Electronic Conduction in Biphenyl Liquid Crystals

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A series of 4-alkyl-4′-alkoxylbiphenyls, which are one of the representative calamitic liquid crystals having a small aromatic core moiety, has been synthesized and their charge carrier transport properties are characterized in order to examine how small the core size can be for a high mobility. The biphenyls exhibit both smectic B and E phases and the hole transport characterized by a high mobility of $10^{-3}\,cm^2\,V^{-1}\,s^{-1}$ in the smectic mesophases. The mobility depends on temperature in both smectic phases, and furthermore it depends on the electric field in the smectic E phase. The fact that such a small molecule of biphenyl exhibits the mobility comparable to those of triphenylenes and TPD (*N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)[1,1′-biphenyl]-4,4′-diamine) gives an insight into the molecular design of high mobility liquid crystalline materials.

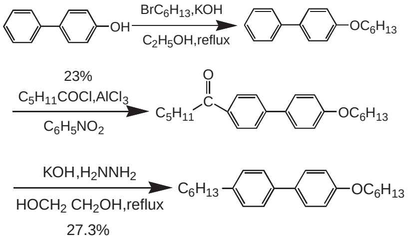
Since the electronic conduction was discovered in both discotic and smectic liquid crystals in the 1990s,[1,2] in which the electrical conduction had been thought to be ionic for a long time, the liquid crystals become recognized to be a new class of organic semiconductors because of their high mobility up to 0.1–$1\,cm^2\,V^{-1}\,s^{-1}$.[3–5] And the liquid crystalline materials are attracting considerable attention increasingly for the device applications to organic FETs.

The high mobility in the liquid crystalline phases is attributed to a short molecular distance among the neighboring molecules resulting from self-organization of liquid crystalline molecules, where the hopping rate of charge carriers are enhanced because of enhanced transfer integral. Thus, the mobility goes up in stepwise when the molecular alignment is sophisticated accompanied with phase transition.[6,7] The mobility, however, is not always determined by a given mesophase that determined a molecular distance: the mobility is quite different in the liquid crystals having various types of core structures even in a particular mesophase.

Because of relatively recent attention to the electronic conduction in the liquid crystals, it has not been established yet how to design the liquid crystalline molecules as an organic semiconductor suitable for device applications, which require a high mobility, HOMO and/or LUMO level alignment to electrode materials, a low and wide temperature range for a mesophase, chemical stability in ambient atmosphere, etc.

Thus, we have studied the charge carrier transport properties in biphenyls (BPs), which is one of the smectic liquid crystals having a small aromatic core moiety in order to examine how the core size affects the charge carrier mobility, and will report the first electronic conduction in the biphenyl derivatives characterized by a fairly high mobility of $10^{-3}\,cm^2\,V^{-1}\,s^{-1}$.

The biphenyls derivatives were synthesized by Wolf–Kishnner reduction of corresponding alkoxybiphenylketones as shown with an example of 6O-BP-6 abbreviating the number of carbon atoms in alkyl and alkoxy chains with numerical values in Scheme 1, and purified carefully by repeating column chromatography and recrystallization a few times.



Scheme 1. Synthetic pathway for 4-alkyl-4′-alkoxybiphenyls.

Table 1. Phase-transition behaviors of biphenyls

Biphenyls	Cryst. - SmE	SmE - SmB	SmB - Isotropic
6O-BP-6	5 °C	68 °C	83 °C
6O-BP-8	30 °C	49 °C	93 °C
6O-BP-9	9 °C	38.7 °C	84.3 °C

The phase-transition behavior of the biphenyls synthesized was determined by both the texture observation under a polarized microscope and differential scanning calorimetry (DSC) measurement. These biphenyls exhibit both smectic B (SmB) and E (SmE) phases at various temperature ranges as summarized in Table 1.

The carrier mobility was determined by conventional time-of-flight experiments, where the photohole injection from the In_2O_3–SnO_2 (ITO) electrode was responsible for a transient photocurrent when illuminated with a 337 nm light-pulse of 600 ps from a nitrogen laser.

Figure 1 shows typical transient photocurrents for positive-

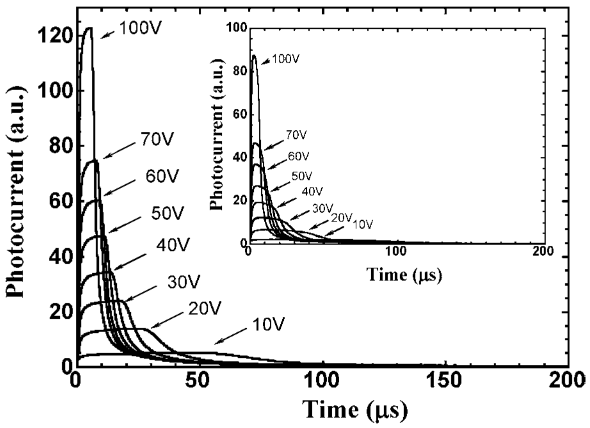


Figure 1. Typical transient photocurrents for positive-charge carriers in SmB (70 °C) and SmE (50 °C, inset) phases of 6O-BP-6 in a 10 μm thick cell with ITO electrodes at various applied voltages.

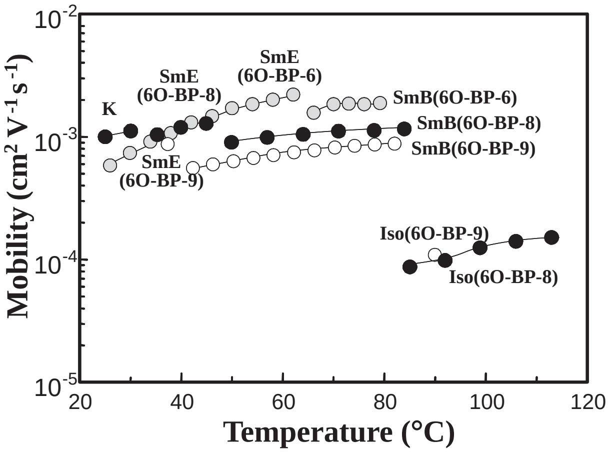
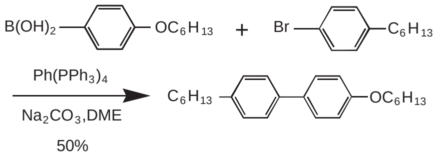


Figure 2. Mobilities of positive-charge carriers in various phases of biphenyls, 6O-BP-6(◎), 6O-BP-8(●), and 6O-BP-9(○) at the electric field of 10^5 V cm^{-1}.

charge carriers in the SmB and SmE phases of 6O-BP-6 in a 10 μm thick cell as a function of applied biases. The photocurrents are non-dispersive and show a clear shoulder, which indicates a transit time when the positive carriers arrive at the counter electrode. The mobility is estimated to be 10^{-3} cm^2 V^{-1} s^{-1} from the transit time and a given applied bias. The mobility of biphenyls studied including 6O-BP-6 is almost the same around 10^{-3} cm^2 V^{-1} s^{-1} irrespective of the smectic phases, which is quite different from the mobility of 6O-BP-8 reported previously, i.e., 10^{-6}–10^{-5} cm^2 V^{-1} s^{-1}.[8]

Judging from a high mobility of 10^{-3} cm^2 V^{-1} s^{-1}, no doubt this charge transport is attributed to hole conduction. Considering that the electronic conduction in the liquid crystal is quite sensitive to trace amounts of chemical impurities,[9] e.g., less than a few ppm, the low mobility of 10^{-6}–10^{-5} cm^2 V^{-1} s^{-1} reported results from the ionic conduction caused by contamination of the impurities. In fact, it showed the Arrhenius type of behavior and the activation energy was determined to be 0.1 eV, which is the same as that of viscosity for hydrocarbons.[10] This coincidence is not accidental, because the ionic conduction in the smectic mesophase takes place at the region where flexible hydrocarbon chains attached to the core moiety are aggregated.[11]

Figure 2 shows the mobilities of biphenyls studied in various phases including isotropic and crystal phases as a function of temperature. Unlike the mobility in the smectic mesophases of 2-phenynaphthalene and terthiophene derivatives,[6,7] the present mobilities in both SmB and SmE phases depend on temperature, although it is more appreciable in the SmE phase. Furthermore, the mobility depends on the electric field in the SmE phase, while not in the SmB phase. It is very unlikely that these different behaviors in these smectic mesophases are explained by trap-controlled hopping caused by contamination of chemical impurities responsible for trap states in the bulk, because they depend on the phase in the same material: in fact, the Arrhenius plots of the mobilities for the SmB and SmE phases do not give a linear relation, while the $1/T^2$ plot, where T is the absolute temperature, gives a good linear relation in the SmE phase, indicating a Gaussian distribution of the density of states responsible for hole transport.[12]



Scheme 2. Alternative synthetic pathway for 6O-BP-6.

For additional support on the discussion described above, we synthesized another 6-OBP-6 via a different synthetic pathway to build up a biphenyl moiety as shown in Scheme 2, rather than functional group transformation in the biphenyl in Scheme 1, in which we expect little contamination of unknown by-products that have the ionization potential smaller than that of 6O-BP-6 compared with the 6O-BP-6 synthesized via Scheme 1.

Comparing the charge carrier transport properties in these 6O-BP-6s synthesized via the Schemes 1 and 2, we could not find any significant difference in their charge carrier transport properties, even though the transient photocurrents in newly synthesized 6O-BP-6 look more perfect. Thus, we come to a conclusion that the present Pool–Frenckel type of behavior in the SmE phase is attributed to the intrinsic nature in this type of biphenyls.

With respect to the core size effect on the mobility, it is generally accepted that the larger the core size is, the higher the mobility becomes in the discotic liquid crystals.[13] The mobility of 10^{-3} cm^2 V^{-1} s^{-1} in the biphenyls is not less high than that of triphenylene derivatives such as H5T and H6T, although the biphenyl moiety is far small compared with a triphenylene moiety. Moreover, the shortest molecular distance of 4.4 and 4.1 Å in the SmB and SmE layers is longer than that of 3.6 Å in the columnar phases of triphenylene derivatives. These facts indicate that we have still lacked the full understanding of the relation between the molecular structure and its charge carrier transport properties in the liquid crystals. The present mobility in the biphenyls gives an insight into the material design for high mobility liquid crystals when we refer the relation between the core structure and the mobility in the smectic liquid crystals.

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