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 unoccupied 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 \( \eta_{max} \) is therefore given by:

\[
\eta_{max} = \frac{\int_{E_{g1}}^{E_{i1}} N(E)dE + \int_{E_{g2}}^{E_{i2}} N(E)dE + \int_{E_{g3}}^{E_{i3}} N(E)dE}{\int_0^\infty E N(E)dE}, \quad \text{with } E_{g1} > E_{g2} > E_{g3}
\]

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 cutoff wavelength \( \lambda_{g1} \) (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 \( \eta_{max} \) for a monolithic organic triple-junction cell is given by:

\[
\eta_{max} = \frac{(E_{i1} + E_{i2} + E_{i3}) \cdot \min\left(\int_{E_{g1}}^{E_{i1}} N(E)dE, \int_{E_{g2}}^{E_{i2}} N(E)dE, \int_{E_{g3}}^{E_{i3}} N(E)dE\right)}{\int_0^\infty E N(E)dE}, \quad \text{with } E_{g1} > E_{g2} > E_{g3}
\]
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 \( \frac{E_i + E_{i2} + E_{i3}}{q} \), 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 (\( \Delta \text{LUMO} \)) is higher than the exciton binding energy [4]. The value of the exciton binding energy (and the minimal \( \Delta \text{LUMO} \)) 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 \( \Delta \text{LUMO} \), we calculate the maximum efficiency in this ideal scenario by changing this parameter, and determine for each \( \Delta \text{LUMO} \) the optimal bandgaps for the different subcells. First, we only change \( \Delta \text{LUMO}_1 \) (the \( \Delta \text{LUMO} \) of the first subcell) and keep \( \Delta \text{LUMO}_2 \) and \( \Delta \text{LUMO}_3 \) 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 \( \Delta \text{LUMO}_1 = 0.3 \) 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 \( \Delta \text{LUMO}_1 \). The optimal bandgap \( E_{g1} \) increases with increasing \( \Delta \text{LUMO}_1 \) 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 \( \Delta \text{LUMO}_1 \). This was to be expected. Indeed, a high \( \Delta \text{LUMO}_1 \) 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 \( \Delta \text{LUMO} \) 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 \( \Delta \text{LUMO}_2 \) (with \( \Delta \text{LUMO}_1 = \Delta \text{LUMO}_3 = 0.3 \) 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 \( \Delta \text{LUMO}_2 \) values. The explanation is analogous as for \( \Delta \text{LUMO}_1 \). For higher
ΔLUMO₂ values, this decrease diminishes fast. Analogous conclusions as for ΔLUMO₁ can be drawn for the optimal bandgaps: the ideal bandgap of the second subcell increases with higher ΔLUMO₂ 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 ΔLUMO₂ 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 ΔLUMO₃ (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) ΔLUMO₁, (b) ΔLUMO₂ and (c) ΔLUMO₃. (right axis) The optimal bandgaps of the three subcells as function of (a) ΔLUMO₁, (b) ΔLUMO₂ and (c) ΔLUMO₃ 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 $\Delta$LUMO 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 $\Delta$LUMOs with one subcell with a high $\Delta$LUMO, than combining three subcells with average $\Delta$LUMOs. This conclusion follows from the increasingly smaller decrease in efficiency with increasing $\Delta$LUMOs.

Conflicts of Interest

The authors declare no conflict of interest.

References and Notes


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