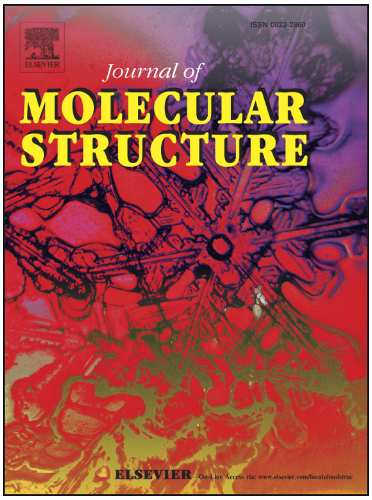

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Aerobic Synthetic Approach and Characterisation of Some Acetylide-thiourea Derivatives for the Detection of Carbon Monoxide (CO) Gas

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Running Tittle: Single Molecule for the Detection of Carbon Monoxide Gas

Keywords: Acetylide, Thiourea, Chemosensor, Gaussian

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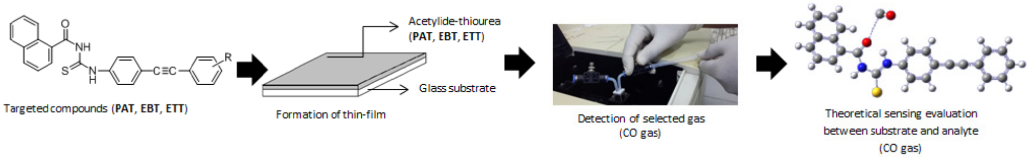
ABSTRACT

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.

Graphical Abstract:



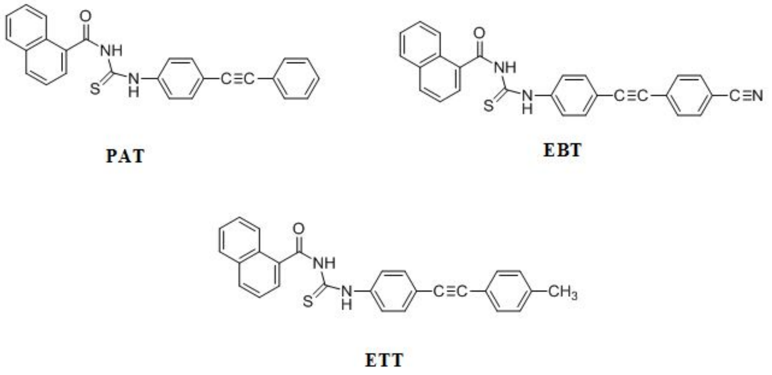
1. Introduction

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 [7-9], and carbon nano-tubes based materials [10-12], which used large instrumentation that requires high temperature and inert environment. Alternatively, single molecules can be employed as an active layer for sensing the 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 [13].

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]ethynlbenzonitrile)-*N*'-(1-naphthoyl)thiourea (**EBT**), and *N*-([4-aminophenyl]ethynl toluene)-*N*'-(1-naphthanoyl)thiourea (**ETT**), in the form of thin-films entrapped in a PVC matrix, as new materials for the detection of CO gas. For **EBT**, the synthesis and the ability of the compound to detect CO have been reported by our group in previous occasion [14]. 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 [15,16]. Poly(vinyl chloride) (PVC) was used for the preparation of membrane thin films due to its relatively low cost and ability to be plasticised [17].

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 [18,19], especially in molecular electronics [20,21]. 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 synthesise, 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. Figure 1 depicts all molecular structures of interest synthesised in this study.



PAT **EBT** **ETT**

Figure 1: The molecular structure of acetylide-thiourea derivatives (**PAT**, **EBT**, and **ETT**)

2.0 Results and discussion

2.1. 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≡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 [22-24]. 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} [25]. Moreover, the ν(C≡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≡C and C≡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 [26,27]. 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 [28,29].

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 x 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 (ε=44760-74080 M^{-1} 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 [30,31]. 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≡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 ^{1}H 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 ($-CH_3$) 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 [32,33]. 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 [34,35].

The ^{13}C NMR spectra for all of the synthesised derivatives showed resonances of acetylide carbons, C≡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≡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 the electronegativity contributed by the oxygen and sulphur atoms [36,37].

2.2 Thermal-stability analysis for the synthesised materials

The thermal stability of the material is the crucial factor to be investigated for fabrication for gas sensor applications. The thermal properties of the synthesised compounds were investigated by thermogravimetric analysis (TGA) at the heating rate of 283K/min under nitrogen atmosphere (Figure 2). The observed thermogram had revealed that no weight loss occurred below 373K, which showed that there were no trace of water molecules or solvents present in the synthesised compounds. It was observed that the onset temperature at which **PAT**, **EBT**, and **ETT** started to degrade was 473K-520K, with maximum degradation. Indeed, the range of decomposition of **EBT** is larger, with **EBT** starting to degrade at 520K (onset) with a large range of decomposition to 821K (offset) because **EBT** had a higher molecular weight than **PAT** and **ETT** and also because of the abundance of C≡N with highly conjugated bonds in the compound. Therefore, the synthesised thiourea derivatives exhibited stability at high temperature and should provide great potential for various fabrication methods at high temperature.

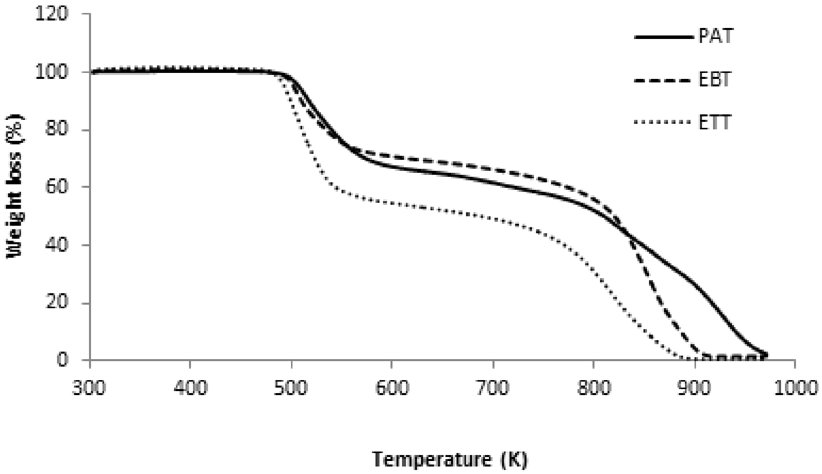


Figure 2: The thermogram of the synthesised compounds

2.3 Studies on the sensing of CO via UV-Vis spectroscopy

The **PAT**, **EBT**, and **ETT** sensors were investigated for three different carbon monoxide (CO) concentrations, which were 10, 20, and 30 ppm (each gas sample was purchased commercially from Gas Sensor Sdn. Bhd., Kuala Lumpur, Malaysia). The absorption spectra of the optical carbon monoxide gas sensor in the presence of increasing concentrations of CO with thin films were investigated in advance to determine the sensitivity of the film substrate for the detection of CO. Results from all of the absorption spectra revealed that significant changes occurred in the electronic transitions of the synthesised compounds (**PAT**, **EBT**, and **ETT**), which were studied as thin films, before and after exposure to various concentrations of CO (10, 20, and 30 ppm). From the spectra, it can be seen that absorption of **PAT**, **EBT**, and **ETT** with CO gas produced similar trends in the absorption spectra. There were two shifted bands that resulted from the electronic-transition changes of the HUMO and LUMO after the synthesised compounds had interacted with CO. However, obvious and most changes of absorbance can be observed within 1st band of wavelength range at λ_{max} = 256-258 nm. Therefore, λ_{max}=256 nm (**PAT**), λ_{max}=258 nm (**EBT**) and λ_{max}= 257 nm (**ETT**) were monitored to evaluate the response of the sensor to CO gas concentrations. The results revealed that, upon exposure to an increased CO concentration, the maximal absorbance of the film substrate decreased to a lower absorbance, showing that an interaction of the acetylide-thiourea film substrate with CO occurred.

The results obtained for the sensing properties show that the sensor response (sensitivity) of **PAT** and **EBT** featuring the electron-withdrawing substituents of the hydrogen (-H) and cyano (CN) moieties decreased with increased CO concentration. **PAT** exhibits the highest sensitivity, compared to **EBT** and **ETT**, to 10 ppm of CO with a 35.82% response, followed by 25.87% (20 ppm), and 13.93% (30 ppm), respectively. In contrast, **EBT** exhibited a 31.02% response to 10 ppm of CO, followed by 25.00% (20 ppm), and 21.30% (30 ppm). In fact, **PAT** and **EBT** feature electron-withdrawing substituents with a lack of electron density to facilitate interaction with the π-molecular orbital of CO [38,39], thus, due to the presence of a high CO concentration, a saturation effect occurred. This finding appears to be consistent with those reported by Tavoli and coworkers [40].

In contrast, **ETT** featuring electron-donating substituted exhibits a higher sensitivity to a high CO concentration with 55.26% for 30 ppm of CO, 25.44% for 20 ppm of CO and only 18.71% for 10 ppm of CO. The gas response of **ETT** increased linearly with no sign of saturation. This is because **ETT** with an electron-donating substituent has sufficient electron density to facilitate interaction with the π-molecular orbital of CO in the presence of a high CO concentration. Theoretically, CO is a well-known, strong pi-accepting molecule that is able to accept electron donation from **ETT** molecules to form an **ETT**-CO complex at a high CO concentration. Figure 3 illustrates the sensor response (sensitivity) bar chart of the film substrates (**PAT**, **EBT**, and **ETT**) to CO after exposure to various concentrations of CO (from 10 to 30 ppm).

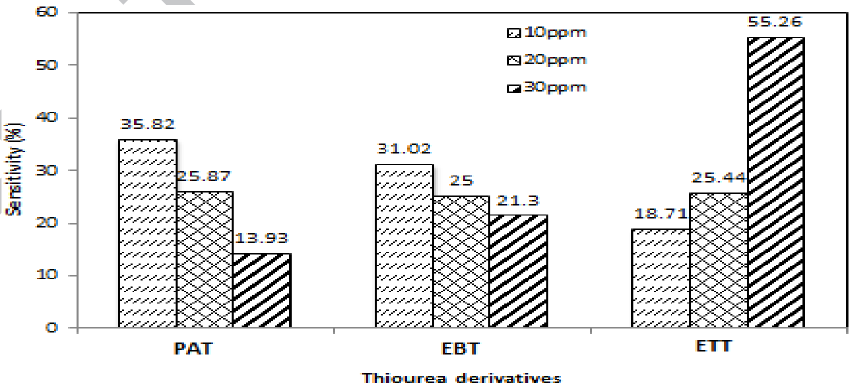


Figure 3: The bar chart of materials sensitivity towards 10, 20, and 30 ppm CO

2.4 Theoretical evaluation: Insight from density functional theory (DFT) calculations

The targeted acetylide-thiourea molecules, also known as free-sensor molecules, and the possible sensor-analyte complex with the CO molecule were optimised to the minimal potential energy using the Gaussian 09 quantum mechanical software package at the theoretical level of DFT (B3LYP)/6-31G (d,p). From the computational modelling studies, it was discovered that the various substituents of thiourea affect the stabilisation energy and the interaction distance of the sensor-analyte complexes.

Theoretically, to predict the possible interaction between **PAT**, **EBT**, and **ETT** with CO, the Mulliken charge values were measured. The Mulliken charges on the selected atoms of **PAT**, **EBT**, and **ETT**, as well as the possible interaction distances, are listed in Table 1. The analysis shows that all of the charges on the oxygen atom of the (C=O amide) were two times higher than those of the sulphur atom of (C=S) in the thiourea moiety. The values of the Mulliken charges of oxygen in the (C=O amide) were observed to be in the range of -0.533 to -0.537, compared to only approximately -0.247 to -0.256 for a sulphur atom. Due to the highly negative values of the charges on the oxygen atoms, we believe that the interactions that were formed between the acetylide-thiourea derivatives of **PAT**, **EBT**, and **ETT** with CO are able to interact at the oxygen atom of the (C=O amide). The presence of various substituents on the thiourea derivatives also affected the stabilisation energy of the interactions. The total electronic energies of the compounds and their stabilisation energies, along with the values for the individual thiourea and CO molecules are listed in Table 2.

Table 1: Mulliken effective charges on selected oxygen and sulfur of **PAT**, **EBT**, and **ETT** and the interaction distance between CO and C=O

Compound	Mulliken charges		Calculated distance between CO and C=O, (Å)
	O (C=O)	S (C=S)	
PAT	-0.533	-0.255	3.14
EBT	-0.536	-0.247	3.14
ETT	-0.537	-0.256	3.14

Note: Mulliken charge of C (C=O) = +0.174

The results show that, of the three complexes, **PAT** was the most sensitive material to CO, with the value -6.56 kJ/mol, followed by **ETT** (-6.54 kJ/mol) and **EBT** (-6.30 kJ/mol). All of the complexes were stabilised by van der Waals bonds (non-bonding interaction), which were caused by the quantum mechanical fluctuating in the electron density of the interacting atoms. The binding that occurred was realised by the electrostatic interaction between the delocalised conducting electrons and the positive ions localised within the compounds. The expected results obtained were in accordance with **PAT>ETT>EBT** at an equimolar concentration of the free-sensor molecule and CO. In summary, from these theoretical evaluations, the interaction of **PAT**, **EBT**, and **ETT** with CO is possible with significant interaction distance and stabilisation energy of the complexes (**PAT/ EBT /ETT** + CO).

Table 2: SCF energy of sensor-analyte complexes, CO, and acetylide-thiourea (**PAT**, **EBT**, and **ETT**) during their interaction and stabilisation with CO

Compound	SCF energy, a.u. (complex)	SCF energy, a.u. (CO)	SCF energy, a.u. (acetylide-thiourea)	Stabilization energy, (kJ/mol)
PAT	-1697.8665	-113.3095	-1584.5545	-6.56 [1]
EBT	-1790.1083	-113.3095	-1676.7964	-6.30 [3]
ETT	-1737.1874	-113.3095	-1623.8754	-6.54 [2]

3. Conclusion

These new acetylide-thiourea materials (**PAT**, **EBT**, and **ETT**) that were highly sensitive for the determination of carbon monoxide (CO) had been successfully synthesised and characterised prior to forming active film substrates entrapped in a PVC matrix for the detection of CO gas. The response of the film substrates to CO at room temperature was observed using the difference in the spectral features prior to and upon interaction with CO. The **PAT** and **EBT** film substrates exhibited good sensitivity to low CO concentrations of 10 and 20 ppm and possessed low sensitivity to a high CO concentration of 30 ppm. Although **ETT** exhibited good sensitivity to a high CO concentration of 30 ppm, it gave low responses with lower CO concentrations of 10 and 20 ppm. The differences in the sensor performances of these newly synthesised derivatives were influenced by the materials' molecular system behaviour. In fact, the theoretical analysis proved that **PAT**, **EBT**, and **ETT** exhibited ideal interaction energies (-6.30 kJ/mol to -6.56 kJ/mol) for sensing CO. In conclusion, a novel approach involving a single-molecular acetylide-thiourea system (**PAT**, **EBT**, and **ETT**) exhibited promising ability and potential for carbon monoxide sensing.

4. Experimental

4.1 Reagents

All reagents, including solvents, chemicals and materials, were commercially purchased from various standard suppliers and used as received without further purification. Most of the chemicals used, namely, ammonium thiocyanate, 1-naphthoyl chloride, 4-ethynylbenzonitrile, palladium chloride ($PdCl_2$), triphenylphosphine, polyvinyl chloride, sodium tetraphenyl borate, triphenyl phosphate, and sodium sulphate, were purchased from Merck, Sigma-Aldrich, Acrós Organics, and R & M Chemical. The catalyst, $Pd(PPh_3)_2Cl_2$ was prepared by literature method [41]. 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 the gas-sensing studies, carbon monoxide (CO) gas with concentrations of 10, 20, and 30 ppm was purchased from Gas Sensor Sdn. Bhd., UKM-MTDC Technology Centre, Bangi, Selangor, Malaysia.

4.2 Characterisation

CHNS microanalysis was performed using a FLASHEA 1112 CHNS analyser for determination of the percentage of CHNS elements present in the synthesised compounds. IR spectra were recorded using a Perkin Elmer 100 FTIR spectrophotometer within the spectral range 4000 to 450 cm^{-1}. Additionally, the UV-Vis spectra of the synthesised compounds were recorded using a Shidmazu 1601 series UV-Vis spectrophotometer in 1 cm path length quartz cell with acetonitrile as solvent and sample concentration of 1×10^{-5} M. Thermogravimetric analysis was performed using a Perkin-Elmer TGA analyser from 273-1073K at a heating rate of 283K/min in the presence of a constant nitrogen flow. NMR spectra were recorded on Bruker Avance III 400 (^1H 400.11 MHz, ^{13}C 100.61 MHz) using deuterated chloroform ($CDCl_3$) at room temperature acting as the solvent and an internal standard within the ranges δ_H 0-15 ppm for ^1H NMR and δ_C 0-200 ppm for ^{13}C NMR. Finally, the ab initio quantum mechanical software package of Gaussian 09 was used to calculate the stabilisation energy and the intermolecular distance of the interaction between the synthesised compounds and carbon monoxide at a minimum potential at the theoretical level of DFT B3LYP/6-31G (d,p).

*4.3 Sonogashira cross-coupling reaction: Preparation of the precursors (**PHE, AEB, AET**)*

*4.3.1 Synthesis of 4-phenylethynylaniline (**PHE**)*

The experimental details with regard to the synthesise of the precursors (**PHE**, **AEB**, and **AET**) had already been reported in the previous literature [42,43,14]. However, several modifications in the synthetic work-up were made, improved and discussed in this report. The synthesis of **PHE** proceeded via $Pd(PPh_3)_2Cl_2$/CuI (5 mmol%)-catalysed coupling of 4-iodoaniline (1 g, 4.56 mmol) with two molar equivalents of phenylacetylene (1 g, 9.13 mmol). The reaction was refluxed using water as the solvent and triethylamine as a base under ambient atmosphere for *ca.* 24 hours, forming two layers of solution. The organic phase was collected, dried over sodium sulphate, and evaporated to dryness. The crude product obtained was then purified via column chromatography, eluted with a mixture of hexane and dichloromethane (7:3). Evaporation of the solvents afforded the product **PHE** as a brown solid (70% yield). ^{1}H NMR (400.11 MHz, $CDCl_3$): δ 3.83 (s br, 2H, NH_2); 6.67 (pseudo-d, J_{HH}=9 Hz, 2H, C_6H_4); 7.52 (pseudo-d, J_{HH}= 9Hz, 2H, C_6H_4); 7.29-7.39 (m, 5H, C_6H_5);^{13}C NMR (100.61 MHz, $CDCl_3$): δ 87.3, 90.1 (2 x s, 2 x C C); 112.6, 114.7, 123.9, 127.6, 128.2, 131.3, 132.9, 146.6 (8 x s, Ar); Elemental analysis for $C_{15}H_{10}N_2$: [Found (Calcd.): C = 86.51 (87.01); H = 5.53 (5.74); N = 7.24 (7.25).

*4.3.2 Synthesis of 4[(4-aminophenyl)ethynylbenzonitrile](**AEB**)*

The yellow solid of the compound **AEB** (0.7 g, 70%) was prepared from 4-iodoaniline (1 g, 4.56 mmol), 4-ethynylbenzonitrile (1.16 g, 9.13 mmol), and the palladium catalyst $Pd(PPh_3)_2Cl_2$, using copper iodide (5 mmol%) as a co-catalyst in the same manner as for **PHE**. ^{1}H NMR (400.11 MHz, $CDCl_3$): δ 3.94 (s br, 2H, NH_2); 6.67 (pseudo-d, J_{HH}=9 Hz, 2H, C_6H_4); 7.38 (pseudo-d, J_{HH}= 8Hz, 2H, C_6H_4); 7.58 (pseudo-d, J_{HH}=8 Hz, 2H, C_6H_4); 7.61 (pseudo-d, J_{HH}=9 Hz, 2H, C_6H_4);^{13}C NMR (100.61 MHz, $CDCl_3$): δ 86.1, 95.1 (2 x s, 2 x C C); 147.4 (s, C N); 110.6, 111.3, 114.7, 118.7, 129.0, 131.7, 131.9, 133.3 (8 x 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).

*4.3.3 Synthesis of 4[(4-aminophenyl)ethynyltoulene](**AET**)*

The pale-brown solid of the compound **AET** (0.85 g, 89%) was prepared from 4-iodoaniline (1 g, 4.56 mmol), 4-ethynyltoluene (1.06 g, 9.13 mmol), and the palladium catalyst $Pd(PPh_3)_2Cl_2$, using copper iodide (5 mmol%) as a co-catalyst in the same manner as for **PHE**. ^1H NMR (400.11 MHz, $CDCl_3$): δ 2.39 (s, 3H, CH_3); 3.83 (s br, 2H, NH_2); 6.66 (pseudo-d, J_{HH}=8 Hz, 2H, C_6H_4); 7.17 (pseudo-d, J_{HH}= 8Hz, 2H, C_6H_4); 7.35 (pseudo-d, J_{HH}=9 Hz, 2H, C_6H_4); 7.36 (pseudo-d, J_{HH}=9 Hz, 2H, C_6H_4);^{13}C NMR (100.61 MHz, $CDCl_3$): δ 87.4, 89.3 (2 x s, 2 x C C); 21.4 (s, CH_3); 112.8, 114.7, 120.8, 129.0, 131.2, 132.9, 137.7, 146.5 (8 x s, Ar); Elemental analysis for $C_{15}H_{10}N_2$: [Found (Calcd.): C = 86.19 (86.92); H = 6.13 (6.32); N = 6.73 (6.76).

*4.4 Synthesis of N-(4-phenylethynylaniline)-N'-(1-naphthoyl)thiourea (**PAT**)*

The general synthetic pathway to produce **PAT** is as shown in Scheme 1. The intermediate 1-naphthoyl thiocyanate was produced by the reaction between 1-naphthoyl chloride and an equimolar amount of ammonium thiocyanate in acetone. The reaction progress was monitored by TLC (hexane:CH_2Cl_2:3:2). Treatment of the latter with an equimolar amount of **PHE** in acetone produced *N*-(4-phenylethynylaniline)-*N*'-(1-naphthoyl)thiourea (**PAT**) as the targeted product. The product was then recrystallised from acetonitrile, yielding the yellow crystalline solid of **PAT** (70% yield) in a needle-like shape. ^1H NMR (400.11 MHz, $CDCl_3$): δ 7.38-7.39 (m, 3H, C_6H_5); 7.56-7.77 (m, 7H, naphthoyl); 7.88 (pseudo-d, J_{HH}=7 Hz, 2H, C_6H_4); 8.09 (pseudo-d, J_{HH}=8 Hz, 2H, C_6H_4); 8.11 (pseudo-d, J_{HH}=8 Hz, 1H, C_6H_4); 8.43 (pseudo-d, J_{HH}=8 Hz, 1H, C_6H_4); 9.10, 12.78 (2 x s, 1H, NH); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 88.8, 90.0 (2 x s, 2 x C≡C); 121.6, 123.1, 123.4, 124.5, 126.4, 127.1, 128.3, 130.6, 131.6, 132.2, 133.3, 133.8, 137.4 (18 x s, Ar); 169.2 (s, C=O); 177.8 (s, C=S); Elemental analysis for

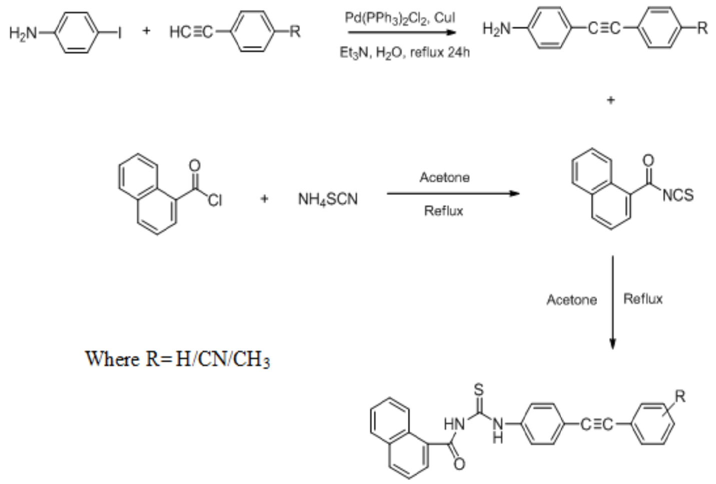
$C_{27}H_{17}N_3S$: [Found (Calcd.): C = 77.13 (76.82); H = 4.30 (4.46); N = 7.17 (6.89); S = 8.13 (7.89).

*4.5 Synthesis of N-(4[4-aminophenyl]ethynylbenzonitrile)-N'-(1-naphthoyl)thiourea (**EBT**)*

Yielding pale-yellow single crystals (64% yield) in a rectangular-like shape, **EBT** was prepared from 1-naphthoyl chloride (2 g, 10.49 mmol), ammonium thiocyanate (0.79 g, 10.49 mmol), and 4[(4-aminophenyl)ethynylbenzonitrile] (2.29 g,10.49 mmol) in same manner as reported by Daud *et al*., 2014 [14]. ^{1}H NMR (400.11 MHz, $CDCl_3$): δ 7.56-7.71 (m, 7H, naphthoyl); 7.86 (pseudo-d, J_{HH}=7 Hz, 2H, C_6H_4); 7.91 (pseudo-d, J_{HH}=8 Hz, 2H, C_6H_4); 7.96 (pseudo-d, J_{HH}=7 Hz, 2H, C_6H_4); 8.43 (pseudo-d, J_{HH}=8 Hz, 2H, C_6H_4); 9.15, 12.83 (2 x s, 1H, NH); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 88.3, 93.2 (2 x s, 2 x 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 x s, Ar); 169.2 (s, C=O); 177.8 (s, C=S); Elemental analysis for $C_{27}H_{17}N_3S$: [Found (Calcd.): C = 75.74 (75.15); H = 3.76 (3.97); N = 9.97 (9.74); S = 7.23 (7.62).

*4.6 Synthesis of N-([4-aminophenyl]ethynyltoluene)-N'-(1-naphthoyl)thiourea (**ETT**)*

Yielding pale-yellow single crystals (72% yield) in a needle-like shape, **ETT** was prepared from 1-naphthanoyl chloride (2 g, 10.49 mmol), ammonium thiocyanate (0.79 g, 10.49 mmol), and 4(4-aminophenyl)ethynyltoluene, (2.17 g, 10.49 mmol) in the same manner as for **PAT**. ^{1}H NMR (400.11 MHz, $CDCl_3$): δ 2.41 (s, 3H, CH_3); 7.21 (pseudo-d, J_{HH}= 8 Hz, 2H, C_6H_4); 7.56 (pseudo-d, J_{HH}=7 Hz, 2H, C_6H_4); 7.63-7.87 (m, 7H, naphthoyl); 7.98 (pseudo-d, J_{HH}=8 Hz, 1H, C_6H_4); 8.11 (pseudo-d, J_{HH}=8 Hz, 1H, C_6H_4); 8.43 (pseudo-d, J_{HH}=8 Hz, 2H, C_6H_4); 9.09, 12.77 (2 x s, 1H, NH); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 21.5 (s, CH_3); 88.2, 90.2 (2 x s, 2 x C≡C); 120.0, 121.8, 123.4, 124.5, 124.6, 126.4, 127.1, 128.2, 128.8, 129.1, 129.8, 130.6, 131.5, 132.1, 133.2, 133.8, 137.2, 138.5 (18 x s, Ar); 169.2 (s, C=O); 177.7 (s, C=S); Elemental analysis for $C_{27}H_{17}N_3S$: [Found (Calcd.): C = 77.00 (77.12); H = 4.67 (4.79); N = 6.86 (6.66); S = 7.25 (7.62).



Scheme 1: General overview of synthetic work-up

4.7 Preparation of the polymer-film substrate

The film precursor solution was prepared by dissolving a mixture of 120 mg of polyvinylchloride (PVC), 240 mg of the plasticiser tributyl phosphate (TBP), 1.5 mg of sodium tetraphenyl borate and 1.6 mg of acetylide-thiourea (**PAT**, **EBT**, **ETT**) in 4 ml of dried tetrahydrofuran (THF) in a glass vial. The solution was stirred for *ca.* six hours to achieve complete homogeneity. The prepared precursor solution contained a ratio of 33% PVC: 66% plasticisers by weight (1:2), which is in accordance with the literature [44,14]. The solution was then spread onto a glass substrate by dip-coating. The films obtained were stored in a desiccator to avoid undesirable reaction with any gases/pollutants in the ambient air. The absorption spectra of the thin film before and after exposure to CO were recorded in closed, designated quartz cells. All the experiments were performed at room temperature under aerobic environment.

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Highlights:

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