

AWARD ACCOUNTS

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Development of Liquid-Crystalline Semiconductors with High Carrier Mobilities and Their Application to Thin-film Transistors

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Carrier transport in liquid-crystal phases, design of liquid-crystalline semiconductors with high carrier mobilities, and their application to field-effect transistors are reviewed. High carrier mobility has been observed in the smectic phases of oligothiophene derivatives as well as in the columnar phases of triphenylene and hexabenzocoronene derivatives. The mobility increases with the molecular ordering in the mesophases and extension of the π -conjugated system of the liquid-crystal molecules. Asymmetrically substituted liquid-crystalline oligothiophene derivatives retain the highly ordered smectic phases below room temperature. The liquid crystals are solution-processable and can be used in high-performance field-effect transistors. The transistors exhibit high hole mobility and on/off ratio of $4 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 10^7 , respectively.

KEY WORDS: Organic Semiconductor / Liquid Crystal / Liquid-Crystalline Semiconductor / Smectic Phase / Columnar Phase / Time-of-Flight Technique / Field-Effect Transistor /

Currently, organic semiconductors are being used in various electronics devices such as disposal xerographic photoreceptors.¹ Electroluminescence devices also have several practical applications.² Bulk heterojunction solar cells, in which p-type and n-type organic semiconductors form nanosegregated structures, have also attracted significant attention.³ Extensive studies on thin-film transistors (TFTs) based on crystalline films of aromatic compounds have been reported.^{4,5} Unlike inorganic semiconductors, whose fabrication requires the use of an expensive vacuum process, most organic semiconductors are solution-processable and can be incorporated into a variety of electronic devices *via* an inexpensive solution process.⁶ One of the recent researches is the development of flexible devices, including electronic papers.⁷ For use in electronic papers, it is indispensable to produce organic semiconductors with high carrier mobility as well as high flexibility.

It is not easy to construct a molecular system that has high carrier mobility, excellent solution processability, and high flexibility. A closely packed molecular structure, which is commonly observed in molecular crystals, facilitates carrier mobility. In aromatic molecular crystals, carrier mobilities exceeding $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ are sometimes observed.⁵ However, precise control of the crystal growth process is essential for high-quality crystalline thin films. Weak intermolecular interactions are indispensable for soft structures of solution-processable and flexible materials. However, such weak intermolecular interactions may result in the formation of amorphous structures with pendant polymers such as polyvinylcarbazole and low-molecular-weight aromatic amines, which exhibit low carrier mobility.⁸ Typically, carrier mobilities in amorphous organic semiconductors fall in the range of 10^{-7} – $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁸

One of the approaches to overcome the above-mentioned difficulty is to make use of the property of liquid crystallinity. Dynamic anisotropic nanostructures have been constructed in liquid crystal phases based on the weak intermolecular interactions and various enhanced electric and optical functionalities can be realized utilizing the nanostructure.⁹ Liquid crystals with highly ordered smectic or columnar phases have a crystal-like molecular packing structure, which is favorable for the fast transport of electronic charge carriers. In addition, a normal liquid-crystal molecule has a few alkyl chains, which make them soluble in organic solvents. The thermal motion of the alkyl chains also contributes to the flexibility and softness of the mesomorphic structures.

For application to fast-response field-effect transistors (FETs), crystalline organic semiconductors must have high carrier mobility. A few solution-processable organic semiconductors that can be used in the fabrication of high-quality polycrystalline thin films have been designed; thin films deposited using soluble precursor molecules are subsequently converted to polycrystalline thin films by thermal treatment.¹⁰ Solution-processable pentacene-bearing bulky substituents can be used to obtain homogeneous crystalline thin films by the spin-coating method.¹¹ However, control of crystal growth in solution processes is difficult, and hence, devices obtained by this process deliver an inferior performance as compared to those fabricated by the vacuum process. High-performance FETs have been fabricated using poly(3-alkylthiophene) and the related compounds;¹² their performance is strongly dependent on the rot of the polymers, and the reproducibility of their characteristics is found to be unsatisfactory.¹³ Both high-molecular-weight and low-molecular-weight liquid crystals are expected to constitute a new class of flexible, solution-

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processable organic semiconductors with high carrier mobilities.

HISTORICAL BACKGROUND^{14–17}

The idea of liquid-crystalline semiconductors was conceived in the 1970s. Yoshino *et al.* carried out detailed studies on electrical conduction in nematic, smectic, and cholesteric phases.^{18,19} Kusabayashi *et al.* synthesized liquid-crystalline compounds containing carbazole or fluorenone moieties, which are known to be good carrier transport materials.²⁰ They found that only ionic conduction occurs in liquid-crystal phases. Because of the increased industrial production of display devices using nematic liquid crystals, a number of researchers have carried out detailed investigations on the electrical conductivity in nematic liquid crystals.^{21–23} These liquid crystals were not so stable, and the contaminants or degraded species present in them caused ionic conduction. Ikeda *et al.* synthesized nematic polymers having carbazolyl groups as pendants. However, their hole mobilities were comparable to those of conventional amorphous photoconductive polymers.²⁴

In order to realize electronic conduction in liquid-crystal phases, it is necessary to enhance the rate of intermolecular charge transfer. Columnar phases or smectic phases, which have closely packed columnar or layer structures, are expected to facilitate rapid intermolecular charge transfer, although transport of electronic charge carriers has recently been confirmed in the nematic and cholesteric phases of oligothiophene derivatives as well.^{25–27} J. Simon *et al.* focused on the one-dimensional energy transfer in the columnar phases of mesomorphic phthalocyanines.²⁸ N. Boden *et al.* studied the discotic columnar phases of AlCl₃-doped hexaalkoxytriphenylene,²⁹ and D. Haarer *et al.* confirmed the transport of electronic charge carriers in the columnar phases using the time-of-flight (TOF) technique.^{30–32} M. Funahashi and J. Hanna synthesized derivatives of 2-phenylbenzothiazole and 2-phenylnaphthalene and confirmed the occurrence of electronic conduction in their smectic phases.^{33,34} It should be noted that the fast electronic charge carrier transport proceeds in liquid-like smectic A or B hexatic phases unlike the columnar phases having closed molecular stacking structures.

The remarkable development of organic electronics in this decade has led to the application of liquid-crystalline semiconductors in various electronic devices such as electroluminescence devices,^{35–39} solar cells,⁴⁰ and TFTs.¹⁵ From the viewpoint of processability, the high solubility of liquid-crystalline semiconductors in conventional organic solvents makes them suitable for device fabrication *via* solution processes. However, most of the previously reported discotic and smectic liquid-crystalline semiconductors crystallize at around room temperature, which limits their use in the fabrication of homogeneous thin films. Moreover, controlling the alignment of columns is difficult in the discotic columnar phases. For application to FETs, the columns in these semiconductors must be aligned parallel to the substrate surface, although a perpendicular alignment is preferred when using

these semiconductors in electroluminescence devices and solar cells.¹⁷

THE BULK CARRIER TRANSPORT CHARACTERISTICS IN THE LIQUID CRYSTAL PHASES AND THEIR STRUCTURE

In the past, carrier transport in the nematic phases of liquid crystals has been studied extensively by several researchers. However, only ionic conduction, which was caused by ionic impurities, was found to occur in these nematic phases. The carrier mobility was found to be on the order of 10^{-6} cm² V⁻¹ s⁻¹, which was the typical value observed for ionic species in low-molecular-weight organic liquids.^{18–23} The low viscosity of the nematic phase was found to favor ionic conduction, and moreover, the small transfer integral which was caused by the low molecular order, resulted in a decrease in the rate of intermolecular electronic charge transfer.

In contrast to the nematic phases, discotic columnar and smectic phases have one- or two-dimensional molecular condensation structures that enhance intermolecular electronic charge transfer.^{41,42} Since the 1990s, transport of electronic charge carriers has been studied in the discotic columnar phases of hexaalkyltriphenylene,^{30,31} hexaalkylthiotriphenylene,³² hexaalkoxyhexabenzocoronene,⁴³ and perylene tetracarboxylate derivatives.⁴⁴ Transport of electronic charge carriers has also been confirmed in calamitic systems such as the smectic phases of 2-phenylbenzothiazole,³³ 2-phenylnaphthalene,³⁴ oligothiophene,^{45–47} and bisthiénylbenzene derivatives.⁴⁸ The molecular structures of typical liquid-crystalline semiconductors are shown in Figure 1. The carrier mobilities were determined by the TOF technique,^{30–34,45–48} microwave absorption measurements,⁴³ and space-charge-limited current measurements.⁴⁴ The drift mobility in these phases, which was determined to be in the range of 10^{-4} – 10^{-1} cm² V⁻¹ s⁻¹ by the TOF technique, was found to be strongly affected by the structure of the liquid crystal phase.^{49,50}

The relationship between the carrier transport characteristics and structures of the columnar phases of triphenylene derivatives⁴⁹ and those of the smectic phases of 2-phenylnaphthalene and terthiophene derivatives was studied by the TOF method.⁵⁰

Three typical columnar phases present in triphenylene derivatives are shown in Figure 2. In the disordered columnar phase, the disk-like liquid-crystal molecules are randomly arranged within the columns. In contrast, the plastic phase has an ordered columnar structure, and each column rotates cooperatively. The helical phase is characterized by a more closely packed columnar structure and a stronger correlation between the molecular orientations in the columns. The carrier transport characteristics in these three phases in hexaalkoxytriphenylene and hexaalkylthiotriphenylene derivatives are studied by the TOF technique, as shown in Figure 2.⁴⁹ The hole mobility in the columnar disordered phase is on the order of 10^{-3} cm² V⁻¹ s⁻¹,^{30,31} however, it increases to a value on the order of 10^{-2} cm² V⁻¹ s⁻¹ in the plastic phase, which has a

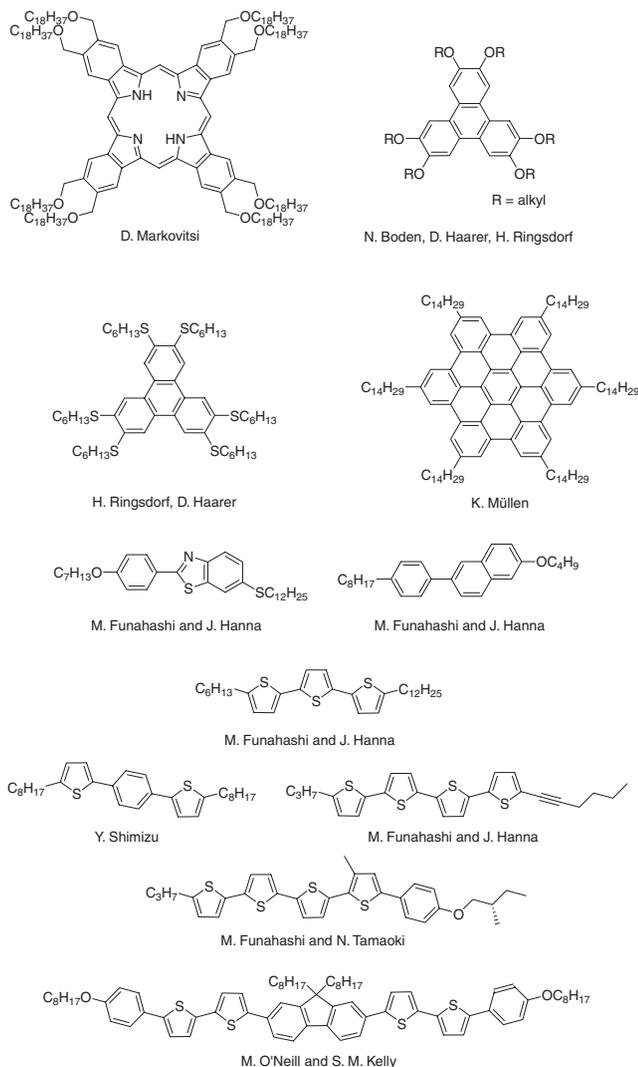
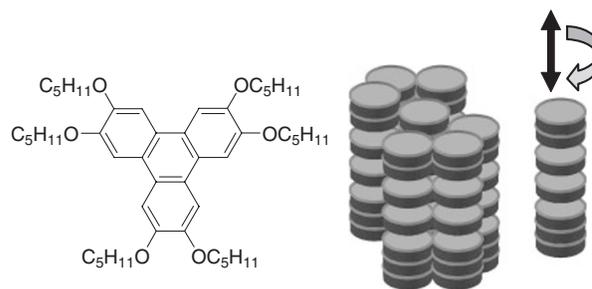


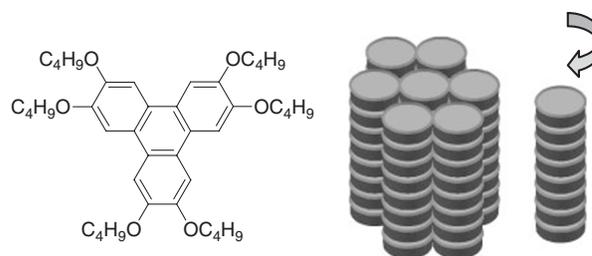
Figure 1. Molecular structures of typical liquid-crystalline semiconductors.

more closely stacked structure than the disordered phase.⁵¹ The hole mobility in the helical phase of hexahexylthiotriphenylene in which a crystal-like long-range molecular order exists within the columns,^{30–32} increases to $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; this is comparable to the hole mobility in molecular crystals.

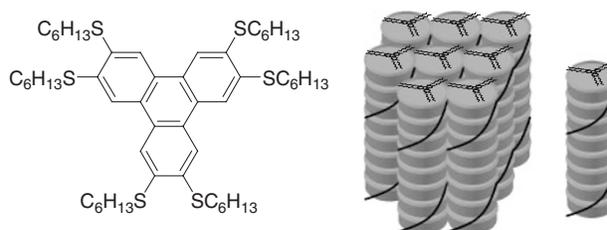
The same tendency was observed in the smectic phases of 2-phenylnaphthalene and terthiophene derivatives, as shown in Figure 3.⁵⁰ 2-(*p*-Octylphenyl)-6-alkoxynaphthalene derivatives exhibit smectic phases in which the director lies parallel to the layer normal, such as smectic A (SmA), smectic B (SmB), and smectic E (SmE) phases. In contrast, 5,5''-dialkyl-2,2':5',2''-terthiophene derivatives exhibit smectic phases in which the director is tilted with respect to the layer normal, such as smectic C (SmC), smectic F (SmF), and smectic G (SmG) phases. Regardless of the tilt angle of the director and the molecular structure, the carrier mobility is found to be on the order of $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ both in the SmA and SmC phases, in which there is no positional order within the smectic layers. The carrier mobility increases to a value of the order of 10^{-3}



Discotic disordered (D_{nd}) phase



Discotic plastic (D_p) phase



Helical (H) phase

Figure 2. Structures of columnar phases of triphenylene derivatives.

$\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the SmB and SmF phases, with a hexatic bond order.^{34,45} In the SmE and SmG phases, in which the molecules are highly ordered within the smectic layers, the mobility is on the order of $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^{45,52} Carrier mobility is thus confirmed to be strongly affected by the molecular ordering within the smectic layers. The relation between the carrier mobility and the mesophase structure is summarized in Figure 3.

DEPENDENCE OF CARRIER MOBILITY IN MESOPHASES ON THE FIELD ELECTRIC STRENGTH AND TEMPERATURE

One of the remarkable characteristics of carrier transport in the smectic and columnar phases is the small dependence of the

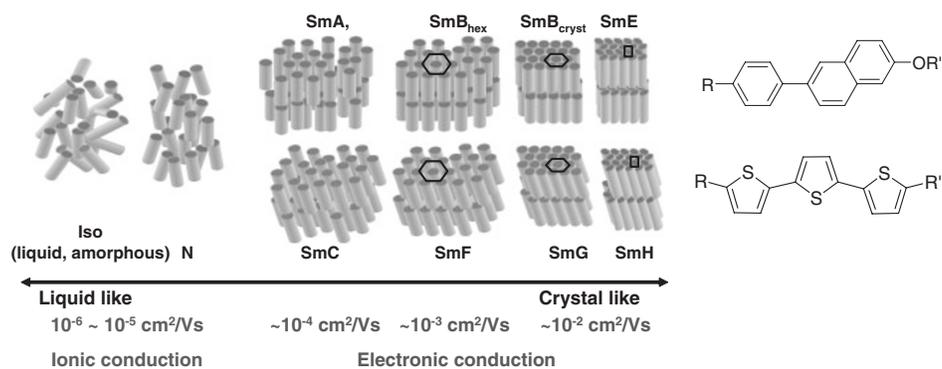


Figure 3. Relationship between the carrier mobility and the structure of the smectic phases.

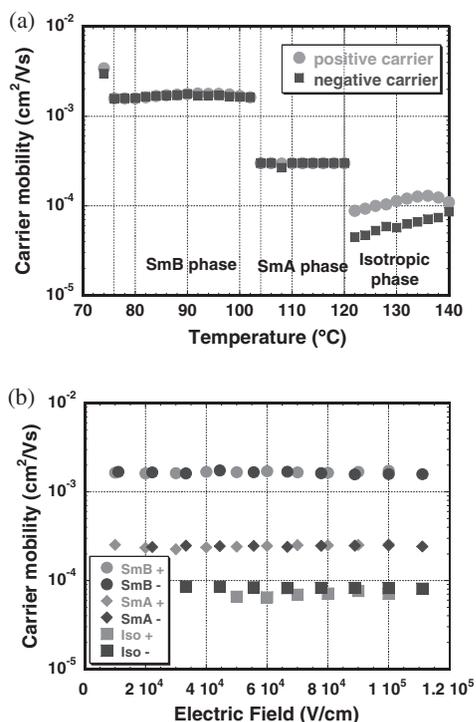


Figure 4. Carrier mobility of 2-(4'-octylphenyl)-6-dodecyloxynaphthalene **1** as a function of (a) the temperature at the electric field of 10^5 V cm^{-1} and (b) the electric field strength.

carrier mobility on the temperature and electric field strength above room temperature.^{30–34,45–47} This behavior is markedly different from that of amorphous organic semiconductors, in which the carrier mobility strongly depends on the electric field strength and temperature.^{53,54} Figure 4 shows the carrier mobility as a function of the temperature and electric field in the smectic phases of 2-(4'-octylphenyl)-6-dodecylphenylnaphthalene **1**.³⁴ In contrast to the isotropic phase, where ionic conduction is dominant, the mobilities of the positive and negative carriers are almost independent of the temperature and electric field strength. Such field- and temperature-independent mobilities are observed in the columnar phases of the hexaalkoxytriphenylene derivatives. The mobility of ionic carriers

is determined by the viscosity of the medium.²¹ The viscosity of organic fluids decreases with an increase in the temperature, resulting in positive temperature dependence of the ionic mobility. In amorphous semiconductors, the carrier mobility increases with the electric field strength and temperature. Amorphous semiconductors are characterized by energetic and structural disorders and the carrier transport involves a carrier hopping process, which is activated by the heat and electric fields.^{53,54} The temperature- and electric field-independent nature of the carrier mobility in smectic and columnar phases is similar to that of the carrier transport in molecular crystals, in which band-like conduction is dominant because of the large transfer integral and small disorders.⁵⁵ In smectic and columnar phases, the dense molecular packing within the layers and columnar structures is expected to increase the transfer integral and decrease the energetic and positional disorders, thus enhancing intermolecular charge transfer.

Liquid crystals **2**, **3**, and **4**, shown in Figure 5, exhibit the mesophases over wide temperature range including room temperature. In these compounds, carrier transport characteristics in the low-temperature region are different from those in the high-temperature region. In contrast to the carrier mobilities in the high-temperature regions in columnar and smectic phases, those in the low-temperature region are dependent on the electric field strength and temperature. The hole transport characteristics in the columnar phases of the triphenylene dimer **2**, as shown in Figure 5, are studied over a wide temperature range.^{56,57} Above 0°C , the hole mobility is almost independent of the electric field and the temperature; in contrast, below 0°C , it increases with the electric field strength and temperature. The dependence of the hole mobility on electric field strength becomes more pronounced at low temperatures.^{56,57} This behavior is described by the one-dimensional Gaussian disorder model (GDM), which was proposed for the carrier transport in amorphous organic semiconductors.⁵⁸ A similar behavior was observed in the columnar phase of a hexabenzocoronene derivative.⁵⁹

The carrier mobilities in the highly ordered smectic phases of alkynylterthiophene derivatives **3** and **4** are measured over a wide temperature range, *i.e.*, between 100°C and -100°C , by the TOF method. In particular, an ambipolar carrier transport is

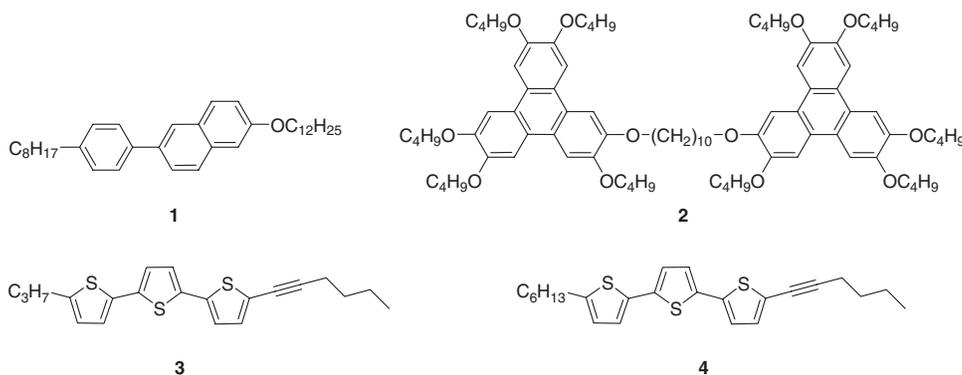


Figure 5. Molecular structures of triphenylene dimer, phenylnaphthalene, and alkylnylterthiophene derivatives.

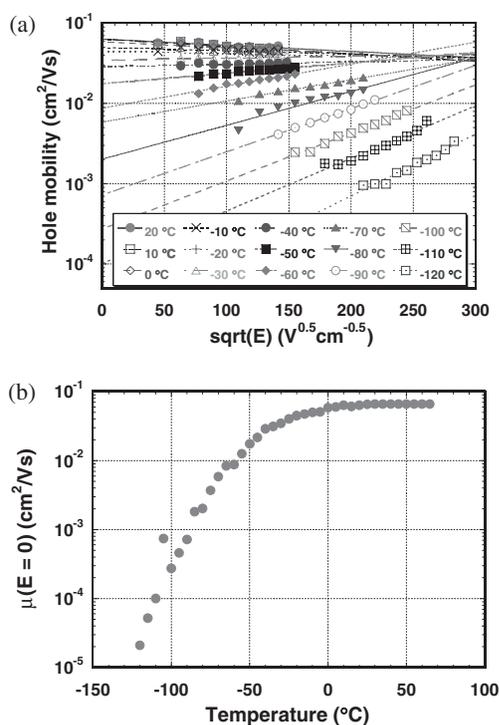


Figure 6. (a) The hole mobility as a function of the electric field strength. (b) Hole mobility extrapolated to zero-field as function of the temperature in the highly ordered smectic phase of 5-propyl-5'-hexynyl-2,2':5',2''-terthiophene (3).

observed in the smectic phase of compound 4.^{46,60} Figure 6 shows the hole mobilities as a function of the electric field strength and temperature. In the smectic phases, the hole and electron mobilities are on the order of $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; above the critical temperature, the mobilities become independent of the electric field strength and temperature, but below the critical temperature, they decrease with a decrease in the electric field strength and temperature. This behavior has also been described by the GDM. The energetic disorders in the columnar and smectic phases are approximately 50 meV; this value is 50% of that observed in amorphous organic semiconductors.⁶⁰ These results indicate that the energetic and structural disorders in columnar and smectic phases are lower

than those in amorphous organic semiconductors. In the high-temperature region, most of the carriers are excited into the transport states, and the carrier mobility should be independent of the temperature and electric field strength.

MOLECULAR STRUCTURE AND CARRIER MOBILITY

Warman and Müllen studied the microscopic carrier mobilities in the discotic columnar phases of various discotic mesogenic compounds by pulse-radiolysis time-resolved microwave conductivity (PR-TRMC).^{43,61} Their results indicated that the microscopic carrier mobility increased with the number of the electrons in π -conjugated systems.⁶² Funahashi and Hanna also confirmed a similar behavior in the macroscopic hole mobilities, which were determined by the TOF technique, in the smectic phases of alkylnylterthiophene and alkylnylquaterthiophene derivatives.⁴⁷

They also showed the relationship between carrier mobility and intermolecular distance within the smectic layers.^{42,50} During hopping transport, the carrier mobility μ is determined from the intermolecular distance r and the extension of molecular orbitals γ , as described in eq 1.⁶³

$$\mu \propto \exp\left(\frac{-r}{2\gamma}\right) \quad (1)$$

Figure 7 shows the relationship between μ and r within the smectic layers in the smectic phases of 2-phenylnaphthalene and dialkylnylterthiophene derivatives. The plots of the 2-phenylnaphthalene and terthiophene derivatives are fitted to different curves on the basis of eq 1. This result indicates that carrier mobility is mainly determined by r and γ . In the highly ordered smectic phases, the closely packed molecular structures bring about in a decrease in the intermolecular distance and an increase in the transfer integral. In contrast to 2-phenylnaphthalene derivatives, dialkylnylterthiophene derivatives contain sulfur atoms with large van der Waals radii; hence, because of their extended molecular orbitals, the carrier mobility in these compounds is significantly high. High carrier mobilities exceeding $1 \times 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ are observed in the highly ordered mesophase of 1,4-di(5'-octyl-2'-thienyl)benzene⁴⁸ and

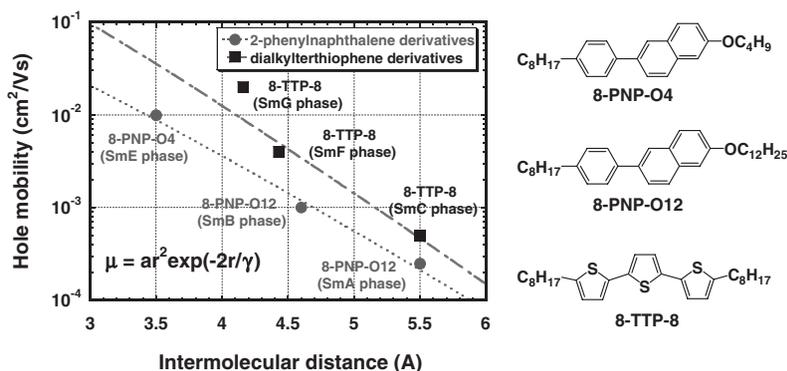


Figure 7. Carrier mobilities in the smectic phases of 2-(4-alkylphenyl)-6-alkoxynaphthalene and dialkylterthiophene derivatives as a function of intermolecular distance within the smectic layers.

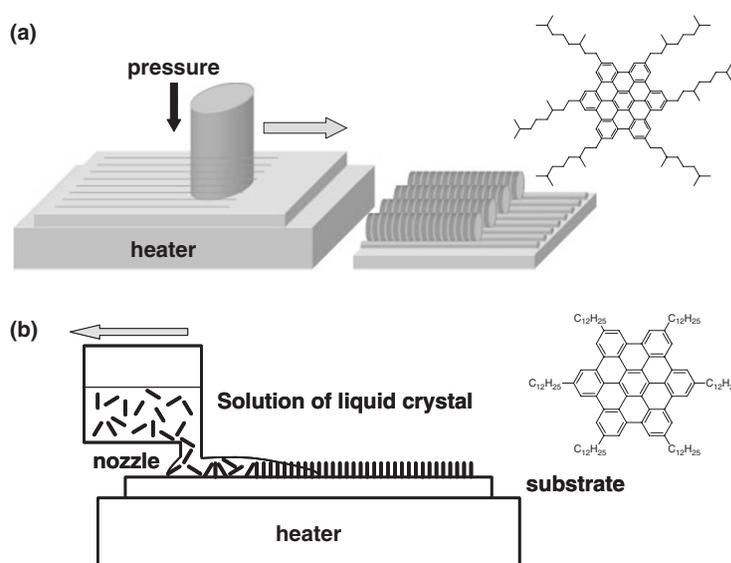


Figure 8. Schematic images of preparation of columnar liquid-crystalline thin films with uniaxially aligned columns. (a) Friction-transfer method. (b) Zone-casting method.

in the smectic phase of alkynylquaterthiophene derivatives with extended π -conjugated systems.⁴⁷

SOLUTION-PROCESSABLE LIQUID-CRYSTALLINE SEMICONDUCTORS WITH HIGH CARRIER MOBILITIES

As mentioned above, extension of the π -conjugated system in liquid-crystalline semiconductors results in increased carrier mobility. However, this extended conjugation decreases the solubility of these semiconductor compounds in organic solvents and increases the mesomorphic temperature range. The linear or branched alkyl chains in the liquid-crystal molecules increase their solubility in organic solvents and lower the mesomorphic temperature range.

FETs Based on Disk-like Liquid-Crystal Molecules

Carrier transport in the columnar phases of hexabenzocoronene derivatives has been investigated by the PR-TRMC

method.^{46,61,62} It reveals quite high microscopic carrier mobility in the columnar phases of the compounds. However this result indicates that the high carrier mobility would be realized in the ideal columnar structure without defects and disorders. The macroscopic drift mobility, which is associated with the device performance, should be lower than the microscopic drift mobility. For the fabrication of FETs, the macroscopic alignment of the columns should essentially be parallel to the surface of the gate dielectric layers. Such a parallel alignment of the columns cannot be achieved by conventional solution processes such as spin-coating and casting. Monobe and Shimizu succeeded in controlling the molecular alignment in the columnar phases of hexaalkoxytriphenylene derivatives by IR laser illumination.^{64–66} However, control of the molecular alignment in columnar phases still remains a challenge.

Müllen *et al.* succeeded in uniaxially aligning the columnar phases of hexaalkylhexabenzocoronene derivatives by friction-transfer⁶⁷ and zone-casting⁶⁸ methods, as shown in Figure 8.

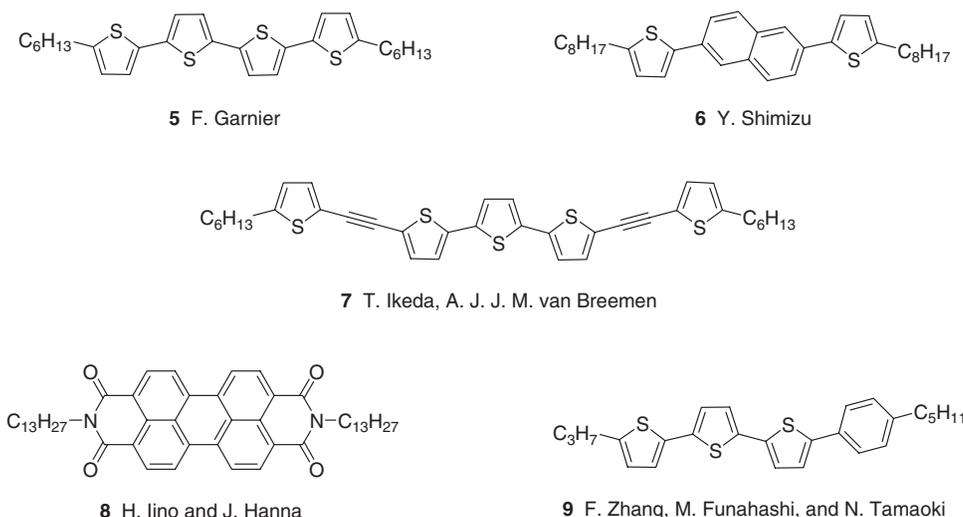


Figure 9. Liquid-crystalline semiconductors used for fabricating FETs.

By the friction transfer method, a uniaxially aligned teflon thin film can be deposited on a substrate. The columnar liquid crystal forms a homogeneous thin films in which the columns are uniaxially aligned parallel to the Teflon film surface when the solution of the liquid crystal is casted on the Teflon film. Thin-film transistors based on the uniaxially aligned columnar liquid crystals exhibited the hole mobility on the order of $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and the on/off ratio of 10^4 .⁶⁷

In the zone-casting method, the continuously supplied solution of the liquid crystal is spread on a moving substrate using a nozzle. Under the optimized conditions, a stationary concentration gradient causes directional crystallization. The hole mobilities in transistors fabricated on uniaxially aligned columnar liquid crystal films improved to $1 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁶⁸

FETs Based on Rod-like Liquid-Crystal Molecules

Control of molecular alignment in the smectic phases consisting of rod-like molecules is relatively easier than that in columnar phases consisting of disk-like molecules. A few examples of smectic liquid-crystalline semiconductors used in FETs are shown in Figure 9.

Garnier *et al.* fabricated FETs based on liquid-crystalline dihexylquaterthiophene (**5**).⁶⁹ They found that two-dimensional arrangement of molecules at the interface between the dielectric and semiconductor layers enhanced the performance of FETs based on organic polycrystalline semiconductors. Vacuum deposition and spin-coating methods could be used to fabricate polycrystalline thin films of liquid-crystalline dihexylquaterthiophene, in which the molecules align themselves perpendicular to the dielectric surface because of their liquid crystallinity. The carrier mobilities in the devices fabricated by the vacuum deposition and spin-coating method were 0.03 and $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. These values were higher than those observed in devices fabricated from non-liquid-crystalline quaterthiophene without alkyl chains.

Shimizu *et al.* fabricated FETs based on vacuum-deposited thin films of bis(2-alkylthienyl)naphthalene derivatives **6**.⁷⁰ The hole mobility in these FETs reached $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which was comparable to that in FETs based on vacuum-deposited polycrystalline thin films. In this study, thin films of the liquid crystalline compounds were in the crystal state, and the devices were operated in the crystalline state.

Van Breemen *et al.* fabricated uniaxially aligned crystalline thin films having a large area from a liquid-crystalline semiconductor, 5,5''-bis(5-hexyl-2-thienylethynyl)-2,2':5',2''-terthiophene **7**,⁷¹ by the spin-coating method. This compound crystallizes at room temperature; however, the molecular order gradually increases when it is cooled from the isotropic phase to the crystal phase. This is because various smectic phases appear successively between the isotropic and crystal phases.⁷² In the smectic phases, the liquid-crystal molecules are aligned uniaxially, and this alignment is maintained in the crystalline state. FETs fabricated using such uniaxially aligned crystalline thin films exhibit good hole mobilities up to $2 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Iino and Hanna also used the spin-coating method to fabricate well-aligned crystalline thin films of mesomorphic dialkylquaterthiophene and perylenetetracarboxylic acid diimide derivatives **8** at their mesomorphic temperatures.⁷³

In the above approaches, liquid crystallinity is a method to align the semiconductor molecules and the crystallized thin films are utilized for the device operation. However, in these films, defect formation resulting from volume shrinkage during the transition from the liquid crystal phase to the crystal phase is observed. Liquid-crystalline thin films can be easily fabricated by spin-coating from the materials that exhibit the liquid-crystalline phase at room temperature. Such liquid-crystalline thin films are expected to have a low defect density because of the thermal movement of molecules. On the other hand, the highly ordered smectic phases of rod-like molecules are waxy and have sufficiently mechanical strength for the fabrication of FETs.

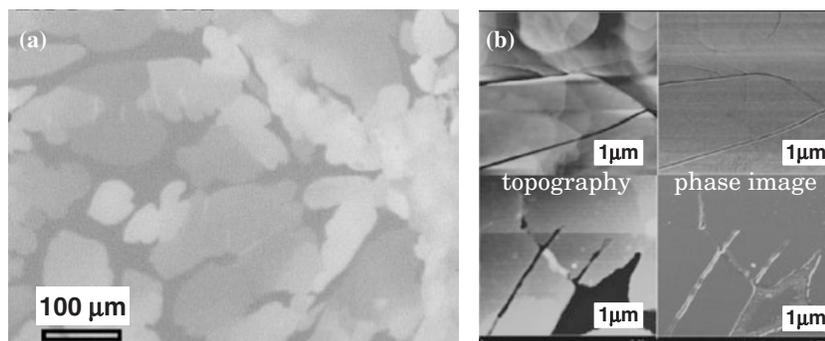


Figure 10. (a) Polarized light microscopic image of a thin film of **9** produced by the spin-coating method (b) AFM images of the thin film surface. The two images on the top are as-deposited thin film. The two images at the bottom show the thermally annealed thin film.

Funahashi *et al.* synthesized 5-alkyl-5''-(4-alkylphenyl)-2,2':5',2''-terthiophene derivatives, which exhibit a highly ordered smectic phase over a wide temperature range, including room temperature.⁷⁴ TOF measurements revealed fast ambipolar carrier transport in the bulk smectic phase of 5-propyl-5''-(4-pentylphenyl)-2,2':5',2''-terthiophene **9** around room temperature. The electron and hole mobilities were 0.2 and 0.07 cm² V⁻¹ s⁻¹, respectively.

Compound **9** is soluble in various organic solvents, and homogeneous liquid-crystalline thin films with thicknesses of several tens of nanometers can be deposited by spin-coating a chlorobenzene solution of **9**. Figure 10 shows the micrographic texture and surface morphology of a liquid-crystalline thin film observed under a polarized light microscope and an atomic force microscope (AFM), respectively. Optical texture observations under a polarized light microscope reveal the formation of very large domains with sizes of several hundreds of micrometers. In conventional FETs, the channel length is around several tens of micrometers, which is sufficiently smaller than the domain size. This fact suggests that carriers can be transported smoothly without being affected by the domain boundaries.

X-Ray diffraction (XRD) analysis of the liquid-crystalline film obtained from **9** reveals the existence of a layered structure and the long-range order in the position of the molecules within the layers. As shown in Figure 11, diffraction peaks appear in the low-angle ($2\theta < 5$ deg.) and high-angle (15 deg. $< 2\theta < 25$ deg.) regions, while no peaks are observed between the two regions, indicating that this thin film has a two-dimensional mesomorphic structure.⁷⁵ The liquid-crystalline molecules in the thin films are aligned perpendicular to the substrate surface.

FETs were fabricated by vacuum-deposition of Au source and drain electrodes through a shadow mask onto the liquid-crystalline thin films spun on Si/SiO₂ substrates. The typical length and width of the channel were 20–50 μm and 5 mm, respectively. Figure 12 shows the output and transfer characteristics of the FET based on the liquid-crystalline film. In this FET, p-type operation was observed, and the hole mobility and on/off ratio were 2 × 10⁻² cm² V⁻¹ s⁻¹ and 10⁶, respectively. As in the case of FETs obtained from organic polycrystalline films, treatment of the surface of the dielectric layer with a

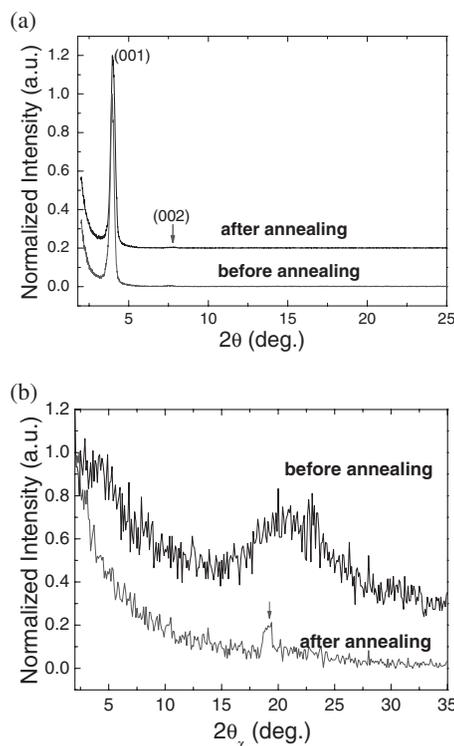


Figure 11. XRD pattern of liquid-crystalline thin film of 5-propyl-5''-(4-pentylphenyl)-2,2':5',2''-terthiophene (**9**) measured (a) in the out-of-plane configuration and (b) in the in-plane setup.

silane coupling reagent resulted in improvement of the device performance. When octyltrichlorosilane was used for the treatment, the field-effect hole mobility and on/off ratio increased to 4 × 10⁻² cm² V⁻¹ s⁻¹ and 10⁷, respectively.⁷⁵

One of the remarkable characteristics of liquid crystals is their softness. Liquid-crystalline semiconductors are expected to be superior to molecular crystals in terms of their flexibility. Someya *et al.* carried out commendable research on flexible transistor arrays based on vacuum-deposited polycrystalline films of pentacene.^{76,77} However, the liquid crystalline semiconductors can offer more flexible electronics devices.

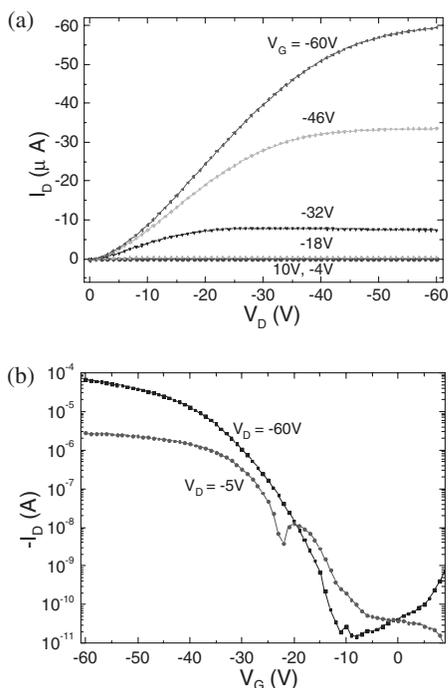


Figure 12. (a) Output characteristics of the FET of **9** on the octyltrichlorosilane-treated SiO₂ surface. (b) Transfer characteristics of the FETs built on the SiO₂ surface treated by octyltrichlorosilane. The channel length and width are 20 μm and 5 mm, respectively.

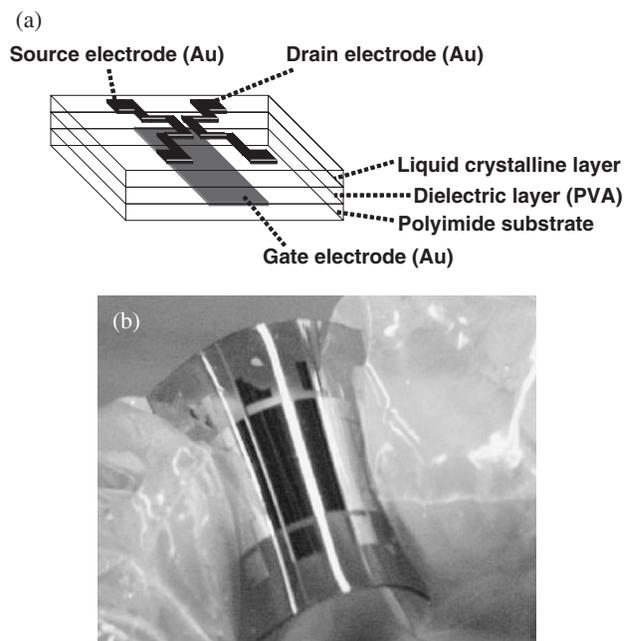


Figure 13. (a) Structure of a FET fabricated on a polymer substrate (b) Photograph of the flexible FET fabricated on a polymer substrate.

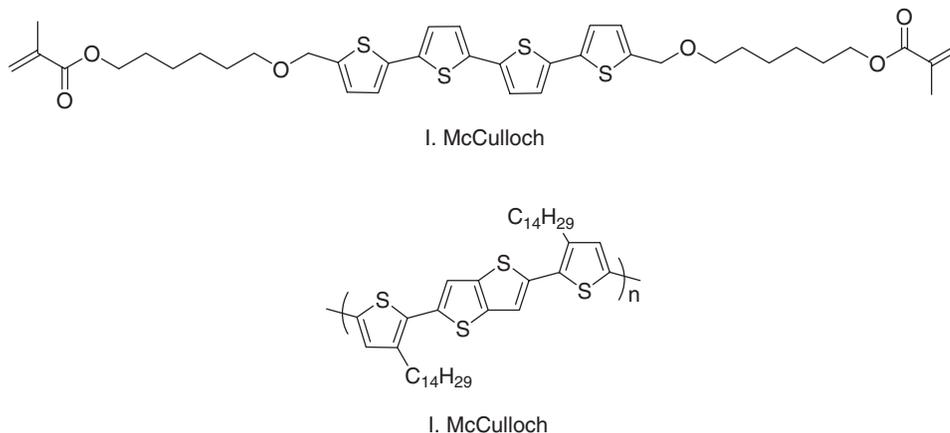


Figure 14. Liquid-crystalline polymers used for fabricating FETs.

A dielectric layer was formed by spin-coating an aqueous solution of polyvinyl alcohol (PVA) on a Au-deposited polyimide film, as shown in Figure 13a. A chlorobenzene solution of **9** was spun on the PVA dielectric layer. The Au source and drain electrodes were vacuum-deposited on the liquid-crystalline layer. The FETs fabricated on the polyimide films exhibited good carrier mobilities of $2 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and on/off ratios of 10^4 . The characteristics did not change even when the devices were subjected to strain up to 3%. The performance of the FETs based on polycrystalline films of pentacene degraded when the strain exceeded 2%. This result indicates that liquid-crystalline semiconductors are favorable for flexible devices.⁷⁸

Liquid-Crystalline Polymer Systems

Carrier transport has been investigated in side-chain liquid-crystal polymers;²⁴ however, none of these polymers can be used to fabricate FETs since their carrier mobilities are not sufficiently high. The Merck research group produced semiconductor thin films by photopolymerization of mesomorphic oligothiophene derivatives bearing reactive functional groups, as shown in Figure 14. The thin films were used to fabricate FETs whose hole mobilities were $5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁷⁹ It should be difficult to maintain the molecular ordered state during the photopolymerization process.

The liquid crystallinity of conjugated polymers such as poly(3-alkylthiophene) has already been reported by Yoshino

*et al.*⁸⁰ McCulloch *et al.* realized high-performance FET devices using liquid-crystalline poly(thienylthiophene) derivatives, as shown in Figure 12.⁸¹ They deposited thin films of the liquid-crystalline conjugated polymer by the spin-coating method. Then, they carried out thermal annealing of the thin films in the liquid-crystalline phase to promote crystallization of the thin films and obtained high-quality semiconductor thin films with large grain sizes and high crystallinity. The hole mobilities of the devices thus fabricated exceeded $6 \times 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

CONCLUSION AND FUTURE PROSPECTS

Liquid-crystalline semiconductors can be used to produce electronics devices by the solution process. FETs based on such semiconductors deliver good performances, with carrier mobilities of the order on $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and the on/off ratio around 10^7 . The performance of the devices is one of the best among those fabricated by the solution process. Moreover, the flexibility of the liquid-crystalline semiconductors is superior to that of organic crystalline semiconductors. Owing to their good carrier transport characteristics and high flexibility, liquid-crystalline semiconductors have potential for the fabrication of new electronic devices having unique functions.

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REFERENCES

1. P. M. Borsenberger and D. S. Weiss, "Organic Photoreceptors for Xerography," Marcel Dekker Inc., New York, 1998.
2. G. Hughes and M. R. Bryce, *J. Mater. Chem.*, **15**, 94 (2005).
3. C. J. Brabec, N. S. Sariciftci, and J. C. Hummelen, *Adv. Funct. Mater.*, **11**, 15 (2001).

4. C. D. Dimitrakopoulos and P. R. L. Malenfant, *Adv. Mater.*, **14**, 99 (2002).
5. M. Kitamura and Y. Arakawa, *J. Phys.: Condens. Matter*, **20**, 184011 (2008).
6. S. Allard, M. Forster, B. Souharce, H. Thiem, and U. Scherf, *Angew. Chem., Int. Ed.*, **47**, 4070 (2008).
7. A. Dodabalapur, *Mater. Today*, **9**, 24 (2006).
8. Y. Shirota, *J. Mater. Chem.*, **15**, 75 (2005).
9. T. Kato, N. Mizoshita, and K. Kishimoto, *Angew. Chem., Int. Ed.*, **45**, 38 (2006).
10. A. R. Murphy, P. C. Chang, P. VanDyke, J. Liu, J. M. Fréchet, V. Subramanian, D. M. DeLongchamp, S. Sambasivan, D. A. Fischer, and E. K. Lin, *Chem. Mater.*, **17**, 6033 (2005).
11. J. E. Anthony, *Chem. Rev.*, **106**, 5028 (2006).
12. A. Salleo, *Mater. Today*, **10**, 38 (2007).
13. R. J. Kline, M. D. McGehee, E. N. Kadnikova, J. Liu, J. M. J. Fréchet, and M. F. Toney, *Macromolecules*, **38**, 3312 (2005).
14. M. O'Neill and S. M. Kelly, *Adv. Mater.*, **15**, 1135 (2003).
15. Y. Shimizu, K. Oikawa, K. Nakayama, and D. Guillon, *J. Mater. Chem.*, **17**, 4223 (2007).
16. M. Funahashi, H. Shimura, M. Yoshio, and T. Kato, *Struct. Bonding*, **128**, 151 (2008).
17. S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hägele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel, and M. Tosoni, *Angew. Chem., Int. Ed.*, **46**, 4832 (2007).
18. K. Yoshino, N. Tanaka, and Y. Inuishi, *Jpn. J. Appl. Phys.*, **15**, 735 (1976).
19. K. Yoshino, K. Yamashiro, and Y. Inuishi, *Jpn. J. Appl. Phys.*, **13**, 1471 (1974).
20. Y. Shimizu, K. Shigeta, and S. Kusabayashi, *Mol. Cryst. Liq. Cryst.*, **140**, 105 (1986).
21. S. Murakami, H. Naito, M. Okuda, and A. Sugimura, *J. Appl. Phys.*, **78**, 4533 (1995).
22. A. Sawada, K. Tarumi, and S. Naemura, *Jpn. J. Appl. Phys.*, **38**, 1418 (1999).
23. A. Sawada, K. Tarumi, and S. Naemura, *Jpn. J. Appl. Phys.*, **38**, 1423 (1999).
24. T. Ikeda, H. Mochizuki, Y. Hayashi, M. Sisido, and T. Sasakawa, *J. Appl. Phys.*, **70**, 3689 (1991).
25. K. L. Woon, M. P. Aldred, P. Vlachos, G. H. Mehl, T. Stirner, S. M. Kelly, and M. O'Neill, *Chem. Mater.*, **18**, 2311 (2006).
26. M. Funahashi and N. Tamaoki, *ChemPhysChem*, **7**, 1193 (2006).
27. M. Funahashi and N. Tamaoki, *Chem. Mater.*, **19**, 608 (2007).
28. D. Markovitsi, T.-H. Tran-Thi, V. Briois, J. Simon, and K. Ohta, *J. Am. Chem. Soc.*, **110**, 2001 (1988).
29. N. Boden, R. J. Bushby, J. Clements, M. V. Jesudason, P. F. Knowles, and G. Williams, *Chem. Phys. Lett.*, **152**, 94 (1988).
30. D. Adam, F. Closs, T. Frey, D. Funhoff, D. Haarer, H. Ringsdorf, P. Schuhmacher, and K. Siemensmeyer, *Phys. Rev. Lett.*, **70**, 457 (1993).
31. N. Boden, R. J. Bushby, J. Clements, B. Movaghar, K. J. Donovan, and T. Kreouzis, *Phys. Rev. B: Condens. Matter Mater. Phys.*, **52**, 13274 (1995).
32. D. Adam, P. Schuhmacher, J. Simmerer, L. Häubling, K. Siemensmeyer, K. Eitzbach, H. Ringsdorf, and D. Haarer, *Nature*, **371**, 141 (1994).
33. M. Funahashi and J. Hanna, *Phys. Rev. Lett.*, **78**, 2184 (1997).
34. M. Funahashi and J. Hanna, *Appl. Phys. Lett.*, **71**, 602 (1997).
35. K. Kogo, T. Goda, M. Funahashi, and J. Hanna, *Appl. Phys. Lett.*, **73**, 1595 (1998).
36. A. E. A. Contoret, S. R. Farrar, P. O. Jackson, S. M. Khan, L. May, M. O'Neill, J. E. Nicholls, S. M. Kelly, and G. J. Richards, *Adv. Mater.*, **12**, 971 (2000).
37. T. Hassheider, S. A. Benning, H.-S. Kitzerow, M.-F. Achard, and H. Bock, *Angew. Chem., Int. Ed.*, **40**, 2060 (2001).
38. A. Bacher, I. Bleyl, C. H. Erdelen, D. Haarer, W. Paulus, and H.-W.

- Scmidt, *Adv. Mater.*, **9**, 1031 (1997).
39. M. P. Aldred, A. E. A. Contoret, S. R. Farrar, S. M. Kelly, D. Mathieson, M. O'Neill, W. C. Tsoi, and P. Vlachos, *Adv. Mater.*, **17**, 1368 (2005).
 40. L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R. H. Friend, and J. D. MacKenzie, *Science*, **293**, 1119 (2001).
 41. S. Sergeev, W. Pisula, and Y. H. Geerts, *Chem. Soc. Rev.*, **36**, 1902 (2007).
 42. M. Funahashi, *Transworld Research Network, Recent Develop. of Appl. Phys.*, **6**, 839 (2003).
 43. A. M. van de Craats, J. M. Warman, K. Müllen, Y. Geerts, and J. D. Brand, *Adv. Mater.*, **10**, 36 (1998).
 44. Z. An, J. Yu, S. C. Jones, S. Barlow, S. Yoo, B. Domercq, P. Prins, L. D. A. Siebbeles, B. Kippelen, and S. R. Marder, *Adv. Mater.*, **17**, 2580 (2005).
 45. M. Funahashi and J. Hanna, *Appl. Phys. Lett.*, **76**, 2574 (2000).
 46. M. Funahashi and J. Hanna, *Mol. Cryst. Liq. Cryst.*, **410**, 529 (2004).
 47. M. Funahashi and J. Hanna, *Adv. Mater.*, **17**, 594 (2005).
 48. K. Oikawa, H. Monobe, J. Takahashi, K. Tsuchiya, B. Heinrich, D. Guillon, and Y. Shimizu, *Chem. Commun.*, **2005**, 5337.
 49. J. Simmerer, B. Glüsen, W. Paulus, A. Kettner, P. Schuhmacher, D. Adam, K.-H. Eitzbach, K. Siemensmeyer, J. H. Wendorff, H. Ringsdorf, and D. Haarer, *Adv. Mater.*, **8**, 815 (1996).
 50. M. Funahashi and J. Hanna, *Mol. Cryst. Liq. Cryst.*, **368**, 303 (2001).
 51. B. Glüsen, W. Heitz, A. Kettner, and J. H. Wendorff, *Liq. Cryst.*, **20**, 627 (1996).
 52. M. Funahashi and J. Hanna, *Appl. Phys. Lett.*, **73**, 3733 (1998).
 53. M. Van der Auweraer, F. C. De Schryver, P. M. Borsenberger, and H. Bässler, *Adv. Mater.*, **6**, 199 (1994).
 54. D. Hertel and H. Bässler, *ChemPhysChem*, **9**, 666 (2008).
 55. M. Pope and C. Swneberg, "Electronic Processes in Organic Crystals and Polymers," 2nd ed., Oxford University Press, Oxford, 1999.
 56. I. Bleyl, C. Erdelen, H.-W. Schmidt, and D. Haarer, *Philos. Mag.*, **B79**, 463 (1999).
 57. D. Adam, P. Schuhmacher, J. Simmerer, L. Häußling, W. Paulus, K. Siemensmeyer, K.-H. Eitzbach, H. Ringsdorf, and D. Haarer, *Adv. Mater.*, **7**, 276 (1995).
 58. H. Bässler, *Phys. Status Solidi B*, **175**, 15 (1993).
 59. M. Kastler, F. Laquai, K. Müllen, and G. Wegner, *Appl. Phys. Lett.*, **89**, 252103 (2006).
 60. M. Funahashi, F. Zhang, N. Tamaoki, and J. Hanna, *ChemPhysChem*, **9**, 1465 (2008).
 61. A. M. van de Craats, J. M. Warman, A. Fechtenkötter, J. D. Brand, M. A. Harbison, and K. Müllen, *Adv. Mater.*, **11**, 1469 (1999).
 62. A. M. van de Craats and J. M. Warman, *Adv. Mater.*, **13**, 130 (2001).
 63. W. D. Gill, *J. Appl. Phys.*, **43**, 5033 (1972).
 64. H. Monobe, K. Awazu, and Y. Shimizu, *Adv. Mater.*, **12**, 1495 (2000).
 65. H. Monobe, K. Kiyohara, N. Terasawa, M. Heya, K. Awazu, and Y. Shimizu, *Adv. Funct. Mater.*, **13**, 919 (2003).
 66. H. Monobe, K. Awazu, and Y. Shimizu, *Adv. Mater.*, **18**, 607 (2006).
 67. A. M. van de Craats, N. Stutzmann, O. Bunk, M. M. Nielsen, M. Watson, K. Müllen, H. D. Chanzy, H. Sirringhaus, and R. H. Friend, *Adv. Mater.*, **15**, 495 (2003).
 68. W. Pisula, A. Menon, M. Stepputat, I. Lieberwirth, U. Kolb, A. Tracz, H. Sirringhaus, T. Pakula, and K. Müllen, *Adv. Mater.*, **17**, 684 (2005).
 69. F. Garnier, R. Hajlaoui, A. El Kassmi, G. Horowitz, L. Laigre, W. Porzio, M. Armanini, and F. Provasoli, *Chem. Mater.*, **10**, 3334 (1998).
 70. K. Oikawa, H. Monobe, K. Nakayama, T. Kimoto, K. Tsuchiya, B. Heinrich, D. Guillon, Y. Shimizu, and M. Yokoyama, *Adv. Mater.*, **19**, 1864 (2007).
 71. A. J. J. M. van Breemen, P. T. Herwig, C. H. T. Chlon, J. Sweelssen, H. F. M. Schoo, S. Setayesh, W. M. Hardeman, C. A. Martin, D. M. de Leeuw, J. J. P. Valetton, C. W. M. Bastiaansen, D. J. Broer, A. R. Popa-Merticar, and S. C. J. Meskers, *J. Am. Chem. Soc.*, **128**, 2336 (2006).
 72. H. Zhang, S. Shiino, A. Shishido, A. Kanazawa, O. Tsutsumi, T. Shiono, and T. Ikeda, *Adv. Mater.*, **12**, 1336 (2000).
 73. H. Iino and J. Hanna, *Mater. Res. Soc. Symp. Proc.*, **1091**, AA11-82 (2008).
 74. M. Funahashi, F. Zhang, and N. Tamaoki, *Adv. Mater.*, **19**, 353 (2007).
 75. F. Zhang, M. Funahashi, and N. Tamaoki, *Appl. Phys. Lett.*, **91**, 063515 (2007).
 76. T. Someya, T. Sekitani, S. Iba, Y. Kato, H. Kawaguchi, and T. Sakurai, *Proc. Natl. Acad. Sci. U.S.A.*, **101**, 9966 (2004).
 77. T. Someya, Y. Kato, T. Sekitani, S. Iba, Y. Noguchi, Y. Murase, H. Kawaguchi, and T. Sakurai, *Proc. Natl. Acad. Sci. U.S.A.*, **102**, 12321 (2005).
 78. F. Zhang, M. Funahashi, and N. Tamaoki, *Org. Electron.*, **10**, 73 (2009).
 79. I. McCulloch, W. Zhang, M. Heeney, C. Bailey, M. Giles, D. Graham, M. Shkunov, D. Sparrowe, and S. Tierney, *J. Mater. Chem.*, **13**, 2436 (2003).
 80. K. Tashiro, K. Ono, Y. Minagawa, M. Kobayashi, T. Kawai, and K. Yoshino, *J. Polym. Sci., Part B: Polym. Phys.*, **29**, 1223 (1991).
 81. I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. MacDonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, M. L. Chabiny, R. J. Kline, M. D. McGehee, and M. F. Toney, *Nat. Mater.*, **5**, 328 (2006).



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