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Communication

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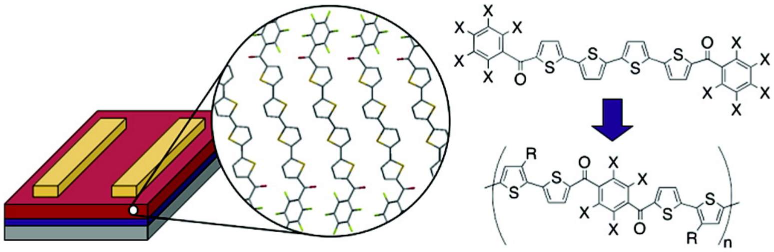

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High Electron Mobility in Solution-Cast and Vapor-Deposited Phenacyl−Quaterthiophene-Based Field-Effect Transistors: Toward N-Type Polythiophenes

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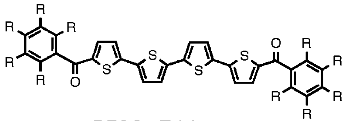
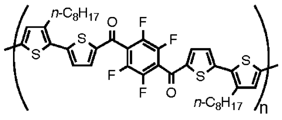
Realization of practical organic electronics has been impaired by the paucity of high-mobility, solution-processable, electron-transporting (n-type) semiconductors for organic field-effect transistors (OFETs).[1] The combination of such materials with hole transporters (p-type)[2,3] should enable inexpensive, high-throughput organic CMOS fabrication via spin-coating, drop-casting, and/or printing. There are two primary challenges to achieving such properties: (i) obtaining favorable crystal packing while maintaining useful solubility, and (ii) achieving n-type transport via appropriate molecular electronic structure/orbital energetics and low-defect density films.[4] To date, postdeposition film processing and chemistries have been explored to address these issues with various outcomes since achieving high purity and highly regular film morphology present significant challenges.[3] This communication describes the synthesis of a new class of soluble oligothiophenes having high electron/hole mobilities *both* in solution-cast (μ_e up to 0.25 $cm^2 \cdot V^{-1} \cdot s^{-1}$) and vapor-deposited ($\mu_e$ up to 0.51 $cm^2 \cdot V^{-1} \cdot s^{-1}$) films with very high current modulation (I_{on}:I_{off} > 10^5 and 10^8, respectively). Furthermore, the structure and energetics of these molecular motifs are models for the synthesis/characteristics of new n-type polythiophenes.

New quaterthiophenes **DFCO-4T** (**1**) and **DPCO-4T** (**2**) and polythiophene **P(COFCO-4T)** (**3**) were synthesized according to Scheme S1 (see Supporting Information) and characterized by conventional chemical and physical methods. Crystals of **1** and **2** suitable for X-ray diffraction were obtained by sublimation. Both crystallize in a herringbone motif (Figure 1), with the shortest intercore distance being 3.50 Å (C14−C15′) and 3.43 Å (C14−C16′) for **1** and **2**, respectively. The average dihedral angle between the phenyl substituent and the adjacent thiophene subunit is ~53° in **1** and ~49° in **2**. The quaterthiophene core of **2** is more planar than that of **1** with a maximum inter-thiophene torsional angle of ~4° versus ~13° in **1**. However, the **1** carbonyl groups lie ~6° out of the plane of the adjacent thiophene ring, while in **2**, this angle increases considerably to ~17°. Both semiconductors are thermally stable and volatile, as indicated by differential scanning calorimetry (Figure S1) and thermogravimetric analysis (Figure S2). Films can be grown from the vapor phase and by solution-casting from common solvents. Wide-angle X-ray diffraction (WAXRD) indicates that vapor-deposited films are highly crystalline, having the same phase as that observed in the crystal structures (Figure S3). The progression of Bragg reflections corresponds to *d*-spacings of 27.62 Å (**1**) and 26.87 Å (**2**). These spacings are consistent with half the unit cell long axes (shown in Figure 1), indicating end-on-substrate molecular orientation. As the substrate temperature during vapor phase film deposition (T_D) is increased progressively from 25 to 90 °C, the films become more crystalline and minority crystallite orientations, present at lower T_D, are no longer observable by WAXRD. Diffraction patterns similar to those of the high T_D vapor-deposited films are also observed for solution-deposited films of **1** (Figure S4).



DFCO-4T (1) : R = F
DHCO-4T (2) : R = H



P(COFCO-4T) (3)

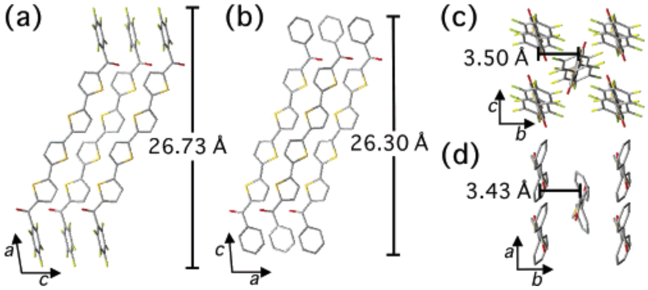


Figure 1. Crystal structures of semiconductors **1** (a) and **2** (b) viewed perpendicular to the long axis of the unit cell (hydrogen atoms not shown). Note the remarkably similar herringbone packing motif in **1** (c) and **2** (d).

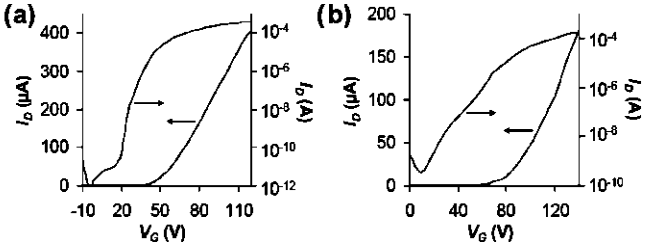


Figure 2. Transfer plots of OFET devices fabricated with **DFCO-4T** vapor-deposited at $T_D = 80$ °C (a) and solution-cast (xylene) at $T_D = 120$ °C (b).

Top-contact OTFTs were fabricated by vapor-deposition/drop-casting of **1**−**3** films onto temperature-controlled HMDS-treated $SiO_2/p^+{-}Si$ substrates, followed by Au deposition through a shadow mask to define the source and drain electrodes. OFET characterization was preformed under argon. High electron mobilities (μ_e) of 0.45 ± 0.07 $cm^2 \cdot V^{-1} \cdot s^{-1}$ are observed for vapor-deposited **1** films ($T_D = 80$ °C) with a threshold voltage (V_T) of ~30 V (I_{on}:I_{off} > 10^8, Figure 2a and Figure S5).

This highly reproducible μ_e value is one of the largest reported to date, doubtless reflecting the favorable crystal packing of this molecule. In solution-cast devices, μ_e is exceptionally high with a value of 0.21 ± 0.05 $cm^2 \cdot V^{-1} \cdot s^{-1}$ (I_{on}:I_{off} = 10^5; V_T = 50−70 V, from xylene, Figure 2b and Figure S6). This is the highest OFET electron mobility for a solution-cast semiconductor reported to date, surpassing that of the previous highest mobility n-type molecular[1n] [0.01 $cm^2 \cdot V^{-1} \cdot s^{-1}$ (I_{on}:I_{off} and V_T not reported) from trifluorotoluene] and polymeric[1l] [0.03 $cm^2 \cdot V^{-1} \cdot s^{-1}$ (I_{on}:I_{off} = 5 × 10^5, V_T (estimated from the reported data) ~30 V)/0.1 $cm^2 \cdot V^{-1} \cdot s^{-1}$ (I_{on}:

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Table 1. Charge Carrier Mobilities (μ, $cm^2 \cdot V^{-1} \cdot s^{-1}$)[a] and Current On/Off Ratios (I_{on}:I_{off}) for OFETs Fabricated with Semiconductors **1** and **2** Measured at 25 °C

deposition method	T_D[b] (°C)	**1**		**2**	
		μ_e	I_{on}:I_{off}	μ_h	I_{on}:I_{off}
vapor	25	0.02	10^4	0.012	10^5
vapor	50	0.17	10^5	0.014	10^5
vapor	70	0.31	10^5	0.028	10^5
vapor	80	0.45	10^8	0.031	10^6
vapor	90	0.17	10^7	0.043	10^6
drop-cast[c]	120	0.21	10^5	8×10^{-4}	10^3

[a] Calculated in the saturation regime. Typical standard deviations are 10−20%. [b] Substrate deposition temperature. [c] From xylenes.

I_{off} (estimated from the reported data) ~5, V_T not reported) from methanesulfonic acid] solution processable semiconductors. Nonfluorinated material **2** exhibits hole mobilities (μ_h) in vapor-deposited films of 0.043 ± 0.008 $cm^2 \cdot V^{-1} \cdot s^{-1}$ (I_{on}:I_{off} = 10^5; $V_T \sim -20$ V, Figure S7), however no electron conduction has been observed. Drop-cast films of this material exhibit $\mu_h = (8 \pm 2) \times 10^{-4}$ $cm^2 \cdot V^{-1} \cdot s^{-1}$. Similar dependencies of mobility on T_D are observed in both semiconductors (Table 1), consistent with the trend in crystallinity observed by WAXRD.

Cyclic voltammetry of the new phenacyl semiconductors in THF reveals two reversible single-electron reductions [E_1/E_2 (V) vs SCE] at −1.05/−1.16 in **1** and at −0.95/−1.30 in **2**. Irreversible oxidative features are observed at +1.07/+1.22 for **1**. UV−vis absorption in THF (Figure S8) indicates that the optical band gap (E_g) is ~2.40 eV for **1** and ~2.46 eV for **2**. Surprisingly, E_1 of n-type **1** is slightly more negative (0.1 V) than that of p-type **2**. On the basis of conventional understanding, redox processes related to MO energetics[1c,d] are primary factors in determining majority charge carrier type; therefore, it is surprising that **1** exhibits electron mobility in the solid state, while **2** preferentially conducts holes. An explanation may lie in subtle crystal structure molecular conformational differences − the dihedral angle between the electron-withdrawing carbonyl groups and the thiophene core (intrinsically p-type) is much greater in **2** than in **1**. This is probably a result of crystal packing forces as the DFT-derived vacuum geometry (Figure S9) indicates that the carbonyl oxygen lies closer to the thiophene plane for both molecules. The resulting greater conjugation in **1** should enhance stabilization of a negatively charged core in the solid state. Since such packing effects are not present in solution, the molecular geometry and, hence, the electronic structure/energetics are more similar, in agreement with MO computation and electrochemical data. Reorganization energies may also effect these mobilities.[1d,2f,4b]

Finally, polymer **3** forms high-quality films when spun-cast from xylene (Figure S10). In THF, **3** undergoes a reversible two-electron reduction at −1.23 V plus an additional irreversible reduction at −1.60 V and three single-electron oxidations at +0.96/+1.13 V (reversible) and +1.40 V. While spin-coated films of the neat polymer exhibit $\mu_e \sim 10^{-6}$ $cm^2 \cdot V^{-1} \cdot s^{-1}$ (optimization in progress), an initial study reveals that blends of **1** and **3** (500−1000 ppm, 1:1 weight ratio from xylenes) yield films with a μ_e of ~0.01 $cm^2 \cdot V^{-1} \cdot s^{-1}$ (I_{on}:I_{off} = 10^4; $V_T \sim 60$ V). Such blends are promising for OFET printing since the polymer adjusts solution rheology, while the molecular semiconductor enhances charge transport.

In summary, two new phenacyl molecular semiconductors were synthesized, crystal structures determined, and OFETs fabricated. **DFCO-4T** exhibits very high μ_e up to ~0.51 $cm^2 \cdot V^{-1} \cdot s^{-1}$ (vapor-deposited) and ~0.25 $cm^2 \cdot V^{-1} \cdot s^{-1}$ (solution-cast) − the latter being unprecedented for a solution-processed organic semiconductor. Any minor air instability can be addressed by core substitution as previously demonstrated.[1c] The corresponding polymer, **P(COFCO-4T)**, was synthesized, and blending **1** and **3** results in good n-type transistor behavior in solution-cast films. The new n-type materials developed in this work have solubility, processability, and performance comparable to or greater than the most studied solution-deposited p-type semiconductors (P3HT[2l] and F8T2[4d]), enabling ready integration into CMOS fabrication. Variable temperature and computational studies are in progress to fully understand this unique class of organic semiconductors.

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Supporting Information Available: 1−3 syntheses, spectroscopic data, crystal structures, and device fabrication details. This material is available free of charge via the Internet at http://pubs.acs.org.

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