

# Synthesis and Characterization of Novel Fused Aromatic Semiconductors

**Qinghua Zhao, Jong-Won Park, Yun-Hi Kim, and Soon-Ki Kwon\***  
**School of Nano and Advanced Materials Engineering, Gyeongsang National**  
**Universtiy, Chinju 660-701, South Korea**  
 Phone: + 82-55-751-5296 , \*E-mail: [skwon@gnu.ac.kr](mailto:skwon@gnu.ac.kr)

## Abstract

The novel oligomers were synthesized by Grignard reaction, the Suzuki coupling reaction, etc. The oligomers were characterized by Infrared (IR), Mass spectrometer (MS). Their thermal properties were investigated by differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA). The new oligomers showed high thermal stability above 300 °C.

## 1. Introduction

Organic semiconductors have been widely studied from viewpoints of their fundamental optoelectronic properties and their potential application such as organic thin film transistor (OTFT)<sup>1-2</sup>, organic light-emitting diodes (OLED) and photovoltaic cells. When compared to their inorganic counterparts, i. e. classical covalent semiconductors such as Si, organic semiconductor present a better difference that fine tuning of the electronic properties of organic molecular semiconductor can be tuned through the modification of the chemical structure of their constituting materials. Because organic semiconductors are molecular materials, formed by assemblies of molecules held together by weak van der Waals forces, which implies that the properties of the solid are directly governed by those of the individual molecules, which form the elemental bricks of the material, and also by the way these bricks are spatially ordered in the material<sup>3</sup>.

Up to date, some semiconductors have been reported to have high mobility. Among all investigated organic semiconductors, fused aromatic compounds such as tetracene and pentacene have shown the most promising performance<sup>4</sup>. Because they facilitate the formation of radical cation (holes) at the interface

between a dielectric and a semiconducting layer, and the extended  $\pi$  system of a higher acene enhances the intermolecular overlap of  $\pi$ - $\pi$  systems in the solid state and leads to high mobility<sup>5-7</sup>. However, they possess relatively low bandgap and a high-energy highest occupied molecular orbital (HOMO) level. Therefore, they are easily oxidized, which results in poor device stability, making them unsuitable for practical electronic circuit application<sup>3</sup>.

To address this problem, design and synthesis of organic semiconductors with high charge carrier mobility as well as good stability is desirable. In a great detail, firstly, highly ordered thin film with large interconnected polycrystalline grains are necessary to achieve high efficiency OTFT. Secondly, to facilitate the charge injection process, the HOMO energy level of the material should match well with the work function of the source or drain electrodes. To adjust the HOMO energy level of the material, it is a better way that the introduction of electron-donating group was considered as "end-cap" substituent. Properly designed end-cap substituents may improve crystallinity, encourage layer growth, and promote dense intermolecular packing in two-dimensional layers, yielding gains in conductivity<sup>8</sup>. In here, fused aromatic compound (naphthalenyl or anthracenyl or thionethiophenyl) was chosen to organize more ordered symmetric molecular structure, which facilitates molecular packing necessary for high mobility.

## 2. Experimental

**Materials.** All starting materials were purchased from Aldrich and used unless otherwise specified. 6-bromonaphthalen-2-ol was purchased from the Aldrich Company. 2,6-

dibromoanthracene<sup>7</sup> and 2,6-dibromothiophene<sup>9</sup> were obtained from the all known procedure.

**Measurements.** The <sup>1</sup>H NMR spectra were recorded with a Bruker AM-300 spectrometer. The FT-IR spectra were measured on a Bomem Michelson series FT-IR spectrometer. The melting points were determined with an Electrothermal Mode 1307 digital analyzer. The thermal analysis were performed on a TA TGA 2100 thermogravimetric analyzer in a nitrogen atmosphere at a heating rate of 20 °C /min. Differential scanning calorimeter(DSC) was conducted under nitrogen on a TA instrument 2100 DSC. The sample was heated with 10 °C /min from 30 °C to 400 °C. UV-vis absorption spectra and photoluminescence spectra were measured by Perkin Elmer LAMBDA-900 UV/VIS/IR spectrophotometer and LS-50B luminescence spectrophotometer, respectively. The photoluminescence spectra were reacted on a Perkin-Elmer LS-50 fluorometer utilizing a lock-in amplifier system with a chopping frequency of 150 Hz.

### Synthesis

**2-Bromo-6-hexyloxy naphthalene:** A 500 ml of 1-neck flask was equipped with 6-bromonaphthalen-2-ol (30 g, 0.135 mol), bromohexane (24 g, 0.145 mol), KOH (8.25 g, 0.147 mol) and NaI (1.35 g, 0.009 mol) dissolved in 300 ml of EtOH. After the reaction mixture was refluxed for 24 h, the ethanol was removed. Then the water was poured into the mixture, extracted by diethyl acetate and dried with MgSO<sub>4</sub>. The pure product was obtained by column chromatography using hexanes as eluent. Yield: 32.98 g (79.8%). mp: 40-42 °C. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm) : 7.92 (s, 1H, Ar-H), 7.58~7.66 (m, 2H, Ar-H), 7.50 (dd, 1H, J=1.61 and 1.62, Ar-H), 7.16 (dd, 1H, J=6.69, Ar-H), 7.10 (s, 1H, Ar-H), 4.07 (t, 2H, J=6.50, -O-CH<sub>2</sub>-), 1.81~1.91 (m, 2H, aliphatic-H), 1.31~1.55 (m, 6H, aliphatic-H), 0.96 (t, 3H, aliphatic-H)

**2-Hexyloxy-naphthalene-6-boronic acid:** 2-Bromo-6-hexyloxy naphthalene (20g, 0.065 mol) dissolved in 150 ml anhydrous THF was added

slowly to fresh magnesium powders (1.74 g, 0.072 mol) after initiation by heating, and the solution was refluxed for 1h under nitrogen atmosphere. After triethylborate (20.9 g, 0.143 mol) was injected into the solution at -78 °C, the solution was stirred for 6 h at room temperature. Then the solution was poured into 2N HCl, and extracted with ethylacetate. The crude product was recrystallized in THF and hexane (1:10). Yield: 9 g (50.8%) mp: 80-82 °C. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm) : 8.69 (s, 1H, Ar-H), 8.21 (d, 1H, J=8.19, Ar-H), 7.95 (d, 1H, J=8.94, Ar-H), 7.83 (d, 1H, J=8.30, Ar-H), 7.15~7.24 (m, 2H, Ar-H), 4.08 (t, 2H, J=6.54, aliphatic-H), 1.84~1.94 (m, 2H, aliphatic-H), 1.40~1.57 (m, 6H, aliphatic-H), 0.98 (t, 3H, J=7.03, aliphatic-H)

### 6,6-Bis-hexyloxy-[2,2',6',2'']ternaphthalene

**(1):** 2,6-dibromonaphthalene (0.5 g, 0.002 mol) and 2-hexyloxy-naphthalene-6-boronic acid (1.09 g, 0.004 mol) were added to 100 ml of 3-neck flask with a solution of 4.37ml 2N K<sub>2</sub>CO<sub>3</sub> and 50 ml THF. After keeping the nitrogen bubbling for 20 min, tetrakis(triphenylphosphine-palladium) (Pd(PPh<sub>3</sub>)<sub>4</sub>) (0.06 g, 5.2x10<sup>-5</sup> mol) was added to the reaction mixture. Then the reaction was refluxed for 24 h. After the reaction was terminated with 2N HCl, filtered to get crude solid. The pure product was obtained by recrystallization from chlorobenzene. Yield: 0.45 g (44 %) mp: 378-380 °C. MS(EI)(m/z): 580.0 (M<sup>+</sup>) FT-IR (KBr, cm<sup>-1</sup>) : 2950, 2920, 2870 (aliphatic C-H), 3010 cm<sup>-1</sup> (Aromatic C=C), 1232 cm<sup>-1</sup> (Ar-C-O)

**2,6-Bis-(6-hexyloxy-naphthalen-2-yl)anthracene (2):** The procedure is the same with that of 6,6''-Bis-hexyloxy-[2,2',6',2''] ternaphthalene . 2,6-dibromoanthracene<sup>7</sup> (1 g, 0.003 mol), 2-Hexyloxy-naphthalene-6-boronic acid (1.8 g, 0.006 mol) , 14 ml 2N K<sub>2</sub>CO<sub>3</sub> , 50 ml THF and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.1 g, 8.2x10<sup>-5</sup> mol) was used for the reaction. Yield: 0.98 g (53.3%) MS(EI) (m/z): 630.0 (M<sup>+</sup>) FT-IR (KBr, cm<sup>-1</sup>) : 2953, 2920, 2860 (aliphatic C-H), 3010 cm<sup>-1</sup> (Aromatic C=C), 1237 cm<sup>-1</sup> (Ar-C-O)

### 2,5-Bis-(6-hexyloxy-naphthalen-2-yl)thieno

**[3,2-b]thiophene (3):** The procedure is the same with that of 6,6-bis-hexyloxy-[2,2',6',2'']ternaphthalene. 2,6-dibromothiophene [3,2-b] thiophene <sup>9</sup>(0.47 g, 0.002 mol) and 2-hexyloxy-naphthalene-6-boronic acid (1 g, 0.004 mol), 5 ml 2N K<sub>2</sub>CO<sub>3</sub>, 30 ml THF and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.037g, 3.2x10<sup>-5</sup> mol) were used for the reaction. Yield: 0.5 g (53.4%) MS(EI)(m/z): 592.0 (M<sup>+</sup>) FT-IR (KBr, cm<sup>-1</sup>): 2958, 2928, 2860 (aliphatic C-H), 3115 cm<sup>-1</sup> (Aromatic C=C), 1240 cm<sup>-1</sup> (Ar-C-O)

### 3. Results and Discussion

The chemical structures of Oligomer 1, 2 and 3 were shown in Figure 1. All materials were p-type active materials of OTFTs based on a combination of hexyloxy naphthalene with naphthalene or anthracene or thienothiophene. Scheme 1 illustrated the synthetic route of the Oligomers.

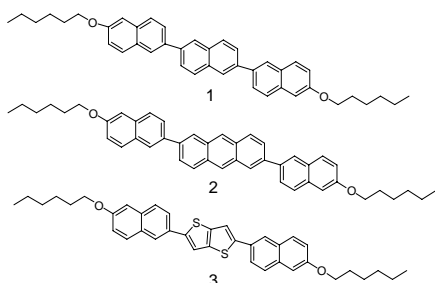
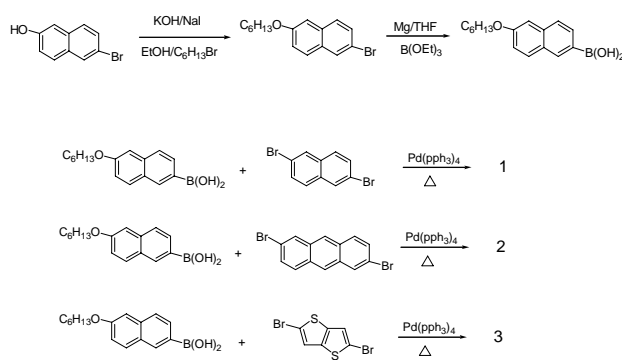


Figure 1. Chemical Structure of Oligomer 1, 2 and 3.



Scheme 1. Synthetic routes for Oligomer 1, 2 and 3.

The oligomers were prepared via a manifold chemical reaction such as Grignard reaction, Suzuki coupling reaction, etc. 2-Bromo-6-

hexyloxy naphthalene was received by alkylation of 6-bromo-2-naphthalenol in the presence of KOH and NaI. After 2-bromo-6-hexyloxy-naphthalene was reacted with magnesium and refluxed for 1 h, triethylborate was injected into the solution at -78 °C to obtain 2-hexyloxy naphthalene-6-boronic acid. Then the oligomers were prepared by palladium-catalyst cross-coupling reaction of boronic acid with 2,6-dibromonaphthalene, 2,6-dibromoanthracene and 2,5-dibromothiophene, respectively.

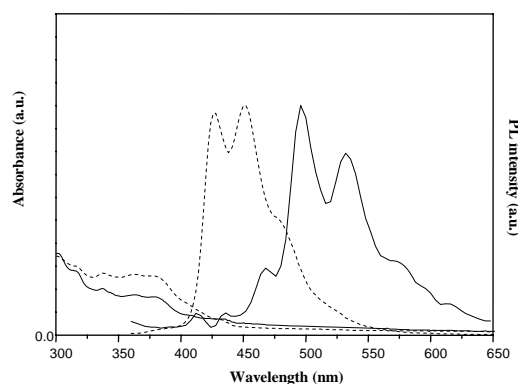


Figure 2. UV and PL spectra of the Oligomer 3 in solution (dotted line) and film (solid line)

The absorption and emission spectra of the oligomer 3 in chlorobenzene and in the solid state, were depicted in Figure 2. The maximum emission of the solid state PL was 413 nm and 450 nm, exhibiting large red-shift (50-90 nm) in comparison with its absorption maximum of 505 nm and 540 nm in dilute chlorobenzene solution. Oligomer 1 and 2 showed smaller red-shift than oligomer 3. From the result, we can suppose that the red-shift could be caused by aggregation or excimer formation, owing to the different interactions between the different molecules, which was expected that the oligomers had high mobility due to high intermolecular interaction.

Table 1. Electrochemical Properties of oligomer 1, 2 and 3.

	Eonset (OX)(ev)	HOMO (ev)	LUMO (ev)	UVedge (nm)	Eg (ev)
1	1.03	5.43	2.32	398	3.11
2	0.99	5.39	2.42	417	2.97
3	1.06	5.46	2.67	443	2.79

Cyclic voltammetry (CV) was employed to estimate its HOMO and LUMO energy level.

Table 1 showed the HOMO, LUMO and energy band gap of oligomer 1, 2 and 3.

Compound 1 had larger band-gap (3.11 eV), which showed it was not oxidized and had better stability in air.

The thermal properties of the oligomers were determined by TGA and DSC. The oligomer 1, 2 and 3 appeared 5% weight loss at 400 °C, 410 °C and 395 °C in the nitrogen, respectively, shown in Figure 3. In the DSC thermograms, the oligomer 1, 2 and 3 showed several transition temperatures (Figure 4). The oligomer 1 have four transition temperatures of 223 °C, 289 °C, 330 °C and 383 °C. Two transitions temperatures for oligomer 2 were 308 °C and 326 °C. Oligomer 3 also showed three transitions temperatures at 268 °C, 304 °C and 329 °C. From the results, it suggested that the novel oligomers had high ordered structures.

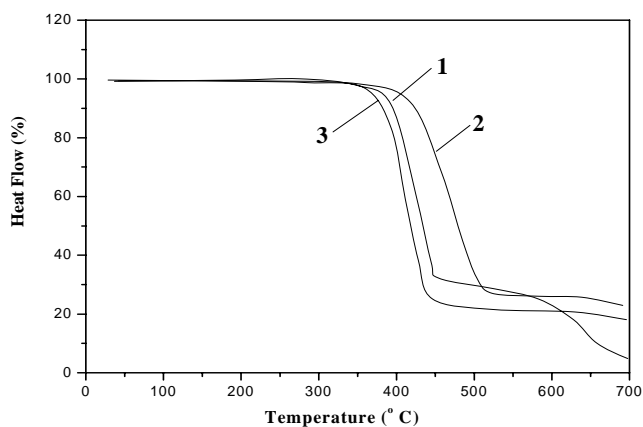


Figure 3. TGA curve of the oligomers

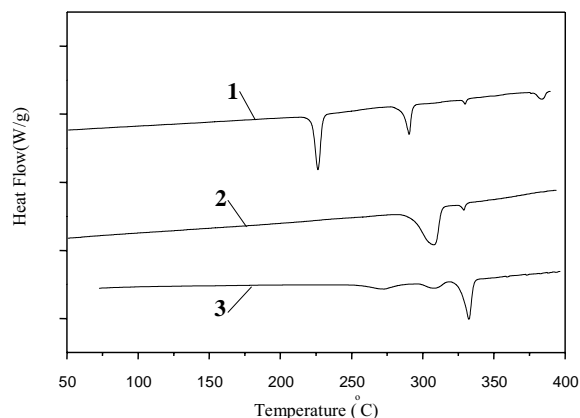


Figure 3. DSC curve of the oligomers .

#### 4. Conclusion

The novel oligomers which are composed of fused aromatic compound were synthesized by Grignard reaction and Suzuki coupling reaction. The obtained oligomers showed ordered molecular structure and stability. From the results, it is expected that the oligomers will have high mobility.

#### 5. Acknowledgements

This work was supported by the 21<sup>st</sup> Century Frontier R & D Program funded by the Ministry of Science and Technology of Korean government.

#### 6. References

- [1] G. B. Blanchet, Y.-L. Loo, J. A. Rogers, F. Gao, C. R. Fincher, *Appl. Phys. Lett.* 82, 463, 2003
- [2] D. Voss, *Nature*, 407, 442, 2000
- [3] F. Garnier, A. Yassar, R. Hajlaoui, G. Horowitz, F. Deloffre, B. Servet, S. Ries, S. Ries, P. Alnot, *J. Am. Chem. Soc.* 115, 8716, 1993
- [4] H. Klauk, M. Halik, U. Zschieschang, G. Schmid, W. Radlik, W. Weber, *J. Appl. Phys.* 92, 5259, 2002
- [5] H. E. Katz, Z. Bao, S. L. Gilat, *Acc. Chem. Res.* 34, 359-369, 2001
- [6] F. Garnier, A. Yassar, R. Hajlaoui, G. Horowitz, F. Deloffre, B. Servet, S. Ries, P.

- Alnot, J. Am. Chem. Soc. 115, 8716 – 8721, 1993.
- [7] K. Ito, T. Suzuki, Y. Sakamoto, D. Kubota, Y. Inoue, F. Sato, S. Tokito, Angew. Chem. Int. 42, 1159, 2003
- [8] T. M. Barday, A. W. Cordes, C. D. Mackinnon, R. T. Oakkey, R. W. Reed, Chem. Mater, 9, 981, 1997
- [9] E. Lim, B. Jung, H. K. Shim, Macromolecules, 36, 4288, 2003