



# AN INTERACTION MODE OF *N*-(DECYLOXYPHENYL)-*N'*-(4-CHLOROBENZOYL)THIOUREA DOPANT IN CARBOXYMETHYL CELLULOSE (CMC) FOR SOLID POLYMER ELECTROLYTE

Wan M. Khairul,<sup>[a]\*</sup> Saidatul Radhiah Ghazali,<sup>[b]</sup> M. I. N. Isa,<sup>[c]</sup> Adibah Izzati Daud<sup>[a,d]</sup> and Rafizah Rahamathullah<sup>[a,d]</sup>

**Keywords:** thiourea, carboxymethyl cellulose, conductive thin film

Alkoxy substituted arylthiourea derivatives provide excellent electronic properties due to the presence of rigid  $\pi$ -systems within their molecular framework. This study introduces a new thiourea derivative, *N*-(decyloxyphenyl)-*N'*-(4-chlorobenzoyl)thiourea (**1A**), belongs to the compounds with general formula A-ArC(O)NHC(S)NHAr-D (A is an aryl group containing chloro (-Cl) substituent, in which acts as electron acceptor, while D represented as  $-OC_nH_{2n+1}$ , the alkoxy chain tail acts as electron donor). Due to its characteristic of D- $\pi$ -A system, alkoxy thiourea derivatives are applied as a dopant in Carboxymethyl Cellulose (CMC) host material to form a conductive biopolymer solid polymer electrolyte (SPE) film. The formation of a biopolymer-thiourea complex (**1A-CMC**) has been analyzed through Fourier Transform Infrared (FTIR) spectroscopy and X-ray diffraction (XRD) to determine the interaction between CMC and thiourea derivative in the form of film as well as Electrical Impedance Spectroscopy (EIS) for their ionic conductivity behavior. The highest conductivity at ambient temperature (303K) exhibits  $1.44 \times 10^{-7} \text{ S cm}^{-1}$  for CMC-thiourea complexation featuring chloro-substitution (**1A**). Indeed, biopolymer electrolyte materials featuring thiourea derivative as a dopant has great potential to be developed as an electrical conductor. Due to these findings, these so-called molecular wires candidate has opened wide possibilities to be applied in many microelectronic devices in the near future.

\* Corresponding Authors

E-Mail: [wmkhairul@umt.edu.my](mailto:wmkhairul@umt.edu.my)

- [a] <sup>1</sup>School of Fundamental Science, Universiti Malaysia Terengganu, 21030, Kuala Nerus, Terengganu, Malaysia  
 [b] Polymer Department, Faculty of Chemical Engineering Technology, TATI University College, 24000 Kemaman, Terengganu, Malaysia  
 [c] Frontier of Materials Research Group, Advanced Materials Team, Faculty of Science and Technology, Universiti Sains Islam Malaysia, Bandar Baru Nilai, 71800 Nilai, Negeri Sembilan, Malaysia  
 [d] <sup>4</sup>Faculty of Engineering Technology, Universiti Malaysia Perlis (UniMAP), Sungai Chuchuh, 02100 Padang Besar, Perlis, Malaysia

context, the synthesis and ability of thiourea derivatives bearing methyl substitution as a dopant in carboxymethyl cellulose (CMC) have been reported by our group in the previous occasion.<sup>6</sup> As a continuation of our previous work, a different type of withdrawing group involving chloro substitution of alkoxy thiourea was doped into CMC in demand to develop new biopolymer electrolyte film and further characterized the film using FTIR, XRD and AC-impedance spectroscopic studies. CMC is also well-known as a cellulose gum with the characteristic of anionic, soluble in water media, biodegradable and exhibit excellent mechanical properties.<sup>7,8</sup> However, the use of CMC itself as a polymer host gave a moderate conductivity performance. To overcome this issue, the use of suitable dopant into the polymer host system is needed to enhance the conductivity performance of solid polymer electrolytes.

## INTRODUCTION

Nowadays, thiourea derivatives have been used widely in numerous advanced materials application such as in drug development for pharmaceutical application,<sup>1</sup> chemical sensors for anions and gas detection,<sup>2,3</sup> active layer for photovoltaic solar cells and catalysis in promoting the cross-coupling reaction.<sup>4,5</sup>

The uniqueness of thiourea derivatives incorporating with varies functional group substitutions make them versatile compounds to be applied in advanced materials application. The presence of diprotic donor group insight thiourea derivatives plays a significant role in providing enough electron to the conjugated system of thiourea derivatives, in which, the  $\pi$ -conjugated system of thiourea derivatives make it as a promising candidate for molecular wires.

Currently, the development of molecular wires featuring conjugated polymers has become exceptional attention. There is an urgent need to explore the ideal materials in the form of the membrane to be applied in microelectronic devices. In this

In addition, the properties of dopant must be suited to the CMC properties in both chemical and mechanical aspects. Thiourea derivatives are known as versatile compounds consist of fair  $\pi$ -system with electronic conjugation on its structure that gave an enormous potential to be an ideal candidate as a dopant for CMC polymer host. Therefore, the purpose of this research was to prepare and characterize a novel thiourea-based conjugated compound prior to the formation of a solid conductive membrane to enhance the conductivity of CMC.

## EXPERIMENTAL

### Synthesis of *N*-decyloxyphenyl-*N'*-(chlorobenzoyl)thiourea(**1A**)

An equimolar amount of 4-chloro benzoyl chloride (5.50 g, 31.20 mmol), ammonium thiocyanate (2.40 g, 31.20 mmol) were suspended into 50 ml of acetone to afford an off-white

solution. The solution was stirred at room temperature for ca. 4 hours followed by the addition of 4-decyloxy aniline (7.8 g, 31.20 mmol). The reaction was then put at reflux for another 1 hour until the observed color of the solution turned from off-white to white. After the reaction was adjudged completion by thin layer chromatography (hexane: dichloromethane: 2:3), the reaction mixture was cooled to room temperature and filtered. The off-white filtrate was added with ice cubes and filtered to yield a crude product of white precipitate. The white precipitate was then recrystallized from methanol to afford the white crystalline solid of the title compound, **1A** (3.40 g, 54 %).

#### Preparation of thiourea carboxymethyl cellulose (CMC) polymer electrolyte (**1A**-CMC)

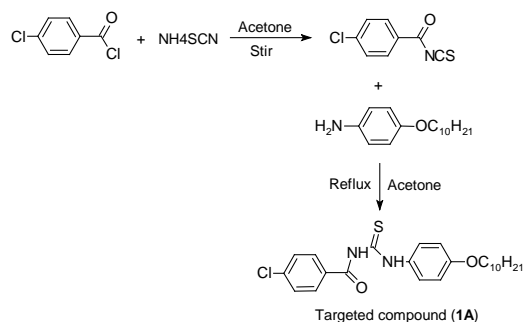
The biodegradable film of solid polymer electrolyte (SPE) was prepared by the solution casting technique. 0.50 g CMC (obtained from standard supplier Across Organic Co.) was dissolved into 50 ml of water, while, in another different beaker, an equal amount of thiourea derivative **1A** was dissolved in 50 ml methanol with constant stirring at 30 – 40 °C. After that, the thiourea solution was added into CMC solution with continuous stirring to form homogenous dissolution. The mixture was then poured into a petri dish and allowed for slowly evaporation at ambient temperature for the formation of thin film (**1A**-CMC).

#### Electrical conductivity measurement of **1A**-CMC

Electrical conductivity measurement was determined using HIOKI 3531 High-tester electrical impedance spectroscopy (EIS) in the frequency range 50 Hz – 1 MHz. The SPE sample of **1A**-CMC was cut into 2cm x 2cm (the same size as the stainless-steel blocking electrode and the sample was sandwiched between them).

## RESULTS AND DISCUSSION

To prepare *N*-decyloxyphenyl-*N'*-(chlorobenzoyl) thiourea (**1A**), equimolar amounts of 4-chlorobenzoyl chloride and ammonium thiocyanate were reacted in acetone at room temperature for 4 h, then 4-decyloxy aniline was added and the reaction mixture was refluxed for 1 h. The synthetic pathway in the preparation of the final product of interest (**1A**) is as described in Scheme 1.



**Scheme 1.** Reaction pathway to the synthesis of **1A**.

The biodegradable film of solid polymer electrolyte (SPE) was prepared by the solution casting technique. An equal amount of thiourea derivative **1A** dissolved in methanol was mixed with an aq. solution of CMC and the mixture was left slowly to evaporate at ambient temperature for the formation of thin film (**1A**-CMC).

The bulk resistance ( $R_b$ ) value was obtained from the plot of negative imaginary impedance versus the real part of impedance, in which the conductivity of the sample was calculated from Eq. 1:

$$\sigma = \frac{t}{R_b a} \quad (1)$$

where

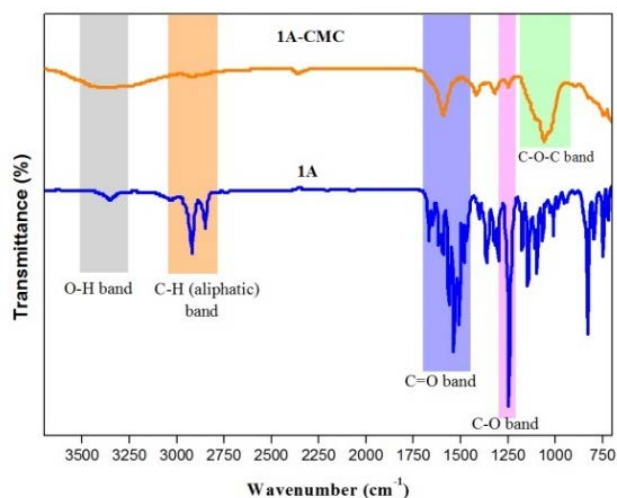
$t$  is the thickness of the film,

$a$  is for the film's area and

$R_b$  represents bulk resistance of the film.

#### Characterisation of polymer electrolyte film (**1A**-CMC)

Fourier-Transform Infrared (FTIR) analysis was carried out to determine the occurrence of complexation between CMC and thiourea (**1A**) compound. CMC was adopted as a host polymer while **1A** acts as dopant material to enhance the conductivity performance of SPE film.



**Figure 1.** Overlay FTIR spectra of **1A**-CMC and its dopant (**1A**)

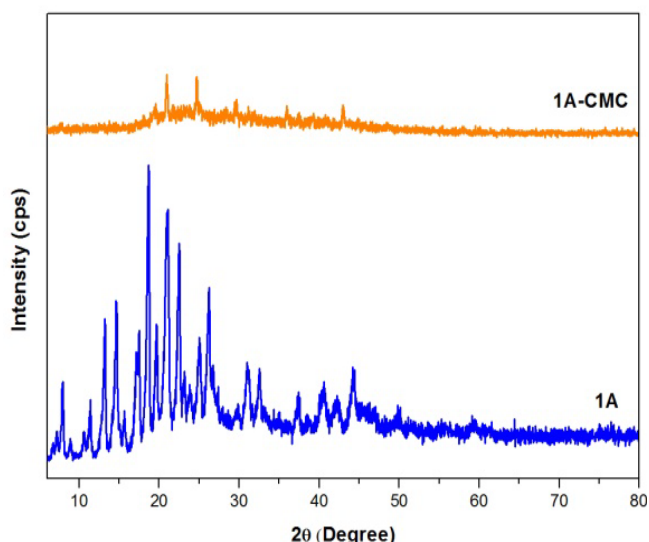
Fig.1 depicts the comparison of FTIR spectra to show evidence of the occurrence of complexation that has been taken place between CMC and **1A**.

From the above spectra, it was clearly shown that there are some changes in the wavenumber and intensity peaks of **1A** dopant upon the addition of CMC. The wavenumber and intensity of major absorption bands represent the main functional groups of **1A** decreases due to the existence of an interaction between **1A** with CMC and the interruption of amorphous nature of CMC to form new SPE film. In this sense, the presence of a new weak broad band of O-H group in the range of 3400-3200  $\text{cm}^{-1}$  in the **1A**-CMC film indicates the functionality of -OH group of CMC and confirms the existence of polymer host in newly developed SPE film.

The strong C=O stretching band and C-O ether bands at  $1650\text{ cm}^{-1}$  and  $1176\text{ cm}^{-1}$  from **1A** is shifted within the range of  $1700 - 1670\text{ cm}^{-1}$  and  $1130-1140\text{ cm}^{-1}$  upon addition of CMC which represents asymmetric stretching carboxylate ( $\text{COO}^-$ ) anions of (C=O) and (C-O) moieties functional group in the system.<sup>9</sup> Noticeable changes in wavenumber and intensity peak of these peaks prove that the interaction has occurred between **1A** as dopant and CMC host polymer to obtain the SPE film featuring **1A-CMC**. The existence of a strong peak at  $1100 - 1000\text{ cm}^{-1}$  attributed to C-O-C stretching band in the SPE system also indicate the presence of polymer host in **1A-CMC**.

### X-Ray diffraction study of 1A-CMC

XRD was used to reveal the nature of complexes of SPE film. The formation of complexes can be identified from the changes in diffraction peaks, the presence of new peak or/and absence of peak from the original position due to the increase of amorphousness of the sample. Fig.2 represents the overlaid XRD diffractogram of **1A** and **1A-CMC**.



**Figure 2.** XRD diffractograms of CMC-thiourea SPE film (**1A-CMC**) and thiourea dopant (**1A**)

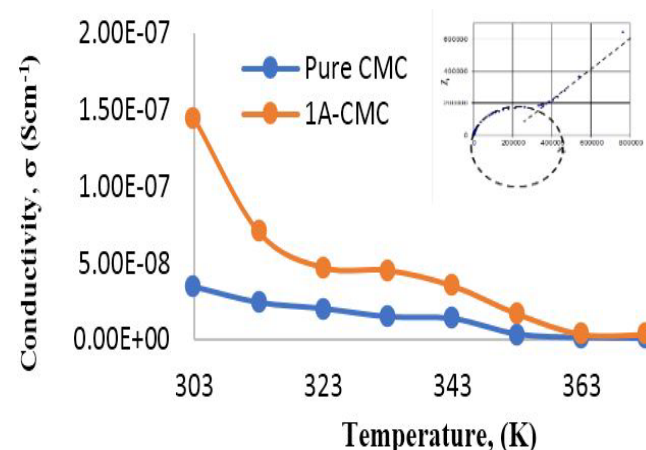
The XRD diffractogram of thiourea dopant (**1A**) at the ambient environment for  $2\theta$  from  $6^\circ$  to  $60^\circ$  shows many broad Bragg peaks at around  $\sim 15-25^\circ$ , indicating semicrystalline nature. By adding CMC, the diffraction peaks become broader and less intense as shown for sample CMC-thiourea (**1A-CMC**) due to the increase of the amorphous content of thiourea which decreases the degree of crystallinity.<sup>10</sup> This,

in turn, has increased the segmental mobility of the **1A-CMC** system and lowers the transition temperature  $T_g$ , which contributed to the increase in conductivity.

### Conductivity study of 1A-CMC

The conductivity of **1A-CMC** was investigated from the EIS study conducted using HIOKI 3232-50 LCR Hi-tester interfaced with a computer in which the resultant Cole-Cole plot and conductivity graph of **1A-CMC** SPE film at elevated temperature reveal that the highest conductivity achieved is  $1.44 \times 10^{-7}\text{ S cm}^{-1}$  at 303 K was obtained as in Fig. 3.

The high frequency of the obtained semicircle is related to the ionic conduction process in the bulk of the polymer electrolytes. While the semicircle possesses a low frequency attributed to the effect of electrode polarization in which related to the charge transfer process.<sup>11</sup> From the Cole-Cole plot, the information of the bulk resistant,  $R_b$  can be obtained to calculate the conductivity of the films. The bulk resistance,  $R_b$  can be retrieved from the intercept of the high-frequency semicircle and the low-frequency spike on the  $Z_r$ -axis. Equation 1 is used to calculate the conductivity,  $\sigma$  of **1A-CMC**.



**Figure 3.** The values of conductivity of pure CMC and **1A-CMC** (Inset: Cole-cole plot)

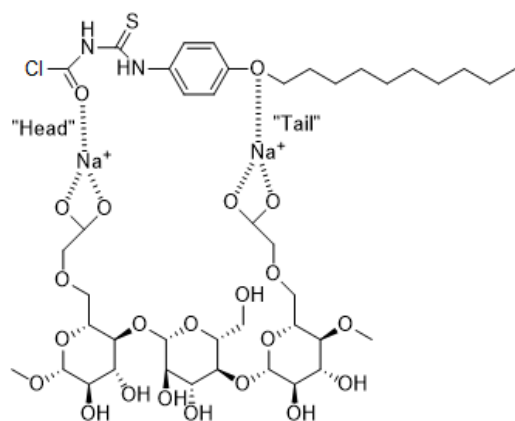
### Predicted Molecular Structure of 1A-CMC complex

To predict the molecular structure of the complex between thiourea and CMC (**1A-CMC**), the Mulliken charges values are measured using theoretical calculation using TD-DFT B3LYP/6-31G (d, p) basis set. The Mulliken charges values on the selected atoms of thiourea dopant (**1A**) is listed in Table 1.

**Table 1.** Mulliken effective charges value of selected atom on thiourea dopant (**1A**)

Thiourea dopant	Mulliken charges			Thiourea-CMC complex	Calculated distance, $\text{Na}^+$ to O, Å	
	O (C=O Amide)	S	O (alkoxy)		O=C	-O <sup>-</sup>
<b>1A</b>	-0.535	-0.262	-0.549	<b>1A-CMC</b>	2.2446	2.3108

From the Mulliken analysis, the charges on the oxygen atom of C=O amide are about two times higher than of sulfur atom of **1A**. While the values of charges observed for oxygen atoms of alkoxy were slightly similar to the oxygen atom of C=O amide. In this sense, we believed that the complexation is formed between the COO<sup>-</sup>Na<sup>+</sup> of CMC and the oxygen of amide as a 'head' and another COO<sup>-</sup>Na<sup>+</sup> of CMC to the oxygen alkoxy as a 'tail' due to the higher negative value of charges on oxygen atoms as depicted in Fig. 4. An attempt also has been made to optimize the complex formed between thiourea and CMC using the binding site of COO<sup>-</sup>Na<sup>+</sup> to the oxygen carbonyl of amide and alkoxy oxygen which resulted in a significant interaction in which the distance between the two poles are in the range of 2.23 to 2.25 Å.



**Figure 4.** The proposed molecular structure of thiourea-CMC (**A1-CMC**) complex

## CONCLUSION

Thiourea derivative featuring chloro substitution (**1A**) has been successfully synthesized and characterized using standard spectroscopic and analytical methods. In turn, **1A** has been doped into CMC host for the formation of SPE thin of **1A-CMC** via solution casting technique. The conductivity behavior of **1A-CMC** has been evaluated using electrical impedance spectroscopy (EIS). Results obtained revealed that, by addition of **1A** as a dopant in CMC host, the electrical conductivity of SPE film has increased from  $10^{-9}$  to  $10^{-7}$  Scm<sup>-1</sup>. This study indicates that **1A** exhibits great promises and show excellent potential to be explored further as conductive biodegradable films for various electronic applications in the near future.

## ACKNOWLEDGMENT

Special acknowledgment is dedicated to Ministry of Education (MOE), Malaysia for the funding of this research (FRGS 59253) and School of Fundamental Science Universiti Malaysia Terengganu (UMT) for research aid and facilities.

The paper was presented at Material Science Forum, Session 10: Biomaterials and Bioengineering in **AMSE-2019**, 21-24, July, Osaka, Japan.

## REFERENCES

- Pingaew, R., Prachayasittikul, V., Anuwongcharoen, N., Prachayasittikul, S., Ruchirawat, S. and Prachayasittikul, V., Synthesis and molecular docking of N,N'-disubstituted thiourea derivatives as novel aromatase inhibitors. *Bioorg. Chem.*, **2018**, *79*, 171-178.  
<https://doi.org/10.1016/j.bioorg.2018.05.002>
- Khairul, W. M., Hasan, M. A., Daud, A. I., Zuki, H. M., Kubulat, K., Kadir, M. A., Theoretical and experimental investigation of pyridylthiourea derivatives as ionophores for Cu(II) ion detection, *Malays. J. Anal. Sci.*, **2016**, *20*, 73-84.  
<https://doi.org/10.17576/mjas-2016-2001-08>
- Daud, A. I., Khairul, W. M., Mohamed H., Zuki, K., Kubulat, K., Synthesis and characterization of N-(4-Aminophenylethynylbenzotrile)-N'-(1-naphthoyl) thiourea as a single molecular chemosensor for carbon monoxide sensing, *J. Sulfur. Chem.*, **2014**, *35(6)*, 691-699.  
<https://doi.org/10.1080/17415993.2014.954248>
- Karthika, P., Ganesan, S., Thomas, A., Rani, T. M. S., Prakash, M., Influence of synthesized thiourea derivatives as a prolific additive with tris (1, 10-phenanthroline) cobalt(II/III) bis/tris (hexafluorophosphate)/hydroxypropyl cellulose gel polymer electrolytes on dye-sensitized solar cells, *Electrochim. Acta*, **2019**, *298*, 237-247.  
<https://doi.org/10.1016/j.electacta.2018.12.099>
- Rahamathullah, R., Khairul, W. M., Kubulat, K., Hussin, Z. M., Influence of curcumin as a natural photosensitizer in the conductive thin film of alkoxy cinnamoyl substituted thiourea. *Main Group Chem.*, **2015**, *14(3)*, 185-198.  
<https://doi.org/10.3233/MGC-150162>
- Ghazali, S. R., Kubulat, K. M., Isa, I. N., Samsudin, A. S., Khairul, W. M., Contribution of methyl substituent on the conductivity properties and behavior of CMC-alkoxy thiourea polymer electrolyte. *Mol. Cryst. Liq. Cryst.*, **2014**, *604(1)*, 126-141.  
<https://doi.org/10.1080/15421406.2014.968058>
- Balaya, P., Goyal, P. S., Non-Debye conductivity relaxation in a mixed glassformer system, *J. Non-Cryst. Solids*, **2005**, *351(19-20)*, 1573-1576.  
<https://doi.org/10.1016/j.jnoncrsol.2005.03.045>
- Marcì, G., Mele, G., Palmisano, L., Pulito, P., Sannino, A., Environmentally sustainable production of cellulose-based superabsorbent hydrogels, *Green Chemistry*, **2006**, *8(5)*, 439-444. <https://doi.org/10.1039/b515247j>
- Pushpamalar, V., Langford, S. J., Ahmad, M., Lim, Y. Y. Optimization of reaction conditions for preparing carboxymethyl cellulose from sago waste. *Carbohydr. Polym.*, **2006**, *64(2)*, 312-318.  
<https://doi.org/10.1016/j.carbpol.2005.12.003>
- Yang, S., Fu, S., Liu, H., Zhou, Y., Li, X., Hydrogel beads based on carboxymethyl cellulose for removal heavy metal ions. *J. Appl. Polym. Sci.*, **2011**, *119(2)*, 1204-1210.  
<https://doi.org/10.1002/app.32822>
- Ho, C. H., Shieh, C. Y., Tseng, C. L., Chen, Y. K., Lin, J. L., Decomposition pathways of glycolic acid on titanium dioxide. *J. Catal.*, **2009**, *261(2)*, 150-157.  
<https://doi.org/10.1016/j.jcat.2008.11.008>

Received: 07.04.2019.

Accepted: 31.05.2019.