

## Supporting Information

### Benzothiadiazole- and pyrrole-based polymers bearing thermally cleavable solubilizing groups as precursors for low bandgap polymers

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**Materials.** All reagents were purchased from Aldrich and used without further purification unless otherwise noted. 4,7-Dibromobenzo[1,2,5]thiadiazole **9** was prepared using a method described by Edelman and al.<sup>1</sup> 2,5-Bis(trimethylstannyl)-1-methylpyrrole **14** was prepared using a method described by Faderl et al.<sup>2</sup> All solvents (reagent grade) were purchased from Fisher or EM Science. Tetrahydrofuran (THF) was distilled over sodium/benzophenone. Methylene chloride, and pyridine were dried prior to use by passing through two columns of neutral alumina. Diisopropylamine was distilled over CaH<sub>2</sub>. *N,N*-Dimethylformamide (DMF) was stored over molecular sieves. *N*-bromosuccinimide (NBS) was recrystallized from acetic acid prior to use. All reactions of air- and water-sensitive materials were performed under nitrogen in flame-dried glassware and degassed solutions. ‘Degassed’ refers to solutions that have been subjected to three successive freeze-thaw cycles on a nitrogen/high-vacuum line. All solvents were removed with a rotary evaporator at aspirator pressure. Reactions were monitored by thin layer chromatography using Whatman<sup>®</sup> 250 μm silica gel plates. Flash column chromatography was performed using Merck Kieselgel 60 silica, 230-400 mesh.

**Characterization.** <sup>1</sup>H NMR and <sup>13</sup>C NMR (using <sup>1</sup>H decoupling) were recorded in CDCl<sub>3</sub> with TMS as standard on Bruker AM-400 and AMX-400. Low and high resolution fast atom bombardment (FAB) and electronic impact (EI) mass spectrometry, and elemental analysis were performed at the UC Berkeley MS

and microanalytical Facilities. High resolution mass spectrometry measurements are valid to  $\pm 5$  ppm. Thermogravimetric Analysis (TGA) was performed using a Seiko instruments SSC 5200 TG/DTA 220, at a speed of  $5^{\circ}\text{C}/\text{min}$ . THF GPC was carried out at  $1.0\text{ mL}/\text{min}$ . Three Plgel columns ( $7.5 \times 300\text{ mm}$ ) with pore sizes of  $10^5$ ,  $10^3$ , and  $500\text{ \AA}$  were used. The particle size was  $5\text{ }\mu\text{m}$ . The GPC system consisted of a Waters 510 pump, a Waters 717 autosampler, a Waters 486 UV-vis detector, a Wyatt DAWN-EOS light scattering detector, and a Wyatt Optilab differential refractive index detector. The columns were thermostatted at  $35^{\circ}\text{C}$ . Absorption spectra were recorded on a Cary 50 UV-Vis spectrometer. FT-IR spectra were obtained on NaCl plates with an ATI Mattson Gemini spectrometer. MALDI-TOF MS was performed on a PerSeptive Biosystems Voyager-DE, using 2,2':5',2''-terthiophene as the matrix.

**4-Nitrophenyl(2-hexadecyl)carbonate.** A solution of 2-hexadecanol (2.38 g, 0.83 mmol) and pyridine (0.81 mL, 10 mmol) in  $\text{CH}_2\text{Cl}_2$  (25 mL) was cooled to  $0^{\circ}\text{C}$ . To this solution was added dropwise a solution of 4-nitrophenylchloroformate (2.00 g, 9.93 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL). The resulting solution was allowed to stir overnight while slowly warming to room temperature. The solution was then poured into water (40 mL). After separating the layers, the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  (40 mL). The combined organic layers were then dried over  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. The resulting oil was purified by flash column chromatography ( $\text{CH}_2\text{Cl}_2$ :hexanes 1:3) to yield 3.60 g (90%) of 4-nitrophenyl(2-hexadecylcarbonate) as a white solid. m.p. =  $46.3\text{--}47.0^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): d 8.28 (d,  $J = 9.2$ , Hz, 2H), 7.39 (d,  $J = 9.2$  Hz), 4.88 (m, 1H), 1.73 (m, 1H), 1.60 (m, 1H), 1.38 (d,  $J = 6.3$  Hz, 3H), 1.26 (br s, 24H), 0.88 (t,  $J = 6.8$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): d 155.91, 152.31, 145.46, 125.46, 122.00, 77.89, 35.93, 32.13, 29.90, 29.87, 29.84, 29.77, 29.70, 29.58, 25.46, 22.90, 19.96, 14.33. HRMS (FAB+)  $m/z$  calcd for ( $\text{C}_{23}\text{H}_{38}\text{NO}_5$ ) 408.2750; found 408.2749. Anal. calcd for ( $\text{C}_{23}\text{H}_{37}\text{NO}_5$ ) C, 67.78; H, 9.15; N, 3.44; found: C, 68.02; H, 9.47; N, 3.45.

**Compound (5).** A suspension of sodium hydride (0.21 g, 8. mmol) in THF (20 mL) was cooled to 0°C, and 0.69 mL (9.9 mmol) of pyrrole (0.69 mL, 9.9 mmol) was added dropwise. After stirring for 5 min, the evolution of gas was observed. After an additional 25 min of stirring, a solution of 4-nitrophenyl(2-hexadecyl)carbonate (3.36 g, 8.25 mmol) in THF (5 mL) was added dropwise, resulting in the formation of copious amounts of an orange precipitate. The solution was then stirred overnight as it slowly warmed to room temperature. After removing the solvent under reduced pressure, the resulting solid was suspended in ethyl acetate (100 mL), then extracted with dilute NaHCO<sub>3</sub> (100 mL) followed by water (2 x 100 mL) and brine (100 mL). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, and then concentrated under reduced pressure. The resulting oil was purified by flash column chromatography (CH<sub>2</sub>Cl<sub>2</sub>:hexanes 1:3) to yield 2.23 g (81%) of **5** as a clear oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): d 7.27 (t, *J* = 2.2 Hz, 2H), 6.23 (t, *J* = 2.3 Hz, 2H), 5.06 (m, 1H), 1.73 (m, 1H), 1.60 (m, 1H), 1.35 (d, *J* = 6.3 Hz, 3H), 1.26 (br s, 24H), 0.88 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): d 150.24, 120.13, 112.30, 75.19, 36.05, 32.13, 31.05, 29.88, 29.86, 29.83, 29.75, 29.69, 29.60, 29.57, 25.49, 22.89, 20.13, 14.31. MS (FAB+): *m/z* = 336 (M + H). Anal. calcd for (C<sub>21</sub>H<sub>37</sub>NO<sub>2</sub>) C, 75.17; H, 11.11; N, 4.40; found: C, 75.19; H, 11.51; N, 4.40.

**Compound (6).** A solution of **5** (640 mg, 1.90 mmol) in THF (20 ml) was cooled to -78 °C. The flask was covered to exclude light, and *N*-bromosuccinimide (680 mg, 3.80 mmol) was added in portions over 5 minutes. The resulting suspension was allowed to stir overnight while slowly warming to room temperature. The solution was then concentrated under reduced pressure without using any heat. The resulting crude product was dissolved in hexanes (10 mL), filtered, and then concentrated to yield 884 mg of **6** (94%) as a yellow oil which was used immediately in the next step without further purification. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): d 6.27 (s, 1H), 5.14 (m, 1H), 1.82 (m, 1H), 1.66 (m, 1H), 1.43 (d, *J* = 6.3 Hz, 3H), 1.25 (br s, 24H), 0.88 (t, *J* = 6.7 Hz, 3H). <sup>13</sup>C NMR (100 MHz,

CDCl<sub>3</sub>): d 148.92, 116.82, 100.78, 77.73, 35.83, 32.14, 29.90, 29.87, 29.83, 29.75, 29.68, 29.58, 25.48, 22.91, 19.89, 14.34.

**Compound (7).** To a solution of 2-(tributylstannyl)thiophene (1.6 mL, 5.1 mmol) in THF (10 mL) was added 850 mg (1.7 mmol) of **6** (850 mg, 1.70 mmol). The solution was degassed using three freeze/pump/thaw cycles. Under high nitrogen pressure, dichlorobis(triphenylphosphine)palladium(II) (60 mg, 0.09 mmol) was added quickly. The resulting solution was stirred at 60 °C overnight. The solution was then concentrated under reduced pressure, and the crude product was purified by flash column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/hexanes 1:2) to yield 611 mg (71%) of **7** as a yellow oil which crystallized after extensive drying under high vacuum. m.p. = 37-41 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): d 7.31 (d, *J* = 5.1 Hz, 2H), 7.09 (d, *J* = 3.4 Hz, 2H), 7.03 (t, *J* = 4.3 Hz, 2H), 6.35 (s, 2H), 4.79 (m, 1H), 1.26 (br s, 24H), 1.63 (m, 1H), 1.01 (d, *J* = 6.2 Hz, 3H), 0.88 (t, *J* = 6.7 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): d 134.54, 129.06, 127.46, 126.97, 125.91, 114.24, 76.31, 35.44, 32.15, 29.92, 29.88, 29.77, 29.66, 29.59, 28.49, 22.92, 19.13, 14.35, 13.82. HRMS (FAB+) *m/z* calcd for (C<sub>29</sub>H<sub>41</sub>NO<sub>2</sub>S<sub>2</sub>) 499.2579; found 499.2588.

**Compound (8).** A solution of diisopropylamine (0.27 mL, 1.9 mmol) in THF (10 mL) was cooled to -78 °C and butyllithium (2.5 M in hexanes, 0.71 mL, 1.8 mmol) was added dropwise. After stirring for 5 min at -78 °C, the solution was allowed to warm slowly to room temperature over 30 min. The solution was then cooled to -78 °C in a dry ice/isopropanol bath, and **7** (402 mg, 0.81 mmol) dissolved in THF (5 mL) was added dropwise. After stirring the solution for 60 min, trimethyltin chloride (1.0 M in THF, 2.0 mL, 2.0 mmol) was added dropwise. The resulting solution was then allowed to warm slowly to room temperature. After stirring overnight, the solution was concentrated under reduced pressure, and the resulting oil was filtered through a short (4 cm) plug of basic alumina using a 30% solution of methylene chloride in hexanes. Removal of the solvent yielded 607 mg (91%) of **8** as a dark green oil. <sup>1</sup>H NMR (400 MHz,

CDCl<sub>3</sub>): d 7.19 (d, *J* = 3.2 Hz, 2H), 7.10 (d, *J* = 3.4 Hz, 2H), 6.32 (s, 2H), 1.25 (br s, 26H), 1.00 (d, *J* = 6.2 Hz, 3H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.38 (s, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): d 151.32, 140.28, 138.39, 135.06, 129.26, 128.40, 113.82, 76.10, 35.42, 32.15, 29.92, 29.88, 29.83, 29.71, 29.58, 25.11, 22.92, 19.04, 14.35, -8.00. HRMS (FAB+) *m/z* calcd for (C<sub>35</sub>H<sub>57</sub>NO<sub>2</sub>S<sub>2</sub><sup>118</sup>Sn<sup>120</sup>Sn) 823.1893, found 823.1906.

**Polymer (1).** A solution containing **8** (184 mg, 0.23 mmol) and 4,7-dibromo-2,1,3-benzothiadiazole **9** (55.0 mg, 0.190 mmol) in THF (4 mL) was degassed using three freeze/pump/thaw cycles. Under high nitrogen pressure, dichlorobis-(triphenylphosphine)palladium(II) (4 mg, 0.06 mmol) was added quickly. The solution was heated at 60 °C for 18 h, during which time the color changed from light yellow to dark purple. The solution was then poured into methanol (150 mL), producing a dark precipitate that was collected by filtration through an extraction thimble. The solid was washed in a Soxhlet extractor for at least twelve hours with each of the following solvents: hexanes, methanol, and acetone. Soxhlet extraction with THF followed by precipitation from methanol afforded 62 mg of **1** as a brown powder. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 8.10 (m, 2H), 7.89 (br s, 2H), 7.25 (d, *J* = 3.7 Hz, 2H), 6.54 (br s, 2H), 4.94 (m, 1H), 1.0-1.4 (br m), 0.87 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): d 128.01, 127.73, 125.51, 114.64, 35.62, 32.16, 29.89, 29.80, 29.61, 25.18, 22.92, 19.39, 14.36. FTIR (film on NaCl, cm<sup>-1</sup>): 2921, 2851, 1753, 1482, 1445, 1274, 787. MALDI-TOF: 2402 (H-(TPTB)<sub>3</sub>-TPT-H), 3035 (H-(TPTB)<sub>4</sub>-TPT-H), 3668 (H-(TPTB)<sub>5</sub>-TPT-H). UV-Vis: (CHCl<sub>3</sub>, nm): 370, 540; (dropcast on glass from CH<sub>3</sub>Cl solution, nm): 390, 580. Anal. calcd for (C<sub>35</sub>H<sub>41</sub>N<sub>3</sub>O<sub>2</sub>S<sub>3</sub>)<sub>n</sub> C, 66.52; H, 6.54; N, 6.65; S, 15.22.; found: C, 66.35; H, 6.81; N, 6.34; S, 14.82.

**Compound (10).** The esterification was carried out using 2-chloro-3,5-dinitropyridine as a condensing agent.<sup>3</sup> To a mixture of thiophene-3-carboxylic acid (3.73 g, 29.1 mmol) and 2-methyl-2-hexanol (5.40 mL, 37.7 mmol) in pyridine (40 mL) was added 2-chloro-3,5-dinitropyridine (5.92 g, 29.1 mmol). The

mixture was stirred at 115°C for 45 min, and then cooled to room temperature. The solution was poured into half saturated aqueous NaHCO<sub>3</sub> (250 mL) and extracted with diethyl ether (2 × 250 mL). The combined organic layers were washed with water (3 × 150 mL), dried over anhydrous sodium sulfate, filtered, and the solvent was removed by rotary evaporation. The resulting crude product was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>:hexanes) to afford 3.10 g (13.7 mmol, 47%) of **10** as a colorless liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): d 8.04 (dd, *J* = 3 and 1 Hz, 1H), 7.51 (dd, *J* = 5 and 1 Hz, 1H), 7.30 (dd, *J* = 5 and 3 Hz, 1H), 1.89 (m, 2H), 1.59 (s, 6H), 1.39 (m, 4H), 0.96 (t, *J* = 7 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): d 23.06, 14.12 (C<sub>prim</sub>); 40.90, 26.19 (C<sub>sec</sub>); 131.89, 128.01, 125.64 (C<sub>tert</sub>); 162.08, 135.74, 83.22 (C<sub>quat</sub>). Anal. Calcd for C<sub>12</sub>H<sub>18</sub>O<sub>2</sub>S: C, 63.68; H, 8.02; Found C, 63.59; H, 8.12.

**Compound (11).** To a solution of diisopropylamine (2.30 mL, 16.4 mmol,) in THF (15 mL) was added dropwise *n*-butyllithium (5.60 mL, 14.0 mmol, 2.5 M in hexanes) at -78°C. The mixture was warmed at 0°C for 5 min and then recooled to -78°C. To this solution was added **10** (3.00 g, 13.3 mmol) in THF (15 mL) and the mixture was stirred at -78°C for 30 min, trimethyltin chloride (16.5 mL, 16.5 mmol, 1.0 M in THF) was added dropwise, and the resulting mixture was stirred at -78°C for 4 h and then allowed to warm to room temperature overnight. The solution was poured into half-saturated sodium chloride solution and the resulting solution was extracted twice with dichloromethane. The combined organic layers were separated dried over anhydrous sodium sulfate, and filtered. The solvent was removed by rotary evaporation to afford 5.17 g (13.3 mmol, 100%) of **11** as an orange liquid, which was used in the next step without further modification. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): d 7.57 (m, 1H), 7.53 (d, *J* = 4 Hz, 1H), 1.87 (m, 2H), 1.57 (s, 6H), 1.36 (m, 4H), 0.92 (t, *J* = 7 Hz, 3H), 0.38 (m, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): d 26.14, 14.07, -7.10 (C<sub>prim</sub>); 40.64, 26.08, 23.02 (C<sub>sec</sub>); 131.00, 129.15 (C<sub>tert</sub>); 163.62, 150.38, 141.51, 82.86 (C<sub>quat</sub>).

**Compound (12).** To a solution of **9** (1.08 g, 3.67 mmol) in THF (15 mL) and DMF (15 mL) was added **11** (3.14 g, 8.07 mmol). The solution was degassed using three freeze/pump/thaw cycles. Under high nitrogen pressure, dichlorobis-(triphenylphosphine)palladium(II) (4-10 mol%) was added quickly. The solution was stirred at 90°C overnight, and let cooled to room temperature. The resulting mixture was poured into a half saturated ammonium chloride solution and extracted twice with dichloromethane. The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>:hexanes 7:3) to afford 1.38 g (2.36 mmol, 64%) of **12** as an orange oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): d 7.74 (s, 2H), 7.63 (d, *J* = 5.4 Hz, 2H), 7.44 (d, *J* = 5.4 Hz, 2H), 1.49 (m, 4H), 1.24 (s, 12H), 1.19 (m, 4H), 1.10 (m, 4H), 0.86 (t, *J* = 7 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): d 25.79, 14.14 (C<sub>prim</sub>); 40.52, 25.92, 23.00 (C<sub>sec</sub>); 130.13, 129.17, 125.26 (C<sub>tert</sub>); 162.32, 153.76, 142.58, 133.46, 127.95, 83.22 (C<sub>quat</sub>). HRMS (FAB+) *m/z* calcd for (C<sub>30</sub>H<sub>36</sub>N<sub>2</sub>O<sub>4</sub>S<sub>3</sub>) 584.1837; found 584.1837. Anal. calcd for (C<sub>30</sub>H<sub>36</sub>N<sub>2</sub>O<sub>4</sub>S<sub>3</sub>) C, 61.62; H, 6.20; N, 4.79; found C, 61.66; H, 6.28; N, 4.94.

**Compound (13).** To a solution of **12** (1.00 g, 1.71 mmol) in DMF (28 mL) was added 1,3-dibromo-5,5-dimethylhydantoin (0.500 g, 1.75 mmol). The resulting mixture was then stirred at room temperature over 48 h. During this period, the reaction was monitored by TLC and additional portions of 1,3-dibromo-5,5-dimethylhydantoin (8 x 0.250 g, 0.875 mmol) were added until the conversion was complete. The resulting mixture was poured into water and extracted several times with dichloromethane. The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>:hexanes 3:7), and recrystallized in hot ethanol to afford 0.902 g (1.21 mmol, 71%) of **13** as pale yellow crystals. m.p. = 94-96°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): d 7.71 (s, 2H), 7.57 (s, 2H), 1.52 (m, 4H), 1.25 (s, 12H), 1.19 (m, 4H), 1.10 (m, 4H), 0.84 (t, *J* = 7 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):

d 25.81, 14.11 ( $C_{\text{prim}}$ ); 40.33, 25.94, 22.97 ( $C_{\text{sec}}$ ); 132.45, 129.29 ( $C_{\text{tert}}$ ); 161.00, 153.40, 143.56, 133.71, 127.06, 112.46, 83.88 ( $C_{\text{quat}}$ ). HRMS (FAB+)  $m/z$  calcd for ( $C_{30}H_{34}Br_2N_2O_4S_3$ ) 740.0047; found 740.0038. Anal. calcd for ( $C_{30}H_{36}N_2O_4S_3$ ) C, 48.52; H, 4.61; N, 3.77; found C, 48.57; H, 4.69; N, 3.76.

**Polymer (3).** To a solution of **13** (224 mg, 0.302 mmol) in THF (6 mL) was added bis(trimethylstannyl)-1-methylpyrrole **14** (123 g, 0.302 mmol). The solution was degassed using three freeze/pump/thaw cycles. Under high nitrogen pressure, dichlorobis(triphenylphosphine)palladium(II) (0.05-10 mol%) was added quickly. The mixture was stirred at 70 °C for 24 h, during which time the color changed from yellow to red. The mixture was cooled to room temperature and poured into methanol under vigorous stirring. A red-orange solid was filtered through an extraction thimble for subsequent Soxhlet extraction. The solid was washed thoroughly with methanol, and then extracted with THF. The THF fraction was concentrated in vacuum and suspended in MeOH. Filtration of the suspension gave 179 mg of polymer **3** as a dark red powder.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 7.82 (br s, 2H), 7.62 (br s, 2H), 6.53 (br s, 2H), 6.54 (br s, 2H), 4.01 (br s, 3H), 1.61 (m, 4H), 1.3-1.2 (m, 16H), 1.11 (m, 4H), 0.89 (t,  $J = 7$  Hz, 6H). UV-Vis: (ODCB, nm): 355, 460; (dropcast on glass from  $\text{CH}_3\text{Cl}$  solution, nm): 320, 460.

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