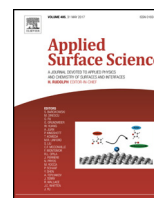




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Full Length Article

# Evaluation on the electrochemically deposited alkoxy thiourea as liquid crystalline semiconductor film

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## ABSTRACT

A new class of liquid crystalline film of alkoxy thiourea which was successfully deposited on indium tin oxide (ITO) coated substrate via electrochemical deposition method. The relationship between liquid crystal molecular structure, phase transition temperature and electrical performance was evaluated. The mesomorphic properties were identified via polarized optic microscopy (POM) which displayed cholesteric phase and their corresponding transition enthalpies were respectively recorded at 20.25 kJ mol<sup>-1</sup>. The findings from the conductivity analysis revealed that the fabricated film exhibits good electrical performance with an increasing conductivity up to 0.2170 S cm<sup>-1</sup> under maximum light intensity of 100 W m<sup>-2</sup>. Therefore, this proposed type of molecular framework has given an ideal indication to act as semiconductor materials and has opened wide potential for application in organic electronic devices.

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## 1. Introduction

Research on organic semiconductor have attracted intensive attention in the area of molecular electronic applications [1–4]. This is due to their unique characteristics such as having low cost of production, lightness and compatibility with large-scale flexible substrates [5–7]. In these contexts, a number of organic semiconductor classes have been extensively studied based on small molecules and polymers derived from pentacene [8,9], naphthalene [10,11] and oligothiophenes [12–14]. These promising candidates consist of conjugated molecular unit which comprises electronic delocalization in extended  $\pi$ -orbital system, through which electrons can flow from one reservoir to another that resulted into the effective properties of electrical conductivity. In addition, the unique and interesting chemistry of these materials which potentially can act as active layer in semiconductor thin film which in turn, may offer exciting characteristics in term of optical, electronic properties and high charge transport mobility [15–17].

Nevertheless, the quest on preparation of ideal materials with appropriate deposition method for thin film fabrication lies upon the favourable alignment which leads to efficient charge transport that can be rather challenging [18–20]. Thus, organic semiconduc-

tors can be fabricated by simple processing techniques, possess excellent electrical performance and perform carrier mobility at an optimum level which are the key requirements in the progress of organic electronics [21]. A large variety of techniques have been developed for thin film deposition process via chemical bath deposition, spray pyrolysis technique, solution process and vacuum deposition to improve device performances [22–24]. It is noteworthy that electrochemical deposition (ECD) is an alternative approach that exhibits low cost and easily prepared with only one-step procedure. This approach can proceed at low temperature as well as able to form uniform and well ordered films on conductive substrates [25,26]. Therefore, insertion of linear  $\pi$ -conjugated molecular systems derived from a number of aromatic rings incorporated with alkyl chains [21,27–29] should promote planar arrangement particularly in the liquid crystalline compounds.

Regarding to this matter, we utilise thiourea which consists naphthyl and alkoxy groups and has become our subject of interest for liquid crystalline materials as active layer in semiconductor film prepared via simple electrochemical deposition method. Considering their versatile properties, such as having delocalized two fused aromatic rings with relatively high thermal stabilities, presence of resonance interactions between nitrogen lone pairs and the C=O and C=S double bonds [30–32] are anticipated to transform into new materials with leads to liquid crystalline phases in semiconductor film. Due to this matter with highly

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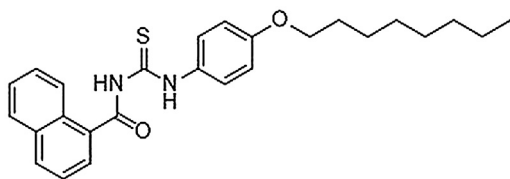


Fig. 1. Molecular structure of *N*-(octyloxy)phenyl-*N'*-(naphthoyl) thiourea (ONTU).

interest in developing semiconducting liquid-crystalline material, we are presenting new alkoxy substituted thiourea derivative namely, *N*-(octyloxy)phenyl-*N'*-(naphthoyl) thiourea (ONTU) as active semiconductor material candidate for this interest as shown in Fig. 1. This compound contains naphthyl group as acceptor linking to terminal alkylation of 8 carbon chain as donor group which makes them soluble in organic solvents, enhances charge carrier mobilities and the thermal motion from alkoxy chains which can contribute to rather interesting flexibility and softness of the mesomorphic structures [15]. The motivation in introducing 8 carbon chain is due to the fact that an increasing length of the alkoxy chain when  $n \geq 7$  enhances temperature range of the phase and plays an important role in the formation of mesophases [29]. Thus, the study involves combination of chemical modeling as in Gaussian studies, synthesis and characterisation; in turn, the molecule deposited into thin film via simple deposition technique prior to form active layer in liquid crystalline semiconductor film.

## 2. Experimental

### 2.1. Materials and instrumentation

All chemicals and solvents were purchased from standard commercial suppliers namely Sigma Aldrich, Merck, Fisher Scientific and R&M Chemical, and were used as received without any special precautions taken during the experimental work-up. The infrared (IR) spectra were recorded on Perkin Elmer 100 Fourier Transform Infrared Spectroscopy by using potassium bromide (KBr) pellets in the spectral range of 4000–400  $\text{cm}^{-1}$ . Electronic absorption spectra of the samples were recorded by using Spectrophotometer Shimadzu UV-1601PC in 1 cm path length quartz cell in methanolic solution with concentration  $1 \times 10^{-5}$  M for absorbance analysis. The C, H, N and S microanalysis of the synthesized compounds were carried out with FLASH EA 1112 CHNS analyzer. The NMR spectra were recorded using Bruker Avance III 400 spectrometer  $^1\text{H}$  (400.11 MHz) and  $^{13}\text{C}$  (100.61 MHz) by using deuterated chloroform ( $\text{CDCl}_3$ ) at room temperature as solvent and internal standard in the range between  $\delta_{\text{H}}$  0–15 ppm ( $^1\text{H}$ ) and  $\delta_{\text{C}}$  0–200 ppm ( $^{13}\text{C}$ ). Thermogravimetric analysis was performed using PerkinElmer TGA Analyzer from 30 °C to 700 °C at a heating rate of 10 °C/min under nitrogen atmosphere. The thermal properties like phase transition temperatures and enthalpy values of liquid crystal mesogens were investigated by modulated DSC Q2000 where the heating and cooling rate at a scanning rate 10 °C/min under nitrogen atmosphere. The liquid crystal phase transitions were investigated by an Olympus polarized light microscope (POM) equipped with Mettler Toledo FP90 hot stage FN82HT [33]. The temperature scanning rate for heating was determined at 10 °C/min while cooling 5 °C/min. Cyclic voltammetry analysis was carried out via Electrochemical Impedance Spectroscopy (EIS) PGSTAT302. The theoretical study was evaluated via Gaussian 09 software employing DFT approach with set of basis function B3LYP/6-31G(d,p) with required physical parameters such as total energy and energy band gap.

### 2.2. General overview of synthetic work

In the synthetic work, it comprised three major parts which were the formation of precursor, *N*-(4-(octyloxy)phenyl) acetamide (1) and the reaction was continued with the formation of 4-octyloxy aniline (2) as an intermediate and in turn, it was reacted with aryl chloride to afford *N*-(octyloxy)phenyl-*N'*-(naphthoyl) thiourea (ONTU) as focalpoint compound in this study. However, the experimental details with regard to the synthesis of precursor 1 and 2 have been reported previously in literatures [34–36]. The synthetic approach for the preparation of ONTU is summarized in Scheme 1.

#### 2.2.1. *N*-(4-(Octyloxy)phenyl) acetamide (1)

The preparation of 1 was accomplished via Williamson ether synthesis through equimolar amount of *N*-(4-hydroxyphenyl) acetamide (10.02 g, 66.2 mmol), octyl bromide (11.4 mL, 66.2 mmol) and potassium carbonate (9.17 g, 66.2 mmol). The mixture of these reactants was suspended in ca. 100 mL acetone and put at reflux for ca. 48 h with continuous constant stirring to afford white precipitate with colourless solution at the end of the reaction. When adjudged completion by thin layer chromatography (TLC) using the solvent system of (hexane:ethyl acetate; 3:2), the reaction mixture was allowed to come to room temperature before the solvent was removed *in vacuo* to afford white solids. The white solids obtained was then stirred with 50 mL of 2% of sodium hydroxide for ca. 1 h and the brown solution with white precipitate was obtained. The resulting cloudy solution with white precipitate was filtered and then the precipitate was washed by little diethyl ether to attain 1 (85% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400.11 MHz):  $\delta$  0.89 (t,  $^3J_{\text{HH}} = 7$  Hz, 3H,  $\text{CH}_3$ ); 1.31–2.14 (m, 12H, 6x  $\text{CH}_2$ ); 3.93 (s, 2H,  $\text{OCH}_2$ ); 6.81 (pseudo-d,  $^3J_{\text{HH}} = 9$  Hz, 2H,  $\text{C}_6\text{H}_4$ ); 6.84 (pseudo-d,  $^3J_{\text{HH}} = 9$  Hz, 2H,  $\text{C}_6\text{H}_4$ ); 7.37 (pseudo-d,  $^3J_{\text{HH}} = 9$  Hz, 2H,  $\text{C}_6\text{H}_4$ ); 7.39 (pseudo-d,  $^3J_{\text{HH}} = 9$  Hz, 2H,  $\text{C}_6\text{H}_4$ ); 7.91 (s, 1H, NH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.61 MHz):  $\delta$  14.09 ( $\text{CH}_3$ ); 22.65, 24.11, 26.04, 29.24, 29.29, 31.81 (6x  $\text{CH}_2$ ); 68.31 ( $\text{CH}_2\text{O}$ ); 114.71, 122.07, 130.85, 156.05 (Ar- $\text{C}_6\text{H}_4$ ); 168.72 (C=O). Elemental Analysis Calculated for  $\text{C}_{16}\text{H}_{25}\text{NO}_2$  (1): C 72.96; H 9.57; N 5.32. Found: C 72.68; H 9.68; N 5.29.

#### 2.2.2. 4-Octyloxy aniline (2)

White solid of 1 (10.80 g, 66.2 mol) was treated in 50 mL ethanol and 50 mL concentrated hydrochloric acid and then put at reflux with constant stirring for ca. 2 h. The solution mixture with light brown colour formed at the end of the reaction afforded 4-octyloxy aniline hydrochloride. Then, the reaction mixture was allowed to come to room temperature before being partitioned between dichloromethane (100 mL) and water (100 mL), the organic layer was collected, dried over  $\text{MgSO}_4$  and finally dried *in vacuo* to afford off-white solid of 2 (57% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400.11 MHz):  $\delta$  0.91 (t,  $^3J_{\text{HH}} = 7$  Hz, 3H,  $\text{CH}_3$ ); 1.31–1.79 (m, 12H, 6x  $\text{CH}_2$ ); 3.91 (s, 2H,  $\text{OCH}_2$ ); 6.73 (pseudo-d,  $^3J_{\text{HH}} = 9$  Hz, 2H,  $\text{C}_6\text{H}_4$ ); 6.75 (pseudo-d,  $^3J_{\text{HH}} = 9$  Hz, 2H,  $\text{C}_6\text{H}_4$ ); 7.29 (pseudo-d,  $^3J_{\text{HH}} = 9$  Hz, 2H,  $\text{C}_6\text{H}_4$ ); 7.37 (pseudo-d,  $^3J_{\text{HH}} = 9$  Hz, 2H,  $\text{C}_6\text{H}_4$ ); 10.24 (s, 2H,  $\text{NH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.61 MHz):  $\delta$  14.08 ( $\text{CH}_3$ ); 22.65, 24.16, 26.04, 29.40, 29.29, 31.82 (6x  $\text{CH}_2$ ); 68.31 ( $\text{CH}_2\text{O}$ ); 114.70, 122.05, 130.96, 155.99 (Ar- $\text{C}_6\text{H}_4$ ). Elemental Analysis Calculated for  $\text{C}_{14}\text{H}_{23}\text{NO}$  (2): C 74.48; H 10.47; N 6.33. Found: C 73.45; H 9.32; N 6.46.

#### 2.2.3. *N*-(Octyloxy)phenyl-*N'*-(naphthoyl) thiourea (ONTU)

The experimental details regarding to the synthesis of ONTU was adapted from the approach carried out by Douglas-Dains [37] involving suspension of 1-naphthoyl chloride (2.85 g, 15 mmol) in 50 mL acetone was added dropwise to a solution of ammonium thiocyanate (1.14 g, 15 mmol) in 50 mL acetone. The mixture was stirred at room temperature with presence of inorganic salt as by product. Then, it was put at reflux with constant stirring for ca. 4 h,

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