

Supplementary Information

Hole Mobility of 3.56 cm²/Vs Accomplished Using More Extended Dithienothiophene Block with Furan Flanked Diketopyrrolopyrrole

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Experimental

General

Chemicals 2,6-dibromodithieno[3,2-b:2',3'-d]thiophene (**3**), n-butyl lithium, trimethyltin chloride, Pd₂(dba)₃, P(oTol)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-decyltetradecyl)-3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**1**), 3,6-bis(5-bromofuran-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**2**) and 2,6-bis(trimethylstannyl)dithieno[3,2-b:2',3'-d]thiophene (**4**) were synthesized accordingly to previously reported procedure.

Synthesis of PDPPF-DTT

To a Schlenk flask, 3,6-bis(5-bromofuran-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**2**) (0.220 g, 0.20mmol), 2,6-bis(trimethylstannyl)dithieno[3,2-b:2',3'-d]thiophene (**4**) (0.104 g, 0.20 mmol), Pd₂(dba)₃ (8 mg), and P(oTol)₃ (11 mg) 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 (0.160 g, 69 % yield).

M_w/M_n (GPC) = 24,726 / 55,035. UV-vis-Near IR: 782 nm (in chloroform); 785 nm (thin film).

Device fabrication and characterization:

Top contact/bottom gate OFET 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°C 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 OFET device reported here, the source-drain channel length (L) and channel width (W) was 100 μm and 1 mm, respectively. The device characteristics of the OFETs 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.

GIWAXS collection

GIWAXS measurements were taken using 9 keV monochromatic photons, aligned parallel to the sample within 0.01 degrees through use of a Si crystal analyser. Exposures were collected using a Polatus 1M detector, which was tiled in 3 1-second exposures to fill in the gaps of the detector, and produce a single gapless 2D scattering pattern. Scattering patterns were collected from 0.05 degrees to 0.4 degrees with a resolution of 0.01 degrees near the critical angle of 0.17 degrees. The critical angle was determined as the incident angle at which scattering dramatically increased.

XRD Measurement

Two-dimensional X-ray diffraction (2-D XRD) measurements were prepared by first forming a polymer thin film (~100 nm) on the wall of a round-bottom flask *via* vacuum evaporation of a dilute polymer solution in chloroform, which were detached from the wall of the flask as disk-like flakes by soaking in methanol, and collected by filtration. A stack of thin films (with a thickness of about 100 μm and a diameter of about 1 mm) were then used for the 2-D XRD measurements on a Bruker AXS D8 system using Cu K_{α} source in air. Data were analyzed with the GADDS software.

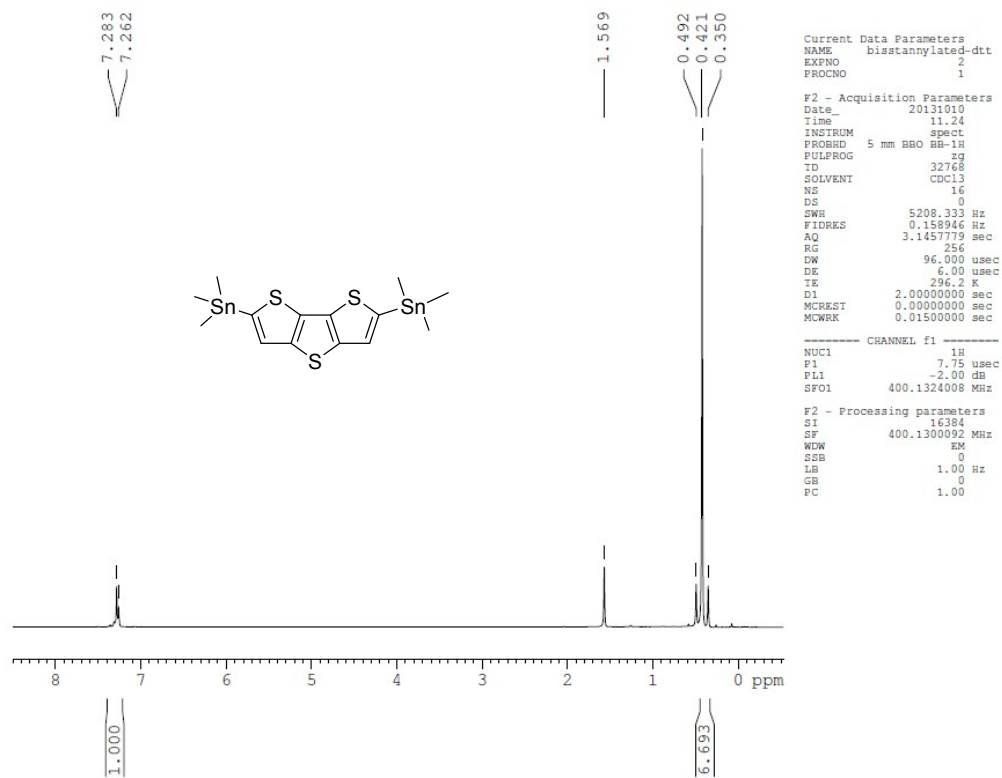


Figure S1. ¹H NMR spectra of bis(trimethylstannyl)dithieno[3,2-b:2',3'-d]thiophene (**4**).

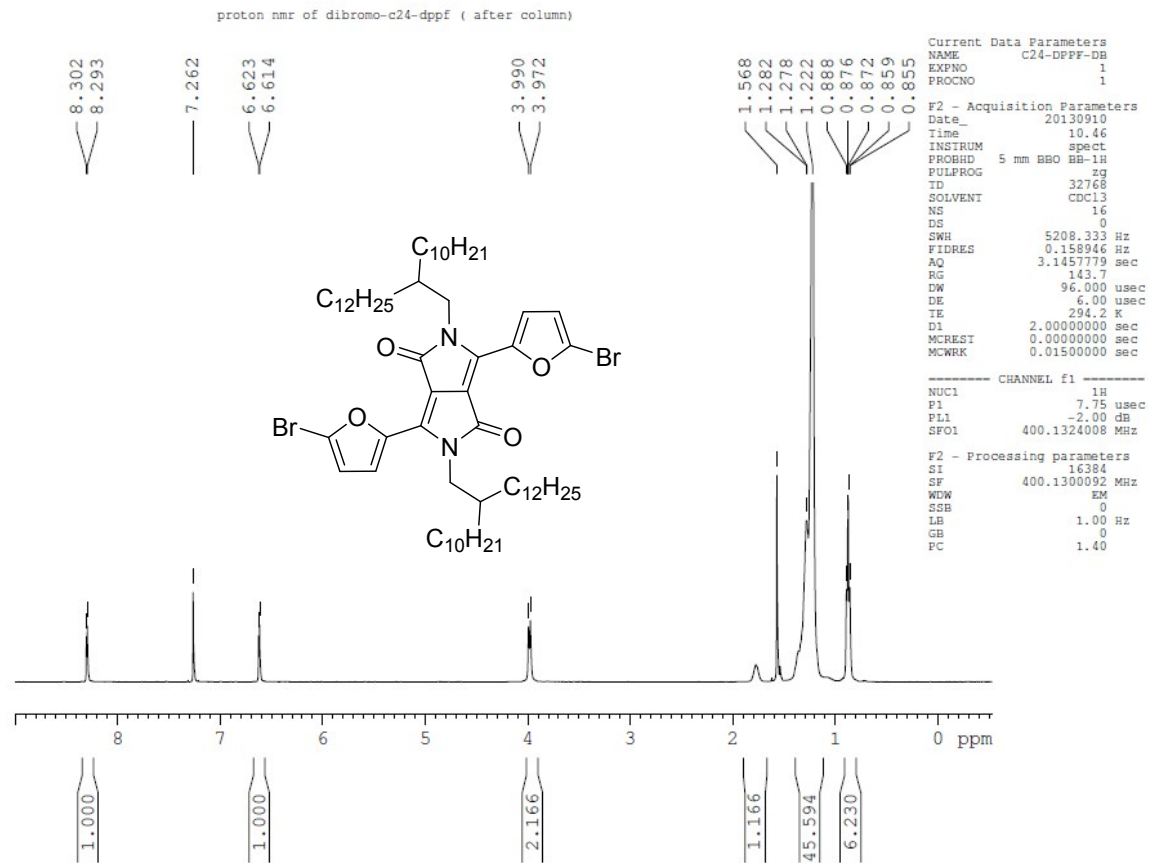


Figure S2. ^1H NMR spectra of 3,6-bis(5-bromofuran-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**2**).

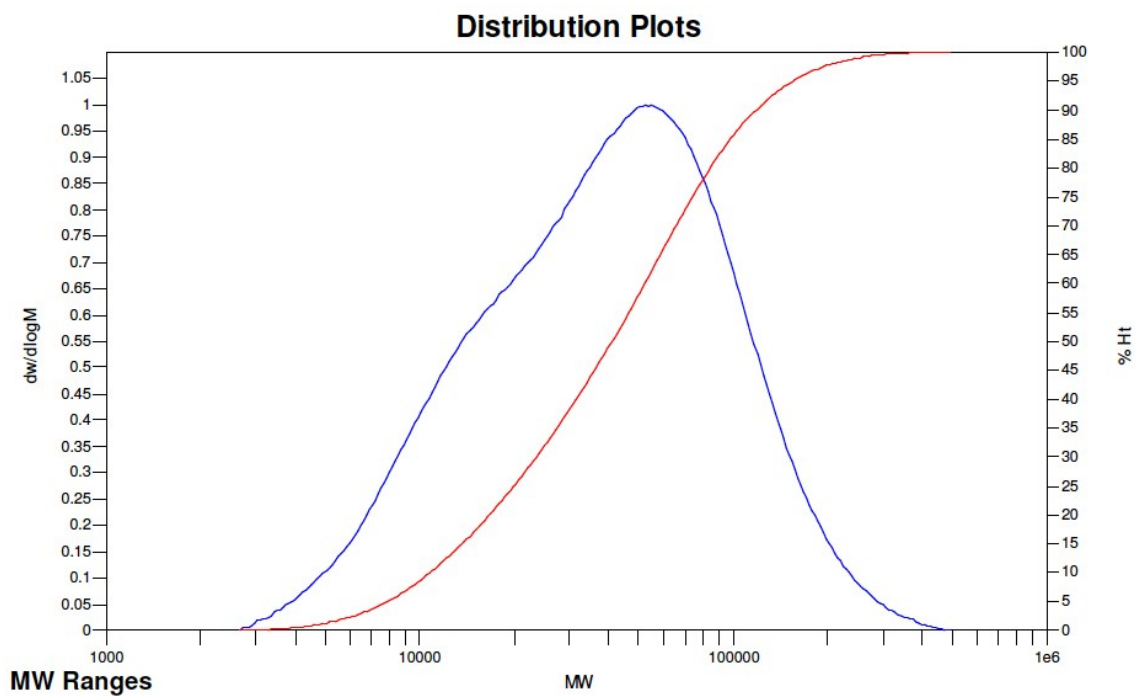


Figure S3. Gel permeation chromatogram of polymer **PDPPF-DTT** in trichlorobenzene using PMMA internal standard at 160°C.

MW Averages

Mp: 54603

Mn: 24726

Mv: 49530

Mw: 55035

Mz: 100872

Mz+1: 154347

PD: 2.2258

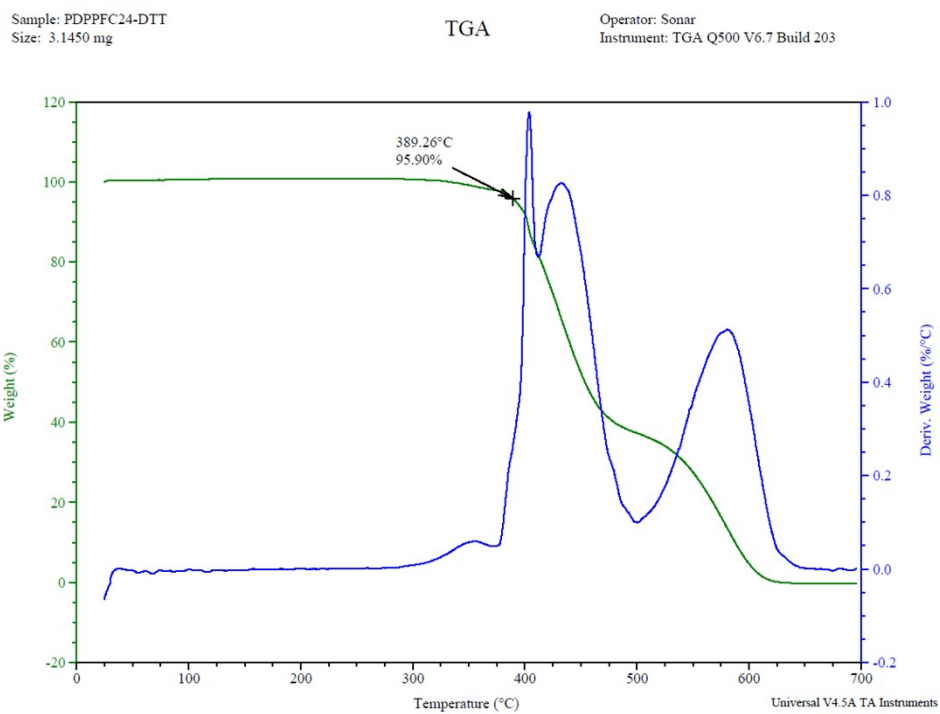
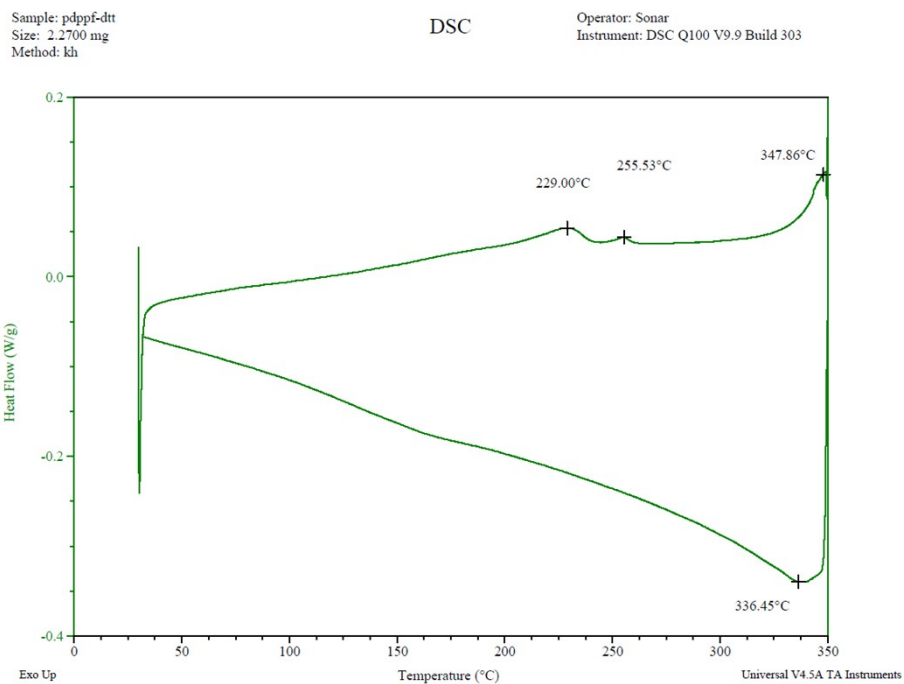


Figure S4. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) data of polymer **PDPPF-DTT**.

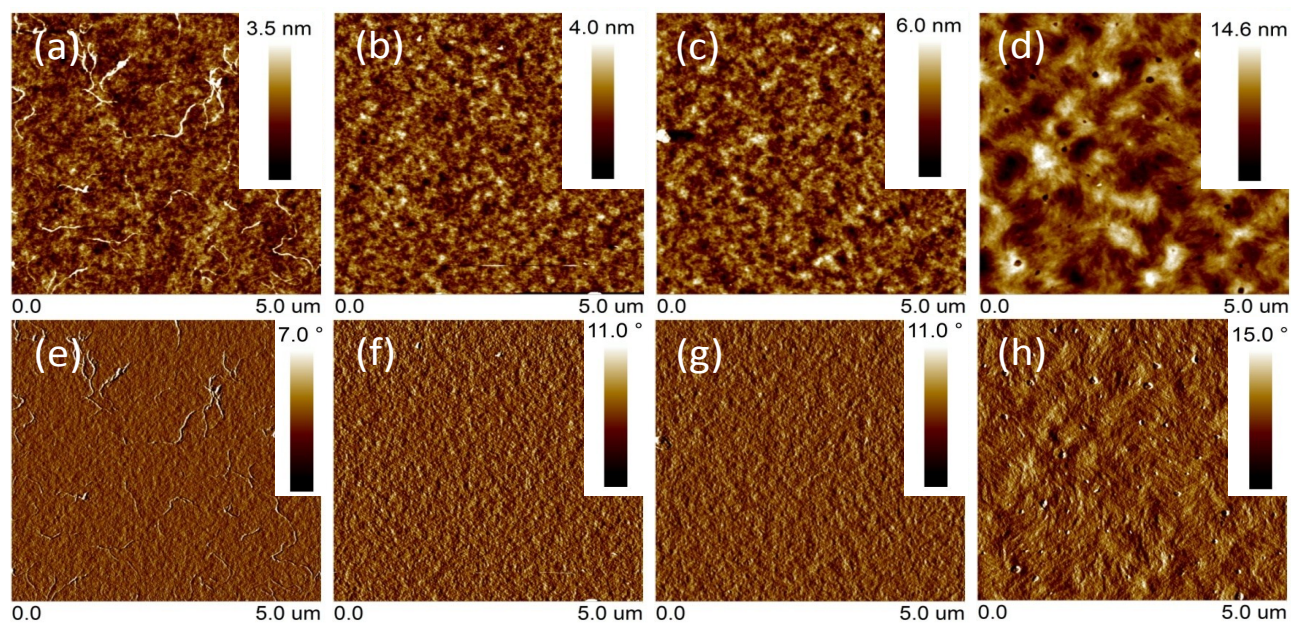


Figure. S5 Atomic Force Microscopic (AFM) height (up) and phase (down) images of PDPPF-DTT thin films annealed at 100°C (a, e), 150°C (b, f), 200°C (c, g) and 250°C (d, h) on OTS treated Si/SiO₂ substrates.

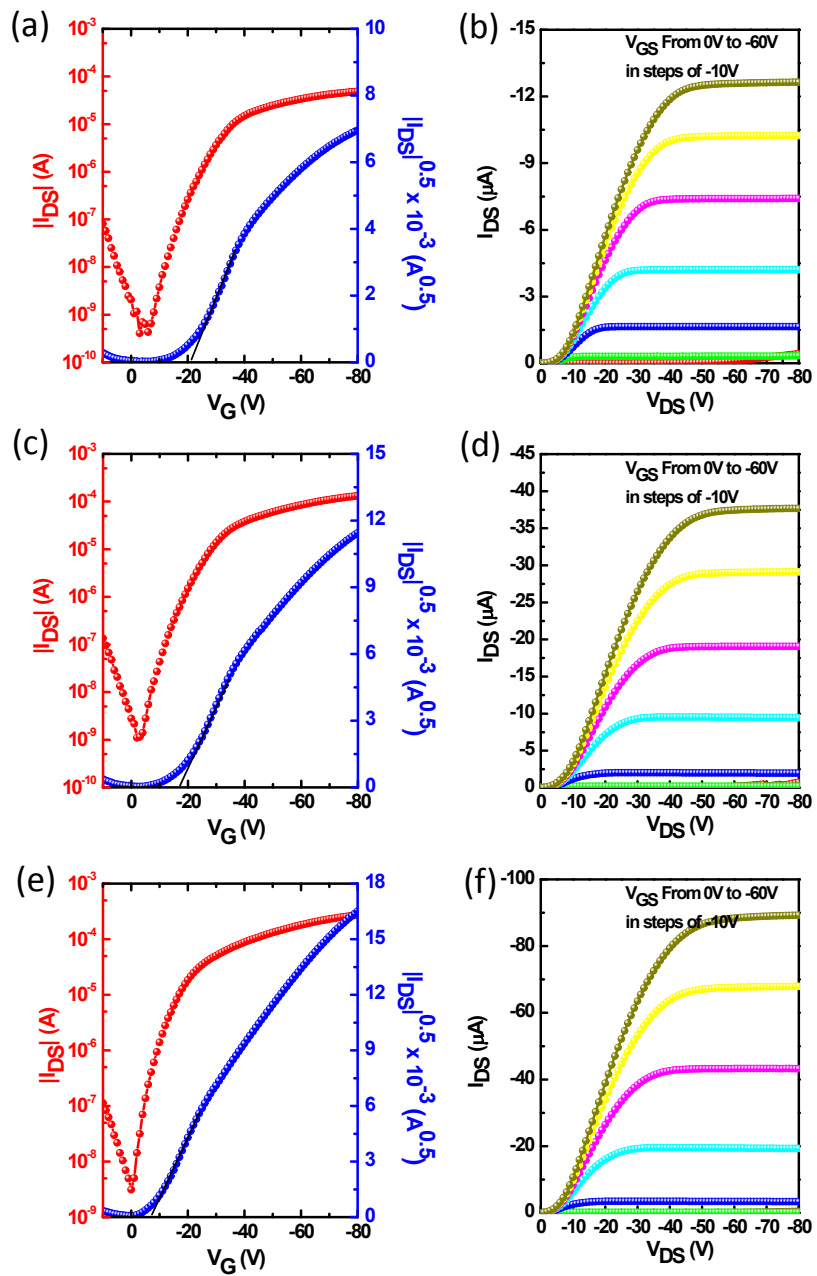


Figure S6. The transfer and output characteristics of the of PDPPF-DTT OFET devices pre-annealed at 100°C (a, b), 150°C (c, d) and 200°C (e, f).