

## Organic Transistors Based on Octamethylenetetrafulvalenes

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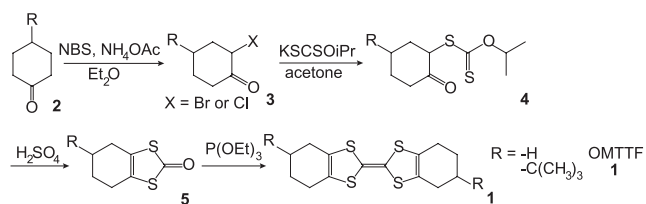
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Organic field-effect transistors (OFET) based on octamethylenetetrafulvalene (OMTTF) and the *t*-butyl derivative are investigated. The parent OMTTF shows poor transistor performance owing to the flat molecular arrangement, but the *t*-butyl substitution realizes standing molecular arrangement and high OFET performance. The tetracyanoquinodimethane (TCNQ) complex of OMTTF exhibits n-channel properties despite the strong donor ability of OMTTF.

Organic field-effect transistors (OFET) have attracted considerable attention for electronic applications such as large-area low-cost integrated circuits and flexible displays.<sup>1</sup> A variety of organic semiconductors have been developed to be used in OFETs,<sup>2</sup> in which field-effect mobility exceeding  $1\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  has been attained in evaporated pentacene films and several solution films,<sup>3</sup> and even more than  $10\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  has been achieved in single crystal devices based on rubrene.<sup>4</sup> Tetrathiafulvalene (TTF) derivatives are well known as excellent donors in charge-transfer complexes,<sup>5</sup> but have been also used as good OFET materials.<sup>6,7</sup> In particular, mobility of hexamethylenetetrafulvalene (HMTTF) has been reported to be more than  $10\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  in a single crystal transistor.<sup>8</sup> We have reported that the HMTTF derivative substituted with *t*-butyl groups show stable high performance ( $\mu = 0.98\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ ) and small threshold voltage  $V_{\text{th}} = -2\text{ V}$  in a thin film transistor.<sup>9</sup> In order to explore steric effects of nonplanar fused rings, in the present paper OFET properties of octamethylenetetrafulvalene (OMTTF, 4,4',5,5',6,6',7,7'-octahydrodibenzotetrafulvalene) with cyclohexane rings (Scheme 1) are investigated together with the *t*-butyl-substituted OMTTF **1**.<sup>10,11</sup>

A mixed-stack dibenzotetrafulvalene (DBTTF) complex of TCNQ shows n-channel properties in single-crystal and thin-film OFETs with (TTF)(TCNQ) source and drain (S/D) electrodes.<sup>12</sup> This has been attributed to the lower HOMO level of DBTTF than that of TTF. Since (HMTTF)(TCNQ) has highly conducting segregate stacks, this compound has been utilized as a S/D material rather than an active layer.<sup>9</sup> By contrast, (OMTTF)(TCNQ) is a mixed-stack insulator,<sup>11a</sup> so we have also investigated the thin-film OFET by using this complex as an active layer.

Although OMTTF was previously prepared from the

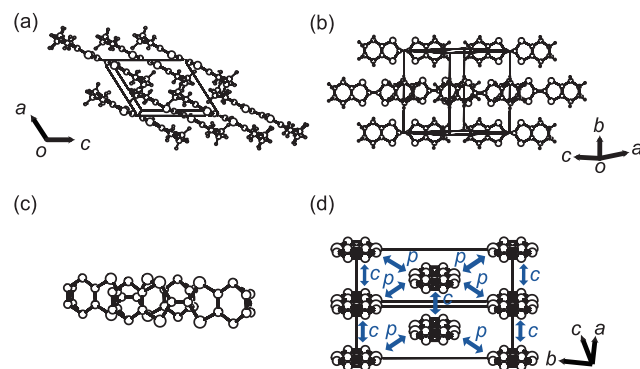
Scheme 1. Synthesis of OMTTF and **1**.

coupling of a 1,3-dithiolium cation,<sup>10</sup> OMTTF and **1** were prepared on a basis of a phosphite-mediated coupling reaction similarly to our previous synthesis of HMTTF derivatives (Scheme 1).<sup>9,13,14</sup> (OMTTF)(TCNQ) was prepared by mixing hot acetonitrile solutions of OMTTF and TCNQ.<sup>15</sup>

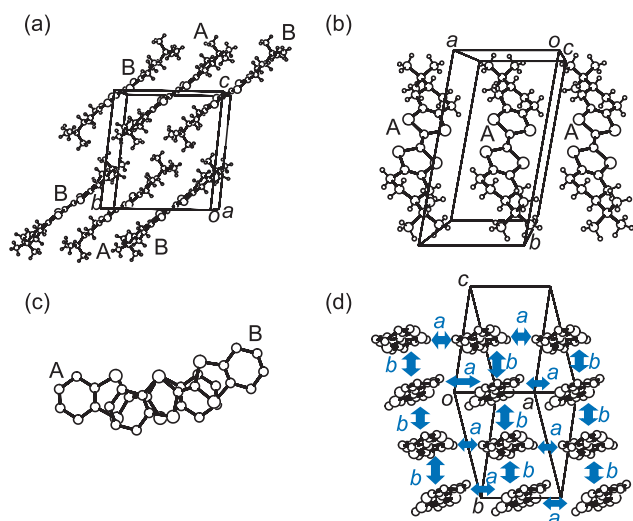
The redox potentials were investigated by cyclic voltammetry.<sup>14</sup> The first redox potentials of OMTTF (0.24 V vs. SCE) and **1** (0.23 V) are approximately the same, and lower than that of TTF (0.34 V), indicating even stronger donor ability than TTF. These results are comparable to 0.25 V of HMTTF.<sup>9</sup>

The molecular and crystal structures of OMTTF and **1** were investigated by X-ray single-crystal structure analysis.<sup>16</sup> OMTTF crystallizes in the space group  $C2/m$ , and the molecule is located on a  $2/m$  position, where a quarter of the molecule is crystallographically independent, and the mirror plane is perpendicular to the molecular plane (Figure 1). The outer carbon atom of the cyclohexane ring is disordered above and below the TTF plane so that the cyclohexane part forms chair conformation. The molecules form a  $C$  centered lattice, constructing a conducting network parallel to the  $bc$  plane. In the stacking along the  $c$  axis, the molecules are slipped by  $6.4\text{ \AA}$  along the molecular long axis in order to avoid the steric hindrance of the cyclohexane part. Consequently, the molecules are largely tilted ( $63^\circ$ ) from normal to the conducting ( $bc$ ) sheet.

The molecule of **1** is located on an inversion center (Figure 2), and there are two kinds of molecules, A and B, in each of which half of the molecule is crystallographically independent. The final coupling reaction potentially produces *cis* and *trans* isomers with respect to the molecular long axis. In addition, the *t*-butyl groups generate potential *R* and *S* optical isomers. Since the molecule is located on an inversion center, the



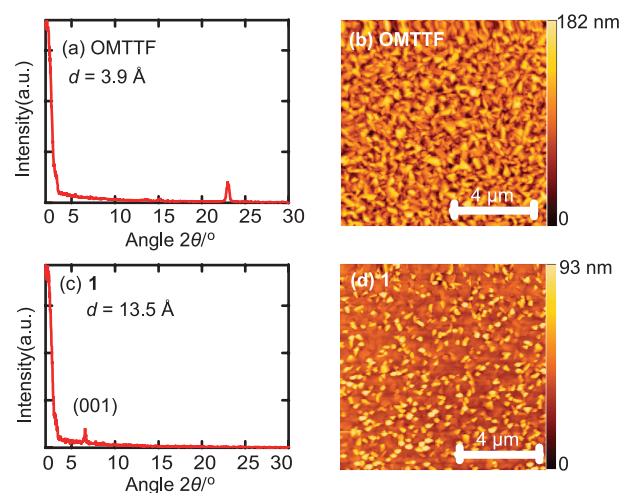
**Figure 1.** Crystal structure of OMTTF, (a) viewed along the  $b$  axis, (b) viewed perpendicular to the molecular plane, (c) overlap mode of OMTTF, and (d) projection along the molecular long axis with the intermolecular overlaps. Shortest S–S contacts are  $p$ :  $3.7\text{ \AA}$ ,  $a$ :  $6.7\text{ \AA}$ , and  $c$ :  $5.4\text{ \AA}$ . Transfer integrals are  $p$ : 34,  $a$ : 2.0, and  $c$ : 14 meV.



**Figure 2.** Crystal structure of **1**, (a) viewed along the *a* axis, (b) viewed along the *c* axis, (c) overlap mode in the stack, and (d) projection along the molecular long axis with the intermolecular overlaps. Short S–S contacts are *a*: 3.9 Å (S1–S2), and *b*: 4.2 Å (S1–S4\*).

crystal contains only a *trans* and *meso* (*RS*) isomer. We have attempted to solve the structure assuming noncentro-symmetric space group *P1*, but have not succeeded in improving the results. Judging from the molecular packing (Figure 2b), the existence of different isomers seems to be impossible. We have obtained a single isomer by recrystallization, and this single isomer is used for further device fabrication. The long axes of molecules A and B are not parallel to each other, where the long axes make an angle of 19°. In general, linear molecules of organic semiconductors are arranged parallel to each other both in stacking and herringbone structures. Even bent oligothiophenes are packed so as to make the linear parts parallel to each other.<sup>17</sup> The present structure is reminiscent of the twisted stacking structure called the  $\delta$ -phase in charge-transfer salts,<sup>18</sup> where the twisted angle is typically 30°. The twisted overlap of the present compound, however, comes from the steric hindrance of the *t*-butyl groups, and the twisted angle is different. In the  $\delta$ -phase, an alternating stack of twisted and parallel overlaps, which has four-molecule periodicity, is more common,<sup>18</sup> but there are examples of “all twisted” stacks with two-molecule periodicity.<sup>19</sup> The present structure is similar to the latter. Accordingly, all intermolecular interactions designated as *b* in Figure 2d are equivalent, making a uniform network parallel to the *ab* plane. The transfer integrals estimated from the molecular orbital calculation (*a*: 23 and *b*: 19 meV) indicate a relatively isotropic two-dimensional conducting sheet. It is also noteworthy that the molecular tilt angle, 47°, from normal to this conducting sheet is smaller than that of OMTTF.

X-ray diffraction (XRD) diagrams of the thin films, vacuum deposited on octyltrichlorosilane (OTS)-treated SiO<sub>2</sub>/Si substrates, show sharp peaks with *d*-spacings of 3.9 Å for OMTTF, and 13.5 Å for **1** (Figures 3a and 3c). The *d*-spacing of **1** is in good agreement with the crystallographic *c* axis. Therefore, molecules are standing perpendicular to the substrate, and the conducting *ab* plane is parallel to the substrate. In contrast, the *d*-spacing of OMTTF corresponds to the interplanar spacing.



**Figure 3.** XRD patterns of (a) OMTTF and (c) **1**, and AFM images of thin-films of (b) OMTTF, and (d) **1** deposited on OTS-treated SiO<sub>2</sub>.

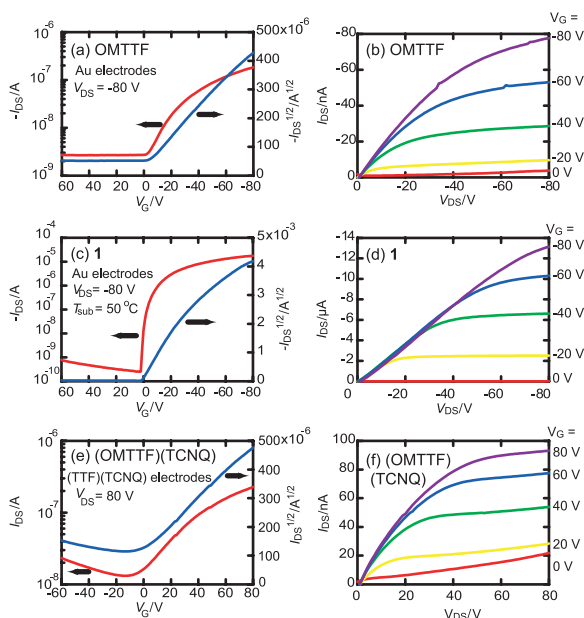
**Table 1.** FET characteristics of OMTTF, **1**, and (OMTTF)(TCNQ)

Compounds Substrate <sup>b</sup>	Electrode <sup>a</sup>	Mobility /cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup>	On/off ratio	<i>V</i> <sub>th</sub> / <i>V</i>
OMTTF <sup>c</sup> rt	Au (TC)	$4.2 \times 10^{-4}$	70	5.4
<b>1</b> <sup>c</sup> rt	Au (TC)	0.020	$4 \times 10^3$	-2.7
	Au (TC)	0.11	$7 \times 10^4$	0.7
(OMTTF)(TCNQ) <sup>d</sup>	Au (TC)	$5.8 \times 10^{-4}$	22	-25
	(TTF)(TCNQ) (BC)	$3.3 \times 10^{-4}$	1	-23

<sup>a</sup>Source and drain electrode materials with top-contact (TC) or bottom-contact (BC) configurations. <sup>b</sup>Substrate temperatures at the time of deposition. <sup>c</sup>p-Type transistor. <sup>d</sup>n-Type transistors.

This may not be surprising because HMTTF is reported to stack parallel to the substrate. As a consequence, however, the most conducting (*bc*) plane is not parallel to the substrate. Atomic force microscopy (AFM) images of the thin films, evaporated on OTS-treated SiO<sub>2</sub>/Si substrates, are shown in Figures 3b and 3d. The thin film of **1** forms as fine domains as 1 μm, and the mean root square roughness is as small as 18 nm. The thin film of OMTTF is composed of similar fine domains.

The transistors are fabricated by vacuum deposition on OTS-treated SiO<sub>2</sub>/Si substrates (Table 1). Several devices are investigated by using Au and (TTF)(TCNQ) S/D electrodes with top-contact (TC) and bottom-contact (BC) configurations. The best performance is recorded for a device on which **1** is deposited at *T*<sub>sub</sub> = 50 °C, showing a field-effect mobility of 0.11 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> (Figures 4c and 4d). Strong donor ability is believed to be disadvantageous in realizing small threshold voltage and long-term device stability, but **1** shows small threshold voltage *V*<sub>th</sub> similarly to *t*-butyl-substituted HMTTF.<sup>9</sup> OMTTF shows lower mobility than **1** by about three orders (Figures 4a and 4b). This is associated with the unfavorable molecular arrangement in the thin film, suggested by XRD. Transistor characteristics of (OMTTF)(TCNQ) thin film are shown in Figures 4e and 4f. Both for Au (TC) and (TTF)(TCNQ) (BC) electrodes, n-channel characteristics are observed (Table 1). It should be noted that these n-channel



**Figure 4.** (a) Transfer and (b) output characteristics of OMTTF, for a device deposited on an OTS-treated SiO<sub>2</sub> substrate with TC Au electrodes. (c) Transfer and (d) output characteristics of **1**, for a device deposited at 50 °C with TC Au electrodes. (e) Transfer and (f) output characteristics of (OMTTF)(TCNQ) thin-film transistor vacuum deposited on an OTS-treated SiO<sub>2</sub> substrate with BC (TTF)(TCNQ) electrodes.

characteristics are stably observed in air. The hole mobility is, if anything, much smaller than the electron mobility. This is surprising because the HOMO level of OMTTF is higher than that of TTF (4.78 eV) (OMTTF is a stronger donor than TTF), and the work function of Au (5.1 eV) is ever larger (deeper) than that of (TTF)(TCNQ) (4.64–4.78 eV).<sup>20</sup> The origin is not certain, but the calculated inter-donor transfers (0.9 meV//*b* and –4.7 meV//*a*) are smaller than the inter-acceptor transfer (8.7 meV//*b*), and the wider TCNQ band may be responsible for the predominately electron-transporting character. This discussion is, however, based on the assumption that the bulk crystal and the thin film have the same structure, but the thin film does not afford clear XRD peaks.

In summary, steric hindrance of nonplanar cyclohexane rings in OMTTF does not improve the OFET performance, but *t*-butyl substitution of OMTTF realizes standing arrangement of the molecules and consequently good OFET performance. The *t*-butyl derivative has characteristic twisted stacks owing to the steric hindrance.

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## References and Notes

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- 16 Crystal data of OMTTF: C<sub>16</sub>H<sub>16</sub>S<sub>4</sub>, monoclinic C2/*m* *a* = 9.622(1), *b* = 11.804(2), *c* = 7.721(1) Å, β = 122.26(1)°, *V* = 741.6(2) Å<sup>3</sup>, *Z* = 2, and *R*<sub>1</sub> = 0.038. Crystal data of **1**: C<sub>22</sub>H<sub>32</sub>S<sub>4</sub>, triclinic *P*1̄ *a* = 6.625(14), *b* = 12.474(3), *c* = 13.655(3) Å, α = 84.56(15)°, β = 84.49(14)°, γ = 79.82(15)°, *V* = 1102.0(2) Å<sup>3</sup>, *Z* = 2, and *R*<sub>1</sub> = 0.096. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-768077 and -768078.
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