

Polymer Bulk Heterojunction Solar Cells: Function and Utility of Inserting a Hole Transport and Electron Blocking Layer into the Device Structure

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Supporting Information

1. General information

Regioregular P3HT (4002-E) was purchased from Rieke Metals, Inc. and used as received. PCBM was supplied from Konarka Technologies, Inc. TPA-PFCB was synthesized in our laboratory according to reference.¹

All FET devices were fabricated on heavily n-type doped silicon (Si) wafers with a 200 nm thick thermally grown SiO₂ layer. Bipolar FETs were fabricated using the top contact geometry. The n-type doped Si substrate functioned as the gate electrode and the SiO₂ layer functioned as the gate dielectric. The active layer was spin cast on top of SiO₂ without any surface treatment (P3HT:PCBM in chlorobenzene, ratio 1:0.7; the concentration of P3HT is 15 mg/ml). Then, a thin TPA-PFCB film was formed on top of the active layer by spin coating method. Consequently, the films were heated at 200 °C for 1 hr under N₂. Please note that the control device (no TPA-PFCB) was also

heated at 200 °C for 1 hr under N₂. Al (~50 nm) was deposited as the source and drain electrodes by thermal evaporation using a shadow mask. The channel length (L) and channel width (W) were 50 μm and 1.5 mm, respectively. Electrical characterization was performed using a Keithley semiconductor parametric analyzer (Keithley 4200). All the operations including measurement were performed in a glove box filled with N₂.

Polymer BHJ solar cells were fabricated on ITO-coated glass substrates. The ITO-coated glass substrate was first cleaned with detergent, ultrasonicated in water, acetone and isopropyl alcohol, and subsequently dried overnight in an oven. A solution of TPA-PFCB dissolved in 1,2-dichloroethane (DCE, concentration of 5 mg/ml) was spin cast on top of ITO with thickness approximately 10 nm. Then, the TPA-PFCB was polymerized at 225 °C for 45 min under N₂. A layer of PEDOT:PSS (Baytron P 4083) diluted with isopropyl alcohol with a thickness of about 20 nm was spin cast on top of the TPA-PFCB. The substrates were dried at 140 °C for 10 min in air and then transferred into a glove box to spin cast the active layer. A solution containing a mixture of P3HT/PCBM in chlorobenzene was then spin cast on top of PEDOT:PSS layer. Subsequently, the thin films were heated at 70 °C for 30 min in glove box. Then, after cooling down to room temperature, the devices were transferred to another glove box and the Ca/Al electrode (Ca: ~15 nm and Al: ~100 nm) were deposited by thermal evaporation in a vacuum of about 3×10^{-6} torr. Current density-voltage (J-V) characteristics of the devices were measured using a Keithley 236 Source Measure Unit. Solar cell performance used an Air Mass 1.5 Global (AM 1.5 G) solar simulator

with an irradiation intensity of 1000 W m^{-2} . The spectral mismatch factor was calculated by comparison of the solar simulator spectrum and the AM 1.5 spectrum at room temperature. The devices were first encapsulated with UV epoxy glue in glove box and were then measured in air.

The IPCE spectra for the PSCs were measured on an IPCE measuring system; the device area is about 19 mm^2 . Before J-V measurements, we first measured the IPCE of PSCs. The integrated IPCE values always agreed with the measured short-circuit current to within a few percent.

The UV-Vis absorption measurements were recorded on the Agilent 8453 spectrophotometer at room temperature. AFM imaging was carried out in air using an Asylum Research MFP-3D AFM. The UPS measurement was performed using Kratos Ultra spectrometer equipped with a He I (21.2 eV) discharge lamp. The base pressure of the analysis chamber was maintained at 1.0×10^{-8} torr. The electron energy analyzer was operated at constant pass energy of 10 eV . A sample bias of -9 V was used in order to separate the sample and the secondary edge for the analyzer. All samples were kept inside a high-vacuum chamber overnight to remove solvent.

2. UV absorption and transmission analysis

After polymerization, TPA-PFCB film is resistant to common organic solvents, such as toluene, chlorobenzene (CB) and dichlorobenzene (DCB). The resistance to DCB via UV/vis spectroscopy was investigated. After immersing the TPA-PFCB film

into DCB for 1 min, the UV absorption intensity did not change, showing the complete resistance to DCB.

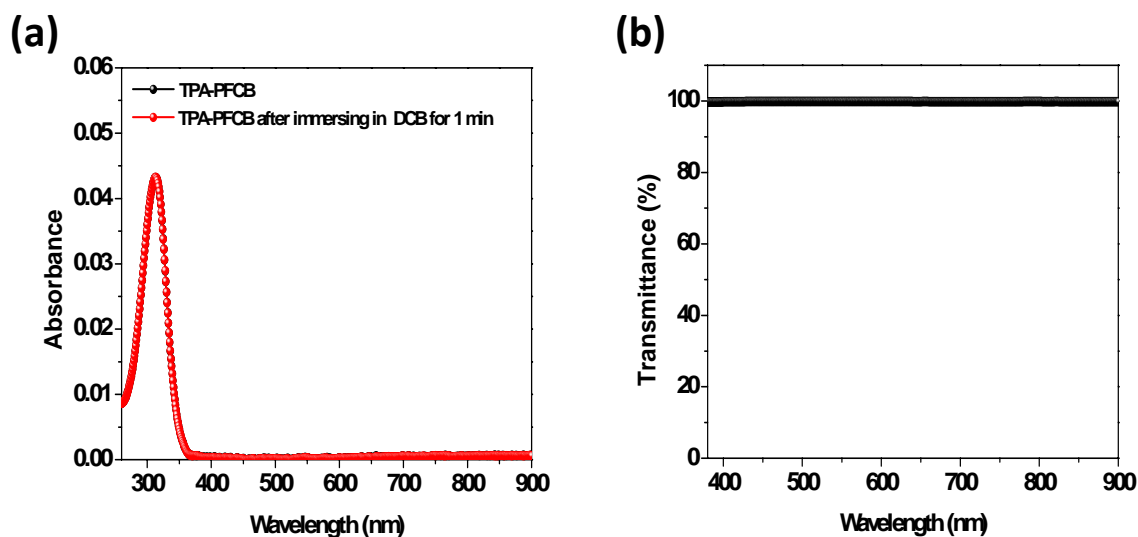


Figure S1. (a) UV-vis absorption spectra of TPA-PFCB film on quartz substrate before and after immersing in DCB solvent for 1 min. (b) The transmission of TPA-PFCB films on quartz substrate after polymerization.

3. UPS analysis

The work function of metals can be “tuned” by using polar molecules (e.g. 1H,1H,2H,2H-perfluoroalkanethiols) which self-assemble on the surface and form an interface dipole.²⁻⁴ There are 6 fluorine atoms (-F) in each monomer unit of TPA-PFCB. Thus, an interface dipole might be expected. Ultraviolet photoelectron spectroscopy (UPS) measurements were carried out on ITO and TPA-PFCB/ITO to probe changes in work function. The work function of ITO can be determined from UPS spectrum.⁵⁻⁸ For ITO, the work function is 4.9 eV and for TPA-PFCB/ITO, the

work function of ITO is 4.87 eV. The TPA-PFCB thin film does not significantly change the work function of the anode.

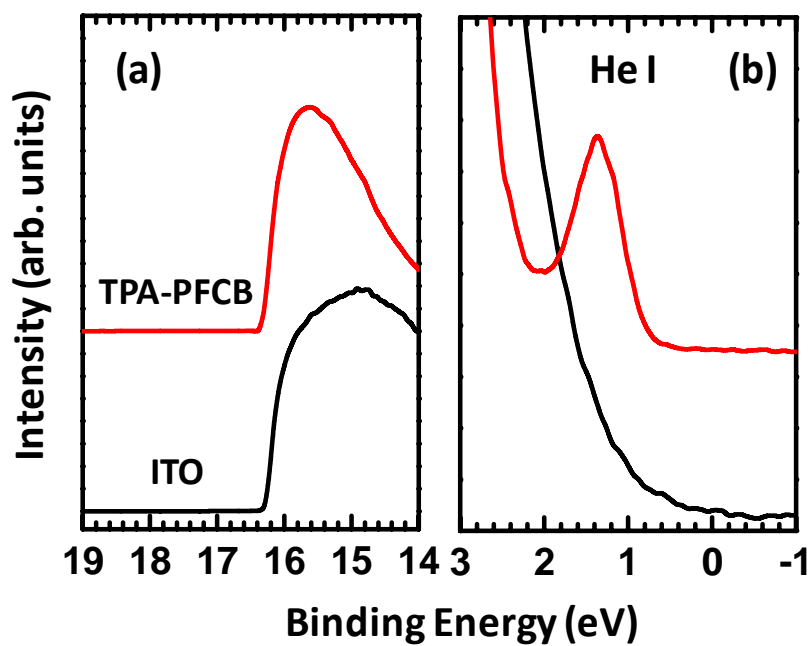


Figure S2. UPS spectra of the high binding energy region (a) and the HOMO region (b) of ITO and TPA-PFCB on ITO with a bilayer structure.

4. IPCE of organic solar cells based on P3HT/PCBM blend with TPA-PFCB.

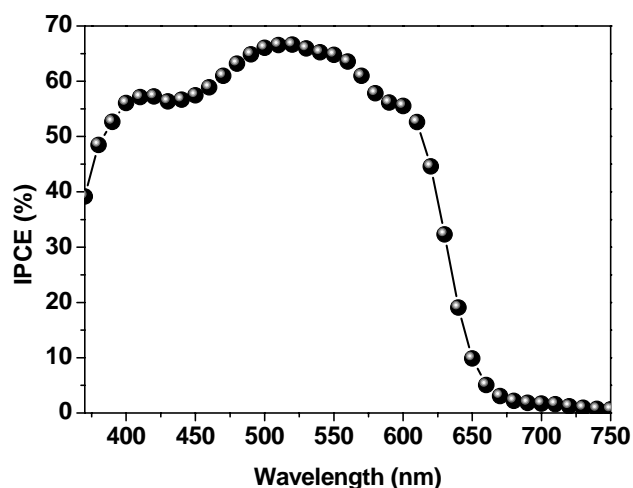


Figure S3. IPCE spectrum of PSC with a thin TPA-PFCB layer (ITO/TPA-PFCB/PEDOT:PSS/ P3HT:PCBM /Ca/Al).

5. Output characteristics of FETs based on P3HT/PCBM blend with TPA-PFCB.

Bipolar field-effect transistors based on P3HT/PCM blend were fabricated with a TPA-PFCB layer on the top. From the output characteristics of devices, the electron transport was blocked by TPA-PFCB layer.

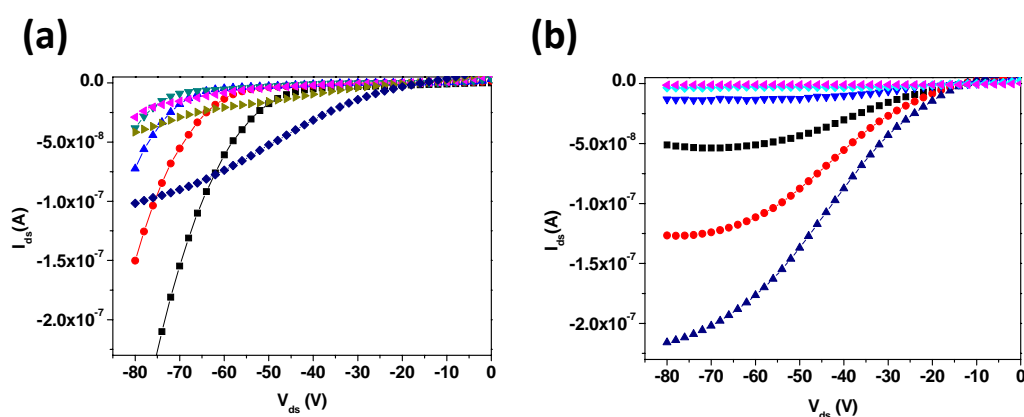


Figure S4. Output curves of device based on P3HT/PCBM blend without TPA-PFCB (a) and with TPA-PFCB (b). The V_{gs} was increased from 0 V to -60 V and the step is -10 V.

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