

Novel Liquid Crystalline Thiophene Oligomers Containing Alkylene Linkage as OTFT Materials

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Abstract

New Oligothiophene derivatives having liquid crystalline property have been designed, synthesized and characterized. New oligothiophene derivatives were prepared by a palladium-catalyzed cross-coupling reaction via zinc-substituted thiophene. The structures of materials were characterized by various spectroscopies. The new obtained oligothiophene derivatives showed high thermal stability above 300 °C and exhibited several transition temperatures, evidence of mesophase. In field-effect transistors, a charge carrier mobility of $1.9 \times 10^{-2} \text{ cm}^2/\text{Vs}$ was observed.

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 $0.01 \text{ cm}^2/\text{Vs}$ and high on/off current ratios of greater than 10^6 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 $0.1 \text{ cm}^2/\text{Vs}$ 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 report, we report the synthesis and characterization of new oligothiophene derivatives containing alkylene linkage for their behavior as FET semiconductors.

2. Experimental

Materials. All starting materials were purchased from Aldrich and used as received unless otherwise specified. Tetrahydrofuran (THF) and diethyl ether 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 $800\text{ }^\circ\text{C}$. 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 $30\text{ }^\circ\text{C}$ to $400\text{ }^\circ\text{C}$. UV-vis absorption spectra and photoluminescence (PL) spectra were measured by Perkin Elmer LAMBDA-900 UV/VIS/NIR spectrophotometer and LS-50B luminescence spectrophotometer, respectively.

2-Hexylthiophene (HTh) (1) n-Butyl lithium (2.5 M in hexane) (82.4 g, 0.29 mol) was added dropwise to a solution of thiophene (30 g, 0.36 mol) in 500 mL of THF at $-78\text{ }^\circ\text{C}$. After 1 hour upon addition, 1-bromohexane (52 g, 0.31 mol) were 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. (40 g, 66 %, bp : $90\text{ }^\circ\text{C}/1\text{ mm Hg}$)

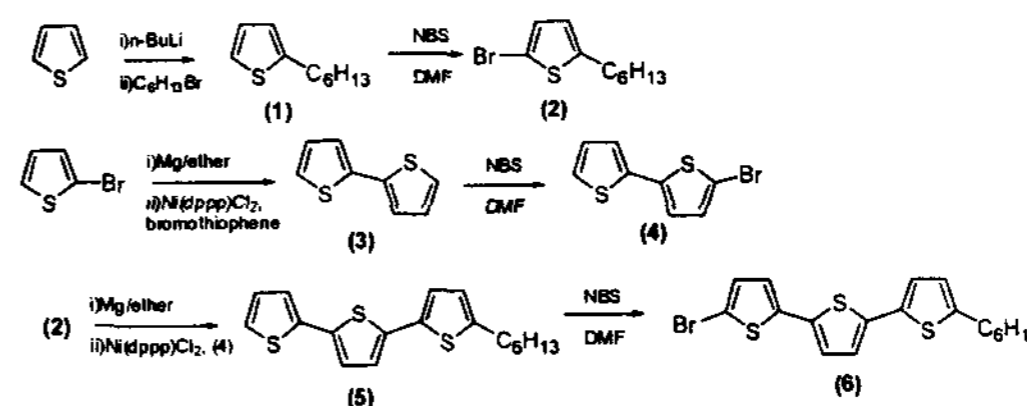
2-Bromo-5-hexylthiophene (BHT) (2) NBS (32.36 g, 0.182 mol) in 50 mL of DMF was added dropwise to a solution of 2-hexylthiophene (30 g, 0.178 mol) in DMF at $0\text{ }^\circ\text{C}$. The reaction mixture was stirred at room temperature for another 10 hours before being poured into water. After extraction with methylene chloride, the organic phase was separated, dried over magnesium sulfate. The pure product was obtained through vacuum distillation. (35.9 g, 82 %, bp : $110\text{ }^\circ\text{C}/1\text{ mmHg}$)

2,2'-Bithiophene (3) 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), $\text{Ni}(\text{dppp})\text{Cl}_2$ (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 $32 - 33\text{ }^\circ\text{C}$)

5-Bromo-[2,2']bithiophene (BBT) (4) The procedure is the same as with 2-bromo-5-hexylthiophene. The pure product was obtained through vacuum distillation. (42 g, 71 %, bp : $110\text{ }^\circ\text{C}/1\text{ mmHg}$)

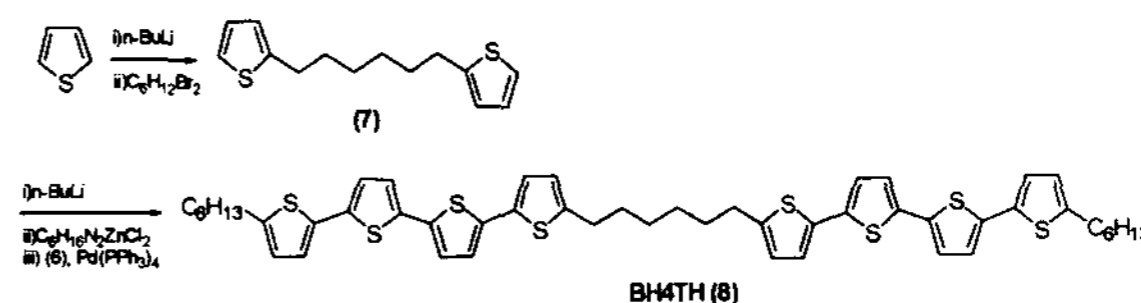
2-Hexyl-[2,2':5',2'']terthiophene (H3T) (5) The procedure is the same as with 2,2'-bithiophene. The pure product was obtained through column chromatography. (24 g, 90 %, mp : $58 - 59\text{ }^\circ\text{C}$)

2-Bromo-5-hexyl-[2,2':5,2'']terthiophene (BH3T) (6) The procedure is the same as with 5-bromo-[2,2']bithiophene. The pure product was obtained after recrystallization from hexane. (10 g, 81 %, mp : 124 - 125 °C)



Scheme 1. Synthesis of the 2-Bromo-5-hexyl-[2,2':5,2'']terthiophene)

1,2-Bis(2'-thiophenyl)hexane (BTH) (7) n-Butyl lithium (2.5 M in hexane) (88.6 g, 0.32 mol) was added dropwise to a solution of thiophene (31.1 g, 0.369 mol) in 500 mL of THF at -78 °C. After 1 hour upon addition, 1,6-dibromohexane (30 g, 0.123 mol) were 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. (22.3 g, 73 %, bp : 164 °C/1 mmHg)



Scheme 2. Synthesis of the 1,2-Bis(2'-hexyl[2,2':5'2'':5'',2'']quarterthiophenyl)hexane (BH4TH)

1,2-Bis(2'-hexyl[2,2':5'2'':5'',2'']quarterthiophenyl)hexane (BH4TH) (8) n-Butyl lithium (2.5 M in hexane) (2.8 g, 10 mmol) was added dropwise to a solution of BTH (1 g, 4 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 (10 mL, 10 mmol) was added to a solution. After 1 hour, BH3T (4.9 g, 12 mmol) and Pd(PPh₃)₄ (0.09 g, 0.08 mmol) was added slowly to the solution containing the zinc BTH derivative, and the reaction was refluxed under a nitrogen atmosphere for 12 hours. Near the end of the reaction, a yellow precipitate of BH4TH appeared.

After cooling, the precipitate was collected and washed several times with hexane, methanol. The product was dried in vacuum oven. (2.5 g, 70 %, mp: 218 °C) Additional purification can be achieved by multiple gradient sublimation.

3. Results and Discussion

Scheme 1 and 2 illustrates the synthetic route of oligothiophene derivatives containing alkylene linkage. The desired compound in each steps were obtained in high yield and were confirmed by various spectroscopies.

Thiophene was reacted with n-butyllithium and 1-bromohexane, followed by bromination with NBS/DMF to give BHT. The pure product was obtained by distillation under reduced pressure.

The synthesis of 2-bromo-5-hexyl-[2,2':5,2'']terthiophene) (BH3T) was achieved by using Grignard coupling reactions and bromination with NBS in DMF. BHT were reacted with magnesium to afford the corresponding Grignard reagents, which were then coupled with BBT in the presence of a catalytic amount of Ni(dppp)Cl₂, followed by bromination with NBS/DMF to give BH3T.

BTH was synthesized by reaction of thiophene with n-butyllithium and 1,6-dibromohexane at nitrogen atmosphere. BH4TH was prepared by a palladium-catalyzed cross-coupling reaction via zinc-

substituted BTH. The first step of this reaction involved the lithiation of the BTH. The organolithium compound was converted with dichloro(*N,N,N',N'*-tetramethylethylenediamine)zinc to the corresponding organozinc compound. The cross-coupling of H3T in THF in the presence of a catalytic amount of Pd(PPh₃)₄ lead to BH4T.

The structures of obtained compounds were characterized by ¹H-NMR, FT-IR and elemental analysis.

The thermal properties of these compounds were determined by a heating-cooling cycle using DSC under nitrogen. The BH4TH exhibit at least one transition temperature, as illustrated in Figure 1, evidence of mesophase formation. It is showed that BH4TH has liquid-crystal-like structure. The transition temperature of BH4TH was detected 170, 218, 234, and 248 °C.

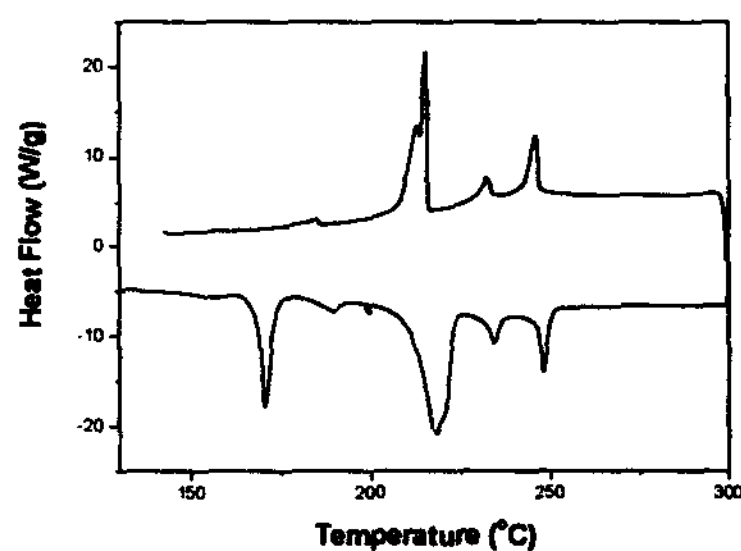


Figure 1. DSC thermographs of BH4TH under a N₂ atmosphere.

Field-effect transistors were made in a bottom contact device configuration. BH4TH performed as good *p*-type transistors. As a representative, Figure 2 shows the drain-source current (I_{DS}) characteristics with different voltages (V_G) for a FET device using BH4TH deposited.

The FET mobility calculated using the I_{DS} in the saturation regions is 0.08 cm² V⁻¹s⁻¹, and the on/off ratio is 3.6 x 10⁵.

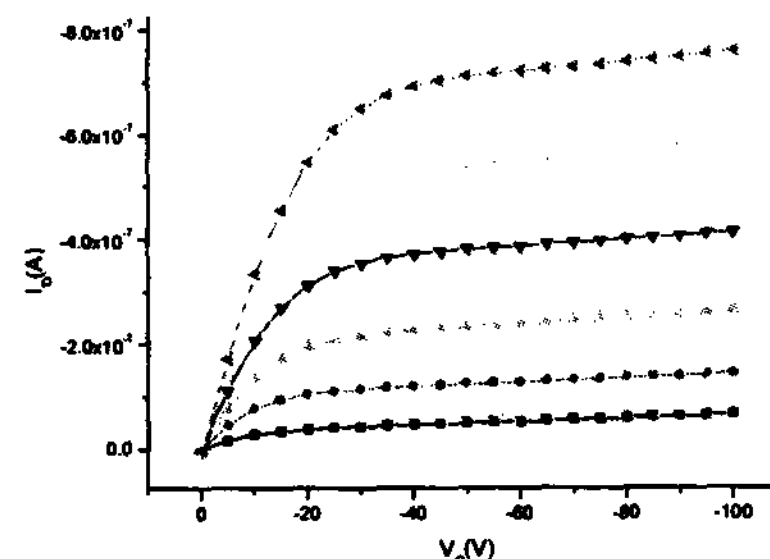


Figure 2. Drain-Source current (I_{DS}) versus drain-source voltage (V_{DS}) characteristic for BH4TH

4. Acknowledgements

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