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Device physics of donor/acceptor-blend solar cells

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Improving the efficiency of bulk heterojunction solar cells

Summary

In this chapter, various ways to improve the efficiency of bulk heterojunction solar cells are identified by using the MIM model as outlined in chapter 2. A much pursued way to enhance the performance is to increase the amount of photons absorbed by the film by decreasing the band gap of the polymer. Calculations based on the MIM model confirm that this would indeed improve the performance. However, it is demonstrated that the effect of minimizing the energy loss in the electron transfer from the polymer to the fullerene derivative is even more beneficial. By combining these two effects, it turns out that the optimal band gap of the polymer would be 1.9 eV. With balanced charge transport, polymer/fullerene solar cells can reach power conversion efficiencies of at least 10.8%.

6.1 Introduction

How efficient can bulk heterojunction solar cells be? Which material requirements must be fulfilled? These are the most important questions in this thesis. For p - n junction based solar cells, the former question was addressed in the 1950's. Shockley and Queisser studied the detailed balance limit to the efficiency of p - n junction solar cells by treating the sun and the solar cell as two black bodies at temperatures $T_{\text{sun}} = 6000$ K and $T_{\text{cell}} = 300$ K, respectively.^[1] Araújo and Martí generalized these arguments and found that the optimal band gap $E_{\text{gap}}^{\text{op}}$ is equal to 1.3 eV, with a maximal efficiency of 31%.^[2] Loferski pointed out that atmospheric conditions change the value of $E_{\text{gap}}^{\text{op}}$ because the spectrum of the incident light is affected. Therefore, the optimal band gap for p - n junction solar cells under AM1.5 illumination is equal to 1.4 eV.^[3] The voltage $V_{\text{MPP}}^{\text{op}}$ corresponding to the maximum power point for an optimized band gap (under full concentration) is given by^[2]

$$V_{\text{MPP}}^{\text{op}} = \frac{E_{\text{gap}}^{\text{op}}}{q} \left(1 - \frac{T_{\text{cell}}}{T_{\text{sun}}} \right), \quad (6.1)$$

showing that $V_{\text{MPP}}^{\text{op}}$ is very close to $E_{\text{gap}}^{\text{op}}/q$. Under normal intensity (1 Sun), it can easily be shown that

$$V_{\text{MPP}}^{\text{op}} \approx 0.95 \frac{E_{\text{gap}}^{\text{op}}}{q} - 0.27. \quad (6.2)$$

This limit cannot be directly applied to BHJ solar cells: Due to the offset between the LUMOs of the donor and the acceptor, necessary for charge transfer, the V_{oc} of BHJ solar cells is limited to $E_{\text{gap}}^{\text{eff}}/q$ (see chapter 3), even for an idealized situation. As a consequence, $V_{\text{MPP}}^{\text{op}}$ for a BHJ device will be smaller than the value predicted by Eq. (6.2). Therefore, the detailed balance limit for BHJ solar cells is significantly lower than the value predicted for p - n junctions and it follows that the optimal value of the band gap of the absorbing polymer will be significantly larger than 1.4 eV.*

In this chapter, a calculation of the detailed balance limit of BHJ solar cells will not be attempted. Instead, ways to improve existing devices will be identified. As a first approximation Coakley and McGehee predicted that an efficiency of 10% may be within reach.^[4] In their calculation it is assumed, among other things, that the fill factor is equal to unity and recombination, either geminate or bimolecular, is neglected. By using the numerical model outlined in chapter 2, a more detailed calculation can be performed. The starting point of this investigation will be the P3HT/PCBM system, with an efficiency of 3.5%. By combining charge carrier mobility measurements^[5] with current-voltage measurements performed on illuminated solar cells, the experimental current-voltage characteristics of these solar cells are quantitatively modeled. The thus obtained

*As the Shockley equation for p - n junctions directly follows from this detailed balance analysis, it is easy to see that, since the detailed balance limit for BHJs is different, the current-voltage characteristics of BHJs cannot be described by the Shockley equation.

theoretical description of P3HT/PCBM solar cells enables one to investigate the enhancement of the efficiency when a number of solar cell parameters is varied.

Scharber *et al.* have also predicted that an efficiency of 10% is achievable,^[6] with an optimal polymer band gap of 1.4 eV. In their calculation it is assumed that the fill factor is equal to 65%, regardless of the HOMO and LUMO positions of the materials. However, if the effective band gap $E_{\text{gap}}^{\text{eff}}$ is increased, the fill factor also increases, thereby favoring larger values of the band gap of the polymer. Therefore, the optimal value of the polymer's band gap is underestimated in their calculation.

6.2 Improving polymer/fullerene solar cells

Let us take a closer look at two important parameters: the energy loss in electron transfer and the band gap of the absorber. 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 by minimizing this loss. This comes as no surprise when one considers that only photons with an energy larger than 2 eV are absorbed, while $V_{\text{oc}} = 0.6$ 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.^[7-11] 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, it is found 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 reduction of the band gap is accompanied by a decrease of the open-circuit voltage, canceling the benefit of an absorption increase. With energy levels, band gaps and mobilities simultaneously optimized polymer/fullerene solar cells can reach nearly 11% efficiency.*

The devices used in this chapter are BHJs of P3HT and PCBM annealed at 110°C with an active layer thickness of 97 nm. Figure 6.1 shows the current density under illumination (J_L) as a function of applied bias (V_a) of a P3HT/PCBM solar cell. To describe the current-voltage characteristics of polymer/fullerene solar cells the MIM model, as outlined in chapter 2, is used, see Fig. 6.1.

The inset of Fig. 6.1 shows the positions of 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 quickly dissipated. This energy 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, see chapter 3.^[12,13] Concomitantly, the need for a LUMO(A)-LUMO(D) offset reduces the output power (and hence efficiency) of the solar cell.

*Although this is not a strictly limiting value.

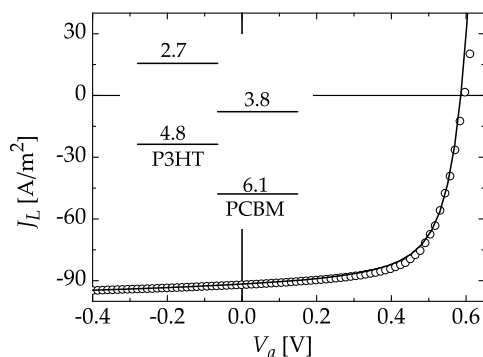


Figure 6.1: The current-voltage characteristics of a P3HT/PCBM bulk heterojunction solar cell (symbols) illuminated at 1 kW/m^2 and the fit to the data (line). The inset shows the energy levels of P3HT and PCBM (energies given in eV with respect to vacuum).

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,^[14] which is known to be approximately 0.4 eV.^[15] Since the difference in LUMO levels is much larger than the exciton binding energy, it should 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 6.2 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 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 small band gap polymer/fullerene device with a LUMO(A)-LUMO(D) offset of only 0.3 eV.^[9] The possibility of triplet formation from the charge transfer state, which can become more probable when the LUMO(A)-LUMO(D) offset is decreased, is ignored.^[16] 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.

Now we turn to the influence of the polymer's band gap. Since P3HT has a relatively large band gap (2.1 eV), improvement of the overlap of the absorption spectrum of the materials used with the solar spectrum may also increase device performance. The effect of lowering the polymer band gap is studied by shifting the P3HT part in the absorption spectrum of a P3HT/PCBM blend film down in energy. In this way, a realistic

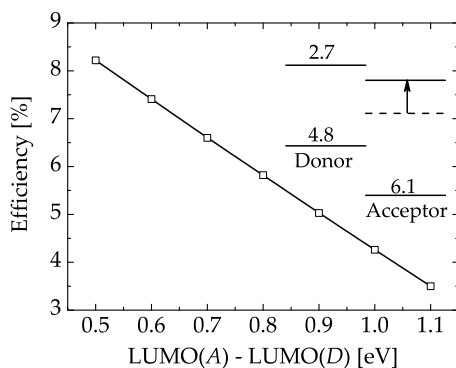


Figure 6.2: The influence of the offset between the LUMO of the donor and the acceptor (symbols), the line is drawn as a guide to the eye.

absorption spectrum for the polymer is taken, both in shape and in magnitude and the assumption that all above band gap photons are absorbed and contribute to the photocurrent is not made.* The HOMO level of the polymer phase is taken constant, so the open-circuit voltage is not affected by the decrease in band gap, and the energy levels of PCBM remain unchanged. Subsequently, the resulting increase in absorption is calculated and the exciton generation rate is modified accordingly. By using this as input for the numerical model, together with the parameters obtained in fitting the current-voltage data of the real P3HT/PCBM device (see Fig. 6.1), the resulting device efficiency is calculated, see Fig. 6.3. Clearly, the device performance benefits from lowering the band gap, 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. The increase in performance is accounted for by enhancement of the short-circuit current. 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.

As a next step the combined effect of lowering the band gap of the polymer whilst keeping the LUMO(A)-LUMO(D) offset to 0.5 eV is studied, see Fig. 6.4. For a band gap of 1.5 eV the efficiency amounts to 6.6%, corresponding to the maximum of Fig. 6.3. 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 reducing the absorption. As shown before in Fig. 6.2, the efficiency corresponding to a 2.1 eV band gap is more than 8%. However, the efficiency shows a broad maximum

*As the band gap of the polymer is decreased, the generation of charges will be due to longer wavelengths, which in turn need a thicker active layer to be absorbed. This optical effect is ignored in the present analysis, overestimating the efficiency of small band gap devices.

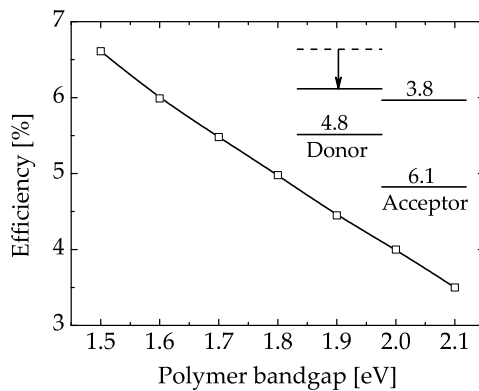


Figure 6.3: The influence of the band gap of the polymer on device efficiency (symbols). The line is drawn as a guide to the eye.

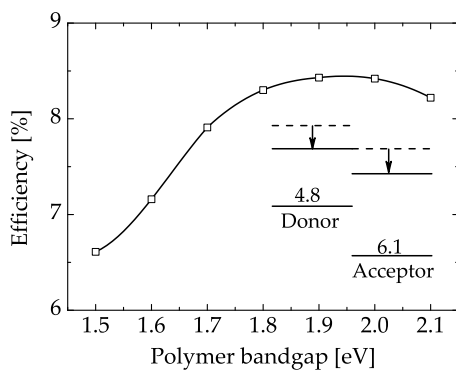


Figure 6.4: The combined effect of tuning the LUMO(A)-LUMO(D) offset to 0.5 eV and changing the polymer band gap (symbols). The line is drawn as a guide to the eye.

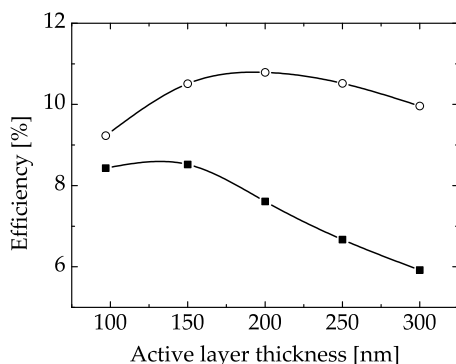


Figure 6.5: The influence of the active layer thickness on the efficiency taking the hole mobility as is (squares) or increasing it to $2.0 \times 10^{-7} \text{ m}^2/\text{Vs}$ (circles). The lines are drawn as guides to the eye.

with the optimal band gap in between 1.9 eV and 2.0 eV, reaching an efficiency of 8.6%. Surprisingly, the optimal band gap when the LUMO(A)-LUMO(D) offset 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.

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.^[17] 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., $2.0 \times 10^{-7} \text{ m}^2/\text{Vs}$ 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. 6.5. Such a high value of the hole mobility in polymer systems is not unrealistic: By optimizing the processing conditions, an even slightly higher value has been obtained.^[18]

In order to vary the active layer thickness, it is necessary to recalculate the volume generation rate of electron-hole pairs. The absorption at each wavelength is calculated from the absorption coefficient, taking into account the reflection of the aluminum electrode. By integrating this over the AM1.5 spectrum, one gets the relative value for the generation rate.^[5] By performing this calculation for various layer thicknesses, the resulting efficiency can be estimated. It should be noted that this is a simplified procedure and it would be more accurate to incorporate optical interference effects in the device,^[19] however, the inclusion of an absorption profile as found by Hoppe *et al.* influences the outcome by less than 0.2%.

Figure 6.5 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.

It is worthy of note, that in the present analysis—by taking P3HT/PCBM as a starting point and *only* changing the parameters under investigation—several (implicit) assumptions are made. First of all, in this calculation, the absorption of the fullerene is neglected. Depending on the chemical structure of the fullerene, this may or may not be a serious omission. Furthermore, it is assumed that the dissociation of electron-hole pairs is not affected by changing the energy levels of the materials: Neither the possibility of triplet formation,^[16] nor the possible influence of the LUMO(A)-LUMO(D) offset on the separation distance a has been included. All in all, the P3HT/PCBM system functions only as an example of a generic strategy and, therefore, is not as general as the detailed balance limit for p - n junctions.

6.3 Conclusions

In this chapter, it was shown that the device efficiency of P3HT/PCBM bulk heterojunction solar cells would greatly benefit from tuning of the LUMO level of PCBM in such a way that the LUMO(A)-LUMO(D) offset would be 0.5 eV. In that case the efficiency could be as high as 8%. Another, much pursued, way to improve the performance is to increase the amount of photons absorbed by the film by decreasing the band gap of the polymer. Calculations based on the MIM model confirm that this would indeed enhance the performance. However, the best efficiency is reached when both effects are combined, i.e., favourable LUMO's of both donor and acceptor and tuning of the polymeric band gap. The optimal band gap lies rather close to the present value, however. This indicates that, although lowering the polymeric band gap enhances the efficiency, it would be more beneficial to either lower the LUMO of PCBM or find another acceptor with a more favourable LUMO level combined with good charge transporting properties. With balanced charge transport, polymer/fullerene solar cells can reach power conversion efficiencies of at least 10.8%.

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