Synthesis and Solution-processed Field Effect Transistors of Liquid Crystalline Oligothiophenes

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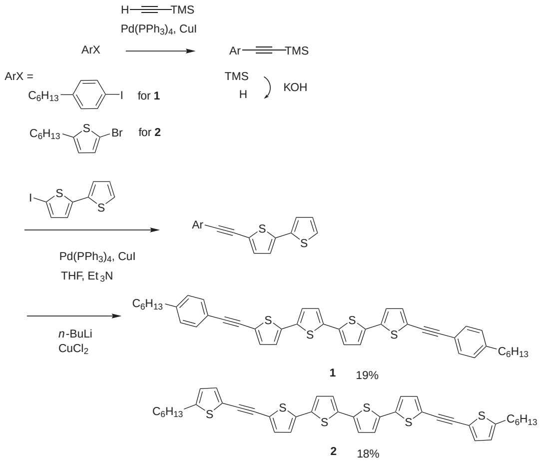
An organic field-effect transistor (OFET), showing a mobility 0.015 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ and an on/off ratio 10^4, which are as high as those of a dry-processed OFET of oligothiophenes, has been built by wet process using a solution of a newly synthesized quaterthiophenes-base liquid crystalline molecule.

There has been growing interest in organic thin–film transistors (OTFTs) over the last several years due to their potential for the fabrication process of large area, low cost, and flexible devices.[1] For industrial use, solution-processed methods such as spin-coating, inkjet printing, and screen printing are highly desirable. Soluble π-systems have been widely studied for this purpose. For example, regioregular head-to-tail poly(3-hexylthiophene) (P3HT) show the marked charge carrier mobilities.[2] The requirement to improve TFT performance is to form the highly crystalline domains in the thin films obtained from solution, in which the molecules self-organize and make cofacially stacked π-frameworks. The resulting close π-stacks facilitate charge carrier transport. Soluble liquid crystalline (LC) semiconductors exhibiting excellent TFT performance have potentials to enhance device performance by manipulating its film morphologies through LC phases.[3] However, it is noted that LC molecules in themselves would have strong tendency of self-organization with highly organized fluidity from their concentrated solutions, resulting in the crystalline domains of their thin films without LC phase assistance.

In this paper, we focus on synthesis and simple drop-casted FET of liquid crystalline quaterthiophenes **1** and **2**, which consist of a central quaterthiophene core with ethyne spacers connecting hexyl chain containing two benzene or thiophene rings. A central quaterthiophene (4T) core keeps molecular linearity at two α-positions of the outside thiophene rings in comparison with odd number rings of oligothiophene core.[4] This linearity is thought to be useful for face-to-face intermolecular π-stacking, making π-conduction paths.

The present compounds **1** and **2** were prepared as shown in Scheme 1 (yield: 19% for **1** and 18% for **2** by four steps).[5] The synthesis involves the two-step Sonogashira cross-coupling reactions.[6] A central quaterthiophene core was constructed at the final dimerization step by lithiation followed by $\mathrm{CuCl_2}$ oxidation, to avoid difficulties due to poor solubility of quaterthiophene unit. Both **1** and **2** are moderately soluble in common organic solvents.

On the cyclic voltammetry measurements, **1** and **2** showed a similar quasireversible oxidation wave: anodic peak potential, $E_{\mathrm{pa}} = 0.68\,\mathrm{V}$ for **1** and 0.67 V for **2** (vs $\mathrm{Ag/AgNO_3}$ in PhCN with 0.1 M n-$\mathrm{Bu_4NPF_6}$, grassy carbon working electrode, and scan rate 100 $\mathrm{mV\,s^{-1}}$). The HOMO (highest occupied molecular orbital) levels of the materials (−5.28 eV for **1** and −5.26 eV for **2**) are determined using the onset positions of the oxidation processes according to the previous report.[7] The thermal properties of **1** and **2** were examined by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). Figure 1 illustrates the heating and cooling DSC scans of **1**. **1** and **2** showed LC phase characteristics with two endothermic peaks of **1** and three endothermic peaks of **2**: crystalline-to-smectic C phase at ≈170 °C and smectic C phase-to-nematic phase with partial decomposition at ≈245 °C for **1**, and crystalline-to-unknown smectic phase (smectic X) at ≈140 °C, smectic X-to-smectic C phase at ≈190 °C, and smectic C phase-to-nematic phase with partial decomposition at ≈210 °C for **2** (POM images of smectic C phase of **1** and **2** are shown in Figure S1). The replacement of the phenyl rings of **1** with the thienyl rings gives



Scheme 1.

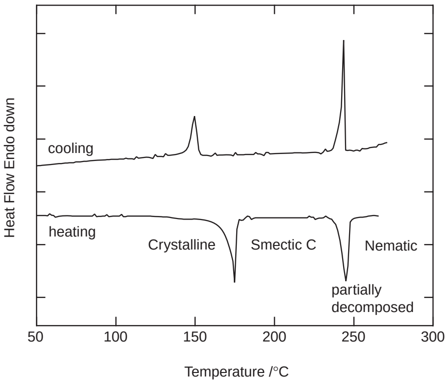


Figure 1. Heating and cooling DSC traces at 5 °C/min for **1**.

rise to a more ordered smectic phase (smectic X) of **2**. This phase could not be distinguished from smectic C only by POM images, but this smectic X phase appears to come from the difference in the orientation of end-capped hexyl chains.

Thin film of **1**, obtained by drop-casting on a SiO_2 substrate from a CS_2 solution followed by annealing below crystal-LC phase-transition temperature (150 °C), showed multiple X-ray diffraction patterns (Figure S2).[5] The most significant Bragg diffraction peaks (*d*-spacing of 20.6 Å) up to the ninth order were recorded, indicating well-defined molecular layers, but multiple patterns imply the co-existence of grains with different molecular orientations. These orientations would be associated with self-organization corresponding to the layered structure of smectic C phase. The *d*-spacing of 20.6 Å corresponds to half of the molecular length (ca. 40 Å) of **1**. Therefore, the molecules are largely tilted (ca. 60°) from the normal direction to the substrate.

Thin film transistors were fabricated by drop casting from CS_2 or toluene solutions of **1** and **2** onto bottom gate, bottom contact HMDS (Hexamethyldisilazane)-treated SiO_2 substrates with photographically patterned gold source and drain electrodes. Devices were annealed at 100 °C under air (below the LC phase temperature) prior to measurement (SEM images are shown in Figure S3). All the devices exhibited p-channel behavior with current modulation. The FET characteristics of thin film of **1** from CS_2 solution are shown in Figure 2. The output characteristics show typical linear and saturated regions together with nonohmic behavior at low V_D region, probably due to mismatch (≈0.3 eV) with the work function of gold metal, resulting in large contact resistance. The FET mobility estimated from the saturation region is $1.5 \times 10^{-2}\,cm^2\,V^{-1}\,s^{-1}$ (at $V_D = -40\,V$, $W = 10000\,\mu m$, $L = 20\,\mu m$) with an on/off ratio of 10^4. On the other hand, devices of **2** showed only linear region of output characteristics under an identical condition with **1**. The estimated linear mobility is $4.3 \times 10^{-4}\,cm^2\,V^{-1}\,s^{-1}$ (at $V_D = -40\,V$, $W = 5000\,\mu m$, $L = 10\,\mu m$) with an on/off ratio of 10^2. The present FET performance is comparable to those of thermally grown oligothiophene thin films. The solution process dramatically decrease device fabrication time in comparison with vacuum deposition, and is suitable for industrial application. It should be noted that the reported devices upon herein were fabricated by simple drop-casting and annealing under normal atmospheric conditions. Self-organization (molecular order) of the present compounds from various concentrated solutions should be investigated to improve film morphology for the enhancement of the FET performance. Further manipulation in or above LC phase temperature to improve the FET performance is also expected.

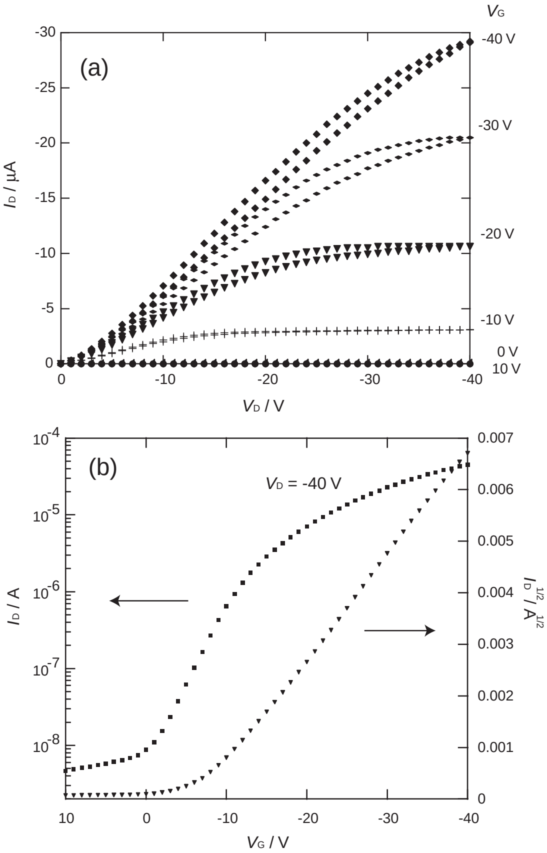


Figure 2. Output (a) and transfer (b) characteristics of a TFT fabricated with **1** as a semiconductor channel layer.

In summary, the new solution-processable LC quaterthiophenes **1** and **2** have been prepared. We have demonstrated that TFTs made by even simple drop-casting film of **1** and **2** show competing FET properties to dry-processed oligothiophene devices. The ordered film structure of **1** without the LC phase assistance indicates that the LC molecules are attractive candidates applicable for the low-cost fabrication technique like the inkjet printing.

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5 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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