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Poly(3,3″-dialkylterthiophene)s: Room-Temperature, Solution-Processed, High-Mobility Semiconductors for Organic Thin-Film Transistors

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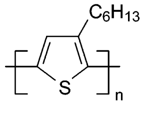
Organic thin film transistors (OTFTs) are potentially low-cost alternatives to amorphous hydrogenated silicon-based technologies for electronic applications,[1−7] particularly in devices where large-area formats and not high processing speeds are needed (e.g., active-matrix displays).[4,5] Organic semiconductors are solution processable, rendering their deposition via conventional low-cost liquid deposition techniques possible.[2,7,8] Organic materials such as polymers may also possess excellent flexibility characteristics, enabling fabrication on flexible substrates[4,6] (e.g., plastic sheets) to provide structurally flexible and mechanically robust electronic devices (e.g., e-paper). However, most solution processable organic semiconductor materials are either low-performing because of their inability to achieve proper structural orders from solution, or are prone to oxidative doping by atmospheric oxygen, which degrades performance. Those that are air-stable generally provide low field-effect transistor (FET) mobility due to their relatively wide band gaps and/or energetic mismatch with the electrode contacts. For example, regioregular head-to-tail poly(3-hexylthiophene), **1** (HT-P3HT), yielded poorer FET properties when processed in air[9] than in inert atmospheres[4]—a consequence of its sensitivity to atmospheric oxygen. On the other hand, the relatively air-stable poly(9,9′-dioctylfluorene-*co*-bithiophene) provided useful FET mobility only after very-high-temperature annealing.[10] Small organic semiconductor molecules such as short-chained oligothiophenes gave high mobility when vacuum-deposited, but yielded significantly lower mobility when fabricated from solution.[11] This was obviously due to their difficulties in forming quality films with desirable structural ordering from solution.



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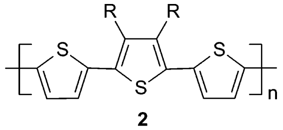

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Recently we demonstrated that proper control on the extended π-conjugation system of regioregular polythiophenes led to attainment of sufficient air stability to enable solution fabrication of functionally useful OTFTs under ambient conditions.[12] Specifically, polythiophene **2** afforded FET mobility similar to that of **1** when processed in air, but it exhibited much greater air stability by virtue of its shorter effective π-conjugation length. We now report that poly(3,3″-dialkyl-terthiophene), **3**, a regioisomer of **2**, achieved significantly higher FET mobility when solution-processed at room temperature without thermally assisted molecular organization. This is significant in that for most OTFTs with solution-processed semiconductors, functionally useful FET properties were achieved either via high-temperature in situ reactions[13] or through postdeposition thermal annealing.[7b,10]

Compound **3** differs from **2** only in the regiochemistry of alkyl side-chains. The "spaced-out" distribution of alkyl side-chains along the backbone of **3** has led to enhanced self-assembly ability. While **2** formed only 2-dimensional face-to-face $\pi-\pi$ stacks in thin films,[12] **3** readily self-assembled into a 3-dimensional lamellar π-stacking order when deposited from solution, a result of its extensive intermolecular side-chain interaction. Through poly(3,3″-di-*n*-octylterthiophene), **3a** (**3**, R = *n*-octyl), we demonstrate herein the critical influence of side-chain regiochemistry on self-assembly behavior, and the ensuing impact on FET performance. **3a** was prepared via a controlled $FeCl_3$-mediated polymerization in chlorobenzene instead of chloroform[14] to enable achievement of consistently well-defined, high-molecular-weight properties (Scheme 1). Specifically, the synthesis involved polymerization of 3,3″-dioctyl-2,2′:5′,2″-terthiophene **4a** (**4**, R = *n*-octyl) in the presence of excess anhydrous $FeCl_3$ in chlorobenzene at an elevated temperature under a dried atmosphere. After polymerization, the reaction mixture was processed accordingly and then extracted with

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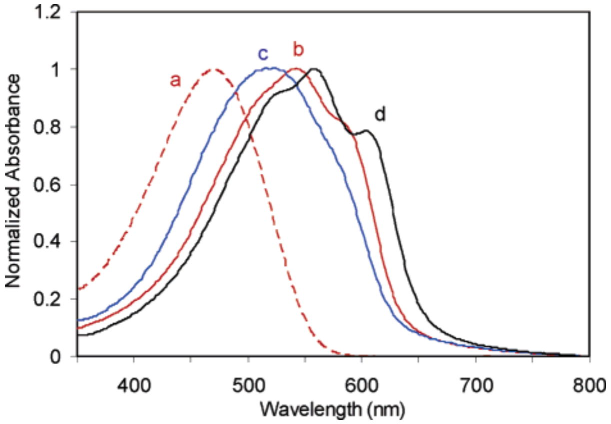
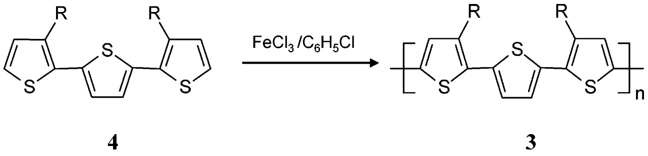


Figure 1. UV-vis spectral properties: (a) dilute solution of **3a** in dichlorobenzene; (b) thin film of **3a** showing vibronic splitting; (c) thin film of **2**; and (d) thin film of **1** showing vibronic splitting.

Scheme 1. Synthesis of Poly(3,3″-dialkyl-terthiophene) 3 via $FeCl_3$-mediated Oxidative Coupling Polymerization of 3,3″-dialkyl-2,2′:5′,2″-terthiophene 4



heptane and chlorobenzene to give electrically pure samples for OTFT fabrication. The sample of **3a** used in our experimental OTFTs had an M_n of 15 800 and M_w of 38 900, relative to polystyrene standards. Its differential scanning calorimeter thermogram showed a melting peak at 150 °C on heating and the corresponding crystallization peak at 97 °C on cooling.

The absorption spectrum of a dilute solution of **3a** in dichlorobenzene (Figure 1a) showed a broad absorption at λ_{max} ~470 nm, typical of a twisted polythiophene conformation. In thin films, the absorption was significantly red shifted with concomitant appearance of vibronic splitting at λ_{max} ~510 (shoulder), 540, and 583 nm (Figure 1b), manifesting a higher structural order in the solid state. The thin-film spectral properties of **3a** are essentially similar to those of **1** (Figure 1d) with a lamellar π-stacking structural order,[15] in sharp contrast to those of **2** (Figure 1c) which displayed indiscernible vibronic feature due to lack of lamellar ordering.

The structural order of **3a** in thin films was further established by X-ray diffraction (XRD) and transmission electron microscopic (TEM) studies. XRD of a thin film of **3a** deposited on an octyltrichlorosilane (OTS-8)-modified wafer showed distinctive diffraction peaks at $2\theta = 5.8°$ (100), 11.8° (200), and 17.8° (300), corresponding to *d* spacing of 15.1 Å (Figure 2a) for the interchain distance between two neighboring polythiophene chains within the lamellar structure. Lamellar structural orders of this type had earlier been observed in regioregular polythiophenes.[15] Since the *n*-octyl chain (~10 Å long) is tilted at ~50° against the backbone in the coplanar polythiophene conformation,[16] its vertical height from the center of the backbone would therefore be at least 8.5 Å. On this basis, the lamellar structure of **3a** is expected to involve some side-chain interdigitation as schematically represented in Figure 2c. TEM of a free-standing thin film of **3a** showed a diffraction corresponding to a face-to-face $\pi-\pi$ stacking distance of 4.0 Å (Figure 2b). This is wider than the normal value of 3.5−3.8 Å for the polythiophene $\pi-\pi$ stacking, thus reflecting the loosely packed lamellar π-stacking structure of **3a**. This was presumably due to the steric interference between the two octyl side-chains on the same repeating units of **3a**, twisting the substituted thienylene moieties slightly out of coplanarity and hindering the lamellar layers from packing closer together. The lamellar structures of **3a** also assumed a preferential orientation with their lamellar (100)-axes normal to the substrate, as revealed by the absence of a $\pi-\pi$ stacking XRD peak. This was a manifestation of the directional effects of OTS-8-modified surface chemistry on the orientation of lamellar structures of **3a**.

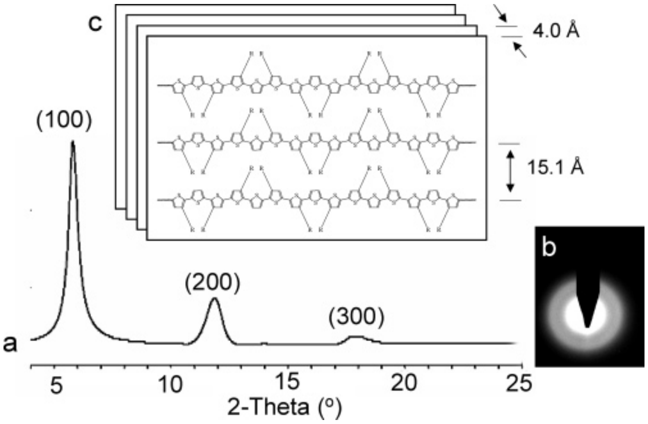


Figure 2. (a) XRD of thin film of **3a**, showing diffraction peaks at $2\theta =$ 5.8° (100), 11.8° (200), and 17.8° (300); (b) TEM of a free-standing film of **3a**, showing diffraction equivalent to a $\pi-\pi$ stacking distance of 4.0 Å; (c) schematic depiction of lamellar π-stacking structure of **3**.

The fabrication and characterization of OTFT devices were carried out under ambient conditions without any precautionary measures being taken to isolate the material and devices from exposure to ambient oxygen, moisture, or light. Bottom-gate, top-contact OTFTs were built on n-doped silicon wafer with a 100-nm thermal silicon oxide (SiO_2) dielectric layer. The silicon wafer was first cleaned with argon plasma, and then immersed in 0.1 M solution of OTS-8 in toluene at 60 °C for 20 min to modify the surface of the dielectric layer. The wafer was subsequently rinsed twice with toluene, rinsed once with 2-propanol, and then blown dry with an air stream. The semiconductor layer (~20−50 nm) was deposited on the OTS-8-modified SiO_2 surface by spin coating a 0.5 wt % solution of **3a** in chlorobenzene, and vacuum-dried. Subsequently, the gold source and drain electrodes were deposited by vacuum evaporation through a shadow mask, thus creating a series of experimental OTFTs with various channel lengths (*L*) and widths (*W*). Patterned transistors with channel length of 90 or 190 μm and channel width of 1 or 5 mm were used for studying their current−voltage charac-

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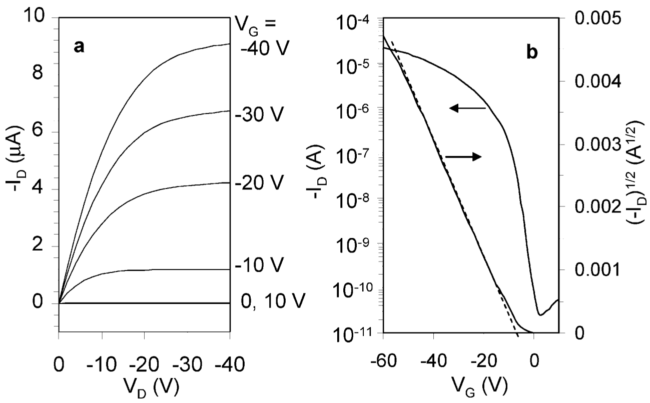

Figure 3. Output (a) and transfer (b) characteristics of a typical OTFT fabricated with **3a** as the semiconductor channel layer, with channel length of 90 μm and channel width of 5000 μm.

teristics. The mobility of OTFT devices in the saturated regime was then extracted from the following equation:

$$I_D = C_i\mu(W/2L)(V_G - V_T)^2$$

where I_D is the drain current, C_i is the capacitance per unit area of the gate dielectric layer, and V_G and V_T are, respectively, the gate voltage and threshold voltage. V_T of the device was determined from the relationship between the square root of I_D at the saturated regime, and V_G of the device was determined by extrapolating the measured data to $I_D = 0$.

All the OTFTs using **3a** exhibited near-ideal FET behaviors. The current−voltage characteristics conform well to the conventional transistor models in both the linear and saturated regimes (Figure 3). The output curves show no contact resistance and very good saturation behavior. The transfer curve in the saturated regime shows a near-quadratic increase of current as a function of gate bias, except for slight deviations at high voltages, which were likely due to bias stress effects. The devices switched on at around 0 V, with a sub-threshold slope of around 2−3 V dec^{-1}. Extracted mobility of up to 0.03 cm^2 V^{-1} s^{-1} was obtained, which is a factor of 3 better than those of corresponding devices with its isomeric form **2a** (**2**, R = *n*-octyl).[12a] The average mobility and current on/off ratio of **3a**-devices were, respectively, in the ranges of 0.015−0.022 cm^2 V^{-1} s^{-1} and 10^5−10^6. These are among the best properties reported for solution-processed OTFTs fabricated at room temperature in air without the temperature-assisted structural ordering. Thus, we have conclusively demonstrated the profound impact of side-chain regiochemistry of a poly(terthiophene) system on molecular ordering and thus on field-effect characteristics.

In addition, the OTFTs using **3a** as the channel semiconductor also exhibited much greater ambient stability as compared to those using other organic semiconductors such as HT-P3HT. The ambient stability of OTFT devices was monitored through the time dependence of their electrical characteristics. The device with **3a** generally provided a high initial on/off ratio of about 10^6 in magnitude, with no significant degradation in performance after prolonged exposure to air in the dark. The current on/off ratio decreased slightly to about 10^5 after 30 days. Conversely, the HT-P3HT-device exhibited a lower initial on/off ratio of about 10^5 and it essentially lost its FET activity with an on/off ratio of 10^2 in about 10 days under similar conditions.[12a] These results clearly attest to the enhanced air stability of **3a** as a channel semiconductor for OTFTs.

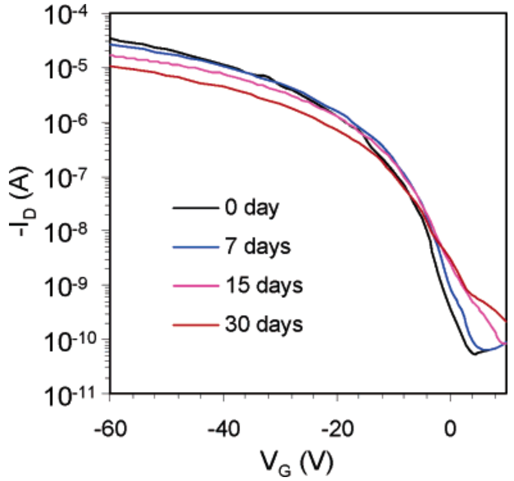

Figure 4. Transfer characteristics in the saturation regime of a typical **3a** OTFT as a function of time in the dark. The source-drain voltage is −60 V, L = 90 μm, W = 5000 μm.

In conclusion, we have shown that through proper control on the side-chain regiochemistry of a poly(terthiophene) system, excellent structural orders conducive to charge carrier transport can be established. The excellent self-organization ability in thin films from solution at room temperature without thermal assistance and its air stability may render poly(3,3″-dialkylterthiophene) an ideal channel semiconductor for low-cost OTFTs.

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Supporting Information Available: Details on instrumentation and characterization, and synthesis of the polymer (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

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