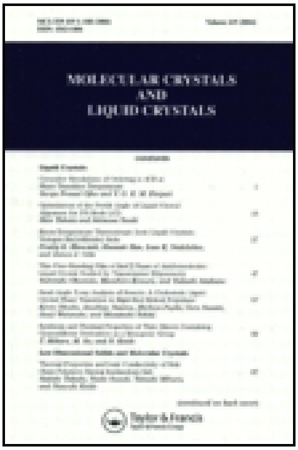

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Organic Field-Effect Transistors Based on 2,6-Diphenylbenzo[1,2-b:5,4-b′]-Dithiophene and -Diselenophene (iso-DPh-BDXs)

Kazuo Takimiya [a], Yasushi Konda [a], Hideaki Ebata [a], Tetsuo Otsubo [a] & Yoshihito Kunugi [b]
[a] Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Kagamiyama, Higashi-Hiroshima, Japan
[b] Department of Applied Chemistry, Tokai University, Kitakaname, Hiratsuka, Japan

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Organic Field-Effect Transistors Based on 2,6-Diphenylbenzo [1,2-*b*:5,4-*b*′]-Dithiophene and -Diselenophene (*iso*-DPh-BDXs)

Kazuo Takimiya
Yasushi Konda
Hideaki Ebata
Tetsuo Otsubo
Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Kagamiyama, Higashi-Hiroshima, Japan

Yoshihito Kunugi
Department of Applied Chemistry, Tokai University, Kitakaname, Hiratsuka, Japan

The title heteroaromatic compounds were prepared as novel organic semiconductors, and field-effect transistors possessing them as an active layer were fabricated and evaluated.

Keywords: chalcogen atoms; fused aromatic molecules; organic field-effect transistors; organic semiconductors

INTRODUCTION

Organic field-effect transistors (OFETs) are regarded as promising alternatives in terms of the fabrication of low cost, flexible, printing circuits to amorphous silicons in modern semiconductor technology [1]. One of the main issues for marketing OFETs is to enhance field-effect mobility (μ_{FET}), and in this regard, recent research efforts have achieved impressive improvements of OFET performances, e.g., realization of high-μ OFET based on pentacene ($\mu_{\mathrm{FET}} = \sim 1.5\,\mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$

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Address correspondence to Kazuo Takimiya, Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Kagamiyama 1-4-1, Higashi-Hiroshima 739-857, Japan. E-mail: ktakimi@hiroshima-u.ac.jp

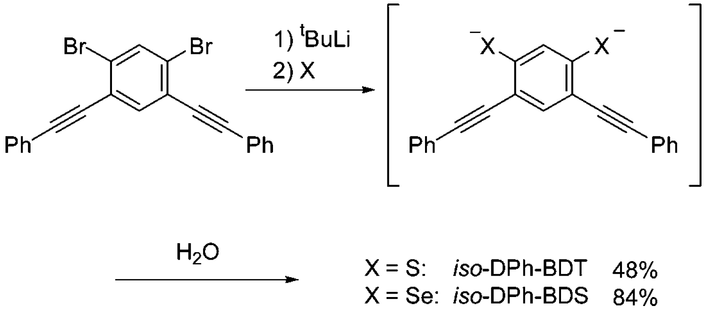
and development of new OFET materials with high mobility ($\mu_{\mathrm{FET}} > 0.1\,\mathrm{cm}^2\,\mathrm{V}^{-1}\mathrm{s}^{-1}$) [2].

We have been engaged in developing new high-performance organic semiconductors for OFETs, focusing our attention on novel rodlike heteroaromatic compounds suitable for charge migration [3], and recently found that 2,6-diphenylbenzo[1,2-*b*:4,5-*b*′]dichalcogenophenes (abbreviated as DPh-BDX) show high mobilities $\mu_{\mathrm{FET}} = {\sim}0.2\,\mathrm{cm}^2\,\mathrm{V}^{-1}\mathrm{s}^{-1}$ [4]. From the molecular structural point of view, we are further interested in 2,6-diphenylbenzo[1,2-*b*:5,4-*b*′]dichalcogenophenes (*iso*-DPh-BDX) with non-centrosymmetric C_{2v} symmetry, which are structural isomers of the C_{2h} symmetrical DPh-BDX. A comparison of both DPh-BDX types of compounds as active layers of OFET devices might allow us to evaluate the symmetry effects of isomeric molecules on the OFET characteristics. In this paper we report on the synthesis and FET characteristics of two new compounds, *iso*-DPh-BDT (X = S) and *iso*-DPh-BDS (X = Se) (Figure 1).

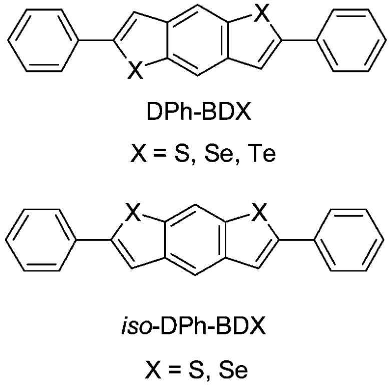
RESULTS AND DISCUSSION

Synthesis

The synthesis of *iso*-DPh-BDX was carried out as shown in Scheme 1, featuring the simultaneous one-pot annelation of two chalcogenophene rings on the central benzene ring [5]. Thus, 1,5-dibromo-2,4-bis(phenylethynyl)benzene prepared from 1,3-dibromobenzene according to the protocol reported by Tour and co-workers [6] was treated with t-BuLi followed by a reaction with elemental sulfur or selenium to give the *iso*-DPh-BDX as a yellow solid after aqueous workup. Both *iso*-DPh-BDT and *iso*-DPh-BDSc were purified by vacuum sublimation and were stable without decomposition until 300°C.



SCHEME 1 Synthesis of *iso*-DPh-BDXs.


DPh-BDX

X = S, Se, Te

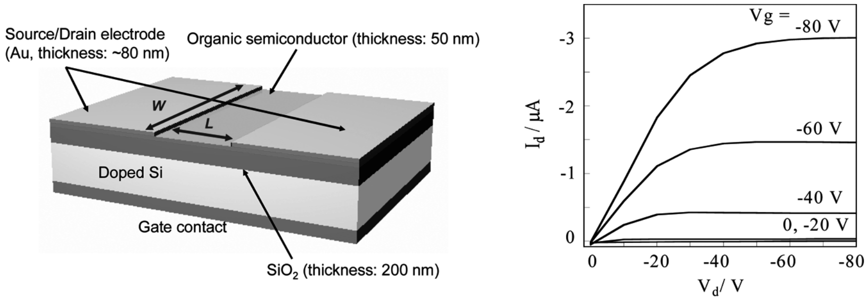
iso-DPh-BDX

X = S, Se

FIGURE 1 Molecular structures of DPh-BDX and *iso*-DPh-BDX.

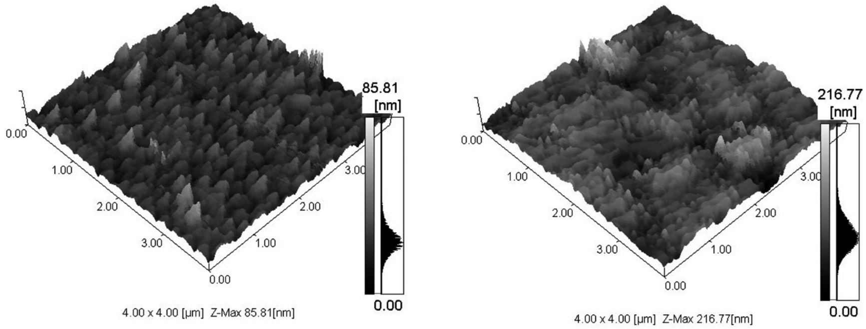
Device Fabrication and Evaluation

OFET devices based on *iso*-DPh-BDXs were fabricated on an *n*-doped SiO_2/Si substrate in a top-contact manner (Fig. 2a). During vacuum deposition of the organic layer, the SiO_2/Si substrate was maintained at rt, 60°C, and 100°C to investigate the substrate temperature (T_{sub}) dependence of film quality and OFET characteristics. The *iso*-DPh-BDT OFET fabricated at $T_{sub} = \text{rt}$ showed a typical *p*-channel FET response as shown in Figure 2b with $\mu_{FET} = 4.2 \times 10^{-4}\,cm^2V^{-1}s^{-1}$. The mobility of *iso*-DPh-BDT-based OFET gradually enhanced with raising the T_{sub}: at $T_{sub} = 60°C$, $\mu_{FET} = 8.1 \times 10^{-4}\,cm^2V^{-1}s^{-1}$ and at $T_{sub} = 100°C$, $\mu_{FET} = 3 \times 10^{-3}\,cm^2V^{-1}s^{-1}$, which is, however, still about



(a) (b)

FIGURE 2 A schematic picture of OFET device; $L = 50\,\mu m$, $W = 1.5\,mm$ (a), and $V_d - I_d$ plot of *iso*-DPh-BDT-based OFET fabricated at $T_{sub} = 100°C$ (b).



(a) (b)

FIGURE 3 AFM images of evaporated thin films of *iso*-DPh-BDS: $T_{sub} = \text{rt}$ (a), and $T_{sub} = 60°\text{C}$ (b).

thirty times lower than the C_{2h} isomer, DPh-BDT ($0.08\,\text{cm}^2\text{V}^{-1}\text{s}^{-1}$). On the other hand, the *iso*-DPh-BDS-based OFET device fabricated at $T_{sub} = \text{rt}$ showed a better μ_{FET}, $0.02\,\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ than that of *iso*-DPh-BDT-based OFETs, indicating that the large selenium atoms contribute to enhance the mobility. This value is almost comparable to that of the DPh-BDS-based OFET fabricated at $T_{sub} = \text{rt}$ ($0.02\,\text{cm}^2\text{V}^{-1}\text{s}^{-1}$). In contrast to the case of the *iso*-DPh-BDT-based OFET devices, the *iso*-DPh-BDS-based OFET devices fabricated at elevated T_{sub} failed to show OFET responses.

The *iso*-DPh-BDS thin film deposited at $T_{sub} = \text{rt}$ has a metallic luster with a specular surface, whereas the thin films deposited at $T_{sub} = 60°\text{C}$ and 100°C are nonluminous and looked pale gray in color. Their AFM images indicated that the different appearances of these thin-films arose from their different microscopic morphologies (Fig. 3). The film deposited at rt consists of small crystal grains of a similar size ($\sim 0.2\,\mu\text{m}$ in diameter) without significant height difference ($\sim 85\,\text{nm}$). In contrast, the AFM image of the film deposited at 60°C shows a larger height difference than 200 nm, though the grain size is not significantly different from the former one. This indicates that the continuous aggregation is not formed in the latter film, and inter-grain charge migration hardly takes place in the non-continuous film.

CONCLUSION

We have successfully synthesized *iso*-DPh-BDT and *iso*-DPh-BDS as new organic semiconductors and fabricated their OFET devices.

Both compounds act as a *p*-channel organic semiconductors with moderate carrier mobility. The OFET device based on sulfur homologue, *iso*-DPh-BDT, showed enhanced mobility depending on elevation of T_{sub}, and the highest mobility, $\mu_{\mathrm{FET}} = 3 \times 10^{-3}\,\mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$, was recorded at $T_{sub} = 100^{\circ}\mathrm{C}$. In contrast, the *iso*-DPh-BDS-based device acted as a better FET with $\mu_{\mathrm{FET}} = 0.02\,\mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$, when fabricated at $T_{sub} = \mathrm{rt}$, but no FET response was observed from OFET fabricated at $T_{sub} = 60$ and $100^{\circ}\mathrm{C}$. Compared to the OFET devices based on the preceding $\mathrm{C_{2h}}$ isomers, the OFETs based on the present $\mathrm{C_{2v}}$ isomers are inferior in FET characteristics both for the sulfur and selenium series. It is speculated that the non-centrosymmetric molecular structure of *iso*-DPh-BDX is not suitable for formation of high quality thin-films, which is critical for high-performance OFET devices.

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[5] Synthesis of *iso*-DPh-BDT: To a solution of 1,5-dibromo-2,4-bis(phenylethynyl)benzene [6] (0.5 g, 1.1 mmol) in THF (15 mL) at $-78^{\circ}\mathrm{C}$ was added a pentane solution of t-BuLi (1.45 M, 4.6 mL, 6.6 mmol). The resulting mixture was stirred at the same temperature for 15 min, and then gradually warmed to room temperature. Elemental sulfur (70 mg, 2.2 mmol) was then added in one portion, and the mixture was stirred for 15 min. Addition of water (40 mL) precipitated a yellow solid, which was collected by filtration, washed successively with hexane, and chloroform, and dried (0.18 g, 48%). The crude product was purified by vacuum sublimation (source temperature: $270^{\circ}\mathrm{C}/10^{-3}\,\mathrm{Pa}$) before device preparation. mp > 300°C; MS (EI) m/z 342 (M^+). Anal. Calcd for $\mathrm{C_{22}H_{14}S_2}$: C, 77.15; H, 4.12. Found: C, 77.10; H, 4.18. *iso*-DPh-BDS was synthesized in a similar way; a yellow solid; 84% yield. mp > 300°C; MS (EI) m/z 438 (M^+). Anal. Calcd. for $\mathrm{C_{22}H_{14}Se_2}$: C, 60.57; H, 3.23. Found: C, 60.58; H, 3.25. *iso*-DPh-BDS was further purified by vacuum sublimation (source temperature: $280^{\circ}\mathrm{C}/10^{-3}\,\mathrm{Pa}$) for device preparation.

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