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Facile Synthesis of Highly π-Extended Heteroarenes, Dinaphtho[2,3-*b*:2′,3′-*f*]chalcogenopheno[3,2-*b*]chalcogenophenes, and Their Application to Field-Effect Transistors

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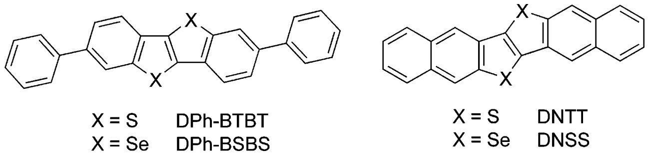
Highly π-extended aromatic compounds are attracting current attention as organic semiconductors for various applications including organic light-emitting diodes (OLEDs), photovoltaic cells, and field-effect transistors (OFETs).[1] Among such aromatic compounds, higher oligoacenes such as naphthacene[2] and pentacene[3] are essential as an active layer of high-performance OFETs. The current benchmark of field-effect mobility (μ_{FET}) in thin-film-based OFETs, which is as high as 3.0 cm^2 V^{-1} s^{-1}, was reported for pentacene-based OFETs.[3b] However, higher oligoacenes are less stable owing to their reduced aromaticity,[4] which makes their devices less stable under ambient conditions.

Recently developed organic semiconductors based on fused chalcogenophene compounds, 2,7-diphenyl[1]benzothieno[3,2-*b*][1]benzothiophene (DPh-BTBT) and its selenophene analogue (DPh-BSBS),[5] have afforded high-performance, air-stable OFET devices ($\mu_{\mathrm{FET}} = \sim 2.0$ cm^2 V^{-1} s^{-1} for DPh-BTBT; $\mu_{\mathrm{FET}} = \sim 0.3$ cm^2 V^{-1} s^{-1} for DPh-BSBS). On the basis of experimental and theoretical studies of their electronic structures, we concluded that the device stability originated from the relatively low-lying HOMO levels and the large HOMO−LUMO energy gaps of the heteroarenes, although they contain a highly extended fused aromatic core with four aromatic rings, similar to naphthacene. Detailed examination of the electronic structure of the heteroarene core, [1]benzochalcogenopheno[3,2-*b*][1]benzochalcogenophene, however, indicates that the core is isoelectronic not with naphthacene but with chrysene, one of the cata-condensed "phenes" with four benzene rings. It is well-known that the acenes having all of their benzene rings fused in a linear array are unstable compared with their structural isomers that have the same number of benzene rings.[4]

With the above consideration, we focused our attention on highly π-extended heteroarenes with six fused aromatic rings, dinaphtho[2,3-*b*:2′,3′-*f*]chalcogenopheno[3,2-*b*]chalcogenophene (DNTT and DNSS, Figure 1), as new promising organic semiconductors. Molecular orbital (MO) calculation predicts that these compounds still retain relatively low-lying HOMO levels and large HOMO−LUMO energy gaps (see Supporting Information).[6] We here report the facile three-step syntheses of DNTT and DNSS and their application to thin-film-based OFETs.

Although there are several possible synthetic approaches to the target compounds, we examined a synthetic route that starts from a naphthalene moiety, and constructed the central heteroaromatic rings at the final step (Scheme 1). Taking advantage of an ortho-directing lithiation procedure using lithium *N,N,N'*-trimethylethylenediamide and excess *n*-BuLi,[7] selective functionalization at the 3-position of commercially available 2-naphthaldehyde with a methylthio or methylseleno substituent was achieved in moderate yields. The aldehyde functionality of 3-methylchalcogeno-2-naphthaldehyde (**1**) was easily converted into a C=C double bond via the low-valence titanium-mediated McMurry coupling to give olefin intermediate (**2**).[8] Finally, **2** was treated with excess iodine to effect ring-closing reaction, forming the thienothiophene or selenophenoselenophene moieties in good yields. It should be noted that the present three-step synthesis, which starts from an aromatic aldehyde to produce π-extended heteroaromatic systems, is a versatile tool to obtain various novel heteroarenes.

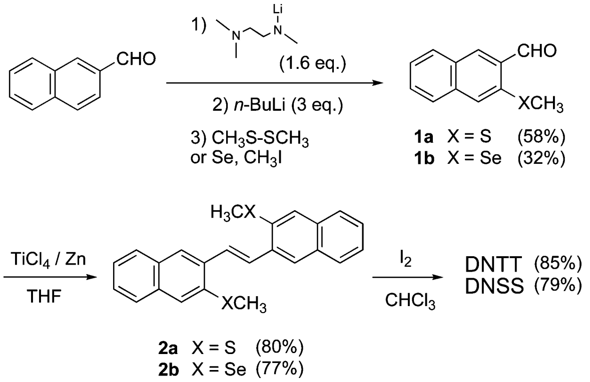


X = S DPh-BTBT
X = Se DPh-BSBS

X = S DNTT
X = Se DNSS

Figure 1. Fused-chalcogenophene-based organic semiconductors.

Scheme 1. Three-Step Synthesis of DNTT and DNSS



DNTT and DNSS are thermally stable yellow crystals that are readily purified by recrystallization or vacuum sublimation. Figure 2 shows the solution UV−vis spectra of DNTT and DNSS. Optical HOMO−LUMO gaps estimated from the absorption edges are ca.

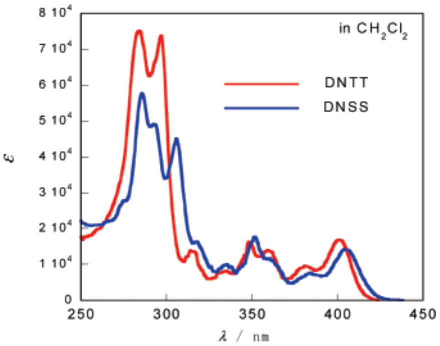


Figure 2. UV−vis absorption spectra of DNTT and DNSS.

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10.1021/ja068429z CCC: $37.00

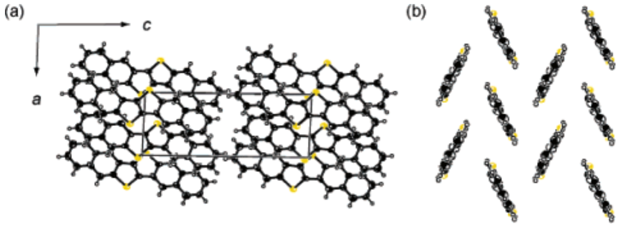

Figure 3. Crystal structure of DNTT: (a) *b*-axis projection; (b) herringbone packing in the layered structure.

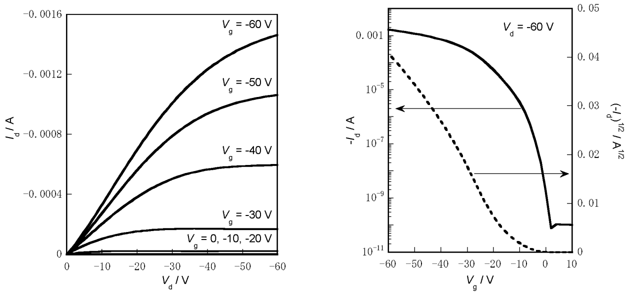

Figure 4. FET characteristics of DNTT-based OFET on OTS-treated substrate (T_{sub} = 60 °C): output characteristics (left) and transfer characteristics at $V_d = -60$ V (right).

3.0 and 2.9 eV for DNTT and DNSS, respectively. Electrochemically defined HOMO levels for DNTT and DNSS by means of cyclic voltammetry (Figure S1) are 5.44 and 5.38 eV below the vacuum level, respectively.[9] These experimental HOMO levels as well as HOMO−LUMO gaps are qualitatively consistent with the results obtained from MO calculations. Judging from these data, we expect that DNTT and DNSS are stable organic semiconductors, similar to DPh-BTBT and DPh-BSBS.

Figure 3 shows the crystal structure of DNTT elucidated by single-crystal X-ray structural analysis. Almost planar molecules with a small standard deviation of 0.058 Å form a layer-by-layer structure in the crystal (Figure 3a). In each layer, herringbone packing typical of poly fused aromatic compounds was observed, resulting in the two-dimensional molecular network (Figure 3b).

Preliminary OFET studies were carried out using "top-contact"-type devices with W/L = ca. 30, which were fabricated by vacuum deposition on Si/SiO_2 substrates whose surfaces were treated with octyltrichlorosilane (OTS) or hexamethyldisilazane (HMDS). All the devices fabricated under various conditions showed typical p-channel FET characteristics with μ_{FET} higher than 0.3 cm^2 V^{-1} s^{-1} and $I_{\mathrm{on}}/I_{\mathrm{off}} > 10^6$ under ambient conditions (Figure 4 and Table 1). In particular, excellent FET characteristics with μ_{FET} higher than 2.0 cm^2 V^{-1} s^{-1} and $I_{\mathrm{on}}/I_{\mathrm{off}}$ of 10^7 were observed in DNTT-based devices fabricated on the OTS-treated substrate at T_{sub} = 60 °C. The present FET characteristics are almost comparable or slightly better than those for DPh-BTBT- and DPh-BSBS-based devices.

In summary, we have established a straightforward three-step procedure for the synthesis of highly π-extended heteroarenes, DNTT and DNSS. Solution UV−vis spectra and electrochemical measurements indicated that they have relatively low-lying HOMO levels and large HOMO−LUMO energy gaps, despite the fact that they are highly π-extended arenes consisting of six fused aromatic rings. These physicochemical properties are reflected by the stability in air of OFETs fabricated with DNTT and DNSS thin films as the active layer. In addition, the highly extended π-framework contributes to effective molecular overlap, which can lead to high carrier mobility in the thin-film transistor setting. From the experimental results, we conclude that the present design strategy for air-stable, high-performance organic semiconductors is quite valid. Further studies to optimize DNTT- and DNSS-based devices are under way.

Table 1. FET Characteristics of DNTT and DNSS Devices Fabricated on Si/SiO_2 Substrates with Different Surface Treatments and under Different Substrate Temperatures (T_{sub})

	surface-treatment reagent	T_{sub}/ °C[a]	μ_{FET}[b]/ cm^2 V^{-1} s^{-1}	$I_{\mathrm{on}}/I_{\mathrm{off}}$	V_{th}/ V
DNTT	HMDS	rt	0.73−0.83	5×10^6	-8.5 ± 2.5
		60	1.1−1.2	5×10^6	-12.5 ± 2.5
		100	1.1−1.3	10^7	-5.5 ± 1.5
	OTS	rt	1.6−1.8	10^7	-13 ± 2.0
		60	2.1−2.9	10^7	-11.0 ± 2.0
		100	1.6−1.9	10^7	-6.5 ± 2.5
DNSS	HMDS	rt	0.54−0.57	5×10^6	-4.5 ± 0.5
		60	0.71−1.3	5×10^6	-3.0 ± 1.0
		100	0.31−0.59	5×10^6	-6.5 ± 1.5
	OTS	rt	0.99−1.9	5×10^6	-7.5 ± 2.5
		60	0.97−1.0	10^7	-7.5 ± 2.5
		100	0.43−0.66	5×10^6	-9.5 ± 2.5

[a] rt = room temperature. [b] Data from more than 10 devices.

Acknowledgment. We thank Dr. E. Miyazaki (Hiroshima University) for helpful discussion on X-ray structural analysis. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and an Industrial Technology Research Grant Program in 2006 from the New Energy and Industrial Technology Development Organization (NEDO), Japan.

Supporting Information Available: Experimental details for the synthesis and characterization of DNTT and DNSS, crystallographic information file (CIF) for DNTT, device fabrication, XRDs, DFT calculations, AFM images of thin films, and FET characteristics of devices fabricated on bare Si/SiO_2 substrates. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA068429Z