Supplemental information for:

Tuning Open-Circuit Voltage in Organic Solar Cells with Molecular Orientation

Brent Kitchen,[1] *Omar Awartani,*[1] *R. Joseph Kline,*[2] *Terry McAfee,*[3] *Harald Ade,*[3] *Brendan T. O'Connor*[1] *

[1]North Carolina State University, Department of Mechanical and Aerospace Engineering, Raleigh, NC 27695

[2]National Institute of Standards and Technology, Material Measurement Laboratory, Gaithersburg, MD, 20899

[3]North Carolina State University, Department of Physics, Raleigh, NC 27695

*btoconno@ncsu.edu

1.0. MORPHOLOGY CONSIDERATIONS

The H-aggregrate model absorbance fits are given in **Figure S1**. The best-fit values are found by minimizing the difference between the modeled absorbance and experimental absorbance over the wavelength range of 500 nm to 650 nm with fitting parameters W, σ, and E_{00}.[1-3] From the model fits, the percent aggregate P3HT is calculated following a previously described method.[2] The absolute absorbance of the various bilayer films is given in **Figure S2**.

The X-ray scatting pole figure for the cross strain films is given in **Figure S3**. When considering the pole figures using the area detector, there is a minimum ω that will meet the necessary Bragg condition. The minimum detectable ω has a polar angle of θ_B, defined by, |q| = ($4\pi/\lambda$□□□□(θ_B). When considering the (100) P3HT diffraction peak at q ≈ 0.39 $Å^{-1}$, results in $\theta_B = 1.73°$.

2.0. PHOTOVOLTAIC DEVICE CONSIDERATIONS

The series resistance (R_S), shunt resistance (R_P), and reverse saturation dark current (J_0) are determined by fitting the dark current-voltage curves to the equivalent circuit model given as,[4]

$$J = \frac{R_P}{R_S + R_P}\left\{ J_0\left[\exp\left(\frac{e(V - JR_S)}{nKT}\right) - 1\right] + \frac{V}{R_P}\right\} \quad (S.1)$$

where J is current density, J_0 is reverse saturation current, e is electron charge, n is the ideality factor, K_B is Boltzmann's constant, T is temperature, and V is voltage. The fits to the dark jV curves are given in **Figure S4**.

The equivalent circuit model fits of the various devices resulted in a variation of the shunt and series resistance between films that may influence V_{OC}. To determine if the variation in R_S and R_P significantly influence V_{OC}, we consider the equivalent circuit fits of two devices: the PHJ device with a slow spin speed cast P3HT layer from chloroform (CF-S) and a biaxially strained P3HT layer cast from chloroform (CF-X). In these devices, we vary R_S and R_P while holding other variable constant (namely J_0, and n). The results of these variations is given in **Table S2** and **Table S3**. We find that over the range of R_p and R_{sh} observed in this study, the change in V_{OC} is much smaller than observed experimentally and thus not believed to be a major contribution to the change in V_{OC} observed between devices.

3.0. HOLE-ONLY DIODES

The *j*-V curves of hole-only diodes with P3HT cast using various processing conditions were measured to determine the out-of-plane hole mobility. The mobility is determined using the following equation,

$$J = \frac{9}{8}\varepsilon_r\varepsilon_0\mu_h\frac{V^2}{L^3}, \tag{S.2}$$

where ε_0 is the permittivity of free space, ε_r is the dielectric constant of the polymer, μ_h is the hole mobility, *V* is the voltage drop across the device, and *L* is the P3HT thickness, following a previously described process.[5] To obtain fits to the *j*-V curves, the voltage drop due to contact and series resistance as well as the built in voltage (V_{bi}) is subtracted from the voltage drop across the device.[5] The calculated μ_h and V_{bi} are plotted in **Figure S5**.

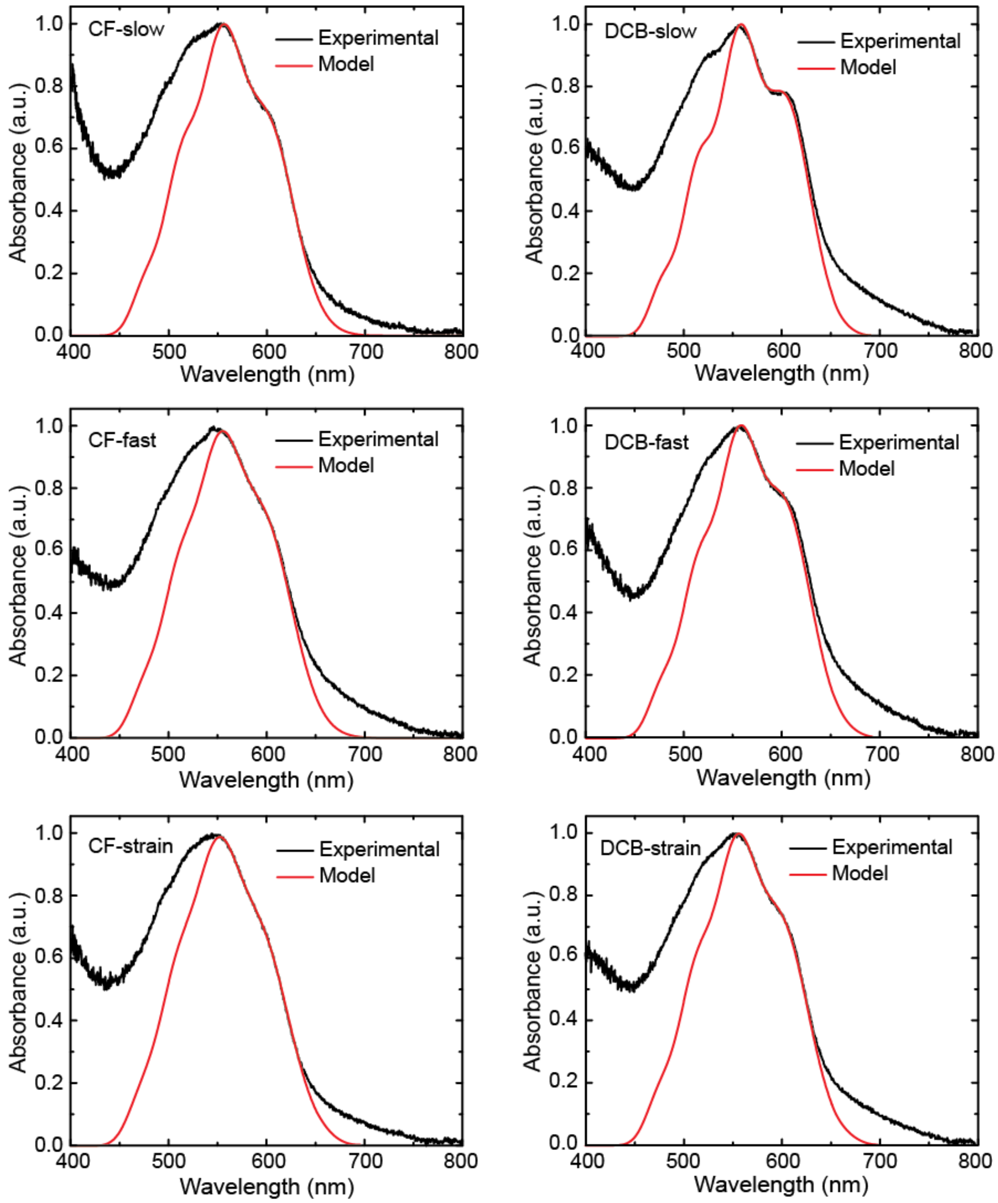

Figure S1. Absorbance model fit to P3HT absorbance. The absorbance is taken to be the absorbance of the bilayer stack minus the absorbance of a neat PCBM film.

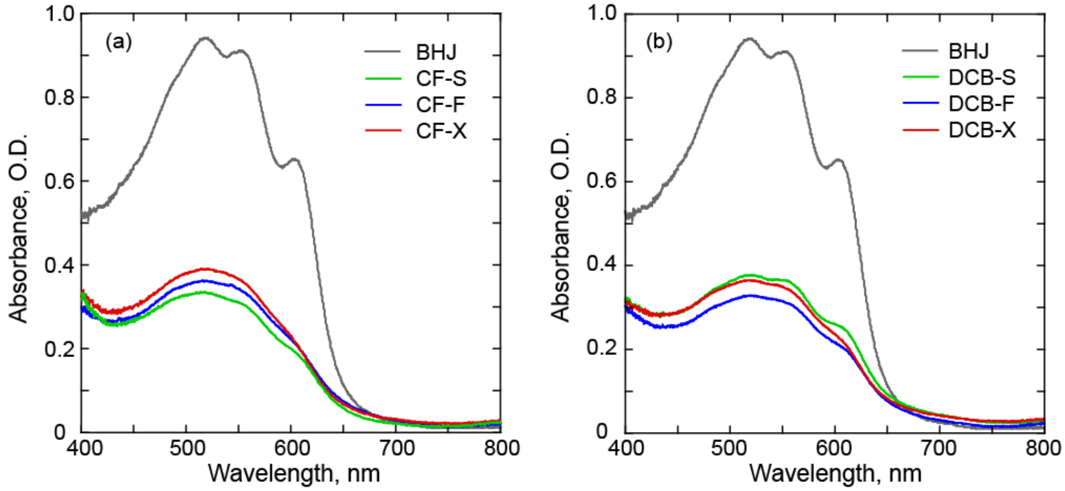

Figure S2. Absolute absorbance of the bulk heterojunction device (BHJ), and bilayer devices with (a) chloroform, and (b) dichlorobenzene.

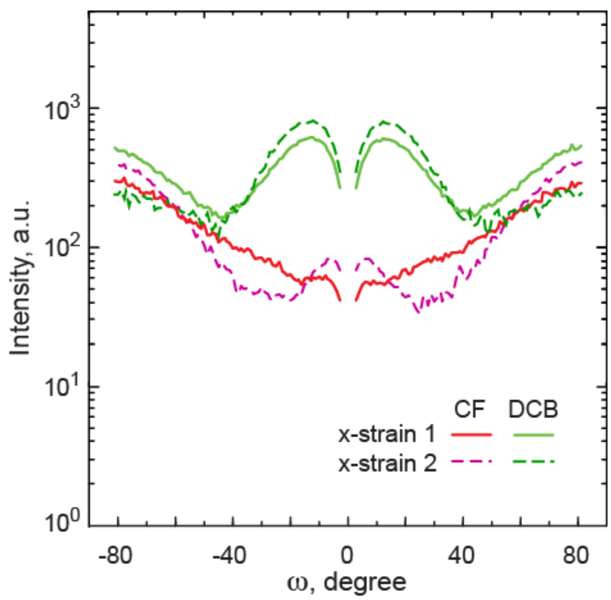

Figure S3. The X-ray scattering pole figure for the biaxially strained P3HT films. The data is taken from the 2-D GIXD image plate data with the X-ray beam parallel to the first strain direction (x-strain 1), and with the X-ray beam parallel to the second strain direction (x-strain 2). The data is normalized by the sum of the intensity for each film, and then corrected by sin(ω).

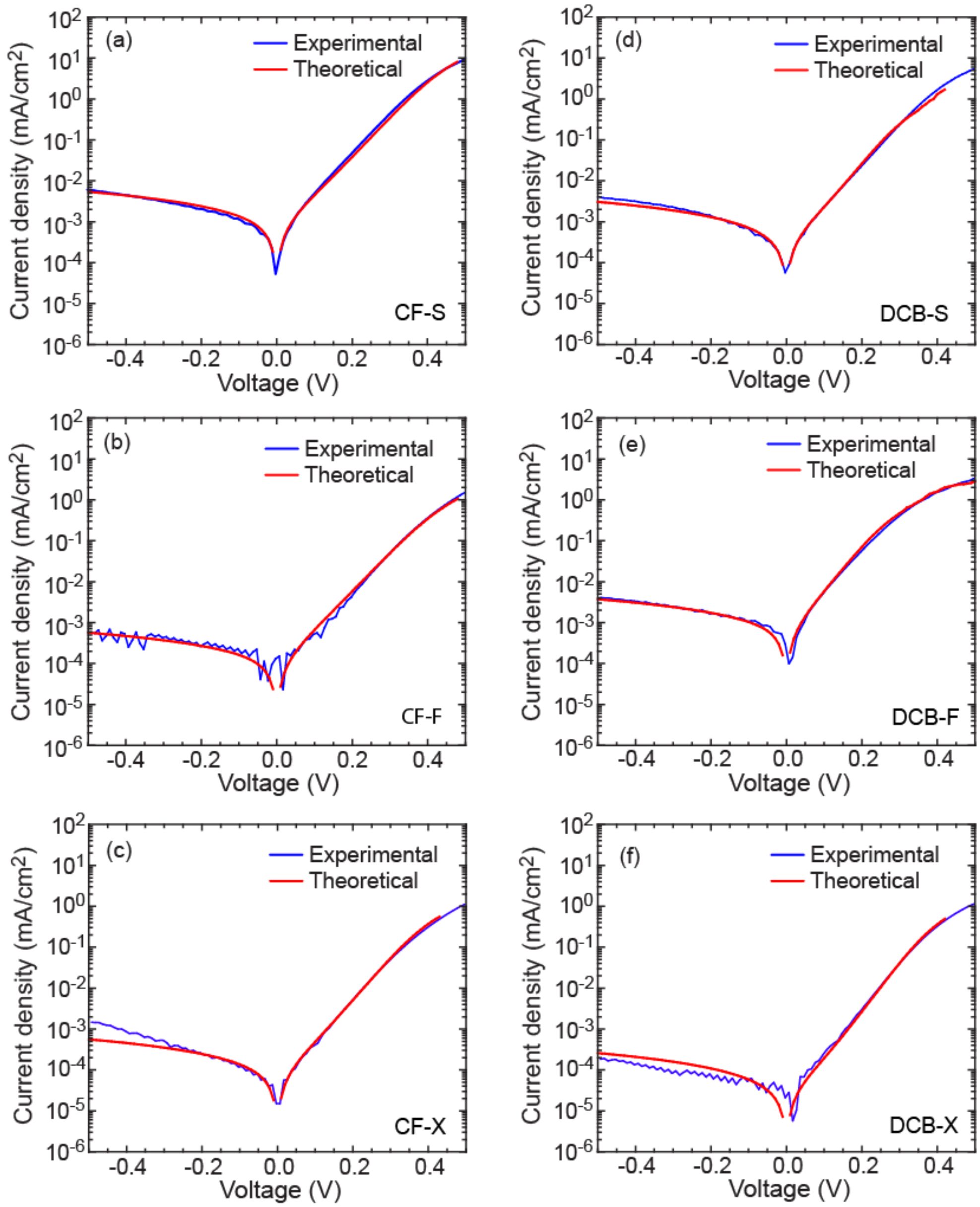

Figure S4. Equivalent circuit model fit of dark current voltage characteristics for the PHJ OPV cells with the following P3HT processing conditions, (a) CF-S (b) CF-F, (c) CF-X, (d) DCB-S, (e) DCB-F, (f) DCB-X.

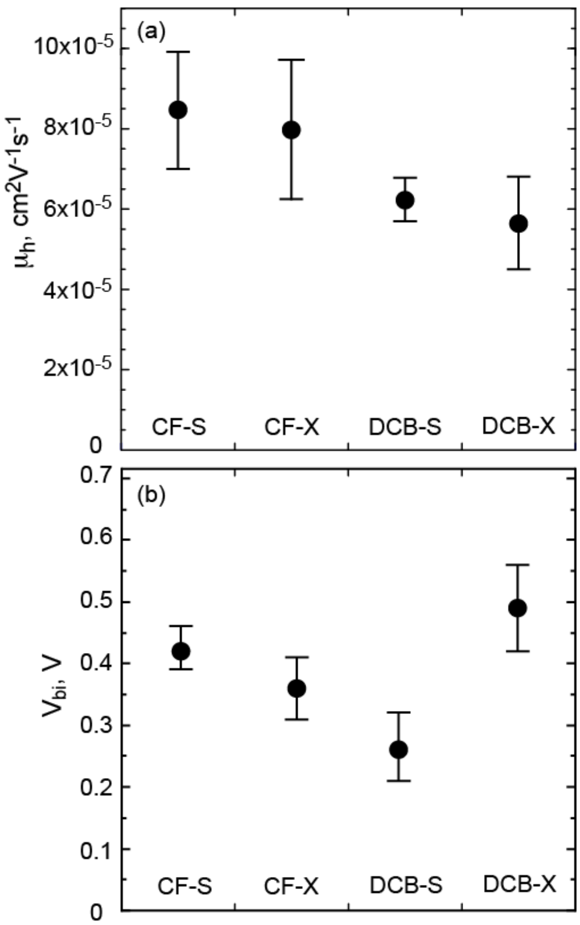

Figure S5. (a) The hole mobility (μ_h) for P3HT in hole only diodes, and (b) the built in voltage subtracted from the voltage drop measured across the device in the *J-V* curves for the various devices.

Table S1. A comparison of the short circuit current predicted by integrating the external quantum efficiency (EQE) multiplied by the AM1.5G solar photon flux between 350 nm to 900 nm and the experimentally measured J_{SC} of the same OPV cell used to measure the EQE given in Figure 7 with the solar simulator (S.S.).

	CF-S (mA/cm^2)	CF-F (mA/cm^2)	CF-X (mA/cm^2)	DCB-S (mA/cm^2)	DCB-F (mA/cm^2)	DCB-X (mA/cm^2)
Predicted from EQE	1.28	0.94	1.05	1.04	1.02	0.76
Measured with S.S.	1.47	0.92	1.19	0.95	1.20	1.17

Table S2. The open circuit voltage (V_{OC}) calculated from an equivalent circuit model based on the CF-S planar heterojunction OPV cell with variation in the R_s and R_p fitting parameters. The V_{OC} values in bold correspond to the range of R_s and R_p modeled in all devices.

R_s (Ohm)	$R_p = 10^0$ Ohm	$R_p = 10^1$ Ohm	$R_p = 10^2$ Ohm	$R_p = 10^3$ Ohm
	V_{OC} (V)	V_{OC} (V)	V_{OC} (V)	V_{OC} (V)
10^0	0.003	0.014	0.120	0.375
10^1	0.014	0.025	0.130	0.373
10^2	0.120	0.129	0.212	0.361
10^3	0.306	0.307	0.311	0.335
10^4	0.320	0.320	0.321	0.323
10^5	**0.321**	**0.321**	**0.322**	0.322
10^6	**0.322**	**0.322**	**0.322**	0.322
10^7	0.322	0.322	0.322	0.322

Table S3. The open circuit voltage (V_{OC}) calculated from an equivalent circuit model based on the CF-X planar heterojunction OPV cell with variation in the R_p and R_s fitting parameters. The V_{OC} values in bold correspond to the range of R_s and R_p modeled in all devices.

R_s (Ohm)	$R_p = 10^0$ Ohm	$R_p = 10^1$ Ohm	$R_p = 10^2$ Ohm	$R_p = 10^3$ Ohm
	V_{OC} (V)	V_{OC} (V)	V_{OC} (V)	V_{OC} (V)
10^0	0.003	0.014	0.120	0.375
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10^4	0.320	0.320	0.321	0.323
10^5	**0.321**	**0.321**	**0.322**	0.322
10^6	**0.322**	**0.322**	**0.322**	0.322
10^7	0.322	0.322	0.322	0.322

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