

Low-Temperature, Solution-Processed, High-Mobility Polymer Semiconductors for Thin-Film Transistors

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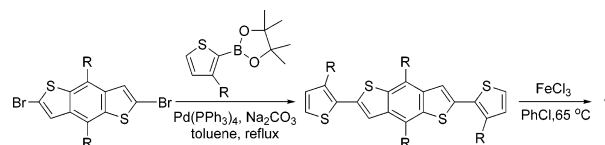
Solution-processable, high-mobility organic semiconductors are required for printing low-cost thin-film transistor (TFT) circuits via solution deposition/patterning processes. This has been widely perceived to be a potentially low-cost alternative to traditional silicon-based technologies to enable ubiquitous flexible electronics.^{1,2} In this regard, several solution-processable, functionally capable polymer semiconductors have been developed,^{3–5} but most, if not all, require postdeposition thermal annealing at above 100 °C in vacuum or an inert atmosphere to achieve high field-effect transistor (FET) mobility.^{4,5} Such a postdeposition annealing step is time-consuming, thus not amenable to high-speed roll-to-roll manufacturing processes for low-cost TFT circuits.

Two critical properties of solution-processed polymer semiconductors are needed to enable printing low-cost TFT circuits:^{2e,4a,5b} (1) an ability to self-organize into a higher structural order for efficient charge carrier transport; and (2) a sufficient stability to permit processing under ambient conditions without a costly protective environmental setup. Several recently reported regioregular polythiophene semiconductors, such as poly(3,3'-dido-decylquaterthiophene) (PQT-12) and analogous polythiophenes, appear to fulfill these requirements. Controlled effective π -conjugation has been employed to impart sufficient ambient stability to these polythiophenes for low-cost processing, while strategically placed long alkyl side-chain substituents have led to increased solution processability and efficient self-assembly via intermolecular interdigitation.^{4a,b} Nonetheless, to achieve higher structural orders via intermolecular interdigitation for improved FET performance, thermal annealing of these polymer thin-film semiconductors after deposition is still necessary.

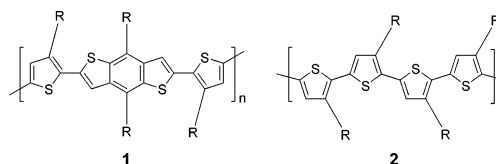
We report here a new solution-processable polythiophene semiconductor system, poly(4,8-dialkyl-2,6-bis(3-alkylthiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene) **1**, which exhibited high FET mobility in TFTs without postdeposition thermal annealing during fabrication. It would thus enable a high-throughput roll-to-roll mass manufacturing process for TFT circuits. The close proximity of alkyl side-chain substituents in **1a** (**1**, R = hexyl) is reminiscent of that of regioregular head-to-tail poly(3-hexylthiophene), P3HT **2a** (**2**, R = hexyl) in that efficient self-assembly could be achieved at room temperature via intermolecular end-to-end side-chain alignment.^{3d}

The synthesis of **1a** is described in Scheme 1 (see also Supporting Information). 4,8-Dihexyl-2,6-bis(3-hexylthiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene monomer was prepared by Suzuki coupling of 2,6-dibromo-4,8-dihexylbenzo[1,2-*b*:4,5-*b'*]dithiophene and 3-hexylthiophene-2-boronic acid pinacol ester in good yield. Subsequent ferric chloride-mediated oxidative coupling polymerization provided

Scheme 1. Synthesis of Poly(4,8-dialkyl-2,6-bis(3-alkylthiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene) **1** (**1a**: R = Hexyl)



1a in reasonable yield. GPC analysis gave a number-average molecular weight (M_n) of 16 300 with a polydispersity of 3.9 against polystyrene standards.



The UV-vis spectrum of **1a** in a warm 1,2-dichlorobenzene solution (~50 °C) showed a strong absorption with λ_{max} at 475 nm, which was similar to that of PQT-12 (λ_{max} = 480 nm) but was red-shifted from that of regioregular P3HT (**2a**, λ_{max} = 458 nm). Two new strong absorption peaks with λ_{max} at 533 and 581 nm appeared when the solution was cooled to room temperature, demonstrating attainment of higher structural orders at lower temperatures. A solution-cast thin film of **1a** displayed similar but broader absorption peaks, which were about 20 nm blue-shifted from those of regioregular P3HT, indicative of a shorter effective conjugation length of **1a** in the solid state. Cyclic voltammetric measurement of a thin film of **1a** provided an ionization potential which was 0.22 eV higher than that of regioregular P3HT, thus a greater stability against oxidative doping. DSC profile of **1a** showed a phase transition at 395 °C from backbone melting. The fact that only one thermal transition was observed was consistent with the absence of intermolecular side-chain interdigitation.

Two-dimensional grazing-incidence X-ray diffraction (GIXRD, incident X-ray angle of 2.5°) measurement (Figure 1a) of a spin-coated thin film (~100 nm) of **1a** from a 1,2-dichlorobenzene solution on an OTS-8-modified silicon wafer substrate showed only a strong primary diffraction pattern (100) at 2θ 5.6° (d -spacing of 16.1 Å; Figure 1c), demonstrating a well-organized lamellar layered structure which was oriented normal to the substrate.^{3b,6} The (010) diffraction from π - π stacking was not observed due to blockage by the substrate. The highly ordered structure of **1a** in thin films was unambiguously demonstrated via two-dimensional transmission X-ray diffraction of a stack of thin films of **1a**, as schematically depicted in Figure 1b. Figure 1d is the diffraction pattern obtained when the incident X-ray was normal to the film stack, showing both a strong π - π stacking (010) at 2θ 22.6° (d -spacing, 3.9 Å)

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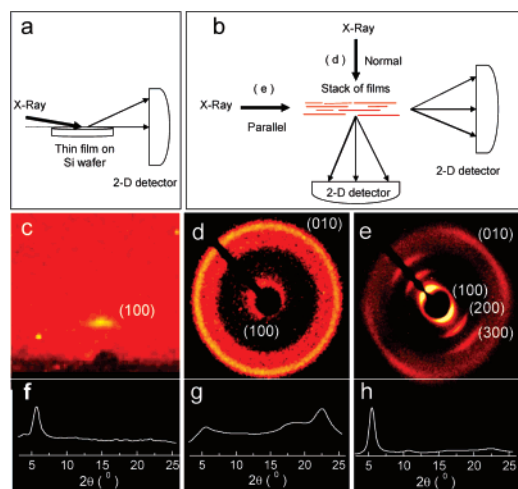


Figure 1. Schematic illustrations of 2-D GIXRD measurement (incident X-ray angle at 2.5°) of a thin film of **1a** (a) and 2-D transmission XRD measurement of a stack of thin films of **1a** (b); 2-D GIXRD images of a thin film of **1a** (c); 2-D transmission XRD images obtained with the incident X-ray normal (d) and parallel (e) to the film stack of **1a**; (f), (g), and (h) are respective XRD diffractograms of pattern intensities of (c), (d), and (e) [obtained by integration of Chi ($0-360^\circ$) with GADDS software].

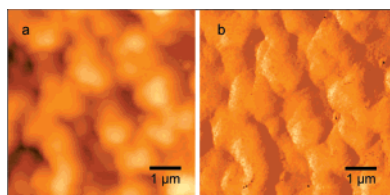


Figure 2. AFM images of an illustrative thin film of **1a**: (a) topography image; (b) phase image showing large domains of $1\ \mu\text{m}$ in width and $>1\ \mu\text{m}$ in length.

and a weak interlayer (100) diffraction. Strong (100), (200), (300), and (010) diffraction patterns were detected when the incident X-ray was parallel to the film stack (Figure 1e), showing the π - π stacking and interlayer diffraction patterns which were normal to each other. Accordingly, the molecular organization of **1a** in thin films was essentially similar to that of **2a**. The highly organized nature of **1a** in a solution-processed thin film was manifested by the formation of extraordinarily large domains of $\sim 1\ \mu\text{m}$ in width and $>1\ \mu\text{m}$ in length, in comparison to those of other polythiophenes,^{4c,5b} as visualized in the AFM images (Figure 2).

The FET properties of **1a** as a solution-processed thin-film semiconductor were evaluated using a bottom-gate, top-contact TFT configuration built on an n-doped silicon wafer with evaporated gold source/drain electrodes and OTS-8-modified SiO_2 gate dielectric (see Supporting Information). Figure 3 shows the typical output and transfer curves of a representative as-prepared TFT device without postdeposition thermal annealing. The output behaviors followed closely the metal oxide–semiconductor FET gradual channel model with very good saturation and no observable contact resistance. The transfer characteristics showed near-zero turn-on voltage, a small threshold voltage of $-5.9\ \text{V}$, and a sub-threshold slope of $\sim 2\ \text{V/decade}$. The device gave a saturation mobility of $0.15\text{--}0.25\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$ with a current on/off ratio of $10^5\text{--}10^6$ when measured in ambient conditions. Annealing at $100\text{--}150\ ^\circ\text{C}$ in vacuum did not lead to improved FET performance, in sharp contrast to the behaviors of most polymer thin-film semiconductors such as PQT and its analogues. The TFT devices using **1a** as the semiconductor also exhibited relatively stable performance over time as no significant degradation in mobility was observed

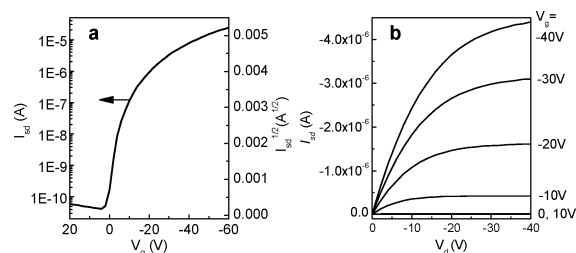


Figure 3. I - V characteristics of an illustrative as-prepared TFT device using **1a** semiconductor (channel length = $90\ \mu\text{m}$; channel width = $1000\ \mu\text{m}$): (a) transfer curve in saturated regime at a constant source-drain voltage of $-60\ \text{V}$ and square root of absolute value of drain current as a function of gate voltage; and (b) output curves at different gate voltages.

after standing over an extended period of time in an ambient environment at 20% relative humidity. In sharp contrast, the devices fabricated with **2a** under similar conditions displayed poorer performance and failed within a few days.^{4a,d} The mobility of the test device decreased slightly from 0.20 to about $0.16\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$ over a period of 30 days under these conditions.

In summary, we have designed a new solution-processable, high-mobility polythiophene semiconductor with enhanced stability for fabrication of low-cost TFTs. Of particular significance is that this semiconductor exhibited high FET mobility even without the usual time-consuming postdeposition thermal annealing step, thus potentially enabling high-throughput, roll-to-roll mass manufacturing processes for TFT circuits. In addition, recent progress in structural optimization has led to greatly improved mobility of $\sim 0.4\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$.

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Supporting Information Available: Instrumentation, details of experimental procedures, and additional figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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