Supporting Information

Investigation of Random Copolymer Analogues of a Semi-Random Conjugated Polymer Incorporating Thieno[3,4-*b*]pyrazine

*Jenna B. Howard, Seyma Ekiz, Alejandro J. Cuellar De Lucio, Barry C. Thompson**

Department of Chemistry, Loker Hydrocarbon Research Institute, University of Southern California, Los Angeles, California 90089-1661, United States

*E-mail: barrycth@usc.edu

Materials and Methods: All reagents from commercial sources were used without further purification, unless otherwise noted. All reactions were performed under dry N_2, unless otherwise noted. All dry reactions were performed with glassware that was flamed under high vacuum and backfilled with N_2. Flash chromatography was performed using a Teledyne CombiFlash R_f instrument in combination with RediSep R_f normal phase disposable columns. Solvents were purchased from VWR and used without further purification except for THF, which was dried over sodium/benzophenone before being distilled.

All compounds were characterized by ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) on a Mercury 400. Polymer ^{1}H NMRs (500 MHz) were obtained on a Varian VNMRS-500. High Resolution Mas Spectrometry (HRMS) by electrospray ionization (ESI) was performed at the UCLA Pasarow Mass Spectrometry Laboratory. For polymer molecular weight determination, polymer samples were dissolved in HPLC grade *o*-dichlorobenzene at a concentration of 0.5 mg/ml, briefly heated and then allowed to turn to room temperature prior to filtering through a 0.2 μm PTFE filter. SEC was performed using HPLC grade *o*-dichlorobenzene at a flow rate of 1 ml/min on one 300 x 7.8 mm TSK-Gel GMH$_{H\ R}$-H column (Tosoh Corporation) at 70 °C using a Viscotek GPC Max VE 2001 separation module and a Viscotek TDA 305 RI detector. The instrument was calibrated vs. polystyrene standards (1,050 – 3,800 000 g/mol) and data was analyzed using OmniSec 4.6.0 software.

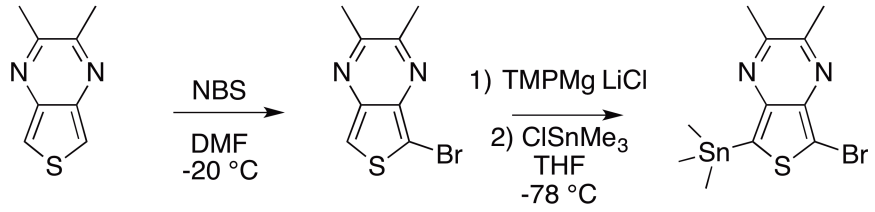
Cyclic voltammetry was collected using an EG&G instruments Model 263A potentiostat under the control of PowerSuite Software. A standard three electrode cell based on a Pt wire working electrode, a silver wire pseudo reference electrode (calibrated vs. Fc/Fc^+

which is taken as 5.1 eV vs. vacuum) and a Pt wire counter electrode was purged with nitrogen and maintained under nitrogen atmosphere during all measurements. Acetonitrile was distilled over CaH_2 prior to use. Tetrabutyl ammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte for polymer films. Polymer films were made by repeatedly dipping the Pt wire in a 1% (w/w) polymer solution in chloroform or *o*-dichlorobenzene and dried under nitrogen prior to measurement.

For thin film measurements polymers were spin coated onto pre-cleaned glass slides from *o*- dichlorobenzene solutions (7 mg/ml). UV-vis absorption spectra were obtained on a Perkin- Elmer Lambda 950 spectrophotometer. The thickness and crystallinity of the thin films and GIXRD measurements were obtained using Rigaku Diffractometer Ultima IV using Cu Kα radiation source (λ= 1.54 Å) in the reflectivity and grazing incidence X-Ray diffraction mode, respectively.

Synthetic Procedures:

Synthetic procedures for the synthesis of 2-bromo-5-trimethyltin-3-hexylthiopehene, poly(3-hexyl thiophene), 2,5-bis(trimethyltin)thiophene, 2-bromo-5-(trimethylstannyl)thiophene, (3-hexyl-5-(trimethylstannyl)thiophene-2-yl)trimethylsilane, 2,3-dimethyl-thieno[3,4-*b*]pyrazine, and 5,7-dibromo-2,3-dimethyl-thieno[3,4-*b*]pyrazine were used without modifications as reported in the literature.[1–3] Synthesis of (3-hexylthiophen-2-yl)trimethylstannane was completed using modified literature conditions.[4]



1; 64% **2; 95%**

Scheme S1.

5-bromo-2,3-dimethyl-thieno[3,4-*b*]pyrazine (1). 2,3-dimethyl-thieno[3,4-*b*]pyrazine (337.7 mg, 2.06 mmol) was dissolved in DMF (41 mL, 0.05 M) and cooled to -20 °C. A solution of NBS (384.8 mg, 2.16 mmol) in DMF (20 mL) was added slowly over the course of 2 h. The reaction mixture was covered from light and left to stir overnight and warm to RT. The reaction mixture was extracted with ether and washed with water several times. The organic layer was dried with $MgSO_4$ and subsequently concentrated *in vacuo* to an orange solid. The extract was purified via flash chromatography with DCM then dried in a dessicator (318.5 mg, 64% yield). ^{1}H NMR: (400 MHz, *$CDCl_3$)* δ 7.81 (s, 1H) 2.66 (s, 3H), 2.64 (s, 3H). ^{13}C NMR: (500 MHz, *$CDCl_3$)* δ 154.57, 153.90, 141.11,

139.61, 115.88, 104.34, 23.73, 23.41. HRMS: *m/z* 241.95074 [M+] (calcd for $C_8H_7N_2SBr$ 241.95078).

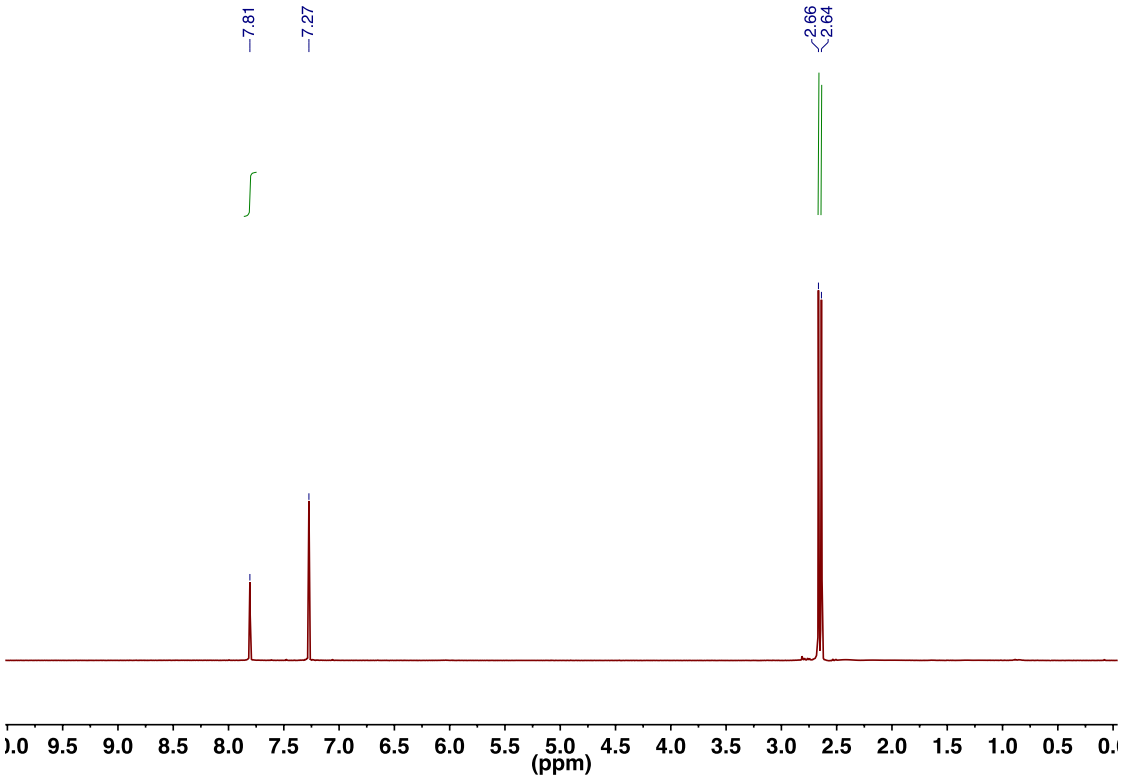


Figure S1. ^{1}H NMR spectrum of **1**.

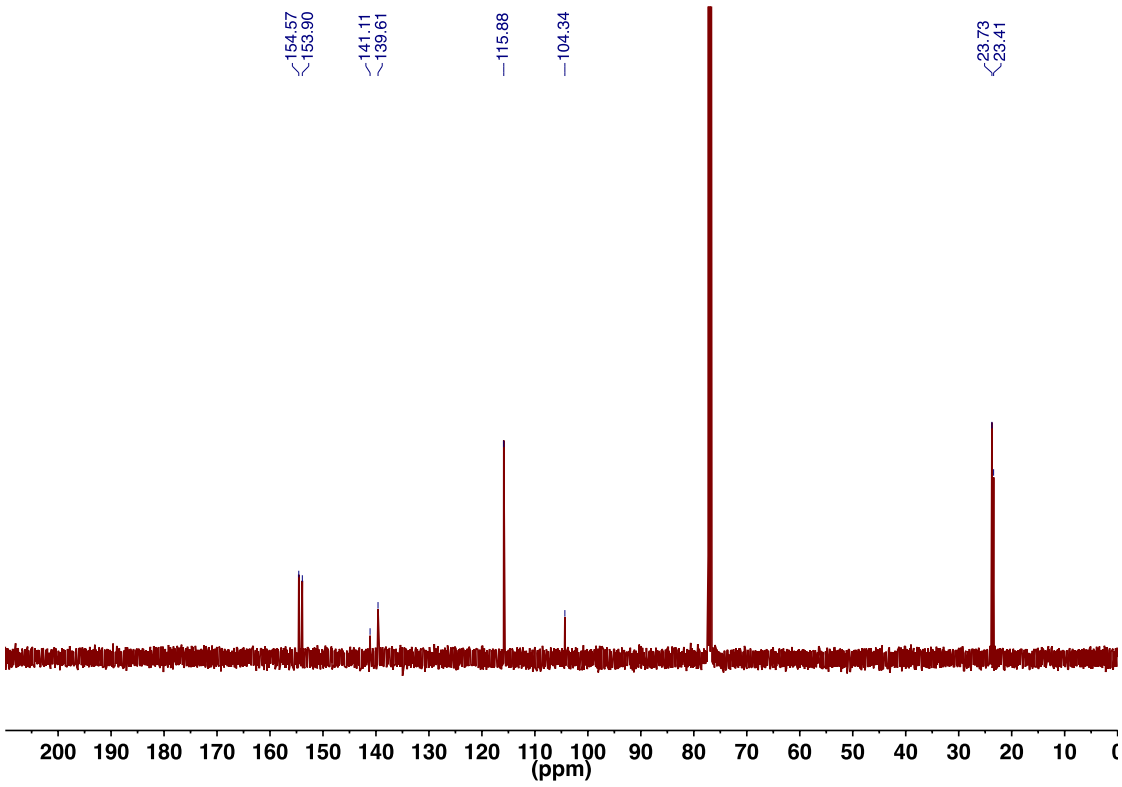


Figure S2. ^{13}C NMR spectrum of **1**.

5-bromo-2,3-dimethyl-7-(trimethylstannyl)thieno[3,4-*b*]pyrazine (2). Compound **1** (178.5 mg, 0.735 mmol) was dissolved in THF (5 mL, 0.15 M) and cooled to -78 °C followed by the dropwise addition of TMP MgCl LiCl in THF/Toluene solution (1.0 M, 1.10 mL). Reaction mixture was left to stir for 3 hours at -78 °C followed by dropwise addition of trimethyl tin chloride in hexanes solution (1.0 M, 1.6 mL). Reaction mixture was left to stir overnight and warm to RT. Reaction mixture was extracted with ether and washed with water and brine several times. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The extract was dissolved in chloroform and passed through a celite plug, pretreated with triethylamine, and concentrated *in vacuo* to an orange solid (300 mg, 95%). ^1H NMR: (500 MHz, *$CDCl_3$)* δ 2.64 (s, 3H), 2.60 (s, 3H), 0.50 (s, 9H).

^{13}C NMR: (500 MHz, *$CDCl_3$)* δ 152.10, 128.43, 128.38, 128.26, 125.65, 115.51, 23.68, 23.50, 7.59. HRMS, found by GC/EI-MS the most abundant form at 406.92258 *m/z* [MH+] (calcd for $C_{11}H_{15}N_2SBrSn$ 406.92341)

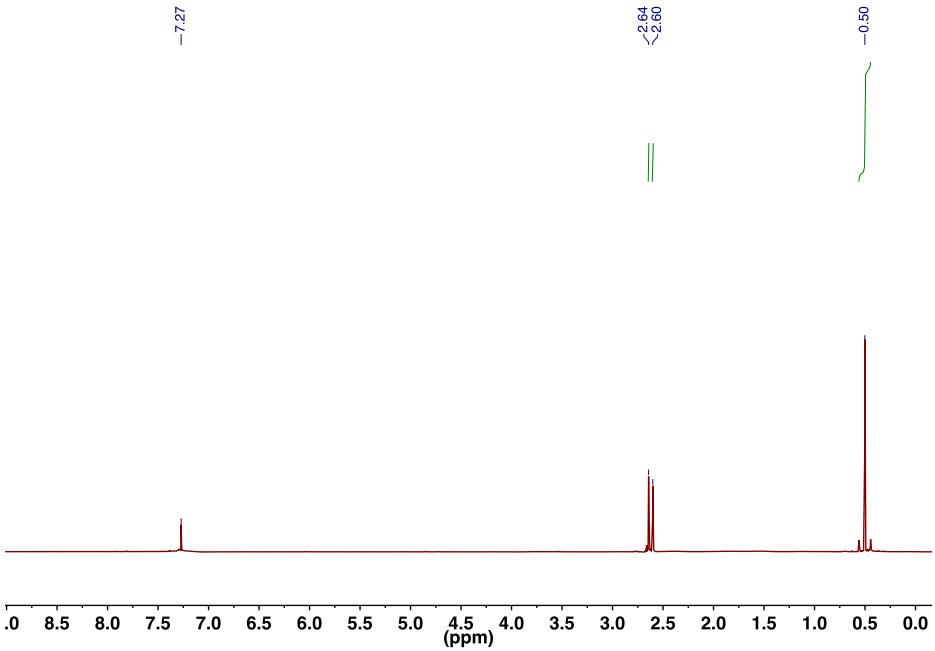


Figure S3. ^{1}H NMR spectrum of compound **2**.

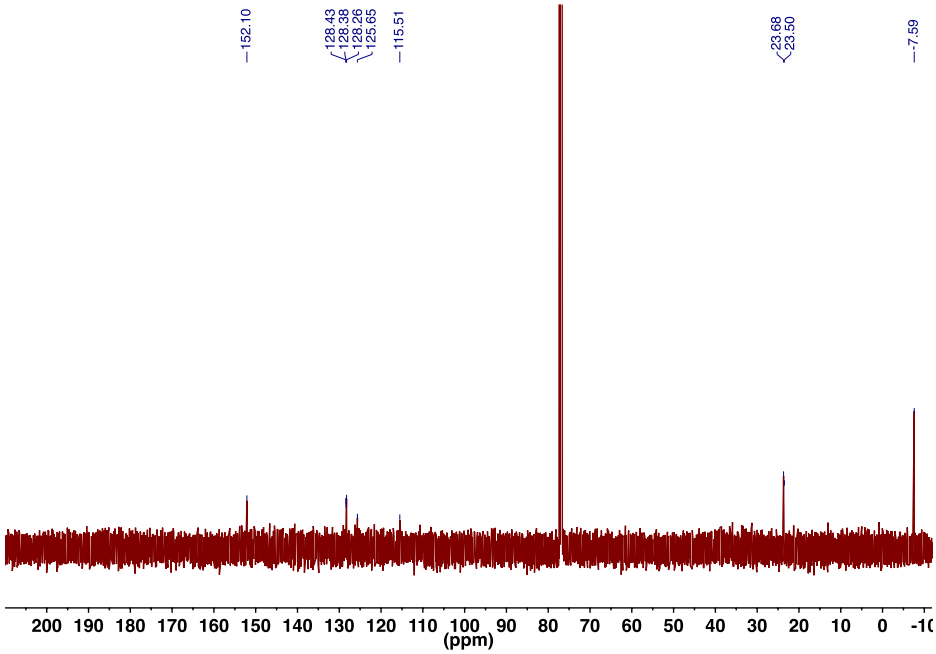
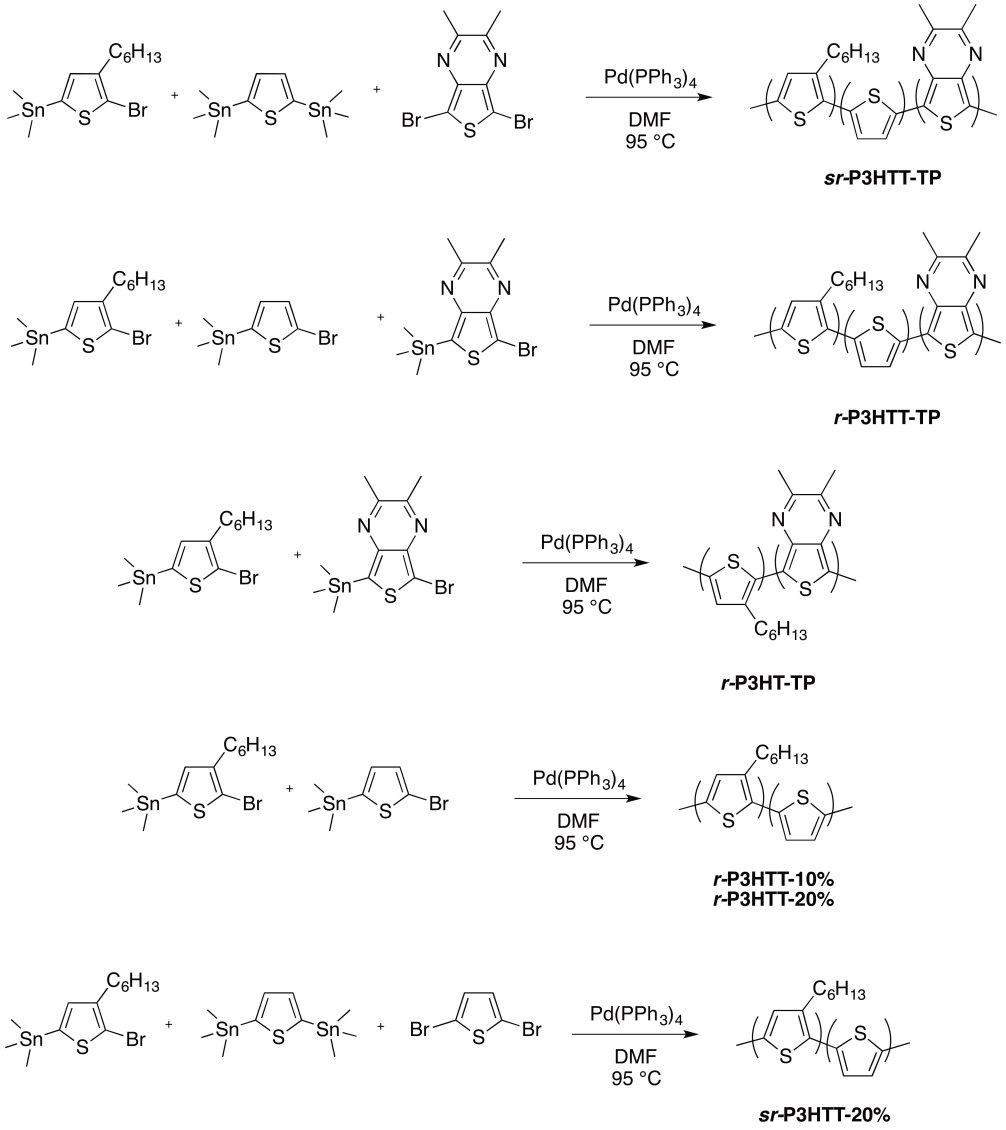


Figure S4. ^{13}C NMR spectrum of compound **2**.



Scheme S2. Copolymerizations of P3HT based random and semi-random polymers.

General Procedure for Stille Copolymerizations for P3HTT, P3HTT-TP and P3HT-TP Polymers. Monomers were dissolved in dry DMF at an overall concentration of 0.04 M, followed by addition of 4 mol % of $Pd(PPh_3)_4$ in one portion. The solution was degassed for 20 minutes with nitrogen, then heated to 95 °C for 48 hours. The reaction mixture was cooled to room temperature and precipitated in stirring methanol followed

by addition of 5 mL NH_4OH. The polymer was then filtered into a soxhlet thimble and purified via soxhlet extraction using MeOH, followed by hexanes. Polymers were collected in hot chloroform, concentrated in vacuo, then precipitated in cold stirring methanol. Polymers were then vacuum filtered and dried in a dessicator.

***sr*-P3HTT-TP.** Yield 69% (107.7 mg). ^{1}H NMR: (500 MHz, *$CDCl_3$)* δ 7.48 (s, 0.25 H), 7.13 (s, 0.19 H), 7.06 (s, 0.24 H), 7.00 (s, 0.44 H), 2.84 (t, 1.77 H), 2.70 (s, 0.75 H), 2.XX (m, 0.15H), 1.73 (m, 1.94 H), 0.94 (t, 3.00 H)

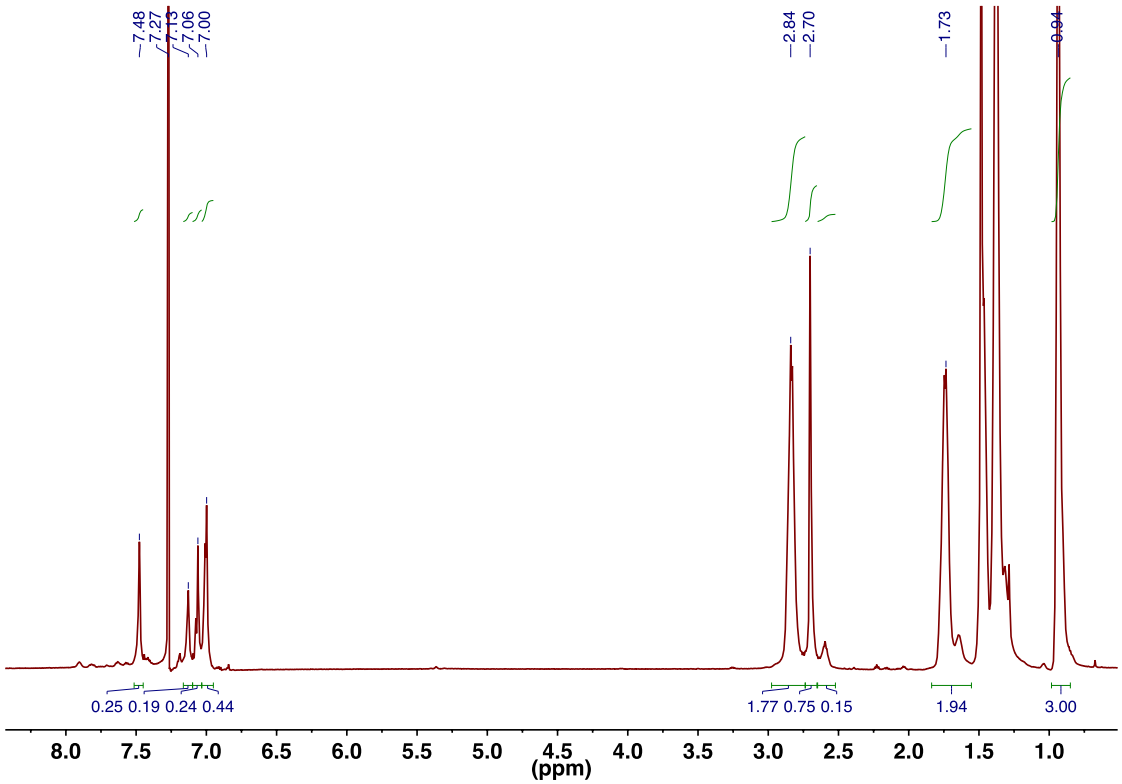


Figure S5. *sr*-P3HTT-TP ^{1}H NMR spectrum.

***r*-P3HTT-TP.** Yield 61% (96.6 mg). ^{1}H NMR: (500 MHz, *$CDCl_3$)* δ 7.50 (s, 0.11 H), 7.14 (s, 0.17 H), 7.07 (s, 0.40 H), 6.99 (s, 0.52 H), 2.XX (m, 0.18H), 2.82 (t, 1.56 H), 2.72 – 2.68 (s, 0.55 H), 2.XX (m, 0.21H), 1.73 (m, 1.99 H), 0.93 (t, 3.00 H)

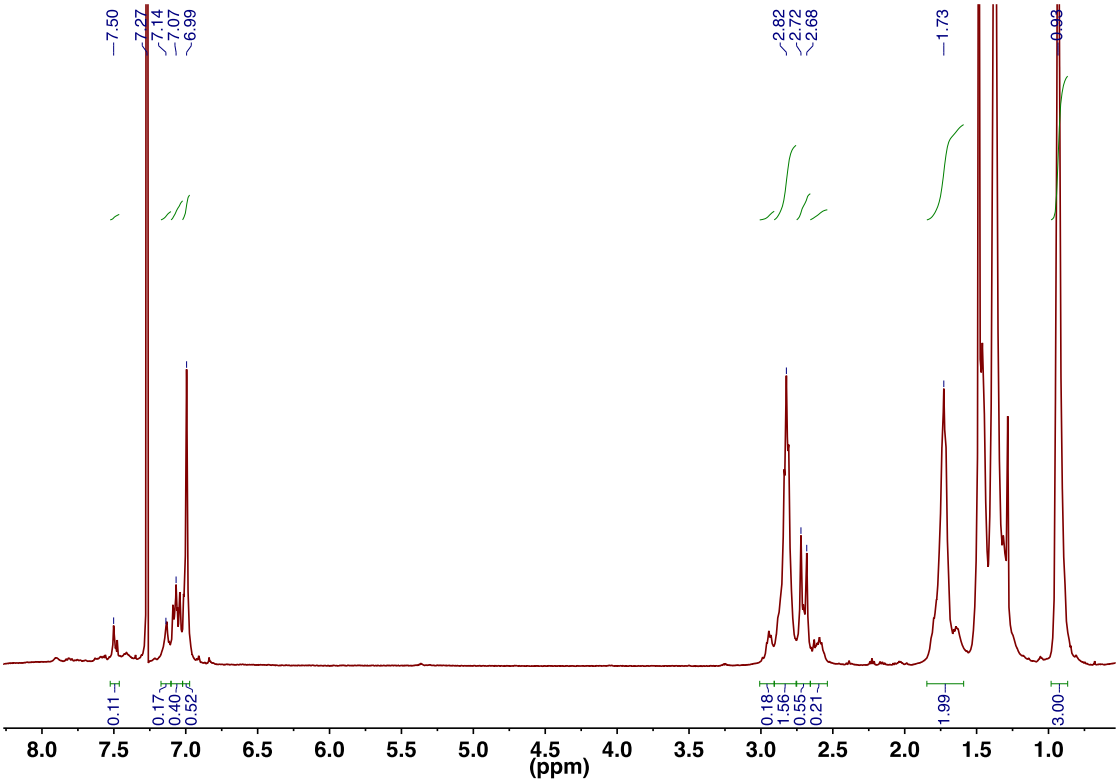


Figure S6. *r*-P3HTT-TP ^{1}H NMR spectrum.

***r*-P3HT-TP.** Yield 92% (147.4 mg). ^{1}H NMR: (500 MHz, *$CDCl_3$)* δ 7.50 (s, 0.16 H), 7.09 - 6.99 (s, 0.83 H), 2.XX (m, 0.32H), 2.82 (t, 1.56 H), 2.72 – 2.68 (s, 0.55 H), 2.XX (m, 0.23H), 1.73 (m, 2.04 H), 0.93 (t, 3.00 H)

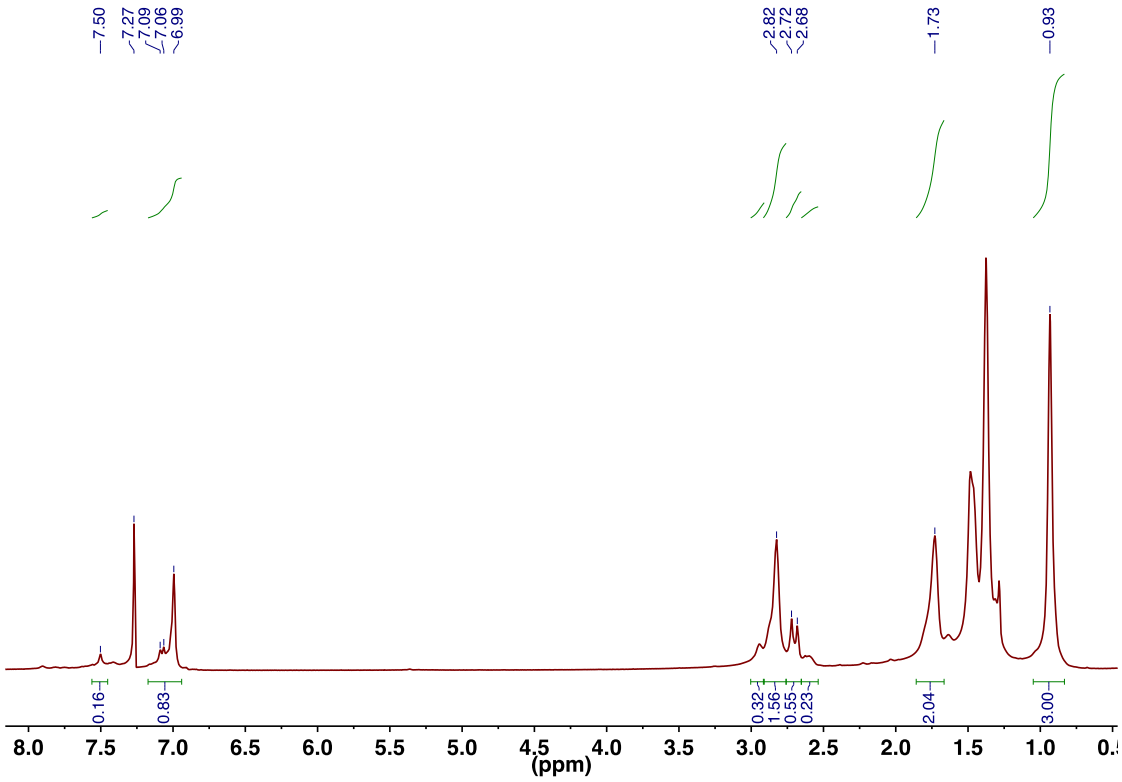


Figure S7. *r*-P3HT-TP ^{1}H NMR spectrum.

***r*-P3HTT-10%.** Yield 88% (191 mg). ^{1}H NMR: (500 MHz, *$CDCl_3$)* δ 7.14 (s, 0.14 H), 7.07 (s, 0.19 H), 6.99 (s, 0.88 H), 2.82 (t, 1.97 H), 1.72 (m, 2.01 H), 0.93 (t, 3.00 H)

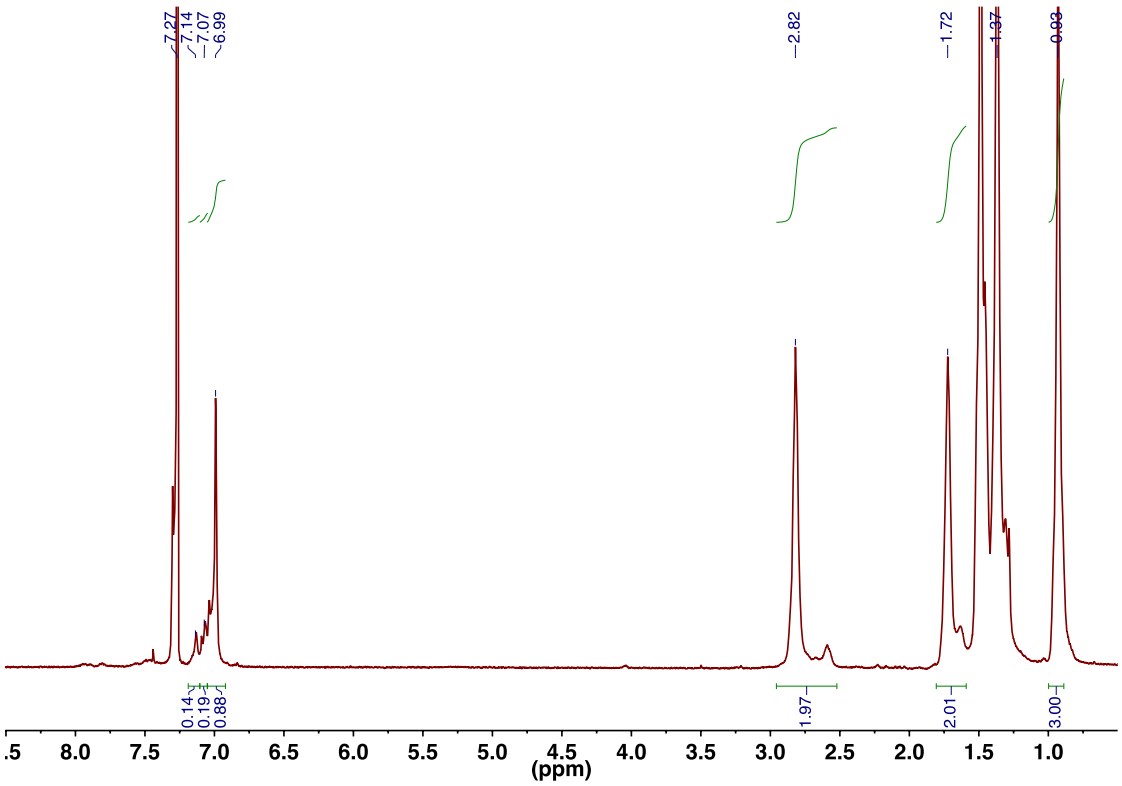


Figure S8. *r*-P3HTT-10% ^{1}H NMR spectrum.

***r*-P3HTT-20%.** Yield 49% (80.8 mg). ^{1}H NMR: (500 MHz, *$CDCl_3$)* δ 7.13 (s, 0.29 H), 7.07 (s, 0.31 H), 6.99 (s, 0.88 H), 2.82 (t, 1.99 H), 1.72 (m, 2.07 H), 0.93 (t, 3.00 H)

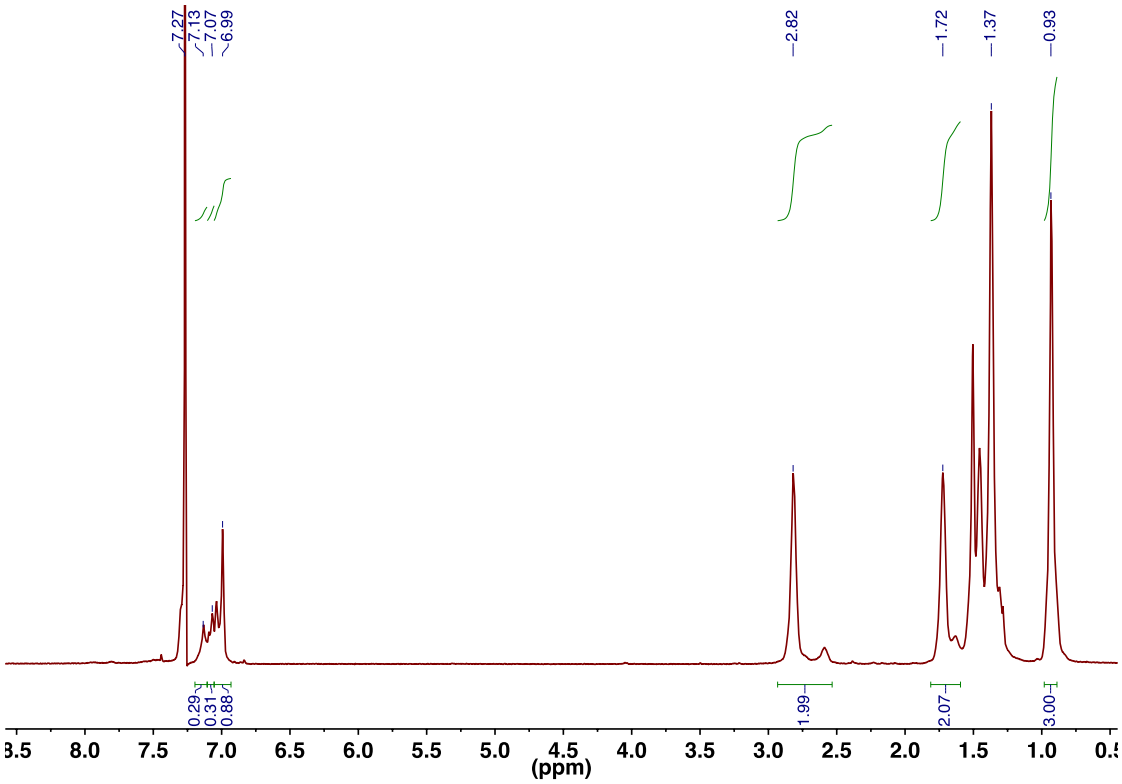


Figure S9. *r*-P3HTT-20% ^{1}H NMR spectrum.

***sr*-P3HTT-20%.** Yield 71% (137.8 mg). ^{1}H NMR: (500 MHz, *$CDCl_3$)* δ 7.13 (s, 0.23 H), 7.08 (s, 0.25 H), 7.00 (s, 0.94 H), 2.82 (t, 2.08 H), 1.73 (m, 2.11 H), 0.94 (t, 3.00 H)

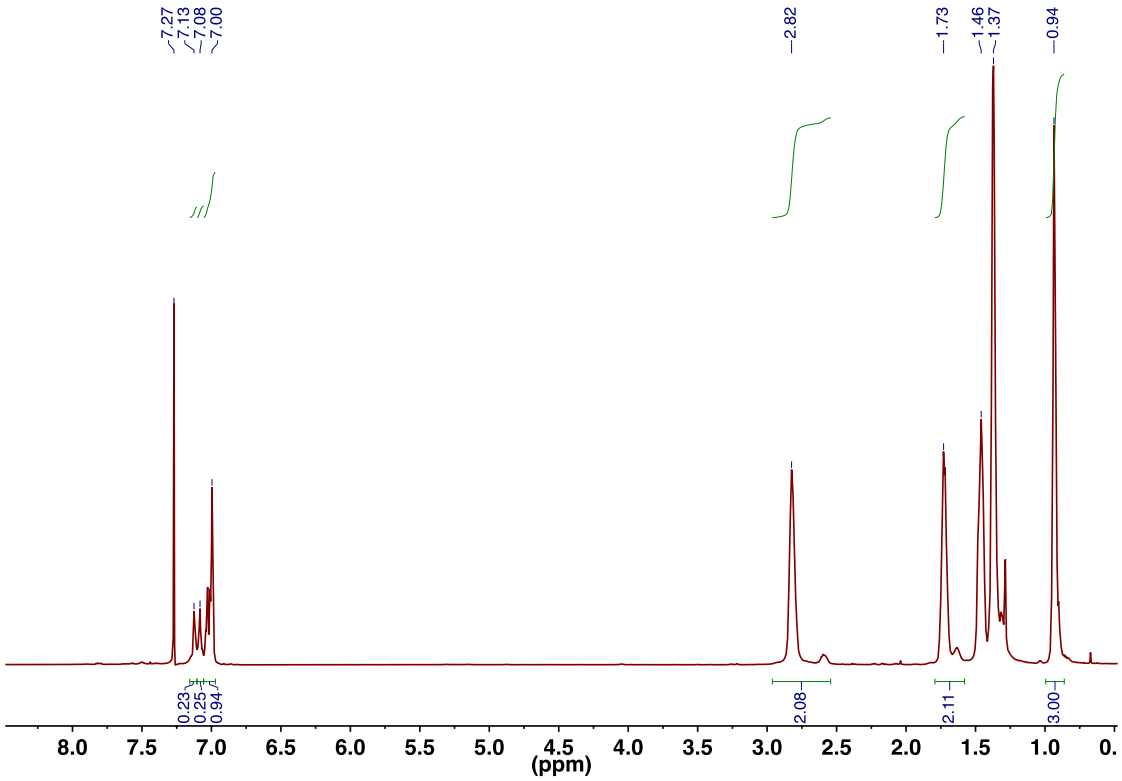
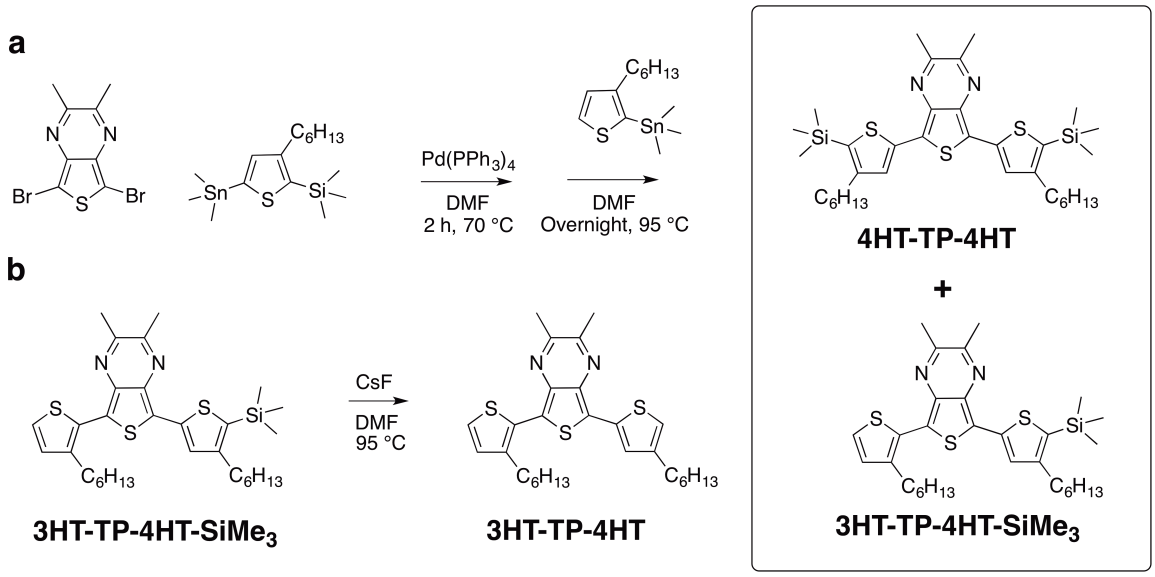


Figure S10. *sr*-P3HTT-20% ^{1}H NMR spectrum.



Scheme S3. Synthesis of 2,3-dimethylthieno[3,4-*b*]pyrazine oligomers, **4HT-TP-4HT, 3HT-TP-4HT-SiMe$_3$,** and **3HT-TP-4HT.**

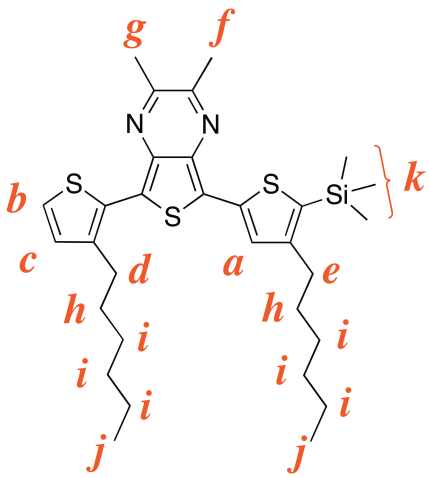
Synthesis of (3-hexylthiophen-2-yl)trimethylstannane. In a flame-dried three-neck flask backfilled with dry nitrogen, 2-bromo-3-hexylthiophene (1.5g, 6.07 mmol) was dissolved in 20 mL of dry THF then cooled to -78°C for 30 minutes. A 1.6M solution of n-BuLi in hexanes (3.98 mL, 6.37 mmol) was added dropwise over 10 minutes. This mixture was allowed to stir for 2 hours at -78°C before a 1.0M solution of trimethyltinchloride in hexanes was added slowly (6.67 mL, 6.67 mmol). The solution was stirred at -78°C for an hour before being allowed to gradually warm to room temperature overnight. The reaction mixture was subsequently poured into water and extracted with ether. The organic phase was combined and washed with water before being dried over $MgSO_4$. The solvent was concentrated under reduced pressure to afford a brown-orange liquid. This was distilled twice under high vacuum to produce the desired

product as a colorless oil (72% yield). 1H-NMR (400 MHz, CDCL3): 7.52 (d, 1H), 7.08 (d, 1H), 2.61 (t, 2H), 1.58 (t, 2H), 1.31 (m, 6H), 0.89 (t, 3H), 0.37 (t, 9H).

Synthesis of 2,3-dimethylthieno[3,4-*b*]pyrazine oligomers. Both TP oligomers, 5-(4-hexyl-5-(trimethylsilyl)thiophene-2-yl)-7-(3-hexylthiophen-2-yl)-2,3-dimethylthieno[3,4-*b*]pyrazine and 5,7-bis(4-hexyl-5-(trimethylsilyl)thiophene-2-yl)-2,3-dimethylthieno[3,4-*b*]pyrazine, were prepared in a one-pot reaction by the following method. A 3-necked round bottom flask was flame dried under vacuum and backfilled with N_2 gas. Subsequently, 5,7-dibromo-2,3-dimethylthieno[3,4-*b*]pyrazine and (3-hexyl-5-(trimethylstannyl)thiophene-2-yl)trimethylsilane were added and dissolved in dry DMF. $Pd(PPh_3)_4$ was added and the solution was degassed with N_2 gas for 10 minutes. The reaction mixture was heated to 70 °C for 2 hours, followed by addition of (3-hexylthiophen-2-yl)trimethylstannane. The reaction mixture was then heated to 95 °C and left to stir overnight (approximately 20 hours). The reaction was cooled to room temperature, diluted in ether and transferred to a separatory funnel with ether. The organic layer was washed with water five times, then dried over $MgSO_4$. The extract was concentrated *in vacuo*, then purified by flash chromatography with Hexanes:DCM (slow gradient from 100% hexanes to 75:25) to separate the two oligomer products.

5-(4-hexyl-5-(trimethylsilyl)thiophene-2-yl)-7-(3-hexylthiophen-2-yl)-2,3-dimethylthieno[3,4-*b*]pyrazine (3HT-TP-4HT-SiMe$_3$). ^{1}H NMR: (500 MHz, *$CDCl_3$)* δ 7.61 (s, 1H), 7.36 (d, 1H), 7.03 (d, 1H), 2.87 (t, 2 H), 2.72 – 2.69 (triplet overlapped with a singlet, 5H total), 2.64 (s, 3H), 2.68 (m, 4H), 1.31 (m, 12H), 0.89 (m, 6H), 0.49 (s, 9H).

^{13}C NMR (500 MHz, *CDCl$_3$)* δ: 153.10, 153.04, 150.88, 141.26, 139.00, 138.13, 137.40, 134.13, 129.48, 128.17, 127.74, 126.35, 125.46, 122.64, 31.78, 31.69, 31.46, 30.35, 30.00, 29.71, 29.44, 29.32, 23.78, 23.62, 22.65, 22.63, 14.10, 0.43. HRMS: *m/z* 569.24957 [MH+] (calcd for $C_{31}H_{44}N_2S_3Si$ 569.25086]



Scheme S4. Structure of **3HT-TP-4HT-SiMe$_3$**, with proton assignments.

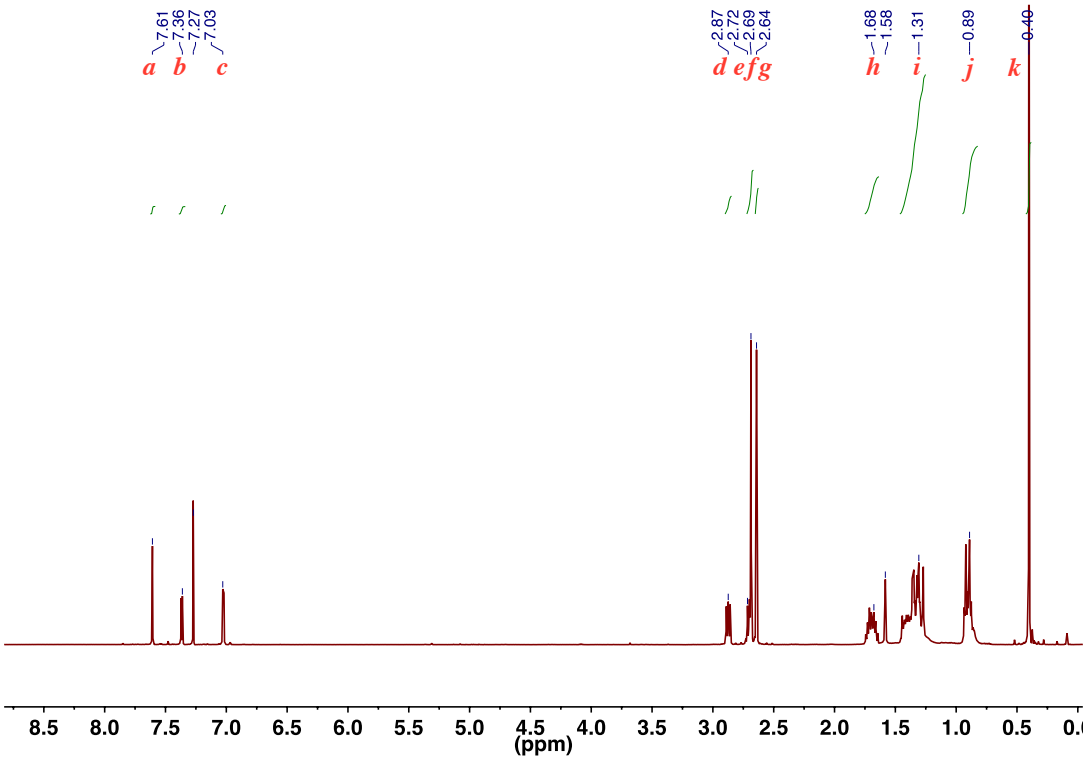


Figure S11. ^{1}H NMR spectrum of **3HT-TP-4HT-SiMe$_3$.**

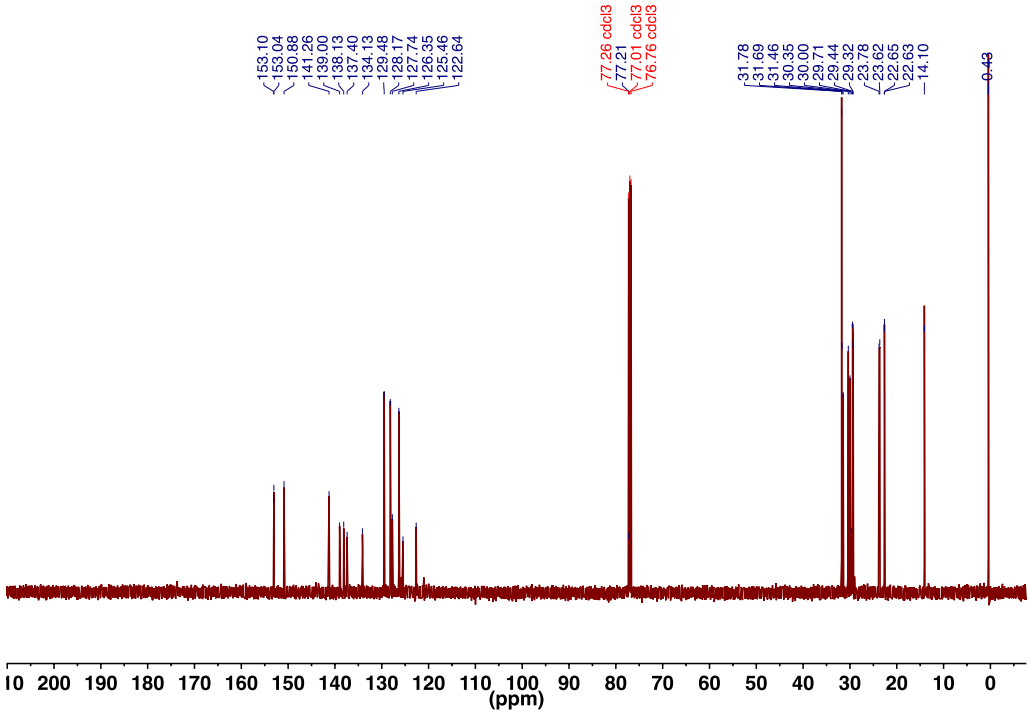
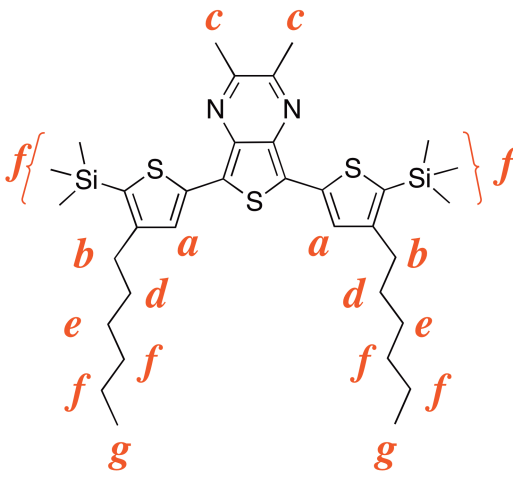


Figure S12. ^{13}C NMR spectrum of **3HT-TP-4HT-SiMe$_3$.**

5,7-bis(4-hexyl-5-(trimethylsilyl)thiophene-2-yl)-2,3-dimethylthieno[3,4-*b*]pyrazine (4HT-TP-4HT). ^{1}H NMR: (500 MHz, *$CDCl_3$)* δ 7.60 (s, 2H), 2.69 – 2.67 (triplet overlapped with a singlet, 10 H), 1.67 (m, 4H), 1.42 (m, 4H), 1.36 (m, 8H), 3.96 (t, 6H), 0.40 (s, 18H). ^{13}C NMR (500 MHz, *$CDCl_3$)* δ: 153.27, 150.86, 138.28, 138.00, 134.06, 128.12, 123.83, 31.78, 31.44, 29.43, 23.80, 22.65, 14.10, 0.42. HRMS: *m/z* 641.29039 [MH+] (calcd for $C_{34}H_{52}N_2S_3Si_2$ 641.30859]



Scheme S5. Structure of **4HT-TP-4HT**, with proton assignments.

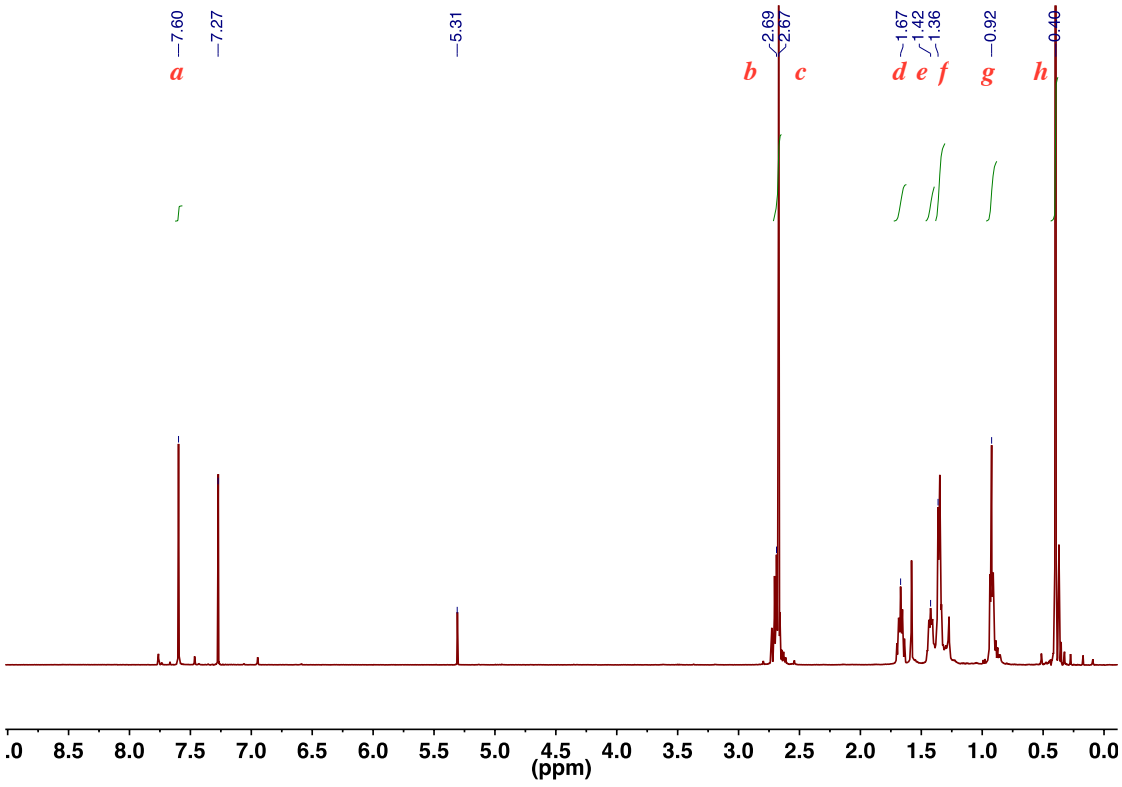


Figure S13. ^{1}H NMR spectrum of **4HT-TP-4HT.** Singlet at 7.27 is $CHCl_3$, 5.31 is CH_2Cl_2, 1.56 is H_2O.

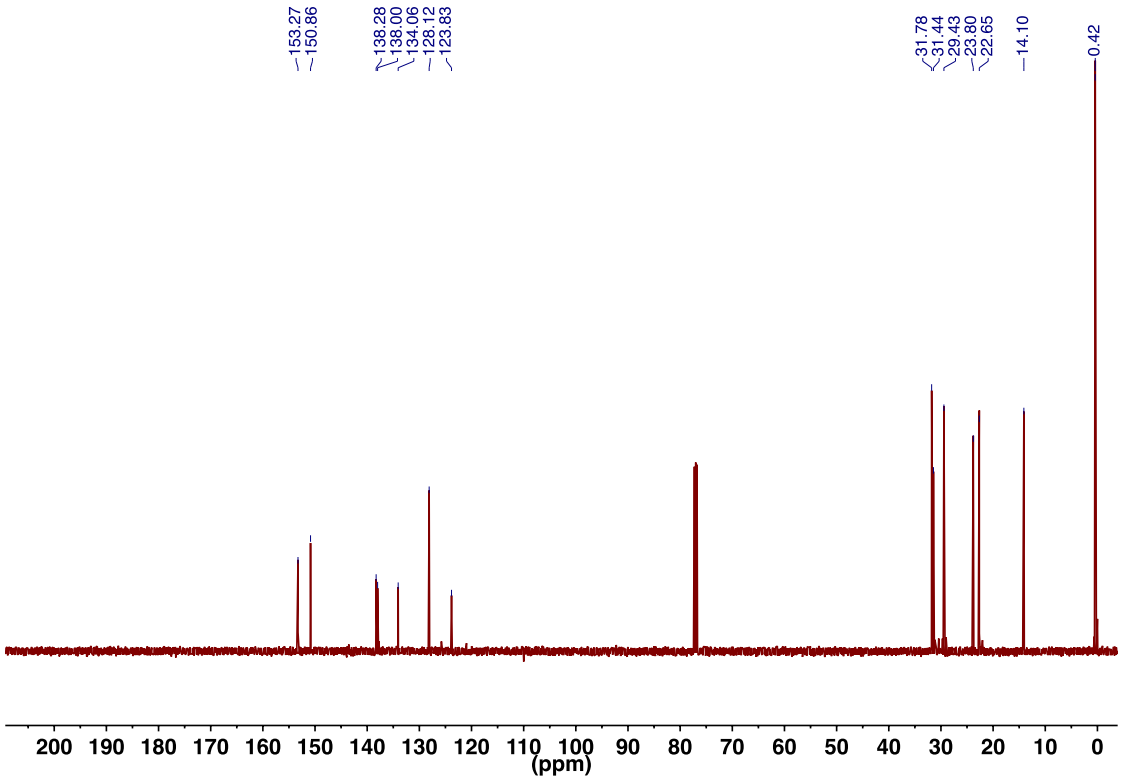
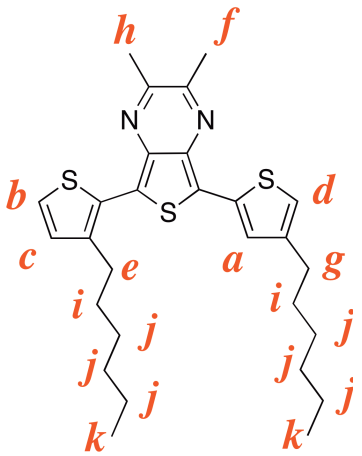


Figure S14. ^{13}C NMR spectrum of **4HT-TP-4HT.**

5-(3-hexylthiophen-2-yl)-7-(4-hexylthiophen-2-yl)-2,3-dimethylthieno[3,4-*b*]pyrazine (3HT-TP-4HT). Cesium fluoride and **3HT-TP-4HT-SiMe$_3$** were dissolved in dry DMF and heated to 95 °C under N_2, overnight. The reaction mixture was cooled to room temperature, diluted in ether, then transferred to a separatory funnel with ether. The organic layer was washed with water five times, then dried over $MgSO_4$. Extract was purified using flash chromatography (95:5 Hexanes/DCM). ^{1}H NMR: (500 MHz, *CDCl$_3$)* δ 7.47 (s, 1H), 7.35 (d, 1H), 7.01 (d, 1H), 6.96 (d, 1H), 2.85 (t, 2H), 2.67 – 2.63 (triplet overlapped with two singlets, 8H total), 1.68 (m, 4H), 1.26 (m)*, 0.88 (m)*. *peaks overlapped by hexanes, unable to accurately integrate. ^{13}C NMR: (500 MHz, *CDCl$_3$)* δ 153.16, 143.56, 141.37, 141.29, 140.74, 137.41, 134.27, 129.51, 127.67, 126.39, 125.81, 122.42, 121.05, 110.02, 34.69, 31.72, 31.61*, 30.49, 30.47, 30.40, 30.00, 29.73, 29.35, 29.05, 25.30, 23.73, 23.65, 22.68*, 20.72, 14.14*, 11.45. *Hexanes. HRMS: *m/z* 497.21024 [MH+] (calcd for $C_{28}H_{34}N_2S_3$ 497.21134]



Scheme S6. Structure of **3HT-TP-4HT**, with proton assignments.

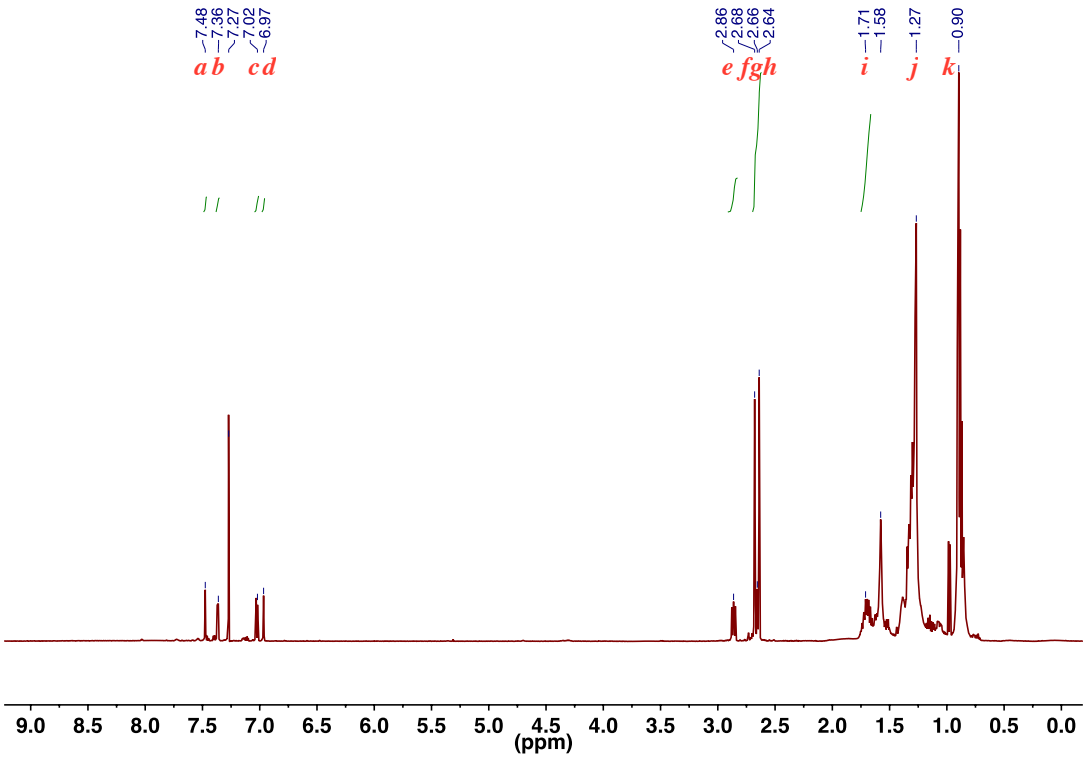


Figure S15. ^{1}H NMR spectrum of **3HT-TP-4HT.**

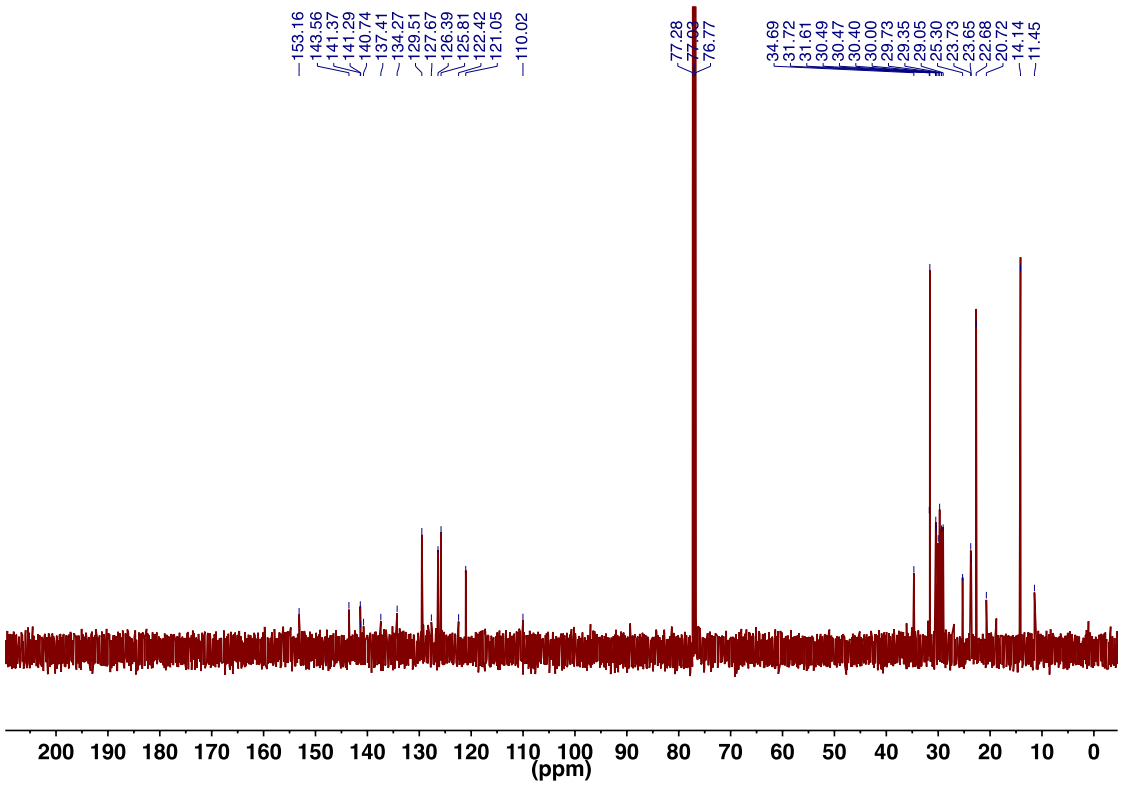


Figure S16. ^{13}C NMR spectrum of **3HT-TP-4HT.**

^{1}H 1D-NOESY Spectroscopy

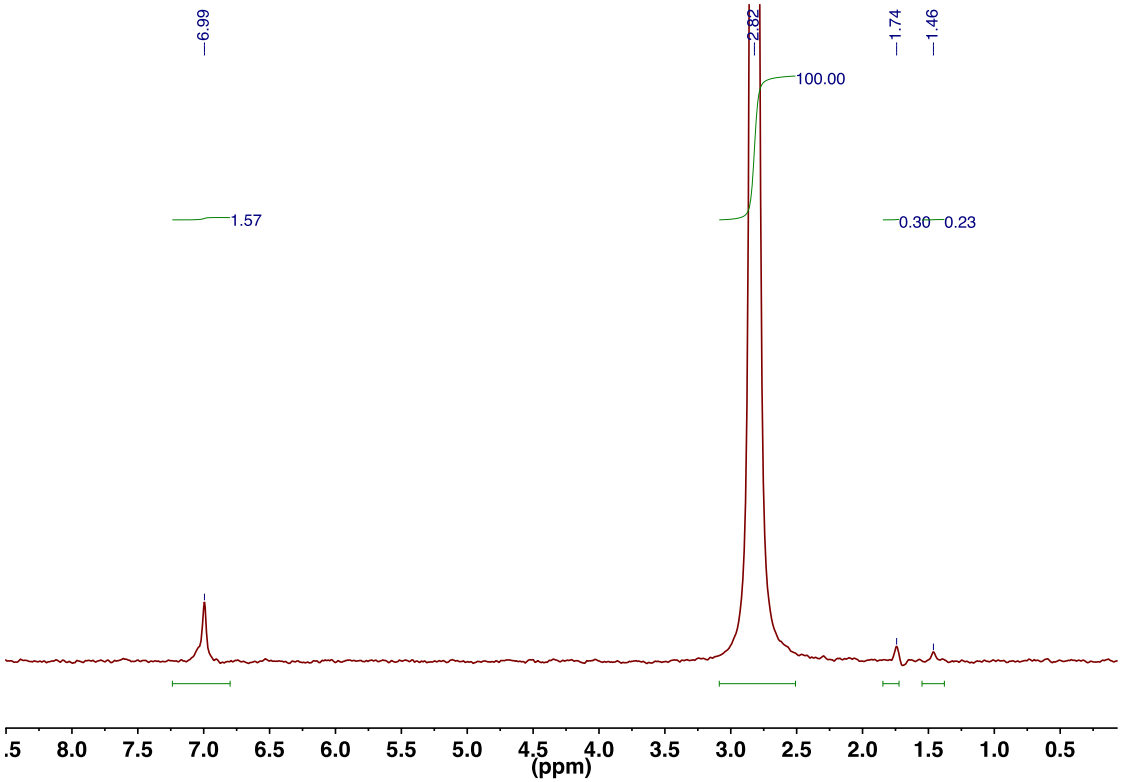


Figure S17. Selective excitation at 2.82 ppm of *r*-P3HT-TP.

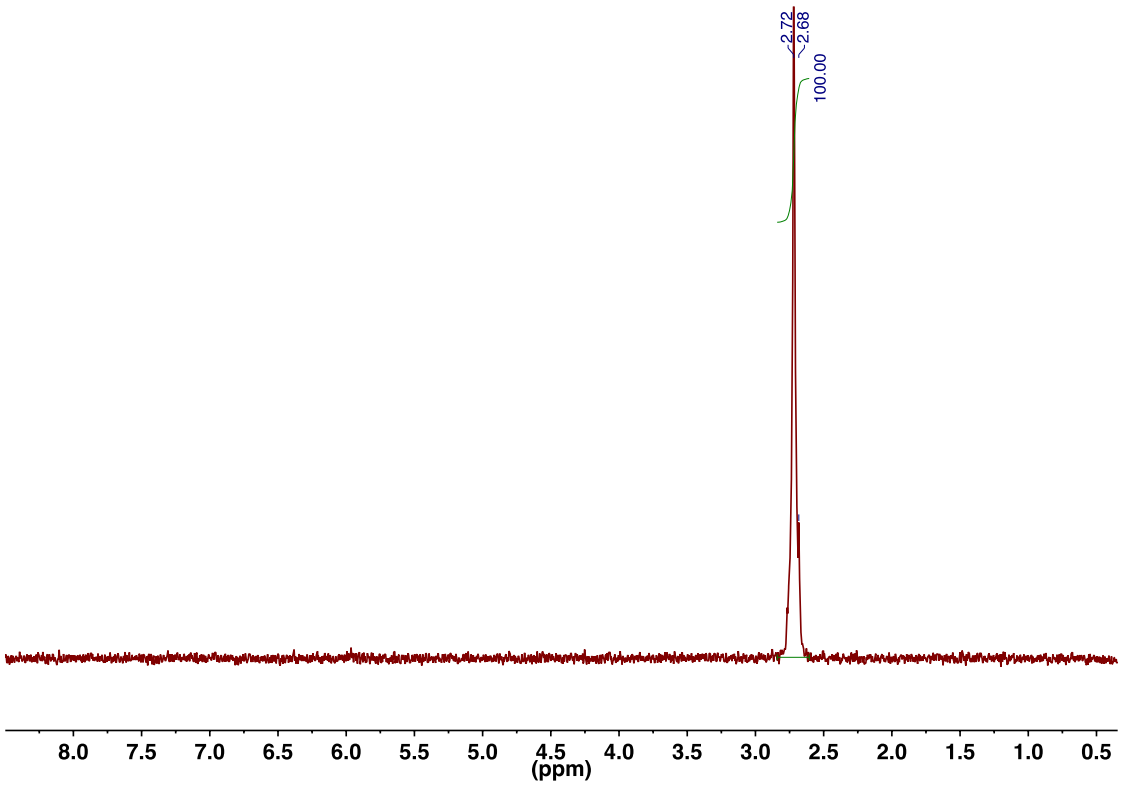


Figure S18. Selective excitation at 2.72 ppm of *r*-P3HT-TP.

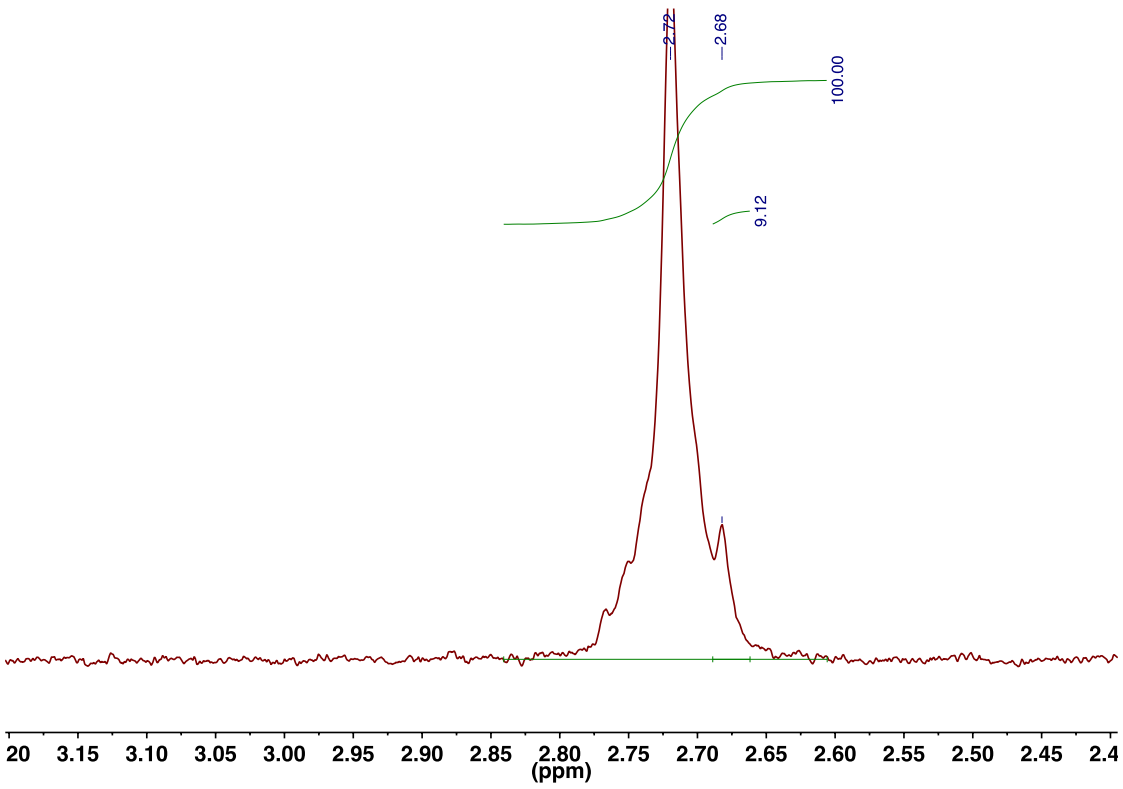


Figure S19. Selective excitation at 2.72 ppm zoomed in, *r*-P3HT-TP.

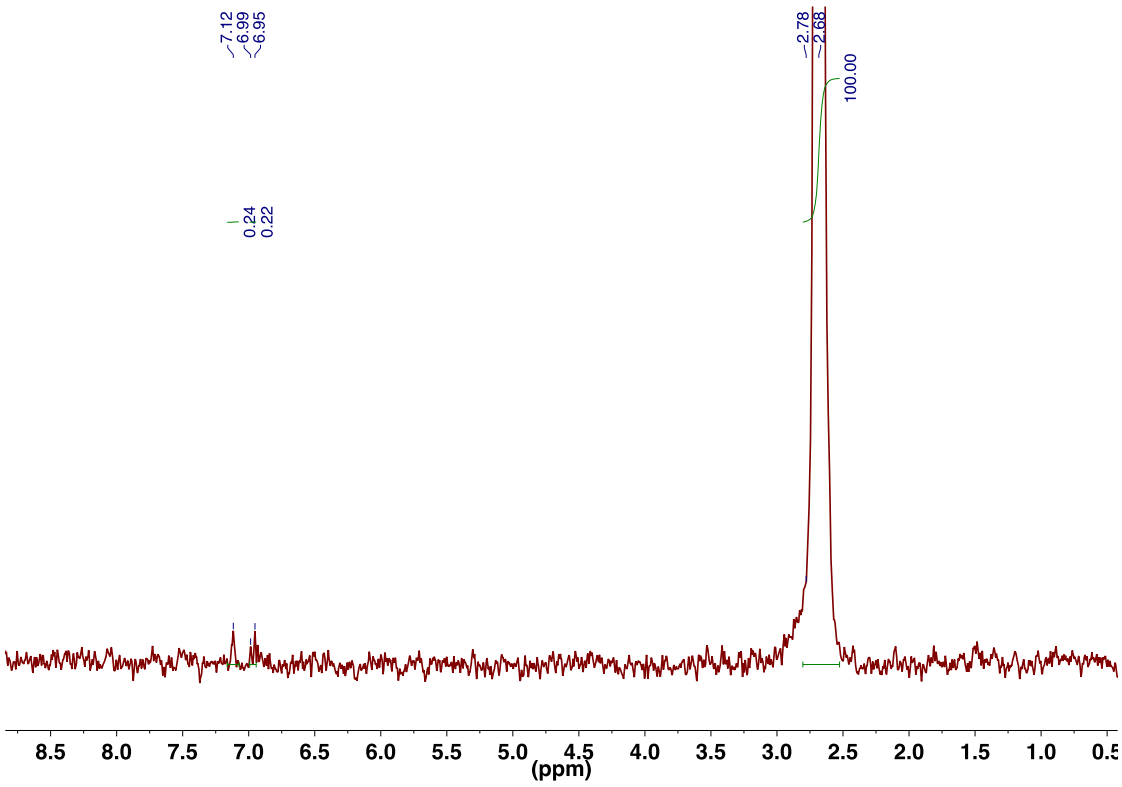


Figure S20. Selective excitation at 2.68 ppm, *r*-P3HT-TP.

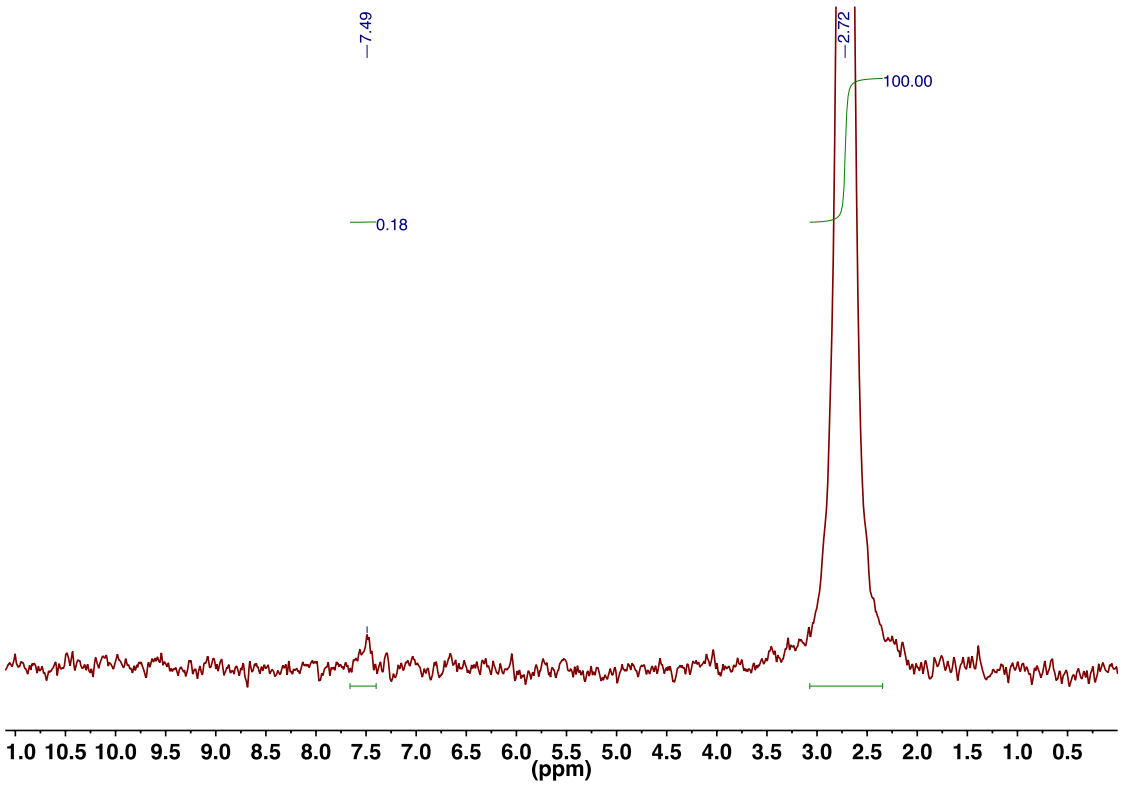


Figure S21. Selective excitation at 2.70 ppm, *sr*-P3HTT-TP.

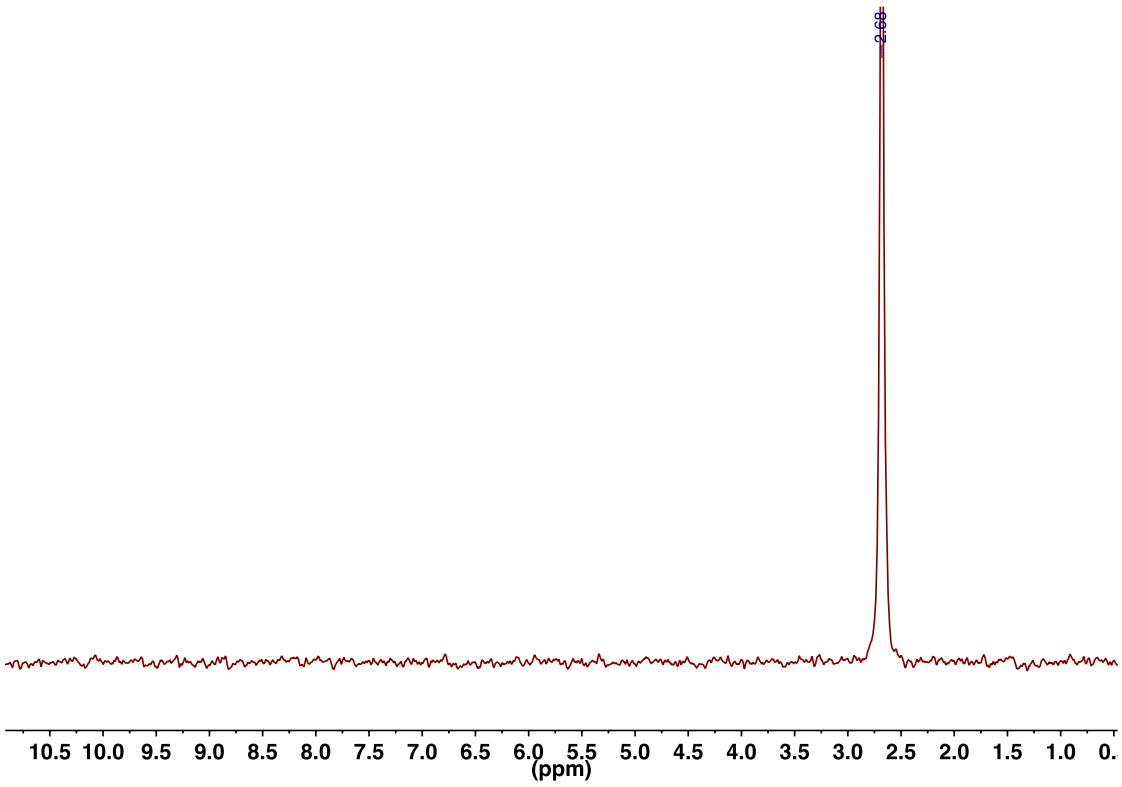


Figure S22. Selective excitation at 2.68 ppm, *r*-P3HTT-TP.

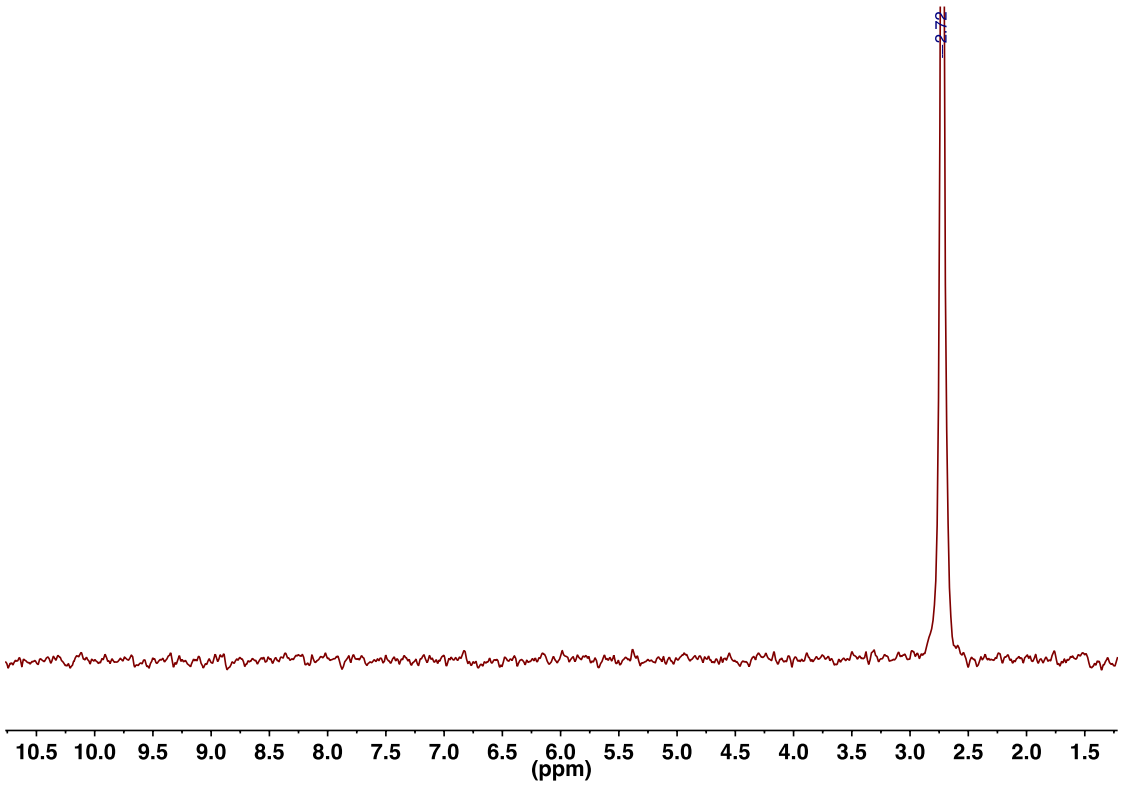


Figure S23. Selective excitation at 2.72 ppm, *r*-P3HTT-TP.

UV-Vis Spectroscopy

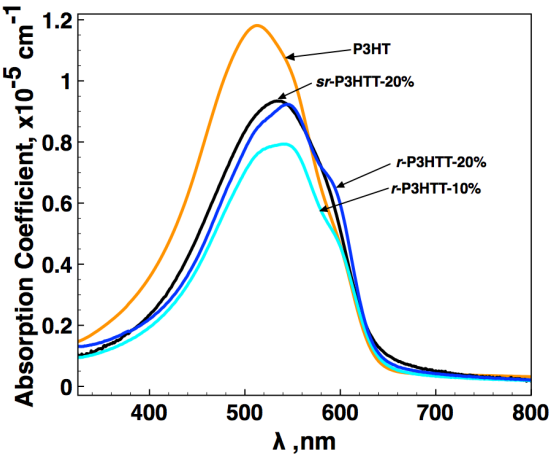


Figure S24. Absorption profiles of P3HT (orange), *r*-P3HTT-10% (light blue), *r*-P3HTT-20% (dark blue), *sr*-P3HTT-20% (black).

Grazing Incidence X-Ray Diffraction

Crystallite size was calculated using the Scherrer equation:

$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

Where,

K is a dimensionless shape factor, 0.9.

λ is the X-ray wavelength, 0.154 nm.

β is the full width at half maximum (FWHM) of the peak, in radians.

θ is the Bragg angle, in degrees.

Table S1. GIXRD data of P3HT, random, and semi-random polymers.

Polymer	2θ ±0.05, degrees	d(100) ±0.2 Å	FWHM, degrees	FWHM, radians	τ, nm
P3HT	5.59	15.7	0.660	0.0156	12.0
***r*-P3HTT-10%**	5.50	16.0	0.725	0.0131	10.5
***r*-P3HTT-20%**	5.89	14.9	0.688	0.0120	11.5
***sr*-P3HTT-20%**	5.79	15.2	0.896	0.0115	8.87
***r*-P3HTT-TP**	5.74	15.3	0.824	0.0144	9.65
***r*-P3HT-TP**	5.49	16.0	0.934	0.0163	8.51
***sr*-P3HTT-TP**	-	-	-	-	-

Cyclic Voltammetry

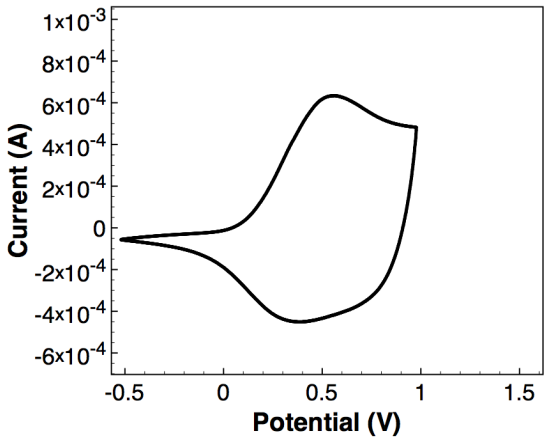


Figure S25. *sr*-P3HTT-TP film CV.

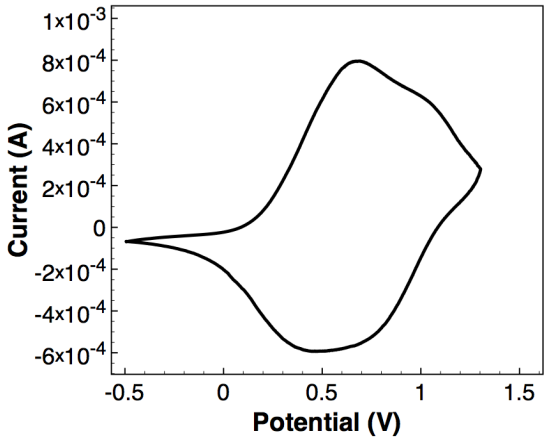


Figure S26. *r*-P3HTT-TP film CV.

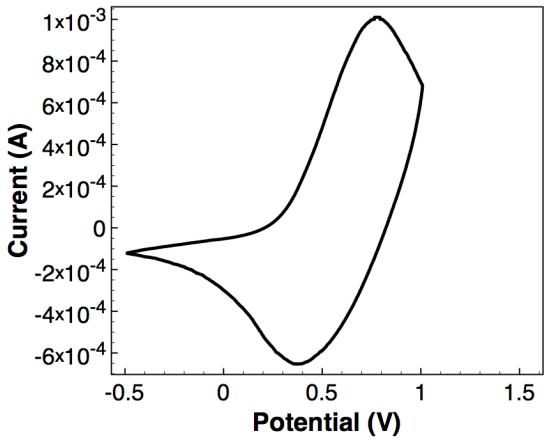


Figure S27. *r*-P3HT-TP film CV.

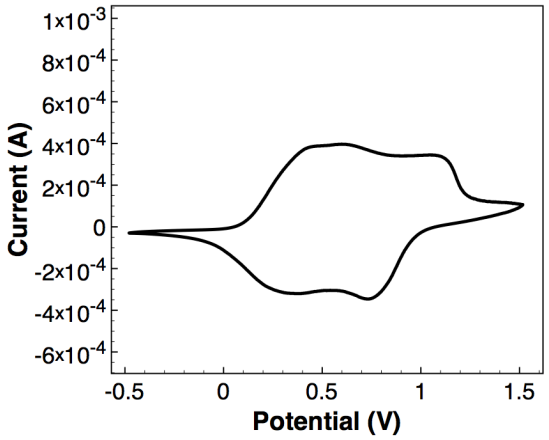


Figure S28. *r*-P3HTT-10% film CV.

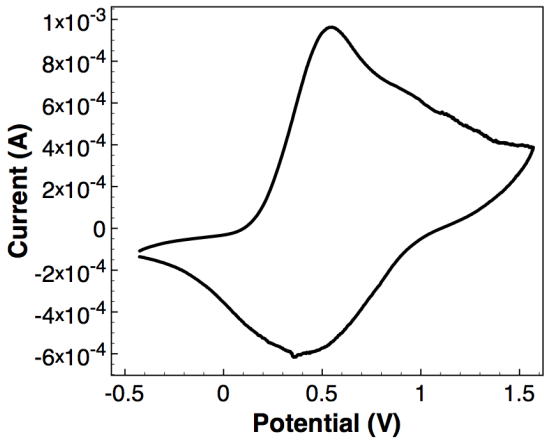


Figure S29. *r*-P3HTT-20% film CV.

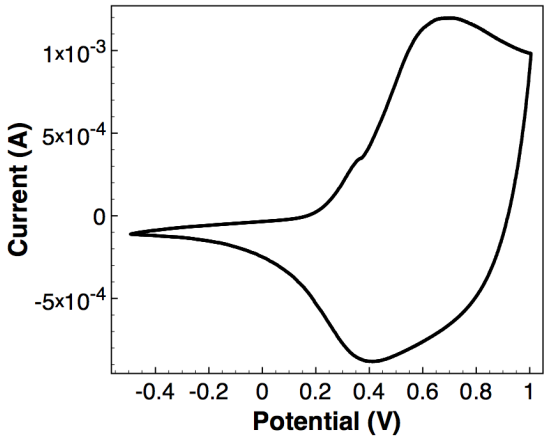


Figure S30. *sr*-P3HTT-20% film CV.

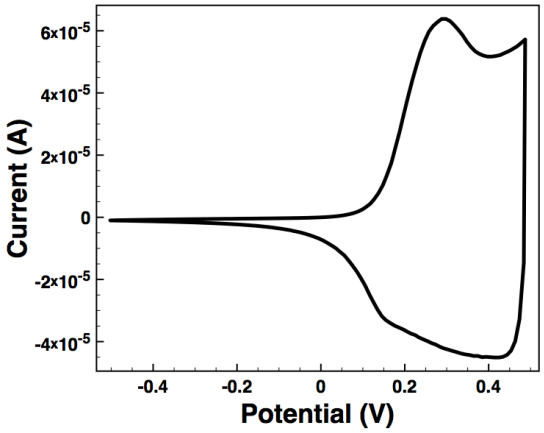


Figure S31. P3HT Film CV

Differential Scanning Calorimetry

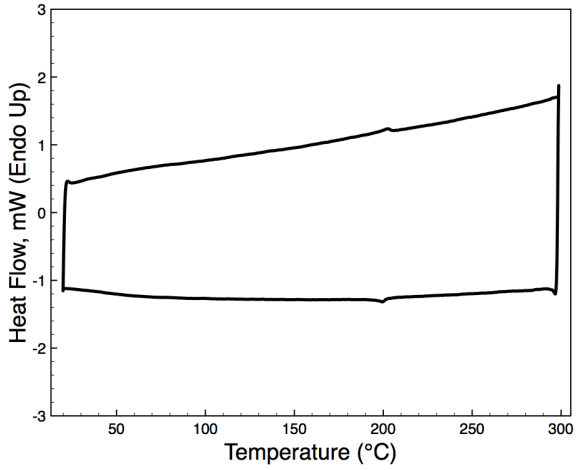


Figure S32. *sr*-P3HTT-TP DSC trace.

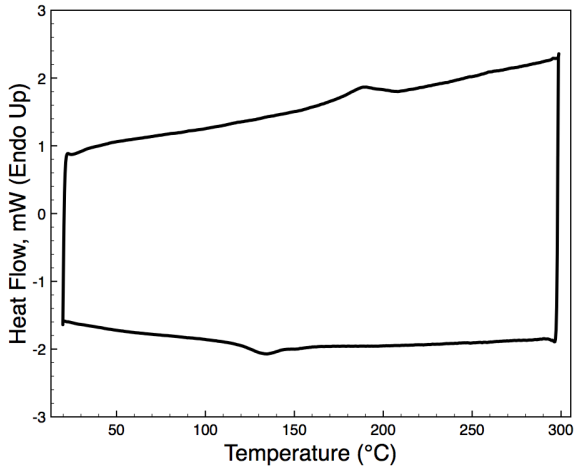


Figure S33. *r*-P3HTT-TP DSC trace.

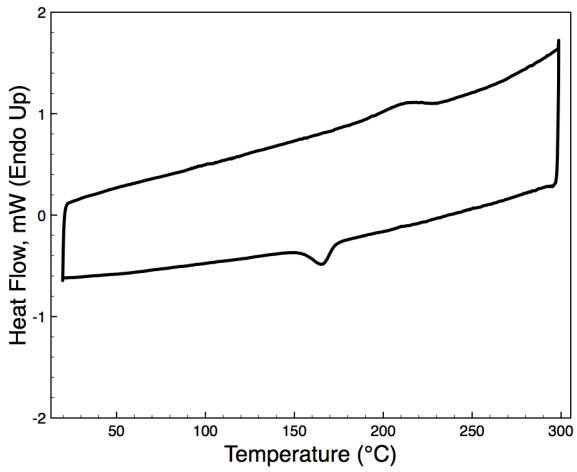


Figure S34. *r*-P3HT-TP DSC trace.

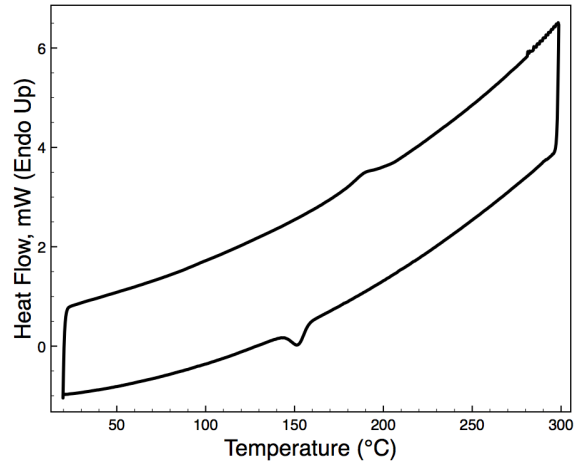


Figure S35. *r*-P3HTT-10% DSC trace.

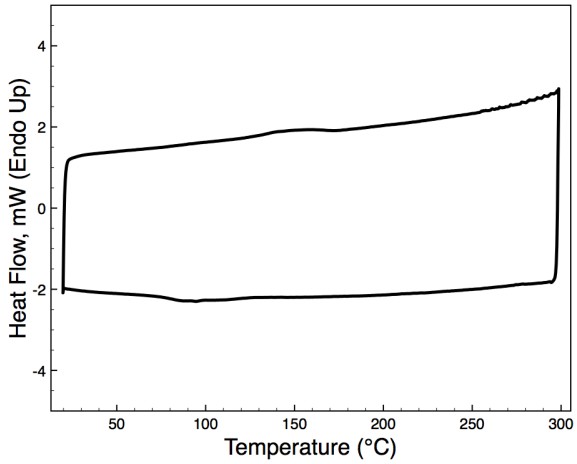


Figure S36. *r*-P3HTT-20% DSC trace.

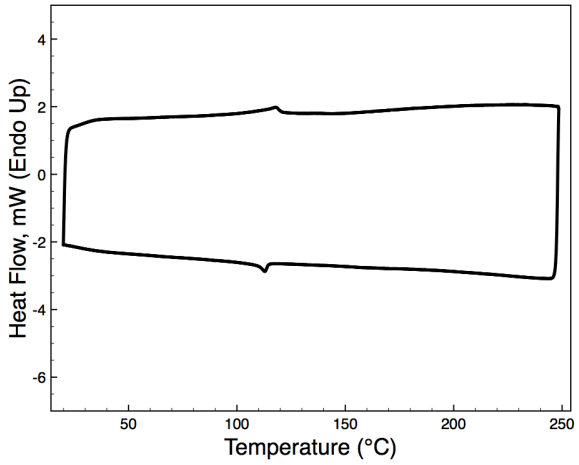


Figure S37. *sr*-P3HTT-20% DSC trace.

References.

(1) Burkhart, B.; Khlyabich, P. P.; Cakir Canak, T.; LaJoie, T. W.; Thompson, B. C. *Macromolecules* **2011**, *44* (6), 1242–1246.
(2) Wen, L.; Heth, C. L.; Rasmussen, S. C. *Phys. Chem. Chem. Phys.* **2014**, *16* (16), 7231–7240.
(3) Fei, Z.; Pattanasattayavong, P.; Han, Y.; Schroeder, B. C.; Yan, F.; Kline, R. J.; Anthopoulos, T. D.; Heeney, M. *Journal of the American Chemical Society* **2014**, *136* (43), 15154–15157.
(4) Crouch, D. J.; Sparrowe, D.; Heeney, M.; McCulloch, I.; Skabara, P. J. *Macromol. Chem. Phys.* **2010**, *211* (24), 2642–2648.