Impact of donor-acceptor morphology on the charge carrier generation in organic photovoltaic devices

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Abstract. We investigate the impact of donor-acceptor morphology on the generation of charge carriers in organic photovoltaic cells and photodiodes based on a recently proposed model. It is found that for devices with typical values of permittivity and actual charge carrier mobilities, the donor-acceptor morphology plays an important role in the charge carrier generation, practically at all operating electric fields. Higher permittivity and actual mobilities increase the charge carrier generation, and also decrease the effect of donor-acceptor morphology on the charge carrier generation. Although the donor-acceptor morphology is important for charge carrier generation in general, but having permittivity and/or actual mobilities that are significantly higher than the typical values are more desirable in order to maximize the charge carrier generation.

1. Introduction
Organic photovoltaic (OPV) devices (a term used here to refer both organic solar cells and photodiodes) have distinctive and interesting properties that could lead to various applications. They are also relatively cheap to fabricate, which mean that organic solar cells have the potential to be a viable energy source.

When light is absorbed by the organic photoactive layer (PL), excitons (strongly bound electron-hole pairs) are produced. In order to efficiently generate free charge carriers, the PLs are made by combining (usually two) different organic semiconductors with different energy levels, where one semiconductor acts as the electron donating material while the other one acts as the electron accepting material. How free charge carriers are generated is a fundamental step in the working operation of OPV devices.

At the donor-acceptor (DA) interface, excitons are generally transformed into charge-transfer (CT) states. A CT state consists of an electron in the acceptor and a hole in the donor that are still bound to each other. Several models have been proposed to explain how a CT state can overcome its binding energy to produce a free electron and a free hole. Since CT states are produced with excess energies, it has been suggested that the energy required to overcome the binding energy is provided by the excess energies [1,2].

Another situation is that CT states with excess energies relax to the ground CT states before dissociating into free charge carriers. The dissociation via the relaxed CT states has been supported experimentally [3–7]. The Onsager–Braun (OB) model [8] is widely used to describe the dissociation of relaxed CT states. However, the OB model has several fundamental issues [9].
Very recently, Ref. [9] has made an improvement to the OB model by including the effect of DA morphology and by employing the correct charge carrier mobilities. However, the detailed investigation on the impact of DA morphology on the generation of charge carriers using the modified OB model [9] has not been done yet. A more efficient charge carrier generation of course would increase the potential efficiency of the device.

The impacts of the PL’s properties such as the carrier mobilities and the permittivity on the performance of OPV devices have been investigated by many studies (for example by Refs. [10-12]) and well understood. However, the impact of the DA morphology of the PL on the charge carrier generation is still unclear. The aim of this paper is to investigate how the DA morphology impacts the generation of charge carriers based on the new model proposed by Ref. [9].

2. Model and procedures

The dissociation probability of a CT state is defined as [8]

\[ P_d = \frac{k_d}{k_d + k_f} \]

where \( k_d \) is the CT state dissociation rate coefficient, and \( k_f \) is the CT state decay rate coefficient. According to the modified OB model proposed by Ref. [9], \( k_d \) is given by

\[ k_d = \frac{3q(\mu_{n,i} + \mu_{p,i})}{4\pi\varepsilon a^3} \exp \left( \frac{-E_b}{k_B T} \right) \frac{J_1(2\sqrt{-2b_{eff}})}{\sqrt{-2b_{eff}}} \]  

(2)

where \( q \) is the elementary charge, \( \mu_{n,i} \) is the actual electron mobility at DA interface, \( \mu_{p,i} \) is the actual hole mobility at DA interface, \( \varepsilon \) is the effective permittivity of the photoactive layer (PL), \( a \) is the separation distance between the electron and the hole of the CT state, \( E_b = q^2/(4\pi a) \) is the binding energy of the CT state, \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature, \( J_1 \) is the Bessel function of the first kind of order 1, and \( b_{eff} \) is

\[ b_{eff} = \frac{q^3 \lambda |F|}{8\pi\varepsilon k_B^2 T^2} \]  

(3)

where \( |F| \) is the magnitude of the electric field, and \( \lambda \) is a parameter that describes how the DA morphology influences the CT state dissociation. Note that \( \mu_{n,i} \) and \( \mu_{p,i} \) are generally not the same as (can be higher than) the conventional carrier mobilities that are used to calculate the electric current [9]. \( \mu_{n,i} \) and \( \mu_{p,i} \) are fixed for any given DA mixture (independent of the DA morphology and device architecture) unlike the conventional carrier mobilities [9]. The detailed explanation on the actual carrier mobilities can be obtained in Ref. [9].

A CT state’s direction is defined as the direction from the electron to the hole of the CT state. A more positive value of \( \lambda \) means the effective direction of the CT states inside the PL is more aligned in the direction of the electric field inside the PL, while a more negative value of \( \lambda \) means the effective direction of the CT states inside the PL is more aligned in the direction opposite to the direction of the electric field. \( \lambda = 1 \) (the maximum value) means that all the CT states inside the PL are in the same direction as the direction of the electric field. \( \lambda = -1 \) (the minimum value) means that all the CT states inside the PL are exactly opposite to the direction of the electric field. \( \lambda = 0 \) means the effective direction of the CT states is perpendicular to the direction of the electric field. In other words, \( \lambda = 0 \) means that the electric field effectively does not contribute to the CT state dissociation. However, since \( \lambda = 0 \) gives an undefined value of \( k_d \) according to equation (2), we simply neglect

\[ k_d = \frac{3q(\mu_{n,i} + \mu_{p,i})}{4\pi\varepsilon a^3} \exp \left( \frac{-E_b}{k_B T} \right) \frac{J_1(2\sqrt{-2b_{eff}})}{\sqrt{-2b_{eff}}} \]  

(2)
the term \( J_1 \left( 2 \sqrt{-2b_{\text{eff}}^2} \right)/\sqrt{-2b_{\text{eff}}^2} \) in equation (2) in order to represent \( k_d \) (and thus \( P_d \)) when \( \lambda = 0 \).

As explained in Ref. [9], the value of \( \lambda \) can be controlled by properly designing the distributions (morphologies) and/or the architectures of the DA mixture.

The generation rate of free charge carriers is given by \( P_d G_{\text{CT}} \), where \( P_d \) is CT state dissociation probability, and \( G_{\text{CT}} \) is the generation rate of CT states. Since \( P_d \) is very closely linked to the charge carrier generation, understanding of the impact of DA morphology on the charge carrier generation can be meaningfully achieved by understanding the impact of DA morphology on \( P_d \). In fact, \( P_d \) may also be called the free charge carrier generation probability, which will be used from here on.

As can be seen from the equations above, the electric field also affects the charge carrier generation. If the electric field is uniform, \(|F|\) inside the PL can be given by (see Ref. [13] for example)

\[
|F| = \left| \frac{V_{\text{bi}} - V_a}{L} \right|
\]

where \( V_{\text{bi}} \) is the built in voltage, \( V_a \) is the applied voltage, and \( L \) is the PL’s thickness. The operating \(|F|\) inside the PL of an OPV device can be up to several \( 10^7 \text{ Vm}^{-1} \). For example, an organic ultraviolet photodetector may have \( V_{\text{bi}} = 3.5 \text{ eV} \) and may operate at \( V_a = -1 \text{ V} \) (reverse bias) with \( L = 100 \text{ nm} \), which means \(|F| = 4.5 \times 10^7 \text{ Vm}^{-1} \) inside the PL. Our analysis must obviously cover the range of the possible operating \(|F|\) in OPV devices.

In order to achieve a comprehensive understanding on how the charge carrier generation is influenced by the DA morphology, we will calculate and analyze the charge carrier generation probabilities with respect to \( \lambda \) (which represents the DA morphology) together with other relevant parameters, which are the effective permittivity, the actual mobilities, and the electric field.

3. Results

Table 1 shows the values of the parameters used for calculations. The PL’s effective permittivity \( \varepsilon \) is given by \( \varepsilon = \varepsilon_0 \varepsilon_r \), where \( \varepsilon_0 \) is the vacuum permittivity, and \( \varepsilon_r \) is the effective relative permittivity of the PL.
Table 1. Values of the parameters.

| Parameter (symbol)                          | Value                        |
|--------------------------------------------|------------------------------|
| Actual electron mobility at DA interface (\(\mu_{n,i}\)) | See text                    |
| Actual hole mobility at DA interface (\(\mu_{p,i}\)) | See text                    |
| Relative permittivity (\(\varepsilon_r\))   | See text                    |
| CT state decay rate coefficient (\(k_f\))    | 1.0 \times 10^8 \text{s}^{-1}|
| Electron-hole separation (\(a\))           | 1.3 \times 10^{-9} \text{m}  |
| Temperature (\(T\))                        | 300 \text{K}                |

Figure 1 shows the charge carrier generation probabilities \(P_d\)'s calculated using \(\varepsilon_r = 3.5\), \(\mu_{n,i} = \mu_{p,i} = 2 \times 10^{-6} \text{m}^2\text{V}^{-1}\text{s}^{-1}\), and several different values of \(\lambda\) as functions of the magnitude of the electric field \(|F|\). The values of \(\varepsilon_r\), \(\mu_{n,i}\), and \(\mu_{p,i}\) used for figure 1 are the typical values for organic PLs. It can be seen that for the OPV device of figure 1, the value of \(\lambda\) (and thus the DA morphology) plays an important role in the charge carrier generation. In fact, it is important for the PL of the OPV device of figure 1 to have \(\lambda\) of at least around 0.75 in order to produce a relatively good \(P_d\) in comparison to \(P_d\) when \(\lambda = 1\). At \(|F| \approx 0 \text{Vm}^{-1}\), the impact of DA morphology on \(P_d\) is not important.
Figure 1. Charge carrier generation probabilities $P_d$'s for several values of $\lambda$ as functions of the magnitude of the electric field $|F|$. The parameters as given in table 1 with $\epsilon_r = 3.5$ and $\mu_{n,i} = \mu_{p,i} = 2 \times 10^{-6} \text{m}^2\text{V}^{-1}\text{s}^{-1}$ are used for calculations.

Figure 2 shows $P_d$'s for several different values of $\lambda$ as functions of $|F|$ using the same $\mu_{n,i}$ and $\mu_{p,i}$ as used in figure 1 but with $\epsilon_r = 5$. From figure 2, it is clear that increasing $\epsilon_r$ increases $P_d$ at any given $|F|$. Increasing $\epsilon_r$ from 3.5 to 5 significantly increases $P_d$ in general. For example, at $|F| = 0$, increasing $\epsilon_r$ from 3.5 to 5 increases $P_d$ from 0.1 to 0.75. For the OPV device of figure 2, it is important for the PL to have $\lambda$ of at least about 0.5 in order to produce a relatively good $P_d$ in comparison to $P_d$ when $\lambda = 1$. However, for the device of figure 2, even a very low (but positive) $\lambda$ produce a quite high $P_d$ at practically the whole range of the studied $|F|$. 
Figure 2. Charge carrier generation probabilities $P_d$ for several values of $\lambda$ as functions of the magnitude of the electric field $|F|$. The parameters as given in table 1 with $\varepsilon_r = 5$ and $\mu_{n,i} = \mu_{p,i} = 2 \times 10^{-6} \text{m}^2\text{V}^{-1}\text{s}^{-1}$ are used for calculations.

Figure 3 shows $P_d$ for several different values of $\lambda$ as functions of $|F|$ using the same $\mu_{n,i}$ and $\mu_{p,i}$ as used in figure 1 but with $\varepsilon_r = 6.5$. For the OPV device of figure 3, the role of $\lambda$ (and thus the DA morphology) is generally not important for the generation of charge carriers. However, it is still quite important to at least have $\lambda > 0$ in general.

Figure 3. Charge carrier generation probabilities $P_d$ for several values of $\lambda$ as functions of the magnitude of the electric field $|F|$. The parameters as given in table 1 with $\varepsilon_r = 6.5$ and $\mu_{n,i} = \mu_{p,i} = 2 \times 10^{-6} \text{m}^2\text{V}^{-1}\text{s}^{-1}$ are used for calculations.
Figure 4 shows $P_d$’s calculated using $\varepsilon_r = 3.5$, $\mu_{n,i} = \mu_{p,i} = 6 \times 10^{-5} \text{m}^2\text{V}^{-1}\text{s}^{-1}$, and several different values of $\lambda$ as functions of $|F|$. From figure 4, it can be seen that higher $\mu_{n,i} + \mu_{p,i}$ increases $P_d$, similar as the effect of a higher $\varepsilon_r$. A higher $\mu_{n,i} + \mu_{p,i}$ makes the role of $\lambda$ (and thus the DA morphology) to be less significant in generating the charge carriers.

![Figure 4](image-url)

**Figure 4.** Charge carrier generation probabilities $P_d$’s for several values of $\lambda$ as functions of the magnitude of the electric field $|F|$. The parameters as given in table 1 with $\varepsilon_r = 3.5$ and $\mu_{n,i} = \mu_{p,i} = 6 \times 10^{-5} \text{m}^2\text{V}^{-1}\text{s}^{-1}$ are used for calculations.

It can be concluded that OPV devices with relatively low $\lambda$ but with $\varepsilon_r$ and/or $\mu_{n,i} + \mu_{p,i}$ that are significantly higher than the typical values are likely to have better charge carrier generation than OPV devices with very high $\lambda$ but with typical values of $\varepsilon_r$ and $\mu_{n,i} + \mu_{p,i}$. Hence, to maximize the charge carrier generation, devices with relatively low $\lambda$ but having $\varepsilon_r$ and/or $\mu_{n,i} + \mu_{p,i}$ that are significantly higher than the (current) typical values are more desirable than devices with very high $\lambda$ but having typical values of $\varepsilon_r$ and $\mu_{n,i} + \mu_{p,i}$. However, for devices with typical values of $\varepsilon_r$ and $\mu_{n,i} + \mu_{p,i}$, having a very high $\lambda$ is important to maximize the charge carrier generation.
4. Summary

Based on a recently proposed model, we have performed a study on the impact of DA morphology on the generation of charge carriers in OPV devices by calculating and analyzing the charge carrier generation probabilities $P_d$ with respect to the parameter $\lambda$ (which represents the DA morphology), the effective permittivity, the actual mobilities, and the electric field. It is found that for OPV devices with typical values of $\varepsilon_r$ (or $\varepsilon$) and $\mu_{n,i} + \mu_{p,i}$, the DA morphology plays an important role in the charge carrier generation, practically at all possible operating electric fields. Increasing the values of $\varepsilon_r$ and/or $\mu_{n,i} + \mu_{p,i}$ increase $P_d$ and at the same time making the effect of DA morphology to be less significant. In order to maximize charge carrier generation, devices with relatively poorly-designed donor-acceptor morphology (low $\lambda$) but having $\varepsilon_r$ and/or $\mu_{n,i} + \mu_{p,i}$ that are significantly higher than the (current) typical values are more desirable than devices with excellently-designed donor-acceptor morphology (very high $\lambda$) but having typical values of $\varepsilon_r$ and $\mu_{n,i} + \mu_{p,i}$.

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