

Synthesis and Characterization of Oligothiophene Derivative

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Abstract

Oligothiophene derivatives have been well-known as a p-type channel material.¹ Here, we report novel oligothiophene derivative containing methylene linkage as a p-type channel material. Oligothiophene derivative containing methylene linkage BHTM was synthesized and characterized. BHTM was prepared by a palladium-catalyzed cross-coupling reaction via zinc-substituted thiophene. BHTM exhibited high thermal stability and at least one transition temperature.

1. Introduction

Organic field-effect transistors (OTFTs) based on molecular and polymeric organic semiconductors are a focus of considerable current interest, motivated by their potential applications for organic integrated circuit sensors,¹ low-cost memories, smart cards, and driving circuits for large-area display device applications such as active-matrix flat-panel liquid-crystal display (AMFPDs), organic light-emitting diodes, electrophoretic materials, and electronic paper displays.^{2,3}

Many of the organic semiconductors used for the fabrication of the p-channel in OTFTs have been derived from thiophene-based π -conjugated systems, oligothiophene, carbon-sulfur fused rings, acenes, phthalocyanines, polythiophene, polythienylenevinylenes, and polypyrroles. The most important criteria for a FET semiconductor are high charge mobility,

high current modulation (on/off current ratio), stability and processability. High field-effect mobilities of above 0.01 cm²/Vs and high on/off current ratios of greater than 10⁶ have been achieved in some of the systems under carefully controlled conditions such as strict exclusion of oxygen and material purification. α,ω -Dialkylsubstituted oligothiophenes, are with pentacene, the most promising p-type materials, due to their capacity for self-assembling into close-packed structures. As reported by different groups, when synthesized and purified according to optimized procedures, oligothiophenes can reach field-effect mobilities of up to 0.1 cm²/Vs for, e.g., vacuum-evaporated 2,5''''-dihexylsexithiophene.⁴

Oligothiophenes with five or more rings have limited solubility in organic solvents. 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. Thus, we tried to synthesize new oligothiophene-based TFT materials containing alkylene linkage, which are expected to give good solubility and high planarity and good device performance.

In this paper, we report the synthesis and characterization of new oligothiophene

derivatives containing alkylene linkage for their behavior as FET semiconductors. The new oligothiophenes containing alkylene linkage were prepared by a palladium-catalyzed cross-coupling reaction via zinc-substituted thiophene.

2. Experimental

Materials. All starting materials were purchased from Aldrich and used as received unless otherwise specified. Tetrahydrofuran (THF) and diethylether were distilled from sodium benzophenone ketyl.

Measurements. A Genesis II FT-IR spectrometer was used to record IR spectra. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded with the use of DRX 300 and 500 MHz NMR Bruker spectrometers, and chemical shifts are reported in ppm units with tetramethylsilane as internal standard. Thermogravimetric analysis (TGA) was performed under nitrogen on a TA instrument 2050 thermogravimetric analyzer. The sample was heated using a $10\text{ }^\circ\text{C}/\text{min}$ heating rate from $50\text{ }^\circ\text{C}$ to $600\text{ }^\circ\text{C}$. Differential scanning calorimeter (DSC) was conducted under nitrogen on a TA instrument 2100 differential scanning calorimeter. The sample was heated with $10\text{ }^\circ\text{C}/\text{min}$ from $35\text{ }^\circ\text{C}$ to $300\text{ }^\circ\text{C}$.

Synthesis

The oligothiophene derivative was synthesized according to the following scheme depicted in Scheme 1.

2,2'-Dithienylcarbinol n-Butyl lithium (2.5 M in hexane) (62.59 g, 0.226 mol) was added dropwise to a solution of thiophene (20 g, 0.238 mol) in 300 mL of ether at $-78\text{ }^\circ\text{C}$. After 1 hour upon addition, ethylformate (8.8 g, 0.118 mol) was added to the solution. The reaction mixture was then warmed to room temperature, stirred for another 10 hours and poured into water. The mixture was extracted with ether, dried over magnesium sulfate, and the solvent

evaporated. The pure product was obtained after recrystallization from ether. (16.5 g, 71%)

2,2'-Dithienylmethane To a suspension of LAH (4.64 g, 0.122 mol) in 50 mL dry ether was added a solution of AlCl_3 (16.3 g, 0.122 mol) in 70 mL dry ether. A solution of 2,2'-dithienylcarbinol (16.6 g, 0.082 mol) in 120 mL dry ether was added to this stirred reducing mixture at such a rate as to cause gentle refluxing (about 20 min.). After boiling under reflux for 2 hours the reaction mixture was cooled in ice bath. The resulting suspension was poured into a mixture of 200 mL of ice-water and 40 mL of concn HCl. The layers were separated and the aqueous phase was extracted with ether. The combined organic layers were washed with NaHCO_3 solution and with water. The product was obtained a flash column chromatography using hexanes as eluent. (12.3, 84%, mp: $35\text{ }^\circ\text{C}$)

2,2'-Bithiophene The Grignard reagent formed from 60 g of 2-bromothiophene (0.368 mol) and magnesium (9.7 g 0.404 mol) was slowly added to a mixture of 2-bromothiophene (50 g, 0.307 mol), Ni(dppp)Cl_2 (1.66 g, 3 mmol), and 150 mL ether at $0\text{ }^\circ\text{C}$, then warmed to room temperature. The reaction was quenched by dilute HCl after 20 hours. The organic phase was separated, and combined with the ether extraction from the aqueous phase. The solvent was evaporated after drying over magnesium sulfate. The product was obtained a flash column using hexanes as eluent. (40 g, yield : 80 %, mp $32 - 33\text{ }^\circ\text{C}$)

2-Hexyl-[2,2']-bithiophene n-Butyl lithium (2.5 M in hexane) (75 g, 0.27 mol) was added dropwise to a solution of 2,2'-bithiophene (50 g, 0.3 mol) in 500 mL of THF at $-78\text{ }^\circ\text{C}$. After 1 hour upon addition, 1-bromohexane (59 g, 0.36 mol) was added to the solution. The reaction mixture was then warmed to room temperature, stirred for another 5 hours and poured into water.

The mixture was extracted with ether, dried over magnesium sulfate, and the solvent evaporated. The product was purified by vacuum distillation. (50 g, 66 %, bp : 140 °C/1 mm Hg)

2-Bromo-5-hexyl-[2,2']-bithiophene

NBS (27.4 g, 0.154 mol) in 100 mL of DMF was added dropwise to a solution of 2-hexyl-[2,2']-bithiophene (35 g, 0.139 mol) in DMF at 0 °C. The reaction mixture was stirred at room temperature for another 10 hours before being poured into water. After extraction with methylene chloride, the organic phase was separated, dried over magnesium sulfate. The product was obtained a flash column chromatography using hexanes as eluent. (44.3 g, 96%)

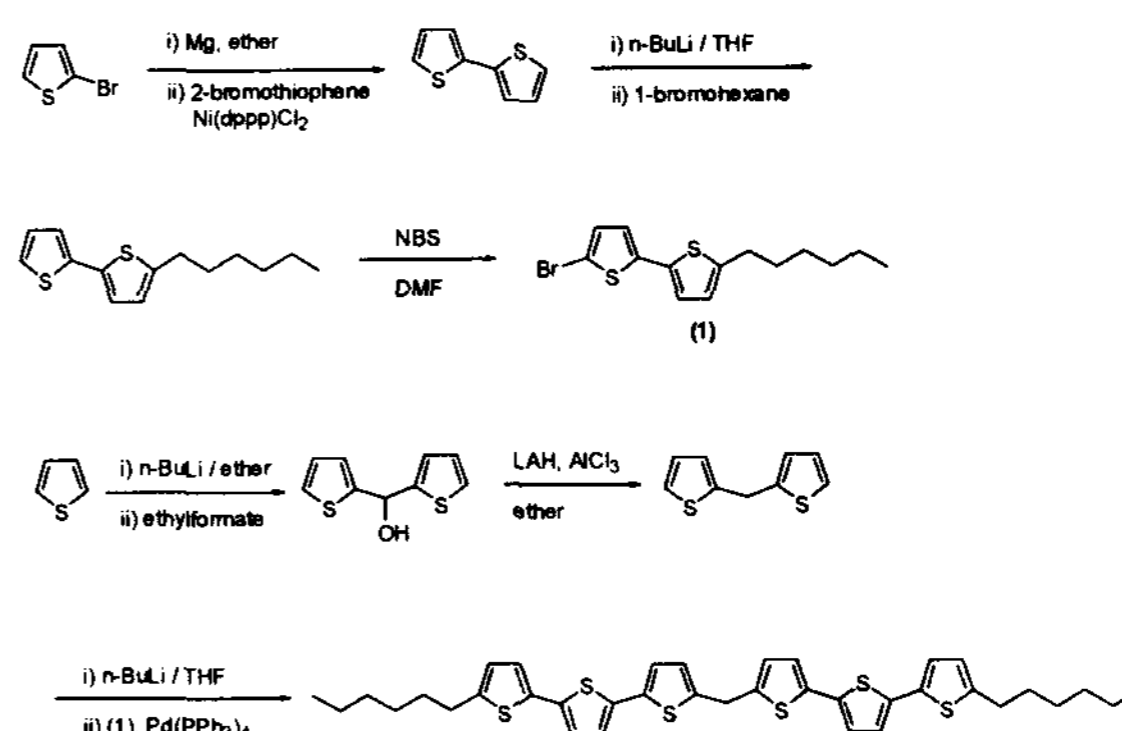
Bis-2-hexyl-[2,2':5',2'']terthiophene-5-yl-methane (BHTM) n-Butyl lithium (2.5 M in hexane) (3.85 g, 13.8 mmol) was added dropwise to a solution of 2,2'-dithienylmethane (1 g, 5.5 mmol) in 50 mL of THF at -78 °C. After 1 hour at room temperature, 1 M solution of dichloro(N,N,N',N'-tetramethylethylenediamine)zinc (13.8 mL, 13.8 mmol) was added to a solution. After 1 hour, 2-Bromo-5-hexyl-[2,2']-bithiophene (4.56 g, 13.8 mmol) and Pd(PPh₃)₄ (0.13 g, 0.11 mmol) was added slowly to the solution containing the zinc 2,2'-dithienylmethane derivative, and the reaction was refluxed under a nitrogen atmosphere for 12 hours. Near the end of the reaction, a yellow precipitate of bis-2-hexyl-[2,2':5',2'']terthiophene-5-yl-methane appeared.

After cooling, the precipitate was collected and washed several times with THF and with methanol. The pure product was obtained after recrystallization from THF. (1.48 g, 40%)

3. Results and Discussion

Scheme 1 illustrates the synthetic route of oligothiophene derivative containing methylene linkage. The desired compound

in each steps were obtained in high yield and were confirmed by various spectroscopic methods.



Scheme 1 Synthetic scheme of oligothiophene derivative.

The synthesis of 2-bromo-5-hexyl-[2,2]bithiophene was achieved by using Grignard coupling reactions and bromination with NBS in DMF. 2,2'-Bithiophene was reacted with magnesium to afford the corresponding Grignard reagents, which were then coupled with 2-bromothiophene in the presence of a catalytic amount of Ni(dppp)Cl₂, followed by alkylation and bromination with NBS/DMF to give 2-bromo-5-hexyl-[2,2]bithiophene.

Thiophene was reacted with n-butyllithium and ethylformate, followed by reduction with LAH/AlCl₃ to give 2,2'-dithienylmethane BHT. The pure product was obtained by recrystallization.

Bis-2-hexyl-[2,2':5',2'']terthiophene-5-yl-methane (BHTM) was prepared by a palladium-catalysed cross-coupling reaction via zinc-substituted 2,2'-dithienylmethane. The first step of this reaction involved the lithiation of the 2,2'-dithienylmethane. The organolithium compound was converted with dichloro(N,N,N',N'-tetramethylethylenediamine)zinc to the corresponding organozinc compound. The cross-coupling of 2-bromo-5-hexyl-[2,2]bithiophene in THF in the presence of a

catalytic amount of $\text{Pd}(\text{PPh}_3)_4$ lead to BHTM.

The structures of obtained compounds were characterized by $^1\text{H-NMR}$, FT-IR and elemental analysis. $^1\text{H-NMR}$ spectrum of BHTM showed in Figure 1.

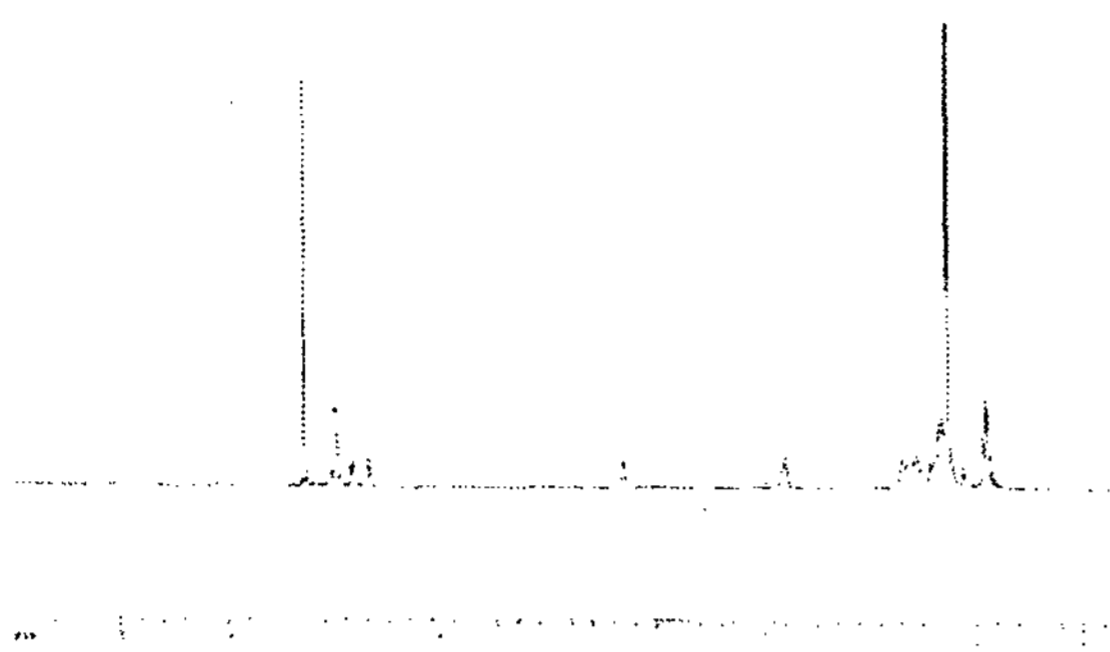


Figure 1. $^1\text{H-NMR}$ spectra of the BHTM. (CDCl_3)

The thermal properties of the BHTM were determined by Thermogravimetric analysis (TGA) and a heating-cooling cycle using Difference Scanning Calorimetry (DSC) under nitrogen atmosphere.

The BHTM appeared 5% weight loss at 358°C in nitrogen as measured by TGA and exhibited at least one transition temperature, as illustrated in Figure 3, evidence of mesophase formation. It is showed that BHTM has liquid-crystal-like structure. The transition temperature of BHTM was detected 170°C and 174°C .

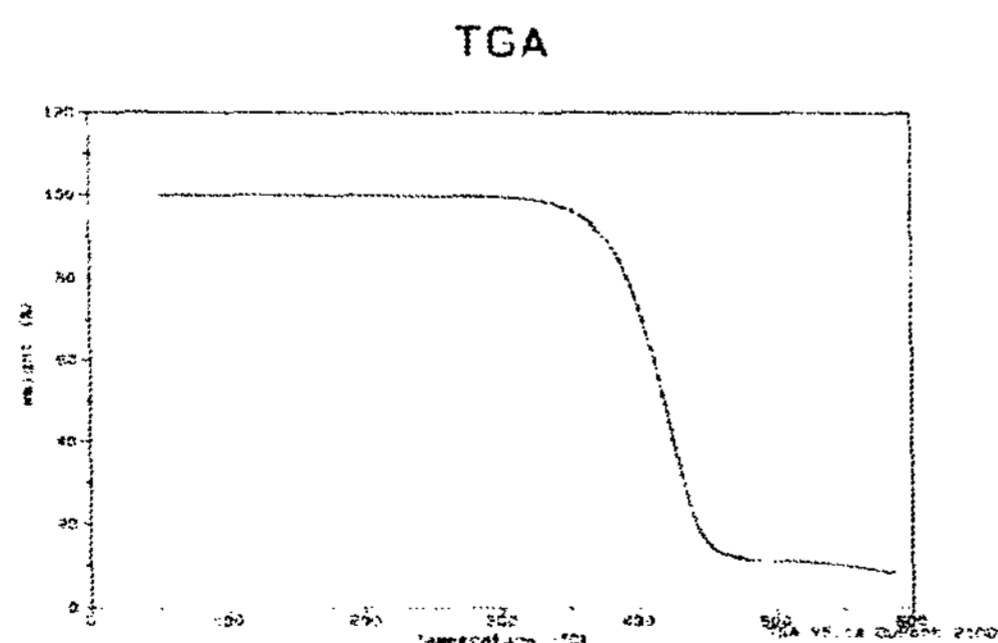


Figure 2. TGA curve of the BHTM.

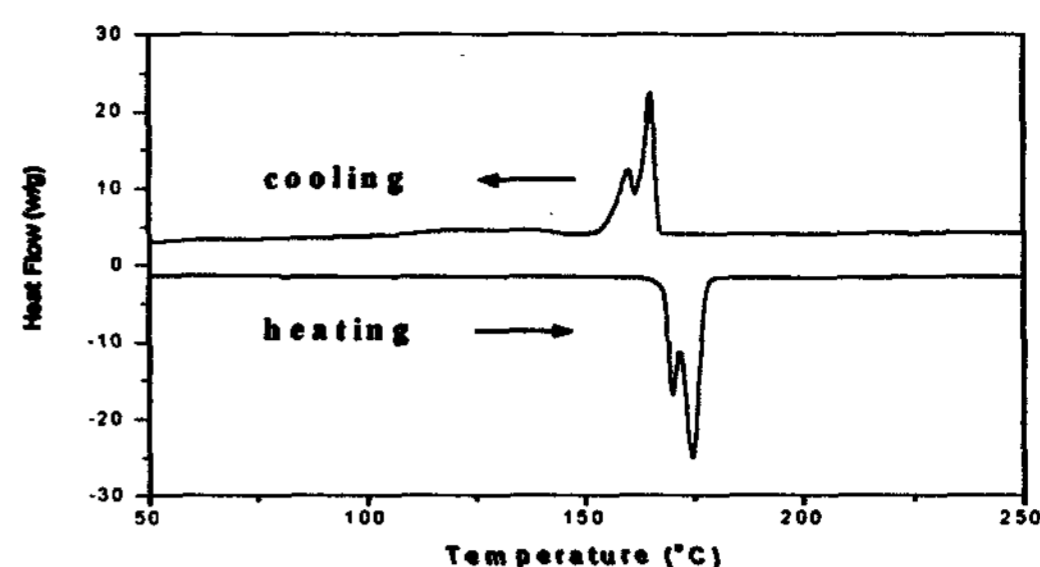


Figure 3. DSC curve of the BHTM.

4. Acknowledgements

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