ABSTRACT

KITCHEN, BRENT THOMAS. The Influence of Polythiophene Orientation at the Heterojunction Interface on Energy Conversion in Organic Solar Cells. (Under the direction of Dr. Brendan O’Connor).

Organic solar cells are have the potential to provide a cost effective source of renewable energy, however many aspects of the energy conversion processes in these devices remains unknown. In this study, a planar heterojunction (PHJ) that provides a sharp interface between poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM) is used as a model system to research energy conversion in these devices. More specifically, the molecular orientation of the P3HT is varied relative to the interface to study the effects of the orientation on the energy conversion process. Films are characterized as either edge-on or face-on by grazing incidence X-ray diffraction (GIXD) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. UV-visible spectroscopy is used to determine general film order. It is found that PHJs composed of face-on P3HT layers exhibit higher open-circuit voltage ($V_{OC}$) than those composed of edge-on P3HT layers. This shift is attributed to a shift in the donor molecule’s highest occupied molecular orbital (HOMO) level relative to the PCBM acceptor’s lowest unoccupied molecular orbital (LUMO) level which is consistent with theoretical studies. When compared to a BHJ, normalized by the short-circuit current ($J_{SC}$), the BHJ has a higher $V_{OC}$ than the PHJ suggesting the energy landscape at the heterojunction interface more closely resembles the conditions at the face-on P3HT/PCBM interface. In addition, annealing the bilayer films is used to form BHJ solar cells while maintaining the out-of-plane orientation of the P3HT. It is found that the $V_{OC}$ is independent of out-of-plain P3HT packing in the BHJ solar cell.
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The Influence of Polythiophene Orientation at the Heterojunction Interface on Energy Conversion in Organic Solar Cells

by
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A thesis submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Master of Science

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1. Introduction

Organic solar cells have seen tremendous performance gains over the past several years, with the ultimate goal of providing low cost, efficient devices for widespread use. These gains in performance have been accompanied by an increased understanding of the mechanisms involved in the energy conversion process.[1] These mechanisms include the absorption of light to form an exciton, the diffusion of the exciton to the heterojunction interface, the dissociation of the exciton, and the charge collection of the electron and hole at the cathode and anode respectively. A kinetic representation and simplified energy level diagram of representing these processes from Deibel and Dyakonov is shown in **Figure 1**.[1]

![Figure 1](image_url)

**Figure 1.** Kinetic representation and simplified energy level diagram of energy conversion in organic solar cells from Deibel and Dyakonov.[1] (i) Light absorption forming an exciton, (ii) diffusion of exciton to the heterojunction, (iii) dissociation of the exciton, (iv) separation of the exciton, and (v) charge transport to the electrode.
Critical to these processes are the interfaces between the active components that comprise the device. In particular, the photoactive layer consists of an electron donor and an electron acceptor material with an energy level offset. This energy offset provides a driving force to dissociate the photogenerated excitons into free carriers that are then collected at the solar cell electrodes.[1–3] The energy level difference between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor also provides an upper limit to the open circuit voltage of the cell.[1, 2, 4] Given the critical nature of the donor-acceptor interface, it has been the focus of a number of research studies.[3, 5–9] Of particular interest to this study is the role of the molecular orientation at the heterojunction interface as well as the bulk of the film on the energy conversion process.
2. Background

2.1. Orientation Effects at the Interface

The molecular orientation at the heterojunction interface has recently been investigated in a number of small molecule organic photovoltaic devices.[6], [10], [11] In these studies, the focus is typically on planar heterojunctions (PHJ) photovoltaic devices that provide a simpler structure to isolate the heterojunction than similar bulk heterojunction (BHJ) structures.[5], [6], [12], [13] Bulk heterojunctions consist of an active layer comprised of mixed donor and acceptor molecules. BHJ solar cells are more efficient than PHJ solar cells because of increased heterojunction surface area. However, the mixed state of the molecules does not allow for a probing of the interface between molecules. A planar heterojunction, however, allows for the investigation of interface effects by subsequent layering donor and acceptor films. These studies showed how the molecular orientation of the dye molecule influenced the charge transfer dissociation and recombination rates, and molecular energy levels. Depending on the details of molecular orbital coupling strength, this can have a significant effect on device performance.[2], [10] In addition, molecular packing anisotropy in the film bulk can result in exciton diffusion length anisotropy.[10], [14]

In this thesis, the molecular orientation of poly(3-hexylthiophene) (P3HT) in, P3HT/PCBM [(6,6)-phenyl C61-butyric acid methyl ester] PHJ photovoltaic cells is investigated. While previous work has been done to optimize the performance of bilayers to compete with BHJ solar cells, that is beyond the scope of this work.[15] Instead, this study will look at the effects of molecular orientation of the donor P3HT in both the PHJ and the BHJ device configurations. Of note, is that previous studies focused on small molecule solar...
cells deposited by vacuum deposition methods. Here, the widely studied polymer P3HT is considered. Given the widespread use of P3HT, details of the energy conversion process in P3HT/PCBM solar cells have been considered at length.[1], [16] However a focus on the P3HT orientation with respect to PCBM in the energy conversion process has only been considered theoretically, or implicitly deduced from bulk heterojunction solar cells.[17] Previous work has also shown that there exists a difference in the energy level alignment of P3HT based on its molecular orientation relative to a gold electrode.[7] This energy shift at the heterojunction would create a variation in the open-circuit voltage of the PHJ.[4], [5], [8], [18] Figure 2 shows a schematic of energy level alignment in organic solar cells with respect to donor molecule orientation from Heimel, et al.[17] While a large number of conjugated polymers have been developed, given the structural commonalities in many conjugated polymers of having a conjugated ring backbone with aliphatic side-chains to assist dissolution in solvents, P3HT may provide general features as to the difference in interface character.
Figure 2. Schematic of energy-level alignment at the interface in organic solar cells from Ref [17]. At left, the edge on orientation of the donor molecule results in a higher HOMO level. Center, in between orientations of the donor result in a HOMO level between that of edge-on and face-on orientations. At right, the face on orientation of the donor results in a lower HOMO level.

2.2. Sharp Heterojunction Interface

A planar heterojunction, similar to the small molecule structures would be an optimal structure to investigate the role of P3HT molecular packing orientation. However, until recently it has been difficult to fabricate polymer/fullerene bilayers with a sharp interface.[19–21] Two prominent methods recently demonstrated include the use of orthogonal solvents, and the use of transfer printing processes.[12], [15], [20], [22] The challenge with orthogonal solvents is to create a sharp interface between two materials where intermolecular diffusion has been shown to take place using common orthogonal solvent methods.[15], [19], [23] Here, we apply transfer printing methods previously applied to P3HT/PCBM films to form sharp bilayers.[12], [13], [20], [22]

To fabricate planar heterojunction devices with a sharp interface between donor and acceptor layers, we process the organic semiconductor layers on separate substrates and use
transfer-printing techniques to construct the solar cell. This processing approach allows each film to be individual processed on a separate substrate to manipulate film morphology. Briefly, the P3HT films are initially spun cast onto OTS-treated silicon substrates. The film is then removed using a polydimethylsiloxane (PDMS) stamp and printed onto poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) coated indium tin oxide (ITO) substrates. The PCBM layer is then spin cast on a separate substrate and printed onto the P3HT layer. The printing of the individual layers is done at room temperature to avoid intermixing.[13], [24], [25] This sharp interface allows for the assumption that the surface orientation of the P3HT films is equivalent to the orientation at the P3HT/PCBM interface.

2.3. P3HT/PCBM Intermixing

While this study looks primarily at the effects of orientation at the interface, also of concern is the effect of P3HT orientation in a BHJ on organic photovoltaic (OPV) device performance. To achieve highly oriented bulk heterojunctions, we first construct planar heterojunctions with sharp interfaces. Previous research has shown that the application of heat during or following the printing process causes intermixing between the two polymers.[24], [25] Of particular interest is the work by Ro, et al. which shows a nearly uniform mixing of layers following annealing at 140°C for 60 seconds.[25] This intermixing of layers can be seen in Figure 3. Complete intermixing implies that the heterojunction is no longer locally defined, but rather that it exists at all orientations throughout the film. This allows for the probing of the effects of bulk orientation on the performance of the solar cell.
2.4. Orientation Variation

In this study we vary the out-of-plane orientation on the P3HT layer using a combination spin cast speed and large plastic strains.[26], [27] Shown in Figure 4 is an illustrative definition of the terms “face-on” and “edge-on” used to describe P3HT orientation in this thesis.

**Figure 3.** Depth-dependent PCBM volume fraction for the bilayer with P3HT as determined by neutron reflectivity from Ref [25].
Figure 4. Illustrative representation of (a) face-on and (b) edge on P3HT orientation. The (010) and (100) refer to the associated out-of-plane X-ray scattering peak.

It has been shown spin cast speed can directly influence out-of-plane molecular packing orientation.[26] We exploit this dependence, along with a novel technique to biaxially strain neat P3HT films to allow for the variance of out-of-plane alignment of the P3HT molecules from highly edge-on to predominantly face-on.[27], [28] This process consists of straining a P3HT film in one direction, then straining it in a second direction perpendicular to the first before transferring it to the solar cell stack. The processing condition of the PCBM layer remains constant to isolate the effects of the P3HT orientation. In processing the P3HT, the solution concentrations are varied to ensure that the final film thicknesses are within 10 nm of each other.
3. Experimental

3.1. Materials

The P3HT was obtained from Plextronics, Inc. with a number-averaged molecular mass Mn = 50 kD, a regioregularity of 99%, and a polydispersity of 2.1. The PCBM was obtained from Nano-C with a purity of 99%. The PEDOT:PSS solution was type PVP AI4083, obtained from Heraeus Materials Technology. PDMS was made from SYLGARD 184 Elastomer Kit from Dow Corning at a ratio between 15:1 and 20:1. OTS was obtained from Gelest, Inc.

3.2. Film preparation

The processing conditions of P3HT films under study are given in Table 1.

Table 1. List of processing conditions for P3HT films in study.

<table>
<thead>
<tr>
<th>No.</th>
<th>Solution Concentration (mg/ml)</th>
<th>Solvent</th>
<th>Spin Speed (rpm)</th>
<th>Strain Treatment</th>
<th>Thickness (nm)</th>
<th>Post Cast Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>CF</td>
<td>500</td>
<td>Unstrained</td>
<td>42</td>
<td>As Cast</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>CF</td>
<td>3000</td>
<td>Unstrained</td>
<td>36</td>
<td>As Cast</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>CF</td>
<td>750</td>
<td>Biaxially Strained</td>
<td>41</td>
<td>As Cast</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>DCB</td>
<td>625</td>
<td>Unstrained</td>
<td>42</td>
<td>As Cast</td>
</tr>
<tr>
<td>5</td>
<td>12</td>
<td>DCB</td>
<td>3000</td>
<td>Unstrained</td>
<td>37</td>
<td>As Cast</td>
</tr>
<tr>
<td>6</td>
<td>12</td>
<td>DCB</td>
<td>850</td>
<td>Biaxially Strained</td>
<td>45</td>
<td>As Cast</td>
</tr>
<tr>
<td>Basic BHJ</td>
<td>30</td>
<td>DCB</td>
<td>600</td>
<td>Unstrained</td>
<td>215-234[29]</td>
<td>Annealed</td>
</tr>
</tbody>
</table>
As can be seen in Table 1, P3HT films are cast from both chloroform (CF) and dichlorobenzene (DCB) solvents. This allows for a comparison of aggregate order and a larger variation in out-of-plane packing orientation as discussed below in more detail. The total thickness of the P3HT layer is between 36 nm and 45 nm. The neat P3HT films are spun cast on OTS coated silicon. The PCBM layer is held constant at 38 nm. These layer thicknesses are based on a bilayer device optimization. Neat PCBM films are spun on silicon at 2250 rpm from 35 mg/ml DCB solution. A basic BHJ is prepared for comparison purposes. It is cast from a 1:1 solution of P3HT:PCBM. After spinning, it is solvent annealed for 20 minutes and thermally annealed at 110°C for 10 minutes.[29] All solutions are prepared in a nitrogen filled glovebox and placed on a hotplate at 75°C for a minimum of 12 hours and then allowed to cool down to room temperature before casting. All substrates are cleaned by sonication for 10 minutes in deionized (DI) water, acetone and isopropanol, followed by UV-ozone treatment for 10 minutes, and then rinsed with DI water. PEDOT:PSS films are spun on ITO coated glass at 5000 rpm for 60s and then annealed inside a glovebox at 120°C for 20 minutes.

3.3. Device Construction

Devices are constructed by transfer printing subsequent layers of P3HT and PCBM. P3HT transfer printing is performed in a glovebox while PCBM transfer printing is performed in atmosphere. Removal of the film from the initial substrate is performed by laminating a pre-strained PDMS stamp to the film and then quickly pulling perpendicularly away from the (donor) substrate resulting in the film being completely removed from the
initial substrate and adhering to the PDMS surface. The film on the PDMS is then printed onto a secondary (receiver) substrate by laminating the film stack to the substrate, slowly removing the strain on the PDMS while pulling away from the receiving substrate surface. Biaxially strained P3HT is formed by straining the film by 100% while on PDMS, and printing the film back to an OTS substrate. The uniaxially strained film is then picked up by PDMS a second time, strained 100% perpendicular to the original strain direction, then printed onto the final substrate. The biaxial strain process is illustrated in Figure 5.

![Figure 5. Biaxial strain process for P3HT films.](image)

PCBM films are transferred to strained PDMS via water immersion, then printed by strain release on top of the P3HT film. The film stacks are printed onto glass/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), Glass/indium tin oxide (ITO)/PEDOT:PSS, and Silicon substrate for both film morphology characterization and device fabrication. Thermally annealed films are annealed inside a glove box at 140°C for 10
minutes. The basic BHJ is spin coated onto Glass:ITO:PEDOT:PSS. It is solvent annealed for 20 minutes, then thermally annealed at 110°C for 10 minutes. The cathode is deposited by vacuum thermal evaporation at a pressure of 1x10^{-6} torr. The cathode consists of ~1 nm lithium fluoride and ~100 nm aluminum film.

### 3.4. Morphology and Device Characterization

The thickness of the films is determined using a Woollam variable-angle spectroscopic ellipsometer (VASE). A 4 layer (ambient, PCBM or P3HT, oxide, silicon) model is used. To allow for variations in the optical properties due to processing, the P3HT is modeled using a biaxial model over the optical range of 750-1100 nm fitting thickness. Absorbance measurements are made using an Ocean Optics Jazz spectrometer. Absorbance is measured on P3HT:PCBM films on PEDOT:PSS, ITO-glass substrates. The organic photovoltaic devices are tested using a Newport 150 W solar simulator with an AM1.5G filter under 100 mW/cm² as determined by an NREL traceable diode. The OPV device area is 3.14 mm², and the device performance is not corrected for spectral mismatch. The reported device performance is the average performance for each casting condition. The external quantum efficiency is measured using light from a Newport 150 W solar simulator with an AM1.5G filter in combination with Newport 7400 Cornerstone 130 1/8m monochromator. The response is recorded as the current over a 1 MΩ resistance, using a Stanford research Systems SR830 lock-in amplifier. A Newport 818-UV silicon low power detector is used as reference to obtain external quantum efficiencies.
4. Results and Discussion

4.1. Bilayer Morphology Characterization

Critical to the interpretation of results is the ability to know the structure of the final photovoltaic device with relative certainty. Previously, it has been shown that the transfer printing techniques used in this study form sharp bilayer structures though characterization with X-ray reflectivity and neutron reflectivity.\[25\] We focus here on the P3HT film morphology, characterized using a combination of UV-visible spectroscopy, atomic force microscopy (AFM), X-ray diffraction, and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy.

AFM revealed that fast spun P3HT films had lower RMS roughness values than slow spun films. Biaxially strained films had higher roughness values than non-strained films. The RMS roughness values can be found in Table 2. AFM images can be found in Figure 6.

Table 2. RMS roughness values of P3HT films found using AFM with 2.5 μm scans.

<table>
<thead>
<tr>
<th>No.</th>
<th>RMS Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.75</td>
</tr>
<tr>
<td>2</td>
<td>0.58</td>
</tr>
<tr>
<td>3</td>
<td>1.51</td>
</tr>
<tr>
<td>4</td>
<td>2.8</td>
</tr>
<tr>
<td>5</td>
<td>1.29</td>
</tr>
<tr>
<td>6</td>
<td>6.5</td>
</tr>
</tbody>
</table>
Figure 6. AFM Images of P3HT films under study.
The absorbance of the P3HT films, given in Figure 7, provides information on the level of P3HT aggregation as well as aggregate quality. As shown in Figure 7, the P3HT films cast from chloroform have weaker vibronic character than the films cast from dicholorobenzene. However, none of the films exhibit sharp features characteristic of highly ordered films.[16], [30] In addition, we find that the variation in P3HT film preparation conditions result in similar absorbance spectra when starting with the same solvent.

![Figure 7. Absorbance of bilayers of all casting conditions.](image)

For a more quantitative analysis, the absorption of P3HT is modeled based on weakly interacting H-aggregates.[16], [30], [31] The absorbance is fit over the range 550 nm to 610 nm, with the exciton bandwidth ($W$), Gaussian line width ($\sigma$), and the $0\rightarrow0$ transition energy ($E_{00}$) as fitting parameters.[16], [30], [31] These fits were performed on the absorbance of the bilayer stack without subtraction of the PCBM. The model fit for each PHJ is given in
Figure 8, with best-fit values are provided in Table 3. It is important to note that the experimental absorbance includes absorbance from the PCBM layer. However, the absorption is PCBM will be most significant at wavelengths below 550 nm and will not alter the fitting values substantially. Future work will be done to subtract the PCBM absorbance from the data; however, in the given films the PCBM layer is fabricated the same way for all measured films such that a relative comparison of P3HT aggregate quality and size should remain. Because of the similar appearance of the absorbance spectra of all films under study, it can be qualitatively said that the percent aggregate of all bilayers is similar. The similarity of the model fit parameters suggests that the P3HT films have similar levels of local order.

Table 3. Optical properties of PHJs.

<table>
<thead>
<tr>
<th>No.</th>
<th>W (meV)</th>
<th>$\sigma$ (meV)</th>
<th>$E_{00}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>135.4</td>
<td>84.7</td>
<td>2.03</td>
</tr>
<tr>
<td>2</td>
<td>125.6</td>
<td>88.0</td>
<td>2.04</td>
</tr>
<tr>
<td>3</td>
<td>133.6</td>
<td>90.7</td>
<td>2.05</td>
</tr>
<tr>
<td>4</td>
<td>110.1</td>
<td>78.8</td>
<td>2.03</td>
</tr>
<tr>
<td>5</td>
<td>118.4</td>
<td>83.5</td>
<td>2.03</td>
</tr>
<tr>
<td>6</td>
<td>126.0</td>
<td>85.4</td>
<td>2.04</td>
</tr>
<tr>
<td>BHJ</td>
<td>99.8</td>
<td>72.3</td>
<td>2.03</td>
</tr>
</tbody>
</table>
Figure 8. Absorbance model fit to P3HT absorbance. The absorbance is for PCBM/P3HT bilayers and thus include a contribution from PCBM absorption.
The packing characteristics of the crystalline P3HT are characterized by grazing incidence X-ray diffraction (GIXD). The GIXD image plate data for bilayer films are given in Figure 9. It can be seen that slow spun P3HT films cast in the low boiling point CF exhibit more edge-on stacking crystals with alkyl-stacking (h00) peaks out-of-plane and π-π stacking (010) peaks detected both in-plane with a relatively broad orientation distribution.

**Figure 9.** GIXD image plates of bilayer devices.
This is in agreement with near-edge X-ray absorption fine structure (NEXAFS) measurements on similarly cast P3HT films from CF.[26], [28] It can also be seen that for the higher boiling point solvent DCB, this difference is not as distinct and slow and fast cast films have similar edge-on packing character. The films that are biaxially strained are found to have the highest degree of face-on packing character (conjugated ring placed parallel to the substrate), similar to that previously reported.[27], [28] The biaxially strained films initially cast from CF result in films with the highest degree of face-on packing character of the films considered in this report. It is important to note that it has previously been demonstrated that biaxially strained films result in very weak in-plane alignment.[28]

Critical to the heterojunction is the molecular orientation of the P3HT right at the interface with the PCBM layer. To determine the surface orientation, NEXAFS measurements are conducted on the neat P3HT films from slow-cast DCB and biaxially strained DCB films, with results shown in Figure 10. The NEXAFS measurements are done on the surface that will be in contact with the PCBM layer in the PHJ OPV devices. NEXAFS will measure the average molecular orientation of the amorphous and crystalline P3HT within the first 6 nm of the film in contrast to the GIXD diffraction.[32]
Figure 10. NEXAFS measurements of slow spun (4) and biaxially strained (6) DCB films.

The measurements are for the partial electron yield (PEY) mode, where the average orientation of the conjugation plane ($\pi^*$ orbital) can be quantitatively determined by collecting carbon K-edge spectra with multiple incident angles of the linearly polarized soft X-rays. The average orientation of the $\pi^*$ orbitals is given by the dichroic ratio ($R_{\pi^*}$), which is the difference between the extrapolated intensities at 90° and 0° incidence divided by the sum.[20], [26] $R_{\pi^*}$ can vary from 0.7 for perfectly edge-on to -1 for perfectly face-on conjugated ring orientation.[26] The values of $R_{\pi^*}$ for the DCB film surface that will be in contact with the PCBM layer in the PHJ solar cell is 0.32 for slow cast films and -0.14 for biaxially strained films. The $R_{\pi^*}$ values are consistent with the GIXD results showing that the slow cast films have a high edge-on packing character and straining the film increases face-on packing. Qualitatively we find that the NEXAFS orientation is consistent with the
GIXD data suggesting the surface and the bulk of the films have similar packing characteristic.

4.2. Photovoltaic Device Characteristics

While the efficiency of these devices is fairly low (~0.15-0.2 %), they are comparable to other P3HT/PCBM PHJ solar cells.[12] The current voltage characteristics of the bilayer solar cells under 1-sun illumination conditions are shown in Figure 11 with key performance metrics reported in Table 4. In this table the series resistance (Rs), and reverse saturation dark current (Js) are determined by fitting the dark J-V curves to the equivalent circuit model given as,[3]

\[
J = \frac{R_p}{R_s + R_p} \left( J_s \left[ \exp \left( \frac{q(V-J)R_s}{nk_BT} \right) - 1 \right] + \frac{V}{R_p} \right)
\]  

(1)

where J is current density, Rp is shunt resistance, Rs is series resistance, Js is reverse saturation current, q is the charge of an electron, n is ideality factor, k_B is Boltzmann’s constant, T is temperature, and V is voltage.

The reported performance values are average performance values without outliers. Outliers are defined as those more than two standard deviations from the average. Figure 11 shows the current-voltage characteristics of the highest performing devices.
Figure 11. Current voltage curves of highest performing bilayer devices. The processing conditions of the P3HT layer in the device is given in Table 1.

Table 4. Performance of planar heterojunction devices.

<table>
<thead>
<tr>
<th>No.</th>
<th>$J_{sc}$† (mA/cm^2)</th>
<th>$V_{oc}$† (V)</th>
<th>Fill Factor†</th>
<th>Efficiency† (%)</th>
<th>$R_p$‡ (MOhm)</th>
<th>$R_s$‡ (Ohm)</th>
<th>$J_s$‡ (mA/cm^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.11±0.25</td>
<td>0.34±0.05</td>
<td>0.50±0.04</td>
<td>0.19±0.05</td>
<td>0.10</td>
<td>10.4</td>
<td>0.4</td>
</tr>
<tr>
<td>2</td>
<td>0.82±0.17</td>
<td>0.40±0.02</td>
<td>0.53±0.01</td>
<td>0.18±0.05</td>
<td>0.95</td>
<td>35.7</td>
<td>0.02</td>
</tr>
<tr>
<td>3</td>
<td>0.88±0.15</td>
<td>0.43±0.04</td>
<td>0.47±0.06</td>
<td>0.18±0.04</td>
<td>0.81</td>
<td>94.0</td>
<td>0.01</td>
</tr>
<tr>
<td>4</td>
<td>1.07±0.09</td>
<td>0.30±0.07</td>
<td>0.49±0.03</td>
<td>0.15±0.02</td>
<td>0.14</td>
<td>13.9</td>
<td>0.13</td>
</tr>
<tr>
<td>5</td>
<td>1.03±0.36</td>
<td>0.28±0.05</td>
<td>0.49±0.04</td>
<td>0.14±0.05</td>
<td>0.13</td>
<td>50.8</td>
<td>0.51</td>
</tr>
<tr>
<td>6</td>
<td>0.72±0.24</td>
<td>0.41±0.08</td>
<td>0.48±0.04</td>
<td>0.15±0.08</td>
<td>3.40</td>
<td>59.7</td>
<td>0.02</td>
</tr>
</tbody>
</table>

† - Represents average values with standard deviation given  
‡ - Represents data from highest efficiency device

These JV curves with equivalent circuit fits are provided in Figure 12. As discussed above, the efficiency of these devices is considerably lower than their BHJ counterpart, but are comparable to other bilayer devices.[12], [13], [33] A key difference observed in the device performance is that solar cells with more edge-on stacking P3HT exhibit lower $V_{oc}$ than the more face-on stacking films, with the reverse trend observed for $J_{sc}$. The origin of the difference in $V_{oc}$ and $J_{sc}$ is now discussed individually.
Figure 12. Equivalent circuit model fit of dark J-V curves.
It has been demonstrated that the ionization energy of small molecules and polymers can have a significant dependence on molecular orientation.[17], [34] Theoretically, density functional theory was applied to P3HT films showing that a decrease of the ionization energy and electron affinity by up to 0.4 eV between perfectly face-on and edge-on configurations.[17] This is attributed to an intrinsic surface dipole along the conjugated backbone of the polymer. Experimentally, we find a variation in open circuit voltage of 0.15 V when going from the film with highest edge-on to highest face-on packing character. We attribute this change to the shift in the IP of the P3HT at the interface with PCBM. From the dark-current J-V model, the reverse saturation current ($J_s$) can be related to this change through,[3]

$$J_s = J_{SO} \exp \left( -\frac{E_g}{2nk_BT} \right)$$

(2)

where $J_{SO}$ is a current prefactor, $n$ is the ideality factor, $T$ is temperature, and $E_g$ is the difference between the IP of the donor and EA of the acceptor. As shown in Figure 13, there is a clear correlation between $J_s$ and $V_{OC}$.
Figure 13. Reverse saturation current ($J_s$) with measured open circuit voltage change in each device under 1-sun illumination.

The change in $E_g$ is attributed to the change in the IP of the P3HT donor as predicted by Heimel et al.[17] Because $E_g$ and $V_{OC}$ are both related to the difference between IP of the donor and EA of the acceptor, it is possible to correlate the change in $V_{OC}$ to a change in $E_g$.

It is important to note that we do not see the maximum possible shift in $V_{OC}$ as predicted by Heimel, but our films do have a significant orientation distribution as observed by the arching scattering peaks in the GIXD image plates, particularly for the face on packing films. This likely results in parallel diode type behavior at the heterojunction interface which will effectively average the variation in output voltage potential.[35] Note that the $V_{OC}$ of 0.28-0.43 V is significantly lower than a comparable BHJ solar cell (~0.6 V).[29] However, the $V_{OC}$ will have a charge carrier dependence; normalizing the output voltage by the short circuit current of the device through variation in incident light intensity allows for a more
meaningful comparison.[36] A comparison between films cast from DCB is given in Figure 14, showing that for common short carrier densities the output voltage of the face-on P3HT bilayer device is comparable to the BHJ device. Therefore, there is no fundamental difference between the devices causing this discrepancy.

![Graph showing comparison of V_{OC} between DCB cast devices with variable J_{SC}](image)

**Figure 14.** Comparison of V_{OC} between DCB cast devices with variable J_{SC}.

Interestingly, the V_{OC} of the face-on film is close to that of the BHJ cell suggesting that the energy landscape at the heterojunction in the BHJ film may more closely resemble that of the face-on P3HT / PCBM heterojunction. We believe this is due to the reduced potential energy state associated with the face-on orientation at the interface. A higher V_{OC} is related to a reduced donor HOMO level relative to the acceptor LUMO level.[37] Because the PCBM processing is kept constant, the LUMO of the acceptor is believed to remain constant. The choice of electrodes can also alter the V_{OC} of the solar cells.[38], [39]
However, there is Fermi level pinning at the interface between P3HT and PEDOT:PSS.[2] This should result in the IP of the P3HT film dictating the output voltage rather than the PEDOT:PSS influencing the output voltage. Therefore, all variation in $V_{OC}$ is due to a change in the HOMO level in the P3HT at the interface. While the sharp interface of the PHJs in this study restricts the orientation angle, and thus the interface energy level of the donor material, in the BHJ, the heterojunction can be thought to exist at a wide range of orientations simultaneously. It would follow that the preferred energy transfer state would be that with the lowest potential energy/lowest donor HOMO level. This is consistent with the BHJ having a higher Voc than our face-on bilayers. In addition, the slope of $V_{OC}$ with $J_{SC}$ for the BHJ film is slightly reduced compared to the bilayer cell, which is attributed to increased bimolecular recombination in the BHJ which is not expected to occur in a bilayer film.[40]

The variation in short circuit current may be attributed to a number of factors including interfacial roughness increasing the heterojunction interface, a variation in exciton diffusion, or a difference in charge transfer state coupling and dissociation efficiency. However, the aforementioned AFM measurements show that the films cast from CF have a slightly lower roughness, and the films that are biaxially strained are slightly rougher. Therefore, roughness variation is not a cause for short-circuit current variation. To gain additional information about the $J_{SC}$, the external quantum efficiency (EQE) of the solar cells is provide in Figure 15. These EQE have been normalized to the $J_{SC}$ of the highest efficiency PHJ of each casting condition.
Figure 15. External Quantum Efficiency (EQE) of bilayer devices.

As expected films with lower short circuit current have a reduced EQE spectra. The variation in EQE is greatest for the portion of the spectrum dominated by absorption in P3HT. This change can thus be attributed to anisotropic exciton diffusion, or a variation in charge transfer coupling at the heterojunction. Recently, small molecular polycrystalline and single crystal films where shown to have anisotropic exciton diffusion.[10] The films under study have a relatively large variation in angular distribution suggesting that the diffusion anisotropy may be relatively low. Similar to the work on the variation in CuPc orientation at a heterojunction with C60, the coupling is more significantly altered for the donor material, whereas excitons generated in the fullerene do not have a strong dependence on donor orientation for dissociation rates. This is similar to our work where the EQE spectra shows that at low wavelengths the charge photogeneration from the PCBM remains relatively constant independent of P3HT processing conditions. However, determining the exact
recombination differences between bilayers of varying orientation remains a topic for future work.

4.3. Annealed Device Characteristics

Bilayer devices are also annealed at 140 °C for 10 minutes to allow for interdiffusion of the donor and acceptor layers, allowing for a study on the effects of bulk orientation on performance. The preparation of these devices is described in Table 5.

<table>
<thead>
<tr>
<th>No.</th>
<th>Solution Concentration (mg/ml)</th>
<th>Solvent</th>
<th>Spin Speed (rpm)</th>
<th>Strain Treatment</th>
<th>Post Cast Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>3</td>
<td>CF</td>
<td>500</td>
<td>Unstrained</td>
<td>Annealed</td>
</tr>
<tr>
<td>8</td>
<td>6</td>
<td>CF</td>
<td>3000</td>
<td>Unstrained</td>
<td>Annealed</td>
</tr>
<tr>
<td>9</td>
<td>7</td>
<td>CF</td>
<td>750</td>
<td>Biaxially Strained</td>
<td>Annealed</td>
</tr>
<tr>
<td>10</td>
<td>6</td>
<td>DCB</td>
<td>625</td>
<td>Unstrained</td>
<td>Annealed</td>
</tr>
<tr>
<td>11</td>
<td>12</td>
<td>DCB</td>
<td>3000</td>
<td>Unstrained</td>
<td>Annealed</td>
</tr>
<tr>
<td>12</td>
<td>12</td>
<td>DCB</td>
<td>850</td>
<td>Biaxially Strained</td>
<td>Annealed</td>
</tr>
</tbody>
</table>

Upon annealing, the PCBM diffuses into the P3HT layer, creating a bulk heterojunction.[25] These devices can be thought to have the heterojunction at all orientations of P3HT simultaneously. That is to say that PCBM surrounds the P3HT in the bulk, whereas in the planar heterojunction, the heterojunction is restricted to a single interface. Additionally, GIXD image plates, shown in Figure 16, reveal that qualitatively, the P3HT in the bulk maintains the same orientation as in the bilayer.
Figure 16. GIXD image plates of annealed bilayer devices.

Absorbance data for the annealed bilayers is found in Figure 17. It can be seen that the order of the films increases as is expected upon annealing.[41]
Figure 17. Absorbance of annealed bilayer devices.

The current voltage characteristics of the annealed solar cells under 1-sun illumination conditions are shown in Figure 18 with key performance metrics reported in Table 6.

Figure 18. Current-voltage characteristics of annealed bilayers.
Table 6. Performance of annealed bilayer devices.

<table>
<thead>
<tr>
<th>No.</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>Fill Factor</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>6.08</td>
<td>0.63</td>
<td>0.53</td>
<td>2.05</td>
</tr>
<tr>
<td>8</td>
<td>4.95</td>
<td>0.61</td>
<td>0.51</td>
<td>1.53</td>
</tr>
<tr>
<td>9</td>
<td>6.19</td>
<td>0.62</td>
<td>0.60</td>
<td>2.32</td>
</tr>
<tr>
<td>10</td>
<td>7.03</td>
<td>0.56</td>
<td>0.58</td>
<td>2.29</td>
</tr>
<tr>
<td>11</td>
<td>5.50</td>
<td>0.56</td>
<td>0.51</td>
<td>1.57</td>
</tr>
<tr>
<td>12</td>
<td>6.40</td>
<td>0.62</td>
<td>0.50</td>
<td>2.00</td>
</tr>
</tbody>
</table>

It can be seen that the difference in $V_{oc}$ and $J_{sc}$ disappear upon annealing. Additionally, EQE testing revealed that differences in performance at wavelengths associated with P3HT are no longer present. The EQE for these devices are shown in Figure 19.

Figure 19. EQE for annealed devices.
Despite the differences in bulk orientation between the annealed devices, the performance characteristics are similar indicating that the orientation in the bulk is not as influential on electrical performance as interface orientation.
5. Conclusion

The relative orientation of P3HT had a significant impact on the open circuit voltage of the planar heterojunction organic solar cell because of a shift in the band gap energy of the organic layers.[5], [7] A face-on orientation of the P3HT at the heterojunction is found to correspond to a lower donor HOMO level and therefore an increased $V_{OC}$. We also found that the $V_{OC}$ of a BHJ at a comparable $J_{SC}$ has a higher $V_{OC}$, indicating that the energy transfer occurs between a lower donor HOMO level than our face-on PHJs. This would suggest that the charge transfer occurs preferentially in the face-on direction in the BHJ. While the PHJs have fixed orientations at the heterojunction, the heterojunction in BHJs exists in a range of orientations simultaneously allowing for charge transfer to occur at the lowest donor HOMO level, producing the greatest possible $V_{OC}$. 
REFERENCES


