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High-Performance, Solution-Processed Organic Thin Film Transistors from a Novel Pentacene Precursor

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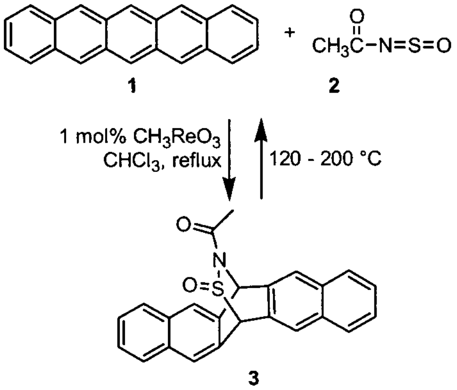
We describe the preparation of a soluble precursor to the organic semiconductor pentacene and its use in the solution-based fabrication of high-performance organic thin film transistors (OTFTs). These devices exhibit the highest field-effect mobilities reported to date for solution-processed OTFTs. Our synthetic approach uses an efficient Lewis acid-catalyzed Diels−Alder reaction of pentacene, a virtually insoluble compound in organic solvents at room temperature, with a hetero dienophile under moderate conditions to form an adduct that is highly soluble in chlorinated solvents and ethers. Heating spin-coated thin films of this adduct at moderate temperatures causes a retro Diels−Alder reaction that converts the adduct film to a pentacene thin film. Our one-step synthetic approach is a straightforward route to a soluble pentacene precursor that can be used for solution-based, large area deposition of pentacene on substrates, including plastic substrates, for the fabrication of high-performance OTFTs.

Over the past two decades, organic semiconductors have been studied for their use in devices such as light-emitting diodes,[1] field-effect transistors,[2−5] and photovoltaic cells.[6,7] The drive to incorporate organic semiconductors in these devices stems from their attractive processing characteristics; they can be deposited over large areas and at temperatures low enough to be compatible with flexible plastic substrates. Among organic semiconductors, commercially available pentacene **1** has been the subject of special attention. Field-effect mobilities of greater than 1.0 $cm^2/(V\ s)$ have been reported for OTFTs using vacuum-deposited pentacene.[8,9] Furthermore, pentacene has been shown to be the most environmentally stable organic semiconductor.[10] The main drawback for pentacene is that it is essentially insoluble in organic solvents at room temperature. Solubility is a desirable characteristic for organic semiconductors because of the low cost offered by solution deposition of thin films. Müllen and co-workers reported the preparation of a soluble precursor of pentacene that can be spin-coated and then heated to form pentacene.[11] OTFTs with pentacene formed by this precursor method showed field-effect mobilities (μ) ranging from $10^{-4}-9 \times 10^{-3}$ $cm^2\ V^{-1}\ s^{-1}$ for $T = 140$ °C[12,13] to 0.1−0.2 $cm^2\ V^{-1}\ s^{-1}$ for $T = 200$ °C.[11] The limitation of Müllen's approach is that the precursor is not easily accessible; it is prepared in a multistep synthesis with low overall yield. Furthermore, the mobility at the lowest conversion temperature, which is desirable for plastic substrates, is very low.

Our goal was to develop a one-step synthesis of a soluble pentacene precursor that reverts to pentacene at moderate temperatures while retaining transport properties comparable to those of vacuum-deposited pentacene films. We employed a Diels−Alder reaction using a reactive *N*-sulfinylamide as hetero dienophile. The Diels−Alder chemistry of activated *N*-sulfinyl compounds in organic synthesis has been well documented.[14] Pentacene **1** was treated with excess *N*-sulfinylacetamide **2**[15] in refluxing chloroform in the presence of a catalytic amount of methyltrioxorhenium[16] to give the Diels−Alder adduct **3** in greater than 90% yield (Scheme 1). The product is purified by flash column chromatography to give analytically pure samples of **3** as an air-stable, white, microcrystalline compound that is highly soluble (>50 mg/mL) in chlorinated hydrocarbons, THF, and dioxane. Samples of **3** may be stored for months at −10 °C without decomposition. The structure of **3** was deduced from its ^1H NMR spectrum,[17] IR spectrum,[18] and elemental analysis.[19]

Scheme 1



Thermogravimetric analysis of adduct **3** (Figure 1) shows that it undergoes a retro Diels−Alder reaction starting at 120 °C and reaches a plateau at 160 °C. The weight loss of about 27% is in accordance with the loss of *N*-sulfinylacetamide **2** from the adduct **3**. Further proof for the thermal conversion of **3** to pentacene was obtained by UV−vis spectroscopy. Figure 2 shows the UV−vis spectrum of a thin film of adduct **3** with an absorption maximum at 254 nm, consistent with the naphthalene moiety. After heating the substrate under nitrogen at 150 °C for 10 min, we obtained a blue compound with several absorption peaks between 500 and 700 nm that match the absorption spectrum reported for pentacene.[11]

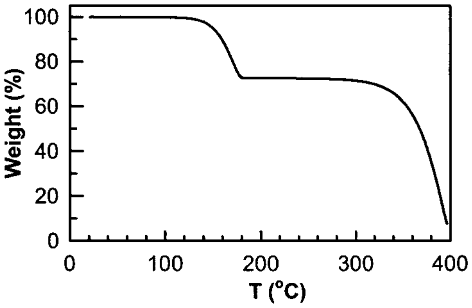


Figure 1. Thermogravimetric analysis curve for the retro Diels−Alder reaction of precursor **3** (heating rate: 10 °C/min).

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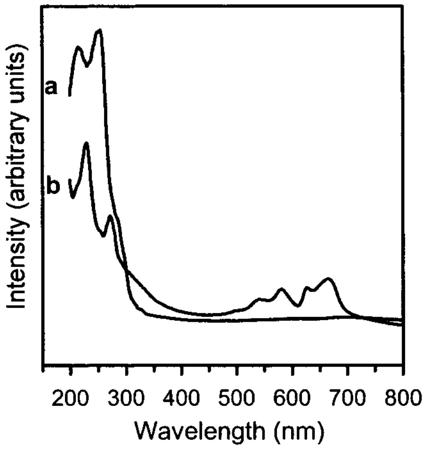

Figure 2. UV−vis spectra of thin films of (a) precursor **3** and (b) pentacene formed by annealing **3** under nitrogen at 150 °C for 5 min.

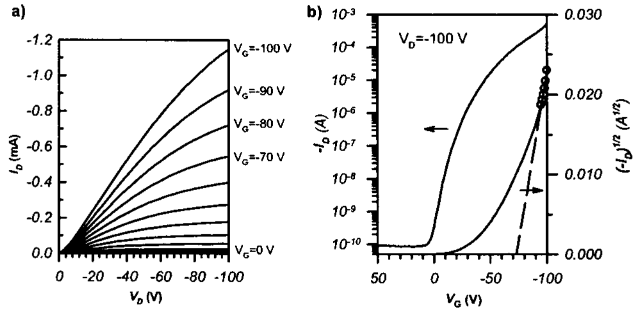

Figure 3. (a) Drain current, I_D, versus drain voltage, V_D, as a function of gate voltage, V_G, for an OTFT with pentacene as the active channel. The pentacene film was obtained by spin-coating a solution of precursor **3** and then heating the substrate at 200 °C for 1.5 min under a nitrogen atmosphere. Channel length $L = 4.8$ μm and channel width $W = 1.5$ mm were defined by gold source and drain electrodes. (b) Plots of I_D and $I_D^{1/2}$ versus V_G at constant $V_D = -100$ V for the device in (a).

Field-effect measurements were carried out on bottom-contact OTFTs[20] fabricated by spin-coating a chloroform solution (1−2% solid) of **3** on the substrate followed by annealing (200 °C, 1.5 min or 130 °C, 25 min) under a nitrogen atmosphere to convert adduct **3** to pentacene. OTFTs fabricated using pentacene films produced from precursor **3** as the active layer exhibit p-type characteristics, as expected from previous results of vapor-deposited pentacene OTFTs[4,8] and pentacene OTFTs deposited via the precursor route of Müllen et al.[11,12] A typical plot (for 200 °C annealing of the precursor) of drain current I_D versus drain voltage V_D at various gate voltages V_G obtained from pentacene OTFTs fabricated from precursor **3** is shown in Figure 3a.

Models developed for inorganic semiconductors can adequately describe the I−V characteristics of OTFTs.[21] The field effect mobility, μ, was calculated in the linear regime from the transconductance[21] to be 0.29 cm^2 V^{-1} s^{-1} at $V_D = -20$ V for a device with a channel length, L, of 15 μm and a channel width, W, of 1500 μm. Because of the nonlinearity of the I_D versus V_D curves at low V_D, the relatively high value of $V_D = -20$ V was chosen so that it lay in the linear regime. Figure 3b shows a graph that contains a semilogarithmic plot of $-I_D$ versus V_G and a plot of $(-I_D)^{1/2}$ versus V_G and corresponds to the same device as Figure 3a. The mobility calculated in the saturation regime[21] from Figure 3b was 0.42 cm^2 V^{-1} s^{-1}. The current modulation, which is the ratio of the current in accumulation over the current in depletion, also referred to as the I_{on}/I_{off} ratio, was above 2×10^7. The highest mobility exhibited in the saturation regime was 0.89 cm^2 V^{-1} s^{-1} with equally good current modulation. These are the highest mobilities reported to date for OTFTs fabricated by solution processing an organic semiconductor. OTFTs fabricated by annealing the precursor **3** at a lower temperature (130 °C, 25 min) resulted in field-effect mobilities of 0.13 cm^2 V^{-1} s^{-1} measured both for the linear and for the saturation regime. Similar to OTFTs with vacuum sublimed pentacene films,[4] substantial gate voltage dependence of the mobility is observed.

In summary, we have demonstrated a versatile, high-yield synthesis of a soluble pentacene precursor that enables the fabrication of high-performance, solution-processed OTFTs. This synthetic approach can potentially be used for the preparation of a variety of pentacene precursors to tailor their solubility, melting point, and other physical properties. The present results demonstrate that the performance of OTFTs with solution-deposited channels rivals that of vacuum-deposited OTFTs and amorphous Si TFTs. Furthermore, the conversion temperature of the precursor has been lowered enough to make its processing compatible with plastic substrates, without substantially sacrificing performance. Such characteristics are necessary for the fabrication of low-cost, but high-performance, OTFTs on plastic substrates for large area electronics applications.

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(17) ^{1}H NMR (CDCl$_3$), δ (ppm downfield from TMS, 400 MHz): 2.35 (s, 3H), 5.95 (s, 1H), 7.2 (s, 1H), 7.5 (m, 4H), 7.8 (m, 2H), 7.85 (m, 2H), 7.9 (s, 1H), 8.0 (s, 1H), 8.02 (s, 1H), and 8.05 (s, 1H).
(18) KBr, $\nu_{C=O}$ 1740 cm $^{-1}$, $\nu_{N=S=O}$ 1245 cm^{-1}.
(19) Calculated for $C_{24}H_{17}NO_2S$: C, 75.19; H, 4.43; N, 3.65. Found: C, 75.40; H, 4.33; N, 3.58.
(20) For the bottom-contact OTFT, a highly doped silicon wafer was used as the gate electrode, thermally grown SiO$_2$ (500 nm), in which the surface was modified with a layer of hexamethyldisilazane (HMDS), was used as the gate insulator, and gold source and drain electrodes were vacuum-deposited through a stencil mask.
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