Electronic Supplementary Information (ESI) for

Donor−Acceptor Polymers with Tunable Infrared Photoresponse

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Computation. All DFT and TD-DFT calculations were carried out with the Gaussian 09 package (version C.01)[1] employing the B3LYP exchange-correlation functional[2] and a polarized 6-31G(d) basis set using default SCF convergence criteria (density matrix converged to at least 10^{-8}), DFT integration grid (75 radial and 302 angular quadrature points) and optimization convergence criteria (RMS force of at least 0.0003 Hartree/Bohr). The HOMO and LUMO figures for the **P2** and **P3** tetramers are shown in Figures S1-S4.

Table S1. Calculated data for (**P1**–**P5**) at the B3LYP/6-31G(d) level of theory.

	HOMO[a]	LUMO[a]	E_g [b]	f [c]	$E_g^{vert}(n\rightarrow\infty)$ [d]
P1b[e]	−4.62	−3.15	1.47	6.82	1.08
P1	−4.32	−2.98	1.34	7.02	1.04
P2	−4.25	−3.01	1.24	6.56	0.94
P3	−4.40	−3.28	1.12	5.91	0.88
P4	−4.16	−3.25	0.91	10.01	0.68
P5	−4.14	−3.26	0.88	9.74	0.63

[a]Frontier molecular orbital energies as determined at the at the B3LYP/6-31G(d) level of theory. [b]HOMO/LUMO orbital energy gap (E_g). [c]Oscillator strength (f). [d]S_0 to S_1 vertical transition energy extrapolated to $n = \infty$ using the Kuhn equation ($E_g^{vert}(n\rightarrow\infty)$). All energies are in eV and oscillator strength is a unitless quantity. [e]Data adopted from reference 3.

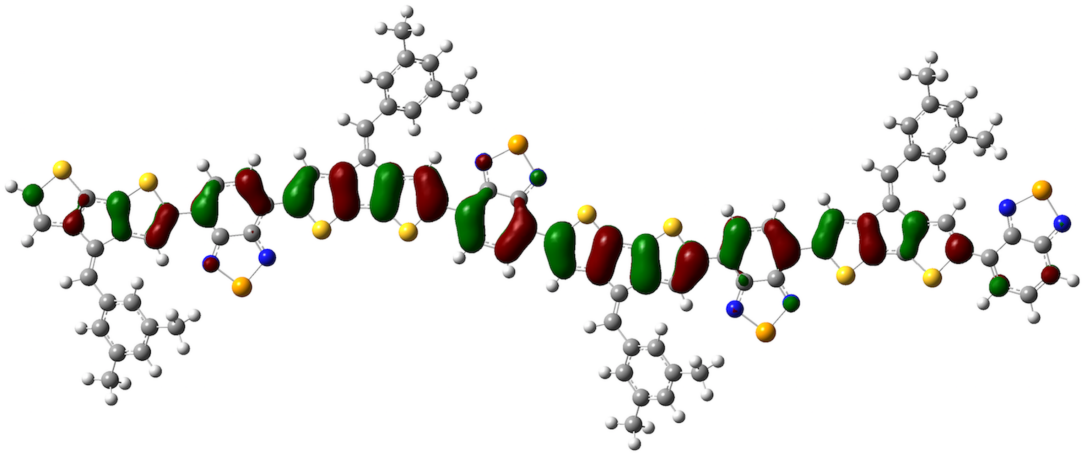

Figure S1. Optimized ground-state (S_0) geometric structures for the **P2** tetramer (n = 4) and pictorial representation of the HOMO wavefunction as determined at the B3LYP/6-31G(d) level of theory.

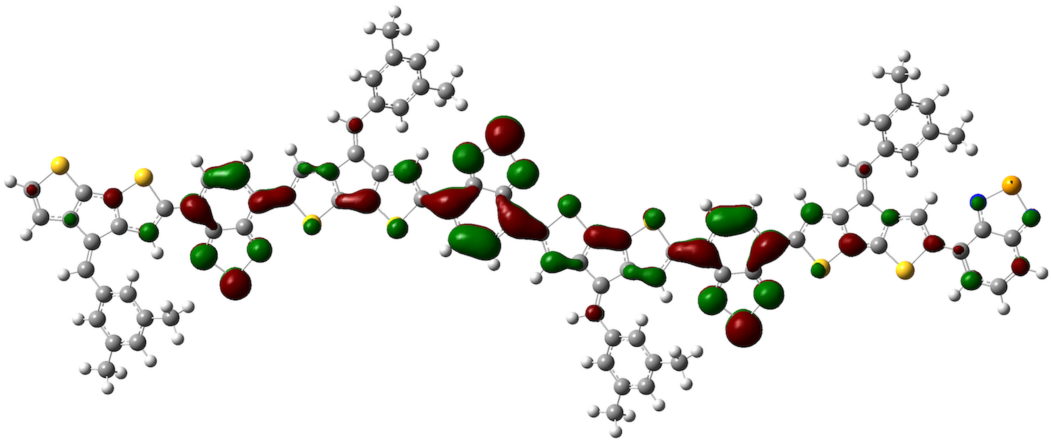

Figure S2. Pictorial representation of the LUMO wavefunction for the **P2** tetramer (n = 4) as determined at the B3LYP/6-31G(d) level of theory.

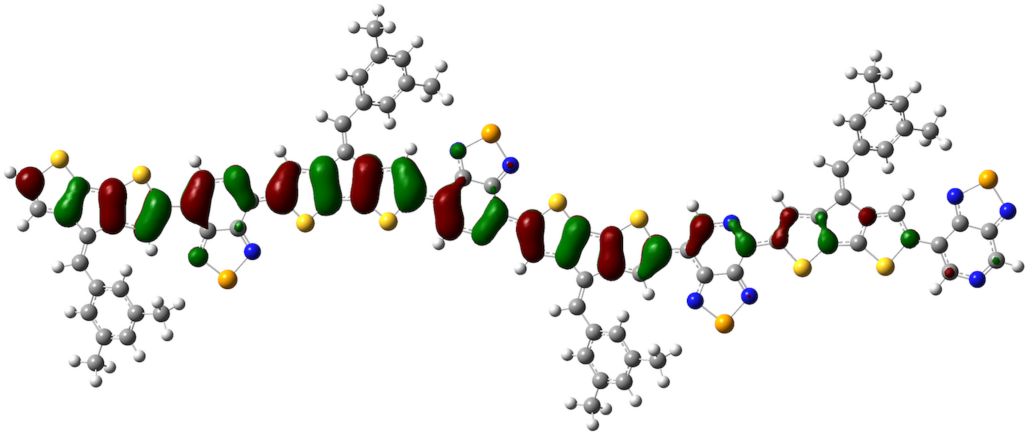

Figure S3. Optimized ground-state (S_0) geometric structures for the **P3** tetramer (n = 4) and pictorial representation of the HOMO wavefunction as determined at the B3LYP/6-31G(d) level of theory.

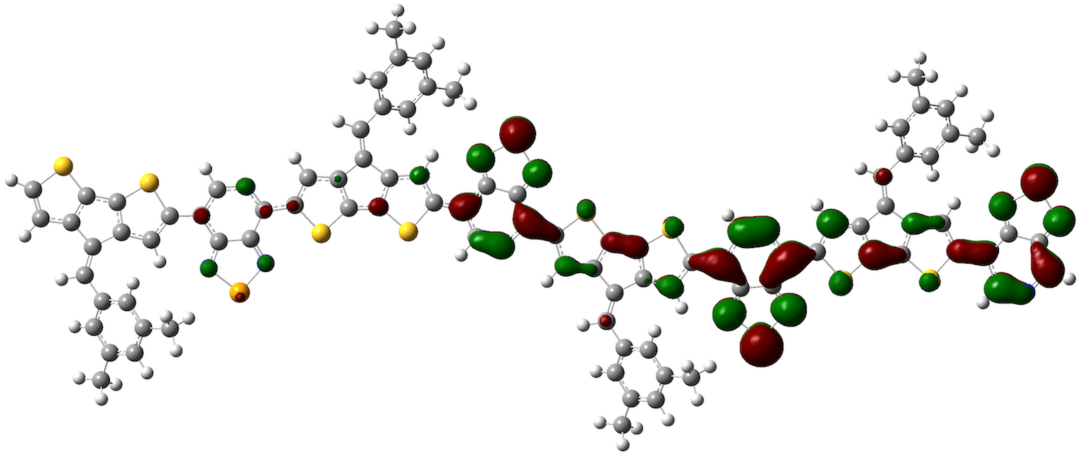

Figure S4. Pictorial representation of the LUMO wavefunction for the **P3** tetramer (n = 4) as determined at the B3LYP/6-31G(d) level of theory.

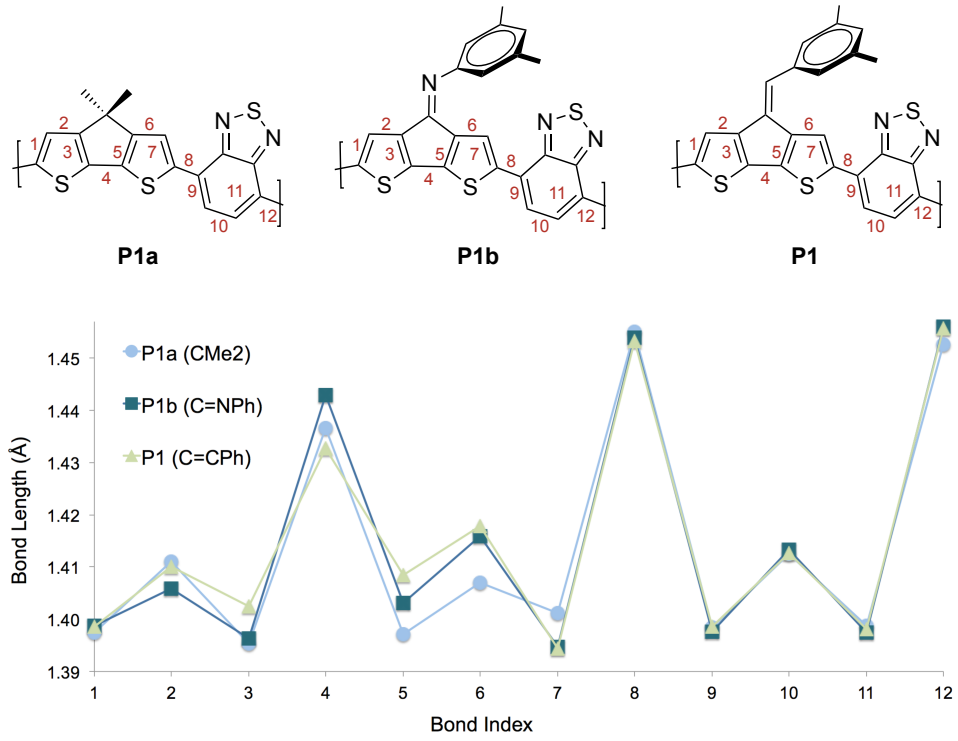

Figure S5. Repeat unit of **P1a**, **P1b**, and **P1** and bond length plots of the (central dimer) of the oligomers with $n = 6$ (C_1-C_{12} shown for clarity). Bond length values are in Å.

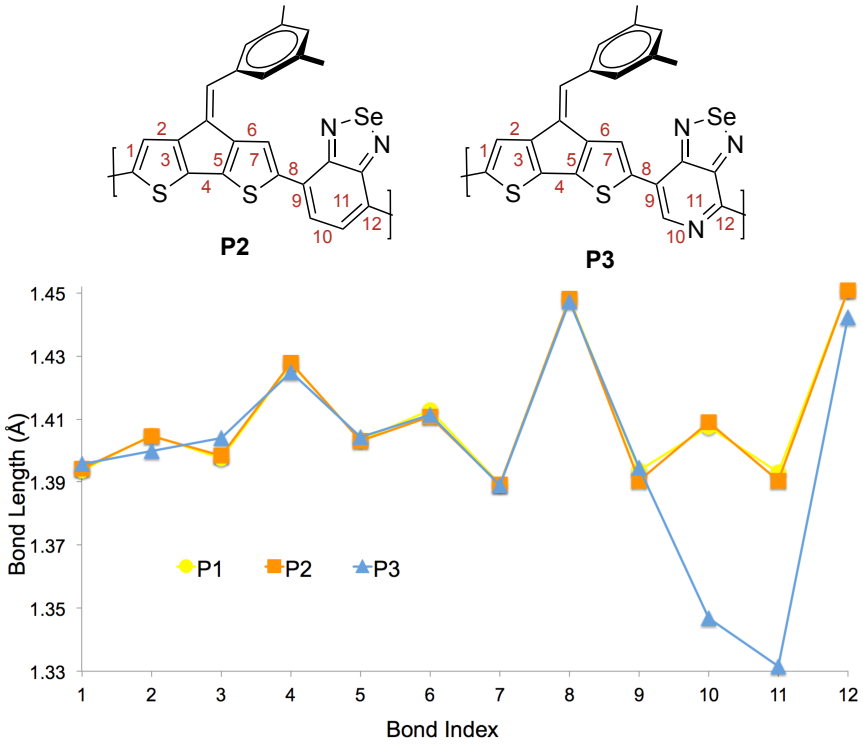

Figure S6. Repeat unit of **P1-P3** and bond length plots of the (central dimer) of the oligomers with $n = 6$ (C_1-C_{12} shown for clarity). Bond length values are in Å.

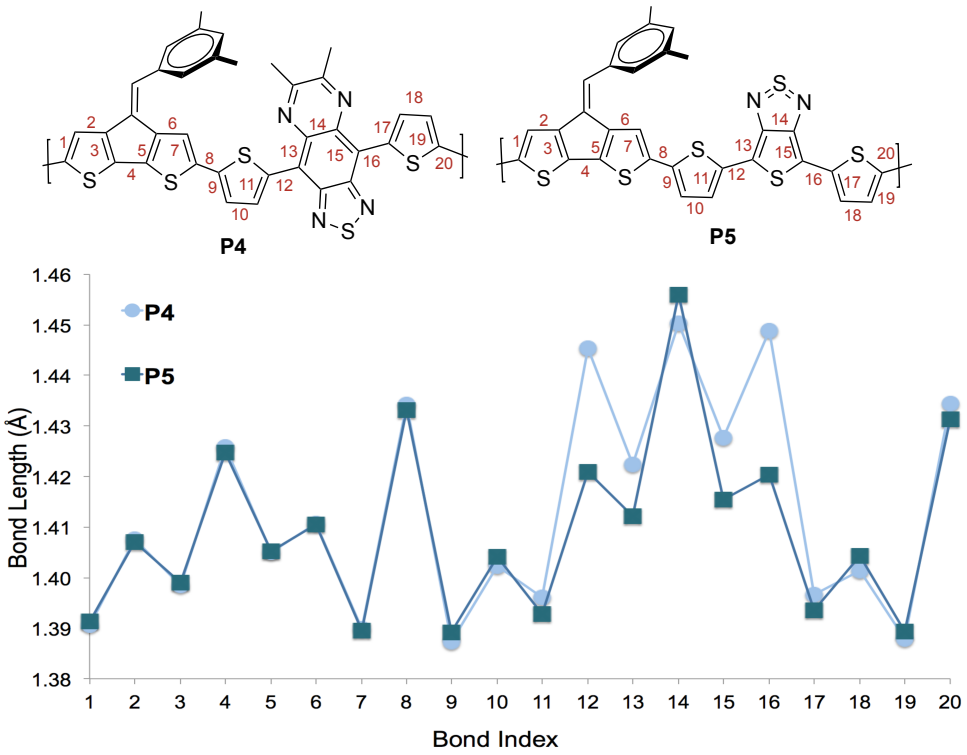

Figure S7. Repeat unit of **P4** and **P5** and bond length plots of the (central dimer) of the oligomers with $n = 6$ (C_1-C_{20} shown for clarity). Bond length values are in Å.

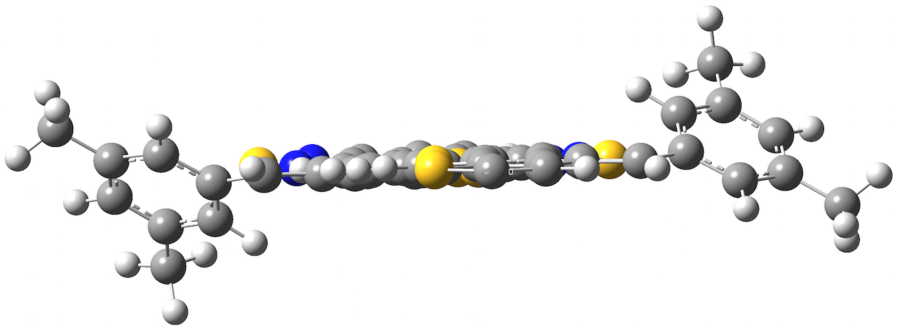

Figure S8. Side view of the optimized geometry of $(\mathbf{P1})_4$.

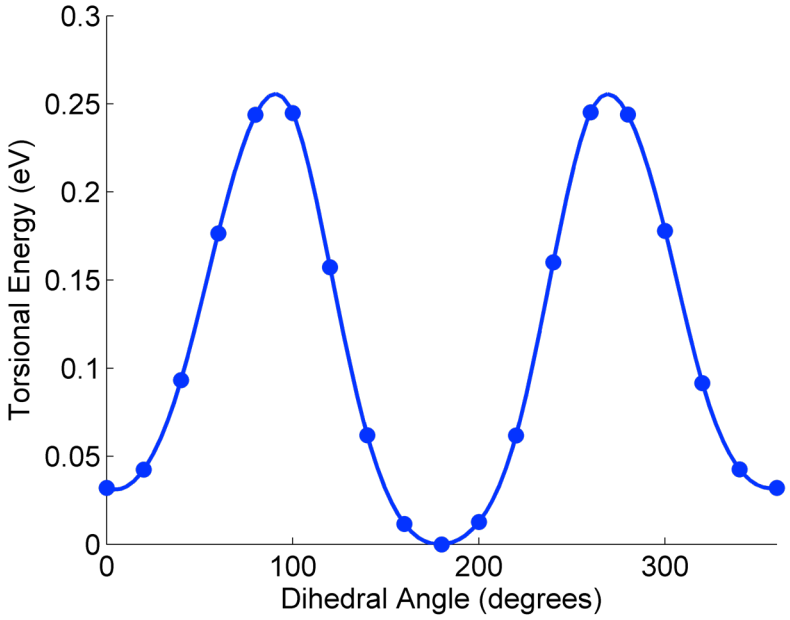

Figure S9. Torsional energy as a function of the dihedral angle for the **P1** dimer calculated at the B3LYP/6-31G(d) level of theory.

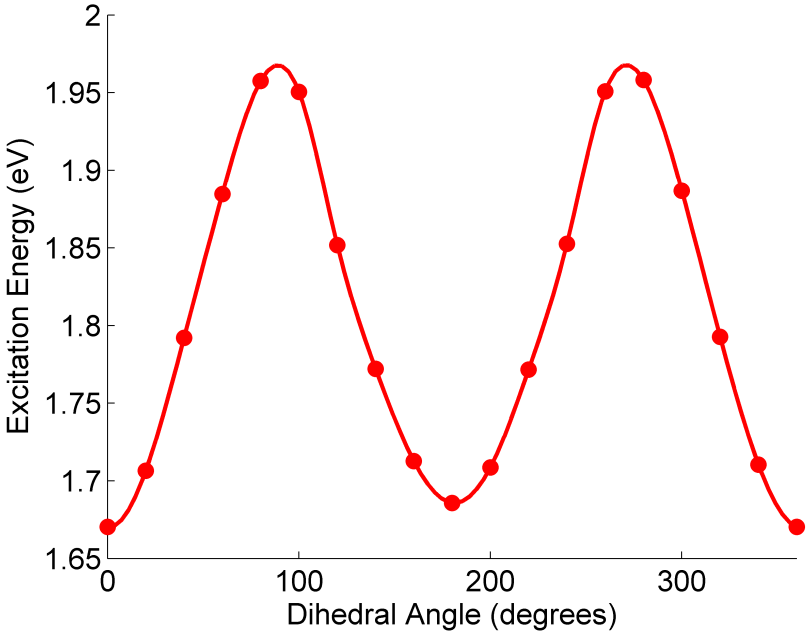

Figure S10. S_1 excitation energy as a function of the dihedral angle for the **P1** dimer calculated with time-dependent DFT at the B3LYP/6-31G(d) level of theory.

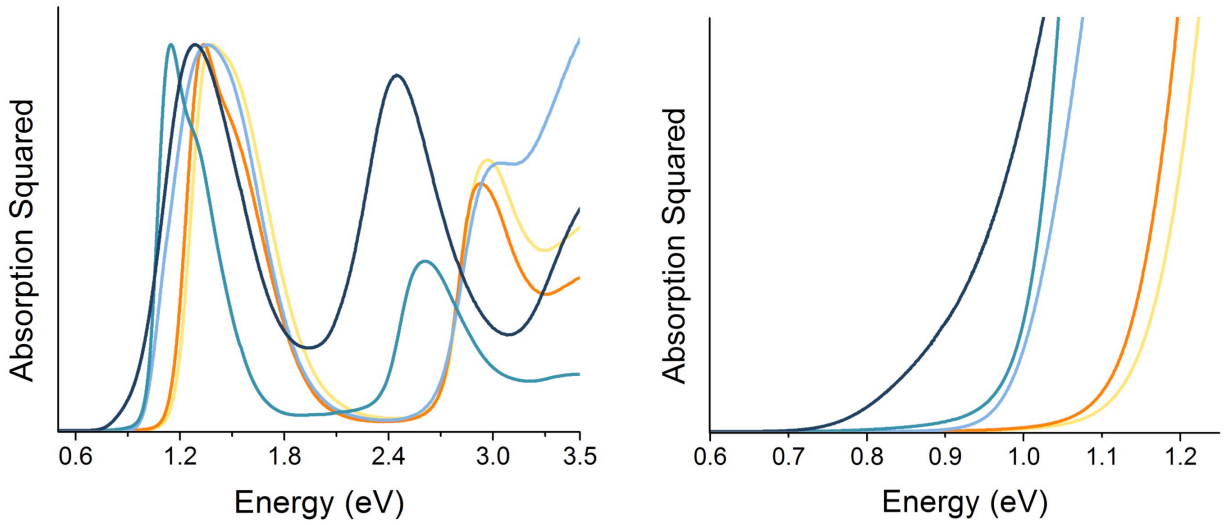

Figure S11. Absorption squared plots of **P1**-**P5** as thin films.

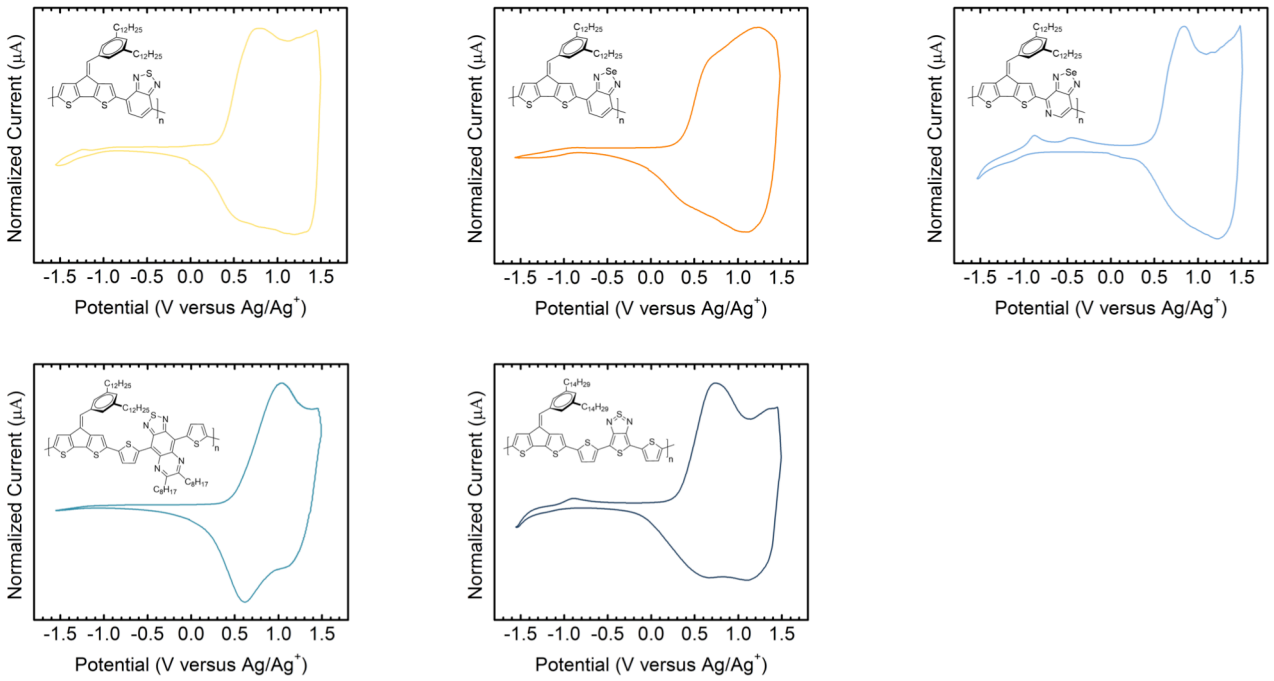

Figure S12. CV of **P1**–**P5** (third scan).

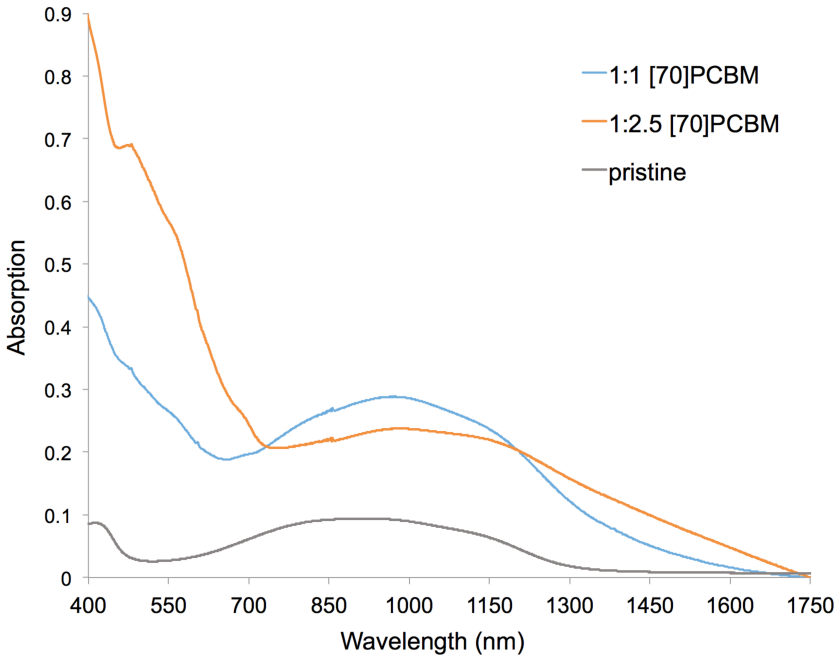

Figure S13. Absorption spectra of **P3** thin films with varying ratios of [70]PCBM.

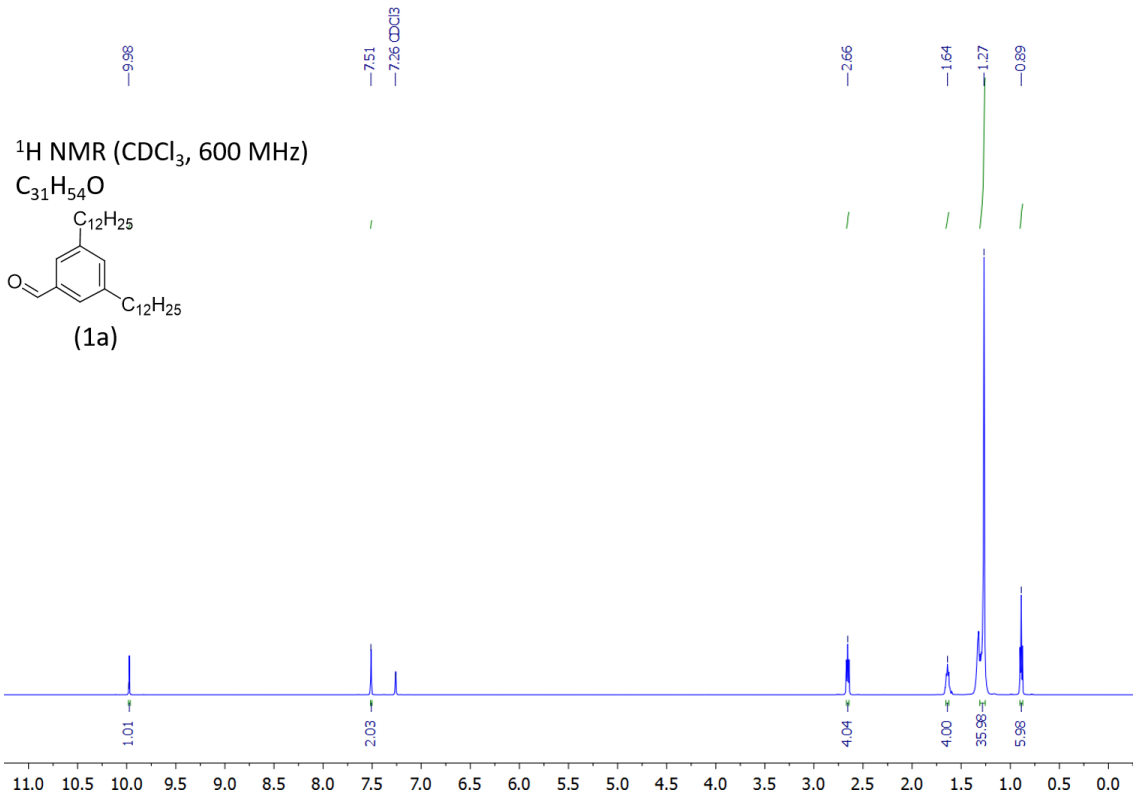

Figure S14. ^{1}H NMR spectra of **1a**.

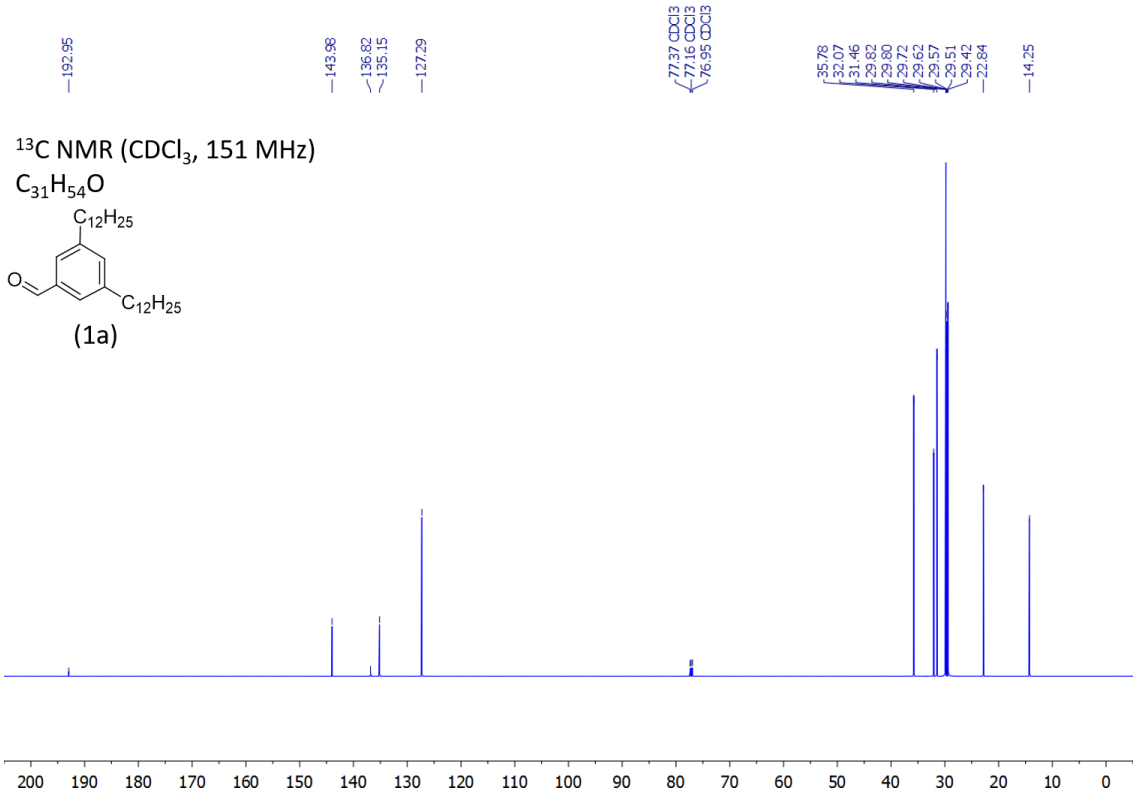

Figure S15. ^{13}C NMR spectra of **1a**.

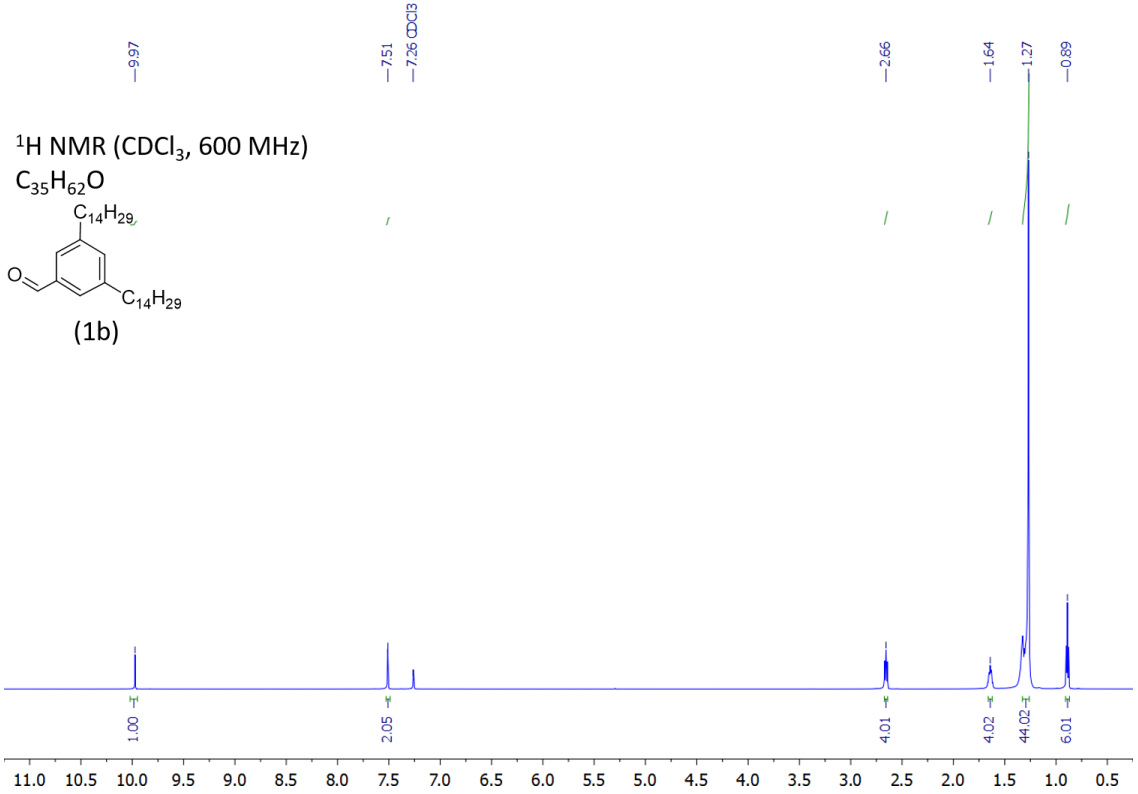

Figure S16. ^{1}H NMR spectra of **1b**.

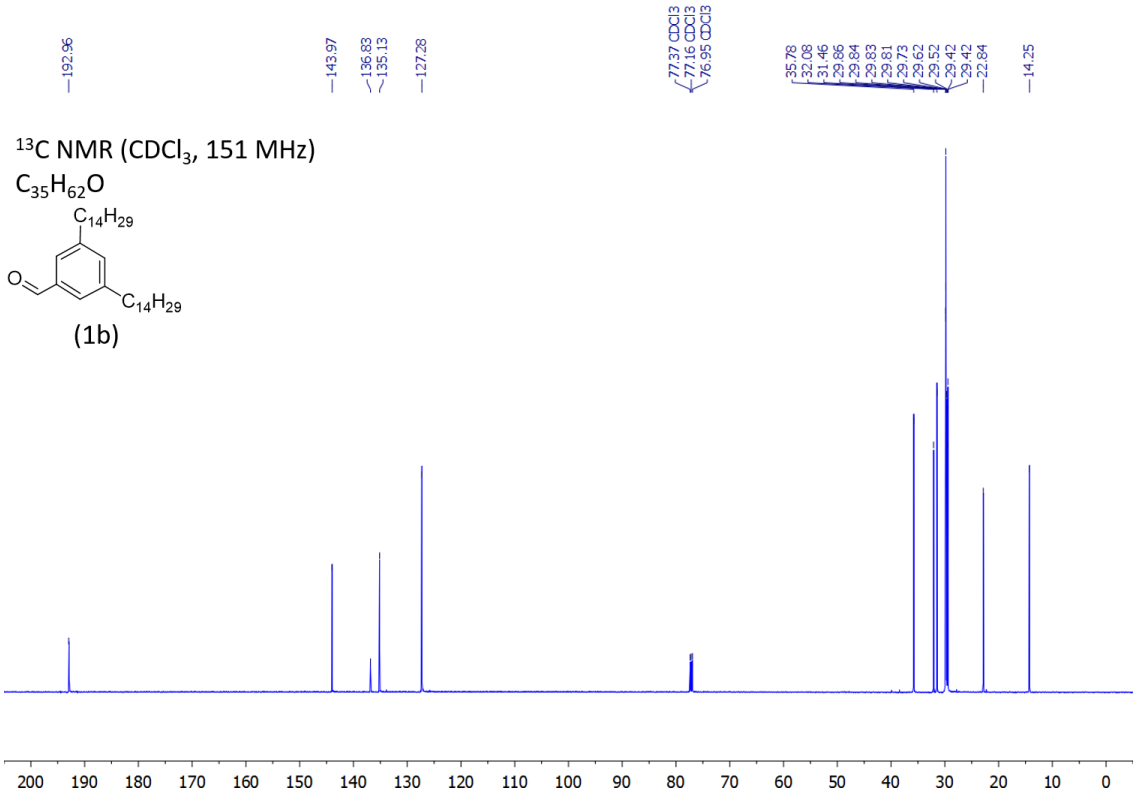

Figure S17. ^{13}C NMR spectra of **1b**.

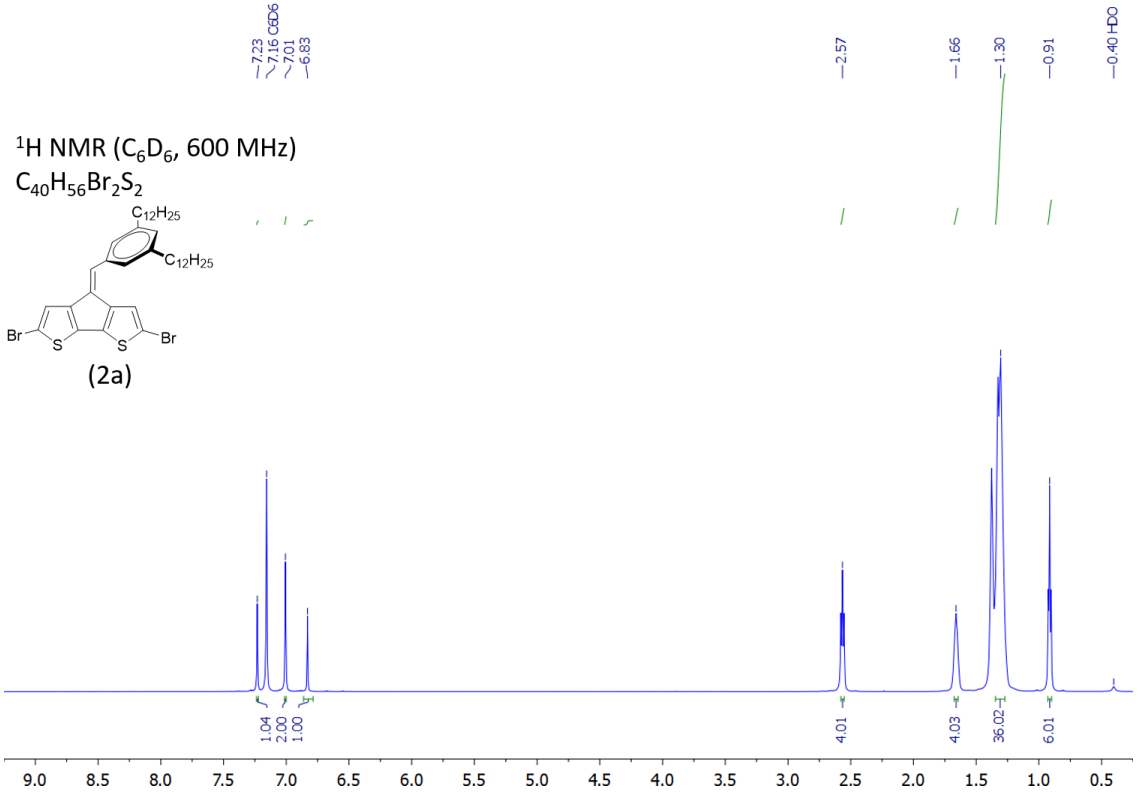

Figure S18. ^{1}H NMR spectra of **2a**.

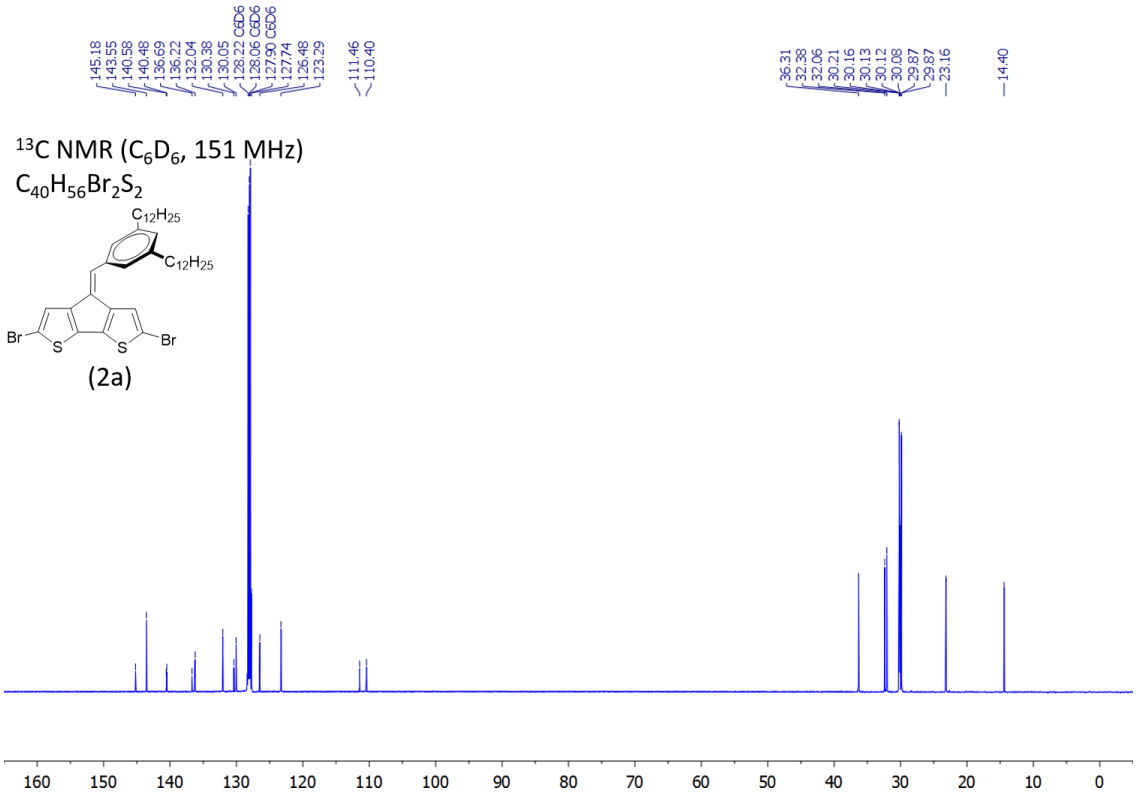

Figure S19. ^{13}C NMR spectra of **2a**.

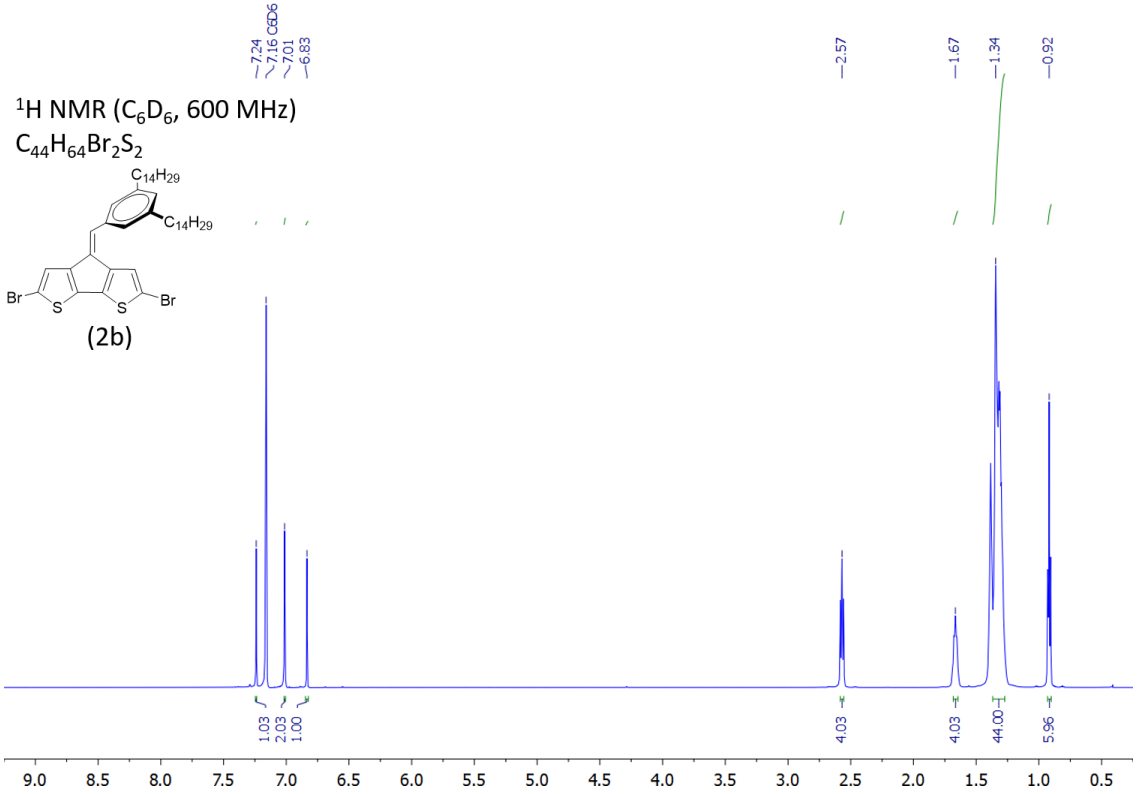

Figure S20. ^{1}H NMR spectra of **2b**.

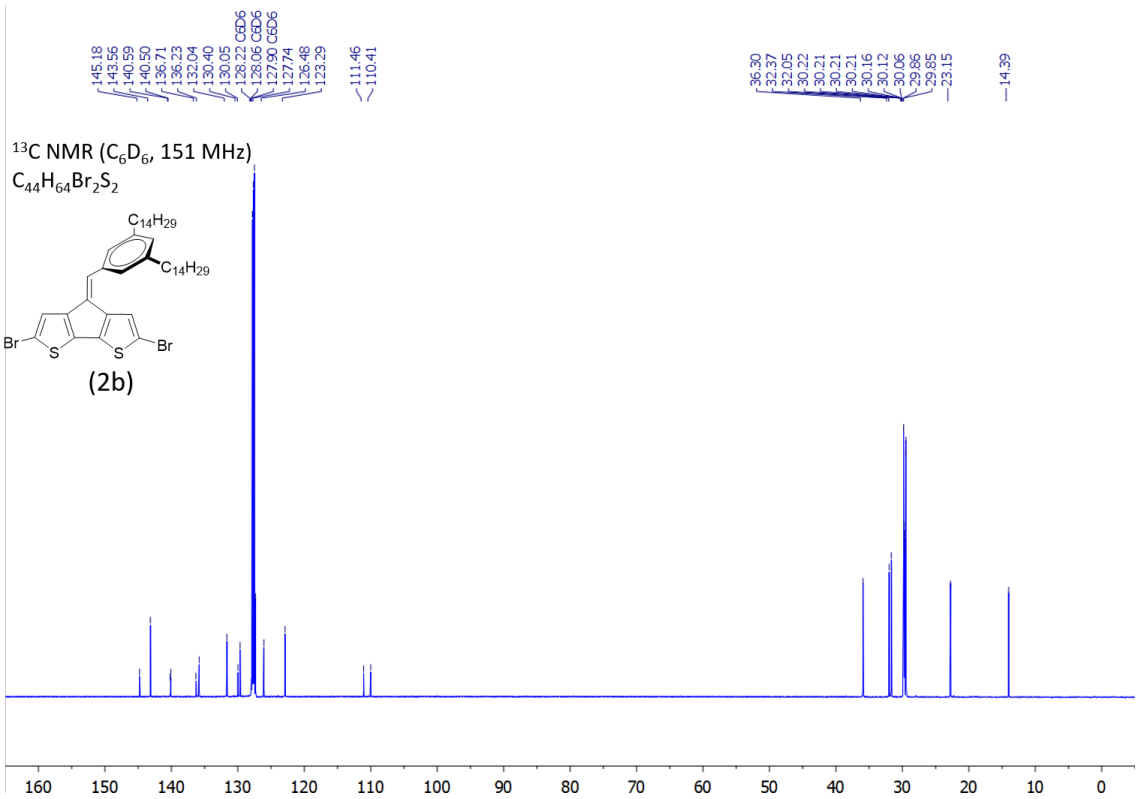

Figure S21. ^{13}C NMR spectra of **2b**.

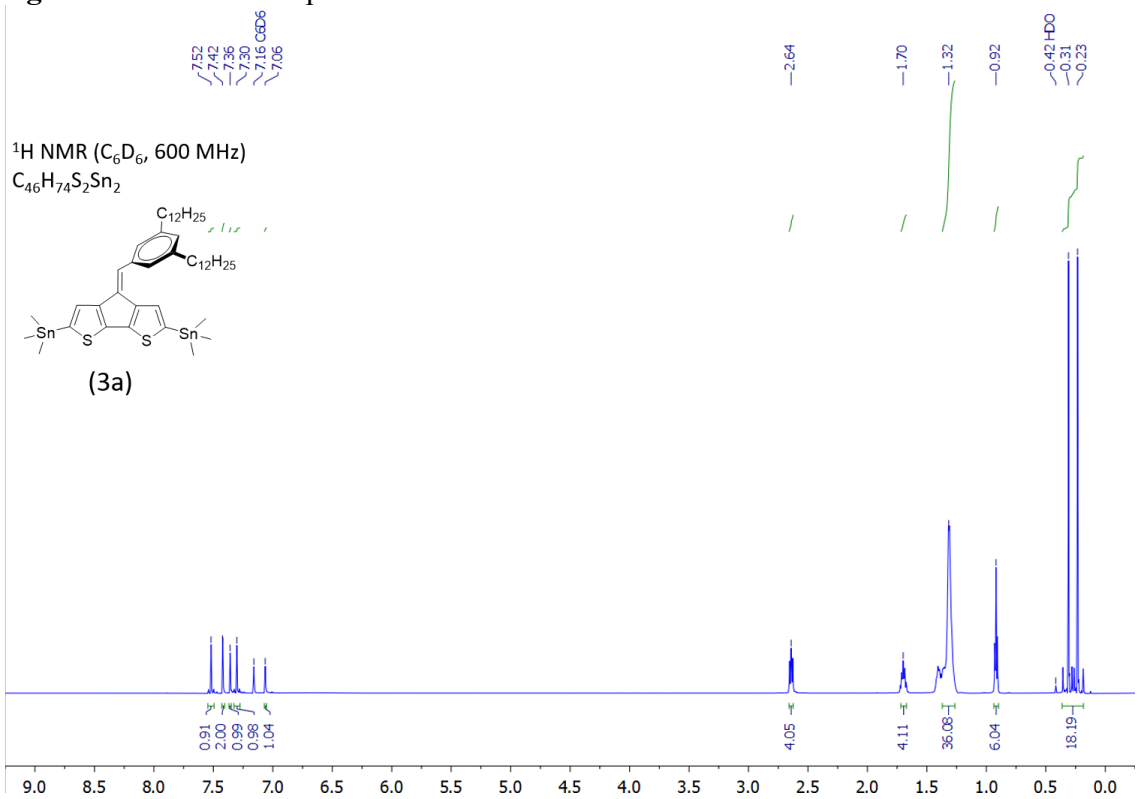

Figure S22. ^{1}H NMR spectra of **3a**.

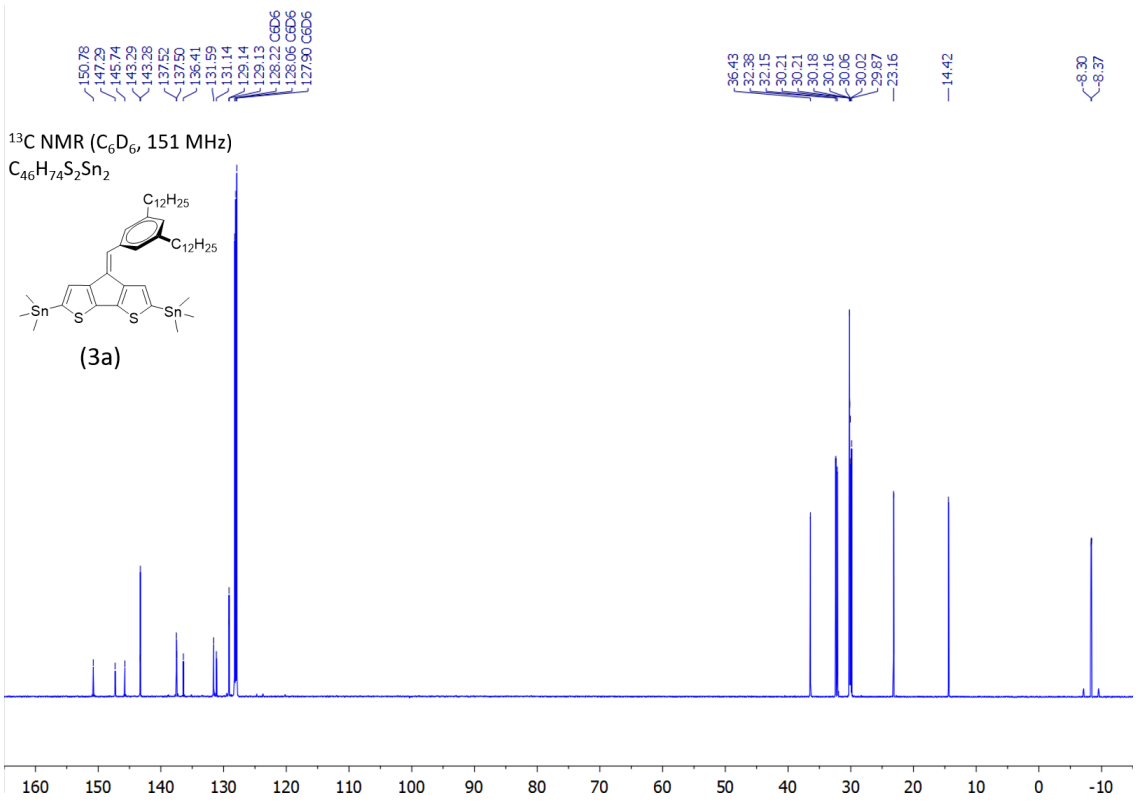

Figure S23. ^{13}C NMR spectra of **3a**.

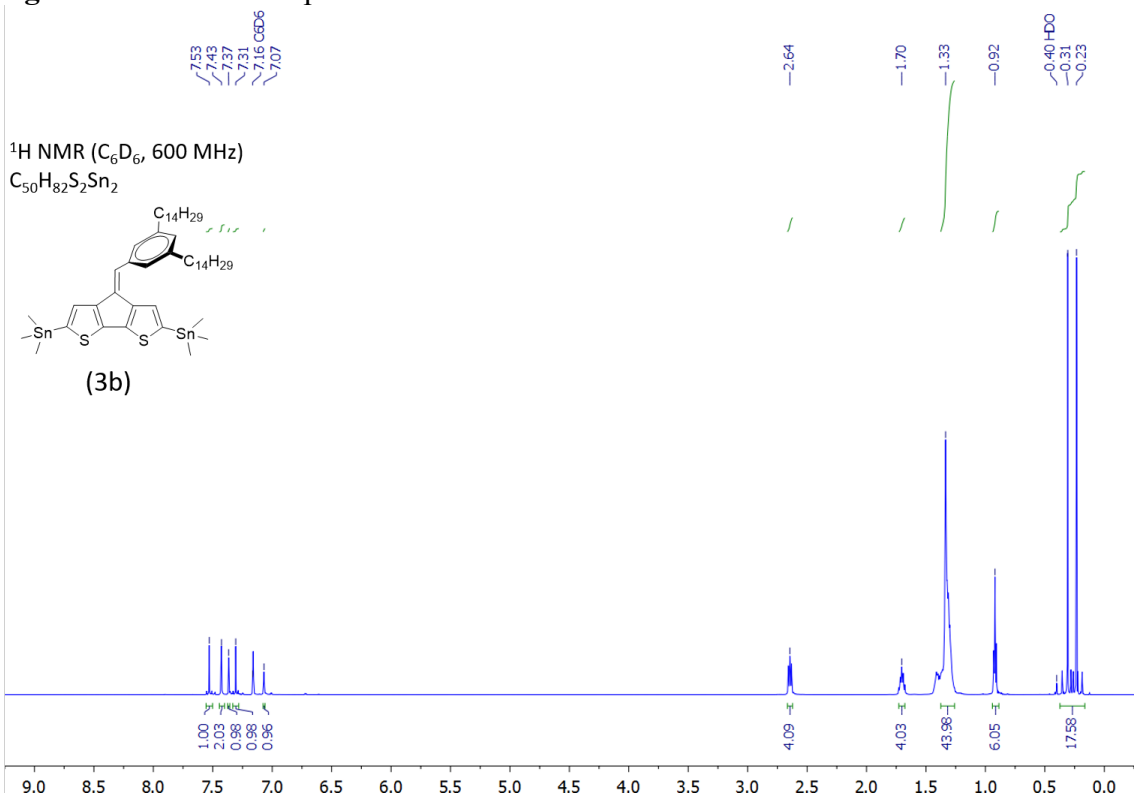

Figure S24. ^{1}H NMR spectra of **3b**.

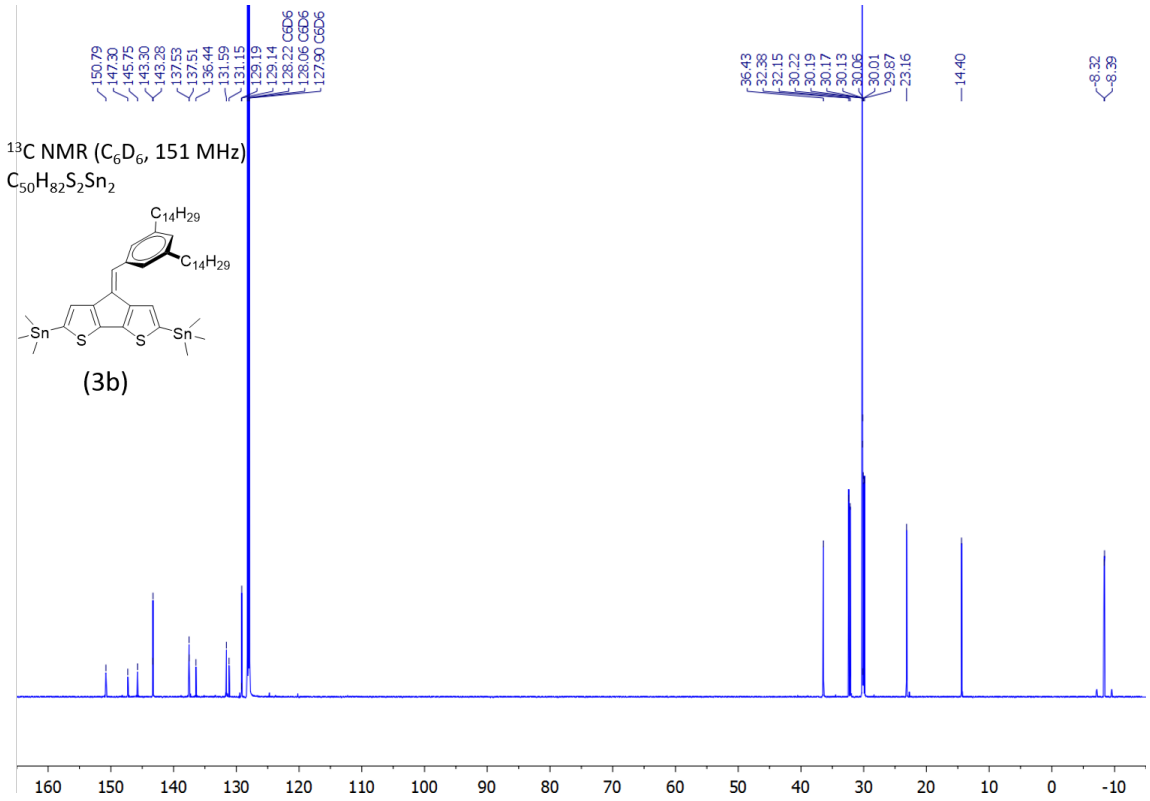

Figure S25. ^{13}C NMR spectra of **3b**.

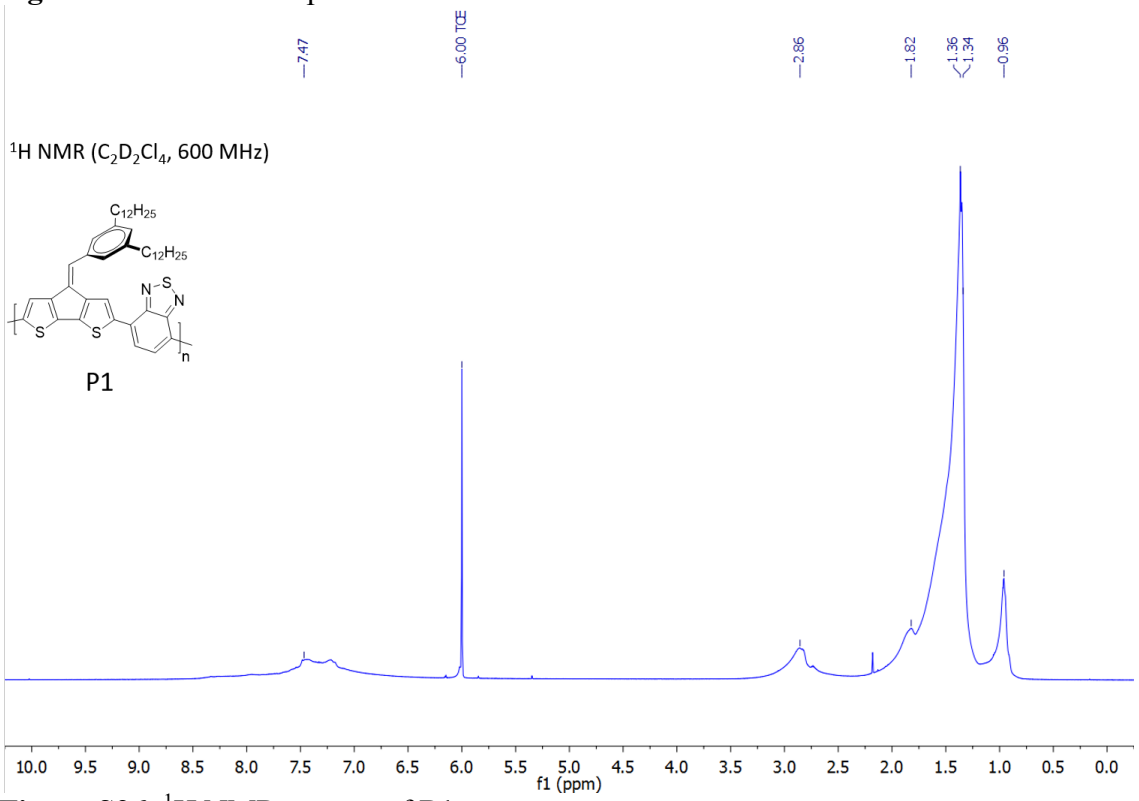

Figure S26. ^{1}H NMR spectra of **P1**.

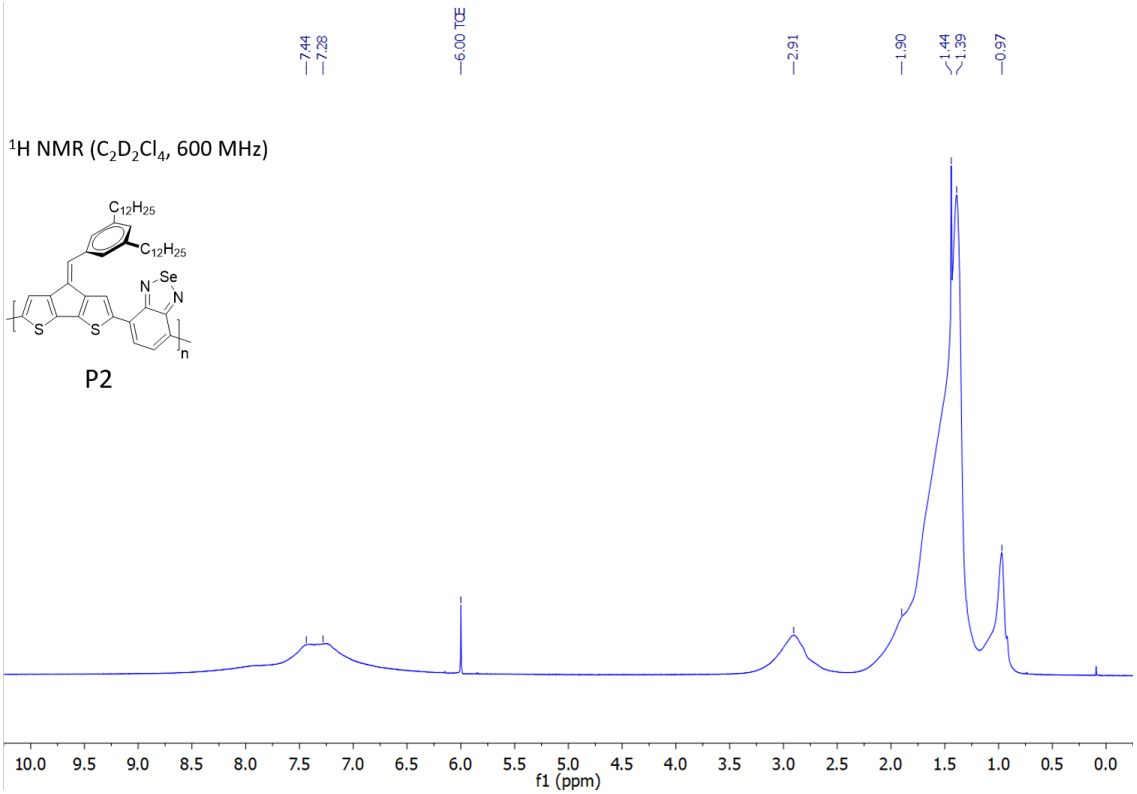

Figure S27. ^{1}H NMR spectra of **P2**.

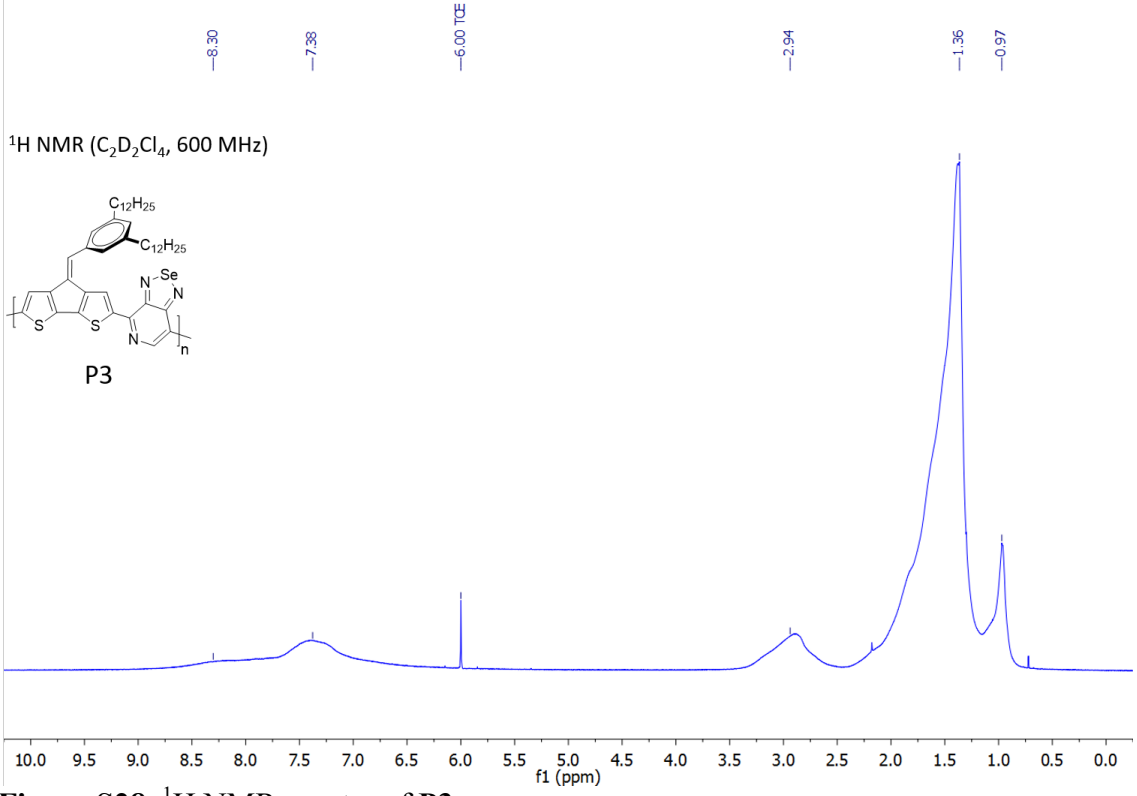

Figure S28. ^{1}H NMR spectra of **P3**.

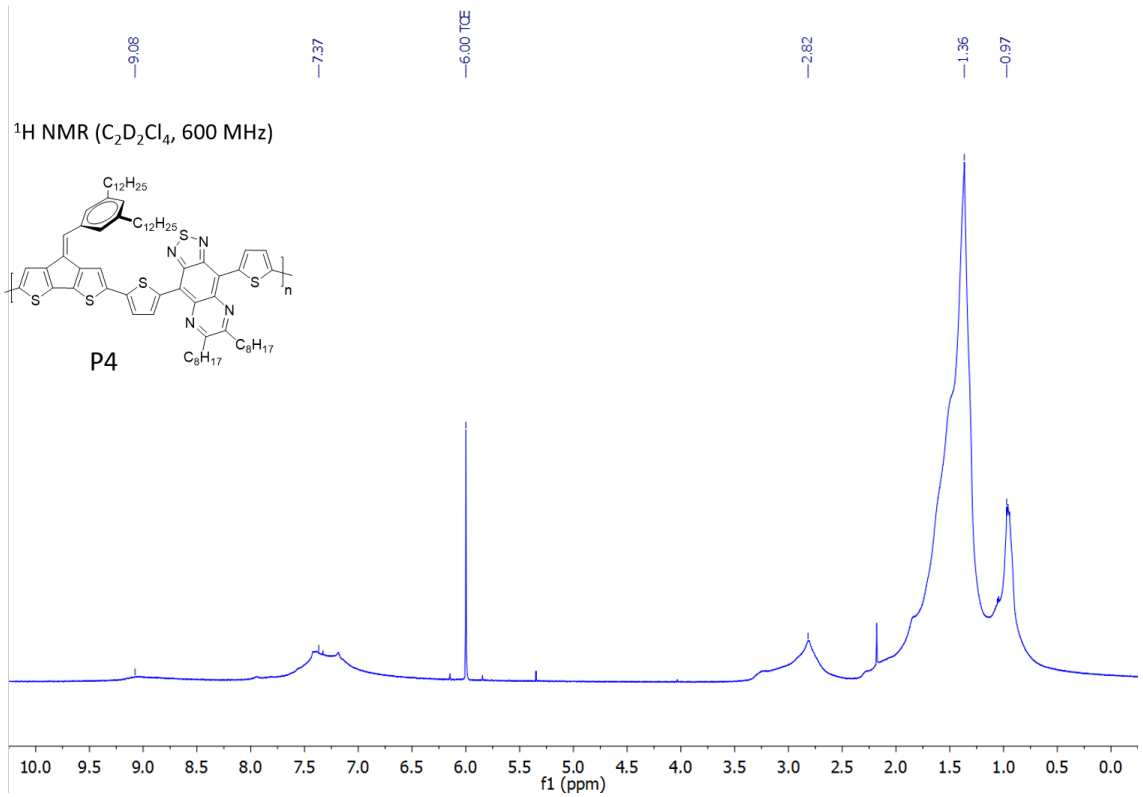

Figure S29. ^{1}H NMR spectra of **P4**.

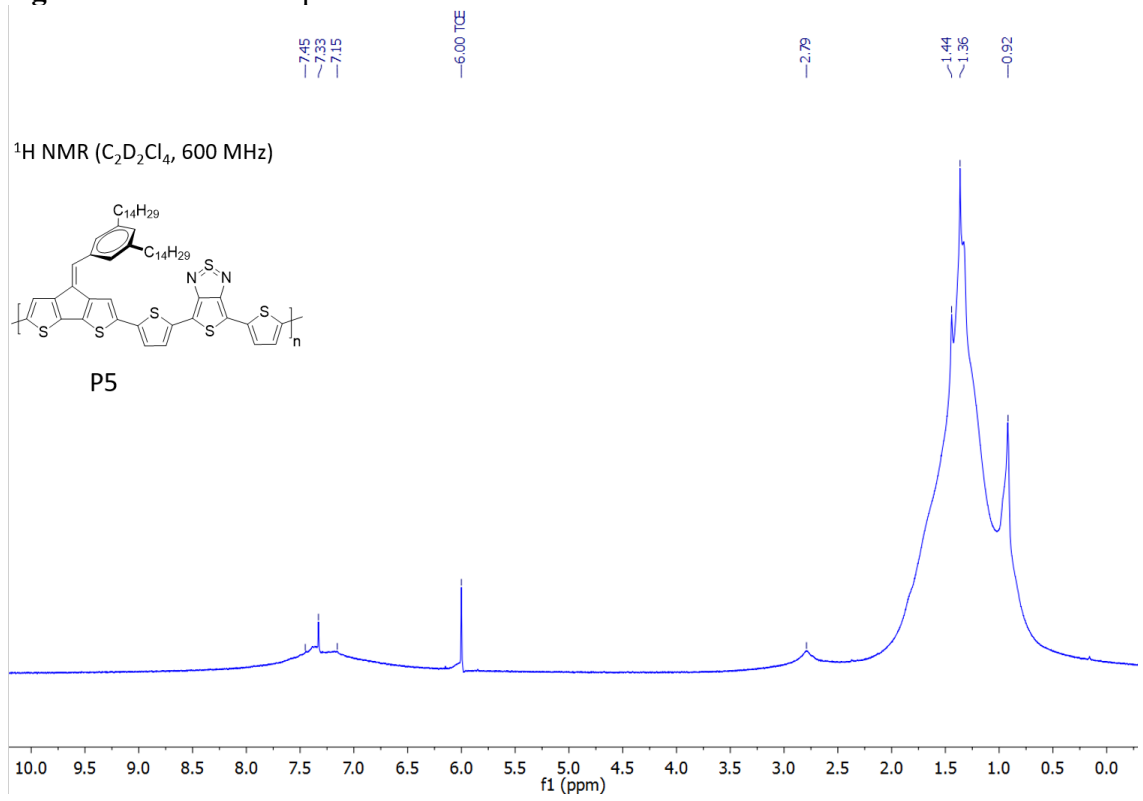

Figure S30. ^{1}H NMR spectra of **P5**.

References

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2. A.D. Becke, *J. Chem. Phys.*, **1993**, *98*, 5648-5652.
3. M. E. Foster, B. A. Zhang, D. Murtagh, Y. Liu, M. Y. Sfeir, B. M. Wong and J. D. Azoulay, *Macromol. Rapid Commun.*, **2014**, *35*, 1516-1521.