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SYNTHESIS AND CHARACTERIZATION OF LIQUID CRYSTALLINE SEMICONDUCTING MATERIALS, DIALKYL-2-PHENYLNAPHTHALENE DERIVATIVES—MESOMORPHIC BEHAVIOR AND CHARGE CARRIER TRANSPORT

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For establishment of high electronic charge carrier transport at ambient temperature, dialkyl derivatives of 2-phenylnaphthalene have been synthesized and characterized their liquid crystalline behaviors and photoelectrical properties. These materials exhibited smectic mesophases (Smectic A, B and E phases), at fairly low temperature range extended down below ambient temperature. Fast electronic transport of positive carriers was observed in SmE phase of 2-(4'-octylphenyl)-6-butyl-naphthalene at 30°C, whose mobility was over $10^{-2} \text{ cm}^2/\text{Vs}$.

Keywords: calamitic liquid crystal; carrier transport; hole mobility; photoconductivity; 2-phenylnaphthalene; smectic phase

INTRODUCTION

Recently it was discovered that some types of liquid crystals including not only the discotics [1] but also the calamitics [2] exhibit very fast electronic carrier mobility over $10^{-2} \text{ cm}^2/\text{V}$, which is 3 to 4 orders of magnitude higher than that of the conventional amorphous organic semiconductors practically used. Liquid crystalline molecules self-organization in columnar or layered structure, in which the molecules are closely packed and aligned in some orders. Therefore, now, liquid crystals are being recognized as

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a new class of organic semiconductors, i.e., *self-organizing molecular semiconductor (SOMS)*.

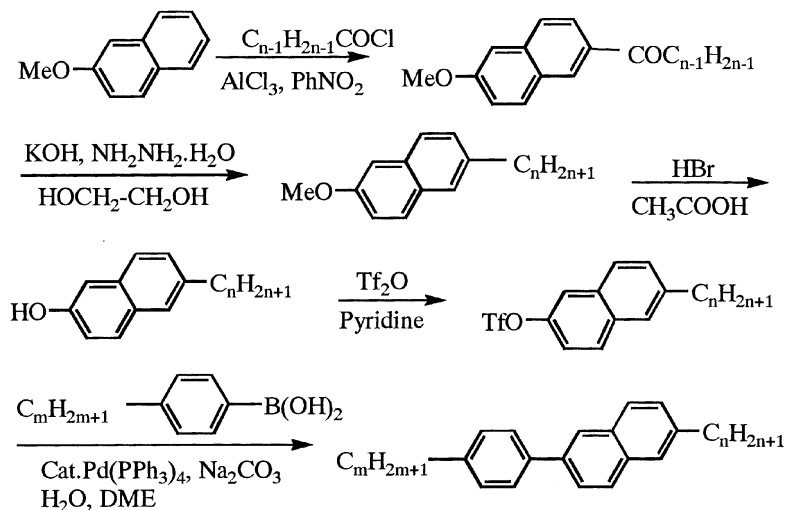
We have reported that as a typical example, 6-(4'-alkylphenyl)-2-alkoxynaphthalene derivatives (m-PNP-On), which are calamitic liquid crystals [3–10] and exhibit preferentially smectic mesophases (SmA, SmB, and SmE phases), show the fast charge carrier transport characterized by bipolar mobility over $10^{-4} \text{ cm}^2/\text{Vs}$ and $10^{-2} \text{ cm}^2/\text{Vs}$ at best. But temperature ranges of mesophases in these compounds are higher than 55°C , where the fast carrier transport is observed. Therefore, it would be very attractive for device application that a material exhibits liquid crystallinity and high carrier mobility at ambient temperature: in display applications, a liquid crystalline mixture is very convenient for reduction of mesophase temperature down below ambient temperature indeed, but it is not always acceptable in this new property; this is because the guest material can be a charge carrier trap or a diluent, often resulting in deterioration of the carrier transport properties. In this study, for establishment of high electronic carrier transport at ambient temperature, we designed and synthesized several dialkyl-2-phenylnaphthalene derivatives, i.e., 2-(4'-alkylphenyl)-6-alkylnaphthalene derivatives (m-PNP-n) on the basis of our previous results of 6-alkoxynaphthalene derivatives. In this report, we have characterized and discussed their mesophase behaviors and photoconductive and carrier transport properties in comparison with those of 6-alkoxynaphthalene derivatives.

SYNTHESIS

We used 2-Methoxynaphthalene as the starting material and derived it to 6-alkyl-2-naphthol via Friedel Craft acylation, and successive hydrazine reduction, and followed by demethylation by hydrobromic acid. And the resulting 2-naphthols were derived to their triflate and exploited for Suzuki coupling reaction [11,12] with 4-alkylphenylboronic acid in the presence of palladium catalyst, as shown in Scheme 1. The resulting dialkyl derivatives of 2-phenylnaphthalene (m-PNP-n) were purified by flush column chromatography with hexane as eluent, and followed by successive recrystallization several times.

CHARACTERIZATION

The mesophoric behaviors in these 6-alkyl-2-phenylnaphthalenes were studied with observation of optical texture under polarized optical microscope, DSC measurements (Seiko Instruments Inc.) and X-ray diffraction analysis.



SCHEME 1 Synthetic route of Dialkynaphthalene derivatives.

Phase transition temperature of 6-alkyl-2-phenylnaphthalene are summarized in Table 1. These materials exhibited smectic mesophases such as smectic A (SmA), SmB, and sometimes SmE phase. These behaviors were similar to alkoxy-naphthalene analogues, but their mesophase temperature ranges were fairly low compared with the alkoxy-naphthalene analogues. Some of them exhibited the highly ordered smectic phase below room temperature. The texture profiles of 8-PNP-4, for example, are shown in Figure 1, and X-ray diffraction data are shown Table 2, respectively.

Judging from these results, it is clear that the distance of intersmectic layers is determined by the molecular length and the intermolecular distance in a smectic layer by the molecular order in the smectic layer but they did not depend on temperature. These data were almost same as those of Alkoxy-naphthalene analogues.

TABLE 1 Phase Transition Behavior of Dialkynaphthalene Derivatives

8-PNP-4	Cryst. -3.5 SmE 75.2 SmB 88.8 SmA 93.0 Iso.
8-PNP 6	Cryst. 7.6 SmE 77.2 SmB 98.2 SmA 102.5 Iso.
8-PNP-12	Cryst. 39.1 SmB 92.7 SmA 97.2 Iso.
10-PNP-10	Cryst. 67.6 SmB 94.7 SmA 100.4 Iso.
10-PNP-12	Cryst. 67.4 SmB 92.1 SmA 97.8 Iso.

unit: °C.

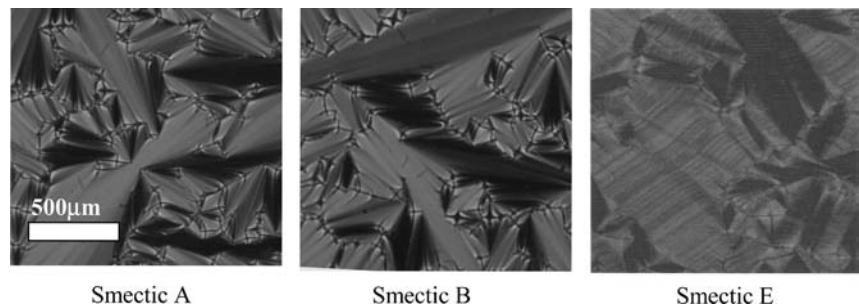


FIGURE 1 Micrographic texture profiles of 8-PNP-4.

TABLE 2 X ray Diffraction Data for Layer Spacing and Intermolecular Distance in Smectic Layers in the Smectic B Phase of 6-alkynaphthalene Derivatives

m–n	Smectic A	Smectic B	Distance of intermolecules	Crystal
8–12	34.2	35.9	4.6	33.4
10–10		36.5	4.6	34.0

unit of length: Å

PHOTOCONDUCTIVE MEASUREMENT

All the measurements on photo-electronic properties were carried out with a symmetrical sandwich-type cell consisting of two indium-tin oxide (ITO)-coated glass plates rubbed mechanically to realize homogeneous alignment in liquid crystalline phase. The cell was prepared by capillary-filled with the liquid crystals under isotropic phase temperature. The cell thickness was 15 μm. The resulting cell exhibit the polydomain texture consisting of fairly large fan-like domains on the order of 100 μm, so that it is quite possible that each domain has no boundaries between two electrodes. The cell was mounted on a hot stage whose temperature was controlled by thermocontroller (Mettler corp.) within an accuracy of 0.1°C.

To confirm their photoconductivity, photocurrent in steady-state was measured under UV light illumination from Xe lamp (500 W) equipped with a band-pass filter (UV33DS, Toshiba Glass Co. Ltd.) and a IR cut filter. The light intensity was 2.5 mW/cm². The carrier transport properties were evaluated with a transient photocurrent measured by time-of-flight (TOF) technique with N₂ laser (λ = 337 nm, 40 μJ/pulse, pulse width = 600 ps).

RESULT AND DISCUSSION

The photocurrent response was observed clearly irrespective of bias polarity of illuminated electrode in all the phases including isotropic phase. The dark conductivities in mesophases were estimated to be on the order of $10^{-12} - 10^{-13}$ S/cm from a linear relation in current-voltage characteristic at low electric field. The photocurrent was little smaller than 6-alkoxynaphthalene analogues at the same condition. Photocurrent response and current-voltage characteristics are shown in Figure 2 and Figure 3, respectively.

The typical transient photocurrents as a function of applied bias are shown in Figure 4. These curves are a little dispersive. We think that this is due to insufficient purification of the material. In fact, even in a trace amount of impurity contamination results in dispersive transport in the smectic liquid crystals. We could determine clearly the transit time from the inflection point of in their double logarithmic plots. The carrier mobility of dialkyl 2-phenylnaphthalene derivatives was on the order of 10^{-4} cm²/Vs in SmA phase, 10^{-3} cm²/Vs in SmB phase, and 10^{-2} cm²/Vs in SmE phase. It was absolutely independent of temperature and electric field in each mesophase, as shown in Figure 5 and Figure 6, and was not influenced even by the domain size in the cell [13,14]. These were the same results with alkoxy-naphthalene analogues.

The fact that the higher molecular order in mesophase becomes, the faster carrier mobility in these two series of phenylnaphthalene analogues indicates that the intermolecular distance between calamitic molecules in

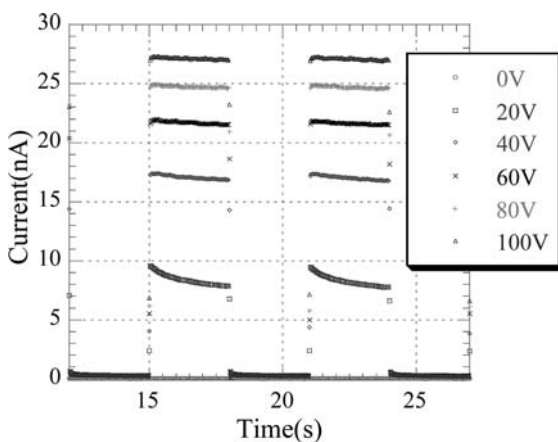


FIGURE 2 Photocurrent response at 31°C in the smectic E phase of 8-PNP-4. ($d = 15 \mu\text{m}$, $S = 16 \text{ mm}^2$, ITO/ITO)

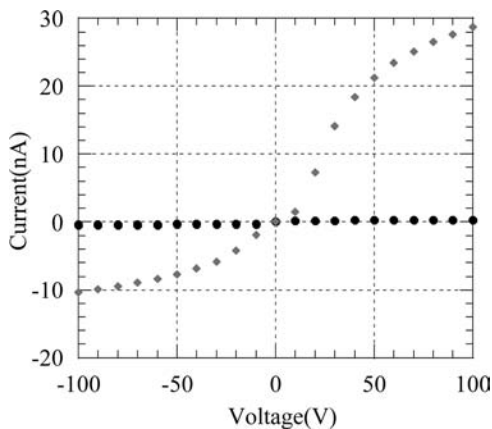


FIGURE 3 Photocurrent response at 31°C in the smectic E phase. of 8-PNP-4. ($d = 15 \mu\text{m}$, $S = 16 \text{ mm}^2$, ITO/ITO)

smectic layer determines the carrier mobility primarily. This is well understood in considering that the carrier transport in the smectic is governed by hopping transport among the molecular hopping sites.

CONCLUSION

2-(4'-alkylphenyl)-6-alkylnaphthalene derivatives that have very simple and stable molecular structure exhibited smectic mesophases even below

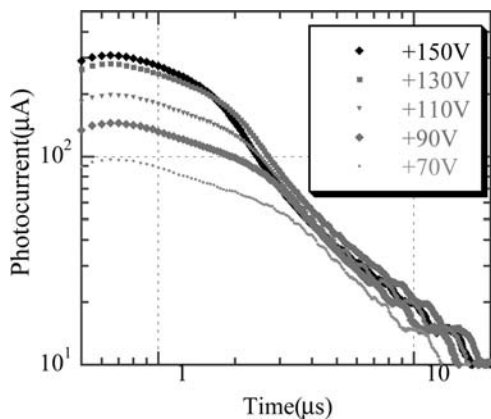


FIGURE 4 Transient photocurrent curves at 31°C in the smectic E phase of 8-PNP-4. ($d = 15 \mu\text{m}$, $S = 100 \text{ mm}^2$, ITO/ITO)

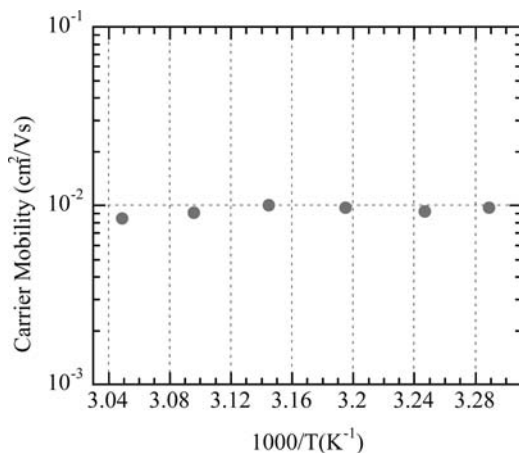


FIGURE 5 Temperature dependence on hole carrier mobility in the smectic E phase of 8-PNP-4. ($d = 15 \mu\text{m}$, $S = 100 \text{ mm}^2$, ITO/ITO)

room temperature, whose positive carrier mobility was on the order of $10^{-2} \text{ cm}^2/\text{Vs}$ in SmE phase irrespective of different carbon chains. This is the highest mobility ever achieved in calamitic mesophases in a single material at room temperature. No significant difference in mobility of 6-alkyl and alkoxy-2-phenylnaphthalene derivatives in each phase indicates

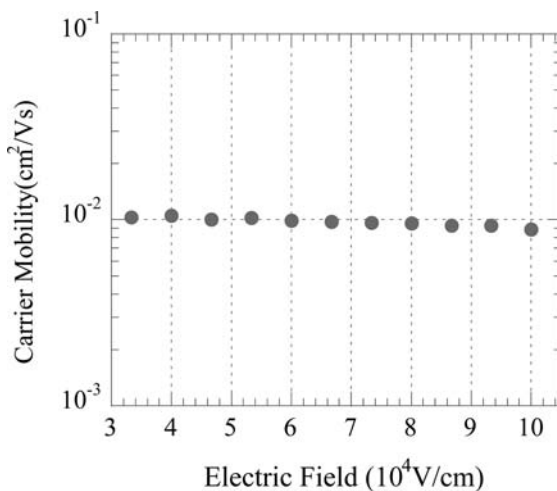


FIGURE 6 Electric field dependence on hole carrier mobility at 31°C in the smectic E phase of 8-PNP-4. ($d = 15 \mu\text{m}$, $S = 100 \text{ mm}^2$, ITO/ITO)

that the carrier transport is governed by molecular alignment in the smectic layer and affected little by chemical modification of core moiety. The present results are the first step to get a guiding principle for the materials design of high mobility self-organizing molecular semiconductor.

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