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Supporting Information

A random donor polymer based on an asymmetric building block to tune the morphology of non-fullerene organic solar cells

Jing Liu¹[†], Lik-Kuen Ma¹[†], Zhengke Li¹, Huawei Hu¹, Tingxuan Ma¹, Chenhui Zhu², Harald Ade³, & He Yan^{1,4*}

¹ Department of Chemistry and Energy Institute, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong.

² Advance Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

³ Department of Physics, North Carolina State University, Raleigh, North Carolina 27695, USA.

⁴ The Hong Kong University of Science and Technology-Shenzhen Research Institute No. 9 Yuexing

1st RD, Hi-tech Park, Nanshan Shenzhen 518057, China.

[†]These authors contributed equally to this work.

*email: hyan@ust.hk.

Solar cell fabrication and testing. Pre-patterned ITO-coated glass with a sheet resistance of ~15 Ω per square was used as the substrate. It was cleaned by sequential sonications in soap deionized water, deionized water, acetone, and isopropanol for 30 min at each step. After UV/ozone treatment for 60 min, a ZnO electron transport layer was prepared by spin-coating at 5000 rpm from a ZnO precursor solution (diethyl zinc). Active layer solutions (D/A ratio 1:1.5, polymer concentration 8 mg/ml) were prepared in chlorobenzene (CB). To completely dissolve the polymer, the active layer solution should be stirred on hotplate at 90 °C for at least 1 hour. Before spin coating, both the polymer solution and ITO substrate are preheated on a hotplate at about 100 °C. Active layers were spin-coated from the warm polymer solution on the preheated substrate in a N_2 glovebox at 1800 rpm to obtain thicknesses of ~120 nm. The polymer:SMA blend films were then thermally annealed before being transferred to the vacuum chamber of a thermal evaporator inside the same glovebox. At a vacuum level of 3×10^{-6} Torr, a thin layer (20 nm) of V₂O₅ was deposited as the anode interlayer, followed by deposition of 100 nm of Al as the top electrode. All cells were encapsulated using epoxy inside the glovebox. Device J-V characteristics was measured in forward direction under AM1.5G (100 mW cm⁻²) at room temperature using a Newport solar simulator. The dwell times is 2 s and the speed is 0.8 V/s. The light intensity was calibrated using a standard Si diode (with KG5 filter, purchased from PV Measurement) to bring spectral mismatch to unity. J-V characteristics were recorded using a Keithley 236 source meter unit. Typical cells have devices area of 5.9 mm², which is defined by a metal mask with an aperture aligned with the device area. EQE was characterized using a Newport EQE system equipped with a standard Si diode. Monochromatic light was generated from a Newport 300W lamp source.

AFM analysis. AFM measurements were acquired by using a Scanning Probe Microscope-Dimension 3100 in tapping mode. All film samples were spincast on ITO/ZnO substrates.

Optical characterizations. Film ultraviolet–visible absorption spectra were acquired on a Perkin Elmer Lambda 20 ultraviolet/visible Spectrophotometer. All film samples were spincast on ITO/ZnO substrates. Solution ultraviolet-visible absorption spectra at elevated temperatures were collected on a Perkin Elmer Lambda 950 ultraviolet/visible/NIR Spectrophotometer. The temperature of the cuvette was controlled with a Perkin Elmer PTP 6+6 Peltier System, which is supplied by a Perkin Elmer PCB 1,500 Water Peltier System. Before each measurement, the system was held for at least 5 min at the target temperature to reach thermal equilibrium. A cuvette with a stopper (Sigma Z600628) was used to avoid volatilization during the measurement.

Cyclic voltammetry. Cyclic voltammetry was performed in an electrolyte solution of 0.1M tetrabutylammonium hexafluorophosphate, both working and counter electrodes were platinum electrode. Ag/AgCl electrode was used as the reference electrode; the Fc/Fc^+ redox couple was used as an external standard.

GIWAXS characterizations. GIWAXS measurements¹ were performed at beamline 7.3.3 at the Advanced Light Source (ALS). Samples were prepared on Si substrates using identical blend solutions as those used in devices. The 10k eV X-ray beam was incident at a grazing angle of 0.13° -0.17°, which maximized the scattering intensity from the samples. The scattered X-rays were detected using a Dectris Pilatus 2 M photon counting detector.

R-SoXS characterization. R-SoXS transmission measurements were performed at beamline 11.0.1.2 at the ALS.² Samples for R-SoXS measurements were prepared on a PSS modified Si substrate under the same conditions as those used for device fabrication, and then transferred by floating in water to a 1.5×1.5 mm, 100 nm thick Si₃N₄ membrane supported by a 5×5 mm, 200 mm thick Si frame (Norcada Inc.). Two dimensional scattering patterns were collected on an in-vacuum CCD camera (Princeton Instrument PI-MTE). The beam size at the sample is ~100

mm by 200 mm. The composition variation (or relative domain purity) over the length scales probed can be extracted by integrating scattering profiles to yield the total scattering intensity. The median domain spacing is calculated from $2\pi/q$, where q here corresponds to half the total scattering intensity. ³ The purer the average domains are, the higher the total scattering intensity. Owing to a lack of absolute flux normalization, the absolute composition cannot be obtained by only R-SoXS.

Hole-mobility measurements. The hole-mobilities were measured using the SCLC method, employing a device architecture of ITO/V2O5/blend film/V2O5/Al. The mobilities were obtained by taking current-voltage curves and fitting the results to a space charge limited form, where the SCLC is described by:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu(V_{appl} - V_{bi} - V_S)^2}{8L^3}$$

Where ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material (assumed to be 3), μ is the hole mobility, V_{appl} is the applied voltage, V_{bi} is the built-in voltage (0V), V_S is the voltage drop from the substrate's series resistance ($V_S = IR$, R is measured to be 10.8 Ω) and L is the thickness of the film. By linearly fitting $J^{1/2}$ with $V_{appl} - V_{bi} - V_S$, the mobilities were extracted from the slope and L:

$$\mu = \frac{slope^2 \times 8L^3}{9\varepsilon_0\varepsilon_r}$$

Electron mobility measurements. The electron mobilities were measured using the SCLC method, employing a device architecture of ITO/ZnO/blend film/Ca/Al. The mobilities were obtained by taking current-voltage curves and fitting the results to a space charge limited form, where the SCLC is described by:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu(V_{appl} - V_{bi} - V_S)^2}{8L^3}$$

Where ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material (assumed to be 3), μ is the hole mobility and L is the thickness of the film. From the plots of $J^{1/2}$ versus V, electron mobilities can be deduced. The mobilities were extracted from the slope and L:

$$\mu = \frac{slope^2 \times 8L^3}{9\varepsilon_0\varepsilon_r}$$

Molecular interaction parameter (\chi) calculation. We can obtain an estimate of the Flory-Huggins interaction parameter, χ , following the Flory-Huggins equation:^{4, 5}

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_f} \frac{v_m}{v_s} (\Phi_s - \chi \Phi_s^2)$$

where T_m is the melting point of the mixture, T_m^0 is the melting point of pure polymer, R is the ideal gas constant, ΔH_f is the heat of fusion of pure polymer, v_m is the monomer molar volume of polymer and v_s is the solvent molar volume (polymer and small molecule density was found to be ~1.15 and ~1.3 g/cm³, respectively). Based on the DSC data as shown in Figure 4b, interaction parameters χ of 0.97 and 1.40 are calculated for the PTFB-P:ITIC-Th and PTFB-M:ITIC-Th blends, respectively.

Supplementary figures and tables



Fig. S1 Temperature-dependent UV-Vis absorption spectra of polymer PTFB-P.



Fig. S2 Electrochemical cyclic voltammetry of PTFB-M.



Fig. S3 Density functional theory (DFT) optimized conformation by Spartan of (a) PTFB-M dimer and (b) PTFB-P dimer.



Fig. S4 $J^{1/2} \sim V_{appl} - V_{bi} - V_S$ characteristics of (a) hole-only for pure polymers. (b) electron-only and (c) hole-only for devices. Dash lines are fits.



Fig. S5 AFM (1 μ m × 1 μ m) height (left) and phase (right) images of (a) PTFB-M:ITIC-Th and (b) PTFB-P:ITIC-Th blend films.



Fig. S6 TGA curves for two polymers.



Fig. S7 Jsc versus light intensity of the devices. The lines are linear fitting results.

Synthesis Section:

General information. All reagents and solvents were purchased from commercial sources (Aldrich, Acros, and J&K) and used without further purification unless stated otherwise. Solvents were purified by distillation when necessary. 4,7-bis(5-bromo-4-(2-decyltetradecyl)thiophen-2-yl)-5,6-difluoro-2-propyl-2H-benzo[d][1,2,3]triazole and polymer PTFB-P were synthesized according to literature procedure.⁶ ITIC-Th was purchased from solarmer company. Microwave assisted polymerizations were conducted in a CEM Discover microwave reactor. ¹H, ¹⁹F and ¹³C NMR spectra were recorded on a Bruker AV-400 MHz NMR spectrometer. Chemical shifts were reported in parts per million (ppm, δ). ¹H NMR and ¹³C NMR spectra were referenced to tetramethylsilane (0 ppm) for CDCl₃. Mass spectra were collected on a MALDI Micro MX mass spectrometer.

2,2'-(2,6-difluoro-1,4-phenylene)dithiophene (T-FB-T-M). To a 10 mL microwave tube, 2,5-dibromo-1,3-difluorobenzene (557 mg, 2.0 mmol), tributyl(thiophen-2-yl)stannane (1.87 g, 5.0 mmol), $Pd_2(dba)_3$ (91.5 mg, 0.1 mmol), $P(o-tol)_3$ (182 mg, 0.6 mmol) were added. Toluene was also added as the solvent. The mixture was then put into microwave reactor and heated at 110 °C for 1h. After being cooled to room temperature, the reaction mixture was filtered, diluted with chloroform and washed with potassium fluoride solution, water and brine for 3 times. The organic layer was dried over Na₂SO₄, filtered and concentrated. Then the residue was recrystallized from methanol to yield pure product as a light yellow solid (283 mg, yield: 61%).

¹H NMR (400 MHz, CDCl₃) δ 7.71 – 7.55 (m, 1H), 7.48 (dd, *J* = 5.2, 1.1 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.29 – 7.20 (m, 2H), 7.19 – 7.14 (m, 1H), 7.11 (dd, *J* = 5.0, 3.8 Hz, 1H).

¹⁹F NMR (376 MHz, CDCl₃) δ -109.76 (d, *J* = 9.7 Hz).

¹³C NMR (101 MHz, CDCl₃) δ 161.28 (d, *J* = 8.3 Hz), 158.79 (d, *J* = 8.3 Hz), 141.82 (s), 134.90 (t, *J* = 11.2 Hz), 129.50 (dd, *J* = 18.7, 12.8 Hz), 128.63 (s), 127.50 – 126.98 (m), 126.54 (s), 124.74 (s), 116.88 – 109.26 (m), 109.20 (s).

HRMS (MALDI+) Calcd for C14H8F2S2 (M +): 278.0035, Found: 278.0027.

((2,6-difluoro-1,4-phenylene)bis(thiophene-5,2-diyl))bis(trimethylstannane) (T-FB-T-M-ditin). To a solution of T-FB-T-M (278 mg, 1.0 mmol) in 20 mL fresh distilled anhydrous THF, 2.0 M *n*-BuLi in hexane (1.38mL, 2.2 mmol) was added dropwise at -78 °C under N₂. The mixture was warmed and stirred at 0 °C for 1h. 1.0 M Me₃SnCl in hexane (2.5mL, 2.5 mmol) was then added at -78 °C and then the reaction mixture was warmed to room temperature

and stirred overnight. The resulted solution was quenched by potassium fluoride solution. The mixture was extracted by ethyl acetate for 3 times and then the organic layer was washed with potassium fluoride solution, water and brine for 3 times. The organic layer was dried over Na₂SO₄, filtered and concentrated. Then the residue was recrystallized from CHCl₃/Methanol to yield pure product as a white solid (450 mg, 74% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.70 (dd, *J* = 2.4, 1.1 Hz, 1H), 7.50 – 7.41 (m, 1H), 7.32 – 7.22 (m, 3H), 7.22 – 7.13 (m, 1H), 0.75 – 0.16 (m, 18H).

¹⁹F NMR (376 MHz, CDCl₃) δ -109.83 (d, *J* = 9.9 Hz).

¹³C NMR (101 MHz, CDCl₃) δ 161.05 (d, J = 8.4 Hz), 158.56 (d, J = 8.5 Hz), 147.54 (s), 140.10 (d, J = 11.6 Hz), 136.64 (s), 135.30 (s), 134.67 (t, J = 11.0 Hz), 130.25 (t, J = 5.5 Hz), 125.84 (d, J = 19.6 Hz), 111.16 (d, J = 17.5 Hz), 109.34 (s), 109.07 (s), -6.10 (d, J = 8.4 Hz), -7.92 (s), -9.74 (d, J = 8.3 Hz).

HRMS (MALDI+) Calcd for $C_{20}H_{24}F_2S_2Sn_2$ (M +): 605.9331, Found: 605.9375.



¹H NMR of T-FB-T-M



¹³C NMR of T-FB-T-M



¹⁹F NMR of T-FB-T-M



¹³C NMR of T-FB-T-M-ditin



¹⁹F NMR of T-FB-T-M-ditin

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