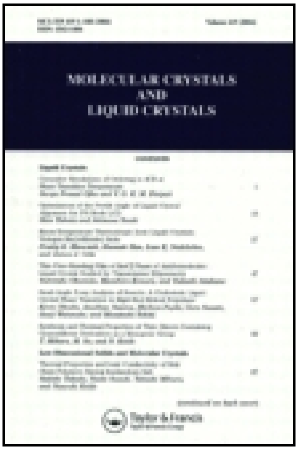

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Electronic Carrier Transport in Liquid Crystalline Semiconductors - Increase in Carrier Mobility and Extension of Mesomorphic Temperature Range

Masahiro Funahashi [a]

[a] Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan

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Electronic Carrier Transport in Liquid Crystalline Semiconductors – Increase in Carrier Mobility and Extension of Mesomorphic Temperature Range

Masahiro Funahashi
Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan

Liquid crystalline semiconductors have been recognized as one of promising materials potential for opto-electronics applications. However increase in carrier mobility as well as extension of mesomorphic temperature range is indispensable for practical applications, such as electroluminescence and thin film transistors. In this report, carrier transport in highly ordered smectic phases of oligothiophene derivatives is reported.

Keywords: carrier transport; organic semiconductor; smectic phase; time-of-flight technique

1. INTRODUCTION

Recently organic semiconductors have been extensively investigated for their application to electroluminescence and thin film transistors. For practical device application, property to produce homogeneous thin films with high quality is necessary, as well as high carrier mobility. Polycrystalline thin films of aromatic compounds such as pentacene exhibit high carrier mobility over $0.1\,\mathrm{cm}^2/\mathrm{Vs}$, however vacuum crystal growth process under rigorously controlled condition is indispensable to produce homogeneous thin films with high quality [1]. Liquid crystals with crystal-like packing structure and molecular order in addition to fluidity and softness have a potential to form

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Address correspondence to Masahiro Funahashi, Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology, Higashi 1-1-1, Tsukuba, Ibaraki 305-8565, Japan. E-mail: masahiro-funahashi@aist.go.jp

homogeneous films with low defect density as well as high carrier mobility.

Electronic charge carrier transport has been confirmed in smectic phases of 2-phenylnaphthalene, 2-phenylbenzothiazole, and dialkylterthiophene derivatives [2–6]. In particular, high carrier mobility exceeding 10^{-2} cm^2/Vs was observed in highly ordered smectic phases [4–6]. However, mesomorphic temperature ranges of these materials are quite narrow above room temperature. For practical applications and understanding carrier transport mechanism, it is indispensable to design and synthesize liquid crystalline semiconductors which exhibit highly ordered smectic phases over wide temperature range including ambient temperature.

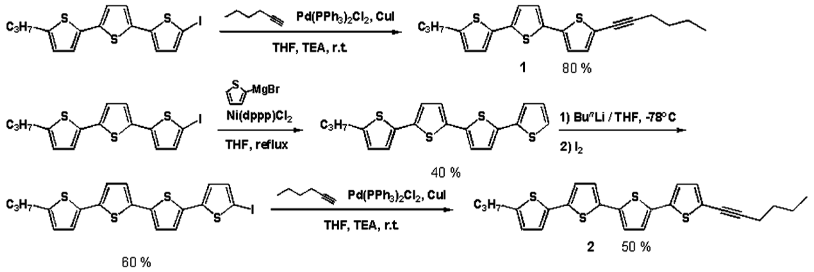
In this work we synthesized new liquid crystalline semiconductors, alkynylterthiophene and alkynylquaterthiophene derivatives exhibiting highly ordered smectic phases over wide temperature range including room temperature and their carrier transport properties were investigated. And material design for increase in carrier mobility is also discussed.

2. MATERIAL DESIGN AND MESOMORPHIC BEHAVIORS

In order to extend mesomorphic temperature range below room temperature, inhibition of crystallization is effective. We have already reported carrier transport below room temperature in smectic phases of 2-(*trans*-4-pentylcyclohexyl)ethyl-5″-propylterthiophene which has bulky substituent to inhibit crystallization. However, the carrier mobility was on the order of 10^{-3} cm^2/Vs which were insufficient for application to switching devices such as thin film transistors [7]. In this study asymmetric structure was adopted in order to inhibit crystallization.

Hexynylpropyl terthiophene (**1**) and hexynylpropylquaterthiophene (**2**) derivatives were synthesized as shown in Scheme 1 [8]. 2-Alkylterthiophene and 2-alkylquaterthiophene skeletons are constructed by Ni-catalyzed coupling reaction between Grignard reagent and corresponding aryl bromide. After iodination of the corresponding 2-alkyloligothiophene, alkynyl group is introduced into the 2-alkyloligothiophene skeleton with Hagiwara–Sonogashira coupling reaction [9].

Mesomorphic behaviors of oligothiophene **1** and **2** were determined by observation of optical texture under polarizing light microscope, differential scanning caloriemetry (DSC), and X-ray diffraction. Under polarizing light microscope, mosaic textures which are characteristics for highly ordered smectic phases are observed for compound **1** and **2** cooled from their isotropic liquid phases and the optical textures are



SCHEME 1 Synthetic route of terthiophene derivative **1** and quaterthiophene derivative **2**.

maintained when they are cooled below room temperature. In DSC measurement, a large exothermal peak appears at 96°C for compound **1** and 196°C for compound **2**, corresponding to isotropic–smectic phase transition. And no other peaks are observed for both compounds below the isotropic-smectic transition points in cooling process, indicating that smectic phases of the both compounds are frozen below room temperature. In X-ray diffraction, the both compounds exhibit smectic phases having hexagonal long range order below room temperature, as shown in Table 1. In compound **1**, the layer spacing is almost as long as the molecular length of the compound, and therefore the smectic phase is identified to be smectic B crystal phase. In contrast, the smectic phase of compound **2** is identified to be smectic G or smectic I where molecules tilt to the layer nomal because the determined layer spacing is shorter than the molecular length of compound **2**.

3. CARRIER TRANSPORT CHARACTERISTICS

Carrier mobility was determined by conventional time-of-flight technique using N_2 pulse laser ($\lambda = 337\,\mathrm{nm}$, pulse duration $= 600\,\mathrm{ps}$) as an excitation light source. Sample was a liquid crystal cell consisting

TABLE 1 X-ray Diffraction Peaks and Lattice Constants in the Highly Ordered Smectic Phases of Compound **1** and **2** at 23°C

Phase transition temp. in cooling process	Diffraction angle 2θ (degree)				Lattice constants (A)		
	[001]	[002]	[100]	[110]	[001]	[100]	[110]
1 Iso 96°C $\mathrm{SmB_{cryst}}$	3.27		19.71	22.78	21.04	3.82	4.56
2 Iso 196°C SmG or I	3.67	6.90	19.70	22.97	24.11	3.87	4.50

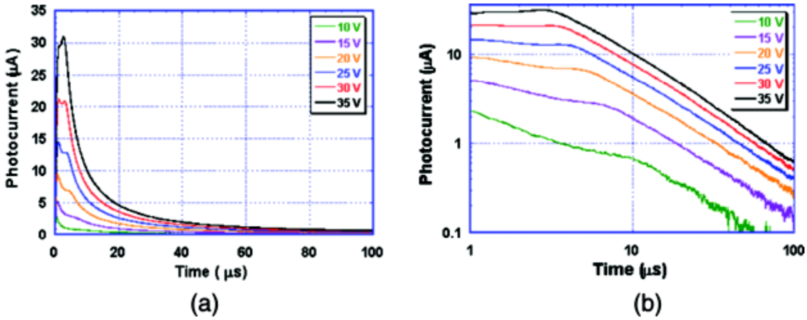


FIGURE 1 Transient photocurrent curves for hole in the $\mathrm{SmB_{cryst}}$ phase of compound 1 at 15°C. The sample thickness is 25 μm, (a) linear plot and (b) double logarithmic plot.

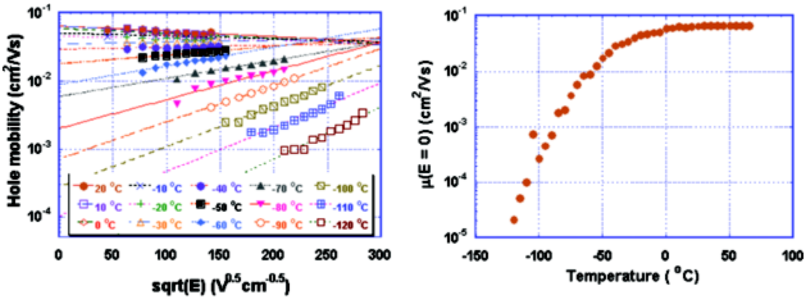
of two ITO-coated glass plates spaced by silica particles, whose thickness was 25μm. Photocurrent signal was recorded as a change of voltage drop through a serial resistor (100 Ω). In the measurement, liquid crystal molecules aligned parallel to the electrode surface, and therefore carrier transport was measured within smectic layers. The molecular alignment did not change when electric field was applied to the sample, because of large viscosity and rigid structure of these highly ordered smectic phases. Carrier mobility μ is expressed as Eq. (1) where d, V, and t_T is sample thickness, applied voltage, and transit time, respectively.

$$\mu = d^2/Vt_T \tag{1}$$

3.1. Carrier Transport Characteristics of Terthiophene Derivative 1

For compound **1**, non-dispersive transient photocurrent curves were observed as shown in Figure 1 and carrier mobility was determined precisely for positive carrier in all temperature range from 100°C to –100°C. Hole mobility at 30°C was $6 \times 10^{-2}\,\mathrm{cm^2/Vs}$ which is 4 order of magnitude larger than conventional amorphous organic semiconductors and slightly smaller than that of polycrystalline films of aromatic compounds [10]. It should be emphasized that high carrier mobility comparable to that of molecular crystals is achieved in the smectic phases with disorders.

Above −20°C, the hole mobility is almost independent of temperature and electric field, while field-dependence of carrier mobility was remarkable below −20°C, and the dependence increased with decrease



(a) (b)

FIGURE 2 (a) Carrier mobility as a function of electric field at various temperature and (b) Carrier mobility as a function of temperature.

in temperature as shown in Figure 2. This behavior resembles to organic amorphous semiconductors rather than aromatic molecular crystals [11], in spite of molecular packing and ordering structure of the highly ordered smectic phase.

In amorphous organic semiconductors, carrier transport process is described as charge carrier hopping between hopping sites via intermolecular orbital overlaps. In disordered systems such as amorphous materials, energy level of hopping sites and intermolecular distance are distributed by disorder of local electric field formed by dipole moment of each molecule, producing low carrier mobility which is strongly dependent on electric field and temperature. Gaussian disorder model can explain carrier transport characteristics in amorphous organic semiconductors. This model assumes Gaussian distribution with a width of σ in the energy level of hopping sites and distribution of transfer integral Σ which corresponds to disorder in intermolecular distance. Carrier mobility μ is expressed as Eq. (2) using σ, Σ and pre-exponential factor μ_0, electric field F, and temperature T [11].

$$\mu = \mu_0 \cdot \exp\left[\left(\frac{2}{3}\frac{\sigma}{kT}\right)^2\right] \cdot \exp\left[C\left\{\left(\frac{\sigma}{kT}\right)^2 - \Sigma^2\right\}\sqrt{F}\right] \quad \Sigma > 1.5$$

$$\mu = \mu_0 \cdot \exp\left[\left(\frac{2}{3}\frac{\sigma}{kT}\right)^2\right] \cdot \exp\left[C\left\{\left(\frac{\sigma}{kT}\right)^2 - 2.25\right\}\sqrt{F}\right] \quad \Sigma < 1.5 \qquad (2)$$

From a slope of a plot between carrier mobility when electric field is 0 and square of 1/kT, σ and μ_0 can be obtained. Σ can be calculated from a slope of a plot between $\partial(\ln\mu)/\partial(\sqrt{F})$ and square of 1/kT as shown in Fig. 3.

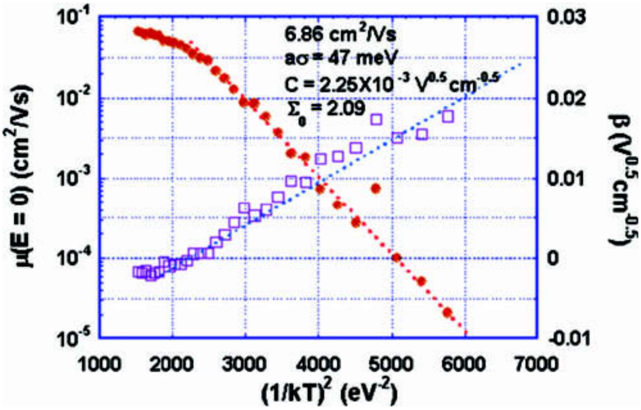
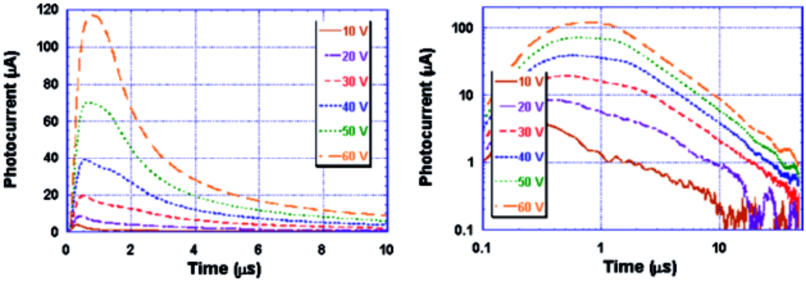


FIGURE 3 Carrier mobility at zero-field and $\partial(\ln\mu)/\partial(\sqrt{F})(=\beta)$ as a function of $1/\mathrm{kT}^2$.

Below −20°C, logarithms of hole mobility is proportional to square root of electric field as shown in Figure 2(a). And the dependence of the mobility on electric field increases with decrease in temperature. This behavior is characteristics to organic amorphous semiconductors. Therefore based on Gaussian disorder model, disorder parameters, σ, Σ, and μ_0 were extracted from the measured hole mobility and its dependence upon electric field and temperature in low temperature region below −20°C as shown in Fig. 3. Energetic disorder σ was 47 eV, positional disorder Σ 2.1. They were surely smaller than those of amorphous organic semiconductors, but not so remarkably small. In contrast, pre-exponential parameter μ_0 corresponding to intermolecular transfer integral, was 6.9 cm^2/Vs which was remarkably larger than that of amorphous organic semiconductors and comparable to carrier mobility of molecular crystals. This indicates that intermolecular closer packing structure increases transfer integral, rather than decrease in disorder, resulting in high carrier mobility around room temperature.

3.2. High Carrier Mobility of 2 up to 0.1 cm^2/Vs Around Room Temperature

Quaterthiophene derivative **2** has larger π-conjugated system than that of terthiophene derivative **1** although intermolecular distance within smectic layers of these compounds **1** and **2** is almost same. Therefore larger transfer integral is expected in the smectic phase of quaterthiophene derivative **2**. In TOF measurement, slightly dispersive transient photocurrent curves with clear kink point in a double



(a) (b)

FIGURE 4 Transient photocurrent curves in the highly ordered smectic phase of **2** at 30°C. The sample thickness was 25 μm.

logarithmic plot are obtained in the highly ordered smectic phase of compound **2**, indicating that hole mobility reached up to $0.1\,\mathrm{cm}^2/\mathrm{Vs}$ at room temperature, as shown in Figure 4. This value is comparable to that of molecular crystals. The intermolecular distance within smectic layers was almost the same as that of **1**, however the larger π-conjugated system of **2** increased intermolecular transfer integral, resulting in higher carrier mobility. This result indicates that carrier mobility in smectic phases can be enhanced to be comparable to molecular crystals.

4. RELATIONSHIP BETWEEN CARRIER MOBILITY AND MOLECULAR STRUCTURE

In smectic B hexatic ($\mathrm{SmB_{hex}}$) phase of cyclohexylethylterthiophene derivative which was previously reported [7], carrier mobility was only $1 \times 10^{-3}\,\mathrm{cm}^2/\mathrm{Vs}$, which was two orders of magnitude smaller than that in the highly ordered smectic phases of compound **1** and **2**. In the $\mathrm{SmB_{hex}}$ phase of the compound, average intermolecular distance deremined by X-ray diffraction was 4.53A, which is longer than those in the highly ordered smectic phases of compounds **1** and **2** perhaps because the compound has a bulky cyclohexylethyl group. Compound **2** which has larger π-conjugated system exhibits higher carrier mobility than compound **1** in spite of the same intermolecular distance within smectic layers. Therefore short intermolecular distance in the highly ordered smectic phases should contribute to large carrier mobility as well as large π-conjugated system. Carrier mobility should be mainly determined by intermolecular distance within smectic layer and extension of π-molecular orbital rather than energetic and spatial disorders because disorder parameters, σ and Σ, are not so reduced in contrast to pre-exponential parameter μ_0 in the highly ordered smectic phase of terthiophene derivative **1**.

5. CONCLUSION

High carrier mobility comparable to molecular crystals was observed in the highly ordered smectic phases of oligothiophene liquid crystalline semiconductors around room temperature. Carrier mobility in smectic phases should be determined by intermolecular distance within smectic layers and extension of π-molecular orbital rather than energetic and spatial disorders.

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