# Performance Enhancement of Poly(3hexylthiophene):Methanofullerene Bulk-Heterojunction Solar Cells

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## ABSTRACT

Using a newly developed device model we have studied the effect of controlled thermal annealing on charge transport and photogeneration in bulk-heterojunction solar cells (BHJ) made from blend films of regioregular poly(3hexylthiophene) (P3HT) and methanofullerene (PCBM). With respect to the charge transport, we demonstrate that the hole mobility in the P3HT phase of the blend is dramatically affected by thermal annealing. It increases more than three orders of magnitude, to reach a value up to  $\approx 2 \times 10^{-8} \text{ m}^2/\text{Vs}$  after the annealing process, as a result of an improved crystallinity of the film. Slow drying leads to an additional 33-fold enhancement of the hole mobility even up to  $5.0 \times 10^{-7} \text{ m}^2\text{V}^{-1}\text{s}^{-1}$ , thereby balancing the transport of electrons and holes in the blend. The resulting reduction of space-charge accumulation enables the use of thick films (~300 nm), absorbing most of the incoming photons, without losses in the fill factor and short-circuit current of the device.

As a next step we performed model calculations to exploit the potential of polymer/fullerene bulk heterojunction solar cells. Lowering the polymeric band will lead to a device efficiency exceeding 6%. Tuning the electronic levels of PCBM in such a way that less energy is lost in the electron transfer process enhances the efficiency to values in excess of 8%. Ultimately, with an optimized level tuning, band gap and balanced mobilities polymeric solar cells can reach power conversion efficiencies approaching 11%.

Keywords: organic photovoltaics, modeling, polymers, charge transport

# 1. INTRODUCTION

Solar cells based on a blend of conjugated polymers and functionalized fullerenes are an attractive option for cost effective, large area and light-weight applications.<sup>1</sup> Their working principle is based on the ultra-fast photo-induced charge transfer (~45 fs) of an electron from the polymer donor towards the fullerene acceptor.<sup>2</sup> After dissociation of the exciton, a geminate pair of a hole at the donor and an electron at the acceptor is formed across the interface, which needs to be further separated into free charge carriers through the assistance of an electric field. After separation the photogenerated electron and hole are transported through the donor and acceptor phase of the bulk heterojunction (BHJ) towards the electrodes, leading to an external photocurrent density  $J_{I}$ . Until two-three years ago the attention has mainly been focused on blends of poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-p-phenylene vinylene) (MDMO-PPV) and [6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester (PCBM). By optimizing the morphology of the MDMO-PPV:PCBM BHJ, certified AM1.5 power efficiencies of 2.5% (with [60]PCBM) and 3% (with [70]PCBM) have been achieved.<sup>3,4</sup> Recently, we have developed a device model that quantitatively describes the operation characteristics of PPV:PCBM BHJ solar cells.<sup>5</sup> An important process that limits the photocurrent is the dissociation of bound electron-hole pairs, formed after the ultrafast electron transfer at the donor/acceptor interface.<sup>6</sup> Another remarkable feature of MDMO-PPV:PCBM solar cells is that the optimum performance is reached adding up to 80 wt. % of PCBM, a hardly absorbing material in the solar spectral region.<sup>3</sup> The necessity of such a large amount of PCBM arises from a strong enhancement of the hole transport in MDMO-PPV when blended with PCBM,<sup>7</sup> combined with an enhanced dissociation efficiency due to the increase of the dielectric constant.<sup>8</sup> For PPV-based compounds with lower hole mobilities we have demonstrated that the photocurrent reaches a fundamental space-charge limit, which is detrimental for the fill factor and efficiency.<sup>9</sup> Therefore, an intrinsically higher hole mobility in the blend permits to reduce the amount of PCBM and inhibits the occurrence of space-charge, which will further increase the magnitude of the photogenerated current and enhance the efficiency.

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In the last 2-3 years attention has shifted from PPV-based devices towards BHJ solar cells based on regioregular poly(3-hexylthiophene) (P3HT). Regioregular P3HT has demonstrated promising physical properties such as environmental stability, reasonably high hole mobility and an improved absorption as compared with PPV-based devices. It has been demonstrated that thermal annealing of P3HT:PCBM blend devices strongly improves the energy conversion efficiencies up to 3.5%.<sup>10</sup> This strong increase of the efficiency has been attributed to an increase of the hole transport due to crystallization of the polymer, a better morphology, and an improved overlap with the solar spectrum due to a red shift of the absorption upon annealing.<sup>11-13</sup> In a recent paper by Yang and coworkers it was demonstrated that the efficiency can exceed 4% by controlling the growth rate of the active layer.<sup>14</sup> Slowing down the drying process of the wet films leads to an enhanced self-organization. In this paper we address the effects of thermal annealing and slow drying on the solar cell performance in terms of physical parameters as the charge carrier mobility and photocurrent generation efficiency in these devices.

This study enables us to quantify the parameters that limit the device performance and to exploit the potential of polymer/fullerene bulk heterojunction solar cells in terms of the maximum attainable efficiency.



**Figure 1.** Experimental photocurrent  $(J_{ph})$  versus effective applied voltage  $(V_0 - V)$  of the P3HT:PCBM devices at room temperature; for as-cast device and after thermally annealing of the photoactive layers (see legend). The device thickness (*L*) is 96 nm and the arrow indicates the position of the short-circuit current  $(J_{SC})$ . The dashed lines represent the square-root dependence of the  $J_{ph}$  on voltage.

### 2. EFFECTS OF THERMAL ANNEALING

In Fig. 1 the photocurrent  $J_{ph}$  of a P3HT:PCBM blend (50:50 wt.-%) BHJ solar cell is shown in a double logarithm plot as a function of effective applied voltage  $(V_0-V)$ .<sup>15</sup> This effective applied voltage is a measure for the average electric field in the device. The curves correspond to the different postproduction treatments, namely as cast, thermally annealed at a temperature where the enhancement in efficiency  $\eta$  is maximized (120 °C), and annealed at lower temperature (70 °C). Thermal annealing was performed on complete devices, i.e., with the photoactive layer between the electrodes, on the hot plate for a period of 4 minutes. It appears from Fig. 1 that for the complete annealed device (at 120 °C), the short-circuit current ( $J_{SC}$ ) increases by a factor of 5, the fill factor (FF) by a factor of 2 and the overall enhancement of  $\eta$  is about one order of magnitude when compared with the device as-cast. In order to quantify this strong improvement of the photocurrent of the P3HT:PCBM blends, knowledge about the charge transport properties is indispensable. The hole mobility of pristine P3HT has been measured using field-effect transistors (FET),<sup>16,17</sup> time-of-flight (TOF) photocurrent measurements,<sup>18</sup> and space-charge limited (SCL) current in a sandwich structures.<sup>19</sup> The measured hole mobility ranges from  $10^{-8}$  m<sup>2</sup>/Vs in TOF and SCL current, up to  $10^{-5}$  m<sup>2</sup>/Vs in FET. In this study the SCL technique is applied, where suitable electrodes either suppress the injection of electrons or holes. resulting in a hole- or electron-only device, respectively. To fabricate the hole-only devices palladium was evaporated as oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) electrode indium tin а top on

(PEDOT:PSS)/P3HT:PCBM structure. The work function of PEDOT:PSS matches the highest occupied molecular orbital (HOMO) of P3HT at 4.9 eV, forming an Ohmic contact for hole injection,<sup>12,19</sup> whereas palladium strongly suppresses electron injection into PCBM due to the large mismatch between its work function and lowest unoccupied molecular orbital (LUMO) of PCBM.<sup>20</sup> In order to suppress the hole injection into P3HT, the bottom contact must have a low work function. For this we use a silver electrode of which the work function is modified using a self-assembled monolayer (SAM).<sup>21</sup> As a top electrode a LiF/Al contact is evaporated that matches the LUMO of PCBM.



**Figure 2.** Room temperature electron (•) and hole ( $\circ$ ) zero-field mobilities in 50:50 wt.% blends of P3HT:PCBM as a function of postproduction annealing temperature of the completed devices. For comparison, the hole mobility measured in pristine P3HT devices ( $\Delta$ ) is also shown. The mobilities were calculated from the SCL current measured using the electron- and hole-only device configuration.

Figure 2 shows the measured mobility of electrons and holes from the SCL currents in 50:50 wt.-% blends of P3HT:PCBM devices as a function of the annealing temperature. For comparison, the hole mobility of pristine P3HT, measured under the same experimental conditions, is also shown. It appears from Fig. 2 that the hole mobility in pristine P3HT is hardly affected by thermal annealing, with a typical value of  $(1.4-3.0) \times 10^{-8} \text{ m}^2/\text{Vs}$ . In contrast, the hole mobility of P3HT in the blend is strongly affected by the presence of PCBM and it drops almost 4 orders of magnitude for an as-cast device. Upon annealing, however, the mobility starts to increase sharply with an onset at 50–60 °C, followed by saturation to approximately the value of the pristine polymer when the devices are annealed above 120 °C. Furthermore, the electron mobility of PCBM in the blend is also affected by thermal annealing: For as-cast films the electron mobility is  $(1-2) \times 10^{-8} \text{ m}^2/\text{Vs}$ , being typically a factor of 5000 higher than the hole mobility. As a result, the charge transport in as-cast films is strongly unbalanced and the current is fully dominated by the electrons. Thermal annealing of P3HT:PCBM films results in an enhanced electron mobility by typically a factor of 30, with an onset corresponding to the same temperature observed for the hole mobility. These experimental charge-carrier mobilities will now be used to analyze the photocurrent

Recently, we have demonstrated that the photocurrent in polymer/fullerene blends can be limited by the buildup of space-charge, even under normal operation conditions (1 Sun illumination). This space-charge limited photocurrent occurs when the difference between electron and hole mobility is too large.<sup>9</sup> The fingerprints of a SCL photocurrent are its square-root dependence on voltage and a three-quarter dependence on light intensity.<sup>9</sup> The mobility measurements presented in Fig. 2 show that there is more than two orders of magnitude difference between the electron and hole mobility in as-cast and devices annealed up to 90 °C. As expected, the photocurrents shown in Fig. 1 indeed exhibit a square-root dependence on voltage for both the as-cast film and the device annealed at 70 °C. As a next step the light intensity ( $P_{\text{light}}$ ) dependence of the photocurrent has been studied for the device annealed at 70 °C). The  $P_{\text{light}}$ was varied from 1000 W/m<sup>2</sup> (upper curve) down to 76 W/m<sup>2</sup> using a set of neutral density filters with a constant optical density over the spectral range of the light source.



**Figure 3.** Light intensity dependence of the photocurrent  $(J_{ph})$  versus effective applied voltage  $(V_0 - V)$  of the device thermally annealed at 70 °C. The intensity was varied from 1000 (upper curve) down to 76 W/m<sup>2</sup>, whereas the arrow indicated the position of the short-circuit current  $(J_{SC})$ .

Figure 3 shows the  $J_{ph}$ -( $V_0$ -V) characteristics of the P3HT:PCBM device, after thermal annealing at 70 °C as shown in the Fig. 1, as a function of  $P_{\text{light}}$ . It is observed that for  $V_0$ -V < 0.03 V, the  $J_{\text{ph}}$  shows linear dependence on voltage at all light intensities, which is caused by the opposite effect of drift and diffusion of charge carriers.<sup>5,6,9</sup> Above 0.03 V, however, a square-root dependence on voltage of the experimental  $J_{ph}$  is observed, as is predicted for blends with a large difference in electron and hole mobilities.<sup>9</sup> At even larger voltages the  $J_{ph}$  shows a clear transition to the saturation regime where it becomes limited by the field- and temperature dependence of the dissociation of bound electron-hole pairs;  $J_{ph}=qG(E,T)L$ .<sup>6</sup> These results are distinctly different when the devices are annealed at higher temperature, where the electron and hole transport is more balanced. In that case, no square-root dependence of  $J_{\rm ph}$  is observed, as seen in the Fig. 1 by the curve at 120 °C. Figure 4 displays, on the double-logarithmic scale, the experimental  $J_{\rm ph}$  taken form Fig. 3 as a function of light intensity for two different voltages; at  $V_0$ -V=0.1 V in the square-root regime and at  $V_0$ -V=3 V in the saturation regime. The slope S determined from the linear fit (lines) to the experimental data (as shown in Fig. 4) clearly proves that  $J_{\rm ph}$  is limited by the build-up of space-charge in the square-root regime and becomes space-chargefree in the saturation regime.<sup>9</sup> It is clear that the build-up of space charge dramatically reduces the device performance, since it causes a fundamental limitation on FF and  $J_{SC}$ . Due to the strongly increased hole mobility, leading to a better balanced transport, this limitation is prevented under normal operation condition in the device annealed above 110 °C. Thus, the enhancement in the device efficiency by a factor of 10 upon thermal annealing is mainly due to the improved hole mobility of P3HT inside the blend by more than three orders of magnitude. With increasing hole transport the devices recover from the space-charge limitation to become space-charge-free, as a result of a more balanced transport. The absence of the square-root voltage dependence in the device annealed at 110 °C leads to a strong enhancement of both FF and  $J_{SC}$ .



**Figure 4** Light intensity dependence of the photocurrent ( $J_{ph}$ ) taken from Fig. 3 at an effective voltage of  $V_0$ -V=0.1 V and  $V_0$ -V=3.0 V (symbols). The slope (S) determined from the linear fit (solid lines) to the experimental data is written on the figure.

# 3. EFFECT OF SLOW DRYING

In recent experiments by Yang et al. the efficiency of P3HT:PCBM BHJ solar cells was enhanced up to 4% by controlling the growth rate of the active layer.14 Slowing down the drying process of the wet films leads to an enhanced self-organization. Such an improvement of the sefl-organization might also enhance the hole transport in the P3HT. However, the charge transport in these slowly dried P3HT:PCBM blends has been investigated using time-of-flight (TOF) measurements. It was demonstrated that slow drying leads to an enhanced hole transport. Electron and hole mobilities of  $\mu = 7.7 \times 10-9 \text{ m2V-1s-1}$  and  $\mu = 5.1 \times 10-9 \text{ m2V-1s-1}$  were reported, respectively.14 It is remarkable that the reported mobility values for these slowly dried films with superior photovoltaic performance are much lower than the values reported for MDMO-PPV:PCBM and annealed P3HT:PCBM devices: For MDMO-PPV:PCBM (1:4 wt. %) values of  $\mu = 2.0 \times 10-7 \text{ m2V-1s-1}$  and  $\mu h = 1.4 \times 10-8 \text{ m2V-1s-1}$  have been found,8 and for P3HT:PCBM (1:1 wt.%) using fast drying and annealing similar values of  $\mu = 3.0 \times 10-7 \text{ m2V-1s-1}$  and  $\mu h = 1.5 \times 10-8 \text{ m2V-1s-1}$  have been measured, as shown in section 2.22 Therefore, from the reported values it is not clear whether an enhanced hole transport is responsible for the improved performance after slow drying, or for example an improved balance between electron and hole transport.

For fast drying films as discussed in section 2 the active layer was fabricated by spin coating a solution of regioregular P3HT and PCBM (1:1 w/w) in chloroform on top of the PEDOT:PSS coated substrate. To complete the devices, a LiF (1 nm)/Al (100 nm) top electrode was deposited by thermal evaporation. To get the optimum performance the devices were subsequently annealed in the nitrogen glove box on a hot plate at a temperature of 110 °C for 4 minutes. For slow drying films the P3HT:PCBM layer was spun from an ODCB solution on the ITO/PEDOT:PSS substrate, followed by drying of the films at room temperature in a closed Petri dish overnight.<sup>14</sup> Subsequently, a LiF/Al top electrode was thermally evaporated to complete the devices. As a first step we compare the photocurrent of solar cells prepared with either fast drying and subsequent annealing or the slow drying procedure, as shown on Fig. 5. The first type of devices reach their optimum performance at a layer thickness L of  $\sim 100$  nm. With a short-circuit current density  $J_{sc}$ =79 A/m<sup>2</sup>, an open-circuit voltage  $V_{oc}$ =0.6 V and a fill factor FF=66% the efficiency of these devices amounts to 3.1%. For the slowly dried films, however, the optimum performance is obtained at considerably thicker films with thickesses of typically L~300 nm. In these devices values of  $J_{sc}=105$  A/m<sup>2</sup>,  $V_{oc}=0.59$  V and FF=60% have been obtained. The strong increase of  $J_{sc}$  and the relatively small loss in FF leads to an enhanced efficiency of 3.7%. The efficiency increase found here is similar to the one reported by Yang et al. when measured under standard AM1.5 conditions.<sup>14</sup> In order to further investigate the origin of this enhanced performance we study the hole transport in the various blend using single carrier SCL devices as described in section 2. For the fast dried and annealed film a hole mobility of  $\mu_h = 1.1 \times 10^{-8} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$  is obtained, similar to the value reported before.<sup>22</sup> For the slowly dried films a mobility of  $\mu_h = 5.0 \times 10^{-7} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$  is obtained. Thus, applying slow drying we observe that the hole mobility in the P3HT phase increases by a factor of 45 with respect to the annealed films.



**Figure 5.** Experimental photocurrent  $(J_L)$  versus applied voltage (*V*) of the ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al devices fabricated by two different recipes: ( $\circ$ ) the active layer was spun from a chloroform solution, resulting in a fast drying of the film during the spin-coating process, followed by thermal annealing of the completed device at 110 °C for 4 minutes; ( $\Box$ ) the active layer was spun from an ODCB solution and subsequently dried in a covered Petri dish overnight before the actual top electrode was thermally deposited. Also shown are the model calculation (solid line) using the measured hole and the electron mobilities for the fast drying film. The remaining model parameters are identical to the ones determined in a previous study.<sup>22</sup> As a comparison, also the photocurrent for a 304 nm device is calculated (dashed line) using the model parameters of the quickly dried and annealed device.

In order to study the effect of such a mobility increase on the solar cell efficiency we apply our numerical device model<sup>5</sup> to analyze the photocurrent  $J_L$  of the solar cells, as represented in Fig. 5. The input parameters required to calculate the photocurrent in the model are:  $\mu_e$  and  $\mu_h$ , the spatially averaged dielectric constant < r > of P3HT and PCBM, the dissociation parameters a and  $k_F^{-1}$ , and maximum generation rate  $G_{\text{max}}$ . For the annealed devices using  $\mu_h=1.1\times10^{-8} \text{ m}^2\text{V}^{-1}\text{s}^{-1}$  and  $\mu_e=3.0\times10^{-7}\text{m}^2\text{V}^{-1}\text{s}^{-1}$ , a=1.8 nm and  $k_F^{-1}=7\times10^{-5}$  s, and  $G_{\text{max}}=6\times10^{27} \text{ m}^{-3}\text{s}^{-1}$  the photocurrent is consistently described, as shown in Fig. 5. For comparison, we also calculated the photocurrent for a device with a thickness L=304 nm, keeping all other parameters fixed. It is evident from the curve that the fill factor strongly reduces to a value of only 42%, which is detrimental for the performance. Such a low fill factor is indicative for the formation of space-charge in such a thick active layer device. In Fig. 6 the photocurrent of the slowly dried device is modeled using the enhanced mobility of  $\mu_h = 5.0 \times 10^{-7} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$  as input, while the other parameters were kept the same, except for G<sub>max</sub> that was fitted from the photocurrent under reverse bias. Taking the enhanced mobility into account, the calculated photocurrent is in excellent agreement with the measurements. As a reference the dashed line of Fig. 6, using the lower mobility, is also included in the plot. As expected, the increase of the mobility leads to a strong enhancement of the FF, going from 42% to 61%. The small loss compared to the thin device shown in Fig. 3 (FF=66%) is overruled by a significant increase of the  $J_{sc}$  due to the increased absorption, enhancing the power efficiency from 3.1% to 3.7%. The role of the increased mobility is that the transition from non-SCL towards the SCL regime is extended to higher thickness. With a mobility of  $\mu_h = 5.0 \times 10^{-7} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$ , the 304 nm device is still in the regime where space-charge effects do not play a role. This is also confirmed by the linear intensity dependence of  $J_{sc}$ .



Figure 6. Experimental photocurrent  $(J_L)$  of a P3HT:PCBM blend solar cell device, prepared by the slow drying method of the photoactive layer (squares), together with the model calculation, using a hole mobility measured in the fast drying film (dashed line) and slow drying film (solid line).

## 4. OPTIMIZATION OF THE PERFORMANCE OF P3HT:PCBM SOLAR CELLS

How to enhance the performance of these promising devices? Coakley and McGehee predicted that efficiencies higher than 10% can be achieved by optimizing the cell's architecture to promote efficient exciton splitting and charge transport and by reducing the band gap of the polymer so that a larger fraction of the solar spectrum can be absorbed.<sup>23</sup> In their calculation, several simplifying assumptions are made, such as the fill factor being unity, and recombination (either geminate or bimolecular) is neglected. In order to make a more detailed calculation, our numerical model is used.<sup>5</sup> As a starting point for our investigation we use annealed P3HT:PCBM BHJs. Since we know the mobilities of the charge carriers in P3TH:PCBM blends, we can quantitatively model the experimental current-voltage characteristics of these devices. The current-voltage characteristics of an illuminated P3HT:PCBM devices (annealed at 110 °C) is shown in Fig. 7, together with the numerical result. The thus obtained theoretical description of P3HT:PCBM solar cells enables us to investigate the enhancement of the efficiency when a number of solar cell parameters is varied.

We focus on two effects: First the effect of minimizing the energy loss in the electron transfer from donor to acceptor material is found to be of paramount importance; an efficiency of 8.4% is predicted. This comes as no surprise when one considers that only photons with an energy larger than approximately 2 eV are absorbed, while the opencircuit voltage is only 0.6 V. Subsequently, the effect of decreasing the polymeric band gap is studied. Several research groups have put a lot of effort in the synthesis and application of these polymers.<sup>24-28</sup> At a first glance a small band gap polymer seems beneficial. Due to an improved overlap with the solar spectrum the absorption is enhanced, leading to efficiencies larger than 6%. Surprisingly, we show that once the energy loss in electron transfer is minimized, the best performing solar cell comprises a polymer with a band gap of around 2 eV, clearly not a small band gap. In these cells a lowering of the band gap is accompanied by a decrease of the open-circuit voltage, canceling the benfit of an absorption increase. Ultimately, with energy levels, band gaps and mobilities simultaneously optimized polymer/fullerene solar cells can reach nearly 11% efficiency.

The inset of Fig. 7 shows the LUMO and HOMO of P3HT and PCBM. Due to the large offset between the LUMO of the donor, LUMO(D), and the LUMO of the acceptor, LUMO(A), electron transfer from the donor onto the acceptor takes place, thereby breaking up the exciton. However, the excess energy of the electron and the hole is dissipated quickly. This energetic loss is reflected in the open-circuit voltage, which is limited by the difference between the HOMO of the donor and the LUMO of the acceptor.<sup>29,30</sup> Concomitantly, the LUMO(A)-LUMO(D) offset reduces the hence efficiency of the solar cell. Experimental and theoretical investigations of polymer/polymer BHJs show that electron transfer occurs provided that the difference in LUMO levels is larger than the binding energy of the intrachain exciton,<sup>31</sup> which is known to be approximately 0.4 eV.<sup>32</sup> Since the difference in LUMO levels is much larger than the electron transfer efficiency and thereby increasing the energy difference between the HOMO of the donor and the LUMO be possible to decrease the LUMO(A)-LUMO(D) offset without decreasing the electron transfer efficiency and thereby increasing the energy difference between the HOMO of the donor and the LUMO of the acceptor.



**Figure 7**. The current-voltage characteristics of a P3HT/PCBM bulk heterojunction solar cell (symbols) and the fit to the data (line). The inset shows the energy levels, energies given in eV with respect to vacuum, of a P3HT:PCBM BHJ, together with the process of electron transfer from P3HT to PCBM.

Figure 8 shows the influence of the LUMO(A)-LUMO(D) offset on the device efficiency when all other parameters are kept the same as for the annealed P3HT:PCBM device. The performance of the photovoltaic devices is greatly enhanced by lowering the LUMO(A)-LUMO(D) offset, primarily caused by an increase in open-circuit voltage. For the P3HT/PCBM system, the LUMO(A)-LUMO(D) offset amounts to 1.1 eV, leading to 3.5 % efficiency. To be on the safe side, the LUMO(A)-LUMO(D) offset is not lowered below 0.5 eV, although Brabec *et al.* have shown that efficient charge transfer takes place in a low band gap polymer/fullerene device with a LUMO(A)-LUMO(D) offset of only 0.3 eV.<sup>25</sup> By lowering this offset to 0.5 eV the device efficiency would increase to more than 8 %, showing the great importance of matching the electronic levels of donor and acceptor.

Since P3HT has a relatively high band gap (approximately 2.1 eV), improvement of the overlap of the absorption spectrum of the materials used with the solar spectrum may also increase device performance. We study the effect of lowering the polymer band gap by shifting the P3HT part in the absorption spectrum of a P3HT:PCBM blend film down in energy. This ensures that the shape and magnitude of the absorption spectrum of the polymer is realistic, and the assumption that all above band gap photons are absorbed and contribute to the photocurrent is not made. Subsequently, the resulting increase in absorption is calculated and the exciton generation rate is modified accordingly. The results for the efficiency as a function of the band gap of the polymer are shown in Fig. 9. Evidently, the performance benefits from lowering the band gap, ultimately reaching 6.6 % for a 1.5 eV band gap. The band gap is not lowered beyond 1.5 eV, which corresponds to a LUMO(A)-LUMO(D) offset of 0.5 eV, to ensure efficient electron transfer from the polymer to PCBM. This calculation shows that the effect of only tuning the LUMO(A)-LUMO(D) offset is more beneficial than only lowering the polymeric band gap.



Figure 8. The influence of the offset between the LUMO of the donor and the acceptor (symbols), the line is drawn as a guide to the eye.



Figure 9. The influence of the band gap of the polymer on device efficiency (symbols). The line is drawn as a guide to the eye.

As a next step the combined effect of lowering the band gap of the polymer and tuning the LUMO(A)-LUMO(D) offset to 0.5 eV is studied, see Fig. 10. For a band gap of 1.5 eV the efficiency amounts to 6.6%, corresponding to the maximum of Fig. 9. However, when the band gap is increased the now fixed LUMO(A)-LUMO(D) offset leads to an increase of the open-circuit voltage, thereby enhancing the efficiency in spite of the reduced absorption. As shown before in Fig. 8, the efficiency corresponding to a 2.1 eV band gap is more than 8%. However, the efficiency shows a broad maximum with the optimal band gap in between 1.9 eV and 2.0 eV, reaching an ultimate efficiency of 8.6%. Surprisingly, the optimal band gap when LUMO(A)-LUMO(D) is kept at 0.5 eV is very close to the present P3HT value of 2.1 eV, demonstrating that the usage of small band gap polymers is not the most efficient way of increasing the performance of single layer devices.

Up to this point we have not considered the influence of charge carrier mobility. The thickness of current polymer:fullerene BHJs is limited by the rather low hole mobility of the polymer phase as compared to the electron mobility of the fullerene. Typically, increasing the thickness of the active layer beyond 150 nm leads to a decrease in fill factor. Lenes et al. have shown that the decrease in fill factor is due to a combination of charge recombination and space charge effects.<sup>33</sup> On the other hand, device performance is expected to be enhanced by a thicker active layer since more light is absorbed. Therefore, the effect of increasing the hole mobility to the value for the electron mobility, i.e.,  $2.0 \times 10^{7}$  m<sup>2</sup>/Vs is studied, in combination with a polymeric band gap of 1.9 eV and a LUMO(A)-LUMO(D) offset of 0.5 eV, corresponding to an optimal situation. A 97 nm thick device with these specifications would yield an efficiency of 9.2%, see Fig. 11. Such a high value of the hole mobility in polymer systems is not unrealistic, as supported by the high hole mobility found in slowly dried P3HT:PCBM blends. Figure 11 shows the variation of the efficiency with active layer thickness for both values of the hole mobility. As expected, the optimal thickness for the situation with the current hole mobility is around 100-150 nm, as observed experimentally. Increasing the hole mobility causes the optimum to shift toward 200 nm. The efficiency at this thickness is 10.8%, showing the great potential of polymer/fullerene based solar cells.



Figure 10. The combined effect of tuning the LUMO(A)-LUMO(D) offset to 0.5 eV and changing the polymer band gap (symbols). The line is drawn as a guide to the eye.



Figure 11. The influence of the active layer thickness on the efficiency taking the hole mobility as is (squares) or increasing it to 2.0  $\times 10^{-7}$  m<sup>2</sup>/Vs (circles). The lines are drawn as guides to the eye.

#### 5. CONCLUSIONS

The origin of the enhanced performance in P3HT:PCBM bulk heterojunction solar cells after thermal annealing and slow drying was investigated. Using hole transport measurements, we demonstrate that due to thermal annealing the hole mobility is increased by more than two orders of magnitude. An additional 33-fold enhancement of the hole mobility is obtained by slow drying, reaching a value as large as  $5.0 \times 10-7$  m2V-1s-1 in the P3HT phase of the blend. This mobility increase reduces the accumulation of space-charges in films, enabling the use of thicker films. The resulting increase in short-circuit current together with the preserved fill factor increases the power conversion efficiency of these cells to a value of 3.7%. Model calculations demonstrate that optimization of the LUMOs of both donor and acceptor combined with tuning of the polymeric band gap would strongly enhance the performance. Ultimately, with balanced charge transport polymeric solar cells can reach power conversion efficiencies of 10.8 %.

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