Synthesis of 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-3-substituted thiophenes

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Supporting Information:

General Methods: All chemicals were purchased from Aldrich, except for 3,4-ethylenedioxythiophene, which was donated by Bayer AG. Reactions were carried out on a Schlenk line under an argon atmosphere using inert air atmosphere techniques. 3,4-ethylenedioxythiophene was degassed with argon and then vacuum distilled from CaH₂. THF and diethyl ether were distilled from sodium benzophenone ketyl. Sulfur powder was sublimed prior to use. 3-bromothiophene was dried over CaCl₂, distilled and degassed with argon. 2,5-dibromo-3-(butylsulfanyl)thiophene was degassed with argon and vacuum distilled. 2,5-dibromo-3-(4'-methoxyphenyl)thiophene was dried in vacuo. *n*-butyllithium (2.5 M in hexanes) was titrated prior to use by the method of Watson and Eastham.¹ [1,3-bis(diphenylphosphino)propane]dichloronickel(II) was opened, manipulated, and stored in an MBraun glove box under a nitrogen atmosphere with <1 ppm H₂O and O₂. Magnesium turnings were dried by heating under vacuum. 1,2-dibromoethane was dried over CaCl₂ and distilled. Other chemicals were used as received. ¹H and ¹³C NMR were conducted on a Bruker AC-300 FT-NMR using CDCl₃ as a solvent unless otherwise stated. All chemical shifts were reported relative to tetramethylsilane (TMS) at 0.0 ppm, or the CDCl₃ triplet at 77.0 ppm. Microanalyses were performed by Galbraith Laboratories.

Spectroscopy. Absorbance spectra were obtained on a Shimadzu UVPC-3101 spectrometer using a slow scanning speed and 1 nm slit width. Photoluminescence spectra were obtained on a Perkin Elmer LS 50B. The excitation slit width was 15 nm, while the emission slit width was 5 nm. Emission spectra were corrected using standard spectra of quinine sulfate and *N,N'*-dimethyl-*m*-nitroaniline.² The quantum yield of the BEDOT derivatives was estimated by comparison with a quantum yield standard.³ With this method, the fluorescence quantum yield, ϕ_f , of a material is calculated by equation (1) in which I is the integrated emission intensity, A is the absorbance, and n is the refractive index.

$$\phi_f = \phi_r \frac{I}{I_r} \frac{A_r}{A} \frac{n^2}{n_r^2} \quad (1)$$

The subscript, r , refers to the reference material, in this case quinine sulfate in 0.1 M H₂SO₄ ($\phi_r = 0.577$ at 22 °C for excitation at 350 nm).⁴ Emission spectra for quantum yield measurements were obtained at the same temperature and excitation wavelength as the standard. To minimize reabsorption and inner filter effects, the solutions were diluted such that the absorbance was below 0.05 at the excitation wavelength. Quantum yield measurements were carried out in chloroform and was purged with nitrogen to minimize the influence of O₂ quenching. The sodium D-line (589 nm) refractive index of the solutions was measured with a Thermospectronic Abbé 3L refractometer at 23 °C.

Electrochemistry. Cyclic voltammetry was conducted with a Bioanalytical Systems BAS-100B/W electrochemical analyzer equipped with the C2 cell stand. A non-aqueous cell was used for the electrochemical analysis consisting of acetonitrile (distilled over Ca₂H₂) as the solvent, tetrabutylammonium hexafluorophosphate (recrystallized from ethanol) as the electrolyte (0.1 M). The three electrodes used were a Pt auxiliary electrode, a glassy carbon working electrode, and a Ag/Ag⁺ reference electrode. The reference electrode solution was 0.01 M AgNO₃ in the 0.1 M electrolyte solution. Monomer solutions were prepared at concentrations of 1.0 mM. Cyclic voltammograms were obtained over a broad potential range at a scan rate of 100 mV/s. Cyclic voltammetry of polymers was performed in monomer free electrolyte with various scan rates.

2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-3-butylthiophene (2). To a Schlenk flask equipped with a teflon stirbar and rubber septum was added 1.00 g (7.04 mmol) of 3,4-ethylenedioxythiophene and 25 ml of THF. The flask was cooled to -78 °C and 2.85 ml (7.11 mmol) of *n*-BuLi was added dropwise and reacted at -78 °C for 1 h, warmed to 0 °C and reacted for 1 h. The MgBr₂·THF suspension [from 0.256 g (10.61 mmol) of magnesium turnings, 1.323 g (7.04 mmol) of 1,2-dibromoethane and 30 ml of THF] was transferred to the 2-lithio adduct through a frit, transfer was completed with 3x15 ml of THF washings, and was reacted at 0 °C for 1 h. This was then transferred dropwise to a Schlenk flask at 0 °C containing 1.049 g (3.52 mmol) of 2,5-dibromo-3-butylthiophene, 0.0725 g (0.134 mmol, 1.9 mol%) of [1,3-bis(diphenylphosphino)propane]dichloronickel(II), 30 ml of THF and was reacted for 36 h at RT. It was then poured into crushed ice acidified with 2N HCl and the layers were separated. The aqueous layer was extracted with 3x25 ml of Et₂O, the organics were combined, washed with 3x100 ml of H₂O, 30 ml of NaHCO₃, 2x100 ml of H₂O, dried over MgSO₄, filtered, and the solvent was removed under reduced pressure. Column chromatography (silica gel 230-400 mesh) of the brown residue eluting with pentane:CHCl₃ (1:1 v/v) afforded 1.00 g (67%) of the title compound as a tan solid. ¹H NMR: δ 7.04 (s, 1H), 6.34 (s, 1H), 6.20 (s, 1H), 4.31 (m, 2H), 4.27 (m, 2H), 4.23 (m, 4H), 2.67 (t, 2H $J = 8.0$ Hz), 1.61 (m, 2H), 1.33 (m, 2H), 0.91 (t, 3H $J = 7.3$ Hz). ¹³C NMR: δ 141.77, 141.41, 140.83, 138.04, 137.39, 133.64, 125.69, 125.01, 112.23, 110.35, 98.67, 96.71, 64.91, 64.76, 64.52, 64.44, 32.62, 29.11, 22.63, 13.90. Anal. Calcd: C₂₀H₂₀O₄S₃. C 57.12; H 4.79; O 15.22; S 22.87. Found: C 56.95; H 4.83; O 15.11; S 23.03.

2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-3-octylthiophene (3). **3** was prepared as **2** and column chromatography (silica gel 230-400 mesh) of the brown residue eluting with pentane:CHCl₃ (1:1 v/v) afforded 1.00 g (60%) of the title compound as a tan viscous oil. ¹H NMR: **δ** 7.04 (s, 1H), 6.33 (s, 1H), 6.18 (s, 1H), 4.31 (m, 2H), 4.27 (m, 2H), 4.23 (m, 4H), 2.66 (t, 2H *J* = 8.1 Hz), 1.62 (m, 2H), 1.26 (bs, 10H), 0.85 (t, 3H). ¹³C NMR: **δ** 141.76, 141.40, 140.85, 138.62, 137.38, 133.62, 125.67, 124.98, 112.20, 110.33, 98.65, 96.68, 64.88, 64.74, 64.49, 64.41, 31.82, 30.47, 29.54, 29.46, 29.37, 29.13, 22.61, 14.06. Anal. Calcd: C₂₄H₂₈O₄S₃. C 60.48; H 5.92; O 13.43; S 20.18;. Found: C 59.98; H 6.05; O 13.43; S 20.03.

2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-3-(butylsulfanyl)thiophene (4). **4** was prepared as **2** and column chromatography (silica gel 230-400 mesh) of the brown residue eluting with pentane:CHCl₃ (1:1 v/v) afforded 1.00 g (60%) of the title compound as a red viscous oil which solidifies upon standing. ¹H NMR 300 MHz (CDCl₃) **δ**: 7.16 (s, 1H), 6.35 (s, 1H), 6.25 (s, 1H), 4.32 (m, 4H), 4.25 (m, 4H), 2.86 (t, 2H), 1.58, (m, 2H), 1.39 (m, 2H), 0.89 (t, 3H). ¹³C NMR 75 MHz (CDCl₃) **δ**: 141.75, 141.02, 138.57, 137.68, 136.88, 132.38, 131.91, 127.25, 111.46, 111.07, 99.42, 97.04, 64.99, 64.88, 64.43, 64.32, 36.25, 31.47, 21.78, 13.37. Anal. Calcd: C₂₀H₂₀O₄S₄. C 53.07; H 4.45; O 14.14; S 28.34. Found: C 52.95; H 4.23; O 14.05; S 28.64.

2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-3-(4'-methoxyphenyl)thiophene (5). **5** was prepared as **2** and column chromatography (silica gel 230-400 mesh) of the brown residue eluting with petroleum ether:CHCl₃ (1:1 v/v) afforded 1.92 g (58%) of the title compound as a yellow solid. ¹H NMR 300 MHz (CDCl₃) **δ**: 7.31 (d, 2H *J* = 4.9 Hz), 7.17 (s, 1H), 6.87 (d, 2H *J* = 4.9 Hz), 6.21 (s, 1H), 6.19 (s, 1H), 4.29 (m, 2H *J* = 2.5, 1.2, 2.7, 3.4 Hz), 4.21 (m, 2H *J* = 3.5, 2.7, 1.1, 2.5 Hz), 4.13 (s, 4H), 3.75 (s, 3H). ¹³C NMR 75 MHz (CDCl₃) **δ**: 158.99, 141.78, 141.16, 139.05, 138.30, 137.66, 133.42, 130.23, 128.93, 126.16, 125.39, 113.58, 111.92, 110.73, 98.96, 96.97, 64.91, 64.70, 64.50, 64.37, 55.17. Anal. Calcd: C₂₃H₁₈O₅S₃. C 58.70; H 3.86; O 17.00; S 20.44. Found: C 58.95; H 4.00; O 16.92; S 19.65.

3-(butylsulfanyl)thiophene. To a Schlenk flask equipped with a teflon stirbar and rubber septum was added 6.252 g (40.00 mmol) of 3-bromothiophene and 100 ml of Et₂O. The flask was cooled to -78 °C and 16 ml (40 mmol) of *n*-BuLi was added dropwise and reacted at -78 °C for 1 h. Sulfur powder 1.28 g (40 mmol) was added in one portion, reacted at -78 °C for 2 h, when 5.48 g (40 mmol) of bromobutane was added dropwise via syringe. The contents of the flask were allowed to react overnight when it was then poured into crushed ice containing NH₄Cl and the layers were separated. The aqueous layer was extracted with 3x25 ml of Et₂O, the organics were combined, washed with 3x100 ml of H₂O, 30 ml of NaHCO₃, 2x100 ml of H₂O, dried over MgSO₄, filtered, and the solvent was removed under reduced pressure. Kugelrohr distillation of the yellow oil (92 °C / 2 mm Hg) afforded (35%) of the title compound as a light yellow oil. ¹H NMR: **δ** 7.31 (dd, 1H *J* = 1.9, 3.0 Hz), 7.11 (dd, 1H *J* = 1.7, 1.1 Hz), 7.00 (dd, 1H *J* = 3.9, 1.1 Hz), 2.83 (t, 2H *J* = 7.3 Hz), 1.59 (m, 2H), 1.43 (m, 2H), 0.97 (t, 3H *J* = 7.3 Hz). ¹³C NMR: **δ** 132.23, 129.52, 125.90, 122.70, 34.87, 31.37, 21.74, 13.56. Anal. Calcd: C₈H₁₂S₂. C 55.76; H 7.02; S 37.22. Found: C 55.71; H 6.96; S 36.97.

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