

Organic Thin Film Transistors based Oligothiophene Derivatives using α,ω -Dihexyl(quarter- & sexi-)Thiophene

Jae-Hong Kwon, Myung-Ho Chung, Tae-Yeon Oh, Hyeon-Seok Bae, and Byeong-Kwon Ju

Abstract—End-substitution of quarterthiophene and sexithiophene with hexyl groups leads to highly soluble conjugated oligomers, α,ω -dihexylquarterthiophene (DH-4T) and α,ω -dihexylsexithiophene (DH-6T). We have characterized these oligomers for optical and electrical properties. We fabricated an organic thin film transistor (OTFT) using the above two air-stable *p*-type organic semiconductor materials. We obtained a stable characteristic curve. The field effect mobility, μ , was calculated to be 3.29×10^{-4} cm²/Vs for DH-6T based OTFT; while the DH-4T based OTFT had 1.88×10^{-5} cm²/Vs.

Keywords—Organic thin film transistor, α,ω -dihexylquarterthiophene, α,ω -dihexylsexithiophene.

I. INTRODUCTION

MANY groups have developed organic thin film transistors (OTFTs). These organic thin film transistors (OTFTs) have been fabricated using a soluble process. This process has included spin coating [1], screen printing [2], drop casting [3], and nanoimprint lithography [4]. These techniques for soluble processes can be easily used in coating processes to form circuits for disposable electronics on a plastic substrate. There are several advantages; a large-area coverage, structural flexibility, low-temperature fabrication processing, and especially low-cost.

One critical material for OTFTs is the semiconductor channel which dictates transistor performance. Functionally capable organic semiconductors (OSCs) for low-cost OTFTs are rare because most OSCs are either insoluble or very sensitive to air under ambient conditions. Material insolubility precludes the use of liquid patterning and deposition. Also, the materials' sensitivity to air increases the manufacture cost

Jae-Hong Kwon is with Display and Nanosystem Laboratory, College of Engineering, Korea University, Anam-dong, Seongbuk-gu, Seoul 136-713, Republic of Korea (corresponding author to provide phone: 82-2-3290-3665; fax: 82-2-3290-3791; e-mail: jhkwon@korea.ac.kr).

Myung-Ho Chung, Tae-Yeon Oh, and Hyeon-Seok Bae are with Display and Nanosystem Laboratory, College of Engineering, Korea University, Anam-dong, Seongbuk-gu, Seoul 136-713, Republic of Korea (e-mail: maengho@korea.ac.kr, hopeofsoul@korea.ac.kr, skipio701@korea.ac.kr).

Byeong-Kwon Ju is with School of Electrical Engineering, College of Engineering, Korea University, Anam-dong, Seongbuk-gu, Seoul 136-713, Republic of Korea (e-mail: bkju@korea.ac.kr).

thereby nullifying the fundamental economic advantage of OTFTs. Until relatively recently, the challenges of designing a liquid process capable of producing high performing OSCs with sufficient air-stability to enable low-cost OTFTs seemed to be insurmountable.

Recently, however, great strides have been made in the design of air-stable OSCs with a solution-process which is capable of producing OSCs with excellent OTFT properties. These latest advances in semiconductor development are very encouraging and have strengthened the prospect of bringing low-cost OTFT circuits from the laboratory to the commercial world in the near future.

Of various soluble OSCs current in use, α,ω -dihexylquarterthiophene (DH-4T) and α,ω -dihexylsexithiophene (DH-6T) have become the most promising candidates for all organic semiconductor integration because of air stability, good solubility, and easy synthesis [5-7]. In the following sections, the synthesis and characterizations of DH-4T and DH-6T and their applications in TFTs are presented. We discuss these results obtained for optical properties and device performance.

II. EXPERIMENTS

A. Synthesis of materials

A synthesis of materials - α,ω -dihexylquarterthiophene (DH-4T), 5,5''-dihexyl-2,2',5',2''-dihexylquarterthiophene. A standard BuLi/CuCl₂ coupling was performed on 2.4 g of hexylbithiophene prepared as described above. A standard aqueous/organic workup was performed including quenching with dilute HCl and adding toluene to the organic layer. The concentrated organic reaction mixture was triturated with hexane and methanol to obtain a solid product, pure by nuclear magnetic resonance (NMR). The yield was 58 % based on the consumed starting material (not accounting for lithiate quenched by adventitious water or HCl). Also, for the α,ω -dihexylsexithiophene, DH-6T, A mixture of 5,5'-bis(tri-n-butylstannyl)-2,2'-bithiophene (1.40 g, 1.88 mmol), 5-hexyl-5'-bromo-2,2'-bithiophene (1.23 g, 3.76 mmol), and [Pd(PPh₃)₄](0.05g, 0.04 mmol) in dry dimethylformamide (DMF) (40 mL) was deaerated twice with nitrogen. The reaction mixture was then heated at 80 °C for 7 hours during which time a precipitate formed. After cooling,

the bright red solid was collected and washed several times with hexane, methanol, and acetone to produce the product (1.02 g, 82 % yield). In this work, all solutions were filtered through a 0.45 μm PTFE membrane syringe filter before use. The synthesis is schematically shown in figure 1.

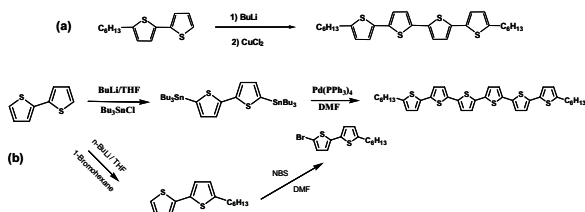


Fig. 1 The synthesis of α,ω -dihexylquaterthiophene and α,ω -dihexylsexithiophene

B. Device fabrication and measurements

A bottom contact configuration for the OTFTs was used in this work (Figure 2). A highly doped *p*-type Si wafer (resistivity 0.005 $\Omega\text{-cm}$) was used both as a substrate and as a gate electrode for the bottom-contact structure. Initially, the gate insulator (GI: SiO_2) for most of the devices was thermally grown to a thickness of 100 nm. Sequentially, gold (Au, 70 nm thickness) source/drain electrodes including titanium (Ti, 30 nm thickness), which acted as an adhesion layer, were deposited by electron-beam evaporation. Also, a shadow mask was used to define the source and drain electrodes. The channel width, W , and length, L , were 500 μm and 20 μm , respectively. Next, a 200 nm thin film of the DH-4T and DH-6T OSCs was deposited by a spin coating system (Shinumst Co. SC-40P), respectively. Finally, their OSCs were annealed using an oven (Daehan Science Co. SH-HF) at room temperature in air, respectively.

The absorption spectra of the samples in solution (chloroform, conc. 1×10^{-5} mole/l) and the thin films were obtained using ultraviolet-visible (UV-Vis) spectrometry (HP 8453, PDA, type $\lambda = 190\text{-}1100$ nm). The photoluminescence (PL) spectra of the solutions were acquired on an Aminco-Bowman series-2 luminescence spectrometer. A Keithley 4200-SCS semiconductor characterization system was used to probe the devices in air ambient at room temperature and in dark condition.

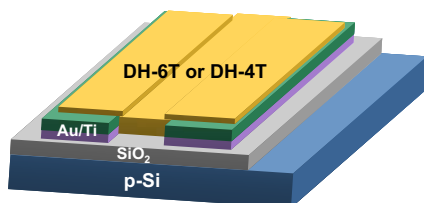


Fig. 2 A cross-sectional diagram of the organic thin film transistor structure

III. RESULTS AND DISCUSSION

Thiophene based polymers and oligomers are without doubt,

among the most studied OSCs for OTFTs. The performance of oligothiophene based TFTs is strongly dependent on the chemical structure of the molecules and consequently, on the structural arrangement of the OSC layer on top of the GI layer. It is well-known that the introduction of an alkyl chain, at the terminal α -positions of quarter- & sexi- thiophenes, has led to a significant increase of hole mobility as a result of stronger intermolecular relations between the π -conjugated systems induced by the occurrence of van der Waals interactions between lipophilic alkyl chains. [8,9] Therefore, the well-studied and documented DH-4T and DH-6T were chosen as the OSCs.

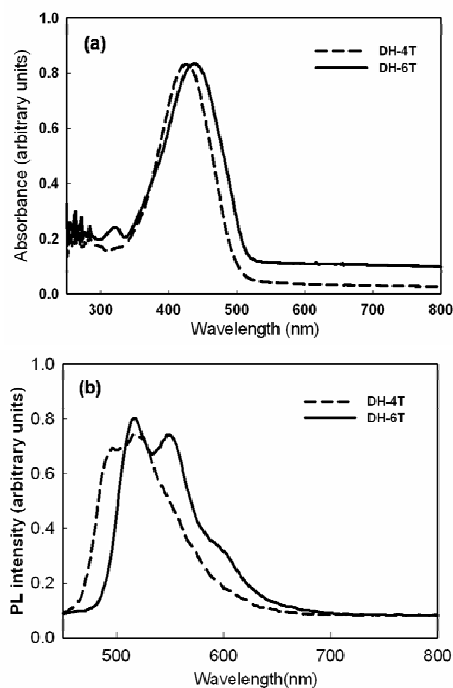


Fig. 3 Optical absorption (UV-Vis) and emission (PL) spectra of DH-4T (dash line) and DH-6T (solid line) in chloroform

Figure 3 compares the optical absorption and emission (PL) spectra of DH-4T and DH-6T in solution. Remarkably, the solution spectra were nearly superimposable which suggested that the energy differences between the ground and excited states of the thiophene core were only marginally sensitive to α,ω -substitution. This also suggested that the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gaps were nearly identical at approximately 2.4 eV [10]. The absorption peaks ($\lambda_{\text{max}}^{\text{abs}}$) were observed at 426 nm (dash line: DH-4T) and 441 nm (solid line: DH-6T) and exhibited violet and blue fluorescence, respectively. The PL spectra were recorded with an excitation at a maximum of 520 nm with a shoulder at 496 nm (DH-4T) and at a maximum of 520 nm with a shoulder at 550 nm (DH-6T).

We characterized the electronic properties of the OSCs' transistors using a Si wafer as the bottom gate. Typical output and transfer characteristics of DH-6T and DH-4T based OTFTs

shown in figure 4.

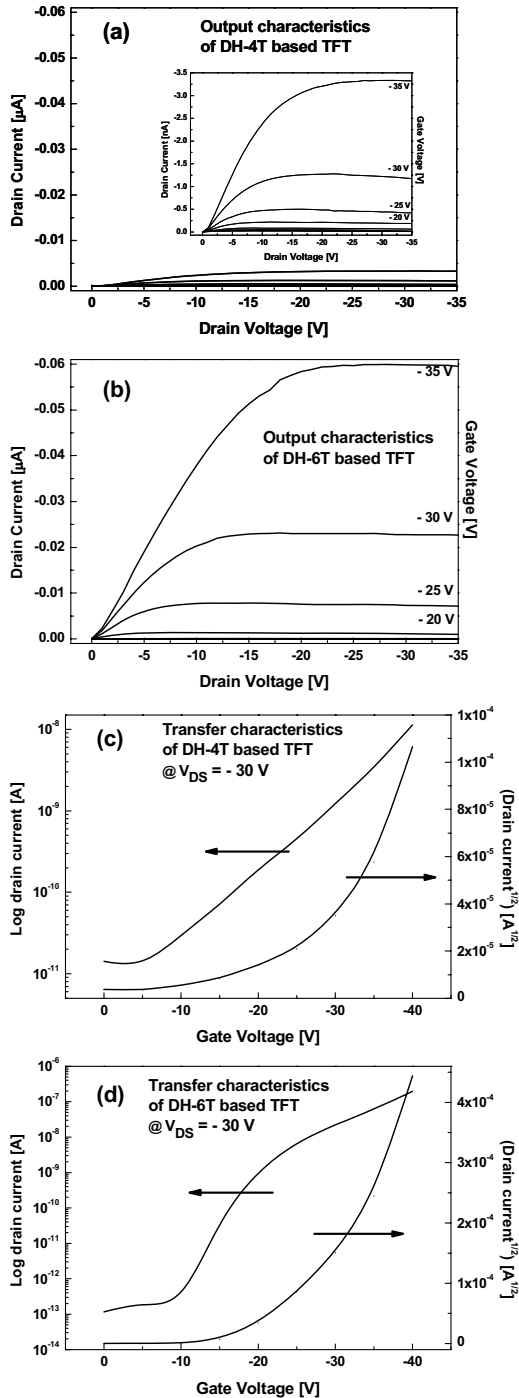


Fig. 4 The drain current versus voltage characteristics of an OTFT based DH-4T (a) such as that shown in the inset and an OTFT based DH-6T (b) composite at various gate voltages. The square root of the drain current versus gate voltage of the OTFT based DH-4T (c) and the OTFT based DH-6T (d) at a drain voltage of -30 V

The DH-4T and DH-6T based OTFTs showed characteristics typical of a *p*-channel field effect transistor, i.e. when a negative bias was applied, the drain-source current scaled with

the negative gate voltage due to the increased number of charge carriers (holes). The output curves [i.e. $I_D = f(V_G)$] at different gate biased and the transfer curves [i.e. $I_D = f(V_G)$] at constant V_D for the DH-4T and DH-6T films are shown in figures 4(a) and (c) and figures 4(b) and (d), respectively. The output curves showed very good saturation behavior. The field effect motilities, μ , were calculated in the saturation regime using the equation $I_D = (WC_i/2L) \mu (V_G - V_T)^2$ where C_i was the capacitance of the SiO₂ insulator ($C_i = 3.50 \times 10^{-8}$ F/cm²) and V_G and V_T were the gate and threshold voltages, respectively. Also, The subthreshold swing (*SS*) was usually extracted from the TFT subtransfer characteristic in the subthreshold regime using the equation $SS = (dV_{GS}/d\log(I_D))$. The performance parameters for our fabricated devices were summarized in TABLE 1. The OTFT based DH-4T showed a hole mobility of 1.88×10^{-5} cm²/Vs, a current on/off ratio of 9.34×10^2 , a threshold voltage of -21 V, and a subthreshold swing of ~ 11.63 V/decade when annealing at a temperature of 195 °C; while DH-6T had a hole mobility of 3.29×10^{-4} cm²/Vs, a current on/off ratio of 1.3×10^6 , a threshold voltage of -19 V, and a subthreshold swing of ~ 2.57 V/decade under the same conditions. Considering that the OTFTs were fabricated using bottom contact geometry with a SiO₂ gate dielectric, this TFT performance was among the best among thin film OSCs. In addition, the high work function of Au is expected to improve the injection of holes into the OSCs. However, spin on DH-4T and DH-6T based OTFTs are relatively low TFT performance parameters. Because the carrier channel in which the electronic charges are transported in the device is formed in close proximity to the interface, the properties of the GI surface and of the OSC/GI interface are of critical importance.[11] Hence, treatment of the interface between the OSC and GI layer using physical or chemical cleaning techniques has been studied by other groups [11,12] to improve the characteristics of the OTFT.

TABLE I
MEASURED FIELD EFFECT MOTILITIES, CURRENT ON/OFF RATIOS, THRESHOLD VOLTAGES, AND THE SUB-THRESHOLD SWING FOR SPIN ON DH-4T AND DH-6T ORGANIC THIN FILM TRANSISTORS

	Mobility [cm ² /Vs]	Current on/off ratio	Threshold voltage [V]	Sub-threshold swing [V/decade]
DH-4T	1.88×10^{-5}	9.34×10^2	-21 V	11.63
DH-6T	3.29×10^{-4}	1.3×10^6	-19 V	2.57

IV. CONCLUSION

Significant progress has been achieved recently in the research on and development of organic semiconductors based on polymers and oligomers of thiophene derivatives. The OTFT is the essential component for future flexible display devices accompanying electroluminescence devices. Therefore, in order to realize the potential of organic electronics, using simple processing, we require these semiconductors to have the ability to form devices with solution deposition methods, preferably using simple, inexpensive, easily synthesized materials. We have reported here on DH-4T and DH-6T characterizations obtained by

optical properties. We have fabricated OTFTs using air-stable DH-4T and DH-6T coated as active layers using a soluble process. From electrical measurements such as the typical I-V characteristics of the TFT, we have confirmed that the devices formed using this process have good potential in organic electronics.

ACKNOWLEDGMENT

This work was supported by the National Research Laboratory (NRL, R0A-2007-000-20111-0) Program of the Ministry of Science and Technology (Korea Science and Engineering Foundation), the IT R&D program of Ministry of Knowledge Economy of Korea/Institute for Information Technology Advancement (MKE/IITA, 009-F-018-01, TFT backplane technology for next generation display), and the Industrial-Educational Cooperation Program between Korea University and LG Display. We thank Professor Dong Hoon Choi and Kyung-Hwan Kim (Department of Chemistry, Korea University, Anam-dong, Seongbuk-gu, Seoul 136-713, Republic of Korea) for supplying the DH-6T powder. Also, Jung-Hun Kim (Thin Film Materials Research Center, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, Republic of Korea) thanks for electron-beam evaporation process.

REFERENCES

- [1] J. -H. Kwon, J. -H. Seo, S. -I. Shin, K. -H. Kim, D. H. Choi, I. B. Kang, H. Kang, and B. -K. Ju, "A 6,13-bis(Triisopropylsilylethynyl) Pentacene Thin-Film Transistor Using a Spin-On Inorganic Gate-Dielectric", *Electron Devices, IEEE Transactions on*, vol.55, no.2, pp.500-505, Jan., 2008.
- [2] J. -H. Kwon, S. H. Lee, and B. -K. Ju, "Screen-printed multi-crystalline silicon solar cells with porous silicon antireflective layer formed by electrochemical etching", *J. Appl. Phys.*, vol.101, no.9, p.104515, May, 2007.
- [3] J. -H. Kwon, S. -I. Shin, K. -H. Kim, M. -J. Cho, K. -N. Kim, D. -H. Choi, and B. -K. Ju, "Organic thin film transistors using 6,13-bis(triisopropyl-silylethynyl)-pentacene embedded into polymer binders", *Appl. Phys. Lett.*, vol.94, No.1, p.013506, Jan., 2009.
- [4] M. Austin and S. Chou, "Fabrication of 70 nm channel length polymer organic thin-film transistors using nanoimprint lithography", *Appl. Phys. Lett.*, vol.81, no.23, p.4431, Dec., 2002.
- [5] J. -H. Kwon, J. -H. Seo, H. Kang, D. H. Choi, and B. -K. Ju, "p-type semiconducting α,ω -dihexylsexithiophene for an organic thin film transistor", *J. Appl. Phys.*, vol.101, no.6, p.064502, Mar., 2007.
- [6] A. Facchetti, M. Yoon, C. L. Stern, G. R. Hutchison, M. Ratner and T. Marks, "Building Blocks for N-Type Molecular and Polymeric Electronics. Perfluoroalkyl- versus Alkyl-Functionalized Oligothiophenes (nTs; n = 2-6). Systematic Synthesis, Spectroscopy, Electrochemistry, and Solid-State Organization", *J. Am. Chem. Soc.*, vol.126, no.41, pp.13480-13501, Sep., 2004.
- [7] F. Garnier, A. Yassar, R. Hajlaoui, G. Horowitz, F. Deloffre, B. Servet, S. Ries, and P. Alnot, "Molecular engineering of organic semiconductors: design of self-assembly properties in conjugated thiophene oligomers", *J. Am. Chem. Soc.*, vol.115, no.19, pp.8716-8721, Sep., 1993.
- [8] F. Garnier, R. Hajlaoui, A. E. Kassmi, G. Horowitz, L. Laigre, W. Porzio, M. Armanini, and F. Provasoli, "Dihexylquaterthiophene, A Two-Dimensional Liquid Crystal-like Organic Semiconductor with High Transport Properties", *Chem. Mater.*, vol.10, no.11, pp.3334-3339, Oct., 1998.
- [9] H. E. Katz, A. Dodabalapur, L. Torsi and D. Elder, "Precursor Synthesis, Coupling, and TFT Evaluation of End-Substituted Thiophene Hexamers", *Chem. Mater.*, vol.7, no.12, pp. 2238-2240, Dec., 1995.
- [10] A. Facchetti, Y. Deng, A. Wang, Y. Koide, H. Sirringhaus, T. Marks and R. Friend, "Tuning the Semiconducting Properties of Sexithiophene by α,ω -Substitution α,ω -Diperfluorohexylsexithiophene: The First n-Type Sexithiophene for Thin-Film Transistors", *Angew. Chem. Int. Ed.*, vol.39, no.24, pp.4547-4551, Dec., 2000.
- [11] D.-H. Lee, G.-W. Hyung and Y.-K. Kim, "The Influence of a Polymeric Adhesion Layer on Gate Insulators in Organic Thin-Film-Transistors", *J. Korean Phys. Soc.*, vol.49, no.3, pp.1111-1116, Sep., 2006.
- [12] J. H. Lee, S. H. Kim, J. B. Koo, J. W. Lim, S. C. Lim, G. H. Kim, S. J. Yun, K. S. Suh, C. H. Ku and J. Jang, "Isolation Effect on Organic Thin Film Transistors for Low Hysteresis Characteristics", *J. Korean Phys. Soc.*, vol.49, no.3, pp.1148-1151, Sep., 2006.

Jaehong Kwon received the B.S. and M.S. degrees in electronics engineering from Sejong University, Seoul, Korea, in 2003 and 2005, respectively. He is currently working toward the Ph.D. degree at Korea University, Seoul, Korea. During 2003, he was an Intern Researcher with the Corporate R&D Center, Samsung SDI Company, Ltd., Korea. Since 2005, he has been a Researcher in the Semiconductor Research Center, Korea University. Since 2006, he has been an Electronics and Electrical Engineer at Korea University. His current research interests include flexible printed electronics (circuitry, memory, display, and sensor) and silicon solar cell.

Myung-Ho Chung received the B.S. degree in electrical engineering from Korea University, Seoul, Korea, in 2008. From 2008, he is currently working toward the M.S. degree in electronics and electrical engineering at Korea University, Seoul, Korea. His current research interests include flexible organic electronics with organic thin-film transistors (OTFTs).

Tae-Yeon Oh received the B.S. degree in electrical engineering from Korea University, Seoul, Korea, in 2009. From 2009, he is currently working toward the M.S. degree in electronics and electrical engineering at Korea University, Seoul, Korea. His current research interests include flexible organic electronics with organic thin-film transistors (OTFTs) using nano imprinting method.

Hyeon-Seok Bae received the B.S. degree in electrical engineering from Kwangju University, Seoul, Korea, in 2004. From 2008, he is currently working toward the M.S. degree in electronics and electrical engineering at Korea University, Seoul, Korea. His current research interests include flexible electronics with oxide thin-film transistors.

Byeong-Kwon Ju (M'00) received the M.S. degree in electronic engineering from the University of Seoul, Seoul, Korea, in 1988, and the Ph.D. degree in semiconductor engineering from Korea University, Seoul, in 1995. In 1988, he joined Korea Institute of Science and Technology (KIST), Seoul, as a Principal Research Scientist, and was engaged in the development of mainly silicon micromachining and microsensors. In 1996, he was a Visiting Research Fellow with the Microelectronics Centre, University of South Australia, South Australia, Australia. Since 2005, he has been an Professor with Korea University, Seoul. He is the author or coauthor of more than 300 journal articles. His current research interests include flexible electronics (organic light-emitting diodes (OLEDs) and organic thin-film transistors (OTFTs)), field emission device, microelectromechanical systems (MEMS) (Bio and RF), and carbon nanotube-based nano systems. Prof. Ju is a member of the Society for Information Display (SID), the Korea Institute of Electrical Engineering (KIEE), and the Korea Sensor Society.