

## Tetrathiafulvalene-Derivatives-Based Single-Crystal Organic Transistors with Organic Metal Electrodes

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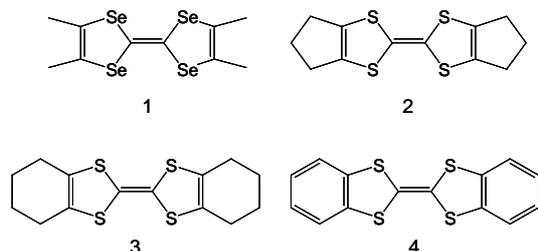
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### 1. Introduction

In recent years, a large number of molecular materials with relatively high carrier mobilities have been reported for the use as channels of organic field-effect transistors (OFETs), which are envisioned as key components of low-cost, large-area, and flexible electronic devices [1]. Attention is being focused on modifications of polycyclic aromatic hydrocarbons like pentacene to realize a high performance and easy processability. Other potential candidates are tetrathiafulvalene (TTF) analogues [2-6], which are well known as electron-donor molecules in organic charge-transfer (CT) complexes. The ability of these compounds to form a wide variety of organic metals and superconductors should permit their use in high-performance, single-component semiconducting materials. In fact, a mobility of about 0.1–1.4 cm<sup>2</sup>/Vs has been reported for some TTF analogues. In this report, we present device characteristics of single crystal OFETs based on four kinds of TTF analogues (TMTSF **1** (tetramethyl-tetrathiafulvalene) [2], HMTTF **2** (Hexamethyl-tetrathiafulvalene) [7], OMTTF **3** (octa methyl-tetrathiafulvalene), and DBTTF **4** (dibenzo-tetrathiafulvalene) [4-6]) as channel semiconducting materials. To achieve the optimum electrical contact with these materials, we used TTF-TCNQ thin-films (TCNQ = tetracyanoquinodimethane) as source/drain electrodes [10]. We discuss the relationship between the device properties and molecular packing in the crystals.

### 2. Experiments

Single crystals were obtained by sublimation in sealed glass tube with 2 ~ 3 mbar nitrogen gas for all the compounds. For HMTTF, single crystals were also obtained by recrystallization in chlorobenzene solution. We chose crystals with sizes larger than 0.5 × 0.2 × 0.2 mm<sup>3</sup> with shiny as-grown surfaces for the device fabrications. We evaporated TTF-TCNQ thin films as source/drain



electrodes on top of crystal surfaces. Sheet resistance of the films is 1 ~ 1.5 kΩ/□ at the thickness of 300 nm. We used Parylene C with thickness of 1 μm ( $C_i = 2.12$  nF/cm<sup>2</sup>) as gate insulator layers. The gate electrodes were fabricated with gold paint on top of the gate dielectric layers.

### 3. Results and discussions

The device properties and molecular packing scheme are summarized in Table 1 for the TTF derivatives. All the devices exhibited p-type feature. The field effect mobility is estimated in linear regime. Figure 1 shows transfer characteristics of single crystal OFETs for TMTSF, OMTTF and DBTTF. The mobility is in the range from 0.01 to 1 cm<sup>2</sup>/Vs. In contrast, the mobility for HMTTF exceeds 10 cm<sup>2</sup>/Vs. Figures 2 shows the transfer characteristics of HMTTF OFETs composed of solution- (broken-line) and vapor-transport (solid-line) grown channel single crystals, in

Table 1 The device properties and molecular packing

compounds	process	$\mu$ (cm <sup>2</sup> /Vs)	on/off	packing
<b>1</b>	sublimation	0.8	6	<i>regular</i>
<b>2</b>	sublimation	11.2	600	<i>brickworks</i>
<b>2</b>	solution	10.4	8	<i>brickworks</i>
<b>3</b>	sublimation	0.05	1000	<i>herringbone</i>
<b>4</b>	sublimation	0.6	300	<i>herringbone</i>

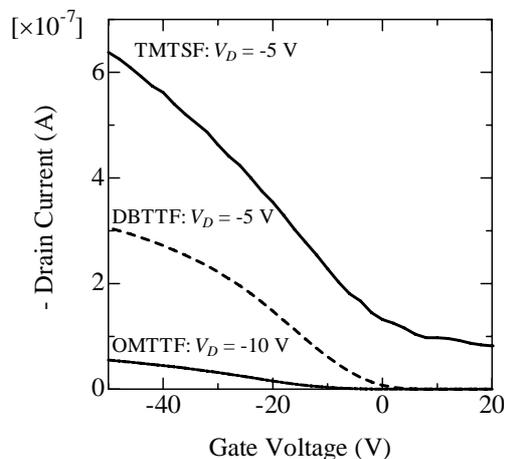


Figure 1 The transfer characteristics of TMTSF, DBTTF, and OMTTF single crystal transistors.

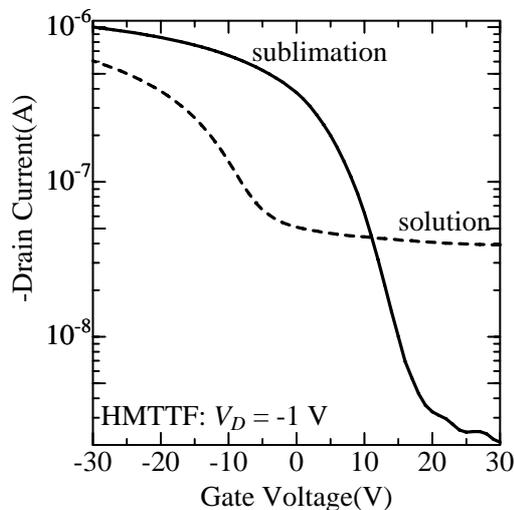


Figure 2 The transfer characteristics of HMTTF single crystal transistors which are fabricated by sublimation process (solid line) and solution process (broken line).

logarithmic scale. In the devices, the field effect mobility in the linear region reached  $11.2 \text{ cm}^2/\text{Vs}$  in vapor-transport grown crystals and  $10.4 \text{ cm}^2/\text{Vs}$  in solution-grown ones. The on/off ratios of the both devices were estimated about 600 and 10 respectively. We also found that the devices keep high performance at atmospheric conditions for several weeks. The mobility of the former device was estimated as  $7 \text{ cm}^2/\text{Vs}$  after two months of fabrication.

The vapor-transport grown and solution-grown crystals are isostructural in HMTTF. The high performance could be attributed to the close *side-by-side* and *brickwork* molecular packing in the crystals. The shortest intermolecular sulfur-sulfur contact is  $3.55 \text{ \AA}$  that affords large  $\pi$ - $\pi$  overlaps. This distance is shorter than twice of van der Waals radii of sulfur ( $\sim 1.8 \text{ \AA}$ ). Extended Hückel molecular orbital calculations [11] allow us to estimate the intermolecular transfer integrals as  $0.1151 \text{ eV}$  (*side-by-side*),  $-0.0113 \text{ eV}$  (*slipped stacks*), and  $0.0176 \text{ eV}$  (*slipped stacks*). These results demonstrate the origin of high performance in HMTTF single crystal OFETs.

In sharp contrast, molecular packings both in OMTTF and DBTTF are *herringbone*-type, where the shortest intermolecular sulfur-sulfur contacts are larger than  $3.8 \text{ \AA}$ . This may be the reason for the lower performance in OFTTF and DBTTF single crystal OFETs. Molecular packing in TMTSF is *regular* arrangement, where the shortest intermolecular sulfur-sulfur contacts is about  $3.8 \text{ \AA}$  [12]. The distance is almost same as twice of van der Waals radii for selenium ( $1.9 \text{ \AA}$ ). However, the performance is not satisfactory, possibly due to the degradation in air.

#### 4. Conclusions

We fabricated single crystal OFETs with four kinds of TTF derivatives, TMTSF, HMTTF, OMTTF, and DBTTF,

as channel semiconductors and TTF-TCNQ molecular conductor films as source/drain electrodes. Among them, HMTTF-based OFETs show high mobility, exceeding  $10 \text{ cm}^2/\text{Vs}$ , both for vapor-transport grown and solution-grown single crystals. In contrast, the mobility of single crystal OFETs based on TMTSF, OMTTF, and DBTTF is limited in the range of  $0.01 - 1 \text{ cm}^2/\text{Vs}$ . We discuss the origin of the different performances in terms of the molecular packing and intermolecular sulfur-sulfur interactions.

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