

Electronic Supplementary Information

Zwitterionic Side Chain-Modified Conjugated Polymers with Greatly Enhanced Ambipolar Charge Transport Mobilities

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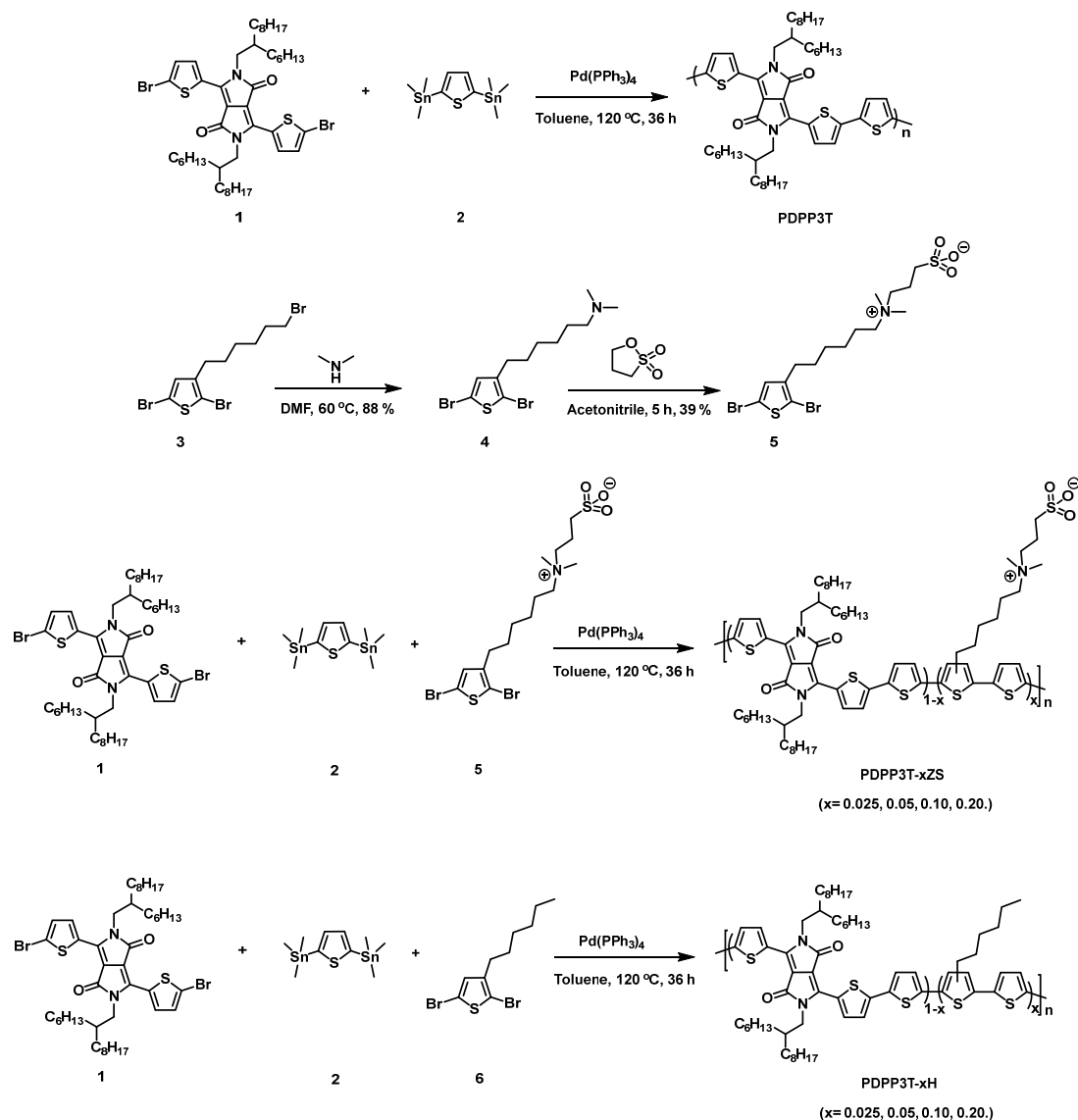
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1. Materials and synthesis



Scheme S1 Synthetic routes of polymer **PDPP3T**, **PDPP3T-xZS** ($x = 0.025, 0.05, 0.10, 0.20$) and **PDPP3T-xH** ($x = 0.025, 0.05, 0.10, 0.20$)

All reagents were brought from TCI, J&K, Suna Tech Inc., and used without further purification. Anhydrous toluene was obtained by distilling with Na/benzophenone. 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-hexyldecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**1**) was purchased from Suna Tech Inc., while 2,5-bis(trimethylstannyl)thiophene (**2**) and 2,5-dibromo-3-(6-bromohexyl)thiophene (**3**) were prepared following previously reported

methods.^{S1, S2}

Synthesis of PDPP3T.

Into a dried 25 mL three-necked flask, 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-hexyldecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (Monomer **1**, 181.40 mg, 0.20 mmol,) and 2,5-bis(trimethylstannyl)thiophene (Monomer **2**, 81.95 mg, 0.20 mmol) were added. After vacuumed and filled back with argon, the flask was added with 10 mL anhydrous toluene and subjected to freezing-pump-thaw cycle for getting rid of oxygen. After the first cycle, Pd(PPh₃)₄ was added and the residue oxygen was further removed by the additional two cycles of freezing-pump-thaw. Finally, argon was filled back into the flask, and the reaction mixture was heated to 120 °C and refluxed for 36 h. After the temperature was cooled down to room temperature, the reaction mixture was dropped into 100 mL methanol to precipitate the product. After filtration, the crude product was Soxhlet extracted with methanol, acetone, n-hexane, dichloromethane and chloroform, respectively, and the chloroform fraction was collected. After concentrated under reduced pressure, the crude product was further subjected to size-exclusion chromatography (SEC) with a column filled with Bio-Beads S-X1 resin. The high molecular weight fraction was collected, concentrated, precipitated with methanol, and dried in vacuum at 50 °C, affording 145 mg PDPP3T product as black solid. Yield: 87.4 %. ¹H NMR (400 MHz, 1,1,2,2-tetrachloroethane-*d*₂, 100 °C) δ 8.82-8.75 (br, 2H), 7.23-7.04 (br, 4H), 3.98 (br, 4H), 1.95 (br, 2H), 1.37-1.21 (br, 46H), 0.83-0.81 (br, 14H). Element Anal. Found for (C₅₀H₇₂N₂O₂S₃)_n: C 71.03, H 8.85, N 3.03. GPC (1,2,4-trichlorobenzene, 145 °C): *M*_n = 17.9 kDa, *M*_w = 39.1 kDa, Đ = 2.2.

Synthesis of 6-(2,5-dibromothiophen-3-yl)-N,N-dimethylhexan-1-amine (**4**)

In a 100 mL pressure flask, compound **3** (0.6 g, 1.48 mmol) was added. After the atmosphere was changed into argon, 20 mL DMF and 8 mL dimethylamine were added, and the reaction mixture was heated to 60 °C. During the reaction, white precipitation was produced. After the reaction was over, the reaction mixture was cooled to room temperature, poured into ice water, and extracted with dichloromethane for three times. The organic fractions were combined, washed with deionized water and saturated salt, and concentrated under reduced pressure. The residue was subjected to column chromatography using petroleum ether/ethyl acetate (v/v: 1/1)

as eluent, affording 0.52 g compound **4** as light yellow oily liquid. Yield: 88 %. ^1H NMR (400 MHz, CDCl_3) δ 6.77 (s, 1H), 2.76 (dd, $J = 7.2$ Hz, $J = 14.4$ Hz, 2H), 2.50 (t, $J = 7.6$ Hz, 2H), 2.28 (t, $J = 7.6$ Hz, 2H), 2.25 (s, 6H), 1.57-1.47 (m, 2H), 1.35-1.31 (m, 2H), 1.19 (t, $J = 7.2$ Hz, 2H).

Synthesis of 3-((6-(2,5-dibromothiophen-3-yl)hexyl)dimethylammonio)propane-1-sulfonate (5)

Compound **4** (0.37g, 1.00 mmol) was added into a 25mL three-necked flask. After the atmosphere was changed into argon, anhydrous acetonitrile (10 mL) and 1,3-propane sulfonate (0.49 g, 4.00 mmol) were added. The reaction mixture was heated to reflux for 5 h, and then cooled back to room temperature. During the reaction, white suspended precipitate was formed gradually. After filtration, the crude product was subsequently washed with acetonitrile and ether, affording 191 mg compound **5** as white solid. Yield: 39 %. ^1H NMR (400 MHz, CD_3OD) δ 6.96 (s, 1H), 3.52-3.48 (m, 2H), 3.30-3.28 (m, 2H), 3.08 (s, 6H), 2.87 (t, $J = 6.8$ Hz, 2H), 2.58 (t, $J = 7.6$ Hz, 2H), 2.20-2.16 (m, 2H), 1.79-1.76 (m, 2H), 1.66-1.59 (m, 2H), 1.45-1.40 (m, 4H). LRMS (EI) m/z : 491.9 (M^+).

Synthesis of PDPP3T-xZS and PDPP3T-xH (x = 0.025, 0.05, 0.10, 0.20).

General procedure of Stille coupling polymerization: Into a fully-dried 25 mL three-necked flask, monomer **1** (1-x equiv., **1**), monomer **2** (1 equiv.), and monomer **5** or monomer **6** (x equiv.) were added. After the atmosphere was replaced with argon, 10 mL newly distilled anhydrous toluene was added and the reaction mixture was subjected to three freezing-pump-thaw cycles to remove oxygen. $\text{Pd}(\text{PPh}_3)_4$ (0.06 equiv.) was added during the second cycle. Afterwards, the reaction mixture was heated to 120 °C for 36 h, and then cooled back to room temperature. After precipitated with methanol and filtered, the crude product was Soxhlet extracted with methanol, acetone, n-hexane, dichloromethane and chloroform, respectively, and the chloroform fraction was collected. After concentrated under reduced pressure, the crude product was further subjected to size-exclusion chromatography (SEC) with a column filled with Bio-Beads S-X1 resin. The high molecular weight fraction was collected, concentrated, precipitated with methanol, and dried in vacuum at 50 °C, affording **PDPP3T-xZS** or **PDPP3T-xH** as black solid.

PDPP3T-0.025ZS: 112 mg black powder was obtained in a yield of 68 % by using monomer **1** (176.87 mg, 0.195 mmol), monomer **2** (81.95 mg, 0.20 mmol), monomer **5** (2.46 mg, 0.0050

mmol), and Pd(PPh₃)₄ (13.87 mg, 0.012 mmol). ¹H NMR (400 MHz, 1,1,2,2-tetrachloroethane-*d*₂, 100 °C) δ 8.81-8.75 (m), 7.31-7.04 (m), 3.98 (m), 2.56 (m), 2.47 (m), 1.94 (m), 1.37-1.21 (m), 0.83-0.81 (m). Element Anal. Found C 72.46%, H 8.85%, N 3.00%. GPC (1,2,4-trichlorobenzene, 145 °C): *M*_n = 16.0 kDa, *M*_w = 30.5 kDa, Đ = 1.9.

PDPP3T-0.05ZS: 123 mg black powder was obtained in a yield of 76 % by using monomer **1** (172.32 mg, 0.19 mmol), monomer **2** (81.95 mg, 0.20 mmol), monomer **5** (4.92 mg, 0.010 mmol), and Pd(PPh₃)₄ (13.87 mg, 0.012 mmol). ¹H NMR (400 MHz, 1,1,2,2-tetrachloroethane-*d*₂, 100 °C) δ 8.75 (m), 7.30-7.02 (m), 3.98 (m), 2.56 (m), 2.47 (m), 1.94 (m), 1.37-1.22 (m), 0.83-0.81 (m). Element Anal. Found C 72.54%, H 9.00%, N 3.19%. GPC (1,2,4-trichlorobenzene, 145 °C): *M*_n = 17.6 kDa, *M*_w = 34.1 kDa, Đ = 1.9.

PDPP3T-0.10ZS: 120 mg black powder was obtained in a yield of 76 % by using monomer **1** (163.26 mg, 0.18 mmol), monomer **5** (9.84 mg, 0.020 mmol), monomer **2** (81.95 mg, 0.20 mmol) and Pd(PPh₃)₄ (13.87 mg, 0.012 mmol). ¹H NMR (400 MHz, 1,1,2,2-tetrachloroethane-*d*₂, 100 °C) δ 8.74 (m), 7.30-7.00 (m), 3.98 (m), 2.56 (m), 2.47 (m), 1.94 (m), 1.37-1.21 (m), 0.93-0.81 (m). Element Anal. Found C 72.40%, H 8.83%, N 3.06%. GPC (1,2,4-trichlorobenzene, 145 °C): *M*_n = 18.2 kDa, *M*_w = 34.5 kDa, Đ = 1.9.

PDPP3T-0.20ZS: 103 mg black powder was obtained in a yield of 69 % by using monomer **1** (145.1 mg, 0.16 mmol), monomer **5** (19.68 mg, 0.040 mmol), monomer **2** (81.95 mg, 0.20 mmol) and Pd(PPh₃)₄ (13.87 mg, 0.012 mmol). ¹H NMR (400 MHz, 1,1,2,2-tetrachloroethane-*d*₂, 100 °C) δ 8.78-8.74 (m), 7.31-7.07 (m), 3.98 (m), 2.56 (m), 2.47 (m), 1.94 (m), 1.37-1.21 (m), 0.83-0.81 (m). Element Anal. Found C 72.25%, H 8.61%, N 2.96%. GPC (1,2,4-trichlorobenzene, 145 °C): *M*_n = 14.9 kDa, *M*_w = 28.8 kDa, Đ = 1.9.

PDPP3T-0.025H: 120 mg black powder was obtained in a yield of 74 % by using monomer **1** (176.87 mg, 0.195 mmol), monomer **6** (1.63 mg, 0.0050 mmol), monomer **2** (81.95 mg, 0.20 mmol) and Pd(PPh₃)₄ (13.87 mg, 0.012 mmol). ¹H NMR (400 MHz, 1,1,2,2-tetrachloroethane-*d*₂, 100 °C) δ 8.74 (m), 7.30-6.98 (m), 3.98 (m), 2.56 (m), 2.47 (m), 1.95 (m), 1.37-1.23 (m), 0.83-0.81 (m). Element Anal. Found C 70.8%, H 8.81%, N 3.00%. GPC (1,2,4-trichlorobenzene, 145 °C): *M*_n = 31.1 kDa, *M*_w = 68.7 kDa, Đ = 2.2.

PDPP3T-0.05H: 117 mg black powder was obtained in a yield of 73 % by using monomer **1**

(172.32 mg, 0.19 mmol), monomer **6** (3.26 mg, 0.01 mmol), monomer **2** (81.95 mg, 0.20 mmol) and Pd(PPh₃)₄ (13.87 mg, 0.012 mmol). ¹H NMR (400 MHz, 1,1,2,2-tetrachloroethane- *d*₂, 100 °C) δ 8.75 (m), 7.30-7.00 (m), 4.00-3.96 (m), 2.56 (m), 2.47 (m), 1.94 (m), 1.38-1.21 (m), 0.92-0.71 (m). Element Anal. Found C 72.00%, H 8.70%, N 2.99%. GPC (1,2,4-trichlorobenzene, 145 °C): *M*_n = 20.3 kDa, *M*_w = 42.4 kDa, Đ = 2.1.

PDPP3T-0.10H: 97 mg black powder was obtained in a yield of 63 % by using monomer **1** (163.26 mg, 0.18 mmol), monomer **6** (6.52 mg, 0.02 mmol), monomer **2** (81.95 mg, 0.20 mmol) and Pd(PPh₃)₄ (13.87 mg, 0.012 mmol). ¹H NMR (400 MHz, 1,1,2,2-tetrachloroethane- *d*₂, 100 °C) δ 8.76 (m), 7.30-7.02 (m), 3.98 (m), 2.56 (m), 2.47 (m), 1.94 (m), 1.38-1.21 (m), 0.93-0.71 (m). Element Anal. Found C 73.11%, H 8.77%, N 3.10%. GPC (1,2,4-trichlorobenzene, 145 °C): *M*_n = 19.4 kDa, *M*_w = 38.5 kDa, Đ = 2.0.

PDPP3T-0.20H: 84 mg black powder was obtained in a yield of 59 % by using monomer **1** (145.12 mg, 0.16 mmol), monomer **6** (13.04 mg, 0.04 mmol), monomer **2** (81.95 mg, 0.20 mmol) and Pd(PPh₃)₄ (13.87 mg, 0.012 mmol). ¹H NMR (400 MHz, 1,1,2,2-tetrachloroethane- *d*₂, 100 °C) δ 8.70 (m), 7.74-6.42 (m), 3.98 (m), 2.56 (m), 2.47 (m), 1.94 (m), 1.48-1.21 (m), 0.93-0.81 (m). Element Anal. Found C 72.95%, H 9.06%, N 2.96%. GPC (1,2,4-trichlorobenzene, 145 °C): *M*_n = 18.7 kDa, *M*_w = 37.7 kDa, Đ = 2.0.

2. Instruments and measurements

Characterization of nuclear magnetic resonance spectroscopy (¹H NMR, ¹³C NMR) was determined by a Bruker DRX 400, Bruker DRX 500, or Varian Mercury 300 NMR spectrometer using CHCl₃ or 1,1,2, 2-tetrachloroethane-*D*₂ as the solvent and tetramethylsilane as the internal standard. Agilent Technologies Model 5973N, Simadzu Biotech Axima Performance and Thermo Fisher Scientific LTQ FT Ultra Mass Spectrometer (MS) were used for the mass characterization. Elemental analysis (E.A.) were measured on an elemental analyzer with the model Elementar Vario EL III. Polymer molecular weight was determined by high temperature gel permeation chromatography (GPC) at 145 °C on a PL-GPC220 gel permeation chromatographer equipped with a RI detector and using 1,2,4-trichlorobenzene as eluent. Thermogravimetric analysis (TGA) was tested in nitrogen atmosphere on a TGA Q500 thermogravimetric analyzer with a heating rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC) analysis was performed in

nitrogen atmosphere at heating/cooling rate of 10 °C min⁻¹ on a DSC Q2000 instrument. Ultraviolet visible near infrared (UV-vis-NIR) absorption spectroscopy was measured with a Hitachi U-3310 UV-vis spectrometer. Cyclic voltammetry (CV) was conducted at a scanning rate of 100 mV s⁻¹ on a CHI610D electrochemical workstation using a traditional three-electrode cell with a glassy carbon as working electrode, a Ag/Ag⁺ electrode as reference electrode, a platinum disk as a counter electrode in acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate electrolyte (Bu₄NPF₆). Polymer film samples were prepared by casting their chloroform solution onto glassy carbon working electrode. Atomic force microscope (AFM) was measured on a JPK Nano Wizard AFM instrument. Density functional theoretical (DFT) computations were performed by a Gaussian09 program using B3LYP method with 6-31G basis set. 2-Dimensional grazing incidence wide-angle X-ray scattering (2D GIWAXS) was recorded at the beamline BL14B1 of Shanghai Synchrotron Radiation Facility with an incident X-ray beam light having a wavelength of 1.2398 Å. Sample films with a thickness around 40 nm were prepared by spin-coating from their chloroform solutions with a concentration of 10 mg mL⁻¹ onto silicon wafers and annealing at their optimized temperatures. In the measurements, samples were placed at a position with a sample-to-detector distance of 425 cm, and lanthanum hexaboride was used as standard to calibrate the diffraction pattern. The incident angles for all samples were set to be about 0.18 ° for ensuring all the incident beam light was used similarly for scattering. A Rayonix MX225 detector was used to record the scattering patterns and the exposure time was set to 20 seconds.

3. Fabrication and characterization of organic field effect transistors

All devices were fabricated with a bottom gate top contact (BGTC) configuration. A heavily n-doped silicon wafer with a 300 nm-thick SiO₂ layer as gate dielectric layer was used as the substrate. Before fabrication, octadecyltrichlorosilane (OTS) was coated onto it according to the literature method.⁵³ Then, the polymer active layer was deposited on the substrate by spin-coating their chloroform solution, and annealed at different temperatures in nitrogen atmosphere. Finally, 50 nm-thick gold electrodes were deposited as source/drain electrodes through a mask under high vacuum condition. The channel length (*L*) and width (*W*) were 273

and 31 μm , respectively. The device was tested in a glove box with nitrogen atmosphere at room temperature using a Keithley 4200 semiconductor parametric analyzer. The charge mobility was calculated in saturation regime on the basis of the following equation:

$$I_{DS} = (\mu WC_i/2L)(V_G - V_T)^2,$$

where I_{DS} is the drain–source current, μ is the mobility, W is the channel width, C_i is the capacitance per unit area of the gate dielectric layer, L is the channel length, V_G is the gate voltage, and V_T is the threshold voltage, respectively.

4. Supporting figures and tables

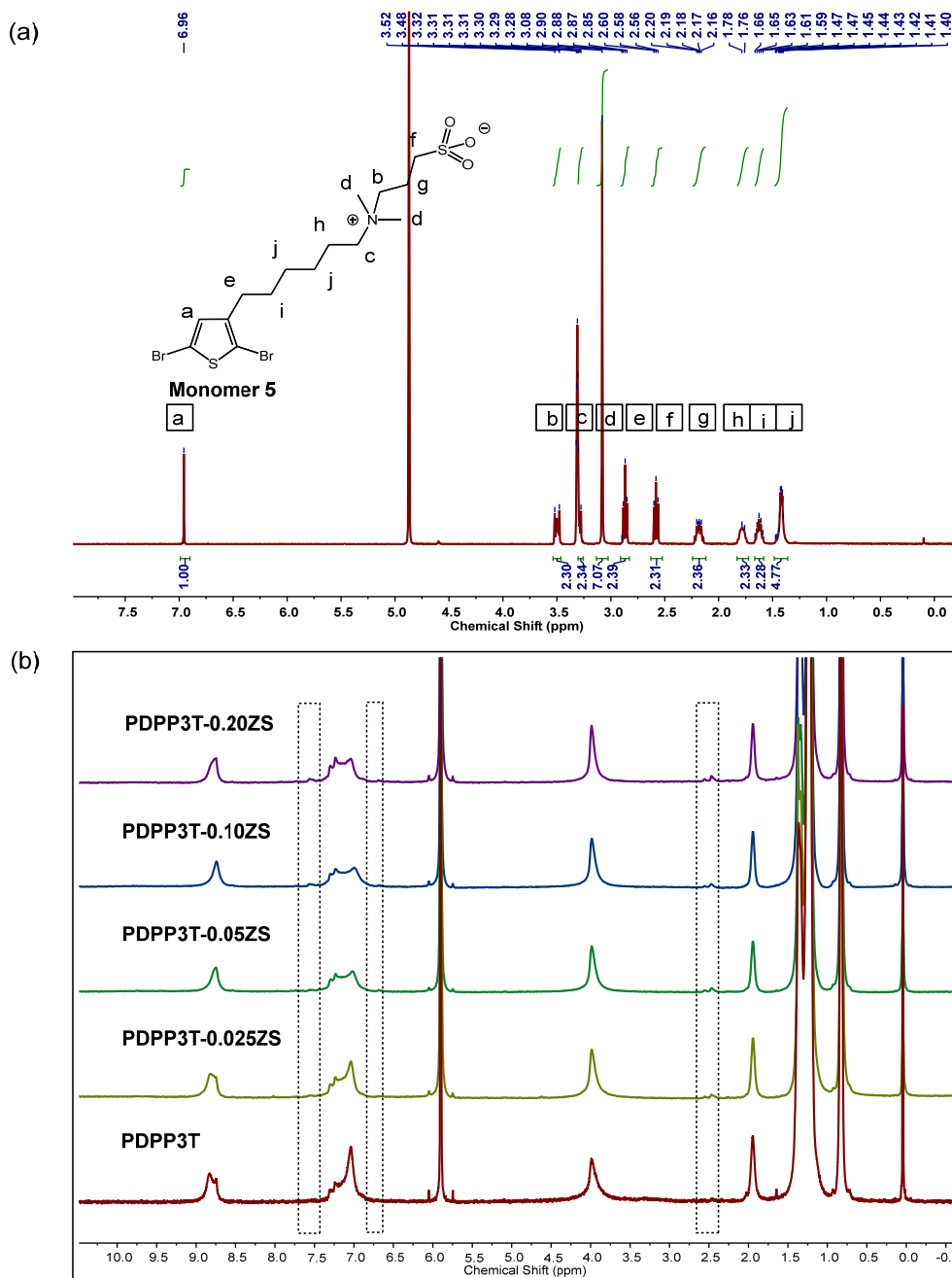


Fig. S1 ^1H NMR spectra of (a) Monomer **5** and (b) polymer **PDPP3T**, **PDPP3T-xZS** ($x = 0.025, 0.05, 0.10, 0.20$). As compared to that of **PDPP3T**, **PDPP3T-xZS** displayed three new peaks around 2.5, 6.7 and 7.6 ppm. The former is assignable to the $\alpha\text{-CH}_2$ unit in zwitterionic side chain (adjacent to its attached thiophene unit), while the latter two peaks originate from bithiophene unit. Based on this fact, the amount of zwitterionic side chain-appended unit in **PDPP3T-xZS** were calculated by the following equation:

$$\frac{6(1-x) + 3x}{2x} = \frac{S_2}{S_1}$$

in which S_1 and S_2 are the integrals of 2.5 ppm-peak and all aromatic peaks, respectively. The results were 1.9% for **PDPP3T-0.025ZS**, 3.8% for **PDPP3T-0.05ZS**, 8.1% for **PDPP3T-0.10ZS** and 16.5% for **PDPP3T-0.20ZS**.

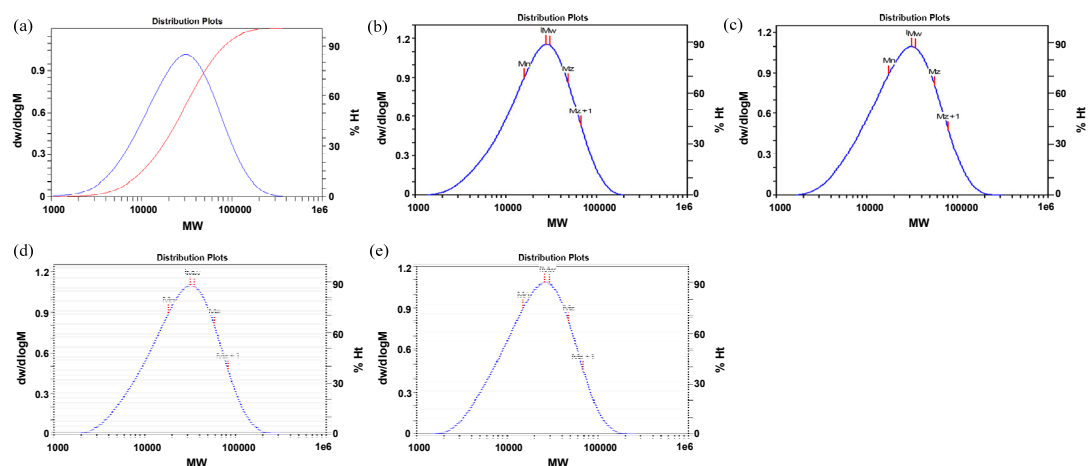


Fig. S2 High temperature GPC charts of (a) **PDPP3T**, (b) **PDPP3T-0.025ZS**, (c) **PDPP3T-0.05ZS**, (d) **PDPP3T-0.10ZS**, (e) **PDPP3T-0.20ZS**.

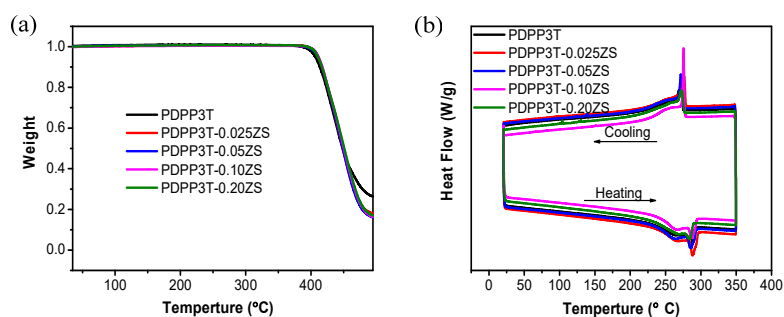


Fig. S3 (a) TGA, (b) DSC of polymer **PDPP3T** and **PDPP3T-xZS** ($x = 0.025, 0.05, 0.10, 0.20$)

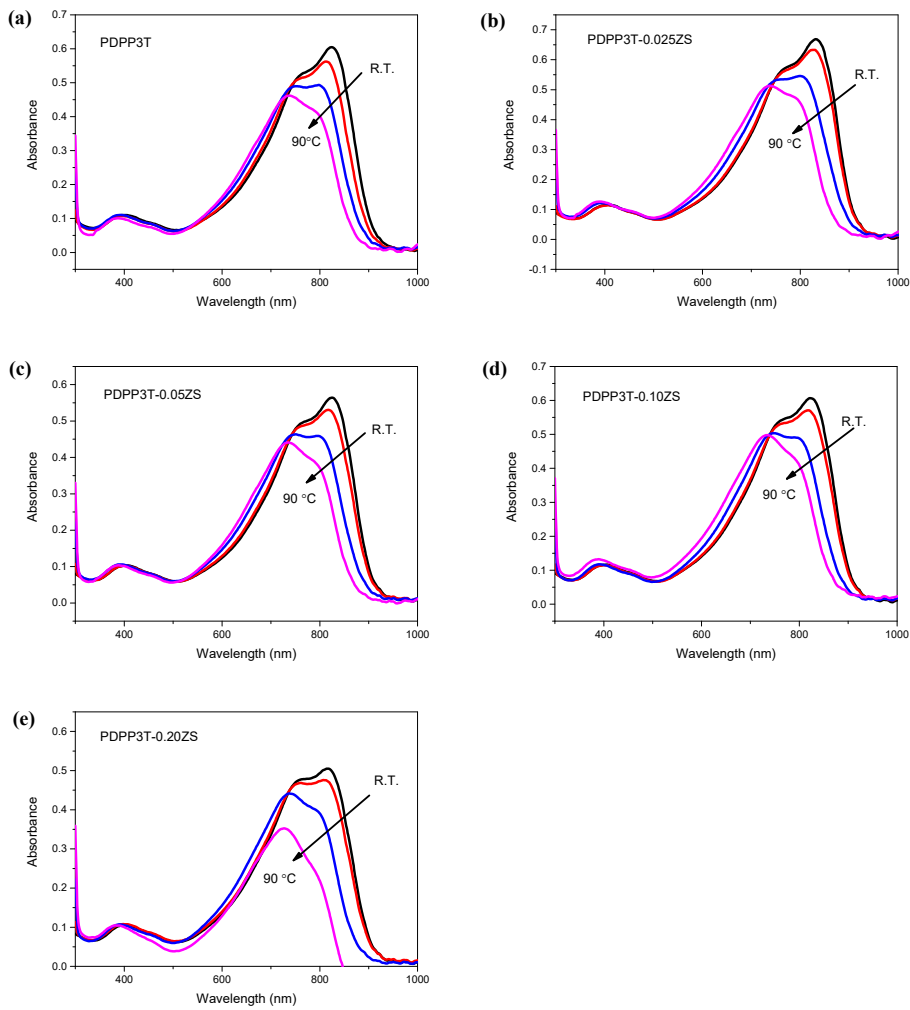


Fig. S4 Temperature-dependent UV-vis-NIR spectra in *o*-DCB solution of (a) PDPP3T, (b) PDPP3T-0.025ZS, (c) PDPP3T-0.05ZS, (d) PDPP3T-0.10ZS and (e) PDPP3T-0.20ZS.

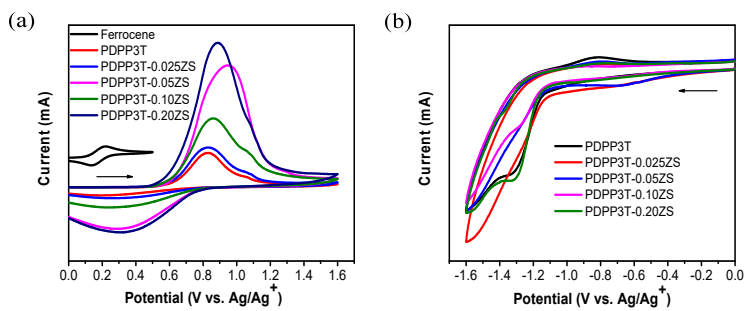


Fig. S5 CV Curves of PDPP3T and PDPP3T-*x*ZS (*x* = 0.025, 0.05, 0.10, 0.20)

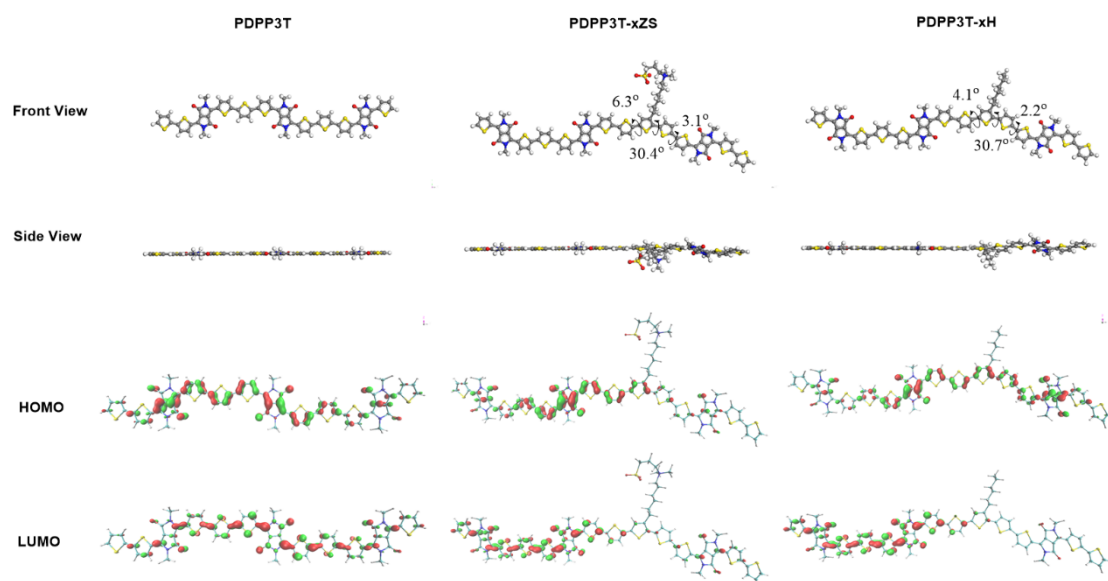


Fig. S6 DFT-calculated geometries and frontier orbitals of a trimeric fragment model of **PDPP3T** and two same fragments but separately inserted with a zwitterionic side chain or a hexyl side chain-appended 2,2'-bithiophene unit.

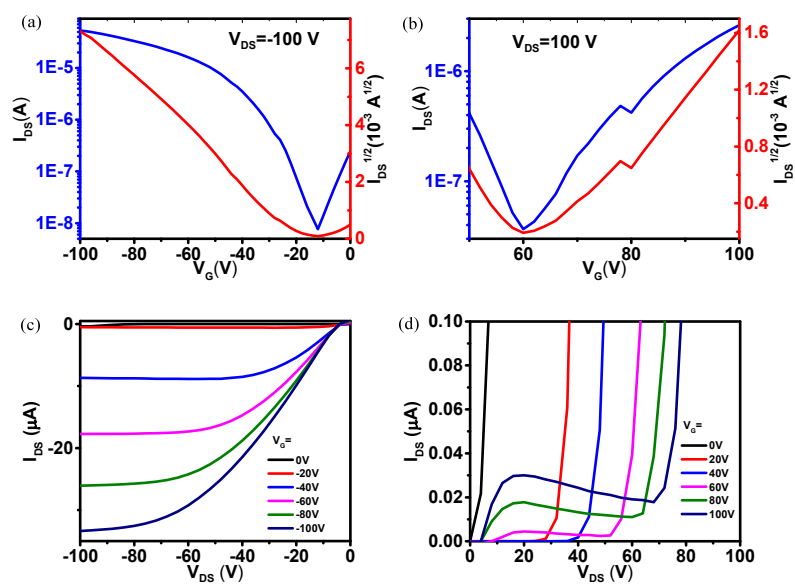


Fig. S7 The transfer curves and output Curves of **PDPP3T** after 150 °C annealing.

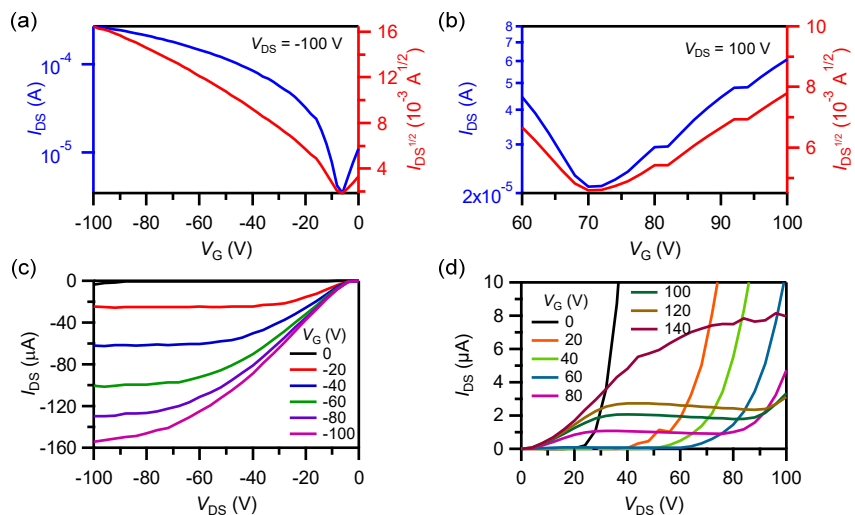


Fig. S8 The transfer and output curves of PDPP3T-0.025ZS after 240 °C annealing.

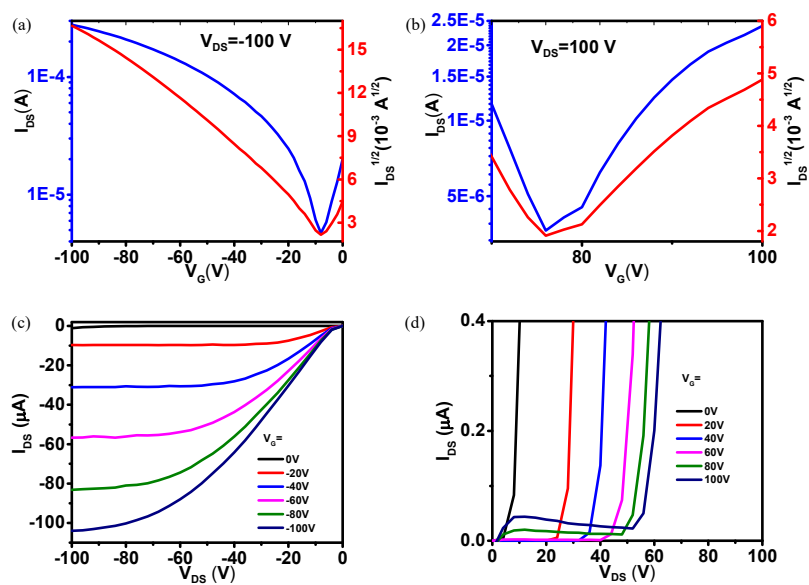


Fig. S9 The transfer and output curves of PDPP3T-0.05ZS after 240 °C annealing.

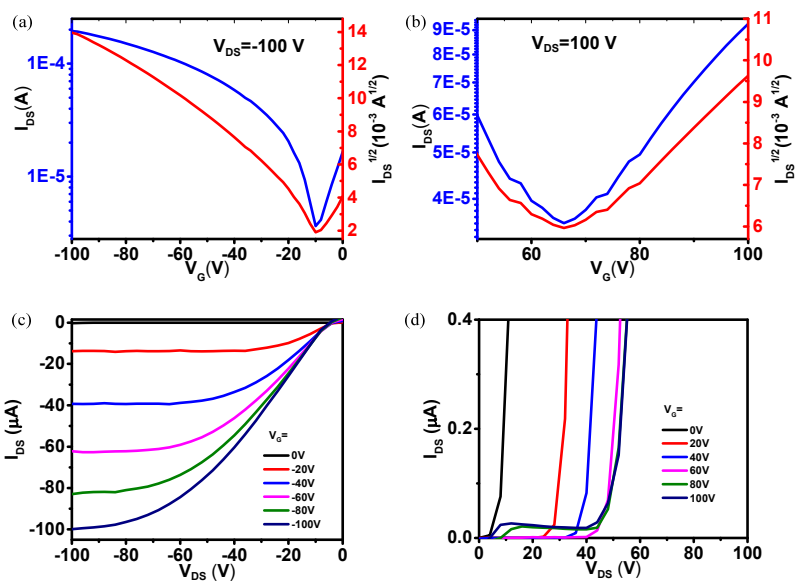


Fig. S10 The transfer and output curves of **PDPP3T-0.10ZS** after 240 °C annealing.

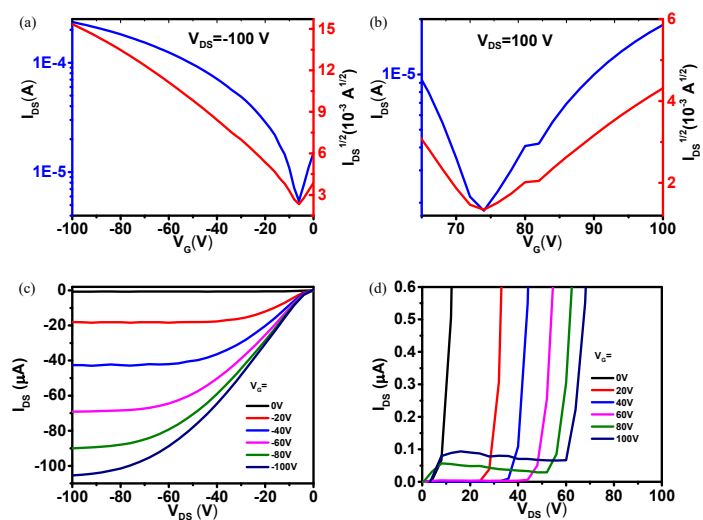


Fig. S11 The transfer and output curves of **PDPP3T-0.20ZS** after 240 °C annealing.

Table S1 Characteristics of OFET devices based on **PDPP3T** and **PDPP3T-xZS** (x = 0.025, 0.05, 0.10, 0.20)^a

Polymer	T_{anneal} / °C	p-channel			n-channel		
		μ_h ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	V_T (V)	$I_{\text{on}}/I_{\text{off}}$	μ_e ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	V_T (V)	$I_{\text{on}}/I_{\text{off}}$
PDPP3T	As cast	0.14±0.042	-12.45	10^3 - 10^4	0.010±0.003	62.38	10^0 - 10^1
	120	0.20±0.051	-19.36	10^4 - 10^5	0.032±0.01	60.80	10^0 - 10^1
	150	0.27±0.066	-16.71	10^3 - 10^4	0.038±0.016	63.95	10^1 - 10^2
	180	0.16±0.014	-7.15	10^2 - 10^3	0.014±0.001	70.68	10^1 - 10^2
PDPP3T-0.025ZS	As cast	0.26±0.021	-7.48	10^2 - 10^3	0.070±0.035	41.82	10^0 - 10^1
	80	0.29±0.038	-15.00	10^2 - 10^3	0.058±0.016	55.41	10^0 - 10^1
	160	0.55±0.054	-2.68	10^2 - 10^3	0.26±0.11	49.94	10^0 - 10^1
	240	1.06±0.25	-2.51	10^1 - 10^2	0.31±0.085	32.92	10^0 - 10^1
PDPP3T-0.05ZS	As cast	0.27±0.025	-9.26	10^2 - 10^3	0.010±0.0040	31.52	10^0 - 10^1
	80	0.33±0.033	11.29	10^2 - 10^3	0.018±0.0078	46.17	10^0 - 10^1
	160	0.60±0.087	-5.24	10^2 - 10^3	0.29±0.031	49.79	10^0 - 10^1
	240	0.84±0.13	3.71	10^1 - 10^2	0.27±0.089	33.12	10^0 - 10^1
PDPP3T-0.10ZS	As cast	0.39±0.030	-7.19	10^2 - 10^3	0.037±0.025	45.69	10^0 - 10^1
	80	0.46±0.076	10.72	10^2 - 10^3	0.032±0.0056	44.93	10^0 - 10^1
	160	0.59±0.087	-0.36	10^1 - 10^2	0.34±0.13	43.26	10^0 - 10^1
	240	0.73±0.19	-4.12	10^1 - 10^2	0.24±0.099	26.84	10^0 - 10^1
PDPP3T-0.20ZS	As cast	0.31±0.049	-7.20	10^2 - 10^3	0.064±0.017	18.58	10^0 - 10^1
	80	0.45±0.085	7.48	10^1 - 10^2	0.078±0.033	35.39	10^0 - 10^1
	160	0.51±0.074	0.055	10^1 - 10^2	0.23±0.072	42.77	10^0 - 10^1
	240	0.69±0.14	1.28	10^1 - 10^2	0.21±0.043	23.45	10^0 - 10^1

^a The data are obtained by statistical analysis of more than 10 devices tested in nitrogen, while the V_T data are the average values.

Table S2 Performance of **PDPP3T-0.025ZS** devices by different batch fabrication

Batch	p-channel			n-channel		
	μ_h ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	V_T (V)	$I_{\text{on}}/I_{\text{off}}$	μ_e ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	V_T (V)	$I_{\text{on}}/I_{\text{off}}$
1 st	1.06 ± 0.25	-2.51	10^1 - 10^2	0.31 ± 0.085	32.92	10^0 - 10^1
2 nd	1.20 ± 0.13	1.63	10^1 - 10^2	0.24 ± 0.028	30.33	10^0 - 10^1
3 rd	0.92 ± 0.29	-0.88	10^1 - 10^2	0.39 ± 0.007	35.50	10^0 - 10^1

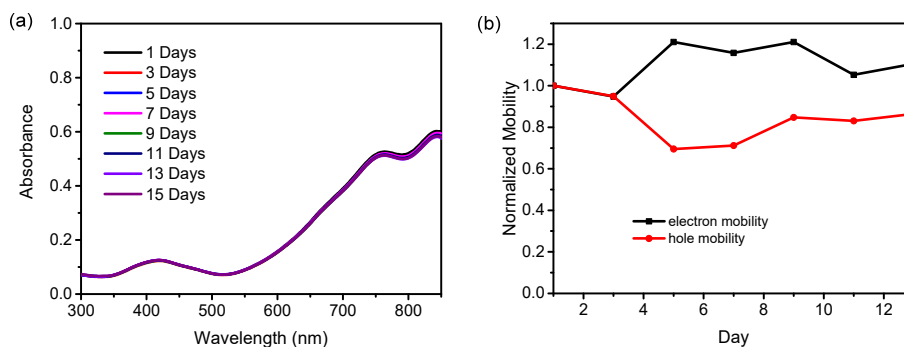


Fig. S12 Stability studies on (a) a film sample and (b) an OFET device of **PDPP3T-0.025ZS** stored in the glove box with N₂ atmosphere.

Table S3 Thermal analysis data, optical, electrochemical properties of **PDPP3T-xH** (x = 0.025, 0.05, 0.10, 0.20)

Polymer	M_n^a	\mathcal{D}^a	λ_{\max} (nm)		E_{HOMO}^c (eV)	E_{LUMO}^c (eV)	$E_{g,\text{CV}}^d$ (eV)
			Solution	Film			
PDPP3T-0.025H	18.3	1.9	408, 812	404, 769, 843	-5.19	-3.59	1.60
PDPP3T-0.05H	20.3	2.1	414, 833	406, 761, 844	-5.26	-3.60	1.66
PDPP3T-0.10H	19.4	2.0	417, 822	395, 768, 845	-5.22	-3.62	1.60
PDPP3T-0.20H	18.7	2.0	413, 802	414, 761, 840	-5.17	-3.60	1.57

^aDetermined by high temperature gel chromatography using 1,2,4-trichlorobenzene as eluent at 145 °C; ^b $E_{g,\text{opt}} = 1240/\lambda_{\text{onset}}$; ^cFc/Fc⁺ ($E_{\text{HOMO}} = -4.8$ eV) as external standard; ^d $E_{g,\text{CV}} = E_{\text{LUMO}} - E_{\text{HOMO}}$.

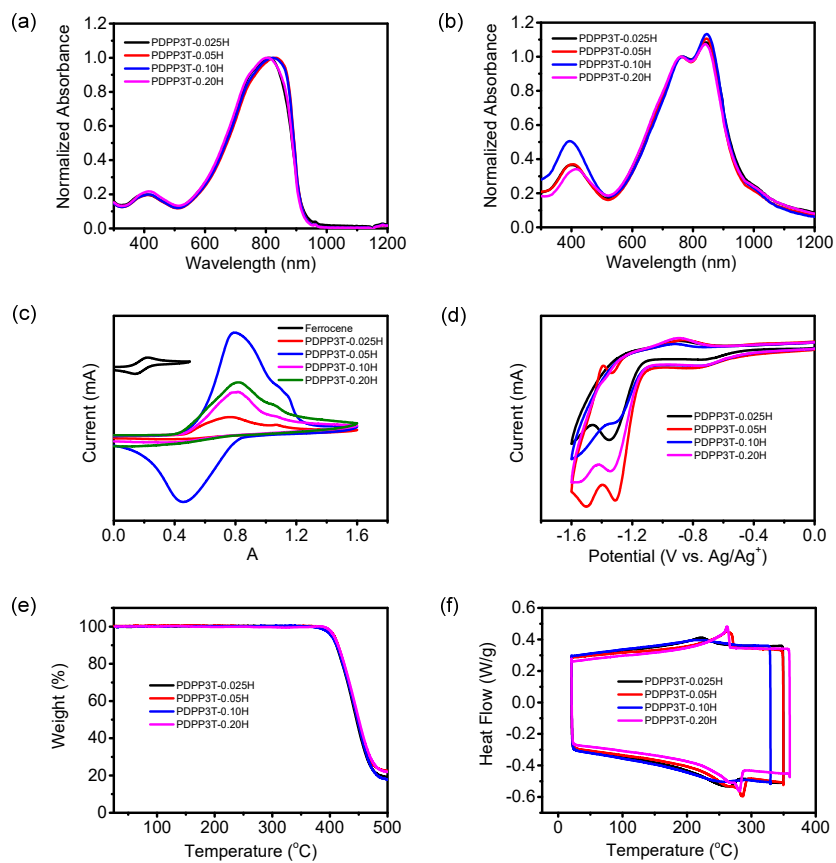


Fig. S13 (a) Normalized UV-Vis-NIR absorption spectra in solution and (b) in film, (c-d) CV, (e) TGA curve, and (f) DSC curves of **PDPP3T-xH** ($x = 0.025, 0.05, 0.10, 0.20$)

Table S4 The OFET mobilities of **PDPP3T-xH** ($x = 0.025, 0.05, 0.10, 0.20$) in N_2 ^a

Polymer	T_{anneal} (°C)	p-channel	n-channel
		μ_h ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	μ_e ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)
PDPP3T-0.025H	As cast	0.063±0.014	0.0003±0.00008
	120	0.066±0.024	0.0008±0.0008
	160	0.025±0.0065	0.012±0.0015
	200	0.014±0.0055	0.0022±0.0008
	240	0.047±0.0083	0.012±0.0006
PDPP3T-0.05H	As cast	0.030±0.0069	0.00045±0.00013
	120	0.037±0.022	0.0021±0.0020
	160	0.029±0.011	0.018±0.0092
	200	0.015±0.011	0.0039±0.0013
	240	0.012±0.0078	0.0035±0.0018
PDPP3T-0.10H	As cast	0.052±0.0007	0.00055±0.00007
	120	0.066±0.015	0.0011±0.00007
	160	0.056±0.014	0.024±0.0097
	200	0.022±0.0047	0.0039±0.00080
	240	0.022±0.0086	0.0075±0.022
PDPP3T-0.20H	As cast	0.017±0.0042	0.0004±0.00007
	120	0.026±0.0032	0.0006±0.0005
	160	0.049±0.028	0.025±0.012
	200	0.0057±0.0015	0.0029±0.0018
	240	0.0055±0.0028	0.0019±0.0017

^a The data are obtained by statistical analysis of more than 10 devices tested in nitrogen.

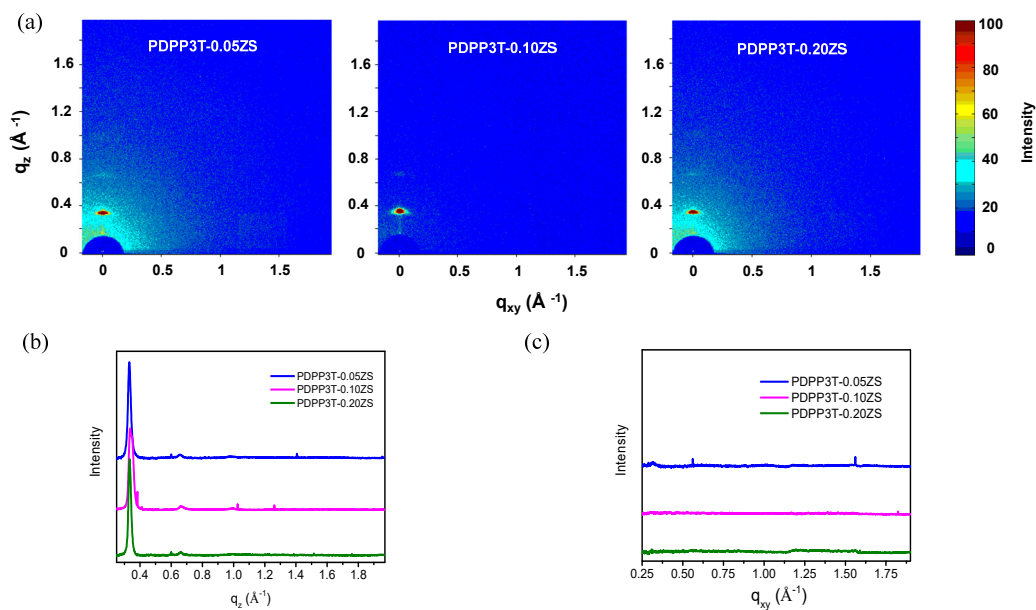


Fig. S14 (a) 2D GIWAXS patterns, and their (b) out-of-plane and (c) in-plane line-cuts of **PDPP3T-0.05XS**, **PDPP3T-0.10ZS** and **PDPP3T-0.20XS**.

5. References

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