

Synthesis and Characterization of Novel Fused Aromatic Materials

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Abstract

A series of new oligomers were synthesized by Grignard reaction, the Suzuki coupling reaction, etc. The oligomers showed excellent TFT performance with mobilities higher than $0.5 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$ and on/off ratios higher than 5×10^5 . Their electronic and optical properties were investigated using many analysis methods, such as X-ray diffraction (XRD), UV-vis and photoluminescence spectroscopies.

1. Introduction

Organic semiconductors that consist of conjugated oligomers or polymer have been widely studied from viewpoints of their fundamental optoelectronic properties and their potential application such as organic thin film transistor(OTFT)¹⁻², organic light emitting diodes(OLED) and photovoltaic cells. Among all investigated organic semiconductors, fused aromatic compounds(pentacene) have attracted great interest, owing to its high OTFT performance: mobility of $0.3\text{-}0.7 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$ on SiO_2/Si substrate, $1.5 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$ on chemically modified SiO_2/Si substrate, and $3 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$ on polymer gate dielectrics³⁻⁵. However, pentacene is subject to rapid degradation in ambient conditions, presumably to form the endoperoxide or Diels-Alder adducts.⁶⁻⁷ Over the past ten years, significant progress has been made with respect to increasing the performance of organic semiconductors, such as improving their charge-carrier mobility and on/off ratio⁸⁻¹¹, especially for oligothiophenes. Recently, Meng et al. reported a

mobility of $0.50 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$ for bis(5'-alkylthiophen-2'-yl)-2,6-anthracene evaporated onto a $\text{SiO}_2/n\text{-doped-Si}$ substrate¹². In this communication, the novel fused aromatic materials were synthesized and their properties were investigated. OTFT based on the oligomers were fabricated and showed good performance with mobility higher than $0.5 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$, on/off ratios higher than 5×10^5 . The high mobility was achieved, owing to organize more ordered symmetric molecular structure using fused aromatic compound (naphthalenyl or anthracenyl or thionethiophenyl), 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 and 2,6-dibromothienothiophene were obtained from the all known procedure.

Synthesis.

2-Bromo-6-hexyloxy naphthalene: A 500 ml of 1-neck flask was equipped with 6-bromo-2-naphthol (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_4 . The pure product was obtained by column chromatography using hexanes as eluent. Yield: 32.98 g (79.8 %). M.P.:

40-42 °C. $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ [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-CH₂-), 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 2 N HCl, and extracted with ethylacetate. The crude product was recrystallized in THF and hexane (1:10). Yield: 9 g (50.8 %). M.P.: 80-82 °C. $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ [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)

Compound 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 2 N K_2CO_3 (4.37ml) and THF (50 ml). After keeping the nitrogen bubbling for 20 min, tetrakis(triphenylphosphine-palladium) ($\text{Pd}(\text{PPh}_3)_4$) (0.06 g, 5.2×10^{-5} mol) was added to the reaction mixture. Then the reaction was refluxed for 24 h. After the reaction was terminated with 2 N HCl, filtered to get crude solid. The pure product was obtained by recrystallization from chlorobenzene. Yield: 0.45 g (44 %). M.P.: 378-380 °C. MS(EI)(m/z): 580.0 (M^+). FT-IR (KBr, cm^{-1}) : 2950, 2920, 2870 (aliphatic C-H), 3010 cm^{-1} (Aromatic C=C), 1232 cm^{-1} (Ar-C-O)

Compound 2: The procedure is the same with that of compound 1. 2,6-dibromoanthracene (1 g, 0.003 mol), 2-Hexyloxy-naphthalene-6-boronic acid (1.8 g, 0.006 mol), 14 ml 2 N K_2CO_3 , 50 ml THF and $\text{Pd}(\text{PPh}_3)_4$ (0.1 g, 8.2×10^{-5} mol) was used for the reaction. Yield: 0.98 g (53.3 %). M.P.: 396-398 °C. MS(EI) (m/z): 630.0 (M^+). FT-

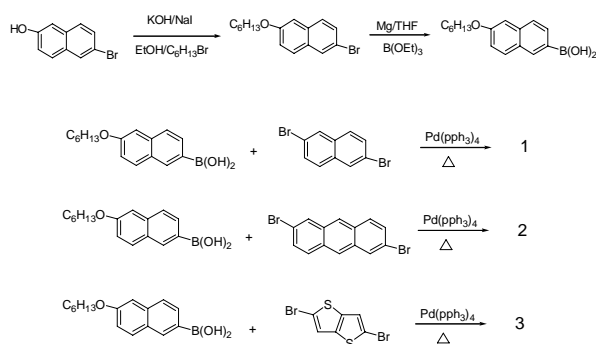
IR (KBr, cm^{-1}) : 2953, 2920, 2860 (aliphatic C-H), 3010 cm^{-1} (Aromatic C=C), 1237 cm^{-1} (Ar-C-O)

Compound 3: The procedure is the same with that of compound 1. 2,6-dibromothieno [3,2-b] thiophene (0.47 g, 0.002 mol) and 2-hexyloxy-naphthalene-6-boronic acid (1 g, 0.004 mol), 5 ml 2 N K_2CO_3 , 30 ml THF and $\text{Pd}(\text{PPh}_3)_4$ (0.037g, 3.2×10^{-5} mol) were used for the reaction. Yield: 0.5 g (53.4 %). M.P.: 368-370 °C. MS(EI)(m/z): 592.0 (M^+) FT-IR (KBr, cm^{-1}) : 2958, 2928, 2860 (aliphatic C-H), 3115 cm^{-1} (Aromatic C=C), 1240 cm^{-1} (Ar-C-O)

Fabrication and Measurement of OTFTs: OTFTs were constructed on heavily doped n-type silicon wafers with a resistivity of 0.01-0.015 Ω cm, covered with 600 Å thick thermally grown silicon dioxide (SiO_2) (1-10). The compound was deposited on SiO_2 by vacuum evaporation at rates between $0.8\text{-}1.0 \text{ \AA s}^{-1}$ under a base pressure of 10^{-6} torr. The thickness of the semiconductor layer was 60 nm. Gold (50 nm) was used for the source and drain electrodes and deposited on the organic semiconductor layer through a shadow mask with a channel width (W) of 1000 μm and a channel length (L) of 50 μm .

Atomic force microscope (AFM) images were taken with a Digital Instrument Nanoscope IV operating in tapping mode in air based on a low-force imaging technique to get a high-resolution image. Wide angle X-ray diffraction (XRD) measurements were performed at room temperature using a Rigaku diffractometer (Model D/MAX-2200V). The CuK α radiation source was operated at 40 kV and 60 mA.

3. Results and Discussion



Scheme 1. Synthetic scheme of oligomers

Scheme 1 illustrates the synthetic route of oligomeric p-type OTFT materials. The oligomers were prepared via a manifold chemical reaction such as Grignard reaction, Suzuki coupling reaction, etc.

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.

Table 1. Electrochemical Properties of oligomers.

	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

The thermal properties of the oligomers were determined by TGA and DSC. The compound 1, 2 and 3 appeared 5% weight loss at 400 °C, 410 °C and 395 °C in the nitrogen, respectively. In the DSC thermograms, the compound 1, 2 and 3 showed several transition temperatures. The compound 1 have four transition temperatures of 223 °C, 289 °C, 330 °C and 383 °C. Two transition temperatures for compound 2 were 308 °C and 326 °C. Compound 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. Top contact OTFT was employed for electrical analysis in this study. Compound 2 was used as a semiconductor and silicon oxide modified with hexamethyldisilazane (HMDS) was used as a gate insulator. The output characteristic curves [for drain current (I_{ds}) vs drain voltage (V_{ds})] of OTFTs (channel length = 50 μm , width = 1000 μm) were shown in Fig 1(left). The OTFTs showed typical p-type characteristics with a clear transition from linear to saturation behaviour. At a given negative gate voltage, I_{ds} initially increased linearly with a small negative V_{ds} and then saturates due to a pinch off of accumulation layer at the interface between semiconductor and gate insulator. Fig 1b) showed transfer characteristic curves of OTFTs fabricated with compound 2, respectively, where gate voltage (V_{gs}) was swept from 10V to -20V and V_{ds} was set at -10V. The OTFTs with compound 2 deposited at of T_{sub} (substrate temperature) = 140 °C showed mobility as high as 0.64 cm^2/Vs . Other performance parameters were extracted from the transfer characteristic curve [Fig 1b)] and it showed I_{on}/I_{off} current ratio of 7.5×10^5 , threshold voltage as low as 4.4 V, and subthreshold slop of 0.8 V/dec when respectively. The film of the compound 2 was investigated by using XRD in reflection mode. Highly crystalline film was observed, as seen in Figure 2 a). In film, the first order reflection is very intense, and

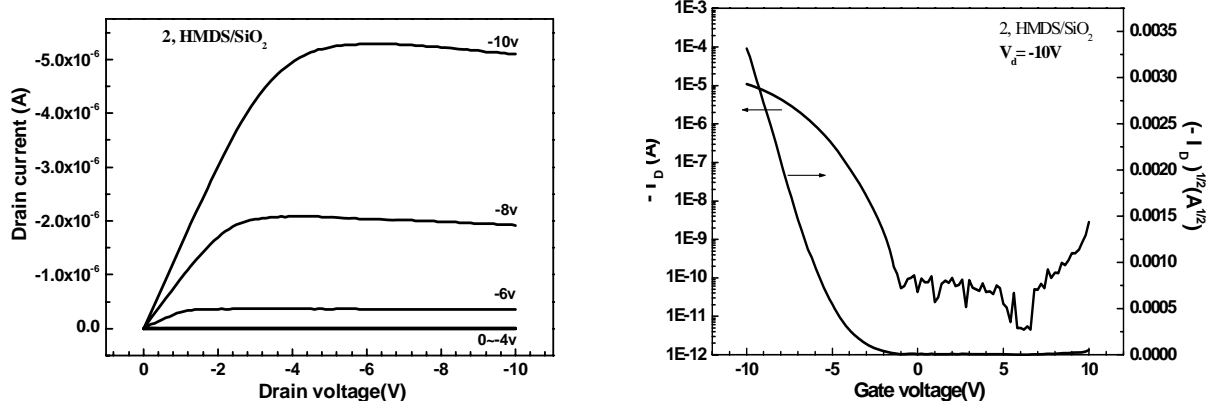


Figure 1. Plot of drain current (I_D) versus drain voltage (V_D) characteristics of compound 2 at different gate voltages (V_G) (left); I_D versus V_G and $I_D^{1/2}$ versus V_G for TFT prepared using compound 2 as the semiconductor material (right).

multiple order of reflection, preferred orientation is also exhibited, indicating the film to be well-ordered, layered microstructure. From the XRD data of the thin film, the interplanar d spacings of the compound was calculated. From the first layer line, the monolayer thickness is 38.38 Å for compound 2, which corresponds well to the length of the molecule determined by theoretical calculation. From the result, it is suggested that the molecule is oriented with its long axis almost normal to the film, with the π - π stacking direction parallel to the substrate, and in that case the charge carriers could transport easily with high mobility.

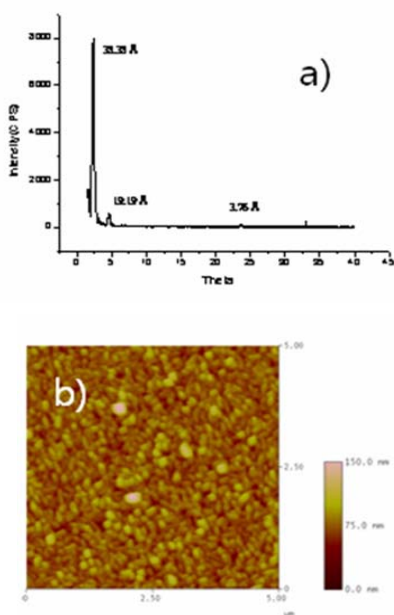


Figure 2. a) XRD patterns and b) AFM image of a 60 nm thick compound 2 film on Si/SiO₂ deposited at a substrate temperature of 140 °C

AFM image of compound 2 is shown in Figure 2 b). It is observed that the full covering of the substrate with the material and good network inter connection between the crystallites that is probably, responsible for good charge carrier mobility, measured in OTFT.

4. Conclusion

The novel oligomers which are composed of fused aromatic compound 1,2 and 3 were synthesized by Grignard reaction and Suzuki coupling reaction. The obtained oligomers showed high thermal stability, oxidative stability and liquid crystal behaviors. In the TFT device, compound 2 show high mobility (0.64 cm²/Vs).

Acknowledgements

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5. References

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