

## **Supplementary Information**

### **Fluorenone Based Low Band Gap Solution Processable Copolymer for Air Stable and High Mobility Organic Field Effect Transistors**

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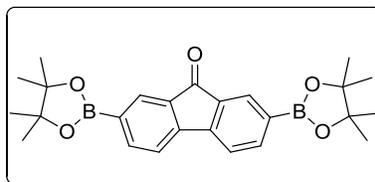
## Experimental

### General

All the chemicals 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 was synthesized similarly according to the earlier published procedure using decyltetradecyl bromide and diketopyrrolopyrrole (DPP) core compounds.<sup>1</sup>

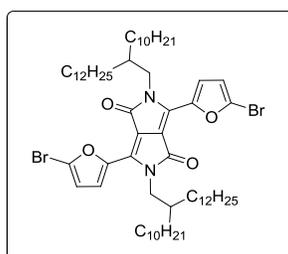
### Characterization

<sup>1</sup>H and <sup>13</sup>C NMR data were performed on a Bruker DPX 300 MHz or 400 MHz spectrometer using solvent CDCl<sub>3</sub>. The chemical shifts were recorded in ppm using TMS as an internal standard. 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 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<sup>6</sup>). UV-Vis spectra were recorded on a Shimadzu model 2501-PC. Photoelectron spectroscopy in air (PESA) measurement was done on the thin film of PFN-DPPF polymer spin coated on glass 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<sup>-1</sup>). Thermal gravimetric analysis (TGA) was carried out using a TA Instrument TGA Q500 instrument (heating rate of 10°C min<sup>-1</sup>).



**Synthesis of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluoren-9-one (2):** (3)

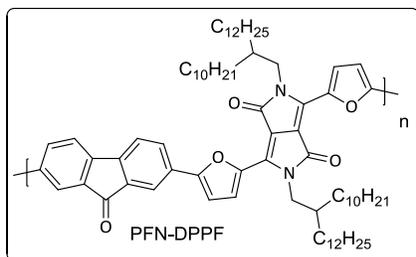
2,7-dibromo-9H-fluoren-9-one (3.0 g, 8.87 mmol), bis(pinacolato)diboron (5.31 g, 20.91 mmol), PdCl<sub>2</sub>(dppf) (0.381 g, 0.457 mmol), and KOAc (8.0 g, 44.3 mmol) was kept under vacuum for 10 min and then degassed before 1,4-dioxane (50 mL) was added under argon. The reaction mixture was stirred at 80 °C overnight and quenched by adding water. The resulting mixture was extracted with chloroform (100 mL). The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and filtered. After removing the solvent, a dark red solid was obtained, which was purified by silica gel chromatography by using 3 % ethyl acetate in hexane as eluent to give the title compound as a yellow solid (2.4 g, 62 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.12 (s, 2H), 7.95-7.93 (d, 2H), 7.56-7.54 (d, 2H), 1.34 (s, 24H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 147.08, 141.73, 134.077, 130.876, 120.39, 84.52, 25.27. MS (MALDI-TOF, m/z) calcd. for C<sub>25</sub>H<sub>30</sub>B<sub>2</sub>O<sub>5</sub> =432.23, found, 434.38.



**Synthesis of 3,6-bis(5-bromofuran-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (4):**

2,5-bis(2-decyltetradecyl)-3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (5.0 g, 5.31 mmol) and chloroform (50 mL) were charged to a 100 mL three neck flask equipped with a stirring bar, a condenser, and a dropping funnel. Bromine (Br<sub>2</sub>) (1.74 g, 10.88 mmol) in chloroform (20 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 MgSO<sub>4</sub>. 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 (4.50 g, 77%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.29-8.28 (d, 2H), 6.61-6.60 (d, 2H), 3.98-3.96 (d, 4H), 1.78-1.76 (s, 2 H), 1.35-1.26 (m, 80H), 0.88-0.85 (t, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.28, 146.63, 133.18, 126.60, 122.61, 115.90, 106.70, 47.02, 39.22, 32.33, 31.87, 30.52, 30.06, 29.99, 29.76, 26.90, 23.09, 14.51. MS (MALDI-TOF,  $m/z$ ): calcd. for  $\text{C}_{62}\text{H}_{102}\text{Br}_2\text{N}_2\text{O}_4=1096.62$ ; found, 1097.21.



### Synthesis of poly{2,7-9H-fluoren-9-one alt- (furan-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione} (PFN-DPPF):

To a 50 mL Schlenk flask, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluoren-9-one (0.133 g, 0.30 mmol) and 3,6-bis(5-bromofuran-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (0.350 g, 0.30 mmol) were dissolved in toluene (15 mL). 2M  $\text{K}_2\text{CO}_3$  (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 (76 % yield).

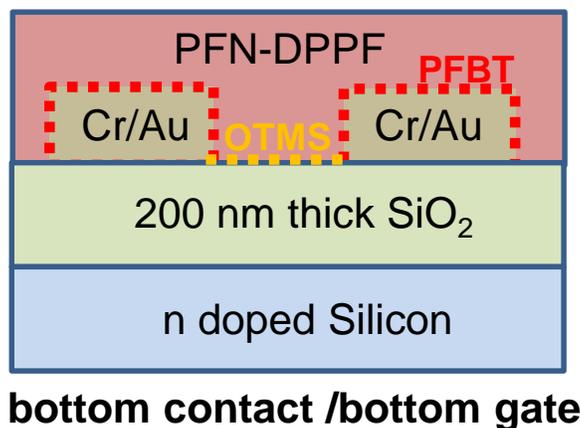
$M_w/M_n$  (GPC) = 28,300/ 70,000, polydispersity index (PDI) =2.93,  $\lambda_{\text{max}}$  (UV-vis-Near IR): 711 nm (in chloroform); 712 nm (thin film). Absorption cutoff from thin film= 764 nm.

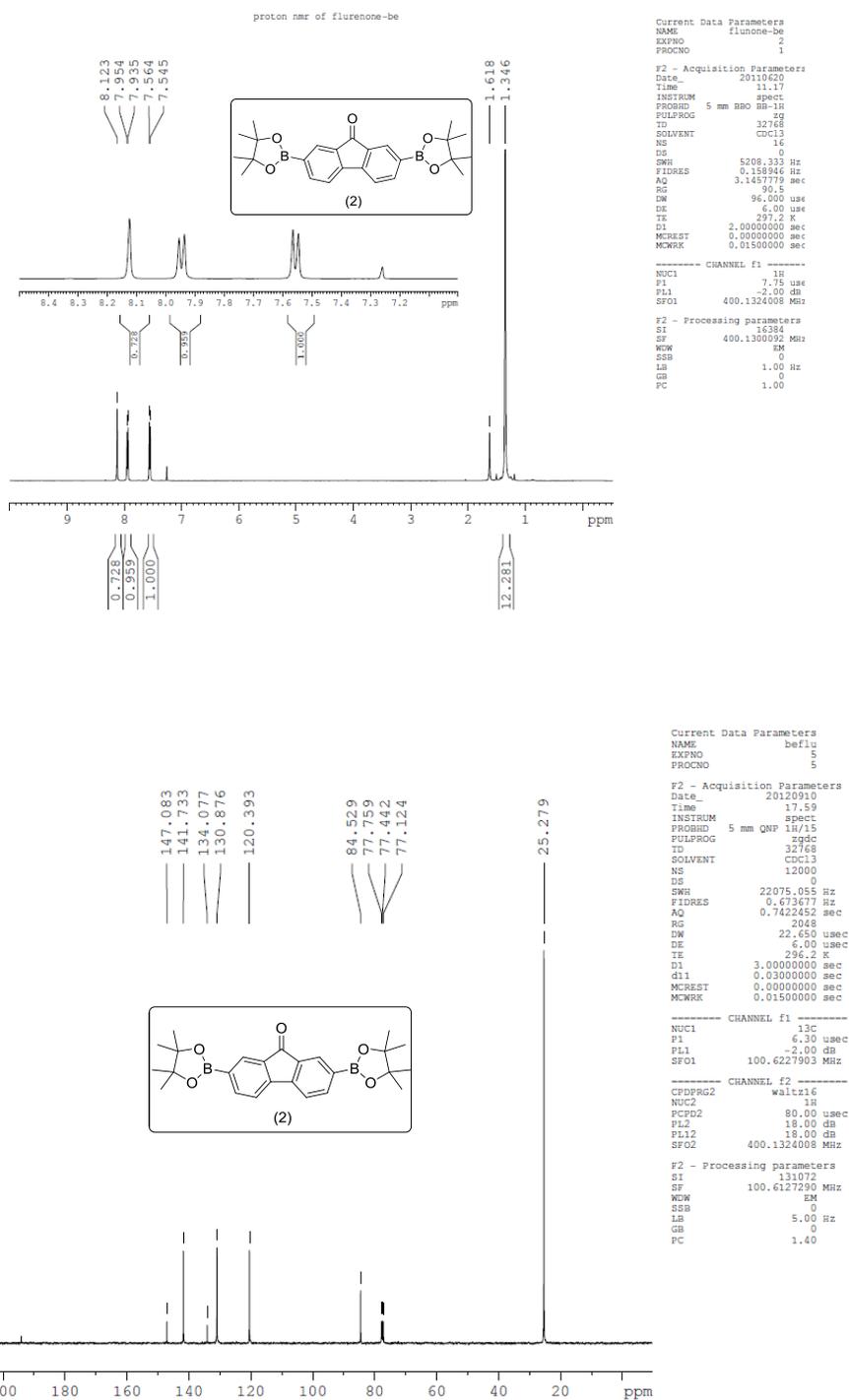
### OTFT Fabrication and Characterization

Bottom contact/bottom gate OFET devices fabricated using Si/SiO<sub>2</sub> substrates where n doped Si and SiO<sub>2</sub> 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<sup>2</sup>. 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.

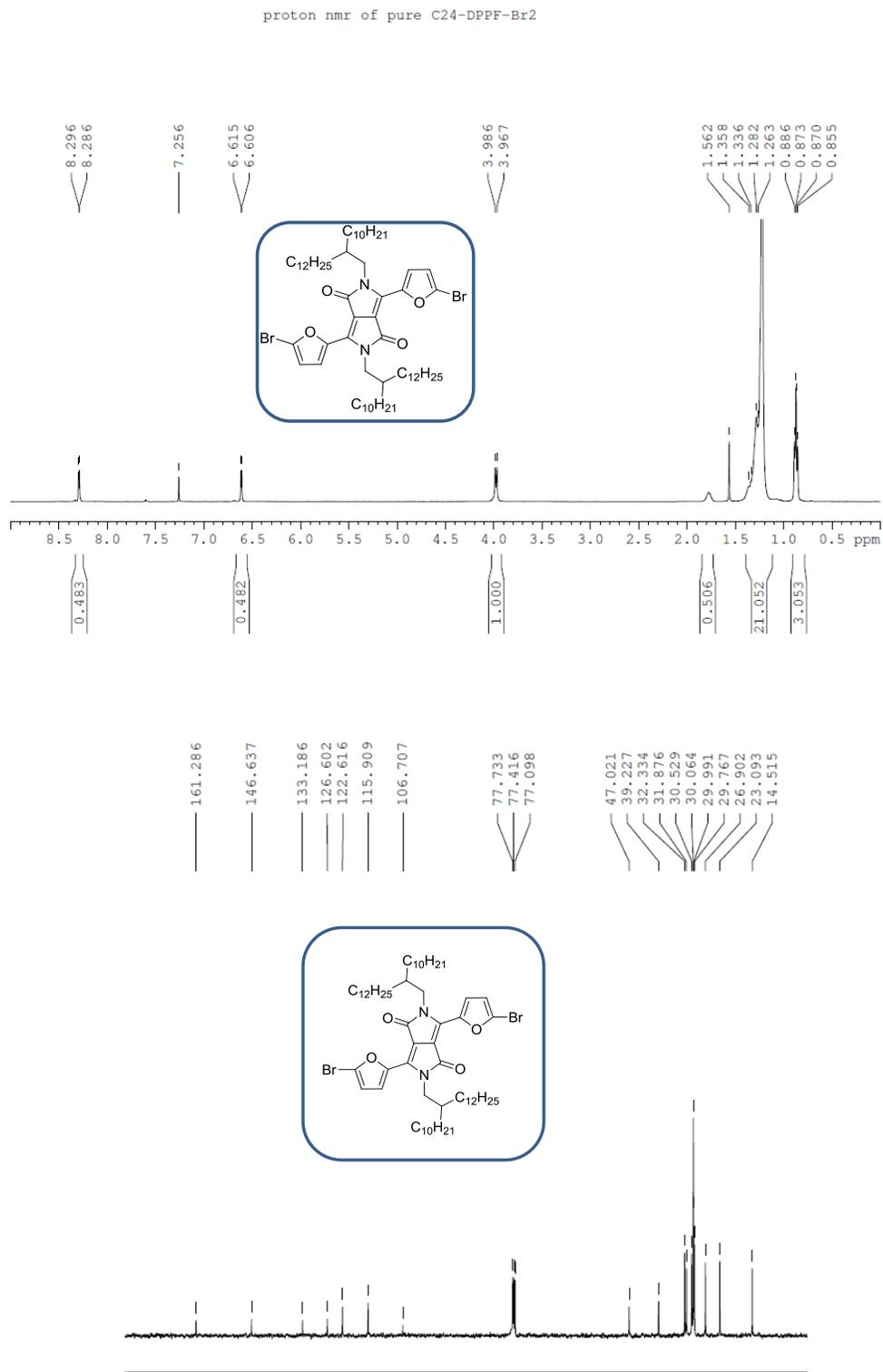
PFN-DPPF polymer thin film was deposited via spin coating using 8 mg/ml solution in chloroform on the OTMS treated Si/SiO<sub>2</sub> substrate. For a typical OFET device reported here, the source-drain channel length (L) and channel width (W) was 4 μm and 80 μm, respectively. The device characteristics 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:

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





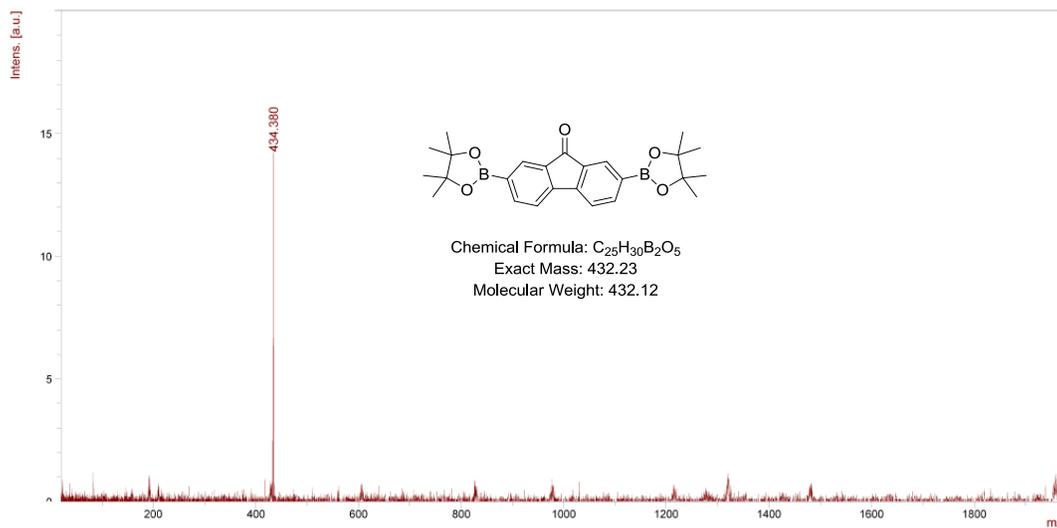
**Figure S1.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  spectra of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluoren-9-one (2).



**Figure S2.** <sup>1</sup>H NMR and <sup>13</sup>C spectra of 3,6-bis(5-bromofuran-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione in CDCl<sub>3</sub> (4).

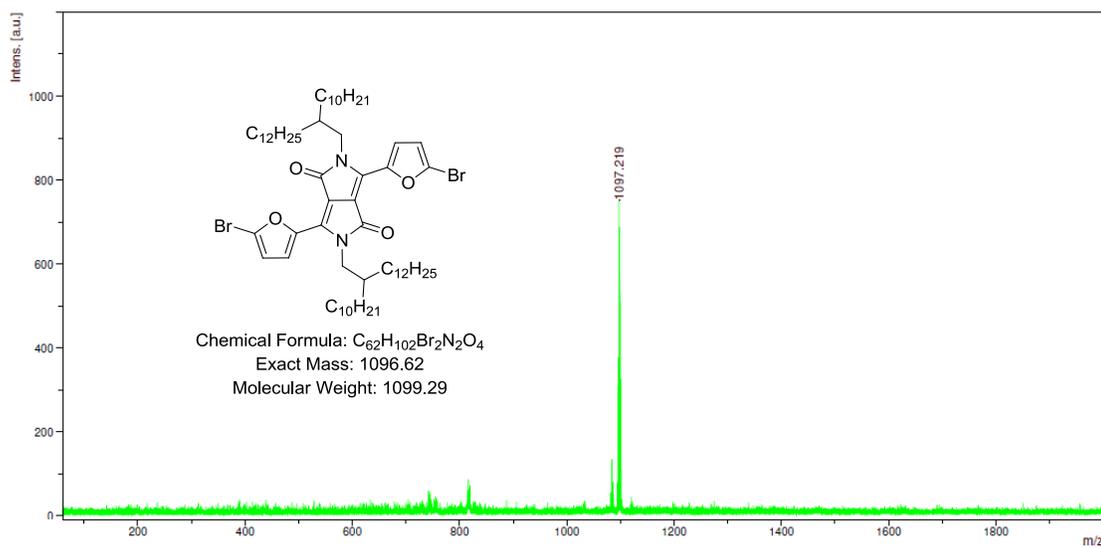
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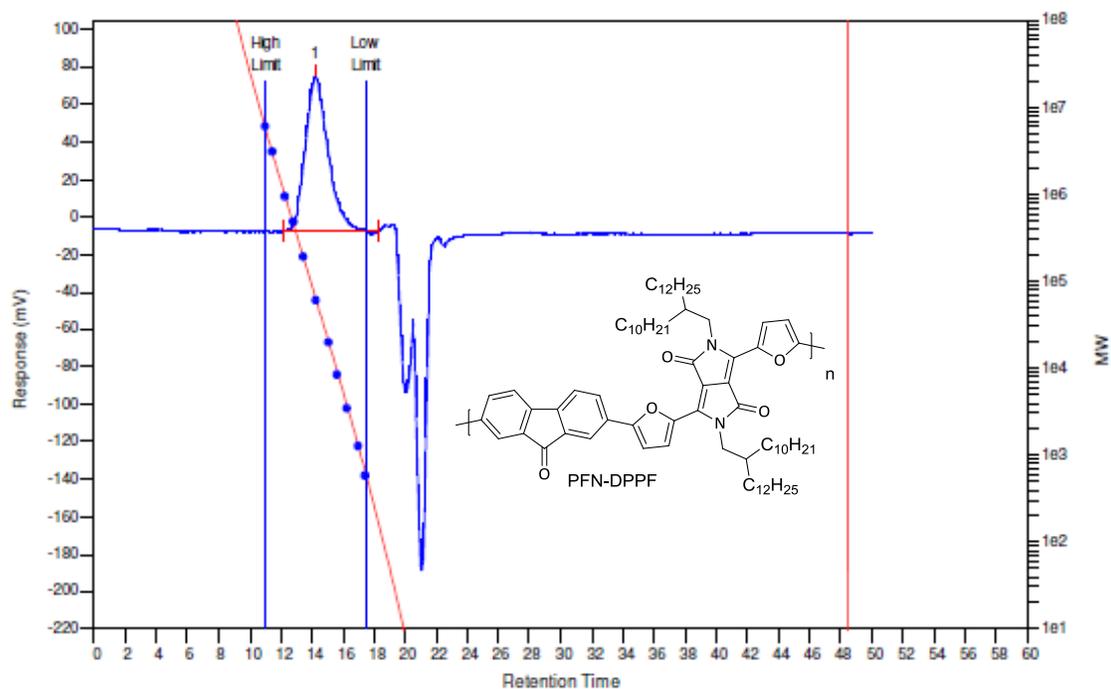


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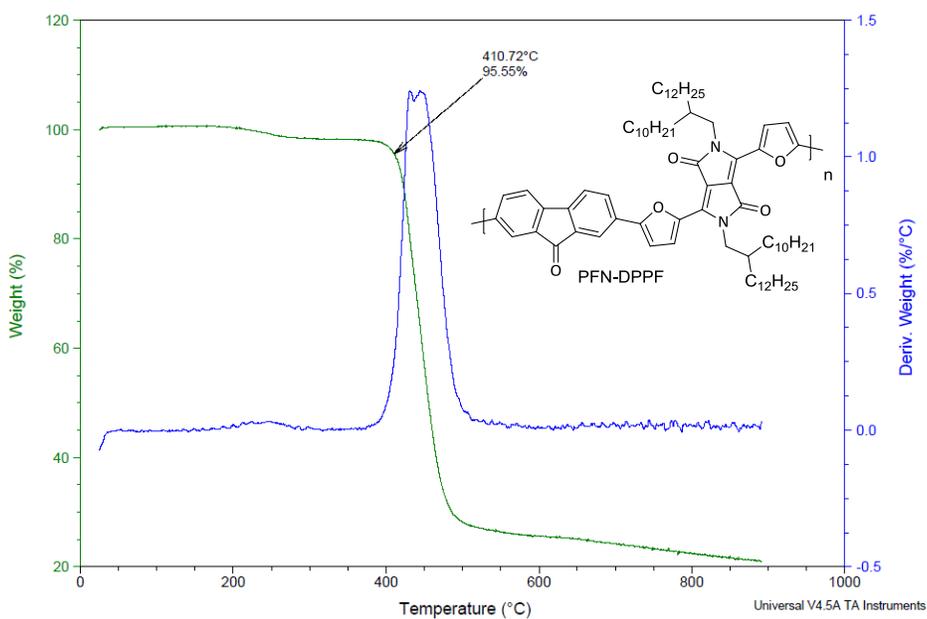
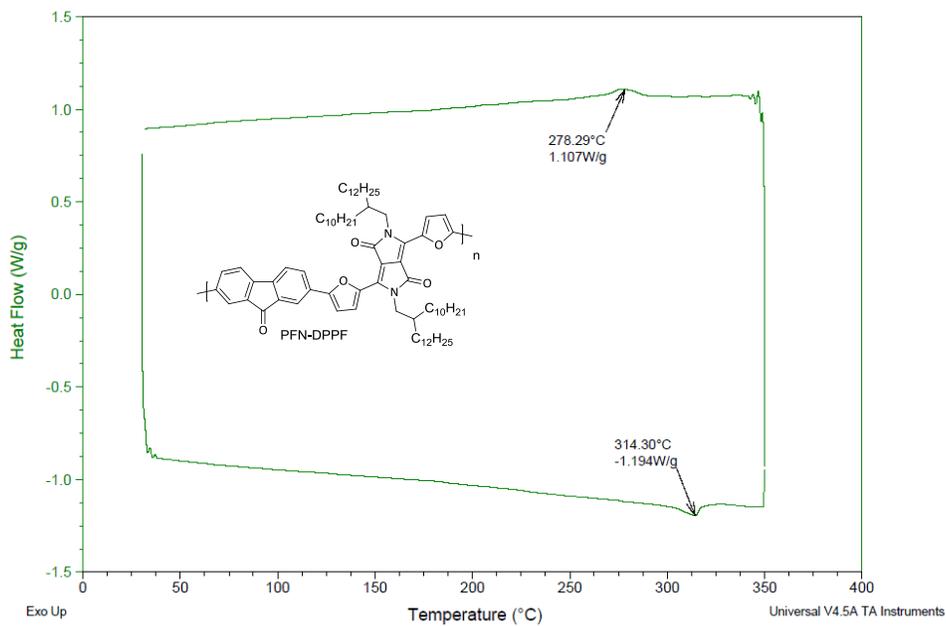
**Figure S3.** Matrix assisted laser deposition-time of flight (MALDI-TOF) spectra of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluoren-9-one (2) and 3,6-bis(5-bromofuran-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (4).



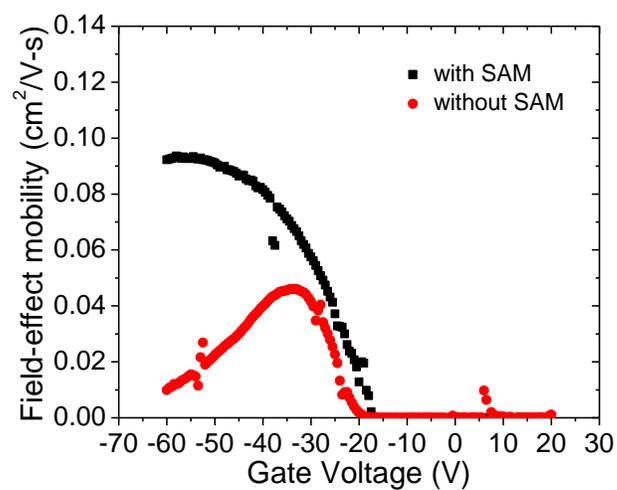
Sample Injection Report

MW Averages							
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	70010	28381	83364	165849	273464	73967	2.93732

**Figure S4.** Gel permeation chromatogram of polymer **PFN-DPPF** in THF and Chloroform using PMMA internal standard.



**Fig. S5** Differential Scanning Calorimetry (DSC) and thermo gravimetric analysis (TGA) of PFN-DPPF polymer.



**Fig. S6** Effect of SAM treatment **PFN-DPPF** based OFET devices on OTMS modified SiO<sub>2</sub>/Si substrates.

#### References

1. Y. Li, P. Sonar, S. P. Singh, W. Zeng, M. S. Soh, *J. Mater. Chem.* 2011, **21**,10829.