

Oligothiophene Derivatives Containing Alkylene Linkage as New Semiconductor for OTFT

Hyung-Sun Kim¹, Kyung-Hwa Son¹, Jong-Won Park¹, Yun-Hi Kim¹,
and Soon-Ki Kwon^{1*}

¹ Department of Polymer Science & Engineering and Engineering Research Institute,
Gyeongsang National University, Chinju 660-701, South Korea
Phone : +82-55-751-5296, *e-mail : skwon@nongae.gsnu.ac.kr

Lee-Mi Do²,

² Basic Research Laboratory, ETRI, Taejon 305-350, South Korea

Abstract

Oligothiophene derivatives have been well-known as a p-type channel material.¹ Here, we report novel oligothiophene derivative containing alkylene linkage as a p-type channel material. Oligothiophene derivative containing alkylene linkage BE4TH was synthesized and characterized. BE4TH was prepared by a palladium-catalyzed cross-coupling reaction via zinc-substituted thiophene. B4TH and BH4TH 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.

A valuable characteristic to decide the

performance of OTFTs is the field effect mobility of the charge carriers in the organic semiconductor layer and by the efficiency of injecting and extracting carriers at the source and drain contacts. For virtually all classes of organic semiconductors, the intrinsic carrier mobility depends critically on the degree of molecular ordering and on the extent of the π - π stacking in the material. Consequently, optimizing the chemical structure of the organic semiconductor with regard to optimum molecular ordering and maximum orbital overlap continues to be of great importance for the further advancement of organic TFT technology.

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, such as 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

The research of relationships between molecular structure and electrical performance have been reported mainly the number of repeat units and the length of alkyl substituents⁵. Due to the ease in synthesis and chemical modification of their structures can potentially allow us to fine-tune their optical and electronic properties, the oligothiophenes particularly are suitable for model compounds for this type of investigation.

For many years, oligothiophenes and their alkyl-substituted derivatives have been among the most intensely investigated organic semiconductors and have even led to the demonstration of fast integrated circuits. However, in many previous studies, new materials were developed using a shape of the a,a'-dialkylsubstituted oligothiophene skeletons which have one mesogen and two spacers. No OTFTs made from the molecule of two mesogens and one spacer or two mesogens and three spacers have so far been reported.

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 Suzuki cross-coupling reaction.

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. ¹H-NMR and ¹³C-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 °C/min heating rate from 50 °C to 600 °C. Differential scanning calorimeter (DSC) was conducted under nitrogen on a TA instrument 2100 differential scanning calorimeter. The sample was heated with 10 °C/min from 35 °C to 300 °C.

Synthesis

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

2-Bromo-[2,2':5',2'']terthiophene (2)

NBS (7.52 g, 42.3 mmol) in 50 mL of DMF was added dropwise to a solution of [2,2':5',2'']terthiophene (10 g, 40.2 mmol) 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 dichloromethane as eluent. Yield: 8 g (61 %), mp: 124 - 125 °C, ¹H-NMR (300 MHz, CDCl₃, ppm):

1,6-Bis(thiophene-2-yl)hexane (3) n-Butyllithium (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. Yield: 22.3 g (73%), bp : 164 °C/1 mmHg, ¹H-NMR (300 MHz, CDCl₃, ppm):

1,6-(Dithiophene-2'-yl)hexane-bis-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4) To a solution of compound 3 (8 g, 32 mmol) in THF (100 mL) at -78 °C was added dropwise 22 g (0.08 mol) of n-butyllithium (2.5 M solution in hexane). After the mixture had been stirred at -78 °C for 1 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14.8 g, 0.08 mol) was

added to the mixture, and the resulting mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h and then warmed to room temperature and further stirred for overnight. The mixture was poured into water, extracted with diethylether, and then dried over MgSO_4 . The solvent was removed by rotary evaporation, the yellow oil was obtained a flash column chromatography using hexane:ethylacetate(10:1) as eluent. Yield: 6 g (37.5%), $^1\text{H-NMR}$ (300 MHz, CDCl_3 , ppm):

1,6-Bis(quarterthiophene-2-yl)hexane

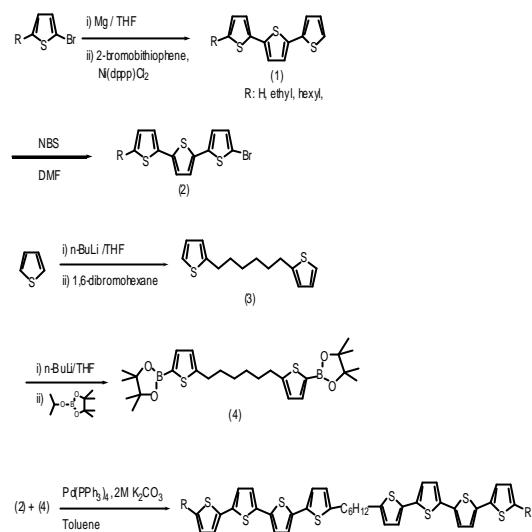
(B4TH) To a solution of compound **4** (1 g, 2 mmol) and compound **2** (1.56 g, 4.8 mmol) dissolved in toluene (50 ml) was added a aqueous 2M sodium carbonate solution (20 mL). The mixture was bubbled with nitrogen for 30 min.

Then, tetrakis(triphenylphosphine)palladium(0) (0.046 g, 2 mol%) was added. The mixture was heated to $90\text{ }^{\circ}\text{C}$ for 48 h. under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and poured into methanol (400 mL) and aqueous 2N HCl (200 mL). The orange precipitate was filtered off, washed with water, methanol, then with acetone three times to remove the starting material as well as the mono-substituted by-product. The crude product was purified by Soxhlet extraction with methanol and toluene.

3. Results and Discussion

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

The synthesis of 2-Bromo-[2,2':5',2'']terthiophene was achieved by using Grignard coupling reactions and bromination with NBS in DMF. BTH was synthesized by reaction of thiophene with *n*-butyllithium and 1,6-dibromohexane at nitrogen atmosphere. B4TH was prepared by a Suzuki cross-coupling reaction. The structures of obtained compounds were characterized by $^1\text{H-NMR}$, FT-IR and elemental analysis.



Scheme 1 Synthetic scheme of oligothiophene derivative.

The thermal properties of the BE4TH were determined by Thermogravimetric analysis (TGA) and a heating-cooling cycle using Difference Scanning Calorimetry (DSC) under nitrogen atmosphere.

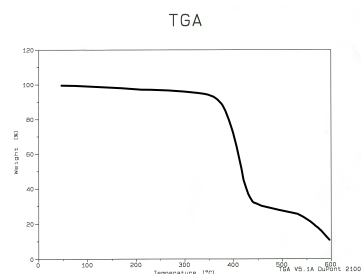


Figure 1. TGA curve of the B4TH.

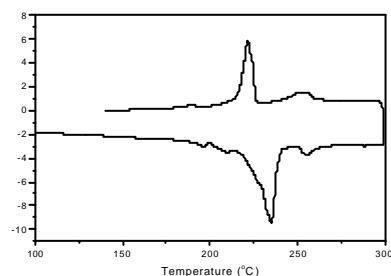


Figure 2. DSC curve of the B4TH.

The B4TH and BH4TH appeared 5% weight loss at 350, 345 °C, in nitrogen as measured by TGA and exhibited at least one transition temperature, as illustrated in Figure 2, evidence of mesophase formation. It is showed that B4TH has liquid-crystal-like structure. The transition temperature of B4TH was detected 235 and 255 °C.

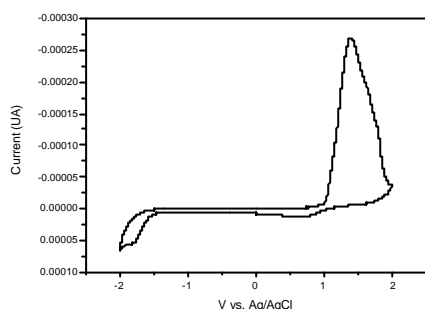


Figure 3. Cyclic voltammogram of the B4TH films on glassy carbon in 0.1 M Bu₄NPF₆, CH₃CN solution.

The electrochemical behavior of the B4TH was investigated by cyclic voltammetry (CV) (Figure 3). The onset of oxidation and reduction process is at 1.02 V, -1.54 V, respectively. HOMO and LUMO levels calculated according to an empirical formula ($E_{\text{HOMO}} = -e(\text{EOX} + 4.4)$ eV and $E_{\text{LUMO}} = -e(\text{Ered} + 4.4)$ eV). HOMO and LUMO levels of B4TH were 5.58 eV, 3.02 eV, respectively and bandgap is 2.56 eV.

4. Acknowledgements

This research was supported by a grant(M1-02-KR-01-0001-02-K18-01-003-2-0) from Information Display R&D Center, one of the 21st Century Frontier R&D Program funded by Ministry of Science and Technology of Korean government.

5. References

4. C. D. Dimitrakopoulos, S. Purushothaman, J. Kymissis, A. Callegari, J. M. Shaw, *Science*. 1999, 283, 822.

5. M. Halik, H. Klauk, U. Zschieschang, G. Schmid, S. Ponomarenko, S. Kirchmeyer, W. Weber, *Adv. Mater.* 2003, 15, 917.
6. H. Akimichi, K. Waragai, S. Hotta, H. Kano, H. Sakaki, *Appl. Phys. Lett.* 1991, 58, 1500.
7. Z. Bao, A. J. Lovinger, J. Brown, *J. Am. Chem. Soc.* 1998, 120, 207.
8. G. Horowitz, F. Kouki, P. Spearman, D. Fichou, C. Nogues, X. Pan, F. Garnier, *Adv. Mater.* 1996, 8, 242.
9. A. Facchetti, M. Mushrush, H. E. Katz, T. J. Marks, *Adv. Mater.* 2003, 15, 33.
10. C. Vidolot, J. Ackermann, P. Blanchard, J. M. Raimundo, P. Frere, M. Allain, R. Bettignies, E. Levillain, J. Roncali, *Adv. Mater.* 2003, 15, 306.
11. H. S. Kim, S. O. Jung, Y. H. Kim, S. K. Kwon, *Polym. Print*, 2003, 44, 423.
12. S. Mohapatra, B. T. Holmes, C. R. Newman, C. F. Prendergast, C. D. Frisbie, M. D. Ward, *Adv. Funct. Mater.*, 2004, 14, 605.