Beyond Amorphous Organic Semiconductors

Jun-ichi Hanna*

Imaging Science and Engineering Laboratory, Tokyo Institute of Technology

ABSTRACT

Recently it has been discovered that some types of liquid crystals, which believed to be governed by ionic conduction, exhibit a very fast electronic conduction. Their charge carrier transport is characterized by high mobility over 10^{-2} cm^2/Vs independent of electric field and temperature. Now, the liquid crystals are being recognized as a new class of organic semiconductors. In this article, a new aspect of liquid crystals as a self-organizing molecular semiconductor are reviewed, focused on their basic charge carrier transport properties and discussed in comparison with those of molecular crystals and amorphous materials. And it is concluded that the that the liquid crystal is promising as a quality organic semiconductor for the devices that require a high mobility.

Keywords: Organic semiconductor, Molecular crystal, Liquid crystalline semiconductor, Discotic liquid crystal, Smectic liquid crystal, Charge carrier transport, Mobility

1. INTRODUCTION

20 years later since the electrical properties in the molecular crystals of aromatic compounds had been extensively studied in 1950s to 1960s, the organic semiconductors was first applied to the photoreceptors for xerography practically[1], which is often called organic photoconductive coatings (OPCs). With a need of fast and non-impact printers for computer outputs, the xerographic photoreceptor have rapidly come into wide use in these ten years not only for photocopiers but also for laser printers. Furthermore, the second commercial application of the organic semiconductors has launched in the organic light emitting diodes (OLEDs)[2] a few yeas ago. Now, much attention is paid to the organic thin film transistors (OTFTs) for the next one.

In these commercialized products such as OPCs and OLEDs, the organic semiconductors are used in amorphous thin films, which are prepared by either wet-coating or vacuum evaporation of the materials. Indeed, the amorphous materials have no long range order in molecular alignment, that is, isotropic, so that we can prepare their uniform films in large-area easily.

In these two decades, the carrier transport properties in the amorphous organic solids have been well understood with the continuous effort by late Bosenberger[1], Bässler [3,4], and the others [5,6]. The carrier transport in the amorphous films is governed by hopping conduction via molecularly localized states basically, which is quite different from the band conduction in the molecular crystals. The hopping conduction in the amorphous solids was modeled as the charge migration with an assist of electric field and temperature among the sites Gaussian-distributed spatially and energetically, and simulated by computer-aided Monte Carlo simulation by Bässler[3]. According his formalism based on the simulated results, the mobility, μ, is described as a function of the Gaussian width of the density of states, σ, a parameter related to the distribution of molecular distance, Σ, and electric field, E, and temperature, T, the Boltzman constant, k, as shown in the following equation.

$$\text{For } \Sigma \geqq 1.5 \quad \mu(\sigma, \Sigma, E, T) = \mu_0 \, exp\,[-(2\sigma/3kT)^2]\,exp[C\{(\sigma/kT)^2 - \Sigma^2\}E^{1/2}]$$

$$\text{For } \Sigma < 1.5 \quad \mu(\sigma, \Sigma, E, T) = \mu_0 \, exp\,[-(2\sigma/3kT)^2]\,exp\,[C\{(\sigma/kT)^2 - 1.5^2)\}E^{1/2}]$$

n fact, this equation well explains the experimental results on the charge carrier transport in the amorphous thin films prepared by coating a solusion of a small molecular semiconductor and a polymer binder or a polymeric organic semiconductor, or by vacuum evaporation of a small molecule semiconductor[2]. It is very clear from the mobility described as a function of σ and Σ in the equation that the carrier transport in the amorphous organic solids is subject to the inherent nature of the amorphous materials, i.e., the distribution of the density of localized states.

* hanna@isl.titech.ac.jp; Phone +81-45-924-5176; Fax +81-45-924-5175; Imaging Science and Engineering Laboratory, Tokyo Institute of Technology, Nagatsuta Midori-ku, Yokohama, 226-8503, JAPAN

Organic Photonic Materials and Devices V, James G. Grote, Toshikuni Kaino, Editors,
Proceedings of SPIE Vol. 4991 (2003) © 2003 SPIE · 0277-786X/03/$15.00

In comparison with the molecular crystals, which are the best material in terms of the fast charge transport as is the case of the inorganic counterparts as well, the charge carrier transport properties in the amorphous materials are very poor: a mobile carrier is either electron or hole, and the bipolar transport seldom happens; the charge carrier mobility is one millionth of that in the molecular crystals, i.e., 10^{-6}~10^{-5} cm^2/Vs typically, and 10^{-3} cm^2/Vs at most; to make the matter worse, the mobility depends on temperature and electric field heavily. According to the Gaussian disorder model as described above, a typical deviation in the density of states, , ie., a Gaussian width, is 100 to 120 meV[1], which is fairly large compared with a thermal energy of kT at ambient temperature, e.g., 25 meV. This can explain the temperature-and-field dependent mobility observed in the amorphous materials. This hopping model provides us with a clear image for a material design of the amorphous organic semiconductors: the molecules having a spatially extended molecular structure, which is favorable for an efficient overlap of the wave function in the semiconductor molecules associating with the charge hopping, may give us high mobility. In fact, N,N'-diphenyl-N,N'-di(*m*-tolyl)-*p*-benzidine (TPD)[7], which is often used in the photoreceptors and the charge transport layer for OLEDs, has a spatially extended molecular structure and exhibits a high mobility on the order of 10^{-3} cm^2/Vs in a vacuum evaporated thin film. In addition, we have to pay attention to the crystallization when we deal with the amorphous material, because it is a thermally non-equilibrated material and often the crystallization occurs, leading to a significant deterioration of the carrier transport attributed to the deep defects at the boundaries of crystal grains.

2. PRACTICAL BASIS OF AMORPHOUS MATERIALS IN DEVICE APPLICATIONS

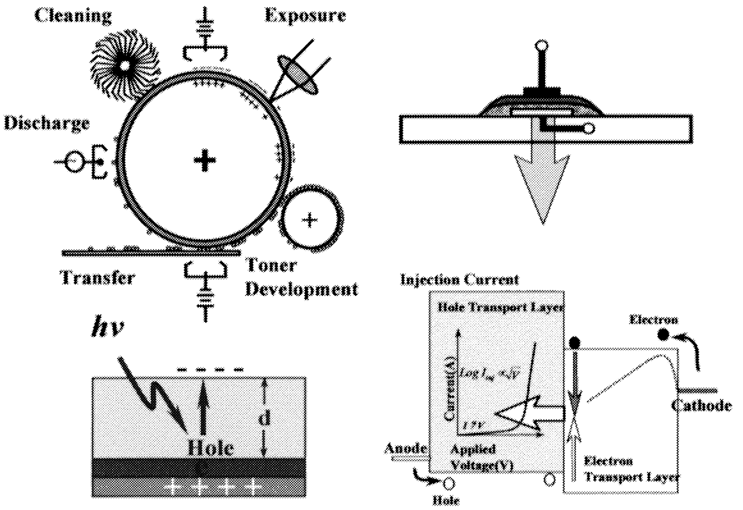

Fig. 1 Xerographic photoreceptor and organic light emitting diode

It is true that the amorphous materials are used practically as a key material for the charge carrier transport layer in the OPCs and OLEDs in spite of the poor charge carrier transport properties as described in the previous section. For the discussion followed, it is worth describing how such the amorphous materials can be available for the practical applications. In the OPCs for the xerography, their essential requirement in the materials is a carrier range larger, $\mu\tau E$ than a photoreceptor thickness, d, as shown in Fig.1, which is a distance for a photogenerated carrier of mobility, μ to reach at a given electric field, E within its life time, τ. Indeed the mobility is quite small in the amorphous materials, e.g, $10^{-6} cm^2/Vs$, but the life time of carriers is usually fairly long and exceeds msec. In addition, the applied electric field is over $10^5 V/cm$ when the photoreceptor is corona-charged. Therefore, this requirement of the carrier range is well satisfied when a carrier-lifetime products, $\mu\tau$ is over $10^{-8} cm^2/V$. The unipolar carrier transport is well compensated in the photoreceptors by adopting a layered structure consisting of a carrier generation layer and a carrier transport layer. Furthermore, a slow driving frequency of 1Hz for the photoreceptors allows us to use such a slow material because a transit time of carriers in the photoreceptor is only a few msec and negligible short compared with a xerographic process time of 1 sec (60 copies/min). This slow driving frequency is quite favorable also for the thermal relaxation of trapped charges at deep states in the photoreceptor, which are caused during photodecay of surface charges. Thus we can utilize the amorphous materials whose mobility is on the order of $10^{-6} cm^2/Vs$ for the xerographic photoreceptors. Here, the isotropic nature of the amorphous materials is quite beneficial to establish a large-area uniformity, and the low-cost and easy fabrication of organic thin films by wet-coating is a good basis of industrial production.

What is discussed on the xerographic photoreceptors above is also true in the case of OLEDs. An efficient carrier injection of both electrons and holes from the electrodes is crucial for a high brightness in OLEDs as shown in Fig.1, which requires high electric fields over 10^6cm/Vs and a close alignment of HOMO and LUMO levels with a work function of electrodes materials. Adopting a very thin device structure less than 100nm in thickness, the high electric filed over 10^6V/cm is established at a few volt, leading to an efficient electron and hole injection. Moreover, a response time for device operation also enjoys a great benefit of a thin device thickness and a high electric field established, resulting in a fast response less than a few microsecond in spite of a slow transport as described above. Furthermore, the unipolar carrier transport in amorphous materials is well compensated by adopting both electron and hole transport layers.

Thus, the amorphous materials having such the poor charge carrier transport properties are available for the OPCs and OLEDs on these basis back-upped by the structural design of devices and generous device requirements.

On the other hand, the amorphous materials are not available for the organic TFTs, because they require a high mobility for a high speed switching and a high current density essentially. Therefore, there must be something else for TFT applications.

This is also true for improvement of the device performance in OLEDs because the high mobility is beneficial for the enhancement of charge injection from the electrodes as well. The next target in the practical organic devices will be organic TFTs, which will be followed by organic photovoltaics and organic laser. These devices challenge us to realize a high mobility, well-defined ohmic contacts, and establishment of a local high field by junctions, which can hardly be performed by the amorphous organic semiconductors. Thus, a recent revived attention has been paid to the organic crystalline materials such as pentacene[8] and oligothiophes[9], whose mobilities are 5 to 6 orders of magnitude higher than those of amorphous materials.

3. ORGANIC CRYSTALLINE SEMICONDUCTORS

It is well known that molecular crystals of aromatic compounds exhibit excellent charge carrier transport properties, which had been studied in 1950s to1960s extensively. In crystalline materials, the electrical properties are very sensitive to the impurity, if it is electrically active: a trace amount of impurities, e.g., 1 ppm, often cause a serious degradation of their electrical properties[10]. Therefore, a special care has to be taken of the purification of materials, where the zone-refining technique is often used[11]. The most sophisticated material is a single crystal prepared from the material zone-refined. In such a single crystal, bipolar carrier transport is often observed. A typical mobility is around 1 cm^2/Vs independent of electric field and temperature at a certain temperature range. However, the carrier transport cannot escape from the harmful effect of grain boundaries in polycrystals, although the crystals are composed of molecules that never cause point defects such as dangling bonds. It is retarded by shallow and deep trapping states at the boundaries, where the impurities contaminated in the bulk are often accumulated. To make the matter worse, the boundaries often easily absorb oxygen in the ambient atmosphere, leading to an electrical instability in a long term in general. As for the practical applications of the molecular crystals, there remain several tough problems to be overcome, including how we can prepare large-area uniform films ?, how we can compensate the ill effect of grain boundaries in polycrystals ?, and how we can process the molecular crystals for devices ?.

Indeed, we do not know which way we should go for quality organic semiconductors available for TFTs and other advanced organic devices, but it is sure that the quality materials beyond the amorphous organic semiconductors have to have a molecular order, because the poor electrical properties in the amorphous organic semiconductors are attributed to the intrinsic nature of disordered molecular systems as described above.

4. LIQUID CRYSTALLINE SEMICONDUCTORS

4.1 Historical studies

Nowadays, the liquid crystals have been well established as a display material and are indispensable to display devices. The liquid crystals enjoy liquid-like fluidity and crystal-like molecular alignment. These unique nature gifts optical anisotropy and a feasibility of controlling the molecular orientation by external electric field, which are utilized in the display devices. In addition, the feasibility of fabricating uniform large-area and the stability as a thermally equilibrated material are a good basis for industrial applications.

In these ten years, it has been discovered that some types of liquid crystals exhibit very fast electronic conduction, which is 1000 to 10000 times faster than those of organic amorphous semiconductors practically used. The mobility exceeds 10^{-2}cm^2/Vs. Fig.2 shows typical examples: one is called the discotic liquid crystal and the other the smectic liquid crystals, which has a disk-like molecular shape and self-organizes in columns, and has a rod-like molecular shape and self-organizes in layers, respectively. Now the liquid crystals are being recognized as a new class of quality organic semiconductors.

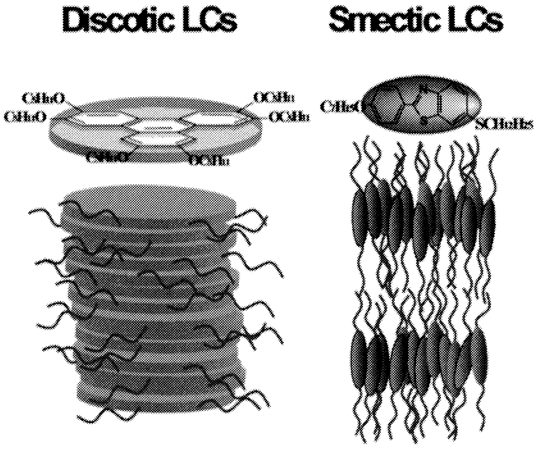

Fig.2 Discotic and smectic liquid crystals

Before describing the major topics in the liquid crystals, it is worth while to review historical studies on electrical properties in liquid crystals shortly, which is shown schematically in Fig. 3. The first attention to the electrical properties in liquid crystals goes back to late 1960s[12, 13]. Heilmeier in Philips paid his attention to charge carrier transport in the *p*-azoxyanisole[12] for his new invention[14], that is, the display device based on so-called dynamic scattering which was caused by ions drift in liquid crystalline phase. This called a considerable attention at that time. Many people looked at the electrical properties of liquid crystals and found that the conduction was always ionic[15]. This was quite acceptable at that time because of the fluid nature in liquid crystals.

After the discovery of the discotic liquid crystals by Chandraskhal in1977[16], the major interest in the electrical properties of liquid crystals was shifted from calamitics to the discotics which are more like a molecular crystal and hardly exhibit liquid-like fluidity. In late 1980's, Leeds and Delft groups had studied the electrical properties in chemically doped triphenylenes and porphyrins by time-resolved microwave conductivity measurements[17, 18], suggesting that these materials have a high mobility over 10^{-3}cm^2/Vs. After these pioneer works, finally, in 1993, the first electronic conduction was established in a triphenylene by means of the time-of-flight measurement conducted by Prof. Haarer and his coworkers in Bayreuth[19].

Two year later, we discovered independently that the smectic liquid crystal of a 2-phenylbenzothiazole derivative exhibits no less fast carrier transport than that of discotics[20] i.e., 5 ×10^{-3}cm^2/Vs which had been believed to be ionic for a long time. Since then, the various materials exhibiting fast electronic conduction have been discovered as listed in Fig. 3.

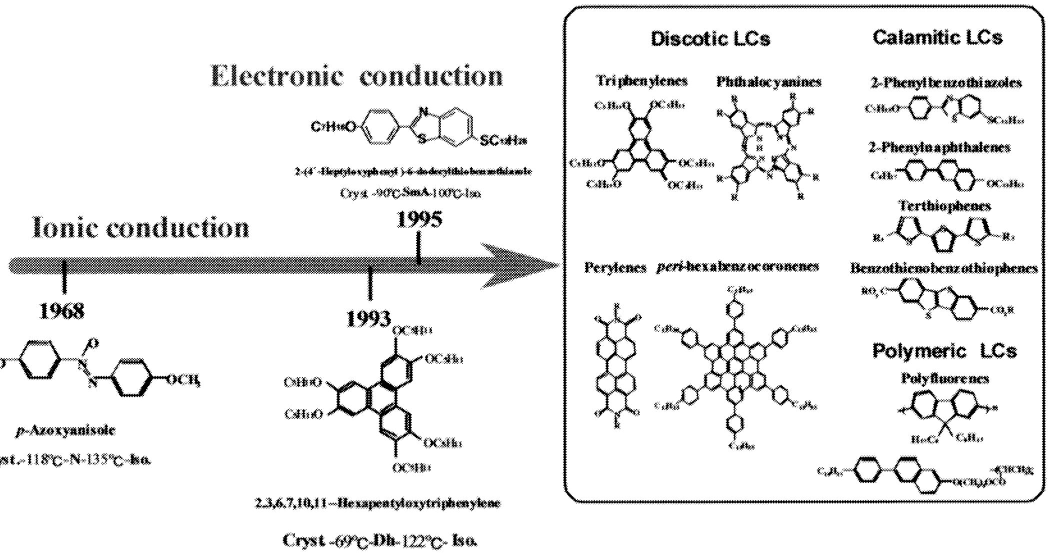

Fig. 3 Historical studies on electrical properties in liquid crystals.

4.2 Discotics

The discotic liquid crystals self-organizes in columns, in which the disk-like molecules are closely packed with thermal fluctuation. The average molecular distance is about ~3.5 A within a column and ~20 A or more in intercolumns. Therefore, the charge carriers are transported very fast along with the column. Fig. 4 shows the liquid crystalline material in which the electronic conduction was established for the first time. This material, i.e., hexapentyoxytriphenylene (HTP), exhibits a high hole mobility of 10^{-3} cm^2/Vs in the discotic hexagonal phase (D_h), which does not depend on temperature and electric field, while the mobility for negative carriers are on the order of 10^{-6} cm^2/Vs and very likely to be ionic.

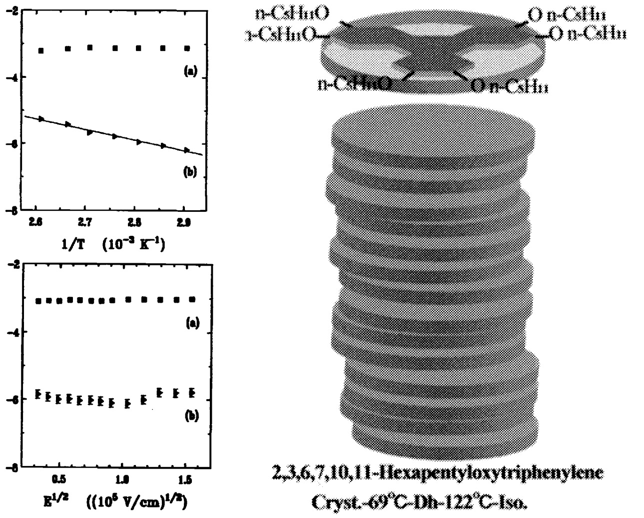

Fig. 4 Electronic conduction in Triphenylene (HPT).

The discotic liquid crystals most extensively studied are triphenylenes. The carrier transport properties in their various derivatives including a dimer[21] and polymers have been investigated[22, 23]. Fig. 5 shows these examples of the discotics in which the fast electronic conduction is confirmed either by time-of-flight technique or time-resolved microwave conductivity measurement, including triphenylene derivatives, the hexabenzocoronene called supercoronene[24], perylemes[25], phthalocyanes[26], small dendrons[27] that self-organize into the columnar hexagonal mesophase, and a discotic pair that stabilizes the columnar mesophase[28,29]. The highest mobility ever achieved is 8×10^{-2} cm^2/Vs in a herical phase of a thioalkyl derivative[30], while the higher mobility on the order of 10^{-1} cm^2/Vs determined by time-resolved microwave conductivity measurement was reported in the derivatives of hexabenzocolonene and lutetium phthalocyanine[26]. An interesting relation between a core size in discotic liquid crystals and their mobility is reported[31].

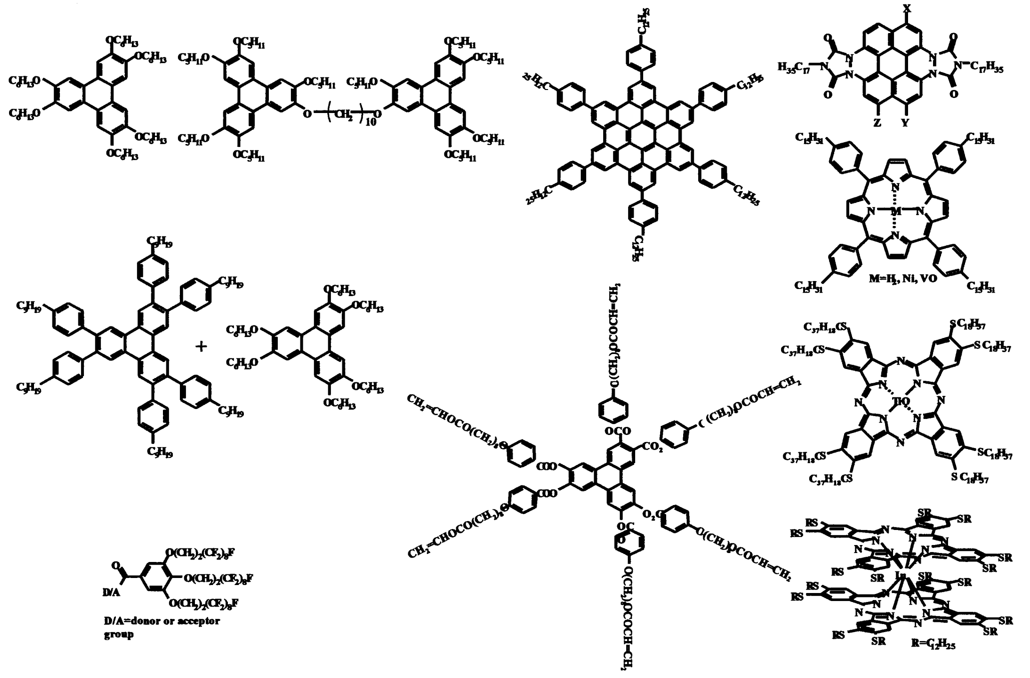

Fig. 5 Electronic conduction in various discotics

Recently Bushby et al found a unique discotic pair exhibiting 1:1 molecularly complexed mesophase called CPI disctics, which is stabilized by complementary polytropic interactions. This 1:1 mixture gives high mobility up to 10^{-2} cm^2/Vs, which is more than one order of magnitude higher than each discotic material alone. The carrier transport properties have been explained with several models including 1-dimensional disorder model[21] and a miniband models[32].

4.3 Smectics

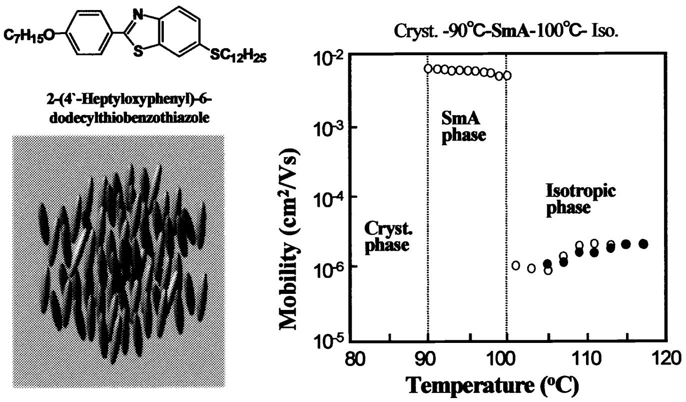

Fig. 6 First electronic conduction in smectic liquid crystal

The electrical conduction in calamitic (rod-like) liquid crystals including smectic liquid crystals had been believed to be governed by ionic conduction for a long time[33, 34]. In fact, many experimental results were reported to support the ionic conduction in the nematic and smectic liquid crystals before. The first electronic conduction was discovered in a smectic liquid crystal of 2-phenylbenzothiazole derivative in 1995[20], which is shown in Fig. 6. This lead to a general recognition that the liquid crystalline mesophase exhibits a fast electronic conduction. Now, it is has been recognized that there are two critical factors to determine the conduction mechanism in liquid crystals, i.e., which conduction takes place in a particular liquid crystal, the electronic or ionic conduction ? Of these critical factors is a viscosity in a given mesophase.

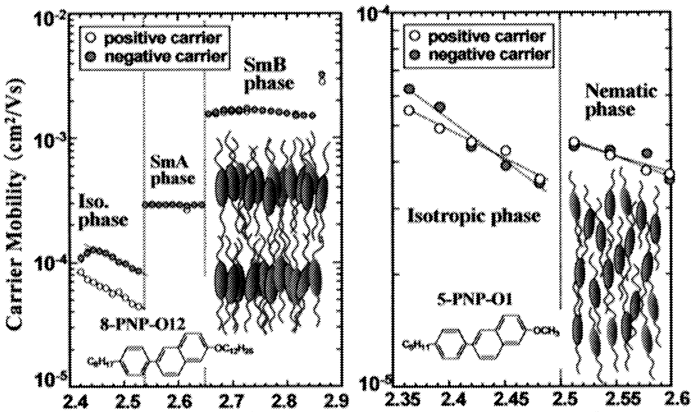

Fig. 7 Electronic and ionic conduction in 2-phenylnaphthalene derivatives.

In principle, the ionic conduction is possible in the liquid crystal due to its fluidity. Fig.7 shows the carrier mobility in different phases of 2-phanylnaphthalene derivatives as a function of temperature[35]. In smectic mesophases of 8-PNP-O12, i.e., SmA and SmB, the mobility is very high, i.e., on the order of 10^{-4} cm^2/Vs and 10^{-3} cm^2/Vs, respectively, which does not depend on temperature. This is attributed to the electronic conduction. On the other hand, in nematic and isotropic phases of 5-PNP-O1, the carrier mobility is very small, i.e., on the order of 10^{-5} cm^2/Vs that exhibits Arrhenius type behavior[35] due to the ionic conduction induced by a low viscosity in these phase. In addition, taking into account of a fact that the amorphous films of 2-phenylnaphthalene exhibit electronic conduction, it is very clear how important the viscosity is for the conduction mechanism, which is associated with a molecular alignment in the material. Another important factor to determine the conduction mechanism is a purity of the liquid crystals: doping experiments with a chemical impurity in the 2-phenylnephthalene derivative revealed that the conduction mechanism changed from "electronic" to "ionic" with a trace amount of the impurity, e.g., a few ppm or less, when it causes a deep states in the liquid crystals[36]. The trapped charge in a deep state in the liquid crystals does not mean a space harge that often occurs in the solid: once electron or hole is trapped at a deep state, i.e., a contaminated chemical impurity, the localized charge on the impurity starts to move as an ion because of the fluidity in the mesophase. Therefore, it is very plausible that the most of experimental results reporting the ionic conduction in smectic liquid crystals previously studied could result from a trace amount of chemical impurities contaminated in the liquid crystals.

In general, the carrier transport in smectic liquid crystals is upgraded from phase to phase in a discontinuous manner according to the sophistication of the molecular alignment when the phase transition takes place: for example, the mobility is enhanced from 10^{-4} cm^2/Vs to 10^{-3}cm^2/Vs, and 10^{-3} cm^2/Vs to 10^{-2} cm^2/Vs when the phase transition takes place in 2-phenylnaphthalene derivatives from SmA to SmB and from SmB to SmE[37], respectively. The thiophene derivatives follow this trend, which exhibit a series of SmC, SmF, and SmG phases[38]. The carrier mobility in deferent phases seems to be governed primarily by a molecular distance to the nearest neighbor: the mobility in the series of smectic mesophases of 2-phenylnaphtalene derivatives follows a relation between the molecular distance and the mobility in the hopping conduction regime.

Various smectic liquid crystals exhibiting a fast mobility have been discovered since 1995, which is summarized in Fig. 8. These include a sanidic liquid crystal exhibiting a lamello-columnar phase[39, 40]. In addition, the fast hole conduction is reported in oligosilanes exhibiting SmB phase [41,42,43]. The highest mobility ever achieved is 5×10^{-2} cm^2/Vs in a terthiphene derivative[44], which will be broken over 10^{-1} cm^2/Vs o sooner or later. It should be noticed that the chemical structure of the molecules listed in Fig. 8 is quite small and simple compared with those of amorphous materials such as TPD and its related materials popular in OLED and OPC applications, indicating how effective the closely packed molecular alignment is to establish the fast electronic conduction. However, any relation between a chemical structure and the mobility has not been established yet, which can be a guiding principle to design a liquid crystal molecule of a high mobility, although an interesting relation between a core size and a mobility is pointed out in the discotics[31].

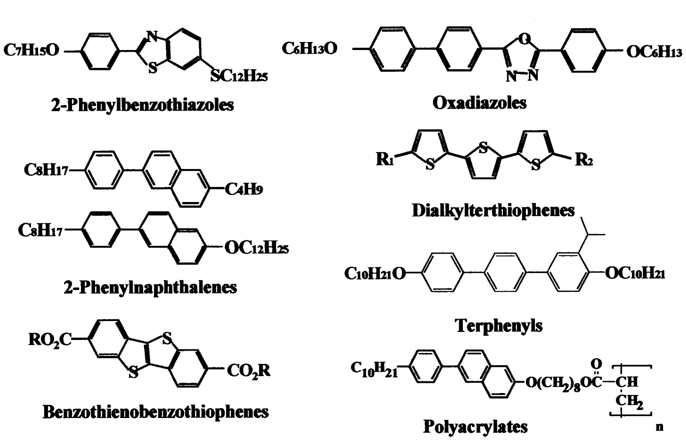

Fig. 8 Electronic conduction in various smectics.

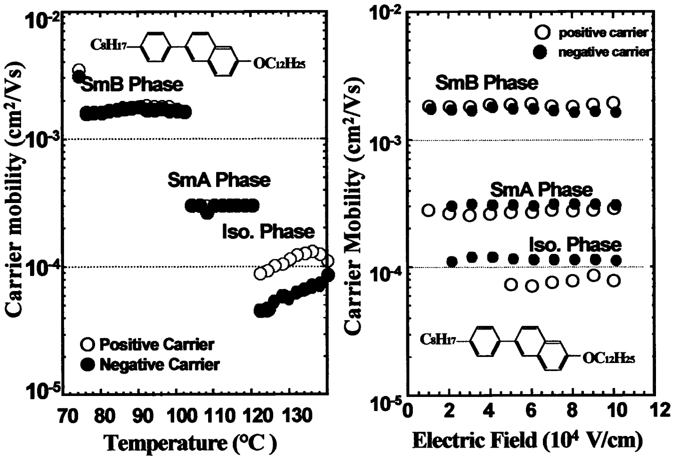

Fig. 9 Field-and-temperature independent mobility in 2-phenylnaphthalene derivative.

The carrier transport in smectics has some unique features. The bipolar carrier transport takes place in smectic liquid crystals, in which electron and hole are mobile. In fact, almost same mobilities for electron and hole are observed in 2-phenylnaphthalene and terthiphene derivatives. This seems to be a general feature in this type of materials, although the bipolar electronic transport has been seldom reported in the discotics so far[45,46]. Furthermore, the intrinsic mobility does not depend on the temperature and electric field in each mesophase basically as shown in Fig. 9, although the ionic conduction or the trap-controlled conduction, which is induced by contaminated impurities, depend on temperature. This field-and temperature independent carrier transport seems to be also common in the liquid crystals, and it is very different from those described by Poole-Frenkel type of behaviors in the amorphous materials. In this connection, there is an interesting question, i.e., does the smectic mesophase in polymeric liquid crystals also exhibit a high mobility as in the case of those in small molecules ? This was investigated by a side chain polymer having a pendant group of 2-phenylnaphthalene moiety as a core part[47]. This material exhibits SmA phase over 110°C and a high mobility of 10^{-3} cm^2/Vs at that phase. Interestingly, its glassy phase containing 20wt % of 8-PNP-O12 exhibits a high mobility of 10^{-3} cm^2/Vs at ambient temperature. There is another example of the polymeric liquid crystals exhibiting a high mobility. It is not a smectic but a nematic liquid crystal of π-conjugate main chain polymer, i.e., a polyfluorene , which exhibits nematic phase over 160°C. This material has a high mobility of 8×10^{-3} cm^2/Vs in nematic glassy phaset[48]. In fact, this mobility is fairly high, in spite of a low-molecular order of nematic phase. This probably due to a long coherent length of π-conjugate molecular system, which enhances charge hopping from molecule to molecule.

The charge carrier transport in smectic liquid crystals have not been fully understood yet. A few models are proposed to explain its unique feature as described above, including 2-dimensional hopping model in Gaussian-distributed density of states with a small deviation[49], a compensation of temperature dependence in two charge transport processes of non-thermally activated molecular polaron and thermally activated small lattice polaron[50], and a narrow band model[51].

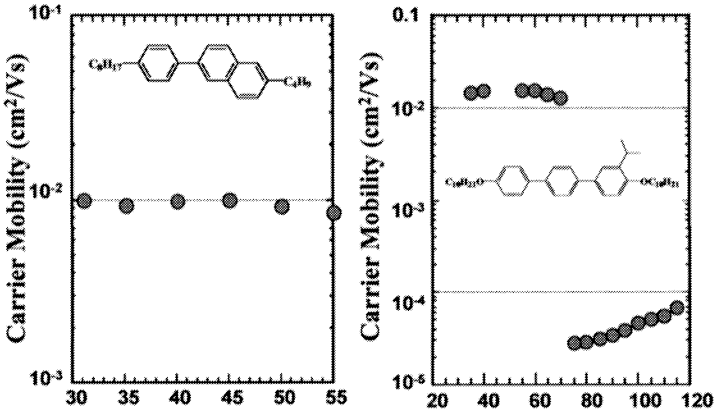

Fig. 10 High mobility at ambient temperatures.

There must be a high mobility material exhibiting a wide temperature range for a highly ordered mesophase at ambient temperature for the practical applications. It does not seem to be easy indeed, but a few examples satisfying this requirement have been demonstrated already, even though the guiding principle for the materials design has not been established yet: Fig. 10 shows a charge carrier transport properties of dialkylated 2-phenyl nathpathalenes[52] and terphenyl derivatives[53]. Both of the materials exhibit a high mobility over 10^{-2}cm^2/Vs at a wide temperature rage including ambient temperatures.

In addition, the fixation of the fluidity in the liquid may be required for extending their potential in the practical applications, which provides us with thin films on substrates. This was demonstrated by fabricating a composite with a cross-linked polymer, i.e., a liquid crystalline gel[54]. The charge carrier mobility in a pure 2-phenynathalene derivative of 8-PNP-O12 is well preserved when a mixture of 8-PNP-O12 and hexamethylene diacrylate of 20 wt% is photopolymerized in smectic mesophase, and a mixture of 8-PNP-O12 and diacrylate having 2-phenynaphthalene moiety of 50 wt%. Of course, the polymeric liquid crystals is an alternative for this approch as demonstrated by and an acrylate having 2-phenylnaphthalene moiety[47] and a polyfluorenes[48].

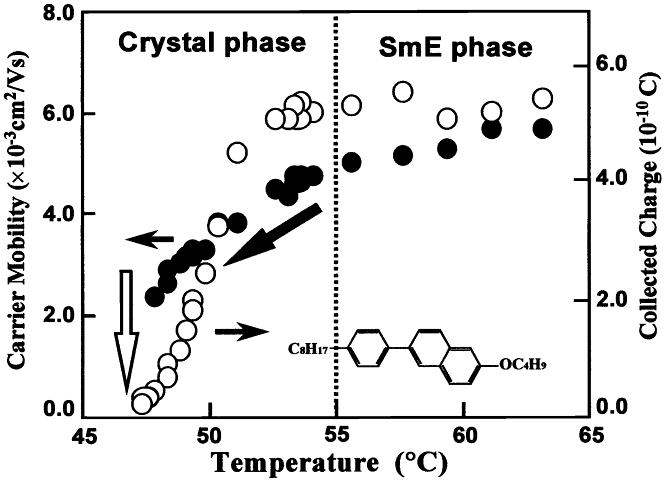

Fig.11 Boundary effect on charge carrier transport in polycrystal and smectic E phases of 2-phenylnaphthalene derivative.

Different from the isotropic amorphous materials, the liquid crystals exhibit molecular order in the mesophases. Therefore, there are any kinds of structural defects including disclination and domain boundaries, which is attributed to mis-orientation of liquid crystalline molecules. In organic polycrystals, such defects are electrically active and cause shallow and deep trapping states in polycrystals, which is not limited in the case of inorganic crystals. In fact, the recent increasing studies on organic polycrystals for OTFTs pointed out this problems repeatedly. The structural defects in the liquid crystals, however, are electrically inactive and does not cause any shallow and deep defects in mesophases[55, 56]. Fig. 11 shows a very interesting comparison between the grain boundaries in the polycrystal and the domain boundaries in liquid crystalline mesophase. In this figure, the carrier mobility and collected charges obtained by time-of-flight experiments, which are good indicators for evaluating formation of shallow and deep trapping states, respectively, is plotted as a function of temperature in SmE and crystalline phases of 2-phenylnaphthalene derivative of 8-PNP-O4. The dotted line indicates a phase transition temperature from SmE phase to crystalline phase. As is indicated clearly in the figure, the mobility goes down when the phase transition into the crystalline phase takes place at 55°C, and the collected charges also steeply go down neither when the temperature is reduced. These are attributed to the formation of shallow and deep trap states, respectively. On the other hand, there is no significant change in the mobility and the collected charges for SmE phese when the temperature is reduced. This tells us that the grain boundary of polycrystals is electrically active and forms shallow and deep trap states when the crystalline lattice is contracted as the temperature goes down. However, it is not the case in the liquid crystalline domains. The exact reason why the domain boundary does not show the ill effect on the charge carrier transport in the smectic liquid crystals obviously has not been answered yet, but it is likely that the molecular orientation at the interface of the domain boundaries is well aligned compatible enough for the carriers to hop from domain to domain thanks to liquid-like fluidity, even though th molecular orientation in th bulk is different in each domain. What is discussed here is a great advantage of the soft mesophase materials over the hard crystalline counterparts, especially for large-area applications.

4.4 Applications

Several applications with liquid crystalline semiconductors have been demonstrated so far, even though their industrial importance has not been recognized yet. These include a photosensor[57,58], light emitting diodes[59,60,61,62,63,64,65,66], photovoltaics[67, 68, 69], and xerographic photoreceptors[70]. The high mobility over 10^{-2}cm^2/Vs independent of electric field and temperature, the bipolar carrier transport, and various anisotropic properties including mobility, photocarrier generation, and optical absorption and emission in the liquid crystals provide us with high device performances such as a µsec fast photo-response in photosensor and polrized electrolumimescence in a light eiting diode, and a high efficincy in a solar cell.

The liquid crystals have several advantage for practical applications: for example, the cell technologies have been well established already for liquid crystal displays, which is also favorable for protecting the liquid crystalline materials from the ambient atmosphere. The fluidity is not always troublesome and provides us with a very convenient methods for device preparation. As a matter of fact, the highly ordered mesophases, which are always favorable for a high mobility, show not a liquid-like fluidity but a wax-like solidity. From the application point of view, the development of device structures and their device fabrication processes utilizing the unique properties in the liquid crystalline materials will extend further its high potential for device applications.

5. CONCLUDING REMARKS

A new aspect of liquid crystals as a self-organizing molecular semiconductor (SOMS) is reviewed to show a new direction for materials studies beyond organic amorphous semiconductors.

The charge carrier mobility in the liquid crystalline materials is two to three orders of magnitude higher than those of amorphous organic semiconductors, but one order of magnitude lower than those of organic crystalline semiconductors. However, the liquid crystals has an essential advantage over crystalline counterparts in terms of electrically inactive boundaries thanks to its liquid-like nature. The amorphous materials practically used stand between the molecular crystal and the liquid in terms of molecular alignment and the state of matters as shown in Fig. 12. That is, the amorphous material is more-like a molecular crystal in terms of the state of matters and more-like a liquid in terms of the molecular alignment. The feasibility of establishing large-area uniformity in large-area is achieved by their isotropic nature given by an entire loss of molecular orientation. In this point of view, the liquid crystals, or self-organizing molecular semiconductors are very similar to the amorphous materials, but are just opposite to them: the liquid crystal is more-like a molecular crystal in terms of molecular alignment and more-like a liquid in terms of the state of matters. The feasibility of large-area uniformity can be achieved as well thanks to the liquid-like fluidity. In addition, the liquid crystal is a thermally equilibrated material, so that it is never crystallized in mesophases. This is another big advantage over the amorphous materials.

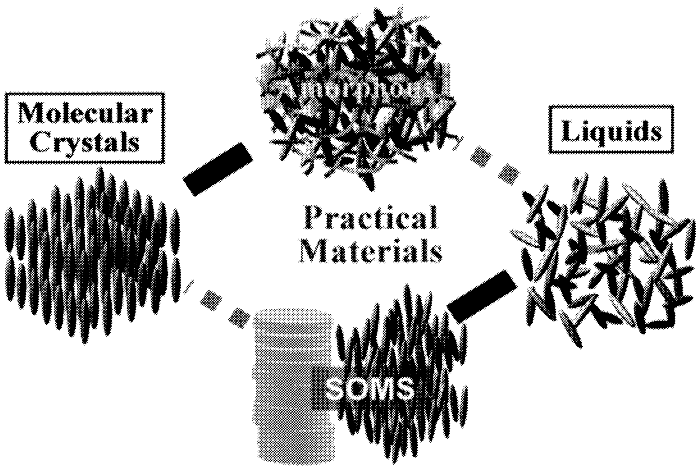

Fig. 12 Where SOMS stands ?

Since the first discovery of electronic conduction in discotics and smectics in 1993 and 1995, respectively, their basic properties including the charge carrier transport have been clarified, thus, the liquid crystals are being recognized as high quality organic semiconductors. However, the liquid crystals research in this new direction has just taken a first step for its vast future development. Therefore, there remain many questions to be answered, which includes:

1. What are the most important factors that influence charge mobility in SOMS?
2. How can the carrier transport in SOMS be understood theoretically?
3. What are the theoretical or practical limits of charge mobility in SOMS?
4. How can SOMS be designed with both high mobility and other important ancillary properties?
5. How can the carrier injection at the interface with the electrode materials be controlled and optimized?
6. What are the most unique phenomena and device structures involving SOMS?
7. What are the most promising technological applications for exploitation of SOMS?

In conclusion, we would like to stress that the materials research of the liquid crystals has just launched in this new direction and we are knocking on a door to a new materials field beyond the organic amorphous semiconductors, where has not been mined yet. We expect the SOMS opens a new materials world in the future.

ACKNOWLEDGMENT

This research was supported in part by the NEDO grant for international joint research.

REFERENCES

1 P. M. Borsenberger and D. S. Weiss, *Organic Photoreceptors for Xerography*, Marcel Dekker, Inc. New York, (1998).

2. C. W. Tang and S. A. Van Slyke, "Organic electroluminescent diodes,". *Appl. Phy. Lett.,* **51**, pp.913-915 (1987).

3. H. Bässler, “Charge Transport in Disordered Organic Photoconductors”, *Material Phys. Status. Solid, B* **175**, 15 (1993).

4.Y. N. Gartstein and E. M. Conwell, *J. Chem. Phys.,* **100**, 9175 (1994).

5. D. H. Dunlap, P. E. Parris, and V. M. Kenkre, *Phys. Rev. Lett.,* **77**, 542- (1996).

6. D. Hertel, H. Bässler, U. Scherf, and H. H. Horhold, *J. Chem. Phys.,* **110**, 9214 (1999).

7. M. Stolka, H-J. Yuh, K. McGrane, and D. M. Pai, *J. Phys. Chem.*, **88**, 4707 (1984).

8. S. F. Nelson, Y.-Y. Lin, D. J. Gundlach, and T. N. Jackson, “Temperature-independent transport in high-mobility pentacene transistors”, *Appl. Phys. Lett.*, 72, pp.1854-1856 (1998).

9. H. Sirringhaus and R. H. Friend, X. C. Li, S. C. Moratti, and A. B. Holmes and N. Feeder, "Bis(dithienothiophene) organic field-effect transistors with a high ON/OFF ratio", *Appl. Phys. Lett.*, **71**, pp.3871-3873 (1997).

10. H. Probst and N. Karl, *Phys.Stat. Sol. A*, 27, 499 (1975).

11. W. G Pfann, *Zone Melting*, J. Wiley, New York (1958).

12. G H. Heilmeirer and P. M. Heyman, “Note onTransient Current Measurement in Liqid Crystals and Related Systemsn”, *Phys. Rev. Lett.*, **18**, 583 (1967).

13. S. Kusabayashi and M. M. Labes, “Condictivity in Liquid Crystals”, *Mol. Cryst. Liq. Cryst.*, **7**, pp. 395-405 (1969).

14. G H. Heimeier, L. A. Zanoni, and L. A. Burton, *Proc. IEEE,* **56** pp.1162 (1968).

15. G Drefel and A. Lipnski, “Charge Carrier Mobility Measurements in Nematic Liquid Crystsal”, *Mol. Cryst. Liq. Cryst.*, **55**, pp.89-100 (1979).

16. S. Chandrasekhal and B. K. Sadashiva and K.A. Suresh, *Pramana*, **7,** 471 (1977).

17. N. Boden, R. J. Bushby, J. Clements, M. V. Jesudason, P. F. Knowles, and G. Williams, “One-dimensional electronic conductivity in discotic liquid crystals“, *Chem. Phys. Lett.*, **152**, 94 (1988).

18. P. G. Shouten, J. M. Warman, M. P. de Haas, M- A. Fox, and H.-L. Pan, "Charge Migration in Columnar Aggregates of Peripherally Substituted Porphyrins", *Nature*, **353**, 736 (1991).

19. D. Adam, F. Closs, T. Frey, D. Funhoff, D. Harrer, J. Ringsdorf, P. Schuhmacher, and K. Siemensmeyer, " Transient Photoconductivity in a Discotic Liquid Crystal," *Phys. Rev. Lett.*, **70**, pp. 457-460 (1993).

20. M. Funahashi and J. Hanna, “Fast Hole Transport in a New Calamitic Liquid Crystal of 2-(4'-Hepthyloxyphenyl)-6-dodecylthiobenzothiazole”, *Phys. Rev. Lett.*, **78**, pp. 2184-2187 (1997).

21. A. M. Van de Craats, L. D. A. Siebbeles, I. Bleyl, D. Haarer, Y. A. Berlin, A. A. Zharikov, J. M. Warman, “Mechanism of Charge Tranport along Columnar Stacks of a Triphenylene Dimer”, *J. Phy. Chem. B.*, **102**, pp.99625-9634 (1998).

22. A. Bacher, C. H. Erdelene, W. Paulus, H. Ringsdorf, H.W. Schmidt, P. Schumacher, “Photo-cross-linked triphenylene as novel insoluble hole transport materials in organic LEDs”, *Macromolecules*, **32**, pp.4551-4557 (1999).

23. M. Inoue, M. Ukon, H. Monobe, T. Sugimoto, and Y. Shimizu, “Effect of photopolymerization on photoconductivebehavior in triphenylene discotic liquid crystals”, *Mol. Cryst. Liq. Cryst.*, **365**, pp.1395-1402 (2001).

24. A. M .de Craats, J. M. Warman, A. Fechtenkotter, J. D. Brand, M. A. Harbison, and K. Mullen, “Record Charge Carrier Mobility in Room-Temperature Discotic Liquid Crystalline Derivative of Hexabenzocoronene”, *Adv. Mater.*, **11**, pp. 1469-1472 (1999).

25. C. W. Struijk, A. B. Sieal, J. E. Dakhorst, M.van Dijk, P. Kimkes, r. B. M. Koehorst, H. Donler, T. J. Schaafsma, J. P. Picken, A. M. Van de Craats, J. M. Warman, H. Zuohof, and E. J. R. Sundholter, “Liquid Crystalline Perylene Diimides: Architecture and Charge Carrier Mobilities”, *J. Amer. Chem. Soc.*, **122**, pp. 11057-11066 (2000).

26.K. Ban, K. Nishizawa, K. Ohta, A.M. van de Caats, J. M. Warman, I. Yamoamoto, H. Shirai, “Discotic liquid ctratls of trnsition metal complexes, 29, Mesomorphism and charge transport properties of alkylthio-substituted phthalocyanine rare-earth metal sandwich complexses”, *J. Mat. Chem.,* **11**, pp.321-331 (2001).

27. V. Percec, M. Glodde, T. K. Bera, Y. Miura, I. Shiyanovskaya, K. D. Singer, V. S. K. Balagurusamy, P. A. Heiney, I. Schnell, A. Rapp, H.-W. Spiess, S. D. Hudsonk, and H. Duank, "Self-organization of supramolecular helical dendrimers into complex electronic materials", *Nature*, **417**, pp.384-387 (2002).

28. T. Kreouzis, K. Scott, K.J. Donovan, N. Boden, R.J. Bushby, O.R. Lozman, Q. Liu “Enhanced electronic transport properties in complementary binary discotic liquid crystal systems”, *Chem. Phys.*, **262**, pp.489-497 (2000).

29. N. Boden R. J. Bushby, G. Cooke, O.R. Lozman, Z.B. Lu, “ A Recipe for Improving Applicable Properties of Discotic Liquid Crystals”, *J. Am. Chem. Soc.*, **123**, pp.7915-7916 (2001).

30. D. Adam, P. Schuhmacher, J. Simmerer, L. Haussling, K. Siemensmeyer, K. H. Etzbach, H. Ringsdorf, and D.Haarer, “Fast Photoconduction in the Highly ordered columnar phase of a Discotic Liquid Crystals*”, Nature*, **371**, 141 (1994).

31. A. M. van de Craats, J. M. Warman, “The Core-Size Effect on the Mobility of Charge in Discotic Liquid Crystalline Materials”, *Adv. Mater.,* **13**, pp.130-133 (2001).

32. N. Boden, R. J. Bushby, J. Clements, and B. Movaghar, “Mechanism of charge transport in discotic liquid crystals*”, Phys. Rev. B*, **52** 13274 (1995).

33. K. Okamoto, S. Nakajima, M. Ueda, A. Itaya and S. Kusabayashi, “Charge-carrier transport in nematic 2-[p-(decyloxy)benzylideneamino]-9-fluorenone”, *Bull. Chem. Soc. Jpn.*, **56**, pp. 3545-3548 (1983).

34. K. Okamoto, S. Nakajima, M. Ueda, A. Itaya, and S. Kusabayashi, “Electrical dark conductivities and photoconductivities of 2-[p-(decyloxy)benzylideneamino]-9-fluorenone in the nematic state”, *Bull. Chem. Soc. Jpn.*, **56**, pp.3830-3832 (1983).

35. M. Funahashi and J. Hanna, “Carrier Transport in Calamitic Mesophase s of Liquid Crystalkline Photoconductor 2-Phenylnaphthalene Drivatives”, *Mol. Cryst. Liq. Cryst.*, **331**, pp.509-516 (1999).

36. T. Kamitani, H. Fujita, M. Funahashi, and J. Hanna, to be submitted. (2003).

37. M. Funahashi and J. Hanna, "Anomalous High Mobility in Smectic E Phase of a 2-Phenylnaphthalene derivative", *Appl. Phys. Lett.*, **73**, pp. 3733-3735 (1998).

38. M. Funahashi and J. Hanna, "Fast ambipolar carrier transport in self-organizing Terthiophene derivatives", *Appl. Phys. Lett.* , **76**, pp.2574-2576 (2000).

39. D. Haristoy, S. Mary, B. Heinrich, L. Mager, J.F. Nicoud, D. Guillon, "Structure and photoconductive behavior of a sanidic liquid crystal", *Liq,. Cryst.*, **27**, pp.321-328 (2000).

40. S. Mary, D. Haristoy, J.F. Nicoud, D. Guillon, S. Diele, H. Monobe, Y. Shimizu, "Bipolar carriertransport in a lamello-columnar mesophase of a sanidic liquid crystals", *J. Mat. Chem.*, **12**, pp.37-41 (2002).

41. H. Okamoto, H. Yatabe, M. Shimomura, A. Kaito, N. Minami, and Y. Tanabe, "Self-organized oligosilanes; a new class of organic hole-transport materials", *Adv. Mater.*, **13**, pp.72-75 (2001).

42. H. Okamoto, H. Yatabe, J. Pewng, A. Kaito,and N. Minami, "Hole transport properties of Self-organized oligosilane films in a polycrystalline and a mesophase", *Synth. Met.*, **121**, pp.1507-1508 (2001).

43. H. Okamoto, H. Yatabe, M. Shimomura, A. Kaito, N .Minami, and Y. Tanabe, "High hole mobility in the ,olecularly ordered oligosilanes", *Synth. Met.*, **116**, pp.385-388 (2001).

44. M. Funahashi and J. Hanna, to be submitted. (2003).

45.Y. Yuan, B. A. Gregg, M. F. Lawrence, "Time-of-glight study of electrical charge mobilities in liquid crystalline zinc octakis(β-octaoxyethyl)porphyrin films", *J. Mat. Res.*, **15**, pp.2494-2498 (2000).

46. M. Funahashi and J. Hanna, "Fast Ambipolar Carrier Transport in Smectic phases of Phenyl naphthalene liquid crystal", *Appl. Phys. Lett.*, **71**, pp.602-604 (1997).

47. T. Shimakawa, T. Tani, and J. Hanna, to be submitted. (2003).

48. M. Redecker, and D. D. C. Bradley, M. Inbasekaran and E. P. Woo, "Mobility enhancement through homogeneous nematic alignment of a liquid-crystalline polyfluorene", *Appl. Phys. Lett.*, **74**, pp.1400-14002 (1999).

49. A. Ohno and J. Hanna, "Simulated carrier transport in smectic mesophase and its comparison with experimental result", *Appl. Phys. Lett.*, **82**, pp.751-752 (2003).

50. I. Shiyanovskaya and K. D. Singer, R. J. Twieg, L. Sukhomlinova, and V. Gettwert, "Electronic transport in smectic liquid crystals", *Phys. Rev. E*, **65**, pp.41714-41728 (2002).

51. B. Movaghar, L. Siebbles, and A. Pecchia, "Charge carrier mobility in smectic and discotic mesophases", to be published in *Proceedings of SPIE 4991* (2003)

52. Y. Takayashiki and J. Hanna, "Synthesis ans Characteriaztion of Liquid Crystalline Semiconducting Materials, Dialkyl-2-phenylnaphthalene Derivatives, -Mespmorphic behavior and Charge carrier trannsport-", *Mol. Cryst. Liq. Cryst.*, in press (2003).

53. Y. Takayashiki, T. Shmakawa, and J. Hanna, to be submitted. (2003).

54. N. Yoshimoto and J. Hanna, "A Novel Charge Transport Materials Fabricated Using Liquid Crystalline Semiconductor and Crossliked Polymer", *Adv. Mater.*, **14**, pp.988-991 (2002).

55. H. Maeda, M. Funahashi, and J. Hanna, "Effect of Domain Boundary on Carrier Transport of Calamitic Liquid Crystalline Photoconductive Materials", *Mol. Cryst. Liq. Cryst.*, **346**, pp.193-192 (2000).

56. H. Maeda. M. Funahashi, and J. Hanna, "Electrical Properties of Domain Boundaries in Photoconductive Smectic Mesophases and Crystal Phases", *Mol. Cryst. Liq Cryst.*, **366**, pp.369-376 (2001).

57. M. Funahashi and J. Hanna, "Micosecond photo-response in Liquid Crystalline photoconductor doped with C_{70} under Illumination of Visible Light", *Appl. Phys. Lett.*, **75**, pp.2484-2486 (1999).

58. H. Maeda, M. Funahashi, and J. Hanna, "New Aspects of Organic Electric Materials in Calamitic Liquid Crystalline Photoconductors", *Mat. Res. Soc. Symp. Proc.*, **598** BB3.61.1 (1999).

59. I. H. Stapff, V. Stumpflen, J. H. Wendorf, D. B. Spohn, D. Mobius, " Multilayer light emitting diodes based on columnar discotics", *Liq. Cryst.*, **23**,pp. 613-617 (1997).

60. K. Kogo, T. Goda, M. Funahashi, and J. Hanna, "Polarized Emission from Liquid Crystalline Semiconductor doped with dye", *Appl. Phys Lett.*, **73**, 1595 (1998).

61. H. Tokuhisa, M. Era, and T. Tsutsui, "Polarized electroluminescence from smectic mesophase", *Appl. Phys. Lett.*, **72**, pp.2639-2641 (1998).

62. S. Tanaka, C. Adachi, T. Koyama, Y. Taniguchi, "Organic light emitting didodes, usung triphenylene derivatives as a hole transport materials", *Chem. Lett.*, pp.975-976 (1998).

63. M. Funahashi and J. Hanna, *Proceedings of Annual Meeting in Japanese Society of Liquid Crystals*, in Japanese, pp.250-252, (1999).

64. I. Seguy, P. Destruel, H. Bock, "An all-columnar bilayer light emitting diode", *Synth. Met.*, **111**, pp.15-18 (2000).

65. T. Frauenheim, H. S. Kitzerrow, "Absorption and luminescence spectra of electrluminescent liquid crystals with triphenylene, pyrene and perylene units", *Liq. Cryst.*, **28**, pp.1105-1113 (2001).

66. R. Freudenmann, B.Behnisch, M. Hanack,"Stnthesis of conjugated-bridged triphentlenes and application in OLEDs", *J. Mat. Chem.*, **11**, pp.1618-1624 (2001).

67. K. Perisch, R.H. Friend, A. Lux, G. Rozenberg, S.C. Moratti, A.B. Homes, "Liquid crystalline phthalocyanines in organic solar cells", *Synth. Met.*, **102**, pp.1776-1777 (1999).

68. L. Schmidt-Mende, R. H. Friend, and J. D. MacKenzie, " Self-Organized Discotic Liquid Crystals for High-Efficiency Organic Photovoltaics", *Science*, **293**, pp.1119-1122 (2001).

69. L. Schmidt-Monde, A. Mullen, R. H. Friend, J.D. MacKenzie, "Efficient organicphotovoltaics from soluble discotic liquid crystalline materials", *Physica E*, **14**, pp.263-267 (2002).

70. H. Maeda and J. Hanna, *Proceedings of Japan Hardocopy'99*, in Japanese, pp.117-120 (1999).