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Heteroatom Substituted Naphthodithiophene-Benzothiadiazole Copolymers and Their Effects on Photovoltaic and Charge Mobility Properties

Bao Wang,[a] Ji Zhang,[c] Keli Shi,[c] Hoi Lam Tam,[b] Weifeng Zhang,[c] Lei Guo,[a] Feng Pan,[d] Gui Yu,*[c] Furong Zhu*[b] and Man Shing Wong*[a]

[a] *Institute of Molecular Functional Materials[#], Department of Chemistry and Institute of Advanced Materials, Hong Kong Baptist University, Kowloon Tong, Hong Kong SAR, China. E-mail: mswong@hkbu.edu.hk*

[b] *Department of Physics and Institute of Advanced Materials, Hong Kong Baptist University, Kowloon Tong, Hong Kong SAR, China. E-mail: frzhu@ hkbu.edu.hk*

[c] *Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China. E-mail: yugui@iccas.ac.cn*

[d] *School of Advanced Materials, Peking University Shenzhen Graduate School, Shenzhen University Town, Xili, Nanshan District, Shenzhen, 518055, P.R. China*

[#]*Areas of Excellence Scheme, University Grants Committee (Hong Kong)*

E-mail: mswong@hkbu.edu.hk; frzhu@hkbu.edu.hk; yugui@iccas.ac.cn

Materials Characterization

All reagents and starting materials were purchased from commercial sources and used as received, unless otherwise noted, The $Pd(PPh_3)_4$ was purchased from Sigma-Aldrich. The synthetic routes of monomers are shown in **Scheme 1** and **2**, respectively. The key intermediates are prepared according to reported procedures with modification. All the solvents were dried by the standard methods wherever needed. ^1H NMR spectra were recorded using a Bruker-400 NMR spectrometer and referenced to the residual $CHCl_3$ 7.26 ppm. ^{13}C NMR spectra were

recorded using a Bruker-400 NMR spectrometer and referenced to the $CDCl_3$ 77 ppm. Thermal stabilities were determined by thermal gravimetric analyzer (PE-TGA6) with a heating rate of 10 ^oC /min under N_2. All absorption measurements were performed with Varian Cary 100-UV-Vis spectrophotometer. Cyclic voltammetry (CV) were carried out on a CH Instrument 630C using platinum wires as working electrode and counter-electrode at a scan rate of 100 mV/s. The reference electrode was Ag/AgCl and the electrolyte was a solution of 0.1 M hexafluorophosphate (Bu_4NPF_6) in dry acetonitrile. Under these conditions, the half wave potential of oxidation of ferrocene was 0.07 V versus Ag/Ag^+. The HOMO energy level was determined from the oxidation onset from the cyclic voltammograms and reported values were calculated with reference to ferrocene (4.8 eV vs vacuum), the LUMO energy level was determined by LUMO = (HOMO + E_g^{opt}) eV. The molecular weight and polydispersity index (PDI) of the polymer were determined by gel permeation chromatography (GPC) using Agilent 1050 HPLC system with VWD and waters 515 HPLC pump. THF was used as eluent and commercial polystyrenes were used as standards.

Fabrication of Field – Effect Transistor Devices

Organic field-effect transistors (OFETs) were fabricated in a bottom-gate bottom-contact

(BGBC) configuration (gold electrode on Si/SiO_2 substrates). Before the deposition of organic semiconductors, the gate dielectric was treated with octadecyltrichlorosilane (OTS) and annealed at 120 °C in a vacuum oven for 3 hours to form an OTS self-assembled monolayer on its surface. Then the polymer thin films were spin-coated on the OTS modified SiO_2/Si substrates from the solutions (In chlorobenzene, 2.5–5 mg/mL, spin-coated at 1500−2000 rpm, 60s). The polymer OFETs were annealed successively at 80 °C, 120 °C, 160 °C, 200 °C, 220 °C 240 °C, 280 °C for 5-6 min in air. The performance of OFETs was measured at room temperature in air by using a Keithley 4200 Semiconductor Characterization System. As contrast, the characteristics of as-prepared devices were also measured. The mobility of the OFETs was calculated in the saturation regime. The equation is listed as follows:

$$I_{DS} = (W / 2L)\, C_i\, \mu\, (V_{GS}\text{-}V_{th})^2,$$

where W/L is the ratio of the channel width (W) to channel length (L), Ci is the insulator capacitance per unit area, and V_{GS} and V_{th} are the gate voltage and threshold voltage, respectively.

Fabrication of Photovoltaic Devices

Organic solar cells (OSCs) with an inverted device structure of ITO/ZnO/Al (1.2 nm)/Polymer:$PC_{71}BM$ (80 nm)(1:1)/MoO_3/ Ag were fabricated by spin-coating of a ZnO layer, a vacuum deposition of Al layer, and then a blend of the polymer:$PC_{71}BM$ layer in chlorobenzene

(with 3% DIO) followed by deposition of anode contact of MoO_3 and Ag layers in vacuum, with an active cell area of 3.0 mm × 3.0 mm. The concentration of the polymer/$PC_{71}BM$ blend solution for spin coating was 6 mg/ml (polymer/chlorobenzene), and the thickness of the active layer is ~ 80 nm. The performance of OSCs was measured under AM 1.5 simulated solar illumination at an irradiation intensity of 100 mW cm^2. The devices were tested under glove-box (filled with Nitrogen) environment.

Jsc of the OSCs usually increases linearly with the intensity of the solar simulator. Measurement errors can be easily encountered to overestimate the photocurrent with a solar simulator having the intensity adjusted greater than one sun condition. In order to avoid the possible overestimate in OSC measurement, and for the correct characterization of OSCs, the optical power in the visible region in the solar simulator in our lab is calibrated using a silicon diode with a KG5 filter. Therefore, it is possible that the Jsc, hence the PCE, derived from the J-V measurements may appear slightly lower than that calibrated from IPCE spectrum, which represents the best achievable Jsc of the testing cells.

3-Octylthiophene (1): To a mixture of magnesium turnings (1.02 g, 42 mmol), anhydrous ether (100 mL) and a small amount of iodine in a 250 mL round-bottom flask, a solution of 3-(bromomethyl)heptane (7.9 g, 41 mmol) was added slowly at 0 °C under N_2. After refluxing for 1 h, the reaction mixture was added dropwise to a mixture of 3-bromothiophene (5 g, 31 mmol), Ni(dppp)Cl_2 (170 mg, 0.3 mmol) placed in a 500 mL flask at 0 °C. After being stirred overnight at room temperature, the reaction was quenched with cold HCl aq. (2 M). The solution was extracted with $CHCl_3$ and dried over anhydrous Mg_2SO_4. The crude product was further purified by column chromatography using hexane as eluent to give a clear liquid (5.1 g, 86% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28-7.26 (m, 1H), 6.98-6.95 (m, 2H), 2.67 (t, *J* = 7.6Hz, 2H), 1.69-1.65 (m, 2H), 1.36-1.32 (m, 10H), 0.95-0.92 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 143.3, 128.3, 125.0, 119.8, 32.0, 30.7, 30.4, 29.5, 29.4, 29.4, 22.8, 14.2.

(4-(2-Ethylhexyl)thiophen-2-yl)boronic acid (2): To a mixture of 3-(2-ethylhexyl)thiophene (1.96 g, 10 mol) and anhydrous THF (20 mL) cooled in a liquid nitrogen/acetone bath was added 2.5 M *n*-butyl lithium (10 mmol, 4 mL) dropwise over 15 min. After stirring for 2 h at -78 ^{o}C, trimethyl borate (1.04 g, 10 mmol) was added in one portion. The solution mixture was stirred for 1 h at -78 ^{o}C and then at room temperature overnight. The reaction was quenched with cold HCl (2 M) and the solution was adjusted to pH = 3-4. The product was extracted with ethyl acetate and dried over anhydrous Mg_2SO_4. After removal of the solvent under reduced pressure,

the corresponding boronic acid was used directly in the next step without further purification.

2,5-Dibromopyridine-3,4-diamine (3): To a solution of 3,4-diaminopyridine (3.93 g, 36 mmol) in 50 mL 48% aqueous hydrobromic acid was added slowly bromine (6 mL, 116 mmol) and the mixture subsequently was allowed to reflux overnight. The mixture was cooled down to room temperature and then filtered. The resultant precipitation was washed sequentially with aq. Na_2CO_3, aq. $Na_2S_2O_3$ and water. The crude product was further refluxed in a 10% solution of Na_2CO_3 for 1 h and then obtained by filtration. Purification by silica gel chromatography (eluent: dichloromethane/ethyl acetate = 10/1) gave product as a yellow solid. Yield: 3.5 g (37%). ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.05 (s, 1H), 5.96 (brs, 2H), 5.07 (brs, 2H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 140.7, 140.4, 129.8, 128.3, 106.2. HRMS (MALDI-TOF) m/z Calcd for $C_5H_5Br_2N_3$ 267.8834 found 267.8816 $[M+H]^+$.

4,7-Dibromo-[1,2,5]thiadiazolo[3,4-c]pyridine (4): To a stirred, cooled solution of 3,4-diamino-2,5-dibromopyridine (1 g, 3.78 mmol) in pyridine (12 mL) at 0 ^{o}C was added dropwise $SOCl_2$ (4 mmol, 0.4 mL). Stirring was continued for an additional 2 h and then the mixture was poured into water. The crude product was collected by filtration and washed with water. Further purification by silica column chromatography (eluent: hexane/dichloromethane = 4/1) afforded product as a pale yellow solid. Yield: 0.62 g (56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 150.3, 145.3, 136.7, 111.7. MS (MALDI-TOF) m/z

295.8109 $[M+H]^+$.

4,7-Dibromobenzo[c][1,2,5]oxadiazole (5): To a 100 mL round bottom flask, benzo[c][1,2,5]oxadiazole (4.8 g, 40 mmol) and iron dust (93 mg, 1.6 mmol) were added, the mixture was heated to 90 oC, bromine (15.2 g, 95 mmol) was added dropwise to the hot system. After stirring 2 h at 90 ^oC the mixture was poured out in water. A solution of sodium bisulfite was added until no gas evolution was observed. The solid was filtered off and impregnated on silica. This was subjected to column chromatography (silica, eluent heptane). The resulting yellow solid was recrystallized in ethanol to yield 8.4 g (75%) as yellow crystals.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 134.2, 108.7.

5-Fluorobenzo[c][1,2,5]thiadiazole (6a): To a 250 mL round bottom flask containing 4-fluoro-1,2-phenylamine (10.0 g, 79.28 mmol), 100 mL toluene and triethylamine (46 mL, 327.6 mmol) were added. This reaction mixture was cooled down with acetone/liquid nitrogen. After that thionyl chloride (12 mL, 163.9 mmol) was slowly added. The reaction mixture was allowed to reflux for one hour. After cooling down to room temperature the mixture was given to ice water, diluted with toluene. The solid was filtered off and the filtrate was washed several times with water and dried with MgSO4. After filtration the toluene was evaporated and the remaining product was further purified by column chromatography on silica gel with hexane/ ethyl acetate 10:1 as mobile phase affording the desired product as a white solid (5.25 g, 43%). ^{1}H NMR (400

MHz, $CDCl_3$) δ 7.96 dd, (*J* = 9.6, 5.1 Hz, 1H), 7.60 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.40 (td, *J* = 8.7, 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 162.3, 155.0 154.8, 152.0, 129.3, 122.6, 122.5, 121.5, 121.2, 104.9, 104.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.34 ppm.

5,6-Difluorobenzo[c][1,2,5]thiadiazole (6b): This material was synthesized following the same procedure as for **6a**. After purification by column chromatography, the product was obtained as colorless oil (6.1 g, 88% yield). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.23-7.21 (m, 1H), 6.93-6.90 (m, 2H), 2.63 (t, *J* = 5.7 Hz, 2H), 1.65-1.57 (m, 2H), 1.30-1.26 (m, 14H), 0.89 (t, *J* = 5.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.3, 128.3, 124.9, 119.7, 31.9, 30.6, 30.3, 29.6, 29.5, 29.3, 22.7.

4,7-Dibromo-5-fluorobenzo[c][1,2,5]thiadiazole (7a): 5-Fluoro-2,1,3-benzothiadiazol (10.40g, 67.5 mmol) and 45.8 mL HBr were added in a 100 mL round bottom flask. After that bromine (11.1 mL, 190 mmol) was added dropwise. The reaction mixture was stirred for two days at 95°C, additionally two days at room temperature. The reaction mixture was put in water and the solid was filtered off, washed several times with water to be neutral and dried. The product was then recrystallized from methanol and 5% toluene. Affording the desired product as a white solid (5.97 g, 33%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.28 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 158.9, 152.8, 152.7, 150.3, 132.4, 124.0, 123.7, 114.1, 113.9, 98.3, 98.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.27 ppm.

4,7-Dibromo-5,6-difluorobenzo[c][1,2,5]thiadiazole (7b): This material was synthesized following the same procedure as for **7a**. After purification by column chromatography, the product was obtained as colorless oil (6.1 g, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23-7.21 (m, 1H), 6.93-6.90 (m, 2H), 2.63 (t, *J* = 5.7 Hz, 2H), 1.65-1.57 (m, 2H), 1.30-1.26 (m, 14H), 0.89 (t, *J* = 5.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.3, 128.3, 124.9, 119.7, 31.9, 30.6, 30.3, 29.6, 29.5, 29.3, 22.7.

4,7-Bis(4-(2-ethylhexyl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridine (8a): To a 50 mL 2-neck round-bottom flask with a condenser, (4-(2-ethylhexyl)thiophen-2-yl)boronic acid (1.08 g, 4.2 mmol), 4,7-dibromo-[1,2,5]thiadiazolo[3,4-c]pyridine (0.294 g, 1 mmol), nitrogen-saturated 2 M K2CO3 solution 10 mL and THF 10 mL were added. The mixture was then purged with nitrogen for 15 min. Then $Pd(PPh_3)_4$ (10 mg) was added and the reaction mixture was heated to reflux overnight. The reaction mixture was then cooled to room temperature and the solvent was evaporated. The crude red product was re-dissolved in THF and filtered through a short silica gel. The solvent was evaporated and the product was recrystallized from ethanol. Yield: 0.42 g (80 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.49 (d, *J* = 1.2 Hz, 1H), 7.93 (d, *J* = 1.2 Hz, 1H), 7.17-7.15 (m, 1H), 7.05-7.03 (m, 1H), 2.64-2.61 (m, 4H), 1.67-1.65 (m, 2H), 1.21-1.42 (m, 16H), 0.95-0.90 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 148.1, 146.4, 144.0, 143.2, 141.2, 140.7, 136.4, 133.6, 129.8, 126.6, 122.9, 120.5, 40.4, 40.3, 34.7, 34.6, 32.5, 28.9, 25.7,

24.8, 23.1, 14.2, 10.9. HRMS (MALDI-TOF) m/z Calcd for $C_{29}H_{39}N_3S_3$ 525.2300 found 525.2305 $[M+H]^+$.

4,7-Bis(4-(2-ethylhexyl)thiophen-2-yl)benzo[c][1,2,5]oxadiazole (8b): This material was synthesized following the same procedure as for **8a**. After purification by column chromatography, the product was obtained as white solid (80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 1.2 Hz, 2H), 7.55 (s, 2H), 6.99 (d, *J* = 1.2 Hz, 2H), 2.61 (d, *J* = 6.8 Hz, 4H), 1.66-1.63 (m, 4H), 1.39-1.34 (m, 16H), 0.93-0.88 (m, 12H).^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 143.8, 137.4, 130.6, 126.1, 122.5, 122.1, 40.3, 34.7, 32.5, 28.9, 25.6, 23.1, 14.2, 10.9. HRMS (MALDI-TOF) *m/z* Calcd for $C_{30}H_{40}N_2OS_2$ 508.2577 found 508.2590 $[M+H]^+$.

4,7-Bis(4-(2-ethylhexyl)thiophen-2-yl)-5-fluorobenzo[c][1,2,5]thiadiazole (8c): This material was synthesized following the same procedure as for **8a**. After purification by column chromatography, the product was obtained as orange solid, yield 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.96 (s, 1H), 7.74 (d, *J* = 13 Hz, 1H), 7.13 (s, 1H), 7.07 (s, 1H). 2.67-2.63 (m, 4H), 1.67-1.64 (m, 2H), 1.36-1.27 (m, 16H), 0.94-0.87 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 157.4, 153.2, 153.1, 149.5, 143.0, 141.9, 137.4, 137.4, 132.1, 132.1, 132.0, 131.9, 130.2, 125.4, 123.8, 123.8, 123.5, 116.4, 116.1, 111.1, 111.0, 40.4, 40.4, 34.7, 34.6, 32.6, 31.7, 29.0, 25.8, 25.7, 23.2, 22.8, 14.3, 14.2, 11.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.19 ppm. HRMS (MALDI-TOF) *m/z* Calcd $C_{30}H_{39}FN_2S_3$ for 542.2253 found 542.2268 $[M+H]^+$.

4,7-Bis(4-(2-ethylhexyl)thiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (8d): This material was synthesized following the same procedure as for **8a**. After purification by column chromatography, the product was obtained as orange solid (68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 2H), 7.18 (s, 2H), 2.65 (d, J = 6.8 Hz, 4H), 1.68-1.63 (m, 2H), 1.37-1.28 (m, 16 H), 0.94-0.90 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 151.0, 149.0 (d), 148.6, 148.4, 142.4, 132.8, 132.8, 132.7, 131.0, 128.8, 128.8, 127.3, 127.2, 124.9, 111.8, 111.7, 111.7, 111.6, 40.4, 34.5, 32.5, 28.9, 25.7, 23.1, 14.2, 10.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -128.24 ppm. HRMS (MALDI-TOF) *m/z* Calcd for $C_{30}H_{38}F_2N_2S_3$ 560.2159 found 560.2170 $[M+H]^+$.

4,7-Bis(5-bromo-4-(2-ethylhexyl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridine (9a): To a stirred solution of 4,7-bis(4-(2-ethylhexyl)thiophen-2-yl)-[1,2,5]-thia-diazolo[3,4-c]pyridine (0.24 g, 0.456 mmol) in THF (10 mL), NBS (0.178 g, 0.1 mmol) was added in small portions. The reaction mixture was stirred at room temperature for 6 h, then the reaction mixture washed with washed with brine and dried over anhydrous sodium sulfate. The solvent was removed at a reduced pressure to give the product as a red solid. Needle-like crystal was obtained by recrystallizing from ethanol. Yield: 0.249 g (80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.33 (s, 1H), 7.75 (s, 1H), 2.60-2.57 (m, 4H), 1.56-1.36 (m, 2H), 1.20-1.40 (m, 16H), 0.91-0.89 (m, 12H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 154.6, 145.7, 145.4, 143.5, 142.5, 140.8, 140.1, 135.7, 133.1, 129.0, 119.8, 117.1, 112.6, 40.0 (d), 34.0, 33.8, 32.5, 28.5, 25.7, 25.7, 23.1, 14.2, 10.9.

HRMS (MALDI-TOF) *m/z* Calcd for $C_{29}H_{37}Br_2N_3S_3$ 683.0491 found 683.0444 $[M+H]^+$.

4,7-Bis(5-bromo-4-(2-ethylhexyl)thiophen-2-yl)benzo[c][1,2,5]oxadiazole (9b): This material was synthesized following the same procedure as for **9a**. After purification by column chromatography, the product was obtained as orange solid (68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 2H), 7.43 (s, 2H), 2.55 (d, *J* = 7.2 Hz, 4H), 1.72-1.69 (m, 2H), 1.38-1.30 (m, 16 H), 0.94-0.88 (m, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 143.2, 137.0, 130.3, 125.8, 121.5, 112.2, 40.0, 33.9, 32.5, 28.8, 25.7, 23.1, 14.2, 10.9. HRMS (MALDI-TOF) *m/z* Calcd for $C_{30}H_{38}Br_2N_2OS_2$ 666.0768 found 666.0746 $[M+H]^+$.

4,7-Bis(5-bromo-4-(2-ethylhexyl)thiophen-2-yl)-5-fluorobenzo[c][1,2,5]thiadiazo-le (9c): This material was synthesized following the same procedure as for **9a**. After purification by column chromatography, the product was obtained as orange solid (88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.95 (s, 1H), 7.74 (d, *J* = 13.2 Hz, 1H), 7.13(s, 1H), 7.07 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 157.6, 153.0, 152.9, 149.4, 142.4, 141.5, 136.9, 136.9, 132.0, 132.0, 131.6, 131.5, 129.3, 125.0, 124.9, 116.2, 115.8, 113.9 (d), 113.8, 110.8, 110.6, 40.0 (d), 33.9, 33.8, 32.5, 28.8 (d), 25.7, 23.1, 14.2, 10.9 (d). ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.31 ppm. HRMS (MALDI-TOF) *m/z* Calcd for $C_{30}H_{37}Br_2FN_2S_3$ 700.0478 found 700.0445 $[M+H]^+$.

4,7-Bis(5-bromo-4-(2-ethylhexyl)thiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thia-diazole (9d): This material was synthesized following the same procedure as for **7a**. After purification by

column chromatography, the product was obtained as orange solid (86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 2H), 2.59 (d, *J* = 7.2 Hz, 4h), 1.72-1.69 (m, 2H), 1.37-1.32 (m, 16H), 0.93-0.90 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 150.8, 148.4 (d), 148.3, 141.8, 132.3, 1323, 132.2, 131.0, 115.0, 111.1, 111.0, 39.8, 33.7, 32.4, 28.8, 25.7, 23.1 14.2, 10.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -128.13 ppm. HRMS (MALDI-TOF) *m/z* Calcd for $C_{30}H_{36}Br_2F_2N_2S_3$ 718.0355 found 718.0321 $[M+H]^+$.

1,2-Bis(2-ethylhexyloxy)benzene (10): A mixture of catechol (3.3 g, 30 mmol), KOH (6.7 g, 120 mmol) and 3-(bromomethyl)heptane (19.3 g, 100 mmol) in DMSO (60 mL) was refluxed overnight under N_2. After being cooled to room temperature, the reaction mixture was poured to water and then extracted with hexane. The organic phase was washed with water, brine, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was purified by silica gel column chromatography using petroleum ether as eluent affording the desired product as a colorless oil (8.9 g, 88 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.88 (s, 4H), 3.87-3.85 (m, 4H), 1.77-1.73 (m, 2H), 1.56-1.30 (m, 16H), 0.95-0.88 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 149.5, 120.8, 113.8, 71.5, 39.5, 30.6, 29.1, 23.9, 23.0, 14.0, 11.1.

1,2-Dibromo-4,5-bis(2-ethylhexyloxy)benzene (11):. To a stirred solution of compound **1** (7.0 g, 21 mmol) in AcOH/$CHCl_3$ (25 mL/25 mL) at room temperature, NBS (8.9 g, 50 mmol) was added in portions. After complete addition, the mixture was stirred for 10 h. The reaction was

quenched with water and extracted with hexane. The organic phase was separated and washed with brine, dried over anhydrous Na_2SO_4. The crude was purified by silica gel column chromatography using petroleum ether as eluent affording the desired product as a colorless oil (9.7 g, 88 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.05 (s, 2H), 3.82-3.80 (m, 4H), 1.77-1.71 (m, 2H), 1.52-1.25 (m, 16H), 0.94-0.88 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 149.3, 117.6, 114.3, 71.8, 39.3, 30.4, 29.0, 23.8, 22.9, 13.9, 11.0.

1,2-Bis(2'-ethylhexyloxy)-4,5-bis(3-thienyl)benzene (12). To a 100 mL two-neck round-bottom flask was added 3-thiopheneboronic acid, (3.8 g, 30 mmol), 1,2-dibromo-4,5-bis(2-ethylhexyloxy)benzene (4.9 g, 10 mmol), $Pd(PPh_3)_4$ (100 mg), THF (100 mL) and 2 M K_2CO_3 (30 mL). The solution mixture was heated to 80 ^{o}C overnight under N_2. After being cooled to room temperature, the mixture was poured into water and extracted with dichloromethane (3 × 50 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude product was purified by silica gel column chromatography eluting with petroleum ether/dichloromethane affording the desired product (3.5 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.17 (dd, 2H, J = 3.0, 4.96 Hz), 7.02 (dd, 2H, J = 1.28 Hz, 3.0 Hz), 6.78 (dd, 2H, J = 1.24, 4.96 Hz), 3.93-3.91 (m, 4H), 1.81-1.78 (m, 2H), 1.56-1.33 (m, 16H), 0.97-0.92 (m, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 148.7, 142.2, 129.1, 127.8, 124.5, 122.2, 71.8, 39.6, 30.6, 29.1, 23.9, 23.1, 14.1, 11.1.

Synthesis of compound (**13**). A solution of iron(III) chloride (953 mg, 5.88 mmol) in nitromethane (20 mL) was added dropwise to a solution of 1,2-*bis*(2-ethylhexyloxy)-4,5-*bis*(3-thienyl)benzene **3** (1.0 g, 2 mmol) in DCM (200 mL) under N_2. After complete addition in 30 min, methanol (10 mL) was added and the reaction was stirred for another 30 min. The solvent was removed and the residue was purified by silica gel column chromatography giving the desired product (940 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, J = 5.36 Hz, 2H), 7.68 (s, 2H), 7.47 (d, J = 5.32 Hz, 2H), 4.11-4.04 (m, 4H), 1.90-1.87 (m, 2H), 1.60-1.36 (m, 16H), 1.00 (t, J = 7.44 Hz, 6H), 0.93 (t, J = 7.04 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 149.2, 133.9, 130.3, 123.4, 122.7, 122.6, 106.4, 71.5, 39.6, 30.7, 29.2, 24.1, 23.1, 14.1, 11.3.

Synthesis of compound (**14**). To a 100 mL two-neck round bottom flask was added 5,6-*bis*(2-ethylhexyloxy)naphtho[2,1-b:3,4-b']dithiophene **4** (400 mg, 0.8 mmol) and anhydrous THF (10 mL). After deoxygenating with nitrogen three times, the solution was cooled to -78 ^{o}C and 1.6 M of *n*-BuLi (1.3 mL, 2.0 mmol) was added dropwise. The resulting white suspension was stirred at -78 ^{o}C for 1 h and *tri*-*n*-butyltin chloride (651 mg, 2.0 mmol) was added in one portion. Upon complete addition, the reaction mixture was stirred at -78 ^{o}C for 10 min, and then warmed to room temperature stirring for 3 h. The reaction mixture was poured into ethyl acetate (100 mL), washed with H_2O (2 × 30 mL), brine (2 × 30 mL), and dried over anhydrous Na_2SO_4. After removal of solvent, the residue was purified by silica gel column chromatography (silica gel was

immersed in hexane containing 15% triethylamine for 1 h before use) using hexane as the eluent affording the desired product as a colorless liquid (810 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (s, 2H), 7.81 (s, 2H), 4.22-4.15 (m, 4H), 1.99-1.93(m, 2H), 1.80-1.26 (m, 52H), 0.96-0.88 (m, 30H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 148.5, 136.1, 135.4, 134.6, 130.3, 122.5, 107.3, 69.4, 31.9, 29.7, 29.6, 29.5, 29.4, 29.0, 27.3, 26.2, 22.7, 14.1, 13.7, 10.9. MS (MALDI-TOF), m/z 1077.4831 (M^+).

Synthesis of **PNBO**.

This polymer was synthesized following the same procedure as for PNTP. After purification by Soxhlet extraction affording the polymer as a black solid (35 mg, 34%). GPC: Mn (71 kDa), PDI (2.49).

Synthesis of **PNfTB**.

This polymer was synthesized following the same procedure as for **PNTP**. After purification by Soxhlet extraction affording the polymer as a black solid (70 mg, 67%). GPC: Mn (47 kDa), PDI (1.60).

Synthesis of **PNffTB**.

This polymer was synthesized following the same procedure as for **PNTP**. After purification by Soxhlet extraction affording the polymer as a black solid (40 mg, 37%). GPC: Mn (46 kDa), PDI (2.07).

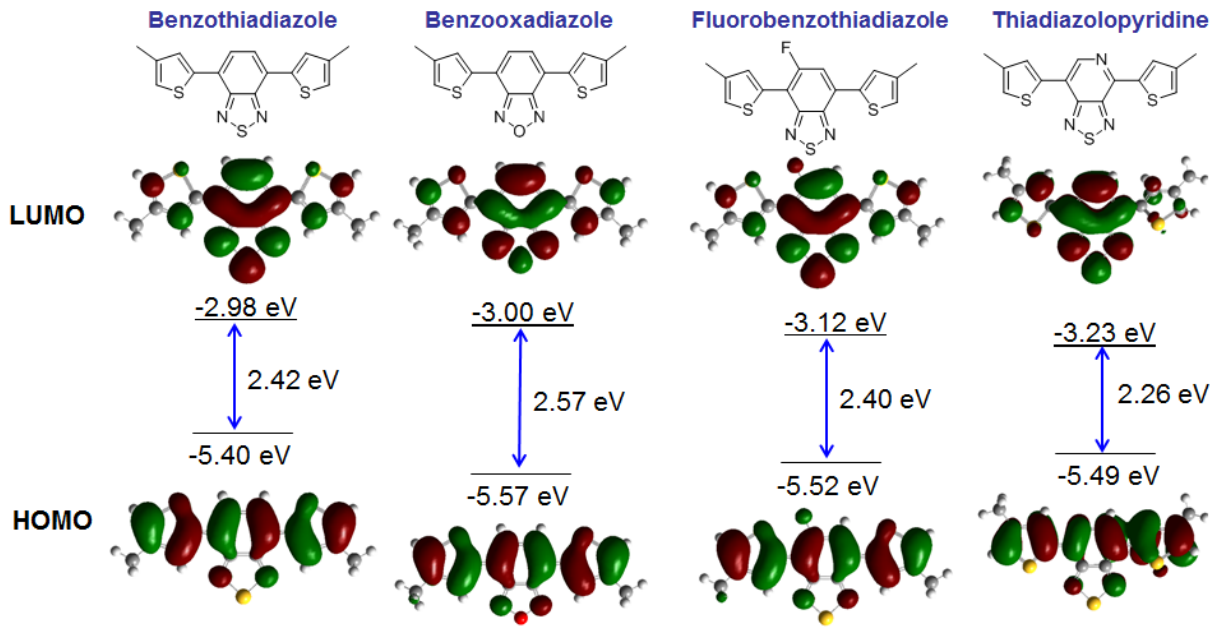

Fig. S1. Results of frontier molecular orbital energy level calculations by Gaussian 09 using Density Functional theory (DFT) with B3LYP and 6-31G basis set.

(a) (b)

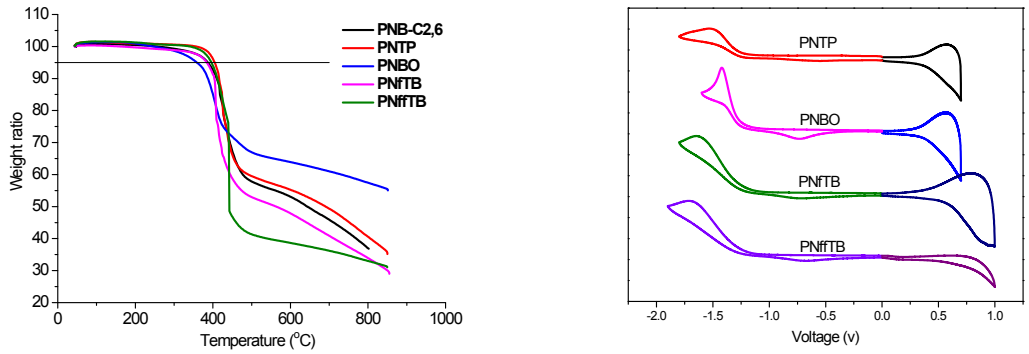

Fig. S2. (a) TGA plots of polymers with a heating rate of 10 °C / min under an inert atmosphere. (b) CV traces of copolymers

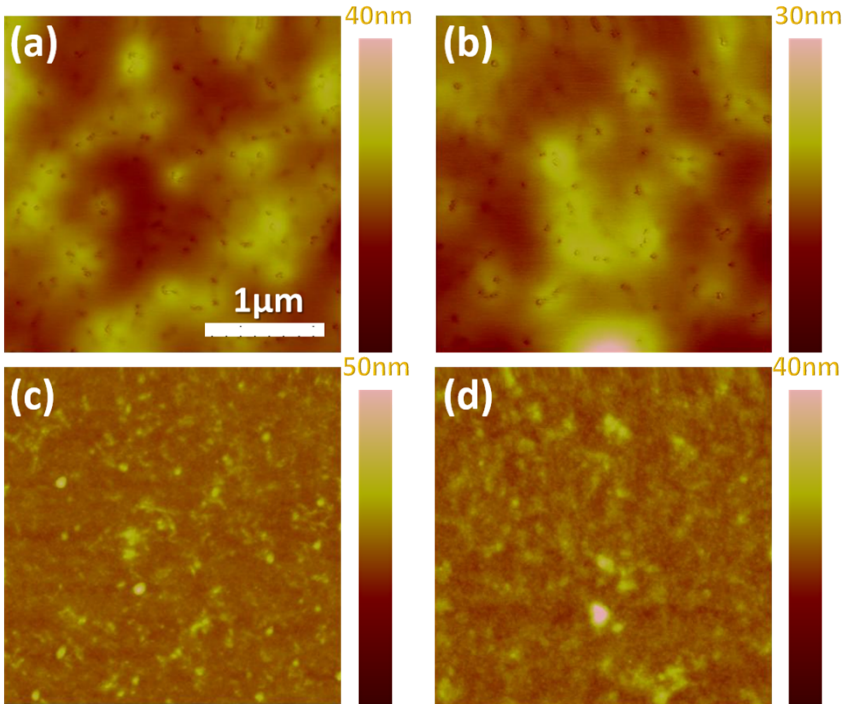

Fig. S3. AFM height images of **PNfTB** thin film annealed at (a) room temperature and b) 200 °C; **PNffTB** thin film annealed at (c) room temperature and (d) 240 °C.