

Supporting Information

Organic Thin-Film Transistors Based on Carbonyl- Functionalized Quaterthiophenes. High Mobility N-Channel Semiconductors and Ambipolar Behavior

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Materials.

The reagent 2-thiophenylaldehyde and 2-bromothiophene are commercially available. The reagent 5,5'-bis(tri-*n*-butylstannyl)-2,2'-dithiophene was prepared according to the known procedure (Wei, Y.; Yang, Y.; Yeh, J.-M. *Chem. Mater.* **1996**, 8, 2659). Compound **8** was prepared following a known procedure (Brzezinski, J. Z.; Reynolds, J. R. *Synthesis* **2002**, 8, 1053, respectively).

Synthesis of 5, 5'''-diheptanoyl-2,2':5',2'':5'',2'''-quaterthiophene (DHCO-4T, 1). A mixture of compound **4** (0.64 g, 2.33 mmol), 5,5'-bis(tri-*n*-butylstannyl)-2,2'-dithiophene (0.744 g, 1.00 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.07 g, 0.06 mmol) in dry DMF (5 mL) was deaerated three times with N₂. The reaction mixture was stirred overnight at 100 °C during which time a precipitate formed. After cooling, the orange solid was collected by filtration and washed several times with hexane, then MeOH. The solid was recrystallized from xylene and dried in vacuum oven (120 °C) yielding pure compound (0.36 g, 65 %). mp 290 °C; ¹H NMR (CD₂Cl₂) δ 7.60 (d, 2H, ²J=3.6 Hz), 7.25 (d, 2H, ²J=3.6 Hz), 7.19 (d, 2H, ²J=3.6 Hz), 7.16 (d, 2H, ²J=3.6 Hz), 2.85 (t, 4H, ³J=7.6 Hz), 1.72-1.70 (m, 4H), 1.36-1.31 (m, 12H), 0.88 (t, 4H, ³J=6.0 Hz); Anal. Calcd for C₃₀H₃₄O₂S₄: C 64.94, H 6.18. Found: C 64.80, H 6.21; MS (EI): *m/z* (%) 553.9 (100) [M⁺]

Synthesis of 5, 5'''-diperfluorohexylcarbonyl-2,2':5',2'':5'',2'''-quaterthiophene (DFHCO-4T, 2). A mixture of compound **3** (1.86 g, 3.66 mmol), 5,5'-bis(tri-*n*-butylstannyl)-2,2'-dithiophene (1.36 g, 1.83 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.13 g, 0.11 mmol) in dry DMF (10 mL) was deaerated three times with N₂. The reaction mixture was stirred overnight at 100 °C during which time a precipitate formed. After cooling, the dark red solid was collected by filtration and washed several times with hexane, then MeOH. Further purification was achieved by gradient vacuum sublimation (1.22 g, 65 %). mp 248 °C; ¹H NMR (CD₂Cl₂) 120°C δ 7.93 (2H), 7.39 (2H), 7.32 (2H), 7.27 (2H); ¹⁹F NMR (CD₂Cl₂) 120°C δ -79.88 (6F), -113.42 (4F), -120.18 (8F), -121.62 (4F), -124.90 (4F). Anal. Calcd for C₃₀H₈F₂₆O₂S₄: C 35.24, H 0.79, F 48.30. Found: C 35.13, H 0.84, F 48.51; MS (EI): *m/z* (%) 1021.5 (100) [M⁺].

Synthesis of 2,7-[bis-(5-perfluorohexylcarbonylthien-2-yl)]-4H-cyclopenta[2,1-*b*:3,4-*b'*]-dithiophen-4-one (DFHCO-4TCO, 3). Molecule **7** (0.50 g, 0.46 mmol) was dissolved in 75 mL acetic acid while refluxing. After addition of concentrated HCl (2 mL), the solution turned from purple to brown, and a dark green precipitate formed immediately. The reaction was quenched with H₂O (20 mL). The solution was then decanted off while warm and the product was collected as a dark green solid (0.45 g). The solid was washed with acetone (2 x 10 mL) and chloroform (6 x 10 mL), dried overnight in vacuum oven, and purified by gradient sublimation twice. The pure portion was collected and washed with boiling chloroform (20 mL). The red solution was decanted leaving the product as a black solid. It was washed with chloroform and purified by gradient sublimation (0.265 g, 60 % yield): mp 297 °C; Anal. Calcd for C₃₁H₆F₂₆O₃S₄: C 35.51, H 0.58. Found: C 35.40, H 0.71; MS (EI, 70 eV) *m/z*: calcd (M⁺) for C₃₁H₆F₂₆S₄O₃, 1048.0; found, 1048.0.

Synthesis of 2-heptanoyl-5-bromothiophene (4). The reagent of 2-bromothiophene (1.63 g, 10.0 mmol) and heptanoyl chloride (1.78g, 12.0 mmol) were dissolved in dry benzene (15 mL) and AlCl₃ was added in portions with stirring over a period of 10 min. The resulting dark brown solution was refluxed for 1 h and left to cool down to room temperature. The reaction mixture was quenched with 2M HCl (15 mL) while carefully stirring. The organic layer was separated, washed with 2M HCl, 2M NaOH, and water, and passed through silica column (d = 3 cm, l = 8 cm). The collected solution was dried over MgSO₄, and concentrated in vacuo (2.40 g, 87 %). ¹H NMR (CDCl₃): δ 7.44 (d, 1H, ²J=3.8 Hz), 7.10 (d, 1H, ²J=3.8 Hz), 2.81 (t, 2H, ³J=7.4 Hz), 1.74-1.68 (m, 2H), 1.38-1.23 (m, 6H), 0.89 (t, 3H, ³J=6.4 Hz); HRMS (EI, 70 eV) *m/z*: calcd (M⁺) for C₁₁H₁₅BrOS, 274.00; found, 274.0016.

Synthesis of perfluorohexyl-thien-2-yl-methanol (5). MeLi (1.6 M, 15.9 mL) was added dropwise to a solution of 5-thiophenyl aldehyde (2.80g, 25.0 mmol) and perfluorohexyliode (11.73 g, 26.3 g) in dry Et₂O (70mL) at -78 °C with stirring. The mixture was stirred for additional 40 min and quenched with 3N HCl (70 mL). The organic layer was separated, washed with water twice, dried over MgSO₄, filtered, and concentrated in vacuo. Column chromatography of the residue over silica gel (hexane: ethyl acetate = 1:1) yielded **5** (6.20 g, 57 %). ¹H NMR (CDCl₃): δ 7.45 (d, 1H, ²J=4.5 Hz), 7.24 (d, 1H, ²J=3.0 Hz), 7.10-7.06 (dd, 1H, J=4.5, 3.8 Hz), 5.54-5.46 (m, 1H), 2.56 (d, 1H, ²J=5.7 Hz); HRMS (EI, 70 eV) *m/z*: calcd (M⁺) for C₁₁H₅F₁₃OS, 431.99; found, 431.9838.

Synthesis of perfluorohexyl-(5-bromothiophen-2-yl)-methanol (6). Bromine (0.698 g, 4.37 mmol) was added to a solution of **1** (1.80 g, 4.16 mmol) in CH₂Cl₂ (15 mL). After stirring overnight at room temperature, the mixture was neutralized with saturated aqueous NaHCO₃ solution and extracted with CH₂Cl₂ (3 x 20 mL). The organic layers were combined, dried over MgSO₄, filtered, and concentrated in vacuo (1.90 g, 89 %). ¹H NMR (CDCl₃): δ 7.02 (d, 1H, ²J=3.7 Hz), 6.97 (d, 1H, ²J=3.8 Hz), 5.46-5.38 (m, 1H), 2.64 (d, 1H, ²J=5.2 Hz); HRMS (EI, 70 eV) *m/z*: calcd (M⁺) for C₁₁H₄F₁₃BrOS, 509.90; found, 509.8945.

Synthesis of 2-perfluorohexylcarbonyl-5-bromothiophene (7). A solution of compound **2** (1.90 g, 3.72 mmol) and activated MnO₂ (5 g) was stirred overnight. The mixture was filtered through Celite. The filtrate was dried over MgSO₄, and the solvent evaporated in vacuum (1.85 g, 98 %). The mixture was purified by sublimation; mp 27 °C; ¹H NMR (CDCl₃): δ 7.74 (d, 1H, ²J=3.8 Hz), 7.23 (d, 1H, ²J=3.8 Hz); ¹⁹F NMR (CDCl₃) δ -81.20 (3F), -115.20 (2F), -121.77 (4F), -123.18 (2F), -126.53 (2F); Anal. Calcd for C₁₁H₂BrF₁₃OS: C 25.95, H 0.40. Found: C 26.11, H 0.54; MS (EI, 70 eV) *m/z*: (M⁺) calcd for C₁₁H₂BrF₁₃OS 509.8; found 509.8.

Synthesis of spiro[4H-cyclopenta[2,1-b:3,4-b']dithiophene-4,2'-[1,3]dioxolane], 2,6-bis(tri-*n*-butylstannyl) (9). Spiro[4H-cyclopenta[2,1-b:3,4-b']dithiophene-4,2'-[1,3]dioxolane] (1.71 g, 7.35 mmol) was dissolved in dry THF (20 mL) under nitrogen and cooled to -78°C. Two equivalents of *n*-BuLi were added dropwise (5.92 mL, 14.85 mmol) and the reaction mixture stirred for 30 min. The solution was allowed to warm to room temperature and stirred for an additional 1.5 h. The resulting thick brown suspension was cooled again to -78°C and tri-*n*-butyltin chloride (4.78 g, 14.7 mmol) was added. The solution was then stirred at room temperature for 4 h. The reaction was quenched with 100 mL H₂O and extracted with hexane. The organic layer was washed with H₂O (6 x 50 mL) and dried over MgSO₄. After filtration, evaporation of the solvent left a brown oil (5.7g, 95 % yield): ¹H NMR (CDCl₃): δ 6.96 (s, 2H), 4.33 (s, 4H), 1.57 (m, 12H), 1.33 (m, 12H), 1.10 (m, 12H), 0.91 (t, 18H, ³J=6.8 Hz); HRMS (ACPI, CH₂Cl₂) *m/z*: ((M+H)⁺) calcd for C₃₅H₆₀S₂O₂Sn₂, 814.4; found, 815.2.

Synthesis of spiro[4H-cyclopenta[2,1-b:3,4-b']dithiophene-4,2'-[1,3]dioxolane], 2,6-bis-(5-perfluorohexyl carbonylthien-2-yl) (10). A mixture of compound **6** (2.00 g, 2.46 mmol), compound **3** (2.50 g, 4.91 mmol), and Pd[PPh₃]₄ (0.193 g, 0.167 mmol) in dry DMF (60 mL) was stirred at 90°C for 6 h. After 15 min a purple solid precipitated. Filtration of the red solution left the disubstituted product as a dark green solid (2.18 g, 81.04 % yield). The solid was washed with ether (3 x 20 mL) and hexane (3 x 10 mL), dried overnight in vacuum oven, and purified by gradient sublimation: mp 218 °C; ¹H NMR (CDCl₃): δ 7.88 (2H), 7.32 (4H), 4.39 (4H); ¹⁹F NMR (DMSO) -85.88 (6F), -119.69 (4H), -126.43 (8F), -127.85 (4F), -131.21 (4F); Anal. Calcd for C₃₃H₁₀F₂₆O₄S₄: C 36.27, H 0.92. Found: C 36.15, H 1.01; MS (EI, 70 eV) *m/z*: (M⁺) calcd for C₃₃H₁₀F₂₆S₄O₄, 1092.4; found 1092.2.

Device Fabrication and Thin Film Characterization.

Prime grade *n*-doped silicon wafers (100) having 300 nm thermally grown oxide (Process Specialties Inc.) were used as device substrates. They were rinsed with water, methanol, and acetone before film deposition. Trimethylsilyl functionalization of the Si/SiO₂ surface was carried out by exposing the silicon wafers to hexamethyldisilazane (HMDS) vapor at room temperature in a closed container under nitrogen overnight. Organic compounds were deposited by either vacuum evaporation (pressures < 10⁻⁵ Torr) at a growth rate of 0.2-0.3 Ås⁻¹, or by casting films from THF solutions (concentrations 200 - 400 ppm, 10⁻⁴ - 10⁻² M). Evaporated films were 500 Å thick (as determined by a calibrated in situ quartz crystal monitor), and solution-cast films were variable and thicker, on the order of microns. For solution depositions, a region of the substrate surface (~1-2 cm²) was defined using 3M Novec™ EGC-1700 electronic coating (comparable to the previously used 3M FC-722 product) before casting. The room temperature or warm solution was transferred inside the defined area and allowed to evaporate, with no special care taken to avoid dust in the environment (a clean hood is optional). For FET device fabrication, top-contact electrodes (500 Å) were deposited by evaporating gold (pressure < 10⁻⁵ Torr); channel dimensions were 50/100 μm (L) by 5.0 mm (W). The capacitance of the insulator is 2 x 10⁻⁸ F/cm² for 300 nm SiO₂. TFT device measurements were carried out in a customized vacuum probe station (8 x 10⁻⁵ Torr) or in air. Coaxial and/or triaxial shielding was incorporated into Signatone probe stations to minimize the noise level. TFT characterization was performed with a Keithly 6430 subfemtoammeter and a Keithly 2400 source meter, operated by a locally written Labview program and GPIB communication.

Thin films were analyzed by X-ray film diffractometry (XRD), using standard θ - 2θ techniques, with Cu K α radiation and a monochromator. All θ - 2θ scans were calibrated in situ with the reflection of the Si (100)

substrates. Films were coated with 3 nm of sputtered Au before analysis by scanning electron microscopy (SEM) using a Hitachi S4500 FE microscope.

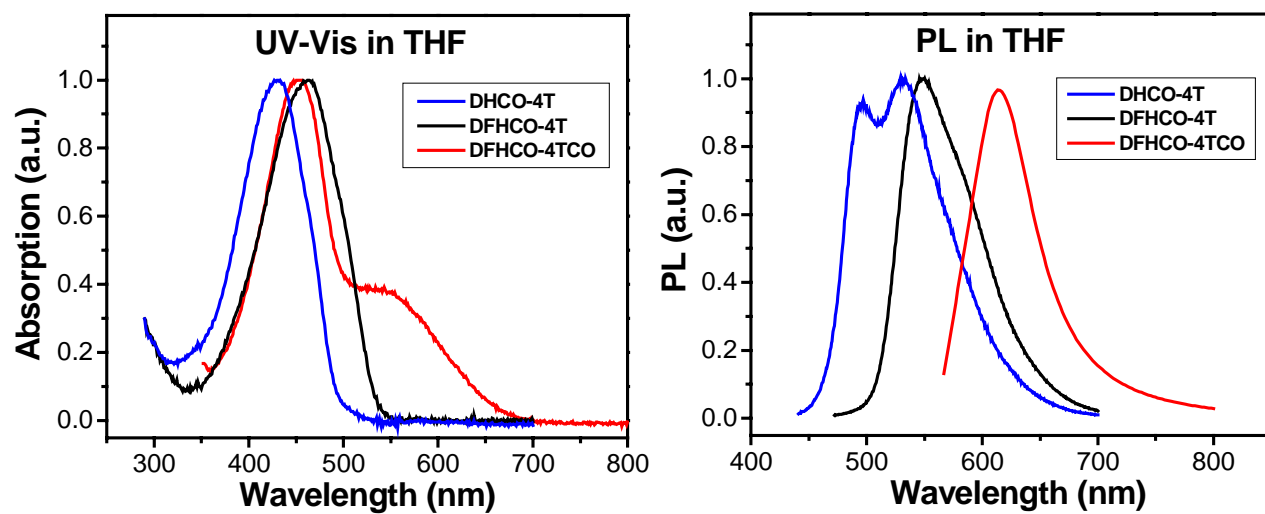


Figure S1. UV-vis/Photoluminescence (PL) spectra of **DHCO-4T**, **DFHCO-4T** and **DFHCO-4TCO**.

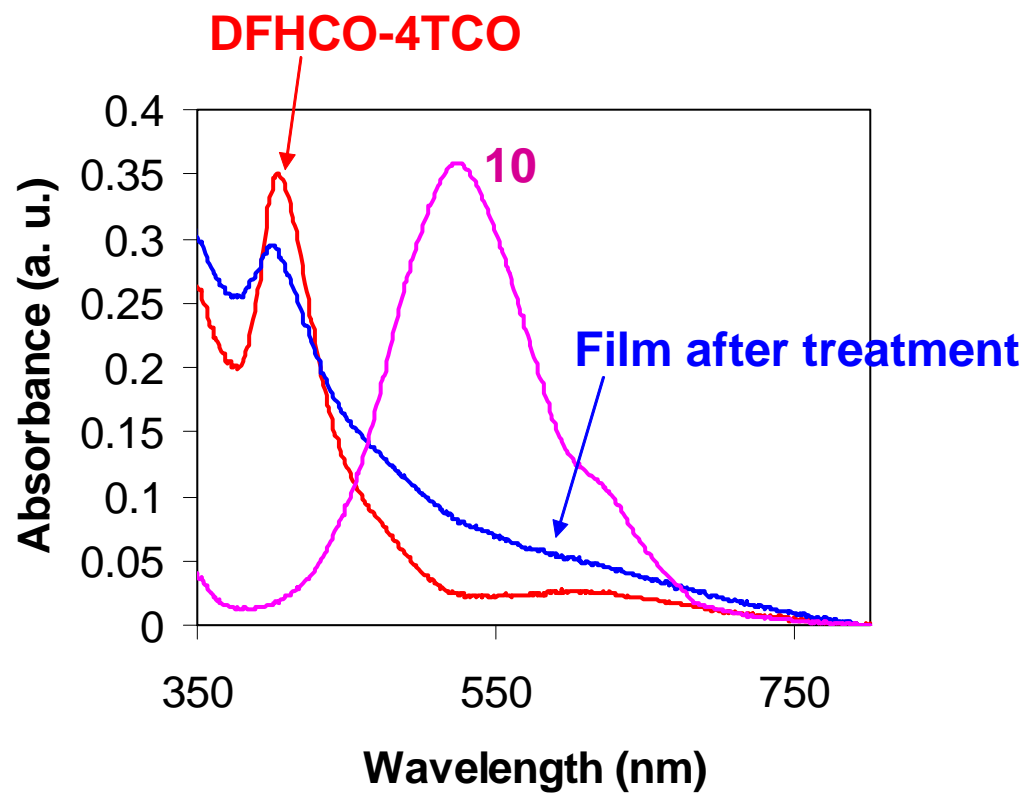


Figure S2. UV-Vis spectra of **DFHCO-4TCO** (red) and **10** (pink) films and that of film **10** after H₂O-HCl vapor treatment and annealing.