

## A First Synthesis and Physical Properties of Asymmetric Anthracenes-Thiophenes Bridged with Ethylene

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Here we report our recent result of a new semiconductor material, which has an asymmetric structure. The synthesized molecules consist of anthracene and thiophene connected by bridged ethylene and substituted with hexyl or dodecyl groups as pendants. The semiconductors were synthesized using a McMurry coupling reaction between anthracene-2-carbaldehyde and corresponding 5-hexyl(or dodecyl)thiophene-2-carbaldehyde. A first investigation of synthesized asymmetry AVHT (**9a**) and AVDT (**9b**) for the physical properties showed that they have high oxidation potential and thermal stability. The devices prepared by using AVHT (**9a**) and AVDT (**9b**) showed the mobility of  $2.6 \times 10^{-2}$  cm<sup>2</sup>/Vs and  $4.4 \times 10^{-3}$  cm<sup>2</sup>/Vs, respectively, in solution processed OTFTs.

**Key Words** : Organic thin-film transistors, McMurry coupling, Asymmetric anthracene derivatives, Solution-processing, p-Type charge carrier mobility

### Introduction

During the past decades, organic thin-film transistors (OTFTs) have attracted intense interest because of their potential application in active-matrix display and integrated circuits (ICs) for logic and memory chips. Several types of conjugated oligomers and polymers were synthesized as new organic semiconductor candidates.<sup>1-11</sup> Among of the synthesized compounds for OTFTs candidates, many investigators have interest in anthracene moiety because of the characteristic results such as hole mobility. The hole mobility in anthracene single crystals was measured by the time-of-flight photocurrent technique and found to reach up to 3 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> at 300 K.<sup>2</sup> Since anthracene have shown good character for OTFTs, many research groups want to develop and find out more better structure of anthracene derivatives which have conjugated systems as OTFTs. The anthracenes conjugated triple bond and aromatic or heteroaromatics with end-capped *n*-alkyl chain were synthesized and reported for the OTFTs properties.<sup>12-20</sup> The synthesized anthracene derivatives have a symmetry and were exhibited as a good OTFT device performances but still remain severe limitation in large scale device fabrication because of the complexity of the process. On the other hand, one of the reported results for the asymmetric molecule (quaterthiophene) exhibited somewhat good charge carrier mobility.<sup>21</sup> It's means asymmetric material also seems to have possibility to develop as organic semiconductors. Therefore we designed and synthesized a new structure of asymmetric anthracene derivatives

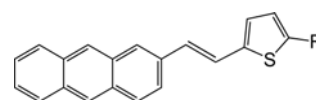
and investigated the physical and organic semiconductor properties of synthesized molecules for the first time.

We decide to introduce double bond instead of triple bond between anthracene and monothiophene which has alkyl group as a pendant to confirm the length effect of alkyl chain.<sup>22</sup> The alkyl side chain of the end-groups leads to a good molecular ordering at high temperature, so the device became more stable and increase the solubility.<sup>23,24</sup>

Herein, we report the synthesis and characteristics of novel asymmetric anthracene derivatives for OTFTs, composed of anthracene and 5-alkyl-2-ethenylthiophene (Figure 1). The asymmetric molecules AVHT and AVDT were synthesized and characterized. Their physical properties were also measured with various instruments.

### Experimental

**General and Materials.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a 300 MHz spectrometer with chemical shift values reported in  $\delta$  units (ppm) relative to an internal standard (TMS). IR spectra were obtained on a Mattson Genesis Series FT-IR spectrophotometer. Elemental analysis



AVHT, R = C<sub>6</sub>H<sub>13</sub>, AVDT, R = C<sub>12</sub>H<sub>25</sub>

**Figure 1.** Structure of synthesized asymmetry OTFTs candidates.

were performed with a Perkin-Elmer 240C. Mass spectra were obtained on a JMS-700, JEOL. UV-visible absorption and photoluminescence (PL) spectra were measured with a Perkin Elmer LAMBDA-900 UV/VIS/NIR spectrophotometer and a LS-50B luminescence spectrophotometer, respectively. The melting points were determined using an Electrothermal Mode 1307 digital analyzer and were uncorrected. The open-bed chromatography was carried out on silica gel (70-230 mesh, Merck) using gravity flow. The column was packed with slurries made from the elution solvent. Thiophene, 2-aminoanthraquinone, 2-methyl-3-butyn-2-ol, bithiophene and other chemicals were purchased from Aldrich Chemical Co and used without further purification. The solvents such as tetrahydrofuran (THF), diethyl ether, toluene and acetonitrile were purified with sodium/benzophenone or calcium hydride under nitrogen gas.

**Measurements.** Thermogravimetric analysis (TGA) was performed under nitrogen using a TA instruments 2050 thermogravimetric analyzer. The sample was heated at a 10 °C/min heating rate from 30 °C to 700 °C. Differential scanning calorimeter (DSC) studies were carried out under nitrogen using a TA instruments 2100 differential scanning calorimeter. The sample was heated from 30 °C to 300 °C with a heating rate of 10 °C/min. Cyclic voltammogram (CV) of the sample was recorded using a Epsilon E3 at room temperature in a 0.1 M solution of tetrabutylammonium perchlorate ( $\text{Bu}_4\text{NClO}_4$ ) in acetonitrile under nitrogen environment at a scan rate of 50 mV/s. A Pt wire and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. Top-contact OFETs were fabricated on a common gate of highly n-doped silicon with a 300 nm thick thermally grown  $\text{SiO}_2$  dielectric layer. The octadecyltrichlorosilane monolayer was treated in toluene solution for 2 h. Solutions of the organic semiconductors were spin-coated at 2000 rpm from 0.5 wt % chloroform solutions to form thin films with a nominal thickness of 45 nm, confirmed using a surface profiler (Alpha Step 500, Tencor). Gold source and drain electrodes were evaporated on top of the semiconductor layers (100 nm). For all measurements, we used channel lengths (L) of 100  $\mu\text{m}$  and channel widths (W) of 2000  $\mu\text{m}$ . The electrical characteristics of the FETs were measured in air using both KEITHLEY 2400 and 236 source/measure units. Field-effect mobilities were extracted in the saturation regime from the slope of the source-drain current.

### Material Synthesis and Characterization

**2-Bromoanthraquinone (2), 2-Bromoanthracene (3) and Anthracene-2-carbaldehyde (4)** were prepared according to literature report and spectral data were coincidence.<sup>25,26</sup>

**2-Hexylthiophene (6a).** A solution of **5** (5.0 g, 60 mmol) in THF (50 mL) was added dropwise *n*-BuLi (40.6 mL, 65 mmol, 1.6 M in hexane) at -78 °C. The reaction mixture was stirred for 1 h at -78 °C under nitrogen. To the reaction mixture added slowly 1-bromohexane (10.7 g, 65 mmol), and elevated to rt and stirred for 12 h. The reaction was

quenched with water and product was extracted with diethyl ether. The organic layer was washed with water, brine, and dried over  $\text{MgSO}_4$ , and then evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (*n*-hexane) to give compound **6a** as colorless liquid. Yield: 8.3 g (82%); IR (KBr): 3071  $\text{cm}^{-1}$  ( $\text{sp}^2$  C-H), 2921-2854  $\text{cm}^{-1}$  ( $\text{sp}^3$  C-H), 1470  $\text{cm}^{-1}$  (C=C);  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.08 (d, 1H,  $J = 4.8$  Hz), 6.88 (dd, 1H,  $J = 4.8$  Hz), 6.69 (d, 1H,  $J = 3.3$  Hz), 2.81 (t, 2H,  $J = 7.7$  Hz), 1.68-1.61 (m, 2H), 1.34-1.26 (m, 6H), 1.02-0.98 (t, 3H,  $J = 1.8$  Hz); EI, MS  $m/z$  (%): 168 (100,  $\text{M}^+$ ).

**2-Dodecylthiophene (6b).** The procedure used the same as that for preparation of compound **6a**. Yield: 81%; IR (KBr): 3106-3038  $\text{cm}^{-1}$  ( $\text{sp}^2$  C-H), 2923-2856  $\text{cm}^{-1}$  ( $\text{sp}^3$  C-H), 1475  $\text{cm}^{-1}$  (C=C);  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.20-7.18 (dd, 1H,  $J = 1.2$  Hz), 7.03-7.00 (dd, 1H,  $J = 3.3$  Hz), 6.89-6.88 (dd, 1H,  $J = 0.9$  Hz), 2.96-2.91 (t, 2H,  $J = 7.3$  Hz), 1.85-1.75 (m, 2H), 1.41 (m, 18H), 1.05-1.00 (t, 3H,  $J = 6.6$  Hz);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  145.85, 126.65, 122.74, 32.10, 30.06, 29.83, 29.55, 22.86, 14.25 Hz; EI, MS  $m/z$  (%): 252 (100,  $\text{M}^+$ ).

**2-Bromo-5-hexylthiophene (7a).** Compound **6a** (30 g, 178 mmol) was dissolved in chloroform/acetic acid (100 mL/100 mL, v/v) and added NBS (34.9 g, 198 mmol) at rt. The reaction mixture was stirred for 2 h and quenched with water (100 mL). The product was extracted with  $\text{CH}_2\text{Cl}_2$  and washed with water, brine, and dried over  $\text{MgSO}_4$ , and then evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (*n*-hexane) to give compound **7a** as colorless liquid. Yield: 39 g (90%); IR (KBr): 3068  $\text{cm}^{-1}$  ( $\text{sp}^2$  C-H), 2951-2852  $\text{cm}^{-1}$  ( $\text{sp}^3$  C-H), 1521-1436  $\text{cm}^{-1}$  (C=C);  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.86-6.85 (d, 1H,  $J = 3.6$  Hz), 6.55-6.54 (d, 1H,  $J = 3.6$  Hz), 2.78-2.73 (t, 2H,  $J = 7.2$  Hz), 1.67-1.62 (m, 2H), 1.35-1.32 (m, 6H), 1.12-0.91 (t, 3H,  $J = 1.8$  Hz);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  147.66, 129.37, 124.33, 108.55, 31.53, 31.43, 30.34, 28.66, 22.57, 14.08 Hz; EI, MS  $m/z$  (%): 246 (100,  $\text{M}^+$ ).

**2-Bromo-5-dodecylthiophene (7b).** The procedure used the same as that for preparation of compound **7a**. Yield: 98%; IR (KBr): 3065  $\text{cm}^{-1}$  ( $\text{sp}^2$  C-H), 2956-2858  $\text{cm}^{-1}$  ( $\text{sp}^3$  C-H), 1525-1433  $\text{cm}^{-1}$  (C=C);  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.87-6.86 (d, 1H,  $J = 3.6$  Hz), 6.56-6.55 (d, 1H,  $J = 3.6$  Hz), 2.80-2.75 (t, 2H,  $J = 7.6$  Hz), 1.72-1.62 (m, 2H), 1.35-1.31 (m, 18H), 0.95-0.91 (t, 3H,  $J = 6.6$  Hz);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  147.63, 129.36, 124.32, 108.59, 31.99, 31.51, 29.70, 29.60, 22.76, 14.18 Hz; EI, MS  $m/z$  (%): 330 (100,  $\text{M}^+$ ).

**5-Hexylthiophene-2-carbaldehyde (8a).** Compound **7a** (3.6 g, 14.5 mmol) was dissolved in THF (40 mL) and added dropwise *n*-BuLi (11.8 mL, 19 mmol, 1.6 M in hexane) at -78 °C. The reaction mixture was stirred for 1 h at -78 °C under nitrogen. To the reaction mixture added slowly dimethyl formamide (1.4 g, 19 mmol), and elevated to rt and stirred for 12 h. The reaction quenched with water, and product was extracted with diethyl ether. The organic layer washed with water, brine, and dried over  $\text{MgSO}_4$ , and then

evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (*n*-hexane) to give compound **8a** as yellow color liquid. Yield: 1.8 g (63%); IR (KBr): 3108  $\text{cm}^{-1}$  ( $\text{sp}^2$  C-H), 2925-2850  $\text{cm}^{-1}$  ( $\text{sp}^3$  C-H), 1674  $\text{cm}^{-1}$  (C=O), 1439  $\text{cm}^{-1}$  (C=C);  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  9.77 (s, 1H), 7.58-7.57 (d, 1H,  $J = 3.9$  Hz), 6.87-6.86 (d, 1H,  $J = 3.6$  Hz), 2.84-2.79 (t, 2H,  $J = 7.65$  Hz), 1.71-1.61 (m, 2H), 1.30-1.24 (m, 6H), 0.87-0.82 (t, 3H,  $J = 6.75$  Hz);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  182.33, 157.47, 141.60, 136.95, 125.79, 31.91, 31.26, 30.76, 29.63, 29.51, 29.36, 29.28, 29.02, 22.68, 14.09 Hz; EI, MS  $m/z$  (%): 196 (100,  $\text{M}^+$ ).

**5-Dodecylthiophene-2-carbaldehyde (8b).** The procedure used the same as that for preparation of compound **8a**. Yield: 91%; IR (KBr): 3102  $\text{cm}^{-1}$  ( $\text{sp}^2$  C-H), 2931-2856  $\text{cm}^{-1}$  ( $\text{sp}^3$  C-H), 1674  $\text{cm}^{-1}$  (C=O), 1429  $\text{cm}^{-1}$  (C=C);  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  9.74 (s, 1H), 7.54-7.53 (d, 1H,  $J = 3.6$  Hz), 6.84-6.83 (d, 1H,  $J = 3.6$  Hz), 2.82-2.79 (t, 2H,  $J = 7.65$  Hz), 1.69-1.59 (m, 2H), 1.21 (m, 18H), 0.85-0.80 (t, 3H,  $J = 6.6$  Hz);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  182.33, 157.47, 141.60, 136.95, 125.79, 31.91, 31.26, 30.76, 29.63, 29.51, 29.36, 29.28, 29.02, 29.68, 14.09 Hz; EI, MS  $m/z$  (%): 280 (100,  $\text{M}^+$ ).

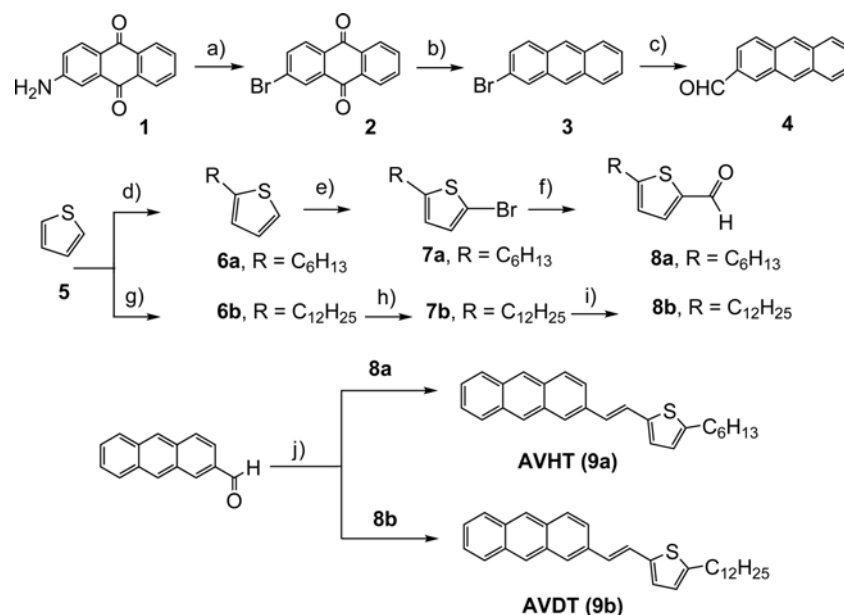
**(E)-2-(2-(anthracen-2-yl)vinyl)-5-hexylthiophene, AVHT (9a).** To the suspension of Zn (2.28 g, 11 mmol) in THF (50 mL) added dropwise  $\text{TiCl}_4$  (2.4 mL, 22 mmol) and stirred for 2.5 h at  $-18$  °C. To the reaction mixture added dropwise pyridine (0.9 mL, 11 mmol) and stirred for 10 min at  $-18$  °C. The mixed solution of **4** and **8a** in THF (10 mL) was added dropwise to the reaction mixture and elevated to 60 °C and stirred for 12 h under nitrogen. The reaction was quenched with  $\text{NaHCO}_3$  (10%, 5 mL), and product was extracted with diethyl ether. The organic layer washed with water, brine,

and dried over  $\text{MgSO}_4$ , and then evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (*n*-hexane) to give compound **9a** as yellow color solid. Yield: 0.4 g (68%); mp 165 °C; IR (KBr): 2958-2916  $\text{cm}^{-1}$  ( $\text{sp}^2$  C-H), 2846  $\text{cm}^{-1}$  ( $\text{sp}^3$  C-H), 1465  $\text{cm}^{-1}$  (C=C);  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.37 (s, 2H), 8.01-7.91 (m, 4H), 7.72-7.68 (d, 1H,  $J = 10.5$  Hz), 7.49-7.45 (m, 2H), 7.36-7.31 (d, 1H,  $J = 15.9$  Hz), 7.06-7.00 (d, 1H,  $J = 15.9$  Hz), 6.95-6.94 (d, 1H,  $J = 3.6$  Hz), 6.72-6.71 (d, 1H,  $J = 3.6$  Hz), 2.86-2.81 (t, 2H,  $J = 7.65$  Hz), 1.74-1.67 (m, 2H), 1.27 (m, 6H), 0.92-0.88 (t, 3H,  $J = 6.6$  Hz); EI, MS  $m/z$  (%): 370 (100,  $\text{M}^+$ ).

**(E)-2-(2-(anthracen-2-yl)vinyl)-5-dodecylthiophene, AVDT (9b).** The procedure used the same as that for preparation of compound **9a**. Yield: 91%; mp 150 °C; IR (KBr): 2959-2915  $\text{cm}^{-1}$  ( $\text{sp}^2$  C-H), 2845  $\text{cm}^{-1}$  ( $\text{sp}^3$  C-H), 1467  $\text{cm}^{-1}$  (C=C);  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.38 (s, 2H), 8.01-7.99 (m, 3H), 7.96-7.91 (d, 1H,  $J = 14.4$  Hz), 7.72-7.69 (d, 1H,  $J = 10.5$  Hz), 7.49-7.46 (m, 2H), 7.36-7.31 (d, 1H,  $J = 15.9$  Hz), 7.06-7.00 (d, 1H,  $J = 15.9$  Hz), 6.95-6.94 (d, 1H,  $J = 3.6$  Hz), 6.72-6.71 (d, 1H,  $J = 3.6$  Hz), 2.86-2.80 (t, 2H,  $J = 7.65$  Hz), 1.77-1.67 (m, 2H), 1.28-1.27 (m, 18H), 0.92-0.87 (t, 3H,  $J = 6.6$  Hz); EI, MS  $m/z$  (%): 454 (100,  $\text{M}^+$ ).

## Result and Discussion

**Synthesis and Characterization.** The synthetic strategy to obtain desired molecules is illustrated in Scheme 1. Compound **1** was converted to **4** via **2** and **3** following reactions; 1) treat with *tert*-butyl nitrite and copper(I) bromide, 2) reduce under vigorous conditions with hydroiodic acid and hypophosphorus acid, 3) formylation reaction. 2-Bromo-5-hexylthiophene (**7a**) and 2-bromo-5-dodecylthiophene



**Scheme 1.** Synthesis of asymmetry OTFT candidates.

Reagents and conditions. a) *t*-BuONO,  $\text{CuBr}_2$ ,  $\text{CH}_3\text{CN}$ , 4 h, 65 °C, 61%. b) HI,  $\text{H}_3\text{PO}_2$ , AcOH, 4 day, 150 °C, 58%. c) *n*-BuLi, DMF, THF, 94%. d) *n*-BuLi, 1-bromohexane, 82%. e) NBS, AcOH, chloroform, 90%. f) *n*-BuLi, DMF, THF, 63%. g) *n*-BuLi, 1-bromododecane, 81%. h) NBS, AcOH, chloroform, 98%. i) *n*-BuLi, DMF, THF, 91%. j)  $\text{TiCl}_4$ , Zn, pyridine, THF, **9a**: 68%, **9b**: 91%.

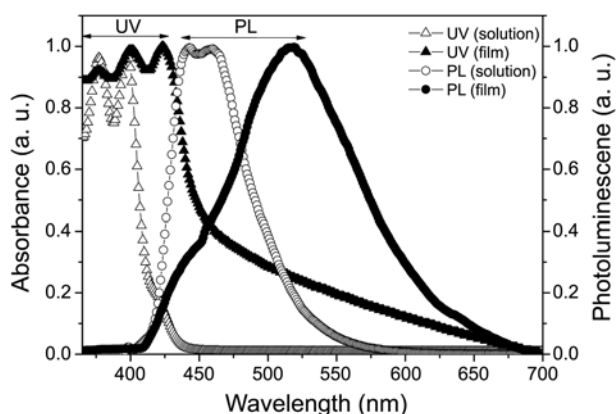
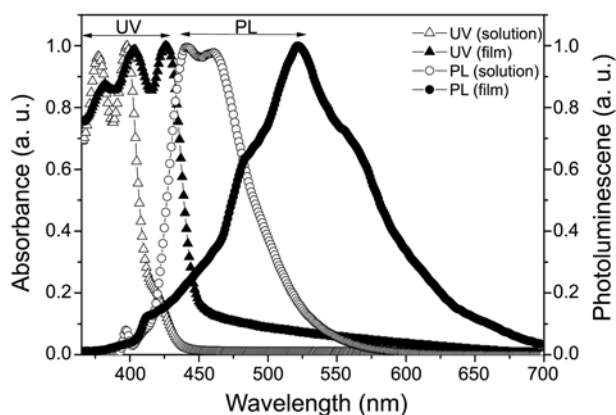
**Table 1.** UV-visible and PL spectra of AVHT and AVDT

Compound	$\lambda_{\text{abs/nm}}^a$		$\lambda_{\text{em/nm}}^b$	
	Solution	Film	Solution	Film
AVHT	376, 397	400, 423	442	516
AVDT	376, 397	403, 426	443	522

<sup>a</sup>Measured in dilute  $\text{CHCl}_3$  solution and thin film state. <sup>b</sup>Excited at the absorption maxima.

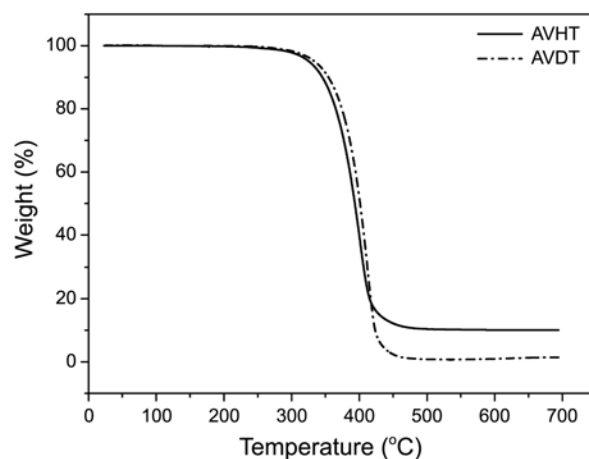
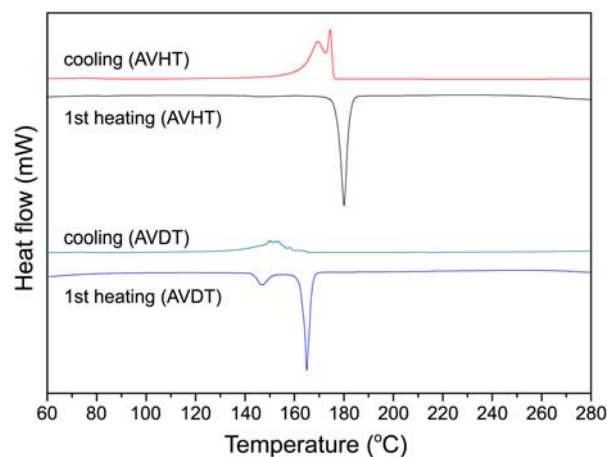
(7b) were readily obtained by alkylation of thiophene with *n*-BuLi and corresponding haloalkane and followed by bromination with *N*-bromosuccinimide in the presence of acetic acid. Formylation of  $\alpha$ -position of thiophene proceeded by treated with *n*-BuLi and DMF and to give 8a. The target material AVHT (9a) and AVDT (9b) were synthesized by reaction of 4 with 8a and 8b under the conditions of McMurry coupling reactions in the presence of  $\text{TiCl}_4$  and Zn in THF. The synthesized AVHT and AVDT were confirmed by FT-IR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , and mass analysis.

**Optical Properties.** The optical properties of synthesized materials were investigated using UV-visible absorption and photoluminescence (PL) in dilute  $\text{CHCl}_3$  solution and on thin films. The results are shown in Figure 2 and 3. The films of AVHT and AVDT were prepared on quartz substrates by dip-coating from the chloroform solutions at room temper-

**Figure 2.** UV-visible absorption and Photoluminescence spectra of AVHT in dilute  $\text{CHCl}_3$  solution and thin film.**Figure 3.** UV-visible absorption and Photoluminescence spectra of AVDT in dilute  $\text{CHCl}_3$  solution and thin film.

ature. UV-visible absorption and PL emission spectral data of AVHT and AVDT are shown in Table 1. As depicted in Figure 2 and 3, AVHT and AVDT of films show about 25–30 nm red shift of the main absorption peak compared to that obtained in dilute chloroform solution. This red shift effects derived from the formation of aggregation or excimer in thin film due to  $\pi$ - $\pi^*$  stacking or intermolecular interaction caused by their planar structure. This phenomenon was known generally as H- or J- aggregates<sup>27–30</sup> in the conjugated materials.

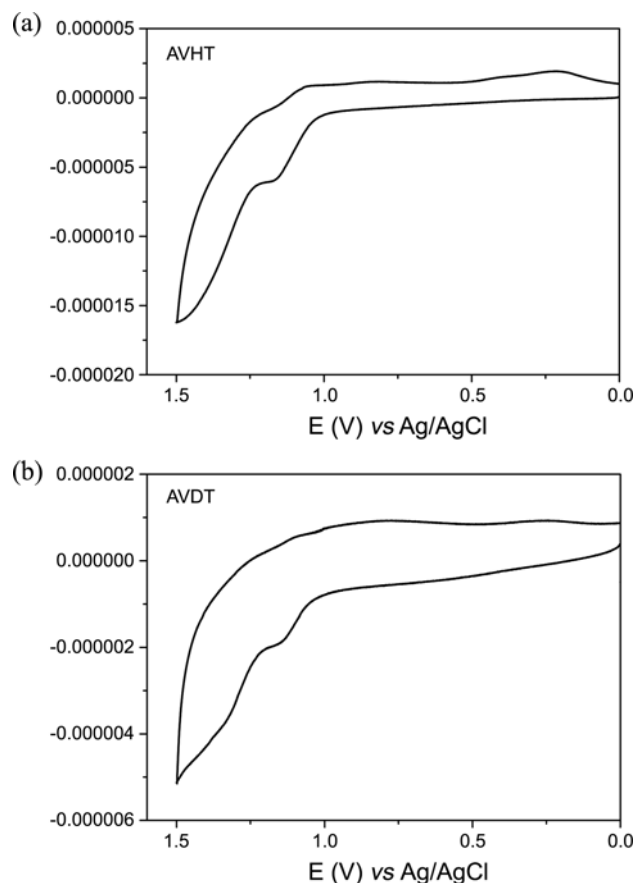
**Thermal Properties.** The thermal properties of AVHT and AVDT were investigated by thermogravimetric analysis (TGA). TGA diagram reveals that both AVHT and AVDT have high thermal stability with decomposition temperatures ( $T_d$ ) of 325 °C and 337 °C, respectively (Figure 4). The thermal phase transitions of AVHT and AVDT were analyzed by differential scanning calorimetry (DSC) (Figure 5). The major endothermic melting peak of AVHT was shown at 180 °C and AVDT was shown at 164 °C. As expected, increase of the length of alkyl chain results slightly decrease of the phase transition temperature. Figure 5 illustrates the heating and cooling process for AVHT and AVDT. The thermal features of AVHT and AVDT show that two materials

**Figure 4.** TGA thermogram of AVHT and AVDT in nitrogen atmosphere at a scan rate of 10 °C/min.**Figure 5.** DSC curve of AVHT and AVDT in nitrogen atmosphere at a scan rate of 10 °C/min.

**Table 2.** Electrochemical properties of AVHT and AVDT

Compound	Oxidation $E_{\text{onset}}$ (V)	HOMO/eV	LUMO/eV	$E_g$ /eV
AVHT	1.03	-5.47	-2.65	2.82
AVDT	1.04	-5.48	-2.66	2.82

※ HOMO-LUMO gap measured according to the onset of UV absorption ( $= 1240/\lambda_{\text{onset}}$  eV). HOMO (eV) measured according to the onset of oxidation (HOMO =  $4.44 + E_{\text{onset}}$ ; ferrocene =  $4.84 - E_{\text{onset}}$  (oxidation of ferrocene) =  $4.84 - 0.40 = 4.44$ ).



**Figure 6.** (a) Cyclic voltammogram of AVHT. (b) Cyclic voltammogram of AVDT (working electrode: glassy carbon, reference electrode: Ag/AgCl in KCl (sat'd), counter electrode: Pt wire, electrolyte: 0.1 M TBAP in methylene chloride, purge time: 60 s, scan rate: 50 mV/s).

are crystalline. Therefore, it is expected that their thin films are well-ordered under heat treatment.

**Electrochemical Properties.** In order to investigate the electrochemical behaviors such as charge transport properties and assess the ionization potentials and electrochemical stability of AVHT and AVDT, cyclic voltammetry (CV) measurements have been performed on thin films of the two synthesized materials (Figure 6). The CV of the AVHT and AVDT were recorded in a  $1.0 \times 10^{-3}$  M  $\text{CHCl}_3$  solution containing 0.1 M  $\text{Bu}_4\text{NClO}_4$ . The oxidation peak potentials of AVHT and AVDT are summarized in Table 2. The oxidation potential  $E_{\text{ox}}$  was 1.03 V for AVHT, 1.04 V for AVDT, respectively. As a result, two materials showed good electro-

**Table 3.** TFT properties of AVHT and AVDT

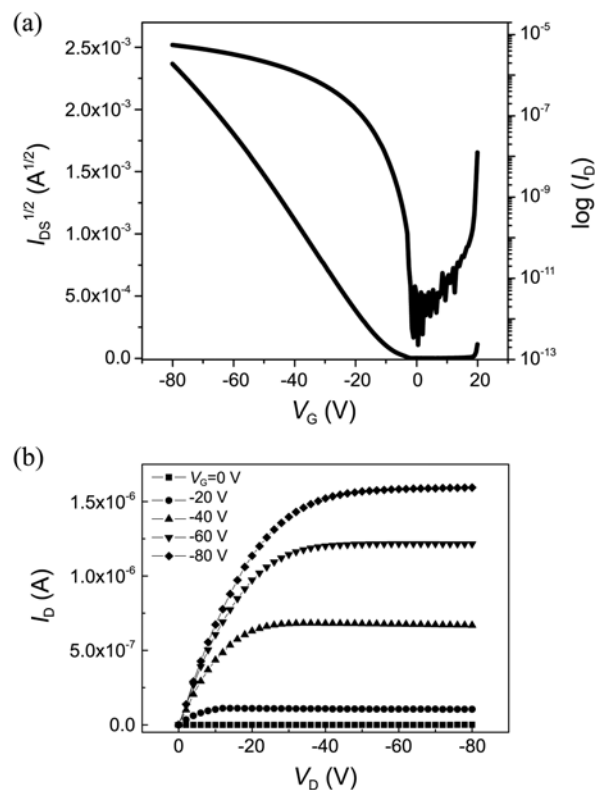
Compound	Mobility	On/off Ratio <sup>a</sup>	Threshold voltage	Subthreshold voltage
AVHT	0.026 $\text{cm}^2/\text{Vs}$	$1.60 \times 10^7$	-9.41 V	0.494 V/dec
AVDT	0.004 $\text{cm}^2/\text{Vs}$	$3.82 \times 10^6$	-7.70 V	0.357 V/dec

<sup>a</sup>Top-contact, OTS, spin-coating.

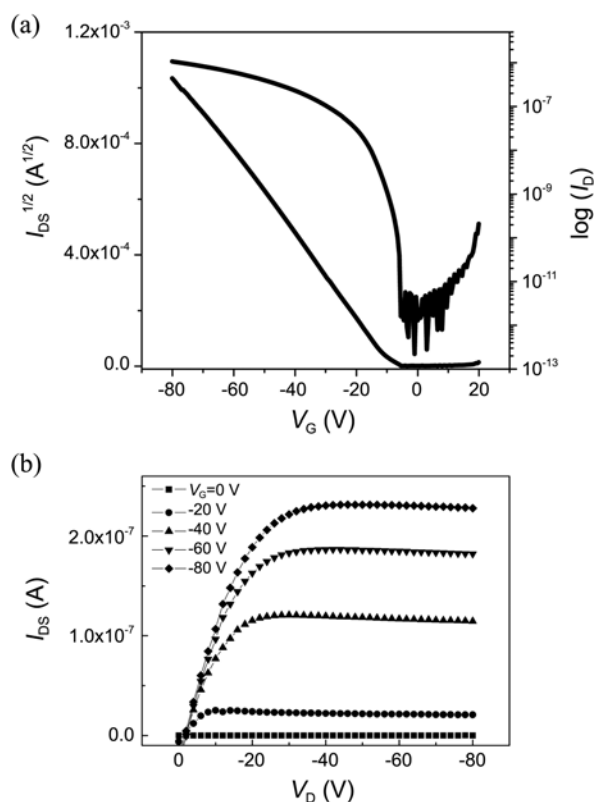
chemical stability.

HOMO energy level of AVHT and AVDT were calculated from the empirical equation shown in the range of -5.47 eV and -5.48 eV, which are lower than that of pentacene (HOMO level: -5.0 eV). These results indicate that AVHT and AVDT have high oxidation stability but oxidation potential is lower than that of pentacene. The optical band gap ( $E_g$ ) of AVHT and AVDT were determined from absorption onset and found to be 2.82 eV.

**OTFT Characterization.** The semiconducting properties of AVHT and AVDT were investigated by fabricating OTFT devices in top-contact configuration. For preliminary transistor measurements, the active layers of AVHT and AVDT were spin-coated from 0.5 wt % chloroform solutions without further thermal treatment. The investigation proceeded without annealing. TFT device characteristics cooperating with AVHT and AVDT are summarized in Table 3. Figure 7(a) and Figure 8(a) shows a plot of the drain current ( $I_d$ ) versus gate voltage ( $V_g$ ), and Figure 7(b) and Figure 8(b)



**Figure 7.** (a) Drain current ( $I_d$ ) versus gate voltage ( $V_g$ ) characteristics of AVHT. (b) Drain current ( $I_d$ ) versus drain-source voltage ( $V_d$ ) characteristics of AVHT OTFT at different gate voltages ( $V_g$ ).



**Figure 8.** (a) Drain current ( $I_d$ ) versus gate voltage ( $V_g$ ) characteristics of AVDT. (b) Drain current ( $I_d$ ) versus drain-source voltage ( $V_d$ ) characteristics of AVDT OTFT at different gate voltages ( $V_g$ ).

shows a plot of the drain current ( $I_d$ ) versus drain-source voltage ( $V_d$ ) for a AVHT and AVDT-based OTFT.

The graph for drain current ( $I_d$ ) versus gate voltage ( $V_g$ ) in Figures 7 and 8 of AVHT and AVDT were shown that a gate voltage ( $V_g$ ) applied to the device a significant change was occur in the drain current. As showing in Figures 7 and 8, when the gate voltage decreased to below zero, drain current flow increase suddenly. This means both of AVHT and AVDT have typical p-channel FET characteristics. AVHT-based OTFT showed higher performance in terms of both mobility ( $0.026 \text{ cm}^2/\text{Vs}$ ) and on/off ratio ( $1.60 \times 10^7$ ). This results may comes through AVHT has relatively shorter alkyl chain to compare with AVDT, therefore, the J- or H-aggregation effect increased in crystalline states. On the other hands, the longer alkyl chain of AVDT could have hindered the formation of a crystalline structure, and led to unforeseen low mobility ( $0.004 \text{ cm}^2/\text{Vs}$ ) and on/off ratio ( $3.82 \times 10^6$ ) to compare with AVHT. From the results, we can say the mobility of AVHT and AVDT depends on their alky chain length.

### Conclusion

We synthesized novel AVHT and AVDT from McMurry coupling reaction and investigated their optical, thermal and electrophysical properties. These performances are among the first results reported so far for conjugated asymmetric

materials. Investigation of their thermal properties revealed that two materials had good thermal stability ( $325 \text{ }^\circ\text{C}$  and  $337 \text{ }^\circ\text{C}$ , respectively). Investigation of their optical and electrophysical properties showed that AVHT and AVDT have higher oxidation potentials due to their HOMO energy levels ( $-5.47 \text{ eV}$  for AVHT,  $-5.48 \text{ eV}$  for AVDT). Devices using AVHT thin films deposited by spin coating as an active semiconductor have exhibited mobilities as high as  $0.026 \text{ cm}^2/\text{Vs}$  with on/off current ratios of up to  $1.6 \times 10^7$  and threshold voltage of  $-9.41 \text{ V}$ , which is very simple and asymmetry structure materials for device application. From the obtained results, AVHT seems to be more compact structure or high degree of ordering than AVDT. This is somehow related to the high field-effect mobility observed for AVHT. These results suggest that the presence of a short chain alkyl group preferable to maximize ordering in thin films as well as charge-carrier mobility.

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### References

- Locklin, J.; Li, D.; Mannsfeld, W. S. C. B.; Brokent, E. J.; Meng, H.; Advincula, R.; Bao, Z. *Chem. Mater.* **2005**, *17*, 3366.
- Meng, H.; Zheng, J.; Lovinger, A. J.; Wang, B.; Van Patten, P. G.; Bao, Z. *Chem. Mater.* **2003**, *15*, 1778.
- Mushrush, M.; Facchetti, A.; Lefenfeld, M.; Katz, H. E.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 9414.
- Kim, H. S.; Kim, Y. H.; Kim, T. H.; Noh, Y. Y.; Pyo, S.; Yi, M. H.; Kim, D. Y.; Kim, S. K. *Chem. Mater.* **2007**, *19*, 3561.
- Hongkun, T.; Jianwu, S.; Donghang, Y.; Lixiang, W.; Yanhou, G.; Fosong, W. *Adv. Mater.* **2006**, *18*, 2149.
- Gao, X.; Di, C.; Hu, Y.; Yang, X.; Fan, H.; Zhang, F.; Liu, Y.; Li, H.; Zhu, D. *J. Am. Chem. Soc.* **2010**, *132*, 3697.
- Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99.
- Facchetti, A.; Yoon, M. H.; Marks, T. J. *Adv. Mater.* **2005**, *17*, 1705.
- Barbarella, G.; Melucci, M.; Sotgiu, G. *Adv. Mater.* **2005**, *17*, 1581.
- Shirota, Y.; Kageyama, Y. *Chem. Rev.* **2007**, *107*, 953.
- Murphy, A. R.; Fréchet, J. M. J. *Chem. Rev.* **2007**, *107*, 1066.
- Park, J. H.; Jung, D. S.; Park, J. W.; Ahn, T.; Kong, H.; Jung, Y. K.; Lee, J.; Yi, M. H.; Park, C. E.; Kwon, S. K.; Shim, H. K. *Org. Lett.* **2007**, *9*, 2573.
- Jung, K. H.; Bae, S. Y.; Kim, K. H.; Cho, M. J.; Lee, K.; Kim, Z. H.; Choi, D. H.; Lee, D. H.; Chung, D. S.; Park, C. E. *Chem. Comm.* **2009**, 5290.
- Tang, M. L.; Reichardt, A. D.; Siegrist, T.; Mannsfeld, S. C. B.; Bao, Z. *Chem. Mater.* **2008**, *20*, 4669.
- Jang, S. H.; Tai, T. B.; Kim, M. K.; Han, J. W.; Kim, Y. H.; Shin, S. C.; Yoon, Y. J.; Kim, S. K.; Lee, S.-G. *Bull. Korean Chem. Soc.* **2009**, *30*, 618.
- Jiang, L.; Hu, W.; Wei, Z.; Xu, W.; Meng, H. *Adv. Mater.* **2009**,

- 21, 3469.
17. Zhao, Q.; Kim, T. H.; Park, J. W.; Kim, S. O.; Jung, S. O.; Kim, J. W.; Ahn, T.; Kim, Y. H.; Yi, M. H.; Kwon, S. K. *Adv. Mater.* **2008**, *20*, 4868.
18. Meng, H.; Sun, F.; Goldfinger, M. B.; Jaycox, G. D.; Li, Z.; Marshall, W. J.; Blackman, G. S. *J. Am. Chem. Soc.* **2005**, *127*, 2406.
19. Ito, K.; Suzuki, T.; Sakamoto, Y.; Kubota, D.; Inoue, Y.; Sato, F.; Tokito, S. *Angew. Chem. Int. Ed.* **2003**, *42*, 1159.
20. Meng, H.; Sun, F.; Goldfinger, M. B.; Gao, F.; Londono, D. J.; Marshall, W. J.; Blackman, G. S.; Dobbs, K. D.; Keys, D. E. *J. Am. Chem. Soc.* **2006**, *128*, 9304.
21. Kim, S. O.; An, T. K.; Chen, J.; Kang, I.; Kang, S. H.; Chung, D. S.; Park, C. E.; Kim, Y. H.; Kwon, S. K. *Adv. Funct. Mater.* **2011**, *21*, 1616.
22. Garnier, F.; Yassar, A.; Hajlaoui, R.; Horowitz, G.; Deloffre, F.; Servet, B.; Ries, S.; Alnot, P. *J. Am. Chem. Soc.* **1993**, *115*, 8716.
23. Merlo, J. A.; Newman, C. R.; Gerlach, C. P.; Kelley, T. W.; Muyres, D. V.; Fritz, S. E.; Toney, M. F.; Frisbie, C. D. *J. Am. Chem. Soc.* **2005**, *127*, 3997.
24. Lee, S. K.; Yang, W. J.; Choi, J. J.; Kim, C. H.; Jeon, S. J.; Cho, B. R. *Org. Lett.* **2005**, *7*, 323.
25. Ando, S.; Nishida, J.; Fujiwara, E.; Tada, H.; Inoue, Y.; Tokito, S.; Yamashita, Y. *Synth. Met.* **2006**, *156*, 327.
26. Drolet, N.; Morin, J. F.; Leclerc, N.; Wakim, S.; Tao, Y.; Leclerc, M. *Adv. Funct. Mater.* **2005**, *15*, 1671.
27. Kim, R.; Yun, H.-J.; Yi, M. H.; Shin, S. C.; Kwon, S.-K.; Kim, Y.-H. *Bull. Korean Chem. Soc.* **2012**, *33*, 420.
28. Estrada, L. A.; Montes, V. A.; Zyryanov, G.; Anzenbacher, R. Jr. *J. Phys. Chem. B Lett.* **2007**, *111*, 6983.
29. Meng, H.; Zheng, J.; Lovinger, J.; Wang, B.-C.; Patten, P. G. V.; Bao, Z. *Chem. Mater.* **2003**, *15*, 1778.
30. Horowitz, G. *Adv. Mater.* **1998**, *10*, 5259.
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