Supporting Information

Nano-Structured Organic Semiconductors *via* Directed Supramolecular Assembly

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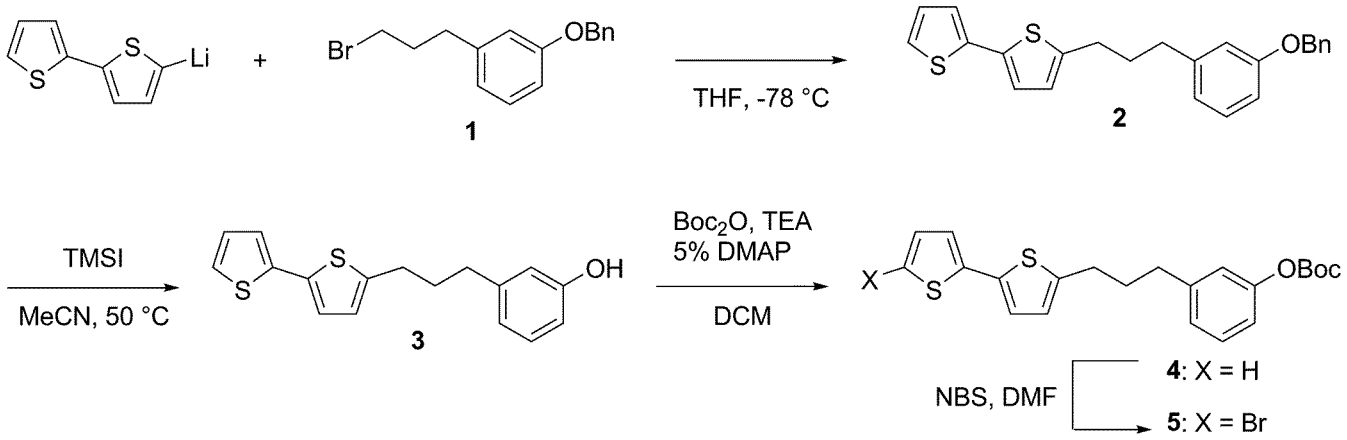
Method Section

Materials. N-bromosuccinimide was recrystallized from water prior to use. All other chemicals were purchased from Aldrich and used as received. All reactions were performed under dry N_2 unless otherwise noted. All extracts were dried over $MgSO_4$ and solvents were removed by rotary evaporation with aspirator pressure. Flash chromatography was performed using Merck Kieselgel 60 (230-400 mesh) silica. Methylene chloride, THF, toluene, pyridine, DMF, and triethylamine were purchased from Fisher and vigorously purged with nitrogen for 1h. The solvents were further purified by passing them under nitrogen pressure through two packed columns (Glass Contour) of neutral alumina (for THF and methylene chloride), neutral alumina and copper(II) oxide (for toluene), or activated molecular sieves (for DMF).

Sample Preparation and Characterization. ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker AV-300, AVQ 400, or DRX-500 instruments using $CDCl_3$ as the solvent. High Resolution Mass Spectometry (HRMS) using Fast Atom Bombardment (FAB) was done with a Micromass ZAB2-EZ double focusing mass spectrometer (BE geometry). Elemental analyses were performed at the UC Berkeley Microanalysis Laboratory. Differential scanning calorimetry measurements were performed on a TA instrument DSC Q200. The samples (~2 mg) were heated from 30 °C to 200 °C at a heating rate of 10 °C/min under nitrogen.

Synthesis. The target disubstituted quaterthiophene was assembled via cross-coupling of functionalized 2,2'-bithiophene partners. First, 2,2'-bithiophene was metallated with *n*-BuLi and quenched with **1** to yield the alkylated product **2**. The benzyl ether **2** was converted to the free phenol **3** with TMS iodide generated *in situ*. A Boc protecting group was then installed to yield **4,** which could be cleanly brominated with NBS at the unsubstituted bithiophene α-carbon to yield coupling partner **5**. Coupling partner **7** was prepared by treating 2,2'-bithiophene with *n*-BuLi and quenching with 3,7-dimethyloctyl bromide to yield **6**, which was treated again with *n*-BuLi and quenched with

trimethylstannyl chloride. A Stille cross-coupling of **5** and **7** followed by removal of the Boc group with silica yielded **4T**.



1-(benzyloxy)-3-(3-bromopropyl)benzene (1) was prepared according to a previously published procedure.[1] ^{1}H NMR (400 MHz): δ 2.13-2.20 (m, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 3.39 (t, *J* = 6.4 Hz, 2H), 5.06 (s, 2H), 6.81-6.84 (m, 3H), 7.20-7.24 (m, 1H), 7.32-7.46 (m, 5H). ^{13}C NMR (100 MHz): δ 33.16, 34.02, 34.04, 69.96, 112.37, 115.36, 121.28, 127.58, 128.01, 128.63, 129.55, 137.05, 142.23, 158.98.

5-(3-(3-(benzyloxy)phenyl)propyl)-[2,2']bithiophene (2). A solution of 2.18 g (13.1 mmol) 2,2'-bithiophene in 80 mL THF was cooled to -78 °C and 4.22 mL (10.6 mmol) 2.5 M *n*-BuLi in hexanes was added slowly via syringe. The mixture was stirred at -78 °C for 1 hour and then 2.68 g (8.8 mmol) **1** was added via syringe. The mixture was then stirred at room temperature overnight followed by evaporation of the solvent under reduced pressure. The resulting oil was purified by flash chromatography through silica using 5% ethyl ether in hexanes as the eluent. The solvent was evaporated and the product dried *in vacuo* to afford 1.76 g (51 %) of a white solid. ^{1}H NMR (400 MHz): δ 1.98-2.06 (m, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.82 (t, *J* = 7.4 Hz, 2H), 5.07 (s, 2H), 6.69 (d, *J* = 3.2 Hz, 1H), 6.81-6.84 (m, 3H), 6.99-7.01 (m, 2H), 7.11 (d, *J* = 3.6 Hz, 1H), 7.17 (d, *J* = 5.2 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.31-7.46 (m, 5H). ^{13}C NMR (100 MHz): δ 29.47, 32.85, 35.05, 69.87, 112.03, 115.19, 121.17, 123.02, 123.37, 123.76, 124.97, 127.49, 127.66, 127.90, 128.54, 129.33, 134.94, 137.06, 137.82,

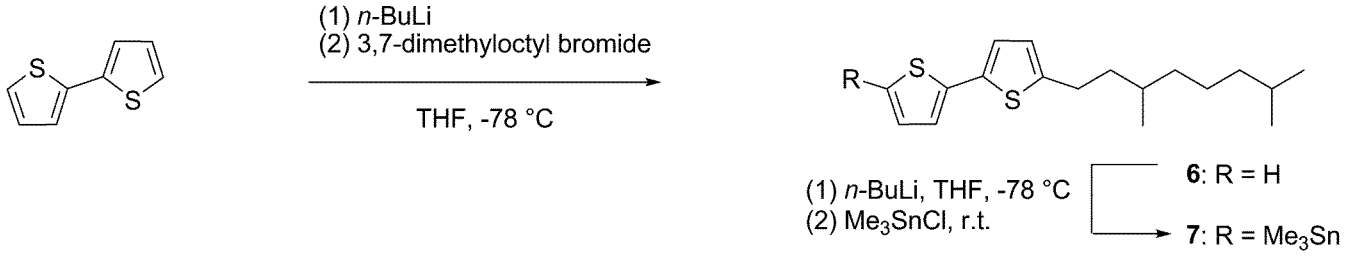
143.42, 144.53, 158.85. HRMS (FAB) *m/z* calc for ($C_{24}H_{22}OS_2$) 390.1112; found 390.1117. Anal. Calcd for $C_{24}H_{22}OS_2$: C, 73.81; H, 5.68; S, 16.42. Found C, 74.11; H, 5.45; S, 16.29.

3-(3-([2,2']bithiophen-5-yl)propyl)phenol (3). A mixture of 1.40 g (3.6 mmol) **2** and 1.6 g (10.7 mmol) NaI was dissolved in 20 mL anhydrous acetonitrile and 1.17 g (10.7 mmol) chlorotrimethylsilane was added via syringe. The resulting mixture was stirred at 50 °C overnight and then quenched with methanol. The solvent was evaporated and the resulting mixture was dissolved in 100 mL ethyl acetate and washed twice with 1 M HCl and water and once with brine. The organic layer was dried and the solvent evaporated. The resulting product was purified by flash chromatography through silica using 20% ethyl acetate in hexanes. The solvent was then evaporated and the product was dried *in vacuo* to afford 1.02 g (94%) of a white solid. ^{1}H NMR (400 MHz): δ 1.97-2.06 (m, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.82 (t, *J* = 7.4 Hz, 2H), 4.66 (s, 1H), 6.66 (m, 3H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.99-7.01 (m, 2H), 7.11 (dd, *J* = 1.0 Hz and 3.4 Hz, 1H), 7.15-7.18 (m, 2H). ^{13}C (100 MHz): δ 29.54, 32.86, 34.94, 112.85, 115.41, 121.01, 123.21, 123.46, 123.85, 125.05, 127.73, 129.80, 135.04, 137.89, 143.83, 144.55, 155.54. HRMS (FAB) *m/z* calc for ($C_{17}H_{16}OS_2$) 300.0643; found 300.0635. Anal. Calcd for $C_{17}H_{16}OS_2$: C, 67.96; H, 5.37; S, 21.35. Found C, 68.11; H, 5.28; S, 21.21.

3-(3-([2,2']bithiophen-5-yl)propyl)phenyl *tert*-butyl carbonate (4). A mixture of 1.02 g (3.4 mmol) **3**, 0.56 mL (4.0 mmol) triethylamine, and 21 mg (0.2 mmol) DMAP was dissolved in 10 mL DCM, and 0.89 g (4.1 mmol) di-*tert*-butyl dicarbonate was added under air. The mixture was stirred for 2 hours during which time vigorous gas evolution occurred. The resulting mixture was diluted with 100 mL ethyl acetate and was washed twice with water and once with brine. The organic layer was dried and the solvent evaporated. The product was dried *in vacuo* to yield 1.30 g (96%) of a white solid. ^{1}H NMR (400 MHz): δ 1.57 (s, 9H), 1.99-2.06 (m, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.83 (t, *J* = 7.4 Hz, 2H), 6.69 (d, *J* = 3.6 Hz, 1H), 6.99-7.02 (m, 4H), 7.06 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 3.6 Hz, 1H), 7.17 (d, *J* = 5.2 Hz, 1H), 7.27-7.31 (m, 1H). ^{13}C (100 MHz): δ 27.76, 29.50, 32.77, 34.81, 83.44, 118.79, 121.30, 123.12, 123.46, 123.84, 125.13, 125.92, 127.71, 129.27, 135.09, 137.87, 143.48, 144.37, 151.16, 151.98.

HRMS (FAB) *m/z* calc for ($C_{22}H_{24}O_3S_2$) 400.1166; found 400.1159. Anal. Calcd for $C_{22}H_{24}O_3S_2$: C, 65.97; H, 6.04; S, 16.01. Found C, 66.14; H, 6.32; S, 15.72.

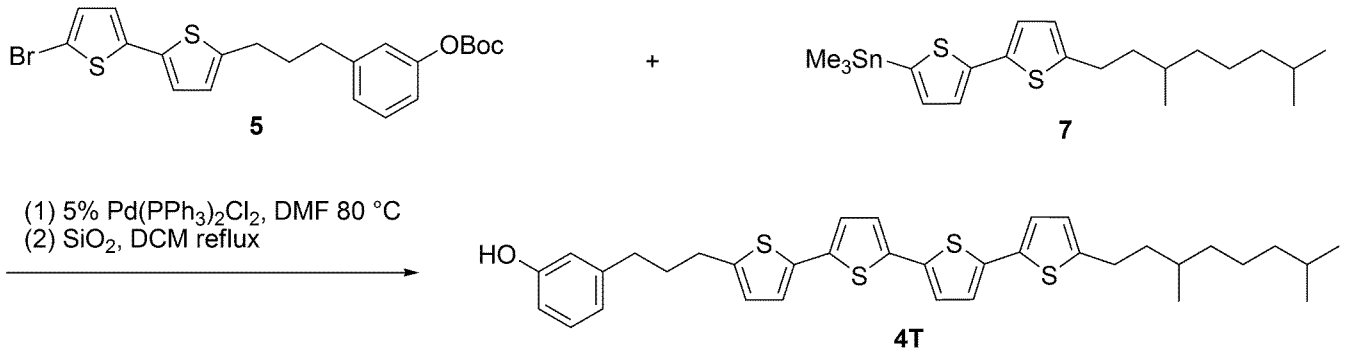
3-(3-(5'-bromo-[2,2']bithiophen-5-yl)propyl)phenyl *tert*-butyl carbonate (5). A flask containing 1.29 g (3.2 mmol) **4** in 10 mL DMF was protected from light and 0.57 g (3.2 mmol) NBS was added. The mixture was stirred overnight and was then diluted with 100 mL ethyl acetate. The resulting solution was washed twice with water and once with brine. The organic layer was dried and the solvent evaporated to yield a product that was dried *in vacuo* to yield 1.48 g (97%) of a white solid. ^{1}H NMR (500 MHz): δ 1.56 (s, 9H), 1.98-2.05 (m, 2H), 2.70 (t, *J* = 7.5 Hz, 2H), 2.81 (t, *J* = 7.3 Hz, 2H), 6.68 (d, *J* = 4.0 Hz, 1H), 6.84 (d, *J* = 4.0 Hz, 1H), 6.92 (d, *J* = 3.5 Hz, 1H), 6.94 (d, *J* = 3.5 Hz, 1H), 7.00-7.06 (m, 3H), 7.27-7.30 (m, 1H). ^{13}C (125 MHz): δ 27.68, 29.41, 32.65, 34.71, 83.40, 110.20, 118.75, 121.22, 123.10, 123.70, 125.15, 125.84, 129.22, 130.46, 133.99, 139.28, 143.31, 144.87, 151.07, 151.91. HRMS (FAB) *m/z* calc for ($C_{22}H_{23}BrO_3S_2$) 478.0272; found 478.0266. Anal. Calcd for $C_{22}H_{23}BrO_3S_2$: C, 55.11; H, 4.84; S, 13.38. Found C, 54.95; H, 4.89; S, 13.05.



5-(3,7-dimethyloctyl)-[2,2']bithiophene (6). A solution of 1.20 g (7.2 mmol) 2,2'-bithiophene in 40 mL THF was cooled to -78 °C and 3.4 mL (7.2 mmol) 2.1 M *n*-BuLi in hexanes was added slowly via syringe. The mixture was stirred for 1 hour at -78 °C and then 1.5 mL (7.2 mmol) 3,7-dimethyloctyl bromide was added slowly via syringe. The mixture was then stirred overnight at room temperature followed by quenching with 1 M HCl. The solvent was evaporated and the product was purified via flash chromatography with 5% DCM in hexanes. The product was dried *in vacuo* to yield 1.12 g (51%) of a colorless oil. ^{1}H NMR (400 MHz): δ 0.88 (d, *J* = 6.8, 6H), 0.93 (d, *J* = 6.4, 3H), 1.09-1.37 (m, 7H),

1.46-1.59 (m, 2H), 1.68-1.74 (m, 1H), 2.73-2.88 (m, 2H), 6.68 (d, J = 3.6 Hz, 1H), 6.98-7.00 (m, 2H), 7.10 (dd, J = 1.0 Hz and 3.4 Hz, 1H), 7.16 (dd, J = 5.2 Hz and 1.2 Hz, 1H). ^{13}C (100 MHz): δ 19.55, 22.70, 22.79, 24.75, 27.85, 28.04, 32.33, 37.11, 38.95, 39.36, 123.01, 123.42, 123.74, 124.62, 127.71, 134.76, 138.03, 145.65. HRMS (FAB) *m/z* calc for ($C_{18}H_{26}S_2$) 306.1476; found 306.1476. Anal. Calcd for $C_{18}H_{26}S_2$: C, 70.53; H, 8.55; S, 20.92. Found C, 70.82; H, 8.91; S, 20.69.

(5'-(3,7-dimethyloctyl)-[2,2']bithiophen-5-yl)trimethylstannane (7). A solution of 0.71 g (2.3 mmol) **6** in 30 mL THF was cooled to -78 °C and 1.2 mL (2.5 mmol) 2.1 M *n*-BuLi in hexanes was added slowly via syringe. The mixture was stirred for 1 hour at -78 °C and then the reaction was quenched by adding 2.3 mL (2.3 mmol) 1.0 M chlorotrimethylstannane in THF via syringe. The mixture was allowed to warm to room temperature and was stirred overnight. The solvent was evaporated and the resulting product was taken up in 100 mL ethyl acetate and washed twice with dilute aqueous HCl and once with brine. The organic layer was dried and the solvent was evaporated to yield 0.99 g (91%) of a green oil that was used without further purification. ^{1}H NMR (300 MHz): δ 0.28-0.47 (m, 9H), 0.87 (d, J = 6.6 Hz, 6H), 0.92 (d, J = 6.3 Hz, 3H), 1.07-1.33 (m, 7H), 1.44-1.60 (m, 2H), 1.67-1.75 (m, 1H), 2.70-2.89 (m, 2H), 6.67-6.68 (m, 1H), 6.97 (d, J = 3.6 Hz, 1H), 7.07 (d, J = 3.3 Hz, 1H), 7.20 (d, J = 3.3 Hz, 1H).



5'''-(3,7-dimethyloctyl)-5-(3-(3-hydroxyphenyl)propyl)-[2,2';5',2'';5'',2'''] quaterthiophene (4T). A flask was charged with 0.54 g (1.1 mmol) **5** and 0.81 g (1.7 mmol) **7**, 38 mg $Pd(PPh_3)Cl_2$ and 20 mL DMF. The mixture was degassed with one freeze-pump-thaw cycle and then stirred at 80 °C overnight. The mixture was then diluted to 200 mL with methanol and a little water to ensure complete

precipitation of the crude yellow product. The solids were filtered and washed with copious amounts of water. The crude product was air dried and then dissolved in 150 mL DCM. The mixture was then heated at reflux with silica until conversion of the *tert*-butylcarbonate to the phenol was complete, as indicated by thin-layer chromatography. The DCM was then evaporated from the silica, which was then loaded onto a silica column. The product was eluted with 3:1 DCM:hexanes to yield 0.57 g (86%) of a yellow solid. ^{1}H NMR (500 MHz): δ 0.87 (d, *J* = 6.5 Hz, 6H), 0.93 (d, *J* = 6.0 Hz, 3H), 1.14-1.33 (m, 6H), 1.51-1.54 (m, 3H), 1.68-1.73 (m, 1H), 1.98-2.04 (m, 2H), 2.66 (t, 7.5 Hz, 2H), 2.74-2.87 (m, 4H), 6.67-6.70 (m, 4H), 6.80 (d, *J* = 7.5 Hz, 1H), 6.97-7.00 (m, 4H), 7.03-7.04 (m, 2H), 7.15-7.18 (m, 1H). ^{13}C (125 MHz): δ 19.44, 22.58, 22.68, 24.63, 27.79, 27.92, 29.50, 32.22, 32.78, 34.85, 36.99, 38.82, 39.24, 112.77, 115.32, 121.03, 123.34, 123.36, 123.52, 123.62, 123.97, 124.01, 124.69, 125.13, 129.54, 134.35, 134,67, 135.25, 135.42, 136.53, 136,73, 143.69, 144.74, 145.90, 155.46. HRMS (FAB) *m/z* calc for ($C_{35}H_{40}OS_4$) 604.1962; found 604.1965. Anal. Calcd for $C_{35}H_{40}OS_4$: C, 69.49; H, 6.66; S, 21.20. Found C, 69.20; H, 6.87; S, 21.02.

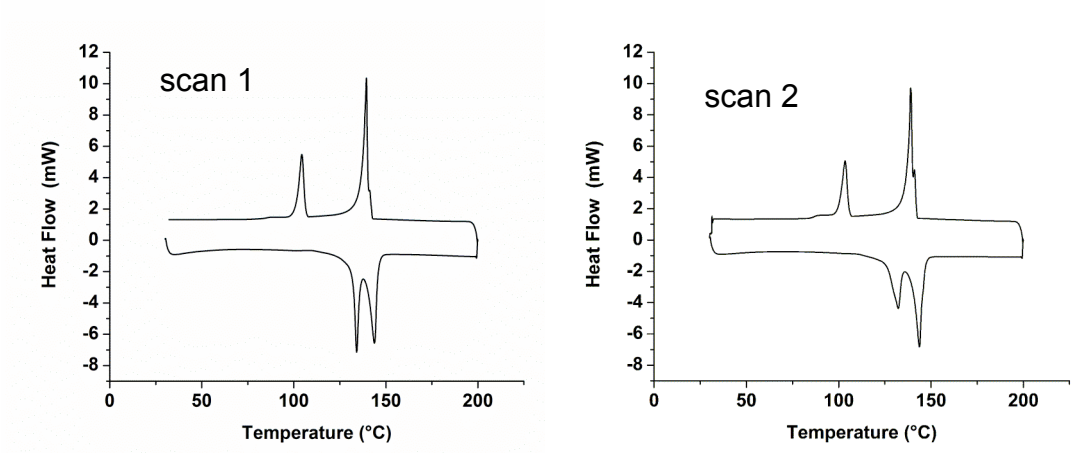


Figure S1. DSC thermograms of **4T** from first and second scan.

References

1. Murphy, W. S.; Wattanasin, S. Intramolecular alkylation of phenols. Part 5. A regiospecific anionic ring closure of phenols *via* quinone methides. *J. Chem. Soc., Perkin Trans. 1.* **1980**, *7*, 1567-1577.