

Organic Semiconductor Material Featuring 4-Ethylbenzoyl-3-(4-ethynylbenzotrile-phenyl)-thiourea (CYT-1) of Donor- π -acceptor for Chemiresistive Carbon Dioxide (CO₂) Sensing

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ABSTRACT: *In this work, a new member of acetylide-thiourea namely 4-ethylbenzoyl-3-(4-ethynylbenzotrile-phenyl)-thiourea (CYT-1) was successfully designed, synthesised, and characterised by nuclear magnetic resonance (NMR) analysis. In turn, CYT-1 acting as sensor was fabricated onto interdigitated electrodes (IDEs) by drop-casting method. The performance of CYT-1 on reaction response and sensitivity characteristics towards carbon dioxide (CO₂) as chosen gas was measured at different CO₂ concentration (10–1000 ppm) for 30 min of time exposure. The investigation was carried out at room temperature via studying the changes in resistivity measurement before and upon CO₂ exposure. The unique molecular characteristic of CYT-1 is due to the presence of two potential active sites of –NH-C=O and acetylide -C≡C- for H-bonding and π - π interaction to take place between molecule and CO₂ analyte.*

Keywords: Acetylide-thiourea, spectroscopic, organic semiconductor, CO₂ gas sensor, resistivity

1. INTRODUCTION

Carbon dioxide (CO₂) is one of the dominant greenhouse gas emissions which takes up around 77% of total gas in air.¹ The most comprehensive research conducted stated that a safe level of CO₂ concentration in a closed environment should not exceed 350 ppm.² A concern on global warming has motivated researchers to conduct intense research in the aspects of sense, capture and CO₂ storage.^{3,4} Conventionally, active sensing materials that are commercially used nowadays are based on inorganic and conductive polymeric materials, with ideal sensitivity at high operating temperatures.⁵⁻⁹ However, the disadvantages of these readily available materials are that they exhibit low ability of reversibility, less stability performances, and highly sensitive in ambient atmosphere.¹⁰ Hence, in the present work, a new derivative of acetylide-thiourea featuring 4-ethylbenzoyl-3-(4-ethynylbenzonitrile-phenyl)-thiourea (CYT-1) as illustrated in Figure 1 becomes an ideal molecular candidate to act as semiconductor molecular system in the implementation of fundamental importance of the interaction with CO₂ at highly stable response. It also works at ambient atmosphere with high reversibility performance.

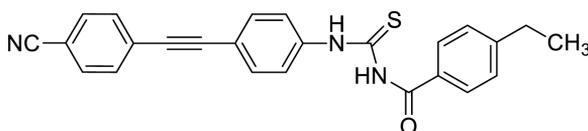


Figure 1: The general molecular structure of CYT-1 so called CO₂ sensor.

The derivative of CYT-1 is having two reactive sites of carbonyl amide (-NH-C=O) and acetylide (C≡C) regions which make it distinctive from other typical thiourea derivatives. By observing its molecular framework, CYT-1 has gained much importance due to the presence of electron withdrawing group, cyano (CN) which has the ability to form highly uniform and compactly adhered film on interdigitated electrodes (IDEs). In this contribution, we discuss the resistive-type semiconductor properties based study on sensing ability of CYT-1 towards CO₂ gas. CYT-1 is modelled for CO₂ gas sensing and our findings reveal that CYT-1 gave high sensitivity towards high CO₂ concentration (1000 ppm) with 25.8%.

2. EXPERIMENTAL

2.1 Synthesis of 4-Ethylbenzoyl-3-(4-ethynylbenzonitrile-phenyl) Thiourea (CYT-1)

A 4-ethylbenzoyl chloride solution (2.29 mmol) was slowly added into ammonium thiocyanate (2.29 mmol) solution in 15 ml acetone. The reaction mixture was

stirred for 10 min to give pale yellow solution in presence of white precipitate of ammonium chloride. Then, a solution of equimolar 4[(4-aminophenyl) ethynylbenzonitrile] in 10 ml acetone was added dropwise into the reaction mixture and continuously put at reflux for another 8 h. The colour of the solution changed to bright yellow. The reaction was adjudged completion via thin layer chromatography (TLC) (hexane:ethylacetate:4:1). Yellow precipitate was formed once the solution mixture was poured into several small ice blocks. The obtained precipitate was filtered, washed with little cold water, and recrystallised from acetonitrile to yield yellowish crystalline solids of CYT-1 (0.6 g, 67% yield).

2.2 CO₂ Gas Sensing System

The gas sensing evaluation was performed in a tightly enclosed stainless steel chamber to achieve controllable inert, temperature, and humidity conditions during experimental tasks. The fabricated gas sensing electrode with 100 μm thickness of layered CYT-1 on IDEs was placed (hanging) inside the chamber near the gas inlet valve in a highly pure, nitrogenous environment with a controlled humidity between 65–70% RH for 1–2 h to equilibrate the chamber environment. The gas flow rate was controlled by a gas flow meter. The changes in resistivity of the electrode before and after exposure with CO₂ gas were recorded using HIOKI IM3570-LCR-Hi tester analyser at constant voltage of 1 V. Nitrogen gas was purged over sensing module after every exposure cycle. The changes in resistivity measurement of the sensing material, CYT-1 successive to exposure with gas were evaluated by the formula as stated in Equation 1:

$$S = \frac{R_g - R_a}{R_a} \times 100\% \quad (1)$$

where R_g is the responsive resistivity of the sensing material upon exposure with CO₂ gas and R_a is the responsive resistivity of the sensing material without CO₂ in the high purity of nitrogen gas flow. Response time (τ_{res}) and recovery time (τ_{rec}) were evaluated as time required for 90% of maximum response of CYT-1 with CO₂ gas, and time needed for recovering 90% of the original resistivity in the inert environment respectively.

3. RESULTS AND DISCUSSION

3.1 Spectroscopic and Characterisation of CYT-1

For structural elucidation, both ¹H and ¹³C NMR spectra of CYT-1 are consistent with the proposed molecular structure. Two singlet proton resonances were

deshielded at two distinctive environments δ_H 9.09 ppm and δ_H 12.86 ppm respectively, in which they were assigned for NH-C=O and NH-C=S moieties due to the anisotropic effect and intramolecular hydrogen bonding in the *trans-cis* conformation. The resonance presence in the range of δ_H 7.37–7.85 ppm was attributed to aromatic protons. Besides, a shielded triplet resonances at δ_H 1.29 ppm was assigned for methyl (CH₃). Whilst a quartet resonances at δ_H 2.75 ppm was due to the presence of ethyl (CH₂) substituted at the aromatic ring. For ¹³C NMR spectrum of CYT-1, it revealed shielded resonance of methyl (CH₃) carbon located at δ_C 15.1 ppm and ethyl (CH₂) carbon at δ_C 28.9 ppm. There were two different carbon resonances at δ_C 88.2 ppm and δ_C 93.3 ppm attributed to acetylide carbons (C≡C). Additionally, the resonance of carbon cyano (C≡N) was located in the deshielded region at δ_C 151.2 ppm arising from the electronegative nitrogen atom delocalised π -orbital attached to the C≡N carbon. Aromatic carbons were found to resonate in the region δ_C 111.5–138.3 ppm. Two distinctive resonances at downfield region located at δ_C 167.0 ppm and δ_C 177.9 ppm corresponded to the presence of C=O and C=S moieties. Both C=O and C=S resonances were deshielded at higher chemical shift due to the effect of intramolecular hydrogen bonding and electronegativity of S and O atoms.¹¹

3.2 Evaluation of CO₂ Sensing Performance

The dynamic response of the gas sensor and its sensitivity for different concentrations of CO₂ gas at room temperature have been carried out with an applied bias of 1 V as shown in Figure 2. The designing principle for this sensor was to exploit the chemical interaction of CO₂ with the amide moiety (NH-C=O; NH-C=S) as well as acetylide –C≡C– functional groups that present in CYT-1 which in turn changed the signal resistivity before and upon exposure with CO₂. CYT-1 based CO₂ gas sensor showed weak to moderate response at room temperature, which was observed to increase upon the increase in CO₂ concentrations from 10 ppm to 1000 ppm.¹¹ CYT-1 exhibited high response of $8.24 \times 10^6 \Omega$ at the CO₂ concentration of 1000 ppm from $6.55 \times 10^6 \Omega$ (resistivity in air) with 25.8% of

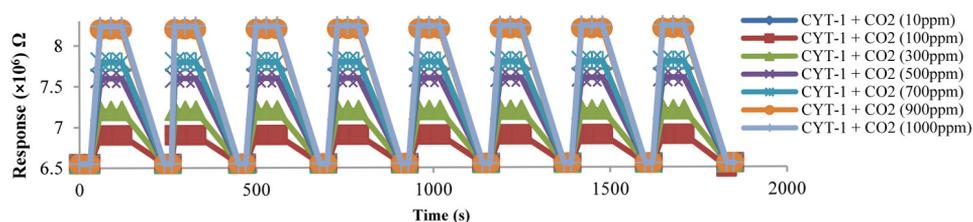


Figure 2: Response and recovery curve of CYT-1 towards various CO₂ concentrations (10–1000 ppm) between 65%–70% RH at room temperature (1V DC, 2 kHz).

sensitivity in N_2 environment. The response and recovery times for 10–1000 ppm concentrations of the CO_2 gas to be approximately 1 min and 3 min respectively. Besides, Figure 3 shows the linearity graph of CYT-1 towards 10–1000 ppm CO_2 gas with the efficiency of $R^2 = 0.9873$.

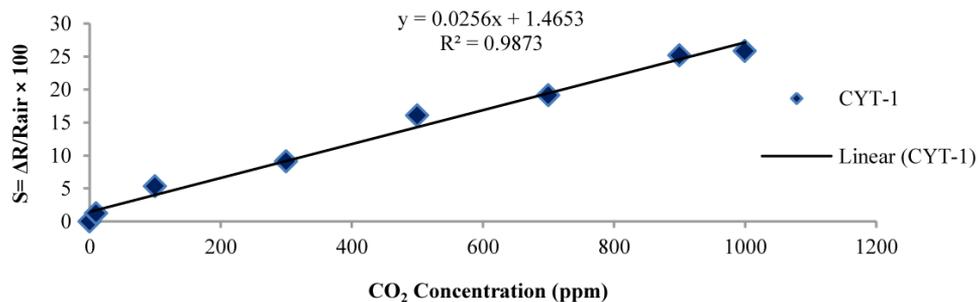


Figure 3: The sensitivity (%) linearity graph for CYT-1 towards various CO_2 concentrations.

Referring to the linear graph in Figure 3, limit of detection (LOD) of CYT-1 towards CO_2 gas was examined to investigate the efficiency and sensitivity of the sensor for CO_2 gas detection which was calculated using Equation 2:

$$LOD = \frac{3.3s}{\sigma} \quad (2)$$

where s is the standard deviation and σ is the slope from the linearity graph. The LOD for CYT-1 sensor for CO_2 detection is the lowest with 249 ppm. According to World Health Organisation (WHO), the maximum permissible CO_2 concentration in closed working environment for 8 h of exposure is about 350 ppm.² Indeed, in this contribution, LOD value of CYT-1 exhibited to be lower than the permissible CO_2 concentration which was good indication for CYT-1 to be applied further as chemiresistive CO_2 sensor.

4. CONCLUSION

A new member of organic semiconductor featuring acetylide-thiourea, CYT-1 has been successfully designed, synthesised and characterised as chemiresistive-type CO_2 sensor. Its properties and behaviours were investigated via electrical properties characterisation which revealed good sensitivity response of 25.8% with 1 min response time and 3 min recovery time operated at room temperature. CYT-1 revealed possible interaction towards CO_2 due to the H-bonding interaction occurred at $NH-C=O$ and $\pi-\pi$ interaction occurred at $C\equiv C$ site.

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6. REFERENCES

1. Rahman, F. A. et al. (2017). Pollution to solution: Capture and sequestration of carbon dioxide (CO₂) and its utilization as a renewable energy source for a sustainable future. *Renew. Sust. Energ. Rev.*, 71, 112–126, <https://doi.org/10.1016/j.rser.2017.01.011>.
2. Wennersten, R., Sun, Q. & Li, H. (2015). The future potential for carbon capture and storage in climate change mitigation – An overview from perspectives of technology, economy and risk. *J. Clean Prod.*, 103, 724–736, <https://doi.org/10.1016/j.jclepro.2014.09.023>.
3. Spinelle, L. et al. (2017). Field calibration of a cluster of low-cost commercially available sensors for air quality monitoring. Part B: NO, CO and CO₂. *Sens. Actuat. B Chem.*, 238, 706–715, <https://doi.org/10.1016/j.snb.2016.07.036>.
4. Al-Kayssi, A. W. & Mustafa, S. H. (2016). Impact of elevated carbon dioxide on soil heat storage and heat flux under unheated low-tunnels conditions. *J. Environ. Manage.*, 182, 176–186, <https://doi.org/10.1016/j.jenvman.2016.07.048>.
5. Kim, D. Y. et al. (2017). A carbon dioxide gas sensor based on cobalt oxide containing barium carbonate. *Sens. Actuat. B Chem.*, 248, 987–992. <http://dx.doi.org/10.1016/j.snb.2017.02.160>.
6. Baltrusaitis, J. et al. (2011). Carbon dioxide adsorption on oxide nanoparticle surfaces. *Chem. Eng. J.*, 170(2), 471–481. <https://doi.org/10.1016/j.cej.2010.12.041>.
7. Mendoza, F. et al. (2014). Room temperature gas sensor based on tin dioxide-carbon nanotubes composite films. *Sens. Actuat. B Chem.*, 190, 227–233, <https://doi.org/10.1016/j.snb.2013.08.050>.
8. Fratoddi, I. et al. (2015). Chemiresistive polyaniline-based gas sensors: A mini review. *Sens. Actuat. B Chem.*, 220, 534–548, <https://doi.org/10.1016/j.snb.2015.05.107>.
9. Chen, X. et al. (2012). Impact of the functional group on the working range of polyaniline as carbon dioxide sensors. *Sens. Actuat. B Chem.*, 175, 15–21, <https://doi.org/10.1016/j.snb.2011.11.054>.

10. Çiftyürek, E., Sabolsky, K. & Sabolsky, E. M. (2016). Molybdenum and tungsten oxide based gas sensors for high temperature detection of environmentally hazardous sulfur species. *Sens. Actuat. B Chem.*, 237, 262–274, <https://doi.org/10.1016/j.snb.2016.06.071>.
11. Saeed, A., Erben, M. F. & Bolte, M. (2013). Synthesis, structural and vibrational properties of 1-(adamantane-1-carbonyl)-3-halophenyl thioureas. *Spectrochim. Acta A*, 102, 408–413, <https://doi.org/10.1016/j.saa.2012.10.043>.
12. Kumar, R., Avasthi, D. K. & Kaur, A. (2017). Fabrication of chemiresistive gas sensors based on multistep reduced graphene oxide for low parts per million monitoring of sulfur dioxide at room temperature. *Sens. Actuat. B Chem.*, 242, 461–468, <https://doi.org/10.1016/j.snb.2016.11.018>.