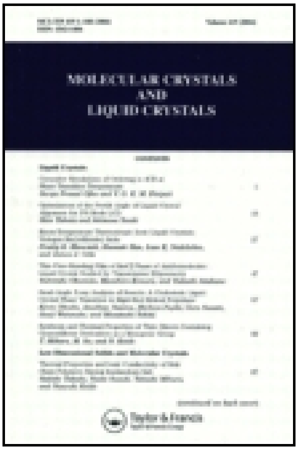

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Effect of Dipoles on Charge Carrier Transport in Smectic Liquid Crystal

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We first investigated the dipolar-dopant effects on the electronic charge transport in mesophases. We used phenylnaphthalene derivatives as a host smectic liquid crystal and cyanobiphenyls as a variable dipolar guest, and characterized the charge carrier transport properties of doped smectic mesophases by time-of-flight experiments. Comparing the experimental results with analytical calculation based on Gaussian disorder model, we found that the effect of dipoles is well explained by additional energetic disorder induced by carrier-dipole interaction, and that the induced energetic disorder is proportional to the square root of the dopant concentration c ($\sim c^{1/2}$) for smectic mesophases, while it is proportional to $c^{2/3}$ for non-oriented materials. This indicates that the ordered molecular alignment in smectic mesophases lowers energetic disorder. This study gives us an insight into the effect of dipoles in ordered molecular systems and the better molecular design of liquid crystals as an organic semiconductor.

Keywords: dipole moment; hopping transport; organic semiconductor

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I. INTRODUCTION

Since the electronic conduction was discovered in the columnar and smectic mesophases, various liquid crystals have been investigated for a new type of organic semiconductor exhibiting self-organization and high mobility [1–3]. At the same time, the mechanism of electronic

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transport in liquid crystals has been studied in both experimental and theoretical points of view. In fact, we have clarified that the charge transport properties in the smectic mesophases are well-understood by a hopping transport in a narrowly Gaussian-distributed localized states, i.e., density of states (DOS) [4], where carriers can hop at a high rate from molecule to molecule. Thus, liquid crystals are very attractive for opto-electronic device applications. This new aspect of mesophase materials has been recognized recently and is leading to a new development of liquid crystals as a new type of organic semiconductors [5].

The "liquid-like" nature in mesophases enables us to prepare a self-organized homogeneous film with large domains of ten micrometers easily by wet-processes. On the other hand, the "crystal-like" nature in them provides self-organized conduction channels for an effective carrier transport with few defects.

In molecularly doped polymers, it is well-known that dipoles originating from both semiconductor molecules and a host matrix govern their charge transport properties due to carrier-dipole interaction dominantly [6]. The distribution of the DOS in such disordered systems can be described by a formalism based on the Gaussian-disorder model proposed by Bässler [7]. The energetic disorder of the DOS causes a reduction in the mobility as well as its field and temperature dependence. Thus the concentration and strength of dipoles are the major factors to determine the charge transport properties in disordered materials systems.

As described above, the charge carrier transport in the mesophases is described in the same framework as the charge carrier transport in disordered material systems, but it is characterized by a small Gaussian width of 40 to 60 meV instead of a large width of 100 to 120 meV for disordered materials including the molecularly doped polymers [4,6]. If dipolar materials are doped into a mesophase, additional energetic disorder would give rise due to the carrier-dipole interaction. Their effects, however, would be different because of the "ordered" nature of the mesophase where the doped dipolar materials also align and orient according to the host liquid crystalline molecules: the randomness of the dipolar orientation would be limited.

In this paper, we have investigated the effect of the dipolar dopants on the charge-carrier transport properties in the smectic phases of phenyl naphthalene derivatives, which is a typical rod-like liquid crystals exhibiting smectic mesophases and whose carrier transport properties are well characterized: how the dipoles affect the charge carrier transport properties in smectic mesophases and how the mobility is changed by doped dipoles.

II. EXPERIMENT

For the present study, we prepared mixtures of a liquid crystal and a dipolar dopant. They were filled into the liquid crystal cells having ITO electrodes in capillary action at an isotropic temperature: we used 2-phenylnaphthalene derivatives, 2-(4′-octylphenyl)-6-dodecyloxynaphthalene (8-PNP-O12) [2] and 2-(4′-octylphenyl)-6-butyloxynaphthalene (8-PNP-O4) for a host liquid crystal, whose chemical structures are shown in Figure 1(a); we adopted cyano compounds such as 6-(4′-octylphenyl)-2-dodecyloxynaphthalene (10CB) and octylcyanide (8-CN) for a dipolar dopant having variable dipoles, which

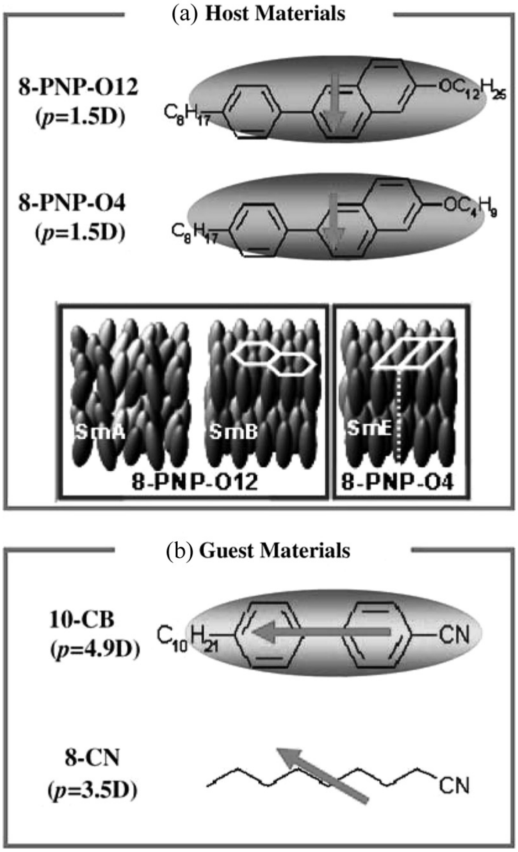

FIGURE 1 Chemical structures of (a) host and (b) guest materials values and arrows attached to each structure are calculated dipole moment by MOPAC PM3 method.

have strong dipole moments. Their dipole moments calculated by PM3-based calculations [8] (MOPAC7) are listed in Figure 1. The cell thickness was varied in the range of 5–10 μm. We confirmed that the molecules in the cells sit parallel to the substrate naturally in spite of no alignment layer, i.e., the planar alignment, wherein the smectic layers were perpendicular to the electrode surface.

Liquid crystalline molecules self-organize into mesophases and often separate guest materials out smectic layers. Therefore, we have to be careful about the inhomogeneity when we mix liquid crystals with non-liquid crystalline materials.

The doped samples prepared as described above were used in the time of flight (TOF) experiments to characterize their charge carrier transport properties. We used a N_2 laser (a pulse width = 600 ps) for photo-excitation. Experimental details were described elsewhere [2]. The transit time t_T was determined by a shoulder ("Kink point") in the linear plot of the resulting transient photocurrent, where we were careful to take shoulders originating from a RC-time constant $RE \ll t_T$ and space charge: $q \ll CV$, where R is external register, C is cell capacitance, and V is applied voltage. The mobility, μ at various applied voltage V was calculated from $\mu = L^2/t_T V$, where L is a cell thickness.

III. RESULTS AND DISCUSSION

Figure 2 shows double logarithmic plots of typical photocurrents for doped samples. All of signals have a clear kink point exhibiting a transit time. As is clear, the transit times depend on a concentration of

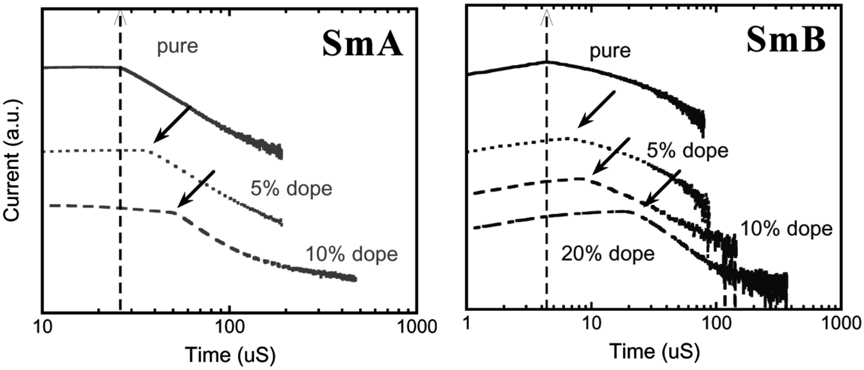

FIGURE 2 Typical photo transient current for 10CB doped 8-PNP-O12 parametric in dopant-molar concentration.

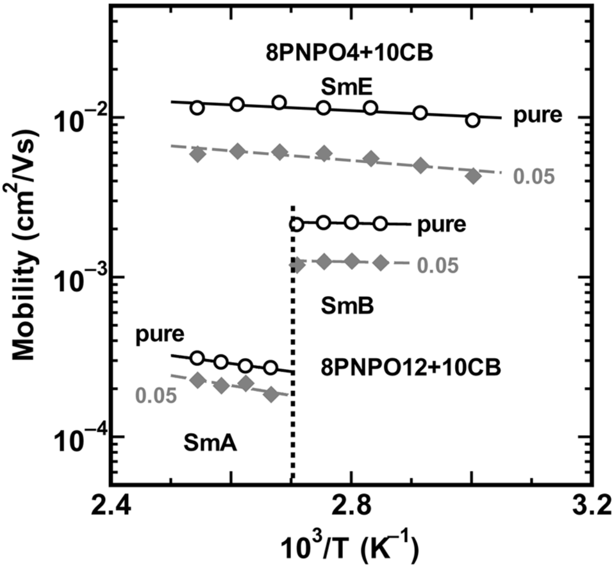

FIGURE 3 Temperature dependence of the mobility in 10CB doped 8-PNP-O12 (for Iso, SmA and SmB phase) and 10CB doped 8-PNP-O4 parametric in molar concentration of dopants.

dopant. The mobility decreases with increasing its concentration. This dependence was found in both SmA and SmB phases.

Figure 3 shows the mobility for 10CB-doped samples as a function of temperature for non-doped and 5% 10CB-doped samples. The mobility decreases with an increase in 10CB-concentration. All of the plots depend on temperature *T*, indicating thermally activation type of behavior. Before discussing the effect of dipoles, we consider the origin of such a reduction of mobility in the doped samples. There are some possible candidates to cause the reduction such as chemical traps associated with dopant molecules that follow Hoesterey-Letson formalism [9] and a dilution effect of dopant molecules that results in increase of average intermolecular distance in the smectic layer. We confirmed that the results plotted in Figure 3 fail to follow the Hoesterey-Letson formalism, and exhibit a reduction of mobility as a function of average distance of LC molecules steeper than that expected from the exponential relation resulting from the dilution effect. Thus we attributed the present behavior of the mobility in the doped samples to the effect of dipolar dopants.

It is well accepted that the mechanism of charge transport in amorphous organic materials is explained by disorder formalism proposed by Bässler [7]. In this model, temperature dependence is dominated not by activation energy but by energetic disorder of the DOS. This model also explains the field dependent mobility that is always observed in the amorphous materials. We could not see any field dependence of the mobility in the doped samples. In our Monte-Carlo simulation based on the disorder model for mesophases [4], however, we found that the mobility does depend on temperature as denoted by Eq. (1) at certain temperature range where the mobility does not depends on electric field:

$$\mu = \frac{e}{kT} A \exp\left[-B\left(\frac{\sigma}{k_{\mathrm{B}}T}\right)^2\right], \tag{1}$$

where A is $2.9 \times 10^{-4}\,\mathrm{cm}^2/\mathrm{Vs}$ and $B = 0.67$. This model is based on the fact that the localized states where carriers can hop have energetic disorder, which form Gaussian density of states. In the Gaussian DOS, photo-generated carriers also distribute in a Gaussian. In this case, the average level of the carrier distribution has temperature dependence. Then the activation energy depends on temperature: $\sim\sigma^2/k_{\mathrm{B}}T$. Thus the mobility follows Eq. (1). Using this equation, all of the plots can be fit and the energetic disorder induced by carrier-dipole interaction in smectic mesophases is evaluated. The detail discussion will be described in elsewhere [10].

The important point of this paper is that the energetic fluctuation forms Gaussian DOS and the induced energetic disorder is proportional to the square root of c: $\Delta\sigma_{\mathrm{d}} \sim \sqrt{c}$, where c is a concentration of dipolar dopant. This relation is completely different from the case of isotropic system including the amorphous materials.

However, the mobility of 8-CN doped 8-PNP-O12 hardly depend on a concentration of 8-CN. It is quite interesting because 8-CN has a large dipole moment comparable to 10-CB. In order to clarify the reason why 8-CN has little effect on the charge carrier transport in both SmA and SmB phases, we studied X-ray diffraction in 8-CN doped samples. And it shows that the layer spacing of smectic layers was increased with an increase in the 8-CN concentration, while it never happened in the 10-CB doped samples. This fact indicates that 8-CN, which had no core moiety such as a biphenyl, is phase-separated into the inter-smectic layers. Therefore, the carriers in the smectic layers are hardly affected by the dipoles of phase-separated 8-CN because of a long distance between the carriers and the dipoles, whose minimum distance is a half of molecular length of the host molecules, 8-PNP-O12 and 8-PNP-O4, i.e., ~18 Å and ~14 Å. This distance is 10 times longer than that of the minimum intermolecular distance between carriers and (~3–5 Å) dipoles in a smectic layer, so that it is quite reasonable that the induced energetic disorder for 8-CN doped samples becomes is one-tenth compared with that for 10CB doped samples. These are completely different from the case of disordered system such as amorphous organic materials whose dipolar effects are more obvious and depend on $c^{2/3}$ [6]. The present concentration dependence of $c^{1/2}$ observed in the 10CB doped samples obviously reflects the molecular alignment of dipolar dopant in the smectic layer.

IV. CONCLUSION

We have investigated the dipolar effect on the charge carrier transport in smectic mesophase with a host-guest system of liquid crystalline 2-phenylnaphthalene derivatives and cyano compounds. As a result, we found that the contribution of an additional energetic disorder from dipolar dopants depends on where the dopant molecules are located: their contribution to $\Delta\sigma_{\mathrm{d}}$ is quite obvious when the dopant molecules sit in the smectic layers, while it is negligible when they sit in the inter-smectic layers. The value of $\Delta\sigma_{\mathrm{d}}$ is proportional to $\sim c^{1/2}$ which is completely different from the case of amorphous organic semiconductors. This indicates that the smectic molecular alignment affects lowering of energetic disorder attributed to the dipolar dopants. Thus, it should be noted that the liquid crystalline alignment has an advantage over isotropic materials in terms of the energetic disorder in the charge carrier transport. This is backed up by 2-dimensional charge carrier transport in the smectic layer and a unique nature of phase-separation of dopants from the conductive channel.

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