

## Supporting Information:

# Isoindigo-Based Donor-Acceptor Conjugated Polymers

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## Materials and Methods.

All reagents and starting materials were purchased from commercial sources and used without further purification, unless otherwise noted. The Et<sub>4</sub>NOH (1M) aqueous solution was degassed by three freeze-pump-thaw cycles. Anhydrous solvents were obtained from an anhydrous solvent system. All <sup>1</sup>H NMR (300 MHz) spectra were recorded on a Varian Mercury 300 spectrometer. Chemical shifts for <sup>1</sup>H were referenced to residual signals from CDCl<sub>3</sub> (<sup>1</sup>H 7.26 ppm). UV-vis spectra were recorded on a Varian Cary 500 Scan UV-vis-near-IR spectrophotometer. Free standing films of **P1** were obtained by slow evaporation of a toluene solution cast into a 20cm-diameter glass Petri dish. Thermogravimetric analysis (TGA) was performed on TA Instruments TGA Q1000 Series using dynamic scans under nitrogen. Differential scanning calorimetry (DSC) analysis was performed using a TA Instruments Q1000 series equipped with a controlled cooling accessory (liquid nitrogen cooling system) at 10 °C/min. Gel permeation chromatography (GPC) was performed at 40°C using a Waters Associates GPCV2000 liquid chromatography system with an internal differential refractive index detector and two Waters Styragel HR-5E columns (10 μm PD, 7.8 mm i.d., 300 mm length) using HPLC grade THF as the mobile phase at a flow rate of 1.0 mL/min.

## Electrochemical Studies.

Tetra-n-butylammonium hexafluorophosphate was purchased (98%, Acros) and used without further purification. The salt was transferred to an argon-filled drybox (OmniLab model, Vacuum Atmospheres). Acetonitrile was distilled over calcium hydride and kept under inert atmosphere before being transferred to the drybox in which the electrolyte solutions were made. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) studies were performed using an EG&G Princeton Applied Research model 273A potentiostat/galvanostat in the argon-filled drybox. Experiments were carried out in a one compartment electrochemical cell using Ag/Ag<sup>+</sup> reference electrode and platinum foil as a counter electrode; all potentials were reported vs Fc/Fc<sup>+</sup> redox couple. The polymer films were dropcast from toluene solution (0.2 g/mL) onto platinum disk electrodes (0.02 cm<sup>2</sup>) and switched 10 times at a scan rate 50 mV s<sup>-1</sup> in the

corresponding range of potentials prior to characterization until a complete stabilization of the current responses was reached. The following setup parameters were applied for the DPV studies: a step size of 1.4 mV, a step time of 0.035 s, and amplitude of 55 mV.

#### General procedure for Suzuki polycondensations (for **P1**, **P2** and **P3**).

In a 100 mL flame-dried Schlenk flask, the dibromoisindigo monomer **4** (0.5 mmol, 1 equiv.), the bis(pinacolato)diboron comonomer (0.5 mmol, 1 equiv.), Pd<sub>2</sub>(dba)<sub>3</sub> (15 mg) and P(*o*-tyl)<sub>3</sub> (10 mg) were subjected to three cycles of evacuation/argon purging, and then dissolved with 5 mL of degassed toluene after which 1.5 mL (1M) of degassed aqueous solution of Et<sub>4</sub>NOH was added. The reaction mixture was stirred at 85°C for 36 hours under argon, and then cooled down to room temperature. The mixture was precipitated in 100 mL of methanol and filtered through a 0.45µm nylon filter. The dark solids were purified using a Soxhlet apparatus with methanol until the extracts appeared colorless. The polymers were then fractionated in the Soxhlet apparatus using hexanes and chloroform fractions which contained varying amounts of polymer after complete extraction depending on the nature of the comonomer used. Concentration and reprecipitation in methanol allowed filtering the solids through a 0.45µm nylon filter to afford the targeted polymer after complete drying in vacuo.

*Poly[9,9'-dihexyl-2,7-fluorene-alt-N,N'-(2-ethylhexyl)-6,6'-isindigo](P1)*: The general Suzuki polymerization procedure was followed using 322 mg of compound **4** and 293 mg of 2,2'-(9,9-dihexyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) to afford a shiny brown solid. (466 mg, yield: 93%, chloroform fraction). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): 9.40-9.30 (br, 2H), 7.90-7.80 (br, 2H), 7.70-7.60 (br, 4H), 7.45-7.35 (br, 2H), 7.10-7.05 (br, 2H), 4.00-3.50 (br, 4H), 2.15-1.90 (br, 2H), 1.65-1.30 (br, 16H), 1.10-1.05 (br, 20H), 1.05-0.95 (br, 6H), 0.95-0.80 (br, 6H), 0.80-0.70 (br, 6H). M<sub>n</sub>: 21.2 kDa ; PDI: 1.96. Anal. Calcd for C<sub>57</sub>H<sub>72</sub>N<sub>2</sub>O<sub>2</sub>: C, 83.78; H, 8.88; N, 3.43. Found: C, 82.72; H, 8.84; N, 3.42.

*Poly[2,5-dioctyloxy-1,4-phenyl-alt-N,N'-(2-ethylhexyl)-6,6'-isindigo](P2)*: The general Suzuki polymerization procedure was followed using 322 mg of compound **4** and 265 mg of 2,2'-(2,5-bis(octyloxy)-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) to afford a dark brown fluffy solid. (116 mg, yield: 31%, hexanes fraction); (241 mg, yield: 63%, chloroform fraction). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): 9.30-9.20 (br, 2H), 7.35-7.25 (br, 2H), 7.20-7.15 (br, 2H), 7.10-7.05 (br, 2H), 4.05-3.90 (br, 4H), 3.85-3.65 (br, 4H), 1.95-1.85 (br, 2H), 1.85-1.65 (br, 4H), 1.40-1.20 (br, 32H), 1.00-0.75 (br, 18H). M<sub>n</sub>: 10.5 kDa ; PDI: 2.13. Anal. Calcd for C<sub>50</sub>H<sub>68</sub>N<sub>2</sub>O<sub>4</sub>: C, 78.91; H, 9.01; N, 3.68. Found: C, 78.97; H, 9.01; N, 3.57.

*Poly[3,4-dioctyl-2,5-thiophene-alt-N,N'-(2-ethylhexyl)-6,6'-isindigo](P3)*: The general Suzuki polymerization procedure was followed using 322 mg of compound **4** and 280 mg of 2,2'-(3,4-dioctylthiophene-2,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) to afford a dark brown fluffy powder. (109 mg, yield: 28%, hexanes fraction); (224 mg, yield: 57%, chloroform fraction). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): 9.35-8.90 (br, 2H), 7.40-7.10 (br, 2H), 7.10-6.75

(br, 2H), 3.90-3.45 (br, 4H), 3.05-2.50 (br, 4H), 2.05-1.80 (br, 2H), 1.80-1.15 (br, 40H), 1.15-0.75 (br, 12H), 0.75-0.45 (br, 6H).  $M_n$ : 16.7 kDa ; PDI: 1.94. Anal. Calcd for  $C_{52}H_{74}N_2O_2S$ : C, 78.94; H, 9.43; N, 3.54. Found: C, 79.26; H, 9.45; N, 3.58.

#### General procedure for Stille polycondensations (for **P4**, **P5** and **P6**).

The dibromoisindigo monomer **4** (0.5 mmol, 1 equiv.),  $Pd_2(dba)_3$  (15 mg) and  $P(o\text{-}t\text{-}yl)_3$  (10 mg) were added to a flame-dried Schlenk flask which was evacuated and backfilled with argon three times. The bis(trimethylstannyl) comonomer (0.5 mmol, 1 equiv.) was dissolved in a dried separate vial in 5 mL of toluene (except for **P5** for which chlorobenzene was used in place of toluene), subsequently degassed with argon for one hour. The solution was then added to the Schlenk flask and the reaction mixture was stirred at 85 °C for 36 hours. The mixture was precipitated in 100 mL of methanol and filtered through a 0.45 $\mu$ m nylon filter. The dark solids were purified using a Soxhlet apparatus with methanol until the extracts appeared colorless. The polymers were then fractionated in the Soxhlet apparatus using hexanes, chloroform and chlorobenzene fractions which contained varying amounts of polymer after complete extraction depending on the the nature of comonomer used. Concentration and reprecipitation in methanol allowed filtering the solids through a 0.45 $\mu$ m nylon filter to afford the targeted polymer after complete drying in vacuo.

*Poly[2,5-thiophene-*alt*-N,N'-(2-ethylhexyl)-6,6'-isoindigo](**P4**):* The general procedure for Stille polymerization was followed using 322 mg of compound **4** and 205 mg of 2,5-bis(trimethylstannyl)thiophene to afford a deep blue solid after extraction. (120 mg, yield: 42%, chloroform fraction)  $^1H$  NMR (300 MHz,  $CDCl_3$ , ppm): 9.20-8.90 (br, 2H), 7.30-7.15 (br, 2H), 7.15-6.90 (br, 2H), 6.75-6.60 (br, 2H), 3.75-3.45 (br, 4H), 1.95-1.70 (br, 2H), 1.55-1.20 (br, 16H), 1.20-0.80 (br, 12H).  $M_n$ : 2.4 kDa ; PDI: 1.13. Anal. Calcd for  $C_{36}H_{42}N_2O_2S$ : C, 76.29; H, 7.47; N, 4.94. Found: C, 75.88; H, 7.31; N, 4.75.

*Poly[1,2-vinylene-*alt*-N,N'-(2-ethylhexyl)-6,6'-isoindigo](**P5**):* The general procedure for Stille polymerization using chlorobenzene instead of toluene was followed using 322 mg of compound **4** and 303 mg 1,2-bis(tributylstannyl)vinylene to afford a black solid after extraction using methanol, hexanes, chloroform and chlorobenzene. (92 mg, yield: 36%, chloroform fraction) ; (34 mg, yield: 13%, chlorobenzene fraction).  $^1H$  NMR (300 MHz,  $CDCl_3$ , ppm): 9.25-9.00 (br, 2H), 7.45-7.05 (br, 4H), 6.95-6.80 (br, 2H), 3.90-3.45 (br, 4H), 2.00-1.75 (br, 2H), 1.50-1.20 (br, 16H), 1.05-0.85 (br, 12H).  $M_n$ : 1.9 kDa ; PDI: 1.20. Anal. Calcd for  $C_{34}H_{42}N_2O_2$ : C, 79.96; H, 8.29; N, 5.49. Found: C, 79.75; H, 8.01; N, 4.97.

*Poly[2,5-propylenedioxythiophene-*alt*-N,N'-(2-ethylhexyl)-6,6'-isoindigo] (**P6**):* The general procedure for Stille polymerization was followed using 322 mg of compound **4** and 383 mg of (3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-6,8-diyl)bis(trimethylstannane) to afford a dark blue solid. (290 mg, yield: 63%, hexanes fraction) ; (161 mg, yield: 34%, chloroform fraction).  $^1H$  NMR (300 MHz,  $CDCl_3$ , ppm): 9.20-9.05 (br,

2H), 7.45-7.35 (br, 2H), 7.35-7.25 (br, 2H), 4.30-4.15 (br, 4H), 3.65-3.50 (br, 4H), 3.55-3.45 (br, 4H), 3.45-3.25 (br, 4H), 1.95-1.75 (br, 4H), 1.50-1.20 (br, 32H), 1.05-0.80 (br, 24H).  $M_n$ : 19.3 kDa ; PDI: 1.70. Anal. Calcd for  $C_{57}H_{82}N_2O_6S$ : C, 74.15; H, 8.95; N, 3.03. Found: C, 73.65; H, 8.65; N, 3.10.

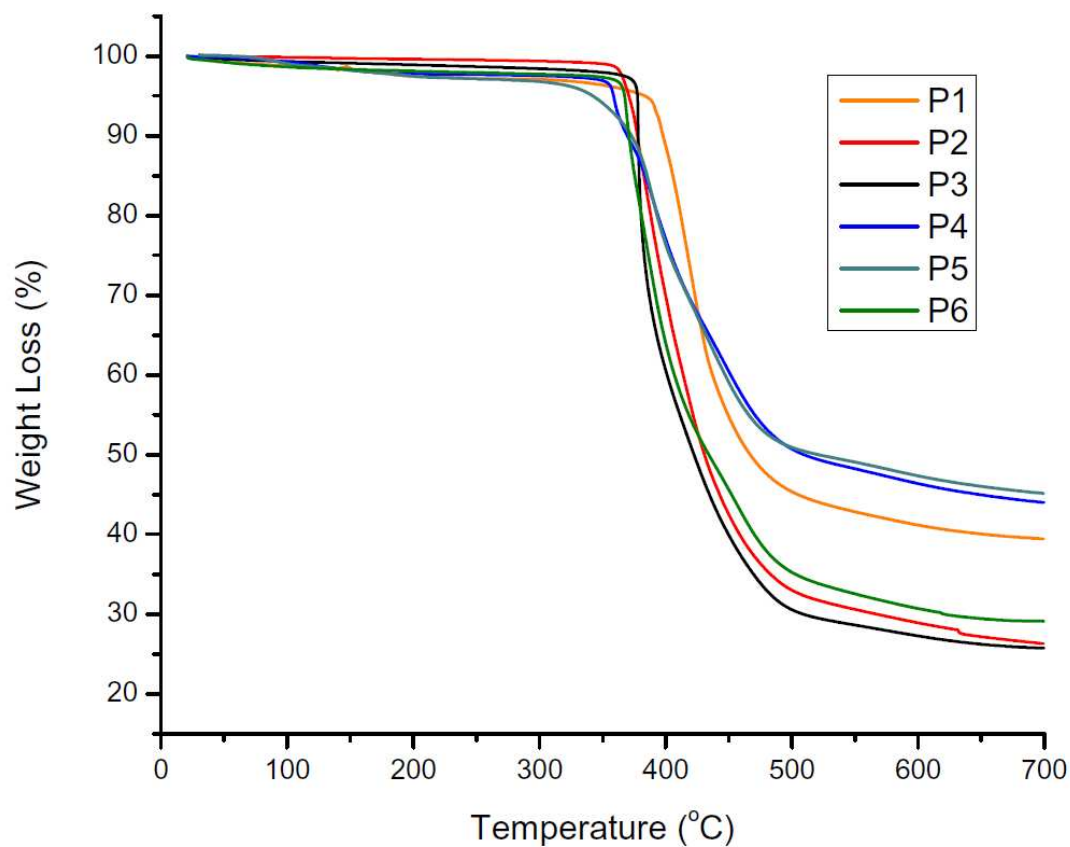


**Figure S1:** TGA thermograms of **P1** through **P6** under nitrogen atmosphere; scan rate 10°C/min.

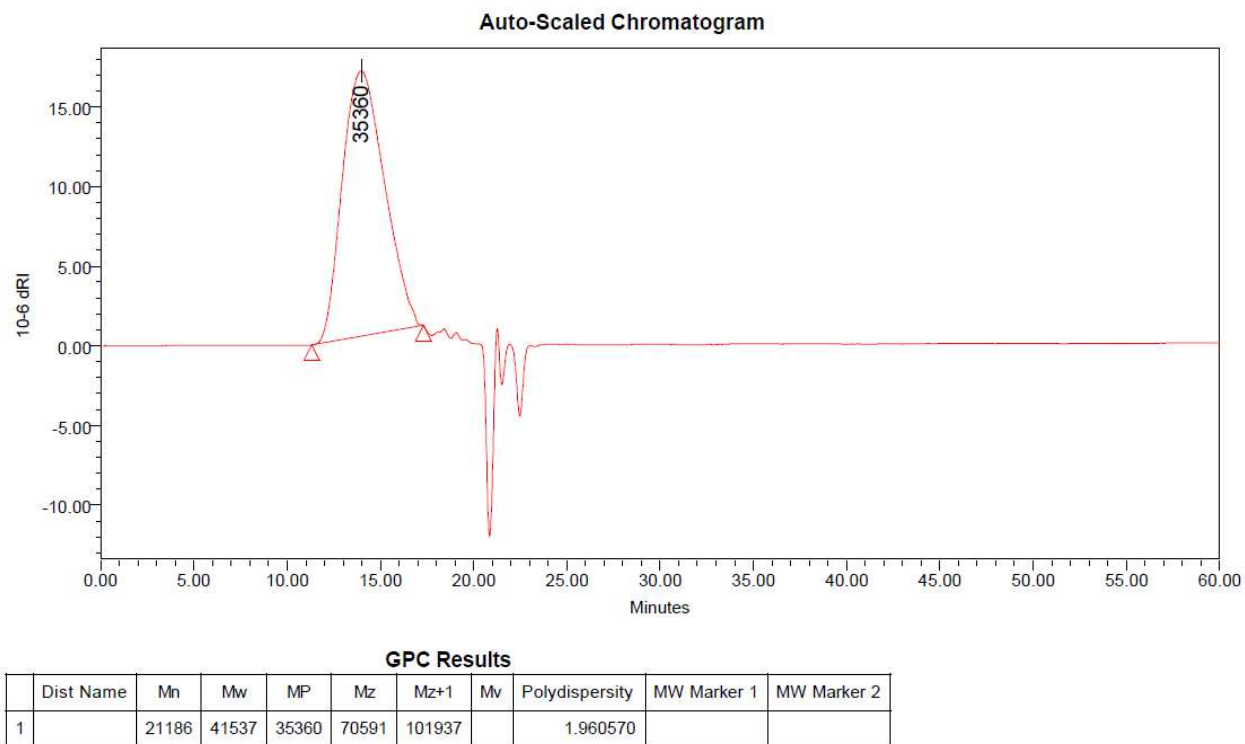


**Figure S2-1:** GPC trace for **P1** at 40°C in THF, against polystyrene standards.

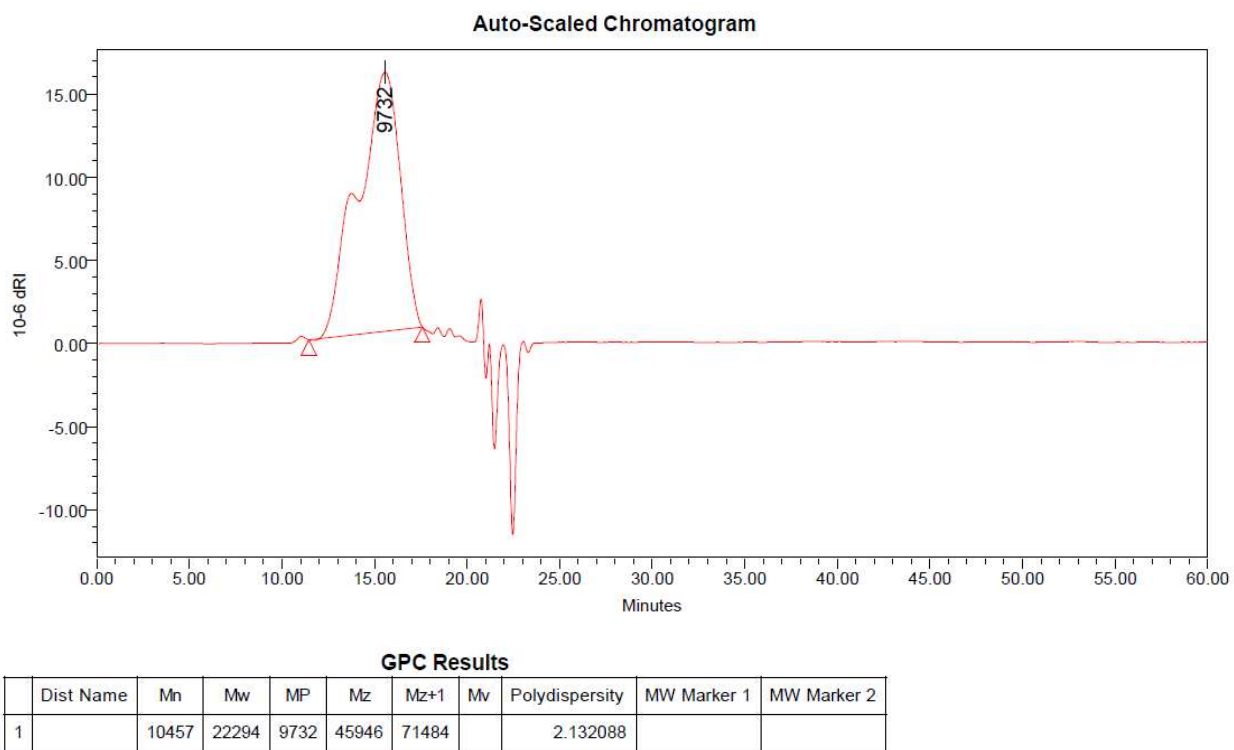


**Figure S2-2:** GPC trace for **P2** at 40°C in THF, against polystyrene standards.

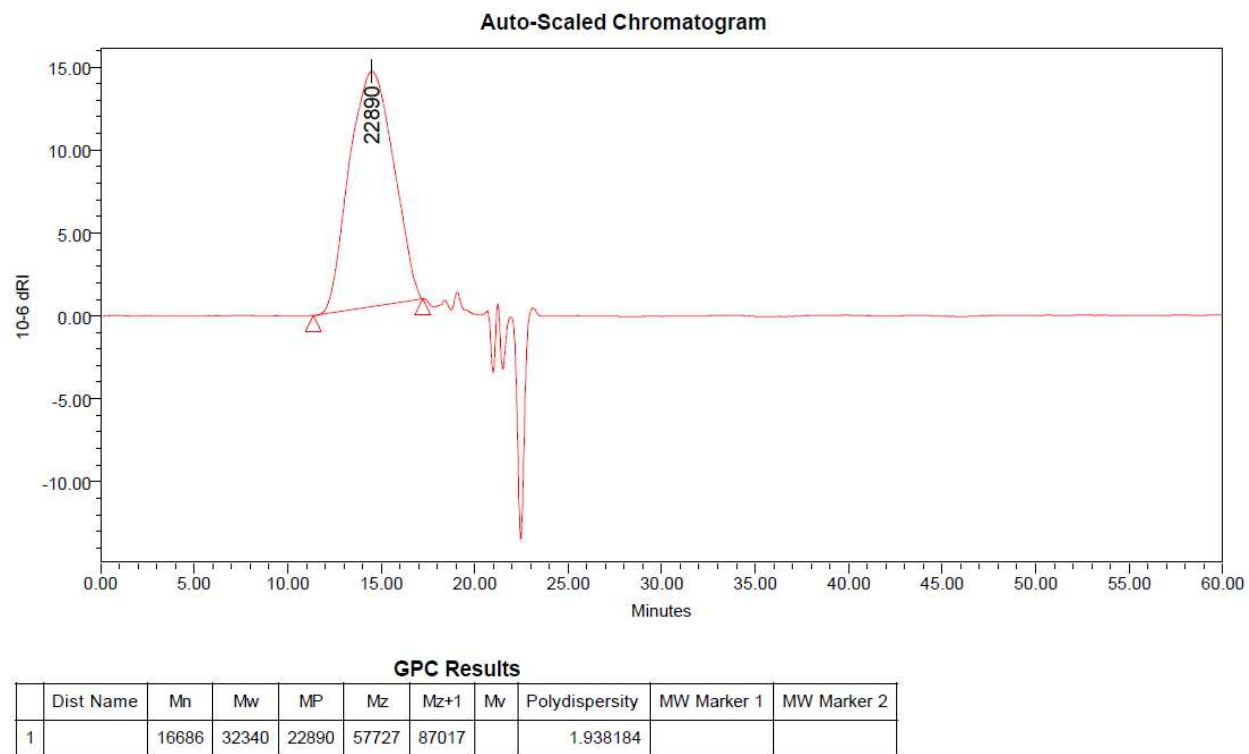


**Figure S2-3:** GPC trace for **P3** at 40°C in THF, against polystyrene standards.

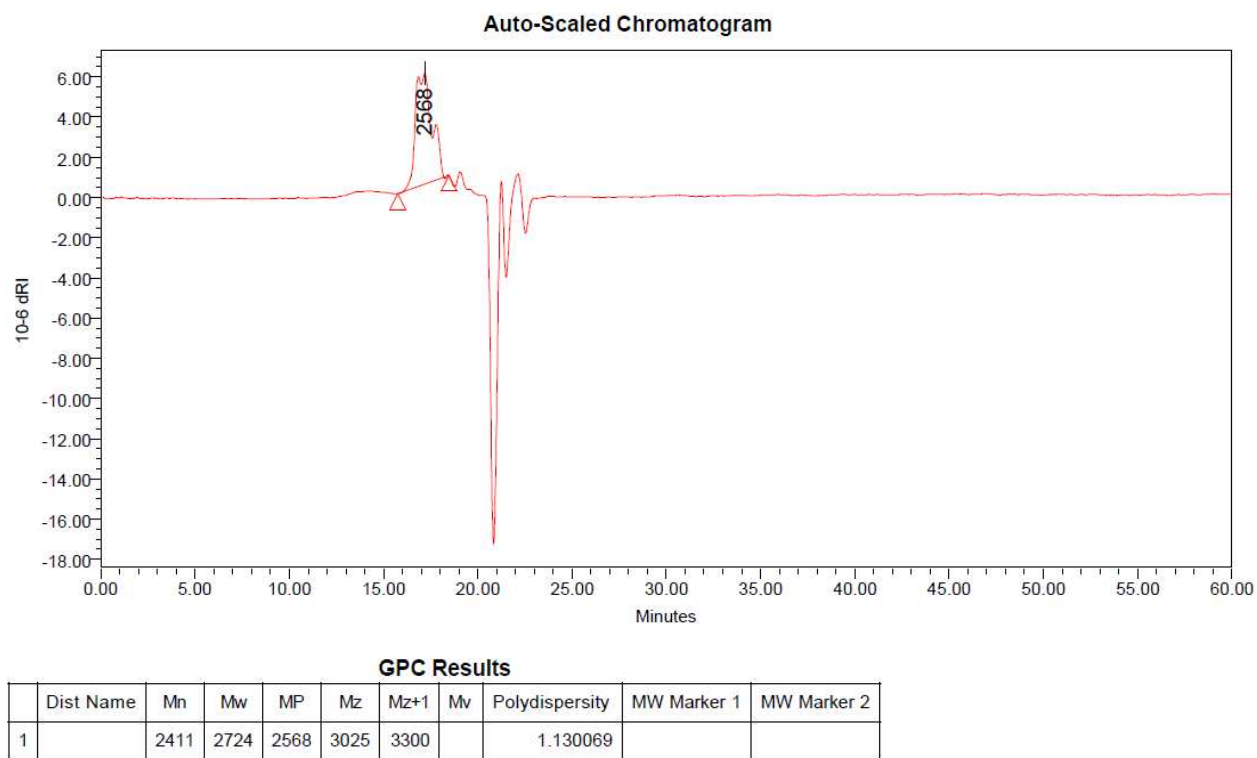


**Figure S2-4:** GPC trace for **P4** at 40°C in THF, against polystyrene standards.

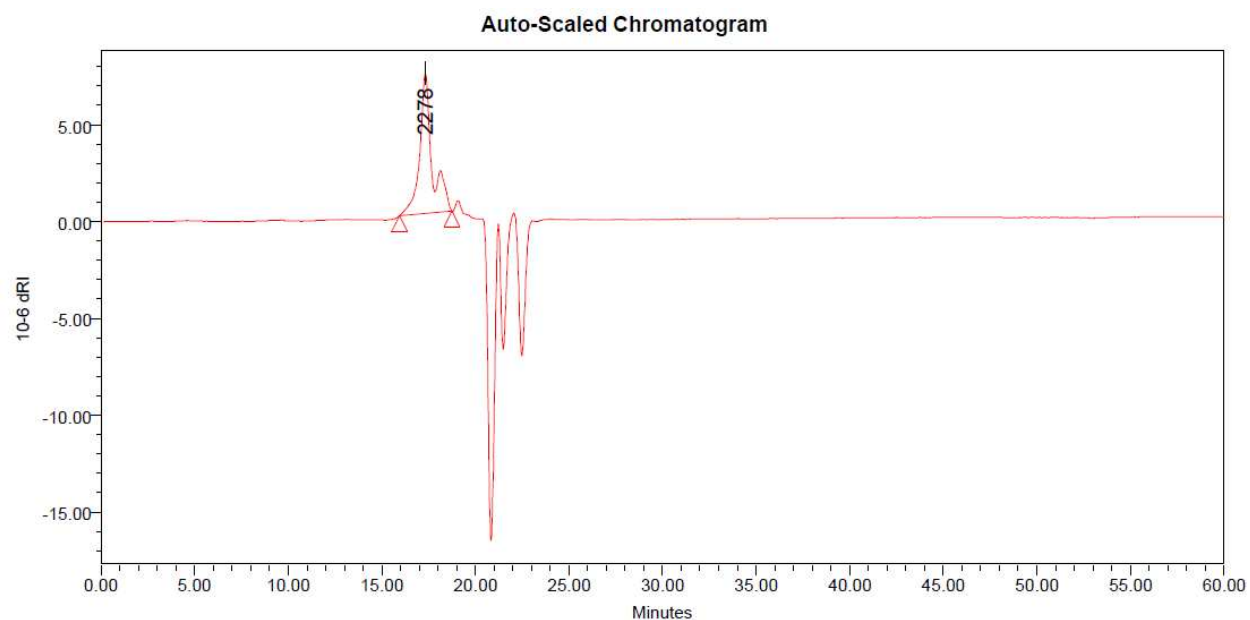


**Figure S2-5:** GPC trace for **P5** at 40°C in THF, against polystyrene standards.

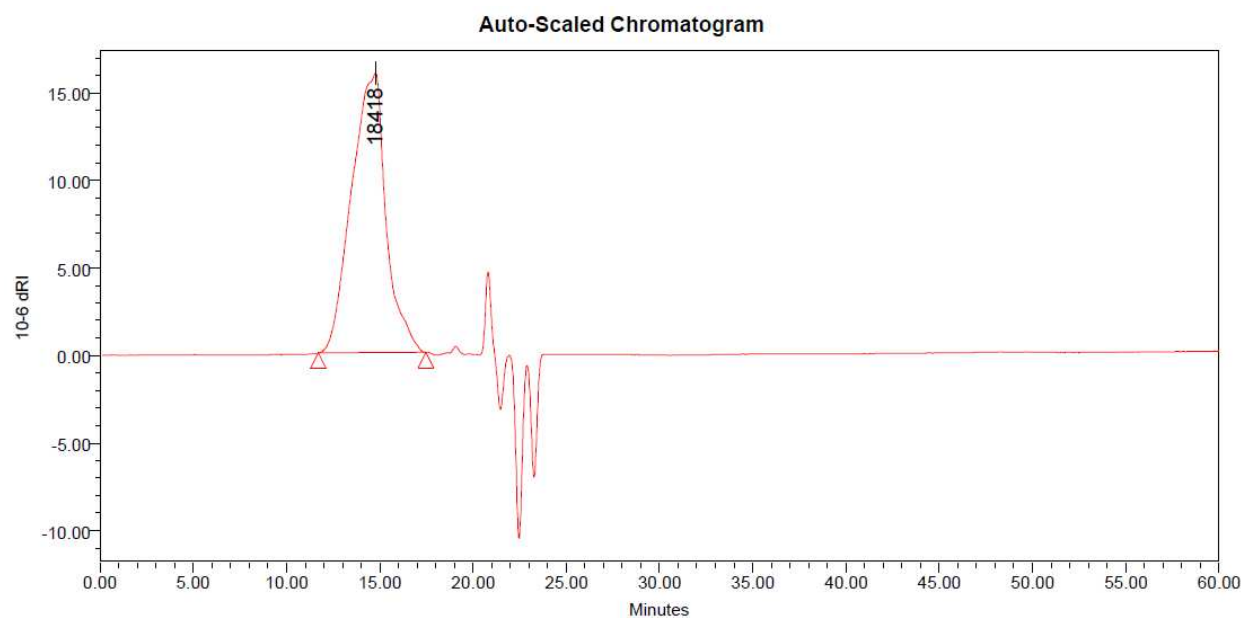


**Figure S2-6:** GPC trace for **P6** at 40°C in THF, against polystyrene standards.

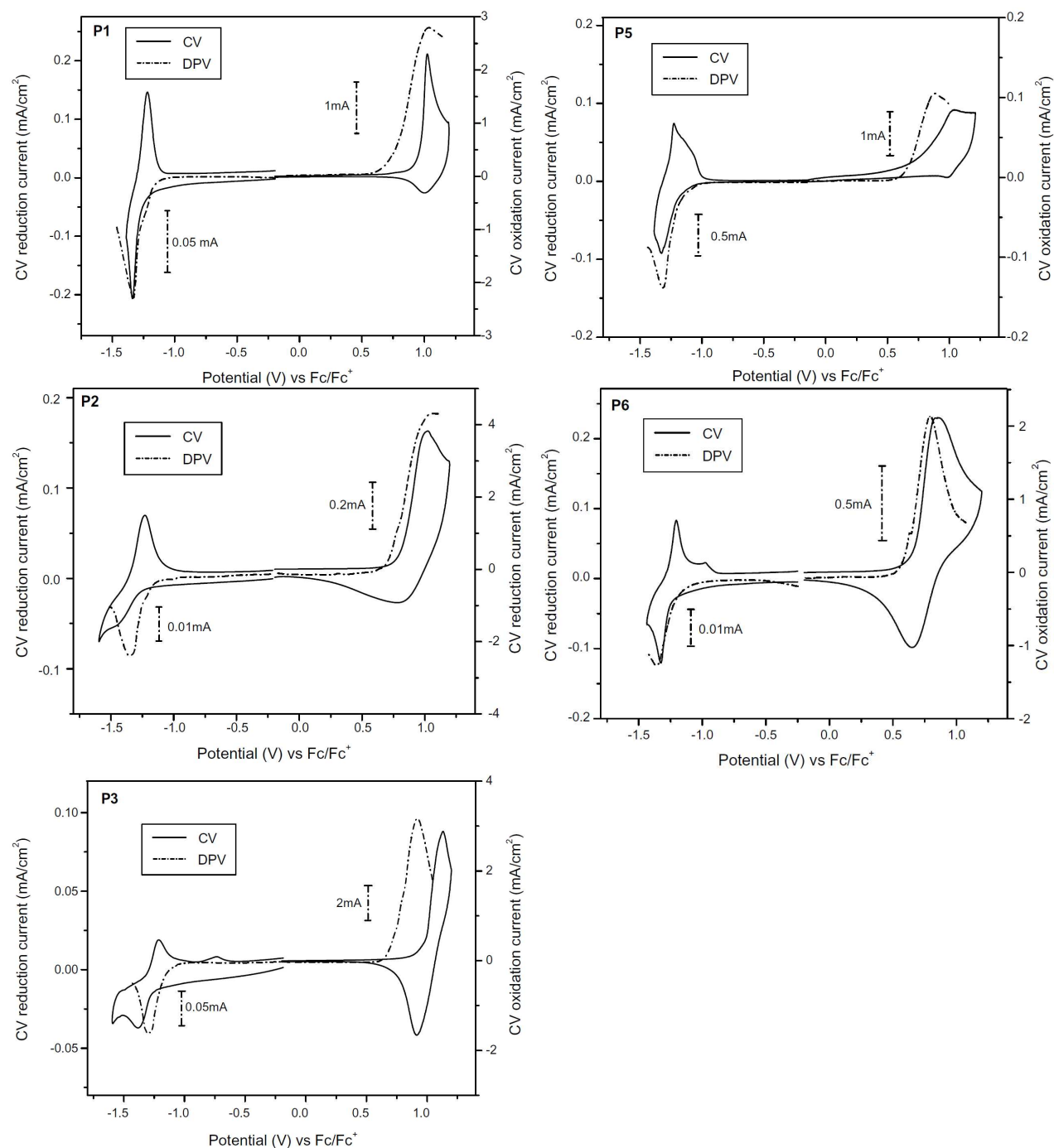


**Figure S3:** Cyclic voltammograms and differential pulse voltammograms of **P1**, **P2**, **P3**, **P5** and **P6** thin films on Pt-button electrodes, recorded at a 50mV/s scan rate in 0.1M TBAPF<sub>6</sub> acetonitrile solution.

**Table S1:** Molar absorptivities  $\epsilon$  of **P1** through **P6** in toluene solution.

| Polymer                                        | <b>P1</b> | <b>P2</b> | <b>P3</b> | <b>P4</b> | <b>P5</b> | <b>P6</b> |
|------------------------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|
| $\epsilon$ (M <sup>-1</sup> cm <sup>-1</sup> ) | 24,900    | 17,000    | 22,000    | 14,400    | 12,200    | 40,500    |