

Electronic Supplementary Information

Phenanthro[1,10,9,8-*cdefg*]carbazole-containing copolymer for high performance thin-film transistors and polymer solar cells

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Experimental section

Materials: All starting materials were purchased from Alfar Aesar and used without further purification. Toluene and tetrahydrofuran (THF) were distilled from benzophenone ketyl and sodium. 4,8-dibromo-6-(2-octyldodecyl)-phenanthro[1,10,9,8-*cdefg*]carbazole ¹ and 2,5-bis(5-bromo-3-dodecylthiophen-2-yl)thiazolo[5,4-*d*]thiazole (**M2**) ² were prepared according to the literature methods.

Synthesis of N-(2-octyldodecyl)-4,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenanthro[1,10,9,8-*cdefg*]carbazole (M1):

To a solution of 4,8-dibromo-6-(2-octyldodecyl)-phenanthro[1,10,9,8-*cdefg*]carbazole (3.5 g, 5 mmol) in 100 mL dry THF at -78 °C was added dropwise 5.2 mL of 2.5 M solution of *n*-butyllithium in *n*-hexane. The mixture was stirred at -78 °C, warmed to 0 °C for 30 min, and then cooled down to -78 °C, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.8 g, 15 mmol) was added rapidly into the solution and allowed to stir at room temperature overnight. The resultant mixture was quenched with 10 mL of water and extracted with dichloromethane. The organic extracts were washed with brine and dried over

magnesium sulfate and concentrated in vacuum. The crude product was purified by chromatography using petroleum ether/dichloromethane (3:1) as an eluent to give a yellow solid. Yield: 1.28 g, 32%. ^1H NMR (400 MHz, CDCl_3): 8.97–8.99 (d, 2H), 8.68–8.70 (d, 2H), 8.45 (s, 2H), 7.86 (t, 2H), 4.64–4.65 (d, 2H), 2.35 (m, 1H), 1.49 (s, 24H), 1.36–1.40 (m, 6H), 1.19–1.27 (m, 26H), 0.81–0.87 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3): 132.97, 132.41, 130.74, 126.76, 124.99, 124.40, 122.91, 120.66, 119.90, 83.76, 49.91, 39.89, 32.08, 32.05, 31.79, 30.08, 29.80, 29.71, 29.50, 29.45, 26.54, 25.24, 22.84, 22.82, 14.29. MALDI-TOF: Found, 797.7; Calcd, 797.6. Elemental Analysis (%) Calcd, for $\text{C}_{52}\text{H}_{73}\text{B}_2\text{NO}_4$: C, 78.29; H, 9.22; N, 1.76. Found: C, 78.01; H, 9.23; N, 1.79.

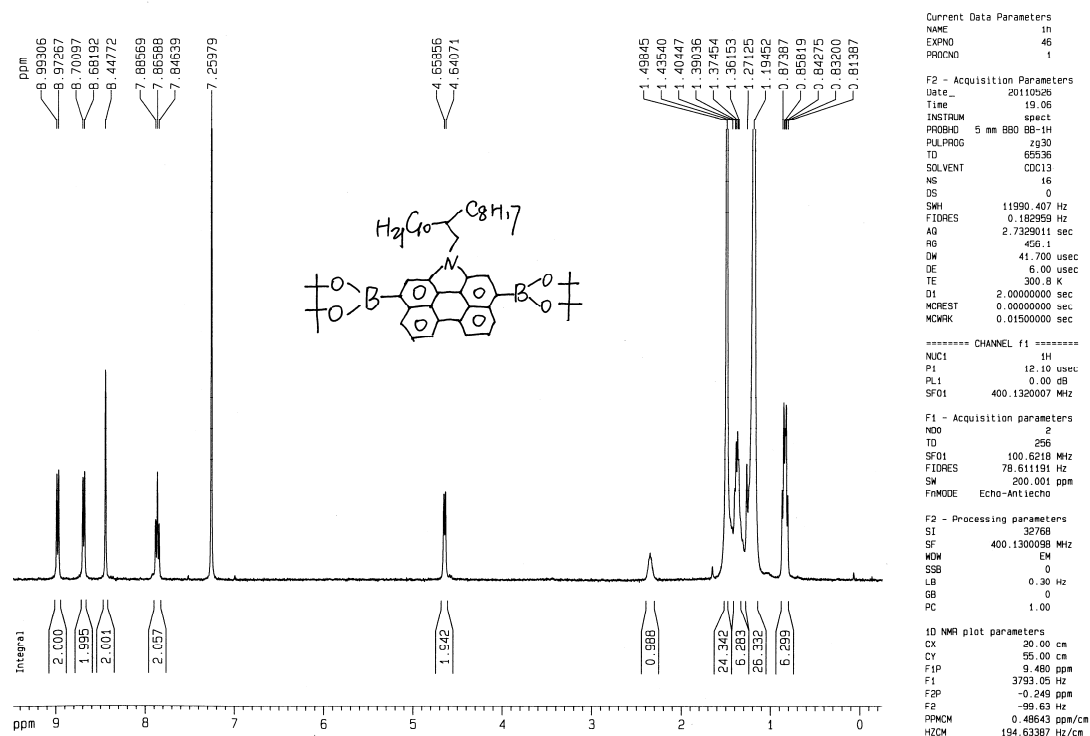


Figure S1. ^1H NMR spectrum of the monomer M1

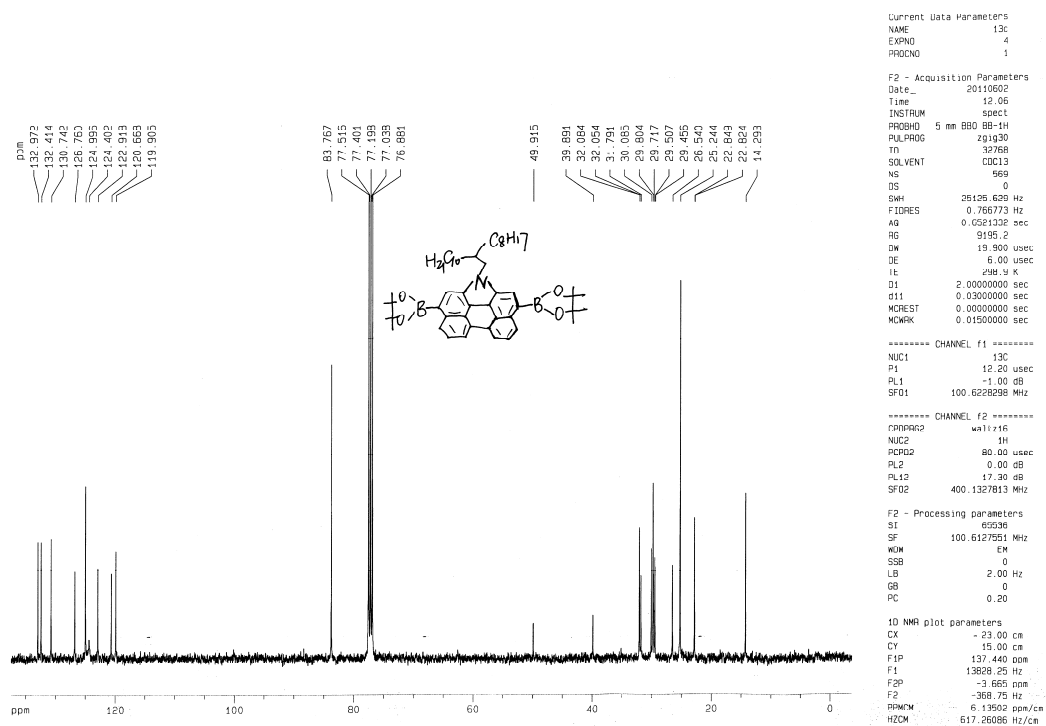


Figure S2. ^{13}C NMR spectrum of the monomer **M1**

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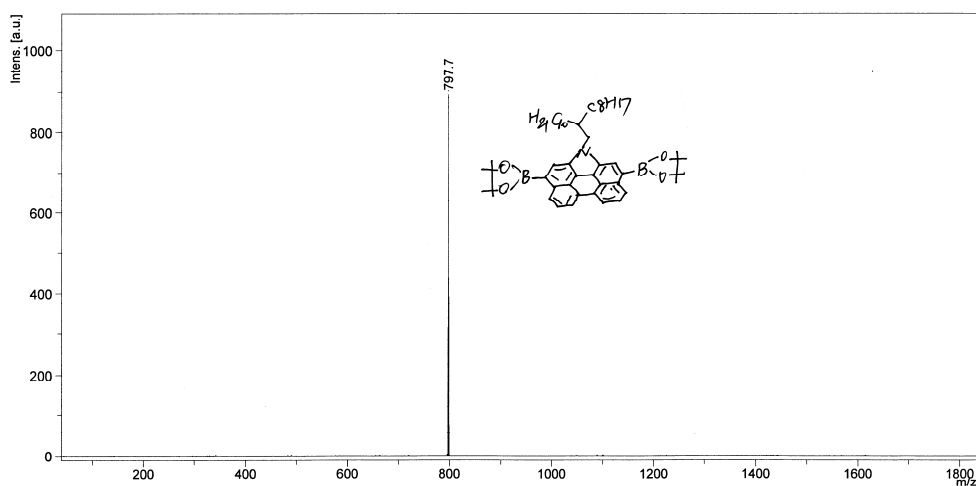


Figure S3. MALDI-TOF spectrum of the monomer **M1**

Synthesis of PPTT: In a Schlenk flask, monomer **M1** (0.16 g, 0.2 mmol), monomer

M2 (0.16 g, 0.2 mmol), 2 M aqueous K_2CO_3 solution (4 mL), and 2 drops of *N*-methyl-*N*, *N*-dioctyloctan-1-ammonium chloride (Aliquat 336) were dissolved in dry toluene (10 mL). The solution was charged with nitrogen through a freeze–pump–thaw cycle for three times, and then tetrakis(triphenylphosphine)palladium (15 mg) was added. The mixture was stirred for 48 h at 110 °C under nitrogen atmosphere. Then phenylboronic acid (0.3 g, 2.5 mmol) was added and stirred at reflux for 3 h. Bromobenzene (5 mL) was then added under nitrogen, and the mixture was stirred for another 3 h. After the reactant was cooled down to room temperature, the polymer was precipitated by addition of 200 mL of methanol and 10 mL of hydrochloric acid. The precipitate was filtered and washed by methanol. Finally, the polymer was subjected to Soxhlet extraction with methanol, hexane, and chloroform. The evaporation of chloroform fractions afforded a dark solid. Yield: 161 mg, 68%. GPC: $M_w = 21900$, $M_n = 14100$, PDI = 1.55.

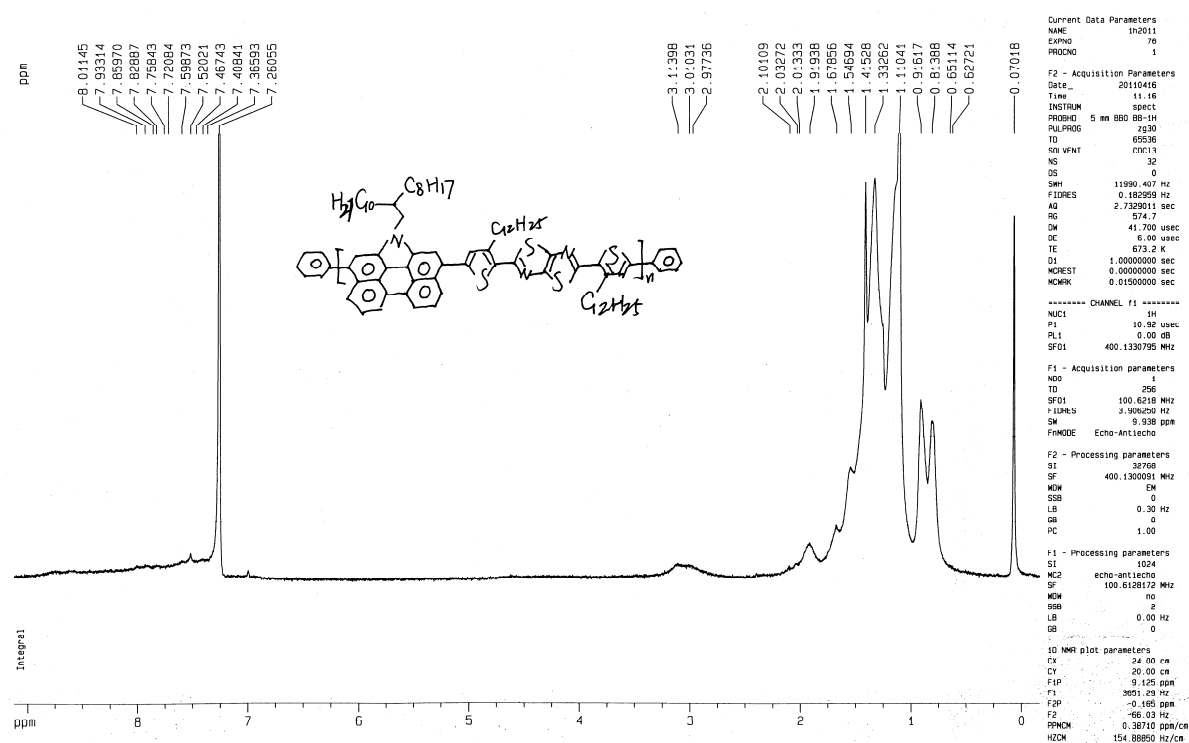


Figure S4. 1H NMR spectrum of the copolymer **PPTT**.

Characterization: Gel-permeation chromatography (GPC) was performed on a Waters 2690 separations module apparatus using polystyrene as a standard and THF as an eluent. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. UV-vis absorption spectra were measured in the polymer solutions and polymer thin-films using a PE Lamada 25 spectrometer. Cyclic voltammetry (CV) experiments were conducted on an electrochemistry workstation (CHI660A, Chenhua Shanghai) using a three-electrode cell. The platinum stick electrode coated with a thin film layer of polymer was used as a working electrode. Ag/AgCl (Ag in a 0.01 mol L^{-1} KCl) electrode was used as a reference electrode. Platinum wire was used as a counter electrode. An anhydrous and N_2 -saturated solution of 0.1 M tetrabutylammonium hexylfluorophosphate in acetonitrile was employed as an electrolyte. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7 with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under inert atmosphere. The PPTT films were imaged in air using a Digital Instruments Nanoscope III atomic force microscope operated in a tapping mode.

Fabrication and characterization of organic photovoltaic devices (OPVs): The organic solar cells were fabricated in the configuration of the traditional sandwich structure with an indium tin oxide (ITO) glass resistance of $20\ \Omega/\square$ purchased from CSG Holding Co., Ltd. (China). The ITO-coated glass substrates were cleaned stepwise in water, acetone, and isopropyl alcohol, and finally the ITO glass was treated in a UV-ozone oven for 30 min. PEDOT: PSS (Baytron PVP A1 4083) was then spin-coated onto the top of the ITO-glass substrate and dried at $150\text{ }^\circ\text{C}$ for 30 min. The thickness of the PEDOT: PSS layer was ca. 40 nm. Subsequently, PPTT/[6,6]-phenyl- C_{71} -butyric acid methyl ester (PC_{71}BM) photoactive layer was then spin-coated from the *o*-dichlorobenzene solution of the polymer/ PC_{71}BM (1:2, w/w) on the top of the PEDOT : PSS layer, giving a thickness of ca. 80 nm determined by a surface profilometer (XP-2, USA). Finally, the substrates were transferred into an evaporator and pumped down to $5\times 10^{-5}\text{ Pa}$ to deposit 10 nm of Ca and 80 nm of aluminum cathodes, producing an active area of 4 mm^2 for each cell. The current

density–voltage (J – V) characteristics of the OPVs were measured on a computer controlled Keithley 236 source measure unit under AM 1.5 illumination conditions, 100 mW cm^{-2} . The external quantum efficiency (EQE) measurements of the OPVs were performed by a Stanford Research Systems model SR830 DSP lock–in amplifier coupled with a WDG3 monochromator and a 500 W xenon lamp. The light intensity at each wavelength was calibrated with a standard single–crystal Si photovoltaic cell. All these measurements were automatically controlled by a computer system and performed under ambient atmosphere at room temperature.

Fabrication and characterization of thin film transistors (OTFTs): To study the characterization of OTFTs performance, bottom–gate/bottom–contact OTFT devices were fabricated using n^+ –Si/SiO₂ substrates with a channel width (W) of 1400 μm and different channel length (L) of 5 ~ 50 μm . The substrates were subjected to cleaning using ultrasonication in deionized water, ethanol, and acetone, respectively. The cleaned substrates were dried under vacuum at 80 °C. Before spin–coating PPTT semiconductor, octadecyltrichlorosilane (OTS) treatment was performed on the SiO₂ gate dielectrics in a vacuum to form an OTS self–assembled monolayer. A layer of polymer film was then deposited on the OTS–treated SiO₂ surface by spin–coating from a PPTT solution in *o*–dichlorobenzene (8 mg mL^{-1}) at a speed of 1500 rpm for 60 s. For annealed OTFTs, the samples were further placed on a hotplate in air for 5 minutes before cooling down to room temperature. The OTFTs characteristics of the devices were determined at room temperature in air by using a Keithley 4200 SCS semiconductor parameter analyzer. The mobility of the devices was calculated in the saturation regime. The equation is listed as follows:

$$I_{DS} = (W / 2L) C_i \mu (V_{GS} - V_{th})^2$$

where W/L is the channel width/length, C_i is the insulator capacitance per unit area, and V_{GS} and V_{th} are the gate voltage and threshold voltage, respectively.

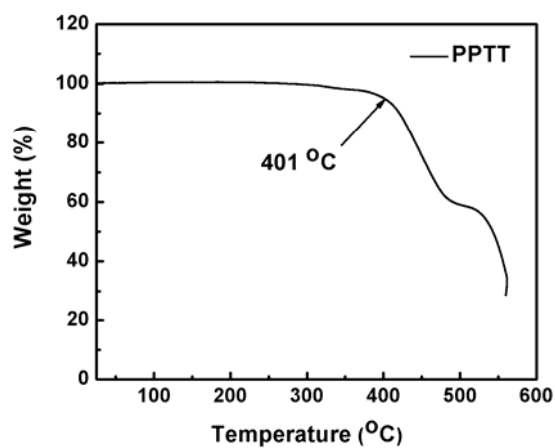


Figure S5. TGA curve of PPTT with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under inert atmosphere.

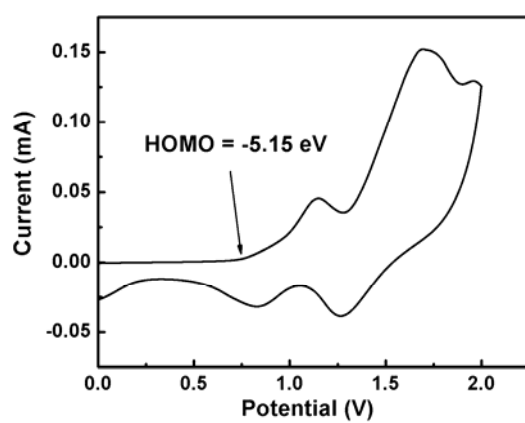


Figure S6. Cyclic voltammograms of the PPTT film on a platinum electrode.

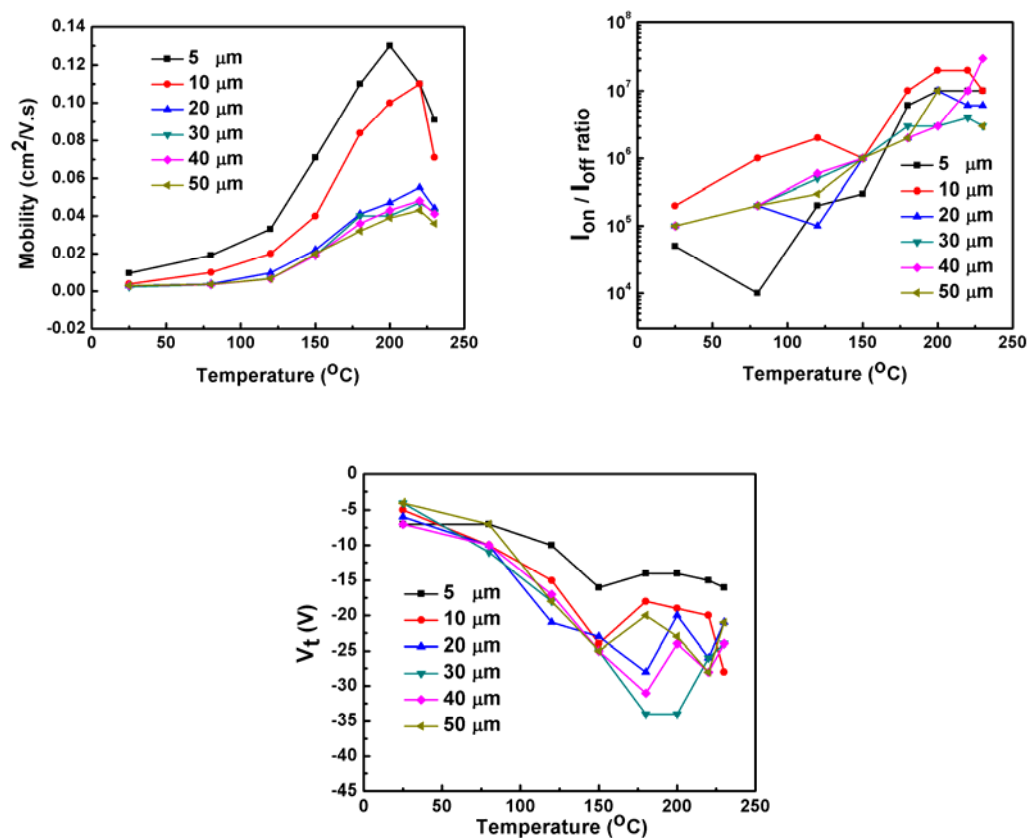


Figure S7. Detailed electrical parameters of the PPTT-based OTFTs with different channel length (L) and under different annealing temperature (T).

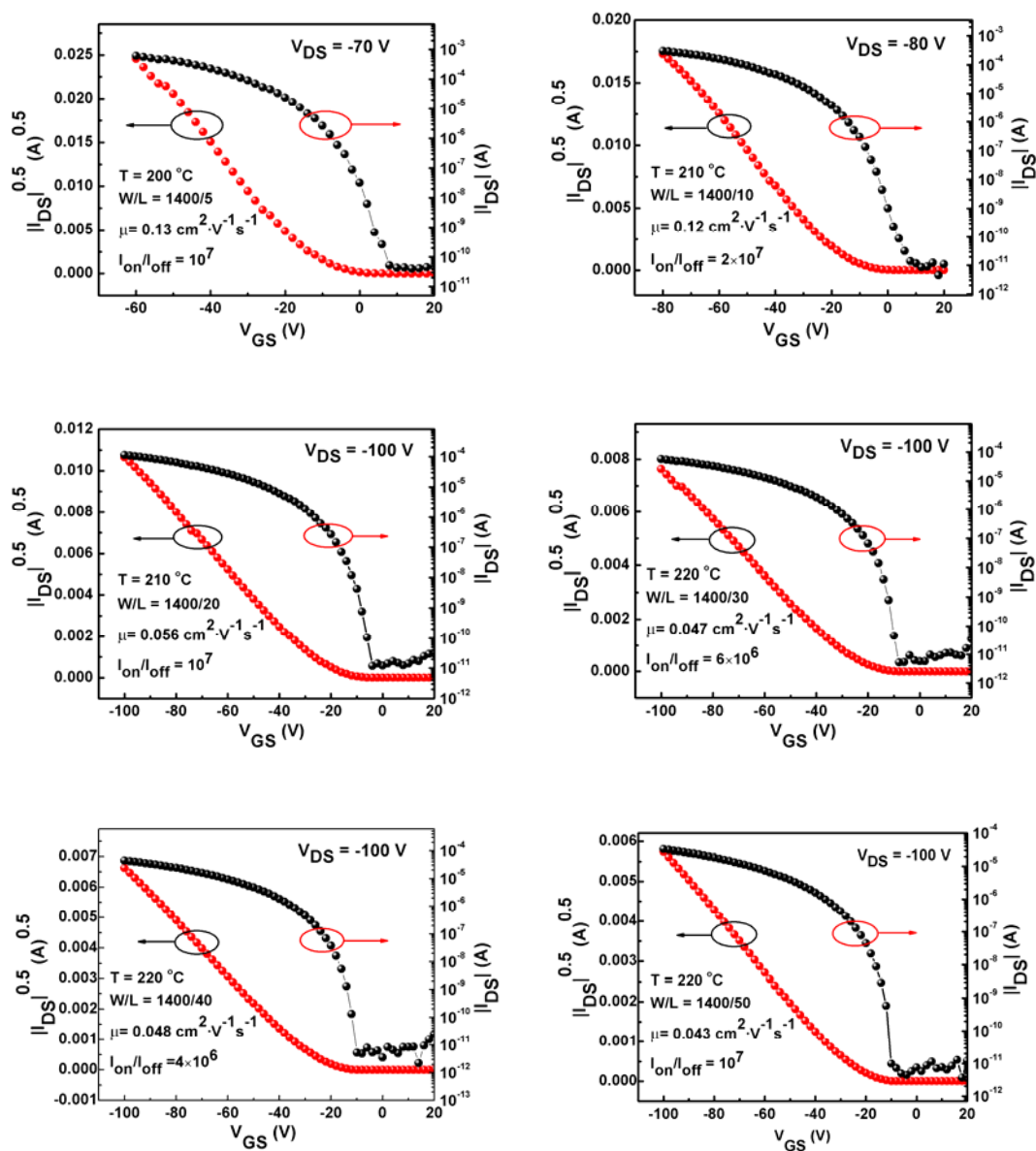


Figure S8. Typical transfer curves of the PPTT-based OTFTs with different channel length (L) and under different annealing temperature (T).

References

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