2,6-Bis(benzo[b]thiophen-2-yl)-3,7-dipentadecyltetrathienoacene (DBT-TTAR2) as an Alternative of Highly Soluble p-type Organic Semiconductor for Organic Thin Film Transistor (OTFT) Application

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Received 12 October 2012; Accepted 12 January 2013; Published online for 1 April 2013

ABSTRACT

A new compound of organic semiconductor based on tetrathienoacene (TTA) derivatives structure, DBT-TTAR2 was synthesized and characterized. The corporation of dibenzo[b,d]thiophene (DBT) group and alkyl substituent in both ends of TTA core have a significant effect on their π-π molecular conjugation length, energy gaps value and solubility properties. DBT-TTAR2 was fabricated as p-type organic semiconductor of organic thin film transistor (OTFT) by solution process at Industrial Technology Research Institute, Taiwan. A good optical, electrochemical, and thermal properties of DBT-TTAR2 showed that its exhibits a better performance as highly soluble p-type organic semiconductor.

Key word: Organic semiconductor, thin film transistor, tetrathienoacene, DBT-TTAR2

INTRODUCTION

Transistor is a fundamental building block for all modern electronics. Nowadays, there were two types of transistors, thin film transistors (TFTs) which is the conventional ones and organic thin film transistors (OTFTs). Fundamentally, the arrangement of TFT and OTFT are the same, they are composed of three electrodes (source, drain and gate), a gate dielectric layer as an insulating material and a thin semiconductor layer as a conducting material [6]. The different between TFT and OTFT are on their semiconductor. The TFT have an inorganic semiconductor, such as silicon (Si), germanium (Ge), gallium arsenide (GaS) and other III/V or II/VI compounds, meanwhile OTFT constructed of an organic or polymer semiconductor [2, 4].

Figure 1 shows a schematic layout of a bottom-gate top-contact OTFT. Note that several other device architectures can be fabricated depending on the relative position of the contacts and the dielectric/semiconductor layers (not shown). In this device, negligible source-drain current (\(I_{SD} = 0\ A\)) flows when the gate voltage is zero (\(V_{G} = 0\ V\)) independently of the bias applied between the source and drain contacts (\(V_{SD}\)). The device turns on (\(I_{SD} \neq 0\ A\)) when a gate field is applied (\(V_{G} \neq 0\ V\)), which is induces charge carrier in the semiconductor at the interface with dielectric layer [3].
Recent years, OTFTs have received bigger attention because they have many advantages compared to the TFTs. Common reason the OTFTs more important option in many applications for electronic technology due to its easily fabricated even at lower temperature than that of TFT. Wide application of OTFT for electronic industry can be found as an active matrix display for mobile phone, electronic papers, flexible microelectronics, smart cards, radio frequency identification (RFID) tags and chemical sensors [2, 4, 5].

The most important of OTFT is an organic semiconductor in which the charge carriers can be induced to migrate under the influence of electric fields, with the mobility generally a thermally activated doping process from one molecules or chain to another. It also has some process ability advantages which can be fabricated by low-cost and low-energy processes. And also it offer a unique physical features from those conventional semiconductors (i.e., electrical, optical, thermal, and magnetic properties) [7, 9]. Therefore organic semiconductor is a critical component that can improve the performance of OTFT. Performance of OTFTs is primarily determined by the field effect mobility of the charge carriers in the layers, efficiency of injection and extraction carriers at the source and drain contacts [5].
Based on its charge carriers, organic semiconductor can be divided into two groups, i.e. as a p-type and n-type organic semiconductor. For the p-type, majority carriers are holes, while in n-type the majority carriers are electrons (Figure 2). Most organic semiconductor that has been investigated is p-type form, because p-type semiconductors are stable in air and relative high its mobility. On the other hands, most of n-type semiconductors are sensitive to air and moisture. Furthermore, the n-type relatively have low field-effect mobility [1, 5, 15].

Many kinds of organic semiconductors have been synthesized and evaluated for applying in OTFTs. But until nowadays the investigation of the relationship between molecular structure and electrical OTFTs performance lack and have not been reported. In other word, the investigation to get a high performance organic semiconductor under ongoing research [5]. There were some properties that should have by the organic semiconductor materials, such as a good solubility, long-term thermal and oxidative stability, and enhanced π-stacking for superior electrical conductivity [5, 10].

Recently, there were significant achievements for the development of organic semiconductor materials such as π-conjugated polymers, heteroacenes, oligo- and polythiophenes include their derivatives. Among of these, thienoacenes form attract as organic semiconductor, which consists of fused thiophene rings in a ladder-type of molecular structure. Synthesis of fused thiophene substructures is interesting due to their utility as bioactive materials, pharmaceuticals and intermediates in the manufacture of dyes. They were also employed as key units for the development of electronic materials, such as a narrow band gap polymers and electron donors or acceptors for conductive charge transfer salts. In many recent years, thienoacenes have been widely synthesized and evaluated as organic semiconductors [14, 19]. Accordingly, Youn et al. (2010) reported fused thiophene, thienoacenes is the most interesting alternative material for organic semiconductor because of their extensive conjugation, strong intermolecular S•••S interactions, large band gap, and high ambient stability. Fused ring thiophene also became an important representative system of p-type organic semiconductor material because the synthetic availability and widespread possibility [16, 18].

Halik et al. (2003) explained one of most useful and practical strategy to investigate the properties of an organic semiconductor for OTFT application is focused on its chemical structure [14]. It can be done either by varying the number of units in the conjugated backbone of the molecule, or by varying the length of alkyl substituent. Unfortunately, these variants of organic semiconductor materials still lack an under investigation due to difficulty to synthesized [11, 18]. However, there were several derivatives of fused thiophene and thienoacene with three or four thiophene rings which have been explored and demonstrated as a model for p-type charge transport performance. The mobility value was very differs, 0.1 cm² V⁻¹ s⁻¹ > μ > 2 cm² V⁻¹ s⁻¹ [16].

One example of organic semiconductors based on thienoacene derivatives which used dithienothiophene (DTT) as a core, which is a 2,5-diphenyl-dithieno[2,3-b:3′,2′-d]thiophene (DP-DTT) (Figure 3). DTT represents a sulfur-rich, planar, and rigid π-conjugated system, which has been widely used as a building block in functional materials. These compounds have a high stability and good mobility value, which is 0.42 cm²/Vs [13]. But DP-DTT has poor solubility properties, and should be fabricated using vapour deposition process. Here, our groups develop a new derivative of thienoacenes with the derivative of polythiophene compounds, tetrathienoacene (TTA) as the core. TTA were chosen because of their synthetic availability and widespread possibility for modifying [11, 14, 17, 18]. Next, TTA core will be
conjugated with benzene thiophene (BT) group, especially its basic structural unit of the BT system, dibenzo[b,d]thiophene (DBT). The structure of DBT showed a possibility of its variety compound to induce the strong π-π intermolecular interactions, include in some compounds which presented short S⋯S interactions, such as various thiophene oligomers as the backbone. And it would provide an additional channel for charge carrier transport and if it’s happened, we can get the high performance of organic semiconductors for OTFT application \[11, 18\]. In addition to increase the solubility with an expectation to get a good performance of those compounds, so each compound will be conjugated with alkyl substituent, pentadecyl (C\(_{15}\)H\(_{31}\)).

Based on the structural properties and our last experience, we estimate that DBT-TTA-diC\(_{15}\)H\(_{31}\) (DBT-TTAR2) (Figure 3), would have a good performance as highly soluble p-type organic semiconductor. Finally, DBT-TTAR2 can act as a new compound which could enrich organic semiconductors based on fused thiophene derivative.

![Figure 3. Structure of DP-DTT and DBT-TTAR2](image)

**EXPERIMENT**

**Materials and Methods**

All chemicals have synthetic grade and purchased from Sigma Aldrich. \(^1\)H-NMR (200 MHz, 300 MHz) and \(^1^3\)C-NMR (300 MHz) spectra were obtained on Bruker Model NMR Spectrometer using CDCl\(_3\) as solvent. MS spectra were obtained on JEOL JMS-700 Mstation high resolution MS spectrometer (Germany). Optical, thermal and electrochemical properties were determined by using Hitachi UV-Visible spectrometer, Mettler Toledo TGA and DPV, respectively.

**Synthesis procedure**

The synthetic route and the chemical structures of compound used in this study are shown in Figure 4. The procedure of the synthesis is presented as below.

**2,5-Di(1,1'-pentadecanone)-3,6-dibromo-thieno[3,2-b]thiophene (1)**

Under nitrogen and anhydrous conditions, 2,3,5,6-tetra- bromo-thieno[3,2-b]thiophene (5.43 g; 0.012 mol) was dissolved in anhydrous tetrahydrofuran (200 mL), added \(n\)-buthyl lithium (2.5 M; 9.769 mL; 24.42 mmol) slowly and the reaction mixture was stirred at 0 °C for 1 h. Then, the anhydrous pentadecanoyl chloride (13.098 mL; 0.048 mmol) was added slowly and stirred at – 40 °C for 1 h. The reaction mixture was stirred continuously at room temperature for 12 h. After reaction completed, the reaction mixture temperature should be decreased to – 40 °C, filtered and washed with acetone 99 %. Removal all the solvent under vacuum condition afforded the title compound 1 (3.86 g; 0.005 mol; 41.82 % yield) as a white solids which was used for the next step without further purification. \(^1\)H NMR (200
MHz, CDCl₃): δ 3.082 ppm (t, 2H, J = 14.4 Hz), δ 1.768 ppm (t, 2H, J = 14.3 Hz), δ 1.252 ppm (br, 24H), δ 0.876 ppm (t, 3H, J = 13.2 Hz).

2,6-Dicarboethoxy-3,7-dipentadecyltetrathienoacene (2)

Under the ambient condition, potassium carbonate (3.11 g; 0.023 mol) and the compound 1 (3.86 g; 0.005 mol) was dissolved in dimethyl formamide (150 mL) until the reaction mixture homogen. The reaction mixture was stirred, heated to 60 °C and protected it from air. Then ethyl-2-mercaptoacetate or ethyl-2-sulfanylacetate (1.09 g/mL; 1.378 mL; 165.59 mmol) was added slowly and stirred for 48 h at 60 °C. After the reaction completed, the mixture was quenched with hydrochloric acid (6 M, 200 mL) in cold condition using an ice bath. The quenched reaction mixture was extracted with ethyl ether and water. The organic layer was dried with anhydrous sodium sulfate and filtered. The solvent was removed by evaporation under vacuum condition, afforded the title compound 2 (2.77 g; 0.003 mol; 68 % yield) as a white solids, which was used in the next step without further purification. ¹H NMR (200 MHz, CDCl₃) : δ 4.345 ppm (m, 2H, J = 7.2 Hz), δ 3.147 ppm (d, 2H, J = 8 Hz), δ 1.410 ppm (t, 3H, J = 14.4 Hz), δ 1.243 ppm (br, 26H), δ 0.868 ppm (t, 3H, J = 12.6 Hz).

3,7-Dipentadecyltetrathienoacene-2,6-dicarboxylate acid (3)

Sodium hydroxide (0.504 g; 0.013 mol) was dissolved in distilled water (5 mL) and added slowly to the reaction mixture of compound 2 (2.77 g; 0.003 mol) in tetrahydrofuran : methanol (5 : 1). The reaction mixture was heated at 200 °C for 12 h and further refluxed. The reaction mixture was quenched using hydrochloric acid (6 M; 200 mL) under cold condition with an ice bath. Then the quenched reaction mixture was filtered, and removed the solvents under vacuum condition and gave the title compound 3 (2.53 g; 0.003 mol; 98 % yield) as a white solids which was used in the next step without further purification.

3,7-Dipentadecyltetrathienoacene (4)

Under nitrogen and anhydrous condition, the title compound 3 (2.53 g; 0.003 mol) was added with copper powder (0.587 g; 0.009 mol) and dissolved in anhydrous quinoline solvent (100 mL). The reaction mixture was refluxed at 265 °C using the hot mantle for 12 h. After the reaction completed, decreasing the reaction mixture temperature and then quenched with hydrochloric acid (6 M; 200 mL) in a cold condition using an ice bath, filtered and washed with hot toluene. The liquid phase was extracted using hot toluene and water. Then the organic layer was removed from the solvents by evaporation under vacuum condition. Purification with column chromatography (silica, hot toluene 70 °C as eluent), and recrystallization, respectively third times, and concentrated under vacuum condition. The solid phase afforded was recrystallized using hot toluene (70 °C), respectively third times and concentrated under vacuum condition. Purification and recrystallization were afforded the title compound 4 (1.8 g; 0.003 mol; 80.45 % yield) as a white solids which was used in the next step. ¹H NMR (200 MHz, CDCl₃) : δ 6.989 ppm (s, 1H), δ 2.773 ppm (t, 2H, J = 14.6 Hz), δ 1.792 ppm (d, 2H, J = 6.6 Hz), δ 1.289 ppm (br, 24H), δ 0.913 ppm (t, 3H, J = 27.4 Hz).

2,6-Dibromo-3,7-dipentadecyltetrathienoacene (5)

Compound 4 (1.55 g; 0.002 mol) and n-bromosuccinimide (0.942 g; 0.0046 mol) was dissolved in tetrahydrofuran : methanol (5 : 1) and heated to 40 °C. The reaction mixture was stirred at ambient condition for 12 h. After the reaction completed, the reaction mixture was
filtered and washed using hexane solvents. Removal the solvents under the vacuum condition and subsequently afforded the title compound 5 (1.6 g; 0.002 mol; 83.62 % yield) as a yellow solids which was used for the next step. $^1$H NMR (200 MHz, CDCl$_3$) : $\delta$ 2.738 ppm (t, 2H, J = 15 Hz), $\delta$ 1.635 ppm (t, 2H, J = 63 Hz), $\delta$ 1.377 ppm (br, 24H), $\delta$ 0.872 ppm (t, 3H, J = 15 Hz).

2,6-Bis(benzo[b]thiophen-2-yl)-3,7-dipentadecyltetrathienoacene or DBT-TTAR2 (6)

Under nitrogen and anhydrous condition, the title compound 5 (0.95 g; 0.001 mol) and tetrakis(triphenylphosphine)palladium (0.053 g; 0.000004 mol) were dissolved in anhydrous toluene solvent (150 mL) which was filtered through celite. Then the reaction mixture was added slowly with 1-benzothiophen-2-yltributylstannane (1.113 g; 0.0023 mol) and refluxed at 200 °C for 12 h. After the reaction completed, the reaction mixture was quenched with hydrochloric acid (6 M, 200 mL) and filtered through celite : silica (1:1). The solvents was removed from the filtrate with evaporated under vacuum condition and subsequently afforded the crude product. Recrystalization of crude product under a hot toluene (70 °C), respectively third times, and concentrated under vacuum was afforded the final compound called as DBT-TTAR2 (0.7 g; 0.001 mol; 65.31 % yield) as a bright yellow solids. $^1$H NMR (300 MHz, CDCl$_3$) : $\delta$ 7.816 ppm (m, 2H, J = 19.8 Hz), $\delta$ 7.402 ppm (m, 1H, J= 8.7 Hz), $\delta$ 7.344 ppm (m, 2H, J = 16.2 Hz), $\delta$ 3.009 ppm (t, 2H, J = 15.6 Hz), $\delta$ 1.828 ppm (m, 2H, J = 30 Hz), $\delta$ 1.249 ppm (br, 24H), $\delta$ 0.871 ppm (t, 3H, J = 13.5 Hz). $^{13}$C NMR (300 MHz, CDCl$_3$) : $\delta$ 14.11, 22.68, 28.91~29.68, 31.92, 122.02, 122.53, 123.60, 124.60, 124.74, 129.94, 131.21, 132.26, 133.94, 136.35, 139.84, 139.99, 142.84. HRMS (EI) m/z : C$_{56}$H$_{150}$S$_6$ calculated = 937.5669 (M+); found = 936.3958.

RESULT AND DISCUSSION

Synthesis of DBT-TTAR2

DBT-TTAR2 synthetic route described in Figure 4. The synthesis of DBT-TTAR2 used 2,3,5,6-tetrabromothieno[3,2-b]thiophene as the starting material which lithiated with BuLi and followed by the addition of C$_{15}$H$_{31}$COCl. Side chain ketone was formed on both sides diBr-TT. Cyclization reaction using ethyl-2-mercaptoacetate and potassium carbonate as catalyst formed TTAR2-(COOCH$_2$CH$_3$)$_2$. This reaction was continued by saponification and decarboxylation reaction, subsequently using NaOH 10% and copper powder to result TTAR2. Bromination reaction using NBS and Stille coupling reaction between diBr-TTAR2, C$_{12}$H$_{27}$ClSn, and catalysed by Pd(PPh$_3$)$_4$ formed the final compound, DBT-TTAR2. This final product was purified by recrystalization and characterized by mass spectroscopy (MS), UV-Visible spectroscopy (UV-Vis), thermogravimetric analysis (TGA), and differential pulse voltammetry (DPV).

Optical Properties

The UV-Vis absorptions of the DBT-TTAR2 was analyzed in o-dichlorobenzene solution to investigate the maximum absorbance, onset absorption, and energy gap. The onset absorption and energy gap data to describe details about the electrochemical properties of DBT-TTAR2 were showed in Table 1. According to the absorption spectra, the maximum wavelength value for DBT-TTAR2 is 406.5 nm. This maximum wavelength compared with DP-DTT, one example of p-type organic semiconductor that has been synthesized by Sun et al. (2006). Sun et al. (2006) described that DP-DTT which have a high mobility value (0.42 cm$^2$/Vs) and
a good stability as an p-type organic semiconductor, these maximum wavelength value is 373.0 nm (Figure 5). DP-DTT is one of thienoacene derivatives which is consist of DTT core as a backbone and DT (dithiophene) as a chain on its both side. Its π-π molecular conjugation made the DP-DTT have better properties as p-type organic semiconductor through a vapour deposition process.

![Figure 4. Synthetic route of DBT-TTAR2](image)

![Figure 5. Comparison of optical absorption spectra between DP-DTT and DBT-TTAR2](image)
The difference of maximum wavelength between DP-DTT and DBT-TTAR2 explained the $\pi-\pi$ molecular conjugation length of DBT-TTAR2 increase importantly. The DBT-TTAR2 maximum wavelength more shifted to red region than that of DP-DTT. DBT-TTAR2 have a longer $\pi-\pi$ molecular conjugation which was added on the thiophene core and dibenzo[b,d]thiophene (DBT) substitutents on both side.

The shifts of maximum wavelength have a relationship with the requirement of energy for electronic excitation. And the presence of extended $\pi-\pi$ molecular conjugation decreased the energy require for electronic excitation. The longer $\pi-\pi$ molecular conjugation, the energy level from an occupied electronic energy level to an unoccupied level will narrower and the maximum wavelength shifted broader.

**Electrochemical properties**

Knupfer et al. (2001) described the performance of most devices is related to the transport properties. A central parameter to model the transport behavior of material is the energy gap, which is the energy difference between a free electron in the conduction band (LUMO) and a free hole in the valence bond (HOMO). Energy gap is binding energy (BE) of lowest lying optical excitation, which is defined as the energy difference between the excitation energy as measured in optical experiment (optical gap) and transport gap.

Differential Pulse Voltammograms (DPV) of DBT-TTAR2 was analyzed in $o$-dichlorobenzene at 25 °C which provided description of the HOMO/LUMO levels. The electrochemically derived HOMO level of the DBT-TTAR2 is significantly up-shifted compares with DP-DTT (Figure 6). There is a consideration about the relationship between $\pi-\pi$ molecular conjugations length, HOMO and LUMO level. The $\pi-\pi$ molecular conjugation length of DBT-TTAR2 is extent than DP-DTT means the HOMO level of the previous is higher than the latter and the LUMO level of DBT-TTAR2 lower than DP-DTT.

![Figure 6. Comparison of electrochemically derived HOMO and LUMO energy levels of DP-DTT and DBT-TTAR2](image)

**Table 1. Optical and electrochemical data of DBT-TTAR2**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\lambda_{\text{onset}}$ (nm)</th>
<th>$E_{\text{onset}}$ (eV)</th>
<th>$^a$ HOMO (eV)</th>
<th>$^b$ $E_g$ (eV)</th>
<th>$^c$ LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBT-TTAR2</td>
<td>406.5</td>
<td>468</td>
<td>1.112</td>
<td>-5.312</td>
<td>2.651</td>
<td>-2.661</td>
</tr>
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$^a$ Calculated based on HOMO = $\frac{\text{E}_{\text{opt}}}{(4.2 \text{ eV})}$. $^b$ Estimated the $E_g$ (eV) = 1240.8 / $\lambda_{\text{onset}}$. $^c$ Calculated LUMO = HOMO + $E_g$. 

Ag/Pt in $o$-dichlorobenzene with 0.1 M Tetrabuthylammonium haexafluorophosphate as a supporting electrolyte.
The increasing of HOMO level and decreasing of LUMO level resulted the decreasing of the energy gap, and the closer of the energy level provided the lower of the energy gap (Eg) (Table 1).

**Thermal properties**

High purity organic semiconductor material is preferable to achieve better properties in OTFT and may help increase the device lifetime. The sublimation technique is a very good purification method and because a number of organic semiconducting materials sublime at high temperatures and high vacuum, high purity materials can be obtained. One of sublimation technique analysis is using Thermal Gravimetric Analysis (TGA) method.

Thermal analysis describes the techniques used in characterizing materials by measuring a physical or mechanical property as a function of temperature or time at a constant temperature or as a function of temperature. TGA method is normally used to obtain the onset temperature of initial polymer or small molecule weight loss, as well as the extent of oxidative effects. The main purposes of thermal analysis were to investigate the thermal stability of a compound, it was important, since it is likely related to practical concerns such as ease of purification and device longevity.

As a result of TGA analysis, DBT-TTAR2 has a high 5% weight loss temperature which is 405 °C. This value indicated DBT-TTAR2 have high purity, and able to provide a better performance of OTFT. Besides that, OTFT based on DBT-TTAR2 as its organic semiconductor materials will have a high thermal stability and become a longevity device.

**CONCLUSION**

We have successfully synthesized a highly soluble p-type organic semiconductor based on structure tetrathienoacene derivatives (TTA) which is called DBT-TTAR2 by chemical modification of DP-DTT. The comparative analysis of the optical absorptions, electrochemical potentials, and thermal properties of DBT-TTAR2 showed enhancement of \( \pi-\pi \) molecular conjugation length, through the corporation of DBT substituent in both ends of tetrathienoacene (TTA) core. This provides a major effect on compound performance as an organic semiconductor. The addition of alkyl substituent in both ends of tetrathienoacene (TTA) core, also give more advantage to DBT-TTAR2, and also this addition of increase the solubility. This compounds potential to be fabricated by solution technique deposition.

**ACKNOWLEDGEMENT**

The authors are grateful to Dr. Elvina Dhiaul Iftitah from Department of Chemistry, Mathematics and Science Faculty, Brawijaya University for motivation, discussion and helpful comments.

**REFERENCE**