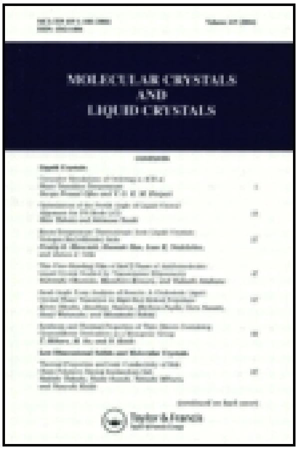

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Probe of Molecular Ordering in Photoconductive Smectic Mesophases by Transient Photocurrent Measurement

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Probe of Molecular Ordering in Photoconductive Smectic Mesophases by Transient Photocurrent Measurement

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We have studied the carrier transport properties of the two series of smectic mesophases, from SmA to SmE phases, and from SmC to SmG phases in 2-pahenynaphthalene and terthiophene derivatives by time of flight measurements. We examine the experimental data with the hopping transport formalism as a function of the molecular distance with the reference to that from X-ray diffraction. We propose another aspect of the carrier transport characteristics as a probe for elucidating the molecular alignment in the smectic layer.

Keywords: carrier transport; photoconductivity; smectic phases; time-of-flight technique; terthiophene; 2-phenylnaphthalene

Introduction

Variety of liquid crystal phases is a specific feature in calamitic liquid crystals, which is originated from the molecular alignment of rod-like molecules. This provides us with unique optical and electrical properties in each phase applicable to opto-electronic devices.

The macroscopic molecular order in the liquid crystal can be determined by spectroscopic anisotropy and more detailed information from X ray diffraction[1].

Recently it has been found that electronic charge transport takes place in some discotic[2, 3] and smectic liquid crystal phases[4, 5, 6], in which a localized charge on an aromatic core moiety of the liquid crystalline molecule, hops to the nearest neighbor molecule one after another along with the electric field. Therefore, the hopping probability of the charge to adjacent molecules, which determines the carrier mobility of carrier velocity at unit electric field, depend on the distance between the hopping sites significantly. It is well known that this electronic hopping transport is described on the basis of intermolecular orbital overlap as the following equation (1) :

$$\mu = r^2 \exp\left(-\frac{2r}{\gamma}\right) \tag{1}$$

where μ is carrier mobility, r hopping distance between the localized states, and γ a decay constant of the wave function characterizing the molecular orbitals[7]. Thus, it is plausible that the carrier mobility provides us with microscopic information on the molecular order in the liquid crystals.

In smectic phases, there exists a clear anisotropy in the intermolecular distance in the direction vertical to the smectic layers and within the layers: a short distance of 3~5 A between rod-like molecules within the smectic layers and a long distance of 20~40 A between the layers separated with insulative long alkyl chains[8]. Therefore, the carrier transport in homogeneous alignment is dominated within the smectic layer, which is characterized by two dimensional hopping in the smectic layers. In fact, this is confirmed experimentally by anisotropy in photoconductivity in the smectic phases and the studies of carrier transport in the smectic phases doped with carrier traps.

From this point of view, we have studied the carrier transport characteristics in two series of smectic phases in which molecular director is perpendicular to the smectic layer (SmA, SmB and SmE phases in 2-phenylnaphthalen derivatives) and tilted towards the layer (SmC, SmF, and SmG phases in terthiophene derivatives). In this report, we will discuss the molecular ordering in the smectic layer through the carrier transport in those phases with reference to the lattice parameters measured by X ray diffraction.

Materials and their characterization

The 2-phenylnaphthalene derivatives are synthesized by Suzuki coupling reaction[10] between 4-alkylphenylboric acid and 2-brom-6-alkoxyonaphthalene which was previously reported elsewhere[5]. A symmetric terthiophen derivative, 8-TTP-8, was synthesized from 2,5-dibromothiophene and 2-octylthienyl Grignard reagent, and the asymetric dialkylterthiophene one, 6-TTP-12 by Ni(II)dpppCl$_2$-catalyzed coupling reaction between corresponding thienyl Grignard reagent and thienyl bromides step by step [12] in a good yield as shown in Fig. 1

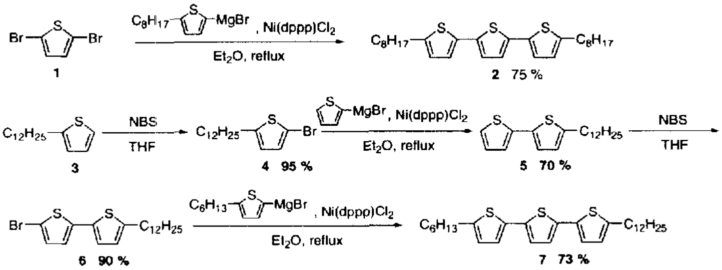

FIGURE 1 Synthetic route of dialkylterthiophene derivatives.

Mesophase characterization was carried out with the observation of optical texture and a miscibility test under a polarized light microscope. Phase transition temperatures are determined by differential scanning caloriemetry as shown in Table 1.

Table 1 Phase transition temperature of the 2-phenylnaphthalene and terthiophene derivatives.

8-TTP-8	K 55℃ SmG 72℃ SmF 87℃ SmC 91℃ Iso
6-TTP-12	K 56℃ SmF 88℃ Iso
8-PNP-O12	K 79℃ SmB 100℃ SmA 121℃ Iso
8-PNP-O4	K 55℃ SmE 125℃ SmA 128℃ Iso

Carrier mobility measurement

The liquid crystal cells were made from two ITO-coated glass plates whose surfaces were rubbed with filter paper, spaced with silica particles. The liquid crystal material was capillary-filled into the cells at isotropic phase. The resulting molecular alignment was homogeneous with poly-domain structure with the fairly large domain size of 100 μm over the cell thickness.

Time-of-flight (TOF) technique was used to determine the transit time of carrier drifting across the sample[13], using N_2 pulse laser pulse (λ = 337 nm, pulse duration = 600 ps, intensity = 40 mJ/pulse) for excitation.

The carrier mobility was calculated by the equation (2) with the transient time t_T determined as a kink point in double logarithmic plot of the transient photocurrent as a function of time.

$$\mu = \frac{d^2}{Vt_T} \tag{2}$$

where d is sample thickness, V applied voltage.

Results and discussion

In the smectic series of the SmA, SmB, and SmE phases of 2-phenylnaphthalene derivatives, in which molecular director is vertical to the smectic layer, ambipolar carrier mobility had no dependence on electric field and temperature, and increased stepwise from 2.5X10^{-4} cm^2/Vs in the SmA phase , via 1.6X10^{-3} cm^2/Vs in the SmB phase, and up to 1X10^{-2} cm^2/Vs in the SmE phase, as reported previously[6].

In the other series of SmC, SmF, and SmG phases of terthiophene derivatives, in which molecular director tilts to the layer, so it did from 5X10^{-4} cm^2/Vs in the SmC phase, via 4X10^{-3} cm^2/Vs in SmF phase, and up to 2X10^{-2} cm^2/Vs in the SmG phase as shown in Fig. 2. The SmF phases in 6-TTP-12 and 8-TTP-8 exhibited the same mobility of 4X10^{-3} cm^2/Vs in as described above, indicating the intrinsic properties of the present phase. These mobility are summarized in Fig. 3 and Fig. 4, repectively.

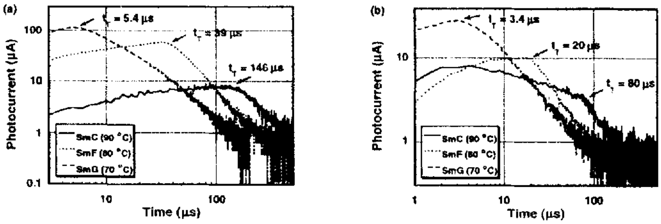

FIGURE 2 Transient photocurrent in the SmC, SmF, SmG phases for (a) positive (d = 20 μm) and (b) negative carrier (d = 15 μm) at 50 V.

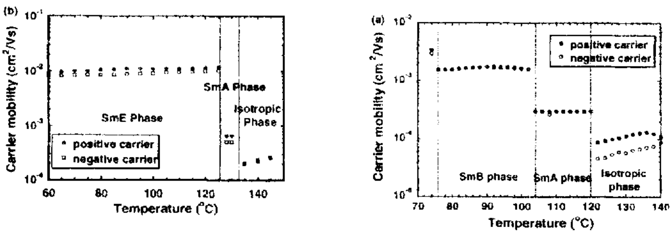

FIGURE 3 Mobility of (a) 8-PNP-O12 and (b) 8-PNP-O4 as a function of temperature.

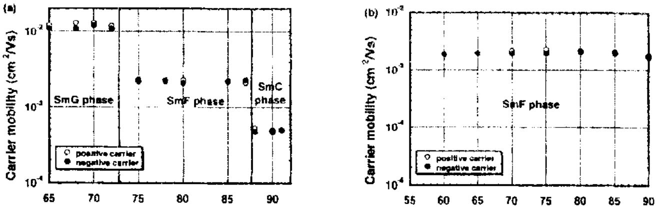

FIGURE 4 Mobility of (a) 8-TTP-8 and (b) 6-TTP-12 as a function of temperature.

This mobility upgrade in accordance with the phase transition was quite similar in both series of the smectic phases. X-ray diffraction study revealed the detailed molecular distances in inter-and intra smectic layers as summarized in Table 2.

Table 2 Lattice constants of the different phases in 2-phaenylnaphthalene and terthiophene derivatives determined from X ray diffraction

8-TTP-8	SmC	SmF		SmG			
	30.89 A	31.6 A	4.43 A	28.9 A	4.16 A	4.47 A	4.63 A
8-PNP-O12	SmA	SmB					
	36.1 A	37.4 A	4.61 A				
8-PNP-O4	SmA			SmE			
	27.80 A			28.1 A	3.49 A	4.33 A	4.78 A

According to the hopping transport model, it is natural that the mobility is enhanced by the upgrade of the molecular order accompanied with the phase transition due to the reduction of intermolecular distance, which is estimated by the relationship described as eq. (1),.

Assuming a density of 0.9 for both of the liquid crystals and the interlayer distance, 36.1 A for SmA phase and 30.89 A for SmC phase listed in Table 2, we estimated the average molecular distance to be 5.5 A and 5.7 A in SmA and SmC pahse of 8-PNP-O12 and 8–TTP-8, respectively. With this average distance, we calculated the γ in equation (2) to be 0.81A for 2-phenylnaphthalene and to be 0.82 A for terthipohene derivatives, which are relatively small compared with a typical value of 1~2 A for organic amorphous semiconductors[7]. We estimated the mobility for each phase on the basis of the experimental mobility for the SmA and SmC phases according to the equation (2) with the molecular distance listed in Table 2 and the γ determined. Interestingly, it is revealed that the estimated mobility of $1.6X10^{-3}$ cm^2/Vs for the SmB phase, $1.1X10^{-2}$ cm^2/Vs for the SmE phase, $5.3X10^{-3}$cm^2/Vs for the SmF phase, and $9X10^{-3}$ cm^2/Vs for the SmG phase, give fairly good agreement with the experimental values in each series as described above. This indicates that the carrier transport within the smectic layer is primarily determined by the molecular distance in the smectic layer. In other words, we can get the information on the molecular alignment in the layer through the carrier transport properties. It should be noted that the experimental mobility of $2X10^{-2}$ cm^2/Vs in the SmG phase, which is corresponding to crystal SmB phase in the smectic series with the director vertical to the layers, is not only higher than that estimated value of $9X10^{-3}$ cm^2/Vs but also that of the SmE phase of 8-PNP-O4. We think that this large mobility observed should be attributed to the increase of carrier hopping probability caused by the enhanced local orbital overlap due to the hindered molecular rotation around the molecular axis[1] and/or sulfur atoms with large van der Waals radius in the core moiety.

With the assumption that the decay constant characterizing the spatial extent of the wave function for the hopping sites is 1~2 A similar to that for the organic semiconductors, the estimated mobilities become higher in the SmA and SmC phases than the experimental mobilitites and smaller in the SmE and SmG phases. These disagreement on the experimental data may be attributed to the disordered molecular alignment in the SmA and SmC phases and to the hindered molecular rotation in the highly ordered SmE and SmG phases, which enhances the local molecular overlap between the hoping site. In fact, the average hopping time for each hopping event is estimated to be 1 ns for the mobility on the order of 10^{-3} cm^2/Vs, which implies that the molecular rotation may affect the hopping probability at each site.

In conclusion, we have studied the carrier transport properties of the two series of smectic mesophases, from SmA to SmE phases, and from SmC to SmG phases in 2-pahenynaphthalene and terthiophene derivatives and examined the mobilities measured with the hopping transport formalism as a function of the intermolecular distance with the reference to that from X-ray diffraction. We found that the carrier mobility is determined primarily by the hopping distance among the adjacent molecules irrespective of the two series of the liquid crystals and that the highly ordered phase tends to exhibit enhanced carrier mobility compared with that estimated by the molecular distance, suggesting the contribution of local molecular interaction.

We draw the conclusion that the carrier transport characteristic properties provide us with a new probe for elucidating the molecular alignment in the mesophases and give some detailed information about the local molecular alignment, although we need accumulation of the carrier transport data in different materials systems before judging the effectiveness of the present discussion.

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