Naphthodithiophene-2,1,3-Benzothiadiazole Copolymers for Bulk Heterojunction Solar Cells

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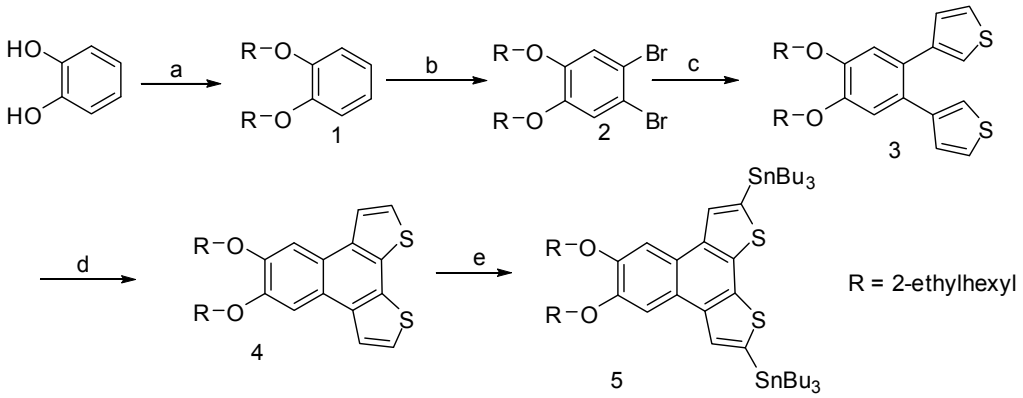
Experimental:

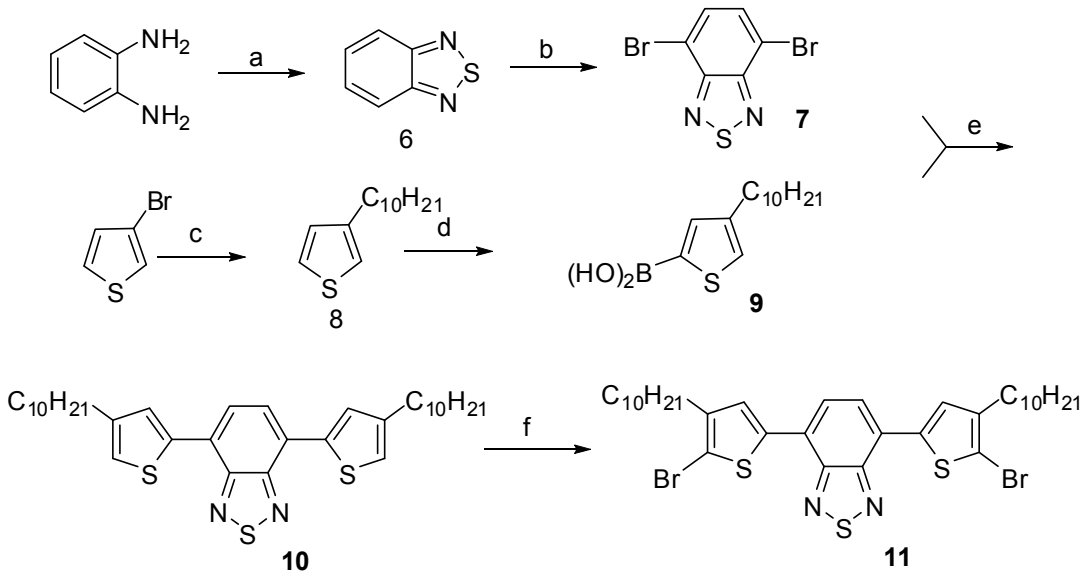
Materials and method

All reagents and starting materials were purchased from commercial sources and used as received, unless otherwise noted. The synthetic routes of monomers are shown in Scheme 1 and 2, respectively. The key intermediates 3 and 7 are prepared according to reported procedures. All the solvents were dried by the standard methods wherever needed. ^{1}H NMR spectra were recorded using a Bruker-400 NMR spectrometer and referenced to the residual $CHCl_3$ 7.26 ppm or DMSO-d_6 2.5 ppm. ^{13}C NMR spectra were recorded using a Bruker-400 NMR spectrometer and referenced to the $CDCl_3$ 77 ppm or DMSO-d_6 39.5 ppm. Thermal stabilities were determined by thermal gravimetric analyzer (PE-TGA6) with a heating rate of 10 ^{o}C /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 0.44 V versus Ag/Ag^{+}. The HOMO and LUMO energy levels were determined from the oxidation and reduction onsets from the cyclic voltammograms and reported values were calculated with reference to ferrocene (4.8 eV vs vacuum). 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.



Reagents and conditions: a) EtOH, KOH, $C_8H_{17}Br$, 88%; b) NBS, $CHCl_3$/AcOH, 86%; c) 3-thiopheneboronic acid, $Pd(PPh_3)_4$, 2 M K_2CO_3, THF, 84%; d) $FeCl_3$, $MeNO_2$, DCM, 78%; e) *n*-BuLi, Bu_3SnCl, 94%.

Scheme S1 Synthetic route for donor moiety **5**.



Reagents and conditions: a) $SOCl_2$, Et_3N, DCM, 76%; b) Br_2, HBr, 91%; c) (i) Mg, $C_{10}H_{21}Br$, (ii) $Ni(dppf)Cl_2$, 88%; d) *n*-BuLi, $B(OMe)_3$, 82%; e) $Pd(PPh_3)_4$, 2 M K_2CO_3, THF, 90%; f) NBS, $CHCl_3$/AcOH, 93%.

Scheme S2 Synthetic route for acceptor moieties, **7** and **11**.

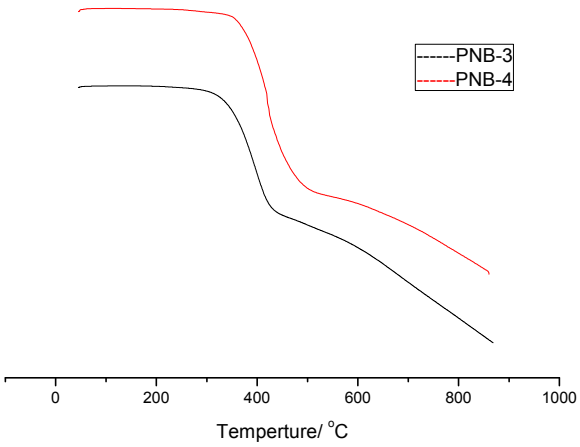


Fig. S1 TGA traces of **PNB-3** and **PNB-4**.

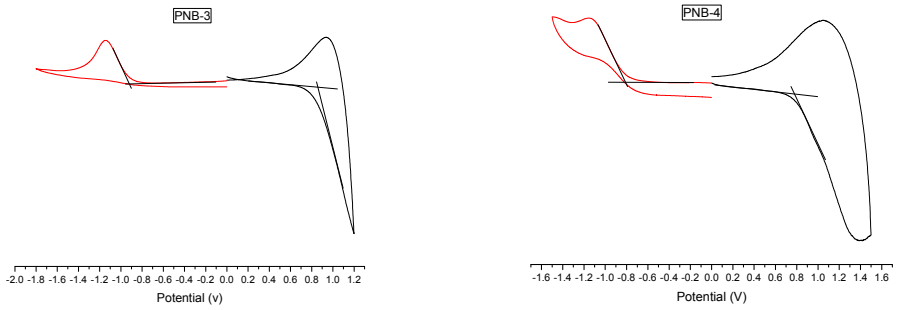


Fig. S2 CV traces of PNB-3 and PNB-4

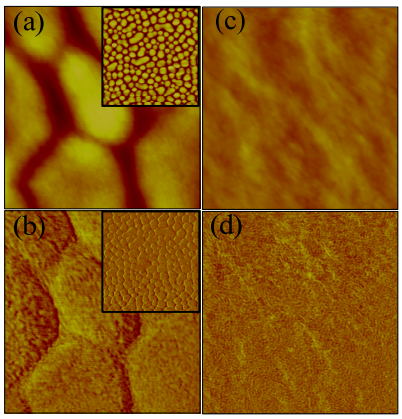


Fig. S3 AFM images of PNB-4 : $PC_{71}BM$ blend films prepared from chlorobenzene with scan size of 1 × 1 μm. (a) and (b) are the morphology and phase images of the blend film without the addition of DIO, respectively. The insets in (a) and (b) are the scan size of 5 × 5 μm of the corresponding films. (c) and (d) are the morphology and phase images of the blend film with the addition of 3% DIO respectively.

Experimental section

1,2-bis(2-ethylhexyloxy)benzene ***(1)***[1]. The mixture of catechol (3.3 g, 30 mmol), KOH (6.7 g, 120 mmol) and 3-(bromomethyl)heptane (4.2 g, 22 mmol) in EtOH (60 mL) was refluxed overnight under N_2. The reaction mixture was cooled to room temperature and then poured into water. The solution mixture was extracted with hexane twice. The combined organic phase was washed with water, brine, and dried over anhydrous Na_2SO_4. The crude product 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, $CDCl_3$) δ: 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 ***(2)***. To a stirred solution of compound **1** (7.0 g, 21 mmol) in AcOH/$CHCl_3$ (25 ml/25 ml) at room temperature was added NBS (8.9 g, 50 mmol) in portions. After complete addition, the solution mixture was stirred for 10 h at r.t. The reaction mixture was then poured into water and extracted with hexane twice. The organic phase was separated, washed with brine, dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude product was purified by silica gel column chromatography using petroleum ether as eluent affording the desired product as an 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, $CDCl_3$) δ: 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 ***(3)***[2]. To a 100 mL two-neck round-bottom flask was added 3-thiophenebonoric acid, (3.8 g, 30 mmol), compound **2** (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 cooling 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, 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, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 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.

5,6-Bis(2'-ethylhexyloxy)naphtho[2,1-b:3,4-b']dithiophene ***(4)***[2]. A solution of iron(III) chloride (953 mg, 5.88 mmol) in nitromethane (20 mL) was added dropwise to a stirred solution of compound **3** (1.0 g, 2 mmol) in DCM (50 mL) under N_2. After stirring for 30 min, methanol (10 mL) was added and the reaction was stirred for another 30 min. After removal of solvent, the residue was purified by silica gel column chromatography to give the desired product (940 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (dd, 2H, J = 5.36 Hz), 7.68 (s, 2H), 7.47 (dd, 2H, J = 5.32 Hz), 4.11-4.04 (m, 4H), 1.90-1.87 (m, 2H), 1.60-1.36 (m, 16H), 1.00 (t, 6H, J = 7.44 Hz), 0.93 (t, 6H, J = 7.04 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 1492, 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. (Note: For a 2.0 gram-scale reaction, the reaction yield drops to 78%).

5,6-bis(2'-ethylhexyloxy)-2,5-bis(tri-n-butylstannyl)-naphtho-[2,1-b:3,4-b']dithiophene ***(5)***. To a 100 mL two-neck round bottom flask was added compound **4** (400 mg, 0.8 mmol) and dry THF (10 mL). After deoxygenated 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 mixture was stirred at -78 ^{o}C for 10 min, and then warmed to room temperature to stir 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 added 5 mL of triethylamine and stirred at room temperature for 2 h. After triethylamine was removed, the residue was purified by silica gel column chromatography 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), 1.8-1.26 (m, 52H), 0.96-0.88 (m,

30H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 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.

2,1,3-Benzothiadiazole ***(6)***[3]. To a 1000 mL flask were added commercially purchased o-phenylenediamine (10.0 g, 92.5 mmol), CH_2Cl_2 (300 mL), and triethylamine (37.4 g, 370 mmol). The solution mixture was stirred vigouously until a complete dissolution of di-amine. Thionyl chloride (13.4 mL, 184.9 mmol) was very slowly added dropwise. After complete addition, the reaction mixture was heated to reflux for 5 h. The solvent was then removed under reduced pressure. The residue was added with water (700 mL) and then concentrated HCl to adjust the pH to 1. The desired product was purified by direct steam distillation. The distillate was extracted with CH_2Cl_2 (5 × 200 mL), dried with anhydrous $MgSO_4$, and filtered. The solvent was removed to afford pure product **6** (19.6 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, J = 3.2 Hz and J = 5.7 Hz, 2H), 7.57 (dd, J = 3.2 Hz and J = 5.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.8, 129.3, 121.6.

4,7-Dibromo-2,1,3-benzothiadiazole ***(7)***. To a 500 mL two-necked round-bottomed flask containing benzothiadiazole **6** (10.0 g, 73.4 mmol) and HBr (150 mL, 48%) was carefully added dropwise a solution of Br_2 (35.2 g, 220.3 mmol) in HBr (100 mL, 48%). After complete addition of Br_2, the solution mixture was heated to reflux for 6 h. Precipitation of a dark orange solid was noted. The reaction mixture was cooled to room temperature and a sufficient amount of a saturated solution of $NaHSO_3$ was added to completely consume the excess Br_2. The mixture was then filtered under vacuum and the solid was washed exhaustively with water and cold Et_2O. The solid was finally dried under vacuum for 20 h to afford dibrominated product in 95% yield (20.5 g, 69.8 mmol). ^{1}H NMR (400 MHz, $CDCl_3$/[D_6] DMSO, 8:2): δ = 7.73 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.9, 132.3, 113.9. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.9, 132.3, 113.9.

3-Decylthiophene ***(8)***. To magnesium turnings (7.68 g, 320 mmol) in diethyl ether (100 mL) was added 1-bromodecane dropwise (31.8 mL, 160 mmol). After complete addition, the mixture was refluxed for 3 h and then transferred to a solution of 3-bromothiophene (13.0 g,

80 mmol) and Ni(dppp)Cl_2 (150 mg) at 0 ºC. The solution mixture was refluxed overnight under N_2. The reaction mixture was poured into ice-water and extracted with diethyl ether. The combined organic extract was washed with brine, water and then dried over anhydrous Na_2SO_4. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography using petroleum ether as eluent affording the desired product as colorless liquid (15.8 g, 88%). ^{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.

3-Decylthiophene-5-boronic acid ***(9)***. To a dry 100 mL two-neck flask containing diisopropylamine (3.32 g, 4.6 mL, 32.8 mmol) and dry THF (40 mL) was added 1.6 M of *n*-butyl lithium (20.6 mL, 32.9 mmol) dropwise under N_2 at 0 ^{o}C. The solution mixture was stirred for 0.5 h at 0 ^{o}C and then cooled to -78 ^{o}C. To the solution mixture was added a solution of 3-decylthiophene (6.7 g, 29.8 mmol) in dry THF (20 mL). The resulting mixture was stirred for 1 h at -78 ^{o}C and allowed to warm to r.t. for 1 h. After cooling to -78 ^{o}C, trimethyl borate (7 mL, 61 mmol) was added in one portion and the reaction mixture was allowed to warm up to r.t. for 2 h. Water and 3 M HCl were in turn added. The reaction mixture was poured into water and then extracted with ethyl acetate (3 × 50 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and evaporated to dryness under 35 ^{o}C. The crude product was then loaded on silica gel column and eluted with petroleum ether/dichloromethane and petroleum ether/ethyl acetate affording the desired product as a yellow viscous liquid (6.6 g, 82%). The material was carried forward without further purification.

4,7-Bis(3'-decylthiophen-2-yl)-2,1,3-benzothiadiazole ***(10)***. To a 100 mL two-neck round bottom flask was added 3-decylthiophene-5-boronic acid (3.86 g, 1.44 mmol), 4,7-dibromo-2,1,3-benzothiadiazole (1.76 g, 1 mmol), $Pd(PPh_3)_4$ (100 mg), THF (60 mL) and 2 M K_2CO_3 (3 mL). The solution mixture was heated to 80 ^{o}C overnight under N_2. After cooling to room temperature, the reaction mixture was poured into water and extracted with dichloromethane

(3 × 60 mL). The combined organic phase was dried over anhydrous sodium sulfate, and evaporated to dryness. The crude product was then loaded on silica gel column and eluted with petroleum ether/dichloromethane affording the desired product as a red solid (2.9 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, *J* = 1.2 Hz, 2H), 7.76 (s, 2H), 7.01 (d, *J* = 1.2 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 4H), 1.73-1.65 (m, 4H), 1.38-1.26 (m, 28H), 0.89 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.5, 144.3, 138.9, 128.9, 125.9, 125.4, 121.4, 31.9, 30.6, 30.5, 29.6, 29.5, 29.4, 29.38, 29.34, 22.7, 14.1. MS (MALDI-TOF): m/z 580.3 (M^+).

4,7-Bis(5′-bromo-3′-(2-decylthiophen-2-yl)-2,1,3-benzothiadiazole ***(11)***. To a solution of 4,7-*bis*(3′-decylthiophen-2-yl)-2,1,3-benzothiadiazole (2.32 g, 40 mmol), AcOH (30 mL) and $CHCl_3$ (60 mL) was added *N*-bromosuccinimide (15.7 g, 88 mmol) in portions at 0 ^{o}C. After stirring for 24 h, the reaction mixture was poured into H_2O (150 mL) and then extracted with dichloromethane (3 × 80 mL). The combined organic extract was washed with brine, water and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by silica gel column chromatography using petroleum ether/dichloromethane as eluent affording the desired product as a red solid (2.54, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (s, 2H), 7.71 (d, *J* = 0.8 Hz, 2H), 2.64 (t, *J* = 7.8 Hz, 4H), 1.70-1.62 (m, 4H), 1.39-1.26 (m, 28H), 0.89 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.9, 135.9, 135.4, 134.7, 130.4, 122.4, 106.8, 71.6, 39.7, 30.8, 29.3, 29.1, 27.5, 24.1, 23.2, 14.2, 13.8, 11.4, 11.0. MS (MALDI-TOF): m/z 738.1 (M^+).

PNB-3. To a 50 mL round-bottom flask containing 4,7-dibromo-2,1,3-benzothiadiazole **7** (58 mg, 0.20 mmol), 5,6-*bis*(2′-ethylhexyloxy)-2,5-*bis*(*tri*-*n*-butylstannyl)-naphtho[2,1-*b*:3,4-*b*′]-dithiophene **5** (215 mg, 0.20 mmol) were added $Pd(PPh_3)_4$ (10 mg). After three successive deoxygenation-refilling with N_2 cycles, anhydrous toluene (64 mL) were added via a syringe. The polymerization was carried out at refluxing for 42 h under N_2. The polymer was precipitated in MeOH and collected by filtration. Low-molecular-weight oligomers were removed by Soxhlet extraction with MeOH and hexane, respectively. The remaining high-molecular-weight solid was extracted with chloroform. The desired polymer was precipitated from methanol, collected and dried in vacuum for 12 h affording the product as a black solid

(108 mg, 86%). GPC: *Mn* (14.8 Kg/mol), PDI (1.79).

PNB-4. The synthetic procedure of **PNB-3** was followed using 4,7-*bis*(5′-bromo-3′-(2-decylthiophen-2-yl)-2,1,3-benzothiadiazole **11** (74 mg, 0.10 mmol), 5,6-*bis*(2′-ethylhexyloxy)-2,5-*bis*(*tri*-*n*-butylstannyl)naphtho[2,1-*b*:3,4-*b*′]dithiophene **5** (107 mg, 0.10 mmol), $Pd(PPh_3)_4$ (10 mg), in DMF (30 mL) refluxing for 42 h. The polymer was precipitated in MeOH and collected by filtration. Low-molecular-weight oligomers were removed by Soxhlet extraction with MeOH and hexane, respectively. The remaining high-molecular-weight solid was extracted with toluene. The desired polymer was precipitated from methanol, collected and dried in vacuum for 12 h affording the desired polymer product as a black solid (69 mg, 64%). GPC: *Mn* (33.4 Kg/mol), PDI (1.62).

References:

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