Organic Thin Film Transistors from a Soluble Oligothiophene Derivative Containing Thermally Removable Solubilizing Groups

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The solubility of organic semiconducting materials is a particularly important consideration when evaluating candidates for use in low-cost electronic devices such as organic thin film transistors (OTFTs),[1] since the desired processing of these materials includes solution-based methods such as spin coating,[2] stamping,[3] or ink-jet printing.[4] These methods have the advantage of being conducted at ambient temperatures, allowing for the use of a great variety of substrates such as plastic or fabric, and they are also amenable to large-area or continuous applications. However, highly conjugated organic materials are notoriously difficult to manipulate due to their low solubility. Therefore, our focus in designing the next generation of organic semiconductors has been to impart solubility to the materials through the use of strategically placed substituents.[5] Herein we report the synthesis and characterization of a symmetrical α,ω-substituted sexithiophene derivative containing thermally removable solubilizing groups for use in solution-processed OTFTs.

Thiophene oligomers, particularly α,ω-dihexyl-sexithiophene (DH6T), have recently been reported to exhibit thin film charge mobilities as high as 1.0 cm^2/(V s),[6] but due to limited solubility they need to undergo vacuum deposition to form thin films.[7] Solution processing has been attempted with α,ω-dihexyltetra-,[8] penta-,[9] and sexithiophene,[10] giving OTFT devices with mobilities on the order of 10^{-2} cm^2/(V s) with on/off ratios of 10^3. However, high temperatures are required of both the substrate and the spinning solvent. Improvements in solubility of sexithiophene oligomers has been demonstrated by incorporating polar functionalities such as alkyl phosphonates[11] and poly(ethylene oxide)[12] at the α- and ω-positions at the cost of decreasing mobilities to 10^{-3} cm^2/(V s) and 10^{-4} cm^2/(V s), respectively. Substituents impart solubility by interrupting the natural tendency of a material to π-stack; therefore, semiconducting materials that rely heavily on π-orbital overlap to achieve high charge mobility suffer as a result of functionalization. Furthermore, typical substituents consist of insulating saturated alkane derivatives that may lower the intrinsic electronic properties of a material.

To overcome the negative effects of these necessary solubilizing groups, it would be advantageous to be able to remove these groups in a postprocessing step. The thermal removal of solubilizing groups, key to our design of chemically amplified photoresists,[13] was also used in the Durham polyacetylene[14] and more recently for solution-processible pentacene.[15] Our specific target was the diester-functionalized sexithiophene derivative 6 (Scheme 1). This target contains activated secondary esters at the α- and ω-positions which are known to undergo thermolysis between 150 and 300 °C. The branched nature of the ester renders the oligomer soluble in common organic solvents, facilitating synthesis, purification, and processing. These oligomers can be solution cast into thin films

Scheme 1. Thermolysis of the Ester-Substituted Sexithiophene.
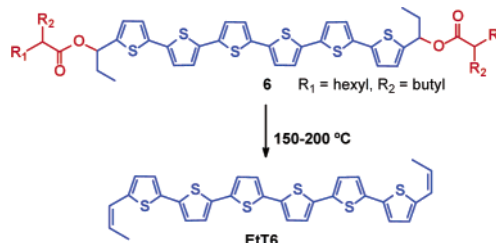
Scheme 2. Synthesis of Ester-Terminated Sexithiophene 6
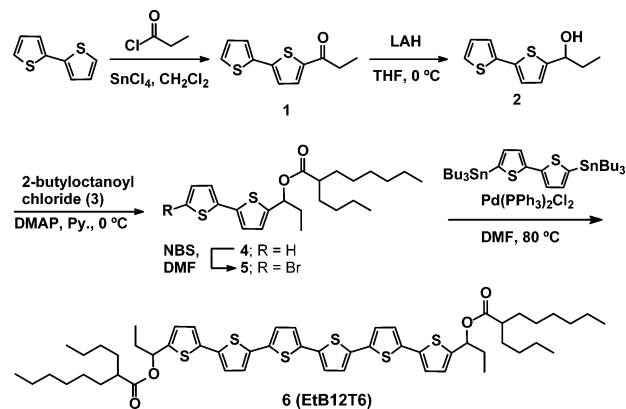
and then thermolyzed with a relatively low-temperature heating cycle, leaving pendant alkene groups on the oligomer.

Compound 6 was synthesized by linking a central bis-stannylated bithiophene with terminal α-functionalized bithiophene units through a Stille cross-coupling reaction (Scheme 2). The α-functionalized bithiophene 2 is prepared by a Friedel−Crafts reaction between bithiophene and propionyl chloride, followed by a reduction of the carbonyl with LAH. Following esterification of 2 with 2-butyloctanoyl chloride to form ester 4 and bromination to 5, Stille coupling was carried out with 5,5′-di(tributylstannyl)-2,2′-bithiophene[16] to afford compound 6. As a result of the presence of its branched ester side chains, the orange semicrystalline product is highly soluble in most organic solvents.

Thermogravimetric analysis (TGA) of the product verified the expected ester thermolysis reaction (Figure 1). A 41% loss of the total mass, corresponding to a loss of the carboxylic acid, initiates at 120 °C and is complete by 210 °C. The thermolysis reaction was also monitored by MALDI-TOF showing the expected mass loss upon heating the sample of 6 (Figure 2).

The morphologies of thin films of 6 on Si/SiO$_2$ were imaged with AFM before and after heating. The initial unheated films are microcrystalline and show only local aggregation (Figure 3a). However, after thermolysis the films reorganize into large crystalline terraces, which increase in height with increasing annealing
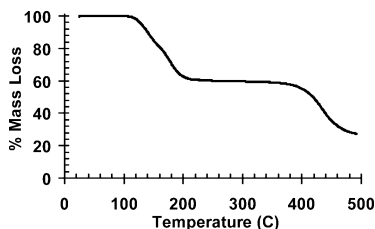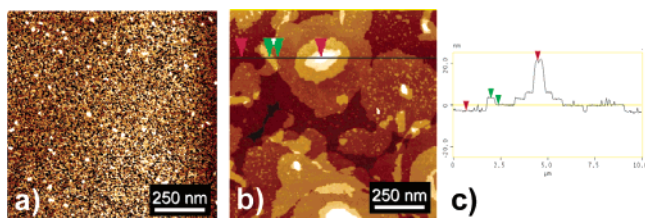
Figure 1. Thermogravimetric analysis of **6** heating at 5 °C/min. The expected loss of 41% of the mass occurs between 120 and 210 °C.
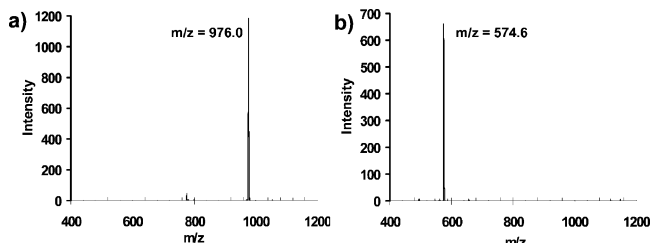
Figure 2. MALDI-TOF MS of **6** (a) before heating (calc MW = 975.5) and (b) after heating to 150 °C for 10 min (calc MW = 574.9).
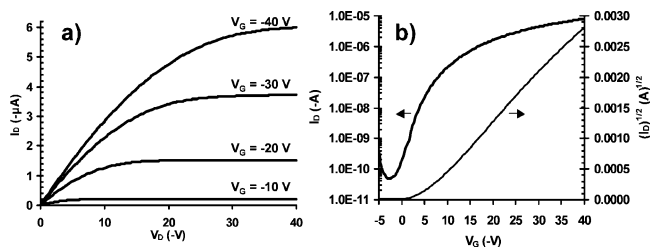

Figure 3. AFM Images of thin films of **6** (a) before heating (b) after heating to 200 °C for 20 min. (c) Height profile of (b). The initial microcrystalline film transforms into crystalline molecular terraces after thermolysis.

Figure 4. Electrical characterization of OTFTs after heating to 200 °C. (a) Drain current I_D vs drain voltage V_D as a function of gate voltage for a top-contact device with $L = 200$ μm and $W = 20$ μm. (b) I_D and $I_D^{1/2}$ vs V_G at $V_D = -22$ V.

temperature (Figure 3b,c). When annealed at 200 °C, step heights of 3 nm, corresponding to the length of the molecule, can be seen as well as islands as tall as 30 nm (Figure 3c).

This increased order in the films after thermolysis and removal of the insulating ester groups also gives rise to increased charge mobility through the material. OTFTs were fabricated on a doped silicon gate, using thermally grown 1250 Å SiO_2 as a dielectric with gold electrodes in top-contact geometry. A film was deposited by spin-coating 2−3 mg/mL solutions of **6** in $CHCl_3$. Devices tested before heating had low mobilities, on the order of 10^{-5} cm^2/(V s) with on/off ratios of <100. However, annealing the substrates between 180 and 200 °C for 20 min produced devices with mobilities averaging 0.03 cm^2/(V s), with many devices exhibiting mobilities as high as 0.05 cm^2/(V s) in both the linear and saturation regime (Figure 4). These devices also possess very high on/off ratios of >10^5. The on/off ratios are maintained after exposure to air for 7 days, demonstrating low oxygen sensitivity, but experience a 10−20% reduction in mobility. These mobilities and on/off values are among the highest ever reported for solution-processed thiophene oligomers.

This method of adding thermally labile solubilizing groups offers an attractive route to easily processed thiophene oligomers. The solubility can be tuned to facilitate processing without adversely affecting the performance of the final material. Further refinement of the substituents may allow even further enhancement in properties. These materials show great promise for use in solution-processed low-cost electronics.

Supporting Information Available: Complete experimental procedures and characterization of **1−6** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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