# Charge carrier transport properties of liquid crystalline biphenyl dimers

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## Abstract

In recent years, liquid crystals have attracted increasing attention as a new type of quality organic semiconductors due to the superior charge carrier transport properties when compared to conventional amorphous organic semiconductors. In order to determine how best to design the molecular structure of "liquid crystalline semiconductors", a liquid crystalline biphenyl dimer  $\{\alpha, \beta\}$  $\omega$ -bis (4-propylbiphenyl-4'-yloxy) dodecane}: (B3BO12) and its derivative, { $\alpha$ ,  $\omega$ -bis (4-propylbiphenyl-4'-yloxy) octane}: (B3BO8) were synthesized and purified. The flexible spacer lengths were varied from 8 to 12 methylene units. The electrical properties of the dark and photo-conductivity were investigated by I-V measurement and carrier transport properties in the liquid crystal phase, using the time-of-flight (TOF) technique. The effect of dimer structure in terms of liquid crystallinity and charge carrier transport properties in comparison with the corresponding monomer is also discussed.

#### 1. Introduction

Recent revived attention to organic crystals for organic field effect transistors (OFETs) reminds us of the historical studies on the electrical properties of organic single crystals in the 1950's [1]. Those lead to a new paradigm of organic semiconductor [2].

Because of a crystal-like molecular alignment in liquid crystals, it was very natural that a new curiosity was extended to the liquid crystal in the late 1960's [3]. However, this did not result in showing up another aspect of liquid crystals as a selforganizing molecular semiconductor. This is probably because of an accidental coincidence with Heilmier's attractive invention of the first display device utilizing a liquid crystal [4]. The electronic conduction in liquid crystals might be discovered at that time, if Heilmier's display device had not been proposed: his invention attracted considerable attention indeed and triggered a new study on the ionic conduction in liquid crystals [5], because this display device was based on so-called "dynamic scattering mode", where the drift of ions in a liquid crystal cell played a major role for display performance; in fact, many reports described the ionic conduction in various liquid crystals including smectics in the 1970's [6]. As a result, it was very natural that "a wrong recognition" that the intrinsic electrical properties in liquid crystals were governed by ionic conduction had been accepted since then. Thus, the exploration of electronic conduction in liquid crystals was succeeded in discotics having a large disc-shape core moiety and more-like molecular crystal [7,8], after Chandraschal's discovery of a discotic liquid crystal in1977 [9].

It is indeed in a discotic liquid crystal, i.e., hexaheptyloxytriphenylene (H6T) that the first electronic conduction in the liquid crystal was established in 1993 [10]. A

few years later, the electronic conduction was discovered in a calamitic liquid crystal, i.e., a 2-phenylbenzothiazole derivative (7O-PBT-S12) as well [11]. Since then, the electronic conduction was established in various liquid crystals, and it has become recognized to be a common feature in liquid crystals having an aromatic  $\pi$ -conjugated system. Thus, the continuous efforts to find a new aspect of electrical properties in liquid crystals and to understand their unique properties of charge carrier transport have been made in this decade. Nowadays, the liquid crystal is being recognized as a new class of quality organic semiconductors, which is characterized by a high mobility exceeding  $10^{-3}$  cm<sup>2</sup>/Vs and up to  $10^{-1}$  cm<sup>2</sup>/Vs, which is  $10^3$  to  $10^4$  times higher than those in amorphous organic semiconductors practically used.

In this paper, the charge carrier transport properties of liquid crystalline biphenyl dimer { $\alpha$ ,  $\omega$ -bis (4-propylbiphenyl-4'-yloxy) dodecane}: (B3BO12) are investigated and the effect of dimer structure in terms of liquid crystallinity and charge carrier transport properties in comparison with the corresponding monomer is also discussed.



Figure 1. Molecular structure of B3BO12.

# 2. Experiment

## A. Material Preparation

The two biphenyl dimer { $\alpha$ ,  $\omega$ -bis (4-propylbiphenyl-4'-yloxy) octane}: (B3BO8) and { $\alpha$ ,  $\omega$ -bis (4-propylbiphenyl-4'-yloxy) dodecane}: (B3BO12) were prepared by the reaction of 4-propyl-4'hydroxybiphenyl with dibromooctane and dibromododecane, respectively in dry enthanol with sodium hydroxide as base according to the reported procedure [12].



Scheme 1. Synthetic pathway for B3BOn.

The final crude product was purified carefully by repeating recretallization a few times.

## **B.** Measurements

Differential Scanning Calorimetry (DSC) experiments were performed on a Seiko Inst. DSC 5400C at a heating rate of  $10^{\circ}C/min$  and a cooling rate of  $10^{\circ}C/min$ . The instrument was calibrated with standard samples of indium.

Polarizing Optical Microscopy (POM) studies were carried out on a Nikon optical polarizing microscope equipped with a Mettler Toledo FP900 hot stage. Each powder-like sample was paced on a glass slide, covered with a glass cover slip, and heated or cooled on the hot stage at a rate of 10°C/min.

X-ray Diffractometry (XRD) experiments were carried out on a Rigaku RAD-2B. The powder samples were sealed in glass capillaries and placed into a homemade hot stage. Powder samples were heated above their respective clearing temperatures and then cooled to room temperature to ensure that all of the samples had equivalent thermal histories.

UV Absorption spectrum measurements were performed on a HITACHI 228 spectrophotometer equipped with a homemade hot stage.

Transient photocurrents were measured by a conventional time-of-flight (TOF) setup. In this work, TOF measurements were done using a N<sub>2</sub> laser ( $\lambda$ =337nm, pulse duration=600ps) as an excitation light source. Bias voltage was applied by Kikusui PVA250 and the transient photocurrent was recorded by a digital oscilloscope Nicolet.

# 3. Results and Discussion

#### 3.1 Structural and Thermal Properties

The transitional properties of the  $\alpha$ ,  $\omega$ -bis (4-propylbiphenyl-4'-yloxy) dodecane (B3BO12) are shown in the Figure 2. The sample was treated as follows, first heated at 40 °C/min into the isotropic phase, then cooled to -30 °C at 40 °C/min, held at that temperature for 5 min, subsequently reheated into isotropic phase at 10 °C/min and then cooled to -30 °C at 10 °C/min. The melting points and the liquid crystalline transition temperatures given are the peak maxima in the DSC trace. It shows that the melting point from cooling and heating run is about 158 °C and 166 °C, respectively. The phase transition temperature from crystal to liquid crystal on cooling process is about 131 °C and the width range of the mesophase of B3BO12 is around 30 °C. The mesophase texture of B3BO12 at 150 °C is shown in Figure 3. However, its derivative,  $\alpha$ ,  $\omega$ -bis (4-propylbiphenyl-4'-yloxy) octane: (B3BO8), the phase transition temperature from crystal to isotropic is around 165 °C. Figure 4 shows the transitional properties of B3BO8 and no mesophase is observed. The reason might be that the crystallization becomes easier due to the stronger intermolecular interaction in which the mesogenic units were linked by shorter alkyl spacer, and for its corresponding monomer 4-propyl-4'hydroxybiphenyl (3HB), the transition temperature from crystal to isotropic is around 150 °C and no mesophase is observed too, which maybe caused by the strong effects of H-bond from end to end.



Figure 2. DSC curve of B3BO12 (heating and cooling processes at 10 °C/min)



Figure 3. Photomicrograph under crossed polarizers of B3BO12 at 150 °C.



Figure 4. DSC curve of B3BO8 (heating and cooling processes at 10 °C/min)

The X-ray diffraction data obtained for the liquid crystalline B3BO12 are shown in Figure 5 and the molecular length of B3BO12 calculated by WinMoPac is around 40 Å. This plot shows that the molecular alignment is highly ordered in this Sm X phase, but It is difficult to determine which Smectic phase it is only by these measurements.



Figure 5. X-ray diffraction pattern for B3BO12 at 150 °C.

#### 3.2 Optical Properties

The absorption properties of B3BO12 for UV-VS spectrum is shown in Figure 6, which indicates that this biphenyl compound almost can not absorb the incident light at 337 nm which is used as excitation light in time-of-flight (TOF) measurement to generate the photo carriers under different temperature.



**Figure 6.** Absorption spectrum of B3BO12 in condensed phase in quartz cell at different temperature. (the quartz cell thickness was 1.5  $\mu$ m)

## 3.3 Electric Properties

The photocurrent and dark current of B3BO12 are shown in Figure 7. In the Sm X phase, the values of dark current are under the order of nA and no obvious photocurrent response was obtained by the stationary irradiation, which is because the biphenyl dimer can hardly absorb the incident light from 350~400 nm.



**Figure 7.** Photocurrent respons to UV light illumination in the Sm X phase (150 °C). ITO/ITO cell was used, the thickness was 15 µm, electrode area 16 mm<sup>2</sup>. Wavelength and intensity of excitation light was 350 ~ 400 nm and 2.5mW/cm<sup>2</sup>, respectively.

On the other hand, the transient photocurrent of B3BO12 was observed by conventional time-of-flight (TOF) experiments. The value of the transient photocurrent is small under the order of nA which is from the photohole injection from the  $In_2O_3$ -SnO<sub>2</sub> (ITO) electrode when illuminated with a 337 nm light pulse of 600 ps from a nitrogen laser. Figure 8 shows a transient photocurrent of B3BO12 for positive charge carriers in the crystal phase (55 °C) in a 15 µm thick ITO cell as a function of applied biases.



**Figure 8.** Transient photocurrent for positive charge carriers of B3BO12 in the crystal phase (55 °C). ITO/ITO cell was used, the cell thickness was 15  $\mu$ m and electrode area 16 mm<sup>2</sup>. Wavelength of excitation light was 337 nm, and intensity 10 mJ/pulse.

As the photocurrent is quite small, we must use the large resistance to get the signal which maybe increases the influences of RC delay. The double logarithmic plot shows a kink point, which indicates a transit time when the positive carriers arrive at the counter electrode and the mobility is estimated to be around  $2.5 \times 10^{-3} \text{ cm}^2 \text{v}^{-1} \text{s}^{-1}$  by the equation (1).

$$\mu = \frac{d}{Et_T} = \frac{d^2}{Vt_T} \tag{1}$$

Where  $\mu$  is the mobility, d is the sample thickness, E is the electric field, V is a given applied voltage and  $t_T$  is the transit time. Here the transit time is determined by a kink point of two lines in the double logarithmic plot of the current as a function of time.

Figure 9 shows a transient photocurrent for positive carriers of B3BO12 in the Sm X phase (150 °C). The mobility of B3BO12 in this mesophase is around  $1.4 \times 10^{-3}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> calculated by equation (1).



**Figure 9.** Transient photocurrent for positive charges of B3BO12 in the Sm X phase (150 °C). ITO/ITO cell was used, the cell thickness was 15 µm and electrode area 16 mm<sup>2</sup>. Wavelength of excitation light was 337 nm, and intensity 10 mJ/pulse.

Judging from this high mobility of 10<sup>-3</sup> cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, It is not the ionic conduction caused by contamination of the impurities, but hole conduction. In order to increase the photocurrent and get nondispersive transient photocurrent, this sample needs to be further purified by chromatography and recrystallization. Maybe we could obtain more precious transient time. Furthermore, we will investigate the charge carrier mobility of dependence on temperature and electric field compared with that of monomer 4hexyl-4'-hexyloxybiphenyls (6O-BP-6) which has strong temperature and electric field dependence of carrier mobility [13].

## 4. Conclusion

Dimeric liquid crystals are a class of liquid crystals in which two rigid mesogenic units are joined by a flexible spacer and the symmetric dimer liquid crystals proved useful as model compounds for the polymers [14]. In this study, two biphenyl dimers B3BO8 and B3BO12 were prepared. The phase transition temperature of B3BO12 from crystal to liquid crystal on cooling process is about 131 °C and the width range of this mesophase is about 30 °C. however, it is found that there is not any mesophase for B3BO8. The charge carrier transport properties of B3BO12 are investigated by TOF technique at 337 nm and the mobility at Sm X and crystal phase is estimated to be around  $10^{-3}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> which is attributed to the hole conduction.

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## References

- [1] H. Akamatsu and H. Inokuchi, J. Chem. Phys., 18, 810-811 (1950).
- [2] H. Inokuchi, Bull. Chem. Soc. Japan, 27, 22-27 (1954).
- [3] S. Kusabayashi and M.M. Labes, Mol. Cryst. Liq. Cryst., 7, 395-405 (1969).
- [4] G.H. Heimeier, L.A. Zanoni, and L.A. Burton, Dynamic scattering: A new electrooptic effect in certain classes of nematic liquid crystals, Proc. IEEE 56, pg. 1162-1171. (1986).
- [5] G.H. Heilmeir and P.M. Heyman, Phys. Rev. Lett., 18, 583-585 (1967).
- [6] G. Drefel and A. Lipnski, Mol. Cryst. Liq. Cryst., 55, 89-100 (1979).
- [7] N. Boden, R.J. Bushby, J. Clements, M.V. Jesudason, P.F. Knowles, and G. Williams, Chem. Phys. Lett., 152, 94 (1988).
- [8] P.G. Shouten, J.M. Warman, M.p. de Haas, M.A. Fox, and H.L. Pan, Nature, 353, 736 (1991).
- [9] S. Chandrasekhal, B.K. Sadashiva, and K.A. Suresh, Pramana, 7, 471 (1977).
- [10] D. Adam, F. Closs, T. Frey, D. Funhoff, D. Harrer, J. Ringsdorf, P. Schuhmacher, and K. Siemensmeyer, Phys. Rev. Lett., 70, 457-460 (1993).
- [11] M. Funahashi and J. Hanna, Phys. Rev. Lett., 78, 2184-2187 (1997).
- [12] H.K. Bisoyi and S. Kumar, Phase Transitions, 79, 285-292 (2006).
- [13] K. Kurotaki, H. Haruyama, Y. Takayashiki and J. Hanna, Chemistry Letters, 35, 1194 (2006).
- [14] C.B. Zhang, Z.G. Huang, Z.Q. Cong, and B.Z. Yin, Chinese J. of Liquid Crystals and Displays, 5, 375-383 (2005).