Supplementary Information

Synthesis, Characterization and Organic Field Effect Transistor Performance of Diketopyrrolopyrrole- Fluorenone Copolymer

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Experimental

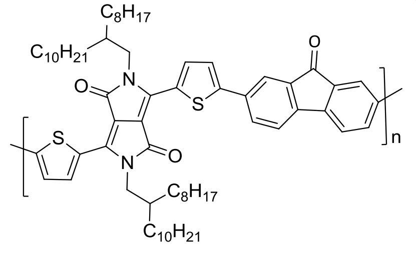
General

All the solvents, catalysts and reagents were purchased from Sigma-Aldrich, Strem, Acros and used without further purification. Most of the reactions were conducted using Schlenk techniques in an argon or nitrogen atmosphere with anhydrous solvents. Compounds 1, 2, 3 and 5 were synthesized according to earlier reported procedures.[1, 2]

Characterization

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy measurements were conducted on a Bruker DPX 300 MHz or 400 MHz spectrometer using solvent $CDCl_3$. The chemical shifts were recorded in ppm using TMS as an internal standard. High temperature gel-permeation chromatography (HT-GPC) measurements were performed 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. The measured data were analyzed with

Cirrus software, using narrow MWD polystyrene standards as a reference (PL EasiVial PS, range of calibration 103 to 6×10^6). Ultraviolet-visible (UV-Vis) spectra were recorded on a Shimadzu model 2501-PC. Photoelectron spectroscopy in air (PESA) measurement was done on the thin film of PDPPT- *alt*- FN polymer spin coated on glass using Riken Photoelectron Spectrometer (Model AC-2). Thermal gravimetric analysis (TGA) was carried out using a TA Instrument TGA Q500 instrument (heating rate of 10°C min^{-1}). Differential scanning calorimetry (DSC) was carried out under nitrogen on a TA Instrument DSC Q100 instrument (scanning rate of 10°C min^{-1}).



PDPP-*alt*-FN

Synthesis of poly{3,6-dithiophene-2-yl-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione-alt- fluorenone} (PDPP-*alt*-FN):

To a 50 mL Schlenk flask, 3,6-bis-(5-bromo-thiophen-2-yl)-N,N'-bis((2-octyldodecyl)-1,4-dioxo-pyrrolo[3,4-c]pyrrole (0.350 g, 0.34 mmol) and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluoren-9-one (0.150 g, 0.34 mmol) were dissolved in toluene (15 mL). 2M K_2CO_3 (5 mL) and 2 drops of Aliquat 336 were added in the above reaction mixture. The solution was purged with argon for 30 min, and then tetrakis(triphenylphosphine)palladium (20 mg, 0.017 mmol) was added. The reaction was stirred at 80°C for 3 d. Then a solution of phenylboronic acid was added, followed by the addition of bromobenzene and stirred overnight. 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 re--dissolved 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 (68 % yield).

*M*w/*M*n (GPC) = 42,600/ 135615, polydispersity index (PDI) =3.18, λmax (UV-vis-Near IR): 711 nm (in chloroform); 712 nm (thin film). Absorption cutoff from thin film= 764 nm.

OTFT Fabrication and Characterization

Bottom contact/bottom gate OFET devices fabricated using Si/SiO_2 substrates where n doped Si and SiO_2 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 15 nF/cm^2. Substrates were cleaned using ultrasonication in acetone, methanol and isopropanol alcohol. The cleaned substrates were dried under a nitrogen flow and heated at 120°C for 5 min. The substrates were then treated in UV-ozone for 5 minutes. The source/drain electrodes were defined by photolithography and chrome/gold (2.5 nm/50 nm) bi-layers were deposited by thermal evaporation. Self-assembled mono-layer (SAM) was treated by soaking a dilute solution of pentafluorobenzenethiol (PFBT) and isopropyl alcohol (10mM) for 1 hour, then rinsed with pure isopropyl alcohol to remove residual PFBT and annealed at 120°C for 30 minutes. These samples were immersed in a dilute octadecyltrimethoxysilane (OTMS) solution with isopropanol (concentration= 1:20) for 5 minutes under the nitrogen atmosphere. The substrate was rinsed with isopropanol, and dried under a nitrogen flow. The substrates were placed on the hot plate at 120 °C for 30 minutes. PDPPT- *alt*- FN polymer thin film was deposited via spin coating using 8 mg/ml solution in chloroform on the OTMS treated Si/SiO_2 substrate. For a typical OFET device reported here, the source-drain channel length (L) and channel width (W) was 4 μm and 80 μm, respectively. The device characteristics of the OFETs were measured at room temperature in air. The field effect mobility (μ) was calculated from the saturation regime of transfer characteristics. The saturation mobility $\mu_{sat.}$ is calculated from the slope of $\sqrt{|I_{DS}|}$ vs. V_G that is obtained from the output characteristics in the saturation region:

$$\mu_{sat.} = \left(\frac{\sqrt{|I_{DS}|}}{V_G} \right)^2_{V_{DS}} \frac{2L}{WC_i}$$

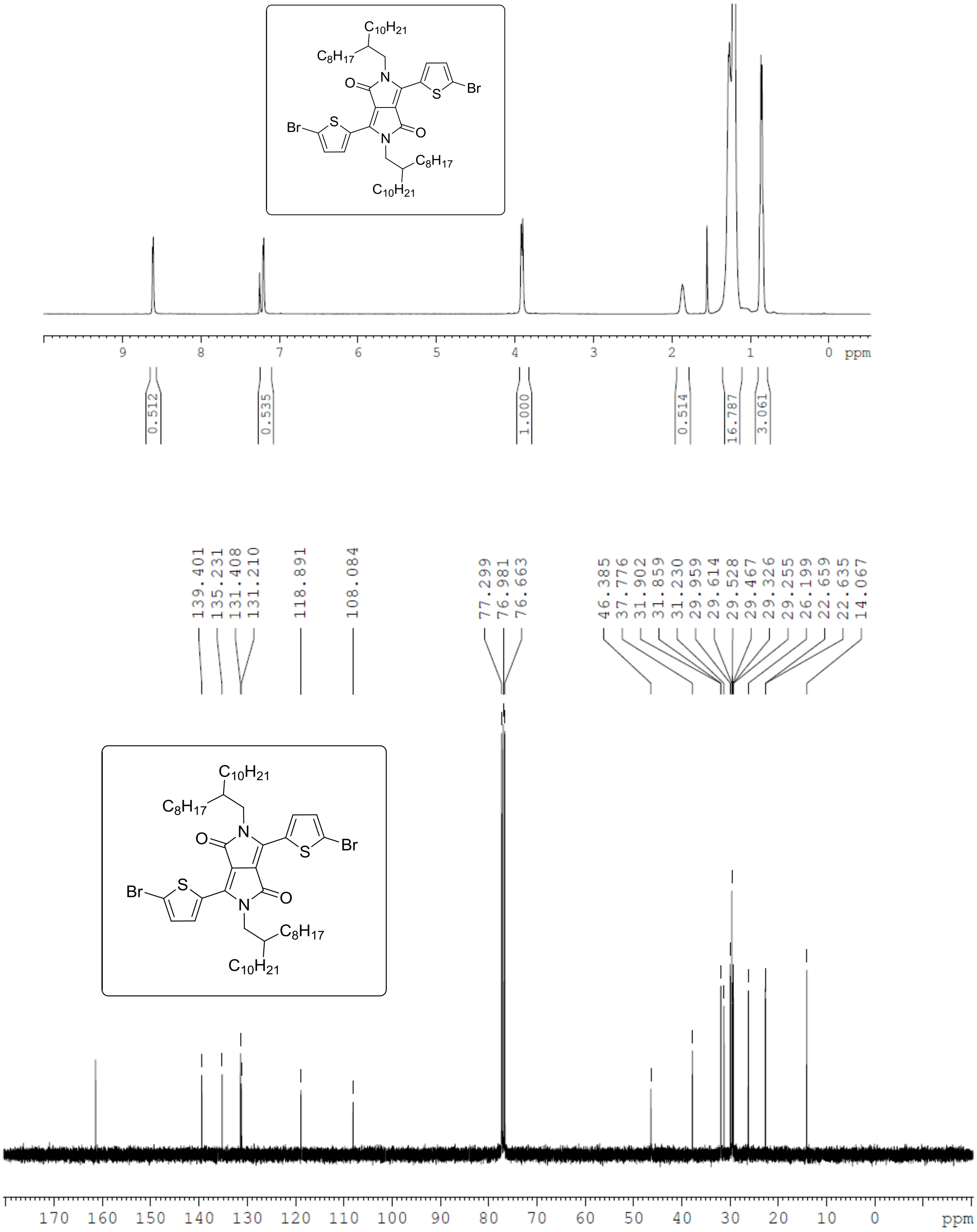
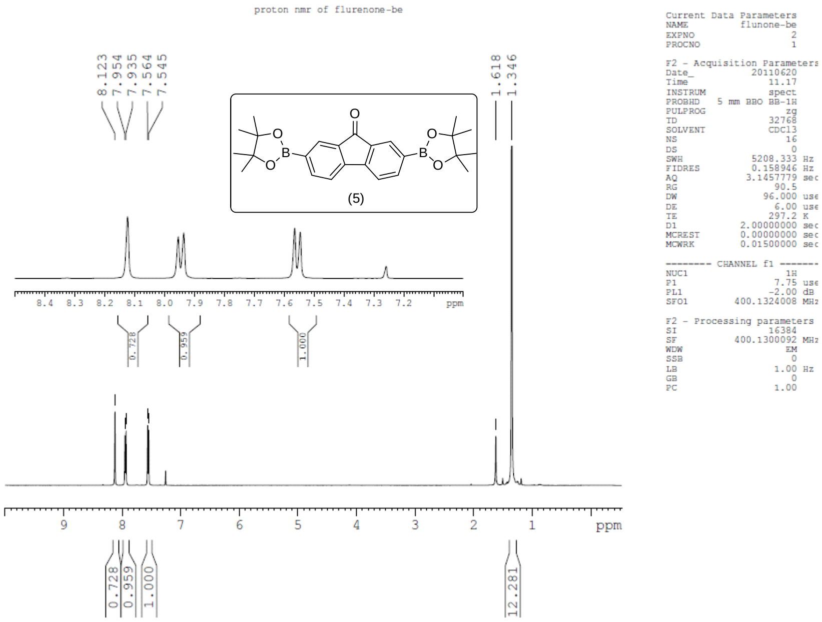


Figure S1. ^{1}H NMR and ^{13}C spectra of 3,6-bis-(5-bromo-thiophen-2-yl)-N,N'-bis((2-octyldodecyl)-1,4-dioxo-pyrrolo[3,4-c]pyrrole in $CDCl_3$ (**3**).



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TD                 32768
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DS                     0
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FIDRES          0.158946 Hz
AQ             3.1457779 sec
RG                  90.5
DW                96.000 use
DE                  6.00 use
TE                 297.2 K
D1            2.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 =======
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P1                  7.75 use
PL1                -2.00 dB
SFO1         400.1324008 MHz

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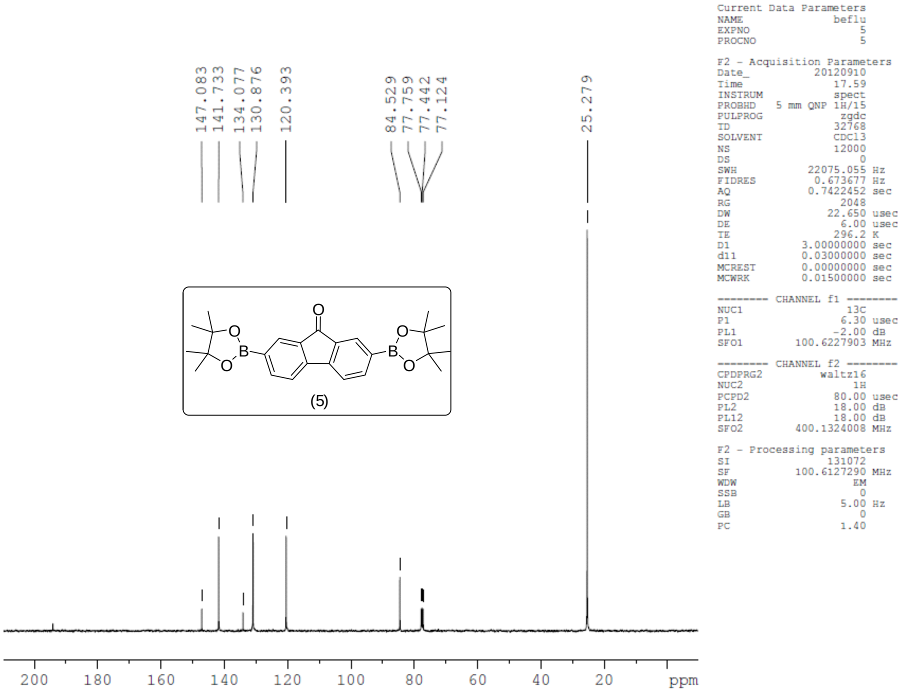

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DE                  6.00 usec
TE                 296.2 K
D1            3.00000000 sec
d11           0.03000000 sec
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MCWRK         0.01500000 sec

======== CHANNEL f1 ========
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PL1                -2.00 dB
SFO1         100.6227903 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                18.00 dB
PL12               18.00 dB
SFO2         400.1324008 MHz

F2 - Processing parameters
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SF           100.6127290 MHz
WDW                   EM
SSB                    0
LB                  5.00 Hz
GB                     0
PC                  1.40
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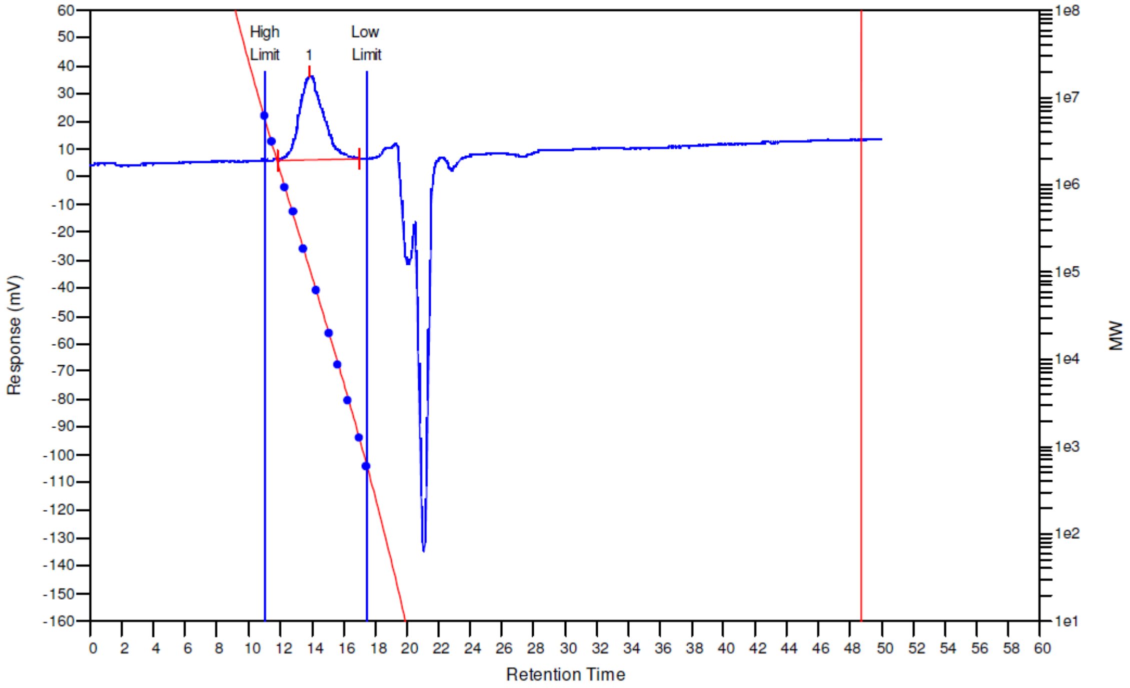
Figure S2. ^{1}H NMR and ^{13}C spectra of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluoren-9-one (5).

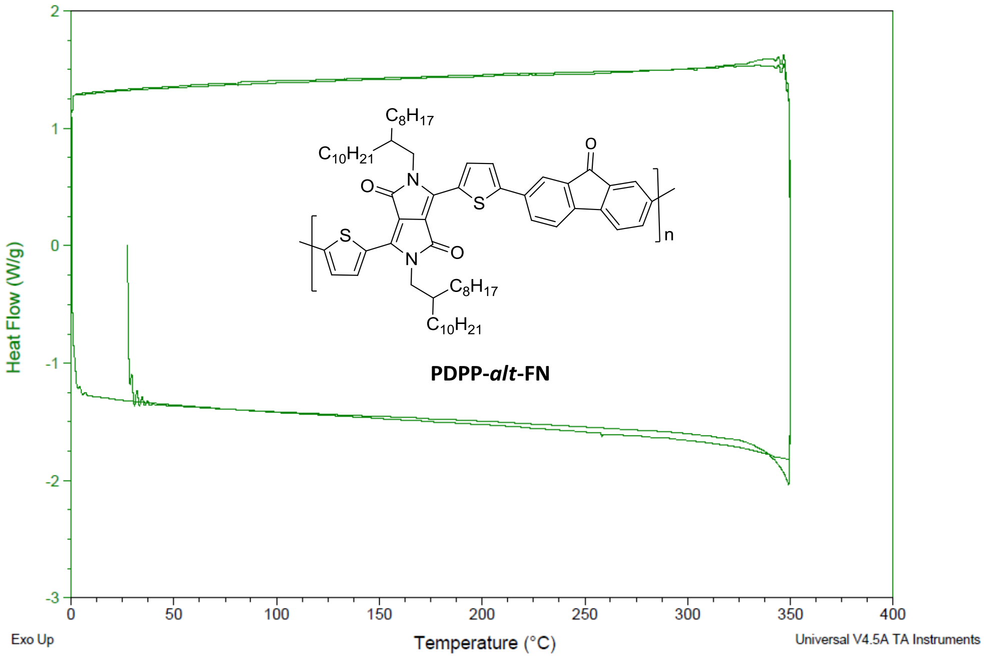


Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	105684	42604	135615	288117	510347	119275	3.18315

Figure S3. Gel permeation chromatogram of polymer **PDPPT-** ***alt-*** **FN** in 1,2,4-trichlorobenzene (TCB) using PS internal standard.



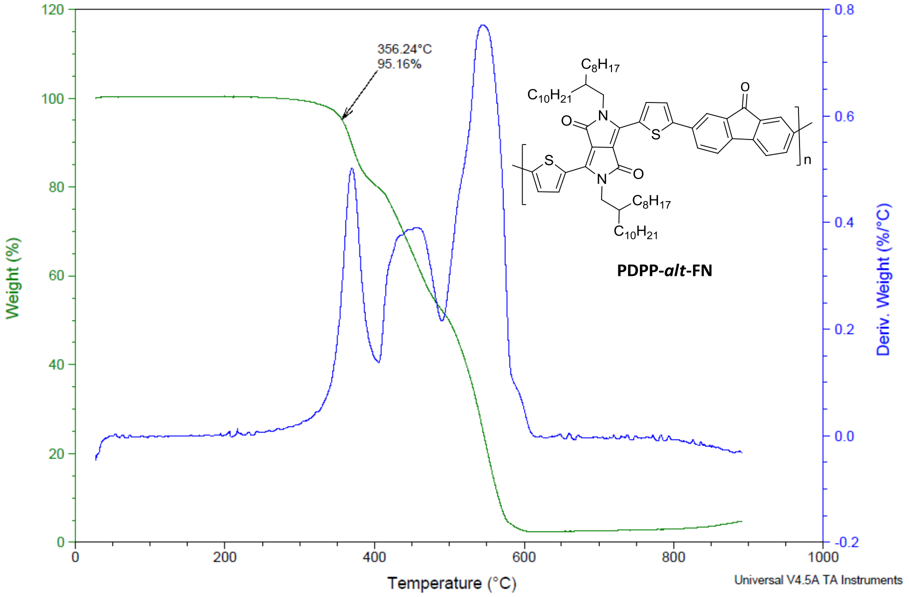


Fig. S4 Differential Scanning Calorimetry (DSC) and thermo gravimetric analysis (TGA) of **PDPPT-** ***alt*****-FN** polymer.

1. Y. Li, S. P. Singh and P. Sonar, *Adv. Mater*. 2010, **22**, 4862

2. P. Sonar, T. J. Ha, A. Dodabalapur, *Chem. Commun*. DOI: 10.1039/C2CC37131F