Ambipolar charge carrier transport in liquid crystals

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We review the electron transport in both smectic and discotic liquid crystals with the updated experimental results, and discuss the ambipolar carrier transport in these materials. We indicate that the intrinsic nature of charge carrier transport in liquid crystals is probably ambipolar, in which both electronic and ionic charges are transported basically irrespective of their polarity, and that the ionic transport in these liquid crystals is extrinsic and induced by photo-ionization of chemical impurities. Furthermore, we discuss the importance of this unique features of charge carrier transport in the liquid crystals in the future development of new optoelectronic device applications that cannot be achieved with conventional organic semiconductors.

1. Introduction

Organic semiconductors have come to be used practically in xerographic photoreceptors for photocopiers and laser printers in the 1970's and 1980's [1], respectively, and more recently in organic light emitting diodes (OLEDs). Because of large-area uniformity required in these applications, the materials are used in a form of amorphous thin films. The charge carrier transport properties in amorphous materials, however, have several drawbacks compared with those of crystalline materials. These include a small mobility of 10^{-3} cm^2/Vs at most, its field and temperature dependence, and unipolar charge transport [1]. Therefore, various devices for compensating these degraded properties are made in the practical applications described above: in the xerographic applications, the photoreceptors adopt a layered structure consisting of a charge generation material (CGM) and a charge transport material (CTM) for compensating the unipolar charge transport and utilizing hole transport richly in material [2], in addition to a thick charge transport layer for establishing a high surface potential of ~10^3 V; in the OLEDs, a very thin layer of emissive hole and electron transport materials, e.g., 100 nm, is adopted to have a high electric field of 10^6 V/cm at a few volt for promoting charge carrier injection from electrodes [3].

In this point, it is noted that the establishment of ambipolar charge carrier transport is another important issue in the organic semiconductor for extension of device applications with organic semiconductors, in addition to upgrade of charge carrier mobility.

In amorphous organic semiconductors, p-type materials are major compared with n-type counterparts, in which hole and electron are mobile, respectively. It is thought that the reason why the n-type materials are minor is probably due to oxygen adsorbed in the materials, which has a high electron affinity and traps electron deeply, in fact, the materials known as a n-type organic semiconductor such as 2,4,7-trinitrofluorenone (TNF), 7,7,8,8-tetracyanoquinodimethane (TCNQ), and 3,3',5,5'-tetra-*t*-butyl-4,4'-diphenoquinone have electron affinity higher than that of oxygen, i.e., 1.46 eV, which supports this idea [4]. The recent report on n-type conduction in a titanyl-phthalocyanine thin film transistor, which was fabricated in an ultra-high vacuum chamber and characterized without exposing it with oxygen, is another experimental result to support it [5]. Therefore, the ambipolar charge carrier transports in the amorphous organic semiconductors have been established basically in the molecular composites combined with a set of hole and electron transport materials. The PVK-TNF system is the most well known. Another examples are molecularly doped polymers consisting of p-type and n-type materials such as diphenoquinone and triphenylamine derivatives [6,7,8], while the ambipolar charge carrier transport in a single material has been reported recently [9,10].

On the other hand, the ambipolar carrier transport is often observed in organic crystals including polyacenes, N-*iso*-propylcarbazole, and β-phthalocyanine [11]. Interestingly, the hole and electron mobilities in the organic crystals are not so different, while very different in inorganic semiconductors. As a matter of fact, there remains a question about why the ambipolar charge carrier transport is often observed in the organic crystals to be explained.

As for the liquid crystals, since their electronic conduction was established in discotic and smectic liquid crystals

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[12,13], there is no systematic data and conclusive discussion on the ambipolar transport in the discotic liquid crystals, while the ambipolar charge transport was often reported in various smectic liquid crystals.

In this article, we review the negative charge carrier transport in liquid crystals including its updated results in both smectic and discotic liquid crystals that have been re-investigated in detail recently, and discuss the ambipolar charge carrier transport in liquid crystals.

2. Charge transport for positive and negative carriers in calamitic liquid crystals

Since the first hole conduction was established in a smectic liquid crystals of 2-phenylbenzothiazole derivative (7O-PBT-S12) [13], the electronic conduction also has come to be reported in various smectic liquid crystals including 2-phenylnapthtalene [14,15], oxadiazole [16], terthiophene [17,18], bisbenzothiophene [19] derivatives. The charge carrier transport in these materials is ambipolar naturally, in which electron and hole mobilities are comparable as summarized in Table 1.

However, the experimental results reported on the negative carrier transport in some of calamitic liquid crystals show inconsistency in various points, for example, a transient photocurrent for negative carriers in the 2-phenyl-benzothiazole derivative (7O-PBT-S12) exhibits no transit and an exponential decay in stead as shown in the inset of Fig. 1 [13], a shape of transient photocurrents for negative carriers in a 2-phenylnaphthalene derivative (8-PNP-O12) is different from those for positive carriers and has a long

tail after a transit time [14], which is never observed in positive transient photocurrents as shown in Fig. 2. Furthermore, the carrier mobility reported for negative carriers in the 8-PNP-O12 is quite different in terms of its absolute value and temperature dependence from research group to research group [4,20].

In order to make these inconsistencies clear, we have re-investigated the negative carrier transport in 8-PNP-O12 in detail. We found that there existed an additional slow transit at a longer time range of millisecond as shown in Fig. 3, which was responsible for the long tail and corresponded to a mobility of ~10^{-5} cm²/Vs. We clarified the origin of this slow transit to be the ionic conduction induced by drift of chemical impurities photo-ionized in 8-PNP-O12 [23], even though their chemical structures have not been clarified yet. It should be noted that the electronic conduction depends on neither temperature nor electric field at a temperature range higher than ambient temperatures because of a small Gaussian distribution of density of state [22], while the ionic conduction does depend on temperature because of temperature-dependent viscosity. In fact, a temperature-dependent small mobility of 10^{-5} cm²/Vs reported by Singer *et al.* [20] for negative carriers in 8-PNP-O12 is attributed to this ionic conduction induced by photo-ionization of chemical impurities in 8-PNP-O12 and shows a good agreement with the mobility corresponding to the second transit as described above. Furthermore, we also found a slow transit in a long time range of millisecond in 7O-PBT-S12 as well, which followed the exponential decay of photocurrent at a short time range of microsecond and corresponded to a mobility of 10^{-5} cm²/Vs [24].

Table 1. Positive and negative charge carrier mobility in discotic liquid crystalline semiconductors.

	Hole (cm²/Vs)	Electron (cm²/Vs)	Anion (cm²/Vs)	Phase	Temp. (°C)	Thickness (µm)	Ref.
8-PNP-O12	2.5×10^{-4} 1.6×10^{-3}	2.5×10^{-4} 1.6×10^{-3}	4×10^{-5} 5×10^{-5}	SmA SmB	110 90	9	14,20,21
8-PNP-O4	4×10^{-4} 1×10^{-2}	4×10^{-4} 1×10^{-2}	10^{-6}–10^{-5} 10^{-6}–10^{-5}	SmA SmE	125 100	15	15
8-TTP-8	5×10^{-4} 2×10^{-3} 2×10^{-2}	5×10^{-4} 2×10^{-3} 2×10^{-2}	6×10^{-5} 5×10^{-5} 4×10^{-5}	SmC SmF SmG	90C 80 70	9	17
8-QTP-8	1×10^{-2}	1×10^{-2}	—^{c}	SmG	120	9	22
7O-PBT-S12	5×10^{-3}	—^{c}	8×10^{-6}	SmA	95	9	13,22
BTBT^a	2.2×10^{-3}	2.7×10^{-3}	1.2×10^{-6}	SmA	90	35	19
HOBP-OXD^b	?^{d} ?^{d}	1×10^{-4} 8×10^{-4}	?^{d} ?^{d}	SmA SmX^e	95 70	17	16

a – [1]benzothieno[3,2-b][1]benzothiophene-2,7-dicarboxylate,
b – Hexyloxyphenyl-hexyloxybiphenyloxadiazole,
c – No signal within a limit of S/N ratio for transient photocurrent measurement,
d – No description in the original paper,
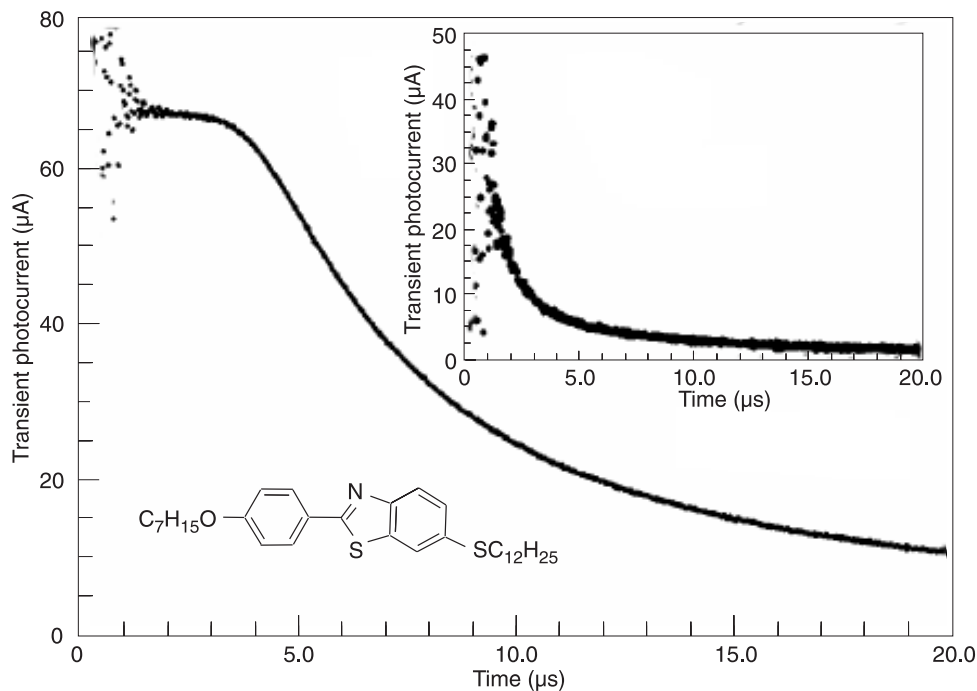e – Un-identified mesophase.

Fig. 1. Typical transient photocurrents for positive and negative carriers in the smectic A phase of 2-(4'-hepthyloxyphenyl)-6-dodecylthio-benzothiazole (7O-PBT-S12). The transient photo current was measured with a cell of 28 μm at 1×10^5 V/cm and 95°C.
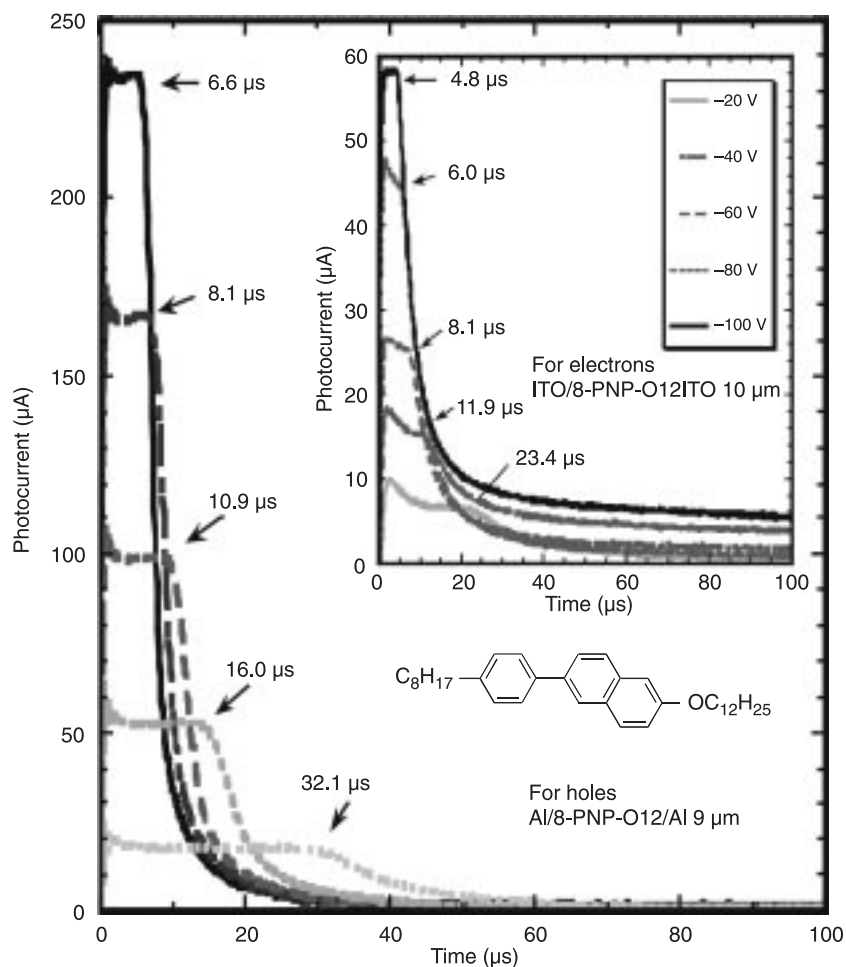

Fig. 2. Typical transient photocurrents for positive and negative carriers in the smectic B phase of 6-(4'-octylphenyl)-2-dodecyloxyna-phthalene (8-PNP-O12). The transient photocurrent was measured with a 9-μm thick cell at 95°C.
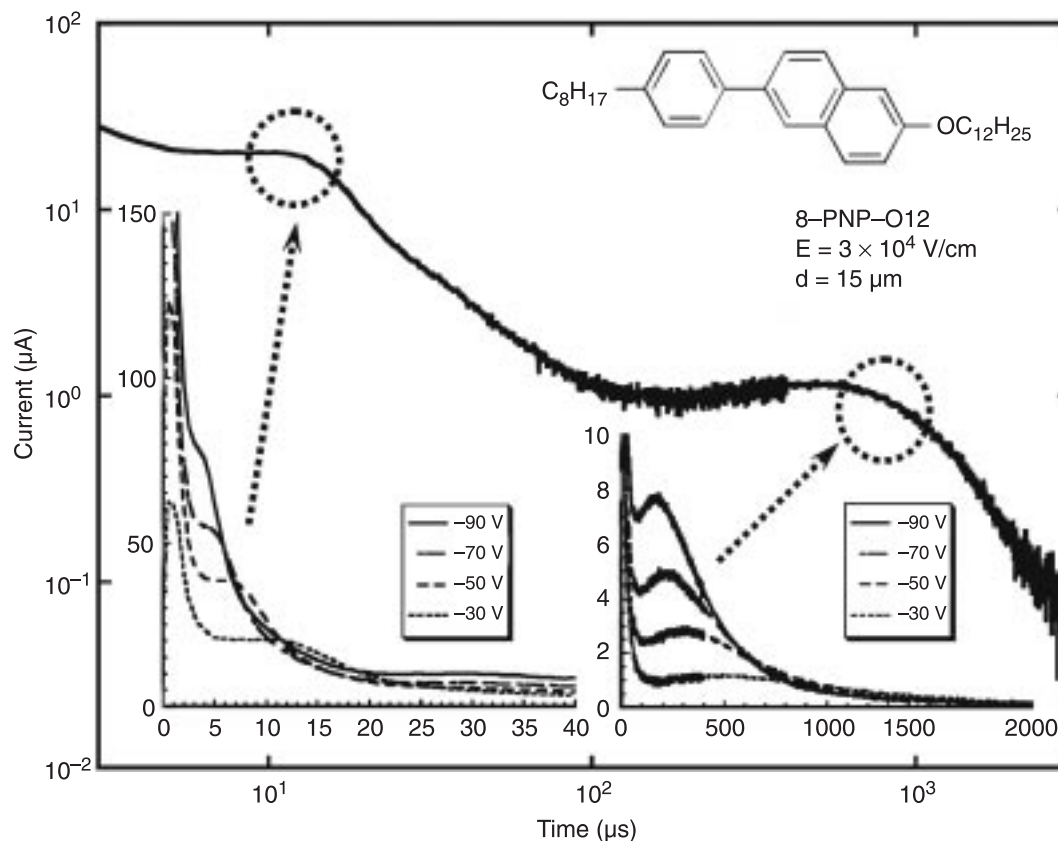
Fig. 3. Double logarithmic transient photocurrent for negative carriers in the SmB phase of 6-(4'-octylphenyl)-2-dodecyloxynaphthalene (8-PNP-O12). The insets show the first and second transient photocurrents at different applied electric fields.

Thus, all the inconsistencies in the negative charge carrier transport of the smectic liquid crystals described above has been solved, taking account of photo-induced ionic conduction attributed to the chemical impurities contaminating the liquid crystal during its synthesis. According to this knowledge, we can attribute the fast and slow transits for both positive and negative carriers reported in the bisbenzothiophene [19] to either hole or electron fast transport and the ion slow transport, respectively.

3. Charge transport for positive and negative carriers in discotic liquid crystals

Although the hole conduction was established in a triphenylene derivative (H5T) by means of time-of-flight experiments in 1993, there has been little information about the electron transport in discotic liquid crystals. This is partly due to their less feasibility of controlling molecular alignment suitable for time-of-flight experiments, which provide useful information about each charge transport property of materials for positive and negative carriers separately. In fact, the pulsed radiolysis time-resolved microwave conductivity (PR-TRMC) measurement has been utilized often for characterizing the charge transport properties in discotic liquid crystals, which cannot tell anything about each contribution of electrons and holes to the charge

transport separately [25]. Among discotic liquid crystals, the ambipolar charge transport was proved in two materials, i.e., porphyrin and phthalocyanine derivatives recently [26,27].

As for the triphenylene derivatives in which the hole conduction was established firstly, the Arrhenius-type mobility of slow transit for negative carriers in H5T was reported in the original paper [12], but its origin was not discussed. This result was confirmed in the following experiments with H6T [28], in which the slow negative mobility, i.e., 2.8×10^{-5} cm^2/Vs, was interpreted to be due to the ionic conduction without any additional experimental evidence.

On the basis of our experimental results on the negative charge transport in the smectic liquid crystals, we suspected that the slow transit of negative carriers in triphenylene derivatives was due to the extrinsic ionic transport induced by chemical impurities. Then, we re-investigated the charge carrier transport for negative carriers in detail with extensively purified triphenylene derivatives including 2,3,6,7,10,11-hexabutyloxytriphenylene (H4T: R = OC$_4$H$_9$) [29], 2,3,6,7,10,11-hexapentyloxytriphenylene (H5T: R = OC$_5$H$_{11}$) [30], and 2,3,6,7,10,11-hexahexyloxytriphenylene (H6T: R = OC$_6$H$_{13}$), 2,3,6,7,10,11-hexahexylthiotriphenylene (HHTT: R = S C$_6$H$_{13}$) [31], and a phthalocyanine derivative [32], whose chemical structures are illustrated in Fig. 4.
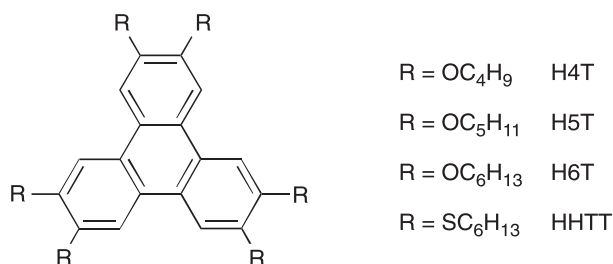
R = OC$_4$H$_9$ H4T

R = OC$_5$H$_{11}$ H5T

R = OC$_6$H$_{13}$ H6T

R = SC$_6$H$_{13}$ HHTT

Fig. 4. Chemical structures for triphenylene derivatives: 2,3,6,7, 10,11-hexabutyloxytriphenylene (H4T: R = OC$_4$H$_9$), 2,3,6,7, 10, 11-hexapentyloxytriphenylene (H5T: R = OC$_5$H$_{11}$), and 2,3,6, 7,10,11-hexahexyloxy triphenylene (H6T: R = OC$_6$H$_{13}$), and 2,3, 6,7,10,11-hexahexythiotriphenylene (HHTT: R = SC$_6$H$_{13}$).

As a result, we found that transient photocurrents had two transits in H5T as was the case of 8-PNP-O12 as shown in Fig. 5, and so did in H4T, and H6T: the fast transit at a short time range of microseconds corresponded to the mobilities of 10^{-4} ~10^{-2} cm^2/Vs and depended on the columnar phases; the slow transit at long time range of millisecond corresponded to 10^{-6} ~10^{-5} cm^2/Vs and did not depend on columnar phases as shown in Fig. 6. With the aid of a dilution experiment with a less-viscous organic solvent such as a hydrocarbon [23,30], we finally came to a conclusion that the slow transit often observed in discotic liquid crystals was due to the ionic transport. In fact, the electronic transport depended on neither temperature nor electric field, but the

ionic mobility did depend on temperature, which was very similar to those in smectic liquid crystals.

In the HHTT showing the highest hole mobility of 0.1 cm^2/Vs ever reported in the bulk of discotic liquid crystals [33], we also established the high electron mobility of 0.1 cm^2/Vs comparable to the hole mobility after intensive purification by means of repeated recrystallization [31].

We extended the characterization of charge transport in purified discotic liquid crystals to a phthalocyanine derivative, which is one of the most well known p-type materials. To our surprise, we found that 1,4,8,11,15,18,22,25-octa-octylphthalocyanine (8H$_2$Pc) exhibited extremely high electron mobility of 0.3 cm^2/Vs even in the ambient atmosphere [32], which is the highest electron mobility ever achieved in the bulk of non-crystalline organic materials and higher than the hole mobility of 0.2 cm^2/Vs in its own in the Col$_r$ phase [21].

Table 2 shows a summary of ambipolar charge carrier transport in discotic liquid crystals.

4. Ionic and electronic conduction in liquid crystals

As we described above, we often observe the slow ionic transport in the liquid crystalline materials, if their purity is not highly enough to find the electronic conduction. The ionic species in the liquid crystal that are responsible for
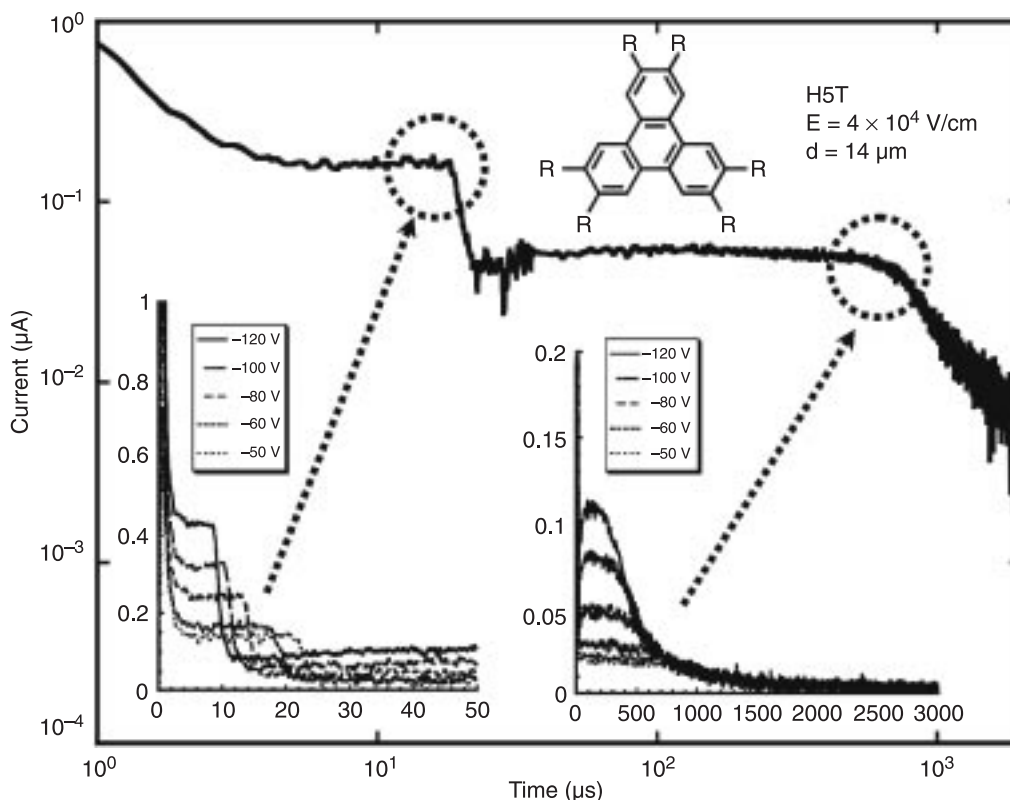

Fig. 5. Double logarithm plots of transient photocurrents for negative carriers in Col$_h$ phase of H5T at 100°C. The insets show the first and second transient photocurrents at different applied electric fields. The sample thickness was 14 μm. The electrodes were semi transparence aluminum.
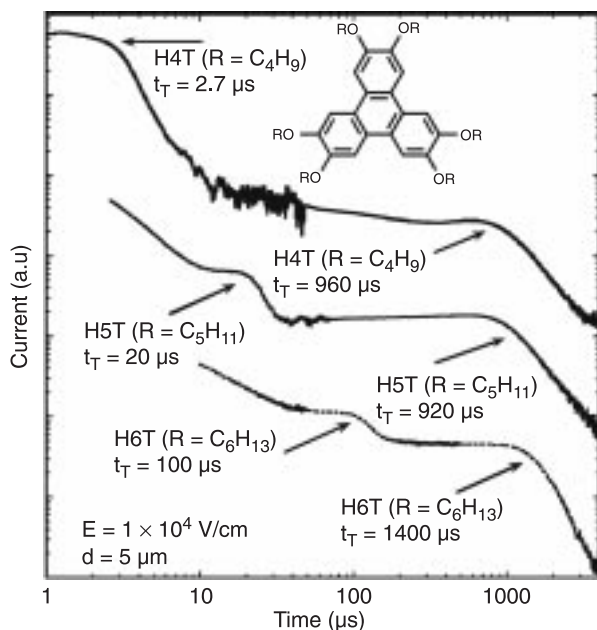
Fig. 6. Double logarithmic plots of transient photocurrents for negative carriers in the Col_h phases of H4T at 100°C, H5T at 100°C and H6T at 95°C, respectively. The thicknesses and applied voltages of three samples are same, 5 µm and –5 V. The grey area is a guide for eyes to indicate a time range for the second transits.

the slow transient photocurrent in the time-of-flight experiments have not been identified yet, but their origins are photo-ionized chemical impurities, which are originally neutral molecules contaminating liquid crystals during synthetic processes. The amount of the impurities that causes a devastating effect on electronic conduction in the liquid crystals is estimated to be less than a few ppm [34], and the effect can be detected even in a trace amount of 0.1 ppm [35]. In this point, the liquid crystalline mesophase is very

similar to the single crystal of organic materials, even though its mobility is not higer than those for organic polycrystals.

Taking account of microphase-separated structure in the mesophase materials, it is very plausible that the ions migrate to "a soft fluid-like region" consisting of hydrocarbon side chains aggregating loosely, while the electronic charges, i.e., electrons and holes, are transported via "a rigid solid-like region" consisting of closely packed π-conjugate core moiety of liquid crystalline molecules. In fact, the activation energies of ionic mobility in liquid crystals are 0.1~0.3 eV typically [23,30], which coincides with a activation energy of viscosity for hydrocarbons [36]. If so, we can draw a very interesting conclusion that there exist two distinctive channels for charge carrier transport in the mesophase in its intrinsic nature, that is, one for ions and the other for electronic charges. Therefore, the present discussion implies that the ambipolar electronic transport is very likely to be encountered in the mesophases of both discotic and calamitic liquid crystals as long as they are highly purified.

There remains an interesting question to be answered, concerning with the ambipolar transport in crystalline and liquid crystalline materials, why does it happen so often in these materials? It is not so easy to answer this question with any experimental ambiguities indeed, but the previous experimental results on the charge carrier transport properties in poly-(N-vinyl carbazole) (PVK) and a single crystal of its model compound, N-*iso*-propylcarbazole (NIPC) tell us a possible story about this question, an amorphous film of PVK is a typical p-type material and shows a very small hole mobility of 10^{-6} cm^2/Vs [37], while a single crystal of NIPC exhibits ambipolar charge carrier transport characterized by high mobilities of 0.33 cm^2/Vs and 1.0 cm^2/Vs for holes and electrons, respectively [38]. Taking account of a

Table. 2. Positive and negative charge carrier mobility in discotic liquid crystalline semiconductors.

	Hole (cm^2/Vs)	Electron (cm^2/Vs)	Anion (cm^2/Vs)	Phase	Temp. (°C)	Thickness (µm)	Ref.
H4T	2.3×10^{-2}	2.5×10^{-2}	4×10^{-5}	Col_{hp}	80	7	26,29
H5T	1.7×10^{-3}	1.9×10^{-3}	5×10^{-5}	Col_h	80	5	12,30
H6T	4×10^{-4}	4×10^{-4}	3×10^{-5}	Col_h	80	5	28,31
HHTT	1.4×10^{-3} 0.08	1.4×10^{-3} 0.08	7×10^{-6} —c	Col_h Helical	80 45	15	34,32
8H$_2$Pc	0.1 0.2	0.2 0.3	—c —c	Col_h Col_r	120 85	13	35,33
ZnOOEP^a	1×10^{-2}	8×10^{-3}	?^{d}	D^e	60	3.5	26
CuPc^b	2.2×10^{-3}	2.4×10^{-3}	?^{d}	Col_h	110	5	27

a – Zinc octakis (*β*-octoxyethyl) porphyrin,

b – 2-(12-Hydroxydodecyloxy)-3-methoxy-9,10,16,17,23,24- hexakis(3,4-didecyloxy phenoxy) phthalocyaninato copper(II),

c – No signal within a limit of S/N ratio for transient photocurrent measurement,

d – No description in the original papers,

c – Un-identified mesophase.

strong electron trapping effect of oxygen absorbed in the p-type of materials, it is plausible that closely packed molecules in ordered materials including liquid crystalline mesophases suppress oxygen diffusion from the surface into the bulk, preventing from the devastating effect of oxygen on electron transport. This idea needs to be proved by appropriate experiments.

5. Device applications utilizing ambipolar carrier transport in liquid crystals

As we describe in the introduction, the present device applications of organic semiconductors are backed up by various devices to compensate the unipolar carrier transport in amorphous organic semiconductors that are thought to be indispensable for fabricating large-area uniform films. Therefore, the unique features of high ambipolar mobility and electrically inactive structural defects including domain boundaries in the liquid crystals are very effective in improving the present devices and extending the present applications limited by charge transport properties of amorphous organic semiconductors, as for the xerographic photoreceptor for laser printers and photocopiers, the liquid crystal has a high potential to realize a single-layered photoreceptor. Furthermore, it helps to realize a single-material complementary FET, in photovoltaic applications, it is very promising because of ambipolar field-independent fast charge transport even at a low electric field of $10^3 \sim 10^4$ V/cm [39].

6. Conclusions

We have summarized the ambipolar carrier transport in discotic and smectic liquid crystals based on the updated experimental results until now, and discussed the intrinsic nature of charge carrier transport in the liquid crystals.

We indicate that the intrinsic nature of charge carrier transport in liquid crystals is probably ambipolar, where both electronic and ionic charges are transported basically irrespective of their polarity, and that this unique feature will play a very important role in further extension of organic semiconductors to new device applications in the future.

Acknowledgements

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