พอลิเมอร์ฐานเมทัลโลซาเลนสำหรับรีดักชันของคาร์บอนไดออกไซด์

นายจีรวัฒน์ แก้วใหญ่

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METALLOSALEN-BASED POLYMERS FOR REDUCTION OF CARBON DIOXIDE

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งานวิจัยนี้แสดงการสังเคราะห์ชุดของคอปเปอร์และนิกเกิลซาเลนที่มีโครงสร้างไม่สมมาตรแบบไม่สมมาตรที่มีหมู่แทนที่เป็นอนุพันธ์ของไทโอฟีน และพิสูจน์เอกลักษณ์โดยเทคนิคเนวเคลียร์แม็กเนติคเนวเคลียร์แมก เนติคเนวเคลียร์แมกนิตอิลิโตร์กิวสมมติและแมสสเปกโทรscopy ความสามารถในการเป็นตัวเร่งปฏิกิริยาด้วยเคมีไฟฟ้าในระบบเอกพันธุ์ของสารประกอบเป็นหายสำหรับเรติคชันของคาร์บอนไดออกไซด์ที่ต้องการออกตัวอย่างมีค่าเดี่ยวของสารประกอบโดยใช้เทคนิคไซคลิกวอลแทมเมตري การศึกษาทางเคมีไฟฟ้าแสดงให้เห็นว่าสารประกอบเป็นไม่สามารถในการเป็นตัวเร่งปฏิกิริยาสำหรับเรติคชันของคาร์บอนไดออกไซด์เนื่องจากการเพิ่มขึ้นอย่างมีนัยสำคัญของค่ากระแสไฟฟ้าภายใต้ภาวะที่อิ่มตัวด้วยคาร์บอนไดออกไซด์เทียบกับภาวะที่อิ่มตัวด้วยไนโตรเจน ผลการศึกษาแสดงให้เห็นว่าการแทรกตัวของพันธะสามของคาร์บอน-คาร์บอนระหว่างหมู่ที่มาจากไทโอฟีนและโครงสร้างหลักของซาเลดน้ำไปสู่ความต้องการเคมี่ไฟฟ้าดีขึ้นที่ดังนี้ ในขณะที่การเพิ่มขึ้นของไทโอฟีนไม่มีอิทธิพลอย่างมีนัยสำคัญในด้านนี้ นอกจากนี้ การเติมน้ำมันอย่าง 3 เล็กเป็นแหล่งโปรตอนส่งผลให้เกิดการเพิ่มมากขึ้นของค่ากระแสไฟฟ้าที่ใช้ในการปฏิกิริยาของคาร์บอนไดออกไซด์อยู่ด้วย ผลการศึกษาจากปฏิกิริยาพอลิเมอร์ใช้เคมีการใช้ของสารประกอบเป็นหมายเหตุใหญ่ที่มาจากไทโอฟีนให้พอลิเมอร์ฐานเมทัลโลซาเลนที่ต้องการในกระบวนการพอลิเมอร์เรซิซัน แสดงให้เห็นว่าการเพิ่มขึ้นของไทโอฟีนนี้ง่ากลับความต้องการเคมี่ไฟฟ้าออกตัวดีขึ้นที่ดังนี้ ในขณะที่อนุพันธ์ที่มีหมู่เชื่อมต่อที่เป็นพันธะสามของคาร์บอน-คาร์บอนต่อการเคมี่ไฟฟ้าออกตัวดีขึ้นที่มากขึ้น อย่างไรก็ตาม ภาวะในกระบวนการพอลิเมอร์เรซิซันยังจำเป็นต้องได้รับการปรับปรุงเพิ่มเติม เพื่อให้ได้รับพิกัดที่ประสิทธิภาพมากขึ้นสำหรับเรติคชันของคาร์บอนไดออกไซด์
In this research, a series of novel asymmetric copper- and nickel-salens bearing thiophene-based substituents were successfully synthesized and characterized by nuclear magnetic resonance spectroscopy and mass spectrometry. Homogeneous electrocatalytic activities of these monomers toward reduction of CO₂ were investigated using cyclic voltammetry technique. Electrochemical studies showed these salen monomers are able to serve as catalysts in the electrochemical reduction of CO₂ due to the significantly increase of the current observed under CO₂-saturated condition, compared with those found under the N₂-saturated one. Results also revealed that insertion of the carbon-carbon triple-bond between the thiophene-based substituents and the salen core led to the lower required reduction potential, while the additional thiophene rings did not significantly influence in this aspect. Furthermore, addition of 3% of H₂O as a proton source resulted in even higher current enhancement in the reduction of CO₂. Electropolymerization of the target monomers through their thiophene-based units gave desirable metallosalen-based polymers in most cases. In the polymerization process, results showed that the introduction of bithiophenyl rings led to the lower required oxidation potential, while the derivatives containing carbon-carbon triple-bond spacers required higher oxidation potential than those having the thiophene-based substituents directly linked to the salen cores. However, further optimization of the polymerization condition is required to obtain more efficient films for the reduction of CO₂.
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<th>Description</th>
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<td>°C</td>
<td>degree Celcius</td>
</tr>
<tr>
<td>calcd</td>
<td>calculated</td>
</tr>
<tr>
<td>CDCl$_3$</td>
<td>deuterated chloroform</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>carbon dioxide</td>
</tr>
<tr>
<td>$^{13}$C-NMR</td>
<td>carbon nuclear magnetic resonance spectroscopy</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
</tr>
<tr>
<td>DMF</td>
<td>$N,N'$-dimethylformamide</td>
</tr>
<tr>
<td>d</td>
<td>doublet (NMR)</td>
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CHAPTER I
INTRODUCTION

In the present scenario, the world has global warming problem because of a concentration of greenhouse gases in the atmosphere that absorbed the sunlight and solar radiation without letting them bounce off the surface’s earth. Carbon dioxide (CO$_2$), is a one of greenhouse gases which has been released continuously from human activities,$^{1}$ including burning of fuel in industry and household. Subsequent climate change leads to ecological impacts, such as a change the amount of carbon in vegetation, sea-level rise, hotter heat waves, and more frequent natural disaster.$^{2-5}$ Because of this, there are several researches trying to find out ways to reduce CO$_2$ in the atmosphere by conversion of CO$_2$ to value added products.

The electrocatalytic reduction (ECR) of CO$_2$ is an attractive way to reduce and convert CO$_2$ to several fuels and chemicals,$^{6-9}$ such as carbon monoxide (CO), alcohol, aldehyde and hydrocarbon.$^{10-11}$ CO and/or formate (HCOO$^-$) were obtained from two-electron reduction of CO$_2$ system, whereas methanol (CH$_3$OH) and methane (CH$_4$) were obtained from six and eight-electron reduction of CO$_2$, respectively.$^{12-14}$ Many types of metals, such as copper (Cu), ruthenium (Ru) and molybdenum (Mo), have been studied for the ECR of CO$_2$ owing to their ability to proceed multi-electron transfer to reduce CO$_2$, but one of common drawbacks of this process is large overpotential required for the formation of desired products. Consequently, metal complexes become of interest so as to reduce the overpotential by well-designed ligand and suitable central metal to improve catalytic properties.$^{15}$ One of attractive metal complexes for the ECR of CO$_2$ is metal-salen complexes, also called as metallosalen. In the past few years, the metallosalen was investigated as catalyst for ECR of CO$_2$ to give many possible products could be obtained including CO, CH$_4$, ethylene (C$_2$H$_4$), ethane (C$_2$H$_6$), depending on applied potential and central metal of metallosalen.$^{16}$ Copper (Cu) and nickel (Ni) were used to form metallosalen electrocatalysts. Cu(0) is well known to facilitate the formation of hydrocarbons,$^{17-18}$ while Ni(0) reportedly promotes in H$_2$ production with slight formation of CO.$^{19}$
In this work, we are interested in synthesizing and investigating monomers and polymers of the metallosalen for the ECR of CO\textsubscript{2}. The target monomers contain thiophene-based substituents on peripheral phenol rings, and a Cu(II) or Ni(II) metal center as shown in Figure I–1. Thiophene is known to be easy to electrochemically polymerize to give polythiophene that has conductive property\textsuperscript{20}. Polythiophene derivatives had been used in various applications, such as organic light-emitting diodes (OLEDs),\textsuperscript{21-27} solar cells\textsuperscript{28-35} and chemical sensors.\textsuperscript{36-40} The metallosalen-embedded polythiophenes was previously synthesized by electropolymerization with lower potential, affording conductive polymer\textsuperscript{41-42}. Moreover, it was efficiently used for the ECR of O\textsubscript{2} to give H\textsubscript{2}O and H\textsubscript{2}O\textsubscript{2} as products.\textsuperscript{43}

\[
\begin{align*}
\text{MS-nT} & \quad & \text{MS-CC-nT} \\
\text{MS} & = & \text{Cu or Ni} \\
n & = & 1 \text{ or } 2
\end{align*}
\]

\textbf{Figure I–1: Structures of the target molecules}

Since it was found that unsymmetrical metallosalens served as versatile asymmetric catalysts leading to highly reactive and enantioselective catalytic reactions,\textsuperscript{44-48} the target salens for this work are designed to have a cyclohexyl stereocenter in the molecules. The resulting monomers will be subject to electropolymerization. Both monomers and polymers will be investigated for their physical properties and electrochemical properties, and their catalytic abilities for the ECR of CO\textsubscript{2}.

\textbf{1.1 Objectives of this research}

Synthesis and investigation of physical and electrochemical properties, as well as their catalytic abilities towards the ECR of CO\textsubscript{2} of unsymmetrical metallosalen monomers and polymers.
1.2 Scopes of this research

Each target unsymmetrical metallosalen monomers contains thienyl or bithiophenyl para-substituents on its phenolic groups and a Cu(II) or Ni(II) metal center as shown in Figure I–1. All target monomers will be characterized by spectroscopic techniques, including $^1$H- and $^{13}$C-nuclear magnetic resonance (NMR) spectroscopy, and mass spectrometry. The polymerization will be performed by cyclic voltammetry (CV). Both target monomers and polymers will be studied for their possible use as catalysts for the ECR of CO$_2$. 
CHAPTER II
THEORY AND LITERATURE REVIEWS

2.1 Electrochemical reduction of CO$_2$

The ECR of CO$_2$ is the conversion of CO$_2$ into the fuel or others value added chemicals.\textsuperscript{59-56} Considering thermodynamics of this reaction, the reduction of CO$_2$ by proton-coupled multi-electron processes are normally more favorable than single-electron step process because the latter requires high energy to convert CO$_2$ to CO$_2$\textsuperscript{−}.

Moreover, several thermodynamically stable products are produced in the proton-coupled multi-electron processes,\textsuperscript{57} corresponding to equations (1)–(6) from calculation of the standard reduction potential ($E^0$) in a 1 M aqueous solution of other solutes at pH 7 vs. normal hydrogen electrode (NHE) at 25ºC under 1 atm gas pressure.\textsuperscript{58}

\begin{align*}
\text{CO}_2 + e^- & \rightarrow \text{CO}_2\textsuperscript{−} \quad E^0 = -1.90 \text{ V} \quad (1) \\
\text{CO}_2 + 2\text{H}^+ + 2e^- & \rightarrow \text{HCOOH} \quad E^0 = -0.61 \text{ V} \quad (2) \\
\text{CO}_2 + 2\text{H}^+ + 2e^- & \rightarrow \text{CO} + \text{H}_2\text{O} \quad E^0 = -0.53 \text{ V} \quad (3) \\
\text{CO}_2 + 4\text{H}^+ + 4e^- & \rightarrow \text{HCHO} + \text{H}_2\text{O} \quad E^0 = -0.48 \text{ V} \quad (4) \\
\text{CO}_2 + 6\text{H}^+ + 6e^- & \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad E^0 = -0.38 \text{ V} \quad (5) \\
\text{CO}_2 + 8\text{H}^+ + 8e^- & \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad E^0 = -0.24 \text{ V} \quad (6)
\end{align*}

In kinetic aspect, a major challenge is a formation of nuclei and chemical bonds to convert CO$_2$ into other carbon-based molecules. Two mechanistic pathways have been proposed: one is the conversion of CO$_2$ to syngas (CO/H$_2$), followed by transformation to liquid fuel, such as gasoline, by Fisher-Tröpsch technologies;\textsuperscript{59} and the other is the direct conversion of CO$_2$ to liquid fuel, such as methanol, by electrocatalytic processes. Efficient electrocatalysis of CO$_2$ requires fast electron transfer at an electrode surface and acceleration of a chemical conversion.\textsuperscript{60} As a result, both electron transfer and chemical kinetics must be optimized, or in other words, the electrocatalysts must exhibit good thermodynamic match between the redox potential for the electron transfer reaction and the chemical reaction that is being catalyzed.\textsuperscript{61}
Several groups of organometallic compounds were reported to be efficient
elecrocatalysts for reduction of CO\textsubscript{2} because of their high efficiencies, selectivities and
turnover numbers,\textsuperscript{6} for example metal complexes of porphyrins,\textsuperscript{62-69} phthalo-
cyaines,\textsuperscript{70-76} cyclams,\textsuperscript{77-83} phosphines,\textsuperscript{84-93} bipyridines,\textsuperscript{94-101} and salen ligands.\textsuperscript{16}

2.2 Cyclic voltammetry (CV)

CV is a one of the most widely used techniques to determine the efficiency of
the electrocatalysts for the ECR of CO\textsubscript{2}\textsuperscript{102} due to its non-destructive nature, versatility
and informative details that can be relatively quickly extracted. Furthermore, it can
be used for a wide range of applications in organic and inorganic chemistry as well as
material development.\textsuperscript{103-104} In addition, both qualitative and quantitative information
about analyte in the electrochemical reaction can be obtained from this technique.\textsuperscript{105}
The electrochemical cell consists of three electrodes, i.e. a working electrode (WE), a
counter electrode (CE) (also called as an auxiliary electrode) and a reference electrode
(RE), which are immersed in an electrolyte solution\textsuperscript{106} as depicted in Figure II–1a.
During measurement, oxidation and/or reduction of the analyte occur at the WE
surface corresponding to applied potential (E\textsubscript{appl}). CV consists of the linearity of
potential scanning with a triangular waveform,\textsuperscript{106} sweeping through a potential range
and reversing the direction of the sweep in a cyclic wave as depicted in Figure II–1b.
The E\textsubscript{appl} value is simultaneously measured across the WE and the RE having a large
resistance and therefore no passing current. The current is then measured in response
to E\textsubscript{appl} across the WE and the CE, resulting in a plot between the current response
and E\textsubscript{appl}, which is called a cyclic voltammogram\textsuperscript{105} as shown in Figure II–1c. A forward
scan produces cathodic peak current (I\textsubscript{pc}) for reducing the analyte in a range of E\textsubscript{appl}
with a maximum cathodic current called cathodic peak potential (E\textsubscript{pc}). On the other
hand, a reverse scan produces anodic peak current (I\textsubscript{pa}) for oxidizing the reduced form
of the analyte back to the original form with a maximum anodic current as anodic peak
potential (E\textsubscript{pa}).
In a study of the electrocatalytic activity for the CO$_2$ reduction, the cyclic voltammogram of the electrocatalyst under a dry inert atmosphere (Ar or N$_2$) should show a reversible or quasi-reversible redox couple. When CO$_2$ was added in system, the diffusion limited current should increase significantly, while the potential shifts anodically, and the reversibility in the return oxidation wave may lose because of the chemical reaction between CO$_2$ and the electrocatalyst. For instance, Figure II–2a shows a cyclic voltammogram of cobalt(II)-tetraphenylporphyrin (CoTPP). When the CoTPP solution was saturated with CO$_2$, the first reduction for a Co$^{II}$/Co$^{I}$ step was unaffected but the second reduction for a Co$^{I}$/Co$^{0}$ step exhibited significant increase in current, compared with that obtained in the Ar-saturated condition. This catalytic reduction of CO$_2$ took place at a potential about 0.3 V less negative than that required for direct reduction of CO$_2$ in a similar solution without CoTPP (−2.02 vs. −2.32 V, vs. saturated calomel electrode (SCE)) (Figure II–2b). These results indicated that CoTPP can lower overpotential and increase the reaction kinetics of the CO$_2$ reduction.
Electropolymerization has been studied for a long time because of its several advantages, e.g. it is a catalyst-free procedure, it provides direct deposition of a doped polymer onto an electrode surface, control of film thickness is quite easy in situ characterization of the polymerization by electrochemical and/or spectroscopic techniques is possible. Moreover, rate of initiation can be easily controlled by varying electrochemical parameters and it can be carried out under mild condition. A great number of experiments have been performed in organic solvent (non-aqueous) systems with various kinds of supporting electrolytes. The widely used organic solvents include dimethylformamide (DMF), dimethylsulfoxide (DMSO) and acetonitrile (ACN), while the examples of the commonly used supporting electrolytes are tetra-butylammonium phosphate (TBAP), tetraethylammonium tetrafluoroborate (Et₄NBF₄), tetraethylammonium perchlorate (Et₄NCIO₄) and tetrabutylammonium perchlorate (nBu₄NCIO₄). Recently, aqueous systems have been of interest for the electropolymerization due to environmental friendliness and economic advantage. However, the selection of the solvent systems depends on the solubility of the monomers.
The electropolymerization can be classified according to occurrence of the polymer. If the polymer forms at a cathode, it will be called electroreduction polymerization (ERP). If the polymer forms at an anode, it will be called electrooxidation polymerization (EOP). In general, the EOP of organic materials has received more interest than the ERP because the formation of the polymer often occurs by the oxidation of the aromatic compounds. The examples of compounds that can be polymerized by the EOP include pyrrole, thiophene, indole, furan, benzene and derivatives, while the compounds that can be polymerized by ERP include methyl methacrylate, acrylonitrile and methacrylonitrile.

2.4 Metallosalen

Salen is an anionic tetradeutate ligand and widely used in coordination chemistry and homogeneous catalysis. The name of salen is an abbreviation from salicylaldehyde and ethylenediamine, which are substrates for condensation to give salen ligand. The salen ligand is a yellow micaceous solid that is favorably soluble in polar organic solvents. The structure of the salen ligand generally consists of two phenoxy groups connected by two methyne carbons via two imine bridges, which are formed by condensation between carbonyl group at ortho-positions of the phenoxy groups and amine groups of the ethylenediamine (Figure II–3).

![Figure II–3: A general structure of the salen ligand](image)

There are several methods for structural modification of the salen ligands, including the substitution on the phenoxy groups or the ethylene bridge and the metalation to give a complex called a metallosalen. Metallosalens were well known as chemical catalyst in various reactions such as enantioselective pinacol coupling, copolymerization, enantioselective Nazarov cyclization, asymmetric sulffimidation and sigmatropic rearrangement. Later, the catalytic efficiency of metallosalen was improved by substitution on salen ligand in order to use as a catalyst.
for copolymerization between cyclohexene oxide and CO$_2$\textsuperscript{140-141}. Moreover, the substitution of acetylene derivatives on the metallosalen structure at peripheral phenol rings was investigated for catalytic efficiency in Henry reaction\textsuperscript{142-143}.

### 2.4.1 Synthesis of metallosalen

Synthesis of the metallosalen was reported for the first time in 1933 by Pfeiffer and co-workers\textsuperscript{130}. In 1950, Diehl\textsuperscript{131} suggested a simple route of synthesis of the salen ligand via condensation between salicylaldehyde and ethylenediamine in hot ethanol (Scheme II–1).

![Scheme II–1: Synthesis of the salen ligand under a Diehl’s condition.](image)

Later, condensation between salicylaldehyde derivatives and 1,2-diamine derivatives in ethanol in the similar manner was reported to give the corresponding salen ligands as precipitates in 50–80% yield (Scheme II–2). The metallosalens can be quantitatively prepared via metallation between the salen ligands and various metal salts in appropriate solvents\textsuperscript{140-141} (Scheme II–3).

![Scheme II–2: Synthesis of substituted-salen ligands](image)

![Scheme II–3: Metallation of substituted-metallosalens](image)
2.5 Thiophene

Thiophene is a five-membered ring heterocyclic aromatic compound, which can be polymerized to be polythiophene (Figure II-4), which exhibits conductive properties. Its conductive properties are caused by delocalization of electrons throughout its conjugated backbone. Furthermore, high environmental stability and well-established structural modification of polythiophene enable great developments of its derivatives for several electronic applications, such as capacitors, light-emitting diodes, field-effect transistors, solar cells and electrochromic device.

![Figure II-4: A structure of polythiophene.](image)

Polythiophenes can be prepared by means of two routes, chemical and electrochemical synthesis. In case of chemical synthetic routes, nickel- and palladium-based cross coupling chemistry are adapted to the efficient synthesis of polythiophene and its derivatives. Two important features of these cross-coupling reactions are selective C-C bond formation and regioselectivity of the catalyst. Scheme II-4 shows published preparation procedures of polythiophenes using nickel- and palladium-based catalysts. The upper route involves in the formation of two intermediates by reacting a 2,5-dibromothiophene derivative with Rieke zinc (Zn*) under a Rieke’s method. The resulting Zn-complexes were accessed in the cross-coupling reaction using Pd(PPh₃)₄, affording a corresponding polythiophene derivative. The lower way starts from synthesis of intermediates through Grignard metathesis, followed by nickel-catalyzed coupling reaction to get the corresponding polymer.
As regards the electrochemical polymerization, the cyclic voltammograms and the proposed mechanism of the electropolymerization of thiophene are depicted in Figure II–5. The electrochemical processes of thiophene starts from the oxidation step generating cation radical species, followed by coupling and aromatization to form its dimer. After that, a sequence of subsequent dimerization steps proceeds to the formation of oligomers and polymers. The cyclic voltammogram shows a current density increased as more polythiophene was formed on the electrode surface.  

2.6 Thiophene-substituted metallosalen derivatives

In 1998, Kingsborough and Swager studied electroactivity of the thiophene-substituted cobalt-salen (CoS-T) which was synthesized through the palladium-based cross coupling, followed by the condensation and the cobalt metallation (Scheme II–
After that, CoS-T was successfully polymerized by oxidative polymerization, while no film growth was observed for the metal-free derivative.

**Scheme II–5: Synthesis and oxidative polymerization of CoS-T**

Furthermore, EDOT-substituted cobalt-salen (CoS-EDOT), where EDOT stands for 3,4-ethylenedioxythiophene (Figure II–6), was synthesized and polymerized in the similar manner as CoS-T. Compared with the cyclic voltammograms of electro-polymerization of CoS-T, those of CoS-EDOT showed overall decrease in the oxidation potential as depicted in Figure II–7, indicating that a more electron-rich EDOT led to easier oxidative polymerization. In addition, an EDOT-substituted cobalt-salen polymer (poly(CoS-EDOT)) was investigated for the electrocatalytic activity for oxygen (O₂) reduction. The result showed that poly(CoS-EDOT) was a highly conducting hybrid material capable of O₂ reduction by four-electron reduction process to produce H₂O and H₂O₂.

**Figure II–6: A structure of CoS-EDOT**
Figure II–7: Cyclic voltammograms of oxidative polymerization of (a) CoS–T and (b) CoS–EDOT\textsuperscript{41}

In 2006, asymmetric thiophene-derivatives metallosalens 1, 2 and 3 (Figure II–8) were synthesized and polymerized to investigate effects of their structures on the electroactivity.\textsuperscript{187} The [1S,2S]-cyclohexyl bridge was introduced to these molecules to improve the catalytic activities for Nozaki-Hiyama-Kishi reaction and enantioselectivities of the metallosalen,\textsuperscript{188} which was found that asymmetric metallosalen gave better those properties than symmetric one.\textsuperscript{189–190} Moreover, thienyl rings were used to improve the stability, reversibility of redox couples and conductivity of the resulting polymers.\textsuperscript{41–42}

Figure II–8: Structures of 1, 2 and 3
CHAPTER III
EXPERIMENTS

3.1 Synthesis

3.1.1 Materials and methods

All chemicals were commercially available and used as received unless noted otherwise.

$^1$H- and $^{13}$C-NMR spectra were recorded on a Varian Mercury 400 NMR Spectrometer and a Bruker Avance 400 NMR Spectrometer respectively and obtained in CDCl$_3$. Chemical shifts (δ) were reported in parts per million (ppm) relative to the residual CHCl$_3$ signal (7.26 ppm for $^1$H-NMR spectroscopy and 77.0 ppm for $^{13}$C-NMR spectroscopy.

Mass spectra were obtained using high-resolution electrospray ionization (HR-ESI) and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometers using α-dithranol as a matrix.

3.1.2 2-Hydroxy-5-thiophen-2-yl-benzaldehyde (H-1T-B)

Following a reported procedure with slight modification by using a protected boronic acid derivative instead of thiophenyl-2-boronic acid, a mixture of 5-bromosalicylaldehyde (0.396 g, 1.97 mmol), 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-thiophene (0.496 g, 2.36 mmol), [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) complex with CH$_2$Cl$_2$ (PdCl$_2$(dpdpf)-CH$_2$Cl$_2$, 0.082 g, 0.10 mmol) and sodium carbonate (Na$_2$CO$_3$, 0.209 g, 1.97 mmol) in dimethoxyethane (DME)/water (3/1, 6 mL, degassed with N$_2$) was stirred under N$_2$ atmosphere at 100 °C for 5 h. After cooling to room temperature, the reaction mixture was poured into deionized water (20 mL). The aqueous mixture was extracted with CH$_2$Cl$_2$ (3x15 mL), and the combined organic
phase was dried over anhydrous MgSO₄. The solvent was removed under reduced pressure and the resulting crude was purified by column chromatography over silica gel (diethyl ether (Et₂O)/hexanes 1/1) to give a yellow powder. After recrystallization in hexanes, compound H-1T-B was obtained as yellow crystals (0.254 g, 63%). m.p. 108–110 °C. ¹H NMR δ 7.00 (d, J = 8.4 Hz, 1H), 7.04–7.11 (m, 1H), 7.20–7.24 (m, 1H), 7.24–7.28 (m, 1H), 7.70–7.76 (m, 2H), 9.90 (s, 1H), 11.00 (s, 1H) (Figure A-1); ¹³C NMR δ 118.3, 120.7, 122.9, 124.7, 126.9, 128.2, 130.6, 134.6, 142.6, 161.0, 196.5 (Figure A-2). These characterization data are consistent with those described in a published report.¹⁸⁸

3.1.3 2-Hydroxy-5-(2,2′-bithiophen-5-yl)-benzaldehyde (H-2T-B)

In a similar manner to the synthesis of H-1T-B, a mixture of 5-bromosalicylaldehyde (0.396 g, 1.97 mmol), 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2′-bithiophene (0.689 g, 2.36 mmol), PdCl₂(dppf)-CH₂Cl₂ (0.082 g, 0.10 mmol) and Na₂CO₃ (0.209 g, 1.97 mmol) in DME/H₂O (3/1, 6 mL, degassed with N₂) was stirred under N₂ atmosphere at 100 °C for 5 h. After above-mentioned work-up process, the resulting crude was purified by column chromatography over silica gel (CH₂Cl₂/hexanes 1/1) to provide dark yellow powder. After recrystallization in hexanes, compound H-2T-B was obtained as a dark yellow solid (0.338 g, 60%). m.p. 179–181 °C. ¹H NMR δ 7.02–7.05 (m, 2H), 7.14 (s, 1H), 7.19 (d, J = 2.4 Hz, 1H), 7.23 (d, J = 4.0 Hz, 1H), 7.24–7.26 (m, 1H), 7.73–7.77 (m, 2H), 9.95 (s, 1H), 11.01 (s, 1H) (Figure A-3); ¹³C NMR δ 118.5, 120.8, 123.6, 123.9, 124.7, 124.8, 126.7, 128.0, 130.4, 134.3, 136.8, 137.2, 141.3, 161.2, 196.5 (Figure A-4); HR-ESI-MS m/z: [M⁺] calcd for C₁₅H₁₀O₂S₂, 286.0122; found, 286.0123 (Figure A-5).
3.1.4 2-Hydroxy-5-(2-(thiophen-2-yl)-ethyn-1-yl)-benzaldehyde (H-CC-1T-B)

Following a reported procedure, a mixture of 5-iodosalicyladehyde (0.496 g, 2.00 mmol), 2-ethynylthiophene (0.270 g, 2.50 mmol), bis[triphenylphosphine]-dichloropalladium(II) (PdCl₂(PPh₃)₂, 0.070 g, 0.10 mmol), Cul (0.038 g, 0.20 mmol) and PPh₃ (0.052 g, 0.20 mmol) in toluene (6 mL, degassed with N₂) was stirred at room temperature for 15 min. After that, triethylamine (NEt₃, 3 mL) was added slowly, and then a mixture was stirred under N₂ atmosphere at room temperature for 18 h. Then, the reaction mixture was poured into CH₂Cl₂ (25 mL) and the resulting solution was extracted with a saturated aqueous solution of NH₄Cl (3x15 mL) and a saturated aqueous solution of NaCl (1x15 mL). The combined organic phase was dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure. The resulting crude was purified by column chromatography over silica gel (CH₂Cl₂/hexanes 1/4) to give an off-white powder which was recrystallized in hexanes to yield compound H-CC-1T-B as white crystals (0.268 g, 59%). m.p. 103–105 °C. ¹H NMR δ 6.95–7.05 (m, 2H), 7.23–7.34 (m, 2H), 7.64 (dd, J = 8.8, 2.0 Hz, 1H), 7.73 (d, J = 1.6 Hz, 1H), 9.88 (s, 1H), 11.12 (s, 1H) (Figure A–6); ¹³C NMR δ 82.3, 91.3, 115.0, 118.3, 120.7, 123.1, 127.3, 127.5, 132.1, 136.9, 139.7, 161.6, 196.1 (Figure A–7); HR-ESI-MS m/z: [M⁺] calcd for C₁₃H₈O₂S, 228.0245; found, 228.0240 (Figure A–8).

3.1.5 2-Hydroxy-5-(2-(2,2'-bithiophen-5-yl)-ethyn-1-yl)-benzaldehyde (H-CC-2T-B)

In a similar manner to synthesis of H-CC-1T-B, a mixture of 5-iodosalicyladehyde (0.496 g, 2.00 mmol), 5-ethynyl-2,2'-bithiophene (0.476 g, 2.50 mmol), PdCl₂(PPh₃) (0.070 g, 0.10 mmol), Cul (0.038 g, 0.20 mmol) and PPh₃ (0.052 g, ...
0.20 mmol) in toluene (6 mL, degassed with N₂) was stirred at room temperature for 15 min, NEt₃ (3 mL) was added slowly, and then a mixture was stirred continuously under N₂ atmosphere at room temperature for 18 h. After above-mentioned work-up process, the resulting crude was purified by column chromatography over silica gel (CH₂Cl₂/hexanes 1/2) to give yellow powder which was recrystallized in hexanes to yield compound H-CC-2T-B as a light-yellow solid (0.310 g, 50%). m.p. 146–148 °C.

³¹H NMR δ 6.99 (d, J = 8.4 Hz, 1H), 7.03 (dd, J = 5.2, 3.6 Hz, 1H), 7.07 (d, J = 3.6 Hz, 1H), 7.17 (d, J = 4.0 Hz, 1H), 7.20 (d, J = 2.8 Hz, 1H), 7.23–7.26 (m, 1H), 7.64 (dd, J = 8.4, 1.6 Hz, 1H), 7.73 (d, J = 1.6 Hz, 1H), 9.88 (s, 1H), 11.13 (s, 1H) (Figure A-9); ¹³C NMR δ 82.3, 92.3, 115.0, 118.4, 120.7, 121.7, 123.7, 124.4, 125.2, 128.1, 133.0, 136.8, 139.2, 139.7, 161.7 196.1 (Figure A-10); HR-ESI-MS m/z: [M⁺] calcd for C₁₇H₁₀O₂S₂, 310.0122; found, 310.0127 (Figure A-11).

3.1.6 General procedure for salen ligand formation

Following a reported procedure,¹⁸⁶ to a solution of a salicylaldehyde derivative (1.70 equivalent) in ethanol (15 mL) was treated with (S,S)-1,2-cyclohexanediocamine (1.00 equivalent) at 60 °C for 1.5 h. After the reaction mixture was cooled to room temperature, the resulting solid was filtered, washed with ethanol, methanol and hexane, and recrystallized in chloroform and hexane to afforded desired products.

3.1.6.1 (S,S)-N,N'-bis(salicylidene-5-thiophen-2-yl)-cyclohexane-1,2-diamine (H₂S-1T)

H-1T-B (0.402 g, 1.97 mmol) was reacted with (S,S)-1,2-cyclohexanediocamine (0.116 g, 1.02 mmol) to give the title compound as a yellow crystal (0.312 g, 65%); m.p.
115–117 °C.  

$^1$H NMR δ 1.45–1.53 (m, 2H), 1.68–1.80 (m, 2H), 1.84–2.03 (m, 4H), 3.31–3.38 (m, 2H), 6.91 (d, J = 8.4 Hz, 2H), 7.00–7.04 (m, 2H), 7.10–7.14 (m, 2H), 7.18 (d, J = 4.8 Hz, 2H), 7.37 (s, 2H), 7.44–7.52 (m, 2H), 8.30 (s, 2H), 13.38 (s, 2H) (Figure A–12).  

$^{13}$C NMR δ 24.2, 33.1, 72.8, 117.5, 118.7, 122.2, 123.9, 125.6, 128.0, 128.9, 130.2, 143.8, 160.7, 164.6 (Figure A–13); MALDI-TOF-MS m/z: found, 486.586 (100) [M$^+$]; calcd avg mass, 486.648 (M$^+$; $M = C_{28}H_{26}N_2O_2$) (Figure A–14). These characterization data are consistent with those described in a published report.$^{188}$

3.1.6.2 (S,S)-N,N$'$-bis(salicylidene-5-(2,2$'$-bithiophen-5-yl)-cyclohexane-1,2-diamine (H$_2$S-2T) 

H-2T-B (0.292 g, 1.02 mmol) was reacted with (S,S)-1,2-cyclohexanediylamine (0.069 g, 0.60 mmol) to give the title compound as a light orange crystal (0.183 g, 55%); m.p. 240–242 °C.  

$^1$H NMR δ 1.47–1.60 (m, 2H), 1.70–1.81 (m, 2H), 1.86–2.04 (m, 4H), 3.33–3.39 (m, 2H), 6.92 (d, J = 8.4 Hz, 2H), 6.98–7.04 (m, J = 3.4 Hz, 2H), 7.08 (d, J = 3.6 Hz, 2H), 7.15 (d, J = 2.8 Hz, 2H), 7.19 (d, J = 4.0 Hz, 2H), 7.24–7.29 (m, 2H), 7.35 (d, J = 1.6 Hz, 2H), 7.47 (dd, J = 8.4, 2.0 Hz, 2H), 8.30 (s, 2H), 13.40 (s, 2H) (Figure A–15).  

$^{13}$C NMR δ 24.3, 33.1, 72.8, 117.7, 118.8, 122.8, 123.5, 124.3, 124.6, 125.3, 127.9, 128.6, 129.9, 135.8, 137.6, 142.6, 160.9, 164.7 (Figure A–16); MALDI-TOF-MS m/z (mol%): found, 650.646 (100) [M$^+$]; calcd avg mass, 650.888 (M$^+$; $M = C_{38}H_{30}N_2O_2$) (Figure A–17); HR-ESI-MS m/z: [(M+$+$H)$^+$] calcd for $C_{38}H_{30}N_2O_2$ 651.1263; found, 651.1261 (Figure A–18).

3.1.6.3 (S,S)-N,N$'$-bis(salicylidene-5-(2-thiophen-2-yl)-ethyn-1-yl)-cyclohexane-1,2-diamine (H$_2$S-CC-1T) 

H-CC-1T-B (0.233 g, 1.02 mmol) was reacted with (S,S)-1,2-cyclohexanediylamine (0.069 g, 0.60 mmol) to give the title compound as a light-yellow crystal (0.243 g, 52%); m.p. 193–195 °C.  

$^1$H NMR δ 1.35–1.44 (m, 2H), 1.58–1.69 (m, 2H), 1.78–1.90 (m, 4H), 3.21–3.28 (m, 2H), 6.80 (d, J = 8.4 Hz, 2H), 6.89–6.93 (m, 2H), 7.15 (d, J = 2.4 Hz, 2H), 7.17 (d, J = 5.2 Hz, 2H), 7.26 (s, 2H), 7.30–7.34 (m, 2H), 8.14 (s, 2H), 13.49 (s, 2H) (Figure A–19).  

$^{13}$C NMR δ 24.2, 33.0, 72.6, 81.2, 92.5, 113.2, 117.6, 118.6, 123.7, 127.0, 127.2, 131.6, 134.8, 135.5, 161.6, 164.18 (Figure A–20); MALDI-TOF-MS m/z (mol%): found, 534.713
(100) [M⁺]; calcd avg mass, 534.692 (M⁺; M = C₃₂H₆₀N₂O₂S₂) (Figure A–21); HR-ESI-MS m/z: [(M+H)⁺] calcd for C₃₂H₆₀N₂O₂S₂ 535.1508; found, 535.1505 (Figure A–22).

3.1.6.4 (S,S)-N,N’-bis(salicylidene-5-(2-(2,2′-bithiophen-5-yl)-ethyn-1-yl)-cyclohexane-1,2-diamine (H₂S-CC-2T)

H-CC-2T-B (0.317 g, 1.02 mmol) was reacted with (S,S)-1,2-cyclohexanediamine (0.069 g, 0.60 mmol) to give the title compound as a dark yellow crystal (0.390 g, 49%); m.p. 129–131 °C. ¹H NMR δ 1.45–1.54 (m, 2H), 1.68–1.78 (m, 2H), 1.85–2.01 (m, 4H), 3.32–3.38 (m, 2H), 6.89 (d, J = 8.4 Hz, 2H), 7.00–7.03 (m, 2H), 7.04 (d, J = 3.6 Hz, 2H), 7.11 (d, J = 3.6 Hz, 2H), 7.18 (d, J = 2.4 Hz, 2H), 7.23 (d, J = 4.0 Hz, 2H), 7.32–7.36 (m, 2H), 7.40 (dd, J = 8.4, 1.6 Hz, 2H), 8.23 (s, 2H), 13.59 (s, 2H) (Figure A–23); ¹³C NMR δ 24.1, 32.9, 72.5, 81.2, 93.5, 113.1, 117.5, 118.5, 122.2, 123.5, 124.1, 124.9, 127.9, 132.3, 134.7, 135.4, 136.8, 138.5, 161.6, 164.0 (Figure A–24); MALDI-TOF-MS m/z (%): found, 699.010 (100) [M⁺]; calcd avg mass, 698.932 (M⁺; M = C₄₀H₄₀N₂O₂S₄) (Figure A–25); HR-ESI-MS m/z: [(M+H)⁺] calcd for C₄₀H₄₀N₂O₂S₄ 699.1263; found, 699.1269 (Figure A–26).

3.1.7 General procedure for salen complexation

Following a reported procedure,¹⁸⁸ a solution of salen ligand (0.50 mmol) in CH₂Cl₂ (30 mL) was reacted with Ni(OAc)₂ or Cu(OAc)₂ (0.55 mmol, 1.1 mol equivalent) in MeOH (15 mL) at room temperature. After 5 h, the reaction mixture was poured into water (25 mL), and the separated organic phase was extracted with a saturated aqueous solution of NH₄Cl (3x15 mL) and a saturated aqueous solution of NaCl (3x15 mL). The combined extract was dried over anhydrous MgSO₄, and the solvent was removed under reduced pressure. The resulting crude was filtered and washed with methanol and hexane to afford the desired product.

CuS-1Th (0.219 g, 80%), a dark green solid; m.p. > 250 °C. MALDI-TOF-MS m/z (%): found, 547.748 (100) [M⁺]; calcd avg mass, 548.178 (M⁺; M = C₂₈H₂₆CuN₂O₂S₂) (Figure A–27).
NiS-1Th (0.231 g, 85%), a dark yellow solid; m.p. > 250 °C. MALDI-TOF-MS m/z (%): found, 542.257 (100) [M⁺]; calcd avg mass, 543.325 (M⁺; M = C_{28}H_{28}N_{2}NiO_{2}S_2) (Figure A–28).

CuS-2Th (0.249 g, 70%), a brown green solid; m.p. > 250 °C. MALDI-TOF-MS m/z (%): found, 711.954 (100) [M⁺]; calcd avg mass, 712.418 (M⁺; M = C_{36}H_{26}CuN_{2}O_{2}S_4) (Figure A–29).

NiS-2Th (0.255 g, 73%), a brown yellow solid; m.p. > 250 °C. MALDI-TOF-MS m/z (%): found, 705.727 (100) [M⁺]; calcd avg mass, 707.565 (M⁺; M = C_{36}H_{26}N_{2}NiO_{2}S_4) (Figure A–30).

CuS-CC-1T (0.223 g, 75%), a dark green solid; m.p. > 250 °C. MALDI-TOF-MS m/z (%): found, 594.774 (100) [M⁺]; [M+Na]⁺, 659.909 [(M+Cu)⁺]; calcd avg mass, 596.222 (M⁺; M = C_{32}H_{24}CuN_{2}O_{2}S_2) (Figure A–31); HR-ESI-MS m/z: [(M+H)⁺] calcd for C_{32}H_{24}CuN_{2}O_{2}S_2, 596.0648; found, 596.0645 (Figure A–32).

NiS-CC-1T (0.236 g, 80%), a dark yellow solid; m.p. > 250 °C. MALDI-TOF-MS m/z (%): found, 590.290 (100) [M⁺]; calcd avg mass, 591.369 (M⁺; M = C_{32}H_{24}N_{2}NiO_{2}S_2) (Figure A–33); HR-ESI-MS m/z: [(M+H)⁺] calcd for C_{32}H_{24}N_{2}NiO_{2}S_2, 591.0705; found, 591.0712 (Figure A–34).

CuS-CC-2T (0.269 g, 71%), a brown green solid; m.p. > 250 °C. MALDI-TOF-MS m/z (%): found, 758.324 (100) [M⁺], 823.316 [(M+Cu)⁺]; calcd avg mass, 760.462 (M⁺; M = C_{40}H_{28}CuN_{2}O_{2}S_4) (Figure A–35); HR-ESI-MS m/z: [(M+H)⁺] calcd for C_{40}H_{28}CuN_{2}O_{2}S_4, 760.0402; found, 760.0407 (Figure A–36).

NiS-CC-2T (0.279 g, 74%), a brown yellow solid; m.p. > 250 °C. MALDI-TOF-MS m/z (%): found, 753.408 (100) [M⁺]; calcd avg mass, 755.609 (M⁺; M = C_{40}H_{28}N_{2}NiO_{2}S_4) (Figure A–37); HR-ESI-MS m/z: [(M+H)⁺] calcd for C_{40}H_{28}N_{2}NiO_{2}S_4, 755.0460; found, 755.0434 (Figure A–38).
3.2 Electrochemistry

3.2.1 Electropolymerization

The electropolymerization was performed using a Metrohm-Autolab PGSTAT101 potentiostat in a three-electrode cell containing the ITO-coated glass as the WE, Pt plate as the CE and a silver chloride coated on silver wire (Ag/AgCl) as a quasi-reference electrode (QRE). The concentration of monomers at their maximum solubility (0.50–0.10 mM) in dry CH₂Cl₂ containing 0.1 M nBu₄NPF₆ was used. The solution was degassed with N₂ for 15 min prior to the electropolymerization. The polymerization was carried out at cyclic potential between −0.2 V and 1.8 V versus Ag/AgCl QRE at a scan rate of 100 mV·s⁻¹ with the number of repeated scanning of 10 cycles.

3.3.2 ECR of CO₂

The ECR of CO₂ was performed using a Metrohm-Autolab PGSTAT101 potentiostat. For a homogeneous condition, the electrochemical reduction was conducted in the three-electrode cell containing a glassy carbon as the WE, Pt plate as the CE and the Ag/AgCl QRE. The concentration of the monomers was 0.50 mM in dry DMF containing 0.1 M nBu₄NPF₆. The electrochemical behavior of the monomers was studied by purging N₂ to the solution for 15 min prior to the measurements which were proceeded at cyclic potential between 0.0 V and −2.0 V versus Ag/AgCl QRE at a scan rate of 50 mV·s⁻¹, for 3 cycles. After that the same solution was purged with CO₂ for 15 min to determine their electrocatalytic activities for the ECR of CO₂ by using the same potential range, scan rate and number of scan. For the heterogeneous ECR of CO₂, the same cyclic voltammetry setup on that described for the monomers was used, except that the WE in this case was the polymer films on the ITO-coated glass, the electrolyte solution contained no salen monomer and the potential range was between 0.0 V and −1.7 V.
CHAPTER IV
RESULTS AND DISCUSSION

This research mainly focuses on synthesis, characterization and investigation of physical properties and electrochemical properties of novel unsymmetrical metallosalen bearing thienyl derivatives substituents, which are shown in Figure IV-1. Target compounds MS-nT consist the metallosalen bear thienyl or bithiophenyl units directly attached on their phenoxy rings, while target compounds MS-CC-nT have carbon-carbon triple bonds between the metallosalen and their thienyl or bithiophenyl units. These compounds will be used as monomers for the electropolymerization. After that, the target monomers and the resulting polymers will be investigated for their possible use for electrocatalytic reduction of CO\textsubscript{2}. Thus, in this chapter, the content includes synthesis and characterization of the target monomers, the investigation of the electrocatalytic activity of the monomers towards the ECR of CO\textsubscript{2}, and electropolymerization of the monomers and the determination of the potential use of the resulting polymers for the ECR of CO\textsubscript{2}.

4.1 Synthesis of salen monomers

Synthesis of MS-nT started with Suzuki cross-coupling of 5-bromosalicylaldehyde with an excess amount of thiophene-2-boronic acid pinacol ester or 2,2'-bithiophene-5-boronic acid pinacol ester in the presence of PdCl\textsubscript{2}(dppf)-CH\textsubscript{2}Cl\textsubscript{2} and Na\textsubscript{2}CO\textsubscript{3} in a DME/H\textsubscript{2}O mixture\textsuperscript{188} as depicted in Scheme IV-1, leading to compound H-1T-B or H-2T-B in 63% or 60%, respectively. Formation of compound H-1T-B was
confirmed by a $^1$H-NMR spectrum showing a singlet peak of a hydroxyl proton at 11.00 ppm, a singlet peak of an aldehyde proton at 9.90 ppm, and a group of peaks corresponding to protons on the benzene and thiophene rings at around 7.00–7.76 ppm. These spectral data are consistent with those reported in a literature.\textsuperscript{188} In a similar manner, a $^1$H-NMR spectrum of H-2T-B showed a singlet peak of a hydroxyl proton at 11.01 ppm, a singlet peak of an aldehyde proton at 9.95 ppm, and a group of peaks indicating protons on benzene and bithiophene rings at around 7.02–7.77 ppm. Furthermore, a HS-ESI mass spectrometry showed a molecular ion peak of H-2T-B at $m/z$ 286.0123 [(M+H)$^+$], confirming successful formation of H-2T-B.

Scheme IV–1: Synthesis of MS-nT derivatives
After that, H-1T-B and H-2T-B were condensed with an excess amount of (S,S)-1,2-cyclohexanediamine at 60°C in ethanol to avoid complication due to the co-precipitation of H-1T-B and H-2T-B with the desirable products. The reactions were completed to afford compounds H$_2$S-1T and H$_2$S-2T in 65% and 55%, respectively. Each of their $^1$H-NMR spectra exhibited a singlet of two protons of the hydroxyl groups at 13.38–13.40 ppm due to deshielding effect from electron withdrawing phenyl rings and imine groups. Their two imine protons gave a singlet peak at 8.30 ppm, while the singlet peaks of the aldehyde protons observed in H-1T-B and H-2T-B disappeared. Besides, protons of their cyclohexane units gave three multiplet peaks at 1.47–3.39 ppm. Additionally, formation of the H$_2$S-1T and H$_2$S-2T was also confirmed by their spectra from mass spectrometry, which exhibited their molecular ion peaks at m/z 486.586 and 650.646, respectively. Furthermore, a HS-ESI mass spectrum showed the molecular ion peaks of H$_2$S-2T at m/z 651.1261 [(M+H)$^+$].

Finally, metallation of H$_2$S-1T with Cu(OAc)$_2$ or Ni(OAc)$_2$ was achieved to give CuS-1T or NiS-1T in 80% or 85% yield, respectively. Likewise, H$_2$S-2T was Cu- and Ni-metalated, resulting in CuS-2T and NiS-2T in 70% and 73%, respectively. The formation of CuS-1T, NiS-1T, CuS-2T and NiS-2T was confirmed by mass spectra, exhibiting their molecular ion peaks at m/z 547.748, 542.257, 711.954 and 705.727, respectively. However, the melting point of them could not be obtained because a temperature was too high to measure.

The first attempt to synthesize MS-CC-1T was made by Sonogashira cross-coupling of 5-bromosalicylaldehyde with an excess amount of 2-(thiophen-2-yl)-acetylene in the presence of PdCl$_2$(PPh$_3$)$_2$, Cul, and NEt$_3$ in refluxing THF under N$_2$ for 5 h. However, based on $^1$H-NMR spectrometry, the desired product could not be obtained. The $^1$H-NMR spectrum of a product separated from the reaction mixture showed a group of peaks indicating protons on thiophene rings but two peaks of protons on hydroxyl and aldehyde groups were not found. It is likely that Glaser coupling of 2-(thiophen-2-yl)-acetylene occurred, leading to a diacetylene byproduct as shown in Scheme IV–2. This way be because of low reactivity of the 5-bromosalicylaldehyde.
To enhance productivity of the reaction, 5-iodosalicylaldehyde\(^{192}\) was therefore used instead of 5-bromosalicylaldehyde because a rate of reaction of an aryl iodide in the Sonogashira coupling was higher than an aryl bromide with a milder condition required.\(^{196}\) Compounds H-CC-1T-B and H-CC-2T-B were successfully prepared in 59% and 50%, respectively, through the Sonogashira cross-coupling of 5-iodosalicylaldehyde with an excess amount of 2-ethynylthiophene and 5-ethynyl-2,2’-bithiophene,\(^{193}\) respectively, in the presence of PdCl\(_2\)(PPh\(_3\))\(_2\), Cul, PPh\(_3\) and NEt\(_3\) in toluene at room temperature under N\(_2\) for 18 h as shown in Scheme IV–3. Formation of compounds H-CC-1T-B and H-CC-2T-B was confirmed by their \(^1\)H-NMR spectra showing singlet peaks of each of their hydroxyl protons at 11.12–11.13 ppm, singlet peaks of the aldehyde protons at 9.88 ppm, and multiplet signals indicating protons on their benzene and thiophene rings at around 6.99–7.73 ppm. Furthermore, HS-ESI mass spectrometry showed molecular ion peaks of H-CC-1T-B and H-CC-2T-B at \(m/z\) 228.040 and 310.0127 [(M+H)\(^+\)], respectively.

\[\text{Scheme IV–2: Formation of the diacetylene byproduct}\]
Scheme IV–3: Synthesis of MS-CC-nT derivatives

After that, H-CC-1T-B and H-CC-2T-B were condensed with excess amount of (S,S)-1,2-cyclohexanediamine at 60°C in ethanol to avoid complication due to the co-precipitation of H-CC-1T-B and H-CC-2T-B with the desirable products. The reactions were completed to afford compounds H$_2$S-CC-1T and H$_2$S-CC-2T in 52% and 49%, respectively. Each of their $^1$H-NMR spectra exhibited a singlet of two protons of the hydroxyl groups at 13.40–13.49 ppm due to deshielding effect from electron withdrawing phenyl rings and imine groups. Their two imine protons gave a singlet peak at 8.14–8.30 ppm, while the singlet peaks of the aldehyde protons observed in H-CC-1T-B and H-CC-2T-B disappeared. Besides, protons of their cyclohexane units gave three multiplet peaks at 1.35–3.38 ppm. Additionally, formation of the H$_2$S-CC-1T and H$_2$S-CC-2T was also confirmed by their spectra from mass spectrometry, which
exhibited their molecular ion peaks at \( m/\text{z} \) 534.692 and 699.010, respectively. Furthermore, a HS-ESI mass spectrum showed the molecular ion peaks of \( \text{H}_2\text{S-CC-1T} \) and \( \text{H}_2\text{S-CC-2T} \) at \( m/\text{z} \) 535.1505 and 699.1269 \([\text{M+H}]^+\), respectively.

Finally, metallation of \( \text{H}_2\text{S-CC-1T} \) with \( \text{Cu(OAc)}_2 \) or \( \text{Ni(OAc)}_2 \) was achieved to give \( \text{CuS-CC-1T} \) or \( \text{NiS-CC-1T} \) in 75% or 80% yield, respectively. Likewise, \( \text{H}_2\text{S-CC-2T} \) was Cu- and Ni-metalated, resulting in \( \text{CuS-CC-2T} \) and \( \text{NiS-CC-2T} \) in 71% and 74%, respectively. The formation of \( \text{CuS-CC-1T}, \text{NiS-CC-1T}, \text{CuS-CC-2T} \) and \( \text{NiS-CC-2T} \) was confirmed by mass spectra, exhibiting their molecular ion peaks at \( m/\text{z} \) 596.0645, 591.0712, 760.0407 and 755.0434 \([\text{M+H}]^+\), respectively, and the melting point of them could not be obtained because a temperature was too high to measure.

4.2 Electrochemical investigations

4.2.1 Electrochemical reduction of \( \text{CO}_2 \) of target monomers

The electrochemical reduction (ECR) of \( \text{CO}_2 \) was performed by cyclic voltammetry using the one-compartment three-electrode electrochemical cell consisting of the glassy carbon as the WE, the Pt plate as the CE and the Ag/AgCl QRE. Cyclic voltammograms were recorded in a DMF solution containing 0.1 M \( \text{nBu}_4\text{NPF}_6 \) as the supporting electrolyte at the potential between 0.0 V and -2.0 V vs. Ag/AgCl QRE with the scan rate of 50 mV·s\(^{-1}\). The concentration of the metallosalen analyte was 0.5 mM, which is approximately the level where most of metallosalens in the series can be dissolved (Table IV-1), and in case where a proton source was needed, 3% \( \text{H}_2\text{O} \) v/v was added. As for the solubility of the target metallosalen monomers in various solvents, DMF was selected as a solvent for ECR of \( \text{CO}_2 \) because of the highest solubility of the metallosalens, compared with \( \text{CH}_2\text{Cl}_2 \) and \( \text{CH}_3\text{CN} \), and because it can mix well with water. However, due to very low solubility of \( \text{CuS-2T} \) and \( \text{NiS-2T} \), their electrocatalytic activities could not be determined. By comparing the solubility of the \( \text{MS-nT} \) and \( \text{MS-CC-nT} \) series, results from Table IV-1 revealed that insertion of a carbon-carbon triple bond between the peripheral thiophene rings and that salen core significantly reduced the solubility of the metallosalens in \( \text{CH}_2\text{Cl}_2 \) and DMF. Moreover, the derivatives having the bithiophenyl units were found to have less solubility than
those containing the thienyl units. Additionally, in most of the cases the copper-salen exhibited higher solubilities than their nickel-chelated analogs.

**Table IV–1**: Solubilities of the target metallosalen monomers in various solvents

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility / mM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH₂Cl₂</td>
</tr>
<tr>
<td>CuS-1T</td>
<td>0.91</td>
</tr>
<tr>
<td>NiS-1T</td>
<td>0.50</td>
</tr>
<tr>
<td>CuS-2T</td>
<td>0.04</td>
</tr>
<tr>
<td>NiS-2T</td>
<td>0.03</td>
</tr>
<tr>
<td>CuS-CC-1T</td>
<td>0.45</td>
</tr>
<tr>
<td>NiS-CC-1T</td>
<td>0.29</td>
</tr>
<tr>
<td>CuS-CC-2T</td>
<td>0.20</td>
</tr>
<tr>
<td>NiS-CC-2T</td>
<td>0.10</td>
</tr>
</tbody>
</table>

To characterize the electrochemical behavior of the target metallosalens, the electrolyte solution of each compound was purged with N₂ for 15 min prior to the measurement, while it was purged with CO₂ for 15 min to study the electrocatalytic activities for the CO₂ reduction. The cyclic voltammograms of the electrolyte solution under N₂- and CO₂-saturated condition with and without 3% H₂O are summarized in **Figure IV–2**. In comparison between N₂- and CO₂-saturated condition, results revealed that current was slightly increased in the CO₂-saturated one when the reduction potential was raised towards −2.0 V vs. Ag/AgCl QRE, which is attributed to transfer of a single electron proceed through the formation of carbon dioxide radical, and the current was even higher due to H₂-evolution when H₂O was added. This observation suggested that the ECR of CO₂ in our studies was able to perform in a potential range between 0.0 V and −2.0 V vs. Ag/AgCl QRE.
Figure IV–2: Cyclic voltammograms of the 0.1 M nBu₄NPF₆ solution in DMF under the N₂-saturated condition in the absence of H₂O (black solid line), under CO₂-saturated condition in the absence of H₂O (black dashed line), under N₂-saturated condition in the absence of H₂O (red solid line) and under the CO₂-saturated condition in the presence of H₂O (red dashed line).

Under the N₂ atmosphere in absence of H₂O, the cyclic voltammograms of CuS-1T, CuS-CC-1T and CuS-CC-2T showed similarly reversible reduction peaks at –1.42 V, –1.42 V and –1.35 V vs. Ag/AgCl QRE, respectively (Figure IV–3 and Table IV–2), corresponding to the published value for unsubstituted copper-salen with slight increase of the reduction potential due to the introduction of thiophene groups in our case. In comparison between the cyclic voltammograms of CuS-1T and CuS-CC-1T, the results indicated that the insertion of the carbon-carbon triple bond between the thienyl units and the salen core did not significantly influence a reduction process of both target molecules. On the other hand, by comparing the reduction process of CuS-CC-1T and that of CuS-CC-2T, their cyclic voltammograms suggested that the introduction of the additional thiophene ring seemed to decrease the reduction potential.
Figure IV–3: Cyclic voltammograms of a 0.1 M nBu$_4$NPF$_6$ solution (grey solid line) containing (a) CuS-1T (black solid line), CuS-CC-1T (red dashed line) and CuS-CC-2T (blue dotted line) under the N$_2$-saturated condition, (b) the 0.1 M nBu$_4$NPF$_6$ solution containing CuS-1T under N$_2$- (solid line) and CO$_2$-saturated condition (dashed line) in the absence (black line) and in the presence of H$_2$O (red line), (c) the 0.1 M nBu$_4$NPF$_6$ solution containing CuS-CC-1T under N$_2$- (solid line) and CO$_2$-saturated condition (dashed line) in the absence (black line) and in the presence of H$_2$O (red line) and (d) the 0.1 M nBu$_4$NPF$_6$ solution containing CuS-CC-2T under N$_2$- (solid line) and CO$_2$-saturated condition (dashed line) in the absence (black line) and in the presence of H$_2$O (red line). The concentration of each compound was 0.5 mM and the cyclic voltammograms were collected at the scan rate of 50 mV/s$^{-1}$. 
**Table IV–2: Electrochemical data of CuS-1T, CuS-CC-1T and CuS-CC-2T**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Condition</th>
<th>$E_{\text{peak}}$ ($E_{\text{onset}}$) / V vs. Ag/AgCl</th>
<th>Current at $E_{\text{peak}}$ / mA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CuS-1T</strong></td>
<td>Without 3% H$_2$O</td>
<td>Nitrogen: -1.42 (–1.22) carbon dioxide: -1.42 (–1.22)</td>
<td>0.086</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nitrogen: -1.41 (–1.23) carbon dioxide: -1.88 (–1.60)</td>
<td>0.064</td>
</tr>
<tr>
<td></td>
<td>With 3% H$_2$O</td>
<td>Nitrogen: -1.39 (–1.20) carbon dioxide: -1.88 (–1.60)</td>
<td>0.095</td>
</tr>
<tr>
<td><strong>CuS-CC-1T</strong></td>
<td>Without 3% H$_2$O</td>
<td>Nitrogen: -1.42 (–1.23) carbon dioxide: -1.42 (–1.22), -1.89 (–1.73)</td>
<td>0.059</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nitrogen: -1.35 (–1.18) carbon dioxide: -1.33 (–1.15), -1.81 (–1.55)</td>
<td>0.056</td>
</tr>
<tr>
<td><strong>CuS-CC-2T</strong></td>
<td>Without 3% H$_2$O</td>
<td>Nitrogen: -1.35 (–1.15) carbon dioxide: -1.35 (–1.15), -1.83 (–1.63)</td>
<td>0.057</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nitrogen: -1.31 (–1.14) carbon dioxide: -1.29 (–1.12), -1.73 (–1.50)</td>
<td>0.035</td>
</tr>
</tbody>
</table>

$^a$ $E_{\text{peak}}$ could not be determined.

$^b$ The current value at the potential of –2.0 V was reported.
Under the CO\(_2\) saturation in the absence of H\(_2\)O, the cyclic voltammogram of CuS-1T (Figure IV–3b) showed its first reduction process occurred at the same potential (−1.42 V vs. Ag/AgCl QRE) as that observed in the N\(_2\) atmosphere in the absence of H\(_2\)O with slight increase in current from 0.086 to 0.102 mA. After that potential, current was continuously increased to 0.478 mA when potential reached −2.0 V. This observation indicated that CuS-1T could promote in the ECR of CO\(_2\). Under the N\(_2\) atmosphere in the presence of 3% H\(_2\)O, the first reduction of CuS-1T was observed at −1.41 V vs. Ag/AgCl QRE (Figure IV–3b), indicating that H\(_2\)O did not significantly affect the reduction process of this compound. However, under the CO\(_2\)-saturated condition in the presence of 3% H\(_2\)O, the reduction process occurred at −1.39 V and −1.88 V vs. Ag/AgCl QRE with the current of 0.095 and 0.322 mA, respectively (Figure IV–3b). Since the first reduction peak appears at the similar potential as that observed in the anhydrous CO\(_2\)-saturated condition with slight decrease in current from 0.102 to 0.095 mA, it can be concluded that the first reduction of CuS-1T did not significantly related to the ECR of CO\(_2\). Nevertheless, the appearance of the second reduction peak with the peak current of 0.322 mA when 3% H\(_2\)O was added, suggested that the second reduction of CuS-1T and H\(_2\)O should involve in the ECR of CO\(_2\).

In case of CuS-CC-1T, the cyclic voltammogram obtained from the anhydrous CO\(_2\)-saturated condition showed that the reduction process of CuS-CC-1T occurred at the same peak potential (−1.42 V vs. Ag/AgCl QRE) as that observed in the anhydrous N\(_2\)-saturated one with negligible increase in current from 0.051 to 0.059 mA (black dashed line, Figure IV–3c). Furthermore, an additional reduction peak was found at −1.89 V vs. Ag/AgCl QRE with the current of 0.100 mA. This observation indicated that the first reduction process of CuS-CC-1T did not significantly related to the ECR of CO\(_2\), its the second reduction may involve in the ECR of CO\(_2\). Under the N\(_2\) atmosphere in the presence of 3% H\(_2\)O, the cyclic voltammogram of CuS-CC-1T exhibited a reduction peak at −1.35 V vs. Ag/AgCl QRE without significant peak current increase, compared with those observed under the anhydrous N\(_2\)-saturated condition (red solid line, Figure IV–3c). This suggested that the addition of H\(_2\)O slightly facilitate the reduction process of the target monomers. Under the CO\(_2\) atmosphere in the presence of 3% H\(_2\)O, the cyclic voltammogram of CuS-CC-1T exhibited the reduction peaks at −1.33 V and
-1.81 V vs. Ag/AgCl QRE with the current of 0.071 and 0.204 mA, respectively, (red dashed line, Figure IV-3c). The very small change in the peak potential and current of the first reduction observed under this condition, compared with those found under the anhydrous CO$_2$-saturated one, suggested that the first reduction of CuS-CC-1T may not involve in the ECR of CO$_2$. On the contrary, the second reduction at the similar potential with significant current increase suggested that the second reduction of CuS-CC-1T and H$_2$O should involve in the ECR of CO$_2$. In comparison between the electrochemical behavior of CuS-1T and that of CuS-CC-1T in the above-mentioned conditions, it can be concluded that the insertion of the carbon-carbon triple bond between the thienyl units and the salen core brought about significant decrease in the reduction potential of the ECR of CO$_2$ in the presence of H$_2$O with, however, smaller reduction currents both in the absence and presence of H$_2$O.

As regards CuS-CC-2T, under the CO$_2$ saturation in the absence of H$_2$O (black dashed line, Figure IV-3d), its reduction process of CuS-CC-2T occurred at the same peak potential (−1.35 V vs. Ag/AgCl QRE) as that observed in the anhydrous N$_2$ atmosphere (black solid line, Figure IV-3d) with negligible increase in the peak current. Moreover, an additional reduction peak was found at −1.83 V vs. Ag/AgCl with the current of 0.130 mA. This observation indicated that the first reduction process of CuS-CC-2T did not significantly related to the ECR of CO$_2$, whereas its second reduction was likely to participate the ECR of CO$_2$. Under the N$_2$ atmosphere in the presence of 3% H$_2$O, the reduction of CuS-CC-2T was observed at a slightly lower potential −1.31 V vs. Ag/AgCl QRE (red solid line, Figure IV-3d), compared with those found in the anhydrous CO$_2$-saturated one, suggesting the negligible effect of the addition of H$_2$O on the reduction process of CuS-CC-2T. Under the CO$_2$ atmosphere in presence of 3% H$_2$O, two reduction processes of CuS-CC-2T were observed at −1.29 V and −1.73 V vs. Ag/AgCl QRE with the peak currents of 0.035 and 0.145 mA, respectively, (red dashed line, Figure IV-3d). The very small change in the peak potential and current of the first reduction observed in this condition, compared with those found in the anhydrous CO$_2$-saturated one, suggested that the first reduction of CuS-CC-2T may not involve in the ECR of CO$_2$. Conversely, the appearance of the second reduction peak with the significant current increase to 0.145 mA suggested that the second
reduction of CuS-CC-2T and H₂O should involve in the ECR of CO₂. In comparison between the electrochemical behavior of CuS-CC-1T and that of CuS-CC-2T in the above-mentioned conditions, it can be summerized that the addition of thiophene ring in CuS-CC-2T led to significant decrease in the reduction potential of the ECR of CO₂ both in the absence and presence of H₂O. However, the addition of H₂O did not significantly affected the reduction process under the N₂-saturated conditon, but it obviously increased the peak current under the CO₂-saturated condition, indicating the possible role of H₂O as the proton source for the ECR of CO₂. To confirm the role of H₂O in the ECR of CO₂, further investigation of the products from the ECR of CO₂ with and without H₂O by, for example, bulk electrolysis still has to be performed.

Under the anhydrous N₂-saturated condition, the cyclic voltammograms of NiS-1T, NiS-CC-1T and NiS-CC-2T showed reversible reduction peaks at −1.78 V, −1.72 V and −1.69 V vs. Ag/AgCl QRE, respectively (Figure IV-4a and Table IV-3), corresponding to redox processes of the nickel-salen complexes from Ni(II) to Ni(I)201-202. In a similar manner observed for the copper-derivatives, the comparison between the cyclic voltammograms of NiS-1T and those of NiS-CC-1T indicated that the insertion of the carbon-carbon triple bond between the thienyl units and the salen core did not significantly influence a reduction process of both target molecules. Furthermore, the comparison between the electrochemical behavior of NiS-CC-1T and that of NiS-CC-2T suggested that the introduction of the additional thiophene ring seemed to decrease the reduction potential.
Figure IV-4: Cyclic voltammograms of a 0.1 M nBu_4NPF_6 solution (grey solid line) containing (a) NiS-1T (black solid line), NiS-CC-1T (red dashed line) and NiS-CC-2T (blue dotted line) under the N_2-saturated condition, (b) the 0.1 M nBu_4NPF_6 solution containing NiS-1T under N_2- (solid line) and CO_2-saturated condition (dashed line) in the absence (black line) and in the presence of H_2O (red line), (c) the 0.1 M nBu_4NPF_6 solution containing NiS-CC-1T under N_2- (solid line) and CO_2-saturated condition (dashed line) in the absence (black line) and in the presence of H_2O (red line) and (d) the 0.1 M nBu_4NPF_6 solution containing NiS-CC-2T under N_2- (solid line) and CO_2-saturated condition (dashed line) in the absence (black line) and in the presence of H_2O (red line). The concentration of each compound was 0.5 mM and the cyclic voltammograms were collected at the scan rate of 50 mV·s⁻¹.
Table IV–3: Electrochemical data of NiS-1T, NiS-CC-1T and NiS-CC-2T

<table>
<thead>
<tr>
<th>Compound</th>
<th>Condition</th>
<th>$E_{\text{peak}}$ (E$_{\text{onset}}$) / V vs. Ag/AgCl</th>
<th>Current at $E_{\text{peak}}$ / mA</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiS-1T</td>
<td>Without 3% H$_2$O</td>
<td>N$_2$: -1.78 (–1.60) CO$_2$: -1.79 (–1.60)</td>
<td>0.119</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N$_2$: -1.75 (–1.55) CO$_2$: -1.80 (–1.62)</td>
<td>0.106</td>
</tr>
<tr>
<td>NiS-CC-1T</td>
<td>Without 3% H$_2$O</td>
<td>N$_2$: -1.72 (–1.52) CO$_2$: -1.74 (–1.52)</td>
<td>0.051</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N$_2$: -1.69 (–1.49) CO$_2$: -1.76 (–1.54)</td>
<td>0.079</td>
</tr>
<tr>
<td>NiS-CC-2T</td>
<td>Without 3% H$_2$O</td>
<td>N$_2$: -1.69 (–1.51) CO$_2$: -1.72 (–1.52)</td>
<td>0.069</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N$_2$: -1.67 (–1.49) CO$_2$: -1.75 (–1.50)</td>
<td>0.231</td>
</tr>
</tbody>
</table>
Under the anhydrous CO$_2$-saturated condition, results in Figure IV–4b showed that the reduction process of NiS-1T (black dashed line) occurred at the similar potential (−1.79 V vs. Ag/AgCl QRE) as that observed under the anhydrous N$_2$-saturated one (black solid line, Figure IV–4b) with significant current increase from 0.119 to 0.146 mA. This observation indicated that NiS-1T might play a role in the ECR of CO$_2$. Under the N$_2$ atmosphere in the presence of 3% H$_2$O, the reduction potential of NiS-1T was observed a similar potential as that observed under the anhydrous condition (−1.75 V vs. Ag/AgCl QRE) with a current of 0.106 mA (red solid line, Figure IV–4b). When this analyte solution was saturated with CO$_2$, the reduction process was found to occur at −1.80 V vs. Ag/AgCl QRE with the current increase to 0.306 mA (red dashed line, Figure IV–4b). The large increase in current from 0.146 to 0.306 mA indicated that H$_2$O significantly affected the reduction process of this compound.

The cyclic voltammogram of NiS-CC-1T under the anhydrous CO$_2$-saturated condition (black dashed line, Figure IV–4c) showed that the reduction process of NiS-CC-1T occurred at the similar peak potential (−1.74 V vs. Ag/AgCl QRE) as that observed in the anhydrous N$_2$-saturated one (black solid line, Figure IV–4c) with the current increase from 0.051 to 0.111 mA. This observation indicated that NiS-CC-1T might participate the ECR of CO$_2$. Under the N$_2$ atmosphere in the presence of 3% H$_2$O, the cyclic voltammogram of NiS-CC-1T exhibited a reduction peak at the comparable potential as that observed under the anhydrous condition (−1.69 V vs. Ag/AgCl QRE, red solid line, Figure IV–4c) with a current of 0.079 mA. Under the CO$_2$ atmosphere in presence of 3% H$_2$O, the reduction process of NiS-CC-1T occurred at −1.76 V vs. Ag/AgCl QRE with the current of 0.226 mA (red dashed line, Figure IV–4c). The current increase from 0.111 to 0.226 mA indicated the significant catalytic activity of NiS-CC-1T in the ECR of CO$_2$. In comparison between the electrochemical behavior of NiS-1T and that of NiS-CC-1T, the similar effect of the insertion of the carbon-carbon triple bond between the thienyl units and the salen core on the increase in the reduction potential of the ECR of CO$_2$ as observed for the copper series was also detected.

As regards NiS-CC-2T, under the CO$_2$ saturation in the absence of H$_2$O (black dashed line, Figure IV–4d), its reduction process occurred at the same peak potential (−1.72 V vs. Ag/AgCl QRE) as that observed in the anhydrous N$_2$-saturated one (black
solid line, Figure IV-4d) with the current increase from 0.069 to 0.099 mA. This observation indicated that NiS-CC-2T might participate the ECR of CO$_2$. Under the N$_2$ atmosphere in the presence of 3% H$_2$O (red solid line, Figure IV-4d), the cyclic voltammogram of NiS-CC-2T exhibited a reduction peak at the comparable potential ($\sim$1.67 V vs. Ag/AgCl QRE) as that observed under the anhydrous N$_2$-condition (black solid line, Figure IV-4d). Under the CO$_2$ atmosphere in presence of 3% H$_2$O (red dashed line, Figure IV-4d), the reduction process of NiS-CC-2T occurred at $\sim$1.75 V vs. Ag/AgCl QRE with the current of 0.231 mA. This reduction peak was observed at a similar potential with that observed under the anhydrous CO$_2$-saturated condition with current increase from 0.099 to 0.231 mA, indicating the significant catalytic activity of NiS-CC-2T in the ECR of CO$_2$. In contrast to the case of the copper-derivatives, the comparison between the electrochemical behavior of NiS-CC-1T and that of NiS-CC-2T indicated that the introduction of the addition thiophene unit did not bring about significant change of the reduction potential of the ECR of CO$_2$. In comparison between the copper- and the nickel-salen monomers, the first reduction of the copper-salen monomers, which occurred in a range between $\sim$1.29 V and $\sim$1.42 V vs. Ag/AgCl QRE, seem not to significantly involve in the ECR of CO$_2$, but the electrochemical catalytic activity of these compounds become significant at the potential higher than $\sim$1.50 V vs. Ag/AgCl QRE. On the other hand, there was only one reduction peak observed in a range between $\sim$1.67 V and $\sim$1.80 V vs. Ag/AgCl QRE for the nickel-salen monomers, and these processes also involved in the ECR of CO$_2$. Furthermore, the addition of H$_2$O significantly affected the reduction process for the ECR of CO$_2$ in both series. Considering the current increase, the results suggested that the MS-nT monomers gave the larger current increase than the MS-CC-nT ones. Moreover, in term of the reduction potential, the results suggested that the MS-CC-nT monomers gave the lower reduction potential than the MS-nT ones. However, the bulk electrolysis should be performed for more realistic comparison. This experiment will be done and its results will be described elsewhere.
4.2.2 Electrochemical polymerization of target monomers

In order to prepare stable films of the target metallosalen for using as heterogeneous electrocatalysts for the ERC of CO$_2$, their electropolymerization was performed in this study. Although the target metallosalen could be greatly dissolved in DMF, the potential window in the DMF system is quite narrow for oxidative polymerization. Therefore, the electropolymerization was performed in CH$_2$Cl$_2$ having the wider potential range than DMF. From the solubilities of the target metallosalens reported in CH$_2$Cl$_2$ in Table IV–1, it can be seen that to perform the electropolymerization of each monomer series, i.e. MS-1T, MS-2T, MS-CC-1T and MS-CC-2T, the concentration of choice had to be approximately the maximum solubilities of the Ni-chelated derivatives. Therefore, the electropolymerization of MS-1T, MS-2T, MS-CC-1T and MS-CC-2T series was performed at the concentration of 0.50, 0.03, 0.25 and 0.10 mM, respectively. A cyclic voltammogram of the 0.1 M nBu$_4$NPF$_6$ solution in CH$_2$Cl$_2$ is shown in Figure IV–5, indicating that a suitable potential range for the oxidative polymerization was between –0.2 V and 1.6 V vs. Ag/AgCl QRE.

![Cyclic voltammogram](image)

*Figure IV–5:* Cyclic voltammogram of a 0.1 M nBu$_4$NPF$_6$ solution in CH$_2$Cl$_2$ measured by using ITO-coated glass and Pt-plate as the WE and CE, respectively, against Ag/AgCl QRE at a scan rate of 100 mV·s$^{-1}$. 
According to a previous study, a chromium salen complex containing the thienyl groups was successfully electrochemically polymerized under oxidative polymerization at the applied voltage between −0.20 V and +1.60 V vs Ag/AgCl QRE with a scan rate of 100 mV·s⁻¹, leading to formation of the polymer film that fully covered on the WE. By using the similar condition, the oxidative polymerization of CuS-1T and NiS-1T was carried out on the ITO-coated glass at the potential between −0.20 V and +1.30 V vs Ag/AgCl QRE. The cyclic voltammograms had significant increase in current from the first to the tenth cycles with small positive shift of $E_{pa}$, indicating the progress of the polymerization of the thienyl unit (Figure IV-6) with a increased film. As a result, the polymers of CuS-1T (poly-CuS-1T) and NiS-1T (poly-NiS-1T) were obtained as a dark green and yellowish green films, respectively, which were stable under the ambient atmosphere.
Figure IV-6: Cyclic voltammograms of oxidative polymerization of a 0.1 M \( \text{Bu}_4\text{NPF}_6 \) in \( \text{CH}_2\text{Cl}_2 \) containing (a) 0.50 mM CuS-1T to give (b) the resulting poly-CuS-1T film on the ITO-coated glass, and (c) 0.50 mM NiS-1T to give (d) the resulting poly-NiS-1T film on the ITO-coated glass. The oxidative polymerization was performed at a scan rate of 100 mV·s\(^{-1}\) for up to 10 cycles.
In case of CuS-2T and NiS-2T monomers, the oxidative polymerization was performed at the potential between 0.0 V and +1.50 V vs Ag/AgCl QRE with a scan rate of 100 mV·s⁻¹. Upon the increase in the number of scanning cycle up to 10 cycles, the increase in the anodic current at +0.90 V, and +1.49 V, and the cathodic current at +0.80 V and +0.35 V vs Ag/AgCl QRE was observed for CuS-2T (Figure IV–7a), while the anodic current increase was not detected for NiS-2T (Figure IV–7c). However, the resulting film from the polymerization of CuS-2T was found to be very thin (Figure IV–7b), whereas the polymerization of NiS-2T failed to give a visible film, although the number of the scanning cycle was increased up to 50 cycles in both cases. This is attributed to low solubility of both compounds. In comparison between the polymerization of MS-1T and that of MS-2T series, the required potential for the polymerization of MS-2T (approximately +0.90 V vs Ag/AgCl QRE) is slightly lower than that of MS-1T (+1.15 V vs Ag/AgCl QRE). The former value was consistent with the potential reported for the oxidative polymerization of a thienyl-substituted chromium-salen in a previous study. It can be concluded that the introduction of the additional thiophene ring in MS-2T brought about significant decrease in the required potential for the oxidative polymerization.
Figure IV-7: Cyclic voltammograms of oxidative polymerization of a 0.1 M nBu₄NPF₆ in CH₂Cl₂ containing (a) 0.03 mM CuS-2T to give (b) the resulting poly-CuS-2T film on the ITO-coated glass, and (c) 0.03 mM NiS-1T. The oxidative polymerization was performed at a scan rate of 100 mV·s⁻¹ for up to 10 cycles.
In a similar manner, the oxidative polymerization of CuS-CC-1T and NiS-CC-1T was carried out at the potential between 0.0 V and +1.50 V and between 0.0 V and +1.60 V vs Ag/AgCl QRE, respectively, with a scan rate of 100 mV·s⁻¹. Upon continuous scanning from the first to the tenth cycles, the anodic and cathodic current in both cases was found to decrease as shown in Figure IV–8. This is attributed to the increase of the resistivity of the resulting film, which suppresses the progress of the electrochemical polymerization. Consequently, the light browish green and light brown films of polymers of CuS-CC-1T (poly-CuS-CC-1T) and NiS-CC-1T (poly-NiS-CC-1T), respectively, were obtained (Figure IV–8b and Figure IV–8d, respectively) and found to be stable under ambient atmosphere. Compared with the MS-1T series, the MS-CC-1T series required more positive potential for electropolymerization, possible due to the stronger electronic communication between the salen and thiophene units via linear carbon-carbon triple bonds that creates electron-withdrawing effect at the polymerizable α-position of the thiophene rings or, in other words, causes the peripheral thienyl unit less reactive to the electrochemical oxidative polymerization.
Figure IV-8: Cyclic voltammograms of oxidative polymerization of a 0.1 M $n$Bu$_4$NPF$_6$ in CH$_2$Cl$_2$ containing (a) 0.25 mM CuS-CC-1T to give (b) the resulting poly-CuS-CC-1T film on the ITO-coated glass, and (c) 0.25 mM NiS-CC-1T to give (d) the resulting poly-NiS-CC-1T film on the ITO-coated glass. The oxidative polymerization was performed at a scan rate of 100 mV·s$^{-1}$ for up to 10 cycles.
In case of CuS-CC-2T and NiS-CC-2T monomers, the oxidative polymerization was performed at the potential between −0.20 V and +1.50 V and between −0.20 V and +1.55 V vs Ag/AgCl QRE, respectively, with a scan rate of 100 mV·s⁻¹. The increase in the anodic current at +0.95 V and +1.48 V, and the cathodic current at +0.89 V and +0.36 V vs Ag/AgCl QRE was observed for CuS-CC-2T and the increase in the anodic current at +0.92 V and +1.52 V, and the cathodic current at +0.88 V and +0.35 V vs Ag/AgCl QRE was observed for NiS-CC-2T (Figure IV–9). In both cases, the cyclic voltammograms exhibited significant increase in current from the first to the tenth cycles with slight positive shift of $E_{pa}$ and negative shift of $E_{pc}$. As a result, polymers of CuS-CC-2T (poly-CuS-CC-2T) and NiS-CC-2T (poly-NiS-CC-2T) were obtained as a stable yellowish brown and light yellow films as shown in Figure IV–9b and Figure IV–9d, respectively. In comparison between the polymerization of MS-CC-1T and that of MS-CC-2T series, the result showed that the polymerization of MS-CC-2T required less potential than that of MS-CC-1T, possibly due to higher susceptibility of the bithiophenyl unit to the electrochemical polymerization, compared with that of the thienyl one as described in previous studies.¹⁸⁶, ²⁰₃, ²¹¹ However, the comparison between the polymerization of MS-CC-2T and that of MS-2T series indicated the stronger electronic communication between the salen and bithiophene units that creates electron-withdrawing effect at the polymerizable α-position on the bithiophene rings in MS-CC-2T led to require more positive potential than MS-2T for the electrochemical oxidative polymerization.
Figure IV-9: Cyclic voltammograms of oxidative polymerization of a 0.1 M nBu₄NPF₆ in CH₂Cl₂ containing (a) 0.10 mM CuS-CC-2T to give (b) the resulting poly-CuS-CC-2T film on the ITO-coated glass, and (c) 0.10 mM NiS-CC-2T to give (d) the resulting poly-NiS-CC-2T film on the ITO-coated glass. The oxidative polymerization was performed at a scan rate of 100 mV·s⁻¹ for up to 10 cycles.
4.2.3 Electrochemical reduction of CO$_2$ of target polymers

The ECR of CO$_2$ of poly-CuS-1T, poly-CuS-CC-1T, poly-CuS-CC-2T, poly-NiS-1T, poly-NiS-CC-1T and poly-NiS-CC-2T was studied by using the same cyclic voltammetry setup as that described for their monomers in Section 4.2.1, except that the WE in this case was the polymer films on the ITO-coated glass and the electrolyte solution contained no salen monomer. The electrochemical window was determined by the cyclic voltammograms of a 0.1 M $n$Bu$_4$NPF$_6$ solution using a clean ITO-coated glass as the WE. The results in Figure IV–10 showed that although the current under the N$_2$ atmosphere did not significantly change up to –2.0 V vs Ag/AgCl QRE, that under the CO$_2$ atmosphere drastically increased at the potential higher than –1.7 V vs Ag/AgCl QRE. Therefore, the potential range chosen for the heterogeneous ECR of CO$_2$ was between 0.0 V and –1.7 V vs Ag/AgCl QRE.

![Figure IV–10](image)

Figure IV–10: Cyclic voltammograms of a 0.1 M $n$Bu$_4$NPF$_6$ solution in DMF under the N$_2$- (solid line) and CO$_2$-saturated condition (dashed line).

When the polymer films on the ITO-coated glasses were used on the WE, it is surprising that the electrochemical features of the films under the N$_2$ atmosphere were not consistent with those observed for their corresponding monomers (Figure IV–11). Moreover, under the CO$_2$ atmosphere, these polymer films gave no significant current enhancement. This observation was confirmed by using the freshly made polymer films under the same conditions and setup. This unexpected result may be explained by high resistance of the films due to possible aggregation of the repeating units in the polymer chains or unfavorable morphology of the polymer films. To investigate the detailed cause of this, further optimization of the polymerization condition and in-
depth film studies have to be performed. Therefore, the ECR of CO$_2$ of these films was not continued in this work.

![Cyclic voltammograms of different films](image)

Figure IV-11: Cyclic voltammograms of (a) poly-CuS-1T, (b) poly-NiS-1T, (c) poly-CuS-CC-1T, (d) poly-NiS-CC-1T, (e) poly-CuS-CC-2T and (f) poly-NiS-CC-2T under N$_2$ (black solid line) and CO$_2$-saturated condition (red dashed line). The cyclic voltammograms were recorded in a 0.1 M $n$Bu$_4$NPF$_6$ solution in DMF at the scan rate of 50 mV·s$^{-1}$. 


A series of the novel asymmetric copper- and nickel-salens bearing the thienyl and bithiophenyl units attached on their phenoxy rings directly and via the carbon-carbon triple-bond spacer was successfully synthesized. The characterization of the target compounds was carried out by $^1$H-NMR and $^{13}$C-NMR spectroscopy and mass spectrometry. The solubilities of the target compounds were found to vary in a range of 0.03–0.90, 0.01–0.05 and 0.04–2.74 mM in CH$_2$Cl$_2$, CH$_3$CN and DMF, respectively. Their electrocatalytic activities for the homogeneous ECR of CO$_2$ in DMF were determined by cyclic voltammetry. Under the CO$_2$-saturated condition, results revealed that both copper- and nickel-salens should be able to work as catalysts for the ECR of CO$_2$ by showing the current increase of the reduction peaks compared with those observed under the N$_2$ atmosphere. Moreover, the results showed that the insertion of the carbon-carbon triple bond between the thienyl units and the salen core led to the decrease in the required reduction potential. Furthermore, the introduction of the thienyl rings also encouraged the current increase in reduction process of both in copper- and nickel-salen, while the additional thiophene rings did not play a significant role in this aspect. In addition, the water gave significant contribution in the reduction of CO$_2$ by increasing the peak current in most cases. The oxidative polymerization of all target monomers, except the ones bearing the bithiophenyl groups directly linked to the salen core that exhibited low solubilities, gave stable thin films of the corresponding polymers. The results indicated that the monomers having the carbon-carbon triple-bond spacer required higher potential for the polymerization, compared to the ones having the thiophene-based groups directly linked to the salen core. Additionally, the monomers containing the bithiophenyl groups required lower potential to proceed the polymerization than those bearing the thienyl rings. Due to unexpected electrochemical behavior of the resulting polymers, the electrocatalytic activities of these polymers for the ECR of CO$_2$ could not be yet investigated, and will be further described elsewhere. Possible future work is to
analyze the products from the homogeneous ECR of CO$_2$ by the bulk electrolysis for more realistic comparison of the catalytic efficiency of each monomer. Furthermore, the further optimization of the polymerization condition should be performed to obtain the efficient polymeric catalyst for the heterogeneous ECR of CO$_2$, as well as the determination of products from this process in a similar manner to the homogeneous one.
REFERENCES


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Figure A-1: $^1$H-NMR spectrum of compound H-1T-B
Figure A-2: $^{13}$C-NMR spectrum of compound H-1T-B
Figure A-3: $^1$H-NMR spectrum of compound H-2T-B
Figure A-4: $^{13}$C-NMR spectrum of compound H-2T-B
Figure A-5: HR-ESI spectrum of compound H-2T-B
Figure A-6: \(^1\)H-NMR spectrum of compound H-CC-1T-B
Figure A-7: $^{13}$C-NMR spectrum of compound H-CC-1T-B
Figure A-8: HR-ESI spectrum of compound H-CC-1T-B
Figure A–9: $^1$H-NMR spectrum of compound H-CC-2T-B
Figure A-10: $^{13}$C-NMR spectrum of compound H-CC-2T-B
Figure A-11: HR-ESI spectrum of compound H-CC-2T-B
Figure A-12: $^1$H-NMR spectrum of compound $\text{H}_2\text{S}-1\text{T}$
Figure A-13: $^{13}$C-NMR spectrum of compound H$_2$S-1T
Figure A-14: MALDI-TOF spectrum of compound H$_2$S-1T
Figure A-15: $^1$H-NMR spectrum of compound H$_2$S-2T
Figure A-16: $^{13}$C-NMR spectrum of compound $H_2S\text{-}2T$
Chemical Formula: $C_{36}H_{30}N_{2}O_{2}S_{4}$
Molecular Weight: 650.888

Figure A-17: MALDI-TOF spectrum of compound $H_2S$-2T
Figure A-18: HR-ESI spectrum of compound $\text{H}_2\text{S}_{2}\text{T}$

Mass Spectrum List Report

Analysis Info
Analysis Name: OSCK00531001.d
Method: Tune wide_POS_Natee20130403.m
Sample Name: H2S-2T

Acquisition Date: 6/2/2017 9:35:39 AM
Operator: Administrator
Instrument: microTOF

Acquisition Parameter
Source Type: ESI
Scan Range: m/z
Scan Begin: 50 m/z
Scan End: 3000 m/z
Ion Polarity: Positive
Capillary Exit: 200.0 V
Hexapole RF: 600.0 V
Hexapole 1: 70.0 V
Hexapole 2: 25.0 V
Set Corrector Fill: 50 V
Set Pulsar Pull: 337 V
Set Pulsar Push: 337 V
Set Reflector: 1300 V
Set Flight Tube: 9000 V
Set Detector TOF: 2295 V

Chemical Formula: C$_{36}$H$_{30}$N$_2$O$_2$S$_4$

Exact Mass: 650.1190

([M+H]$^+$): 651.1263

$\text{H}_2\text{S}_{2}\text{T}$

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Figure A–19: $^1$H-NMR spectrum of compound H$_2$S-CC-1T
Figure A-20: $^{13}$C-NMR spectrum of compound H$_2$S-CC-1T
Figure A-21: MALDI-TOF spectrum of compound $\text{H}_2\text{S-CC-1T}$
Figure A-22: HR-ESI spectrum of compound H₂S-CC-1T
Figure A-23: $^1$H-NMR spectrum of compound H$_2$S-CC-2T
Figure A-24: $^{13}$C-NMR spectrum of compound H$_2$S-CC-2T
Chemical Formula: $C_{40}H_{30}N_2O_2S_4$

Molecular Weight: 698.932

Figure A-25: MALDI-TOF spectrum of compound H$_2$S-CC-2T
Figure A–26: HR-ESI spectrum of compound $\text{H}_2\text{S-CC-2T}$

Chemical Formula: $\text{C}_{40}\text{H}_{30}\text{N}_2\text{O}_2\text{S}_4$

Exact Mass: 698.1150

$[(\text{M+H})^+]$: 699.1263
Figure A-27: MALDI-TOF spectrum of compound CuS-1T
Figure A-28: MALDI-TOF spectrum of compound NiS-1T

NiS-1T

Chemical Formula: $C_{28}H_{24}N_{2}NiO_2S_2$

Molecular Weight: 543.325
Figure A–29: MALDI-TOF spectrum of compound CuS-2T

Chemical Formula: $C_{36}H_{28}CuN_{2}O_{2}S_{4}$
Molecular Weight: 712.418
Figure A-30: MALDI-TOF spectrum of compound NiS-2T
Chemical Formula: $C_{32}H_{24}CuN_2O_2S_2$

Molecular Weight: 596.222

Figure A-31: MALDI-TOF spectrum of compound CuS-CC-1T
Figure A-32: HR-ESI spectrum of compound CuS-CC-1T
Chemical Formula: $\text{C}_{32}\text{H}_{24}\text{N}_{2}\text{NiO}_{2}\text{S}_{2}$

Molecular Weight: 591.369

Figure A–33: MALDI-TOF spectrum of compound NiS-CC-1T
Figure A–34: HR-ESI spectrum of compound NiS-CC-1T
Figure A.35: MALDI-TOF spectrum of compound CuS-CC-2T
Figure A–36: HR-ESI spectrum of compound CuS-CC-2T

Analysis Info

Analysis Name: OSCK00531006_1.d
Method: TuneWide_POS_pin_800.m
Sample Name: CuS-CC-2Th
CuS-CC-2Th

Acquisition Parameter

Source Type: ESI
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Scan End: 3000 m/z
Ion Polarity: Positive
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Hexapole 1: 75.0 V
Skimmer 1: 25.0 V

Set Injector Fill: 50 V
Set Pulsar Pull: 337 V
Set Pulsar Push: 337 V
Set Reflector: 1300 V
Set Flight Tube: 9000 V
Set Detector TCF: 2265 V

Chemical Formula: C_{40}H_{28}CuN_{2}O_{2}S_{4}

Exact Mass: 759.0330

[(M+H)\(^{+}\)]: 760.0402

CuS-CC-2T

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Figure A–37: MALDI-TOF spectrum of compound NiS-CC-2T
**Mass Spectrum List Report**

**Analysis Info**
- **Analysis Name**: OSCK005310C9_4 d
- **Method**: Tune_wide_POS_pin_600.m
- **Sample Name**: NiS-CC-2TH

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**Chemical Formula**: C_{40}H_{28}N_{2}NiO_{2}S_{4}

**Exact Mass**: 754.0387

**[M+H]^+**: 755.0460

---

**Figure A-38**: HR-ESI spectrum of compound NiS-CC-2T
VITA

Mr. Cherawat Kaewyai was born on Sunday 19th September, 1993, in Bangkok, Thailand. In 2015, he graduated with a Bachelor’s degree of Science in Chemistry, from Srinakharinwirot University. Next, he has been studied for a Master’s degree of Science in Petrochemical and polymer science, Faculty of Science, Chulalongkorn University in 2015. His poster presentation and proceeding "Synthesis of Thiophene-substituted Metallosalen for Reduction of Carbon Dioxide" have been submitted at The 44th National Graduate Research Conference (NGRC 44) in Ubon Ratchathani University, 19-20th October, 2017, Thailand.