CHAPTER 2

CHARGE TRANSPORT AND RECOMBINATION IN PDPP5T:[70]PCBM SOLAR CELLS

Summary

The performance of organic bulk heterojunction solar cells is strongly dependent on the donor/acceptor morphology. Morphological parameters, such as the extent and the composition of donor- and acceptor-rich domains, influence both the charge generation and the charge transport throughout the active layer. The first part of this thesis focuses on a polymer:fullerene system based on a small bandgap diketopyrrolopyrrole-quinquethiophene alternating copolymer (PDPP5T) mixed with [6,6]-phenyl-C$_{71}$-butyric acid methyl ester ([70]PCBM) that is capable of efficiencies higher than 6%. By changing the processing conditions, the morphology can be varied from a coarse separated morphology, with fullerene domains (blobs) embedded in a polymer-rich matrix, to a completely mixed layer. The experimental characterization of charge carrier transport and bimolecular recombination in PDPP5T:[70]PCBM blends with different morphologies and fullerene concentrations is presented in this chapter.
2.1 Introduction

This chapter and the next focus on the performance of solar cells based on the blend of a small band gap ($E_g \approx 1.46\text{eV}$) diketopyrrolopyrrole-quinquethiophene alternating copolymer (PDPP5T)\cite{1,2} with [6,6]-phenyl-C$_{71}$-butyric acid methyl ester ([70]PCBM) (Figure 2.1). We aim at establishing a relation between the morphology of the active layer and the performance of the solar cell; PDPP5T is an excellent tool for achieving this goal, because its blend with [70]PCBM can yield a wide range of morphologies, depending on the processing conditions.\cite{3}

![Molecular structures of PDPP5T and [70]PCBM.](image)

A PCE exceeding 6% can be achieved when the blend PDPP5T:[70]PCBM 1:2 wt. ratio is spin cast from a chloroform (CF) solution with a 5 vol% of ortho-dichlorobenzene (oDCB) as a co-solvent.\cite{3} The presence of oDCB results in the deposition of an active layer with a fine phase separation, ideal for efficient dissociation of excitons. A fine phase separation can also be obtained without co-solvent, but only if the concentration of [70]PCBM is kept below a certain threshold (around 28 vol%). Conversely, when the blend PDPP5T:[70]PCBM 1:2 wt. ratio is spin cast from a chloroform solution, the extension of phase separation is greatly increased, the active layer now being composed by domains of [70]PCBM dispersed in a matrix of polymer and fullerene. Thus, both a finely dispersed donor-acceptor mixture and a phase-separated morphology, representative of many polymer:fullerene systems, can be achieved with PDPP5T:[70]PCBM blends.

In a recent publication, Kouijzer et al. showed that the phase separation is due to liquid-liquid demixing during film formation, and that the size of the domains and the composition of the matrix depend on the drying time of the layer.\cite{3} They also suggested that the photocurrent of these devices consists of two contributions: one is rather independent of the layer thickness; the other is linearly dependent on the reverse bias, and the slope of this dependency increases when the thickness decreases.

We measure the electrical properties of PDPP5T:[70]PCBM blends. We perform steady-state measurements of the mobility of electrons and holes and of the strength of bimolecular recombination in blends with different concentration of fullerene and with different morphologies. In this chapter, we report the results of our measurements. In
the next, we will use the measured quantities to describe the $J$-$V$ characteristics of the PDPPP5T:[70]PCBM solar cells.

## 2.2 PDPPP5T:[70]PCBM solar cells: performance and morphology

Figure 2.2 shows the $J$-$V$ characteristics of the PDPPP5T:[70]PCBM blends, spin cast from chloroform solution or from chloroform/oDCB solution. The parameters of these solar cells are listed in Table 2.1. Clearly, the device processed from a chloroform/oDCB (95:5 vol. ratio) solution is the most efficient. The other devices give a much lower $J_{sc}$, and for the device with a low concentration of [70]PCBM in the active layer, the FF is also small.

![Figure 2.2: $J$-$V$ curves of PDPPP5T:[70]PCBM solar cells. The device with optimized active layer (green curve) clearly outperforms the devices with non-optimal morphology (red and blue curves) or donor:acceptor ratio (black curve).](image)

We study the topography of the active layers by atomic force microscopy (AFM) imaging of films cast on glass substrates. Figure 2.3 presents the AFM images; the layer spin cast from a chloroform/oDCB solution presents the optimal morphology, a finely dispersed mixture of polymer and fullerene which yields efficient charge separation and transport. A finely dispersed structure is also obtained without the addition of co-solvent, provided that the blend does not contain enough [70]PCBM to form aggregates. It is the case of the PDPPP5T:[70]PCBM 4:1 wt. ratio blend. As shown in Section 2.3, this blend exhibits poor electron transport properties, and this explains the loss in efficiency if compared to the optimal device (see next chapter).
Chapter 2. Charge transport and recombination in PDPP5T:[70]PCBM solar cells

Table 2.1: Solar cell parameters of the $JV$ curves reported in Figure 2.2.

<table>
<thead>
<tr>
<th>PDP5T:[70]PCBM w/w ratio</th>
<th>Solvent</th>
<th>Thickness (nm)</th>
<th>$J_{sc}$ (A m$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF [-]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4:1</td>
<td>CF</td>
<td>130</td>
<td>14.78</td>
<td>0.662</td>
<td>0.29</td>
<td>0.28</td>
</tr>
<tr>
<td>1:2</td>
<td>CF</td>
<td>110</td>
<td>39.71</td>
<td>0.622</td>
<td>0.57</td>
<td>1.41</td>
</tr>
<tr>
<td>1:2</td>
<td>CF/oDCB</td>
<td>260</td>
<td>19.28</td>
<td>0.613</td>
<td>0.60</td>
<td>0.71</td>
</tr>
<tr>
<td>1:2</td>
<td>CF</td>
<td>150</td>
<td>174.36</td>
<td>0.540</td>
<td>0.61</td>
<td>5.77</td>
</tr>
</tbody>
</table>

A different morphology characterizes the blends with high [70]PCBM load spin cast from chloroform, which presents a coarse phase separation with fullerene blobs embedded in a polymer-rich matrix. It is shown in Ref. 3 that the domains of [70]PCBM are bigger if the drying time of the blend is longer. This is in agreement with our experimental observations: for the blends PDPP5T:[70]PCBM 1:2 wt. ratio, the size of the fullerene blobs increases for films cast at a lower spin rate, which also implies a larger thickness. The different extent of phase separation influences the performance of the devices. The dissociation of excitons occurs at the polymer/fullerene interface, which is reduced when the blob size is increased; therefore, the thicker device has a lower short circuit current with respect to the thinner one. The difference in short circuit current is not only due to the different extent of phase separation, but also to the different transport properties of the polymer matrices of the two devices (see next chapter).

It is interesting to know how much [70]PCBM can be dissolved into the polymer-rich matrix. We perform atomic force microscopy imaging on blends with different amount of [70]PCBM, keeping the concentration of polymer in solution fixed at 6 mg/ml (Figure 2.4). The aggregation of the fullerene derivative into pure domains starts at [70]PCBM concentration between 2 and 2.5 mg/ml. From this, we conclude that the maximum [70]PCBM concentration in the mixed, polymer-rich phase is around 35% by weight, which corresponds to 28 vol%*.

*assuming the density of PDPP5T equals 1 g/ml and the density of [70]PCBM equals 1.4 g/ml$^{4,5}$
2.2. PDPP5T:[70]PCBM solar cells: performance and morphology

Figure 2.3: AFM images of PDPP5T:[70]PCBM blends: a) 4:1 wt. ratio cast from chloroform; b) 1:2 wt. ratio cast from chloroform/ODCB; c) and d) 1:2 wt. ratio cast from chloroform, respectively 260 and 110 nm thick.

Figure 2.4: AFM images of PDPP5T:[70]PCBM blend cast from chloroform. The concentration of PDPP5T in solution is 6 mg/ml, the concentration of [70]PCBM is a) 2 mg/ml and b) 2.5 mg/ml.
2.3 Charge transport

In this section we briefly describe the space charge limited current (SCLC) method, which we use to measure the mobilities of holes and electrons in PDPP5T:[70]PCBM blends. Then, we present the results of our measurements, showing in particular how the mobilities are influenced by the amount of [70]PCBM in the blend.

2.3.1 Space charge limited current

When a layer of organic semiconductor is sandwiched between two selective contacts, which can inject/extract either only electrons or only holes, and a bias is applied to the contacts, the current flowing through the layer is limited by the build-up of space charge. If at least one of the contacts is ohmic and the mobility of the charge carrier flowing through the device is constant, the analytical expression for the current density \( J_{\text{SCL}} \) is given by:

\[
J_{\text{SCL}} = \frac{9}{8} \varepsilon \mu \frac{V_{\text{int}}^2}{L^3},
\]

where \( \varepsilon \) is the dielectric constant of the material, \( \mu \) is the mobility of the charge carrier, \( L \) is the thickness of the semiconductor layer and \( V_{\text{int}} \) is the internal voltage drop across the layer. \( V_{\text{int}} \) is given by the applied voltage \( V_a \) corrected for the built-in voltage \( V_{\text{bi}} \) and for the series resistance, according to:

\[
V_{\text{int}} = V_a - V_{\text{bi}} - V_{\text{Rs}}.
\]

Here, \( V_{\text{Rs}} \) represents the voltage drop across the series resistance of the substrates. For the single carrier devices presented in this thesis, the series resistance is around 10 - 15 \( \Omega \)/square, while for the device fabricated on ITO substrates the series resistance is in the range 30 - 40 \( \Omega \)/square. The built-in voltage arises from the difference in work function of the electrodes.

If the mobility of the charge carrier under investigation is not constant, Equation 2.1 is not valid. An example relevant to this thesis is the case in which the mobility is dependent on the electric field. In previous works, this dependence has been described empirically by:

\[
\mu = \mu_0 \exp \left( \gamma \sqrt{F} \right),
\]

where \( \mu_0 \) is the zero-field mobility, \( \gamma \) is the field activation factor, and \( F \) is the field strength. The mobility may also depend on the charge carrier density, e.g. as described in the work by Pasveer et al.\[8\]

Beside the analytical approach, the current flowing through a single carrier device can be numerically calculated by means of drift-diffusion simulation. Here, we use a numerical code\[9\] that incorporates the field-dependency of mobility in the form described by Equation 2.3 and the density dependence as described in Ref. 8.
2.3. Charge transport

The SCLC method is a suitable tool for the characterization of transport in solar cells, because the experimental conditions (device structure, electric field, charge density) under which SCLC measurements are performed are similar to the working conditions of a BHJ device.

2.3.2 Charge transport in PDPP5T:[70]PCBM blends

We fabricate electron-only and hole-only devices according to the procedure described in the Section 1.6. The $JV$ characteristics of these devices are shown in Figure 2.5. The applied voltage is corrected for the series resistance of the substrate (14 $\Omega$/square for the hole-only devices, 10 $\Omega$/square for the electron-only devices). To investigate the effect of the co-solvent on the transport of electrons, we measure the mobility both for the blends spin cast from chloroform and for the ones spin cast from chloroform/oDCB. Figure 2.5 also reports numerical fit of the experimental data.\[^{[9]}\] It was not necessary to include the dependence of mobility on charge density,\[^{[8]}\] because this effect is, in these blends, largely overcome by the field dependence.

![Figure 2.5: J/V curves of PDPP5T:[70]PCBM single carrier devices. a) PDPP5T:[70]PCBM 4:1 wt. ratio, spin cast from chloroform (thicknesses: hole-only 118 nm, electron-only 96 nm); b) PDPP5T:[70]PCBM 1:2 wt. ratio spin cast from chloroform/oDCB (thicknesses: hole-only 179 nm, electron-only 122 nm). Symbols: experimental data; solid lines: numerical fits.](image)

The zero field mobilities and field activation factors of electrons and holes in the PDPP5T:[70]PCBM blends analysed are extracted as fit parameters and are reported in Figure 2.6 against the vol% of [70]PCBM in the blend.\[^{[*]}\] In the range analysed the mobility of holes is not dependent on the amount of [70]PCBM in the blend, and its value is sim-

\[^{[*]}\]For reasons of brevity, we do not present in this thesis all the $JV$ curves of the single carrier devices with different [70]PCBM load.
ilar to the hole mobility in the pristine polymer ($\mu_{0p} = 1.1 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$). The mobility of electrons strongly depends on the concentration of [70]PCBM, because the electrons travel through the fullerene molecules. We verify this by measuring the electron current in the pristine polymer, which was significantly lower than the electron current in the blend with the lowest [70]PCBM concentration (data not shown).

When the [70]PCBM load is reduced, the transport of electrons becomes more dependent on the electric field. For the fit of the electron-only $J-V$ of the 1:2 blend (Figure 2.5b), we used a field activation factor $\gamma = 3 \times 10^{-5} \text{m}^{1/2} \text{V}^{-1/2}$; for the 4:1 blend (Figure 2.5a), it was necessary to increase $\gamma$ to $5.3 \times 10^{-4} \text{m}^{1/2} \text{V}^{-1/2}$.

It should be noted that for the blends with low content of [70]PCBM the mobility of holes is several order of magnitudes higher than the mobility of electrons; this unbalanced transport will lead to a build-up of space charge\textsuperscript{[10]} for the solar cells fabricated from these blends. This space charge effect makes it necessary to take into account the generation profile of charge carriers through the active layer in order to model the bulk heterojunction solar cells (see next chapter).

### 2.3.3 Thickness dependence of the electron mobility

To prove that the electron mobility in blends with low concentration of [70]PCBM is not strongly dependent on the charge density, we plot the effective electron mobility versus layer thickness for the PDPP5T:[70]PCBM blend with 19 vol.% of fullerene (Figure 2.7). As our devices have ohmic contacts for electron injection, varying the thickness will change the carrier density in the device: electrons diffuse into the active layer.\textsuperscript{[11]} The enhancement of carrier density due to diffusion from the contacts is important for small thicknesses, the effect is smaller for very thick layers. Thus, if mobility depends on charge density, it will increase in thin layers.
2.3. Charge transport

The values of mobility are calculated by inverting the Equation 2.1 and using the experimental data from electron-only devices with different thicknesses. As can be seen, the electron mobility is independent of layer thickness. It should be noted that the experimental values of mobility presented here are calculated with the inversion of Mott-Gurney law, which considers a constant mobility. They cannot be directly compared with the value of zero-field electron mobility presented in Figure 2.6 for the blend with the same composition (which has been obtained by fitting the $J$-$V$ data using a field-dependent mobility).

To illustrate the effect of a density-dependent mobility, we use the drift-diffusion simulator together with a mobility that depends on the carrier density as described in Ref. 8. Such a density dependence does indeed show up as a mobility (again calculated by inverting the Mott-Gurney law) that depends on thickness. From the comparison between experiment and simulation we conclude that the density dependence is not important for the blends we are considering.

![Figure 2.7: Electron mobility for PDPP5T:[70]PCBM devices with 19 vol.% of [70]PCBM, calculated for devices with different thickness by inverting Equation 2.1 for $V = 0.5V$. The dots represent experimental data, the dashed line is obtained from the simulation of electron-only devices with density dependent mobility. For the simulation, we use the mobility expression given in Ref. 8, with $\sigma = 0.073eV$ and $a = 3.4nm.$]
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2.4 Charge recombination

In this section, we describe the steady state method used to characterize the strength of the bimolecular recombination in PDPP5T:[70]PCBM solar cells. The method relies on the assumption that the bimolecular recombination is the only recombination pathway active in this polymer:fullerene blend. Next, we present the bimolecular recombination strength for blends with different morphologies.

2.4.1 Reduced Langevin recombination in organic solar cells

The recombination of photogenerated free charge carriers is one of the main limiting factors for the power-conversion efficiency of organic solar cells.\cite{12} In pristine organic semiconductors, the recombination is bimolecular, and has a strength $\gamma_L$ given by the Langevin equation:\cite{13}

$$\gamma_L = \frac{q}{\varepsilon} (\mu_n + \mu_p), \quad (2.4)$$

where $q$ is the elementary charge.

In organic solar cells, the strength of the bimolecular recombination is reduced with respect to the classical Langevin expression.\cite{14,15} Equation 2.4 can still be used to describe bimolecular recombination in BHJs, but it is necessary to apply a prefactor $\gamma_{\text{pre}} \leq 1$:

$$\gamma = \gamma_{\text{pre}} \gamma_L = \gamma_{\text{pre}} \frac{q}{\varepsilon} (\mu_n + \mu_p), \quad (2.5)$$

with $\gamma$ the total recombination strength. It is therefore necessary to determine the Langevin prefactor in order to model the $JV$ characteristic of the devices.

Wetzelaer et al.\cite{16} derived an expression for the Langevin prefactor which allows to estimate it from simple, steady-state current voltage measurements. It is possible to express the prefactor in terms of mobilities, according to

$$\gamma_{\text{pre}} = \frac{16\pi}{9} \frac{\mu_n \mu_p}{\mu_{\text{eff}}^2 - (\mu_n + \mu_p)^2}. \quad (2.6)$$

The effective double carrier mobility $\mu_{\text{eff}}$ is obtained by fitting the dark current of the solar cells with the same model used for the single carrier devices (Figure 2.8).

2.4.2 Recombination strength in PDPP5T:[70]PCBM blends

We measured $\mu_n, \mu_p$ and $\mu_{\text{eff}}$ following the SCLC method described in Section 2.3.1. To investigate the effect of the dimension of [70]PCBM aggregates on the strength of the bimolecular recombination, single and double carrier devices with different thicknesses have been made with the PDPP5T:[70]PCBM 1:2 wt. ratio blend from chloroform. Figure 2.9a presents the three mobilities measured for different thicknesses of the active layer.
Interpolation of these data allowed to calculate the Langevin prefactor and to plot it as a function of the thickness, as shown in Figure 2.9b.

![Figure 2.8: Dark current of three solar cells made with the blend PDPP5T:[70]PCBM 1:2 wt. ratio spin cast from chloroform. Symbols: experimental data; solid lines: numerical fits.](image1)

![Figure 2.9: a) Mobility of electrons and holes and b) Langevin prefactor of PDPP5T:[70]PCBM blends spin cast from chloroform, as a function of the thickness of the active layer.](image2)
Interestingly, the Langevin prefactor clearly follows a decreasing trend with increasing thickness. We assigned this trend to the larger size of [70]PCBM blobs in thicker devices, which reduces the interfacial area between donor and acceptor phase, where bimolecular recombination occurs.

To validate this hypothesis, we determined the Langevin prefactor, with the same procedure, for the PDPP5T:[70]PCBM 1:2 wt. ratio blend spun from chloroform/oDCB solution. As highlighted in Section 2.2, the addition of oDCB as co-solvent yielded a finely dispersed blend. In such a homogeneous film, there is a high probability for the charges to recombine. From the $J\nu$ characteristics of single and double carrier devices made with this blend, the values of $2.7\times10^{-7}$, $3.1\times10^{-7}$ and $9.9\times10^{-7}$ m$^2$ V$^{-1}$ s$^{-1}$ have been extracted for $\mu_p$, $\mu_n$ and $\mu_{eff}$ respectively. Substituting this values in Equation 2.6 gave a Langevin prefactor of 0.77 for this blend, which confirms the hypothesis that the relative strength of the bimolecular recombination is higher for more finely dispersed systems.

### 2.5 Conclusion

To understand the performance of PDPP5T:[70]PCBM devices, we measured the mobility of charge carriers, the exciton generation rates and the strength of bimolecular recombination in the active layer. We performed the measurements for different concentrations of [70]PCBM and for different morphologies of the active layers.

A strong dependency of the electron mobility on the amount of [70]PCBM in the blend was observed, while the mobility of hole is always high ($\mu_0p \approx 1.1\times10^{-7}$ m$^2$ V$^{-1}$ s$^{-1}$). Furthermore, we observed an increasing dependency of the electron mobility on the electric field when the concentration of fullerene in the blend is reduced.

The strength of the bimolecular recombination decreases when the phase-separation of the blend is increased, because the bimolecular recombination occurs at the donor:acceptor interface, which is larger for homogeneous blends. We proved this by keeping the polymer:fullerene ratio constant and modifying the extent of phase-separation by changing the drying conditions of the film; for films with smaller domain size, the strength of the bimolecular recombination is closer to the value measured for the homogeneous blend.

The data presented here will be used in the next chapter to model the $J\nu$ characteristics of PDPP5T:[70]PCBM solar cells.
References


