Supporting Information

Direct Arylation Polymerization of Asymmetirc Push-Pull Aryl Halides

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Experimental Section

Materials and characterizations

All reagents were purchased from Sigma Aldrich and used without further purification unless otherwise noted. Anhydrous *N*,*N*-dimethylformamide is prepared from MB-SPS solvent purifying system. ¹H and ¹³C NMR spectra were recorded on a Brucker ARX 400 at 293 K with deuterized chlorofrom as solvent. Size exclusive chromatography (SEC) was performed in tetrahydrofuran or trichlorobenzene under room temperature or 140°C with calibration curve based on polystyrene standards. UV-vis-NIR spectra were measured with an Agilent Technologies Cary 6000i UV-Vis-NIR spectrophotometer (300-1300 nm). All solution spectra were collected in chloroform and thin film spectra from drop-casted samples on glass substrate.

Organic field-effect transistors fabrication

For FET devices, a heavily n-doped Si wafer with a 300-nm SiO₂ surface layer (capacitance of 11 nF/cm²) was employed as the substrate with Si wafer serving as the gate electrode and SiO₂ as the dielectric. The gold S/D electrodes were sputtered and patterned by photolithography technique. The device channel length was 20 μ m, and the channel width was 1400 μ m. For the octadecyltrichlorosilane (OTS) modification, the silicon wafer (with Au bottom contact) was first cleaned with hot piranha solution (H₂SO₄ (98%): H₂O₂ (30% water solution) = 7 : 3). It was then further subjected to sonication sequentially in water and acetone for 6 min each. After drying at an oven, the silicon wafer was then put in a petri dish with a small drop of OTS. The dish was then covered and heated in a vacuum oven at 120 °C for 3 hours resulting in the formation of an OTS self-assembled monolayer on the surface. The OTS modified substrates were

rinsed successively with hexane, ethanol, and chloroform, and dried by nitrogen. The semiconductor layer was deposited on the OTS-treated Si/SiO_2 substrates by spin coating 10 mg/mL semiconductor solution in chloroform with spin speed of 2000 r.p.m. and spin time of 60 s. The devices were then annealed in nitrogen golvebox at 120 °C for 10 minutes.

Device characterization

Device characterization was carried out using Keithley 4200 in ambient air. The field-effect mobility was calculated in the saturation regime by using the equation $I_{DS} = (\mu W C_i/2L)(V_G - V_T)^2$, where I_{DS} is the drain-source current, μ is the field-effect mobility, W is the channel width, L is the channel length, C_i is the capacitance per unit area of the gate dielectric layer, V_G is the gate voltage, and V_T is the threshold voltage.

General method for polymerization

General method for the direct arylation polymerization.

To a Schlenk tube was added the monomer TBII-Br, catalyst, ligand, base, additive, then vacuum for about 5min and purge with N_2 , and repeated the vacuum and purge for three times. After then, added the degassed solvent into the tube and heated in oil bath. When the reaction was done added chloroform and water into the tube collected the organic phase and precipitated with methanol. The precipitate solid was submit to soxhlet extraction with methanol, acetone, hexane and chloroform, collected the hexane fraction and chloroform fraction, precipitate with methanol to get the solid product.

General method for the Suzuki coupling polymerization.



To a Schlenk tube was added the monomer II-2B (44 mg, 0.046mmol, 1.0 eq), TII-2Br(30 mg, 0.046mmol, 1.0 eq), Pd(Ph₃)₄ (2.6mg, 0.002mmol, 0.05eq), then vacuum for about 5min and purge with N₂, and repeat the vacuum and purge for three times. After then, added the degassed 1 mL toluene and aqueous potassium carbonate (2.0 M, 0.3 mL) into the tube and heat to 100°C in oil bath. After 96 hours added chloroform 10mL and 1M HCl solution 5mL into the tube collect the organic phase and precipitate with methanol. The precipitate solid was submit to soxhlet extraction with methanol, acetone, hexane and chloroform, collect the chloroform fraction, precipitate with methanol to get the solid product.

Synthesis



Scheme 1. Synthetic routes for monomers II-2Br and TII.



A round schlenk flask was charged with tribasic potassium phosphate (26.04 g, 122.68 mmol, 2.0 equiv.), copper (I) iodide (1.17 g, 6.13 mmol, 0.1 equiv.) and a stir bar, after vacuum and purged with N_2 for three times 3-bromothiophene (10.0 g, 61.3 mmol, 1.0 equiv.), octylamine (9.59 g, 73.6 mmol, 1.2 equiv.), N,N-dimethylaminoethanol (61 mL, 1M based on 3-bromothiophene) was added. This mixture was heated at 80 °C for 48 h, after which it was poured into saturated NH₄Cl, extracted three times with hexanes, dried on MgSO₄, filtered, and concentrated via rotary evaporation. The residue was purified by flash silica gel chromatography (10% EtOAc/hexanes), 9.7g(45.9 mmol) vellow oil was got. 75%. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.15 (dd, 1H, J_1 = 4.8 Hz, $J_2 = 3.0$ Hz), 6.62 (d, 1H, J = 4.8 Hz), 5.95 (s, 1H), 3.57 (s, 1H), 3.07 (t, 2H, J = 6.8 Hz), 1.66-1.59 (m, 2H), 1.40-1.29 (m, 10H), 0.90 (t, 3H, *J* = 6.8 Hz). To a solution of oxalyl chloride (8.9 g, 70 mmol) diluted in anhydrous dichloromethane (30 mL) cooled at 0 [°]Cunder an nitrogen atmosphere, a solution of compound 2 (11 g, 52.04 mmol)diluted in anhydrous dichloromethane (10 mL) was added dropwise over 30 min. After 30 min, triethylamine (23.17 g, 229.0 mmol) was added dropwise over 30 min. The resulting mixture was allowed to warm to room temperature. After stirring for 15 h at room temperature, the mixture was quenched with water then extract with dichloromethane. The organic phase was evaporated under reduced pressure. The residue was purified by silica gel chromatography, eluting with (CH₂Cl₂) then re-crystal with hexane to provide 4.9 g (35.5%) as a red solid. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 8.00 (d, 1H, J = 4.8

Hz), 6.78 (d, 1H, J = 4.8 Hz), 3.65 (t, 2H, J = 7.2 Hz), 1.68-1.61 (m, 2H), 1.31-1.25 (m, 10H), 0.86 (t, 3H, J = 6.4 Hz). IR(cm⁻¹): 1362.4, 1471.3,1699.0,1736.8, 2852.9,2919.6, 2945.0, 3085.9.



Sodium hydride 60% dispersion in mineral oil (850 mg, 21.4 mmol) was dispersed in dry DMF (100 ml) at 0 °C before addition of 5-bromoisatin (4.00 g, 17.7 mmol). After stirring for 30 minutes 1-bromo-2-hexyldecane (6.10 g, 20.0 mmol) was added and the mixture heated to 65 °C for 24h. After cooling the mixture was extracted with water and ethyl acetate and the organic fractions washed with brine and dried over MgSO₄. After remove the solvent the yellow oil was directly used for the next step. In a mixture of N₂H₄ (10 ml) and DMSO (20 ml) 6-bromo-1-(2-hexyldecyl)indoline-2,3-dione (4.8 g, 10.66 mmol) was dissolved and heated to 140 °C for 2h. After cooling H₂O:HClcon. (1:1) (50 ml) was added and the mixture was subsequently extracted with ethyl acetate. Organic fractions were combined and washed with brine and dried over MgSO4 to give a yellow crude oil that was purified by silica column chromatography using EtOAc/hexanes= $1/20 \sim 1/10$ as mobile phase. The pure fractions were concentrated in vacuum to give 2.7 g of yellow oil (yield 35% two steps). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.15 (d, 1H, J = 8.0 Hz), 7.08 (d, 1H, J = 8.0 Hz), 6.92 (s, 1H), 3.54 (d, 2H, J =7.2 Hz), 3.45 (s, 1H), 1.83 (br, 1H), 1.26-1.24 (br, 24H), 0.87 (t, 6H, J = 7.2 Hz).



TosOH (106 mg, 0.62 mmol) was added to a solution of compound 3 (1.64 g, 6.18 mmol) and compound 6 (2.7 g, 6.19 mmol) in acetic acid (30 ml). This mixture was reacted at 110 °C for 24h before quenching it by pouring the mixture over ice. The mixture was extracted with hexane and washed with brine. The crude product was submit to silica gel column chromatography using DCM/hexanes= $1/3 \sim 1/2$ as mobile phase. 2.8g black solid was got with 66% yield. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 9.13 (d, 1H, J = 8.4 Hz), 7.61 (d, 1H, J = 5.6 Hz), 7.22 (dd, 1H, J₁ = 8.4 Hz, J₂ = 1.6 Hz), 6.97 (d, 1H, J = 1.6 Hz), 6.77 (d, 1H, J = 5.2 Hz), 3.77 (t, 2H, J = 7.2 Hz), 3.69 (d, 2H, J = 7.6 Hz), 1.91 (br, 1H), 1.74-1.68 (m, 2H), 1.30-1.24 (m, 36H), 0.86-0.84 (m, 12H). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 170.3, 169.0, 152.7, 145.0, 136.7, 130.0, 129.7, 124.9, 124.8, 121.5, 119.9, 114.7, 111.4, 110.7, 44.5, 41.7, 35.9, 31.8, 31.7, 31.3, 29.9, 29.6, 29.4, 29.2, 29.1, 29.1, 28.3, 26.8, 26.2, 22.6, 14.0. IR(cm⁻¹): 1509.9, 1598.8, 1675.6, 2853.9, 2922.8, 2956.4. HRMS (ESI): Calcd for C38H56BrN2O2S 683.3240. Found: 683.3233 [M + H]⁺. Anal. Calcd for C38H55BrN2O2S: C, 66.74; H, 8.11; N, 4.1.; S, 4.69. Found: C, 67.00; H, 7.79; N, 4.80; S,4.72.



7-(bromomethyl)pentadecane (0.872 g, 2.86 mmol), II-NH-2Br (0.5 g, 1.19 mmol),

K₂CO₃ (0.987 g, 7.14 mmol) was added into a flask then DMF 7 mL was added. The mixture was stirred at 100°C for 16h. Add water 50mL into flask the extract with EtOAc(50mL) for twice. Submit to column chromatography(Hexane:EtOAc=30:1-20:1) to get 0.9g product then precipitate with methanol to get 0.7g red solid with 67% yield. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 9.06 (d, 2H, J = 8.4 Hz), 7.16 (dd, 2H, $J_I = 8.4$ Hz, $J_2 = 1.2$ Hz), 6.90 (d, 2H, J = 1.2 Hz), 3.62 (d, 4H, J = 7.2 Hz), 1.88 (br, 2H), 1.31-1.25 (m, 48H), 0.86 (t, 12H, J = 6.0 Hz). IR(cm⁻¹): 1594.1,1691.5, 2853.1, 2922.0. Anal. Calcd for C48H72Br2N2O2: C, 66.35; H, 8.35; N, 3.22. Found: C, 66.08; H, 8.46; N, 3.89.



To Schlenk tube added II-2Br (0.3)0.35mmol), a was g, 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (0.193 g, 0.76 mmol), AcOK (0.203 g, 2.1 mmol), Pd(dppf)Cl₂ (0.014 mg, 0.017 mmol), then vacuum and purge with N₂ for three times. Then added de-gas 1,4-dioxane 10mL and heat to 80°C for 18hrs. When the reaction is done extract with 30mL EtOAc and 50mL water. Then submit to column chromatography(Hexane:EtOAc=20:1) to get product as red solid 0.205g, yield=60%. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 9.13 (d, 2H, J = 8.0 Hz), 7.47 (d, 2H, J = 8.0 Hz), 7.16 (s, 2H), 3.69 (d, 4H, J = 7.2 Hz), 1.95 (br, 2H), 1.36-1.25 (m, 72H), 0.86 (t, 12H, J = 6.0 Hz). ¹³C NMR (100 MHz, CDCl₃), δ (ppm):168.0, 144.4, 134.2, 128.8, 128.6, 124.1, 113.4, 83.9, 44.3, 36.0, 31.8, 31.7, 31.5, 29.9, 29.5, 29.5, 29.2, 26.3,

24.8, 22.6, 22.5, 14.0. HRMS (ESI): Calcd for C60H97B2N2O6 963.7527. Found: 963.7539 [M + H]⁺



To a Schlenk tube was added compound 4 (1g, 3.77mmol), Lawessin reagent (1.52 g, 3.77mmol), then 20mL of toluene was added and heat to 60°C for 2hrs. When the reaction is done evaporated the solvent then submitted to column chromatography (DCM:Hexane=1:1) to get 0.34g red sold. Yiled=36%.¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.54 (d, 2H, J = 5.2 Hz), 6.82 (d, 2H, J = 5.2 Hz), 3.81 (t, 4H, J = 7.2 Hz), 1.73 (t, 4H, J = 6.8 Hz), 1.34-1.26 (m, 18H), 0.87 (t, 6H, J = 6.4 Hz). IR(cm⁻¹): 1307.2, 1605.1, 1681.4, 2852.7, 2924.0, 2952.4. Anal. Calcd for C28H38N2O2S2: C, 67.43; H, 7.68; N, 5.62.; S,12.86. Found: C, 67.20; H, 7.66; N, 6.15; S,12.02.



To a flask was added TII (0.2g, 0.4mmol), NBS (N-Bromobutanimide) (0.157g, 0.88mmol), then add DCM 10mL to stir at 25°C for 4hrs. Then run column chromatography (DCM:Hexane=1:1) to get the desired product as purple solid. 0.184g, yield=70%.¹H NMR (400 MHz, CDCl₃), δ (ppm): 6.77 (s, 2H), 3.71 (t, 4H, J = 7.2 Hz), 1.67 (br, 4H), 1.31-1.25 (m, 20H), 0.86 (t, 6H, J = 5.6 Hz).¹³C NMR (100 MHz, CDCl₃),

δ (ppm):169.8, 149.7, 123.0, 119.4, 114.7, 114.5, 41.8, 31.7, 29.1, 29.1, 28.5, 26.8, 22.5, 14.0. HRMS (ESI): Calcd for C28H37Br2N2O2S2 655.0658. Found: 655.0657 [M + H]⁺



To a schlenk tube was added the monomer TII (70 mg, 0.14mmol, 1.0 eq), II-2Br(122 mg, 0.14mmol, 1.0 eq), Pd₂(dba)₃CHCl₃ (1.3mg, 0.0014mmol, 0.01eq), *o*-MeOPh₃P(1.0mg, 0.0028mmol, 0.02eq), PivOH(4.3mg, 0.042mmol, 0.3eq),K₂CO₃(58.2mg, 0.42mmol, 3.0eq), then vacuum for about 5-10min and purge with N₂, and repeat the vacuum and purge for three times. After then, added the degassed *o*-xylene 0.6mL into the tube and heat in a 140°C oil bath for 160h. When the reaction is done added chloroform and water into the tube collect the organic phase and precipitate with methanol. The precipitate solid was submitted to soxhlet extraction with methanol, acetone, hexane and chloroform, collect the hexane fraction, precipitate with methanol to get the solid product PTII-II (111mg), yield 92%,*Mn*=3.6k,PDI=1.6.



Figure S1. ¹H NMR spectrum of compound 3.



Figure S2. ¹H NMR spectrum of compound 4.



Figure S3. ¹H NMR spectrum of TBII-Br.



Figure S4. ¹³C NMR spectrum of TBII-Br.



Figure S5. ¹H NMR spectrum of II-2B.



Figure S6. ¹³C NMR spectrum of II-2B.



Figure S7. ¹H NMR spectrum of **TII**.



Figure S8. ¹H NMR spectrum of TII-2Br.



Figure S9. ¹³C NMR spectrum of TII-2Br.



Figure S10. ¹H NMR spectrum of **PTBII** in CDCl₂CDCl₂ at 80°C.



Figure S11. ¹H NMR spectrum of PTII-II in CDCl₂CDCl₂ at 80°C.



Figure S12. ¹H NMR spectrum of PTBII gets from five equivalents of thiophene control

experiment.



Figure S13. UV-Vis-NIR spectrum of PTBII from the thiophene control experiment.



Figure S14. UV-Vis-NIR spectrum of PTBII with different molecular weight.



Figure S15. TGA curves of PTBII.



Figure S16. TGA curves of PTII-II.



Figure S17. (a) Transfer and (b) output characteristics for **PTBII** OFETs, respectively. (c) Transfer and (d) output characteristics for **PTII-II** OFETs, respectively.