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Symmetric Long Alkyl Chain End-Capped Anthracene Derivatives for Solution-Processed Organic Thin-Film Transistors

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Three new anthracene derivatives, 2,6-bis(4-decylphenyl)anthracene (DDPAnt), 2-decyl-5-(2-(5-decylthiophen-2-yl)anthracen-6-yl)thiophene (DDTAnt), and 2,6-bis(4-decyloxy phenyl) anthracene (DDPXAnt) were synthesized by Suzuki cross-coupling reaction. The obtained oligomers were characterized by ^{1}H NMR, FT-IR, Mass, UV-visible spectroscopy, cyclovotammetry, differencial scanning calorimetry, and thermogravimetric analysis. The thermal studies show that these oligomers are stable up to 400 °C. The solution processed OTFTs were fabricated using synthesized oligomers by spin-coating and drop casting processes on Si/SiO$_2$. OTFTs based on DDPAnt showed the mobility of 7.6×10^{-3} cm^2/Vs and on/off ratio of 10^5.

Keywords: Solution-Processing, Anthracene Derivatives, Suzuki Coupling, Organic Thin-Film Transistors.

1. INTRODUCTION

Organic thin-film transistors (OTFTs) have attracted intense interest in recent years because of their potential applications in active-matrix displays and integrated circuits (ICs) for logic and memory chips.[1,2] To realize the full potential of these applications, it is necessary to identify conjugated semiconductors with high mobility and robust environmental stability. Organic oligomers investigated to date include *p*-type, *n*-type, and *p*/*n*-type bipolar semiconductors.[3,4] *n*-Linked benzene rings ($n = 3$: anthracene; $n = 4$: tetracene; $n = 5$: pentacene) are promising candidates for organic semiconductors because their planar shapes facilitate crystal packing and the extended system over molecules enables the intermolecular overlap of π systems.[5] Especially, pentacene has been used as a benchmark *p*-type semiconductor material with a charge mobility over 1.0 cm^{-2}/V · s, as reported by the several groups.[6] Yet the stability of these semiconductor types is limited.[7]

Recent developments by several groups have resulted in the improved stability, primarily through the judicious choice of conjugated units and side chains.[8,9] Meng's group reported two novel organic semiconductors based on thiophene-anthracene molecules, which show remarkably high stability and very good electrical characteristics. These anthracene derivatives introduced thiophene moiety to improve the TFT performance (mobility of 0.5 cm^2/Vs, on/off ratio of 2.8×10^7). Also introduction of hexyl side chain in thiophene-anthracene has showed the greater stability due to large band gap and good molecular ordering of the alkyl side chain, especially at high substrate temperatures.[10–12]

Thus we modified phenyl-, phenoxyl-as fused aromatic unit instead thiophene unit to increase oxidation stability and crystallinity. Also the anthracene derivatives with long decyl end group increase solubility and fine molecular ordering due to improved self-assembly properties.[12,13] In this paper, we report synthesis and characterization of semiconductors based on anthracene-fused aromatic hybride and their TFT characteristics.

2. EXPERIMENTAL DETAILS

2.1. Device Fabrication

SiO$_2$ (300 nm) as the dielectric layer. The hydrophobic surface treatments of the dielectric surface such as with hexamethyldisilazane (HMDS), octadecyltrichloro silane

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(OTS-18), and polydimethylsiloxane (PDMS), were performed via the well-known solution method. The water contact angles for each case were measured to $25 \pm 2°$ (untreated), $68 \pm 2°$ (HMDS), $99 \pm 2°$ (OTS-8), $108 \pm 1°$ (OTS-18), $109 \pm 2°$ (PDMS). Semiconducting materials were usually deposited onto modified dielectric surface via spin-casting, drop-casting using chloroform, toluene, and chlorobenzene and in some cases, substrates were annealed to fabricate a more uniform layer. The Au source and drain electrodes were thermally evaporated for 100 nm, and a shadow mask was used to make the patterns and a channel region 1500 μm long and 150 μm wide. The field effect mobility was extracted from the saturation regime from transfer characteristics, using the equation $\mu_{\text{sat}} = (2I_{\text{DS}}L)/(WC(V_g–V_{\text{th}})^2)$, where I_{DS} is the saturation drain current, C is the capacitance of the oxide dielectric, V_g is the gate bias, and V_{th} is the threshold voltage.

2.2. Synthesis of DDPAnt

DDPAnt. To a solution of 2,6-dibromoanthracene (2.0 g, 5.95 mmol) and 2-(4-decyl-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (4.51 g, 13.09 mmol) dissolved in toluene (40 mL). The reaction mixture was added 6 mL of (2 M Na_2CO_3) sodium carbonate (3.16 g, 29.8 mmol), followed by the addition of the phase-transfer agent Aliquat® 336 (1.2 g, 2.98 mmol). The mixture was deoxygenated with a stream of nitrogen. Then, $Pd(PPh_3)_4$ (0.14 g, 0.42 mmol) was added. The mixture was heated to 90 °C for three days under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and poured into methanol (50 mL). The precipitate was filtered off, washed with water, dilute acid (5% HCl), water, methanol and then with acetone three times to remove the starting material as well as the mono-substituted byproduct. The crude product was purified by soxhlet (silica gel, toluene) and finally by recrystallization from toluene to give DDPAnt (2.9 g, 80%) as pale yellowish green powder. mp 227 °C; IR (KBr, cm^{-1}): 3036 (sp^2 C–H), 2917–2848 (sp^3 C–H), 1465 (C=C); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.49 (s, 2 H), 8.21 (s, 2 H), 8.11–8.08 (d, 2 H, $J = 8.3$ Hz), 7.79–7.77 (d, 2 H, $J = 7.8$ Hz), 7.74–7.71 (d, 4 H, $J = 6.99$ Hz), 7.36–7.33 (d, 4 H, $J = 6.81$ Hz), 2.70 (t, 4 H, $J = 7.2$ Hz), 1.7–1.65 (m, 4 H), 1.3 (m, 28 H), 0.91 (t, 6 H, $J = 6.37$ Hz); EI, MS m/z (%): 610 (100, $M+$).

2.3. Synthesis of DDTAnt

DDTAnt. Following the procedure reported for DDPAnt. DDTAnt was prepared using 2,6-dibromoanthracene (1 g, 2.98 mmol), 2-(5-decylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-di-oxaborolane (1.9 g, 6.56 mmol), $Pd(PPh_3)_4$ (45 mg, 0.06 mmol), Aliquat® 336 (0.6 g, 1.49 mmol), (2 M Na_2CO_3) sodium carbonate (1.48 g, 14 mmol), toluene (48 mL) and water (7 mL), respectively. The crude product was purified by soxhlet (silica gel, toluene) and finally by recrystallization from toluene to give DDTAnt (0.80 g, 43%) as pale yellow powder. mp 233 °C; IR (KBr, cm^{-1}): 3050 (sp^2 C–H), 2953–2847 (sp^3 C–H), 1495 (C=C); EI, MS m/z (%): 622 (100, $M+$).

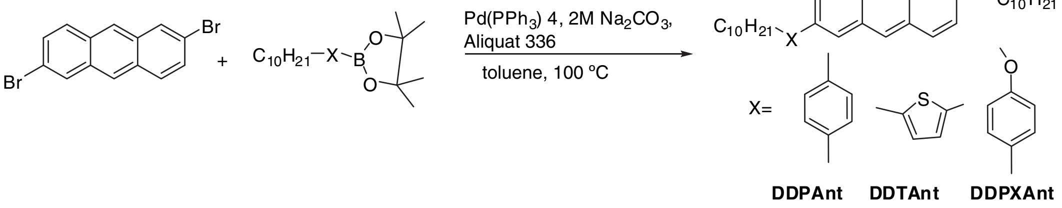
2.4. Synthesis of DDPXAnt

DDPXAnt. Following the procedure reported for DDPAnt. DDPXAnt was prepared using 2,6-dibromoanthracene (0.97 g, 2.9 mmol), 2-(4-(decyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxa -borolane (2.3 g, 6.38 mmol), $Pd(PPh_3)_4$ (70 mg, 0.06 mmol), Aliquat® 336 (0.59 g, 1.45 mmol), (2 M Na_2CO_3) sodium carbonate (1.54 g, 14.5 mmol), toluene (48 mL) and water (8 mL), respectively. The crude product was purified by soxhlet (silica gel, toluene) and finally by recrystallization from toluene to give DDPXAnt (0.92 g, 50%) as pale yellowish green powder. mp 213 °C; IR (KBr, cm^{-1}): 3080 (sp^2 C–H), 2953–2850 (sp^3 C–H), 1604–1517 (C=C); EI, MS m/z (%): 643 (100, $M+$).

3. RESULTS AND DISCUSSION

The anthracene derivatives DDPAnt, DDTAnt and DDPXAnt with different aromatic unit were designed to have each phenyl, thiophene and phenoxyl unit between anthracene and decyl end group. The anthracene derivatives were synthesized as depicted in Scheme 1. The materials DDPAnt, DDTAnt and DDPXAnt were synthesized under the conditions of Suzuki coupling reaction in the presence of palladium catalyst in water:toluene (1:6) to give 80%, 43% and 50% yield, respectively. Their structures were confirmed by FT-IR, ^{1}H-NMR, ^{13}C-NMR and mass analysis. The synthesized materials have good solubility in organic solvents under heating.

Figure 1 shows the UV-visible and photoluminescence (PL) spectra in dilute $CHCl_3$ solution and thin film and



Scheme 1. Synthesis of DDPAnt, DDTAnt, DDPXAnt.

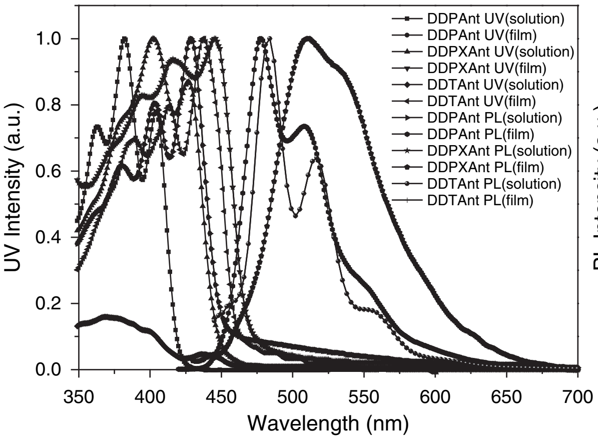


Fig. 1. Optical absorption (UV) and emission (PL) of DDPAnt, DDTAnt and DDPXAnt in dilute $CHCl_3$ solution and in the solid state.

data are summarized in Table I. Thin films of DDPAnt, DDTAnt and DDPXAnt show a red shift about 40–60 nm of the main absorption peak compared to that obtained in dilute chloroform solution. These results can be originated from the formation of aggregation or excimer in thin film due to $\pi-\pi^*$ stacking or intermolecular interaction caused by their planar structure.

The electrochemical behaviors of oligomers were investigated by cyclic voltammetry (CV) in Bu_4NClO_4 (0.1 M) in $CHCl_3$ at a scan rate of 50 mV/s under nitrogen. A platinum electrode was used as working electrode. A Pt wire was used as a counter electrode and an $Ag/AgNO_3$ electrode was used as the reference electrode. All measurements were calibrated using ferrocene value of −4.4 eV as standard (Table I). HOMO energy level of oligomers were shown in the range of −5.79 eV to −5.45 eV, which are lower than that of pentacene (HOMO level of −5.0 eV). These results indicate that the synthesized oligomers have high oxidation stability. Moreover, these HOMO levels are closed and therefore match well to the work function of gold electrode (−5.4 eV) in OTFTs,[17] which increases the efficiency of the injection and transport of holes.

The thermal properties of oligomers were investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) in a nitrogen atmosphere. TGA curve reveals that the oligomers have high thermal stability. Five percent weight loss (T_{5d}) is observed at 438 °C, 333 °C and 384 °C for DDPAnt, DDTAnt and DDPXAnt (Table I). From DSC, DDPAnt exhibits four endothermic peaks at 131 °C, 193 °C, 220 °C and 226 °C and four exothermic transition at at 83 °C, 178 °C, 215 °C and 224 °C. DSC of DDTAnt reveals two endothermic peaks at 213 °C and 223 °C and two exothermic peaks at 210 °C and 218 °C. DDTAnt also exhibited good thermal feature under heating and cooling cycle. DSC of DDPXAnt reveals two endothermic peaks at 125 °C and 233 °C and an exothermic peaks were observed at 228 °C respectively. All revealed thermal features of DDPAnt, DDTAnt and DDPXAnt showed that all of the three oligomers are crystalline and it is expected that their thin films are well ordered under heat treatment. DDPAnt, and DDPXAnt were used as active layer of OTFT device, and their electrical characteristics were shown in Figure 2. In case of DDPXEAnt, no semiconducting characteristics were observed, and it may possibly be due to the poor film structure. Both DDPAnt, and DDPXAnt showed semiconducting performance after thermal annealing above 140 °C.

Table I. Summary of the physical data of DDPAnt, DDTAnt and DDPXAnt.

	λ_{abs}/nm		λ_{em}/nm						
Compound	Solution	Film	Solution	Film	E_{ox}/eV	T_{5d}/°C	E_g/eV	HOMO/eV	LUMO/eV
DDPAnt	360, 385, 402	380, 403, 428	405, 429, 470	478, 511	1.19	438	2.87	−5.63	−2.76
DDTAnt	373, 436	386, 415, 444	482, 515, 555	484, 519, 560	1.35	333	2.59	−5.79	−2.93
DDPXAnt	393, 403, 425	417, 445	446, 471	510, 533	1.01	384	2.70	−5.45	−2.98

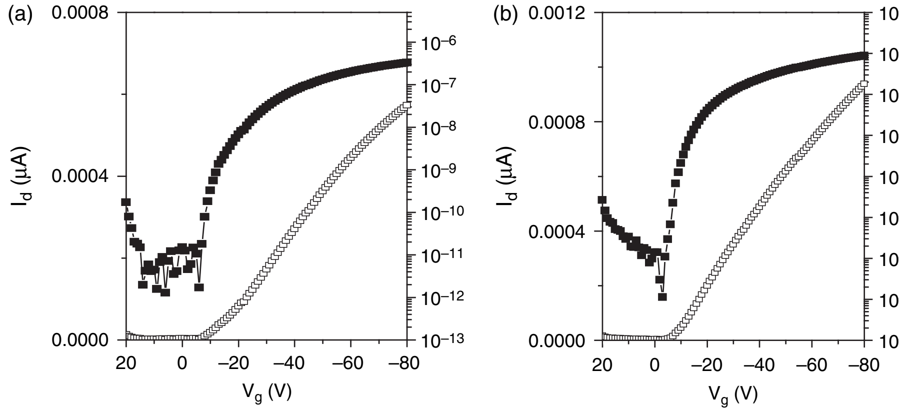


Fig. 2. Drain current (I_d) versus gate voltage (V_g) characteristics of (a) DDPAnt (b) DDPXAnt.

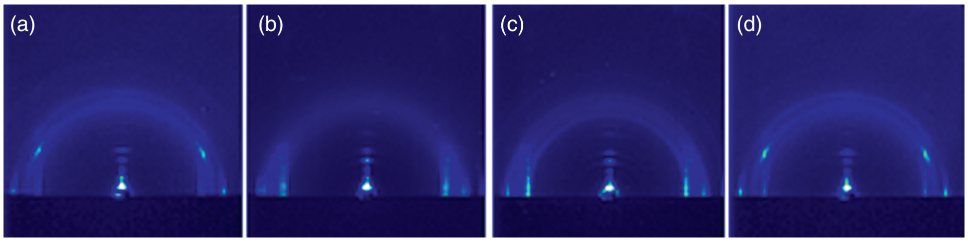


Fig. 3. GIXD data of DDPAnt (a) as-spun film, (b) annealed at 140 °C and DDPXAnt (c) as-spun film, (d) annealed at 140 °C.

To study the crystalline structure of both films in more detail, we have measured GIXD of DDPAnt and DDPXAnt (Fig. 3). In both cases, the intensity of (00*l*) diffraction peaks increased as a result of annealing, originated from re-ordering of semiconducting molecules. At the same time, the number of deffraction spots along the q_z (out-of-plane) direction at a given q_{xy} (in-plane) of DDPAnt is larger than DDPXAnt, and their intensities also show same trend. These results strongly suggested that DDPAnt forms more densely packed three-dimensional (3D) multi-layered structures rather than DDPXAnt, which may result in higher charge carrier mobility. Maximum mobility of DDPAnt was measured as 3.7×10^{-3} cm^2/Vs, but around half of this value (2.0×10^{-3} cm^2/Vs) was exhibited in the device based on DDPXAnt. This observation is followed by general relationship between crystallinity of film and device performance. In output curves, better output characteristic was observed in 160 °C annealed DDPAnt film, compared to 180 °C annealed DDPXAnt film. In output curves, better output characteristic was observed in 160 °C annealed DDPAnt film, compared to 180 °C annealed DDPXAnt film. This observation is followed by general relationship between crystallinity of film and device performance. DDPXAnt is slightly tilted on the substrate composed to DDPAnt because molecules inserted oxygens are inclinded to have less ridigity.

4. CONCLUSION

We synthesized new 4-alkyl/alkoxybenzene end-capped oligomers by Suzuki coupling reaction. Their thermal properties revealed that all oligomers had good thermal stability (between 333 °C and 438 °C). Investigation on the optical and electrochemical properties showed that the synthesized oligomers have higher oxidation potentials due to their high HOMO energy levels (−5.63 eV for DDPAnt, −5.79 eV for DDTAnt and −5.45 eV for DDPXAnt). OTFTs showed the mobility of 3.3×10^{-3} cm^2/Vs at 140 °C for DDPAnt and 3.3×10^{-3} cm^2/Vs at 180 °C for DDPXAnt. In the case DDPAnt, only slightly better mobility (7.6×10^{-3} cm^2/Vs) was obtained by thermal annealing at 160 °C.

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