

Highlight Review

Organic Charge-transfer Salts and the Component Molecules in Organic Transistors

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Abstract

Electron donors and acceptors such as tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ), which have been long known as components of organic metals, act as p- and n-channel organic semiconductors in organic field-effect transistors. High performance, good thin-film properties, and long-term stability have been achieved on the basis of appropriate molecular design. In addition, their charge-transfer complexes work as the active layers as well as conducting electrode materials showing low contact resistance.

Introduction

Organic field-effect transistors (OFETs) have been the subject of intensive scientific and technological research due to the potential application to flexible, large-area, and low-cost electronic devices.¹ A variety of organic semiconductors have been developed for use in OFET,² and mobility has significantly improved over the past two decades (Figure 1). Recent rapid development of new materials is notable,³ and high-performance materials whose mobility exceeding $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ have been successively reported. Particularly, progress has been remarkable for solution-process materials,⁴ and for single-crystal transistors.⁵

When we turn attention to conductivity instead of mobility, highly conducting organic materials and even organic super-

conductors have been investigated in inherently doped organic materials,⁶ namely, organic charge-transfer salts.⁷ Such high-conducting materials are achieved by using stable organic electron donors and acceptors; the representative materials are tetrathiafulvalene (TTF) as a donor, and tetracyanoquinodimethane (TCNQ) as an acceptor. Actually these molecules act as good OFET materials. The history of TTF derivatives in OFETs is plotted in Figure 1. A very high mobility of $11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ has been reported for single-crystal HM-TTF (hexamethylene-TTF),⁸ this is next to the present record mobility of $40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for single-crystal rubrene.⁹

In this highlight review, first, OFETs based on TTF derivatives are reviewed.¹⁰ Second, n-channel OFETs constructed from organic acceptors such as dicyanoquinonediimines (DCNQI) are discussed. Charge-transfer salts themselves act as active layers in OFETs. Highly conducting charge-transfer salts are also used as electrode materials, so the merit of using organic/organic interface instead of the conventional metal/organic interface is described. We have investigated carbon electrodes because carbon/organic interfaces bear some resemblance to organic/organic interfaces, and this leads to “self-contact” OFETs.

OFETs Based on TTF

Since the history of TTF-based OFETs has been summarized previously,¹⁰ the author describes here the recent progress according to materials. Although thin-film transistors of unsubstituted TTF (**1**, Scheme 1) do not work well because TTF gradually goes away under vacuum, single-crystal transistors of micro TTF crystals prepared from solution have been investigated,¹¹ based on the recent efforts on making micro crystals of organic semiconductors.¹² TTF takes two different crystal forms, uniformly stacked α -phase, which seems to correspond to the bulk phase,¹³ exhibits a high mobility ($1.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), whereas a β -phase shows a relatively low mobility ($0.23 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).

DibenzoTTF (DB-TTF, **2**) is a well-investigated material, probably because the thin films are easily prepared. Various mobility values are reported for evaporated thin films,^{14,15} but recently a value of $0.55 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ has been realized by optimizing the substrate contact angle.¹⁶ Solution-processed single-crystal devices have been also reported ($1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).¹⁷ Although the crystal has a herringbone structure,¹⁸ the dihedral angle (130°) is much larger than the usual herringbone structures (typically 50°), so these should be

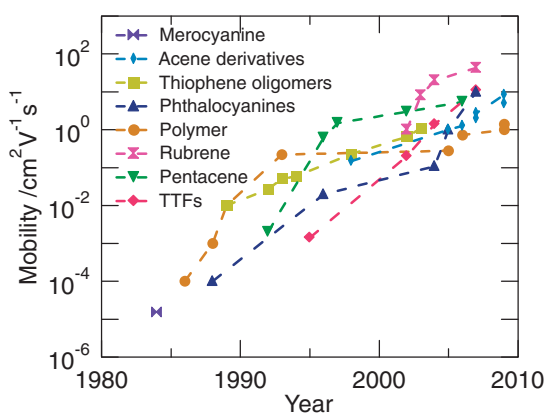
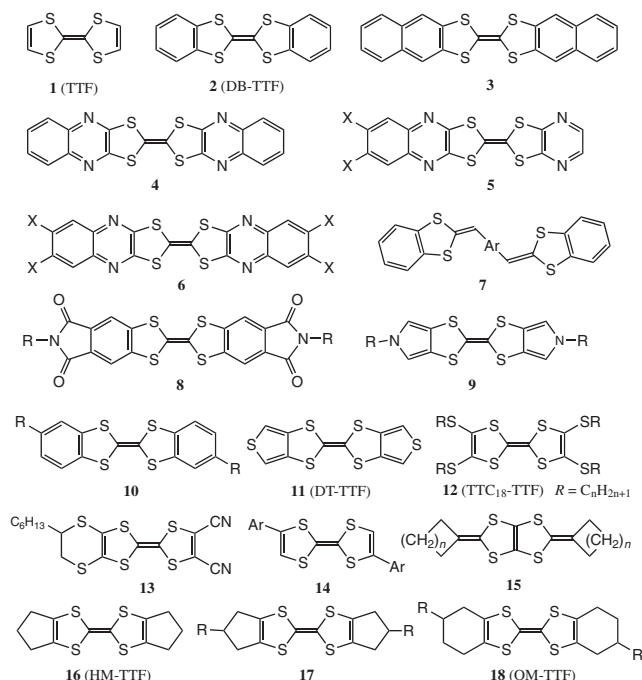


Figure 1. Evolution of OFET hole mobility for representative organic semiconductors.

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Scheme 1. TTF-based OFET materials. Mobilities are for evaporated thin films except for otherwise stated. **1** (TTF) crystal $1.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,¹¹ **2** (DB-TTF): $0.55 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,¹⁶ crystal $1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,¹⁷ **3**: $0.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,²⁰ **4**: $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,²⁰ **5**: $X = \text{F}$ $0.20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $X = \text{Cl}$ $0.64 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,²⁴ **6**: $X = \text{H}$ $0.20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $X = \text{F}$ $0.10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (n), $X = \text{Cl}$ $0.11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (n),²⁴ **7**: $Ar = \text{thiophene}$ $0.097 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $Ar = \text{thienothiophene}$ $0.29 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,²⁴ **8**: $R = n\text{-C}_4\text{H}_9$ $0.22 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,²⁶ **9**: $R = n\text{-C}_{16}\text{H}_{33}$ solution $0.012 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,²⁷ **10**: $R = n\text{-C}_8\text{H}_{17}$ solution $0.11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,²⁸ **11** (DT-TTF): crystal $3.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,³⁰ **12** (TTC_n-TTF) $n = 18$ zone casting $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,³⁴ **13**: $0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,³⁶ **14**: $Ar = \text{biphenyl}$ $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,³⁷ **15**: $n = 1$ $0.013 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $n = 2$ $0.27 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $n = 3$ $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,³⁸ **16** (HM-TTF) $6.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,³⁹ crystal $11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,^{8a} **17**: $R = t\text{-C}_4\text{H}_9$ $0.98 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, crystal $2.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $R = t\text{-C}_5\text{H}_{11}$ $0.60 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, crystal $1.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $R = n\text{-C}_4\text{H}_9$ $0.19 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,⁴⁰ **18** (OM-TTF): $R = \text{H}$ $4.2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $R = t\text{-butyl}$ $0.11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,⁴¹

recognized as essentially different structures.¹⁹ It has been, however, reported that the thin-film structures are somewhat different from the single-crystal structure.²⁰ Although TTF is a strong electron donor with a small ionization potential (4.8 eV),^{21,22} DB-TTF is a relatively weak electron donor whose energy level (5.1 eV) is even lower than that of pentacene (4.9 eV).²³ Usually low energy level is advantageous in device stability, but DB-TTF transistors are not particularly stable. Naphthalene TTF **3** and pyrazine-fused TTF **4** have been prepared, and improved performance has been reported.¹⁴ n-Channel performance has been observed in the halogen-substituted pyrazine derivative **6**,²⁴ though unsubstituted **6** and halogenated **5** show p-channel characteristics. DB-TTF derivatives **7** with thiophene spacers have been also investigated.²⁵ DB-TTF bisimides **8** with *N*-alkyl groups have been prepared, and average mobility of $0.22 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ has been reported for vacuum deposited films.²⁶ *N*-Alkylation is a good way to

improve the solubility, so solution-processible transistors are reported for **9**.²⁷ DB-TTF shows poor solubility, but the direct alkylation **10** achieves relatively high performance in solution process ($0.11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), that is on the same order as the evaporated films.²⁸

DT-TTF (**11**) has been investigated since pioneering work on solution-deposited crystals.²⁹ Improved performance as well as temperature-dependent measurements of the characteristics has been reported.³⁰ DT-TTF also shows polymorphs, where the newly found thin-film β -phase exhibits lower performance by one order.³¹ Similar solution processes have been applied to many TTF derivatives.³² Although BEDT-TTF (bis(ethylenedithio)TTF) exhibits relatively low mobility ($0.005 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), several thiophene-fused transistors show good performance. Light sensitivity of DT-TTF transistors has been demonstrated.³³ Solution-process transistors of TTC₁₈-TTF (**12**) have been achieved by using zone casting.³⁴ Monoalkyl-substituted BEDT-TTFs do not show transistor properties,³⁵ but the cyano analog **13** has a liquid-crystalline phase and shows transistor properties.³⁶ Biphenyl-TTF (**14**) exhibits relatively good transistor properties.³⁷ Among the tetrathiapentalene (TTP) derivatives **15** with different terminal rings, the cyclopentane compound ($n = 2$) shows the best transistor properties.³⁸ The crystal structure sensitively changes depending on the terminal cycloalkane groups; the cyclopentane compound ($n = 2$) has a herringbone structure with a large dihedral angle (128°) similarly to DB-TTF, the cyclobutane compound ($n = 1$) has simple uniform stacks, and the cyclohexane compound ($n = 3$) shows uniform stacking structure of bent molecules.

HM-TTF (**16**) shows excellent performance: $11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for single-crystal and $6.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for thin-film transistors.^{8a,39} It is characteristic of this compound that the molecules are stacked, and molecular planes are parallel to the substrate in the thin films.³⁹ Therefore, the high performance is not related to the transport along the stacking but is maintained by the transport along the transverse interactions. This is not surprising because the stacking direction is considerably dimerized, while the transverse direction has much larger uniform overlap.^{8a}

When alkyl groups are attached at the ends of the molecule like **17**, the molecules are still stacked in the crystals, but standing in the thin films.⁴⁰ In particular, the *t*-butyl derivative of **17** exhibits high performance of $0.98 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for films and $2.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for crystals. Although the performance is not as high as HM-TTF, the threshold voltage is reduced from 20 to 30 to -2 V . At the same time, the device shows excellent long-term stability; the performance does not change much even after 3 month storage under ambient conditions. When the *t*-butyl groups are replaced by *t*-pentyl groups, similarly high performance is attained, but *n*-butyl groups do not show such high performance. More recent work shows *s*-groups work similarly to *n*-groups. Accordingly the *t*-groups are necessary to realize high performance and low threshold voltage together with the long-term stability, probably due to some kind of passivation effect of the bulky substituent. HM-TTF is an extremely strong electron donor with the ionization potential of 4.7 eV, and it is not much changed by the alkyl substitution. Substitution by bulky *t*-groups is a new strategy to attain low threshold voltage and long-term stability without changing the energy levels.

Expecting similar steric effect, cyclohexane-substituted TTF **18** has been investigated, which is called octamethylene-TTF

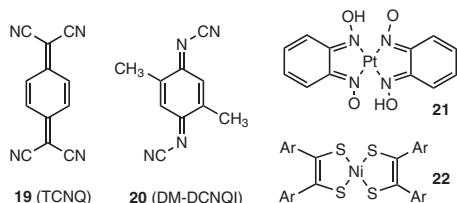
(OM-TTF),⁴¹ but this compound does not show good performance. However, good performance is obtained when *t*-butyl groups are attached.

In summary, thanks to the large S–S interaction and large band width (1 eV),⁴² TTF transistors show extraordinarily high performance in single crystals, as exemplified by HM-TTF, and solution-processed crystals in DT-TTF, DB-TTF, and TTF. However, usual TTF derivatives show very strong tendency to aggregate in crystals, which is not very suitable for thin-film transistors. Nonetheless, DB-TTF and HM-TTF make high performance thin-film transistors. The alkyl substitution improves the film quality, and even solution processing is possible for such compounds as **9** and **10**. The strong donor ability of TTF tends to result in large threshold voltage and reduced device stability, but these drawbacks are removed by bulky *t*-butyl substitution.

◆ OFETs Based on Acceptors

n-Channel organic semiconductors are limited in comparison with p-channel organic semiconductors, and much efforts have been devoted to develop n-channel materials.⁴³ Organic anions are unstable against oxygen and water,⁴⁴ and it is particularly difficult to realize n-channel organic semiconductors that make air-stable devices. Although a considerable number of air-stable n-channel organic semiconductors have been reported recently,^{3b,43} it is reasonable to explore strong electron acceptors such as TCNQ (**19**, Scheme 2) to make air-stable devices. Actually, TCNQ single crystals afford air-stable high-performance n-channel transistors, though the reported performance in thin-film devices is low.⁴⁵ DM-DCNQI (dimethyldicyanoquinonodiiimine, **20**) is also a strong electron acceptor and makes air-stable n-channel thin-film transistors.⁴⁶

Since metal complexes exhibit a wide variety of redox potentials, several metal complexes are excellent electron acceptors. Some metal complexes show n-channel performance, though others show p-channel performance. Metal phthalocyanine (Pc) is a representative p-channel material,² but TiOPc shows n-channel behavior under high vacuum,⁴⁷ and perfluorinated Pc is a well-known n-channel material.⁴⁸ Ni and Pt make square-planar complexes, and crystals of **21** afford n-channel transistors.⁴⁹ However, these metal complexes are hardly vacuum deposited, and as an exception, phenyl-substituted complexes like **22** make thin-film transistors.⁵⁰



Scheme 2. n-Channel OFET materials based on electron acceptors. Mobilities are for evaporated thin films except for otherwise stated. **19** (TCNQ): $3 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, crystal $2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,⁴⁵ **20** (DM-DCNQI): $0.012 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,^{46,71} **21**: crystal $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,⁴⁹ **22**: Ar = *p*-CH₃Ph $1.3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,⁵⁰

◆ OFETs Based on Charge-transfer Complexes

The use of organic charge-transfer complexes in OFETs dates back to the late 1990's,⁵¹ where field-effect transport in single-crystal (TTF)(TCNQ) at 12 K has been detected. (TMTSF)(TCNQ) is also evaporated from a single source,⁵² in which the electron-like transport on a substrate at 25 °C changes to hole-like at 35 °C.⁵³ Electron-like transport is observed in (TTF)(TCNQ). The charge polarity in these materials has been attributed to the excess component depending on the evaporation temperatures. Molecular wires of (TTF)(TCNQ) formed under electric fields are investigated, and electron-like transport has been observed, which has been also ascribed to the TCNQ-rich situation.⁵⁴ (BEDT-TTF)(TCNQ) behaves as a Mott insulator below the metal–insulator transition temperature at 330 K. Ambipolar transport is observed, and the mobility increases down to 240 K.⁵⁵ Additional dielectric anomaly at 285 K has been suggested.⁵⁵ Single-crystal transistors of (BEDT-TTF)(F₂TCNQ) are also investigated at low temperatures, and ambipolar transport has been observed.⁵⁶ κ -(BEDT-TTF)₂-Cu[N(CN)₂]Br is an organic superconductor with the transition temperature of 11.8 K but located on the border of the Mott insulator. When placed on a silicon substrate, the crystal exhibits an insulating behavior at low temperatures owing to the strain and shows an extremely high n-channel field-effect mobility of $94 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 4 K.⁵⁷

◆ Charge-transfer Complexes as Electrodes

Takahashi et al. have reported electrodes composed of (TTF)(TCNQ) charge-transfer salts vacuum deposited on (DB-TTF)(TCNQ) single crystals.⁵⁸ By changing TTF and TCNQ to similar molecules, they have controlled work functions and achieved hole, electron, and ambipolar transport. Although these authors have used single-crystal (DB-TTF)(TCNQ), we have later investigated thin-film transistors based on (DB-TTF)(TCNQ) and (OM-TTF)(TCNQ) (Table 1).^{15,41} Although the performance is not very high, all these transistors show n-channel characteristics even under ambient conditions. This is reasonable because the oxidation potential of DB-TTF (0.72 V)

Table 1. Mobilities ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) of thin-film transistors using (TTF)(TCNQ) electrodes

Organic semiconductors	Au TC	(TTF)(TCNQ) BC	Ref
Pentacene	0.49	0.34	59
DB-TTF (2)	0.19	0.013	15
F ₁₆ CuPc	0.0008 ^a	0.0061 ^a	69
CuPc/F ₁₆ CuPc (hetero)		0.00042/0.0016 ^a	69
DM-DCNQI (20)	0.01 ^a	0.0036 ^a	46
HM-TTF (16)	3.6	0.91 (1.1) ^b	40
<i>t</i> -Butyl-HMTTF (17)	0.98	0.54 (0.69) ^b	40
Cyclopentyl-TTF (15)	0.27	0.17	38
Cyclohexyl-TTF (15)	0.10	0.024	38
(DB-TTF)(TCNQ)		5.9×10^{-4} ^a	15
(OM-TTF)(TCNQ)		5.9×10^{-4} ^a	41

^an-Channel. ^b(HM-TTF)(TCNQ) instead of (TTF)(TCNQ).

is higher than TTF (0.38 V), while surprising for (OM-TTF)-(TCNQ) because OM-TTF (0.24 V) is a stronger donor than TTF. This has been attributed to larger intermolecular transfers in TCNQ than OM-TTF. Energy levels do not seem to be a unique factor to determine the polarity of carriers in these charge-transfer salts.

It has been well known that bottom-contact (BC) transistors in which organic semiconductors are deposited on the source and drain (S/D) electrodes, exhibit considerably reduced performance in comparison with top-contact (TC) transistors where the S/D electrodes are constructed on the thin films of organic semiconductors.^{1a,59} This has been attributed to (1) morphological discontinuity where organic molecules are standing in the channel region but deposited in a face-on manner on the metal S/D electrodes^{1a,59} and (2) interfacial potentials in which organic molecules at the metal/organic interface are usually charged in the direction to increase the injection barrier.⁶⁰

Attempted remedies to recover the performance of BC transistors are: (1) thiol treatment on Au electrodes⁶¹ and (2) the use of conducting polymer electrodes.⁶² As another way, a thin layer of oppositely charged molecules between the electrode and the active layer improves the performance. For example, a thin layer of TCNQ or F₄TCNQ on metal electrodes has been used as a buffer layer of p-channel organic transistors.⁶³ When a thin layer of TCNQ is deposited on Ag or Cu electrodes before evaporating pentacene, improved performance has been reported.⁶⁴ However, metal TCNQ complexes are low-conducting insulators with 1:1 composition.⁶⁵ When DM-DCNQI is deposited from a solution between Ag or Cu electrodes and pentacene, the resulting performance (0.3 cm² V⁻¹ s⁻¹ for Cu) is almost comparable to that of Au TC transistors (0.49 cm² V⁻¹ s⁻¹),⁶⁶ because the complex, Cu(DM-DCNQI)₂ is a highly conducting metal.⁶⁷

In this connection, we have attempted to replace the electrode material with highly conducting organic charge-transfer salts such as (TTF)(TCNQ) and obtained as high performance as the Au TC devices in pentacene transistors.⁵⁹ In the (TTF)(TCNQ) devices, the BC device exhibits almost the same performance as the TC device. In DB-TTF transistors, we have investigated different metal electrodes as well as (TTF)(TCNQ) and found that the performance is in the order of the metal work functions, Au > Cu > Ag. (TTF)(TCNQ) electrodes afford performance that does not depend on BC and TC.¹⁵ If the performance is determined by the injection barrier from the electrode metal to the organic semiconductor, the mobility μ is proportional to $\exp(-n\Delta\Phi_m)$,⁶⁸ where $\Delta\Phi_m$ is the difference between the electrode metal work function and organic semiconductor ionization potential. The electrode dependence of the DB-TTF transistors follows this naïve expectation. (TTF)(TCNQ) electrodes also work well in n-channel transistors based on DM-DCNQI and F₁₆CuPc.^{46,69} In the latter case, we have constructed ambipolar transistors using a heterostructure consisting of a double layer of CuPc and F₁₆CuPc. In the former case, the expected order of the electrode metal dependence is Ag > Cu > Au, but the actually observed one is Au > (TTF)(TCNQ) > Ag > Cu. When we assume that the (TTF)(TCNQ) electrode is “null” of the interfacial potential shift Δ , Δ works in the direction to increase the injection barrier for Ag and Cu but to decrease the barrier for Au (Figure 2). This

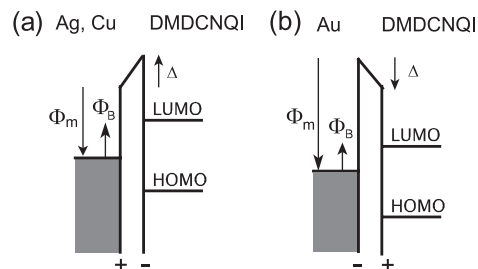


Figure 2. Interfacial energy diagram of (a) DM-DCNQI/Ag or Cu, and (b) DM-DCNQI/Au, representing enhancement and reduction, respectively, of electron injection barrier Φ_B due to the interfacial vacuum energy shift Δ .

is the reason that Au is generally a good electrode material even for n-channel transistors, though Au work function is relatively large.

(TTF)(TCNQ) electrodes are also adopted to TTP and HM-TTF derivatives,^{38,40} in which performance is almost comparable to the Au TC devices. Up to now we have applied (TTF)(TCNQ) electrodes to a considerable number of materials (Table 1).

The heart of this method that the two-component complex, (TTF)(TCNQ), is easily vacuum deposited from a single crucible. This is based on similar sublimation temperatures of the two components (120 °C). Therefore, this method is not applicable to other complexes containing hardly evaporating components. We have also used (HM-TTF)(TCNQ), which is another metallic conductor. (HM-TTF)(TCNQ) seems to show a little better performance than (TTF)(TCNQ) probably because of the fine grain size.⁴⁰ Alternatively, double-shot inkjet printing from individual TTF and TCNQ solutions has been reported.⁷⁰ We have recently used (TTF)(TCNQ) nanoparticles stabilized by ionic liquid and fabricated (TTF)(TCNQ) electrodes from a solution method.⁷¹ This method is applicable to nonevaporating components.

Recently, we have used conducting carbon instead of (TTF)(TCNQ), expecting that the carbon/organic interface is not as heterogeneous as a metal/organic interface.⁷² Although carbon electrodes in organic transistors have been attempted for chemical vapor deposition (CVD) carbon films,⁷³ we have used a dispersed carbon solution. For patterning, we have used surface selective deposition (Figure 3a),⁷⁴ where self-assembled monolayers (SAMs) are selectively removed by irradiating ultraviolet light using a metal mask, and carbon dispersion in polar ethyl acetate is deposited on the hydrophilic bare SiO₂ region. After depositing various organic semiconductors by evaporation or solution, the resulting transistors have exhibited excellent performance even though this is a kind of BC transistor.⁷² As another patterning method, a carbon film is selectively irradiated by laser (Figure 3b).⁷⁵ When washed with a polar solvent such as ethyl acetate, the nonirradiated part is removed and laser irradiated carbon film remains. By this laser sintering method, we can make short-channel patterns down to 2 μ m and relatively complicated patterns without using photolithography. The resulting carbon film is practically transparent because the thickness is as thin as 60 nm, affording a transparent conducting film, which is interesting as a replacement of indium tin oxide (ITO). The laser sintering reminds us that many organic polymers are transformed to conducting carbon by laser

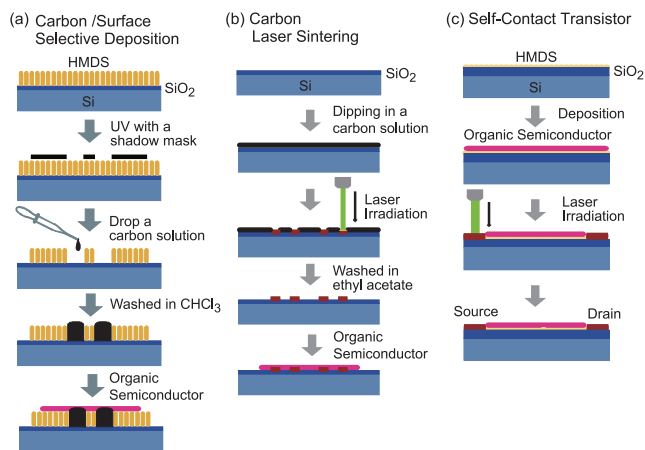


Figure 3. Patterning methods of carbon and self-contact transistors. Hexamethyldisilazane (HMDS) is used as SAMs.

irradiation.⁷⁶ Then films of pentacene or other organic semiconductors are selectively irradiated by laser to transform to conducting carbon (Figure 3c). Using this part as S/D electrodes, “self-contact” organic transistors are constructed.⁷⁷ This is an ultimately easy way to fabricate organic transistors.

◆ Summary

Although TTF derivatives are strong electron donors and have a strong tendency to aggregate into crystals, they show with appropriate molecular design excellent transistor properties. Charge-transfer complexes such as (DB-TTF)(TCNQ) are also used as the active layers and easily make air-stable n-channel organic transistors. Organic transistors with (TTF)(TCNQ) electrodes afford an insight into problems in the conventional metal/organic interface, which lead to such fabrication methods as carbon electrodes, laser sintering, and self-contact transistors. Through this work, we can explore charge transfer at the interface of organic materials.

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