Supporting Information

Synthesis of Side-Chain Regioregular and Main-Chain Alternating Poly(bi chalcogenophenes) and an ABC-Type Periodic Poly(terchalcogenophene)

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Table of Contents

Experimental procedures .....................................................................................................2
Synthetic Procedures............................................................................................................4
NMR Spectra of Intermediates and Polymers ...................................................................14
Procedure for \( M_n \) versus Monomer Conversion Plot ......................................................16
MALDI-TOF Mass Spectrometry of PSSeTe ...................................................................17
Characteristics of OFETs .................................................................................................17
NMR Spectra .....................................................................................................................19
GPC Traces ........................................................................................................................47
DFT Computation and Analysis ........................................................................................49
References.........................................................................................................................56
Experimental Procedures

**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⁺ electrode as the reference electrode, while 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) 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 $\text{HOMO} = - (E_{\text{ox onset}} - E_{\text{ferrocene onset}} + 4.8) \text{ eV}$. The LUMO levels were obtained from the equation $\text{LUMO} = - (E_{\text{red onset}} - E_{\text{ferrocene onset}} + 4.8) \text{ eV}$. High resolution mass spectra (HRMS) were obtained on a JEOL AccuTOF GCX (EI). MALDI spectra were recorded on an Bruker Autoflex III system using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as a matrix in THF (5 mg/mL). GIXRD measurements were performed at the BL23A station of the National Synchrotron Radiation Research Center (NSRRC), Taiwan. Polymer molecular weights were determined with a 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.

**Film preparation for GIWAXRD.** The wafers with thermal grown 300 nm SiO₂ 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 from 20 mg/mL solutions in oDCB on 1.4 × 1.4 cm silicon wafers. The post-annealing of the thin films was carried out in the glovebox to prevent oxidation.

**OFET fabrication.** A n-type heavily doped Si wafer with a SiO₂ layer of 300 nm and a capacitance of 11.5 nF cm⁻² as the gate electrode and dielectric layer was ultrasonically cleaned sequentially in detergent, water and isopropyl alcohol. Octadecyltrichlorosilane (ODTS) was used as a self-assembled monolayer. The polychalcogenophene samples were
prepared form 20 mg/mL solutions in chloroform and were spin-coated on the ODTStreated 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 4156C instrument. The mobility calculation was based on the equation

$$I_{ds}(W/2L)\mu Ci(V_g - V_t)^2$$

in the saturation regime, where $I_{ds}$ is the drain–source current, $W$ is the channel width (1 mm), $L$ is the channel length (100 mm), $\mu$ is the field-effect mobility, $Ci$ is the capacitance per unit area of the dielectric layer, $V_g$ is the gate voltage, and $V_t$ is the threshold voltage.
Synthetic Procedures

All chemicals were purchased from Aldrich, Acros or TCI and used as received unless specified. $^1$H and $^{13}$C NMR spectra were obtained in deuterium-substituted chloroform by Varian 400 MHz spectrometers and 0.5 wt% TMS also used as reference. 3-hexyltellurophene$^1$, compound 1$^2$, compound 2$^3$, compound 3$^4$ and compound SeS$^5$ were synthesized as reported.

Scheme S1. Synthetic routes for SSeI$_2$, SeSI$_2$, STeI$_2$, SeTeI$_2$, and SSeTeI$_2$ monomers and their polymers.

Synthesis of 2-bromo-3-hexylselenophene (4). To a solution of 3-hexyltellurophene (2.5
g, 9.40 mmol) in anhydrous THF (40 mL) was added a solution of 2.5 M \( n \)-BuLi (3.95 mL, 9.87 mmol) dropwisely under 0 °C for 1 h. Then a solution of 1 M trimethyltin chloride (9.4 mL, 9.40 mmol) was added. The reaction mixture was stirred at room temperature for 16 h then extracted with dichloromethane and water. The organic layer was collected and dried with MgSO\(_4\). After removal of the solvent under reduced pressure, a crude brown oil was obtain (3.84 g, 95 %), the crude compound was used for further reaction without purification.

**Synthesis of 3-hexyl-2-(4-hexylselenophen-2-yl)thiophene (SSe).** A mixture of (4-hexylselenophen-2-yl)trimethylstannane 3 (2 g, 5.26 mmol), 2-bromo-3-hexylthiophene 1 (1.29 g, 5.26 mmol), tetrakis(triphenylphosphine)palladium (121 mg, 0.11 mmol) in toluene (50 mL) under N\(_2\) was stirred at 120 °C for 16 h. After removal of the solvent under reduced pressure, the residue was purified by silica gel chromatography with hexane as the eluent to give a yellow oil (1.12 g, 56 %). \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\) ppm): 0.87-0.92 (m, 6H), 1.28-1.40 (m, 12H), 1.59-1.67 (m, 4H), 2.58 (t, 2H, \(J = 7.6\) Hz), 2.73 (t, 2H, \(J = 8.0\) Hz), 6.92 (d, 1H, \(J = 5.2\) Hz), 7.13 (d, 1H, \(J = 5.6\) Hz), 7.14 (s, 1H), 7.50 (d, 1H, \(J = 1.2\) Hz). \(^13\)C NMR (CDCl\(_3\), 100 MHz, \(\delta\) ppm): 14.0, 14.1, 22.6, 29.0, 29.1, 29.2, 30.2, 30.7, 31.6, 31.7, 32.2, 123.3, 124.3, 129.9, 130.0, 133.3, 139.0, 140.1, 145.4. HRMS (C\(_{20}\)H\(_{30}\)SSe): calcd, 382.1228; found (EI\(^+\)), 382.1228.
Synthesis of 3-hexyl-2-(4-hexyl-5-iodoselenophen-2-yl) thiophene (SSeI). N-iodosuccinimide (0.89 g, 3.9 mmol) was added in portions to a solution of SSe (1 g, 2.6 mmol) in DMF (50 mL). The mixture was stirred at room temperature for 3 h. The mixture was quenched in Na₂S₂O₃ aqueous solution, followed by the extraction with dichloromethane and water. The organic layer was collected and dried with MgSO₄. After removal of the solvent under reduced pressure, the residue was purified by silica gel chromatography with hexane as the eluent to give a brown oil (1.27 g, 95%).¹H NMR (400 MHz, CDCl₃, δ ppm): 0.87-0.90 (m, 6H), 1.29-1.37 (m, 12H), 1.54-1.59 (m, 4H), 2.50 (t, 2H, J = 7.8 Hz), 2.68 (t, 2H, J = 8.0 Hz), 6.903 (d, 1H, J = 5.2 Hz), 6.905 (s, 1H), 7.15 (d, 1H, J = 5.2 Hz).¹³C NMR (CDCl₃, 100 MHz, δ ppm): 14.0, 14.1, 22.6, 28.9, 29.2, 29.8, 30.7, 31.6, 34.0, 75.5, 123.9, 129.0, 130.0, 132.6, 139.7, 145.0, 149.5. HRMS (C₂₀H₂₉ISSe): calcd, 508.0194; found (EI⁺), 508.0171.

![Diagram of SSェI](image)

Synthesis of 3-hexyl-2-(4-hexyltellurophen-2-yl)thiophene (STe). A mixture of (4-hexyltellurophen-2-yl)trimethylstannane 4 (2.5 g, 5.81 mmol), 2-bromo-3-hexylthiophene 1 (1.43 g, 5.81 mmol), tetrakis(triphenylphosphine)palladium (134 mg, 0.12 mmol) in toluene (55 mL) under N₂ was stirred at 120 °C for 16 h. After removal of the solvent under reduced pressure, the residue was purified by silica gel chromatography with hexane as the eluent to give a yellow oil (0.8 g, 32 %).¹H NMR (400 MHz, CDCl₃, δ ppm): 0.90-0.94 (m, 6H), 1.29-1.42 (m, 12H), 1.61-1.67 (m, 4H), 2.61 (t, 2H, J = 7.6 Hz), 2.71 (t, 2H, J = 8.0 Hz), 6.92 (d, 1H, J = 5.2 Hz), 7.09 (d, 1H, J = 5.2 Hz), 7.59 (d, 1H, J = 1.2 Hz), 8.31 (d, 1H, J = 0.8 Hz).¹³C NMR (CDCl₃, 100 MHz, δ ppm): 14.1, 14.1, 22.6, 29.0, 29.3, 29.4, 30.3, 30.6, 31.6, 31.7, 35.2, 118.9, 122.9, 130.1, 134.9, 137.6, 137.9, 138.1, 152.4. HRMS (C₂₀H₃₀STe): calcd, 432.1125; found (EI⁺), 432.1122.
Synthesis of 3-hexyl-2-(4-hexyltellurophen-2-yl)selenophene (SeTe). A mixture of (4-hexyltellurophen-2-yl)trimethylstannane 4 (2.5 g, 5.81 mmol), 2-bromo-3-hexylselenophene 2 (1.71 g, 5.81 mmol), 2-bromo-3-hexylthiophene (1.43 g, 5.81 mmol), tetrakis(triphenylphosphine)palladium (134 mg, 0.12 mmol) in toluene (55 mL) under N₂ was stirred at 120 °C for 16 h. After removal of the solvent under reduced pressure, the residue was purified by silica gel chromatography with hexane as the eluent to give a yellow oil (1.84 g, 66 %). \(^1\)H NMR (400 MHz, CDCl₃, δ ppm): 0.86-0.90 (m, 6H), 1.29-1.37 (m, 12H), 1.59-1.63 (m, 4H), 2.58 (m, 2H), 2.67 (t, 2H, \(J = 8.0\) Hz), 7.19 (d, 1H, \(J = 6.0\) Hz), 7.51 (d, 1H, \(J = 1.6\) Hz), 7.74 (d, 1H, \(J = 5.6\) Hz), 8.31 (t, 1H, \(J = 0.8\) Hz). \(^{13}\)C NMR (CDCl₃, 100 MHz, δ ppm): 14.0, 14.1, 22.6, 29.0, 29.3, 30.2, 30.4, 30.6, 31.6, 31.7, 35.2, 119.2, 127.8, 133.6, 137.0, 138.6, 139.8, 142.4, 152.2. HRMS (C₂₀H₃₀SeTe): calcd, 480.0569; found (EI⁺), 480.0559.

Synthesis of 3-hexyl-2-(4-hexyl-5-(4-hexyltellurophen-2-yl)selenophen-2-yl)thiophene (SSeTe). A mixture of (4-hexyltellurophen-2-yl)trimethylstannane (92.4 g, 0.217 mmol), SSeI (100 mg, 0.197 mmol), and tetrakis(triphenylphosphine)palladium(0) (11.4 mg, 0.01 mmol) in toluene (1.9 mL) under N₂ was stirred at 120 °C for 16 h. After removal of the solvent under reduced pressure, the residue was purified by silica gel chromatography with hexane as the eluent to give a yellow oil (127 mg, 79%). \(^1\)H NMR (400 MHz, CDCl₃, δ ppm): 0.86-0.90 (m, 9H), 1.29-1.40 (m, 18H), 1.60-1.66 (m, 6H), 2.58 (t, 2H, \(J = 7.6\) Hz), 2.66 (t, 2H, \(J = 7.8\) Hz), 2.75 (t, 2H, \(J = 7.8\) Hz), 6.91 (d, 1H, \(J = 5.2\) Hz), 7.130 (s, 1H),
7.131 (d, 1H, \( J = 5.2 \) Hz), 7.52 (s, 1H), 8.32 (s, 1H). \(^{13}\text{C}\) NMR (CDCl\(_3\), 100 MHz, \( \delta \) ppm): 14.1, 22.6, 29.0, 29.3, 29.4, 29.7, 30.3, 30.5, 30.6, 30.7, 31.7, 35.2, 119.4, 123.4, 130.2, 131.8, 133.0, 136.3, 137.7, 138.3, 139.3, 140.1, 142.5, 152.3. HRMS (C\(_{30}\)H\(_{44}\)SSeTe): calcd, 646.1386; found (EI\(^+\)), 646.1411.

**Synthesis of 3-hexyl-2-(4-hexyl-5-iodoselenophen-2-yl)-5-iodothiophene (SSeI\(_2\)).** To a solution of SSe (1 g, 2.62 mmol) and p-toluenesulfonic acid (1g, 5.24 mmol) in CH\(_2\)Cl\(_2\) (30 mL) was added N-iodosuccinimide (1.3 g, 5.76 mmol) in portions. The reaction was stirred at room temperature for 3 h. The mixture was then quenched in Na\(_2\)S\(_2\)O\(_3\) aqueous solution, and followed by the extraction with dichloromethane and water. The organic layer was collected and dried with MgSO\(_4\). After removal of the solvent under reduced pressure, the residue was purified by silica gel chromatography with hexane as the eluent to give a brown oil (0.58 g, 35 %). \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\), \( \delta \) ppm): 0.87-0.90 (m, 6H), 1.29-1.37 (m, 12H), 1.54-1.59 (m, 4H), 2.50 (t, 2H, \( J = 7.8 \) Hz), 2.63 (t, 2H, \( J = 7.8 \) Hz), 6.85 (s, 1H), 7.04 (s, 1H). \(^{13}\text{C}\) NMR (CDCl\(_3\), 100 MHz, \( \delta \) ppm): 14.0, 14.1, 22.6, 28.9, 29.1, 29.8, 30.6, 31.5, 31.6, 33.9, 72.0, 76.4, 129.5, 138.6, 139.7, 141.5, 143.3, 149.6. HRMS (C\(_{20}\)H\(_{28}\)I\(_2\)SSe): calcd, 633.9161; found (EI\(^+\)), 633.9187.

**Synthesis of 3-hexyl-2-(4-hexyl-5-iodothiophen-2-yl)-5-iodoselenophene (SeSI\(_2\)).** To a solution of SeS (300 mg, 0.787 mmol) and p-toluene sulfonic acid (299 mg, 1.57 mmol) in
CH₂Cl₂ (15 mL), N-iodosuccinimide (265 mg, 1.18 mmol) was added in portions, the reaction was stirred at room temperature for 3 h. The mixture was then quenched in Na₂S₂O₃ aqueous solution, and followed by the extraction with dichloromethane and water. The organic layer was collected and dried with MgSO₄. After removal of the solvent under reduced pressure, the residue was purified by silica gel chromatography with hexane as the eluent to give a brown oil (230 mg, 46%). 

1H NMR (400 MHz, CDCl₃, δ ppm): 0.87-0.90 (m, 6H), 1.29-1.37 (m, 12H), 1.54-1.59 (m, 4H), 2.51 (t, 2H, J = 7.8 Hz), 2.62 (t, 2H, J = 7.8 Hz), 6.63 (s, 1H), 7.37 (s, 1H). 

13C NMR (CDCl₃, 100 MHz, δ ppm): 14.1, 22.5, 22.6, 28.9, 29.1, 29.7, 29.8, 29.9, 30.7, 31.5, 31.6, 32.3, 73.8, 74.8, 127.3, 140.5, 141.5, 143.4, 143.5, 147.6. HRMS (C₂₀H₂₈I₂SSe): calcd, 633.9161; found (EI⁺), 633.9159.

**Synthesis of 3-hexyl-2-(4-hexyl-5-iodotellurophen-2-yl)-5-iodothiophene (STeI₂).** To a solution of STe (1 g, 2.31 mmol) and p-toluenesulfonic acid (0.88g, 4.62 mmol) in CH₂Cl₂ (25 mL) was added N-iodosuccinimide (1.3 g, 5.08 mmol) in portions. The reaction was stirred at room temperature for 3 h. The mixture was then quenched in Na₂S₂O₃ aqueous solution, and followed by the extraction with dichloromethane and water. The organic layer was collected and dried with MgSO₄. After removal of the solvent under reduced pressure, the residue was purified by silica gel chromatography with hexane as the eluent to give a brown oil (0.21 g, 13%). 

1H NMR (400 MHz, CDCl₃, δ ppm): 0.87-0.90 (m, 6H), 1.26-1.36 (m, 12H), 1.55-1.59 (m, 4H), 2.51-2.59 (m, 2H), 7.03 (s, 1H), 7.20 (s, 1H). 

13C NMR (CDCl₃, 100 MHz, δ ppm): 14.0, 14.1, 22.5, 22.6, 28.9, 29.0, 29.2, 29.8, 30.6, 31.5, 31.6, 36.5, 67.8, 71.6, 136.5, 138.0, 139.8, 140.6, 143.0, 155.4. HRMS (C₂₀H₂₈I₂STe): calcd, 683.9058; found (EI⁺), 683.9062.
Synthesis of 3-hexyl-2-(4-hexyl-5-iodotellurophen-2-yl)-5-iodoselenophene (SeTeI₂).

N-iodosuccinimide (1.3 g, 4.58 mmol) was added to a solution of SeTe (1 g, 2.08 mmol) and p-toluenesulfonic acid (0.79 g, 4.16 mmol) in CH₂Cl₂ (25 mL) in portions. The reaction was stirred at room temperature for 3 h. The mixture was then quenched in Na₂S₂O₃ aqueous solution, and followed by the extraction with dichloromethane and water. The organic layer was collected and dried with MgSO₄. After removal of the solvent under reduced pressure, the residue was purified by silica gel chromatography with hexane as the eluent to give a brown oil (0.73 g, 48 %). ¹H NMR (400 MHz, CDCl₃, δ ppm): 0.87-0.91 (m, 6H), 1.30-1.35 (m, 12H), 1.53-1.57 (m, 4H), 2.52 (t, 2H, J = 8.0 Hz), 2.55 (t, 2H, J = 8.0 Hz), 7.13 (s, 1H), 7.36 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz, δ ppm): 14.0, 14.1, 22.5, 22.6, 28.9, 29.2, 29.8, 30.0, 30.1, 31.5, 31.6, 36.5, 68.1, 73.3, 137.1, 140.2, 142.2, 143.8, 147.8, 155.3. HRMS (C₂₀H₂₈I₂TeSe): calcd, 731.8502; found (EI⁺), 731.8507.

Synthesis of 3-hexyl-2-(4-hexyl-5-(4-hexyl-5-iodohexyltellurophen-2-yl)selenophen-2-yl)-5-iodothiophene (SSeTeI₂). To a solution of SSeTe (0.5 g, 0.78 mmol), p-toluenesulfonic acid (0.29 g, 1.56 mmol) in CH₂Cl₂ (25 mL) was added N-iodosuccinimide (0.44 g, 1.94 mmol) in portions. The mixture was stirred at room temperature for 3 h. The mixture was then quenched in Na₂S₂O₃ aqueous solution, followed by the extraction with dichloromethane and water. The organic layer was collected and dried with MgSO₄. After removal of the solvent under reduced pressure, the residue was purified by silica gel chromatography with hexane as the eluent to give a yellow solid (0.54 g, 78%). ¹H NMR
(400 MHz, CDCl₃, δ ppm): 0.87-0.91 (m, 9H), 1.30-1.36 (m, 18H), 1.55-1.60 (m, 6H), 2.53 (t, 2H, J = 8.0 Hz), 2.57 (t, 2H, J = 8.0 Hz), 2.68 (t, 2H, J = 8.0 Hz), 7.04 (s, 1H), 7.05 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz, δ ppm): 14.1, 22.61, 22.64, 29.0, 29.1, 29.2, 29.3, 29.7, 29.9, 30.59, 30.63, 31.63, 31.66, 31.68, 36.5, 67.3, 71.7, 132.1, 136.5, 136.6, 138.8, 139.9, 140.76, 140.79, 141.2, 142.5, 155.3. HRMS (C₃₀H₄₂I₂STeSe): calcd, 897.9319; found (EI⁺), 897.9306.

Synthesis of poly(3-hexylselenophene-alt-3-hexylthiophene) (PSSe). To a solution of 1.3 M isopropylmagnesium chloride lithium chloride complex (0.25 mL, 0.32 mmol) diluted by dried THF (8 mL) was added dropwisely a solution of SSeI₂ (200 mg, 0.32 mmol) in dried THF (8 mL) in a glovebox. After Grignard metathesis was completed (monitored by thin layer chromatography), [1,3-bis(diphenylphosphino)propane]dichloronickel(II) (1.7 mg, 0.0032 mmol) was added. The reaction was stirred at room temperature for 16 h. After PSSe was precipitated with 6 M HCl/MeOH solution and washed with methanol, a deep purple solid was yielded (43 mg, 36 %). ¹H NMR (400 MHz, CDCl₃, δ ppm): 0.91 (br, 6H), 1.25-1.43 (br, 12H), 1.68-1.70 (br, 4H), 2.76 (br, 4H), 6.92 (s, 1H), 7.19 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz, δ ppm): 13.90, 13.92, 22.5, 29.1, 29.2, 29.5, 30.39, 30.44, 30.5, 30.6, 31.6, 129.1, 131.6, 133.2, 135.2, 135.8, 138.0, 139.7, 141.6.
Synthesis of poly(3-hexyltellurophene-alt-3-hexylthiophene) (PSTe). To a solution of 1.3 M isopropylmagnesium chloride lithium chloride complex (0.22 mL, 0.29 mmol) diluted by dried THF (8 mL) was added dropwise a solution of STeI$_2$ (200 mg, 0.29 mmol) in dried THF (8 mL) in a glovebox. After Grignard metathesis was completed (monitored by thin layer chromatography), [1,3-bis(diphenylphosphino)propane]dichloronickel(II) (1.6 mg, 0.0029 mmol) was added. The reaction was stirred at room temperature for 16 h. After PSTe was precipitated with 6 M HCl/MeOH solution and washed with methanol, a deep purple solid was yielded (56 mg, 44 %). $^1$H NMR (400 MHz, CDCl$_3$, $\delta$ ppm): 0.90-0.93 (br, 6H), 1.34-1.42 (br, 12H), 1.66-1.68 (br, 4H), 2.65-2.67 (br, 2H), 2.69-2.78 (br, 2H), 6.82 (s, 1H), 7.65 (s, 1H). $^{13}$C NMR (CDCl$_3$, 100 MHz, $\delta$ ppm): 14.0, 14.1, 22.7, 29.3, 29.4, 29.8, 30.6, 30.8, 31.75, 31.77, 32.5, 129.5, 131.4, 133.0, 137.7, 139.2, 139.7, 139.8, 148.2.

![Polymer Structure](attachment:image.png)

Synthesis of poly(3-hexyltellurophene-alt-3-hexylselenophene) (PSeTe). To a solution of 1.3 M isopropylmagnesium chloride lithium chloride complex (0.21 mL, 0.27 mmol) diluted by dried THF (8 mL) was added dropwisely a solution of SeTeI$_2$ (200 mg, 0.27 mmol) in dried THF (8 mL) in a glovebox. After Grignard metathesis was completed (monitored by thin layer chromatography), [1,3-bis(diphenylphosphino)propane]dichloronickel(II) (1.4 mg, 0.0027 mmol) was added. The reaction was stirred at room temperature for 16 h. After PSeTe was precipitated with 6 M HCl/MeOH solution and washed with methanol, a deep purple solid was yielded (70 mg, 53 %). $^1$H NMR (400 MHz, CDCl$_3$, $\delta$ ppm): 0.92-0.95 (br, 6H), 1.27-1.44 (br, 12H), 1.67 (br, 4H), 2.63 (br, 2H), 2.74 (br, 2H), 6.97 (s, 1H), 7.54 (s, 1H). $^{13}$C NMR (CDCl$_3$, 100 MHz, $\delta$ ppm): 14.05, 14.06, 22.7, 29.0, 29.3, 29.4, 30.3, 30.61, 30.63, 30.7, 30.87, 30.91, 31.76, 31.77, 32.5, 35.3, 132.9, 134.6, 134.8, 140.5, 144.0, 143.0, 143.9, 147.7.
Synthesis of ABC-type periodic terpolymer, poly(3-hexyltellurophene-per-3-hexylselenophene-per-3-hexylthiophene) (PSSeTe). To a solution of 1.3 M isopropylmagnesium chloride lithium chloride complex (0.17 mL, 0.22 mmol) diluted by dried THF (8 mL) was added dropwisely a solution of SSeTeI\(_2\) (200 mg, 0.22 mmol) in dried THF (8 mL) in a glovebox. After Grignard metathesis was completed (monitored by thin layer chromatography), [1,3-bis(diphenylphosphino)propane]dichloronickel(II) (1.2 mg, 0.0022 mmol) was added. The reaction was stirred at room temperature for 16 h. After PSSeTe was precipitated with 6 M HCl/MeOH solution and washed with methanol, a deep purple solid was yielded (110 mg, 77 %). \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\) ppm): 0.92-0.95 (br, 9H), 1.27-1.44 (br, 18H), 1.67 (br, 6H), 2.69 (br, 2H), 2.77 (br, 4H), 6.83 (s, 1H), 7.17 (s, 1H), 7.58 (s, 1H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz, \(\delta\) ppm): 14.05, 14.06, 22.68, 22.69, 29.0, 29.31, 29.34, 29.4, 29.7, 30.3, 30.6, 30.7, 30.8, 31.76, 31.77, 31.78, 32.5, 35.3, 129.5, 131.8, 131.9, 133.3, 135.0, 137.6, 140.0, 140.1, 140.5, 140.8, 142.5, 148.1.
NMR Spectra of Intermediates and Polymers

Figure S1. $^1$H NMR spectra of the crude products from Grignard metathesis/acidic quenching of (a) SSeI$_2$, STeI$_2$, and SeTeI$_2$ and (b) SScTeI$_2$.

Figure S2. Crude $^1$H-NMR spectrum for Grignard metathesis of SSeI$_2$ followed by acid quenching.
Figure S3. $^1$H NMR spectra of PSSe, PSTe, PSeTe, and PSSeTe.

Figure S4. $^{13}$C NMR spectra (aromatic region) of PSSe, PSTe, PSeTe, and PSSeTe.
Procedure for \( M_n \) versus Monomer Conversion Plot

To a solution of isopropylmagnesium chloride lithium chloride complex (1.3 M, 0.169 mL, 0.22 mmol) diluted by dried THF (6 mL) was added dropwisely a solution of \( \text{STeI}_2 \) (150 mg, 0.22 mmol) with nonadecane (59 mg, 0.22 mmol) in dried THF (6 mL) as the internal standard. An aliquot was subjected to GC-MS analysis to determine the initial ratio of monomer to the internal standard (nonadecane). [1,3-bis(diphenylphosphino)propane]dichloronickel(II) (1.2 mg, 0.0022 mmol) was quickly added to the solution in one portion. Aliquots (1 mL) were taken periodically over a period of 5 min to determine the monomer conversion (GC-MS) and number average molecular weight (GPC).

Table S1. \( M_n \) and PDI versus monomer conversion of PSTe.

| Monomer conversion (%) | \( M_n \) | PDI |
|-----------------------|----------|-----|
| 8.3                   | 552      | 1.20|
| 70.8                  | 10267    | 1.35|
| 95.9                  | 14931    | 1.19|
| 97.3                  | 15663    | 1.20|
| 98.3                  | 16162    | 1.19|

Figure S5. Dependence of \( M_n \) and PDI on monomer conversion for PSTe.
MALDI-TOF Mass Spectrometry of PSSeTe

Figure S6. MALDI-TOF-MS of PSSeTe.

Characteristics of OFETs

Figure S7. Output characteristics of OFETs based on (a) PSSe, (b) PSTe, (c) PSeTe, and (d) PSSeTe.
Figure S8. Transfer characteristics of OFETs based on (a) PSSe, (b) PSTe, (c) PSeTe, and (d) PSSeTe.
Figure S9. $^1$H NMR spectrum of SSe.
Figure S10. $^{13}$C NMR spectrum of SSe.
Figure S11. $^1$H NMR spectrum of STe.
Figure S12. $^{13}$C NMR spectrum of STe.
Figure S13. $^1$H NMR spectrum of SeTe.
Figure S14. $^{13}$C NMR spectrum of SeTe.

S24
Figure S15. $^1$H NMR spectrum of SSeI.
Figure S16. $^{13}$C NMR spectrum of SSel.
Figure S17. $^1$H NMR spectrum of SSeTe.
Figure S18. $^{13}$C NMR spectrum of SSeTe.
Figure S19. $^1$H NMR spectrum of SSeI$_2$. 

S29
Figure S20. $^{13}$C NMR spectrum of SSeI$_2$.
Figure S21 $^1$H NMR spectrum of SeSI$_2$. 
Figure S22 $^{13}$C NMR spectrum of SeSI$_2$. 
Figure S23. $^1$H NMR spectrum of STel$_2$. 

S33
Figure S24. $^{13}$C NMR spectrum of STeI$_2$. S34
Figure S25. $^1$H NMR spectrum of SeTeI$_2$. 

S35
Figure S26. $^{13}$C NMR spectrum of SeTeI$_2$. 

S36
Figure S27. $^1$H NMR spectrum of SSeTeI$_2$. 
Figure S28. $^{13}$C NMR spectrum of SSeTeI$_2$. 
Figure S29. $^1$H NMR spectrum of PSSe.
Figure S30. $^{13}$C NMR spectrum of PSSe.
Figure S31. $^1$H NMR spectrum of PSTe.
Figure S32. $^{13}$C NMR spectrum of PSTe.
Figure S33. $^1$H NMR spectrum of PSeTe.
Figure S34. $^{13}$C NMR spectrum of PSeTe.
Figure S35. $^1$H NMR spectrum of PSSeTe.
Figure S36. $^{13}$C NMR spectrum of PSSeTe.

GPC Traces
Figure S37. GPC chromatogram and analysis of PSSe (M/Cat. = 50).

Figure S38. GPC chromatogram and analysis of PSTe (M/Cat. = 50).
Figure S39. GPC chromatogram and analysis of PSeTe (M/Cat. = 50).

Figure S40. GPC chromatogram and analysis of PSSeTe (M/Cat. = 50).
DFT Computation and Analysis

Computational details.

Quantum-chemical calculations were performed with the Gaussian09 suite employing the cam-B3LYP density functional in combination with the LANL2DZ(d,P) basis set for the chalcogens, phosphine, and iodine, the LANL2DZ basis set for nickel, and the 6-311G(d,p) basis set for the remaining atoms. Geometry optimizations were performed with tight SCF and convergence criteria and an ultrafine integration grid, applying the GEDIIS optimization algorithm. The nature of each stationary point was confirmed by a frequency analysis.
3-Hexyl-2-(4-hexyl-5-iodo-selenophen-2-yl)-5-iodo-thiophene

\[
\begin{align*}
\text{C} & \quad 2.245111877258 & 1.014266772530 & -0.847914146666 \\
\text{C} & \quad 2.161050676785 & 0.359055612288 & 0.340945918701 \\
\text{C} & \quad 0.861144734280 & -0.191349123933 & 0.584402291982 \\
\text{C} & \quad -0.089494763217 & 0.017151855755 & -0.361924668779 \\
\text{H} & \quad 0.640366469535 & -0.735840763442 & 1.495249250091 \\
\text{C} & \quad -1.462595036652 & -0.482448210242 & -0.361924668779 \\
\text{C} & \quad -2.649336795618 & 0.196090718589 & -0.426670627317 \\
\text{C} & \quad -3.776515847383 & -0.681905034343 & -0.391457765455 \\
\text{C} & \quad -3.438013842415 & -1.99231300236 & -0.300937693647 \\
\text{I} & \quad 0.640366469535 & -0.735840763442 & 1.495249250091 \\
\text{C} & \quad -1.462595036652 & -0.482448210242 & -0.361924668779 \\
\end{align*}
\]

3-Hexyl-2-(4-hexyl-5-iodo-tellurophen-2-yl)-5-iodo-thiophene

\[
\begin{align*}
\text{C} & \quad 2.245111877258 & 1.014266772530 & -0.847914146666 \\
\text{C} & \quad 2.161050676785 & 0.359055612288 & 0.340945918701 \\
\text{C} & \quad 0.861144734280 & -0.191349123933 & 0.584402291982 \\
\text{C} & \quad -0.089494763217 & 0.017151855755 & -0.361924668779 \\
\text{H} & \quad 0.640366469535 & -0.735840763442 & 1.495249250091 \\
\text{C} & \quad -1.462595036652 & -0.482448210242 & -0.361924668779 \\
\text{C} & \quad -2.649336795618 & 0.196090718589 & -0.426670627317 \\
\text{C} & \quad -3.776515847383 & -0.681905034343 & -0.391457765455 \\
\text{C} & \quad -3.438013842415 & -1.99231300236 & -0.300937693647 \\
\text{I} & \quad 0.640366469535 & -0.735840763442 & 1.495249250091 \\
\text{C} & \quad -1.462595036652 & -0.482448210242 & -0.361924668779 \\
\end{align*}
\]

3-Hexyl-2-(4-hexyl-5-iodo-tellurophen-2-yl)-5-iodo-thiophene

\[
\begin{align*}
\text{C} & \quad 2.245111877258 & 1.014266772530 & -0.847914146666 \\
\text{C} & \quad 2.161050676785 & 0.359055612288 & 0.340945918701 \\
\text{C} & \quad 0.861144734280 & -0.191349123933 & 0.584402291982 \\
\text{C} & \quad -0.089494763217 & 0.017151855755 & -0.361924668779 \\
\text{H} & \quad 0.640366469535 & -0.735840763442 & 1.495249250091 \\
\text{C} & \quad -1.462595036652 & -0.482448210242 & -0.361924668779 \\
\text{C} & \quad -2.649336795618 & 0.196090718589 & -0.426670627317 \\
\text{C} & \quad -3.776515847383 & -0.681905034343 & -0.391457765455 \\
\text{C} & \quad -3.438013842415 & -1.99231300236 & -0.300937693647 \\
\text{I} & \quad 0.640366469535 & -0.735840763442 & 1.495249250091 \\
\text{C} & \quad -1.462595036652 & -0.482448210242 & -0.361924668779 \\
\end{align*}
\]
3-Hexyl-2-(4-hexyl-5-iodo-tellurophen-2-yl)-5-iodo-selenophene
3-Hexyl-5-(3-hexyl-5-iodo-selenophen-2-yl)-2-iodo-thiophene

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3-Hexyl-5-(3-hexyl-5-iodotellurophen-2-yl)-2-iodo-thiophene
3-Hexyl-5-(3-hexyl-5-iodo-tellurophen-2-yl)-2-iodo-selenophene

C 2.341720467166 0.750267112581 -1.333394179000
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C -2.979558492937 6.367610957607 1.591601214110
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