High open-circuit voltage, high fill factor single-junction organic solar cells

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We demonstrate a high open circuit voltage (V_{oc}), high fill factor, single-junction organic photovoltaic (OPV) cell consisting of tetraphenyldibenzoperiflanthene (DBP) as the donor and pyrrolo[3,4-c]pyrrole- 1,4-dione, 3,6-bis(4-chlorophenyl)-2, 5-dihydro (DPP) as the acceptor in a vapor-deposited, fullerene free organic solar cell. Under one sun illumination, the DBP/DPP based planar heterojunction solar cell exhibits a V_{oc} of 1.19 V with a fill factor of 0.67, leading to a final power conversion efficiency (PCE) of 2.2%. Our achieved V_{oc} is the highest value reported thus far for a single-junction, high fill factor organic solar cell. A planar-mixed device architecture allows for high exciton generation while maintaining high exciton dissociation, leading to a PCE of 3.2%. The DBP and DPP interface creates a high interface energy gap (ΔE_{DA}) and relatively low saturation current (J_S) due to poor coupling across the donor-acceptor interface. These results support earlier theories that high V_{oc} values are dependent on large ΔE_{DA} and low J_S for a given donor-acceptor combination in OPVs. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4894089]

Organic photovoltaics (OPVs) have drawn increasing attention as a potential low-cost and easy-processing renewable energy.[1,2] Although the power conversion efficiency (PCE) of organic solar cells has made remarkable progress in the past 30 years, OPVs still suffer from low open circuit voltage (V_{oc}), a limitation for the development of OPVs as high performance devices. The main reason is that the acceptor materials in OPVs have been dominated by fullerene molecules and their derivatives, which have a narrow range of electronic bandgaps.[3] As several publications have demonstrated, the value of V_{oc} depends significantly on the donor (D)/acceptor (A) interface energy gap (ΔE_{DA}), which is the difference between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the fullerene acceptor.[4] The second reason is that the donor/fullerene heterointerface necessary for exciton dissociation in an OPV often leads to a relatively high magnitude of the diode saturation current density, J_s, which negatively affects the maximum achievable V_{oc}. Third, the preference for materials displaying long exciton diffusion lengths narrows the various possible donor-acceptor combinations.

These problems have stimulated investigation into non-fullerene acceptors. Currently, the sate-of -the-art, fullerene-free OPV uses a subphthalocyanine chloride (SubPc) donor and a fused fluorinated SubPc dimer acceptor to achieve a comparable PCE as the standard SubPc/C_{60} OPV.[5] Long-range exciton transfer between SubPc and subnaphthalocyanine chloride (SubNc) was also exploited to create an 8.4% efficient fullerene-free OPV.[6] We note, however, that the V_{oc} for the fullerene-free OPVs reported thus far remains largely limited to $\leq$1 V. In this paper, we present a high V_{oc}, high fill factor (FF) single-junction organic photovoltaic cell that consists of tetraphenyldibenzoperiflanthene (DBP) as a donor and pyrrolo[3,4-c]pyrrole-1,4-dione, 3,6-bis(4-chlorophenyl)–2, 5-dihydro (DPP) as a non-fullerene acceptor. Devices using the small molecule DPP as the acceptor component in vapor-deposited, fullerene-free organic solar cells are sparse, although diketo-pyrrolo[3,4-c]pyrrole moieties were previously incorporated into the donor component of various solution-processed devices.[7] Planar-mixed (PM-HJ) devices[8] containing DBP/DPP are presented as efficient architectures with which to increase exciton photogeneration while maintaining high V_{oc} and FF. We also explore the importance of molecular composition and intermolecular coupling at the D/A heterointerface in determining a high V_{oc} in OPVs, independent of ΔE_{DA} values.

Both planar heterojunction (PHJ) and PM-HJ OPVs were fabricated on pre-patterned indium tin oxide (ITO) on glass substrates with the following device structure: Molybdenum oxide (MoO_3)/DBP/DPP/Bathocuproine (BCP)/Ag. In this structure, MoO_3 served as an efficient hole transport layer and BCP as an effective exciton blocking layer to reduce the series resistance and improve the FF and PCE of the device.[9] All the layers of the photovoltaic devices were deposited by thermal evaporation under ultrahigh vacuum ($<10^{-6}$Torr). MoO_3 and the subsequent organic layers were blanket deposited without a vacuum break, while the top Ag cathode was deposited with a metal shadow mask after a vacuum break. The final device area was 1.21 mm^2. All device handling and transfer operations, and electrical measurements, were performed in nitrogen filled gloveboxes. Electrical characterizations were performed under dark conditions and 1 sun illumination, and results were not corrected for spectral mismatch. The morphology of the DBP and DPP active layers were investigated using atomic force microscopy and X-ray diffraction.[10]

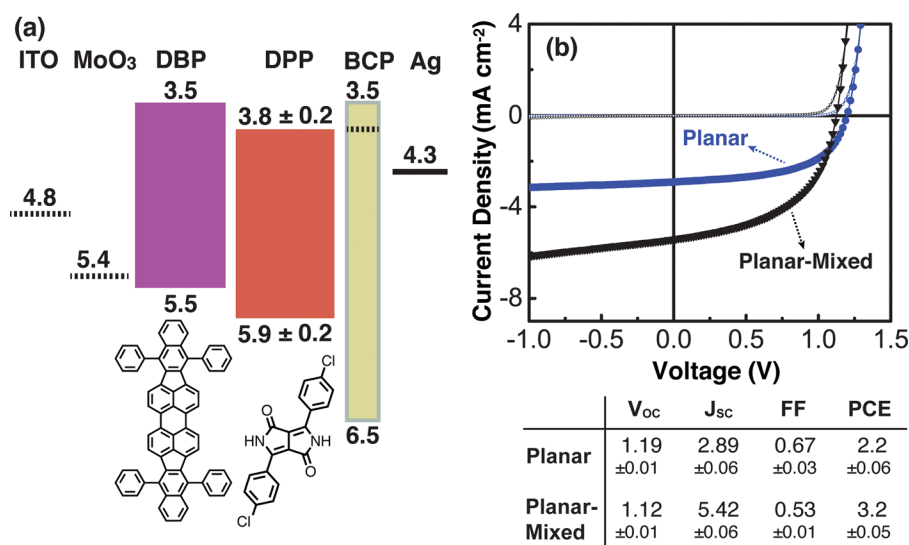[a]Author to whom correspondence should be addressed. Electronic mail: tlandrew@wisc.edu

FIG. 1. (a) The energy band structure of a fullerene-free solar cell containing a DBP-DPP planar heterojunction, including the chemical structures of DBP and DPP. (b) Representative current density-voltage characteristics of both planar and planar-mixed DBP/DPP heterojunction solar cells. The current densities under light (filled symbols) were measured under 1 sun. The inset details median values of pertinent device metrics obtained over 20 devices.

	V_{OC}	J_{SC}	FF	PCE
Planar	1.19 ±0.01	2.89 ±0.06	0.67 ±0.03	2.2 ±0.06
Planar-Mixed	1.12 ±0.01	5.42 ±0.06	0.53 ±0.01	3.2 ±0.05

The energy band structure of the PHJ solar cell is shown in Figure 1(a). The oxidation onset of DPP films were measured using cyclic voltammetry (CV), and the corresponding valence band edge was calculated using a calibrated correction.[10,11] The conduction band edge was estimated using the transport gap, which was calculated from the optical band gap recorded for neat DPP films.[12] The energy band positions of the other materials employed in this solar cell are previously reported.[13] As illustrated in Figure 1(a), DPP forms a Type II heterojunction with DBP. Figure 1(b) shows the current density-voltage characteristics of our optimized PHJ and PM-HJ solar cells in the dark and under 100 mW/cm^2 white light (1 sun) illumination. The thicknesses of MoO$_3$, DBP, DPP, and BCP in the PHJ device are 5 nm, 25 nm, 15 nm, and 7.5 nm, respectively. The planar junction solar cell exhibits a power conversion efficiency of 2.2% with a V$_{oc}$ of 1.19 V, a short circuit current density (J$_{sc}$) of 2.89 mA/cm^2, and a FF above 0.67. A V$_{oc}$ value of 1.19 V with a concurrently high FF value of 0.67 is the highest reported for a single-junction organic solar cell. The PM-HJ structure is as follows: glass/ITO 150 nm/MoO$_3$ 5 nm/DBP 5 nm/DBP:DPP 30 nm/DPP 5 nm/BCP 7.5 nm/Ag 100 nm. The J$_{sc}$ of the PM-HJ device is 5.42 mA/cm^2, which is considerably higher than that of the PHJ device because of higher exciton photogeneration in the bulk heterojunction

layer of the PM-HJ device. However, the FF of the PM-HJ cell is significantly lower than that of the PHJ cell due to increased recombination in the mixed layer. The V$_{oc}$ values of the PM-HJ cell are only slightly lower than those of the PHJ cell and reach 1.13 V. The comparison of these two device architectures shows that a PCE value of 3.2% can be achieved with the PM-HJ structure. Notably, the fill factors of all the devices reported herein are not limited by the close conduction band offset (0.3 ± 0.2 V) between donor and acceptor.[14]

The optimal thickness of the photoactive layers in an organic solar cell depends on exciton diffusion lengths and absorption coefficients.[15] To optimize device performance, various layer thicknesses for MoO$_3$, DPP, DBP, and BCP layers were investigated. The dependence of the cell response on each layer's thickness is shown in Figure 2. At first, we varied the thickness of MoO$_3$ between 5–25 nm, with the rest of the solar cell structure being fixed as: glass/ITO 150 nm/MoO$_3$ /DBP 25 nm/DPP 15 nm/BCP 10 nm/Ag 100 nm. The values of J$_{sc}$, V$_{oc}$, FF, and PCE were observed to increase monotonically as the MoO$_3$ thickness decreased. Next, the DPP layer thickness was varied between 10–20 nm. Optimal performance was achieved with a DPP thickness of 15 nm. Then the thickness of DBP donor layer was varied within 20–30 nm, while the rest of the device structure was fixed as
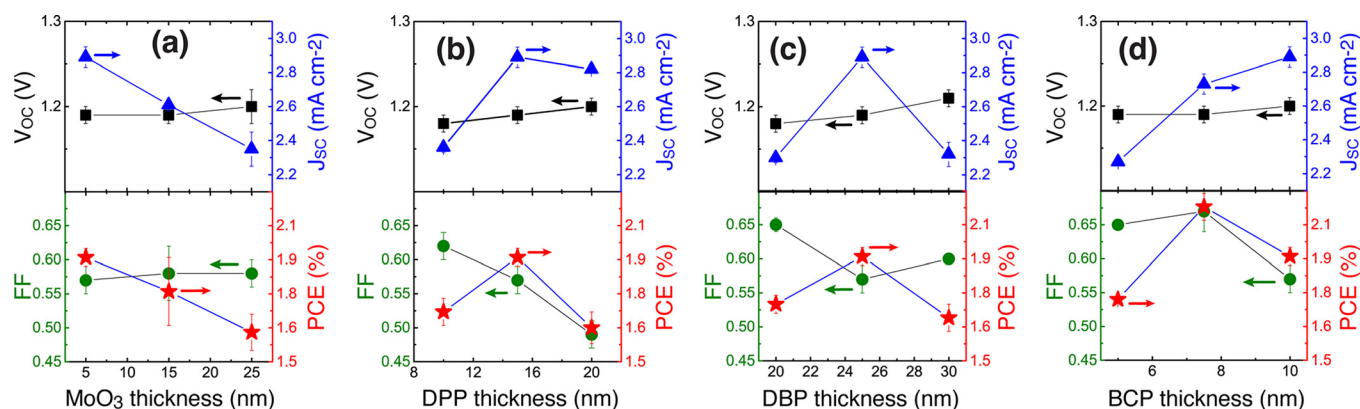

FIG. 2. Variation of V$_{oc}$ (black squares), J$_{sc}$ (blue triangles), FF (green dots), and PCE (red stars) for planar heterojunction devices with different MoO$_3$, DPP, DBP, and BCP layer thicknesses. All devices were measured under 1 sun.
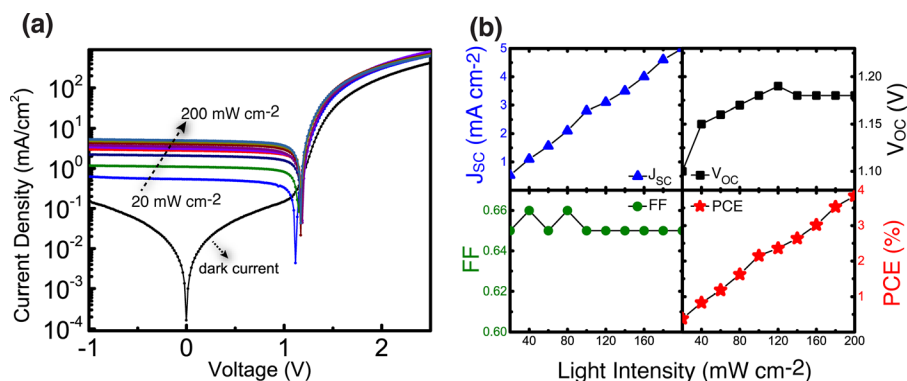
FIG. 3. Performance characteristics (J_{sc}, V_{oc}, FF, and PCE) of the optimized DBP/DPP PHJ solar cell as a function of incident light intensity. A maximum PCE of 3.8% is achieved at 200 mW/cm².

follows: glass/ITO 150 nm/MoO₃ 5 nm/DBP/DPP 15 nm/ BCP 10 nm/Ag 100 nm. As seen in Figure 2, a DBP layer thickness of 25 nm leads to maximal power conversion efficiency. We infer from these results that desirable balance between exciton diffusion length and photon absorption in the DBP and DPP layers can be obtained with layer thicknesses of 25 and 15 nm, respectively. Last, the BCP layer thickness was varied within 5–10 nm. We found that when the thickness of BCP is 7.5 nm, the FF reached its maximum value, which leads to the maximal PCE value. Notably, the values of V_{oc} of the solar cells remained constant at 1.19 V with negligible error, independent of the thickness of any layer of the solar cell. This observation suggests that a strong and stable electric field is generated at the DBP/DPP interface irrespective of device structure, which maximizes exciton dissociation and minimizes detrimental band bending of donor and acceptor energy levels at the DA interface.

To further characterize solar cell behavior, the current density-voltage response of the optimized PHJ device was recorded under various incident light intensities between 20 and 200 mW/cm² with 20 mW/cm² increments. As shown in Figure 3, the J_{sc} of the solar cell increases linearly with incident light intensity, indicating an absence of substantial space charge accumulation in the active layer.[16] A small increase in V_{oc} is also observed between 20 to 120 mW/cm², with the values stabilizing at 1.18V past 120 mW/cm² incident light intensity. Notably, the FF remains stable at 0.65 between 20–200 mW/cm²; in comparison, the fill factor of most OPVs is known to decrease at higher incident light intensities due to exciton-polaron annihilation.[3,17] A

maximum PCE of 3.8% is observed for the DBP/DPP PHJ solar cell at 200 mW/cm².

A control device with vapor deposited C₆₀ as the acceptor was fabricated to further explore the performance of DPP as a fullerene alternative and to investigate the relationship between material properties and V_{oc}. The following structure was used: glass/ITO 150 nm/ MoO₃ 15 nm/DBP 20 nm/C₆₀ 40 nm/BCP 6.5 nm/Ag 100 nm. Based on the D/A heterojunctions formed between DBP and either DPP or C₆₀, the estimated values of ΔE_{DA} are 1.7 and 1.5 eV, respectively. It is clear that our observed V_{oc} values do not follow the thermodynamic ΔE_{DA} model, since as Figure 4 shows, the V_{oc} of the two solar cells are not comparable. This observation prompted us to explore another model to explain the origin of V_{oc}.

For most organic heterojunction diodes with ideality factor (n) close to 2,[10] the saturation current J_s can be expressed as Eq. (1) shows:

$$J_s = J_{so} \exp\left(-\frac{\Delta E_{DA}}{2nkT}\right), \qquad (1)$$

where n is the diode ideality factor, q is the fundamental charge, and T is the absolute temperature. Further, V_{oc} can be expressed as follows:

$$V_{oc} = \frac{nkT}{q} \ln\left(\frac{J_{sc}}{J_{so}}\right) + \frac{\Delta E_{DA}}{2q}. \qquad (2)$$

Equation (2) describes the dependence of V_{oc} on ΔE_{DA} and J_{so}, which quantifies the strength of intermolecular coupling at the D/A heterointerface.[18,19] Mathematically, J_{so} must be minimized in order to get the maximum V_{oc} for a given D/A pair. The DBP/DPP and DBP/C₆₀ heterojunctions have similar calculated ΔE_{DA} values, and the resulting DBP/DPP solar cell displays smaller J_{sc}; however, the DPP based solar cell has a lower J_s and a surprisingly higher V_{oc}. Therefore, we conclude that a lower saturation current value, arising from a reduced J_{so}, leads to the high observed V_{oc} with DPP. The lower J_{so} in DBP/DPP planar heterojunction devices likely kinetically suppresses dark recombination at the D/A interface and can be attributed to weaker intermolecular D/A coupling across the DBP/DPP heterointerface compared to DBP/ C₆₀ heterojunctions.[10] This result strongly supports the importance of J_{so} in determining the V_{oc}.

The external quantum efficiency (EQE) of the DBP/DPP PHJ solar cell reported herein was also measured, and the corresponding internal quantum efficiency (IQE) was
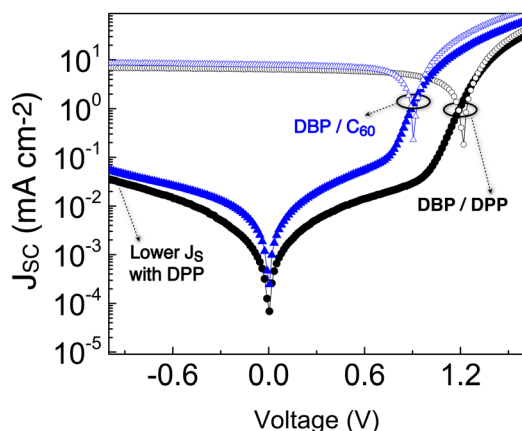

FIG. 4. Semi-log scale J-V curve in the dark (filled) and under 1 sun (open) for DPP (black circles) and C₆₀ (blue triangles) based OPVs.
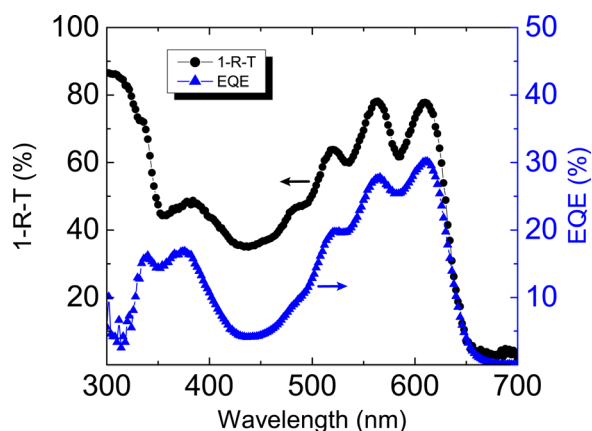
FIG. 5. 1-R-T spectrum (black dots) and EQE (blue triangles) as a function of the wavelength of the DBP/DPP planar heterojunction solar cell.

calculated by dividing the recorded EQE by the light absorbed by the device (defined as 1-reflection (R)-transmission (T)). As seen in Figure 5, the EQE spectrum is largely coincident with the device absorption spectrum. A maximum EQE of 30% is observed at 610 nm, corresponding to an IQE of 40%. This relatively low EQE is attributed to the low absorption coefficient of DPP. Considering that the absorption spectrum of the device mostly resembles the absorption spectrum of DBP, we posit that excitons generated in the DBP layer are predominantly responsible for the photocurrent generated by the solar cell. Another hypothesized reason for the low EQE is the thin DBP layer, which overcomes the issue of short exciton diffusion length but limits the overall light absorption of the device.

We report a high open circuit voltage (V_{oc}), high fill factor single-junction OPV cell using a DBP/DPP heterojunction. The optimized planar heterojunction solar cell exhibits a power conversion efficiency of 2.2% and a surprisingly high V_{oc} of 1.19 V, which is the highest V_{oc} value ever reported for an OPV. Planar-mixed heterojunction devices allow for higher exciton photogeneration and exhibit a PCE of 3.2%. These results demonstrate that DPP can serve as an efficient fullerene alternative in vapor-deposited OPVs. With DBP as the donor, the donor-acceptor (D/A) interface of the reported solar cell displays a high interface energy gap (ΔE_{DA}) and a relatively low diode saturation current (J_S) due to desirably weak D/A coupling across the heterointerface.

These results provide evidence for the importance of high ΔE_{DA} and low J_S to create high observed V_{oc}. While previous studies established the relationship between V_{oc}, ΔE_{DA} and J_S for various donor materials with fullerene acceptors, our work demonstrates that a similar relationship can be posited for non-fullerene acceptors in OPVs.

[1]C. W. Tang, Appl. Phys. Lett. 48, 183 (1986).
[2]R. F. Service, Science 332, 293 (2011).
[3]E. T. Hoke, K. Vandewal, J. A. Bartelt, W. R. Mateker, J. D. Douglas, R. Noriega, K. R. Graham, J. M. J. Fréchet, A. Salleo, and M. D. McGehee, Adv. Energy Mater. 3, 220 (2013).
[4]B. P. Rand, D. P. Burk, and S. R. Forrest, Phys. Rev. B. 75, 115327 (2007).
[5]B. Verreet, B. P. Rand, D. Cheyns, A. Hadipour, T. Aernouts, P. Heremans, A. Medina, C. G. Claessens, and T. Torres, Adv. Energy Mater. 1, 565 (2011).
[6]K. Cnops, B. P. Rand, D. Cheyns, B. Verreet, M. A. Empl, and P. Heremans, Nat. Commun. 5, 3406 (2014).
[7]B. Walker, C. Kim, and T.-Q. Nguyen, Chem. Mater. 23, 470 (2011).
[8]J. Wagner, M. Gruber, A. Hinderhofer, A. Wilke, B. Bröker, J. Frisch, P. Amsalem, A. Vollmer, A. Opitz, N. Koch, F. Schreiber, and W. Brütting, Adv. Funct. Mater. 20, 4295 (2010).
[9]D. F. O'Brien, M. A. Baldo, M. E. Thompson, and S. R. Forrest, Appl. Phys. Lett. 74, 442 (1999).
[10]See supplementary material at http://dx.doi.org/10.1063/1.4894089 for cyclic voltammograms, absorption spectra, AFMs, and XRD of compounds described herein, calculated diode ideality factors and space-filling simulations of the DBP-DPP and DBP-C$_{60}$ heterojunctions.
[11]B. Dandrade, S. Datta, S. Forrest, P. Djurovich, E. Polikarpov, and M. Thompson, Org. Electron. 6, 11 (2005).
[12]P. I. Djurovich, E. I. Mayo, S. R. Forrest, and M. E. Thompson, Org. Electron. 10, 515 (2009).
[13]J. A. Macko, R. R. Lunt, T. P. Osedach, P. R. Brown, M. C. Barr, K. K. Gleason, and V. Bulović, Phys. Chem. Chem. Phys. 14, 14548 (2012).
[14]N. S. Sariciftci, C. J. Brabec, and G. Dennler, in Semiconducting Polymers, edited by G. Hadziioannou and G. G. Malliaras (Wiley-VCH: Weinheim, Germany, 2006).
[15]V. P. Singh, D. L. Linam, D. W. Dils, J. C. McClure, and G. B. Lush, Sol. Energy Mater. Sol. Cells 63, 445 (2000).
[16]J. Y. Kim, K. Lee, N. E. Coates, D. Moses, T. Q. Nguyen, M. Dante, and A. J. Heeger, Science 317, 222 (2007).
[17]L. Tzabari, V. Zayats, and N. Tessler, J. Appl. Phys. 114, 154514 (2013).
[18]M. D. Perez, C. Borek, S. R. Forrest, and M. E. Thompson, J. Am. Chem. Soc. 131, 9281 (2009).
[19]C. W. Schlenker and M. E. Thompson, Chem. Commun. 47, 3702 (2011).