Supporting information

2,9-Dibenzo[*b,def*]chrysene as a Building Block for Organic Electronics

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TABLE OF CONTENTS

Apparatus

NMR spectra were recorded using a Varian Inova AS400 spectrometer (Varian, Palo Alto, USA) at 400 MHz or an Agilent DD2 500 MHz. Signals are reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), dt (doublet of triplets), m (multiplet) and coupling constants (J) are reported in hertz (Hz). The chemical shifts are reported in ppm (δ) relative to residual solvent peak. High-resolution mass spectra (HRMS) were recorded using an Agilent 6210 time-of-flight (TOF) LCMS apparatus equipped with an ESI and APPI ion source (Agilent Technologies, Toronto, Canada). Number-average (M_n) and weight-average (M_w) molecular weights were obtained by size-exclusion chromatography (SEC) using a high temperature Varian Polymer Laboratories GPC220 equipped with an RI detector. The column set consists of 2 PL gel Mixed C (300 x 7.5 mm) columns and a PL gel Mixed C guard column. The flow rate was fixed at 1 mL min^{-1} using 1,2,4- trichlorobenzene (TCB) (with 0.0125% BHT w/v) as the eluent. The temperature of the system was set to 110 º C. All the samples were prepared at a nominal concentration of 1.0 mg mL^{-1} in TCB.[1] Dissolution was performed using a Varian Polymer Laboratories PL-SP 260VC sample preparation system. The sample vials were held at 110 ºC with shaking for 1 h for complete dissolution. The solutions were filtered through a 2 mm porous stainless-steel filter used with a 0.40 mm glass filter into a 4 mL chromatography vial. The calibration method used to generate the reported data was the classical polystyrene method using polystyrene narrow standards Easi-Vials PS-M from Varian Polymer Laboratories which were dissolved in TCB. UV-visible spectra of monomers were recorded on a Varian diode-array spectrophotometer (model Cary 7000) using 10 mm path length quartz cells. Cyclic voltammograms (CVs) were recorded on a Solartron 1287 potentiostat using platinum electrodes at a scan rate of 50 mV s^{-1} and a Ag/Ag$^+$ (0.01 M of AgNO$_3$ in acetonitrile) reference electrode in an anhydrous and argon-saturated solution of 0.1 M of tetrabutylammonium tetrafluoborate (Bu$_4$NBF$_4$) in acetonitrile. Tetrabutylammonium

S-3

tetrafluoborate (98%, Aldrich) was recrystallized from methanol/water and dried at 70 °C under reduced pressure.[2] In these conditions, for a freshly prepared reference electrode, the half-wave oxidation potential ($E_{1/2}$) of ferrocene should be around 0.091 V versus Ag/Ag^+ as reported by Li *and al.*[3] The HOMO and LUMO energy levels are determined from the oxidation and reduction onset.[4-5] The onsets potential $\left(E'\right)$ are determined at the position where the current starts to differ from the baseline.

$$E_{HOMO} = -[(E^{'}_{ox\ vs\ Ag/Ag^+}) - (E^{1/2}_{Ferrocene\ vs\ Ag/Ag^+}) + 4.8]$$

$$E_{LUMO} = -[(E^{'}_{red\ vs\ Ag/Ag^+}) - (E^{1/2}_{Ferrocene\ vs\ Ag/Ag^+}) + 4.8]$$

TGA spectra were recorded using a Mettler TGA/SDTA-851e/SF/1100 °C instrument equipped with a MT1 model balance. The balance was protected with a constant flow of PP nitrogen at a flow of 20 mL/min. 2 mg of samples were weight and heated from 50 °C to 600 °C at 20 °C/min.

General Methods

Chemical reagents were purchased from Sigma–Aldrich Co. Canada, Oakwood Products, Inc. or Strem Chemicals, Inc. and were used as received. Vat Orange 1 was purchased from Hangzhou Chungyo Chemical Co. Ltd.

Experimental section

C$_{10}$H$_{21}$ C$_8$H$_{17}$

Br
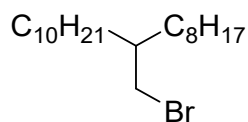
Compound A1: The product was prepared according to the methods reported in the literature.[6]

C$_8$H$_{17}$ C$_{10}$H$_{21}$

Br

Br

C$_{10}$H$_{21}$ C$_8$H$_{17}$
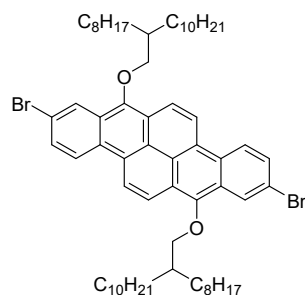
Compound 1: In a round bottom flash equipped with a magnetic stir bar, Aliquat 336 (0.22 mL, 0.49 mmol) was added to distilled water (12 mL). The mixture was stirred vigorously and degassed with nitrogen to make an emulsion. Vat orange 1 (200 mg, 0.41 mmol) was added to the mixture. The mixture was stirred and degassed with nitrogen for 30 min. at 75 °C. Sodium hydroxide (81.5 mg, 2.04 mmol) and sodium dithionite (184.5 mg, 1.06 mmol) was added to the reaction. The reaction was stirred 15 min. at 75 °C before adding 9-(bromomethyl)nonadecane. The reaction was stirred for 72 hours at 75 °C before it was cooled down at room temperature and poured into cold methanol. The solid was purified through column chromatography (hexanes as eluent), followed by a precipitation in cold methanol from a warm tetrahydrofuran solution to provide the desired compound as a yellow solid (222 mg, 52%). ^{1}H NMR (400 MHz, chloroform-d) δ 8.74 (d, J = 9.2 Hz, 2H), 8.69 (d, J = 9.6 Hz, 2H), 8.65 (d, J = 2.1 Hz, 2H), 8.37 (d, J = 9.5 Hz, 2H), 7.80 (dd, J = 9.1, 2.1 Hz, 2H), 4.09 (d, J = 5.4 Hz, 4H), 2.09 (p, J = 6.1 Hz, 2H), 1.89 – 1.75 (m, 4H), 1.66 (ddd, J = 13.8, 8.0, 5.9 Hz, 4H), 1.56 – 1.21 (m, 56H), 0.90 (dt, J = 9.5, 6.9 Hz, 12H). ^{13}C NMR (101 MHz, chloroform-d) δ 149.09, 129.17, 126.84, 126.61, 125.19, 125.16, 125.02, 124.03, 122.76, 122.05, 121.14, 120.51, 79.09, 39.67, 32.00, 31.97, 31.39, 30.22, 29.82, 29.80, 29.78, 29.74, 29.46, 29.43, 27.17, 22.75, 22.73, 14.17, 14.15. HRMS (APPI$^+$): C$_{64}$H$_{92}$Br$_2$O$_2$ [M]$^+$ 1050.54641 m/z, found 1050.55010 m/z, diff 3.61 ppm.
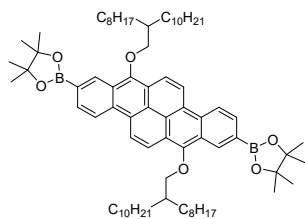
Compound 2: A screw-capped pressure vessel under nitrogen equipped with a magnetic stir bar was charged with compound **1** (400 mg, 0.379 mmol), bis(pinacolato)diboron (385 mg, 1.52 mmol), anhydrous potassium acetate (167 mg, 1.71 mmol) and [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) dichloride (16.6 mg, 0.023 mmol). The mixture was purged three times with nitrogen. In a separate flask, 1,4-dioxane (3.5 mL) was degassed with nitrogen for 15 min. before it was added to the reaction mixture. The reaction mixture was stirred for 24 h at 100 °C, extracted with dichloromethane and washed three times with water. The organic layer was dried with magnesium sulfate, filtered under vacuum and the solvent was removed under reduced pressure. The resulting solid was purified through column chromatography (hexanes:dichloromethane 1:1 as eluent) followed by a precipitation in cold methanol from a warm tetrahydrofuran solution to provide the desired compound as a yellow solid (231 mg, 53%). ^{1}H NMR (500 MHz, chloroform-*d*) δ 9.20 (d, *J* = 1.2 Hz, 2H), 9.02 (d, *J* = 8.7 Hz, 2H), 8.95 (d, *J* = 9.7 Hz, 2H), 8.58 (d, *J* = 9.5 Hz, 2H), 8.18 (dd, *J* = 8.6, 1.2 Hz, 2H), 4.24 (d, *J* = 5.4 Hz, 4H), 2.21 (p, *J* = 6.0 Hz, 2H), 1.97 – 1.85 (m, 4H), 1.72 (ddd, *J* = 14.0, 8.0, 6.3 Hz, 4H), 1.61 – 1.56 (m, 8H), 1.53 – 1.47 (m, 8H), 1.47 (s, 24H), 1.46 – 1.26 (m, 40H), 0.91 (dt, *J* = 11.2, 6.9 Hz, 12H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 150.77, 131.56, 130.29, 130.00, 126.24, 124.96, 124.16, 122.45, 122.39, 122.12, 121.11, 83.95, 79.67, 39.77, 31.99, 31.96, 31.59, 30.23, 29.81, 29.78, 29.74, 29.47, 29.42, 27.24, 25.03, 22.75, 22.72, 14.16, 14.13. HRMS (APPI$^+$): $C_{76}H_{117}B_2O_6$ [M]$^+$ 1144.90307 m/z, found 1144.89859 m/z, diff -3.91 ppm.
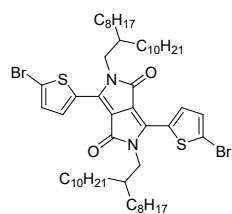
**Monomer DPP**: The product was prepared according to the methods reported in the literature.[7]
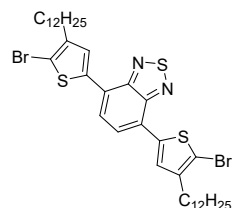
Monomer TBT: The was product was prepared according to the methods reported in the literature.[8]
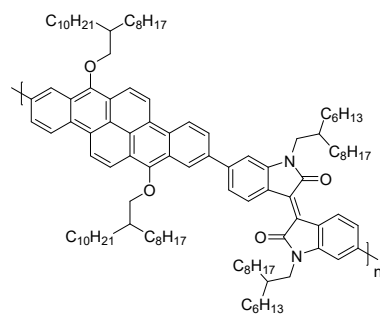
Polymer P1: A screw-capped flask equipped with a magnetic stir bar was charged with compound **2** (90.0 mg, 0.08 mmol), *N,N'*-bis(2-hexyldodecyl)-6,6'-dibromoisoindigo (68.1 mg, 0.08 mmol), tetrakis(triphenylphosphine) palladium (1.8 mg, 1.5 µmol) and Aliquat 336 (1 drop). The vessel was put under vacuum for an hour and purged 3 times with nitrogen. Degassed toluene (1.6 mL) was added and the reaction mixture was degassed while the temperature was increased to 75 °C to solubilize all the reactant in the flask. When a homogenous solution was obtained, a degassed solution of potassium carbonate (2 M, 0.2 mL, 0.4 mmol) was added. The flask was then sealed and the reaction mixture was stirred for 3 days at 110 °C. The reaction was allowed to cool down before it was precipitated in cold methanol. The precipitate was filtered under vacuum and washed with methanol followed by hexanes using a Soxhlet apparatus. The solvent was removed under reduced pressure and the polymer was solubilised in chloroform (25 mL). A solution of sodium diethyldithiocarbamate trihydrate (20 mL of a solution of 25.3 g of salt in 500 mL of water) was added and the resulting mixture was stirred vigorously for 6 hours at 75 °C. The mixture was extracted with chloroform

and washed three times with water. The organic layer was dried over magnesium sulfate, filtered and the solvent was removed under reduced pressure. Using hot chloroform, the polymer was precipitated in cold methanol and dried to give the desired polymer as a charcoal solid (112 mg, 57 %), (M_n = 33 kg·mol^{-1}, M_w = 53 kg·mol^{-1}, PDI = 1.6). ^{1}H NMR was performed in deuterated 1,1,2,2-tetrachloroethane at 75 °C, but no peaks were found.
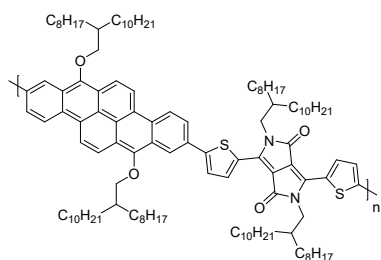
Polymer P2: A screw-capped flask equipped with a magnetic stir bar was charged with compound **2** (110.0 mg, 0.10 mmol), **DPP** (97.7 mg, 0.10 mmol), tetrakis(triphenylphosphine) palladium (2.2 mg, 1.9 µmol) and Aliquat 336 (1 drop). The vessel was put under vacuum for an hour and purged 3 times with nitrogen. Degassed toluene (1.9 mL) was added and the reaction mixture was degassed while the temperature was increased to 75 °C to solubilize all the reactant in the flask. When a homogenous solution was obtained, a degassed solution of potassium carbonate (2 M, 0.2 mL, 0.5 mmol) was added. The flask was then sealed and the reaction mixture was stirred for 3 days at 110 °C. The reaction was allowed to cool down before it was precipitated in cold methanol. The precipitate was filtered under vacuum and washed with methanol followed by hexanes and chloroform using a Soxhlet apparatus. The solvent was removed under reduced pressure and the polymer was solubilised in chloroform (40 mL). A solution of sodium diethyldithiocarbamate trihydrate (32 mL of a solution of 25.3 g of salt in 500 mL of water) was added and the resulting mixture was stirred vigorously for 6 hours at 75 °C. The mixture was extracted with chloroform and washed three times with water. The organic layer was dried over magnesium sulfate, filtered and the solvent was removed under reduced pressure. Using hot chloroform, the polymer was precipitated in cold methanol and dried to give the desired polymer

as a deep purple solid (152 mg, 90 %), (M_n = 46 kg·mol^{-1}, M_w = 119 kg·mol^{-1}, PDI = 2.6). ^{1}H NMR was performed in deuterated 1,1,2,2-tetrachloroethane at 75 °C, but no peaks were found.
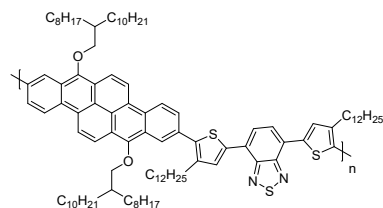
Polymer P3: A screw-capped flask equipped with a magnetic stir bar was charged with compound **2** (110.0 mg, 0.10 mmol), **TBT** (76.2 mg, 0.10 mmol), tetrakis(triphenylphosphine) palladium (2.2 mg, 1.9 µmol) and Aliquat 336 (1 drop). The vessel was put under vacuum for an hour and purged 3 times with nitrogen. Degassed toluene (1.9 mL) was added and the reaction mixture was degassed while the temperature was increased to 75 °C to solubilize all the reactant in the flask. When a homogenous solution was obtained, a degassed solution of potassium carbonate (2 M, 0.2 mL, 0.5 mmol) was added. The flask was then sealed and the reaction mixture was stirred for 3 days at 110 °C. The reaction was allowed to cool down before it was precipitated in cold methanol. The precipitate was filtered under vacuum and washed with methanol followed by hexanes using a Soxhlet apparatus. The solvent was removed under reduced pressure and the polymer was solubilised in chloroform (35 mL). A solution of sodium diethyldithiocarbamate trihydrate (28 mL of a solution of 25.3 g of salt in 500 mL of water) was added and the resulting mixture was stirred vigorously for 6 hours at 75 °C. The mixture was extracted with chloroform and washed three times with water. The organic layer was dried over magnesium sulfate, filtered and the solvent was removed under reduced pressure. Using hot chloroform, the polymer was precipitated in cold methanol and dried to give the desired polymer as a dark brown solid (122 mg, 83 %), (M_n = 42 kg·mol^{-1}, M_w = 95 kg·mol^{-1}, PDI = 2.2). Proton magnetic nuclear resonance spectroscopy was performed in deuterated 1,1,2,2-tetrachloroethane at 75 °C on the polymer, but not peaks was found.
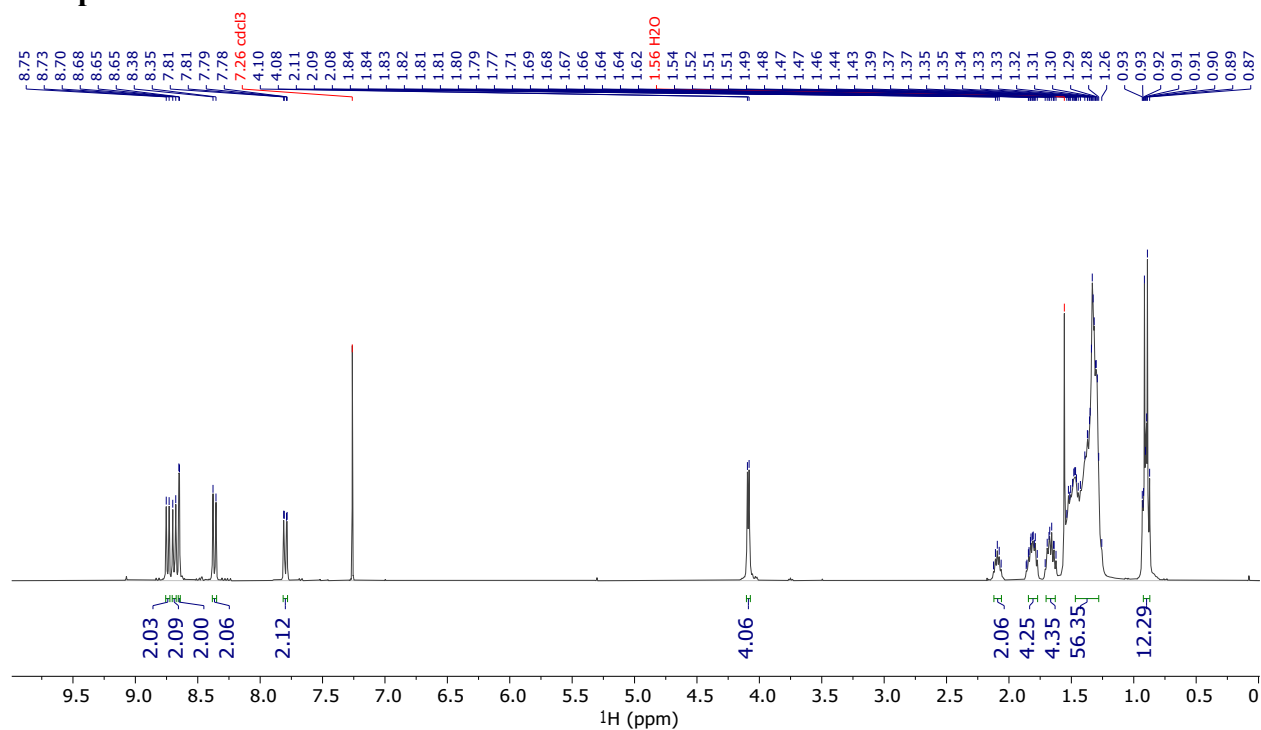
NMR Spectra

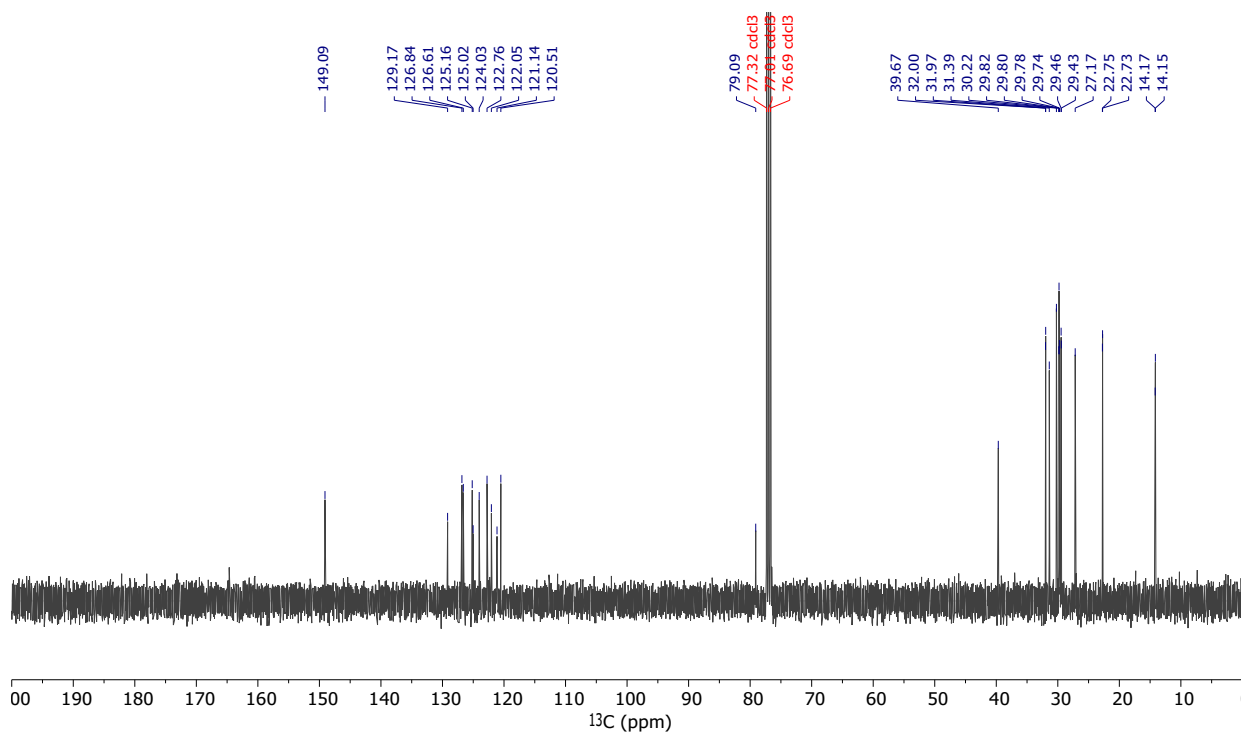## Compound 1

Figure S1: ^{1}H NMR spectrum of compound **1** in CDCl$_3$.

Figure S2: ^{13}C NMR spectrum of compound **1** in CDCl$_3$.

Compound 2
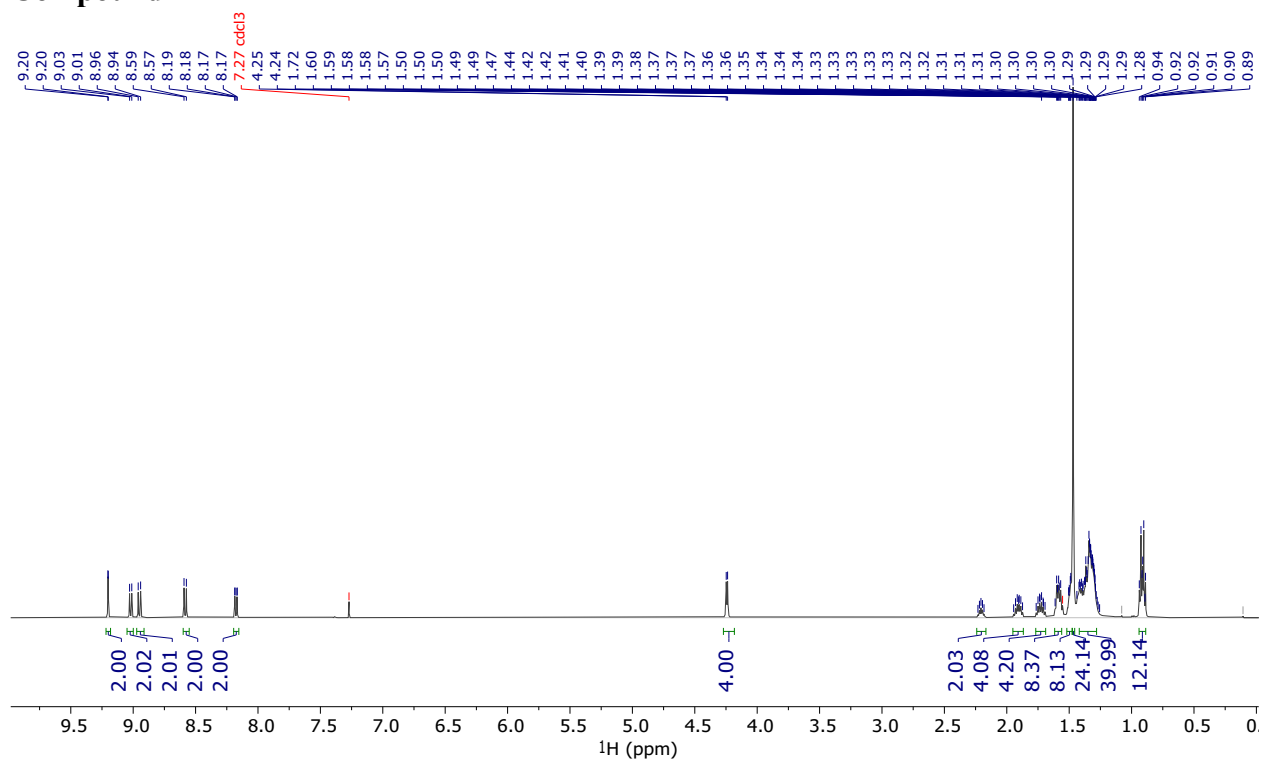
Figure S3: ^{1}H NMR spectrum of compound **2** in CDCl$_3$.
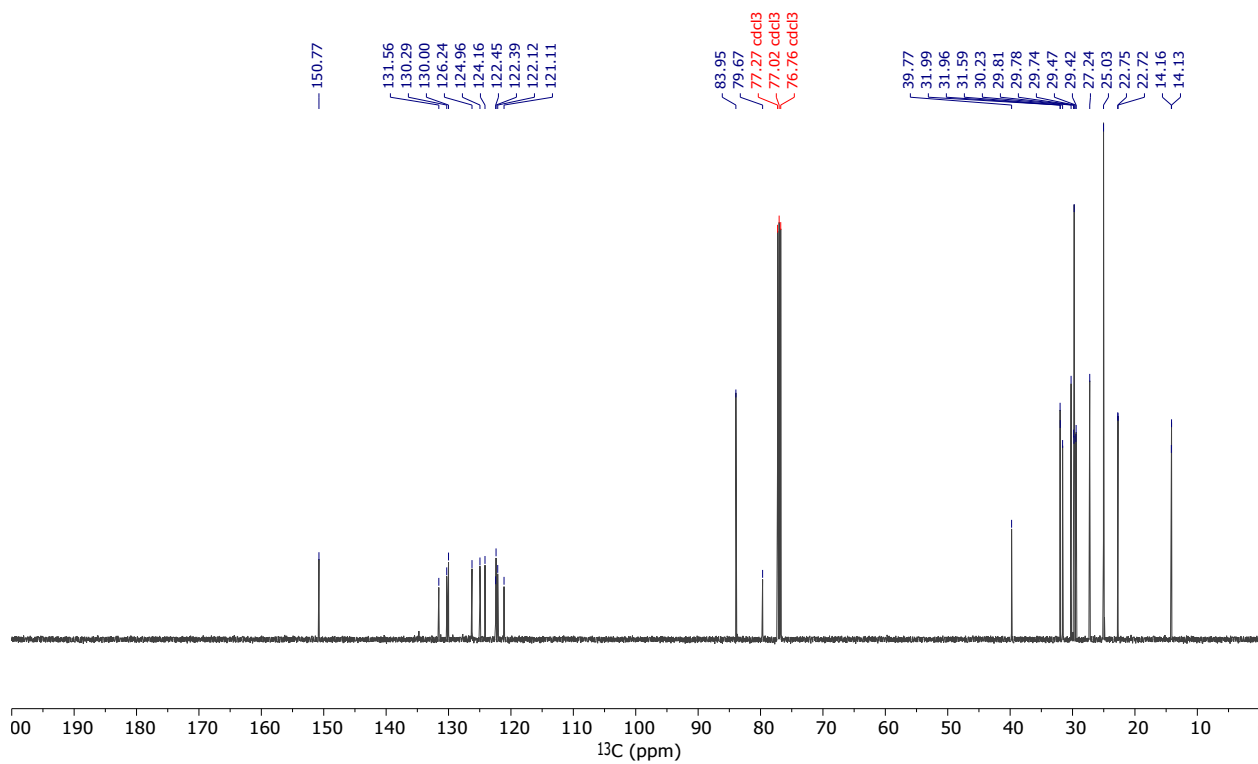
Figure S4: ^{13}C NMR spectrum of compound **2** in CDCl$_3$.

Polymer P1
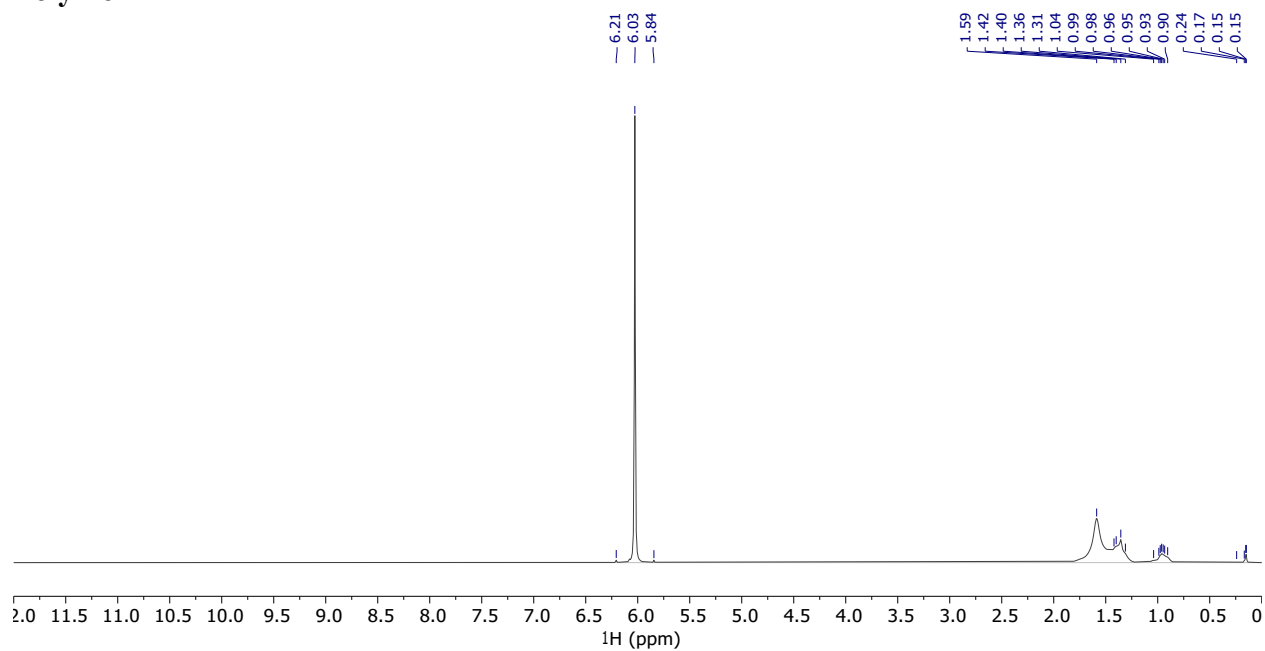
Figure S5: ^{1}H NMR spectrum of polymer **P1** 1 in TCE-d_2 at 75 °C.
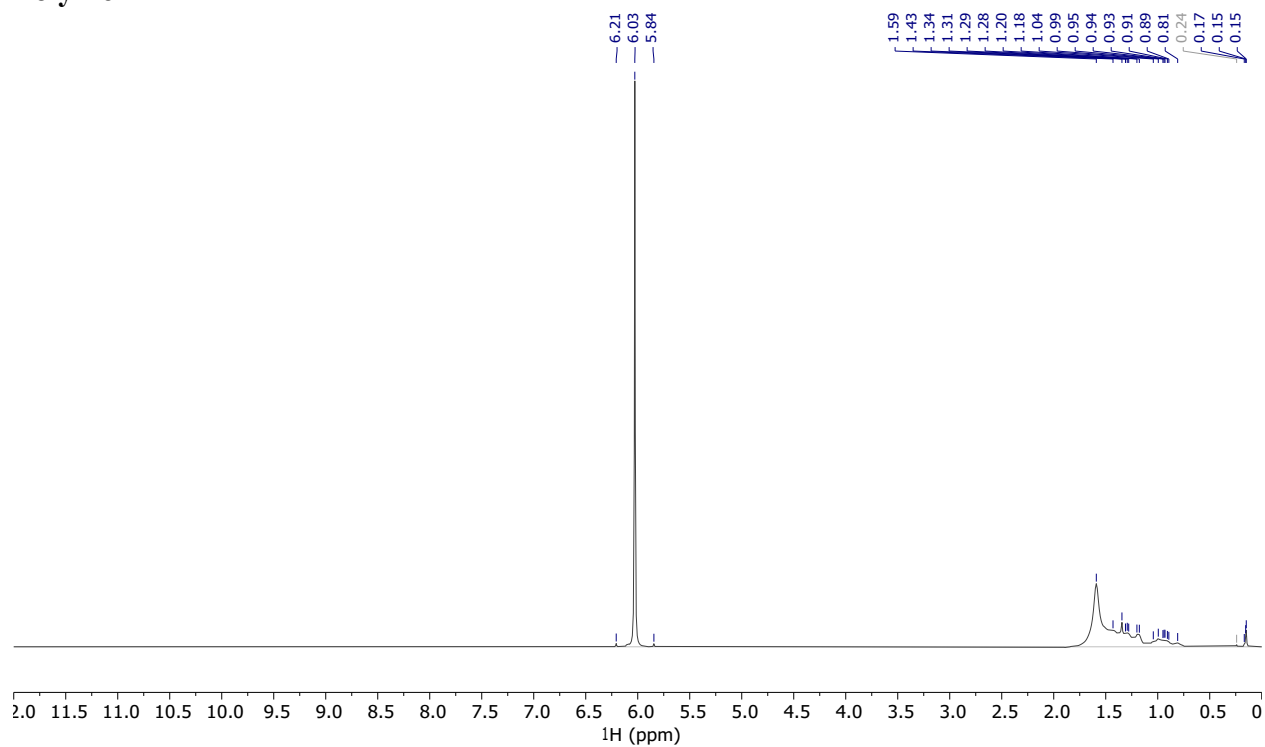
Polymer P2

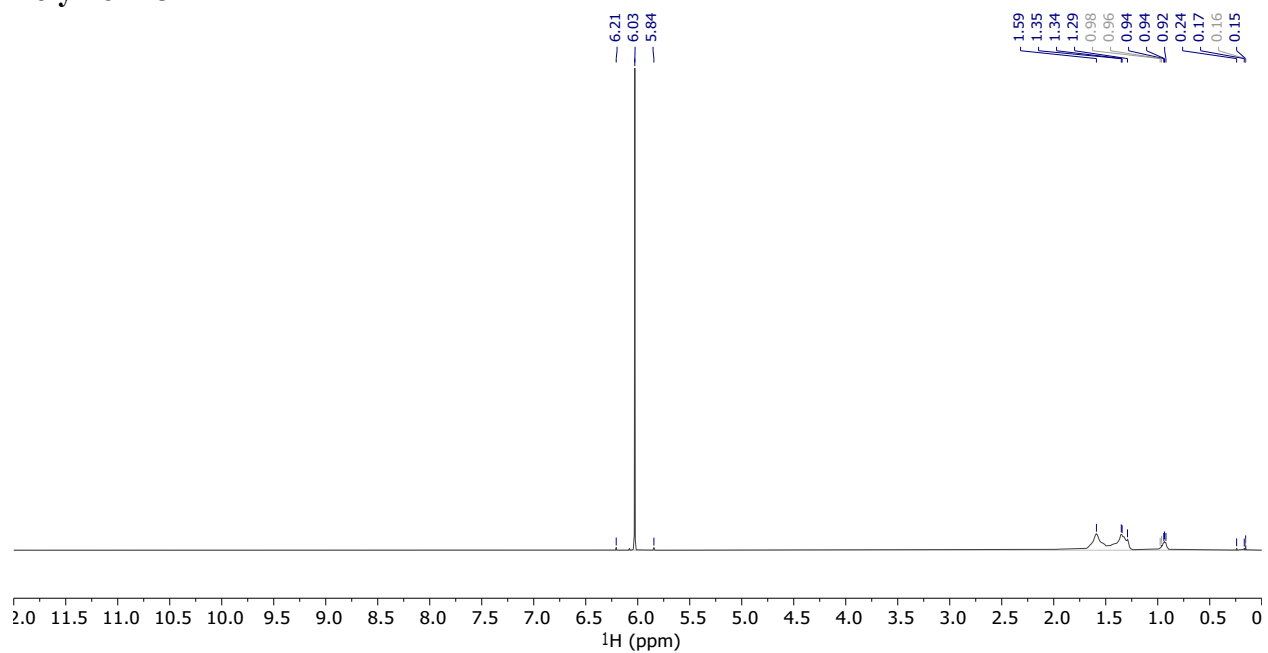**Figure S5**: ^{1}H NMR spectrum of polymer **P2** 1 in TCE-d_2 at 75 °C.

Polymer P3

Figure S5: ^{1}H NMR spectrum of polymer **P3** 1 in TCE-d_2 at 75 °C.
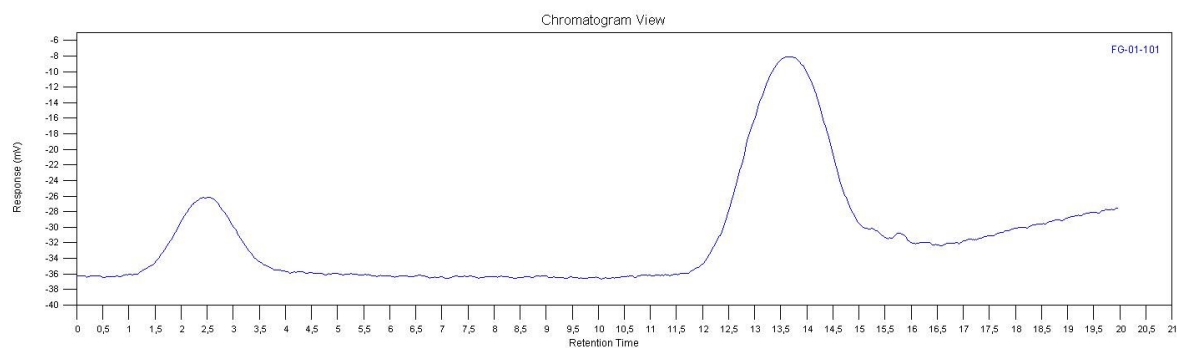
Size-exclusion chromatography

Figure S6: Size exclusion chromatography traces for polymer **P1** (M_n: 33.4 kg·mol^{-1}, M_w: 53.0 kg·mol^{-1}, polydispersity index (PDI): 1.6, X_n: 21).
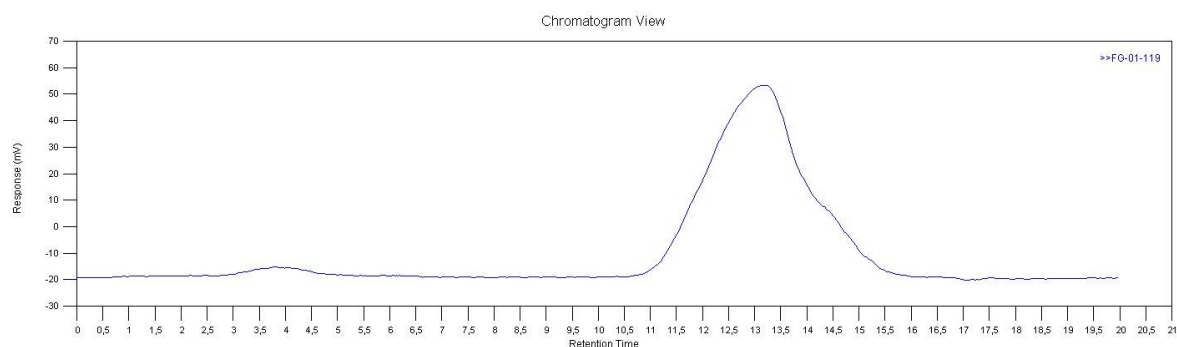

Figure S7: Size exclusion chromatography traces for polymer **P2** (M_n: 45.8 kg·mol^{-1}, M_w: 119.4 kg·mol^{-1}, polydispersity index (PDI): 2.6, X_n: 26).
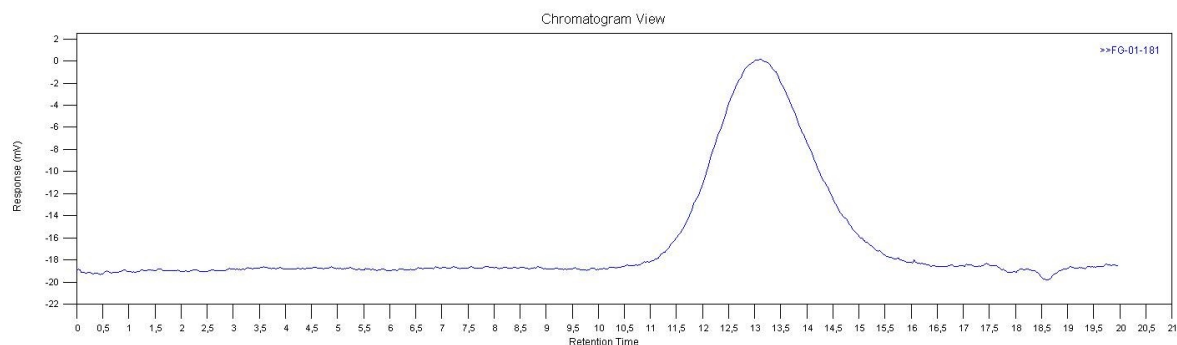

Figure S8: Size exclusion chromatography traces for polymer **P3** (M_n: 42.3 kg·mol^{-1}, M_w: 94.9 kg·mol^{-1}, polydispersity index (PDI): 2.2 X_n: 28).
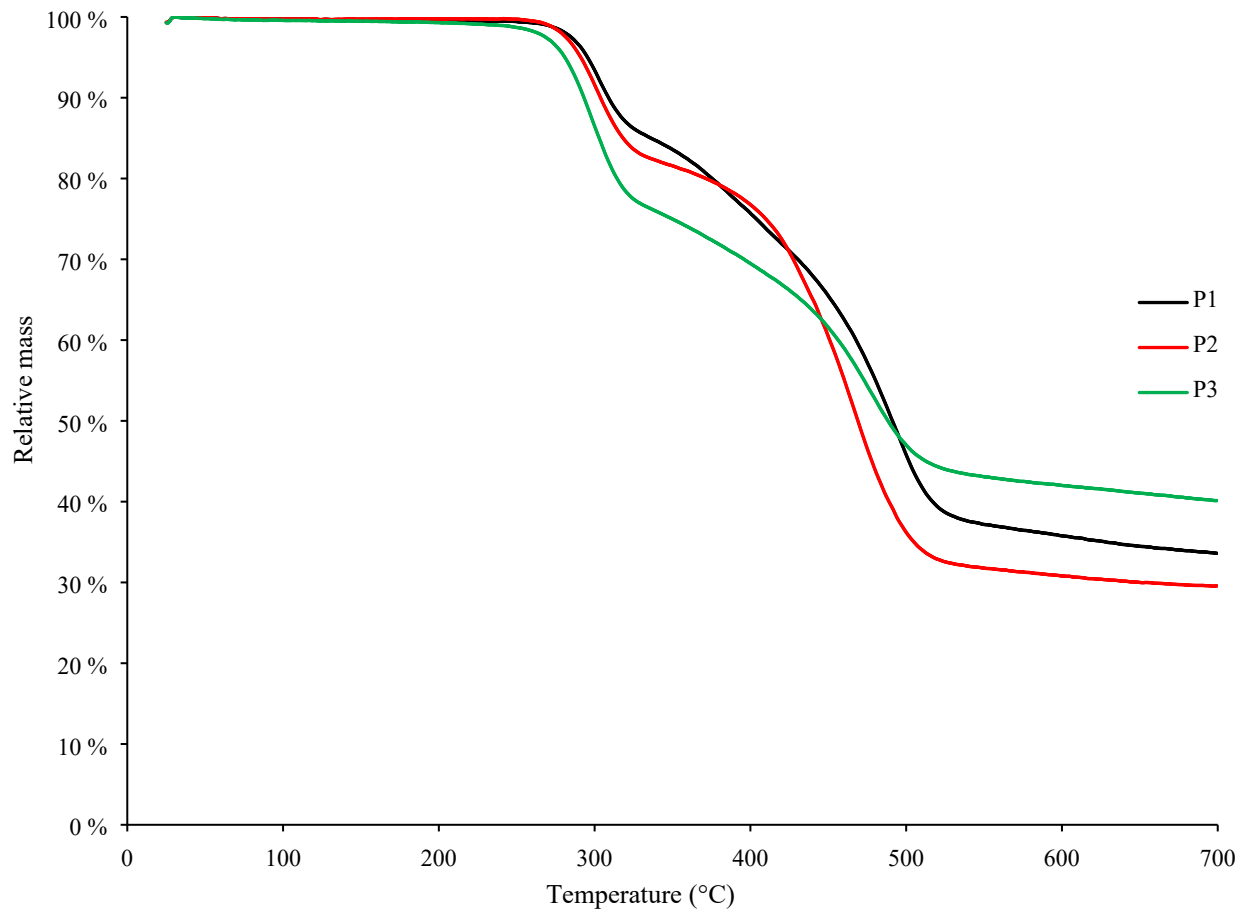
Thermogravimetric analysis

Figure S9: Thermogravimetric analysis curves for polymers **P1-P3.**

Table S1: Decomposition temperature of **P1-P3**.

POLYMER	DECOMPOSITION TEMPERATURE [a] (°C)
P1	295
P2	290
P3	280

[a] 5% weight loss

Differential scanning calorimetry

Figure S10: Differential scanning calorimetry plots of polymer **P1** (T_g: (110 ± 10) °C, T_m: (230 ± 10) °C), cooling curve was reversed.

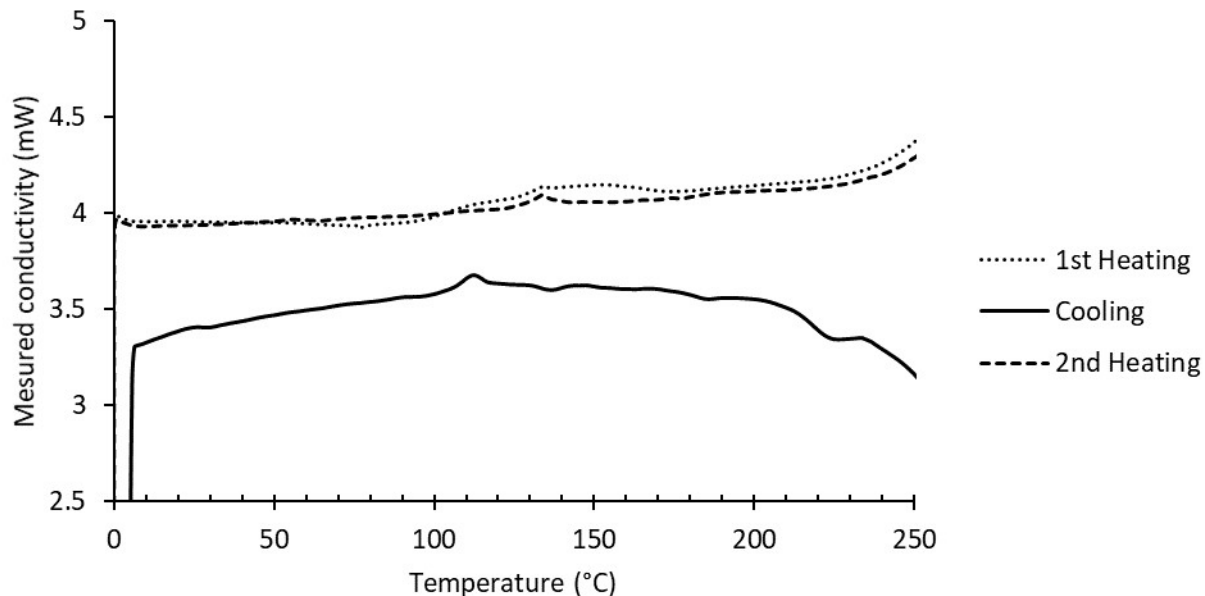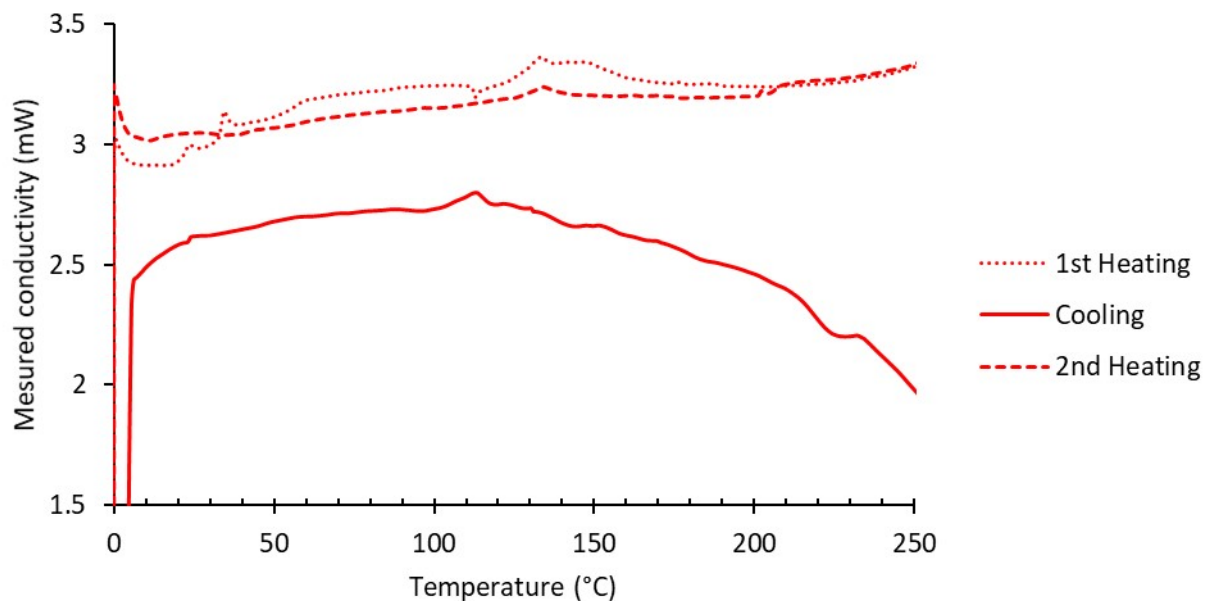

Figure S11: Differential scanning calorimetry plots of polymer **P2** (T_g: (110 ± 10) °C, T_m: (230 ± 10) °C), cooling curve was reversed.
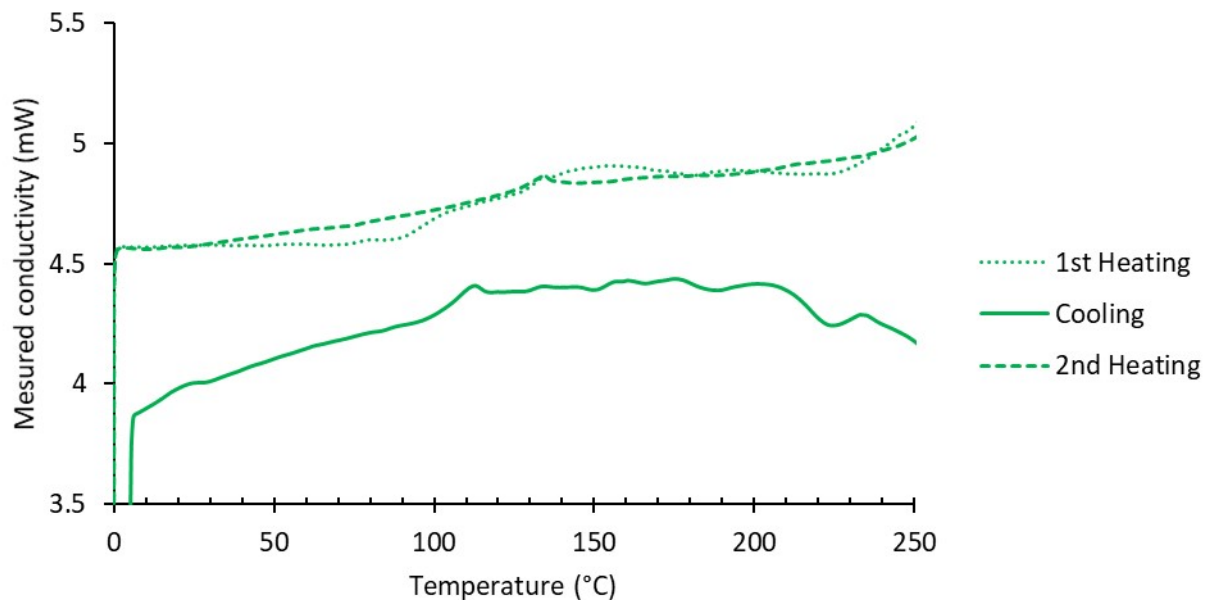
Figure S12: Differential scanning calorimetry plots of polymer **P3** (T_g: (110 ± 10) °C, T_m: (220 ± 10) °C), cooling curve was reversed.

Cyclic voltammetry

Figure S13: Film Cyclic Voltammetry of polymer **P1** in acetonitrile solution with 0.1M [Bu$_4$N][BF$_4$] as the supporting electrolyte with a scan rate of 50 mV·s^{-1}.

Figure S14: Film Cyclic Voltammetry of polymer **P2** in acetonitrile solution with 0.1M [Bu$_4$N][BF$_4$] as the supporting electrolyte with a scan rate of 50 mV·s^{-1}.
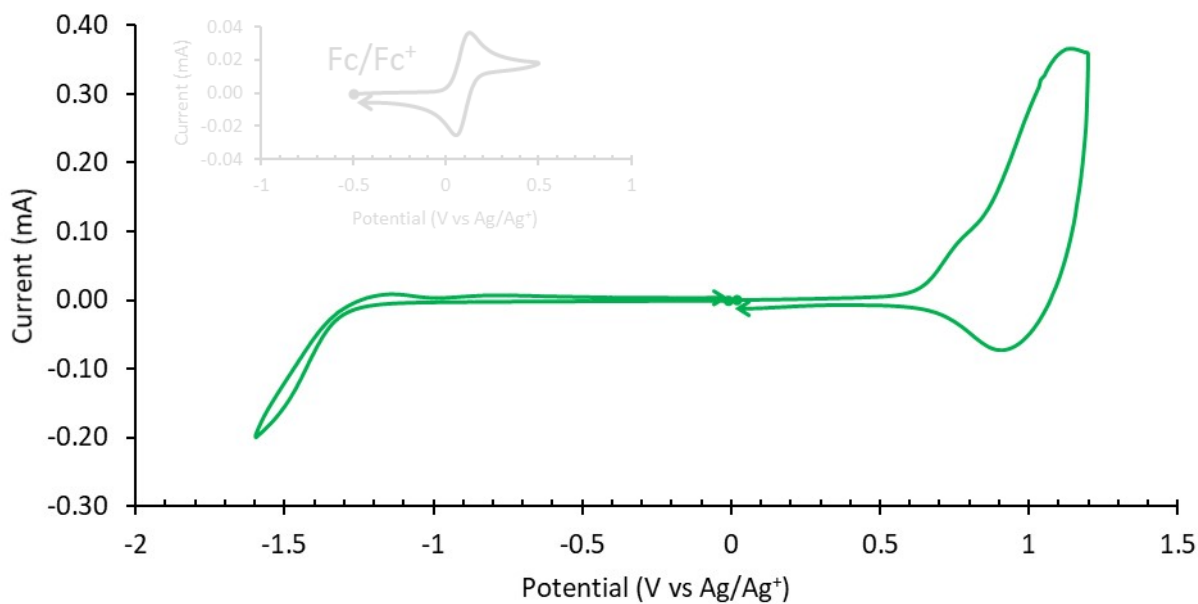
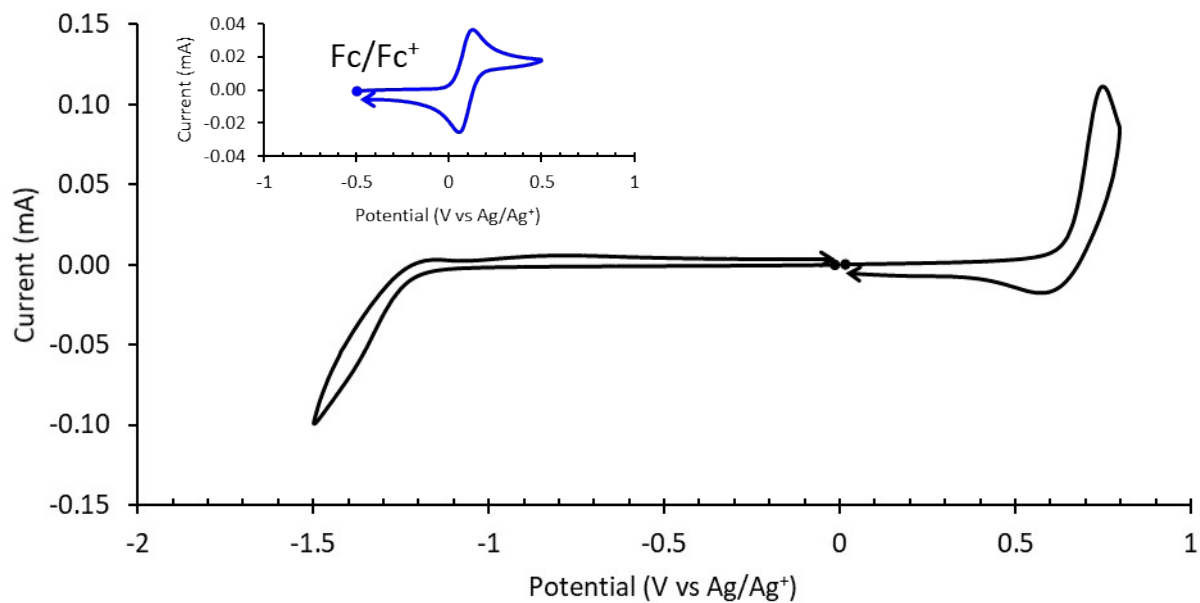**Figure S15**: Film Cyclic Voltammetry of polymer **P3** in acetonitrile solution with 0.1M [Bu$_4$N][BF$_4$] as the supporting electrolyte with a scan rate of 50 mV·s^{-1}.
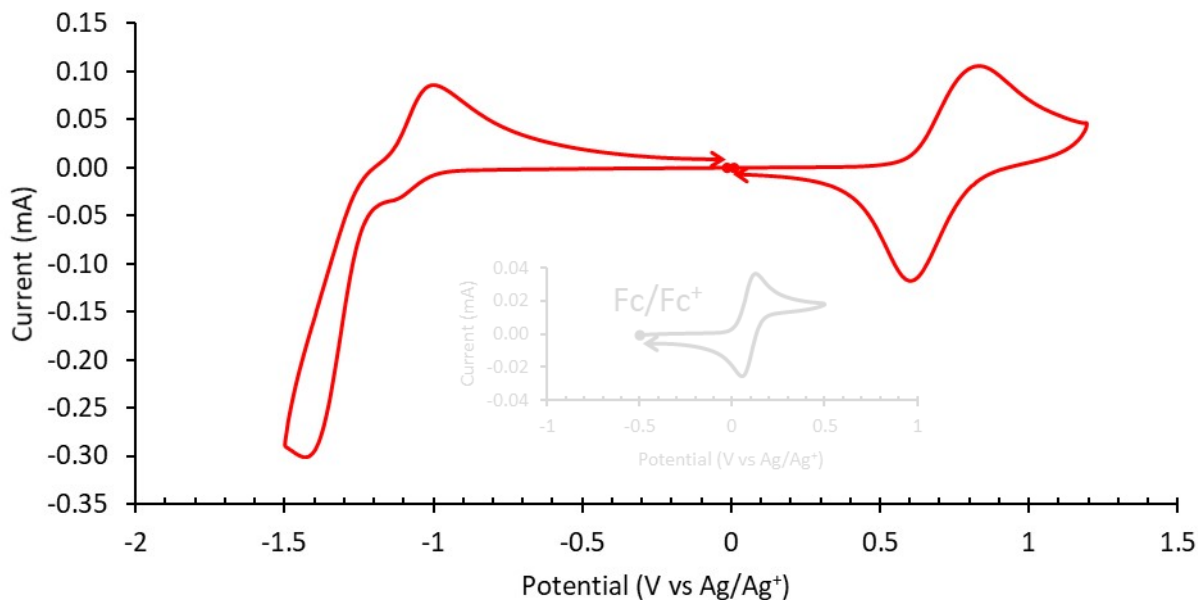
UV-vis spectroscopy
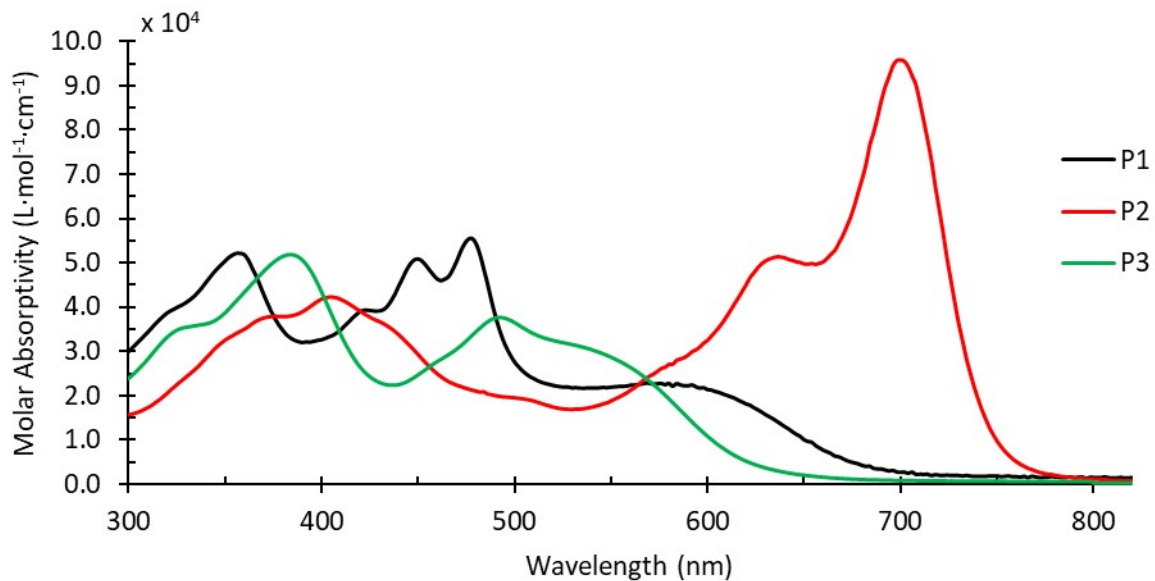
Figure S16: UV-vis molar absorptivity spectra of polymers **P1-P3** in solution of CHCl₃.
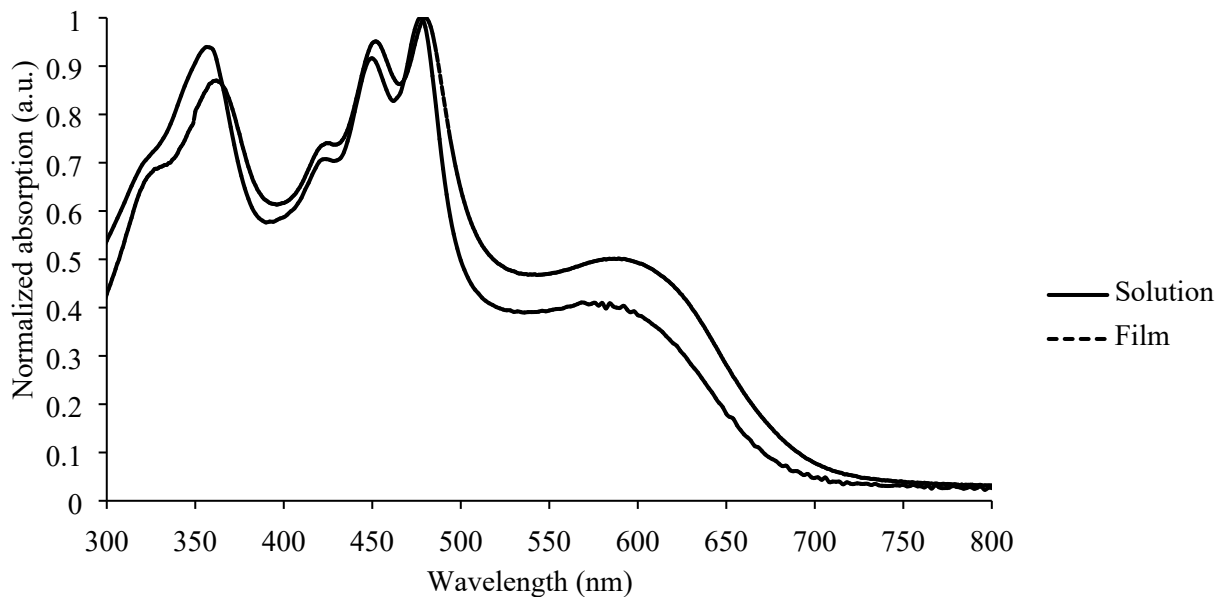
Figure S17: Normalized UV-vis absorption spectra of polymer **P1** in solution of CHCl₃ and in film.

Figure S18: Normalized UV-vis absorption spectra of polymer **P2** in solution of CHCl$_3$ and in film.

Figure S19: Normalized UV-vis absorption spectra of polymer **P3** in solution of CHCl$_3$ and in film.

Organic solar cells devices

Organic solar cells processing: The devices were prepared in an inverted geometry under ambient atmosphere. The geometry was ITO/ZnO/Polymer:PC$_{61}$BM/MoO$_3$/Ag. The devices were prepared using commercial ITO-coated glass substrates (10 Ω/square, Thin Film 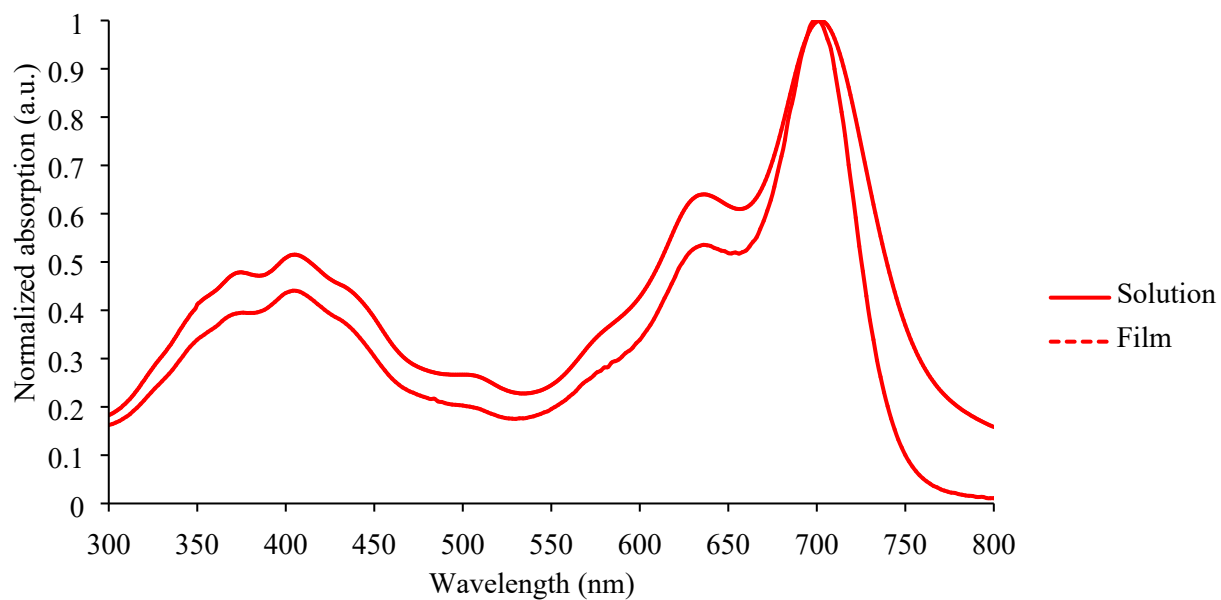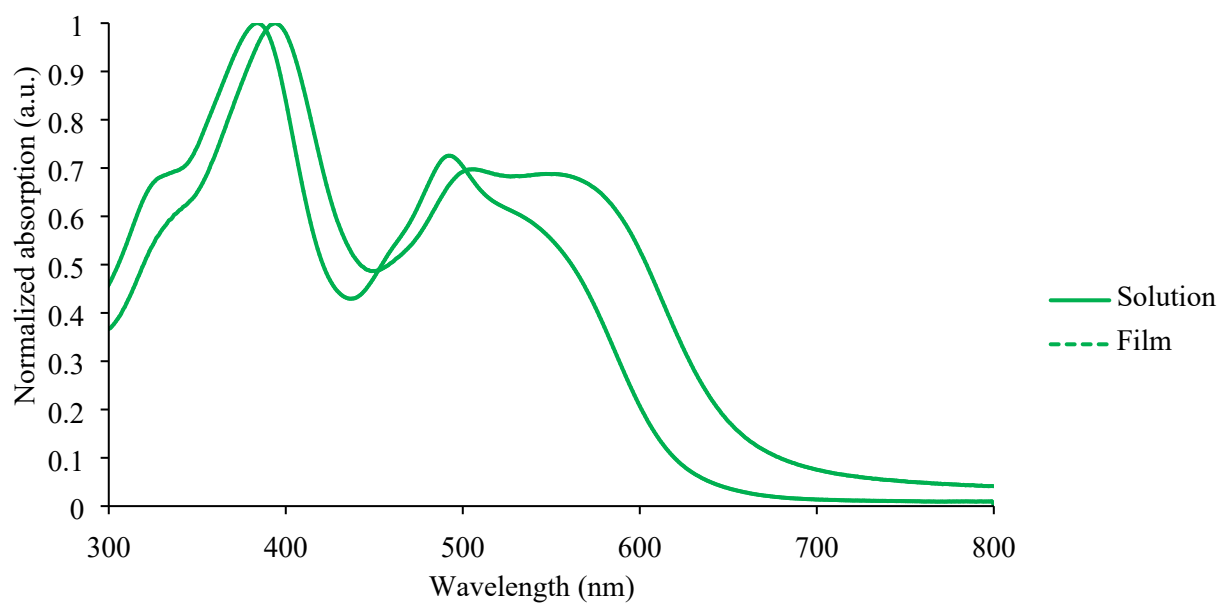Devices). The substrates were cleaned using cleanroom detergent water, acetone, and isopropyl alcohol. The ITO was then treated in a Plasma-Oxygen chamber for 5 minutes. The sol-gel ZnO was then spin-coated on the ITO glass substrates and annealed at 200 °C for at least 10 minutes. The polymer:PC$_{61}$BM solution was spin-coated at 60 °C, with spin speeds between 300 and 800 rpm. The active layer solution was previously prepared from a 1:2 D:A weight ratio in a 12 mg/mL polymer concentration. *o*-Dichlorobenzene was added to **P1-P3** and PC$_{61}$BM and the solution was stirred overnight at 60 °C. Diphenyl ether was added in solution 2 hours prior to the solution deposition. No annealing processes were made. Finally, the substrates were taken to a vacuum-deposition chamber and placed under high vacuum at 5x10^{-7} torr. 8 nm of MoO$_3$ (0.2 Å/s) and 100 nm of silver (1.5 Å/s) were evaporated. The current density-voltage curves (J-V) were measured using a Keithley 2400 source meter on active area of 0.09 cm^2. The AM 1.5 spectrum was reproduced with a light intensity of 100 mW cm^{-2} from an Oriel Instruments Solar Simulator. The active layer thicknesses were measured with a Veeco Deltak IIA Surface Profiler.
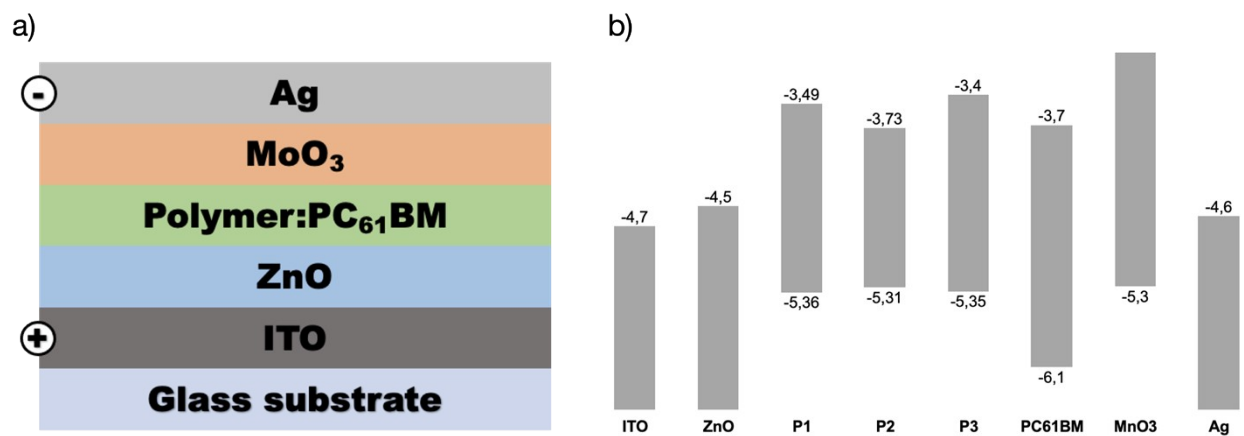
Figure S20: Solar cells configuration (a) and Energy diagram of the solar cells components (b).
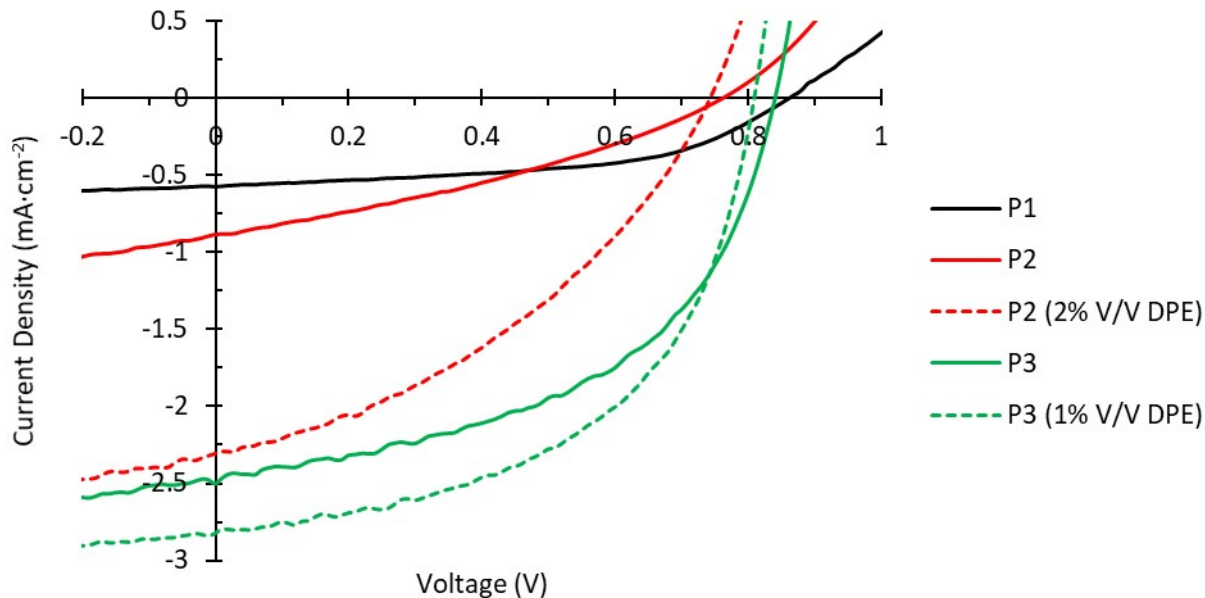
Figure S21: J-V curves of polymers **P1-P3** without diphenyl ether as additive and the one's using the best ratio of additive.

Table S2: Organic solar cell results[a] for devices without additive in the active layer and conditions who gives the higher power conversion efficiency for polymers **P1-P3**.

Polymer	Thickness (nm)	Additive Ratio[b] (% V/V)	J_{sc} (mA/cm²)	V_{oc} (V)	FF	PCE (%)
P1[c]	100 ± 20	-	0.577 (0.571)	0.86 (0.80)	0.51 (0.49)	0.25 (0.22)
P2	100 ± 30	-	0.9 (0.7)	0.8 (0.4)	0.33 (0.35)	0.2 (0.1)
	70 ± 10	2	2.30 (2.31)	0.74 (0.73)	0.387 (0.384)	0.66 (0.65)
P3	110 ± 10	-	2.50 (2.44)	0.84 (0.83)	0.50 (0.49)	1.05 (1.00)
	90 ± 30	1	2.8 (2.4)	0.810 (0.815)	0.53 (0.53)	1.2 (1.0)

[a] Maximum value reached presented, average value in parenthesis. [b] Diphenyl ether as additive.

[c] No increase of performance observed using additive.

Organic field-effect transistors

FET Device Fabrication and Characterization: FET devices were fabricated on highly doped n-type Si(100) wafer with a 300 nm thick SiO_2 functionalized with an n-octadecyltrimethoxysilane (OTS) self-assembled monolayer. The OTS-treated substrate was washed with toluene, acetone and isopropyl alcohol, and then dried with nitrogen before use. The organic semiconductor thin films were spin-cast at 1500 RPM on the OTS-treated substrates to produce films with thicknesses of ~40 nm from prepared polymer solutions in chlorobenzene (5 mg mL^{-1}). The thermal annealing process was carried out for an hour in a vacuum oven. A top-contact gold electrode (50 nm) was subsequently deposited by evaporation through a shadow mask with a channel length (L) and width (W) defined as 50 and 1000 μm, respectively. All transistor measurements were conducted using a Keithley 4200-SCS semiconductor parameter analyzer (Keithley Instruments Inc., Cleveland, OH, USA) in an N_2-filled glove box at room temperature. Mobility values were calculated through linear fitting of the transfer curve in the saturation regime and using the equation $\mu_{sat} = 2L/CW$ $(\delta(I_D)^{1/2}/\delta V_G)^2$. Transfer curves were obtained through measuring the I_{DS} with a V_{DS} held at -60 V and sweeping the V_G from 0 to -60V. A V_{DS} of -60V was used to ensure that the transfer curve was measured in the saturation regime of the output curve and that linear fitting of the transfer curve would result in extrapolation of the saturation mobility.
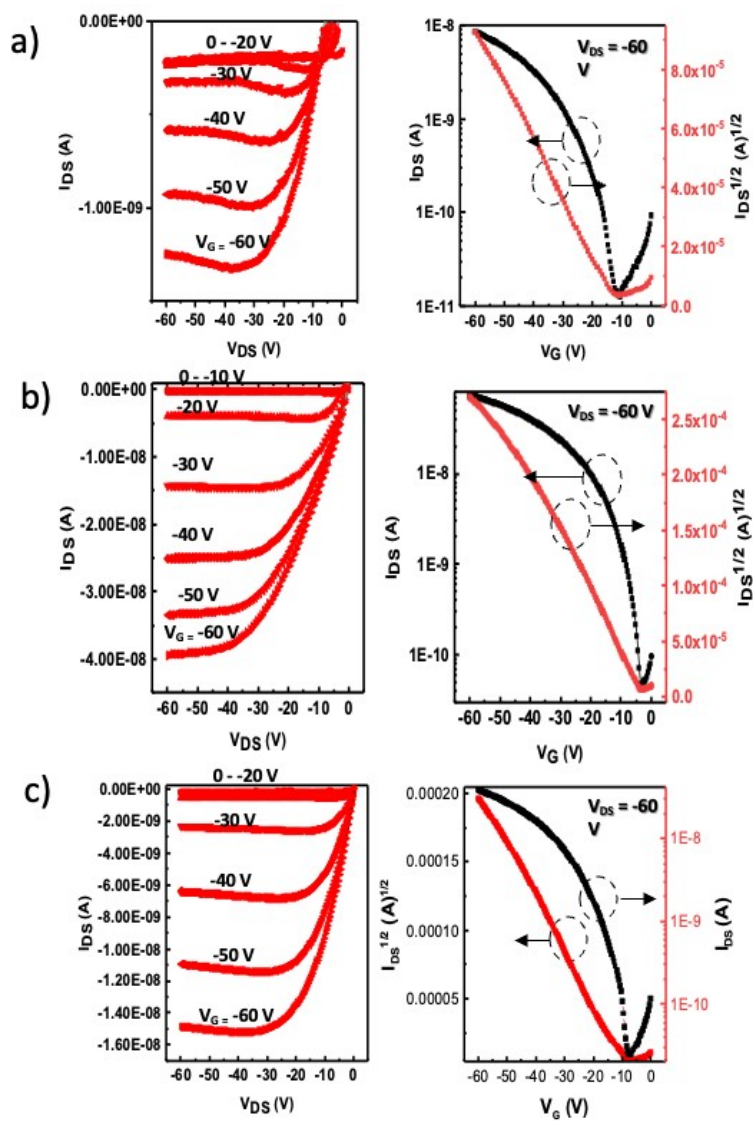
Figure S22. Typical output (left) and transfer (right) (V_{DS} = -60 V) characteristics of a) **P1**, b) **P2**, and c) **P3** after thermal annealing for 1 hour at 150 °C.

DFT Calculations

Table S3. Values of the torsion for the minimum in energy for compounds **P1**, **P2** and **P3**, and the potential energy barrier to reach another minimum. Calculations were performed using 6-31g**/B3LYP method

Polymer	Torsion of minimum energy (deg.)	Activation energy (kcal/mol)
P1	40.6	5.9
P2	30.3	0.5
P3	44.9	1.7

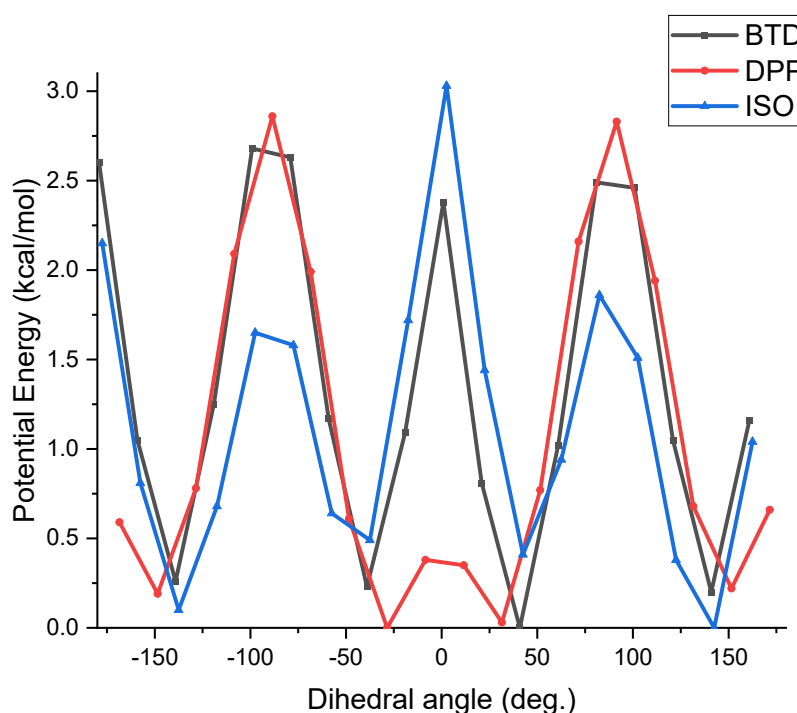**Figure S23. Dihedral scan of P1 (ISO), P2 (DPP) and P3 (BTD).**

Considering the configuration of minimum energy, as reported in Table S3, computation of the UV/vis spectra was carried out using the time dependent DFT (TD-DFT) approach (Table S4). However, specific treatment for the non-local exchange were needed.[9] More specifically, some hybrid functionals can ameliorate greatly the results.[10]

Table S4. TDDFT computed maximum wavelength, using 2 different basis sets (double and triple zeta), and 3 different functionals (B3LYP, PBE, wB97xd), are compared with experimental data.

Polymer	λ_{max}^{film} nm	B3LYP/ 6-31g**	B3LYP/ 6-311g**	PBE/ 6-31g**	wB97xd/ 6-311g**
P1	701	1205	1199	756	432
P2	772	894	878	640	448
P3	666	939	923	674	425

From Table S4, it is observed that functionals B3LYP or PBE, and extended basis set, led to **P1** as the compound showing the first excited state with the longer absorption wavelength. The wB97-xd functional exhibits the stronger charge transfer character and lead to the right order in the maximum wavelength. However, values are clearly higher than the experimental ones. These differences in the ranking and in the absolute values can also be retrieved by computing the gap between HOMO and LUMO orbitals, as revealed in Table S5, where the computed gaps are compared with the experimental gap.

Table S5. TD-DFT computed band gap, using 2 different basis sets (double and triple zeta), and 3 different functionals (B3LYP, PBE, wB97xd), are compared with experimental data.

Polymer	E_g^{elec} (eV)	B3LYP/ 6-31g**	B3LYP/ 6-311g**	PBE/ 6-31g**	wB97xd/ 6-311g**
P1	1.86	1.27	1.28	0.50	6.23
P2	1.58	1.70	1.69	0.92	5.92
P3	1.95	4.05	1.59	0.57	6.22

Classical functionals are not able to accurately describe absorption spectra, and the gap of the three compounds, despite values that approach experimental data. We need to consider hybrid functional with the long-range exchange described by Hartree-Fock exchange.[11] Such consideration agrees with molecular characteristics displayed by the configuration of minimum energy of the three molecules. **P2** exhibits the greatest planarity, which should lead to the highest absorption wavelength.

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