

# Synthesis and Characterization of Anthracene Derivative for Organic Field-Effect Transistor Fabrication

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Here we report on the synthesis and characterization of anthracene derivative for solution processable organic field-effect transistors. The transistor devices with bottom-contact geometry provided a maximum field-effect mobility of  $3.74 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> as well as current on/off ratio of  $5.05 \times 10^4$ and low threshold voltage. Structural information in the solid state is obtained by thermal analysis and two-dimensional wide angle X-ray scattering (2D-WAXS). From the 2D-WAXS, it is clear that the planes of anthracene rings and benzene ring of the molecule are different in solid state. We assume similar arrangement in the thin-film which limit the effective hopping and thus charge mobility.

**Keywords:** Organic Field-Effect Transistors, Anthracene Derivative, Supramolecular Organization.

Delivered by Publishing Technology to: University of Waterloo IP: 192.81.0.87 On: Wed, 14 Oct 2015 18:26:28 Copyright: American Scientific Publishers and stability compared to the most studied pentacene

# 1. INTRODUCTION

Organic field-effect transistors (OFETs) have attracted great attention over the past decades to replace vacuumdeposited amorphous silicon-based thin-film transistors because of their potential for low cost, light weight and large-area processability.<sup>1-6</sup> They have proved to be highly suitable for applications in flexible displays, electronic papers, radio frequency identification (RF-ID) tags, and sensors.<sup>7-10</sup> The most important aspect of OFET is flexibility realized by fabrication on polymer substrates.<sup>11</sup> High mobility and on-off current ratio are the most important requirements for wider application of an organic semiconductor.<sup>12</sup> In metals and inorganic semiconductors, charge transport occurs in delocalized states where as in organic semiconductors, the charge delocalization can only occur between the  $\pi$ -orbitals of adjacent molecules. Therefore, charge transport in organic materials is believed to occur through charge hopping mechanism.13 For effective hopping the molecule should possess structural ordering through strong  $\pi - \pi$  stacking.<sup>14</sup> It has been proved that the charge carrier mobility strongly depends on the supramolecular organization of the molecules.<sup>15</sup> For our studies, we have considered anthracene-based molecules because of their easy derivatization, higher solubility

alted diethynyl benzene core. The alkoxy chains increase the solubility and the rigid acetylene bonds extend the π-conjugation of the molecule.<sup>18</sup> Wide angle X-ray diffraction was used to understand the structural ordering of the molecule in solid state. **2. EXPERIMENTAL DETAILS**

# 2.1. Reagents and Solvents

2-Aminoanthraquinone (technical grade) and other reagents were purchased from Sigma Aldrich and were used as received. Solvents were dried according to conventional methods prior to the reactions. 1,4-Diiodo-2,5-didodecyloxybenzene **4** was synthesized according to reported literature procedures.<sup>19</sup>

derivatives.<sup>17</sup> Here we report the synthesis and OFET per-

formance of an anthracene-based semiconducting material

bearing two anthracene units connected to a dialkoxy-

## 2.2. Instrumentation

Proton nuclear magnetic resonance (<sup>1</sup>H NMR) and <sup>13</sup>C NMR spectra were obtained at 300 MHz on a Varian Oxford-300 NMR spectrometer. Mass spectra were recorded on a JMS-AX505WA mass spectrometer. Differential scanning calorimetry (DSC) analysis was performed

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in nitrogen atmosphere with a heating rate of 10 °C/min using a TA Instrument 2100 equipped with differential scanning calorimetry cell. The thermograms were obtained on powder sample after it had been heated to 200 °C and air-cooled to room temperature. Thermogravimetric analysis (TGA) was performed in nitrogen atmosphere with a heating rate of 10 °C/min using a TA Hi-Res TGA 2950 thermogravimetric analyzer. UV-vis absorption spectra and photoluminescence (PL) spectra were measured by a Shimadzu UV-2401 and LS-50B luminescence spectrophotometer, respectively. The two-dimensional wideangle X-ray diffraction experiments were performed by means of a rotating anode (Rigaku 18 kW) X-ray beam with a pinhole collimation and a 2D Siemens detector with a beam diameter of 1 mm. A double graphite monochromator for the CrK<sub> $\alpha$ </sub> radiation ( $\lambda = 0.154$  nm) was used. The sample was prepared by filament extrusion at elevated temperatures.

#### 2.3. Synthetic Procedures

#### 2.3.1. Synthesis of Bromoanthraquinone (2)

Into a 1 L, two-necked round-bottom flask, were placed cupric bromide (46 g, 206 mmol) and acetonitrile (300 mL). To the reaction mixture, tert-butyl nitrite (25 mL, 210.4 mmol) was added with vigorous stirring. A solution of 2-aminoanthraquinone 1 (20 g, 89.6 mmol) in dry THF (350 mL) was added drop wise at room temperature. After stirring for 20 h, the reaction mixture was concentrated and the solid residue was triturated with water. This slurry was filtered, washed with dichloromethane and the filtrate was concentrated. The crude product was purified by column chromatography using ethyl acetate/hexane (1:4) as eluent to afford 20 g of 2-bromoanthraquinone 2 (80%). <sup>1</sup>H NMR  $(CDCl_3)$ :  $\delta$  8.5 (d, J = 2.0 Hz, 1 H), 8.3 (m, 2 H), 8.1 (d, J = 8.3 Hz, 1 H), 7.9 (dd, J = 8.3, 2.0 Hz, 1 H), 7.8(*m*, 2 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 182.10, 135.10, 134, 133.61, 132.60, 132.10, 128.20, 128.30, 126.81, 126.50. EI-Mass specta m/z, calcd for C<sub>14</sub>H<sub>7</sub>BrO<sub>2</sub>: 287.11. Found: 286.90.

#### 2.3.2. Synthesis of 2-Bromoanthracene (3)

Into a 500 mL two-necked round-bottom flask were placed 2-bromoanthraquinone 2 (20 g, 69.7 mmol) and isopropanol (300 mL). After the mixture was stirred at room temperature for 30 min, sodium borohydride (11.4 g, 301 mmol) was added. After stirring for 12 h, the suspension was poured into 1 L of cold water and a solid obtained by filtration. The solid was treated with aqueous 3 M HCl (500 mL), and heated at 75 °C for 6 h. The suspension was cooled and filtered to give a brownish– yellow solid that was placed in a 500 mL round-bottom flask and dissolved in isopropanol (300 mL). The reaction mixture was treated with sodium borohydride (15.9 g, 420.3 mmol) at room temperature and the mixture was heated at reflux for 12 h. Aqueous 3 M HCl was added until bubbling ceased and the mixture was filtered and residue was washed with dichloromethane. The filtrate was concentrated and purified by column chromatography using dichloromethane/hexane (1:9) as eluent to afford 2-bromoanthracene **3** (9.8 g, 55%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ 8.44 (*s*, 1 H), 8.34 (*s*, 1 H), 8.19 (*d*, *J* = 1.0, 1 H), 8.01 (*m*, 2 H), 7.89 (*d*, *J* = 9.2 Hz, 1 H), 7.51 (*m*, 3 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 132.50, 132.40, 131.91, 129.90, 129.70, 129.60, 128.42, 128.11, 128.20, 125.60, 125.40, 119.11. EI-Mass specta *m*/*z*, calcd for C<sub>14</sub>H<sub>9</sub>Br: 257.13. Found: 257.0.

# 2.3.3. Synthesis of 1,4-Bis(dodecyloxy)-2, 5-Diethynyl-Benzene (4)

This compound was prepared by using previously reported two-step procedure from 1,4-bis(dodecyloxy)-2,5-diiodobenzene.<sup>19</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.95 (*s*, 2 H), 3.97 (*t*, 4 H), 3.33 (*s*, 2 H), 1.8–0.9 (*m*, 46 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 151.40, 118.30, 113.0, 82.30, 81.41, 31.90, 29.60, 29.30, 25.90, 22.70, 14.11. EI-Mass specta *m*/*z*, calcd for C<sub>34</sub>H<sub>54</sub>O<sub>2</sub>: 494.79. Found: 494.7.

# 2.3.4. Synthesis of 1,4-Bis(anthracen-2-ylethynyl)-2, 5-Bis(dodecyloxy) Benzene (P2)

Into a 100 mL two-necked round-bottom flask equipped with a reflux condenser were placed compound 4 (0.5 g, 1.0 mmol), diisopropylamine (24 mL), compound 3 (0.52 g, 2.0 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.16 g, 0.2 mmol), CuI (0.04 g, 0.2 mmol) and dry THF (40 mL). After overnight reflux, the reaction mixture was cooled to room temperature, filtered, and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried over MgSO<sub>4</sub> and the solvent was evaporated. The crude product was purified by column chromatography using hexane/chloroform (3:1) as eluent to yield 0.5 g of **P2** (56%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.40 (s, 4 H), 8.22 (s, 2 H), 8.0 (m, 6 H), 7.60-7.45 (m, 6 H), 7.10 (s, 2 H), 4.10 (t, 4 H), 1.90 (m, 4 H), 1.70 (m, 4 H), 1.50–1.10 (*m*, 32 H), 0.98 (*t*, 6 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 151.3, 131.7, 131.3, 128.9, 128.10, 127.70, 126.50, 125.60, 119.10, 118.31, 112.31, 93.30, 84.20, 68.10, 64.0, 31.9, 29.6, 29.3, 22.7, 14.1. EI-Mass specta m/z, calcd for C<sub>62</sub>H<sub>70</sub>O<sub>2</sub>: 847.22. Found: 847.0.

#### 2.4. Fabrication of the OFET Devices

Bottom-contact and top-contact FET devices were fabricated on a common gate of highly *n*-doped silicon with a 200 nm thermally grown  $SiO_2$  dielectric layer. For some of the devices, octyltrichlorosilane (OTS) and hexamethyldisilazane (HMDS) were used to produce hydrophobic dielectric surface. For bottom-contact devices, gold was evaporated through a shadow mask to form source and

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Scheme 1. Reagents and conditions: (I) *t*-BuONO, acetonitrile, CuBr<sub>2</sub>, THF, 60 °C; (II) NaBH<sub>4</sub>, isopropanol, 25 °C; (III) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, diisopropylamine, THF, 80 °C.

drain electrodes. The channel length and channel width of the devices were 20  $\mu$ m and 1400  $\mu$ m respectively. Thin layers of **P2** were spin-coated at 2000 rpm for 60 seconds from a 2 wt% chloroform solution, with a thickness of 50 nm. For top-contact devices, gold source and drain electrodes were evaporated on the organic semiconducting layer through a shadow mask. The channel width and length were the same as mentioned above. All the preparations and electrical measurements using a Keithley 4200 semiconductor parameter analyzer were performed under nitrogen atmosphere at room temperature. The saturated field-effect mobilities were extracted in the saturation regime from the slopes of the source–drain currents using the classical equations describing field-effect transistors.

# 3. RESULTS AND DISCUSSION

#### 3.1. Synthesis

A novel anthracene derivative **P2** was synthesized using the procedure shown in Scheme **1**. Compound 2 was prepared by bromo substitution of compound **1** with 80% yield. Reduction of compound 2 with sodium borohydride yielded compound **3**. Sonogashira cross-coupling reaction of compound **3** and compound 4 provided target molecule **P2** with 56% yield.

### 3.2. Optical and Thermal Properties

The optical properties of **P2** were investigated using UVvis and photoluminescence spectroscopies. Solution of **P2** in chloroform exhibited absorption between 300 and 450 nm with absorption maxima at 312, 325, 366, 390 and 411 nm and emission maximum at 441 nm. The UV-vis and PL spectra are shown in Figure 1 which are comparable to previously reported anthracene derivatives.<sup>20</sup> The thermal properties of **P2** were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in nitrogen atmosphere (Fig. 2). TGA revealed good thermal stability of the compound. Three percent weight loss was observed at 390 °C. The DSC scan during heating revealed multiple peaks for **P2**, whereby the material entered the isotropic melt at 161 °C. During this scan also two other endothermic phase transitions appeared at 116 °C and 152 °C which were attributed to transitions between crystalline states (see X-ray analysis below). Additionally, one exothermic peak was observed at 83 °C, which could be correlated to the solid state rearrangement. Interestingly, only one exothermic peak at 128 °C during cooling arose probably due to a quick cooling rate. This is the reason why any birefringence through cross-polarized optical microscope could be discerned since the material remained in an amorphous and/or disordered state after fast cooling from the isotropic state.

## 3.3. Structural Studies

Solid state order was investigated by two-dimensional wide-angle X-ray diffraction (2D-WAXS) from mechanically aligned fibers of **P2**. The fiber samples were mounted perpendicular to the incident X-ray beam, and diffracted X-rays were collected with an area detector. The pattern recorded at 30 °C is presented in Figure 3(a) and is characteristic for a crystalline state of matter.



Fig. 1. Absorption and emission spectra of P2 in chloroform solution.

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**Fig. 2.** (a) TGA thermogram obtained at a heating rate of 10 °C/min (b) DSC thermograms obtained at a heating and cooling rate of 10 °C/min.

The equatorial reflections indicated that the molecules are arranged in stacks which were oriented along the fiber axis in the extrusion direction. A distance between the stacks of 1.51 nm was derived and is in accordance to the molecular structure. The meridional reflection (I) corresponded to an intermolecular distance of 0.51 nm along the stacks, while the wide-angle equatorial scattering intensities (II) were related to the  $\pi$ -stacking distance of 0.37 nm of the anthracene units. As depicted in the schematic illustration of the supramolecular organization in Figure 3(b), the molecules are stacked on top of each other due to  $\pi$ -stacking interactions. Furthermore, the anthracene units are out-of-plane tilted towards the molecular plane by an angle of ca 90° leading to the wide-angle equatorial reflections. For this molecular arrangement, the benzenes are most probably slightly shifted laterally towards each other. This is the reason for the larger distance of 0.51 nm between the packed benzene building blocks. Interestingly, this crystalline organization is maintained above the phase transitions at 116 °C and 152 °C. An identical observation has been made for other reported crystalline small molecules.<sup>18</sup> At elevated temperatures only the  $\pi$ -stacking distance increases slightly to 0.38 nm (above 116 °C) and 0.39 nm (above 152 °C).



Fig. 3. (a) 2D-WAXS pattern of P2 at 30 °C, and (b) schematic illustration of the organization.

## 3.4. OFET Properties

To investigate the charge transport properties of **P2**, topcontact and bottom-contact FETs were fabricated and annealed at different temperatures. Various devices were made with and without surface treatments using HMDS or OTS. The best device performances were obtained from the bottom-contact device which was fabricated without surface treatment with a hole mobility of  $3.74 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, current on/off ratio of  $5.05 \times 10^{4}$  and threshold voltage of -3.5 V. This particular device was made by spin-coating 2 wt% solution of **P2** in chloroform on silicon substrate at a speed of 2000 rpm for 60 seconds and OFET characteristics were measured at room temperature



**Fig. 4.** (a) Drain current  $(I_D)$  versus drain–source voltage  $(V_D)$  characteristics of **P2** at different gate voltages  $(V_G)$ . (b) Drain current  $(I_D)$  versus gate voltages  $(V_G)$  characteristics of **P2** at a drain voltage of -40 V.

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under nitrogen atmosphere. The output and transfer characteristics of the bottom-contact OFET device are shown in Figure 4.

Among top-contact OTFTs, the device made by spincoating 2 wt% solution of **P2** in chloroform on OTS treated silicon substrate and annealed at 80 °C showed a best performance with a hole mobility of  $5 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.

The molecular organization in the solid state evidenced an out-of-plane tilting of anthracene rings and this type of tilting can also be assumed in the case of thin-film which can affect the hopping mechanism of charge transport and thus limit OFET performance.

## 4. CONCLUSION

OFETs were made from solution processable, anthracenebased organic semiconductor P2 and a hole mobility of  $3.74 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> with on/off ratio of  $5.05 \times 10^{4}$  and threshold voltage of -3.5 V was obtained from bottomcontact devices. Charge transport properties are expected to be influenced by the supramolecular arrangement of the molecule. The solid state order was studied by DSC and X-ray. In extruded fibers, the molecule arranged on  $\pi$ -stacked layers with intermolecular molecular distances of 0.37 and 0.51 nm between anthracene rings and benzene rings respectively. Similar phenomenon can be predicted in the thin-film and the existence of anthracene rings and benzene rings in different planes may affect the close packing of the adjacent layers. As the charge transport in organic semiconductors occurs through hopping, the tilting of the aromatic planes may limit the charge mobility.

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