

## Sequence-Controlled Alternating Block Poly(3-hexylchalcogenophenes): Synthesis, Structural Characterization, Molecular Properties, and Transistors for Bromine Detection

Kuo-Hsiu Huang<sup>a</sup>, Huai-Hsuan Liu<sup>a</sup>, Kuang-Yi Cheng<sup>a</sup>, Chia-Lin Tsai<sup>a</sup> and Yen-Ju Cheng<sup>\*ab</sup>

<sup>a</sup>Department of Applied Chemistry, National Yang Ming Chiao Tung University, 1001 University Road, Hsinchu, 30010, Taiwan

<sup>b</sup>Center for Emergent Functional Matter Science, National Chiao Tung University, 1001 University Road, Hsinchu, 30010, Taiwan

E-mail: [yjcheng@nycu.edu.tw](mailto:yjcheng@nycu.edu.tw)

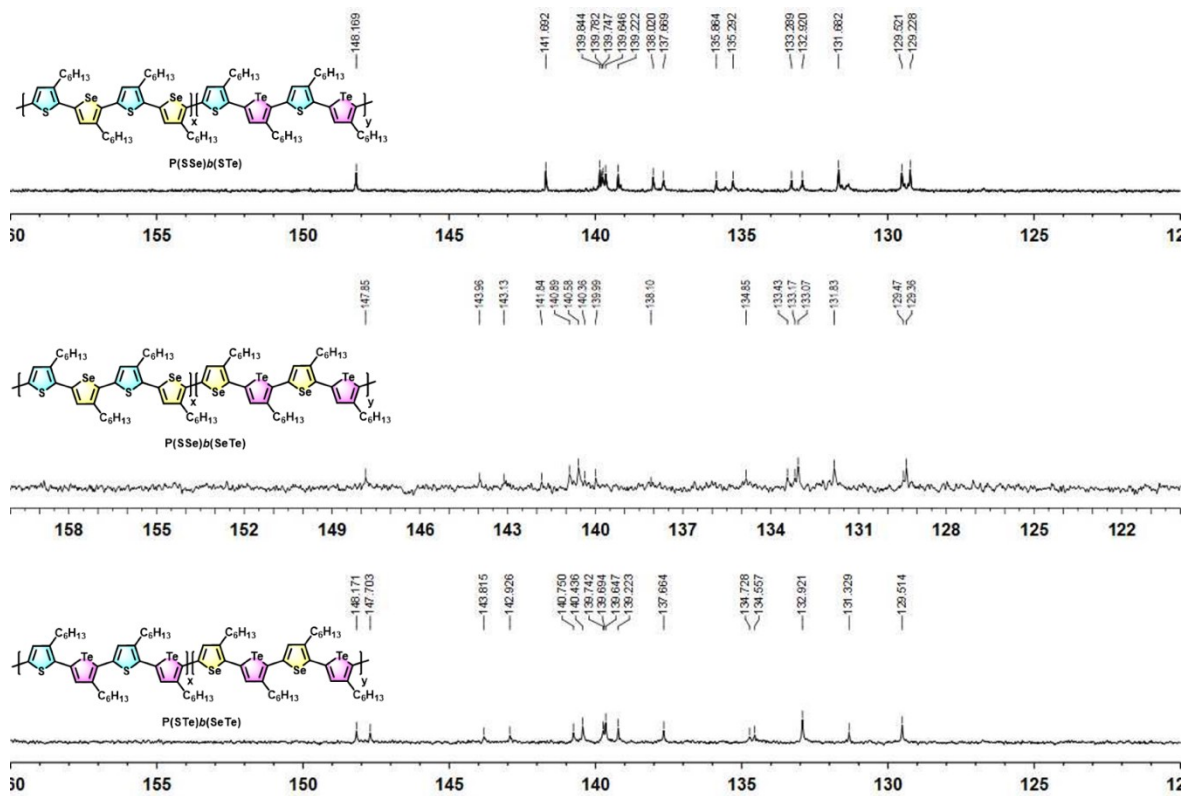
### Experimental Details

**General measurement and characterization.** UV data were collected by the HITACHI U-4100 spectrophotometer. The electrochemical cyclic voltammetry (CV) was conducted on a CH Instruments Model 611D. A carbon glass coated with a thin polymer film was used as the working electrode and Ag/Ag<sup>+</sup> electrode as the reference electrode, while 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) in acetonitrile was the electrolyte. CV curves were calibrated using ferrocene as the standard, whose HOMO is set at -4.8 eV with respect to zero vacuum level. The HOMO energy levels were obtained from the equation  $\text{HOMO} = - (E_{\text{ox}}^{\text{onset}} - E_{(\text{ferrocene})}^{\text{onset}} + 4.8) \text{ eV}$ . The LUMO levels were obtained from the equation  $\text{LUMO} = - (E_{\text{red}}^{\text{onset}} - E_{(\text{ferrocene})}^{\text{onset}} + 4.8) \text{ eV}$ . High resolution mass spectra (HRMS) were obtained on a JEOL AccuTOF GCX (EI). Polymer molecular weights were determined with HLC-8321GPC/HT (1,2,4-trichlorobenzene, 140 °C, 1 mL/min flow rate) using Tosoh Bioscience LLC TSKgel GMHHR-HHT2 mixed-bed columns and narrow molecular weight distribution polystyrene standards. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were measured using Varian 600 MHz instrument spectrometer and obtained in deuterated

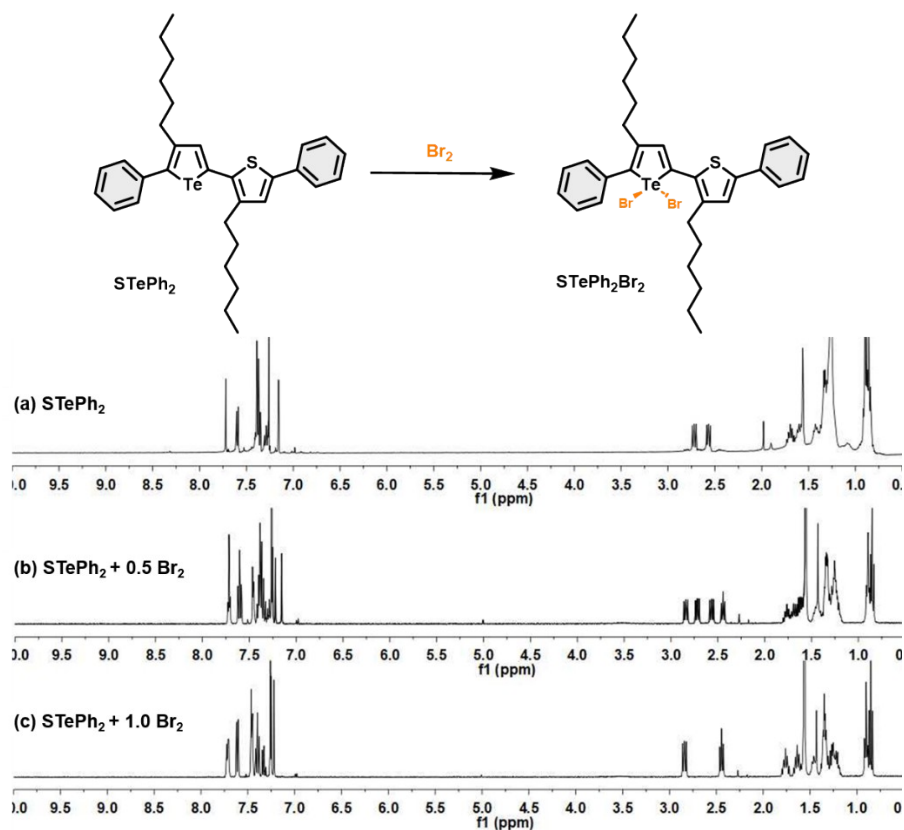
chloroform ( $\text{CDCl}_3$ ) with 0.5 wt% TMS as internal reference unless otherwise stated, and chemical shifts ( $\delta$ ) are reported in parts per million. GIWAXS measurements were performed at the BL23A end-station of the National Synchrotron Radiation Research Center (NSRRC), Taiwan.

**Films fabrication for GIWAXS.** The wafers with thermal grown 300 nm  $\text{SiO}_2$  were ultrasonically cleaned in sequential detergent, water, acetone, isopropyl alcohol and dried under nitrogen purging, followed by UV/Ozone treatment for 20 min. The polychalcogenophene thin films were prepared by spin-coating of 20 mg/mL *o*-DCB solutions on  $1.4 \times 1.4$  cm silicon wafers under a dry nitrogen environment in a glovebox. The post-annealing for films of polychalcogenophenes was carried out in the glovebox to prevent further oxidation.

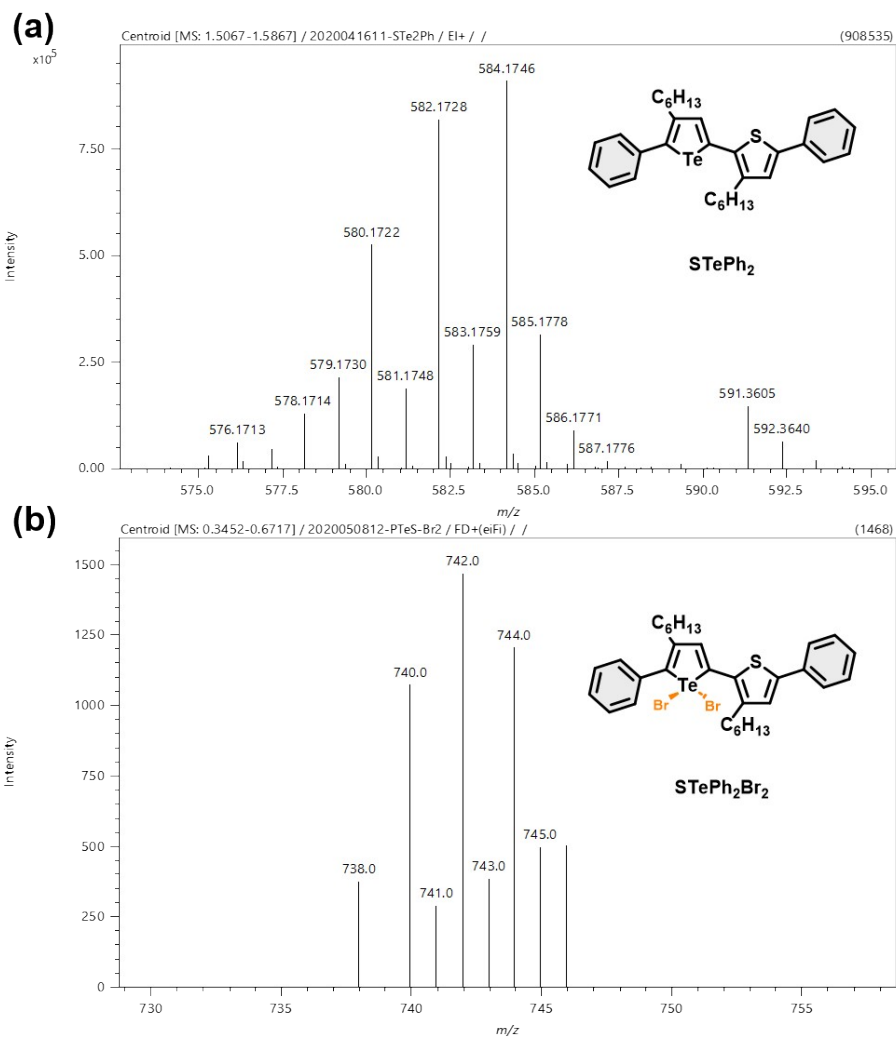
**OFET fabrication.** A n-type heavily doped Si wafer with a  $\text{SiO}_2$  layer of 300 nm and a capacitance of  $11.5 \text{ nF cm}^{-2}$  as the gate electrode and dielectric layer was ultrasonically cleaned sequentially in detergent, water and isopropyl alcohol. *n*-Octadecyltrichlorosilane (ODTS) was used as a self-assembled monolayer. The polychalcogenophene samples were prepared from 20 mg/mL solutions in chloroform and were spin-coated on ODTS-treated silicon wafers. The gold source and drain electrodes (40 nm in thickness) were then deposited on the organic layer by vacuum evaporation through a shadow mask, affording a bottom-gate, top-contact device configuration. OFET measurement was carried out at room temperature under a nitrogen atmosphere using an Agilent Technologies B1500A instrument. The mobility calculation was based on the equation  $I_{\text{DS}} = (W/2L)\mu C_i(V_g - V_t)^2$  in the saturation regime, where  $I_{\text{DS}}$  is the drain–source current,  $W$  is the channel width (1 mm),  $L$  is the channel length (100  $\mu\text{m}$ ),  $\mu$  is the field-effect mobility,  $C_i$  is the capacitance per unit area of the dielectric layer,  $V_g$  is the gate voltage, and  $V_t$  is the threshold voltage.



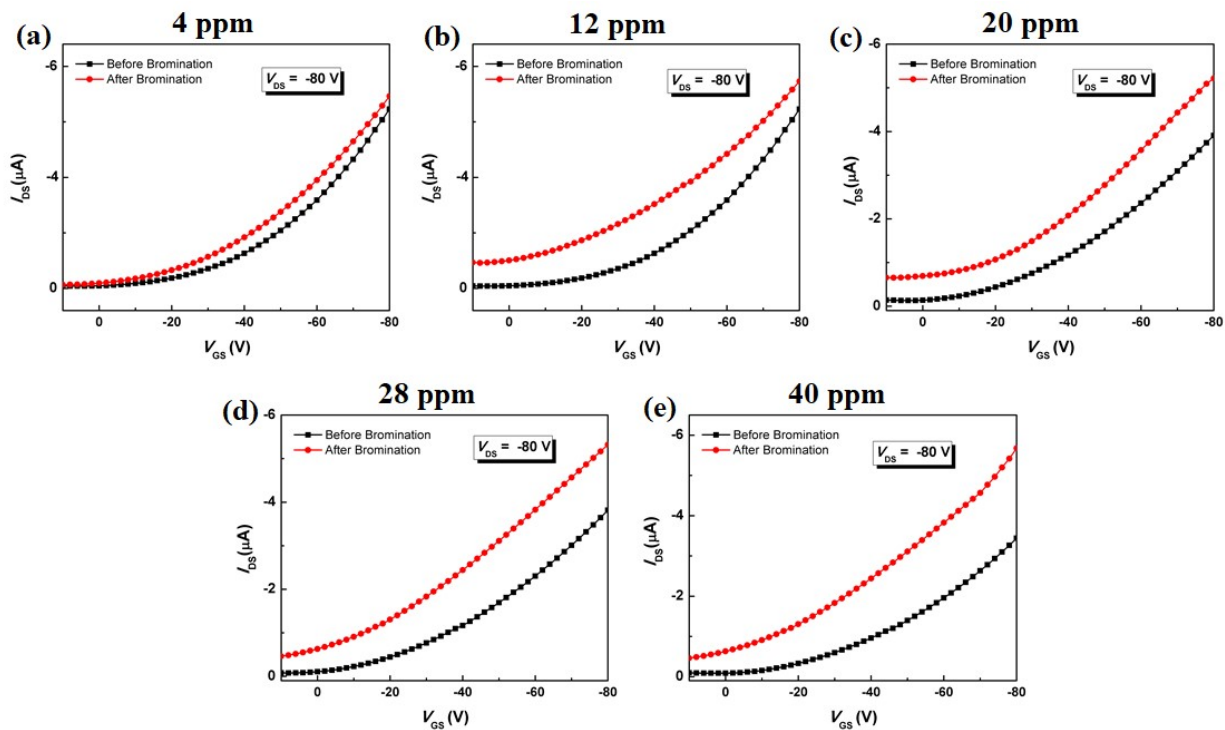
**Figure S1.**  $^{13}\text{C}$ -NMR spectra of **P(SSe)b(STe)**, **P(SSe)b(SeTe)** and **P(STe)b(SeTe)** in *d*-chloroform at temperature of 50 °C. 16 peaks in the aromatic region are observed for each polymer.



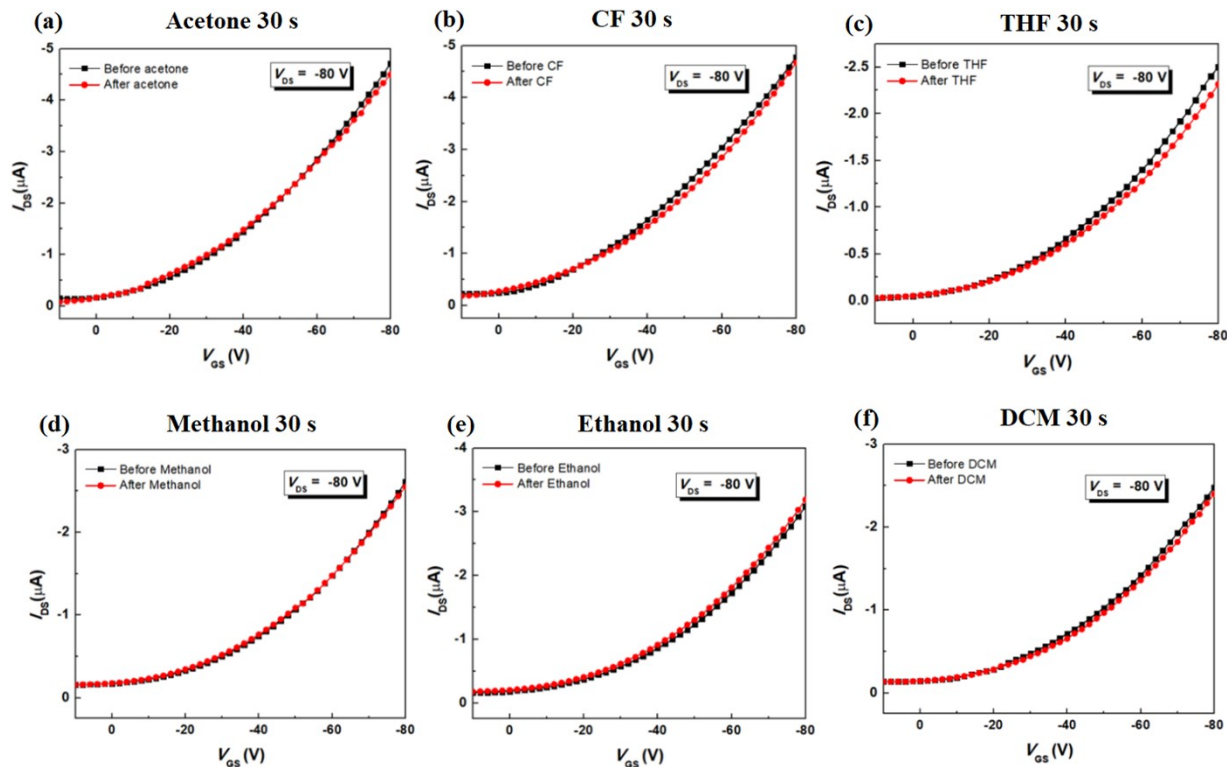
**Figure S2.**  $^1\text{H}$  NMR spectra of (a)  $\text{STePh}_2$ , (b)  $\text{STePh}_2$  with 0.5 eq. of  $\text{Br}_2$  and (c)  $\text{STePh}_2$  with 1 eq. of  $\text{Br}_2$  in *d*-chloroform.



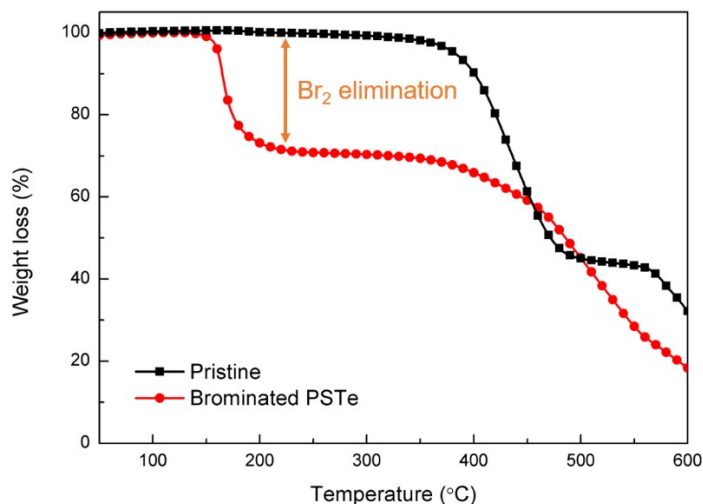
**Figure S3.** Mass spectra of (a) **STePh<sub>2</sub>** and (b) **STePh<sub>2</sub>Br<sub>2</sub>** showing the molecular weight of 584 and 742 m/z, respectively.



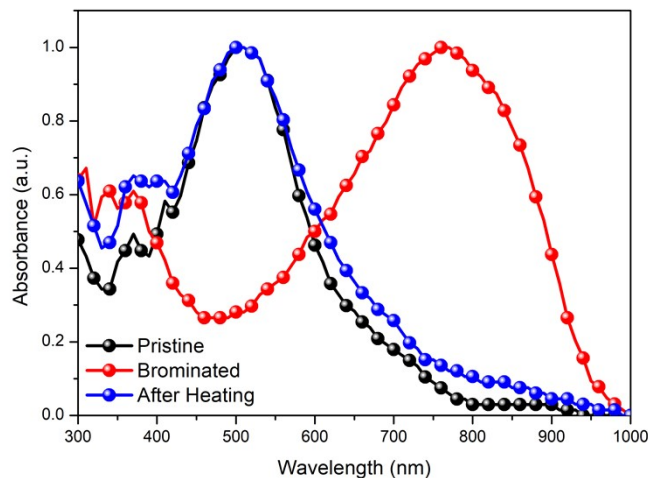
**Figure S4.** The  $I_{DS}/V_{GS}$  curves of the PSTe-based OFETs ( $V_{DS} = -80\text{ V}$ ) before and after exposure to different concentration of  $\text{Br}_2$ .



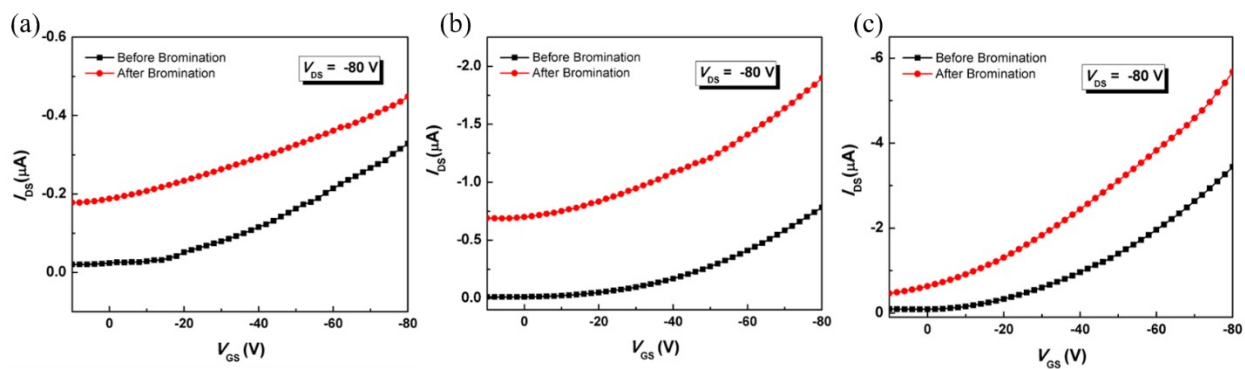
**Figure S5.** The  $I_{DS}/V_{GS}$  curves of the **PSTe**-based OFETs ( $V_{DS} = -80$  V) before and after exposure to different organic solvent vapors for 30 seconds (a) acetone, (b) chloroform, (c) THF, (d) methanol, (e) ethanol, and (f) dichloromethane.



**Figure S6.** Thermogravimetric analysis of **PSTe** ( $T_d = 382$  °C) and **PSTeBr<sub>2</sub>** (first  $T_d = 150$  °C, second  $T_d = 382$  °C) at a ramping rate of  $10$  °C  $\text{min}^{-1}$ . **PSTeBr<sub>2</sub>** shows a 27% weight loss at 150 °C, which is attributed to  $\text{Br}_2$  elimination.



**Figure S7.** UV-vis absorption spectra of the **PSTe** and brominated **PSTeBr<sub>2</sub>** thin films. After thermal annealing at 150 °C for 10 min, **PSTeBr<sub>2</sub>** returns back to the original profile of **PSTe**.

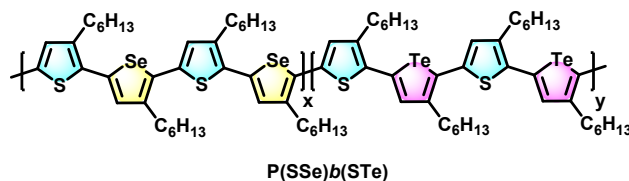


**Figure S8.** The  $I_{DS}/V_{GS}$  curves of the **P(SSe)*b*(STe)**, **P(SSe)*b*(STe)**, and **P(STe)*b*(SeTe)**-based OFETs ( $V_{DS} = -80$  V) before and after exposure to  $\text{Br}_2$  of 4 ppm.

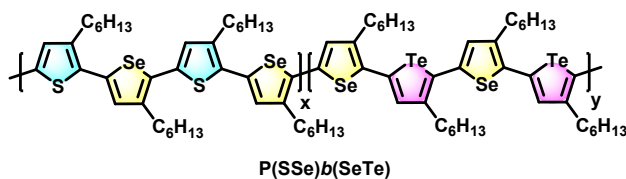
## Synthetic Procedures

All chemicals were purchased from Aldrich, Acros or TCI and used as received unless specified.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were obtained in deuterium-substituted chloroform by Varian 600 MHz spectrometers and 0.5 wt% TMS also used as reference. Compound **SSeI<sub>2</sub>**, compound **STeI<sub>2</sub>**, and compound **SeTeI<sub>2</sub>** were synthesized as reported.

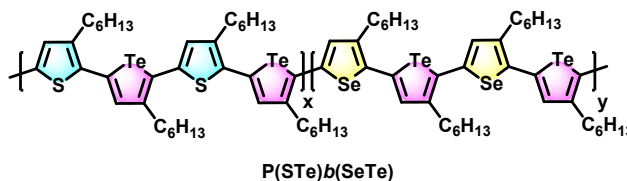




**Synthesis of poly(3-hexylthiophene-*alt*-3-hexylselenophene-*block*-3-hexylthiophene-*alt*-3-hexyltellurophene) (P(SSe)*b*(STe)).** To a solution of 1.3 M isopropylmagnesium chloride lithium chloride complex (60.8  $\mu$ L, 0.079 mmol) diluted by dried THF (3 mL) was added dropwise a solution of **SSeI<sub>2</sub>** (50 mg, 0.079 mmol) in dried THF (1 mL) in a glovebox. After Grignard metathesis was completed (monitored by thin layer chromatography), [1,3-bis(diphenylphosphino)propane]dichloronickel(II) (0.85 mg, 0.00158 mmol) was added. The reaction was stirred at room temperature for 30 min to form the first block polymer. At the same time, **STeI<sub>2</sub>** (53.9 mg, 0.079 mmol in 4 mL THF) was treated with 1.3 M isopropylmagnesium chloride lithium chloride complex (60.8  $\mu$ L, 0.079 mmol). The **MgSTeI<sub>2</sub>** solution was transferred to the above solution for the second block polymerization. The reaction was continued for another 2 h. After the solution was precipitated with 6 M HCl/MeOH solution and washed with methanol, a deep purple solid **P(SSe)*b*(STe)** was yielded. <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 7.65 (s, 1H), 7.19 (s, 1H), 6.93 (s, 1H), 6.83 (s, 1H), 2.78 (br, 6H), 2.67 (br, 2H), 1.70-1.71 (br, 8H), 1.25-1.44 (br, 24H), 0.92 (br, 12H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz,  $\delta$  ppm): 148.3, 141.8, 140.0, 139.92, 139.88, 139.78, 139.4, 138.2, 137.8, 136.0, 135.4, 133.4, 133.1, 131.8, 129.7, 129.4, 32.6, 31.9, 31.0, 30.83, 30.76, 29.8, 29.6, 29.5, 29.1, 22.8, 14.2.



**Synthesis of poly(3-hexylthiophene-*alt*-3-hexylselenophene-*block*-3-hexylselenophene-*alt*-3-hexyltellurophene) (P(SSe)*b*(SeTe)).** To a solution of 1.3 M isopropylmagnesium chloride lithium chloride complex (60.8  $\mu$ L, 0.079 mmol) diluted by dried THF (3 mL) was added dropwise a solution of SSeI<sub>2</sub> (50 mg, 0.079 mmol) in dried THF (1 mL) in a glovebox. After Grignard metathesis was completed (monitored by thin layer chromatography), [1,3-bis(diphenylphosphino)propane]dichloronickel(II) (0.85 mg, 0.00158 mmol) was added. The reaction was stirred at room temperature for 30 min to form the first block polymer. At the same time, SeTeI<sub>2</sub> (57.6 mg, 0.079 mmol in 4 mL THF) was treated with and 1.3 M isopropylmagnesium chloride lithium chloride complex (60.8  $\mu$ L, 0.079 mmol). The MgSeTeI<sub>2</sub> solution was transferred to the above solution for the second block polymerization. The reaction was continued for another 2 h. After the solution was precipitated with 6 M HCl/MeOH solution and washed with methanol, a deep purple solid P(SSe)*b*(SeTe) was yielded. <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 7.57 (s, 1H), 7.18 (s, 1H), 7.00 (s, 1H), 6.92 (s, 1H), 2.75 (br, 4H), 2.51-2.68 (br, 4H), 1.68-1.75 (br, 8H), 1.25-1.43 (br, 24H), 0.91 (br, 12H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz,  $\delta$  ppm): 147.9, 144.0, 143.1, 141.8, 140.9, 140.6, 140.4, 140.0, 138.1, 134.9, 133.4, 133.2, 133.1, 131.8, 129.5, 129.4, 32.6, 31.9, 31.0, 30.83, 30.76, 29.8, 29.6, 29.5, 29.1, 22.8, 14.2.



**Synthesis of poly(3-hexylthiophene-*alt*-3-hexyltellurophene-*block*-3-hexylselenophene-*alt*-3-hexyltellurophene) (P(STe)*b*(SeTe)).** To a solution of 1.3 M isopropylmagnesium chloride lithium chloride complex (60.8  $\mu$ L, 0.079 mmol) diluted by dried THF (3 mL) was added dropwise a solution of STeI<sub>2</sub> (53.9 mg, 0.079 mmol) in dried THF (1 mL) in a glovebox. After Grignard

metathesis was completed (monitored by thin layer chromatography), [1,3-bis(diphenylphosphino)propane]dichloronickel(II) (0.85 mg, 0.00158 mmol) was added. The reaction was stirred at room temperature for 30 min to form the first block. At the same time, **SeTeI<sub>2</sub>** (57.6 mg, 0.079 mmol) was treated with THF (4 mL) and 1.3 M isopropylmagnesium chloride lithium chloride complex (60.8  $\mu$ L, 0.079 mmol). The **MgSeTeI<sub>2</sub>** solution was transferred to the above solution for the second block polymerization. The reaction was continued for another 2 h. After solution was precipitated with 6 M HCl/MeOH solution and washed with methanol, a deep purple solid **P(STe)*b*(SeTe)** was yielded. <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 7.64 (s, 1H), 7.57 (s, 1H), 7.00 (s, 1H), 6.82 (s, 1H), 2.77-2.78 (br, 4H), 2.65-2.68 (br, 4H), 1.69 (br, 8H), 1.35-1.48 (br, 24H), 0.91-0.92 (br, 12H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz,  $\delta$  ppm): 148.3, 147.8, 144.0, 143.1, 140.9, 140.6, 139.9, 139.83, 139.78, 139.4, 137.8, 134.9, 134.7, 133.1, 131.5, 129.7, 32.6, 31.9, 31.04, 30.98, 30.8, 30.7, 29.9, 29.6, 29.5, 29.4, 22.8, 14.2.

# NMR spectra

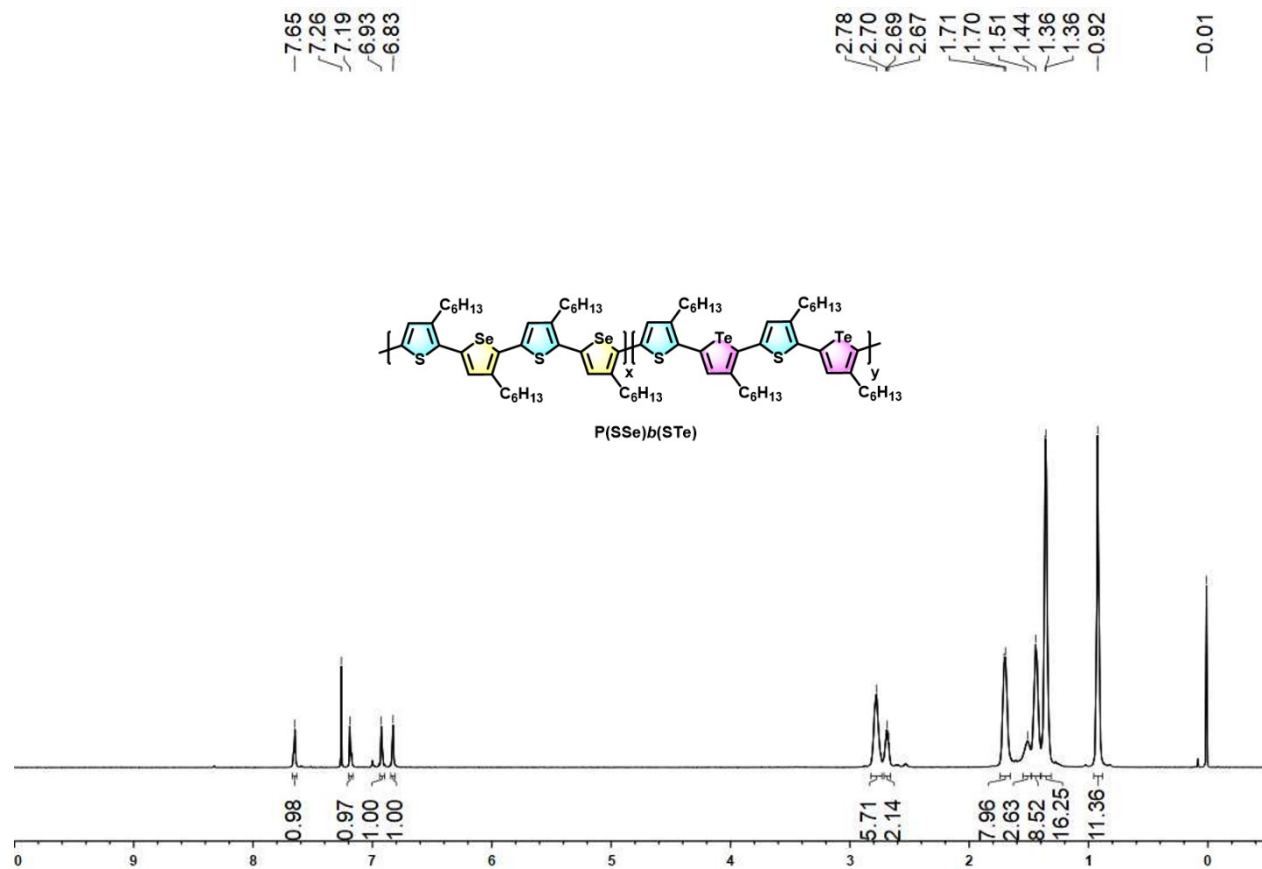
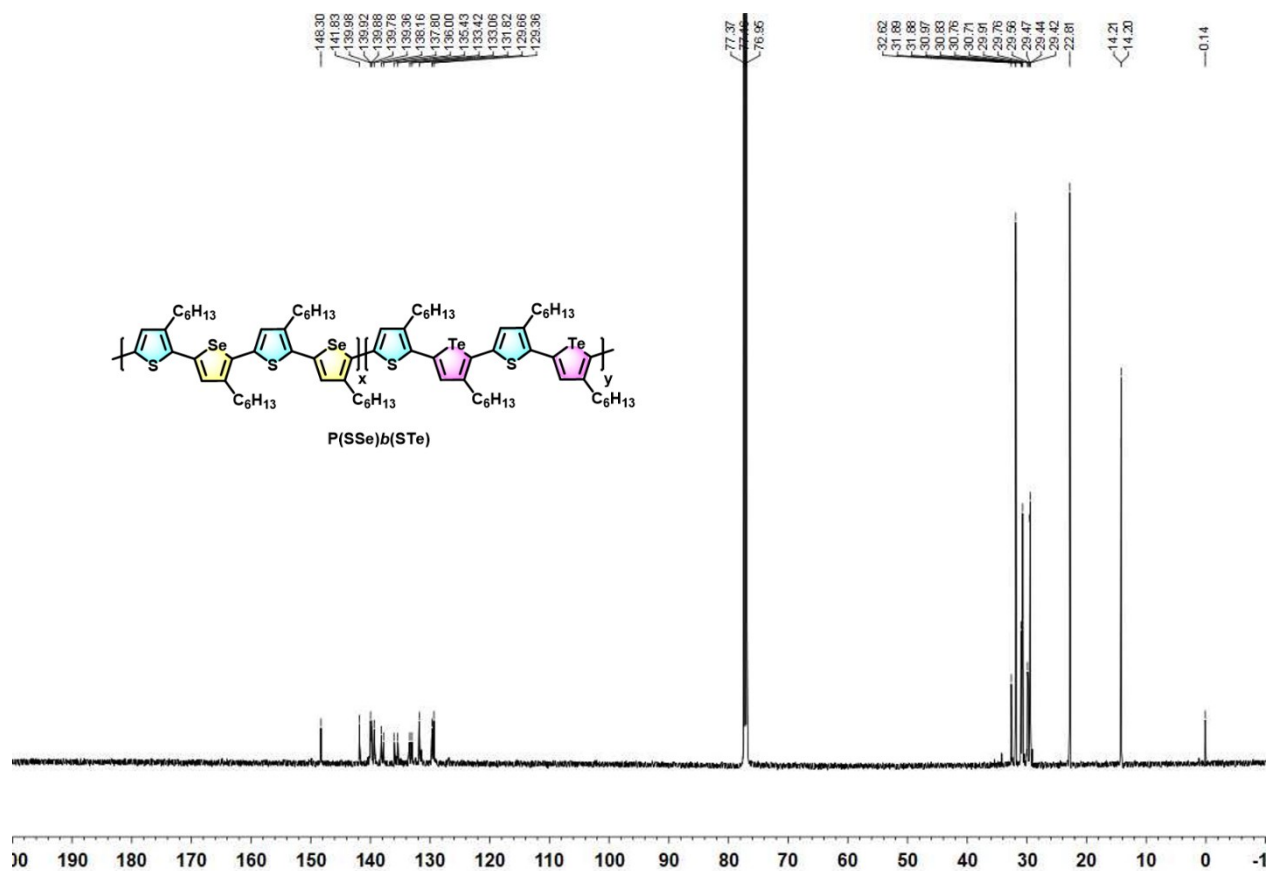
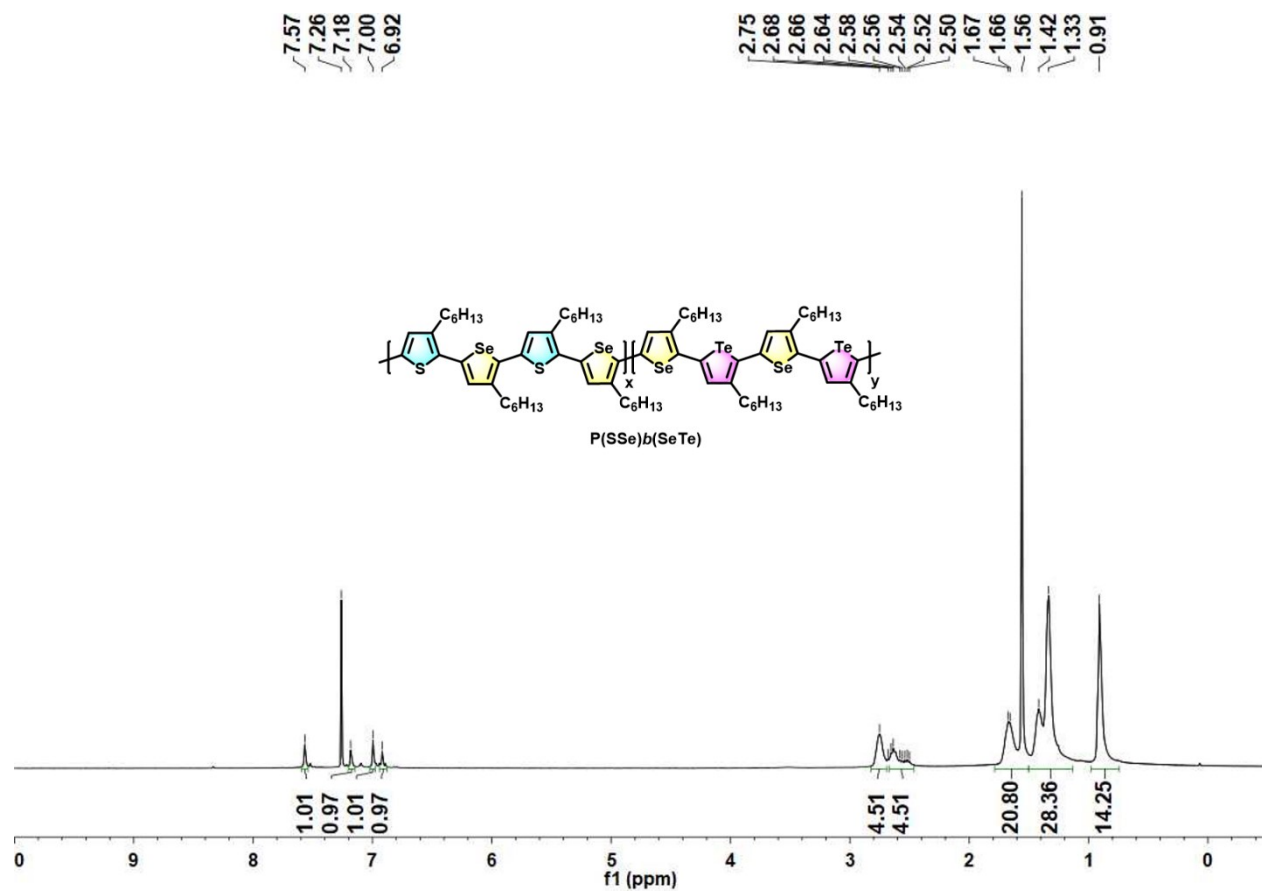


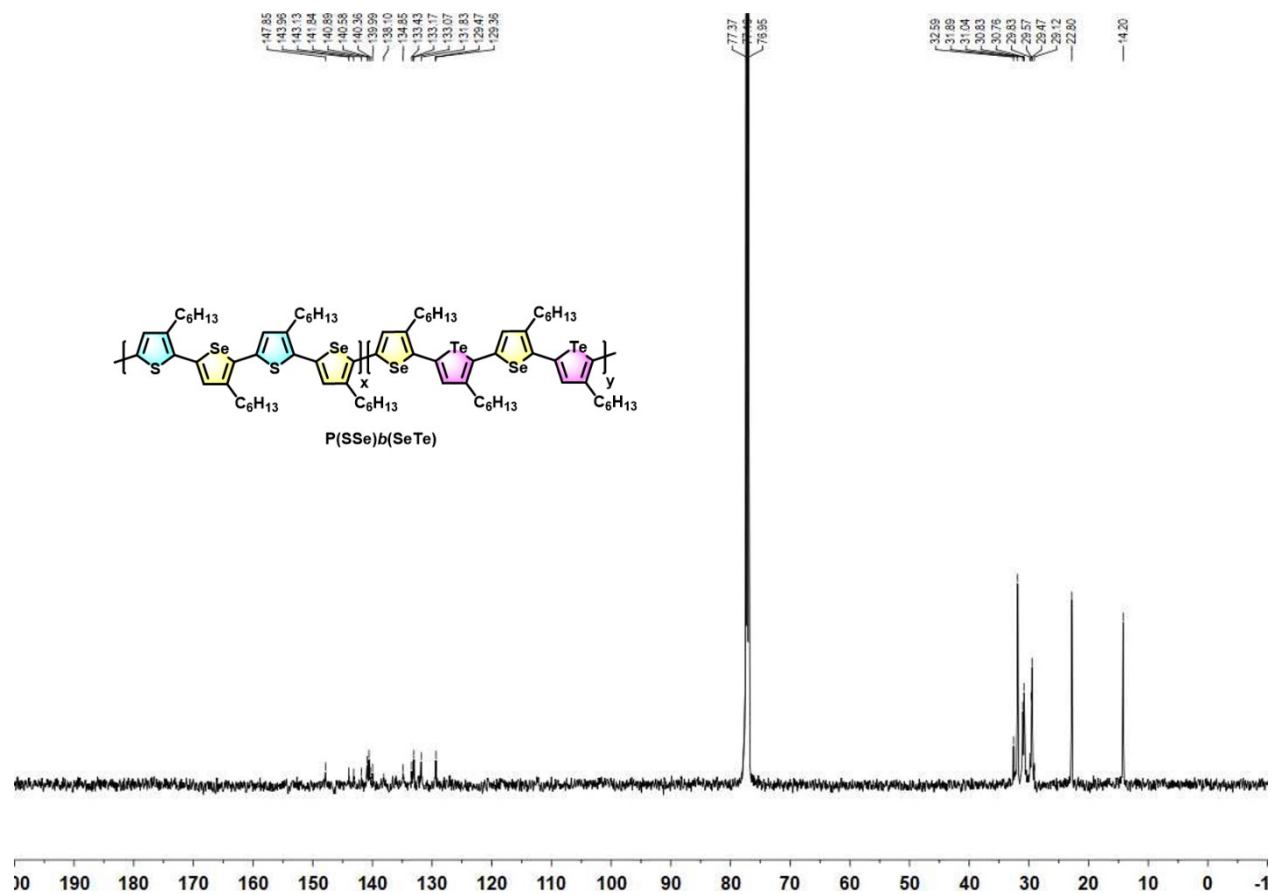
Figure S9. <sup>1</sup>H NMR spectrum of P(SSe)*b*(STe) in CDCl<sub>3</sub>.



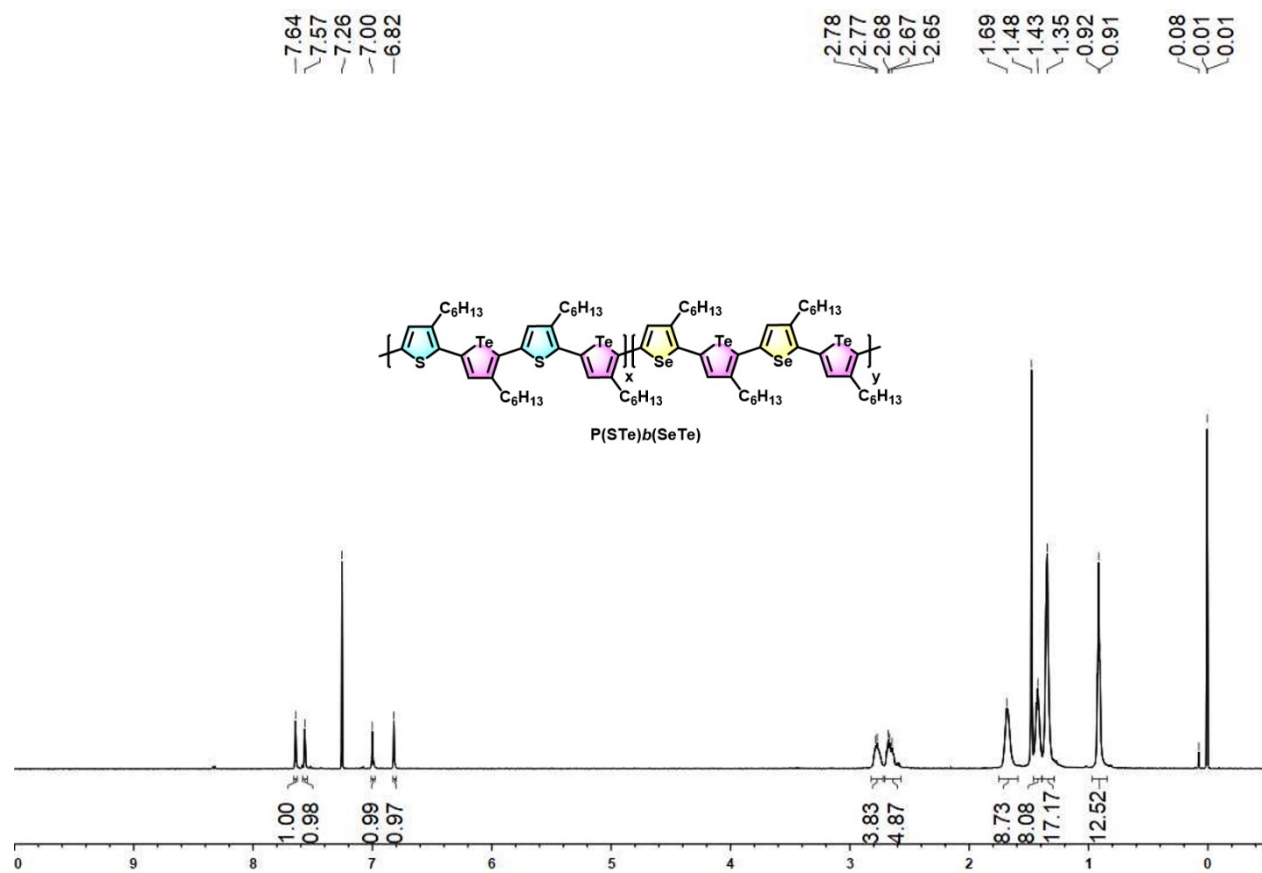
**Figure S10.**  $^{13}\text{C}$  NMR spectrum of  $\text{P}(\text{SSe})_x\text{b}(\text{STe})_y$  in  $\text{CDCl}_3$ .



**Figure S11.** <sup>1</sup>H NMR spectrum of P(SSe)*b*(SeTe) in CDCl<sub>3</sub>.

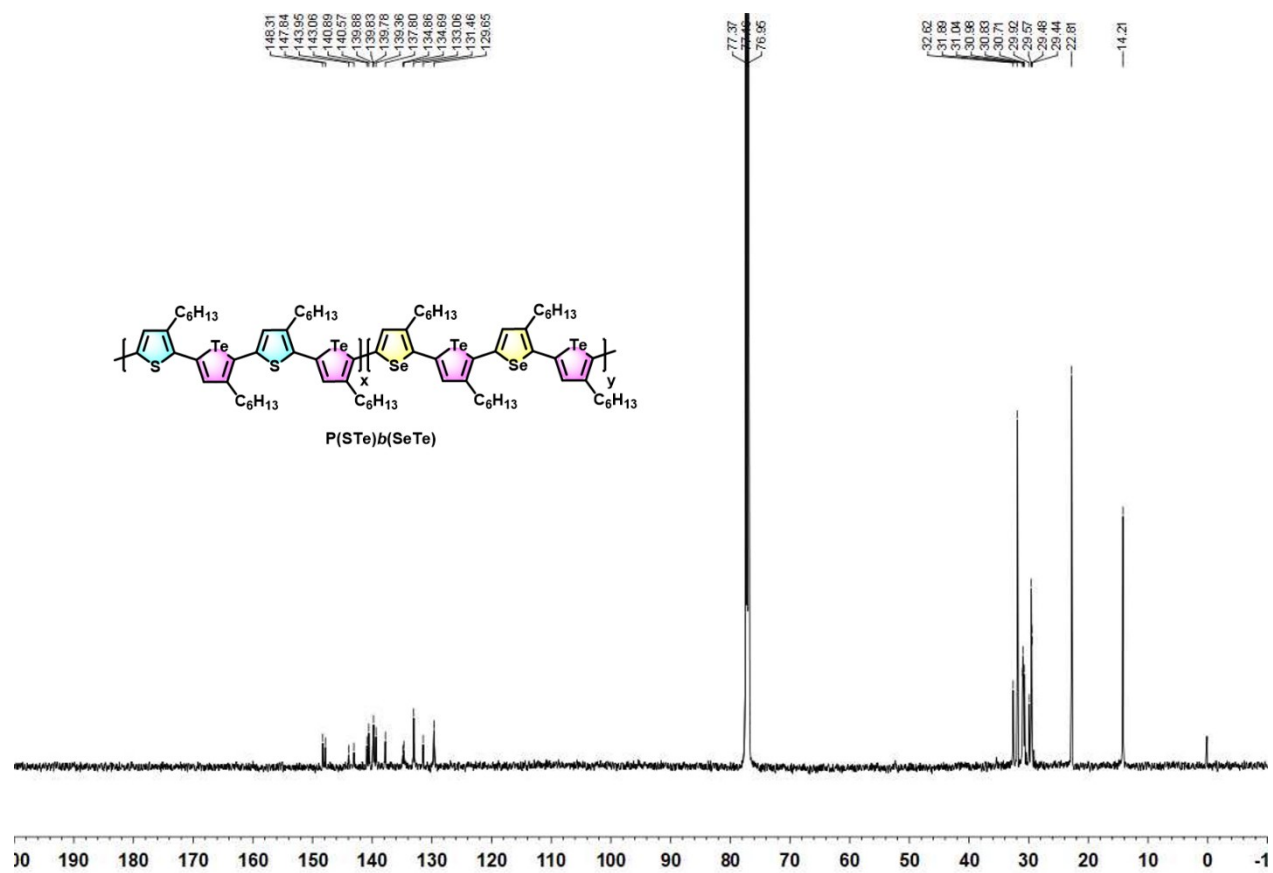


**Figure S12.**  $^{13}\text{C}$  NMR spectrum of  $\text{P}(\text{SSe})_x\text{b}(\text{SeTe})_y$  in  $\text{CDCl}_3$ .



**Figure S13.**  $^1H$  NMR spectrum of  $P(STe)_x(SeTe)_y$  in  $CDCl_3$ .





**Figure S14.**  $^{13}\text{C}$  NMR spectrum of  $\text{P}(\text{STe})_x\text{b}(\text{SeTe})_y$  in  $\text{CDCl}_3$ .