

# An Efficient Synthesis of Symmetrical Oligothiophenes: Synthesis and Transport Properties of a Soluble Sexithiophene Derivative

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We report a new approach for the synthesis of symmetrical oligothiophenes based on a highly efficient palladium-catalyzed Ullmann coupling reaction. This synthetic route enables the simple preparation of substituted oligothiophenes with a wider range of functionalities and in higher yield compared to previously reported syntheses. We demonstrate our procedure by preparing a novel, highly soluble  $\alpha,\omega$ -substituted sexithiophene, dibutylphosphonate- $\alpha$ -sexithiophene (DBP- $\alpha$ -6T). We present spectroscopic characterization of this compound in solution and solution cast thin films. Thin film transistors (TFTs) fabricated using solution cast thin films of DBP- $\alpha$ -6T as the p-type semiconducting channel have high on/off ratios, demonstrating the utility of this synthetic approach in the preparation of highly pure materials for solution-deposited organic electronic devices.

## Introduction

Current demand for low-cost, lightweight, and flexible electronic devices relies on the development of soluble semiconducting materials that can be used in solution-based fabrication schemes such as spin-coating, dip-coating, ink-jet printing, and screen printing. Organic thin film transistors (TFTs) have attracted much attention in the past decade for large area applications where high switching speeds are not required. Field-effect mobilities of up to 0.1 cm<sup>2</sup>/(V s) have been achieved for several thiophene-based conjugated organic materials,<sup>1,2</sup> and integrated electronic devices based on organic semiconductors using printing techniques have been demonstrated.<sup>3–5</sup> For further development of this field and realization of the potential of organic-based devices in low-cost and large area electronic components, availability of soluble organic semiconductors in sufficient purity is essential. The synthesis of soluble organic semiconductors, however, remains challenging due to the limited number of synthetic methods suitable for the preparation of conjugated systems. Therefore, it is necessary to devise new synthetic chemistry for the preparation of a range of processable and highly pure organic semiconductors that have high carrier mobilities and current modulation ( $I_{ON}/I_{OFF}$ ) for use as channel materials in TFTs.

Many of the approaches to date have focused on synthetic routes to soluble derivatives of thiophene polymers and oligomers. Regioregular poly(3-hexylthiophene) (P3HT) is among the best known polymeric semiconductors and has been widely used as the semi-

conducting channel material in the fabrication of TFTs by solution-based processes.<sup>6–8</sup> Although TFT devices using P3HT as the semiconducting channel have shown modest carrier mobilities (up to 0.05 cm<sup>2</sup>/(V s)), the on/off ratio suffers from the presence of intractable impurities, introduced by polymerization catalyst, and partial doping of the material in air. Use of thiophene oligomers overcomes this problem, and on/off ratios of up to 10<sup>6</sup> have been reported for sexithiophene and its alkylated derivatives.<sup>9,10</sup> High on/off ratios require materials of high purity and free of any inorganic residue that is usually present in various coupling reactions employed in the synthesis of oligothiophenes.<sup>11</sup> Oligothiophenes with five or more rings have limited solubility in organic solvents, and consequently purification of these compounds is always tedious, often requiring repeated column chromatography and/or gradient sublimation. Therefore, synthesis of soluble oligothiophenes not only is desirable for solution processing and large area applications but also is crucial to obtain the highly pure compounds necessary for electronic applications. The common approach for solubilization of oligothiophenes has been substitution of alkyl chains of varying length on thiophene rings. Introduction of alkyl chains on middle rings of oligothiophenes greatly increases their solubility, but steric hindrance introduced by the alkyl chains reduces oligomer planarity and makes close packing of the molecules more difficult, resulting in poor device performance. The effect of alkyl substitution on the terminal rings ( $\alpha$  and  $\omega$  positions) of oligothiophenes

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on their solubility is not significant to make them useful for solution processing at room temperature. The only other alternative is the introduction of polar functional groups like hydroxy, carboxyl, phosphonate esters, etc., to enhance solubility. Unfortunately, most of the synthetic methods commonly used for the preparation of oligo- and polythiophenes<sup>11</sup> are not tolerant of polar functionalities. Introduction of these functionalities requires protection and deprotection that complicates the synthesis.

In this paper, we present a new approach to the synthesis of soluble oligothiophene derivatives based on an improved Ullmann coupling of  $\alpha$ -bromo-substituted terthiophene derivative. The exceptional functional group tolerance of this reaction allows the incorporation of reactive polar functionalities. We demonstrate the effectiveness of this method by synthesizing a highly soluble, functionalized sexithiophene compound, dibutylphosphonate- $\alpha$ -sexithiophene (DBP- $\alpha$ -6T), not easily accessible by established synthetic methods. We use solution-based deposition techniques, namely spin-coating, to fabricate TFTs with DBP- $\alpha$ -6T as the semiconducting channel material.

### Experimental Section

All chemicals were purchased from Aldrich Chemical Co. and used as received. Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN. Melting points and thermal transitions were measured on a Dupont differential scanning calorimeter (DSC). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on 250 and 400 MHz Bruker spectrometers, and chemical shifts are reported in ppm downfield of TMS. UV-vis absorption spectra were collected on an HP8453 diode array spectrometer.

**Diethyl-4-(2-thienyl)butylphosphonate (2).** A solution of 1-bromo-4-(2-thienyl)butane (**1**)<sup>12</sup> (4.58 g, 0.02 mol) in 20 mL of triethyl phosphite was heated at 160 °C for 20 h, with nitrogen bubbling directly into the solution. The solution was cooled to room temperature, and 50 mL of water was added; the resulting mixture was stirred for 4 h. The product was extracted with carbon tetrachloride. The organic layer was separated, washed with brine, and dried over anhydrous magnesium sulfate. Evaporation of the solvent yielded an oily residue that was distilled under vacuum (0.12 mmHg, 135 °C) to give **2** as a colorless oil (6.0 g, 82%). <sup>1</sup>H NMR (250 MHz, 25 °C, CDCl<sub>3</sub>):  $\delta$  7.06 (m, 1H, Ar-*H*), 6.85 (m, 1H, Ar-*H*), 6.72 (m, 1H, Ar-*H*), 4.03 (m, 4H, POCH<sub>2</sub>CH<sub>3</sub>), 2.79 (t, 2H, Ar-CH<sub>2</sub>), 1.72 (m, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>P), 1.26 (t, 6H, POCH<sub>2</sub>CH<sub>3</sub>).

**Diethyl-4-(2-bromothieryl)butylphosphonate (3).** *N*-Bromosuccinimide (1.78 g, 0.01 mol) was added portionwise to a solution of **2** (2.78, 0.01 mol) in dimethylformamide (DMF) (20 mL), and the solution was stirred at room temperature overnight. Diethyl ether (50 mL) was added to the reaction mixture, and then the mixture was washed twice (50 mL each) with water, washed once with brine, and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave **3** as a light yellow oil (3.2 g, 87%) which was used without further purification in the next step. <sup>1</sup>H NMR (250 MHz, 25 °C, CDCl<sub>3</sub>):  $\delta$  6.80 (d, 1H, Ar-*H*), 6.49 (d, 1H, Ar-*H*), 4.03 (m, 4H, POCH<sub>2</sub>CH<sub>3</sub>), 2.72 (t, 2H, Ar-CH<sub>2</sub>), 1.67 (m, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>P), 1.27 (t, 6H, POCH<sub>2</sub>CH<sub>3</sub>).

**4-[5-(2,2':5',2''-Terthienyl)]butane-1-phosphonic Acid Diethyl Ester (5a).** 5-Tri-*n*-butylstannyl-2,2'-bithiophene (**4**) (4.54 g, 0.01 mol) was added to a solution of **3** (3.55 g, 0.01 mol) in anhydrous DMF (30 mL) under a nitrogen atmosphere. To this solution was added 500 mg of bis(triphenylphosphine)-palladium(II) chloride, and the mixture was heated to 60 °C for 3 h and then stirred at room temperature for 20 h. Diethyl

ether (100 mL) was added, and the mixture was washed several times with water and then with brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a yellow-orange solid residue that was purified by chromatography on a column of silica gel. Elution with ethyl acetate gave, after evaporation of the solvent, an orange solid (3.0 g, 83%). Crystallization from hexane afforded analytically pure **5a**; mp = 92 °C. <sup>1</sup>H NMR (250 MHz, 25 °C, CDCl<sub>3</sub>):  $\delta$  7.16–6.94 (m, 6H, Ar-*H*), 6.66 (m, 1H, Ar-*H*), 4.08 (m, 4H, POCH<sub>2</sub>CH<sub>3</sub>), 2.79 (t, 2H, Ar-CH<sub>2</sub>), 1.75 (m, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>P), 1.29 (t, 6H, POCH<sub>2</sub>CH<sub>3</sub>). Calcd for C<sub>20</sub>H<sub>25</sub>O<sub>3</sub>PS<sub>3</sub>: C, 54.44; H, 5.68; S, 21.81. Found: C, 53.86; H, 6.02; S, 21.95.

**4-[5''-Bromo-5-(2,2':5',2''-terthienyl)]butane-1-phosphonic Acid Diethyl Ester (5b).** *N*-Bromosuccinimide (356 mg, 2 mmol) was added portionwise to a solution of terthiophene phosphonate **5a** (880 mg, 2 mmol) in 10 mL of anhydrous DMF. After completion of the addition, the reaction mixture was stirred at room temperature for an additional 5 h. Ether (50 mL) was added, and the precipitate was filtered and washed with 1:1 ether-hexane mixture and dried. Crystallization from 2:1 ether-hexane afforded analytically pure brominated terthiophene **5b** (820 mg, 79%) as yellow needles; mp = 114–115 °C.

**Phosphonic Acid, [5,5''''-(2,2':5'2'':5',2''':5''',2''''':5''''',2''''''-Sexithiophenedi-4,1-butanediyl)]bis(tetraethyl) Ester 6 (DBP- $\alpha$ -6T).** A solution of palladium acetate (20 mg, 0.09 mmol) and tri-*p*-tolylphosphine (30 mg, 0.1 mmol) in anhydrous DMF (10 mL) was added to a mixture of 5-bromo-2,2':5',2''-terthienylbutylphosphonate (**5b**) (870 mg, 1.67 mmol), hydroquinone (160 mg, 1.4 mmol), and cesium carbonate (700 mg, 2.1 mmol), and the mixture was deaerated by three freeze-thaw cycles and backfilled with nitrogen. The mixture was then heated at 70 °C for 4 h, cooled to room temperature, and then stirred further for 20 h. The dark orange solid was separated by filtration, washed several times with diethyl ether, and dried in vacuo. Crystallization from 1,2-dichlorobenzene afforded **6** as a bright red-orange microcrystalline product (900 mg, 62%); mp = 245–246 °C. <sup>1</sup>H NMR (400 MHz, 25 °C, CDCl<sub>3</sub>):  $\delta$  7.04 (m, 6H, Ar-*H*), 6.97 (m, 4H, Ar-*H*), 6.66 (m, 2H, Ar-*H*), 4.05 (m, 8H, -POCH<sub>2</sub>-CH<sub>3</sub>), 2.8 (t, 4H, Ar-CH<sub>2</sub>), 1.6–1.8 (m, 12H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>) and 1.29 (t, 12H, -POCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, 25 °C, CDCl<sub>3</sub>):  $\delta$  144.9 (s, quat), 137.3 (s, quat), 136.6 (s, quat), 136.2 (s, quat), 135.6 (s, quat), 135.1 (s, quat), 125.6 (s, arom CH), 124.8 (s, arom CH), 124.7 (s, arom CH), 124.6 (s, arom CH), 124.1 (s, arom CH), 123.9 (s, arom CH), 61.9 (d, |*J*| = 6.5 Hz, POCH<sub>2</sub>), 32.7 (d, |*J*| = 16.3 Hz, CH<sub>2</sub>), 30.1 (s, CH<sub>2</sub>-Ar), 25.9 (d, |*J*| = 140.3 Hz, CH<sub>2</sub>P), 22.3 (d, |*J*| = 5.1 Hz, CH<sub>2</sub>), 16.9 (d, |*J*| = 5.9 Hz, POCH<sub>2</sub>CH<sub>3</sub>). Calcd for C<sub>40</sub>H<sub>48</sub>O<sub>6</sub>P<sub>2</sub>S<sub>6</sub>: C, 54.67%; H, 5.46; S, 21.86. Found: C, 54.10; H, 5.72; S, 22.03.

**Device Fabrication.** Device test structures were fabricated on highly doped silicon wafers, which served as the gate electrode, with 500 nm thermally grown SiO<sub>2</sub>, that forms the gate insulator. Gold source and drain electrodes were deposited on the SiO<sub>2</sub> surface by e-beam evaporation through a silicon membrane shadow mask used to define the width and length of the transistor channel. Thin films of sexithiophene derivative **6** were deposited on top of these test structures, forming a bottom contact TFT geometry (Figure 4), by spin-coating dilute solutions (2–5 mg/mL) of DBP- $\alpha$ -6T from a variety of chlorinated solvents at 2000 rpm for 1 min. The samples were deposited in a nitrogen box and annealed on a digital hot plate held at various temperatures for 5 min to study the effects of postdeposition curing on device performance. Current/voltage characteristics were measured in a nitrogen atmosphere using an HP4156 semiconductor parameter analyzer.

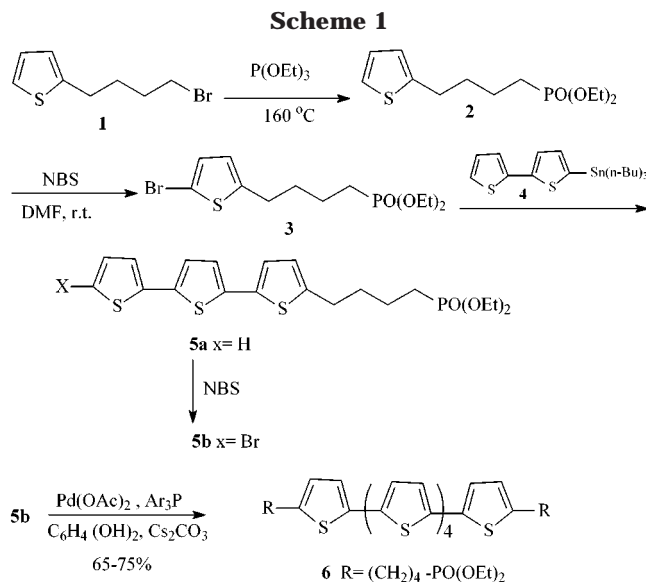
### Results and Discussion

**Synthesis.** The most common approach for the synthesis of sexithiophene and its derivatives has been lithiation of the corresponding terthiophenes, followed by copper-catalyzed oxidative coupling of the lithiated

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species.<sup>13</sup> This approach has two drawbacks. First, ring-chlorinated compounds are always formed as byproducts, and their separation from the desired products is very difficult and often requires column chromatography and/or gradient sublimation. Second, use of alkyllithium for lithiation of the thiophene ring excludes the presence of reactive polar groups such as carboxylic acids, esters, amines (including the majority of protected amines), and any other functionality that reacts with alkyllithium, including the phosphonate groups used in this paper. This particular limitation has been a major road block in the synthesis of oligothiophenes having polar functionalities as evidenced by the paucity of the reported derivatives. A second approach for the preparation of oligothiophenes is the McCullough<sup>14</sup> coupling of lithiated (or Grignard) thiophene monomers with bromo- or iodothiophenes in the presence of a nickel catalyst. In addition to the formation of undesired self-coupling products of halogenated thiophenes and/or lithiated (or Grignard) reagents, this reaction also limits the nature of functional groups that can be present in the starting thiophene derivatives due to the presence of the highly reactive aryllithium or Grignard reagents. Finally, a third synthetic approach is Stille coupling<sup>15</sup> of trialkyltin-substituted thiophenes with bromothiophenes, which has recently been used in the preparation of several oligothiophenes. Stille coupling is a versatile synthetic tool that is carried out at moderate temperatures, resulting in moderate yields of coupling products. It is tolerant of many polar groups and has been used in the synthesis of substituted sexithiophenes with reactive polar functionalities, including carboxylic esters and aldehydes.<sup>16</sup> However, this synthetic approach has several drawbacks. It employs highly toxic organotin reagents, and side products such as self-coupling products of tin compounds are formed which require tedious purification often using repeated column chromatography to obtain pure products.

Our strategy for the introduction of a polar functionality, the phosphonate ester group which was known to us to impart high solubility, was to construct the diphosphonate-substituted sexithiophene DBP- $\alpha$ -6T (**6**) from Ullmann coupling of monophosphonate terthiophene **5b**. Ullmann coupling of aryl halides has been known for more than a century, and in its original form aryl halides were heated at high temperature in the presence of copper powder. Although Ullmann coupling is tolerant of a variety of polar functionalities, the yield of symmetrical biaryls is very low. A recent report on a high yielding, palladium-catalyzed reductive coupling of aryl iodides and bromides<sup>17</sup> prompted us to extend the application of this method to the synthesis of oligothiophenes and specifically to sexithiophene derivative DBP- $\alpha$ -6T (**6**). Therefore, bromoterthiophene phosphonate (**5b**) was synthesized in 40% overall yield starting



from 1-bromo-4-(2-thienyl)butane (**1**)<sup>12</sup> as shown in Scheme 1. Arbuzov<sup>18</sup> reaction of the 1-bromo-4-(2-thienyl)butane (**1**) with triethyl phosphite proceeded to give the phosphonate ester **2** in more than 90% yield. NBS bromination of **2**, followed by Stille coupling with tri-*n*-butylstannylbithiophene (**4**),<sup>19</sup> afforded, after chromatography, terthiophene butylphosphonate (**5a**).  $\alpha$ -Bromination of terthiophene **5a** with NBS at room temperature gave **5b** in quantitative yield. Following the procedure of Rawal et al., Ullmann coupling of **5b**, catalyzed by palladium acetate and tri-*p*-tolylphosphine, was carried out at 80 °C in DMF, and upon cooling the reaction mixture the desired sexithiophene derivative DBP- $\alpha$ -6T **6** was precipitated from the reaction mixture as a brown-red powder. There are no detectable side products in this reaction, and highly soluble unreacted starting materials are the only impurities present. Filtration and crystallization from dichlorobenzene afforded analytically pure DBP- $\alpha$ -6T **6** as bright orange crystalline compound in 65–70% yield. The ease of purification of the products combined with the accessibility of  $\alpha$ -bromothiophene oligomers and moderately high yield makes this reaction very useful for the preparation of symmetrical oligothiophenes substituted with a variety of reactive functional groups.

We characterized DBP- $\alpha$ -6T **6** by NMR and UV–vis spectroscopy. The proton NMR spectrum, shown in Figure 1, is consistent with the molecular structure of DBP- $\alpha$ -6T **6**, does not show evidence of impurities, and integrates accordingly. To our knowledge, this is the first reported example of a solution NMR spectrum of an  $\alpha,\omega$ -substituted sexithiophene. The UV–vis absorption spectrum of DBP- $\alpha$ -6T **6** (Figure 3) in chloroform shows the main absorption maximum at  $\lambda_{\max} = 442$  nm, consistent with reported values for the  $\pi$ – $\pi^*$  transition in dispersed, unsubstituted, and planar sexithiophene oligomers.<sup>20</sup> The absorption spectrum for the spin-coated thin film shows one higher energy absorption resonance at 425 nm and two lower energy resonances at 476 and 519 nm as the absorption band of isolated 6T is split

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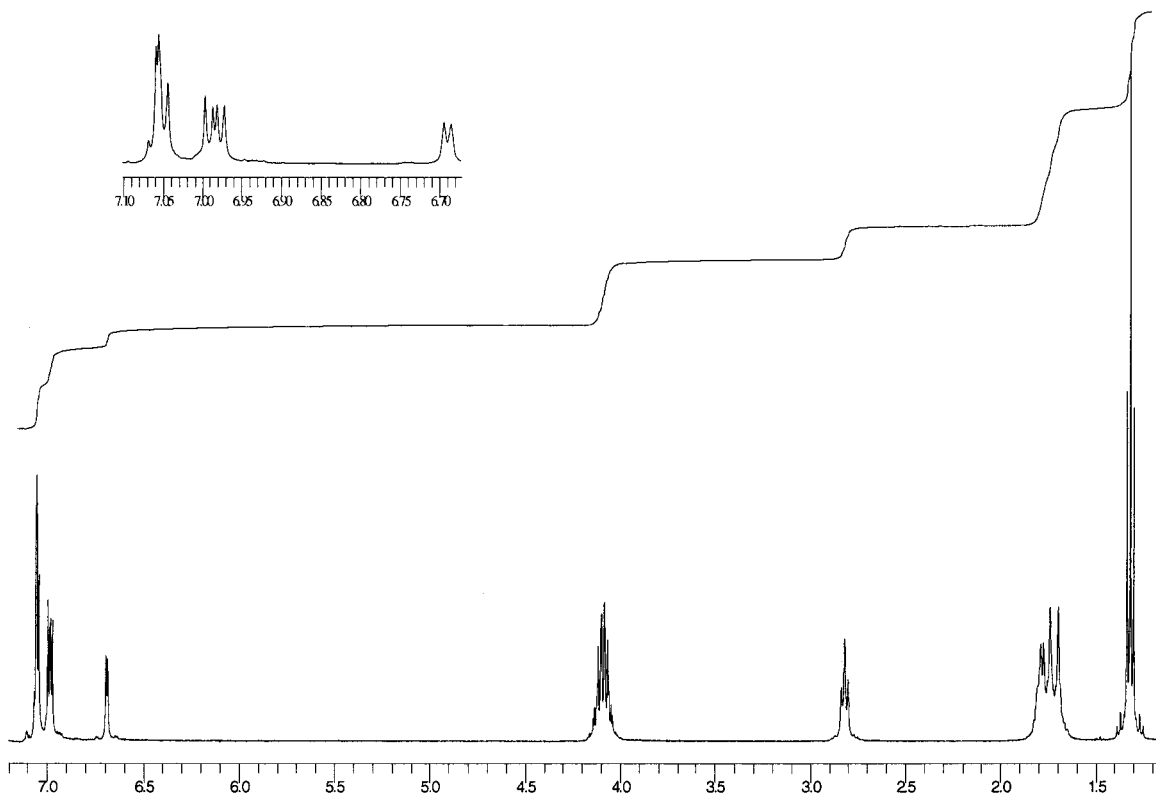
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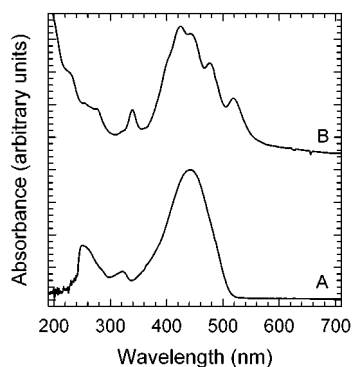
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**Figure 1.**  $^1\text{H}$  NMR spectrum of DBP- $\alpha$ -6T **6** in  $\text{CDCl}_3$ . Inset: aromatic region.

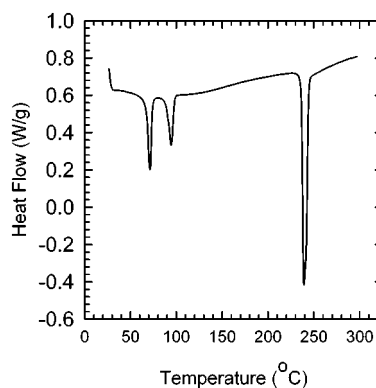


**Figure 2.** UV-vis absorption spectrum for DBP- $\alpha$ -6T **6** (a) in chloroform and (b) thin solid film.

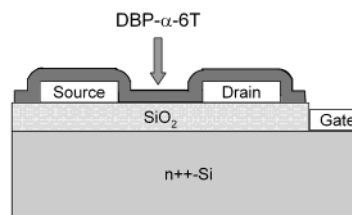
due to aggregation and/or electron-phonon coupling in the solid state.<sup>21</sup>

Differential scanning calorimetry of DBP- $\alpha$ -6T **6** (Figure 3) shows two thermal transitions at 78 and 99 °C. Since polarized light microscopy at elevated temperature (25–120 °C) did not reveal any mesophase, it was concluded that these two transitions are simply due to two different crystalline phases of DBP- $\alpha$ -6T **6**. A sharp melting point at 284 °C is also present in the DSC.

**Thin Film Transistors.**  $I$ - $V$  characteristics for a TFT (device geometry shown in Figure 4) having DBP- $\alpha$ -6T **6** as the semiconducting channel are shown in Figure 5. Plots of drain current,  $I_D$ , vs source-drain voltage,  $V_{DS}$ , as a function of the applied gate voltage,  $V_G$ , inset in Figure 5, show DBP- $\alpha$ -6T **6** forms a typical p-channel transistor operating in accumulation mode. These devices are adequately modeled by the standard



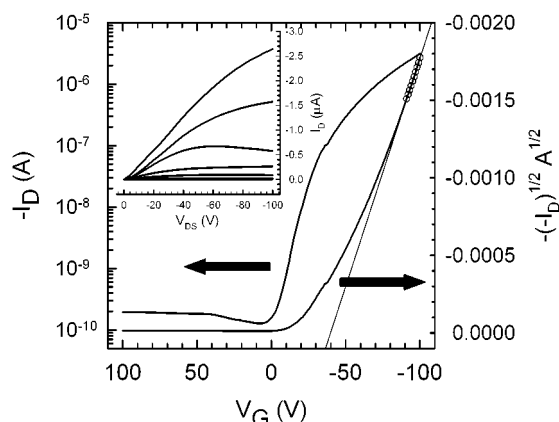
**Figure 3.** Differential scanning calorimetry (DSC) curves of DBP- $\alpha$ -6T **6**, heated at 10 °C/min.



**Figure 4.** Device geometry used for fabrication of TFT devices.

equations for field-effect transistors. Field-effect mobility ( $\mu$ ) and current modulation ( $I_{ON}/I_{OFF}$ ) are calculated in the saturation regime from  $I_D^{1/2}$  vs  $V_G$  and  $I_D$  vs  $V_G$ , respectively (Figure 5). For the device shown  $\mu$  is  $4 \times 10^{-3} \text{ cm}^2/(\text{V s})$  and  $I_{ON}/I_{OFF} > 10^4$ . The off current is limited by leakage to the gate electrode as the material was not patterned sufficiently to eliminate that current path as evidenced by current on the gate. The  $I$ - $V$  characteristics are representative of devices fabricated by spin-coating DBP- $\alpha$ -6T **6** from chloroform and an-

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**Figure 5.** Plots of drain current,  $I_D$ , vs gate voltage,  $V_G$ , and (inset)  $I_D$  vs source-drain voltage,  $V_{DS}$ , for a TFT device having DBP- $\alpha$ -6T as the semiconducting channel. Channel length ( $L$ ) = 15.4  $\mu\text{m}$  and channel width ( $w$ ) = 1000  $\mu\text{m}$ .

**Table 1. Dependence of the I–V Characteristics on Carrier Solvent<sup>a</sup>**

solvent	mobility ( $\text{cm}^2/(\text{V s})$ )	$I_{ON}/I_{OFF}$
dichloromethane	$5 \times 10^{-4}$	6000
chloroform	$3.9 \times 10^{-3}$	16250
1:1 chloroform:tetrachloroethylene	$2.8 \times 10^{-3}$	15800
tetrachloroethane	$3.8 \times 10^{-4}$	3300

<sup>a</sup> All films are spun at 2000 rpm for 60 s and annealed at 100 °C for 5 min.

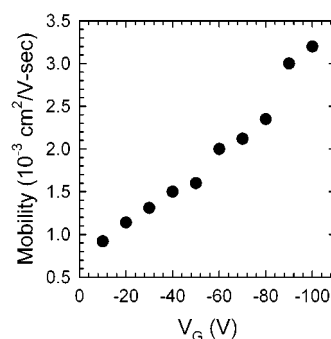
**Table 2. Dependence of the I–V Characteristics on the Postdeposition Anneal Temperature<sup>a</sup>**

anneal temp (°C)	mobility ( $\text{cm}^2/(\text{V s})$ )	$I_{ON}/I_{OFF}$
60	$1 \times 10^{-4}$	2025
80	$2.3 \times 10^{-3}$	19 800
90	$2.1 \times 10^{-3}$	18 600
110	$1.3 \times 10^{-3}$	11 600
120	$1 \times 10^{-3}$	9400

<sup>a</sup> All films are spun at 2000 rpm for 60 s from chloroform and annealed for 5 min.

nealing the film at 100 °C for 5 min. While the example shown was measured in a  $\text{N}_2$  box, similar characteristics, within the sample-to-sample variability, were measured in air.

We fabricated devices by spin-coating DBP- $\alpha$ -6T **6** from dichloromethane, chloroform, tetrachloroethane, or 1:1 chloroform:trichloroethylene onto device test structures. Field-effect mobility and  $I_{ON}/I_{OFF}$  were measured after annealing the films, at various temperatures below, between, and above the two phase transitions measured by DSC, and cooling to room temperature. As shown in Table 1, chloroform-containing solutions formed films having the best device characteristics and visibly the smoothest appearance. While data for DBP- $\alpha$ -6T **6** spun from chloroform are reported, the same trend was observed for the other chlorinated solvents. Table 2 shows the effects of postdeposition curing on the mobility of TFTs having DBP- $\alpha$ -6T **6** as the semiconducting channel. The mobility is negligible without postdeposition annealing. The mobility increases as the substrate is heated to 60 °C and especially after heating to 80 °C, which is just above the first phase transition temperature shown in DSC (Figure 3). Curing the TFTs to temperatures between the first and second phase transition (between 80 and 100 °C) does not affect the device performance (field-effect mobility and  $I_{ON}/I_{OFF}$ ). Further



**Figure 6.** Field dependence of TTF with DBP- $\alpha$ -6T **6** as active semiconducting channel.

heating the substrate above 100 °C, the second thermal transition, reduces the device  $\mu$  and  $I_{ON}/I_{OFF}$ , and by 200 °C the mobility is reduced to near zero.

Figure 6 shows the field-dependent mobility ( $\mu$  vs  $V_G$ ) for DBP- $\alpha$ -6T **6**. The field-effect mobility shows the same increase with increasing applied gate voltage as has been observed more generally for organic TFTs.<sup>22</sup> The increase in mobility is attributed to a filling of traps as carriers move with mobilities more characteristic of the intrinsic semiconductor with increasing applied gate voltage. While organic TFTs often show a saturation in mobility at high applied gate voltages, DBP- $\alpha$ -6T **6** does not saturate up to  $\pm 100$  V (note: devices are fabricated with a 5000 Å gate oxide). This suggests that even at high applied gate voltage we do not fill all of the traps. Reducing traps, whether in the bulk or at interfaces, may enable higher mobilities to be achieved in this material.

In addition to field-effect mobility the second yardstick for evaluation of semiconductors is the current modulation ( $I_{ON}/I_{OFF}$ ). For vacuum-deposited films of sexithiophene ( $\alpha$ -6T) or dihexyl- $\alpha$ -6T,  $I_{ON}/I_{OFF}$  is in the range  $10^5$ – $10^6$ , but for solution cast films of regioregular poly-(3-alkylthiophene)  $I_{ON}/I_{OFF}$  is significantly reduced to less than few hundred. In the case of solution cast, unpatterned thin films of DBP- $\alpha$ -6T **6**, the on/off ratio was consistently measured greater than  $10^4$ , indicative of the high purity of the material prepared by this method.

In conclusion, we extended a highly efficient Ullmann-type coupling of aryl halides to the synthesis of symmetrical oligothiophenes. This reaction can easily be applied to the synthesis of oligothiophenes substituted with a variety of functionalities, in particular, polar functionalities, not readily accessible by other synthetic methods.<sup>23</sup> We demonstrated the feasibility of this approach by synthesizing a highly soluble  $\alpha,\omega$ -disubstituted sexithiophene DBP- $\alpha$ -6T **6**. Because of the lack of side products in this reaction, oligothiophenes prepared by this method can easily be purified by simple crystallization, eliminating the need for tedious column chromatography or sublimation. TFT devices fabricated using solution processed thin films of the soluble sexithiophene, while having modest carrier mobility, have high on/off ratios, indicative of the high purity of materials prepared by this synthetic route.

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(23) We have prepared oligothiophenes bearing other polar functionalities like carboxylic esters or carbamates using this approach; unpublished reports.