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Should A Good Organic Solar Cell Be A Good Organic LED ?

Blaise Godefroid and Gregory Kozyreff *

Physics Department, Université libre de Bruxelles (U.L.B.), C.P. 231, Belgium

* Correspondence: gkozyref@ulb.ac.be

Abstract: We revisit the argument that link the efficiency of a solar cell to its reverse operation as a LED, in the case where the material is organic. In organic cells, exciton transport is an intermediate process between sunlight absorption and the generation of electric current. We show that quenching exciton radiation can be beneficial to cell efficiency, without contradicting the general rule prevailing for semiconductor cells. Our treatment allows us to discuss both bulk heterojunction and planar junctions.

Keywords: organic solar cells; heterojunction; IQE; organic LED

1. Introduction

“A good solar cell should be a good LED” – This simple rule rapidly became a central design principle for solar cells after it was first enacted by Owen D. Miller, Eli Yablonovitch, and Sarah R. Kurtz in 2012 [1]. However, it only strictly holds for semi-conductor cells. In this communication, we revisit the derivation of this statement and explain how to apply it to organic solar cells. What makes organic cells distinct from inorganic ones is the limiting role played by excitons. In organic cells, the absorption of a photon first gives rise to a long-lived exciton. It is only at the interface between the donor and acceptor materials that the local electric gradient can break the exciton into a free hole and a free electron. Counter-intuitively, we show here that if the exciton emissivity can be reduced, as in [2], while leaving electron emission unaffected, then one may improve the open-circuit voltage V_{oc} .

2. Classical theory

The famous statement by Miller, Yablonovitch and Kurtz directly comes from Shockley and Queisser’s theory of solar cells. In its simplest form, this theory expresses the conservation of the number of particles : the current of electron-hole pairs generated by photon absorption, I_s , is eventually converted either into a particle current in the external circuit $I(V)$, where V is the electric potential, or into a recombination current. We write the latter as $I_{R,e}(V) + I_{NR,e}(V)$, where “R” and “NR” stand for “radiative” and “non radiative”, respectively, and the subscript “e” is there to express that the processes in question involve electrons. In particular, $I_{R,e}(V)$ is a current of photons re-emitted by the cell through electrons-hole recombination. The detailed balance reads

$$I_s = I_{R,e}(V) + I_{NR,e}(V) + I(V). \quad (1)$$

With good approximation, the recombination terms follow the classical expression of an ideal diode [3–5], so that one may rewrite the previous equation as

$$I(V) = I_s - [I_{R,e}(0) + I_{NR,e}(0)] e^{q\beta V}, \quad (2)$$

where q is the absolute electric charge and $\beta = 1/k_B T$. From this, one can compute the open-circuit voltage V_{oc} :

$$q\beta V_{oc} = \ln \left(\frac{I_s}{I_{R,e}(0) + I_{NR,e}(0)} \right). \quad (3)$$

Suppose now that the solar cell operates in reverse, with electric current being injected into it. Then the cell becomes a Light Emitting Diode and the injected electrons produce photons with an LED quantum efficiency Q^{LED} defined as

$$Q^{LED} = \frac{I_{R,e}(0)}{I_{R,e}(0) + I_{NR,e}(0)}. \quad (4)$$

With this efficiency in mind, we can express the V_{oc} in terms of its ideal value, V_{oc}^{rad} as [6]

$$q\beta V_{oc} = \ln \left(\frac{I_s}{I_{R,e}(0) + I_{NR,e}(0)} \right) \quad (5)$$

$$= \ln \left(\frac{I_s}{I_{R,e}(0)} \frac{I_{R,e}(0)}{I_{R,e}(0) + I_{NR,e}(0)} \right) \quad (6)$$

$$= \ln \left(\frac{I_s}{I_{R,e}(0)} \right) + \ln \left(\frac{I_{R,e}(0)}{I_{R,e}(0) + I_{NR,e}(0)} \right) \quad (7)$$

$$= q\beta V_{oc}^{rad} + \ln \left(Q^{LED} \right). \quad (8)$$

If $Q^{LED} = 1$, recombination is only radiative and the second term vanishes, yielding $V_{oc} = V_{oc}^{rad}$. Otherwise ($Q^{LED} < 1$), V_{oc} is reduced by non-radiative recombination. From this follows the famous statement at the centre of this communication.

3. Organic solar cells

In organic solar cells, the absorbed photons first produce excitons, which must migrate to the donor-acceptor interface before any usable electric current can be produced. Denoting the exciton current at the interface by I_χ , Eqs. (1) and (2) become [2,7–9]

$$I_\chi = I(V) + I_{R,e}(V) + I_{NR,e}(V) \quad \rightarrow \quad I(V) = I_\chi - [I_{R,e}(0) + I_{NR,e}(0)] e^{q\beta V}. \quad (9)$$

At open-circuit, we now have

$$q\beta V_{oc} = \ln \left(\frac{I_\chi}{I_{R,e}(0) + I_{NR,e}(0)} \right) \quad (10)$$

$$= \ln \left(\frac{I_s}{I_{R,e}(0) + I_{NR,e}(0)} \right) + \ln \left(\frac{I_\chi}{I_s} \right) \quad (11)$$

$$= q\beta V_{oc}^{rad} + \ln \left(Q^{LED} \right) + \ln (\text{IQE}). \quad (12)$$

The last expression differs from (8) by the last term which is the logarithm of the ratio between the generated free carriers and the absorbed photons, *i.e.* the internal quantum efficiency (IQE), if a perfect charge collection efficiency is assumed at short-circuit condition, which is commonly the case [10–12]. Hence, if IQE is less than unity, V_{oc} is further decreased due to the incomplete transport and dissociation of generated excitons. From equation (12), we can make two important observations.

Firstly, bulk and planar heterojunction are characterized by distinct realization of Eq. (12). On the one hand, bulk-heterojunctions make IQE as close to 1 as possible, but can have poor Q^{LED} due to

dead-ends in the electron path toward the electrodes. On the other hand, with planar heterojunctions, interferences can be optimized in order to maximise Q^{LED} . However IQE decreases rapidly as soon as the thickness of the active layer exceeds the diffusion length of excitons, which severely limits photon absorption. Fortunately, photonic management can significantly increase the diffusion length for exciton with large fluorescence quantum yield, allowing one to guarantee a good IQE [2].

Secondly, as excitons diffuse in direction to a dissociation interface, some of them disintegrate, either radiatively or non-radiatively, making $I_{\chi} < I_s$. Explicitly,

$$I_{\chi} = I_s - I_{R,\chi} - I_{NR,\chi}, \quad (13)$$

where $I_{R,\chi}$ and $I_{NR,\chi}$ are the radiative and non-radiative exciton recombination current, respectively. Here, it is important to note that $I_{R,\chi}$ is quite distinct from $I_{R,e}(V)$, since the two quantities relate to distinct particles. Crucially, since excitons are electrically neutral, their radiation is independent of the voltage V . For the same reason, their transport within the cell, contrary to electron, is insensitive to the local electric field. Using (13), we can rewrite the IQE as

$$IQE = 1 - \frac{I_{R,\chi} + I_{NR,\chi}}{I_s} \quad (14)$$

As I_s is far larger than the total exciton recombination current, the logarithm of the IQE in (12) can be expanded and we finally get

$$q\beta V_{oc} = q\beta V_{oc}^{rad} + \ln(Q^{LED}) - \frac{I_{R,\chi} + I_{NR,\chi}}{I_s}. \quad (15)$$

Hence, if one manages to decrease $I_{R,\chi}$, while keeping $I_{NR,\chi}$ as small as possible, one can improve the V_{oc} . As it turns out, it is possible, in principle to reduce drastically $I_{R,\chi}$ through interference management, without affecting I_s . Indeed, organic cells are ultra-thin compared to optical wavelengths and, in such confined environment, exciton fluorescence can be tuned by properly adjusting the cell geometry [13].

That one can reduce $I_{R,\chi}$ while maintaining I_s may seem slightly counter-intuitive because one usually assumes that the emissivity of the cell is equal to its absorptivity. Consequently, decreasing the emitted current should decrease the absorbed photons current. However, as far as exciton is concerned, absorption takes place at energies larger than the bandgap while exciton emission occurs only at sub-bandgap energies. Secondly, and more importantly, absorption involves sun photons that enter the cell at nearly-normal incidence, whereas radiation by excitons occurs in all directions. In such a strongly confined environment as an organic solar cell, photon emission becomes highly anisotropic. As a result, there exists an asymmetry between absorption of sun photons and radiative decay of excitons, see Figure 1. Thermodynamically speaking, this is a non-classical effect.

In conclusion, while it remains true that a good organic solar cell must be a good LED, it is only desirable to have good LED luminescence from electron-hole recombination. Meanwhile, exciton being electrically neutral, their fluorescence should be minimized so as to maximize IQE.

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Abbreviations

The following abbreviations are used in this manuscript:

LED	Light Emitting Diode
IQE	Internal Quantum Efficiency

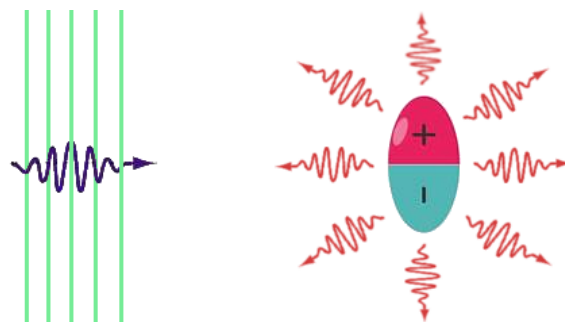


Figure 1. Left: incident photons coming at normal incidence with energies larger than the bandgap. Right: emitted photons by the excitons in any direction and with energies lower than the bandgap.

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