Supporting Information

N-Type Charge Carrier Transport Properties of BDOPV-Benzothiadiazole-Based Semiconducting Polymers

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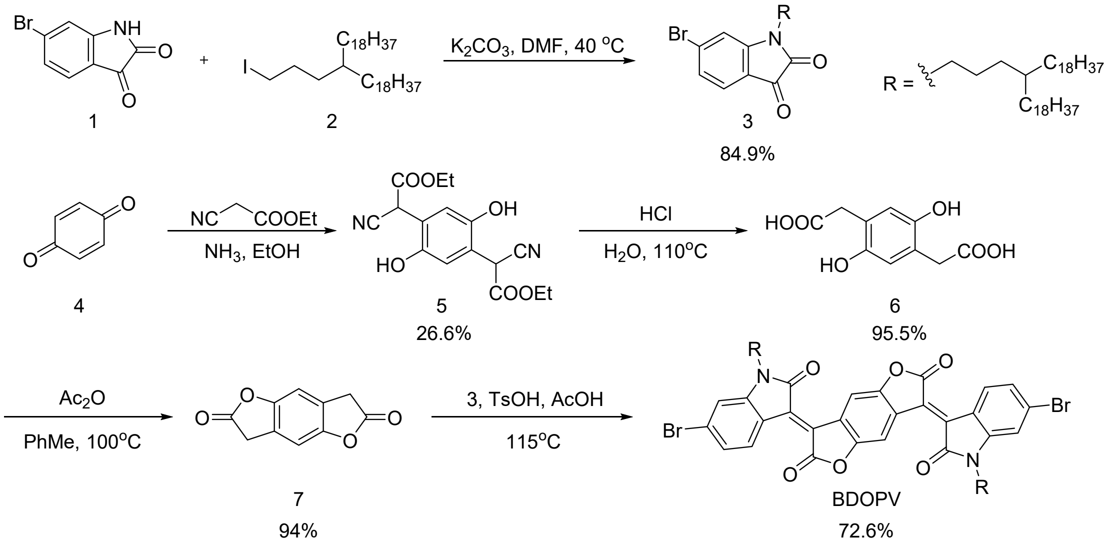
1. Monomer synthesis



Compound 2 was purchased from JiuJiang Design Optoelectronic Materials Co., Ltd.

Compound 3. [S1] To a solution of 2 (1.52 g, 2.20 mmol) in a mixture of THF (20 mL) and *N,N*-dimethylformamide (DMF) (20 mL), 6-bromoisatin (compound 1, 500 mg, 2.20 mmol) and K_2CO_3 (611 mg, 4.40 mmol) were added. The mixture was stirred at 50 °C for 16 h and then the solvents were removed under reduced pressure. The residues were dissolved in $CHCl_3$ (150 mL), washed with water and brine, and then dried over anhydrous magnesium sulfate. After removal of the solvents under reduced pressure, the residue was purified by silica gel chromatography with eluent (hexane:CH_2Cl_2 = 1:1) to give 3 as an orange solid (1.47 g, 84.9%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.05 (s, 1H), 3.67 (t, *J* = 7.0 Hz, 2H), 1.65 (s, 2H), 1.24 (d, *J* = 1.4 Hz, 114H), 0.96–0.82 (m, 8H).

Compound 5. [S1] A mixture of 1 mL of ethyl cyanoacetate and 4 mL of ethanol was placed in a 20 mL flask. Meanwhile, 2.00 g (18.5 mmol) of 1,4-benzoquinone (4) in 20 mL of ethanol was heated to 40 °C in a 50 mL flask. When most of the quinone was dissolved, 2 mL of ethyl cyanoacetate was added and the mixture was stirred for another 10 minutes. After that, the mixture was transferred to a 50 mL of dropping funnel by a glass syringe. Then, 1 mL of concentrated ammonium hydroxide was added to a three-necked 300 mL flask. A solution of 4 mL of concentrated ammonium hydroxide in 6 mL of water was placed in one another 50 mL dropping funnel, which was loosely stoppered. After 1 mL of concentrated ammonium hydroxide solution in the 300 mL flask started to stir, the other two solutions were added through the dropping funnels at a constant rate over 5 minutes. After that, stirring was continued for additional 10 minutes. The mixture was left stand for 1 hour. The precipitate was collected by filtration and washed with ethanol several times to give a purple solid (1.36 g, 26.6%). The product was directly used in the next step.

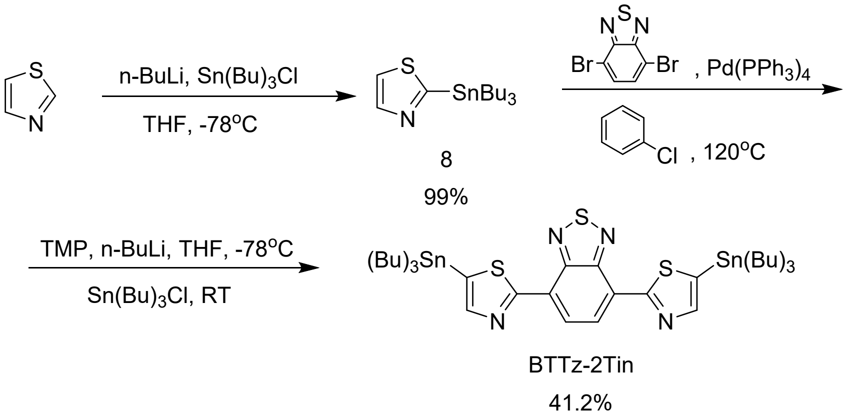
Compound 6. [S1] 1.36 g of compound 5 and 8 mL of concentrated hydrochloric acid in 7 mL of deionized water were added to a 30 mL flask equipped with a reflux condenser. Then, the mixture was heated up to 110 °C for 20 h to complete the hydrolysis. At first, the mixture needed to be refluxed gently, and then vigorously. After 20 h, 7 mL of deionized water and 150 mg of activated charcoal were added and the mixture was stirred and boiled for 3 minutes, after which it was rapidly filtered with suction through 2 layers of filter paper. The filtrate was put in the fridge for 5 h, and the precipitates were collected and dried to give 6 as a snow-white solid (884 mg, 95.5%). The resulting compound was used directly for the next step.

Compound 7. To a suspension of 6 (880 mg, 3.89 mmol) in toluene (40 mL), Ac_2O (8 mL) was added. The mixture was stirred at 100 °C for 5 h and then the solvent was removed under reduced pressure. The residue was recrystallized from toluene to give 7 as a pink crystal (695 mg, 94%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.07 (s, 1H), 3.78 (s, 2H).

BDOPV. [S2] To a solution of 1-alkyl-6-bromoisatin (compound 3) (1.00 g, 1.27 mmol) in acetic acid (15 mL), compound 7 (100 mg, 0.530 mmol) and toluene sulfonic acid monohydrate (28 mg, 0.15 mmol) were added. The mixture was stirred at 115 °C under argon atmosphere for 17 h, and then cooled down to room temperature and filtered with suction. After washed with acetic acid and methanol, the filtration residues were dissolved in $CHCl_3$ and then washed with water and brine, and dried over anhydrous magnesium sulfate. After removal of the solvents under reduced pressure, the products were collected to give a deep blue solid (665 mg, 72.6%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.14 (s, 3H), 8.96 (d, *J* = 8.7 Hz, 2H), 7.21 (d, *J* = 7.1 Hz, 2H), 6.97 (s, 1H), 3.74 (s, 1H).



Compound 8. [S3] *n*-Butyllithium (1.59 M in hexane, 8.1 mL, 12.9 mmol) was added dropwise to a stirred solution of thiazole (1.00 g, 11.74 mmol) in anhydrous THF (40 mL) held at −78 °C under N_2 atmosphere over 30 min. The reaction mixture was stirred for 2 h at −50 °C and then *n*-Bu_3SnCl (3.5 mL, 13 mmol) was added to the mixture. The mixture was allowed to warm to room temperature and stirred overnight. The solvent was mostly removed under reduced pressure at a temperature below 40 °C before it was poured into deionized water to quench. Then, the mixture was diluted and extracted with dichloromethane, washed with deionized water, then dried over anhydrous magnesium sulfate and filtered. The solvent was removed at a temperature below 40 °C to leave light yellow oil (99%), which was directly used in the next step as soon as possible.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16 (d, *J* = 3.0 Hz, 1H), 7.54 (d, *J* = 3.0 Hz, 1H), 1.74–0.78 (m, 108H).

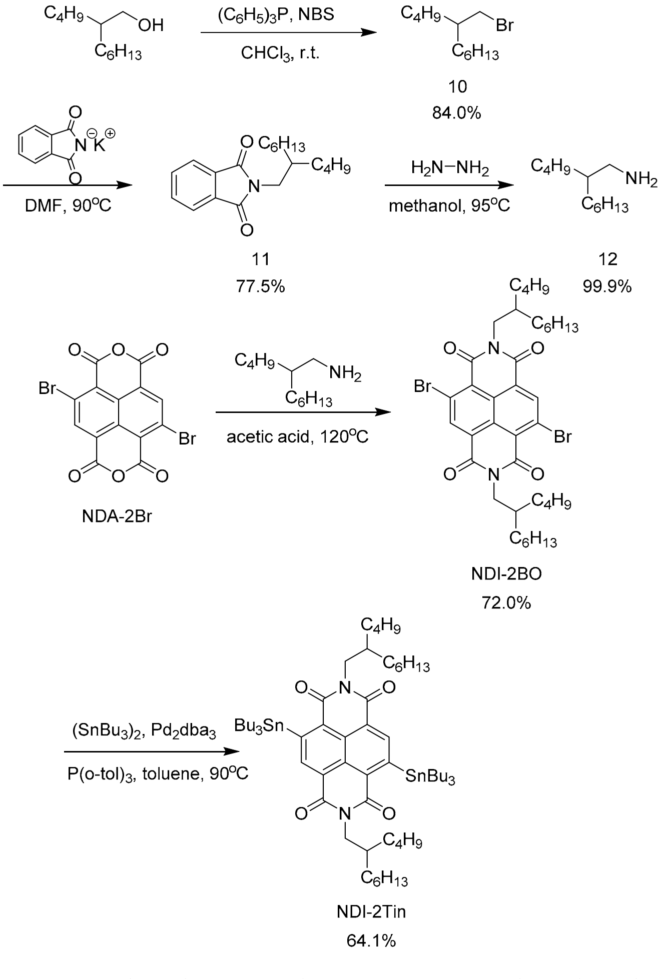
Compound 9. [S4] To a solution of 4,7-dibromo-2,1,3-benzothiadiazole (1.15 g, 3.91 mmol) and compound 8 (11.74 mmol) in anhydrous chlorobenzene (35 mL), catalyst $Pd(PPh_3)_4$ (226 mg, 5% mmol) was added. The mixture was heated at 120 °C and then refluxed. After 17 h, the mixture was cooled to room temperature, the solvent was removed under reduced pressure and diluted with chloroform. The solution was washed with deionized water, dried over anhydrous magnesium sulfate and filtered. The solvent was removed completely under reduced pressure and recrystallized from chloroform/methanol to give an orange needle-like crystal (768 mg, 65%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.75 (s, 1H), 8.07 (d, *J* = 3.2 Hz, 1H), 7.64 (d, *J* = 3.2 Hz, 1H).

BTTz-2Tin. [S5] 2,2,6,6-Tetramethylpiperidine (TMP, 0.14 mL ,0.83 mmol) was dissolved in 2 mL of THF, and then *n*-butyllithium (1.59 M in hexane, 0.52 mL, 0.83 mmol) was added dropwise at 0 °C. After stirring for 15 min at 0 °C, the mixture was transferred into a solution of compound 9 (100 mg, 0.330 mmol) in 10 mL of anhydrous THF via a syringe at −78 °C. The mixture was stirred at −50 °C for 90 min and then *n*-Bu_3SnCl (0.27 mL, 1.0 mmol) was added.

The reaction mixture was allowed to warm to room temperature and stirred overnight. The mixture was quenched with deionized water and extracted with ethyl acetate. The organic extracts were washed with deionized water, dried over anhydrous magnesium sulfate and filtered. After removal of the solvents under reduced pressure, the residue was purified via a short column (silica gel, hexane: EA = 1:1). It was further purified by using a recycling HPLC to give orange oil (120 mg, 41.2%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.71 (s, 1H), 7.99 (s, 1H), 1.72–0.78 (m, 53H).



Compound 10. [S6] To 2-butyl-1-octanol (10.0 g, 53.7 mmol) and triphenylphosphine (16.9 g, 64.4 mmol) in $CHCl_3$ (80 mL) in an ice-water bath, NBS (11.5 g, 64.4 mmol) was added in several portions within 15 min and stirred for 21 h. After removal of the solvent, a large amount of hexane was added to the reaction mixture and it was filtered with suction. The organic phase was evaporated and then purified by short column chromatography (silica gel, hexane) to give colorless oil (11.2 g, 84.0%), which was assumed pure and directly used in the next step.

Compound 11. [S6] Potassium phthalimide (1.23 g, 6.65 mmol) was added to a solution of compound 10 (1.50 g, 6.04 mmol) in 15 mL of dry DMF. The reaction mixture was stirred for 16 h at 90 °C. After cooling to room temperature, the reaction mixture was poured into deionized water and extracted with dichloromethane. The combined organic extracts were washed with 0.2N KOH solution, deionized water, and saturated ammonium chloride solution, dried over anhydrous magnesium sulfate, and the solvents were removed under reduced pressure. The resulting crude yellow oil was purified via column chromatography (silica gel, dichloromethane: hexane = 1:1), giving 11 as pale yellow oil (1.47 g, 77.5%), which was assumed pure and directly used in the next step.

Compound 12. [S6] Compound 11 (1.47 g, 4.68 mmol), hydrazine hydrate (hydrazine, 51%) (1.0 mL) and 20 mL methanol were added to a flask. The mixture was stirred at 95 °C and the reaction progress was monitored by TLC. After the disappearance of the starting imide, methanol was removed under reduced pressure, and the residue was diluted with dichloromethane and washed with 10% KOH solution. Aqueous layers were combined and extracted with dichloromethane. The organic extracts were then washed with brine and dried over anhydrous magnesium sulfate. After removal of dichloromethane, yellow oil was obtained (4.68 mmol), which was directly used in the next step without further purification.

NDI-2BO. [S6] A flask was charged with NDA-2Br (498 mg, 1.17 mmol), compound 12 (866 mg, 4.68 mmol) and 10 mL of acetic acid, and the mixture was stirred at 120 °C under argon for 12 h. After that, approximately 2/3 of the solvent was removed under reduced pressure and the concentrate was added to methanol. The resulting red solid was collected by filtration and washed with methanol. The red solid was dissolved in dichloromethane completely and then purified via column chromatography (silica gel, dichloromethane: hexane = 1:1). The resulting orange solid was further purified via recrystallization from hexane to give a yellow solid as NDI-2BO (638.5 mg, 72.0%).

^{1}H NMR (300 MHz, CDCl$_3$): δ 9.00 (s, 1H), 4.24–4.07 (m, 2H), 2.03 (s, 1H), 1.51–0.76 (m, 31H).

NDI-2Tin. [S7] To a two-necked 30 mL flask, NDI-2BO (100 mg, 0.132 mmol), bis(tributyltin) (157 mg, 0.270 mmol), tri(*o*-tolyl)phosphine (8.00 mg, 0.0264 mmol) and tris(dibenzylideneacetone)dipalladium(0) (6.0 mg, 0.0066 mmol) were added and degassed with argon for 5 min. After that, 2 mL of dry toluene was syringed into the flask and the reaction mixture was heated to 90 °C for 24 h. After cooling to room temperature, the reaction mixture was directly purified by a short column chromatography (silica gel, chloroform: hexane = 1:1) and then further purified by HPLC to afford yellow oil (100 mg, 64.1%).

^{1}H NMR (300 MHz, CDCl$_3$): δ 8.97 (s, 1H), 4.15 (d, *J* = 7.2 Hz, 3H), 1.99 (s, 1H), 1.70–0.61 (m, 100H). 13C NMR (75 MHz, CDCl$_3$): δ 161.33, 139.32, 128.55, 125.41, 45.47, 36.49, 31.97, 31.93, 31.56, 30.07, 29.69, 29.68, 29.64, 29.60, 29.40, 29.35, 26.36, 22.71, 14.15. IR (neat): υ 2960, 2922, 2852, 2364, 2357, 2338, 2330, 1700, 1657, 1635, 1545, 1464,1439, 1374, 1308,1242, 1204, 1065, 790, 770, 725, 697, 686, 654, 643, 627, 611 cm^{-1}. MALDI-TOF MS (dithranol): m/z calcd for 1067.19.

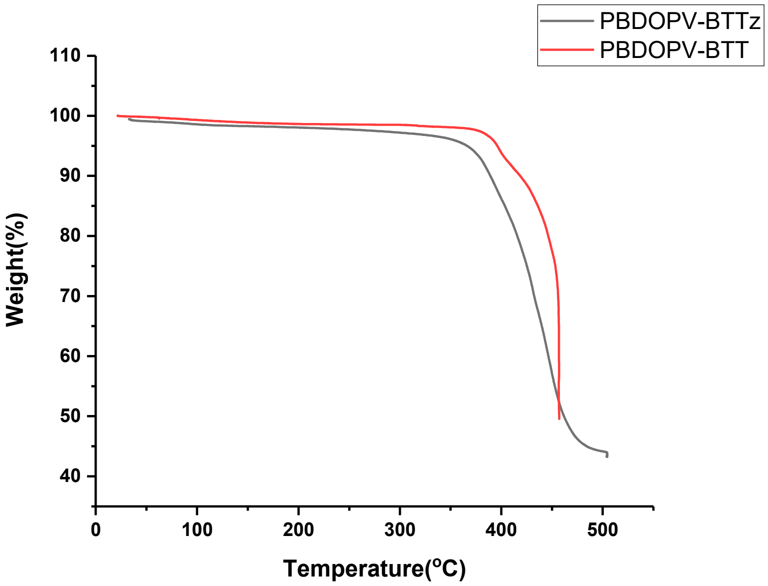


Figure S1. Thermogravimetric analysis (TGA) curves of the copolymers under nitrogen atmosphere at the heating rate of 10 °C min⁻¹.

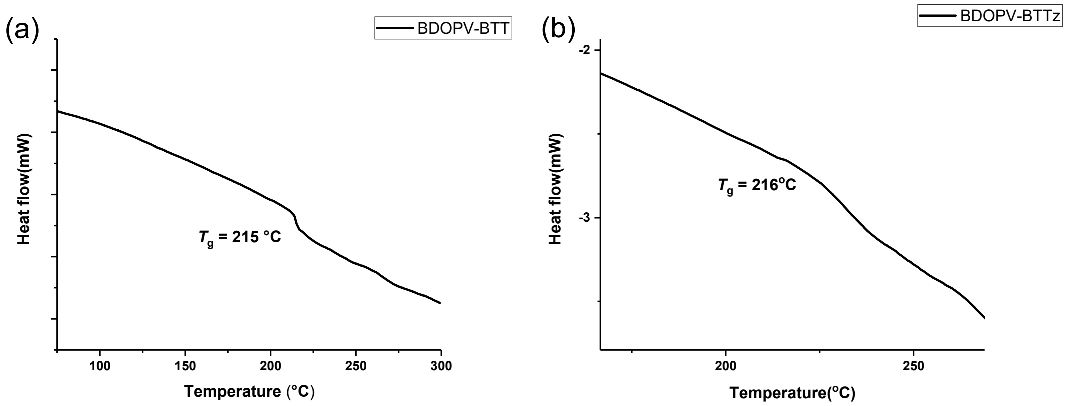


Figure S2. Differential scanning calorimetry (DSC) curves of the copolymers. All the DSC curves are the second heating and cooling processes under nitrogen flow (50 mL min⁻¹) at the scan rate of 10 °C min⁻¹.

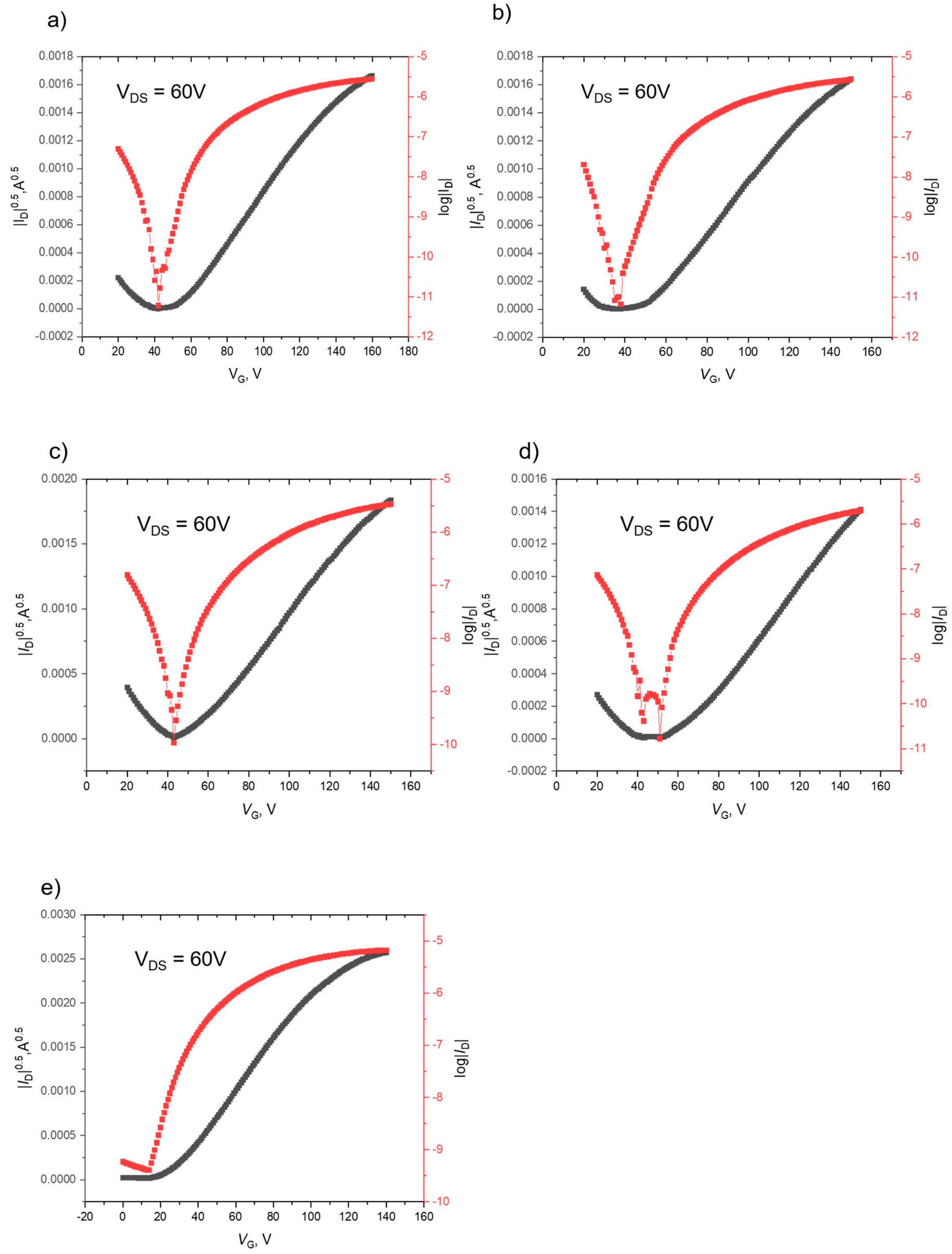


Figure 3-1. Transfer curves of thin film transistors based on PBDOPV-BTT: (**a**) as cast, after thermal annealing at (**b**) 150 °C, (**c**) 180 °C, (**d**) 210 °C, and (**e**) 240 °C (L = 100 m and W = 1000 m).

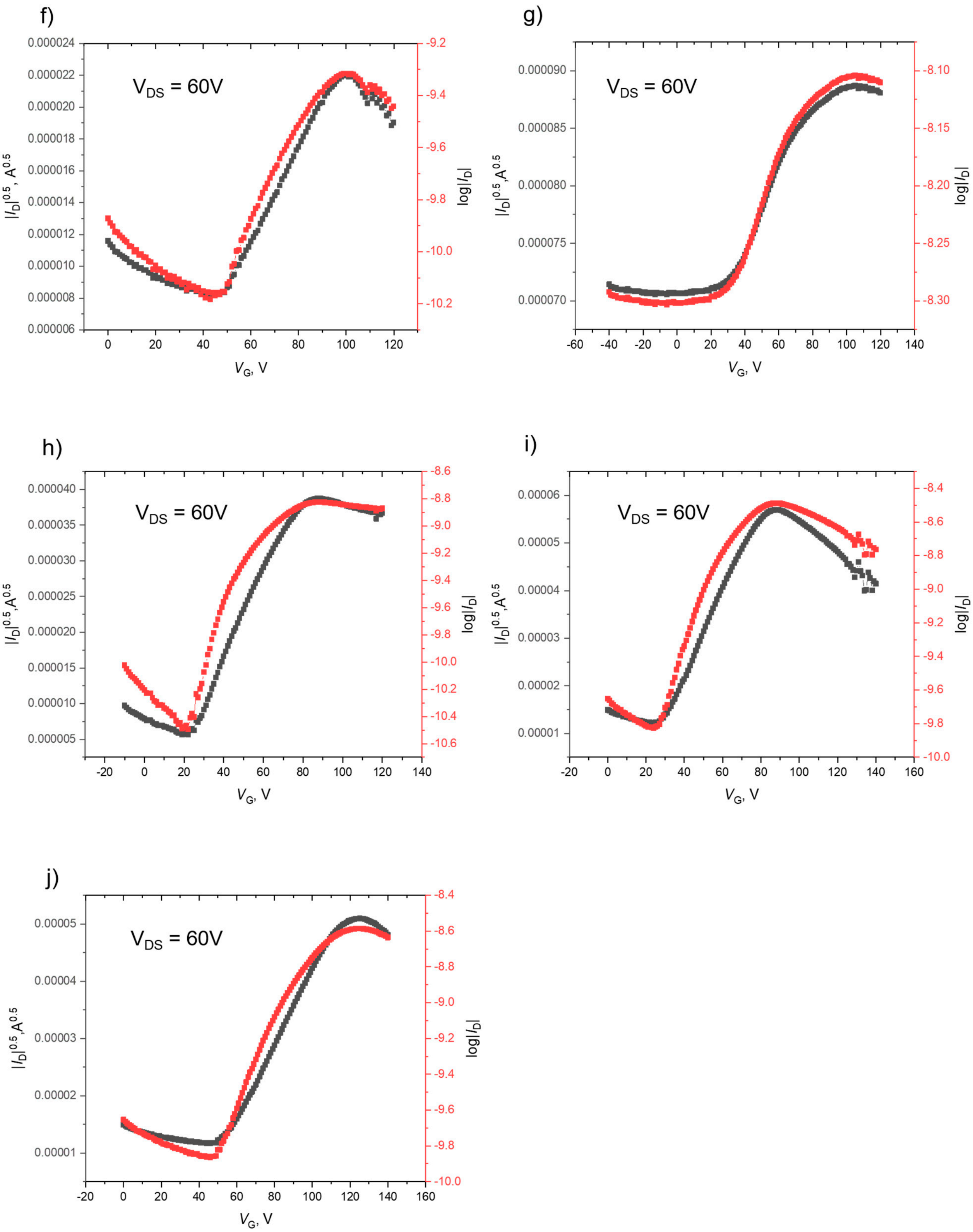


Figure S3-2. Transfer curves of thin film transistors based on PBDOPV-BTTz: (**a**) as cast, after thermal annealing at (**b**) 150 °C, (**c**) 180 °C, (**d**) 210 °C, and (**e**) 240 °C (*L* = 100 m and *W* = 1000 m).

Table S1. Dihedral angles between BTT(z) and BDOPV monomer units in PBDOPV-BTT(z) obtained by DFT (B3LYP, 6-31G(d)).

	Average dihedral angle between BTT(z) and BDOPV monomers (°)			
	Dimer	**Tetramer**	**Hexamer**	**Average**
PBDOPV-BTT	18.54	18.95	18.91	18.80
PBDOPV-BTTz	20.85	21.38	19.92	20.72

Table S2. Average HOMO and LUMO energy levels and energy gaps of PBDOPV-BTT(z) and their different conformations obtained by DFT (B3LYP, 6-31G(d)).

	Energy Levels/Gap Conformer A (eV)			Energy Levels/Gap Conformer B (eV)		
	E_{HOMO}	E_{LUMO}	E_g^{calc}	E_{HOMO}	E_{LUMO}	E_g^{calc}
PBDOPV-BTT	−5.324	−3.429	1.895	−5.379	−3.598	1.781
PBDOPV-BTTz	−5.587	−3.480	2.107	−5.589	−3.651	1.938
ΔE (eV)	−0.263	−0.051	+0.212	−0.210	−0.053	+0.157

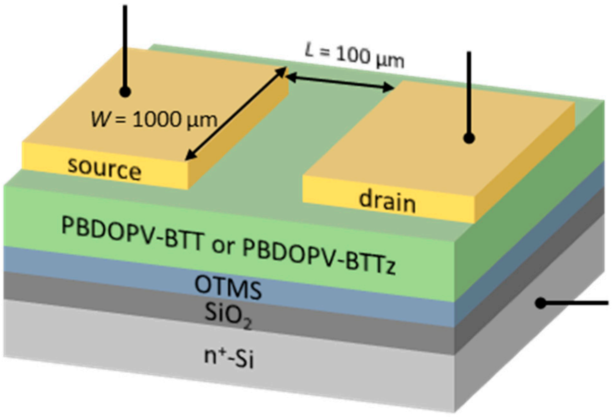


Figure S4. Schematic illustration of the thin film transistor structure, where n$^+$-Si is a heavily *n*-doped Si wafer coated with a SiO_2 layer, OTMS is octadecyltrimethoxysilane self-assembly monolayer, source and drain electrodes are vacuum-deposited Au, *W* and *L* are channel width and length, respectively.

References

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