

Supplementary Materials

Enhancement in Charge Carrier Mobility by Using Furan as Spacer in Thieno[3,2-*b*]pyrrole and Alkylated-Diketopyrrolopyrrole Based Conjugated Copolymers

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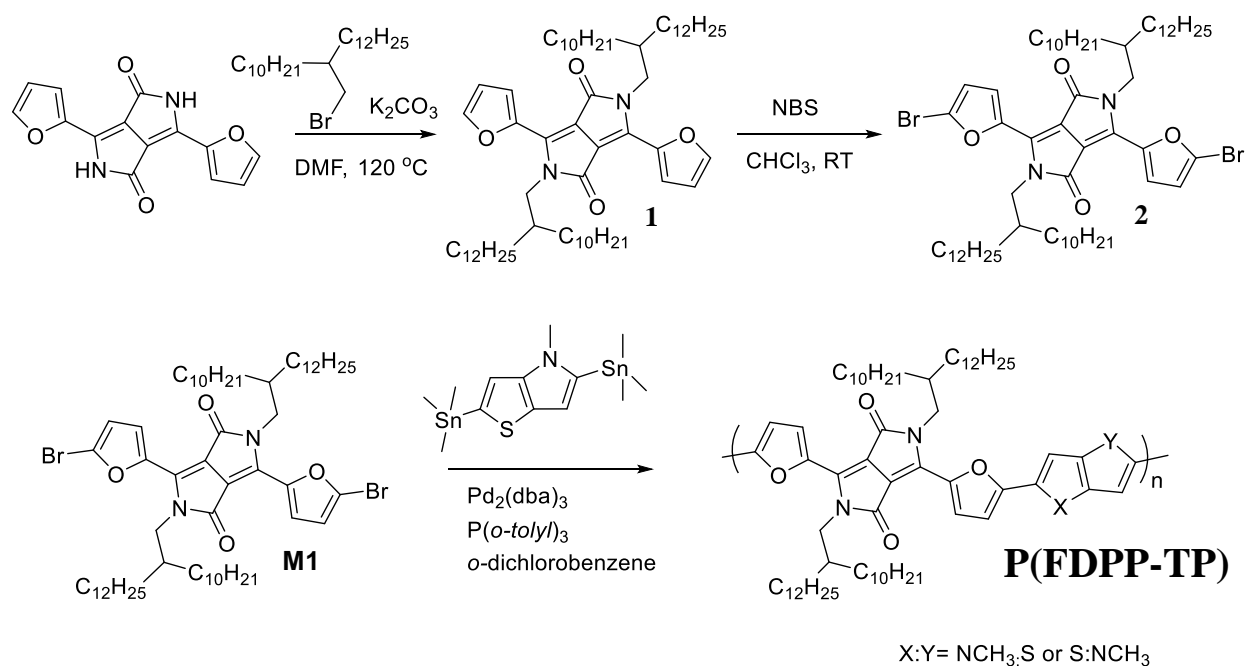
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Experimental methods

The reagents were acquired from Fisher Scientific and Sigma-Aldrich and used without further purification. Except for the bromination, all the other reactions were performed in closed vessels in a nitrogen environment. Compound 4-methyl-2,5-bis(trimethylstannyl)-4*H*-thieno[3,2-*b*]pyrrole was synthesized according to a procedure in the literature [1]. The hydrogen (¹H) and carbon (¹³C) NMR spectra were acquired with a Bruker AVANCE 500 MHz spectrometer and processed with the TopSpin software. The polymer molecular weight was measured by size-exclusion chromatography (SEC) using a Viscotec VE 3580 system with CLM3009 columns, linked to a UV detector with a 254 nm laser source. Tetrahydrofuran eluent was used, and polystyrene-standard calibration was employed for SEC analysis. Thermal properties were examined on a Mettler Toledo TGA/DSC-1 system under inert gas conditions. Thermal gravimetric analysis (TGA) was carried out at a scanning rate of 10 °C/min and differential scanning calorimetry (DSC) analysis was carried out at a scanning rate of 20 °C/min. An Agilent 8453 UV-Vis spectrometer was used to obtain UV-Vis spectra for both solution (chloroform) and thin films. BAS CV-50W voltammetric analyzer with a three-electrode system (Pt wire counter electrode, glassy carbon working electrode, and Ag/Ag⁺ reference electrode) was employed for cyclic voltammetry analysis using 0.1 M tetrabutylammonium hexafluorophosphate solution as the electrolyte. Rigaku III SmartLab XRD instrument using Cu K α ($\lambda=1.54059$ Å) with a nickel filter was used for GIXRD measurements of samples prepared by spin coating a 10 mg/mL solution at 500 rpm on a cleaned Si substrate treated with octadecyltrimethoxysilane (OTMS). For the surface morphology studies, a Nanoscope IV Multimode Veeco instrument (Cantilever: Bruker NTESPA; Frequency: 300kHz; force constant: 40N/m) was used to obtain TMAFM images by scanning the channel region. The scanning area for the images was $2 \times 2 \mu\text{m}^2$ with a frequency of 1 Hz. To fabricate OFET devices, a highly doped n-type silicon wafer with a 200 nm thick SiO₂ layer (capacitance = 17 nF cm⁻²) was used. In the bottom-gate bottom-contact (BGBC) device, the drain and source electrodes were furnished with 5 nm Cr and 100 nm Au, while in bottom-gate top-contact (BGTC) devices, drain and source electrodes were 100 nm Au. The channel width and channel length of BGTC devices were 100 μm and 1000 μm , while those of the BGBC devices were 20 μm and 475 μm , respectively, defined by the masks used for the fabrication. The mobilities over six devices were measured at each annealing temperature, and maximum and average values were reported. The SiO₂ surface was cleaned with a piranha solution (30% H₂O₂: Conc.H₂SO₄ = 3:7 v/v) before it was treated with a 3 μM octadecyltrimethoxysilane

(OTMS) solution. A 10 mg/mL solution of the polymer was spin-coated under a nitrogen environment at 500 rpm and annealed at different temperatures for 5 minutes. The polymer thin-film thickness was determined with a Veeco Dektak VIII Profilometer. The films had a thickness ranging between 33 and 38 nm. All the electrical measurements were obtained at ambient conditions using a Keithley 4200-SCS system coupled with a Cascade Microtech probe station.

Detailed synthesis methods



Scheme S1. Synthesis of the poly(((methylthionopyrrolo)furanyl)diketopyrrolopyrrol) **P(FDPP-TP)**.

Synthesis of 2,5-bis(2-decyltetradecyl)-3,6-di(furan-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**1**)

3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (1.00 g, 3.72 mmol) and anhydrous potassium carbonate (1.55 g, 11.16 mmol) were measured into a three-neck round bottom flask under nitrogen. Anhydrous DMF (15 mL) was added, and the reaction mixture was stirred at 120°C for 2 hours before 9-(bromomethyl)nonadecane (4.03 g, 11.16 mmol) was injected. The reaction mixture was stirred at 120°C for 24 hours and quenched into an ice–water mixture and extracted with dichloromethane (100 mL \times 2). The organic layer was dried over magnesium sulfate, and a red color solid was recovered after the solvent was removed. The crude product was purified by using silica gel chromatography with dichloromethane and hexane (3:7) as eluent to give a dark red solid as the pure product (yield 61%). ^1H NMR (CDCl_3 , 500 MHz): δ_{H} 0.86–0.89 (m, 6H), 1.22–1.29 (m, 40H), 1.79 (m, 1H), 4.05 (s, 1H), 4.03 (d, $J = 7.5\text{Hz}$, 2H), 6.68 (dd, $J_1 = 3.5\text{Hz}$, $J_2 = 1.5\text{Hz}$, 1H), 7.59 (d, $J = 1.5\text{Hz}$, 1H), 8.32 (d, $J = 3.5\text{Hz}$, 1H). ^{13}C NMR (CDCl_3 , 125 MHz): 14.25, 22.83, 26.66, 29.48, 29.50, 29.76, 29.78, 29.80, 29.83, 30.16, 31.47, 32.07, 38.66, 46.70, 106.64, 119.59, 120.29, 134.08, 144.91, 144.95, 161.38.

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

2,5-bis(2-decyltetradecyl)-3,6-di(furan-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (0.300 g, 0.32 mmol) was dissolved in chloroform (45 mL) at 0 °C under nitrogen conditions. *N*-bromosuccinimide (0.125 g, 0.70 mmol) was dissolved in chloroform (5 mL) and slowly injected into reaction mixture over 10 minutes at 0 °C while stirring. Then the reaction mixture was further stirred for 1.5 hours at 0 °C. The reaction was monitored by thin-layer chromatography, and completion of the reaction was confirmed by proton NMR. Reaction mixture was poured into deionized water, extracted with two more chloroform portions (50 mL ×2), washed with deionized water, and dried over anhydrous magnesium sulfate. Then the solvent was removed under vacuum to obtain crude product. Crude was purified by column chromatography using silica and 30% dichloromethane in hexane as eluent to obtain purple solid product (0.185 g, 53%). ¹H NMR (CDCl₃, 500 MHz): δ_H 0.83–0.87 (m, 6H), 1.22–1.28 (m, 40H), 1.77 (m, 1H), 3.98 (d, *J* = 7.5 Hz, 2H), 6.61 (d, *J* = 3.5 Hz, 1H), 8.29 (d, *J* = 3.5 Hz, 1H). ¹³C NMR (CDCl₃, 125 MHz): δ_C 14.26, 22.84, 26.65, 29.51, 29.73, 29.81, 29.85, 30.28, 31.63, 32.08, 38.97, 46.78, 106.47, 115.65, 122.36, 126.35, 132.95, 146.39, 161.05.

Synthesis of P(FDPP-TP) polymer

3,6-bis(5-bromofuran-2-yl)-2,5-bis(2-octadecyl)pyrrolo[3,4-c]pyrrole-1,4-(2*H*,5*H*)-dione (110 mg, 0.11 mmol), 4-methyl-2,5-bis(trimethylstannyl)-4*H*-thieno[3,2*b*]pyrrole (50 mg, 0.11 mmol), tris(dibenzylideneacetone)dipalladium (2.0 mg, 2.1 μmol), and tri(*o*-tolyl)phosphine (2.5 mg, 8.4 μmol) were dissolved in 5 mL *o*-dichlorobenzene under a nitrogen atmosphere in a 50 mL pressure flask. Mixture was sealed and stirred at 130 °C for 36 hours. Reaction was cooled to room temperature and quenched in 250 mL of methanol. The solid obtained was Soxhlet extracted with methanol, hexanes, and acetone before it was extracted into chloroform. After removing the chloroform, final polymer was obtained as a dark blue solid (61 mg, yield=58%, *M_n*=18.6 kDa, *M_w*= 30.3 kDa, PDI= 1.62).

Table S1. Optoelectronic properties of P(FDPP-TP).

Polymer	HOMO ^a (eV)	LUMO ^b (eV)	E _g ^c (ec) (eV)	E _g ^d (opt) (eV)	λ _{max} sol (nm)	λ _{max} film (nm)	λ _{onset} (nm)
P(FDPP-TP)	-4.64	-2.77	1.87	1.25	395,832	402,870	1040

^a Estimated from the oxidation potential in CV. ^b Estimated from the reduction potential in CV. ^c Calculated from LUMO–HOMO. ^d Calculated from the onset of thin-film absorption in UV-Vis.

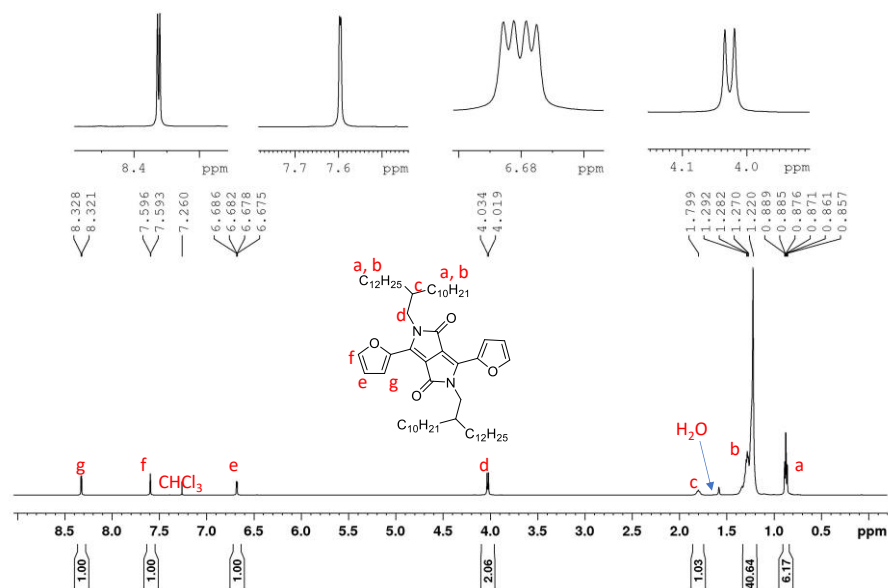


Figure S1. ^1H NMR spectrum of 2,5-bis(2-decyltetradecyl)-3,6-di(furan-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione.

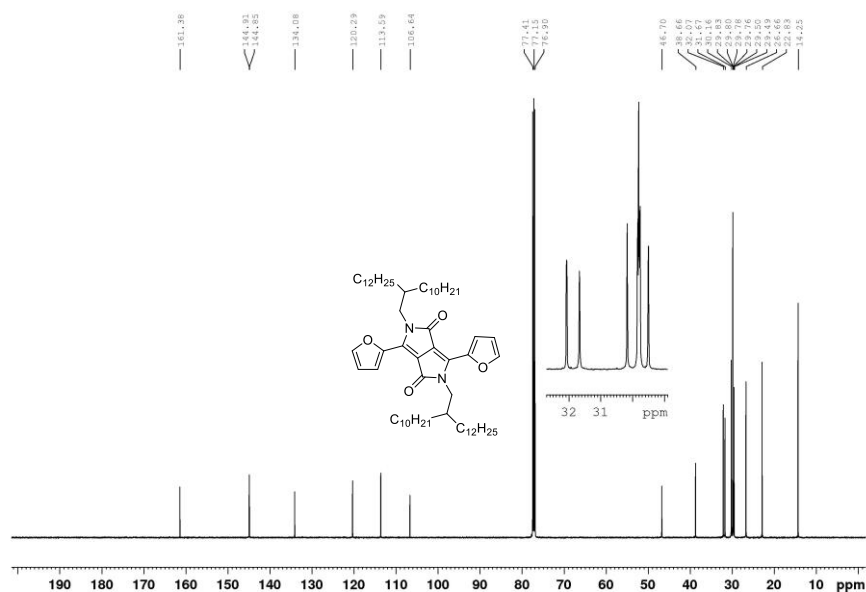


Figure S2. ^{13}C NMR spectrum of 2,5-bis(2-decyltetradecyl)-3,6-di(furan-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione.

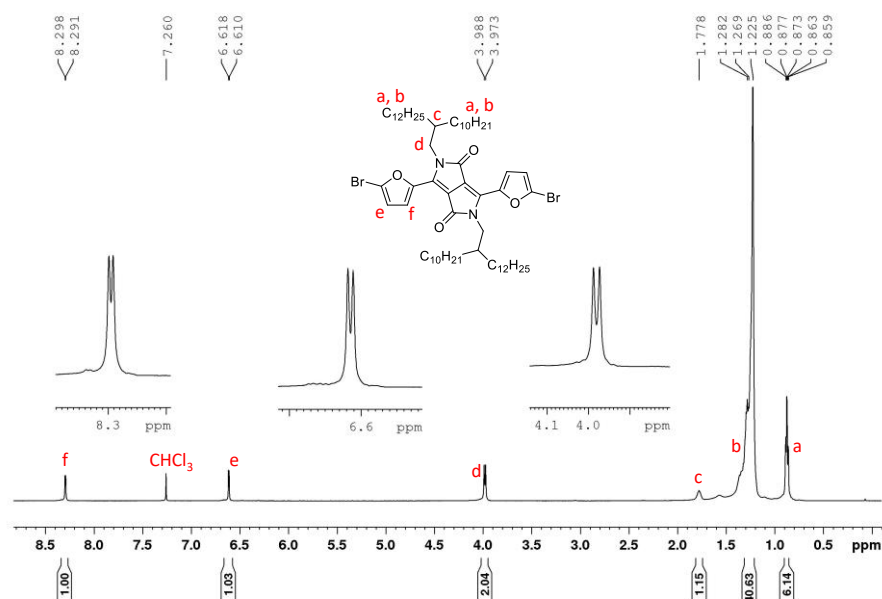


Figure S3. ^1H NMR spectrum of 3,6-bis(5-bromofuran-2-yl)-2,5-bis(2-decyltetradecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione. .

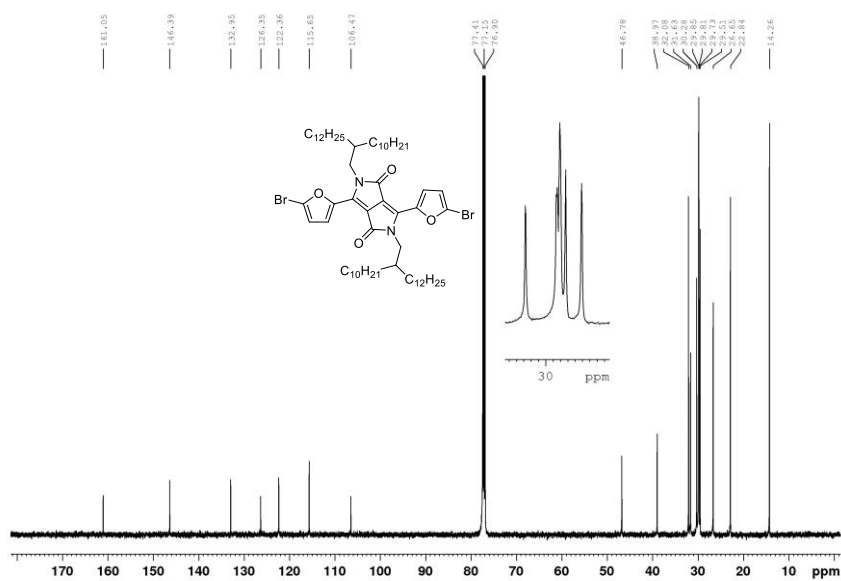


Figure S4. ^{13}C NMR spectrum of 3,6-bis(5-bromofuran-2-yl)-2,5-bis(2-decyltetradecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione. .

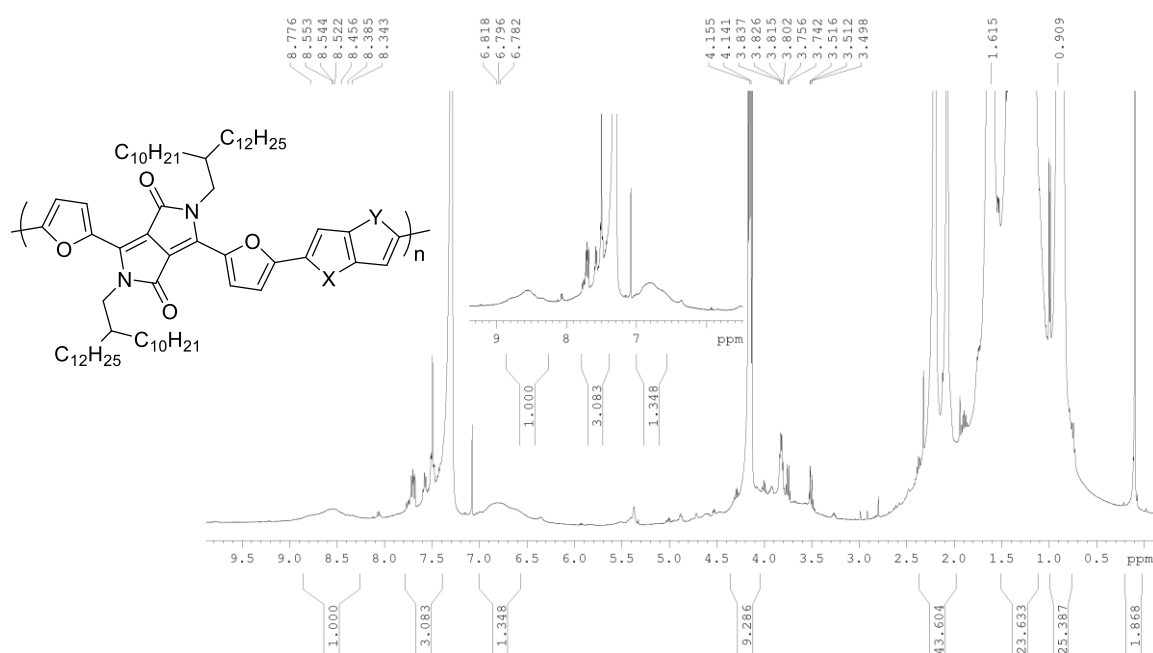


Figure S5. ^1H NMR spectrum of P(FDPP-TP) polymer.

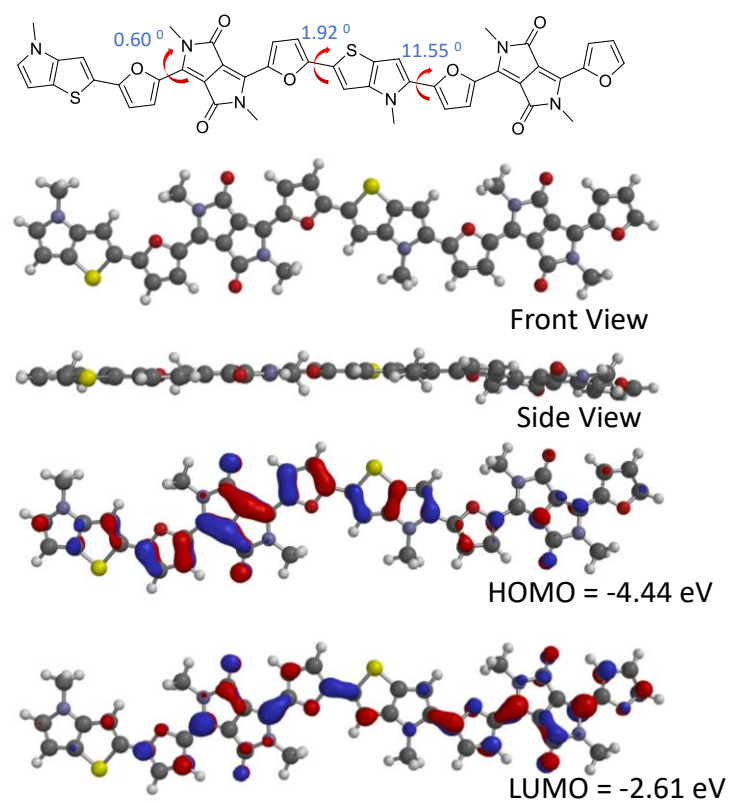


Figure S6. DFT calculation data of Spartan'16 software (B3LYP/6-31G*).

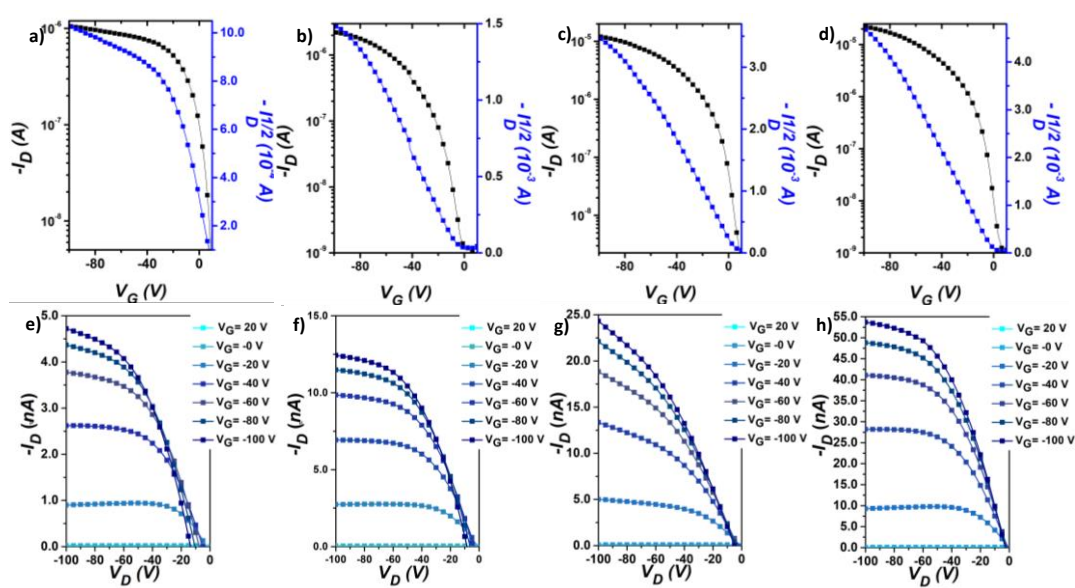


Figure S7. OFET transfer curves (a-d) and output curves (e-h) of bottom-gate top-contact devices: (a,e) RT, (b,f) 100 °C, (c,g) 150 °C, and (d,h) 200 °C.

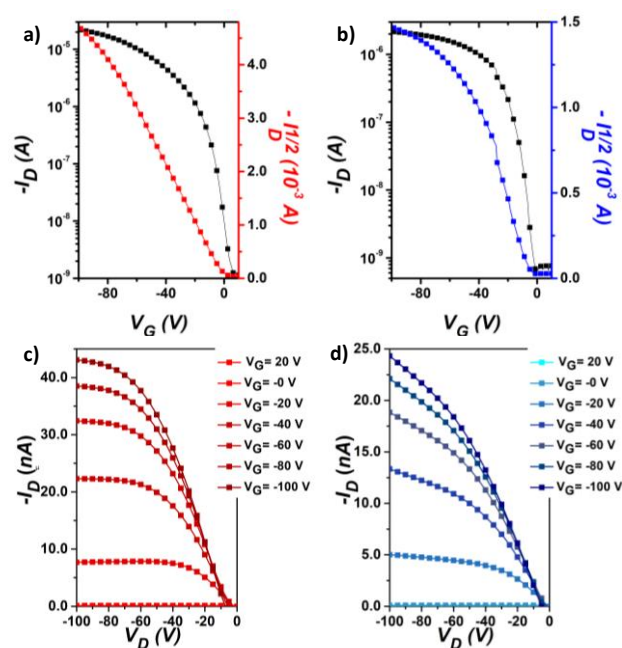


Figure S8. OFET transfer curves (a,b) and output curves (c,d) at 225 °C of (a,c) BGBC and (b,d) BGTC.

Table S2. BGBC OFET data of P(FDPP-TP).

Temperature (°C)	Maximum hole mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	Average hole mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	Threshold voltage (V)	On/off ratio
RT	4.46×10^{-3}	$3.11 (\pm 0.48) \times 10^{-3}$	-4 to (-7)	$>10^3$
100	8.45×10^{-3}	$6.95 (\pm 0.39) \times 10^{-3}$	2 to 5	$>10^4$
150	7.91×10^{-2}	$6.80 (\pm 0.36) \times 10^{-2}$	-1 to (+2)	$>10^5$
200	4.20×10^{-1}	$3.32 (\pm 0.40) \times 10^{-1}$	0 to 2	$>10^5$
225	8.92×10^{-2}	$7.71 (\pm 0.56) \times 10^{-2}$	1 to 4	$>10^5$

^a Average mobility was measured over six devices; the film thickness ranged between 33 and 38 nm.

Table S3. OFET data of BGTC devices of P(FDPP-TP).

Temperature (°C)	Maximum hole mobility (cm ² V ⁻¹ s ⁻¹)	^a Average hole mobility (cm ² V ⁻¹ s ⁻¹)	Threshold voltage (V)	On/off ratio
RT	2.62 × 10 ⁻³	1.81 (±0.31) × 10 ⁻³	7 to 10	>10 ²
100	6.40 × 10 ⁻³	5.42 (±0.40) × 10 ⁻³	-1 to (+3)	>10 ³
150	1.56 × 10 ⁻²	1.18 (±0.23) × 10 ⁻²	-3 to (-5)	>10 ⁴
200	1.27 × 10 ⁻¹	9.84 (±0.37) × 10 ⁻²	0 to (+3)	>10 ⁵
225	5.68 × 10 ⁻²	4.08 (±0.54) × 10 ⁻²	2 to 6	>10 ⁴

^a Average was measured over six devices; the film thickness ranged between 33 and 38 nm.

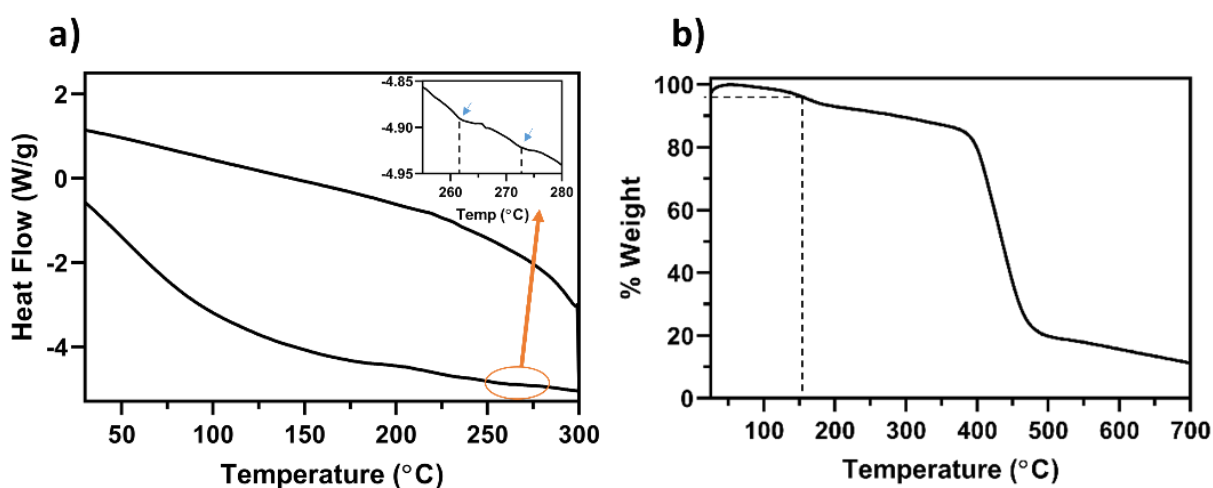


Figure S9. (a) DSC thermogram and (b) TGA thermogram of P(FDPP-TP).

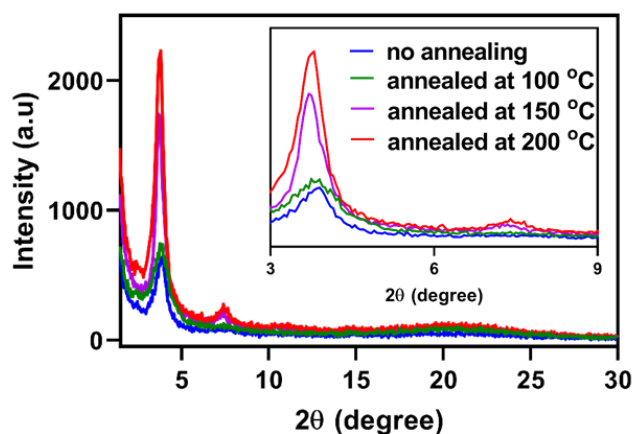


Figure S10. GIXRD pattern of P(FDPP-TP) thin films on SiO₂ substrates at different temperatures. The crystallite sizes considering (100) peak from XRD patterns were calculated by using Scherrer formula as 7.44 nm, 7.53 nm, 8.91 nm, and 9.23 nm for samples not annealed, annealed at 100 °C, annealed at 150 °C, and annealed at 200 °C, respectively [2].

Reference

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2. Patterson, A. L. The Scherrer formula for X-ray particle size determination. *Physical review* **1939**, *56*, 978–982.