

Supporting Information

Controlling Phase Separation and Optical Properties in Conjugated Polymers Through Selenophene-Thiophene Copolymerization

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Experimental Methods

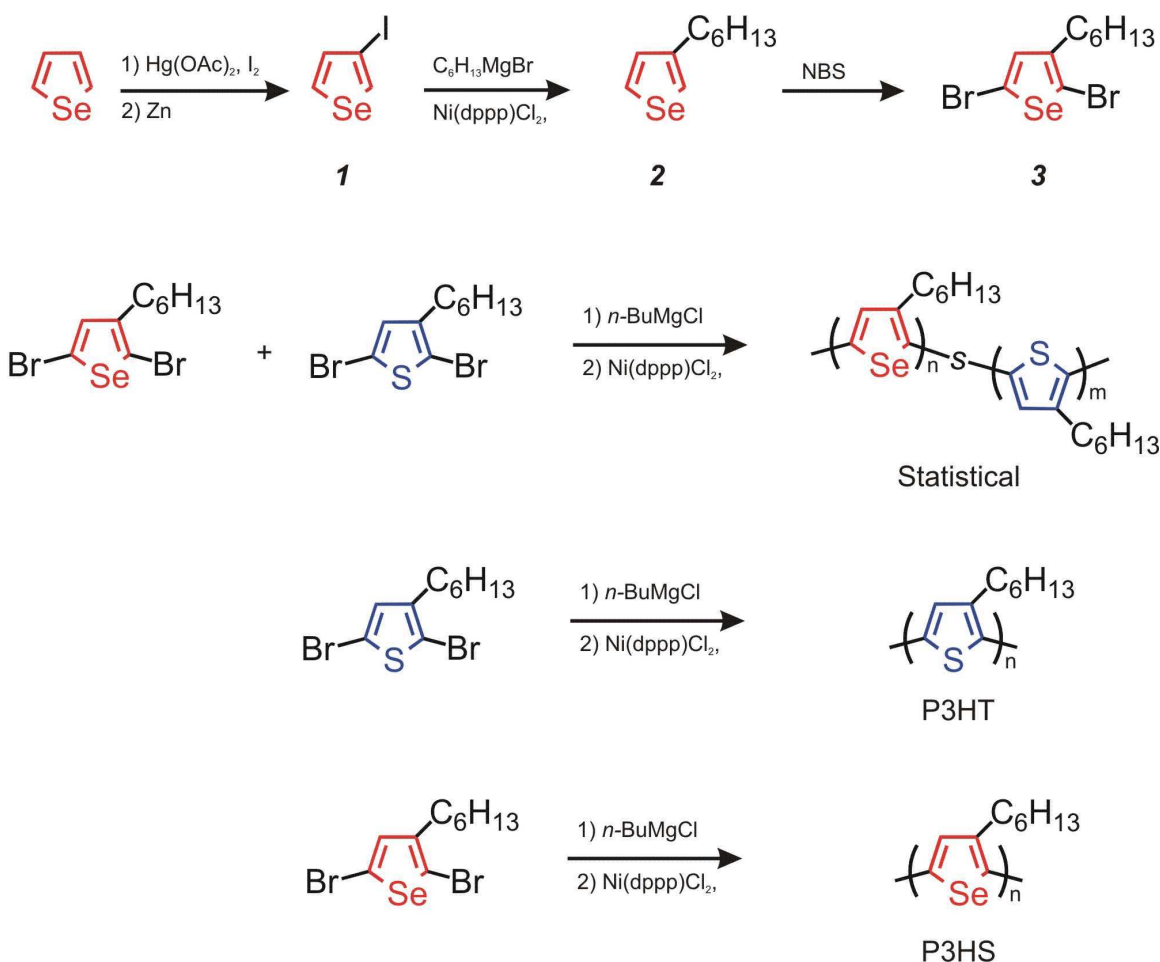
General Considerations

All reagents were used as received unless otherwise noted. Selenophene, *n*-hexylmagnesium bromide in diethyl ether (2.0 M), *n*-butylmagnesium chloride in THF (2.0 M), 3-hexylthiophene, and anhydrous chlorobenzene were purchased from Sigma-Aldrich. [1,3-Bis(diphenylphosphino)propane]nickel(II) chloride (Ni(dppp)Cl_2), N-bromosuccinimide (NBS), and powdered zinc were purchased from Acros Organics. Mercury acetate was purchased from Alfa Aesar.

Instrumentation

Absorption spectra were recorded using a Varian Cary 5000 spectrometer. Solution measurements were made in chlorobenzene at ~ 0.02 mg/mL. NMR spectra were recorded on a Varian Mercury 300 spectrometer (300MHz). Fluorescence spectra were recorded using a SPEX Fluorolog-3 spectrofluorometer in chlorobenzene at ~ 0.002 mg/mL. Masses were determined on a Waters GCT Premier ToF mass spectrometer (EI). Polymer molecular weights were determined using a Varian PL220 GPC (1,2,4-trichlorobenzene, 150 °C) with narrow weight distribution polystyrene standards. AFM images were obtained with a Veeco Dimension 3000 microscope. STEM imaging was carried out at 200 kV using a Hitachi HD-2000 instrument.

Synthesis



Scheme S1. Synthetic routes used to prepare the selenophene monomer, statistical copolymer, poly-(3-hexylthiophene) (P3HT), and poly-(3-hexylselenophene) (P3HS).

3-Iodoselenophene (1).¹ Mercury acetate (50.1 g, 157 mmol) was added to a solution of selenophene (5.15g, 39.3 mmol) in acetic acid (200 mL). The solution was heated to 90 °C and crushed iodine (40.0 g, 157 mmol) was added in portions over 15 minutes. After 60 minutes an orange solid formed, the reaction was allowed to cool to room temperature and water (300 mL) was added. The mixture was stored at 4 °C for 16 hours, filtered, and the solids were collected and treated with a solution of potassium iodide

(0.60 M) at room temperature for 3 hours with constant stirring and filtered. This intermediate (tetraiodoselenophene) was used immediately in the next step without further purification. Tetraiodoselenophene (17.1 g, 26.9 mmol) was placed in a Schlenk flask with freshly purified zinc powder (9.2 g, 135 mmol). A 4:1 (v/v) mixture of acetic acid:water (80 mL) was added to the flask under a nitrogen atmosphere and the apparatus was placed in an ultrasonic bath and sonicated for 2.5 hours at 40 °C. The resulting mixture was diluted with ethyl acetate; washed with water, saturated sodium bicarbonate, and brine; dried over MgSO₄; filtered and concentrated. The resulting yellow oil was distilled under reduced pressure (60 °C, 1.5 mmHg) to afford the title compound (3.1 g, 31%). ¹H NMR (CDCl₃, 300 MHz): δ 8.09 (m, 1H), 7.85 (dd, *J*₁ = 2.7, *J*₂ = 5.6 Hz, 1H), 7.32 (m, 1H); ¹³C NMR (CDCl₃, 75 MHz): 137.6, 132.7, 132.5. HRMS-EI: calc. 257.8445, found 257.8450, Δ = 1.9 ppm.

3-Hexylselenophene (2). A Schlenk flask with a nitrogen atmosphere was charged with 3-iodoselenophene (3.1 g, 12.1 mmol) and diethyl ether (10 mL), and cooled in an ice bath. Ni(dppp)Cl₂ (65 mg, 0.12 mmol) was added to the solution and *n*-hexylmagnesium bromide (7.2 mL, 2.0 M in diethyl ether, 14.4 mmol) was then added drop-wise. The reaction mixture was allowed to warm to room temperature over 16 hours with constant stirring. The mixture was quenched with dilute HCl and diluted with diethyl ether. The organic phase was washed with water and brine; dried over MgSO₄; filtered and concentrated. The resulting black oil was distilled under reduced pressure (75 °C, 1.5 mmHg) to afford the title compound (1.3 g, 50%). ¹H NMR (CDCl₃, 300 MHz): δ 7.91 (dd, *J*₁ = 2.7 Hz, *J*₂ = 5.3 Hz, 1H), 7.54 (m, 1H), 7.21 (d, *J* = 5.4 Hz, 1H), 2.61 (t, *J* =

7.8 Hz, 2 H), 1.62 (q, $J = 7.8$ Hz, 2H), 1.27-1.38 (m, 6H), 0.89 (t, $J = 6.3$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 145.6, 131.8, 130.0, 124.0, 32.3, 32.0, 30.7, 29.4, 23.0, 14.5. HRMS-EI: calc. 216.0417, found 216.0420, $\Delta = 1.4$ ppm.

2,5-Dibromo-3-hexylselenophene (3). A degassed solution of 3-hexylselenophene (1.1 g, 5.1 mmol) in DMF (40 mL) was treated drop-wise with a degassed solution of N-bromosuccinimide (1.8 g, 10.2 mmol) in DMF (40 mL) in the dark at 0 °C. The mixture was allowed to warm to room temperature over 16 hours with constant stirring. The mixture was diluted with diethyl ether; washed with 10 % sodium bisulfite, water, and brine; dried over MgSO_4 ; filtered and concentrated. The resulting yellow oil was purified by column chromatography (hexanes) to afford the title compound (0.9 g, 47%). ^1H NMR (CDCl_3 , 300 MHz): δ 6.98 (s, 1H), 2.49 (t, $J=7.8$ Hz, 2H), 1.53 (m, 2H), 1.26-1.31 (m, 6H), 0.88 (t, $J=6.0$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 145.2, 134.6, 113.9, 111.3, 31.9, 31.0, 29.8, 29.1, 22.9, 14.4. HRMS-EI: calc. 371.8627, found 371.834, $\Delta = 1.9$ ppm.

2,5-Dibromo-3-hexylthiophene. This compound was synthesized in a manner similar to 2,5-dibromo-3-hexylselenophene starting from 3-hexylthiophene. ^1H NMR (CDCl_3 , 300 MHz): δ 6.78 (s, 1H), 2.50 (t, $J=7.8$ Hz, 2H), 1.53 (m, 2H), 1.23-1.36 (m, 6H), 0.89 (t, $J=6.6$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 143.3, 131.3, 110.7, 108.3, 31.9, 29.9, 29.8, 29.1, 22.9, 14.4. HRMS-EI: calc. 323.9183, found 323.9187, $\Delta = 1.2$ ppm.

Poly-(3-hexylselenophene-*block*-3-hexylthiophene). *n*-Butylmagnesium chloride (0.14 mL, 2.0 M in THF, 0.28 mmol) was added drop-wise to a solution of 2,5-dibromo-3-hexylselenophene (100 mg, 0.27 mmol) in dry THF (1.5 mL) under a nitrogen atmosphere. This mixture was allowed to reflux for 1 hour, then the solution was transferred to a nitrogen filled flask containing Ni(dppp)Cl₂ (3.0 mg, 5.4 nmol) (Solution A). In a separate flask *n*-butylmagnesium chloride (0.14mL, 2.0 M in THF, 0.28 mmol) was added to 2,5-dibromo-3-hexylthiophene (87 mg, 0.27 mmol) in dry THF (1.5 mL) and the solution was refluxed for 1 hour (Solution B). Solution A was refluxed for 10 hours at which time Solution B was added drop-wise. The combined mixture was refluxed for an additional 10 hours, then quenched with dilute hydrochloric acid and precipitated into methanol. The precipitated solid was purified by Soxhlet extraction using hexanes, methanol, and chloroform. The chloroform fraction was concentrated to afford the polymer as a deep purple solid (20 mg, 29%, regioregularity (RR) = 77 %). ¹H NMR (CDCl₃, 300 MHz): δ 7.12 (s, 1H), 6.98 (s, 1H), 2.72-2.82 (4H), 1.65-1.72 (4H), 1.25-1.46 (12H), 0.90-0.93 (6H). *M_n*=7.4 kg/mol, *M_w*=13.2 kg/mol, PDI = 1.8. To synthesize the block oligomer the same procedure was used as above with a catalyst:total monomer ratio of 5:100.

Poly-(3-hexylselenophene-*stat*-3-hexylthiophene). *n*-Butylmagnesium chloride (0.27 mL, 2.0 M in THF, 0.54 mmol) was added drop-wise to a solution of 2,5-dibromo-3-hexylselenophene (100 mg, 0.27 mmol) and 2,5-dibromo-3-hexylthiophene (87 mg, 0.27 mmol) in dry THF (9 mL) under a nitrogen atmosphere. The mixture was refluxed for 1 hour then transferred to a nitrogen filled flask containing Ni(dppp)Cl₂ (7.6 mg,

14.0 nmol). This mixture was refluxed for 20 hours then quenched with dilute hydrochloric acid. The resulting deep red solution was precipitated into methanol and purified by Soxhlet extraction using hexanes, methanol, and chloroform. The chloroform fraction was concentrated to afford the polymer as a deep purple solid (23 mg, 22%, RR = 77%). ^1H NMR (CDCl_3 , 300 MHz): δ 7.19 (s, 0.25H), 7.12 (s, 0.21H), 6.98 (s, 0.29H), 6.92 (s, 0.25H), 2.77 (4H), 1.70 (4H), 1.26-1.44 (12H), 0.88-0.93(6H). M_n =9.9 kg/mol, M_w =17.8 kg/mol, PDI = 1.8.

Poly-(3-hexylthiophene) (P3HT). *n*-Butylmagnesium chloride (0.77 mL, 2.0 M in THF, 1.54 mmol) was added drop-wise to a solution of 2,5-dibromo-3-hexylthiophene (500 mg, 1.54 mmol) in dry THF (9 mL) under a nitrogen atmosphere. The mixture was refluxed for 1 hour, then transferred to a flask containing Ni(dppp)Cl_2 (8 mg, 0.015 mmol). The solution was refluxed for 20 hours then quenched with dilute hydrochloric acid. The deep red solution was precipitated into methanol and purified by Soxhlet extraction using hexanes, methanol, and chloroform. The chloroform fraction was concentrated to afford the polymer as a purple solid (206 mg, 80%, RR = 91%). ^1H NMR (CDCl_3 , 300 MHz): δ 6.98 (s, 1H), 2.78-2.83 (2H), 1.66-1.75 (2H), 1.31-1.46 (6H), 0.89-0.94 (3H). M_n =14.6 kg/mol, M_w =25.6 kg/mol, PDI = 1.8.

Poly-(3-hexylselenophene) (P3HS). Prepared in an analogous manner as P3HT. The crude product was purified by Soxhlet extraction using hexanes, methanol, chloroform, and chlorobenzene. The chlorobenzene fraction was concentrated to afford the polymer as a deep blue solid (20 mg, 17%, RR = 75%). ^1H NMR (CDCl_3 , 300 MHz): δ 7.12 (s,

1H), 2.73 (2H), 2.25 (2H), 1.26-1.43 (6H), 0.91 (3H). M_n = 15.6 kg/mol, M_w = 20.6 kg/mol, PDI = 1.3.

Film Preparation

Solutions of polymers (5-8 mg/mL) in chlorobenzene were spun-cast at 1000 RPM onto glass substrates that had been washed with methanol. The films were annealed at 150 °C for one hour in a nitrogen atmosphere.

Additional Figures

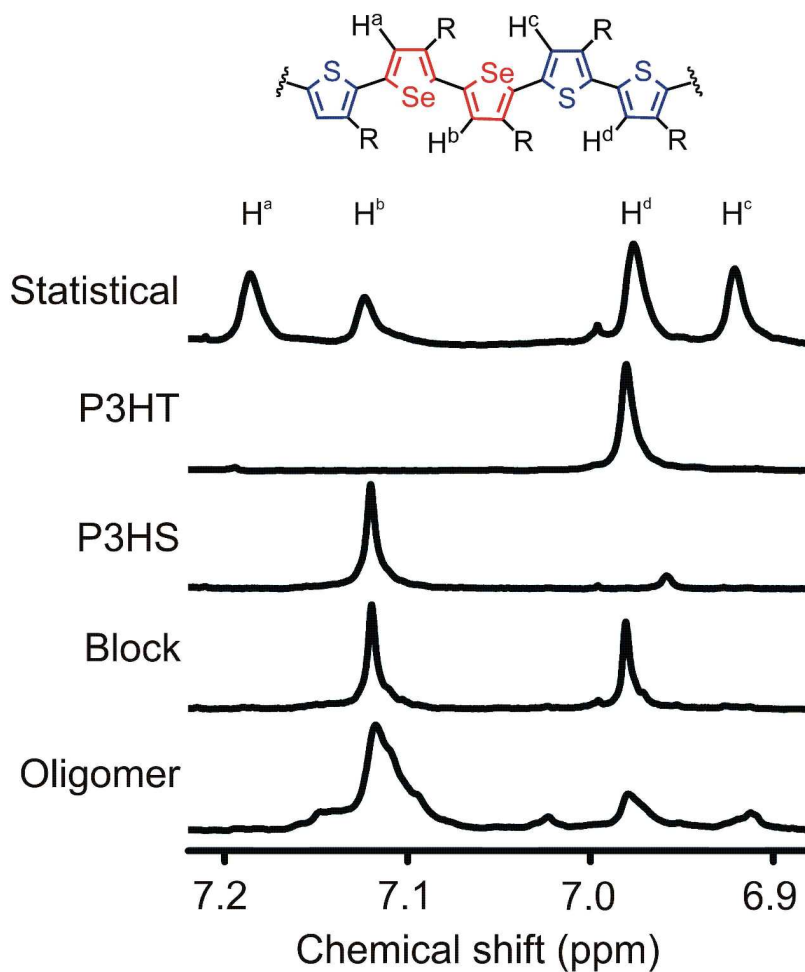


Figure S1. Partial ^1H NMR spectra of the aromatic region of statistical, P3HT, P3HS, block polymers, and block oligomer (additional peaks are attributed to end-group effects²). The structure is a representative portion of poly-(3-hexylselenophene-*stat*-3-hexylthiophene) ($\text{R} = n\text{-C}_6\text{H}_{13}$).

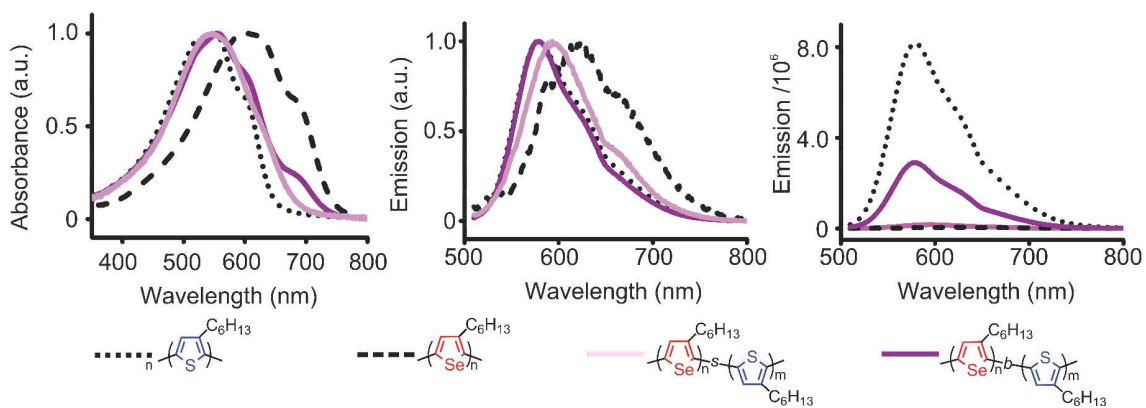


Figure S2. Solution absorbance (left) normalized (center) and relative (right) emission spectra. The key shows the polymer structures and their corresponding line colors in the spectra.

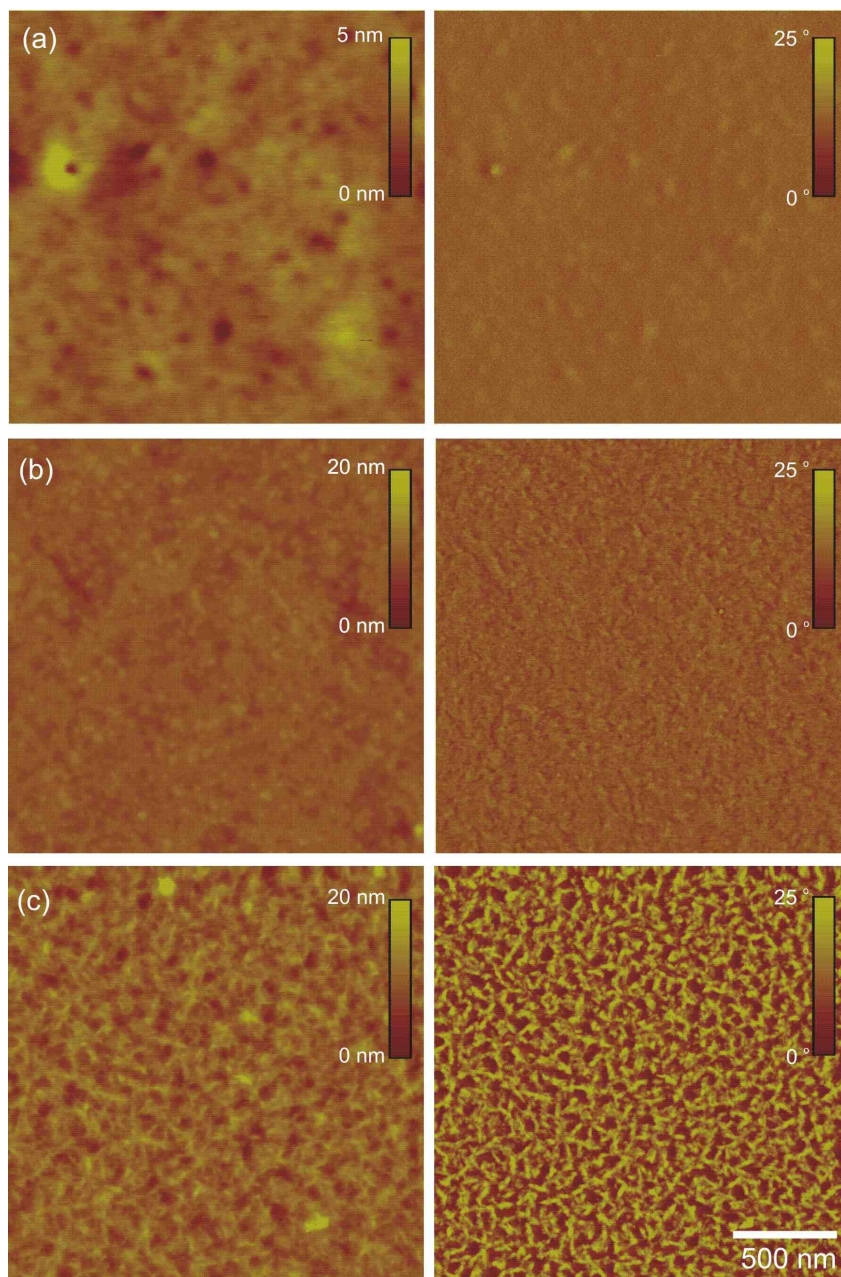


Figure S3. AFM height (left) and phase (right) image of (a) 1:1 wt % blend of P3HT and P3HS, (b) poly-(3-hexylselenophene-*stat*-3-hexylthiophene), and (c) poly-(3-hexylselenophene-*block*-3-hexylthiophene).

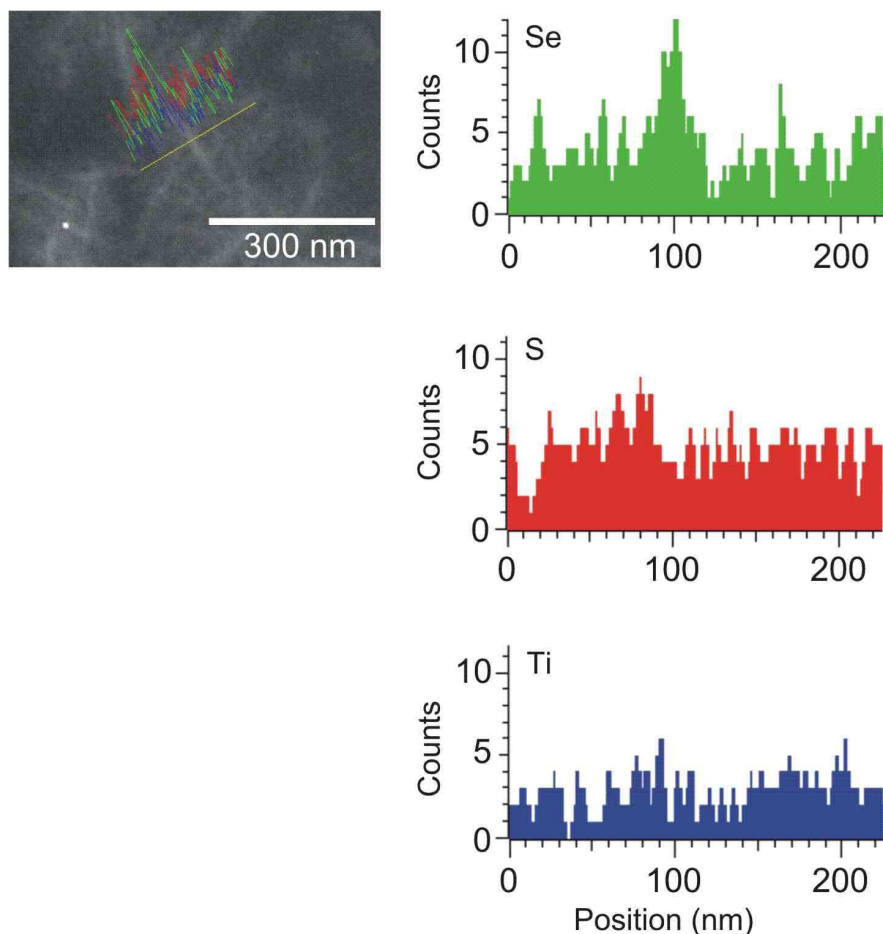


Figure S4. STEM image and elemental mapping of a poly-(3-hexylselenophene-*block*-3-hexylthiophene) film showing selenium, sulfur, and titanium content as a function of position.

Additional References

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2. Trznadel M.; Pron, A.; Zagorska, M.; Chrzaszcz, R.; Pielichowski, J. *Macromolecules*, **1998**, *31*, 5051.