

Study on Semiconductor Properties of Acetylide-Thiourea Fabricated onto Interdigitated Electrodes (IDES) Platform Towards Application In Gas Sensing Technology

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Abstract

In the past few decades, the unique properties of acetylide and thiourea moieties individually have attracted great attention from researchers in various fields to be developed in numerous applications in advanced materials technology, especially as an active layer in gas sensing devices. The molecular systems of acetylide and thiourea provide a wide range of electronic properties as they possess rigid π -systems in their designated structures. In this study, a derivative of acetylide-thiourea featuring *N*-(4[4-aminophenyl] ethynyl benzonitrile)-*N'*-(4-ethyl benzoyl) thiourea (**TCN**) has been synthesised with the general formula of $\text{ArC}(\text{O})\text{NHC}(\text{S})\text{NHC}\equiv\text{CAr}$ adopted the system of D- π -A for the significant development of conductive materials. The derivative consists of donating substituent characterised by typical spectroscopic techniques, such as infrared spectroscopy, UV-visible spectroscopy, and ¹H and ¹³C Nuclear Magnetic Resonance. In turn, **TCN** was deposited onto interdigitated electrode (IDE) for the measurement of thin-film resistance. The resistance values of synthesised compound is caused the effect of donating substituent attached to the acetylide-thiourea, which indeed altered the conductivity performances of fabricated IDE substrate. In fact, the theoretical calculation also was carried out using Gaussian 09 to evaluate the relationship between experimental and theoretical analyses of acetylide-thiourea semiconductor properties in term of energy band gap and the sensing response to the selected analyte.

Abstract

Studi Sifat Semikonduktor Asetilida-Thiourea sebagai Substrat Elektroda Terdigitasi (IDES) menuju Aplikasi dalam Teknologi Penginderaan Gas. Bio ethanol adalah salah satu bahan bakar potensial di masa depan. Namun campuran etanol dalam air memiliki titik azeotrop pada konsentrasi 95,6 % berat, sehingga sulit untuk dimurnikan lebih lanjut. Metode umum yang dipakai dalam pemurnian etanol adalah menggunakan kolom distilasi azeotropik yang membutuhkan energi yang intensif dan penambahan solven tertentu. Pada penelitian ini, pemurnian etanol dilakukan dengan kolom adsorpsi dengan bahan isian cincin zeolite di dalamnya. Zeolit alam sebelum digunakan dimodifikasi dengan larutan NaOH agar kemampuan penyerapan (adsorpsi) air menjadi meningkat. Kemurnian etanol dapat mencapai lebih dari 99% dengan zeolite termodifikasi. Modifikasi ini juga meningkatkan waktu saturasi kolom sehingga kolom bisa dijalankan dengan efisien.

Keywords: acetylide, conductivity, IDE, semiconductor, thiourea

1. Introduction

The development of a single molecular system as an active electronic unit has currently attracted huge attention from both researchers and industry [1],[2]. The first kick-off regarding active molecular electronic was

introduced by Aviram and Ratner in 1973, with the current rectifying behaviour consisting of D- σ -A, where *D* represents an electron-donor unit, *A* represents an electron – acceptor unit, and σ is a conducting molecular bridge that connects *D* with *A* [3]-[5]. The existence of extremely large number of chemicals with

various chemical substitutions can lead to various electrical functions which can open up new possibilities in electronic devices that have never been offered [6]. Electron hopping within single molecular junction is determined by charge instillation barriers at the electrode-molecule surface [7], which in turn characterised by the energy configuration between the electrode Fermi level and a single discrete energy level of molecules, known to be either the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO) levels [8]. Thus, noteworthy efforts have been given to attain modulation of the HOMO-LUMO molecules with external stimulus such as electric field, light, and mechanical forces, for understanding and controlling the unique electrical characteristics of single-molecule junctions [9].

For the past few years, thiourea derivatives are known as one of the single molecular types which have been applied widely in numerous advanced materials fields such as in pharmaceutical [10],[11], organic light emitting diode [12], dopant in conductive polymer electrolyte [13], organic solar cells [14] and also as active sensing materials [15]. Referring to the previous literatures, thiourea derivatives have unique properties as single molecular organic materials that allows it to be versatile compounds and applied in above mentioned applications. The existence of diprotic donor group of thiourea derivatives make it able to act as good receptors for anion and other molecules detection [16]. In fact, the utilization of thiourea molecular backbone featuring π - conjugation system makes it as an excellent candidate to act as molecular wires by utilizing electronic properties that can be produced in-situ at the level of molecular framework [17],[18]. Indeed, the introduction of new materials with hybrid moieties containing acetylide ($C\equiv C$) and thiourea moieties are considerably interesting because they potentially combine the physical properties derived individually from the presence of both moieties. Therefore, the applications of these materials cover a wide range of electronic and optical functionalities, for instance, including as sensing elements. Previously, inorganic materials such as tin oxide [19], zinc oxide [20], and magnesium oxide [21] are commercially used as conductive active sensing materials which possess high sensitivity and good response in high operating temperatures. However, they are also associated with lack of reversibility and durability performances [22]. Nowadays, published reports on the use of single molecule of acetylide-thiourea as gas conductive sensing elements has brought these materials in competition with commercial metal oxide active sensing elements. Acetylide-thioureas have been reported to exhibit semiconductor properties with low energy band gap that have high sensitivity operated at room temperature towards carbon monoxide ($C\equiv O$) gas [23].

The presence of gases such as carbon dioxide (CO_2) is classified as one of the greenhouse gases that contributes to the global warming problems that are harmful to our environment which is considered severe threats to living beings [24]. Thus, a great interest in using gas sensors to detect and monitor the existence of carbon dioxide in atmosphere is crucial with a variety of carbon dioxide sensors that have been introduced for the determination of carbon dioxide concentration. Usually, the change in electrical responses when exposed to carbon dioxide is used as a method for carbon dioxide detection. The electrical responses such as electronic current or capacitance measurements in a resistivity-type and capacitance-type sensor play a key role in sensing CO_2 in which the physical signals such as currents may change when exposed to selected CO_2 analyte [25].

In addition, acetylide-thiourea derivative **TCN** with ethyl substitution consists of two reactive site which are carbonyl amide ($NH-C=O$) and acetylide ($C\equiv C$) making it different from other common thiourea derivatives. Acetylide-thiourea gets a lot of attention because the highly uniform formation and compactly adhered film on various metal substrates due to the presence of several functional groups with the ability to bind with metals (i.e. $C=O$, $C=S$, $C\equiv N$). A film with uniform thickness can be obtained easily via spin-coating technique. Besides, theoretical calculations was also carried out via density functional theory (DFT) based on the study of sensing ability of acetylide-thiourea for carbon dioxide (CO_2) gas to evaluate the sensing distance between reactive site and targeted analyte as well as their binding energy. Using theoretical simulations, acetylide-thiourea was found to be responsive to CO_2 via intermolecular hydrogen bonding sensing mechanism.

2. Experimental

Sonogashira cross-coupling reaction: Preparation of 4-aminophenylethynyl benzonitrile (CYT). The experimental procedure regarding to the synthesis of Sonogashira cross-coupling reaction as intermediate compound (CYT) was already reported in literatures [26]-[28]. However, some modifications in synthetic process using low Pd-catalyst loading (1 mmol %) was applied with high yield afforded. A mixture of iodoaniline (1 mmol), 4-ethynylbenzonitrile (1.5 mmol), $Pd(PPh_3)_2Cl_2$ (1 mmol %), copper(I) iodide (0.5 mmol %), triethylamine (1 mmol) as a base, and 30 mL of tetrahydrofuran (THF) as a solvent. The reaction was then put at reflux with continuous stirring for *ca.* 12 hours. The progress of the reaction was monitored via thin layer chromatography technique (TLC) (hexane: ethyl acetate). Once the reaction was adjudged completed, the mixture was filtered and the solvent was removed under low pressure. The crude obtained was

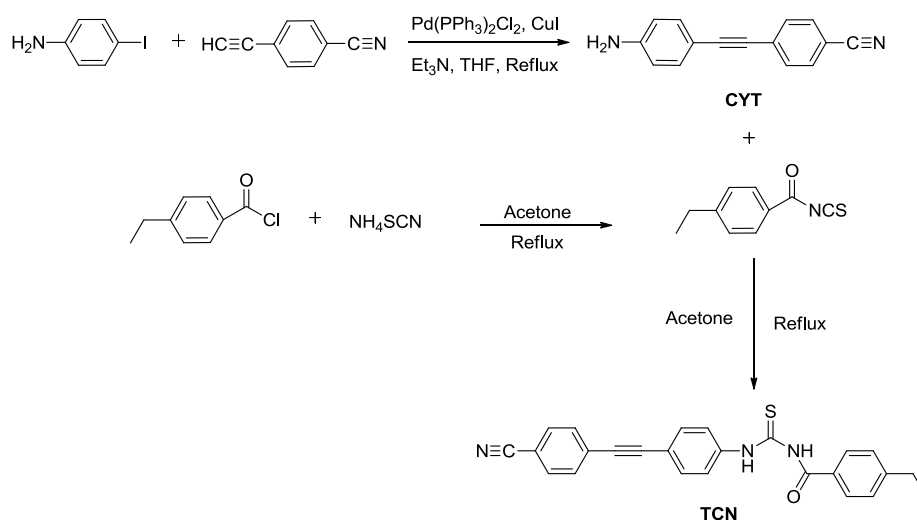


Figure. The Reaction Route for Synthesis of *N*-(4-[4-aminophenyl] ethynyl benzonitrile)-*N'*-(4-ethyl benzoyl)thiourea (TCN)

purified by flash column chromatography on silica gel to yield **CYT** with 95 % yield.

Synthesis of *N*-(4-[4-aminophenyl] ethynyl benzonitrile)-*N'*-(4-ethyl benzoyl)thiourea (TCN). General synthetic pathway to obtain **TCN** is as shown in Scheme 1. The intermediate 4-ethyl thiocyanate was obtained by the reaction between 4-ethylbenzoyl chloride and an equimolar ratio of ammonium thiocyanate in acetone. The progress of reaction was assessed by TLC (hexane: ethyl acetate). Later, the equimolar amount of 4-aminophenylethynyl benzonitrile (**CYT**) in acetone yield *N*-(4-[4-aminophenyl]ethynyl benzonitrile)-*N'*-(4-ethyl benzoyl) thiourea (**TCN**) was added as targeted compound. The obtained compound was the recrystallised from acetonitrile to produce white-off crystalline solid of **TCN** (80% yield).

Deposition of TCN onto interdigitated electrode (IDE). This part of studies was carried out in collaboration with MIMOS Berhad, Malaysia. Interdigitated electrode (IDE) with dimensions of 10 mm x 10 mm x 2 μm was fabricated with an excess amount of **TCN** as active materials in solution form using spin-coater and rotated at high speed at 3000 rpm for *ca.* 30 seconds. **TCN** was spread by centrifugal force to obtain the uniform thickness using annealing process at 90 $^{\circ}\text{C}$ for 5 minutes.

Conductivity measurement of TCN. The sample of **TCN** fabricated onto IDE was used for resistivity analysis using Impedance Analyzer HIOKI IM 3570 LCR Hi-tester with 100 kHz frequency. The sheet resistance (R_s) value was obtained and the conductivity of (σ) was calculated from Equation (1):

$$\sigma = 1/R_s \quad (1)$$

3. Results and Discussion

Spectroscopic and characterisation studies. The infrared spectrum of **TCN** indicated six important absorption bands namely $\nu(\text{N-H})$, $\nu(\text{C-N})$, $\nu(\text{C=O})$, $\nu(\text{C=S})$, $\nu(\text{C}\equiv\text{C})$, and $\nu(\text{C}\equiv\text{N})$. Strong absorption band of $\nu(\text{C=O})$ was assigned at 1669 cm^{-1} associated to the resonance effect of aromatic conjugation of benzoyl ring along with the existence of intramolecular hydrogen bonding with N-H moiety which have same arguments with previous reported literatures [29],[30]. Moreover, the presence of asymmetric and symmetric stretching vibrations of secondary thioamide $\nu(\text{N-H})$ is located at 3379 cm^{-1} [31], which examined to be above 3000 cm^{-1} due to the occurrence of intramolecular hydrogen bonding between carbonyl $\nu(\text{C=O})$ and thiol $\nu(\text{C=S})$ group. In addition, the overlapping band of $\nu(\text{C}\equiv\text{C})$ and $\nu(\text{C}\equiv\text{N})$ stretching vibration in **TCN** was observed at 2216 cm^{-1} with medium intensity. Whilst, stretching frequencies at 1341 cm^{-1} corresponds to vibration of $\nu(\text{C-N})$. Indeed, the most important functional group was observed for the existence of C=S band with medium intensity at 833 cm^{-1} [32] which located at low frequency due to the less double bond character with low nucleophilic character of the sulfur atom [33] in C=S moiety of **TCN**.

In ^1H NMR spectrum of **TCN**, the unresolved resonance of conjugated aromatic proton can be observed as multiplet at chemical shift between δ_{H} 7.37-7.85 ppm [34] arising from the overlapping proton signals of aromatic including pseudo-doublet system affected by para-substituted behaviour on aromatic moiety. In fact, there were two singlet resonances for amine protons (N-H), which located at two distinct environments at δ_{H} 9.09 and δ_{H} 12.86 ppm for the two consecutive amine (N-H) groups respectively resulting from intramolecular hydrogen bonding of N-H in both trans and cis-

conformers [35]. Additionally, the ^{13}C NMR spectrum for **TCN** exhibited important resonances of acetylide $\text{C}\equiv\text{C}$, which located at δ_{C} 88.2 and δ_{C} 93.2 ppm. However, the aromatic carbon resonances were observed in between δ_{C} 111.5 – 138.2 ppm attributed to the phenyl rings of **TCN**. Two resonances which were obtained at higher chemical shift were assigned for the carbon of $\text{C}=\text{O}$ and $\text{C}=\text{S}$ at δ_{C} 167.0 and δ_{C} 177.9 respectively caused by the intermolecular hydrogen bonding and existence of high electronegativity atoms of oxygen and sulfur [36].

Electronic properties

UV-Visible spectrum and frontier molecular orbital analysis of TCN. UV spectral analysis is essential in determining the transmittance and absorption of an active optical semiconductor material. The electronic spectrum of **TCN** was recorded in acetonitrile. The absorption spectrum for **TCN** comprises of mainly two major bands of interest. The first band occurred in the region of 285 nm ($\epsilon = 44,000 \text{ L mol}^{-1} \text{ cm}^{-1}$) which is attributed to $\pi\text{-}\pi^*$ transition which was assigned to arise from overlapping of phenyl ring and acetylide ($\text{C}\equiv\text{C}$) moieties, located at longer wavelength due to the effect of π -conjugation of acetylide derivatives. The second band assigned in the region of 326 nm ($\epsilon = 42,200 \text{ L mol}^{-1} \text{ cm}^{-1}$) due to the transition of $n\text{-}\pi^*$ for the occurrence of amine (N-H), carbonyl ($\text{C}=\text{O}$), and thione ($\text{C}=\text{S}$) moieties. Subsequently, the energy band gap (E_{g}) of **TCN** was calculated from the maximum absorption of UV-vis (λ_{max}) within range 200 – 500 nm by using equation as stated in Equation (1) [32], giving the E_{g} value for **TCN** was 3.80 eV. Therefore, **TCN** is classified as semiconductor material.

$$E_{\text{g}} = hc/\lambda \quad (2)$$

where h = plank constant; c = speed of light; λ = wavelength at absorption maximum

The uniqueness between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of a molecular system lead to the calculation of excitation energies and also provides the information about the chemical steadiness of **TCN** [37]. The HOMO is located throughout the molecule, where the interaction arose between HOMO and LUMO nominated by $\pi\text{-}\pi^*$. Theoretical investigation for HOMO-LUMO was carried out at TD-SCF B3LYP/6-31G (d,p) and its involved machinations are as shown in Figure 1. Therefore, the energy gap obtained was responsible for the electronic transition that exists within the molecule [38]. In this case, HOMO-1 and LUMO were involved in the electronic transition of **TCN**. The HOMO-1 energy obtained was -6.114 eV and the energy level for LUMO was -2.276 eV. Therefore, the calculated energy band gap HOMO (-1) - LUMO was

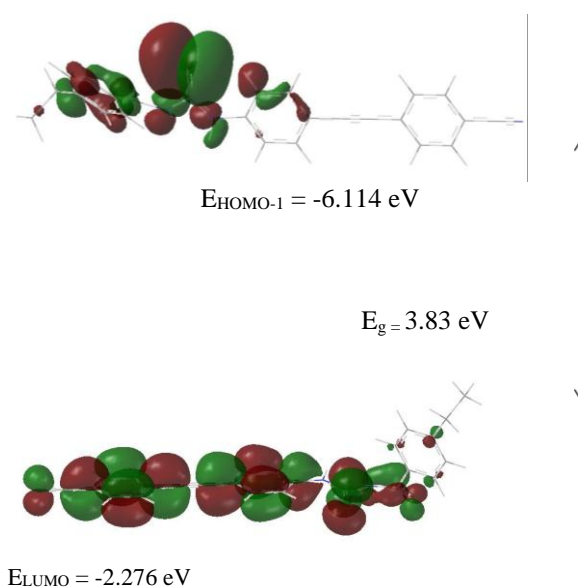


Figure 1. The Atomic Orbital Compositions of the Frontier Molecular Orbital of TCN Represent HOMO-1 and LUMO

3.83 eV which is almost in same argument with experimental result.

Conductivity studies. The sample of **TCN** fabricated onto IDE was used for conductivity analysis using the HIOKI3532-50 LCR Hi-tester, and the resultant resistivity (R) result was directly obtained from the LCR reading and applied for the conductivity calculation as in Equation 1 above, σ of **TCN** which was $3.66 \times 10^{-6} \text{ Scm}^{-1}$ with resistance value of 366235Ω from the sample at room temperature. In fact, the conductivity of each semiconductor materials depends on several factors such as ionic or electron concentration in the designed molecules, cationic or anionic types charge carries, and also the presence of suitable substitution of “push-pull” electron throughout molecules. The results can be observed that conductivity of **TCN** was within the range and in compliment with other thiourea derivatives [13],[39]. The presence of alkyl substitution and rigid structure of $\text{C}\equiv\text{C}$ made it an ideal electron donor in the system to enhance the rich electron density within the molecular framework system.

Optimized geometric parameters for carbon dioxide (CO_2) sensing by DFT methods. The optimization of **TCN**, CO_2 , and **TCN-CO₂** either at $\text{NH-C}=\text{O}$ or acetylide ($\text{C}\equiv\text{C}$) site was obtained for investigating the effect of analyte on geometric parameters such as bond length, and stabilization energy of the complexes (**TCN-CO₂**). The structures of optimized **TCN**, CO_2 bounded complexes (**TCN-CO₂** ($\text{NH-C}=\text{O}$) & **TCN-CO₂** ($\text{C}\equiv\text{C}$)) are illustrated in Figure 2 and 3. Geometric parameters such as bond length of **TCN-CO₂** are listed in Table 1 where the atomic labelling in the table is corresponding to Figure 2 and Figure 3.

The sensing response can be evaluated by investigating the extent of intermolecular distance between TCN and CO₂ analyte. The intermolecular distance between TCN and CO₂ at NH-C=O site ($d_{H29...O51}$) was about 2.14 Å. However, the intermolecular distance between TCN and CO₂ at acetylide (C≡C) site ($d_{H9...O51}$ & $d_{H19...O52}$) increased gradually to 2.6 Å, indicating decreased interaction of hydrogen bonding at C≡C site due to the

Table 1. Optimised geometric parameter (bond length, Å), for TCN-CO₂ (at NH-C=O site) and TCN-CO₂ (at C≡C site)

Species	TCN-CO ₂	
	at NH-C=O site $d_{H29...O51}$ (Å)	at C≡C site $d_{H9...O51}$ & $d_{H19...O52}$ (Å)
	2.14	2.56

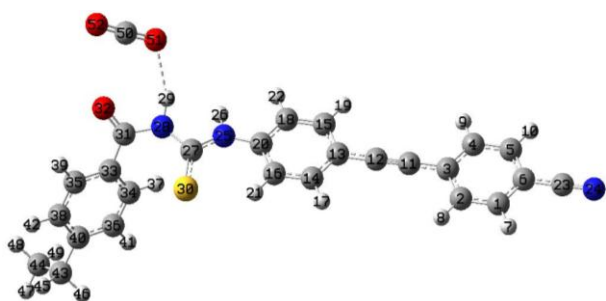


Figure 2. The Optimised Geometries of TCN and their Complexes with CO₂ at NH-C=O site

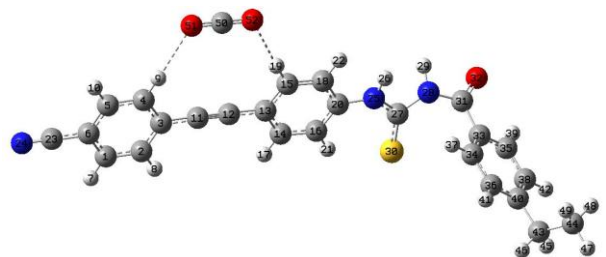


Figure 3. The Optimised Geometries of TCN and their Complexes with CO₂ at Acetylide Site

Table 2. Calculated stabilisation energy of TCN, CO₂, and TCN-CO₂ complexes at NH-C=O site and C≡C site

Species	SCF	SCF	SCF	Stabilisation energy (kJ/mol)
	energy of TCN (a.u.)	energy of CO ₂ (a.u.)	energy of TCN-CO ₂ (a.u.)	
TCN-CO ₂ (at NH-C=O site)	1601.655	188.264	1790.244	853.81
TCN-CO ₂ (at C≡C site)	1601.655	188.264	1790.238	839.03

low electropositive site of both hydrogen (H19 and H29). In addition, interaction energy analysis is a basic approach to evaluate the sensing ability and mechanism of individual substances that precisely predicts the strength of occurred interactive force between two species of TCN and CO₂ analyte was simulated using simple stabilisation energy calculations. All the calculated stabilisation energies of TCN and CO₂ complexes are as tabulated in Table 2. Stabilisation energy of TCN-CO₂ at NH-C=O site was 853.81 kJ/mol which was generally known to have hydrogen bonding interaction [40] between H...O of TCN and CO₂ due to the high obtained stabilisation energy. Whilst, the stabilisation energy was slightly decrease to 839 kJ/mol when the TCN interacted with CO₂ at acetylide region.

The results obtained can be considered reasonable for the sensing properties because the stabilisation energy was high and stable enough for H-bonding to occur which were caused by the electron fluctuating in the electron density of the interacting atoms which was suitable for sensing mechanism. Theoretical calculations show that single molecule of TCN with NH-C=O and C≡C moieties can interact with CO₂ due to the suitable electropositive and electronegative atoms of oxygen and hydrogen.

4. Conclusion

The new hybrid single molecule of acetylide-thiourea featuring TCN with potential to act as active materials in gas sensing technology has been successfully synthesised and characterised prior to be deposited onto interdigitated electrode (IDE) for detection of selected analyte (i.e. carbon dioxide). TCN exhibited semiconductor properties with energy band gap of 3.8 eV for both experimental and theoretical calculations. The conductivity value for TCN was about $3.66 \times 10^{-6} \text{ Scm}^{-1}$ possesses great ability to further developed as conductive single molecular material in detection any gases not only in the case of CO₂.

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