doi:10.1246/cl.2012.435
Published on the web April 4, 2012

A Soluble α-Dithienotetrathiafulvalene Derivative for Organic Field-effect Transistors

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Bis(octylthio) derivative of α-dithienotetrathiafulvalene (α-DT-TTF) was synthesized, characterized, and examined as a semiconductor for organic field-effect transistors (OFETs). In contrast to no field-effect responses of devices based on evaporated thin-film of the parent α-DT-TTF, the octylthio derivative afforded solution-processed OFETs showing apparent normally-on behaviors with field-effect mobility of up to $0.6\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$. Characterization of the thin-film revealed that the octylthio groups had significant impact on self-assembly, affording high quality thin films with well-oriented molecular array.

Organic field-effect transistors (OFETs) have been actively investigated in the last decade because of possible use in flexible device applications.[1–3] Among many π systems reported to date, tetrathiafulvalene (TTF) is a promising π-conjugated framework for high-performance p-channel organic semiconductors.[4–8] Dithienotetrathiafulvalene (DT-TTF, Figure 1) is a representative TTF-based semiconductor, and DT-TTF-based OFETs have shown high mobilities up to $3.6\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ with the single-crystal devices and $0.1\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ with thin-film devices.[9,10]

These high performances of DT-TTF have attracted our attention to its isomeric thiophene-fused TTF, α-dithienotetrathiafulvalene (α-DT-TTF, **1**, Figure 1).[11,12] Another interesting feature of **1** is that **1** has vacant α-carbon atoms in the thiophene rings, on which introduction of substituents can be done. Introduction of solubilizing groups, for example, can make new solution-processable materials. In fact, related pyrrole-fused TTF systems can afford soluble organic semiconductors by N-alkylation.[13,14] In this paper, we report the synthesis, properties, and solution-processed OFET characteristics of bis(octylthio)-α-dithienotetrathiafulvalene **2**. By comparing the packing structures of **1** and **2** in the solid state, it turned out that introduction of octylthio groups has significant impact on the molecular ordering, which brings about a suitable molecular array of **2** in the thin film state to an active semiconducting channel.

For the synthesis of **2**, we first attempted direct introduction of octylthio groups on **1**, which was prepared according to a reported procedure by a phosphate-mediated coupling reaction of the corresponding thiophene-fused 1,3-dithiole-2-thione **3**.[15] The initial lithiation of **1** with LDA followed by subsequent reactions with elemental sulfur and 1-iodooctane, however, did not gave **2**, probably owing to poor reactivity of the resulting α-anions of **1**. On the other hand, similar reactions on **3** gave the corresponding octylthio-substituted 1,3-dithiole-2-thione **4** in 56% isolated yield (Scheme 1). After conversion of **4** to corresponding ketone **5**, a phosphite-mediated coupling reaction gave **2** in 36% isolated yield. In sharp contrast to poor solubility of **1**, high solubility in common organic solvents was found for **2** as expected.

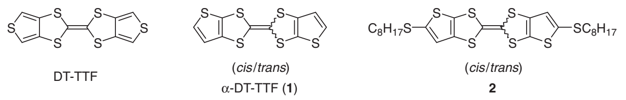
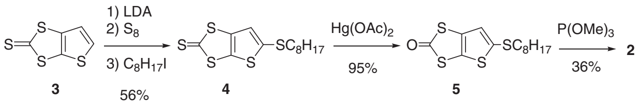


Figure 1. Molecular structures of DT-TTF, α-DT-TTF (**1**), octylthio-substituted α-DT-TTF **2**.

Cyclic voltammograms of **1** and **2** shown in Figure 2 demonstrate clear reversible two-step oxidation processes for both compounds. The oxidation potentials of **1** and **2** are similar to each other, and the onset voltages of the first oxidation waves are almost the same (0.38 V for **1** and 0.39 V for **2** vs. Ag/AgCl, Table S1).[22] The estimated HOMO energy levels are −4.75 V for **1** and −4.76 V for **2**. These experimentally estimated energy levels qualitatively agree with the values calculated by DFT (Figure 3 and Table S2).[16,22] The calculated HOMO densities of **1** and **2** are very similar to each other, and it should be also noted that the HOMO density is high on the sulfur atoms in the TTF core but is negligible on the sulfur atoms in the thiophene rings.

Recrystallization of **1** and **2** from toluene solutions afforded single crystals suitable for single-crystal X-ray analysis (Figure 4).[17] Depending on the mutual direction of two thiophene rings, **1** and **2** can have *cis*- and *trans*-isomers. In



Scheme 1. Synthesis of **2**.

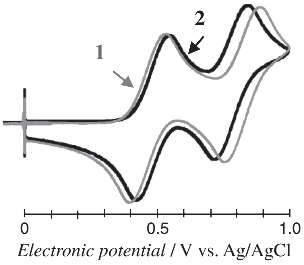


Figure 2. Cyclic voltammograms of **1** (gray line) and **2** (black line) in dichloromethane solutions.

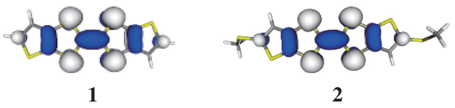


Figure 3. The HOMO coefficients on **1** and **2** (methyl derivative) calculated with DFT method at B3LYP/6-31G(d) level.

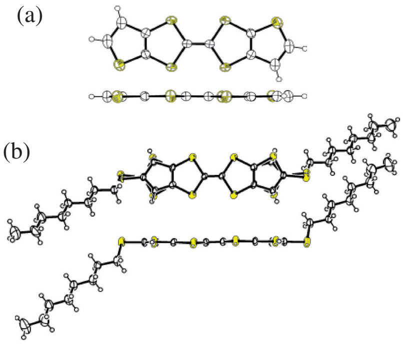


Figure 4. Molecular structures of **1** (a) and **2** (b). Disorder of the thiophene rings is observed for both molecules. Two different structural representations are used: a *trans* only model for **1** and superimposing model of *cis*- and *trans*-forms for **2**.

fact, the crystallographic analyses of **1** and **2** suggested that the position of the sulfur atoms in the thiophene rings are somewhat disordered (ca. 30%). However, it is not clear whether the disorders in the crystallographic analyses were caused by the existence of isomer and/or random orientation in a single isomer. It is interesting to note that octylthio groups in **2** are not significantly disordered, owing to the fact that the relative position of the α-carbon atoms in both isomers is not very different.[18] In addition, since the HOMO density is mainly on the central TTF cores as mentioned above, the intermolecular HOMO interactions should be determined by the TTF cores and not affected significantly by the directional disorder of the thiophene rings.

In sharp contrast to similar molecular structures and the HOMO densities of **1** and **2**, their packing structures are markedly different; **1** forms characteristic trimers that pack in a herringbone manner (Figure 5a), being totally different from the packing structure of DT-TTF,[9] where a two-dimensional (2D) interactive structure is characteristic. Thus, **1** appears to hardly form an effective semiconducting layer in the solid state. On the other hand, the packing structure of **2** can be characterized as an infinite π-stacking structure with side-by-side nonbonded sulfur–sulfur intermolecular contacts (3.46 Å) shorter than the sum of van der Waals radii of sulfur atoms (Figure 5b). In addition, **2** forms a lamella-like layer-by-layer structure along the crystallographic *c* axis direction, where the alkyl layer and the TTF core layer stack alternately, reminiscent of high-performance OFETs based on alkyl-substituted extended π-conjugated systems.[19,20] Comparison of the packing structures of **1** and **2** in the solid state clearly shows that the octylthio groups in **2** act as a self-assembling group that renders **2** packs in the lamella structure, which may be suitable for the OFET channels.

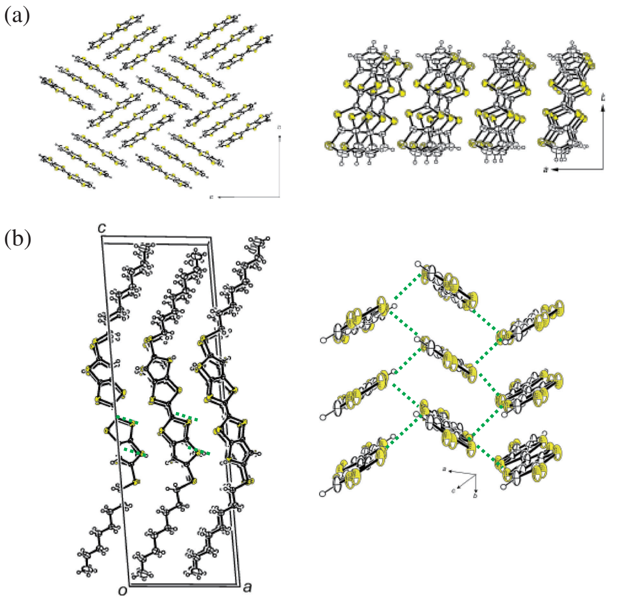


Figure 5. Molecular arrangements in single crystals of **1** (a) and **2** (b). Alkyl moieties are omitted for clarity. Green dash lines show short S–S contacts (3.46 Å).

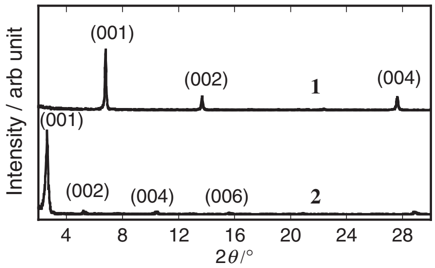


Figure 6. XRD patterns of thin films of **1** (top) and **2** (bottom) on Si/SiO_2 substrates.

Thin films of **2** were readily deposited on Si/SiO_2 substrates by spin-coating a 0.6 wt% toluene solution. X-ray diffraction (XRD) measurements of the **2** thin-film showed a series of peaks assignable to crystallographic (00*l*) reflections, indicating that the thin films are highly crystalline with the same packing structure as in the bulk crystal (Figure 6). The *d*-spacing calculated from the (00*l*) refraction is 34 Å, meaning that the crystallographic *c* axis (34.1 Å) is the preferred orientation on the substrate. On the other hand, thin films of **1** were fabricated by vacuum deposition. Although the film showed sharp XRD peaks with *d*-spacing of 13.0 Å corresponding to the molecular-long axis of **1** (ca. 12.7 Å), the AFM image shows that the surface of the film was quite rough, indicating that the coverage of the surface with **1** was quite poor (Figure S2[22]). Such noncontinuous film should not be suitable for semiconducting a channel in OFETs, and in fact **1**-based OFETs did not work (vide infra).

Fabrication of OFET devices with the top-contact configuration was completed by vacuum deposition of gold source–drain electrodes on top of the thin films. **2**-based OFETs showed normally-on p-channel FET characteristics under ambient conditions (Figure 7). The extracted μ_{FET}'s are up to 0.6 $cm^2 V^{-1} s^{-1}$ and are comparable to those of devices based on DT-TTF fabricated by vacuum-deposition.[21] In addition, the mobility is quite high for solution-processed OTFTs with TTF-based materials. In sharp contrast, **1**-based OFETs showed no field-effect responses at all. These completely different results on **1** and **2** can be understood by the film morphology and the packing structure in the solid states; the former hardly forms effective semiconducting channels in the thin-film state, whereas the latter afforded a 2D semiconducting layer on the substrate (Figure 5b).

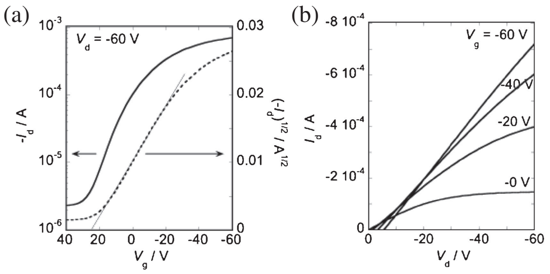


Figure 7. Transfer (a) and output (b) characteristics of **2**-based OFETs measured in air.

Although the mobilities of **2**-based OFETs are fairly high, their high off-current (10^{-6} A) and normally-on behavior are apparent drawbacks for practical applications. These can be explained by the HOMO energy level of **2** (−4.76 eV below the vacuum level determined by the cyclic voltammogram); p-channel semiconductor with such high-lying HOMO energy level can be largely affected by air oxidation. However, OFETs based on p-channel semiconductors with similar HOMO energy levels, e.g., poly(3-hexylthiophene) (P3HT) and pyrrole-fused TTFs, did not show such apparent normally-on behavior with significantly high off-current.[13] To understand the behavior of **2**-based OFETs, we measured the ionization potentials (IPs) of **1** and **2** by photoelectron emission yield spectroscopy (PESA) of the thin films (Figure S5[22]). To our surprise, the IP of **2** thin-film was determined to be ca. 4.3 eV, which is much smaller than the value expected from the cyclic voltammetry. In sharp contrast, the IP of **1** thin-film was determined to be 4.7 eV, which is identical with the value expected from the cyclic voltammetry. Despite the fact that both **1** and **2** have the same π core, such significant difference in the IP in the thin-film state can cause the marked normally-on behavior of **2**-based OFETs. At the moment, such large difference in IP is not clearly explained, but we speculated that strong intermolecular interaction in the solid state causes effective electronic coupling of the frontier orbitals between the neighboring molecules, lowering the effective IP in the thin-film state.

In summary, synthesis, properties, solid-state structures, and FET characteristics of α-DT-TTF (**1**) and its bis(octylthio) derivative **2** were reported. Characterizations of their thin films revealed that the octylthio groups introduced had significant impact on self-assembly bringing about enormous perturbation on its solid-state electronic structures. As a result, fairly high mobility (0.6 $cm^2 V^{-1} s^{-1}$) was obtained from solution-processed **2**-based OFETs, whereas **1** did not act as an active semiconducting material. On the other hand, the strong intermolecular interaction in the solid state may lower the effective IP of **2** thin-films, rendering **2**-based OFETs to be normally-on devices. These results indicate that the long alkyl groups can affect significantly not just self-assembling nature but also solid-state electronic structures.

References and Notes

1 H. Klauk, *Chem. Soc. Rev.* **2010**, *39*, 2643.
2 K. Takimiya, Y. Kunugi, T. Otsubo, *Chem. Lett.* **2007**, *36*, 578.
3 Y. Yamashita, *Chem. Lett.* **2009**, *38*, 870.
4 M. Mas-Torrent, C. Rovira, *Chem. Rev.* **2011**, *111*, 4833.
5 C. Rovira, *Chem. Rev.* **2004**, *104*, 5289.
6 Naraso, J.-i. Nishida, S. Ando, J. Yamaguchi, K. Itaka, H. Koinuma, H. Tada, S. Tokito, Y. Yamashita, *J. Am. Chem. Soc.* **2005**, *127*, 10142.
7 X. Gao, W. Qiu, Y. Liu, G. Yu, D. Zhu, *Pure Appl. Chem.* **2008**, *80*, 2405.
8 M. Kanno, Y. Bando, T. Shirahata, J.-i. Inoue, H. Wada, T. Mori, *J. Mater. Chem.* **2009**, *19*, 6548.
9 M. Mas-Torrent, M. Durkut, P. Hadley, X. Ribas, C. Rovira, *J. Am. Chem. Soc.* **2004**, *126*, 984.
10 M. Leufgen, O. Rost, C. Gould, G. Schmidt, J. Geurts, L. W. Molenkamp, N. S. Oxtoby, M. Mas-Torrent, N. Crivillers, J. Veciana, C. Rovira, *Org. Electron.* **2008**, *9*, 1101.
11 C. Rovira, J. Veciana, N. Santaló, J. Tarrés, J. Cirujeda, E. Molins, J. Llorca, E. Espinosa, *J. Org. Chem.* **1994**, *59*, 3307.
12 E. M. Engler, V. V. Patel, J. R. Andersen, R. R. Schumaker, A. A. Fukushima, *J. Am. Chem. Soc.* **1978**, *100*, 3769.
13 I. Doi, E. Miyazaki, K. Takimiya, Y. Kunugi, *Chem. Mater.* **2007**, *19*, 5230.
14 I. Doi, E. Miyazaki, K. Takimiya, *Chem. Lett.* **2008**, *37*, 1088.
15 T. Jigami, K. Takimiya, T. Otsubo, Y. Aso, *J. Org. Chem.* **1998**, *63*, 8865.
16 MO calculations were carried out with DFT methods at B3LYP/6-31G(d) level using a PC GAMESS program. http://www.msg.ameslab.gov/games/.
17 Crystallographic data for **1** and **2**: **1**: *monoclinic*, $C_{10}H_4S_6$: $Mr = 316.50$, $P2_1/n$ (#14), $a = 6.1828(5)$, $b = 15.456(1)$, $c = 18.617(1)$ Å, $\beta = 95.090(2)°$, $V = 1772.0(2)$ Å^3, $Z = 6$, $R = 0.042$. **2**: *monoclinic*, $C_{26}H_{36}S_8$: $Mr = 605.03$, $P2_1/a$ (#14), $a = 10.326(2)$, $b = 4.2141(2)$, $c = 34.056(2)$ Å, $\beta = 94.81(1)°$, $V = 1476.7$ Å^3, $Z = 2$, $R = 0.086$. See Supporting Information[22] for detail.
18 Similar directional disorder of the thiophene rings with ordered alkyl substituents at the α-positions was observed in 2-hexylthiophene-fused porphyrazine, see: E. Miyazaki, A. Kaku, H. Mori, M. Iwatani, K. Takimiya, *J. Mater. Chem.* **2009**, *19*, 5913.
19 H. Ebata, T. Izawa, E. Miyazaki, K. Takimiya, M. Ikeda, H. Kuwabara, T. Yui, *J. Am. Chem. Soc.* **2007**, *129*, 15732.
20 M. J. Kang, I. Doi, H. Mori, E. Miyazaki, K. Takimiya, M. Ikeda, H. Kuwabara, *Adv. Mater.* **2011**, *23*, 1222.
21 The DT-TTF-based thin-film OFETs with top-contact configuration fabricated on HMDS-treated Si/SiO_2 substrates by vacuum deposition showed mobilities up to 0.3 $cm^2 V^{-1} s^{-1}$. See Supporting Information.[22]
22 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.