Impurity Effect in Self-organizing Molecular Semiconductors

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Abstract

The impurity effect on the carrier transport in a 2-phenylnaphthalene derivative of 6-(4'-octylphenyl)- 2-dodecyloxynaphthlene (8-PNP-O12), which is a liquid crystalline photoconductor and we call *Self-organizing Molecular Semiconductors (SOMS),* was investigated with a two series of impurity materials, i.e., polyacenes and terthiophenes. The carrier transport in impurity doped 8-PNP-O12 exhibited curious impurity effects which were never observed in solid materials systems: the carrier transport was affected not only by an energy level of impurity materials but also their molecular structure; its activation energy depended not only on the energy level of impurity molecules but also on their concentration; the carriers were transported by two different mechanisms, i.e., the electronic and ionic conduction. All these unique properties are discussed in relation to the nature of liquid crystalline molecules. i.e., fluidity and self-organization.

Introduction

Recently, it has been discovered that some of liquid crystals exhibit the very fast electronic conduction characterized by a fast mobility over 10^{-3} cm^2/Vs in mesophases.[1,2] Interestingly, this mobility depends on neither temperature nor electric field, which is quite different from the conventional amorphous semiconductors such as molecularly doped polymers with small organic semiconductors and their vacuum evaporated thin films. Thus, these materials are being recognized as a new class of organic semiconductors. Typical examples are triphenylenes of discotic liquid crystals and 2-phenylbenzothiazole of smectic liquid crystals. Above all, in the latter, it had been believed for a long time that the electrical conduction was ionic for a long time since the electrical properties of liquid crystals were reported first in late 1960s. It is understandable because the smectic liquid crystals often exhibit liquid-like fluidity.

These types of materials exhibit self-organization spontaneously when condensed, as shown in Fig. 1.

Therefore, we call this new type of organic semiconductors *Self-organizing molecular semiconductor (SOMS)*. On the basis of our study on the smectic liquid crystals,[2-8] we can describe the general features of carrier transport in self-organizing molecular semiconductors as follows:

(1) Anisotropic carrier transport
(2) Two-dimensional hopping transport in smectic layers
(3) Very fast carrier mobility ranges from 10^{-4} to 10^{-2} cm^2/Vs
(4) Bipolar carrier transport
(5) Independence of electric field
(6) Independence of temperature in each mesophase

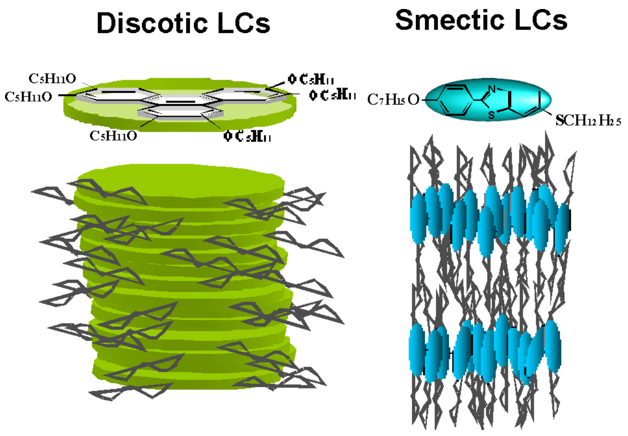

Figure 1. Self-organization of liquid crystalline molecules

These unique features give a clear contrast to conventional amorphous organic photoconductors/semiconductors whose molecular alignment is random. The self-organizing molecular semiconductor enjoys unique properties as described above. In addition, it should be noted that the fluidity allows us to fabricate uniform large-area device, and furthermore the boundary in the polydomain, which corresponds to polycrystals in crystalline materials, is electrically inactive and never cause deep defects states. For these reasons, the self-organizing molecular semiconductor is a promising material that extends practical application of organic semiconductors over the limitation of the conventional organic semiconductors. Because of the recent discovery of these materials, however, there is no basis where the device application should be established.

In this paper, we describe the unique carrier transport in a doped 2-phenylnaphthalene with two series of impurity materials, i.e., polyacenes and terthiophenes, and discuss the interesting experimental results in terms of *liquid crystallinity*.

Experimental

Materials and Liquid Crystal Cells

We used 2-phenylnaphthalene derivative of 6-(4'-octylphenyl)- 2-dodecyloxynaphthlene, 8-PNP-O12[3] as a model compound of SOMS and synthesized it with Suzuki coupling reaction catalyzed by $Pd(PPh_3)_4$ between 4-octyl-phenylboric acid and 2-bromo-6-dodecyloxy-naphthalene. The crude product was purified by recrystallization from hexane. As for the impurities, we used a series of polyacenes, i.e., anthracene, naphthalene, and naphthacene, and another series of terthiohenes, i.e., terthiophene (TTP), dodecylterthipophene (12-TTP) and dihexylterthiophene (6-TTP-6), whose molecular structures are shown in Fig.2. 8-PNP-O12 exhibits SmA and SmB phases, whose phase transition temperatures are 90°C and 101°C, respectively.

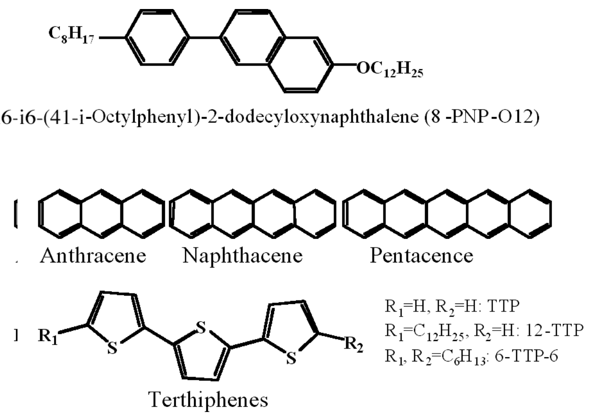

Figure 2. Chemical structures of materials used

Liquid crystal cells were prepared by capillary-filling the doped 8-PNP-O12 with the impurity material of a given concentration into the two ITO (In_2O_3). No particular treatment was done on electrode surface, resulting in polydomain structure with homogeneous molecular alignment, where rod-like liquid crystalline molecules are arranged parallel to the electrode surface. The average domain size was on the order of a few tens μm that was larger than the cell thickness. The resulting molecular alignment was stable under the electric field applied in the present study.

Measurement of Electrical Properties

The liquid crystal cell was mounted on the hot stage controlled at a given temperature by PID thermocontroller within an accuracy of 0.1 K. The carrier transport properties were evaluated by measuring transient photocurrents induced by a short pulse of N_2 laser (337nm, 600ps). The transient photo-signals were pre-amplified and recorded by a digital oscilloscope (Model Pro92, Nicolet Co.Ltd.). 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. With this transit time, carrier mobility was calculated from the equation : $\mu = d^2/V \tau_T$ (1), where μ is a carrier mobility, d a sample thickness, V an applied voltage, and τ_T a transit time.

Results and Discussion

1. A Series of Polyacenes

It is well known that the chemical impurities often form trap states in the host carrier transport materials, according to their relative energy levels of the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO) to the conduction levels of the host materials. One of the clear examples is the carrier transport in naphthacene-doped anthracene, in which the naphthacene molecules form hole-trap states and slow down the carrier mobility even in a small concentration of a few ppm. In this example, the mobility exhibits Arrhenium-type of activation energy of 0.4 eV, which does not depend on the impurity concentration.[9] This kind of trap-controlled carrier transport was observed also in the amorphous materials in which the conduction level is distributed, as is clearly demonstrated with a moleculary doped polymer with triphenylamine (TPA) and N-isopropylcarbazole (NIPC) system.[10]

In different phases of 8-PNP-O12 doped with anthracene including smectic mesophases and isotropic phase, there was no change in the mobility and its temperature dependence irrespective of carrier signs, compared with those of non-doped 8-PNP-O12. On the other hand, the carrier transport was significantly changed in the naphthacene doped 8-PNP-O12, which depended on the mesophases. For positive charges, the transient photocurrents became dispersive and the carrier mobility was decreased in SmB phase. Curiously, the activation energy was increase with an increase in the doping concentration as shown in Fig. 3.

In SmA phase, the transient photocurrents exhibited two kinks in different time regions interestingly, indicating two transit with different origins, as shown in Fig. 4. The fast transit corresponded to the mobility of 10^{-4} cm^2/Vs, which is slightly slower than that of undoped 8-PNP-O12. The second one was on the order of 10^{-5}~10^{-6} cm^2/Vs. Therefore, we attributed these two transits to the hole conduction dominated by shallow traps and ionic conduction due to the positively charged molecules. In fact, we observed two different activation energy of 0.26~0.35eV and 0.55~0.67eV corresponding to the first and second transits, respectively. In isotropic phase, the mobility was on the order of 10^{-5} cm^2/Vs and depended on the temperature irrespective of carrier signs and the doping concentration, whose activation energy was 0.26~0.37eV. For negative charges, we observed one transit in each transient photocurrent except for that in 1ppm doped SmB phase, where the mobility did not depend on the doping concentration irrespective of mesophases, whose activation energy was determined to be 0.55~0.62eV and 0.33~0.45eV for SmA and SmB phases, respectively.

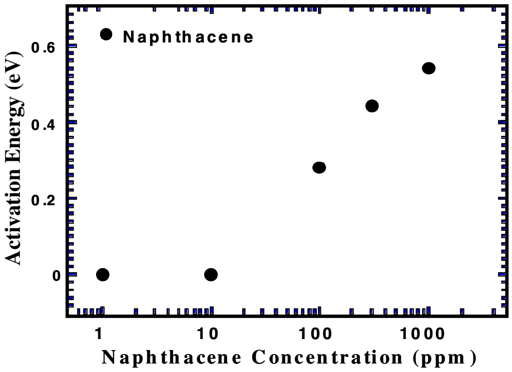

Figure 3. Activation energy of mobility in Naphthacene-doped 8-PNP-O12

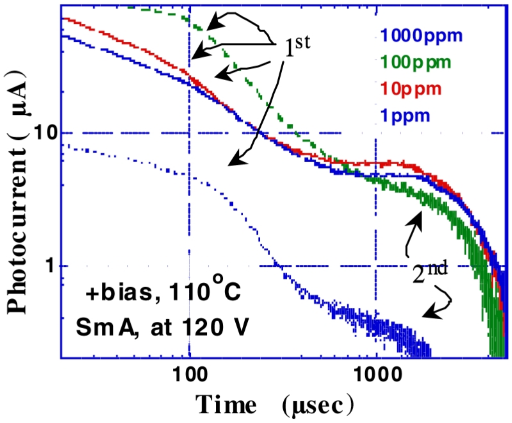

Figure 4. Transient photocurrents in SmA phase of Naphthacene-doped 8-PNP-O12

We could not measure the carrier transport properties in pentacene-doped 8-PNP-O12 systematically, because of very small solubility in organic solvents. In a slightly doped 8-PNP-O12, probably less than several tens ppm, we observed serious decrease in the mobility down to 10^{-5}~10^{-6} cm^2/Vs, which depended on the temperature. The activation energy in SmB phase depended on the carrier signs, and was 0.54eV and 0.33eV for positive and negative carriers, respectively. On the other hand, we observed almost same activation energy irrespective of the carrier signs in SmA and isotropic phases, and was 0.55~0.57eV and 0.29~0.31eV, respectively.

2. A Series of Terthiophenes

Next, we investigated the effect of terthiophenes, i.e., TTP, 12-TTP, and 6-TTP-6 as shown in Fig.1, on the carrier transport of 8-PNP-O12. All these materials show almost same HOMO and LUMO levels according to the molecular calculation. In fact, they show the ionization potential of 5.0~5.1eV determined by XPS. Therefore, it is expected that they play electron and hole traps with the trap depth of 0.3eV and 0.5eV in the 8-PNP-O12, respectively.

In TTP-doped 8-PNP-O12, the positive carrier mobility was not heavily degraded until TTP concentration exceeded over 1000ppm and gradually decreased down to $10^{-4}cm^2/Vs$. The activation energy of the mobility curiously depended on the doping concentration. In addition, we observed two transits in a small doping concentration, e.g., 100ppm: the fast one corresponds to the mobility slightly slower than that of the undoped 8-PNP-O12; the slow one does to the mobility on the order of 10^{-5} cm^2/Vs, indicating the ionic conduction. For negative carriers, we observed two transits the same as the positive ones did when the doping concentration was low, e.g., 100 ppm. With an increase in the doping concentration, the transport was degraded seriously and the mobility went down to the order of 10^{-5} ~10^{-6} cm^2/Vs. These behavior was very similar to those in the polyacenes doped 8-PNP-O12.

On the contrary, the carrier transport was seriously degraded when 6-TTP-6 was doped even in a very small concentration. Figure 5 shows the carrier mobility in the different phases of 6-TTP-6-doped 8-PNP-O12 as a function of doping concentration of 6-TTP-6.

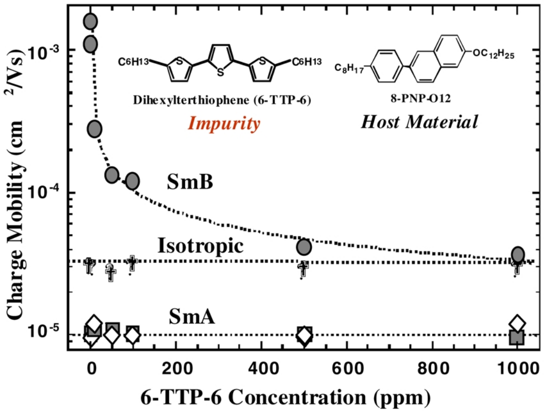

Figure 5. The carrier mobility of 6-TTP-6 doped 8-PNP-O12 as a function of the doping concentration.

In SmB phase, the positive carrier mobility was decreased from 10^{-3} cm^2/Vs to 10^{-4} cm^2/Vs with a small amount of 6-TTP-6 of 100ppm. The activation energy of mobility was 0.45eV and independent of the doping concentration. On the other hand, the carrier mobility in both SmA and isotropic phases was independent of the doping concentration. Interestingly, the mobility of SmA phase was smaller than that of the isotropic phase. This is due to the ionic conduction in SmA phase which is more viscous than isotropic phase.

In 12-TTP-doped 8-PNP-O12, its carrier transport properties were similar to those of the 6-TTP-6-doped ones, but its activation energy of hole mobility was 0.3eV and smaller than 0.45eV of 6-TTP-6-doped one, although the activation energy did not depend on the doping concentration.

Figure 6 shows the activation energy of positive mobility in TTP, 6-TTP-6, and 12-TTP doped 8-PNP-O12 as function of doping concentration. All these mobility is due to the electronic conduction. In 6-TTP-6 and 12-TTP-doped 8-PNP-O12, the activation energy was independent of the doping concentration while it depended on the doping concentration in TTP-doped one.

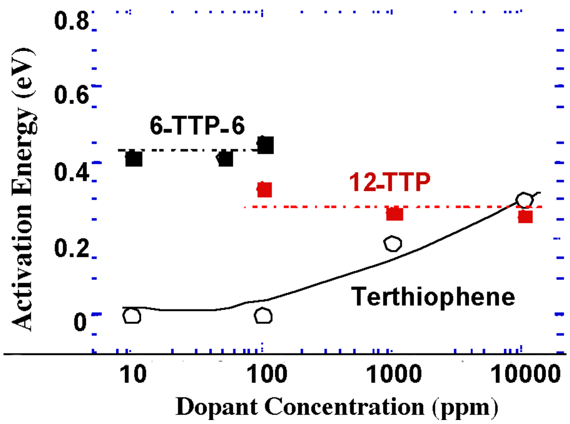

Figure 6. *Activation energy of 8-PNP-O12 doped with different terthiophenes as a function of doping concentration.*

This variable activation energy in TTP-doped 8-PNP-O12 is also observed in polyacenes doped one as described above.

We think that these curious carrier transport characteristics in doped 8-PNP-12 are attributed to microscopic inhomogeneous doping of the impurity molecules in the smectic layers: the impurity molecules should affect the carrier transport seriously even in a small concentration, if they sit within the smectic layer; however, the carrier transport should be tolerant of the impurity, if the impurity molecules sit in the inter-smectic layers. It is plausible that where the impurity molecules sit depends on the molecular structure of impurity molecule. Thus, we conclude that the alkylated terthiophenes favor substitutional doping in the smectic layers, where the impurity molecules work as efficient hole trap states and non-alkylated molecules including polyacenes do the interstitial doping in inter- smectic layers, resulting in inefficient carrier traps with a small capture cross-section for carriers.

In addition, it should be noted that the fluidity is another essential factor that determines the charge transport mechanism in doped liquid crystalline molecular semiconductors. It is likely that the ionized molecules start to move as ions once the electrons and holes are trapped in the impurity molecules that cause deep trap states in the smectic layers. Taking account of low viscosity in SmA and isotropic phases compared with that of SmB phase, we can explain why the ionic conduction takes place in SmA and isotropic phase of doped 8-PNP-O12.

Conclusion

The impurity-doped self-organizing molecular semiconductor exhibited very curious carrier transport properties such as the molecular structure-sensitive trap formation and concentration-dependent trap depth. These unique trap behaviors are closely related to the nature of liquid crystals, i.e., fluidity and self-organization.

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Biography

Jun-ichi Hanna received his B.S. and M.S. in Chemistry from Tokyo Institute of Technology in 1974 and 1976, respectively, and his Doctor degree in Imaging Science and Engineering from the same Institute in 1982. He joined the present laboratory as a research associate in Tokyo Institute of Technology in 1977 and promoted to professor of Faculty of Engineering in 1993. He has studied new imaging materials and their application to the imaging systems. His recent interests are in large-area electronic materials including low-temperature CVD poly-Si thin films and liquid crystalline semiconductors for imaging devices. hanna@isl.titech.ac.jp