# **SUPPORTING INFORMATION**

# Cyano-Substituted Head-to-Head Polythiophenes: Enabling High-Performance n-Type Organic Thin-Film Transistors

Hang Wang,<sup>†,‡</sup> Jun Huang,<sup>‡,§</sup> Mohammad Afsar Uddin,<sup>#</sup> Bin Liu,<sup>‡</sup> Peng Chen,<sup>‡</sup> Shengbin Shi,<sup>‡</sup> Yumin Tang,<sup>‡</sup> Guichuan Xing,<sup>†</sup> Shiming Zhang,<sup>†,</sup> \* Han Young Woo,<sup>#, \*</sup> Han Guo,<sup>‡,\*</sup> Xugang Guo<sup>‡,\*</sup>

<sup>†</sup> Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University, 30 South Puzhu Road, Nanjing 211816, Jiangsu, China

<sup>‡</sup> Department of Materials Science and Engineering, The Shenzhen Key Laboratory for Printed Organic Electronics, Southern University of Science and Technology (SUSTech), No. 1088, Xueyuan Road, Shenzhen 518055, Guangdong, China

<sup>#</sup> Research Institute for Natural Sciences, Department of Chemistry, Korea University, Seoul 136-713, South Korea

§ Center for Advanced Low-dimension Materials, State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620, China

<sup>1</sup> Institute of Applied Physics and Materials Engineering, University of Macau, Macao 999078, China

\*Email: iamsmzhang@njtech.edu.cn (S.Z.); hywoo@korea.ac.kr (H.Y.W.); guoh3 @sustc.edu.cn (H.G.); guoxg@sustc.edu.cn (X.G.)

# **Table of Contents**

1.	Materials and InstrumentsS-3
2.	Synthesis of Monomers and PolymersS-4
3.	Optical, Electrochemical, and Thermal Properties of PolymersS-14
4.	OTFT Performance Characteristics of Polymers P1-P3 and P3HTS-16
5.	Polymer Film MorphologyS-20
6.	<sup>1</sup> H and <sup>13</sup> C NMR Spectra of Monomers and PolymersS-22

#### 1. Materials and Instruments.

All commercially available chemicals and reagents were used as received without any further purifications unless otherwise specified. The known 3,3'-dialkoxy-4,4'dicyano-2,2'-bithiophene (BTCNOR) with 2-ethylhexyl or *n*-dodecyl side chain was prepared according to published procedure.<sup>1</sup> Dry tetrahydrofuran (THF) and toluene were distilled from benzophenone/sodium under argon before use. All air and moisture sensitive reactions were carried out with a standard Schlenk line technique. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were collected on a Bruker AV-400 (400 MHz) spectrometer using tetramethylsilane (TMS) as the internal reference. Elemental analysis (EA) was performed on a vario EL cube instrument (Elementar). High-Resolution Mass Spectrometry (HMRS) data were collected on a Q-Exactive mass spectrometer (ThermoFisher Scientific). Polymer molecular weights were determined by hightemperature gel permeation chromatography (GPC) at 150 °C using 1,2,4trichlorobenzene as the eluent with respect to a polystyrene standard. Thermal analysis of polymers was performed on a METTLER TOLEDO instrument (TGA Mettler STAR<sup>e</sup> System and DSC MettleR STAR<sup>e</sup> System) under nitrogen. Cyclic voltammetry (CV) measurements of polymer films were performed on a CHI660A electrochemical workstation at a scan rate of 50 mV s<sup>-1</sup> under nitrogen, using platinum electrodes and  $Ag/Ag^+$  reference electrode with 0.1 M tetra(*n*-butyl)ammonium hexafluorophosphate in acetonitrile as the supporting electrolyte. UV-vis spectra were recorded on a SHIMADZU UV-3600 spectrometer. Atomic force microscopy images were collected on a Dimension Icon Scanning Probe Microscope (Asylum Research, MFP-3D-

Standard Alone) under tapping mode. Two-dimensional grazing-incidence wide-angle X-ray Scattering (2D-GIWAXS) measurements were carried out at Beamline PLS-II 9A SAXS in the Pohang Accelerator Laboratory, Republic of Korea.

#### 2. Synthesis of Monomers and Polymers.

$$C_{16}H_{33}-OH \longrightarrow C_{16}H_{33}-O-S-CH_{3}$$

*n*-Hexadecyl methanesulfonate. To a solution of hexadecan-1-ol (32.7 mL, 110.3 mmol) and triethylamine (18 mL, 1.2 equiv) in THF (60 mL) was dropwise added methanesulfonyl chloride (10.2 mL, 1.2 equiv) at 0 °C for 30 min under argon atmosphere. The resulting light brown suspension was warmed to room temperature and stirred overnight. Then, a saturated solution of ammonium chloride (100 mL) was added. The aqueous layer was extracted with 100 mL dichloromethane for three times. The organic layers were combined and dried over anhydrous magnesium sulfate followed by filtration. After removal of the solvent, a light brown oil was obtained as the crude product, which was subjected to flash column chromatography. Finally, the product was obtained as a colorless solid (35 g, 99%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 4.22 (t, 2H), 3.00 (s, 3H), 1.74 (m, 2H), 1.41-1.25 (m, 26H), 0.88 (t, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 70.34, 37.52, 32.06, 29.82, 29.79, 29.75, 29.66, 29.56, 29.28, 29.18, 29.17, 25.56, 22.83, 14.25. (Note: some peaks in <sup>13</sup>C NMR spectrum overlap).



**2-Butyloctyl methanesulfonate.** This compound was synthesized using a similar method to the *n*-hexadecyl methanesulfonate with a yield of 80%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 4.11 (d, 2H), 2.99 (s, 3H), 1.67 (m, 1H), 1.35-1.27 (m, 16H), 0.87 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 72.66, 37.86, 37.25, 31.87, 30.75, 30.43, 29.61, 28.85, 26.63, 22.99, 22.74, 14.19, 14.13.



**4-(***n***-Hexadecyloxy)-2,5-dihydrothiophene-3-carbonitrile.** To a solution of 4-cyano-3-tetrahydrothiophene (2.01 g, 15.7 mmol) in dimethylformamide (DMF) (10 mL),  $Cs_2CO_3$  (5.62 g, 1.1 equiv) and hexadecyl methanesulfonate (6.03 g, 1.2 equiv) were added. The reaction mixture was heated under microwave irradiation at 80 °C for 10 min. After completion of the reaction, the mixture was poured into water and then extracted with dichloromethane (20 mL × 3). The combined organic layer was dried over anhydrous magnesium sulfate, filtrated, and then concentrated to give the crude product, which was subjected to a short column chromatography to afford a colorless yellow oil and directly used for the next step.



**4-(2-Butyloctyloxy)-2,5-dihydrothiophene-3-carbonitrile.** This compound was S-5

synthesized using a similar method to 4-(*n*-hexadecyloxy)-2,5-dihydrothiophene-3carbonitrile and directly used for the next step.



4-(*n*-Hexadecyloxy)thiophene-3-carbonitrile. To a solution of 4-(*n*-hexadecyloxy)-2,5-dihydrothiophene-3-carbonitrile (12.9 g, 36.7 mmol) in dichloromethane (50 mL) was added a solution of 2,3-dicyano-5,6-dichlorobenzoquinone (DDQ) (10.0 g, 1.2 equiv) in THF (20 mL) at 50 °C under argon atmosphere. After completion of the addition, the mixture was stirred overnight at the same temperature. Then the mixture was cooled to room temperature and extracted with dichloromethane (40 mL  $\times$  3). The combined organic layer was dried over anhydrous magnesium sulfate followed by filtration. After removal of the solvent, the residue was subjected to column chromatography using petroleum ether: ethyl acetate (10:1) as the eluent to afford a white solid as the product with a yield of 45.5% for the above two steps). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.77 (d, 1H), 6.25 (d, 1H), 3.99 (t, 2H), 1.79 (m, 2H), 1.47-1.26 (m, 26H), 0.88 (t, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 157.67, 134.06, 113.44, 101.14, 97.94, 71.30, 31.92, 29.61, 29.60, 29.53, 29.32, 28.90, 25.89, 22.69, 14.12. Elemental analysis: cacld. for: C<sub>21</sub>H<sub>35</sub>NOS, C, 72.15; H, 10.09; N, 4.01; S, 9.17. Found: C, 72.11; H, 10.68; N, 4.27; S, 9.80.



**4-(2-Butyloctyloxy)thiophene-3-carbonitrile.** This compound was synthesized using a similar method to 4-(*n*-hexadecyloxy)thiophene-3-carbonitrile with a yield of 38% for the above two steps after purification . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.78 (d, 1H), 6.28 (d, 1H), 3.98 (d, 2H), 1.84 (m, 1H), 1.45-1.31 (m, 16H), 0.92 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 157.95, 134.16, 113.51, 104.28, 97.92, 74.22, 37.85, 31.96, 31.33, 31.02, 29.75, 29.15, 26.92, 23.11, 22.80, 14.24, 14.21. Elemental analysis: cacld. for: C<sub>17</sub>H<sub>27</sub>NOS, C, 69.58; H, 9.27; N, 4.77; S, 10.92. Found: C, 69.95; H, 10.05; N, 4.82; S, 10.96.



**4-(***n***-Hexadecyloxy)-2-(triisopropylsilyl)thiophene-3-carbonitrile.** To a solution of 4-(*n*-hexadecyloxy)thiophene-3-carbonitrile (3.02 g, 8.64 mmol) in THF (30 mL) was dropwise added *n*-BuLi (2.4 M, 4 mL, 1.1 equiv) at -78 °C under argon atmosphere. After addition, the reaction mixture was stirred at this temperature for 1 h. Then triisopropylsilyl chloride (2.0 mL, 1.1 equiv) was added in one portion. The mixture was warmed to room temperature and stirred overnight. Then the mixture was quenched with water and extracted with dichloromethane (25 mL × 3). The combined organic layer was dried over anhydrous magnesium sulfate followed by filtration. After removal of the solvent, the crude product was subjected to a short column chromatography to afford a colorless oil as the product and directly used for the next step.



**4-(2-Butyloctyloxy)-2-(triisopropylsilyl)thiophene-3-carbonitrile.** This compound was synthesized using a similar method to 4-(*n*-hexadecyloxy)-2-(triisopropylsilyl)thiophene-3-carbonitrile and directly used for the next step.



3,3'-Bis(n-hexadecyloxy)-5,5'-bis(triisopropylsilyl)-2,2'-bithiophene-4,4'-

**dicarbonitrile.** To a solution of 4-(*n*-hexadecyloxy)-2-(triisopropylsilyl)thiophene-3carbonitrile (4.01 g, 7.93 mmol) in THF (30 mL), *n*-BuLi (2.4 M, 3.63 mL, 1.1 equiv) was slowly added at -78 °C under argon. After completion of the addition, the reaction mixture was stirred at this temperature for 45 min, and warmed to room temperature and stirred at this temperature for 1 h. The mixture was cooled to 0 °C and a solution of Fe(acac)<sub>3</sub> (3.08 g, 1.1 equiv) in THF (10 mL) was then added in one portion. The mixture was stirred at 80 °C for 2 h. Then the reaction was quenched with water and extracted with dichloromethane (75 mL × 3). The combined organic layer was dried over anhydrous magnesium sulfate followed by filtration. After removal of the solvent, the residue was subjected to column chromatography using petroleum ether as the eluent to afford a yellow solid as the product with a yield of 33% for the above two steps. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 4.29 (t, 4H), 1.91 (m, 4H), 1.59 (m, 6H), 1.28-1.25 (m, 52H), 1.17 (d, 36H), 0.90 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 155.67, 144.45, 123.16, 115.81, 111.37, 75.34, 32.08, 30.50, 29.89, 29.85, 29.81, 29.77, 29.75, 29.52, 26.22, 22.84, 19.98, 18.72, 18.66, 14.28, 11.82. (Note: some peaks in <sup>13</sup>C NMR spectrum overlap). Elemental Analysis: cacld. for C<sub>60</sub>H<sub>108</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>Si<sub>2</sub>: C, 71.36; H, 10.78; N, 2.77; S, 6.35. Found: C, 71.45; H, 10.74; N, 2.68; S, 6.45.



3,3'-Bis(2-butyloctyloxy)-5,5'-bis(triisopropylsilyl)-2,2'-bithiophene-4,4'-

**dicarbonitrile:** This compound was synthesized using a similar method to 3,3'-bis(*n*-hexadecyloxy)-5,5'-bis(triisopropylsilyl)-2,2'-bithiophene-4,4'-dicarbonitrile with a yield of 51% after purification for the above two steps. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 4.18 (d, 4H), 1.96 (m, 2H), 1.61 (m, 6H), 1.34-1.32 (m, 32H), 1.19 (d, 36H), 0.90 (m, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 155.84, 144.57, 122.50, 115.87, 111.19, 78.32, 39.25, 32.02, 31.19, 30.82, 27.08, 23.19, 22.84, 19.28, 18.63, 14.25, 14.23, 12.71, 11.81. Elemental analysis: calcd for: C<sub>52</sub>H<sub>92</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>Si<sub>2</sub>, C, 69.58; H, 10.33; N, 3.12; S, 7.14. Found: C, 69.89; H, 10.51; N, 3.16; S, 7.22.



**3,3'-Bis**(*n*-hexadecyloxy)-**2,2'-bithiophene-4,4'-dicarbonitrile.** To a solution of 3,3'-bis(*n*-hexadecyloxy)-**5**,5'-bis(triisopropylsilyl)-**2**,2'-bithiophene-**4**,4'-dicarbonitrile

(1.2 g, 1.19 mmol) in THF (25 mL) was added (*n*-tetrabutyl)ammonium fluoride (1 M, 3.6 mL, 3 equiv) slowly at -78 °C under argon. After completion of the addition, the mixture was warmed to room temperature. The mixture was quenched with water and extracted with dichloromethane (45 mL × 3). The combined organic layer was dried over anhydrous magnesium sulfate followed by filtration. After removal of the solvent, a white solid was obtained as the product (702 mg, 85%), which can be used for the following reaction without further purification. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.76 (s, 2H), 4.30 (t, 4H), 1.88 (m, 4H), 1.51-1.14 (m, 52H), 0.87 (t, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 152.38, 133.35, 118.04, 114.02, 75.10, 32.08, 32.06, 30.17, 29.85, 29.84, 29.81, 29.77, 29.73, 29.67, 29.52, 29.48, 25.89, 22.85, 14.28. (Note: some peaks in <sup>13</sup>C NMR spectrum overlap). Elemental analysis: cacld. for C<sub>42</sub>H<sub>68</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 72.36; H, 9.83; N, 4.02; S, 9.20. Found: C, 72.48; H, 9.76; N, 4.10; S, 9.44.



**3,3'-Bis(2-butyloctyloxy)-2,2'-bithiophene-4,4'-dicarbonitrile.** This compound was synthesized using a similar method as 3,3'-bis(*n*-hexadecyloxy)-2,2'-bithiophene-4,4'-dicarbonitrile with a yield of 78% after purification. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ (ppm): 7.76 (s, 2H), 4.46 (d, 4H), 1.88 (m, 2H), 1.51-1.14 (m, 32H), 0.88 (m, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>), δ (ppm): 152.71, 133.48, 117.38, 114.17, 104.52, 77.98, 39.96, 31.97, 31.08, 30.76, 29.80, 29.07, 26.85, 23.17, 22.82, 17.84, 14.22, 12.41. S-10

Elemental analysis: cacld. for C<sub>34</sub>H<sub>52</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 69.82; H, 8.96; N, 4.79; S, 10.96. Found: C, 70.04; H, 8.85; N, 4.88; S, 11.47.



5,5'-Dibromo-3,3'-bis(hexadecyloxy)-2,2'-bithiophene-4,4'-dicarbonitrile: To a solution of 3,3'-bis(hexadecyloxy)-2,2'-bithiophene-4,4'-dicarbonitrile (430.6 mg, 0.62 mmol) in THF (20 mL) was added n-BuLi (2.4 M, 0.62 mL, 2.4 equiv) slowly at -78 °C under argon. After completion of the addition, the mixture was stirred at this temperature for 1 h. Then the solution was warmed to room temperature and stirred for 1 h. The mixture was cooled to -78 °C again and Br<sub>2</sub> (0.2 mL, 6 equiv) was added in one portion. The mixture was warmed to room temperature and stirred overnight. The reaction was quenched with water and extracted with dichloromethane (50 mL  $\times$  3). The combined organic layer was dried over anhydrous magnesium sulfate followed by filtration. After removal of the solvent, the residue was subjected to flash chromatograph using dichloromethane:petroleum ether (1:1) as the eluent. A pale yellow solid was obtained as the product (492 mg, 93%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ (ppm): 4.3 (d, 4H), 1.87(m, 4H), 1.50-1.25 (m, 52H), 0.88 (t, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 150.99, 122.63, 118.16, 112.83, 107.93, 75.36, 32.07, 30.05, 29.85, 29.83, 29.81, 29.72, 29.66, 29.52, 29.40, 25.80, 22.84, 14.28. (Note: some peaks in <sup>13</sup>C NMR spectrum overlap). Elemental Analysis: calcd. for  $C_{42}H_{66}Br_2N_2O_2S_2$ : C, 59.01; H, 7.78; N, 3.28; S, 7.50. Found: C, 59.45; H, 7.88; N, 3.77; S, 7.13. ESI-HRMS: m/z for [C<sub>42</sub>H<sub>66</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>+HCOO]<sup>-</sup>: 899.28940, found: 899.28890.



**5,5'-Dibromo-3,3'-bis((2-ethylhexyl)oxy)-[2,2'-bithiophene]-4,4'-dicarbonitrile:** This compound was synthesized according to reported literature.<sup>1 1</sup>H NMR (400 MHz, CDCl3), δ (ppm): 4.20 (dd, 4H), 1.83 (m, 2H), 1.54–1.34 (m, 16H), 0.98–0.96 (m, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 151.32, 122.66, 117.54, 112.90, 107.91, 77.98, 40.32, 30.14, 29.01, 23.59, 23.16, 14.23, 11.15. Elemental analysis: calcd. for  $C_{26}H_{34}Br_2N_2O_2S_2$ : C, 49.53; H, 5.44; N, 4.44; S, 10.17. Found: C, 49.65; H, 5.56; N, 4.48; S, 10.13. ESI-HRMS: m/z for [ $C_{26}H_{34}Br_2N_2O_2S_2$ +HCOO]<sup>-</sup>: 675.03900, found: 675.03956.



5,5'-Dibromo-3,3'-bis(2-butyloctyloxy)-2,2'-bithiophene-4,4'-dicarbonitrile: This compound was synthesized using a similar method to 5,5'-dibromo-3,3' bis(hexadecyloxy)-2,2'-bithiophene-4,4'-dicarbonitrile with a yield of 86%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 4.19 (d, 4H), 1.89(m, 2H), 1.54-1.21 (m, 32H), 0.96-0.85 (m, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 151.32, 122.66, 117.53, 112.91,

107.90, 78.31, 38.93, 31.98, 31.04, 30.72, 29.80, 29.04, 28.83, 23.17, 22.84, 14.28, 14.24. (Note: some peaks in <sup>13</sup>C NMR spectrum overlap). Elemental analysis: calcd. for C<sub>34</sub>H<sub>50</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 54.98; H, 6.79; N, 3.77; S, 8.63. Found: C, 55.06; H, 6.97; N, 3.28; S, 8.54. ESI-HRMS: m/z for [C<sub>34</sub>H<sub>50</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>+HCOO]<sup>-</sup>: 787.16420, found: 787.16297.

**General polymerization procedure.** To a dried microwave tube was added the 5,5'dibromo-3,3'-bis(alkoxy)-2,2'-bithiophene-4,4'-dicarbonitrile (0.1 mmol), hexa(*n*butyl)ditin (1.0 equiv), Pd<sub>2</sub> (dba)<sub>3</sub> (0.015 equiv), and P(*o*-tol)<sub>3</sub> (0.12 equiv). The mixture was vacuumed and refilled with argon for three times, followed by the addition of dry toluene (5 mL) under argon flow. The solution was stirred at 80 °C for 10 min, 100 °C for 10 min, and 150 °C for 3 h under microwave irradiation. Then the polymers were end-capped with 2-(tributylstannyl)thiophene and 2-bromothiophene, sequentially. After cooled to room temperature, the mixture was dripped into 200 mL methanol (containing 5 mL 12 N hydrochloric acid) under vigorous stirring. The precipitation was collected and poured into a Soxhlet thimble, and then extracted with methanol, acetone, hexane, dichloromethane, and chloroform in sequence. The final chloroform fraction was concentrated and dripped into methanol again under vigorously stirring, and the precipitates were collected via filtration to afford the final polymer product.

**Polymer**  $P_{ins}$ . This polymer with *n*-decyloxy side chain is insoluble in common organic solvents (e.g., chloroform, chlorobenzene, etc.) even at high temperature, preventing further materials characterization and device fabrication.

Polymer P1. The polymer was obtained as a deep colored solid (82%). <sup>1</sup>H NMR (400

MHz, 1,1,2,2-tetrachloroethane-D2 ( $C_2D_2Cl_4$ )): 4.50-4.39 (br, 4H), 2.04-21.96 (br, 4H), 1.70-1.25 (br, 52H), 0.96-0.91 (br, 6H). Elemental analysis: calcd. for  $C_{42}H_{66}N_2O_2S_2$ : C, 72.57; H, 9.57; N, 4.03; S, 9.22; found: C, 71.08; H, 9.34; N, 3.90; S, 8.84.  $M_n =$ 13.3 kDa, D = 1.3.

**Polymer P2.** The polymer was obtained as a deep colored solid (87%). <sup>1</sup>H NMR (400 MHz,  $C_2D_2Cl_4$ ): 4.41-4.33 (br, 4H), 2.07-2.00 (br, 2H), 1.25-0.75 (br, 16H), 1.07-0.92 (br, 12H). Elemental analysis: calcd. for  $C_{26}H_{34}N_2O_2S_2$ : C, 66.35; H, 7.28; N, 5.95; S, 13.62; found: C, 65.98; H, 7.15; N, 5.78; S, 13.19.  $M_n = 16.6$  kDa, D = 1.4.

**Polymer P3.** The polymer was obtained as a deep colored solid (91%). <sup>1</sup>H NMR (400 Hz,  $C_2D_2Cl_4$ ): 4.40-4.37 (br, 4H), 2.12-2.09 (br, 2H), 1.65–1.30 (br, 32H), 0.97-0.89 (br, 12H). Elemental analysis: calcd. for  $C_{34}H_{50}N_2O_2S_2$ : C, 70.06; H, 8.65; N, 4.81; S, 11.00; found: C, 69.88; H, 8.17; N, 4.79; S, 10.30.  $M_n = 10.1$  kDa, D = 1.8.



3. Optical, Electrochemical, and Thermal Properties of Polymers.

Figure S1. Temperature-dependent UV-Vis absorption spectra of (a) P1, (b) P2, and (c) P3 in diluted chlorobenzene solutions (ca.  $10^{-5}$  M).



**Figure S2.** The optical properties of (a) **P1**, (b) **P2**, and (c) **P3** thin film after annealing at different temperatures.



**Figure S3.** Cyclic voltammogram of rr-P3HT polymer film with a Fc/Fc<sup>+</sup> redox couple as the reference.



Figure S4. (a) TGA and (b) DSC curves of the BTCNOR-based homopolymers P1– P3. The upper temperature limits in the DSC scans of P2 and P3 are lower than that of P1 due to their lower thermal decomposition temperatures. Further increasing the upper temperature limit in the DSC scan leads to much reduced peak intensity.

### 4. OTFT Performance Characteristics of Polymers P1-P3 and P3HT.

Polymer $\frac{T_{\text{anneal}}}{(^{\circ}\text{C})}$		$\mu_{e,lin}{}^a$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$\mu_{ m e,sat}{}^a$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$V_{t,avg}^{b}$ (V)	$I_{\rm on}/I_{\rm off}^{\rm c}$
	as-cast	$3.3 \times 10^{-3} (2.1 \times 10^{-3} \pm 9.6 \times 10^{-4})$	$4.6 \times 10^{-3} (3.4 \times 10^{-3} \pm 1.3 \times 10^{-3})$	47 ± 5	10 <sup>5</sup>
	160	$2.8 \times 10^{-3} (2.2 \times 10^{-3} \pm 1.4 \times 10^{-3})$	$6.1 \times 10^{-3} (5.6 \times 10^{-3} \pm 5.3 \times 10^{-4})$	$30\pm9$	105
	190	$6.8 \times 10^{-3} (3.8 \times 10^{-3} \pm 2.6 \times 10^{-3})$	$0.011~(7.6\times10^{-3}\pm3.3\times10^{-3})$	$44\pm7$	106
P1	190 <sup><i>d</i></sup>	$5.2 \times 10^{-3} (3.3 \times 10^{-3} \pm 1.4 \times 10^{-3})$	$9.7 \times 10^{-3} (6.8 \times 10^{-3} \pm 2.9 \times 10^{-3})$	$40 \pm 5$	105
	220	$5.9 \times 10^{-3} (5.2 \times 10^{-3} \pm 5.8 \times 10^{-4})$	$8.8 \times 10^{-3} (8.5 \times 10^{-3} \pm 2.7 \times 10^{-4})$	37 ± 4	105
	250	$4.6 \times 10^{-3}  (4.4 \times 10^{-3} \pm 2.1 \times 10^{-4})$	$8.4 \times 10^{-3} (6.5 \times 10^{-3} \pm 2.0 \times 10^{-4})$	45 ± 6	104
	as-cast	$0.010\ (0.0082\pm 0.0015)$	$0.022\ (0.015\pm 0.0068)$	$52\pm9$	106
	160	$0.12 \ (0.087 \pm 0.034)$	0.14 (0.12 ± 0.017)	$34 \pm 5$	106
DA	190	$0.10~(0.074\pm0.020)$	0.19 (0.17 ± 0.021)	$34 \pm 7$	106
P2	190 <sup>d</sup>	0.16 (0.11 ± 0.028)	$0.31(0.23 \pm 0.042)$	$32 \pm 4$	106
	220	$0.090 \ (0.074 \pm 0.0015)$	$0.076 \ (0.069 \pm 0.010)$	$28 \pm 5$	106
	250	$4.4 \times 10^{-3} (3.2 \times 10^{-3} \pm 1.0 \times 10^{-3})$	$6.3 \times 10^{-3} (4.8 \times 10^{-3} \pm 1.2 \times 10^{-3})$	$45\pm4$	105
	as-cast	$8.9 \times 10^{-4} (7.8 \times 10^{-4} \pm 7.6 \times 10^{-5})$	$9.6 \times 10^{-4} (8.3 \times 10^{-4} \pm 8.8 \times 10^{-5})$	33 ± 3	104
	160	$6.5 \times 10^{-3} (4.4 \times 10^{-3} \pm 2.5 \times 10^{-4})$	$1.1 \times 10^{-3} (9.0 \times 10^{-4} \pm 3.1 \times 10^{-5})$	$20\pm 8$	104
<b>D</b> 2	190	$1.5 \times 10^{-3} (1.1 \times 10^{-3} \pm 2.7 \times 10^{-4})$	$1.9 \times 10^{-3} (1.8 \times 10^{-3} \pm 1.2 \times 10^{-5})$	$29 \pm 4$	104
РJ	190 <sup>d</sup>	$1.4 \times 10^{-3} (1.0 \times 10^{-3} \pm 1.4 \times 10^{-4})$	$2.1 \times 10^{-3} (2.0 \times 10^{-3} \pm 8.7 \times 10^{-5})$	$28 \pm 3$	104
	220	$1.0 \times 10^{-3} (8.2 \times 10^{-4} \pm 1.4 \times 10^{-4})$	$1.2 \times 10^{-3} (9.5 \times 10^{-4} \pm 2.0 \times 10^{-4})$	36 ± 5	104
	250	$2.7 \times 10^{-4} (2.3 \times 10^{-4} \pm 2.9 \times 10^{-5})$	$8.5  imes 10^{-4}  (7.1  imes 10^{-4} \pm 1.3  imes 10^{-4})$	$43 \pm 3$	104

Table S1. Device Performance parameters of P1-P3-based TG/BC OTFTs using CsF

electrode surface modification layer.

<sup>*a*</sup> The highest  $\mu_e$  with the average  $\mu_e$  from at least five devices given in parentheses; mobility calculated using average slope within  $V_g$  from 70 to 80 V. <sup>*b*</sup> Average values from at least five devices. <sup>*c*</sup> Current on/off ratio for the transfer curve in the saturation region ( $V_d = 80$  V). <sup>*d*</sup> Spin-coated method: off-center spin-coat.

Polymer	T <sub>anneal</sub> (°C)	$\mu_{e}^{a}$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$\mu_{ m h}^{a}$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$V_{t,avg}^{b}$ (V)	$I_{\rm on}/I_{\rm off}$
P1	190	$2.1 \times 10^{-3} (1.7 \times 10^{-3})$	$8.4 \times 10^{-5} (6.9 \times 10^{-5})$	n: 61; p: -65	n: 10 <sup>3</sup> ; p: 10 <sup>2</sup>
P2	190	$3.4  imes 10^{-2} (2.6  imes 10^{-2})$	1.5×10 <sup>-3</sup> (9.2 × 10 <sup>-4</sup> )	n: 60; p: -62	n: 10 <sup>3</sup> ; p: 10 <sup>3</sup>
P3	190	$4.6 \times 10^{-4} (4.1 \times 10^{-4})$	$1.2 \times 10^{-5} (1.0 \times 10^{-5})$	n: 55; p: -67	n: 10 <sup>3</sup> ; p: 10 <sup>2</sup>

 Table S2. Device Performance parameters of P1-P3-based TG/BC OTFTs without using electrode surface modification layer.

<sup>*a*</sup> Maximum mobility from at least 5 devices with average value shown in parentheses; <sup>*b*</sup> Average threshold value from at least 5 devices shown.

 Table S3. TG/BC OTFTs performance parameters of P1-P3 using PEIE electrode

 surface modification layer.

Polymer	$T_{\text{anneal}}$ $\mu_{\text{e,lin}^{a}}$ (°C)(cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )		$\frac{\mu_{e,\text{sat}}^a}{(\text{cm}^2 \text{V}^{-1} \text{s}^{-1})}$	$V_{t,avg}^{b}$ (V)	$I_{\rm on}/I_{\rm off}$
P1	190	$5.7\times 10^{-4} (5.2\times 10^{-4}\pm 4.6\times 10^{-5})$	$1.5 \times 10^{-3} (1.2 \times 10^{-3} \pm 1.9 \times 10^{-4})$	$10 \pm 4$	105
P2	190	$0.022 \ (0.015 \pm 3.8 \times 10^{-3})$	$0.055 \ (0.034 \pm 0.011)$	$7\pm5$	105
P3	190	$1.5 \times 10^{-4} (1.1 \times 10^{-4} \pm 3.1 \times 10^{-5})$	$5.4 \times 10^{-4} (4.9 \times 10^{-4} \pm 6.5 \times 10^{-5})$	24 ± 9	104

<sup>a</sup> Maximum mobility from at least 5 devices with average value shown in parentheses;

<sup>b</sup> Average threshold value from at least 5 devices shown.



Figure S5. TG/BC OTFT output and transfer characteristics of (a, d) P1, (b, e) P2, and (c, f) P3 using PEIE electrode surface modification layer. Gate voltage range in the output plots is 0–80 V with 10 V intervals. L = 20 um and W = 5 mm for all plots.



Figure S6. TG/BC OTFT output and transfer characteristics of (a, d) P1, (b, e) P2, and (c, f) P3 doped with 1.0 wt% of CsF. Gate voltage range in the output plots is 0–80 V with 10 V intervals. L = 20 um and W = 5 mm for all plots.

Polymer	T <sub>anneal</sub> (°C)	$\mu_{ m e,lin}$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$\mu_{\rm e,sat}$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$V_{t,avg}^{a}$ (V)	$I_{\rm on}/I_{\rm off}$
P1	190	$4.9 \times 10^{-3}  (4.2 \times 10^{-3} \pm 9.4 \times 10^{-4})$	$7.0 \times 10^{-3}  (6.4 \times 10^{-3} \pm 6.4 \times 10^{-4})$	$39 \pm 2$	10 <sup>3</sup>
P2	190	0.052 (0.031 ± 0.016)	$0.091 \ (0.070 \pm 0.014)$	$48 \pm 6$	10 <sup>3</sup>
P3	190	$6.7 \times 10^{-4} (5.5 \times 10^{-4} \pm 1.0 \times 10^{-4})$	$8.9 \times 10^{-4} (6.3 \times 10^{-4} \pm 1.5 \times 10^{-4})$	$30 \pm 4$	104

 Table S4. TG/BC OTFTs performance parameters of P1-P3 doped with 1.0 wt% of

<sup>a</sup> Maximum mobility from at least 5 devices with average value shown in parentheses;

<sup>b</sup> Average threshold value from at least 5 devices shown.

CsF.



**Figure S7.** (a) Transfer and (b) output characteristics of P3HT-based TG/BC OTFT device. The channel length and width are 20  $\mu$ m and 5 mm, respectively. The gate voltage scanning range in the output plot is 0 to -80 V with a 10 V interval.

Table S5. Device Performance parameters of P3HT-based TG/BC OTFTs.

Polymer	$T_{a}(^{\circ}\mathrm{C})$	$\mu_{ m h,lin}$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ) <sup><i>a</i></sup>	$\mu_{ m h,sat}$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ) <sup><i>a</i></sup>	V <sub>t,avg</sub> (V) <sup>b</sup>	$I_{\rm on}/I_{\rm off}$
РЗНТ	190	0.16 (0.14)	0.23 (0.21)	-21	103

<sup>a</sup> Maximum mobility from at least 5 devices with average value shown in parentheses;

<sup>b</sup> Average threshold value from at least 5 devices shown.

5. Polymer Film Morphology.



**Figure S8.** Tapping-mode AFM height images (above) and phase images (below) of as-cast polymer film of (a, d) **P1**, (b, e) **P2**, and (c, f) **P3**.



**Figure S9**. In-plane (IP) and out-of-plane (OOP) line-cut profiles of 2D-GIWAXS of (a) as-cast and (b) thermally annealed polymer films.

Polymer	Crystallographic parameters		Pristine	Annealed
	$q_{xy}$ profile	$q(A^{-1})$	0.34	0.34
	(100)	d-spacing (Å)	18.47	18.47
P1	a profile	$q(A^{-1})$	0.37	0.37
	$q_z$ prome	d-spacing (Å)	16.97	16.97
	(100)	CCL(Å)	137.4	155.1
	$q_{xy}$ profile	$q(Å^{-1})$	0.32	0.32
	(100)	d-spacing (Å)	19.63	19.63
		$q(Å^{-1})$	0.32	0.33
P2	$q_{z}$ profile	d-spacing (Å)	19.63	19.63
	(100)	CCL (Å)	264.5	337.6
	$q_{xy}$ profile	$q(Å^{-1})$	0.17	0.17
	(100)	d-spacing (Å)	36.94	36.94
P3	$q_z$ profile	$q(Å^{-1})$	0.19	0.19
		d-spacing (Å)	33.05	33.05
	(100)	CCL (Å)	111.2	129.9

 Table S6. Packing parameters derived from 2D-GIWAXS measurements of the polymer films.



## 6. <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Monomers and Polymers

**Figure S10.** <sup>1</sup>H NMR spectrum of 5,5'-dibromo-3,3'-bis(hexadecyloxy)-2,2'-bithiophene-4,4'-dicarbonitrile in CDCl<sub>3</sub> at room temperature (400 MHz).



bithiophene-4,4'-dicarbonitrile in CDCl<sub>3</sub> at room temperature (100 MHz).



-7.26

**Figure S12.** <sup>1</sup>H NMR spectrum of 5,5'-dibromo-3,3'-bis((2-ethylhexyl)oxy)-[2,2'bithiophene]-4,4'-dicarbonitrile in CDCl<sub>3</sub> at room temperature (400 MHz).



155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10

**Figure S13.** <sup>13</sup>C NMR spectrum of 5,5'-dibromo-3,3'-bis((2-ethylhexyl)oxy)-[2,2'-bithiophene]-4,4'-dicarbonitrile in CDCl<sub>3</sub> at room temperature (100 MHz).



**Figure S14.** <sup>1</sup>H NMR spectrum of 5,5'-Dibromo-3,3'-bis(2-butyloctyloxy)-2,2'bithiophene-4,4'-dicarbonitrile in CDCl<sub>3</sub> at room temperature (400 MHz).



**Figure S15.** <sup>13</sup>C NMR spectrum of 5,5'-dibromo-3,3'-bis(2-butyloctyloxy)-2,2'bithiophene-4,4'-dicarbonitrile in CDCl<sub>3</sub> at room temperature (100 MHz).

CLB SLB

-7.26



Figure S16. <sup>1</sup>H NMR spectrum of polymer P1 in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 80 °C (400 MHz).



Figure S17. <sup>1</sup>H NMR spectrum of polymer P2 in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 80 °C (400 MHz).



Figure S18. <sup>1</sup>H NMR spectrum of P3 in  $C_2D_2Cl_4$  at 80 °C (400 MHz).

#### Reference

1. Huang, J.; Tang, Y.; Gao, K.; Liu, F.; Guo, H.; Russell, T. P.; Yang, T.; Liang, Y.; Cheng, X.; Guo, X. Head-to-Head Linkage Containing Dialkoxybithiophene-Based Polymeric Semiconductors for Polymer Solar Cells with Large Open-Circuit Voltages. *Macromolecules* **2017**, *50*, 137-150.