#### Supplementary Information for

## Effects of Varying the Lengths of the Donor Units in $\pi$ -Extended Thienothiophene Isoindigo-Based Polymer Semiconductors

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<sup>†</sup> Electronic supplementary information (ESI) available: Synthetic procedures, material characterizations (NMR, mass spectrum, TGA, DSC, CV), 2D-GIXD, molecular conformations (DFT), OFET characteristics (output curves and n-type device performance).

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#### **Synthesis**

*Synthesis of N-(7-decylnonadecyl)thieno[3,2-b]thiophen-3-amine (1)*: 3-Bromothieno[3,2-b]thiophene (9.30 g, 42.4 mmol), 15-(6-bromohexyl)hentriacontane (27.0 g, 63.70 mmol), copper (0.13 g, 2.12 mmol), copper(I) iodide (0.40 g, 2.12 mmol) and potassium phosphate tribasic (18.0 g, 63.7 mmol) were stirred in 100 mL of dimethyl aminoethanol at 80 °C for 48 h. The mixture is filtered and solvent removed by vacuum. The crude product dissolved in hexane, and the solution was passed through a short silica gel column. Evaporation of the solvent gave crude compound (1) that could be used directly without further purification. 4.7 g, yield 19%.

*Synthesis of 7-(7-decylnonadecyl)-5H-thieno[2',3':4,5]thieno[3,2-b]pyrrole-5,6(7H)-dione (2)*: Compound (1) (4.7 g, 8.36 mmol) in 17 mL of DCM was added dropwise to oxalyl dichloride (1.433 g, 11.32 mmol) in 25 mL of DCM at 0 °C. After 30 min, triethylamine (3.85 g, 38.04 mmol) in 16 mL DCM was added dropwise and stirred overnight at room temperature. Solvents were removed under vacuum and crude product was purified by chromatography on silica gel in hexane : ethyl acetate (5:1). Compound (2) was obtained as red viscous oil. 1.67 g, yield 35 %. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ/ppm: 7.86-7.84 (d, 1H), 7.38-7.37 (d, 1H), 3.83-3.80 (t, 2H), 1.81-1.78 (m, 2H), 1.33-1.22 (bm, 49H), 0.91-0.88 (m, 6H). <sup>13</sup>C- NMR (CDCl<sub>3</sub>, 125 MHz): 172.65, 161.74, 157.63, 154.23, 136.83, 123.87, 111.50, 42.47, 37.39, 33.66, 33.61, 31.94, 30.16, 30.06, 29.73, 29.67, 29.37, 26.83, 26.56, 22.70, 14.13, 1.03. MS ES+(m/e): 615.41 (M+, 100%).

#### Synthesis of (E)-7,7'-bis(7-decylnonadecyl)-[5,5'-bithieno[2',3':4,5]thieno[3,2-

*b]pyrrolylidene]-6,6'(7H,7'H)-dione (TTID)*: A solution of compound (2) (1.6 g, 2.85 mmol) and Lawesson's Reagent (0.577 g, 1.43 mmol) in 45 mL o-xylene was stirred at 60 °C for 8h. The progress of reaction was monitored by TLC and change in colour (from red to dark green). The reaction mixture was then cooled down to room temperature. After evaporated solvent, the crude product was purified by chromatography on silica gel in hexane : DCM (3:1). 0.74 g, yield 35%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$ /ppm: 7.53-7.52 (d, 2H), 7.34-7.33 (d, 2H), 3.98-3.95 (m, 4H), 1.87-1.84 (m, 4H), 1.31-1.21 (bm, 98H), 0.90-0.88 (m, 12H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$ /ppm: 170.78, 148.45, 142.83, 129.97, 123.53, 121.15, 116.24, 37.38, 33.66, 33.61, 31.94, 30.26, 30.17, 29.73, 29.67, 29.38, 26.96, 26.71, 26.58, 22.70, 14.13. FAB MS ES+(m/e): 1198.9 (M+, 100%).

Synthesis of (E)-2,2'-dibromo-7,7'-bis(7-decylnonadecyl)-[5,5'-bithieno[2',3':4,5]thieno[3,2b]pyrrolylidene]-6,6'(7H,7'H)-dione (TTIDBr): N-bromosuccinimide (NBS, 0.23 g, 1.34 mmol) was added slowly to a solution of (E)-7,7'-bis(7-decylnonadecyl)-[5,5'bithieno[2',3':4,5]thieno[3,2-b]pyrrolylidene]-6,6'(7H,7'H)-dione (0.70 g, 0.58 mmol) in THF (18 mL) at 0°C. The solution was protected from light and stirred at room temperature for 12 h. The reaction mixture was poured into water (60 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried over MgSO<sub>4</sub> and the solvent was evaporated under reduced pressure. The crude product was purified by silica gel chromatography (hexane-methylene dichloride, gradient from 10:1 to 3:1). The dark green solid was obtained (0.6 g, 75%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$ /ppm: 7.37 (s, 2H), 3.90 (m, 4H), 1.84-1.77 (m, 4H), 1.33-1.24 (bm, 98H), 0.93-0.88 (m, 12H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$ /ppm: 170.40, 155.84, 150.26, 149.00, 142.41, 134.94, 123.89, 115.42, 37.33, 33.60, 33.54, 31.93, 30.17, 30.12, 29.70, 29.66, 29.36, 26.86, 26.63, 26.48, 22.69, 13.88. TOF MS ES+(m/e): 1357.6 (M+, 100%).

Synthesis of poly[(E)-7,7'-bis(7-decylnonadecyl)-[5,5'-bithieno[2',3':4,5]thieno[3,2b]pyrrolylidene]-6,6'(7H,7'H)-dione-co-thiophene] (PTTID-T) : PTTID-T was prepared using a Pd-catalyzed Stille coupling reaction. (E)-2,2'-dibromo-7,7'-bis(7-decylnonadecyl)-[5,5'bithieno[2',3':4,5]thieno[3,2-b]pyrrolylidene]-6,6'(7H,7'H)-dione (0.3 g, 0.22 mmol) and 2,5bis(trimethylstannyl)thiophene (0.09 g, 0.22 mmol) were dissolved in dry chlorobenzene (4.5 mL). After degassing with N<sub>2</sub> for 30 min, Pd<sub>2</sub>(dba)<sub>3</sub> (0.0040g, 0.004 mmol) and P(o-Tol)<sub>3</sub> (0.0053 g , 0.0176 mmol) were added to the mixture and stirred at 100 °C under nitrogen atmosphere for 48 h. Tributyl(thiophen-2-yl)stannane and 2-bromothiophene were injected at a time interval of 6 h for end-capping, respectively. The polymer was precipitated in methanol. The crude polymer was collected by filtration and then purified by soxhlet with methanol, acetone, hexane, toluene and chloroform, successively. The final product was obtained by precipitation on methanol and dried under vacuum. Yield: 0.21 g (70%) <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$ /ppm: 8.15-7.45 (br, 2H), 7.25-6.89 (br 2H), 3.85-3.80 (br, 4H), 1.90-1.79 (br, 4H), 1.40-1.24 (br, 98H), 0.97-0.87 (br, 12H).

# Synthesis of poly[(E)-7,7'-bis(7-decylnonadecyl)-[5,5'-bithieno[2',3':4,5]thieno[3,2-b]pyrrolylidene]-6,6'(7H,7'H)-dione-co-bithiophene] (PTTID-BT)

PTTID-BT was prepared in the same method as.PTTID-T by using (E)-2,2'-dibromo-7,7'-bis(7-decylnonadecyl)-[5,5'-bithieno[2',3':4,5]thieno[3,2-b]pyrrolylidene]-6,6'(7H,7'H)-dione (0.3 g, 0.22 mmol) and 2,5'-bis(trimethylstannyl)bithiophene (0.1082 g, 0.22 mmol), Yield: 0.19 g (63%) <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$ /ppm: 8.17-7.45 (br, 2H), 7.25-7.09 (br 2H), 6.70- 6.32 (br 2H), 3.81-3.70 (br, 4H), 1.91-1.78 (br, 4H), 1.39-1.24 (br, 98H), 0.97-0.88 (br, 12H)

### Synthesis of poly[(E)-7,7'-bis(7-decylnonadecyl)-[5,5'-bithieno[2',3':4,5]thieno[3,2b]pyrrolylidene]-6,6'(7H,7'H)-dione-co-thienothiophene] (PTTID-TT)

PTTID-TT was prepared in the same method as.PTTID-T by using (E)-2,2'-dibromo-7,7'-bis(7 decylnonadecyl)-[5,5'-bithieno[2',3':4,5]thieno[3,2-b]pyrrolylidene]-6,6'(7H,7'H)-dione (0.3 g, 0.22 mmol) and 2,2'-bis(trimethylstannyl)thieonthiophene (0.1024 g g, 0.22 mmol) Yield: 0.23 g (76%) <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz): δ/ppm: 8.16-7.55 (br, 2H), 7.25-7.09 (br 2H), 3.79-3.75 (br, 4H), 1.89-1.74 (br, 4H), 1.35-1.22 (br, 98H), 0.98-0.90 (br, 12H)

#### Synthesis of poly[(E)-7,7'-bis(7-decylnonadecyl)-[5,5'-bithieno[2',3':4,5]thieno[3,2b]pyrrolylidene]-6,6'(7H,7'H)-dione-co-thienothiophene-vinylene-thiophene] (PTTID-TVT) PTTID-TVT was prepared in the same method as. PTTID-T by using (E)-2,2'-dibromo-7,7'bis(7-decylnonadecyl)-[5,5'-bithieno[2',3':4,5]thieno[3,2-b]pyrrolylidene]-6,6'(7H,7'H)-dione

(0.3 g, 0.22 mmol) and 2,5'-bis(trimethylstannyl)thiophene-vinylene-thiophene vbithiophene (0.1139 g, 0.22 mmol)

Yield: 0.20 g (66%) <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$ /ppm: 8.15-7.45 (br, 2H), 7.25-6.89 (br, 4H), 6.72- 6.42 (br 2H), 3.85-3.82 (br, 4H), 1.89-1.79 (br, 4H), 1.42-1.6 (br, 98H), 0.96-0.88 (br, 12H).

# Synthesis of poly[(E)-7,7'-bis(7-decylnonadecyl)-[5,5'-bithieno[2',3':4,5]thieno[3,2-b]pyrrolylidene]-6,6'(7H,7'H)-dione-co-thienothiophene] (PTTID-SVS)

PTTID-SVS was prepared in the same method as.PTTID-T by using (E)-2,2'-dibromo-7,7'-bis(7-decylnonadecyl)-[5,5'-bithieno[2',3':4,5]thieno[3,2-b]pyrrolylidene]-6,6'(7H,7'H)-dione (0.3 g, 0.22 mmol) and 2,5'-bis(trimethylstannyl)selenophene-vinylene-selenophene (0.1345 g , 0.22 mmol)

Yield: 0.22 g (73%) <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz): δ/ppm: 8.25-7.55 (br, 2H), 7.37-6.89 (br, 4H), 6.52- 6.32 (br 2H), 3.85-3.82 (br, 4H), 1.89-1.79 (br, 4H), 1.42-1.6 (br, 98H), 0.96-0.88 (br, 12H).







Figure S3. Mass spectrum of Compound (1).





Figure S5. <sup>13</sup>C NMR spectrum of TTID.



Figure S6. Mass spectrum of TTID.



Figure S7. <sup>1</sup>H NMR spectrum of TTIDBr.



**Figure S8**. <sup>13</sup>C NMR spectrum of TTIDBr.



Figure S9. Mass spectrum (MADI-TOF) of TTIDBr.





**Figure S11**. <sup>1</sup>H NMR spectrum of PTTID-BT.



**Figure S12**. <sup>1</sup>H NMR spectrum of PTTID-TT.



Figure S13. <sup>1</sup>H NMR spectrum of PTTID-TVT.



Figure S14. <sup>1</sup>H NMR spectrum of PTTID-SVS.



**Figure S15**. (a) TGA and (b-f) DSC results of (b) PTTID-T, (c) PTTID-BT, (d) PTTID-TT, (e) PTTID-TVT and (f) PTTID-SVS.

Table S1. The summary of TGA results of the TTID-based copolymers

Polymers	$T_{\rm d}$ (°C)
PTTID-T	423
PTTID-BT	425
PTTID-TT	413
PTTID-TVT	405
PTTID-SVS	402



**Figure S16.** Top and side views of the energy minimized structures of the TTID-based polymers and their dihedral angles: (a) PTTID-T, (b) PTTID-BT, (c) PTTID-TT, (d) PTTID-TVT, and (e) PTTID-SVS.



**Figure S17.** The cyclic voltammograms of the TTID-based polymers. HOMO and LUMO energy levels were obtained by the following equations;  $E_{\text{HOMO}} = -(E_{\text{ox}}^{\text{onset}} + 4.4)$  eV and  $E_{\text{LUMO}} = -(E_{\text{RE}}^{\text{onset}} + 4.4)$  eV.



**Figure S18.** 2D-GIXD patterns of TTID-based polymer films (a) before being annealed and after being annealed (b) at 100 °C or 150 °C (150 °C for PTTID-T and 100 °C for the others), and (c) at 200 °C.



**Figure S19.** The molecular conformations of (a) TTID-T, (b) TTID-BT, (c) TTID-TT, (d) TTID-TVT, and (e)TTID-SVS dimers, which were obtained by DFT calculations. The lines are a guide to see and were drawn from the C-H bond of the last aromatic ring to C-H or C-C bonds of the first or intermediate aromatic rings.



**Figure S20.** Output curves of OFETs with TTID-based copolymers without annealing (left) and after annealing at each optimal temperature (right): (a) PTTID-T, (b) PTTID-BT, (c) PTTID-TT, (d) PTTID-TVT, and (e) PTTID-SVS.



Figure S21. Transfer characteristics of BG/TC OTFTs fabricated with aluminum source and drain electrodes under a positive drain bias ( $V_D = 100$  V) in the n-channel operation mode.