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# Hole Transport of a Liquid-crystalline Phenylterthiophene Derivative Exhibiting the Nematic Phase at Ambient Temperature

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A liquid-crystalline phenylterthiophene derivative which exhibits a nematic phase at room temperature has been prepared. The hole mobility in the nematic phase at room temperature reaches $4 \times 10^{-4}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$. This value is two orders of magnitude larger than those of amorphous organic semiconductors and comparable to those in the smectic A or C phases of liquid-crystalline semiconductors.

Electroactive liquid crystals with π-conjugated moieties can exhibit new enhanced or anisotropic properties such as electronic functions.[1–6] Recently, fast electronic charge-carrier mobilities have been observed in columnar[2,3] and smectic phases.[2,4] They have been applied to solution-processable field-effect transistors.[3d,5]

The electronic charge-carrier transport has been observed even in the nematic and cholesteric phases without columnar or layer structures.[6] The carrier mobilities in these phases are on the order of $10^{-4}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ which is lower than those in the columnar and smectic phases.[3,4] Photopolymerized glassy nematic fluorene derivatives have been used for electroluminescence devices emitting linearly polarized light.[7] In the fluidic nematic phase, molecular orientation can be changed by an electric field. This property can be coupled with the electronic functions. For example, fluidic nematic semiconductors are expected to improve the performance of photorefractive devices.[8] However, they exhibit the nematic or cholesteric phases only at high temperature and lose the fluidity because of the crystallization or glass transition at room temperature.[6,7]

Herein we report a liquid-crystalline phenylterthiophene derivative which exhibits a nematic phase at room temperature. A branched alkyl chain[9] and a lateral methyl group[6b] lower the nematic temperature range of this compound, and an extended π-conjugated core enhances the hole transport.[6a,6b]

Liquid-crystalline phenylterthiophene **1** was synthesized by the Pd(0)-catalyzed Suzuki coupling reaction[10,11] between corresponding bromoterthiophene and boronic ester derivatives (Figure 1).

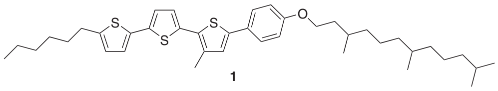
**1**

**Figure 1.** Chemical structure of liquid-crystalline phenylterthiophene derivative **1**.

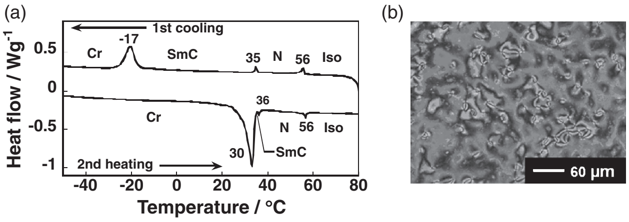

**Figure 2.** (a) DSC thermograms of compound **1**. The heating and cooling rates were $5\,^\circ\mathrm{C\,min^{-1}}$. (b) A polarizing optical photomicrograph of compound **1** in the N phase at 40 °C.

Compound **1** exhibits the nematic phase between 56 and 35 °C and the smectic C phase between 35 and −17 °C during cooling. The phase-transition behavior of compound **1** was determined by differential scanning calorimetry (DSC), a polarizing optical microscope, and X-ray diffraction. The DSC thermogram reveals that two mesophases appear on cooling as shown in Figure 2a.[11] The polarizing optical micrograph and an X-ray diffraction pattern for the sample of **1** show that the mesophases are nematic and smectic C phases, respectively. Figure 2b presents a polarizing micrograph of compound **1** at room temperature. The schlieren textures which are characteristic of the nematic phase are observed in the photograph. At room temperature, the X-ray diffraction pattern shows a broad halo in the wide angle region and a weak cybotactic peak at 37 Å. This pattern is typical of a nematic phase without layer structures.

The carrier-transport properties in the nematic phase of compound **1** were studied by time-of-flight (TOF) technique.[12] At room temperature, compound **1** exhibiting the fluidic nematic phase was capillary-filled into a cell consisting of two indium tin oxide (ITO) electrodes. The gap between the two electrodes was 2 μm. The sample was mounted on a hot stage. The induced transient photocurrent by a laser illumination (Third harmonic generation of Nd:YAG laser, $\lambda = 356\,\mathrm{nm}$) under the application of DC voltage was recorded in a digital oscilloscope.

The micrographic texture shows the molecular alignment is homeotropic at the voltage over 10 V during the TOF measurements. The obtained mobility is thus parallel to the director of the nematic phase.

Figure 3 shows a transient photocurrent curve for positive charge carriers in the nematic phase at room temperature. Non-dispersive transient photocurrents are observed. The mobility of the positive charge carrier is $4 \times 10^{-4}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ at the electric field of $1 \times 10^{5}\,\mathrm{V\,cm^{-1}}$. This value is much higher than the ionic mobilities on the order of $10^{-6}$–$10^{-5}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ in the conventional nematic liquid crystals.[13] Moreover, the positive carrier mobility in the nematic phase of compound **1** is independent of the temperature. In the ionic conduction, the ionic carrier mobility increases with an increase in the temperature because the ionic mobility is determined by the viscosity and that of the nematic phase generally decreases with an increase in the temperature.[13] The positive charge-carrier transport in the

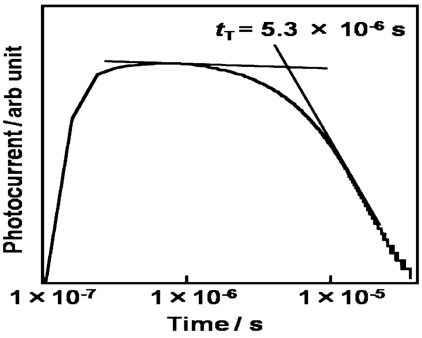

**Figure 3.** A double logarithmic plot of a transient photocurrent for positive carriers in the N phase of compound **1** at 20 V at 40 °C. Sample thickness was 2 µm.

nematic phase should be attributed to the electronic process, but not the ionic. Fast transport of the negative charge carrier is not observed.

The electronic charge-carrier transport was observed in the fluidic nematic and cholesteric phases of the liquid crystals with an extended $\pi$-conjugated system.[6] The carrier mobilities were on the order of $10^{-4}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$. The materials exhibited the nematic or cholesteric phases at high temperatures.[6] A few liquid-crystalline fluorene derivatives exhibited a glassy nematic phase without the fluidity below room temperature.[6e]

The hole mobility in the nematic phase of compound **1** is several times higher than those of liquid-crystalline phenylquaterthiophene derivatives,[6a,6b] which exhibit the mesophases at high temperature; therefore, charge-carrier transport should be enhanced by thermal activation. In the case of compound **1**, the mesomorphic temperature range is around room temperature and the thermal activation effect of the carrier transport is not so remarkable. Moreover, compound **1** has a smaller $\pi$-conjugated system than the phenylquaterthiophene derivatives. This is unfavorable for the fast electronic charge-carrier transport. It is notable that high hole mobility of $4 \times 10^{-4}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ is observed in the nematic phase of compound **1**, in spite of the smaller thermal activation effect and $\pi$-conjugated system. This high hole mobility should be attributed to the formation of microscopic smectic clusters[6b] which is suggested by the cybotactic peak in the X-ray diffraction in the nematic phase.[11] In the cholesteric phase of phenylquaterthiophene derivatives, the enhancement of the hole transport is observed by the formation of the smectic clusters.[6b]

The electronic charge-carrier transport in the fluidic nematic phase could be combined with the dynamic control of the molecular orientation. They should be applied to photorefractive devices and have a potential for tunable or stimuli-responsive electronics devices.

In summary, we have synthesized a liquid-crystalline phenylterthiophene derivative exhibiting a nematic phase at room temperature. The hole mobility in the nematic phase at room temperature has been $4 \times 10^{-4}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$.

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