# Organic Field-effect Transistors Based on Solution-processible Dibenzotetrathiafulvalene Derivatives

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Organic field-effect transistors based on alkyl-substituted dibenzotetrathiafulvalenes (DBTTF) are fabricated by solution process. The molecules with butyl or longer alkyl groups are standing perpendicular to the substrates in the thin films, and the transistors exhibit comparable performance to the vacuum-deposited DBTTF devices.

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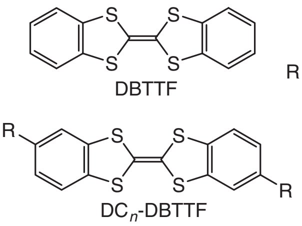
Solution-processible organic semiconductors have been attracting considerable interest due to their potential applications to organic field-effect transistors (OFETs). Although solution-processed OFETs have generally offered lower performance than the vacuum-deposited counterparts, recent investigations have attained high mobilities exceeding 1.0 $cm^2 V^{-1} s^{-1}$ by using functionalized pentacenes and benzothiophene derivatives.[1,2] Considerably high mobilities reaching 0.1–0.6 $cm^2 V^{-1} s^{-1}$ have been realized in poly(3-hexylthiophene) (P3HT) derivatives as well.[3] Tetrathiafulvalene (TTF) derivatives also afford high-performance OFETs exceeding 1.0 $cm^2 V^{-1} s^{-1}$ in solution-processed crystals[4] and in the range of 0.1–0.4 $cm^2 V^{-1} s^{-1}$ by vacuum-deposited thin films.[5] However, solution-processed thin-film OFETs of TTF derivatives still usually remain in the order of $10^{-2}$ $cm^2 V^{-1} s^{-1}$.[6] Among them, dibenzo-TTF (DBTTF) is a representative material,[5b,5d] but the solubility is very low. Here we report alkyl-substituted DBTTFs ($DC_n$-DBTTF, Chart 1) with improved solubility. The OFETs fabricated by spin coating attain 0.11 $cm^2 V^{-1} s^{-1}$, that is almost comparable to 0.19 $cm^2 V^{-1} s^{-1}$ of the vacuum-deposited DBTTF.[5d]

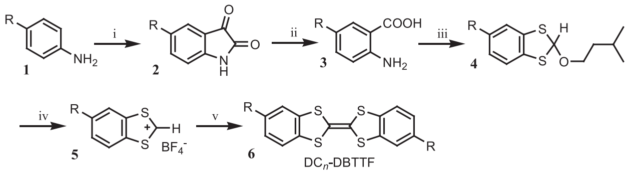
A series of $DC_n$-DBTTFs were synthesized similarly to DBTTF from the corresponding anthranilic acid (**3** in Scheme 1)[7–9] and purified by recrystallization and/or sublimation. The oxidation potentials, 0.55 and 0.97 V for $DC_8$-DBTTF,[9] were slightly smaller than 0.59 and 1.01 V of DBTTF, reflecting the enhanced donor ability owing to the electron-donating alkyl substitution.

The molecular and crystal structures of $DC_1$-DBTTF were investigated by X-ray single-crystal structure analysis (Figure 1).[10] The preparation gives potentially cis and trans forms with respect to the alkyl groups, whereas only the cis form is found. The molecular arrangement is a kind of modified herringbone packing, where the molecules are shifted along the molecular long axis from the basic herringbone pattern.[11]



| R = | |
|---|---|
| $C_2H_5$ | $DC_2$-DBTTF |
| $C_3H_7$ | $DC_3$-DBTTF |
| $C_4H_9$ | $DC_4$-DBTTF |
| $C_6H_{13}$ | $DC_6$-DBTTF |
| $C_8H_{17}$ | $DC_8$-DBTTF |
| $C_{12}H_{25}$ | $DC_{12}$-DBTTF |

**Chart 1.**



**Scheme 1.** Synthesis of $DC_n$-DBTTF. i: 1) chlorale hydrate, hydroxylamine hydrochloride, HCl, $Na_2SO_4$, 2) $H_2SO_4$, ii: NaOH, $H_2O_2$, iii: 3-methylbutylnitrite, 3-methylbutanol, $CS_2$, iv: $HBF_4$, v: $Et_3N$.

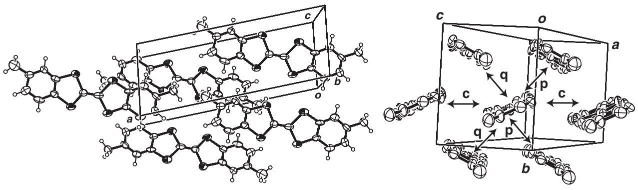


**Figure 1.** Crystal structure of $DC_1$-DBTTF.

Compounds with $n \leq 2$ can be vacuum deposited on hexamethylenedisilazane (HMDS)-treated $Si/SiO_2$ substrates, whereas the $n \geq 2$ compounds are spin coated from the chloroform solutions. The X-ray diffraction (XRD) measurements of the thin films show sharp peaks (Figure 2a), and the evaluated *d* spacings are listed in Table 1. When $n \leq 3$, the observed *d* spacings are considerably shorter than the expected molecular lengths *l*, suggesting tilted or modified layer structures as found in the $DC_1$-DBTTF crystal. For $n \geq 4$, however, the observed *d* spacings are nearly equal to the molecular lengths, indicating that the molecules are standing perpendicular to the substrates.

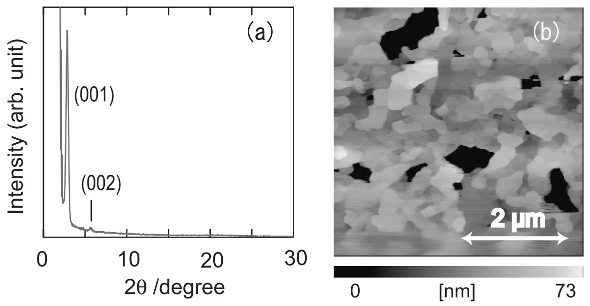


**Figure 2.** (a) X-ray diffraction diagram and (b) AFM image of $DC_8$-DBTTF thin film, spin coated on an HMDS-treated $SiO_2$ substrate, after 80 °C annealing.

**Table 1.** FET characteristics of $DC_n$-DBTTF transistors, with $d$ spacings and the expected molecular lengths ($l$)

| Compounds[a] | | Mobility $/cm^2\,V^{-1}\,s^{-1}$ | On/off ratio | $d$/Å | $l$/Å |
|---|---|---|---|---|---|
| DBTTF | v | 0.17 | $9.2 \times 10^4$ | 13.5 | 13.5 |
| $DC_1$-DBTTF | v | $6.4 \times 10^{-5}$ | 64 | 12.9 | 13.7 |
| $DC_2$-DBTTF | v | 0.079 | $7.4 \times 10^2$ | 14.2 | |
| | s | 0.014 | $1.2 \times 10^2$ | 14.6 | 17.2 |
| $DC_3$-DBTTF | s | 0.013 | $6.2 \times 10^3$ | 13.5, 17.2 | 19.6 |
| $DC_4$-DBTTF | s | 0.054 | $1.4 \times 10^2$ | 22.3 | 22.4 |
| $DC_6$-DBTTF | s | 0.054 | $7.4 \times 10^2$ | 26.7 | 27.2 |
| $DC_8$-DBTTF | s | 0.081 | $1.0 \times 10^3$ | 31.0 | 32.2 |
| $T_{sub}$ 80 °C | s | 0.11 | $3.4 \times 10^4$ | 31.4 | |
| $DC_{12}$-DBTTF | s | 0.0015 | 48 | — | |

[a]s: spin coat, v: vacuum deposition.

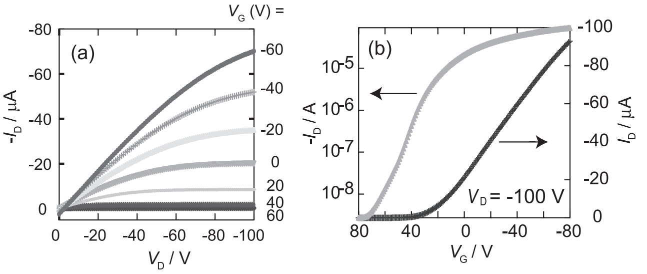


**Figure 3.** (a) Output and (b) transfer characteristics of a $DC_8$-DBTTF transistor after annealing.

The $n = 3$ compound is the boundary, where two independent peaks appear in the thin-film XRD (Table 1). Sharp XRD peaks are obvious in the large $n$ compounds, and at the same time the domain structure, observed by AFM, becomes large (Figure 2b). Significant improvement of the film morphology is observed by increasing the alkyl chain length. Accordingly, the alkyl chains with $n \geq 4$ improve not only the solubility but also molecular packing. Solubility of the $n = 8$ compound is as large as 20 mg in 1 mL of chloroform, but the $n = 12$ compound exhibits reduced solubility (2 mg/1 mL) and relatively poor thin-film quality.

Gold source and drain electrodes were vapor-deposited on the top of the thin films through a shadow mask, and the OFET characteristics were measured in air (Table 1). All compounds exhibit p-channel properties, and the field-effect mobility increases with increasing $n$, but the $n = 12$ compound shows reduced performance on account of the reduced solubility. The best results are obtained for $n = 8$. When the device is annealed at 80 °C for 1 h, the film quality is further improved (Figure 2), and the mobility increases to $0.11\,cm^2\,V^{-1}\,s^{-1}$ (Figure 3), which is comparable to $0.19\,cm^2\,V^{-1}\,s^{-1}$ of the vacuum-deposited DBTTF.[5d] As-grown films of these compounds tend to give relatively large threshold voltages, but it is improved by annealing.

In conclusion, alkyl-substituted DBTTF shows improved solubility and excellent quality of the spin-coated thin films, and the solution-processed OFETs realize comparable performance to the vacuum-deposited DBTTF OFETs.

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9 Supporting Information is available electrically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

10 Crystal data of $DC_1$-DBTTF: $C_{16}H_{12}S_4$, monoclinic $P2_1$, $a = 16.467(6)$, $b = 7.533(4)$, $c = 6.080(2)$ Å, $\beta = 98.81(3)°$, $V = 745.3(5)$ Å$^3$, $Z = 2$, and $R_1 = 0.045$. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-714681.

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