Regioregular poly(3-hexyl)selenophene: A low bandgap organic hole transporting polymer.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-300 (300 MHz), using the residual solvent resonance of CDCl$_3$ or TMS as an internal reference and are given in ppm. [77]Se spectra were recorded at 76.278 MHz using selenophene as an internal reference. Absorption spectra were collected by a Perkin Elmer Lamba 9 UV-VIS spectrophotometer. Microanalyses were obtained with an elementar vario EL analyzer. Mass spectra were obtained from an Agilent GCMS using a 6890 series GC with a 5973 MSD (EI). Molecular weight determinations were carried out in chlorobenzene solution at 60ºC on an Agilent 1100 series HPLC using two Polymer Laboratories mixed B columns in series, and the system was calibrated against narrow weight PL polystyrene calibration standards. DSC measurements were performed on a TA Q100 under nitrogen. Degradation tests were performed upon a Hereaus Suntester using a 1500 W Xenon arc lamp, with a water cooled substrate holder. Cyclic voltammetry measurements were taken on solid samples deposited on the working electrode (glassy carbon) from 1,2-dichlorobenzene in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrode and referenced to ferrocene, which has a HOMO of -4.8 eV.

Thin-film organic field-effect transistors (OFETs) were fabricated in a dry nitrogen glove box environment on highly doped silicon substrates with thermally grown silicon oxide (SiO$_2$) insulating layer (thickness 230 nm), where the substrate served as a common gate electrode. Transistor source-drain gold contacts were photolithographically defined on the SiO$_2$ layer. FET substrates were solvent cleaned and then ozone treated for 10 min in a custom built low-pressure mercury lamp setup. Devices were then treated with octyltrichlorosilane by immersing substrates in 10mM solutions in heated toluene (60ºC) for 15 min, followed by a thorough washing with hexane, acetone and isopropanol. Thin semiconductor films were then deposited by spin-coating solutions in warm 1,2-dichlorobenzene (10 mg/ml) at a spin speed of 3,000 rpm. The samples were then dried and annealed at 100ºC for 10 min and measured in the absence of light. Electrical characteristics were calculated as previously reported.[1] HOMO energy levels were directly determined by an ambient photoelectron spectroscopy method with a Riken-Keiki AC-2 spectrometer.[2]

<u>2,5-Dibromo-3-hexylselenophene:</u>

To a solution of 3-hexylselenophene (0.90 g, 4.6 mmol) in THF (20 ml) at 0ºC was added N-bromosuccinimide (1.66 g, 9.3 mmol) in six portions over 40 min. The resulting solution was stirred in the dark at room temperature for 16 h. The solvent was removed under reduced pressure and the resulting residue was dissolved in ethyl acetate (50 ml) and washed with water (2 x 30 ml). The aqueous washings were combined and further extracted with ethyl acetate. The combined organics were washed with saturated sodium chloride, dried (sodium sulphate), filtered and concentrated under reduced pressure. The resulting pale yellow oil was filtered through silica (eluent: petrol 40-60ºC) to afford a colourless oil (1.39 g, 80%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.98 (s, 1H), 2.48 (t, 2H, J = 7.8 Hz), 1.53 (m, 2H), 1.29 (m, 6H), 0.89 (t, 3H, J = 6.6 Hz). ^{13}C NMR (75 MHz, CDCl$_3$) δ 144.9, 134.2, 113.5, 111.0, 31.6, 30.7, 29.5, 28.8, 22.6, 14.1. MS (EI) 374 (t). Found C, 32.4; H, 3.9. Calc. for C$_{10}$H$_{14}$Br$_2$Se$_1$ C, 32.2; H, 3.8.

<u>Poly(3-hexyl)selenophene (P3HS):</u>

To a solution of 2,5-dibromo-3-hexylselenophene (5.22 g, 14 mmol) in dry THF (50 ml) at 20 ºC was added n-butyl magnesium chloride (6.3 ml of a 2M solution in THF, 12.6 mmol). The resulting solution was stirred for 50 min at 20 ºC and then heated to reflux for 1 h. Heating was removed, and 1,2-(bis(diphenylphosphino)ethane)dichloronickel (II) (41 mg, 0.078 mmol) was added at once as a solid. Once the resulting exotherm had subsided, the reaction was refluxed for 21 h. The reaction was cooled to 20ºC and precipitated into methanol. The resulting suspension was stirred for 20 min. The solid was filtered and washed (Soxhlet) with methanol (20 h), acetone (24 h) and THF (24 h). The residue was dissolved in hot chlorobenzene, filtered and precipitated into methanol. Filtration afforded the polymer as a deep red powder (2.51 g). GPC (C_6H_5Cl, 60ºC) Mn 39,000, Mw 75,500. ^{1}H NMR (300 MHz, $CDCl_3$, 50ºC) δ 7.11 (s, 1H), 2.73 (t, 2H, J = 7.3 Hz), 1.69 (quint, 2H), 1.43 (m, 2H), 1.29 (br m, 4H), 0.91 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 50ºC) δ 141.45, 139.93, 138.12, 132.31, 31.74, 30.73, 30.65, 29.31, 22.64, 14.03. [77]Se ($CDCl_3$) δ 610.61. Found C, 56.5; H, 6.6. Calc. for $(C_{10}H_{14}Se)_n$ C, 56.3; H, 6.6
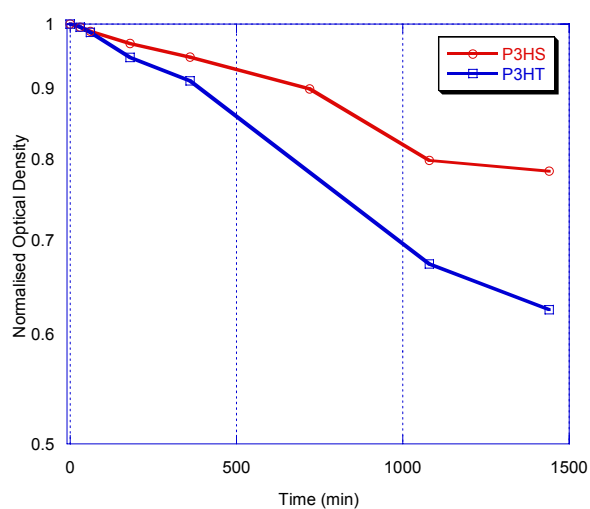

Figure S1. Plot showing ratio of intensity of initial λ_{max} vs exposed λ_{max} as a function of exposure time to 1500W Xenon arc lamp for 25 nm thick spin coated films on a quatz substrate for P3HS (λ_{max} = 626 nm) and P3HT (520 nm)
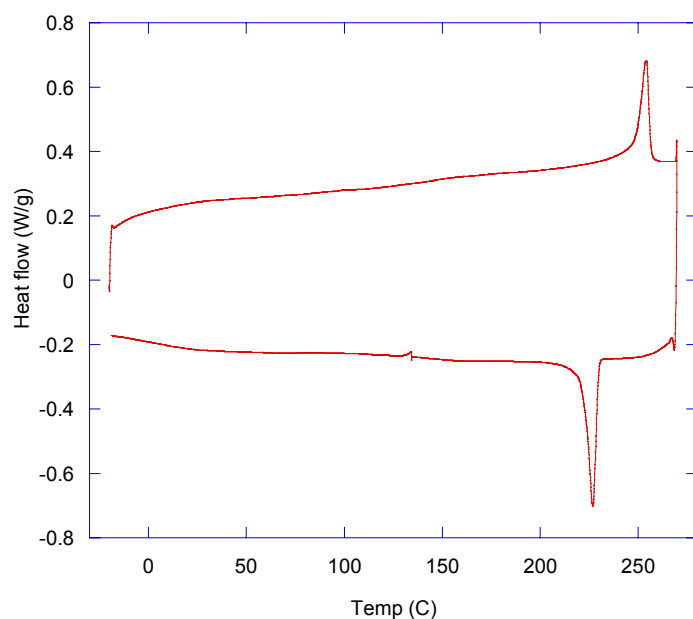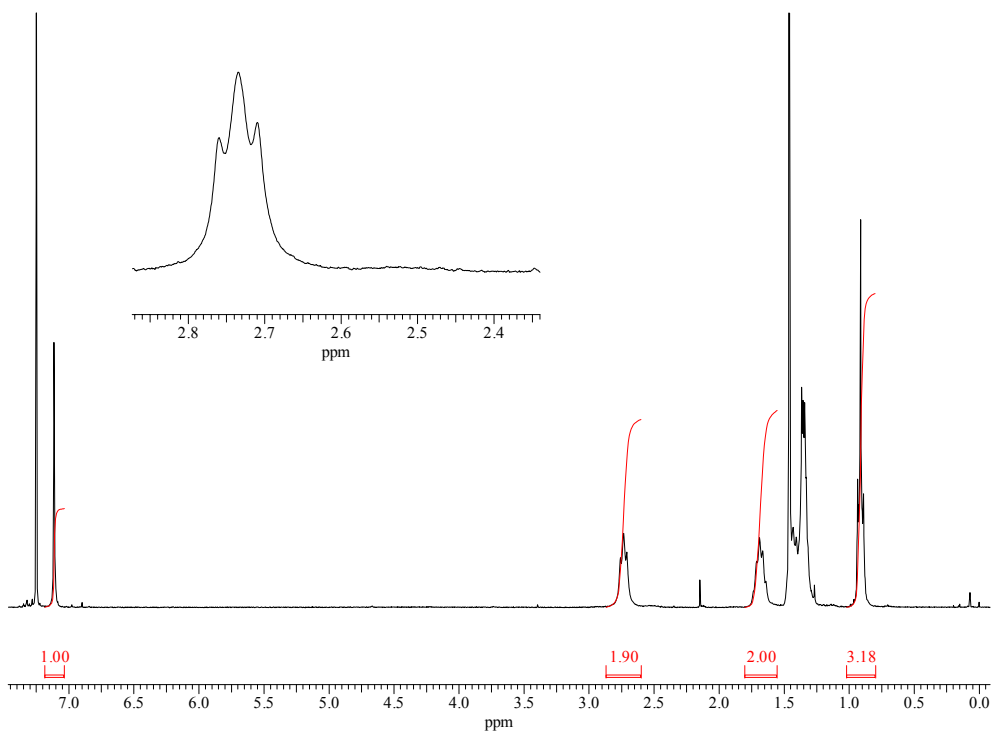
Figure S2. DSC of P3HS (second heating cycle at 10C/min).
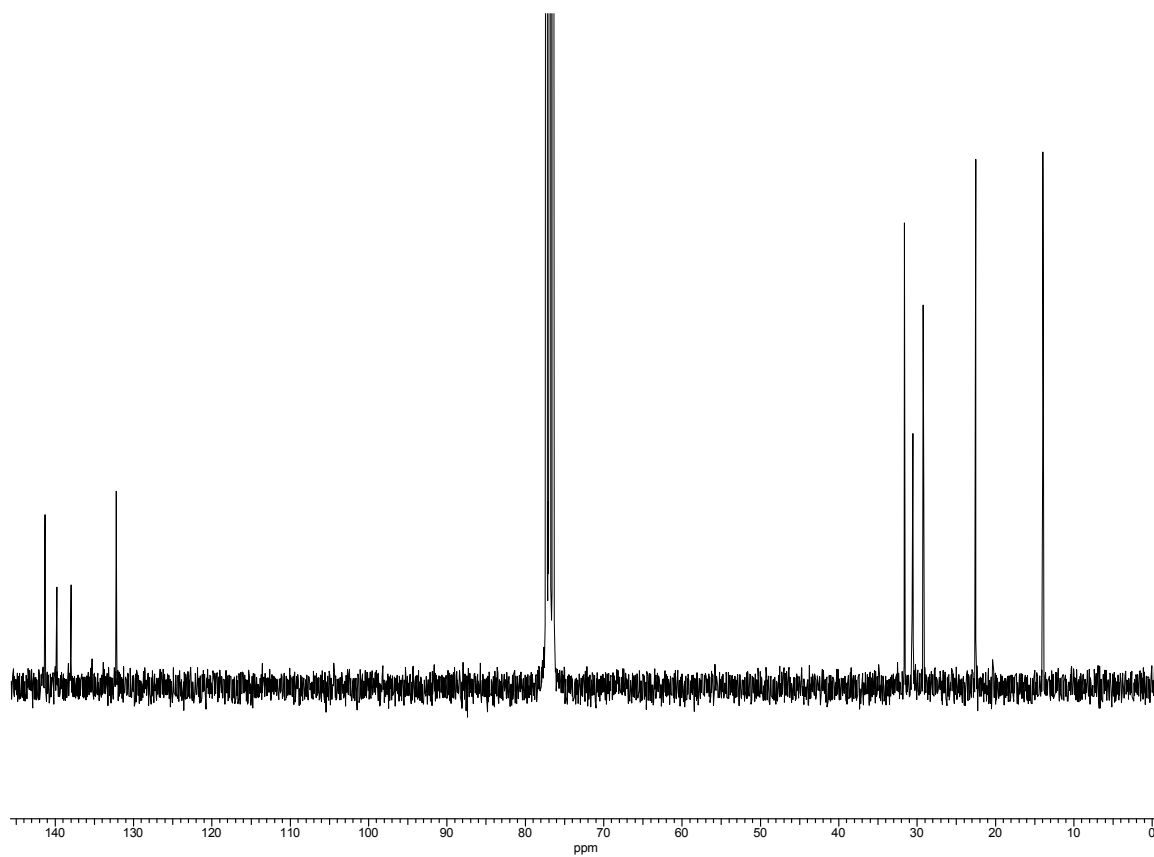

Figure S3. ^{1}H NMR of P3HS in CDCl$_3$.

Figure S4. ^{13}C NMR of P3HS in CDCl$_3$.

X-ray Scattering Measurements. A film of P3HS was spin-coated from a solution in 1,2-dichlorobenzene (5 mg/mL) onto a silicon wafer with native oxide treated with octyltrichlorosilane. The film was subsequently annealed at 250° C under nitrogen. Grazing incidence measurements of x-ray scattering were performed at the Stanford Synchrotron Radiation Laboratory on beam-line 11-3 using an area detector (MAR345 image plate). The incident energy was 12.7 keV and the angle of incidence was ~0.1°. Typical exposure times for the area detector measurements were 20 minutes. Data are expressed as a function of the scattering vector, $\mathbf{q}$, that has magnitude of $(4\pi/\lambda)\sin\theta$, where θ is half the scattering angle and λ is the wavelength of the incident radiation; the *d*-spacing of a peak is simply $2\pi/q$.
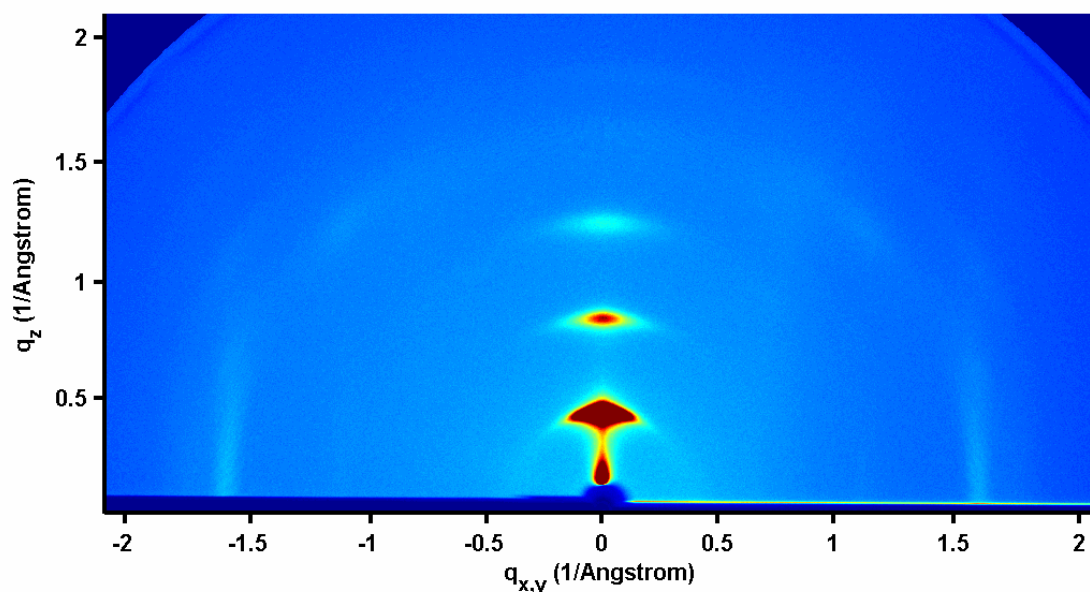

Figure S5. Grazing incidence X-ray scattering from a thin film of P3HS annealed at 250° C.

1.   M. Heeney, C. Bailey, M. Giles, M. Shkunov, D. Sparrowe, S. Tierney, W. Zhang and I. McCulloch, *Macromolecules*, 2004, **37**, 5250.

2.   T. Sano, Y. Hamada and K. Shibata, *IEEE J. Sel. Top. Quantum. Electron.*, 1998, **4**, 34.