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Communications

High-Performance Thin-Film Transistors from Solution-Processed Dithienothiophene Polymer Semiconductor Nanoparticles

Jun Li,[†,‡] Fang Qin,[†] Chang Ming Li,*[,†] Qiaoliang Bao,[†] Mary B. Chan-Park,[†] Wei Zhang,[‡] Jingui Qin,[‡] and Beng S. Ong*[,§]

*School of Chemical & Biomedical Engineering and School of Material Science & Engineering, Nanyang Technological University, 637457 Singapore, Department of Chemistry, Hubei Key Lab on Organic and Polymeric Optoelectronic Materials, Wuhan University, Wuhan 430072, P.R. China, and Institute of Materials Research & Engineering (IMRE), A*STAR, 117602, Singapore*

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Organic thin-film transistors (OTFTs) have received great interest as a promising alternative to amorphous hydrogenated silicon transistors for applications in a large area and flexible electronics.[1–5] The primary driving force is the expectation that OTFT devices can be fabricated using simple solution deposition/patterning processes for significantly lower manufacturing cost. Special attention has thus been devoted to polymer semiconductors in view of their easy solution processability and good film-forming property, as compared to low molecular weight organic molecular compounds, which generally require vacuum fabrication techniques.[6–8] However, most current polymer semiconductors either have low mobility or are prone to photo-oxidative doping/bleaching, yielding poorer performance in air than in inert atmosphere.[9,10] Only very few polymer semiconductors have demonstrated good transistor characteristics (mobility $\geq$ 0.1 cm^2/(V s) and on/off ratio $\geq 10^5$) and environmental stability.[11–18] Accordingly, new functionally capable polymer semiconductors that can be solution processed at low temperatures for OTFTs are of great interest.

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* Coresponding authors. E-mail: ecmli@ntu.edu.sg (C.M.L.); ongb@imre.a-star.edu.sg (B.S.O.).

[†] Nanyang Technological University.

[‡] Wuhan University.

[§] A*STAR.

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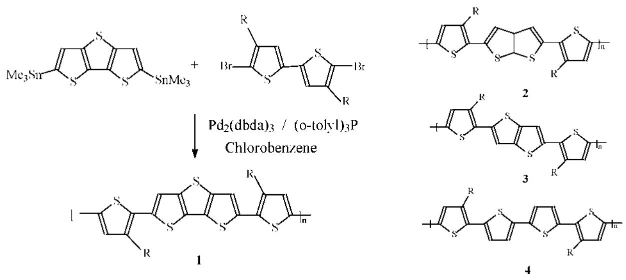
Scheme 1. Synthesis of PBTDT, 1, and Structures of Representative High-Mobility Semiconductor Polymers



While dithieno[3,2-*b*:2′,3′-*d*]thiophene (DDT)-based small molecules have been studied and shown high field-effect transistor (FET) characteristics (mobility ~ 0.42 cm^2/(V s); current on/off ratio ~ 10^8) as vacuum evaporated thin-film semiconductors,[19,20] the corresponding polymers have not been explored for OTFT applications, presumably as a result of their poor solubility.[21–23] In this communication, we describe the synthesis and characterization of a new DTT-based copolymer, poly(2,6-bis(3-alkylthiophen-2-yl)dithieno-[3,2-*b*;2′,3′-*d*]thiophene) (PBTDT) **1**, as an excellent solution-processed semiconductor for OTFTs. Structurally, PBTDT may vaguely be reminiscent of thienothiophene polymer semiconductors **2** and **3**,[16,17] which display profoundly different FET mobility by as much as one order of magnitude (10^{-2} vs 10^{-1} cm^2/(V s)) even though they are structural fused-ring derivatives of PQT **4**.[11] This is primarily the result of different thienothiophene regiochemistry that critically impacts the stereoarrangement of pendant alkyl side chains along the backbone, thus, the efficacy of self-assembly. We show herein that our new polymer **1**, which incorporates a dithienothiophene moiety, not only offers high FET mobility but also other equally important processing and performance attributes including room-temperature processability in environmentally friendlier nonchlorinated solvents. High-mobility polymer semiconductors for OTFTs such as **3** require processing in toxic chlorinated solvents at high temperatures to avoid solution gelling complications during device fabrication.

Copolymer **1** is prepared by Stille coupling polymerization of 2,6-bis-trimethyl-stannanyl-dithieno[3,2-*b*;2′,3′-*d*]thiophene with 5,5′-dibromo-4,4′-dialkyl-[2,2′]bithiophene in good yields (Scheme 1). It is purified by sequential Soxhlet extraction with hexane and then ethanol (see Supporting Information). It is soluble in THF, $CHCl_3$, chlorobenzene, and so forth. Gel-permeation chromatography analysis of PBTDT-12 (**1a**, R = *n*-$C_{12}H_{25}$) in THF solution shows a number-average molecular weight of 7900 with a polydispersity (M_w/M_n) of 1.3 against polystyrene standards. The differential scanning calorimetry thermogram of **1a** does not reveal any obvious phase transitions between 25 and 300 °C.

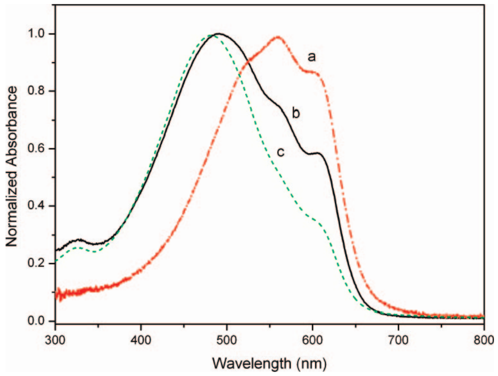


Figure 1. UV–vis absorption spectra of PBTDT-12, **1a**: Trace (a): as-cast thin film (red dashed dotted line); (b) dilute solution in chlorobenzene at 25 °C (black solid line); and (c) dilute hot solution in chlorobenzene above 60 °C (green dashed line).

The UV–vis spectrum of a dilute solution of **1a** in chlorobenzene shows absorption peaks at λ_{max} = 489, 558, and 605 nm with distinct vibronic splitting (Figure 1). The spectral absorptions of a thin film of **1a** are slightly red-shifted with well-defined vibronic splitting at λ_{max} = 520, 558, and 605 nm, reflecting a higher structural ordering in the thin film. The similarity of absorption patterns between the thin-film and the solution spectra suggests that the polymer solution contains a structurally well-organized molecular system. Light-scattering measurements reveal that the solution is a suspension of nanoparticles in chlorobenzene with particle sizes around 90 nm. Atomic force microscopy images of a spin-coated thin film with **1a** before annealing also illustrate that the nanoparticles distribute separately but uniformly in the thin film (Figure S1, Supporting Information). A similar UV–vis absorption phenomenon has been observed with PQT-12.[11,24] However, the nanoparticle suspension of **1a** is far more stable. Specifically, when the dilute suspension of **1a** is heated above 60 °C, its absorption spectrum still retains the vibronic splitting characteristic, and no gelation occurs when the solution is cooled down to room temperature. The solution of polymer semiconductor **3** in dichlorobenzene gels readily; it thus has to be processed in hot solution during device fabrication.[17] The stability of nanoparticles suspension of **1a** renders it an appealing semiconductor candidate for OTFTs as this would potentially enable room-temperature OTFT array/circuit mass-manufacturing process using common printing techniques (e.g., gravure, inkjet).

Cyclic voltammetric measurements of a thin film of **1a** in 0.1 M Bu_4PF6/CH_3CN solution show a multielectron transfer process in the oxidative state (Figure S2, Supporting Information) with an onset oxidation potential (HOMO level) at about 5.14 eV, indicating a great stability against oxidative doping.

The X-ray diffraction (XRD) patterns of **1a** under various processing conditions are shown in Figure 2. A powdered

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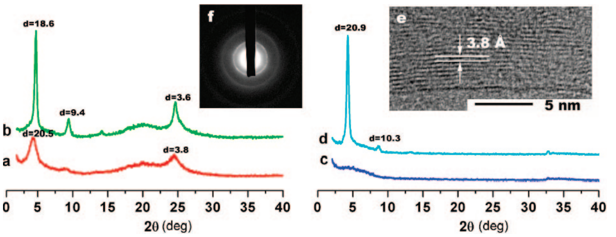

Figure 2. XRD spectra of PBTDT-12, **1a**: (a) powder pellet at room temperature; (b) powder pellet annealed at 160 °C; (c) thin film at room temperature; (d) thin film annealed at 160 °C; (e) HRTEM image of crystalline domains in a thin film on carbon grid; and (f) selected-area electron diffraction of a thin film on carbon grid.

sample of **1a** exhibits two diffractions at $2\theta = 4.3$ and 24.4°, corresponding respectively to an interchain d-spacing of 20.5 Å and a $\pi-\pi$ stacking distance of 3.8 Å. When the powdered sample is annealed at 160 °C, a more distinctive, highly crystalline XRD pattern is observed. However, the XRD pattern of an as-cast thin film of **1a** in chlorobenzene on an octyltrichlorosilane-modified silicon wafer substrate is featureless until annealing at 160 °C. The annealed thin film shows high crystallinity with a strong primary diffraction peak at $2\theta = 4.2°$ and second order peak at 8.6°, which corresponds to an interchain distance of 20.9 Å. Conspicuously absent in the annealed thin film is the prominent $\pi-\pi$ stacking peak of the annealed powdered sample at $2\theta = 24.4°$. This indicates that annealing leads to formation of lamellar $\pi-\pi$ stacks which are oriented normal to the substrate.[9] The high-resolution transmission electron microscopy (HRTEM) image (Figure 2e) clearly shows the crystal lattices of **1a** domains, where the (020) fringes have a d-spacing of 3.8 Å, corresponding to the face-to-face $\pi-\pi$ stacking distance. Electron diffraction analysis (Figure 2f) also confirms a $\pi-\pi$ stacking distance of 3.8 Å.

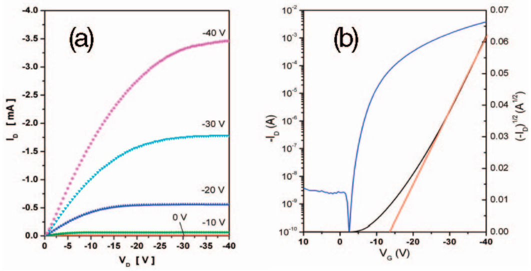

Figure 3. $I-V$ characteristics of an illustrative TFT device using PBTDT-12, **1a** semiconductor: (a) output curves at different gate voltages; (b) transfer curve in saturated regime at constant source−drain voltage of –40 V and square root of the absolute value of the drain current as a function of gate voltage.

Bottom-gate, bottom-contact TFT devices were fabricated using **1a** in chlorobenzene as a dip-coated thin-film semiconductor. The devices were built on an n-doped silicon wafer with octyltrichlorosilane-modified SiO_2 gate dielectric and octylthiol-modified gold source/drain electrodes. The fabrication and characterization of OTFTs are carried out under ambient conditions without taking precautionary measures to isolate the material and devices from exposure to ambient oxygen, moisture, or light. Figure 3 exhibits a characteristic p-type FET behavior of a representative OTFT device after annealing at 160 °C. The output characteristics display very good saturation behavior with no obvious contact resistance. The saturation current is ∼3.5 mA at the gate and the source−drain voltages of –40 V. The transfer characteristics show a near-zero turn-on voltage and a threshold voltage of –14.2 V. The mobility extracted from the saturated regimes is as high as 0.3 $cm^2/(V\ s)$ with a very high current on/off ratio of over 10^7. More importantly, we have found that **1a** can also be processed in environmentally friendly hydrocarbon solvents such as hexane, heptane, and higher homologues with particle sizes around 500 nm, and such fabricated TFT devices still retain high FET performance characteristics (e.g., mobility ∼ 0.17 $cm^2/(V\ s)$; on/off ratio ∼ 10^6), in sharp contrast to most high-mobility polymer semiconductors that have to be processed in toxic solvents (e.g., chlorinated solvents).[11–18] We believe that the FET performance of this class of polymer semiconductors can be further improved through material and device optimizations.

In conclusion, we have developed a new class of solution-processable polymer semiconductors (PBTDT) through rational molecular design to achieve good solution processability, efficient self-assembly, greater ambient stability, and excellent transistor properties. This class of polymer semiconductors has exhibited high FET mobility and current on/off ratio in TFT devices fabricated entirely under ambient conditions. These performance characteristics certainly represent the current benchmark FET properties achieved by a solution-processed polymer semiconductor at room temperature under ambient conditions without precautionary measures in excluding oxygen, light, and moisture during device fabrication and characterization.

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Supporting Information Available: Experimental procedures, cyclic voltammetry measurement, detailed information about the fabrication and measurement of TFTs (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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