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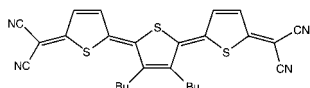
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A π -Stacking Terthiophene-Based Quinodimethane Is an n-Channel Conductor in a Thin Film TransistorTed M. Pappenfus,[†] Reid J. Chesterfield,[‡] C. Daniel Frisbie,^{*,‡} Kent R. Mann,^{*,†} Juan Casado,^{†,§} Jonathan D. Raff,[†] and Larry L. Miller[†]*Departments of Chemistry, Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455 and Departamento de Química Física, Facultad de Ciencias, Universidad de Málaga, 29071-Málaga, Spain*

Received January 9, 2002

An important goal for organic electronics is the synthesis of organic semiconductors with improved performance in thin film transistors (TFTs).¹ This design process should take into account both molecular properties, such as reduction/oxidation potentials, and solid-state crystal packing to achieve materials with enhanced transport properties. Here we report the single-crystal X-ray structure and TFT results for a novel quinodimethane-substituted terthiophene oligomer, compound **1**.



Molecules of **1** have quinoidal character, display reversible electrochemical reduction and oxidation in solution, and form π -stacks in the solid state. The ease of reduction and the π -stacking suggested that polycrystalline films of **1** might be good thin film n-channel conductors in TFTs. There are currently few organic semiconductors that function as good n-channel conductors,² for example, α,ω -diperfluorohexylsexithiophene,^{2f} naphthalenetetracarboxylic diimide,^{2g} and copper fluorophthalocyanine;^{2h} most organic semiconductors show only p-channel conductivity in TFTs. The development of both n- and p-channel materials is important for circuit design because it allows for a broader variety of circuit architectures.³

Compound **1** was prepared from 3',4'-dibutyl-5,5''-dibromoterthiophene using malononitrile and sodium hydride in a Pd-catalyzed coupling, followed by oxidation with Br₂ (see Supporting Information). The product was purified chromatographically and characterized by ¹H NMR and high-resolution mass spectrometry. Cyclic voltammetry experiments were conducted using an Ag/AgCl reference and a glassy carbon working electrode in 0.1 M Bu₄NPF₆/CH₂Cl₂ solution. The voltammograms for **1** showed a reversible one-electron oxidation ($E^\circ = +1.27$ V) and a reversible two-electron reduction ($E^\circ = -0.15$ V). Reversible two-electron reductions have been reported for such compounds,⁴ but reversible oxidations have not.

Single crystals of **1** ($(P2_1/c)$, $a = 16.42$ Å, $b = 7.55$ Å, $c = 21.17$ Å, $\beta = 111.37^\circ$) were grown by slow evaporation of solvent from an acetone/heptane solution. The crystal structure obtained at 173 K, shown in Figure 1, reveals that except for the butyl groups all the atoms in one molecule are in the same plane, that the sulfur

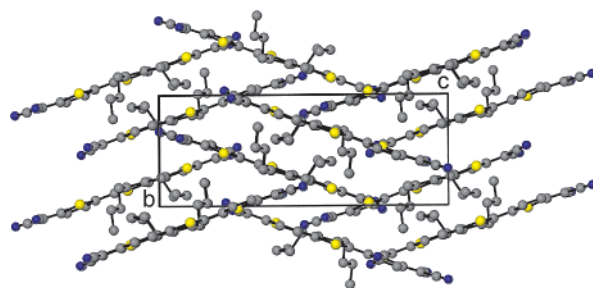


Figure 1. Packing view along the a -axis of **1** (hydrogen atoms omitted).

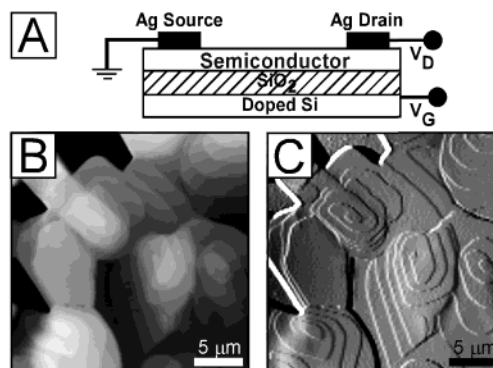


Figure 2. (A) Scheme of a thin film transistor. (B) AFM topographic image (tapping mode) of a thin film of **1** vacuum evaporated onto an SiO₂(300 nm)/Si substrate. The height range varies from 0 (dark) to 150 nm (light). (C) Tip amplitude image taken simultaneously with (B).

atoms in adjacent rings are transoid, and that the molecules form face-to-face slipped π -stacks. The stacks contain π -dimers, and the intermolecular face-to-face distance is alternately 3.47 and 3.63 Å. These stacks are packed in alternating columns that are twisted at an angle of 39.4° from each other.

TFTs were fabricated with the geometry shown in Figure 2A. Compound **1** was thermally evaporated at 230 °C and 1×10^{-6} Torr onto an SiO₂(300 nm)/Si substrate held at 130 °C. After **1** was annealed at 130 °C in a vacuum for 15 min, optical microscopy and atomic force microscopy (AFM) revealed a polycrystalline thin film with grains as large as 10 μ m. AFM images (Figure 2, B and C) show grains of terraced islands with step heights of 17–19 Å. X-ray diffraction (XRD) of the thin film on SiO₂ exhibited a d spacing of 17.8 Å. These dimensions do not correspond directly with either the a -, b -, or c -axes of the single-crystal unit cell. However, 17.8 Å does correspond to the height of π -dimers oriented with the long axis of the molecules tilted 25.3° with respect to the surface normal. The AFM and XRD suggest that the films are a

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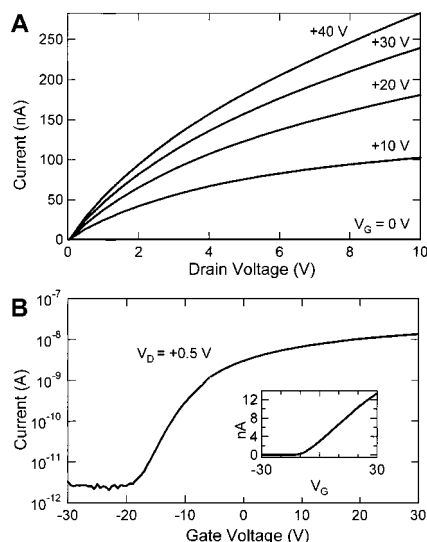


Figure 3. (A) Source-drain current (I_D) versus drain voltage (V_D) for a TFT-based on **1**. (B) Semilog plot of I_D versus V_G for a drain voltage $V_D = +0.5$ V. Inset shows a linear plot of I_D versus V_G , which was used to determine the threshold voltage, V_T .

crystalline polymorph with the π -stacking direction parallel to the SiO_2 substrate, which should optimize electrical transport between source and drain contacts in a TFT.

The TFT structure was completed by evaporating the Ag source and drain electrodes through a shadow mask onto the thin film of **1**. A typical device had a source-drain channel length of 10 μm , with a width of 600 μm , and a semiconductor thickness of 50 nm. To improve electrical performance, devices were annealed in a flowing stream of hydrogen gas at 60 $^\circ\text{C}$ for an hour. Figure 3A shows source-drain current (I_D) versus drain voltage (V_D) at various gate voltages (V_G). Figure 3B shows I_D versus V_G at a V_D of 0.5 V. It is evident from Figure 3, A and B, that the channel conductance increases as V_G becomes more positive, meaning the film is an n-channel conductor.

Scanning V_G to negative values decreased the channel conductance; beyond $V_G = -20$ V I_D equilibrated at 3×10^{-12} A (Figure 3B). Formation of a p-channel was not observed even for V_G as large as -100 V. The V_G dependence of the channel conductance is consistent with the solution cyclic voltammetry that indicates **1** undergoes reversible reduction at relatively small (negative) potentials. TFT mobility (or field effect mobility, μ_{FET}) and threshold voltage (V_T) were extracted from the low- V_D linear region of the curves in Figure 3A.⁵ Mobility was measured as high as $0.005 \text{ cm}^2/\text{Vs}$ in some devices with typical thresholds of -11 V. This mobility is within an order of magnitude of the best n-channel field effect mobilities that have been reported.^{2g,h} The negative V_T indicates that at $V_G = 0$ there are free carriers in the film.

We have observed that V_T becomes more negative upon prolonged exposure of thin films of **1** to air, suggesting that the films become chemically modified. Annealing the TFT in H_2 returns V_T to its original value. We expect that characterization of these devices under inert atmosphere will result in stable V_T values and improved mobility.

Soluble organic semiconductors are attractive because they afford opportunities for solution processing of TFTs.^{2g} The butyl side chains give **1** significant solubility ($> 1 \text{ mg/mL}$) in tetrahydrofuran, acetone, and chlorobenzene. Thin films of **1** cast from chlorobenzene onto SiO_2 substrates showed a field effect mobility as high as $0.002 \text{ cm}^2/\text{Vs}$ in some TFT devices but V_T was very large (-60 V). Significant improvement in device performance is anticipated with improvement in casting methods, and upon characterization in an inert atmosphere.

In summary, a polycrystalline film of **1** functions as an n-channel semiconductor in a TFT. Electron field effect mobility in vapor- and solution-deposited films is 0.005 and $0.002 \text{ cm}^2/\text{Vs}$, respectively. The observation of n-channel conduction and the absence of p-channel conduction corresponds with the finding that **1** is easier to reduce than to oxidize. These results suggest that analogues of **1** with more thiophene rings will be easier to oxidize in solution and will provide ambipolar transport (p- and n-channel conductance). Experiments are underway to test this hypothesis.

Acknowledgment. K.R.M. thanks the NSF for support. C.D.F. thanks the Packard Foundation and the NSF-funded Materials Research Science and Engineering Center at UMN for financial support. R.J.C. thanks the NSF Graduate Research Fellowship Program. J.C. thanks the Ministerio de Educacion y Cultura of Spain for a Postdoctoral Fellowship (PF00 25327895).

Supporting Information Available: Synthesis and characterization information for **1** (PDF). X-ray crystallographic files in CIF format for **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA025553J