Organic Field-effect Transistor Based on Biphenyl Substituted TTF

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Tetrathiafulvalene-based organic semiconductor with biphenyl substituents, DBP-TTF (bis(biphenyl)tetrathiafulvalene) is used as an active layer of an organic field-effect transistor. DBP-TTF forms a good thin film on a SiO₂ substrate, in which the DBP-TTF molecules are arranged almost perpendicular to the substrate. The field-effect mobility of the thin-film transistor amounts to $0.11 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.

Organic field-effect transistors (OFETs) have recently attracted much attention from the viewpoints of low-cost, largearea electronic applications such as flat-panel displays, electronic paper, and chemical sensors.¹ To date, thin-film OFETs with good performance have been based on thiophene oligomers² and acene molecules like pentacene,³ with the field-effect mobility exceeding $1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. To improve the performance of devices, the amount of π overlap is expected to play an important role. In this respect tetrathiafulvalenes (TTF), which have provided many good conductors and superconductors,⁴ realize much larger bandwidth (typically 1 eV) than pentacene (0.2 eV).⁵ A high mobility OFET $(1.4 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1})$ has been reported by using a single crystal of a TTF derivative⁶ and 0.2 cm²V⁻¹s⁻¹ by using an evaporated film.⁷ However, rigid TTF molecules show too strong aggregation to form microcrystals, so that film formability of these TTF derivatives is usually



Scheme 1.

poor.⁸ The authors have reported that TTF derivatives with flexible alkyl groups and polar cyano groups improve the film formability and affinity to inorganic SiO₂ substrates. One of these TTF derivatives forms a good film on SiO₂ substrates and the field-effect mobility of the OFET is $0.02 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.⁹ Recently phenyl substituted oligothiophene derivatives have been reported to have good thin-film properties and high mobility.¹⁰ We have prepared moderately rigid biphenyl substituted TTF, DBP-TTF (bis(biphenyl)tetrathiafulvalene, Scheme 1) to improve film formability and thin-film properties, and used as an active layer of a field-effect transistor. This paper reports thinfilm properties and OFET characteristics of this compound.

To prepare DBP-TTF, since phosphite-mediated coupling reaction of the 1,3-dithiol-2-one resulted in a low yield,¹¹ coupling reaction of the dithiolium salt using triethylamine was adopted (Scheme 1).¹² The final product was purified by column chromatography (silica gel, CS_2). This molecule was obtained as a mixture of trans and cis isomers with respect to the position of the biphenyl groups. DBP-TTF is a little weaker electron donor than TTF; the first oxidation potential is reported to be higher than that of TTF by 0.09 V.¹²

Figure 1 shows an AFM image of a vacuum-deposited film of DBP-TTF. The thin film has been prepared on a thermally grown SiO₂ substrate (300 nm) made on an n-type Si wafer. We can observe small grains and many grain boundaries. Clear X-ray diffraction peaks corresponding to the *d* spacing of 25 Å are observed as shown in Figure 2. This *d* spacing is almost the same as the length of the molecule with the biphenyl groups in the trans position. This indicates that the DBP-TTF molecules stand almost perpendicular to the SiO₂ substrate.

The FET characteristics were measured on a bottom-contact-type FET on a SiO₂ substrate using photolithographically patterned gold as source and drain electrodes. The channel length (*L*) and width (*W*) were 50 and 300 μ m, respectively. The OFET of DBP-TTF shows p-channel behavior (Figure 3).



Figure 1. AFM image of a vacuum deposited film of DBP-TTF on a room-temperature SiO_2 substrate.



Figure 2. X-ray diffraction pattern of a vacuum-deposited film of DBP-TTF on a room-temperature SiO₂ substrate.



Figure 3. FET characteristics of a vacuum-deposited film of DBP-TTF, grown on a room-temperature SiO₂ substrate. (a) Drain current I_D vs source-drain voltage V_D curves for various source-gate voltages V_G at room temperature. I_D curves at V_G of 100 and 80 V nearly overlap. (b) Drain current I_D vs source-gate voltage V_G curves (transconducrance) at a drain-source voltage V_D of -30 and -100 V.

The field-effect mobility is estimated from the linear regime of the transconductance,

$$g_m = \frac{\partial I_{\rm D}}{\partial V_{\rm G}} \Big|_{V_{\rm D}={\rm const.}} = \frac{W C_{\rm i} \mu}{L} V_{\rm D}$$

by plotting drain current $I_{\rm D}$ vs source-gate voltage $V_{\rm G}$ at a constant low source-drain voltage $V_{\rm D}$.¹³ Thus the field-effect mobi-

lity is obtained to be $0.11 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. This value is comparable to those of oligothiophene thin films. Relatively high positive threshold voltage is observed in the transconductance (Figure 3b), indicating the existence of rich carriers in the active layer under zero gate voltage. This could be either due to the poor quality of the film or due to small work function of the TTF molecule. The drain current, however, drops to small values under high positive gate voltages. The resulting on/off ratio amounts to 10^2 (at $V_{\rm D} = -100 \text{ V}$).

In conclusion, an OFET of DBP-TTF has shown relatively high field-effect mobility. In comparison with simple alkyl substituted BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) molecules,⁸ the present molecule forms much improved films. This demonstrates that the substitution by phenyl or biphenyl groups is a versatile tool to modify molecules for the use of thin film OFET. The present work proves that modified TTFs are, at least, as promising materials as oligothiophenes as active layers of OFET.

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