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2,6-Diphenylbenzo[1,2-*b*:4,5-*b*′]dichalcogenophenes: A New Class of High-Performance Semiconductors for Organic Field-Effect Transistors

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Recent high performances of organic field-effect transistors (OFETs) have been accomplished from two approaches: the improvement of device fabrication techniques, as represented by pentacene-based OFETs,[1] and the development of new molecular semiconductors for active OFET materials.[2] Such materials exhibiting high performances are mainly composed of thiophene-comprising molecules, such as oligothiophenes,[3] thienylene−phenylene co-oligomers,[4] thienylene−vinylene co-oligomers,[5] and fused thiophene aromatics.[6] From the theoretical point of view, it is pointed out that transfer integral between neighboring molecules is the basic parameter to determine field-effect mobilities.[7] According to this guideline, one may naturally expect that high-performance OFET materials can be developed by replacement of sulfur atoms in the thiophene-comprising molecules with heavy chalcogen atoms such as selenium and tellurium with enhanced overlap integrals. However, selenophene- and tellurophene-comprising organic semiconductors have not been reported thus far. Very recently, we reported OFETs using quaterselenophene as an active layer, which showed a relatively high mobility (3.6×10^{-3} cm^2 V^{-1} s^{-1}) comparable with that of quaterthiophene.[8] Here we report a new prototypical class of FET materials, 2,6-diphenylbenzo[1,2-*b*:4,5-*b*′]dichalcogenophenes (**1**−**3**), and their remarkably high FET performances (Figure 1).

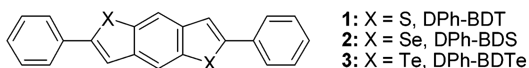

Figure 1. Molecular structures of 2,6-diphenylbenzo[1,2-*b*:4,5-*b*′]dichalcogenophenes.

The conventional methods for the synthesis of benzo[1,2-*b*:4,5-*b*′]dithiophenes using thiophene derivatives as key starting materials[6a,9] are unlikely to be applicable to the selenium and tellurium homologues. Alternatively, we have successfully developed an efficient synthetic method of benzo[1,2-*b*:4,5-*b*′]dichalcogenophenes, which can be applicable to all the chalcogen series (**1**−**3**). This method takes advantage of double heterocycle formation on the central benzene ring, as shown in Scheme 1.[10] Thus, 1,4-dibromo-2,5-bis(phenylethynyl)benzene (**4**), readily prepared from 1,4-dibromobenzene via a two-step conversion,[11] was treated with *t*-BuLi followed by an addition of powdery chalcogen (sulfur, selenium, or tellurium) to give **1**−**3** in moderate to good yields. These new compounds were purified by vacuum sublimation to give yellow powder or fine crystals. Thermal properties of **1**−**3** investigated by differential scanning calorimetry (DSC) indicated that the present compounds are thermally stable: neither phase transition nor thermal decomposition was observed up to 350 °C.

Thin films of **1**−**3** can be deposited on oxidized silicon substrates by thermal evaporation under vacuum. The X-ray diffraction (XRD) of the films reveals highly ordered structures for all the cases. Figure 2A shows an X-ray diffraction of the film of **2** deposited at 60 °C. A series of sharply resolved peaks assignable to multiple (00*l*) reflections can be seen, and from the first-layer line, the monolayer thickness is determined to be ca. 18.0 Å. This value corresponds well to the molecular length of **2** determined by X-ray crystallographic analysis, indicating nearly perfect orthogonal orientation of molecules onto the substrate. Comparing the monolayer thickness in the thin film and the lattice parameter determined by the single-crystal X-ray analysis, one can notice a similarity between these two; the *a*-axis in the unit cell (36.83 Å) is just twice that of the monolayer thickness, implying that the molecular assembly in the thin film is basically the same as that in bulk crystals. Figure 2B shows a crystal packing of **2** projected along the crystallographic *a*-axis direction, which corresponds to the molecular long axis of **2**. The crystal packing of **2** is classified into a herringbone-type, reminiscent of the crystal structure of pentacene[12] and sexithiphene[13] showing high FET mobilities. Although the single-crystal structures of **1** and **3** were not elucidated, we assume that they take similar thin-film structures as seen for **2**, because the monolayer thicknesses of **1** (17.9 Å) and **3** (18.5 Å) determined by X-ray diffractions are similar to that of **2**.

Field-effect transistors were made in a top contact device configuration.[14,15] All the compounds performed as good *p*-type transistors. As a representative, Figure 3 shows the drain-source current (I_{DS}) characteristics with different voltages (V_G) for a FET device using **2** deposited at 60 °C. It demonstrates a typical FET response; I_{DS} scales up with increasing V_G. The FET mobility calculated using the I_{DS} in the saturation regions is 0.17 cm^2 V^{-1} s^{-1}, and the on/off ratio of the I_{DS} between V_G of 0 and −100 V is

Scheme 1. Synthesis of 2,6-Diphenylbenzodichalcogenophenes

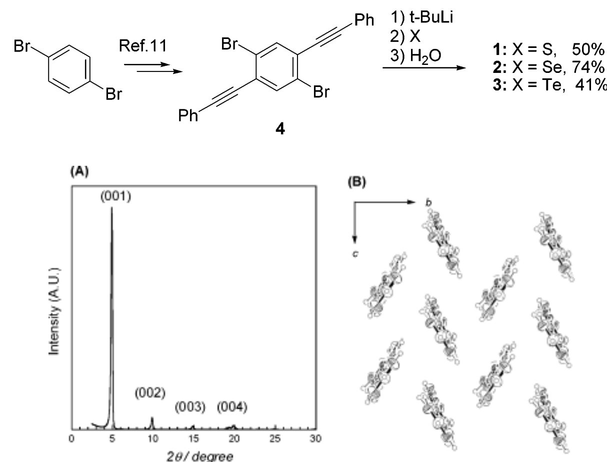

Figure 2. (A) XRD pattern of an evaporated thin film of **2** (T_{sub} = 60 °C). (B) Packing diagram of **2** viewed along *a*-axis in a bulk single crystal.

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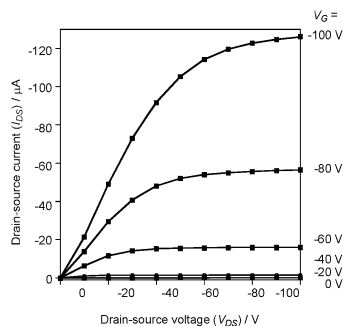

Figure 3. Drain-source current (I_{DS}) versus drain-source voltage (V_{DS}) characteristic for **2** (T_{sub} = 60 °C).

Table 1. Field-Effect Mobility and On/Off Ratio for Transistors of **1**−**3** Prepared at Different Deposition Temperature of the Substrate (T_{sub})

T_{sub}/°C	**1** (DPh-BDT) mobility/cm² V⁻¹ s⁻¹ (on/off ratio)	**2** (DPh-BDS) mobility/cm² V⁻¹ s⁻¹ (on/off ratio)	**3** (DPh-BDTe) mobility/cm² V⁻¹ s⁻¹ (on/off ratio)
rt	4.6×10^{-3} (10^3)	1.6×10^{-2} (10^4)	7.3×10^{-3} (2×10^3)
60	1.8×10^{-2} (2×10^3)	1.7×10^{-1} (10^5)	3.7×10^{-3} (10^3)
100	8.1×10^{-2} (2×10^3)	7.8×10^{-2} (10^2)	4.2×10^{-3} (10^3)

greater than 10^5. This FET performance is among the best class of OFET materials recently developed. Table 1 compares the FET characteristics of three kinds of materials **1**−**3**. It should be noticed that the FET characteristics are fairly dependent not only on the used materials but also on the substrate temperature (T_{sub}) during the film deposition, and the T_{sub} giving the highest mobility is different for each compound. The highest mobility of the selenium homologue **2** is 2 times higher than that of the sulfur counterpart (**1**). This confirms our initial expectations that heavy chalcogen atoms are advantageous for the design of high-performance OFET materials. However, the tellurium homologue **3** fails to meet our expectations; its highest mobility is lower by 1 order of magnitude than that of **1**. This moderate performance may be attributed to the lower aromatic nature of the tellurophene rings, causing less charge delocalization over the whole molecule.[16]

In summary, we have found that a series of diphenylbenzodichalcogenophenes (**1**−**3**) are readily available in three steps from 1,4-dibromobenzene, and all three chalcogen compounds perform as good *p*-type transistors. In particular, the benzodiselenophene derivative **2** demonstrates a remarkably high FET performance. This suggests that similarly fused selenophene compounds have the high potential of providing superior OEFT materials. Further investigation along this line is underway.

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Supporting Information Available: Details for the synthesis and the device fabrication of **1**−**3**, XRDs and AFM images of the thin films of **1**−**3**, crystallographic information files (CIF) for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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