Electronic Supporting Information

Tuning the surface energies in a family of poly-3-alkylthiophenes bearing hydrophilic side-chains synthesized via direct arylation polymerization (DArP)

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General: All reactions were performed under dry N_2 in oven dried glassware, unless otherwise noted. Unless noted otherwise, all reagents were purchased and used as received from commercial sources. Solvents were purchased from VWR and used without purification, unless otherwise noted. Palladium(II) acetate was purchased from Beantown Chemical and used as received.

K_2CO_3 was ground into a fine powder and dried at 120 °C in a vacuum oven before use. Anhydrous *N,N*-dimethylacetamide (DMA) was purchased from Acros Organics and used as received. 2-(thiophen-3-yl)ethanol was purchased from OXCHEM and used as received. 3-bromothiophene was purchased from Matrix Scientific and used as received.

All ^{1}H-NMR were recorded at 25 °C using $CDCl_3$ on either a Varian Mercury 400 MHz, Varian VNMRS-500 MHz, or a Varian VNMR-600 MHz. All spectra were referenced to $CHCl_3$ (7.26 ppm), unless noted otherwise. Number average molecular weights (M_n) and dispersity (Đ) were determined by size exclusion chromatography (SEC) using a Viscotek GPC Max VE 2001 separation module and a Viscotek Model 2501 UV detector with 70 °C HPLC grade 1,2-dichlorobenzenen (*o*-DCB) as eluent at a flow rate of 0.6 mL/min on one 300 × 7.8 mm TSK-Gel GMHHR-H column (Tosoh Corp). The instrument was calibrated vs. polystyrene standards (1050–3,800,000 g/mol), and data were analysed using OmniSec 4.6.0 software. Polymer samples were dissolved in HPLC grade o-dichlorobenzene at a concentration of 0.5 mg ml−1 , stirred at 110-120 °C until dissolved, cooled to room temperature, and filtered through a 0.2 μm PTFE filter.

For polymer thin-film measurements, solutions were spin-coated onto pre-cleaned glass slides from chloroform ($CHCl_3$) solutions at 7 mg/mL. UV-Vis absorption spectra were obtained on a PerkinElmer Lamda 950 spectrophotmeter. The thickness of the thin films and grazing-incidence X-ray diffraction (GIXRD) measurements were obtained using a Rigaku Diffractometer Ultima IV using Cu Kα radiation source (λ = 1.54 Å) in the reflectivity and grazing-incidence mode, respectively.

Surface energy studies of neat polymer films were performed on a Ramé-Hart Instrument Co. contact angle goniometer model 290-F1 and analyzed using Surface Energy (two liquids) tool implemented in DROPimage 2.4.05 software. Films on pre-cleaned glass slides were prepared via spin-coating from 5 mg/mL $CHCl_3$. Water and glycerol were used as the two solvents in the so-called two-liquid model to measure the contact angle, and harmonic mean Wu model[1,2] was used to calculate the average surface energy values for each film according to the following set of equations:

$$(1)\ \gamma_w \cdot (1 + \cos(Z^w)) = \frac{4 \cdot \gamma_w^d \cdot \gamma^d}{\gamma_w^d + \gamma^d} + \frac{4 \cdot \gamma_w^p \cdot \gamma^p}{\gamma_w^p + \gamma^p}$$

$$(2)\ \gamma_g \cdot (1 + \cos(Z^g)) = \frac{4 \cdot \gamma_g^d \cdot \gamma^d}{\gamma_g^d + \gamma^d} + \frac{4 \cdot \gamma_g^p \cdot \gamma^p}{\gamma_g^p + \gamma^p}$$

$$(3)\ \gamma^{tot} = \gamma^d + \gamma^p$$

$$\gamma_w = 72.8\frac{mJ}{m^2}\,;\,\gamma_w^d = 21.8\frac{mJ}{m^2}\,;\,\gamma_w^p = 51.0\frac{mJ}{m^2}$$

$$\gamma_g = 64.0\frac{mJ}{m^2}\,;\,\gamma_g^d = 34.0\frac{mJ}{m^2}\,;\,\gamma_g^p = 30.0\frac{mJ}{m^2}$$

where Z^w is the contact angle with water, Z^g is the contact angle with glycerol, γ^{tot} is the total surface energy, γ^p and γ^d are polar and dispersive surface energy components.

For the one-liquid method with water as the probe liquid the Ramé-Hart DROPimage Advanced software was used to determine the surface energies. For this method the drop shape method is determined by a contour fitting algorithm, and the profile coordinates are used to calculate the surface tension, contact angle and the area and volume of the drops. Calculation of surface tension is accomplished by precise mathematical analysis of the drop profile using cubic interpolation. Curves are fitted with linear polynomials using the method of least squares. The final calculations are accomplished using the theoretical profiles produced by a numerical integration of the Young-Laplace equation. The relevant equations are depicted below where γ_S is the surface energy of the solid, γ_{SL} is the interfacial tension between the solid and the liquid, γ_{LV} is the surface tension of the liquid, $\varTheta$ is the angle the liquid form with the surface and $\beta = 0.000115\ (m^2/mJ)^2$.[3]

$$(4)\ \ \gamma_S = \gamma_{SL} + \gamma_{LV} \cdot \cos\varTheta$$

$$(5)\ \ \gamma_{SL} = \gamma_S + \gamma_{LV} - 2\sqrt{\gamma_{LV}\gamma_S} \cdot e^{-\beta}(\gamma_{LV} - \gamma_S)^2$$

$$(6)\ \ \cos\varTheta = -1 + 2\sqrt{\frac{\gamma_S}{\gamma_{LV}}} \cdot e^{-\beta}(\gamma_{LV} - \gamma_S)^2$$

Cyclic voltammetry (CV) was performed on Princeton Applied Research VersaStat3 potentiostat under the control of VersaStudio 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)[3,4] and a Pt wire counter electrode was purged with nitrogen and maintained under a nitrogen atmosphere during all measurements. Polymer films were made by drop-casting an $CHCl_3$ solution of polymer (10 mg/mL) and tetrabutylammonium hexafluorophosphate (TBAPF6) (30 mg/mL) directly onto the Pt wire and dried under nitrogen prior to measurement. Acetonitrile was distilled over CaH_2 prior to use, and TBAPF6 (0.1 M) was used as the supporting electrolyte.

Differential scanning calorimetry (DSC) profiles were recorded on a Perkin-Elmer DSC 8000 with a scan rate of 10 °C/min. The sample size was ~ 5 mg; polymers were used as obtained after purification. The second cycle for each sample is depicted below. The heating/cooling protocol used is:

1. Hold for 2.0 min at 20.0 °C
2. Heat from 20.0 °C to 250.0 °C at 10.0 °C/min
3. Cool from 250.0 °C to 20.0 °C at 10.0 °C/min
4. Heat from 20.0 °C to 250.0 °C at 10.0 °C/min
5. Cool from 250.0 °C to 20.0 °C at 10.0 °C/min

Mobility was measured using a hole-only device configuration of ITO/PEDOT:PSS/Polymer/Al in the space charge limited current regime (SCLC). All steps of the device fabrication and testing were performed in air. ITO-coated glass substrates (10 Ω/square, Thin Film Devices Inc.) were subsequently cleaned by sonication in detergent, de-ionised water, tetrachloroethylene, acetone and isopropyl alcohol and dried in a N_2 stream. A thin layer of PEDOT:PSS (Baytron® P VP AI 4083, filtered with a 0.45 μm PVDF syringe filter – Pall Life Science) was first spin-coated on the pre-cleaned ITO-coated glass substrate and annealed at 130 °C for 60 minutes under vacuum. Polymer solutions were prepared in chloroform and stirred for 24 hours at 40 °C. The polymer active layer was spin-coated (with a 0.45 μm PTFE syringe filter – Whatman) on top of the PEDOT:PSS layer. Films were placed in a nitrogen cabinet for 20 minutes before being transferred to a vacuum chamber. The substrates were pumped down to a high vacuum and aluminium (100 nm) was thermally evaporated at 3-4 Å/s using a Denton Benchtop Turbo IV Coating System onto the active layer through shadow masks to define the active area of the devices. The dark current was measured under ambient conditions. At sufficient potential the mobilities of charges in the device can be determined by fitting the dark current to the model of SCL current and is described by the following equation where J_{SCLC} is the current density, ε_0 is the permittivity of space, ε_R is the dielectric constant of the polymer (assumed to be 3), μ is the zero-field mobility of the majority charge carriers, V is the effective voltage across the device (V = $V_{applied} - V_{bi} - V_r$), and L is the polymer layer thickness:

$$J_{SCLC} = \frac{9}{8} \cdot \varepsilon_R \cdot \varepsilon_0 \cdot \mu \cdot \frac{V^2}{L^3}$$

The series and contact resistance of the hole-only device was measured using a blank (ITO/PEDOT/Al) configuration and the voltage drop due to this resistance (V_r) was subtracted from the applied voltage. The built-in voltage (V_{bi}), which is based on the relative work function difference of the two electrodes, was also subtracted from the applied voltage. The built-in voltage can be determined from the transition between the ohmic region and the SCL region and is found to be about 1 V. Polymer film thicknesses were measured using GIXRD in the reflectivity mode.

The ratios of functionalized comonomer to 3-hexyl-thiophene monomer in the copolymers which are listed in Table S3 were determined from the respective ^{1}H-NMR spectra by integrating the -CH$_2$- signal of the carbon on the side chain that is directly attached to the thiophene core and then calculating the ratio form those integrals. These calculations are shown for P3HT-eth-50 as an example below.
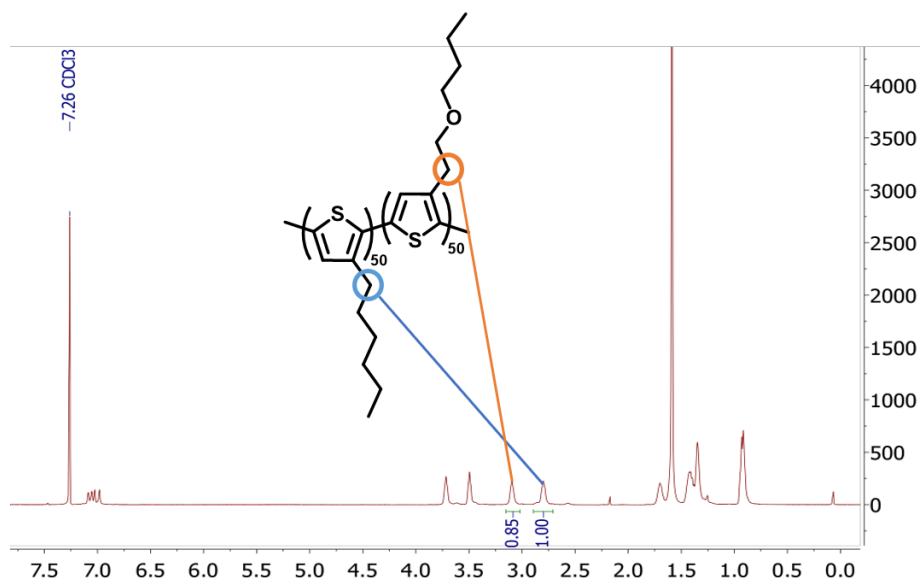
Ratio ether-comonomer in copolymer: $\frac{0.85}{(0.85+1.00)} = 0.46 = 46\%$

Monomer synthesis:
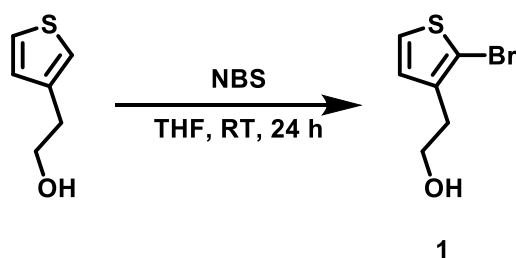
2-(2-bromothiophen-3-yl)ethan-1-ol (1): An oven dried three-neck flask was vacuum backfilled three times and charged with 3.59 mL 2-(3-thionyl)ethanol (4.10 g, 32.0 mmol, 1.00 eq.) and 40.0 mL dry tetrahydrofuran. The reaction mixture was cooled to 0 °C and 5.92 g recrystallized *N*-bromosuccinimide (33.28 mmol, 1.04 eq.) were added in portions under vigorous stirring. Upon addition the flask was wrapped in aluminum-foil, allowed to warm up to room temperature and stirred overnight. The crude mixture was transferred to a separatory funnel with 40.0 mL diethyl ether and the organic phase washed with water (3 × 40 mL), dried over MgSO$_4$, filtered, and concentrated *in vacuo*. The crude product was purified via column chromatography (hexanes/ethyl acetate = 80/20) and subsequently vacuum distillation affording the desired product as a clear, colorless oil in 60% yield (15.966 g). ^{1}H-NMR (500 MHz, Chloroform-*d*): δ = 7.22 (m, 1H), 6.88 (m, 1H), 3.84 (dt, 2H), 2.87 (dt, 2H).
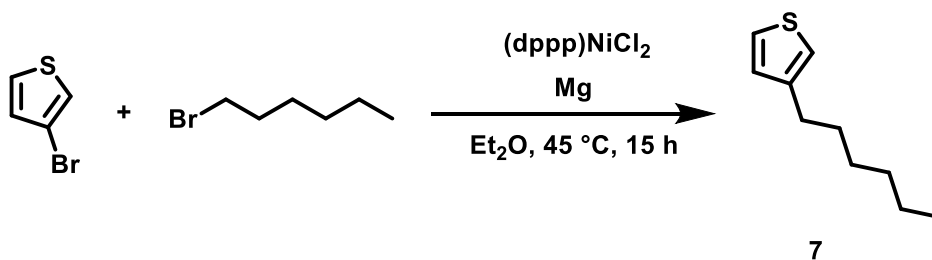
3-hexylthiophene (7): A flame-dried three-neck flask equipped with a condenser and stir-bar was vacuum-backfilled three times. 1.64 g of freshly ground magnesium turnings (67.47 mmol, 1.10 eq.) and a flake of iodine were added and dissolved in 20.0 mL dry diethyl ether. In a separate flask 10.30 mL 1-bromohexane (12.15 g, 73.61 mmol, 1.20 eq.) were dissolved in 20.0 mL dry diethyl ether and the resulting mixture was added dropwise under vigorous stirring to the magnesium mixture. Upon addition the reaction mixture is heated up to 40 °C until all magnesium turnings are dissolved and subsequently cooled to room temperature. 49.87 mg (dppp)NiCl$_2$ (0.0921 mmol, 0.0015 eq.) were added and the mixture stirred at room temperature for 15 min. 5.75 mL 3-bromothiophene (10.0 g, 61.34 mmol, 1.00 eq.) were added dropwise and the resulting mixture heated up to 45 °C for 15 h. Upon cooling to room temperature, the mixture is poured into cold 10% aqueous HCl (100 mL) and the aqueous mixture extracted with diethyl ether (3 × 50 mL). The combined organic phases are washed with water (1 × 50 mL), dried over MgSO$_4$, filtered, and concentrated *in vacuo*. The crude product is purified via vacuum distillation yielding the desired product as a clear, colorless liquid in 67% yield (6.94 g). ^{1}H-NMR (500 MHz, Chloroform-*d*): δ = 7.24 (m, 1H), 6.93 (m, 2H), 2.63 (t, 2H), 1.62 (p, 2H), 1.31 (m, 6H), 0.89 (t, 3H).
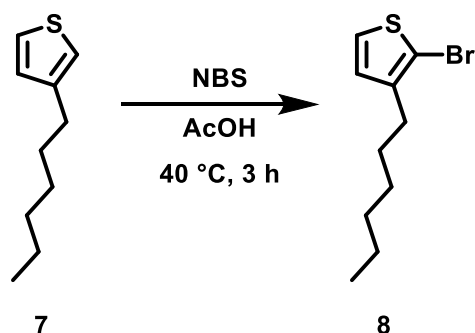
2-bromo-3-hexylthiophene (8): An oven dried three-neck flask was vacuum backfilled three times and then 6.94 g 3-hexylthiophene (41.24 mmol, 1.00 eq.) were added and dissolved in 55.0 mL concentrated acetic acid. Then under N$_2$ 7.34 g recrystallized *N*-bromosuccinimide (41.24 mmol, 1.00 eq.) were added at once and the reaction mixture was heated up to 40 °C and stirred for 3 h. Upon cooling to room temperature, the mixture was poured into 70 mL DI water. The aqueous solution was extracted with diethyl ether (3 × 70 mL), the combined organic layers washed with 10% aqueous sodium chloride solution (2 × 75 mL), dried over MgSO$_4$, filtered, and concentrated *in vacuo*. The crude product was purified via vacuum distillation yielding the desired product as a clear, colorless oil in 68% yield (6.93 g). ^{1}H-NMR (500 MHz, Chloroform-*d*): δ = 7.17 (d, *J* = 5.4 Hz, 1H), 6.80 (d, *J* = 5.4 Hz, 1H), 2.56 (t, 2H), 1.57 (m, 2H), 1.31 (m, 6H), 0.89 (t, 3H).
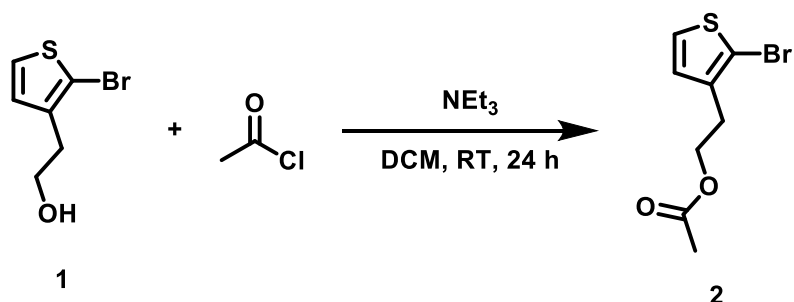
2-(2-bromothiophen-3-yl)ethyl acetate (2): An oven dried three-neck flask was vacuum backfilled three times. 30.0 mL dry dichloromethane were added in and cooled to 0 °C. At 0 °C 800.0 mg 2-(2-bromothiophen-3-yl)ethanol were added in and 4.64 mL 1 M acetyl chloride in dichloromethane (333.56 mg, 4.25 mmol, 1.10 eq.) and 0.646 mL triethylamine (469.11 mg, 4.64 mmol, 1.20 eq.) were added dropwise, the mixture warmed up to room temperature and subsequently stirred overnight. The mixture was quenched with saturated aqueous $NaHCO_3$ (75 mL) and extracted with dichloromethane (3 × 50 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified via column chromatography (100% DCM) yielding the desired product as a clear, colorless liquid in 94% yield (904.1 mg). ^{1}H-NMR (500 MHz, Chloroform-*d*): δ = 7.22 (d, *J* = 5.6 Hz, 1H), 6.84 (d, *J* = 5.6 Hz, 1H), 4.24 (t, 2H), 2.92 (t, 2H), 2.05 (s, 3H).
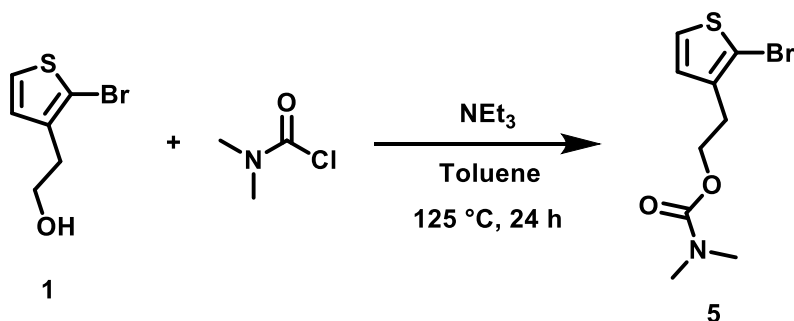
2-(2-bromothiophen-3-yl)ethyl dimethylcarbamate (5): An oven dried three-neck flask is vacuum backfilled three times and then charged with 67.5 mL dry toluene, 3.00 g 2-(2-bromothiophen-3-yl)ethanol (14.49 mmol, 1.00 eq.) and 1.76 g triethylamine (17.40 mmol, 1.20 eq.) and stirred at room temperature for 15 min. 1.59 mL dimethylcarbamic chloride (1.87 g, 17.40 mmol, 1.20 eq.) are added dropwise and the resulting mixture is then heated up to 125 °C overnight. Upon cooling to room temperature saturated aqueous $NaHCO_3$ (50 mL) are added and the resulting aqueous solution is extracted with dichloromethane (3 × 70 mL). The combined organic phases are washed with water (1 × 100 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude mixture is added to another oven dried three-neck flask that was vacuum backfilled three times and dissolved in 60.0 mL dichloromethane. 2.76 g 4-methylbenzenesulfonyl chloride (14.49 mmol, 1.00 eq.) and 1.76 g triethylamine (17.40 mmol, 1.20 eq.) are added dropwise and the mixture is stirred at 30 °C for 24 h. Upon cooling to room temperature saturated aqueous $NaHCO_3$ (50 mL) are added and the resulting

aqueous solution is extracted with dichloromethane (3 × 70 mL). The combined organic phases are dried over MgSO$_4$, filtered, and concentrated *in vacuo*. The crude product is purified via column chromatography (DCM/hexanes = 80/20) yielding the desired product as a clear yellow liquid in 10% yield (412.3 mg). ^{1}H-NMR (500 MHz, Chloroform-*d*): δ = 7.21 (d, *J* = 5.6 Hz, 1H), 6.85 (d, *J* = 5.6 Hz, 1H), 4.24 (t, 2H), 2.93 (t, 2H), 2.89 (m, 6H).
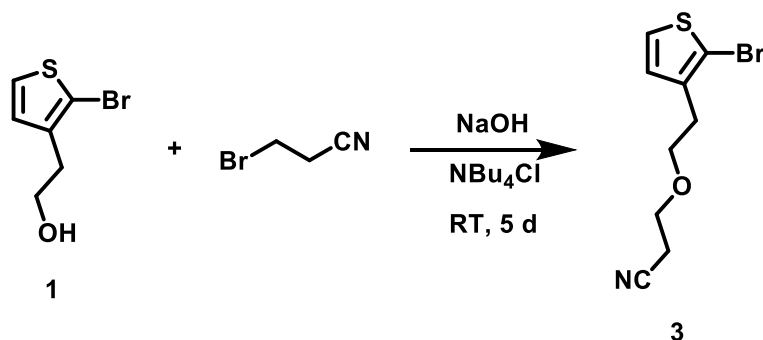

3-(2-(2-bromothiophene-3-yl)ethoxy)propanenitrile (3): In a single neck flask 32.21 mg (0.116 mmol, 0.12 eq.) NBu$_4$Cl are weighed out and dissolved in 0.0322 mL dichloromethane. The mixture is degassed with N$_2$ for 15 min and then 200.0 mg 2-(2-bromothiophene-3-yl)ethanol (0.966 mmol, 1.00 eq.) and 103.51 mg 3-bromopropionenitrile (0.773 mmol, 0.80 eq.) are added in dropwise. In a separate flask 309.03 mg (7.73 mmol, 8.00 eq.) NaOH are dissolved in 0.66 mL DI water and the aqueous solution subsequently added to the reaction mixture. The resulting mixture is stirred at room temperature for 2 days. Then another 55.6 mg of 2-(2-bromothiophene-3-yl)ethanol (0.269 mmol, 0.28 eq.) are added and stirring is continued for another 2 days. The crude mixture is diluted with 15 mL water and extracted with diethyl ether (3 × 20 mL). The combined organic phases are dried over MgSO$_4$, filtered and *concentrated in vacuo*. The crude product is purified via column chromatography (100% DCM) affording the desired product as a clear, colorless oil in 73% yield (146.4 mg). ^{1}H-NMR (500 MHz, Chloroform-*d*): δ = 7.21 (d, *J* = 5.6 Hz, 1H), 6.88 (d, *J* = 5.6 Hz, 1H), 3.67 (t, 2H), 3.66 (t, 2H), 2.88 (t, 2H), 2.59 (t, 2H).
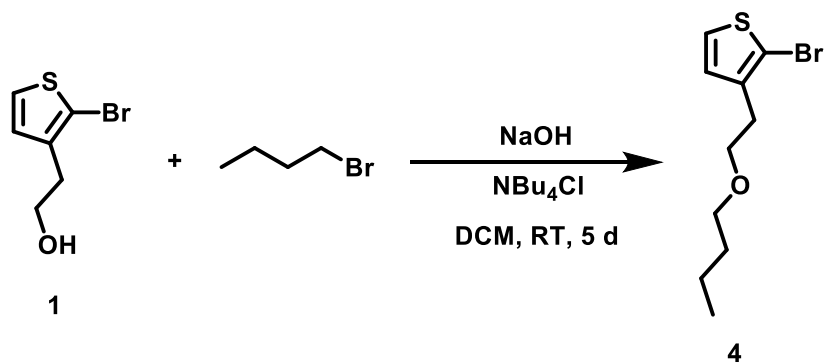
2-bromo-3-(2-butoxyethyl)thiophene (4): In a single neck flask 32.21 mg (0.116 mmol, 0.12 eq.) NBu$_4$Cl are weighed out and dissolved in 0.0322 mL dichloromethane. The mixture is degassed with N$_2$ for 15 min and then 200.0 mg 2-(2-bromothiophene-3-yl)ethanol (0.966

mmol, 1.00 eq.) and 105.87 mg 1-bromobutane (0.773 mmol, 0.80 eq.) are added in dropwise. In a separate flask 309.03 mg (7.73 mmol, 8.00 eq.) NaOH are dissolved in 0.66 mL DI water and the aqueous solution subsequently added to the reaction mixture. The resulting mixture is stirred at room temperature for 2 days. Then another 55.6 mg of 2-(2-bromothiophene-3-yl)ethanol (0.269 mmol, 0.28 eq.) are added and stirring is continued for another 2 days. The crude mixture is diluted with 15 mL water and extracted with diethyl ether (3 × 20 mL). The combined organic phases are dried over MgSO$_4$, filtered and *concentrated in vacuo*. The crude product is purified via column chromatography (100% DCM) affording the desired product as a clear, yellow oil in 84% yield (171.4 mg). ^{1}H-NMR (500 MHz, Chloroform-*d*): δ = 7.19 (d, *J* = 5.6 Hz, 1H), 6.87 (d, *J* = 5.6 Hz, 1H), 3.59 (t, 2H), 3.44 (t, 2H), 2.86 (s, 2H), 1.56 (m, 2H), 1.35 (m, 2H), 0.91 (t, 3H).
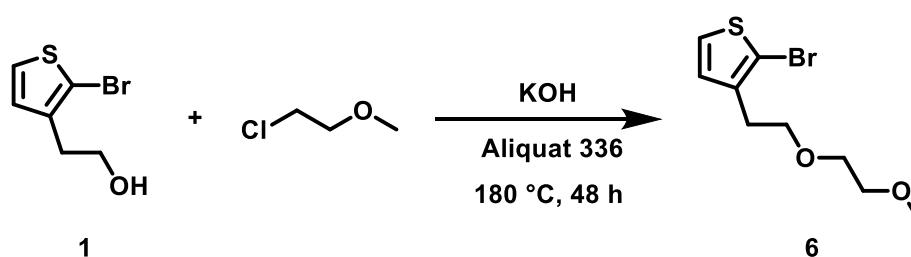
2-Bromo-3(2-(2-methoxyethoxy)ethyl)thiophene (6): An oven dried three-neck flask is vacuum backfilled three times and then charged with 1.22 g freshly ground KOH (21.73 mmol, 3.00 eq.). Under N$_2$ 1.65 mL 2-chloroethylmethylether (1.71 g, 18.11 mmol, 2.50 eq.), 1.50 g 2-(2-bromothiophene-3-yl)ethanol (7.24 mmol, 1.00 eq.) and 0.092 mL Aliquat 336 are added and the resulting mixture heated to 180 °C for 48 h. Upon cooling to room temperature the mixture is diluted with 10 mL water and extracted with diethyl ether (3 × 10 mL). The combined organic phases are washed with 10% aqueous HCl (3 × 30 mL), dried over MgSO$_4$, filtered, and concentrated in vacuo. The crude product is purified via column chromatography (hexanes/ethyl acetate = 75/25) affording the desired product as a clear, colorless liquid in 43% yield (816.1 mg). ^{1}H-NMR (500 MHz, Chloroform-*d*): δ = 7.19 (d, *J* = 5.5 Hz, 1H), 6.87 (d, *J* = 5.5 Hz, 1H), 3.65 (m, 4H), 3.56 (m, 2H), 3.39 (s, 3H), 2.89 (t, 2H).

General polymerization procedure:

An oven-dried three-neck flask equipped with a stir-bar was stoppered with a rubber-septum and a glass stopper, connected to the Schlenck-line and vacuum backfilled three times. Both monomers (a total of 0.4484 mmol), K$_2$CO$_3$ (0.673 mmol, 1.50 eq.) and anhydrous DMA (3.74 mL) were added and the resulting mixture was degassed with N$_2$ for 20 min. Pd(OAc)$_2$ (0.009 mmol, 0.02 eq.) were quickly added and the mixture was degassed with N$_2$ for another 20 min. The rubber-septum was replaced with a glass stopper and the vessel was stirred a room temperature for 5 min. It was then submerged in a pre-heated oil bath at 70 °C with moderate stirring for 24 h. The reaction was then cooled to room temperature, solids were dissolved in hot dichlorobenzene (3-5 mL) and the mixture was precipitated into a cold 10% (v:v)

NH₄OH/methanol solution with high stirring (125 mL). The precipitate was collected via decantation into a thimble and washed with methanol. The crude product was purified via Soxhlet extraction with methanol and hexanes and then collected in chloroform. Polymer solutions were concentrated *in vacuo*, precipitated into cold methanol (125 mL) and collected via filtration. They were then dried under high-vacuum overnight.
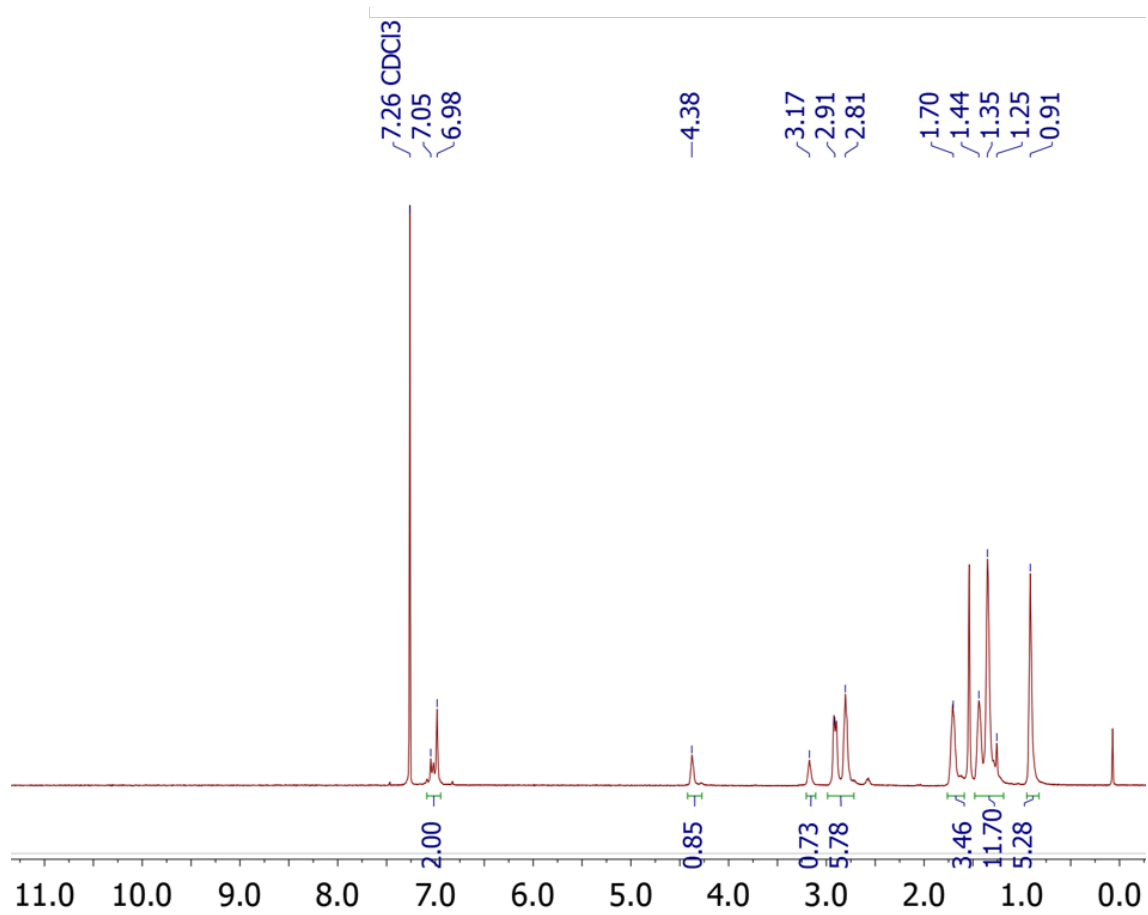
¹H-NMR of Polymers:
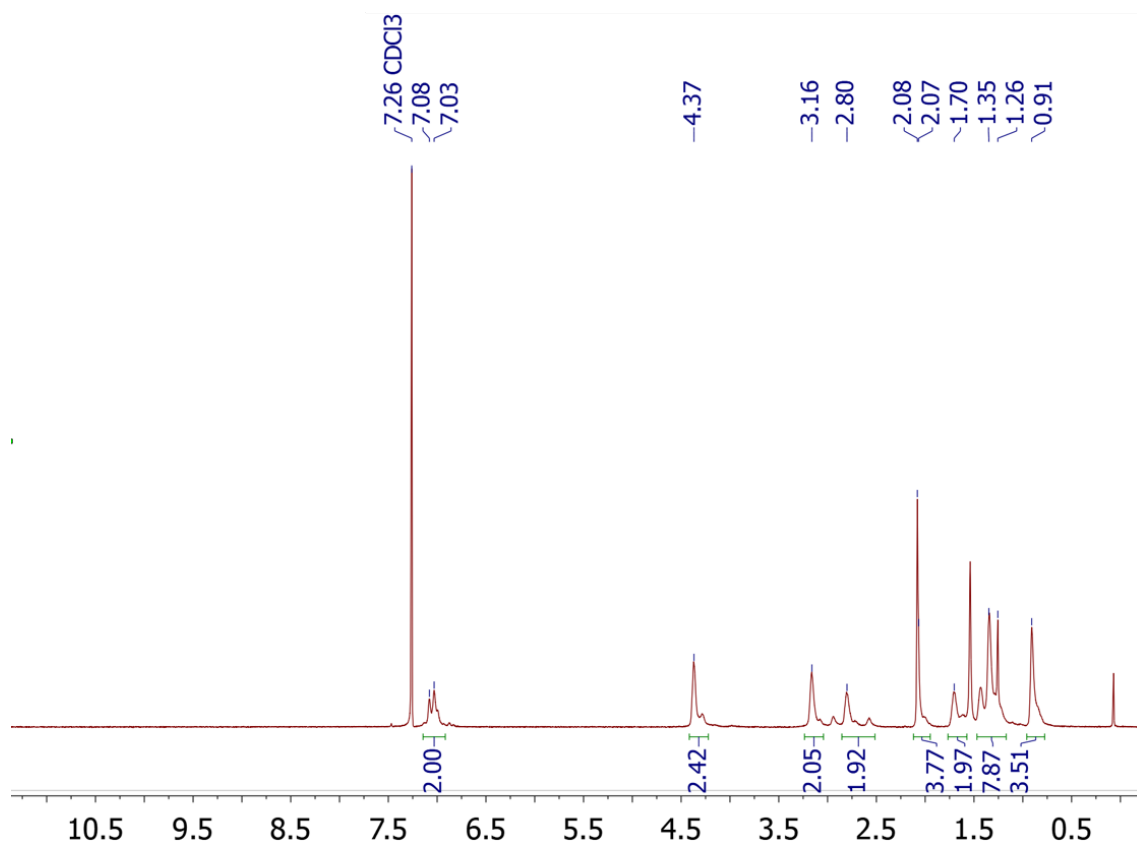
Fig. S1: ¹H-NMR (CDCl₃, 25°C, 500 MHz) spectra of P3HT-est-50.
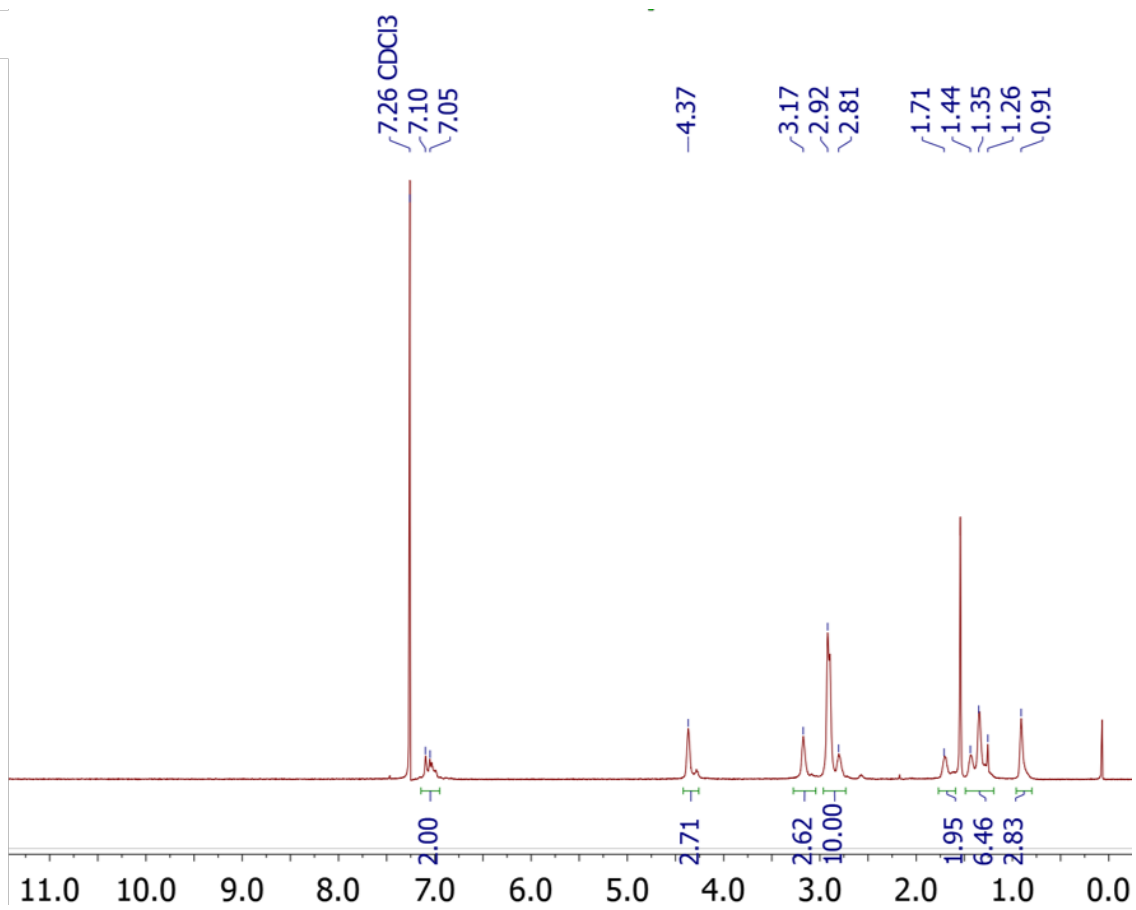
Fig. S2: ^{1}H-NMR (CDCl$_3$, 25°C, 500 MHz) spectra of P3HT-carb-50.
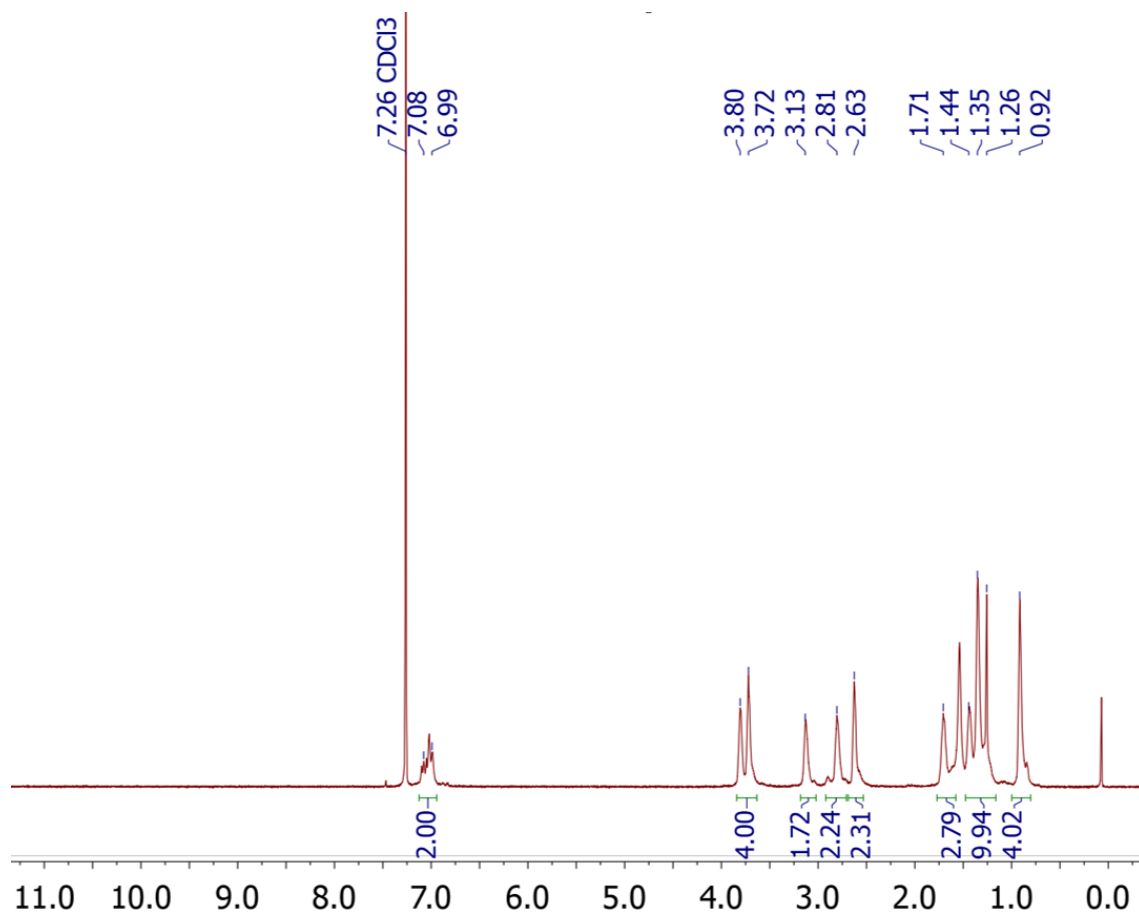
Fig. S3: ^{1}H-NMR (CDCl$_3$, 25°C, 500 MHz) spectra of P3HT-nit-50.

Fig. S4: ^{1}H-NMR (CDCl$_3$, 25°C, 500 MHz) spectra of P3HT-carb-25.
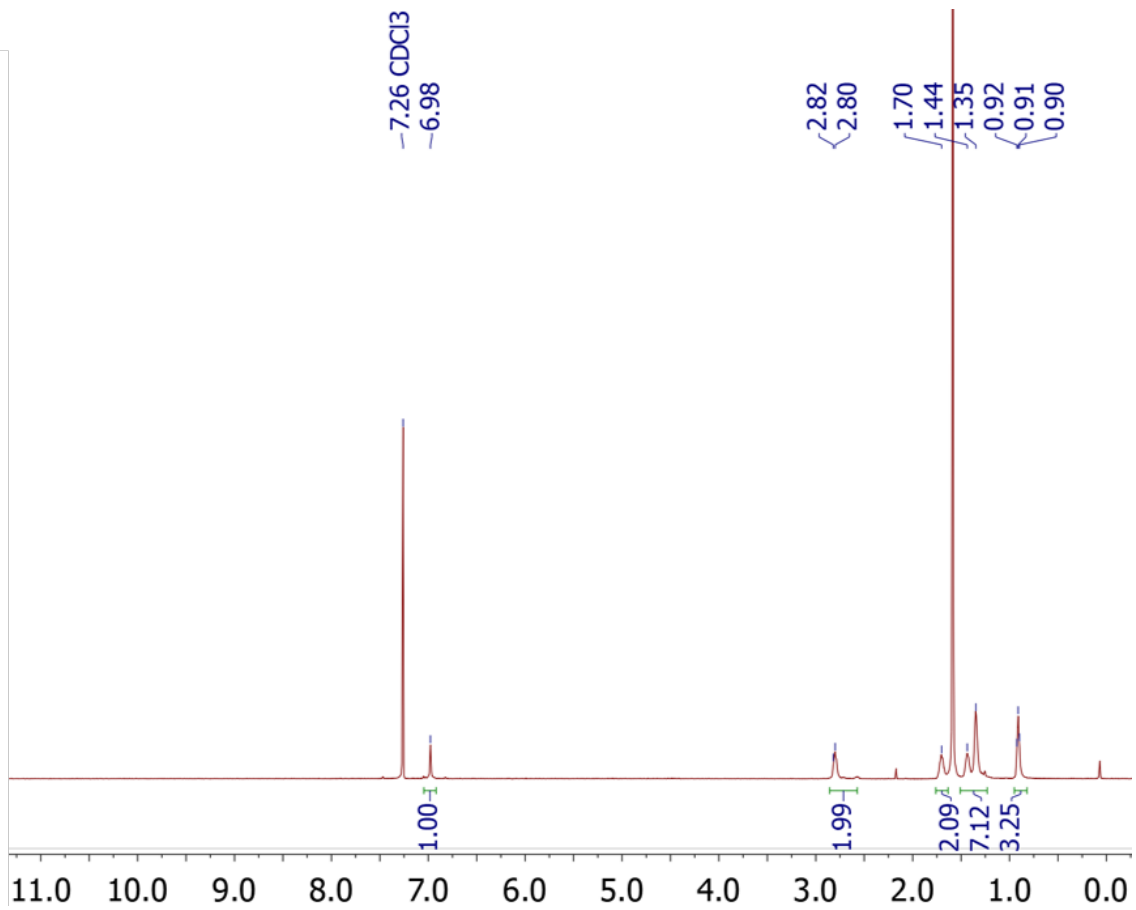
Fig. S5: ^{1}H-NMR (CDCl$_3$, 25°C, 500 MHz) spectra of P3HT.
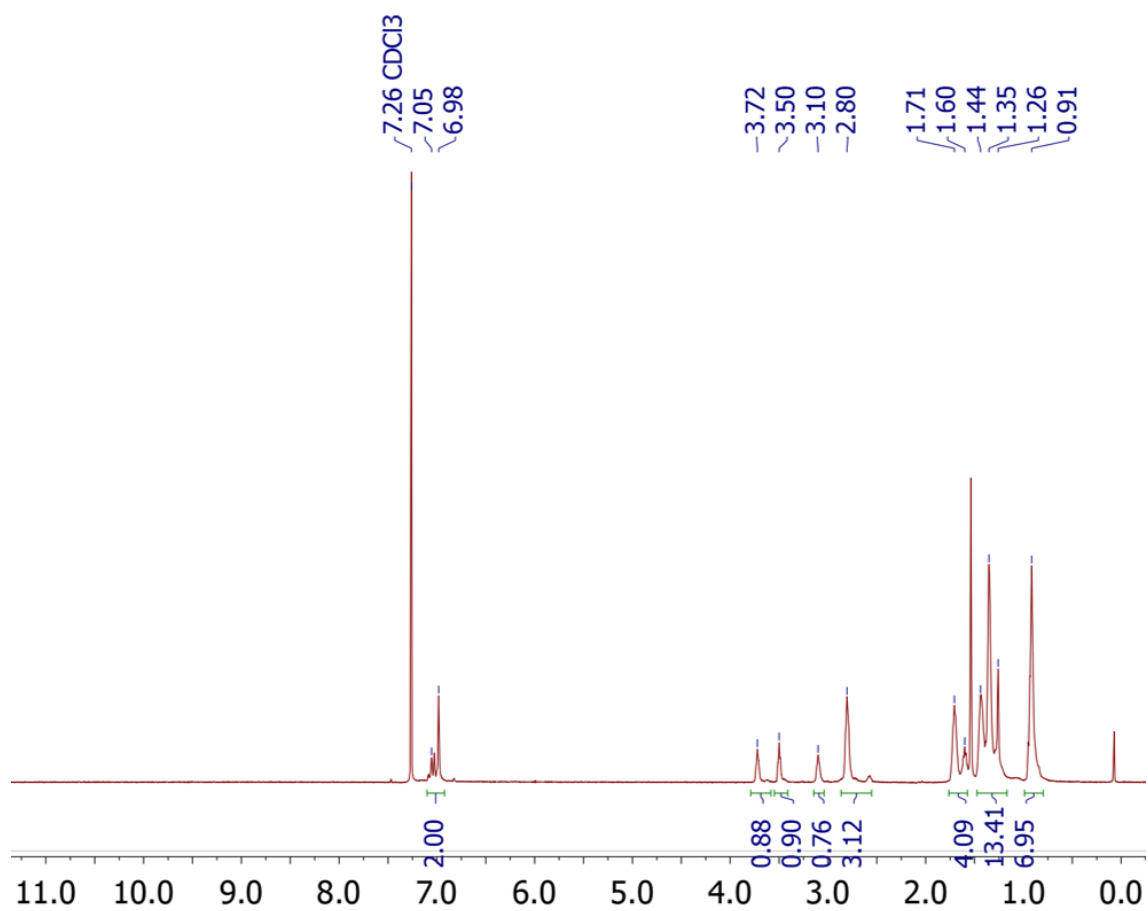
Fig. S6: ^{1}H-NMR (CDCl$_3$, 25°C, 500 MHz) spectra of P3HT-eth-25.
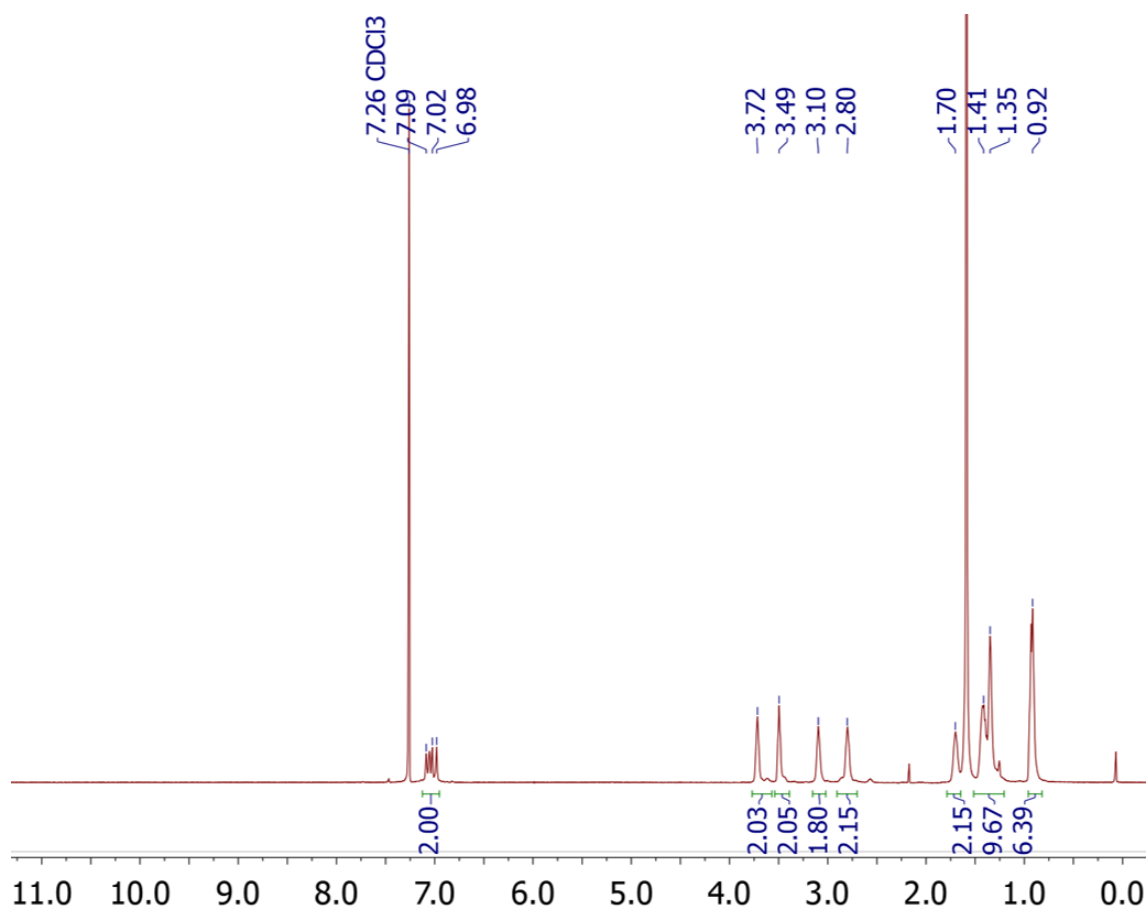
Fig. S7: ^{1}H-NMR (CDCl$_3$, 25°C, 500 MHz) spectra of P3HT-eth-50.
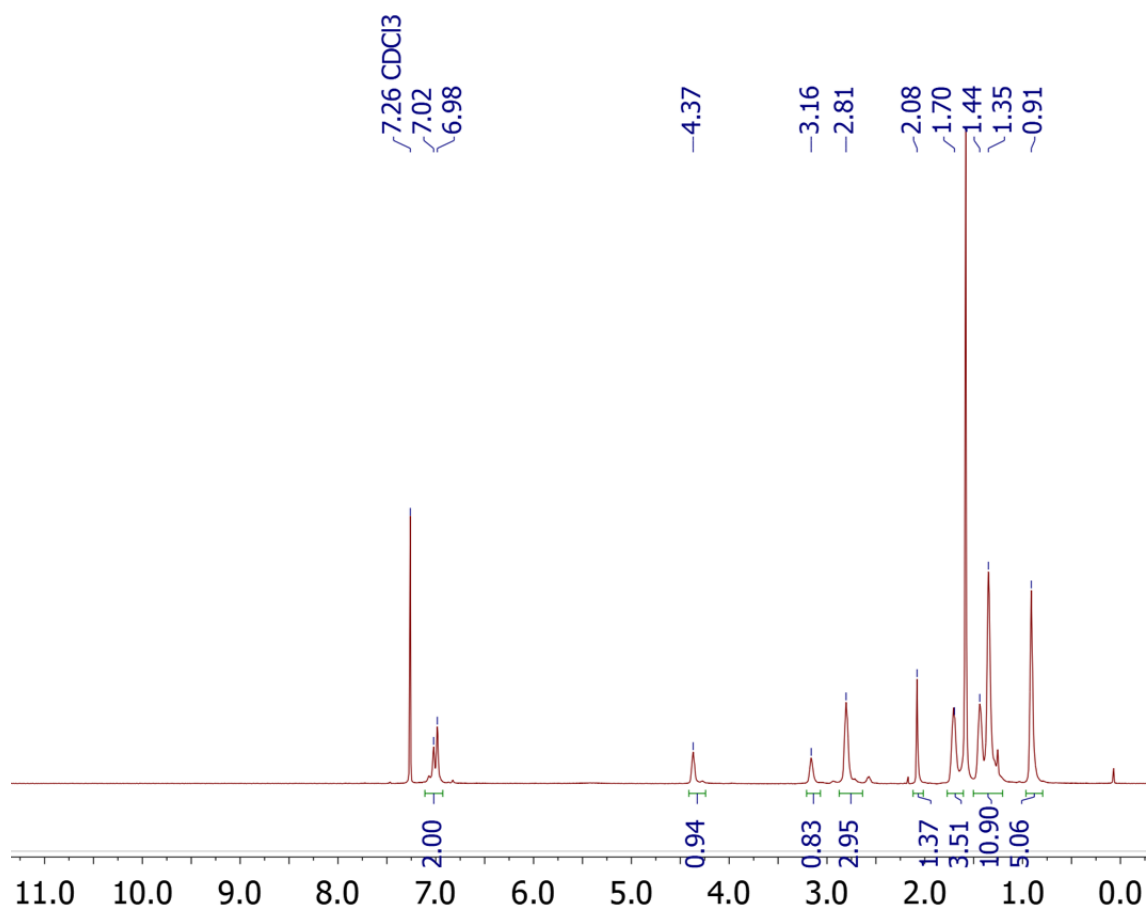
Fig. S8: ^{1}H-NMR (CDCl$_3$, 25°C, 500 MHz) spectra of P3HT-est-25.
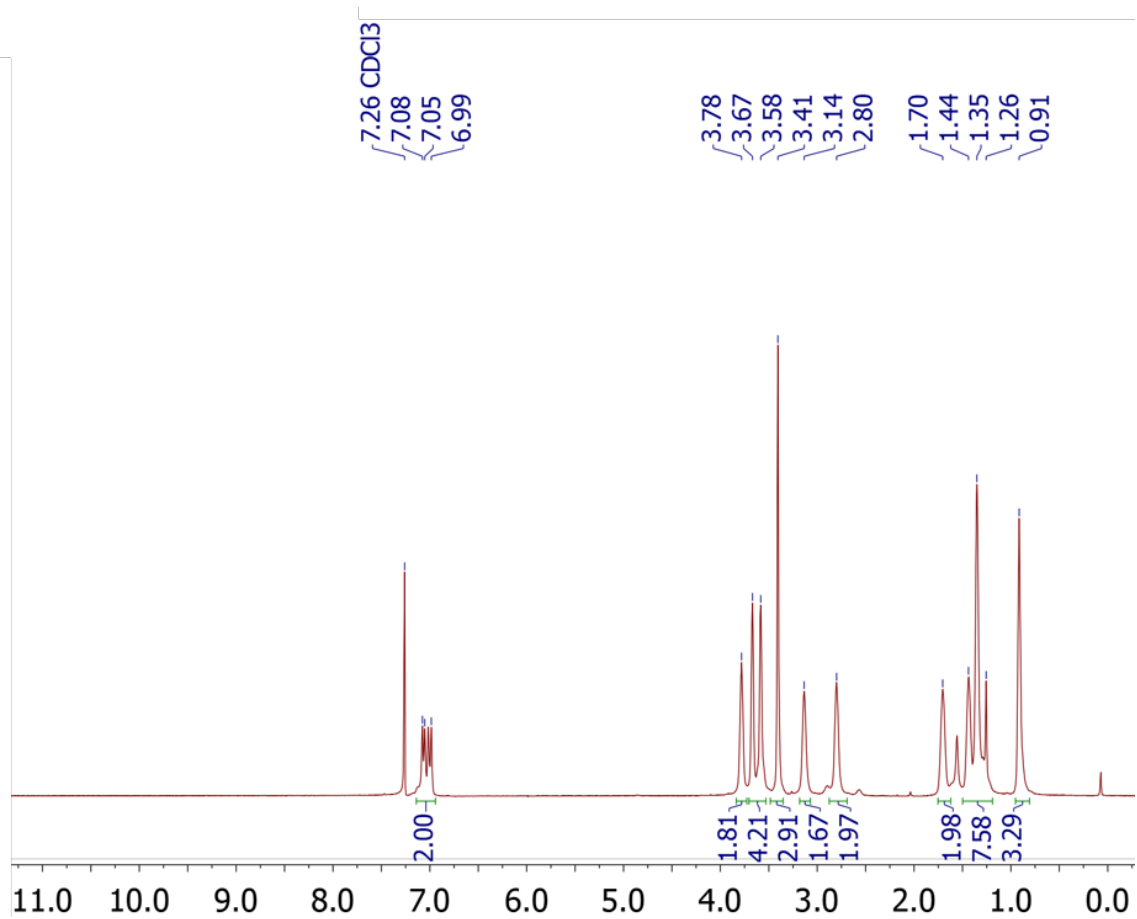
Fig. S9: ^{1}H-NMR (CDCl$_3$, 25°C, 500 MHz) spectra of P3HT-dieth-50.
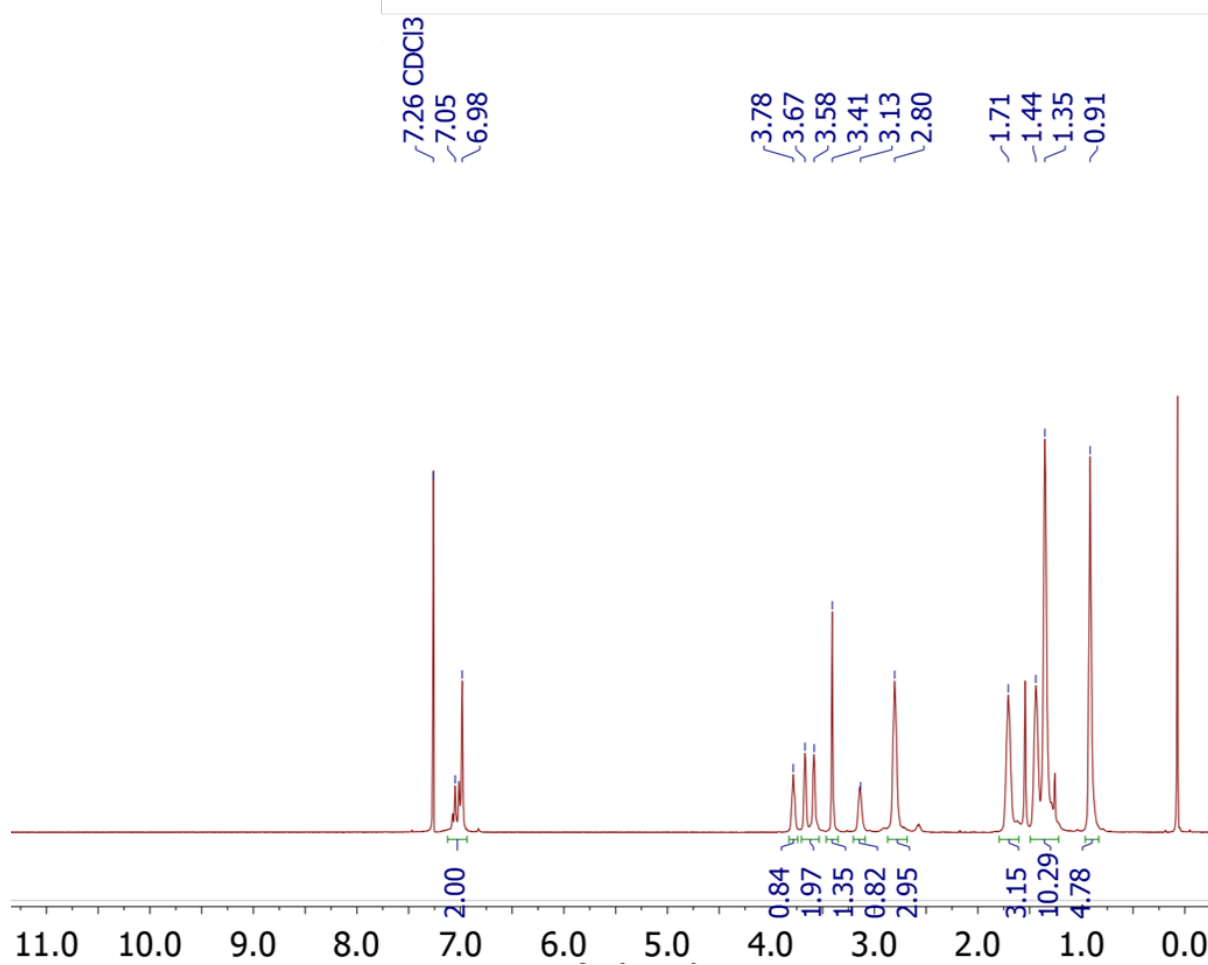
Fig. S10: ^{1}H-NMR (CDCl$_3$, 25°C, 500 MHz) spectra of P3HT-dieth-25.
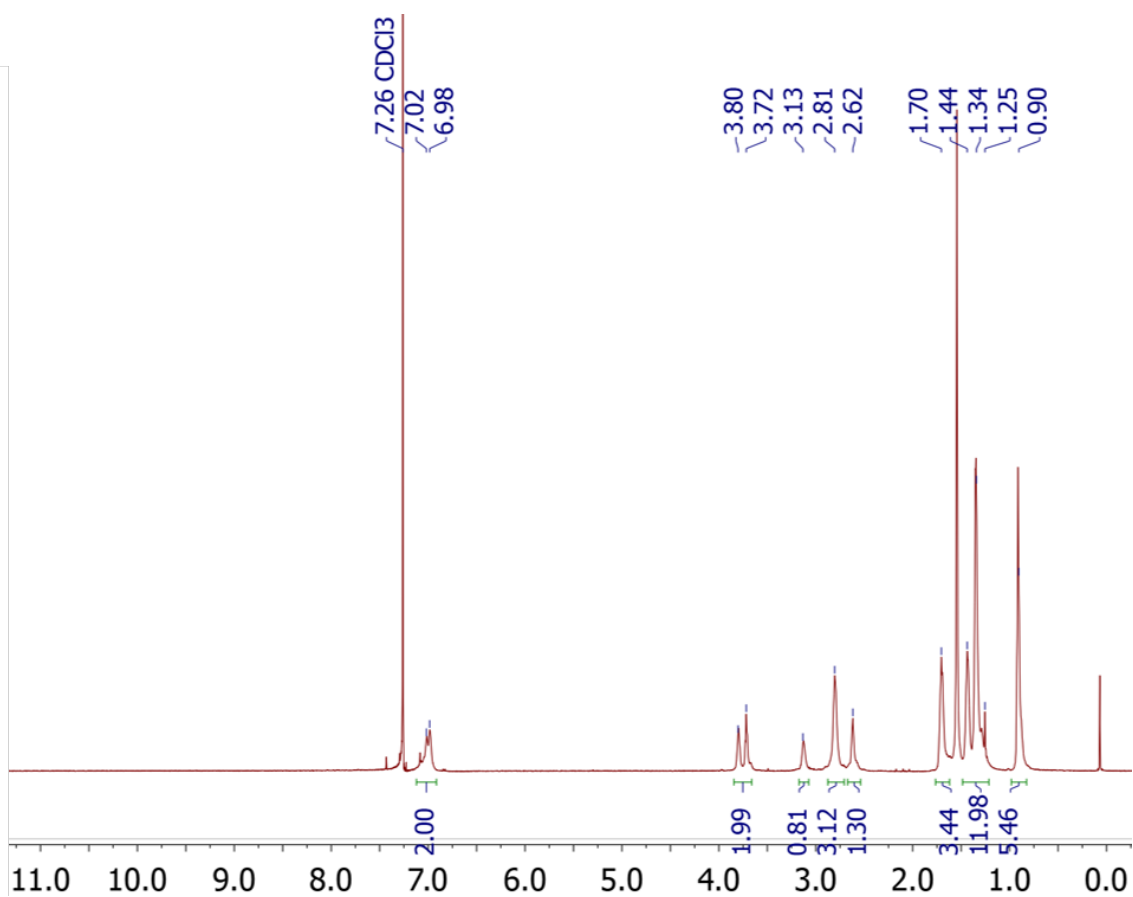
Fig. S11: ^{1}H-NMR (CDCl$_3$, 25°C, 500 MHz) spectra of P3HT-nit-25.

Cyclic Voltammetry:
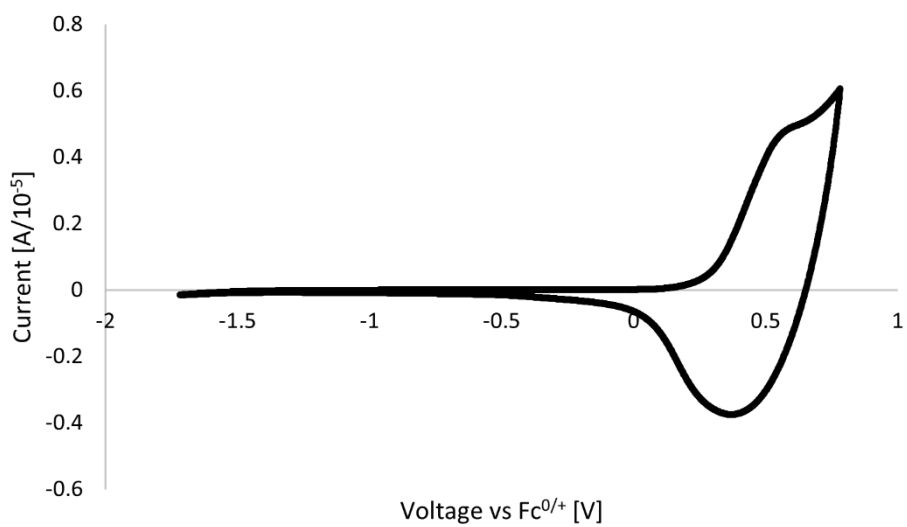
Fig. S12: Cyclic voltammetry of P3HT-est-50.
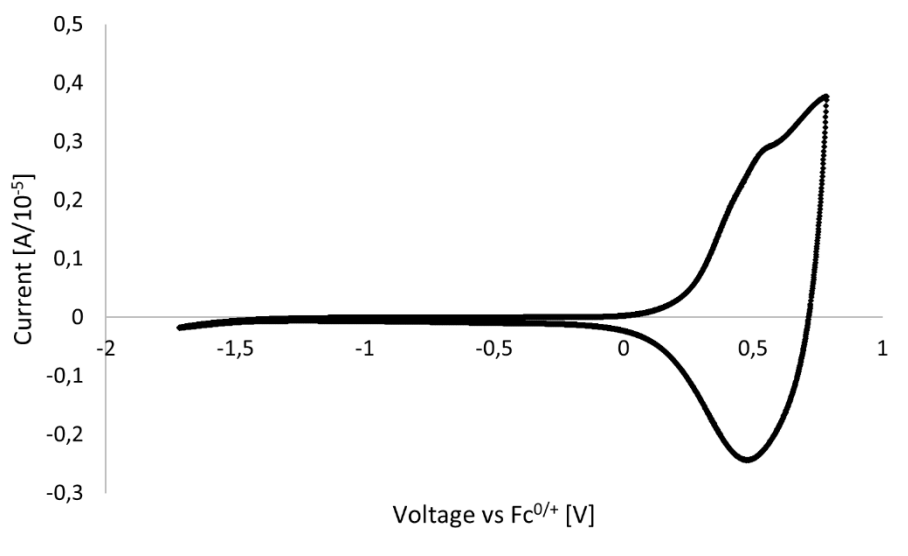
Fig. S13: Cyclic voltammetry of P3HT-carb-50.
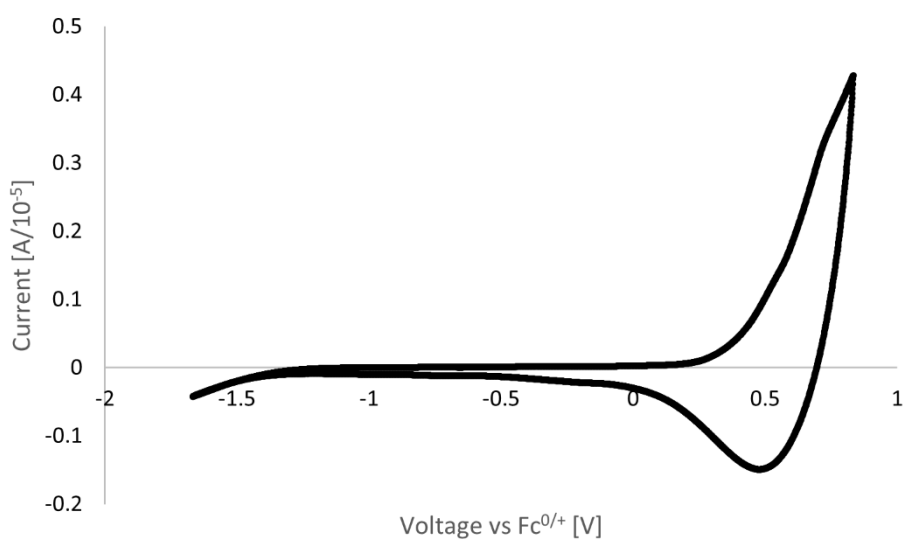
Fig. S14: Cyclic voltammetry of P3HT-eth-50.
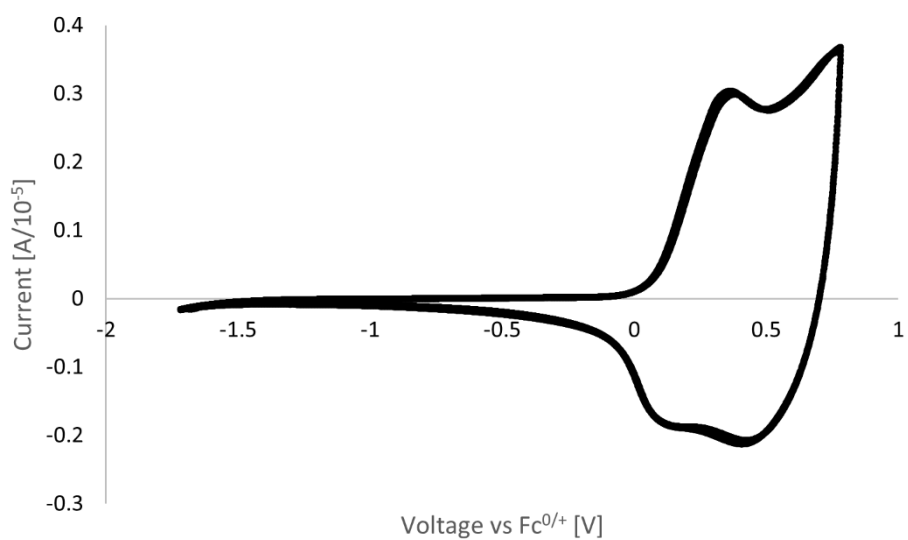
Fig. S15: Cyclic voltammetry of P3HT-nit-50.
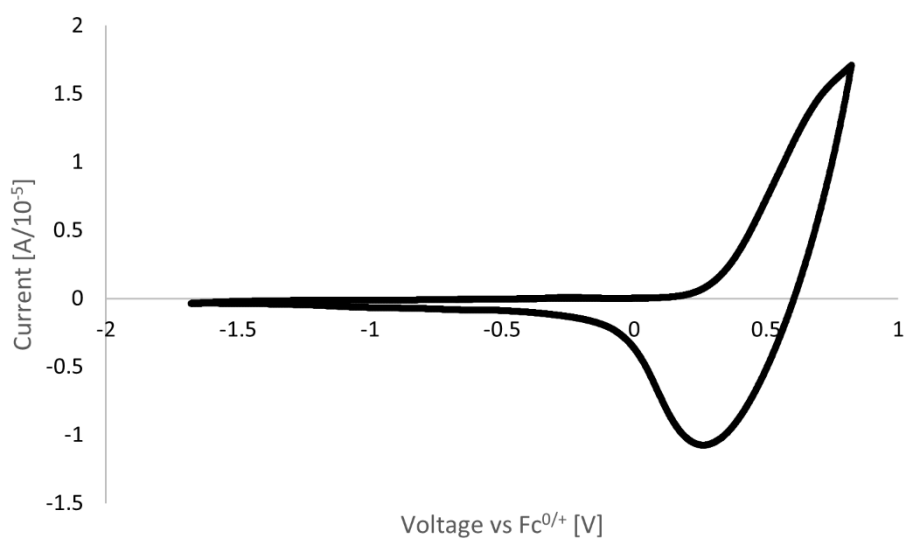

Fig. S16: Cyclic voltammetry of P3HT-dieth-50.
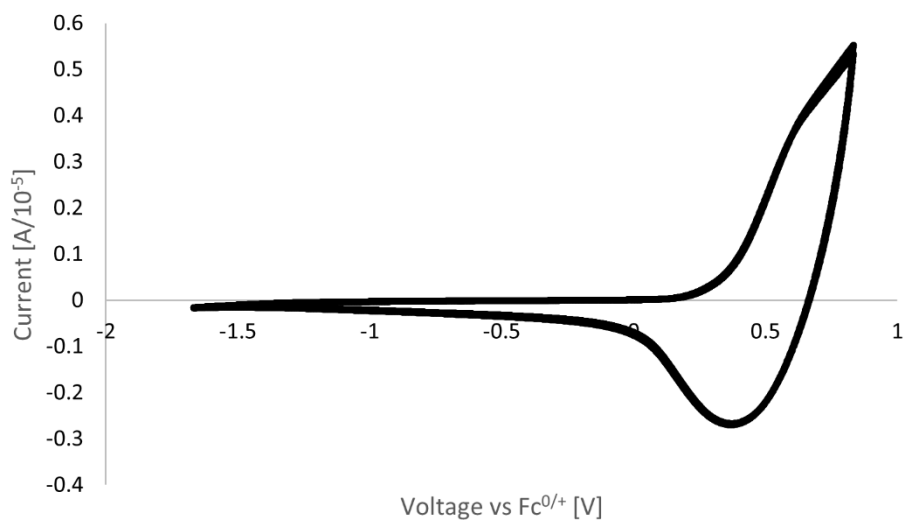
Fig. S17: Cyclic voltammetry of P3HT-est-25.
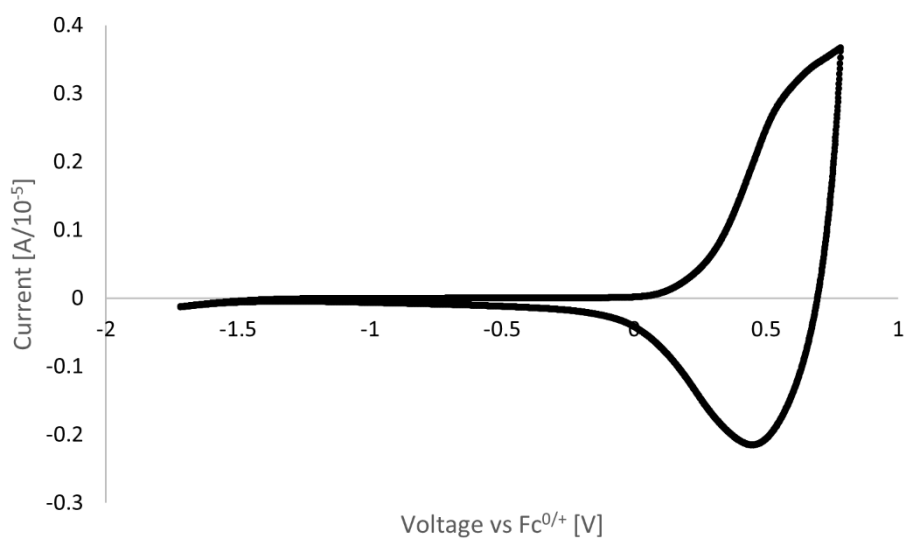
Fig. S18: Cyclic voltammetry of P3HT-carb-25.
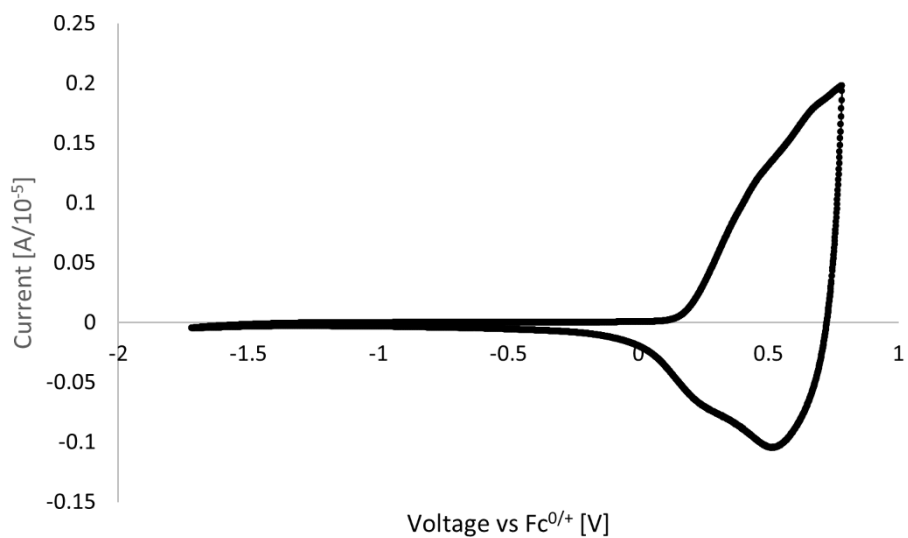
Fig. S19: Cyclic voltammetry of P3HT-eth-25.
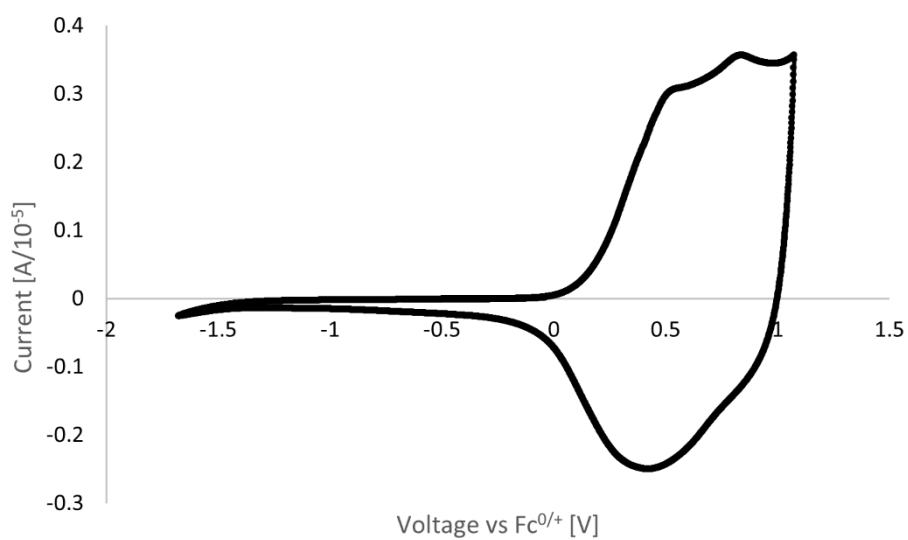
Fig. S20: Cyclic voltammetry of P3HT-nit-25.
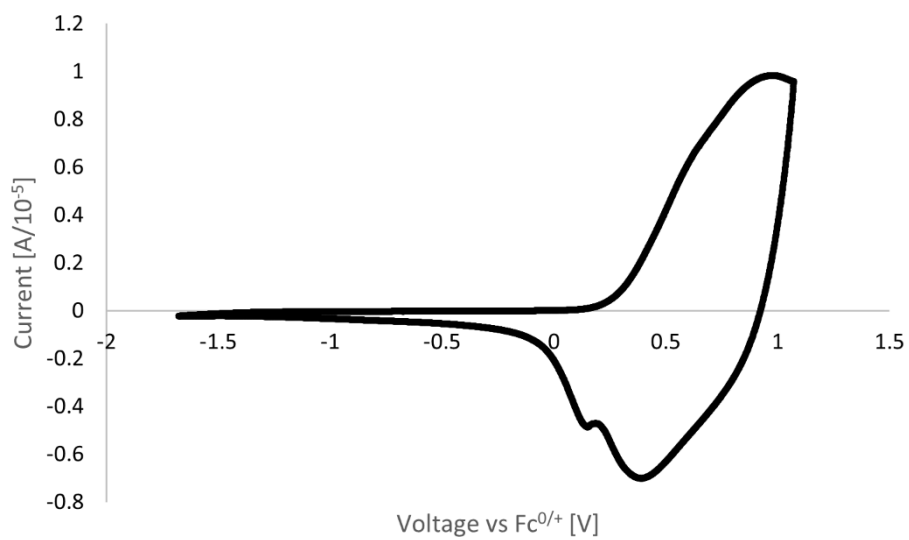
Fig. S21: Cyclic voltammetry of P3HT-dieth-25.
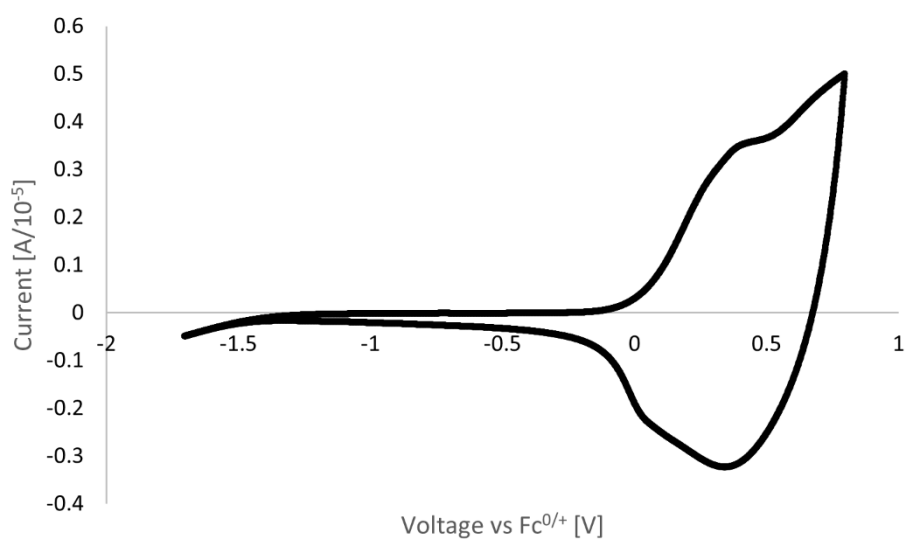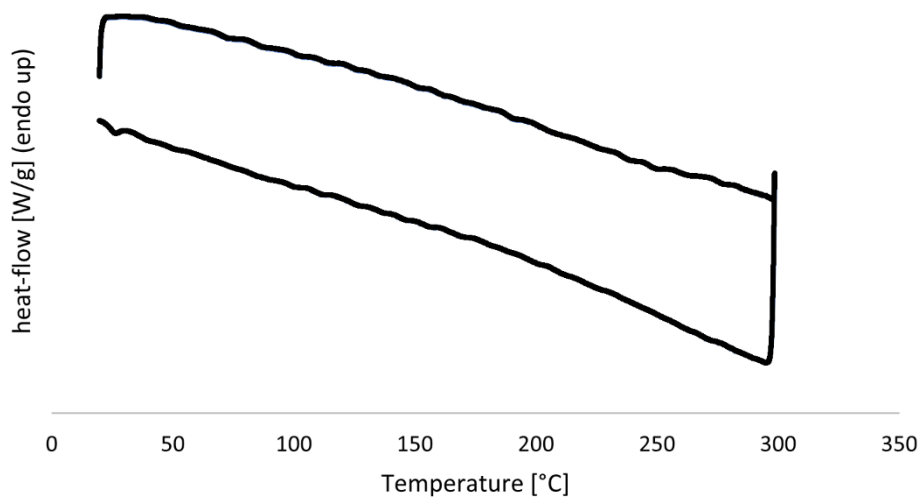

Fig. S22: Cyclic voltammetry of P3HT.
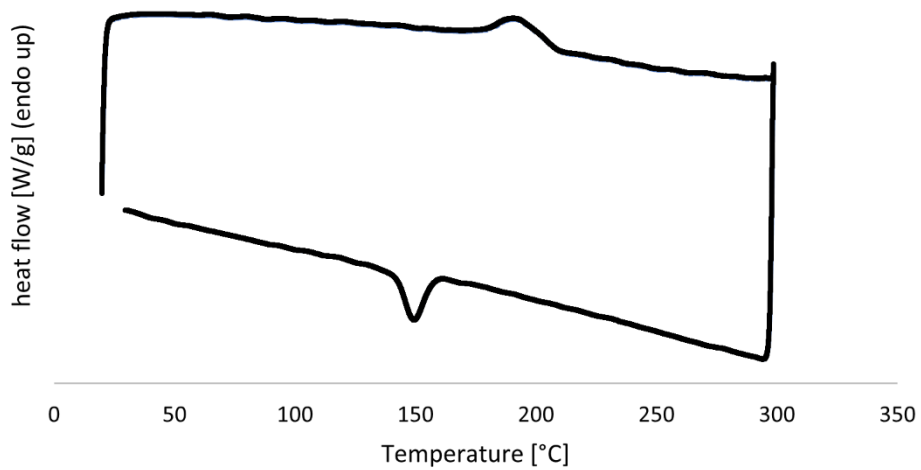
Differential Scanning Calorimetry:
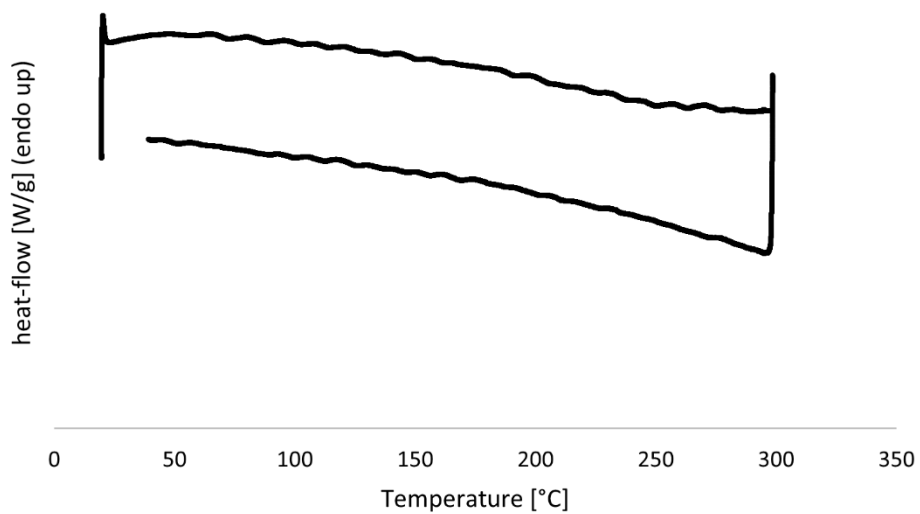
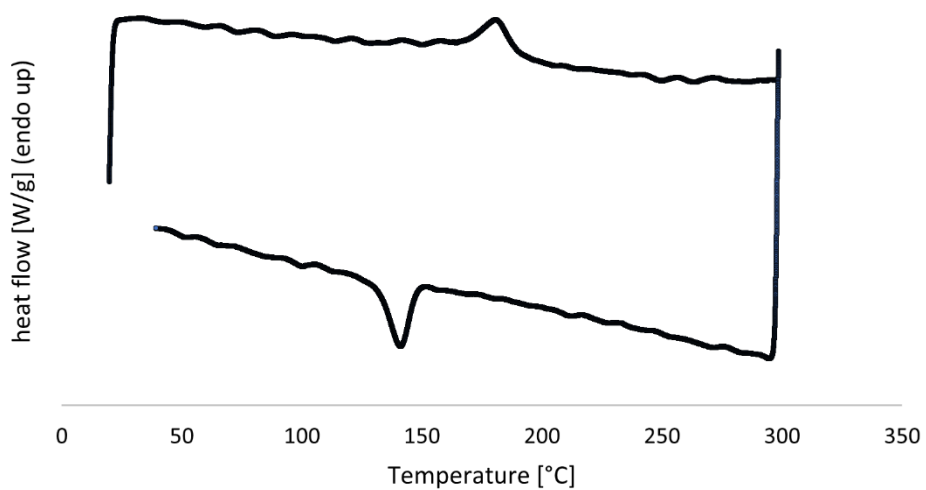**Fig. S23:** Differential scanning calorimeter trace of P3HT-est-50.
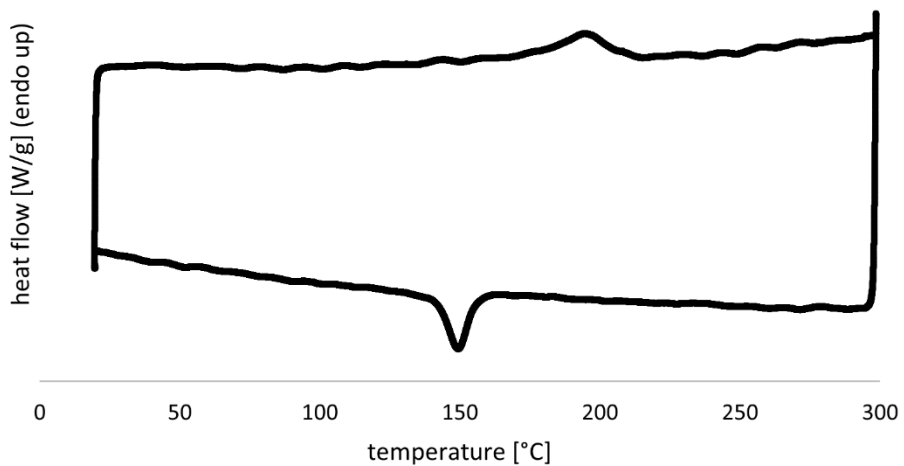
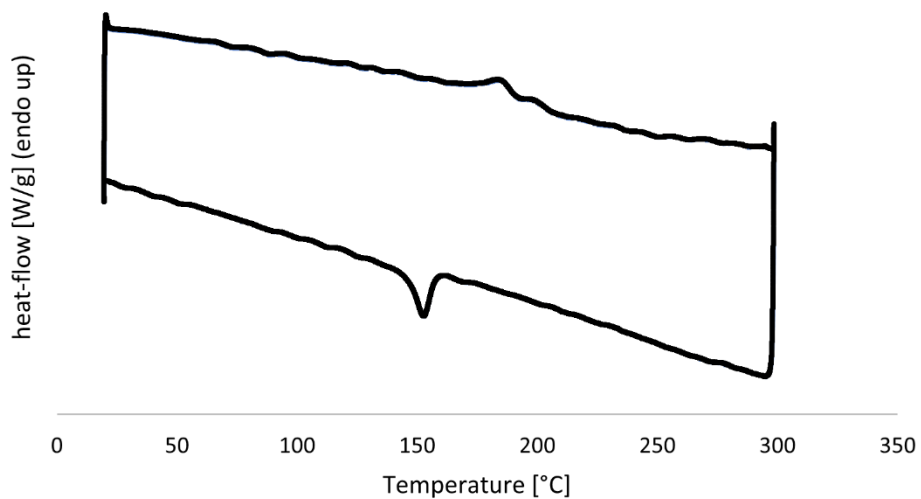**Fig. S24:** Differential scanning calorimeter trace of P3HT-est-25.

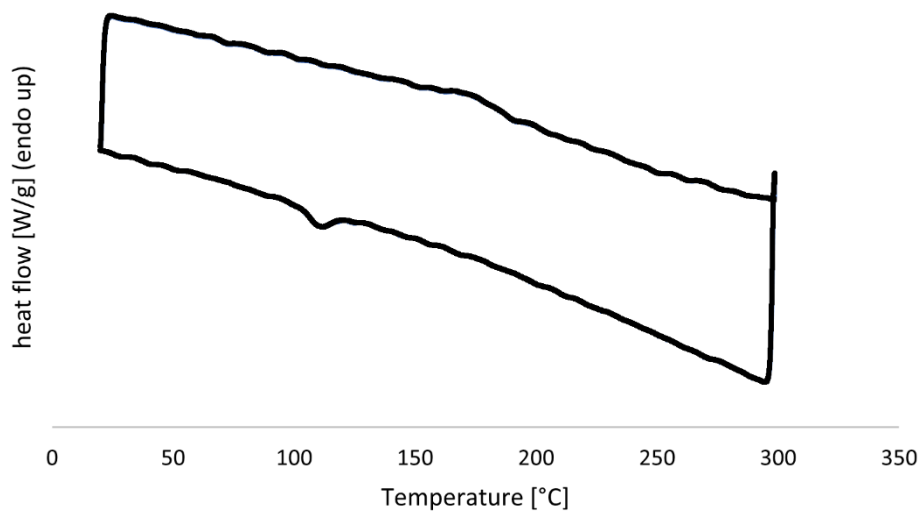**Fig. S25:** Differential scanning calorimeter trace of P3HT-nit-50.

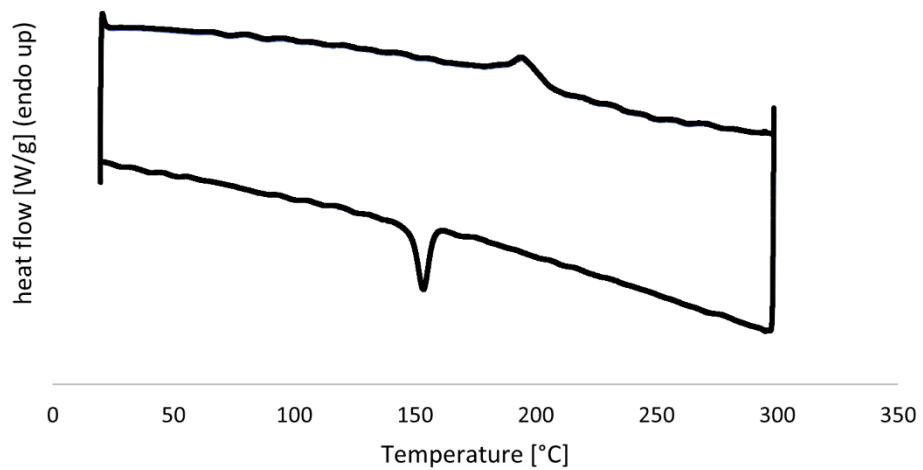**Fig. S26:** Differential scanning calorimeter trace of P3HT-nit-25.

Fig. S27: Differential scanning calorimeter trace of P3HT-eth-50.
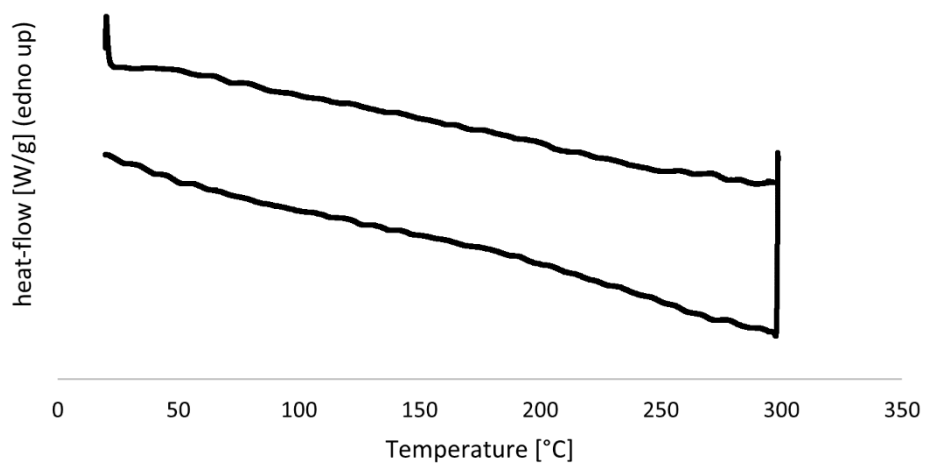

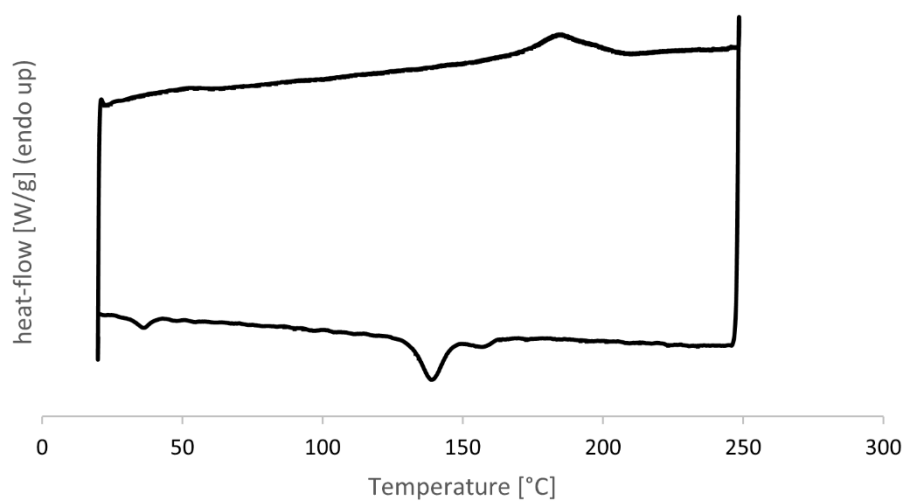**Fig. S28:** Differential scanning calorimeter trace of P3HT-eth-25.

Fig. S29: Differential scanning calorimeter trace of P3HT-dieth-50.
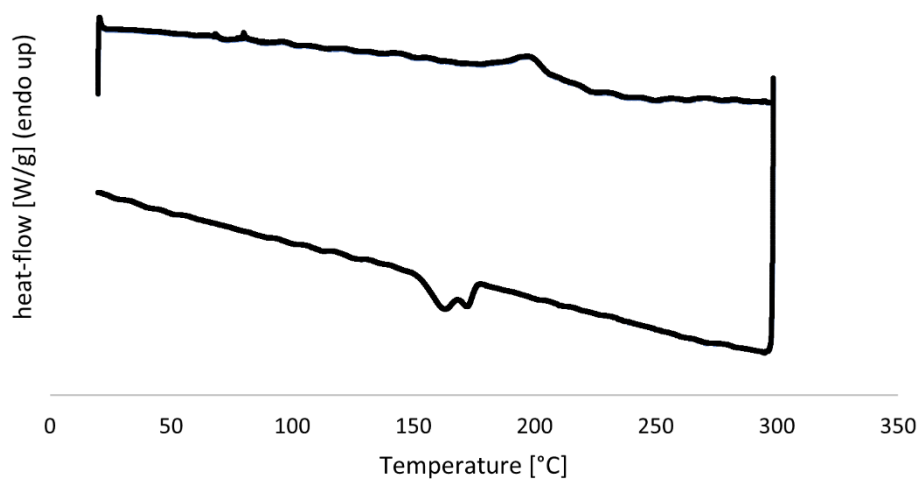

Fig. S30: Differential scanning calorimeter trace of P3HT-dieth-25.

Fig. S31: Differential scanning calorimeter trace of P3HT-carb-50.

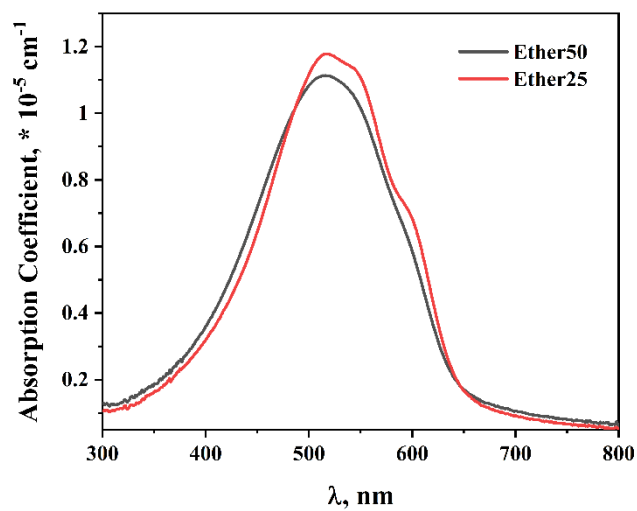**Fig. S32:** Differential scanning calorimeter trace of P3HT-carb-25.

Fig. S33: Differential scanning calorimeter trace of P3HT.

Thin-film UV-Vis Absorption.

Fig. S34: UV/Vis-absorption profiles for P3HT-eth-25 and P3HT-eth-50.
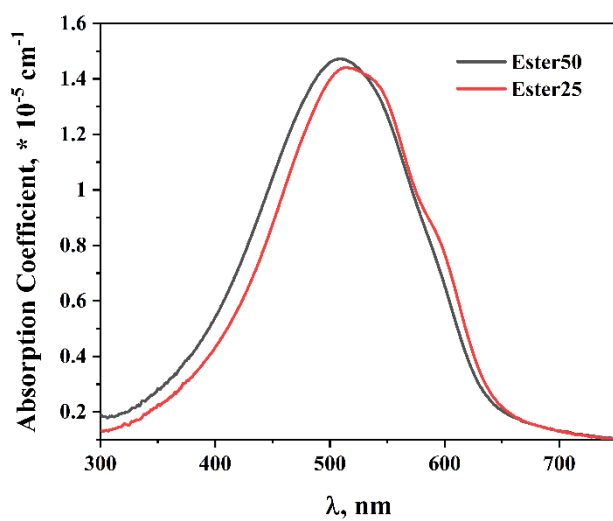
Fig. S35: UV/Vis-absorption profiles for P3HT-est-25 and P3HT-est-50.
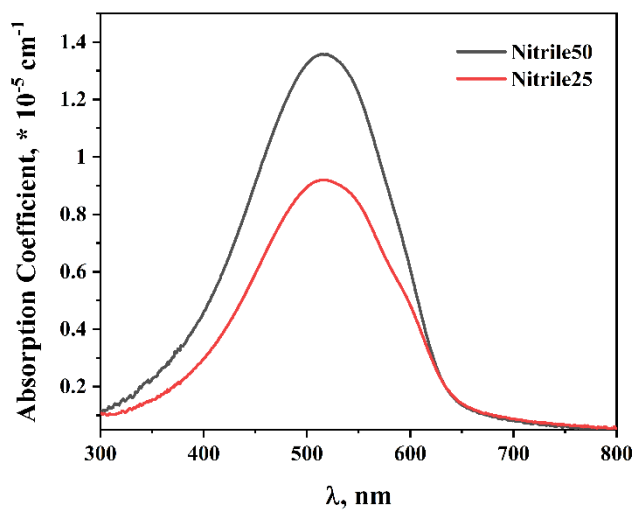
Fig. S36: UV/Vis-absorption profiles for P3HT-nit-25 and P3HT-nit-50.

Fig. S37: UV/Vis-absorption profiles for P3HT-dieth-25 and P3HT-dieth-50.

Fig. S38: UV/Vis-absorption profiles for P3HT-carb-25 and P3HT-carb-50.

GIXRD.

Fig. S39: GIXRD-data for P3HT-eth-25 and P3HT-eth-50.
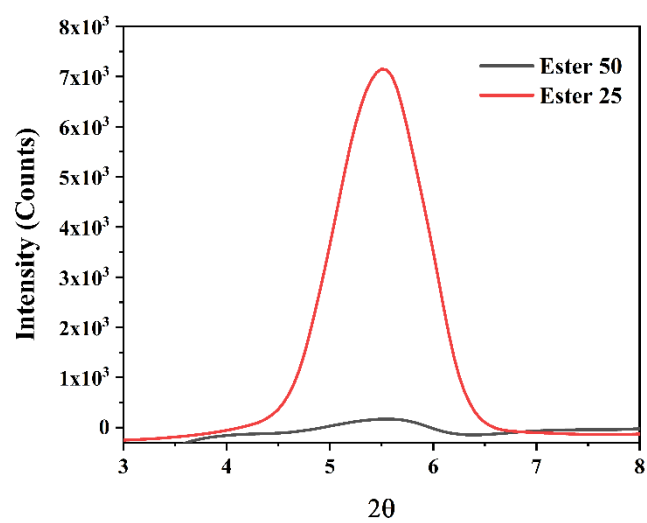
Fig. S40: GIXRD-data for P3HT-est-25 and P3HT-est-50.
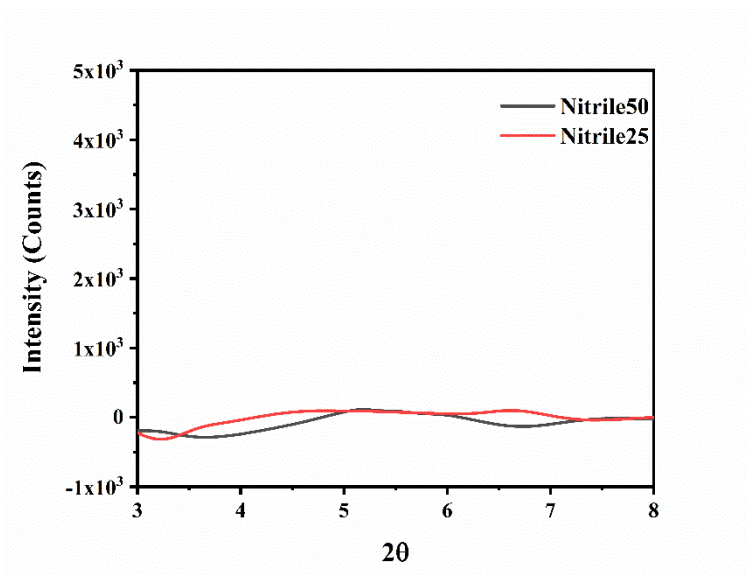
Fig. S41: GIXRD-data for P3HT-nit-25 and P3HT-nit-50.
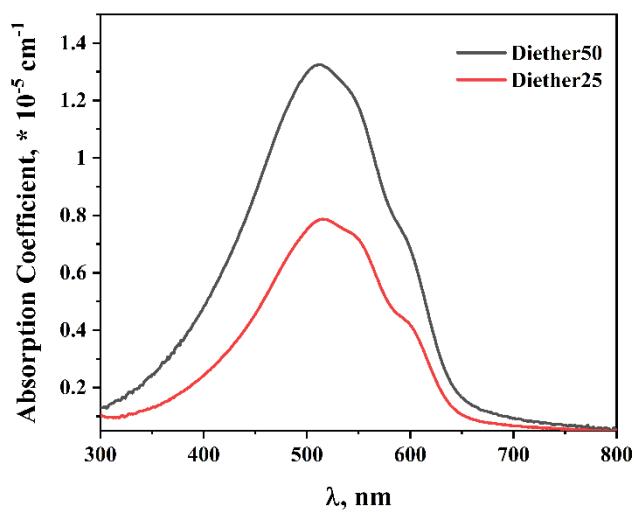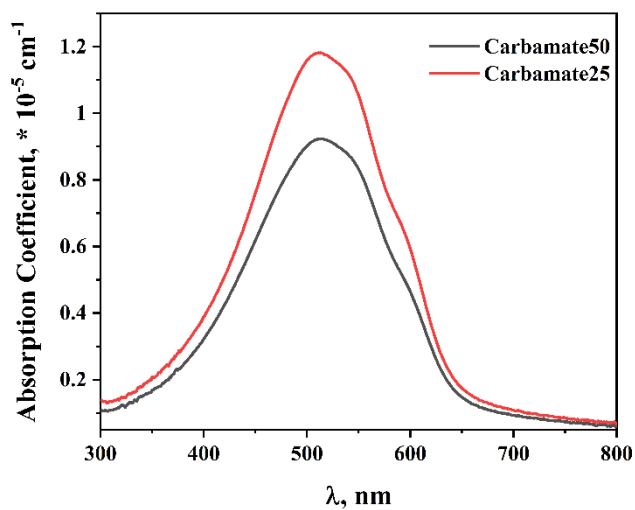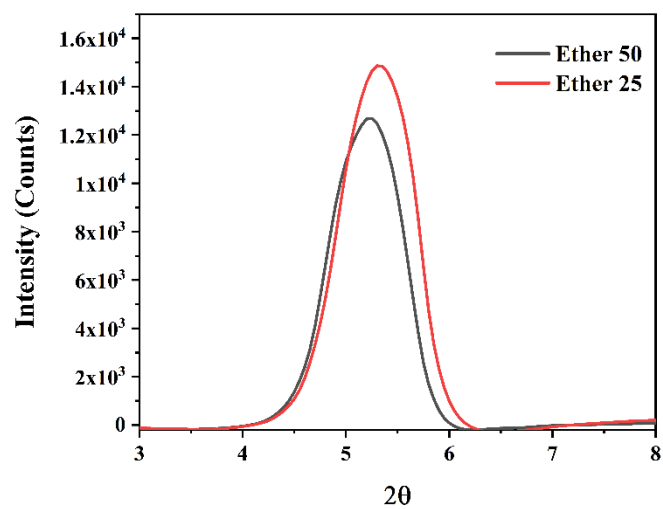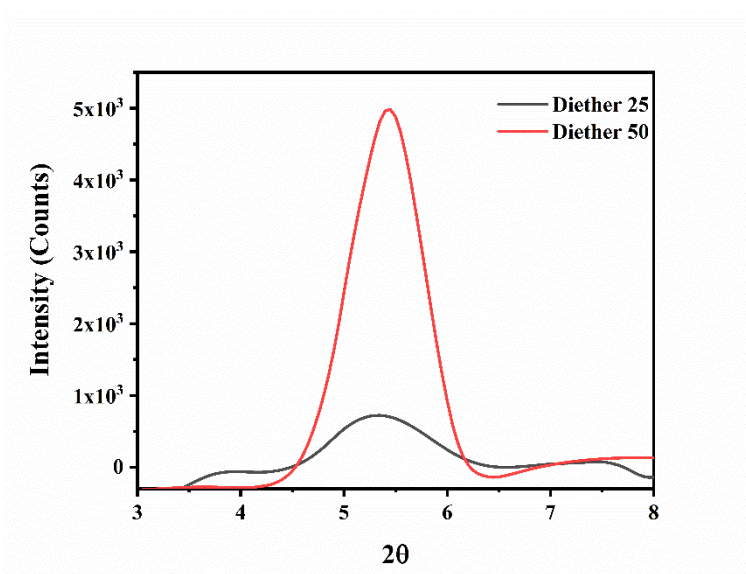

Fig. S42: GIXRD-data for P3HT-dieth-25 and P3HT-dieth-50.
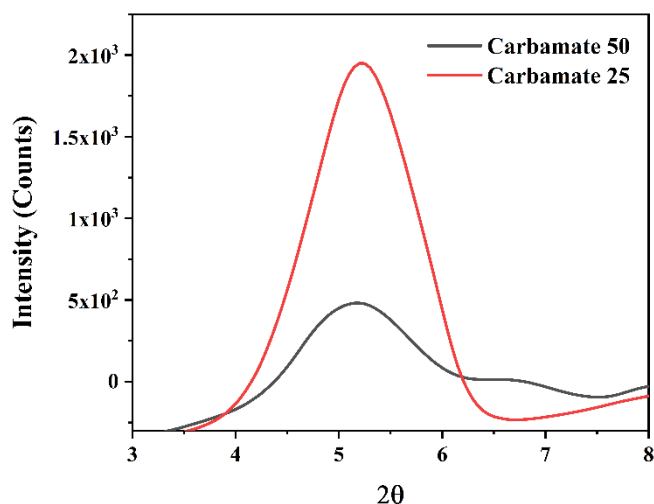
Fig. S43: GIXRD-data for P3HT-carb-25 and P3HT-carb-50.

Surface Energy Data:

Table S1: Contact angles for water and glycerol and Surface energies of all (co-)polymers based on the single-liquid approach and the two-liquid Wu-model approach.

Polymer	Contact angle water [°]	Contact angle glycerol [°]	One-Liquid Surface Energy [mN/m]	Wu Model Surface Energy [mN/m]
P3HT-carb-50	91.0	81.87	28.6	25.6
P3HT-carb-25	96.02	88.04	25.5	22.3
P3HT-dieth-50	95.61	85.91	25.7	23.6
P3HT-dieth-25	100.44	92.39	22.8	20.2
P3HT-nit-50	96.91	85.32	24.9	24.5
P3HT-nit-25	99.46	87.65	23.4	23.6
P3HT-est-50	97.42	88.49	24.6	22.2
P3HT-est-25	100.33	89.97	22.8	21.9
P3HT-eth-50	101.23	92.3	22.3	20.4
P3HT-eth-25	102.93	92.02	21.8	21.3
P3HT	102.08	93.89	21.3	19.5

Mobility Data:

Table S2: Hole mobilities, two theta and theta angles and d-spacing from GIXRD measurements for all (co-)polymers.

Polymer	Hole Mobility (μ_h) [cm^2 V^{-1} s^{-1}]	2Θ	d-spacings [Å]
P3HT-carb-50	$(4.79 \pm 0.53) \cdot 10^{-6}$	5.22	16.916
P3HT-carb-25	$(1.69 \pm 0.18) \cdot 10^{-4}$	5.22	16.916
P3HT-dieth-50	$(1.35 \pm 0.51) \cdot 10^{-4}$	5.38	16.413
P3HT-dieth-25	$(6.28 \pm 0.96) \cdot 10^{-4}$	5.41	16.322
P3HT-nit-50	$(3.96 \pm 0.54) \cdot 10^{-5}$	0	-
P3HT-nit-25	$(3.45 \pm 0.24) \cdot 10^{-4}$	0	-
P3HT-est-50	$(6.22 \pm 0.39) \cdot 10^{-5}$	0	-
P3HT-est-25	$(5.39 \pm 0.39) \cdot 10^{-4}$	5.49	16.084
P3HT-eth-50	$(5.21 \pm 1.23) \cdot 10^{-4}$	5.20	16.981
P3HT-eth-25	$(8.52 \pm 1.47) \cdot 10^{-4}$	5.30	16.661
P3HT	$(2.45 \pm 0.22) \cdot 10^{-3}$	5.44	16.232

Table S3: Reaction conditions, molecular weights, dispersities (Đ), yields and the ratios of the functionalised comonomers in the copolymers as calculated from the ^{1}H-NMR spectra for all polymers.

Entry	Polymer	Conc.	Time	M$_n$ [kDa]	Đ	Yield	Ratio funct. comonomer
1	P3HT	0.25 M	24 h	10.8	2.26	53%	-
2	P3HT-est-50	0.25 M	24 h	14.7	3.49	38%	56%
3	P3HT-est-25	0.25 M	24 h	12.9	2.88	39%	22%
4	P3HT-carb-50	0.25 M	24 h	13.3	2.91	76%	57%
5	P3HT-carb-25	0.25 M	24 h	14.1	2.89	62%	21%
6	P3HT-eth-50	0.12 M	24 h	16.1	2.99	38%	46%
7	P3HT-eth-25	0.12 M	24 h	14.0	3.09	40%	21%
8	P3HT-nit-50	0.05 M	24 h	9.6	3.38	57%	47%

9	P3HT-nit-50	0.05 M	24 h	7.4	2.62	52%	-
10	P3HT-nit-50	0.12 M	24 h	9.4	9.97	28%	-
11	P3HT-nit-25	0.05 M	10 h	7.3	3.51	56%	21%
12	P3HT-nit-25	0.05 M	24 h	14.9	8.79	65%	-
13	P3HT-nit-25	0.02 M	24 h	11.9	4.78	33%	-
14	P3HT-dieth-50	0.05 M	24 h	29.0	2.47	56%	47%
15	P3HT-dieth-25	0.05 M	24 h	18.7	2.91	34%	22%

Table S4: Wavelengths of maximum absorbance (λ_{max}), wavelengths for onset absorbance (λ_{onset}), band gaps calculated from λ_{onset}, film thicknesses for XRD measurements for all polymers.

Polymer	λ_{max} [nm]	λ_{onset} [nm]	E_g [eV]	film thickness [nm]
P3HT-carb-50	512	656	1.89	81
P3HT-carb-25	511	653	1.90	75
P3HT-dieth-50	511	652	1.90	64
P3HT-dieth-25	515	650	1.91	74
P3HT-nit-50	516	649	1.91	61
P3HT-nit-25	515	655	1.89	69
P3HT-est-50	509	662	1.87	56
P3HT-est-25	513	656	1.89	69
P3HT-eth-50	515	657	1.89	57
P3HT-eth-25	515	651	1.90	64
P3HT	518	657	1.89	71

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