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2,7-Diphenyl[1]benzothieno[3,2-*b*]benzothiophene, A New Organic Semiconductor for Air-Stable Organic Field-Effect Transistors with Mobilities up to 2.0 cm^2 V^{-1} s^{-1}

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Organic field-effect transistors (OFETs) have generated great interest in the past decade because of their technological potential as a cheap alternative for the current amorphous silicon-based thin-film transistors (TFTs).[1] Whereas the primary issue facing OFETs for practical applications is the enhancement of field-effect mobility ($\mu_{\rm FET}$), recent intensive research efforts both in the development of new organic semiconductors and in the optimization of device fabrication techniques have improved the $\mu_{\rm FET}$ of OFETs to a level that is almost comparable to those of amorphous silicon-based TFTs.[2] Impressive high performances ($\mu_{\rm FET} \sim 20$ cm^2 V^{-1} s^{-1}) of OFETs fabricated on single crystals have been reported,[2f,g] but such devices are of almost no use in practical applications. In contrast, the $\mu_{\rm FET}$ of thin-film-based OFETs having many potential applications is still lower by 1 or 2 orders of magnitude than that of OFETs fabricated on single crystals. In fact, there are only a limited number of organic semiconductors capable of generating $\mu_{\rm FET}$ higher than 1.0 cm^2 V^{-1} s^{-1} in a TFT setting.[2a−e] In addition, the stability of OFETs under ambient conditions has become increasingly important, and stable *p*-channel organic semiconductors have been recently developed.[3] However, the $\mu_{\rm FET}$ of such stable semiconductors is still lower than 1.0 cm^2 V^{-1} s^{-1}.

In our search for superior semiconductors for OFETs, we have focused our attention on fused chalcogenophene compounds and successfully developed a series of high-performance organic semiconductors.[4] Among the materials we developed, two selenium-containing compounds, 2,6-diphenylbenzo[1,2-*b*:4,5-*b*′]diselenophene (DPh-BDS, $\mu_{\rm FET} = \sim 0.2$ cm^2 V^{-1} s^{-1})[4a] and 2,7-diphenyl[1]benzoselenopheno[3,2-*b*][1]benzoselenophene (DPh-BSBS, $\mu_{\rm FET} = \sim 0.3$ cm^2 V^{-1} s^{-1}),[4d] have proven the utility of fused chalcogenophene compounds as high-performance OFET materials. It should be noted that DPh-BSBS-based OFETs showed high stability both in the shelf lifetime test and in the operation lifetime test in air, indicating that DPh-BSBS is a valuable OFET material possessing both high performance and stability. However, selenium-containing materials present disadvantages in commercial use owing to the safety issue and the problem of waste disposal. For these reasons, the sulfur analogue, 2,7-diphenyl[1]benzothieno[3,2-*b*][1]-benzothiophene (DPh-BTBT), is considered to be a more practical material. We report herein the synthesis of DPh-BTBT, the fabrication of its evaporated thin-film-based OFET, and the excellent FET characteristics in air.

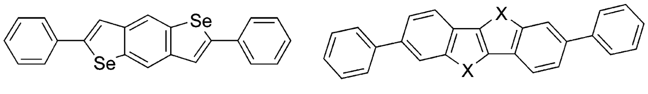
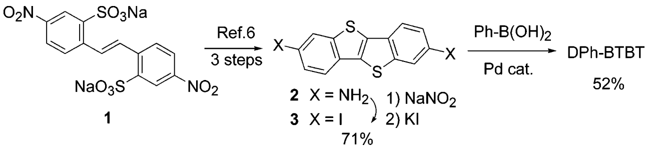


Figure 1. Fused chalcogenophene-based organic semiconductors.

Scheme 1. Synthesis of DPh-BTBT



Since attempts to synthesize DPh-BTBT via a method similar to that which produces DPh-BSBS met with failure, we developed a new synthetic route to DPh-BTBT, as shown in Scheme 1, employing the palladium-catalyzed Suzuki−Miyaura coupling reaction between phenyl boronic acid and 2,7-diiodo[1]benzothieno-[3,2-*b*][1]benzothiophene (**3**),[5] which was readily prepared from corresponding 2,7-diamino compound (**2**) derived from commercial disodium 4,4′-dinitrostilbene-2,2′-disulfonate (**1**).[6] The cyclic voltammogram of DPh-BTBT in benzonitrile showed a reversible oxidation wave at $E_{1/2} = +\,0.91$ V vs Fc/Fc$^+$ (Figure S1). The HOMO level of DPh-BTBT was estimated from the oxidation onset (+0.84 V) to be ca. 5.6 eV. In the solution UV−vis spectrum of DPh-BTBT in THF, the absorption maximum is 336 nm with an absorption edge at 385 nm (Figure S2), corresponding to the HOMO−LUMO energy gap of 3.2 eV. These experimentally estimated energy levels of the frontier orbitals are qualitatively consistent with those obtained from MO calculations (see Supporting Information).

High-quality homogeneous DPh-BTBT thin films on quartz or Si/SiO$_2$ substrate were easily obtained by vacuum deposition. The absorption spectrum of the thin film deposited on the quartz substrate showed red-shifted absorption bands relative to those in the solution spectrum, indicating strong intermolecular interaction in the thin film (Figure S2). X-ray diffraction (XRD) measurement of the thin film on Si/SiO$_2$ substrate showed a series of peaks assignable to (00*h*) reflections (Figure 2). The thus-obtained *d*-spacing (20 Å) is well explained by the molecular arrangement in which DPh-BTBT is nearly perpendicular to the substrate. No significant difference was observed in the XRD patterns of the thin films on the substrates that were subjected to various surface treatments [bare, octyltrichlorosilane (OTS), and hexamethyldisilazane (HMDS)] and/or substrate temperatures during deposition ($T_{\rm sub}$), indicating that the crystalline phase was not affected by these parameters in the vacuum deposition. The thin-film morphology examined by AFM (Figure S5) also showed no apparent dependence

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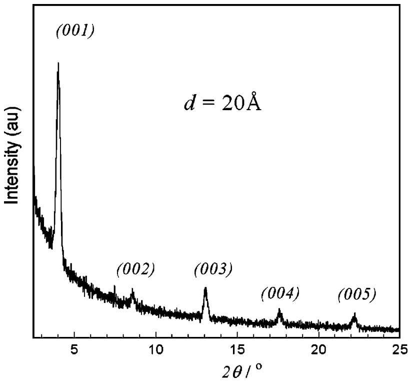

Figure 2. X-ray reflection diagram of DPh-BTBT thin film on OTS-treated Si/SiO$_2$ substrate.

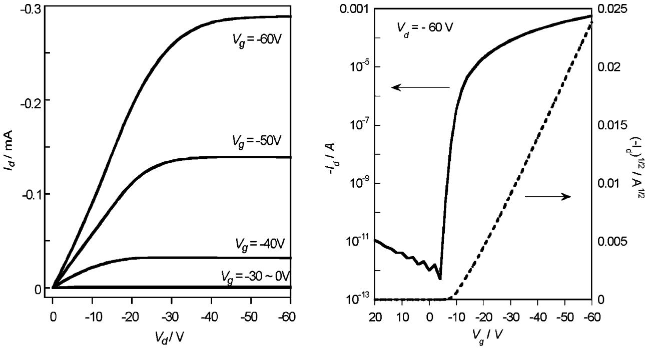

Figure 3. FET characteristics of DPh-BTBT-based OFET on OTS-treated substrate (T_{sub} = 100 °C): output characteristics (left) and transfer characteristics at $V_d = -60$ V (right).

Table 1. FET Characteristics of Devices Fabricated on Si/SiO$_2$ Substrates with Different Surface Treatments and under Different Substrate Temperatures (T_{sub})

	T_{sub}/°C	μ_{FET}^{a}/cm^2 V^{-1} s^{-1}	I_{on}/I_{off}
bare SiO$_2$	rt	0.19−0.22	5×10^6
	60	0.21−0.26	5×10^6
	100	0.12−0.15	5×10^6
HMDS	rt	0.42−0.45	10^6
	60	0.51−0.53	5×10^6
	100	0.93−1.2	10^7
OTS	rt	0.36−0.46	5×10^6
	60	0.43−0.58	10^7
	100	1.0−2.0	$>10^7$

[a] Data from more than 20 devices.

on the surface treatment but on the T_{sub}. Small crystal grains ∼0.3 μm in size were observed in the AFM images of the thin films obtained at T_{sub} = room temperature, and the grain size was increased with elevation of T_{sub}. In the AFM images of the thin films obtained at T_{sub} = 100 °C, large crystal grains with terrace-like step structures were observed.

"Top-contact"-type FET devices with W/L = ca. 30 were fabricated on Si/SiO$_2$ substrates with various surface treatments by vacuum deposition. Regardless of the surface treatment, all the devices showed typical *p*-channel FET response under ambient conditions (Figure 3). The OFETs fabricated on the bare Si/SiO$_2$ substrates showed small dependence of the FET performances (μ_{FET} ∼ 0.3 cm^2 V^{-1} s^{-1} and $I_{on}/I_{off} = 5 \times 10^6$) on T_{sub} (Table 1). These μ_{FET} characteristics are almost the same as those of the DPh-BSBS-based OFETs fabricated on the bare Si/SiO$_2$ substrates.[4d] In contrast, the FET performances of devices fabricated on the silanized substrates showed significant improvement.[7] On the HMDS-treated substrates, the maximum μ_{FET} was ∼1.2 cm^2 V^{-1} s^{-1} at T_{sub} = 100 °C, which is almost 4 times higher than the μ_{FET} on the bare Si/SiO$_2$ substrates. Pronounced enhancement of μ_{FET} was observed for the devices fabricated on the OTS-treated substrates; however, the device-to-device variation of μ_{FET} was relatively large. The devices fabricated at T_{sub} = 100 °C routinely showed $\mu_{FET} > 1.0$ cm^2 V^{-1} s^{-1} and $I_{on}/I_{off} > 10^7$, and the best devices with $\mu_{FET} = 2.0$ cm^2 V^{-1} s^{-1} and $I_{on}/I_{off} \sim 10^8$ were reproducibly obtained. Figure 3 shows the FET characteristics of a typical device with $\mu_{FET} = 1.0$ cm^2 V^{-1} s^{-1}, $I_{on}/I_{off} = 5 \times 10^8$, and subthreshold swing, S = 0.9 V decade^{-1}. It should be emphasized that such high performances recorded in ambient conditions are one of the best among the thin-film-based OFETs so far reported. In preliminary stability tests of the devices, there was almost no change in μ_{FET} after 250 days (Figure S3, Table S4) for the devices fabricated on the bare Si/SiO$_2$ substrates, whereas the devices on the OTS-treated substrates showed a slight decrease in mobility. Further storage and operation stability tests are underway.

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Supporting Information Available: Experimental details for the synthesis and characterization of DPh-BTBT, device fabrication, XRDs, DFT calculations, AFM images of DPh-BTBT thin films, and FET characteristics of DPh-BSBS-based OFETs fabricated on silanized substrates. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) For comparison, DPh-BSBS-based OFETs on silanized substrates were also fabricated and evaluated; see Supporting Information.

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