

Dicyanomethylene-Substituted Fused Tetrathienoquinoid for High-Performance, Ambient-Stable, Solution-Processable n-Channel Organic Thin-Film Transistors.

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 Supporting Information

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N-channel organic semiconductors (OSCs) have received great attention because of their important roles in organic p-n junctions, bipolar transistors and complementary logic circuits.¹ For commercial applications, n-channel semiconductors must meet the following requirements: (i) high mobility (e.g., $\mu_e > 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) to provide sufficiently large drive currents in the circuits; (ii) solution processability to allow for cost-effective deposition methods; and (iii) ambient stability to eliminate encapsulation. Although great progress in OSC have been made recently, the overall performance of n-channel OSCs still lags behind their p-channel counterparts. Indeed, n-channel OSCs with all of the above-described features are still rare (most n-channel OSCs with high electron mobilities are vacuum deposited and/or unstable in ambient conditions).² Therefore, the discovery of high-performance, solution-processable, and ambient-stable n-channel material is crucial for the development of organic electronics.

Dicyanomethylene-substituted quinoidal compounds are superior electron acceptors and have low-lying lowest unoccupied molecular orbital (LUMO) energy levels, which make them good candidates for n-channel organic semiconductors.³ Recently, the charge transport properties of dicyanomethylene-substituted quinoidal oligothiophenes have been studied, and some of them displayed promising device performance.⁴ To date, the highest electron mobility of dicyanomethylene-substituted quinoidal oligothiophenes was $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This system is based on vacuum-deposited transistors and was reported by Frisbie and co-workers.^{4e} For solution-processed transistors, the highest electron mobility reached $0.16 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (in ambient condition, after annealing the film at 150°C), which was recorded by Takimiya and co-workers.^{4f} However, isomers in the oligothienoquinoid were observed, and the electron mobility decreased from $0.16 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ after storing in plastic boxes under ambient conditions for two months.^{4f}

Compared with quinoidal oligothiophenes, the dicyanomethylene-substituted fused thienoquinoids not only share the merits of quinoidal oligothiophenes but also enhance the intermolecular interactions and eliminate the problem of isomerism,⁵ which are very likely to be a class of excellent n-channel organic semiconductors. Unfortunately, up to now, their syntheses and applications as n-channel OFETs materials have been rarely studied.⁶

Very recently, Takimiya et al. explored the charge transport properties of ((alkyloxy)carbonyl)cyanomethylene-substituted quinoids of fused thiophenes (thieno[3,2-b]thiophene (TT), dithieno[3,2-b;2',3'-d]thiophene (DTT) and benzothieno[1,2-b;4,5-b']dithiophene (BDT)). Electron mobility as high as $0.012 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was obtained based on a solution-processed BDT derivative in ambient conditions.⁷ In this communication, we reported the synthesis and charge transport property of dicyanomethylene-substituted fused tetrathienoquinoid **1**. An electron mobility as high as $0.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was observed based on the solution-processed thin film of **1** in ambient conditions without post-treatment. To the best of our knowledge, this electron mobility is one of the highest values for solution-processed n-channel OTFTs tested in ambient conditions.

The chemical structure and synthetic route of **1** was shown in scheme 1. In compound **1**, 3-hexylundecyl alkyl chains were introduced to increase the solubility and minimize the negative effect of side alkyl chains on the self-assembly property. Compound **1** was prepared from dibromotetrathienoacene precursors through a Pd-catalyzed Takahashi coupling reaction, followed by oxidation with bromine, and was isolated as green solid (Scheme 1). The chemical structure of **1** was characterized by NMR, MS and elementary analysis. As expected, compound **1** is highly soluble in chloroform, chlorobenzene and dichlorobenzene (solubility $>10 \text{ mg/mL}$), and it crystallizes readily from the saturated solutions. The good solubility of compound **1** laid a foundation for the fabrication of devices with solution processing.

Solution cyclic voltammetry (CV) revealed two reversible reductions in CH_2Cl_2 for compound **1** with the first half-wave potential ($E_{1/2}^{-1}$) at -0.10 V (Figure 1a). The LUMO energy level calculated from CV was -4.3 eV ($E_{\text{LUMO}} = -(E_{1/2}^{-1} + 4.4) \text{ eV}$),^{2b} similar to that of dicyanomethylene-substituted quinoidal oligothiophenes.⁴ Figure 1b illustrates the absorption spectra of **1** in solution and on thin film. The optical energy gaps (E_g^{opt}) was 1.8 eV as estimated from the onset of absorption in solution. The UV-vis spectrum of the film exhibited a strong absorption band at $\lambda_{\text{max}} = 565 \text{ nm}$, a large blue shift compared with that of

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Scheme 1. Synthetic Route of Compound 1

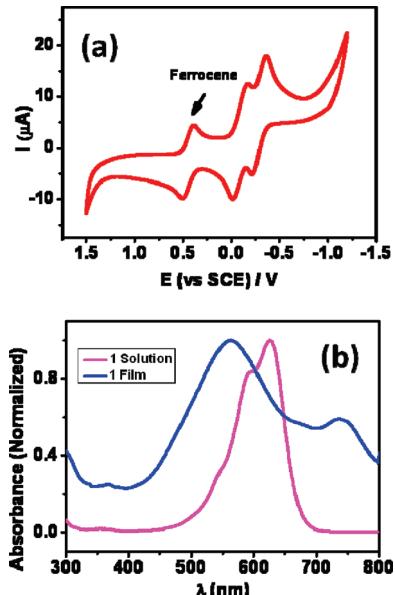
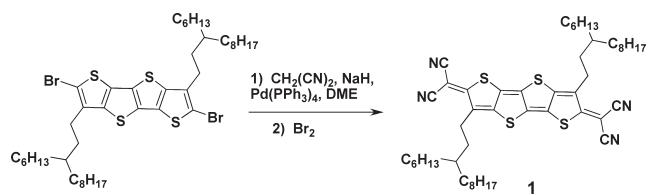


Figure 1. (a) Cyclic voltammogram of compound 1 (0.001 mol/L in CH_2Cl_2 , 0.1 mmol/L Bu_4NPF_6 as electrolyte, scan rate 50 mV/s, SCE as the reference electrode) by using ferrocene as internal standard. (b) UV-vis absorption spectra of compound 1 in dichloromethane solution (1×10^{-6} mol/L) and on thin film (quartz substrate).

solution. In addition, a small absorption peak centered at 736 nm was also observed, which is a typical feature of Davydow splitting. The absorption spectrum of 1 film suggested that 1 exhibits H-type molecular aggregation in film.⁸

The charge transport property of 1 was investigated by solution processed thin film transistors (TFTs). Thin films of 1 were prepared by drop casting a chlorobenzene solution (5 mg/mL) of 1 on octadecyltrichlorosilane (OTS)-treated SiO_2/Si wafers.^{4f} The Au source and drain electrodes were deposited through a shadow mask by vacuum evaporation. The gate is n-type heavily doped Si. A thermally grown SiO_2 layer of 300 nm (the specific capacitance was measured to be 10 nF cm^{-2}) was used as the dielectric layer. The devices had a channel length of $31 \mu\text{m}$ and a width of $273 \mu\text{m}$. All of the devices were fabricated and tested in ambient condition. Compound 1 displayed typical n-channel characteristics. Figure 2 displays a typical output and transfer curves of the devices. We observed a pronounced nonlinear onset in the output-curves at low drain voltage, which was mainly due to the contact resistances between the metal electrodes and the organic semiconductor layer. The field-effect mobility of electrons (μ_e) was calculated by fitting a straight line to the plot of the square root of I_{DS} vs V_G (saturation region), according to the expression $I_{\text{DS}} = (W/2L)\mu_e C_i(V_G - V_{\text{TH}})^2$. The average mobility of the total 54

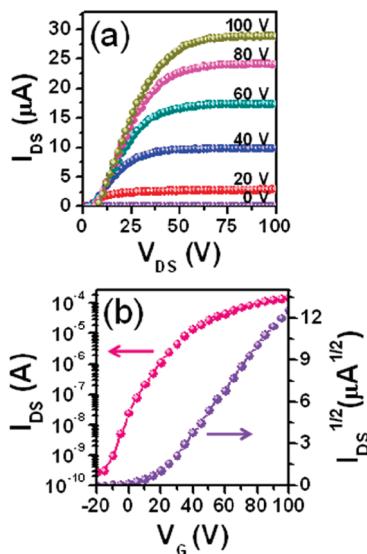


Figure 2. Current-voltage characteristics of the device based on solution-casted thin films of compound 1 without post-treatment. The device was tested in ambient air. (a) Output characteristics (the gate voltage was biased from 0 to 100 V with a step of 20 V from bottom to top of the curves); (b) transfer characteristics ($V_{\text{DS}} = 100$ V).

devices was $0.43 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and the highest value reached $0.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The current on/off ratios were about 1×10^5 . To the best of our knowledge, this electron mobility was one of the highest values among solution-processed, n-channel organic thin film transistors tested in ambient conditions.

Figure 3a shows the optical microscopic images of the casted thin film of 1. Atomic force microscopy (AFM) measurements on the surfaces of the film at random areas revealed that a large part of the film was atomically flat (rms=0.131 nm along the line shown in Figure 3b). Terrace structures with identical heights of about 2.0 nm were also found on some part of the surfaces (Figure 3c,d). Such surface steps are usually found on highly crystallized thin films and single crystals,^{4d,9,10} indicating the high crystallinity of the films. Figure 3e illustrates the XRD result of thin films. The d -spacing determined from the dominant peak was 2.446 nm, close to the simulated molecular length (2.2 nm, see the Supporting Information). Combining with the step height determined from AFM result, we proposed molecules 1 adopted a nearly perpendicular orientation on the substrate in the film. We believe the high-quality of the thin film and the orientation of 1 in film are response for the high mobility of transistors.

It is well-known that post-treatment such as thermal or solvent annealing can increase the crystallinity of the film and ultimately increase the device performance.^{2b,4d,4f,11} As for 1, it should be noted the high electron mobility was obtained without any post-treatment, which meets the requirement of a low-temperature process for organic electronics and facilitates device fabrication.

In addition to high electron mobility, the devices exhibited good stability (especially ambient stability), which is another important index for commercial applications. We assessed the stability of the devices by two methods. One is the stability under continuous working conditions, in which the devices were tested by sweeping the gate voltage from 0 to 100 V and back to 0 V for 100 circles (the drain voltage was stabilized at 100 V). The I - V curves showed good repeatability with the maximum current fluctuating less than

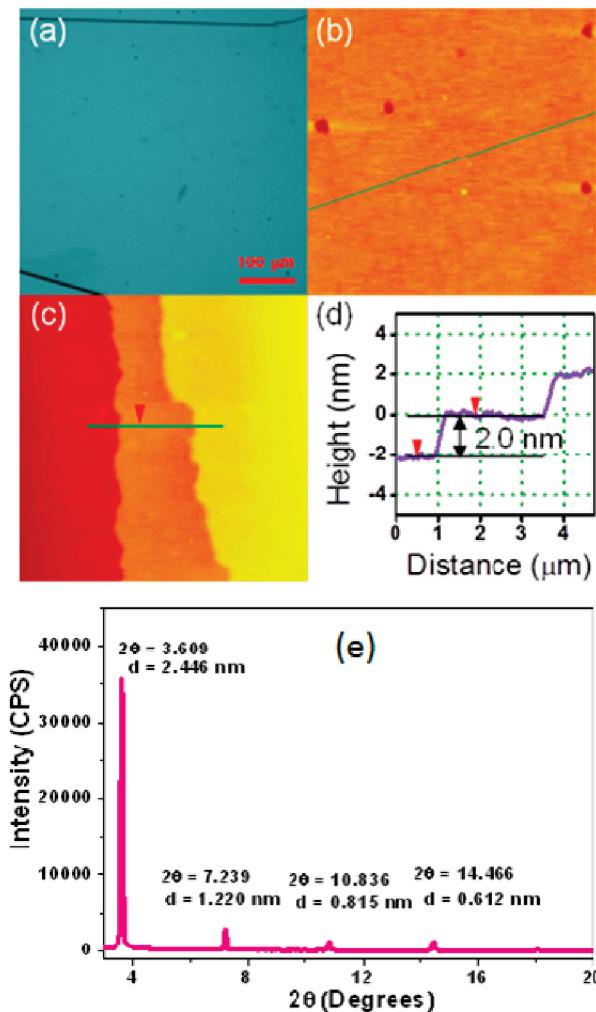


Figure 3. Morphologies and XRD results of the solution-casted films of compound 1. (a) Optical microscopic image; (b) tapping-mode AFM image of a flat area (15 by 15 μm , rms = 0.131 nm along the marked line); (c) AFM images of an area with terrace structures (30 by 30 μm); (d) cross-section analysis of the line marked in c, the height of a single step is about 2.0 nm; (e) the XRD result with d -spacing.

4.5% throughout the measurement (see the Supporting Information). The other is the long-term stability. The electron mobility of transistor was still above $0.18 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ after storage in ambient air for 12 weeks (see the Supporting Information).

In conclusion, the synthesis and electron transport property of a new type of n-channel OSCs dicyanomethylene-substituted fused tetrathienoquinoid were reported. Thin film transistors based on annealing-free, solution-casted films of **1** displayed high stability and high performance with an electron mobility up to $0.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in ambient conditions. The excellent performance of **1** indicated that dicyanomethylene-substituted fused tetrathienoquinoid semiconductors might be a new class of electron-transporting material and have great potential for applications in organic electronics.

ASSOCIATED CONTENT

5 Supporting Information. Experimental details of synthesis of **1**, device fabrication, and characterization. This materials available free of charge via the Internet at <http://pubs.acs.org>.

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