
Gon Namkoong
Old Dominion University, gnamkoon@odu.edu

Patrick Boland
Old Dominion University

Keejoo Lee
Old Dominion University

James Dean
Old Dominion University

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Design of organic tandem solar cells using PCPDTBT:PC$_{61}$BM and P3HT:PC$_{71}$BM

Gon Namkoo1,a, Patrick Boland1, Keejoo Lee2 and James Dean2
1Department of Electrical and Computer Engineering, Applied Research Center, Old Dominion University, 2050 Jefferson Avenue, Newport News, Virginia 23606, USA
2Department of Aerospace Engineering, Old Dominion University, 4750 Elkhorn Avenue, Norfolk, Virginia 23529, USA

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We conducted optical and electrical simulations with the goal of determining the optimal design for conjugated polymer-fullerene tandem solar cells using poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b’]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT): [6,6]-phenyl C$_{61}$ butyric acid methyl ester (PC$_{61}$BM) as a bottom cell and poly(3-hexylthiophene) (P3HT): [6,6]-phenyl C$_{71}$ butyric acid methyl ester (PC$_{71}$BM) as a top cell. The effects of photon density, absorption, balanced and unbalanced charge carrier transport, and bimolecular recombination in the two subcells were incorporated into the simulations. We found that the maximum energy conversion efficiency ($\eta$) is 9% when charge carrier mobilities in both top and bottom cells are balanced. However, the efficiency drops significantly if the carrier mobilities are unbalanced in either the top or bottom cell. In addition, we found that unbalanced carrier mobilities in the top cell require a reduction in the thickness of the bottom cell whereas unbalanced bottom cell mobilities require an increase in the thickness of the bottom cell to compensate for the reduced current.

I. INTRODUCTION

The development of photovoltaics to harness limitless and pollution-free solar energy continues to garner an ever-increasing scientific interest. The need for low-cost, easily-producible, and reliable energy sources has spurred research efforts aimed at addressing the development of organic solar cells. Over the last two decades, comprehensive insights and greater understanding of organic materials1–3 have enabled the continuing evolution of solar energy conversion technology in organic solar cells. Remarkable improvements in performance have been made with bulk heterojunction (BHJ) devices1–3 where organic polymers and fullerene derivatives are randomly mixed to form nanoscale donor/acceptor interfaces. Organic BHJ solar cells have shown drastically improved energy conversion efficiencies of more than 4%.4–6 However, the limited absorption profiles of currently available organic materials prevent the attainment of higher efficiencies.7–9 To overcome this shortcoming, multijunction organic solar cells7–9 have been investigated as a potential design modification for achieving high-efficiency photovoltaics. These multijunction solar cells are arranged in a “tandem” configuration that offers a number of advantages including increasing open circuit voltage ($V_{OC}$) and short circuit current density ($J_{SC}$) when connected in series or parallel,8,9 respectively. The most common configuration comprises a series connection of two or three subcells where the photogenerated current extracted from the tandem structure is determined by the subcell producing the lowest value of photocurrent.5 The $V_{OC}$ of the tandem cell is approximately the sum of each subcell’s $V_{OC}$.5 Therefore, ideal tandem solar cells in a series configuration require that each subcell be engineered such that light absorption is accurately controlled to balance photocurrent. Recently, Dennler et al.,10 used optical transfer matrix methods (TMM) (Ref. 11) to predict organic thin film thickness for matched photocurrents between two different heterojunction organic blends: poly(3-hexylthiophene) (P3HT): [6,6]-phenyl C$_{61}$ butyric acid methyl ester (PC$_{61}$BM), and poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b’]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT): [6,6]-phenyl C$_{71}$ butyric acid methyl ester (PC$_{71}$BM). However, in their simulations the balanced photocurrent is calculated based on an assumption of 100% internal quantum efficiency (IQE) where all absorbed photons in the active layers of each subcell ultimately contribute to photocurrent ($J_{ph}$). In real organic solar cells, several charge transport properties12–14 such as exciton generation and dissociation, bimolecular recombination, and unbalanced charge transport inside the active layers must be considered when designing optimal tandem structures since those factors cause current density ($J_{SC}$) to deviate from photocurrent ($J_{ph}$) obtained when IQE = 100%. Considering all the factors described above, we carried out electrical simulations as well as optical analysis using an organic drift-diffusion model and the optical TMM model tailored for design analysis of tandem organic structures.

II. METHODOLOGY

A. Optical modeling

A schematic of a tandem device is shown in Fig. 1. In the bottom cell, multiple material layers are stacked sequentially: indium tin oxide (140 nm)/poly(3,4 ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDOT:PSS) (25 nm)/PCPDTBT:PC$_{61}$BM ($d_{bottom}$)/TiO$_2$.
(8 nm). The top cell is formed similarly: PEDOT:PSS (25 nm)/P3HT:PC_{71}BM \((d_{\text{top}} = 0-300 \text{nm})\) and finally Al (100 nm) on the top. Note that \(d_{\text{bottom}}\) and \(d_{\text{top}}\) are the thicknesses of the active layers allowed to vary up to a maximum of 300 nm. The P3HT polymer is known to have an effective absorption range between UV and 650 nm (Ref. 10) while a low-band gap \(E_{\text{g}} \sim 1.5\) eV organic material—PCPDTBT—extends the absorption spectra into the infrared region.\(^{5,15,16}\) Therefore, the combination of these two polymer materials covers a wide spectral absorption range from UV to infrared. It should be noted that this tandem structure has produced energy conversion efficiencies as high as 6.5%.\(^{17}\)

For the optical analysis of tandem solar cell structures, TMM is performed over a wavelength range from 350–900 nm using standard AM 1.5 sunlight spectra. The optical properties of all the layers are described based on the complex refractive indices, \(n' = n(\lambda) + i k(\lambda)\), which are either experimentally obtained from spectroscopic ellipsometry or from the literature.\(^{10}\) In particular, the refractive index values for P3HT:PC_{71}BM and PCPDTBT:PC_{61}BM are extracted from Ref. 10. For a given set of \(d_{\text{bottom}}\) and \(d_{\text{top}}\), the number of photons \(N_{\text{abs}}\) absorbed in the top and bottom layers are calculated in each subcell as shown in Fig. 2. The absorbed photons are converted to photocurrent by considering charge carrier transport and bimolecular recombination processes and designing an optimal \(d_{\text{bottom}}\) and \(d_{\text{top}}\) for each subcell. The maximum thickness considered is around 300 nm due to the fact that both bimolecular recombination and internal resistance of the device significantly increase with excessive thickness and adversely affect energy conversion efficiency.

**B. Electrical modeling**

The absorbed photons in organic blends generate electron-hole (e-h) pairs or excitons, some of which subse-

![Image](100x487 to 245x742)

FIG. 1. (Color online) Schematic diagram of a tandem structure used in the simulations. Thicknesses of active layers were varied from 0–300 nm.

![Image](214x760 to 487x1029)

FIG. 2. (Color online) Photon absorption rate profile for a tandem structure composed of active layers of a PCPDTBT:PC_{61}BM bottom cell (130 nm) and a P3HT:PC_{71}BM top cell (150 nm).

sequently dissociate into free-charge carriers at the BHJ interfaces as described by Onsager–Braun theory.\(^{12,13}\) The transport of dissociated free-charge carriers and Langevin bimolecular recombination are incorporated into a one-dimensional drift-diffusion model and used to estimate the current density and efficiency of organic solar cells. In this model, the mobilities of electron and hole carriers are assumed to be independent of the electric field which is taken to be constant within the organic blends. The net generation rate, \(U(x)\), of free-charge carriers can be expressed as\(^{18}\)

\[
U(x) = P(x)[G_{\text{e-h}}(x) + R(x)] - R(x),
\]

where \(P(x)\) is the dissociation probability of bound e-h pairs. \(G_{\text{e-h}}(x)\) is the generation rate of photo-induced e-h pairs and \(R(x)\) is the Langevin bimolecular recombination rate expressed as

\[
R(x) = k_r[n(x)p(x) - n_{\text{int}}^2],
\]

\[
k_r = \frac{q}{e} \min(\mu_e, \mu_h).
\]

The electron and hole charge carriers are recombined at the rate, \(k_r\), with respect to the intrinsic carrier density \(n_{\text{int}}^2\). One should note that \(k_r\) is dictated by the mobility of the slower carrier in Eq. (2).

More specifically, the e-h pair dissociation probability at a given pair distance, \(\xi\), is given by

\[
p[\xi, F(x), T] = \frac{k_d[\xi, F(x), T]}{k_d[\xi, F(x), T] + k_r(T)},
\]

where \(k_d\) is the e-h dissociation rate and \(k_r\) is the decay rate to the ground state. The dissociation rate is a function of the e-h pair distance, field strength \(F\), and temperature \(T\)

\[
k_d[\xi, F(x), T] = \frac{3k_r}{4\pi \xi^2} e^{-E_b/k_B T} J_1(2\sqrt{2b}), \quad b = \frac{q^3 F(x)}{8\pi \xi^2 k_B T^2},
\]

where \(E_b\) is the e-h binding energy and \(J_1\) is the Bessel function of the first kind. In disordered polymer-fullerene systems, the e-h pair distance, \(\xi\), is not constant. Accordingly, the overall dissociation probability of e-h pairs must be treated statistically by integrating the probability function in
Eq. (3) over all spatial e-h pair distances \((\xi=0, \infty)\) as

\[
P[a, F(x), T] = \int_{\xi=0}^{\xi=\infty} p[\xi, F(x), T] \frac{4\epsilon^2}{\sqrt{\pi} a^3} e^{-a(\xi/a)^2} d\xi,
\]

where a Gaussian function normalized to the most probable distance \(a\) is used to represent a selected distribution profile.

Using the Poisson equation, potential \(\phi(x)\) and electric field are calculated at the position \(x\) as

\[
\epsilon \frac{d^2 \phi(x)}{dx^2} = -\frac{e}{\sqrt{\pi} a^3} \int_{\xi=a}^{\xi=\infty} e^{-a(\xi/a)^2} d\xi = q[n(x) - p(x)],
\]

where \(\epsilon\) is the dielectric constant of organic blend, \(q\) is the elementary charge, and \(n(x)\) and \(p(x)\) are the electron and hole densities, respectively.

The current densities in terms of drift-diffusion of the charge carriers are calculated using the continuity equations for the electron \([J_n(x)]\) and hole current densities \([J_p(x)]\)

\[
q \frac{d J_n(x)}{dx} + U(x) = 0,
\]

\[
- q \frac{d J_p(x)}{dx} + U(x) = 0,
\]

\[
J_n(x) = - q \mu_n \left[ n(x) \frac{d \phi(x)}{dx} - V_f \frac{d n(x)}{dx} \right],
\]

\[
J_p(x) = - q \mu_p \left[ p(x) \frac{d \phi(x)}{dx} + V_f \frac{d p(x)}{dx} \right],
\]

where \(\mu_n\) and \(\mu_p\) are the mobilities of the electrons and holes, respectively, and \(V_f = k_B T/q\) is the thermal voltage. The coupled nonlinear equations described above are solved iteratively to obtain the steady state condition for the electric potential, free-charge concentrations, and current densities.

### C. Comparison with experimental data

Using the optical and electrical models, material parameters for P3HT:PCBM and PCPDTBT:PCBM were derived and are summarized in Table I. The parameters for P3HT:PCBM were extracted based on device efficiencies over 4% and an active layer thickness of 175 nm. The reference mobility ratio between electrons and holes \((\mu_e/\mu_h)\) is taken close to 1 which is required to achieve higher energy conversion efficiencies in thicker organic blends. Even though these mobilities listed in Table I are one order of magnitude higher than the experimentally measured values from Ref. 19, our values have been fitted to other experimental data\(^{20}\) where the device thickness exceeded 300 nm as can be seen in Fig. 3(a).

In contrast, device parameters for PCPDTBT:PCBM are not well investigated requiring that we use experimental current-voltage (IV) characteristics from Ref. 5. Results are shown in Fig. 3(b). The best fit values for the pair separation distance, \(a=1.47\) nm, and decay rate, \(k_f =10^5\) 1/s, were determined by comparing experimental IV characteristics with fitting data for an active layer thickness of 110 nm. These values differ somewhat compared to previously reported values\(^{21}\) where \(a=2.1\) nm and the decay

![FIG. 3. (Color online) (a) Comparison of current density and efficiencies between experimental data (dots) and simulation (solid lines) of P3HT:PCBM (Ref. 20) and (b) comparison of simulated and experimentally-measured IV characteristics of PCPDTBT:PCBM having an active layer thickness of 110 nm (Ref. 5).](image)
TABLE II. Mobilities of electrons and holes for Cases I, II, and III.

<table>
<thead>
<tr>
<th></th>
<th>Numerical value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom cell</td>
<td>Top cell</td>
</tr>
<tr>
<td>PCPDTBT:PC61BM</td>
<td>P3HT:PC71BM</td>
</tr>
<tr>
<td>(cm²/V s)</td>
<td>(cm²/V s)</td>
</tr>
<tr>
<td>Case I</td>
<td></td>
</tr>
<tr>
<td>$\mu_e = 6 \times 10^{-3}$</td>
<td>$\mu_e = 9 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\mu_h = 1 \times 10^{-3}$</td>
<td>$\mu_h = 7 \times 10^{-4}$</td>
</tr>
<tr>
<td>Case II</td>
<td></td>
</tr>
<tr>
<td>$\mu_e = 6 \times 10^{-3}$</td>
<td>$\mu_e = 9 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\mu_h = 1 \times 10^{-3}$</td>
<td>$\mu_h = 7 \times 10^{-3}$</td>
</tr>
<tr>
<td>Case III</td>
<td></td>
</tr>
<tr>
<td>$\mu_e = 6 \times 10^{-3}$</td>
<td>$\mu_e = 9 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\mu_h = 1 \times 10^{-4}$</td>
<td>$\mu_h = 7 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

rate $k_f = 1.7 \times 10^7$ 1/s. Such a difference might come from the improvement in optical and electrical performance that results from adding alkane dithiols to PCPDTBT polymer-fullerene blends.

III. RESULTS AND DISCUSSION

Current matching between subcells in series tandem structures is a critical performance requirement where the number of absorbed photons, charge carrier transport, and bimolecular recombination must be optimized to balance the photocurrent. Low charge carrier mobilities and unbalanced charge distribution that results from unbalanced electron/hole mobilities in organic photovoltaics are characteristics of organic solar cells that make it complicated to match current densities between subcells. In this study, three different cases were investigated employing a PCPDTBT:PC61BM bottom subcell and a P3HT:PC71BM top cell: Case I—unbalanced charge carrier mobilities in the P3HT:PC71BM subcell with balanced mobilities in the PCPDTBT:PC61BM cell, Case II—balanced charge carrier mobilities in both top and bottom subcells, and Case III—unbalanced carrier mobility in PCPDTBT:PC61BM with balanced mobilities in P3HT:PC71BM. Table II shows electron and hole mobilities for each subcell in each of the three cases. The values for the electron and hole mobilities for organic blends are varied based on experimental results reported in the literature. To consider unbalanced charge carrier transport, we set hole mobility one order of magnitude lower than that of the electrons as this is consistent with experimentally observed values for organic blends.

Figure 4 shows an isoline graph where the current densities for each case are matched between the top and bottom cells as a function of both cell thicknesses. The $J_{SC}$ values for each case were calculated based on both electrical and optical models described in Sec. II. We first calculated the isoline as a guideline where the total number of photons, $N_{ph}$, absorbed in each cell are matched and converted into photocurrent density, $J_{ph}$, by assuming that IQE was equal to 100%. $J_{SC}$ deviated from the $J_{ph}$ isoline in all three Cases, I, II, and III. When charge carriers in both cells are balanced (Case II), $J_{SC}$ is very close to $J_{ph}$. However, when charge carriers are unbalanced as in Cases I and III, the thickness of each subcell will be modified dependent upon the degree of unbalance of charge carrier mobilities in the bottom or top cell. In Case I where the P3HT:PC71BM top cell has unbalanced carrier mobilities, it is observed that $d_{bottom}$ (PCPDTBT:PC61BM) should be reduced. In contrast, in Case III where the PCPDTBT:PC61BM bottom cell has unbalanced charge mobilities, $d_{bottom}$ (PCPDTBT:PC61BM) should be increased.

To investigate the effect of charge carrier mobility on isoline variations, we calculated the $J_{SC}$ for each cell by fixing $d_{top}$ (P3HT:PC71BM) = 100 nm while varying $d_{bottom}$ (PCPDTBT:PC61BM) from 0 to 300 nm as shown in Fig. 5. Interestingly in Fig. 5(a), $J_{ph}$ for P3HT:PC71BM continuously decreases with increased $d_{bottom}$ while $J_{ph}$ for PCPDTBT:PC61BM continuously increases though at a slower rate from 180 to 300 nm thickness. In this configuration, the $J_{ph}$ in each cell are matched with the active layer thicknesses of $d_{bottom} = 150$ nm and $d_{top} = 100$ nm as shown in Fig. 5(a). When hole mobility dropped by one order of magnitude from $\mu_h = 7 \times 10^{-3}$ to $\mu_h = 7 \times 10^{-4}$ cm²/V s with a constant electron mobility of $\mu_e = 9 \times 10^{-3}$ cm²/V s in P3HT:PC71BM (Case I), a significant drop in $J_{SC}$ was observed. Therefore, $d_{bottom}$ should be modified to have a thinner active layer. The shift toward a thinner $d_{bottom}$ is required to reduce the absorption of $N_{ph}$ in the bottom cell, thereby reducing $J_{SC}$ in PCPDTBT:PC61BM and subsequently matching the reduced $J_{SC}$ of the top cell. It should be also noted that increasing $d_{top}$ will lead to increased bimolecular recombination and subsequently more current density drops in the top solar cell. This in turn will require $d_{bottom}$ to be made thinner. This can be seen in Fig. 4 where increased deviation from $J_{ph}$ is observed with increased $d_{top}$ which leads to a decrease in the thickness of the active layer, $d_{bottom}$, in the bottom cell.

In Case III where the charge carrier mobility of PCPDTBT:PC61BM in the bottom cell is unbalanced, the $J_{SC}$ is shifted toward the right away from $J_{ph}$ in Fig. 4 indicating that a thicker active layer in the bottom solar cell is required to match current between the bottom and top solar cells [Fig. 5(b)]. Since the drop in $J_{SC}$ in the bottom cell occurs due to increased bimolecular recombination that results from de-
rent drop of the bottom solar cell. Consequently, the effect of allowing more photons to be absorbed in the bottom cell. This can be achieved by increasing hole mobility in PCPDTBT:PC 61BM was dropped from 1 × 10⁻³ cm²/V s, a significant current drop was observed. For Case III, when the hole mobility in PCPDTBT:PC61BM was dropped from μₕ=1 × 10⁻³ cm²/V s (blue solid line with spheres) to μₕ=1 × 10⁻⁴ cm²/V s (blue dotted line with spheres) with constant μₑ=6×10⁻³ cm²/V s, a significant current drop was observed. Solid lines indicate the photocurrent Jₚh generated with IQE=100%.

creasing hole mobility from μₕ=1 × 10⁻³ to μₕ=1 × 10⁻⁴ cm²/V s and holding electron mobility constant at μₑ=6×10⁻³ cm²/V s, it is necessary to drop JₜSC in the top cell. This can be achieved by increasing dₕbottom which will have the effect of allowing more photons to be absorbed in the bottom solar cell. Consequently, Nₚh in the bottom cell is increased, thereby, decreasing Nₚh in the top cell and subsequently matching the JₜSC between top and bottom cells.

To estimate energy conversion efficiency in tandem solar cells, we calculated JₜSC, fill factor (FF), and V蔟 using the following relations:

\[ V\text{tandem} = V\text{bottom} + V\text{top}, \]

\[ J\text{tandem} = \min(J\text{bottom}, J\text{top}). \]

The simulated results are shown in Fig. 6. As expected, when charge carriers in both the bottom and top cells are balanced for Case II, the highest JₜSC, V蔟, and energy conversion efficiency are obtained. The JₜSC initially increases but reaches a plateau of ~11 mA/cm² as shown in Fig. 6(a). In contrast, FF in Fig. 6(b) continuously decreases with increased active layer thickness. Therefore, the highest efficiency obtained was about 9% with active layer thicknesses of dₕbottom (PCPDTBT:PC61BM)=146 nm and dₜop (P3HT:PC71BM)=106 nm, as shown in Fig. 6(c). For a wide range of active layer thicknesses for the bottom and top cells for Case II, an overall energy conversion efficiency of 8%–9% can be achieved. However, it should be noted that in our simulations balanced high mobilities in the subcells led to high FF (~0.74) and a corresponding η=9%. If the experimental FF=0.67 is considered, the realistic energy conversion efficiency should reach approximately 8.14%. On the other hand, the energy conversion efficiency for Cases I and III recorded below 6%. For Case I, a rapid drop in current density in Fig. 6(a) is observed and is responsible for the lower η. As shown in Fig. 7(a) for the IV characteristics of individual cells in the tandem structure for Case I, the P3HT:PC71BM top cell has unbalanced charge carrier mobilities that are attributed to the lower current density of the
tandem solar cell design. In contrast, higher current density is observed for Case III but the FF is governed by the PCPDTBT:PC$_{61}$BM bottom cell and is much lower than that of Case I as shown in Fig. 7(b). The reported FF for PCPDTBT:PCBM shows values less than 0.55 (Refs. 5, 17, and 26) while P3HT:PCBM produces FF=0.6–0.69. Therefore, in Case III the lower FF of the bottom PCPDTBT:PC$_{61}$BM cell restricts the efficiency.

IV. CONCLUSION

Based on optical and electrical simulations, we investigated the optimal design of tandem organic solar cells using PCPDTBT:PC$_{61}$BM for the bottom subcell and P3HT:PC$_{71}$BM for the top cell. It is found that the achievable energy conversion efficiency of this device structure can be as high as 9%. However, if charge carriers are unbalanced in either subcell, energy conversion efficiencies can drop to 4%–6% as a result of either lower current density or lower FF in the subcell. Therefore, it is required that charge carrier mobilities be balanced in each subcell to achieve the highest energy conversion efficiencies in organic tandem structures.

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