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Supplementary Information

Isoindigo Benzodifurandione based Conjugated Polymers for High Performance Organic Field-effect Transistors

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1 MATERIALS SYNTHESIS

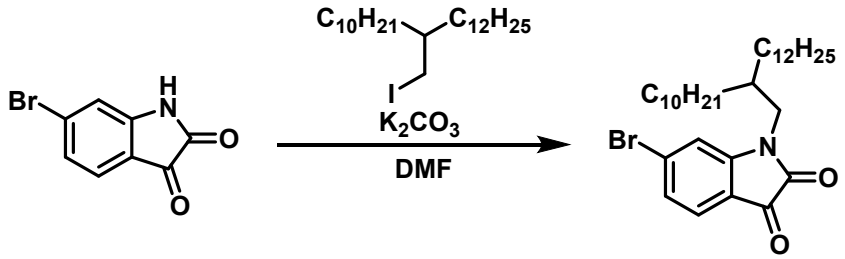

Figure S1. < 6-bromo-1-(2-decyltetradecyl) indoline-2,3-dione synthesis >

Compound 1: 6-bromo-1-(2-decyltetradecyl) indoline-2,3-dione, Fig. S1. 6-bromoindoline-2,3-dione (1.76 g, 7.79 mmol) and 11-(iodomethyl)tricosane (4.35 g, 9.36 mmol) were dissolved in anhydrous *N,N*-dimethylformamide (DMF, 40 ml), and then heated to 80°C under N_2 for 15 min. Anhydrous potassium carbonate (2.15 g, 15.58 mmol) was added and the mixture was heated to 80°C for 6 h. After cooling to room temperature, the solution was filtered under reduced pressure, and the solution was poured into water (200 ml) and extracted with ethyl acetate three times. The organic layer was collected and dried with anhydrous sodium sulfate, residual solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography with *n*-hexane to *n*-hexane/ethyl acetate (7:1) eluent. Yield = 3.82 g, 87%. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm): δ = 7.46 (d, J = 8.0 Hz, 1H); δ = 7.27 (dd, J = 8.0, 1.1 Hz, 1H), δ = 7.03–7.05 (d, 1H); δ = 3.47–3.61 (d, 2H); δ = 1.84 (br, J = 5.4 Hz, 1H); δ = 1.13–1.37 (m, 40H), δ = 0.74–0.95 (t, 6H).

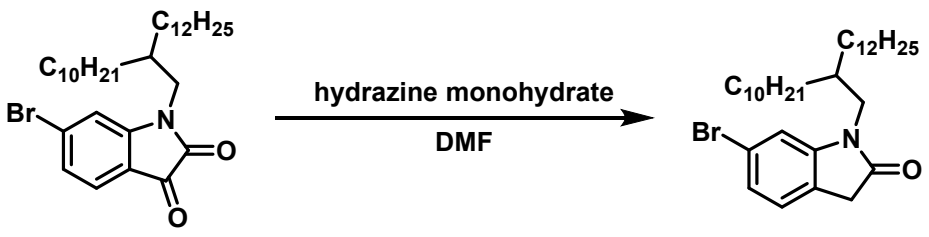

Figure S2. < 6-bromo-1-(2-decyltetradecyl) indolin-2-one synthesis>

Compound 2: 6-bromo-1-(2-decyltetradecyl) indolin-2-one, Fig. S2. Compound 1 (618 mg, 1.10 mmol) and hydrazine monohydrate (1.5 ml) were dissolved in anhydrous DMF (4.0 ml). The mixture was heated to 120 °C for 1.5 h under N_2, then cooled to room temperature, acetic acid (2.0 ml) added, and stirred for 15 min. The reaction mixture was then poured into water (100 ml) and extracted with hexane three times. The organic layer was collected and dried with anhydrous sodium sulfate, residual solvent was removed under reduced pressure, and the

residue was purified by silica gel chromatography with *n*-hexane to *n*-hexane/ethyl acetate (7:1) eluent. Yield = 540 mg, 89%. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm): δ = 7.15 (dd, J = 8.0, 1.7 Hz, 1H); δ = 7.09 (d, J = 8.0 Hz, 1H); δ = 6.93 (d, J = 1.7 Hz, 1H); δ = 3.54 (d, J = 6.6 Hz, 2H); δ = 3.46 (s, 2H); δ = 1.84 (br, J = 5.7 Hz, 1H); δ = 1.15–1.45 (m, 40H); δ = 0.75–0.89 (t, 6H).

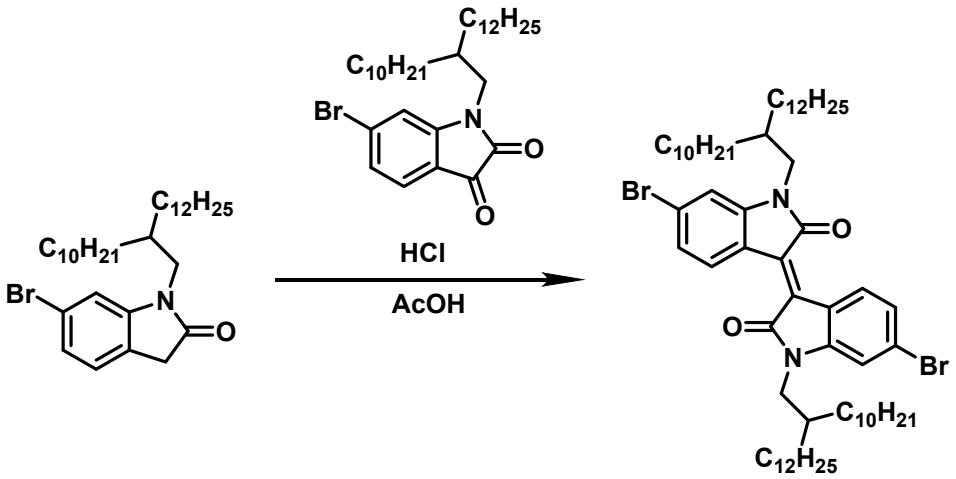

Figure S3. <6, 6'-di-bromo-(2, 2'-di-decyltetradecyl) isoindigo synthesis >

Compound 3: 6, 6'-di-bromo-(2, 2'-di-decyltetradecyl) isoindigo, Fig. S3. Compounds 1 (553 mg, 0.98 mmol), 2 (540 mg, 0.98 mmol), and hydrochloric acid (2 drops) were added to acetic acid (8.0 ml), and the mixture was heated to 120 °C for 18 h under N_2. The reaction mixture was then cooled to room temperature, poured into water (100 ml), and extracted with ethyl acetate three times. The organic layer was collected and dried with anhydrous sodium sulfate, residual solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography with *n*-hexane to *n*-hexane/chloroform (4:1) eluent. Yield = 825 mg, 77%. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm): δ = 9.06 (d, J = 8.6 Hz, 2H); δ = 7.16 (dd, J = 8.6, 1.7 Hz, 2H); δ = 6.90 (d, J = 1.7 Hz, 2H); δ = 3.62 (d, J = 7.4 Hz, 4H); δ = 1.87 (br, J = 6.3 Hz, 2H); δ = 1.23–1.36 (m, 80H); δ = 0.87 (td, J = 6.9, 1.7 Hz, 12H).

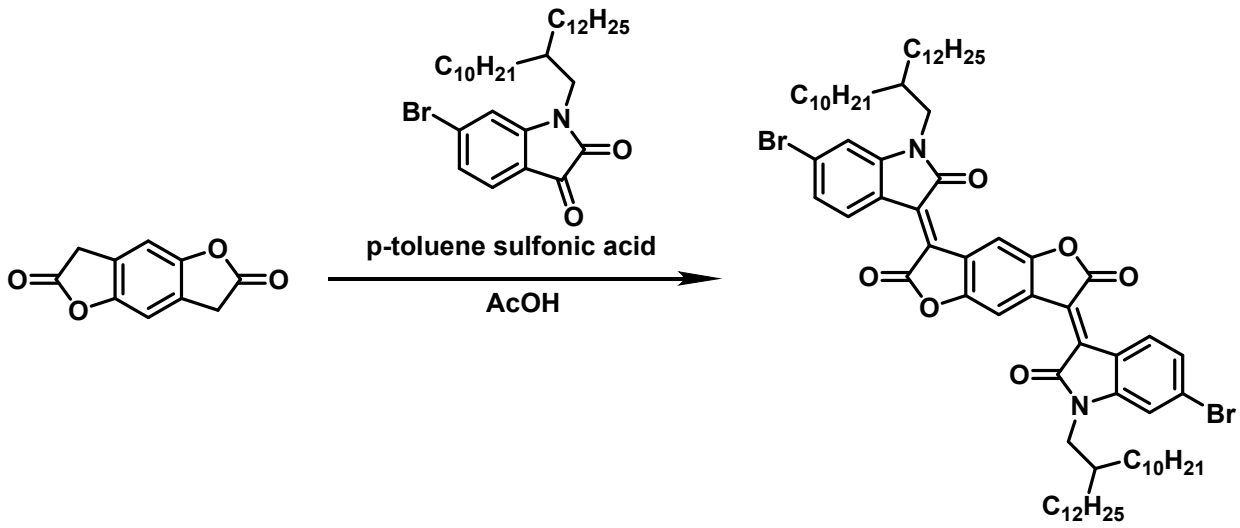

Figure S4. <IBDF synthesis >

Compound 4: IBDF, Fig. S4. 3,7-dihydrobenzo[1,2-b:4,5-b']difuran-2,6-dione (40.0 mg, 0.21 mmol), compound 1 (281 mg, 0.5 mmol), and *p*-toluenesulfonic acid monohydrate ($TsOH \cdot H_2O$, 23.0 mg, 0.121 mmol) was added to acetic acid (3.6 ml), and the mixture was heated to 115°C for 20 h under N_2. The reaction mixture was then cooled to room temperature, poured into water (100 ml), and then extracted with chloroform three times. The organic layer was collected and dried with anhydrous sodium sulfate, residual solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography with *n*-hexane to *n*-hexane/chloroform (1:1) eluent. Yield = 171 mg, 63%. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm): δ = 9.09 (s, 2H); δ = 8.93 (d, J = 8.6 Hz, 2H); δ =7.20 (dd, J = 8.6, 1.7 Hz, 2H); δ = 6.91 (d, J = 1.7 Hz, 2H); δ = 3.63 (d, J = 7.4 Hz, 4H); δ = 1.88 (br, 2H); δ = 1.23–1.39 (m, 80H); δ = 0.73–0.87 (t, 12H).

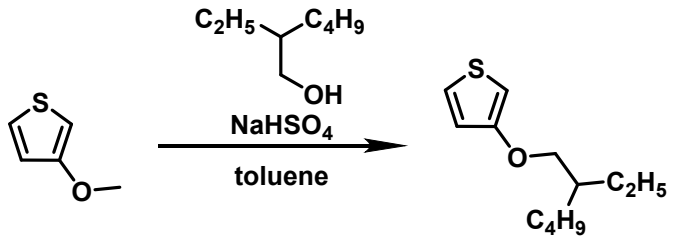

Figure S5. <3-((2-ethylhexyl)oxy)thiophene synthesis>

Compound 5: 3-((2-ethylhexyl)oxy)thiophene, Fig. S5. 3-methoxy thiophene (2.48 ml, 25.0 mmol), 2-ethylhexanol (5.88 ml, 37.5 mmol), and sodium hydrogen sulfate (240 mg, 2.0 mmol) were dissolved in anhydrous toluene (50.0 ml) and heated to 115°C for 18 h under N_2. The reaction mixture was then cooled to room temperature, poured into water (200 ml), and extracted with hexane three times. The organic layer was collected and dried with anhydrous sodium sulfate, residual solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography with *n*-hexane eluent. Yield = 3.57 g, 67%. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm): δ 7.12-7.19 (dd, 1H), 6.75 (dd, J = 5.4, 1.4 Hz, 1H), 6.22-6.26 (dd, 1H), 3.80-3.87 (dd, 2H), 1.67-1.75 (m, 1H), 1.27-1.54 (m, 8H), 0.85-1.00 (m, 6H). ^{13}C-NMR (175 MHz, $CDCl_3$, δ): 11.10, 14.11, 23.04, 23.80, 29.06, 30.47, 30.47, 39.37, 96.68, 119.62, 124.42, 158.26; Calcd. C 67.87, H 9.49; found C 68.11, H 9.65.

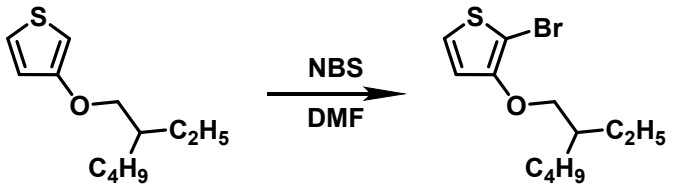

Figure S6. <2-bromo-3-((2-ethylhexyl)oxy)thiophene synthesis >

Compound 6: 2-bromo-3-((2-ethylhexyl)oxy)thiophene, Fig. S6. Compound 5 (3.57 g, 16.8 mmol) was dissolved in DMF (25.0 ml) and stirred at 0°C for 15 min. *N*-bromosuccinimide (NBS, 2.99 g, 16.8 mmol) was added slowly to the solution in the dark. After 1 h, the mixture was warmed to room temperature and stirred for a further 1 h. The reaction was quenched by adding $NaHCO_3$ aqueous solution, the solution was poured into water (100 ml), and extracted with *n*-hexane three times. The organic layer was collected and dried with anhydrous sodium sulfate, residual solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography with *n*-hexane eluent. Yield =0 4.13 g, 85%.^{1}H-NMR (500 MHz, $CDCl_3$, ppm): δ = 7.18 (d, J = 5.3 Hz, 1H); δ = 6.75 (d, J = 5.4 Hz, 1H); δ = 3.87-3.99 (d, 2H); δ = 1.62–1.75 (m, 1H); δ = 1.16–1.57 (m, 8H); δ = 0.77–1.04 (m, 6H).

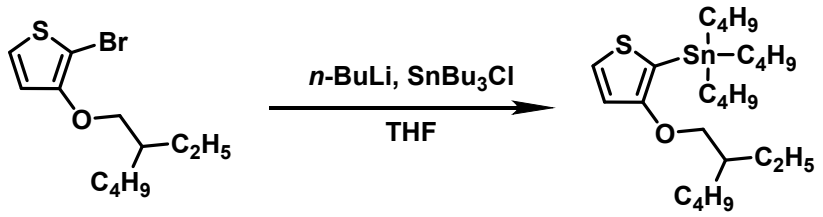

Figure S7. < Tributyl(3-((2-ethylhexyl)oxy)thiophen-2-yl)stannane synthesis>

Compound 7: Tributyl(3-((2-ethylhexyl)oxy)thiophen-2-yl)stannane, Fig. S7. Compound 6 (1.03 g, 3.55 mmol) was dissolved in anhydrous tetrahydrofuran (THF, 17.1 ml) and stirred at -78°C under nitrogen for 30 min. 1.6 M *n*-hexane solution of *n*-BuLi (2.44 ml, 3.9 mmol) was added dropwise to the solution and stirred for 4 h. Tributyltin chloride was added slowly, and then the mixture was warmed to room temperature and stirred for 1 h. The reaction mixture was quenched by adding distilled water, then the solution was poured into water (100 ml) and extracted with *n*-hexane. The organic layer was collected and dried with anhydrous sodium sulfate, and residual solvent was removed under reduced pressure. Yield = 1.57 g, 88%). ^{1}H-

NMR (500 MHz, $CDCl_3$, ppm): δ = 7.49–7.36 (d, 1H); δ = 6.98–6.91 (d, 1H); δ = 3.85–3.81 (d, 2H); δ = 1.69–1.21 (m, 21H); δ = 1.16–0.98 (m, 6H); δ = 0.95–0.80 (m, 15H).

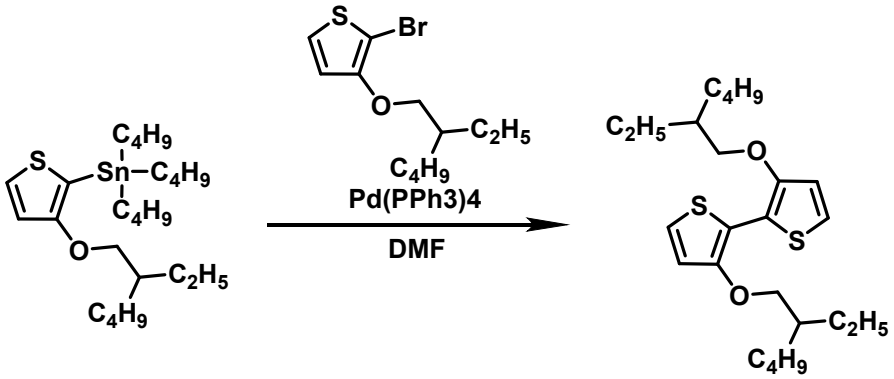

Figure S8. < BTO synthesis >

Compound 8: BTO, Fig. S8. Compounds 6 (866 mg, 2.97 mmol), 7 (1.56 g, 3.12 mmol), and $Pd(PPh_3)_4$ (102 mg, 0.088 mmol) were dissolved in anhydrous DMF (23.0 ml) and heated to 90°C under N_2 for 24 h. After cooling to room temperature the solution was poured into water (100 ml) and extracted with *n*-hexane/ethyl acetate (4:1) three times. The organic layer was collected and dried with anhydrous sodium sulfate, residual solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography with *n*-hexane to *n*-hexane/dichloromethane (9:1) eluent. Yield = 720 mg, 57%. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm): δ = 7.08 (d, J = 5.7 Hz, 2H); δ = 6.84–6.85 (d, 2H); δ = 3.98–4.03 (d, 4H); δ = 1.71–1.81 (m, 2H); δ = 1.18–1.69 (m, 16H); δ = 0.77–1.08 (m, 12H). ^{13}C-NMR (175 MHz, $CDCl_3$, δ): 11.21, 14.14, 23.06, 23.84, 29.12, 30.45, 39.85, 73.08, 113.39, 115.48, 121.39, 151.98; Calcd. C 68.20, H 9.06; found C 68.17, H 9.09.

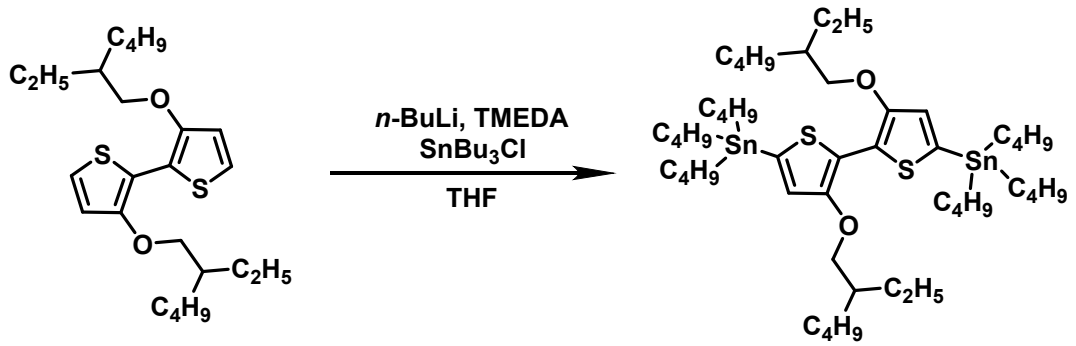

Figure S9. < BTO synthesis >

Compound 9: BTO Fig. S9. Compound 8 (328 mg, 0.776 mmol) and tetramethylethylenediamine (TMEDA, 0.254 ml, 1.71 mmol) were dissolved in anhydrous THF (14.0 ml) and stirred at -78 °C under N_2 for 30 min. 1.6 M hexane solution of *n*-BuLi (1.11 ml, 1.86 mmol) was added dropwise into the solution and stirred for 2 h. Tributyltin chloride was added at -78 °C, the mixture was warmed to room temperature, and stirred for 2 h. The reaction mixture was then cooled with ice water, quenched by adding distilled water, poured into water (100 ml), and extracted with *n*-hexane three times. The organic layer was collected and dried with anhydrous sodium sulfate, residual solvent was removed under reduced pressure, and the residue was purified by recycling gel-permeation liquid chromatography (JAI-GEL 1-H/2-H columns) with chloroform eluent. Yield = 404 mg, 52%. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm): δ = 6.83 (t, J = 12.3 Hz, 2H); δ = 4.02 (dq, J = 13.5, 4.2 Hz, 4H); δ = 1.76 (m, J = 11.9, 6.1 Hz, 2H); δ = 1.25–1.70 (m, 40H); δ = 1.00–1.18 (m, 12H); δ = 0.86–0.96 (m, 30H).

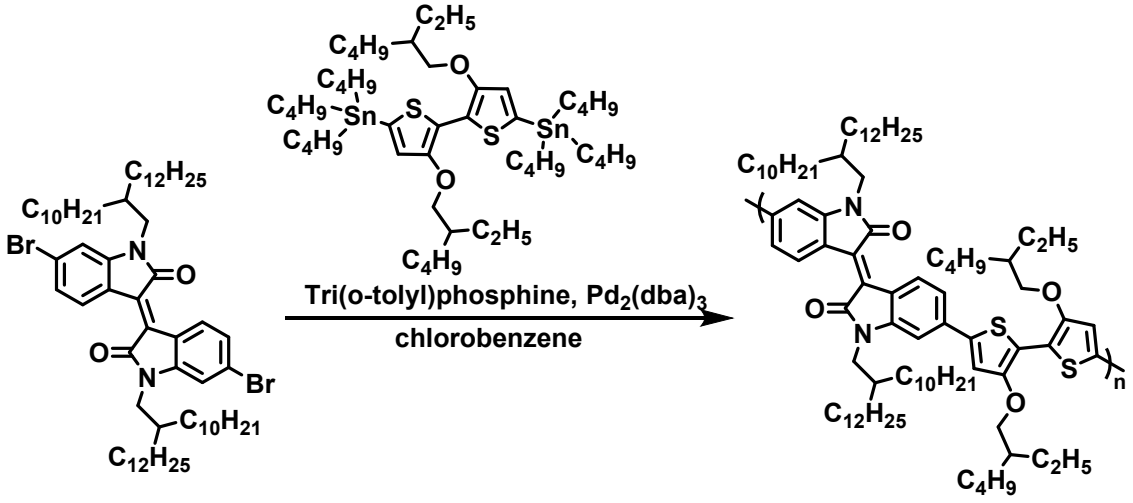

Figure S10. < PI-BTO synthesis >

Compound 10: PI-BTO, Fig. S10. Compounds 3 (112 mg, 0.103mmol), 9 (103 mg, 0.103 mmol), $Pd_2(dba)_3$ (3.76 mg), P(*o*-tol)$_3$ (12.5 mg), and chlorobenzene (4.1 ml) were added in a Schlenk tube, and the tube was charged with N_2 by three freeze-pump-thaw cycles. The mixture was stirred for 18 h at 130°C, cooled to room temperature, poured into methanol (150 ml), and stirred for a further 1 h. Precipitant was filtered and purified by washing with methanol and ethyl acetate. Yield = 116 mg, 83%. GPC: M_w = 155000, M_n = 38700, $Đ_M$ = 4.0, DP_n = 28.5.

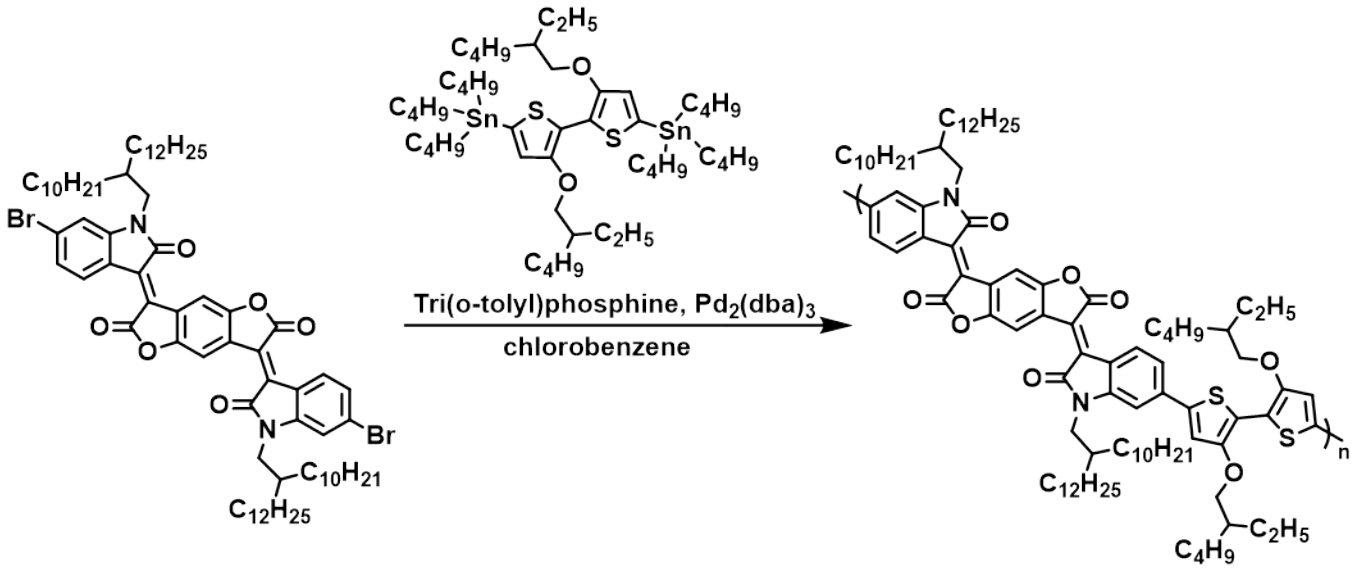

Figure S11. < PIBDF-BTO synthesis>

Compound 11: PIBDF-BTO, Fig. S11. Compounds 4 (123 mg, 0.096 mmol), 9 (96.5 mg, 0.096 mmol), $Pd_2(dba)_3$ (3.53 mg), P(*o*-tol)$_3$ (11.8 mg), and chlorobenzene (3.9 ml) were added to a Schlenk tube, and the tube was charged with N2 by three freeze-pump-thaw cycles. The mixture was stirred for 18 h at 130°C, cooled to room temperature, poured into methanol (150 ml), and stirred for a further 1 h. Precipitant was filtered and purified by washing with methanol and ethyl acetate Yield = 144 mg, 97%). GPC: M_w = 178000, M_n = 53000, $Đ_M$ = 3.7, DP_n = 33.4.

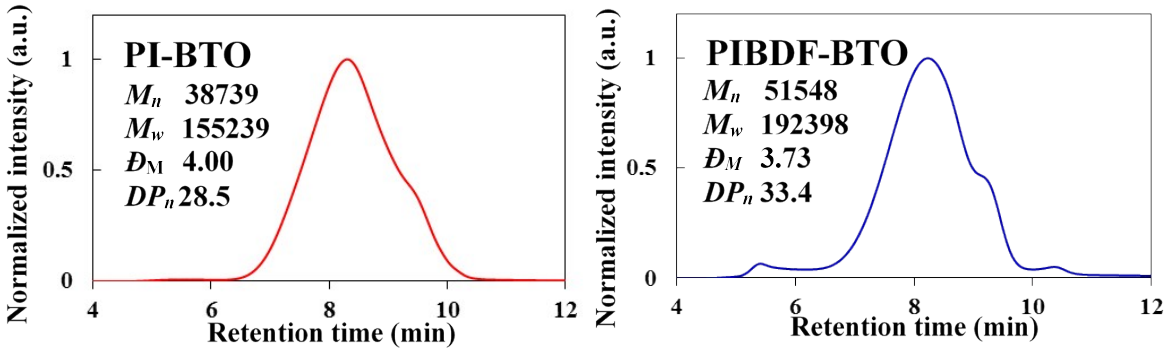

Figure S12. Gel permeation chromatography for PI-BTO and PIBDF-BTO. Molecular weights were determined with THF eluent at 40ºC.

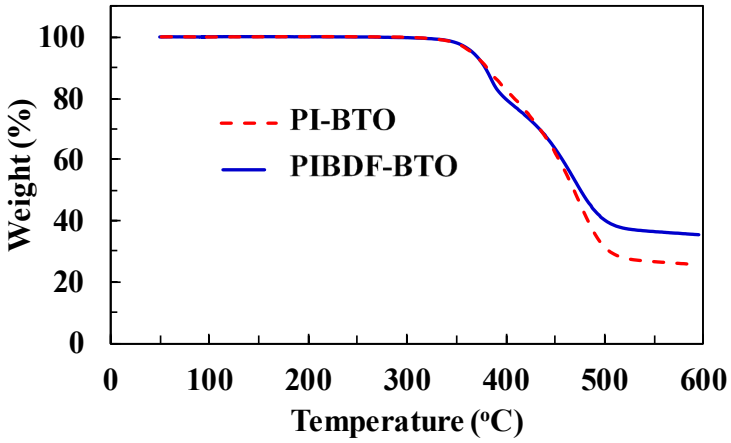

Figure S13. Thermal gravity analysis (TGA) for PI-BTO and PIBDF-BTO

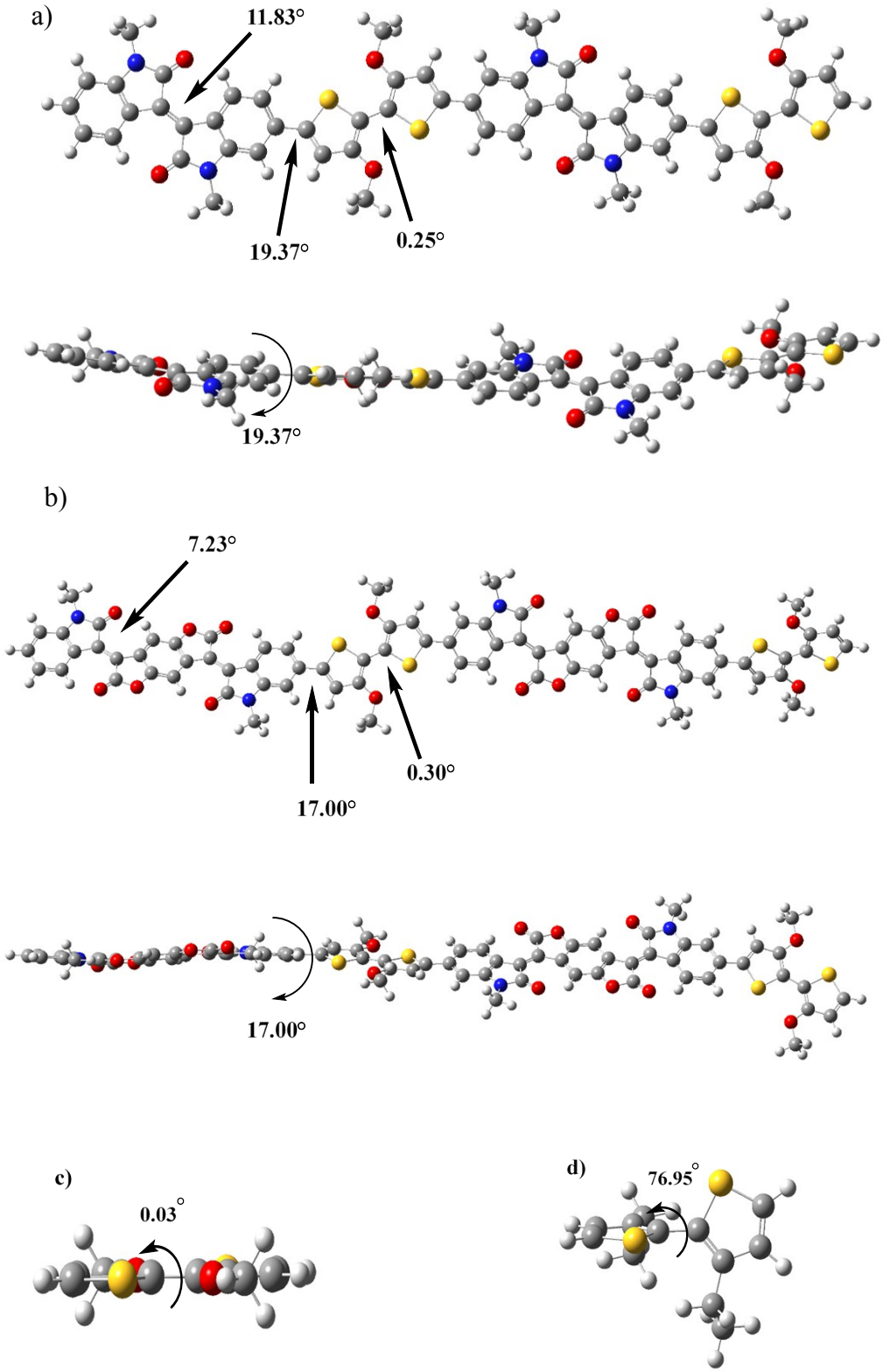

Figure S14. Optimized structures for a) PI-BTO, b) PIBDF-BTO, c) methoxy and d) ethyl substituted dithiophene. All calculations were performed at B3LYP/6-31G level.

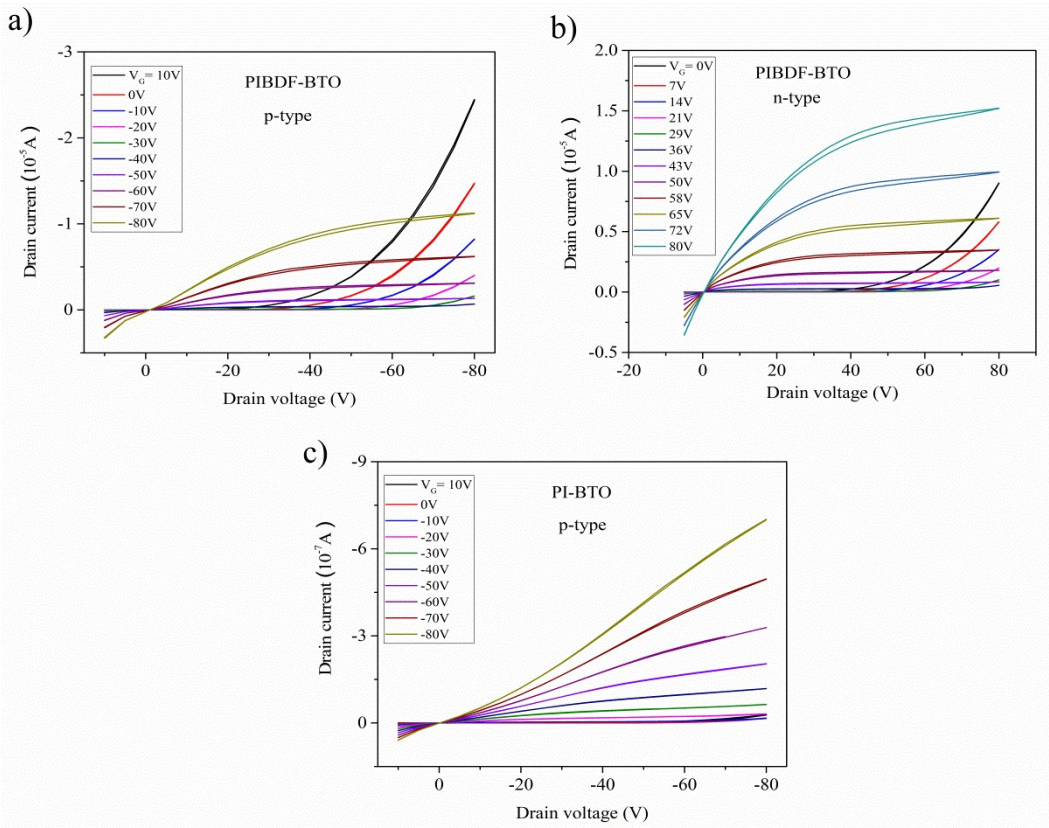

Figure S15. Output curves for (a) PIBDF-BTO p-type, (b) PIBDF-BTO n-type, and (c) PI-BTO p-type FETs