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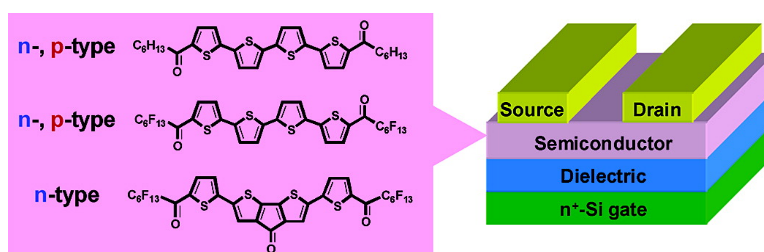

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Organic Thin-Film Transistors Based on Carbonyl-Functionalized Quaterthiophenes: High Mobility N-Channel Semiconductors and Ambipolar Transport

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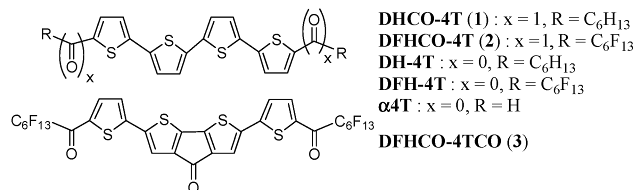
The search for high-performance, environmentally stable electron-transporting (n-type) materials for organic field-effect transistors (OFETs) has just begun.[1,2] Despite the latest impressive results,[2] these materials are, compared to hole transporters (p-type),[3] far less developed in terms of understanding fundamental structure−charge transport properties relationships and carrier activation−deactivation mechanisms. Furthermore, the availability of n-type (semi)conductors that approach or surpass the carrier mobilities of the most efficient p-type materials[3] is important for applications in many organic device technologies[4] including, but not limited to, OFETs and complementary circuits.[1−4]

Our group is pursuing this goal using the strategy of selectively functionalizing and/or replacing oligothiophene moieties with perfluorinated substituents.[2e,5] This approach afforded the first n-type sexithiophene-based OFETs[5c] and progressive increase of oligothiophene electron mobilities (in $cm^2\ V^{-1}\ s^{-1}$, measured in vacuo) from 0.02[5c] to 0.08[2e] and recently to 0.22.[5a] However, these and many other n-type materials perform nonoptimally in air. In this communication, we report the synthesis and OFET properties of three new carbonyl-functionalized quaterthiophenes exhibiting improved stability and unique charge transport characteristics.

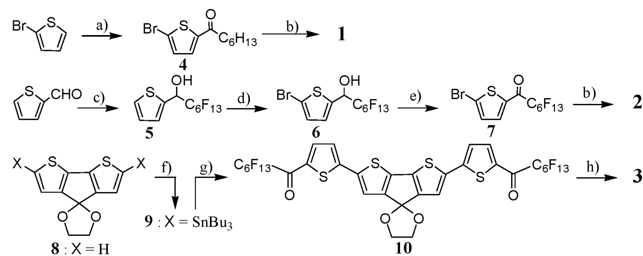


DHCO-4T (**1**) : x = 1, R = C_6H_{13}
DFHCO-4T (**2**) : x = 1, R = C_6F_{13}
DH-4T : x = 0, R = C_6H_{13}
DFH-4T : x = 0, R = C_6F_{13}
α4T : x = 0, R = H
DFHCO-4TCO (**3**)

The design rationale for these new structures is the following. The quaterthiophene core was selected since it exhibits one of the greatest and most reproducible OFET mobilities (μ) and current modulation ratios (I_{on}:I_{off}) in the oligothiophene family, as both p-(α,ω-dihexyl-4T, **DH-4T**) and n-type (α,ω-diperfluorohexyl-4T, **DFH-4T**) semiconductors.[5a] Carbonyl functionalization was chosen because (i) it introduces one of the stronger electron-withdrawing (EWD) primary functionalities, (ii) in contrast to other powerful EWD groups such as CN and NO_2, it allows additional modifications and fuctionalization, (iii) it can be readily incorporated into π-conjugated cores, and (iv) it prevents β-fluoride elimination when inserted between a fluoroalkyl chain and carbanion fragment. The new quaterthiophenes **1**−**3** were synthesized according to Scheme 1 and were characterized by conventional chemical and physical methods.

Cyclic voltammetry[6] of **1**−**3** in THF reveals two reversible one-electron reduction processes (E_1/E_2 (V): **DHCO-4T** −1.06/−1.47; **DFHCO-4T** −0.88/−1.01; **DFHCO-4TCO** −0.65/−0.78), considerably less negative than unsubstituted **α4T** (−1.94/−2.07 V). Oxidation processes are irreversible. UV−vis/PL data (Figure S1) indicate that the C=O groups are effectively conjugated with the 4T core and give rise to substantially red-shifted absorption and emission maxima (λ_{abs}/λ_{em} (nm): **DHCO-4T** 430/530; **DFHCO-4T** 465/550; **DFHCO-4TCO** 545/615) and HOMO−LUMO optical gap reductions (E_g (eV): **DHCO-4T** 2.6; **DFHCO-4T** 2.4; **DFHCO-4TCO** 2.2) vs **4T** (λ_{abs}/λ_{em} = 391/450 nm, E_g = 2.8 eV). HOMO/LUMO energies (E_{HOMO}/E_{LUMO} (eV)) are estimated as follows for **DHCO-4T** (−6.38/−3.78), **DFHCO-4T** (−6.36/−3.96), and **DFHCO-4TCO** (−6.39/−4.19) vs **α4T** (E_{HOMO}/E_{LUMO} = −5.79/−2.90 eV), from the relation $E_{HOMO} = E_{LUMO} - E_g$, where E_{LUMO} is estimated from E_1.[5b] Note that compared to p-type **α4T**, the new systems exhibit a considerably larger depression of LUMO (∼0.9−1.3 eV) vs HOMO (∼0.6 eV) energies, suggesting that carbonyl functionalization of the core should affect electron transport more than hole transport. In marked contrast, on going from **α4T** to **DFH-4T** (E_{HOMO}/E_{LUMO} = −6.19/−3.31 eV) or **DH-4T** (E_{HOMO}/E_{LUMO} = −5.80/−2.89 eV) a uniform E_{HOMO}/E_{LUMO} shift is observed in agreement with σ-EWD substituent effects.[5b] Theoretical and experimental studies on carbonyl-functionalized (oligo)heteroaromatics indicate that HOMO energies are less affected than LUMOs, since the latter are more localized on the molecular core.[7] In marked contrast, the LUMO fully extends to the C=O groups via $S_{thiophene}$→C=O intramolecular charge transfer, enhancing substituent σ/π-EWD effects. Therefore, greater perturbation of the **1**−**3** LUMOs is expected, in excellent agreement with the present electrochemical and optical data.

Scheme 1. Synthetic Route to Semiconductors **1**−**3**



(a) $C_6H_{13}COCl$, $AlCl_3$, C_6H_6, reflux.
(b) Bu_3Sn–(bithiophene)–$SnBu_3$, Pd[PPh_3]$_4$, DMF, 100 °C.
(c) $C_6F_{13}I$, MeLi, Et_2O, -78 °C; HCl. (d) Br_2, CH_2Cl_2.
(e) MnO_2, CH_2Cl_2. (f) *n*-BuLi, Bu_3SnCl, THF.
(g) **7**, Pd[PPh_3]$_4$, DMF, 90 °C. (h) AcOH-HCl, reflux.

The new carbonyl-substituted oligothiophenes are thermally stable and undergo quantitative sublimation. Thin films are readily grown from the vapor phase under vacuum and have been characterized by XRD (revealing molecular edge-on-substrate growth orientation), scanning electron microscopy, and FET *I*−*V* measurements. Full details will be reported separately. Top-contact FET devices were fabricated as reported previously.[5] Briefly, semiconductors **1**−**3** (∼50 nm) were vapor-deposited on HMDS-treated p-doped Si/SiO_2 substrates maintained at deposition temperatures

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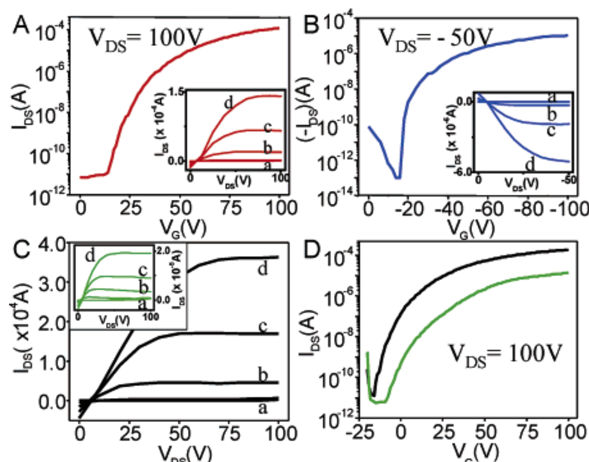

Figure 1. $I_{DS}-V$ plots for: (A) **DHCO-4T** (n-type, vacuum). (B) **DHCO-4T** (p-type, vacuum). (C) **DFHCO-4T** in a vacuum (black) and air (green). (D) **DFHCO-4TCO** transfer plots in a vacuum (black) and air (green) at different source-drain/gate biases. V_G (V); $a = 0-\pm40$, $b = \pm60$, $c = \pm80$, $d = \pm100$.

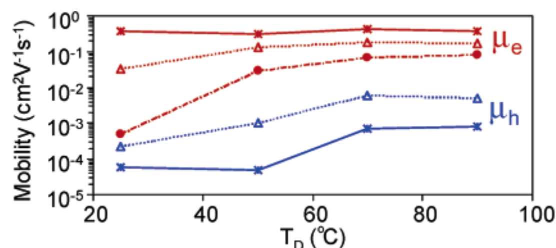

Figure 2. Electron (red) and hole (blue) mobilities vs film deposition temperature (T_D) for **DHCO-4T** (△), **DFHCO-4T** (×), and **DFHCO-4TCO** (●) in a vacuum. μ_e for **DFHCO-4T** is after I_2 vapor treatment.

(T_D) between 25 and 90 °C. OFET fabrication was completed by vapor-depositing source-drain Au contacts (~50 nm). Measurements were performed in air and vacuum (~10^{-5} Torr), and the standard saturation FET equation[8] was employed to calculate carrier mobilities.

Figure 1 shows typical source-drain current−voltage plots for **1**−**3**-based OFETs under different conditions. All of the new oligothiophenes exhibit *very high* electron mobilities (μ_e) in vacuum, with average values as a function of T_D shown in Figure 2. Note that for some **DFHCO-4T** devices, μ_e as high as ~0.6 cm^2 V^{-1} s^{-1} has been measured. Interestingly, **DHCO-4T** films also exhibit relatively *large hole* mobilities (μ_h up to 0.01 cm^2 V^{-1} s^{-1} at T_D = 70 °C) at all deposition temperatures. Ambipolar transport has been observed previously in blend and bilayers and single component OFETs, but with modest figures of merit, large imbalances between μ_e and μ_h, and only for narrow T_D ranges.[2f,9] To our knowledge, **DHCO-4T** is the first organic conductor exhibiting unoptimized μ_e/μ_h values as high as ~0.1/0.01 cm^2 V^{-1} s^{-1} (vacuum, T_D = 70−90 °C). **DFHCO-4T** also exhibits ambipolar behavior but only after I_2 vapor treatment. From the transfer plots, very high I_{on}:I_{off} ratios are observed for electrons: >10^7. Maximum current gains for holes are >10^8 for **DHCO-4T**. The subthreshold swings (S), indicating how sharply the devices turn on, are in the 1.3−4.9 V/decade range, and turn-on voltages $|V_0|$ are ~5−30 V.

More electron-deficient **DFHCO-4T** (Figure 1C) and **DFHCO-4TCO** (Figure 1D) also operate well in air, with μ_e's exhibiting the same T_D dependence as in a vacuum (Figure 2) but with ~5/10× lower magnitudes. In particular, **DFHCO-4TCO**-based devices can be cycled more then 20 times in air without obvious degradation. Finally, since dioxolane-protected 4T **10** is solution-processable and its films are readily converted to **DFHCO-4TCO** films by deprotection via H_2O−HCl vapor treatment and annealing (Figure S2), we are exploring this approach for depositing n-type materials from soluble precursors.

In conclusion, new carbonyl-functionalized quaterthiophenes have been prepared and characterized. These materials possess low-lying LUMOs that allow and facilitate electron injection and transport as well as HOMO energies compatible with respectable hole transport. OFETs fabricated by conventional methods exhibit the largest oligothiophene thin-film μ_e's found to date and approach the performance of pentacene/SiO_2 OFETs.[1]

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Supporting Information Available: **1**−**3** syntheses and spectroscopic data and FET device fabrication. Figures S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.

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