Supporting Information

Synthesis of Bridged Oligothiophenes: Towards a New Class of Thiophene-Based Electroactive Surfactants

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Materials. All reagents were purchased from Aldrich and used without further purification unless otherwise noted. 2,2'-Bithiophene was filtered through silica gel using petroleum ether as the eluent. *N*-bromosuccinimide (NBS) was recrystallized from acetic acid/water. Potassium carbonate was pulverized and dried at 120°C overnight prior use. 2,2'-Bithiophene-5-carboxylic acid **6** was prepared using a method described by Malenfant and al.¹ 5-(Trimethylstannyl)-2,2'-bithiophene was prepared using a method described by Groenendaal et al.² *N,N,N',N'*-tetramethylethylenediamine (TMEDA) and diisopropylamine were distilled over CaH₂. All solvents (reagent grade) were purchased from Fisher or EM Science. *N,N*-Dimethylformamide (DMF) and chloroform were stored over molecular sieves. Tetrahydrofuran (THF) was distilled over sodium/benzophenone. 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.

Characterization. Thin layer chromatography was performed on Merck Kieselgel 60 F₂₅₄. Silica used for flash chromatography was Merck Kieselgel 60 (230-400 mesh). Infrared spectra were collected on a Mattson Genesis II FT-IR using potassium bromide with a diffuse reflectance accessory (Pike). ¹H NMR, ¹³C NMR and ³¹P NMR were recorded on Bruker AM-400 and AMX-400. Low and high resolution fast atom bombardment (FAB) and electronic impact (EI) mass spectrometry was performed at

the UC Berkeley MS Facility. High resolution mass spectrometry measurements are valid to ± 5 ppm.

Compound (1). To a suspension of sodium hydride (6.49 g, 162 mmol, 60% dispersion in mineral oil) in THF (100 mL) was added dropwise 3-thiophenemethanol (12.0 mL, 125 mmol) at 0°C and the mixture was allowed to stir at 0°C for 15 min. 1-Bromobutane (17.4 mL, 160 mmol) was added dropwise to this mixture, the resulting solution was stirred at reflux overnight, and then quenched with water. THF was removed by rotary evaporation and the mixture was extracted with dichloromethane. The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and the solvent was removed by rotary evaporation. The resulting crude product was purified by column chromatography (silica gel, CH₂Cl₂) to afford 17.9 g (105 mmol, 84%) of **1** as a colorless liquid. IR (KBr, cm⁻¹): 3102, 2956, 2931, 2857, 1720, 1566, 1461, 1417, 1381, 1347, 1224, 1154, 1098, 931, 856, 832, 776, 686, 634, 585. ¹H NMR (CDCl₃, 400 MHz): δ 7.28 (dd, J = 5.2 and 3.0 Hz, 1H), 7.19 (m, 1H), 7.08 (dd, J = 5.2 and 1.2 Hz, 1H), 4.51 (s, 2H), 3.47 (t, J = 6.8 Hz, 2H), 1.60 (m, 2H), 1.40 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 13.98 (C_{prim}); 70.15, 68.16, 31.87, 19.43 (C_{sec}); 127.37, 125.88, 122.50 (C_{tert}); 139.93 (C_{quat}). HRMS (EI) m/z calcd for (C₉H₁₄OS) 170.0765; found 170.0770.

Compound (2). A solution of **1** (8.97 g, 52.7 mmol) and NBS (9.38 g, 52.7 mmol) in glacial acetic acid (50 mL) was stirred at room temperature overnight. The resulting mixture was then quenched with water and extracted with dichloromethane. The combined organic layers were washed with sodium hydroxide solution (1 M) and then with water. The organic layers were dried over anhydrous magnesium sulfate, filtered, and the solvent was removed by rotary evaporation. The resulting crude product was purified by column chromatography (silica gel, hexanes) to afford 8.61 g (34.6 mmol, 66%) of **2** as a colorless liquid. IR (KBr, cm⁻¹): 3105, 2955, 2930, 2865, 1462, 1415, 1347, 1219, 1103, 991, 929, 826, 721, 687, 652, 583. ¹H NMR (CDCl₃, 400 MHz): δ 7.24 (d, J = 5.6 Hz, 1H), 6.95 (d, J = 5.6 Hz, 1H), 4.45 (s, 2H), 3.47 (t, J = 6.8 Hz, 2H), 1.59 (m, 2H), 1.40 (m, 2H), 0.93 (t,

$J = 7.4$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 13.98 (C_{prim}); 70.23, 66.79, 31.82, 19.40 (C_{sec}); 128.21, 125.88 (C_{tert}); 138.63, 110.83 (C_{quat}). HRMS (EI) m/z calcd for ($\text{C}_9\text{H}_{13}\text{BrOS}$) 247.9870; found 247.9866.

Compound (3). To a solution of **2** (7.11 g, 28.5 mmol) in THF (50 mL) was added dropwise *n*-butyllithium (12.6 mL, 31.5 mmol, 2.5 M in hexanes) at -78°C . The mixture was stirred at -78°C for 90 min, trimethyltin chloride (32.0 mL, 32.0 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 solvent was removed by rotary evaporation and the resulting mixture was partitioned between dichloromethane and saturated ammonium chloride solution. The organic layer was separated, washed with water, dried over sodium sulfate, and filtered. The solvent was removed by rotary evaporation to afford a slightly orange liquid, which contains 8.63 g (25.9 mmol, 91%) of **3**, along with 0.414 g of starting material **2** (1.66 mmol), as determined by ^1H NMR. Compound **3** will be used at the next step without further purification. ^1H NMR (CDCl_3 , 400 MHz): δ 7.56 (d, $J = 4.6$ Hz, 1H), 7.17 (d, $J = 4.6$ Hz, 1H), 4.52 (s, 2H), 3.48 (t, $J = 6.8$ Hz, 2H), 1.62 (m, 2H), 1.40 (m, 2H), 0.93 (t, $J = 7.4$ Hz, 3H), 0.37 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 13.99, -7.53 (C_{prim}); 70.63, 69.76, 31.78, 19.49 (C_{sec}); 130.70, 128.88 (C_{tert}); 146.88, 134.87 (C_{quat}).

Compound (4). To a solution of 2,2'-bithiophene (5.00 g, 30.1 mmol) in THF (60 mL) was added dropwise *n*-butyllithium (15.2 mL, 38.0 mmol, 2.5 M in hexanes) at -78°C . The mixture was stirred at -78°C for 2 h, diethyl chlorophosphate (4.50 mL, 30.2 mmol) in THF (10 mL) 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 crude product was isolated according to the standard work-up described for **3** and purified by column chromatography (silica gel, EtOAc/hexanes 4:1) to afford 5.74 g (19.0 mmol, 63%) of **4** as a yellow oil. IR (KBr, cm^{-1}): 3073, 2980, 2934, 2903, 1785, 1477, 1444, 1418, 1390, 1297, 1255 (P=O), 1162, 1094, 1020, 968, 800, 758, 700, 630, 573, 544. ^1H NMR (CDCl_3 , 400 MHz): δ 7.50 (dd, $J = 8.4$ and 3.8 Hz, 1H), 7.25 (dd, $J = 5.2$ and 1.0 Hz, 1H), 7.21 (dd, $J = 3.8$ and 1.0 Hz, 1H), 7.16 (m, 1H),

6.99 (dd, $J = 5.2$ and 3.8 Hz, 1H), 4.08 (m, 4H), 1.32 (t, $J = 7.0$ Hz, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 16.29 ($J_{\text{CP}} = 7$ Hz) (C_{prim}); 62.71 ($J_{\text{CP}} = 5$ Hz) (C_{sec}); 137.52 ($J_{\text{CP}} = 11$ Hz), 128.10, 126.00, 125.20, 124.29 ($J_{\text{CP}} = 18$ Hz), (C_{tert}); 145.44 ($J_{\text{CP}} = 8$ Hz), 135.80 ($J_{\text{CP}} = 4$ Hz), 125.93 ($J_{\text{CP}} = 209$ Hz) (C_{quat}). ^{31}P NMR (CDCl_3 , 162 MHz): δ 10.17. HRMS (FAB) m/z calcd for ($\text{C}_{12}\text{H}_{15}\text{O}_3\text{PS}_2$) 302.0200; found 302.0203.

Compound (5). To a solution of *n*-butyllithium (3.40 mL, 8.50 mmol, 2.5 M in hexanes) in THF (20 mL) was added dropwise diisopropylamine (1.20 mL, 8.56 mmol) at -78°C . The mixture was warmed at 0°C for 5 min and then recooled to -78°C . To this solution was added **4** (2.32 g, 7.67 mmol) in THF (20 mL) and the mixture was stirred at -78°C for 1 h, trimethyltin chloride (8.50 mL, 8.50 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 crude product was isolated according to the standard work-up described for **3** to afford a brown oil, which contains 3.18 g (6.84 mmol, 89%) of **5**, along with 0.232 g of starting material **4** (0.767 mmol), as determined by ^1H NMR. Compound **5** will be used at the next step without further purification. ^1H NMR (CDCl_3 , 400 MHz): δ 7.55 (dd, $J = 8.4$ and 3.8 Hz, 1H), 7.37 (d, $J = 3.8$ Hz, 1H), 7.19 (m, 1H), 7.12 (d, $J = 3.8$ Hz, 1H), 4.14 (m, 4H), 1.35 (t, $J = 7.0$ Hz, 6H), 0.40 (s, 9H). ^{31}P NMR (CDCl_3 , 162 MHz): δ 10.42.

Compound (7). A solution of 2,2'-bithiophene-5-carboxylic acid **6** (4.73 g, 22.5 mmol), 1,9-dibromononane (3.02 g, 10.2 mmol), anhydrous potassium carbonate (5.95 g, 43.1 mmol) and 18-crown-6 (0.538 g, 2.04 mmol) in THF (66 mL) was stirred at reflux for 3 days. The solvent was removed by rotary evaporation and the resulting solid was filtered through celite in dichloromethane and then purified by column chromatography (silica gel, CH_2Cl_2 :hexanes 1:1 $\rightarrow$ CH_2Cl_2) to afford 4.97 g (9.12 mmol, 89%) of **7** as a white powder. m.p. 108°C . IR (KBr, cm^{-1}): 3093, 2960, 2921, 2852, 1690 ($\text{C}=\text{O}$), 1511, 1471, 1452, 1420, 1298, 1273, 1109, 1036, 946, 843, 808, 745, 717. ^1H NMR (CDCl_3 , 400 MHz): δ 7.70 (d, $J = 3.8$ Hz, 2H), 7.30 (dd, $J = 5.2$ and 1.2 Hz, 2H), 7.28 (m, 2H),

7.15 (d, $J = 3.8$ Hz, 2H), 7.05 (dd, $J = 5.2$ and 3.8 Hz, 2H), 4.30 (t, $J = 6.6$ Hz, 4H), 1.76 (m, 4H), 1.45-1.35 (m, 10H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 65.22, 29.26, 29.06, 28.60, 25.83 (C_{sec}); 133.94, 128.01, 125.92, 125.08, 123.80 (C_{tert}); 162.05, 144.93, 136.31, 131.72 (C_{quat}). HRMS (FAB) m/z calcd for ($\text{C}_{27}\text{H}_{28}\text{O}_4\text{S}_4$) 544.0870; found 544.0864.

Compound (8). A solution of **7** (4.95 g, 9.09 mmol) and NBS (3.26 g, 18.3 mmol) in CHCl_3 (125 mL) and DMF (75 mL) was stirred at room temperature overnight. The resulting mixture was then washed with water. The organic layer was dried over anhydrous magnesium sulfate, and filtered through silica gel to afford 6.08 g (8.65 mmol, 95%) of **8** as a white powder. m.p. 92°C . IR (KBr, cm^{-1}): 3097, 2961, 2928, 2854, 1708 ($\text{C}=\text{O}$), 1515, 1453, 1424, 1353, 1304, 1256, 1118, 1101, 1039, 969, 877, 807, 787, 742. ^1H NMR (CDCl_3 , 400 MHz): δ 7.68 (d, $J = 3.8$ Hz, 2H), 7.08 (d, $J = 3.8$ Hz, 2H), 7.02 (m, 4H), 4.29 (t, $J = 6.8$ Hz, 4H), 1.75 (m, 4H), 1.45-1.35 (m, 10H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 65.43, 29.36, 29.14, 28.67, 25.92 (C_{sec}); 134.02, 130.95, 125.25, 124.09 (C_{tert}); 162.01, 142.79, 137.85, 132.30, 112.91 (C_{quat}). HRMS (FAB) m/z calcd for ($\text{C}_{27}\text{H}_{26}\text{Br}_2\text{O}_4\text{S}_4$) 699.9081; found 699.9074.

Compound (9). To a solution of **3** (12.0 mmol) and **8** (3.72 g, 5.29 mmol) in THF (100 mL) and DMF (100 mL) was added $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (4-10 mol%). The solution was stirred at 60°C for 3 days. THF was removed by rotary evaporation and the resulting mixture was poured into a saturated ammonium chloride solution and extracted 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_2Cl_2 :hexanes 1:1 $\rightarrow$ CH_2Cl_2 :MeOH 99:1) to afford 3.16 g (3.59 mmol, 68%) of **9** as a yellow oil. IR (KBr, cm^{-1}): 3092, 2955, 2916, 2852, 1690 ($\text{C}=\text{O}$), 1513, 1461, 1297, 1114, 1032, 940, 877, 826, 796, 746, 705, 653, 616. ^1H NMR (CDCl_3 , 400 MHz): δ 7.70 (d, $J = 3.8$ Hz, 2H), 7.24 (d, $J = 3.8$ Hz, 2H), 7.23 (d, $J = 5.2$ Hz, 2H), 7.15 (d, $J = 3.8$ Hz, 2H), 7.13 (m, 4H), 4.55 (s, 4H), 4.30 (t, $J = 6.8$ Hz, 4H), 3.53 (t, $J =$

6.8 Hz, 4H), 1.77 (m, 4H), 1.64 (m, 4H), 1.45-1.35 (m, 14H), 0.94 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 13.96 (C_{prim}); 70.28, 66.52, 65.38, 31.86, 29.39, 29.18, 28.71, 25.95, 19.49 (C_{sec}); 134.12, 131.89, 127.27, 125.69, 124.45, 123.82 (C_{tert}); 162.11, 143.66, 136.59, 136.11, 136.07, 133.48, 130.40 (C_{quat}). HRMS (FAB) m/z calcd for ($\text{C}_{45}\text{H}_{52}\text{O}_6\text{S}_6$) 880.2088; found 880.2084.

Compound (10). A solution of **9** (2.96 g, 3.36 mmol) and NBS (1.19 g, 6.69 mmol) in CHCl_3 (100 mL) and DMF (50 mL) was stirred at room temperature overnight. The resulting mixture was then washed several times with water. The organic layer was dried over anhydrous magnesium sulfate, and filtered through silica gel to afford 3.36 g (3.23 mmol, 96%) of **10** as a yellow oil.

IR (KBr, cm^{-1}): 3071, 2930, 2862, 1712 ($\text{C}=\text{O}$), 1463, 1282, 1245, 1101, 836, 799, 747. ^1H NMR (CDCl_3 , 400 MHz): δ 7.70 (d, $J = 3.8$ Hz, 2H), 7.22 (d, $J = 3.8$ Hz, 2H), 7.15 (d, $J = 3.8$ Hz, 2H), 7.09 (s, 2H), 7.06 (d, $J = 3.8$ Hz, 2H), 4.48 (s, 4H), 4.30 (t, $J = 6.8$ Hz, 4H), 3.51 (t, $J = 6.8$ Hz, 4H), 1.77 (m, 4H), 1.64 (m, 4H), 1.45-1.35 (m, 14H), 0.94 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 13.97 (C_{prim}); 70.43, 66.22, 65.42, 31.82, 29.38, 29.17, 28.70, 25.94, 19.47 (C_{sec}); 134.12, 132.84, 127.58, 125.65, 124.02 (C_{tert}); 162.05, 143.29, 137.11, 136.64, 134.60, 134.57, 132.13, 111.38 (C_{quat}). HRMS (FAB) m/z calcd for ($\text{C}_{45}\text{H}_{50}\text{Br}_2\text{O}_6\text{S}_6$) 1036.0298; found 1036.0313.

Compound (11). To a solution of **3** (2.82 mmol) and **10** (1.53 g, 1.47 mmol) in THF (45 mL) and DMF (45 mL) was added $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (4-10 mol%). The solution was stirred at 60°C for 2 days. The crude product was isolated according to the standard work-up described for **9** and purified by column chromatography (silica gel, CH_2Cl_2) to afford 1.20 g (0.985 mmol, 70%) of **11** as an orange oil.

IR (KBr, cm^{-1}): 2928, 2863, 1707 ($\text{C}=\text{O}$), 1464, 1447, 1278, 1241, 1094, 833, 802, 746, 695, 653. ^1H NMR (CDCl_3 , 400 MHz): δ 7.71 (d, $J = 3.8$ Hz, 2H), 7.26 (d, $J = 3.8$ Hz, 2H), 7.22 (d, $J = 5.2$ Hz, 2H), 7.21 (s, 2H), 7.16 (d, $J = 3.8$ Hz, 4H), 7.13 (d, $J = 5.2$ Hz, 2H), 4.57 (s, 4H), 4.56 (s, 4H), 4.31 (t, $J = 6.8$ Hz, 4H), 3.55 (m, 8H), 1.77

(m, 4H), 1.64 (m, 8H), 1.50-1.35 (m, 18H), 0.94 (m, 12H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 13.98, 13.96 (C_{prim}); 70.42, 70.30, 66.64, 66.57, 65.38, 31.87, 29.38, 29.17, 28.71, 25.94, 19.51 (C_{sec}); 134.12, 130.26, 129.50, 127.22, 125.78, 124.30, 123.86 (C_{tert}); 162.10, 143.57, 136.71, 136.48, 135.93, 135.70, 133.80, 133.47, 131.97 (C_{quat}). HRMS (FAB) m/z calcd for ($\text{C}_{63}\text{H}_{76}\text{O}_8\text{S}_8$) 1216.3306; found 1216.3316.

Compound (12) A solution of **11** (1.09 g, 0.895 mmol) and NBS (0.318 g, 1.79 mmol) in CHCl_3 (26 mL) and DMF (13 mL) was stirred at room temperature overnight. The resulting mixture was then washed with water. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvent removed by rotary evaporation. The crude product was purified by column

chromatography (silica gel, CH_2Cl_2) to afford 1.00 g (0.727 mmol, 81%) of **12** as an orange oil. IR (KBr, cm^{-1}): 2931, 2856, 1707 ($\text{C}=\text{O}$), 1463, 1448, 1277, 1094, 837, 798, 746. ^1H NMR (CDCl_3 , 400 MHz): δ 7.71 (d, $J = 3.8$ Hz, 2H), 7.26 (d, $J = 3.8$ Hz, 2H), 7.16 (m, 6H), 7.09 (s, 2H), 4.54 (s, 4H), 4.50 (s, 4H), 4.31 (t, $J = 6.8$ Hz, 4H), 3.56 (t, $J = 6.8$ Hz, 4H), 3.52 (t, $J = 6.8$ Hz, 4H), 1.77 (m, 4H), 1.63 (m, 8H), 1.50-1.35 (m, 18H), 0.94 (m, 12H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 13.98 (C_{prim}); 70.50, 70.45, 66.59, 66.26, 65.41, 31.86, 31.84, 29.38, 29.18, 28.71, 25.94, 19.51, 19.49 (C_{sec}); 134.13, 132.72, 129.76, 127.38, 125.78, 123.93 (C_{tert}); 162.08, 143.45, 136.94, 136.52, 136.50, 135.35, 134.57, 134.25, 132.68, 132.06, 111.20 (C_{quat}). HRMS (FAB) m/z calcd for ($\text{C}_{63}\text{H}_{74}\text{Br}_2\text{O}_8\text{S}_8$) 1372.1516; found 1372.1475.

Compound (13). To a solution of **5** (0.420 mmol) and **10** (0.218 g, 0.210 mmol) in THF (7 mL) and DMF (5 mL) was added $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (4-10 mol%). The solution was stirred at 60°C overnight. The crude product was isolated according to the standard work-up described for **9** and purified by column

chromatography (silica gel, CH_2Cl_2 :MeOH 99.5:0.5 $\rightarrow$ CH_2Cl_2 :MeOH 98.5:1.5) to afford 0.105 g (0.0709 mmol, 34%) of **13** as a red oil. IR (KBr, cm^{-1}): 2915, 2849, 1704 ($\text{C}=\text{O}$),

1454, 1433, 1276, 1249, 1095, 1048, 1021, 967, 792, 746, 575. ^1H NMR (CDCl_3 , 400 MHz): δ 7.69 (d, $J = 3.8$ Hz, 2H), 7.53 (dd, $J = 8.4$ and 3.8 Hz, 2H), 7.23 (d, $J = 3.8$ Hz, 2H), 7.19 (m, 4H), 7.15 (m, 4H), 7.13 (d, $J = 3.8$ Hz, 2H), 7.08 (d, $J = 3.8$ Hz, 2H), 4.52 (s, 4H), 4.29 (t, $J = 6.8$ Hz, 4H), 4.16 (m, 8H), 3.55 (t, $J = 6.8$ Hz, 4H), 1.64 (m, 4H), 1.57 (m, 4H), 1.50-1.38 (m, 14H), 1.35 (t, $J = 7.0$ Hz, 12H), 0.93 (t, $J = 7.4$ Hz, 6H). ^{31}P NMR (CDCl_3 , 162 MHz): δ 10.05. HRMS (FAB) m/z calcd for ($\text{C}_{69}\text{H}_{78}\text{O}_{12}\text{P}_2\text{S}_{10}$) 1480.2176; found 1480.2144.

Figure 1. ^1H NMR (CDCl_3 , 400 MHz) spectrum of compound **13** (* solvent).

Compound (14). To a solution of **5** (0.154 mmol) and **12** (106 mg, 0.0771 mmol) in THF (5 mL) and DMF (5 mL) was added $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (4-10 mol%). The solution was stirred at 60°C for two days. The crude product was isolated according to the standard work-up described for **9** and purified by column chromatography (silica gel, $\text{CH}_2\text{Cl}_2:\text{MeOH}$ 99.5:0.5 $\rightarrow$ $\text{CH}_2\text{Cl}_2:\text{MeOH}$ 99:1) to afford 0.140 mg (0.00770 mmol, 10%) of **13** as a red wax. IR (KBr, cm^{-1}): 2922, 2853, 1708 ($\text{C}=\text{O}$), 1459, 1259, 1094, 1020, 963, 797, 747, 576. ^1H NMR (CDCl_3 , 400 MHz): δ 7.69 (d, $J = 3.8$ Hz, 2H), 7.55 (dd, $J = 8.4$ and 3.8 Hz, 2H), 7.25-7.15 (m, 12H), 7.12 (d,

$J = 3.8$ Hz, 2H), 7.09 (d, $J = 3.8$ Hz, 2H), 4.54 (s, 8H), 4.29 (t, $J = 6.8$ Hz, 4H), 4.16 (m, 8H), 3.55 (t, $J = 6.8$ Hz, 8H), 1.75 (m, 4H), 1.63 (m, 8H), 1.50-1.38 (m, 18H), 1.35 (t, $J = 7.0$ Hz, 12H), 0.94 (m, 12H). ^{31}P NMR (CDCl_3 , 162 MHz): δ 10.04. LRMS (FAB) m/z 1818.

Compound (15). To magnesium turnings (1.12 g, 46.1 mmol) in THF (10 mL) was added *p*-dibromobenzene (10.0 g, 42.4 mmol) in THF (25 mL). The mixture began to reflux within 1 or 2 min and an ice bath was used to maintain a mild reflux. When the initially vigorous reaction had subsided, the solution was left to stir at room temperature for 4 h, then diluted with THF (80 mL) and cooled to 0°C. The Grignard reagent was then transferred via cannula to a solution of diethylchlorophosphate (9.50 mL, 63.8 mmol) in THF (10 mL) at 0°C. The resulting mixture was stirred at room temperature overnight and a hydrochloric acid solution (1.0 M) was carefully added to quench the reaction. The aqueous layer was extracted with diethyl ether, the combined ether layers were washed with water, dried over anhydrous magnesium sulfate and then filtered. The solvent was removed by rotary evaporation. Distillation (Kugelrohr) afforded 2.74 g (9.35 mmol, 22%) of **15** as a colorless liquid. IR (KBr, cm^{-1}): 3053, 2981, 2904, 1579, 1478, 1443, 1387, 1250 (P=O), 1163, 1127, 1096, 1053, 1024, 964, 769, 726, 582, 527. ^1H NMR (CDCl_3 , 400 MHz): δ 7.67-7.55 (m, 4H), 4.15 (m, 4H), 1.29 (t, $J = 7.0$ Hz, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 16.30 ($J_{\text{CP}} = 6$ Hz) (C_{prim}); 62.27 ($J_{\text{CP}} = 5$ Hz) (C_{sec}); 133.28 ($J_{\text{CP}} = 10$ Hz), 131.77 ($J_{\text{CP}} = 16$ Hz), (C_{tert}); 127.51 ($J_{\text{CP}} = 4$ Hz), 127.48 ($J_{\text{CP}} = 189$ Hz) (C_{quat}). ^{31}P NMR (CDCl_3 , 162 MHz): δ 16.70. HRMS (EI) m/z calcd for ($\text{C}_{10}\text{H}_{14}\text{BrO}_3\text{P}$) 291.9864; found 291.9865.

Compound 16. To a solution of 5-(trimethylstannyl)-2,2'-bithiophene (0.668 g, 2.03 mmol) and **15** (0.594 g, 2.03 mmol) in THF (5 mL) and DMF (5 mL) was added $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (2-5 mol%). The solution was stirred at 60°C overnight. The crude product was isolated according to the standard work-up described for **9** and purified by column chromatography (silica gel, $\text{CH}_2\text{Cl}_2 \rightarrow \text{CH}_2\text{Cl}_2:\text{MeOH}$ 99.3:0.7) to afford 0.533 g (1.41 mmol, 69%) of **16** as a yellow powder. m.p. 79-80°C. IR (KBr, cm^{-1}): 3065, 2980, 2932, 2905, 1599, 1491, 1452, 1424, 1399, 1243 (P=O), 1134, 1055, 1022, 960, 839, 797, 771, 692, 624, 579, 525. ^1H NMR (CDCl_3 ,

400 MHz): δ 7.82 (dd, J = 12.8 and 8.2 Hz, 2H), 7.69 (m, 2H), 7.32 (d, J = 3.8 Hz, 1H), 7.24 (m, 2H), 7.17 (d, J = 3.8 Hz, 1H), 7.04 (dd, J = 5.2 and 3.8 Hz, 1H), 4.14 (m, 4H), 1.34 (t, J = 7.0 Hz, 6H). ^{31}P NMR (CDCl_3 , 162 MHz): δ 17.55. HRMS (FAB) m/z calcd for ($\text{C}_{18}\text{H}_{19}\text{O}_3\text{PS}_2$) 378.0513; found 378.0520.

Compound (17). To a solution of TMEDA (0.500 mL, 3.31 mmol) in THF (2 mL) was added dropwise lithium diisopropylamide (0.200 mL, 0.400 mmol, 2.0 M in heptane/THF/ethylbenzene) at -78°C . To this solution was added dropwise a solution of **16** (0.0800 g, 0.211 mmol) in THF (2 mL) at -78°C . The mixture was stirred at this temperature for 90 min, trimethyltin chloride (0.500 mL, 0.500 mmol, 1.0 M in THF) was added dropwise, and the resulting mixture was stirred at -78°C for 1 h and then allowed to warm to room temperature overnight. The crude product was isolated according to the standard work-up described for **3** to afford 0.113 g (0.209 mmol, 99%) of **17** as an orange oil, which will be used at the next step without further purification. ^1H NMR (CDCl_3 , 400 MHz): δ 7.80 (dd, J = 12.8 and 8.2 Hz, 2H), 7.66 (dd, J = 8.2 and 3.8 Hz, 2H), 7.31 (m, 2H), 7.15 (d, J = 3.8 Hz, 1H), 7.10 (d, J = 3.8 Hz, 1H), 4.12 (m, 4H), 1.31 (t, J = 7.0 Hz, 6H), 0.38 (s, 9H). ^{31}P NMR (CDCl_3 , 162 MHz): δ 17.60.

Compound 18. To a solution of **10** (0.104 g, 0.100 mmol) and **17** (0.106 g, 0.196 mmol) in THF (15 mL) and DMF (5 mL) was added $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (4-10 mol%). The solution was stirred at 60°C for 2 days. The crude product was isolated according to the standard work-up described for **9** and purified by column chromatography (silica gel, $\text{CH}_2\text{Cl}_2 \rightarrow \text{CH}_2\text{Cl}_2:\text{MeOH}$ 98:2) to afford 0.0160 g (0.00980 mmol, 10%) of **18** as a red waxy solid. IR (KBr, cm^{-1}): 2930, 2852, 1706 (C=O), 1597, 1508, 1442, 1246, 1096, 1048, 1024, 958, 825, 793, 708, 578. ^1H NMR (CDCl_3 , 400 MHz): δ 7.80 (dd, J = 12.8 and 8.2 Hz, 4H), 7.68 (m, 6H), 7.32 (d, J = 3.8 Hz, 2H), 7.23 (d, J = 3.8 Hz, 2H), 7.18 (s, 2H), 7.14 (m, 4H), 7.11 (m, 4H), 7.08 (d, J = 3.8 Hz, 2H), 4.52 (s, 4H), 4.27 (t, J = 6.8 Hz, 4H),

4.12 (m, 8H), 3.55 (t, $J = 6.8$ Hz, 4H), 1.75 (m, 4H), 1.62 (m, 4H), 1.50-1.38 (m, 14H), 1.33 (t, $J = 7.0$ Hz, 12H), 0.92 (t, $J = 7.4$ Hz, 6H). ^{31}P NMR (CDCl_3 , 162 MHz): δ 17.48. HRMS (FAB) m/z calcd for ($\text{C}_{81}\text{H}_{86}\text{O}_{12}\text{P}_2\text{S}_{10}$) 1632.2802; found 1632.2812.

Compound (19). To a solution of 3,4-ethylenedioxythiophene (5.36 g, 37.7 mmol) in THF (60 mL) was added dropwise *n*-butyllithium (15.2 mL, 38.0 mmol, 2.5 M in hexanes) at -78°C . The mixture was stirred at room temperature for 1 h and cooled at -78°C . Trimethyltin chloride (38.0 mL, 38.0 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 crude product was isolated according to the standard work-up described for **3** to afford a brown oil, which contains 10.2 g (33.4 mmol, 89%) of **19**, along with 0.597 g of starting material (4.20 mmol), as determined by ^1H NMR. Compound **19** will be used at the next step without further purification. ^1H NMR (CDCl_3 , 400 MHz): δ 6.61 (s, 1H), 4.20 (m, 4H), 0.38 (s, 9H).

Compound (20). To a solution of **8** (2.31 g, 3.29 mmol) and **19** (6.56 mmol) in THF (40 mL) and DMF (40 mL) was added $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (4-10 mol%). The solution was stirred at 60°C for 3 days. The crude product was isolated according to the standard work-up described for **9** and purified by column chromatography (silica gel, CH_2Cl_2) to afford 1.90 g (2.30 mmol, 70%) of **20** as an orange powder. m.p. $139\text{--}140^\circ\text{C}$. IR (KBr, cm^{-1}): 3109, 2984, 2928, 2848, 1707 ($\text{C}=\text{O}$), 1689, 1519, 1490, 1438, 1366, 1287, 1265, 1237, 1163, 1089, 1067, 1015, 969, 911, 869, 831, 792, 747, 672. ^1H NMR (CDCl_3 , 400 MHz): δ 7.69 (d, $J = 3.8$ Hz, 2H), 7.19 (d, $J = 3.8$ Hz, 2H), 7.12 (m, 4H), 6.27 (s, 2H), 4.37 (m, 4H), 4.29 (t, $J = 6.8$ Hz, 4H), 4.26 (m, 4H), 1.76 (m, 4H), 1.45-1.35 (m, 10H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 65.30, 65.11, 64.57, 29.35, 29.15, 28.70, 25.93 (C_{sec}); 134.15, 125.25, 123.38, 123.34, 97.74 (C_{tert}); 162.19, 144.16, 141.90, 138.20, 135.68, 134.24, 131.31, 111.72 (C_{quat}). HRMS (FAB) m/z calcd for ($\text{C}_{39}\text{H}_{36}\text{O}_8\text{S}_6$) 824.0734; found 824.0751.

Compound (21). A solution of **20** (1.85 g, 2.24 mmol) and NBS (0.810 g, 4.55 mmol) in CHCl_3 (85 mL) and DMF (35 mL) was stirred at room temperature overnight. The resulting mixture was then washed with water. The organic layer was dried over anhydrous magnesium sulfate, and filtered through silica to afford 2.16 g (2.20 mmol, 98%) of **21** as a yellow powder.

m.p. 160-161°C. IR (KBr, cm^{-1}): 2954, 2930, 2853, 1694 (C=O), 1542, 1520, 1494, 1450, 1367, 1288, 1273, 1101, 1084, 1029, 954, 910, 842, 787, 749, 546. ^1H NMR (CDCl_3 , 400 MHz): δ 7.68 (d, $J = 3.8$ Hz, 2H), 7.17 (d, $J = 3.8$ Hz, 2H), 7.12 (d, $J = 3.8$ Hz, 2H), 7.05 (d, $J = 3.8$ Hz, 2H), 4.35 (m, 8H), 4.29 (t, $J = 6.8$ Hz, 4H), 1.75 (m, 4H), 1.45-1.35 (m, 10H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 65.21, 64.93, 64.90, 29.21, 29.00, 28.58, 25.80 (C_{sec}); 134.02, 125.11, 123.46, 123.28 (C_{tert}); 162.01, 143.77, 140.16, 137.13, 134.59, 134.46, 131.44, 111.78, 85.90 (C_{quat}). HRMS (FAB) m/z calcd for ($\text{C}_{39}\text{H}_{34}\text{Br}_2\text{O}_8\text{S}_6$) 979.8945; found 979.8944.

Compound (22). To a solution of **5** (1.78 mmol) and **21** (0.856 g, 0.871 mmol) in THF (30 mL) and DMF (20 mL) was added $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (4-10 mol%). The solution was stirred at 60°C for 3 days. The crude product was isolated according to the standard work-up described for **9** and purified by column

chromatography (silica gel, EtOAc, EtOAc:MeOH 98:2, CH_2Cl_2 :MeOH 99:1) to afford 0.712 g (0.499 mmol, 57%) of **22** as a red powder. m.p. 150-153°C. IR (KBr, cm^{-1}): 2987, 2928, 2857, 1700 (C=O), 1447, 1287, 1270, 1253, 1084, 1054, 1019, 957, 785, 747, 576. ^1H NMR (CDCl_3 , 400 MHz): δ 7.69 (d, $J = 3.8$ Hz, 2H), 7.55 (dd, $J = 8.4$ and 3.8 Hz, 2H), 7.19 (d, $J = 3.8$ Hz, 4H), 7.17 (d, $J = 3.8$ Hz, 2H), 7.12 (m, 6H), 4.43 (s, 8H), 4.29 (t, $J = 6.8$ Hz, 4H), 4.18 (m, 8H), 1.76 (m, 4H), 1.50-1.38 (m, 10H), 1.35 (t, $J = 7.0$ Hz, 12H). ^{31}P NMR (CDCl_3 , 162 MHz): δ 10.27. HRMS (FAB) m/z calcd for ($\text{C}_{63}\text{H}_{62}\text{O}_{14}\text{P}_2\text{S}_{10}$) 1424.0822; found 1424.0785.

Figure 2. ^1H NMR (CDCl_3 , 400 MHz) spectrum of compound **22** (* solvent).

Compound (23). A solution of 2,2'-bithiophene-5-carboxylic acid **6** (1.60 g, 7.61 mmol), α,α' -dibromo-*m*-xylene (1.02 g, 3.75 mmol), anhydrous potassium carbonate (2.13 g, 15.4 mmol) and 18-crown-6 (0.199 g, 0.753 mmol) in THF (36 mL) was stirred at reflux for 2 days. The solvent was removed by rotary evaporation and the resulting solid was filtered through celite in dichloromethane and then purified by column chromatography (silica gel, CH_2Cl_2 :hexanes 1:1 $\rightarrow$ CH_2Cl_2) to afford 1.61 g (3.08 mmol, 82%) of **23** as a white powder. m.p. 117°C . IR (KBr, cm^{-1}): 3100, 3077, 1695 (C=O), 1510, 1450, 1423, 1383, 1317, 1291, 1257, 1227, 1109, 1091, 1043, 963, 890, 840, 807, 786, 746, 694. ^1H NMR (CDCl_3 , 400 MHz): δ 7.74 (d, $J = 3.8$ Hz, 2H), 7.52 (s_{broad} , 1H), 7.43 (s_{broad} , 3H), 7.31 (d, $J = 5.2$ Hz, 2H), 7.28 (d, $J = 3.8$ Hz, 2H), 7.14 (d, $J = 3.8$ Hz, 2H), 7.04 (dd, $J = 5.2$ and 3.8 Hz, 2H), 5.37 (s, 4H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 66.47 (C_{sec}); 134.58, 128.97, 128.16, 127.99, 127.61, 126.17, 125.33, 123.98 (C_{tert}); 161.86, 144.55, 136.35, 136.29, 131.14 (C_{quat}). HRMS (FAB) m/z calcd for ($\text{C}_{26}\text{H}_{18}\text{O}_4\text{S}_4$) 522.0088; found 522.0093.

Compound (24). A solution of **23** (1.55 g, 2.97 mmol) and NBS (1.06 g, 5.96 mmol) in CHCl_3 (25 mL) and DMF (15 mL) was stirred at room temperature overnight. The resulting mixture was then washed with water. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvent removed by rotary evaporation. The crude product was recrystallized from dichloromethane/hexanes to afford 1.87 g (2.75 mmol, 93%) of **24** as a white powder. m.p. 157-158°C. IR (KBr, cm^{-1}): 3092, 2929, 2878, 1690 (C=O), 1512, 1455, 1424, 1374, 1296, 1246, 1105, 1085, 1046, 971, 878, 809, 782, 746, 703. ^1H NMR (CDCl_3 , 400 MHz): δ 7.72 (d, J = 3.8 Hz, 2H), 7.51 (s_{broad} , 1H), 7.42 (s_{broad} , 3H), 7.06 (d, J = 3.8 Hz, 2H), 7.00 (m, 4H), 5.37 (s, 4H). HRMS (FAB) m/z calcd for ($\text{C}_{26}\text{H}_{16}\text{Br}_2\text{O}_4\text{S}_4$) 677.8298; found 677.8295.

Compound (25). To a solution of **3** (1.94 mmol) and **24** (0.645 g, 0.948 mmol) in THF (55 mL) and DMF (25 mL) was added $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (4-10 mol%). The solution was stirred at 60°C for 2 days. The crude product was isolated according to the standard work-up described for **9** and purified by column chromatography (silica gel, CH_2Cl_2 :hexanes 3:2 $\rightarrow$ CH_2Cl_2) to afford 0.613 g (0.713 mmol, 75%) of **25** as a yellow oil. IR (KBr, cm^{-1}): 3100, 2955, 2928, 2863, 1706 (C=O), 1462, 1439, 1374, 1275, 1240, 1090, 797, 745, 697. ^1H NMR (CDCl_3 , 400 MHz): δ 7.75 (d, J = 3.8 Hz, 2H), 7.53 (s_{broad} , 1H), 7.44 (s_{broad} , 3H), 7.23 (m, 4H), 7.15 (d, J = 3.8 Hz, 2H), 7.12 (m, 4H), 5.38 (s, 4H), 4.55 (s, 4H), 3.52 (t, J = 6.8 Hz, 4H), 1.63 (m, 4H), 1.43 (m, 4H), 0.93 (t, J = 7.4 Hz, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 13.95 (C_{prim}); 70.28, 66.52, 66.50, 31.86, 19.48 (C_{sec}); 134.62, 130.39, 128.97, 127.98, 127.59, 127.28, 125.83, 124.47, 123.86 (C_{tert}); 161.79, 144.16, 136.43, 136.34, 136.28, 136.12, 133.43, 131.21 (C_{quat}). HRMS (FAB) m/z calcd for ($\text{C}_{44}\text{H}_{42}\text{O}_6\text{S}_6$) 858.1306; found 858.1335.

Compound (26). A solution of **25** (0.456 g, 0.531 mmol) and NBS (0.189 g, 1.06 mmol) in CHCl_3 (15 mL) and DMF (7.5 mL) was stirred at room temperature overnight. The resulting mixture was then washed several times with water. The organic layer was dried over anhydrous magnesium sulfate, and filtered through silica gel to afford 0.503 g (0.495 mmol, 93%) of **26** as an orange oil. IR (KBr, cm^{-1}): 3077, 2956, 2870, 1709 (C=O), 1458, 1372, 1273, 1086, 796, 744, 698. ^1H NMR (CDCl_3 , 400 MHz): δ 7.74 (d, J = 3.8 Hz, 2H), 7.53 (s_{broad} , 1H), 7.43 (s_{broad} , 3H), 7.20 (d, J = 3.8 Hz, 2H), 7.13 (d, J = 3.8 Hz, 2H), 7.09 (s, 2H), 7.04 (d, J = 3.8 Hz, 2H), 5.38 (s, 4H), 4.47 (s, 4H), 3.50 (t, J = 6.8 Hz, 4H), 1.62 (m, 4H), 1.43 (m, 4H), 0.94 (t, J = 7.4 Hz, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 13.95 (C_{prim}); 70.44, 66.51, 66.23, 31.82, 19.46 (C_{sec}); 134.61, 132.84, 128.97, 127.96, 127.56, 127.51, 125.79, 124.06 (C_{tert}); 161.72, 143.79, 136.93, 136.71, 136.33, 134.79, 134.48, 131.47, 111.44 (C_{quat}). HRMS (FAB) m/z calcd for ($\text{C}_{44}\text{H}_{40}\text{Br}_2\text{O}_6\text{S}_6$) 1013.9516; found 1013.9525.

Compound (27). To a solution of **5** (0.374 mmol) and **26** (0.190 g, 0.187 mmol) in THF (15 mL) and DMF (15 mL) was added $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (4-10 mol%). The solution was stirred at 60°C for two days. The crude product was isolated according to the standard work-up described for **9** and purified by column chromatography (silica gel, $\text{CH}_2\text{Cl}_2:\text{MeOH}$ 99.5:0.5 $\rightarrow$ $\text{CH}_2\text{Cl}_2:\text{MeOH}$ 99:1) to afford 0.030 g (0.0206 mmol, 11%) of **27** as a red oil. IR (KBr, cm^{-1}): 3066, 2956, 2929, 2863, 1706 (C=O), 1451, 1255 (P=O), 1091, 1020, 966, 792, 746, 576. ^1H NMR (CDCl_3 , 400 MHz): δ 7.73 (d, J = 3.8 Hz, 2H), 7.54 (dd, J = 8.4 and 3.8 Hz, 2H), 7.52 (s_{broad} , 1H), 7.41 (s_{broad} , 3H), 7.20 (d, J = 3.8 Hz, 2H), 7.18 (m, 4H), 7.13 (m, 4H), 7.10 (d, J = 3.8 Hz, 2H), 7.06 (d, J = 3.8 Hz, 2H), 5.37 (s, 4H), 4.49 (s, 4H), 4.11 (m, 8H), 3.54 (t, J = 6.8 Hz, 4H), 1.63 (m, 4H), 1.43 (m, 4H), 1.35 (t, J = 7.0 Hz, 12H), 0.92 (t, J = 7.4 Hz, 6H).

^{31}P NMR (CDCl_3 , 162 MHz): δ 10.05. HRMS (FAB) m/z calcd for ($\text{C}_{68}\text{H}_{68}\text{O}_{12}\text{P}_2\text{S}_{10}$) 1458.1393; found 1458.1425.

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