

## Electronic Supplementary Information

# Dithienosilole-*co*-5-Fluoro-2,1,3-Benzothiadiazole- Containing Regio-Isomeric Polymers for Organic Field- Effect Transistors

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## Experimental Section

*Materials and Instruments:* 4-fluoro-*o*-penylenediamine and 2,6-dibromo-4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophene were purchased from AK Scientific and Solarmer Materials Inc., respectively. All other chemicals and reagents were purchased from Sigma-Aldrich, Alfa Aesar Chemical Company, and Tokyo Chemical Industry Co., Ltd. and used without any further purification. All solvents were ACS and anhydrous grade by distillation. 4,4-bis(2-ethylhexyl)-2,6-bis(trimethylstannyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophene (**2**), 4,7-dibromo-5-fluorobenzo-2,1,3-thiadiazole (**3**), 7,7'-(4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(4-bromo-5-fluorobenzo[*c*][1,2,5]thiadiazole) (**4**) and 4,4-bis(2-ethylhexyl)-2-(trimethylstannyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophene (**7**) were synthesized according to the reported literature. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on an Agilent 400 MHz spectrometer using deuterated CDCl<sub>3</sub> as a solvent and tetramethylsilane (TMS) as an internal standard. Elementary analyses were carried out with a Flash 2000 element analyzer (Thermo Scientific, Netherlands) and MALDI-TOF MS spectra were checked by Ultraflex III (Bruker, Germany). UV-vis-NIR absorption spectra in solution and in thin films were measured with a UV-1800 (SHIMADZU) spectrophotometer. The number-average ( $M_n$ ) and weight-average ( $M_w$ ) molecular weights, and polydispersity indices (PDI) of the polymer products were determined by gel permeation chromatography (GPC) with a FUTECS NS-4000 using a series of monodisperse polystyrene as standards in 1,2,4-trichlorobenzene (HPLC grade) at 100 °C. Cyclic voltammetry (CV) measurements were performed on an AMETEK Versa STAT 3 with a three-electrode cell system in a nitrogen bubbled 0.1 M tetra-*n*-butylammonium hexafluorophosphate (*n*-Bu<sub>4</sub>NPF<sub>6</sub>) solution in acetonitrile at a scan rate of 100 mV<sup>1</sup> s<sup>-1</sup> at room temperature. An Ag/Ag<sup>+</sup> electrode, platinum wire, and platinum were used as the reference electrode, counter electrode, and working electrode, respectively. The Ag/Ag<sup>+</sup> reference electrode was calibrated using a ferrocene/ferrocenium redox couple as an internal

standard whose oxidation potential was set at  $-4.8$  eV with respect to the zero-vacuum level. Subsequently, HOMO energy levels were obtained from the equation  $\text{HOMO (eV)} = - (E_{(\text{ox})}^{\text{onset}} - E_{(\text{ferrocene})}^{\text{onset}} + 4.8)$  and LUMO levels from the equation  $\text{LUMO (eV)} = - (E_{(\text{red})}^{\text{onset}} - E_{(\text{ferrocene})}^{\text{onset}} + 4.8)$ . DFT calculations were performed using the Gaussian 09 package with the nonlocal hybrid Becke three-parameter Lee-Yang-Parr (B3LYP) function and the 6-31G basis set to investigate the HOMO and LUMO levels, charge density isosurfaces, torsion angles between the internal moiety planes and the magnitude of dipole moment vectors for the theoretically optimized geometries of 2CIBT-based polymers. HOMO and LUMO levels were calculated by multiplying 27 from the value of optimized structures.

*Synthesis of and 4,4-bis(2-ethylhexyl)-2,6-bis(tributylstannyl)-4H-silolo[3,2-b:4,5-b']dithiophene (5)*: 1 (1.60g, 2.60 mmol) was dissolved in 30 mL of tetrahydrofuran and purged with argon for 30 min. To the solution, 2.5 M n-BuLi (2.30 mL, 5.72 mmol) was added dropwise to the solution at  $-78$  °C. The mixture was stirred at  $-78$  °C for 1 h. After tributyltin chloride was added, the mixture was allowed to warm to room temperature and stirred overnight. The resulting mixture was quenched with water and extracted with diethyl ether. The organic layer was evaporated after washing three times with water and drying over  $\text{MgSO}_4$ . The crude product was purified by a short column chromatography with aluminum oxide using 5% triethylamine in hexane as the eluent to afford 2.76 g (yield 99.8 %) of a sticky green solid as a product.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.03 (s, 2H), 1.66–1.61 (m, 6H), 1.59–1.55 (m, 14H), 1.39–1.29 (m, 34H), 1.18–1.12 (m, 24H), 0.94–0.87 (m, 44H), 0.84–0.79 (m, 14H), 0.77–0.73 (m, 12H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 154.63, 143.61, 138.13, 136.24, 35.88, 35.65, 29.27, 28.98, 28.80, 27.40, 27.25, 22.97, 17.83, 14.17, 13.64, 10.85, 10.79, 8.74.

MALDI-TOF MS ( $m/z$ ) Calcd: 996.43. Found: 995.53 ( $\text{MH}^+$ ). Anal. Calcd. for  $\text{C}_{48}\text{H}_{90}\text{S}_2\text{SiSn}_2$ :

C, 57.83; H, 9.10; S, 6.43. Found: C, 56.41; H, 9.03; S, 5.80.

*Synthesis of and 7-(4,4-bis(2-ethylhexyl)-6-(tributylstannyl)-4H-silolo[3,2-b:4,5-b']dithiophen-2-yl)-4-bromo-5-fluorobenzo[c][1,2,5]thiadiazole (6):* **5** (1.50 g, 1.50 mmol), **3** (844 mg, 2.71 mmol), tetrakis(triphenylphosphine)palladium(0) (52.2 mg, 45.1  $\mu$ mol), and 25 mL of anhydrous toluene were mixed in a 30 mL microwave vessel and purged with argon for 30 min. The reaction mixture was subjected to microwave irradiation with heating at 110 °C for 3 h. After cooling to room temperature, the solvent was evaporated, and the crude product was purified by silica column chromatography using a solvent gradient of 0–10% chloroform in hexane–1% triethylamine as the eluent, which afforded 363 mg (yield 25.7%) of a sticky red solid as the product.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.14 (s, 1H), 7.66 (d, 1H,  $J$  = 10.3 Hz), 7.11 (s, 1H), 1.62–1.56 (m, 4H), 1.49–1.41 (m, 2H), 1.40–1.31 (m, 6H), 1.31–1.09 (m, 22H), 1.03–0.95 (m, 4H), 0.91 (t, 9H,  $J$  = 7.4 Hz), 0.79 (q, 12H,  $J$  = 7.4 Hz).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 162.13, 159.63, 152.33, 148.98, 145.50, 143.95, 139.69, 138.27, 137.18, 132.33, 128.25, 114.79, 114.48, 94.78, 77.31, 76.99, 76.67, 35.93, 35.71, 35.63, 28.97, 28.92, 28.87, 28.84, 27.25, 22.97, 17.73, 14.15, 13.65, 10.95, 10.81, 10.79.

MALDI-TOF MS ( $m/z$ ) Calcd: 938.22. Found: 938.24 (MH<sup>+</sup>). Anal. Calcd. for C<sub>54</sub>H<sub>74</sub>Cl<sub>2</sub>N<sub>2</sub>S<sub>5</sub>Si<sub>2</sub>: C, 53.73; H, 6.87; N, 2.98; S, 10.25. Found: C, 55.36; H, 7.00; N, 2.93; S, 10.45.

*Synthesis of and 7-(4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophen-2-yl)-4-bromo-5-fluorobenzo[c][1,2,5]thiadiazole (8):* **7** (1.00 g, 1.72 mmol), **3** (590 mg, 1.89 mmol), tetrakis(triphenylphosphine)palladium(0) (59.6 mg, 51.6  $\mu$ mol), and 20 mL of anhydrous toluene were mixed in a 30 mL microwave vessel and purged with argon for 30 min. The reaction mixture was subjected to microwave irradiation with heating at 110 °C for 3 h. After cooling to room temperature, the solvent was evaporated, and the crude product was purified

by silica column chromatography using a solvent gradient of 0–20% chloroform in hexane as the eluent, which afforded 550 mg (yield 49.2%) of a sticky red solid as the product.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.13 (s, 1H), 7.68 (d, 1H,  $J = 10.4$  Hz), 7.30 (t, 1H,  $J = 5.2$  Hz), 7.09 (s, 1H), 1.47–1.41 (m, 2H), 1.32–1.12 (m, 20H), 1.03–0.97 (m, 3H), 0.82–0.77 (m, 9H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 162.09, 159.59, 152.08, 148.94, 148.31, 144.24, 144.15, 144.10, 144.07, 132.06, 132.02, 130.02, 128.08, 127.98, 126.69, 115.02, 114.71, 35.92, 35.89, 35.67, 35.64, 28.90, 28.87, 28.84, 22.96, 22.94, 17.69, 17.65, 17.63, 17.59, 14.12, 10.79, 10.77.

MALDI-TOF MS ( $m/z$ ) Calcd: 650.11. Found: 650.12 ( $\text{MH}^+$ ). Anal. Calcd. for  $\text{C}_{30}\text{H}_{38}\text{BrFN}_2\text{S}_3\text{Si}$ : C, 55.45; H, 5.89; N, 4.31; S, 14.80. Found: C, 55.42; H, 6.01; N, 4.32; S, 14.77.

*Typical Procedure for Stille Polymerization and Polymer Purification:* dibrominated co-monomer (100 mg, 1 eq) (**3** or **4**)–bis-stannylated co-monomer (1 eq) (**2**) combination or mono-stannylated–monobrominated monomer (150 mg, 1eq) (**6**) and tetrakis(triphenylphosphine)palladium(0) (0.03 eq) in 5 mL of anhydrous p-xylene were mixed in a 30 mL microwave vessel and purged with argon for 30 min. Afterwards, the reaction mixture was heated at 180 °C for 3h. The crude product was poured into methanol (400 mL), and the mixture was filtrated. The precipitate was subjected to sequential Soxhlet extraction with methanol, acetone, and hexane for a day for each step to remove the low molecular weight fractions of the material. The residue was extracted with chloroform to produce a product after precipitating in methanol and drying *in vacuo*.

*Synthesis of PI:* Using the same procedure described above, a mixture of **2** and **3** was used to polymerize to give a dark purple powder. Isolated yield = 80%.  $M_n = 5.26$  kDa, PDI = 1.65.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.86–7.82 (br, 2H), 7.21–7.17 (br, 2H), 7.13–7.07 (br, 2H), 1.53–1.49 (br, 4H), 1.34–1.20 (br, 32H), 1.09–1.01 (br, 8H), 0.87–0.80 (br, 24H).

Anal. calcd. for  $C_{60}H_{74}F_2N_4S_6Si_2$ : C, 63.34; H, 6.56; N, 4.92; S, 16.91; found: C, 62.29; H, 6.70; N, 2.49; S, 17.19.

*Synthesis of P2*: Using the same procedure described above, a mixture of **4** and **2** was used to polymerize, resulting in a dark purple powder. Isolated yield = 75%.  $M_n$  = 5.85 kDa, PDI = 2.37.

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  (ppm) 7.89–7.81 (br, 2H), 7.34–7.28 (br, 2H), 7.22–7.18 (br, 2H), 1.51–1.49 (br, 4H), 1.28–1.20 (br, 32H), 1.08–1.04 (br, 8H), 0.85–0.80 (br, 24H).

Anal. calcd. for  $C_{60}H_{74}F_2N_4S_6Si_2$ : C, 63.34; H, 6.56; N, 4.92; S, 16.91; found: C, 62.29; H, 6.70; N, 2.49; S, 17.19.

*Synthesis of P3*: Using the same procedure described above, **6** was used to polymerize, resulting in a dark purple powder. Isolated yield = 48%.  $M_n$  = 6.97 kDa, PDI = 1.98.

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  (ppm) 7.87–7.81 (br, 2H), 7.19–7.16 (br, 2H), 7.13–7.04 (br, 4H), 1.52–1.48 (br, 4H), 1.28–1.19 (br, 32H), 1.07–1.01 (br, 8H), 0.85–0.80 (br, 24H).

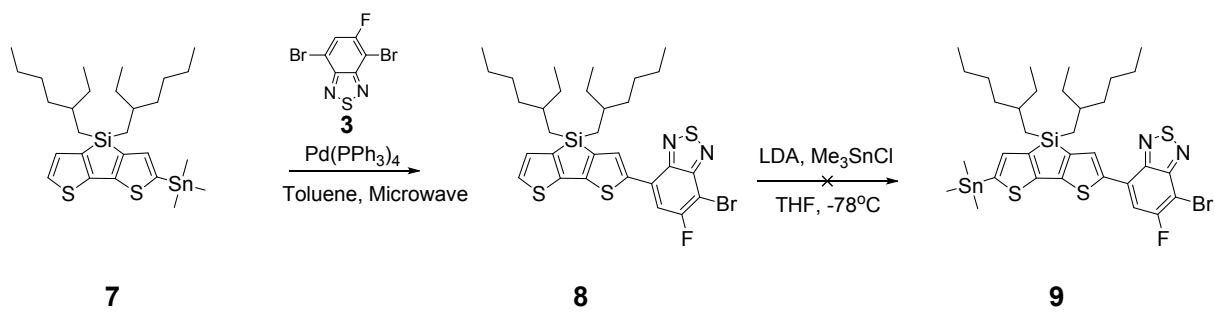
Anal. calcd. for  $C_{60}H_{74}F_2N_4S_6Si_2$ : C, 63.34; H, 6.56; N, 4.92; S, 16.91; found: C, 62.29; H, 6.70; N, 2.49; S, 17.19.

*Thin-Film Microstructure Analyses*: Samples for thin-film microstructure analyses were prepared by spin-coating the polymer solutions (5 mg mL<sup>-1</sup> in chlorobenzene at 2000 rpm for 60 s) onto SiO<sub>2</sub>/Si substrates. An Agilent 5500 scanning probe microscope with a Nanoscope V controller was used to obtain AFM images. Grazing incidence X-ray diffraction (GIXD) measurements were performed at the PLS-II 6D UNIST-PAL beamline of the Pohang Accelerator Laboratory in Korea. X-rays coming from the in-vacuum undulator (IVU) were monochromated ( $E_k$  = 11.6 keV and  $\lambda$  = 1.069 Å). The incidence angle of the X-rays was adjusted to 0.12°, which was close to the critical angle of the samples. GIXD patterns were recorded by a 2D CCD detector (SX165, Rayonix, USA) located at approximately 245 mm from the sample center. The raw data were processed and analyzed using the Igor-Pro software

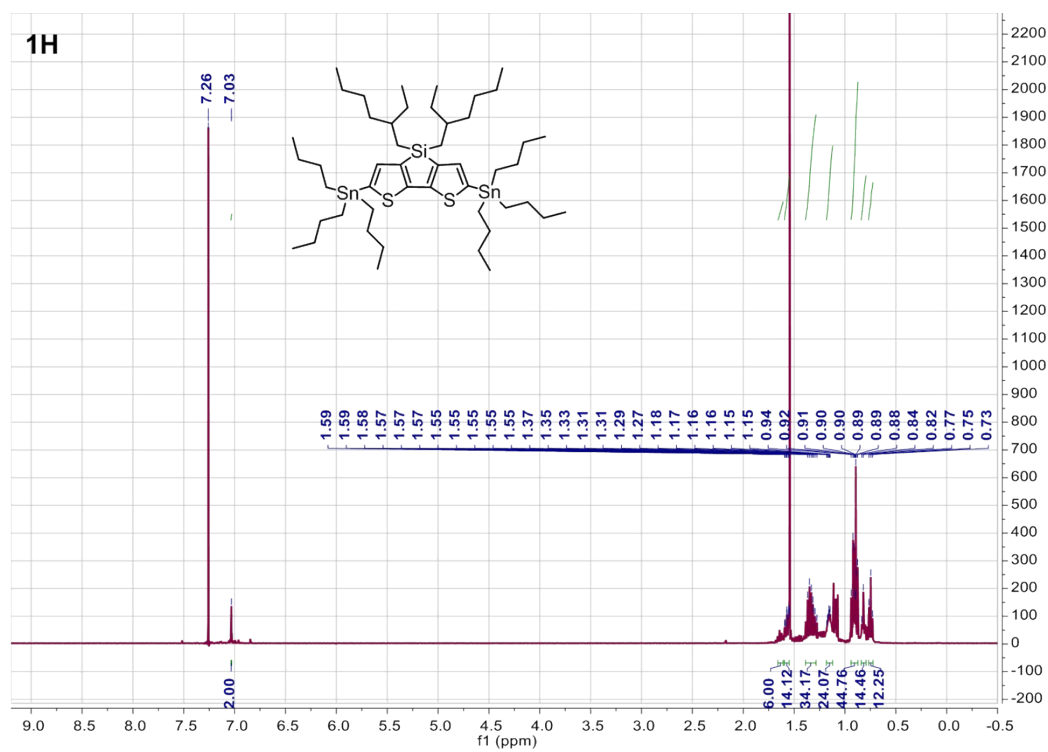
package.

*OFET Fabrication and Measurement:* OFET devices based on bottom-gate/bottom-contact (BGBC) geometry were fabricated by spin-casting polymer solutions onto  $n^{++}\text{Si}/\text{SiO}_2$  substrates. The  $n^{++}\text{Si}/\text{SiO}_2$  wafers were pre-cleaned sequentially with acetone and isopropanol. After UV-ozone treatment for 10 min, the  $n^{++}\text{Si}/\text{SiO}_2$  substrates were passivated with n-decyltrichlorosilane in a toluene solution ( $50 \mu\text{m}/5 \text{ mL}$ ). Then, the substrates were transferred to a nitrogen-filled glove box and the P1, P2 or P3 was spin-cast onto  $\text{SiO}_2$  substrates at 1500 rpm for 40 s. After thermal annealing of the polymer thin films at  $200 \text{ }^\circ\text{C}$  for 5 min, transfer and output characteristics were measured by using Keithley 4200A-SCS Parameter Analyzer. All measurements were performed in a nitrogen-filled glove box.

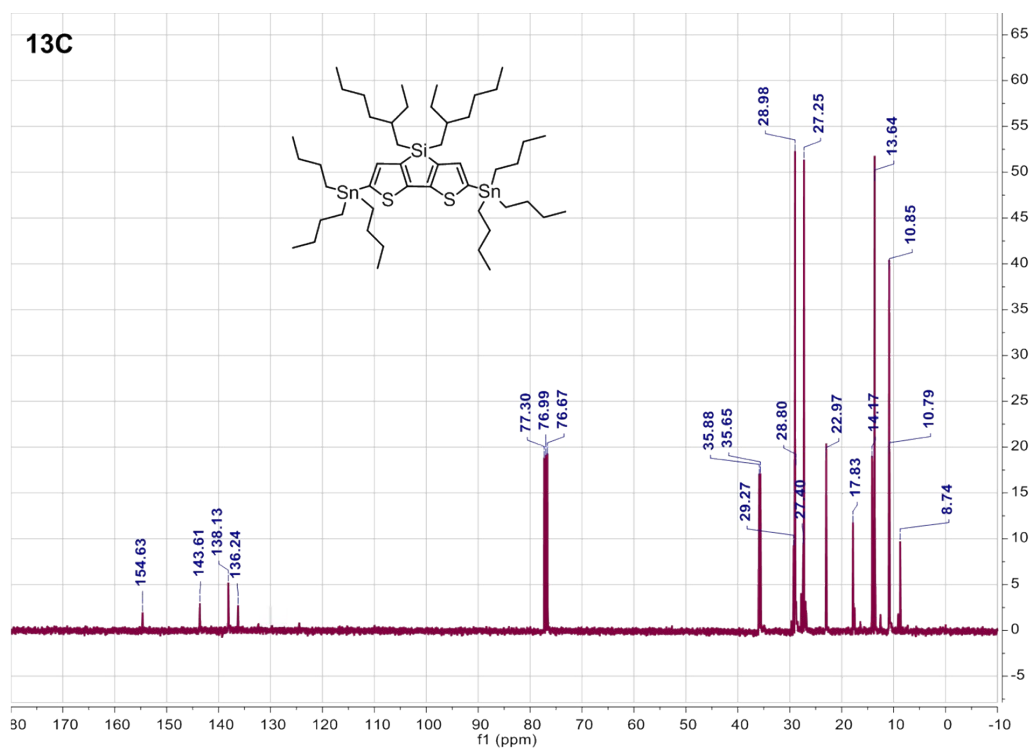




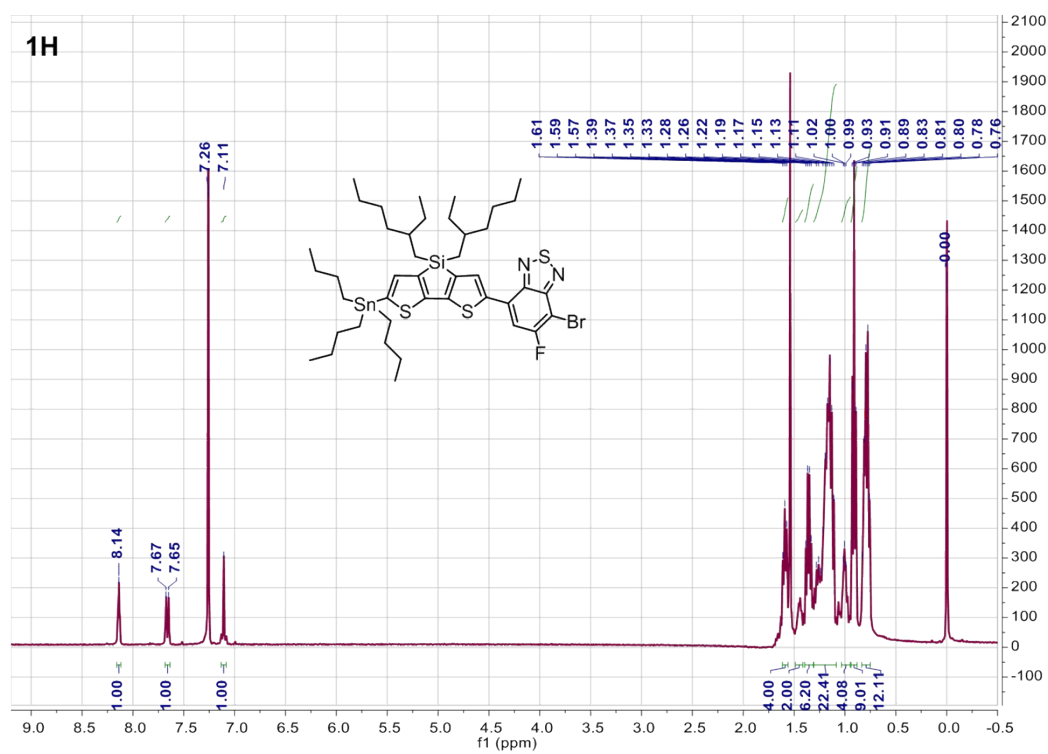
**Scheme S1.** Initial synthetic routes for intermediates of P3.



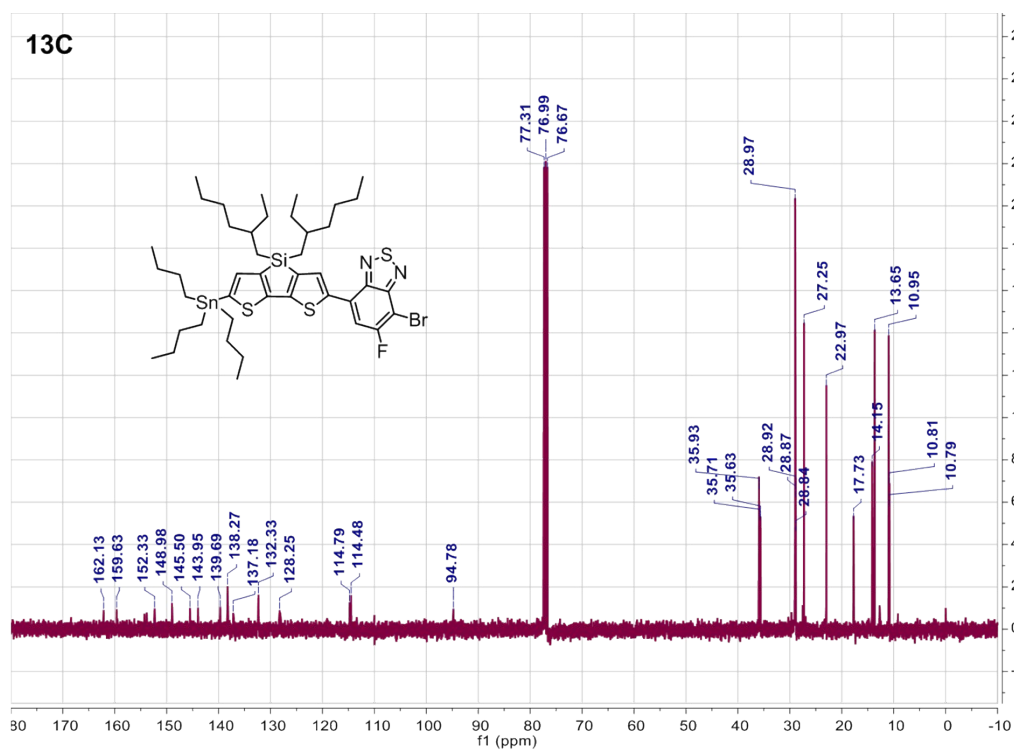
**Figure S1.** The  $^1\text{H}$  NMR spectroscopy for **5**.



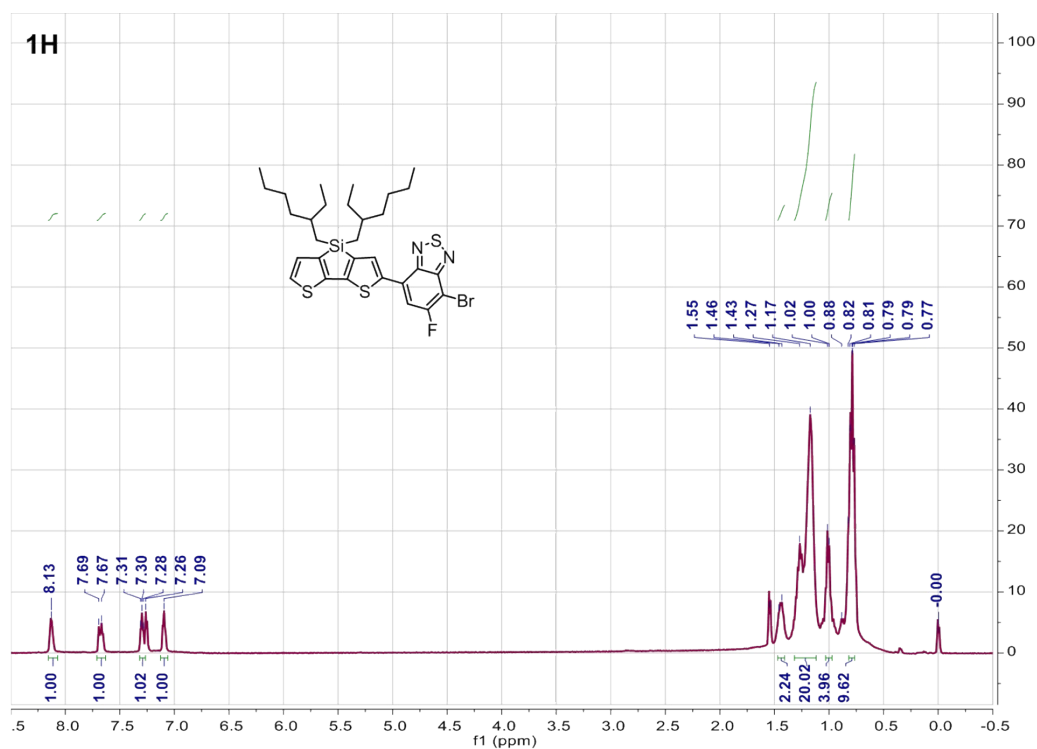
**Figure S2.** The  $^{13}\text{C}$  NMR spectroscopy for **5**.



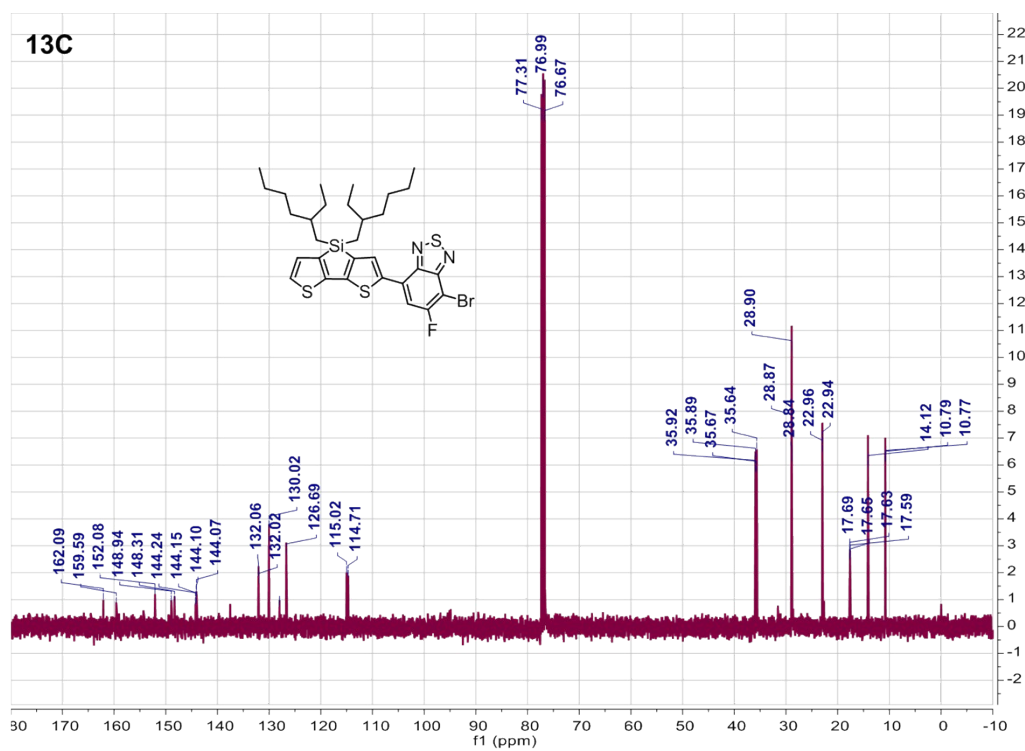
**Figure S3.** The  $^1\text{H}$  NMR spectroscopy for **6**.



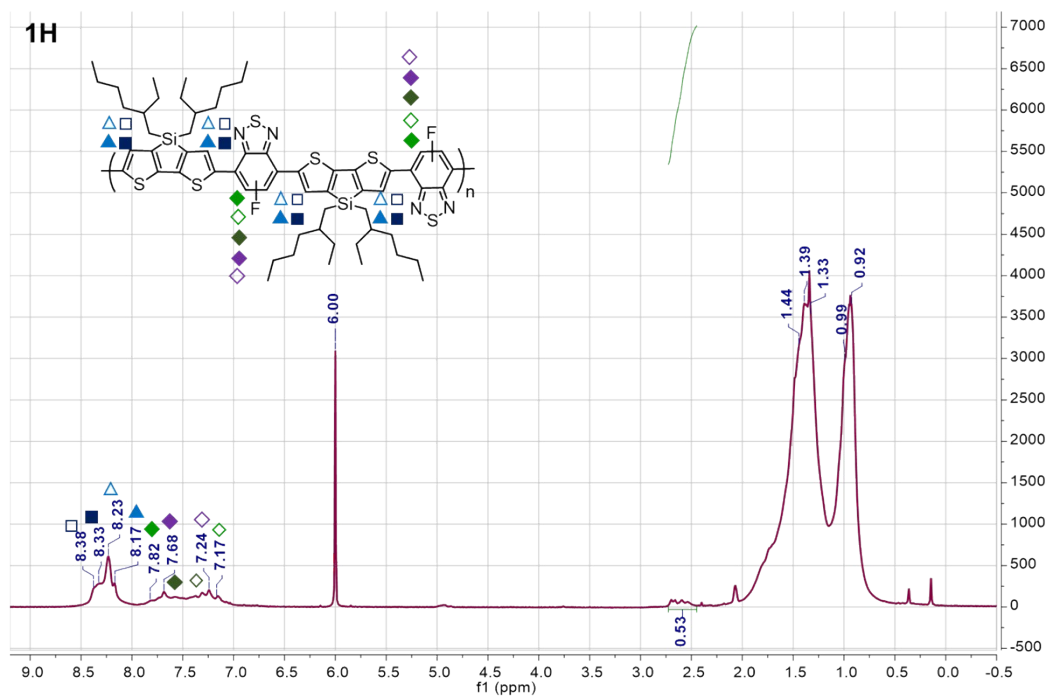
**Figure S4.** The  $^{13}\text{C}$  NMR spectroscopy for **6**.



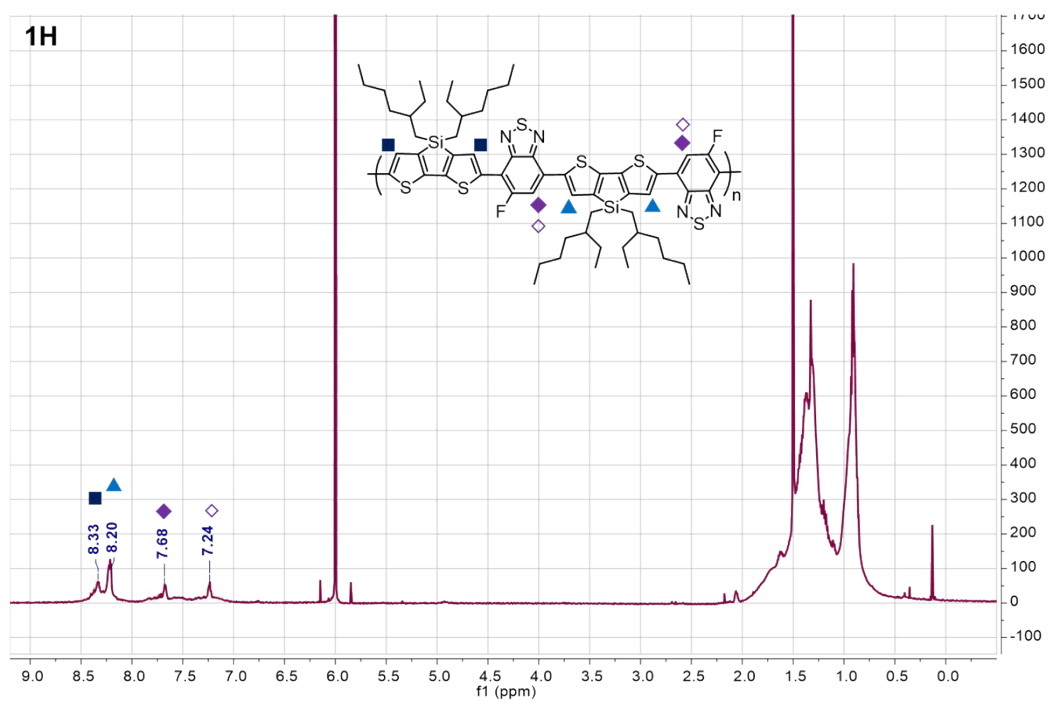
**Figure S5.** The  $^1\text{H}$  NMR spectroscopy for **8**.



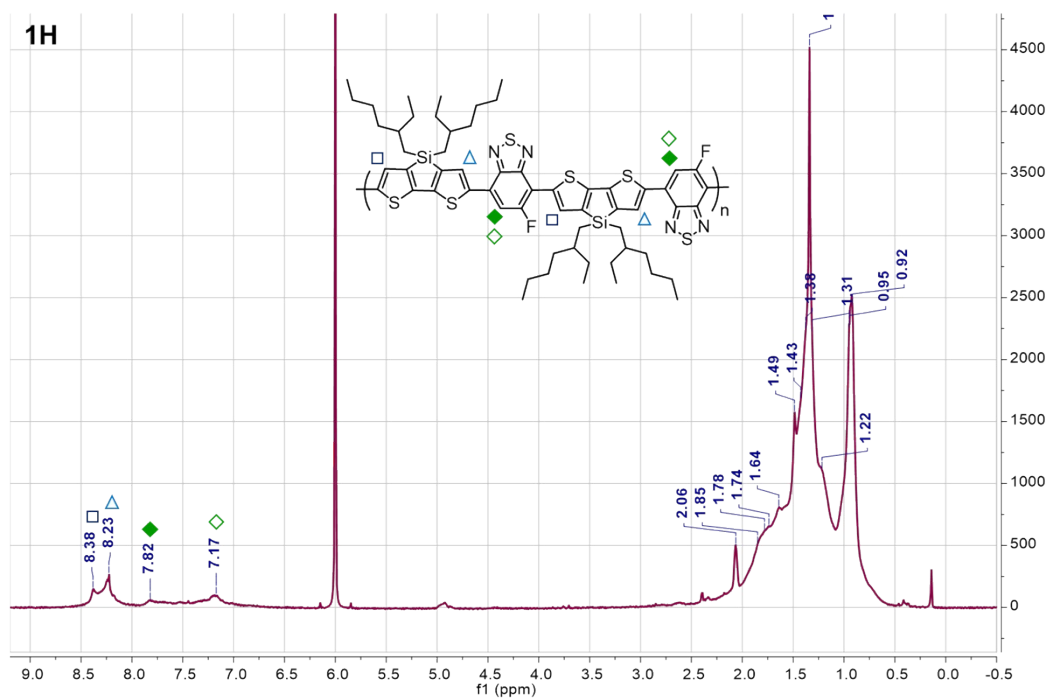
**Figure S6.** The  $^{13}\text{C}$  NMR spectroscopy for **8**.



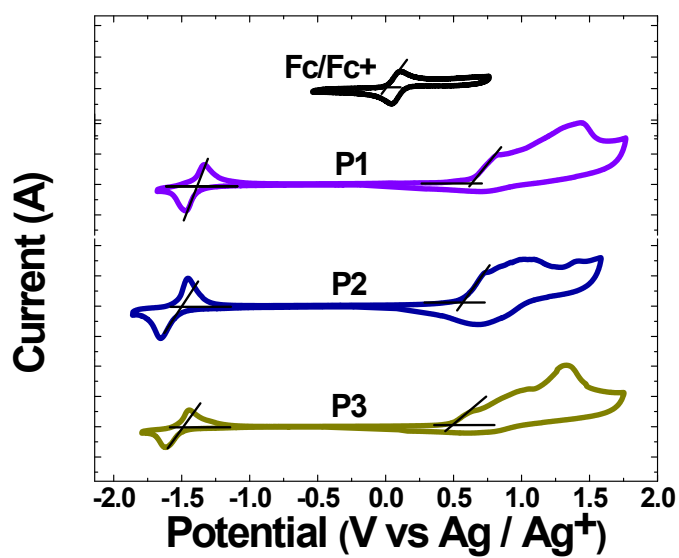
**Figure S7.** The  $^1\text{H}$  NMR spectroscopy for P1.



**Figure S8.** The  $^1\text{H}$  NMR spectroscopy for P2.



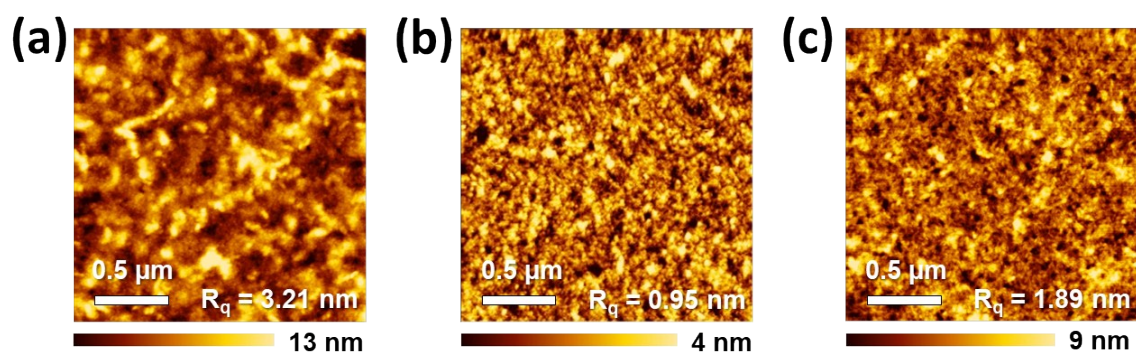
**Figure S9.** The  $^1\text{H}$  NMR spectroscopy for P3.



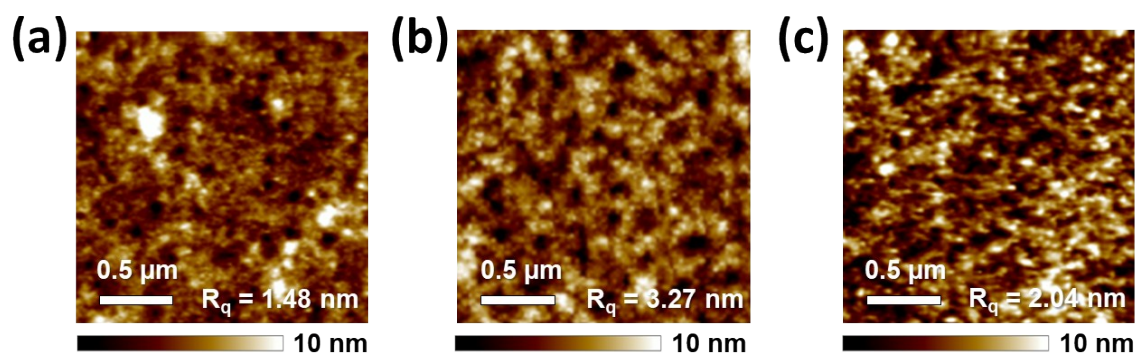
**Figure S10.** Cyclic voltammograms of the polymers in  $n\text{-Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$  solution (scan rate:  $100 \text{ mV s}^{-1}$ ).

**Table S1.** Calculated dipole moments and energy levels of the dimeric units of the polymers by DFT.

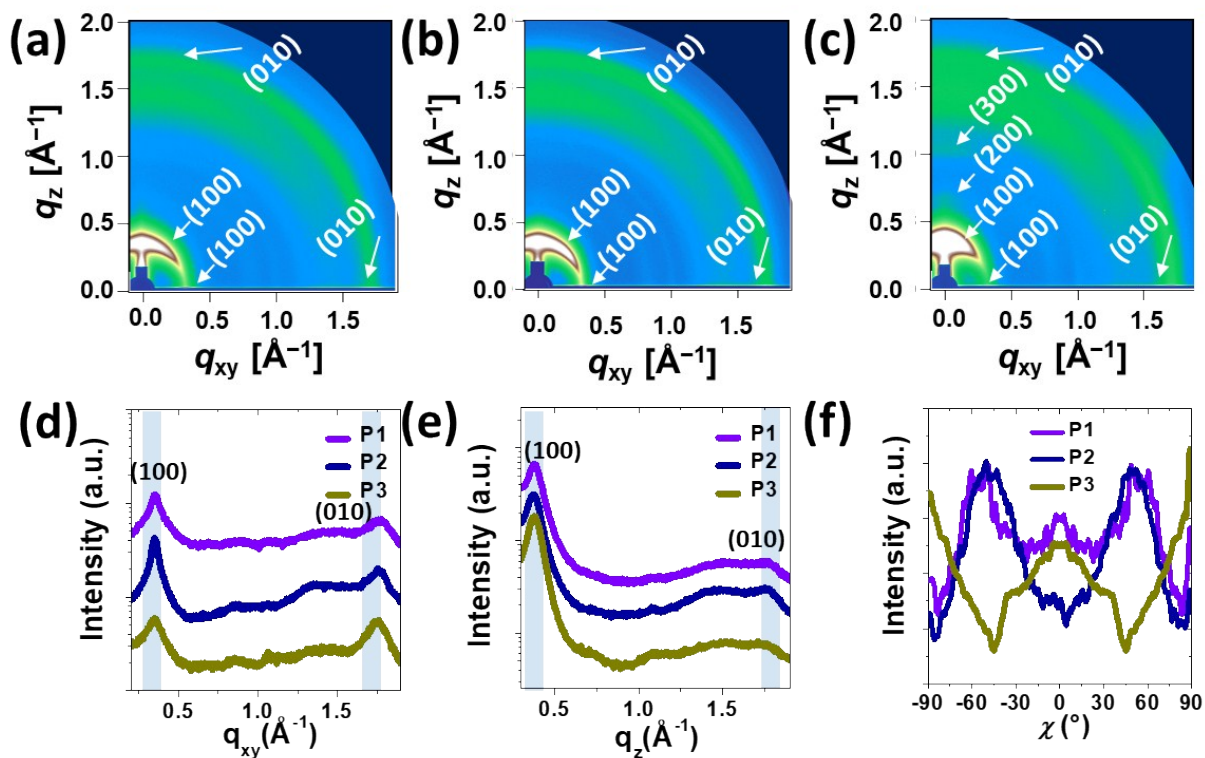
	Vector			Dipole Moment [D]	$E_{\text{HOMO}}^{\text{DFT}}$ [eV]	$E_{\text{LUMO}}^{\text{DFT}}$ [eV]
	x	y	z			
M1	-5.0892	0.0483	0.0008	5.0894	-4.79	-3.44
M2	-5.0606	1.4633	-0.0004	5.2679	-4.76	-3.39
M3	-10.2921	-6.9581	-0.0002	12.4234	-4.79	-3.38



**Figure S11.** AFM height images of (a) P1, (b) P2 and (c) P3 annealed films at 200 °C.



**Figure S12.** The AFM height images of (a) P1, (b) P2 and (c) P3 as-cast films.



**Figure S13.** 2D-GIXD images of as-cast (a) P1, (b) P2 and (c) P3 polymer films fabricated by spin-casting method and the 1D-GIXD profiles of polymer films along (d) in-plane and (e) out-of-plane orientations. (f) Pole figures for  $\pi$ - $\pi$  stacking of the polymer films.



**Table S2.** Crystallographic parameters of spin-cast polymer films annealed at 200 °C.<sup>a</sup>

Polymer film	$T_a$ [°C]	Lamellar spacing <sup>b</sup>			$\pi$ - $\pi$ spacing <sup>c</sup>		
		$q_z$ [Å <sup>-1</sup> ]	$d_z$ [Å]	$L_c$ [Å]	$q_{xy}$ [Å <sup>-1</sup> ]	$d_{xy}$ [Å]	$L_c$ [Å]
TVT:Se							
P1		0.365	17.21	206.5	1.754	3.58	126.6
P2	200	0.361	17.39	152.3	1.761	3.57	111.0
P3		0.364	17.25	150.4	1.753	3.58	113.3

<sup>a</sup> The parameters were calculated from GIXD profiles; The parameters for <sup>b</sup> the lamellar spacing and <sup>c</sup> the  $\pi$ - $\pi$  spacing were derived from the peaks along  $q_z$  and  $q_{xy}$  axis, respectively.

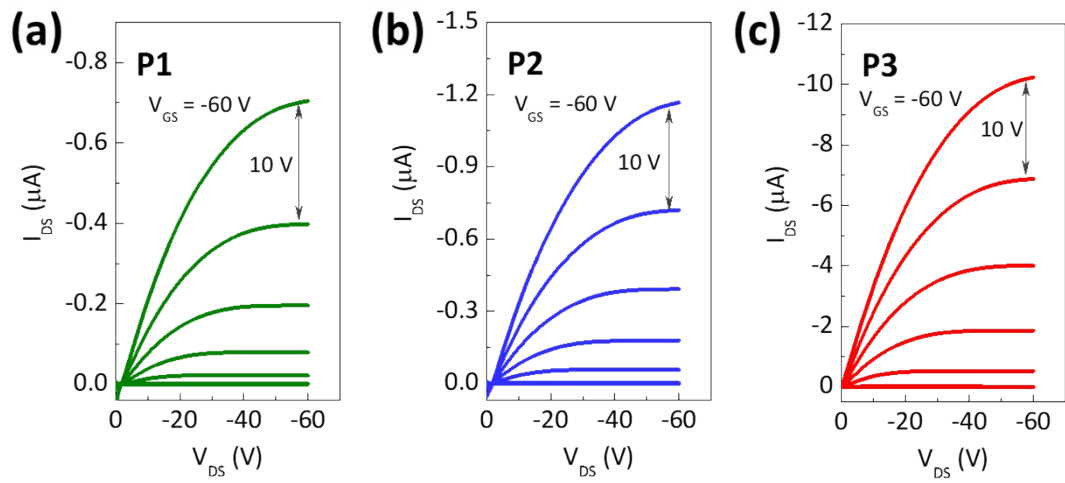
**Table S3.** Crystallographic parameters of as-cast polymer films.<sup>a</sup>

	$T^b$ [°C]	Lamellar Spacing <sup>b</sup>			$\pi$ - $\pi$ stacking <sup>c</sup>		
		$q_{z(100)}$ [Å <sup>-1</sup> ]	$d_{z(100)}$ [Å]	$L_{c,(h00)}$ [Å]	$q_{xy(010)}$ [Å <sup>-1</sup> ]	$d_{xy(010)}$ [Å]	$L_{c,(010)}$ [Å]
P1		0.375	16.75	104.7	1.755	3.58	92.4
P2	RT	0.370	17.00	109.8	1.753	3.58	123.0
P3		0.377	16.67	117.8	1.747	3.60	95.1

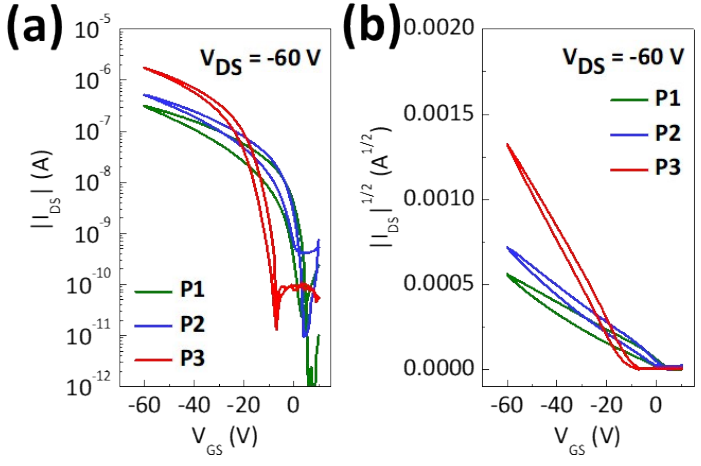
<sup>a</sup> The parameters were calculated from GIXD profiles; The parameters for <sup>b</sup> the lamellar spacing and <sup>c</sup> the  $\pi$ - $\pi$  spacing were derived from the peaks along  $q_z$  and  $q_{xy}$  axis, respectively.

**Table S4.** Crystalline population obtained a pole figure in Figure 3f.

polymer	$\pi$ - $\pi$ stacking orientation ratio (%)	
	Edge-on	Face-on
P1	88.4	11.6
P2	64.2	35.8
P3	82.8	17.2



**Figure S14.** Output characteristics of the devices fabricated with (a) P1, (b) P2 and (c) P3. All device parameters were obtained after thermal annealing at 200 °C for 5 min.

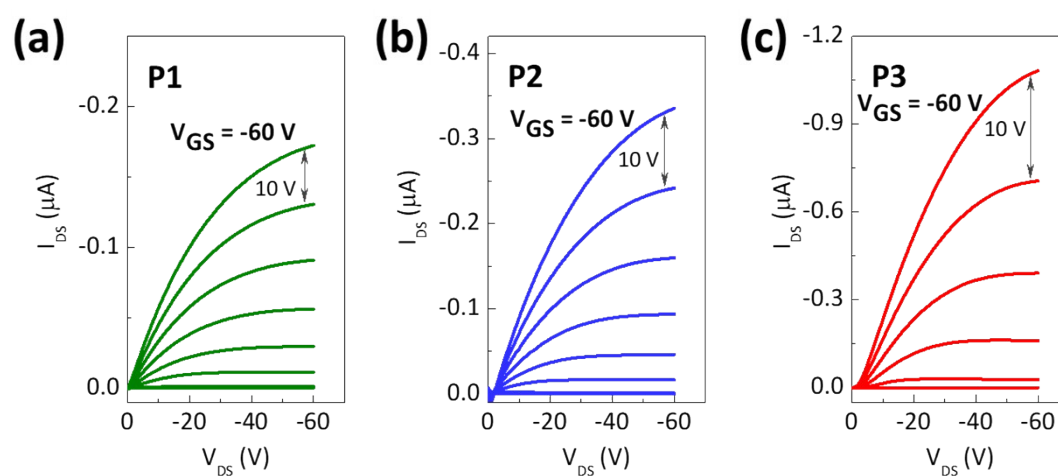


**Figure S15.** (a) Transfer and (b) output characteristics of the devices with various semiconducting polymers in the channel. All device parameters were obtained from the as-cast films.

**Table S5.** Electrical characteristics of the polymer OFET devices of the as-cast films.

Polymer	$\mu_{h,avg}^b$ [ $\text{cm}^2 \text{V}^{-1}\text{s}^{-1}$ ]	$V_{th}$ [V]	$I_{on/off}$
P1	$2.33 \times 10^{-4}$	8.6	$3.14 \times 10^4$
P2	$3.64 \times 10^{-4}$	4.8	$5.14 \times 10^4$
P3	$3.27 \times 10^{-3}$	-6.7	$2.29 \times 10^4$

<sup>a</sup>The maximum and <sup>b</sup>average mobility of the FET devices ( $L = 20 \mu\text{m}$  and  $W = 1,000 \mu\text{m}$ ) obtained from 5 devices.



**Figure S16.** Output characteristics of the devices fabricated with (a) P1, (b) P2 and (c) P3. All device parameters were obtained from the as-cast films.