

Supporting Information

Unravelling the Influence of Side-Chain Symmetry on Device Performance: Insights from Isoindigo-Based Polymers in Thin-Film Transistors

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General Procedure and Materials

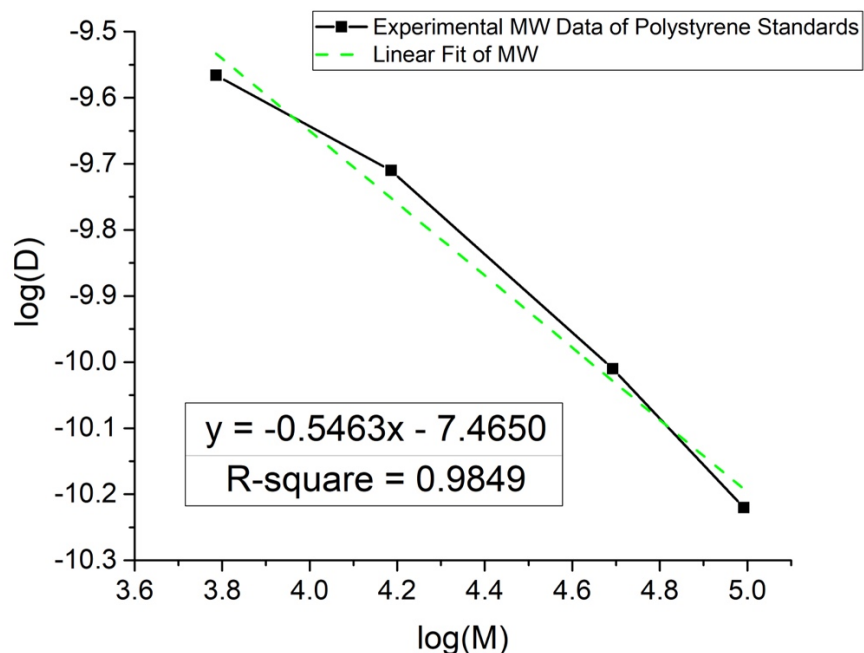
Materials: Chemical reagents were purchased from Oakwood Products Inc., Sigma-Aldrich Canada Co., or Tokyo Chemical Industry Co. Ltd. and were used as received. The 4-decyltetradecan-1-ol reagent was purchased commercially from Lyn (Beijing) Science & Technology Co. Ltd. and used as received. Solvents used for organic synthesis were obtained from Sigma-Aldrich, with dry solvents purified using a Solvent Purifier System (SPS) (Swagelok, Solon, Ohio, USA). Tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct ($\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene were purchased from Sigma-Aldrich and recrystallized following reported procedures.^{1,2} 6,6'-dibromo-isoidigo (il) and compounds **1-3** were synthesized following reported procedures.³⁻⁶ Compounds **M1**, **M2**, and **M3** were synthesized by slightly modified procedures from previous literature.^{4,7,8}

Measurements and Characterization: Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 300 MHz spectrometer. Chemical shifts were given in parts per million (ppm). High-resolution mass spectrometry (HRMS) was performed on an Agilent 6550 (ESI-CE/LCMS QToF) instrument using an ESI MS Orbitrap Velos Pro under positive mode. FTIR spectroscopy was performed on a Bruker ALPHA FTIR spectrometer using a Platinum ATR sampling module. UV-visible spectroscopy was performed on a Varian UV/Visible Cary 50 spectrophotometer. All electrical measurements for OFET devices were conducted using a Keithley 4200 semiconductor parameter analyzer (Keithley Instruments Inc.) under dry N_2 (glovebox). Film surface structure of the polymers was evaluated using a Multimode atomic force microscope (AFM, Digital Instruments) operated in the tapping mode at room temperature. Images were collected using Nanoscope 6 software and processed using WSxM 5.0 Develop 8.0 software. Grazing incidence X-ray diffraction (GIXRD) was performed at the BL13A beamline of the

National Synchrotron Radiation Research Center, Taiwan using a Rayonix SX165 charge coupled device detector to collect 2D X-ray scattering patterns under ambient conditions. The X-ray wavelength was 1.02704 Å with a beam energy of 12.0720 keV and incidence angle of 0.12°. The sample to detector distance was about 228.8 nm. Numerical integration of the diffraction peak areas was performed using the software fit2D.

Molecular weight determination: The number-average molecular weight (M_n), weight-average molecular weight (M_w), and dispersity (\mathcal{D}) for **P1**, **P2**, and **P3** were evaluated by high temperature size exclusion chromatography (SEC) using 1,2,4-trichlorobenzene and performed on an EcoSEC HLC-8321GPC/HT (Tosoh Bioscience) equipped with a single TSK gel GPC column (GMHHR-H; 300 mm \times 7.8 mm) calibrated with monodisperse polystyrene (PS) standards. The samples were prepared using 1 mg mL⁻¹ of sample in 1,2,4-trichlorobenzene (TCB) and were stirred at 80 °C for 12 h prior to injection. The analysis of the samples was performed at 180 °C with a flow rate of 1.0 mL/min with injection quantities of 300 μ L. The data was collected and integrated using EcoSEC 8321GPC HT software suite. The molecular weights (M) of **P1**, **P2**, and **P3** were also estimated by diffusion-order NMR spectroscopy (DOSY) using a Bruker 300 MHz spectrometer calibrated with monodisperse polystyrene (PS) standards in deuterated chloroform (CDCl₃). A previously reported DOSY procedure was followed with slight modifications.⁹ Four different PS samples (1 mg mL⁻¹ each) of known molecular weight were prepared in NMR tubes and analysed by ¹H-NMR spectroscopy and DOSY. The diffusion coefficient (D) for each monodisperse sample was obtained from the DOSY spectra, then the logarithms of each sample's molecular weight (M) and diffusion coefficient (D) were calculated. The graph of log(D) vs. log(M) was then plotted and linearly fit to obtain the calibration curve for molecular weight determination. After obtaining the calibration curve, 1 mg mL⁻¹ of each polymer was prepared in CDCl₃ prior to being placed in a

clean, dry NMR tube for spectroscopic analysis to determine the diffusion coefficient (D) of the polymer. The equation of the linear fit of $\log(D)$ vs. $\log(M)$ for the PS standards was used to determine the molecular weight (M) of each polymer.



Plotted and linearly fitted $\log(D)$ vs. $\log(M)$ graph of polystyrene standards.

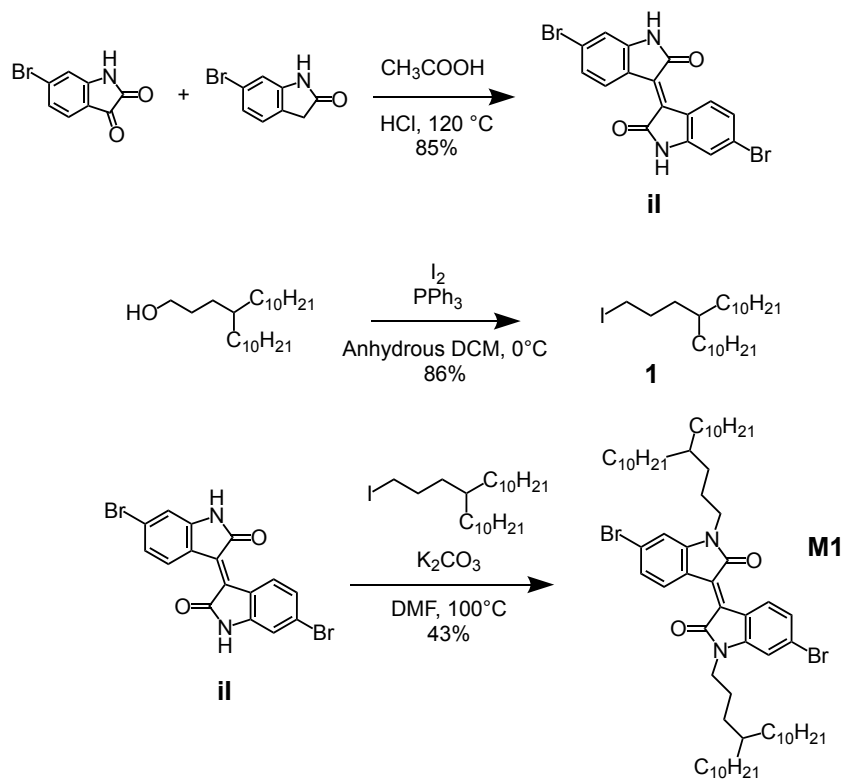
OFET Device Fabrication: Bottom-gate top-contact OFET devices were fabricated on highly doped n -type Si(100) wafer with a 300 nm-thick SiO_2 dielectric layer. Wafers were first functionalized with a phenyltrimethoxysilane (PTS) self-assembled monolayer, according to a reported method.¹⁰ The PTS-treated substrate was washed with toluene, acetone, and isopropanol, then dried with nitrogen before use. Thin films of the polymers were spin-coated at 1000 rpm for 1 min onto PTS-treated substrates from prepared polymer solutions (5 mg mL^{-1} , 1,1,2,2-tetrachloroethane), giving films approximately 50 nm thick. Gold source and drain contacts were then deposited through a shadow mask via e-beam physical vapour deposition (2 \AA s^{-1}). 50 nm of Au were deposited on top of the polymer films, yielding devices with channel length, L , and width,

W , defined as 150 and 1000 μm , respectively. Thermal annealing was carried out using a hot plate at 200 $^{\circ}\text{C}$ inside the glove box under N_2 atmosphere for 30 min. Measurements of the device characteristics were conducted at room temperature using a Keithley 4200-SCS semiconductor parameter analyzer (Keithley Instruments Inc., Cleveland, OH, USA) inside a N_2 -purged glovebox. To study the electrical performance of the OFET, the V_{th} and μ were extracted and averaged from the transfer curves of at least 8 devices per polymer.

OEET Device Fabrication: OEET devices were fabricated on two different substrates. First, electrode patterns were fabricated using conventional photolithography technique on glass substrates treated with an *n*-octadecyltrimethoxysilane (OTS) self-assembled monolayer.¹¹ In short, this was performed by first photopatterning positive photoresist AZ MiR 703 on a hexamethyldisilazane (HMDS)-treated glass substrate. Then, 5 nm Ti and 95 nm Au were deposited by electron beam evaporation (1 \AA s^{-1}). The photoresist was then dissolved in acetone to lift off the unwanted metal area, and the electrodes were further washed with isopropanol and DI water and treated with O_2 plasma for 2 minutes, leaving patterned electrodes. The substrate was then immersed in an *n*-octadecyltrimethoxysilane (OTS) solution to functionalize the exposed non-gold-covered glass with an OTS monolayer, according to a reported method.¹¹ The second substrate upon which OEETs were fabricated was bare silicon wafers treated with a phenyltrimethoxysilane (PTS) self-assembled monolayer, as previously reported.¹⁰ Onto this second substrate, 5 nm Ti and 95 nm Au were deposited by electron beam evaporation (1 \AA s^{-1}) on these wafers. The OEET devices on both the OTS- and PTS-treated substrates had a channel length, L , of 100 μm and a channel width, W , of 4 mm. After electrode deposition and monolayer functionalization, polymer solutions (5 mg mL^{-1} , 1,1,2,2-tetrachloroethane) were prepared, heated to 60 $^{\circ}\text{C}$ in a glovebox, and stirred overnight before use. The polymer solutions were then spin-

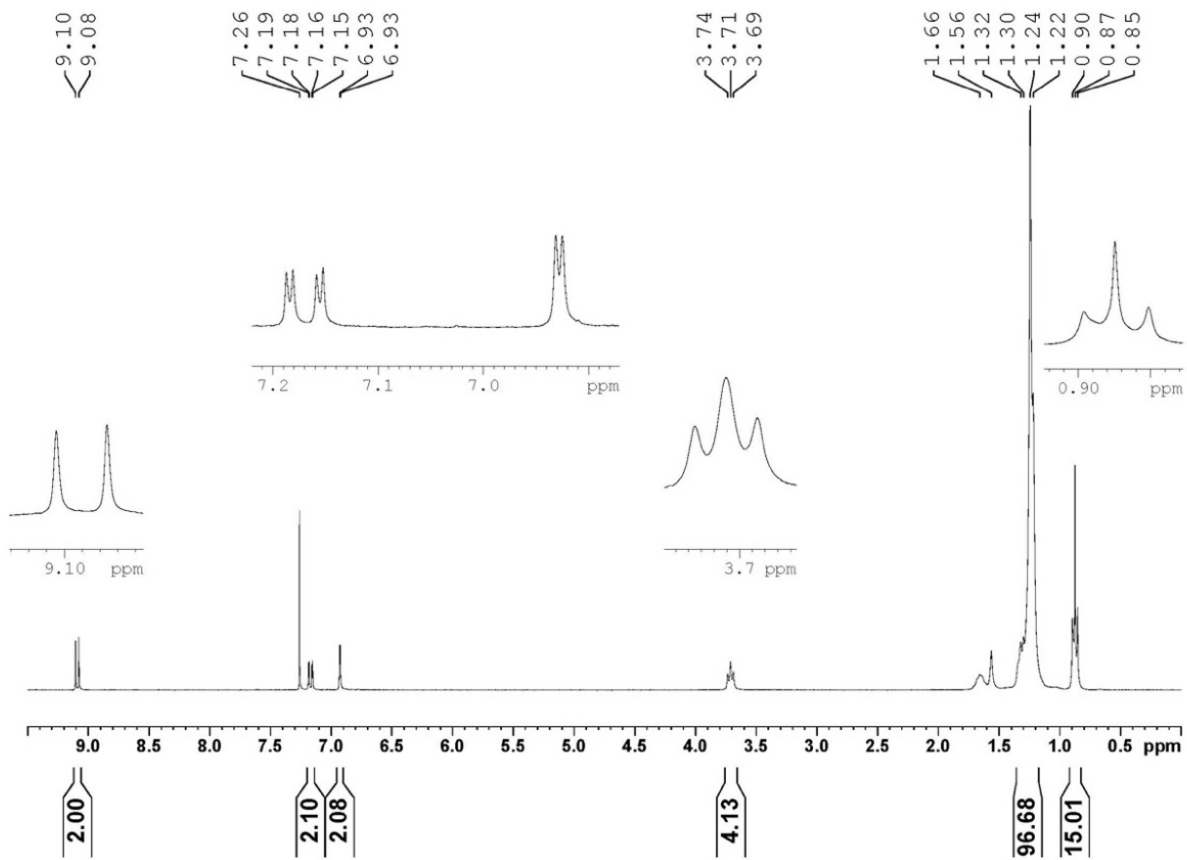
coated at 1000 rpm for 30 seconds onto each of the two different electrode substrates, giving films between 40-70 nm thick. Unwanted polymer material was then removed manually by dissolution in chloroform. Thermal annealing was then carried out using a hot plate at 200 °C inside the glove box for 1 h. For device measurement, a PDMS well (15:1) was placed on the channel to confine the electrolyte. 0.1 M aqueous NaCl solution was dropped on the channel as the electrolyte. An Ag/AgCl pellet (Warner Instruments, E210) was immersed in the electrolyte as the gate electrode. Measurements of the device characteristics were conducted at room temperature in open air using a Keithley 4200-SCS semiconductor parameter analyzer (Keithley Instruments Inc., Cleveland, OH, USA). The electrical performance of at least 3 devices were tested, per polymer sample (**P1**, **P2**, or **P3**) and per monolayer substrate (OTS or PTS).

Experimental Procedure

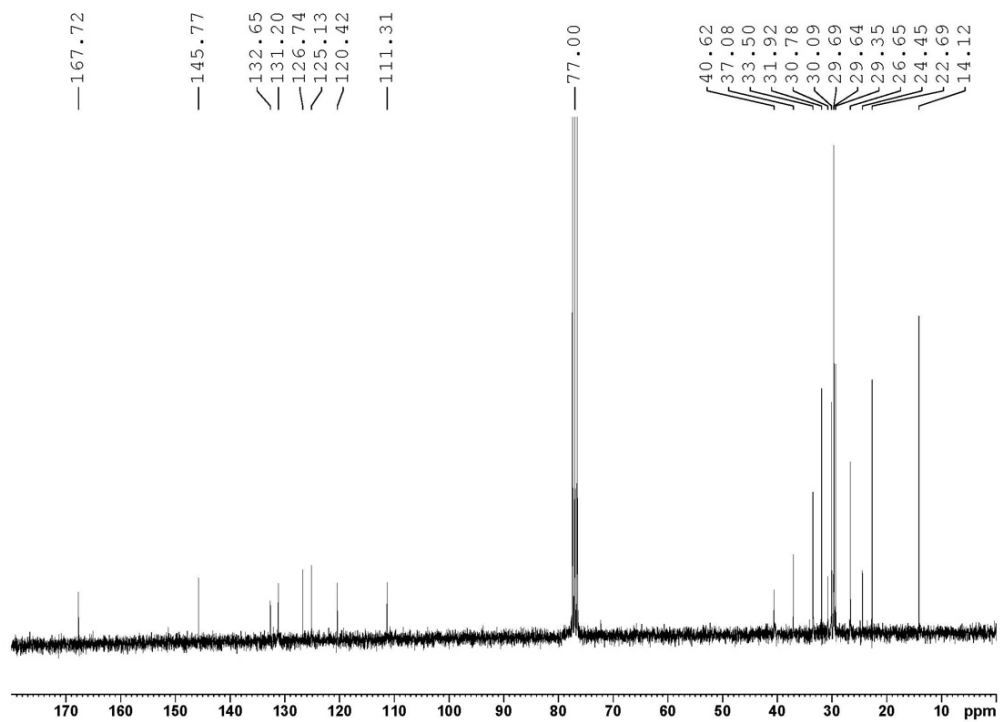


Scheme S1. Synthetic route to **ii** and **M1**.

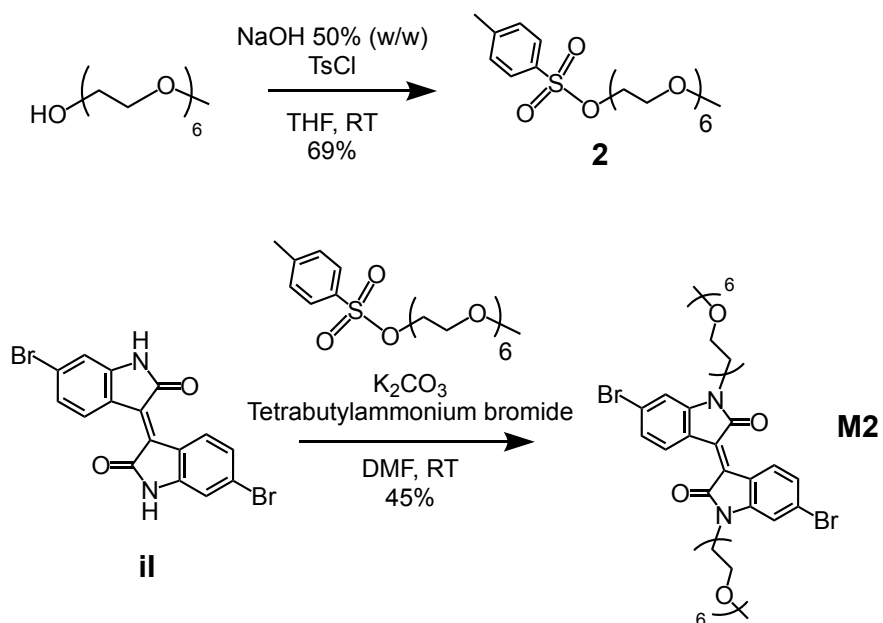
Compound M1. A 250 mL round-bottom flask was equipped with a magnetic stir bar and purged under nitrogen. **ii** (500 mg, 1.19 mmol) and K_2CO_3 (494 mg, 3.57 mmol) were added in anhydrous DMF (30 mL). The mixture was then stirred for approximately 30 minutes. Afterwards, **1** (1382 mg, 2.98 mmol) was added to the flask dropwise. The reaction mixture continued to stir for 12 hours at 100 °C under nitrogen. DMF was then removed under vacuum *via* toluene azeotrope. Extraction was performed on the resulting mixture in water (200 mL). The organic phase was extracted in $CHCl_3$ (2×50 mL), then washed in saturated brine, and dried using $MgSO_4$. Excess solvent was removed under vacuum. The final mixture was recrystallized in IPA and filtered to obtain a dark red solid. Yield of **M1**: 553 mg (43%). 1H NMR ($CDCl_3$) δ : 9.09 (d, 2H, $J = 9.0$ Hz), 7.17 (dd, 2H, $J = 9.0$ Hz, $J = 3.0$ Hz), 6.93 (d, 2H, $J = 3.0$ Hz), 3.71 (t, 4H, $J = 7.5$ Hz), 1.24 (m, 82H), 0.88 (t, 12H, $J = 7.5$ Hz). ^{13}C NMR ($CDCl_3$) δ : 167.7, 145.8, 132.7, 131.2, 126.7, 125.1, 120.4, 111.3, 40.6, 37.1, 33.5, 31.9, 30.8, 30.1, 29.7, 29.6, 29.4, 26.7, 24.5, 22.7, 14.1. HRMS: m/z calculated for $C_{64}H_{104}Br_2N_2O_2$ $[M+H]^+$ 1091.6537; found, 1091.6396.



^1H NMR of compound **M1** (CDCl_3 , 300 MHz, 298 K).

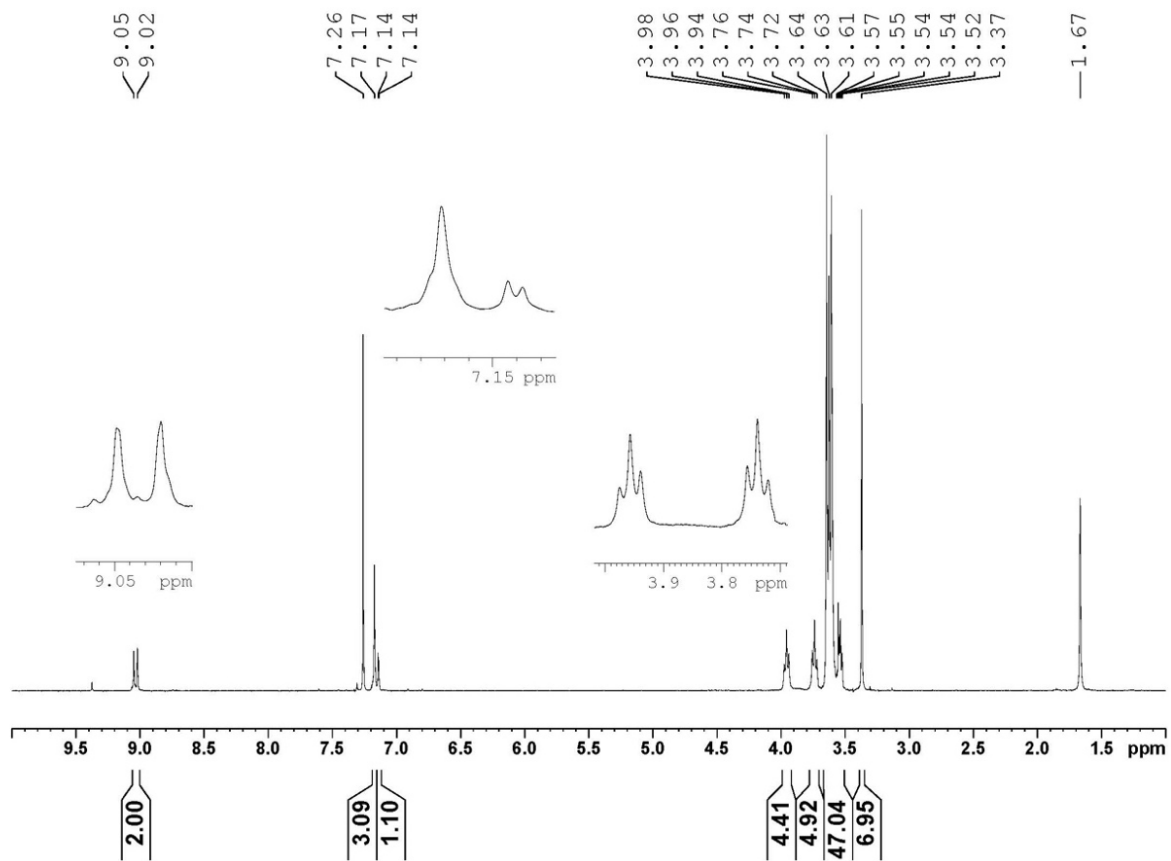


^{13}C NMR of compound **M1** (CDCl_3 , 300 MHz, 298 K).

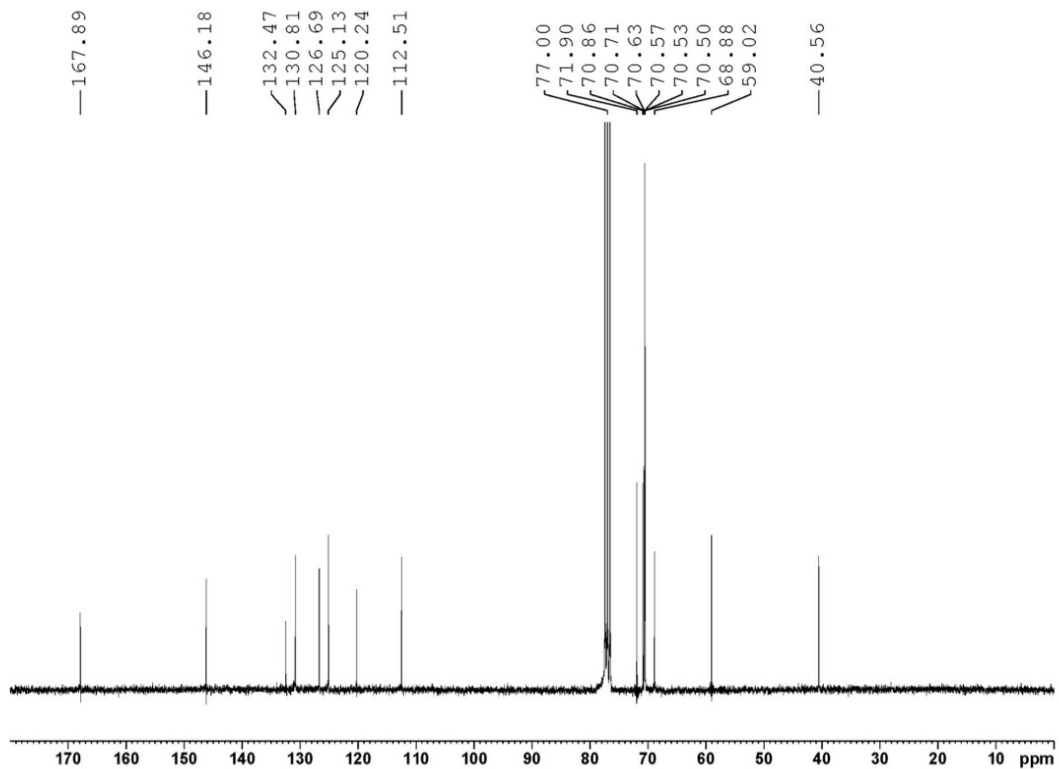


Scheme S2. Synthetic route to **M2**.

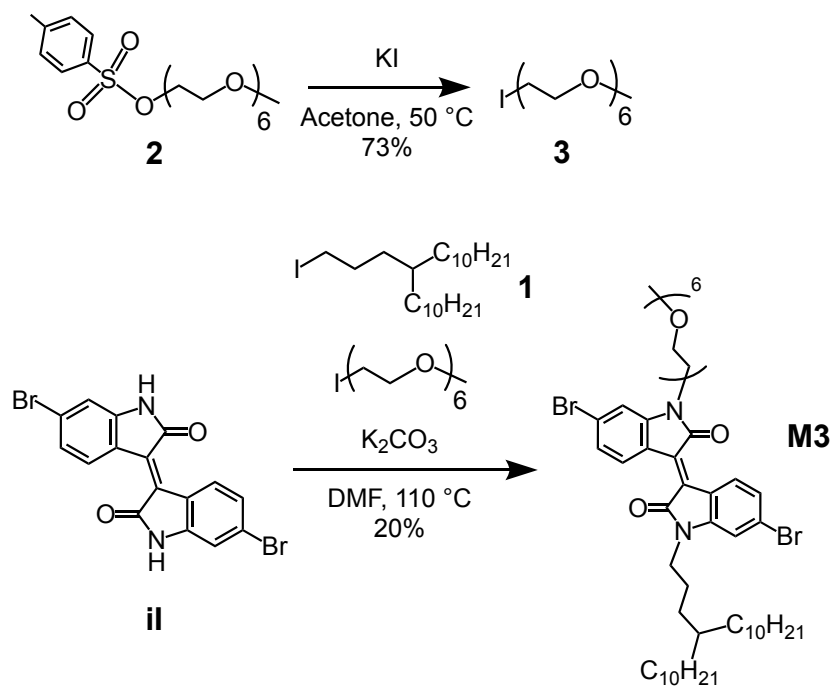
Compound M2. A 100 mL round-bottom flask was equipped with a magnetic stir bar and purged under nitrogen. **11** (190 mg, 0.43 mmol), **2** (525 mg, 1.07 mmol), and K₂CO₃ (188 mg, 1.29 mmol) were added to the flask and stirred for approximately 30 minutes under nitrogen. Afterwards, anhydrous DMF (20 mL) and tetrabutylammonium bromide (73 mg, 0.21 mmol) were added to the mixture. The reaction mixture continued to stir for 5 hours at room temperature under nitrogen. DMF was then removed under vacuum *via* toluene azeotrope. Extraction was performed on the resulting mixture in water (200 mL). The organic phase was extracted in CHCl₃ (2 × 50 mL), then washed in saturated brine, and dried using MgSO₄. Excess solvent was removed under vacuum. The final mixture was purified by silica gel column chromatography, beginning with an eluent of pure DCM, then subsequently increasing the amount of acetone by 5% until a 25:75 acetone to DCM gradient was reached. The product was reduced under pressure. Yield of **M2**: 197 mg (45%). ¹H NMR (CDCl₃) δ: 9.03 (d, 2H, *J* = 7.5 Hz), 7.17 (m, 3H), 7.14 (d, 1H, *J* = 3.0 Hz), 3.96 (t, 4H, *J* = 6.0 Hz), 3.74 (t, 4H, *J* = 6.0 Hz), 3.61 (m, 40H), 3.37 (s, 6H). ¹³C NMR (CDCl₃) δ: 167.9, 146.2, 132.5, 130.8, 126.7, 125.1, 120.2, 112.5, 71.9, 70.9, 70.7, 70.6, 70.6, 70.5, 70.5, 68.9, 59.0, 40.6. HRMS: *m/z* calculated for C₄₂H₆₀Br₂N₂O₁₄ [M+H]⁺ 975.2484; found, 975.2320.



^1H NMR of compound **M2** (CDCl_3 , 300 MHz, 298 K).

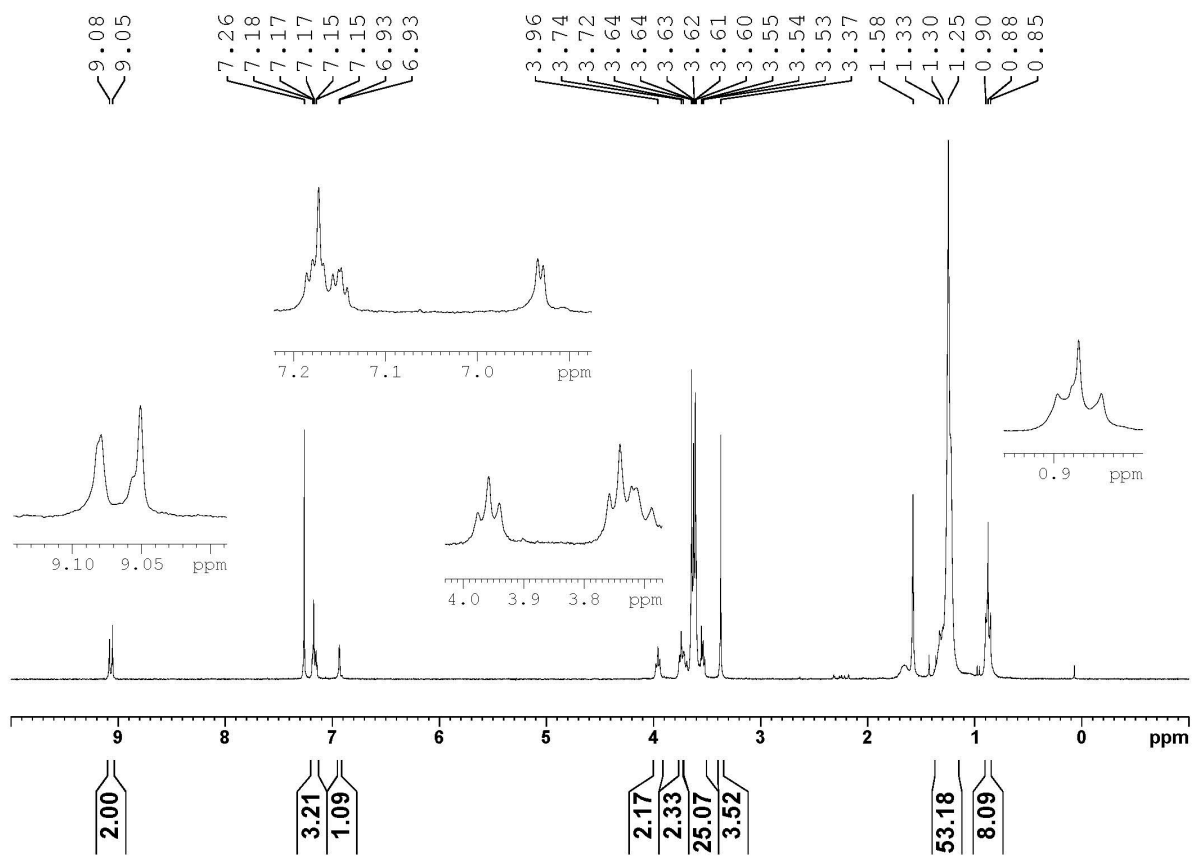


^{13}C NMR of compound **M2** (CDCl_3 , 300 MHz, 298 K).

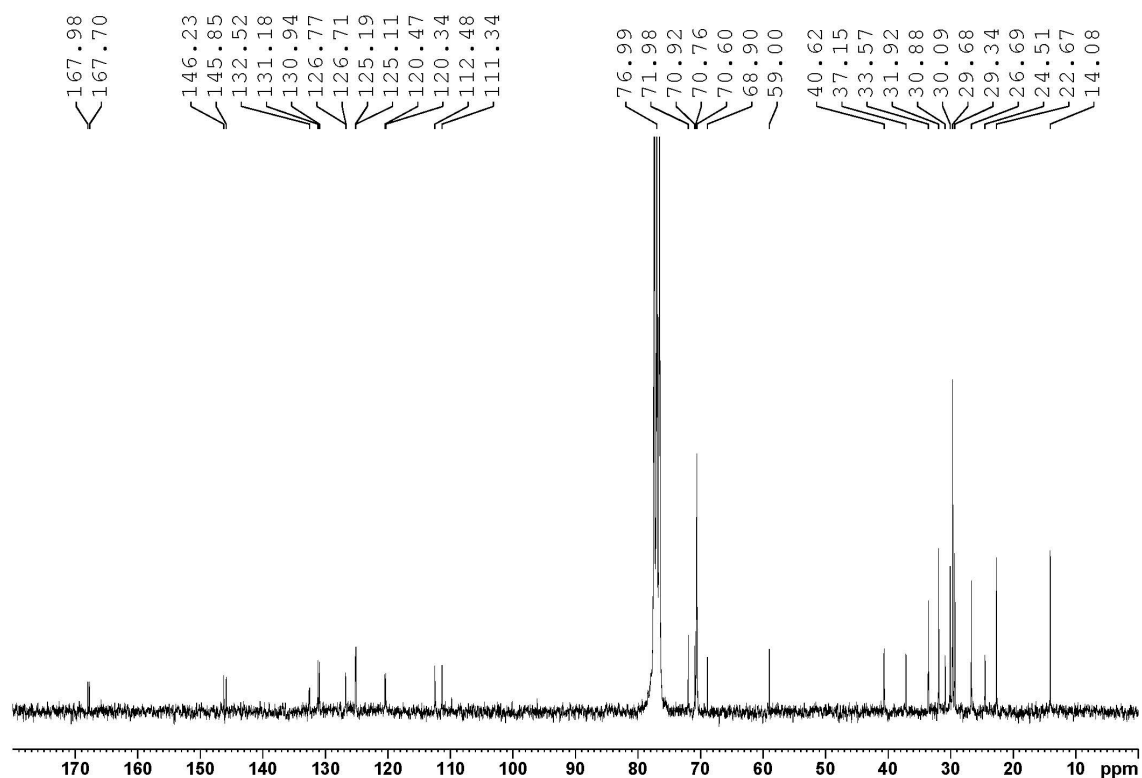


Scheme S3. Synthetic route to **M3**.

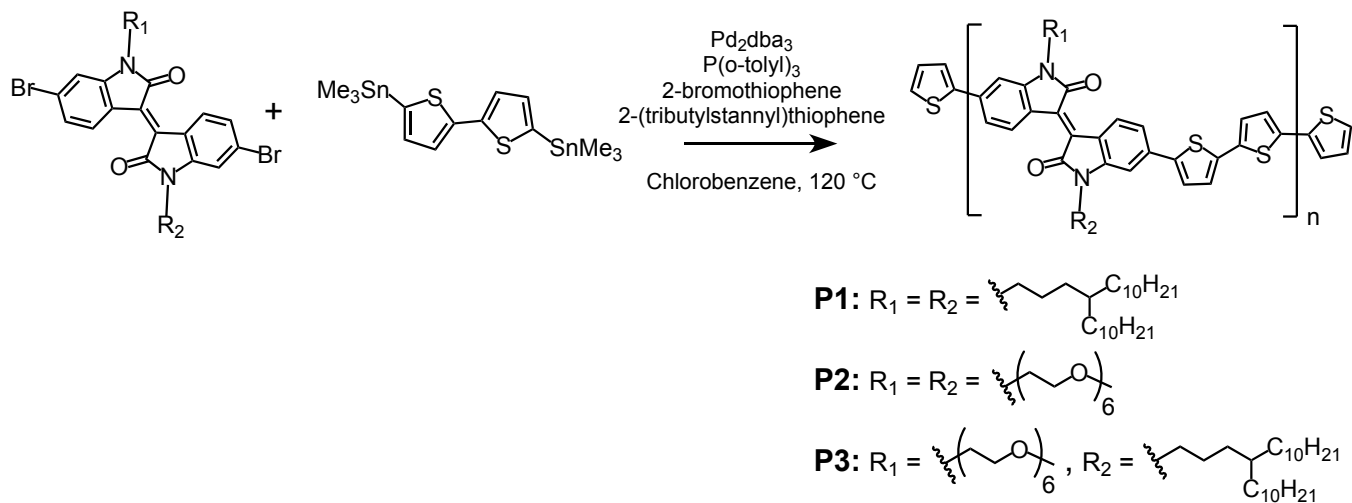
Compound M3. A 100 mL round-bottom flask was equipped with a magnetic stir bar and purged under nitrogen. **ii** (226 mg, 0.54 mmol) and K_2CO_3 (223 mg, 1.61 mmol) were added in anhydrous DMF (10 mL). The mixture was then stirred for approximately 30 minutes. In a new vial, **1** (313 mg, 0.67 mmol) and **3** (273 mg, 0.67 mmol) were added with DMF (5 mL). The vial mixture was then injected all at once into the flask mixture. The reaction in the flask continued to stir for 12 hours at 110 °C under nitrogen. DMF was then removed under vacuum *via* toluene azeotrope. Extraction was performed on the resulting mixture in water (200 mL). The organic phase was extracted in $CHCl_3$ (2 × 50 mL), then washed in saturated brine, and dried using $MgSO_4$. Excess solvent was removed under vacuum. The final mixture was purified by silica gel column chromatography. The purification began in pure hexanes, then the amount of acetone was increased by increments of 2% until a 4:1 hexanes to acetone gradient was reached. The resulting product was reduced under pressure and confirmed through TLC. Yield of **M3**: 111 mg (20%). 1H NMR ($CDCl_3$) δ : 9.07 (d, 2H, $J = 9.0$ Hz), 7.17 (m, 3H), 6.93 (d, 1H, 3.0 Hz), 3.96 (t, 2H, $J = 6.0$ Hz), 3.74 (t, 2H, $J = 6.0$ Hz), 3.63 (m, 20H), 3.37 (s, 3H), 1.25 (s, 51H), 0.88 (t, 6H, $J = 6.0$ Hz). ^{13}C NMR ($CDCl_3$) δ : 168.0, 167.7, 146.2, 145.9, 132.5, 131.2, 130.9, 126.8, 126.7, 125.2, 125.1, 120.5, 120.3, 112.5, 111.3, 72.0, 70.9, 70.8, 70.6, 68.9, 59.0, 40.6, 37.2, 33.6, 31.9, 30.9, 30.1, 29.7, 29.3, 26.7, 24.5, 22.7, 14.1. HRMS: m/z calculated for $C_{53}H_{82}Br_2N_2O_8$ $[M+H]^+$ 1033.4511; found, 1033.4321.



^1H NMR of compound **M3** (CDCl_3 , 300 MHz, 298 K).



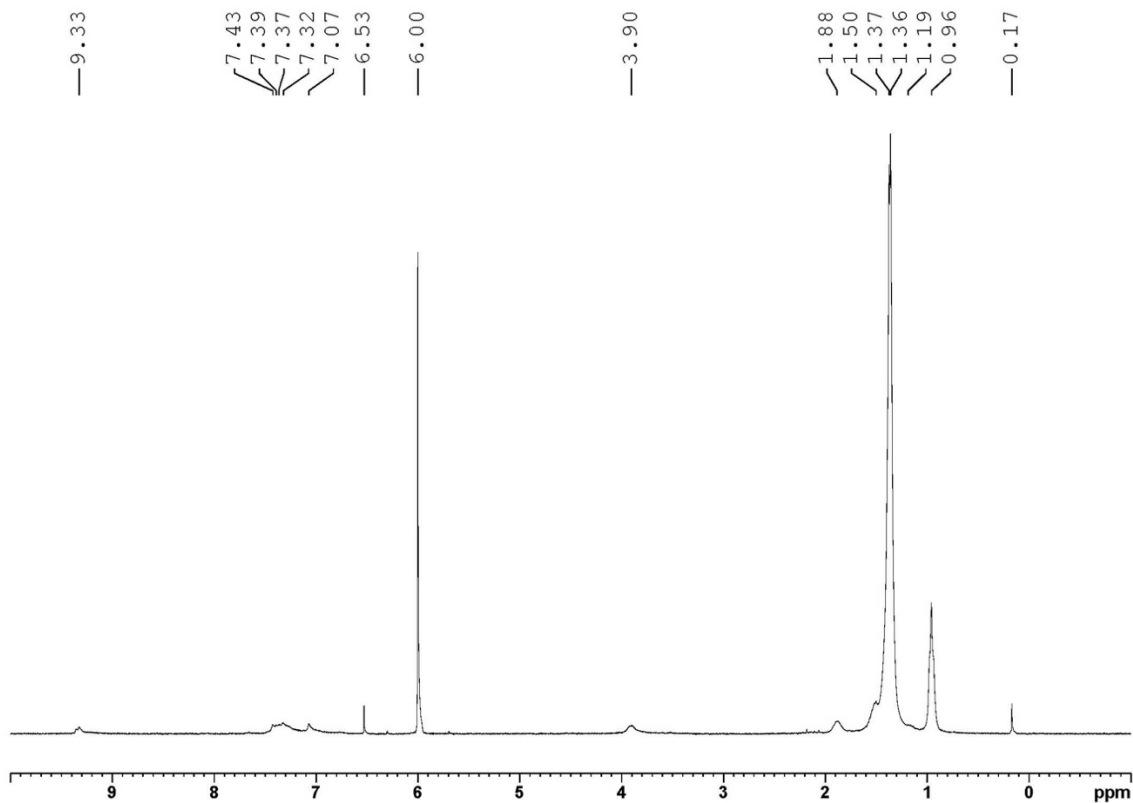
^{13}C NMR of compound **M3** (CDCl_3 , 300 MHz, 298 K).



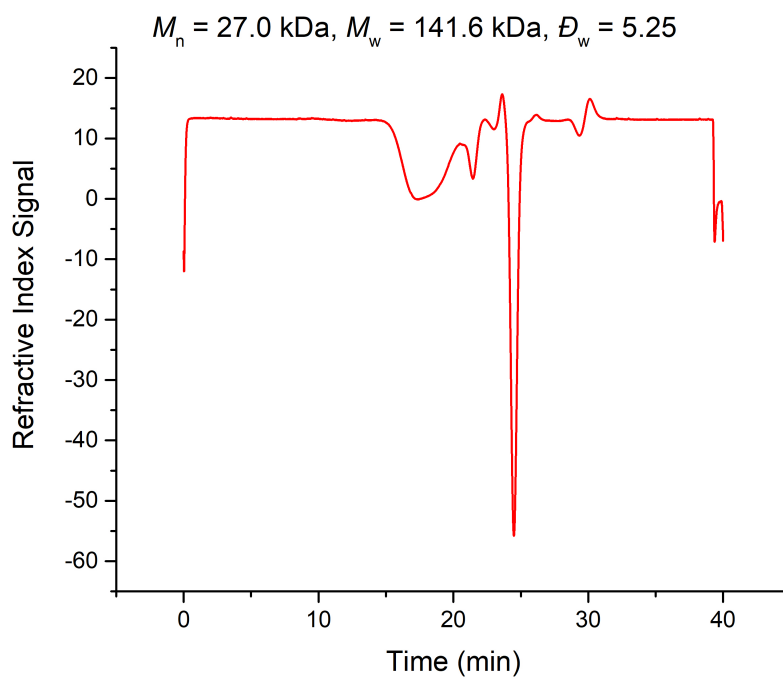
Scheme S4. Synthetic route to the polymers: **P1**, **P2**, and **P3**.

General Polymerization Procedure. An isoindigo monomer and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene were added to a microwave vial equipped with a stir bar, followed by the addition of chlorobenzene (1.5 mL). The solution was degassed under nitrogen for 30 minutes at room temperature using a needle inlet thru a rubber stop cap on the vial. Afterwards, the inlet and cap were removed, and Pd₂(dba)₃ and P(*o*-tolyl)₃ were quickly and simultaneously added to the vial. The vial was then immediately sealed with a snap cap and stirred at 1500 rpm in an oil bath at 120 °C for 72 h. Next, the polymer was end-capped with 2-bromothiophene, and the reaction continued to stir at 120 °C, 1500 rpm for an additional 30 minutes. Then, the second end-capping agent, 2-(tributylstannyl)thiophene, was added to the vial, with the contents continuing to stir at 120 °C, 1500 rpm for a final interval of 30 minutes. After cooling the reaction to room temperature, the polymer was precipitated in methanol and collected by filtration in a glass Soxhlet thimble. The contents of the thimble were then purified by successive Soxhlet extractions in methanol, acetone, hexanes, and chloroform. The chloroform fraction was concentrated and reprecipitated in methanol, then filtered and dried under vacuum to yield a dark blue solid.

P1. M1 (53.2 mg, 0.0487 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (23.9 mg, 0.0487 mmol), Pd₂(dba)₃ (0.89 mg, 0.0010 mmol), P(*o*-tolyl)₃ (1.61 mg, 0.0044 mmol), 2-bromothiophene (9.52 mg, 0.0584 mmol), and 2-(tributylstannyl)thiophene (25.43 mg, 0.0681 mmol). Yield of **P1**: 34.5 mg. ¹H NMR (CDCl₃) δ: 9.33 (m), 7.45-7.15 (m), 7.07 (broad), 3.90 (broad), 1.88 (broad), 1.60-1.10 (m), 0.96 (m). Molecular weight estimated from high temperature GPC: $M_n = 27.0$ kDa, $M_w = 141.6$ kDa, $\bar{D} = 5.3$.

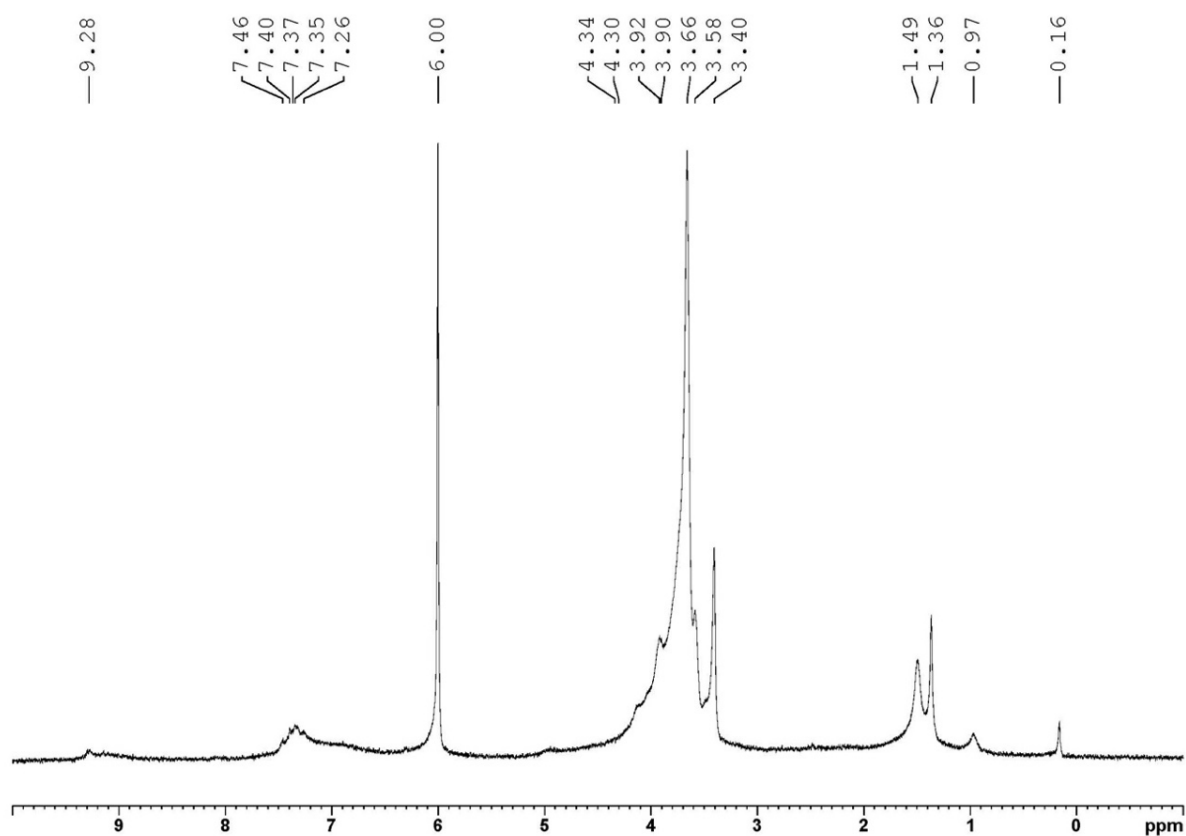


^1H NMR of compound **P1** (1,1,2,2-tetrachloroethane- d_2 , 300 MHz, 393 K).

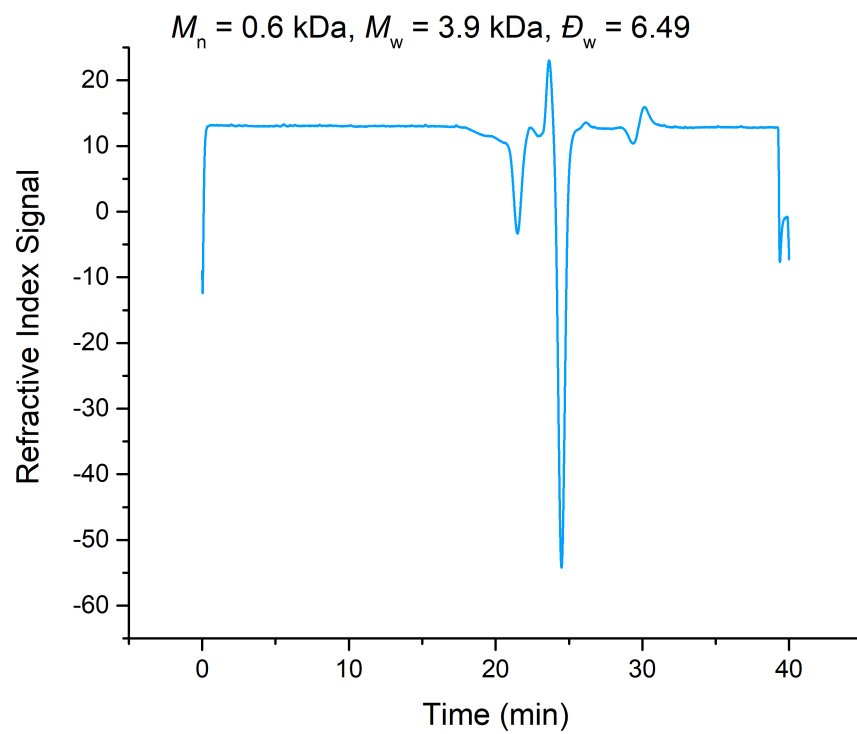


High temperature GPC of compound **P1** using polystyrene standards.

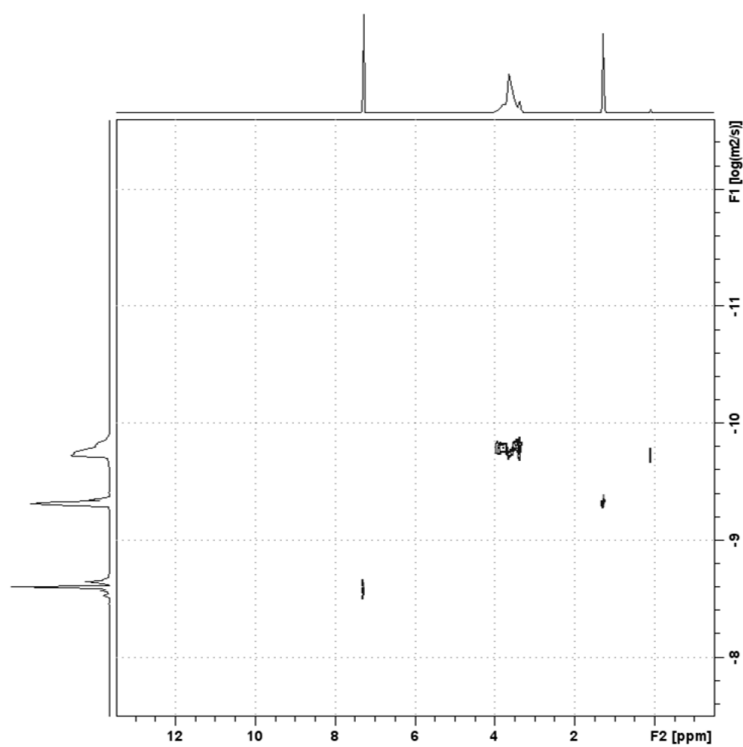
P2. M2 (53.2 mg, 0.0545 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (26.8 mg, 0.0545 mmol), Pd₂(dba)₃ (1.00 mg, 0.0011 mmol), P(o-tolyl)₃ (1.81 mg, 0.0049 mmol), 2-bromothiophene (10.66 mg, 0.0654 mmol), and 2-(tributylstannyl)thiophene (28.5 mg, 0.0763 mmol). Yield of **P2**: 38.0 mg. ¹H NMR (CDCl₃) δ: 9.28 (broad), 7.50-7.10 (m), 4.34-3.50 (m), 3.40 (m), 1.49 (broad), 1.36 (m), 0.97 (broad). Molecular weight estimated from high temperature GPC (unsuccessful for **P2** due to insolubility in 1,2,4-trichlorobenzene): *M*_n = 0.6 kDa, *M*_w = 3.9 kDa, Đ = 6.5. Molecular weight estimated from DOSY (CDCl₃): *M* = 15.55 kDa; experimentally determined log(*D*) of **P2**: -9.755 m² s⁻¹.



¹H NMR of compound **P2** (1,1,2,2-tetrachloroethane-*d*₂, 300 MHz, 393 K).

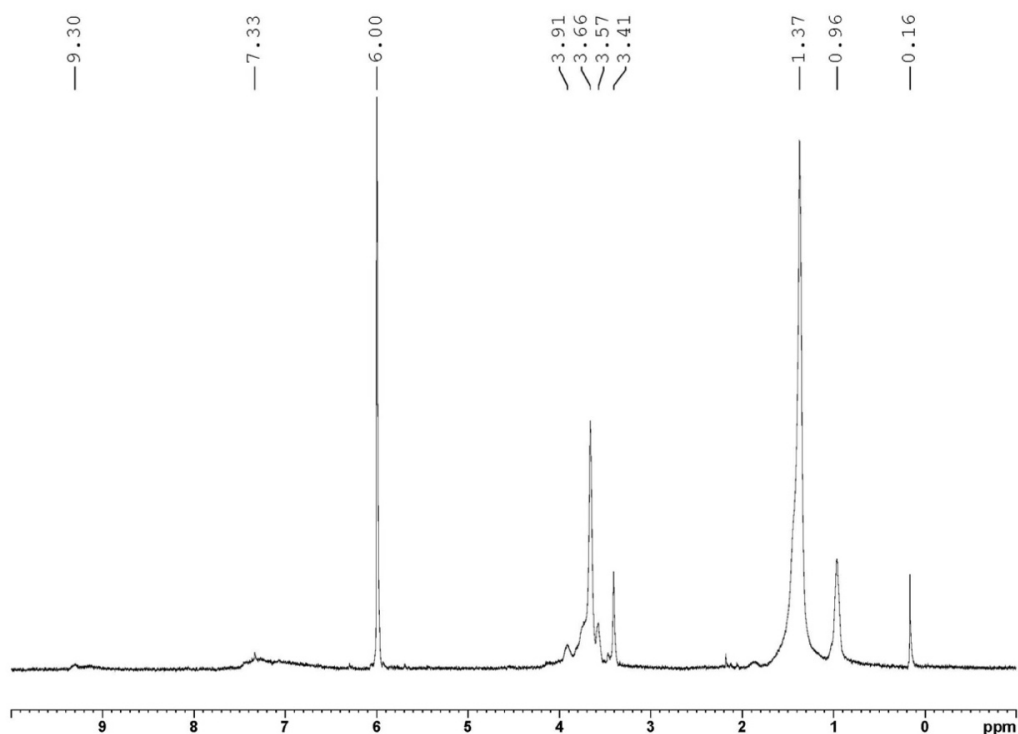


High temperature GPC of compound **P2** using polystyrene standards.

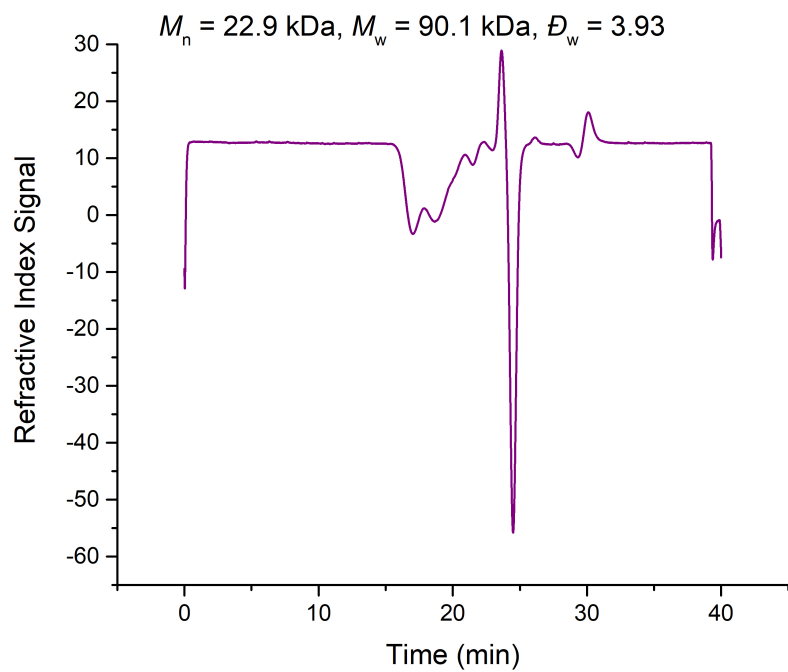


DOSY of compound **P2** (CDCl₃, 300 MHz, 298 K)

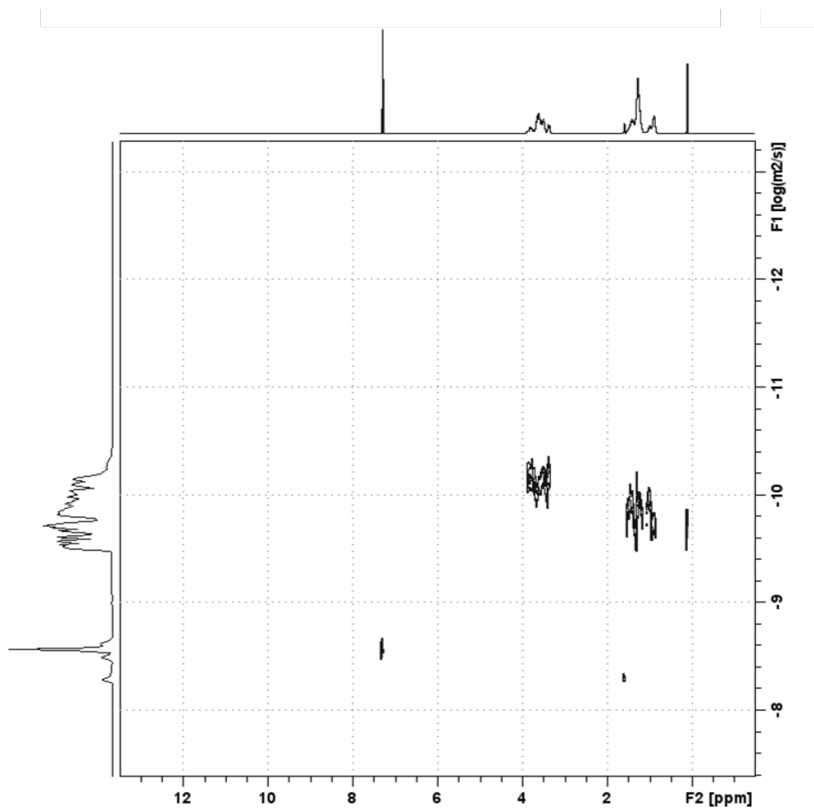
P3. M3 (57.0 mg, 0.0551 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (27.1 mg, 0.0551 mmol), Pd₂(dba)₃ (1.01 mg, 0.0011 mmol), P(o-tolyl)₃ (1.83 mg, 0.0050 mmol), 2-bromothiophene (10.77 mg, 0.0661 mmol), and 2-(tributylstannyl)thiophene (28.8 mg, 0.0771 mmol). Yield of **P3**: 41.4 mg. ¹H NMR (CDCl₃) δ: 9.30 (broad), 7.46-7.10 (m), 4.34-3.50 (m), 3.50-3.35 (m), 3.41 (m), 1.75-1.37-1.10 (m), 0.96 (broad). Molecular weight estimated from high temperature GPC: $M_n = 22.9$ kDa, $M_w = 90.1$ kDa, $\bar{D} = 3.9$. Molecular weight estimated from DOSY (CDCl₃): $M = 15.75$ kDa, 86.10 kDa; experimentally determined $\log(D)$ of **P3**: $-9.758 \text{ m}^2 \text{ s}^{-1}$, $-10.161 \text{ m}^2 \text{ s}^{-1}$.



¹H NMR of compound **P3** (1,1,2,2-tetrachloroethane-*d*₂, 300 MHz, 393 K).



High temperature GPC of compound **P3** using polystyrene standards.



DOSY of compound **P3** (CDCl₃, 300 MHz, 298 K)

Characterization

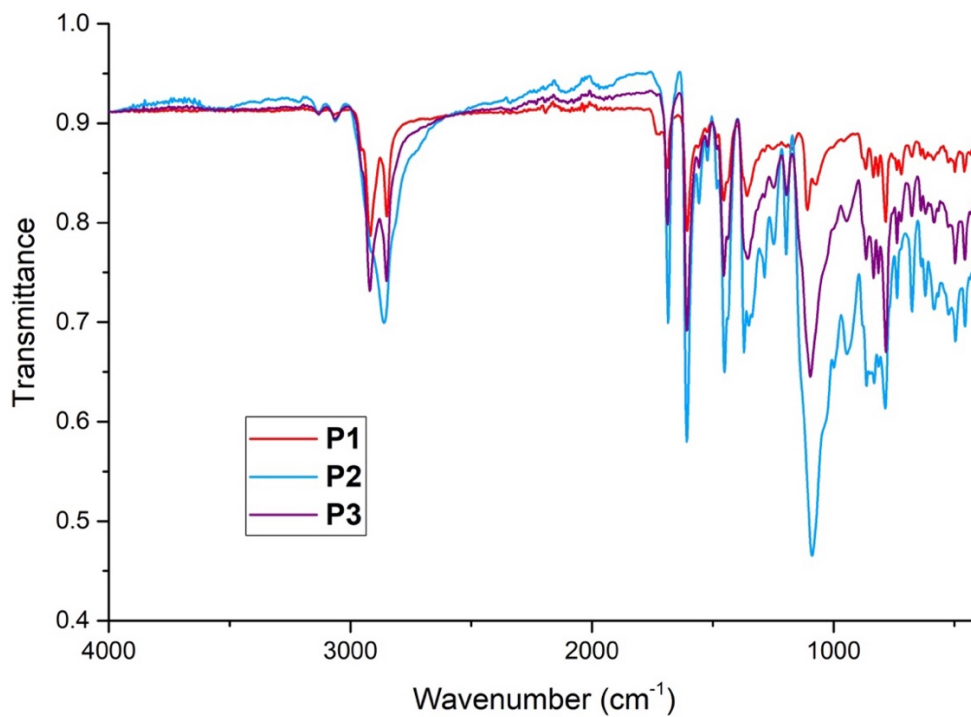


Figure S1. Fourier-Transform Infrared spectroscopy (FTIR) spectrum of polymers **P1** to **P3**.

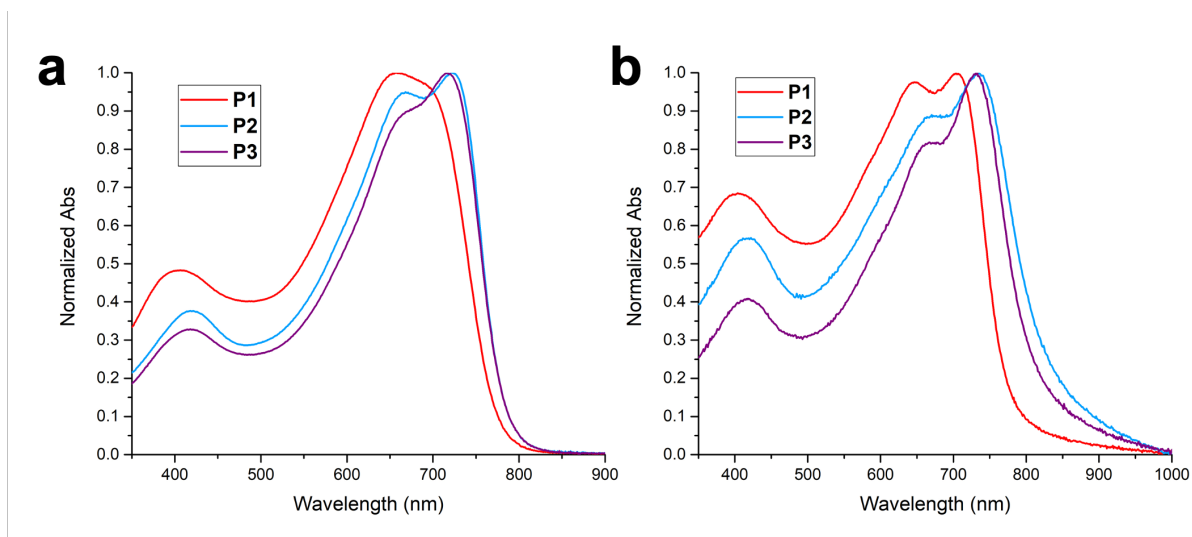


Figure S2. UV-vis spectra of polymers **P1** to **P3** in CHCl₃ in (a) solution and (b) drop-casted thin film.

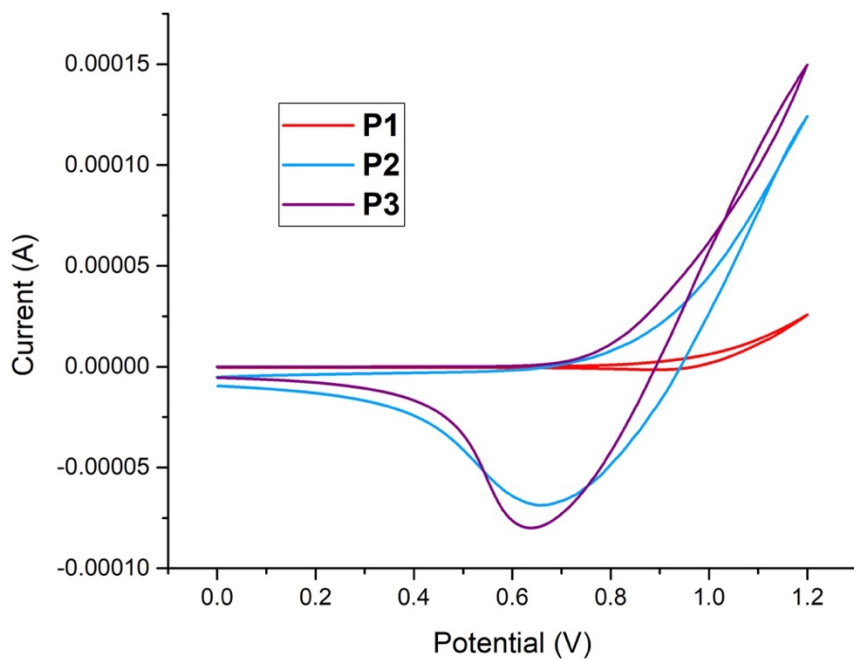


Figure S3. Cyclic voltammetry (CV) of the three polymers vs Fc/Fc^+ using 0.1 M TBAPF_6 in CH_3CN as the electrolyte.

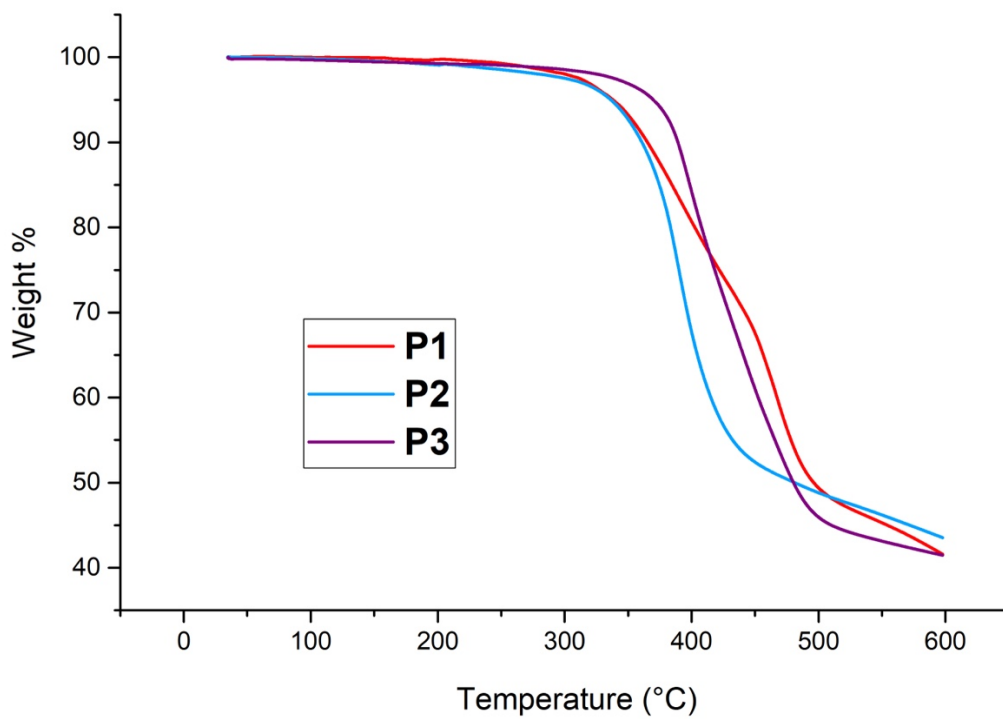


Figure S4. Thermogravimetric analysis (TGA) of the three polymers.

OFET Device Measurements

Each device's saturation charge-carrier mobility (μ_{sat}) was obtained by linearly fitting the $I_{\text{D}}^{1/2}$ vs. V_{G} curve in the saturation regime and extracting the slope of the line to complete the following equation:

$$\mu_{\text{sat}} = \left(\frac{\partial \sqrt{I_{\text{D}}}}{\partial V_{\text{G}}} \right)^2 \times \frac{2L}{WC}$$

where L is the channel length, W is the channel width, and C is the capacitance per unit area of the dielectric material, which was $1.15 \times 10^{-8} \text{ F cm}^{-2}$ for the SiO_2 used in this work.^{8,12}

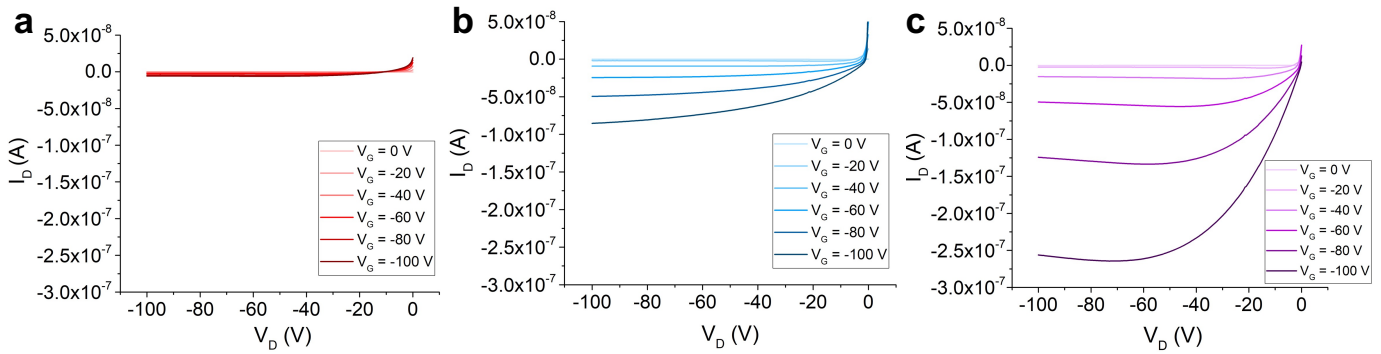


Figure S5. OFET output curves of (a) P1, (b) P2, and (c) P3 along the same source-drain current (I_{d}) scale on PTS-treated substrate.

OEET Device Measurements

The equation for transconductance (g_m) based on the data from an OEET transfer curve is:

$$g_m = \frac{\partial I_D}{\partial V_G}$$

where I_D is the drain current, and V_G is the gate voltage. The g_m was calculated between each data point on an OEET's transfer curve and plotted against V_G to assess doping and de-doping of the polymer layer by the ions in solution.¹³

Upon normalizing the transconductance to the device's channel width, the following relationships exist among the $g_{m, \text{normalized}}$, μC^* , and threshold (V_{th}) and gate voltages (V_G) for an OEET:

$$g_{m, \text{normalized}} = \mu C^* \times (V_{th} - V_G)$$

Thus, μC^* is derived from the above equation.¹⁴

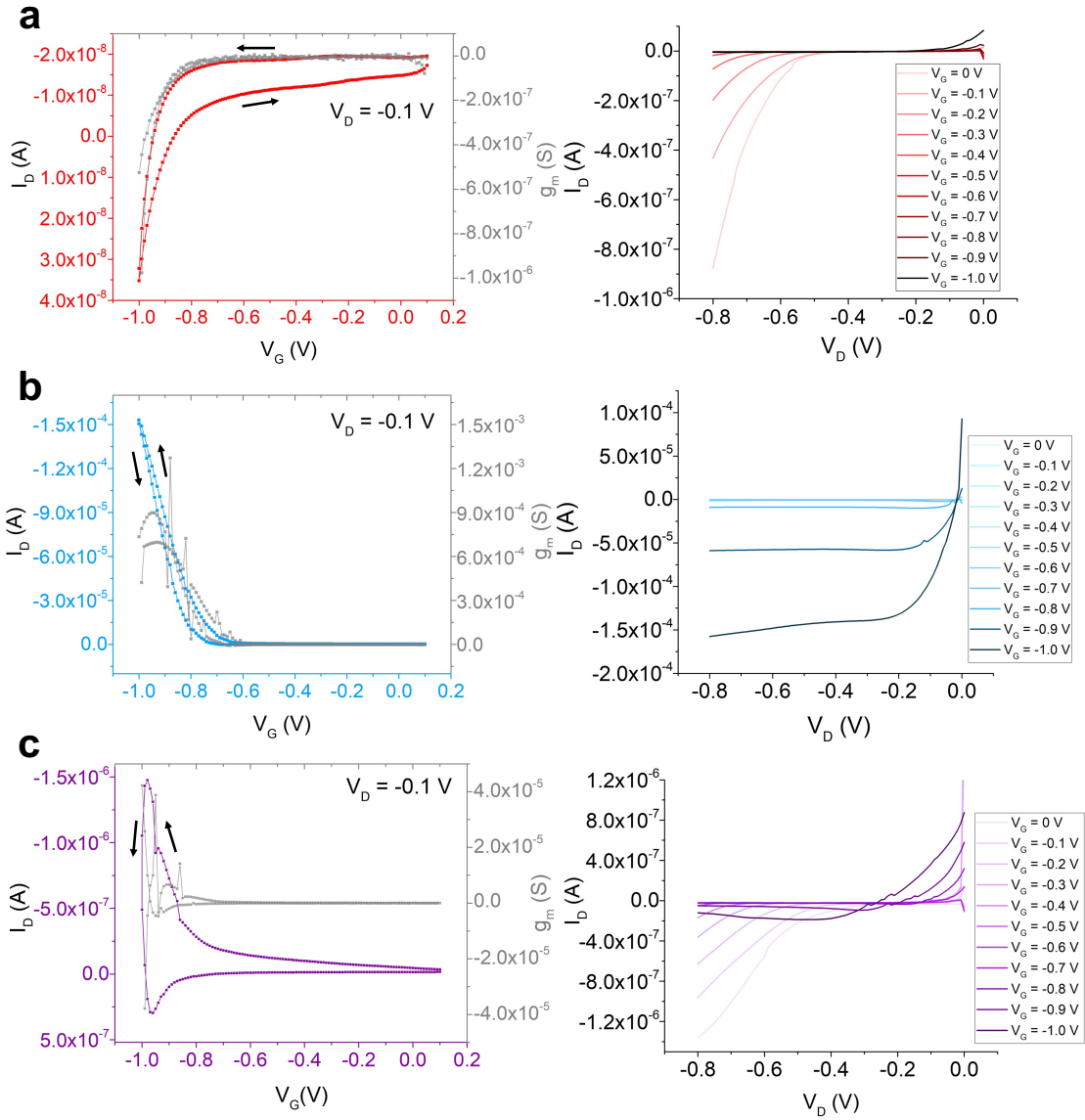


Figure S6. OECT transfer and transconductance curves (left) and output curves (right) of (a) **P1**, (b) **P2**, and (c) **P3** on OTS-treated substrate.

Table S1 Maximum transconductances (g_m^{\max}), $I_{\text{on}}/I_{\text{off}}$ current ratios, and threshold voltages (V_{th}) for the OECTs on OTS-treated substrate.

Film	g_m^{\max} (S)	$[I_{\text{on}}/I_{\text{off}}]^{\text{avg}}$	$V_{\text{th}}^{\text{avg}}$ (V)
P1	1.10×10^{-8}	10^0	N/A
P2	1.27×10^{-3}	10^3	-0.8
P3	4.22×10^{-5}	10^0	-1.2

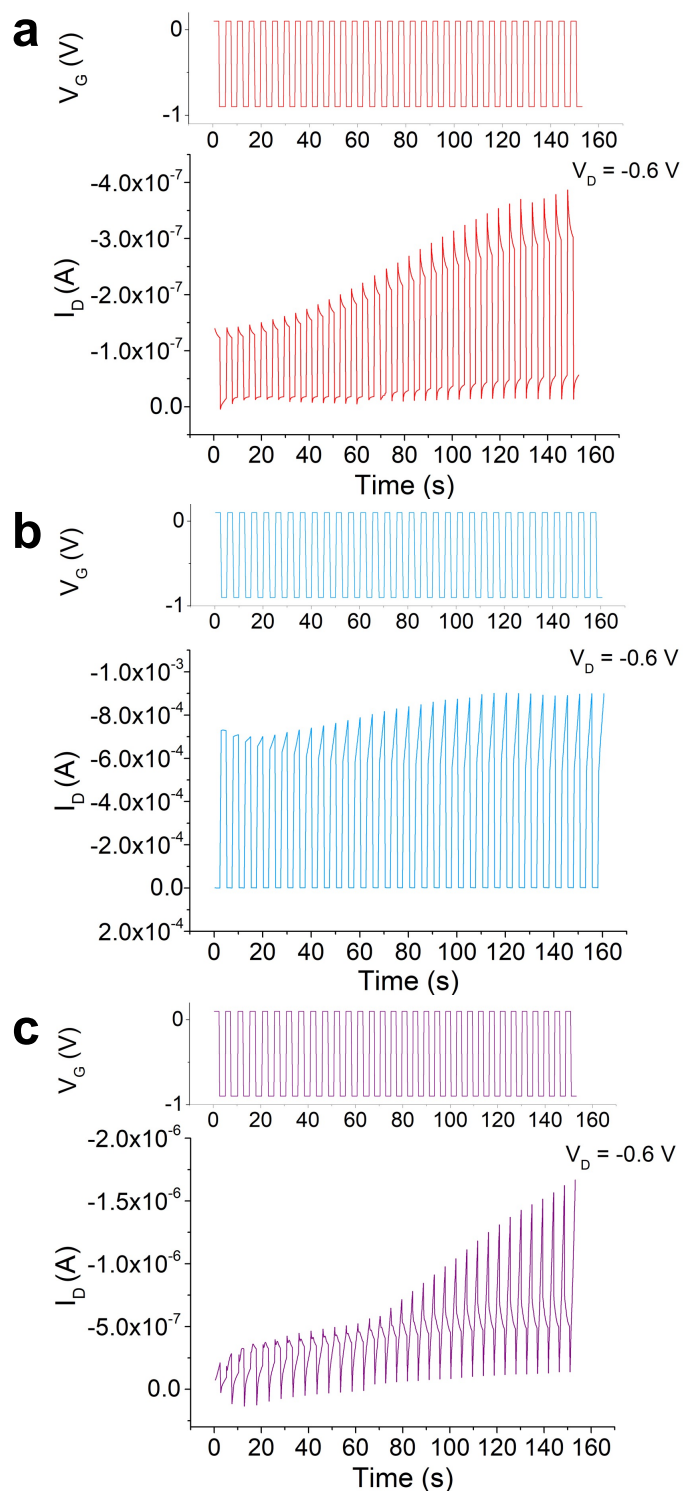


Figure S7. OECT on-off cycling curves of (a) **P1**, (b) **P2**, and (c) **P3**. Devices fabricated on PTS-treated Si wafers.

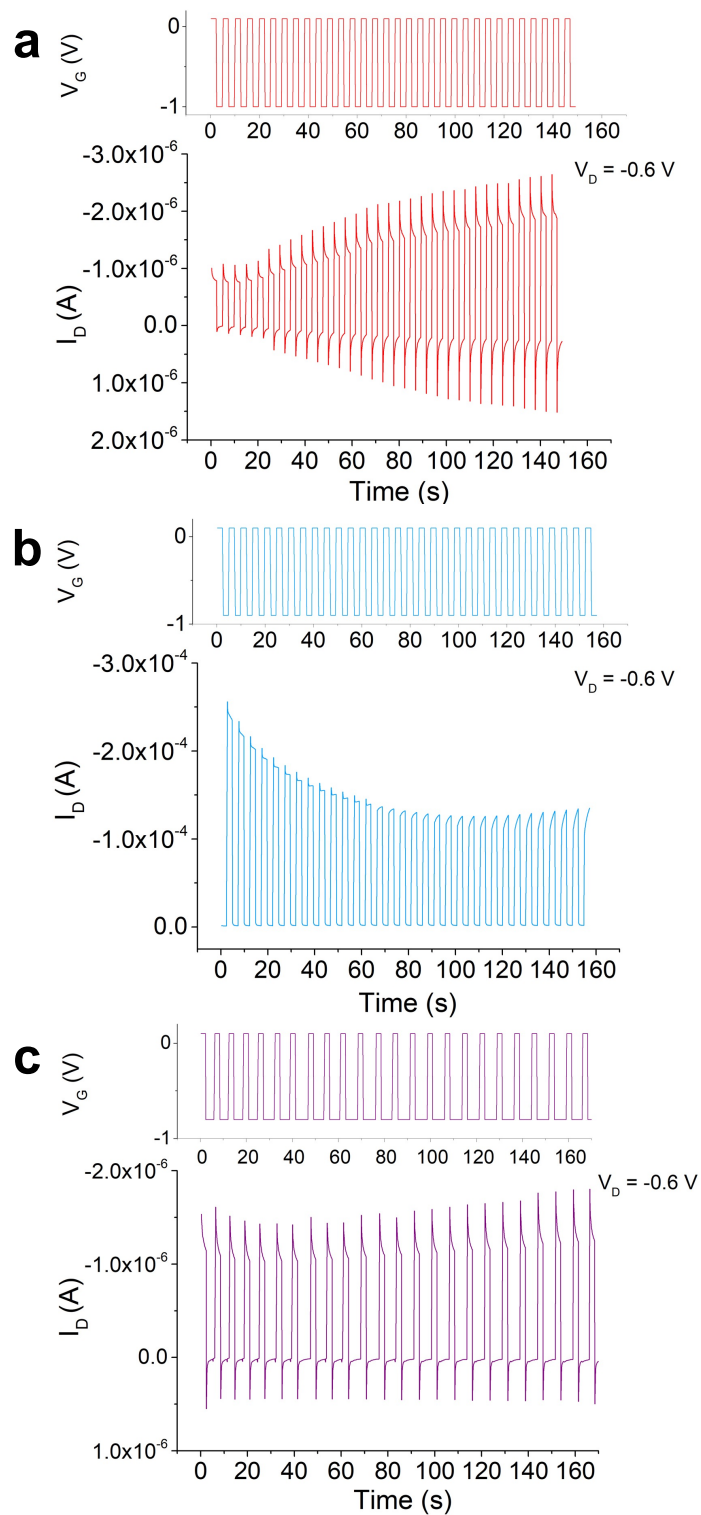


Figure S8. OECT on-off cycling curves of (a) **P1**, (b) **P2**, and (c) **P3**. Devices fabricated on OTS-treated substrate.

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