DPP-Thiazolothiazole Copolymers for High Performance Organic Field-Effect Transistors

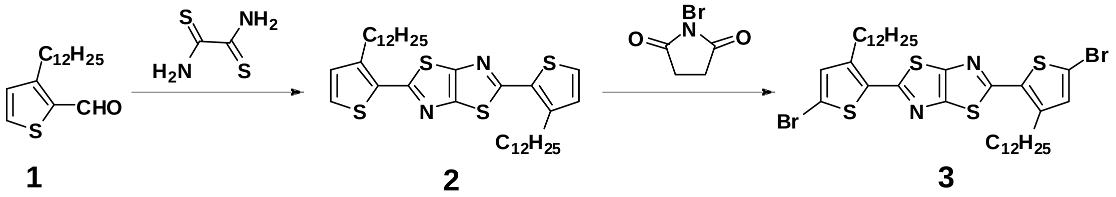
Cheng Cheng, Chunmeng Yu, Yunlong Guo, Huajie Chen, Yu Fang, Gui Yu* and Yunqi Liu**

Supporting Information

Contents

S1. Synthetic procedures and characterization

Materials: All starting materials were purchased from Aldrich, Acros, or Alfar Aesar and used directly without further purification. Toluene and tetrahydrofuran (THF) were distilled from benzophenone ketyl and sodium.

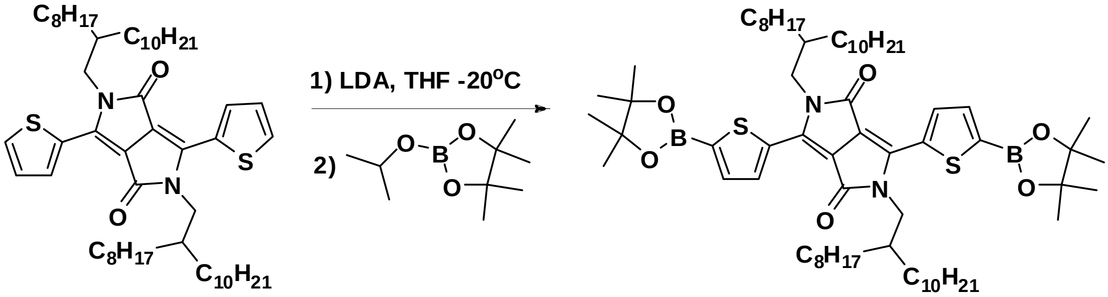


Synthesis of 2,5-Bis(3-dodecylthiophen-2-yl)thiazolo[5,4-d]thiazole

A mixture of 1 (48.8 g, 0.174 mol) and dithiooxamide (6.97 g, 0.058 mol) in a 250 mL round bottom flask equipped with Dean–Stark apparatus was stirred at 200 °C for 5 h. Then the reaction mixture was cooled to room temperature and extracted with chloroform and water. The organic layer was dried over magnesium sulfate and concentrated by evaporation. The brown oil was purified by column chromatography using silica gel (eluent: hexane/chloroform = 5:1, v/v) and resulting dark yellow solid was recrystallized from hexane to give 10.8 g of yellow powder (yield = 29%). ^{1}HNMR ($CDCl_3$, *d*): 7.38 (*d, J* = 5.1 Hz, 2H), 7.02 (*d, J* = 5.1 Hz, 2H), 3.00 (*t, J* = 7.8 Hz, 4H), 1.74 (*q, J* = 7.8 Hz, 4H), 1.29 (*bs*, 36H), 0.90 (*t, J* = 6.7 Hz, 6H). ^{13}CNMR ($CDCl_3$, *d*): 161.6, 150.0, 143.1, 131.8, 130.8, 127.3, 31.92, 30.4, 30.1, 30.0, 29.6, 29.5, 29.4, 22.7, 14.1.

Synthesis of 2,5-Bis(5-bromo-3-dodecylthiophen-2-yl)thiazolo[5,4-d]thiazole:

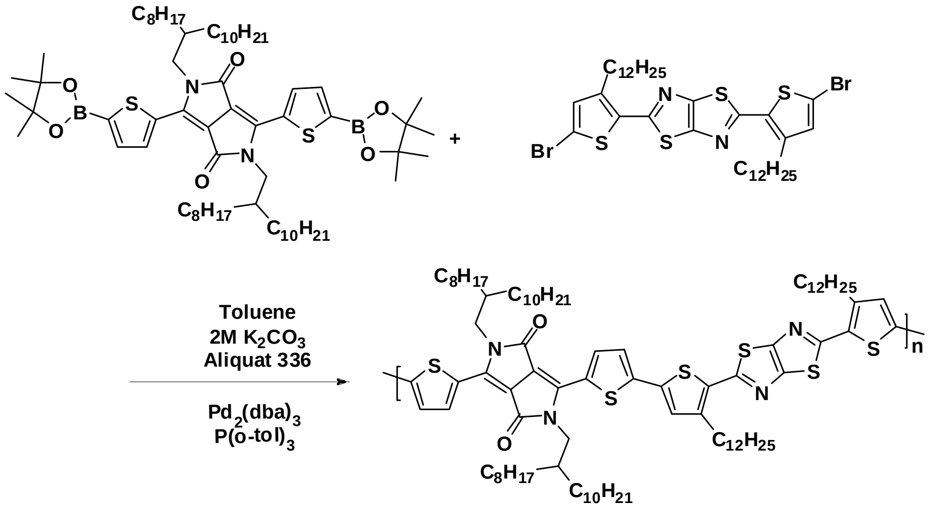
To a solution of 2 (5.4 g, 8.4 mmol) in 150 mL of chloroform, NBS (3.29 g, 18.5 mmol) was added in one portion and stirred under reflux for 3 h. Then the reaction solution was cooled to room temperature and washed twice with 100 mL of water. The solution was dried over magnesium sulfate and concentrated by evaporation. The resulting brown-yellow solid was washed with 100 mL of hexane at room temperature for 1 h to afford 4.9 g of yellow powder (yield = 72%). ^{1}HNMR ($CDCl_3$, *d*): 6.98 (*s*, 2H), 2.91 (*t*, *J* = 7.8 Hz, 4H), 1.67 (*q*, *J* = 7.6 Hz, 4H), 1.29 (*br*, 36H), 0.91 (*t*, *J* = 6.7 Hz, 6H). ^{13}CNMR ($CDCl_3$, d): 160.3, 150.0, 143.4, 133.4, 115.4, 31.9, 30.2, 29.8, 29.7, 29.6, 29.4, 29.3, 22.7, 14.1.



Synthesis of 3,6-bis-(5-(4,4,5,5-tetramethyl-1,3,2-dioxabrolan-2-yl)thiophen-2-yl)-N,N′-bis((octyldodecyl)-1,4-dioxo-pyrrolo[3,4-c]pyrrole:

To a solution of DPP (1.5 g, 1.74 mmol) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxoborolane (1.3 g, 6.98 mmol) in THF (30 mL) under N_2 at -20°C was added dropwise LDA (2M in hexane/THF, 2.6 mL, 5.2 mmol) over 10 minutes. The resulting solution was stirred for 1 hour at 0°C and then quenched with 1 M HCl. The product was extracted by DCM and washed with water and dried over $MgSO_4$. After evaporation of the solvent the residue is dissolved in small amount of DCM and then slowly added to 200 mol of heavily stirred acetone. The precipitate was collected by filtration, washed with acetone and dried under vacuum afford 0.85 g of powder (44%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ ppm 8.90 (*d, J* = 3.6 Hz, 2H), 7.70 (*d, J* = 3.6 Hz, 2H), 4.04 (*d, J* = 8.4 Hz, 4H), 1.89 (*m*, 2H), 1.36 (*m*, 24H), 1.24 (br, 68H), 0.85 (*m*, 12H); ^{13}CNMR ($CDCl^3$, 400 MHz): δ ppm 161.76, 140.53, 137.66, 136.13, 135.68, 108.75, 84.59, 46.28, 37.79, 31.93, 31.88, 31.31, 31.29, 30.03, 30.02, 29.64, 29.59, 29.53, 29.35, 29.29, 26.36, 26.34, 24.78, 22.69, 22.67, 14.12, 14.12.

Synthesis of PDPPTzBT :



PDPPTzBT

In a Schlenk flask 3,6-bis-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-thiophen-2-yl))-N,N'-bis(octyldodecyl)-1,4-dioxopyrrolo[3,4-c]pyrrole (0.300 g, 0.29 mmol) and 2,5-bis(3-dodecylthiophen-2-yl)thiazolo[5,4-d]thiazole] (0.232 g, 0.29 mmol), 2 M aqueous K_2CO_3 solution (1.5 mL), and 2 drops of N-methyl-N,N -dioctyloctan-1-ammonium chloride (Aliquat 336) were dissolved in toluene (6 mL).

The solution was purged with argon for 30 min, then $Pd_2(dba)_3$ (9 mg), and $P(o\text{-}tol)_3$ (24.6 mg) were added. The reaction was stirred at 105 °C for 2 days. Then a toluene solution of phenyl boronic acid was added and the mixture was stirred for an additional 4 h, followed by the addition of a few drops of bromobenzene, after which it was stirred overnight. The resulting mixture was poured into a mixture of methanol and water and stirred overnight. The dark precipitate was re-dissolved in chloroform and added dropwise to methanol (250 mL). The resulting solid was filtered off and subjected to Soxhlet extraction for 2 days successively in methanol, acetone, and hexane for the removal of oligomers and catalytic impurities. The remaining polymer was extracted with chloroform and precipitated again from methanol, filtered, washed with methanol, and dried under vacuum at room temperature. (0.400 g, 75% yield). Mw/Mn (GPC) = 23876/43227. Anal. calcd. for $C_{92}H_{144}N_4O_2S_6$:C 72.20, H 9.48, N 3.36; found: C 72.46, H 9.55, N 3.41.

S2. General procedures and experimental details

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ARX-400 (400MHz) spectrometer. ^1H NMR chemical shifts were referenced to internal tetramethylsilane (TMS). Electron–impact mass spectra (EI-MS) were collected on a Bruker BIFLEX III mass spectrometer. Elemental analyses were carried out using a Carlo Erba model 1160 elemental analyzer. Gel permeation chromatography was carried out at 150 °C using a Polymer Labs PL 220 system using a refractive index detector and 1,2,4-trichlorobenzene as the eluent. UV–vis–NIR absorption spectra were measured on polymer solutions in chloroform and polymer films cast onto quartz glass using a Hitachi U-3010 spectrophotometer. Cyclic voltammetry (CV) experiments were carried out 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 working electrode. Ag/AgCl (Ag in a 0.01 mol/L KCl) electrode was used as the reference electrode. Platinum wire was used as the counter electrode. An anhydrous and N_2 saturated solution 0.1 M tetrabutylammonium hexylfluorophosphate in acetonitrile was employed as the electrolyte. Differential scanning calorimetry analyses (DSC) were recorded on a METTLER TOLEDO Instrument DSC822 calorimeter. Polymer films were imaged in air using a Digital Instruments Nanoscope V atomic force microscope operated in tapping mode. Atomic force microscopy (AFM) measurements were carried out on a Nanoscope V instrument. AFM samples were identical to those used in FET performance analysis. For grazing incidence X-ray scatting (GIXS), the drop-coated films were illuminated at a constant incidence angle of 0.2° ($\lambda = 2d\sin\theta = 1.54$ Å).

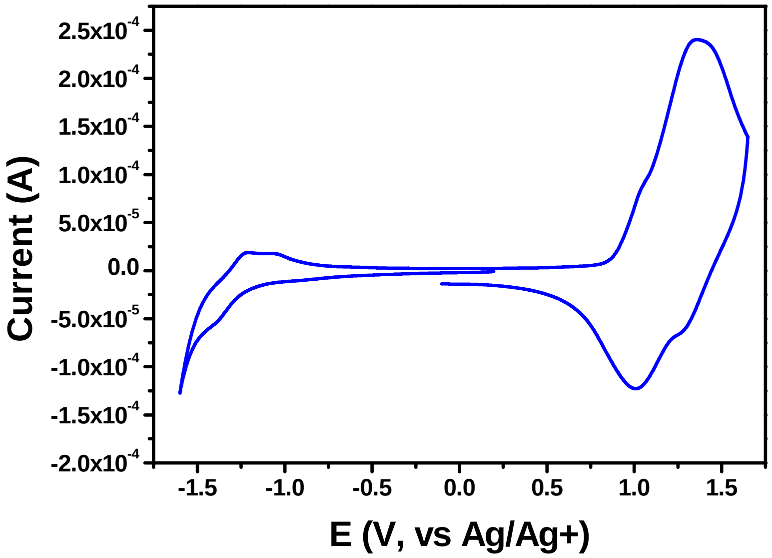


Figure S1. Cyclic voltammetry measurements of the polymers on a platinum electrode in acetonitrile solution. All the polymers exhibited reversible and strong oxidation processes but a weak reduction processes, indicating these polymers might favor p-type transport over n-type transport. The energy level of the highest occupied molecular orbital (HOMO) for the polymer were found to be –5.28 eV for PDPPTzBT, which were calculated from the onset oxidation potential (E_{ox}^{onset}) according to the equation of $E_{HOMO} = - e(E_{ox}^{onset} + 4.4)$ eV.

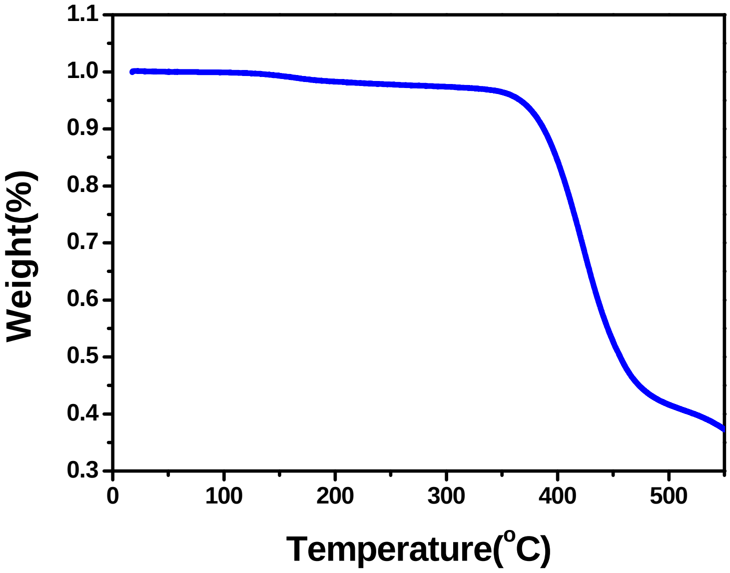


Figure S2. Thermogravimetric analysis plot for PDPPTzBT. Scan rate = 10 °C/min from 20 to 550 °C.

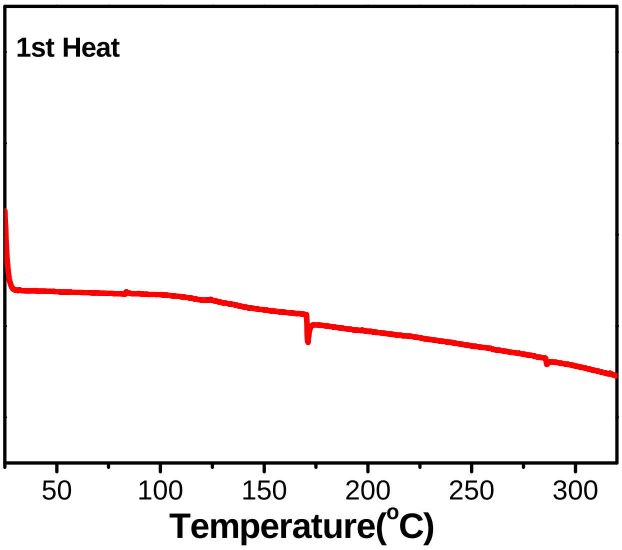
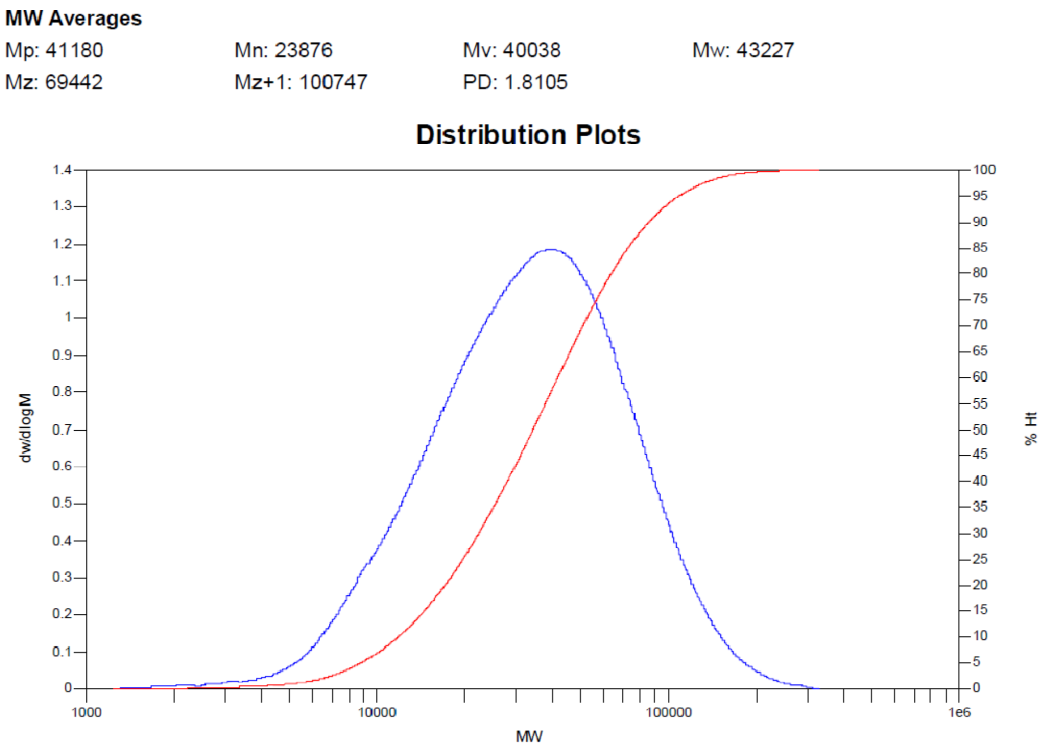


Figure S3. Differential scanning calorimetry plot for Polymer. Scan rate = 10 °C/min from 0 to 320 °C.



MW Averages

Mp: 41180
Mn: 23876
Mv: 40038
Mw: 43227
Mz: 69442
Mz+1: 100747
PD: 1.8105

Figure S4. GPC peak report of PDPPTzBT.

S3. FET device fabrication

Polymer-based FETs were fabricated on highly-doped silicon wafer with 300 nm SiO_2 insulator, which was used as a gate electrode. The source-drain gold electrodes were formed by photolithography. The substrates were then subjected to cleaning using ultrasonication in acetone, deionized water (twice), and ethanol. The cleaned substrates were dried under vacuum at 80 ^{o}C, and then treated with plasma for 15 min. Before the deposition of polymer semiconductors, octadecyltrichlorosilane (OTS) treatment was performed on the SiO_2 gate dielectrics in a vacuum to form an OTS self-assembled monolayer. Then, a layer of polymer semiconductor film (~40 nm) was deposited on the OTS-treated substrates by spin-coating from a polymer solution in hot DCB (3 mg/mL) at a speed of 2000 rpm for 60 s. For annealing FETs, the samples were further placed on a hotplate in air for 5 minutes before cooling down to room temperature. Field-effect characteristics of the devices were determined in air by using a Keithley 4200 SCS semiconductor parameter analyzer. Different channel lengths (L) of the FET devices (L = 10, 20, 30, 40, and 50 μm) and the same channel widths (W) of 1400 μm were used to optimize device performance. The field-effect mobility in saturation (μ) is calculated from equation:

$$I_{DS} = (W/2L)\, C_i\, \mu\, (V_{GS} - V_{th})^2 \qquad (1)$$

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