Efficiency enhancement of polymer fullerene solar cells
Lenes, Martijn

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Chapter 4

Recombination-limited photocurrents in small bandgap polymer:fullerene solar cells

Abstract

The charge transport and photogeneration in solar cells based on the low bandgap conjugated polymer, poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) and a methanofullerene is studied. The efficiency of the solar cells is limited by a relatively low fill factor that contradicts with the observed good and balanced charge transport in these blends. Intensity dependent measurements display a recombination limited photocurrent, characterized by a square root dependence on effective applied voltage, a linear dependence on light intensity, and a constant saturation voltage. Numerical simulations show that the origin of the recombination limited photocurrent stems from the short lifetime of the bound electron-hole pairs at the donor-acceptor interface.

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M. Lenes, M. Morana
C. J. Brabec and P. W. M. Blom
4.1 Introduction

As discussed in chapter 1 the large offset between donor and acceptor LUMO of P3HT and PCBM results in a significant loss of energy. One way to overcome this problem is by decreasing the LUMO level of the polymer creating so called small bandgap donors. Due to the lowering of the donor bandgap the absorption is expanded towards higher wavelengths, allowing more photons to be absorbed, even when one takes into account that not all photons above the bandgap are absorbed. Besides an expected enhanced efficiency compared to P3HT:PCBM when used in single active layers, small bandgap donors are also desired for multijunction solar cells or infrared photodetectors.

One route towards small bandgap polymers is by coupling electron donor and acceptor units together in a polymer. Most of the polymers created using this route, however, have resulted in significantly inferior performances compared to solar cells based on P3HT. The reason for the low performance is mainly due to the poor carrier transport in these polymers, resulting in low fill factors and quantum efficiencies. One of the most promising devices following this approach are based on poly [2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b’]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT), reaching power conversion efficiencies of up to 3.2% when combined with [6,6]-phenyl-C_{71}-butyric acid methyl ester ([70]PCBM). In spite of the increased absorption the power efficiency is still lower than the state-of-the-art P3HT:PCBM cells, of which efficiencies have been reported of more than 5%. The efficiency is mainly limited by a low fill factor \((FF)\) of only 40%. In chapter 2 it has been demonstrated that a strongly unbalanced charge transport leads to space-charge limited photocurrents, characterized by a square-root dependence on applied voltage. This dependence limits the fill factor to about 40%. Remarkably, measurements performed on PCPDTBT-based field effect transistors resulted in hole mobilities of the polymer as high as \(2 \times 10^{-6} \text{ m}^2\text{V}^{-1}\text{s}^{-1}\). Even though field-effect mobilities are quantitatively difficult to relate to charge carrier mobilities in actual solar cells, due to the much lower charge carrier densities in the latter devices, the high field-effect mobilities clearly indicate that the quality of the hole transport in PCPDTBT must be very good. Combined with the electron transport properties of intrinsic PCBM films, which already have been investigated in great detail, a balanced transport is therefore expected. Consequently, the origin of the reduced fill factors and external quantum efficiencies in these blends is not clear. In this chapter the charge transport and photogeneration of PCPDTBT:PCBM solar cells is studied to gain more insight into the loss mechanisms in this type of devices.
4.2 Charge transport in pristine PCPDTBT films

As mentioned above, even though field-effect mobilities give a valuable insight into the quality of the charge carrier transport, ideally one would like to measure the charge carrier mobility in a device geometry similar to the actual solar cell. Here the charge transport is studied in a vertical device geometry, similar to solar cells. By choosing suitable top and bottom contacts one can either inject both charge carriers, or choose to block one carrier and measure either the hole or electron current. The transport through these single carrier devices is modeled with a space-charge limited current (SCLC). Figure 4.1 shows the measured J-V characteristics of a hole only device of PCPDTBT. From the J-V measurements the zero-field mobility is determined to be 5.5x10^{-8} m^2/Vs. This mobility is about a factor of 30 lower than the earlier reported field-effect mobility, due to the density dependence of the mobility. However, the observed hole mobility of 5.5x10^{-8} m^2/Vs for PCPDTBT is about a factor of 2-3 larger than the mobility obtained from diodes based on pristine regio-regular P3HT.\textsuperscript{16} As a result in its pristine form PCPDTBT is at least as good a hole transporter as regio-regular P3HT.

Since the electron transport in polymer:fullerene blends occurs through the fullerene phase, electron transport through the polymer is of no importance for the device operation of organic solar cells. Nevertheless, also the electron transport through pristine PCPDTBT films is studied as shown in Figure 4.1. As reported previously,\textsuperscript{10} the polymer also shows signs of electron transport. In fact, the observed electron mobility of 4x10^{-9} m^2/Vs is only one order of magnitude lower than the hole mobility. Interestingly, the electron transport in the pristine material exhibits normal SCLC behavior where polymers usually show a much stronger voltage dependence due to charge trapping.\textsuperscript{17}

![Figure 4.1: J-V characteristics, corrected for built-in voltage and series resistance, of a PCPDTBT hole and electron only device. Data are fitted (solid line) with a space-charge limited current using a field dependent mobility resulting in a hole mobility of 5.5 \times 10^{-8} m^2/Vs and electron mobility of 4x10^{-9} m^2/Vs, respectively.](image-url)
4.3 Charge transport in PCPDTBT:PCBM blends

Blending a polymer with a fullerene often significantly alters the charge carrier transport in both polymer and fullerene compared to the pristine case. For instance, in the case of MDMO-PPV, a 200 fold increase in hole mobility is observed when blending the polymer with PCBM.\(^{18}\) On the other side, blending P3HT with PCBM results in a reduced hole transport, only to be recovered by thermal or solvent annealing.\(^{19,20}\) Therefore, single carrier measurements on the actual blend used in the solar cell are needed to relate the charge carrier transport to the solar cell performance. Blends of PCPDTBT and PCBM were prepared in a 1 to 4 weight ratio, which was reported to be optimal.\(^{10}\) The charge transport is determined in single carrier devices as described above for pristine polymer films. Figure 4.2 shows the \(J-V\) characteristic of a hole and electron only device of a PCPDTBT:PCBM blend with a weight ratio of (1:4). The determined hole mobility of PCPDTBT in the blend of \(3\times10^{-8}\) m\(^2\)/Vs almost equals the hole mobility in pristine films. This indicates that the hole transport in the polymer is not altered by blending it with PCBM. Furthermore, the determined hole mobility is equal to hole mobilities reported in MDMO-PPV:PCBM (1:4) blends\(^{18}\) and P3HT:PCBM (1:1) blends after annealing.\(^{16}\) The determined electron mobility of \(7\times10^{-8}\) m\(^2\)/Vs is slightly lower than values reported for MDMO-PPV:PCBM and P3HT:PCBM blends, that typically amount to \(1.0\times10^{-7}-2.0\times10^{-7}\) m\(^2\)/Vs.\(^{18,19,20}\) Similar electron and hole mobility values were found by ambipolar transport studies on OFETs at high fullerene loadings.\(^{21}\)

![Figure 4.2: \(J-V\) characteristics, corrected for built-in voltage and series resistance, of a PCPDTBT:PCBM hole- and electron-only device with a weight ratio of (1:4). Data are fitted with a space-charge limited current using a field-dependent mobility, resulting in a hole mobility in the](image)
blend of $3 \times 10^{-8} \text{ m}^2/\text{Vs}$ and an electron mobility of $7 \times 10^{-8} \text{ m}^2/\text{Vs}$.

The single carrier measurements presented here demonstrate that in the blends the hole and electron mobilities are balanced and closely match the mobilities reported for MDMO-PPV and P3HT based blends. It is therefore highly unlikely that the relatively low quantum efficiencies and fill factors are a consequence of unbalanced transport or too low charge carrier mobilities and more investigation of the solar cells is needed.
4.4 PCPDTBT:PCBM Solar Cells

The inset of Figure 4.3 shows the current vs. voltage ($J-V$) curve at room temperature of a typical PCPDTBT:PCBM solar cell made in this study. The external quantum efficiency (see figure 4.4) has been determined at ECN in Petten to estimate the correct short circuit current under AM 1.5 illumination and thus the mismatch factor of our measurements. Efficiencies of 2.2% are obtained which is somewhat lower than the 2.7% reported previously for PCPDTBT:[60]PCBM.\textsuperscript{10} As reported previously the power conversion efficiency is limited by a low external quantum efficiency (<35%) and fill factor (40%).

Figure 4.3: Photocurrent of a PCPDTBT:PCBM solar cell versus effective applied voltage. The black line indicates a square root dependence. Inset: $J-V$ characteristics of a PCPDTBT:PCBM solar cell.
For studying the device physics it is very useful to plot the photocurrent of a solar cell as a function of effective applied voltage. The photocurrent density is defined as \( J_{ph} = J_L - J_D \), where \( J_L \) and \( J_D \) are the current density under illumination and in dark, respectively, and the effective applied voltage as \( V_{eff} = V_0 - V_A \). Here \( V_0 \) is the compensation voltage defined as \( J_{ph}(V0)=0 \) and \( V_A \) is the applied bias. The photocurrent versus effective applied voltage of a PCPDTBT:PCBM solar cell is also shown in figure 4.3. It is clear that at large reverse bias the photocurrent saturates, at which point all generated electron-hole pairs are dissociated and collected at the electrodes, which indicates that the mean electron and hole drift lengths \( \omega_{eh} = \frac{\mu_{eh} \tau_{eh}}{e} \) are equal to, or larger than the sample thickness \( L \) and no recombination occurs. The photocurrent shows a sharp decrease at lower effective applied voltages, resulting in a rather low short circuit current and low fill factor. Furthermore, a square root dependence of the photocurrent as a function of effective voltage is observed, as is indicated by the black line. The origin of such a square root dependence of the photocurrent has been explained by Goodman and Rose in 1971. If the mean electron or hole (or both) drift length becomes smaller than \( L \), recombination of charge carriers becomes considerable. If there is also a difference between hole and electron drift length, a non uniform electric field will occur across the devices, which will give rise to a square-root dependent photocurrent:

\[
J_{ph} = qG\sqrt{\mu_{h(e)} \tau_{h(e)}} \sqrt{V}
\]  

(4.1)

with \( G \) the generation rate of free charge carriers. Here a low mobility or short lifetime of the free carriers, due to recombination or trapping, limits the
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photocurrent. Additionally, at high light intensities the build up of space-charges (which is the origin of the non-uniform electric field) reaches a fundamental limit. In this limit the maximum electrostatically allowed photocurrent is limited by the mobility of the slowest charge carrier and is given by

\[ J_{ph} \leq (qG)^{0.75} \left( \frac{9}{8} \varepsilon_0 \epsilon_r \mu_h \right)^{0.25} \cdot \sqrt{V} \]  

(4.2)

which again has a square-root dependence on voltage. The latter has been experimentally demonstrated in a system where the charge carrier mobilities are heavily unbalanced.\(^\text{12}\) The way to distinguish between these two physically distinct cases is by light-intensity dependent measurements. Where in the first (recombination limited) case the photocurrent scales linearly with light intensity, in the second (the space-charge limited) case it scales with a \(\frac{3}{4}\) power law dependence. Furthermore, the point at which the square root regime forms a transition into the saturation regime, the saturation voltage \(V_{sat}\), is either independent on light intensity (recombination-limited) or scales with a one half power on light intensity (space-charge limited case). From figure 4.5 it is clear that with decreasing light-intensity \(V_{sat}\) is not changing, as expected for a recombination-limited photocurrent. Furthermore, in Fig. 4.6 it is shown that in the square-root regime the photocurrent is linearly scaling with light-intensity. As a result the photocurrent observed for PCPDTBT:PCBM devices clearly shows the fingerprints of a recombination-limited photocurrent. Since the mobilities of the charge carriers in the device are known we can estimate the lifetime using equation (2), resulting in a lifetime of \(\sim 10^{-7}\) s. This value, estimated under the assumption that the dominant limitation comes from the hole transport, may slightly change if electron transport is considered as well.
Figure 4.5: Photocurrent of a PCPDTB:PCBM solar cell versus effective applied voltage at different intensities varying over more than 1 order of magnitude. Solid lines indicate square root and saturation regimes as a guide for the eye where $V_{sat}$ indicates the saturation voltage.

Figure 4.6: Intensity dependence of the photocurrent at different effective voltages. The slope ($S$) determined from the linear fit (solid lines) to the experimental data is indicated in the figure.
4.5 Device Simulations and Discussion

In a polymer:fullerene solar cell the photogenerated excitons dissociate at the donor-acceptor interface via an ultrafast electron transfer from the donor to the acceptor. However, the ultrafast electron transfer to the acceptor does not directly result in free carriers, but in a bound electron-hole pair (due to the Coulomb attraction between the carriers). This pair also needs to be dissociated, assisted by temperature and by the internal electric field, before it decays to the ground state. As proposed by Braun, this bound pair is metastable, enabling multiple dissociations and being revived by the recombination of free charge carriers via Langevin recombination. Finally, the free carriers are transported to the electrodes, a process governed by charge carrier mobility. In the above mentioned Goodman and Rose model a direct generation of free carriers (from now on called $G_{GR}$) is assumed. In a polymer:fullerene solar cell, however, the amount of generated free carriers will not only depend on the amount of generated bound electron-hole pairs ($G_B$), but also on their dissociation probability ($P$). In that case the generation rate of bound pairs $G_B$ is proportional to the incident light intensity and is taken as a measure for the amount of absorbed photons (assuming that all generated excitons dissociate at the donor-acceptor interface). As a result, when equation 4.1 is applied to an organic solar cell the calculated lifetime can only be considered as an effective lifetime ($\tau_{\text{eff}}$). This can be seen more clearly when one considers the device at open circuit voltage: Since no charges are extracted ($J_{\text{ph}}=0$) there is an equilibrium between the generation and recombination of free charge carriers in the device, given by:

$$G_{GR} = \frac{n}{\tau_{\text{eff}}} \quad (4.3)$$

with $n=p$ being the free electron/hole density and $G_{GR}$ the recombination rate of free carriers. Thus, if $\tau_{\text{eff}}$ is small, indicating lots of recombination, also the free carrier density will be small for a given generation rate of free carriers $G_{GR}$. When the formation and dissociation of bound electron-hole pairs as an intermediate step is taken into account the amount of free carriers that are generated will be given by $PG_B$ and hence one can state that

$$PG_B = \frac{n}{\tau} \quad (4.4)$$

where $\tau$ is now the true lifetime of free charge carriers as given by Langevin recombination.

One can also say that
Thus, when the bound-pair generation rate $G_B$ is taken as a measure for the amount of generated charges, as has been done in device modeling, the effective lifetime $\tau_{\text{eff}}$ can be small either due to a small life time $\tau$ of the free carriers or due to a low dissociation probability $P$ of the bound pairs.

In order to disentangle the effects of $P$ and $\tau$ on $\tau_{\text{eff}}$ we performed device simulations using a numerical program which solves Poisson’s equation and the continuity equations, including diffusion, space-charge effects and charge dissociation of bound electron-hole pairs. Relevant parameters for the simulation program are the charge carrier mobilities, including their field and/or density dependence, dielectric constant $\varepsilon$, separation distance $a$ and the decay rate of the bound electron-hole pairs $k_f$. Since the charge carrier mobilities are measured and the dielectric constant is known only $a$ and $k_f$ are used as fitting parameters. Figure 4.7 shows the fit of the simulation program using $a = 2.1 \times 10^9$ m and $k_f = 1.7 \times 10^7$ s$^{-1}$. Using the same fit parameters we can fit all measured light intensities. When the calculated dissociation probability is compared with the measured and simulated photocurrent (as is indicated in figure 4.7) it is clear that the strong field dependence of the photocurrent for effective voltages $> 0.4$ V originates from the field dependent dissociation of the bound electron-hole pairs. What is striking in
the device simulations is the high value of \( k_f \) needed to fit the data. As an indication, for MDMO-PPV:PCBM and P3HT:PCBM cells a value of \( \sim 10^4 \) is found. This indicates that the solar cells are limited by a high decay-rate, and thus short lifetime, of the bound electron-hole pair. Recently Hwang et. al. have shown experimental evidence of such an intermediate charge transfer state with a short lifetime using photoinduced absorption spectra.\textsuperscript{25} To indicate the strong effect this decay rate has on the performance of the solar cells, simulations with a decreasing \( k_f \) have been performed up to the point at which the decay rate is equal to P3HT and MDMO-PPV values (see figure 4.8). Upon lowering of the decay rate the typical square root behavior disappears and the photocurrent becomes significantly less field dependent, manifesting itself in a greatly increased short circuit current and fill factor. The simulations indicate that when \( k_f \) for the PCPDTBT:PCBM devices would be as low as for the P3HT:PCBM cells an efficiency of \( \sim 7\% \) can be achieved. This demonstrates the potential of these low band gap polymer:fullerene devices, when the increased recombination of the bound pairs can be prevented.

Above, we have shown that PCPDTBT:PCBM solar cells show signs of a recombination limited photocurrent as predicted by Goodman and Rose. Using our numerical simulation program we are able to show that the low dissociation probability is the cause of the low effective lifetime of the free carriers \( \tau_{\text{eff}} \). We show the lifetime of the bound electron-hole pair to be significantly shorter.
compared to other polymer:fullerene systems. Moreover, the effective lifetime predicted using equation (4.2) ~ \(10^{-7}\) s, matches the lifetime of the bound pair \(1/k_f\), \((k_f = 1.7 \times 10^7\text{ s}^{-1})\) predicted by the simulation model.

Therefore, we can conclude that the decrease of the photocurrent at low effective voltages, and hence low fill factor of the device, is due to a short lifetime of the bound electron-hole pairs. In earlier work an almost complete intermixing of the PCPDTBT polymer with PCBM at the molecular level was reported.\(^{26}\) When donor and acceptor are too closely intermixed carriers can end up being trapped in dead ends and will not dissociate fully into free carriers leading to a large decay rate and hence small effective lifetime. This hypothesis seems to be confirmed by recent results on PCPDTBT:PCBM solar cells by Peet et al.\(^{27}\) Here they show that the addition of alkanedithiols to the solution results in a dramatic increase in device performance. It is shown that adding alkanedithiol results in larger phase separation of donor and acceptor which in turn results in a much higher fill factor and external quantum efficiency. Apparently the larger phase separation results in an increase of the effective lifetime of the charge carriers, such that the device is no longer recombination limited, as predicted by the simulations.
4.6 Conclusions

The charge transport and photogeneration in PCPDTBT:PCBM solar cells is studied to gain insight into the loss mechanisms in these devices. The hole transport in the polymer phase has been shown to be unaffected upon blending with fullerenes, with a mobility of $5.5 \times 10^{-8}$ m$^2$/Vs. The electron mobility of PCBM in the blend has been determined to be $7 \times 10^{-8}$ m$^2$/Vs, which is slightly lower than the pristine value for PCBM. Thus the electron and hole transport are almost balanced and the mobilities are sufficiently high to reach high fill factors and efficiencies. Nevertheless, the fill factor of PCPDTBT:PCBM solar cells is relatively low, originating from a square root regime in the photocurrent as a function of effective voltage. Where in chapter 2 this square root dependence was shown to be due to an unbalance in charge carrier mobilities this is not the case here. The photocurrent is shown to be recombination limited, characterized by a square-root dependence on effective applied voltage, a linear dependence on light intensity and a constant saturation voltage. Simulations of the photocurrent show that the solar cells are limited by a short lifetime of bound electron-hole pairs. It is suggested that this short lifetime is due to an unfavorable morphology where donor and acceptor are too intimately mixed.
REFERENCES

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