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Article

The theoretical influence of the difference between the LUMO energy levels of donor and acceptor in organic photovoltaic triple-junction solar cells

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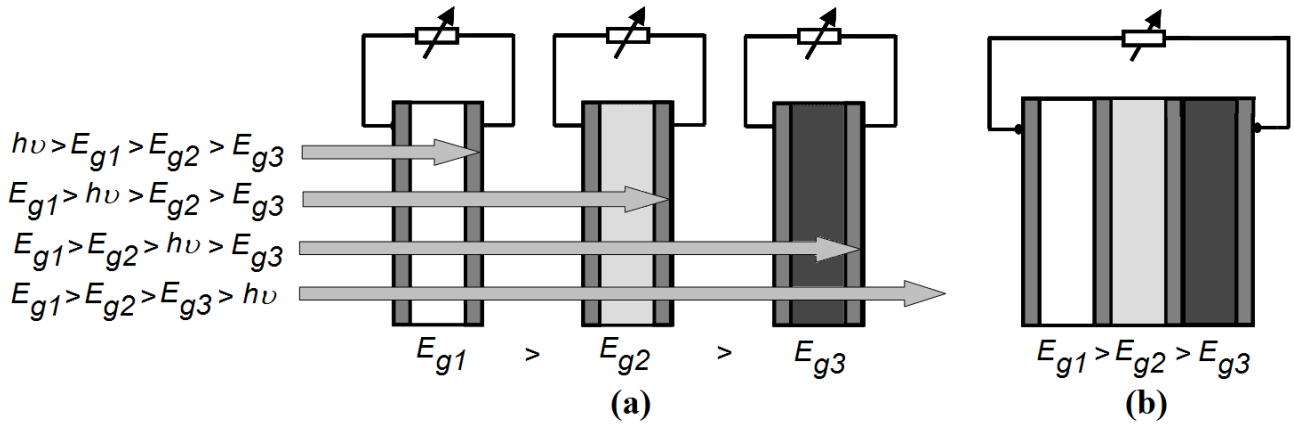
Abstract: In organic photovoltaic solar cells, light absorption does not immediately lead to free charge carriers. Instead, an exciton is created. The highest efficiency is reached when the lowest unoccupied molecular orbital (LUMO) of the donor is as close as possible to the LUMO of the acceptor. However, a necessary condition for efficient dissociation of the created excitons is that the difference between the LUMOs of donor and acceptor is higher than the exciton binding energy. The value of the exciton binding energy in different materials is a subject of discussion. The excess of this necessary minimum of the LUMO-difference corresponds with an energy loss. Moreover, it is often not possible to optimize suitable material combinations for organic photovoltaic cells to an ideal (low) LUMO difference. Another energy loss in organic solar cells is caused by their narrow absorption windows, compared to the absorption band of inorganic solar cells. A way to capture a wider band of the solar radiation is using more solar cells with different bandgaps in a row. In this article, we study three organic cells in a row, i.e. a triple-junction. More specifically, we study the theoretical influence of the difference between the LUMO energy levels of donor and acceptor for an organic triple-junction solar cell. We study as well the monolithic as the stacked configuration.

Keywords: solar cells; photovoltaic energy; triple-junction; organic solar cells; multi-junction; simulation; energy levels; lowest unoccupied molecular orbital; LUMO

1. Introduction

A characteristic of organic solar cells is their narrow absorption window, compared to the absorption band of inorganic semiconductors [1]. A possible way to capture a wider band of the solar spectrum - and thus increasing the power conversion efficiency - is using more solar cells with different bandgaps in a row, referred to as a multi-junction solar cell. In this article, we will focus on triple-junction solar cells, i.e. three cells in a row. The absorber of the first single solar cell in such a triple-junction cell has a large bandgap E_{g1}. High-energy photons with an energy $h\nu > E_{g1}$ are absorbed by the first cell. The second cell, with a lower bandgap E_{g2}, absorbs the middle-energy photons with energy between E_{g1} and E_{g2}. The third cell absorbs the low-energy photons between E_{g2} and E_{g3} (Figure 1). In this configuration, the photon energy is used more efficiently: the voltage at which electrical charge is collected in each subcell is closer to the energy of the photons absorbed in that subcell.

Figure 1. (a) A stacked or 6-terminal triple-junction solar cell: the first single cell absorbs photons with energy higher than E_{g1}. The second and third cell absorb photons with energy between E_{g1} and E_{g2}, respectively, E_{g2} and E_{g3}. Photons with energy below E_{g3} are not absorbed. The three subcells are electrically separated. **(b)** A monolithic or 2-terminal triple-junction solar cell: the single cells are electrically connected in series.



In the ideal configuration, the subcells are electrically separated. This is called the stacked or 6-terminal configuration (Figure 1a). However, experimental and commercial multi-junction solar cells are usually of the monolithic type (Figure 1b). This means that they are not only optically in series, but also electrically in series. This configuration will never reach an efficiency that is higher than that of a stacked (6-terminal) triple-junction cell, because all single cells cannot be operating at their optimal working point at the same time (unless they have an equal maximum-power current).

2. Assumptions

The active material in a single organic bulk heterojunction solar cell consists of an interpenetrating network of an electron acceptor (e.g. fullerene derivatives) and an electron donor (e.g. conjugated polymers), sandwiched between two electrodes with different work functions. The optical bandgap E_g

is defined as the difference between the lowest u noccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the absorber material.

We consider a 6-terminal triple-junction solar cell, consisting of three single organic cells. We assume that in each single cell, only one material absorbs light. Usually, most of the light is absorbed by the donor; this is the case we will consider here onwards. Because we assume full absorption in each subcell, we neglect interference and optical coupling of the subcells, thus overestimating the efficiency potential. The organic cell with the widest absorber bandgap is at top (at the side of the sun), thus $E_{g1} > E_{g2} > E_{g3}$. The distance between the HOMO of the donor and the LUMO of acceptor is considered as the thermodynamic limitation of the useful energy [2]. We call this value the interface bandgap E_i. For an organic solar cell with ohmic contacts, the open circuit voltage V_{oc} is linearly dependent on the interface bandgap E_i. For a cell with non-ohmic contacts, the V_{oc} is dependent on the work function difference of the electrodes. In these calculations, we assume a cell with ohmic contacts.

For our simulation, the following fundamental assumptions are made about the stacked triple-junction cell (Figure 1a): (i) every photon with energy $h\nu$ higher than the bandgap E_{g1} is absorbed by the first cell and leads to a useful energy E_{i1}. This assumption implies that each absorbed photon eventually leads to a free electron and a free hole, with an energy difference of E_{i1} between them. (ii) every photon with energy $h\nu$ between E_{g1} and E_{g2} is absorbed by the second cell and leads to a useful energy E_{i2}. (iii) every photon with energy $h\nu$ between E_{g2} and E_{g3} is absorbed by the third cell and leads to a useful energy E_{i3}. (iii) photons with energy $h\nu$ lower than E_{g3} are fully transmitted. The maximum efficiency η_{max} is therefore given by:

$$\eta_{\max} = \frac{E_{i1}\int_{E_{g1}}^{\infty} N(E)\,dE + E_{i2}\int_{E_{g2}}^{E_{g1}} N(E)\,dE + E_{i3}\int_{E_{g3}}^{E_{g2}} N(E)\,dE}{\int_{0}^{\infty} E\,N(E)\,dE}, \quad with \;\; E_{g1} > E_{g2} > E_{g3} \qquad (1)$$

with $N(E)$ the incident photon flux. For all our simulations, we use the AM 1.5 experimentally measured solar spectrum [3]. In this ideal scenario, the open circuit voltage V_{oc} of the subcells will be given by E_{ij}/q (j=1,2,3) with q the electric charge. The fill factor FF of the subcells is assumed to equal unity, as well as the external quantum efficiency EQE of the first cell for wavelengths below the cut-off wavelength λ_{g1} (corresponding with E_{g1}). Similar conditions apply to the second and third cell.

In a monolithic triple-junction solar cell (Figure 1b), the individual cells are electrically connected in series. This means that the total voltage over the cell is the sum of the voltages over each individual cell, and thus equals the sum of the interface bandgaps of the single cells. Furthermore, the same current flows through all single cells. Hence, the maximum efficiency η_{max} for a monolithic organic triple-junction cell is given by:

$$\eta_{\max} = \frac{(E_{i1}+E_{i2}+E_{i3})\cdot \min\left(\int_{E_{g1}}^{\infty} N(E)\,dE, \int_{E_{g2}}^{E_{g1}} N(E)\,dE, \int_{E_{g3}}^{E_{g2}} N(E)\,dE\right)}{\int_{0}^{\infty} E\,N(E)\,dE}, \quad with \;\; E_{g1} > E_{g2} > E_{g3} \qquad (2)$$

with min(x,y,z) the minimum of x, y and z. The open circuit voltage V_{oc} of the whole monolithic cell will be given by ($E_{i1}+E_{i2}+E_{i3}$)/q, the fill factor FF equals unity, as does the external quantum efficiency EQE for wavelengths below the cut-off wavelength.

In organic bulk heterojunction solar cells, light absorption does not immediately lead to free charge carriers. Instead, an exciton is created. In an ideal scenario, the highest efficiency is reached when the LUMO of the donor is as close as possible to the LUMO of the acceptor. However, a necessary condition for efficient dissociation of the created excitons is that the difference between the LUMOs of donor and acceptor (ΔLUMO) is higher than the exciton binding energy [4]. The value of the exciton binding energy (and the minimal ΔLUMO) in different materials is a subject of discussion, but a value of 0.3 eV was put forward as an empirical threshold necessary for exciton dissociation [5]. The excess of this necessary minimum of the LUMO-difference corresponds with an energy loss.

In the next section, we calculate the theoretical influence of the difference between the LUMO energy levels of donor and acceptor for an organic stacked and monolithic triple-junction solar cell. The absolute value of the maximum efficiency is only relevant for academic purposes. It is the relative difference between the efficiencies that is important in quantifying the influence of the LUMO differences.

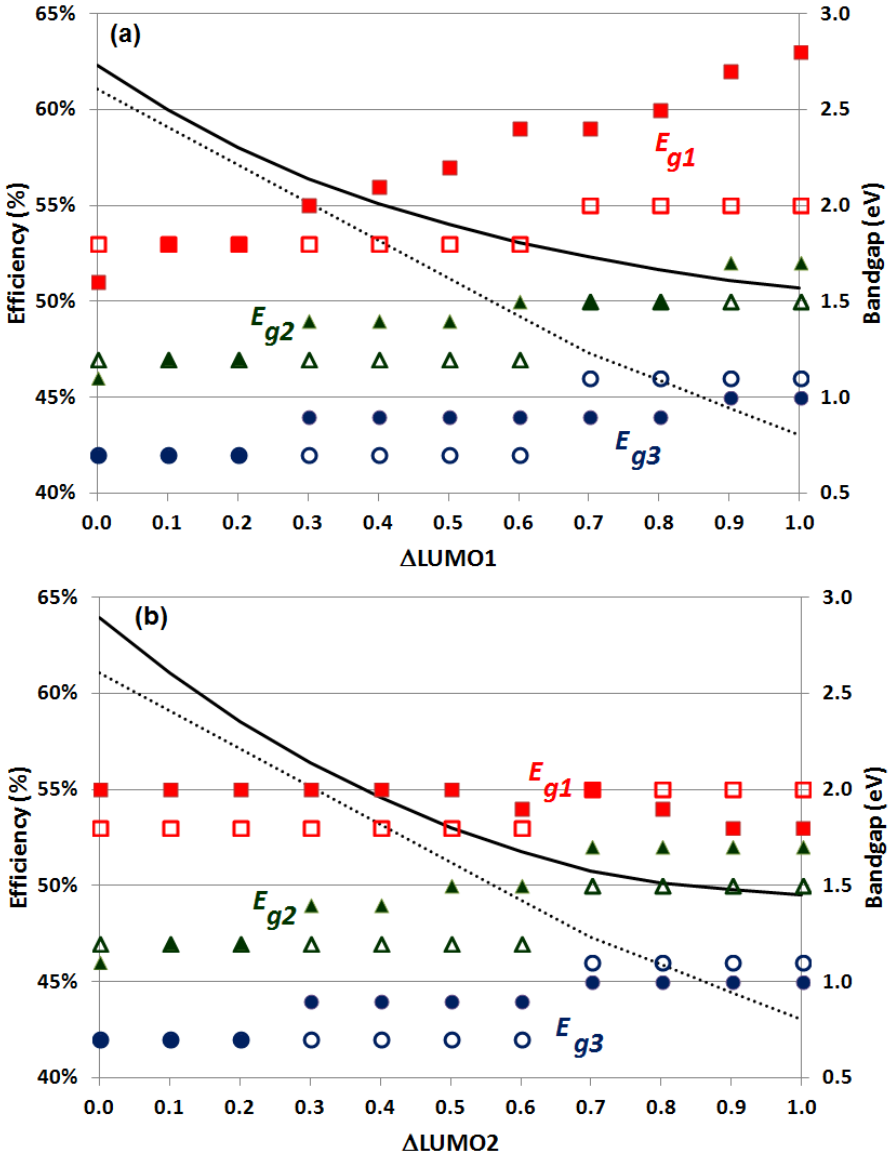
3. Results

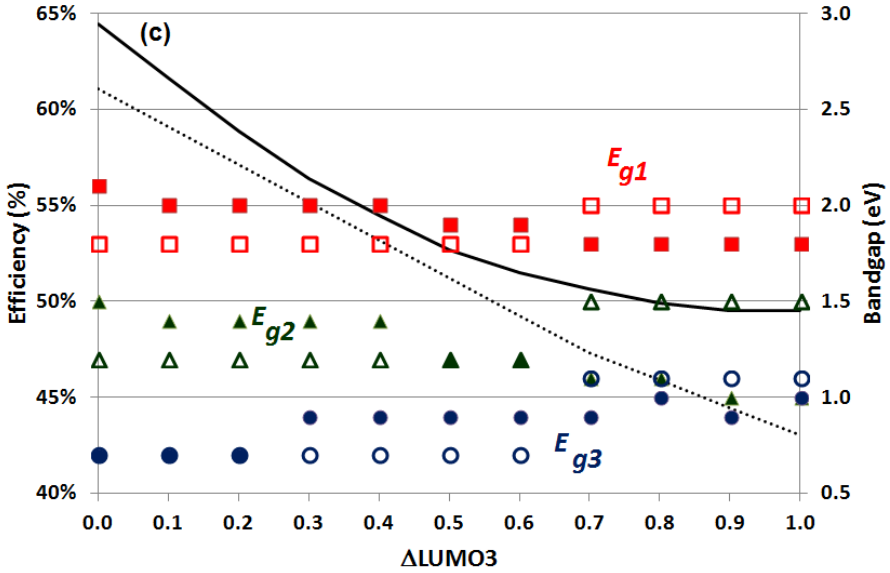
To study the influence of ΔLUMO, we calculate the maximum efficiency in this ideal scenario by changing this parameter, and determine for each ΔLUMO the optimal bandgaps for the different subcells. First, we only change $\Delta LUMO_1$ (the ΔLUMO of the first subcell) and keep $\Delta LUMO_2$ and $\Delta LUMO_3$ constant at 0.3 eV (the empirical threshold necessary for exciton dissociation). If there is no energy difference between the LUMOs of the first subcell, the maximum efficiency reaches 62% and 61% for a stacked and monolithic configuration respectively (Figure 2a). The efficiency at $\Delta LUMO_1$ = 0.3 eV, the minimum threshold for exciton dissociation, is 56% and 55% respectively, a decrease of 10% relative compared to no LUMO difference. The efficiency decreases 1 to 3% relative per 0.1 eV. This relative decrease is higher for lower values of $\Delta LUMO_1$. The optimal bandgap E_{g1} increases with increasing $\Delta LUMO_1$ for both the stacked and the monolithic configuration. The higher the LUMO difference, the smaller the part of the incoming spectrum that is being absorbed. This reduces the relative decrease per 0.1 eV. The optimum of all three bandgaps increase with higher $\Delta LUMO_1$. This was to be expected. Indeed, a high $\Delta LUMO_1$ of the first subcell will lower significantly the useful energy of the absorbed photons in this first subcell. This is compensated by increasing E_{g1}. As a result, a broader part of the solar spectrum is transmitted to the other two subcells, leading to a rearrangement of the optimal bandgaps of those subcells to higher values. The maximum efficiency will never decrease below 49.5%, because this is the efficiency of a tandem cell (i.e. a multi-junction with two subcells) where both ΔLUMOs are 0.3 eV. The bandgap of the first solar cell will then be that big that it will no longer absorb any photons and the triple-junction will act as a tandem cell.

We now consider the influence of $\Delta LUMO_2$ (with $\Delta LUMO_1 = \Delta LUMO_3 = 0.3$ eV). The efficiency drops from 64% / 61% at 0 eV to 56% / 55% for 0.3 eV and 50% / 43% for 1.0 eV for the stacked / monolithic configuration respectively (Figure 2b). We notice a sharp decline in the beginning which decreases for higher $\Delta LUMO_2$ values. The explanation is analogous as for $\Delta LUMO_1$. For higher

$\Delta LUMO_2$ values, this decrease diminishes fast. Analogous conclusions as for $\Delta LUMO_1$ can be drawn for the optimal bandgaps: the ideal bandgap of the second subcell increases with higher $\Delta LUMO_2$ values to compensate for the energy loss caused by the LUMO difference. As a result, the optimal bandgap of the first subcell decreases whereas E_{g3} increases. This reduces the influence of the second (less efficient) subcell. At high $\Delta LUMO_2$ values, the optimal values of E_{g1} and E_{g2} coincide, reducing the triple junction to a tandem cell. Analogous conclusions can be drawn for $\Delta LUMO_3$ (Figure 2c).

Figure 2. (left axis) The maximum efficiency for a stacked (solid line) and monolithic (dashed line) triple-junction solar cell as function of **(a)** $\Delta LUMO_1$, **(b)** $\Delta LUMO_2$ and **(c)** $\Delta LUMO_3$. **(right axis)** The optimal bandgaps of the three subcells as function of **(a)** $\Delta LUMO_1$, **(b)** $\Delta LUMO_2$ and **(c)** $\Delta LUMO_3$ for a stacked (filled symbols) and monolithic (open symbols) triple-junction solar cell.





4. Conclusions

The most important conclusion from this study is that a high ΔLUMO for one subcell is not detrimental for the efficiency of an organic triple-junction solar cell. It is even often better to combine two subcells with low ΔLUMOs with one subcell with a high ΔLUMO, than combining three subcells with average ΔLUMOs. This conclusion follows from the increasingly smaller decrease in efficiency with increasing ΔLUMOs.

Conflicts of Interest

The authors declare no conflict of interest.

References and Notes

1. Winder, C.; Sariciftci, N.S., Low bandgap polymers for photon harvesting in bulk heterojunction solar cells. *J. Mater. Chem.* **2004**, *14*, 1077-1086.
2. Dennler, G.; Sariciftci, N.S., Flexible conjugated polymer-based plastic solar cells: From basics to applications. *Proc. IEEE*. **2005**, *93*, 1429-1439.
3. International Standard, IEC 60904–3, Edition 2, April 2008, Photovoltaic devices - Part 3 : measurement principles for terrestrial photovoltaic (PV) solar devices with reference spectral irradiance data, ISBN 2–8318– 9705-X, International Electrotechnical Commission (2008).
4. Sun, S-S.; Optimal energy offsets for organic solar cells containing a donor/acceptor pair. *Sol. Energy Mater. Solar Cells* **2005**, *85*, 261-267.
5. Scharber, M.C.; Mühlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A.J.; Brabec, C.J., Design rules for donors in bulk -heterojunction solar cells - Towards 10% energy -conversion efficiency. *Adv. Mat.* **2006**, *18*, 789-794.