Practical efficiency limits in organic photovoltaic cells: Functional dependence of fill factor and external quantum efficiency

Jonathan D. Servaites, Mark A. Ratner,[a)] and Tobin J. Marks[b)]
Department Materials Science and Engineering, Department of Chemistry, and the Materials Research Center, Northwestern University, Evanston, Illinois 60208, USA

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We evaluate practical power conversion efficiency limits (η_{lim}) in bulk-heterojunction organic photovoltaic (BHJ OPV) cells and how the field dependence of exciton dissociation affects cell efficiencies. We treat the fill factor limit as a function of the donor-acceptor lowest unoccupied molecular orbital offset energy (E_{LLO}), calculating how this limit varies with decreasing E_{LLO}. We also evaluate OPV external quantum efficiency as a function of wavelength from the optical transmittance and internal quantum efficiency limitations. For a given E_{LLO}, we numerically optimize donor bandgap and η_{lim} and show that $\eta_{\text{lim}}>10\%$ should be possible for hypothetical OPV systems generating free charge carriers efficiently at $E_{\text{LLO}}\sim 0.3$–0.4 eV. Current BHJ OPVs with low E_{LLO} values appear to be limited to cell efficiencies of $\sim 5\%$ largely as a consequence of incomplete exciton dissociation. [doi:10.1063/1.3243986]

Recent advances in bulk heterojunction organic photovoltaics (BHJ OPVs) have demonstrated significant power conversion efficiency (η) advances, crossing the 5% threshold.[1–5] However, $\eta>10\%$ is thought necessary for widespread application,[6] and developing donor (D) and acceptor (A) active layer materials with optimized energy levels is one promising strategy to achieve this goal.[3,5,7–9] A potential drawback in altering D or A energies is that exciton dissociation efficiencies (η_{ED}) may be compromised, particularly for smaller electric fields.[10–14] In OPV systems, where D absorbs large percentages of solar radiation, appropriate offset between the D and A lowest unoccupied molecular orbital (LUMO) energies is critical. In this letter, we assess practical η limits (η_{lim}) in BHJ OPVs by considering the effects of reduced LUMO offset energies (E_{LLO}), as well as addressing potential counter effects involving η_{ED} losses from reduced E_{LLO} values.

Prior studies have addressed efficiency limits in OPVs by building on the original Shockley–Queisser description of *p-n* junction solar cells,[15–19] with overall trends as a function of E_{LLO} discussed using various η modeling approaches.[11,16–18] Here we suggest somewhat higher practical η_{lim} values for single-layer BHJ OPVs may be achievable based upon the following approach. First, applying a diode-based model, we treat fill factor as a function of E_{LLO}, showing how the fill factor limit can increase at lower E_{LLO} values. We also incorporate recent data[4,6] demonstrating that OPV fill factors approaching 70% are achievable at large E_{LLO} values (e.g., 1.0 eV); applying these data to our model yields fill factor limits of $\sim 75\%$ at lower E_{LLO} values (e.g., 0.3–0.5 eV). Furthermore, we treat external quantum efficiency (EQE) as a function of wavelength based upon anode transmittance and internal quantum efficiency (IQE) constraints. Finally, we assess the impact on η when η_{ED} is reduced for smaller E_{LLO} values. Regarding terminology, in accord with most literature, we approximate the photoexcitation energy as the highest occupied molecular orbital (HOMO)-LUMO gap. Note that this is not strictly accurate—upon excitation, all molecular levels relax, and the excited state ionization energy (the LUMO level here) is only approximated by the ground-state LUMO energy.[20] However, "LUMO level" can be replaced by the more precise term "electron affinity," and the discussion then proceeds unchanged.

We begin with basic solar cell efficiency equation[21]

$$\eta=\frac{J_{\text{sc}}V_{\text{oc}}\beta_{\text{FF}}}{P_{\text{solar}}}, \tag{1}$$

where J_{sc} is the short circuit current density, V_{oc} the open circuit voltage, β_{FF} the fill factor, and P_{solar} the incident solar radiation. We employ the standard AM1.5G solar spectrum ($P_{\text{solar}}=1000\ \text{W/m}^2$). Given EQE limits, the J_{sc} calculation is an integration of photon flux over the wavelengths absorbed by the cell

$$J_{\text{sc}}=A_{\text{cell}}^{-1}\int_{\lambda=0}^{\lambda=\lambda_g}\Phi_p(\lambda)\,\eta_{\text{EQE}}(\lambda)\,d\lambda, \tag{2}$$

where A_{cell} is the OPV cell area, λ the wavelength of the light, λ_g the largest absorbed wavelength corresponding to the D bandgap, $\Phi_p(\lambda)$ the photon flux, and $\eta_{\text{EQE}}(\lambda)$ the EQE limit for a given wavelength. Since D materials dominate light absorption in the highest efficiency BHJ OPVs reported to date,[3,5,6,9] we assume that D is the light absorber. Starting with Fig. 1, we numerically integrate these data, applying Eq. (2) to determine J_{sc}. We assume an IQE limit of 90% across all wavelengths to calculate $\eta_{\text{EQE}}(\lambda)$ (for a given wavelength, EQE=IQE × optical transmittance). From the indium tin oxide (ITO)/glass transmittance spectrum, we calculate EQE variation with wavelength, resulting in weighted average EQEs of $\sim 75\%$–80% for the present E_{LLO} values. While these EQEs seem relatively large, comparable values have been achieved in BHJ OPVs having $E_{\text{LLO}}\sim 1.0$ eV.[5,6] Further work is needed to assess the affect of smaller E_{LLO} values on EQE.

Regarding V_{oc}, note that it cannot exceed the energy difference between the LUMO of A ($E_{\text{LUMO(A)}}$) and the HOMO

[a)]Electronic mail: ratner@northwestern.edu.
[b)]Electronic mail: t-marks@northwesten.edu.

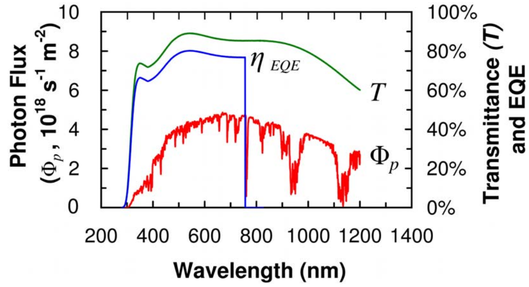

FIG. 1. (Color online) AM1.5G photon flux (Φ_p), anode optical transmittance (t), and EQE (for the case of E_g=1.5 eV) spectra used in the present study. The transmittance spectrum is for ITO on glass from Delta Technologies Ltd. The EQE spectrum is based on applying IQE=90%.

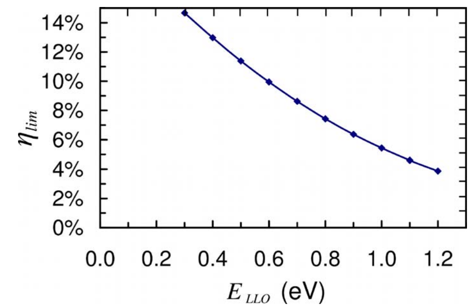

FIG. 2. (Color online) Practical η_{lim} vs LUMO offset, as determined from Eqs. (1)–(3) and (6), taking $\gamma_{\text{ED}}=\infty$. The line is added as a guide to the eye.

of D ($E_{\text{HOMO(D)}}$).[17] However, it has been demonstrated that there is a ~0.3 V reduction in this upper limit to V_{oc} across a wide range of OPV donor materials: $V_{\text{oc}}=(1/e)(E_{\text{HOMO(D)}}-E_{\text{LUMO(A)}})-0.3$, where e is the elementary charge.[17] While theoretically V_{oc} may exceed this relationship, data for state-of-the-art BHJ OPVs suggest it represents a practical V_{oc} limit.[2–6,17] Furthermore, the LUMO offset energy is $E_{\text{LLO}}=|E_{\text{LUMO(A)}}-E_{\text{LUMO(D)}}|$, and the donor bandgap energy is $E_g=|E_{\text{HOMO(D)}}-E_{\text{LUMO(D)}}|$. We can then express V_{oc} in terms of E_g and E_{LLO},

$$V_{\text{oc}}=\frac{1}{e}(E_g-E_{\text{LLO}})-0.3. \quad (3)$$

The remaining part of the η calculation concerns the fill factor limit. Our approach differs from prior approaches in that fill factor is now treated as a part of the η optimization for each value of E_{LLO}, rather than as a fixed parameter. We calculate fill factor by modifying a diode-based model, known to reproduce OPV behavior well,[22–24]

$$J=J_o\left\{\exp\left[\frac{e(V-JR_s)}{nk_BT}\right]-1\right\}+\frac{V-JR_s}{R_{p(\text{eff})}}-J_L, \quad (4)$$

where J_o is the reverse saturation current, V the cell voltage, J the current density, n the diode ideality factor, k_B Boltzmann's constant, T temperature, R_s the series resistance, $R_{p(\text{eff})}$ a modified effective parallel resistance, and J_L the photocurrent generated by the cell before recombination losses.[21,25] We introduce $R_{p(\text{eff})}$ as the effective resistance of two resistors in parallel,

$$R_{p(\text{eff})}=(R_p^{-1}+\gamma_{\text{ED}}^{-1})^{-1}, \quad (5)$$

where R_p is the traditional equivalent circuit parallel resistance[22–24] and γ_{ED} is an exciton dissociation factor representing the exciton dissociation field dependence[26,27] at $V=0$ (i.e., we define $\gamma_{\text{ED}}\equiv\partial V/\partial J_L$ at $V=0$). Like R_p, γ_{ED} predominantly affects the slope of the J-V curve near $V=0$. For our *limits* analysis, we assume the optimal scenario of $\gamma_{\text{ED}}=\infty$, i.e., at $V=0$ any change in V yields no change in J_L. For $E_{\text{LLO}}=\sim 1$ eV, this assumption is well supported in BHJ OPVs;[4,6] however, state-of-the-art BHJ OPVs with lower E_{LLO}(~0.4 eV) values appear to have lower γ_{ED} values (~100–200 Ω cm^2), as evidenced by a least-squares fit of these J-V data.[7,28] The impact of these lower γ_{ED} values on η is addressed below. Finally, a least-squares fit of the current density-voltage (J-V) data also permits extracting the parameters n, R_s, and $R_{p(\text{eff})}$. Here, these are determined using recent data[4] under AM1.5G illumination. This calculation yields: n=2.38, R_s=1.44 Ω cm^2, and $R_{p(\text{eff})}$=3960 Ω cm^2, resulting in a fill factor of 0.69, which is among the highest reported[6] BHJ OPV fill factors. Therefore, we use these parameters to calculate a *practical* BHJ OPV fill factor limit (instead of assuming ideal parameters, which yield higher fill factors). Applying Eq. (4) and Green's method,[29] the relationship for a practical fill factor limit as a function of E_{LLO} is given by

$$\beta_{\text{FF}}=\beta_{\text{FF}(s)}\left[1-\left(\frac{E_g-E_{\text{LLO}}-0.3+0.7nk_BT}{E_g-E_{\text{LLO}}-0.3}\right)\left(\frac{\beta_{\text{FF}(s)}}{r_{p(\text{eff})}}\right)\right], \quad (6)$$

where $\beta_{\text{FF}(s)}$ is β_{FF} based on an idealized R_p, and $r_{p(\text{eff})}$ is the normalized value of $R_{p(\text{eff})}$. Note that Eq. (6) can also be applied to assess how exciton dissociation field dependence reduces the fill factor limit when $\gamma_{\text{ED}}\neq\infty$ (since $r_{p(\text{eff})}$ is a function of γ_{ED}). See Ref. 29 and supporting information[30] here for details on Green's method, its accuracy, and our derivation of Eq. (6).

We now calculate practical η_{lim} variation with E_{LLO}. For a given E_{LLO} there will be an optimal E_g that provides the greatest η. We numerically optimize E_g for a given E_{LLO} via Eq. (1), solving for J_{sc} through Eq. (2), V_{oc} through Eq. (4), and fill factor via Eq. (6), taking $\gamma_{\text{ED}}=\infty$ for this limits analysis. Figure 2 shows the η_{lim} optimization results: reducing E_{LLO} to ~0.3–0.4 eV without reducing η_{ED}, as others have argued may be possible,[6,8] yields η values well over 10%. Ross *et al.*[8] recently demonstrated reduced LUMO offsets (E_{LLO}=~0.7 eV) without reduction in η_{ED} and, therefore, without significant change in γ_{ED}. Figure 3 shows how optimal E_g and fill factor vary with E_{LLO} in this limits analysis.

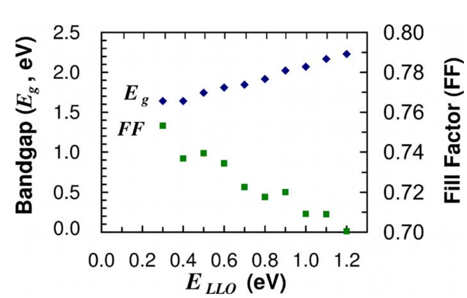

FIG. 3. (Color online) Optimal donor bandgap energy (E_g) and limit of fill factor (FF) vs LUMO level offset. E_g is optimized to maximize η via Eq. (1), and fill factor is determined from Eq. (6). This analysis takes fill factor as a function of LUMO level offset. The scatter in the data points is due to the texture of the terrestrial solar spectrum.

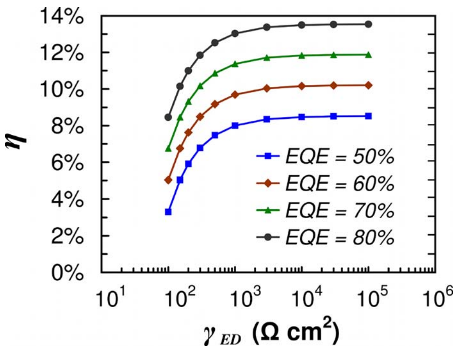

FIG. 4. (Color online) Exciton dissociation field dependence (γ_{ED}) and weighted average EQE vs η for $E_{LLO}=0.4$ eV, as determined from Eqs. (1)–(3), (5), and (6). Note that as $\gamma_{ED}\rightarrow\infty$ for EQE=$\sim$80%, $\eta\rightarrow\eta_{lim}$ for $E_{LLO}=0.4$ eV (Fig. 2). The bandgap energy is held constant at $E_g=1.64$ eV (Fig. 3). Lines are added as guides to the eye.

Fill factor is significantly impacted at low values of γ_{ED} and $R_{p(\mathrm{eff})}$ [Eq. (6)]; this is shown graphically in the supporting information.[30] Note that other than γ_{ED} and R_p, it has been shown that injection barriers at the electrodes[31] can also affect the slope of the J-V curve at $V=0$ (thus reducing fill factor); however, previous results show that these losses can be overcome in optimized systems, as evidenced by a near-zero slopes of J-V curves at $V=0$.[4]

Finally, we consider the impact of exciton dissociation field dependence. Just as a smaller R_p affects the slope of the J-V curve at $V=0$, a smaller γ_{ED} does as well. While there is evidence that E_{LLO} can be lowered without reducing γ_{ED},[8] there are counterexamples at $E_{LLO}<0.5$ eV where exciton dissociation appears to be limited, based on the J-V curve near $V=0$.[7,28] A reduction in γ_{ED} will therefore reduce fill factor, and while the fill factor *limit* increases with E_{LLO} (Fig. 3), there can be a countereffect on actual fill factor based upon reductions in γ_{ED}. Furthermore, projected EQEs are reduced when exciton dissociation is incomplete at $V=0$. While detrimental effects on fill factor and EQE are observed for low E_{LLO} values (e.g., $\sim$0.4 eV),[7,28] the relationship between E_{LLO}, fill factor, and EQE is not well understood. However, we can model how γ_{ED} and EQE changes affect η, as shown in Fig. 4 for the case of $E_{LLO}=0.4$ eV. Current generation OPVs with $E_{LLO}\sim 0.4$ eV exhibit a weighted average EQE=50%–60% at $V=0$ and appear to have a $\gamma_{ED}=100$–$200\ \Omega\ \mathrm{cm}^2$ based upon the J-V data, resulting in $\eta\sim 5\%$.[7,28] It will be critical to develop materials and D-A interfaces that enhance exciton dissociation at such E_{LLO} values (moving up and to the right in Fig. 4). Potential cell strategies include materials with higher dielectric constants,[10,13] greater mobilities,[13,32] and enhanced phonon-electron coupling.

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