

Effect of Molecular Alignment in Smectic Mesophases on Carrier Transport of Self-Organizing Molecular Semiconductors

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Abstract

The general features of electrical properties of a new class of organic photoconductors, i.e., photoconductive liquid crystals, to which we prefer “*Self-organizing Molecular Semiconductors*” as a conceptual name, are reviewed briefly. And in two series of smectic mesophases, i.e., from SmA to SmE and from SmC to SmG in which the liquid crystalline molecules sit perpendicular to the smectic layer and tilted towards the layer, respectively, the effect of molecular alignments on the carrier transport was investigated by transient photocurrent measurements with 2-phenylnaphthalene and terthiophene derivatives corresponding to the two series. All the transient photocurrents measured were non-dispersive and ambipolar irrespective of the mesophases. The mobility increased stepwise in accordance with the upgrade of the molecular alignment and ranged from 10^4 cm²/Vs to 10^2 cm²/Vs, which was independent of electric field and temperature. The highest mobility was observed in SmE phase of 2-phenylnaphthalenes and SmG phase of terthiophenes. Judging from the analysis with two-dimensional hopping model in the smectic layers and the results from X-ray diffraction study, it was concluded that the upgrade of mobility at the phase transition from mesophase to mesophase is attributed primarily to the reduction of the molecular distance in the smectic layer irrespective of the type of the series. In addition, it was suggested that the hopping probability is enhanced possibly through a local overlap of molecular orbitals in highly ordered mesophases in which the molecular motion is limited.

Introduction

Organic photoconductors have been utilized in photoreceptors for xerographic copiers and laser printers,¹ and more recently in active components of electroluminescent devices.² These applications require large-area uniformity in thin films, so that the materials practically used are amorphous and prepared either by polymerization, vacuum evaporation, or molecular doping into polymer films, of photoconductive small molecules. Inevitably the electrical

properties of resulting amorphous films were degraded compared with their own molecular crystals due to the loss of long range order of molecules: the carrier mobility is decreased down to $10^6 \sim 10^5$ cm²/Vs and depends on both electric field and temperature.¹ This is a trade-off for the large-area uniformity in amorphous films. In addition, deep states originated from impurities and carrier-dipole interactions often dominate the response time and retard the carrier transport. Thus, their device configuration and application are limited as is. Recently, considerable improvement in mobility of the molecularly doped films has been achieved up to 10^3 cm²/Vs by utilizing less polar polymer matrices³, but further improvement and unsolved problems of the field and temperature dependence in mobility are still a challenging subject. Thus, in order to relax the present limitation of the organic photoconductors in device application, a new material exhibiting high mobility independent of electric field and temperature with low densities of defect states has to be realized.

From this point of view, we recognized the importance of molecular alignment in the carrier transport and paid our attention to the liquid crystal that has been utilized widely for display devices. The liquid crystal exhibits liquid-like fluidity and crystal-like self-organizing molecular alignment. This unique nature of liquid crystals should be a good basis of not only large-area uniformity but also a high potential of enhanced carrier transport.

In 1995, 2 years later from the first discovery of electronic conduction in triphenylene derivatives of a discotic (disk-shaped) liquid crystal by Haarer's group at Bayreuth University,⁴ we found independently that 2-phenylbenzothiazole derivatives, which is a typical calamitic (rod-shaped) liquid crystal exhibiting the smectic mesophase, shows very fast electronic charge transport.⁴ It is well known that the calamitic liquid crystal is more liquid-like compared with the discotic liquid crystal that are more-like molecular crystals and hardly shows liquid-like fluidity. Therefore, our discovery is something epoch-making because the carrier transport in the calamitic liquid crystals indeed had been believed to be ionic for a long time since Heilmeyer's first report on its electrical conduction in 1968. Since then, we have investigated the basic photo-

electrical properties of the ‘photoconductive’ smectic liquid crystals^{5,6,7} including 2-phenylnaphthalene and terthiophene derivatives.

According to our results have obtained so far, we can describe the general features of carrier transport in self-organizing molecular semiconductors as follows:

- (1) Anisotropic carrier transport⁸
- (2) Two-dimensional hopping transport in smectic layers⁹
- (3) Very fast carrier mobility ranges from $10^4 \sim 10^2$ cm²/Vs
- (4) Ambipolar carrier transport^{6,7}
- (5) Independence of electric field^{5,6,7}
- (6) Independence of temperature in each mesophase^{5,6,7}
- (7) co-occurrence of extrinsic ionic conduction¹⁰
- (8) Electrically inactive domain boundary^{11,12,13}

These unique features give a clear contrast to conventional organic amorphous photoconductors/semiconductors whose molecular alignment is random. The liquid crystals have been utilized in display devices, in which their optical anisotropy that originates from molecular alignment play the major role for giving the optical contrast in display. It is true that these features described above also originate from self-organized molecular alignment, but they afford the liquid crystals quite different aspects from “the liquid crystals” as a display material. Therefore, we prefer to call them *Self-organizing Molecular Semiconductors*, rather than photoconductive liquid crystals.

In this paper, we will overview the electrical properties of the self-organizing molecular semiconductors described above with reference to those in the conventional amorphous materials, and discuss our recent results on the effect of molecular alignment on carrier transport in comparison with two different series of smectic mesophases in 2-phenylnaphthalene and terthiophene derivatives.

Experimental

Materials and Liquid Crystal Cells

2-phenyl naphthalene derivatives, 5-PNPO1, 8-PNP-O4, and 8-PNP-O12 were synthesized with Suzuki coupling reaction catalyzed by Pd(PPh₃)₄ between corresponding 4-alkylphenylboric acids and 2-bromo-6-alkoxy-naphthalenes in dimethoxyethane in the presence of aqueous Na₂CO₃ solution. They were recrystallized from hexane before use. Dialkylated terthiophene derivatives, i.e., 6-TTP-12 and 8-TTP-8, were synthesized with Ni-catalyzed coupling reactions or direct alkylation of terthiophene with alkylbromides in the presence of base. Their chemical structures are shown in Fig. 1.

All these materials exhibited smectic mesophases except 5-PNP-O1. In the smectic mesophases of 2-phenylnaphthalene derivatives, all the molecules organize in layers and sit perpendicular to the layer, resulting in smectic A (SmA), SmB, and SmE phases: in SmA phase, the molecules in the smectic layers have no positional order; in SmB and SmE phases, they have hexatic and rectangular orders in the layer, respectively. On the other hand, all the

molecules organize in layers, but tilt towards the smectic layer in the terthiophene derivatives, resulting in SmC, SmF, and SmG phases: in SmC, the molecules have no positional order in the smectic layer just like in the SmA; SmF and SmG phases are analogous to SmB Phase. Phase transition behavior was characterized by the microscopic observation of textures under polarized illumination and a miscibility test with a standard material such as 4-hexyl-4'-heptyloxybiphenyl. The phase transition characteristics are summarized in Table 1.

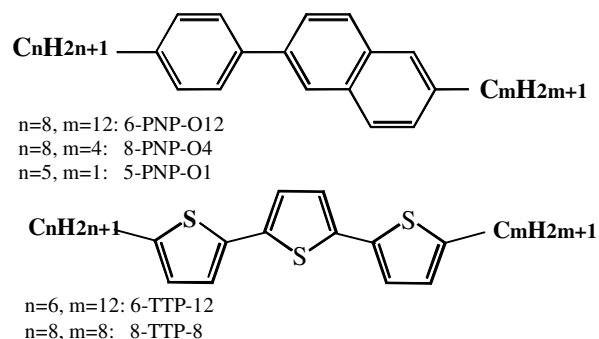


Figure 1. Chemical structures of 2-phenylnaphthalene and dialkylterthiophene derivatives.

Table 1. Phase characteristics of 2-phenylnaphthalene and dialkylterthiophene derivatives.

Materials	Phase transition Behavior
5-PNP-O1 (n=5, m=1)	K -121°C- N -128°C- Iso
8-PNP-O4 (n=8, m=4)	K -50°C- SmE -123°C- SmA -128°C- Iso
8-PNP-O12 (n=8, m=12)	K -79°C- SmB -103°C- SmA -120°C- Iso
6-TTP-12 (n=6, m=12)	K -59.1°C- SmF -90.3°C- Iso
8-TTP-8 (n=8, m=8)	K -63.9°C- SmG -72°C- SmF -87.8°C- SmC -91.3°C- Iso

The n and m indicate a number of carbons in the chemical structure shown in Fig.1, respectively.

Liquid crystal cells were prepared for properties evaluation by capillary-filling the materials into the two ITO (In₂O₃) or Al-coated glass plates spaced with silica particles or polyimide films. No particular treatment of the electrode surface was carried out, resulting in polydomain structure with homogeneous molecular alignment, where rod-like molecules organized parallel to the electrode surface. The resulting molecular alignment was stable under the electric field applied in the present study. The domain size were around several tens μm, larger than the cell thickness.

Measurement of Electrical Properties

The carrier transport properties were evaluated by steady-state and transient photocurrent measurements. For steady-state photocurrent measurements, Xe lamp (500W) equipped with a band pass filter (UV33DS, Toshiba Glass Co.Ltd) was used for UV illumination (300 ~ 380 nm). The light intensity was 2.5 mW/cm². The liquid crystal cell was mounted on the hot stage in which the temperature was controlled by PID thermocontroller within an accuracy of 0.1 K. The photocurrent was recorded with a source measurement unit. For transient photocurrent measurements, conventional time-of-flight set-up equipped with a N₂ laser (37nm, 40 J/pulse, pulse width: 600ps) was used. The signals were pre-amplified and recorded by a digital oscilloscope (Model Pro92, Nicolet Co.Ltd.). For positive carriers, the Al-evaporated electrodes were used, and the ITO electrodes for negative carriers. This is due to minimizing the interface effects of electrodes on carrier trapping of photo-generated carriers. The transit time of photo-generated carriers was determined from an inflection point in a double logarithmic plot of transient photocurrent as a function of time, which was almost same as the onset time of the current decay in normal plot. With this transit time, carrier mobility was calculated from the equation (1)

$$\mu = d^2/V \tau_t \quad (1)$$

where μ is a carrier mobility, d a sample thickness, V an applied voltage, and τ_t a transit time.

Results and Discussions

1. General Features of Carrier Transport

(1) Anisotropic and Two-dimensional hopping transport

In smectic mesophases, carrier transport exhibits anisotropy due to the molecular orientation of rod-like molecules: the fast carrier transport takes place within the smectic layer where the rod-like molecules are closely packed. This is attributed to the big difference in the average molecular distance between inter-layers and intra-layers. In fact, it is estimated to be 4.61 Å and 37.4 Å in intra- and inter-smectic layer of 8-PNP-O12 from X-ray diffraction study, respectively. Therefore, in homogeneous alignment where all the molecules sit parallel to the electrode surface, it is likely that all the carriers are transported exclusively within the smectic layers. In fact, the two-dimensional hopping transport was confirmed by the facts that the trap-controlled mobility is determined by a trap concentration in the smectic layer¹⁴ (a square root of the impurity concentration) as shown Fig.2 and that the mobility in molecularly diluted liquid crystals is determined by the average distance of the hopping sites in the smectic layer.⁹ We have not succeeded in evaluate the carrier mobility across the smectic layers quantitatively yet because of a small TOF signal in the homeotropic alignment cell, but we could observe a very clear photoconductive anisotropy in the steady-state photocurrent measurements.⁸

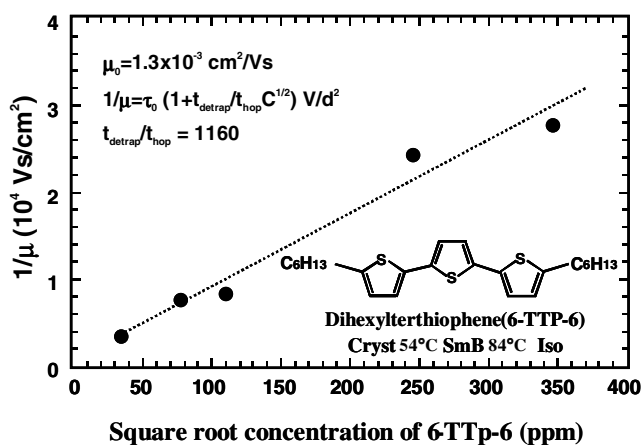


Figure 2. Effect of impurity doping on carrier transport in 2-phenylnaphthalene derivative, 8-PNP-O12 doped with dihexylterthiophene (6-TTp-6)

(2) Fast Electronic Conduction

The carrier transport in smectic mesophases is characterized by a very fast mobility over 10⁴ cm²/Vs. The highest mobility observed so far is on the order of 10² cm²/Vs in SmE phase of the 2-phenylnaphthalene derivative of 8-PNP-O4, and the SmG phase of the terthiophene derivative of 8-TTP-8. This mobility is 10³~10⁴ times faster than those in the conventional organic amorphous photoconductors including molecularly doped polymers.

Interestingly, ambipolar carrier transport is often observed in self-organizing molecular semiconductors as is the case of molecular crystals. In fact, the mobility for electrons and holes is almost same at each mesophase in 2-phenyl-naphthalene and terthiophene derivatives. This is very an attractive feature for device application. In the conventional organic amorphous semiconductors, there is no material that exhibits ambipolar carrier transport, while the combined materials system of electron and hole transport materials such as PVK-TNF¹⁵ and triphenylamine and diphenoquinone derivatives¹⁶ have been reported in the limited range of mobility of 10⁶ cm²/Vs.

(3) Field-and-temperature independency

It is well accepted in the recent understanding of the carrier transport in disordered systems that the temperature- and-field dependence of the mobility results from energetic and positional disorders of the hopping sites. In this point, the carrier transport characteristics in the liquid crystals are quite interesting because this material system have various molecular alignments from "liquid" to "almost crystal", which are thermally fluctuated. Therefore, they will give us insight into further understanding of the carrier transport in the disordered systems.

The carrier mobility in smectic mesophases of self-organizing molecular semiconductors is independent of temperature at each phase as shown in Fig.3 in comparison with those in amorphous films. This is a common feature of this type of materials irrespective of the molecular order in

the smectic layer. In isotropic phase, however, the mobility depends on temperature and follows Arrhenius relation. This is due to the ionic conduction. In fact, that was confirmed experimentally by checking the mobility change when diluted with hydrocarbon, which leads to lower viscosity favorable for ionic conduction and to longer hopping distance unfavorable for electronic conduction. The activation energy of 0.3 eV in isotropic phase is a typical value for the ionic conduction in liquids.

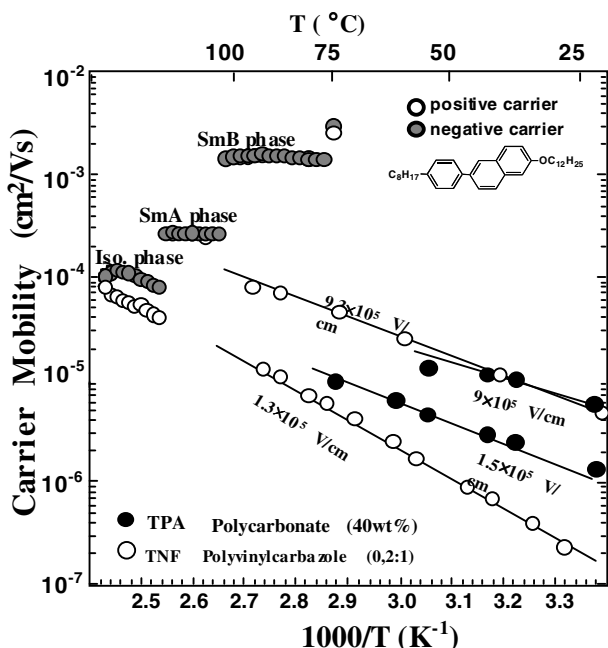


Figure 3. Temperature dependence of carrier mobility in 2-phenylnaphthalene derivative, 8-PNP-O12 and typical polymeric and molecular doped polymers, PVK-TNF and TPA-polycarbonate.

In addition, the electric field does not affect the carrier mobility. The carrier mobility keeps constant even at the lowest electric field on the order of 10^4 V/cm. It is not the case of the organic amorphous semiconductors.

(4) Co-existence of different conduction mechanism

In self-organizing molecular semiconductors, electronic and ionic conduction are possible in principal due to their fluidity. The viscosity and impurity determine the conduction mechanism basically. In fact, in nematic and isotropic phases with lower viscosity, the ionic conduction takes place, where ionized liquid crystalline molecules and/or impurity molecules are responsible for mobile carriers. Not only ionic impurities but also non-ionic ones often play an important role for the conduction mechanism. The non-ionic impurities that form deep trap states behave as ionic carriers once they trap an electrons or a hole. In fact, quite a small concentration of the impurities often traps free electronic carriers efficiently to alter the conduction mechanism to the ionic conduction. This is the main reason why the ionic conduction had always been observed in

calamitic liquid crystals in spite of many studies on their electrical properties since Heilmeyer's first report.¹⁷

(5) Electrical inactive domain boundary

It has been revealed that there is a marked contrast in the electrical nature of the boundaries of crystalline and liquid crystalline materials. In general, the grain boundary in polycrystals often causes defect states irrespective of organic and inorganic materials because of a pile-up of impurities and structural relaxation of accumulated strain. In polydomain of the liquid crystals, however, experimental results indicate that the polydomain boundary is electrically inactive and does not cause defect states at all. This was demonstrated by a transient photocurrent measurements in two liquid crystalline cells of $100 \mu\text{m}$ with different domain sizes on each electrode as shown in Fig. 4, in which no appreciable change is observed in the photocurrents irrespective of the great difference of domain sizes, except for a small difference in the signal intensity originated from light scattering. Interestingly, once the liquid crystalline phases are transformed into polycrystalline phase, the carrier transport is degraded significantly and is often governed by deep traps, while the single crystals exhibit superior electrical properties to those of the liquid crystalline phases.

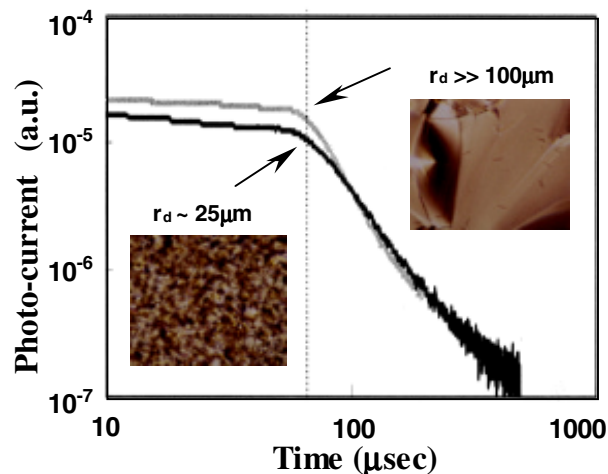


Figure 4. Transient photocurrents in two liquid crystal (8-PNP-O12) cells of $100 \mu\text{m}$ with different domain sizes.

2. Effect of molecular alignment

As described, carrier transport is governed by ionic conduction in nematic and isotropic phases of 2-phenylnaphthalene derivatives. So is the isotropic phase in the terthiophene derivatives. In the nematic phase, all the molecules are oriented to a direction with thermal fluctuation without any positional order, while the molecules are at random in the isotropic phase. The average molecular distance in these phases is around 8 \AA , which is smaller than the typical value of the average hopping distance in molecularly doped polymers. Therefore, it is reasonable that the ionic conduction is originated from low viscosity in these phases. On the other hand, in smectic mesophases, the

molecules are accumulated in layers and tend to be oriented to a direction in the layer, therefore, more closely packed compared with the isotropic and nematic phases. The average molecular distance in SmA and SmC phases is estimated to be around 5.5 Å in 2-phenylnaphthalene and terthiophene derivatives. Thus, the viscosity is enhanced in the resulting closely packed molecular aggregate, i.e., smectic phase, retarding the ionic conduction.

Fig. 5 shows the carrier mobility as a function of temperature for 8-PNP-O4(a) and 8-TTP-8(b). In both materials, the carrier transport is ambipolar and independent of electric field and of temperature at each phases. The mobility is increased abruptly when the phase transition to a higher ordered phase takes place. The carrier mobility in each phase is the same value irrespective of the different length of carbon chains in these two series of the materials. Therefore, it implies that the determined mobility in each phase is originated from the intrinsic properties of each phase: it is on the order of 10^{-4} cm²/Vs for SmA and smC phase, on that of 10^{-3} cm²/Vs for SmB and SmF phases. The highest mobility over 10^2 cm²/Vs is achieved in SmE phase for 2-phenylnaphthalene derivatives and in SmG phase for terthiophene derivatives. The mobility seems to be determined by the molecular alignment in the smectic layer, while the thermal fluctuation of each molecule hardly affects the carrier hopping.

In 2-phenylnaphthalene derivatives, all the molecules sit perpendicular to the smectic layer, while they are tilted towards the smectic layer in the terthiophene derivatives as described. According to the phase transition, the molecular alignment in the smectic layer is sophisticated from ‘isotropic’ in SmA and SmC (tilled SmA) phases, ‘hexatic’ in SmB, SmF and SmG phases, and to ‘rectangular’ in SmE phase. Simultaneously, the average distance is reduced with the upgrade of the molecular alignment, which is demonstrated by X-ray diffraction study, which is summarized in Table 2.

The carrier transport in smectic layer is governed by two-dimensional hopping transport in the smectic layers. In fact, the relative mobility of these two series, i.e., from SmA to SmE and from SmC to SmG, are in good agreement with each other as discussed, but the exact co-relation is not established. For example, SmG phases are categorized not to be tilted SmE but to be tilted SmB phase.¹⁸

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. (2),

$$\mu \propto r^2 \exp(-2r/a_0) \quad (2)$$

where μ is the mobility, r an average hopping distance, a_0 the decay constant of the molecular orbital.

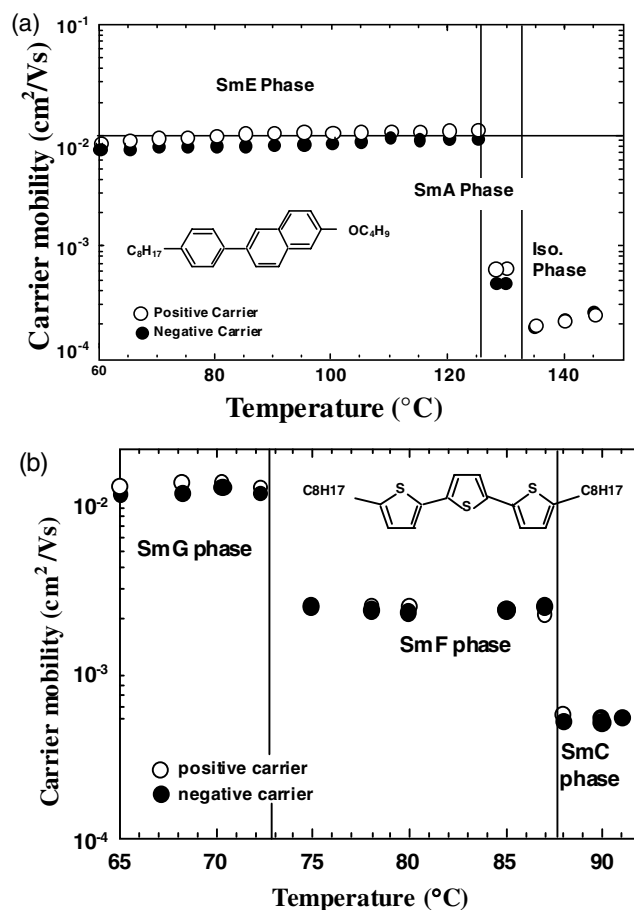


Figure 5. Mobility as a function of temperature in 8-PNP-O4 (a) and 8-TTP-8; (b) for holes (open circles) and electrons (closed circles).

Table 2 Molecular distance in different phases of 2-phenylnaphthalene and terthiophene derivatives.

2-Phenylnaphthalenes	SmA	SmB	SmE
8-PNP-O12 inter-layer	36.1 Å	37.4 Å	-
intra-layer	-	4.61 Å	-
8-PNP-O4 inter-layer	27.8 Å	-	28.1 Å
intra-layer	-	-	3.49 Å 4.33 Å 4.78 Å
Terthiophenes	SmC	SmF	SmG
8-TTP-8 inter-layer	30.89 Å	31.6 Å	28.9 Å
intra-layer	-	4.43 Å	4.16 Å 4.47 Å 4.78 Å

With an assumed density of 0.9 for both of the liquid crystals and the interlayer distance, 36.1 Å for SmA phase and 30.89 Å for SmC phase listed in Table 2, we estimated the average molecular distance to be 5.5 Å and 5.7 Å in SmA and SmC phase of 8-PNP-O12 and 8-TTP-8, respectively. With this average distance, we calculated the γ in equation (2) to be 0.806 Å for 2-phenylnaphthalene and to

be 0.822 Å for terthiophene derivatives, which are relatively small compared with a typical value of 1~2 Å for organic amorphous semiconductors.⁷ We estimated the mobility for each phase on the basis of the experimental mobility for 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 $1.6 \times 10^{-3} \text{ cm}^2/\text{Vs}$ for SmB phase, $1.1 \times 10^{-2} \text{ cm}^2/\text{Vs}$ for SmE phase, $5.3 \times 10^{-3} \text{ cm}^2/\text{Vs}$ for SmF, and $9 \times 10^{-3} \text{ cm}^2/\text{Vs}$ for 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. It should be noted that the experimental mobility of $2 \times 10^{-2} \text{ cm}^2/\text{Vs}$ in SmG phase, which is corresponding to titled SmB phase, is higher than that estimated value of $9 \times 10^{-3} \text{ cm}^2/\text{Vs}$ but also that of the SmE phase of 2-phenylnaphthalene derivative, 8-PNP-O4. We do not know the exact reason for this, but it is plausible that such a high mobility observed is responsible for the increase of carrier hopping probability caused by the enhanced local molecular overlap due to the limited molecular rotation around the molecular axis and/or sulfur atoms with large van der Waals radius in the core moiety.

Conclusion

The carrier transport in two series of smectic mesophases in 2-phenylnaphthalene and terthiophene derivatives, i.e., from SmA to SmE and from SmC to SmG, was investigated by transient photocurrent measurements. It was found that the carrier transport is ambipolar and depends on neither temperature nor electric field. The ambipolar mobility, which ranged in $10^{-4} \sim 10^{-2} \text{ cm}^2/\text{Vs}$, in the two series exhibited abrupt increase in accordance with the upgrade of the molecular alignment. The mobility was analyzed by 2-dimensional hopping model and showed a good agreement with the model, in which the mobility is determined primarily by the molecular distance among the nearest neighbors in the smectic layer.

The photoconductive liquid crystals, that is, self-organizing molecular semiconductors, are promising as organic opto-electronic materials in the next generation.

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Biography

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