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## **Cobaltocenium Containing Polymers: Complexation With Organic Anion And Initial Assesment For Anion Exchange Membranes**

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COBALTOCENIUM CONTAINING POLYMERS: COMPLEXATION WITH  
ORGANIC ANION AND INITIAL ASSESMENT FOR ANION EXCHANGE  
MEMBRANES

by

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Submitted in Partial Fulfillment of the Requirements

For the Degree of Master of Science in

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2016

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## DEDICATION

To my entire family, my high school and undergraduate teachers, my lab mates,  
and all of my friends

## ACKNOWLEDGEMENTS

I would like to express my gratitude to my advisor Dr. Chuanbing Tang for this great opportunity to work in his research group. He has given incredible amount of guidance and support not only in academia but also in life. His knowledge and expertise in polymer chemistry motivated me to work in this area. Without his guidance, encouragement and persistent help this thesis would not have been possible.

I would also like to thank Dr. Richard D. Adams, Dr. Morgan Stefik and Dr. Harry Ploehn for serving on my committee and providing constructive criticism during research plan. I also want to express my appreciation to all my colleagues, Dr. Peng Yang, Parasmani Pageni, Dr. Jifu Wang, Anisur Rahman, Dr. Zhongkai Wang, Liang Yuan, Mitra Ganewatta, Dr. Hui Li, Tianyu Zhu, Meghan Lamm and Xinzhou Zhang. Working with you all has been a lot of fun and I want to thank you all for your advice and support.

Finally, I would like to thank all the funding supports from the University of South Carolina.

## ABSTRACT

In this thesis, cobaltocenium containing monomers and polymers are investigated for guest anion loading and alkaline anion exchange membrane for fuel cells. The properties of these polymers are characterized and discussed.

Chapter 1 describes overall background and potential applications of metallocene and metallocenium containing polymers. The research objectives of metallocenium containing polymers are discussed.

Cobaltocenium containing polymers have potential applications in biomedical science. Therefore, the effect of different parameters such as electrostatic charge, size, conformation,  $\pi$ -electron system and hydrogen bonding on the interactions between these polymers and small anionic probes has been studied qualitatively, as described in Chapter 2. A fluorescence dye was used to make a complex with polymers. Then small anionic probes were used to displace the dye. The released amount of dye was measured by using simple optical spectroscopy techniques, which give the relative binding affinity of organic probes to polymers.

In Chapter 3, the chemical stability of cobaltocenium cation  $[\text{Cp}_2\text{Co}]^+$  having an eighteen electron closed shell valence configuration, similar to alkali metal cations, was studied at 80 °C in 1 M NaOH solutions using  $^1\text{H}$  NMR, mass spectroscopy and UV-Vis spectroscopy. Attempts were made to synthesize side chain cobaltocenium containing monomers and polymers as alkaline anion exchange membrane for fuel cells.

Finally, a summary with the major results from the previous chapters are discussed in Chapter 4. Suggestions are also offered for future investigations.

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## LIST OF SYMBOLS

$\delta$	chemical shift
$\bar{D}$	dispersity
$T_g$	glass transition temperature
$M_n$	number average molecular weight

## LIST OF ABBREVIATIONS

AAEM.....	Alkaline anion exchange membrane
AAEMFC.....	Alkaline anion exchange membrane fuel cell
AIBN.....	2, 2-Azobisisobutyronitrile
CDB .....	Cumyl dithiobenzoate
CF.....	5(6)-carboxyfluorescein
CTA.....	Chain transfer agent
DCM .....	Dichloromethan
DMAP .....	4-(dimethylamino)pyridine
GPC.....	Gel permeation chromatography
PCoAEMACl .....	Poly (2-cobaltoceniumamidoethyl methacrylate chloride)
RAFT .....	Reversible addition-fragmentation chain-transfer
TBACl.....	Tetrabutylammonium chloride
TMS .....	tetramethylsilane

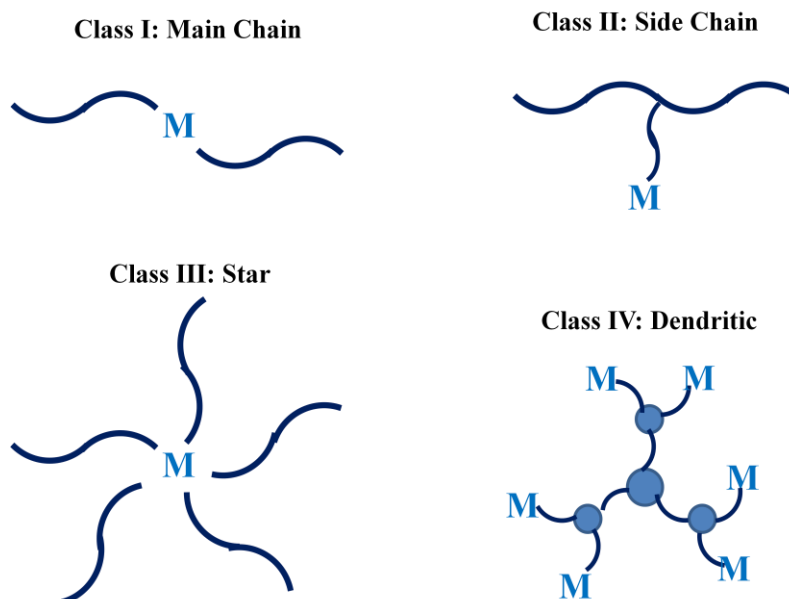
## CHAPTER 1

### GENERAL INTRODUCTION

## 1.1 Metallocene/Metallocenium containing polymer:

Metallopolymers, a class of metal containing polymers, have attracted significant attention during the last decades. These polymers combine metal properties such as catalytic, magnetic, and electronic properties with desirable mechanical and processing properties in polymeric frameworks.<sup>1-3</sup> As a result, they can be utilized in lithography, catalysts, battery materials, redox sensors and biomedical applications.<sup>4-10</sup>

Metallopolymers can be classified into two major categories based on the position of a metal center. First, if the metal center is incorporated into the polymeric backbone, it is called main-chain metallopolymers (Class I). Second, if the metal center is a pendant group attached to the polymeric framework, it is called side-chain metallopolymers (Class II). There are other types of metallopolymers such as star shaped (Class III) and dendritic (Class IV) metallopolymers.<sup>11-16</sup>



**Figure 1.1** Classes of metallopolymers.<sup>1</sup>



Among all the metallopolymers, metallocene containing polymers have attracted significant attention in material science because of their fully reversible redox chemistry and the possibility to synthesize them as tunable and stable materials.<sup>17-18</sup> A metallocene is a compound that has two cyclopentadienyl anions connected to a metal center and has a general formula  $(C_5H_5)_2M$ . Since the metal is present in between two cyclopentadienyl rings, it is placed in the class of sandwich compounds.



**Figure 1.2** A metallocene compound

There are two major states of a metallocene: neutral metallocene and cationic metallocenium. Neutral metallocenes, predominantly 18- $e^-$  ferrocene and ruthenocene, are widely explored.<sup>19-22</sup> In comparison, cationic metalloceniums have received far less attention and have been much less explored.<sup>23-24</sup> One of the main reasons behind the limited research is due to the difficulty in synthesizing substituted derivatives of cationic metallocenium. Neutral metallocenes like ferrocene has 18 valence electrons and can easily undergo electrophilic aromatic substitution reactions, while cobaltocene has 19 valence electrons. Thus, it readily oxidizes to its cobaltocenium salt, which is incapable of undergoing electrophilic aromatic substitution reactions. Besides, cobalt is the smallest atom in the VIIIB family and forms the strongest metal-ring bond, resulting in the most stable cationic metallocenium. As a matter of fact, cationic metalloceniums are fundamentally different from neutral metallocenes.

## 1.2. Research Objectives:

Cobaltocenium polyelectrolytes with chloride anions are water soluble,<sup>25</sup> and forms polycations in aqueous solution, making them a good host for small organic molecules or anions containing antibiotics. Previously, our group reported that water soluble polyelectrolytes have an ability to form bioconjugates with antibiotics like penicillin and amoxicillin through intermolecular interaction in aqueous solution. These bioconjugates displayed antimicrobial properties against different bacteria which are resistant to conventional antibiotics.<sup>26</sup> The ability of polyelectrolytes to form bioconjugates depends on the nature of intermolecular interactions. Therefore, we are motivated to investigate the nature and influence of different parameters like electrostatic charge, size, shape and  $\pi$ -electron system of small organic probes on the binding.

Cobaltocenium cation is extremely stable with decomposition temperature in the range of 250 °C - 350 °C and resistant to attack by strong acids and bases.<sup>27</sup> This cation is also stable at 175°C in the presence of 1M NaOH solution over 4 days.<sup>28</sup> Also cobaltocenium containing polymers have been used as anion-exchange resins<sup>29-30</sup> and water soluble redox-active oligomers/polymers.<sup>24, 31</sup> On the other hand benzyltrimethyl ammonium cation are the mostly used cation for alkaline anion exchange membrane for fuel cells. However, this cation is not stable for a long period of time at high temperature and pH, which motivated us to explore cobaltocenium cation for alkaline anion exchange membrane. We attempted to synthesize cobaltocenium containing highly stable styrene based polymer for alkaline anion exchange membrane.

## CHAPTER 2

### BINDING OF SMALL MOLECULES TO COBALTOCENIUM CONTAINING POLYMERS IN WATER

## 2.1. Abstract

Intermolecular interaction is responsible for the binding between a polyelectrolyte and small organic molecule. We investigated the nature and relative strength of intermolecular interaction between poly (2-cobaltoceniumamidoethyl methacrylate chloride) (PCoAEMACl) and different organic probes in buffer solution by an optical spectroscopic method. We found that electrostatic charge and  $\pi$ -electron moiety in the small molecules are the most influential on the binding between these two compounds. Insights were found by studying the binding of targeted organic probes to water soluble PCoAEMACl polymer. A dye indicator displacement method was used to monitor spectral signals (absorbance and fluorescence emission). This study contributes to a more complete understanding of the fundamental interactions between cobaltocenium polymers and anions.

## 2.2. Introduction:

The binding between small organic molecules and functional macrostructures in water has potential applications in catalysis, sensing and biomedical fields.<sup>32-33</sup> For this purpose, we have studied cobaltocenium containing polyelectrolytes with a methacrylate backbone. These polyelectrolytes with chloride counterion are water soluble at near neutral pH.<sup>25</sup> Previously, our group reported that our water soluble polyelectrolytes have ability to conjugate with antibiotics like penicillin and amoxicillin through intermolecular interaction in solution. These conjugates displayed antimicrobial properties against different bacteria which are resistance to conventional antibiotics.<sup>26</sup>

The ability of forming conjugates depends on the nature of intermolecular interactions between polyelectrolytes and antibiotics. Therefore, it is very important to

know the nature and influence of different parameters like electrostatic charge, size, shape and  $\pi$ -electron system on the binding interactions. However, monitoring the interactions of optically and spectroscopically inactive species is much more challenging. Here, we followed a method to study the relative binding affinities of such spectroscopically silent species.<sup>33</sup> This study provides information about structural features that are valuable to enhance binding to polyelectrolytes, leading to an improved understanding of these interactions.

## **2.3.Experimental**

### **2.3.1. Materials:**

Cyclopentadiene (95%, Acros) dimer was distilled via a 30cm column to obtain cyclopentadiene unimer, Sodium (Sigma-aldrich), n-BuLi solution in hexane, tritylium hexafluorophosphate (97%), RAFT chain transfer agent (CTA), cumyl dithiobenzoate (CDB), 4-(dimethylamino)pyridine (99%, DMAP), 2-aminoethyl methacrylate hydrochloride (90%), N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC-HCl, 98%), Tetrabutylammonium chloride (TBACl) salt was purchased from Sigma Aldrich and used directly. 2, 2-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Triethylamine (99%, Aldrich) was dried over molecular sieves. Cobalt (II) bromide (anhydrous, Alfa Aesar), Sodium hexafluorophosphate (98%, Oakwood Products) were used as received. Tris buffer solution was prepared from Tris(hydroxymethyl)aminomethane (Tris base) (Sigma-Aldrich) and concentrate Hydrochloric acid (Sigma-Aldrich). The fluorescent probe 5(6)-carboxyfluorescein (as a mixture of isomers) was purchased from Sigma-Aldrich. Displacer anion solutions were prepared from succinic acid (Sigma), tricarballic acid and 1,4-Cyclohexanedicarboxylic

acid (Acros), 1,2,3,4-butanetetracarboxylic acid and pimelic acid (Alfa Aesar), trimesic acid and 1,3,5- cyclohexanetricarboxylic acid (TCI America). Water used was from Thermo Scientific Nanopure with ion conductivity at 18.2 MΩ. Grubbs catalyst, 3rd generation, was synthesized following a procedure reported in literatures. All solvents used were dried by using suitable drying agent. All other reagents were from commercial resources and used as received unless otherwise noted.

### **2.3.2. Characterization:**

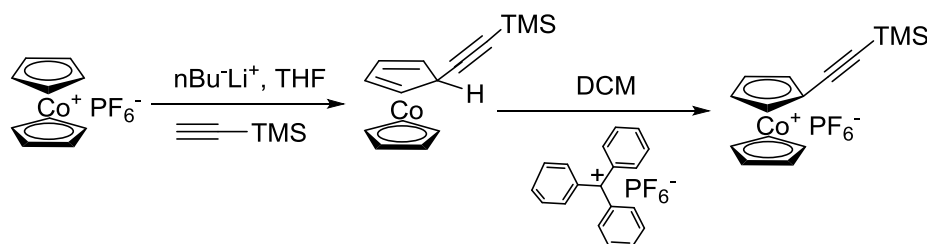
<sup>1</sup>H NMR (300 MHz) was recorded on a Varian Mercury spectrometer with tetramethylsilane (TMS) as an internal reference. UV–visible absorption was carried out on a Shimadzu UV-2450 spectrophotometer with a 10.00 mm quartz cuvette and monochromatic light of various wavelengths over a range of 190–900 nm. Fluorescence emission intensity was measured by using Cary Eclipse Fluorescence Spectrophotometer.

### **2.3.3. Synthesis:**

#### **Synthesis of trimethylsilylethynylcobaltocenium hexafluorophosphate (TMSCoPF<sub>6</sub>):**

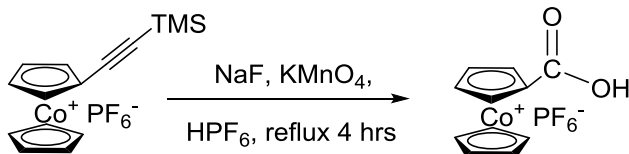
A 500 mL round-bottom flask was charged with magnetic stirring bar and 200 ml of dry THF, 2.36 mL of (trimethylsilyl) acetylene (1.14 equiv, 17 mmol) under protection from air by a nitrogen atmosphere. The mixture was cooled using dry ice/acetone and 6.28 mL (1.05 equiv, 15.6 mmol) of n-BuLi solution was added. It was let to stir for 45 minutes followed by the addition of 5 g of cobaltocenium hexafluorophosphate (1 equiv, 14.9 mmol). The cobaltocenium hexafluorophosphate was synthesized according to modified literature.<sup>31, 34</sup> The reaction mixture was slowly warmed to room temperature to let it react further. There was a change in color from yellow to rusty red which is because of the nucleophilic addition. The solvent was removed in vacuo and passed through an

alumina column using hexane. After removing hexane in vacuo 3.94 g of solid cobaltocenium was obtained which was then dissolved in 150 mL of dry DCM. 6.21 g of triphenylcarbenium hexafluorophosphate (equimolar as cobaltocenium) was added to the stirring solution and let it react at dark for 15 minutes. Then, the reaction mixture was filtered and washed with ether and water until filtrate came off clear. The obtained solid was dried in vacuo to give 79% (5.08 g) overall yield.



#### Synthesis of carboxycobaltocenium hexafluorophosphate:

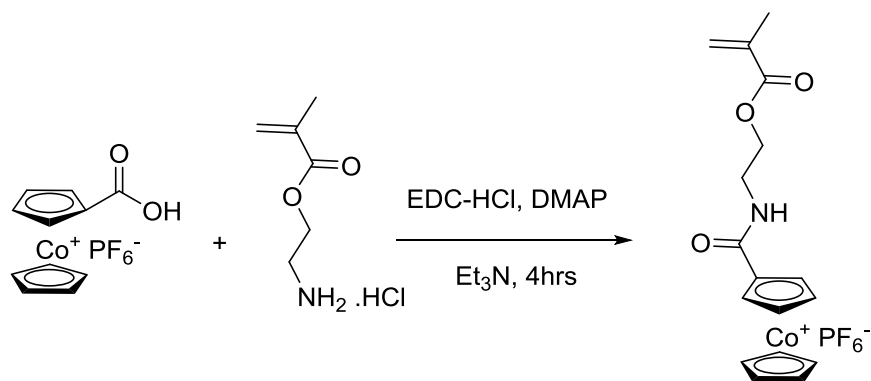
2g of TMSCoPF<sub>6</sub> (1 equiv, 4.65 mmol) was dissolved in 90 mL of acetonitrile and sodium fluoride (1 equiv, 4.65 mmol) was added. It was followed by the addition of an aqueous potassium permanganate solution (2.7 equiv, 12.56 mmol in 150mL water). The reaction mixture was refluxed for 4 hrs at 86 °C. The resulting mixture was then filtered and washed with hot water. The filtrate was concentrated in vacuo at 100 °C and let it cool. Hexafluorophosphoric acid (1.3 equiv, 6.05 mmol) was added and the product was allowed to crystallize in a refrigerator overnight. Thus, obtained yellow powder was filtrated, washed with ice cooled water and dried in vacuo to give 81% yield (1.42 g). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN, δ, ppm): δ 5.75(s, Cp, 5H), 5.79 (t, C<sub>2</sub>/C<sub>5</sub> of substituted Cp, 2H), 6.09 (t, C<sub>2</sub>/C<sub>5</sub> of substituted Cp, 2H); signal of CO<sub>2</sub>H not observed due to rapid exchange.



**Synthesis of 2-Cobaltoceniumamidoethyl methacrylate hexafluorophosphate (CoAEMAPF<sub>6</sub>):**

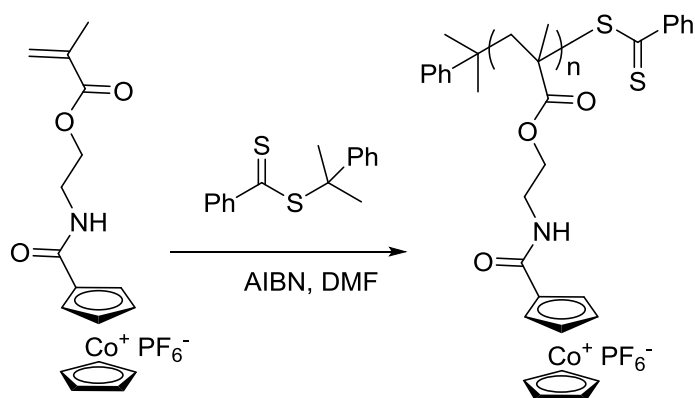
An amidation reaction was employed to synthesize CoAEMAPF<sub>6</sub>. 2g of cobaltoceniumcarboxylic acid hexafluorophosphate (1.0 equiv, 5.29 mmol), 1.14 g of 2-aminoethyl methacrylate hydrochloride (1.3 equiv, 6.88 mmol), and 0.19 g of 4-(Dimethylamino) pyridine (0.3 equiv, 1.59 mmol) were dissolved in 20 mL dry DCM and the solution was cooled to 0 °C. Solution of EDC-HCl (1.32 g, 1.3 equiv 6.88 mmol) was then slowly added into previously cooled solution. Then, dry triethylamine (1.6 g, 2.5 equiv, 13.22 mmol) was immediately added into the reaction mixture and stirred for 4 hours at room temperature. Solution was then extracted by saturated sodium hexafluorophosphate aqueous solution three times to remove unreacted starting materials. The organic phase was condensed and precipitated into diethyl ether. 1.5 g of yellow solids were collected and dried under vacuum overnight. Yield (58%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>, δ, ppm): 8.30 (broad, *NHCH*<sub>2</sub>, 1H), 6.31 (t, Cp, 2H), 6.12 (m, *CH*<sub>2</sub>C, 1H), 6.00 (t, Cp, 2H), 5.95 (s, Cp, 5H), 5.67 (m, *CH*<sub>2</sub>C, 1H), 4.36 (m, *OCH*<sub>2</sub>*CH*<sub>2</sub>*NH*, 2H), 3.70 (m, *OCH*<sub>2</sub>*CH*<sub>2</sub>*NH*, 2H), 1.93 (m, *CH*<sub>3</sub>*CCO*, 3H).





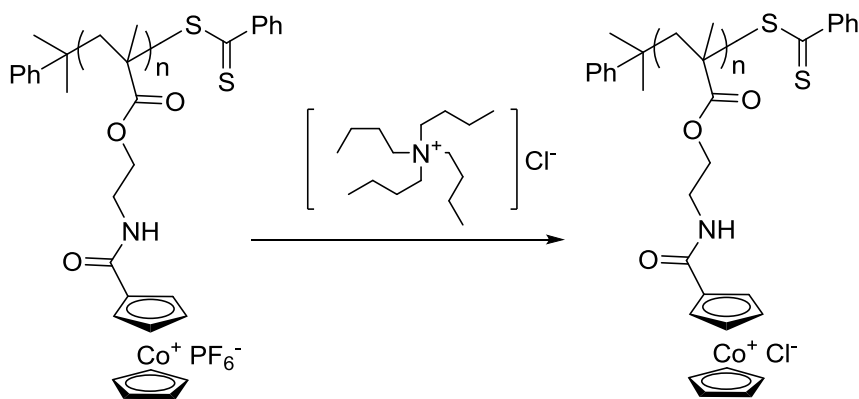
**Synthesis of poly (2-(methacryloyl) ethyl cobaltoceniumcarboxylate hexafluorophosphate) via RAFT polymerization (PCoAEMAPF<sub>6</sub>):**

CoAEMAPF<sub>6</sub> (300 mg, 0.61 mmol), cumyl dithiobenzoate (CDB) (RAFT agent) (1.67mg, 0.0061mmol) and azobisisobutyronitrile (AIBN) (0.20 mg, 1.23 ×10<sup>-3</sup>mmol) were dissolved in 0.4 mL dry DMF in a 10mL Schlenk flask and then purged N<sub>2</sub> for 30 minutes. The polymerization was started by heating the mixture at 90 °C. Samples were taken out periodically to check the monomer conversion. Once the desired conversion was reached, polymerization reaction was quenched by exposing to air. The reaction mixture was then precipitated in cold DCM three times and vacuum dry overnight. Yield: 150 mg, 80%. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN, δ, ppm): 7.4 (broad NHCH<sub>2</sub>, 2H), 6.2, 5.9, 5.8 (m, m, s, Cp, 9H), 4.2(broad, CH<sub>2</sub>OO, 2H) 3.6 (broad, NHCH<sub>2</sub>, 2H), 1.8 (broad, CH<sub>2</sub>C, 2H), 0.6-1.0 (broad, CCH<sub>3</sub>, 3H).



### Ion-exchange of PCoAEMAPF<sub>6</sub>:

1 mL of PCoAEMAPF<sub>6</sub> polymer solution (30 mg/mL in acetonitrile) was slowly added into 5 mL tetrabutylammonium chloride salt solution (40mg/mL in acetonitrile) under vigorous stirring. After stirring for 3~5 minutes, the precipitated polymers were collected and washed by acetonitrile three times to remove PF<sub>6</sub><sup>-</sup> anions and excess tetrabutylammonium salts. The solid polymers were then vacuum-dried and collected. <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O, δ, ppm): 6.14 (broad, Cp, 2H), 5.85 (broad, Cp, 2H), 5.73 (broad, Cp, 5H), 4.43 (broad, CH<sub>2</sub>CH<sub>2</sub>, 2H), 4.15 (broad, CH<sub>2</sub>CH<sub>2</sub>, 2H), 1.50~1.80 (broad, CH<sub>2</sub>C, 2H), 0.50-1.00 (broad, CCH<sub>3</sub>, 3H). <sup>19</sup>F NMR showed no fluorine signal.



### 2.3.4. Ionic Binding Study:

**Titration conditions:** All experiments were carried out in aqueous solutions buffered to pH 7.4 with Tris buffer solution at constant temperature of 25 °C. The pH of the working solutions was adjusted prior to use by addition of NaOH or HCl solutions and spot-checked during a titration to make sure that it had not drifted away from the desired value of 7.4. Drift was generally not a problem, but significant adjustments had to be made when preparing solutions of anions from their corresponding acids. The concentration of polyelectrolytes in all experiment was kept constant at 1.0x10<sup>-6</sup> M

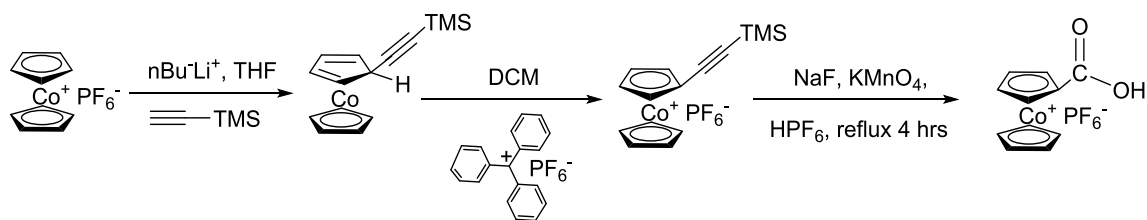
**Binding isotherm:** Stock solutions of dye, polymer, and displacer anions in buffered H<sub>2</sub>O were used as starting points for all experiments. All solutions used in this study were made by dilution of aliquots of these stock solutions. Binding isotherm experiment was conducted using constant polyelectrolytes ( $1.0 \times 10^{-6}$  M) and different fluorophore concentration. Absorbance and fluorescence emission readings were blanked by subtracting the corresponding reading for the buffer. The resulting data were plotted as a function of the [polyelectrolytes]/[fluorophore] ratio to produce binding isotherms.

**General Displacement Titration Protocol:** Displacement experiments were carried out using two separate working solutions: a “titrant” and a “cuvette” solution. Titrant and cuvette solutions were made fresh for each experiment. A cuvette solution contained both the dye ( $[CF] = 2.0 \times 10^{-6}$  M) and the polyelectrolyte ( $[P] = 1 \times 10^{-6}$  M) at the appropriate ratio to form the desired bound dye complex (P·CF<sub>n</sub>). The titrant solution contained a displacer anion at an appropriate concentration to carry out the titration. Titrations on benchtop instruments were carried out by addition of different aliquots of titrant solution to a constant volume of cuvette solution. The total volume of mixture was kept constant by addition of buffer solution. Using this method, the concentration of dye and polyelectrolyte remained constant but the concentration of displacer anion varied throughout the titration. The resulting data from fluorescence and UV-vis spectroscopy were plotted as a function of the [displacer anion]/[fluorophore] ratio to produce fluorescence intensity and absorbance isotherms.

## 2.4. Results and Discussion:

### 2.4.1. Synthesis of carboxycobaltocenium hexafluorophosphate:

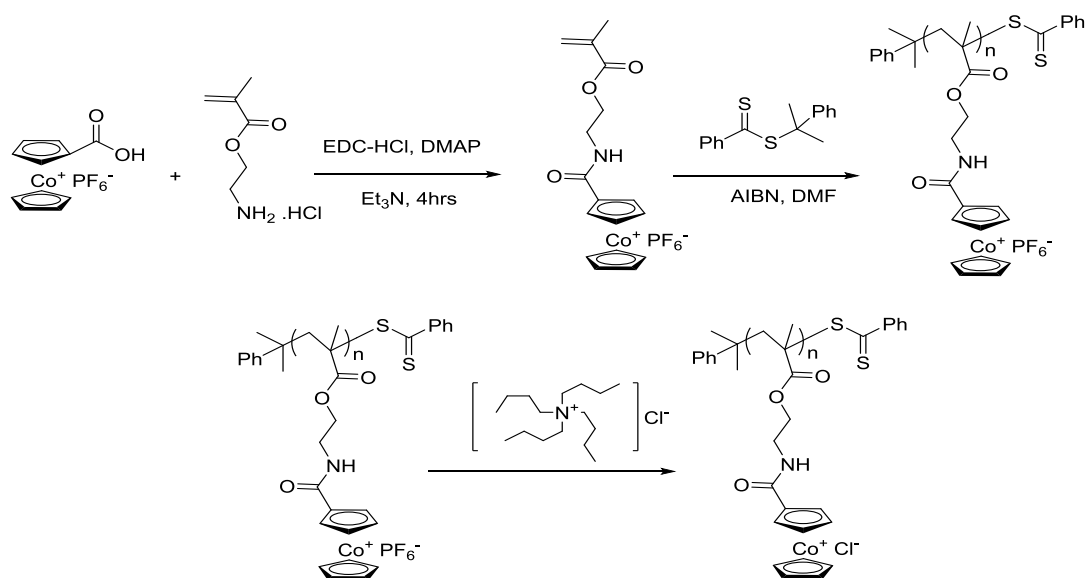
The initial step of preparing side-chain cobaltocenium-containing polymers is to synthesize pure mono-substituted cobaltocenium, as any di-substituted cobaltocenium derivatives can lead to cross-linking between polymer chains. The procedure of Sheats and Rausch was followed, which consisted of a statistical reaction between cyclopentadiene, methyl cyclopentadiene and cobalt chloride followed by methyl side chain oxidation to result cobaltocenium monoacid.<sup>31, 34</sup> The overall yield of this reaction was poor (around 6%) and gave a mixture of product consisting of hexafluorophosphates of cobaltocenium, cobaltocenium carboxylic acid, and cobaltocenium dicarboxylic acid. A more effective synthetic procedure using unsubstituted cobaltocenium and organolithium reagents was followed as shown in Figure 2.1.<sup>35-36</sup> This method consisted of facile nucleophilic addition and selective hydride abstraction of endo-proton followed by the oxidative cleavage by potassium permanganate with an overall yield of around 81%. Thus formed monoacid could be reacted further to give functional monomers.



**Figure 2.1** Synthesis of carboxycobaltocenium hexafluorophosphate

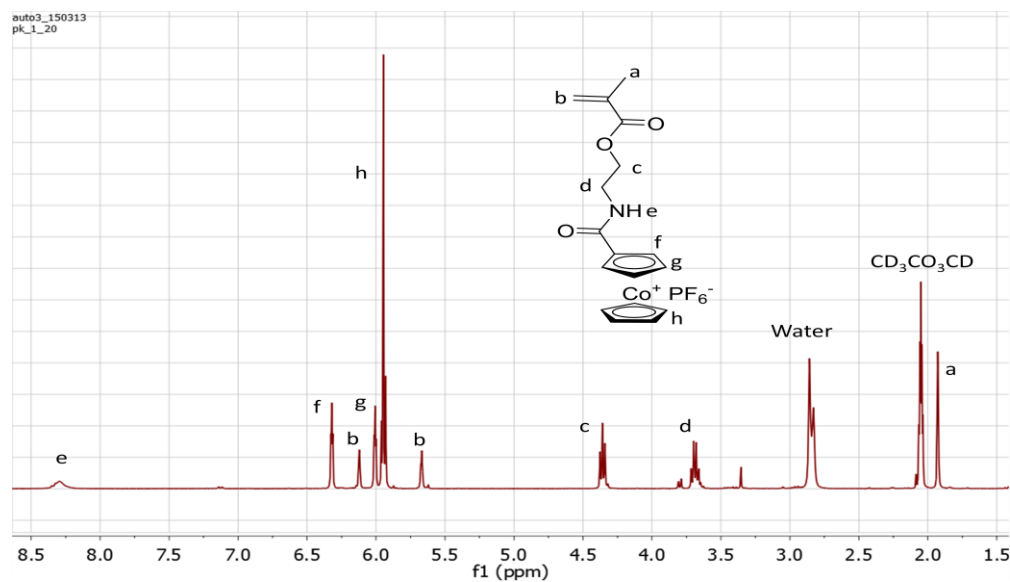
### 2.4.2. Synthesis of cobaltocenium polymer using RAFT:

The monosubstituted cobaltocenium acid was reacted with 2-aminoethyl methacrylate hydrochloride in acetonitrile with EDC as a coupling agent, as shown in Figure 2.2.



**Figure 2.2** Synthesis of cobaltocenium-containing polymers by RAFT polymerization

The protons of  $-\text{CH}_2$  groups at 3.7 ppm and 4.36 ppm and amide proton at 8.3 ppm showed the successful synthesis of monomer, as shown in Figure 2.3. The peaks at 5.67 ppm and 6.12 ppm corresponded to the vinyl protons of methacrylate monomer.



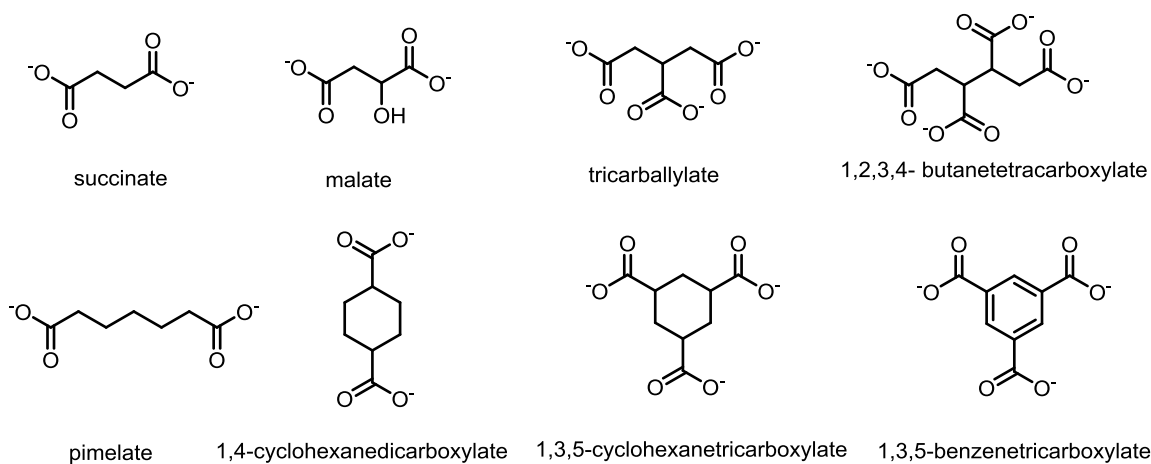
**Figure 2.3**  $^1\text{H}$  NMR spectrum of MAEACoPF<sub>6</sub> in acetone- $\text{d}_6$

The polymerization was conducted by RAFT method with AIBN as an initiator in dry DMF. The reaction temperature was set up at 90 °C. The ratio of [Monomer] / [RAFT] was adjusted to achieve the desired molecular weight (15,000 g/mol). The polymerization was carried out targeting 50% monomer conversion and the conversion was checked periodically by comparing the vinyl proton peaks with cobaltocenium peak. Compared to the  $^1\text{H}$  NMR spectrum of monomer, the vinyl protons disappeared and two new broad peaks showed up at 0.8ppm- 1 ppm in the  $^1\text{H}$  spectrum of PCoAEMAPF<sub>6</sub>. As cobaltocenium-containing polymers cannot be characterized by GPC due to the interaction between the cationic polymers and stationary phase of columns, end group analysis was the method to confirm the final degree of polymerization. According to recent work by our group<sup>23</sup>, cobaltocenium-containing polymers depend on the counterions. Polymers with different anions show different hydrophobicity such as polymer with PF<sub>6</sub><sup>-</sup> and BPh<sub>4</sub><sup>-</sup> are hydrophobic and polymers with inorganic counterions like chloride, bromide and nitrates are extremely hydrophilic. Thus, we attempted to synthesize water soluble polymers through ion exchange phenomenon so that we can use these polymers for biological applications. Tetrabutylammonium chloride (TBACl) was used to carry out the anion exchange. PCoAEMAPF<sub>6</sub> solution in acetonitrile was precipitated in the salt solution (10 times molar ratio of cobaltocenium moiety) under vigorous stirring. The precipitated polymer was washed three times with salt solution and finally by acetonitrile to remove any left-over PCoAEMAPF<sub>6</sub>. Fluorine NMR ( $^{19}\text{F}$ ) confirmed the complete ion-exchange. After the ion-exchange, resulting polymer, PCoAEMACl is not soluble in acetonitrile but soluble in water, which was used for the intermolecular interaction study.

### 2.4.3. Ion-exchange Study:

In this model study we used cobaltocenium polymers with molecular weight 15,000 g/mol. This molecular weight was chosen because it shows an excellent compromise between size and loading properties. Smaller polyelectrolytes do not display high enough affinity towards negative charge.

It was noticed that pH have a significant effect on binding between polyelectrolytes and dye. With the increase of pH the binding capacity first increases then decreases. The maximum binding is at pH 7.4. Thus, all experiments were conducted in H<sub>2</sub>O buffered at pH 7.4 using 50mM Tris buffer solution at 25 °C.



**Figure 2.4** Model carboxylates used as anionic probes

A number of small organic probes (Figure 2.4) were selected to isolate and systematically investigate the relative binding affinity between polyelectrolytes and anion probes in aqueous solution. The anionic probes differ by one key element as shown in Table 2.1; so that comparison of the relative affinities provide us which structural features are important on intermolecular interactions.

**Table 2.1** Sets of organic probes used to elucidate each binding interaction phenomenon

feature under study	anionic probes used
electrostatic interactions	succinate <sup>2-</sup> vs tricarballylate <sup>3-</sup> vs butanetetracarboxylate <sup>4-</sup>
guest size	Succinate (short) vs pimelate (long)
guest shape	tricarballylate (flexible) vs cyclohexanetricarboxylate (rigid)
charge – $\pi$ interactions	cyclohexanetricarboxylate (aliphatic) vs trimesate (aromatic)
hydrogen bonding	succinate (no OH <sup>-</sup> ) vs malate (one OH <sup>-</sup> )

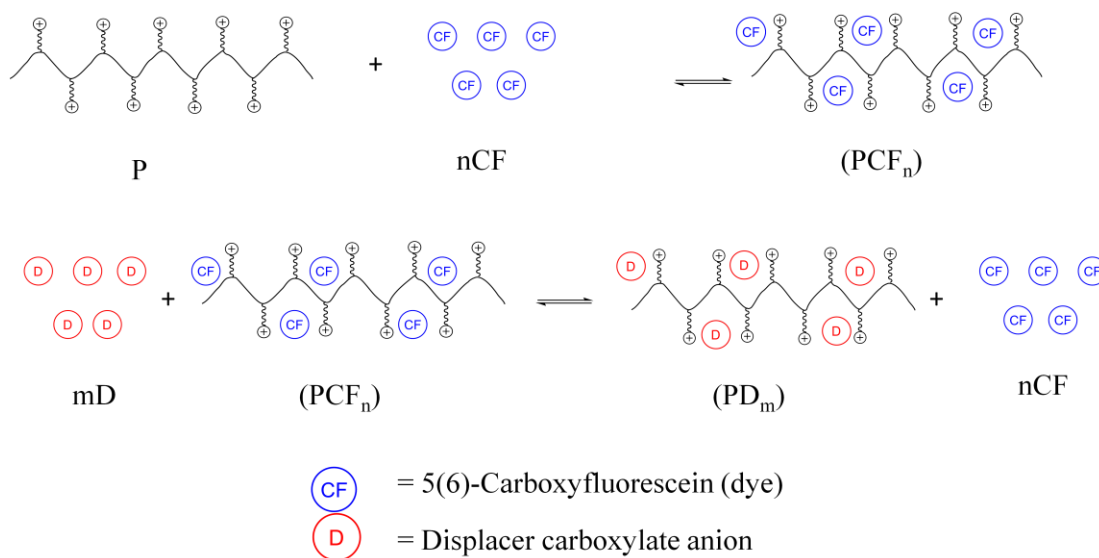
The common methods to investigate such intermolecular interactions like NMR and MS spectroscopic methods are not suitable in this situation because higher concentration required for effective NMR studies but at that much concentrations polymer-dye complex solutions are very viscous, and equilibration is slow.

Therefore, we used an optical spectroscopy method.<sup>33, 37-38</sup> This method is very fast and efficient at low concentration. However, neither the polyelectrolytes nor the organic probes have any significant chromophore or fluorophore by which their binding ability can be monitored, requiring us to introduce a reporting agent in the system. We used a trianion (at pH 7.4), 5(6)-carboxyfluorescein (CF), as a fluorescent indicator because the binding affinity of monoanion and dianion toward polyelectrolytes would be too low at a lower concentration.

In this approach, first polymer-dye complex (P·CF<sup>n</sup> in Figure 2.5) was made. Then the targeted nonfluorescent displacer probe is introduced to displace the dye from its polymer-dye complex and to form the polymer-probe complex, thus the spectroscopic signature represents the free dye anion. The ratio of polymer to dye was fixed such that



all dye molecules are attached to the polymer; the optical properties correspond to the dye-polymer complex.

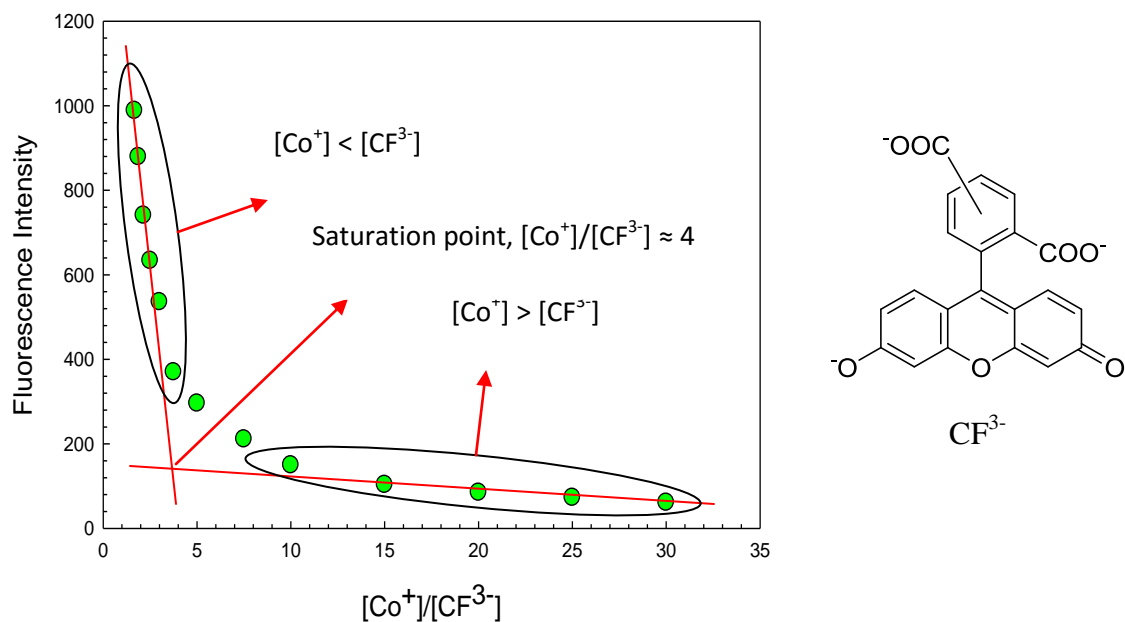


**Figure 2.5** Dye displacement assay used to detect binding affinity of spectroscopically silent anionic guests (D) to the polymer (P) by using trianionic fluorescent dye 5(6)-Carboxyfluorescein (CF)

Although neither the D probes nor the P·Dm polymer-probe complexes have any chromophore or fluorophore, we can still monitor the polymer-probe complex formation process through the change in spectroscopic signature due to the displacement of the dye from its bound state to free state. The studies were conducted by UV-visible and fluorescence emission spectroscopy. The isotherm profiles obtained for the titrations of D probes into a buffered solution of the polymer–dye complex. By comparing isotherm profile for different displacer anions, we can estimate what structural features are important for the binding to these polymers.

The choice of the [polymer]/[dye] ratio is very important in the displacement experiment. If we use too much polymer, the dye would not fully bound to the polymer. There should be some unoccupied space in the polymer, so that we would not see much

signal change because the displaced dye would bind to the unoccupied place without displacing the dye. On the other hand, if we use too little polymer, the excess dye signature would add to the displaced dye signature which would result in wrong estimation. Therefore, we decided to work at a [polymer]/[dye] ratio that gave us at least 85% binding of the total dye.

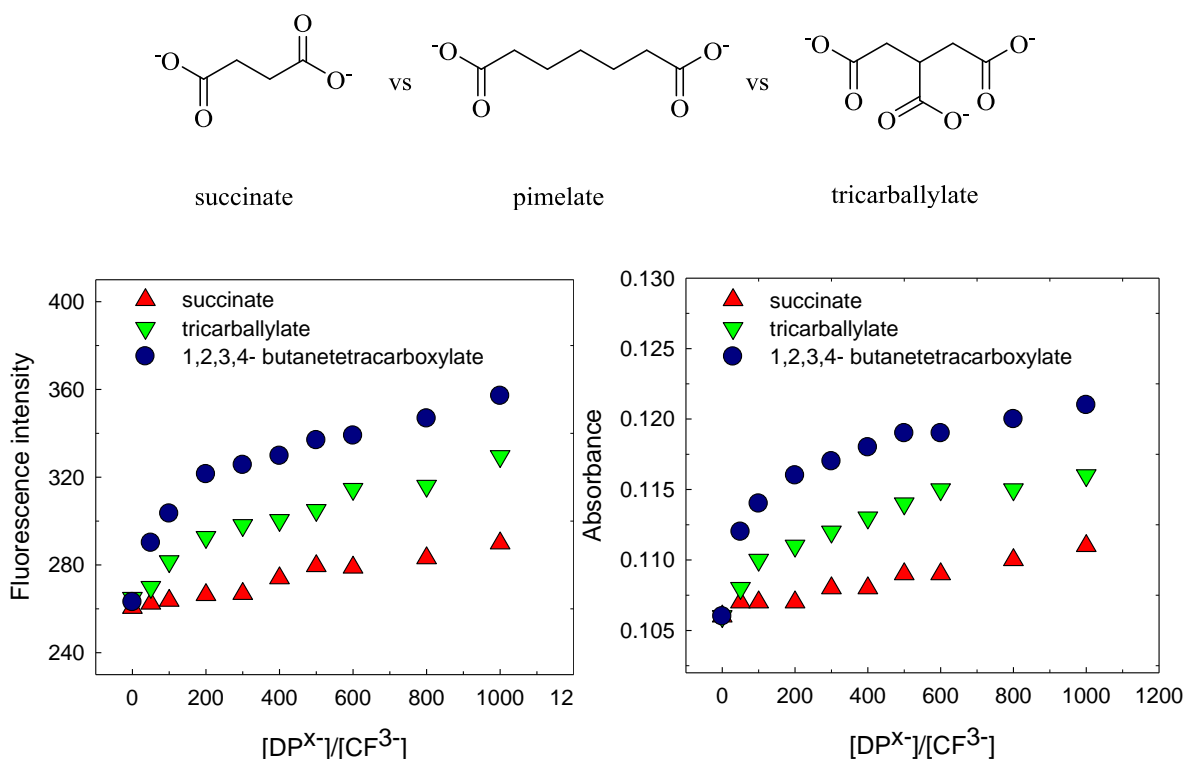


**Figure 2.6** Left: isotherm describing the binding of 5(6)-carboxyfluorescein (CF) to cobaltocenium containing polymer, monitored through fluorescence intensity in a buffered water solution (pH 7.4).  $[CF^{3-}] = 1.0 \times 10^{-6}$  M. Right: structure and protonation state of CF when dissolved in buffered water at pH 7.4.

Finally, it is important to note that we cannot determine the absolute binding constant from this study because of the complexity of the equilibria and the concentrations used were too low. Therefore, we restrict ourselves to determine relative affinity of polymer on different anions.

#### 2.4.4. The effect of electrostatic charge:

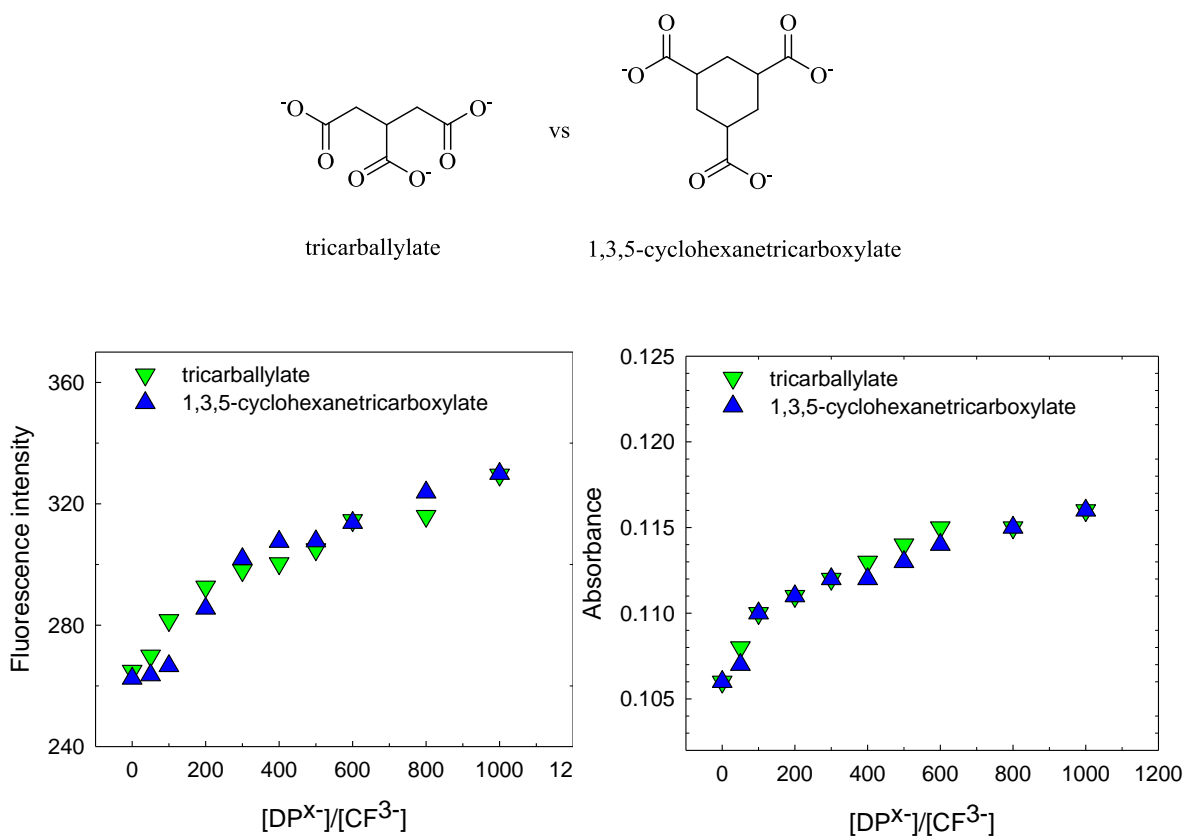
The effect of the electrostatic charge on the relative affinity for cobaltocenium polymers was carried out by using a series of model carboxylate anions such as succinate, propane-1,2,3-tricarboxylate (tricarballylate), and 1,2,3,4-butanetetracarboxylate, which respectively represent two, three, and four negative charges in water at pH 7.4, (Figure 2.1). The results (Figure 2.7) show that the binding affinity of each guest anion increases significantly with increasing electrostatic charge of the guest anion. On average, increasing one negative charge increases the relative binding affinity by one order of magnitude,<sup>39-40</sup> highlighting the paramount importance of electrostatic interactions.



**Figure 2.7** Guest charge: fluorescence intensity and absorbance isotherms from titration of a P·CFn complex with dianionic vs trianionic vs tetraanionic displacer (DP).  $[CF] = 1 \times 10^{-6}$  M,  $[Co^{+}] = 4 \times 10^{-6}$  M in buffered water (50 mM Tris at pH 7.4),  $\lambda_{exc} = 494$  nm.

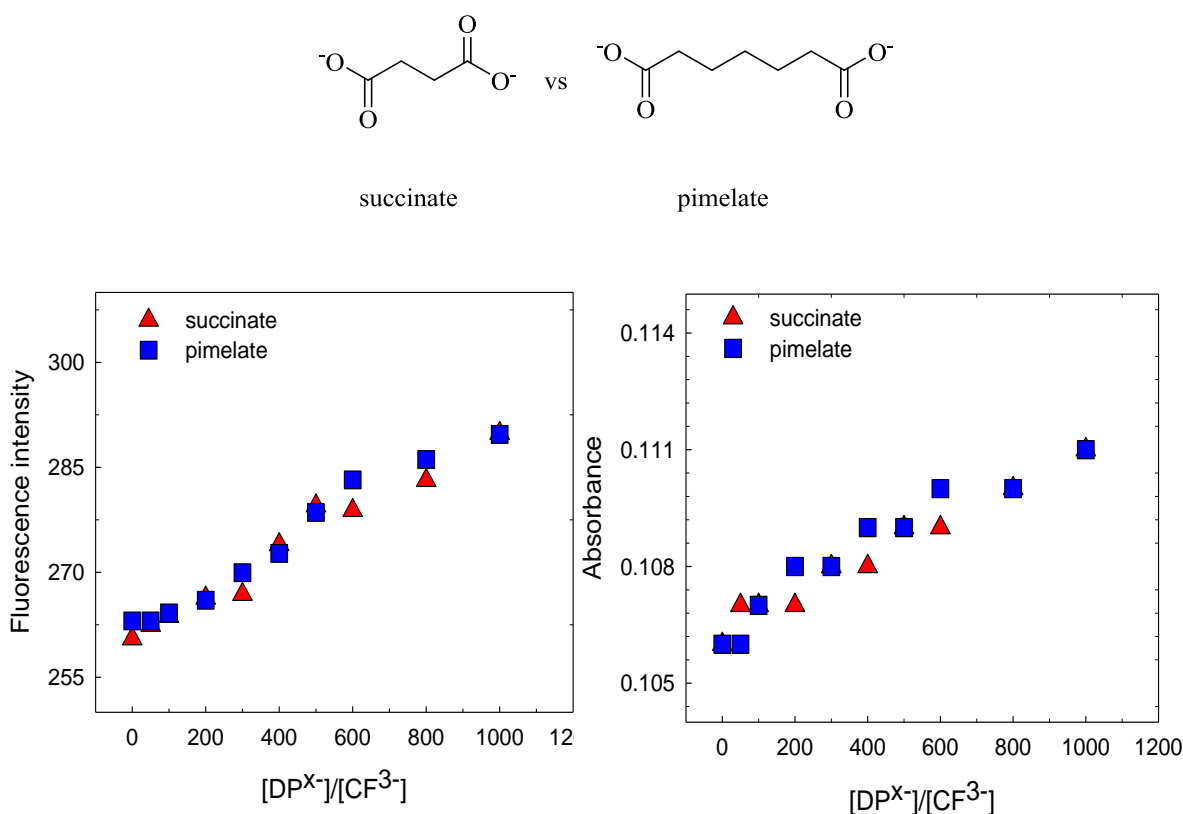
#### 2.4.5. The effect of structure and shape:

We investigated the effect of guest anion's conformation on the relative affinity on the polymer. We compared tricarallylate and 1,3,5- cyclohexanetricarboxylate. Both anions have three negative charges, but cyclohexanetricarboxylate is much more rigid due to its chair conformation whereas tricarallylate have linear backbone results less conformational restrictions. Despite that, the two anions show similar binding affinity, as shown in the isotherms in Figure 2.8.



**Figure 2.8** Guest conformation: fluorescence intensity and absorbance isotherms from titration of a P·CFn complex with trianionic displacers with different shape.  $[CF] = 1 \times 10^{-6}$  M,  $[Co^{+}] = 4 \times 10^{-6}$  M in buffered water (50 mM Tris at pH 7.4),  $\lambda_{exc} = 494$ nm.

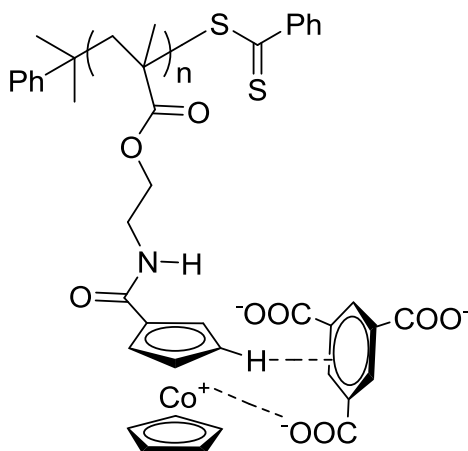
Similarly, in order to explore the effect of guest size on the relative affinity on the polymer, we compared succinate and pimelate, as shown in Figure 2.9. Both anions have two negative charges; therefore, electrostatic contribution would be equal to their binding to the polymers; any difference in structural features between the two displacer anions would reflect in their relative affinity. There is no difference was found in their binding behavior between two linear anions with different chain length. Thus, guest's size and shape do not have significant influence on binding affinity for polymer.



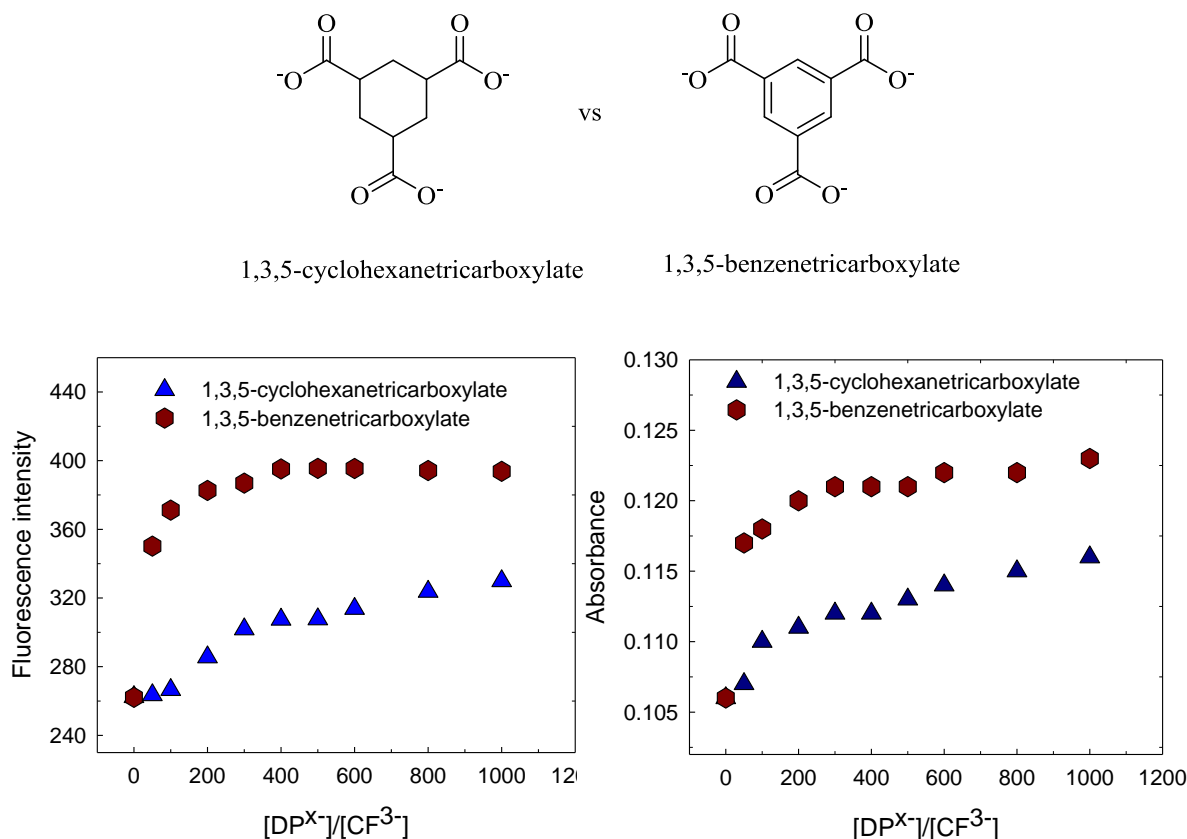
**Figure 2.9** Guest size: fluorescence intensity and absorbance isotherms from titration of a P·CFn complex with different size of displacers. [CF] =  $1 \times 10^{-6}$  M, [Co<sup>+</sup>] =  $4 \times 10^{-6}$  M in buffered water (50 mM Tris at pH 7.4),  $\lambda_{\text{exc}}$  = 494nm.

#### 2.4.6. The effect of $\pi$ -system:

Finally, we investigated the effect of the presence of aromaticity of the displacer probe on the relative affinity. We compared benzene- 1,3,5-tricarboxylate (trimesate) and 1,3,5-cyclohexanetricarboxylate. Both anions have the same number of negative charge, similar size and shape but have significantly different relative affinity due to different  $\pi$ - electron system (Figure 2.11). The Boizzoni group reported that the presence of  $\pi$ -system on guest anion increases the affinity for cationic dendrimer significantly.<sup>40</sup> The difference on the relative affinity is due to an interaction mediated by the aromatic core of the trimesate anion (Figure 2.10). The positive charge of the cobalt induces significant polarization of the C–H bonds in the cyclopentadiene. One of these C–H bonds in cyclopentadiene ring interact with the  $\pi$ -electron cloud of the guest. The overall process of interaction is promoted by the electrostatic charge on cobaltocenium in the polymer as shown in Figure 2.10.



**Figure 2.10 CH- $\pi$  interaction**



**Figure 2.11**  $\pi$ -system: fluorescence intensity and absorbance isotherms from titration of a P·CFn complex with trianionic aliphatic and aromatic guests.  $[CF] = 1 \times 10^{-6}$  M,  $[Co^+] = 4 \times 10^{-6}$  M in buffered water (50 mM Tris at pH 7.4),  $\lambda_{exc} = 494$  nm.

## 2.5. Conclusions:

The function of various intermolecular interactions involved in the binding between small organic probes and PCoAEMACl polymer was investigated using a dye indicator displacement method based on simple optical spectroscopy techniques. The results of these experiments allowed us to evaluate the relative importance of various intermolecular interaction modes to the overall binding process. We found that electrostatic charge and  $\pi$ -electron moiety in the small molecules are the main drivers on the binding between the polymer and organic probes. Hydrogen bonding interactions are also important: the polymer can form hydrogen bond with a molecule containing hydroxyl and carbonyl group. Finally, conformation and size of the guest have no

significant influence on the binding process. Further studies currently underway in our lab will attempt to obtain quantitative measurements of the loading capacity for these hosts to the studied polymer.



## CHAPTER 3

### COBALTOCENIUM CATION FOR ALKALINE ANION EXCHANGE MEMBRANE

### 3.1. Abstract:

The alkaline stability of cobaltocenium cation in 1M NaOD/D<sub>2</sub>O at 80 °C temperature was investigated by <sup>1</sup>H NMR and UV-vis spectroscopy method. We found that deuterium from the reaction media displaces all cyclopentadienyl protons from the cobaltocenium cation but the cation remains stable a period of 13 days. The excellent alkaline stabilities of cobaltocenium cation confirmed that membranes containing cobaltocenium are promising for use in AAEMFCs. Styrene based cobaltocene/cobaltocenium containing monomer were synthesized in one pot reaction without any purification. After synthesizing the monomer, we attempted to polymerize and found that this monomer cannot polymerize due to the stabilizing effect of the cobaltocene/cobaltocenium moiety. In order to avoid stabilizing effect we have synthesized triazole ring containing cobaltocenium styrene monomer via click reaction for future evaluation on polymerization.

### 3.2. Introduction

Due to growing concerns on the depletion of fossil fuels and greenhouse gas emissions, fuel cell technologies have received much attention over the last decade.<sup>41</sup> Fuel cells are electrochemical devices capable of directly converting chemical energy stored in the fuel (e.g. H<sub>2</sub> or CH<sub>3</sub>OH) to electrical energy.<sup>42</sup> The critical component of a fuel cell is the polymeric electrolyte membrane which acts as an ion conducting medium and electric insulator between two electrodes.<sup>43</sup> Nafion, a perfluorinated polymer with pendant sulfonic group, has been using as a proton exchange membrane for proton exchange membrane fuel cells. It has dominated the field due to its processability, stability and high proton exchange capacity.<sup>44-45</sup> However, Nafion has significant

drawbacks such as high cost<sup>46</sup> and methanol crossover, reduced efficiency.<sup>47</sup> Despite being relatively unexplored, alkaline anion exchange membranes (AAEMs) offer important benefits such as reduced methanol crossover and greatly improved oxygen reduction kinetics.<sup>48</sup> These improvements result in higher efficiency as well as permitting the use of non-precious metal catalysts (silver) instead of precious metal catalysts (platinum and its alloys) making this technology economically viable. However, alkaline fuel cells (AFCs) have used alkaline electrolytes containing metal hydroxide (e.g. potassium hydroxide) that react with CO<sub>2</sub> (present in the fuel) forms metal carbonates and bicarbonates. These carbonate salts have lower solubility in aqueous solution, hence precipitation on the bottom of fuel cells, which results in decrease in conductivity and obstructing electrode pores.<sup>49-50</sup> Polymers anchored with organic cation overcome this problem because the cation cannot aggregate with anion to form crystal lattice.

However, ideal AAEMs would be thermally and chemically stable, exhibit good ionic conductivity, reduce methanol crossover and display limited swelling.<sup>41</sup> In order to synthesize ideal AAEMs various cations with a polymer backbone have been investigated. To date, the mostly investigated cationic group for AAEMs is based on the benzyltrimethyl ammonium group because of its good chemical and thermal stability compared to other quaternary ammonium cations.<sup>51-52</sup> The benzyltrimethyl ammonium cation has been incorporated into various polymeric backbones, such as radiation-grafted poly(vinylidene fluoride),<sup>53-56</sup> poly(sulfone),<sup>57-60</sup> poly(phenylene),<sup>61</sup> poly(phenylene oxide)<sup>62</sup> as well as cross-linked polyolefin structures.<sup>63-65</sup> However, the degradation pathways for benzyltrimethyl ammonium cations under alkaline conditions have been investigated by Pivovar and coworkers,<sup>66-67</sup> and the long-term stability of the ammonium

cation under fuel cell operating conditions remains a concern.<sup>68</sup> This motivates to investigate other cationic species anchored to polymeric supports for use in alkaline anion exchange membrane fuel cells (AAMFCs), including guanidinium<sup>69-70</sup> and imidazolium<sup>71-73</sup> cations. Holdcroft and co-workers recently reported a sterically crowded benzimidazolium polymer that exhibits base stability when heated to 60 °C in 2 M KOH over a 13 day period.<sup>71</sup> Coates and co-workers synthesized a cross-linked polyolefin network containing tetraakis(dialkylamino) phosphonium which exhibited high hydroxide conductivity (22 mS/cm at 22 °C in water) and good base stabilities in 1 M KOH at 80 °C.<sup>74</sup> One multivalent metal-cation-based AAEM containing bis(terpyridine)ruthenium(II) complex-functionalized polynorbornenes has also been explored.<sup>75</sup> Cobaltocenium derivatives are good candidates, metal-based cation, for AAEMs because of their excellent thermal,<sup>27, 29</sup> alkaline, and peroxide stabilities.<sup>76</sup> The cobaltocenium cation can be readily incorporated into polymers through functionalization of the cyclopentadienyl rings.<sup>31, 77-78</sup> Moreover, the cobaltocenium ion shows excellent alkaline stability similar to K<sup>+</sup> because of its 18-electron closed valence-shell configuration. Therefore, this suggests that cobaltocenium salts would be electrochemically stable for fuel cell applications. In this chapter, a new monomer, styrenic cobaltocenium hexafluorophosphate (StCp<sub>2</sub>CoPF<sub>6</sub>), was synthesized by one-pot reaction without the requirement of purification by column chromatography.

## 3.2. Experimental

### 3.2.1. Materials:

Cyclopentadiene (95%, Acros) dimers were distilled via a 30cm column to obtain cyclopentadiene unimers respectively. n-BuLi solution in hexane, tritylium

hexafluorophosphate (97%), RAFT chain transfer agent (CTA), cumyl dithiobenzoate (CDB), 4-(dimethylamino)pyridine (99%, DMAP), ethyl vinyl ether (99%, EVE), 2-aminoethyl methacrylate hydrochloride (90%), N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC-HCl, 98%), 5-Norbornene-2-methanol (98%, mixture of exo and endo), Tetrabutylammonium chloride (TBACl) salt and Sodium azide ( $\geq 99.5\%$ ) were purchased from Sigma Aldrich and used directly. 2, 2-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Triethylamine (99%, Aldrich) was dried over molecular sieves. Cobalt (II) bromide (anhydrous, Alfa Aesar), p-Toluenesulfonyl chloride (98%, VWR) and sodium hexafluorophosphate (98%, Oakwood Products) were used as received. Water used was from Thermo Scientific Nanopure with ion conductivity at 18.2 M $\Omega$ . Grubbs catalyst, 3rd generation, was synthesized following a procedure reported in literatures. All solvents used were dried by using suitable drying agent. All other reagents were from commercial resources and used as received unless otherwise noted.

### **3.2.2. Characterization:**

$^1\text{H}$  NMR (300 MHz) was recorded on a Varian Mercury spectrometer with tetramethylsilane (TMS) as an internal reference. Gel permeation chromatography (GPC) was performed in DMF (containing 0.1% LiBr) at a flow rate of 0.8 mL/min at 50 °C on a Varian system equipped with a ProStar 210 pump and a Varian 356-LC RI detector and three 5  $\mu\text{m}$  phenogel columns (Phenomenex Co.) with narrow dispersed polystyrene as standards.

### 3.2.3. Alkaline stability measurement of cobaltocenium chloride ( $\text{Cp}_2\text{CoCl}$ ):

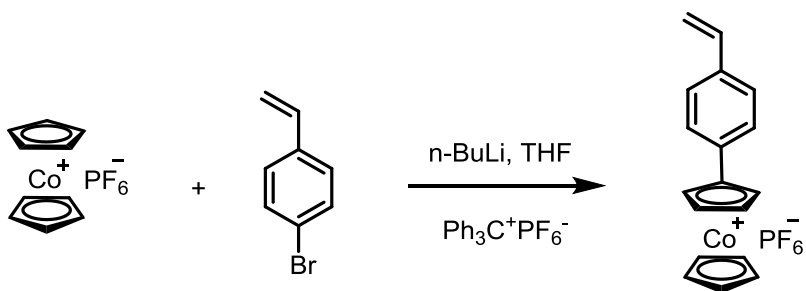
The alkaline stability was measured according to a modified literature procedure.<sup>74</sup> First cobaltocenium chloride was synthesized from cobaltocenium hexafluorophosphate by using chloride ion exchange resin.<sup>25</sup> Cobaltocenium chloride (0.5 M, 0.112.3 mg/mL), 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (0.25 M, 54.6 mg/mL,) and sodium deuterium hydroxide (5 M) stock solution were made by using deuterium hydroxide ( $\text{D}_2\text{O}$ ) in three different vial. 100  $\mu\text{L}$  of each solution was taken in NMR tube. Then, 200  $\mu\text{L}$   $\text{D}_2\text{O}$  was added to the mixture and heated at 80  $^\circ\text{C}$ . The solution was analyzed by  $^1\text{H}$ -NMR and UV-visible spectroscopy in different time period. The degradation of cobaltocenium chloride was measured based on the ratio of integration of cyclopentadienyl rings (2 x 5H) to trimethyl (9H) in 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt.

### 3.2.4. Synthesis:

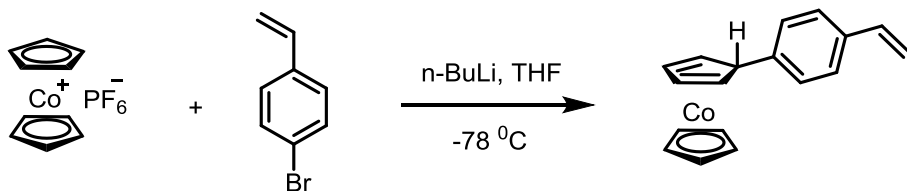
#### Synthesis of styrene cobaltocenium hexafluorophosphate ( $\text{StCp}_2\text{Co}^+\text{PF}_6^-$ ) and styrene cobaltocene ( $\text{StCp}_2\text{CoH}$ ):

4-bromostyrene (3.013 g, 16.46 mmol) was dissolved in 100 ml of freshly distilled THF in 250 mL round bottom flask then purged  $\text{N}_2$  gas for 30 min. The flask was cooled to -78  $^\circ\text{C}$  using a dry ice/acetone bath. 2.5 M n-butyllithium in hexane (6.59 ml, 16.46 mmol) was slowly added into the reaction mixture. After stirring at -78  $^\circ\text{C}$  for 45 min, cobaltocenium hexafluorophosphate (5 g, 14.97 mmol) was added gradually. The yellow suspension turned into a dark red solution after cannulation. The reaction mixture was stirred for 4 h at 0  $^\circ\text{C}$  and then the solvent was evaporated. The product was dissolved in DCM (200 ml) and then triphenylcarbenium tetrafluoroborate (6.392 g, 16.46 mmol) was

added and stirred for 20 min at room temperature, the reaction mixture was poured into 200 ml of water and the organic fraction was extracted with water three times (3 x 200 ml portions). Finally, the organic layer was dried with  $\text{MgSO}_4$ , filtered through Celite and evaporated. The residue was dissolved in 150 ml of DCM. The yellow-brown powder (3.29 g, yield 50.4%) was precipitated by adding 400 ml of ethyl ether for three times.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{COCD}_3$ ,  $\delta$ , ppm) 7.75, 7.57 (dd,  $\text{C}_6\text{H}_4$ , 4H), 6.80 (dd,  $\text{CH}_2=\text{CH}$ , 1H), 6.51 (t, Cp, 2H), 6.14 (t, Cp, 2H), 5.95 (d,  $\text{CH}_2=\text{CH}$ , 1H), 5.75 (s, Cp, 5H), 4.85(d,  $\text{CH}_2=\text{CH}$ , 1H).

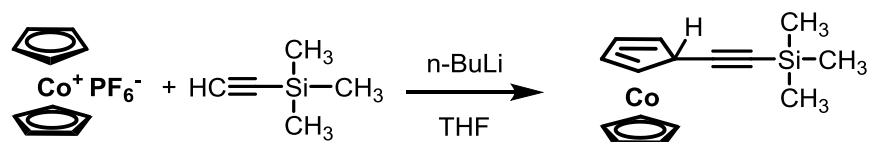


Similar synthetic procedure have used in order to synthesis  $\text{StCp}_2\text{CoH}$ . After nucleophilic addition, the reaction mixture was washed with water three times (3 x 200 ml portions). Then, the organic layer was separated and dried with  $\text{MgSO}_4$ . The solution was filtered through Celite and evaporated. 2.36 g of brown powder (yield 50.4%) was obtained. The structure was confirmed by  $^1\text{H}$  NMR.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm) 7.20, 6.75 (dd,  $\text{C}_6\text{H}_4$ , 4H), 6.57 (dd,  $\text{CH}_2=\text{CH}$ , 1H), 5.63 (d,  $\text{CH}_2=\text{CH}$ , 1H), 5.28 (t, Cp, 2H), 5.07 (d,  $\text{CH}_2=\text{CH}$ , 1H), 4.76 (s, Cp, 5H), 3.81 (s, Cp, 1H), 2.92 (t, Cp, 2H).



**Synthesis of ( $\eta^5$ -Cyclopentadienyl)[ $\eta^4$ -(exo-5-trimethylsilylethynyl)-1,3-cyclopentadiene] Cobalt:**

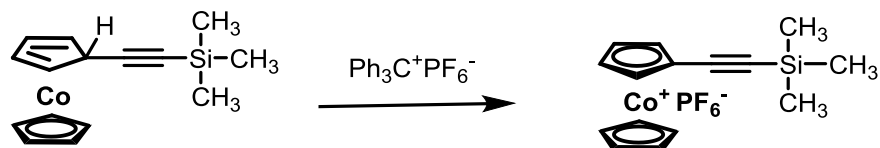
A 500 mL round-bottom flask was charged with magnetic stirring bar and 200ml of dry THF, 2.36 mL of (trimethylsilyl) acetylene (1.14 equiv, 17 mmol) under protection from air by a nitrogen atmosphere. The mixture was cooled using dry ice/acetone and 6.28 mL (1.05 equiv, 15.6 mmol) of n-BuLi solution was added. It was let to stir for 45 minutes followed by the addition of 5 g of cobaltocenium hexafluorophosphate (1 equiv, 14.9 mmol). The reaction mixture was slowly warmed to room temperature to let it react further. There was a change in color from yellow to rusty red which is because of the nucleophilic addition. The solvent was removed in vacuo and passed through an alumina column using hexane. After removing hexane in vacuo 3.94 g (yield 92%) of product was obtained.



**Synthesis of trimethylsilylethynylcobaltocenium hexafluorophosphate (TMSCoPF<sub>6</sub>):**

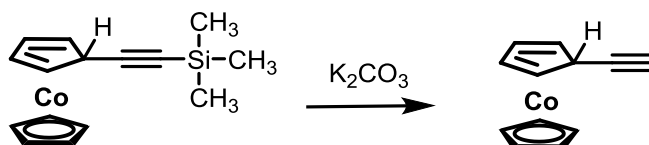
2 g of ( $\eta^5$ -Cyclopentadienyl)[ $\eta^4$ -(exo-5-trimethylsilylethynyl)-1,3-cyclopentadiene] Cobalt was dissolved in 150 mL of dry DCM. 2.7 g of triphenylcarbenium hexafluorophosphate (equimolar) was added to the stirring solution and let it react at dark for 15 minutes. Then, the reaction mixture was filtered and washed with ether and water until filtrate came off clear. The obtained solid was dried in vacuo to give 96% (2.9 g) yield.





**Synthesis of (η5-Cyclopentadienyl)[η4-(exo-5-ethynyl)-1,3-cyclopentadiene] Cobalt (Compound III):**

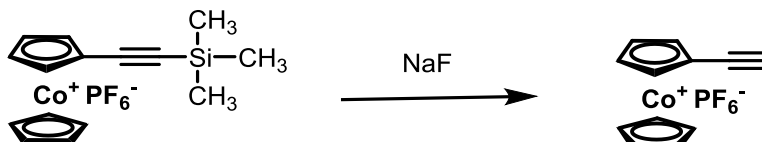
To a solution of compound I (1.0 g, 3.48 mmol) in 50 mL of methanol,  $\text{K}_2\text{CO}_3$  (1.95 g, 13.93 mmol) was added. The reaction mixture was stirred at room temperature for 4 h. The solution was filtered, evaporated, and re-dissolved in dichloromethane, washed with water, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated to give a product 0.78 g (98%) as brown powder.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 5.41(s,  $\text{C}_2/\text{C}_5$  of substituted Cp, 2H), 4.80 (s, Cp, 5H), 3.46 (s, CCH, 1H), 2.77 (s,  $\text{C}_2/\text{C}_5$  of substituted Cp, 2H), 1.87 (s, Cp, 1H).



**Synthesis of ethynel cobaltocenium hexafluorophosphate:**

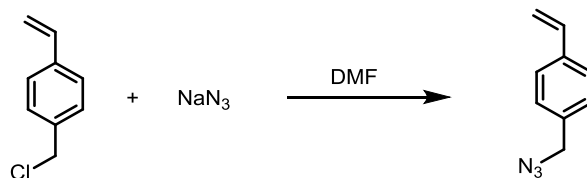
A 1.0 g portion of  $\text{TMSCoPF}_6$  (2.32 mmol, 1 equiv) was dissolved in 25 mL of an acetonitrile–water mixture (3/2 v/v), and 0.106 g of sodium fluoride (1.09 equiv, 2.53 mmol) was added. The solution was refluxed for 2 hrs at 90 °C, and stirred at room temperature overnight. On next day, traces of dark solid byproduct were filtered off and thoroughly washed with acetonitrile. The filtrate was concentrated on a rotary evaporator at a bath temperature of 50 °C to remove acetonitrile completely. Evaporation was continued until the total volume of the aqueous solution was approximately 7 mL. 345  $\mu\text{L}$  of an aqueous hexafluorophosphoric acid solution (1.09 equiv, 2.53 mmol) was added

and the product was allowed to crystallize at 0 °C for 1hr. The yellow powdery product was filtered off and thoroughly washed two times with a small amount of ice cooled water and three times with diethyl ether. The obtained solid was dried in vacuo to give 86% yield (0.72 g, 2.02 mmol):  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{COCD}_3$ ,  $\delta$ , ppm): 5.94 (t, Cp, 2H), 5.65 (s, Cp, 5H), 5.63 (t, Cp, 2H), 3.67 (s, CCH, 1H).



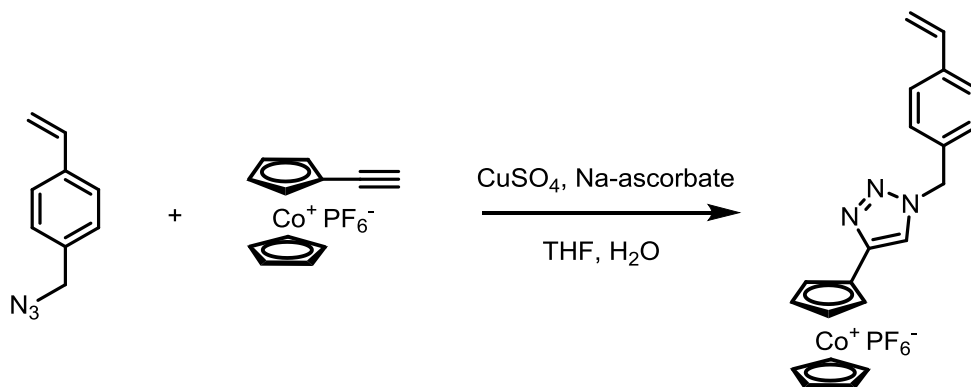
#### Synthesis of 4-Vinylbenzyl azide:

4-vinylbenzyl azide was synthesized by a simple nucleophilic substitution reaction of 4-vinylbenzyl chloride with sodium azide. 2.0 g of 4-vinylbenzyl chloride (13.16 mmol) was dissolved in 20 ml DMF in round bottom flask. 2.56 g of  $\text{NaN}_3$  (39.48 mmol) was added to the solution and stirred overnight at room temperature. The reaction mixture was poured into 50 ml of water and the organic fraction was extracted with water three times (3 x 50 ml portions). Finally, the organic layer was dried with  $\text{MgSO}_4$  and evaporated the solvent. The product was an orange liquid in a 92.6 % yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 7.35 (dd,  $\text{C}_6\text{H}_4$ , 2H), 6.71 (dd,  $\text{CH}_2=\text{CH}$ , 1H), 6.41 (t, Cp, 2H), 6.0 (t, Cp, 2H), 5.71 (t, Cp, 5H), 5.68 (s,  $\text{CH}_2\text{N}_3$ , 2H), 5.50 (d,  $\text{CH}_2=\text{CH}$ , 2H).



**Synthesis of 1-(4-vinylbenzyl)-1H-1,2,3-triazole-4-cobaltocenium hexafluorophosphate:**

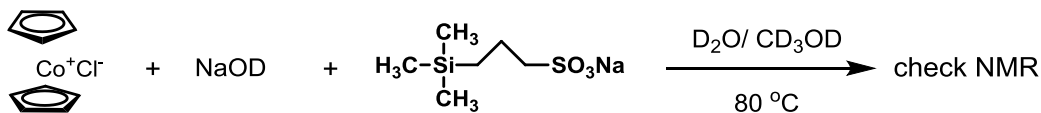
A mixture of 1-(azidomethyl)-4-vinylbenzene (43 mg, 0.28 mmol) and ethynylcobaltocenium hexafluorophosphate (3) (100 mg, 0.28 mmol) were dissolved in 15 mL of 3:2 distilled THF/H<sub>2</sub>O. At 0 °C, CuSO<sub>4</sub> was added (1 equiv.; 1 M aqueous solution), followed by dropwise addition of a freshly prepared solution of sodium ascorbate (2 equiv.; 1 M aqueous solution), then purge N<sub>2</sub> gas for 30 min. The solution was allowed to stir for 12 h at room temperature under N<sub>2</sub>. An aqueous solution of ammonia was added, and the mixture was allowed to stir for 10 min. Extract with dichloromethane 50 mL × 2, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under vacuum. Further purified on silica gel column with a mixture of dichloromethane/methanol 10:1 (v/v) as eluent to give 100 mg monomer 4 as yellow solid with a yield of 70%. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>, δ, ppm): 4.31 (s, CH<sub>2</sub>N<sub>3</sub>, 2H). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>, δ, ppm): 8.53 (s, triazolyl H, 1H), 7.40 (dd, C<sub>6</sub>H<sub>4</sub>, 2H), 6.75 6.71 (dd, CH<sub>2</sub>=CH, 1H), 5.50 (d, CH<sub>2</sub>=CH, 2H), 3.67 (s, CCH, 1H).



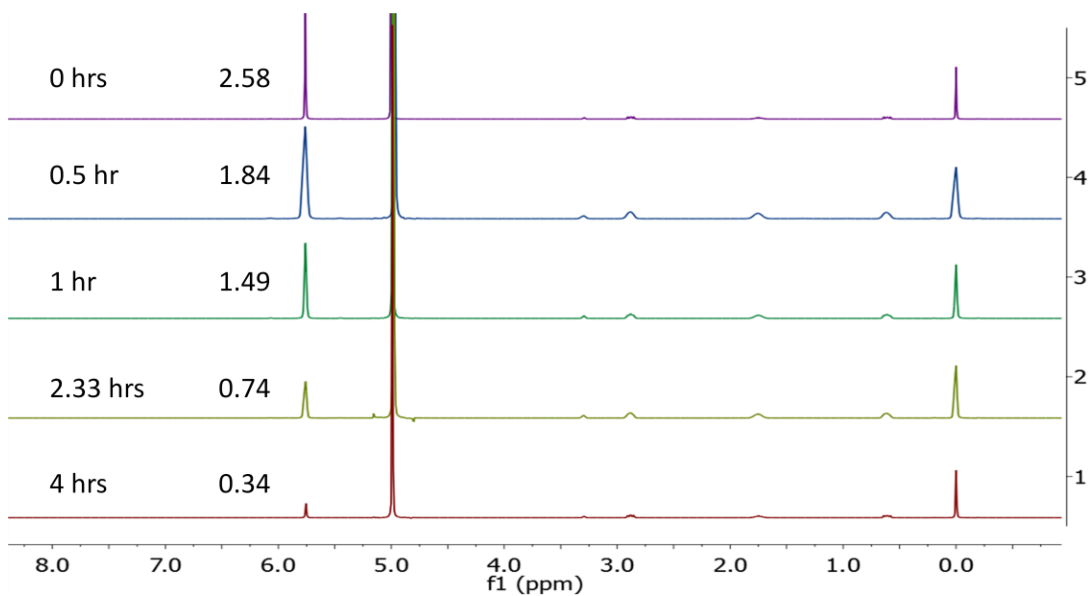
### 3.4. Results and Discussion:

#### 3.4.1. Alkaline stability of cobaltocenium chloride ( $\text{Cp}_2\text{CoCl}$ ):

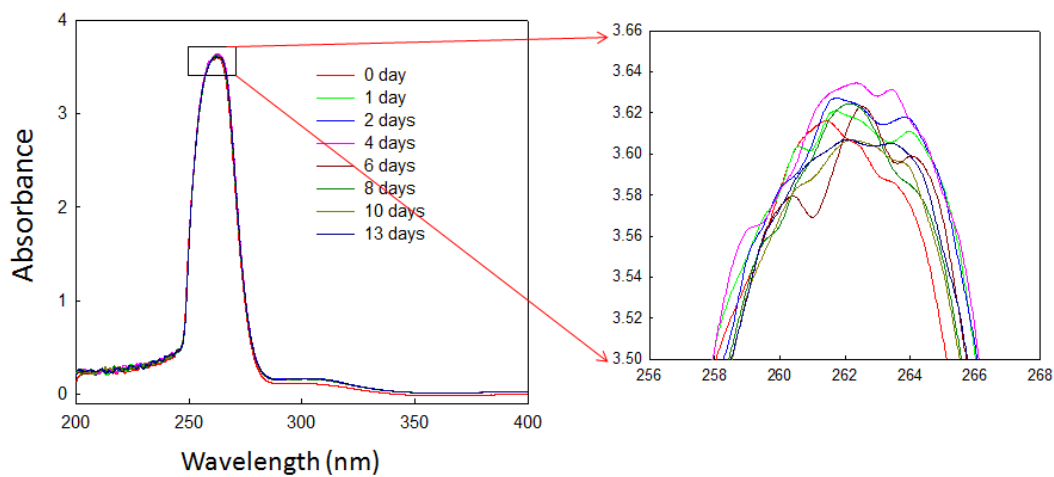
The alkaline stability of cobaltocenium chloride salt was investigated in 1M NaOD/ $\text{D}_2\text{O}$  solution with an internal standard 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt at 80 °C temperature by using  $^1\text{H}$ -NMR and UV-visible spectroscopy (shown in Figure 3.1). The  $^1\text{H}$ -NMR spectrum is shown in Figure 3.2. The singlet at  $\delta$  0.0 ppm ( $\text{CH}_3$ ) and  $\delta$  5.75 ppm (Cp CH) correspond to the internal standard and cobaltocenium Cp ring respectively. After testing for 4 hours, it seemed that significant degradation (87%) occurred from the relative integration of Cp ring in comparison to the internal standard peak. On the other hand, UV-visible spectrum shows no significant change in the absorbance of cobaltocenium cation after 13 days (Figure 3.3). Different results were found in two different spectroscopic methods and no appearance of new resonance peaks imply that the proton in Cp ring could be displaced by deuterium upon heating. Therefore integration value of Cp ring decreased over time but the absorbance of Cp ring didn't change. This finding was further confirmed by Mass spectroscopy of the resulting product (Figure 3.4). The mass spectrum shows that molecular weight of cobaltocenium increased from 189 g/mol to 199 g/mol due to the replacement of 10 hydrogens by 10 deuteriums. These results confirmed the stability of  $(\text{C}_5\text{H}_5)_2\text{CoCl}$  under test conditions, with the unexpected finding of  $^1\text{H}$  to  $^2\text{H}$  exchange.



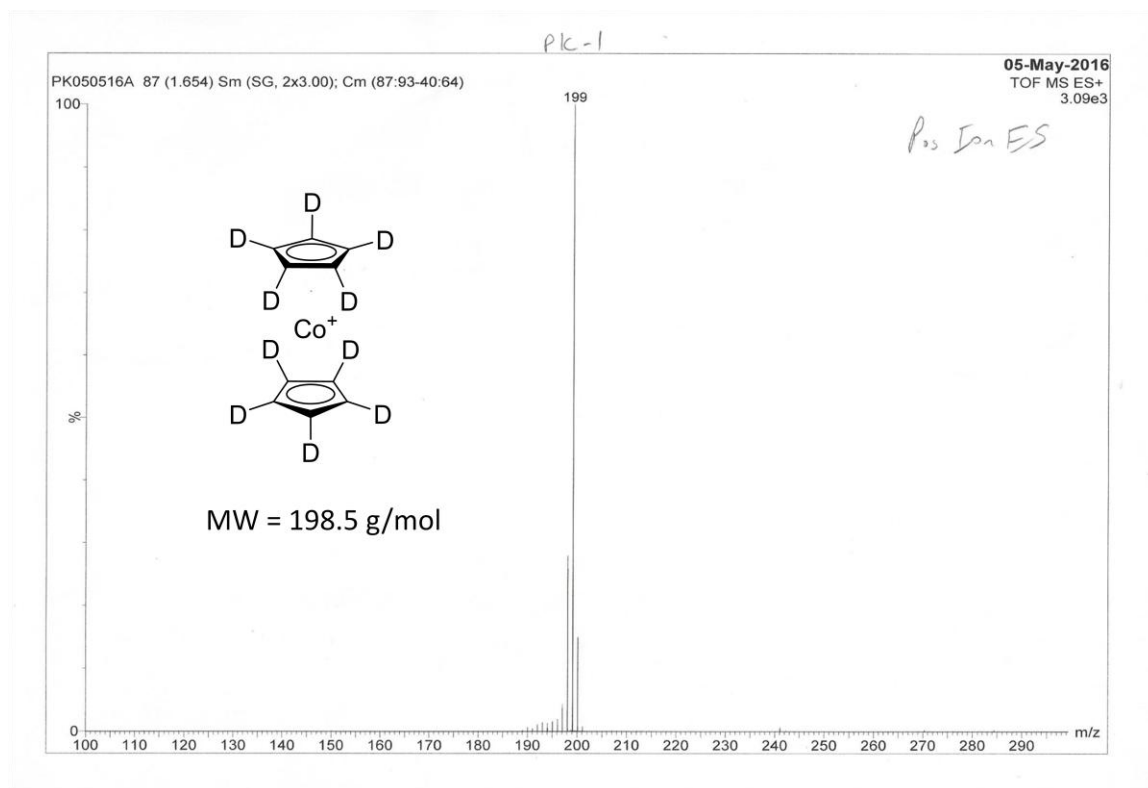
**Figure 3.1** Alkaline stability of Cobaltocenium chloride ( $\text{Cp}_2\text{CoCl}$ )



**Figure 3.2**  $^1\text{H}$  NMR spectrum of  $\text{Cp}_2\text{CoCl}$  in  $1\text{ M NaOD/D}_2\text{O}$  with 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (0.05 M) as an internal standard after heating at  $80\text{ }^\circ\text{C}$  for 4 hours.



**Figure 3.3** UV-vis spectra of  $(\text{C}_5\text{H}_5)_2\text{CoCl}$

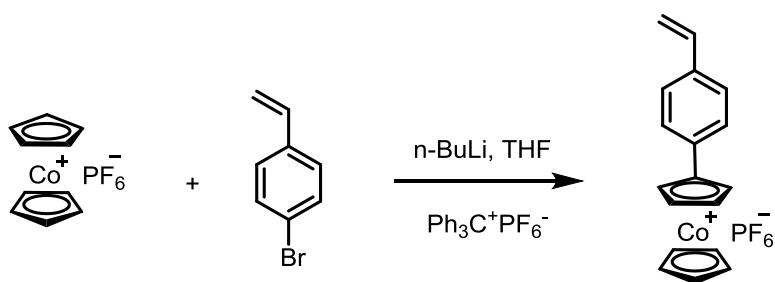


**Figure 3.4** Mass spectra of the product after 4 hours

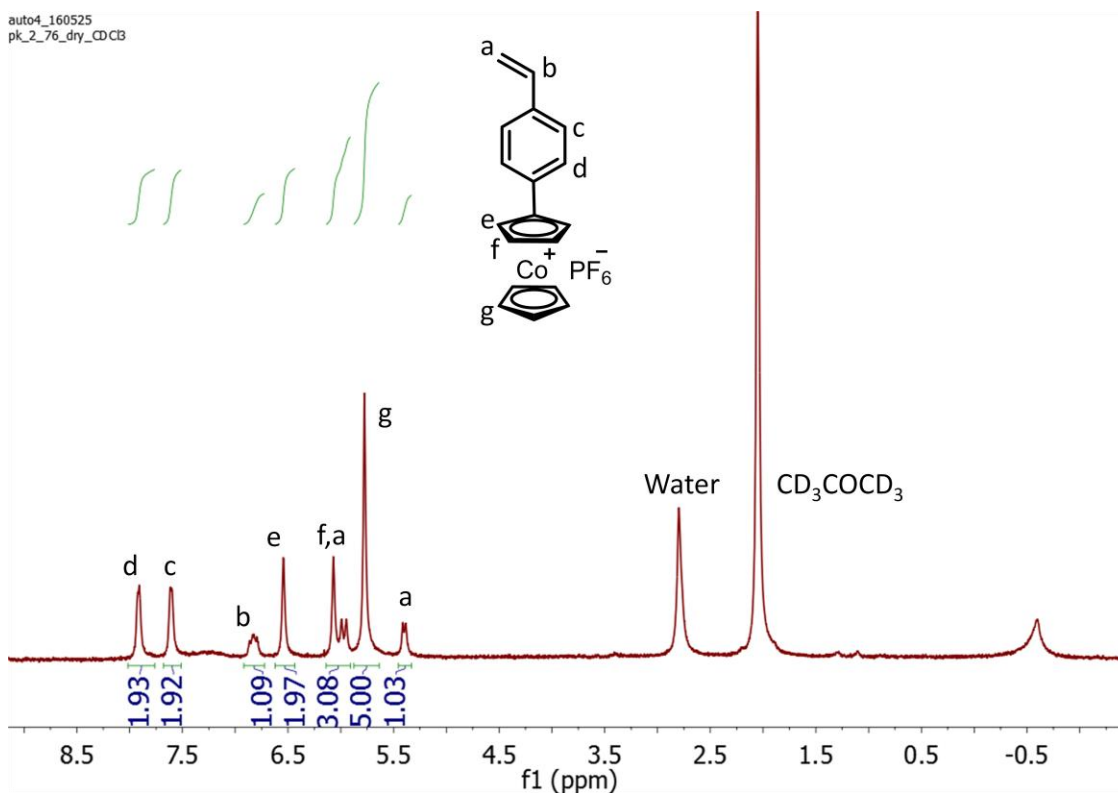
#### 3.4.2. Synthesis of styrene cobaltocenium hexafluorophosphate (StCp<sub>2</sub>CoPF<sub>6</sub>):

Previously, our group synthesized side chain cobaltocenium polymers using monosubstituted cobaltoceniums as monomers.<sup>31, 77-78</sup> Sheats *et al.* synthesized main-chain cobaltocenium polymers via condensation polymerization.<sup>79-80</sup> However, most cobaltocenium polymers contained ester and amide linkage which are not suitable for AAEMFC applications. In order to achieve suitable and stable AAEMs, it is necessary to avoid the presence of ester and amide linkage, and CH<sub>2</sub> or CH group at  $\alpha$  position of cobaltocenium moiety. Because hydroxide ion can cleave the ester and amide bond, and abstracts a proton from the  $\alpha$  position as well, which produces negative charge which can neutralize Co (III) center, resulting reduced efficiency. Here, we synthesized styrene cobaltocenium hexafluorophosphate (StCp<sub>2</sub>CoPF<sub>6</sub>) without any purification. This styrene

based cobaltocenium monomer was chosen because of the steric hindrance of phenyl group would prevent proton abstraction. The synthetic route used to synthesis  $\text{StCp}_2\text{CoPF}_6$  is shown in Figure 3.5. Lithiation of 4-bromostyrene at  $-78^\circ\text{C}$  gives 4-lithiumstyrene, lower temperature is required because styrene would undergo polymerization. Cobaltocenium is functionalized by nucleophilic attack of lithiumstyrene at  $0^\circ\text{C}$ . Cobaltocenium reduced to cobaltocene which was confirmed by the solubility change in THF from a suspension to a purple solution. Finally,  $\text{StCp}_2\text{CoPF}_6$  was successfully synthesized by hydride abstraction by using trityl hexafluorophosphate ( $\text{Ph}_3\text{C}^+\text{PF}_6^-$ ) in dichloromethane at dark followed by precipitation and recrystallization from diethyl ether. Nearly 100% pure  $\text{StCp}_2\text{CoPF}_6$  in a yield of 50% was achieved. The structure and purity was confirmed by  $^1\text{H}$  NMR (shown in Figure 3.6). Three different chemical shifts of cyclopentadienyl (Cp) protons confirmed the successful substitution of cobaltocenium. The chemical shift at  $\delta$  5.59 ppm is from the cyclopentadienyl protons from residual cobaltocenium which can be removed by extraction with water.



**Figure 3.5** Synthetic route of styrene cobaltocenium hexafluorophosphate ( $\text{StCo}^+\text{PF}_6^-$ ).

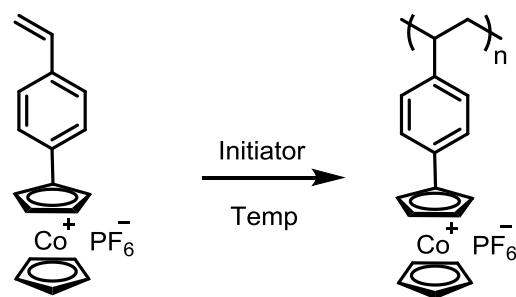


**Figure 3.6**  $^1\text{H}$  NMR spectrum of  $\text{StCo}^+\text{PF}_6^-$  in  $\text{CD}_3\text{COCD}_3$

### 3.4.3. Polymerization of Styrene cobaltocenium hexafluorophosphate ( $\text{StCo}^+\text{PF}_6^-$ ) and Styrene cobaltocene ( $\text{StCp}_2\text{CoH}$ ):

We attempted free radical polymerization of styrene cobaltocenium hexafluorophosphate, by using different initiators including AIBN, BPO and ACHN at different temperature. The polymerization route is shown in Figure 3.7. After stirring for 24 hours, the conversion from monomer to polymer was checked by  $^1\text{H}$  NMR. The NMR shows no disappearance of styrene double bond in all cases, indicating no polymerization.



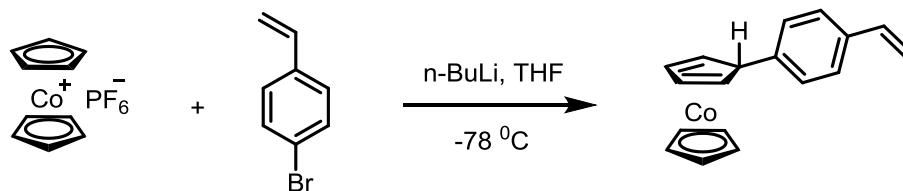


**Figure 3.7** Polymerization of StCp<sub>2</sub>CoPF<sub>6</sub>

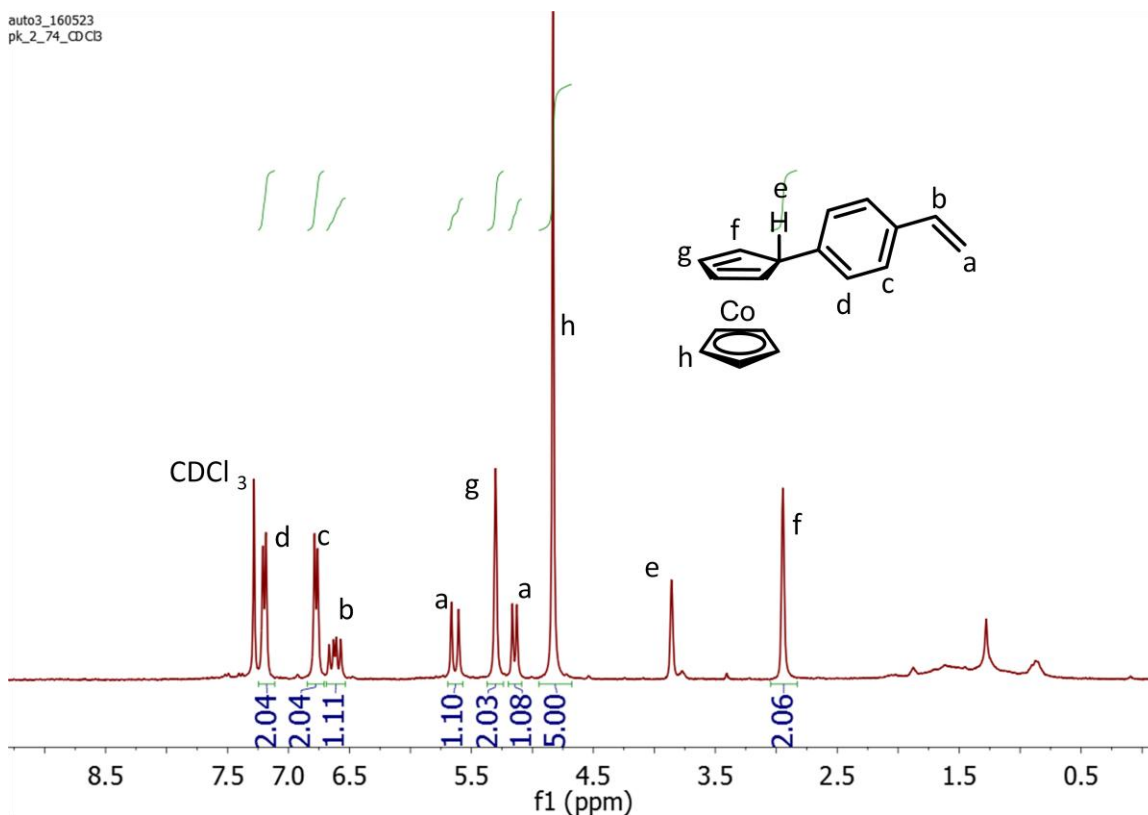
**Table 3.1** Polymerization of StCoPF<sub>6</sub> with different initiators

Initiator	Temp ( °C)	Result
AIBN	70	No
	90	No
BPO	100	No
ACHN	90	No

In StCp<sub>2</sub>CoPF<sub>6</sub> monomer, styrene is connected to the Cp ring of the cobaltocenium cation where cobalt has +3 oxidation state. This cation might quench the free radical from the propagation state in the polymerization. Therefore, we attempted to synthesize and polymerize neutral  $\eta^5\text{Cp } \eta^4\text{Cp}$  containing monomer styrene cobaltocene (StCp<sub>2</sub>CoH). Following a similar synthetic procedure, StCp<sub>2</sub>CoH can be synthesized by one-pot reaction (shown in Figure 3.8) without the need for purification by column chromatography in an overall isolated yield of 57.2%. The structure and purity were confirmed by <sup>1</sup>H NMR (shown in Figure 3.9)



**Figure 3.8** Synthetic route of styrene cobaltocene (StCp<sub>2</sub>CoH)

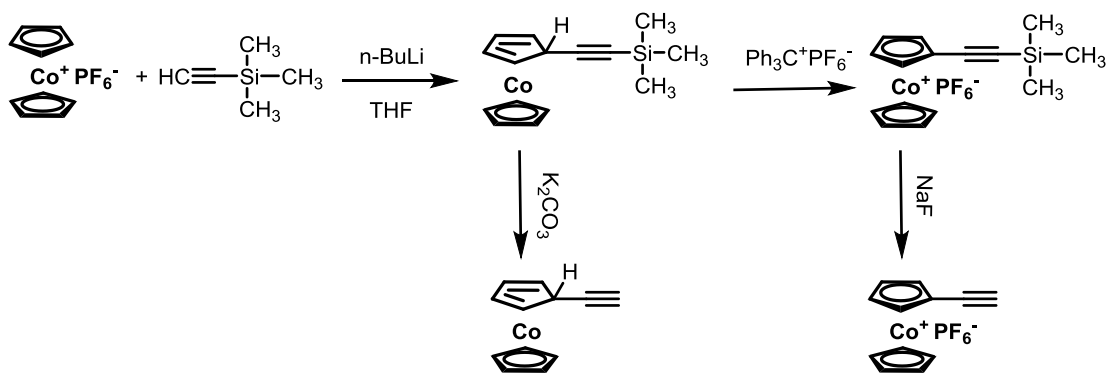


**Figure 3.9** <sup>1</sup>H NMR spectrum of StCp<sub>2</sub>CoH in CDCl<sub>3</sub>

Similarly, we tried to polymerize StCp<sub>2</sub>CoH monomer by using different initiator with different monomer to initiators ratio at different temperature. The <sup>1</sup>H NMR of the resulting mixture shows no conversion after stirring for 24 hours. Due to the difficulties on the polymerization of cobaltocene and cobaltocenium styrene based monomer, we design monomers which have at least one carbon gap between styrene and cobaltocenium moiety shown in Figure 3.15.

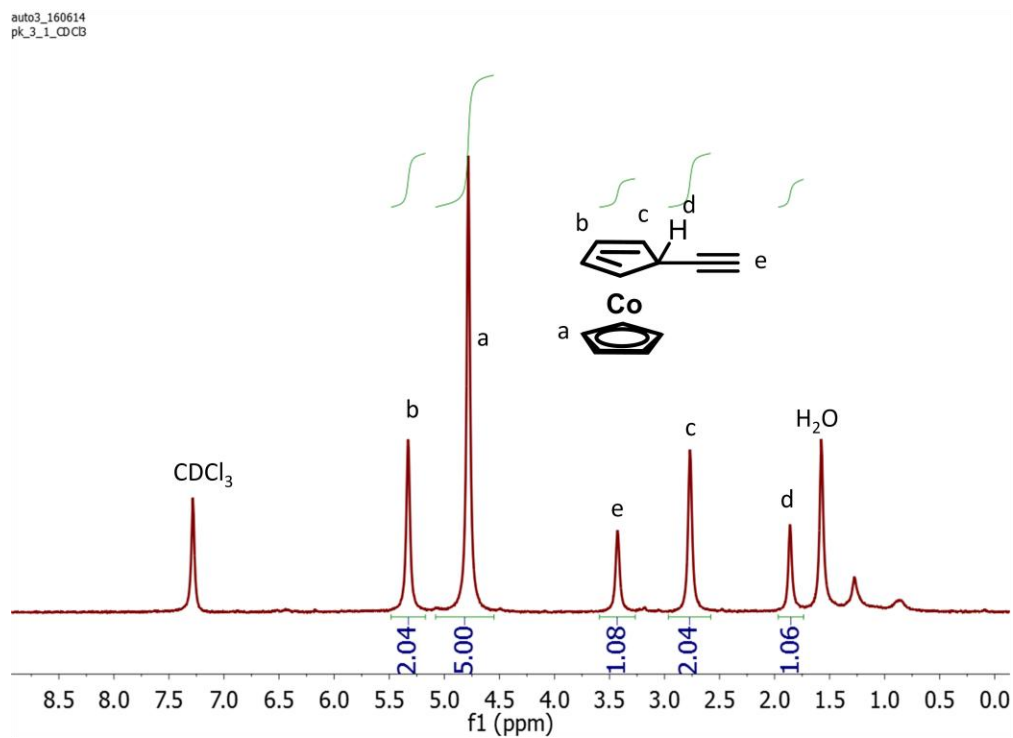
### 3.4.4. Synthesis of Ethynyl cobaltocenium hexafluorophosphate and Cobalt [ $\eta^5$ -cyclopentadienyl- $\eta^4$ -exo-5-ethynyl-1, 3-cyclopentadiene]:

The synthetic route of ethynyl cobaltocenium hexafluorophosphate and cobalt [ $\eta^5$ -cyclopentadienyl- $\eta^4$ -exo-5-ethynyl-1, 3-cyclopentadiene] is shown in Figure 3.10. First the lithiation of trimethyl silylacetylene at  $-78^\circ\text{C}$  gave lithium (trimethylsilyl)acetylide nucleophile. Unsubstituted cobaltocenium hexafluorophosphate was functionalized by nucleophilic addition of lithium (trimethylsilyl)acetylide at  $0^\circ\text{C}$ . Cobaltocenium reduced to cobaltocene which was confirmed by the solubility change in THF from a suspension to a purple solution. Cobalt [ $\eta^5$ -cyclopentadienyl- $\eta^4$ -exo-5-ethynyl-1, 3-cyclopentadiene] was obtained by subsequent deprotection of trimethylsilyl with  $\text{K}_2\text{CO}_3$ .  $^1\text{H}$  NMR (shown in Figure 3.11) confirmed the purity and successful synthesis of the product.

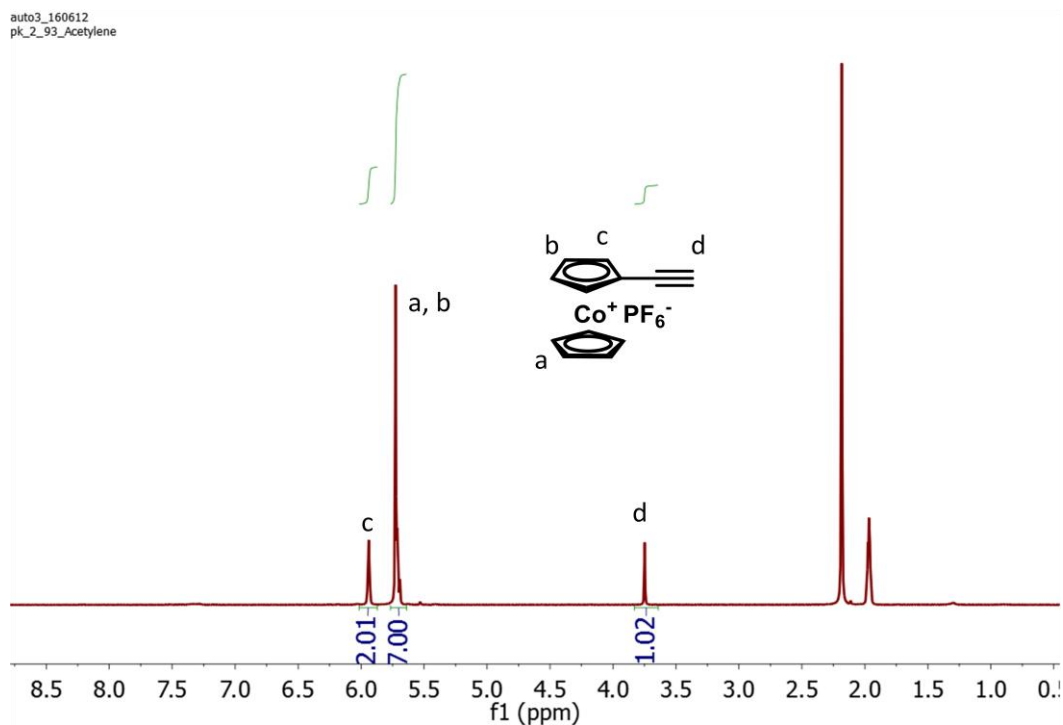


**Figure 3.10** Synthetic route of ethynyl cobaltocenium hexafluorophosphate

Ethynyl cobaltocenium hexafluorophosphate was synthesized from cobalt [ $\eta^5$ -cyclopentadienyl- $\eta^4$ -exo-5-ethynyl-1, 3-cyclopentadiene] by hydride abstraction with trityl hexafluorophosphate and followed by deprotection of trimethylsilyl group with NaF.  $^1\text{H}$  NMR of the product is shown in Figure 3.12.



**Figure 3.11**  $^1\text{H}$  NMR spectrum of ethynyl cobaltocene in  $\text{CDCl}_3$



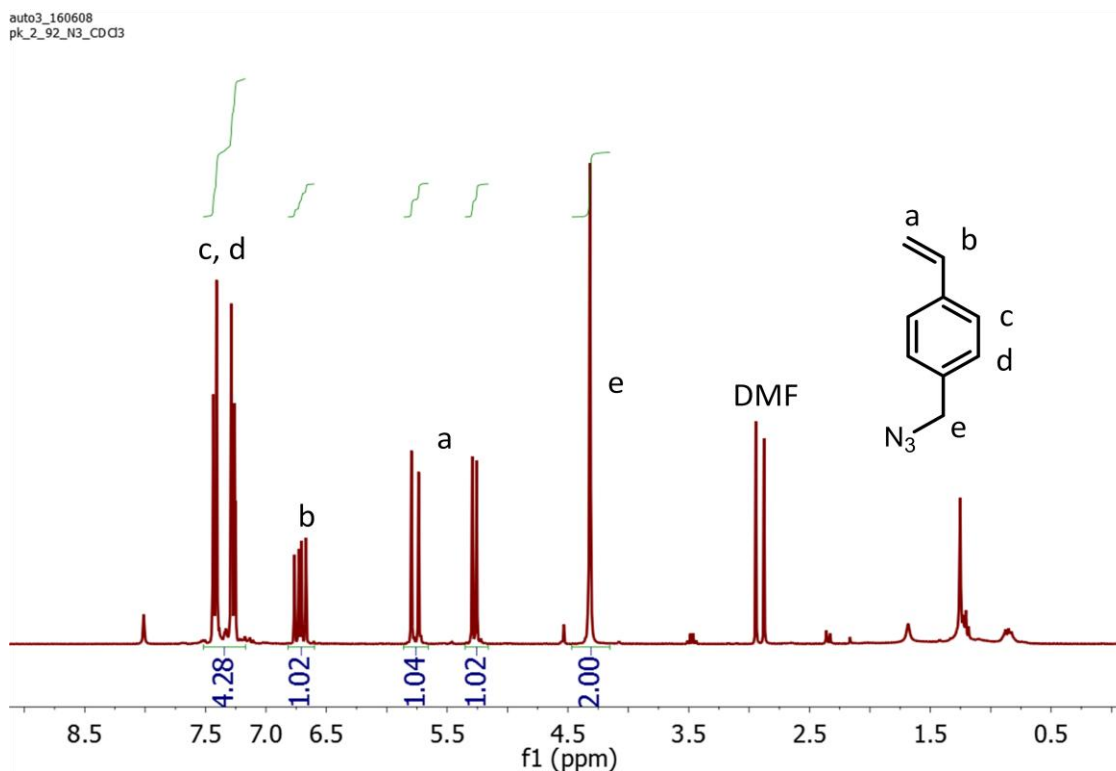
**Figure 3.12**  $^1\text{H}$  NMR spectrum of ethynyl cobaltocenium hexafluorophosphate in  $\text{CD}_3\text{COCD}_3$

### 3.4.5. Synthesis of 4-Vinylbenzyl azide:

The formation of 4-vinylbenzyl azide was carried out by nucleophilic substitution reaction of 4-vinylbenzyl chloride in the presence of  $\text{NaN}_3$  in DMF at room temperature for 24 hours.  $\text{NaN}_3$  is not soluble in DMF, a few drops of water in DMF helped to dissolve azide in the solvent and facilitated the reaction. After washing with water and DCM, product was obtained (yield 98%). The structure and purity was confirmed by  $^1\text{H}$  NMR (shown in Figure 3.14). The chemical shift of benzyl  $\text{CH}_2$  at  $\delta$  4.59 ppm is shifted to  $\delta$  4.32 indicating 100% substitution of Cl by  $\text{N}_3$ .



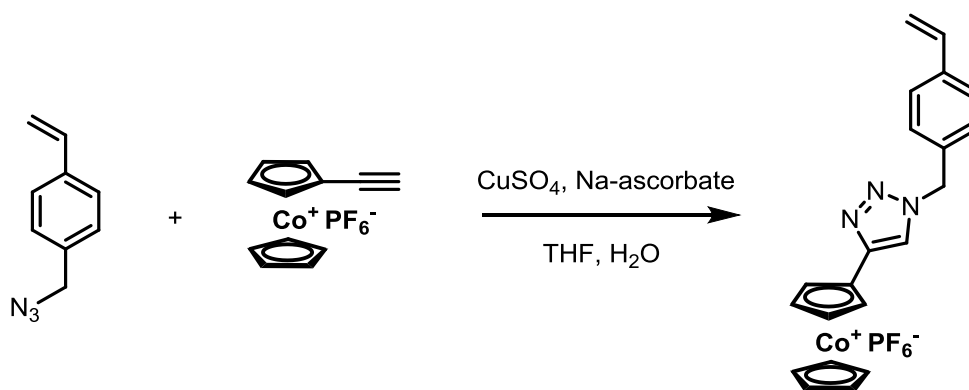
**Figure 3.13** Synthetic route of 4-Vinylbenzyl azide



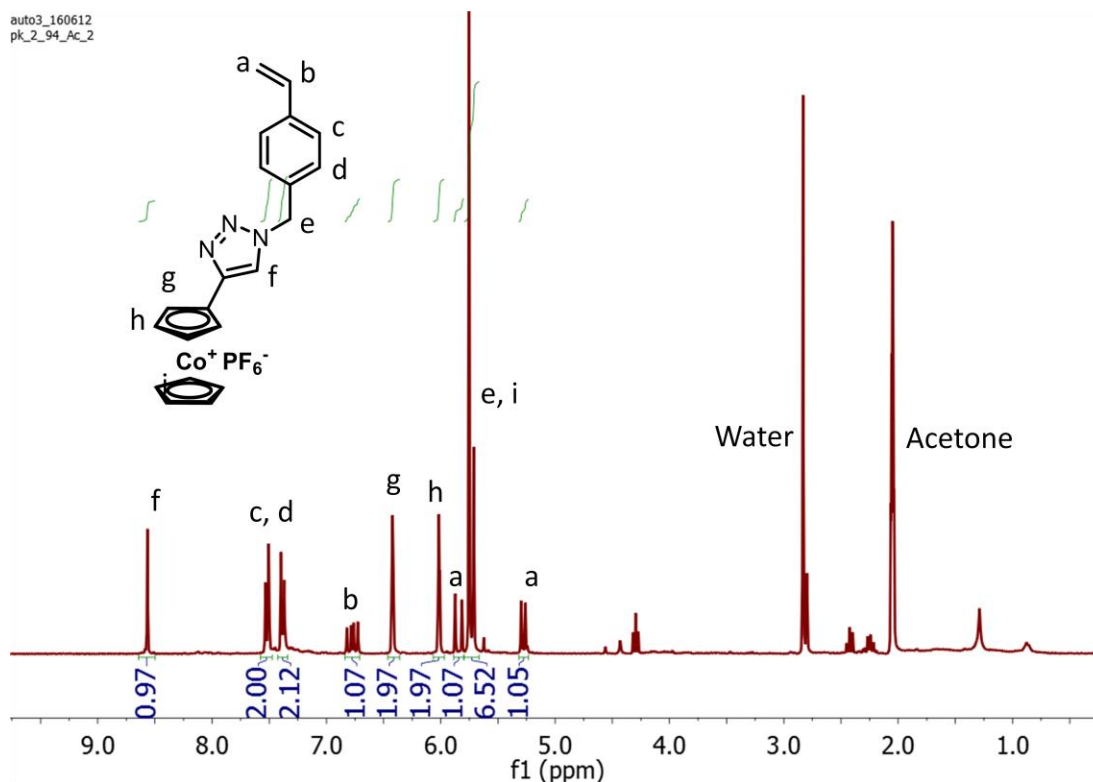
**Figure 3.14**  $^1\text{H}$  NMR spectrum of 4-vinylbenzyl azide in  $\text{CDCl}_3$

### 3.4.6. Synthesis of 1-(4-vinylbenzyl)-1H-1,2,3-triazole-4-cobaltocenium hexafluorophosphate:

Copper-catalyzed azide-alkyne cycloaddition (CuAAC), known as click reaction, between ethynylcobaltocenium hexafluorophosphate and azide-containing 4-vinylbenzyl azide gave the corresponding monomer 1-(4-vinylbenzyl)-1H-1,2,3-triazole-4-cobaltocenium hexafluorophosphate (Figure 3.15). The identity of the desired product was confirmed by  $^1\text{H}$  NMR spectrum as shown in Figure 3.16. The disappearance of the acetylene proton at 3.7 ppm and appearance of the triazole proton at 8.6 ppm demonstrated the successful click reaction.



**Figure 3.15** Synthetic route of 1-(4-vinylbenzyl)-1H-1,2,3-triazole-4-cobaltocenium hexafluorophosphate



**Figure 3.16**  $^1\text{H}$  NMR spectrum of 1-(4-vinylbenzyl)-1H-1,2,3-triazole-4-cobaltocenium hexafluorophosphate in  $\text{CD}_3\text{COCD}_3$

### 3.5. Conclusion

The alkaline stability of cobaltocenium cation in 1M NaOD/ $\text{D}_2\text{O}$  at 80  $^{\circ}\text{C}$  temperature was investigated by  $^1\text{H}$  NMR and UV-vis spectroscopy method. We found that deuterium isotope from the reaction media displaced all cyclopentadiene proton from cobaltocenium. However, cobaltocenium cation remained intact over a 13 day period. The excellent alkaline stability of cobaltocenium cation confirmed that membranes containing cobaltocenium are promising for use in AAEMFC. Styrene based cobaltocene/cobaltocenium containing monomer was synthesized in a one pot reaction without any purification. After synthesizing the monomer, we attempted to polymerize them and found that both monomers cannot undergo polymerization due to the stabilizing

effect of cobaltocene/cobaltocenium moiety. Therefore, we designed a monomer where the double bond containing styrene and cobaltocenium moiety with at least one carbon in between. Finally, we synthesized triazole-ring containing cobaltocenium styrene monomer via click reaction. Further investigation of these monomers could provide further insight on their polymerization.



## CHAPTER 4

### SUMMARY AND OUTLOOK

#### 4.1 Summary:

There were two major goals at the beginning of this project. The first was to investigate the nature and relative strength of intermolecular interaction between PCoAEMACl polyelectrolytes and small organic anions. The organic probes are differ by one variable, so that comparison of the relative affinities provides us which structural features are important on intermolecular interactions. The common methods to investigate such intermolecular interactions like NMR and MS are not suitable in this situation because higher concentration is required for effective NMR, but at higher concentration the polyelectrolytes and anionic probes complex is not soluble. Therefore, we have conducted this study using optical spectroscopy method, an efficient method at low concentration. In this approach, 5(6)-carboxyfluorescein (CF) dye was used as a fluorescent indicator. First we made polymer-dye complex (P·CFn). Then the targeted nonfluorescent displacer probe was then introduced to displace the dye from its polymer-dye complex and to form the polymer-probe complex. The spectroscopic signature of the free dye anion represents the amount of probe bound to the polymer. We found that electrostatic charge and  $\pi$ -electron moiety of small molecules are the most influential, but conformation and size of the guest have no significant influence on the binding process.

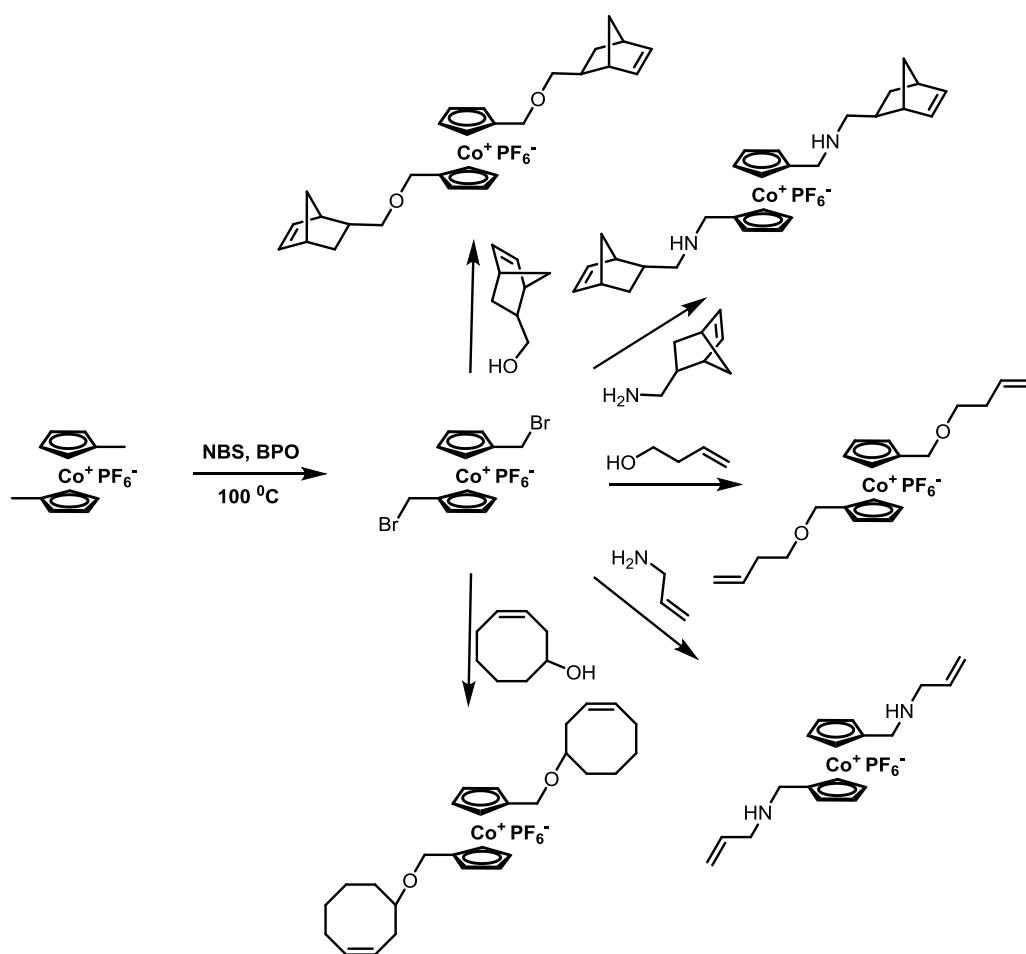
The second goal was to investigate the alkaline stability of cobaltocenium cation and synthesis of styrene based and cobatocenium functionalized alkaline anion exchange membrane. The alkaline stability was conducted in 1M NaOD/D<sub>2</sub>O solution with an internal standard 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt at 80 °C temperature. The excellent alkaline stability of cobaltocenium cation confirmed that membranes containing cobaltocenium are promising for use in AAEMFC. For that

styrene based cobaltocene/cobaltocenium containing monomers were synthesized in one pot reaction and triazole ring containing cobaltocenium styrene monomer via click reaction.

#### **4.2. Future direction:**

##### **Main-chain cobaltocenium containing polymers for AAEMs:**

Along with side-chain cobaltocenium containing polymers, main-chain cobaltocenium containing polymers should be investigated for AAEMs. Polyolefins (saturated hydrocarbon backbone) is relatively inert to nucleophilic attack, or deprotonation by hydroxide ion. Random copolymers norbornene, cyclooctene and diene containing cobaltocenium are promising candidate materials for stable AAEMs. The synthetic routes to these norbornene, cyclooctene and diene containing cobaltocenium monomer are shown in Figure 4.1. The diene containing monomer can be polymerized via acyclic diene metathesis polymerization, and other two monomers can be copolymerized with norbornene, or cyclooctene monomers via ring-opening metathesis polymerization (ROMP) followed by hydrogenation to fabricate flexible, robust and alkaline stable membranes.



**Figure 4.1** Proposed synthetic route to the norbornene, cyclooctene and diene containing cobaltocenium monomer

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