Organic Solar Cells with Open Circuit Voltage over 1.25 V Employing Tetraphenyldibenzoperiﬂanthene as the Acceptor

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Abstract: Organic photovoltaic devices utilizing α-sexithiophene (6T) as a donor and tetraphenyldibenzoperiﬂanthene (DBP) as an acceptor were fabricated and compared to devices utilizing DBP as a donor and C60 as an acceptor. The 6T/DBP devices exhibit substantially higher open circuit voltage, 1.27 V compared to 0.86 V for DBP/C60, as a consequence of the higher energy charge transfer state formed. The 6T/DBP devices yield short-circuit current of 3.9 mA/cm², open-circuit voltage of 1.27 V, and fill factor of 0.55, resulting in a power conversion efficiency of 2.8%. Atomic force microscopy studies show that 6T forms textured films on indium-tin oxide, and subsequent deposition of DBP inﬁlls the surface. Optical modeling provides insight into the ideal active layer and transport layer thicknesses. A power conversion efficiency of close to 3% is achieved for a fairly large process window of layer thickness combinations. The high open-circuit voltage in conjunction with absorption out to a wavelength of 650 nm make this material combination especially attractive for tandem devices.

1. Introduction

Organic photovoltaics (OPVs) have been touted for their low material costs and compatibility with low-cost processing techniques. Nevertheless, their power conversion efficiencies continue to lag behind traditional inorganic solar technologies. Over the past several years, the internal quantum efﬁciency for state of the art organic photovoltaic devices has approached unity. This has been due to the development of precise understanding and control of the morphology present as well as the phenomena occurring within devices. However, despite substantial gains achieved in efﬁcient photocurrent production, the open-circuit voltage (VOC) of organic devices is generally low and serves as a substantial limit to overall device performance. The poor VOC can ultimately be traced back to limitations imposed by fullerenes, which, despite their widespread use, typically exhibit voltages of less than 1 V in devices. To overcome this problem, alternative strategies have been developed to obtain high VOC in organic devices through the judicious selection of active layer materials with lower electron afﬁnity.

Small-molecule OPVs, which incorporate donors related to perylene, such as diindenoperylene (DIP) and tetraphenyldibenzoperiﬂanthene (DBP), have demonstrated high performance as donor materials. Due to their high hole mobilities and favorable film morphologies (although DIP is crystalline and DBP amorphous), devices employing these materials have been shown to exhibit large fill factors (FF) in excess of 0.70 in planar heterojunction devices. Additionally, luminescence quenching measurements have revealed that these materials can have relatively long exciton diffusion lengths (EDL). For DIP an EDL of up to 100 nm has been found, while for DBP the EDL is signiﬁcantly reduced to approximately 10 nm. In conjunction with its high hole mobility, DIP also exhibits high electron mobility, and OPVs utilizing DIP as an acceptor in conjunction with 6T as donor have a reported VOC of 1.24 V, which can further be increased to 1.35 V if substrate heating is used. However, these devices suffer from low photocurrents due to the poor absorption of DIP.

Planar-mixed heterojunction (PHJ) devices comprising a DBP:C70 active layer have exhibited efﬁciencies of 8.1% in single junction devices and a tandem device with 11.1% efﬁciency has been fabricated utilizing two DBP:C70 subcells. Thus, it would be extremely desirable to develop a device utilizing DIP with a substantially enhanced VOC in order to improve both single-cell and tandem device performance.

In this article, we examine the performance of planar heterojunction 6T/DBP solar cells in comparison to DBP/C60. The 6T/DBP devices exhibit a large VOC of 1.27 ± 0.01 V. Variable-temperature device measurements in conjunction with electroluminescence spectroscopy reveal that the large VOC is...
due to a higher energy charge transfer state compared to the value measured for DBP/C₆₀ devices. Further optimization of the devices was performed to illustrate the importance of hole and electron transport layers.

2. RESULTS AND DISCUSSION

The molecular structures and absorption spectra for C₆₀, 6T, and DBP are shown in Figure 1. Both 6T and C₆₀ predominantly absorb in the short wavelength range of the solar spectrum up to a wavelength of 550 nm, while DBP absorbs intensely between 500 and 650 nm. In conjunction, both DBP/C₆₀ and 6T/DBP absorb complementarily. The frontier molecular orbital energies measured for these materials show that DBP has a HOMO of 5.4 eV and LUMO of 3.1 eV, C₆₀ a LUMO of 4.0 eV, and 6T a HOMO of 4.7 (HOMO = highest occupied molecular orbital; LUMO = lowest unoccupied molecular orbital).¹⁴,¹⁶,¹⁷

2.1. Photovoltaic Performance and Optimization. To compare the photovoltaic performance of these materials, OPVs with the structure ITO/6T(60 nm)/DBP(20 nm)/BCP(10 nm)/Al and ITO/MoO₃(10 nm)/DBP(20 nm)/C₆₀(40 nm)/BCP(10 nm)/Al were fabricated through vacuum deposition. For completeness we should also consider OPVs with a 6T donor and C₆₀ acceptor. This device has been reported previously¹⁴,¹⁸ and gives very poor performance. An OPV with the structure ITO/PEDOT:PSS/6T/C₆₀/BCP/Al gives a V₉C of 0.44 V and JₛC and FF of 2.6 mA/cm² and 0.61, respectively, at 1 sun AM1.5 illumination. The poor performance of these devices is due to large energy losses from both the formation of CT states and charge recombination, and we will not include them in our comparison for the present study.

Current vs voltage (J−V), device performance parameters, and external quantum efficiency (EQE) curves are shown in Figure 2 for the two DBP based devices. The DBP/C₆₀ and 6T/DBP devices yield short-circuit currents (JₛC) of 6.1 ± 0.1 and 3.9 ± 0.1 mA/cm², respectively, for the given thicknesses. The error bar indicates variations between nominally identical devices. EQE measurements reveal the lower photocurrent in the 6T/DBP devices derives from a reduced photoresponse in the wavelength range between 400 and 500 nm (where C₆₀ absorbs stronger than 6T (Figure 1)). In contrast to the lower photocurrent, the V₉C of the 6T/DBP device is 1.27 ± 0.01 V, which is substantially larger than the 0.86 ± 0.01 V observed for DBP/C₆₀. The FF of the DBP/C₆₀ and 6T/DBP devices were 0.68 ± 0.01 and 0.55 ± 0.01, respectively. Overall, the power conversion efficiency (η) was 3.6 ± 0.1% for the DBP/C₆₀ device and 2.7 ± 0.1% for 6T/DBP. These values are in the range typically observed in PHJ cells, which have good fill factors but suffer from only moderate currents.¹⁹−²¹ Nevertheless, the V₉C observed for the 6T/DBP device is among the highest reported for a single-junction OPV, which is the main interest of this article. A related OPV has been reported that
utilizes DBP as an acceptor and dinaphthienothiophene (DNTT) as a donor. This DNTT/DBP OPV gave low FF and \( J_{SC} \) (0.29 and 0.65 mA/cm\(^2\), respectively), but a high \( V_{OC} \) of 1.29 V. The authors ascribe the low performance of these DBP acceptor devices to poor exciton dissociation at the DNTT/DBP interface.

In order to optimize the 6T/DBP device, studies to examine the impact of the DBP and 6T thickness as well as electron transport layer (ETL) and hole transport layer (HTL) were performed. Investigation of the effect of 6T layer thickness revealed no significant change in device performance between 60 and 120 nm as it has minor impact on the optical cavity in agreement with previous reports. Devices with thicknesses of DBP varying between 10 and 40 nm were fabricated, with the \( J-V \) curves presented in Figure 3a and device performance characteristics summarized in Table 1. The \( V_{OC} \) increases slightly with increasing DBP thickness from 1.25 \( \pm \) 0.01 V for 10 nm DBP to 1.30 \( \pm \) 0.01 V for 40 nm DBP, probably due to reduced recombination for better coverage of the 6T layer (see the AFM measurements in the next section). The \( J_{SC} \) increases from 2.8 \( \pm \) 0.1 mA/cm\(^2\) for 10 nm DBP to 4.3 \( \pm \) 0.1 mA/cm\(^2\) for 30 nm DBP, and then decreases to 3.9 \( \pm \) 0.1 mA/cm\(^2\) for 40 nm DBP. The FF decreases monotonically from 0.60 \( \pm \) 0.01 for the 10 nm device to 0.43 \( \pm \) 0.01 for the 40 nm device, indicative of an increased series resistance with increasing DBP thickness. As the DBP thickness increases, \( \eta \) increases from 2.1 \( \pm \) 0.1% for 10 nm DBP to a maximum value of 2.8 \( \pm \) 0.1% for 30 nm DBP.

In an attempt to circumvent the loss in FF associated with increasing DBP thickness while simultaneously optimizing the optical electric field (see also simulation results further below), devices with ETL thicknesses between 0 and 20 nm BCP were fabricated, where the DBP thickness was kept fixed at 30 nm. Representative \( J-V \) curves are shown in Figure 3b. \( J_{SC} \) increases monotonically with BCP thickness from 2.9 \( \pm \) 0.1 to 4.4 \( \pm \) 0.1 mA/cm\(^2\). The FF of the devices increased from 0.35 \( \pm \) 0.01 for 0 nm BCP to 0.60 \( \pm \) 0.01 for 5 nm BCP before decreasing to 0.45 \( \pm \) 0.01 for 20 nm BCP. The devices with 0 nm BCP and 20 nm BCP show evidence of “s”-shaped \( J-V \) characteristics indicative of issues with charge injection and extraction.

In addition to the effect of the ETL, the impact of the HTL was investigated. Devices with 10 nm MoO\(_3\) (at 10 nm BCP and 30 nm DBP) were fabricated and compared to those without MoO\(_3\). The device with MoO\(_3\) exhibited a FF of 0.62 \( \pm \) 0.01, significantly larger than the 0.55 \( \pm \) 0.01 observed for the device with no HTL. However, the photocurrent decreased from 3.9 \( \pm \) 0.1 to 3.1 \( \pm \) 0.1 mA/cm\(^2\) upon the addition of MoO\(_3\). These findings are in agreement with previous work, which has shown that the MoO\(_3\)/organic interface quenches excitons. However, this problem can be overcome by using the appropriate exciton blocking layer. The \( V_{OC} \) was unaffected by the presence of the MoO\(_3\) remaining at 1.27 \( \pm \) 0.01 V.

2.2. Morphological Studies. The concomitant increase in photocurrent with DBP thickness is due to a variety of factors related to the film morphology and optical field intensity within the device. To probe the structure of the donor/acceptor (D/A) interface and final active layer, AFM images were collected on films of 6T and 6T covered with various thicknesses of DBP. The AFM images and representative cross sections can be seen in Figure 4. The 60 nm 6T film is extremely textured with surface features on the order of 50 nm and an RMS (root-mean-squared) roughness of 9.2 nm. This large surface roughness leads to an increase in the surface area of the D/A interface, allowing for increased exciton harvesting. Upon deposition of DBP, the surface roughness decreases to exhibit features on the order of 30 nm with an RMS roughness of 6 nm. This decrease in roughness is indicative of the DBP infilling the 6T microstructure rather than simply templating the surface, which would propagate the roughness to the next layer. These results help rationalize the substantial rise in photocurrent from 10 to 20 nm DBP followed by a smaller increase for 30 nm and even a loss for the 40 nm DBP device. For devices with only 10 nm DBP, the trenches in the 6T film become filled, and the interdigitated nature of the D/A interface allows for collection of a large fraction of excitons.
generated in DBP. For 20 nm, the trenches in the 6T film are expected to be filled, the added DBP coats the surface of the film such that excitons must diffuse further to reach the D/A interface, and a (small) fraction is thus lost to recombination. By further increasing the DBP thickness to 30 and 40 nm, respectively, this fraction grows continuously and an increasing proportion of the excited excitons does not contribute to $J_{SC}$.

### Table 1. Device Performance for 6T/DBP Devices with Various Thicknesses of DBP, HTL, and ETL

<table>
<thead>
<tr>
<th>device</th>
<th>$J_{SC}$ (mA/cm²)</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBP (10 nm)</td>
<td>2.8</td>
<td>1.23</td>
<td>0.60</td>
<td>2.6</td>
</tr>
<tr>
<td>DBP (20 nm)</td>
<td>3.9</td>
<td>1.27</td>
<td>0.55</td>
<td>2.7</td>
</tr>
<tr>
<td>DBP (30 nm)</td>
<td>4.3</td>
<td>1.28</td>
<td>0.50</td>
<td>2.8</td>
</tr>
<tr>
<td>DBP (40 nm)</td>
<td>3.9</td>
<td>1.30</td>
<td>0.43</td>
<td>2.1</td>
</tr>
<tr>
<td>BCP (0 nm)</td>
<td>2.9</td>
<td>1.13</td>
<td>0.35</td>
<td>1.1</td>
</tr>
<tr>
<td>BCP (5 nm)</td>
<td>3.5</td>
<td>1.25</td>
<td>0.60</td>
<td>2.6</td>
</tr>
<tr>
<td>BCP (10 nm)</td>
<td>3.9</td>
<td>1.27</td>
<td>0.55</td>
<td>2.7</td>
</tr>
<tr>
<td>BCP (20 nm)</td>
<td>4.4</td>
<td>1.26</td>
<td>0.45</td>
<td>2.5</td>
</tr>
<tr>
<td>MoO₃ (10 nm)</td>
<td>3.1</td>
<td>1.26</td>
<td>0.62</td>
<td>2.4</td>
</tr>
</tbody>
</table>

“The OPVs have the structure ITO/6T(60 nm)/DBP(x nm)/BCP(y nm)/Al, where $y = 10$ nm when the DBP layer thickness is varied and $x = 20$ nm for the BCP variation. The device with MoO₃ between ITO and 6T has 20 nm DBP and 10 nm BCP.

### 2.3. Optical Electric Field Effects

In conjunction with the surface effects studied via AFM, the optical electric field within the device is substantially affected by the DBP layer thickness. Utilizing the transfer matrix formalism, we modeled the 6T/DBP devices with various thicknesses of DBP for an understanding of the optical cavity effects within these devices. As the AFM data reveal substantial surface roughness, while the transfer matrix formalism assumes pristine, flat interfaces, these simulations are intended to be a qualitative guide for understanding but not an absolute predictor of performance.

Absorbed optical power as a function of position are plotted in Figure 5a for 10, 20, 30, and 40 nm DBP devices. To clearly demonstrate the impact on both materials, the absorbed optical power is plotted at individual wavelengths: 450 nm to illustrate 6T and 610 nm for DBP. Two significant trends can be observed with increasing DBP thickness. First, increasing DBP thickness results in increased absorption, which can be calculated by integrating the absorbed power curves with respect to thickness. Normalized to the absorbed optical power of 10 nm DBP, 20 nm results in an increase in absorption by a factor 1.75, 30 nm by a factor of 2.14, and 40 nm by a factor of 2.32. Second, increasing DBP thickness affects the shape and intensity of the absorbed optical power profile within the device. For 10 nm DBP, absorption is most intense at the 6T/DBP interface and decreases sharply with thickness. Twenty nanometer DBP absorbs with the same intensity as 10 nm DBP.

Figure 4. AFM images and characteristic line profiles of 6T(60 nm) (a,d), 6T(60 nm)/DBP(10 nm) (b,e), and 6T(60 nm)/DBP(20 nm) (c,f).
at the 6T/DBP interface, but the slope of the absorbed optical power is decreased. At 30 and 40 nm DBP, the intensity of the absorbed optical power at the 6T/DBP interface decreases, and the slope continues to decrease, too. These simulations corroborate the observed device performance where $J_{SC}$ initially increases with thickness due to enhanced absorption but then plateaus and decreases due to exciton generation shifting away from the D/A interface deeper into the DBP layer. This is due to the short exciton diffusion length of DBP of approximately 10 nm.7

The devices with varying thickness of ETL attempt to maximize the absorbed optical power within a layer thickness that is limited by the exciton diffusion length. Absorbed optical power as a function of position are plotted in Figure 5b for devices with 0, 5, 10, and 20 nm BCP. To clearly demonstrate the impact on both materials, the absorbed optical power is plotted at individual wavelengths: 450 nm to illustrate 6T and 610 nm for DBP. The simulations show that absorbed optical power increases monotonically with BCP thickness. The total absorption can be calculated by integrating the absorbed power curves with respect to thickness. Normalized to the absorbed optical power of 0 nm BCP, 5 nm results in an increase in absorption by a factor 1.16, 10 nm by a factor of 1.30, and 20 nm by a factor of 1.48. These values are in staggeringly good agreement with the observed trend in $J_{SC}$, which increases by a factor of 1.2 for 5 nm, 1.3 for 10 nm, and 1.5 for 20 nm.

2.4. Determination of the Energy of the Charge Transfer State. The energy of the intermolecular charge transfer state ($E_{CT}$) formed between donor and acceptor has been shown to correlate linearly with $V_{OC}$ and the two

Figure 5. (a) Simulated spatial distribution of the absorbed optical power for 6T/DBP devices with various DBP thicknesses at $\lambda = 450$ and 610 nm. (b) Simulated spatial distribution of the absorbed optical power for 6T/DBP devices with various BCP thicknesses at $\lambda = 450$ and 610 nm.

Figure 6. EQE and EL measurements for DBP(20 nm)/C$_{60}$(50 nm) (left) and 6T(60 nm)/DBP(30 nm) (right) planar heterojunction devices. For comparison we have also included a DBP(5 nm)/DBP:C$_{60}$(1:2, 50 nm)/C$_{60}$(10 nm) planar-mixed heterojunction device in the left diagram. EQE curves were fit using eq 2 and EL curves fit with eq 3.
quantities can be related through a modified Shockley–Queisser analysis yielding eq 1.28

\[ V_{OC} = \frac{1}{q} \left( E_{CT} + kT \ln \left( \frac{f \lambda^2}{4 \pi \pi (E_{CT} - \lambda)} \right) + kT \ln(EQE_{EL}) \right) \]

where \( q \) is the elementary charge, \( k \) is Boltzmann’s constant, \( T \) is the temperature, \( h \) is Planck’s constant, \( \lambda \) is the reorganization energy, and \( \text{EQE}_{\text{EL}} \) is the electroluminescence quantum efficiency of the CT state. \( E_{CT} \) can be experimentally determined through sensitive measurements of device EQE and electroluminescence (EL). Values for \( E_{CT} \) can be extracted by fitting the low and high energy portions of the spectra to eqs 2 and 3 for EQE and electroluminescence, respectively:

\[ \text{EQE} \propto \frac{f}{E \sqrt{4 \pi kT}} e^{-\frac{(E_{CT}+\lambda-E)^2}{4 kT}} \]  

(2)

\[ \frac{I_E}{E} \propto \frac{f}{E \sqrt{4 \pi kT}} e^{-\frac{(E_{CT}-\lambda-E)^2}{4 kT}} \]  

(3)

where \( I_E \) is the emission intensity and \( E \) is photon energy.

Figure 6 shows the results of the EQE and EL measurements for DBP/C_{60} and 6T/DBP planar heterojunction devices. The DBP/C_{60} device shows an energetically well separated signal of both CT absorption and emission, which can be fit to an \( E_{CT} \) of 1.45 eV with \( \lambda = 0.22 \) eV. However, in the 6T/DBP device CT absorption and emission features are superimposed by the neat DBP signals. Nevertheless, a CT energy of about 1.75 eV (with \( \lambda = 0.25 \) eV) can be determined. We note that much stronger CT bands are observed for mixtures of DBP and C_{60} (see Figure 6). However, within the uncertainty of this method, the \( E_{CT} \) is almost the same (1.49 eV) and the reorganization energy is only slightly smaller (0.17 eV). For blends of 6T and DBP, the EQE and EL spectra are very similar to the planar heterojunction devices, indicating that both materials are not very well miscible.

An alternative method to determine \( E_{CT} \) is the linear extrapolation of \( V_{OC} \) as a function of temperature to 0 K.13,28 The results of the temperature-dependent measurements of \( V_{OC} \) for DBP/C_{60} and 6T/DBP devices are shown in Figure 7 for varying illumination intensities. Fits to the linear portion of the data reveal \( E_{CT} \) of 1.48 and 1.77 eV for DBP/C_{60} and 6T/DBP, respectively. \( E_{CT} \) has been shown to have a slight temperature dependence thus that the values determined by extrapolation to 0 K provide a lower limit on the value of \( E_{CT} \) at ambient temperature.16 Regarding this uncertainty, the obtained values by optical spectroscopy and temperature-dependent electrical data are in excellent agreement. Thus, the observed increase in \( E_{CT} \) accounts very well for the increase in \( V_{OC} \) from DBP/C_{60} to 6T/DBP.

The 6T/DBP devices are particularly interesting in the context of tandem OPV devices. Tandem devices have exhibited exceptional performance by relaxing some of the extensive requirements placed on OPV materials. For example, in tandem devices, it is possible to specifically target separate portions of the solar spectrum with separate subcells19,29,30 or utilize multiple, thinner identical subcells resulting in reduced resistivity and increased absorption.31,32 However, despite the high power conversion efficiencies exhibited in these devices, the \( V_{OC} \) has not been optimized to maximize subcell voltage. For example, the tandem device with 11.1% efficiency reported by Xiao et al. contains two DBP:C_{70} subcells, which only produce 0.86 V each.15 These subcells absorb photons with energies greater than 1.8 eV and more than half of that energy is lost. By contrast, the total energy loss in 6T/DBP, which has an optical gap of about 1.9 eV, is only about 0.6 eV and is thus right at the minimum energy required for efficient charge generation.33
3. CONCLUSION

In summary, we fabricated a series of OPVs to examine the functionality of DBP as an acceptor in devices with 6T as a donor. The 6T/DBP device exhibits V_{OC} of 1.27 ± 0.01 V, among the highest demonstrated in an OPV, and \eta of 2.8 ± 0.1%. Compared to a DBP/C_{60} device, the 6T/DBP device exhibits substantially larger V_{OC} due to its higher \eta. Studies on the impact of DBP, HTLs, and ETL reveal that selection of the appropriate material and thickness can significantly affect both the J_{SC} and FF of devices. Specifically, the J_{SC} can be increased to 4.4 ± 0.1 mA/cm^2 with 20 nm BCP and the FF to 0.62 ± 0.01 with 10 nm MoO_{3}, although not at the same time. AFM reveals that 6T forms a highly textured surface, which allows for an interdigitated structure of donor and acceptor upon deposition of DBP. Optical modeling shows that shifting the active layer away from the cathode increases absorbed power by a factor of 1.5. Further improvement of the efficiency of the 6T/DBP cell through the fabrication of optimized bulk-heterojunction and planar-mixed heterojunction cells followed by incorporation into tandem devices is expected.

4. EXPERIMENTAL SECTION

Materials. MoO_{3} 99.999% (Alfa-Aesar), DBP (Lumtec), 6T (Sigma-Aldrich), BCP (Sigma-Aldrich), C_{60} (MER), Al 99.9999% (Alfa-Aesar). 6T, BCP, and C_{60} were sublimed before use, and other materials were used as received.

Device Fabrication and Testing. Devices were grown on glass substrates with 150 nm indium tin oxide patterned in 2 mm stripes. Prior to deposition, the substrates were cleaned in a nitrogen atmosphere. A thin 0.05 nm/s was used for the other organics. Finally, a 100 nm-thick Al cathode was deposited at 0.2 nm/s through a shadow mask with a 2 mm slit deﬁned through a 0.01% with 10 nm MoO_{3}, although not at the same time. AFM reveals that 6T forms a highly textured surface, which allows for an interdigitated structure of donor and acceptor upon deposition of DBP. Optical modeling shows that shifting the active layer away from the cathode increases absorbed power by a factor of 1.5. Further improvement of the efficiency of the 6T/DBP cell through the fabrication of optimized bulk-heterojunction and planar-mixed heterojunction cells followed by incorporation into tandem devices is expected.

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