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High-Performance Organic Semiconductors: Asymmetric Linear Acenes Containing Sulphur

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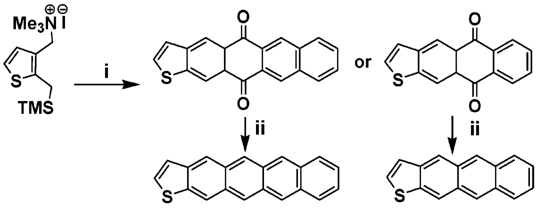
Organic semiconductors show great promise in various low-cost, large-area, electronic applications. Currently, the best performing molecule as the active material in *p*-type organic transistors is pentacene,[1−3] with high mobilities over 1.0 $cm^2\ V^{-1}\ s^{-1}$ and decent on−off ratios. However, pentacene is subject to rapid degradation in ambient conditions, presumably to form the transannular endoperoxide[4] or dimeric Diels−Alder adducts.[5,6] As such, much attention in the field has been focused on designing new organic semiconductor candidates.[7,8] The ideal candidate should be suitable for solution processing, stable in ambient conditions, and possess high-charge mobility. Among the few examples of pentacene derivatives are Anthony's triisopropylsilyl(TIPS)-ethynyl substituted pentacene[9] and anthradithiophene derivatives. In addition to conferring solubility on the parent molecule, the TIPS group enhances packing by introducing π-stacking into the crystal structure,[10] as opposed to the previous herringbone packing. This creates a more densely packed crystal structure, thus optimizing charge transport. However, the synthesis of the anthradithiophene[11] parent molecule and its substituted version creates two isomers that are not easily separable. This may contribute to the disorder in the thin film.

In this work, we present two asymmetric linear pentacene and tetracene derivatives containing fused thiophene units. Compound **1**, tetraceno[2,3-*b*]thiophene, is a reddish purple compound with a conjugation length between tetracene and pentacene, while compound **2**, anthra[2,3-*b*]thiophene, is a bright yellow molecule with a conjugation length between tetracene and anthracene.

Scheme 1 shows the synthesis of **1** and **2**. The quinone precursor of **1**, tetraceno[2,3-*b*]thiophene-5,12-dione was made in one step from a known compound, 2-(trimethylsilylmethyl)-3-(trimethylammonium)-thiophene iodide[12,13] by a Diels−Alder reaction in 60% yield. This precursor quinone was reduced to **1** in 87% yield.[6] In this study, **2** was synthesized in a manner analogous to **1** using naphthoquinone instead of anthraquinone, but anthra[2,3-*b*]thiophene has been made before by condensation reactions.[14] Both molecules were purified by three-zone sublimation three times and characterized by ^1H NMR, mass spectrometry, elemental analysis, and cyclic voltammetry. Thin-films were characterized by atomic force microscopy (AFM), X-ray diffraction (XRD), and transistor measurements.

The optical bandgaps of **1** and **2** and their electrochemical HOMO levels are listed in Table 1 and compared with tetracene[15,16] and pentacene. Structure **1** has a slightly higher oxidation potential than pentacene. Its electrochemical stability is also monitored in solution, where its long wavelength absorption peak outlives that of pentacene. Performing UV−vis absorption measurements in a dilute solution of *o*-dichlorobenzene with similar initial optical densities (OD), we observed that the long-wavelength OD of pentacene decays to nothing in 10 min, while that of tetraceno[2,3-*b*]thiophene decays to zero in 60 min (see Figures S-3 and S-4, Supporting Information).

Scheme 1. Synthesis of Compounds **1** and **2**[a]



1 **2**

Tetraceno[2,3-*b*]thiophene Anthra[2,3-*b*]thiophene

[a] (i) Anthraquinone for **1**, naphthoquinone for **2**, tetrabutylammonium fluoride in THF, DMF; (ii) Al, $HgCl_2$, CBr_4, cyclohexanol.

Table 1. Oxidation Potentials of **1** and **2** vs SCE Reference by Comparison to Ferrocene and Their Optical Bandgaps from Thin Film, Determined at an Onset Absorption Peak

compound	E^{ONSET} (V)	$E_{1/2}$ (V)	IP (eV)	optical E_G (eV)
2	0.86		5.30	2.51
tetracene			5.40	2.25
1	0.64	0.73	5.17	1.96
pentacene	0.63	0.70	5.14	1.77

Table 2. OTFT Data of Tetraceno[2,3-*b*]thiophene, Averaged over at Least Four Devices, Channel Length $L = 50\ \mu m$, $W/L = 20$ (*W*: Channel Width)

	PVP	SiO_2	OTS	temp (°C)
μ (cm^2/Vs)	0.049 ± 0.0007	0.051 ± 0.001	0.10 ± 0.01	room temp
on/off	131	14	5.8×10^5	
V_T (V)	13	44	−14	
μ (cm^2/Vs)	0.054 ± 0.0004	0.062 ± 0.002	0.31 ± 0.11	60
on/off	58	26	1.3×10^6	
V_T (V)	20	40	7	

Thin films of **1** and **2** were evaporated on SiO_2/Si, octadecyltrichlorosilane (OTS) treated SiO_2/Si, and a spin-coated polyvinylphenol (PVP) mixture with a copolymer[3] cured at 200 °C on Si to make organic thin film transistors (OTFTs) with top-contact geometry.[17] The average mobility of **1** is in the range of 0.04−0.31 $cm^2\ V^{-1}\ s^{-1}$, and varies with the surface treatment of the device and substrate temperature, as shown in Table 2. The best performance of **1** is on OTS/SiO_2/Si at 60 °C with a mobility of 0.47 $cm^2\ V^{-1}\ s^{-1}$, while the mobility on SiO_2/Si and PVP/Si is an order of magnitude less. Under similar device fabrication conditions, purified pentacene in our hands gave a mobility of 0.5 $cm^2\ V^{-1}\ s^{-1}$.

For **2**, the mobility ranges from 1×10^{-5} to 0.15 $cm^2\ V^{-1}\ s^{-1}$, with no transistor behavior observed on PVP/Si. The mobility is high for OTS/SiO_2/Si, consistently more than 0.1 $cm^2\ V^{-1}\ s^{-1}$. Interestingly, on SiO_2/Si, 40 nm films have a mobility of 1×10^{-5} $cm^2\ V^{-1}\ s^{-1}$, while 120 nm films show an improved performance,

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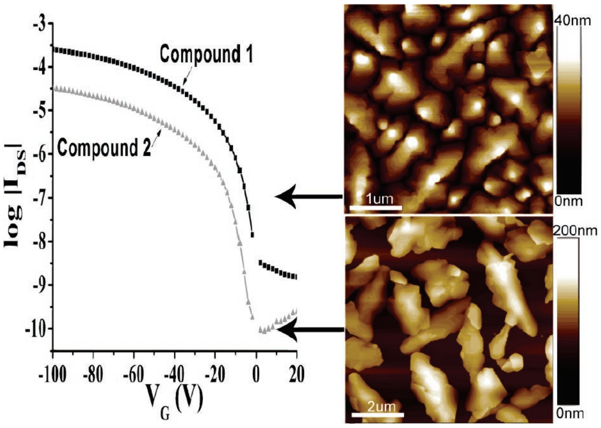

Figure 1. Characteristic transfer curves of **1** and **2** on OTS/SiO_2/Si at 60 °C and room temperature, respectively ($L = 50$ μm, $W/L = 20$), and the corresponding AFM.

with a mobility of 0.006 cm^2 V^{-1} s^{-1}. This may be due to the grains being more connected at the interface with the dielectric for thicker films. For both **1** and **2**, the on/off ratio is on the order of 10^6 for the OTS treated surface but only about 10^2 for the other surfaces.

To probe the morphology of the molecules in an evaporated thin film, we performed AFM scans. AFM images of submonolayer films of **1** on bare SiO_2/Si and OTS/SiO_2/Si reveal grains as large as 1 μm that greatly resemble that of pentacene.[18,19] AFM images of 50 nm films of **1** grown at room temperature on device wafers show a dendritic growth characteristic of pentacene. Dendritic growth is especially apparent on OTS/SiO_2/Si and PVP/Si (see Figure S-10). From room temperature to a substrate temperature of 60 °C, 50 nm films of **1** show larger grains on all substrates, corresponding well with the increase in the thin film mobility (see Figure S-11). At 80 °C, 3D growth dominates on SiO_2/Si and OTS/SiO_2/Si, resulting no working devices. AFM studies of the submonolayer growth of **2** were difficult to perform because of the high roughness of the films. Perhaps this is related to the low molecular weight of **2**, which encouraged desorption at room temperature. However, the morphology of 40 nm films of **2** at room temperature showed grains as large as 3 μm on SiO_2/Si and OTS/SiO_2/Si, with 3D growth occurring much more prominently than for **1**. This is not unexpected, considering tetracene forms towers in thin film and does not give evaporated films with good grain connectivity and thus poor mobility.[20] The 40 nm films of **2** at room temperature on PVP/Si showed disconnected grains with high walls at the boundary of the grains, commensurate with no mobility measured on this surface. Substrate−molecule interactions seem to be less favored than molecule−molecule interactions on the PVP/Si surface. At 40 °C, nothing seems absorbed on SiO_2/Si, while the large disconnected grains exceeding 10 μm on OTS/SiO_2/Si account for nonworking devices made at this temperature (see Figure S-12).

The out-of-plane (OOP) spacing of the molecules in thin film was obtained by X-ray diffraction. For **1**, we observed peaks up to the sixth order, and obtained an average OOP d-spacing of 14.8 Å, which corresponds well with the MM2 minimized molecular length of 14.1 Å. The d-spacing obtained for compound **2** was 12.4 Å, compared to the calculated length of 11.8 Å, with five orders of diffraction observed. In the diffractograms of both **1** and **2**, the intensity of the diffracted peaks on different surfaces and substrate temperatures corresponded with mobility. For instance, for **1**, peak intensities are higher for the films grown on OTS/SiO_2/Si compared to the film grown on SiO_2/Si or PVP dielectric surface at both room temperature and at 60 °C (see Supporting Information).

To conclude, we have synthesized two new asymmetric linear acenes that show high charge mobility and stability. These new conjugated cores can be further functionalized to make a variety of small molecule and polymer based OTFTs, which may aid in the understanding of thin film packing and mobility.

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Supporting Information Available: Details of experimental procedures, UV−vis, cyclic voltammagrams, table content of OTFT device data and X-ray OOP d-spacings, X-ray diffraction graphs, AFM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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