Articles

Precursor Synthesis, Coupling, and TFT Evaluation of End-Substituted Thiophene Hexamers

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Methods for synthesizing pure, monosubstituted α-terthiophenes, and selectively coupling their lithiated derivatives to produce disubstituted sexithiophenes were developed. The terthiophenes were made via carbonyl intermediates that could be readily chromatographed. The coupling reagents were selected to minimize chlorination and lithium−hydrogen exchange. The mobility of the dihexylated hexamer in thin-film transitors was 0.03 cm²/Vs, in agreement with the literature. The on/off ratio was much higher than the literature, due to improved purity. Use of hexylthio as a substituent gave highly conductive, poorly performing transistors.

Introduction

Thiophene oligomers, especially the 2,5-linked hexamer known as α-6T, are under consideration as the semiconducting, hole-transporting materials in various organic-based devices,[1] especially thin-film transistors (TFTs).[2] These devices are prepared using simpler, lower-temperature deposition techniques than are used for silicon-based analogues, and the mechanical properties of the organic devices are compatible with plastic substrates. Seminal work on oligothiophene semiconductors and their use in flexible transistor arrays has been reported by Garnier and his collaborators.[2] The important figures of merit, field effect mobility and on/off ratio, are 0.001 cm²/Vs and 10 000, respectively, in α-6T devices fabricated at room temperature, although higher values have been obtained by using heated substrates. We recently described improvements in these values, achieved via new preparative and fabrication methods, to exceed 0.01 cm²/Vs in mobility and 10⁶ in on/off ratio.[3] While this on/off ratio is sufficient for many applications, it is generally recognized that at least another factor of 10 increase in mobility will be required before organic-based TFTs can be practical. Indeed, the Garnier group succeeded in raising the mobility of α-6T to 0.05 cm²/Vs by affixing hexyl substituents to the 5 and 5'''' carbons and inducing self-assembly of the semiconductor films.[4] The increased

mobility may be attributed to the larger crystalline domain sizes in the deposited films[5] and/or to the greater purity of dihexyl-α-6T (DH-α-6T) compared to the conventionally synthesized unsubstituted compound.

DH-α-6T is made by the dimerization of 5-hexyl-α-terthiophene (H3T). The reported[4] synthesis of this educt, while direct, has certain drawbacks. The sequence depends upon the availability of 2-alkylthiophenes as starting materials and proceeds through intermediates and byproducts that are difficult to separate chromatographically from reagents and targets. Here we describe an alternative synthesis of H3T that proceeds through carbonyl intermediates that are easily separable by chromatography from other reaction components, resulting in purer substituted terthiophenes. The synthesis is generalizable to a wide variety of substituents, starting with commercially available α-terthienyl (α-3T). As an example, we additionally report the synthesis of 5-hexylthio-α-terthiophene (HT3T) and its dimerization to DHT-α-6T. We had hoped that the thio-substituted compounds would have been useful in distinguishing assembly, electronic effects, chemical purity, and stability as variables in the performance of thiophene oligomer films in transistors.

Experimental Section

All procedures were performed under nitrogen. THF was distilled from Na benzophenone ketyl.

2-Hexanoylterthiophene. To a −78 °C solution of 4.0 g (16 mmol) α-terthiophene in 150 mL of THF was added 16 mmol of n-BuLi in hexane over 10 min. After 20 more min. stirring at −78 °C, 4.0 g (15.5 mmol) of MgBr₂-Et₂O was added. The cooling bath was removed. When the suspended solids dissolved, the solution was added to a second solution containing 2.2 g (16 mmol) of hexanoyl chloride (freshly distilled from

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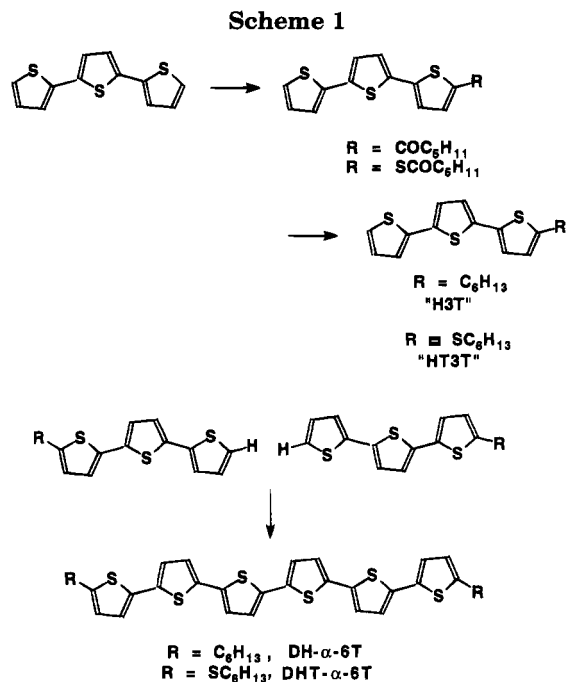[®] Abstract published in *Advance ACS Abstracts*, November 15, 1995.

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Scheme 1

Figure 1. DSC trace for DH-α-6T. The heating rate was 10 °C/min, under N_2.

Results

Synthesis of Thiophene Trimers. The syntheses of H3T and HT3T are shown in Scheme 1. Common to both sequences is a carbonyl intermediate, a ketone or thioester, respectively, that is much more polar than either the α-terthienyl starting material or the nonpolar substituted targets, facilitating purification by column chromatography.

Use of $MgBr_2$ and Li_2MnCl_4 catalyst in the ketone synthesis produced a much cleaner product than directly coupling the lithium reagent, the latter giving erratic yields of <30% due to formation of (α-3T)$_2$RCOH and (α-3T)$_2$C=CHR byproducts. Dihexanoyl-α-3T is also more readily formed in the Li-only system, probably due to facile metal exchange between α-3T-Li and H3T. The addition of α-3T-Li to hexanonitrile was unsuccessful as were the reactions of α-3T-CuLiPR$_3$ complexes with hexanoyl chloride.

The preparation of HT3T was routine, as long as the deprotected thiol or thiolate intermediates were handled as solutions under N_2. In principle, any carboxylic acid chloride could be used to make the thioester; however, diethyl chlorophosphate did not react cleanly with the thiolate.

Dimerization of Thiophene Trimers. We have previously compared $CuCl_2$ and Fe(acac)$_3$ as reagents for oxidatively coupling unsubstituted α-3T-Li[3] and found the latter to be advantageous, because of the avoidance of chlorination at the metallated carbon. However, because of the lesser reactivity of Fe(acac)$_3$, the coupling proceeds at a higher temperature, in a regime where Li–H exchange can occur. Since the hexyl groups at H3T and HT3T possess labile α-hydrogens, Fe(acac)$_3$ is less suitable for coupling these compounds. We therefore employed $CuCl_2$, as described previously,[4] but without TMEDA. Chlorinated side products were observed but were removed by recrystallization from xylene and gradient sublimation. The melting transition of our DH-α-6T is at a higher temperature than the literature value and comprises three endothermic events, as shown in Figure 1, evidence of mesophase formation. This is not surprising, in view of the liquid-crystal-like design of the molecule. DHT-α-6T behaved similarly, with transition temperatures of 290, 298, and 318 °C.

N,N-diethylaniline) and 1 mmol of Li_2MnCl_4[6] in 40 mL of THF at 0 °C, over 30 min. The mixture was kept at 0 °C for 1 h and then allowed to warm to room temperature overnight. Ether or toluene was added, and the solution was washed with dilute HCl and dilute $NaHCO_3$, dried, filtered, and concentrated. The crude material was dissolved in hot toluene, applied to a 70 g silica gel column, and eluted with hexane–CH_2Cl_2, yielding 2.0 g (36%) of product (42% based on recovered α-3T) as a bright, fluorescent yellow solid. NMR (CDCl$_3$) δ 0.88 (t), 1.35 (m), 1.75 (m), 2.87 (t), 7.01–7.25 and 7.58 (2 AB + ABC, ArH). Anal. Calcd for C$_{18}$H$_{18}$OS$_3$: C, 62.4; H, 5.2; S, 27.8. Found C, 62.2; H, 5.4, 5, 27.0.

2-Hexylterthiophene. A sample of 1.06 g of 2-hexanoyl-terthiophene was dissolved in 30 mL of freshly opened anhydrous toluene. This was added to a stirred suspension of 0.79 g of AlCl$_3$ and 0.91g of LiAlH$_4$[7] in 200 mL of ether. After 1 h, the excess reagents were quenched by the addition of 12 mL of EtOAc and 4 mL of concentrated aqueous HCl. The solution was filtered, concentrated, dissolved in warm toluene, and eluted through 20 g of silica gel with hexane. The yield was 0.81 g (80%) of light yellow solid. NMR (CDCl$_3$) δ 0.88 (t), 1.25–1.4 (m), 1.65 (quint), 2.78 (t), 6.67 and 6.96–7.20 (2 AB + ABC, ArH).

2-Hexanoylthioterthiophene. A solution of 4.0 g of α-3T in THF was lithiated as described above and added to a suspension of 0.51 g of sulfur in 40 mL of THF, at −78 °C. After warming to room temperature and stirring for 1.5 h, the resulting red solution was cooled to −78°C and treated with 2.2 g of freshly distilled hexanoyl chloride. After warming to room temperature overnight, the mixture was partitioned between ether and dilute HCl. The organic layer was washed with dilute $NaHCO_3$, dried, filtered, and concentrated to 5.4 g. Chromatography on 90 g of silica gel, eluting with CH_2Cl_2–hexane, gave 2.6 g (43%). NMR (CDCl$_3$) δ 0.88, 1.32, 1.71 (3m), 2.67 (t), 6.99–7.22 (2 AB + ABC, ArH).

2-Hexylthioterthiophene. Hexanoylthioterthiene (1.05 g) was added to 60 mL of THF and 1.5 mL of H_2O, followed by 3 mL of 55% Bu$_4$NOH in H_2O. The solution turned red. Hexyl iodide (0.6 mL) was added after 15 min to titrate the color. Partition between ether and H_2O, followed by chromatography as for hexylterthiophene gave 0.86 g (85%), NMR (CDCl$_3$) δ 0.88 (t), 1.3, 1.4, 1.6 (3 m), 2.88 (t), 6.98–7.22 (2 AB + ABC, ArH). Anal. Calcd for C$_{18}$H$_{20}$S$_4$: C, 59.4; H, 5.5; S, 35.2. Found: C, 59.2; H, 5.5; S, 35.1.

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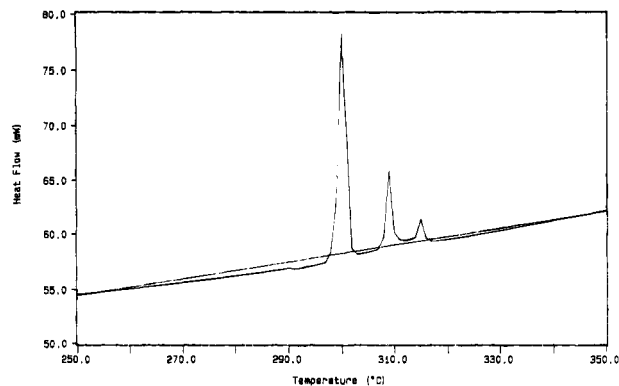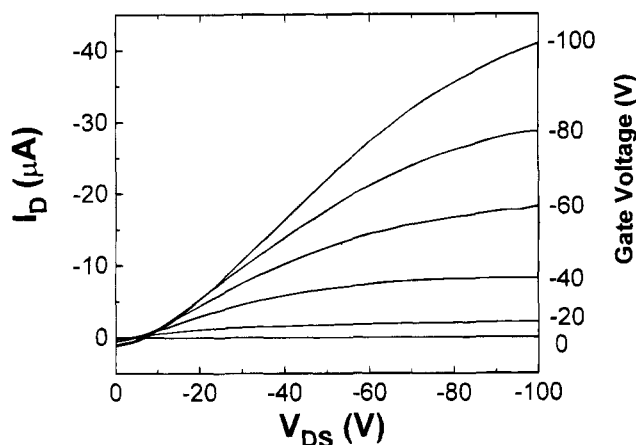(7) Nystrom, R. F.; Berger, C. R. A. *J. Am. Chem. Soc.* **1958**, *80*, 2896.

Figure 2. Transistor characteristics for DH-α-6T, 500 Å on SiO₂/Si, annealed at 195 °C. The gate length was 12 μm. The gate oxide was 300 nm thick.

End-Substituted Thiophene Hexamers in TFTs. TFTs with SiO_2 gate dielectrics and possessing a structure previously described[3,8] were fabricated from DH-α-6T and DHT-α-6T and characterized. The gate widths were 250 μm, and the gate lengths were between 4 and 25 μm. Au and Au/Pt were used as the source/drain electrodes. The high work function of Pt is expected to improve the injection of holes into the active material. As-fabricated TFTs with Au contacts and DH-α-6T active layers sometimes show low mobilities (<10⁻³ cm²/V s), which improve to about 0.03−0.04 cm²/V s following a short anneal at 100−250 °C. The anealing may drive impurities away from the semiconductor−dielectric interface, increase the sizes of continuous crystalline domains, and/or improve the adhesion of the semiconductor to the dielectric. The device characteristics are shown in Figure 2. The higher mobility is of the same magnitude as that reported previously, indicating that, unlike the case of α-6T, differences in the nature and amounts of impurities in DH-α-6T prepared by the CNRS and AT&T groups have not led to differences in mobility. The enhancement due to the hexyl substitution compared to our α-6T is approximately a factor of 2, while an additional order of magnitude increase over the previously described[4,5] α-6T may be attributed to improved purity. In some devices with Au

contacts and in all the devices with Au/Pt contacts, the anneal is not necessary to achieve a high mobility. The *off* current (drain-source current at zero gate-source bias) is high in comparison with α-6T TFTs. Enhancement-mode on/off ratios of ∼10 were common, because of the large off current. In some cases, enhancement mode on/off ratios of ∼1000 were achieved. Running the devices in depletion mode (negative gate bias) lowers the source-drain current to a point that *on/off* ratios > 10⁶ for combined enhancement/depletion mode operation have been attained, far higher than previously reported.[4]

When TFTs were fabricated with DHT-α-6T active layers, the off currents were high, and the shape of the current−voltage characteristics indicate that this material breaks down at lower electric fields in comparison with α-6T and DH-α-6T. The mobility estimated from the characteristics was about 2 orders of magnitude lower than that of α-6T. There was no evidence of drain current saturation. This may have been due to a higher doping level in these more electron-rich films causing a very high off-conductivity or decomposition of the more labile side chain during sublimation or TFT fabrication. Even at a level insignificant when determined by combustion analysis, such decomposition could deteriorate TFT performance.

Conclusions

New, generalizable syntheses of monosubstituted thiophene trimers have been developed, and disubstituted hexamers synthesized therefrom with a high degree of purity. DSC evidence of mesophase behavior has been observed in the hexamers. Mobilities obtained from DH-α-6T are in agreement with literature values. There is no sign that the easier hole injection that might have resulted from using the more electron-rich derivative DHT-α-6T was at all useful. It is therefore likely that the higher on-currents observed in DH-α-6T relative to the unsubstituted compound are in fact due to morphological, rather than hole energy level, differences.

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