Supplementary Information

Carboxylate substitution position influencing polymer properties and enabling non-fullerene organic solar cells with high open circuit

voltage and low voltage loss

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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 7 mg/ml) were prepared in chlorobenzene. 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 2000 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/V_2O_5 /blend film/ V_2O_5 /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:

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

Supplementary figures



Fig. S1 a) Film absorption of P3TAE and P3TEA: the onset of P3TAE and P3TEA are 713 nm and 733 nm, indicating an optical bandgap of 1.74 eV for P3TAE and 1.69 eV for P3TEA. (b) The normalized absorption and emission curves of neat P3TAE films with the crossing point of 1.81 eV.



Fig.S2 Temperature-dependent UV absorption spectra of (a) P3TEA and (b) P3TAE in 0.02 mg/mL chlorobenzene solutions. (c) "Relative aggregation strength" plots of P3TEA and P3TAE in chlorobenzene solutions at different temperature.



Fig.S3 Cyclic voltammetry of P3TAE in solid state.



Fig.S4 LUMO/HOMO distribution of P3TEA and P3TAE dimers calculated by density functional theory.



Fig.S5 $J^{1/2} \sim V_{appl} - V_{bi} - V_S$ characteristics of (a) hole-only for neat P3TEA and P3TAE polymers. (b) hole-only and (c) electron-only for P3TAE:SF-PDI₂ and P3TAE:FTTB-PDI4 devices. Dash lines are fits.



Fig.S6 (a) J-V characteristic curve, and (b) 2D GIWAXS pattern of P3TEA:FTTB-PDI4.



Fig.S7 2D GIWAXS patterns of (a) P3TAE:SF-PDI₂ and (b) P3TAE:FTTB-PDI4 blends.

Synthesis Section:

General information. All reagents and solvents were purchased from commercial sources (Aldrich, Acros, solarmer and J&K) and used without further purification unless stated otherwise. Solvents were purified by distillation when necessary. SF-PDI₂, FTTB-PDI4, 7-bis(5-bromo-4-(2-hexyldecyl)thiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (1) and 2-hexyldecyl 5-(tributylstannyl)-2-(trimethylsilyl)thiophene-3-carboxylate (2) were synthesized according to literature procedure.^{4, 5} 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.

Synthesis of P3TAE polymer.



bis(2-hexyldecyl) 5',5'''-(5,6-difluorobenzo[c][1,2,5]thiadiazole-4,7-diyl)bis(5-bromo-3'-(2-hexyldecyl)-[2,2'-bithiophene]-4-carboxylate) (3). A mixture of chemical **1** (1886 mg, 2 mmol), chemical **2** (3141 mg, 4.4 mmol), $Pd_2(dba)_3$ (92 mg, 0.1 mmol) and $P(o-tol)_3$ (122 mg, 0.4 mmol) were added to a flask. After adding 20 mL Toluene, the mixture was refluxed at 100 °C overnight under N₂. Then a solution of KF in water was added and the system was stirred for another half an hour. The reaction mixture was filtered, diluted with hexane and washed with KF solution, water and brine. The organic layer was dried over Na₂SO₄, filtered and concentrated. Then the residue was simply purified with silica gel chromatography by a short column to give the crude product of red oil, which is directly used for the next step without further purification.

The crude product mixture was added to a 100 mL flask. The N-Bromosuccinimide (712 mg, 4 mmol), a spoon of silica gel, 30 mL chloroform and 6 mL trifluoroacetic acid were added to the system at 0 °C. After reacting for two hours, the reaction mixture was warmed to r.t. and stirred overnight. 10 mL water was added to quench the reaction. After washing with water, the organic phase was dried with Na_2SO_4 and the solvent was removed by rotary evaporator. Then the residue was purified with silica gel chromatography to provide pure product as red liquid (1.381 g, 42 % yield).

¹**H NMR** (400 MHz, CDCl₃) δ 8.09 (s, 2H), 7.48 (s, 2H), 4.23 (d, *J* = 5.5 Hz, 4H), 2.75 (d, *J* = 7.2 Hz, 4H), 1.77 (d, *J* = 5.6 Hz, 4H), 1.45 – 1.09 (m, 96H), 1.02 – 0.66 (m, 24H).

¹³**C NMR** (101 MHz, CDCl₃) δ 162.10 (s), 151.49 (s), 151.28 (s), 148.80 (dd, J = 11.7, 7.8 Hz), 140.52 (s), 135.92 (s), 134.62 (s), 133.18 (s), 132.05 (s), 130.57 (s), 128.35 (s), 119.36 (s), 111.60 – 111.14 (m), 77.47 (d, J = 11.5 Hz), 77.20 (s), 76.89 (s), 68.15 (s), 39.18 (s), 37.59 (s), 33.85 (d, J = 21.0 Hz), 33.66 (d, J = 2.1 Hz), 32.08 (t, J = 3.8 Hz), 31.51 (d, J = 17.9 Hz), 30.20 (d, J = 3.5 Hz), 29.84 (dd, J = 5.8, 5.2

Hz), 29.53 (d, J = 2.8 Hz), 26.95 (d, J = 3.2 Hz), 26.68 (d, J = 4.1 Hz), 22.87 (s), 14.28 (s). ¹⁹F NMR (376 MHz, CDCl₃) δ -127.43 (s).

HRMS (MALDI+) Calcd for $C_{88}H_{136}Br_2F_2N_2O_4S_5$ (M +): 1640.7438, Found: 1640.7430.



Microwave assisted polymerization of P3TAE. A mixture of monomer **3** (41.1 mg, 0.025 mmol), 5,6-difluoro-4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (**4**) (16.6 mg, 0.025 mmol), $Pd_2(dba)_3$ (1.1 mg, 0.00125 mmol) and $P(o-tol)_3$ (1.5 mg, 0.005 mmol) was added to a microwave vial equipped with a stirring bar and then 0.20 mL of chlorobenzene was added in a glove box protected with N₂. The reaction mixture was then sealed and heated to 140 °C for 2 hours using a microwave reactor. Then the mixture was cooled to r.t. and 10 mL of chlorobenzene was added before precipitated with methanol. The solid was collected by filtration, subsequently subjected to Soxhlet extraction with chloroform. This chloroform solution was then concentrated by rotary evaporator, precipitated into methanol. Finally it was collected by filtration and dried in vacuum to get the polymer as dark purple solid (28.7 mg, 63 %). **GPC**: Mn: 44.8 kDa; Mw: 93.6 kDa; PDI=2.09.



¹H NMR of monomer **3**



 19 F NMR of monomer 3

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