Recent Development of New Organic Semiconductors for Thin-Film Transistor Applications

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1. Introduction

Organic field-effect transistors (OFETs) have attracted current attention because of their promising applications to flexible, large-area electronics devices such as bendable display, electronic paper, or ID tag [1]. As our strong interests in molecular electronics materials from synthetic organic chemistry, we have been engaged in the design and synthesis of new organic semiconductors. In particular, we have been developing new organic semiconductors employing chalcogenophene-fused aromatic substructures. Our idea behind this strategy is that heavy chalcogen atoms such as sulfur and selenium having larger atomic radius and higher polarizability can contribute to intermolecular interaction enabling effective intermolecular orbital overlap in the solid state that is highly desirable for effective carrier transport [2-5]. Among novel organic semiconductors in the early stage of our materials development, the most remarkable one was DPh-BTBT showing $\mu_{\text{FET}} \approx 2.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ under ambient conditions. Furthermore, its superior device characteristics were preserved for long period of time (~250 days) without significant changes [5]. With the superior characteristics of DPh-BTBT as p-channel OFET material, molecular modification on the BTBT core seems to be a promising approach to develop new organic semiconductors. We have thus investigated its alkylated analogue, alkyl-BTBTs (C$_n$-BTBTs), and highly $\pi$-extended analogue, DNTT (Fig. 1).

Fig. 1. BTBT and DNTT-based new organic semiconductors.

2. Results and Discussions

$C_n$-BTBTs: Highly Soluble Molecular Semiconductors

A series of $C_n$-BTBT (Fig. 1), in which two solubilizing long alkyl groups are introduced in the molecular $\text{long-axis}$ direction, were readily synthesized via a two-step reaction, namely, Friedel-Crafts acylation and Wolff-Kishner reduction, using the parent BTBT as starting material, or via the palladium-catalyzed Sonogashira coupling of 2,7-diiodo-BTBT with 1-alkynes, followed by catalytic hydrogenation. As expected, C$_n$-BTBTs are highly soluble in common organic solvents.

Homogeneous thin films were deposited on a Si/SiO$_2$ substrate by spin coating using a 0.4 wt% solution of C$_n$-BTBT in chloroform. The spin-coated thin films were highly crystalline as evidenced by X-ray diffraction (XRD) measurements, where a series of peaks assignable to (00$l$) reflections were clearly observed. Gold source and drain electrodes (80 nm) were vapor-deposited on top of the thin films through a shadow mask to complete fabrication of OFET devices with channel length ($L$) and width ($D$) of 50 $\mu$m and 1.5 mm, respectively. Regardless of the length of the alkyl groups, thin films of C$_n$-BTBT derivatives acted as a superior semiconducting channel (Fig. 2), and $\mu_{\text{FET}}$ of the devices was higher than $10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Although no pronounced dependence of $\mu_{\text{FET}}$ on alkyl chain length was observed, C$_n$-BTBT with alkyl groups longer than the decyl (C$_{10}$H$_{21}$) group tended to show higher mobility than derivatives with shorter alkyl groups. It should be noted that the mobility of $2.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is one of the best reported so far among solution-processed OFETs [6].

Fig. 2. FET characteristics of C$_{12}$-BTBT-based OFET: output characteristics (left) and transfer characteristics at $V_D = -60 \text{ V}$ (right).

DNTT: A candidate for Post-pentacene as organic semiconductors

We then focused on a further $\pi$-extended thienoacene molecule with six fused aromatic rings, DNTT (Fig. 1). From the viewpoint of the synthetic organic chemistry, the synthesis of such highly $\pi$-extended molecules is a challenging task. After intensive efforts to find its synthesis method, we finally found a straightforward synthetic route that starts from commercially available 2-naphthaldehyde...
via only three-step reactions. DNTT is a stable crystalline compound that easily purified by vacuum sublimation.

OFET studies were carried out using top-contact device configuration with W/L = ca. 30, which were fabricated by vacuum deposition on Si/SiO₂ substrates whose surfaces were treated with hexamethyldisilazane (HMDS), octyltrichlorosilane (C₈-OTS), or octadecyltrichlorosilane (C₁₈-OTS). All the devices fabricated under various conditions showed typical p-channel FET characteristics with \( \mu_{\text{FET}} \) higher than 0.7 cm² V⁻¹ s⁻¹ under ambient conditions. In particular, excellent FET characteristics with \( \mu_{\text{FET}} \) higher than 2.0 cm² V⁻¹ s⁻¹ and \( I_{\text{on}}/I_{\text{off}} \) of 10⁶ were observed in DNTT-based devices fabricated on the C₈-OTS- or C₁₈-OTS-treated substrates [7].

Alkylated DNTTs: New High Performance Organic Semiconductor with Very High Mobility

As we discussed in the previous sections, we have demonstrated several important design strategies for superior organic semiconductors; (1) the BTBT-based materials are useful platforms for air-stable organic semiconductors, (2) introduction of long alkyl groups in the molecular long axis direction can serve not only as the solubilizing group but also self-assembling group that enables to construct excellent semiconducting channels in the thin film state, and (3) a largely \( \pi \)-extended core such as DNTT can afford much higher \( \mu_{\text{FET}} \) than those of the BTBT-based semiconductors. With these strategies, we have then planned to develop alkylated DNTT (Cₙ-DNTT, Fig. 1), expecting that much better organic semiconducting materials can be realized.

The syntheses of Cₙ-DNTT were achieved by applying the same synthetic methodology for the parent DNTT using alkylated naphthaldehydes as the starting materials. Contrary to our expectations, C₉-DNTTs were poorly soluble in various organic solvents at room temperature, and thus fabrication of their thin films was done by vacuum deposition to evaluate their potentials as organic semiconducting materials. The vapor-processed OFETs in fact showed very high \( \mu_{\text{FET}} \) (~ 4 cm² V⁻¹ s⁻¹) regardless the alkyl chain length. Among the derivatives, we picked didecyl-DNTT (C₁₀-DNTT) up for further device optimization by changing the deposition rate, surface treatments of the substrates, and the channel lengths (L). As a result, optimized C₁₀-DNTT-devices showed very high \( \mu_{\text{FET}} \) up to 8 cm² V⁻¹ s⁻¹, which is among the highest for OFETs based on thin film active layer consisting of multi-crystalline grains [8]. Furthermore, Takeya et al. developed a sophisticated solution-deposition technique that enables to fabricate directly single-crystalline thin films of C₁₀-DNTT on the substrates. The resulting devices gave excellent performances with mobility of up to 12 cm² V⁻¹ s⁻¹. It should be also noted that this methods allow fabricating patterned OFET arrays not only on the Si/SiO₂ substrates but also flexible plastic substrates [9].

Considering the stability, performances of the devices, and easy accessibility (synthetic easiness), we believe that DNTT can be a potential candidate for a “post-pentacene” material, a vapor-processable organic semiconductor of the next generation. On the other hand, C₉-BTBTs are highly soluble organic semiconductors that give solution-processable OFET devices with the highest mobility so far attained among solution-deposited OFETs. This means that conventional conjugated polymers are not only the choice for developing superior solution-processed OFETs; properly designed small \( \pi \)-extended molecules with solubilizing groups are also very intriguing. Furthermore, recent developments both in materials and processes have demonstrated that the OFETs are really promising techniques enabling printed FETs with mobility exceeding 10 cm² V⁻¹ s⁻¹. With these new materials and processes, further applications of OFETs in various devices are expected.

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References


Appendix

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