

# Electronic Properties of Isoindigo-based Conjugated Polymers Bearing Urea-Containing and Linear Alkyl Side Chains

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## General Procedure and Materials

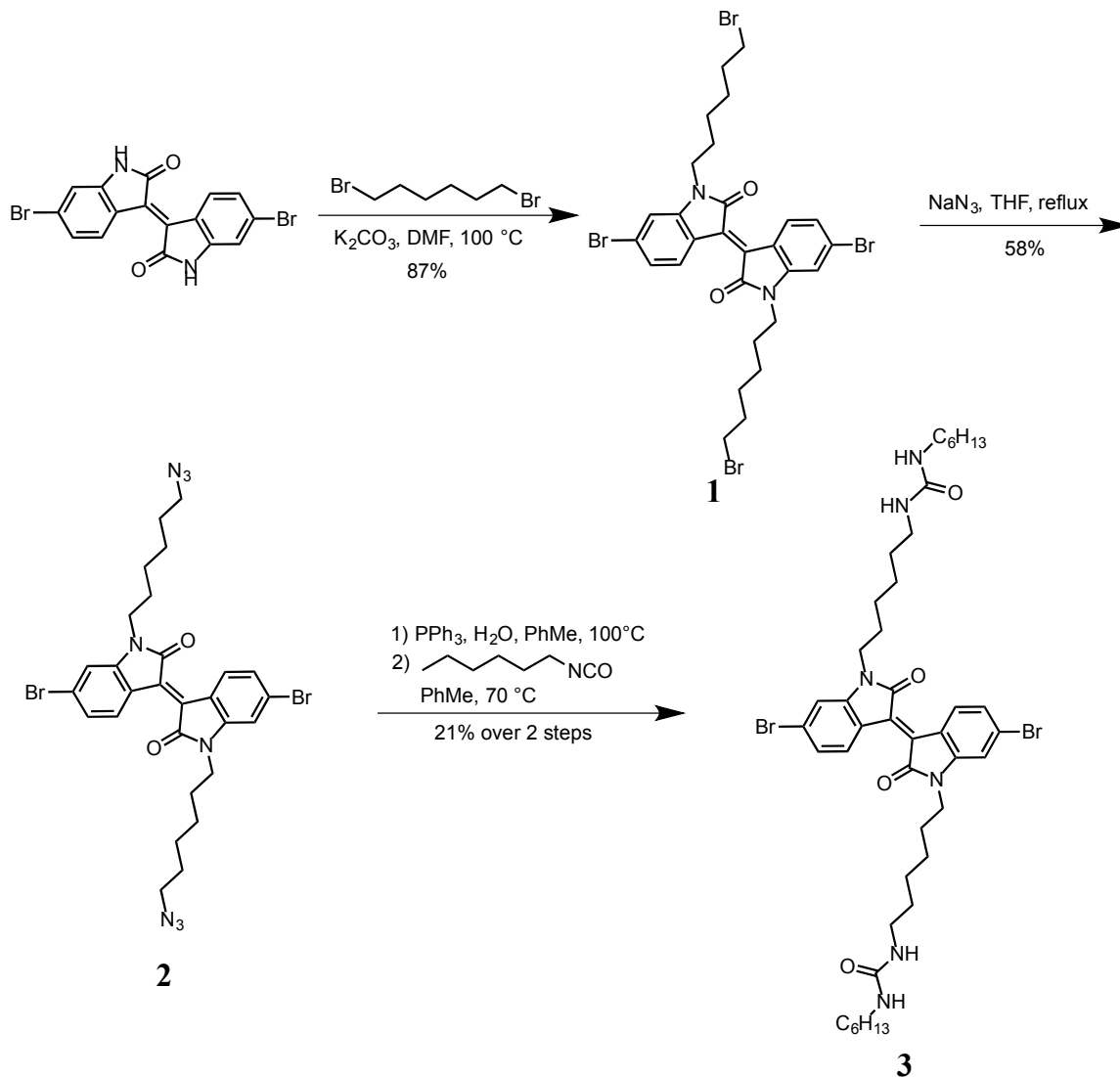
**Materials:** Commercial reactants were used without further purification unless stated otherwise. All the solvents used in these reactions were distilled prior to use. Tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct ( $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ ) was purchased from Sigma Aldrich and recrystallized following a reported procedure.<sup>1</sup> (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (TVT), (*E*)-6,6'-dibromo-1,1'-didodecyl-[3,3'-biindolinylidene]-2,2'-dione, and (*E*)-6,6'-dibromo-1,1'-didodecyl-[3,3'-biindolinylidene]-2,2'-dione were synthesized according to literature.<sup>2-4</sup>

**Measurements and Characterization:** Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 300 MHz. The spectra for all polymers were obtained in deuterated 1,1,2,2-tetrachloroethane ( $\text{TCE-d}_2$ ) at 120 °C. Chemical shifts are given in parts per million (ppm). Number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ), and polydispersity index (PDI) were evaluated by high temperature size exclusion chromatography (SEC) using 1,2,4-trichlorobenzene and performed on a PL-GPC 120 instrument (Agilent

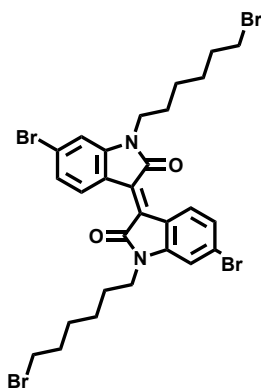
Technologies) equipped with a single TSKgel GPC column (GMH<sub>HR</sub>-H; 300 mm × 7.8 mm) also calibrated by monodisperse polystyrene standards. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo AG-TGA/SDTA851<sup>e</sup>. FTIR spectroscopy was performed on a Bruker ALPHA FTIR Spectrometer using a Platinum ATR sampling module. UV Visible spectroscopy was performed on a Varian UV/Visible Cary 50 spectrophotometer. The surface structure of polymer film was obtained 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. All measurements were conducted using a Keithley 4200 semiconductor parameter analyzer (Keithley Instruments Inc.) under dry N<sub>2</sub> (glovebox) and ambient atmosphere at room temperature. A BASi Epsilon Potentiostat was used to obtain the cyclic voltammetry measurements. Cyclic voltammograms were taken in a 0.1M solution of TBAPF<sub>6</sub> in anhydrous acetonitrile at room temperature. Pt was used as working electrode and counter electrode. Ag|AgCl was used as non-aqueous reference. The scan rate of measurements was 100 mV/s. X-Ray diffraction was performed on a Proto AXRD Benchtop Powder Diffractometer with a Cu source ( $\lambda = 1.5406 \text{ \AA}$ ).

**FET Device Fabrication and Characterization:** FET devices were fabricated on highly doped n-type Si(100) wafer with a 300 nm thick SiO<sub>2</sub> functionalized with an dodecyltrichlorosilane (DDTS) self-assembled monolayer. A bottom-contact gold electrode (70 nm) was subsequently deposited by evaporation through a shadow mask with a channel length (L) and width (W) defined as 33 and 1000  $\mu\text{m}$ , respectively. Before spin-coating the active layers, the DDTS-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 on the DDTS-treated substrates and controlled the thickness at ~40 nm from prepared polymer solutions in chlorobenzene (3 mg mL<sup>-1</sup>). The thermal annealing process was carried out inside a N<sub>2</sub>-filled glove box. All measurements were conducted using a Keithley 4200-SCS semiconductor parameter analyzer (Keithley Instruments Inc., Cleveland, OH, USA) in an N<sub>2</sub>- filled glove box at room temperature.

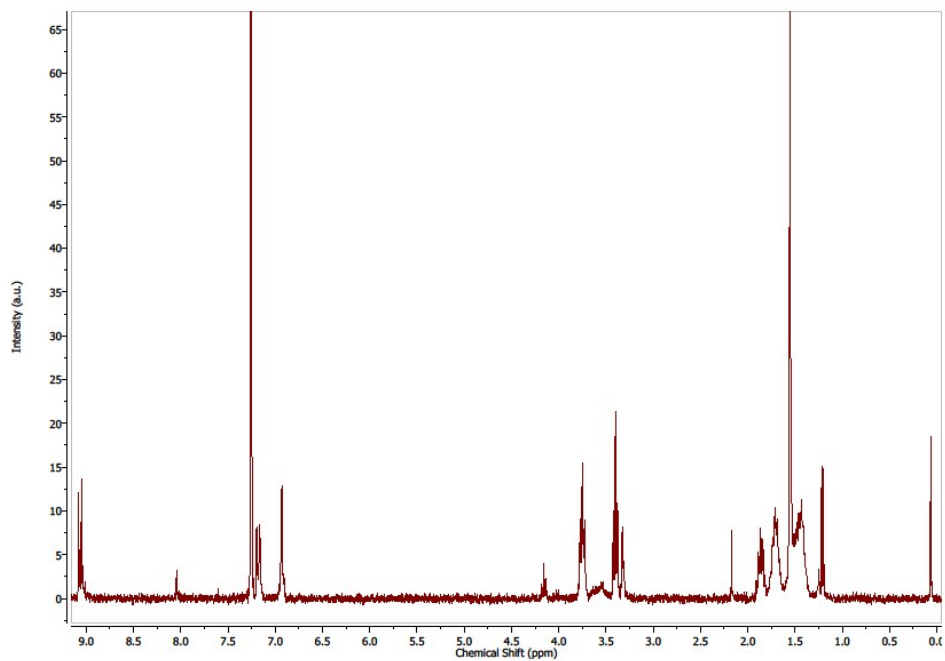
## Experimental Procedure



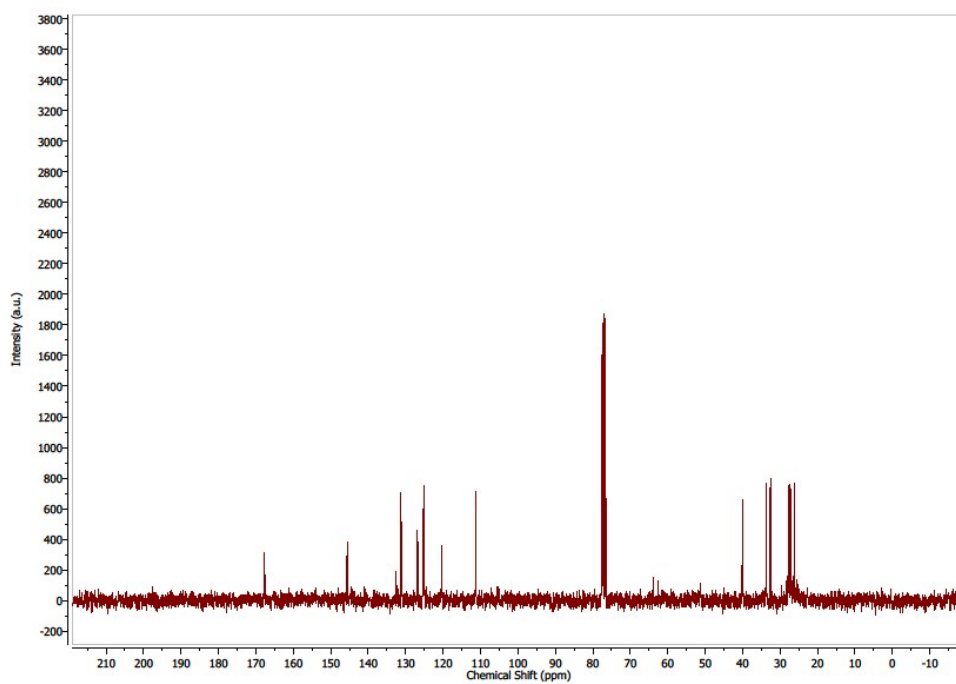
Scheme S1. Synthetic pathway to urea-containing monomer **3**.



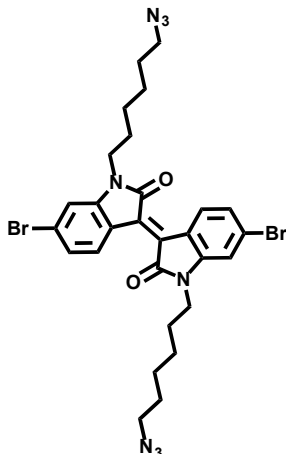
**Compound 1.** A round-bottom flask equipped with a magnetic stir bar was charged with (E)-6,6'-dibromo-[3,3'-biindolinylidene]-2,2'-dione (3.0 g, 7.14 mmol) and DMF (72 mL). Anhydrous potassium carbonate (2.94 g, 21.42 mmol) was then added in one portion and heated to 100 °C. The reaction was stirred for 30 minutes before dropwise addition of 1,6-dibromohexane (13.92 g, 57.12 mmol). The reaction was stirred for 15 h at 90°C. Upon completion, the reaction was diluted in CHCl<sub>3</sub>, extracted with H<sub>2</sub>O and washed with brine. The organic layer was subsequently dried with Sodium sulfate, and the solvent was removed under reduced pressure. The crude mixture was purified by silica flash chromatography using 10% acetone in CHCl<sub>3</sub> as the eluent to afford compound **4** as a bright red solid (4.65 g, 87% yield). <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>, 298 K): 9.06 (d, *J* = 8.5 Hz, 2H), 7.18 (dd, *J* = 8.6 Hz, 1.9 Hz, 2H), 6.93 (d, *J* = 1.9 Hz, 2H), 3.75 (t, *J* = 7.3 Hz, 4H), 3.40 (t, *J* = 6.7 Hz, 4H), 1.43 (m, 16H); HRMS (ESI-ToF) calcd for C<sub>28</sub>H<sub>30</sub>Br<sub>4</sub>N<sub>2</sub>O<sub>2</sub>[M+H]<sup>+</sup>: 746.9000, found 746.9085. <sup>13</sup>C NMR (300MHz, CDCl<sub>3</sub>, 298K): 167.71, 145.63, 132.55, 131.22, 126.82, 125.21, 120.38, 111.25, 40.07, 33.68, 32.58, 27.81, 27.25, 26.17.



$^1\text{H}$  NMR spectrum of **1** in  $\text{CDCl}_3$



$^{13}\text{C}$  NMR spectrum of **1** in  $\text{CDCl}_3$



**Compound 2.** A round-bottom flask equipped with a magnetic stir bar was charged with **1** (1.5 g, 2.01 mmol) and THF (201 mL). Sodium azide (0.392g g, 6.03 mol) dissolved in deionized water (17.23 mL) was added. The reaction was stirred for 48 h at 70°C under reflux. Upon completion, the reaction was diluted in DCM and extracted with H<sub>2</sub>O. The organic layer was subsequently dried with Sodium sulfate, and the solvent was removed under reduced pressure. The crude mixture was purified by silica flash chromatography using DCM as the eluent to afford compound **5** as a deep red solid (0.92 g, 58% yield). <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>, 298 K): 9.07 (d, *J* = 8.6 Hz, 2H), 7.26 (dd, *J* = 8.6 Hz, 1.9 Hz), 6.93 (d, 2H), 3.75 (t, *J* = 7.2 Hz, 4H), 3.26 (t, *J* = 6.7 Hz, 4H), 1.42 (m, 16H); HRMS (ESI-ToF) calcd for C<sub>28</sub>H<sub>30</sub>Br<sub>2</sub>N<sub>8</sub>O<sub>2</sub>[M+H]<sup>+</sup>: 671.0838, found 671.0919. <sup>13</sup>C NMR (300MHz, CDCl<sub>3</sub>, 298K): 167.73, 145.62, 132.57, 131.19, 126.79, 125.21, 120.37,

111.24,

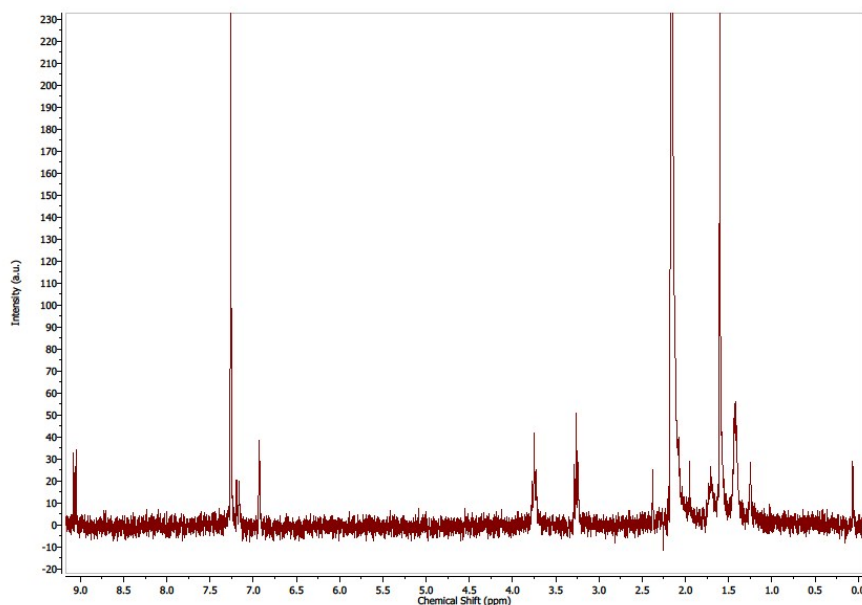
40.02, 29.67,

27.25, 26.48,

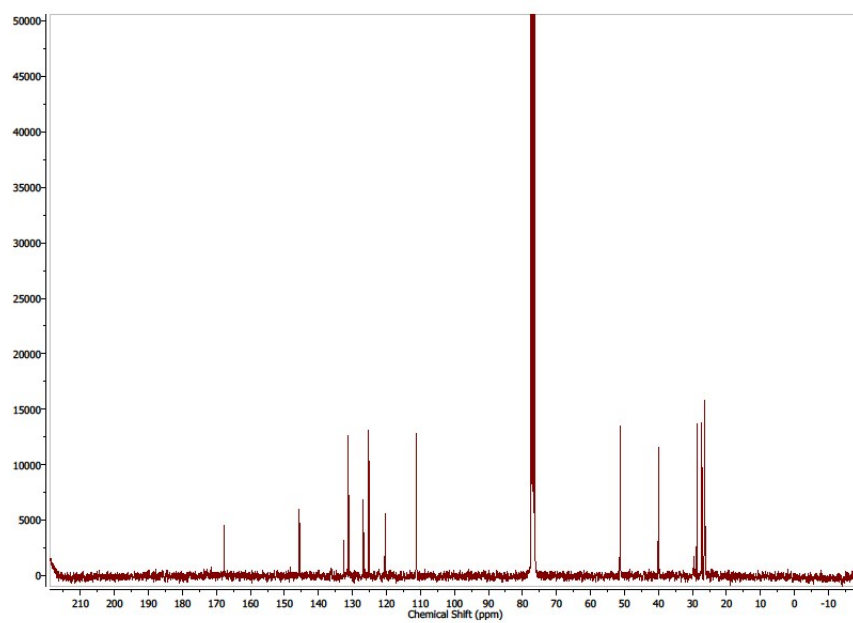
51.27,

28.69,

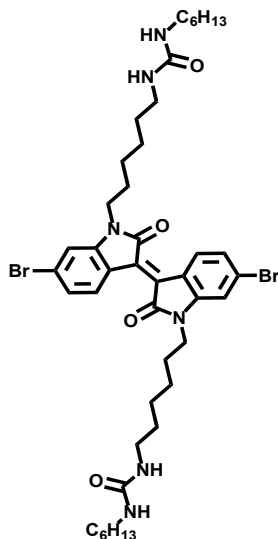
26.37.



$^1\text{H}$  NMR spectrum of **2** in  $\text{CDCl}_3$

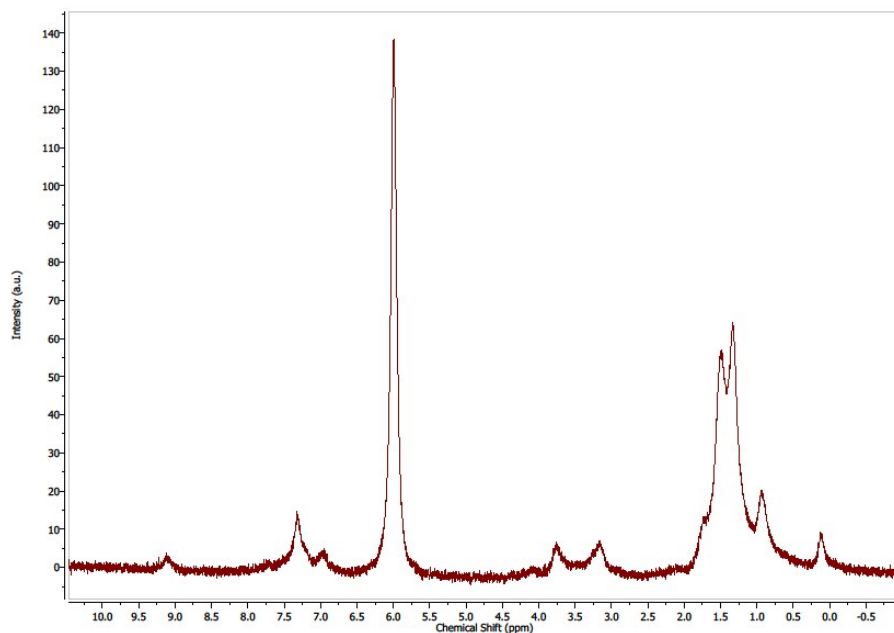


$^{13}\text{C}$  NMR spectrum of **2** in  $\text{CDCl}_3$



**Compound 3.** A round-bottom flask equipped with a magnetic stir bar was charged with **2** (0.70 g, 1.04 mmol), triphenylphosphine (1.64 g, 6.26 mol) and deionized water (0.188 mL, 10.44 mol) were dissolved in toluene (208 mL). The reaction was stirred for 18 h at 80°C under N<sub>2</sub> atmosphere. Upon completion, the reaction was diluted in chloroform and extracted with H<sub>2</sub>O. The organic layer was subsequently dried with Sodium sulfate, and the solvent was removed under reduced pressure. The crude mixture was precipitated in methanol and filtered. The crude product was used directly in the next step without further purifications. The obtained crude mixture and hexyl isocyanate (0.085 mL, 0.582 mol) were dissolved in chloroform (49.7 mL). The reaction mixture was stirred for 18 h at 80°C under N<sub>2</sub> atmosphere. After cooling to room temperature, solvent was removed, and the crude product was recrystallized from chloroform three times. Compound **6** was obtained as dark red solids (0.92 g, 21% yield). <sup>1</sup>H NMR (300MHz, TCE-*d*<sub>2</sub>, 298 K): 9.12 (m, 2H), 7.32 (m, 2H), 6.96 (d, 2H), 3.76 (s, 4H), 3.15 (s, 4H), 1.49 (d, 16H), 1.34 (m, 20H), 0.94 (m, 6H); HRMS (ESI-ToF) calcd for C<sub>42</sub>H<sub>60</sub>Br<sub>2</sub>N<sub>6</sub>O<sub>4</sub> C<sub>42</sub>H<sub>60</sub>Br<sub>2</sub>N<sub>6</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 873.3022, found 873.3099. <sup>13</sup>C NMR was not possible to acquire due to low solubility of compound **3** in deuterated solvents at 120°C.



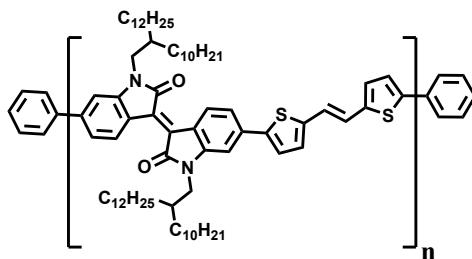


$^1\text{H}$  NMR spectrum of **3** in TCE- $\text{d}_2$  at  $120^\circ\text{C}$

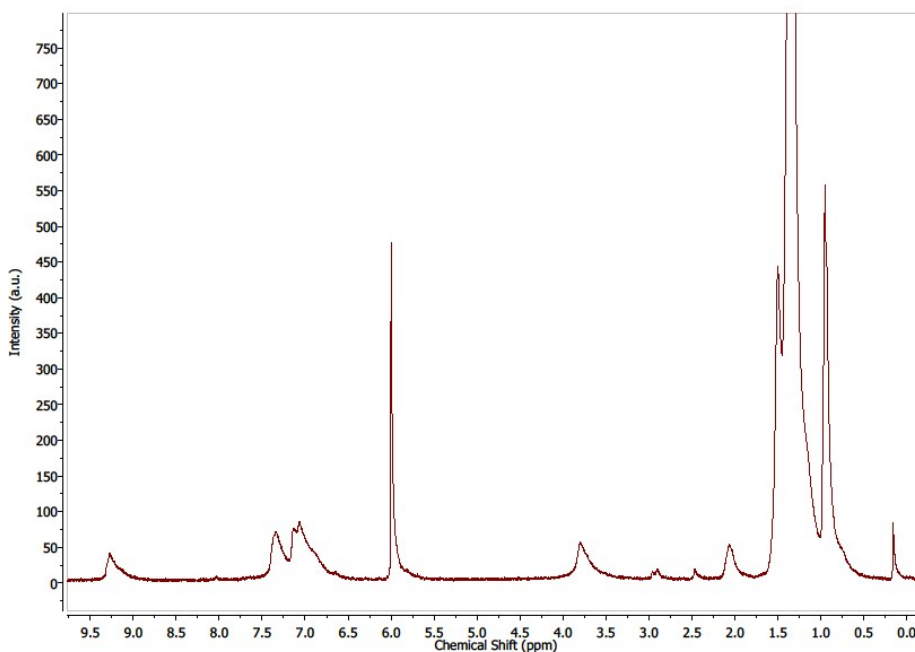
### General procedure for Stille polymerization

A microwave vessel equipped with a stir bar was charged with the appropriate amount of (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (TVT), (*E*)-6,6'-dibromo-1,1'-bis(2-decyltetradecyl)-[3,3'-biindolinylidene]-2,2'-dione and other brominated compound, followed by the addition of anhydrous chlorobenzene. The solution was then bubbled with  $\text{N}_2$  gas for 30 minutes, followed by addition of  $\text{Pd}_2\text{dba}_3$  and  $\text{P}(o\text{-tolyl})_3$ . The vessel was then immediately sealed with a snap cap and microwave irradiated under the following conditions with ramping temperature (Microwave Setup: Biotage Microwave Reactor; Power, 300 W; Temperature and Time, 2 minutes at  $100^\circ\text{C}$ , 2 minutes at  $120^\circ\text{C}$ , 5 minutes at  $140^\circ\text{C}$ , 5 minutes at  $160^\circ\text{C}$ , and 40 minutes at  $180^\circ\text{C}$ ; Pressure, 17 bar; Stirring, 720). After completion, the polymer was end-capped with trimethylphenyl tin and bromobenzene, successively. The reaction was then cooled to room temperature and dissolved in TCE. This solution was then precipitated in methanol and the solid

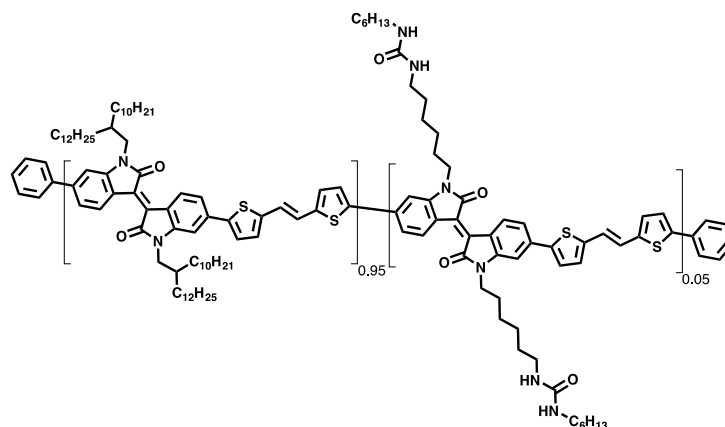
was collected by filtration into a glass thimble. The contents of the thimble were then extracted in a Soxhlet extractor with methanol, acetone, hexane and finally chlorobenzene. The chlorobenzene fraction was concentrated and reprecipitated in methanol, followed by filtration and drying under vacuum.



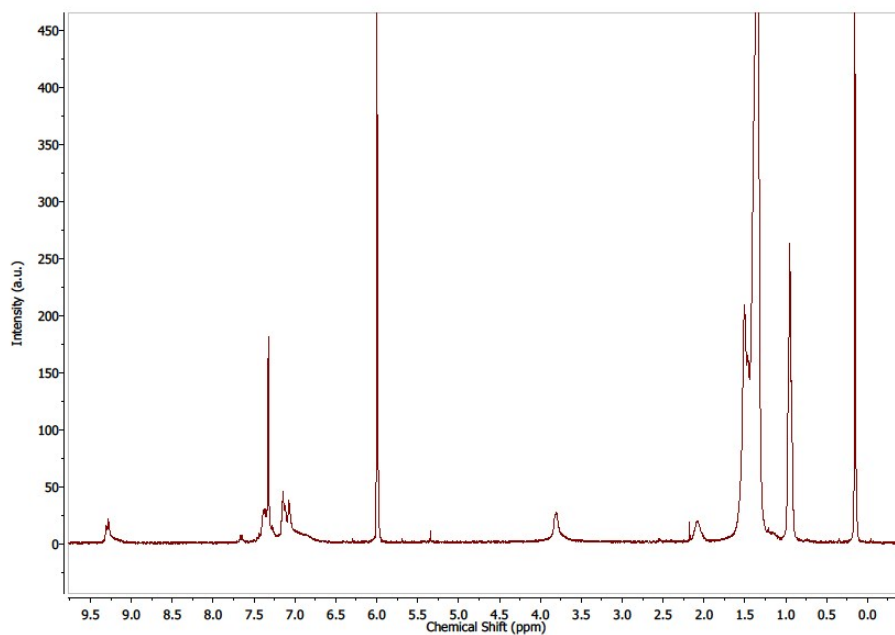
**P1.** (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (44.86 mg, 0.087 mmol), (*E*)-6,6'-dibromo-1,1'-bis(2-decyltetradecyl)-[3,3'-biindolinylidene]-2,2'-dione (95.0 mg, 0.087 mmol), chlorobenzene (3.5 mL), Pd<sub>2</sub>(dba)<sub>3</sub> (1.6 mg, 0.0017 mmol), P(*o*-tolyl)<sub>3</sub> (2.4 mg, 0.0078 mmol), trimethyltin phenyl (20.9 mg, 0.087 mmol) and bromobenzene (13.6 mg, 0.087 mmol). Molecular weight estimated from high temperature GPC: M<sub>n</sub> = 13.0 kDa, M<sub>w</sub> = 59.6 kDa, PDI = 4.6



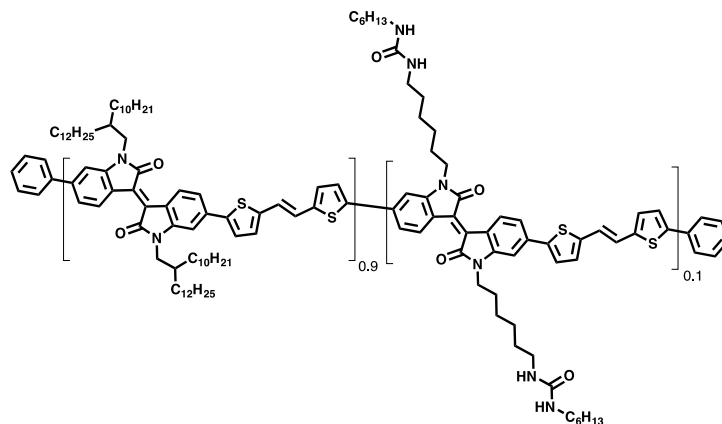
<sup>1</sup>H NMR spectrum of **P1** in TCE-*d*<sub>2</sub> at 120°C



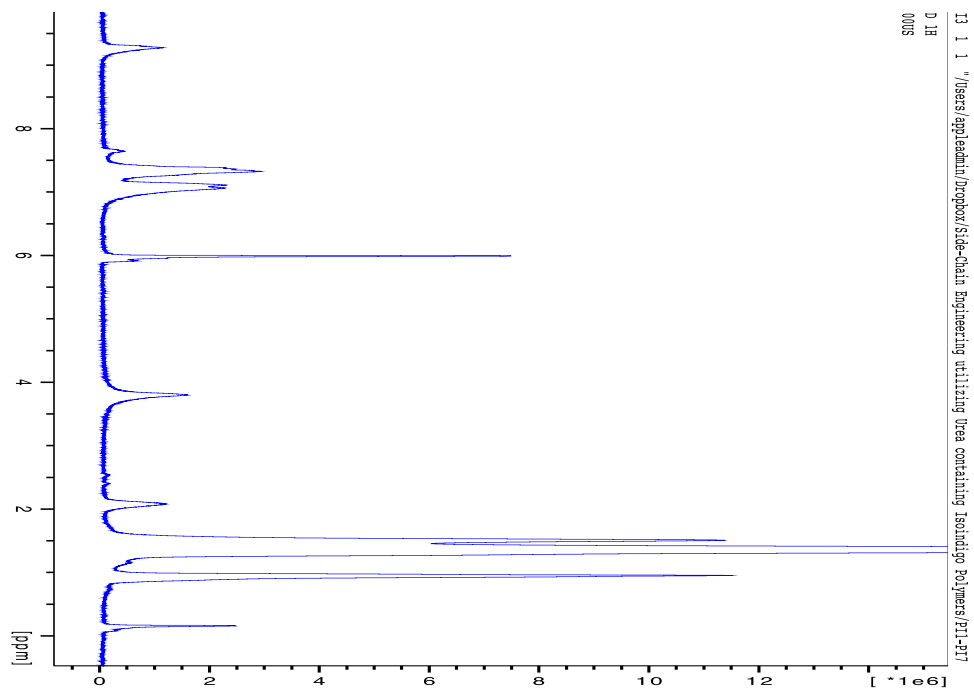
**P2.** (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (45.0 mg, 0.087 mmol), (*E*)-6,6'-dibromo-1,1'-bis(2-decyltetradecyl)-[3,3'-biindolinylidene]-2,2'-dione (90.1 mg, 0.082 mmol), **3** (3.8 mg, 0.0043 mmol), chlorobenzene (3.5 mL), Pd<sub>2</sub>(dba)<sub>3</sub> (1.6 mg, 0.0017 mmol), P(*o*-tolyl)<sub>3</sub> (2.4 mg, 0.0078 mmol), trimethyltin phenyl (20.9 mg, 0.087 mmol) and bromobenzene (13.6 mg, 0.087 mmol). Molecular weight estimated from high temperature GPC: M<sub>n</sub> = 12.2 kDa, M<sub>w</sub> = 75.2 kDa, PDI = 6.2



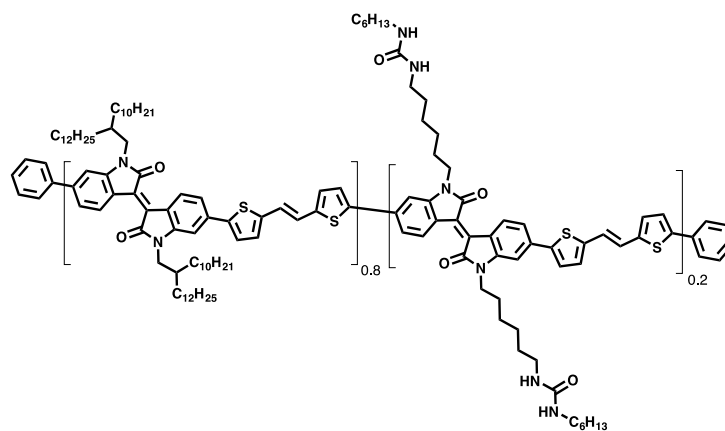
<sup>1</sup>H NMR spectrum of **P2** in TCE-*d*<sub>2</sub> at 120°C



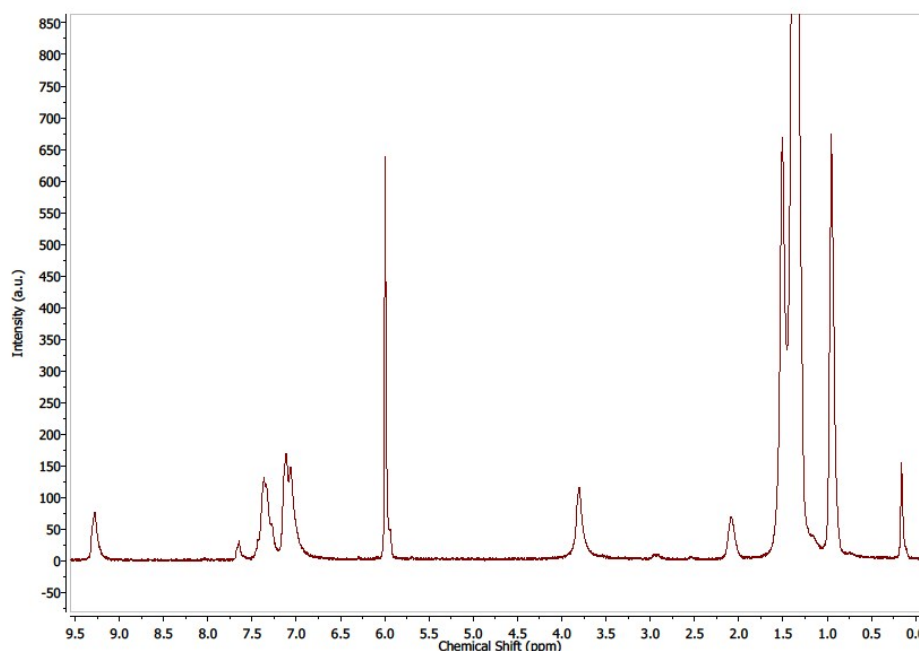
**P3.** (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (45.0 mg, 0.087 mmol), (*E*)-6,6'-dibromo-1,1'-bis(2-decyltetradecyl)-[3,3'-biindolinylidene]-2,2'-dione (85.5 mg, 0.078 mmol), **3** (8.5 mg, 0.0087 mmol), chlorobenzene (3.5 mL), Pd<sub>2</sub>(dba)<sub>3</sub> (1.6 mg, 0.0017 mmol), P(*o*-tolyl)<sub>3</sub> (2.4 mg, 0.0078 mmol), trimethyltin phenyl (20.9 mg, 0.087 mmol) and bromobenzene (13.6 mg, 0.087 mmol). Molecular weight estimated from high temperature GPC: M<sub>n</sub> = 8.7 kDa, M<sub>w</sub> = 33.8 kDa, PDI = 3.9



$^1\text{H}$  NMR spectrum of **P3** in  $\text{TCE-}d_2$  at  $120^\circ\text{C}$

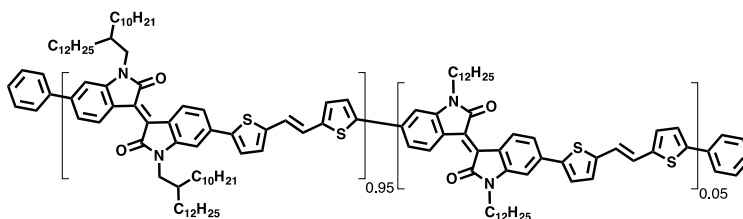


**P4.** (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (45.0 mg, 0.087 mmol), (*E*)-6,6'-dibromo-1,1'-bis(2-decyltetradecyl)-[3,3'-biindolinylidene]-2,2'-dione (76.0 mg, 0.070 mmol), **3** (15.2 mg, 0.017 mmol), chlorobenzene (3.5 mL), Pd<sub>2</sub>(dba)<sub>3</sub> (1.6 mg, 0.0017 mmol), P(*o*-tolyl)<sub>3</sub> (2.4 mg, 0.0078 mmol), trimethyltin phenyl (20.9 mg, 0.087 mmol) and bromobenzene (13.6 mg, 0.087 mmol). Molecular weight estimated from high temperature GPC: M<sub>n</sub> = 9.5 kDa, M<sub>w</sub> = 18.0 kDa, PDI = 1.9

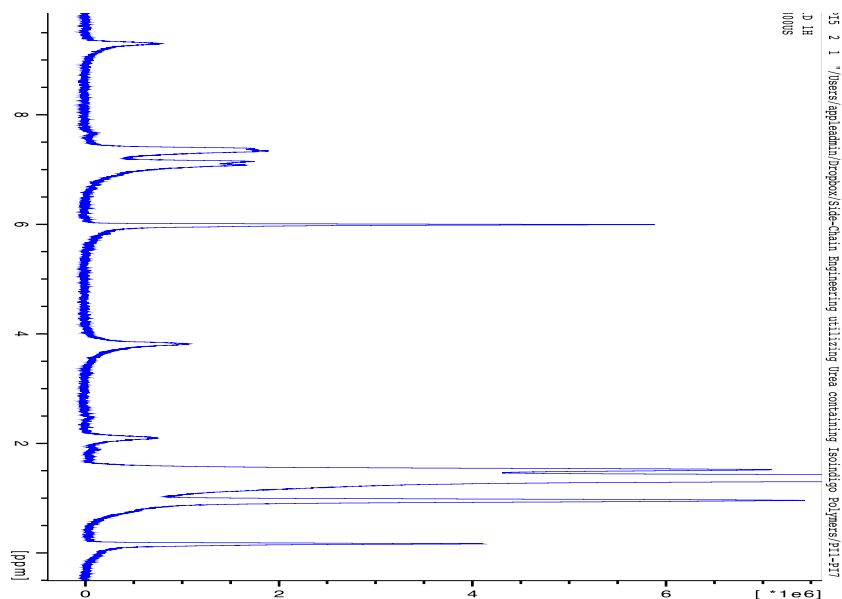


<sup>1</sup>H NMR spectrum of **P4** in TCE-*d*<sub>2</sub> at 120°C

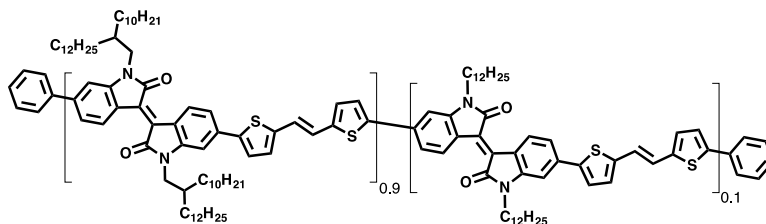
The synthesis of (*E*)-6,6'-dibromo-1,1'-didodecyl-{3,3'-biindolinylidene]-2,2'-dione was completed according to the previously reported conditions for N-alkylation utilizing basic conditions.<sup>ref</sup> **P5** to **P7** were synthesized using the dodecyl-containing monomer as detailed in the following section.



**P5.** (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (45.0 mg, 0.087 mmol), (*E*)-6,6'-dibromo-1,1'-bis(2-decyltetradecyl)-[3,3'-biindolinylidene]-2,2'-dione (90.1 mg, 0.082 mmol), (*E*)-6,6'-dibromo-1,1'-didodecyl-[3,3'-biindolinylidene]-2,2'-dione (3.3 mg, 0.0043 mmol), chlorobenzene (3.5 mL), Pd<sub>2</sub>(dba)<sub>3</sub> (1.6 mg, 0.0017 mmol), P(*o*-tolyl)<sub>3</sub> (2.4 mg, 0.0078 mmol), trimethyltin phenyl (20.9 mg, 0.087 mmol) and bromobenzene (13.6 mg, 0.087 mmol). Molecular weight estimated from high temperature GPC: M<sub>n</sub> = 9.8 kDa, M<sub>w</sub> = 64.0 kDa, PDI = 6.5

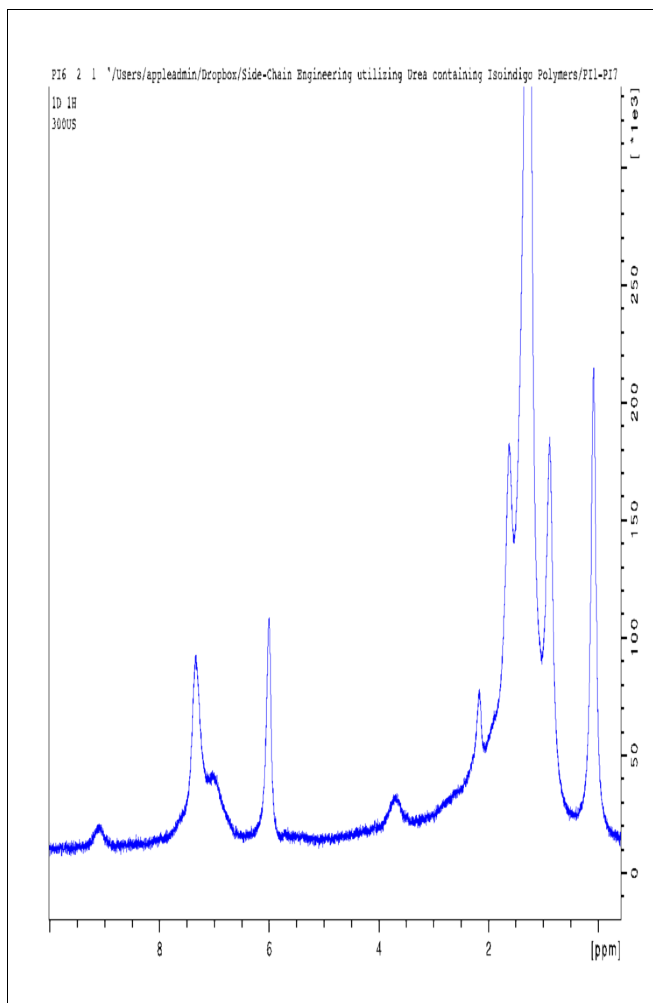


<sup>1</sup>H NMR spectrum of **P5** in TCE-*d*<sub>2</sub> at 120°C

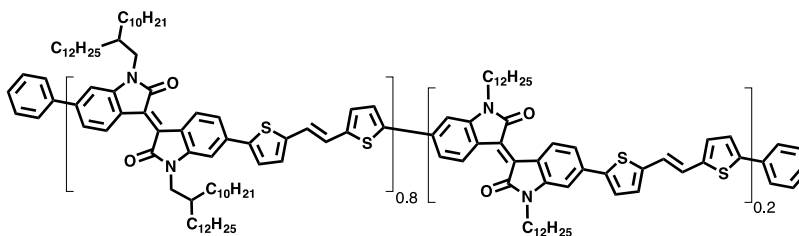


**P6.** (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (45.0 mg, 0.087 mmol), (*E*)-6,6'-dibromo-1,1'-bis(2-decyltetradecyl)-[3,3'-biindolinylidene]-2,2'-dione (85.5 mg, 0.078 mmol), (*E*)-6,6'-dibromo-1,1'-didodecyl-[3,3'-biindolinylidene]-2,2'-dione (6.7 mg, 0.0087 mmol), chlorobenzene (3.5 mL), Pd<sub>2</sub>(dba)<sub>3</sub> (1.6 mg, 0.0017 mmol), P(*o*-tolyl)<sub>3</sub> (2.4 mg, 0.0078 mmol), trimethyltin phenyl (20.9 mg, 0.087 mmol) and bromobenzene (13.6 mg, 0.087 mmol). Molecular weight estimated from high temperature GPC: M<sub>n</sub> = 16.8 kDa, M<sub>w</sub> = 102.7 kDa, PDI = 6.1



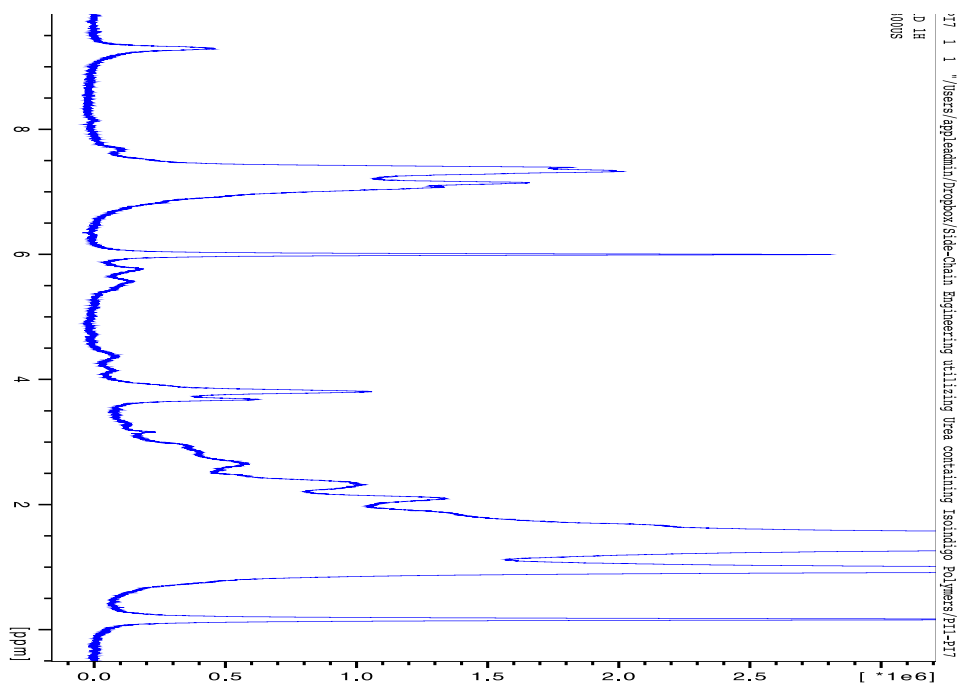


$^1\text{H}$  NMR spectrum of **P6** in  $\text{TCE-}d_2$  at  $120^\circ\text{C}$



**P7.** (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (45.0 mg, 0.087 mmol), (*E*)-6,6'-dibromo-1,1'-bis(2-decyltetradecyl)-[3,3'-biindolinylidene]-2,2'-dione (76.0 mg, 0.070 mmol), (*E*)-6,6'-dibromo-1,1'-didodecyl-[3,3'-biindolinylidene]-2,2'-dione (13.1 mg, 0.017 mmol), chlorobenzene (3.5 mL),  $\text{Pd}_2(\text{dba})_3$  (1.6 mg, 0.0017 mmol),  $\text{P}(o\text{-tolyl})_3$  (2.4 mg, 0.0078 mmol),

trimethyltin phenyl (20.9 mg, 0.087 mmol) and bromobenzene (13.6 mg, 0.087 mmol). Molecular weight estimated from high temperature GPC:  $M_n = 7.0$  kDa,  $M_w = 21.2$  kDa, PDI = 3.0



$^1\text{H}$  NMR spectrum of **P7** in  $\text{TCE-}d_2$  at  $120^\circ\text{C}$

## Materials and Device Characterization

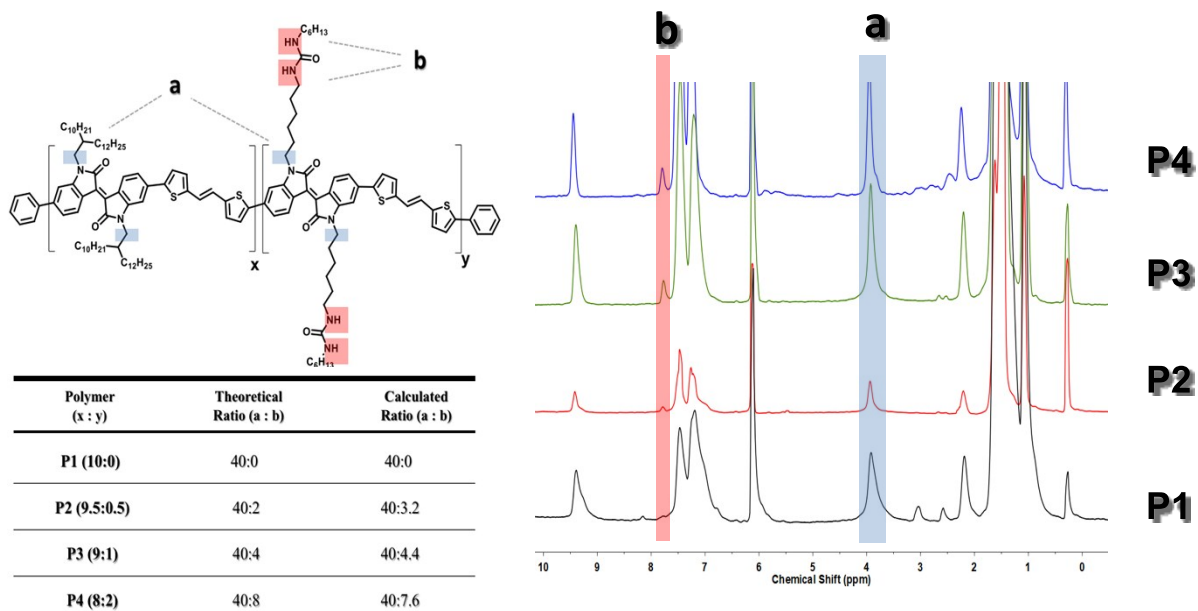


Figure S1. Composition of **P1** to **P4** as determined by variable-temperature  $^1\text{H}$  NMR spectroscopy in 1,1,2,2-tetrachloroethane- $d_2$  at 120  $^\circ\text{C}$ . The theoretical ratios between  $\text{H}_a$  and  $\text{H}_b$  are calculated by assuming 10 repeat units.

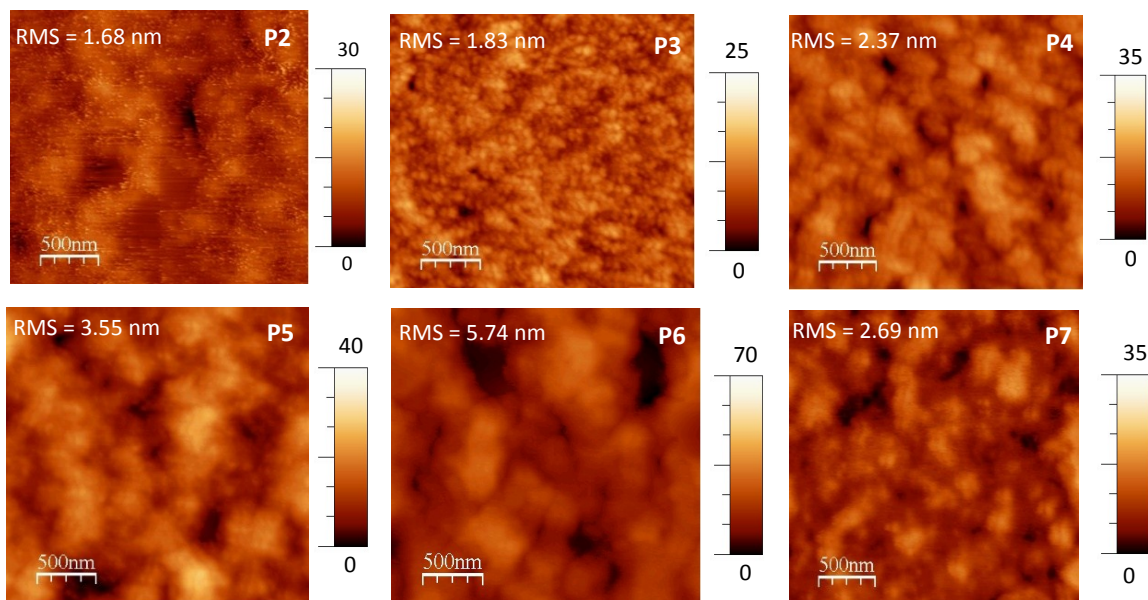


Figure S2. Atomic force microscopy (AFM) height images of **P2** to **P7** before thermal annealing. Scale bars are 500 nm.

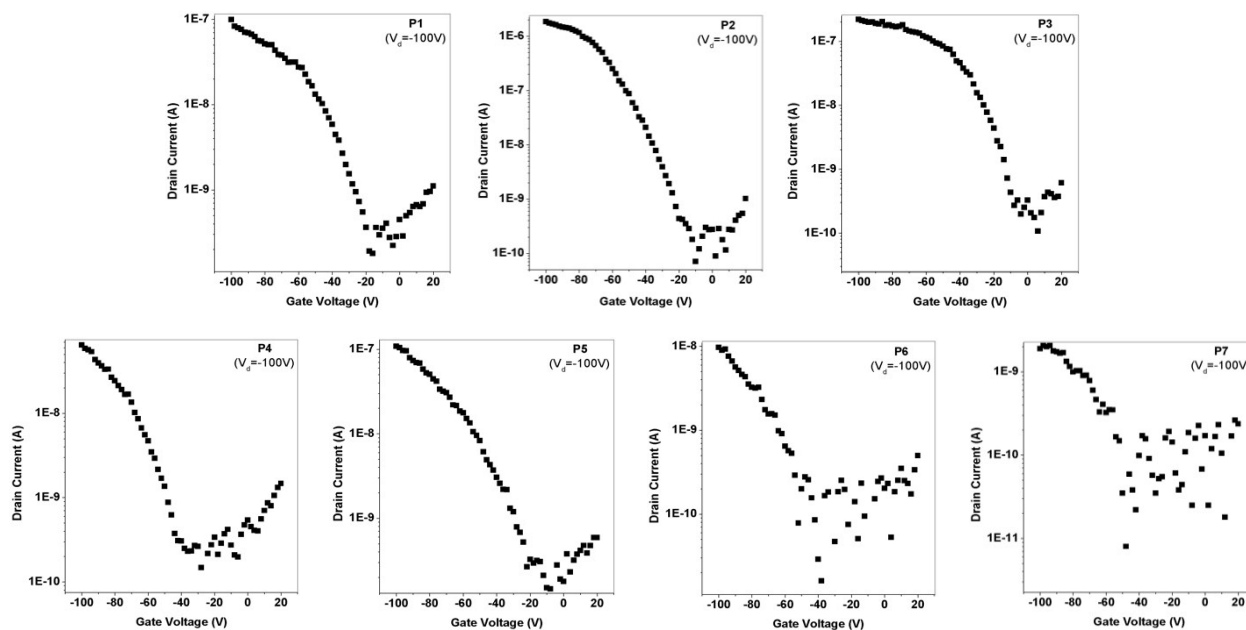


Figure S3. Transfer curves for OFET devices built from **P1** to **P7**, without thermal annealing. Drain voltage is -100V.

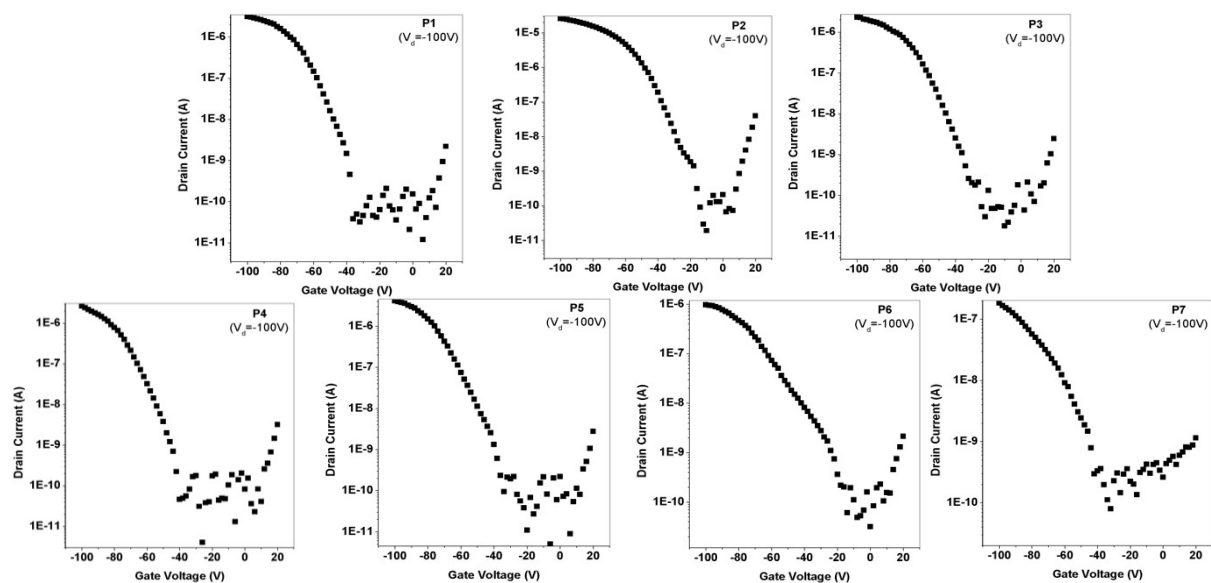


Figure S4. Transfer curves for OFET devices built from **P1** to **P7**, after thermal annealing at 100 °C. Drain voltage is -100V.

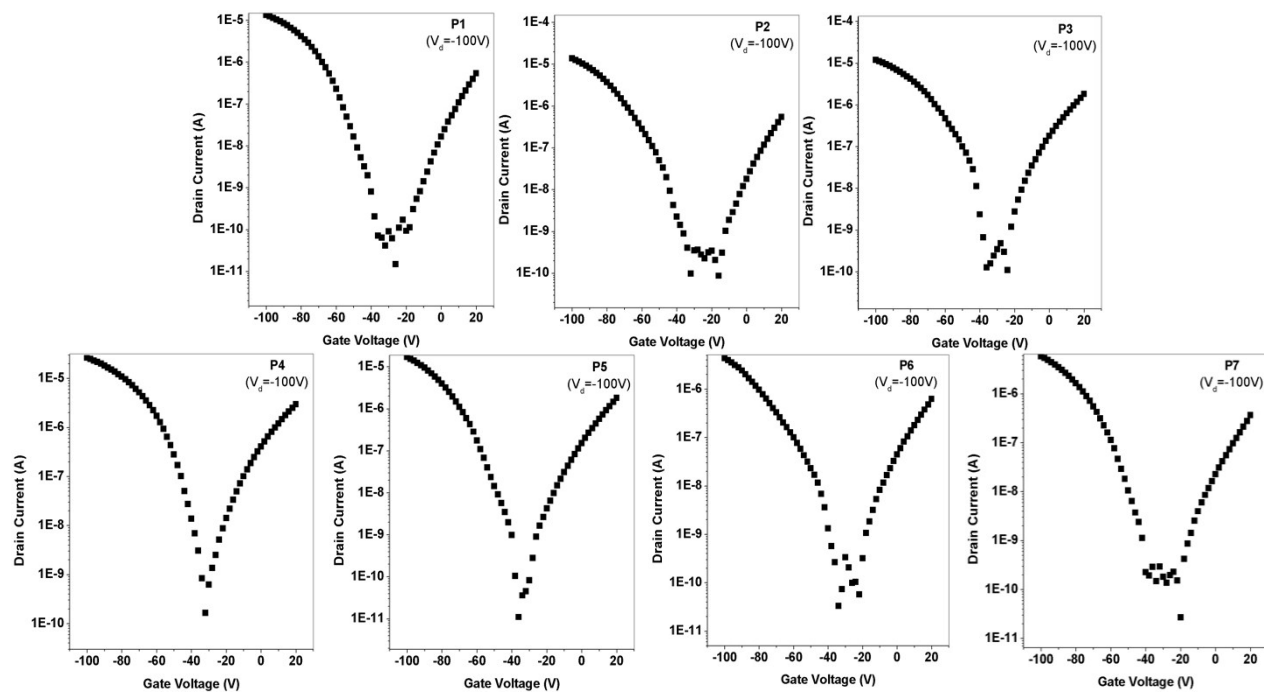


Figure S5. Transfer curves of OFET devices built from **P1** to **P7**, after thermal annealing at 200 °C. Drain voltage is -100V.

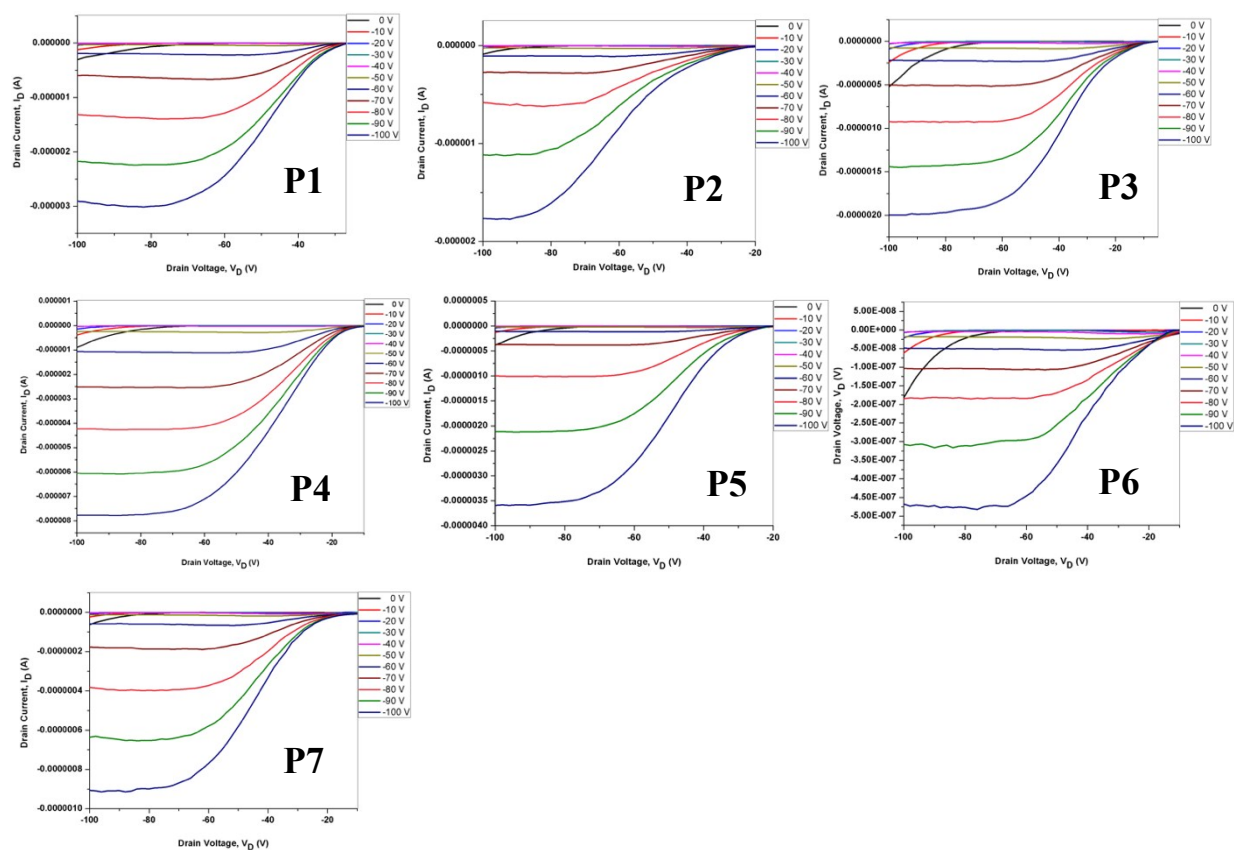


Figure S6. Output characteristics of OFET devices built from **P1** to **P7**, after thermal annealing at 200 °C.

## References

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