

## Supporting Information

# Chlorinated 2,1,3-Benzothiadiazole-Based Polymers for Organic Field-Effect Transistors

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## Experimental Section

*Materials and Instruments:* 4,5-dichlorobenzene-1,2-diamine (**1**) and 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. 5,6-dichloro-2,1,3-benzothiadiazole (**2**), 4,7-dibromo-5,6-dichlorobenzo-2,1,3-thiadiazole, (**3**), 4,4-bis(2-ethylhexyl)-2-(trimethylstannyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophene (**4**), 2,5-bis(trimethylstannyl)thiophene, 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene, 5,5'-bis(trimethylstannyl)-2,2'-bithiophene, and (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene were synthesized according to the reported literature.<sup>1-5</sup> <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 120 °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 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 2ClBT-based polymers. HOMO and LUMO levels were calculated by multiplying 27 from the value of optimized structures.

*Synthesis of 4,7-bis(4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophen-2-yl)-5,6-dichloro-2,1,3-benzothiadiazole (5):* **3** (500 mg, 1.38 mmol), **4** (1.68 g, 2.89 mmol), tetrakis(triphenylphosphine)palladium(0) (47.8 mg, 41.3  $\mu\text{mol}$ ), 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 6 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 0–30% chloroform in hexane as the eluent, which afforded 776 mg (yield 54.2%) of a sticky red solid as the product.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.78 (t, 2H,  $J = 2.2$  Hz), 7.27 (d, 2H,  $J = 4.7$  Hz), 7.09 (d, 2H,  $J = 4.7$  Hz), 1.49–1.44 (m, 4H), 1.29–1.16 (m, 32H), 1.04–0.98 (m, 8H), 0.84–0.77 (m, 24H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 152.54, 148.47, 143.69, 142.20, 135.07, 134.60, 133.54, 129.91, 129.88, 126.15, 125.63, 77.33, 77.01, 76.69, 35.90, 35.87, 35.78, 35.72, 31.59, 28.99, 28.96, 28.86, 28.83, 22.98, 22.66, 17.70, 14.17, 14.12, 10.85, 10.83.

MALDI-TOF MS ( $m/z$ ) Calcd: 1036.34. Found: 1036.46 ( $MH^+$ ). Anal. Calcd. for  $C_{54}H_{74}Cl_2N_2S_5Si_2$ : C, 62.45; H, 7.18; N, 2.70; S, 15.44. Found: C, 62.92; H, 7.32; N, 2.74; S, 15.73.

*Synthesis of 4,7-bis(6-bromo-4,4-bis(2-ethylhexyl)-4H-silolo[3,2-*b*:4,5-*b'*]dithiophen-2-yl)-5,6-dichloro-2,1,3-benzothiadiazole (6)*: To a solution of **5** (500 mg, 0.48 mmol) in 50 mL of anhydrous THF, *N*-bromosuccinimide (NBS, 188 mg, 1.06 mmol) was slowly added at 0 °C. The reaction mixture was allowed to proceed at room temperature and stirred continuously 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  $MgSO_4$ . The crude product was purified by a silica column chromatography using hexane as the eluent to afford 534 mg (yield 92.7%) of a sticky red solid as a product.

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  (ppm) 7.78 (q, 2H,  $J = 2.0$  Hz), 7.05 (s, 2H), 1.49–1.43 (m, 4H), 1.31–1.17 (m, 32H), 1.04–0.97 (m, 8H), 0.86–0.78 (m, 24H).

$^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  (ppm) 152.43, 148.86, 144.04, 141.28, 135.02, 134.97, 132.51, 132.49, 125.52, 113.39, 112.24, 77.32, 77.01, 76.69, 35.89, 35.83, 35.77, 35.69, 28.97, 28.92, 28.88, 28.87, 22.98, 22.97, 17.61, 17.58, 17.58, 14.16, 10.85, 10.83.

MALDI-TOF MS ( $m/z$ ) Calcd: 1196.15. Found: 1196.22 ( $MH^+$ ). Anal. Calcd. for  $C_{54}H_{72}Br_2Cl_2N_2S_5Si_2$ : C, 54.21; H, 6.07; N, 2.34; S, 13.40. Found: C, 54.02; H, 6.06; N, 2.35; S, 13.65.

*Typical Procedure for Stille Polymerization and Polymer Purification*: 4,7-bis(6-bromo-4,4-bis(2-ethylhexyl)-4H-silolo[3,2-*b*:4,5-*b'*]dithiophen-2-yl)-5,6-dichloro-2,1,3-benzothiadiazole (**6**) (100 mg, 83.6  $\mu$ mol), bis-stannylated co-monomers (83.6  $\mu$ mol) (T, TT, DT, or TVT), tetrakis(triphenylphosphine)palladium(0) (2.90 mg, 2.51  $\mu$ mol), and 7 mL of anhydrous toluene were mixed in a Schlenk flask and purged with argon for 30 min. Afterwards, the reaction mixture was heated at 110 °C for 72h. 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 P2ClBT-T*: Using the same procedure described above, a mixture of **6** and 2,5-bis(trimethylstannyl)thiophene was used to polymerize to give a dark blue powder.

Isolated yield = 64%.  $M_n = 27.4$  kDa, PDI = 1.99.

$^1\text{H}$  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  $\text{C}_{58}\text{H}_{74}\text{Cl}_2\text{N}_2\text{S}_6\text{Si}_2$ : C, 62.27; H, 6.67; N, 2.50; S, 17.20; found: C, 62.29; H, 6.70; N, 2.49; S, 17.19.

*Synthesis of P2ClBT-TT*: Using the same procedure described above, a mixture of **6** and 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene was used to polymerize, resulting in a dark blue powder. Isolated yield = 76%.  $M_n = 24.5$  kDa, PDI = 2.51.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (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  $\text{C}_{60}\text{H}_{74}\text{Cl}_2\text{N}_2\text{S}_7\text{Si}_2$ : C, 61.34; H, 6.35; N, 2.38; S, 19.11; found: C, 61.35; H, 6.37; N, 2.35; S, 19.07.

*Synthesis of P2ClBT-DT*: Using the same procedure described above, a mixture of **6** and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene was used to polymerize, resulting in a dark purple powder. Isolated yield = 75%.  $M_n = 44.2$  kDa, PDI = 2.62.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (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  $\text{C}_{62}\text{H}_{76}\text{Cl}_2\text{N}_2\text{S}_7\text{Si}_2$ : C, 62.01; H, 6.38; N, 2.33; S, 18.69; found: C, 61.97; H, 6.41; N, 2.31; S, 18.70.

*Synthesis of P2ClBT-TVT:* Using the same procedure described above, a mixture of **6** and (*E*)-1,2-bis(5-trimethylstannyl)thiophen-2-yl)ethene was used to polymerize, resulting in a dark purple powder. Isolated yield = 83%.  $M_n = 37.0$  kDa, PDI = 2.67.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.87–7.82 (br, 2H), 7.20–7.16 (br, 2H), 7.10–7.04 (br, 2H), 7.00–6.90 (br, 4H), 1.53–1.49 (br, 4H), 1.33–1.18 (br, 32H), 1.09–0.99 (br, 8H), 0.87–0.81 (br, 24H).

Anal. calcd. for  $\text{C}_{64}\text{H}_{78}\text{Cl}_2\text{N}_2\text{S}_7\text{Si}_2$ : C, 62.66; H, 6.41; N, 2.28; S, 18.30; found: C, 62.68; H, 6.44; N, 2.24; S, 18.25.

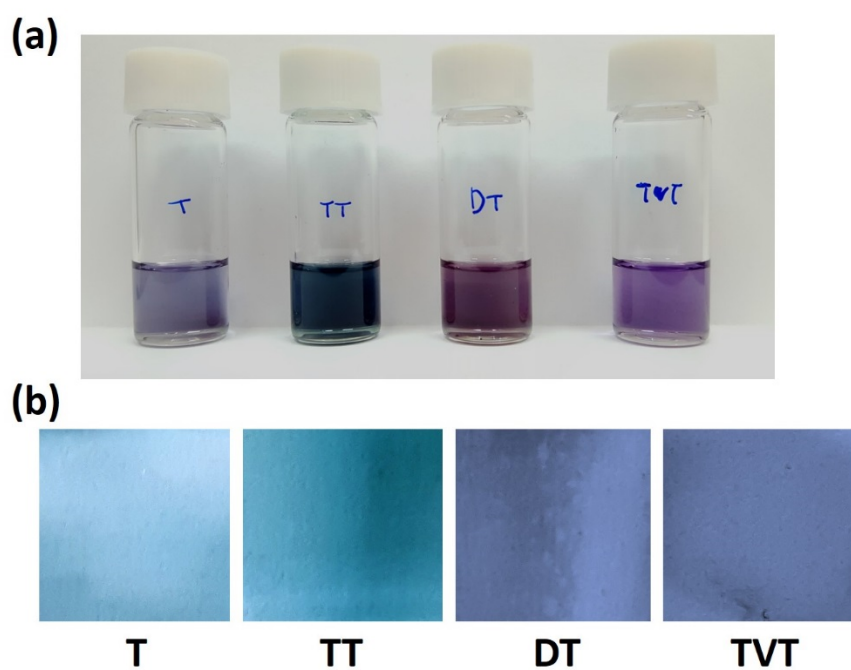
*Thin-Film Microstructure Analyses:* Samples for thin-film microstructure analyses were prepared by spin-coating the polymer solutions ( $5 \text{ mg mL}^{-1}$  in chlorobenzene at 2000 rpm for 60 s) onto  $\text{SiO}_2/\text{Si}$  substrates. An Agilent 5500 scanning probe microscope with a Nanoscope 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 ( $E_k = 11.6 \text{ keV}$  and  $\lambda = 1.069 \text{ \AA}$ ). The incidence angle of the X-rays was adjusted to  $0.12^\circ$ , 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 were fabricated using top-gate/bottom-contact geometry (TG/BC). Using a conventional photolithography method, source and drain contact electrodes (13 nm Au/ 3 nm Ni) were patterned onto glass substrates by thermal-evaporation deposition with a channel length of  $10 \mu\text{m}$  and channel width of  $1000 \mu\text{m}$ . The glass substrates were then cleaned using deionized water, acetone, and isopropanol for 10 min each in a sonication bath. Chlorinated polymer solutions in  $5 \text{ mg mL}^{-1}$  chlorobenzene (from

Sigma Aldrich) were spin-coated at 2000 rpm for 60 s and then thermally annealed at different temperatures (150 and 200 °C) for 30 min. After cooling, PMMA (Sigma Aldrich,  $M_n = 120$  kDa,  $C_i = 6.20$  nF cm<sup>-2</sup>) film from 80 mg mL<sup>-1</sup> solution in *n*-butyl acetate was deposited to act as a gate dielectric at 2000 rpm for 60 s and then baked at 80 °C for 2 h in a N<sub>2</sub>-purged glove box. Completion of the OFET devices was achieved by depositing 50 nm of Al to function as a gate electrode via thermal evaporation using a shadow mask. The devices were characterized through a Keithley 4200 parameter analyzer in a nitrogen filled probe station.

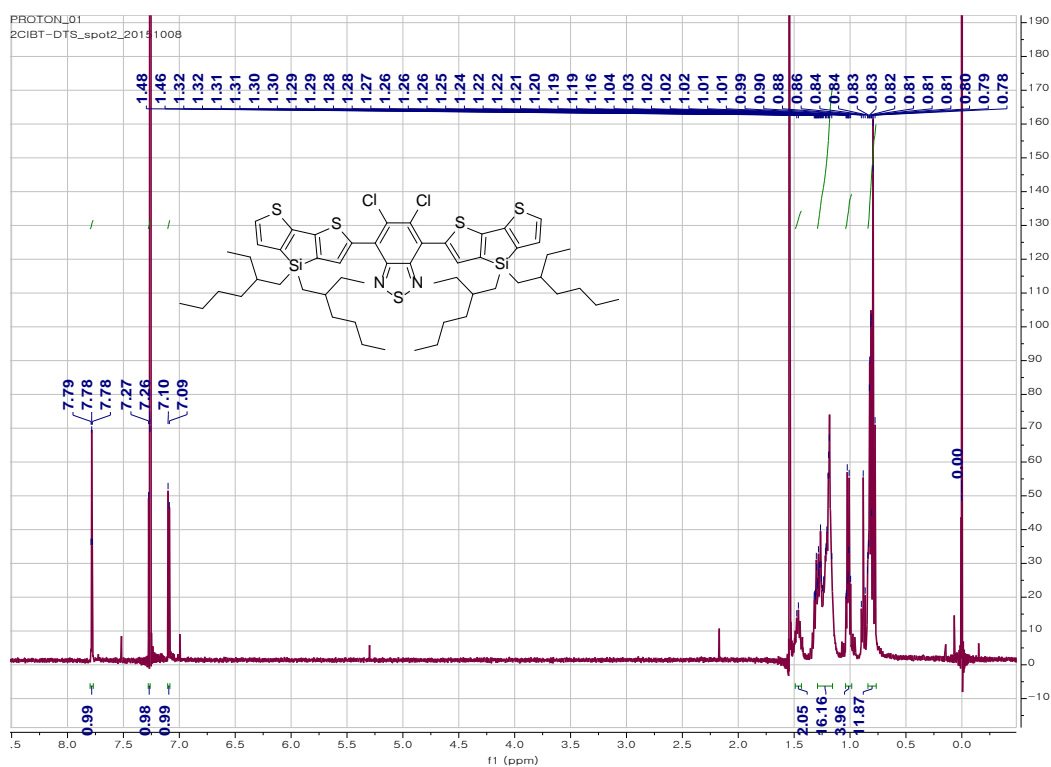
**Table S1.** Calculated dipole moments and energy levels of the BT units by DFT.

	Vector			Dipole Moment [D]	$E_{\text{HOMO}}^{\text{DFT}}$ [eV]	$E_{\text{LUMO}}^{\text{DFT}}$ [eV]
	x	y	z			
<b>BT</b>	-0.0003	-2.89	0.00	2.8900	-6.67	-2.78
<b>1FBT</b>	-0.9254	1.2275	0.0007	1.5372	-6.93	-3.02
<b>1CIBT</b>	0.5145	1.2314	0.0006	1.3346	-6.98	-3.11
<b>2FBT</b>	0.0006	-0.5472	0.00	0.5472	-7.21	-3.23
<b>2CIBT</b>	-0.0006	0.6341	0.00	0.6341	-7.16	-3.37

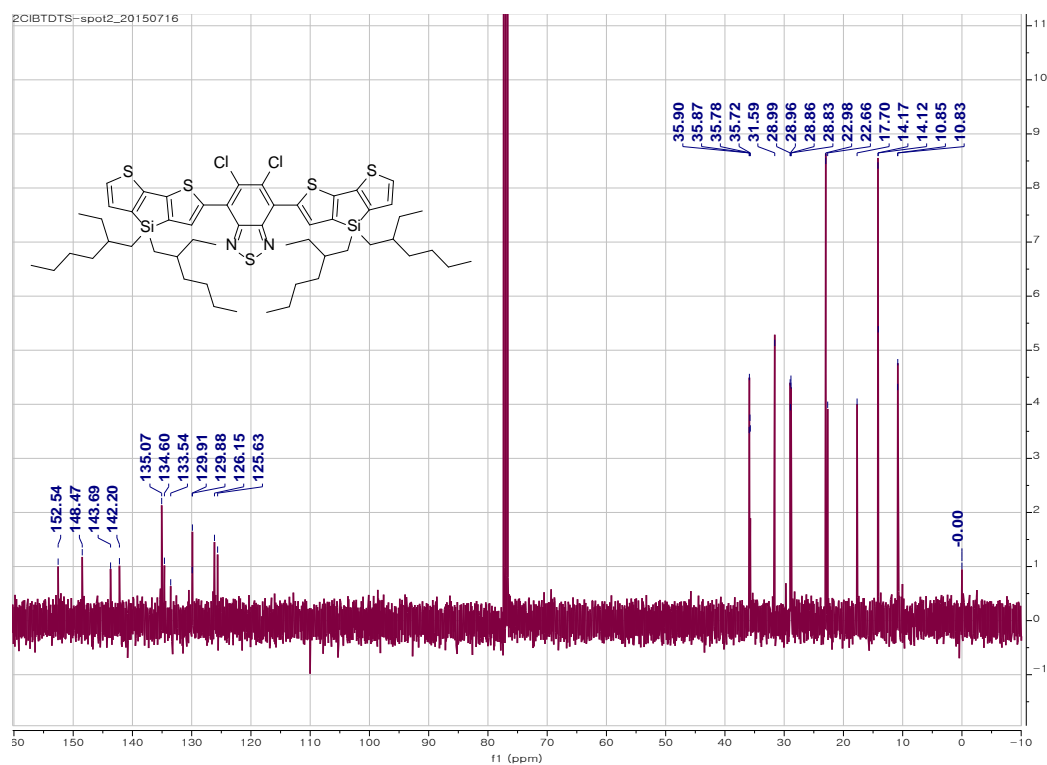


**Figure S1.** Visual images of (a) the polymer solution and (b) solid states.

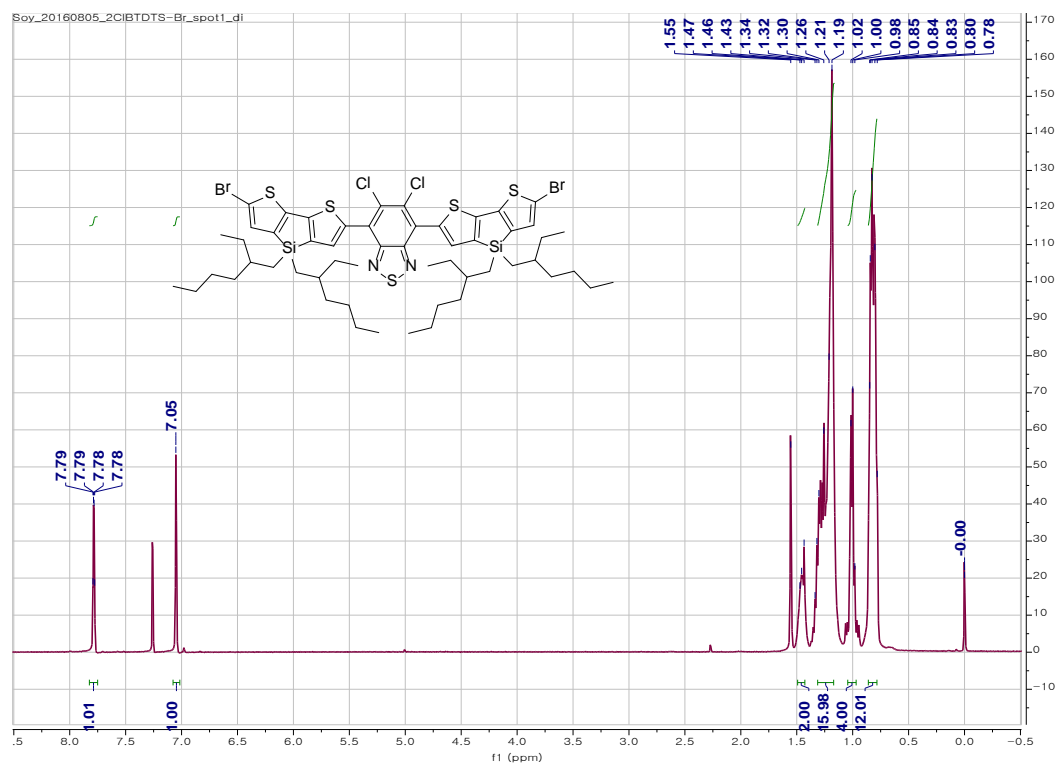




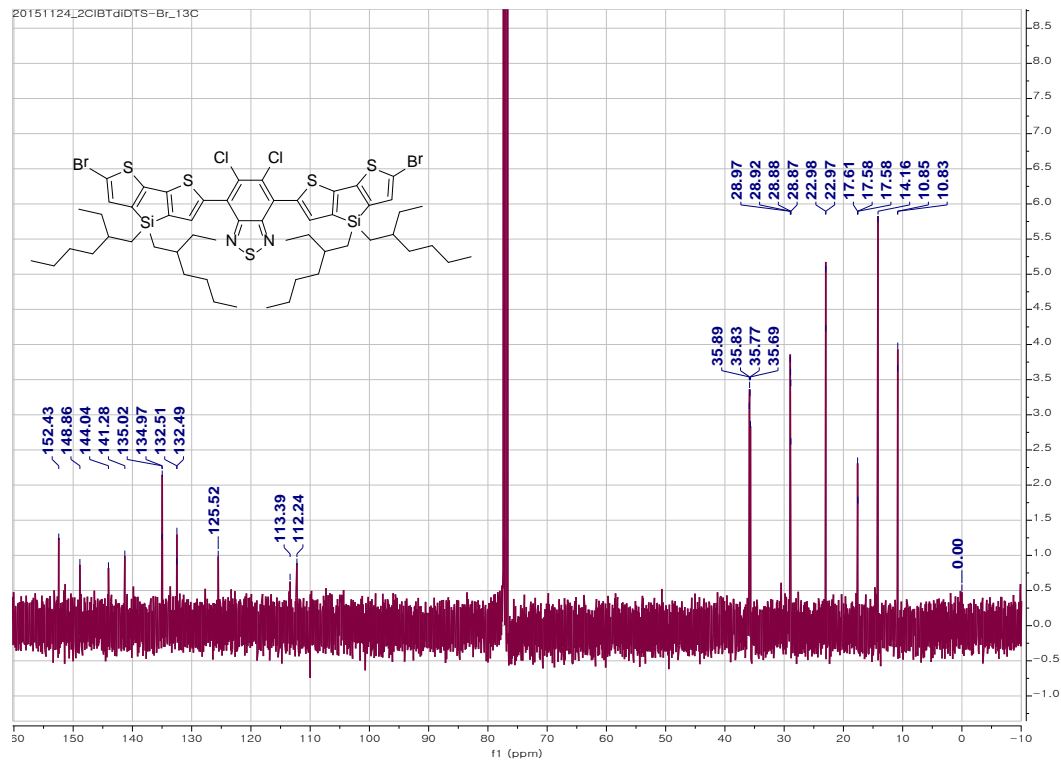
**Figure S2.** The  $^1\text{H}$  NMR spectroscopy for **5**.



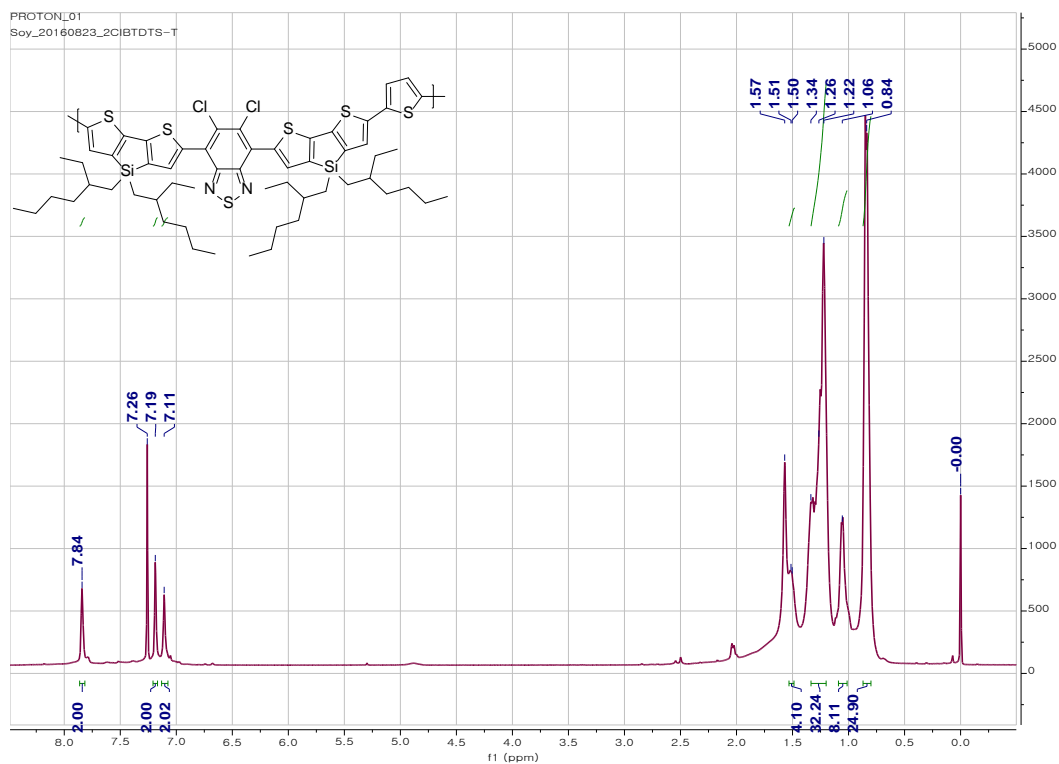
**Figure S3.** The  $^{13}\text{C}$  NMR spectroscopy for **5**.



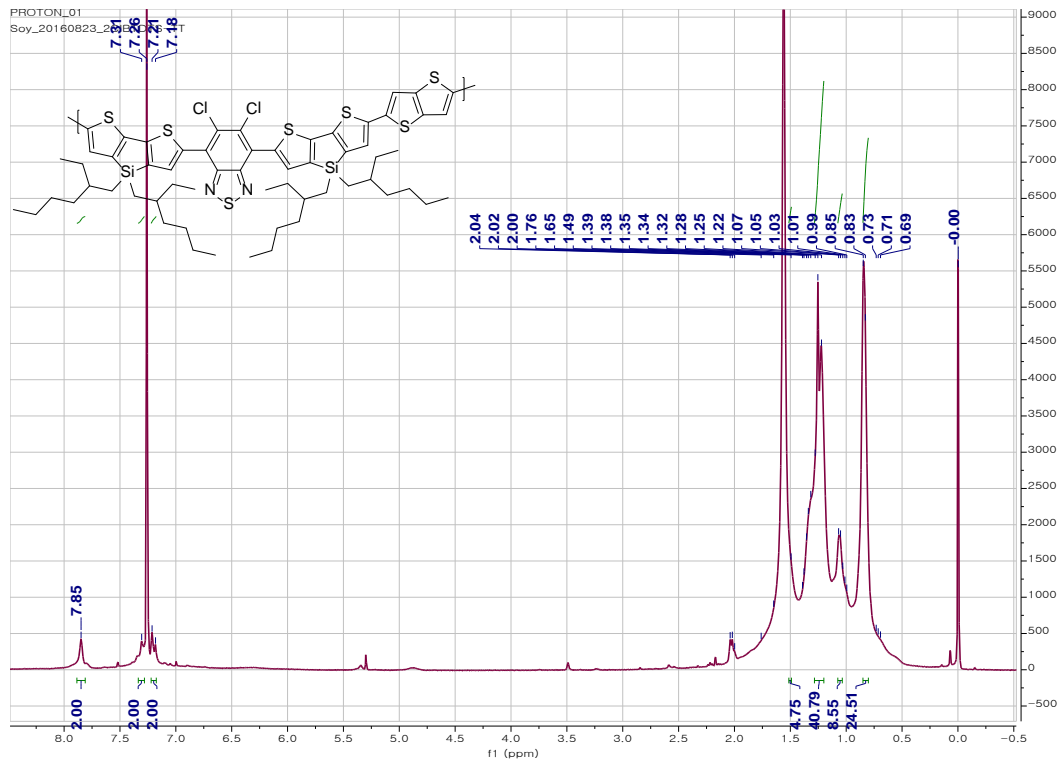
**Figure S4.** The  $^1\text{H}$  NMR spectroscopy for 6.



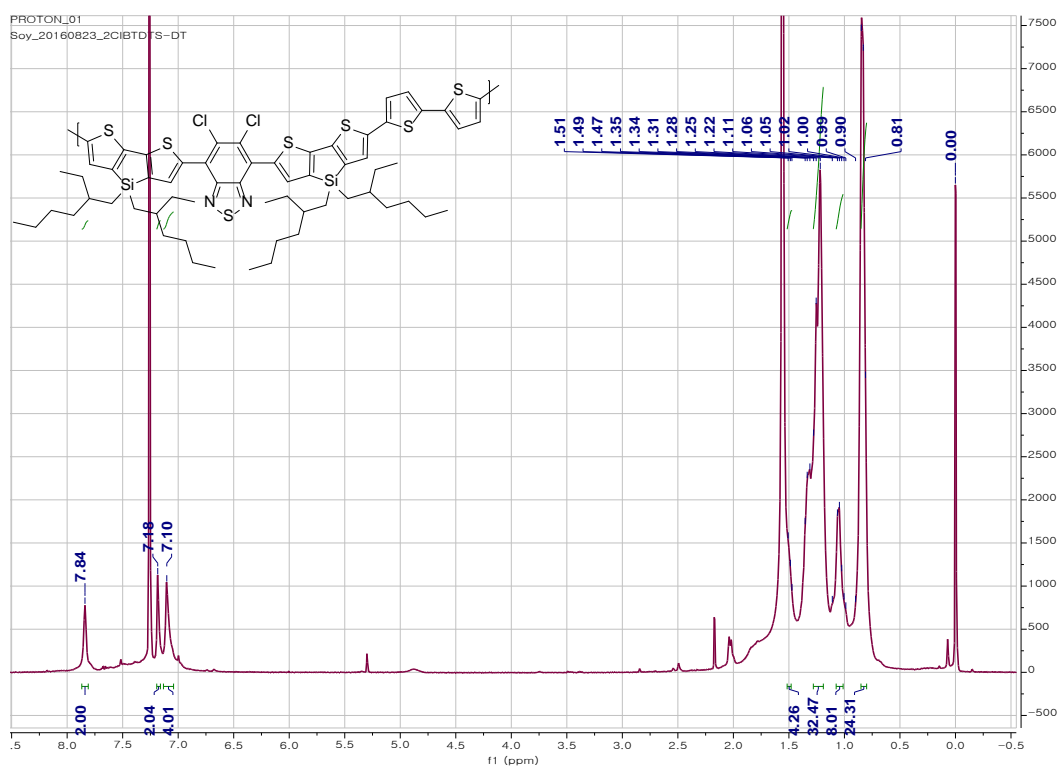
**Figure S5.** The  $^{13}\text{C}$  NMR spectroscopy for 6.



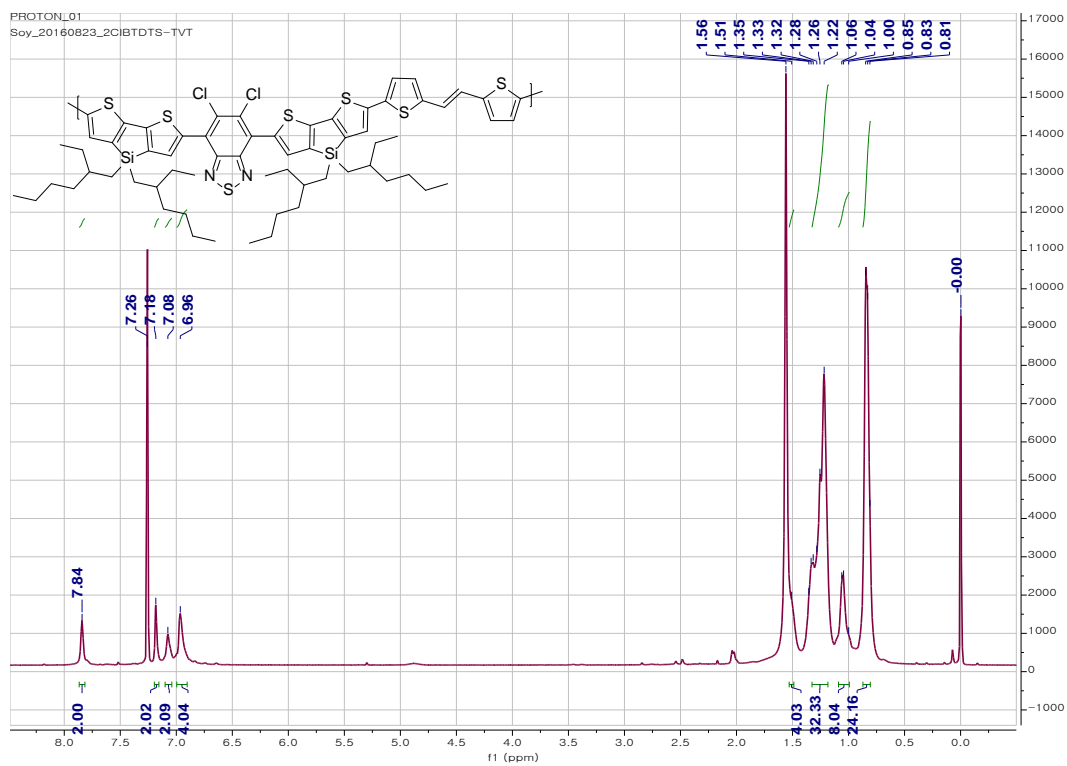
**Figure S6.** The  $^1\text{H}$  NMR spectroscopy for **P2CIBT-T**.



**Figure S7.** The  $^1\text{H}$  NMR spectroscopy for **P2CIBT-TT**.



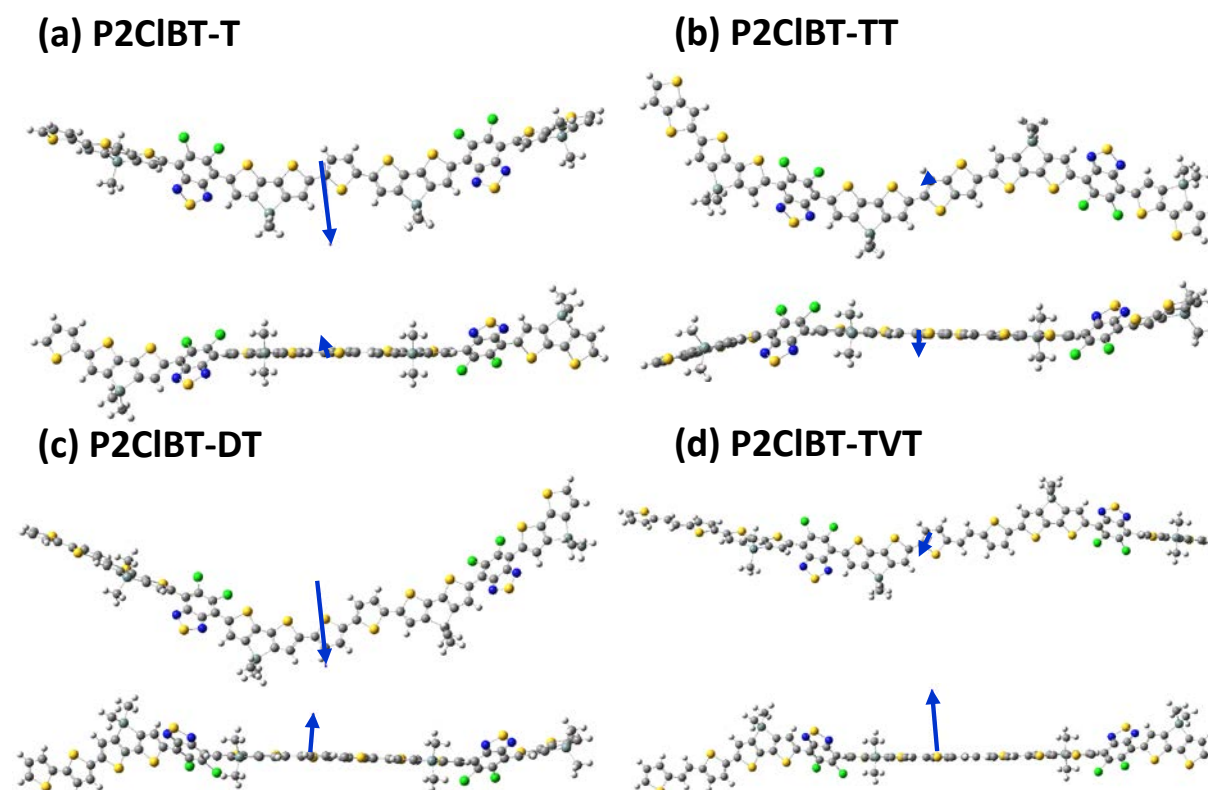
**Figure S8.** The  $^1\text{H}$  NMR spectroscopy for **P2CIBT-DT**.



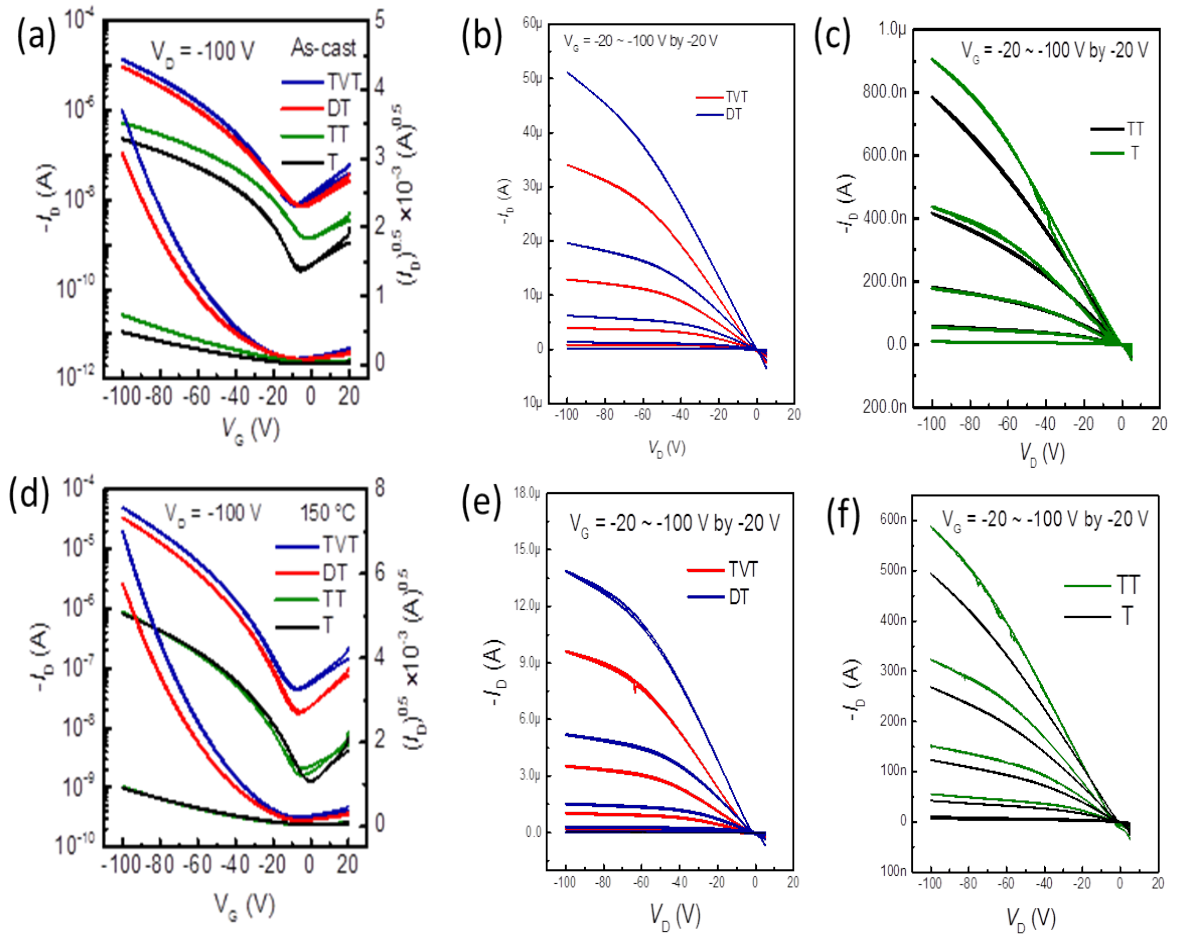
**Figure S9.** The  $^1\text{H}$  NMR spectroscopy for **P2CIBT-TVT**.

**Table S2.** Calculated dipole moments and energy levels of the dimer units of the 2ClBT-based polymers by DFT.

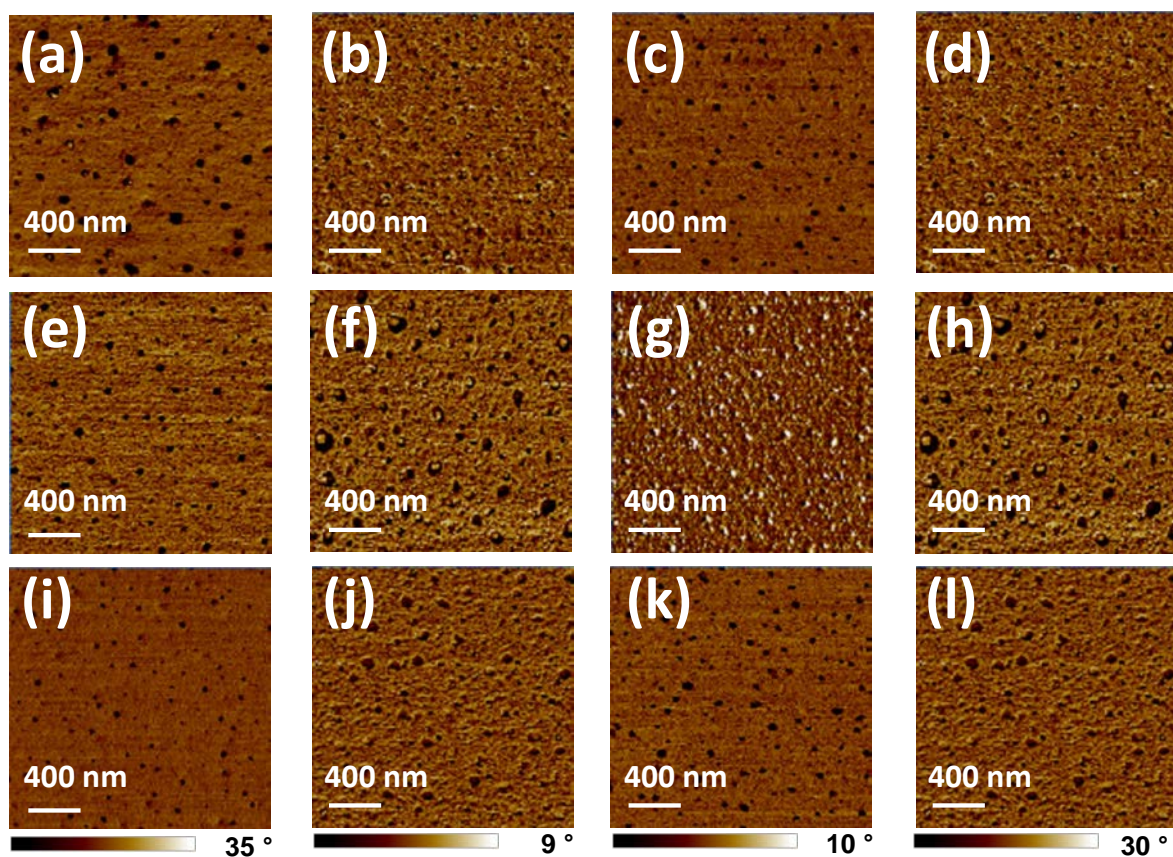
	Vector			Dipole Moment [D]	$E_{\text{HOMO}}^{\text{DFT}}$ [eV]	$E_{\text{LUMO}}^{\text{DFT}}$ [eV]
	x	y	z			
P2ClBT-T	0.3119	6.7936	-1.5863	6.9833	-4.79	-3.21
P2ClBT-TT	-0.0972	0.1342	-0.6264	0.6480	-4.79	-3.24
P2ClBT-DT	-1.0182	-8.5537	-3.2775	9.2166	-4.74	-3.21
P2ClBT-TVT	0.3911	-1.6707	-6.2799	6.5101	-4.70	-3.20



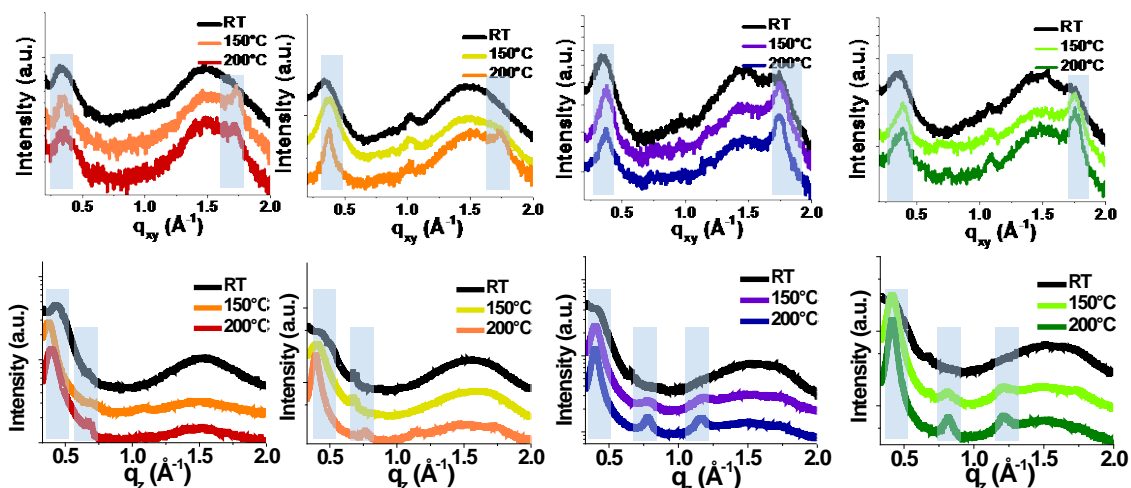
**Figure S10.** Visualized dipole moments of the dimer units of the polymers from the top view (up) and the side view (down) from the DFT calculation data.



**Figure S11.** The transfer (a) and output (b,c) characteristics of the 2ClBT-based polymer OFET devices at 150 °C, and its transfer (d) and output (e,f) characteristics as spun.



**Figure S12.** The AFM phase images of the spin-coated 2ClBT-based polymer films at three different annealing temperatures: P2ClBT-T (a,e,i), P2ClBT-TT (b,f,j), P2ClBT-DT (c,g,k), and P2ClBT-TVT (d,h,l) at three different annealing temperatures: (a-d) pristine films, (e-h) annealed films at 150 °C, and (i-l) annealed films at 200 °C.



**Figure S13.** The 1D-GIXD profiles of the 2CIBT-based polymer films according to annealing temperatures: (a-d) in-plane profiles of P2CIBT-T, P2CIBT-TT, P2CIBT-DT and P2CIBT-TVT, and (e-h) out-of-plane profiles of the polymers in the same order.

**Table S3.** Crystallographic parameters of 2CIBT-based polymer films<sup>a</sup>.

	T <sup>b</sup> [°C]	Lamellar Spacing			$\pi$ - $\pi$ stacking		
		$q_{z(100)}$ [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]
P2CIBT-T	Pristine	0.428	14.69	70.75	-	-	-
	150	0.373	16.83	153.08	1.727	3.64	117.48
	200	0.398	15.78	147.27	1.704	3.69	35.26
P2CIBT-TT	Pristine	0.394	15.96	48.81	-	-	-
	150	0.399	15.74	91.17	-	-	-
	200	0.394	15.95	240.66	1.732	3.63	92.37
P2CIBT-DT	Pristine	0.388	16.20	69.20	-	-	-
	150	0.400	15.69	142.74	1.743	3.60	78.18
	200	0.399	15.76	227.68	1.741	3.61	116.35
P2CIBT-TVT	Pristine	0.389	16.23	60.85	-	-	-
	150	0.414	15.17	153.12	1.743	3.60	86.87
	200	0.415	15.13	220.25	1.748	3.59	98.12

<sup>a</sup>The polymer films were prepared by drop-casting of 5mg mL<sup>-1</sup> solutions and their parameters were calculated from GIXD profiles.

<sup>b</sup>The influence of thermal annealing was investigated.



## References

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