Molecular Modification of 2,6-Diphenylbenzo[1,2-*b*:4,5-*b′*]dichalcogenophenes by Introduction of Strong Electron-withdrawing Groups: Conversion from p- to n-Channel OFET Materials

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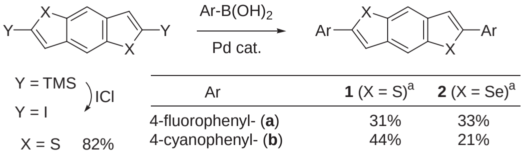
2,6-Diphenylbenzo[1,2-*b*:4,5-*b′*]dithiophene (DPh-BDT) and -diselenophene (DPh-BDS) as p-channel semiconducting materials were modified by introducing fluoro, cyano, or trifluoromethyl groups into the attached phenyl moieties. On examination of organic field-effect transistors fabricated using these modified compounds, the trifluoromethyl-substituted DPh-BDT and BDS derivatives were found to act as n-channel semiconductors with high electron mobilities of 0.044 and 0.10 $cm^2 V^{-1} s^{-1}$, respectively.

Organic filed-effect transistors (OFETs) have attracted current attention from the viewpoints of both material science and practical applications to modern microelectronics.[1] Recent research efforts in the filed have led to the development of many high-performance organic semiconductors nearly competing in mobility with amorphous silicon. However, many of them are p-channel semiconductors. For the reason of a mismatch between the lowest unoccupied molecular orbital (LUMO) of organic molecules and the work functions of metals used for the source and drain electrodes in OFET devices,[2] n-channel semiconductors have been still limited to only specific electron-accepting molecules, such as C_{60},[3] naphthalene or perylene tetracarboximides,[4] and dicyanomethylene-substituted quinoidal oligothiophenes.[5] The recent developments of n-channel semiconductors have been conveniently promoted by introducing strong electron-withdrawing groups into the π-framework of high-performance p-channel semiconductors.[6]

We recently reported that 2,6-dipheneylbenzo[1,2-*b*:4,5-*b′*]dichalcogenophenes (DPh-BDXs) act as high-performance p-channel materials and, in particular, the selenium compound (DPh-BDS) shows very high field-effect mobility (ca. 0.2 $cm^2 V^{-1} s^{-1}$).[7] Further investigation has prompted us to modify the π-framework of these compounds by introducing strong electron-withdrawing groups into the attached phenyl moieties. We report here the synthesis and properties of 4-fluorophenyl, 4-cyanophenyl, 4-trifluoromethylphenyl, and pentafluorophenyl-substituted BDT (**1a**–**1d**) and BDS derivatives (**2a**–**2d**). On examination of OFET devices fabricated using these modified compounds, it has proved that the intended conversion from p- to n-channel OFET materials in this system can be achieved with the 4-trifluoromethylphenyl BDT and BDS derivatives.

As depicted in Scheme 1, the synthesis of **1a**–**1d** and **2a**–**2d** was carried out by a cross-coupling reaction between 2,6-diiodobenzo[1,2-*b*:4,5-*b′*]dichalcogenophene and appropriate substituted phenylboronic acid. Thus, we first synthesized 2,6-diiodo-BDT and -BDS by treatment of the corresponding 2,6-bis(trimethylsilyl) derivatives[8] with iodine monochloride (82 and 86% isolated yield, respectively). The subsequent palladium-catalyzed Suzuki–Miyaura coupling reactions proceeded in moderate yields to give the desired **1a**–**1d** and **2a**–**2d** (for isolated yields, see the inserted table in Scheme 1).[9] These compounds were purified by vacuum sublimation and characterized by spectroscopic and combustion elemental analysis (see Supporting Information).[10]



Ar	**1** (X = S)[a]	**2** (X = Se)[a]
4-fluorophenyl- (**a**)	31%	33%
4-cyanophenyl- (**b**)	44%	21%
4-trifluoromethylphenyl- (**c**)	51%	54%
pentafluorophenyl- (**d**)	37%	26%

[a] Yields after purification by graduent vacuum sublimation.

Scheme 1. Synthesis of DPh-BDT and BDS derivatives.

The LUMO levels of **1** and **2** were estimated by cyclic voltammetry using an Ag/AgCl reference electrode, Pt working and counter electrodes in PhCN containing $^{n}Bu_4NPF_6$ as supporting electrolyte. The 4-fluoro derivatives (**1a** and **2a**) did not show any reduction peak within the given electrochemical window (down to −2.0 V vs Ag/AgCl), indicating that the LUMO levels are higher than ca. 2.5 eV below the vacuum level.[11] Such high LUMO are expected to make too large injection barriers to induce n-channel conduction.[2] On the other hand, all the other derivatives **1b**–**1d** and **2b**–**2d** showed reduction waves in the range of −1.65 to −1.90 V, meaning that the effective lowering of the LUMO levels required for n-channel OFET materials.

Vacuum deposited thin films of **1a**–**1c** and **2a**–**2c** on Si/SiO_2 substrate took on metallic luster on the surface. AFM images revealed that these films have planar surface that consisted of small crystal grains (ca. 0.1 µm in size) with relatively small roughness. On the other hand, the films of the pentafluorophenyl derivatives **1d** and **2d** assumed lackluster gray colors. The AFM images of the films showed rough surfaces with large height-difference (Figures S3 and S4 in Supporting Information).[10] Obviously, the films are not uniformly deposited on the substrate, presumably because of high crystallinity of these compounds.

XRD measurements of the thin films of **1a**–**1c** and **2a**–**2c** gave crucial information on the molecular orientation on the substrate. For the thin films of **1a**, **1c**, **2a**, and **2c**, a series of (00*h*) reflections peaks typical for highly crystalline films were observed. The interlayer distances estimated from the (001) reflection were 18–23 Å, which are nearly equal to their molecular lengths. This indicates that the deposited molecules form assembled layers with nearly upright structures on the substrate. On the other hand, the XRDs of the 4-cyanophenyl derivatives **1b** and

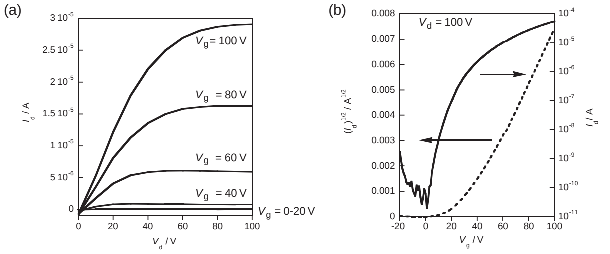


Figure 1. FET characteristics of **1c**-based OFET fabricated at $T_{\mathrm{sub}} = 60\,^{\circ}\mathrm{C}$ with Ag source and drain electrodes: (a) output characteristics and (b) transfer characteristics ($V_{\mathrm{d}} = 100\,\mathrm{V}$).

2b showed no clear peak indicating that these films are not crystalline. It is thus expected that such films are not suitable for carrier transport in OFET devices.

OFET devices using all the BDT and BDS derivatives except poorly filmed **1d** and **2d** were fabricated in a top-contact configuration as follows. First, the thin films (50-nm thick) of the organic semiconductors were deposited on $\mathrm{Si/SiO_2}$ substrate at different substrate temperature (T_{sub}) of rt, 60, and 100 °C. Then, on top of the films, source and drain gold electrodes (80-nm thick) were vacuum-deposited through a shadow mask. The devices of **1c** and **2c** with silver electrodes instead of gold electrodes were also fabricated. The FET characteristics were evaluated in a homemade probe station in vacuo. As expected from the above CV and XRD results, the 4-fluorophenyl derivatives **1a** and **2a** and the 4-cyanophenyl derivatives **1b** and **2b** gave no FET response. On the other hand, the 4-trifluoromethylphenyl derivatives **1c** and **2c** showed typical n-channel FET responses. Figure 1 illustrates the FET characteristics of a **1c**-based OFET device, and Table 1 summarizes the FET performances of all **1c**- and **2c**-based devices fabricated at various T_{sub}s. In comparison of the data measured with gold electrodes, the FET performances of the **1c**-based devices fairly depend on T_{sub}, while those of the **2c**-based devices are almost independent on T_{sub}, though both series of the devices fabricated at $T_{\mathrm{sub}} = 60\,^{\circ}\mathrm{C}$ displayed maximum mobilities (**1c**, $4.8 \times 10^{-3}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ and **2c**, $4.0 \times 10^{-2}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$). In addition, it is worth noticing that the threshold voltages are very high: $V_{\mathrm{th}} = 76$–$77\,\mathrm{V}$ for the **1c**- and 60–63 V for the **2c**-based devices. This suggests that there are still large injection barriers between the electrode and organic semiconducting layers. Consistent with this speculation, the V_{th} values were effectively reduced by using silver electrodes with a lower work function (4.26 eV) than that of gold (5.10 eV).[12] Concomitantly, the mobilities and on/off ratios were enhanced. The mobilities $0.044\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ observed for **1c**-based devices and $0.10\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ for **2c**-based devices are a top level among those for n-channel OFET materials. Interestingly, these values are almost comparable with those previously observed for p-channel DPh-BDT ($0.081\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$) and DPh-BDS ($0.17\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$).[7]

In summary, we have synthesized novel 4-fluorophenyl, 4-cyanophenyl, 4-trifluoromethylphenyl, and pentafluorophenyl-substituted BDT (**1a**–**1d**) and BDS derivatives (**2a**–**2d**) and examined their redox properties and thin film morphologies. On examination of OFET devices fabricated using them, the 4-trifluoromethylphenyl-BDT and -BDS can act as high-performance n-channel semiconductors. The present results evidently demonstrate that novel high-performance n-channel semiconductors can be readily obtained by structural modification of high-performance p-channel semiconductors with electron-withdrawing groups. The concurrent availability of both high-performance p- and n-channel materials with common π-framework would promote the development of effective CMOS-like OFET devices.

Table 1. FET characteristics of **1c** and **2c**-based devices[a]

	T_{sub}/°C	$\mu/\mathrm{cm^2\,V^{-1}\,s^{-1}}$	$I_{\mathrm{on}}/I_{\mathrm{off}}$	V_{th}/V
1c	rt	2.6×10^{-4}	10^4	77
	60	4.8×10^{-3}	10^4	76
	60[b]	4.4×10^{-2}	10^6	31
	100	No FET		
2c	rt	2.2×10^{-2}	10^4	60
	60	4.0×10^{-2}	10^4	63
	60[b]	0.10	10^5	46
	100	1.8×10^{-2}	10^4	62

[a] "Top-contact" configuration with gold source and drain electrodes was used unless otherwise stated. The channel length (L) and channel width (W) are 50 μm and 1.5 mm, respectively. [b] Silver source and drain electrodes were used.

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