Charge Carrier Transport Properties of Biphenyl Liquid Crystals with a Dimer Structure

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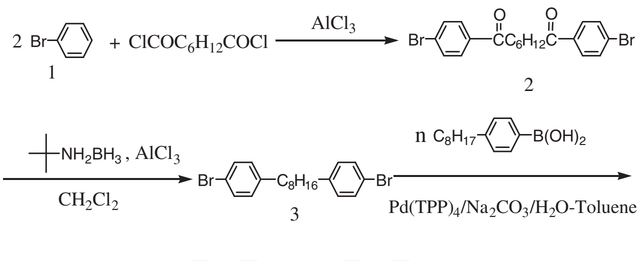
In order to have better understanding design of liquid crystalline molecules as organic semiconductors, we synthesized a series of biphenyl liquid crystals with a dimer structure such as 1,8-bis[4-(4′-butylbiphenyl)]octane (4BP8BP4) and 1,8-bis[4-(4′-octylbiphenyl)]octane (8BP8BP8) as a model material, and characterized their phase-transition behaviors and charge-transport properties. These biphenyl dimers exhibited smectic B (SmB_{hex}) phase at higher temperatures and higher mobility, i.e., 5–6 × 10^{-3} $cm^2 V^{-1} s^{-1}$ that does not depend on temperature, compared with that of a corresponding monomer, 4-octyl-4′-butylbiphenyl (8BP4). We discuss the present result in a framework of disorder in the liquid crystal phase for an organic semiconductor.

Since the discovery of electronic conduction in discotic and smectic liquid crystals in the 1990s,[1–3] the electronic conduction has been reported in various classes of liquid crystals including triphenylenes, porphyrins, naphthalenes, oligothiophenes, benzothiazoles, and biphenyls.[4–8] Their charge carrier transport properties are characterized by high mobility over 10^{-3} $cm^2 V^{-1} s^{-1}$ typically and up to 1 $cm^2 V^{-1} s^{-1}$.

However, there is no guiding principle of how to design liquid crystalline molecules for an organic semiconductor having a high mobility. We synthesized a series of biphenyls with a dimer structure in which two mesogenic moieties are linked via a flexible spacer and studied liquid crystalline behaviors and charge carrier transport properties in comparison with those of corresponding biphenyl monomers on the basis of a previous study.[9]

Scheme 1 shows a schematic diagram of a synthetic route for biphenyl dimers.[10] The chromatographically homogeneous products were further purified by recrystallization from hexane several times for time-of-flight measurement.

The phase-transition behavior of these biphenyl dimers synthesized was determined by texture observation under a polarized microscope, DSC measurement, and XRD studies. These biphenyl dimers exhibit SmB_{hex} phase at a higher temperature range compared with those of corresponding monomers as summarized in Table 1. A higher phase-transition temperature from SmB_{hex} phase to isotropic phase compared with that of the corresponding monomer indicates that the liquid crystalline phase is stabilized in the dimers.



Scheme 1. Synthetic pathway for 8BP8BP8 and chemical structure of corresponding monomer of 8BT4.

Table 1. Phase-transition behaviors of biphenyl dimers

Biphenyls	Cryst.	SmB_{hex}	Isotropic
4BP8BP4		121 °C	136 °C
8BP8BP8		94 °C	138 °C
8BP4		−1.5 °C	43 °C

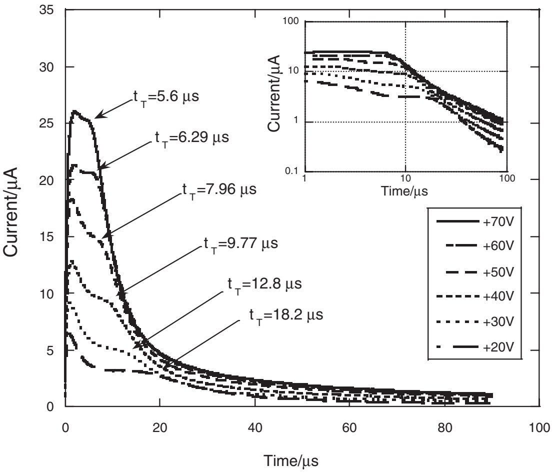


Figure 1. Typical transient photocurrent for positive charge carriers in SmB_{hex} phase (135 °C) of 8BP8BP8 in a 14.1-μm thick quartz cell at various applied voltages. The inset shows double logarithmic plot of transient photocurrents as a function of time.

Figure 1 shows typical transient photocurrents for positive carriers generated by a pulse illumination of 265 nm light from a YAG laser in the SmB_{hex} phase of 8BP8BP8 in a 14.1-μm thick quartz cell as a function of applied biases. We found that molecules were homogeneously aligned to the electrodes in the quartz cell which was confirmed by texture observation under polarized microscope.[11] Each photocurrent in Figure 1 is nondispersive and shows a clear shoulder, which indicates a transit time when the positive carriers arrive at the counter electrode. The photocurrent decay before the transit time is due to charge trapping at deep states probably attributed to trace amounts of chemical impurities.

The mobility is estimated to be 5 × 10^{-3} $cm^2 V^{-1} s^{-1}$ from the transit time and a given applied bias. The mobility of 4BP8BP4 is almost the same as that of 8BP8BP8 and around 6 × 10^{-3} $cm^2 V^{-1} s^{-1}$ in SmB_{hax} phase, which is 5–6 times higher than those of their corresponding monomers. Judging from the same intermolecular distance of biphenyl dimers in SmB_{hex},

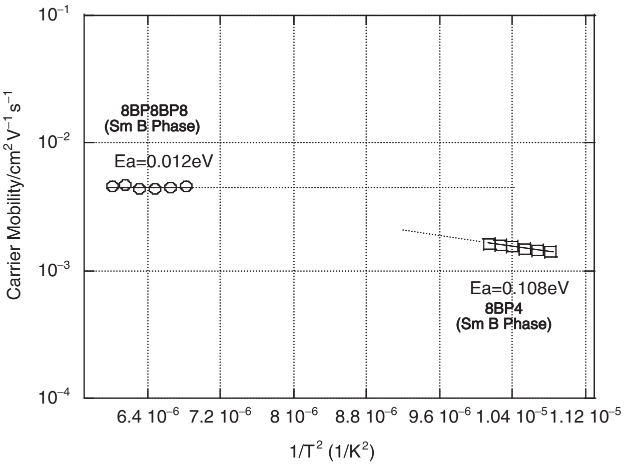


Figure 2. Temperature dependence of positive charge carrier mobility of 8BP8BP8 and 8BP4 in $\mathrm{SmB_{hex}}$.

5.2 Å, which is determined by X-ray diffraction, as those of biphenyl monomers in the same phase, the enhanced mobility is not attributed to a change of the intermolecular distance of smectic layers.

Figure 2 shows the mobility of 8BP8BP8 and 8BP4 as a function of a square inverse of temperature. We can see that the mobility in $\mathrm{SmB_{hex}}$ phase of 8BP8BP8 and 8BP4 exhibit different behaviors, which relate to distribution of the density of states (DOS) responsible for hole conduction:[12] a shallow slope of the dimer, which is typical behavior of mobility in smectic mesophases,[5,6] indicates a narrow distribution of the DOS, while a steep slope of the monomer, which is the same trend as biphenyl derivatives reported previously,[9] does a broad distribution of the DOS.[13] Taking account of no structural difference between 8BP8BP8 and 8BP4 except for a linkage of two monomer units, we can conclude that the stabilized liquid crystalline phase by the linked structure contributes to the reduction of the DOS.

In general, the current decay of transient photocurrent after the transit time reflects a dispersion of carrier velocity for the carriers experiencing hopping events, including diffusion, trapping and thermal releasing at shallow states, and variable range hopping of carriers in distributed DOS. Therefore, the shape of transient photocurrent provides us with additional information about the DOS discussed above.

Figure 3 shows the comparison of transient photocurrents of 4BP8BP4 and 8BP4 as a function of time normalized by their transit times and current. It is very clear that the transient photocurrent of 4BP8BP4 decays more sharply than that of 8BP4. Taking account of a nondispersive electronic transient photocurrent of both the dimers and the monomer that assures a high purity of these materials,[14,15] in addition to a low diffusivity at lower temperature, a sharp decay of transient photocurrent in the dimers support a narrow distribution of their DOS.[12]

Furthermore, the present results suggests that the different charge transport-properties in biphenyl monomers originate from less ordered molecular alignment attributed to a small core moiety of biphenyl.

In summary, we studied liquid crystalline behavior and charge carrier transport properties of liquid crystalline biphenyl dimers, 4BP8BP4 and 8BP8BP8 in comparison with those of corresponding monomers. We conclude that the liquid crystal phase of dimers is stabilized by a dimer structure, leading to a higher temperature range of liquid crystal phase and temperature-independent mobility, which is a few times higher than those of corresponding monomers. This gives an insight into how to design a liquid crystalline molecule for a quality organic semiconductor.

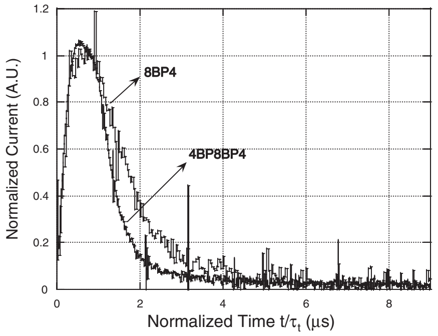


Figure 3. Normalized transient photocurrents of positive charge carriers in $\mathrm{SmB_{hex}}$ phases of biphenyl monomer, 8BP4 and dimer, 4BP8BP4 as a function of time normalized by their transit times.

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