Synthesis, Characterization and Electrical Properties of *N*-([4-(aminophenylethynyl) toluene]-*N*'-(cinnamoyl)thiourea (AECT) as Single Molecular Conductive Film

(Sintesis, Pencirian dan Sifat Elektrik bagi *N*-([4-(aminofenilethynyl) toluena]-*N*'-(cinnamoyl) tiourea (AECT) sebagai Filem Konduktif Molekul Tunggal)

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ABSTRACT

The exploitation of mixed moieties of conjugated acetylide and thiourea system as molecular wire candidates surprisingly unexplored in this distinctive area although the well-known rigid π -systems enhance the electronic field at some extend. Therefore, in the present research, interest has been focused on the design, synthesis, fabrication and evaluation of the performance of a new acetylide-thiourea, N-([4-(aminophenylethynyl)toluene]-N'-(cinnamoyl)thiourea (AECT) based on Donor (**D**)- π -Acceptor (**A**) system as an active layer in conductive film. The compounds were successfully characterized via infrared spectroscopy (IR), UV-visible absorption spectroscopy (UV-Vis), CHNS elemental analysis, ¹H and ¹³C nuclear magnetic resonance spectroscopy (NMR), thermogravimetric analysis (TGA) as well as cyclic voltammetry (CV) analysis. The investigation of its potential as dopant system in conductive film was fabricated on ITO substrate prior to the evaluation of its conductivity properties which was carried out by Four Point Probe. The findings from the conductivity analysis showed that the prepared film, AECT/ITO performed better and exhibited increasing conductivity up to 0.2044 Scm⁻¹ under maximum light intensity of 150 Wm². This proposed molecular framework gives an ideal indication to act as conductive film and has opened wide potential for application in organic electronic devices.

Keywords: Acetylide; conductive film; conductivity; thiourea

ABSTRAK

Eksploitasi moiti tercampur sistem molekul asetilida dan tiourea terkonjugat sebagai calon wayar molekul masih belum diterokai sepenuhnya dalam bidang ini walaupun sistem- π utuh yang dikenali ramai dapat meningkatkan perkembangan dalam bidang elektronik pada tahap tertentu. Oleh yang demikian, dalam kajian ini, perhatian difokuskan kepada reka bentuk, sintesis, fabrikasi dan penilaian prestasi bagi terbitan asetilida-tiourea yang baru, N-([4-(aminofenilethynyl) toluena]-N'-(cinnamoyl)tiourea (AECT) menggunakan sistem penderma (**D**)- π -penerima (**A**) sebagai lapisan aktif dalam filem konduktif. Setiap sebatian telah berjaya dicirikan melalui sinar inframerah (IR), analisis ultra-lembayung sinar nampak (UV-Vis), analisis unsur CHNS, ¹H dan ¹³C multi resonan magnetik nukleus (NMR), analisis termogravimetri (TGA) dan juga analisis voltametri kitaran (CV). Penyelidikan tentang keupayaannya sebagai sistem dopan pada filem konduktif telah dilakukan dengan sebatian ini telah difabrikasikan pada substrat ITO sebelum ciri-ciri kekonduksian dinilai menggunakan Penduga Empat Titik. Daripada kajian kekonduksian, 0.2044 Scm⁻¹ di bawah keamatan cahaya maksimum iaitu 150 Wm². Kerangka molekul yang dicadangkan ini dapat memberikan petunjuk yang ideal untuk bertindak sebagai filem konduktif dan membuka ruang yang luas untuk diaplikasikan sebagai peranti elektronik organik.

Kata kunci: Asetilida; filem konduktif; kekonduksian; tiourea

INTRODUCTION

Development of thin film technology in the field of material sciences has attracted great attention for the past decades due to its special and unique characteristics such as low-cost production, lightweight and flexible (Granqvist & Hultåker 2002; Murphy & Frechet 2007). In these respects, the developed materials based on polymer and organic compounds as active substrates have become primary alternatives over readily available conventional developed films (Cheng et al. 2009; Günes et al. 2007; Horowitz 2004). This is due to the fact that these compounds offer unique properties which consist of conjugated molecular

unit comprising electronic delocalization in extended π -orbital system, in which electrons can move along the molecules (Bayat & Mahdizadeh 2011; Hoeben et al. 2005).

However, the quest to design the ideal molecular system that posseses highly conjugated system, that allows high rate of electrons for utilization in molecular wire, is rather challenging (Guo et al. 2012). There are some requirements needed to design molecular wires, whereby it should be a linear molecule with defined length to span the gap between two components in the circuit and electron or hole conducting in conjugated molecules through π -system

(Jennum & Nielsen 2013; Lamba et al. 2011). Thus, it is crucial to put greater importance on the choice of ideal materials that will facilitate the performance of its functions at optimum levels.

Moving towards this interest, lots of previous studies have been reported on the exploration of 1-acyl-thiourea family to determine their various properties such as synthesis and characterization, crystal structure, thermal behavior and its usage in various applications (Aly et al. 2007; Koch 2001; Saeed et al. 2014b). Due to this matter with high interest in developing single molecule as conductive film, we are presenting a new acetylidethiourea, N-([4-(aminophenylethynyl)toluene]-N'-(cinnamoyl)thiourea (AECT) as organic material candidate to be applied as active layer in conductive film as shown in Figure 1. The unique coordination aspect of acetylidethiourea motif consists of conjugation system and lone pair of N, S and O in which it involves the resonance that leads to electron delocalization all over the molecular backbone of conjugated molecular system that resulted into the effective properties of electrical conductivity. Additionally, acetylide-thiourea system has turned out to be great candidate to construct D-A molecular wire compounds, which can act as excellent transporters. Thus, they can act as the simplest electronic component for the conduction of current along its molecular backbone.

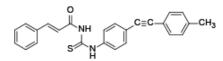


FIGURE 1. *N*-([4-(aminophenylethynyl)toluene]-*N*'-(cinnamoyl)thiourea (AECT)

EXPERIMENTAL DETAILS

MATERIAL AND GENERAL METHODS

All chemicals and solvents were used as received without any special precautions taken during the experimental work-up. All chemicals or reagents used in this study were purchased from standard commercial suppliers namely Sigma Aldrich, Merck, Fisher Scientific and R&M Chemical. The infrared (IR) spectrum was recorded on Perkin Elmer 100 Fourier transform infrared spectroscopy by using potassium bromide (KBr) pellets in the spectral range of 4000-400 cm⁻¹. Meanwhile, for UV-visible absorption spectroscopy (UV-Vis), the spectrum was recorded by using Spectrophotometer Shimadzu UV-1601PC in 1 cm³ cuvette in methanolic solution with concentration 1×10⁻⁵M for absorbance analysis. For the analytical method, the CHNS Analyzer Flashea 1112 series was used to determine the percentage weight of the microelements of C, H, N and S of the synthesized compounds. The NMR spectra of ¹H (400.11 MHz) and ¹³C (100.61 MHz) NMR were recorded using Bruker Avance III

400 spectrometer by using deuterated chloroform (CDCl₃). Thermogravimetric analysis was performed using Perkin– Elmer TGA Analyzer from 30°C to 700°C at a heating rate of 10°C/min under nitrogen atmosphere.

GENERAL OVERVIEW OF SYNTHETIC WORK

For the synthetic work, the Sonogashira cross-coupling protocols were carried out to synthesis tolan derivative, 4-[(4-aminophenylethynyl] toluene to act as precursor compound. From precursor, the preparation of acetylide-thiourea, N-([4-(aminophenylethynyl)toluene]-N'-(cinnamoyl)thiourea (AECT) was obtained as focalpoint compound in this study. However, the experimental details with regard to the synthesis of precursor (4-[(4-aminophenyl)ethynyl]toluene) have been reported before in literatures (Daud et al. 2014; Stiegman et al. 1991). Therefore, some modifications in synthetic work and further characterization on the spectroscopic and analytical tasks carried out are discussed further in this report. The synthetic approach of the AECT is summarized in Scheme 1.

SONOGASHIRA CROSS-COUPLING REACTION: PREPARATION OF 4-[(4-AMINOPHENYL)ETHYNYL]TOLUENE

A mixture of 4-iodoaniline (1 g, 4.56 mmol), 4-ethynyltoluene (0.53 g, 4.56 mmol) and Pd(PPh₂)₂Cl₂/ CuI (5 mmol%) were charged to 100 mL round bottom flask. The reaction was carried out at reflux temperature with using water (H₂O) as solvent and triethylamine (Et₃N) as base for ca. 24 h under ambient atmosphere to give two layers of solution. After adjudged completion by TLC (hexane: ethyl acetate; 3:2), the solution was cooled at room temperature prior to extraction of the organic layer. The organic layer was separated, dried over MgSO₄ and solvent was removed *in-vacuo*. The residue was purified by silica gel column chromatography (n-hexane:dichloromethane; 7:3) to afford title compound (35% yields). IR (KBr); v(NH₂) 3376 s, 3468 s; v (C≡C) 2208 m cm⁻¹. ¹H NMR (400.11MHz, CDCl₃): $\delta_{\rm H}$ 2.28 (s, $3H, CH_3$ 3.73 (s br, 2H, NH₂); 6.57 (pseudo-d, ${}^{3}J_{HH} = 9Hz$, 2H, C_6H_4 ; 7.19 (pseudo-d, ${}^{3}J_{HH} = 8Hz$, 2H, C_6H_4); 7.25 (pseudo-d, ${}^{3}J_{HH} = 8Hz$, 2H, C_6H_4); 7.32 (pseudo-d, ${}^{3}J_{HH} =$ 9Hz, 2H, C_6H_4);¹³C NMR (100.61MHz, CDCl₃): δ_c 21.42 (s, CH₃) 86.27 (s, C≡C); 89.34 (s, C≡C); 110.63, 112.93, 114.76, 120.83, 129.03, 131.25, 137.69, 146.47 (8×s, Ar); Elemental analysis for $C_{15}H_{13}N$: [Found (Calcd.): C = 87.24(86.97); H = 6.06 (6.28); N = 6.17 (6.76%)].

PREPARATION OF N-([4-(AMINOPHENYLETHYNYL) TOLUENE]-N'-(CINNAMOYL)THIOUREA (AECT)

The experimental details regarding to the synthesis of AECT was adapted from the methods carried out by Douglas and Dains (1934) involving suspension of cinnamoyl chloride (1 g, 6 mmol) in 50 mL acetone was added dropwise to a solution of ammonium thiocyanate (0.46 g, 6 mmol) in 50 mL acetone. The mixture was put at reflux with

constant stirring for ca. 4 h, followed by the addition of precursor, (1.24 g, 6 mmol) in 30 mL acetone. After stirring for another 4 h, the colour of the solution changed to yellowish solution. After adjudged completion by thin layer chromatography (TLC) (hexane: ethyl acetate; 3:2), the reaction mixture was allowed to come to room temperature and then filtered. The yellow filtrate was added with several ice cubes and filtered to obtain yellow precipitate which was then recrystallized from acetonitrile to afford title compound (55% yields). IR (KBr); v(NH₂) 3441 s, 3181 s; v (C=C) 2215 m; v (C=O) 1677 s, v (C=S) 729 m cm⁻¹. ${}^{1}\text{H}$ NMR (CDCl₃, 400.11 MHz) δ_{H} : 2.31 (s, 3H, CH₃); 7.10 (pseudo-d, ${}^{3}J_{HH}$ = 9Hz, 2H, C₆H₄); 7.19 (pseudo-d, ${}^{3}J_{HH}$ = 9Hz, 2H, C_6H_4); 7.69 (pseudo-d, ${}^{3}J_{HH} =$ 9Hz, 2H, C_6H_4); 7.76 (pseudo-d, ${}^{3}J_{HH} =$ 9Hz, 2H, C_6H_4); 7.76 (pseudo-d, ${}^{3}J_{HH} =$ 9Hz, 2H, C_6H_4); 7.35-7.49 (m, 5 × H, Ar- C_6H_5); 8.75, 12.67 (2 × s, 1H, NH). ¹³C NMR (CDCl₃, 100.61 MHz): $\delta_{C} 21.53 (CH_{3})$; 88.25, 90.18 (C=C); 118.05, 120.05, 121.79, 123.40, 128.56, 129.14, 129.17, 131.35, 131.53, 132.06, 133.56, 137.28, 138.53, 146.93 (18 \times s, Ar), 165.55 (C=O); 177.89 (C=S). Elemental analysis for $C_{25}H_{20}N_2OS$: (Found (Calcd.): C = 76.32 (75.73); H = 5.27 (5.08); N = 7.06 (7.07); S = 7.63 (8.09%)).

FABRICATION AND ELECTRICAL STUDIES OF THIN FILM FROM AECT ON ITO SUBSTRATE

The fabrication of AECT on ITO substrate has been deposited by electrochemical deposition (ECD) method in 50 mL acetonitrile, 0.5 M sulphuric acid (as supporting electrolyte) with sample concentration of 1×10^{-3} M. Figure 2 shows the general illustration of layers arrangement in thin film. For electrical conductivity characterization, Four-Point Probe system was used to determine the conductivity of AECT in the form of thin film under various intensity of light. The sheet resistivity in produced films was measured by using four point probing system consists of Jandel

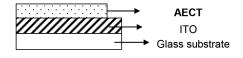


FIGURE 2. The general illustration of arrangement layer thin film

universal probe combined with a Jandel RM3 test unit. Sheet resistance for wafer and film;

$$R_{\rm s} = 4.532 \times {\rm V} / {\rm I},$$
 (1)

where R_s is the sheet resistance (resistivity); 4.532 is the correction factor; V is the voltage measured; and I is the current applied from the test unit. Thus, electrical conductivity can be determined which it is the reciprocal (inverse) of the electrical resistivity, σ as shown in (2).

$$\sigma = 1/R_{\rm s},\tag{2}$$

where σ is the electrical conductivity; and R_s is the sheet resistance (resistivity).

RESULTS AND DISCUSSSION

INFRARED (IR) SPECTROSCOPY ANALYSIS

IR spectrum of AECT showed all the expected bands of interest namely ν (N-H), ν (C=C), ν (C=O), ν (C-N), v(C-O) and v(C=S). Two bands of v(N-H) can be identified at 3441 and 3181 cm⁻¹ which corresponded to two distinctive N-H groups present in the molecule. The assignment of NH at 3181 cm⁻¹ has been examined to be the existance of C=O...H-N intramolecular hydrogen bond characteristic of -C(O)NHS(O)NH- moiety (Karipcin et al. 2013; Saeed et al. 2015a, 2014b, 2013). The broad and not well-resolved bands can be observed near 3000 cm⁻¹ which making the assignment of these features is rather challenging especially to confirm the position of C-H stretching mode is anticipated. According to Weiqun et al. (2003), very low intense signal at 3086 cm⁻¹ was assigned as v(N-H) for the related thiourea species in their work. However, in this present case, the band observed around 3024 cm⁻¹ was assigned as v(C-H) stretching which is almost identical absorption frequencies found in the other reported similar molecular system (Estévez-Hernández et al. 2005; Khairul et al. 2013). The absorption band for $v(C \equiv C)$ stretching vibration occurred at 2215 cm⁻¹ for the formation of acetylide moieties with moderate intensity (Daud et al. 2015; Grigoras et al. 2014). The stretching frequencies at 1431 cm⁻¹ correspond to v(C-N) was assigned by comparing with other thiourea derivatives which should be presence at 1400–1000 cm⁻¹. The strong absorption of v(C=O) stretching band that appeared at 1677 cm⁻¹, apparently decreased in frequency compared to the ordinary carbonyl compounds which a signature for the presence of intramolecular hydrogen bond towards N-H moiety which in the same arguments with previous reported studies (Arslan et al. 2012; Rahamathullah et al. 2015; Weiqun et al. 2003). Additionally, the presence of v(C=S) stretching vibration is the most crucial changes which were observed in the range of 600-800 cm⁻¹ and can be assigned at low frequency of 676 cm⁻¹. This occurrence is due presence of intermolecular interaction between C=S and C-N bond, less double bond character and the lower nucleophilic character of the sulfur atom in C=S moiety (Ataol et al. 2014; Estévez-Hernández et al. 2005; Saeed et al. 2014a).

OPTICAL PROPERTIES

Electronic transition spectrum of AECT was recorded in methanol solution with concentration 1×10^{-5} M and wavelength ranges from λ_{max} 200-400 nm. The absorption spectrum showed two principal bands which were expected to arise from C=O, C=S and phenyl moieties at around λ_{max} 225 and 315 nm. The primary bands of phenyl ring was assigned around λ_{max} 225 nm which can be ascribed as $\pi \rightarrow \pi^*$ transition influenced by the inductive interaction between the aromatic rings and carbonyl group. Strong absorption band centered at around λ_{max} 300-310 nm can be attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions due to the existence of overlapping between C=O and C=S in thiourea moiety (Jasman et al. 2015). The broad absorption band observed in the region at λ_{max} 315 nm was due to π -conjugation of this compound with the phenyl rings ($\pi - \pi^*$ transition).

¹HAND ¹³C NUCLEAR MAGNETIC RESONANCE (NMR) ANALYSIS

The ¹H NMR spectrum showed methyl resonance at $\delta_{\rm H} 2.31$ ppm on the aryl ring that was assigned as singlet resonance due to the effect from the neighbouring proton. Whilst, the unresolved resonances of aromatic protons can be clearly observed as distinctive pseudo-doublet resonances at around $\delta_{\rm H}$ 7.19-7.69 ppm. Expectedly, these characteristics were strongly influenced by para-substituent group at the phenyl ring in the molecule (Otazo-Sánchez et al. 2002). Two singlet resonances can be observed at δ_{H} 8.74 ppm and δ_{μ} 12.67 ppm which attributed to NH group of NHC=O and NHC=S moiety, respectively. The resonance for proton NHC=S which bonded to thiocarbonyl and phenyl group can be noticed at higher chemical shift compared to proton NHC=O that bonded to carbonyl and thiocarbonyl. These signals were different in terms of chemical shift which due to the presence and influences of the electron-withdrawing group and intramolecular hydrogen bond in the molecule (Saeed et al. 2010).

The ¹³C NMR of AECT was consistent with the proposed molecular structure. The methyl resonance can be clearly observed at δ_c 21.53 ppm and carbon resonances for acetylide, C=C were detected at δ_c 88.25 and 88.27 ppm, which showed a good agreement with the previous reports on the similar systems (Daud et al. 2015, 2014). Meanwhile, the resonances for both aromatic ring carbons were assigned in the range of δ_c 119.50 to 148.20 ppm which corresponded to the phenyl rings in these compounds. Two individual and distinctive resonances can be detected at δ_c 165.55 ppm and δ_c 177.89 ppm which represented as C=O and C=S carbons, respectively. These signals were slightly deshielded due to several known reasons which were, formation of intramolecular hydrogen bonding in the molecule, increasing electronegativity of

oxygen and sulphur atoms and different environment as well as geometric conformation.

THERMAL STABILITY

Thermal stability of the material is important to be investigated for fabrication of any thin films application. Thermal properties of AECT was evaluated via thermogravimetric analysis (TGA) at heating rate of 10°C/ min under nitrogen atmosphere with temperature range of 30-700°C as shown in Figure 3. The thermogram showed no mass loss occurred below 100°C which indicate there was no trace of water molecule or solvent presence in the sample. The degradation process of AECT showed two stages of major mass loss. Initial degradation took place at around 220°C (Tonset) and ended at around 300°C (Tonset) with maximum degradation of 235°C which showed good agreement with previous reports on the similar systems (Khairul et al. 2013; Rahamathullah et al. 2015; Saeed et al. 2015b). Whilst, second stage started to degrade at 330°C (Tonset) and ended at 490°C (Toffset) with maximum degradation of 410°C. It showed that the title compound exhibited thermal stability at high temperature and it gave good indications for the potential of thin film fabrication be applied as conductive film for it displays remarkable performance under prolonged thermal stress.

ELECTROCHEMICAL PROPERTIES

The electrochemical properties was investigated further by using cyclic voltammetry analysis in order to determine the redox reaction and potential range of different electrochemical processes. The initial electrochemical study of 1×10^{-3} M of AECT in acetonitrile (CH₃CN) with 0.5 M sulphuric acid as supporting electrolyte on Pt electrode was run at 0.05 V, 0.03 Vs⁻¹ as shown in Figure 4. The cyclic voltammogram of AECT exhibit irreversible redox processes with the presence of oxidation and reduction peaks, respectively. The oxidation peak occurred at $\Delta E_{pa} = 1.502$ V with $I_{pa} = 5.66 \times 10-5$ A while the reduction peak occurred at $\Delta E_{pa} = -0.599$ V with $I_{pc} = -5.66 \times 10-5$ A as shown in Figure 5. It exhibited a pair of peak which became better defined when the potential scan went from -1 to 2.0V. This result was supported by previous literatures describing on similar type of molecular framework where the redox

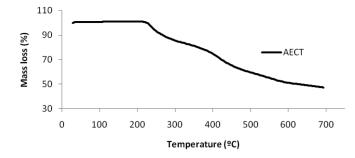


FIGURE 3. TGA thermogram of AECT

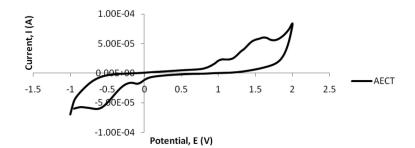


FIGURE 4. Cyclic voltammogram of AECT(1×10⁻³ M) in CH₃CN and 0.5 M sulphuric acid at 0.05 V, 0.03 Vs⁻¹

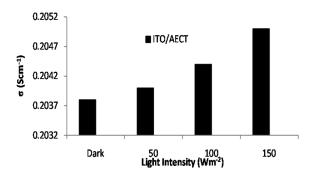
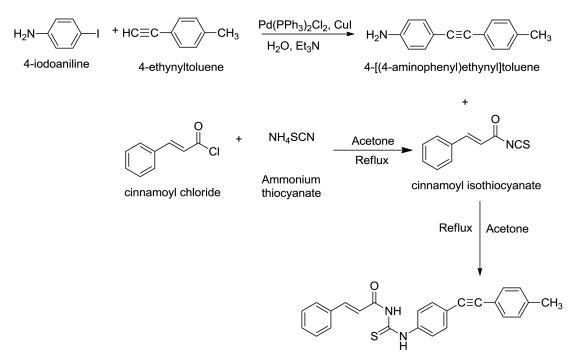


FIGURE 5. Electrical conductivity values under various intensity of light



N-([4-(aminophenylethynyl)toluene]-N'-(cinnamoyl)thiourea (AECT)

SCHEME 1. Synthetic approach for the preparation of AECT

potential in thiourea derivatives with the electro-oxidation stage of thiocarbonyl (Jasman et al. 2015; Khairul et al. 2013; Rahamathullah et al. 2013). Thus, it can be concluded that the redox potential of AECT appeared in the positive region with its electro-oxidation stage as an anodic peak with a separation about 1V. A deprotonated thiourea adsorbate and the soluble species further electroreduced to thiourea which confirm the irreversible behavior of this reaction and the existence of redox potential that subsequently gave good sign for potential of the fabrication of conducting thin film.

ELECTRICAL CONDUCTIVITY OF THIN FILM UNDER INTENSITY OF LIGHT

In order to investigate its conductivity in various conditions, as shown in Figure 5, the electrical conductivity (EC) study of AECT in thin film form coated on the indium tin oxide (ITO) glass was measured under various intensities of light conditions (Wm⁻²) by using Four-Point Probe. It showed the electrical conductivity increased by the increasing amount of light intensities. The highest conductivity was observed for AECT under maximum light intensity (150 Wm⁻²) with the conductivity value, 0.2044 Scm⁻¹ that could be explained by its molecular weight and the conjugation length. In this case, the performance of conductivity that was caused by the introduction of C=O and C=C moieties due its properties, in which the system posses an extensive conjugated bond.

As a conclusion, the electrical conductivity showed positive results under various intensity of light which showed the film was successfully coated on the ITO substrate. Thus, fundament to the resulting conductivity, the AECT system can be applied as an active layer in conducting material.

CONCLUSION

The role and performance of single molecule compound of N-([4-(aminophenylethynyl)toluene]-N'-(cinnamoyl) thiourea (AECT) has been successfully synthesized and characterized as dopant system in conductive film. In fact, ITO/AECT thin film can conduct electricity better under maximum light intensity. From these findings, further investigation on the similar molecular system is suggested to be applied as organic molecular wire for the development and application in any microelectronic devices.

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REFERENCES

- Aly, A.A., Ahmed, E.K., El-Mokadem, K.M. & Hegazy, M.E.A.F. 2007. Update survey on aroyl substituted thioureas and their applications. *Journal of Sulfur Chemistry* 28: 73-93.
- Arslan, N.B., Kazak, C. & Aydın, F. 2012. N-(4-Nitrobenzoyl)-N'-(1, 5-dimethyl-3-oxo-2-phenyl-1H-3 (2H)-pyrazolyl)-thiourea hydrate: Synthesis, spectroscopic characterization, X-ray structure and DFT studies. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 89: 30-38.
- Ataol, Ç.Y. & Ekici, Ö. 2014. Experimental and theoretical studies of (FTIR, FT-NMR, UV–Visible, X-ray and DFT) 2-(4-Allyl-5-pyridin-4-yl-4H-[1, 2, 4] triazol-3-ylsulfanyl)-1-(3-methyl-3-phenyl-cyclobutyl)-ethanone. *Journal of Molecular Structure* 1065: 1-9.
- Bayat, Z. & Mahdizadeh, S.J. 2011. Design of nanoscale molecular wire based on 3, 6-Diphenyl-1, 2, 4, 5-Tetrazine and effect of external electric field on electron transfer in conjugated molecular wire. *Physica E: Low-dimensional Systems and Nanostructures* 43: 1569-1575.
- Cheng, Y.J., Yang, S.H. & Hsu, C.S. 2009. Synthesis of conjugated polymers for organic solar cell applications. *Chemical reviews* 109: 5868-5923.
- Daud, A.I., Khairul, W.M., Zuki, H.M. & Kubulat, K. 2015. Aerobic synthetic approach and characterisation of some acetylide–thiourea derivatives for the detection of carbon monoxide (CO) gas. *Journal of Molecular Structure* 1093: 172-178.
- Daud, A.I., Khairul, W.M., Mohamed Zuki, H. & KuBulat, K. 2014. Synthesis and characterization of N-(4-Aminophenylethynylbenzonitrile)-N'-(1-naphthoyl) thiourea as single molecular chemosensor for carbon monoxide sensing. Journal of Sulfur Chemistry 35: 691-699.
- Douglass, I.B. & Dains, F.B. 1934. Some derivatives of Benzoyl and Furoyl Isothiocyanates and their use in synthesizing heterocyclic compounds. *Journal of the American Chemical Society* 56: 719-721.
- Estévez-Hernández, O., Otazo-Sánchez, E., De Cisneros, J.H.H., Naranjo-Rodríguez, I. & Reguera, E. 2005. A Raman and infrared study of 1-furoyl-3-monosubstituted and 3, 3-disubstituted thioureas. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 62: 964-971.
- Granqvist, C.G. & Hultåker, A. 2002. Transparent and conducting ITO films: New developments and applications. *Thin Solid Films* 411: 1-5.
- Grigoras, M., Ivan, T., Vacareanu, L., Catargiu, A.M. & Tigoianu, R. 2014. Synthesis and optoelectronic characterization of some triphenylamine-based compounds containing strong acceptor substituents. *Journal of Luminescence* 153: 5-11.
- Günes, S., Neugebauer, H. & Sariciftci, N.S. 2007. Conjugated polymer-based organic solar cells. *Chemical Reviews* 107: 1324-1338.
- Guo, C., Zhang, Z.H., Kwong, G., Pan, J.B., Deng, X.Q. & Zhang, J.J. 2012. Enormously enhanced rectifying performances by modification of carbon chains for D-σ-A molecular devices. *The Journal of Physical Chemistry C* 116: 12900-12905.
- Hoeben, F.J., Jonkheijm, P., Meijer, E.W. & Schenning, A.P. 2005. About supramolecular assemblies of π-conjugated systems. *Chemical Reviews* 105: 1491-1546.
- Horowitz, G. 2004. Organic thin film transistors: From theory to real devices. *Journal of Materials Research* 19: 1946-1962.
- Jasman, S.M., Khairul, W.M., Tagg, T., KuBulat, K., Rahamathullah, R., Arshad, S., Razak, I.A. & Tahir, M.I.M. 2015. Synthesis, crystal structure and electrical studies of

Naphthoyl-Thiourea as potential organic light emitting diode. Journal of Chemical Crystallography 45: 338-349.

- Jennum, K. & Nielsen, M.B. 2013. Design and synthesis of organic molecules for molecular electronics. In Organic Synthesis and Molecular Engineering, edited by Nielsen, M.B. Hoboken, New Jersey: John Wiley & Sons, Inc. doi: 10.1002/9781118736449.ch3.
- Karipcin, F., Atis, M., Sariboga, B., Celik, H. & Tas, M. 2013. Structural, spectral, optical and antimicrobial properties of synthesized 1-benzoyl-3-furan-2-ylmethyl-thiourea. *Journal* of Molecular Structure 1048: 69-77.
- Khairul, W.M., Yusof, M.F., Rahamathullah, R., Daud, A.I., Jasman, S.M., Hasan, M.F.A., Salleh, H., Adli, H.K. & Tay, M.G. 2013. Single molecule thin film featuring disubstituted thiourea (TU) doped with chlorophyll as potential active layer in photovoltaic cell. *Int. J. Electrochem. Sci* 8: 8175-8190.
- Koch, K.R. 2001. New chemistry with old ligands: N-alkyl-and N, N-dialkyl-N'-acyl (aroyl) thioureas in co-ordination, analytical and process chemistry of the platinum group metals. *Coordination Chemistry Reviews* 216: 473-488.
- Lamba, V., Wilkinson, S.J. & Arora, C. 2011. Designing molecular devices by altering bond lengths. *Journal of Molecular Modelling* 17: 3251-3255.
- Murphy, A.R. & Frechet, J.M. 2007. Organic semiconducting oligomers for use in thin film transistors. *Chemical Reviews* 107: 1066-1096.
- Otazo-Sánchez, E., Ortiz-del-Toro, P., Estévez-Hernández, O., Pérez-Marin, L., Goicoechea, I., Beltran, A.C. & Villagómez-Ibarra, J.R. 2002. Aroylthioureas: New organic ionophores for heavy metal ion selective electrodes. A nuclear magnetic resonance study. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 58: 2281-2290.
- Rahamathullah, R., Khairul, W.M., Ku Bulat, K. & Hussin, Z.M. 2015. Influence of curcumin as a natural photosensitizer in the conductive thin film of alkoxy cinnamoyl substituted thiourea. *Main Group Chemistry* 14: 185-198.
- Rahamathullah, R., Khairul, W.M., Salleh, H., Adli, H.K., Isa, M.I.N. & Tay, M.G. 2013. Synthesis, characterization and electrochemical analysis of V-shaped disubstituted thioureachlorophyll thin film as active layer in organic solar cells. *Int. J. Electrochem. Sci.* 8: 3333-3348.
- Saeed, A., Ashraf, S., White, J.M., Soria, D.B., Franca, C.A. & Erben, M.F. 2015a. Synthesis, X-ray crystal structure, thermal behavior and spectroscopic analysis of 1-(1-naphthoyl)-3-(halo-phenyl)-thioureas complemented with quantum chemical calculations. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 150: 409-418.
- Saeed, A., Khurshid, A., Bolte, M., Fantoni, A.C. & Erben, M.F. 2015b. Intra-and intermolecular hydrogen bonding and conformation in 1-acyl thioureas: An experimental and theoretical approach on 1-(2-chlorobenzoyl) thiourea. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 143: 59-66.

- Saeed, A., Flörke, U. & Erben, M.F. 2014a. A review on the chemistry, coordination, structure and biological properties of 1-(acyl/aroyl)-3-(substituted) thioureas. *Journal of Sulfur Chemistry* 35: 318-355.
- Saeed, A., Khurshid, A., Jasinski, J.P., Pozzi, C.G., Fantoni, A.C. & Erben, M.F. 2014b. Competing intramolecular N H… O C hydrogen bonds and extended intermolecular network in 1-(4-chlorobenzoyl)-3-(2-methyl-4-oxopentan-2-yl) thiourea analyzed by experimental and theoretical methods. *Chemical Physics* 431: 39-46.
- Saeed, A., Erben, M.F. & Bolte, M. 2013. Synthesis, structural and vibrational properties of 1-(adamantane-1-carbonyl)-3halophenyl thioureas. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 102: 408-413.
- Saeed, S., Rashid, N., Jones, P.G., Ali, M. & Hussain, R. 2010. Synthesis, characterization and biological evaluation of some thiourea derivatives bearing benzothiazole moiety as potential antimicrobial and anticancer agents. *European Journal of Medicinal Chemistry* 45: 1323-1331.
- Stiegman, A.E., Graham, E., Perry, K.J., Khundkar, L.R., Cheng, L.T. & Perry, J.W. 1991. The electronic structure and second-order nonlinear optical properties of donor-acceptor acetylenes: A detailed investigation of structure-property relationships. *Journal of the American Chemical Society* 113: 7658-7666.
- Weiqun, Z., Kuisheng, L., Yong, Z. & Lu, L. 2003. Structural and spectral studies of N-(4-chloro) benzoyl-N'-2-tolylthiourea. *Journal of Molecular Structure* 657: 215-223.

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