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Supplementary Information

Molecular Weight and End Capping Effects on the Optoelectronic Properties of Structurally Related 'Heavy Atom' Donor–acceptor Polymers

*Gregory L. Gibson, Dong Gao, Ashlee A. Jahnke, Jing Sun, Andrew J. Tilley, and Dwight S. Seferos**

Lash Miller Chemical Laboratories, Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, M5S 3H6 Canada

^{1}H NMR Spectra

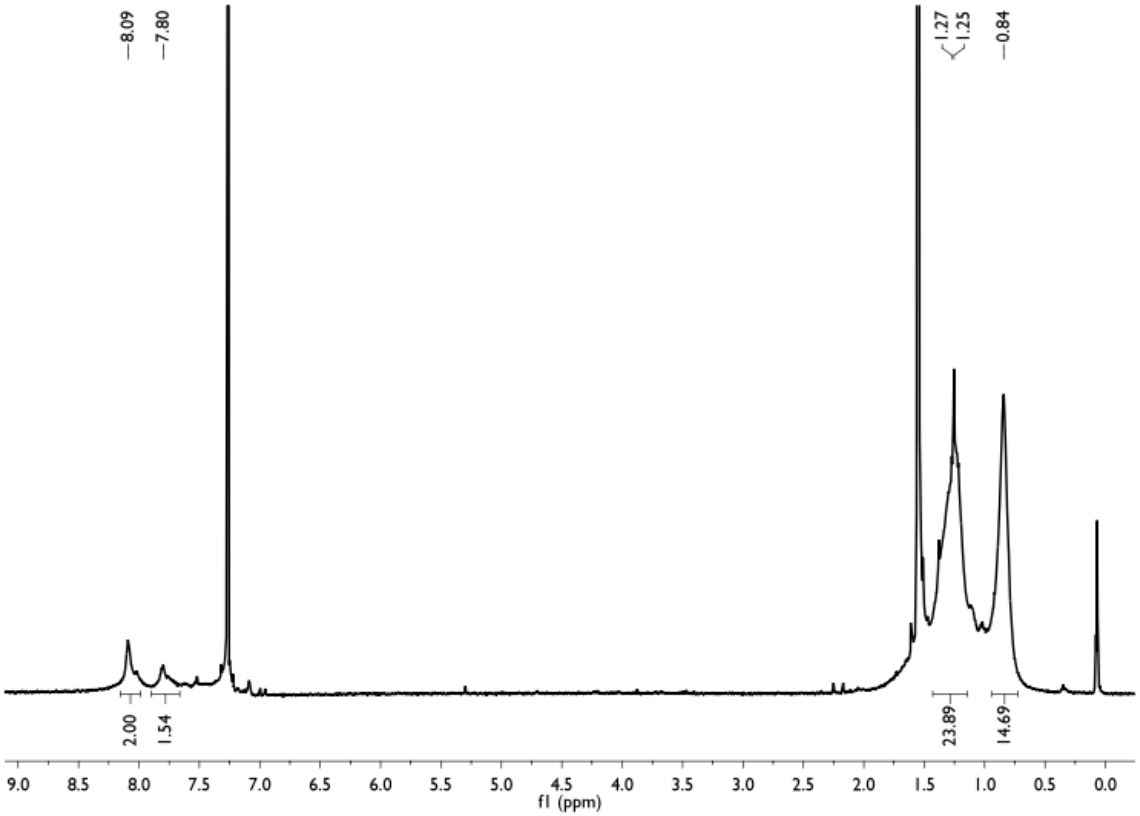

Fig. S1 ^{1}H NMR spectrum of M_n = 8 kg mol^{-1} $\mathbf{P_{SiSe}}$ (400 MHz, $CDCl_3$).

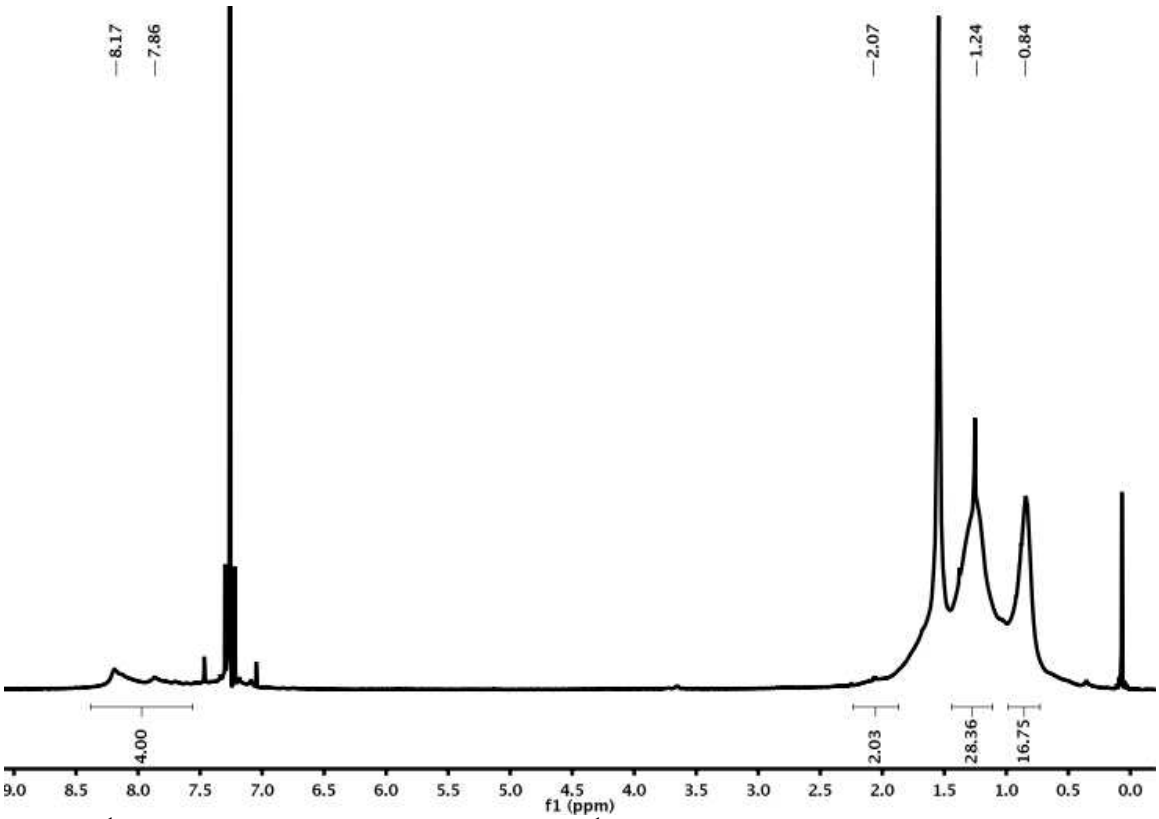

Fig. S2 ^{1}H NMR spectrum of M_n = 11 kg mol^{-1} $\mathbf{P_{SiSe}}$ (400 MHz, $CDCl_3$).

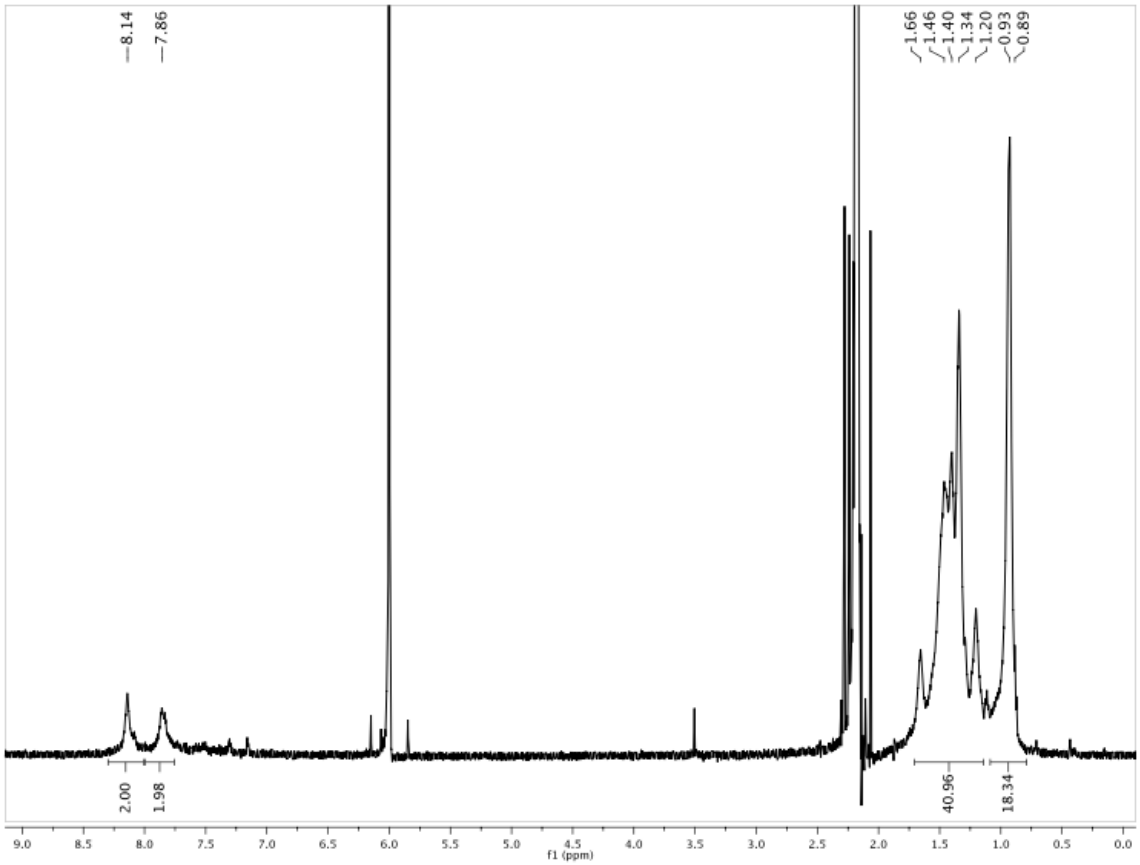

Fig. S3 ^{1}H NMR spectrum of M_n = 18 kg mol^{-1} $\mathbf{P_{SiSe}}$ (130 °C, 600 MHz, 1,1,2,2-tetrachloroethane-d_2).

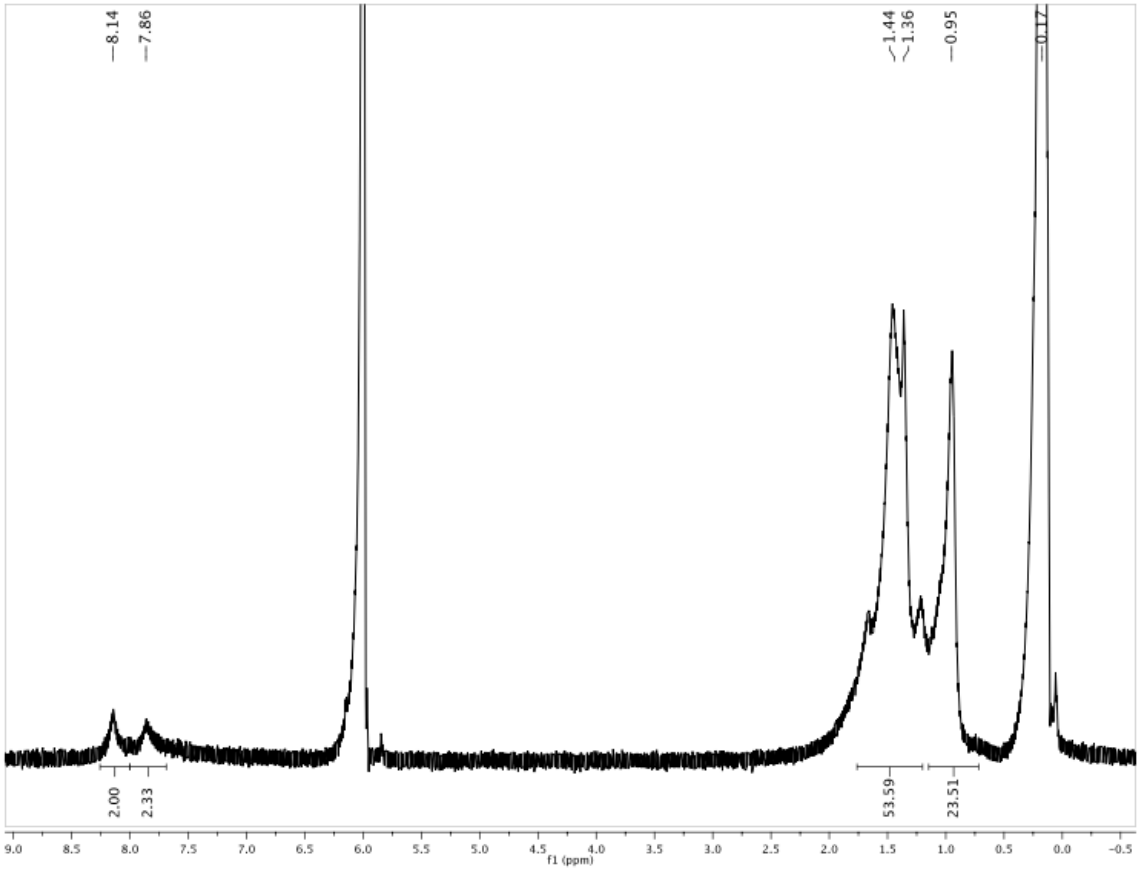

Fig. S4 ^{1}H NMR spectrum of M_n = 33 kg mol^{-1} $\mathbf{P_{SiSe}}$ (130 °C , 600 MHz, 1,1,2,2-tetrachloroethane-d_2).

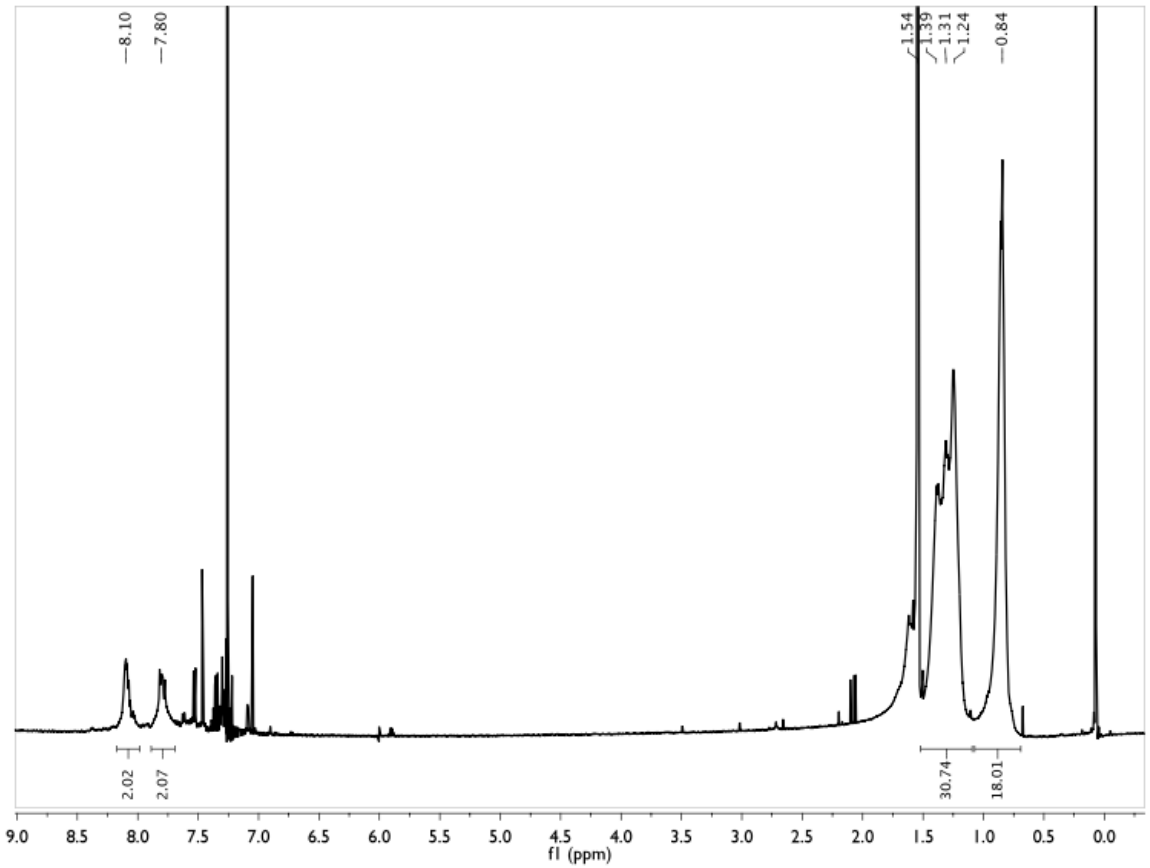

Fig. S5 ^{1}H NMR spectrum of M_n = 5 kg mol^{-1} $\mathbf{P_{GeSe}}$ (400 MHz, $CDCl_3$).

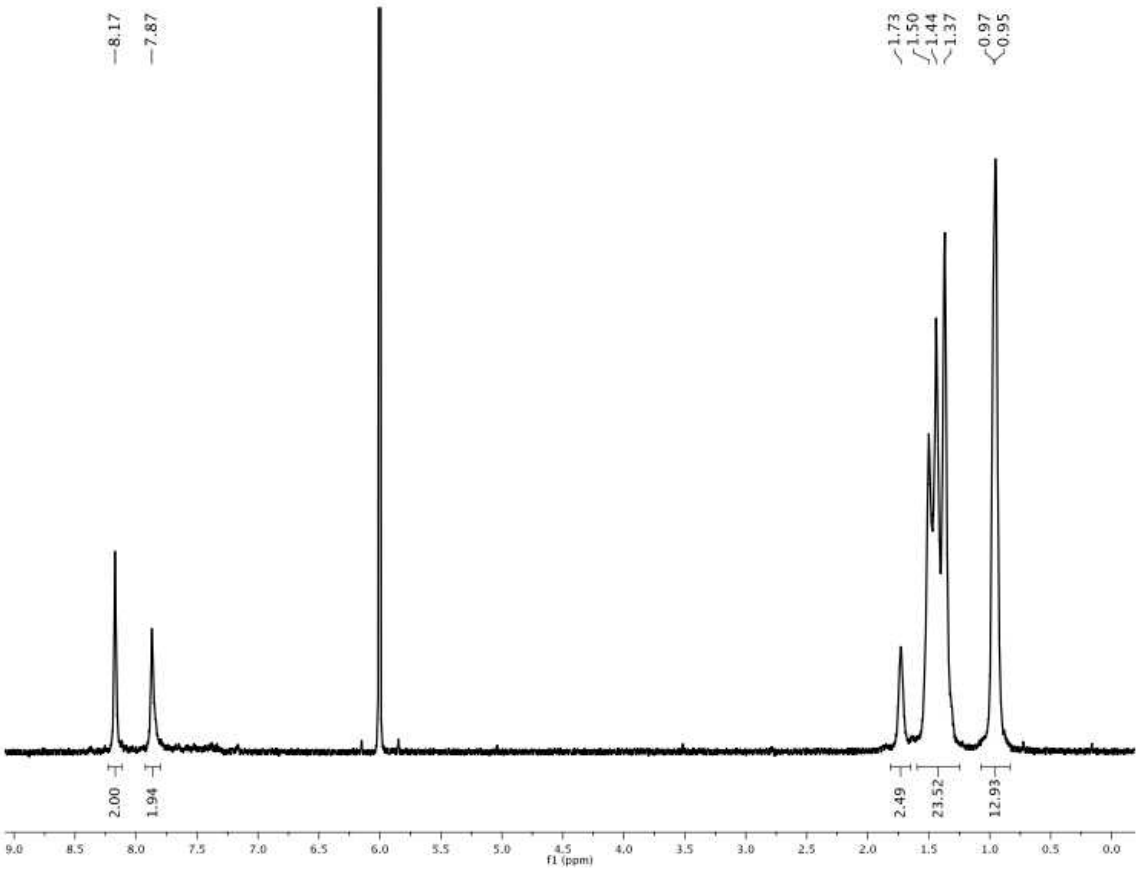

Fig. S6 ^{1}H NMR spectrum of M_n = 16 kg mol^{-1} $\mathbf{P_{GeSe}}$ (130 °C, 600 MHz, 1,1,2,2-tetrachloroethane-d_2).

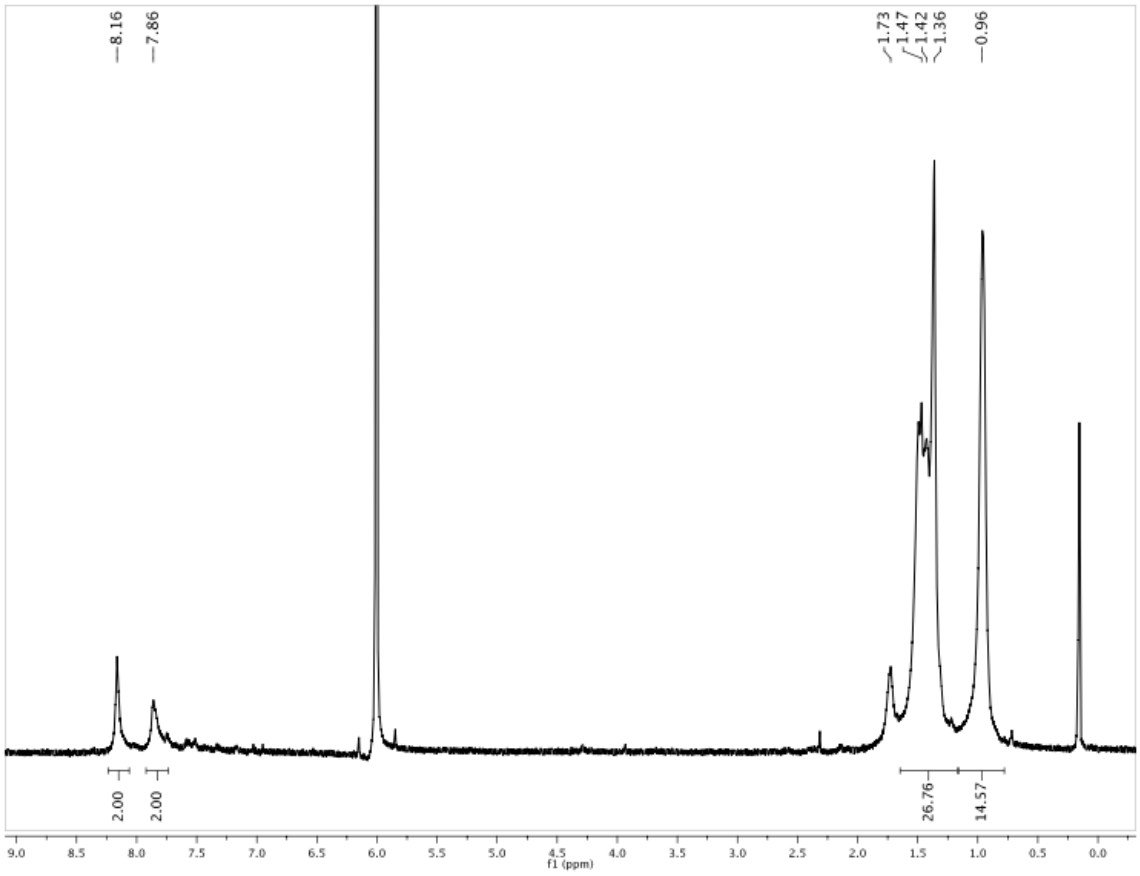

Fig. S7 ^{1}H NMR spectrum of M_n = 24 kg mol^{-1} $\mathbf{P_{GeSe}}$ (130 °C, 600 MHz, 1,1,2,2-tetrachloroethane-d_2).

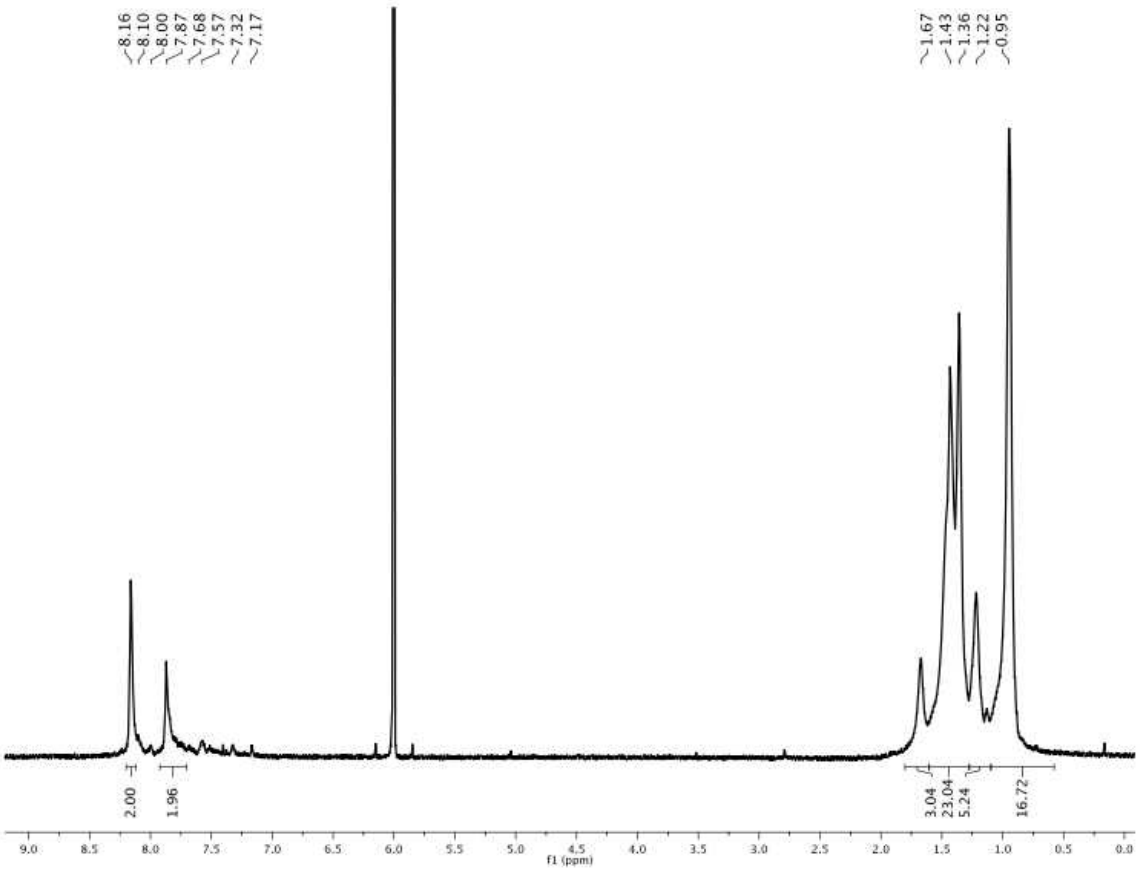

Fig. S8 ^{1}H NMR spectrum of phenyl end-capped M_n = 11 kg mol^{-1} **PhP$_{SiSe}$** (130 °C, 600 MHz, 1,1,2,2-tetrachloroethane-d$_2$).

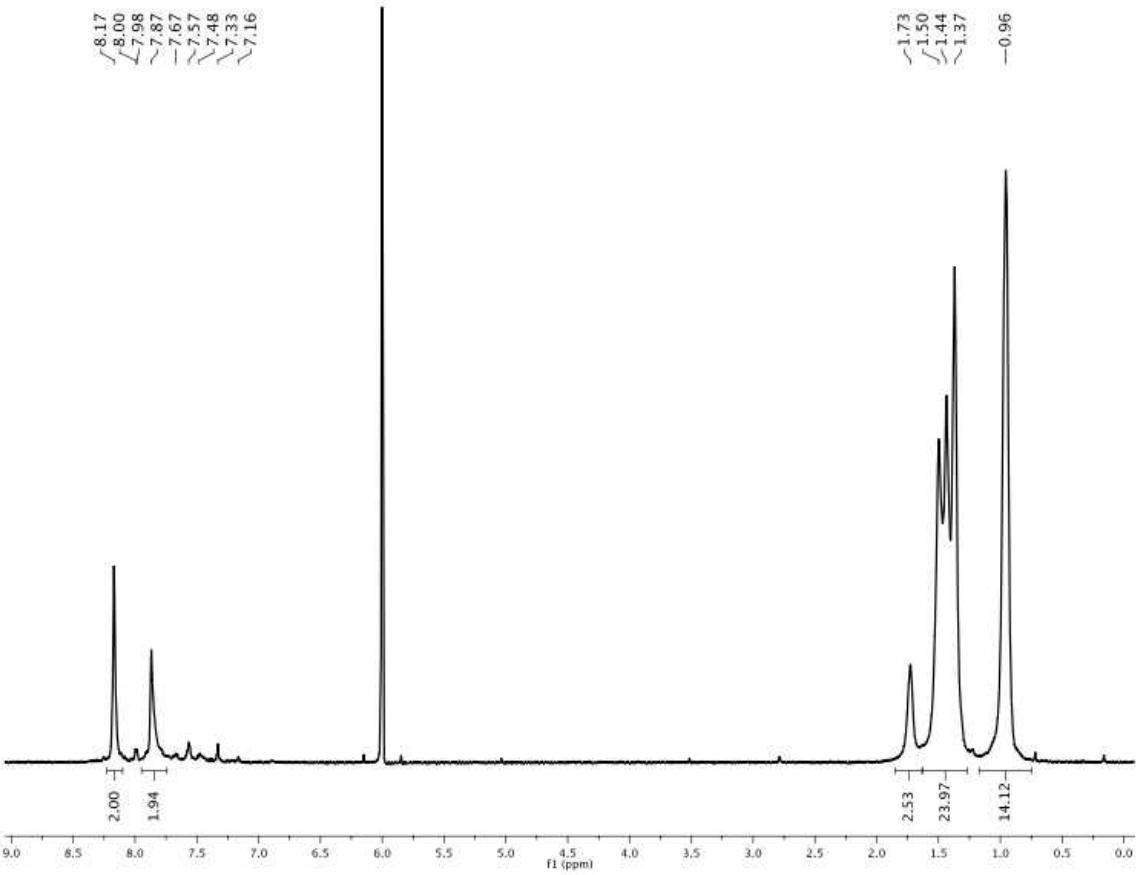

Fig. S9 ^{1}H NMR spectrum of phenyl end-capped M_n = 11 kg mol^{-1} **PhP$_{GeSe}$** (130 °C, 600 MHz, 1,1,2,2-tetrachloroethane-d$_2$).

Additional Spectroscopic Data

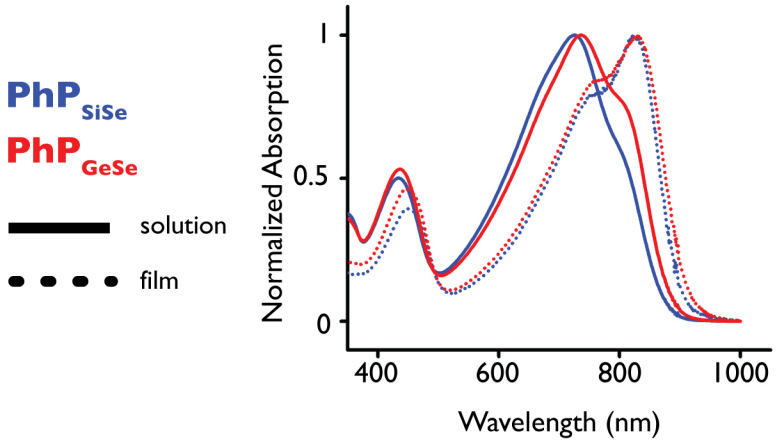

Fig. S10 PhP_{SiSe} and **PhP_{GeSe}** solution and film absorption spectra; solution spectra collected at ~ 10^{-6} M in chlorobenzene; films spin coated from chlorobenzene solution.

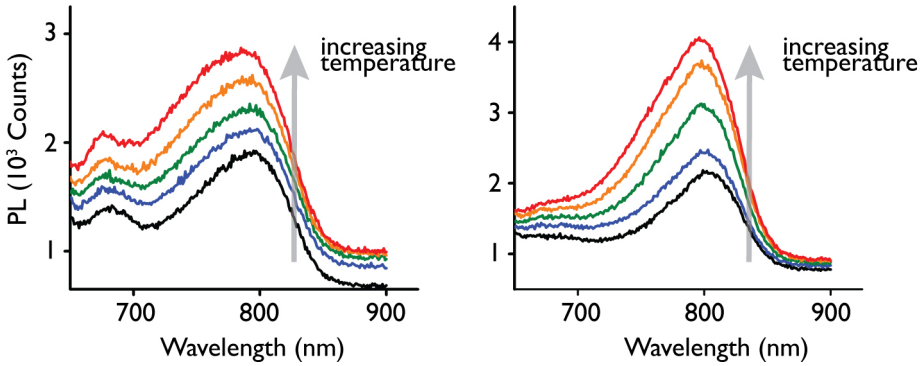

Fig. S11 33P$_{SiSe}$ (left) and **24P$_{GeSe}$** (right) emission spectra in chlorobenzene (~ 10^{-6} M) collected at 20 °C (black), 40 °C (blue), 60 °C (green), 80 °C (orange) and 100 °C (red).

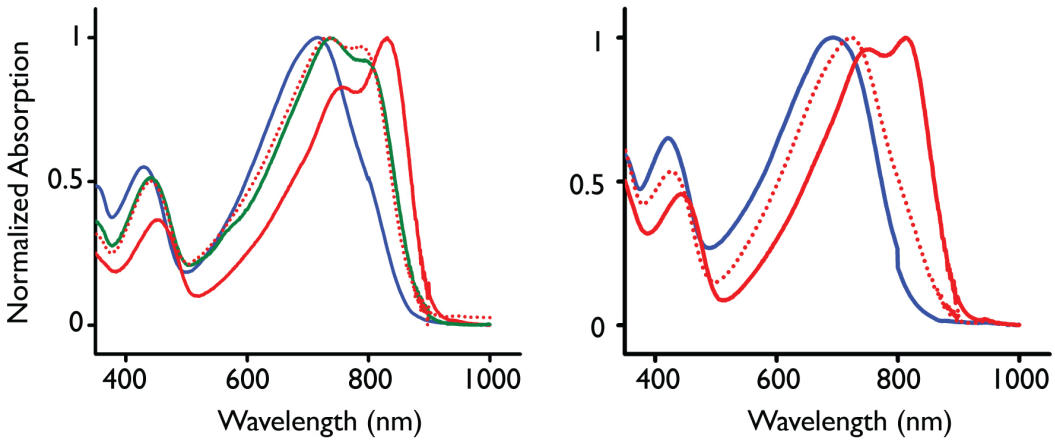

Fig. S12 (left) **33P$_{SiSe}$** solution absorption trace at 80 °C (dotted red) overlaid on solution **11P$_{SiSe}$**, **18P$_{SiSe}$**, and **33P$_{SiSe}$** absorption spectra at 20 °C from Figure 1; (right) **24P$_{GeSe}$** solution absorption trace at 100 °C (dotted red) overlaid on **5P$_{GeSe}$** and **24P$_{GeSe}$** solution absorption spectra at 20 °C from Figure 1.

Cyclic Voltammetry Data

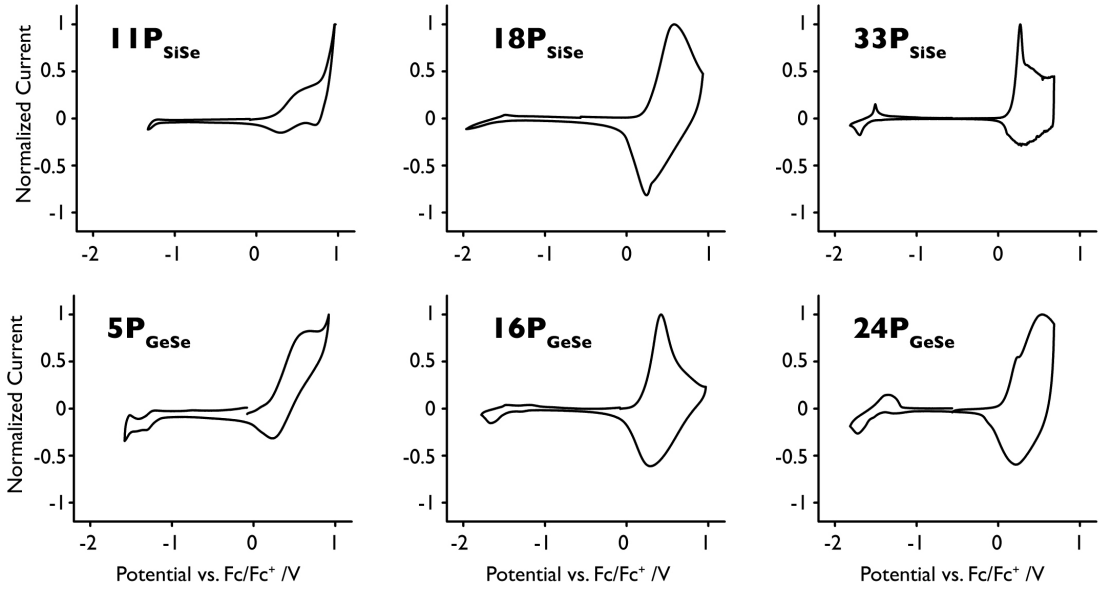

Fig. S13 Polymer film CV traces collected in 0.1M $TBAPF_6$ in acetonitrile at a 50 mv s^{-1} scan rate.

Complete 2D Wide Angle X-ray Scattering Plots

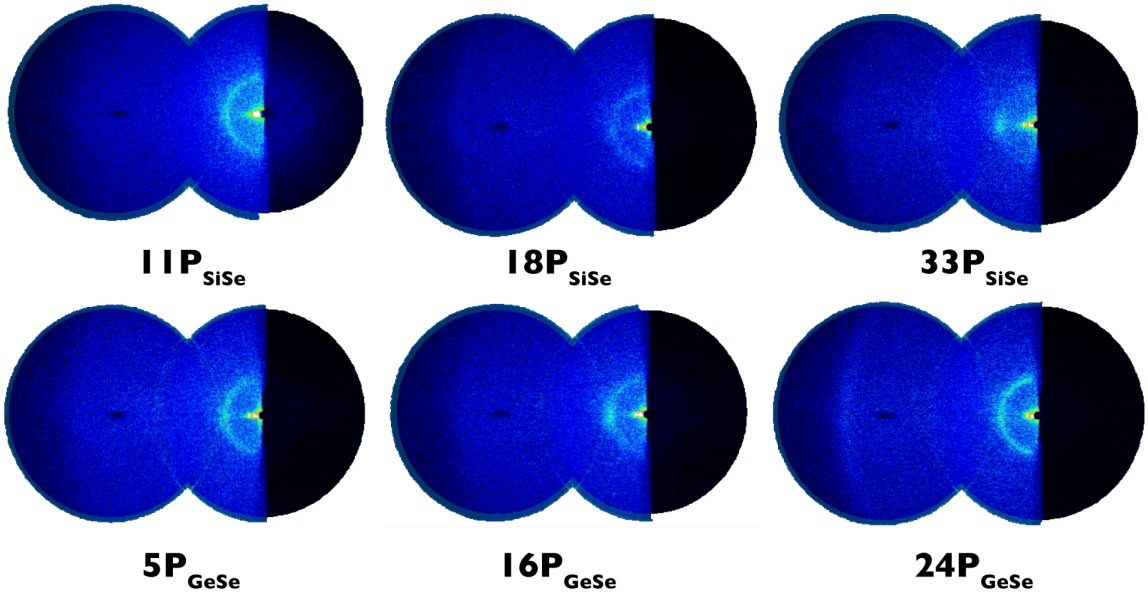

Fig. S14 Polymer film 2D-wide angle x-ray scattering plots.

Additional Microscopy Data

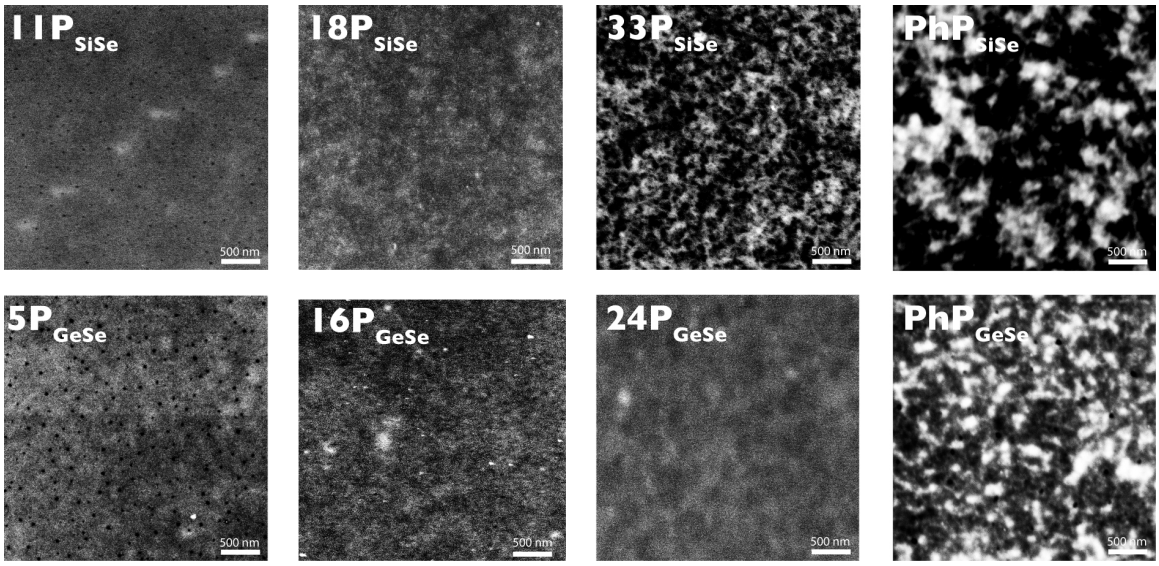

Fig. S15 Scanning transmission electron microscopy images of 1:1 polymer:$PC_{71}BM$ fullerene films.