

Molecular materials for organic field-effect transistors

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TOPICAL REVIEW

Molecular materials for organic field-effect transistors

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Abstract

Organic field-effect transistors are important applications of thin films of molecular materials. A variety of materials have been explored for improving the performance of organic transistors. The materials are conventionally classified as p-channel and n-channel, but not only the performance but also even the carrier polarity is greatly dependent on the combinations of organic semiconductors and electrode materials. In this review, particular emphasis is laid on multi-sulfur compounds such as tetrathiafulvalenes and metal dithiolates. These compounds are components of highly conducting materials such as organic superconductors, but are also used in organic transistors. The charge-transfer complexes are used in organic transistors as active layers as well as electrodes.

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

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1. Introduction

In recent years, research efforts on organic field-effect transistors (OFET) have been particularly intensified on account of the potential applications in low cost alternative of silicon electronics [1–3]. The main advantage of OFET is flexibility realized by fabrication on polymer substrates. Another merit lies in the easy processing from solutions, using such methods as spin coating and inkjet printing; these

processes enable low cost fabrication on large areas [4]. Obviously, the first target for OFET is the active matrix part of flexible displays [5]. Organic electroluminescence (EL) display is currently a commercial product, used in small-size displays in, for example, some mobile phones. Organic EL is, however, applicable for large-size displays in principle. The active matrix part of these displays is still realized with thin-film silicon. The real advantage of organic EL is fabrication on flexible substrates, but for this purpose we have to make the active matrix part with OFET. Recently, ‘all organic’ flexible displays have been reported. Application of flexible electronics is not limited to displays, but has been recently extended to flexible scanners and sensors [6, 7]. Another direction is printed electronics such as RF-ID (radio frequency identification) tags [8]. For high frequency applications, high mobility is required [9–11].

Along these lines, considerable efforts have been devoted to improving the performance of OFET, and a number of new organic semiconductors have been developed [3, 12]. OFET are achieved by using both small molecules and polymers. Since OFET are inherently thin-film devices, they constitute representative applications of thin films of molecular materials. In the present review, the author describes basic principles of

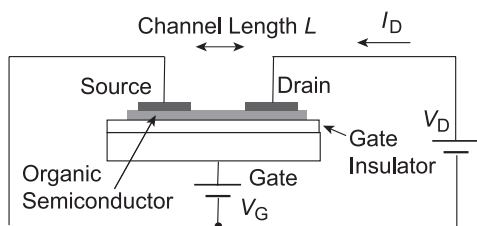


Figure 1. Structure of the OFET.

OFET from the materials point of view. Since an elaborate survey of OFET materials has appeared recently [12], the author lays particular emphasis on multi-sulfur materials such as tetrathiafulvalenes (TTF) and metal dithiolates. These compounds have played important roles in highly conducting organic metals such as organic superconductors [13, 14], but are also used in OFET. Finally, the use of charge-transfer compounds in OFET is mentioned.

2. Structure of OFET

The structure of a representative OFET is depicted in figure 1. First, assume that the organic semiconductor is a conducting material, and is connected to the source and drain (S/D) electrodes. The gate electrode is insulated from these parts. When we apply a gate voltage V_G between the gate electrode and the source electrode, this makes a capacitor. If we apply a positive voltage to the gate, positive charge is accumulated on the gate electrode, and negative charge is induced on the interface between the organic semiconductor and the gate insulator. When we apply some voltage V_D between the source and drain electrodes, the induced charge moves, and some current I_D flows from the drain to the source. If we turn off the gate voltage, the induced charge disappears, and I_D is switched off. When we apply positive V_G , negative charge (that is electron) carries the current, and the device is called n-channel. In the silicon device, doped silicon is called n-type or p-type. By contrast, the organic semiconductor is not chemically doped, and the polarity of the carrier is determined by the gate voltage. In order to distinguish this difference more exactly, some people prefer n-channel and p-channel in OFET instead of n-type and p-type. Then, to achieve p-channel OFET, we have to apply negative V_G .

For the purpose of screening materials in the laboratory, highly doped silicon wafer is conveniently used as the substrate, which works as the gate electrode at the same time. When this substrate is treated in oxygen at about 1000 °C for several hours, SiO₂ of the thickness of several hundred nanometers is formed on the surface [15]. This layer is used as the gate insulator. We can purchase this kind of silicon wafer with SiO₂. After ultrasonic washing successively in several solvents such as acetone, 2-propanol, and pure water, and ozone washing, for SAM (self-assembled monolayer) treatment, the substrates are exposed to HMDS (hexamethyldisilazane) vapor in a small container in an oven, typically at 150 °C for 1 h. Then the organic layer is evaporated or spin coated on the substrates. Finally, S/D electrodes,

typically Au, are vacuum evaporated using a mask. It is possible to make S/D electrodes before depositing the organic layer, and this configuration is called ‘bottom contact’ in contrast to the ‘top contact’ configuration. For the usual metal electrodes such as Au, the top contact device gives orders of magnitude higher performance than the bottom contact device. This is attributed to the contact resistance between the organics and S/D electrodes.

Figure 2 shows typical FET characteristics. A plot of I_D versus V_D is called the output characteristic (figure 2(a)). For different V_G , I_D increases with increase of V_G . However, at high V_D , I_D is almost independent of V_D . When V_D is increased to the same level as V_G , the drain and gate are no longer a capacitor because they are at the same voltage, so charge is no longer induced on the organic semiconductor. When this ‘pinch off’ happens, I_D does not increase any more. This is called the saturated region. By contrast, the region where $V_D < V_G$ is called the linear region, and the characteristics are represented by a quadratic formula:

$$I_D = \frac{W\mu C}{L} \left((V_G - V_T)V_D - \frac{1}{2}V_D^2 \right) \quad (1)$$

L is the channel length (figure 1), and W is the channel width. L is typically several tens of micrometers to several hundred micrometers, and W is usually more than ten times L [3]. C is the capacitance of the gate, and is typically 13 nF cm⁻² for 300 nm SiO₂. Then the mobility μ does not depend on the dimensions of the device, and is regarded as a property of the material.

A plot of I_D versus V_G (figure 2(b)) is called a transfer characteristic. The mobility μ is estimated from the transconductance [3, 16]:

$$g_m = \left. \frac{\partial I_D}{\partial V_G} \right|_{V_D = \text{const}} = \frac{WC}{L} \mu V_D \quad (2)$$

in the linear region. In the saturated region,

$$I_D = \frac{W\mu C}{2L} (V_G - V_T)^2 \quad (3)$$

and μ corresponds to the slope of $I_D^{1/2}$ versus V_G . I_D does not always rise exactly at $V_G = 0$ V, and the shift is represented by the threshold voltage, V_T . If the organic semiconductor has inherent carriers even without applying V_G , the device is ‘normally on’ even at $V_G = 0$ V. By contrast, if there are many traps on the interface, carriers are not accumulated until all traps are occupied, and V_T shifts to make the device a ‘normally off’ state. As equation (3) shows, V_T is evaluated from the plot of $I_D^{1/2}$ versus V_G , by extrapolating the linear part to the horizontal axis. Characteristics of OFET are sometimes measured at high V_G and V_D near 100 V, but low bias around 5–10 V is important for practical applications. In this respect, low and stable V_T is important for practical operation.

It should be mentioned that the structure of OFET is similar to that of thin-film silicon transistors, but different from that of single-crystal silicon transistors [15]. In the latter case, if the channel is made of n-type silicon, the S/D electrodes are made of p-type silicon. The PN junctions at the

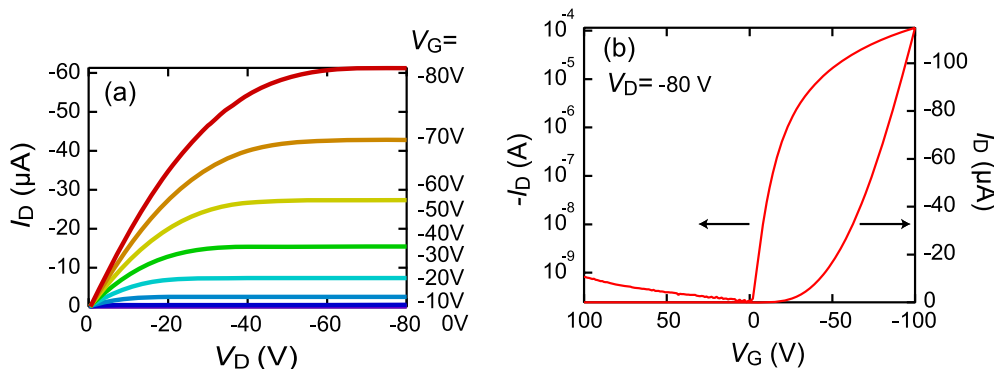


Figure 2. Characteristics of pentacene FET on SiO₂ with HMDS and Au S/D top contact electrodes; (a) output and (b) transfer characteristics. Reused with permission from [33]. Copyright 2007, American Institute of Physics.

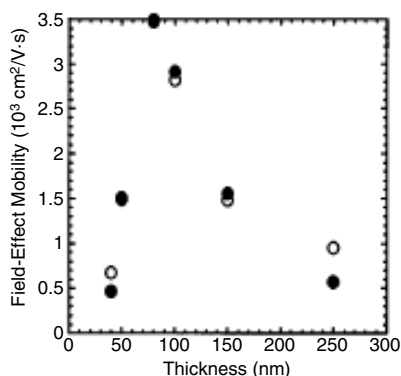


Figure 3. Thickness dependence of the mobility in CuPc FET. Reused with permission from [17]. Copyright 2002, American Institute of Physics.

channel/electrode interface are inversely biased independently of the polarity of V_D . This reduces the off current. Applying V_G , minority carriers are induced on the channel, and an ‘inversion layer’ is constructed in the n-type channel. In this case, these holes can pass to the p-type electrodes, and I_D flows.

The film thickness dependence of OFET has been investigated [17, 18]. Figure 3 shows the thickness dependence of copper phthalocyanine (CuPc) FET [18]. The mobility makes a peak at around 80 nm, and decreases when the film thickness is further increased. It is believed that the field induced charge is confined in a single molecular layer or at most within several layers. The film is, however, not perfectly homogeneous, and needs a little more deposition to cover the entire channel region. Thick film also increases the off current. Accordingly, using film as thin as possible is important for achieving good performance. Even when we make single-crystal transistors, thin crystals are required.

3. Energy levels of organic semiconductors

Energy levels of some organic semiconductors are depicted in figure 4. The ionization potential is regarded as corresponding to the energy level of the HOMO (highest occupied molecular orbital) [19]. The ionization potential is directly measured by

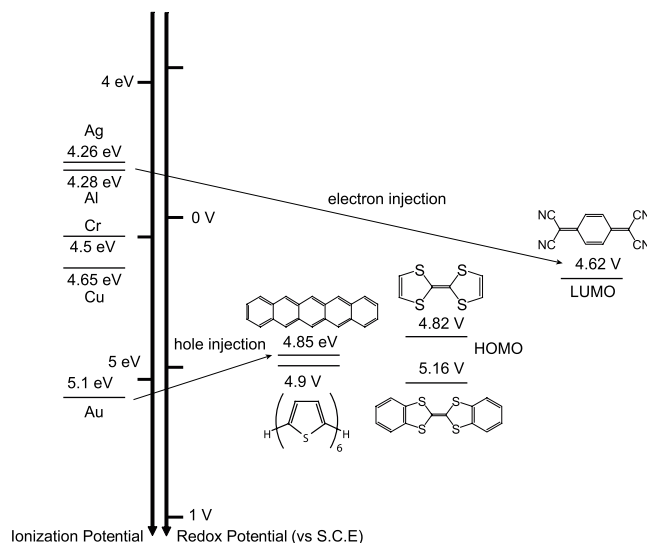


Figure 4. Energy levels of organic semiconductors.

photoelectron spectroscopy, where ultraviolet light or x-rays of frequency ν are used to irradiate the molecule in vacuum, and the kinetic energy E_K of the escaped electron is analyzed, so that the binding energy E_B is estimated from $h\nu = E_K + E_B$. Molecular solids and gaseous molecules afford different E_B values owing to the relaxation in the solids. The ionization energy of the usual electron donor molecule is around 5 eV in the solids, whereas it is 7 eV in the gas phase. We use the former values for the discussion of devices.

We can compare these ionization potentials with work functions of metals, which are the positions of the Fermi levels. For example, the work function of Au (5.1 eV) is located lower than the ionization potential of pentacene (4.85 eV), and hole injection from Au S/D electrodes to pentacene is expected. Although the work function of Au varies between 4 and 5 eV depending on deposition and contamination, 5.1 eV is usually used. The work function of Cr (4.5 eV) is higher than the energy level of pentacene, and naively speaking, the Schottky junction is expected to be between pentacene and Cr.

It is, however, not always easy to measure the ionization potentials by photoelectron spectroscopy. Instead, redox

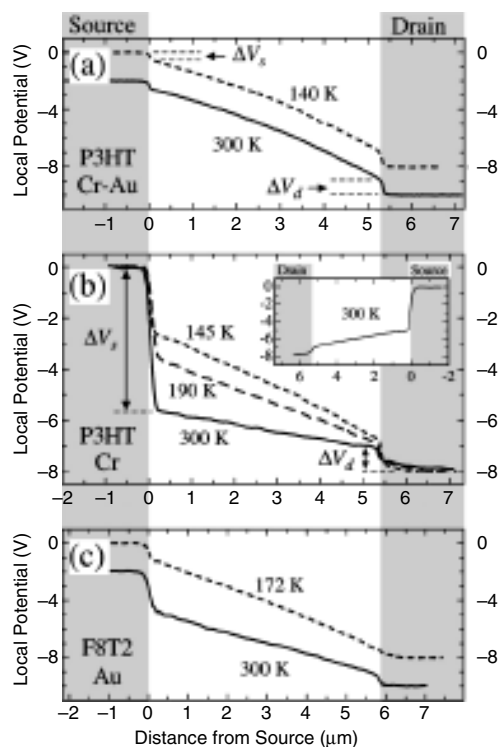


Figure 5. Microscopic potential of (a) P3HT/Au, (b) P3HT/Cr, and (c) F8T2/Au OFET. Reused with permission from [21]. Copyright 2003, American Institute of Physics.

potentials E_{red} (versus SCE) are easily measured in solutions by cyclic voltammetry, and they are converted to the ionization potentials E_{P} via $E_{\text{P}} = E_{\text{red}} + 4.44 \text{ eV}$ [20]. Although this is a very rough estimation, this relation is conveniently used to estimate the energy levels of new materials.

As shown in figure 5, observation of the microscopic potential indicates a considerable potential drop at the interface of the S/D electrode and organic semiconductor [21–23]. In the combination of P3HT (see figure 8) and Au electrodes (figure 5(a)), the work function of Au is lower than the HOMO level of P3HT. Consequently, the hole injection from Au to P3HT is efficient, and no significant potential drop happens at the electrode. When Au is replaced by Cr (figure 5(b)), the Cr level (figure 4) is higher than that of P3HT, and a considerable potential drop is observed at the source electrode. If P3HT is substituted by a fluorinated polymer, F8T2, the HOMO level lowers, and the potential drop occurs similarly (figure 5(c)).

Such an injection barrier is recognized as contact resistance at the S/D electrodes. One method for eliminating the contact resistance is the four-probe method, where two additional electrodes are inserted in the channel region, and the voltage drop is measured at the additional electrodes [24, 25]. Another frequently used approach is the transfer line (or transmission line) method, in which the parasitic resistance is extracted from the devices with varying gate lengths [26–35]. Figure 6 shows an example for pentacene FET, where the S/D electrodes are an organic charge-transfer salt, (TTF)(TCNQ) (discussed in section 8) [35]. Here, several devices with different L are fabricated on the same substrate. Figure 6

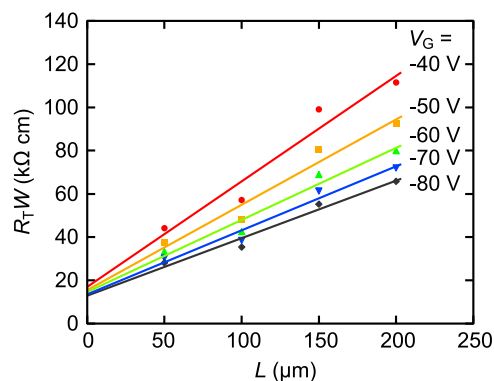


Figure 6. Estimation of contact resistance in OFET by the transfer line method. Pentacene transistor with (TTF)(TCNQ) S/D electrodes. Reused with permission from [33]. Copyright 2007, American Institute of Physics.

shows total resistance $R_{\text{T}} = \Delta V_{\text{D}} / \Delta I_{\text{D}}$ around $V_{\text{D}} = 0 \text{ V}$ as a function of the gate length, L . Since resistance is inversely proportional to the gate width, W , the total resistance is normalized to $R_{\text{T}} W$. From the extrapolation to $L = 0 \mu\text{m}$, we can estimate the contact resistance to be about $15 \text{ k}\Omega \text{ cm}$. The transfer line method is applied to not only pentacene [26, 27], but also polymer transistors [28, 29], and also with varying S/D electrodes to other metals [30], polyanilines [31, 32] charge-transfer salt such as (TTF)(TCNQ) [33], as well as laminated contacts [34, 35].

The contact resistance is, however, not solely energetic in origin. Figure 7 shows AFM images of pentacene thin films on SiO_2 and Au. Pentacene on SiO_2 shows a characteristic pattern (figure 7(a)), but the grain size on Au is dramatically reduced (figure 7(b)) [3, 33]. The latter is expected to be highly resistive. At the edge of the Au electrode, this pattern continues inside to the channel region (figure 7(c)), leading to high contact resistance in the bottom contact transistors. Top contact transistors do not have this transient region, and show much reduced contact resistance. In addition, a thermal effect as well as some reaction of the electrode metal with the organic material during the evaporation may be responsible for the reduced contact resistance in top contact transistors. It should be noted that not only the semiconductor/metal contact but also the semiconductor/dielectric interface is of great importance for the carrier transport.

4. p-channel FET materials

In order to improve the performance of OFET, a large number of materials have been developed and investigated [3, 12, 36]. Representative materials are depicted in figure 8. The first OFET date back to the 1980s, where such materials as polyacetylene and merocyanine are used [37, 38]. In the 1990s, considerable efforts were devoted to investigating oligothiophenes [2]. Oligothiophenes such as 6T are vacuum evaporated to form well ordered thin films, and realize mobility of the order of $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [47]. Introduction of alkyl chains like DH6T and DH4T improves the morphology, and mobility exceeding $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is achieved by optimizing

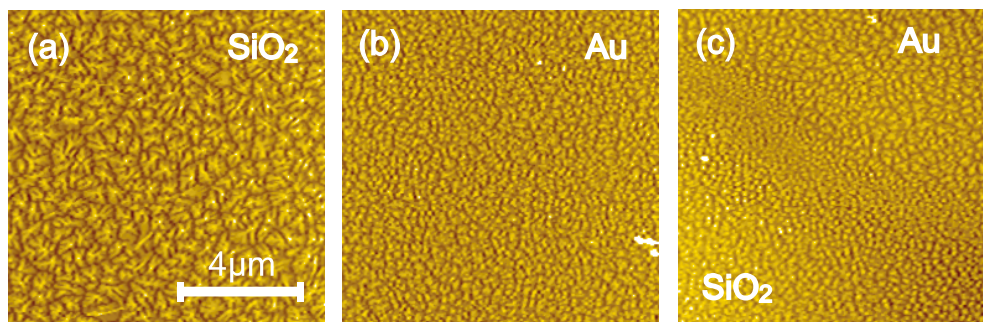


Figure 7. AFM pattern of pentacene on (a) SiO₂, (b) Au, and (c) the edge of the Au electrode. Reused with permission from [33]. Copyright 2007, American Institute of Physics.

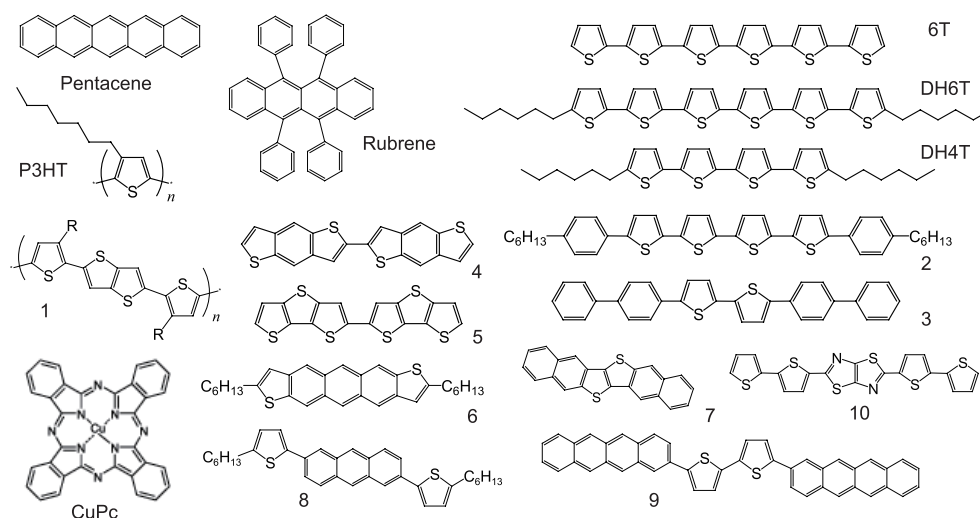


Figure 8. Representative p-channel FET materials. Pentacene: $3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [39], single crystal: $0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [40], P3HT: $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [41], **1** for R = C₁₂H₂₅, C₁₄H₂₉, and C₁₆H₃₃: $0.2\text{--}0.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [42], CuPc: $0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [43], single crystal: $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [44], rubrene: single crystal: $20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [45], 6T: $0.075 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [47], DH6T: $0.13 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [48], DH4T: $0.23 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [49], **2**: $0.028 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [50], **3**: single crystal: $0.66 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [51], **4**: $0.04 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [52], **5**: $0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [53], **6**: $0.15 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [54], **7**: $2.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [55, 56], **8**: $0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [57], **9**: $0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [58], **10**: $0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [59].

the conditions [48, 49]. However, the best performance of evaporated organic films is attained with pentacene, and this is by far the most representative material among OFET materials [39]. A mobility value of more than $3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ has been reported [39]. The mobility of amorphous silicone is about $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and mobility above this value is desirable. Pentacene is, however, hardly soluble in organic solvents, and pentacene thin film is made by vacuum evaporation. Considerable efforts have been devoted to making soluble pentacenes by chemical modifications, and as large mobility as $>1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ has been reported [60]. For the solution processes such as spin coating, soluble polythiophene such as P3HT (poly-3-hexylthiophene) is used, where the solubility is attained by the introduction of the hexyl groups. The mobility is at most $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [41], but recently improved values of $0.2\text{--}0.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were reported in **1** [42]. Rubrene single crystal is the record holder for mobility in organic materials, but the mobility is inversely proportional to the dielectric constant of the insulator, and the best value ($20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) is achieved with the air gap device [45].

Similar inverse proportionality has also been reported for polymer transistors [46].

Co-oligomers of thiophene and phenylene (benzene ring) like **2** and **3** are good FET materials [50, 51]. The phenyl ring tends to increase the ionization potential (lower the HOMO level), and to reduce the off current. It is not necessary to connect six thiophene rings, and four or sometimes two thiophene rings, for example of DH4T and **3**, are sufficient. Fused thiophene rings such as thienothiophenes (**4** and **5**) also work. Recently, fused systems of thiophene and benzene rings were investigated (**6** and **7**). In other words, some of the benzene rings in pentacene or other polyacenes are replaced by thiophene rings. In particular, **7** shows as high mobility ($2.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) as pentacene [55, 56].

5. n-channel FET materials

The number of good n-channel materials is limited, but recently considerable attention has been paid to the development of n-channel materials [61, 62]. Representative n-channel

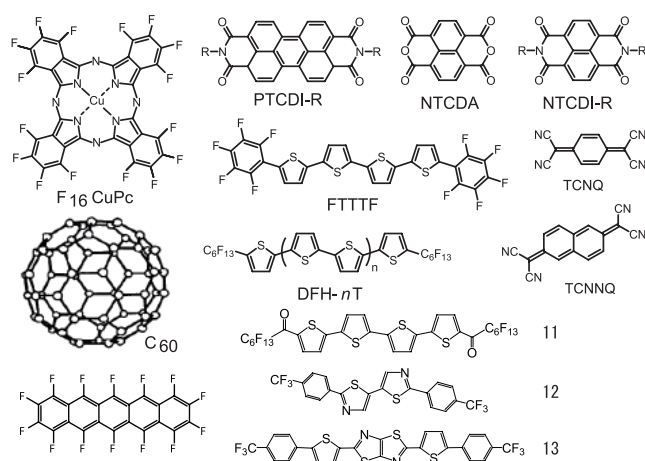


Figure 9. Representative n-channel FET materials. F₁₆CuPc: 0.03 cm² V⁻¹ s⁻¹ [63], C₆₀: 0.3 cm² V⁻¹ s⁻¹ [64], PTCDI-R: 1.7 cm² V⁻¹ s⁻¹ [65], NTCDA: 0.003 cm² V⁻¹ s⁻¹ [66], NTCDI-R: 0.1 cm² V⁻¹ s⁻¹ for R = C₈F₁₇ [67], 0.16 cm² V⁻¹ s⁻¹ for R = C₈H₁₇ [68, 69], FTTTF: 0.43 cm² V⁻¹ s⁻¹ [70], DHF-4T: 0.22 cm² V⁻¹ s⁻¹ [71], TCNQ: 3 × 10⁻⁵ cm² V⁻¹ s⁻¹ [72], TCNNQ: 0.003 cm² V⁻¹ s⁻¹ [73], **11**: 0.6 cm² V⁻¹ s⁻¹ [74], perfluoropentacene: 0.22 cm² V⁻¹ s⁻¹ [75, 76], **12**: 1.83 cm² V⁻¹ s⁻¹ [77], **13**: 0.3 cm² V⁻¹ s⁻¹ [78].

FET materials are depicted in figure 9. C₆₀ and naphthalene tetracarboxylic dianhydride derivatives (PTCDI-R and NTCDI-R) are well known n-channel OFET semiconductors. In addition, a variety of fluoro and trifluoromethyl compounds are known to show n-channel performance. TCNQ (tetracyanoquinodimethane) gives n-channel OFET [72]. Although the reported mobility (3 × 10⁻⁵ cm² V⁻¹ s⁻¹) is not very high, the OFET works in air even after air exposure of several ten days. Recently, record high mobility of 1.83 cm² V⁻¹ s⁻¹ has been reported for **12** [77].

If we use low work function metals as S/D electrodes, it is possible to inject electrons into organic semiconductors with relatively high LUMO (lowest unoccupied molecular orbital) levels. Using Ca as the S/D electrodes, n-channel transistors are achieved for pentacene [79], P3HT, and PPV (polyphenylenevinylene) [80]. Ambipolar characteristics have been observed for the combination of pentacene and Ca [81]. This is not surprising because the LUMO level of pentacene (3.2 eV) is lower than that of Ca (2.9 eV).

It has been reported that n-type organic semiconductors are unstable with respect to oxidations with H₂O and O₂, which take place at redox potentials of -0.66 and 0.57 V (versus SCE), respectively [82]. Compounds with reduction potentials to the monoanionic (1-) states higher than the former (-0.66 V) are reported to be stable in air [83].

6. OFET using tetrathiafulvalenes

TTF is well known to make organic metals and organic superconductors [13, 14]. The high conductivity of the charge-transfer salts is associated with the intermolecular overlap of bulky sulfur orbitals. Actually the bandwidth of TTF conductors, estimated from the energy band calculation, is

about 1 eV, and is larger than those of oligothiophenes (0.43 eV) and pentacenes [84, 85]. Therefore, expecting a large mobility, OFET using TTF derivatives are fabricated [86].

An earlier work on TTF transistors was on BTQBT (**14**, figure 10) [87], though this is not exactly TTF. This material makes a highly crystalline film by vacuum evaporation, and affords hole mobility of 0.2 cm² V⁻¹ s⁻¹. Upon cooling, however, the mobility decreases [88]. Many similar compounds have been examined. Although the mobility values do not exceed the first one, many of them show transistor properties [89].

Mas-Torrent and Rovira have demonstrated the possibility of TTF derivatives in the DT-TTF OFET (**15**) [90]. From the solution, beautiful crystals are grown between the electrodes (figure 11), and these crystals afford high mobility of 1.4 cm² V⁻¹ s⁻¹. They have investigated many TTF derivatives by the same method [91]. Although BEDT-TTF (bis(ethylenedithio)TTF) gives relatively low mobility of 0.005 cm² V⁻¹ s⁻¹, several thiophene fused TTF derivatives give mobility values exceeding 0.1 cm² V⁻¹ s⁻¹. When visible light illuminates a DT-TTF transistor, a considerable increase of the drain current is observed [92]. The increase is particularly large in the off state, rather than the on state.

By the same method, dibenzo-TTF (DB-TTF **16**) gives 1.0 cm² V⁻¹ s⁻¹ [93]. Evaporated film of DB-TTF makes a good OFET as well. A series of fused TTF compounds (**16–19**) were investigated by Yamashita *et al* [94]. The best performance was achieved with the naphthalene fused compound (**17**: 0.4 cm² V⁻¹ s⁻¹), and the value for DB-TTF (0.06 cm² V⁻¹ s⁻¹) is lower than this. However, our recently obtained value for DB-TTF is 0.19 cm² V⁻¹ s⁻¹ [95]. The unsubstituted TTF OFET does not work well because TTF gradually re-evaporates under vacuum. DB-TTF is easily evaporated, and is regarded as a standard for TTF-based OFET. As shown in figure 12, DB-TTF has a herringbone structure in the crystal [96], but the dihedral angle is greatly different from those of the usual herringbone compounds such as oligothiophenes [97]. DB-TTF is closer to the stacking structure. The herringbone structure realizes two-dimensional uniform transfers. In addition, Bromley *et al* have pointed out that small renormalization energy is important to transistor performance [98]. In general, neutral TTF has a greatly bent boat configuration, but TTF⁺ usually has planar structure. Accordingly, the neutral form and the oxidized form have very different energy. By contrast, neutral molecules in the herringbone structure have planar structure, and the renormalization energy is small. This may be related to the good performance of DB-TTF and DT-TTF [99]. When the terminal of DB-TTF is substituted by fluorine or chlorine (**20–23**), interestingly, n-channel behavior is observed [100]. Compounds **22** and **23** have stacking structure rather than herringbone structure. Owing to the uniform stacking, these neutral molecules are entirely planar in the crystal.

We have investigated **24**, where one end of the TTF part is substituted by cyano groups, and another end has an alkyl chain [101]. The affinity of the cyano groups to the SiO₂ substrate, together with the alkyl chain, makes a well ordered thin film. Above 100 °C, this compound shows a liquid

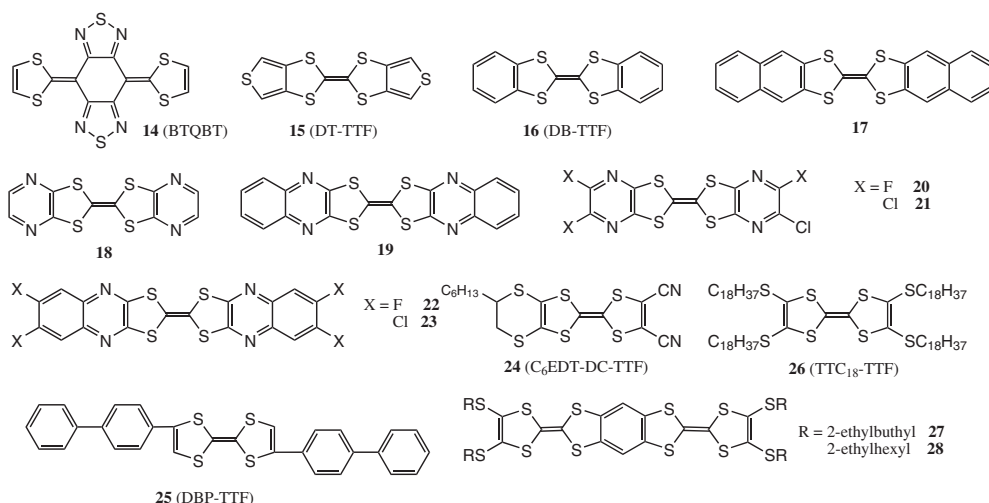


Figure 10. TTF-based OFET materials. **14** (BTQBT): $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [87], **15** (DT-TTF): single crystal: $1.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [90], **16** (DB-TTF): single crystal: $1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [93], $0.19 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [95], **17**: $0.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [94], **18**: $3.3 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [94], **19**: $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [94], **20**: $0.20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (n) [100], **21**: $0.64 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (n) [100], **22**: $0.10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (n) [100], **23**: $0.20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (n) [100], **24**: $0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [101], **25**: $0.11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [105], **26**: zone casting $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [107], **27**: $4.8 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [108], **28**: $2.1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [108].

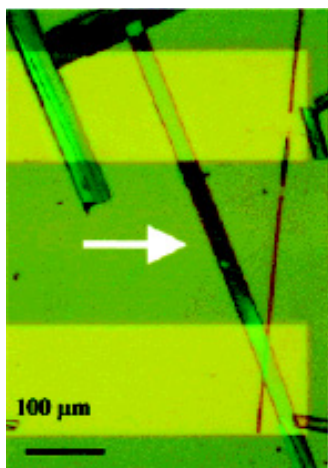


Figure 11. Single crystal of DT-TTF formed on electrodes [90].

crystalline (smectic A) phase. This may be reasonable because, if we imagine the TTF part to be replaced by a biphenyl unit, the resulting structure is cyanobiphenyl, a famous liquid crystalline material. In this analogy, we have synthesized alkyl substituted BEDT-TTF molecules, but these compounds have not shown transistor properties [102]. On the other hand, we have replaced the TTF part with oligothiophenes, and prepared cyano and alkyl substituted oligothiophenes [103]. These compounds do not exhibit transistor properties, but it seems to be a general rule that cyano substituted oligothiophenes do not show transistor properties [104].

Biphenyl substituted TTF **25** shows good transistor properties ($0.11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [105]. The XRD shows that the molecules are standing perpendicular to the substrates, but the crystal structure is not solved. Due to the synthetic procedure, there are two possibilities for the biphenyl substitution: *cis* and *trans* forms. Crystal structures of phenyl and alkylphenyl

substituted TTF have been analyzed, and we have found only the *trans* forms [106]. We draw the *trans* form in figure 10. When the biphenyl part is replaced by a variety of alkylphenyl groups, we obtain various modifications of herringbone structure, where the molecular displacement lowers the performance.

Thin film of TTC₁₈-TTF **26** is fabricated by the solution zone-casting method (figure 13(a)) [107]. By this method, the molecules are aligned along the casting direction (figure 13(b)), and the mobility is high in the aligned direction. Extended molecules such as **27** and **28** are also solution processed, and OFET have been obtained [108].

7. OFET using metal complexes

Recently, considerable attention has been paid to the development of n-channel materials [61, 62]. In this connection, metal coordination compounds are promising because metal complexes show a wide variety of redox potentials in comparison with pure organic compounds. Among the metal complexes, phthalocyanine (Pc) is one of the oldest FET materials, which was used as early as 1964 [109, 110]. Mobility values in the order of $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (p-channel) have been reported from many groups [111, 112]. Recently for single-crystal transistors as high mobility as $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ has been reported [44]. Ambipolar transport has been also observed [111]. Octaethyl platinum porphyrin works as a p-channel semiconductor showing a mobility of $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ as well [113].

Perfluorinated copper phthalocyanine F₁₆CuPc (figure 9) is a famous n-channel material [63], where a mobility of $0.03 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and air stability have been reported [114]. Since F₁₆CuPc is an important n-channel material, many works have been done on this compound. For example, double-layer FET consisting of the first layer of F₁₆CuPc and the

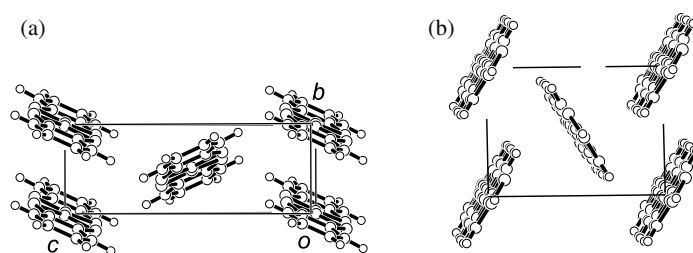


Figure 12. Crystal structure of (a) DB-TTF [96] and (b) sexithiophene [97].

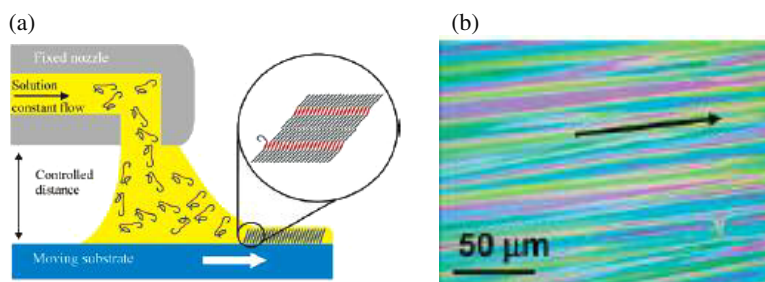


Figure 13. (a) Zone-casting method and (b) the morphology [107].

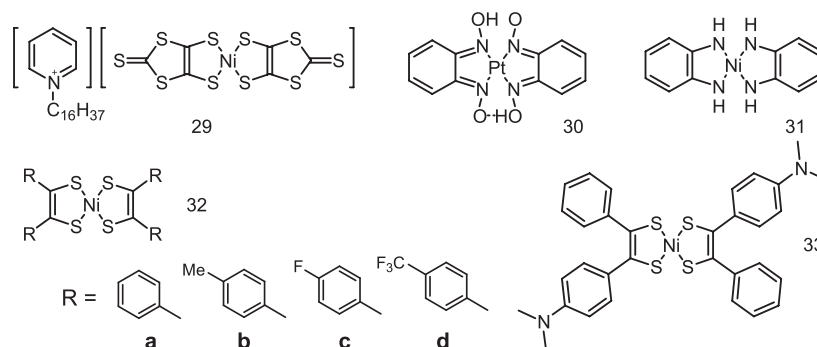


Figure 14. Metal complexes used in OFET. **29**: $2.4 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (n-channel) [123], **30**: single crystal: $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (n) [124], **31**: $0.038 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (p-channel) [125], **32a**: $3.0 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, **32b**: $1.3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, **32c**: $9.0 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, **32d**: $6.6 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (n) [126], **33**: $2.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (p) and $2.0 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (n) [131].

second layer of CuPc have been investigated, and ambipolar transistors have been obtained [115–117], where the hole and electron mobility is attained to be $0.042 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [118]. Ambipolar OFET are also realized with the combination of F_{16}CuPc and 2,5-bis(4-biphenyl)bithiophene (BP2T), where the hole and electron mobility are 0.04 and $0.036 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, by using F_{16}CuPc as the second layer [119]. When CuPc is used only as a buffer layer between the S/D electrodes made of Au, the electron mobility is reported to be $0.076 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [120]. F_{16}CuPc transistors with Ta_2O_5 gate dielectric are also investigated, and the shift of the threshold voltage in the positive direction by the application of the gate bias is reported [121].

Among organic superconductors, many TTF derivatives are known to show superconductivity, but metal dmit (4,5-dimercapto-1,3-dithiol-2-thione) is the only acceptor that shows superconductivity [122]. n-channel FET properties were reported as early as 1994 in *N*-octadecylpyridinium $[\text{Ni}(\text{dmit})_2]$ (**29**) [123].

OFET are also fabricated by using a single crystal of **30** (figure 14), where electron mobility of $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ has been obtained [124].

Bis(1,2-phenylenediamino) nickel **31** is a strong electron donor with the redox potential of about 0 V, and works as a p-type semiconductor [125]. A hole mobility of $0.038 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ has been reported for the evaporated film transistor.

Nickel dithiolates have been studied for a long time due to the intriguing redox properties [126, 127]. Tetraphenyl nickel dithiolate (**32**) is an electron acceptor, and works as an n-channel OFET [128, 129]. On account of the non-planar and dimerized neutral structure [129, 130], the electron mobility is at most in the order of $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, but the fluoromethyl and trifluoromethyl derivatives (**32c** and **32d**) show reasonably air-stable n-channel properties [129]. For these compounds, (TTF)(TCNQ) is used as the S/D electrodes. Since the LUMO level of TCNQ is fairly high, (TTF)(TCNQ) works as a good S/D electrode in n-channel

OFET. Tetraphenyl nickel dithiolates have been investigated as dyes for a long time, and some compounds are commercially available.

The dimethylamino derivative **33** exhibits ambipolar OFET characteristics, where the hole and electron mobility is 2.5×10^{-4} and $2.0 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively [131]. This material is used for complementary FET, and an inverter and a ring oscillator are fabricated [132]. The maximum oscillation frequency of a five-stage ring oscillator is reported to be 710 Hz. Similar tetraphenyl complexes with long alkyl chains are prepared, and field-effect mobility of the order of $1.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ has been reported [133].

8. OFET using charge-transfer salts

It was as early as 1998 that Kudo's group fabricated OFET with a charge-transfer salt (TMTSF)(TCNQ) (TMTSF: tetramethyltetraselenafulvalene) [134]. TMTSF and TCNQ (500 nm each) are successively vacuum deposited on the gate SiO_2/Si , and stacked layers of the donor and the acceptor are formed. When the TMTSF layer is under the TCNQ layer, application of negative gate voltage enhances the drain-source current, suggesting hole transport. By contrast, the lower TCNQ layer results in electron-like gate modulation.

The same group has evaporated (TMTSF)(TCNQ) from a single source [135]. When the substrate temperature is 25°C , electron-like transport is observed, whereas at 35°C hole-like transport is attained. When (TTF)(TCNQ) is evaporated, TTF is re-evaporated, and the film tends to be TCNQ rich [136]. These authors have supposed that in the case of (TMTSF)(TCNQ), TCNQ leaves, and the film becomes TMTSF rich, particularly at elevated substrate temperatures. OFET with Langmuir-Blodgett films made of C_{15}TCNQ (pentadecyl-TCNQ) and TMPD (tetramethyl-p-phenylenediamine) show electron-like transport [137].

Sakai *et al* have succeeded in growing (TTF)(TCNQ) molecular wires between the source and drain electrodes by applying electric fields [138–141]. (TTF)(TCNQ) is co-evaporated from two individual crucibles, and wire-like microcrystals grow between the electrodes typically with 100 μm interval under the applied voltage of 350 V. The conductivities of the molecular wires have been investigated by microscopic potentiometry [142]; that of those grown from the cathode is high ($>100 \text{ S cm}^{-1}$), but that of those from the anode is low (0.3 S cm^{-1}). The conductivity of connected wires varies between 10 and 300 S cm^{-1} . Figure 15 shows the output and transfer characteristics of the (TTF)(TCNQ) transistor. The conductivity at $V_G = 0 \text{ V}$ is 0.2 S cm^{-1} , and large gate modulation, corresponding to the mobility of 1.1 – $2.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, is observed. The n-channel characteristics have been attributed to the partly TCNQ rich composition derived from the re-evaporation of TTF.

(BEDT-TTF)(TCNQ) OFET are made from the solutions [143]. These compounds, composed of segregated stacks of BEDT-TTF and TCNQ, undergo a metal-insulator transition at 330 K [144], and the low temperature state is ascribed

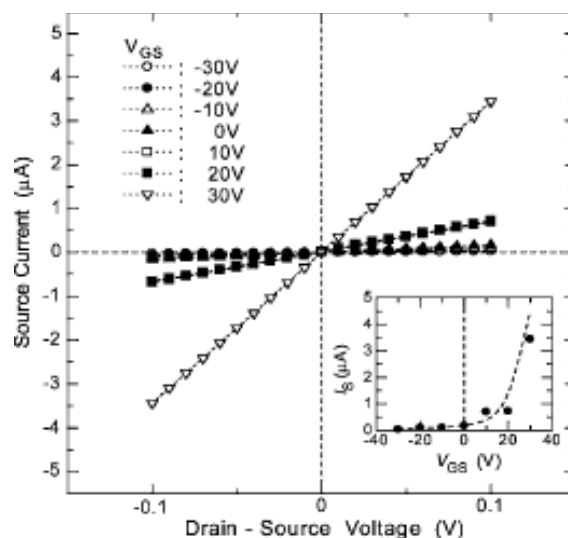


Figure 15. Output characteristics of the (TTF)(TCNQ) FET at room temperature [141]. The inset is the transfer characteristics at $V_{DS} = 0.1 \text{ V}$. Reused with permission from [141]. Copyright 2007, American Institute of Physics.

to a Mott insulating state [145]. The OFET shows ambipolar characteristics, and the mobility increases down to 200–250 K [146]. This indicates that carriers injected by the field effects exhibit metallic behavior below the metal-insulator transition temperature of the bulk material.

Hasegawa *et al* have made a single-crystal transistor of another Mott insulator, (BEDT-TTF)(F_2TCNQ) [147]. This compound consists of fully ionized BEDT-TTF^+ and F_2TCNQ^- , and is a typical Mott insulator. After the fabrication of Au S/D electrodes on the crystal, a Parylene C gate insulator and the gate electrode are fabricated. This device exhibits ambipolar characteristics, and the electron and hole mobilities increase on lowering the temperature. Single crystals of (DB-TTF)(TCNQ) are also used with (TTF)(TCNQ) S/D electrodes, and large n-channel mobility of $1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is observed in air [148]. Furthermore, the S/D materials are changed by using the combinations of TTF, TSF, and DB-TTF as donors and TCNQ, F_1TCNQ , F_2TCNQ , and F_4TCNQ as acceptors, and the energy level is controlled (figure 16) [149]. When the energy level is high from the use of such combinations as (TTF)(TCNQ) and (TTF)(F_1TCNQ) (A and B), n-channel behavior is observed, whereas this changes to ambipolar behavior in (TTF)(F_2TCNQ) and (TSF)(F_1TCNQ) (C and D). Finally, when the energy level is as low as for (TSF)(F_2TCNQ) and (DB-TTF)(F_4TCNQ) (D and F), p-channel behavior is attained.

The same authors have attempted to cover the top of pentacene OFET with F_4TCNQ [150]. When the covered version ratio of the channel is increased, the threshold voltage shifts to positive (normally on) direction. For the fabrication of S/D electrodes by inkjet printing [151], BEDO-TTF (bis(ethylenedioxy)tetrathiafulvalene) and C_{14}TCNQ (tetradecyl-TCNQ) dissolved in dimethylsulfoxide (DMSO) are used [150]. (TTF)(TCNQ) S/D electrodes are made by the double-shot inkjet method, where independent solutions of TTF and TCNQ are used [152].

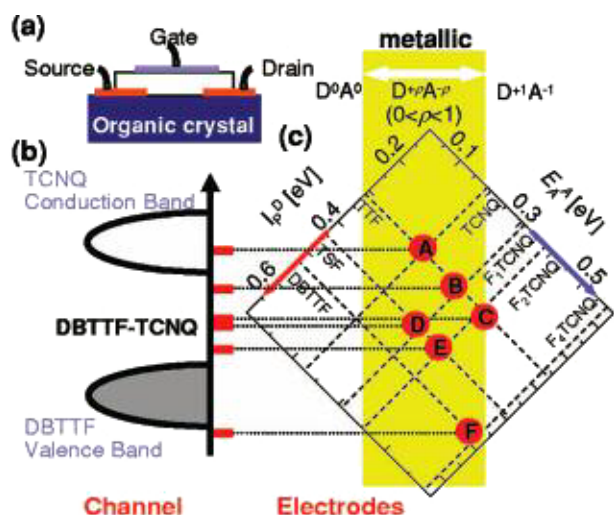


Figure 16. OFET in which both the active layer and the S/D electrodes are composed of organic charge-transfer salts. (a) Structure of the single-crystal transistor, (b) energy bands of the (DB-TTF)(TCNQ) active layer together with (c) the energy levels of the S/D electrodes. Reused with permission from [149]. Copyright 2006, American Institute of Physics.

Table 1. Mobility (μ), on/off ratio, and contact resistance of pentacene thin-film transistors with Au and (TTF)(TCNQ) electrodes.

Electrode	Contact	Overall μ ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	On/off ratio	$R_c W$ ($\text{k}\Omega \text{cm}$)
Au	Top	0.49	10^6	7.6
	Bottom	0.011	10^4	3300
(TTF)(TCNQ)	Top	0.41	10^6	14
	Bottom	0.34	10^6	13
	Bottom	0.29	10^6	50 (without HMDS)

Contact resistance of evaporated (TTF)(TCNQ) S/D electrodes in pentacene thin-film transistors is estimated by the transfer line method (figure 6) [33]. As listed in table 1, contact resistance of the Au bottom contact transistor is several orders larger than that of top contact transistors, though this reduces the overall mobility only to the order of $0.01 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. For (TTF)(TCNQ), the bottom contact and the top contact afford almost the same contact resistance, and the overall performance is comparable to that of the Au top contact transistors. Accordingly, the (TTF)(TCNQ) electrodes are particularly advantageous to the bottom contact configuration. The large contact resistance of the Au bottom contact has been attributed to the microdomain structure of pentacene on the hydrophilic Au, which continues even inside the channel region (figure 7) [3, 22, 33]. The XRD demonstrates that the TTF and the TCNQ molecules are standing in the evaporated thin films. Consequently, the high conduction plane of (TTF)(TCNQ) microcrystals is parallel to the substrate, giving rise to small sheet resistance of $4 \text{ k}\Omega \text{K}^{-1}$, or equivalent bulk resistance of $0.12 \Omega \text{cm}$.

Contact resistances of the (TTF)(TCNQ) electrodes are investigated as well for DB-TTF thin-film transistors [95].

Since the contact resistance of the (TTF)(TCNQ) electrodes deviates from those for the series of metal electrodes such as Au, Cu, and Ag, the small contact resistance is ascribed to preferable organic–organic interface rather than the potential matching between the energy level of the organic semiconductor and the work function of the electrode metal.

In this connection, it has been reported that when Ag and Cu S/D electrodes are modified by a TCNQ solution, the formation of Ag(TCNQ) and Cu(TCNQ) buffer layers improves the transistor performance [153]. An F_4 TCNQ buffer layer inserted between pentacene and Au is also reported to be effective [154].

9. Summary

Here we have surveyed materials aspects of OFET. A variety of materials have been investigated in order to improve the performance of OFET. The TTF family, particularly DB-TTF, are good transistor materials. Metal coordination compounds are relatively unexplored. Not only the energy level but also the morphology is an important factor for determining the performance, whereas, from the practical point of view, ease of fabrication, such as by vacuum evaporation or solubility, is a crucial factor. Care should be given to addressing the fact that mobility is not solely a property of material but greatly depends on the fabrication conditions. Not only the performance but also even the polarity of the carriers is greatly dependent on the combination of organic materials and electrode materials. In this respect, the use of charge-transfer salts as electrode materials should be a new aspect. Single-crystal transistors are interesting as a basic research field, but still pentacene gives the best performance as the film, and solution processing, which is highly desirable for practical applications, gives lower performance. Researchers working in this field seem to have many different origins, including in electronic engineering, applied physics, materials chemistry, and more basic physics. Collaboration of the researchers from different fields is expected to resolve the issues remaining for the coming product applications.

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Note added in proof. Recently it has been reported that one of the two crystal forms of unsubstituted TTF gives high performance OFET ($>1 \text{ cm}^2/\text{V s}$) by the drop cast method [155]. Two different series of TTF derivatives with two alkyl chains are synthesized, where one gives $1.3 \times 10^{-2} \text{ cm}^2/\text{V s}$ by the spin coating [156], and another gives $0.22\text{--}0.40 \text{ cm}^2/\text{V s}$ by thermal evaporation [157].

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