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# SYNTHESIS AND ELECTRICAL PROPERTIES OF COPOLYMERS CONTAINING 3-PHENYL[5]FERROCENOPHANE-1,5-DIMETHYLENE AND VINYLMIDAZOLE

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SYNTHESIS AND ELECTRICAL PROPERTIES OF COPOLYMERS CONTAINING  
3-PHENYL[5]FERROCENOPHANE-1,5-DIMETHYLENE AND VINYLIMIDAZOLE

A Thesis Submitted to the Graduate School  
in Partial Fulfillment of the Requirements  
for the Degree of  
Master of Science

Muteb Alshammari

Pittsburg State University

Pittsburg, Kansas

December 2017

SYNTHESIS AND ELECTRICAL PROPERTIES OF COPOLYMERS CONTAINING  
3-PHENYL[5]FERROCENOPHANE-1,5-DIMETHYLENE AND VINYLIMIDAZOLE

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# SYNTHESIS AND ELECTRICAL PROPERTIES OF COPOLYMERS CONTAINING 3-PHENYL[5]FERROCENOPHANE-1,5-DIMETHYLENE AND VINYLIMIDAZOLE

An Abstract of the Thesis by  
Muteb Hashim Alshammari

Ferrocene is a well-known organometallic compound. Its structure consists of an iron atom sandwiched between two cyclopentadienyl rings. Ferrocene has unique properties such as redox chemistry, high electron density, thermal stability and aromaticity. In addition, the ferrocene can be incorporated into polymers either into the backbone or on the side chains. Ferrocene incorporated polymers have received considerable attention in the areas of electrocatalysis, electrode coating, and battery applications. Therefore, the main purpose of this study is to characterize the electrochemical behavior of copolymers of 3-phenyl[5]ferrocenophane-1,5-dimethylene with vinyl imidazole in aqueous solutions with various electrolytes: sodium perchlorate, zinc perchlorate, cadmium perchlorate, magnesium perchlorate, and lead perchlorate. Using a Wittig reaction, the 3-phenyl[5]ferrocenophane-1,5-dimethylene was synthesized from 3-phenyl[5]ferrocenophane-1,5-dione. Copolymerization with vinyl imidazole was achieved using AIBN as the initiator. The resulting polymers were characterized by FTIR,  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR. Cyclic voltammetry was performed in order to determine electrochemical response of each polymer. Finally, copolymers were investigated by UV-vis spectroscopy as solution in methylene chloride and as thin films to determine electronic communication between the ferrocene and imidazole moieties.

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## LIST OF ABBREVIATIONS

Fc – Ferrocenyl

FE-P- Ferrocene Incorporated Polymers

AIBN -  $\alpha$ ,  $\alpha$ -azobisisobutyronitrile

Bu<sub>4</sub>NPF<sub>6</sub> - Tetrabutylammonium hexafluorophosphate

n-Bu - n-butyl

PPM - Parts Per Million

CME - Chemically Modified Electrodes

Cp - Cyclopentadienyl

CV - Cyclic Voltammetry

E<sub>ox</sub> - Oxidation Potential

E<sub>red</sub> - Reduction Potential

E<sub>1/2</sub> -Redox Potential

EDG - Electron Donating Group

CT - Charge Transfer

HOMO - Highest Occupied Molecular Orbital

LUMO - Lowest Unoccupied Molecular Orbital

NMR-Nuclear Magnetic Resonance

UV-Vis-Ultraviolet-visible spectroscopy

IR-Infrared Spectroscopy

## CHAPTER I

### INTRODUCTION

#### 1.1. Introduction to Ferrocene

Ferrocene is a well-known organometallic compound, and has a sandwich type structural configuration. Its structure consists of an iron (Fe) atom sandwiched between two parallel  $\pi$ -bonded cyclopentadienyl rings, as shown in the

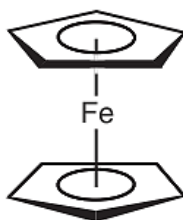


Figure <sup>1</sup>.

**Figure 1:** The structure of Ferrocene<sup>1</sup>

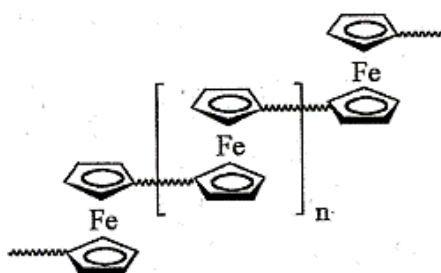
Chemically, it is also termed as bis-cyclopentadienyl-iron, a complex of 18 electrons. This compound first came into the limelight in the year 1951, when its structure was published by Pauson, Miller, and Keally in the journal, Nature. It was an unexpected product of a reaction intended toward production of fulvalene. This reaction involved the oxidation of cyclopentadienyl magnesium bromide with Fe (II) chloride in the presence of ether <sup>1-2</sup>.

Ferrocene is diamagnetic in nature and possesses inherent thermal stability. In addition, it also possesses aromaticity, nontoxicity, and interesting photochemical properties. It can be successfully integrated into long chain polymers as a part of the main chain or as a side-chain. Polymers incorporated with ferrocene side-chains first appeared in the year 1955, with the synthesis of poly (vinyl ferrocene) <sup>3</sup>. The first well characterized polymers having

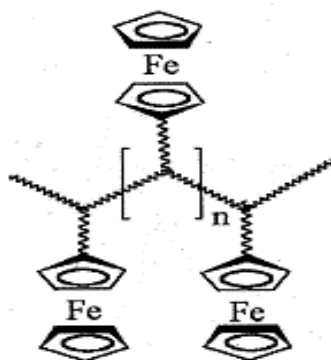
ferrocene in the main polymer backbone were developed in the mid-1970s. However, this area took nearly 15 years to expand because of the limitations of polymerization techniques <sup>1-2,4</sup>. The discovery of new polymerization techniques such as the ring opening polymerization of ferrocenophanes escalated the research in this area <sup>5</sup>.

## 1.2. Ferrocene Incorporated Polymers

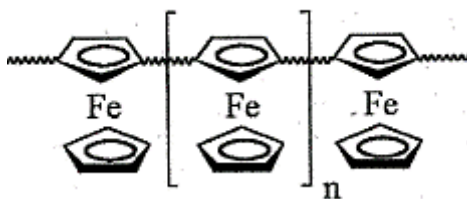
Ferrocene incorporated polymers (FE-P) possess unique properties such as redox stability, reversible oxidation, and charge transfer characteristics <sup>6-8</sup>. Because of these attractive properties, FE-P have received considerable attention in the areas of electro-catalysis <sup>9</sup>, electrode coating <sup>6</sup>, and battery applications <sup>10</sup>. According to a research study <sup>5</sup>, ferrocene polymers can exist in two main structural configurations. These include the following:



**SC-1:** Ferrocene in the main chain of polymers having 1,1'-substitution patterns of spacers about the ferrocene unit

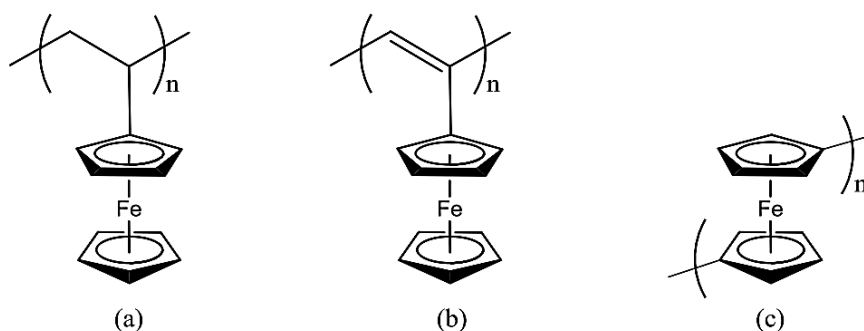


**SC-2:** Ferrocene as side-chains of the main polymer backbone



**SC-3:** Uncommon subclass of SC-2 in which ferrocene is embedded as a lateral attachment of the side-chains of the main polymer backbone

The favorable electronic properties of FE-P have been the focus of many research studies. Recently, a number of FE-P were synthesized and they were studied as a cathode material for rechargeable batteries<sup>10</sup>. These included poly-vinylferrocene and poly-ethynylferrocene having saturated and unsaturated carbon bridges, respectively. The FE-P with no bridges were also studied and their structures are shown in the following figure.



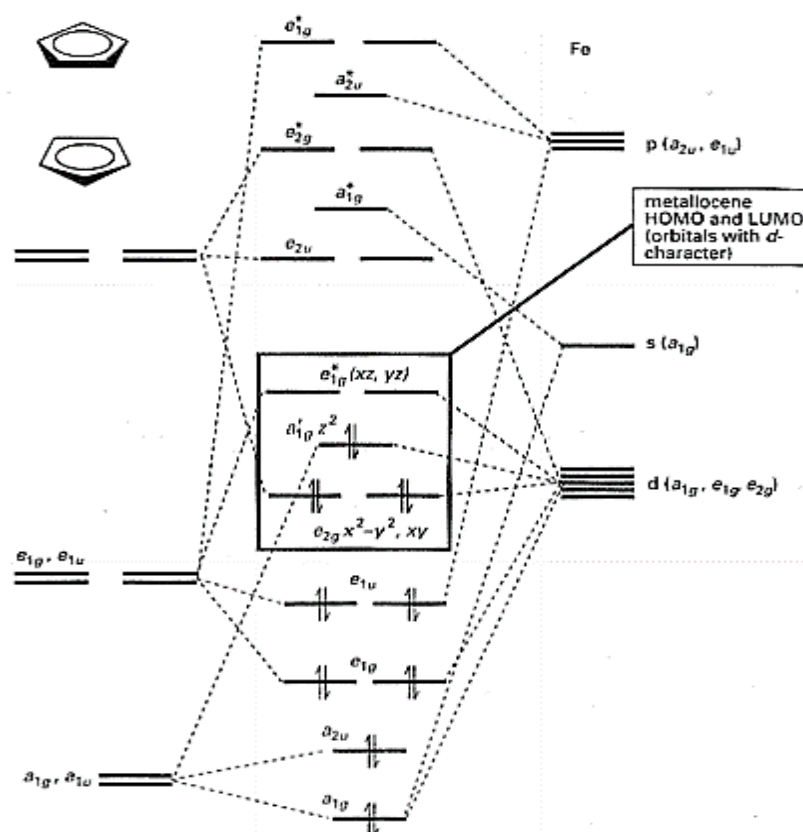
**Figure 2:** The structures of FE-P, a) poly-vinylferrocene, b) Poly-ethynylferrocene, c) FE-P<sup>10</sup>

The charge/discharge characteristics of these polymers exhibited better cycle performance and high discharge capacity (near to theoretical) as compared to polyacetylenes and polynorbornenes<sup>10</sup>. The poly-ferrocenyl-methylsilane and their derivatives were also synthesized and studied as charge storage materials. The charge/discharge studies showed a decrease of nearly 12% after 200 cycles when compared with the poly-vinylferrocene<sup>11</sup>.

### 1.3. Electronic Properties of FE-P

#### 1.3.1. Electronic Structure

Ferrocene is an electrically active material and has unique characteristics such as electron-rich aromatic behavior, facial lithiation (at 1 or 1,1'-position), reversible redox ability, and diversity of substituents<sup>6, 9, 12-13</sup>. It follows the 18-electron rule because the six d-electrons of  $\text{Fe}^{2+}$  ion are bonded with the six  $\pi$ -electrons of the two cyclopentadienyl anions. Its inherent electronic stability is because of the populated bonding, non-bonding orbitals and unpopulated anti-bonding orbitals<sup>1, 10, 14</sup>. A detailed molecular orbital (MO) diagram of ferrocene is shown in the figure as follows,



**Figure 3:** A MO diagram for the ferrocene<sup>4</sup>

In the above figure, the overlapping of molecular orbitals can be predicted by considering the symmetry conditions, respective energies, and overlap integrals of the central iron orbitals (3d, 4s and 4p) along with the ligand orbitals ( $\pi$ )<sup>15</sup>. The different aspects of the Figure are explained in the following steps<sup>14</sup>,

- $a_{1g}$ ,  $a_{2u}$  are the ligand orbitals at the lowest energy
- $3d_z^2/4s$ ,  $4p_z$  are the high energy metal orbitals
- $e_{2g}$  are essentially metal orbitals because of their poor overlapping with the ligand  $e_{2g}$  orbitals
- The overlapping of iron orbitals ( $dx_z$  &  $dy_z$ ) with the ligand orbitals ( $e_{1g}$ ) forms two strong  $\pi$ -bonds. These  $\pi$ -bonds are largely responsible for the stability of a ferrocene molecule
- The ferrocene orbitals such as  $e'_{1g}$ ,  $a'_{1g}$ ,  $e_{2g}$  are the unoccupied weak anti-bonding, non-bonding, and the weakly bonding, respectively
- Here, the degenerate  $e_{2g}$  or  $a'_{1g}$  can be taken as HOMO of ferrocene <sup>16</sup>
- The out of phase  $dx_z/dy_z$  orbitals'  $\pi$ -interaction with the cyclopentadienyl  $e_{1g}$  orbitals gives us the LUMO of ferrocene <sup>17</sup>

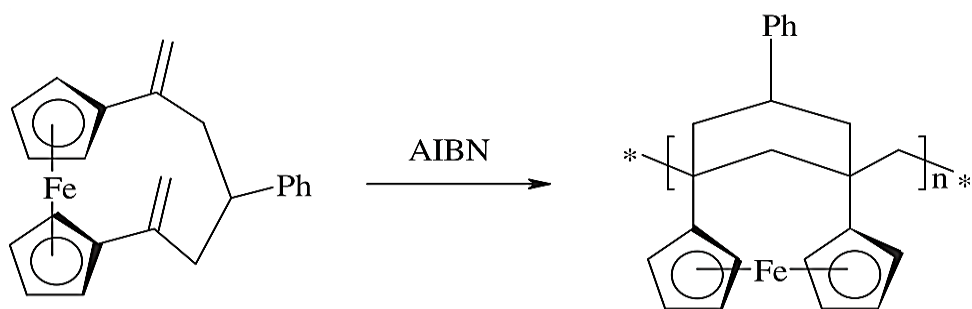
In substituted ferrocene compounds, such as FE-P, the strong  $\pi$ -bonding of cyclopentadienyl rings interact with  $\pi$ -conjugated main chains and exhibit improved electrochemical properties <sup>18-20</sup>.

### 1.3.2. Charge Transfer Characteristics

In polymers, the charge transfer (CT) states are at higher energy as compared with the bottom 1<sup>st</sup> excited state <sup>21</sup>. The separation of charge is usually achieved by dissociation at a defect caused by the presence of impurity or at an interface <sup>22</sup>. A number of research studies <sup>7, 13, 18, 20, 23</sup> have focused on the CT characteristics of ferrocene involving intra-molecular or inter-molecular CT between other redox centers and ferrocene owing to its suitable redox properties. Ferrocene behaves as an electron donor as evident by its vertical ionization potential of IP = 6.85 eV in the gas phase. In addition, its oxidative conversion to ferrocenium ion occurs with almost negligible structural changes. This shows the requirement of very low reorganization energy for electron transfer. It also forms neutral CT complexes with electron deficient acceptors such as quinones, polynitroarenes, and many types of alkyl halides <sup>13</sup>.

The addition of functionalized ferrocene into p-type polymers, such as polythiophene, enhances the formation of CT states. The redox properties of polythiophene are significantly altered by the photo excitation of ferrocene groups <sup>21</sup>. Recently, high molecular weight polymers derived from cyclophanes were incorporated with ferrocenophane units pendant to

the backbone of polymer <sup>9</sup>. In addition, 3-phenyl [5] ferrocenophane-1, 5-dimethylene (**1**) was radically cyclopolymerized and copolymerized with styrene to produce polymers having ferrocenophane units. These polymers exhibited close stacking of ferrocenyl moieties, leading to CT between metallic centers. Their cyclic voltammetry exhibited two redox potentials and infrared spectroscopy indicated the presence of a lower energy barrier to the hopping of electrons <sup>9, 12</sup>. High molecular weight copolymers of **1** with N-substituted maleimides were also studied for electrochemical and thermal properties. They showed one oxidation potential in methylene chloride and good redox activity as thin films using a sodium chloride solution <sup>8</sup>.



**Figure 4:** Polymerization reaction of 3-phenyl [5] ferrocenophane-1,5-dimethylene <sup>8</sup>

#### 1.4. Project Rationale

At present, scientists are exploring new materials for satisfying the energy demands and efficiency requirements of modern day electronic devices. There is a need to develop promising materials that possess high charge density and electronic efficiency. Many prototype molecular electronic devices have been based on FE-P because of their attractive electrochemical, electronic, and chemical properties <sup>24</sup>. In addition, the ferrocene moieties in the main polymer chain of doped FE-P impart semiconducting characteristics owing to the strong metal-metal interaction <sup>25</sup>. Despite these distinguishing characteristics, only a limited number of highly functionalized FE-P have been developed and the scope of this research area is limited <sup>26-27</sup>.

Keeping in view the above-mentioned considerations, in this research we were interested in FE-P with unusual electronic properties especially those which show interaction



between FE-P and neighboring monomers. So, to that extend, 3-phenyl [5] ferrocenophane-1, 5-dimethylene was copolymerized with vinyl imidazole. In addition, the electronic properties of each copolymer will be studied in the presence of different metals. Moreover, the copolymers may display interesting electronic properties by coordinating imidazole to different heavy metals. Using UV-Vis spectroscopy and electrochemistry, the electronic properties of the synthesized copolymers will also be studied in the presence of heavy metals.

## CHAPTER II

### EXPERIMENTAL

#### 2.1. Materials

All beginning materials were commercially available and utilized as received unless otherwise stated. The Wittig reaction was utilized to synthesize the 3-phenyl [5] ferrocenophane-1, 5-dimethylene according to a literature procedure<sup>8</sup>. For chromatography, silica gel (60 Å) (Acros organic) was used as the stationary phase with chloroform or dichloromethane as the mobile phase.

#### 2.2. Instrumentation

All NMR spectra were acquired utilizing a Bruker DPX-300 MHz spectrometer. Fourier Transform Infrared Spectroscopy (FT-IR) was done by utilizing a Perkin Elmer Spectrum 2 Spectrometer. Cyclic Voltammetry was performed utilizing a Gamry Interface 1000 potentiostat with a platinum working electrode, a platinum counter electrode, and an Ag/AgCl counter electrode or Ag wire as pseudo counter electrode. UV-vis spectroscopy was obtained utilizing a Gamry UV-Vis spectro-115u system.

#### 2.3. Synthesis of 3-phenyl [5] ferrocenophane-1,5-dimethylene copolymers

##### 2.3.1. Synthesis of 1,1'-diacetylferrocene<sup>8</sup>

Under a nitrogen atmosphere, dichloromethane (150ml) and aluminum chloride (8.3 g, 62.2 mmol) were added to a dry round bottom flask. Acetyl chloride (4.5 g, 57.3 mmol) was then added and the solution was stirred for half an hour. Ferrocene (4.65 g, 25 mmol) was added and stirring was continued overnight. The reaction mixture was poured into ice water in order to neutralize the AlCl<sub>3</sub>. The organic phase was separated and the solvent was removed with a rotary evaporator. The crude material was recrystallized from isopropanol to yield 1.88 g

(70%) of diacetyl ferrocene. FTIR ( $\text{cm}^{-1}$ ) C-H aromatic 3090, C=O 1695, C=C aromatic 1450.

$^1\text{H}$ -NMR ( $\text{CDCl}_3$ ,  $\delta$ .ppm): 4.75 (4H.CP-ring), 4.46 (4H.CP-ring), 3.51 (6H. C- $\text{CH}_3$ ).

### 2.3.2. Synthesis of 3-phenyl [5] ferrocenophane-1, 5-dione<sup>8</sup>

To a round bottom flask were added 1,1'-diacetylferrocene (1.88 g, 7 mmol) benzaldehyde (0.73 g, 6.9 mmol) and 95% ethanol (50 mL). The solution was stirred for 20 minutes. At room temperature, potassium hydroxide (0.19 g, 3.4 mmol) was added to the reaction and stirring was continued for 16 hours. After 16 hours, the precipitate was collected by filtration and dried under reduced pressure to give 2 g (65%) of 3- phenyl [5] ferrocenophane-1, 5-dione. FTIR ( $\text{cm}^{-1}$ ): C-H aromatic 3075, C=O 1715.  $^1\text{H}$ - NMR ( $\text{CDCl}_3$ ,  $\delta$ .ppm): 7.38 (5H.phenyl), 4.90 (2H.CP-ring), 4.71, 4.60, 4.40, (6H. CP- ring), 4.18(1H.CH-Ph), 2.50(2H.CH- $\text{CH}_2$ ).

### 2.3.3. Synthesis of 3-phenyl [5] ferrocenophane-1, 5-dimethylene<sup>8</sup>

Methyltriphenylphosphonium bromide (5 g, 0.015 mol) and tetrahydrofuran (40 ml) were added to a round bottom flask. A nitrogen atmosphere was established and the reaction mixture was stirred. N-butyllithium (5.5 ml) was added carefully to the reaction, and stirring continued for half an hour. Then 3-phenyl [5] ferrocenophane-1, 5-dione was added and stirring continued for 22 hours. After 22 hours, water (2.5 ml) was added to the solution. The solvent was then removed using a rotary evaporator. Column chromatography was used with silica gel and chloroform as the mobile phase to purify the reaction mixture to yield 1.44g (65%) of 3-phenyl [5] ferrocenophane-1, 5-dimethylene. FTIR ( $\text{cm}^{-1}$ ): =C-H stretch 3090, C-H aromatic 3000, C-H aliphatic 2920, C=C 1670 .  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): (7.25, 5 H, phenyl protons), (5.27, 2H, vinylidene protons), (4.80, 2H, vinylidene protons), (4.49, 4.18, 4.25, 8 H, CP-protons), (4.15, 1H, benzyl proton), (2.64, 4 H, C- $\text{CH}_2$ ).

### 2.3.4. Polymerization of 3-phenyl [5] ferrocenophane-1, 5-dimethylene with vinyl imidazole (3:1) poly 1.

To a round bottom flask were added 3-phenyl [5] ferrocenophane-1, 5-dimethylene (0.1g. 0.2 mmol), vinyl imidazole (0.009 g), and chlorobenzene (0.5 ml). AIBN (0.005 g) was

utilized as an initiator for the polymerization, and a nitrogen atmosphere was established. The mixture was stirred for 16 hours. After cooling to ambient temperature, the solution was added to hexane (25 ml). The precipitate was collected by suction filtration and dried under reduced pressure to yield 0.12 g (80%). FTIR ( $\text{cm}^{-1}$ ): C-H aromatic 3090, C-H aliphatic 2920.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$  ppm): 3.95-4.40 (9H), 7.30-7 (3H), 2.50-0.90 (10H).

### **2.3.5. Polymerization of 3-phenyl [5] ferrocenophane-1, 5-dimethylene with vinyl imidazole (1:3) poly 2.**

To a round bottom flask was added 3-phenyl [5] ferrocenophane-1, 5-dimethylene (0.1 g, 0.2 mmol), vinyl imidazole (0.08 g), AIBN (0.009 g) and chlorobenzene (0.5 ml). The solution was heated at  $80^\circ\text{C}$  and stirred for 16 hours under a nitrogen atmosphere. After the reaction was complete, it was allowed to cool to room temperature and added to hexane (25 ml) to precipitate the copolymer. The resulting solid was collected by vacuum filtration and dried under reduced pressure to provide 0.21 g (77%). FTIR ( $\text{cm}^{-1}$ ): C-H aromatic 3000, C-H aliphatic 2930.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$  ppm): 4.10-4.54 (9H), 7.39-7.15 (3H), 1.90-0. (11H).

### **2.3.6. Polymerization of 3-phenyl [5] ferrocenophane-1,5-dimethylene with vinyl imidazole (1:1) poly 3.**

To a 25-ml round bottom flask with a stir bar, 3-phenyl [5] ferrocenophane-1,5-dimethylene (0.1 g, 0.2 mmol), vinyl imidazole (0.027 g), AIBN (0.006 g) and chlorobenzene (0.5 ml) were added. The reaction was heated at  $70^\circ\text{C}$  under an atmosphere of nitrogen and stirred for 16 hours. After that, the reaction mixture was cooled to room temperature and added to hexane (25 ml). The precipitated copolymer was collected by vacuum filtration and dried under reduced pressure to give 0.15 g (74%). FTIR ( $\text{cm}^{-1}$ ): C-H aromatic 3087, C-H aliphatic 2925.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$  ppm): 4-4.50 (9H), 7.40-7.10 (3H), 2.50-0.90 (10H).

## **2.4. Studies of Electrochemistry and Cast Film Technique**

The preparation of electrochemical solutions was achieved by dissolving each copolymer (1mM) and tetrabutylammonium hexafluorophosphate (100mM), as supporting electrolyte, in dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) (10 mL).

For electrochemistry using thin films, each polymer was dissolving in chloroform. Chloroform solutions for each copolymer (3 mg/ml) were micropipetted (2 $\mu$ L) onto electrodes which were allowed to air dry for 20 minutes. Finally, each electrode was put into various electrolyte solutions for electrochemical testing.

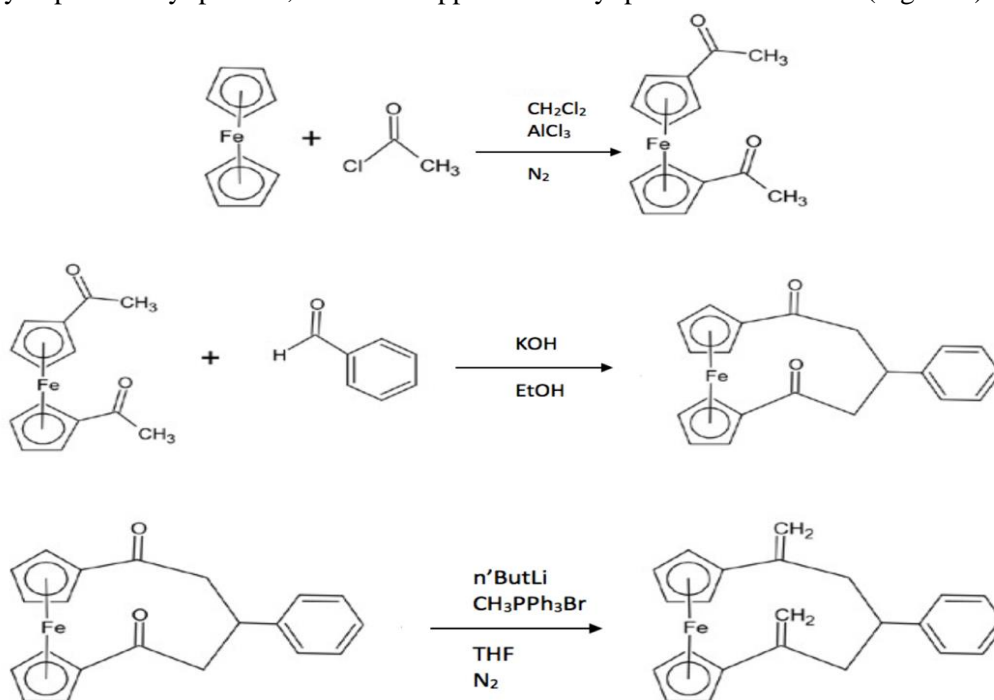
## CHAPTER III

### RESULTS & DISCUSSION

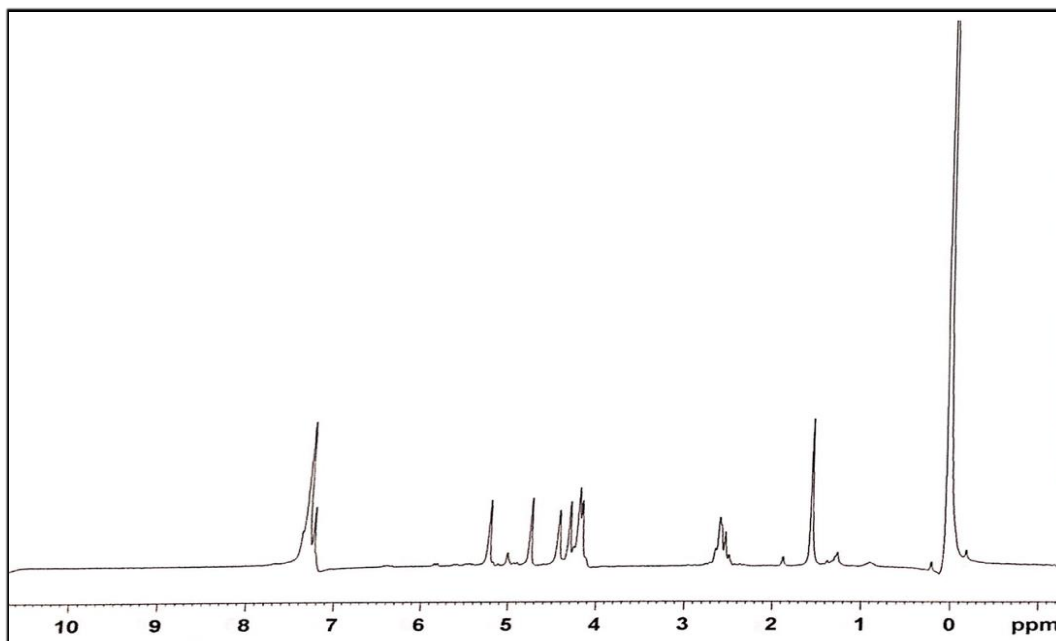
#### 3.1. Synthesis of 3-phenyl [5] ferrocenophane-1, 5-dimethylene with vinyl imidazole

##### 3.1.1. Synthesis of 3-Phenyl [5] ferrocenophane-1, 5-dimethylene<sup>8</sup>

The synthesis of 3-phenyl [5] ferrocenophane-1, 5-dimethylene was achieved according to a literature method<sup>8</sup>. Under Friedel-Crafts conditions, ferrocene was acetylated. Then 3-phenyl [5] ferrocenophane-1, 5-dione was formed by reacting benzaldehyde with 1,1'-diacetylferrocene. Utilizing a Wittig reaction, the dione was converted to the diene. The <sup>1</sup>H NMR spectrum of monomer was consistent with reported spectra in literature<sup>8</sup>. In the <sup>1</sup>H NMR spectrum of 3-phenyl [5] ferrocenophane-1, 5-dimethylene, peaks were observed at 7.2-7.6 ppm for the phenyl protons, at 4.80-5.30 ppm for vinylidene protons, at 4.18-4.49 ppm for cyclopentadienyl protons, and at 4.17 ppm for benzyl protons as shown in (Figure 5).



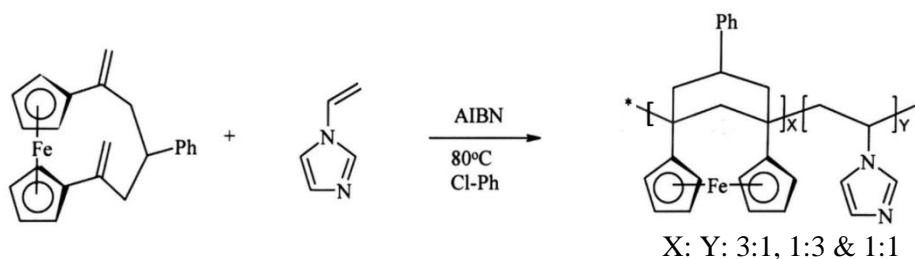
**Scheme 4:** Synthesis of 3-Phenyl [5] ferrocenophane-1, 5-dimethylene<sup>8</sup>



**Figure 5:**  $^1\text{H}$ -NMR Spectrum of 3-phenyl[5]ferroceneophane-1,5-dimethylene

### 3.2. Polymer Synthesis

Using a literature method, 3-phenyl [5] ferrocenophane-1,5-dimethylene was polymerized with vinyl imidazole utilizing  $\alpha, \alpha$ -azobisisobutyronitrile as a free radical initiator in chlorobenzene, affording good polymer yields of 80% as shown in Scheme 5.

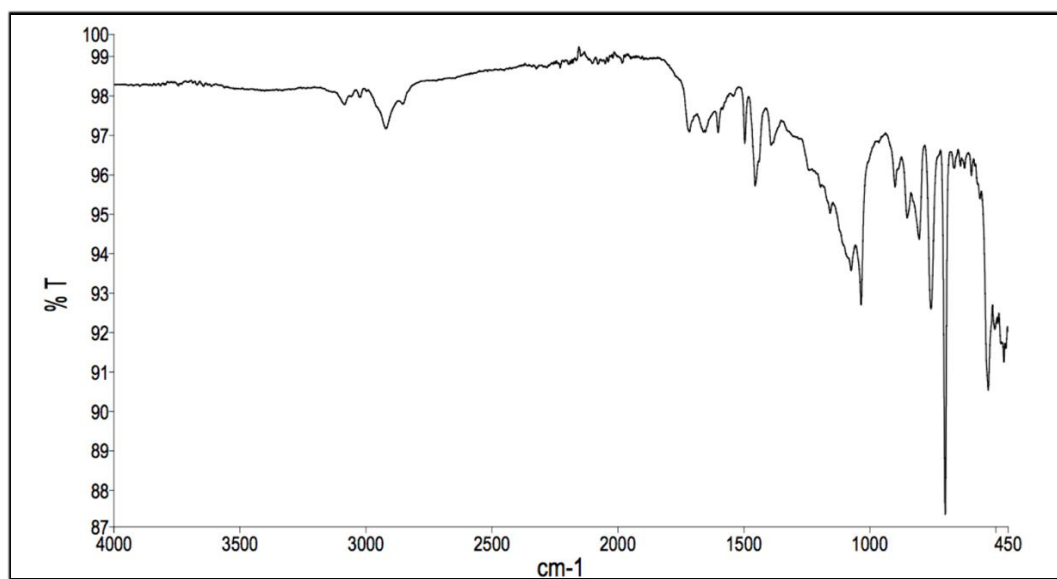


**Scheme 5:** Copolymerization of 3-phenyl [5] ferrocenophane-1, 5-dimethylene with vinyl imidazole

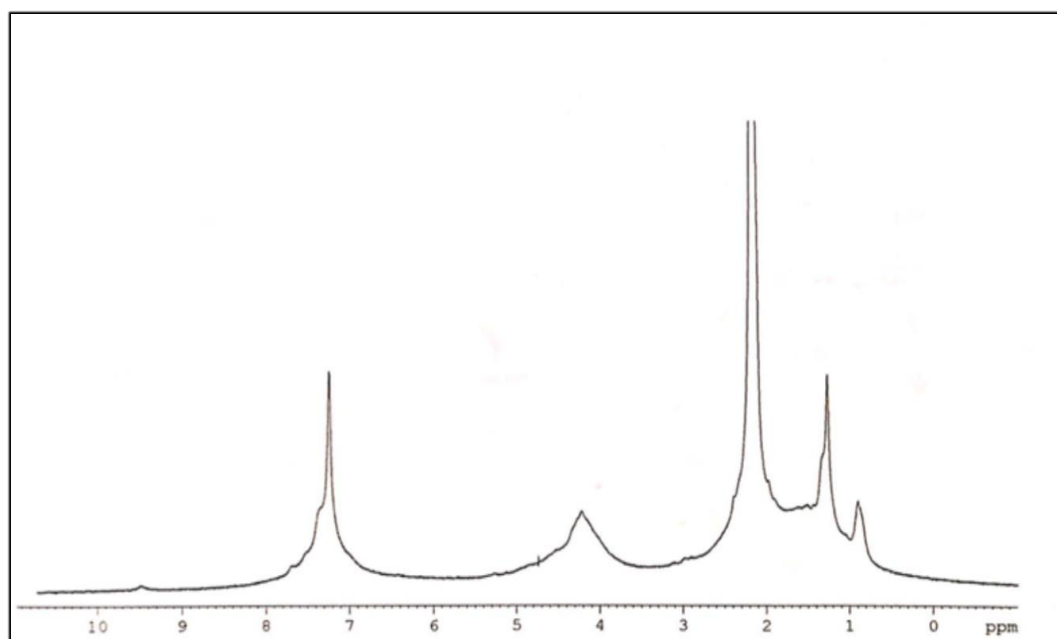
The FTIR,  $^1\text{H}$  NMR, and  $^{13}\text{C}$ -NMR spectra for the 1:1 copolymer are shown in Figures 5, 6, and 7, respectively. The FTIR spectrum displayed absorption peaks at 3087 and 2920  $\text{cm}^{-1}$  for C-H aromatic and C-H aliphatic, respectively. The  $^1\text{H}$  NMR spectrum showed signals from ferrocenyl, imidazole and aliphatic protons at 4-4.3 ppm, 7.1-7.5 ppm, and 0.9-2.5ppm, respectively. In Figure 6, no signals were observed at 4.8-5.4 ppm, indicating the

absence of residual monomer. In the  $^{13}\text{C}$ -NMR spectrum of the 1:1 copolymer, only weak signals were observed. Since the polymer had limited solubility, the solution was not sufficiently concentrated to obtain a good signal: noise ratio.

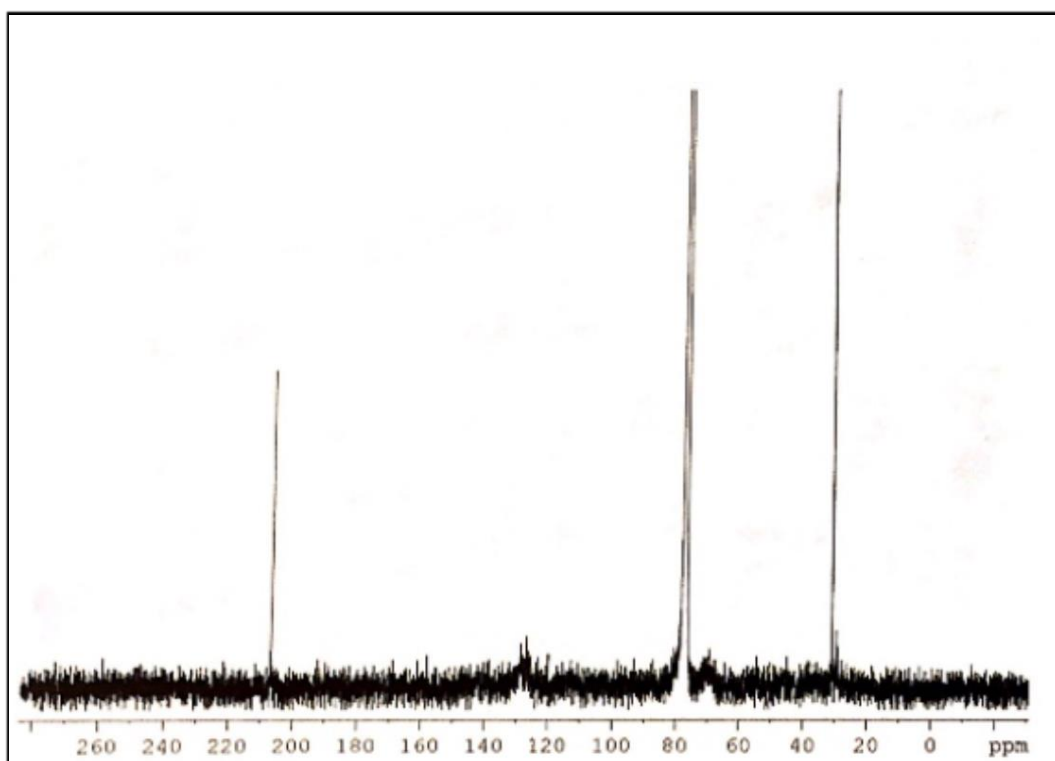




**Figure 6:** FTIR Spectrum of 1:1 Copolymer



**Figure 7:** <sup>1</sup>H NMR Spectrum of 1:1 Copolymer



**Figure 8:**  $^{13}\text{C}$ -NMR Spectrum of 1:1 Copolymer

### 3.3. Electrochemical Measurements

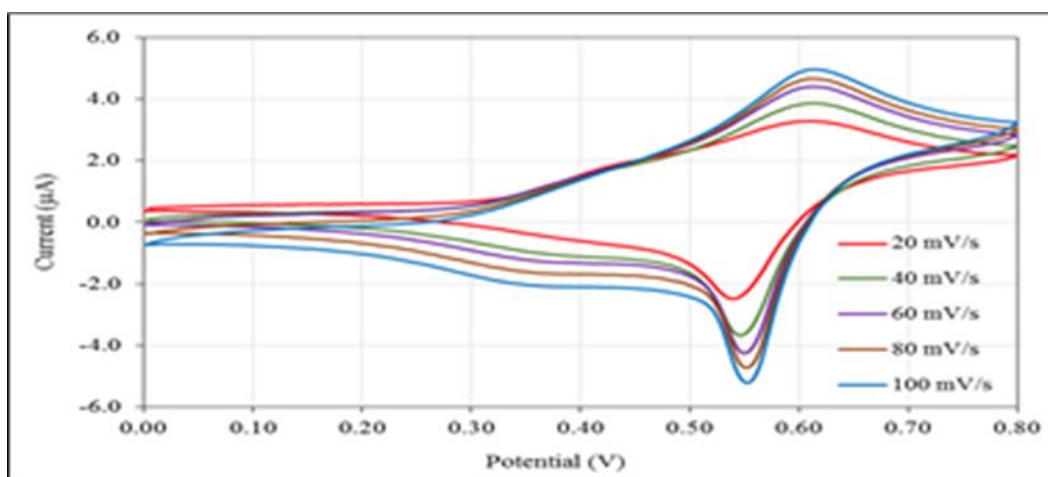
#### 3.3.1. The Solution Electrochemistry of Polymers

Electrochemical solutions were prepared in dichloromethane with tetrabutylammounium hexaflourophosphate ( $\text{NBu}_4\text{PF}_6$ ) as the supporting electrolyte. All polymers were investigated by cyclic voltammetry except 1:3 copolymer, due to a lack of solubility. Cyclic voltammetry (CV) was performed in order to determine the electrochemical behavior regarding each polymer. CV was performed in the range of 0.0V to 0.80V, with scan rates of 20, 40, 60, 80, or 100  $\text{mV/s}^{-1}$ . The oxidation-reduction potentials of each polymer are given in Table 1. Cyclic voltammetry of polymer 1:1 showed one oxidation wave associated with one reduction wave observed at 0.59 V and 0.32 V respectively, at scan rates of 40  $\text{mV/s}^{-1}$  and higher. However, at a scan rate of 20  $\text{mV/s}^{-1}$ , a possible two oxidation processes with one associated reduction peak could be observed. This could indicate that ferrocene was under various electronic environments which may suggest that ferrocene has one or two neighboring imidazole moieties. Also, cyclic voltammetry of polymer 3:1, two oxidation waves at 0.41 and 0.61V associated with two reduction waves were observed at 0.55 and 0.35

V. Each polymer displayed electrochemical reversibility, so the average value of copolymers can be determined by  $E_{1/2} = (E_{pc} + E_{pa})/2$ . In addition, the redox potential ( $E_{1/2}$ ) of polymer 3:1 can be seen at 0.58 and 0.37V as shown in Table1.

**Table1:** Oxidation-Reduction Potential of Each Polymer in  $\text{CH}_2\text{Cl}_2$

Polymer	$E_{ox}$ (V)	$E_{red}$ (V)	$E_{1/2}$ (V)
1:1	0.59	0.33	0.46
	0.38	...	...
3:1	0.61	0.55	0.58
	0.39	0.35	0.37



**Figure 9:** CVs of Copolymer (3:1) in  $\text{CH}_2\text{Cl}_2$  with  $\text{Bu}_4\text{NPF}_4$

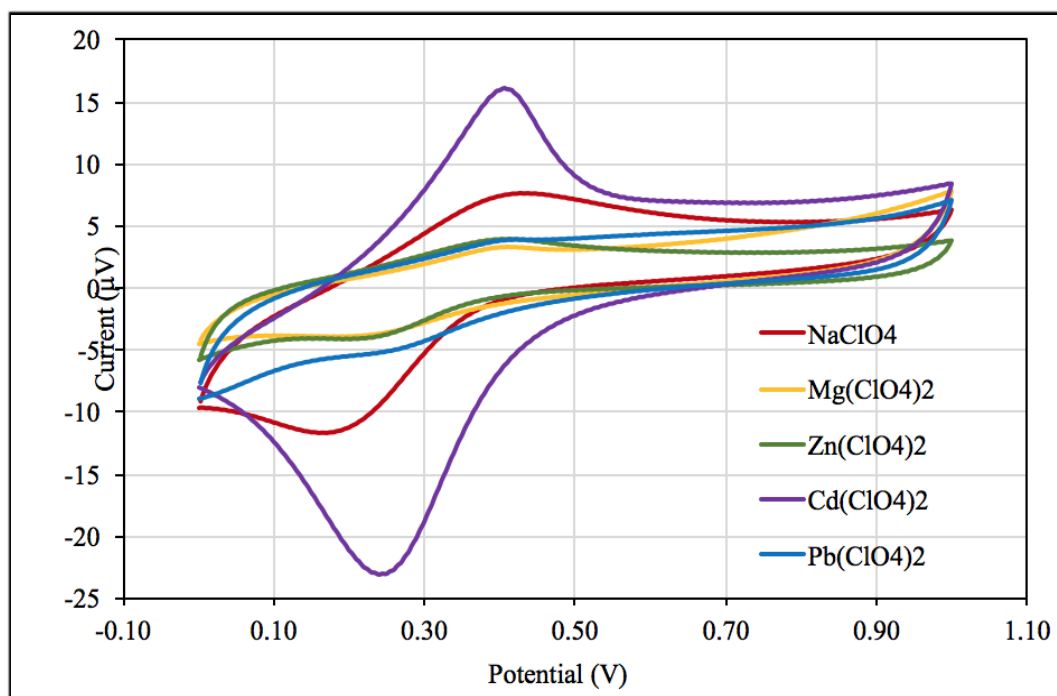
### 3.3.2. Electrochemical Analysis of Chemically Modified Electrodes

Chemically modified electrodes were prepared by casting from chloroform solutions (2  $\mu\text{L}$ ) at a concentration of 3 mg/mL. After casting, the electrodes were put into various electrolyte solutions (0.1M):  $\text{NaClO}_4$ ,  $\text{Mg}(\text{ClO}_4)_2$ ,  $\text{Zn}(\text{ClO}_4)_2$ ,  $\text{Cd}(\text{ClO}_4)_2$ , and  $\text{Pb}(\text{ClO}_4)_2$ . In order to determine the polymer's electrochemical behavior, cyclic voltammetry was used. Redox potentials of 1:1 and 3:1 copolymers in various aqueous electrolytes are given in Table 2. A single anodic wave associated with a single cathodic wave were observed with each metal which may indicate that these metals did not coordinate to imidazole to increases the electron deficiency of the imidazole. Cyclic voltammetry of polymer 3:1 showed one

oxidation wave at 0.41 V associated with one reduction wave at 0.25 V with  $\text{Cd}(\text{ClO}_4)_2$  as a supporting electrolyte. From the cyclic voltammetry figure, the redox potentials ( $E_{1/2}$ ) of polymer 3:1 were obtained at 0.30 V, 0.70 V, 0.71 V, 0.33 V and 0.34 V for  $\text{NaClO}_4$ ,  $\text{Mg}(\text{ClO}_4)_2$ ,  $\text{Zn}(\text{ClO}_4)_2$ ,  $\text{Cd}(\text{ClO}_4)_2$  and  $\text{Pb}(\text{ClO}_4)_2$ , respectively. The changes of redox potentials suggest that there may be a result of differences in ion pair or in solvation of anion.

**Table 2:** Redox Potentials of 1:1 and 3:1 Copolymers with aqueous electrolytes of  $\text{NaClO}_4$ ,  $\text{Mg}(\text{ClO}_4)_2$ ,  $\text{Zn}(\text{ClO}_4)_2$ ,  $\text{Cd}(\text{ClO}_4)_2$ , and  $\text{Pb}(\text{ClO}_4)_2$

<i>Polymer</i>	<i>Electrolyte</i>	<i>E<sub>ox</sub></i> (V)	<i>E<sub>red</sub></i> (V)	<i>E<sub>1/2</sub></i> (V)
1:1	$\text{NaClO}_4$	0.41	0.17	0.29
	$\text{Mg}(\text{ClO}_4)_2$	0.38	0.24	0.31
	$\text{Zn}(\text{ClO}_4)_2$	0.39	0.22	0.305
	$\text{Cd}(\text{ClO}_4)_2$	0.43	0.35	0.39
	$\text{Pb}(\text{ClO}_4)_2$	0.41	0.21	0.31
3:1	$\text{NaClO}_4$	0.42	0.18	0.30
	$\text{Mg}(\text{ClO}_4)_2$	0.40	0.26	0.33
	$\text{Zn}(\text{ClO}_4)_2$	0.42	0.25	0.335
	$\text{Cd}(\text{ClO}_4)_2$	0.41	0.25	0.33
	$\text{Pb}(\text{ClO}_4)_2$	0.40	0.28	0.34



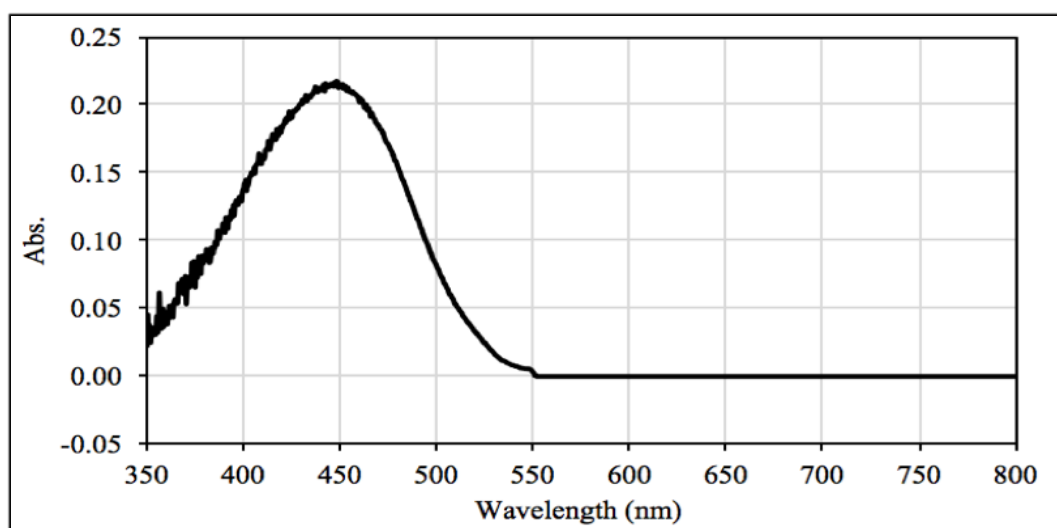
**Figure 10:** CVs of Copolymer (3:1) with Various Metals ( $\text{NaClO}_4$ ,  $\text{Mg}(\text{ClO}_4)_2$ ,  $\text{Zn}(\text{ClO}_4)_2$ ,  $\text{Cd}(\text{ClO}_4)_2$ , and  $\text{Pb}(\text{ClO}_4)_2$ )

### 3.4 UV-Vis Spectroscopy

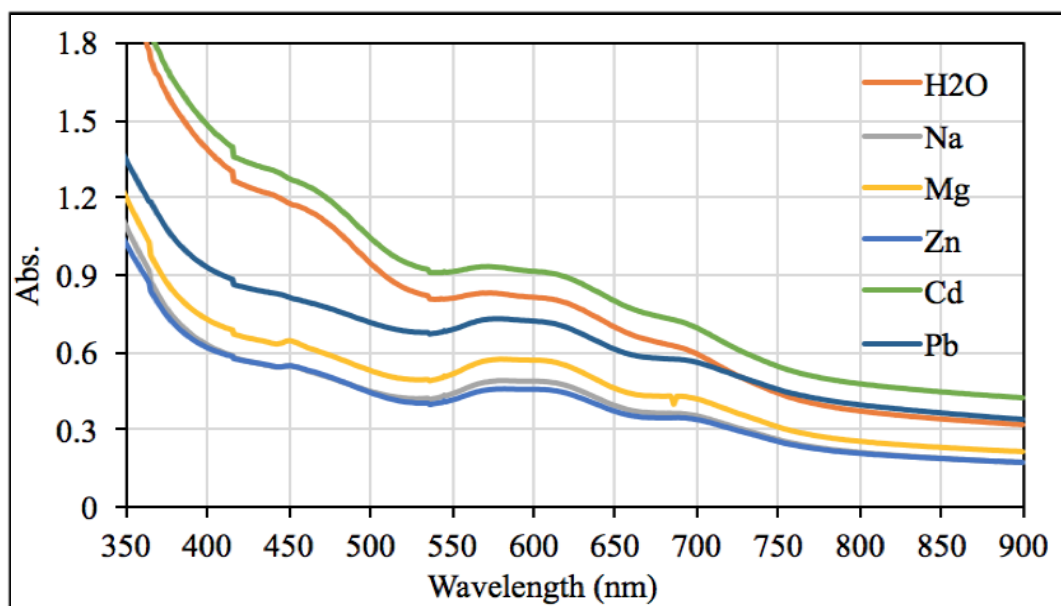
UV-Vis spectroscopy was used to investigate electronic interactions of ferrocene and imidazole moieties. Ferrocenyl groups act as strong electron donors while imidazole groups act as electron acceptors. The charge transfer in ferrocene-imidazole system is accompanied with optical electronic transitions that are located in the UV and visible range. The amount of energy absorbed depends on the energy difference between the LUMO and HOMO electron orbitals of the moieties. The preparation of polymer thin films was achieved by casting from dichloromethane (10  $\mu\text{L}$  at a concentration of 5 mg/mL) on to Indium Tin Oxide plates before testing. After casting, polymer thin films were placed in each of the following electrolytes,  $\text{NaClO}_4$ ,  $\text{Zn}(\text{ClO}_4)_2$ ,  $\text{Mg}(\text{ClO}_4)_2$ ,  $\text{Cd}(\text{ClO}_4)_2$ , and  $\text{Pb}(\text{ClO}_4)_2$  which were tested in the range 350-900nm.

The UV-Vis spectrum of a solution of 3:1 copolymer in Figure10 displayed an absorbance maxima at 450nm which is typical of the ferrocenophane absorption spectrum. UV-vis spectra of the 1:1 polymer thin film in  $\text{H}_2\text{O}$ ,  $\text{NaClO}_4$ ,  $\text{Zn}(\text{ClO}_4)_2$ ,  $\text{Mg}(\text{ClO}_4)_2$ ,  $\text{Cd}(\text{ClO}_4)_2$ , and  $\text{Pb}(\text{ClO}_4)_2$  are shown in Figure 11. UV-vis spectroscopy of polymer 1:1 film

showed the first absorbance maximum at 450 nm as shown in solution which is consistent with ferrocene absorbance. However, additional absorptions were observed at 630 nm and 700 nm. Previous studies have also revealed peaks in this range which indicate interactions of a charge transfer complex<sup>28</sup>. In this case, the absorbance bands at 630 nm and 700 nm may indicate the interaction of the ferrocene and imidazole moieties since these groups are in a close proximity within a thin film. These data suggest that there may be an extended  $\pi$  stacking. However, there was no difference in the UV-spectra in the presence of various aqueous electrolytes which suggest that metals were not migrating into the film. The organic nature of the polymer may prevent sufficient hydration to allow ion migration into the film.



**Figure 11:** UV-vis spectrum of 3:1 copolymer in solution



**Figure 12:** UV-vis spectra of 3:1 copolymer in various electrolytes ( $\text{NaClO}_4$ ,  $\text{Mg}(\text{ClO}_4)_2$ ,  $\text{Zn}(\text{ClO}_4)_2$ ,  $\text{Cd}(\text{ClO}_4)_2$ , and  $\text{Pb}(\text{ClO}_4)_2$ )

## CHAPTER IV

### CONCLUSION

Three new copolymers were synthesized by free radical polymerization using a literature procedure<sup>8</sup>. These three copolymers were prepared by copolymerization of 3-phenyl [5] ferrocenophane-1,5-dimethylene with vinyl imidazole utilizing ABIN as the initiator. All polymers were characterized using <sup>13</sup>C-NMR, <sup>1</sup>H-NMR, and FTIR. The spectra for each polymer were consistent with the corresponding structure.

Electrochemical solutions were prepared in CH<sub>2</sub>Cl<sub>2</sub> using tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The cyclic voltammetry was performed to analyze the electrochemical behavior of each polymer. Cyclic voltammetry of polymers displayed electrochemical reversibility for each polymer include two redox waves for the 3:1 copolymer. Chemically modified electrodes of copolymer films were prepared by casting from chloroform solutions. Cyclic voltammetry of polymer thin films was performed in various the aqueous electrolytes: sodium perchlorate, cadmium perchlorate, zinc perchlorate, magnesium perchlorate, and lead perchlorate. All polymer films in aqueous solutions of electrolytes showed a single redox wave with each metal. Furthermore, the UV-Vis spectroscopy was studied for the electronic communications of the ferrocene and imidazole moieties in the copolymers. Although UV spectroscopy was consistent with electronic interactions, differences were not observed in the presence of different metals. In UV-Vis spectroscopy, all polymers displayed an absorbance at 450 nm in methylene chloride solution or as a thin film with various metals. The UV-vis spectra of the 3:1 copolymer as a thin film compared to the solution showed an increase in absorption at 630nm and 700nm which may be a result of interaction between the ferrocene and imidazole moieties.



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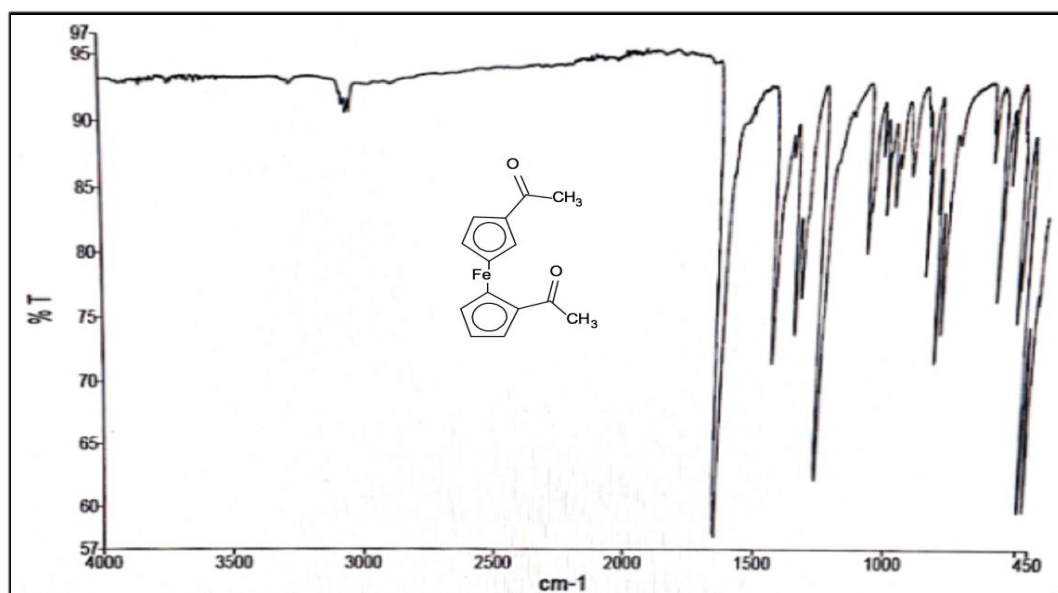
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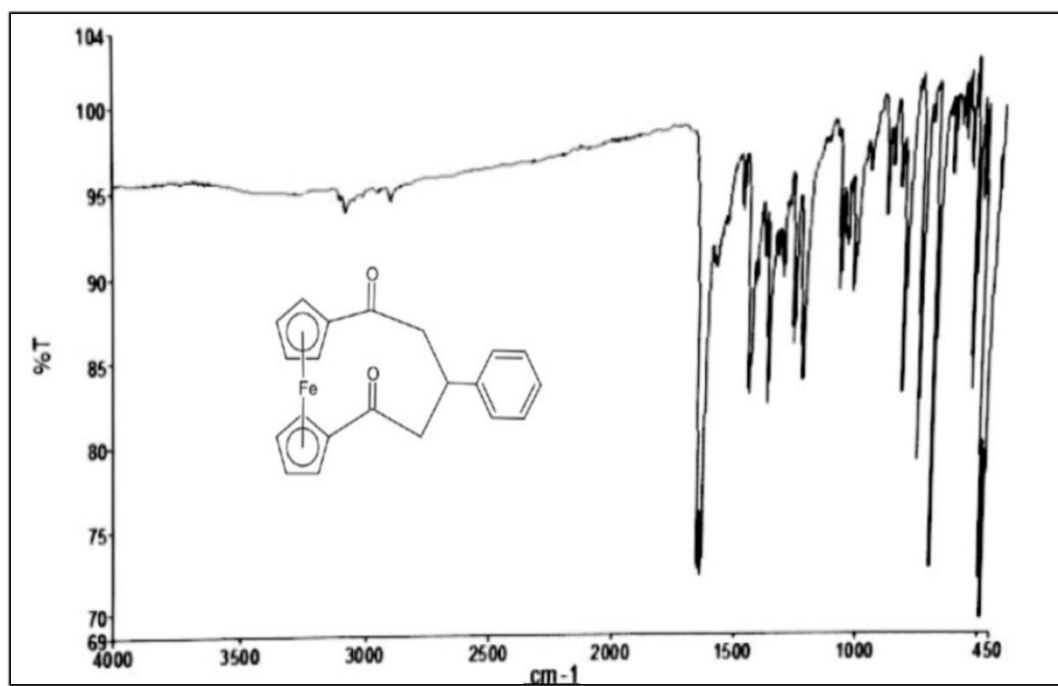
## APPENDIX

## SUPPLEMENTAL LISTS

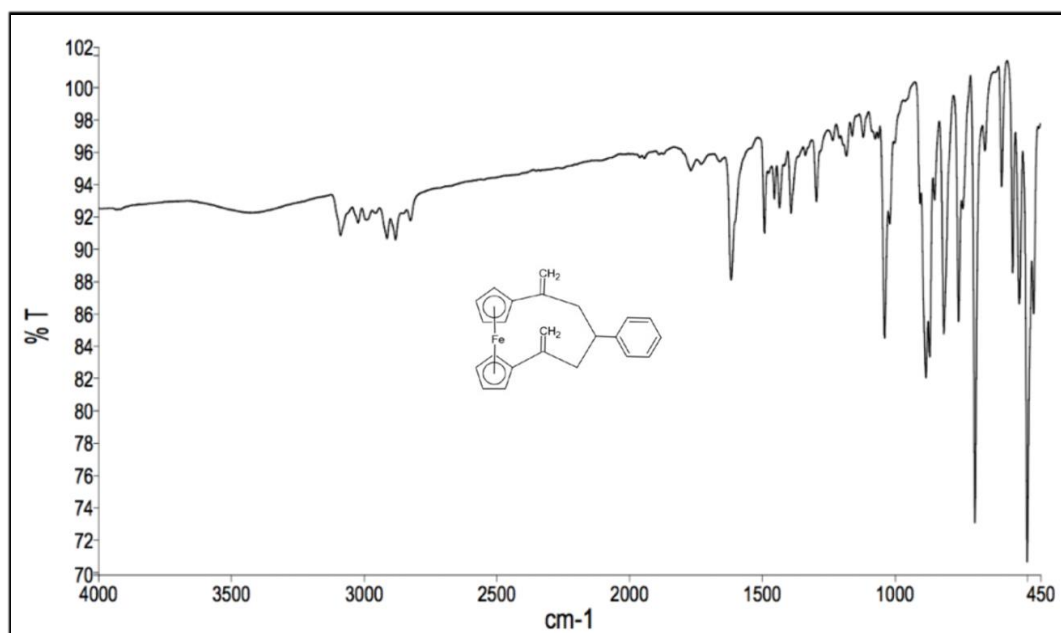
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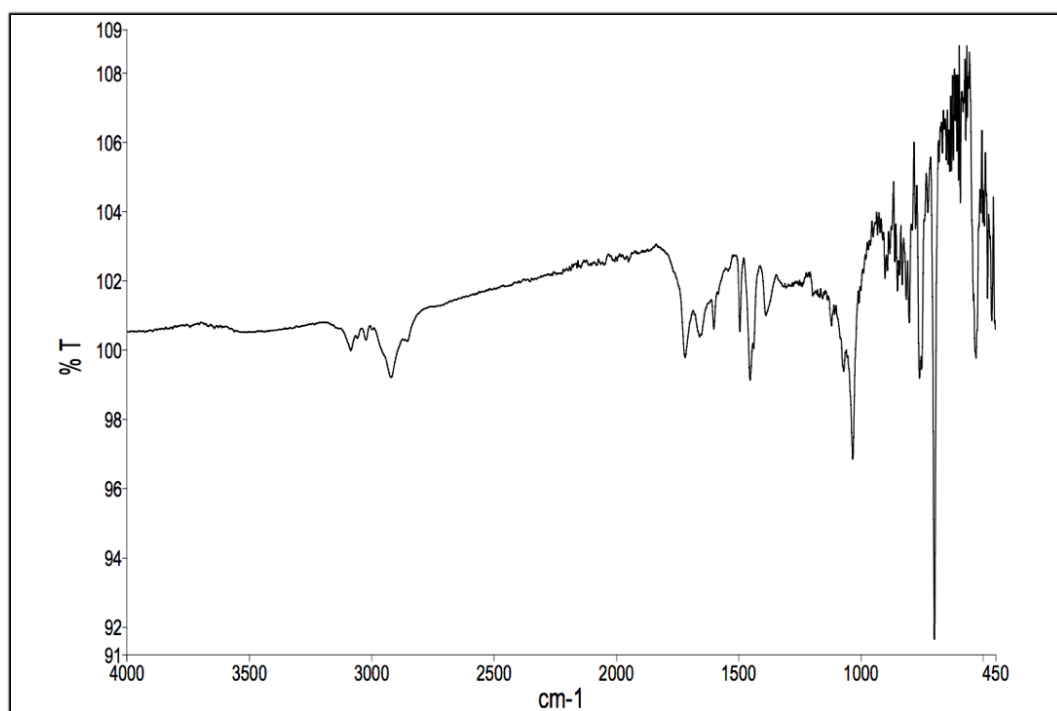
**Figure S1:** FTIR Spectrum of 1, 1'-diacetylferrocene



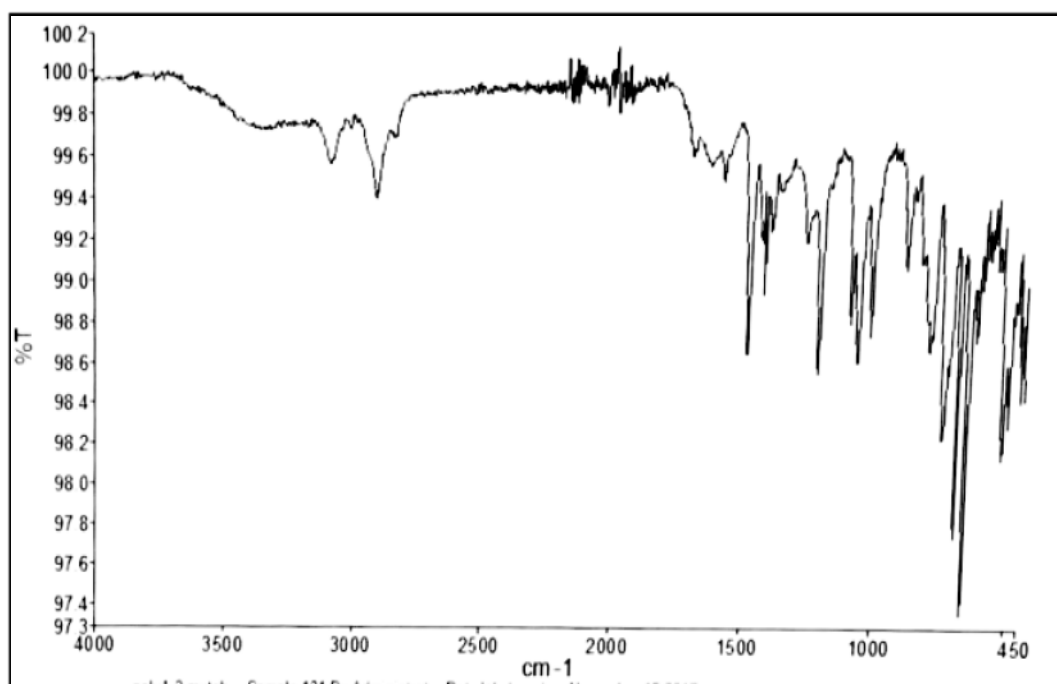
**Figure S2:** FTIR Spectrum of 3-phenyl[5]ferrocenophane-1, 5-dione



**Figure S3:** FTIR Spectrum of 3-phenyl[5]ferroceneophane-1,5-dimethylene

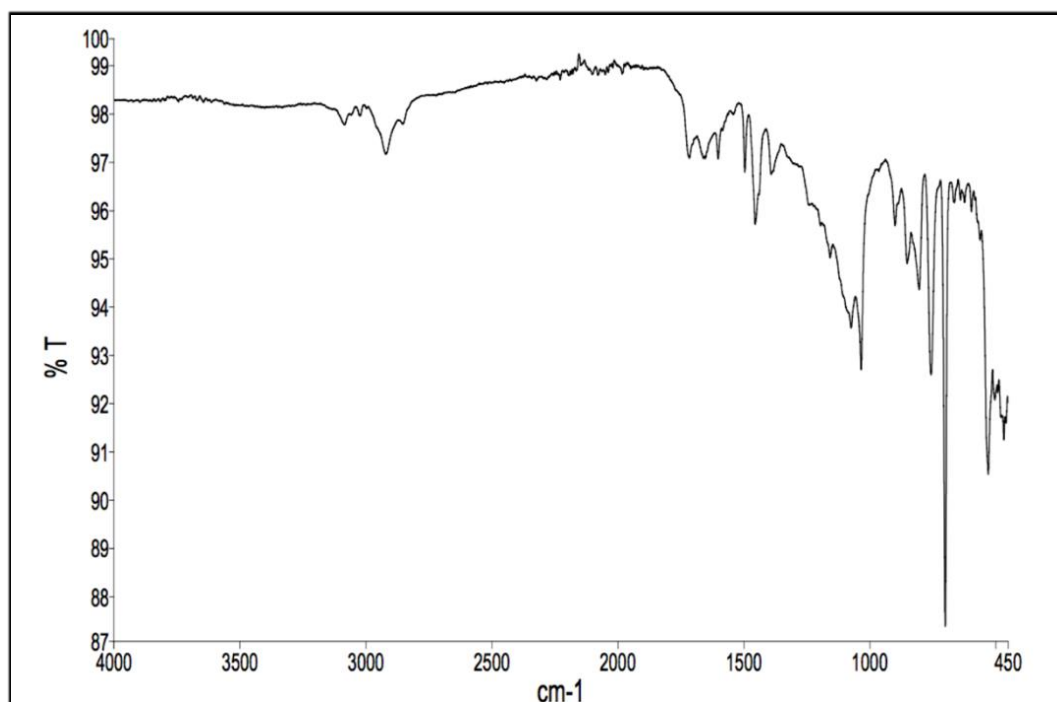


**Figure S4:** FTIR Spectrum of 3:1 Copolymer

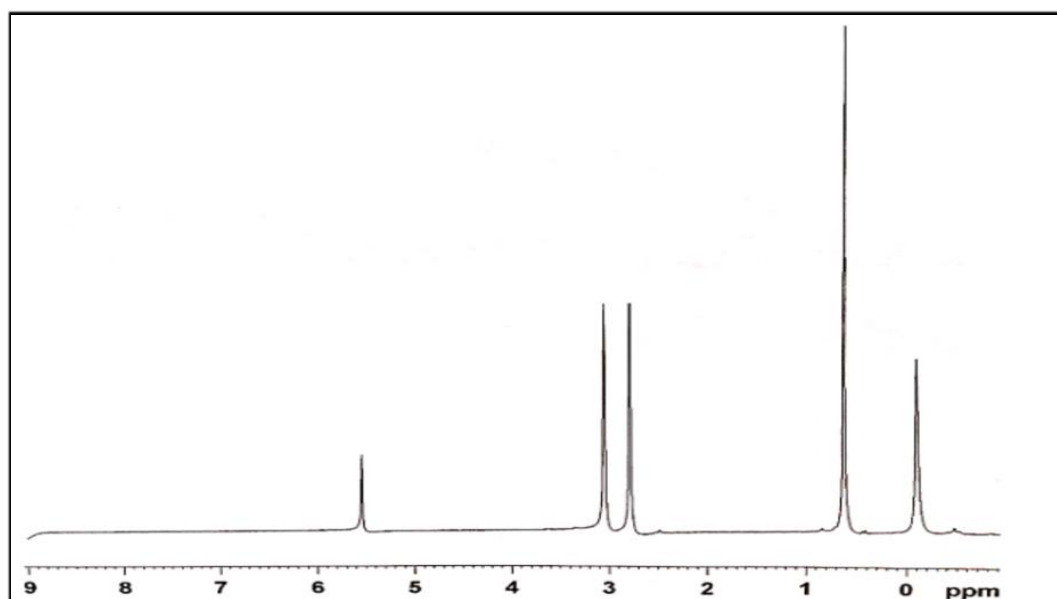


**Figure S5:** FTIR Spectrum of 1:3 Copolymer

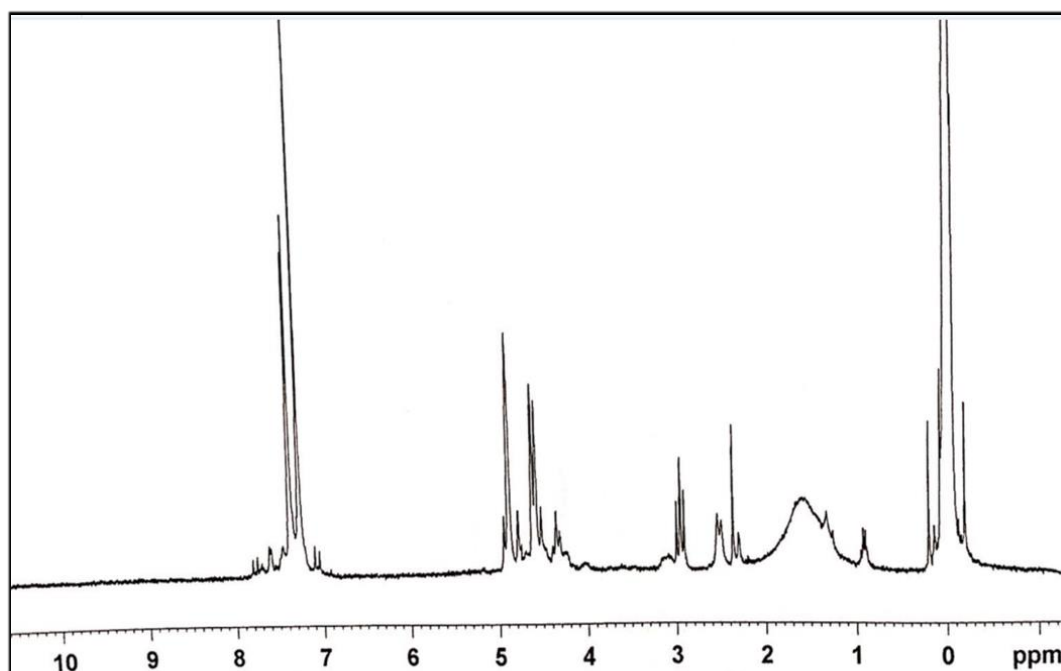




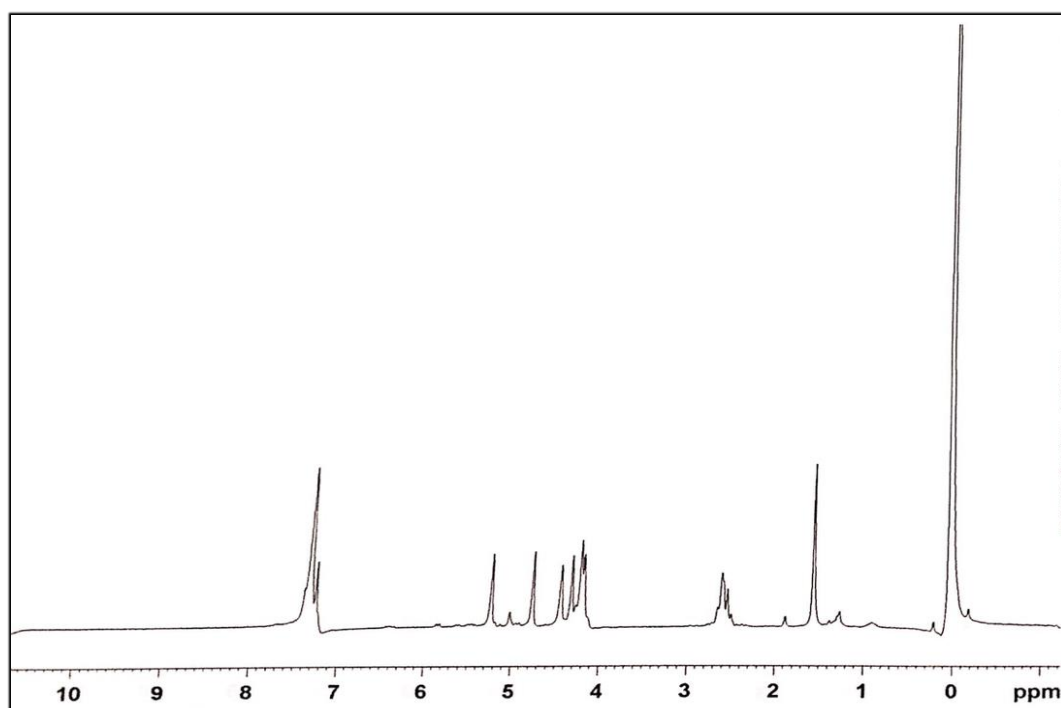
**Figure S6:** FTIR Spectrum of 1:1 Copolymer



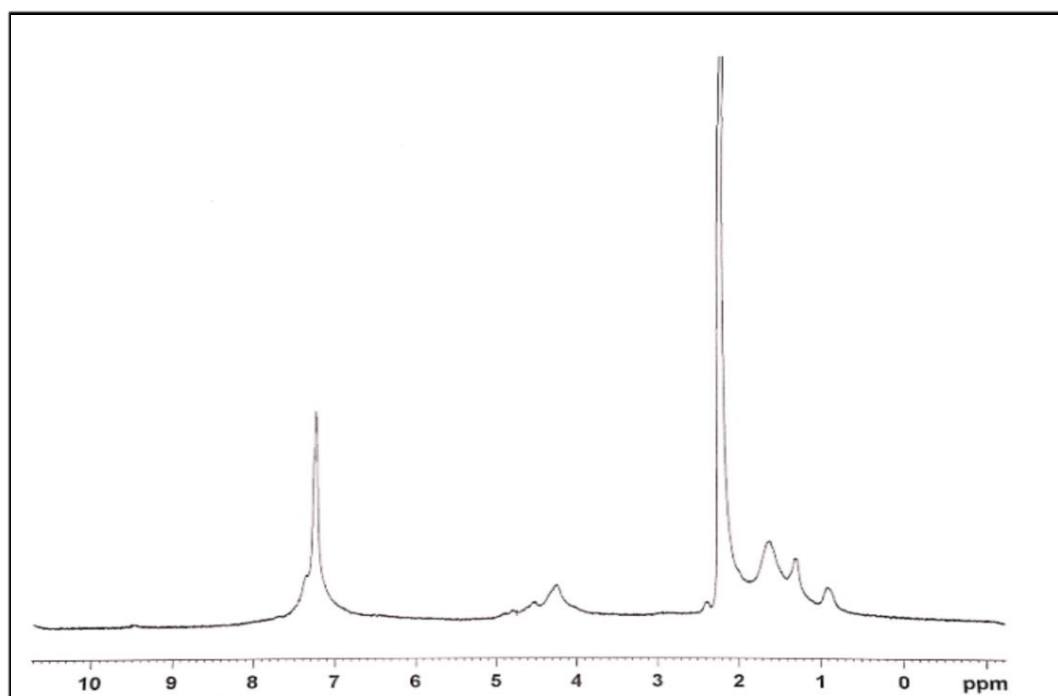
**Figure S7:** <sup>1</sup>H NMR Spectrum of 1,1'-diacetylferrocene



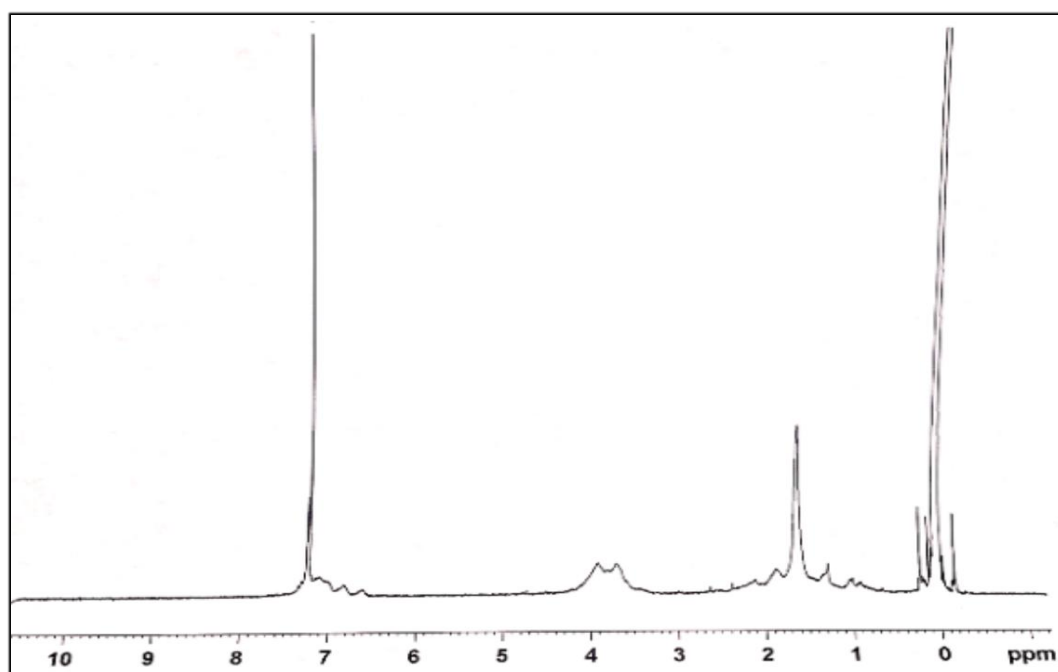
**Figure S8:** <sup>1</sup>H-NMR Spectrum of 3-phenyl[5]ferrocenophane-1,5-dione



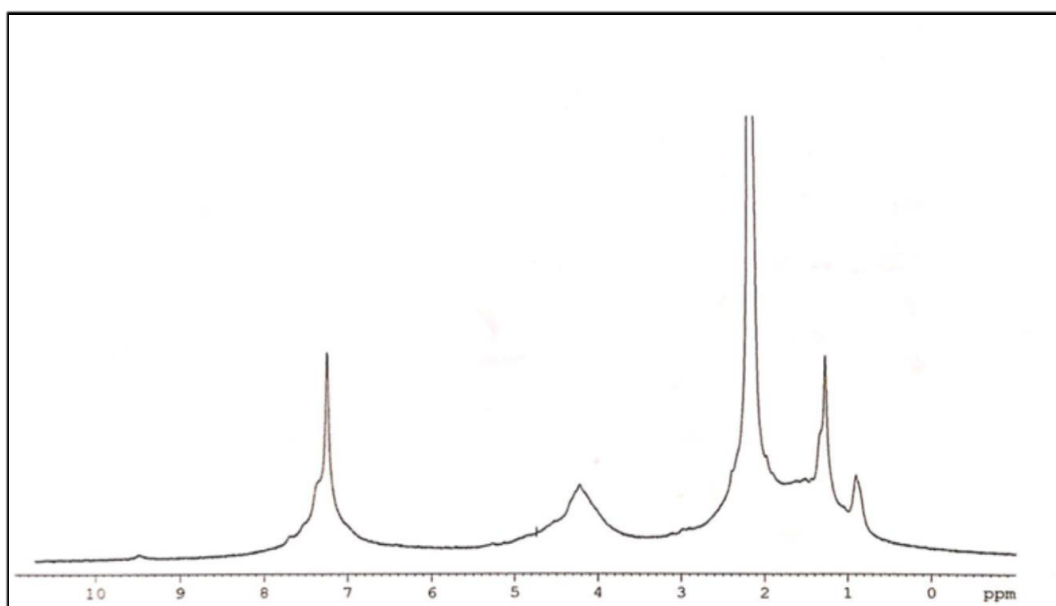
**Figure S9:** <sup>1</sup>H-NMR Spectrum of 3-phenyl[5]ferroceneophane-1,5-dimethylene



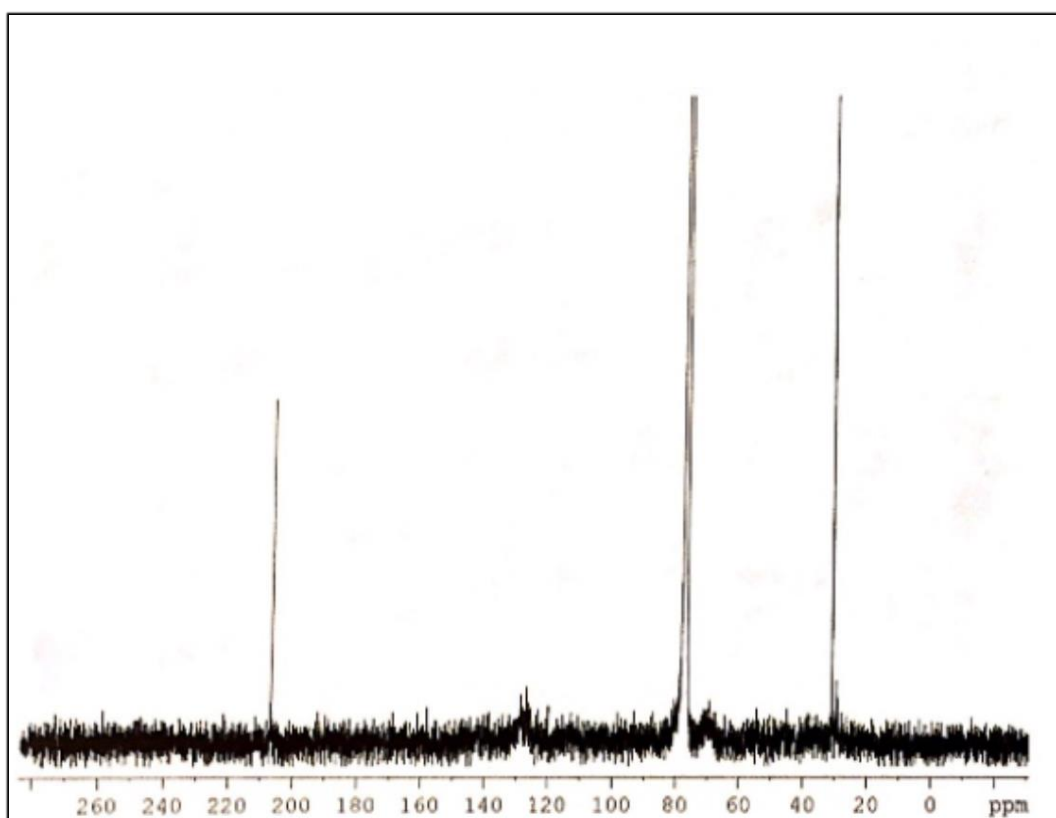
**Figure S10:**  $^1\text{H}$  NMR Spectrum of 3:1 Copolymer



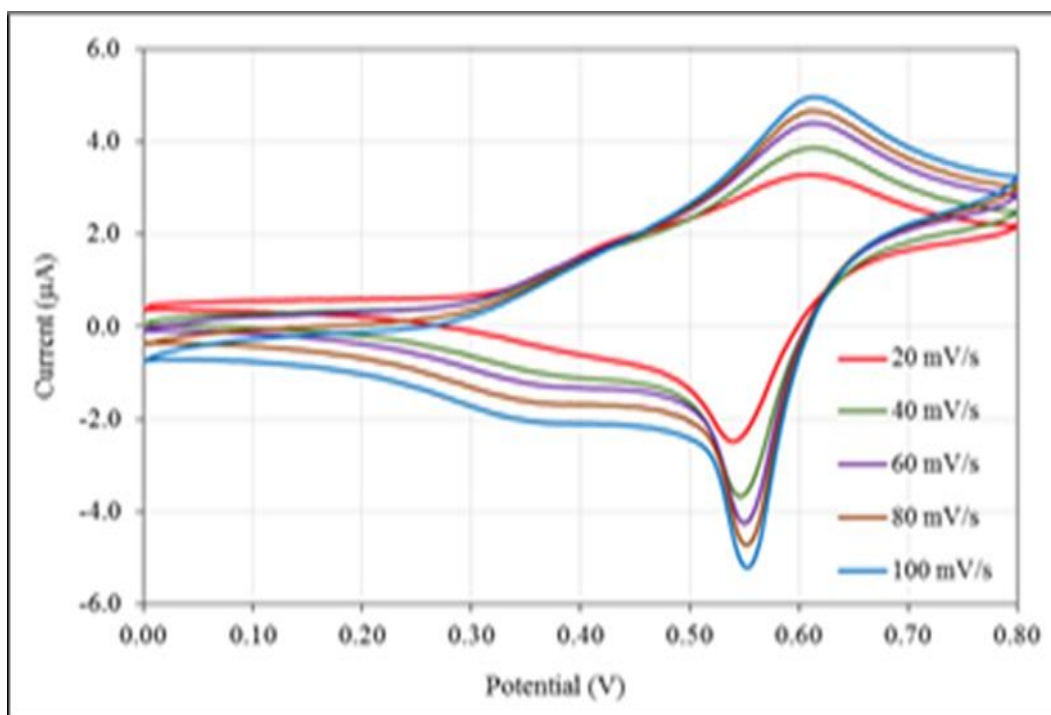
**Figure S11:**  $^1\text{H}$  NMR Spectrum of 1:3 Copolymer



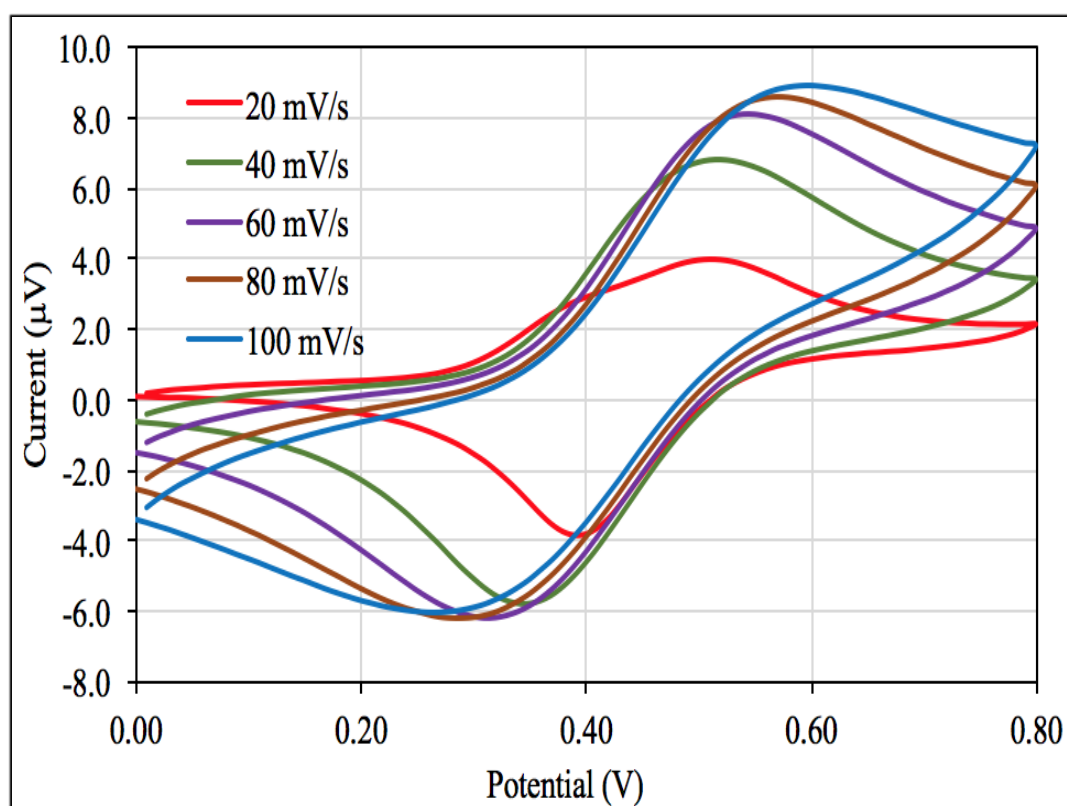
**Figure S12:**  $^1\text{H}$  NMR Spectrum of 1:1 Copolymer



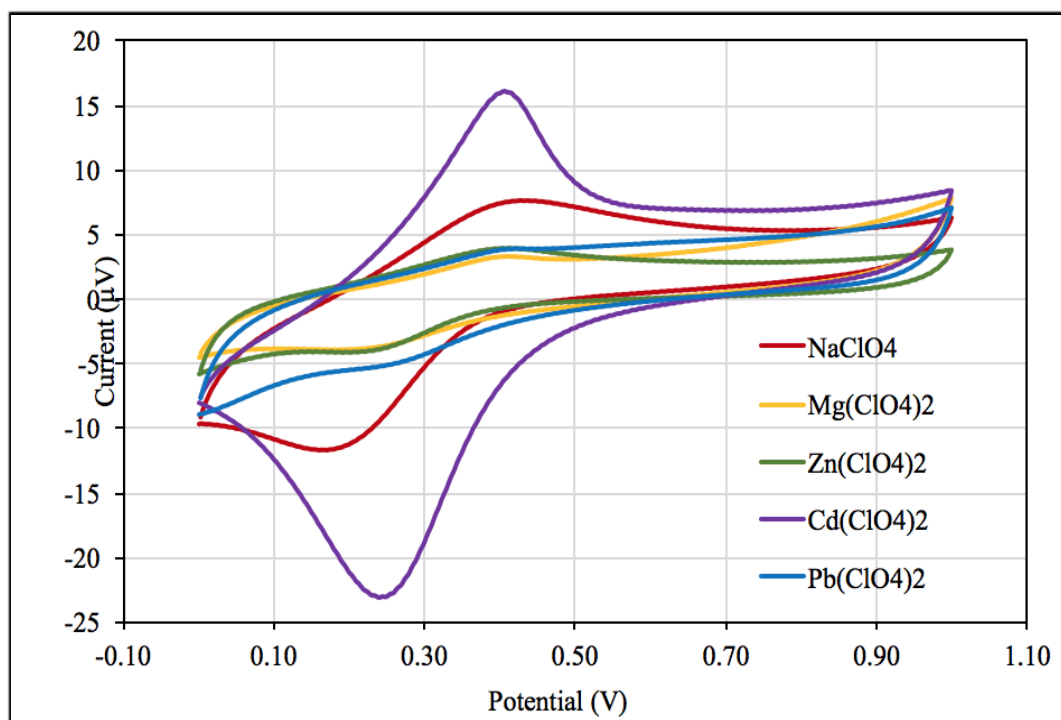
**Figure S13:**  $^{13}\text{C}$ -NMR Spectrum of 1:1 Copolymer



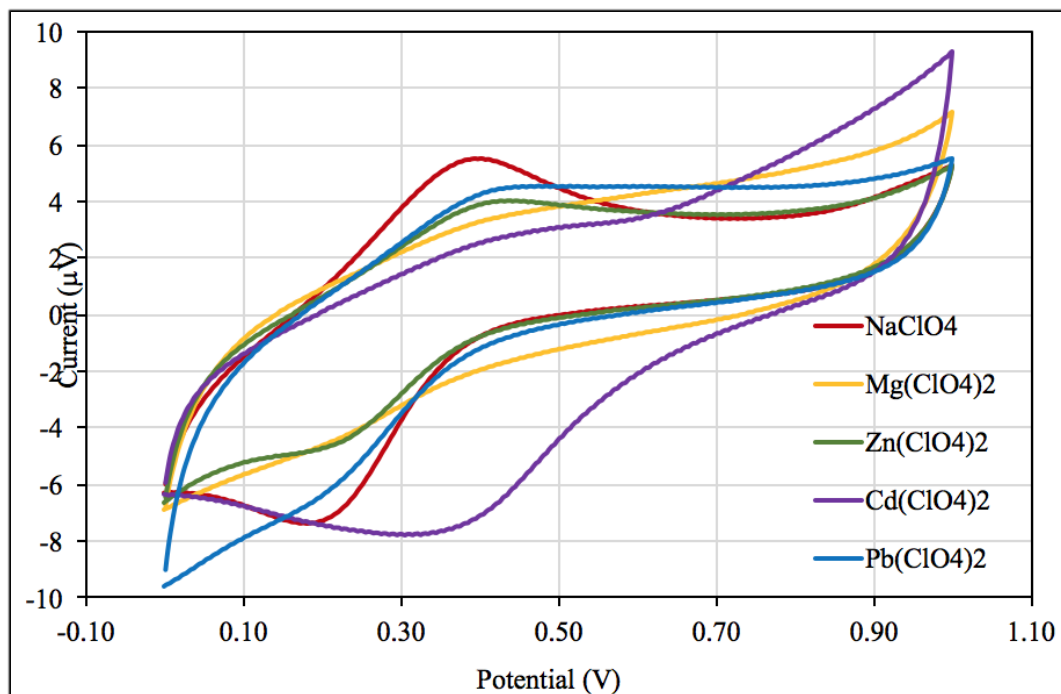
**Figure S14:** CVs of Copolymer (3:1) in  $\text{CH}_2\text{Cl}_2$  with  $\text{Bu}_4\text{NPF}_4$



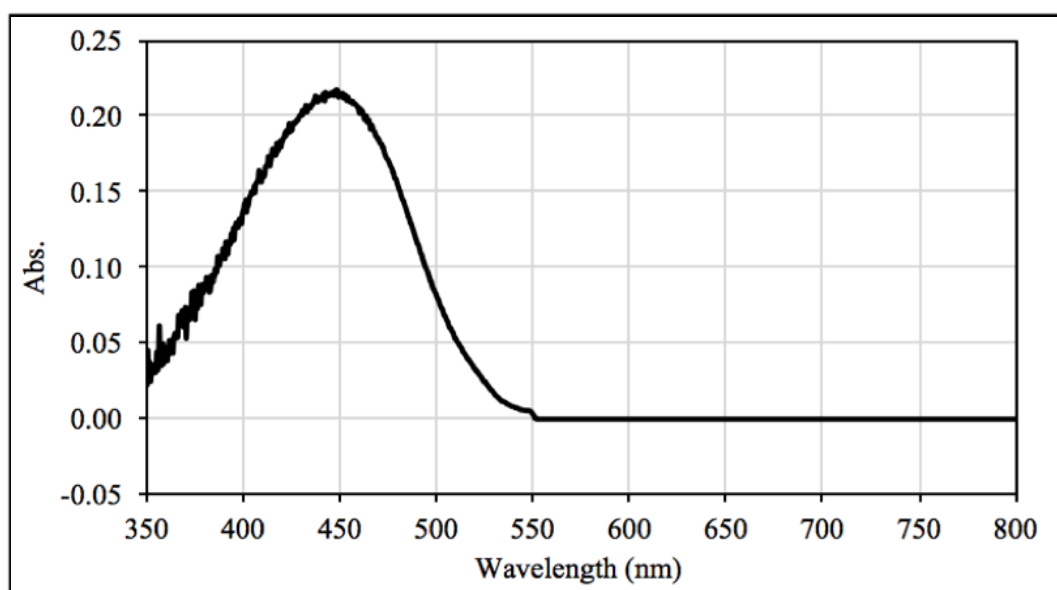
**Figure S15:** CVs of Copolymer (1:1) in  $\text{CH}_2\text{Cl}_2$  with  $\text{Bu}_4\text{NPF}_4$



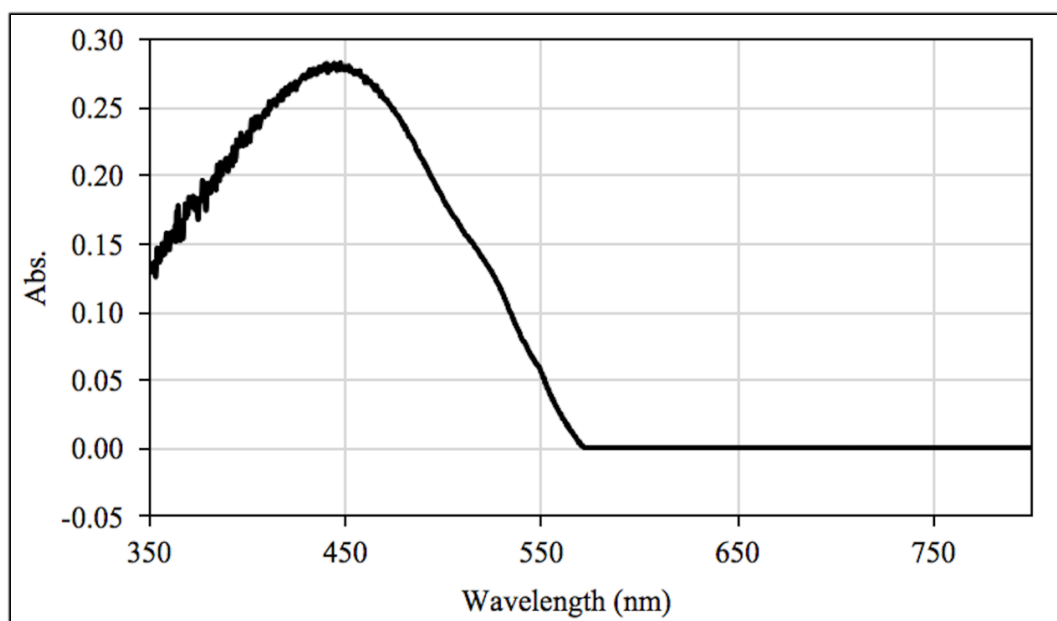
**Figure S16:** CVs of Copolymer (3:1) with Various Metals ( $\text{NaClO}_4$ ,  $\text{Mg}(\text{ClO}_4)_2$ ,  $\text{Zn}(\text{ClO}_4)_2$ ,  $\text{Cd}(\text{ClO}_4)_2$ , and  $\text{Pb}(\text{ClO}_4)_2$ )



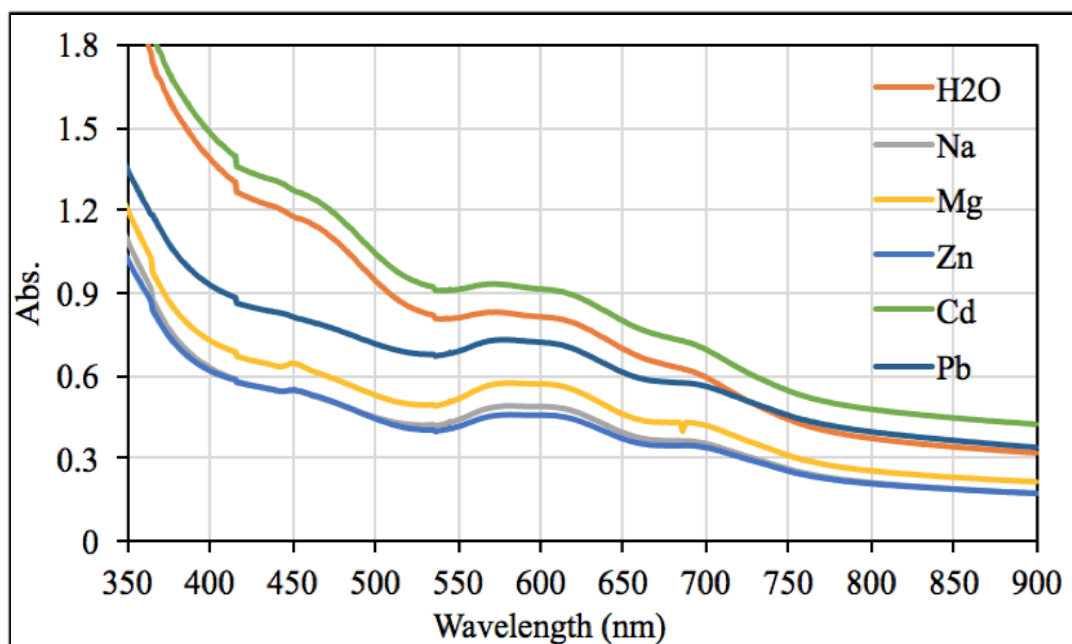
**Figure S17:** CVs of Copolymer (1:1) with Various Metals ( $\text{NaClO}_4$ ,  $\text{Mg}(\text{ClO}_4)_2$ ,  $\text{Zn}(\text{ClO}_4)_2$ ,  $\text{Cd}(\text{ClO}_4)_2$ , and  $\text{Pb}(\text{ClO}_4)_2$ )



**Figure S18:** UV-vis Spectrum of 3:1 copolymer in solution



**Figure S19:** UV-vis spectrum of 1:1 copolymer in solution



**Figure S20:** UV-vis spectra of 3:1 copolymer in various electrolytes (NaClO<sub>4</sub>, Mg(ClO<sub>4</sub>)<sub>2</sub>, Zn(ClO<sub>4</sub>)<sub>2</sub>, Cd(ClO<sub>4</sub>)<sub>2</sub>, and Pb(ClO<sub>4</sub>)<sub>2</sub>)