Enhanced Charge Separation in Organic Photovoltaic Films Doped with Ferroelectric Dipoles

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Supporting Information



Figure S1: AFM phase image (scan size = $2 \ \mu m \ x \ 2 \ \mu m$) showing agglomerates of PVDF-TrFE (dark red) in the BHJ OPV cell with 20% PVDF-TrFE concentration (by weight of P3HT). Maximum phase scale is 40°. Agglomerate size varies from 100-200nm. Such aggregates were not visible in active-layers with 5% and 10% PVDF-TrFE.

Simulation Methodology: For simulations, we assume a dipole of length 10 nm with the positive and negative charges concentrated at opposite ends with a gap of 5 nm between them. This is placed at the center of the active layer with two different orientations, as shown in Fig S2.



Figure S2: Different orientations of dipoles introduced in the active-layer for simulations.

The Poisson equation describing the effect of charge carriers on the electrostatic potential [*Physical Review B*. 2005, 72(8), 1-9] is modified to incorporate the additional influence of the dipole charges.

$$\frac{\partial}{\partial x}\frac{\partial(\varepsilon(x)\psi(x))}{\partial x} = q[n(x) - p(x) + Cn(x) - Cp(x)]$$

Here, Cn(x) and Cp(x) are the charge densities due to the positive and negative charges in the dipole respectively. The value for dipole charge densities, obtained from the experimentally known values of dipole surface charge density ($6\mu C/cm^2$) and radius of gyration (10 nm), is 1E25 m⁻³. The relative dielectric constant of the material in the dipole region is modified to 11.0 from the bulk value of 3.4 for P3HT:PCBM. The current continuity equations remain unchanged.

The electric field dependent dissociation rate constant k_d is described in detail in Koster *et. al* [*Physical Review B* 2005, 72(8), 1-9]. The Poisson equation and the current continuity equations are solved using finite element method with Streamline Upwind Petrov-Galerkin stabilization [*Computer Methods in Applied Mechanics and Engineering* 1982, 32, 199-259]. The electric field, given by $E=-\partial \psi(x)/\partial x$, is calculated at the nodal points of the computational mesh using least-square fitting of the electric field values available at integration points in the finite element method. Kd and Pr are obtained at the nodal points using the calculated values of electric field E. Electron and hole densities were also calculated by solving the drift-diffusion equations.



Figure S3: Simulated electron and hole densities in the active layer for three conditions: (**a**) no dipole, (**b**) dipole orientation -1 i.e. from cathode to anode, and (**c**) dipole orientation +1 i.e. from anode to cathode.

The effect of dipole on calculated charge densities in the active layer is shown in Figure S3. In the case of "Dipole direction -1", there is an accumulation of electrons and holes near the dipole region, which lowers the electric field in the bulk of the device due to screening effect (Figure 2b of main text). However, "Dipole direction +1" decreases the concentration of electrons and holes near the dipole region, thereby alleviating the space charge effect and increasing the built-in field (Figure 2b of main text).



Figure S4: AFM phase image of (a) control (b) P3HT:PCBM films with 20% PVDF concentration (by weight of P3HT). Scan size is 1µm x 1µm and in areas not containing any PVDF agglomerates. Phase scale is 20 degrees. 20% tri-blend film shows coarser blend morphology as compared to the control film. The height image (not shown) reveals a 3.3x difference in the root mean square roughness (7.6nm for 20% and 2.3nm for 0%). This roughness difference could be indicative of larger P3HT domains.



Figure S5: Raman spectra of P3HT:PCBM thin film without and with 10% PVDF-TrFE. Peaks at 1440-1450 and 1380 cm-1 are attributed to the -C=C- symmetric stretching and the -C-C-

skeletal stretching of the thiophene ring, respectively (Nalwa et al., Appl. Phys. Lett. 2011, 98,

093306)



Ferroelectric-poling in bilayer devices:

Figure S6: *Effect of poling on the current-voltage characteristics of (left) interfacial and (right) mixture devices.*

Bilayer devices showed similar dependence on ferroelectric-poling as the bulk-heterojunction devices. Both the mixture and interfacial devices were first subjected to a negative voltage pulse, inducing dipole alignment towards the ITO layer. As stated in the main text, this strong dipole alignment produces an internal electric field that opposes the built-in field. Open circuit voltage (V_{oc}) and fill factor reduced significantly, most likely due to a combination of factors including reduced exciton dissociation and reduced drift transport. With a -10V alignment pulse the V_{oc} of the interface device was reduced by nearly 90%, confirming that the built-in-voltage and drift transport are heavily dependent on the dipole alignment. Similarly, a -12.5V pulse reduced the V_{oc} of the mixture device by nearly 52%. A stepwise reduction could also be achieved with incremental alignment pulses, revealing the dipole-field strength's dependence on the amount of

dipoles polarized (i.e. the number of dipoles aligned by the poling field). For example, a 1%, 11%, and 52% V_{oc} reduction (mixture device) can be achieved by applying an alignment pulse of -7.5V, -10V, -12.5V respectively. These applied fields (43 MV/m, 55.8 MV/m and 69.8 MV/m) correlate well the PVDF-TrFE polarization vs. electric field data available in current literature, where a coercive field of ~50MV/m and a saturation field (i.e 100% polarization) of ~100MV/m are generally reported. Fig. S5 also shows the recovered performance characteristics after positive poling. As displayed, a 12.5V alignment pulse recovered 97% of the interface device's V_{oc} and a 25V pulse recovered 86% of the mixture device's V_{oc} . As in case of BHJ OPVs, positive poling did not improve performance as compared to the unpoled devices, indicating that exciton dissociation and charge transport are equally efficient for random dipoles and dipoles oriented after positive poling.