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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 2.6×10^{-2} cm^2/Vs and 4.4×10^{-3} cm^2/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

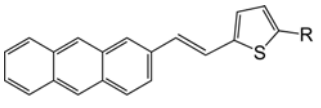
During the past decades, organic thin-film transistors (OTFTs) have attracted intense interest because of their potential application in active-matrix display and integrated circuits (ICs) for logic and memory chips. Several types of conjugated oligomers and polymers were synthesized as new organic semiconductor candidates.[1-11] 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 $cm^2V^{-1}s^{-1}$ at 300 K.[2] 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.[12-20] 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 (quterthiophene) exhibited somewhat good charge carrier mobility.[21] 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.[22] 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.[23,24]

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. ^1H and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer with chemical shift values reported in δ 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_6H_{13}, **AVDT**, R = $C_{12}H_{25}$

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 perchlorite (Bu_4NClO_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 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 μm and channel widths (W) of 2000 μm. 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.[25,26]

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 $MgSO_4$, 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 cm^{-1} (sp^2 C-H), 2921-2854 cm^{-1} (sp^3 C-H), 1470 cm^{-1} (C=C); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 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, M^+).

2-Dodecylthiophene (6b). The procedure used the same as that for preparation of compound **6a**. Yield: 81%; IR (KBr): 3106-3038 cm^{-1} (sp^2 C-H), 2923-2856 cm^{-1} (sp^3 C-H), 1475 cm^{-1} (C=C); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 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}C-NMR (75 MHz, $CDCl_3$) δ 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, 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 CH_2Cl_2 and washed with water, brine, and dried over $MgSO_4$, 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 cm^{-1} (sp^2 C-H), 2951-2852 cm^{-1} (sp^3 C-H), 1521-1436 cm^{-1} (C=C); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 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}C-NMR (75 MHz, $CDCl_3$) δ 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, M^+).

2-Bromo-5-dodecylthiophene (7b). The procedure used the same as that for preparation of compound **7a**. Yield: 98%; IR (KBr): 3065 cm^{-1} (sp^2 C-H), 2956-2858 cm^{-1} (sp^3 C-H), 1525-1433 cm^{-1} (C=C); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 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}C-NMR (75 MHz, $CDCl_3$) δ 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, 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 $MgSO_4$, 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 cm^{-1} (sp^2 C-H), 2925-2850 cm^{-1} (sp^3 C-H), 1674 cm^{-1} (C=O), 1439 cm^{-1} (C=C); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 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}C-NMR (75 MHz, $CDCl_3$) δ 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, M^+).

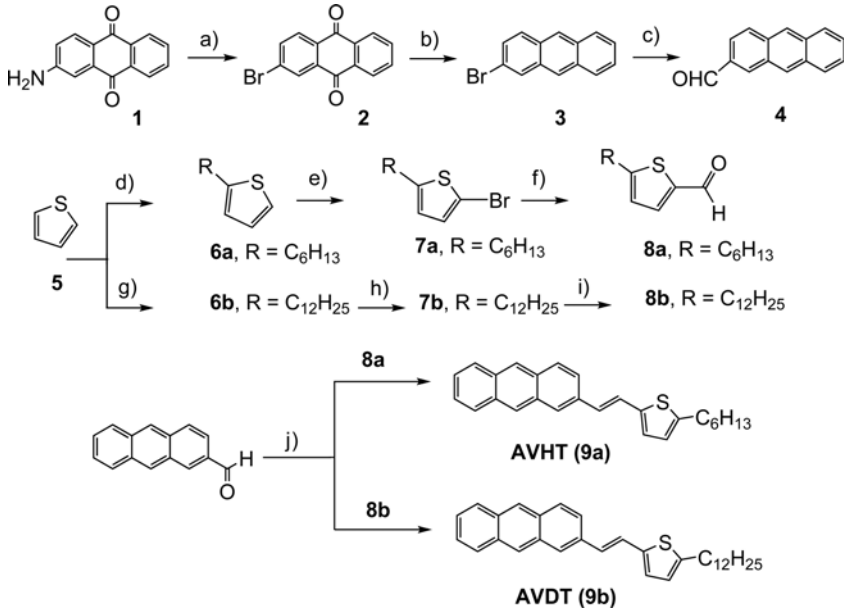
5-Dodecylthiophene-2-carbaldehyde (8b). The procedure used the same as that for preparation of compound **8a**. Yield: 91%; IR (KBr): 3102 cm^{-1} (sp^2 C-H), 2931-2856 cm^{-1} (sp^3 C-H), 1674 cm^{-1} (C=O), 1429 cm^{-1} (C=C); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.54-7.53 (d, 1H, *J* = 3.6 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}C-NMR (75 MHz, $CDCl_3$) δ 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, 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 $TiCl_4$ (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 $NaHCO_3$ (10%, 5 mL), and product was extracted with diethyl ether. The organic layer washed with water, brine, and dried over $MgSO_4$, 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 cm^{-1} (sp^2 C-H), 2846 cm^{-1} (sp^3 C-H), 1465 cm^{-1} (C=C); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 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, 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 cm^{-1} (sp^2 C-H), 2845 cm^{-1} (sp^3 C-H), 1467 cm^{-1} (C=C); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 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, 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 coppper(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, $CuBr_2$, CH_3CN, 4 h, 65 °C, 61%. b) HI, H_3PO_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) $TiCl_4$, Zn, pyridine, THF, **9a**: 68%, **9b**: 91%.

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

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

[a]Measured in dilute $CHCl_3$ solution and thin film state. [b]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 α-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 $TiCl_4$ and Zn in THF. The synthesized **AVHT** and **AVDT** were confirmed by FT-IR, ^{1}H-NMR, ^{13}C-NMR, and mass analysis.

Optical Properties. The optical properties of synthesized materials were investigated using UV-visible absorption and photoluminescence (PL) in dilute $CHCl_3$ 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 temperature. 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 π-π^* stacking or intermolecular interaction caused by their planar structure. This phenomenon was known generally as H- or J- aggregates[27-30] in the conjugated materials.

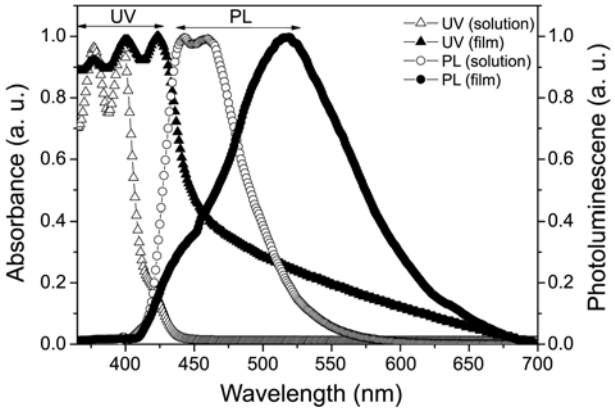


Figure 2. UV-visible absorption and Photoluminescence spectra of **AVHT** in dilute $CHCl_3$ solution and thin film.

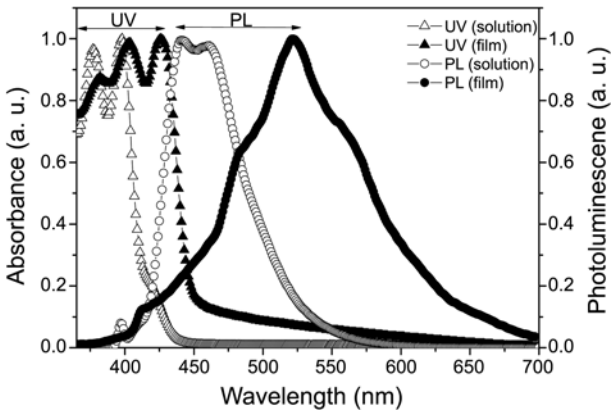


Figure 3. UV-visible absorption and Photoluminescence spectra of **AVDT** in dilute $CHCl_3$ solution and thin film.

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

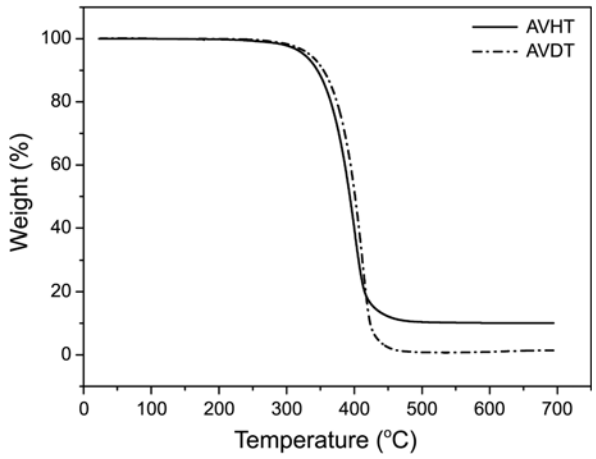


Figure 4. TGA thermogram of **AVHT** and **AVDT** in nitrogen atmosphere at a scan rate of 10 °C/min.

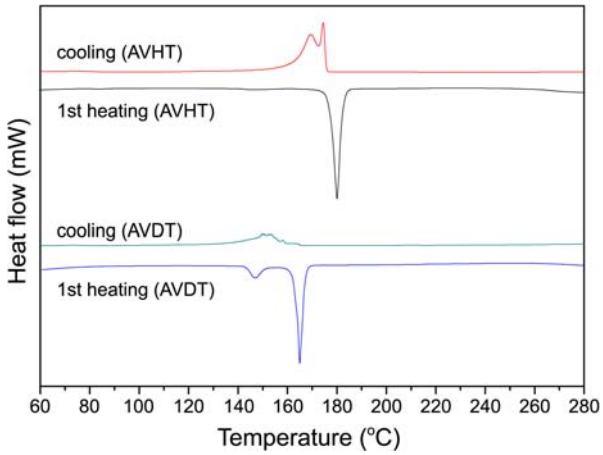


Figure 5. DSC curve of **AVHT** and **AVDT** in nitrogen atmosphere at a scan rate of 10 °C/min.

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

Compound	Oxidation E_{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/λ_{onset} eV). HOMO (eV) measured according to the onset of oxidation (HOMO = 4.44+E_{onset}; ferrocene = 4.84−E_{onset} (oxidation of ferrocene) = 4.84–0.40 = 4.44).

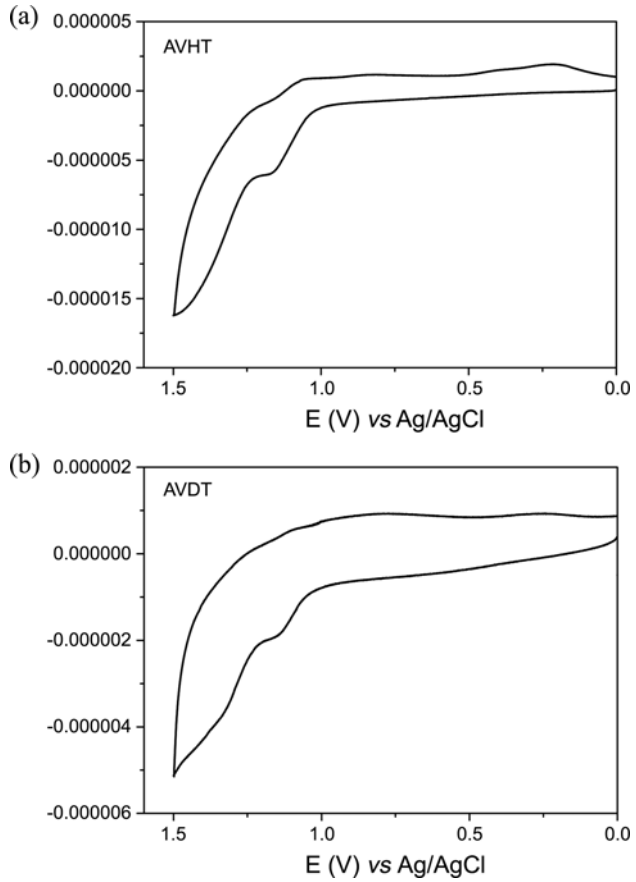


Figure 6. (a) Cyclic voltammogram of **AVHT**. (b) Cyclic voltammogram of **AVDT** (working electrode: glassy carbon, reference electrode: Ag/AgCl in KCl (sat'd), counter electrode: Pt wire, electrolyte: 0.1 M TBAP in methylene chloride, purge time: 60 s, scan rate: 50 mV/s).

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 1.0×10^{-3} M $CHCl_3$ solution containing 0.1 M Bu_4NClO_4. The oxidation peak potentials of **AVHT** and **AVDT** are summarized in Table 2. The oxidation potential E_{ox} was 1.03 V for **AVHT**, 1.04 V for **AVDT**, respectively. As a result, two materials showed good electrochemical stability.

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

Compound	Mobility	On/off Ratio[a]	Threshold voltage	Subthreshold voltage
AVHT	0.026 cm^2/Vs	1.60×10^7	−9.41 V	0.494 V/dec
AVDT	0.004 cm^2/Vs	3.82×10^6	−7.70 V	0.357 V/dec

[a]Top-contact, OTS, spin-coating.

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)

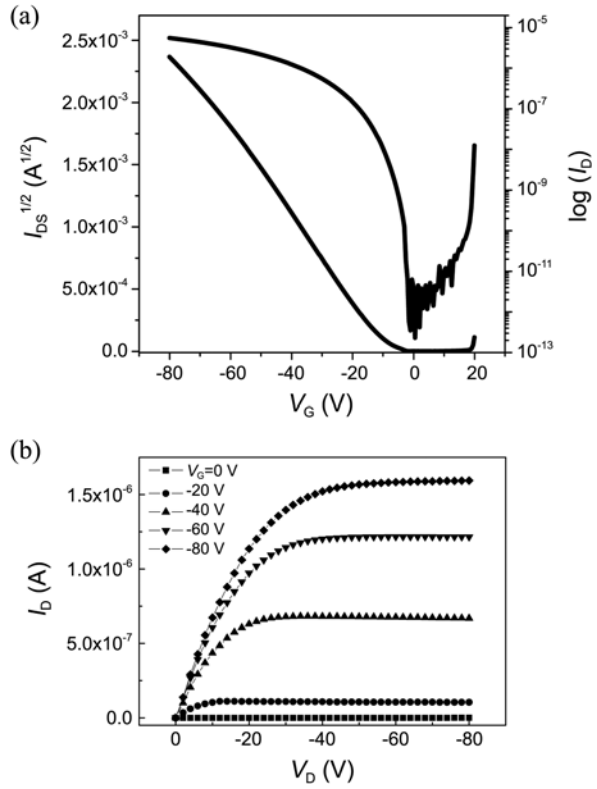


Figure 7. (a) Drain current (I_d) *versus* gate voltage (V_g) characteristics of **AVHT**. (b) Drain current (I_d) *versus* drain-source voltage (V_d) characteristics of **AVHT** OTFT at different gate voltages (V_g).

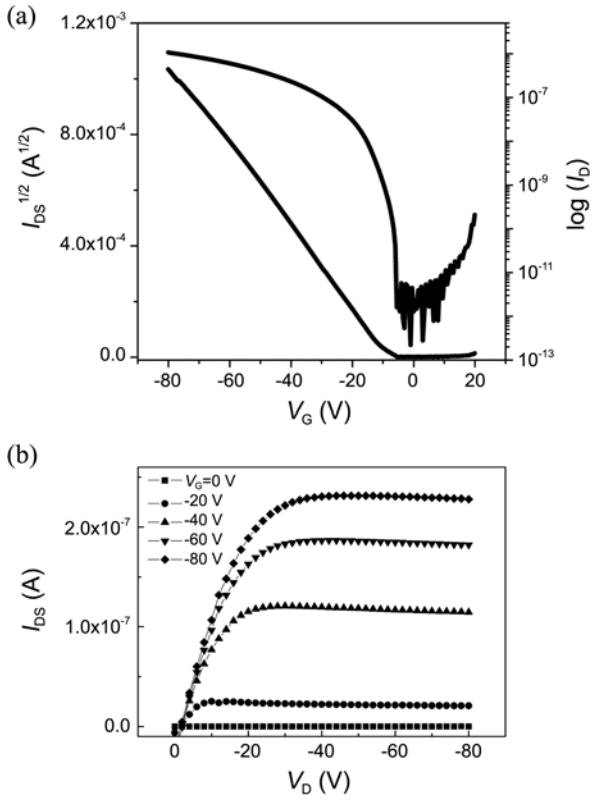


Figure 8. (a) Drain current (I_d) *versus* gate voltage (V_g) characteristics of **AVDT**. (b) Drain current (I_d) *versus* drain-source voltage (V_d) characteristics of **AVDT** OTFT at different gate voltages (V_g).

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 cm^2/Vs) and on/off ratio (1.60×10^7). 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 cm^2/Vs) and on/off ratio (3.82×10^6) 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 °C and 337 °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 eV for **AVHT**, −5.48 eV for **AVDT**). Devices using **AVHT** thin films deposited by spin coating as an active semiconductor have exhibited mobilities as high as 0.026 cm^2/Vs with on/off current ratios of up to 1.6×10^7 and threshold voltage of −9.41 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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