

Electronic and ionic carrier transport in discotic liquid crystalline photoconductor

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We have investigated the negative charge carrier transport in discotic columnar phases of triphenylene derivatives, 2,3,6,7,10,11-hexapentyloxytriphenylene (H5T) and its related derivatives such as H4T and H6T, by time-of-flight experiments. We observed a fast transit for negative charge carriers in the discotic hexagonal columnar phase (D_h) of H5T, which corresponded to a high mobility of $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ comparable to its hole mobility, in addition to a slow transit corresponding to the mobility of $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ reported previously. We observed two transits in H4T and H6T as well, in which the fast mobility was on the order of 10^{-2} and $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in H4T and H6T, respectively, while the slow mobility was almost the same ($3-4 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) in both H4T and H6T. Through dilution experiments with *n*-dodecane, we found that these fast and slow transits were attributable to the electronic and ionic conduction, respectively, and that the latter was caused by negatively ionized impurity molecules trapping photogenerated electrons. We discuss that there exist two distinct carrier transport channels for electronic and ionic charges in the intrinsic nature of discotic columnar phases.

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Since fast electronic conduction was established in the discotic liquid crystal 2,3,6,7,10,11-hexapentyloxytriphenylene (H5T)¹ and the smectic liquid crystal 2-(4'-heptyloxyphenyl)-2-dodecylthiobenzothiazole (7O-PBT-S12)² in the 1990s, it has been found in many liquid crystals including hexabenzocoronenes,³ perylenes,⁴ phthalocyanines,⁵ porphyrins,⁶ 2-phenylnaphthalenes,⁷ terthiophenes,⁸ benzothienobenzothiophenes,⁹ and 2,6-diphenylanthracenes.¹⁰ Thus, electronic conduction has come to be recognized as intrinsic to discotic columnar and smectic mesophases. The charge carrier mobility of these mesophases, ranging from $10^{-4}-1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,^{3,11-13} is comparable to those of organic polycrystals, which are attracting great attention due to their potential application in organic thin film transistors (OTFTs).¹⁴

Furthermore, it has been discovered in the last decade that mesophase materials exhibit several unique features in charge carrier transport, which distinguish liquid crystalline materials from organic amorphous and polycrystalline materials: the mobility changes abruptly upon phase transition: mobility depends on neither electric field nor temperature within a temperature range for each mesophase appearing above room temperature;^{1,7,8} structural defects including disclinations and domain boundaries in polydomain textures are electrically inactive,¹⁵ which is quite different from those in polycrystals. Thus, mesophase materials are being recognized as a new class of quality organic semiconductors.

Interestingly, electron transport is often observed in several calamitic and discotic liquid crystals, while it occurs in far fewer organic amorphous semiconductors: for example, a fast electron transport characterized by a high mobility of over $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, comparable to the hole mobility, was observed in the mesophases 2-phenylnaphthalenes,⁷ terthiophenes,⁸ benzothienobenzothiophene,⁹ porphyrin,⁶ and

phthalocyanine.⁵ By contrast, only slow transport of negative charge carriers characterized by a low, Arrhenius-type mobility of $10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was reported in discotic columnar phases of H5T,¹ in which first fast hole conduction was established, as described above. Similar results were reported for H6T as well.¹⁶ Whether fast electron transport is a general feature of mesophase materials remains an open question.

Thus, we focused on negative charge carrier transport properties in a series of triphenylene derivatives, including H5T, 2,3,6,7,10,11-hexahexyloxytriphenylene(H6T) and 2,3,6,7,10,11-hexabutylxytriphenylene(H4T), by time-of-flight experiments.

In the present report we establish fast electron transport in the discotic columnar phases of triphenylenes, and discuss the intrinsic nature of charge carrier transport in them, including the existence of two carrier transport channels, one for electronic, one for ionic conduction.

Triphenylene derivatives, whose chemical structure is shown in Fig. 1(a), were synthesized by oxidative coupling of *o*-dialkyloxybenzene with MoCl_5 , as reported elsewhere.¹⁷ As-isolated triphenylene derivatives often contain trace amounts of impurities, the main portion of which is partially dealkylated compounds. These compounds give triphenylene derivatives their pink color when exposed to light in the ambient atmosphere. Thus, the isolated product was realkylated with alkyl bromide and sodium hydroxide in an ethanol solution. The resulting product was thoroughly purified several times with both flush chromatography and recrystallization from ethanol and *n*-hexane. H5T, H6T, and H4T exhibited discotic columnar phases in the temperature ranges from 69 °C to 122 °C, 68 °C to 100 °C, and 88 °C to 146 °C, respectively, as reported.^{1,16,18} The purified triphenylene derivatives were capillary filled at the isotropic phase into liquid crystal cells fabricated using two glass plates coated by

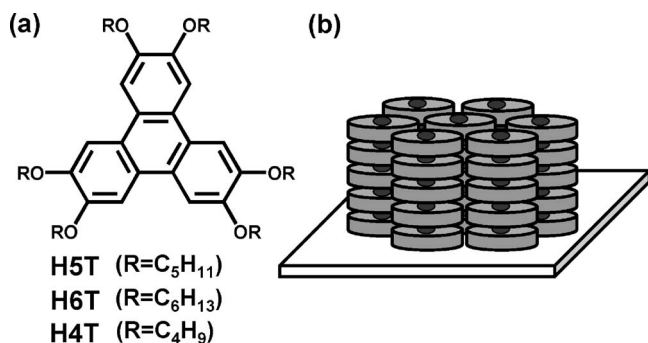


FIG. 1. (a) The chemical structures of H4T, H5T, and H6T; (b) the schematic illustration of its homeotropic alignment for the plane of an electrode in the columnar mesophase.

semitransparent aluminum and silica particle spacers. The cell thickness ranged from 2 to 10 μm , as determined by an interference pattern of the cells in the UV-visible spectrum. Upon slowly cooling from the isotropic phase into the columnar phase, the triphenylene derivatives in the cells were spontaneously aligned in homeotropic alignment [see Fig. 1(b)] without the aid of alignment layers.

The charge carrier transport properties in triphenylene derivatives were characterized by a conventional time of flight setup equipped with a nitrogen laser ($\lambda=337$ nm, pulse duration=600 ps) as an excitation light source: the resulting transient photocurrents were recorded by a digital oscilloscope (Nicolet Pro92), while the cell temperature was maintained at a given temperature by the hot stage with the aid of a PID controller. In these measurements, the one-carrier condition was well established in thicker cells over 5 μm due to the short penetration depth of 0.7 μm for 337 nm excitation light. The transit time for carriers was determined from a shoulder in the transient photocurrent.

Figures 2(a) and 2(b) show the transient photocurrents of H5T at 100 $^\circ\text{C}$ in a 5 μm thick cell for positive and negative charge carriers, respectively. The transient photocurrents were well defined and nondispersive for positive carriers, as shown in Fig. 2(a). The hole mobility was estimated to be $1.6 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is slightly larger than the value reported previously.¹ The inset in Fig. 2(a) shows transient photocurrents in a double logarithmic plot. Past the transit time, each photocurrent decays very rapidly, indicating that the photogenerated holes were transported without a marked dispersion of charge carriers that is often caused by trap sites. The transient photocurrents for negative charge carriers exhibit a curious shape having a shoulder indicative of a transit time with a very long tail [Fig. 2(b)], suggesting another transit at a longer time range: in fact, there were two shoulders at the μs and ms ranges, as shown in the inset for a double logarithmic plot. These two transits correspond to a fast mobility of $1.7 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and a slow mobility of $5 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. This fast mobility is independent of electric field and almost the same as the hole mobility, as described above, while the slow mobility is one order of magnitude higher than that reported originally.¹

In order to determine the origin of the slow transit, we studied the fast and slow charge carrier transport in H5T in detail. Open circles in Fig. 3(a) show the Arrhenius plots of

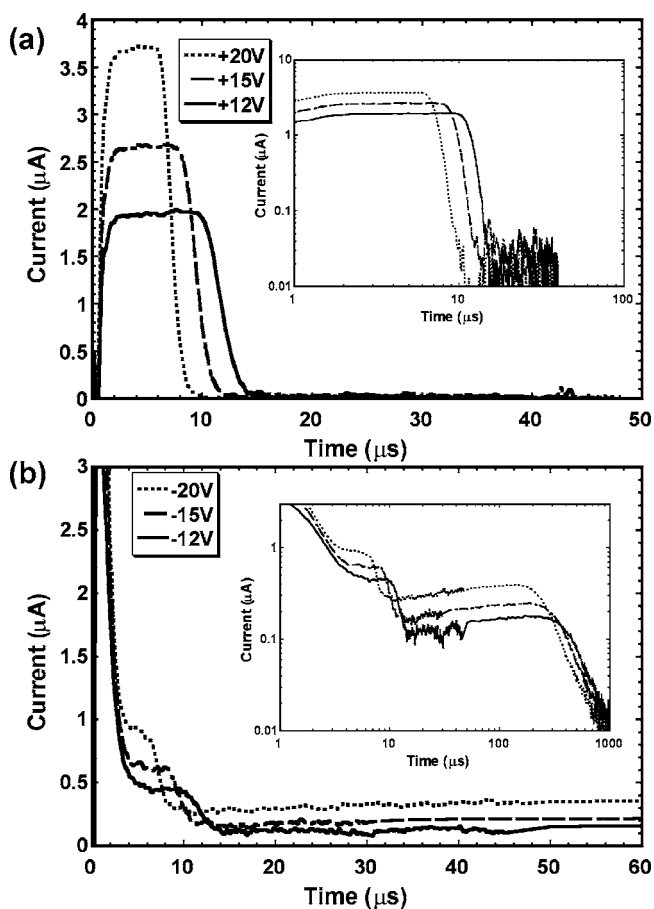


FIG. 2. Linear plots of typical transient photocurrents in the D_h phase of H5T at 100 $^\circ\text{C}$ as a function of time for (a) positive charge carrier and (b) negative charge carrier. The insets show double logarithmic plots of transient photocurrents as a function of time. The sample thickness was 5 μm .

the two mobilities in H5T. Clearly, the fast mobility stayed constant at around $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, while the slow mobility depended on temperature. The activation energy for the slow mobility was estimated to be 0.28 eV. Judging from the characteristic mobility of $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ independent of both the temperature and electric field, the fast mobility for negative charge carriers was attributed to the electron transport. This independence of mobility is well explained by a model based on hopping transport in a narrowly distributed density of states for a hole and an electron in the mesophase, which is described by a Gaussian distribution with a small width of 40–60 meV comparable to kT .^{19–21} The slow, temperature-dependent mobility was attributed to either trap-controlled hopping transport or ionic transport, as we discussed in the smectic mesophases.²²

In order to elucidate the slow transit, we investigated the charge carrier transport in H5T diluted with *n*-dodecane, which was compatible with H5T up to 12 mol% without destroying the mesophases. *n*-dodecane is a hydrocarbon having a long alkyl chain, a low viscosity, and no aromatic moiety to contribute to the electronic charge carrier transport, so that the mobility in diluted H5T decreases if the predominant mechanism is electronic hopping conduction.

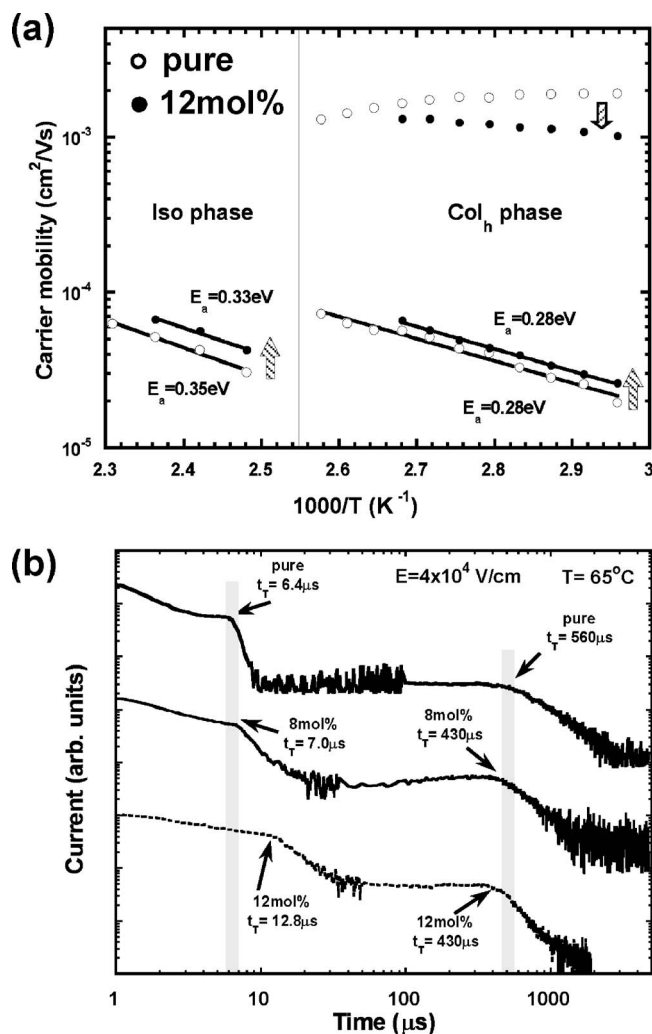


FIG. 3. (a) Transient photocurrents in the D_h phase of nondiluted H5T and diluted H5T with 8 mol% and 12 mol% of *n*-dodecane. The transient photocurrents were measured at an applied bias of -20 V. The sample thickness was $5 \mu\text{m}$. (b) Arrhenius plots of fast and slow mobilities in nondiluted H5T and diluted H5T with *n*-dodecane of 12 mol%.

Otherwise, it increases if the predominant mechanism is ionic conduction. This is because electronic mobility is governed by an average hopping distance that is prolonged by *n*-dodecane dilution and the ionic mobility is governed by the viscosity, which is reduced by dilution.^{23,24}

Figure 3(b) shows typical transient photocurrents for negative charge carriers in nondiluted and diluted H5T with *n*-dodecane. Clearly, the fast transit shifts slightly to a longer time range and the slow transit to a shorter time range as the dilution factor increases. This indicates that the fast mobility is slightly decreased and the slow mobility is slightly increased compared to the corresponding values in nondiluted H5T, as shown with solid circles for these mobilities in Fig. 3(a). Thus, we attributed the slow mobility to ionic conduction.

Figure 4 shows transient photocurrents for negative charge carriers in the D_h phase of H5T as a function of cell thickness at 100°C . Clearly, the fast and slow transit times

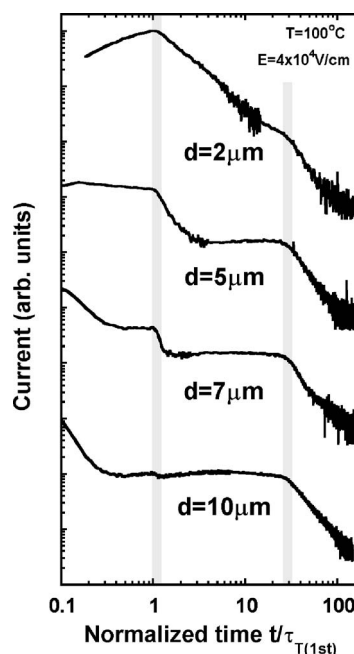


FIG. 4. Logarithmic plots of transient photocurrents in the D_h phase of H5T as a function of time normalized by each first transit time in various cell thickness of 2, 5, 7, and $10 \mu\text{m}$. The shadow areas indicate a guide for eyes to show the fast and slow transient times. These transient photocurrents were measured at a condition of an applied electric field of $4 \times 10^4 \text{ V cm}^{-1}$, and illumination intensities of $2-4 \mu\text{J/pulse}$ where the total collected charges were about 0.07 nC .

scaled as shown in Fig. 4, irrespective of the cell thickness. This confirms that the electron and ionic transits were subject to a common charge transport regime irrespective of the cell thickness. Furthermore, the ionic transport clearly became more dominant with increasing cell thickness, and finally, the electron transit disappeared when the cell thickness exceeded $10 \mu\text{m}$. This indicates that the present transition from the electronic to the ionic transport regime was due to a bulk effect. Indeed, this is supported by the fact that collected charges attributed to the electron transport, which were estimated by integrating the electronic photocurrent extracted from the total transient photocurrent, showed exponential decay as a function of the cell thickness. Thus, it is very likely that ionic transport originates from the negative ions generated when photoelectrons are trapped at chemical impurities distributed uniformly across the bulk, which presumably form during the chemical synthesis of H5T.

The negative charge carrier transport in triphenylene derivatives is summarized in Table I.

Electron mobilities in these triphenylene derivatives are almost the same as the hole mobilities reported for each columnar phase previously.^{1,16,18} It should be noted that the electron mobilities depend on the molecular order of a discotic columnar phase, and change significantly from phase to phase, while the ionic mobility in each phase is almost identical at 80°C .

Clearly, ions can only move in regions where alkyl side chains aggregate, not where the triphenylene moiety aggregates. This implies the existence of two charge transport

TABLE I. Electron and ionic mobility in three triphenylene derivatives. D_{ho} and D_{hp} indicate the discotic columnar ordered and plastic phases, respectively.

	Electron (cm ² /V s)	Ionic (cm ² /V s)	Phase (temp.)
H6T	4×10^{-4}	3×10^{-5}	D_{ho} (80 °C)
H5T	1.9×10^{-3}	3×10^{-5}	D_{ho} (80 °C)
H4T	2.5×10^{-2}	4×10^{-5}	D_{hp} (80 °C)

channels in discotic columnar phases: one for electronic charge carriers of holes and electrons, the other for ions. Taking account of the inhomogeneous, i.e., microphase-separated structure in a molecular aggregate of a discotic columnar phase, it is very likely that the electronic charge carriers are transported via “a solid region” consisting of closely packed π -conjugate core moiety of triphenylene, while the ions migrate through a “fluid region” consisting of hydrocarbon side chains aggregating loosely. The different trends in the electronic and ionic mobilities listed in Table I fit the above structural model of the electronic and ionic transport channels in discotic columnar phases. Taking account of the origin of ionic transport as revealed in the present experiments, the present discussion implies that ambipolar electronic transport is very likely to be encountered

in mesophases of a discotic liquid crystal as long as it is highly purified.

In summary, we have investigated the negative charge carrier transport in triphenylene derivatives including H4T, H5T, and H6T by time-of-flight experiments, in which the hole transport was extensively studied. We found that these materials exhibit the fast electron transport characterized by a high-, and temperature- and field-independent mobility of 10^{-4} – 10^{-2} cm² V⁻¹ s⁻¹, comparable to the hole mobility reported previously, in addition to a slow ionic transport characterized by a slow, Arrhenius-type mobility on the order of 10^{-5} cm² V⁻¹ s⁻¹. Furthermore, we established that ionic transport originated from negatively ionized impurity molecules formed by trapping photoelectrons. Taking account of the microphase-separated aggregate structure in discotic columnar phases, we showed that discotic columnar phases intrinsically exhibit separate transport channels for electronic and ionic charge carriers.

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