EFFICIENCY POTENTIAL OF ORGANIC BULK HETEROJUNCTION SOLAR CELLS

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ABSTRACT

In order for organic bulk heterojunction solar cells to compete with the traditional inorganic cells, power conversion efficiencies of more than 10 % are desirable. Nowadays, efficiencies up to 5 % are reached and the question about the limits for the attainable efficiency of organic cells arises. In this article, we study the efficiency potential of organic bulk heterojunction solar cells. We make realistic assumptions to predict efficiencies obtainable in the near future, and calculate the upper-limit. We study the influence of the difference between the LUMO-energy levels of donor and acceptor, and the absorption window on the efficiency. Ideal material characteristics are obtained from these calculations, giving an idea how the ideal organic solar cell should look like. The calculations show that nowadays, an efficiency of 5.8 % for the single junction bulk heterojunction solar cell should be possible. Considering parameters which are credible to be achieved in the future, an organic solar cell of 15.2 % is in reach, with an optimal bandgap of 1.5 eV for the absorber. We also consider the situation where both the *n*- and *p*-type materials are absorbers. All calculations are not only done for a single junction cell, but also for tandem solar cells. For a tandem structure of organic cells, we find in a realistic scenario a maximum attainable efficiency of 10.1 % and an efficiency of 23.2 % in an optimistic scenario with optimal bandgaps E_{g1} = 1.7 eV and E_{g2} = 1.1 eV.

I. INTRODUCTION

Photovoltaic solar cells based on organic compounds are promising candidates for solar energy conversion. They have the potential for cost effectiveness, mechanical flexibility and easy processing. However, in order to compete with the traditional inorganic cells, power conversion efficiencies of more than 10 % are a desirable. Nowadays, efficiencies up to 5 % are reached [1] and the question about the limits for the attainable efficiency of organic cells arises. In this article, we calculate the upper-limit for the efficiency of organic cells, and make realistic assumptions to predict efficiencies obtainable in the near future. Ideal material characteristics are obtained from these calculations, giving an idea how the ideal organic solar cell should look like. Predicting the efficiency of organic solar cells was already done by multiple authors, e.g. [2, 3], but we include the influence of among others the absorption window. Moreover, these calculations are not only done for one single cell, but also for tandem solar cells.

II. SINGLE JUNCTION ORGANIC SOLAR CELL

The active material in an organic bulk heterojunction solar cell consists of an interpenetrating network of an *n*-type (electron acceptor, e.g. fullerene derivatives) and a *p*-type (semi)conductor (electron donor, e.g. conjugated polymer), sandwiched between two electrodes with different work functions. See Fig. 1(a) for the schematic energy band diagram.

For our simulation, the following assumptions are made: (i) only one material absorbs light. Usually, most light is absorbed by the *p*-type component, and this is the case we will consider from here. In the other case, when the *n*-type material absorbs all the light, the results remain the same by permutation of *n* and *p*. We assume that (ii) every photon with an energy $h\nu$ higher than the bandgap $E_{g,absorber}$ ($=E_{g,p}$) is absorbed, with the bandgap defined as the difference between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the absorber material. (iii) Not any photon with an energy $h\nu$ lower than the bandgap $E_{g,absorber}$ is absorbed. The distance between the HOMO of the donor, and the LUMO of the acceptor is considered as the thermodynamic limitation for the useful energy [4]. This value is often called the interface bandgap $E_{g,i}$. We assume that (iv) every absorbed photon leads to a useful energy $E_{g,i}$. This last assumption means that the absorbed photon leads eventually to a free electron and a free hole, with an energy difference of $E_{g,i}$ between them. In this case, the maximum efficiency η_{max} is given by:

$$\eta_{\max} = \frac{E_{g,i} \int_{E_{g,\,absorber}}^{\infty} N(E)\, dE}{\int_{0}^{\infty} E\, N(E)\, dE} \tag{1}$$

with $N(E)$ the photon flux. For all our simulations, we use the AM 1.5 experimentally measured solar spectrum [5]. Notice that the denominator is the incident photon power density of the solar spectrum and does not depend on the bandgap. The efficiency increases linearly with the interface bandgap $E_{g,i}$. In this ideal scenario, the open circuit voltage V_{oc} will be given by $E_{g,i}/q$, the fill factor *FF* equals unity, as well as the quantum efficiency *QE* for wavelengths lower than the cut-off wavelength λ_g (corresponding with $E_{g,absorber}$).

In Fig. 2 the maximum efficiency for this ideal scenario is plotted for the case where the *p*-type material absorbs the light, and the *n*-type has a bandgap of respectively 1.5 eV (e.g. the widely used fullerene derivative PCBM). Straight lines indicate where the bandgap of the *p*-material is 1.0 eV, 2.0 eV. The position of bulk heterojunction cells with PTV, P3HT, MEH-PPV and MDMO-PPV as *p*-material and respectively PCBM and PCNEPV as *n*-material is given [6, 7]. One notices that the efficiency decreases when LUMO_p increases (i.e. the bandgap of the absorber increases), because less photons are being absorbed. With each LUMO_p, there is an optimum for HOMO_p, being the compromise between the size of the interface bandgap, and the absorber bandgap. The highest efficiency is reached when the LUMO of the *n*-material is as close as possible to the LUMO of the *p*-material. This was expected, because the difference between the LUMO's corresponds with an energy loss of the absorbed photon. With a full absorption window, the optimal bandgap of the absorber is 1.1

eV. Most organic absorbers have a higher bandgap and the production of suitable organic absorbers for photovoltaic applications with such a low bandgap is a problem [8]. However, when we take into account a narrow absorption window (Fig. 1(b) for definition of terms), characteristic for organic materials [8], the optimal bandgap shifts towards higher energies. For an absorption window of e.g. 200 nm, the optimal bandgap is 1.9 eV, which is a realistic value for current organic absorbers.

If we consider the case where not one, but both the *n*- and *p*-type material absorb light, all photons with an energy higher than $E_{g,n}$ or $E_{g,p}$ will ideally be absorbed. Every absorbed photon still leads to a useful energy $E_{g,i}$. Therefore, the maximum efficiency η_{max} is given by:

$$\eta_{\max} = \frac{E_{g,i} \int\limits_{\min(E_{g,p},E_{g,n})}^{\infty} N(E)\,dE}{\int\limits_{0}^{\infty} E\,N(E)\,dE} \qquad (2)$$

In this case, two regions are present. In the region where $E_{g,p}$ is the smallest of the bandgaps, the efficiency is the same as the case with only one material absorbing. In the region where $E_{g,n}$ is the smallest, the efficiency is now higher, because the *n*-material absorbs photons that the *p*-material could not absorb. Summarized, when both materials absorb light, the highest maximum attainable efficiency reached is the same as in the case where only one material absorbs light, but higher efficiencies are reached for materials which have not optimal energy levels. In the continuation of this article, we will only consider one material (the *p*-type material) as the absorber.

In organic bulk heterojunction solar cells, light absorption does not lead immediately to free charge carriers, but an exciton is created. In the ideal scenario, the highest efficiency was reached when the LUMO of the *p*-material is as close as possible to the LUMO of the *n*-material. However, a necessary condition for efficient dissociation of the created excitons is that the difference between the LUMO's of the donor and acceptor is higher than the exciton binding energy. Thus, without a sufficient energy difference between the LUMO's of both materials, the solar cell can not work. The value of the exciton binding energy in different materials is a subject of discussion, values between 0.1 eV and 2 eV are published [9]. The surplus of this necessary minimum of the LUMO-difference corresponds with an energy loss. The optimum efficiency decreases for increasing LUMO-differences. With a full absorption window, each additional difference of 0.1 eV between the LUMO's results approximately in an additional 10 % relative efficiency loss in the maximum attainable efficiency. We now assume for the organic solar cell a difference of 0.2 eV between the LUMO's. This value was put forward as an empirical threshold necessary for exciton dissociation [10].

To estimate the maximum obtainable efficiency in a less ideal situation, we assume two scenarios. In the first scenario, we assume the following realistic values, which are with the current state of technology nowadays reached in organic photovoltaics. We assume an absorption window of 200 nm (Fig. 1(b)), a quantum efficiency *QE* of 70 %, a fill factor *FF* of 60 %, and a voltage factor *f*:

$$f = \frac{q \cdot V_{oc}}{E_{g,i}} \qquad (3)$$

of 60 %, with V_{oc} the open circuit voltage and q the elementary charge. This results in a maximum attainable efficiency of 5.8 % for organic bulk heterojunction solar cells. In the second scenario, we consider optimistic values, which are credible to be achieved in the future (i.e. an absorption window of 400 nm (Fig. 1(b)), *QE*=90 %, *FF*=70 %, *f*=70 %). Then, an efficiency of 15.2 % becomes possible. Notice that in the last case, a bandgap of 1.5 eV is sufficient (see Table 1 for an overview).

Fig. 3 shows how the optimum efficiency decreases for increasing LUMO-differences for different absorption windows (with the values of the optimistic scenario). The ideal bandgap of the absorber for each absorption window is given for no LUMO-difference, and for a LUMO-difference of 0.5 eV. Notice that the LUMO-difference can vary this ideal bandgap. For example, until a difference of 0.1 eV between the LUMO's, the optimum bandgap of the absorber material for an absorption window of 400 nm is 1.5 eV. When the LUMO-difference is 0.2 eV or higher, the optimal bandgap rises to 1.6 eV.

The result that an efficiency of 15.2 % is within reach indicates that organic cells have the potential for improving their efficiencies, which is a necessity for future commercial applications. However, one should focus on developing material combinations with the LUMO-difference between donor and acceptor as small as possible, but with still sufficient exciton dissociation.

III ORGANIC TANDEM SOLAR CELL

The power conversion efficiency can be significantly increased by using several solar cells with different bandgaps in a row, called tandem solar cells. We consider a tandem solar cell, consisting of two single organic photovoltaic cells (Fig. 1(c)). In each single cell, only one material (the *p*-material) absorbs the light. The organic cell with the highest absorber bandgap is in front (side of the sun), thus $E_{g1} > E_{g2}$. We make analogous fundamental assumptions as for the single cell: (i) every photon with an energy $h\nu$ higher than the bandgap E_{g1} is absorbed by the first cell, and leads to a useful energy E_{i1}. (ii) every photon with an energy $h\nu$ between E_{g1} and E_{g2} is absorbed by the second cell, and leads to a useful energy E_{i2}. (iii) photons with an energy $h\nu$ lower than E_{g2} are fully transmitted. The maximum efficiency η_{max} is therefore given by:

$$\eta_{\max} = \frac{E_{i1}\int_{E_{g1}}^{\infty} N(E)\,dE + E_{i2}\int_{E_{g2}}^{E_{g1}} N(E)\,dE}{\int_{0}^{\infty} E\,N(E)\,dE}, \quad with \;\; E_{g,1} > E_{g,2} \qquad (4)$$

Compare η_{max} with equation (1), and notice that now a second term is added, representing the second cell. Notice that when $E_{i1} = E_{i2}$, the efficiency η_{max} is the same as a single cell with bandgap E_{g2}.

Experimental and commercial tandem solar cells are usually of the monolithic or integrated type. This means that they are not only optically in series, but also electrically in series. With the assumptions we made, the tandem solar cell we consider is not electrically connected, and is thus only optically in series. A tandem cell of the monolithic type will never reach a higher efficiency as the one we consider, because both single cells can't operate at the same time at their optimal working point.

The optimum efficiency of 65.4 % in this ideal scenario is reached with a configuration of E_{g1} = 1.54 eV and E_{g2} = 0.71 eV. The requirements for an almost optimal configuration are quite broad, permitting that the values of the bandgaps for optimal cells are not that strict. Comparing with the single junction, adding a second cell results in a relative gain of about 1/3 in power conversion efficiency.

We now take into account the narrow absorption window which is characteristic for organic materials. For the ease of presentation, we suppose that both single cells of the tandem structure have the same absorption window in nm.. As it did for a single cell, the optimum bandgap of the cells shifts towards higher energies for lower absorption windows (Fig. 4). For example, the optimum bandgap shifts from E_{g1} = 1.54 eV and E_{g2} = 0.71 eV for a full absorption band cell to E_{g1} = 2.07 eV and E_{g2} = 1.55 eV for a with an absorption window of 200 nm.

This is a satisfying result, because, as we already mentioned, the production of suitable low bandgap organic materials is difficult. For an absorption window of respectively 400 and 500 nm, already 95 % and 98 % of the maximum attainable efficiency (for a full absorption band) is reached (Fig. 4). Therefore, it would not be worth to try to develop organic materials with an absorption window greater than 400 nm, because hardly any efficiency gain can be achieved by a bigger absorption window. The optimum bandgaps with a sufficient absorption window of 400 nm are E_{g1} = 1.7 eV and E_{g2} = 1.1 eV. Especially the second bandgap is fortunately much higher than the ideal low bandgap 0.7 eV with a full absorption band.

Fig. 4 shows that the optimum bandgap decreases when the absorption window increases. However, for 600 and 700 nm, we notice that the optimal bandgap E_{g1} of the first cell increases again. This is because of the shape of the solar spectrum. The pits in the solar spectrum (caused by absorption by gases in the atmosphere) cause the optimal bandgap to increase a little bit with higher absorption windows. If one considers a smooth approximation of the solar spectrum, the optimal bandgap E_{g1} also decreases for absorption windows of 600 nm and higher.

In Fig. 5 the maximum efficiency η_{max} for a tandem cell with bandgaps E_{g1} and E_{g2} is plotted for the situation where E_{i1} is higher than E_{i2}. The higher E_{g2}, the lower the efficiency, because less photons are being absorbed by the second cell. The higher the bandgap of the first cell E_{g1}, the less photons are absorbed by the first cell. However, with a constant E_{g2}, the higher E_{g1}, more photons are absorbed by the second cell. This means that the higher E_{g1}, the lower the efficiency when $E_{i1} > E_{i2}$, and vice versa when $E_{i1} < E_{i2}$. When $E_{i1} < E_{i2}$, the more photons are absorbed by the second cell, the higher the efficiency, meaning that a first front cell is useless in this case. We can conclude that for a tandem cell, the interface bandgap E_{i1} of the first cell has to be bigger than the interface bandgap E_{i2} of the second cell.

The highest efficiency is again (as for the single junction cell) reached when the LUMO's of both the *p*-materials are as close as possible to the LUMO's of their neighbouring *n*-materials. Again, a sufficiently high difference between the LUMO's of each single cell is necessary for the exciton dissociation. Fig. 6 plots the maximum efficiency in the ideal scenario as a function of the LUMO-difference for different absorption windows (we consider that both single cells of the tandem structure have the same LUMO energy difference and absorption window). With a full absorption window, each additional difference of 0.1 eV between the LUMO's results approximately in an additional 10 % relative efficiency loss in the maximum attainable efficiency. We again assume for the organic solar cell a difference of 0.2 eV between the LUMO's. Only because of this necessary energy difference between the LUMO's, the attainable efficiency for the organic bulk heterojunction tandem solar cell drops

17 % relative in comparison with their inorganic counterpart, purely because of the difficult exciton dissociation.

To estimate the maximum obtainable efficiency in a less ideal situation, we again assume the two scenarios, where we consider that both single cells of the tandem structure have the same *QE*, *FF* and *f*. In the first scenario, with the realistic values, a maximum attainable efficiency of 10.1 % is reached. In the second scenario, with optimistic values which are credible to be achieved in the future, the 20 % threshold is breached with a maximum efficiency of 23.2 % (see Table 1 for an overview).

IV CONCLUSIONS

For a single junction cell, the optimum bandgap of the absorber in an ideal scenario is 1.1 eV, but when taking into account the narrow absorption window of organic materials, this optimum shift to higher values which are in line with current organic absorbers. The highest efficiency is reached when the LUMO of the *n*-material is as close as possible to the LUMO of the *p*-material. However, when considering the empirical threshold of 0.2 eV between the LUMO's, necessary for exciton dissociation, the organic cell loses immediately 18 % relative. In the realistic scenario, with values which are with the current state of technology nowadays reached in organic photovoltaics, a maximum attainable efficiency of 5.8 % is possible. When we consider the optimistic values, which are credible to be achieved in the future, an organic solar cell of 15.2 % is in reach, with an optimal bandgap of 1.5 eV for the absorber. When both *n*- and *p*-materials absorb light, the highest maximum attainable efficiency reached is the same as in the case where only one material absorbs light, but higher efficiencies are reached for materials which have not optimal energy levels. These results indicates that organic bulk heterojunction cells have the efficiency potential of more than 10 %, which is desirable for future commercial applications. However, one should focus on developing material combinations with the LUMO-difference between donor and acceptor as small as possible, but with still sufficient exciton dissociation.

For a tandem solar cell, a maximum efficiency of 65.4 % is possible in the ideal scenario with a configuration of E_{g1} = 1.54 eV and E_{g2} = 0.71 eV. Comparing with the single junction optimum, adding a second cell results in a relative gain of 1/3 in efficiency. However, an absorption window of 400 nm is sufficiently, and then the optimum bandgaps shift to higher values: E_{g1} = 1.7 eV and E_{g2} = 1.1 eV. The highest efficiency is again reached when the LUMO's of both the *p*-materials are as close as possible to the LUMO's of their neighbouring *n*-materials. When considering a LUMO-difference of 0.2 eV, necessary for exciton dissociation, the cell loses 17 % relative in efficiency. For a tandem structure, it was proven that is necessary that the interface bandgap E_{i1} of the first cell is bigger than the interface bandgap E_{i2} of the second cell. In the realistic scenario, a maximum attainable efficiency of 10.1 % is possible with a tandem structure. When we consider the optimistic scenario, a maximum efficiency of 23.2 % can be obtained.

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Table 1

	Single junction		**Tandem junction**		
	η (%)	E_g (eV)	η(%)	E_{g1} (eV)	E_{g2} (eV)
Ideal scenario	39.7	1.1	54.0	1.7	0.9
Present: realistic scenario	5.8	1.9	10.1	2.0	1.5
Future: optimistic scenario	15.2	1.6	23.2	1.7	1.1

Table 1: Optimal efficiency values in the ideal, realistic and optimistic scenarios for a single junction and tandem junction solar cell. Also the optimum bandgap of the absorber material is given. A LUMO difference of 0.2 eV between donor and acceptor was always been taken into account.

Figure 1

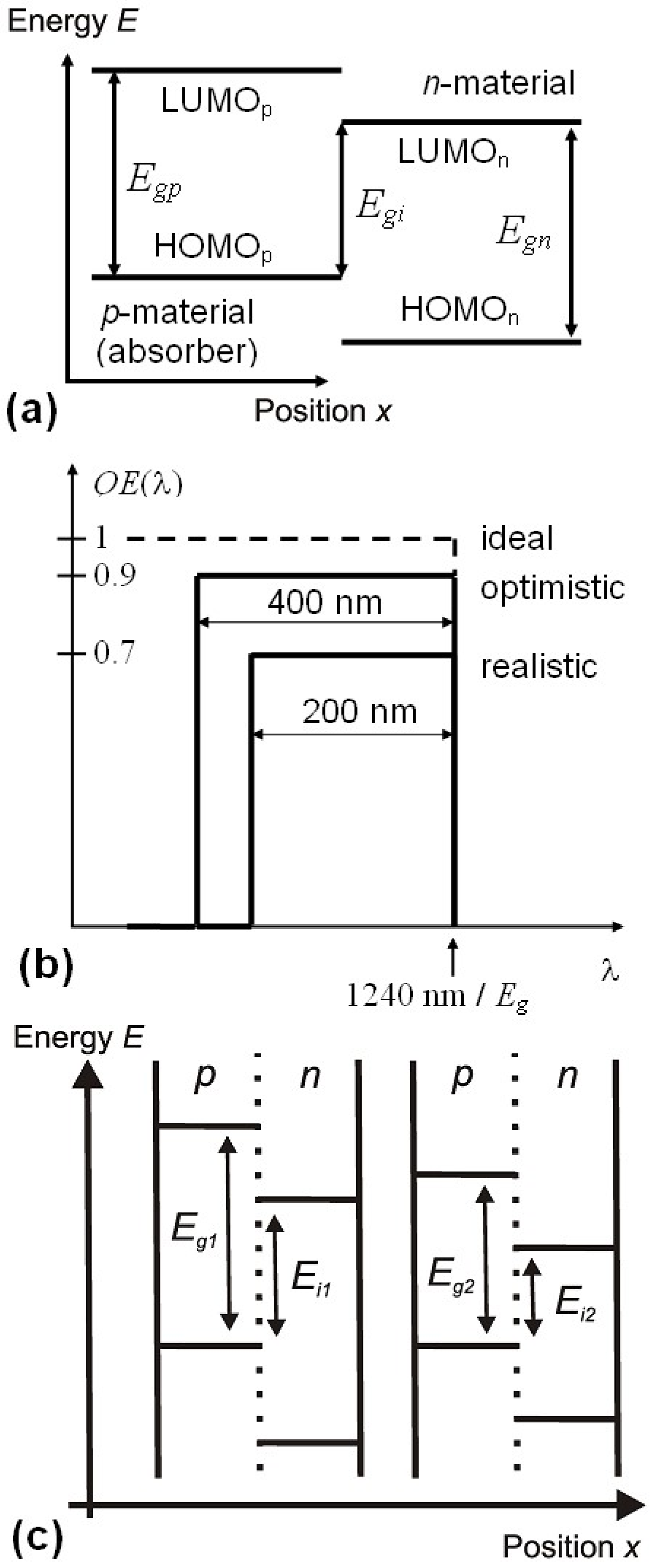
Energy E
LUMO_p
E_{gp}
HOMO_p
p-material
(absorber)
n-material
LUMO_n
E_{gi}
E_{gn}
HOMO_n
(a)
Position x
$OE(\lambda)$
1
0.9
0.7
ideal
optimistic
realistic
400 nm
200 nm
(b)
λ
1240 nm / E_g
Energy E
p
n
p
n
E_{g1}
E_{i1}
E_{g2}
E_{i2}
(c)
Position x

Figure 1: (a) The schematic energy band diagram of a bulk heterojunction single junction organic solar cell with definition of terms: donor and acceptor material, absorber, HOMO and LUMO levels. The HOMO of the *n*-type component is taken as a reference ($HOMO_n$ = 0 eV). (b) Definition of terms: absorption window; ideal (full absorption window), optimistic and realistic scenario for absorption and quantum efficiency *QE*. The cut-off wavelength λ_g corresponds with the bandgap E_g. (c) The schematic energy band diagram of a bulk heterojunction organic tandem solar cell. Only the *p*-material is the absorber. The mutual position of the single cells does not matter, because the cells are only optically and not electrically in series.

Figure 2

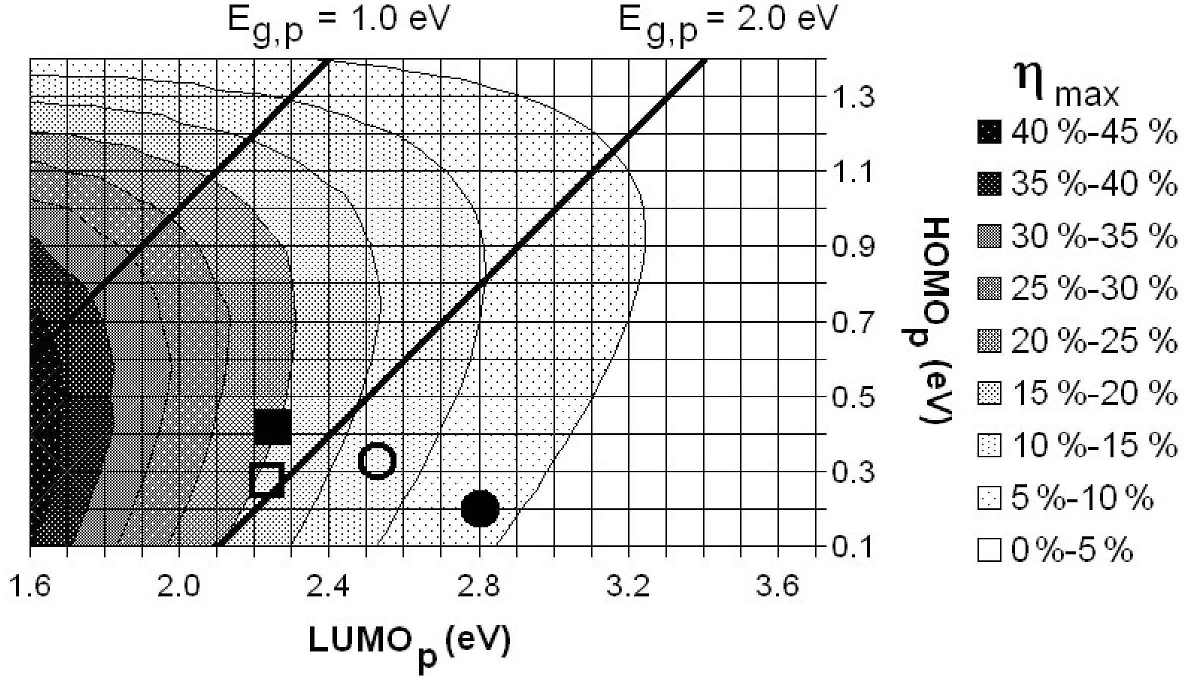

Figure 2: The maximum efficiency η_{max} in the ideal scenario is plotted as a function of the LUMO and the HOMO of the *p*-type material for the case where the *p*-material absorbs the light, and the *n*-type has a bandgap of 1.5 eV (e.g. PCBM). The HOMO of the *n*-material is taken as a reference ($HOMO_n$ = 0 eV). The straight lines indicate where the bandgap of the *p*-material is 1.0 eV, 2.0 eV. The position of bulk heterojunction cells with PTV (■), P3HT (□), MEH-PPV (○), and MDMO-PPV (●) as *p*-material and PCBM as *n*-material is given.

Figure 3

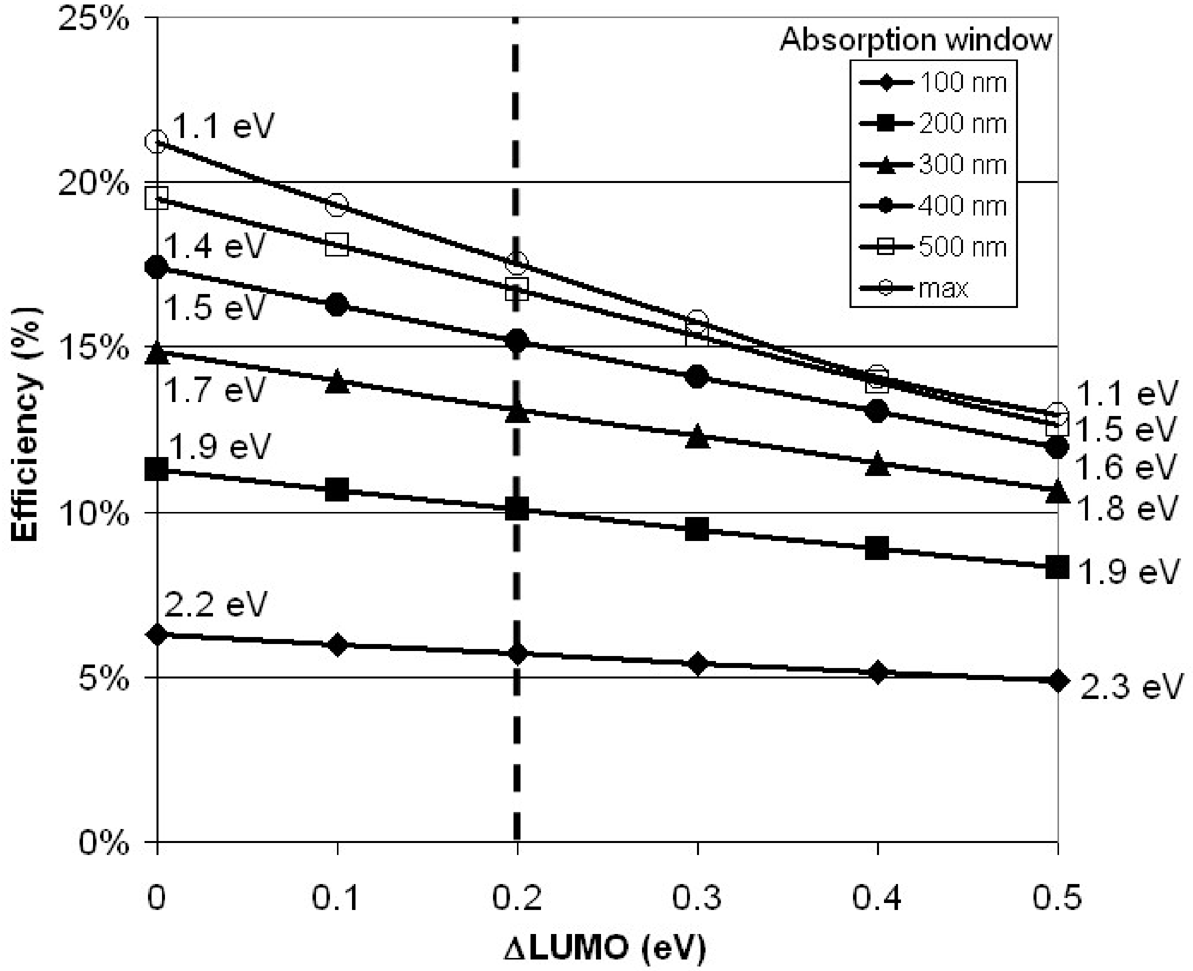

Figure 3: The maximum efficiency η_{max} in the optimistic scenario as a function of the difference between the LUMO's of the *p*- and *n*-material, necessary for exciton dissociation, for different absorption windows. The ideal bandgap of the absorber for each absorption window is given for a LUMO-difference of 0 eV and 0.5 eV. The dotted line indicates the empirical threshold of 0.2 eV.

Figure 4

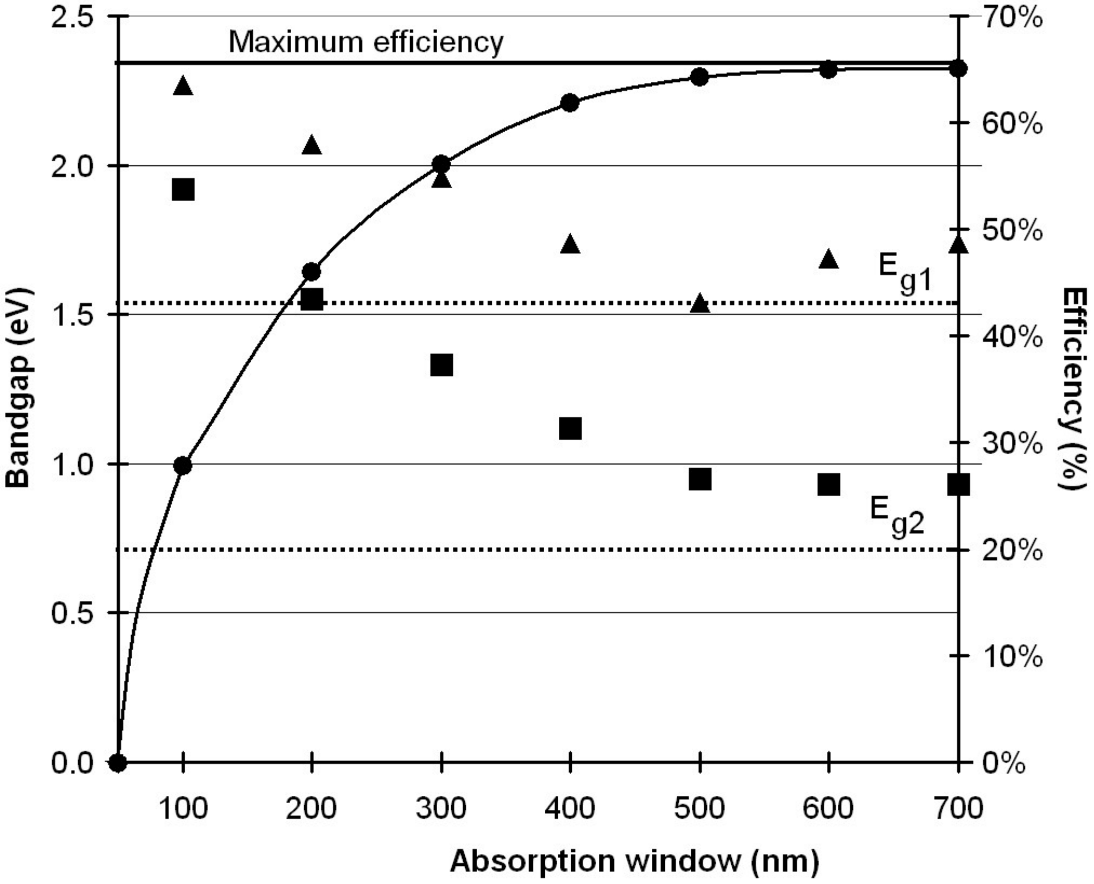

Figure 4: The maximum efficiency η_{max} (●) is plotted in the ideal scenario for a tandem cell as a function of the absorption window. The full line indicates the maximum obtainable efficiency with a full absorption window. Notice that for an absorption window of respectively 400 and 500 nm, already 95 % and 98 % of the maximum attainable efficiency is reached. Also the optimum bandgap E_{g1} (▲) and E_{g2} (■) are plotted as a function of the absorption window. The dotted lines indicate the optimum bandgaps of E_{g1} and E_{g2} with a full absorption window.

Figure 5

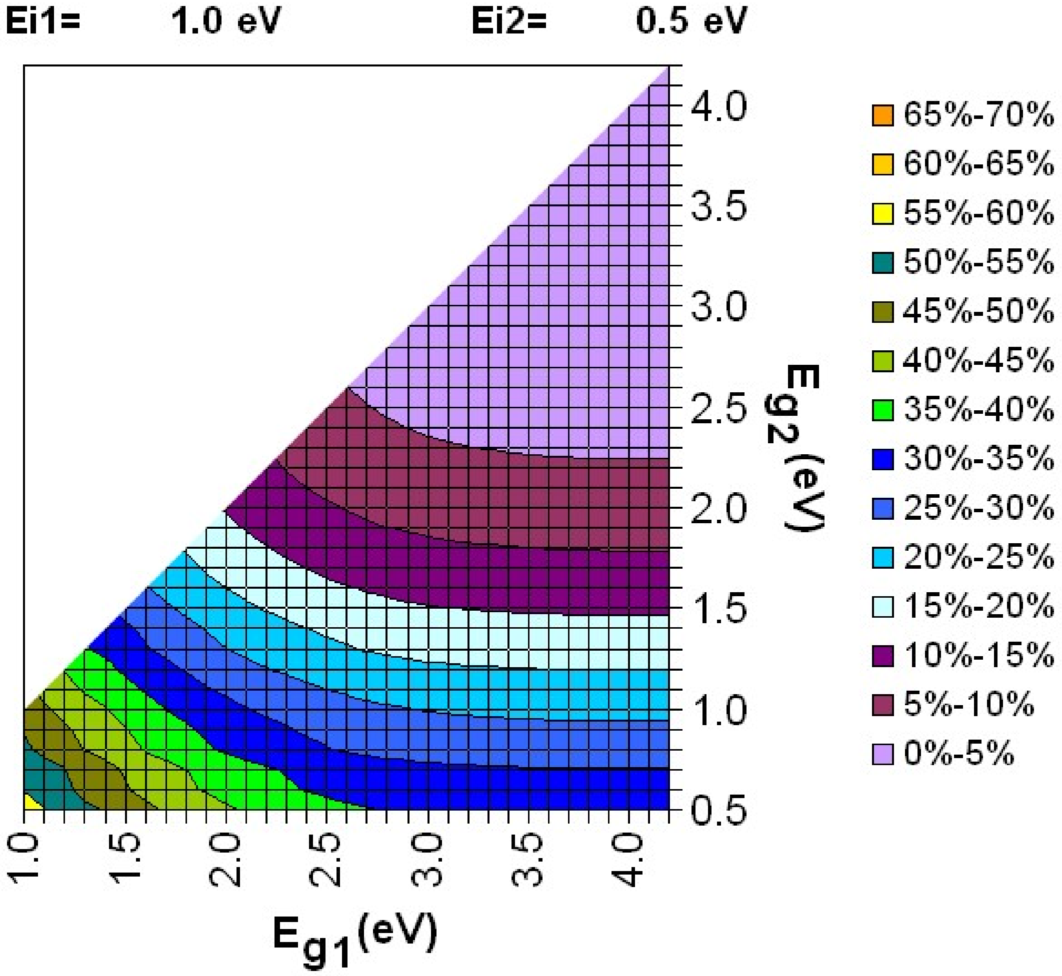

Figure 5: The maximum efficiency η_{max} in the ideal scenario for a tandem cell with bandgaps E_{g1} and E_{g2}, and interface bandgaps E_{i1} = 1.0 eV and E_{i2} = 0.5 eV.

Figure 6

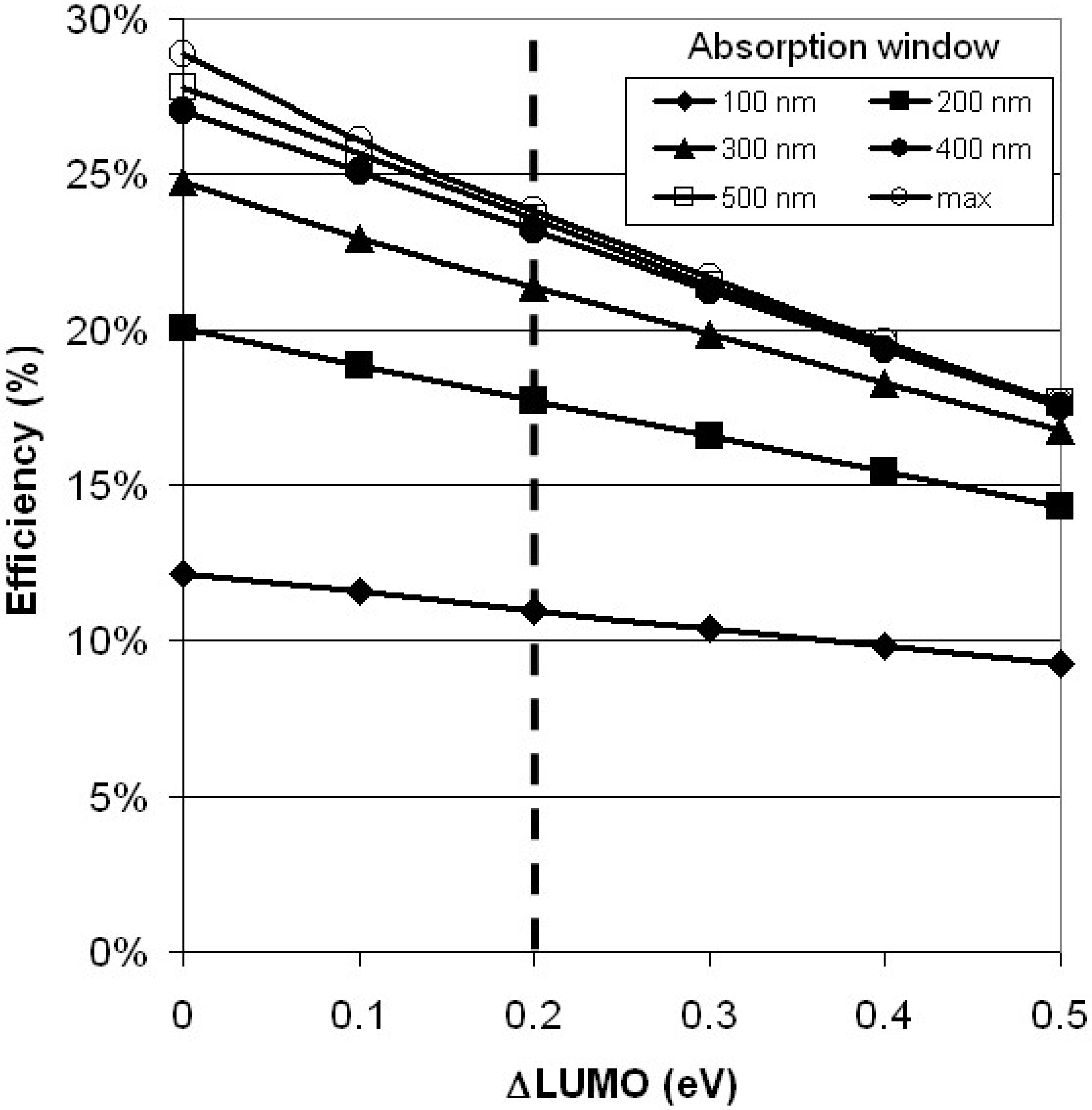

Figure 6: The maximum efficiency η_{max} in the optimistic scenario as a function of the LUMO-difference for different absorption windows. The dotted line indicate the empirical threshold of 0.2 eV.