 orders-of-magnitude-higher electron than hole mobility. We find that small variations in the work function of the anode have a strong effect on the light-intensity dependence of  $V_{OC}$ . Transient measurements and drift-diffusion simulations reveal that this is due to a change in the surface recombination rather than the bulk recombination. We use our numerical model to generalize these findings and determine the circumstances under which the effect of contacts is stronger or weaker compared to the idealized case of balanced charge transport. Finally, we derive analytical expressions for  $V_{OC}$  in the case that a pile-up of space charge is present due to highly imbalanced mobilities.

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### I. INTRODUCTION

Organic solar cells typically consist of a blend of an electron donor and an electron acceptor, sandwiched between two electrical contacts [1–3]. Ideally, the contacts act as semipermeable membranes for electrons (cathode) and holes (anode). In this case, the open-circuit voltage  $V_{OC}$  is solely determined by the splitting of the quasi-Fermi-levels  $E_{F,n} - E_{F,p}$  in the blend [4,5]. If only bimolecular recombination is present,

$$qV_{OC} = E_g - kT \ln \left( \frac{\beta N^2}{G} \right) \quad (1)$$

has been suggested, where  $q$  is the elementary charge,  $E_g$  is the band gap,  $k$  is the Boltzmann constant,  $T$  is the temperature,  $\beta$  is the recombination coefficient,  $N$  is the density of states, and  $G$  is the generation rate [6,7]. The latter part of Eq. (1) predicts a slope of  $kT/q$  when plotting  $V_{OC}$  versus the logarithm of the light intensity.

However, many contacts, such as metals or doped polymers, are nonselective. This means that they have the ability to exchange both minority and majority charge carriers with the photoactive layer. The extraction of minority carriers (electrons at the anode, holes at the cathode)

leads to a reduction of  $V_{OC}$  [8]. Here, we call this loss mechanism surface recombination, with a corresponding recombination current

$$j_S = qSn_{\min}, \quad (2)$$

where  $S$  denotes the surface-recombination velocity and  $n_{\min}$  is the concentration of minority carriers close to the contact under consideration [9,10].

In the case of Ohmic contacts,  $j_S$  is strongly reduced by charge-carrier injection. Because of the high concentration of majority carriers at the interface, minority carriers are much more likely to recombine in the bulk, rather than leaving the device via the “wrong” electrode. As a result,  $V_{OC}$  is still determined solely by properties of the bulk and follows Eq. (1).

The situation changes when one of the contacts is non-Ohmic. For instance, if an injection barrier  $\varphi_{an}$  is present at the anode, fewer holes are injected into the blend, so that  $n_{\min}$  and  $j_S$  are effectively increased. Solak *et al.* [11] showed that the open-circuit voltage at high light intensities may then be described as follows:

$$qV_{OC} = E_g - \varphi_{an} - \frac{kT}{2} \ln \left( \frac{\beta N^2}{G} \right). \quad (3)$$

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Compared to Eq. (1), there are two differences. First, the constant energetic part is reduced by the barrier height. Second, because of the factor  $1/2$  in front of the logarithm, the intensity dependence of  $V_{OC}$  is now given by a slope of  $kT/2q$  (instead of  $kT/q$ ). Such a reduction of the slope has been demonstrated in both experiment and simulation [11–13]. The transition between Eqs. (1) and (3) has been assumed to take place when  $V_{OC}$  equals the built-in voltage  $V_{bi}$  [11].

For large  $S$ , surface recombination is not limited by the interface kinetics but by the transport of carriers toward the contact [12]. Hence the question arises as to how the open-circuit voltage depends on the charge-carrier mobility  $\mu$ . Numerical studies have indicated a decrease of  $V_{OC}(\mu)$  with increasing mobility if the contacts are nonselective [7,14,15]. The result is a finite optimum value of  $\mu$  in terms of the overall device efficiency, independent of the recombination mechanism in the bulk.

In the above considerations, the mobilities of electrons ( $\mu_n$ ) and holes ( $\mu_p$ ) are considered balanced. However, this condition is often not fulfilled in practice. Many polymer-fullerene solar cells, for instance, exhibit a higher electron than hole mobility [16,17], while it is the other way round for devices based on recent nonfullerene acceptors [3,18,19]. It is well known that the imbalanced mobilities lead to a pile-up of space charge close to one contact, which may reduce both the fill factor and the short-circuit current [20,21]. In contrast, little attention has been paid to how this affects the open-circuit voltage. Recently, Spies *et al.* [22] suggested that the additional charge would further reduce the built-in potential and, thus, severely affect the magnitude of  $V_{OC}$ .

In this work, we use an experimental system with a strong mobility mismatch of  $\mu_n/\mu_p = 100$  and a well-calibrated numerical model to discuss the effect of imbalanced transport on the open-circuit voltage in more detail. We show that the ratio between electron and hole mobility critically determines whether  $V_{OC}$  is dominated by surface recombination or bimolecular recombination in the bulk. With the help of the numerical simulations, we expand the analytical framework given by Eq. (3) to the case of imbalanced mobilities.

## II. EXPERIMENTAL AND NUMERICAL FRAMEWORK

### A. Experiment

We fabricate solar cells based on a bulk heterojunction of the small-molecule donor 2,4-bis[4-(*N,N*-diisobutylamino)-2,6-dihydroxyphenyl] squaraine (SQIB) and the fullerene acceptor [6,6]phenyl- $C_{61}$ -butyric acid methyl ester (PCBM). This blend is known for a strong contrast between the mobility of electrons ( $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) and holes ( $10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) [23]. Our devices had the structure ITO/HTL/SQIB:PCBM/LiF/

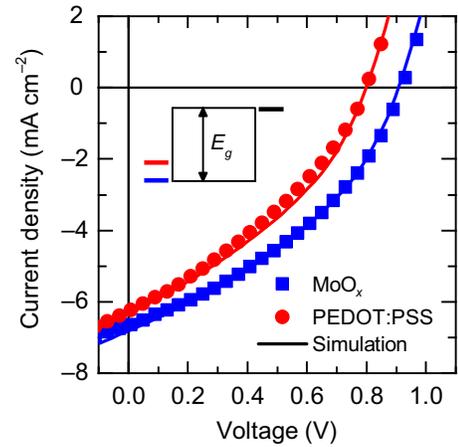


FIG. 1. Current-voltage curves for  $\text{MoO}_x$  (squares) and PEDOT:PSS (circles) devices under simulated AM1.5G illumination ( $100 \text{ mW cm}^{-2}$ ). The solid lines are the result of drift-diffusion simulations using the parameter set in Table I. The only parameter varied is the injection barrier  $\varphi_{an}$  at the anode. The inset shows a schematic energy-level diagram at  $V = V_{OC}$ .

Al, where ITO denotes indium tin oxide and HTL denotes the hole-transport layer. Details regarding the used materials and the device preparation can be found elsewhere [23–25].

To realize both devices with an Ohmic and a non-Ohmic contact, we change the HTL from molybdenum suboxide ( $\text{MoO}_x$ ) to the doped polymer PEDOT:PSS. The energy level of PEDOT:PSS lies within the band gap of the photoactive blend, effectively reducing the built-in voltage by 280 mV. We determine  $V_{bi}$  using a recently developed charge-extraction technique [26] (see the Supplemental Material [27]). As shown in Fig. 1, this reduction results primarily in a significant drop of  $V_{OC}$  from 920 to 800 mV, which is in agreement with previous reports [28–30]. Conversely, the HTL has little effect on the short-circuit current and the fill factor; both current-voltage curves exhibit the typical shape of space-charge-limited collection [20,31]. Averaged photovoltaic characteristics for both types of devices can be found in the Supplemental Material [27].

### B. Numerical model

We aim to understand these findings using a numerical drift-diffusion model [32]. The model treats the bulk heterojunction as an effective semiconductor, sandwiched between two electrical contacts. The alignment of the work function of the contacts and the transport levels of the effective semiconductor is given by the injection barriers  $\varphi_{an}$  (anode) and  $\varphi_{cat}$  (cathode). The injection of charge carriers is then assumed to occur via thermionic emission. Surface recombination at the contacts is treated according to Eq. (2).

TABLE I. Input parameters used for the numerical drift-diffusion simulations.

Parameter	Value	Description
$T$	300 K	Temperature
$E_g$	1.36 eV	Effective band gap
$\varepsilon$	4	Dielectric constant
$d$	100 nm	Active-layer thickness
$N$	$10^{26} \text{ m}^{-3}$	Effective density of states
$\beta$	$10^{-17} \text{ m}^3 \text{ s}^{-1}$	Recombination coefficient
$S$	$10^5 \text{ ms}^{-1}$	Surface-recombination velocity
$\varphi_{\text{cat}}$	0 eV	Injection barrier, cathode
$\varphi_{\text{an}}$	varied	Injection barrier, anode
$\mu_n$	$2 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$	Electron mobility
$\mu_p$	$2 \times 10^{-10} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$	Hole mobility

We then assume that excess charges are generated by illumination through the transparent anode. To take the spatial distribution  $G = G(x)$  of the photogeneration into account, we couple the drift-diffusion model with transfer-matrix calculations [33,34]. The recombination of mobile carriers in the photoactive layer is considered to be solely bimolecular,

$$R = \beta(np - n_i^2), \quad (4)$$

where  $n$  and  $p$  are the density of electrons and holes, respectively, and  $n_i$  is the intrinsic carrier density. This is motivated by a recent study [23], where we show that nongeminate recombination in SQIB:PCBM blends resembles a second-order process with a prefactor  $\beta$  that is independent of the carrier density. However, we note that herein, Eq. (4) is used only as an empirical rate equation, without making any assumptions on the details of the actual recombination mechanism (e.g., whether it is radiative or nonradiative). All relevant input parameters for the simulation are listed in Table I.

With this model, we are able to describe the experimental data only by varying the injection barrier height at the anode, while keeping all other parameters constant (see the solid lines in Fig. 1). This proves that the variation of the HTL only affects the energy-level alignment at the anode but not the bulk properties of the active layer. Thus, we have at hand a suitable model system to study the effect of imbalanced mobilities on  $V_{\text{OC}}$ .

### III. RESULTS AND DISCUSSION

#### A. Impact of an injection barrier

Figure 2(a) shows the experimental light-intensity ( $I$ ) dependence of the open-circuit voltage. For the  $\text{MoO}_x$  device,  $V_{\text{OC}}$  versus  $\ln(I)$  has a slope of nearly  $kT/q$ , as predicted by Eq. (1) for Ohmic contacts. Hence, we can assume that  $V_{\text{OC}}$  is limited by bimolecular recombination in the bulk only. In contrast, the PEDOT:PSS device

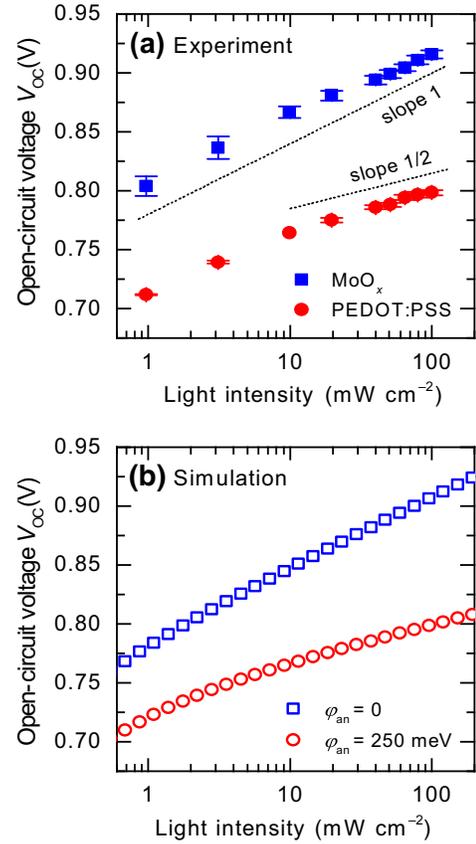


FIG. 2. The light-intensity dependence of  $V_{\text{OC}}$  under AM1.5G illumination for (a) experimental and (b) simulated devices based on  $\text{MoO}_x$  (squares) and PEDOT:PSS (circles). The error bars in (a) are the standard deviation for five individual samples. The dotted lines indicate a scaling of  $kT/q$  (“slope 1”) and  $kT/2q$  (“slope 1/2”).

shows a transition toward a lower slope at mid-to-high light intensity. The reduced slope agrees qualitatively well with Eq. (3). This kind of behavior, with the slope going from approximately  $kT/q$  at low intensity to  $kT/2q$  at higher intensity (while  $V_{\text{OC}}$  remains lower than for the  $\text{MoO}_x$  device over the entire intensity regime), suggests that surface recombination at one non-Ohmic contact is dominating in the PEDOT:PSS device [12].

As can be seen in Fig. 2(b), both the absolute value and the intensity dependence of  $V_{\text{OC}}$  are well captured by our numerical model if we only change the magnitude of  $\varphi_{\text{an}}$ . It is not possible to reproduce the experimental data by varying the surface-recombination velocity at the anode instead (see the Supplemental Material [27]). A significant reduction of  $S$  would give rise to an extraction barrier, which would then result in S-shaped current-voltage curves [9,10,35,36]. Because such an S-kink is not present in the data shown in Fig. 1, we expect the surface-recombination current to be mainly determined by the carrier concentrations at the anode and the transport properties of the bulk.

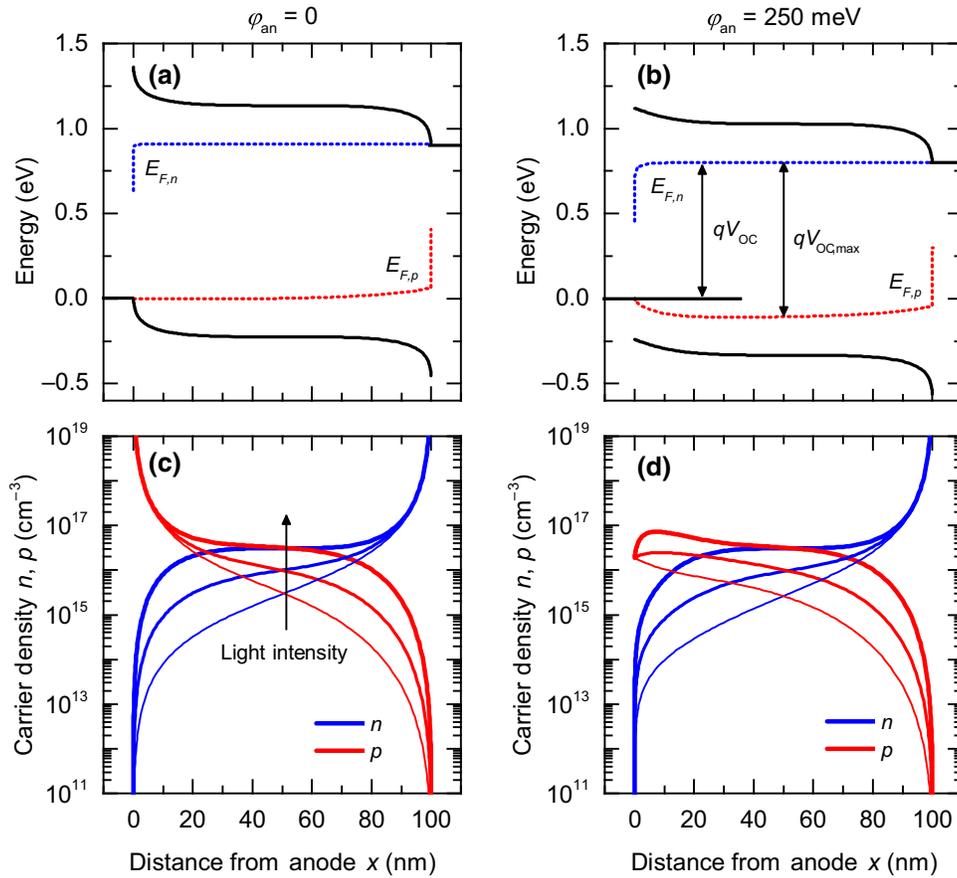


Figure 3 shows the effect of the anode work function on the energy-band diagrams, as well as the electron and hole concentration. The solid lines in panels (a) and (b) denote the transport levels under 1-sun illumination and the dashed lines the quasi-Fermi-levels. The  $\text{MoO}_x$  device shows significant band bending at both electrodes caused by injection of majority carriers into the semiconductor. In the case of the anode, there is a high concentration of holes, exceeding the concentration of photogenerated carriers in the bulk by several orders of magnitude. Because of the high hole concentration, electrons are likely to recombine within the bulk, rather than being extracted. The quasi-Fermi-levels at both electrodes are flat, so that the open-circuit voltage represents the splitting of the quasi-Fermi-levels in the bulk. The situation remains relatively unchanged with increasing photogeneration. Hence, the light-intensity dependence of  $V_{\text{OC}}$  shows a constant slope over the intensity range studied herein and can be described by bimolecular recombination in the bulk.

For the PEDOT:PSS device with a non-Ohmic contact, the concentration of injected holes is much lower, leading to reduced band bending at the anode. Consequently, the electron concentration close to the anode is higher than for the case with an Ohmic contact. According to Eq. (2), this non-negligible concentration of minority carriers induces

a surface-recombination current  $j_s$ . To ensure open-circuit conditions (no net current), it must be compensated by a hole current

$$j_p = p\mu_p \frac{dE_{F,p}}{dx}. \quad (5)$$

Because the magnitude of  $p$  close to the anode is fixed by the barrier height  $\phi_{\text{an}}$  and  $\mu_p$  is considered constant, an increase of  $j_s$  due to increasing photogeneration can only be compensated by a gradient of the quasi-Fermi-level for holes. At 1-sun illumination, the gradient in  $E_{F,p}$  is clearly visible. Consequently, the open-circuit voltage is reduced and no longer a measure of the quasi-Fermi-level splitting in the bulk.

Notably, the drift-diffusion model predicts that beyond a thin region of approximately 15 nm close to the anode, both the quasi-Fermi-level splitting and the carrier concentrations remain unchanged regardless of the anode work function. To check this prediction, we measure the carrier concentration under open-circuit conditions using bias-assisted charge extraction [23,37]. Figure 4(a) shows indeed only a constant voltage shift  $\Delta V_{\text{OC}}$  between the data points for the  $\text{MoO}_x$  and the PEDOT:PSS sample, while the carrier concentration at a given light intensity remains unchanged.

FIG. 3. Simulated band diagrams and local carrier concentrations for (a,c)  $\phi_{\text{an}} = 0$  and (b,d)  $\phi_{\text{an}} = 250$  meV. The anode is positioned at  $x = 0$ . The solid lines in panels (a) and (b) denote the transport bands and the dashed lines the quasi-Fermi-levels under AM1.5G illumination ( $100 \text{ mW cm}^{-2}$ ). Panels (c) and (d) show the total electron and hole concentration for incident-light intensities of 1, 10, and  $100 \text{ mW cm}^{-2}$ . The result of the injection barrier is a gradient of  $E_{F,p}$  at the anode, which reduces  $V_{\text{OC}}$  relative to its optimum value  $V_{\text{OC,max}}$  given by the quasi-Fermi-level splitting in the bulk.

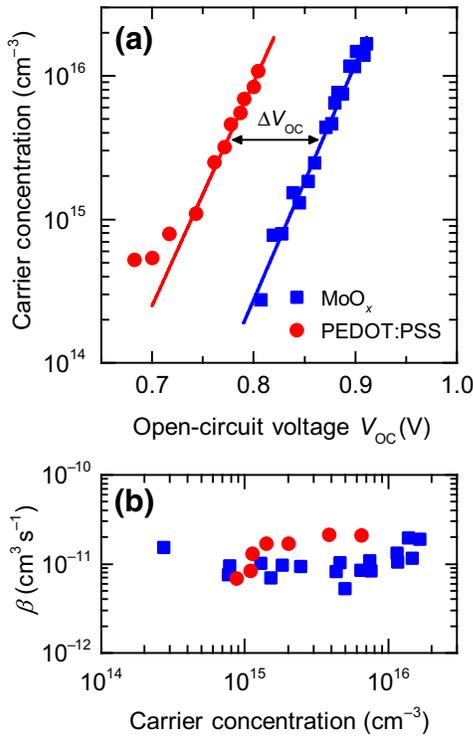


FIG. 4. The results of charge extraction and transient photovoltage measurements for MoO<sub>x</sub> (squares) and PEDOT:PSS (circles) devices. (a) The extracted charge-carrier concentration versus the open-circuit voltage. (b) The recombination rate constant  $\beta$  versus the carrier concentration.

Furthermore, we perform transient photovoltage experiments to determine the carrier lifetime [38]. By plotting the lifetime versus the carrier concentration (see the Supplemental Material [27]), we obtain a reaction order close to 2 in both cases. This indicates that the recombination in the bulk is bimolecular, independent of whether an Ohmic or a non-Ohmic hole contact is present. That the nature of the contact does not affect the recombination in the bulk is also evident from Fig. 4(b), where we plot the recombination-rate constant  $\beta$  as a function of the carrier concentration. For both devices, we find fairly similar values of  $\beta \sim 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ .

Hence, we can conclude that the variation in  $V_{OC}$  between the MoO<sub>x</sub> and PEDOT:PSS devices is solely related to a gradient in the hole quasi-Fermi-level at the anode, while the recombination in the bulk is largely unaffected. This is in line with previous studies on material combinations with balanced mobilities [13,22]. However, it seems surprising that a relatively low injection barrier of 250 meV has such a strong effect on both the magnitude and light-intensity dependence of  $V_{OC}$ . In the following, we show that this is a direct consequence of the highly imbalanced mobilities.

## B. Effect of imbalanced charge transport on the open-circuit voltage

Having shown that our numerical model describes the experimental data well, we will now use it to discuss the effect of charge transport in more detail. Figure 5(a) demonstrates how an injection barrier at the anode (similar to the PEDOT:PSS device) affects the hole quasi-Fermi-level for different ratios between  $\mu_n$  and  $\mu_p$ . For balanced mobilities ( $\mu_n = \mu_p$ ), the injection barrier induces a certain gradient  $dE_{F,p}/dx$ , which leads to a voltage loss  $\Delta V_{OC,1}$  compared to the case with an Ohmic hole contact. If we now lower the hole mobility by 1 or 2 orders of magnitude, the gradient of the quasi-Fermi-level increases significantly. This can be reflected by introducing a second loss component  $\Delta V_{OC,2}$  due to the imbalanced charge transport. Hence, the total loss in  $V_{OC}$  can be expressed as follows:

$$\Delta V_{OC} = \Delta V_{OC,1} + \Delta V_{OC,2}. \quad (6)$$

Another possible loss mechanism would be a reduction of the quasi-Fermi-level splitting (and, thus, the carrier concentration) in the bulk due to very strong surface recombination [22]. However, such a reduction is not present here, as is evident from both the bulk-recombination measurements (see Fig. 4) and the additional band diagrams shown in the Supplemental Material [27].

Figures 5(b) and 5(c) illustrate the effect of imbalanced charge transport in more detail. In Fig. 5(b), an accumulation of holes close to the anode for  $\mu_n/\mu_p \gg 1$  is clearly seen. However, at the same time, the absolute value of  $\mu_p$  is decreased. Hence, it is worthwhile to take a look at the conductivity  $\sigma_p = q\mu_p p$ . Figure 5(c) shows that the increase of the hole concentration is not large enough to compensate the decrease of the hole mobility. At the same time, the conductivity  $\sigma_n$  for electrons is nearly unaffected. Hence, the assumption of more imbalanced charge transport effectively decreases the difference between  $\sigma_p$  and  $\sigma_n$  close to the anode. This can be understood in terms of a further loss of selectivity or a virtual increase of the injection barrier height [8,22].

Figure 6 shows  $V_{OC}$  as a function of  $\mu_p$  for a fixed electron mobility of  $\mu_n = 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and different barrier heights  $\varphi_{an}$ . First, we discuss the case of a constant  $\beta$ , which means that the mobility does not affect the bulk recombination [Fig. 6(a)]. Only a weak variation of  $V_{OC}$  with  $\mu_p$  is then visible for an Ohmic contact ( $\varphi_{an} = 0$ ). The slight decline of  $V_{OC}$  is due to the fact that the cathode is also assumed to be nonselective. When  $\mu_p$  is very large ( $\mu_p \gg \mu_n$ ), the device is dominated by hole transport, so that surface recombination at the cathode becomes limiting. If we now introduce a significant barrier at the anode ( $\varphi_{an} \gg kT$ ), it is clearly seen that the voltage loss  $\Delta V_{OC}$  becomes determined by the mobility ratio. For  $\mu_p = \mu_n$ ,

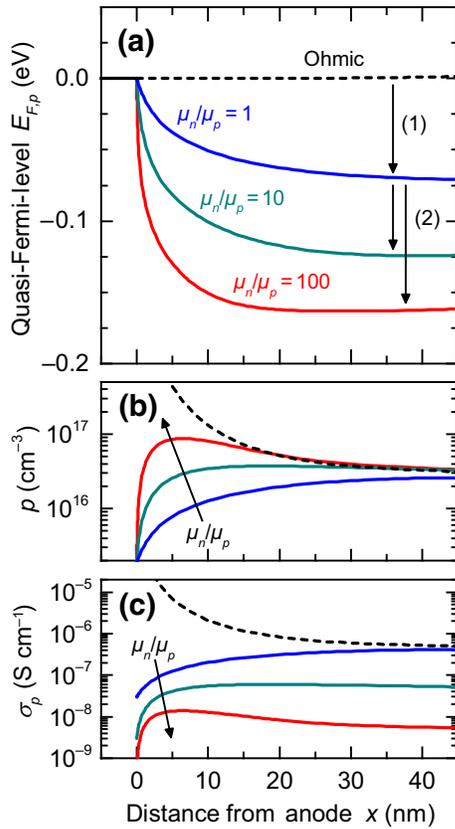


FIG. 5. (a) The quasi-Fermi-level  $E_{F,p}$  close to the anode (located at  $x = 0$ ) for an ideal device with Ohmic contacts and balanced transport (dashed line) and for a device with an injection barrier and varied  $\mu_n/\mu_p$  (solid lines). The arrows indicate the voltage loss due to the barrier height (1) and due to the imbalanced mobilities (2), respectively. Panels (b) and (c) show the corresponding hole concentration  $p$  and hole conductivity  $\sigma_p = q\mu_p p$ .

the reduction of  $V_{OC}$  is solely caused by  $\Delta V_{OC,1}$ , which is proportional to  $\varphi_{an}$ . This no longer holds true for imbalanced mobilities. In the case  $\mu_p \ll \mu_n$ , the voltage loss is further increased by the mobility-dependent  $\Delta V_{OC,2}$  and a logarithmic dependence of  $V_{OC}$  on  $\mu_p$  can be seen. In contrast, for  $\mu_p \gg \mu_n$ , surface recombination is partly compensated, as charges now accumulate at the (Ohmic) cathode. As a result, the total voltage loss is effectively reduced ( $\Delta V_{OC,2} < 0$ ). We also do simulations for  $d = 70$  nm and  $d = 140$  nm (see the Supplemental Material [27]). Previously, we have shown that this thickness range produces clear differences in the competition between charge extraction and bimolecular recombination [23]. However, we find here that the mobility dependence of  $V_{OC}$  is fairly unaffected by the active-layer thickness. This shows that our results are independent of the collection of majority carriers.

Next, we consider the case in which the bulk recombination is also limited by diffusion [Fig. 6(b)]. Such a process

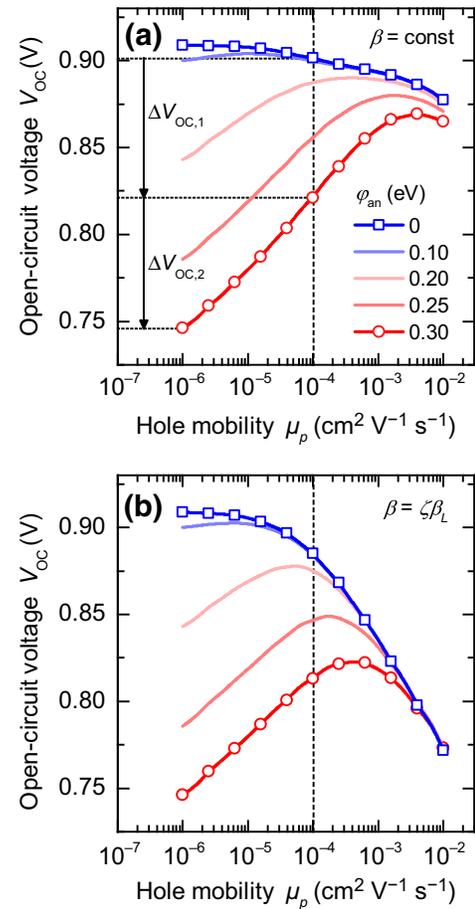


FIG. 6. The simulated  $V_{OC}$  for a varied hole mobility but a fixed electron mobility of  $\mu_n = 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and different barrier heights  $\varphi_{an}$  at the anode. Panel (a) shows the case of a constant  $\beta$ , while for (b) we assume reduced Langevin recombination with  $\beta = \zeta\beta_L$ . The vertical dashed lines indicate the case  $\mu_n = \mu_p$ . The arrows in (a) exemplify the voltage loss  $\Delta V_{OC,1}$  for a barrier of 300 meV and  $\Delta V_{OC,2}$  for a mobility mismatch of  $\mu_n/\mu_p = 100$ , respectively.

is commonly described by the Langevin model, which predicts a mobility-dependent recombination coefficient:

$$\beta_L = \frac{q}{\epsilon\epsilon_0}(\mu_n + \mu_p). \quad (7)$$

However, it is known that the recombination in phase-separated organic blends is reduced compared to the Langevin model,  $\beta = \zeta\beta_L$ , where  $\zeta$  is a reduction factor [39–41]. Here, we choose  $\zeta = 0.1$ , so that with the given mobilities of the SQIB:PCBM system, the experimental value of  $\beta$  is reproduced. For  $\mu_p \ll \mu_n$ , no difference in the mobility dependence of  $V_{OC}$  can be seen between Figs. 6(a) and 6(b), as  $\beta$  is largely determined by the fixed  $\mu_n$ . If the mobilities are similar, there is a significant contribution of  $\mu_p$  to the magnitude of  $\beta$ . In the case  $\mu_p \gg \mu_n$ , the coefficient  $\beta$  becomes so large that the device is entirely dominated by bulk recombination and the barrier at the

anode is no longer relevant. Altogether, this results in a maximum of  $V_{OC}(\mu_p)$ , which shifts toward larger values of  $\mu_p$  with increasing  $\varphi_{an}$ . Such an optimum value of  $V_{OC}$  is unique for imbalanced charge transport and has not been observed in previous studies, where  $\mu_n$  and  $\mu_p$  have been varied simultaneously [7,14,15].

Our numerical results show that independent of the bulk recombination mechanism, surface recombination at the anode critically determines  $V_{OC}$  for imbalanced mobilities with  $\mu_p \ll \mu_n$ . In contrast, for  $\mu_p \gg \mu_n$ , the quality of the anode is less important. We note that our conclusions are directly transferable to the case of a non-Ohmic cathode. A significant barrier  $\varphi_{cat}$  would severely limit  $V_{OC}$  for  $\mu_n \ll \mu_p$ , which is a relevant scenario for nonfullerene solar cells [3,18,19].

### C. Analytical expression for $V_{OC}$ in the case of imbalanced mobilities

Recently, Sandberg *et al.* [12] provided analytical means to describe  $V_{OC}$  for different cases related to surface recombination. If one contact is non-Ohmic (here, the anode) and surface recombination is limited by the diffusion of minority carriers (here, electrons; effective velocity  $v_{d,n}$ ) rather than the interface kinetics ( $S \gg v_{d,n}$ ), the authors derived the expression

$$qV_{OC} = E_g - \varphi_{an} - kT \ln \left( \frac{v_{d,n}N}{Gd} \right) \quad (8)$$

for low light intensities, where bulk recombination is negligible. When  $V_{OC}$  is far from flat-band conditions, we have  $v_{d,n} \approx \mu_n |F(0)|$ , where  $F(0)$  is the electric field close to the anode. Equation (8) is valid as long as  $L_p^* \gg d$ , with the effective diffusion length

$$L_p^* \approx \left( \frac{\mu_{eff}kT}{q\sqrt{\beta G}} \right)^{1/2}, \quad (9)$$

where  $\mu_{eff} = 2\sqrt{\mu_n\mu_p}$  is an effective mobility. At high enough light intensities, so that  $L_p^* \ll d$  and flat-band conditions prevail on the anode side of the active layer, the surface recombination is restricted to a region given by the effective diffusion length. Under these conditions,  $V_{OC}$  can be approximated by [10,12]

$$qV_{OC} \approx E_g - \varphi_{an} - \frac{kT}{2} \ln \left( \frac{\mu_n \beta N^2}{\mu_p G} \right), \quad (10)$$

which in the limit  $\mu_n \rightarrow \mu_p$  is equivalent to the result of Solak *et al.* [11]. We note that Eq. (10) already provides a framework to predict  $V_{OC}$  for moderate mobility contrasts; however, its derivation assumes that flat-band conditions prevail close to the surface-recombination-dominated region near the anode. This is no longer valid for highly imbalanced mobilities.

For  $\mu_p \ll \mu_n$ , a considerable pile-up of holes is taking place close to the anode at high light intensities, as is clearly visible in Fig. 3(d). As is evident from Fig. 3(b), the resulting space-charge region of holes gives rise to a photo-induced upward energy-level bending near the anode. In the hole-dominated space-charge region, the bulk recombination of holes is negligibly small. Instead, at open-circuit conditions, the hole current within this region is balanced by an equal but opposite surface-recombination current of electrons, diffusing against the band bending at the anode. After accounting for the hole-induced energy-level bending and the associated electron diffusion, Eq. (10) is modified to

$$qV_{OC} = E_g - \varphi_{an} - \frac{kT}{2} \ln \left( \frac{q\mu_n^2 N^2}{\varepsilon\varepsilon_0\mu_p G} \right), \quad (11)$$

as shown in the Supplemental Material [27]. The main feature of Eq. (11) is that it no longer depends on the bimolecular recombination strength  $\beta$ . Hence, in the limit of highly imbalanced mobilities and at high enough light intensities,  $V_{OC}$  becomes independent of bulk recombination and is solely given by the contacts and the charge transport in the active layer. Equation (11) also explains the logarithmic  $\mu_p$  dependence at high mobility contrasts  $\mu_n/\mu_p \gg 1$  seen in Fig. 6. The voltage loss due to the imbalanced mobilities is then given by the following:

$$\Delta V_{OC,2} = \frac{kT}{2} \ln \left( \frac{q\mu_n^2}{\varepsilon\varepsilon_0\mu_p\beta} \right). \quad (12)$$

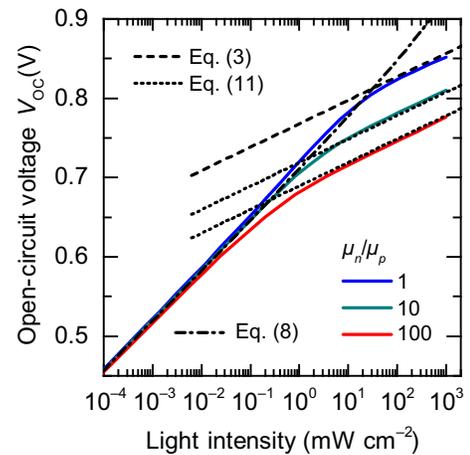


FIG. 7. The simulated value of  $V_{OC}$  (solid lines) versus the light intensity for a device having a non-Ohmic anode ( $\varphi_{an} = 0.3$  eV) at different ratios between  $\mu_n$  and  $\mu_p$ . Equations (3) and (11) are indicated by the dashed and dotted lines, respectively. Our extended analytical expression, Eq. (11), shows striking agreement with the simulations for highly imbalanced mobilities. The dash-dotted line indicates Eq. (8), valid in the low-intensity regime, with  $v_{d,n}$  approximated according to Ref. [12].

As shown in Fig. 7 for mobility contrasts of 1 and 2 orders of magnitude, the modified analytical expression in Eq. (11) describes the numerical data well in the high-intensity regime. We note that as long as the anode can be considered as non-Ohmic ( $\varphi_{\text{an}} \gg kT$ ), this also holds true for other injection barrier heights (see the Supplemental Material [27]). In the low-intensity regime,  $V_{\text{OC}}$  becomes independent of the mobility contrast and can be described by Eq. (8) instead. Our analysis demonstrates that the transition is shifted toward lower photogeneration for increasing  $\mu_n/\mu_p$ .

Furthermore, we check the validity of our analytical framework, as detailed in the Supplemental Material [27]. We find that Eq. (11) predicts the open-circuit voltage for mobility contrasts  $\mu_n/\mu_p \geq 5$  with a relative error below 1% (for the parameters in Table I). It is worth noting that Eq. (10), which neglects band bending in the hole-induced space-charge region, reaches a similar accuracy only for a mobility imbalance of less than a factor of 2. Finally, we point out that in none of the cases presented in Fig. 7 is Eq. (1) suitable to describe the data, even in the low-intensity regime and even though only pure bimolecular recombination is assumed in the simulation. Hence, special care has to be taken when trying to assess information about the bulk recombination from the slope of  $V_{\text{OC}}$  versus  $\ln(I)$ , also called the light ideality factor [42]. If the contacts are not sufficiently selective, the ideality factor will always be affected by surface recombination.

#### IV. CONCLUSION

In summary, we study how imbalanced charge transport affects the interplay of bulk and surface recombination in organic solar cells. Combining experiments and simulations for a blend system with a strong mobility mismatch, we identify two cases with respect to the energy-level alignment at the electrodes: For Ohmic contacts, the open-circuit voltage  $V_{\text{OC}}$  still is representative of the quasi-Fermi-level splitting in the bulk, even though the mobilities  $\mu_n$  and  $\mu_p$  are highly imbalanced. However, if one contact is non-Ohmic,  $V_{\text{OC}}$  becomes critically determined by the mobility ratio. For the devices studied herein ( $\mu_n/\mu_p \gg 1$ ), we find that surface recombination at the anode reduces  $V_{\text{OC}}$  more strongly than would be the case with balanced mobilities. The reason is that with decreasing  $\mu_p$ , a larger gradient of the quasi-Fermi-level is required to cancel out the surface-recombination current of electrons. An analogous situation occurs for a device dominated by hole transport ( $\mu_n/\mu_p \ll 1$ ) at the cathode. Hence, it is properties of the photoactive blend that decide whether an electrode can be considered appropriate.

We also derive analytical equations for  $V_{\text{OC}}$  that take into account the pile-up of space charge due to highly imbalanced mobilities. In particular, Eq. (11) shows excellent agreement with the data from our experimentally

validated numerical device model. With this, we hope to provide a framework that helps researchers to design efficient organic photovoltaics using materials with imbalanced charge transport.

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