Electronic supplementary information for

n-Type conjugated polymers comprising bithiophene imide and multifluorinated thiophene moieties synthesized by direct arylation polycondensation

Houji Cai,^a Xuwen Zhang,^a Yibo Shi,^a Chenhui Xu,^a Tianzuo Wang,^a Cheng Wang,^a Tian Du,^a Yunfeng Deng^{*a} and Yanhou Geng^{a,b}

^aSchool of Materials Science and Engineering and Tianjin Key Laboratory of Molecular Optoelectronic Science, Tianjin University, Tianjin 300072, P. R. China.

^bJoint School of National University of Singapore and Tianjin University, International Campus of Tianjin University, Fuzhou 350207, China.

E-mail: <u>yunfeng.deng@tju.edu.cn</u>.

General methods

¹H NMR spectra were recorded using a Bruker AVANCE III spectrometer in chloroform-d (CDCl₃) at 25 °C or in 1,1,2,2-tetrachloroethane-d ($C_2D_2Cl_4$) at 120 °C. High-temperature gel permeation chromatography analysis was conducted on a PL-GPC 220 system at 150 °C with 1,2,4-trichlorobenzene as the eluent and polystyrene as the standard. Thermogravimetric analysis (TGA) was conducted on a TA Q50 thermogravimetric analyzer under nitrogen flow with a heating rate of 10 °C min-1. Differential scanning calorimetry (DSC) was carried out on a TA Q25 instrument with a heating/cooling rate of 10 °C min⁻¹ under nitrogen flow. UV-vis-NIR absorption spectra were recorded by Shimadzu UV-3600Plus spectrometer. Solution spectra were measured in 1,2-dichlorobenzene (o-DCB) with a concentration of 10⁻⁵ mol L⁻¹ of the repeating unit. Thin films were prepared by spin-coating the o-DCB solutions on the guartz substrates. Film cyclic voltammetry (CV) measurement was performed on a CHI660E electrochemical analyzer with a three-electrode cell at a scan rate of 100 mV s⁻¹ in anhydrous acetonitrile. A glassy carbon electrode with a diameter of 6 mm, a Pt wire, and a saturated calomel electrode (SCE) were used as the working, counter, and reference electrodes. respectively. Tetrabutylammonium hexafluorophosphate (Bu₄NPF₆, 0.1 mol L⁻¹) was used as the supporting electrolyte. In plane and out of plane X-ray diffraction (XRD) of the films were measured by a Rigaku Smart Lab with Cu K α source (λ = 1.54 Å) in air. Atomic force microscopy (AFM) measurements were performed in tapping mode on a Bruker MultiMode 8 instrument. Density functional theory (DFT) optimized molecular geometries and calculated energy levels and frontier molecular orbital (FMO) distribution were conducted by Gaussian 09 at the B3LYP/6-31G(d,p) level. The branched alkyl side chains were replaced by methyl groups to simplify the calculations.

Fabrication and characterization of organic thin-film transistors (OTFTs)

The silicon wafers with a 300 nm thick SiO₂ layer were washed by an ultrasonic cleaner with deionized water, acetone and isopropanol, then dried under a nitrogen flow and heated at 120 °C for 10 min. Au (30 nm) was vacuum-evaporated on the substrate as the source and drain electrodes with an interdigitated electrode pattern (W = 5.6 mm, L = 50 μ m). The prepatterned substrates were treated with UV-zone for 15 min, and then 0.04 wt% PEIE solution (prepared by diluting 37 wt% PEIE water solution with 2methoxyethanol) was spin-coated at 5000 rpm for 60 s, followed by thermal annealing at 100 °C for 10 min. Subsequently, the semiconductor films were prepared by spin-coating at 1500 rpm from polymer solutions (5.0 mg mL⁻¹) with o-DCB as the solvent, followed by thermal annealing at 150 °C for 30 min. As the dielectric layer, CYTOP (Asahi Glass, type CTL-809M) was spincoated at 2000 rpm for 2 min, and annealed at 100 °C in argon for 40 min. The thickness of dielectric layer is 900 nm, which is thick enough to prevent pin-holes and the resultant gate leakage. The corresponding capacitance is 2.1 nF cm⁻². Finally, AI (80 nm) was vacuum evaporated as gate electrode. All the spin-coating processes were conducted in a glovebox and the devices were measured under ambient conditions with Keysight B1500A semiconductor analyzer. Saturation and linear mobilities were calculated according to equation (1) and (2), respectively:

$$\mu_{sat}(V_G) = \frac{\partial I_{D, sat}}{\partial V_G} \cdot \frac{L}{WC_i} \cdot \frac{1}{(V_G - V_T)}$$
(1)

and

$$\mu_{lin} = \frac{\partial I_D}{\partial V_G} \cdot \frac{L}{WC_i V_D}$$
(2)

where *W*/*L* is the channel width/length, I_D the drain-source current, μ the fieldeffect mobility, C_i the capacitance per unit area of the gate dielectric layer, V_G , V_D and V_T the gate voltage, drain voltage and threshold voltage, respectively.

Synthesis procedure

Toluene was dried over sodium with benzophenone as an indicator. 4FBT, 4FTVT and compound 4 were synthesized according to previously reported procedures.¹⁻³ Other chemical reagents were purchased from Sigma-Aldrich, Alfa-Aesar Energy Chemical and J&K Scientific and used as received.



Synthesis of compound **2**: To a solution of compound **1** (5 g, 8.63 mmol), phthalimide (1.27 g, 8.63 mmol), and triphenylphosphine (2.26 g, 8.63 mmol) in dry diethyl ether (40 mL), a solution of diisopropylazodicarboxylate (DIAD, 1.75 g, 8.63 mmol) in dry diethyl ether (5 mL) was added dropwise. The mixture was stirred overnight at room temperature. After removal of the solvent, the residue was purified by column chromatography on silica gel with petroleum ether/dichloromethane (5/1) as the eluent to afford compound **2** as a white solid (5.50 g, 90%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.84 (m, 2H), 7.62 (m, 2H), 3.65 (t, *J*=7.6 Hz, 2H), 1.70-1.59 (m, 2H), 1.39-1.14 (m, 71H), 0.88 (t, *J*=6.8 Hz, 6H).



Synthesis of compound **3**: To a solution of compound **2** (4.3 g, 6.04 mmol) in ethanol (40 mL), hydrazine monohydrate (0.9 mL, 18.48 mmol) was added dropwise. The mixture was stirred overnight at 100 °C. Ethanol was removed under reduced pressure, then the residue was dissolved with dichloromethane and washed with 10% NaOH. The dichloromethane solution was washed with brine and dried over Na₂SO₄. After removal of the solvent, compound **3** was

obtained as a white solid (2.63 g, 75%). The product was used in the next step without further purification. ¹H NMR (400 MHz, CDCl₃, ppm): δ 2.66 (d, *J*=7.2 Hz, 2H), 1.4-1.35 (m, 2H), 1.35-1.14 (m, 71H), 0.87 (t, *J* =6.8 Hz, 6H).



Synthesis of BTI: Compounds 3 (2.35 g, 4.06 mmol), 4 (0.8 g, 3.39 mmol) and 4-dimethylaminopyridine (DMAP, 496 mg, 4.06 mmol) were dissolved in anhydrous 1, 4-dioxane (40 mL). The mixture was stirred at 100 °C for overnight. Then acetic anhydride (4 mL) was added and the solution was stirred at 140 °C for 4 h. After cooling to room temperature, 1, 4-dioxane was removed under reduced pressure and the residue was dissolved in dichloromethane, then washed with brine and dried over MgSO₄. The solvent was removed under a reduced pressure and the residue was purified by column chromatography over silica gel using petroleum ether/dichloromethane (3/1) as the eluent to give BTI as a white solid (2.60 g)96%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.75 (d, J=5.6 Hz, 2H), 7.23 (d, J=5.2 Hz, 2H), 4.17 (t, J=8.0 Hz, 2H), 1.73-1.60 (m, 2H), 1.47-1.04 (m, 71H), 0.88 (t, J=6.8 Hz, 6H).



Synthesis of BTI-2Br: To a solution of BTI (2.6 g, 3.26 mmol) in 32 mL dichloromethane, Br_2 (1.3 g, 8.16 mmol) and iron (III) chloride (10 mg) were added successively. The reaction mixture was stirred at room temperature for overnight in dark. $Na_2S_2O_3$ saturated solution was added to the reaction mixture and stirred for 0.5 h. Then the mixture was extracted with dichloromethane three times and the combined organic layer was dried over MgSO₄. The solvent was removed under a reduced pressure and the residue

was purified by column chromatography over silica gel using petroleum ether/dichloromethane (4/1) as the eluent to give BTI-2Br as a white solid (2.35 g, 75%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.69 (s, 2H), 4.12 (t, *J*=7.6 Hz, 2H), 1.65-1.50 (m, 2H), 1.45-1.02 (m, 71H), 0.88 (t, *J*=6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 160.24, 137.51, 135.50, 133.25, 112.48, 46.70, 37.14, 33.49, 31.92, 30.90, 30.10, 29.72, 29.66, 29.37, 26.62, 24.76, 22.70, 14.14.



Synthesis of BTI-Br: BTI-Br was synthesized following the same procedure for BTI-2Br with 1.0 eq. of Br₂ and 0.02 eq. of FeCl₃. The product was obtained as a white solid (530 mg, 20%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.86 (s, 1H), δ 7.77 (d, *J*=5.2 Hz, 1H), 7.29 (d, *J*=5.2 Hz, 1H), 4.16 (t, *J*=7.6 Hz, 2H), 1.75-1.60 (m, 2H), 1.45-1.04 (m, 71H), 0.89 (t, *J*=6.8 Hz, 6H).



Synthesis of BTI2: BTI-Br (483 mg, 0.55 mmol), hexamethyldistannane (160 mg, 0.28 mmol), Pd(PPh₃)₄ (32 mg, 0.028 mmol) were dissolved in anhydrous toluene (50 mL). The reaction mixture was stirred at 120 °C for 48 h. After cooling to room temperature, the solvent was removed under a reduced pressure and the residue was purified by column chromatography over silica gel using petroleum ether/dichloromethane (2/1) as the eluent to give BTI2 as a yellow solid (350 mg, 80%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.75 (d, *J*=5.2 Hz, 2H), δ 7.70 (s, 2H), 7.24 (d, *J*=5.2 Hz, 2H), 4.14 (t, *J*=7.8 Hz, 4H), 1.72-1.60 (m, 4H), 1.47-1.02 (m, 142H), 0.88 (t, *J*=6.8 Hz, 12H).



Synthesis of BTI2-2Br: BTI2-2Br was synthesized following the same procedure for BTI-2Br. The product was obtained as a white solid (330 mg, 88%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.84 (s, 2H), 7.72 (d, 2H), 4.15 (t, *J*=7.8 Hz, 4H), 1.73-1.60 (m, 2H), 1.47-1.04 (m, 71H), 0.87 (t, *J*=6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 160.79, 160.26, 137.80, 135.89, 135.87, 133.89, 133.57, 130.67, 112.96, 46.73, 37.29, 37.14, 33.69, 31.94, 30.14, 30.06, 29.71, 29.67, 29.36, 26.74, 22.69, 14.07.

Synthesis of P(BTI-4FBT): BTI-2Br (100 mg, 0.1 mmol), 4FBT (25.0 mg, 0.1 mmol), Pd(OAc)₂ (0.5 mg, 2.1 µmol, 2 mol%), K₂CO₃ (36.2 mg, 0.26 mmol, 2.5 eq.) and PivOH (3.2 mg, 31.4 µmol, 0.3 eq.) were added into a pressure-proof-tube. Then anhydrous toluene (4.4 mL) and DMAc (0.9 mL) was added. The reaction mixture was stirred at 100 °C for 24 h. After cooling to room temperature, the mixture was precipitated in methanol. The crude polymer was collected by filtration, and purified by Soxhlet extraction with ethanol, acetone and hexane in succession. The remaining solid dissolved in *o*-DCB, and filtered by 0.45 µm filter. P(BTI-4FBT) was obtained as a brown solid by precipitating the *o*-DCB solution in methanol, filtrated, and then dried in a vacuum (100 mg, 90%). GPC: $M_n = 20.5$ kDa, D = 2.1.

Synthesis of P(BTI-4FTVT) : P(BTI-4FTVT) was synthesized by BTI-2Br (100 mg, 0.1 mmol) and 4FTVT (27.7 mg, 0.1 mmol) following the same procedure for P(BTI-4FBT) (102 mg, 92%). GPC: M_n = 19.0 kDa, D = 3.2.

Synthesis of P(BTI2-4FBT) : P(BTI2-4FBT) was synthesized by BTI2-2Br (60 mg, 34.3 µmol) and 4FBT (8.2 mg, 34.3 µmol) following the same procedure for P(BTI-4FBT) (60 mg, 95%). GPC: $M_n = 37.4$ kDa, D = 2.1.

Synthesis of P(BTI2-4FTVT) : P(BTI2-4FTVT) was synthesized by BTI2-2Br (60 mg, 34.3 µmol) and 4FTVT (9 mg, 34.3 µmol) following the same

procedure for P(BTI-4FBT) (59 mg, 93%). GPC: M_n = 47.7 kDa, D = 2.4.

Supplementary data

Table S1. The results of direct arylation polycondensation toward P(BTI-4FBT).



Entry	Pd source (mol%)	Ligand (mol%)	Base Acid (eq.) (eq.)	Solvent (M)	Temp (°C)	Time (h)	<i>M</i> n (kDa)	Ð
1 ^a	Herrmann's cat (2.0)	P(o-MeOPh) ₃ (4.0)	Cs ₂ CO ₃ PivOH (3.0) (1.0)	Tol (0.02)	120	24	3.5	1.6
2 ^b	Pd₂(dba)₃·CHCl₃ (2.0)	P(o-MeOPh) ₃ (4.0)	Cs ₂ CO ₃ PivOH (3.0) (1.0)	Tol (0.02)	100	24	5.7	1.4
3 ^c	Pd(OAc) ₂ (2.0)	1	K ₂ CO ₃ PivOH (2.5) (0.3)	Tol/DMAc = 3/1 (0.02)	100	24	16.5	2.4
4 ^c	Pd(OAc) ₂ (2.0)	1	K ₂ CO ₃ PivOH (2.5) (0.3)	Tol/DMAc = 5/1 (0.02)	100	24	20.5	2.1
5°	Pd(OAc) ₂ (2.0)	1	K ₂ CO ₃ PivOH (2.5) (0.3)	Tol/DMAc = 7/1 (0.02)	100	24	12.5	1.6
6°	Pd(OAc) ₂ (2.0)	1	K ₂ CO ₃ PivOH (2.5) (0.3)	Tol/DMAc = 10/1 (0.02)	100	24	11.0	1.7

^aHerrmann's catalyst (2 mol%), P(o-MeOPh)₃ (2 mol%), Toluene (0.02 M), PivOH (1.0 eq.) and CS₂CO₃ (3.0 eq.); ^bPd₂(dba)₃·CHCl₃ (2 mol%), P(o-MeOPh)₃ (4 mol%), Toluene (0.02 M), PivOH (1.0 eq.) and CS₂CO₃ (3.0 eq.); ^oPd(OAc)₂ (2 mol%), Tol/DMAc mixed solvent (0.02 M), PivOH (0.3 eq.) and K₂CO₃ (2.5 eq.).



Figure S1. GPC curves of the polymers.



Figure S2. TGA curves of the polymers.



Figure S4. Optimized molecular geometries and energy levels for (a) P(BTI-TVT), (b) P(BTI-4FTVT) and (c) P(BTI2-4FTVT) trimers. The calculation was performed at the B3LYP/6-31G(d,p) level, and the alkyl chain was replaced with a methyl group for calculation simplicity.



Figure S5. The variable-temperature UV-vis-NIR absorption spectra of the polymers.



Figure S6. Cyclic voltammetry curves of the polymers.



Figure S7. Transfer curves of the TGBC OTFT devices without PEIE treatment based on (a) P(BTI-4FBT), (b) P(BTI-4FTVT), (c) P(BTI2-4FBT), and (d) P(BTI2-4FTVT).



Figure S8. Linear mobility versus V_{GS} curves of the PEIE modified TGBC OTFT devices based on (a) P(BTI-4FBT), (b) P(BTI-4FTVT), (c) P(BTI2-4FBT), and (d) P(BTI2-4FTVT).



Figure S9. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of compound 2.



Figure S10. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of compound 3.



Figure S11. ¹H NMR spectrum (400 MHz, CDCI₃, 25 °C) of BTI.



Figure S12. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of BTI-2Br.



Figure S13. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of BTI-Br.

 $< \frac{7.75}{7.70} < \frac{7.26}{7.24}$

1.65 1.31 1.25 1.25 0.88



Figure S14. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of BTI2.



Figure S15. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of BTI2-2Br.



Figure S16. ¹H NMR spectrum (400 MHz, C₂D₂Cl₄, 120 °C) of P(BTI-4FBT)



Figure S17. ¹H NMR spectrum (400 MHz, C₂D₂Cl₄, 120 °C) of P(BTI-4FTVT)



Figure S18. ¹H NMR spectrum (400 MHz, C₂D₂Cl₄, 120 °C) of P(BTI2-4FBT)



Figure S19. ¹H NMR spectrum (400 MHz, C₂D₂Cl₄, 120 °C) of P(BTI2-4FTVT)

Reference

- 1. Y. Gao, X. Zhang, H. Tian, J. Zhang, D. Yan, Y. Geng and F. Wang, *Adv. Mater.*, 2015, **27**, 6753-6759.
- 2. Y. Gao, Y. Deng, H. Tian, J. Zhang, D. Yan, Y. Geng and F. Wang, *Adv. Mater.*, 2017, **29**, 1606217-1606223.
- 3. J. A. Letizia, M. R. Salata, C. M. Tribout, A. Facchetti, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, 2008, **130**, 9679-9694.