TOPICAL REVIEW

Organic field-effect transistors using single crystals

Tatsuo Hasegawa¹ and Jun Takeya²

¹ Photonics Research Institute (PRI), National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba 305-8562, Japan
² Graduate School of Science, Osaka University, 1-1 Machikaneyama, Toyonaka 560-0043, Japan
E-mail: t-hasegawa@aist.go.jp and takeya@chem.sci.osaka-u.ac.jp

Received 27 January 2009
Accepted for publication 22 March 2009
Published 6 July 2009
Online at stacks.iop.org/STAM/10/024314

Abstract

Organic field-effect transistors using small-molecule organic single crystals are developed to investigate fundamental aspects of organic thin-film transistors that have been widely studied for possible future markets for ‘plastic electronics’. In reviewing the physics and chemistry of single-crystal organic field-effect transistors (SC-OFETs), the nature of intrinsic charge dynamics is elucidated for the carriers induced at the single crystal surfaces of molecular semiconductors. Materials for SC-OFETs are first reviewed with descriptions of the fabrication methods and the field-effect characteristics. In particular, a benchmark carrier mobility of 20–40 cm²Vs⁻¹, achieved with thin platelets of rubrene single crystals, demonstrates the significance of the SC-OFETs and clarifies material limitations for organic devices. In the latter part of this review, we discuss the physics of microscopic charge transport by using SC-OFETs at metal/semiconductor contacts and along semiconductor/insulator interfaces. Most importantly, Hall effect and electron spin resonance (ESR) measurements reveal that interface charge transport in molecular semiconductors is properly described in terms of band transport and localization by charge traps.

Keywords: organic transistor, single crystal, rubrene, pentacene, tetrathiafulvalene, tetracyanoquinodimethane, charge-transfer compound, band transport, Hall effect, electron-spin resonance

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Charge transport in organic molecular semiconductors is grounded in the intermolecular dynamics of charge carriers, meaning that a degree of molecular order is absolutely crucial for electrical conductivity [1]. Clean organic semiconductor single crystals are therefore the best candidate to realize ideal carrier transport in organic field-effect transistors (OFETs). For recent decades, OFETs have been attracting considerable attention both for applications and in academia.

OFETs are the key components in next-generation semiconductors for flexible organic electronics, and they have the advantage of low-cost and energy-efficient production [2, 3]. Among the intensive research activities in this field, studies of single-crystal OFETs (SC-OFETs) are relevant for seeking for the highest performance with idealized semiconductor channels of perfectly ordered molecules as compared with those of varieties of organic thin-film transistors. The reported benchmark values of carrier mobility (20–40 cm²Vs⁻¹) are one order of magnitude larger in SC-OFETs than those typically reported for conventional
thin-film transistors of polycrystalline semiconductors [4–8]. At the same time, the challenge has arisen to selectively grow crystalline channels at intended positions on substrates using surface modification techniques [9], to make use of the high carrier mobility of the single-crystal semiconductors for real devices. SC-OFETs are also more convenient for the study of more intrinsic material properties of organic semiconductors than polycrystalline thin-film devices, because of the absence of the extrinsic influence of grain boundaries. Thus far, a number of molecular compounds have been studied in SC-OFETs [10–31]. In addition to popular polycrystene devices, high-mobility SC-OFETs of tetrathiafulvalene (TTF)-based compounds and air-stable n-type SC-OFETs of tetra-cyano-quo-no-dimethane (TCNQ) and perylene tetracarboxylic dianhydride (PTCD) are described in this review. In section 2, materials for SC-OFETs are reviewed with descriptions of development, structures and various semiconductors for single-crystal devices.

In addition, it is crucial to give a proper description of the carrier dynamics in electronic systems that allow significant structural deformation, by incorporating the ‘softness’ into the carrier transport model. Organic single-crystal transistors play an important role in providing a platform on which to study intrinsic charge transport mechanisms in molecular semiconductor systems, because of the nearly perfect periodicity of the molecular potential and of the absence of complexity due to grain boundaries. In particular, for decades a decisive answer has been sought to the fundamental question of whether or not ‘band transport’ can be realized in small-molecule organic semiconductors, which may be associated with the efforts in elaborate fundamental question of whether or not ‘band transport’ for decades a decisive answer has been sought to the fundamental question of whether or not ‘band transport’ can be realized in small-molecule organic semiconductors, which may be associated with the efforts in elaborate organic syntheses to develop organic metals of one molecular species [32]. Recent Hall effect measurements on SC-OFETs clearly revealed that ‘band transport’ can be achieved in high-mobility molecular semiconductor systems, being yet on the verge of localization [33, 34]. Even more recently, high-precision electron spin resonance (ESR) measurements successfully probed the coherent local dynamics of the field-induced carriers in pentacene systems [35, 36]. Section 3 in this review is devoted to descriptions of the physics of SC-OFETs to investigate detailed mechanisms for the intrinsic charge transport at the surface of small-molecule organic semiconductors generated by the electric-field after providing microscopic energetics on charge injection to the organic semiconductors. Finally, a brief summary and future perspectives are given in section 4.

2. Materials for single crystal OFETs

2.1. Development of SC-OFETs

It is obvious that single crystals of organic semiconductors are preferable for achieving higher transistor performance, simply because high carrier mobility is expected owing to perfect molecular order, although polycrystalline thin films are much more prevalent for application that make the best advantage of relatively easy fabrication processes for organic electronic devices. SC-OFETs were first developed of simple aromatic molecules such as pentacene, tetracene and rubrene [10–13]. The important technical tricks have been the methods of preparing interfaces between organic single-crystal surfaces and gate insulating layers without introducing significant damage at the semiconductor surface, which make the carrier-conducting channels themselves. SC-OFETs based on a Mott insulator were also developed at almost the same time, which is conceptually new in that the mechanism of transistor switching is not merely grounded on carrier accumulation but on ‘electronic phase transition’ [14]. Both types of devices are described in this review.

Organic crystal FETs were prepared either by ‘crystal-lamination’ or ‘parylene-coating’ techniques [10–14]. In the former, thin platelets of single crystals, typically less than 1 µm thick, are grown by physical vapor transport (PVT) and are simply laminated electrostatically on gate-insulating layers. Usually, a few hundred nm thick SiO₂ layers [12, 13] or polymeric insulators such as poly-4-vinylphenol (PVP) or amorphous fluoropolymers, which are also common in thin-film transistors [37, 38], are used for the gate insulators [7, 39–41]. Few nm thick gold electrodes are evaporated and patterned by photolithography beforehand, so that the electrical contacts between the semiconductors and the metal are also made by the mere electrostatic bonding. A typical structure of the ‘laminated-crystal’ SC-OFET is illustrated in figure 1(a), and the top view is given in figure 1(b).

The SiO₂ layers were formed by usual thermal oxidization to a thickness of 500 nm. The PVP gate insulators are prepared as follows: a solution of poly-4- vinylphenol and polyemelamine-co-formaldehyde in propylene glycol monomethyl ether acetate (PGMEA) is deposited by spin-coating and is cross-linked at 200 °C for 20 min. With independent measurement of the PVP-film thickness d with a 3D laser microscope, the relative dielectric constant ε₁ is estimated as ~4.0 [7]. On the other hand, the technique of forming polymeric gate insulators with parylene was developed to softly coat the surface of the organic molecular single crystals [10, 11, 14]. For this method, thicker free-standing crystals (typically thicker than 10 µm) are used. Source and drain electrodes are formed by painting carbon or metallic pastes. Then, a thin film of parylene is deposited to a thickness of ~1 µm on top of the crystal in a reactor; the reactor consists of a quartz tube with one closed end and three temperature zones. The dimer para-xyllelve vaporizes in

![Figure 1](image-url)
the vaporization zone at 100 °C, cleaves in the pyrolysis zone at 700 °C, and polymerizes in the deposition zone, where the samples are located at room temperature and at a pressure of ~0.1 torr. Finally, gate electrodes are painted on the parylene gate dielectric to cover the region between the source and drain electrodes. Figure 2(a) shows an illustration of this structure.

It is to be noted that the key technology for the above two methods to successfully fabricate high-performance SC-OFETs is the minimization of damage to the surface of fragile organic semiconductor crystals during the process of forming the interfaces to gate insulators. Yet another method reported by Sundar et al involved ‘vacuum-gap’ space being utilized for the gate insulating layer. The use of polydimethyl-siloxane elastomer enables such construction as shown in figure 2(b), so that the ‘interface’ of the rubrene single crystals with the vacuum results in high mobility of 20–30 cm²Vs⁻¹ at the crystal surface [4, 5]. This value is comparable to the mobility reaching 25–40 cm²Vs⁻¹ reported by Takeya et al for inner crystal channels of rubrene SC-OFETs, measured with very weak gate electric fields [6, 7].

To characterize the intrinsic carrier transport property of the SC-OFETs, four-terminal conductivity measurement can be useful in addition to conventional methods of measuring the drain current \( I_D \) between two (source and drain) electrodes as functions of drain voltage \( V_D \) and gate voltage \( V_G \), because this can exclude the influence of parasitic contacts [11, 12]. Figure 3 shows a schematic of an electrical circuit for measuring \( I_D \) and gate leakage current \( I_G \), by applying \( V_G \) and \( V_D \). By detecting voltages \( V_1 \) and \( V_2 \) at two positions on the crystal, longitudinal sheet conductivity \( \sigma_L = I_D/(V_2 - V_1)L_{12}/W \) is evaluated, where \( L_{12} \) is the distance between the two voltage probes in the current direction and \( W \) is the channel width. Mobility \( \mu^{4T} \) is estimated from the measured transfer characteristics \( \sigma_L(V_G) \) using the formula

\[
\mu^{4T} = 1/C_i \times d\sigma_L/dV_G.
\]

based on

\[
\sigma_L = pe\mu^{4T} = C_i(V_G - V_{th})\mu^{4T}.
\]

Here \( p \) denotes density of the holes, \( e \) is the electron charge, \( C_i \) is the capacitance of the gate insulator per unit area and \( V_{th} \) represents threshold gate voltage. The more commonly used two-terminal mobility \( \mu^{2T} \) can be estimated from the equation

\[
\mu^{2T} = 1/C_i \times dI_D/dV_G \times 1/V_D \times L/W,
\]

where \( L \) is the distance between the source and drain electrodes. In addition, saturation mobility \( \mu^{sat} \) can be estimated when the measurement reaches the saturation regime with \( V_D \) typically larger than \( V_G - V_{th} \) as

\[
I_D^{sat} = C_i\mu^{sat}(V_G - V_{th})^2/2.
\]

\( I_D^{sat} \) represents the saturation current.

The history of the growth of carrier mobility in OFETs is given in figure 4. Developing high-mobility OFETs is a key technology for establishing an extensive market for organic electronics in the future, providing easy-to-fabricate switching components in integrated logic circuits. For example, beyond being a candidate for active matrix-controlling elements, organic transistors could be applied to driving-circuit components in all organic display frames, with mobility more than one-order higher than presently achieved. Attempts have been made to maximize transistor mobility by employing organic single crystals as the active semiconductors in order to generate serious consideration of applicability of organic transistors further extended to the material limit and predict the ultimate size of the market in the future.

2.2. SC-OFETs of rubrene

The representative semiconductor material for SC-OFETs is rubrene, whose molecular and crystal structures are shown in figure 5. Such SC-OFETs were first constructed by Podzorov et al with parylene gate dielectrics [10], after which...
Figure 5. Molecular and crystal structures of rubrene.

Figure 6. A molecularly flat surface extends a few tens of micrometers at the surface of rubrene crystals (an AFM image).

Laminated-crystal OFETs were also developed [15, 42]. This compound turned out to be highly compatible with both device structures, resulting in benchmark mobility values in all OFETs [4–7].

To fabricate SC-OFETs by the lamination technique, platelets of crystals only 1 µm thick are used. Figure 6 shows an atomic force microscopy (AFM) image of the surface of a rubrene crystal, revealing a remarkably flat surface. The surface quality is apparently important for carrier transport in OFETs because the field-induced carriers are mostly confined to the vicinity of the interfaces to the gate dielectric layers, suggesting that the property is partially responsible for the achieving high mobility.

A very high mobility is achieved for devices with self-assembled monolayers (SAMs) coated on SiO$_2$ dielectrics [6]. The surface treatment procedure appears effective in reducing the influence of both defects in SiO$_2$ and the amount of absorbants such as water molecules. Silane self-assembled molecules are carefully attached by chemical vapor deposition. As the result of the mobility estimation, some of the devices exhibit record high values with the application of a weak electric field, as shown in figure 7. It is discussed that carriers can distribute more into the crystal, so that they are less subject to the random potential at the surface of amorphous SiO$_2$ dielectrics [6, 7].

The method of crystal lamination allows the use of any materials of gate insulators for fabrication of SC-OFETs because the crystals are laminated on independently prepared gate dielectric surfaces at room temperature in air. Thus far, various gate dielectric materials other than SiO$_2$ have been tested with rubrene single crystals as the standard material, and most of them showed good transistor performances [43, 44]. The materials range from spin-coated polymers such as poly(vinylpyrrolidone) (PVP) [7], fluoropolymer CYTOP (Asahi Glass Co.) [40, 41], high-κ oxides such as Ta$_2$O$_5$ [43, 45], and even an organic single-crystal insulator [46] and electrolytes such as ionic liquids [47, 48]. Hulea et al reported systematic dependence of the mobility on dielectric constants of the gate dielectric materials and proposed the formation of polarons coupled with the polarization of the gate dielectric materials, owing to the additional mass gained in the renormalized quasiparticles as a result of the dressing effect [43]. The fluoropolymer devices are characterized by very small hysteresis with respect to the gate voltage sweep and also by good reproducibility among devices. Typical for this type of device output characteristics are shown in figure 8 with a high saturation mobility of 30 cm$^2$/Vs$^{-1}$.

Rubrene SC-OFETs are formed even at solid-to-liquid interfaces with ionic liquids, as reported in [48]. Interest in room-temperature ionic liquids is growing because of the prospect of nonvolatile ‘green solvents’ and owing to the development of chemically stable, water-proof, and nontoxic compounds during the last decade [49]. Such materials have been attractive not only for technologies for the production of chemicals without volatilizing organic solvents, both in industry and chemistry laboratories, but also for applications...
to energy conversion and energy storage devices, making use of their fast ionic diffusion. The materials are indeed being applied to electrolytes for lithium ion batteries and fuel cells. However, the use of the ionic liquids for electronic devices is not as developed as the above areas. Solid-to-liquid interfaces are formed between organic semiconductor single crystals and ionic liquids, so that the structures work as fast-switching organic field-effect transistors (OFETs) with the highest transconductance, i.e. the most efficient response of the output current to the input voltage, among all OFETs.

Unlike conventional OFETs, the ionic liquid devices enable minimized operational gate voltage: when $V_G$ is applied to the ionic liquid layer, the electric double layers are formed as a result of the motion of the ions. Noting that gate electric field is confined only to electric double-layers 1 nm thick, only a fraction of a volt is necessary to accumulate the same carrier density as when 100 V is applied to gate dielectrics more than two orders of magnitude thicker. There have been reports on the use of polymer electrolytes such as LiClO$_4$ dissolved in poly(ethylene oxide) or ionic liquids maintained in a polymer gel [51–55]. However, these devices suffer from either poor mobility or slow response to the applied $V_G$ because of relatively slow ionic diffusion in the polymer platforms. The ionic-liquid gel device exhibits the best performance among the electrolyte OFETs, realizing a maximum response frequency of 5 kHz and a mobility up to 1 cm$^2$/Vs. To make the best use of ionic conduction in the ionic liquids, a well structure is useful to hold the liquid underneath organic single crystals by capillary force (figure 9(a)); the structure is formed with a polydimethylsiloxan (PDMS) elastomer on which a rubrene single crystal is electrostatically attached. When a pure ionic liquid of 1-ethyl-3-methylimidazolium bis(trifluoro-methyl-sulfonyl)imide [emimTFSI] (figure 9(b)) is used, whose ionic conductivity may be as high as $10^{-2}$ S cm$^{-1}$, the maximum cutoff frequency is in the MHz range with a well height of 20 $\mu$m.

High mobility of the rubrene single crystals and high capacitance of the electric double layer result in the best performance. As shown in figure 10, the device in figure 9 exhibits high current amplification efficiency with the application of only a fraction of a volt as the gate voltage.

The sheet transconductance $\sigma_T$, defined by $L/W dI_D/dV_G$, measures the rate of the current amplification for OFET devices and therefore directly determines the transistor performance. Since $\sigma_T$ is the product of mobility and the capacitance of the device, both parameters should be large to have the best sheet transconductance. $\sigma_T$ is as high as 20 $\mu$S when $V_D = -1$ V, which is the best performance among all reported OFETs [50].

As has been shown in this section, rubrene has been the standard organic semiconductor material for SC-OFETs. The above-mentioned devices realized the benchmark mobility of organic transistors, and have been and will continue to be a useful platform to study the influence of the gate dielectric.
Figure 11. Molecular and crystal structures of pentacene. ‘Z’ represents the axis perpendicular to the molecular layers.

Figure 12. (a) Channel conductivity versus gate voltage at different temperatures from 160 to 260 K. (b) Field-effect mobility as a function of temperature for three different pentacene single-crystal devices (reproduced with permission from [12]).

2.3. SC-OFETs of pentacene

Molecular and crystal structures of pentacene, the most popular organic semiconductor, are shown in figure 11. Pentacene has been the most common material for OFETs since the 1980s; therefore, it is useful to use it for comparison. However, fabrication of pentacene SC-OFETs is far harder than that of rubrene devices that realize similar level of performance. The reason is mostly due to the chemical instability with oxygen in the atmosphere, which easily oxidizes pentacene to pentacene-quinone. In the first report in 2003, a mobility of only 0.5 cm²Vs⁻¹ was obtained with the crystal lamination technique [12], and the value increased to 3 cm²Vs⁻¹ afterwards when the surface treatment on the SiO₂ gate dielectrics was improved [15].

Figure 12(a) presents electric field induced conductivity σ_T as a function of V_G at different temperatures from 160 to 260 K [12]. While the temperature dependence is obvious in the low V_G region, the maximum slope at high V_G does not differ much with changing temperature. For each temperature, the mobility is estimated from the maximum slope, and it is plotted in figure 12(b). The results for two more crystals (samples B and C) are also shown in addition to the one for figure 12(a). The mobility values range from 0.1 to 0.5 cm²Vs⁻¹, with no apparent temperature dependence. The mobility values of our devices are also comparable to those of high-quality pentacene thin-film FETs, though they are somewhat lower than the best metal oxide semiconductor (MOS) device. Since it is not likely that such extrinsic mechanisms dominate μ(T) in our four-terminal measurement of single crystals, the nearly temperature independent μ(T), at least from 150 K to near room temperature, appears to be an intrinsic property of the surface of the pentacene single crystals, motivating us to investigate the fundamental intermolecular charge dynamics more quantitatively. The nearly temperature-independent feature is inconsistent with conventional hopping models which predict strong T dependence. A difficulty also arises in the band picture, because of a naive estimation of the mean free path, resulting in a value shorter than the distance between adjacent molecules. Allowing for polaron formation, which is common in dilute-charge systems, the nearly temperature-independent feature is deduced for naphthalene; however, since the calculation is based on a balance between electronic parameters such as bandwidth and phononic parameters, the applicability to the case of pentacene crystals has to be further explored. The combination of a short mean free path and an almost temperature-independent conductivity is reminiscent of the T independent interlayer charge transport near room temperature in a high-Tc cuprate. There, metallic planes are stacked at a subnanometer distance. It is argued that direct tunneling between the adjacent planes dominates the interlayer transport in such systems.

Jurchescu et al reported that the method of forming pentacene-quinone on pentacene crystals and using it for gate insulating layers results in very high-mobility carrier transport at the interface between pentacene and the quinone layers [8]. The mobility reaches as high as 30–40 cm²Vs⁻¹, though the estimation includes a certain ambiguity of estimating the thickness of the quinone layers. The structure is reminiscent of a silicon MOSFET, which contains a high-quality interface between single-crystal silicon and its oxide layer, thereby realizing high-mobility carrier transport and high-performance transistor functions.

2.4. SC-OFETs of TTF analogues

Tetrathiafulvalene (TTF) and its analogues are known as the most important components of highly conductive organic charge-transfer compounds [56]. It is expected that their ability to afford a vast variety of molecular conductors and superconductors permits their use in high-performance single-component channel materials of OFETs. To date, organic thin-film transistors with a mobility of about 0.1–1.0 cm²Vs⁻¹ have been reported for some TTF analogues [57–63]. Figure 13(a) shows the molecular structures of some TTF analogues studied for OFETs: dithiophene-tetrathiafulvalene (DTTTF), hexamethylene-tetrathiafulvalene (HMTTF), dibenzo-tetrathiafulvalene (DBTTF) and dinaphtho-tetrathiafulvalene (DNTTF). It was
pointed out that the higher solubility of these materials should be advantageous for their use in low-cost solution processing [57]. In fact, SC-OFETs were fabricated by solution processing for some kinds of TTF analogues [64–67].

It was recently reported that SC-OFETs based on solution-grown as well as vapor-transport-grown HMTTF single crystals exhibit high mobility exceeding 10 cm²Vs⁻¹ [67]. Both solution-grown and vapor-transport-grown crystals yield identical monoclinic crystal structures whose packing motif is shown in figure 13(b). An intermolecular lateral arrangement along the a-axis affords large π–π interactions with close S–S contacts of 3.545(3)–3.647(3) Å. On the other hand, molecules are stacked along the b-axis in a brickwork arrangement in which molecules slip by half their length along the molecular long axes. These structural features are in sharp contrast to the herringbone molecular arrangement of polyacenes like rubrene or pentacene.

The HMTTF SC-OFETs were fabricated with parylene C gate dielectric layers. Thermally evaporated Au, Ag, or TTF–TCNQ metallic thin films on top of the crystals were used as the source/drain electrodes. Figure 14 shows transfer characteristics of the devices measured with a source/drain current along the a-axes. The mobility reached 11.2 cm²Vs⁻¹ in vapor-transport grown crystals and 10.4 cm²Vs⁻¹ in solution-grown crystals. It is noted that the output characteristics shown in the inset present the sign of current saturation at high V_D, if we assume the additional bulk current in the current–voltage characteristics. This performance could be attributed to the close lateral and brickwork molecular packing, shown in figure 13(b). Transfer integrals were estimated by extended Hückel molecular orbital calculations, and it was found that the transfer integral is highest (0.1151 eV) along the lateral intermolecular contact (‘t₁’ in figure 13(b)). Here it is noted that the use of TTF-TCNQ organic metal electrodes is essential to achieve a high performance with HMTTF SC-OFETs. As we discuss in subsection 3.1, carrier injections are optimized with TTF-TCNQ organic metal electrodes in TTF analogues.

In the comparison of vapor-transported and solution-processed SC-OFETs, some different features in the device characteristics are observed. A ‘normally on’ state with V_th at 13 V and a high on/off ratio (≈600) is observed in the device containing vapor-transported crystals, whereas a ‘normally off’ state with V_th at about −6 V and a much lower on/off ratio (<3) is seen in the device containing solution-processed crystals. These different features indicate the relationship between processing and device characteristics in OFETs. The vapor-transport-grown crystals could include a larger number of bulk carriers inside the crystals, possibly associated with thermal decomposition during crystal growth at relatively high temperature. Bulk carriers could be depleted by the reverse gate biases. This may provide the origin of the ‘normally on’ behavior in the transfer characteristics and low off current at high positive voltages. In contrast, the larger off-current in the solution-processed crystals may be associated with conductive paths remaining during the drying process just after the recrystallization from solution.

Figure 13. (a) Molecular structures of some TTF analogues studied for OFETs; (b) and (c) crystal structures of hexamethylenetetrathiafulvalene (HMTTF). Molecules at different positions along the b-axis are shown in different colors (reproduced with permission from [67]).

Figure 14. Transfer and output (inset) characteristics of SC-OFETs composed of single crystals grown by (a) vapor transport and (b) recrystallization (reproduced with permission from [67]).
2.5. Air-stable n-type SC-OFETs of TCNQ and PTCDA

High-performance and air-stable OFETs of both p- and n-types are indispensable for extensive applications to organic logic circuits. In particular, it is yet unclear how to build high-performance n-type OFETs with stable operation in air. Reports on such devices are still very limited [46, 68]. Compared with p-type devices, air-stable n-type OFETs suffer from either low carrier mobility or very large threshold gate voltages, which are fatal for application to low-power complementary logic devices.

One reason for the poorer performances in the n-type OFETs is argued to be energy-level mismatch between their Fermi levels and the lowest unoccupied molecular orbital (LUMO) levels of organic semiconductors. This causes inefficient electron injection from noble metal electrodes. Moreover, there are also concerns about the interfaces to the gate insulators where the atmospheric oxidants O₂ and H₂O, absorbed at grain boundaries of organic semiconductors, or OH groups at the surface of SiO₂ may also harm electron transport acting as electron-trapping centers [69]. Therefore, SC-OFETs based on n-type organic single crystals have been developed for more fundamental evaluation of intrinsic device properties, eliminating influences of grain boundaries and film morphology, as have been studied for p-type single-crystal OFETs.

The air-stable n-type single crystal transistors of TCNQ and PTCDA are successfully fabricated by crystal lamination. Au electrodes are used as usual. Figure 15 shows an optical-microscope view of a TCNQ single-crystal transistor. Because of the high electron-affinity of TCNQ, the reported LUMO levels (~4.8 eV lower than vacuum level) are close to the work function of Au electrodes (~5.1 eV) [70]. The transfer and output characteristics of one of the prepared TCNQ single-crystal transistors are shown in figure 16. All five devices exhibit textbook like n-type transistor performance with negligible hysteresis and negligible threshold. Linear-region mobility was calculated using the standard formula as 0.05−0.3 cm²Vs⁻¹ and 0.2−0.5 cm²Vs⁻¹ from transfer curves of two-terminal measurements shown in figure 16(a) and from the evolution of the four-terminal conductivity σ₄T shown in figure 16(b). Also, as the output performance exhibits typical saturation behavior shown in figure 16(c), saturation mobility is deduced as 0.2−0.5 cm²Vs⁻¹. These values are three orders of magnitude higher than those of TCNQ thin-film transistors [71], indicating that the intrinsic material performance of n-type OFETs was not realized in previous experiments with polycrystalline films, presumably because of such extrinsic influence as of grain boundaries.

It is to be emphasized that the threshold voltage $V_{th}$ is negligible in the present TCNQ single-crystal transistors, indicating absence of effective deep trap levels at the interfaces between the single-crystal surfaces and the SiO₂ gate insulators. The result contrasts with the fact that the majority of organic transistors suffer from significant or fatal effects of deep electron traps, causing poor performance of the n-type transistors. As a result of tremendous effort in developing n-channel semiconductors, air-stable and high-mobility devices were reported recently [68, 72, 73]. However, reports on transistors with a $V_{th}$ less than 10 V are very rare and poorly reproducible. To further understand the mechanism of minimizing the threshold, we use other similarly prepared single-crystal transistors for comparison.

As another example of air-stable n-type OFETs, poorer performance of PTCDA single-crystal transistors is reported; a typical mobility value is only ~10⁻³ cm²Vs⁻¹, and $V_{th}$ is typically as high as 30–50 V [31]. Since the LUMO level of PTCDA is ~3.9 eV lower than the vacuum level, which is ~1 eV higher than that of TCNQ, it can be argued that PTCDA devices suffer from more severe barriers for electron injection, if one neglects energy-level renormalization at the interfaces due to such influences as from interface dipoles. We also note that similarly prepared single-crystal transistors based on rubrene, which has an even lower LUMO level
of ~3.2 eV from the vacuum level, never work as n-type transistors in air.

In addition to the argument about electron-injection barriers at the gold-semiconductor interfaces, often concerned is the effect of deep traps at the boundary to the gate insulators. Since the effects of OH and water-based reactions are of particularly concern, we also prepared TCNQ single-crystal devices with highly water-repellent amorphous fluoropolymer gate dielectrics which do not possess OH groups [72, 73]. The exhibited transistor characteristics were almost identical to those of the SiO₂ devices, indicating the minor effects of electron-trapping centers. The advantages of possessing high electron affinity are not only in lowering electron-injection barriers from noble-metal electrodes. More importantly, oxidizing components, such as OH groups and water which are often concerned as electron-trapping centers, are inactivated because the LUMO levels of the semiconductor channels attract electrons more effectively. Therefore, the experiments tell us that intrinsic material properties of organic compounds with high electron affinity suffice high-performance and air-stable n-type transistors indispensable for low-loss organic complementary circuits.

2.6. SC-OFETs of charge-transfer compounds

Charge-transfer compounds are binary systems composed of electron-donor (D) and electron-acceptor (A) molecules or those with inorganic counterparts [56]. These compounds are well known to provide a wide spectrum of metallic materials, including more than 100 kinds of organic superconductors. Most representative components are TTF-based donor molecules as presented in subsection 2.4, and TCNQ-based acceptor molecules as presented in subsection 2.5. Figure 17 shows an example: ‘mixed-stack’ charge-transfer compounds of DBTTF-TCNQ are composed of alternate stacks of DBTTF donors and TCNQ acceptors along the b-axis [74]. A fundamental feature of the charge-transfer compounds is that the intermolecular charge-transfer interaction, or intermolecular charge resonance, binds D and A molecules much more tightly than the van der Waals interaction. The compounds afford a rich variety of narrow-gap molecular semiconductors. Owing to the strong charge-transfer interaction, the band width in such molecular semiconductors is larger than that in single-component molecular materials. Here, we present some examples of SC-OFETs using prototypical semiconducting charge-transfer compounds as channel single crystals.

DBTTF-TCNQ, as presented in figure 17, is composed of D and A molecules with nominally neutral valence states. The semiconducting gap is ascribed to the charge-transfer excitation from the HOMO (highest occupied molecular orbital) band of DBTTF to the LUMO (lowest unoccupied molecular orbital) band of TCNQ along the mixed stacks. From the infrared absorption spectra, the charge-transfer degree from DBTTF to TCNQ is found to be about 0.46, and the optical gap is estimated as 0.9 eV. Figure 18 shows transfer characteristics of SC-OFETs using DBTTF-TCNQ as channel single crystals. In the fabrication of field-effect devices, parylene C was used to form a gate dielectric layer with a typical thickness of about 1.0 μm (Cₛ = 2.12 nF cm⁻²). Three kinds of metallic thin films using TTF–TCNQ, Ag and Au are used, respectively, as source/drain electrodes in the devices. Among them, n-type mobility of about 1.0 cm² V⁻¹ s⁻¹ is obtained with TTF-TCNQ electrodes. In the device with TTF-TCNQ electrodes, electron injections are optimized from electrodes to the channel crystals, as discussed in the next section.

The charge-transfer compounds are also known to afford a variety of functional molecular semiconductors whose gaps result from strong electron–electron or electron–phonon interactions. Field-effect doping in such materials is of particular interest in condensed matter physics. Ambipolar-type field-effect characteristics are observed in SC-OFETs using Mott insulators of (BEDT-TTF)(F₂TCNQ) [BEDT-TTF (=bis(ethylenedithio)tetrathiafulvalene)] [14], and of (BEDT-TTF)(TCNQ) [75] as channel single crystals. The unique ambipolar operations may be associated with the effect of carrier accumulation at the Schottky barriers in the source/drain contacts with Mott insulators [76, 77]. Kawasugi et al have also recently reported field-effect-transistor operations in the semiconducting

![Figure 17. Molecular and crystal structure of a (DBTTF) (TCNQ) charge-transfer compound.](image1)

![Figure 18. Transfer characteristics of DBTTF-TCNQ SC-OFETs with the source and drain electrodes composed of Au, Ag and TTF-TCNQ, measured along the b-axes (reproduced with permission from [16]).](image2)
phase in the vicinity of the superconducting phase in $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br [30].

3. Physics of SC-OFETs

3.1. Charge injections

As discussed in subsection 2.1, SC-OFETs are conventionally fabricated using single crystals of undoped (or ‘intrinsic’) molecular semiconductors where the electrical contacts are formed directly with inorganic metals. This is significantly different from the contacts in typical silicon-based semiconductor devices, in which doping is conventionally utilized to enhance the tunneling efficiency as well as to control $p$- and $n$-type carrier injections. Such simple metal/semiconductor contacts are possible in SC-OFETs, since interfacial states are not as serious as in inorganic devices owing to the weak nature of van der Waals intermolecular interactions. Figure 19 shows a band diagram for the lowest unoccupied conduction band (LUCB) and the highest occupied valence band (HOVB) of some of the molecular semiconductors presented in subsections 2.2–2.5. This figure also includes work functions of various inorganic and organic metals. The starting point for the consideration of the carrier injections is the Mott–Schottky vacuum level alignment for these energy levels at the metal/semiconductor contacts. We must then consider other factors, for example, the formation of a Schottky barrier or an interfacial dipole layer, in case appreciable contact resistance is observed [78].

To discriminate the contact resistance from the resistance of conducting channels, four-terminal conductivity measurement was utilized in some SC-OFETs [11, 12, 15]. The method is quite useful to extract the intrinsic charge-carrier mobility, as discussed in subsection 2.1. Usually the source contact resistance decreases slightly with increasing drain voltage. The behavior is consistent with the Schottky-like barrier formation at metal/semiconductor contacts. Such a dependence of mobility on $V_D$ demonstrates the importance of contacts for a small $V_D$.

From the fundamental viewpoint of charge transport in intrinsic semiconductors, SC-OFETs could support both electron and hole conductions. However, electron and hole injections into molecular semiconductors are restricted owing to the energy difference between semiconducting band states and work functions of electrode materials, as shown in figure 19. An appropriate choice of electrode materials is necessary to optimize carrier injections in terms of appropriate work functions, which should be close to the HOVB or LUCB for efficient hole or electron injections, respectively. It has been recently reported that pentacene and tetracene allow for good electron injections from low-work-function metals like calcium and exhibit $n$-type FET operation [79]. The topic has now been studied in conjunction with organic light-emitting field-effect transistors (OLETs), a novel class of organic multi functional devices [21, 25, 29, 79]. For the operation of OLETs, both $p$- and $n$-type carrier injections are necessary for electron-hole recombination in the channels. Studies have shown that electron transport in SC-OFETs is sensitive to air. To observe $n$-type FET operation, devices are fabricated without exposure to air to prevent the formation of electron traps.

Achieving tunability in carrier injections is a fundamental issue in organic electronics. It is suggested that metallic molecular donor–acceptor compounds are useful for controlling carrier injections at metal/semiconductor contacts; this suggestion is related to the chemical tunability of organic molecules [16, 19]. For example, the electron affinity of component TCNQ molecules can be modified by fluorine substitutions to form $F_n TCNQ$ ($n = 1, 2, 4$). Since the metal Fermi energy of metallic molecular donor–acceptor compounds is located in the midst of the HOMO levels of donors and LUMO levels of acceptors, chemical tunability allows fine control of the metal Fermi energy of metallic molecular donor–acceptor compounds. It was demonstrated, with use of prototypical SC-OFETs, that $p$- and $n$-type operations can be successfully controlled by tuning the Fermi energy in metallic molecular donor–acceptor compounds [19]. Here, we discuss the nature of carrier injections at such organic metal/organic semiconductor interfaces.

In the experiment, three kinds of organic donors ($D$: TTF, TSF=tetraselenafulvalene, and DBTTF) and four kinds of organic acceptors ($A$: TCNQ, $F_1 TCNQ$, $F_2 TCNQ$ and $F_4 TCNQ$) were employed to produce conductive charge-transfer complex films as the electrodes. Single crystals of the semiconducting mixed-stack charge-transfer compound DBTTF–TCNQ, as presented in subsection 2.6, are utilized as channel semiconductors. As presented in figure 18, the device with TTF–TCNQ electrodes shows large field-effect response compared with Ag or Au electrodes. The measured transfer characteristics are presented in figure 20 for devices with six kinds of organic metals as source and drain electrodes. Clearly, the $n$-type behavior with (a) TTF–TCNQ electrodes changes to ambipolar-type for (c) and (d), and then to $p$-type for (e) and (f). The results can be explained in terms of the variation of the metal Fermi energy with respect to the semiconductor band energy. The Fermi energy can be
shows the Schottky barrier formation. These features indicate that the organic vacuum level alignment rule basically holds for Schottky contacts understood in terms of the Mott–Schottky rule, in which the result implies that both electron and hole injections can be carrier injections for devices (a)–(e) shown in figure d.

With permission from [the organic metals used as source and drain electrodes (reproduced with permission from [19]).]

Figure 20. Transfer characteristics at $V_{G} = 5$ V of DBTTF-TCNQ single-crystal field effect transistors with source and drain electrodes composed of (a) TTF-TCNQ, (b) TTF-F$_{1}$TCNQ, (c) TTF-F$_{2}$TCNQ, (d) TSF-F$_{1}$TCNQ, (e) TSF-F$_{2}$TCNQ and (f) DBTTF-F$_{4}$TCNQ measured along the crystal long axes (reproduced with permission from [19]).

Figure 21. Schottky barrier characteristics at organic metal/semiconductor contacts. Linear (left ordinate) and Schottky barrier height (right ordinate) plotted against $(I_{D}^{V} + E_{g}^{C})/2$ (fm) of the organic metals used as source and drain electrodes (reproduced with permission from [19]).

chemically controlled over the range from the conduction band edge to the valence band edge of the DBTTF-TCNQ channel.

In terms of the relative size of the field-effect response, a much larger enhancement was observed in the unipolar devices ((a), (e) and (f)) than in the ambipolar ones ((c) and (d)). For comparison, the values $\mu_{lin} = |dI_{D}/dU_{G}| \times (L/WC, V_{D})$ are plotted in figure 21 for both p- and n-type field-effect responses. Nominal mobility values are plotted since the channel mobility should fundamentally be the same for all devices. Instead, the distinct variation of $\mu_{lin}$ is associated with the change in the injection efficiency at the metal/semiconductor contacts. From the temperature dependence of the transfer characteristics, the mobility is determined by the thermionic emission, i.e. thermally activated charge hopping against the Schottky barriers, $\phi_B$, above 200 K. The upper part of figure 21 shows the Schottky barrier height of all the devices. Clearly, the slope, $S = d\phi_{B}/d\mu_{lin}$, is roughly equal to unity for both p- and n-type carrier injections for devices (a)–(e) shown in figure 20. This result implies that both electron and hole injections can be understood in terms of the Mott–Schottky rule, in which the vacuum level alignment rule basically holds for Schottky barrier formation. These features indicate that the organic metal/semiconductor contacts can form weakly interacting ideal interfaces, free of interface states in the band gaps.

3.2. Hall effect and intrinsic transport of field-induced carriers

One of the important products of developing high-mobility SC-OFTs has been successful Hall-effect measurements, independently reported in 2005 almost at the same time [33, 34]. As a result, it is evidenced that band transport is indeed realized for the carriers generated at organic semiconductor crystals with highly overlapped orbital states between adjacent molecules. Note that Hall-effect measurement later became possible also for pentacene thin-film transistors, showing that the accumulated carriers are nearly band-like [80].

Doped $\pi$-conjugated molecular semiconductors basically provide unique electronic systems with a relatively small intermolecular transfer integral (typically $\sim 0.5$ eV) and significant coupling to molecular vibration, both of which play a major role even at ordinary temperatures. Simply, the two fundamental transport mechanisms would be a band transport with mass-enhanced carriers and a hopping transport with self-localized carriers in predominance of molecular reorganization energy [1]. In reality, however, there is a complex competition between the two extreme cases, grounded on experimental and theoretical works introducing the idea of ‘polaronic band transport’ [81–84]. Though understanding the carrier transport in such ‘soft’ semiconductor crystals is of emergent importance because of recent technological attention to organic flexible electronics, methods of experimental approaches are still under development toward a full description of the fundamental electronic states of the charge carriers, which provided significant motivation for the Hall-effect measurements.

One of the first samples for the measurements were SC-OFTs with laminated thin rubrene crystals on PVP/doped silicon substrates. The samples are further shaped for the Hall-effect measurements into the ‘six-probe Hall-bar’ using laser etching [85]. Measurement of the transverse Hall voltage $V_{H}$ require evaluating voltages at three points on the crystal; $V_{1}$, $V_{2}$ and $V_{3}$ as presented in figure 22(d), using additional source measure units (SMU). It yields longitudinal.
The inverse of the Hall coefficient is plotted in figure 22(d) together with \( \sigma_Y \) as a function of gate voltage. In contrast to the nonlinear profile of \( \sigma_Y(V_G) \), \( 1/R_H \) increases linearly for \( V_G < V_{th} \). Moreover, the line of \( C_i(V_G < V_{th}) \), which shows the amount of charge modulated by \( V_G \), agrees well with the \( 1/R_H(V_G) \) profile. Here \( C_i \) is capacitance of the gate insulator. The result means that \( 1/R_H \) is indeed a good measure of the number of carriers in the rubrene crystal, demonstrating extended electronic states that manifest themselves in significant wave function overlap.

In addition, the linear increase of \( 1/R_H \) with \( V_G \) indicates an absence of anomalous polarization of the gate dielectric layer. Therefore, the change in the slopes of the transfer curves is solely due to the significant \( V_G \) dependence of \( \sigma_Y \). Hall mobility \( \mu_H \) estimated by \( R_H\sigma_Y \) gives the average mobility of mobile carriers and is argued to give an intrinsic carrier mobility excluding the influence of trapping events.

\( \mu_H \) is plotted as a function of \( V_G \) in figure 22(e), showing that \( \mu_H \) decreases rapidly with the negative \( V_G \). The result demonstrates nonequivalence of carriers introduced under different gate electric fields; neglecting electron correlation in such a low-carrier-density system, the \( \mu_H(V_G) \) profile comes from variation of the mobility values depending on the spatial distribution of the carriers. Under high gate fields, the carriers are localized at the interface because of a larger attractive electrostatic force and a shorter screening length. Therefore, the result of figure 22(e) indicates that \( \mu_H \) of the carriers located near the interface is reduced by significant scattering subjected to random potential on the amorphous polymers. On the other hand, carriers are more spread into the inner crystal because of more pronounced thermal diffusion against weaker gate fields. Since diffusive band-like transport is assumed in the above mechanism, we examine whether the mean free path \( l \) can be sufficiently long with the maximum mobility of \( \sim 8 \text{ cm}^2\text{ V}^{-1}\text{ s}^{-1} \) in figure 22(e). Within the nondegenerate electron gas model, \( l \) can be evaluated at least \( \sim 0.75 \text{ nm} \) at 300 K, assuming the effective mass of the holes \( m \) to be more than twice as large as the free electron mass. As compared with the intermolecular distance \( b (\sim 0.37 \text{ nm}) \) in the stacking direction, \( l \) is more than a few times longer, leaving a room to be reduced by additional scattering. When \( \mu_H \) decreases down to \( \sim 2.5 \text{ cm}^2\text{ V}^{-1}\text{ s}^{-1} \) at higher gate voltage, the above simplified calculation gives \( l \) comparable to \( b \), so that the picture of the diffusive model becomes marginal.

To have more microscopic ideas, one can employ a simple argument of the competition between (i) the gate electric field to confine the carriers to the interface and (ii) their tendency to thermally diffuse into the crystal. A length scale \( L_a \) is introduced for the carrier distribution in the direction of thickness in the organic crystal, based on the Poisson’s equation as discussed in [86]. \( L_a \) can be given as \( \sim 2\varepsilon c k_B T/[\varepsilon e^2 C_i(V_G - V_{th})] \), where \( \varepsilon, k_B \) and \( T \) are the dielectric constant of rubrene in the thickness direction, the Boltzmann constant and temperature, respectively. Assuming that \( \varepsilon c \sim 3\varepsilon_0 \) (\( \varepsilon_0 \) is the dielectric constant in vacuum) and that \( V_{th} \sim 50 \text{ V} \), \( L_a \) is estimated for each \( V_G \) as shown in figure 22(e) in the unit of the lattice constant \( c \) in the thickness direction. Since \( \mu_H \) drastically varies as \( V_G \) with...
the carrier distribution of a few-monolayer thicknesses, the $\mu_H(V_G)$ profile in figure 22(e) can be viewed as a crossover from in-crystal to surface (a few monolayer) carrier transport in the rubrene crystals. Therefore, the above simple estimation of $L_s$ appears consistent with the present experiment, though more precise evaluation is needed to define the exact crossover point avoiding ambiguities in $V_D$ and the residual interface charge.

3.3. Microscopic study by ESR

One of the difficulties in revealing microscopic charge transport in OFETs originates in the small number of accumulated charges at channel/gate dielectric interfaces. This prevents us from applying a variety of microscopic measurements used for bulk materials. It is crucially important to find out a possible experimental method to investigate microscopic states of conduction as well as localized carriers in channel semiconducting materials. Recently, it has been demonstrated that field-induced electron spin resonance (FI-ESR; ESR induced by gate electric field) is a powerful method to investigate charge transport in OFETs [35, 36]. Here we discuss methods and results of FI-ESR, mainly on the results for pentacene TFTs. It is also shown that the method is applicable in rubrene SC-OFTFs.

ESR spectroscopy is a method to detect magnetic resonance absorption of microwaves by Zeeman splitting of electron spins [87]. It is possible to discuss the dynamic as well as the static nature of charge carriers that possess spin moments by analyzing the ESR spectral line shapes and widths. Sensitive measurements are possible, especially in organic materials, since the materials are composed of light elements and show sharp ESR absorption spectra associated with small spin-orbit interactions [88]. Observation of FI-ESR signals was first reported for relatively low mobility OFETs, for which temperature-independent Gaussian-type FI-ESR spectra were obtained and discussed [35]. A subsequent report used relatively high-mobility pentacene TFTs, where the effect of motional narrowing was clearly confirmed with gate-field-dependent and temperature-dependent single-Lorentzian FI-ESR spectra [36]. The observation of motional narrowing enables us to characterize the movements of charge carriers along semiconductor/insulator interfaces.

Figure 23(a) shows the scheme for high-sensitive FI-ESR measurements of relatively high-mobility pentacene TFTs with large-area semiconducting channel layers ($2.5 \times 20$ mm$^2$). Poly(ethylene naphthalate) (PEN) films and high-quality parylene C films were used as nonmagnetic substrates and gate dielectric layers (capacitance of 4.5 nF cm$^{-2}$), respectively. In the devices, a high density of carriers up to $7 \times 10^{12}$ cm$^{-2}$ can be accumulated at the channel/insulator interfaces without electrical breakdown. The channel is composed of vacuum-deposited polycrystalline pentacene films with a grain size of about 200–600 nm. The field-effect mobility is estimated as 0.6 cm$^2$ Vs$^{-1}$ at $V_G = -200$ V.

In the devices, the FI-ESR signal is detected only after application of a negative $V_G$. No ESR signal is detected at a positive gate bias. In addition, the spin number estimated from the FI-ESR signal agrees well with the number of charge carriers calculated from the gate capacitance. The features provide clear evidence that the observed FI-ESR signals originate from the field-induced carriers. Figure 23(b) shows typical FI-ESR spectra at $V_G = -200$ V. The spectra agree well with first derivatives of single Lorentzian curves over the entire range of measured $V_G$ values and temperatures. The linewidth $\Delta B_{1/2}$, defined as the half width at half maximum (HWHM), is as small as 30 mT at 200 K. It broadens as the temperature decreases in the range 200–50 K, as shown in figure 23(c). Such temperature dependence gives clear evidence of the motional narrowing effect: resonance spectrum becomes narrower due to the motion of holes because they perceive averaged magnetic field as they move. The increase of ESR linewidth with decreasing temperature indicates that thermal carrier motion is deactivated at lower temperatures, which then suppresses the narrowing effect. In fact, field-effect mobility decreases as the temperature decreases, as presented in the lower panel of figure 23(c). Figure 23(c) also indicates saturation of $\Delta B_{1/2}$ at about 180 mT below 50 K. Continuous wave saturation experiments reveal inhomogeneous broadening of the FI-ESR spectra at temperatures below 50 K, where the motional narrowing may no longer be effective. In contrast, the spectra become more homogeneous at temperatures above 50 K, which is consistent with the motional narrowing effects.

From the motional narrowing theory, the average residence time of carriers at respective sites can be estimated by the following equation [89]:

$$\Delta B_{1/2} = \gamma (\Delta B_{\text{in}})^2 \tau_C. \quad (5)$$

Here, $\gamma$ is the gyromagnetic ratio, $\Delta B_{\text{in}}$ is the inhomogeneity of the local magnetic field at respective sites, and $\tau_C$ is the autocorrelation time of the Larmor frequency. $\Delta B_{\text{in}}$ could be regarded as the saturated linewidth of about 180 mT at low temperature, rather than the inhomogeneous linewidth of 500 mT for isolated pentacene.
cations as measured in solution [90]. The difference in the hyperfine broadening could be ascribed to the extension of localized electronic states over several molecules in the films. It is also interesting that the saturated value is roughly the same as the temperature-independent linewidth reported for the low-mobility device [35]. This means that the motional narrowing effect is not effective in low-mobility devices even at room temperature, and also that the hyperfine broadening should be common for pentacene films. Using the value of $\Delta B_{\text{inhomo}} = 180 \mu T$, the $\tau_{\text{c}}$ can be estimated as about 4 ns at $V_G = -200$ V at room temperature.

If we assume trap-free band transport, the residence time for each molecule is around 1 ps–10 fs from the calculated bandwidth (∼0.3 eV) for pentacene layers. It is clear that the estimated value for $\tau_{\text{c}}$ is much larger than the expectation. It is reasonable to attribute $\tau_{\text{c}}$ to the residence time at shallow or deep traps within the channels. Then, the average traveling length $d$ between the traps can be simply estimated by diffusion theory as 100 nm using the mobility value of 0.6 cm$^2$/Vs [91]. These results agree well with the picture for multiple trap-and-release (MTR) transport in OFETs — the average time at traps is much longer than that for traveling from trap to trap [86]. We may conclude that the observation of the motional narrowing effect in the FI-ESR spectra should give direct evidence for trap-dominated conduction along channel/insulator interfaces.

Within the channels, carriers should be activated to the band states by thermal energy at an average interval of about 4 ns and move from one trap site to another at a relatively high speed, as schematically shown in figure 24(a). From the Arrhenius plot of ESR linewidth shown in figure 23(c), we estimated average shallow trap depths of about 10–15 meV, depending on the gate voltages. On the other hand, the activation energy of field-effect mobility is larger, estimated as 62 meV at $V_G = -200$ V [92]. These features indicate that intragrain charge transport is limited by shallow traps with trap energies of about 10–15 meV, while the charge transport between the source and drain electrodes is strongly affected by areas with a small number of carriers such as Schottky barriers at the source–drain contacts or grain boundaries.

Figure 24. (a) Schematic picture of multiple trap and release (MTR) processes in a pentacene crystal. (b) Gate-voltage-dependence of ESR linewidth (HWHM) of rubrene SC-OFETs at room temperature.

High-quality single crystals are prerequisites for the development of silicon-based semiconductor devices, in which homogeneous and well-defined structures are required to characterize and theoretically describe the materials, interfaces and devices [96]. As exemplified in this review, the use of SC-OFETs gives us a new insight into the potential of organic electronic devices. It is demonstrated that the SC-OFETs are useful to evaluate the upper limit of the mobility of materials as well as for gaining a better understanding of the underlying device physics. Although the benchmark carrier mobility of 20–40 cm$^2$/Vs is achieved with rubrene SC-OFETs, it is also found that this performance might still be below the ultimate limit of organic materials owing to the charge trap mechanism in the channel crystals. It is also noteworthy that these findings are based on extremely facile handling techniques used to prepare fairly clean interfaces between molecular single crystals and gate insulating layers. Although the direct use of the SC-OFETs may be incompatible with ‘plastic electronics’ with their target of simple, flexible, and most of all cost-efficient fabrication, commercial success will clearly depend on continuing scientific progress in the understanding of the interface charge transport of $\pi$-conjugated organic semiconducting materials using SC-OFETs.

Acknowledgments

The authors thank T Uemura, K Yamada, Y Takahashi and H Matsui for collaboration and discussions on most of the issues focused on in this review. This study was partially supported by a Grant-in-Aid for Scientific Research ‘Molecular Conductors’ (No. 15073201, 2003–2008) by the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

[1] Pope M and Swenberg C 1999 Electronic Processes in Organic Crystals and Polymers 2nd edn (London: Oxford University Press)
[2] Klauk H 2006 Organic Electronics: Materials, Manufacturing, and Applications (Weinheim, Germany: Wiley-VCH Verlag GmbH)
[67] Takahashi Y, Hasegawa T, Horiuchi S, Kumai R, Tokura Y and Saito G 2007 Chem. Mater. 19 6382
[68] Yan H, Zheng Y, Blache R, Newman C, Lu S, Woerle J and Facchetti A 2008 Adv. Mater. 20 3393
[69] Chua L-L, Zausmei J, Chang J-F, Ou E C-W, Ho P K-H, Siritringhaus H and Friend R H 2005 Nature 434 194
[70] Hiroma S, Kuroda H and Akamatu H 1970 Bull. Chem. Soc. Japan 43 3626
[71] Brown A R, de Leeuw D M, Lous E J and Havinga E E 1994 Synth. Met. 66 257
[72] Oh J H, Liu S, Bao Z, Schmidt R and Würthner F 2007 Appl. Phys. Lett. 91 212107
[73] Kumaki D, Ando S, Shimonos S, Yamashita Y, Umeda T and Tokito S 2007 Appl. Phys. Lett. 90 053506
[74] Kobayashi H and Nakayama J 1981 Bull. Chem. Soc. Japan 54 2408
[75] Sakai M, Sakuma H, Ito Y, Saito A, Nakamura M and Kudo K 2007 Phys. Rev. B 76 045111
[76] Yonemitsu K 2005 J. Phys. Soc. Japan 74 2544
[77] Yonemitsu K, Maeshima N and Hasegawa T 2007 Phys. Rev. B 76 235118
[78] Ishii H, Sugiyama K, Ito E and Seki K 1999 Adv. Mater. 11 605
[79] Takahashi T, Takenobu T, Takeya J and Iwasa Y 2007 Adv. Funct. Mater. 17 1623
[80] Sekitani T, Takamatsu Y, Nakano S, Sakurai T and Someya T 2006 Appl. Phys. Lett. 88 253508
[81] Kenkre V M, Andersen J D, Dunlap D H and Duke C B 1989 Phys. Rev. Lett. 62 1165
[82] Podzorov V, Menard E, Borissov A, Kiriyukhin V, Rogers J A and Gershenson M E 2004 Phys. Rev. Lett. 93 086602
[83] Troisi A and Orlandi G 2006 Phys. Rev. Lett. 96 086601
[84] Karl N 2001 Organic Electronic Materials: Conjugated Polymers and Low Molecular Weight Organic Solids ed Farchioni R and Grosso G (New York: Springer)
[85] Yagi I, Tsukagoshi K and Aoyagi Y 2004 Appl. Phys. Lett. 84 813
[86] Horowitz G, Hijaoui M E and Hijaoui R 2000 J. Appl. Phys. 87 4456
[87] Weil J A, Bolton J R and Wertz J E 1994 Electron Paramagnetic Resonance—Elementary Theory and Practical Applications (New York: Wiley Interscience)
[88] Mizoguchi K and Kuroda S 1997 Handbook of Conductive Organic Molecules and Polymers vol 3 ed Nalwa H S (Chichester: Wiley) p 251
[89] Kubo R and Tomita K 1954 J. Phys. Soc. Japan 9 888
[90] James R and Bolton J 1967 Chem. Phys. 46 408
[91] Calhoun M F, Hsieh C and Podzorov V 2007 Phys. Rev. Lett. 98 096402
[92] Matsui H and Hasegawa T 2009 Japan J. Appl. Phys. 48 04C175
[93] Hasegawa T and Matsui H 2008 Kotai Butsuri (Solid State Physics in Japanese) 43 351
[94] Matsui H and Hasegawa T 2009 MRS Spring Meeting Proc. at press
[95] Marumoto K, Arai N, Goto H, Tomimori Y, Takeya J, Tanaka H, Kuroda S, Takenobu T and Iwasa Y 2008 Meeting Abst. Phys. Soc. Japan (in Japanese) 63 831
[96] Seitz F and Einspruch N G 1998 Electronic Genie — The Tangled History of Silicon (Champaign, IL: University of Illinois Press)