Electronic Supplementary Information

Thiophene-Tetrafluorophenyl-Thiophene- A Promising Building Block for Ambipolar Organic Field Effect Transistors

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Experimental

<u>General</u>

Chemicals 1, 4-dibromo-2,3,5,6-tetrafluorobenzene, tributyl(thiophen-2-yl)stannane, trimethyltin chloride, n-butyl lithium, Pd2(dba)₃, P(*o*Tol)₃ were purchased from Sigma-Aldrich, Strem, Acros and used without further purification. All reactions were carried out using Schlenk techniques in an argon or nitrogen atmosphere with anhydrous solvents. 2,5-bis(2-octyl-1-dodecyl)-3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione was synthesized accordingly to previously reported procedure.¹

Characterization

¹H and ¹³C NMR data were performed on a Bruker DPX 300 MHz or 400 MHz spectrometer using solvent CDCl₃. The chemical shifts were recorded in ppm using TMS as an internal standard. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Bruker Autoflex TOF/TOF instrument using dithranol as a matrix. High temperature gel permeation chromatography (HT-GPC) measurements were measured on a Polymer Labs GPC-220 equipped with a refractive index detector, a 500 µm injection loop, two

PLgel Olexis columns (300 mm×7.5 mm, particle size: 13 µm) and one PLgel Olexis 13 µm guard column (50 mm×7.5 mm) at 160 °C using 1,2,4-trichlorobenzene (TCB) stabilized with 0.0125 g/L BHT as the eluent. Polymer solutions were prepared at a concentration of 0.3 mg/mL using a Polymer Labs SP260 sample preparation system at 160 °C for 1 min, which resulted in complete dissolution of the polymers, followed by transfer to the GPC vials. UV-Vis spectra were recorded on a Shimadzu model 2501-PC. The photoelectron spectroscopy in air (PESA) measurements was recorded on the spin coated thin film of PDPP-TFPT samples using Riken Photoelectron Spectrometer (Model AC-2). Differential scanning calorimetry (DSC) was carried out under nitrogen on a TA Instrument DSC Q100 instrument (scanning rate of 10°C min-1). Thermal gravimetric analysis (TGA) was carried out using a TA Instrument TGA Q500 instrument (heating rate of 10°C min-1).



2,2'-(perfluoro-1,4-phenylene)dithiophene (3)

To a 50 mL shlenk tube, tributyl(thiophen-2-yl)stannane (14 mmol, 5.22 g) and 1,4-dibromo-2,3,5,6-tetrafluorobenzene (5 mmol, 1.53 g) were added. Then the Shlenk tube was transferred into glove box, 0.5 mmol Pd(PPh₃)₄ and 20 mL anhydrous toluene were subsequently added. The reaction mixture was heated at 110 °C for 3 days. After removing solvent under reduced pressure, the residue was directly subjected to column chromatography purification with hexane as eluent, to give white solid product 1.4 g, in 89% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.67 (d, J = 3.6 Hz, 2H), 7.56 (d, J = 4.8 Hz,2H), 7.22 (d, J = 4.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 146, 143, 131, 129, 128, 127.



(5,5'-(perfluoro-1,4-phenylene)bis(thiophene-5,2-diyl))bis(trimethylstannane) (4)

2,2'-(perfluoro-1,4-phenylene)dithiophene **3** (1.41g, 4.5 mmol) was dissolved in 20 mL anhydrous THF, then the solution was cooled down to -78 °C with dry ice-acetone bath. 9.8 mmol Butyl lithium was added dropwise at -78 °C, and then the reaction mixture was stirred at same temperature for 1 hour. (1.95 g 9.8 mmol) trimethyl stanyl chloride was added in one portion. The reaction mixture was slowly warm to room temperature and stirred overnight. Recrystallization from ethanol give pure product 2.7 g, in 95% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, *J* = 3.6 Hz, 2H), 7.32 (d, *J* = 3.6 Hz, 2H), 0.45 (s, 18H). ¹³C NMR (100 MHz, CDCl₃): δ 145, 143, 142, 135, 133, 131, 112.



Synthesis of 3,6-bis(5-bromofuran-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-c]pyrrole-2,5-bis(2-octyl-1-dodecyl)-3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (5): 1,4(2H,5H)-dione (2.0 g, 2.41 mmol) and chloroform (20 mL) were charged to a 100 mL three neck flask equipped with a stirring bar, a condenser, and a dropping funnel. Bromine (Br₂) (0.25 mL, 4.82 mmol) in chloroform (10 mL) was then added drop wise to the flask at room temperature through the dropping funnel. The mixture was stirred at room temperature overnight, then slowly poured to an aqueous solution of sodium thiosulfate and stirred for additional 30 min. The product was extracted with chloroform, then washed with DI water, and dried over anhydrous MgSO₄. Removal of the solvent afforded the crude product which was further purified using column chromatography on silica gel (a mixture of hexane and chloroform as eluent) to give the product as a dark red solid (1.50 g, 63%). ¹H NMR (400 MHz, CDCl₃): δ 0.85 (t, J = 6.2 Hz, 12 H), 1.10-1.40 (m, 64 H), 1.76 (s, 2 H), 3.96 (d, J = 6.7 Hz, 4 H), 6.59 (d, J = 3.4 Hz, 2H), 8.27 (d, J = 3.4 Hz, 2 H). ¹³C NMR (100 MHz, CDCl3): δ 160.87, 146.23, 132.78, 126.13, 122.14, 115.45, 106.34, 46.63, 38.78, 31.87, 31.84, 31.47, 30.07, 29.59, 29.52, 29.46, 29.29, 29.24, 26.46, 22.62, 14.02. MS (MALDI-TOF, m/z): calcd. for C₅₄H₈₆Br₂N₂O₄, 984.50; found, 986.38 (M+2).



<u>Synthesis</u> of poly{3,6-difuran-2-yl-2,5-di(2-decyltetradecyl)-pyrrolo[3,4-c]pyrrole-1,4dione-alt- 2,2'-(perfluoro-1,4-phenylene)dithiophene} (PDPP-TFPT):

To a 50 mL Schlenk flask, 3,6-bis(5-bromofuran-2-yl)-2,5-bis(2-octyl-1-dodecyl)pyrrolo[3,4c]pyrrole-1,4(2H,5H)-dione (0.220 g, 0.20 mmol), $Pd_2(dba)_3$ (8 mg), $P(oTol)_3$ (11 mg) and (5,5'-(perfluoro-1,4-phenylene)bis(thiophene-5,2-diyl))bis(trimethylstannane) (0.127 g, 0.40 mmol) were dissolved in anhydrous toluene (12 mL) under argon. The solution was purged with argon for 30 min under stirring, and then was heated at 80°C for 3 d. The resulting mixture was poured into a mixture of methanol (100 mL) and water (100 mL) and stirred overnight. The precipitated dark solid was filtered off and redissolved in chloroform and added drop wise to methanol (250 ml). The resulting solid was filtered off and subjected to Soxhlet extraction with methanol (24 h), acetone (24 h), and hexane (24 h), respectively. The residue was finally extracted with chloroform and precipitated again from methanol, filtered, washed with methanol, and dried under vacuum in 74 % yield.

 $M_{\rm w}/M_{\rm n}$ (GPC) = 20,689/ 12,083, polydispersity index (PDI) =2.80, $\lambda_{\rm max}$ (UV-vis-Near IR): 700 nm (in chloroform); 716 nm (thin film). Absorption cutoff from thin film= 900 nm.

OTFT Fabrication and Characterization

Top contact/bottom gate OTFT devices fabricated using n+-Si/SiO₂ substrates where n+-Si and SiO₂ work as gate electrode and gate dielectric, respectively. The thickness of thermally grown silicon oxide layer is around ~200 nm with a capacitance of about 17 nF/cm². The SiO2/Si substrate was cleaned with acetone, IPA. It was then immersed in a piranha solution (V(H2SO4) : V(H2O2) = 2:1) for 20 minutes, followed by rinsing with deionized water, and then kept in a vacuum oven at 120 oC for 3h with a few drops of octadecyltrichlorosilane (OTS). It was then rinsed with CHCl3, IPA, DI water, and then blow dried with nitrogen gas. PDPP-TFPT polymer

thin film was deposited via spin coating using 7 mg/ml solution in chloroform on the OTS treated Si/SiO₂ substrate. Subsequently, on top of the polymer active layer, a 100 nm thick Gold (Au) thin film was deposited for Source (S) and Drain (D) electrodes through a shadow mask. For a typical OTFT device reported here, the source-drain channel length (L) and channel width (W) was 100 μ m and 1 mm, respectively. The device characteristics of the OTFTs were measured at room temperature under nitrogen with a Keithley 4200 source meter. The field effect mobility (μ) was calculated from the saturation regime of transfer characteristics.



Figure S1. ¹H NMR and ¹³C spectrum of (5,5'-(perfluoro-1,4-phenylene)bis(thiophene-5,2-diyl))bis(trimethylstannane) (**4**).



Figure S2. ¹H NMR and ¹³C spectrum of 3,6-bis(5-bromofuran-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione in CDCl₃ (6).



Figure S3. ¹H NMR spectrum of poly {3,6-difuran-2-yl-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione-alt-2,2'-(perfluoro-1,4-phenylene)dithiophene} (**PDPPF-TFPT**).



Figure S4. Gel permeation chromatogram of polymer <u>PDPP-TFPT</u> in tricholoorobenzene eluent.



Figure S5. 2-D XRD pattern intensity graphs and 2-D XRD image for **PDPP-TFPT** spin-coated thin films (~35 nm) on OTS modified SiO₂/Si substrates with the incident X-ray parallel to the thin film stack (right).



Figure S6. Differential Scanning Calorimetry (DSC) and thermo gravimetric analysis (TGA) of **PDPP-TFPT** polymer.