Synthesis and characterization of $N$-(4-Aminophenylethynylbenzonitrile)-$N'$-(1-naphthoyl)thiourea as single molecular chemosensor for carbon monoxide sensing

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This contribution reports on the design, preparation, and characterization of a novel acetylide-thiourea presenting $N$-(4-Aminophenylethynylbenzonitrile)-$N'$-(1-naphthoyl)thiourea (AETU) obtained from continuous reaction of intermediate compound 4[(4-aminophenyl)ethynyl benzonitrile] (AMEB) with 1-naphthoyl chloride prior to form an active substrate for the detection of carbon monoxide (CO). These compounds were then characterized via several spectroscopic and analytical methods, namely Fourier transform infrared spectroscopy, UV–visible spectroscopy, nuclear magnetic resonance ($^1$H and $^{13}$C NMR), carbon, hydrogen, nitrogen, and sulfur elemental analysis, and Thermogravimetric analysis. The performance of sensor response toward CO was measured using difference response in spectral features of UV–VIS spectrophotometry in thin-film studies with and without the presence of CO. The findings revealed that AETU possibly has an interaction with CO of concentrations 10, 20 and 30 ppm. In addition, quantum chemical calculations also proved that AETU exhibits potential sense interaction toward CO with stabilization energy $-6.30$ kJ/mol and interaction distance is about 3.14 Å. This proposed material sensor gives an ideal indication for application in the aspect of direct detection of CO in real sample and for development of single molecule gas sensor devices.

Keywords: acetylide; thiourea; chemosensor; thin-film; quantum chemical calculations

1. Introduction

Manufacturing industries have become the main economic source of growth in most developed countries nowadays.[1,2] The emission of various toxic gases from the industrial sectors
undoubtedly brings great effect of severe problems leading to air pollution toward the environment. Contributing to this issue is carbon monoxide (CO) gas which is one of the harmful and abundant contaminant in our environment that requires serious prevention and monitoring measures to ensure safety protection of public health.[3,4] In fact, CO is a non-irritating gas that is a product of incomplete combustion of carbon-containing fuels produced within industrial working areas and vehicle transportation. CO is classified as a harmful pollutant because of its ability to interfere with the mechanisms of oxygen transport and storage in living systems during the inhalation process.[5]

Therefore, the detection of toxic and combustible gases by simple and affordable-cost chemical sensors have gained a tremendous attention in recent years and many efforts are still working on the synthesis of novel sensing materials with enhanced performance.[6–10] For example, in the last few years, many research groups have been focusing their attention on the development of active materials for detection of CO whether as optical sensors, conductometric sensors, or nano-grained material sensors.[11–13]

Due to this concern with highly interest in developing single molecules as CO gas sensor, we are presenting a novel conjugated acetylide-thiourea featuring \( \text{N}-(4\text{-aminophenylethynylbenzonitrile})-\text{N}'-(1\text{-naphthoyl})\text{thiourea} \) (AETU) with the presence of some functional moieties such as conjugated double and triple bonds, with reactive carbonyl group (C=O), which is believed to have interaction with CO due to the differences in partial charges between carbon and oxygen of C=O moiety and CO.[14] This new acetylide-thiourea (AETU) derivative is chemically and thermally stable compared with the available commercial silicon-based sensors [15] and metal oxide semiconductor technology, which easily respond to the presence of CO pollution. Investigation on this practical gas sensor can be operated by direct spectroscopic measure of changes in optical properties of material both in solution and thin-films exposed to the selected analyte.[16,17]

In addition, this study also involved a contribution of molecular modeling by Gaussian 09 in order to correlate between experimental and theoretical results as well as synthesis, characterization, and examination of its potential to act as a single molecule CO gas sensor by looking at the difference in spectral features of UV–visible spectrophotometer before and after exposure toward CO. Figure 1 shows the molecular structure of AETU.

2. Results

2.1. Spectroscopic studies

The infrared spectrum of AMEB shows three bands of interest, including two bands for primary amine \( \nu(\text{NH}_2) \) located at 3468.43 and 3376.90 cm\(^{-1}\), and overlapping of both \( \nu(\text{C}≡\text{C}) \), and \( \nu(\text{C}≡\text{N}) \) at 2208.44 cm\(^{-1}\). The infrared spectrum of AETU shows six absorption bands, namely \( \nu(\text{N}≡\text{H}) \), \( \nu(\text{C}≡\text{N}) \), \( \nu(\text{C}≡\text{O}) \), \( \nu(\text{C}≡\text{S}) \), \( \nu(\text{C}≡\text{C}) \), and \( \nu(\text{C}≡\text{N}) \). Strong absorption band of \( \nu(\text{C}≡\text{O}) \) of AETU was located at 1671.42 cm\(^{-1}\) related to the resonance effect with the fused-aromatic and phenyl ring as well as the existence of intramolecular hydrogen bonding with N–H. The result is
in the same arguments with previous reported studies.\[18–20\] The band at 3220.02 cm\(^{-1}\) represents an asymmetric and symmetric stretching vibrations of \(\nu(N–H)\) in the secondary thioamide moiety. The assignment of NH above 3000 cm\(^{-1}\) has been examined to be the existence of intramolecular hydrogen bonding. The overlapping bands of \((C≡C)\) and \((C≡N)\) stretching vibrations in AETU occurred at 2215.55 cm\(^{-1}\) for the formation of acetylide and cyano moieties with strong intensity. Stretching frequencies at 1434.95 cm\(^{-1}\) correspond to \(\nu(C–N)\) and was assigned by comparing with other thiourea derivatives which should be presence at 1400–1000 cm\(^{-1}\).[21] In fact, the most crucial changes were observed for the presence of \(C=S\) stretching frequency at 760.82 cm\(^{-1}\). The frequency for \(\nu(C=S)\) was found to be indicated at low frequency due to less double bond character and the lower nucleophilic character of the sulfur atom in \(C=S\) moiety of AETU.

\(^1\)H NMR spectrum of AMEB shows obvious broad resonance regarding from intramolecular hydrogen bonding \[22\] at \(\delta_H 3.94\) ppm contributed by two protons of primary amine of amino group \((NH_2)\). The aromatic protons observed within range \(\delta_H 6.67–7.61\) ppm as pseudodoublet arising from the para-substituted in the aromatic rings. For AETU \(^1\)H NMR spectrum, the unresolved resonance of fused-aromatic protons clearly can be observed as multiplet resonances between \(\delta_H 7.56\) and 7.71 ppm due to the overlapping proton signals of the fused-aromatic system. Besides, aromatic protons of benzoyl moiety can be clearly seen in the range \(\delta_H 7.86–8.43\) ppm as the pseudo-doublet system which was influenced by the para-substituted on benzoyl moiety.

There are two singlet resonances for amine \((N–H)\) protons which can be observed at two different environments at \(\delta_H 9.15\) and \(\delta_H 12.83\) ppm, respectively, due to the presence of two consecutive amine \((N–H)\) groups resulting from intramolecular hydrogen bonding of \(N–H\) in trans and cis-conformation.[23] Indeed, the resonance for amine of \(N–H\) \((C=O)\) was observed at higher chemical shift than amine proton of \(N–H\) \((C=S)\) due to the deshielding effect and intramolecular hydrogen bonding.[24,25]

The \(^{13}\)C NMR spectrum for AETU shows resonances of acetylide carbons, \(C≡C\) which are located at \(\delta_C 88.3\) and 93.2 ppm. The resonance of carbon for cyano \(C≡N\) moiety is located at downfield region \(\delta_C 138.2\) ppm due to the attached nitrogen atom to cyano carbon. Meanwhile, the aromatic carbon resonances can be found in between \(\delta_C 111.5\) and 132.4 ppm attributed to the phenyl rings of AETU compound. Two resonances which are observed at \(\delta_C 169.2\) and 177.8 ppm are corresponded to carbon of \(C=O\) and \(C=S\). Both \(C=O\) and \(C=S\) resonances are slightly deshielded to higher chemical shift due to intramolecular hydrogen bonding formed in the compound and electronegativity effect attributed by oxygen and sulfur atoms.[26–28]

Electronic transition spectrum of AETU was recorded in acetonitrile solution in 1 cm\(^3\) cuvette with concentration \(1 \times 10^{-5}\) M and shows two principal bands which are believed arising from \(C=O\), \(C=S\), and phenyl moiety. The existence of overlapping \(C=O\) and \(C=S\) band can be observed at \(\lambda_{max} 321.50\) nm. The presence of electron withdrawing group \(C≡N\) also pronounced bathochromic shift on the \(n \rightarrow \pi^*\) and \(\pi \rightarrow \pi^*\) transitions with a broad band at \(\lambda_{max} 343.00\) nm as an effect of conjugation. The broad absorption band observed in the region at \(\lambda_{max} 321.50\) nm is due to \(\pi\)-conjugation of AETU with phenyl rings \((\pi \rightarrow \pi^*\) and \(n \rightarrow \pi^*)\) and orbital overlapping between \(C=O\) and \(C=S\) moieties.

### 2.2. Thermal stability analysis

Thermal stability of the material is the crucial part to be investigated for fabrication of gas sensor application. The thermal properties of the synthesized compounds AMEB and AETU were investigated by thermogravimetric analysis (TGA) at a heating rate of 10°C/min under nitrogen atmosphere (Figure 2). The thermogram observed revealed that there were no weight loss occurs
below 100°C which show that there were no trace of water molecules or solvents present in the synthesized compounds. It has found that the onset temperature of AMEB in which AMEB started to degrade is at 146°C with maximum degradation. The range decomposition of AMEB is small, in the range 146°C (onset) to 400°C (offset) in comparison with AETU that have two stages of degradation process show two stages of major weight lost in AETU. Afterwards, for AETU, the first degradation takes place at 212°C (onset) to 359°C with maximum degradation of 243°C. Second stage of degradation takes place at 542°C (onset) to 646°C (offset) with maximum degradation of 654°C. The total weight lost is about 92% over a range of 646°C. Results obtained revealed that AETU is the most stable in thermal based on its range of decomposition of its onset and offset temperature for first stage of degradation. This is due to the reason that AETU have high molecular weight compared with AMEB. Additionally, the higher stability of AETU may also relate to the presence of cyano moiety with high conjugated triple bond in the compound. Therefore, AETU needs high temperature and takes longer time to degrade itself due to their high molecular weight compounds. To conclude, AETU shows stability at high temperature compared with its precursor AMEB. Thus, final compound of AETU should give great potential for the application of gas sensor at high temperature.

2.3. Gas-sensing studies via UV–visible spectrophotometer

The AETU thin-film with 0.6 wt% plasticized polyvinyl chloride (PVC) was fabricated on glass substrate. In this experiment, the operating temperature of the sensor was fixed at room temperature (27°C). The AETU sensor was exposed to three different concentrations of CO which were 10, 20, and 30 ppm (each of the concentration was purchased commercially from standard commercial supplier). As seen from Figure 3, upon addition of the CO concentration, the maximum absorbance of AETU film was shifted to lower absorbance, showing the interaction of AETU thin-film and CO gas was happened. Figure 4 shows the graph of sensor response (sensitivity) of AETU toward 10, 20, and 30 ppm of CO gases. Results indicated that, AETU shows high sensitivity when exposed to lower CO concentration (10 ppm) with sensor response about 31%, followed by 25% (20 ppm), and 21% (30 ppm). Results obtained for sensing properties show that the sensor response of AETU sensor decreases with high CO concentration. This is because when the equilibrium between the gas phases diffused CO into AETU thin-film was obtained, no more variation of absorbance was observed. The signal will reach a saturation point when concentration of CO is high enough to occupy in AETU molecule. In fact, AETU containing electron withdrawing system with lack electron density to facilitate with $\pi$-molecular
orbital of CO, thus, due to increase CO concentration, saturation effect was occurred. The result obtained is in same arguments with previous literature.[6] In addition, for theoretical evaluation using Gaussian 09, the basic set used is DFT B3LYP 6-31G (d,p) in order to calculate the stabilization energy (kJ/mol) of complex between AETU+CO and the possible intermolecular distance occurred between interaction of AETU and CO. The stabilization energy of complex AETU + CO is about $-6.30 \text{kJ/mol}$ with possible intermolecular distance about 3.14 Å. Theoretical results revealed that single molecule of AETU with C=O moiety can interact with CO gas due to the high negative value of charge on oxygen atom ($-0.536$) and highly positive value of carbon atom ($+0.174$) on CO molecule. Figure 5 shows the predicted possible interaction between AETU and CO.
3. Conclusion

Highly sensitive determination of CO gas was accomplished by making the use of the novel thiourea derivatives with acetylide moiety embedded in PVC thin-film. The thin-film responded to CO at room temperature by observing the difference in spectral features before and upon interaction with CO. AETU thin-film responded to CO with high sensitivity of 31% toward low CO concentration of 10 ppm followed by 25% and 21% toward 20 ppm and 30 ppm, respectively. In fact, theoretical evaluation proved that AETU exhibits ideal interaction (−6.30 kJ/mol) of sensing ability with CO. In conclusion, novel approach involving the single molecular system featuring AETU exhibits great ability for CO sensing.

4. Experimental

4.1. Materials

All reagents, including solvents, and the materials were commercially purchased from various standard suppliers and used as received without further purification. In this present work, chemicals used, namely ammonium thiocyanate, 1-naphthoyl chloride, 4-ethynylbenzonitrile, palladium chloride (PdCl₂), triphenylphosphine, PVC (high molecular weight), sodium tetraphenyl borate, triphenyl phosphate, and sodium sulfate were purchased from Merck, Sigma-Aldrich, Acrós Organic, and R & M Chemical. Whilst all solvents used in this study such as acetone, chloroform, dichloromethane, diethyl ether, ethyl acetate, hexane, methanol, acetonitrile, and triethylamine were purchased from Merck, Sigma-Aldrich, and R&M Chemical. For gas-sensing studies, CO gas with concentrations 10, 20, and 30 ppm were purchased from Gas Sensor Sdn. Bhd., UKM-MTDC Technology Centre, Bangi, Selangor, Malaysia.

4.2. Characterization

Carbon, hydrogen, nitrogen, and sulfur (CHNS) microanalysis was carried out using a FLASHEA 1112 CHNS-analyzer for determination of percentage of CHNS elements presence in the synthesized compounds. IR spectra were recorded using FTIR Perkin-Elmer 100 spectrophotometer within spectral range 4000–450 cm⁻¹ with 4.00 cm⁻¹ resolution. Additionally, UV–VIS spectra of synthesized compounds were recorded using UV–VIS Spectrophotometer Shidmazu 1601 series in 1 cm³ cuvette using acetonitrile as a solvent with 1 × 10⁻⁵ M of sample concentration with light source change wavelength within range 364–295 nm. Moreover, thermogravimetric analysis was performed using Perkin-Elmer TGA analyzer from 0°C to 800°C at a heating rate of 10°C/min in the presence of constant nitrogen flow. NMR spectra were then recorded on Bruker Avance III 400 (¹H 400.11 MHz, ¹³C 100.61 MHz) using deuterated chloroform (CDCl₃) at room temperature to act both as solvent and internal standard within range δ₁H 0–15 ppm for ¹H NMR and δC 0–200 ppm for ¹³C NMR. Stuart Scientific Melting Point Apparatus SMP3 was used on determination of melting point for the synthesized compounds. Finally, ab initio quantum mechanical calculations were used to calculate stabilization energy, intermolecular distance of interaction between AETU and CO at minimum potential at the theoretical level of DFT B3LYP/6-31G (d,p).

4.3. Sonogashira cross – coupling reaction: 4[(4aminophenyl)ethynyl benzonitrile] (AMEB)

The experimental details with regard to the synthesis of intermediate (AMEB) is already reported in the literatures.[29,30] However, some modifications in the synthetic work-up and further
characterization on the spectroscopic and analytical tasks have been carried out and thoroughly
discussed in this report. The synthesis of AMEB preceded via Pd(PPh$_3$)$_2$Cl$_2$/CuI (0.005 mol%) catalyzed coupling of 4-iodoaniline (1 g, 4.56 mmol) with 2 equimolar phenylacetylene (1 g, 9.13 mmol). The reaction was put at reflux using water as solvent and triethylamine as base under ambient atmosphere for ca. 24 h forming two layers of solution. The organic phase was collected, dried over sodium sulfate, and was evaporated to dryness. The crude obtained was then purified via column chromatography eluting with a mixture of hexane and dichloromethane (7:3). Evaporation of the solvents afforded the product title AMEB as brown solid (70% yield). Scheme 1 shows the general synthetic work-up of all synthesized compounds in the study.

1H NMR (400.11 MHz, CDCl$_3$): $\delta$ 3.94 (s br, 2H, NH$_2$); 6.67 (pseudo-d, $^3$J$_{HH}$ = 9 Hz, 2H, C$_6$H$_4$); 7.38 (pseudo-d, $^3$J$_{HH}$ = 8 Hz, 2H, C$_6$H$_4$); 7.58 (pseudo-d, $^3$J$_{HH}$ = 8 Hz, 2H, C$_6$H$_4$); 7.61 (pseudo-d, $^3$J$_{HH}$ = 9 Hz, 2H, C$_6$H$_4$); 13C NMR (100.61 MHz, CDCl$_3$): $\delta$ 86.17 (s, C≡C); 95.10 (s, C≡C); 147.4 (s, C≡N); 110.6, 111.3, 114.7, 118.7, 129.0, 131.7, 131.9, 133.3 (8 s, Ar); Elemental analysis for C$_{15}$H$_{10}$N$_2$: [Found (Calcd.): C = 82.22 (82.55); H = 4.54 (4.62); N = 12.55 (12.84) %].

Scheme 1. General overview of synthetic work-up.

4.4. Synthesis of N-(4-aminophenylEthynylbenzonitrile)-N$'$-(1-naphthoyl) thiourea(AETU)

To a solution containing 2 g (10.49 mmol) of 1-naphthoyl chloride in 70 ml acetone, 1 equimolar amount of ammonium thiocyanate (0.97 g, 10.49 mmol) in 70 ml acetone was added. The reaction mixture was heated with constant stirring for ca. 4 h. After the reaction was adjudged completion, the reaction mixture was then filtered off. Then, a solution of 1 equimolar AMEB (2 g, 10.49 mmol) in 30 mL acetone was added dropwise to the resulting filtrate which was then put at reflux for another ca. 4 h. Afterward, the mixture was filtered into a beaker containing several ice cubes. The yellowish precipitate obtained was washed with little methanol and purified by recrystallization from acetonitrile to afford yellowish crystalline solids (64% yield). 1H
NMR (400.11 MHz, CDCl₃): δ 7.56–7.71 (m, 7H, naphthoyl); 7.86 (pseudo-d, 3J_HH = 7 Hz, 2H, C₆H₄); 7.91 (pseudo-d, 3J_HH = 8 Hz, 2H, C₆H₄); 7.96 (pseudo-d, 3J_HH = 7 Hz, 2H, C₆H₄); 8.43 (pseudo-d, 3J_HH = 8 Hz, 2H, C₆H₄); 9.15, 12.83 (2 × s, 1H, NH); 13C NMR (100.61 MHz, CDCl₃): δ 88.3 (s, C≡C); 93.2 (s, C≡C); 138.2 (s, C≡N); 111.5, 118.5, 120.4, 123.5, 124.5, 124.5, 126.4, 126.4, 127.1, 128.0, 128.3, 128.8, 129.8, 130.5, 132.4 (18 × s, Ar); 169.2 (s, C=O); 177.8 (s, C=S); Elemental analysis for C₂₇H₁₇N₃S: [Found (Calcd.): C = 75.74 (75.15); H = 3.76 (3.97); N = 9.97 (9.74); S = 7.23 (7.62) %].

4.5. Preparation of film substrate

The membrane solution was prepared by dissolving a mixture of 120 mg PVC, 1.5 mg sodium tetraphenyl borate, 240 mg plasticizer (tributylphosphate), and 1.6 mg AETU compound in 4 ml tetrahydrofuran (THF) with sample concentration 1 × 10⁻³ M. Then, the glass substrate (0.7 cm × 4 cm) was dipped into the resulting cocktails for about ca. 30 s. The polymer support, PVC, was used because of its optically transparent and exhibit good adhesion.[31] The obtained film then was kept in a vacuum desiccator to avoid any interference with air moisture. UV–VIS spectra of thin-film were recorded in quartz cells with and without exposure of CO gas.

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Supplemental data

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