



Aerobic synthetic approach and characterisation of some acetylide–thiourea derivatives for the detection of carbon monoxide (CO) gas



Adibah Izzati Daud^a, Wan M. Khairul^{a,*}, Hafiza Mohamed Zuki^b, K. Kubulat^a

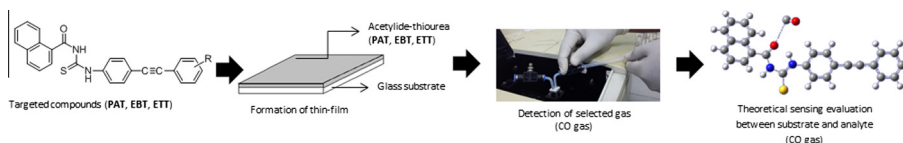
^a School of Fundamental Science, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia

^b School of Marine Science and Environment, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia

HIGHLIGHTS

- Novel derivatives of acetylide–thiourea have been synthesised and characterised.
- They are used as a single molecular sensor towards three concentration of CO gas.
- Thin film formations were deposited via dip-coating technique.
- These derivatives exhibit ideal interaction towards CO gas.
- Synthesised molecules exhibit van der Waals (non-bonding) interaction with CO.

GRAPHICAL ABSTRACT



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ABSTRACT

Novel acetylide–thiourea systems (**PAT**, **EBT**, and **ETT**), that possess both withdrawing and donating system properties were successfully synthesised with good yield (64–72%) and were characterised via several spectroscopic and analytical techniques. In turn, all synthesised derivatives were deposited onto glass substrates by dip-coating, and then their responses towards CO exposure were evaluated via UV–visible spectroscopy to identify their thin-film sensitivity towards CO. Theoretical studies using Gaussian 09 analysis were used to determine the relationship between the experimental and theoretical analyses of the molecules. The data revealed that acetylide–thiourea derivatives exhibit great potential for the detection of CO.

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Introduction

Gas sensors play a crucial role in detecting, monitoring, and controlling the presence of harmful gases in the atmosphere at very low concentrations. Environmental gas monitoring is currently recognised as an important area, in which intense research has been focusing on the development of suitable gas-sensitive materials for the continuous monitoring for the presence of harmful gases beyond the levels specified by Occupational Safety and Health regulations.

Among many different gases present in the atmosphere, carbon monoxide (CO) is classified as a harmful gas that is dangerous for human health, even at very low concentration, due to the ability of CO to interact with oxygen transport in our respiratory system [1–3]. Thus, it is necessary to detect the presence of CO with highly sensitive materials at a very low concentration for early prevention. These materials must be simple, small, low in cost to produce, and easy to fabricate into thin films. Conventionally, CO has been detected mostly by conductive polymer-based materials [4–6], metal-oxide derivatives [7,8,5], and carbon nano-tubes based materials [9–11], which used large instrumentation that requires high temperature and inert environment. Alternatively, single molecules can be employed as an active layer for sensing the

* Corresponding author.

E-mail address: wmkhairul@umt.edu.my (W.M. Khairul).

mechanisms for selected gases. The advantages of using single molecules are that they can act at room temperature in the ambient atmosphere, and they are easy to synthesise, fabricate, tune, and modify, thus, it is suitable for the analyte to be detected [12].

Due to the high level of interest in developing single molecules as CO gas sensors, we are introducing several novel systems of acetylide–thiourea derivatives, *N*-(4-phenylethynylaniline)-*N'*-(1-naphthoyl)thiourea (**PAT**), *N*-(4[4-aminophenyl]ethynylbenzotriazole)-*N'*-(1-naphthoyl)thiourea (**EBT**), and *N*-([4-aminophenyl]ethynyl toluene)-*N'*-(1-naphthoyl)thiourea (**ETT**), in the form of thin-films entrapped in a PVC matrix, as new materials for the detection of CO gas. For **EBT** and **ETT**, the synthesis and the ability of the compounds to detect CO have been reported by our group in previous occasions [13,44]. In this contribution, the comparisons in respect of performance between the other members of the system have been discussed in thorough. To date, there is an obvious loop of reports on the detection of CO based on chemical sensors using acetylide–thiourea derivatives. These acetylide–thiourea derivatives consist of both electron withdrawing and donating systems, that comprise the presence of a number of functional moieties such as conjugated double and triple bonds and a reactive carbonyl (C=O) group, which are believed to contribute an ideal interaction with CO. In this study, all of the synthesised materials were immobilised onto solid supports for application in optical sensing. The substrates were typically entrapped physically by absorption or chemically bonded to the solid support [14,15]. Poly(vinyl chloride) (PVC) was used for the preparation of membrane thin films due to its relatively low cost and ability to be plasticised [16].

For several decades, due to their capacity for electron transport that arises because they have rigid π -conjugated systems, thiourea, acetylide and their resonance structures have been widely studied individually in numerous applications [17,18], especially in molecular electronics [19,20]. Investigation on these practical gas sensors can be performed by direct spectroscopic measurements of the changes in the optical properties of materials in thin films exposed to the selected analyte (CO gas). In addition, this study also involves a combination of molecular modelling by Gaussian 09 software for density functional theory (DFT) calculations in terms of the stabilisation energy (kJ/mol) between the synthesised compounds and CO with the synthesis, characterisation, and investigation of their potential to act as single-molecule CO gas sensors, analysed by examining the differences in the spectral features of UV–visible spectrophotometer before and after exposure to CO. The newly developed optical sensors proposed, had shown significant absorbance signal changes upon exposure to CO gas with concentrations of 10, 20, and 30 ppm. Based on this study, a material that was highly sensitive to a low CO concentration and provided a rapid method for the detection of CO gas was developed with both experimental and theoretical results that were satisfactory. Fig. 1 depicts all molecular structures of interest synthesised in this study.

Results and discussion

Spectroscopic and characterisation studies

The infrared (IR) spectra of the synthesised materials (**PAT**, **EBT**, **ETT**) showed six absorption bands of interest, namely, ν (N–H), ν (C–H), ν (C=O), ν (C–N), ν (C \equiv C), and ν (C–O), ranging from weak to strong intensities. The band in the range of 3169–3220 cm^{-1} represented the asymmetric and symmetric stretching vibrations of ν (N–H) in the secondary thioamide moiety. The assignments of NH above 3000 cm^{-1} had been examined due to the existence of intramolecular hydrogen bonding [21–23]. The stretching frequencies observed in the range of 1405–1441 cm^{-1} corresponded

to ν (C–N) and were assigned by comparison with the spectra of other thiourea derivatives at 1400–1000 cm^{-1} [24]. Moreover, the ν (C \equiv C) stretching vibration in these compounds (**PAT** and **ETT**) occurred at 2214–2218 cm^{-1} as a medium-intensity peak. However, for **EBT**, there was an overlapping band with strong intensity observed between the C \equiv C and C \equiv N moieties at 2214 cm^{-1} . In fact, the strong absorption band for ν (C=O) in **PAT**, **EBT**, and **ETT** was distinguished at 1667–1672 cm^{-1} because of the resonance effect with the fused-aromatic and phenyl rings, as well as the existence of intramolecular hydrogen bonding with N–H. This result agrees with those of previously reported studies [25,26]. The most crucial changes were observed for the presence of the C=S stretching frequency at 741–760 cm^{-1} . The frequencies for ν (C=S) were found at low frequency due to the decreased double-bond character and the lower nucleophilic character of the sulphur atom in the C=S moiety of the synthesised materials [27,28].

The electronic-transition spectra of **PAT**, **EBT** and **ETT** were recorded in an acetonitrile solution obtained in a 1 cm path length quartz cell with concentration of 1×10^{-5} M, and they exhibited two principal bands that are believed to arise from the C=O, C=S, and phenyl moieties. The primary bands observed at λ_{max} 217–301 nm ($\epsilon = 44,760\text{--}74,080 \text{ M}^{-1} \text{ cm}^{-1}$) were assigned to the $\pi \rightarrow \pi^*$ transition of the aromatic moiety, which shifted strongly to lower wavelength with molar absorptivity, influenced by the inductive interaction between the fused aromatic (naphthoyl) and carbonyl group [29,30]. The existence of overlapping C=O and C=S bands can be observed at λ_{max} within the range of 305.00–321.50 nm. For **EBT**, the presence of the electron-withdrawing group C \equiv N also induced a pronounced bathochromic shift of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions with a broad band at λ_{max} 343 nm as an effect of the conjugation. The broad absorption band observed in the region at λ_{max} 305–321.50 nm was due to the π -conjugation of the synthesised materials with phenyl rings ($\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$) and the orbital overlap between the C=O and C=S moieties.

For the ^1H NMR spectra, the unresolved resonance of the fused-aromatic protons can be clearly observed as multiplet resonances between δ_{H} 7.38–7.87, ppm due to the overlapping proton signals of the fused-aromatic system. Additionally, the aromatic protons of the benzoyl moiety can be clearly seen in the range δ_{H} 7.21–8.43 ppm as a pseudo-doublet system that was influenced by the para-substituted benzoyl moiety. For **ETT**, there was a methyl ($-\text{CH}_3$) resonance at a chemical shift of δ_{H} 2.41 ppm on the aryl ring that was assigned as singlet resonance due to the effect from the neighbouring proton. There were two singlet resonances for amide (N–H) protons that can be observed in two different environments within the range of δ_{H} 9.09–9.15 ppm and δ_{H} 12.77–12.83 ppm, respectively, due to the presence of two consecutive amide (N–H) groups resulted from the intramolecular hydrogen bonding of N–H in the trans- and cis-conformation [31,32]. Indeed, the amide resonance of N–H (C=S) was observed at a higher chemical shift than the amide proton of N–H (C=O) due to the deshielding effect and intramolecular hydrogen bonding [33,34].

The ^{13}C NMR spectra for all of the synthesised derivatives showed resonances of acetylide carbons, C \equiv C, which were located at δ_{C} 88.2–88.8 ppm and 90.4–93.2 ppm. For **EBT**, the resonance of the carbon in the cyano C \equiv N moiety was located in the downfield region at δ_{C} 138.2 ppm due to the nitrogen atom attached to the cyano carbon. Additionally, the aromatic carbon resonances can be observed at δ_{C} 111.5–138.5 ppm and are attributed to the phenyl rings of the synthesised materials. Two resonances that were observed at δ_{C} 169.2 ppm and 177.7–177.8 ppm corresponded to the C=O and C=S carbons. Both the C=O and C=S resonances were slightly deshielded to a higher chemical shift due to the intramolecular hydrogen bonding formed in the compound and

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