

**DESIGN AND ELECTROCHEMICAL CHARACTERIZATION OF
NOVEL FUNCTIONALIZED POLYTHIOPHENE AND POLYSILOXANE
DERIVATIVES**

by

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Abstract

Metal-containing conducting polymers are a new and interesting class of materials that combine some of the redox properties of the conducting polymers and metal ions. In metal-containing conjugated polymers, there are several possible arrangements of the metal group relative to the backbone. This research focuses on the development of novel thiophene derivatives, with various side groups using different synthetic approaches and electrochemical polymerization. The resulting polymers could be excellent candidates for chemical sensors, solar cells, photoactive molecular devices and capacitors.

Thiophene-based polymers containing η^6 -(haloarene)- η^5 -cyclopentadienyliron(II) hexafluorophosphate or ferrocene moieties were synthesized. Thiophene monomers which contained organoiron complexes were successfully polymerized using condensation polymerization and electropolymerization. The monomers and their precursors were characterized through nuclear magnetic resonance spectroscopy, infrared spectroscopy, cyclic voltammetry and electrochemical impedance spectroscopy. The thermal properties were studied with thermogravimetric analysis and differential scanning calorimetry.

A novel series of functionalized thiophenes incorporating naphthol, coumarin and pyrene pendants were synthesized by Steglich esterification in the presence of DCC/DMAP and the synthesized monomers were electrochemically deposited onto glassy carbon and carbon fibre microelectrodes as active electrode materials. Another series was prepared with thiophenes using pendant terpyridine groups of varying functionality. The electrochemical impedance

measurements were performed on surface-modified electrodes. Variation of capacitance values was explained according to the different fluorophore groups attached to the thiophene as well as the different substrates. The fluorescence behaviours and the surface morphological analysis were explained in detail.

Additionally, using organoiron-mediated nucleophilic aromatic substitution, a number of allylamine-containing organoiron complexes were prepared. These materials were further hydrosilated with methyldiethoxyhydrosilane to generate cationic organoiron siloxanes and ferrocene-containing siloxane complexes. *In situ* cleavage of the ethoxy groups followed by the addition of H_2SO_4 resulted in the formation of polymeric materials. The synthesized polymers were individually blended with PAN/DMF matrix to form composite thin films. The films indicated porous surface morphology, increasing the surface activity.

Preface

The work contained in this thesis was conducted, analyzed and interpreted by Sibel Dalgakiran. Some parts of the chapters are either published, submitted to, or in preparation to be submitted to scientific journals for publication as below:

- A version of chapter 4 has been published as: Micro and nano-sized polysiloxanes containing organoiron moieties. A.S. Abd-El-Aziz, D.J. Winram, P.O. Shipman, S. Sezgin Dalgakiran, P. Shipley, L. Bichler and B. Patrick (*The New Journal of Chemistry*, 2011, 35, 2341-2348). Diana Winram synthesized the cationic iron including siloxane precursor materials previously; Sibel Dalgakiran conducted syntheses and characterizations of the data and wrote the manuscript with Dr. Patrick O. Shipman. Dr. Paul Shipley helped with the silicone NMR data, Dr. Lukas Bichler achieved the SEM measurements, and crystallographic data was measured by Dr. Brian Patrick. This work was presented at CSC 2010, Toronto by Sibel Dalgakiran.
- Some of the work from chapter 4 has been published as: Design of organoiron-containing polyethers/thioethers and polysiloxanes, enroute to micro- and nano-sized materials. A.S. Abd-El-Aziz, S. Sezgin, and L. Bichler (*Polymer Preprints* 2011, 52(2), 764). The SEM images were conducted by Dr. Lukas Bichler. This work was presented at ACS 2011, Denver by Sibel Dalgakiran.
- Chapter 2 includes organoiron moieties in terms of synthesis and characterizations which have been previously studied by Dr. A.S. Abd-El-Aziz. Sibel Dalgakiran synthesized

novel polymers using organoiron moieties either as side chains or in the backbone. Dr. Lukas Bichler conducted the SEM measurements. This manuscript is ready for submission as follows: Metallo-conjugated EDOT polymer synthesis and characterization. A.S. Abd-El-Aziz, S. Dalgakiran, L. Bichler.

- Chapter 3 is based on the electropolymerization of novel functionalized thiophene derivatives on electrode surfaces. Inan Kucukkaya and Dr. Brian Wagner helped for fluorescence measurements and explanations. This manuscript was submitted to '*Macromolecular Chemistry and Physics*' for publication as follows: synthesis, electrochemistry and fluorescence behaviour of thiophene derivatives decorated with naphthol, coumarin and pyrene. A.S. Abd-El-Aziz, S. Dalgakiran, I. Kucukkaya, B.D. Wagner.
- Some of the work presented in chapter 3 has been prepared as a manuscript. Dr. Wagner conducted the detailed photophysical measurements and Mason Vandel aided in the synthesis of precursor terpyridine compounds. This manuscript is ready for submission for publication as follows: Novel synthesis and electrochemical characterization of thiophenes with pendant terpyridine groups. A.S. Abd-El-Aziz, S. Dalgakiran, M. Vandel, B. D. Wagner.

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List of Symbols and Abbreviations

AC	Alternating current
br	broad
Bu ₄ NClO ₄ ⁻	Tetrabutylammonium perchlorate
°C	Degrees Celsius
CP	Conducting polymer
CV	Cyclic voltammetry
CF	Carbon fibre
CFME	Carbon fibre microelectrode
¹³ C NMR	Carbon 13 nuclear magnetic resonance spectroscopy
¹ H NMR	Proton nuclear magnetic resonance spectroscopy
Cp	cyclopentadienyl ring
C _{sp}	Specific capacitance
C _{dl}	Double layer capacitance
d	Doublet
<i>d</i> ₆	6 deuterium
DCC	Dicyclohexylcarbodiimide
DCM	Dichloromethane
DCU	Dicyclohexylurea
dd	doublet of doublets

ddd	doublet of doublets of doublets
DMAP	N,N'-dimethylaminopyridine
DMF	N,N'-dimethylformamide
DMSO	Dimethylsulfoxide
DSC	Differential scanning calorimetry
dt	Doublet of triplets
E	Voltage
E_g	Band gap
$E_{1/2}$	Half wave potential
EIS	Electrochemical impedance spectroscopy
EDOT	Ethylenedioxythiophene
eV	Electron volt
gHSQC	Gradient heteronuclear single quantum correlation
HOMO	Highest occupied molecular orbital
Hz	Hertz
I	Current
IHP	Inner Helmholtz plane
IR	Infrared spectroscopy
J	J value (Hz)
kohms	kiloohms
LUMO	Lowest unoccupied molecular orbital
M	Molar
m	Multiplet
MHz	Mega hertz

mL	Millilitre
mM	Millimolar
mmol	Millimoles
mol	Moles
MO	Molecular orbital
mS	millisiemens
mV	Millivolt
nm	Nanometer
NMR	Nuclear magnetic resonance spectroscopy
OHP	Outher Helmholtz plane
PAN	Polyacrylonitrile
PEDOT	Poly(3,4-ethylenediothiophene)
ppm	Parts per million
PThPTerpy	thiophene-3-carboxylic acid with 4'-(3-hydroxypropyl) 2,2':6',2''terpyridine
PThHTerpy	thiophene-3-carboxylic acid with 4'-(3-hydroxyhexyl)-2,2':6',2''terpyridine
PThDTERpy	thiophene-3-carboxylic acid with 4'-(3-hydroxydodecyl)-2,2':6',2'' terpyridine
q	Quartet
R _p	Polarization resistor
R _s	Solution resistor
ROMP	Ring opening metathesis polymerization
S	Siemens
s	Singlet
SEM	Scanning electron microscope
t	Triplet

t	tert
TBAPF ₆ ⁻	Tetrabutylammonium hexafluorophosphate
T _g	Glass transition temperature
Th	Thiophene
ThC	2-(3-Thienyl)ethanol with Coumarin-3-carboxylic acid
ThN	3-Thiophenecarboxylic acid with 2-Naphthol
ThP	2-(3-Thienyl)ethanol with 1-Pyrenebutyric acid
THF	Tetrahydrofuran
UV	Ultra violet
V	Volt
VBM	Valeric bimetallic
VBM-EDOT	Valeric bimetallic complex with ethylenedioxythiophene pendant
VBM-Th	Valeric bimetallic complex with thiophene pendant
ΔE	Peak potential difference
ΔQ	Deposition charge
δ	Chemical shift (ppm)
λ	Wavelength

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To my Family

1 Introduction

1.1 Conducting Polymers

Since the electrical conductivity for conjugated polymers was reported in 1977 by Shirakawa, Heeger and MacDiarmid, many researchers have been focused on conducting polymers and their commercial applications [1]. Conducting polymers can be successfully implemented as active components in organic electronic devices, such as light-emitting diodes, field effect transistors, integrated circuits and solar cells, sensors, thin film transistors, electrochromic devices and bioactuators. Due to the electrical characteristics of these polymers, the field of organic conjugated materials and organic electronics exploded and incredible developments took place. Any appropriate molecular combination makes it possible to prepare multifunctional molecules that provide possibility for desired applications [2-4]. The possibility of combining in these new materials the properties of organic polymers and the electronic properties of semiconductors has been the driving force for various applications [5-7]. Electronically conducting polymers, such as polypyrrole, polythiophene or polyaniline, are a class of organic semiconductors with many possible areas of application.

Conducting polymers can be prepared via chemical or electrochemical polymerization [8]. Electrochemical synthesis is rapidly becoming the general preferred method for preparing electrically conducting polymers due to its simplicity, reproducibility and processability at room temperature. Electronically conducting polymer films are coated on a working electrode surface by anodic oxidation of the corresponding monomer in the presence

of an electrolyte solution via electropolymerization. Different electrochemical techniques can be used including potentiostatic (constant potential, chronoamperometry), galvanostatic (constant current, chronopotentiometry) and potentiodynamic (potential scanning, *i.e.* cyclic voltammetry) methods [9].

Electrical conductivity is achieved by oxidation (p-doping) or reduction (n-doping), followed respectively by the insertion of anionic or cationic species [9]. Due to the double bond alternation in the conjugated polymer backbone, the charged species formed upon doping are able to move along the carbon chain (delocalization) allowing electron transport and thus giving an electronically conductive material (Figure 1.1) [10]. The π -electron system along the polymer backbone which confers rigidity and the crosslinking points between polymer chains makes conducting polymers insoluble, infusible and poorly processable. The thickness of the film can be controlled by varying either the potential or current during the electropolymerization process. In this thesis, conductivity is the main purpose. Therefore we should prepare conjugated systems so the charged species could move along the carbon chain and enhance the electrical conductivity.

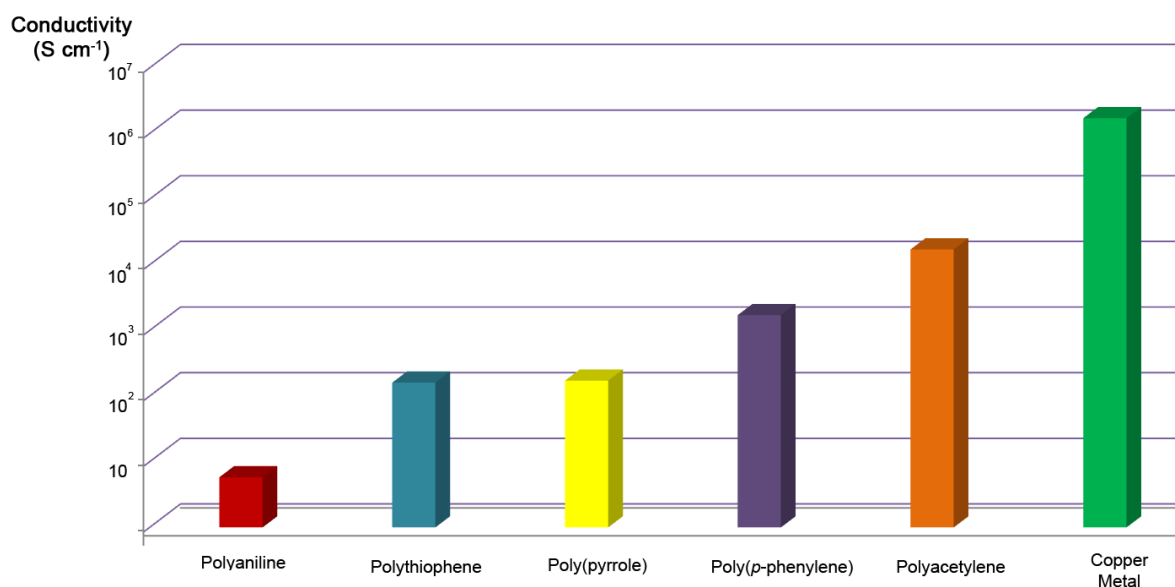


Figure 1.1 Conductivity of some polymers and metals.

1.1.1 Electrical Conductivity for Conjugated Polymers

The electrical conductivity is maintained via electron movement through the conjugated chain. The most common conjugated polymers are illustrated in Figure 1.2. Their structures and electronic properties have been reviewed extensively [7]. Apart from polyaniline, all of these systems share one common structural feature, namely a rigid nature brought about by the sp^2 carbon-based backbone. The utilization of the conjugated construction affords polymer chains possessing extended π -systems, and it is this feature alone that separates conducting polymers from their other polymeric counterparts. In the thesis, thiophene derivatives were preferred to use due to their high conductivity and stability.

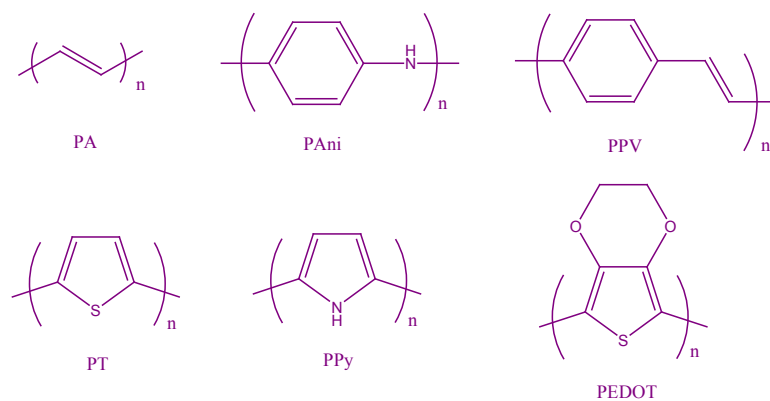


Figure 1.2 The most common conducting polymer structures.

The electrical properties of any material are a result of the material's electronic structure. The conducting polymers form bands through extensive molecular orbital overlap. In this theory, materials are classified as metals, semiconductors, or insulators as indicated in Figure 1.4. Using this generic, lowest energy molecular orbital representation as shown by the π -systems model, the picture of primary concern that is generated by these networks consists of a number of π and π^* levels (Fig. 1.3).

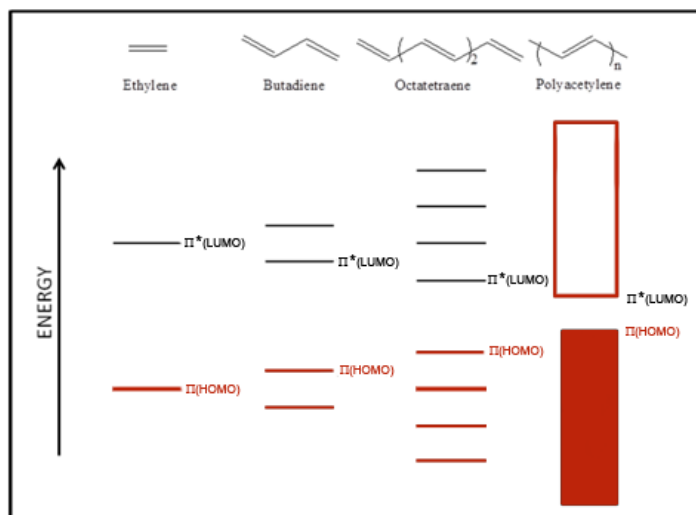


Figure 1.3 Molecular orbital (MO) diagram.

There is enough energy separation between the conduction and valence bands that thermal energy alone is insufficient to excite electrons across the band gap. For electrical conductivity, an electron must have a vacant place to move and occupy. When bands are completely filled or empty, conduction cannot be achieved. Metals are highly conductive because they have unfilled bands. Semiconductors have an energy gap small enough that thermal excitation of electrons from the valence to the conduction bands is sufficient for conductivity; however, the band gap in insulators is too large for thermal excitation of an electron across the band gap. Since we require high electrical conductivity, the band gap of the synthesized polymers should be very low.

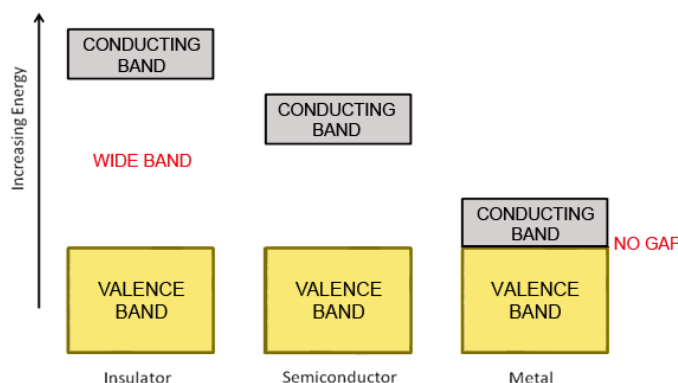


Figure 1.4 Classification of materials and schematic of valence and conduction bands.

1.1.2 Doping Process in Conducting Polymers

The electrochemical switching of a conducting polymer (CP) between the doped and undoped states involves both electron and ion injection into or extraction from the polymer, concomitant with the transport of electronic and ionic charges within the CP. Consequently, the charge transport processes inside the CP bulk, as well as across the CP interfaces, constitute crucial points in many applications and have been the object of extensive research. In particular,

it has been reported that in most cases ion transport is the slow process, i.e. the step limiting the switching rates of, for example, displays and electronic devices based on similar materials [11].

The diffuse nature of the extended π -system readily allows electron removal from, or injection into the polymer. The term "doping" has been borrowed from semiconductor physics with "p-doping" and "n-doping" being used to describe polymer oxidation and reduction, respectively. Doping in regards to semiconductors is quite different as it is a very distinct process carried out at low levels (< 1 %) as compared to CP doping (usually 20-40%). However, the manner by which doping transforms a neutral CP into a conductor remained a mystery for many years. When applied to CP modified electrodes, electrochemical impedance spectroscopy (EIS) has proved to be quite a useful tool for studying the charge transport inside the polymer coating and the charge transfer at the metal/polymer and polymer/solution interfaces [12-16]. By the help of the EIS spectroscopy, we will be able to measure charge storage capabilities, electron transfer rate and electrical conductivities of synthesized polymers.

If only one electron per level is removed, a radical cation is formed and is known as a "polaron". Further oxidation removes this unpaired electron yielding a dicationic species termed a "bipolaron" (Fig.1.5). High dopant concentrations create bipolaron-"rich" materials and eventually lead to band formation of bipolaron levels. Such a theoretical treatment thereby explains the appearance, and subsequent disappearance, of the electron paramagnetic resonance signal of a CP with increased doping as the neutral polymer transitions to the polaronic form and subsequently to the spinless bipolaronic state.

Typical oxidizing dopants used including iodine, arsenic pentachloride, iron (III) and chloride. A typical reductive dopant is sodium naphthalide. The main criteria are its ability to

oxidize or reduce the polymer without lowering its stability and the dopant's capability of initiating side reactions that inhibit the polymer's ability to conduct electricity.

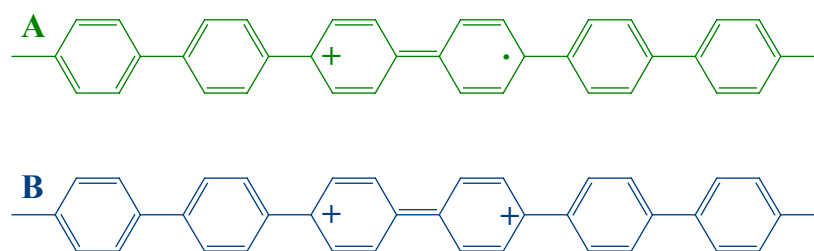


Figure 1.5 Positively charged defects on poly(*p*-phenylene). A: Polaron, B: Bipolaron.

Stabilities for conducting polymers can be divided into two classes: extrinsic and intrinsic. Extrinsic stability is related to sensitivity to external environmental agents such as oxygen, water and peroxides. This is determined by the polymer's susceptibility of charged sites to attack by nucleophiles, electrophiles and free radicals. If a conducting polymer is extrinsically unstable, then it must be protected by a stable coating. Many conducting polymers, however, degrade over time even in dry, oxygen-free environments. This intrinsic instability is thermodynamic in origin. This happens when the charged sites become unstable due to conformational changes in the polymer backbone [17, 20]. Electrical conductivities, stabilities at doped states and electrochemical processing possibilities are shown in Table 1.1.

The quality of the polymers is greatly influenced by many factors, including, impurities, electrode material, pressure, concentrations and temperature. The most important parameters are current density and the electrolyte, particularly the conducting anion X^- [23], because it is incorporated into the polymer as a counterion. The properties of the counterion (size, geometry, charge) influence the properties of the polymer. The amount of counterion incorporated depends

on the reaction conditions. By changing reaction conditions, polymers with different surface morphologies (e.g. an open porous structure) can be obtained.

Table 1.1 Stabilities and processing possibilities of conducting polymers.

POLYMER	Conductivity $\Omega^{-1} \text{ cm}^{-1}$	Stability (doped state)	Processing Possibilities
Polyacetylene	$10^3\text{-}10^5$	poor	limited
Polyphenylene	1000	poor	limited
Polyphenylenesulfide	100	poor	excellent
Polyphenylenevinylene	1000	poor	limited
Polypyrroles	100	good	good
Polythiophenes	100	good	excellent
Polyaniline	10	good	good

The amount of counterion incorporated depends on the reaction conditions. By changing reaction conditions, polymers with different surface morphologies (e.g. an open porous structure) can be obtained. Also, variation of the monomers and their substituted side groups alter the conductivities of the polymer in between 10^2 and 10^{-4} S/cm. Alkyl side chains also increase solubility of the polymers due to flexibility and ease of movement [24- 26]. In the thesis, we used different lengths of alkyl chains in between thiophene precursors and the pendant groups to increase the electropolymerization possibility of the monomers with bulky side groups.

1.1.3 Applications of Conducting Polymers

There are two main groups of applications for conducting polymers (Table 1.2). The first group utilizes their conductivity as its main property whereas the other group utilizes their electronic activities. The extended π -systems of conjugated polymers are highly susceptible to chemical or electrochemical oxidation or reduction. These alter the electrical and optical properties of the polymer, and by controlling this oxidation and reduction, it is possible to precisely control these properties. Since these reactions are often reversible, it is possible to systematically control the electrical and optical properties with a great deal of precision. It is even possible to switch from a conducting state to an insulating state. The two groups of applications are shown in Table 1.2.

Table 1.2 Applications of conducting polymers according to their specialities.

GROUP-1 / CONDUCTIVITY	GROUP-2 / ELECTROACTIVITY
Electrostatic materials	Molecular electronics
Conducting adhesives	Electrical displays
Electromagnetic shielding	Drug release systems
Printed circuit boards	Electromechanical actuators
Artificial nerves	Smart structures
Antistatic clothing	Optical computers
Aircraft structures	Rechargeable batteries, solid electrolytes
Active electronics (diodes, transistors)	Ion exchange membranes
Piezo ceramics	Chemical, biochemical, thermal sensors

The polymer's conductivity and electroactive properties are important for applications. For the first group, the polymers are used because of either their light weight, biological compatibility for ease of manufacturing or cost. By coating an insulator with a very thin layer of conducting polymer it is possible to prevent the build-up of static electricity. This is particularly important where such a discharge is undesirable. By modifying the thermoplastic used by adding a conducting plastic into the resin results in a plastic that can be used for the protection against electrostatic discharge [27]. By placing monomer between two conducting surfaces and allowing it to polymerize it is possible to stick them together. This is a conductive adhesive and is used to stick conducting objects together and allow an electric current to pass through them. Many electrical devices, particularly computers, generate electromagnetic radiation, often radio and microwave frequencies. By coating the inside of the plastic casing with a conductive surface this radiation can be absorbed.

Due to the biocompatibility of some conducting polymers, they may be used to transport small electrical signals through the body, *i.e.* act as artificial nerves. Perhaps modifications to the brain might eventually be contemplated [28]. Modern planes are often made with lightweight composites. This makes them vulnerable to damage from lightning bolts. By coating aircraft with a conducting polymer the electricity can be directed away from the vulnerable internals of the aircraft.

Probably the most publicized and promising of the current applications are lightweight rechargeable batteries. During charging the polymer oxidizes anions in the electrolyte, which enter the porous polymer to balance the charge created [29-31].

Conducting polymers can be used to directly convert electrical energy into mechanical energy. Electrochemical actuators can function by using changes in a dimension of a conducting

polymer, changes in the relative dimensions of a conducting polymer and a counter electrode and changes in total volume of a conducting polymer electrode, electrolyte and counter electrode [32, 33]. In our study, most of the prepared polymers can found application due to their electroactive properties such as capacitors, batteries and biosensors.

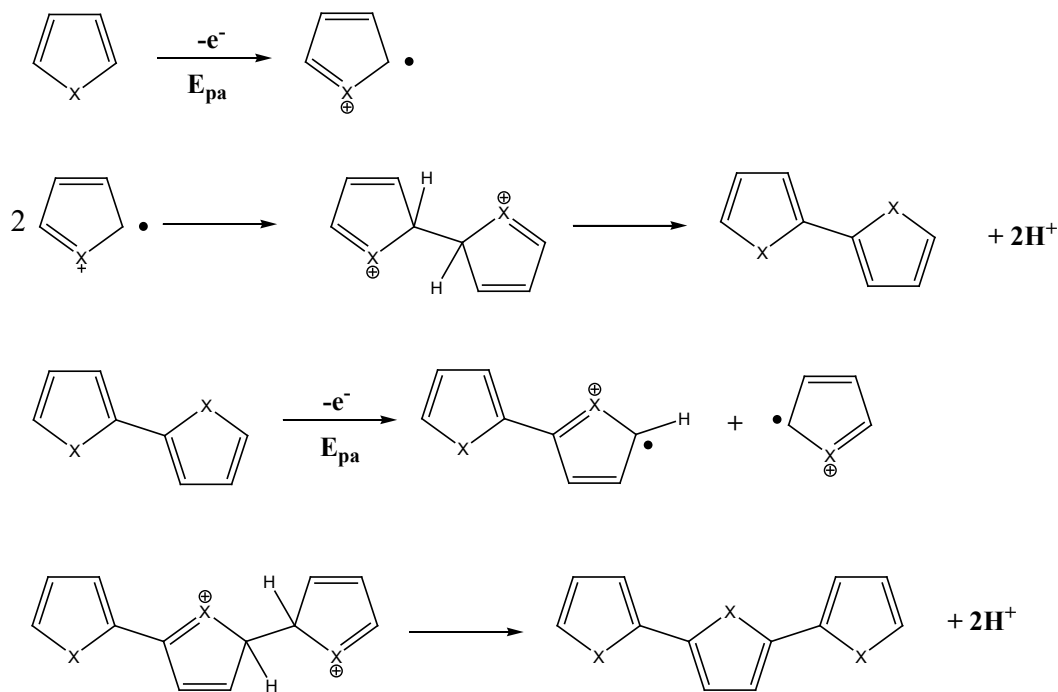
1.2 Electropolymerization

Electrochemical polymerization is recognized as an effective technique for the synthesis of conducting polymers. It is widely used because it is simple and can be used as a one-step method [34]. The electropolymerization procedure offers the advantage of controlling the thickness and functionality of such a ‘reactive’ coating through selective process parameters so uniform coatings can be achieved [35] due to these properties, electropolymerization technique was to polymerize the prepared monomers on to the carbon fibre surfaces.

The electrochemical reaction begins with dissolving the monomer in an appropriate solvent containing the desired anionic doping salt, which oxidizes at the surface of an electrode by application of an anodic potential. The anode can be made of a variety of materials including platinum, carbon fibre, gold, glassy carbon, and tin or indium-tin oxide (ITO) coated glass. During the process, the monomer is electrochemically oxidized at a polymerization potential giving rise to free radicals. These radicals are adsorbed onto the electrode surface and subsequently undergo a wide variety of reactions leading to the polymer network [36]. As a result of the initial oxidation, the radical cation is formed and reacts with other monomers present in solution to form oligomeric products and then the polymer.

In Scheme 1.1, the electrochemical polymerization mechanism of heterocyclic compounds was illustrated. The growth of this polymer depends on its electrical character. If the

polymer is electrically non-conducting, its growth is self-limited due to the unconjugated systems. Such films are very thin (10 - 100 nm). In contrast, the growth of conductive polymers is virtually unlimited.



Scheme 1.1 Electropolymerization pathway for heterocyclic compounds.

The process is governed by the electrode potential and by the reaction time, which allows for control over the thickness of the resulting film [36]. In order to have uniform and reproducible results, the process parameters of electrochemical polymerization have to be optimized. The parameters include type of electrolyte, concentration ratio of monomer and electrolyte, pH of the electrolyte, monomer substitution, scan rate, solvent, temperature and current density, all of which affect the conductivity and morphology of the synthesized polymer film [34]. There are mainly three types of electropolymerization techniques: potentiodynamic by cyclic voltammetry, chronoamperometry (constant potential) and chronopotentiometry (constant current).

1.2.1 Cyclic Voltammetry (CV)

Potentiodynamic techniques, such as cyclic voltammetry, correspond to a repetitive triangular potential waveform applied at the surface of the electrode. Electrochemistry deals with the transfer of electrons from one substance to another. This transfer creates a current, the magnitude of which can give us clues about our substances. This is the method of choice for studying the reversibility of electron transfer, because the oxidation and reduction can be monitored in the form of a current-potential diagram. Intermediate species of very short lifetimes can be observed with microelectrodes using high scanning speed [37].

A cyclic voltamogram traces the transfer of electrons during an oxidation-reduction (redox) reaction. The reaction begins at a certain potential, and as the potential changes, it controls the point at which the redox reaction will take place. Electrodes are placed in an electrolyte solution, containing analyte that will undergo the redox reaction. At the negative electrode, the cathode, electrons are given off, and reduction takes place. At the positive electrode, the anode, the excess electrons are collected, and oxidation occurs. This movement of electrons creates an electric current.

In cyclic voltammetry systems, a conventional three electrode system is usually preferred for use. The working electrode can be made from a variety of materials including platinum, gold, silver, glassy carbon, nickel and palladium. However, carbon fibre micro electrodes were used as a working electrode in the thesis. The counter (auxiliary) electrode conducts the electricity from the signal source into the solution, maintaining the correct current. This electrode is usually an inert conductor such as platinum or graphite. A reference electrode is used in measuring the working electrode potential. This electrode should have a constant electrochemical potential as long as no current flows through it. The potential that is cycled is the potential difference

between the working electrode and the reference electrode. It is usually made from silver/silver chloride (Ag/AgCl) or saturated calomel (SCE). For cyclic voltammetry studies, the current in the cell is measured as a function of potential. The potential of an electrode in solution is linearly cycled from a starting potential to the final potential and back to the starting potential. This process, in turn, cycles the redox reaction. Multiple cycles can take place. During the CV process, the system first starts off with an initial potential at which no redox can take place. Then, at a critical potential during the forward scan, the electro active species will begin to be reduced. After reversal of potential scan direction and depletion of the oxidized species, the reverse reaction, oxidation, takes place. This produces a plot of potential versus current [34]. The knowledge of the initial charge used to polymerize the monomer and the charge involved in the doping process allows the estimation of the doping level in the conducting polymer.

1.2.2 Parameters Affecting Electropolymerization

The presence of alkyl groups gives solubility to copolymers obtained both chemically and electrochemically [39]. N-Substituted conjugated polymers are known to exhibit a conductivity three orders of magnitude lower than that of un-substituted ones [40-42]. The oxidation potential and the yield of polymer were found to be decreased when the size of the alkyl group increased. Bulky substituent attached to the nitrogen atom or to the β -carbon stabilizes the cation radical without stopping the polymerization [53, 54]. The electronic and steric effect of a substituent both contribute to the polymer p-conjugation system [55- 59]. On the other hand, the packing and orientation of polymer molecules in a solid are the important factors in understanding its electric conductivity [60, 61].

One of the first characteristics of a cyclic voltamogram for a conducting polymer film that one searches for is the dependence of the peak current (I_p) on the scan rate (v). According to

well established electrochemical treatments, for a behaviour dominated by diffusion effects, I_p is proportional to $v^{1/2}$, whilst for a material localized on an electrode surface, such as a conducting polymer film, I_p is proportional to v which is explained by the *Randles Sevcik* Equation; $I_p = (2.69 \times 10^5) n^{3/2} v^{1/2} D^{1/2} AC$. (I_p = peak current, c = concentration, n = number of electrons, v scan rate (V/s), A = electrode area (cm^2), D = the analyte's diffusion coefficient (cm^2/s))

The choice of electrolyte is made by considering its solubility and nucleophilicity. The nature of the anion has an impact on the quality of the film produced which depends on the hydrophobic character of the anion and the interactions between the polymer and the anion. For instance, Kassim et al. [52] have shown that in aqueous solution, the utilization of a large aromatic sulphate anion gives stable conducting polymers with better mechanical properties than when a perchlorate anion is used because of their hydrophobic interaction with polymer [53]. The size of the anion controls the microstructure and the porosity of the polymer [54].

As the basicity of the anion increases, the conductivity of the polymer decreases. This phenomenon is due to an increase in the interactions between the positive charges of the polymer and the anions [55]. On the other hand, anion nucleophilicity interferes with the reaction by increasing the formation of soluble products. The polymers of the highest conductivity are produced when elevated concentrations of electrolyte are used.

For both chemical and electrochemical processes, monomer concentration has an affect on the product. For electropolymerization, since the oxidation of the monomer occurs at a higher potential than that of the redox processes of the polymer, side reactions including crosslinking or over-oxidation of the polymer could take place [56].

1.3 Electrochemical Impedance Spectroscopy (EIS)

Electrical resistance is the ability of a circuit element to resist the flow of electrical current. With impedance data, a complete description of an electrochemical system is possible. Representations of the electrified interface have gradually evolved from repeated modifications of the model which was first explained by Helmholtz [57, 58]. Ohm's law defines resistance in terms of the ratio between voltage E and current I . Electrochemical impedance is measured by applying an AC potential to an electrochemical cell and measuring the current passing through the cell. If we apply a sinusoidal potential excitation, an AC current signal will be the response of the excitation, containing the excitation frequency and its harmonics. This current signal can be analyzed as a sum of sinusoidal functions.

EIS could only be used for one circuit element which is an ideal resistor following the Ohm's Law at all current and voltage levels. Also, its resistance value is independent of frequency and AC current and voltage signals though resistors are in phase with each other. Impedance is a measure of the ability of a circuit to resist the flow of electrical current and is not limited by the simplifying properties. Impedance is a complex resistance encountered when current flows through a circuit made of resistors, capacitors, inductors, or any combination of these. Depending on how the electronic components are configured, both the magnitude and the phase shift of an AC can be explained (Fig.1.6).

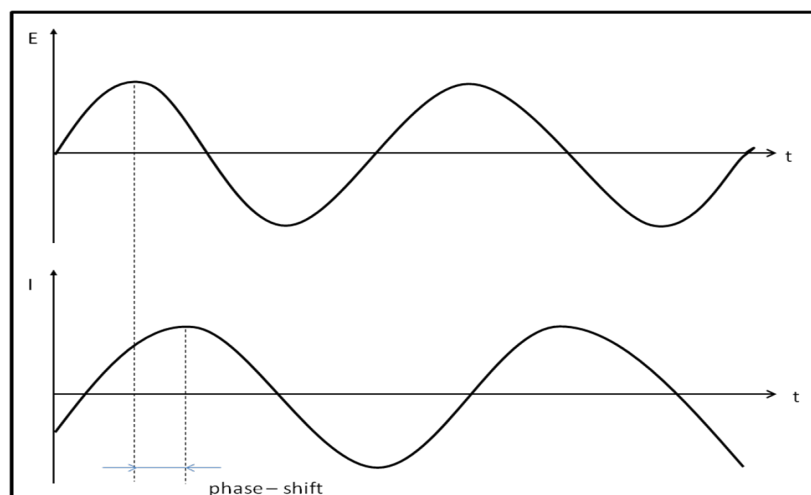


Figure 1.6 Sinusoidal current response in a linear system.

There are two convenient ways of explaining the impedance data: the Nyquist plot, in which imaginary numbers $Z''(\omega)$ are plotted against real numbers $Z'(\omega)$, and the Bode plot, in which absolute values of impedance or phase angle are plotted against the frequency. The Nyquist plot gives all the necessary information about the electrode–electrolyte interface and the reaction. Similar information is obtained by examining the Bode diagram. The $\log R_s$ and $\log (R_p + R_s)$ values are obtained straightforwardly from the $Z(\omega)$ versus $\log \omega$ plot at high and low frequencies from the same argument as the Nyquist plot. Additionally, the mass transport of the electroactive species may limit the electron-transfer process at low frequencies which could be monitored by Warburg impedance.

A Nyquist plot (Fig.17) indicates the low frequency data on the right side of the plot and higher frequencies are on the left. On the Nyquist plot the impedance can be represented as a vector of length $|Z|$. The angle between this vector and the x-axis is ϕ . The resulting impedance plots can be a semicircle or a line perpendicular to y-axis.

The semicircle illustrates the resistive property of polymer including charge transfer resistance and solvent resistance, whereas the perpendicular line indicates the fast electron transfer and charge-discharge ability of the polymer [59].

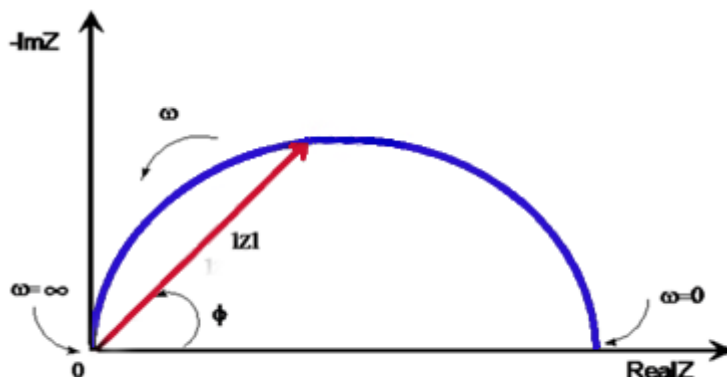


Figure 1.7 Nyquist plot with impedance vector.

One of the other graph is the bode plot, which gives information about double layer capacitance values that exist at the interface between an electrode and its surrounding electrolyte. This layer is formed as ions from the solution "stick on" the electrode surface. Charges in the electrode are separated from the charges of these ions. It varies according to the electrode potential, temperature, ionic concentrations, and types of ions, oxide layers, electrode roughness and impurity adsorption. The impedance is plotted with log frequency on the x-axis and both the absolute value of the impedance ($|Z| = Z_0$) and phase-shift on the y-axis giving information about frequency. The impedance versus frequency behaviour of a capacitor is opposite to that of an inductor. A capacitor's impedance decreases as the frequency is raised. Capacitors also have only an imaginary impedance component. In the thesis, we measured complex impedance data and then analyzed the Nyquist, Bode and Admittance plots, Bode phase and capacitance diagram to be able to characterize the capacitive properties of the modified electrode surfaces.

Solution resistance is an expressive factor in the impedance of an electrochemical cell. Conventional three electrode system compensates for the solution resistance between the counter and reference electrodes. However, any solution resistance between the reference electrode and the working electrode must be considered for modelling. The resistance of an ionic solution depends on the ionic concentration, type of ions, temperature and the geometry of the area in which current is carried.

A polarizing electrode is used to force the electrode away from its value at open circuit that can cause current to flow via electrochemical reactions that occur at the electrode surface. The amount of current is controlled by the kinetics of the reactions and the diffusion of reactants both towards and away from the electrode.

Another resistance is formed by a single controlled electrochemical reaction at equilibrium. Consider a metal substrate in contact with an electrolyte; the metal molecules can electrolytically dissolve into the electrolyte. First, electrons enter the metal, and metal ions then diffuse into the electrolyte. As a result, charge will be transferred with a certain speed depending on the kind of reaction, temperature, concentration of the reaction products and the potential [59].

Most of our prepared modified electrodes indicated capacitive behaviour so they could be used in capacitor device preparation. As an example, a kind of capacitor is formed when two conducting plates are separated by a non-conducting media, called the dielectric (Table 1.3). The value of the capacitance depends on the size of the plates, the distance between the plates and the properties of the dielectric. This relationship is expressed with $C = (\epsilon_0 \cdot \epsilon_r \cdot A)/d$ equation (where ϵ_0 = electrical permittivity, ϵ_r = relative electrical permittivity, A = surface of one plate, d = distances between two plates).

Table 1.3 Typical relative electrical permittivities.

Material	ϵ_r
Vacuum	1
Water	80.1 (20° C)
Organic coating	4-8

1.3.1 Electrochemical Capacitors

The most common electrical energy storage devices are batteries. Batteries have been the technology of choice for most applications, because they can store large amounts of energy in a relatively small volume and weight and provide suitable levels of power for many applications. Shelf and cycle life has been a problem with most types of batteries. Ultracapacitors are being developed as an alternative to pulse batteries. Ultracapacitors must have much higher power and much longer shelf and cycle life compared to batteries. Electrochemical capacitors have much lower energy density than batteries and their low energy density is in most cases the factor that determines the feasibility of their use in a particular high power application (Fig.1.8). In general, a sacrifice in energy density is required to get a large reduction in the time constant so a large increase in power capability can be achieved [60].

Recently, there has been an extensive development in electrode materials for electrochemical capacitors [61, 62] due to the increasing demand for a new kind of accumulator of electrical energy with a high specific power of more than 10 kW/kg and a long durability (over 10^6 cycles). The main advantage of this storage device is the ability of a high dynamic of charge propagation (short term pulse), which is used in hybrid power sources, electrical vehicles, digital telecommunication systems and power supplies for computers and pulse lasers.

Additionally, electrochemical capacitor systems have the possibility of full discharge and short-circuit between the two electrodes is not harmful.

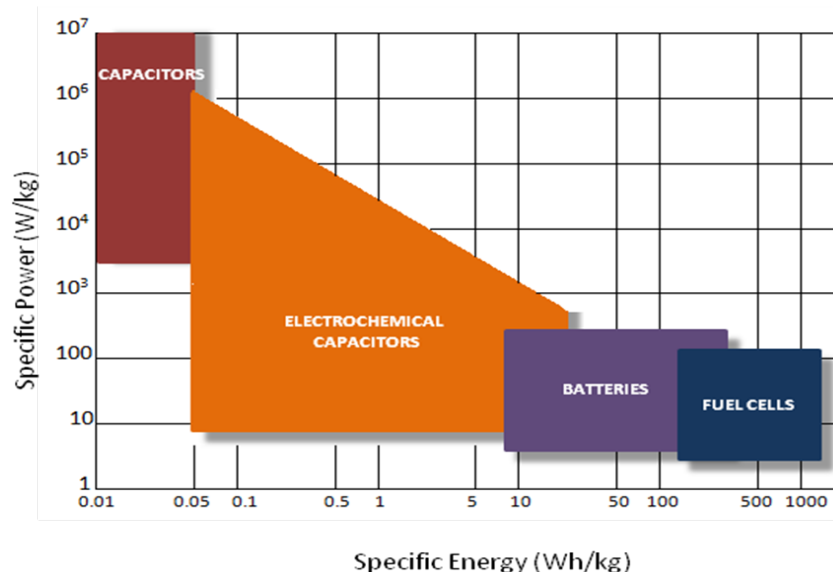


Figure 1.8 Specific energies of capacitors and batteries.

The capacitors that were prepared in the thesis are electrochemical capacitors in which the electrical charge is accumulated in the double layer by electrostatic forces without phase transformation in the electrode materials. The stored electrical energy is based on the separation of charged species in an electrical double layer across the electrode-solution interface represented in Figure 1.9. The charge density is accumulated at the distance of outer Helmholtz plane. Usually electrochemical capacitors contain one positive electrode with electron deficient electrodes built from the same material. On the other hand, ultracapacitors, also known as supercapacitors or electrochemical capacitors, utilize high surface area electrode materials and thin electrolytic dielectrics to achieve capacitances larger than conventional capacitors. Performance of a supercapacitor combines an electrostatic attraction as in electric double layer capacitors and faradaic reactions.

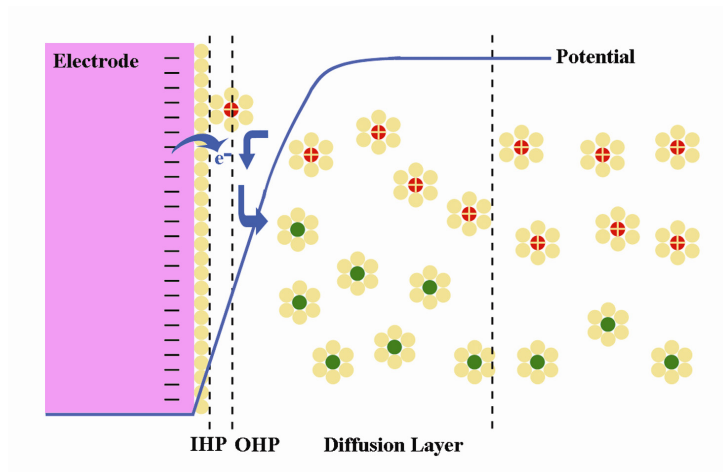


Figure 1.9 Illustration of the electrochemical Helmholtz double layer.

Pseudocapacitance arises when, for thermodynamic reasons, the charge q required for the progression of an electrochemical process is a continuously varying function of potential U . The derivative $C=dq/dU$ then corresponds to a faradaic kind of capacitance. The term *pseudo* originates from the fact that the double layer capacitance arises from quick faradaic charge transfer reactions. An ideal double layer capacitance behavior of an electrode material is expressed in the form of a rectangular shape of the voltammetry characteristic behavior of supercapacitors. In this type of energy storage, the system is purely electrostatic and current is independent on potential. If the electrode material has pseudocapacitance properties then a deviation from such a rectangular shape will be observed. In this case, charge accumulated in the capacitor is strongly dependent on the electrode material [62].

1.4 Carbon Fibres

Carbon fibre can be described as threaded carbon filament that is used for clothing. Moreover, it can also refer to any composite material made with carbon filament. Carbon fibre is a polymer which is a form of graphite, a pure carbon form. In graphite, the carbon atoms are

arranged into planar hexagonal aromatic ring. Carbon fibre is the form of graphite in which these planar hexagonal aromatic rings are long and thin like a sheet. These fibres are usually used to reinforce materials like epoxy resins and other thermosetting materials called *composites* because they have more than one component.

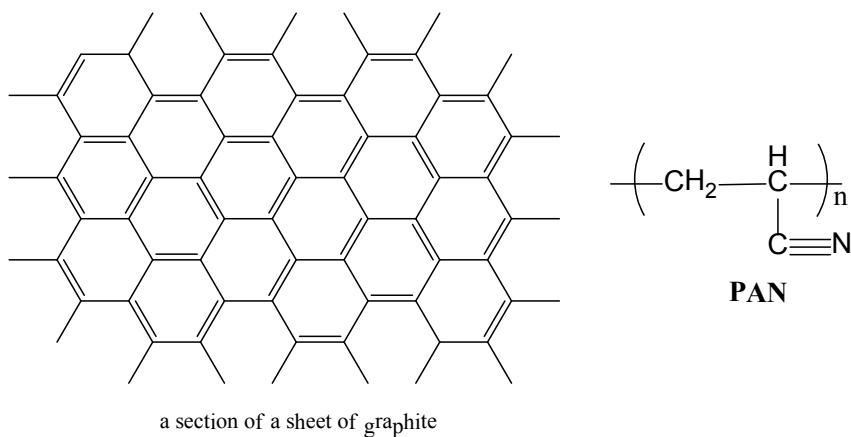


Figure 1.10 Sheet type of graphite and molecular formula of PAN.

Carbon fibre is made from polyacrylonitrile (Fig.1.10), after a complicated heating process. Carbon fibres, which are a new type of high-strength materials are mainly used as reinforcing material in composites such as carbon fibre reinforced plastics, carbon fibre reinforced materials and carbon fibre reinforced cement. Carbon fibre reinforced composites are usually light in weight and stronger than steel so they can be used to replace metals in many uses, from parts for airplanes and the space shuttle to tennis rackets and golf clubs. Carbon fibres demonstrate the better mechanical properties including the highest specific modulus and highest specific strength of all reinforcing fibres. Stress corrosion and stress rupture failures do not affect the carbon fibres at room temperatures, whereas glass and organic polymer fibres are affected. The strength and modulus of carbon fibre are outstanding at high temperature compared to other materials [63]. Carbon fibres also have good electrical conductivity, thermal conductivity, and

low linear coefficient of thermal expansion [64]. Carbon fibre composites are suited to applications where strength, stiffness, lower weight and outstanding mechanical characteristics are required. They are also used where high temperature, good electrical and thermal conductivity chemical inertness and high damping are needed [65, 66]. In the thesis, carbon fibre filaments were used to prepare working electrodes by attaching them to a copper wire with an insulating tape. Therefore, the working electrodes that we prepared could be named as micro electrodes having many advantages such as high rate of mass transport, require small volume of samples and has short response time.

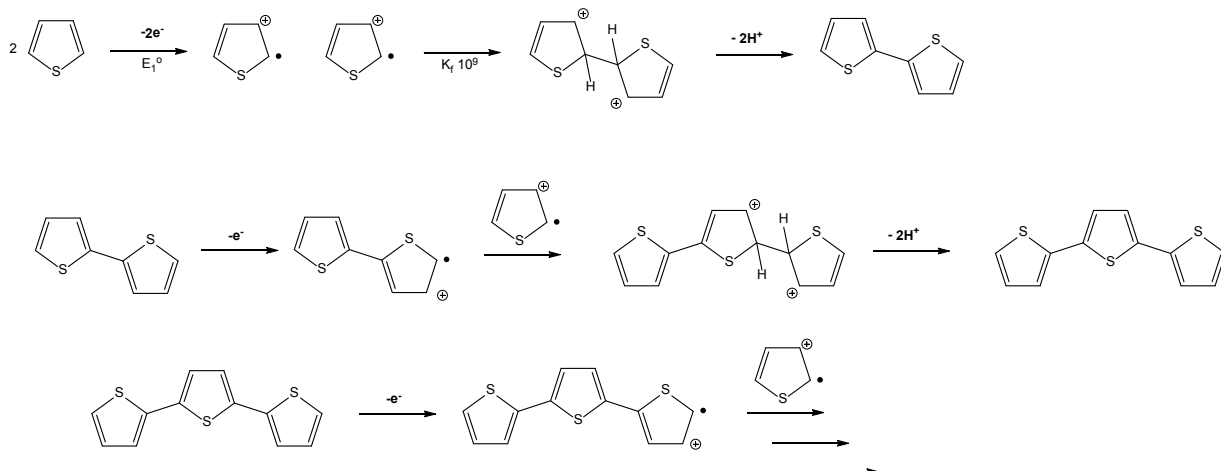
1.5 Polythiophenes

In literature, electropolymerization of thiophene was first mentioned in 1982 [67, 68]. After this initial work, many studies have been devoted to the analysis and optimization of the electropolymerization reaction of thiophene derivatives. In the thesis, thiophene derivatives are preferred to use due to their relatively high electrical conductivity and excellent electrochemical processing possibilities. They are also quite stable at doped states.

Polythiophenes are among the most applicable materials in the field of opto electronics. They are used in organic devices, such as field effect transistors, light-emitting diodes, solar cells, sensors and capacitors [69-77]. Electrochemical techniques are commonly used for both the preparation and the characterization of conjugated systems [78-81]. Usually, an electrochemical anodic process is used to deposit film on an electrode surface. Generally, cyclic voltammetry (CV) or potentiostatic coatings on this class of materials lead to formation of conducting polymers, a process starting from the electrochemical formation of radical ions (Scheme 1.2) followed by nucleation and a phase-growth mechanism. Furthermore, the film

formation and its oxidation occur simultaneously since the oxidation potential of the monomer is always higher than the redox potential for the polymer doping.

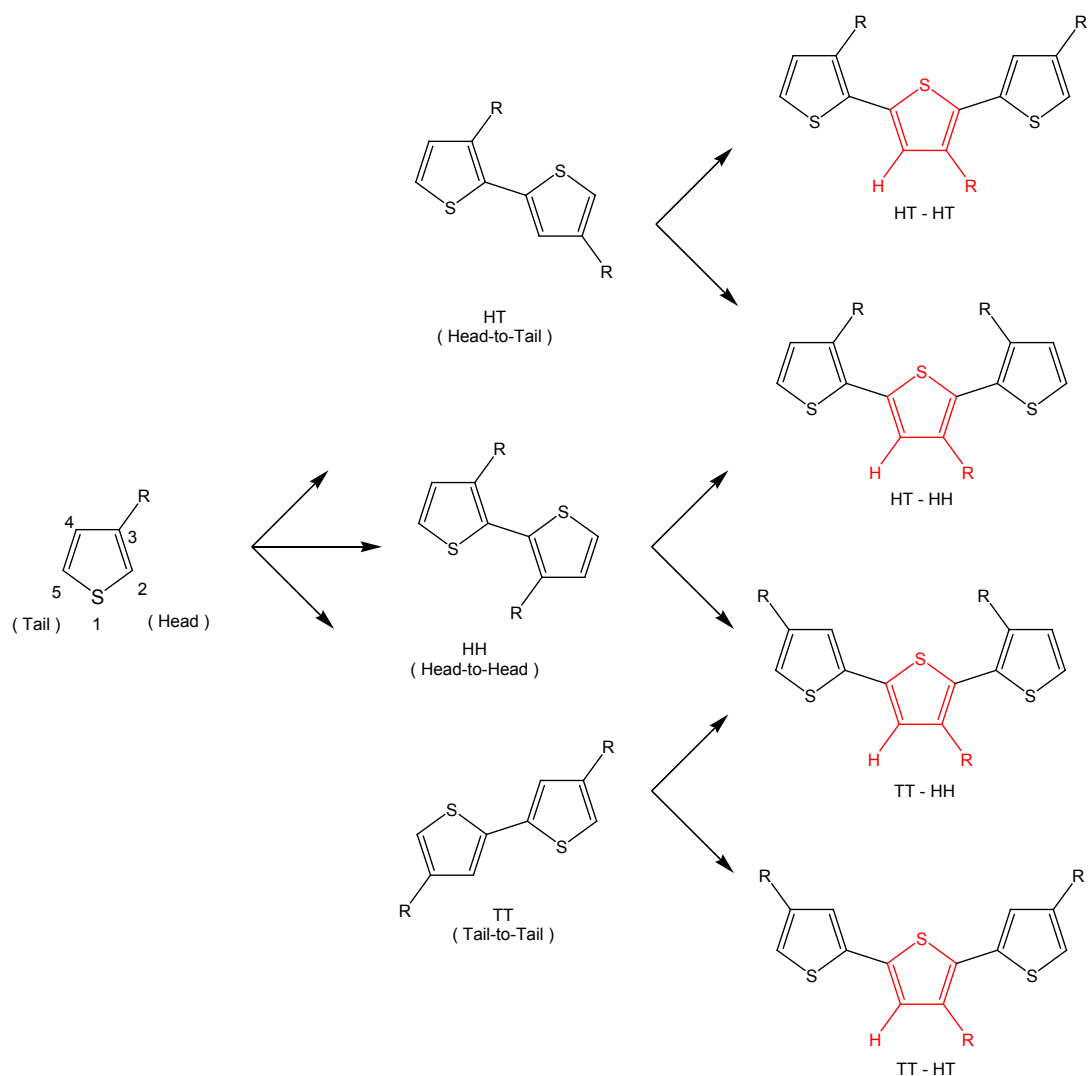
The electrochemical polymerization mechanism including the oxidation step generating a cation radical, coupling and a deprotonation step for generating the dimer and then processing via nucleation and phase-growth deposition is illustrated in Scheme 1.2 [82-85].



Scheme 1.2 Classical mechanism for the electrochemical growth of thiophene.

Polythiophenes (PTs) are often named by adding the first letter of the substituent or a similar abbreviation, as in poly(3-hexylthiophene) (PHT) or poly(3-nonylthiophene) (PNT). Naming the primary structure of 2,5 poly(3-substituted thiophene)s by IUPAC rules can become impracticable when stereochemistry is defined. A common convention instead identifies the sterically crowded 2-position as the ‘head’ and the less congested 5-position as the ‘tail’ which is illustrated in Scheme 1.3. Rings can be joined in three orientations: head-to-head (HH), head-to-tail (HT) or tail-to-tail (TT). The HH orientation in irregular PTs causes an increased twist of thiophene units due to loss of conjugation and steric repulsion and this phenomenon increases the

band gap and causes a blue shift in absorption and luminescence spectra which was observed in the fluorescence characterization sections[86].



Scheme 1.3 Traditional syntheses incorporate multiple regioisomers.

It is proven in the literature that the electropolymerization reaction is strongly dependent on experimental variables such as the solvent, monomer concentration, temperature, nature and geometry of the working electrodes, applied electrical conditions and substituted side groups.

Due to its high oxidation potential, thiophene itself is difficult to polymerize electrochemically. However, upon alkyl substitution the monomer oxidation potential is lowered to an easily accessible range, which has resulted in the extensive study of poly(3-methylthiophene) and other poly(3-alkylthiophene) [87].

Compared with the thiophene monomer, the introduction of one methyl group at the β position of the thiophene ring leads to a decrease in the oxidation potential of 0.2 V due to the inductive effect of the methyl group. In addition, significant increases in conjugation and conductivity were observed for the related polymer [88, 89]. However, increase in the chain length caused significant decrease in conductivity of polymer (Fig.1.11).

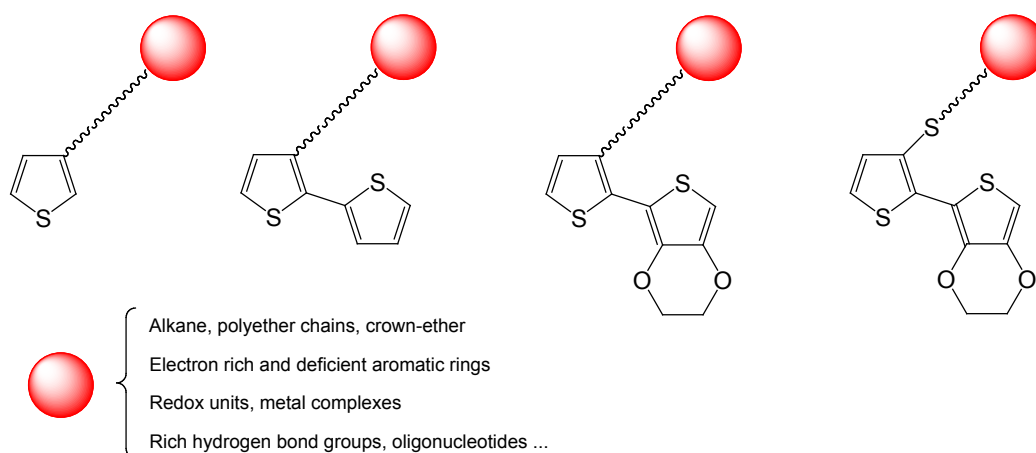


Figure 1.11 Alkyl substituted thiophene derivatives.

The steric hindrance between a bulky alkyl group of one 3-substituted thiophene and the vicinal thiophene ring causes a rotational disorder along the conjugated backbone inducing the electronic delocalization. If the distance between the thiophene ring and the hindered center increases, then the torsion between thiophene ring decreases making the electropolymerization possible (Fig.1.12) [90-92]. According to this hypotheses, we preferred to use long alkyl chains just to increase the distance between thiophene ring and the steric hindered pendant group.

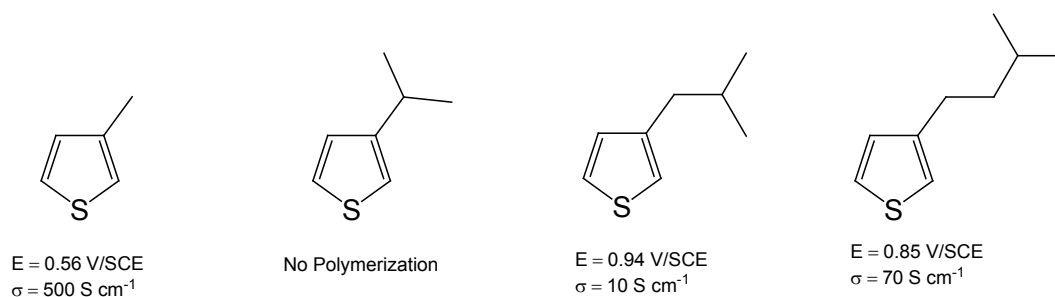


Figure 1.12 Electrical conductivities of 3-substituted thiophene derivatives.

The electron acceptor groups attached to thiophene ring increase the oxidation potential of the monomer whereas electron-donor groups have the opposite effect. In addition, all thiophene monomers in Figure 1.13 indicated an irreversible oxidation peak, suggesting that the intermediate radical cation is unstable and extremely reactive [93-97]. The difficult electropolymerization of monomers with high oxidation potentials is related to the high reactivity of the corresponding radical cations, which likely undergo competing side reactions, with the solvent or the electrolyte [94].

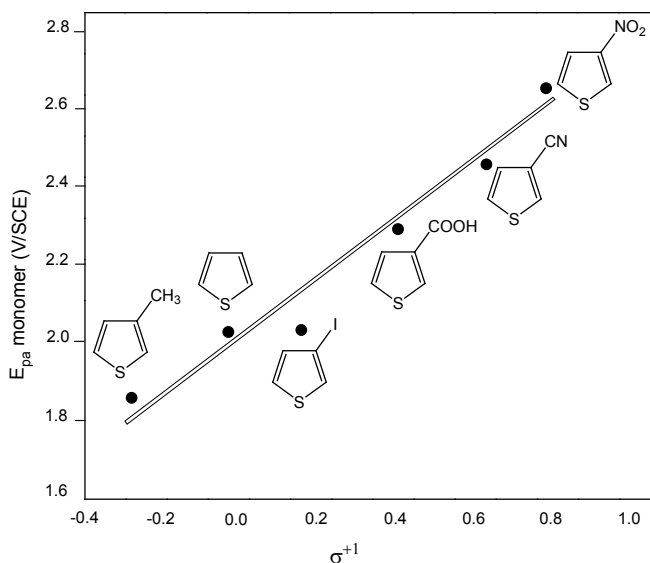


Figure 1.13 Electrochemical oxidation of β -substituted thiophene monomers.

Substitution at the 3- and 4-positions of thiophene prevents the occurrence of α - β and β - β coupling during electropolymerization, yielding more ordered polymers with longer conjugation lengths. Initially, the synthesis of 3,4-disubstituted polythiophenes was carried out with the goal of stabilizing the oxidized form, as well as providing solubility and processability [98]. The PEDOT (Fig.1.14) undergoes both oxidation and reduction. In its p-doped state, PEDOT displays high conductivity, optical transparency and stability. PEDOT is widely used as antistatic coatings and as hole-injecting/electron-blocking layers in light-emitting diodes and solar cells as well as a potential conductor for transparent electrodes.

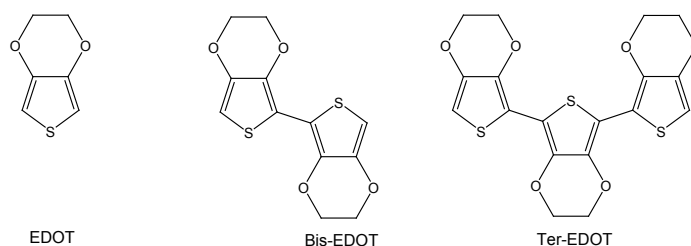
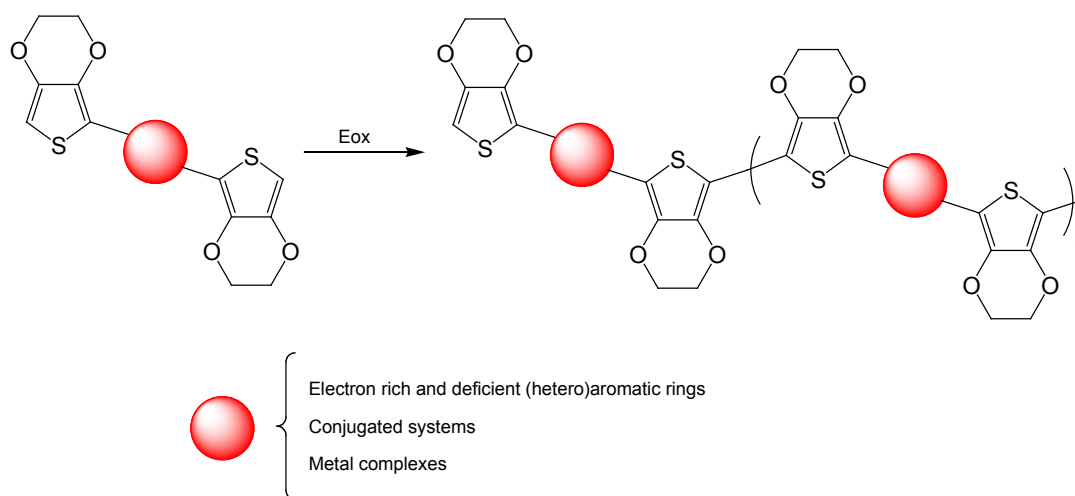


Figure 1.14 Schematic representations of EDOT, Bis-EDOT and Ter-EDOT monomers.

Jonas et al. [99] were the first to anodically polymerize the 3,4-ethylenedioxythiophene. The most important research about PEDOT is studied and commercialized by AGFA-Gevaert N.V. and Bayer AG. In their research, EDOT was used as the core linkage and the prepared materials indicated conductivity less than 10^{-1} Scm^{-1} (Scheme 1.4). The optical properties of PEDOT derivatives can be altered over a broad range as evidenced by the electronic bandgap ranging from 1.0 eV to 2.4 eV. The functionalization was achieved with different side groups according to the applications (Fig.1.15).

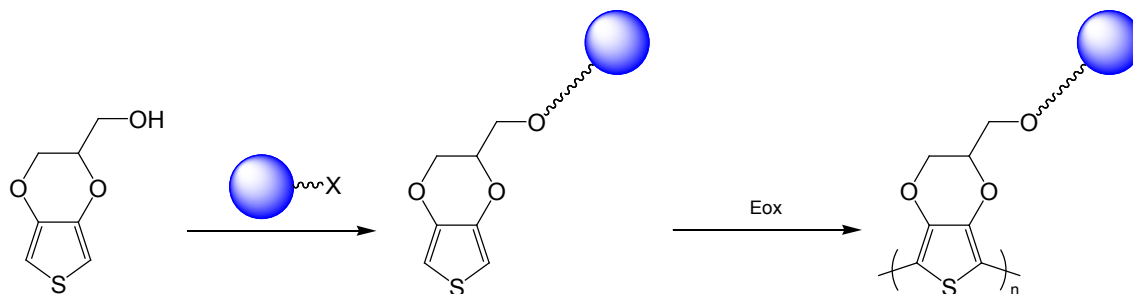
The alkyl-substituted PEDOT derivatives (Scheme1.5) have been compared with unsubstituted one [100-103]. The solvent and electrolyte dependence of EDOT- C_8H_{17} and EDOT- $\text{C}_{14}\text{H}_{29}$ was studied by Sankaran and Reynolds [104]. By repetitive scanning, electroactive

polymer films were deposited onto electrodes. Compared to the parent EDOT monomer, the alkyl derivatives oxidize at lower potentials.



Scheme 1.4 Illustration of electropolymerized EDOT co-monomers.

Introduction of a hydroxymethyl group at the ethylene bridge of EDOT indicates an alternative and practical approach for the functionalization of EDOT [105]. After the introduction of functional groups by Williamson alkylation or esterification reaction starting from hydroxyl methyl EDOT (Scheme 1.5), anodic oxidation led to the corresponding polymer. According to the desired products, EDOT monomers were functionalized with different pendant groups (Fig. 1.15).



Scheme 1.5 Electrochemical oxidation of alkyl substituted hydroxymethyl EDOT.

In this thesis, esterification reaction was used to functionalize the EDOT and Thiophene precursors. The tether lengths which are usually aliphatic chains were altered in between precursor and functional groups. As a functional group we preferred iron containing complexes or chromophores. As illustrated in figure 1.15, we were able to change the functional groups according to the desired application area.

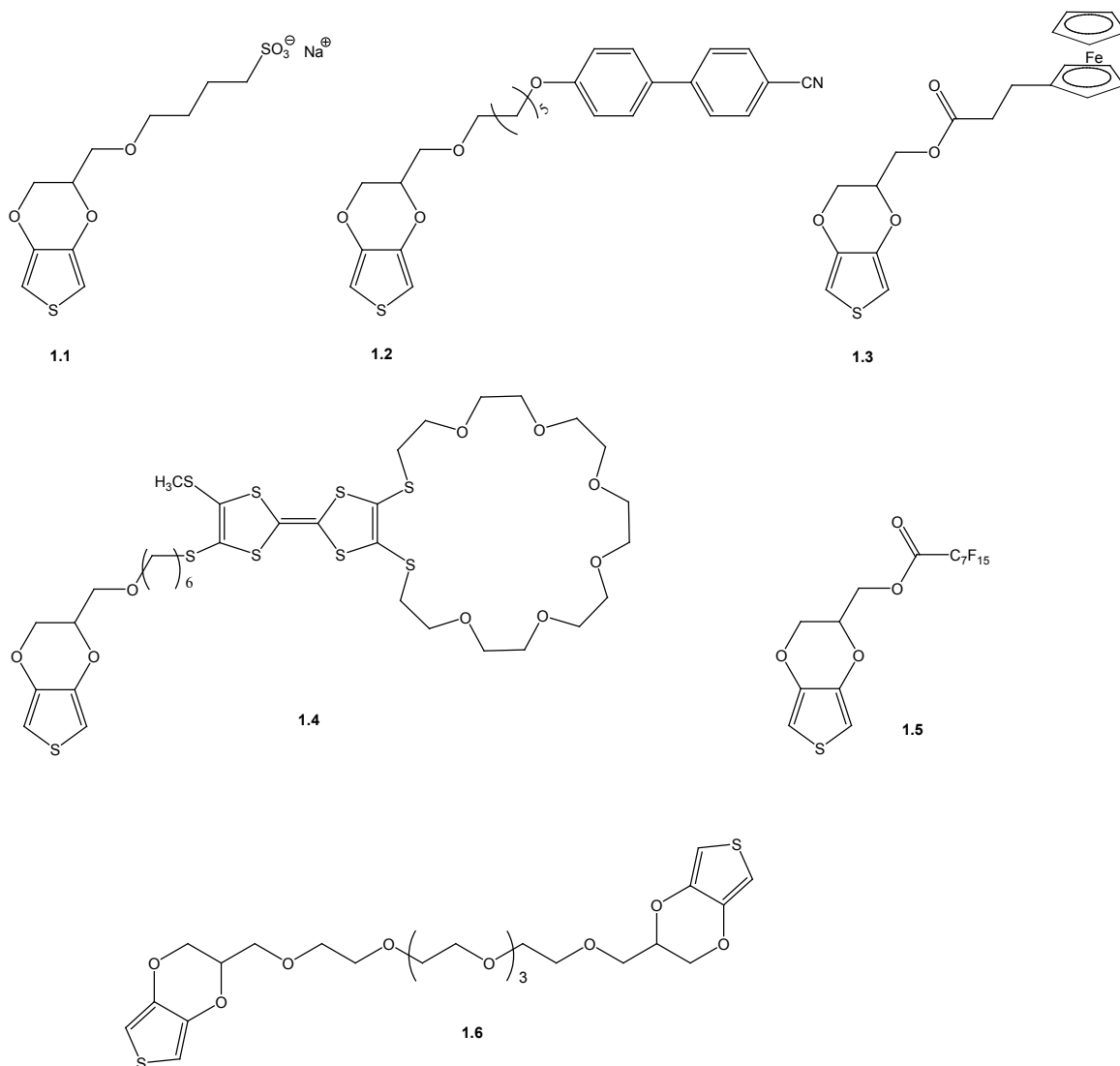


Figure 1.15 Some examples of previously synthesized functional EDOT derivatives.

1.5.1 Polythiophenes Containing Transition Metals

Transition metal-containing polymers are another class of materials [106, 107]. One type of metal-containing polymer involves coupling transition metal complexes to a π -conjugated backbone [108, 109]. Different types of arrangements of the metal group relative to the backbone are possible as illustrated in Figure 1.16.

The metal is tethered to the backbone by a flexible, non-conjugated linker in Type-1. In this case, the polymer behaves as a conductive support and the metal group acts similarly to an untethered complex. Alternatively, the metal and backbone are electronically coupled for Type II materials and the two components may behave differently from uncoupled systems. In Type III materials, the metal group is placed in the conjugated backbone and participate in d- π mixing. These three types of arrangements usually give linear polymer systems but they may also produce dendrimeric, macrocyclic or catenane-type structures. The conductivity could be explained with different types of mechanisms for these materials.

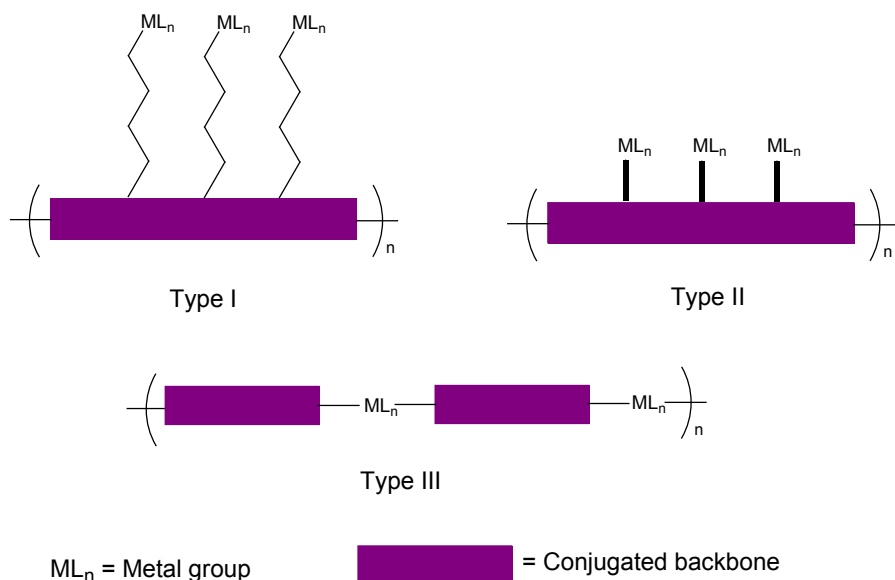


Figure 1.16 Classification of metal-containing conjugated polymers.

Many conjugated polymers without metal groups become conductive through oxidation by introducing mobile charge carriers [109]. Non-conjugated polymers with metal centers, in which the metal can exist in two or more stable redox states, could be conductive as well. In this case, conductivity appears by outer-sphere electron transfer between metal centers of different redox states. If the polymer contains both conjugated backbone units and redox-active metal centers, the conductivity mechanism depends on the type of polymer (I, II or III) as well as the relative redox potentials of the backbone and metal (Table 1.4) [110]. In the thesis, we wanted to insert cationic and neutral iron moieties in the polymer films; therefore we synthesized metal containing conjugated polymers in which the metal is tethered to the backbone with a flexible alkyl chain such as in Type I.

Table 1.4 Mechanisms of conductivity in Type I-II-III polymers.

Polymer type	Relative metal (E_{metal}) and polymer (E_{polymer}) redox potentials^a	Mechanism(s) of conductivity^b
Type I, II, III	$E_{\text{metal}} > E_{\text{polymer}}$	Polaron/bipolarons on polymer
Type I	$E_{\text{metal}} \approx E_{\text{polymer}}$	Polaron/bipolarons on polymer and outer-sphere ET between metals
Type II, III	$E_{\text{metal}} \approx E_{\text{polymer}}$	Inner-sphere ET between metals, polaron/bipolarons on polymer (redox matching)
Type I	$E_{\text{metal}} < E_{\text{polymer}}$	Outer-sphere ET between metals
Type II, III	$E_{\text{metal}} < E_{\text{polymer}}$	Inner- and/or outer-sphere ET between metals

^a Most conjugated polymers have broad redox waves, so E_{polymer} may be a range

^b ET, electron transfer

The synthesis of metal-containing conjugated polymers has been achieved using different types of methods. Condensation routes [111-114], ring-opening metathesis polymerization (ROMP) [115, 116], ring-opening polymerization (ROP) [117, 118] and electrochemical polymerization have been used to prepare metal-containing conjugated polymers [119, 120].

A series of ferrocenyl-capped polythiophenes is illustrated in Figure 1.17 [121]. Generally, the ferrocenyl groups do not show any electrochemical interaction as evidenced by a single ferrocene wave in the cyclic voltammetry, but the difference between the polythiophene

and ferrocene oxidation potential is linearly correlated to the energy of the polythiophene to Fe(III) charge-transfer transitions.

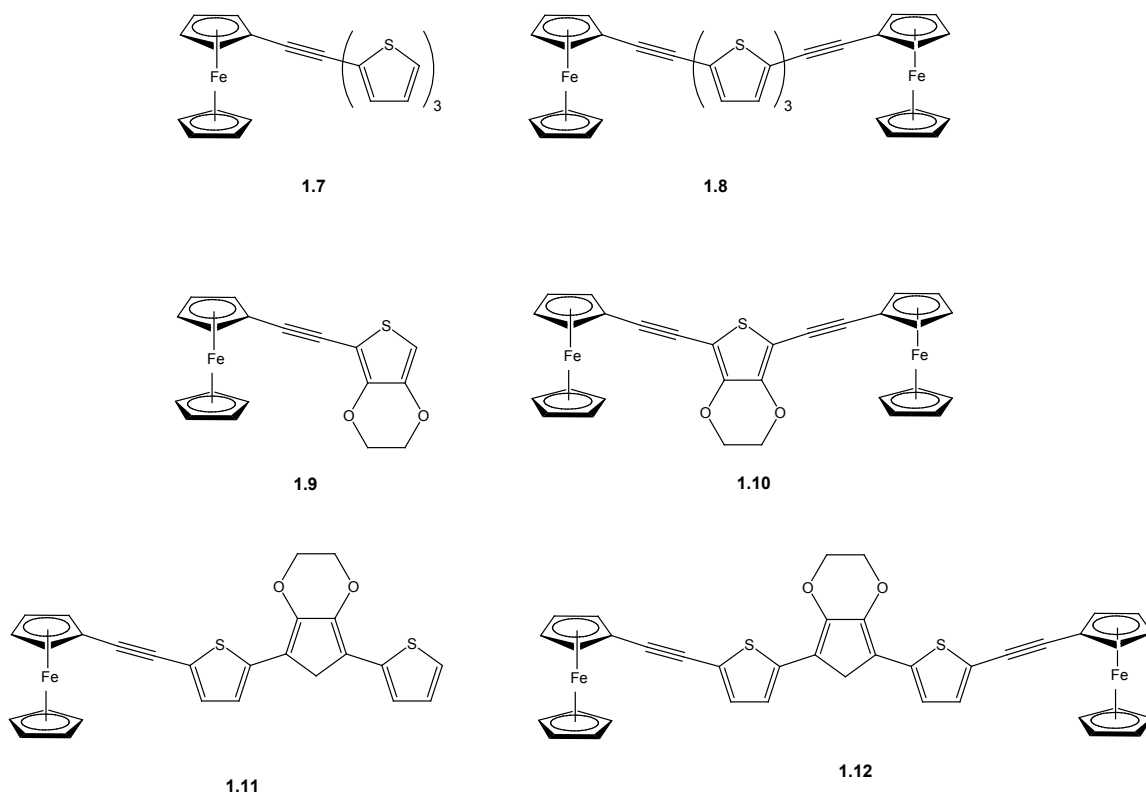


Figure 1.17 Some examples of previously synthesized Ferrocenyl-capped polythiophenes.

As an example, bithiophene derivatives containing tethered ferrocene groups are illustrated in Figure 1.18 to give Type I materials via electropolymerization. [122, 123]. The longer alkyl spacer indicated outer-sphere electron transfer between ferrocene groups, while some conduction was found in the derivatives with shorter linkage. Electropolymerization yielded only very thin polymer films [124].

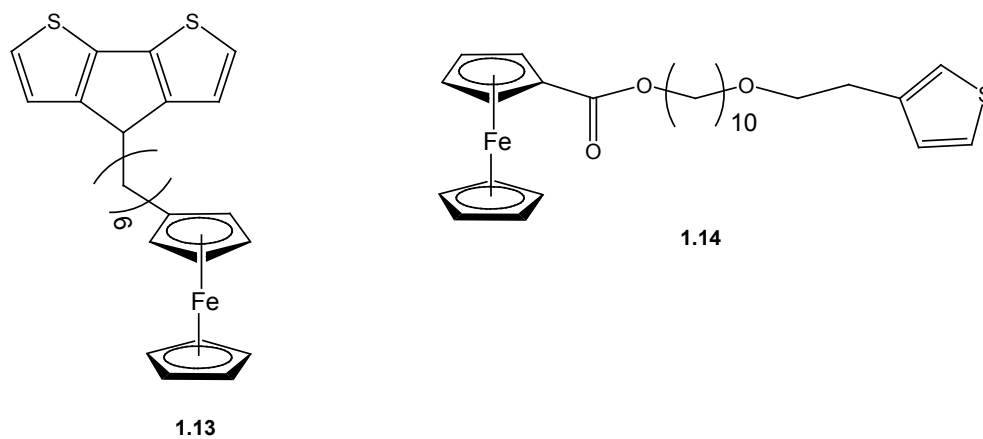


Figure 1.18 Bithiophene derivatives containing tethered ferrocene groups.

Ferrocene-functionalized oligothiophenes are interesting redox functional systems. In this case ferrocene is a donor as well as the oligothiophene backbone, demonstrating unique redox properties. In Figure 1.19, ferrocene was connected to the termini of the oligothiophene or represented the core for the conjugated co-oligomers [125, 126]. Instead of using ferrocene to end-cap the monomer, we preferred to attach ferrocene as pendant group to EDOT and Thiophene precursor.

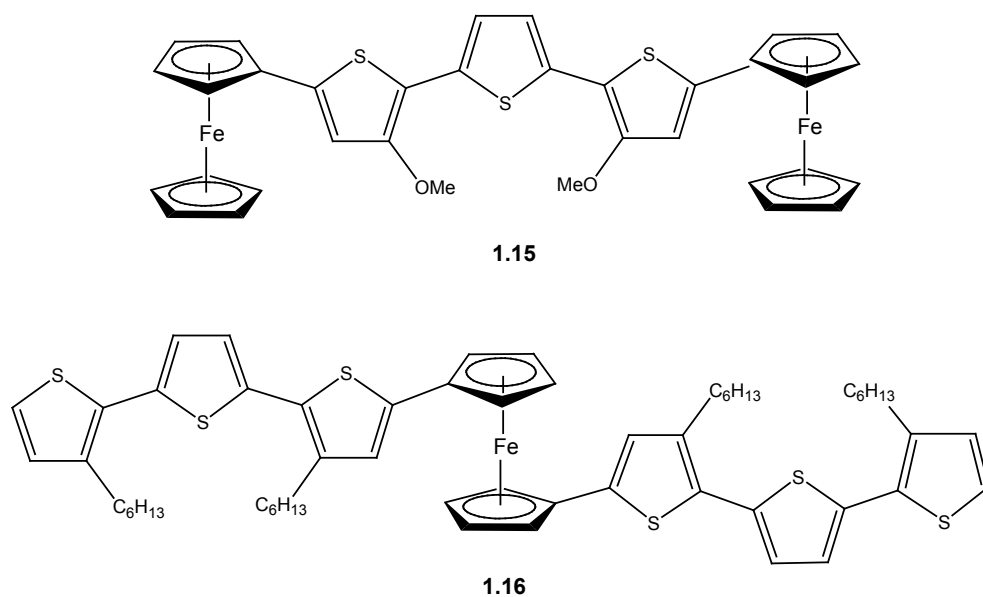


Figure 1.19 Ferrocene-functionalized oligothiophenes.

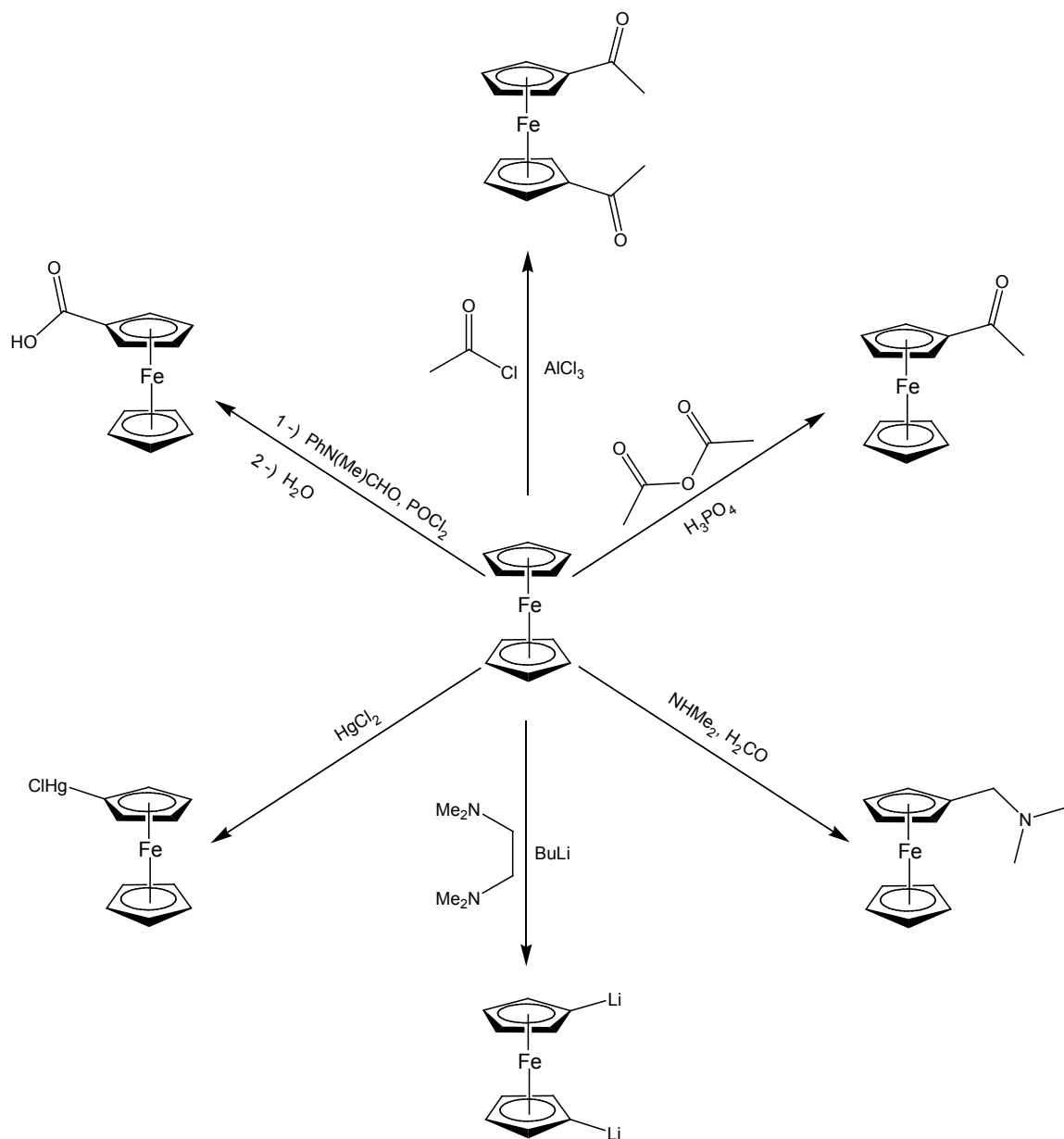
1.6 Metal Containing Polymers

Interest in the synthesis and characterization of metal-containing polymeric materials has increased dramatically due to their specific chemical and physical properties [127]. In recent years, polymers containing transition metals have garnered much attention [128-137]. The diversity of metal-containing polymers is a result of the wide range of oxidation states, coordination numbers, and geometries that transition metals can adopt. Oxidation states can be altered by changing the nature and/or the number of ligands bound to the metal center. In general, there are two primary classes of metal-containing polymers, those where the metal-containing moiety is a part of the main polymer chain (either as part of the backbone itself or directly coordinated to moieties within the polymer backbone), and those in which the metal is part of the pendant group of the polymer.

Polymers containing metals within their backbones have numerous structural features. They can contain metal-carbon σ or π bonds, or the metal can be coordinated to noncarbon elements. As an example, the nitrogen in a porphyrin or phthalocyanine macrocycle, or the nitrogen and oxygen atoms in a Schiff base moiety are bonded to their respective metallic moiety. The properties of these polymers are highly dependent on the coordinated ligands, potentially giving rise to polymer metal sites with properties as diverse as those of coordination compounds themselves. Metal-metal bonds can also be used as part of a polymeric backbone. The coordination of metals directly to atoms within the polymer backbone can commonly be observed in sandwich complex-containing polymers or those containing chelating ligands in the main chain, such as pyridyl groups.

1.6.1 The Chemistry of Ferrocene

The ferrocene synthesis was first reported in 1951 by Pauson and Kealy [138, 139]. After the discovery of ferrocene, it has been widely used as either part of a backbone or a substituent in ancillary ligands due to its unique geometrie and redox properties. The most of ligands formed via substitution of ferrocene using different donor heteroatoms have found applications [140,141]. Ferrocene has two cyclopentadiene rings located in planes above and below an iron atom which are also referred as metallocenes [139, 140]. The cyclopentadiene rings of the ferrocene can give similar reactions to organic aromatic compounds such as Friedel-Crafts acylation of the cyclopentadiene rings which proceed in the presence of a Lewis acid [143, 144, 146]. The Scheme 1.6 below illustrates some kinds of ferrocene derivatives synthesized via organic reactions.



Scheme 1.6 Reactivity of ferrocene.

There are four oxidation states for ferrocene. The 18 e^- ferrocene is an electron rich species that can be oxidized to form its 17 e^- ferrocenium ion by either chemical or electro-oxidation [145]. The reduction of ferrocene to 19 e^- and oxidation to 16 e^- were also demonstrated via cyclic voltammetry (Fig.1.20) [147, 148]. Since this was found to be reversible and reproducible, it has been used as an internal reference for cyclic voltammetry studies.

Electrochemical studies revealed that the redox potentials of ferrocene vary according to the substituent groups. The electron donating substituents lower the redox potentials of ferrocene while electron withdrawing substituents lead to increased redox potentials [149].

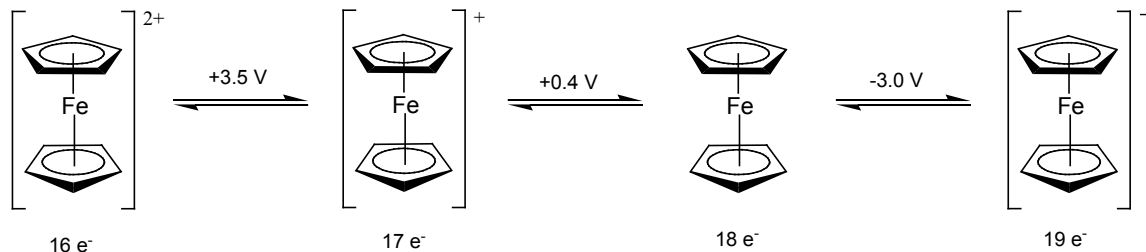


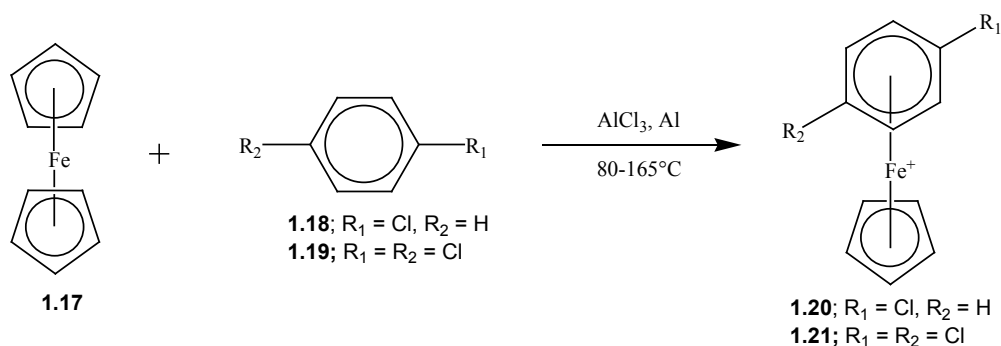
Figure 1.20 Potentials for the oxidation states of ferrocene vs SCE.

Functionalization of ferrocene leads to more chemical reactions and polymerization as well. Ferrocene containing vinyl polymers were first prepared by Arimoto and Haven [150]. After this first attempt, ferrocene has been widely used in polymers both in side chain or backbone due to its high stability towards heat, UV radiation and the reversible electrochemical behaviour [151-154].

1.6.2 Organoiron Complexes Based on Cyclopentadienyliron Cations

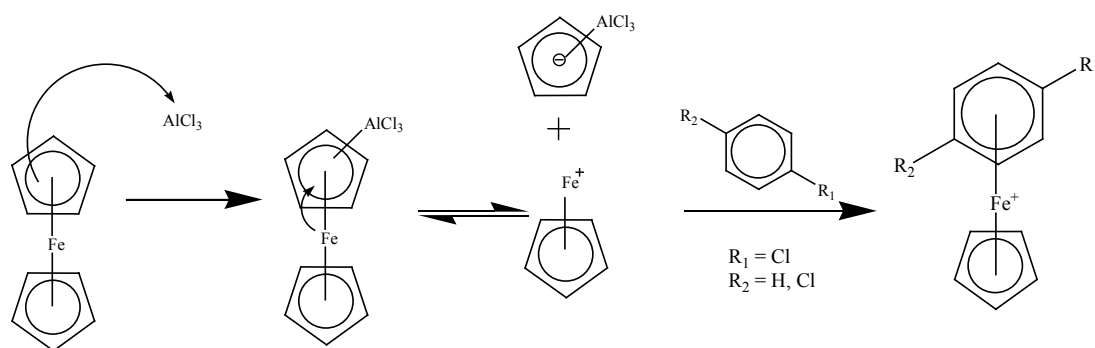
One of the cyclopentadienyl rings of ferrocene can be converted into a cationic η^6 -arene- η^5 -cyclopentadienyliron complex. The η^6 -arene- η^5 -cyclopentadienyliron cation was first synthesized with the reaction of benzene or substituted benzenes with ferrocene and AlCl_3 which is a ligand exchange reaction, by Nesmeyanow [155, 156]. The Scheme 1.7 illustrates the ligand exchange reaction of ferrocene with chlorobenzene or 1,4-dichlorobenzene. The η^6 -dichlorobenzene- η^5 -cyclopentadienyliron complex is treated with ammonium tetrafluoroborate or ammonium hexafluorophosphate and isolated as a neutral salt. The reaction takes places between

80-165°C for 5 hours catalyzed by AlCl_3 since 1,4-dichlorobenzene is liquid under reaction temperatures.



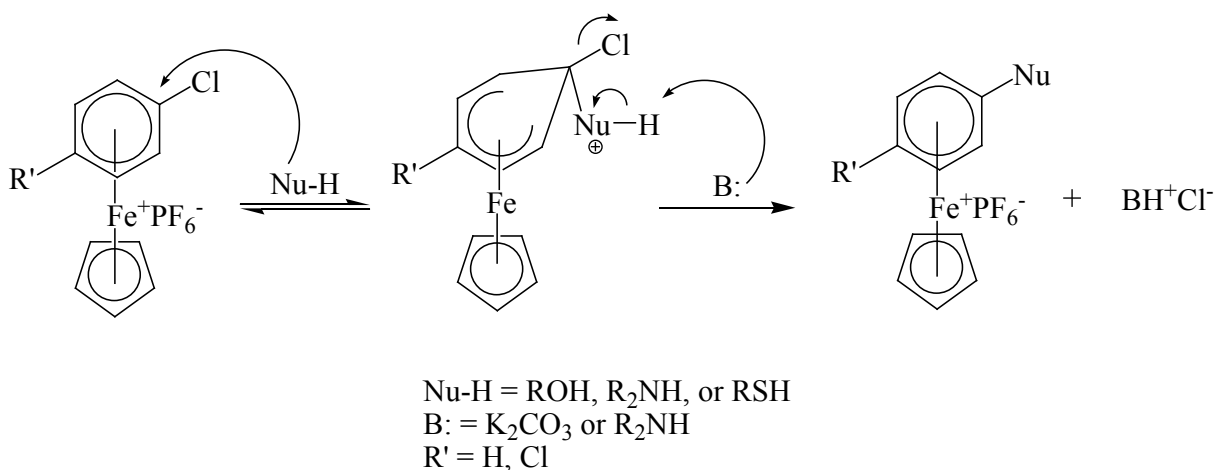
Scheme 1.7 Ligand exchange reaction of ferrocene.

The proposed ligand exchange reaction mechanism is illustrated in Scheme 1.8. The cyclopentadienyliron rings of the ferrocene molecule are coordinated by the AlCl_3 , resulting in a disruption of the bond between the ring and the iron center, cleaving the ring from the ferrocene and creating the cyclopentadienyliron cation. The resulted cyclopentadienyliron cation coordinated to the arene and gave the η^6 -dichlorobenzene- η^5 -cyclopentadienyliron complex [157, 158].



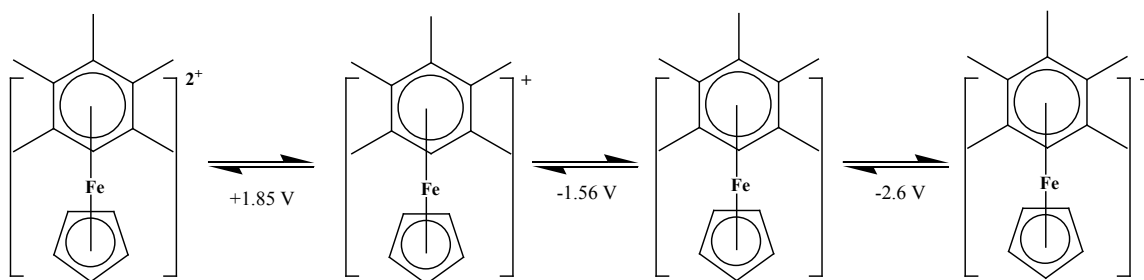
Scheme 1.8 Proposed mechanism for the ligand exchange of ferrocene.

The activity of the arene group is increased to nucleophilic aromatic substitution reactions via coordinating the cationic cyclopentadienyliron moiety to mono- or dihalobenzene due to the electron-withdrawing nature of the cyclopentadienyliron moiety [159-167]. Usually, an aromatic substitution reaction of chlorobenzene with phenolic groups requires long reaction times, high temperature and pressure, or catalysts. However, η^6 -chlorosubstituted arene- η^5 -cyclopentadienyliron complexes are easily substituted by phenolic groups at room temperature in the presence of weak bases, such as K_2CO_3 (Scheme 1.9) [157, 158].



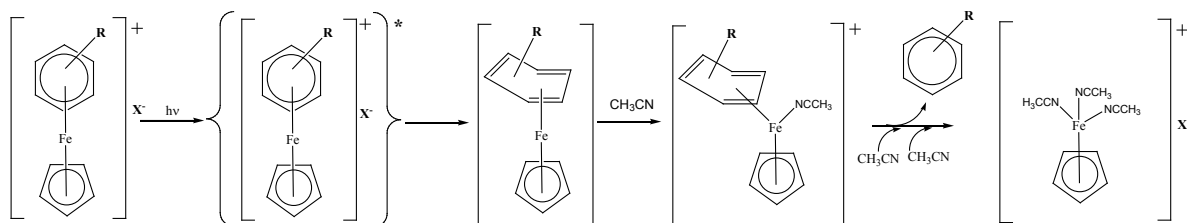
Scheme 1.9 Metal-mediated nucleophilic reaction of an η^6 -dichloroarene- η^5 -cyclopentadienyliron(II) hexafluorophosphate complex.

The cationic cyclopentadienyliron complexes go through two single-electron reductions, providing oxidation states of $17e^-$, $18e^-$, $19e^-$, and $20e^-$, giving them unique electrochemical properties (Scheme 1.10). Depending on the substituent of the arene ring and the cyclopentadienyliron ring, the reduction to form the $20e^-$ species shows the ability to be reversibly reduced to the $19e^-$ state [168].



Scheme 1.10 Potentials for the oxidation states of η^6 -hexamethylbenzene- η^5 -cyclopentadienyliron(II) vs SCE.

The cleavage of the cationic cyclopentadienyl moiety can be achieved via photolysis under UV light to yield the organic analogues of the compound [169-173]. Ferrocene, iron salts, and the organic arene are produced during this procedure, and can be isolated and purified through extractions and column chromatography. The mechanism of photolysis (Scheme 1.11) changes the arene-coordinated cyclopentadienyliron complexes into their triplet states, which results in “ring-slippage” from η^6 to η^4 and makes available a coordination site on the iron atom. In this case, a highly coordinating solvent or the complex’s counter ion can fill the rapidly-formed coordination site, which produces a new intermediate complex that readily decomposes.

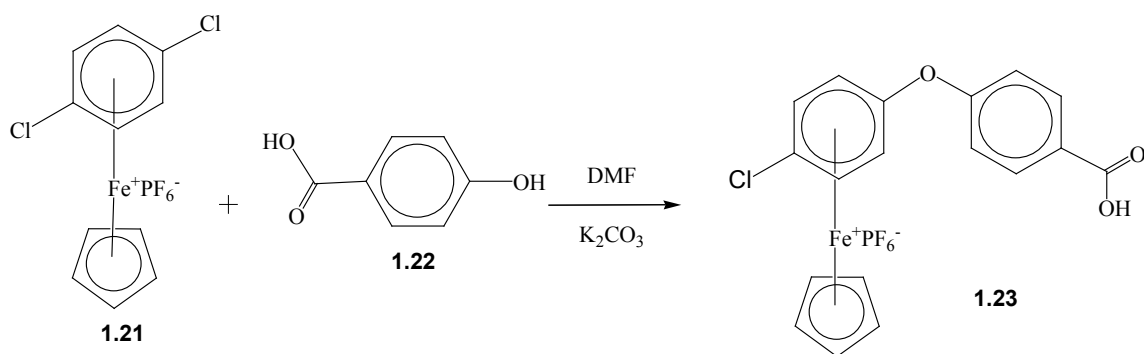


Scheme 1.11 Mechanism of the photolytic cleavage of the cationic cyclopentadienyliron moiety. X^- is a counter ion such as PF_6^- .

1.6.3 The Synthesis and Chemistry of the η^6 -haloarene- η^5 -cyclopentadienyliron(II)

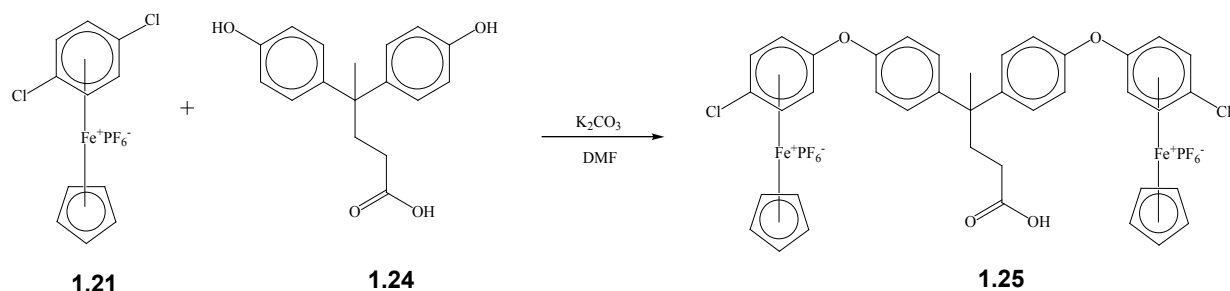
Hexafluorophosphate Complex with Carboxylic Groups

A series of carboxylic acid-functionalized organoiron with mono- and bimetallic complexes were synthesized employing the nucleophilic substitution of the η^6 -chlorosubstituted arene- η^5 -cyclopentadienyliron via Abd-El-Aziz *et al.* The monometallic acid complex was synthesized from the reaction of *p*-dichlorobenzene cyclopentadienyliron hexafluorophosphate with 4-hydroxybenzoic acid in the presence of K_2CO_3 in DMF for 12 hours at room temperature (Scheme 1.12) [173].



Scheme 1.12 Synthesis of the monometallic acid complex.

Bimetallic acid complex was synthesized by the reaction of 4,4-bis(4-hydroxyphenyl)valeric acid with *p*-dichlorobenzene cyclopentadienyliron hexafluorophosphate (Scheme 1.13). The reaction conditions were found to be the same with the mono metallic acid complex. However, a longer reaction time of 36 hours is required to ensure both phenolic groups are metal-mediated due to the ratio of the reagents.



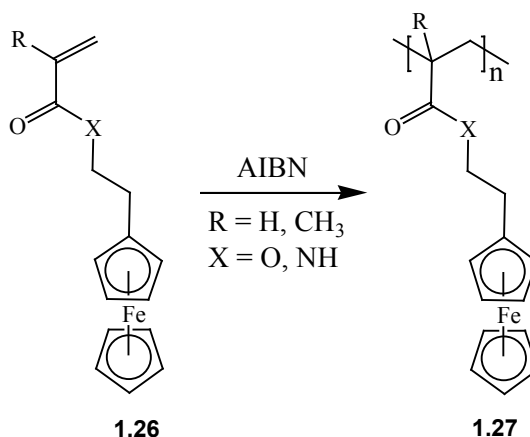
Scheme 1.13 Synthesis of bimetallic carboxylic acid complex.

In the thesis, ferrocene and cationic η^6 -arene- η^5 -cyclopentadienyliron complexes were used to prepare the functional groups which were then attached to the conjugated monomers. By the help of ligand exchange reaction method we prepared cationic η^6 -arene- η^5 -cyclopentadienyliron complex and then it was further reacted with different acid complexes to give monometallic and bimetallic groups for functionalization. The cationic η^6 -arene- η^5 -cyclopentadienyliron complex was also used as precursor for the polysiloxane polymers.

1.6.4 Organoiron Based Polymer

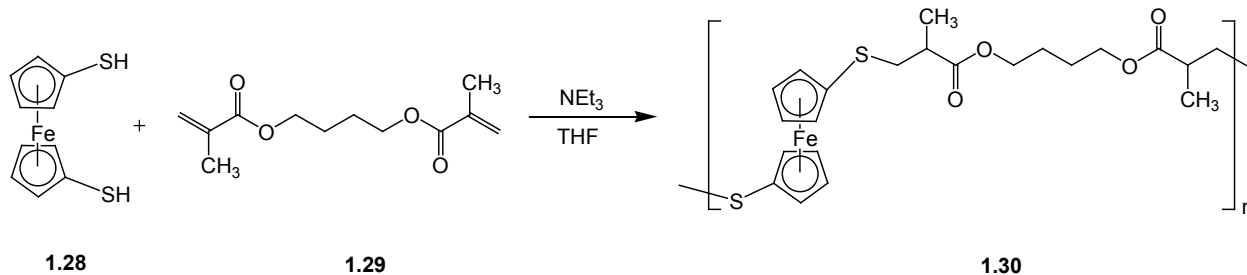
Organoiron based polymer could be prepared via several techniques according to the desired properties. The incorporation of organoiron moieties into the polymers gives materials unique optical, magnetic, and electrochemical properties. Some organoiron containing polymer examples will be given below.

In 2002, the homopolymerization and copolymerization of ferrocene-functionalized acrylates and methacrylates was reported [174]. Polyferrocenylethyl acrylate, methacrylate, acrylamide, and methacrylamide were synthesized using AIBN as initiator, is shown in Scheme 1.14 where the ferrocene was used as pendant group similar to the compounds that we prepared in the second chapter.



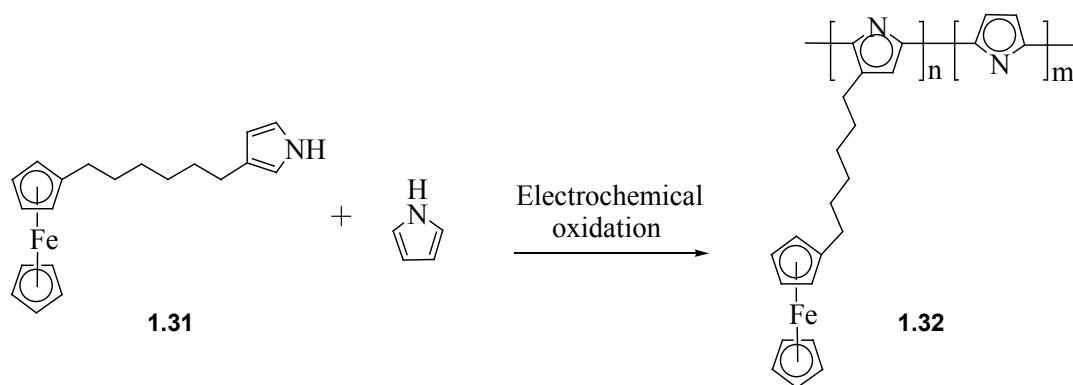
Scheme 1.14 Homopolymerization of ferrocene-functionalized acrylates and methacrylates.

The organometallic polymers were obtained by the reaction of various diolefins with 1,1-dimercaptoferrocene or 1,1-bis(2-mercaptoethyl)ferrocene. The reaction of 1,1-dimercaptoferrocene (**1.28**) with **1.29**, conducted via base-catalyzed polyaddition, is shown in Scheme 1.15 [175].



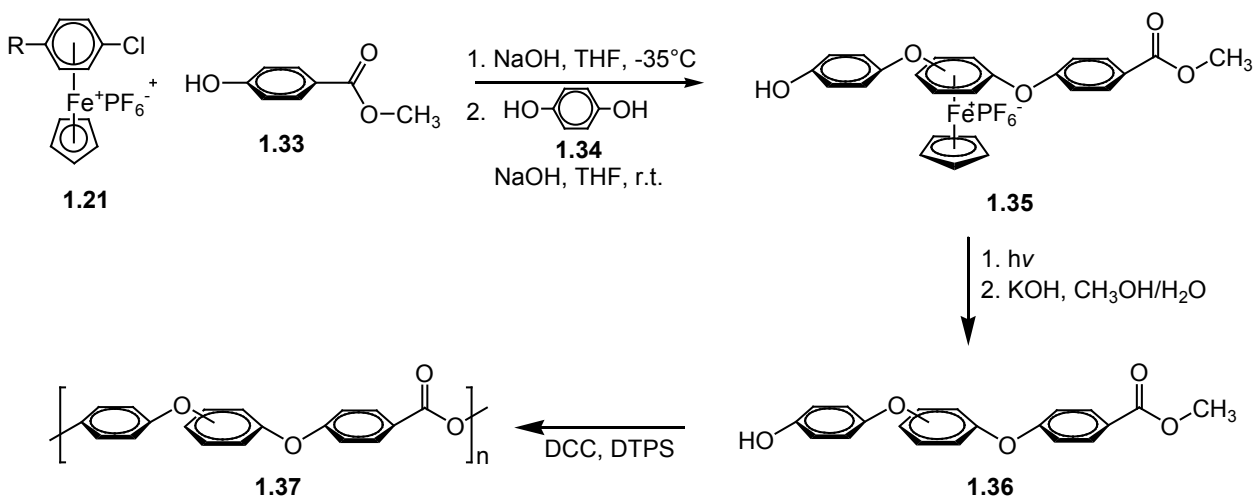
Scheme 1.15 Base-catalyzed polyaddition of 1,1-dimercaptoferrocene (1.28) with 1.29.

Electropolymerization of metallocene-functionalized pyrrole and thiophene derivatives produces organometallic polypyrroles and polythiophenes [176, 177]. Zotti *et al.* studied the electrochemical copolymerization of ferrocene-functionalized pyrrole **1.31** [122,123]. Scheme 1.16 represents the copolymerization of the monomer with pyrrole. The results indicated that polymer **1.32** has an electrical conductivity of $1.5 \times 10^{-2} \text{ Scm}^{-1}$.



Scheme 1.16 Electrochemical copolymerization of ferrocene-functionalized pyrrole with pyrrole.

The synthesis of different aromatic ether monomers using metal mediated S_NAr , as reported by Pearson, is illustrated in Scheme 1.17 [178, 179]. Taking advantage of the selective substitution of the chlorine atoms of the dichlorobenzene complex **1.21** allows for the synthesis of organoiron monomers with different functionalities. Photolytic decomplexation of the iron moieties, followed by a polycondensation reaction, resulted in the formation of high molecular weight polyester. This polymer demonstrated remarkable stability, and some of these materials have also displayed liquid crystallinity.

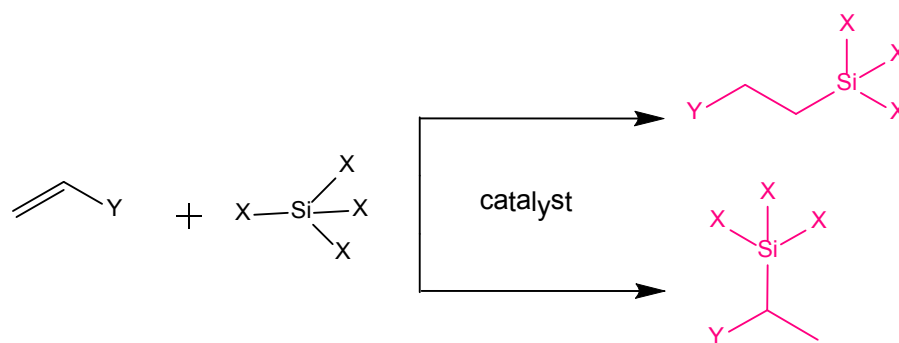


Scheme 1.17 Synthesis of different aromatic ether monomers using metal mediated S_NAr .

1.7 Polysiloxanes

Polysiloxanes are a class of polymeric materials with unique flexible backbones, thermal stability, durability, resistance to biological degradation, and insulation properties [180]. Polysiloxanes have found applications as lubricants, adhesives, mechanical tubing, gaskets, medical tools and implants, and electrical insulators. The low carbon content also makes them precursors for conducting ceramic materials.

The functionalization of siloxanes is achieved via hydrosilation reaction, which is the addition of an organic or inorganic silicon hydride across a double bond (Scheme 1.18). The reaction is quite variable according to the substituents, which can include alkyl, aryl, alkoxy, acyloxy and halogen groups [181, 182]. According to the first reported hydrosilation reaction, extremely high temperature conditions were required to decompose the starting material. However, there have been many transition metal catalysts developed to mediate hydrosilation reactions. These catalysts give products according to the anti-Markovnikov rule [183]. The catalyzed hydrosilation reaction mechanisms vary according to the catalyst, reactants and experimental conditions. Therefore, the mechanisms have not been explained for many of the reactants [184]. On the other hand, hydrosilation reactions with transition metal catalysts often result in side reactions such as oligomerization, polymerization, and isomerization hydrogenation of alkenes and dehydrogenation of silicon hydrides [184].

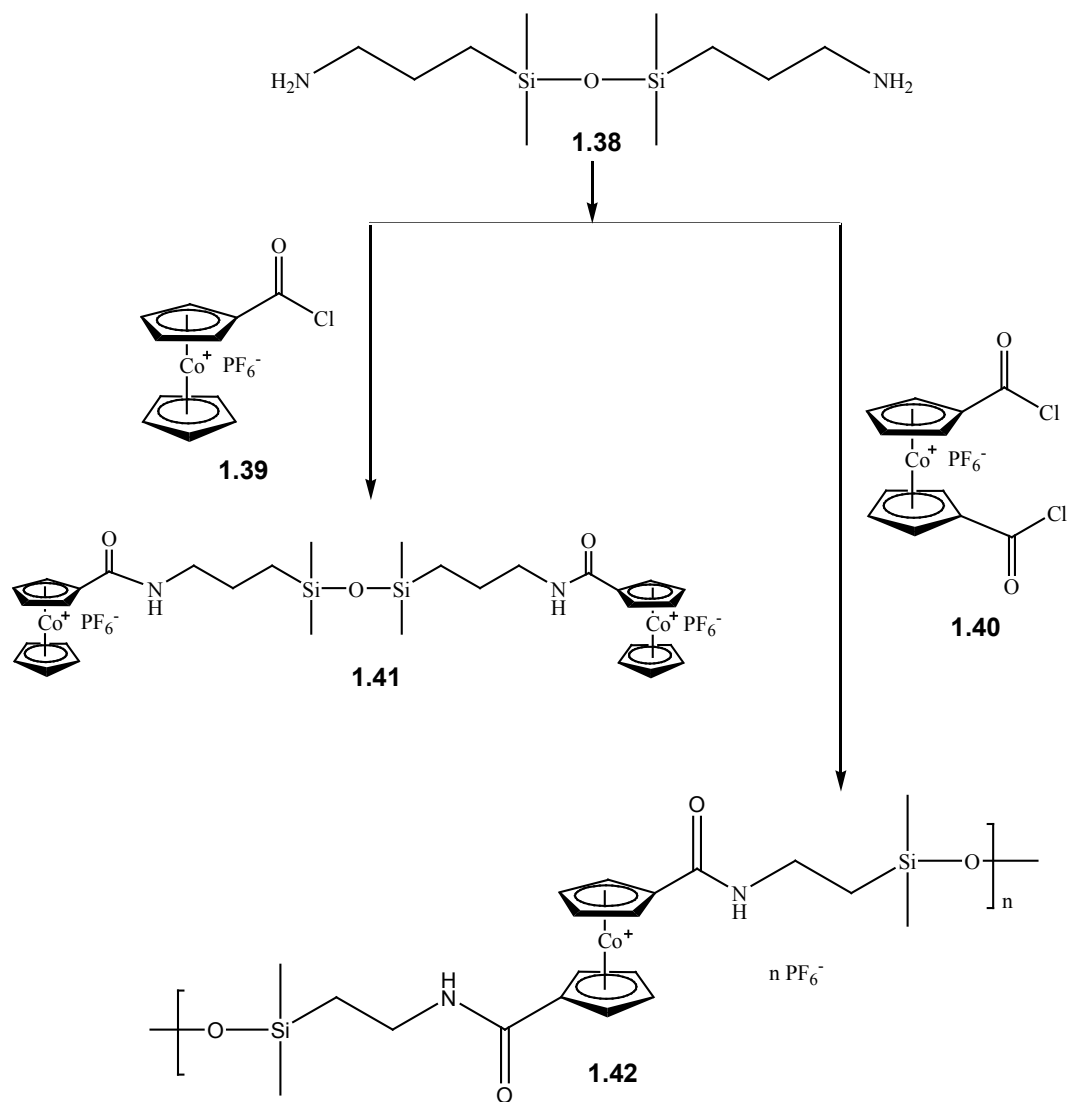


Scheme 1.18 Hydrosilation of terminal alkenes with catalyst.

In recent years, siloxane-based redox-active organometallic polymers have been studied frequently. Cuadrado *et al.* reported siloxane polymers containing ferrocene, $[(\eta^5\text{-C}_5\text{R}_4)\text{Fe}(\text{CO})(\mu\text{-CO})]_2$ ($\text{R} = \text{H}, \text{Me}$), as well as $[(\eta^6\text{-arene})\text{Cr}(\text{CO})_3]$ moieties, which display interesting redox properties [185-186]. Because of its unique electrochemical behaviour and resistance to strong oxidizing agents, cobaltocenium is a valuable moiety to incorporate into polymeric backbones. Interest in obtaining cobaltocenium-containing polysiloxane materials is primarily due to their distinct electrochemical and chemical features, combined with the unique and valuable properties of siloxane backbones.

Cuadrado and coworkers have prepared two different types of siloxane-based cobaltocenium-containing polymers. The polycondensation reaction of 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane with 1,1'-bis(chlorocarbonyl)cobaltocenium hexafluorophosphate was performed under the same reaction conditions as those used to prepare the starting materials, and produced polymer **1.42** with a backbone consisting of alternating dimethylsiloxane segments and cobaltocenium moieties bonded through amide linkages (Scheme 1.19). The polymer, isolated as a greenish solid, was essentially insoluble in most common organic solvents [185]. Using the similar methodology, we prepared linear and crosslinked polysiloxanes including

cationic η^6 -arene- η^5 -cyclopentadienyliron complex and ferrocene instead of cobaltocenium moieties.



Scheme 1.19 Polycondensation of 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane **1.38 with 1,1'-bis(chlorocarbonyl)cobaltocenium hexafluorophosphate **1.40**.**

Conversely, the reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{Cl})]^+\text{PF}_6^-$ with (aminopropyl) methylsiloxane (3-5%)-dimethylsiloxane (95-97%) copolymer, complete with NH₂ functionality, allows facile access to the block copolymer. Polymeric material **1.43** is composed of a

poly(dimethylsiloxane) chain (Fig.1.21), in which pendant amide-linked cobaltocenium moieties are randomly distributed along the methylsiloxane backbone.

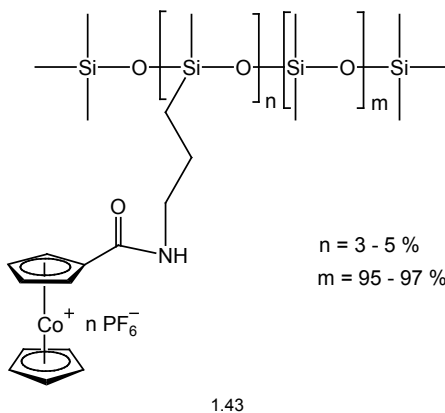


Figure 1.21 Poly(dimethylsiloxane) pendant amide-linked cobaltocenium moieties.

In this thesis, our research objective is to synthesize electrically conductive thiophene derivatives indicating different properties according the pendant groups, by electrochemical polymerization technique. First of all, the effect of cationic and neutral iron moieties in the polymeric films will be observed in terms of capacitance properties and morphology expecting increase in the capacitive properties with the increase of iron moiety.

In the second chapter, we will synthesize thiophene derivatives with different chromophores having different fluorescence properties. We expect an increase in the fluorescence intensity due to the thiophene precursor and flexible spacer group between thiophene and chromophore should increase the electrochemical processing possibility.

Furthermore, in the last chapter, we will blend our previously synthesized polysiloxane and PAN in DMF matrix to make thin films expecting to take the advantage of both compounds. The resulted films are expected to be flexible due to the silicone content.

2 Novel Synthesis and Electropolymerization of Metallo-Conjugated Ethylenedioxythiophene (EDOT) and Thiophene (Th) Derivatives

2.1 Overview

In recent years, there has been great interest in conducting polymers due to their ease of preparation, mechanical processability, and ability to become electrically conducting upon chemical or electrochemical doping. Conducting polymers with metals incorporated into the polymer structure are known as conducting metallopolymers. The incorporation of transition metals into these materials provides many additional applications based on redox, magnetic, optical, or catalytic properties [187-188]. These new metallopolymers have potential applications in solar cells, non-linear optic devices, batteries, molecular actuators, electrocatalysts, and sensors [189-197].

In this study, new conducting metallopolymers were designed with the incorporation of valeric bimetallic carboxylic acid complex and 4-hydroxy benzoic acid based on η^6 -aryl- η^5 -cyclopentadienyliron and ferrocene-3-carboxylic acid to hydroxymethyl EDOT and 2-(3-thienyl)ethanol. The chemistry of η^6 -aryl- η^5 -cyclopentadienyliron complexes has been investigated extensively in literature [130,163,198-202]. The use of arene-coordinated cyclopentadienyliron moieties enhanced the incorporation of cationic metal groups into new materials. The incorporation of cationic cyclopentadienyliron moieties into macromolecules can increase the solubility of the materials compared to their organic analogues and can produce

electrocatalytic properties [203]. The incorporation of cyclopentadienyliron into polyethers, -esters, -norbornenes, and -methacrylates utilizing various functional groups was reported previously [203-207].

Among the numerous polymers developed in recent years, poly(3,4-ethylenedioxythiophene) is one of the most successful materials due to its fundamental and practical features. It has several advantages compared to other polythiophene derivatives, including its ability to combine a low oxidation potential and moderate band gap with good stability in the oxidized state [10]. The formation of α - β linkages during the polymerization is prevented by blocking the β -position of the heterocyclic ring, resulting in a synthesized material better defined as more regiochemical [10,99,208]. PEDOT is not only a highly conductive (~ 400 S/cm) material, but also highly transparent in thin oxidized films [10,99,208,209]. PEDOT derivatives are used in several industrial applications, including antistatic coatings for photographic films, capacitors, biosensors, and hole conducting materials in organic/polymer-based light-emitting diodes [210].

On the other hand, 2-(3-thienyl)ethanol is another popular thiophene derivative with the advantage of the terminal hydroxyl group to give opportunity for several substitution probabilities. Electropolymerization involves electrochemical oxidation or reduction of a monomer to produce a radical anion or cation which are then coupled chemically resulting in a dimer or longer polymer chain. Usually, longer conjugation lengths result from the favored α coupling, but in thiophene rings α - β coupling occurs in most cases [211,71,73].

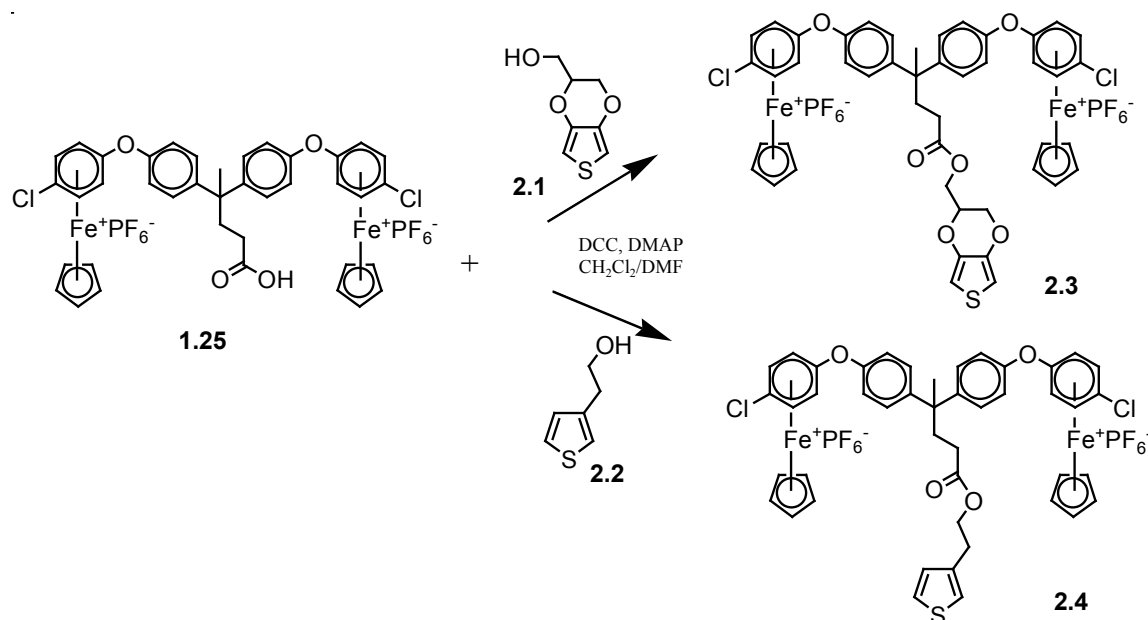
This chapter describes electrochemical polymerization of the newly synthesized monomers including mono and bimetallic cationic iron and neutral ferrocene moieties as pendant groups. In these newly synthesized materials, the metal is tethered to the backbone by a flexible,

non-conjugated linker. Therefore, the polymer acts as a conductive support while the metal groups behave similarly to an untethered complex. The resulting polymers were characterized via electrochemical impedance spectroscopy to measure the capacitive properties and understand the effect of transition metals on capacitance and conductivity.

2.2 Results and Discussion

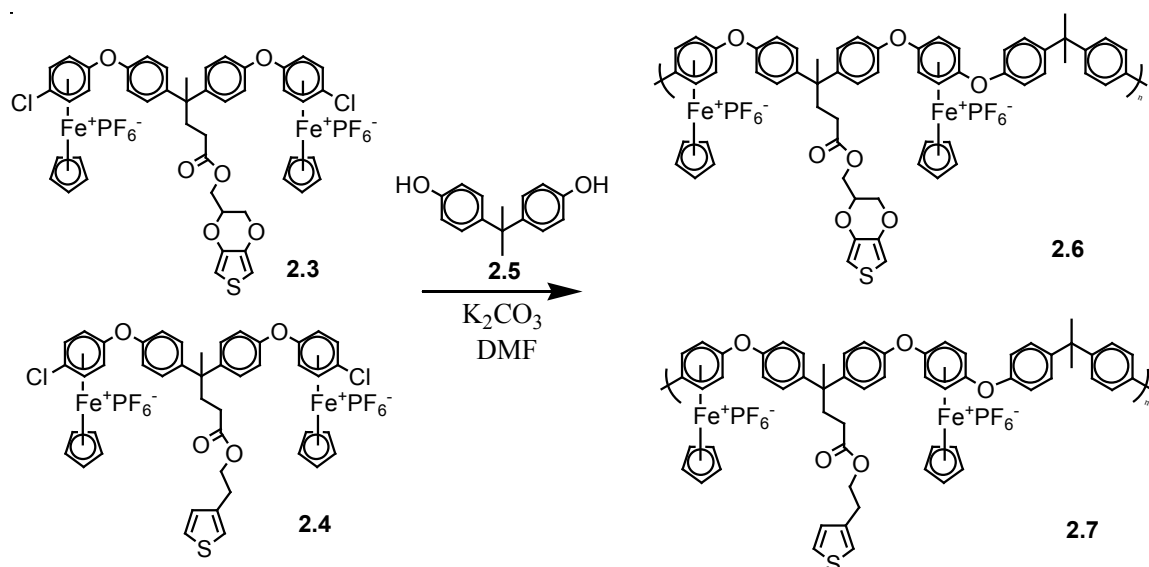
2.2.1 Synthesis of Thiophene Derivatives with Cationic Bimetallic Complex

Polymers can be prepared by using chemical or electrochemical methods of polymerization. The majority of redox polymers have been synthesized by chemical polymerization. Electrochemically active groups are either built into the polymer structure inside the chain or as a pendant group (pre-functionalized polymers), incorporated into the polymer phase in the course of the polymerization, or fixed at the polymer network in an additional step after the coating procedure (post-coating functionalization) in the case of the polymer film electrodes. Herein, the design of bimetallic organoiron incorporated to EDOT and 2-(3-Thienyl)ethanol polymers were achieved via chemical and electrochemical methods. The reaction of arene cyclopentadienyliron cations with a terminal chloro group in the *para*-position with 4,4-bis(4-hydroxyphenyl)valeric acid affords the valeric bimetallic (VBM) complex according to the previously established method [212]. The carboxylic acid group of the synthesized bimetallic organoiron complex was reacted with the terminal hydroxyl group of the hydroxymethyl EDOT and 2-(3-thienyl)ethanol complex to produce the VBM-EDOT and VBM-Th monomer, respectively (Scheme 2.1).



Scheme 2.1 The esterification reaction of Valeric bimetallic complex with hydroxymethyl EDOT and 2-(3-Thienyl)ethanol monomers.

The synthesized monomers were polymerized with bisphenol-A via a condensation polymerization (Scheme 2.2). In this case, we had conjugated EDOT and Th as side groups on polymer chains. The resulting organoiron containing polymers were characterized via NMR and FTIR spectroscopy, and thermal characterization was achieved with TGA and DSC. Furthermore, electrochemical polymerization of the VBM-EDOT complex (**2.3**) was achieved on carbon fibre electrodes in CH₂Cl₂ solution including tetrabutylammonium hexafluorophosphate as supporting electrolyte.



Scheme 2.2 Condensation polymerization of the VBM-EDOT (2.3) and VBM-Th (2.4) monomers with Bisphenol-A.

Identification of the monomer complex and the polymer was accomplished using NMR and IR analysis. In the ^1H NMR spectrum, the disappearance of the OH resonance at 3.56 ppm, as well as the presence of new sets of peaks between 4.04, 4.20, and 4.40 ppm, attributed to the incorporation of the hydroxymethyl EDOT (Fig.2.1) and the presence of new peaks between 7.26, 7.47 ppm attributed to the incorporation of the 2-(3-Thienyl) ethanol (Fig.2.4), indicates successful esterification reactions. Additionally, CH_2 peaks next to the terminal hydroxyl group shifted towards downfield from 3.60 ppm to 4.20 ppm due to the electron withdrawing effect of oxygen. The monomer and polymer spectra also revealed some similarities. For example, the upfield region shows peaks in range of 1.23-1.68 ppm that represent the methyl protons, while the cyclopentadienyl protons of the cationic iron moieties appeared in both spectra around 5.28 ppm. The complexed aromatic protons in both the monomer and the polymer resonated at similar chemical shifts between 6.29 and 6.80 ppm, while the uncomplexed aromatic protons of the monomer and the polymer were found at 7.28 and 7.39 ppm for VBM-EDOT complex.

The ^{13}C NMR spectrum and the HSQC (Fig.2.3, Fig.2.6) spectrum further confirmed the structures. In ^{13}C NMR spectrum, VBM-EDOT (Fig.2.2) monomer indicated that the methyl resonance appeared at 29.51 ppm, while the methyl carbons displayed peaks at 35.79, 26.93, 62.17, and 64.91 ppm. The quaternary aliphatic carbon resonated at 45.01 ppm. The cationic iron Cp carbons showed an intense peak at 79.29 ppm and the complexed arene CH carbons displayed peaks at 76.34 and 86.74 ppm. The uncomplexed aromatic carbons appeared downfield at 120.07 and 129.26 ppm, while peaks at 146.11 and 151.11 ppm represented the quaternary carbons. Additionally, the quaternary carbon of EDOT appeared at 140.90 ppm and the carbonyl carbon showed up at 172.53 ppm whereas the quaternary carbon of 2-(3-Thienyl) ethanol (Fig.2.5) at 120.33 ppm and the carbonyl carbon showed up at 172.79 ppm.

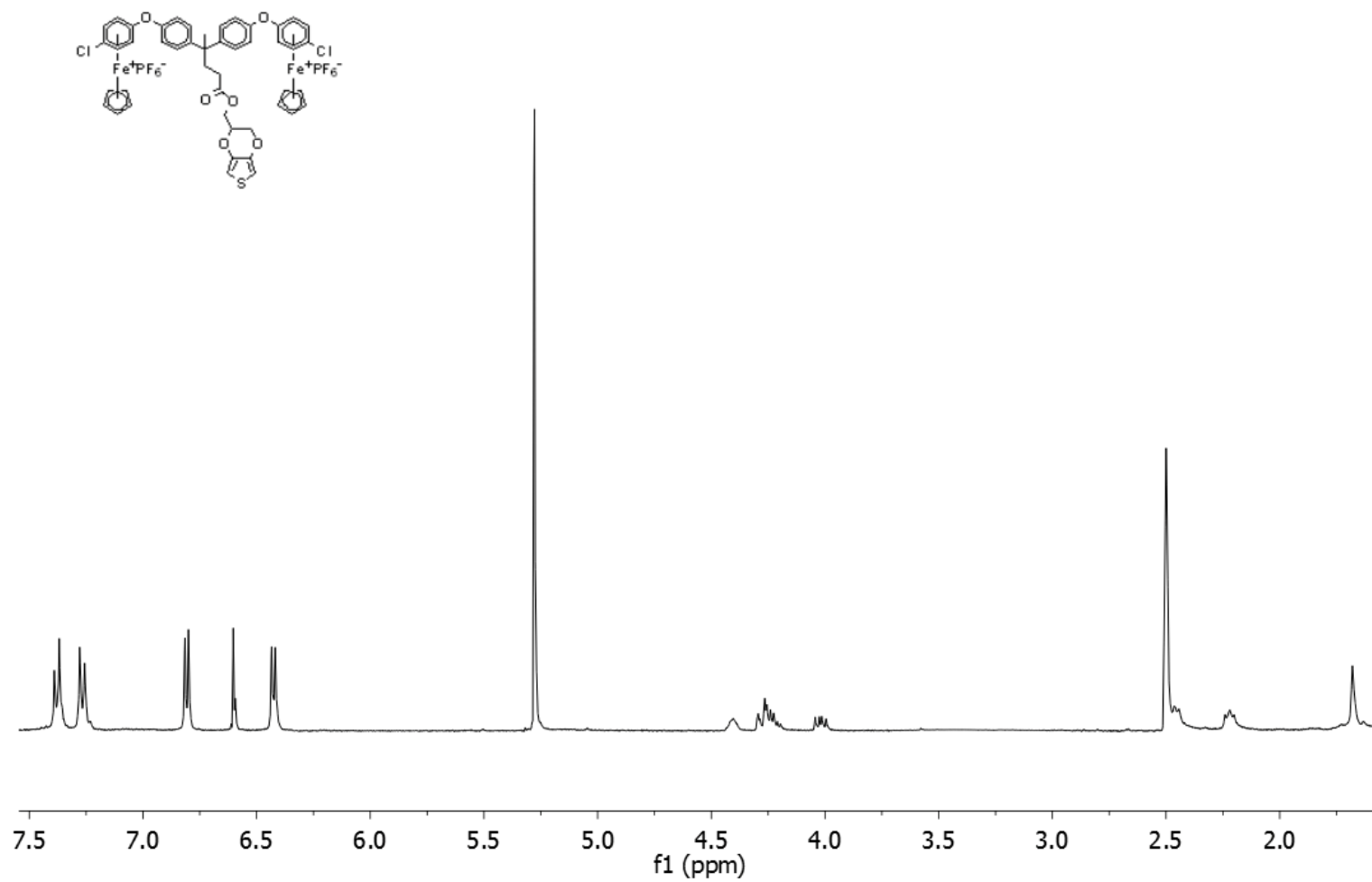


Figure 2.1 ^1H NMR spectrum for VBM-EDOT Complex (2.3).

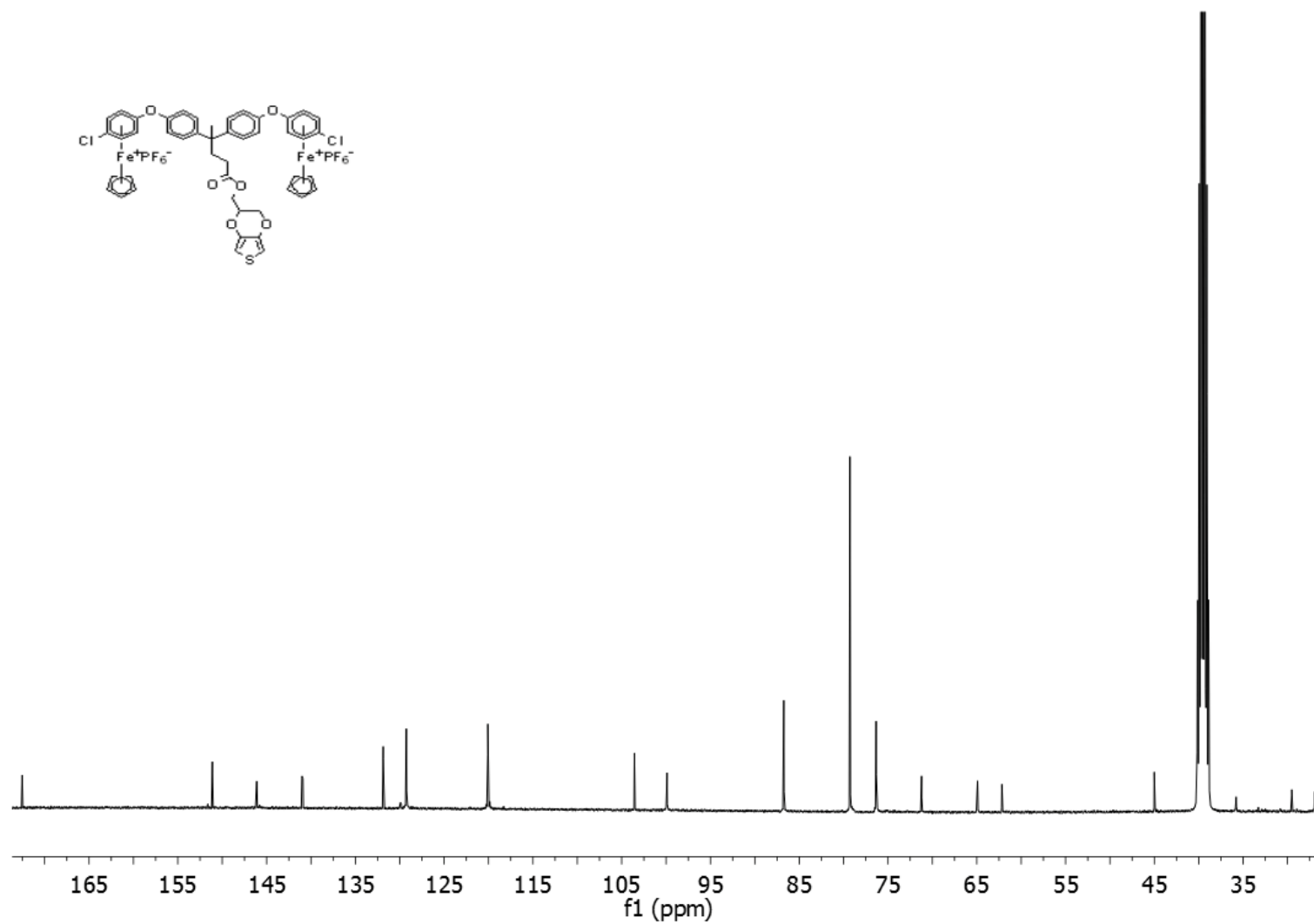


Figure 2.2 ^{13}C NMR spectrum for VBM-EDOT Complex (2.3).

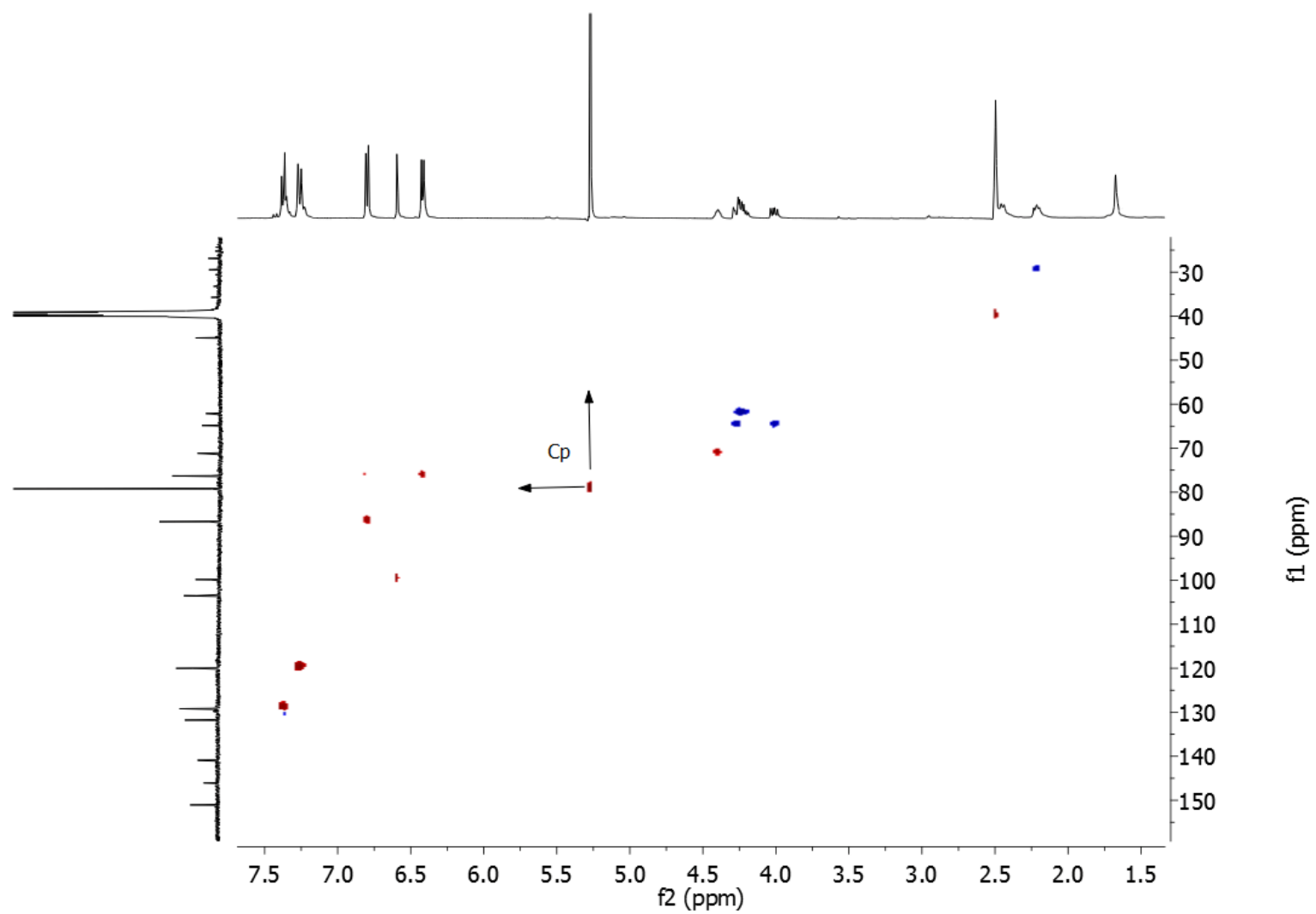


Figure 2.3 2D-HSQC NMR spectrum of the VBM-EDOT monomer (2.3).

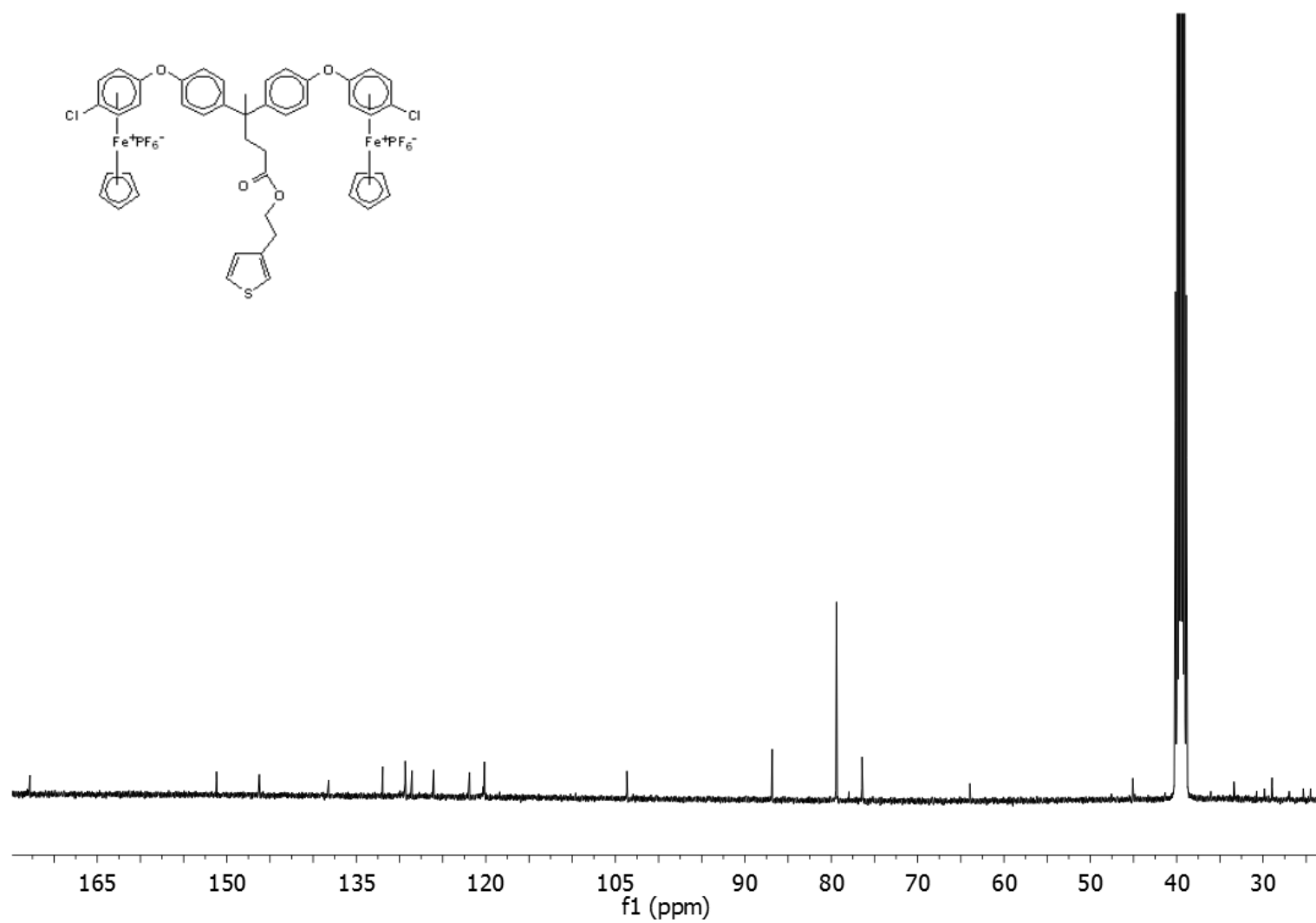


Figure 2.5 ^{13}C NMR spectrum for VBM-Th Complex (2.4).

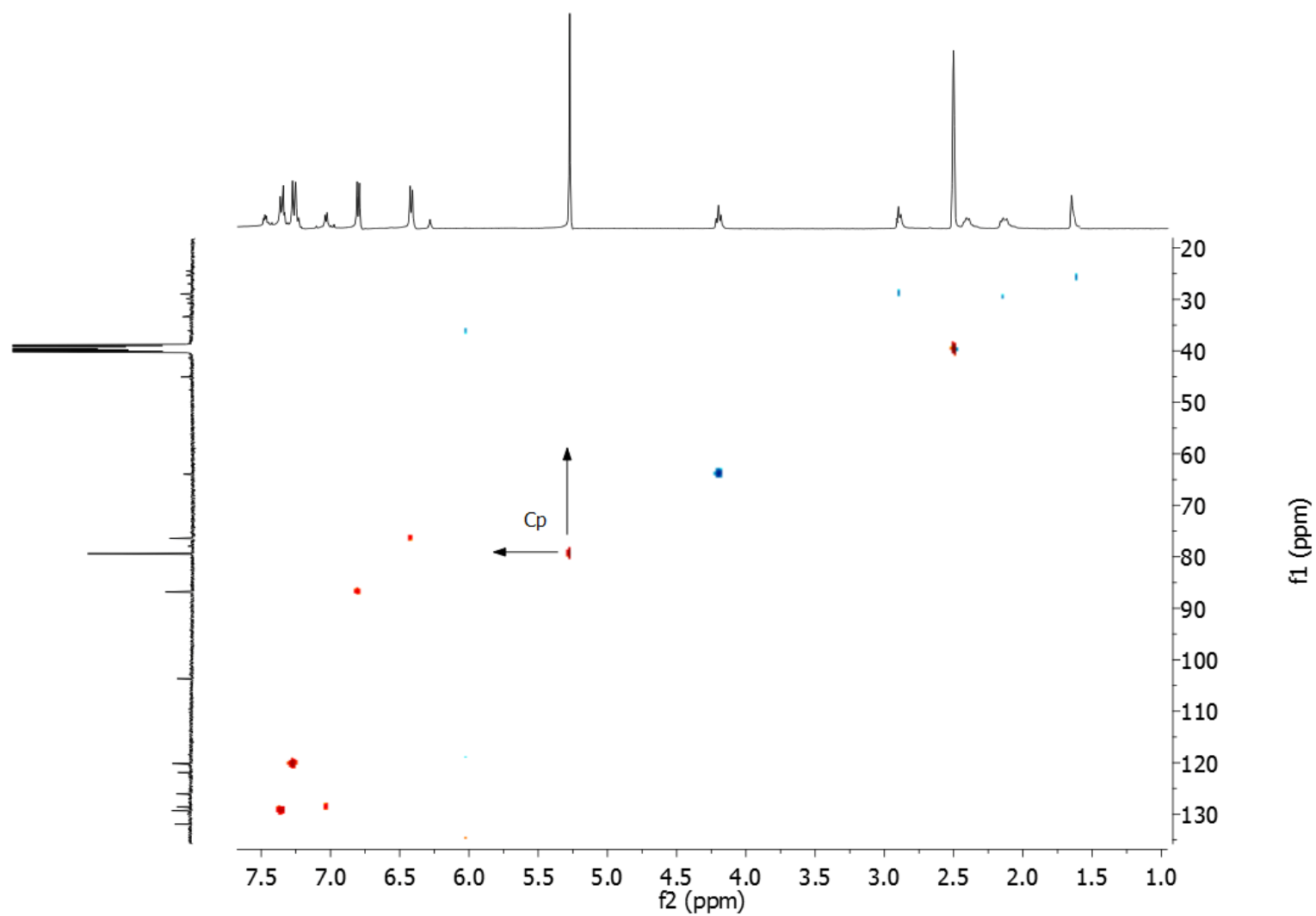


Figure 2.6 2D-HSQC NMR spectrum of the VBM-EDOT monomer (2.4).

The VBM-EDOT and VBM-Th polymers and their corresponding monomers were also characterized by FTIR. The strong band at 840 cm^{-1} and 833 cm^{-1} represents the C-S vibration of the monomer and polymer molecules, respectively. Vibrations at 1500 , 1485 and 1456 cm^{-1} are attributed to the stretching modes of C=C and C-C in the thiophene ring. The bands at 1246 and 1097 cm^{-1} are assigned to the stretching modes of the ethylenedioxy group for VBM-EDOT compound where as the conversion of the OH group in VBM-Th compound could be explained with disappearance of the peak at 3345 cm^{-1} . On the other hand, the aromatic C-H stretch observed around 3105 cm^{-1} belongs to the VBM complex. Another obvious band was seen at 1736 cm^{-1} and 1745 cm^{-1} , which represents the C=O stretch of the bimetallic complex in VBM-EDOT and VBM-Th, respectively.

2.2.1.1 Electropolymerization of VBM-EDOT (2.3) and VBM-Th (2.4) Complexes

Electrochemistry has played a significant role in the preparation and characterization of these novel materials. Electrochemical techniques are especially suitable for controlled synthesis of these compounds and for tuning of a well-defined oxidation state. The preparation, characterization, and application of electrochemically active and electronically conducting polymeric systems are still in the foreground of research activity in electrochemistry. Hydroxymethyl EDOT and 2-(3-Thienyl) ethanol are great precursors for several other EDOT and thiophene derivatives. The synthesized VBM-EDOT and VBM-Th complexes were electrochemically polymerized, yielding the PEDOT and PTh derivatives which are not soluble in common solvents.

Oxidative electropolymerization of VBM-EDOT and VBM-Th was carried out in 0.05M TBAPF₆/DCM as supporting electrolyte solution using the conventional three electrode system at -35°C . Figure 2.7 illustrates the electropolymerized VBM-EDOT compound.

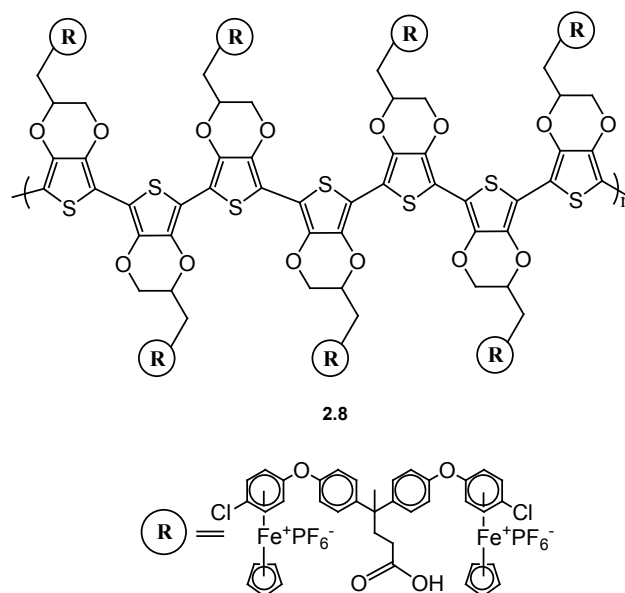


Figure 2.7 Schematic representation of electrochemically polymerized VBM-EDOT conducting polymer.

The quasi-reversible oxidation of the monomer appears clearly on the first cycle. The polymeric films of VBM-EDOT were deposited by cyclic voltammetry over 20 cycles onto a carbon fibre micro electrode. Potentiodynamic growth of VBM-EDOT at 100 mVs^{-1} in $0.05\text{M TBAPF}_6/\text{DCM}$ electrolyte solution was achieved on CFME at -35°C (Figure 2.8). Investigation of the redox switching of the polymer film in monomer-free electrolyte solution showed a well-defined redox process. Figure 2.9 indicates the scan rate dependencies of the VBM-PEDOT film between 100 and 500 mVs^{-1} in $0.05\text{M TBAPF}_6/\text{DCM}$, demonstrating the quasi-reversible redox process of the polymer film.

The first oxidation potential of the monomer (E_{onset}) was observed at 0.246mV . The half-wave oxidation potentials ($E_{1/2}$) of the VBM-PEDOT polymer were observed at -1.28 and 0.473 V ($E_{\text{p,ox1}} = -1.33 \text{ V}$, $E_{\text{p,ox2}} = 0.373 \text{ V}$, $E_{\text{p,red1}} = -1.21 \text{ V}$, $E_{\text{p,red2}} = 0.491 \text{ V}$).

The peak potential difference (ΔE) was calculated as 115mV which is higher than 59mV , indicating that the process was not reversible. The separation between anodic and cathodic peaks

is associated with ion transport resistance involved in these redox reactions. Thus, the difference between anodic and cathodic peaks (ΔE) can serve as an indication for resistance of ion migration in the electrode. The value of ΔE generally increases with the polymer film coated on the electrode. This is expected since an increase in polymer film thickness leads to an increase in resistance for ion penetration. The electropolymerization charge ($\Delta Q=66.22\text{mC}$) was found lower than VBM-Th polymer ($\Delta Q=163.5\text{mC}$) film. The electrochemically prepared polymer exhibits well-defined redox behaviour with a linear dependence between the I_{ox} peak current and the scan rate.

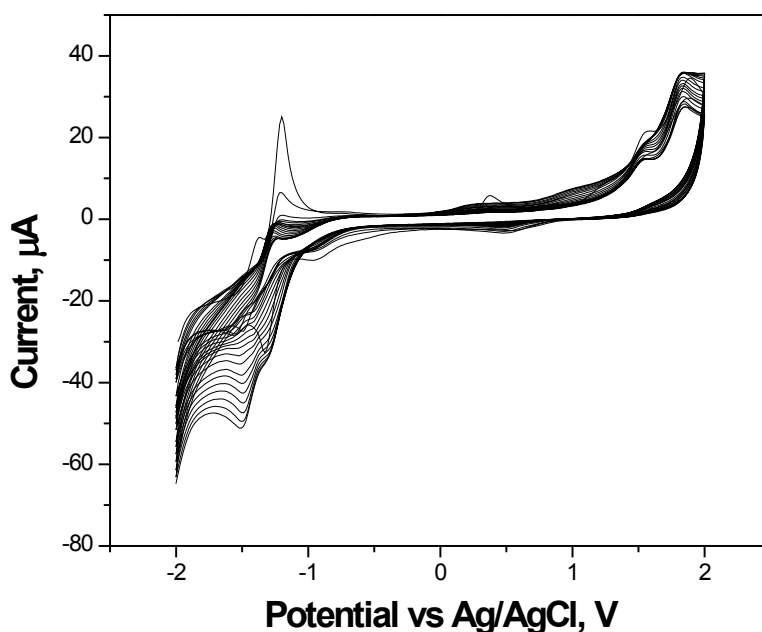


Figure 2.8 Repeated potential scan electropolymerization of the VBM-EDOT (2.3) complex at 100 mVs^{-1} in 0.05 M in $\text{TBAPF}_6/\text{DCM}$ on CFME at $-35\text{ }^\circ\text{C}$.

A single reversible redox wave was found corresponding to the conversion from 18 e^- to 19 e^- iron centres. The cyclic voltammogram of the complex at 100 mVs^{-1} indicated a redox

couple at $E_{1/2} = -1.28$ V, indicating the reduction of the cationic iron moiety. These reductions can occur at more negative potentials than those seen for oxygen-substituted arene complexes. This is characteristic of arene-cyclopentadienyliron complexes containing electron-donating substituent.

The current density is linearly proportional to scan rate indicating all electro-active sites are electrode supported in the monomer-free solution. For the reversible systems, current density (i) is explained by the *Randles-Sevcik* equation at given as: $i = 2.69 \cdot 10^5 \text{ A} \cdot \text{D}^{1/2} \cdot \text{C}_0 \cdot \nu^{1/2}$, where ν (Vs^{-1}) is the scan rate, A (cm^2) is the electrode area, D ($\text{cm}^2 \cdot \text{s}^{-1}$) is the diffusion coefficient of electro-active species, and C_0 ($\text{mol} \cdot \text{l}^{-1}$) is the concentration of electro-active species in solution. For the diffusion controlled redox reactions the peak current is linearly proportional to $\nu^{1/2}$.

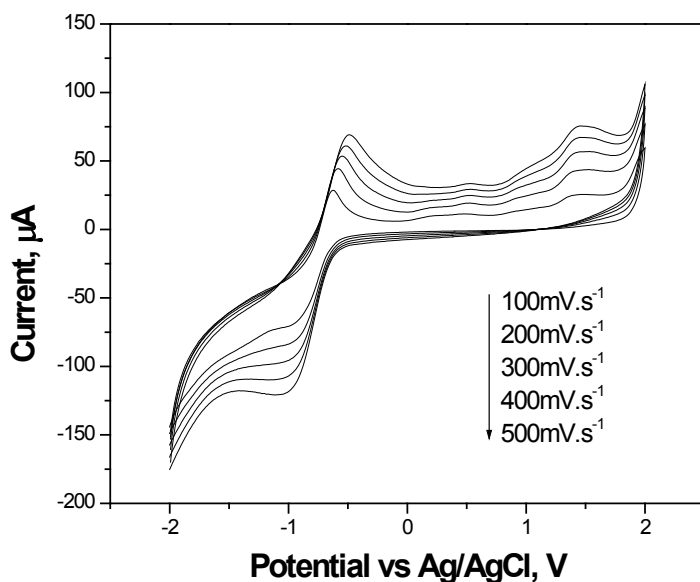


Figure 2.9 Cyclic voltammogram of the VBM-PEDOT (2.8) film in 0.05M TBAPF₆⁻/DCM monomer free electrolyte solution at scan rates of 100, 200, 300, 400 and 500 mVs^{-1} .

The scan rate dependence of the peak currents for both anodic and cathodic peaks is shown in Figure 2.10. Although peaks showed linear dependence, the anodic oxidation peaks correlation coefficient (R_a) was found as 0.984 and the reduction of the same peak R_c was determined to be 0.999, indicating a quasi-reversible property. On the other hand, the correlation coefficient values were found as 0.997 (R_a) for anodic oxidation and 0.989(R_c) for reduction from square root of scan rate ($v^{1/2}$) versus current plot so it could be assigned that the film formed on CFME has diffusion controlled thin layer behaviour.

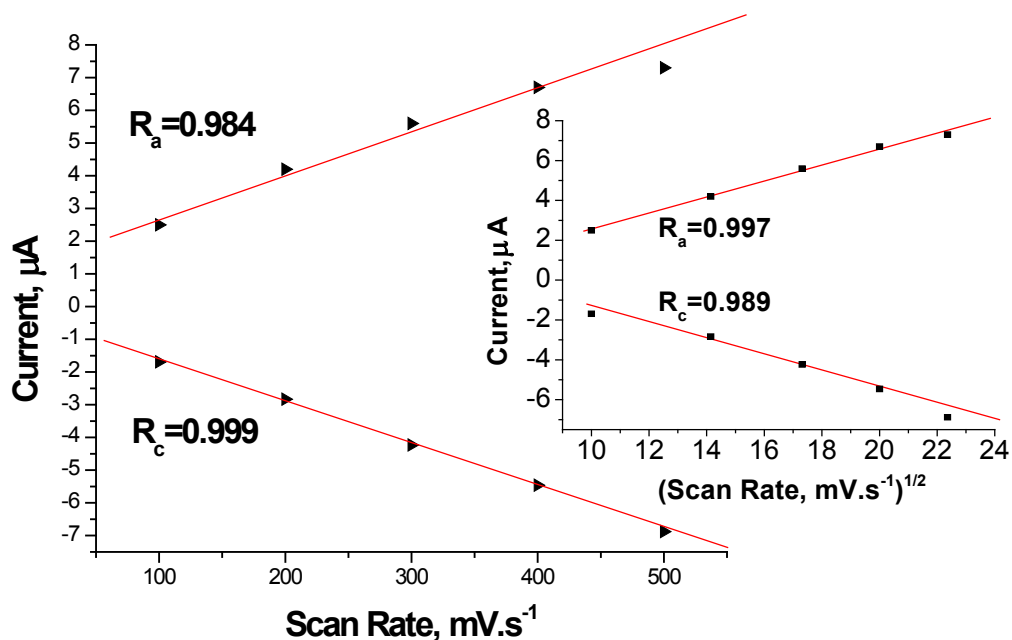


Figure 2.10 Anodic and cathodic peak current density vs. scan rate and dependence of VBM-PEDOT (2.8) thin film in 0.05M TBAPF₆/DCM monomer free electrolyte solution. Inset: Anodic and cathodic peak current density vs. square root of scan rate.

Electrochemical polymerization of VBM-Th was carried out in 0.05M TBAPF₆/DCM as supporting electrolyte solution at -35°C onto CFME. Figure 2.11 illustrates the electrochemically

polymerized VBM-Th conducting polymer. Multi sweep cyclic voltamogram of VBM-Th showed an increase in current value with each cycle, resulting in the formation of conducting polymer film on CFME surfaces. 20 cycles of potentiodynamic growth was achieved and the polymerization charge was obtained as 163.5mC (ΔQ).

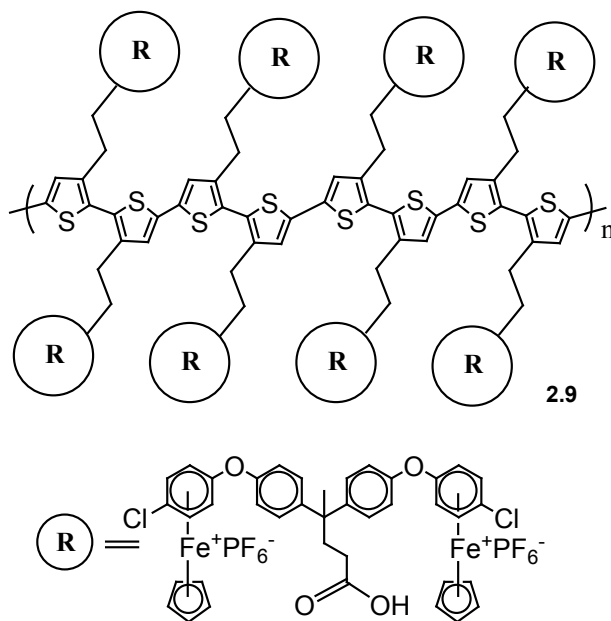


Figure 2.11 Schematic representation of electrochemically polymerized VBM-Th conducting polymer.

Effects of switching potentials on redox parameters were calculated and the onset potential (E_{onset}) value was 0.637mV, which is lower than unsubstituted thiophene monomers. The substitutions of thiophene lowered the onset potential value, which makes oxidation of the monomer and the polymerization easier as well. Also, decrease in the oxidation potential of the polymer provides a better stability in the oxidized state.

Since the VBM-Th shows no clear reduction peaks, the peak potential difference and half wave potentials were not calculated. However, the irreversibility is clearly seen from the cyclic voltamogram (Figure 2.12).

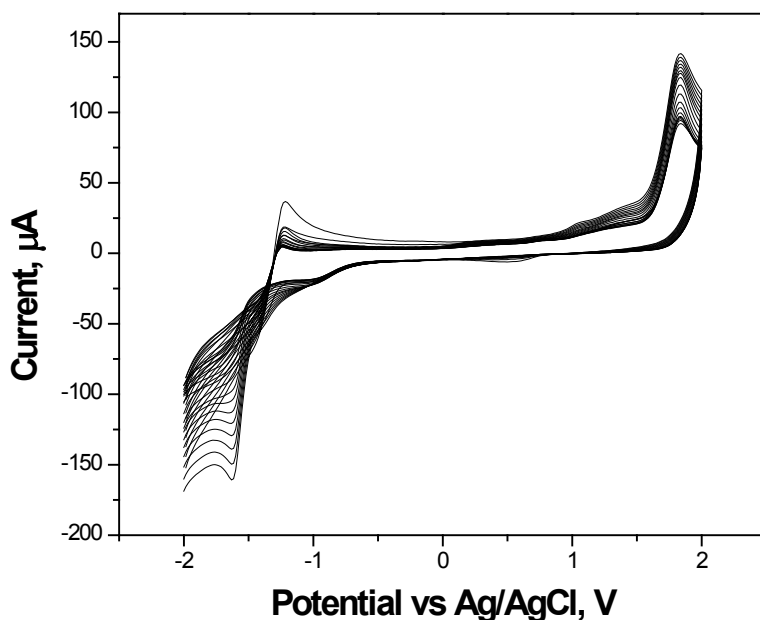


Figure 2.12 Repeated potential scan electropolymerization of the VBM-Th (2.4) complex at 100 mVs^{-1} in 0.05 M in $\text{TBAPF}_6/\text{DCM}$ on CFME at -35°C .

The scan rate dependencies of the VBM-PTh film between 100 and 500 mVs^{-1} in 0.05M $\text{TBAPF}_6/\text{DCM}$ monomer free solution was illustrated in Figure 2.13 indicating the irreversible redox process of the polymer film. The irreversible oxidation of the monomer appears clearly from the first cycle of the scan rate dependency graph followed by a nucleation loop for other cycles.

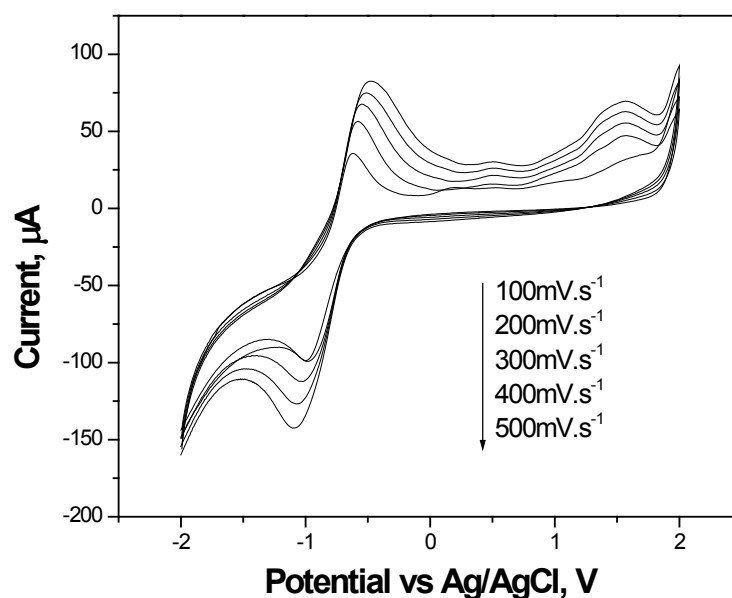


Figure 2.13 Cyclic voltammogram of the VBM-PTh (2.9) film in 0.05M TBAPF₆⁻/DCM monomer free electrolyte solution at scan rates of 100, 200, 300, 400 and 500 mVs⁻¹.

The anodic oxidation peak's correlation coefficient (R_a) was calculated as 0.974 whereas the reduction peak's correlation coefficient (R_c) was determined as 0.998 (Fig.2.14). According to the Randles-Sevcik equation, the correlation coefficient values were found as 0.992 (R_a) for anodic oxidation and 0.984 (R_c) for reduction from square root of scan rate versus current plot. In this case the peak current was linearly proportional to $v^{1/2}$, which indicated that the polymer film formation was a diffusion controlled process.

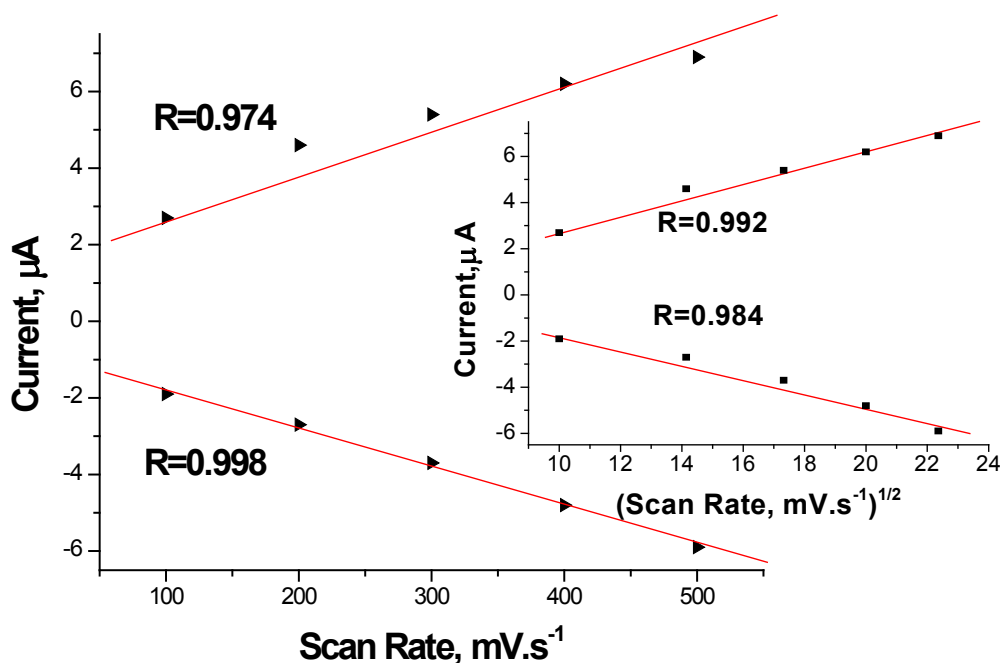


Figure 2.14 Anodic and cathodic peak current density vs. scan rate and dependence of VBM-PTh (2.9) thin film in 0.05M TBAPF₆/DCM monomer free solution. Inset: Anodic and cathodic peak current density vs. square root of scan rate.

2.2.1.2 Electrochemical Impedance Spectroscopic Characterization

Electrochemical impedance spectroscopy (EIS) is an effective tool to figure out the capacitance properties of polymers. EIS has well-developed theoretical and experimental procedures that serve as convenient techniques for obtaining electrochemical information, such as electrolyte resistance, charge transfer resistance, Faradaic capacitance, electrical conductivity, ion diffusion and capacitance of conducting polymer-modified electrodes. The electrochemical impedance spectroscopy (EIS) measurements were taken at room temperature (25°C) using a conventional three electrode cell configuration. EIS measurements were conducted in monomer-free electrolyte solution with perturbation amplitude 10mV over a frequency range of 0.01Hz to 100 kHz with PARSTAT 2273 (software; powersuit).

The Nyquist plots for the VBM-PEDOT and VBM-PTh were performed to estimate the capacitance values for modified CFME (Figure 2.15). At low frequency, there is a sharp increase for the imaginary part of the impedance, and then the plot showed a vertical line characteristic with almost 45° incline along the resistive component. The low frequency capacitance (C_{sp}) values of electrochemically deposited thin films (at 0.01 Hz) were calculated by the following equation: $C_{sp} = (2\pi \cdot f \cdot Z'')^{-1}$, where C_{sp} is the specific capacitance; Z'' is the slope of a plot of the imaginary component of impedance versus the inverse of the frequency (f). The specific capacitance values were calculated as 121.2 μFcm^{-2} and 75.7 μFcm^{-2} for CFME/VBM-PEDOT and CFME/VBM-PTh, respectively. The lower C_{sp} value is preferred for electrochemical capacitor for fast charge/discharge processes. Therefore, electron transfer is going to be faster for VBM-PTh modified electrodes, and it can store more charge than the VBM-PEDOT modified carbon fibre micro electrode.

There is no drastic difference in the Bode phase plot of VBM-PEDOT and VBM-PTh. The bode phase angles approached a plateau (VBM-PEDOT: 82.8°, VBM-PTh: 85.5°), in the frequency region of 0.67Hz-7.2Hz where the films showed capacitor behaviour. The phase transition from capacitor to resistor was observed around the frequency range between 715Hz and 837Hz. However, conducting polymer films indicated resistor behaviour in the range of 1200Hz-81500Hz (Figure 2.16).

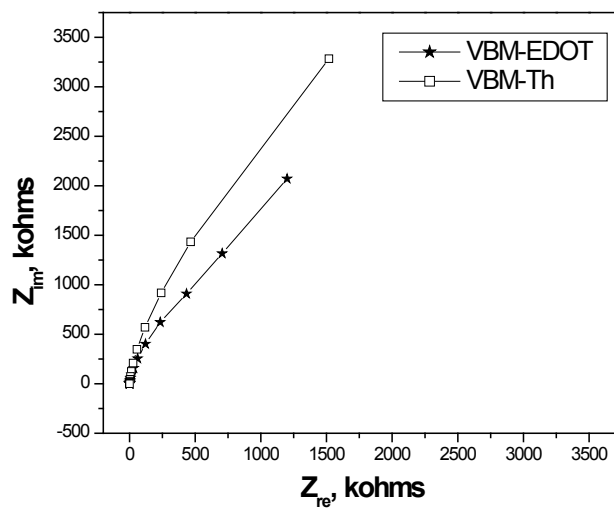


Figure 2.15 Nyquist plots for CFME/VBM-PEDOT (2.8) and CFME/VBM-PTh(2.9) in 0.05M TBAPF₆/DCM monomer free electrolyte solution, measured between 0.01Hz-100 kHz.

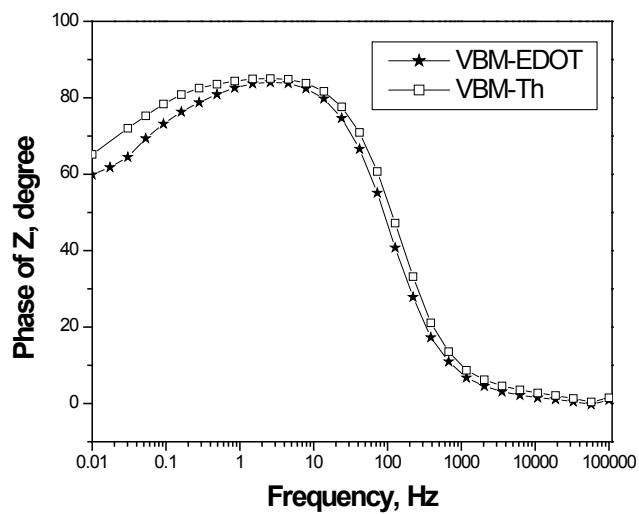


Figure 2.16 Bode Phase diagrams for CFME/VBM-PEDOT (2.8) and CFME/VBM-PTh (2.9) in 0.05M TBAPF₆/DCM monomer free electrolyte solution, measured between 0.01Hz-100 kHz.

Extrapolating a line from the Bode magnitude plot to the log Z axis at $\omega = 1$ ($\log \omega = 0$) yields the value of C_{dl} (double layer capacitance) from the relationship: $|Z|=1/C_{dl}$. Double layer capacitance values were determined as $320 \mu\text{Fcm}^{-2}$ and $225 \mu\text{Fcm}^{-2}$ for VBM-PEDOT and VBM-PTh, respectively (Figure 2.17). The capacitive behaviour increases with the increase in the C_{dl} value and film thickness, therefore VBM-PEDOT film on CFME is thicker than the VBM-PTh film.

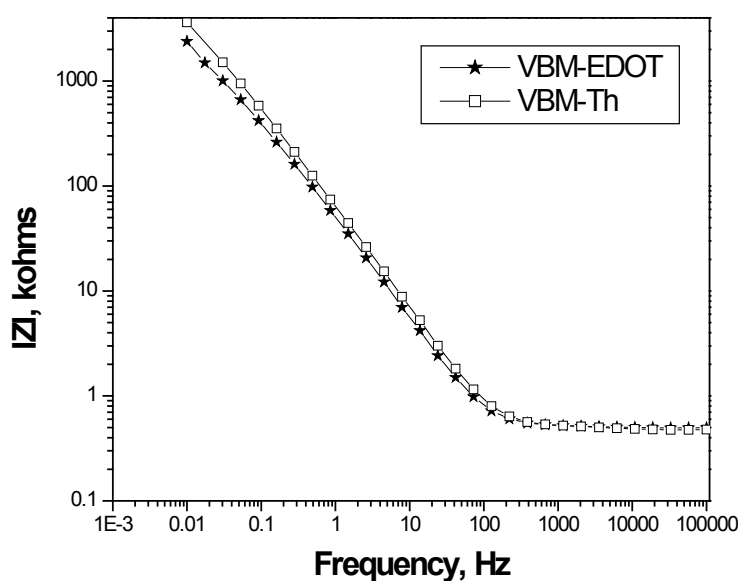


Figure 2.17 Bode Magnitude plots for CFME/VBM-PEDOT (2.8) and CFME/VBM-PTh (2.9) in 0.05M TBAPF₆/DCM monomer free electrolyte solution, measured between 0.01Hz-100 kHz.

On the other hand, an admittance plot gives information how easily a circuit or device will allow a current to flow. Conductivities were determined as 15 mScm^{-2} for VBM-PEDOT whereas the VBM-PTh film has a lower value of 14.2 mScm^{-2} . Admittance (Fig.2.18) and nyquist plots (Fig.2.15) are in a good agreement, indicating that VBM-PEDOT film is better than

VBM-PTh film in terms of conductivity, electron transfer rate and charge storage capability. It is also observed from the capacitance graph (Fig.2.19) that VBM-PEDOT film has higher charge storage ability than VBM-PTh film as well.

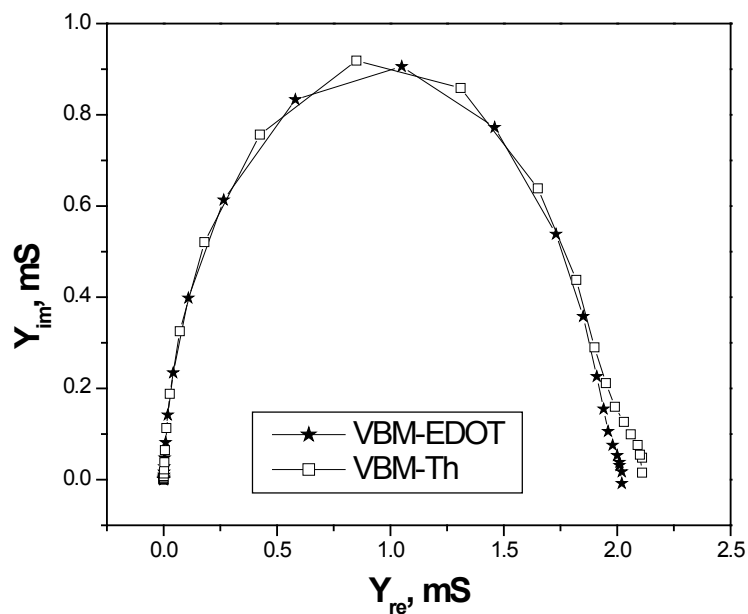


Figure 2.18 Admittance plots for CFME/VBM-PEDOT (2.8) and CFME/VBM-PTh (2.9) in 0.05M TBAPF₆/DCM monomer free electrolyte solution, measured between 0.01Hz-100 kHz.

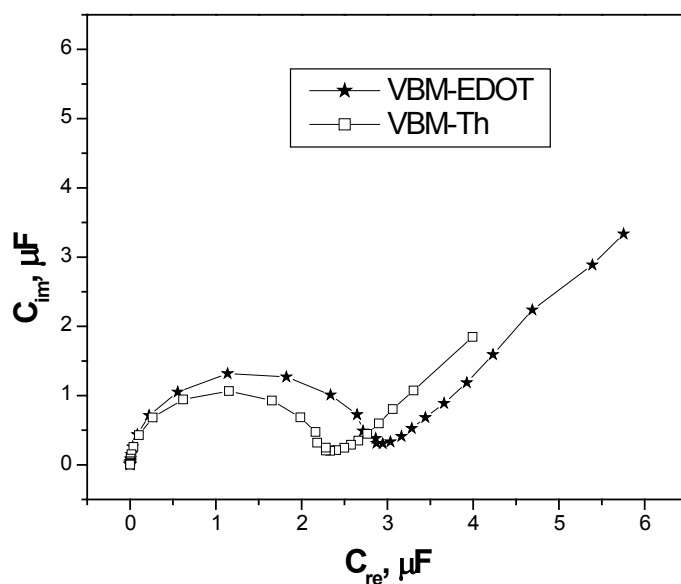


Figure 2.19 Capacitance plots for CFME/VBM-PEDOT (2.8) and CFME/VBM-PTh (2.9) in 0.05M TBAPF₆/DCM monomer free electrolyte solution, measured between 0.01Hz-100 kHz.

2.2.1.3 Thermal Analysis

The thermal properties of the VBM-EDOT and VBM-Th polymers with cationic organoiron moieties were studied using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The polymers containing cyclopentadienyliron cations coordinated to arenes in their backbones underwent at least two weight loss steps, including the first degradation at 148 °C for VBM-Th and 187 °C for VBM-EDOT due to the loss of the pendent iron complexes. Additional weight loss steps were observed starting between 340 °C and 680 °C and attributed to the backbone degradation for both polymers.

DSC analysis of the VBM-EDOT polymer containing the cationic organoiron complex demonstrated a significant glass transition temperature (T_g) at 71.5 °C while the VBM-Th

showed a T_g at 68°C. The TGA data for the cationic organoiron polymer are provided in Figure 2.20. As anticipated, polymers containing cyclopentadienyliron cations coordinated to arenes in their backbone experienced 34.8% weight losses at approximately 187 °C due to the loss of the pendant iron complexes and the polymer backbone degradation started at 310 °C with further 59.2% weight loss for VBM-EDOT polymer. On the other hand, the VBM-Th polymer started to degraded at 148 °C and experienced 22.2% weight loss due to the decomposition of cationic iron moieties and at around 360 °C polymer backbone degradation was observed with 38.3% weight loss.

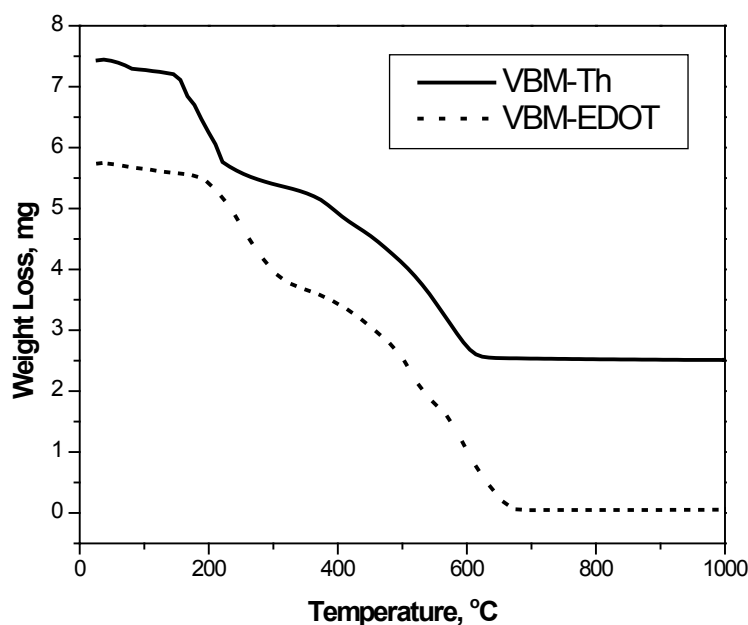


Figure 2.20 Thermal degradation of the VBM-PEDOT (2.8) and VBM-PTh (2.9) polymer with heating rates of 20 °C/min under nitrogen atmosphere.

Table 2.1 Thermal gravimetric analysis of polymer VBM-EDOT and VBM-Th.

Polymer	1st step Onset-Endset °C	Weight Loss (%)	2nd step Onset-Endset °C	Weight Loss (%)
VBM-EDOT (2.6)	187-298	34.8	310-671	59.2
VBM-Th (2.7)	148-231	22.2	361-608	38.3

2.2.1.4 Morphological Characterization

Polymer powders were examined in SEM at low voltages to avoid electron charging during imaging. The micrographs in Figure 2.21 suggest that the material consisted of particles of several scales. As Figure 2.21a (500x magnification) shows, polymer agglomeration on the macroscale occurred, with several large particles being in the 50-100 μm range. However, close examination of these particles (Figures 2.21b, 2.21c) suggest a fine substructure with distinct features. The larger substrate particles (labelled “A” in Figure 2.21c) typically had high aspect ratio morphology with smooth edges. In contrast, formation of fine spherical particulates (<500 nm) were observed (labelled “B” in Figure 2.21c) on the substrate particles. These spherical particulates were seen to form in clusters. Further work will be carried out using X-ray mapping to identify elemental composition of individual particles.

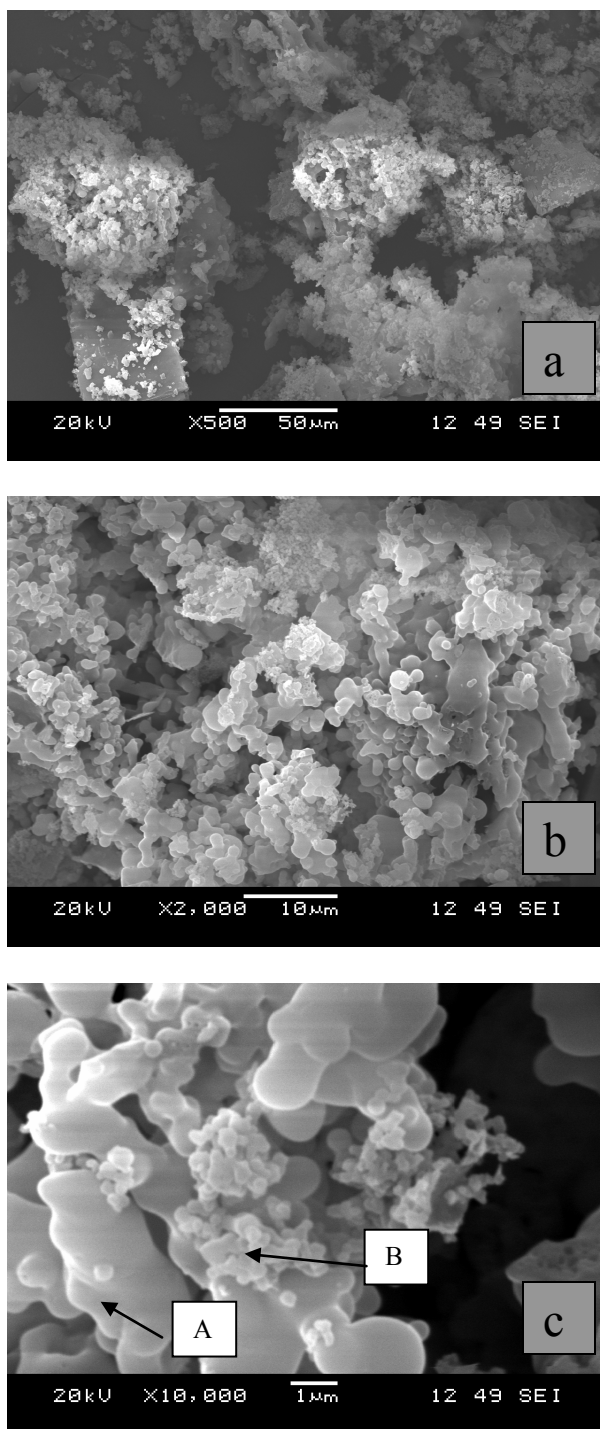


Figure 2.21 Morphological characterization of VBM-EDOT-bisphenol-A polymer (2.6) with SEM a) 500X, b) 2000X, c) 10000X magnifications.

The morphology of the films electrodeposited on CFME was illustrated in Figure 2.22. The SEM images indicate side view of the films deposited on the electrode surface. The

polymers were deposited homogeneously as continuous and very good adhering porous films, which is exhibiting even thickness on the fibre surfaces. The average thicknesses of the films were found to be approximately $0.9\mu\text{m}$ and $0.35\mu\text{m}$ for VBM-PEDOT and VBM-PTh, respectively. Note that bare carbon fibre exhibits striations along the fibre.

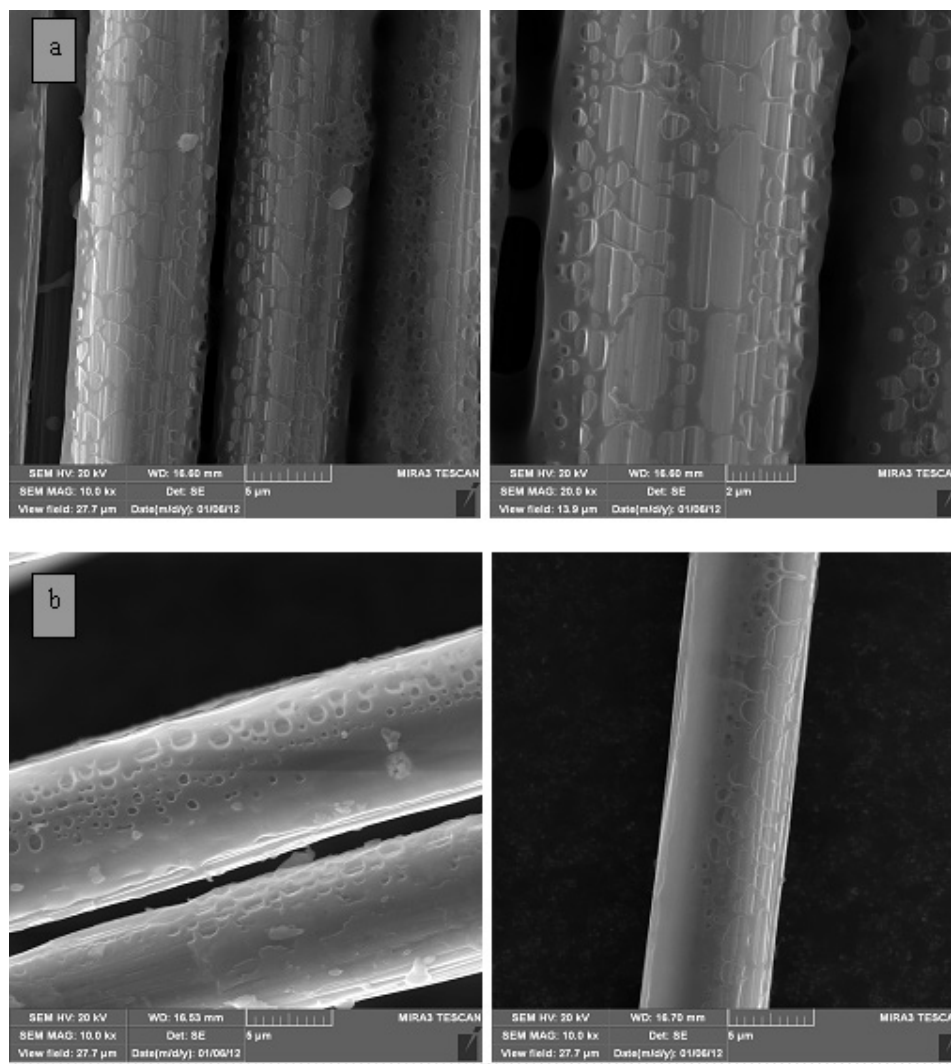
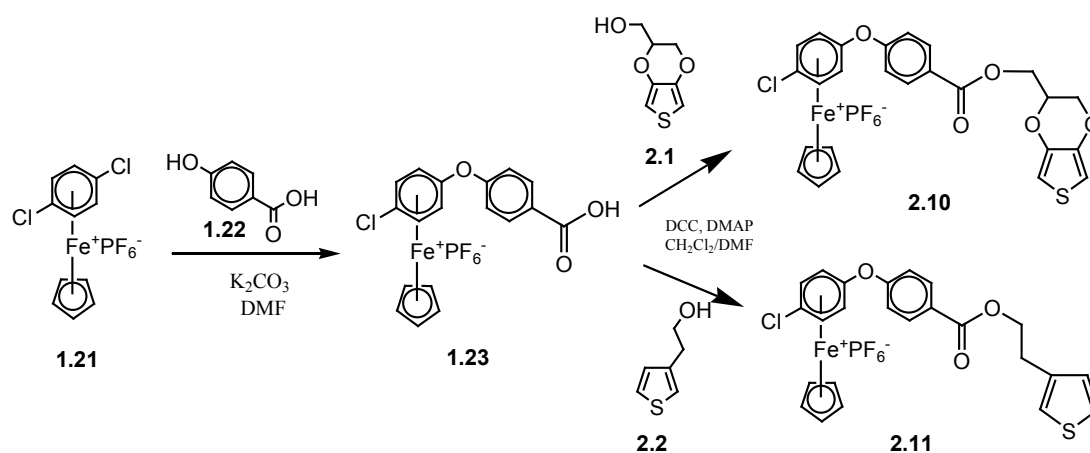


Figure 2.22 SEM images of electrochemically polymerized a) VBM-PEDOT (2.8) and b) VBM-PTh (2.9) on CFME (20 cycles).

2.2.2 Synthesis of Thiophene Derivatives with Cationic Mono-Metallic Complex

The exceptional electron-withdrawing ability of the cationic cyclopentadienyliron moiety allows for facile nucleophilic aromatic substitution reactions of complexed chloroarenes under mild reaction conditions. A monomer containing a single η^6 -arene- η^5 -cyclopentadienyliron (II) hexafluorophosphate moiety was reacted with 4-hydroxybenzoic acid. The acid complex with a cyclopentadienyliron moiety was synthesized at room temperature in DMF for 18 hours. The reaction temperature has to be kept in between 20- 25°C since higher temperatures lead to partial disubstitution of the arene whereas the low temperatures can lead to a mixture of starting material and product. The carboxylic group of this complex was subsequently reacted with terminal hydroxyl groups of hydroxymethyl EDOT and 2-(3-Thienyl)ethanol complex to produce the Acid complex-EDOT and Acid complex-Th via esterification reactions, respectively (Scheme2.3). In this part we report the synthesis and electrochemical characterization of Acid complex-EDOT and Acid complex-Th via esterification reaction polythiophene derivatives containing mono-cationic iron moiety as pendant to the backbone.



Scheme 2.3 Synthesis of Acid complex-EDOT (2.10) and Acid complex-Th (2.11).

Characterization of the monomer complexes were accomplished using NMR and IR analysis. The Cp containing acid complex showed peaks around the upfield region in the ^1H NMR (Fig.2.23 and Fig.2.26) scales. The complexed aromatic protons of the acid complex showed up at 6.84 and 6.55 ppm for both monomers, while the uncomplexed aromatic protons were found at 8.07 and 7.43 ppm for Acid complex-Th and 8.12 ppm and 7.44 ppm for Acid complex-EDOT monomer due to the electron withdrawing effect of ethylenedioxy group. The Cp peak appeared at 5.30 ppm for acid complex. The disappearance of carboxylic OH group (13.0 ppm) and proton of the terminal hydroxyl group of starting material (5.04 ppm for EDOT and 4.67 ppm for 2-(3-Thienyl)ethanol) indicated successful esterification reactions. The incorporation of EDOT is proved by the appearance of peaks at 4.18, 4.40 and 4.57 ppm, whereas 2-(3-Thienyl) ethanol has peaks at 7.11, 7.33 and 7.49 ppm.

The ^{13}C NMR spectrum (Fig.2.24 and Fig.2.27) and the HSQC spectrum (Fig.2.25 and Fig.2.28) also confirmed the structures indicating the shift and new carbon peak assignments. In ^{13}C NMR spectrum the quaternary carbons of EDOT shifted to 141.12 and 141.09 ppm and the carbonyl carbon showed up at 164.55 ppm whereas the quaternary carbon of 2-(3-Thienyl) ethanol appeared at 121.62 ppm and the carbonyl carbon showed up at 164.68 ppm. The Cp carbons assignments appeared at 79.55 and 79.44 for acid complex-EDOT and acid complex-Th, respectively. Additionally, the 2D-HSQC NMR spectrum indicated a good correlation between proton and the carbon environments.

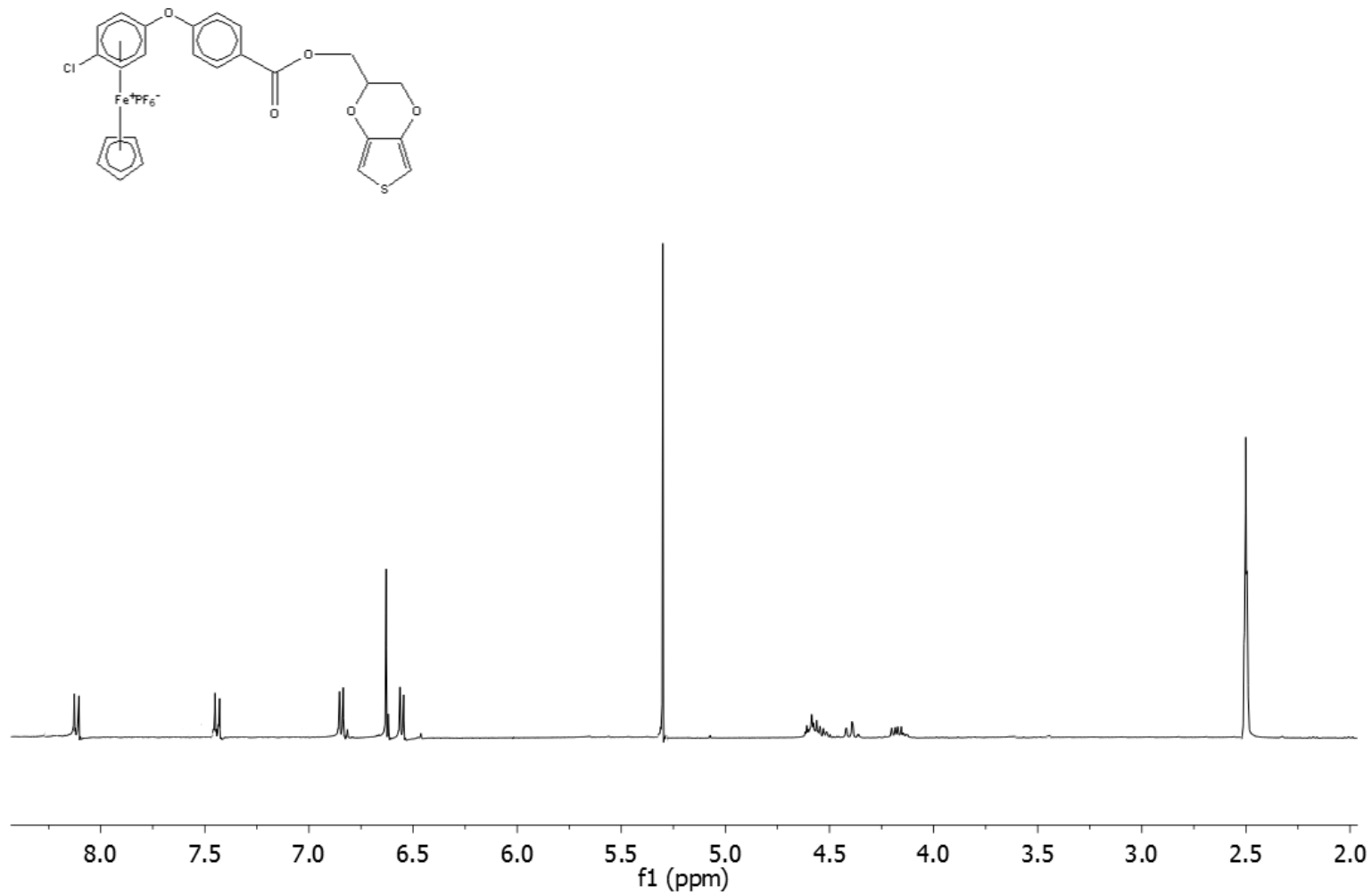


Figure 2.23 ^1H NMR spectrum for Acid complex-EDOT (2.10).

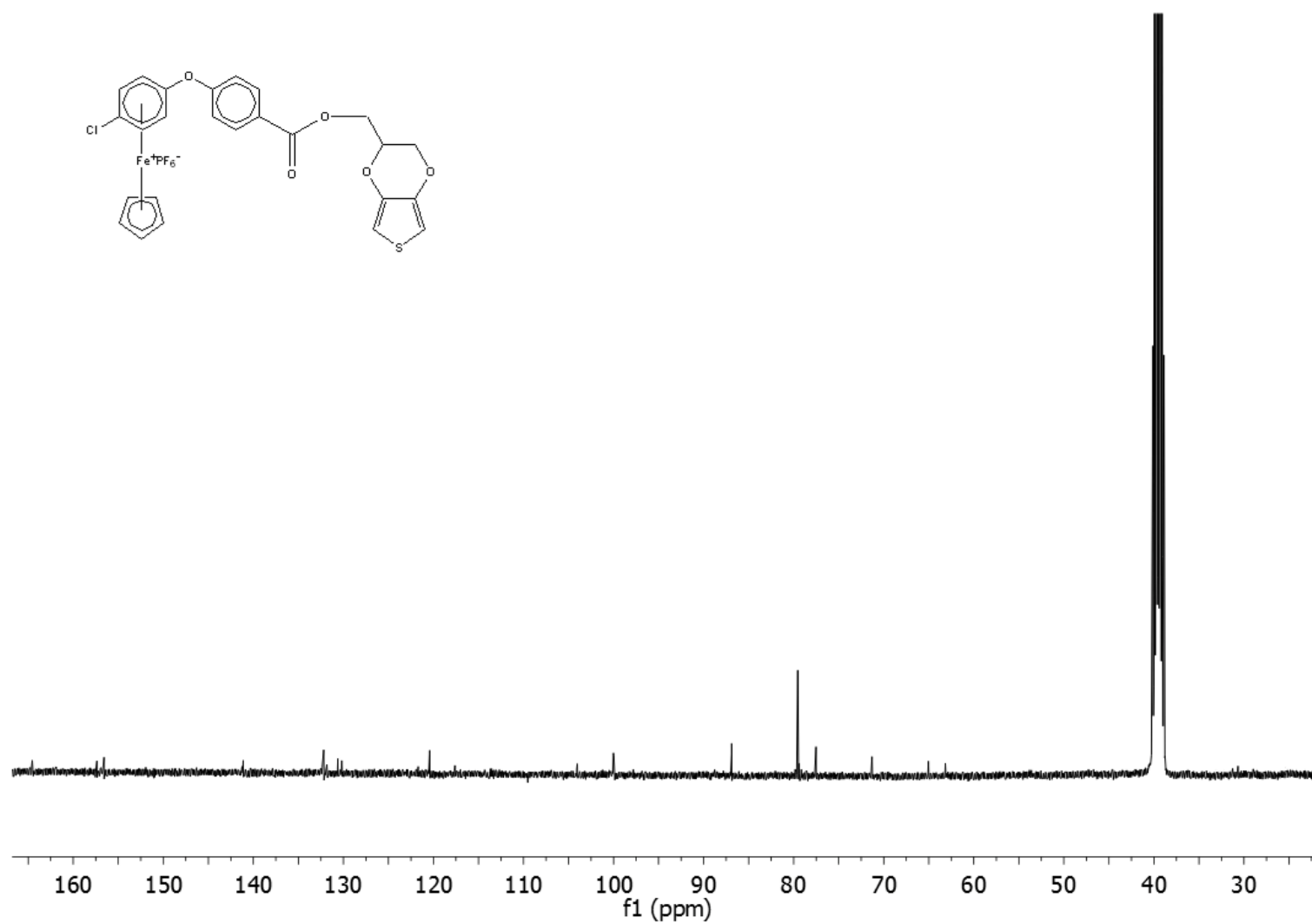


Figure 2.24 ^{13}C NMR spectrum for Acid complex- EDOT (2.10).

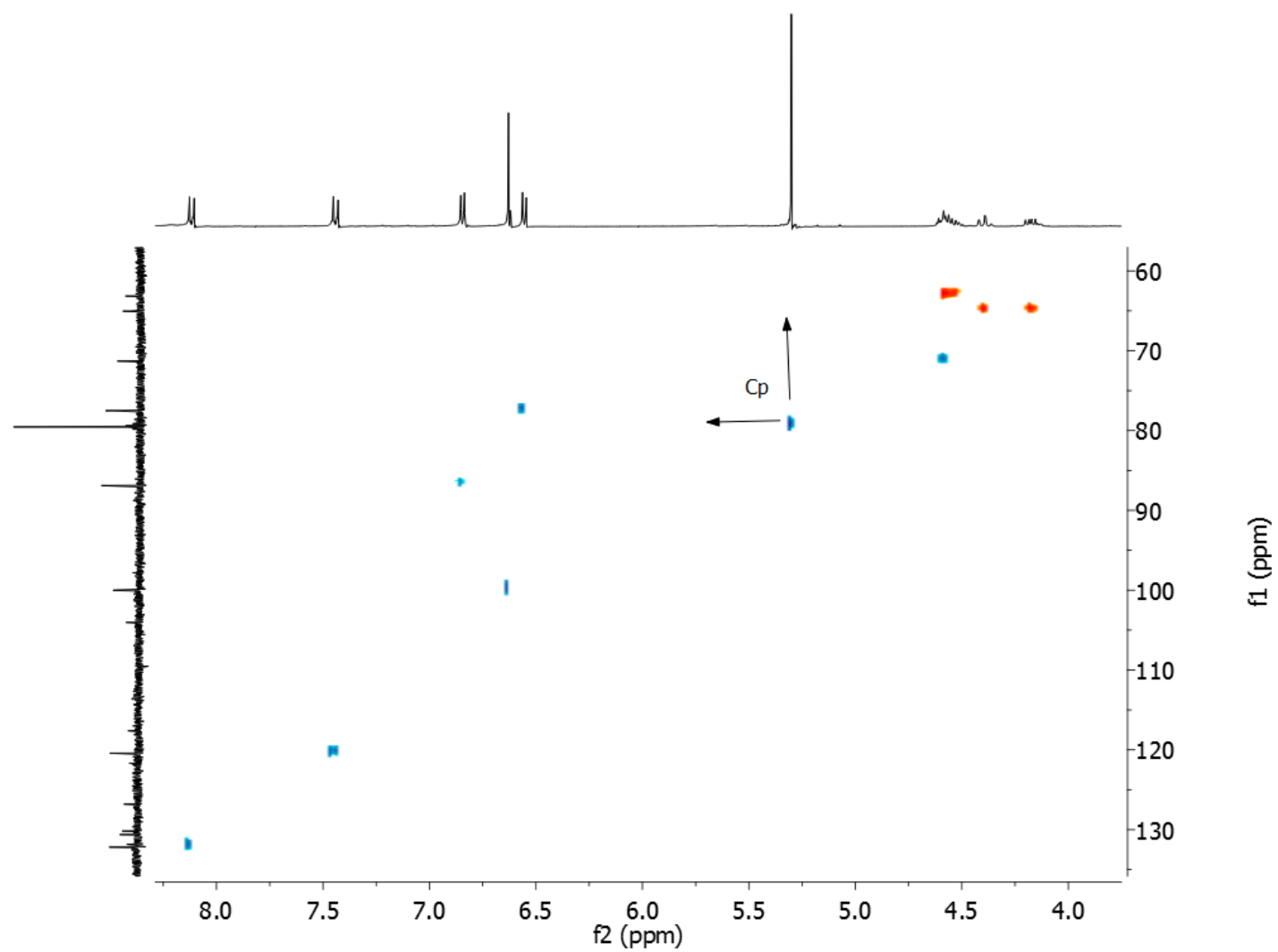


Figure 2.25 2D-HSQC NMR spectrum of the Acid complex- EDOT (2.10).

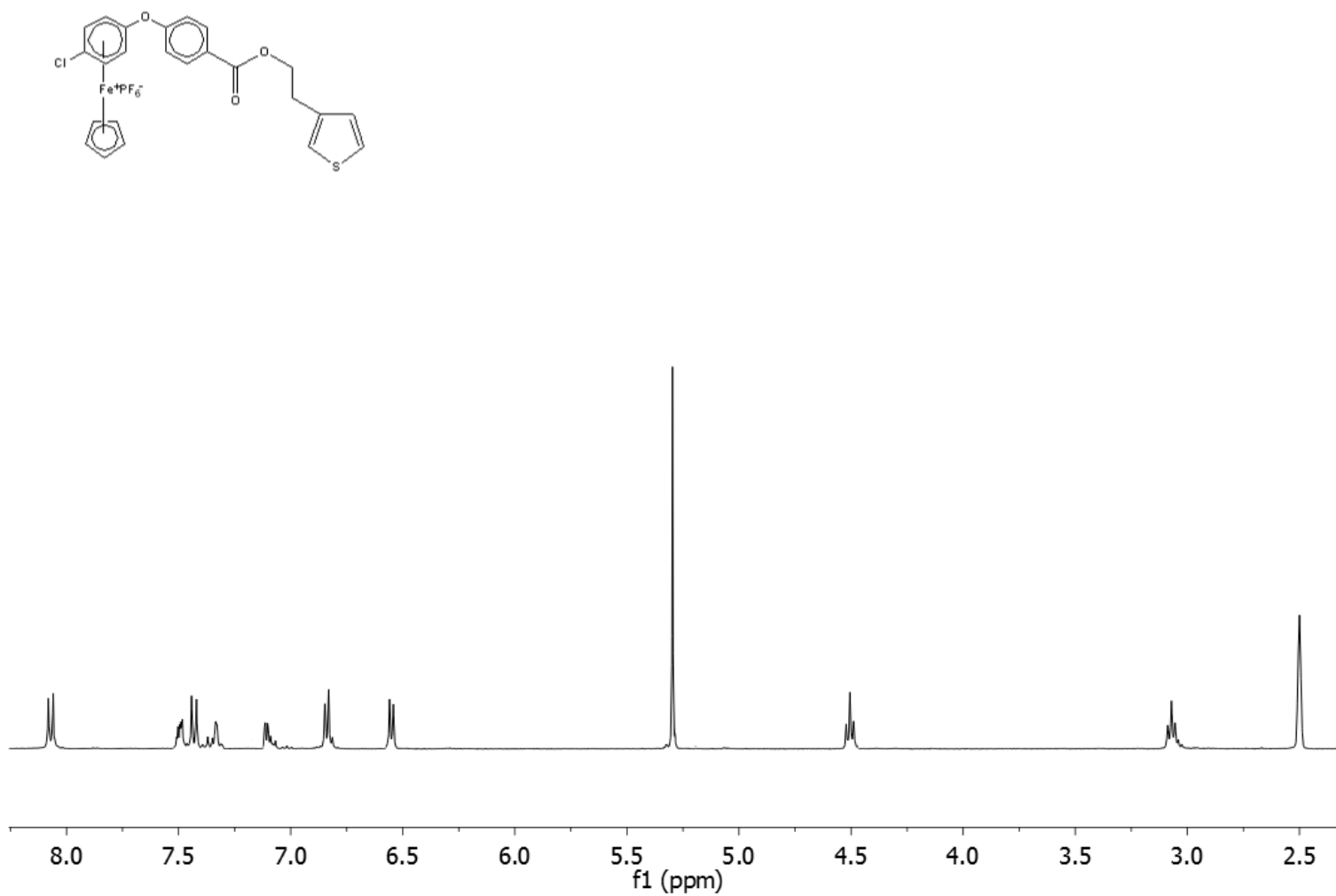


Figure 2.26 ^1H NMR spectrum for Acid complex-Th (2.11).

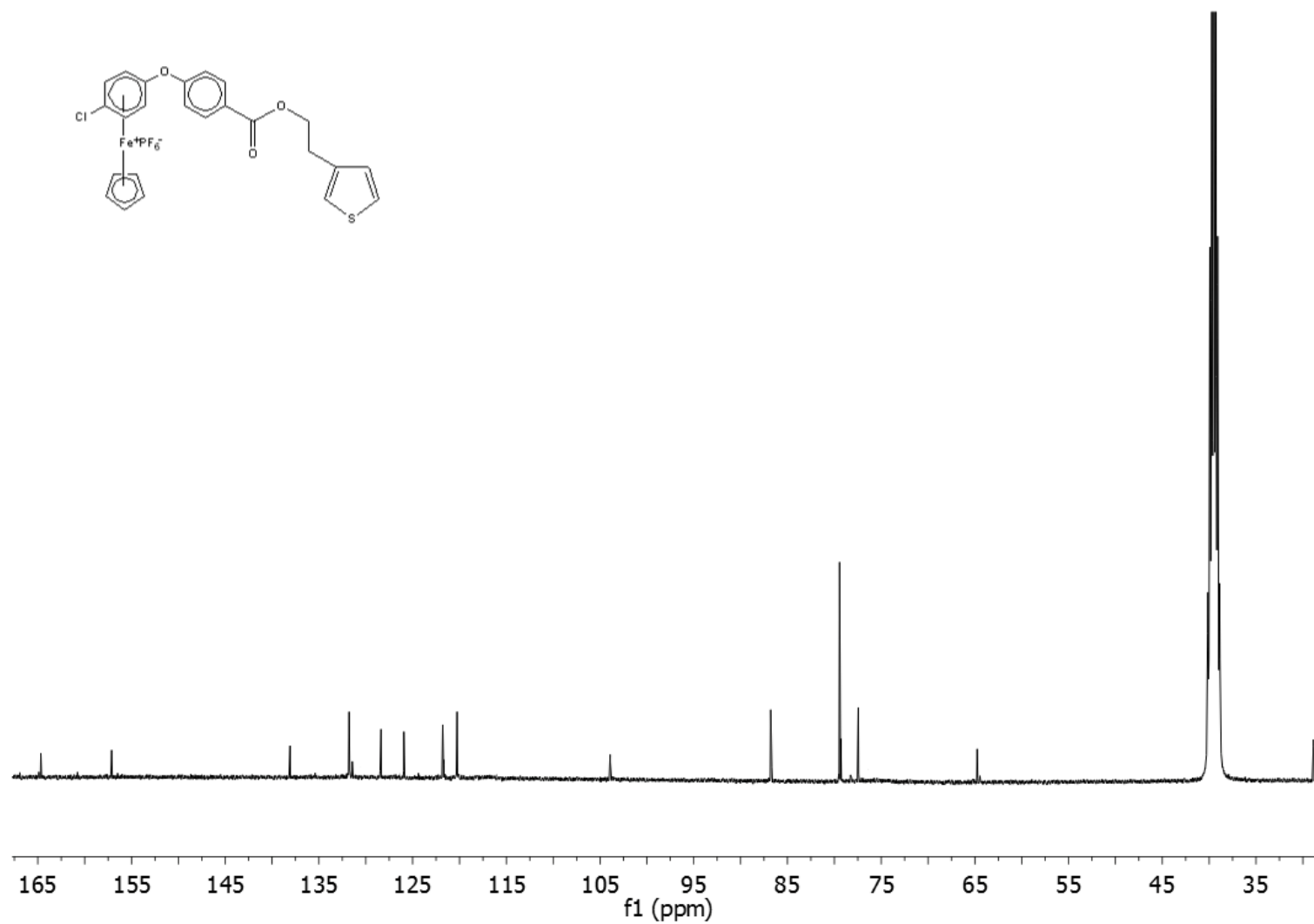


Figure 2.27 ^{13}C NMR spectrum for Acid complex- Th (2.11).

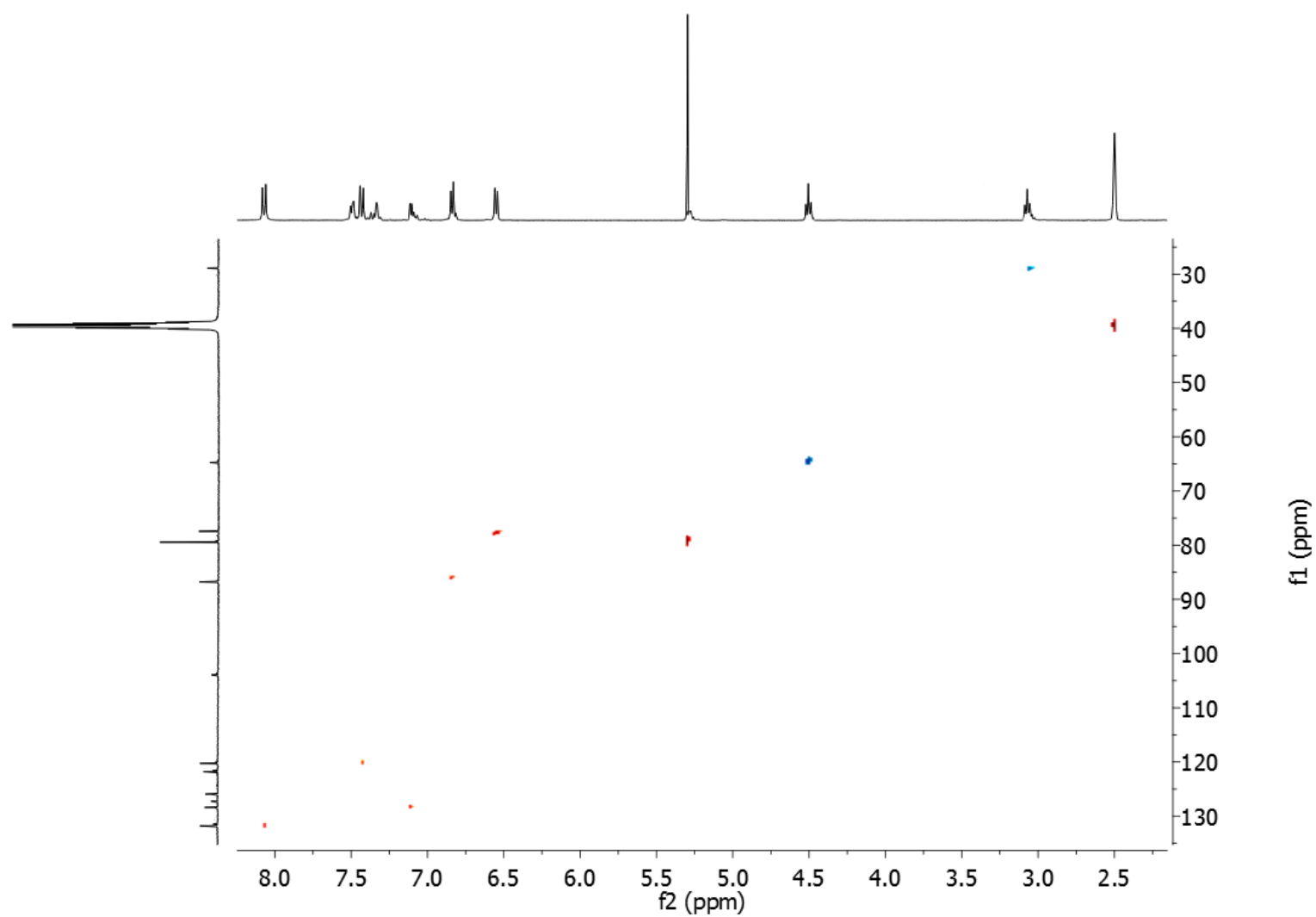


Figure 2.28 2D-HSQC NMR spectrum of the Acid complex- Th (2.11).

2.2.2.1 Electropolymerization of EDOT and Thiophene with Monocationic Acid Complex

The electro-oxidation of Acid complex-EDOT (**2.10**) and Acid complex-Th (**2.11**) was carried out in 0.05M TBAPF₆/DCM as supporting electrolyte solution on carbon fibre micro electrodes with scan rate of 100 mVs⁻¹ at -35°C. The schematic representations of conducting PEDOT and PTh were illustrated in Figure 2.29 and Figure 2.33, respectively.

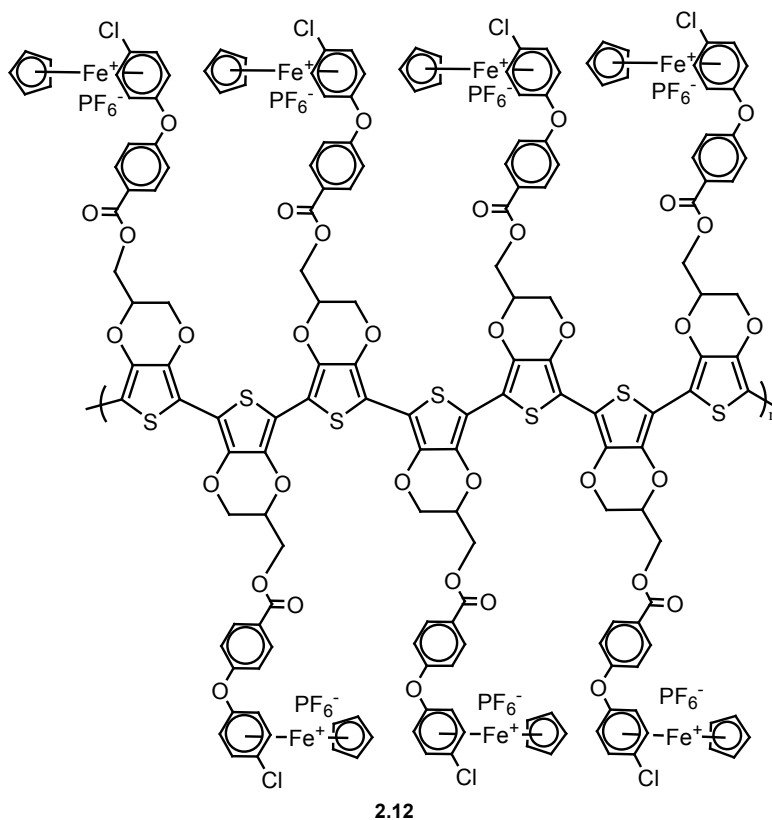


Figure 2.29 Schematic representation of electrochemically polymerized Acid complex-PEDOT (2.12) conducting polymer.

Since the monomer has a cationic iron centre, a single reversible redox wave was observed corresponding to the conversion from 18 e⁻ to 19 e⁻ iron centres. The cyclic voltamogram of the complexes at 100 mVs⁻¹ indicated redox couples at E_{1/2} = -1.32 V (Acid complex-EDOT) (Fig.2.30) and E_{1/2} = -1.46 V (Acid complex-Th) (Fig.2.34), indicating the

reduction of the cationic iron moiety. These half wave potentials are lower than the ones for oxygen-substituted arene complexes due to the characteristic of arene-cyclopentadienyliron complexes containing an electron-donating substituent.

The Acid complex-Th monomer oxidation potential was observed at 1.23 V. Although the cyclic voltamogram exhibits good oxidation waves ($E_{p,ox1} = -1.18$ V, $E_{p,ox2} = 1.76$ V), the cathodic reduction waves ($E_{p,red1} = -1.67$ V, $E_{p,red2} = 1.48$ V) are very weak and unclear.

The peak potential difference (ΔE) for Acid complex-EDOT was calculated as 48mV indicating the reversibility of the electro coating process which is correlated with peak current ratios ($I_a/I_c=0.87$). On the other hand, ΔE for Acid complex-Th polymer was calculated as 280mV proving the irreversibility of the voltamogram. Comparison of ΔE values for polymer films indicated that the Acid complex-Th polymer film has a greater thickness. This is expected since an increase in polymer film thickness leads to an increase in resistance for ion penetration. The electropolymerization charge for Acid complex-Th film ($\Delta Q=58.74$ mC) was found lower than Acid complex-EDOT polymer ($\Delta Q=78.2$ mC) film.

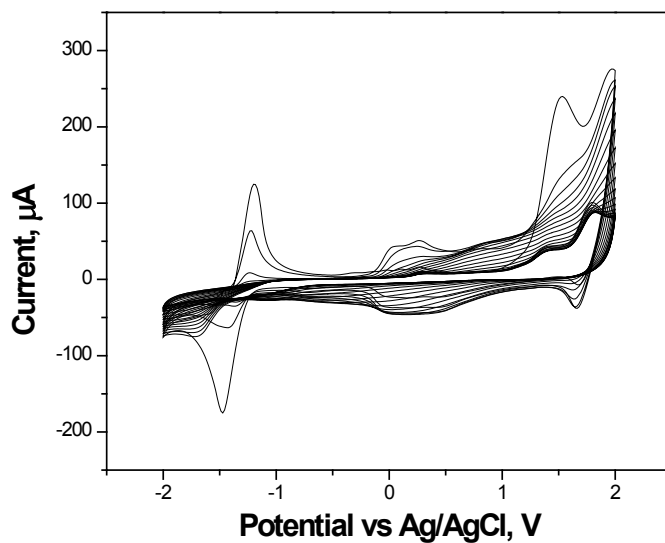


Figure 2.30 Repeated potential scan electropolymerization of the Acid complex-EDOT (2.10) monomer at 100 mVs^{-1} in 0.05 M in $\text{TBAPF}_6^-/\text{DCM}$ on CFME at -35°C .

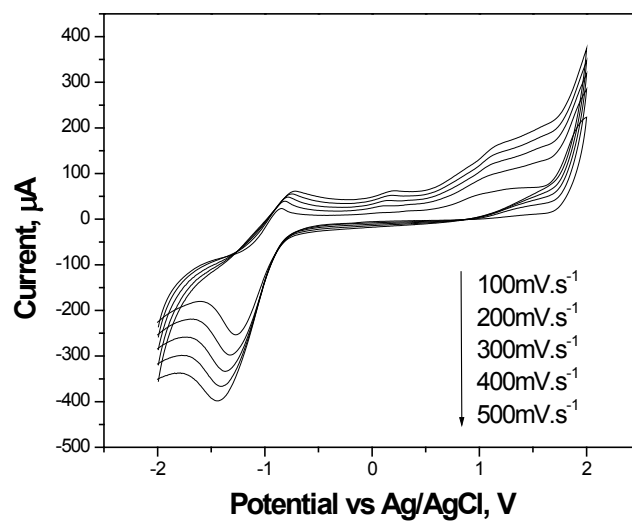


Figure 2.31 Cyclic voltamogram of the Acid complex-PEDOT (2.12) film in 0.05M $\text{TBAPF}_6^-/\text{DCM}$ monomer free solution electrolyte solution at scan rates of $100, 200, 300, 400$ and 500 mVs^{-1} .

Figure 2.31 illustrates the scan rate dependencies of the VBM-PEDOT film between 100 and 500 mVs^{-1} in 0.05M TBAPF₆/DCM, demonstrating the quasi-reversible redox process of the polymer film. The anodic oxidation (R_a) and cathodic reduction (R_c) peak's correlation coefficients were calculated as 0.986 and 0.984 whereas R_a and R_c were found as 0.997 and 0.961 from square root of scan rate versus current plot, respectively (Fig.2.32). According to the *Randles-Sevcik* equation, there is a thin film formation on the electrode surface but it is not a diffusion controlled process.

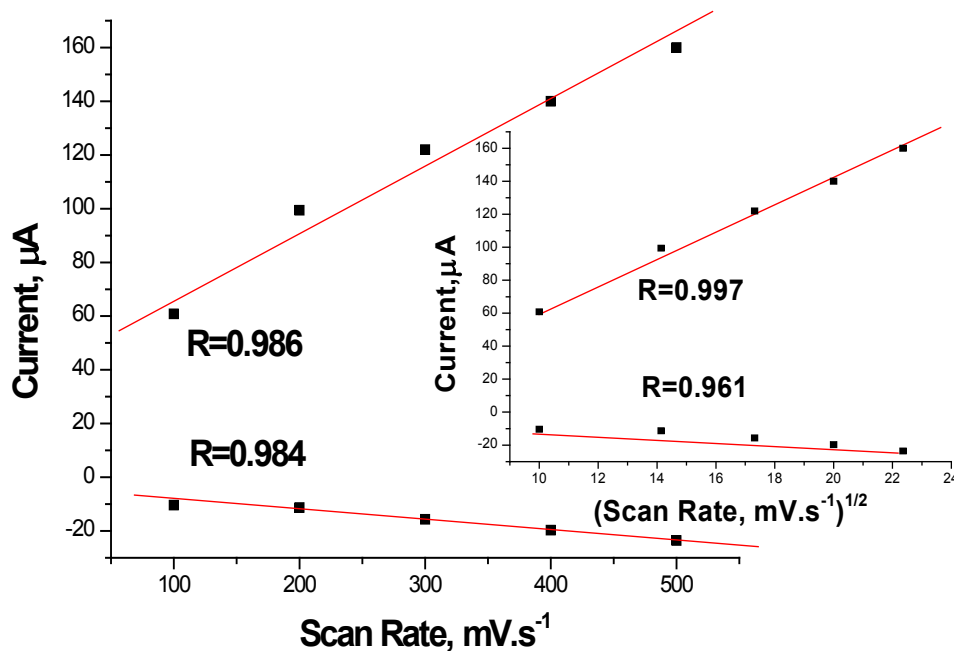


Figure 2.32 Anodic and cathodic peak current density vs. scan rate and dependence of Acid complex-PEDOT (2.12) thin film in 0.05M TBAPF₆/DCM monomer free electrolyte solution. Inset: Anodic and cathodic peak current density vs. square root of scan rate.

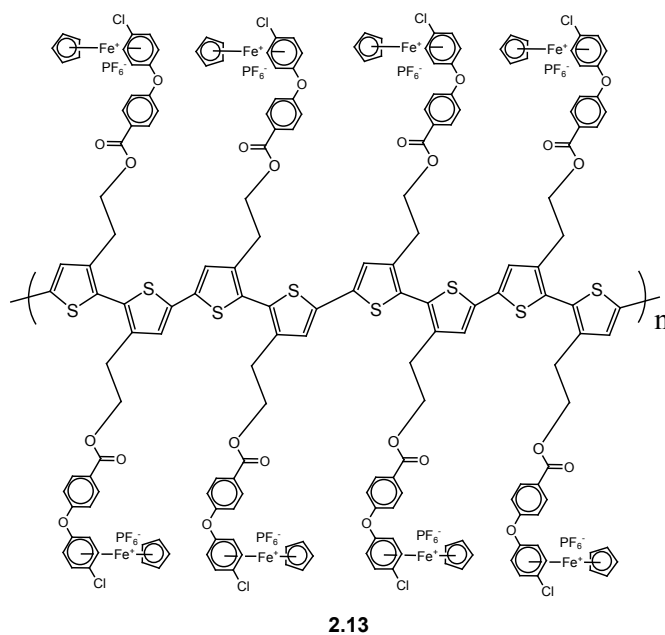


Figure 2.33 Schematic representation of electrochemically polymerized Acid complex-Th conducting polymer.

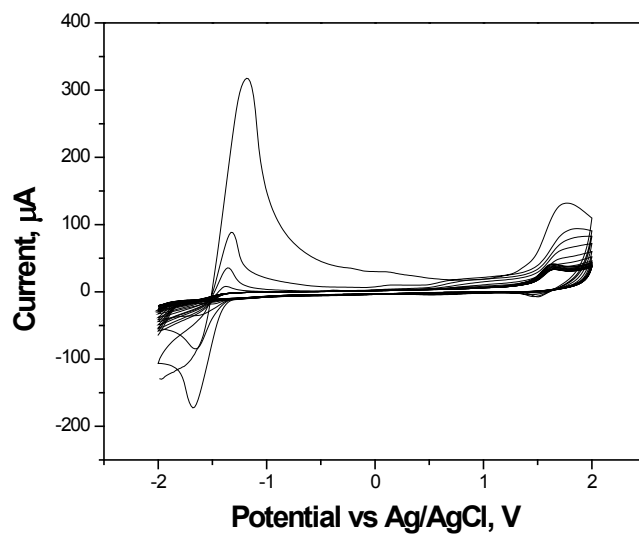


Figure 2.34 Repeated potential scan electropolymerization of the Acid complex-Th (2.11) monomer at 100 mVs⁻¹ in 0.05 M in TBAPF₆/DCM on CFME at -35 °C.

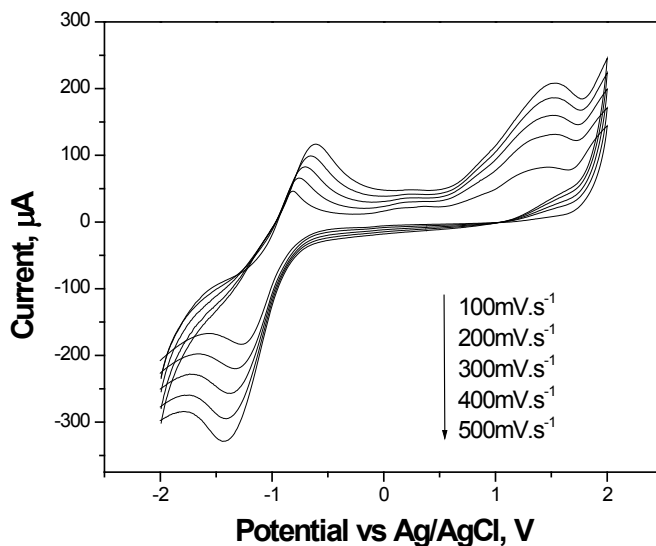


Figure 2.35 Cyclic voltammogram of the Acid complex-PTh (2.13) film 0.05M TBAPF₆/DCM in monomer free solution, at scan rates of 100, 200, 300, 400 and 500 mVs⁻¹.

The scan rate dependencies of the VBM-PTh film (Fig.2.35) between 100 and 500 mVs⁻¹ in 0.05M TBAPF₆/DCM was represented in Figure 2.35. This polymerization reaction was found as diffusion controlled process due to the linearity of the current values ($R_a=0.998$, $R_c=0.987$) according to the Randles-Sevcik equation which provides evidence for chemically reversible redox process as opposed to the cases where redox causes major structural change in the analyte.

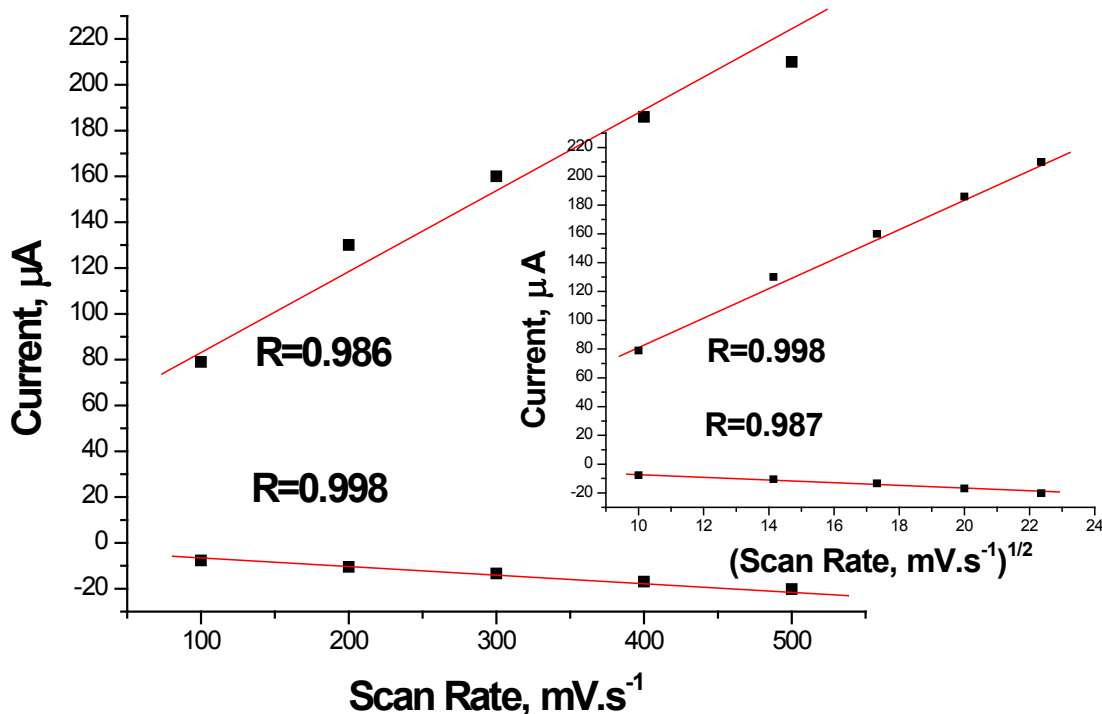


Figure 2.36 Anodic and cathodic peak current density vs. scan rate and dependence of Acid complex-PTh (2.13) thin film in 0.05M TBAPF₆/DCM monomer free solution. Inset: Anodic and cathodic peak current density vs. square root of scan rate.

2.2.2.2 Electrochemical Impedance Spectroscopic Characterization

EIS measurements were achieved in 0.05M TBAPF₆/DCM monomer-free electrolyte solution with perturbation amplitude 10mV over a frequency range of 0.01Hz to 100 kHz with PARSTAT 2273. The Nyquist plots for the Acid complex-PEDOT and Acid complex-PTh were studied to observe the capacitance values for modified CFME (Figure 2.37). The low frequency capacitance (C_{sp}) values of electrochemically deposited thin films (at 0.01 Hz) were calculated as 377 μFcm^{-2} and 151.5 μFcm^{-2} for PEDOT and PTh films, respectively. The data comparison indicates that Acid complex-PTh showed a more perpendicular line to the imaginary axis indicating faster electron transfer and more charge storage capacity. However, at low frequencies

Acid complex-PEDOT showed quite capacitive behaviour, and it approaches the real axis indicating resistive behaviour. In this case, Acid complex-PTh is preferred for electrochemical capacitor applications due to fast charge/discharge processes and faster electron transfer.

The Bode magnitude plot expresses the magnitude of the frequency response gain, whereas the Bode phase plot expresses the frequency response phase shift. In the frequency region of 0.79Hz-2.7Hz phase angles (Acid complex-PEDOT: 81.7°, Acid complex -PTh: 82.6°) approached a plateau for a very short time interval. The phase transition from capacitor to resistor was observed around the frequency range between 7.14Hz and 678Hz, and after 1480Hz polymer films indicated resistor behaviour (Figure 2.38).

Double layer capacitance values were calculated as 606 μFcm^{-2} and 500 μFcm^{-2} for Acid complex-PEDOT and Acid complex-PTh, respectively (Figure 2.39). As a result of the Bode magnitude plots, the Acid complex-PEDOT film was found to be thicker and to have higher capacitive behaviour.

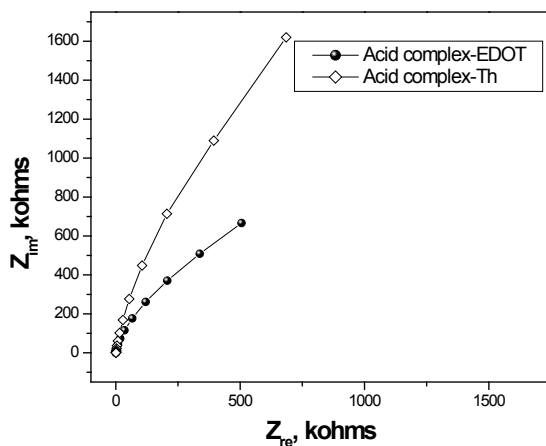


Figure 2.37 Nyquist plots for CFME/Acid complex-PEDOT (2.12) and CFME/Acid complex-PTh (2.13) in 0.05M TBAPF₆/DCM monomer free electrolyte solution, measured between 0.01Hz-100kHz.

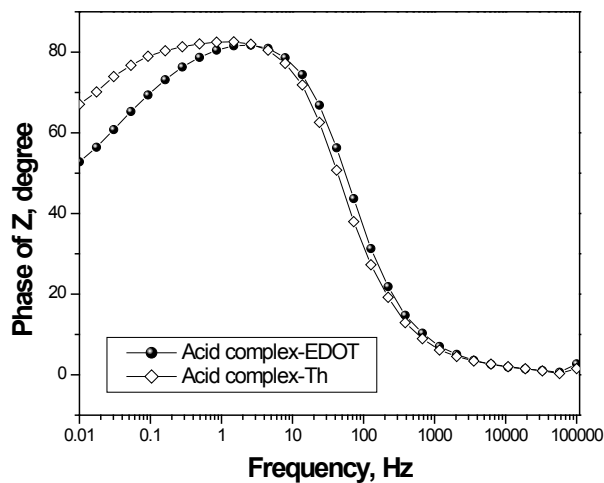


Figure 2.38 Bode Phase diagrams for CFME/Acid complex-PEDOT (2.12) and CFME/Acid complex-PTh (2.13) in 0.05M TBAPF₆/DCM monomer free electrolyte solution, measured between 0.01Hz-100kHz.

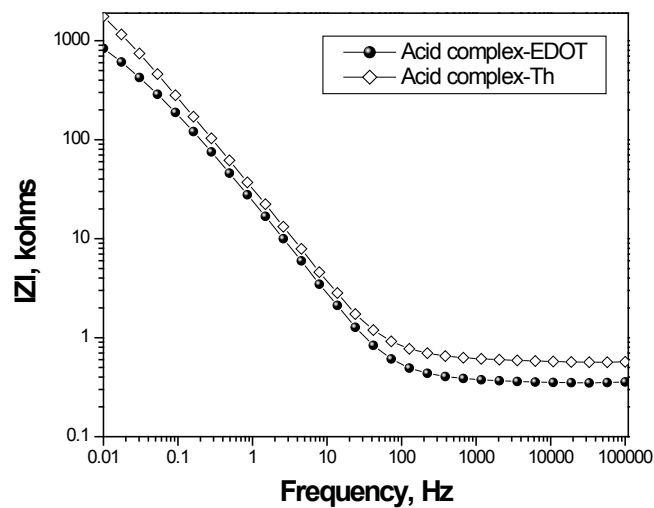


Figure 2.39 Bode magnitude plots for CFME/Acid complex-PEDOT (2.12) and CFME/Acid complex-PTh (2.13) in 0.05M TBAPF₆/DCM monomer free electrolyte solution, measured between 0.01Hz-100kHz.

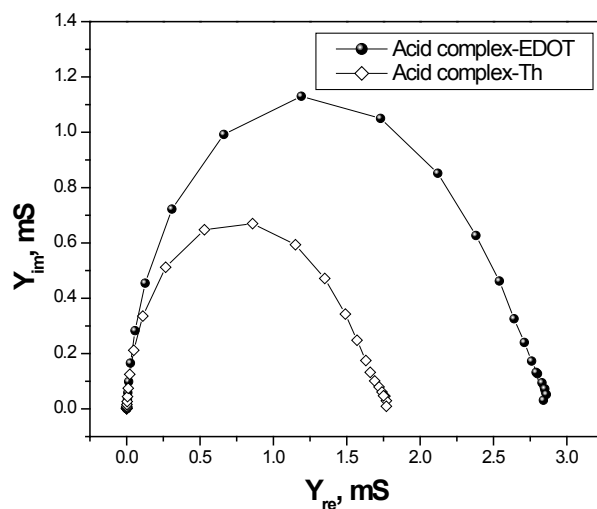


Figure 2.40 Admittance plots for CFME/Acid complex- PEDOT (2.12) and CFME/Acid complex-PTh (2.13) in 0.05M TBAPF₆/DCM monomer free electrolyte solution, measured between 0.01Hz-100kHz.

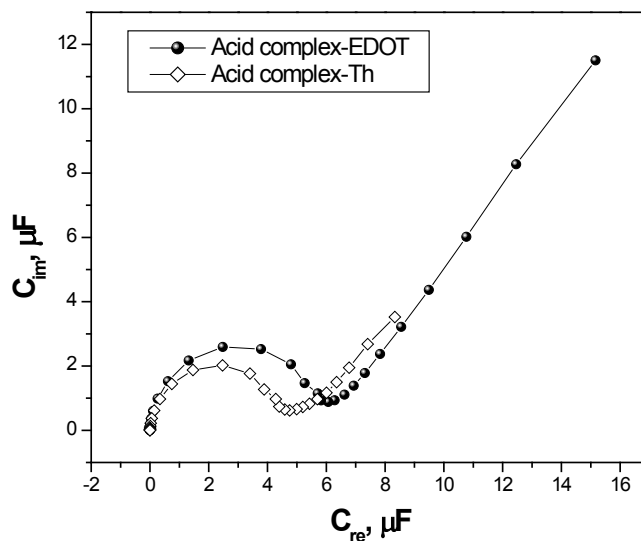


Figure 2.41 Capacitance plots for CFME/Acid complex- PEDOT (2.12) and CFME/Acid complex-PTh (2.13) in 0.05M TBAPF₆/DCM monomer free electrolyte solution, measured between 0.01Hz-100kHz.

The electrochemical conductivities were determined 16 mScm⁻² for Acid complex-PEDOT and 9.84 mScm⁻² for the Acid complex-PTh film. Admittance (Fig.2.40), capacitance (Fig.2.41) and Bode plots (Fig.2.39) all indicate the better film properties for Acid complex-PEDOT polymer in terms of film thickness, electrical conductivity and charge storage ability compared to the Acid complex-PTh.

2.2.2.3 Morphological Analysis

The morphologies of modified CFME were investigated by scanning electron microscopy for the samples obtained by potentiodynamic growth. Morphology of the coated films strongly depends on the deposition charge but film thickness does not show a linear relation with the increase of deposition charge. PEDOT and PTh derivatives are generally electropolymerized in the presence of small anions which affect the morphology of the films. In this case, the nature of

the PF_6^- anion associated with the tetra butyl ammonium cation affected the surface morphology and the electrochemical properties of the Acid complex-PEDOT and Acid complex-PTh compounds.

The film thicknesses were calculated as $2.4\mu\text{m}$ and $1.9\mu\text{m}$ for Acid complex-PEDOT and Acid complex-PTh, respectively. When comparing the electrodeposited films on the surface, the Acid complex-PEDOT indicates a more uniform film with some particles on it whereas the Acid complex-PTh indicated a well-distributed micro-sized porous film. Furthermore, PEDOT films proved to be the most problematic for studying the surface morphology. As seen by SEM micrographs in Figure 2.42, PEDOT films grew both as film and fine precipitate due to the additional solubility imparted by the ethylenedioxy moiety. Rather than rapidly condensing on the electrode surface, oligomeric radical cations generated at the electrode were able to diffuse away from the electrode surface. When they started to precipitate from solution, it appeared as partially flocculating powder. There is also compatibility between organic solvent and polymer; PEDOT films swelled during the coating process.

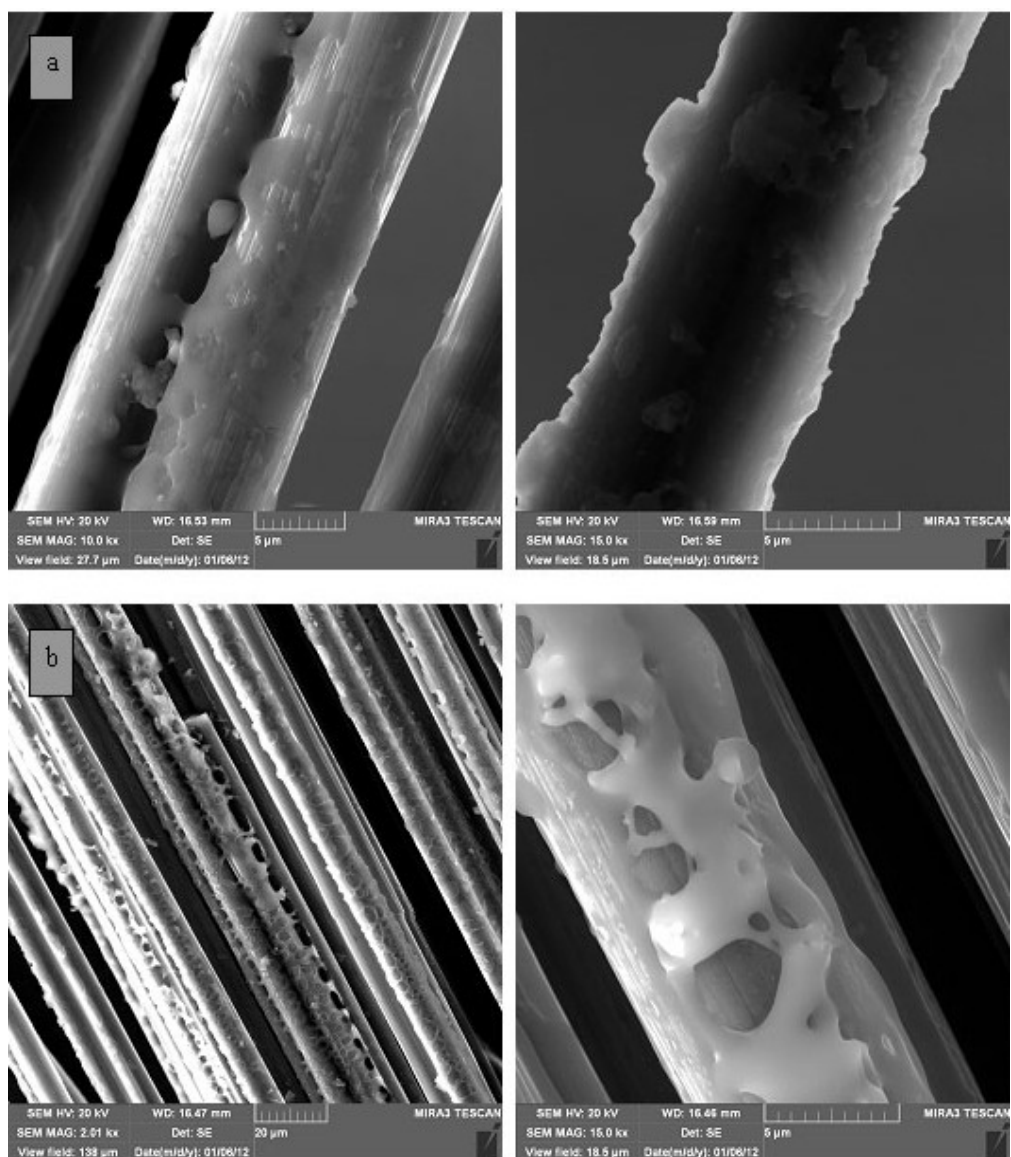


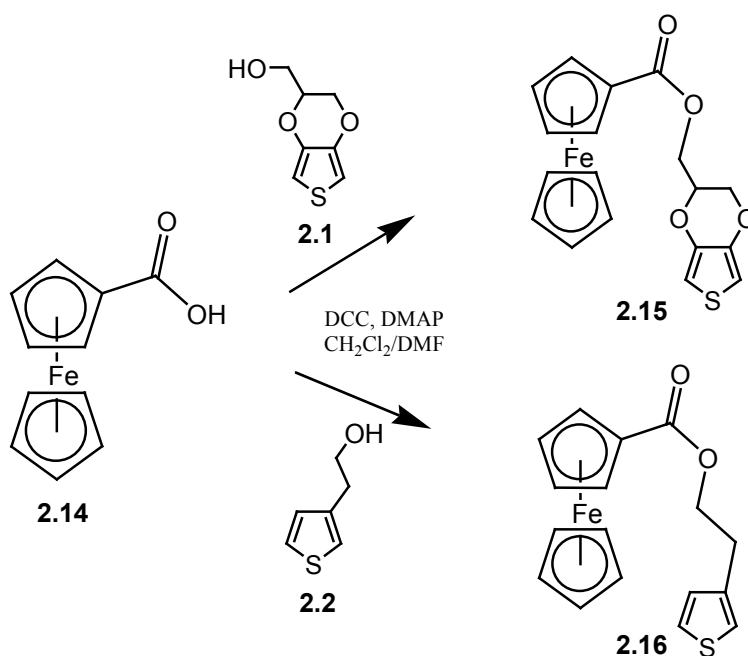
Figure 2.42 SEM images of electropolymerized a) Acid complex-PEDOT (2.12) and b) Acid complex-PTh (2.13) on CFME.

2.2.3 Synthesis of Thiophene Derivatives with Ferrocene Pendant

The electronic interaction between pendant ferrocene groups and a polythiophene backbone was studied via polymer films prepared from Fc-EDOT and Fc-Th monomers (Scheme 2.4). These films show maximum conductivity at the ferrocenyl redox potential. Electrochemical

measurements revealed that the iron-centered oxidations increased the conductivity and the shorter linkers lowered the onset potential.

Introduction of a hydroxymethyl group at the ethylene bridge of EDOT and then further functionalization was achieved via esterification reaction leading Fc-PEDOT polymers through anodic oxidation. On the other hand, 2-(3-Thienyl)ethanol and ferrocene carboxylic acid underwent esterification reactions to have pendant ferrocene groups. The insertion of a ferrocene unit in the precursor structure lead to a further decrease in the polymerization potential and enhanced the efficiency of the electropolymerization process.



Scheme 2.4 Synthesis pathway for Fc-EDOT (2.15) and Fc-Th (2.16).

The esterification reactions were identified by the disappearance of carboxylic OH resonance at 12.13 ppm and the disappearance of terminal hydroxyl protons at 5.04 ppm for EDOT and 4.67 ppm for 2-(3-Thienyl)ethanol). The ¹H NMR spectrum of Fc-EDOT (Fig. 2.43) and Fc-Th (Fig. 2.46) confirmed complete synthesis due to the presence of a new Cp resonance

at 4.15 ppm caused by the non-functionalized Cp ring of the ferrocene as well as by the two resonances due to the functionalized Cp ring at 4.79 ppm and 4.45 ppm for Fc-EDOT monomer while the non-functionalized Cp resonates at 4.12 ppm and the functionalized Cp peaks showed up at 4.47 ppm and 4.71 ppm for Fc-Th monomer. The ester CH₂ of Fc-Th monomer appears at 63.372 ppm in ¹³C NMR spectrum (Fig. 2.44 and Fig. 2.47), which is a large shift from its analogous alcohol at 61.82 ppm. This shift is clearly due to the increased electron withdrawing nature of the ester. Additionally, the quaternary carbon of EDOT appeared at 141.12 ppm and the carbonyl carbon showed up at 170.35 ppm, whereas the quaternary carbon of 2-(3-Thienyl) ethanol at 138.53 ppm and the carbonyl carbon showed up at 170.54 ppm. Further characterization was achieved with 2D HSQC NMR, illustrated in figure 2.45 and figure 2.48.

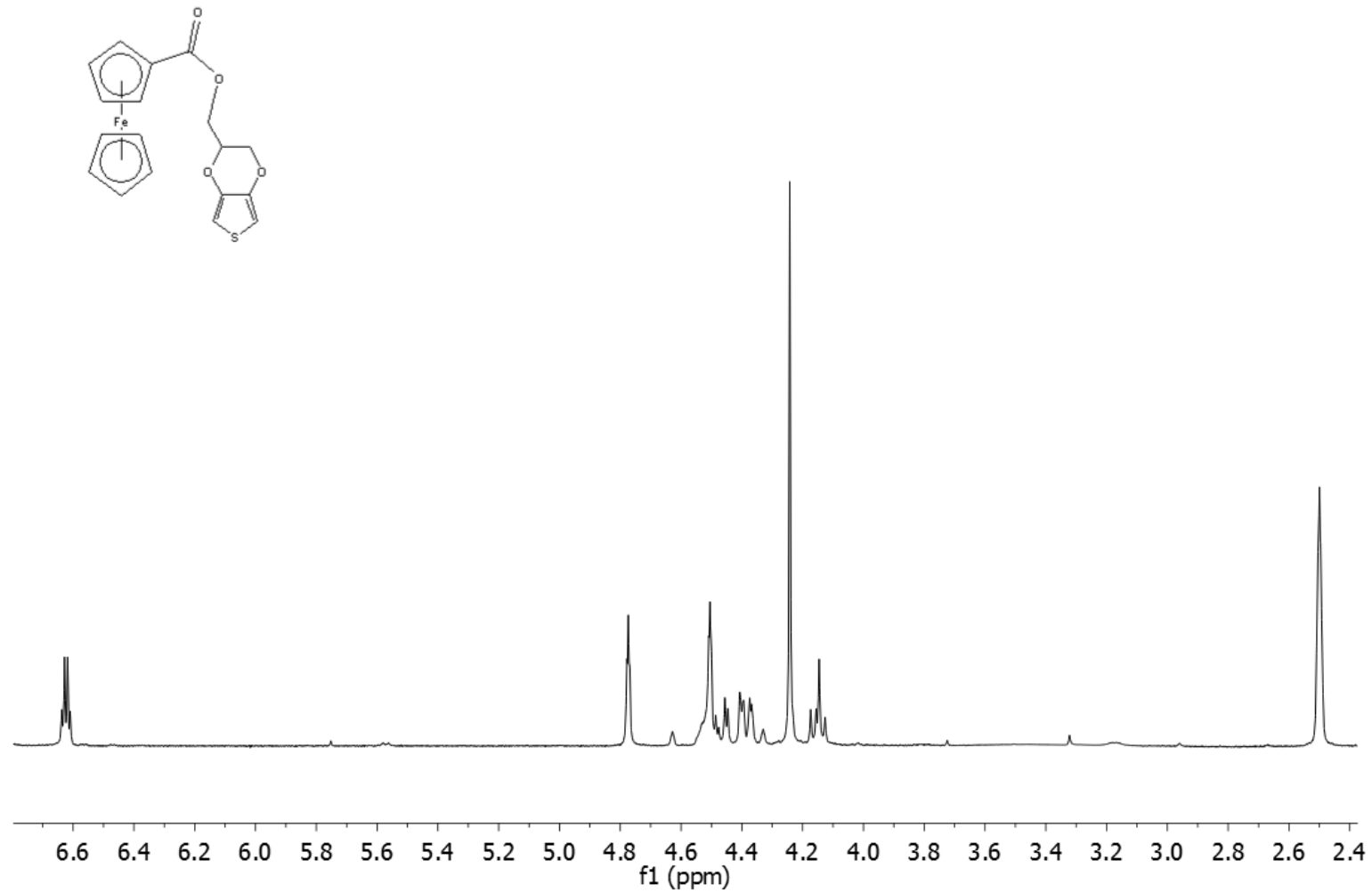


Figure 2.43 ^1H NMR spectrum for Fc-EDOT (2.15).

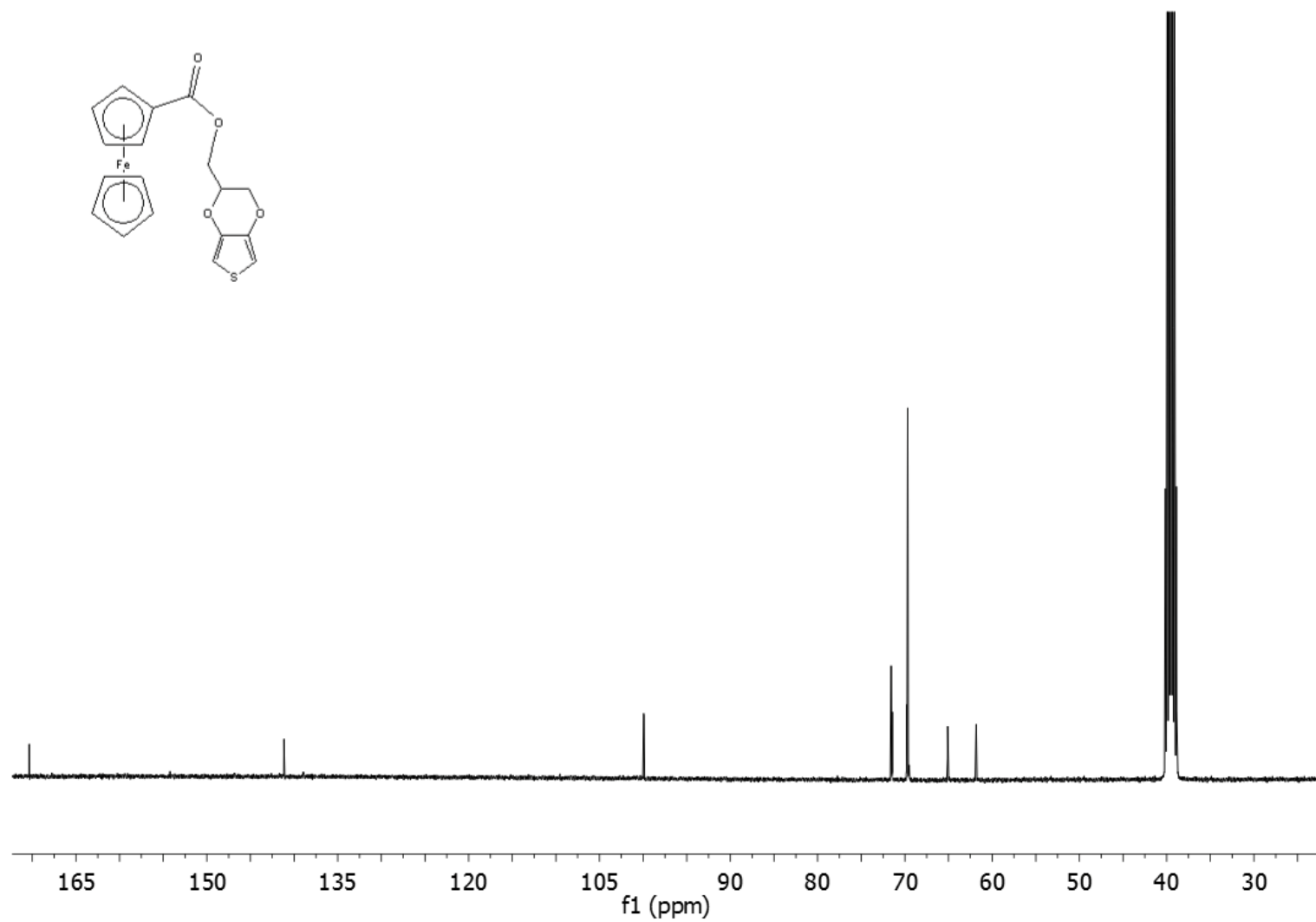


Figure 2.44 ^{13}C NMR spectrum for Fc- EDOT (2.15).

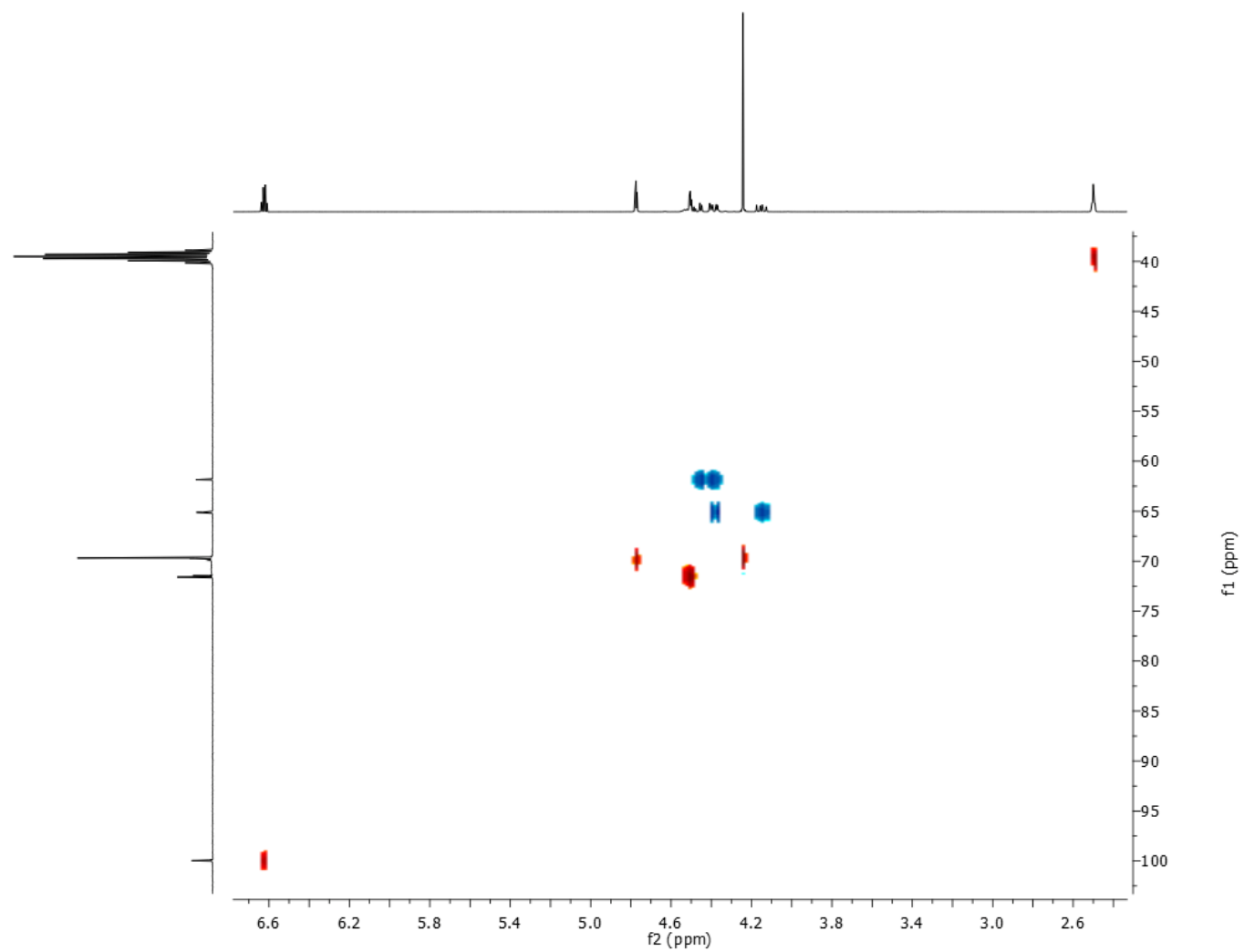


Figure 2.45 2D-HSQC NMR spectrum of the Fc- EDOT (2.15).

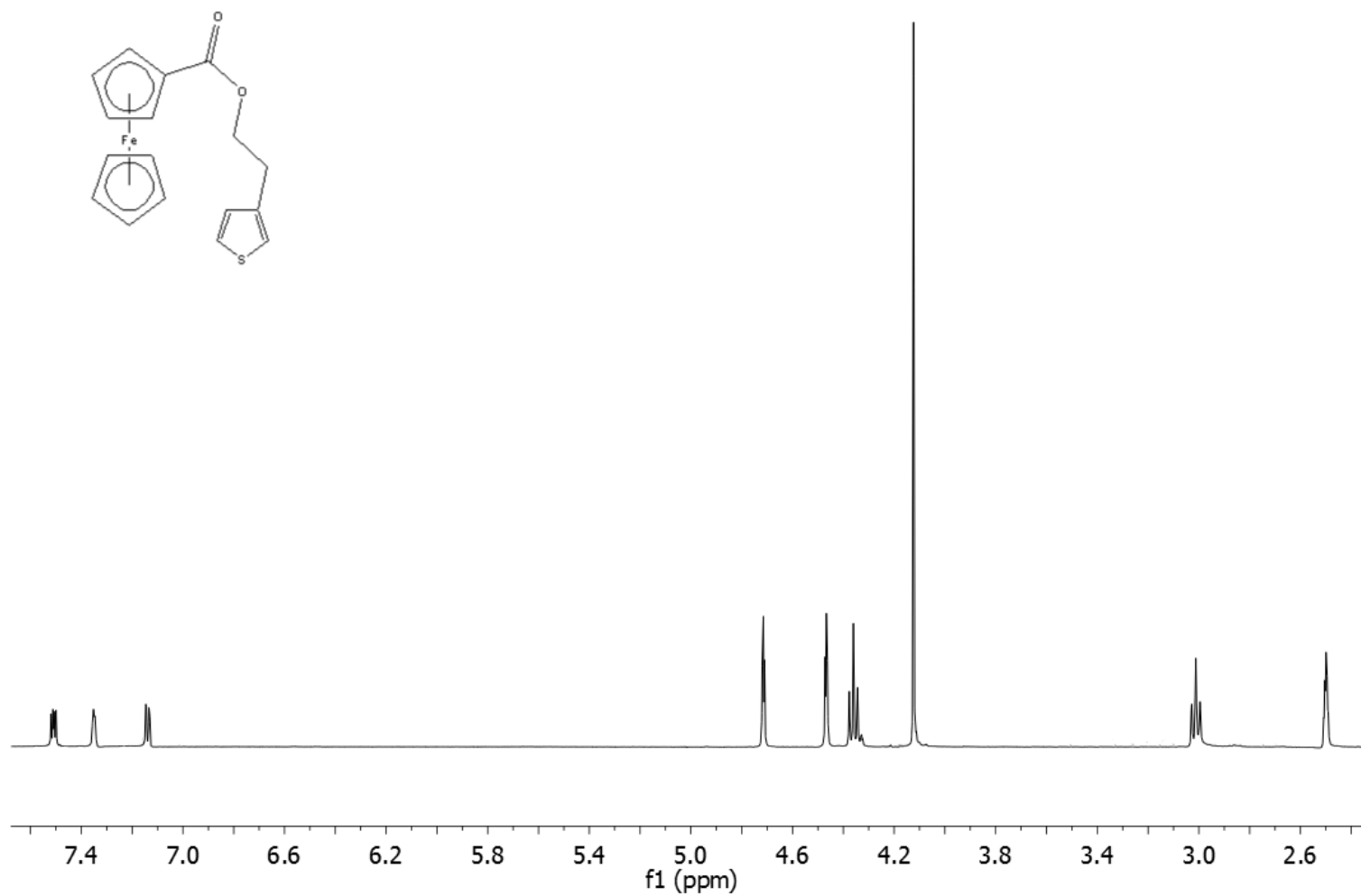


Figure 2.46 ^1H NMR spectrum for Fc-Th (2.16).

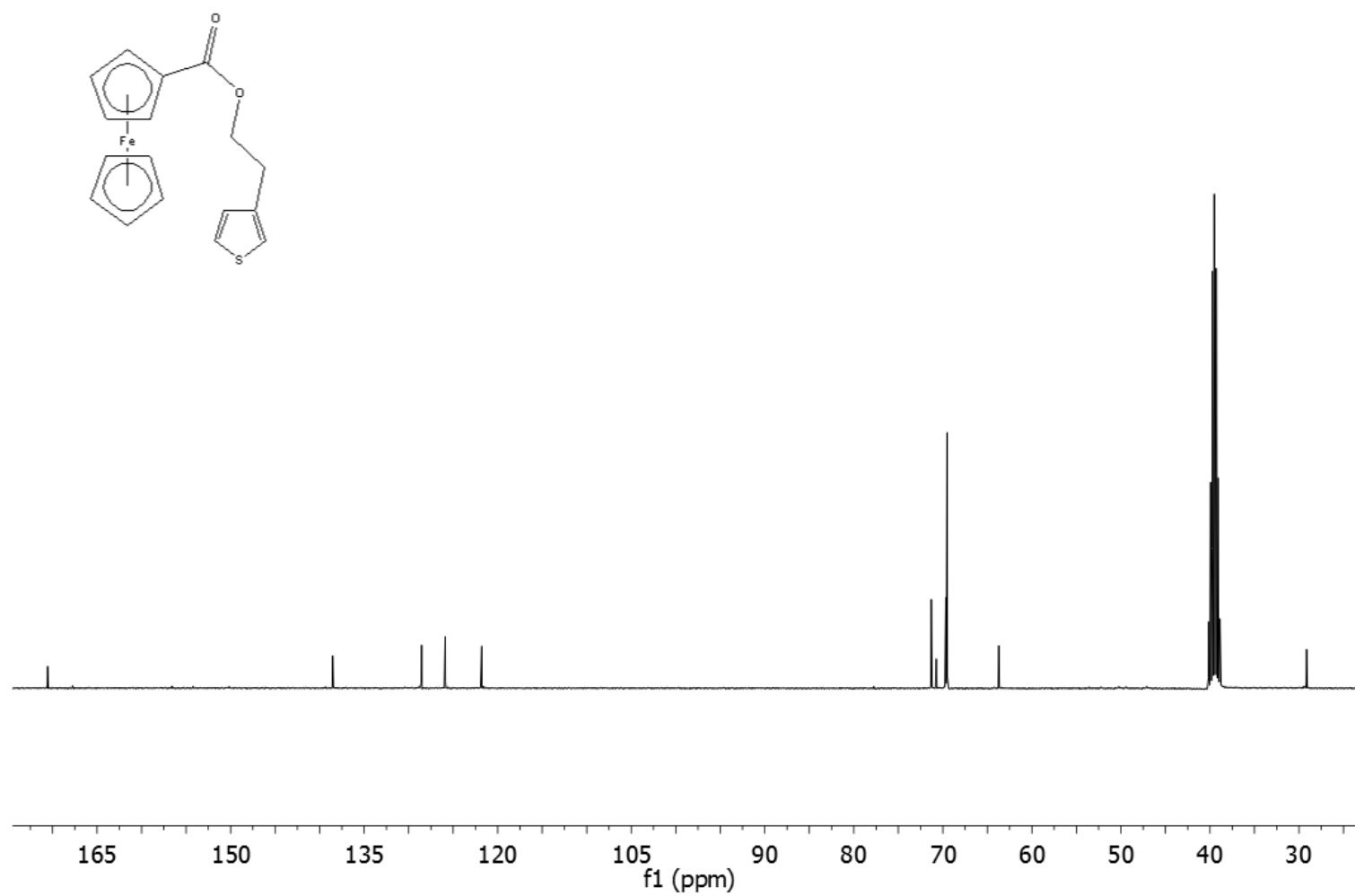


Figure 2.47 ^{13}C NMR spectrum for Fc-Th (2.16).

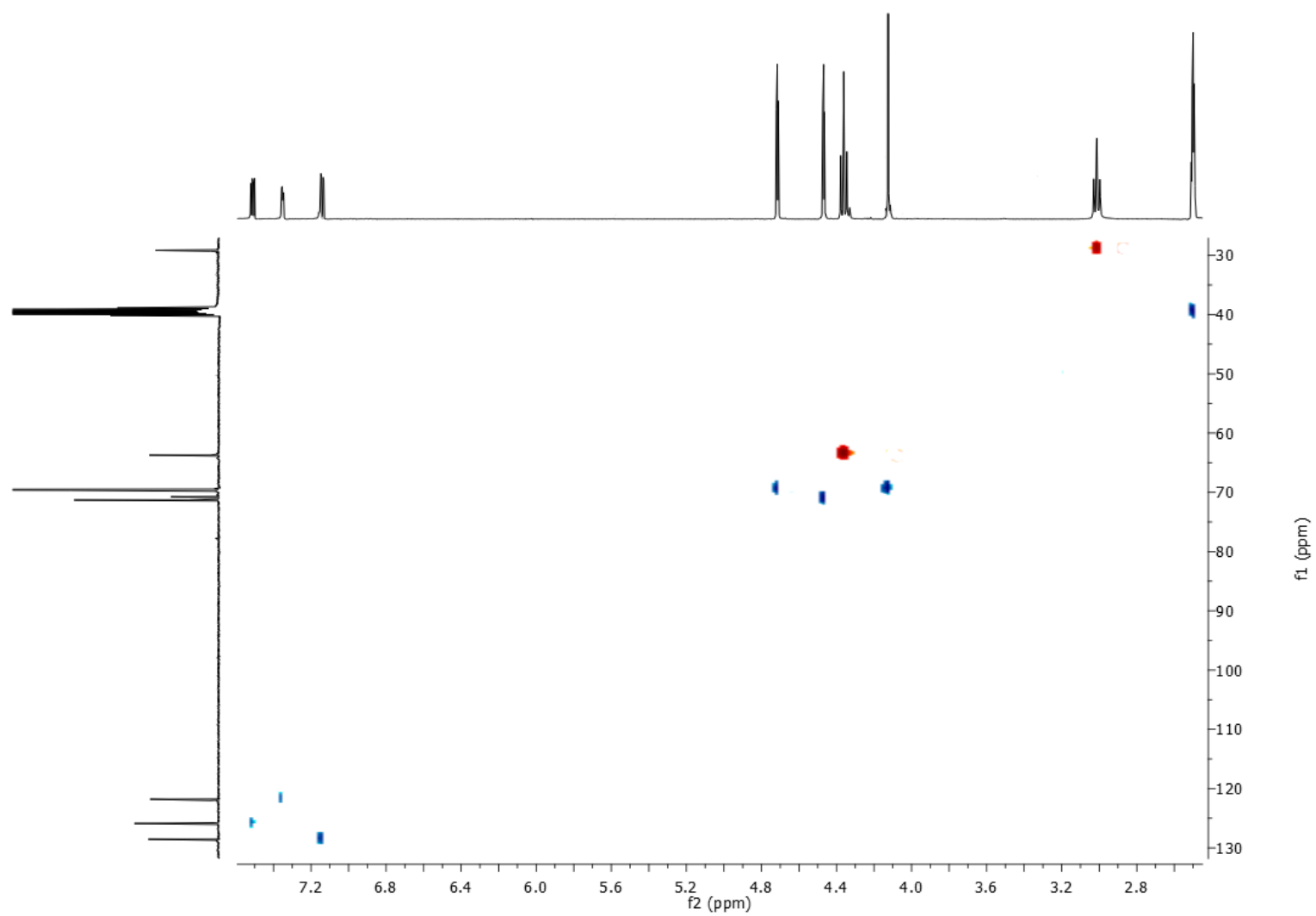


Figure 2.48 2D-HSQC NMR spectrum of the Fc- Th (2.16).

2.2.3.1 Electropolymerization of EDOT and Thiophene with Ferrocene Pendant

Ferrocene-functionalized polythiophenes are interesting redox functional systems; the ferrocene is a donor as well as the polythiophene backbone, and these compounds therefore demonstrate unique redox properties. Although the ferrocenyl groups in these systems do not show any electrochemical interaction as evidenced by a single ferrocene wave in the cyclic voltamogram, the difference between the polythiophene and ferrocene oxidation potential is linearly correlated to the energy of the polythiophene to Fe(III) charge-transfer transitions. A reduction in ΔE results in either greater delocalization of charge or in delocalization further along the rigid ligand.

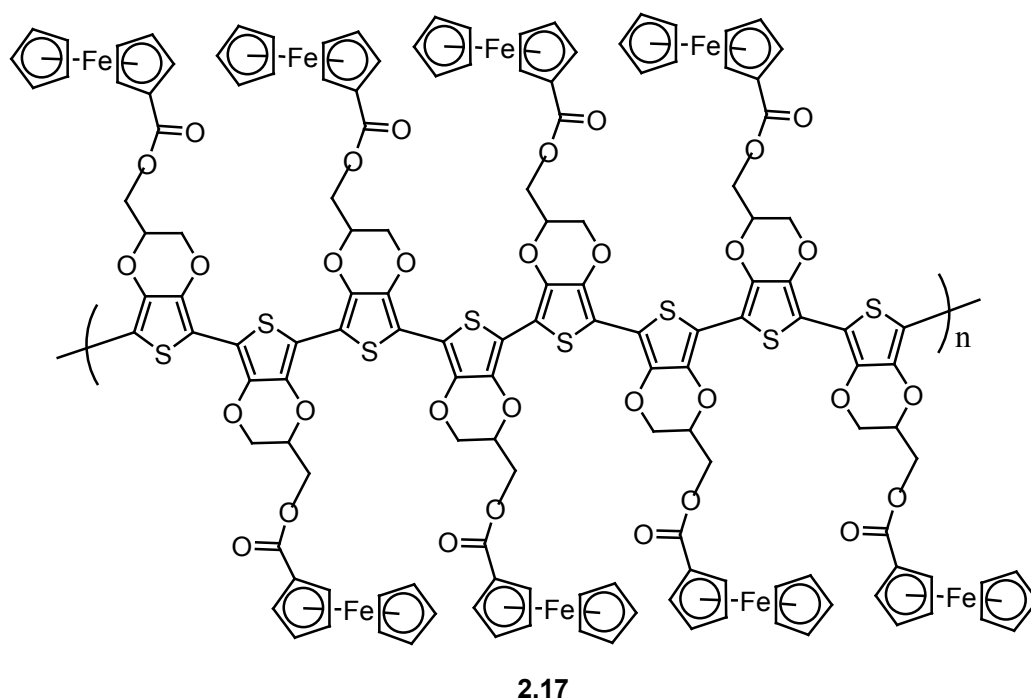


Figure 2.49 Schematic representation of electrochemically polymerized Fc-EDOT conducting polymer (2.17).

The anodic oxidation of Fc-EDOT (Fig.2.50) and Fc-Th (Fig.2.53) was achieved in 0.05M TBAPF₆⁻/DCM as supporting electrolyte solution on carbon fibre micro electrodes with scan rate of 100 mVs⁻¹ at 25°C and the conducting polymers are illustrated in Figure 2.49 and 2.52, respectively.

In the present work, the oxidation of ferrocene, Fe(C₅H₅)₂, to the ferrocenium cation, Fe(C₅H₅)₂⁺, was examined in 0.05M TBAPF₆⁻/DCM. The anodic and cathodic peak separation (ΔE) in the cyclic voltammograms was found to be 0.53V and 0.338 for ferrocene peaks of Fc-EDOT and Fc-Th polymer films, respectively. The ideal value which is indicative of one electron oxidation is in the range between 0.06 V and 0.10 V. However, in this case poor electron donating DCM was used as solvent which increased the potential difference, causing a slow electron transfer and the oxidation of ferrocene to the ferrocenium cation becomes more difficult. The large (ΔE) value can be attributed to the uncompensated resistance effect.

The redox potential for a couple is better expressed as the half-wave potential ($E_{1/2}$) rather than by the anodic peak or cathodic peak potentials since they can change with the scan rate effect whereas the $E_{1/2}$ is independent of the scan rate for reversible systems. The half wave potentials of the Fe(C₅H₅)₂⁺/Fe(C₅H₅)₂ couple was determined for both Fc-EDOT and Fc-Th polymeric films and found to be 0.866V and 0.897V, respectively.

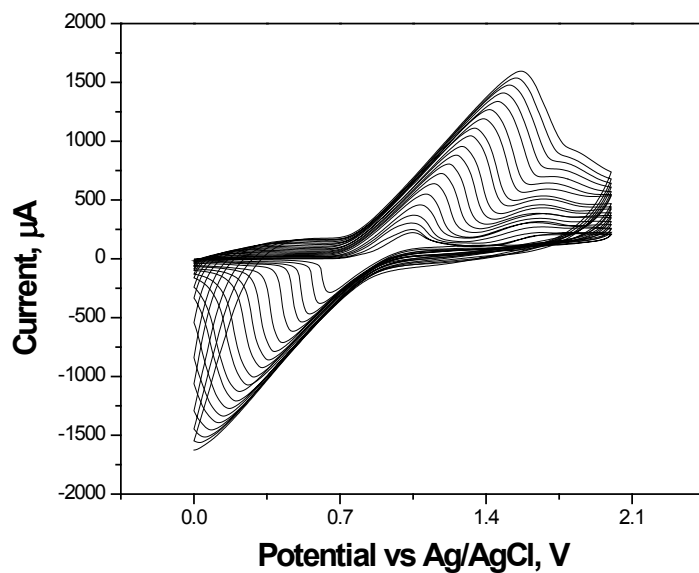


Figure 2.50 Repeated potential scan electropolymerization of the Fc-EDOT (2.15) monomer at 100 mVs^{-1} in 0.05 M in $\text{TBAPF}_6^-/\text{DCM}$ on CFME at 25°C .

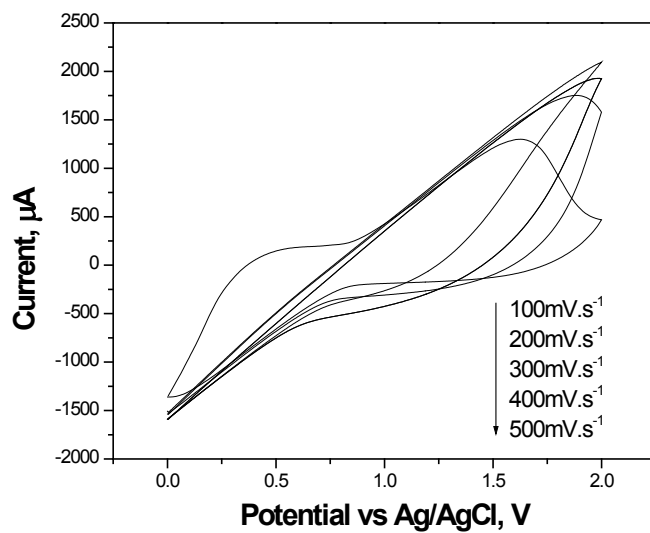


Figure 2.51 Cyclic voltamogram of the Fc-PEDOT (2.17) film in 0.05M $\text{TBAPF}_6^-/\text{DCM}$ monomer free electrolyte solution, at scan rates of 100, 200, 300, 400 and 500 mVs^{-1} .

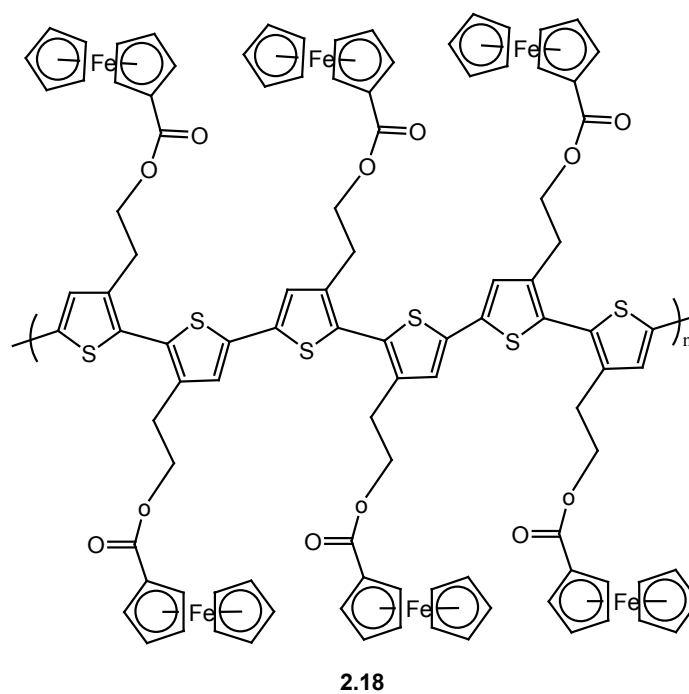


Figure 2.52 Schematic representation of electrochemically polymerized Fc-Th conducting polymer (2.18).

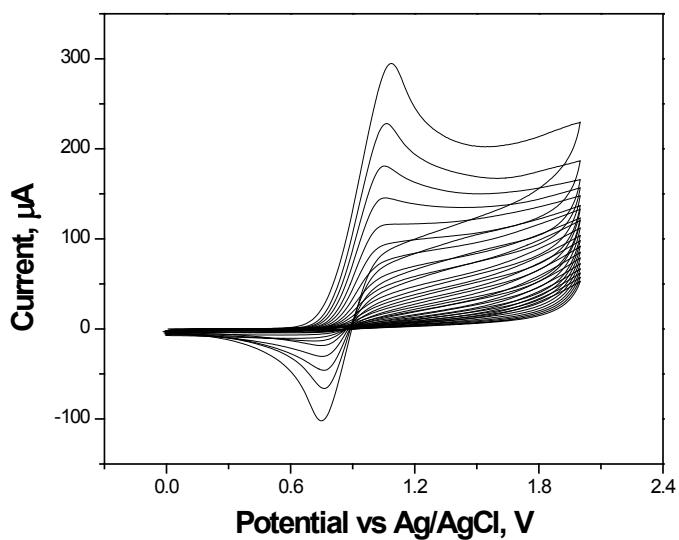


Figure 2.53 Repeated potential scan electropolymerization of the Fc-Th (2.16) monomer at 100 mVs^{-1} in 0.05 M in $\text{TBAPF}_6^-/\text{DCM}$ on CFME at 25°C .

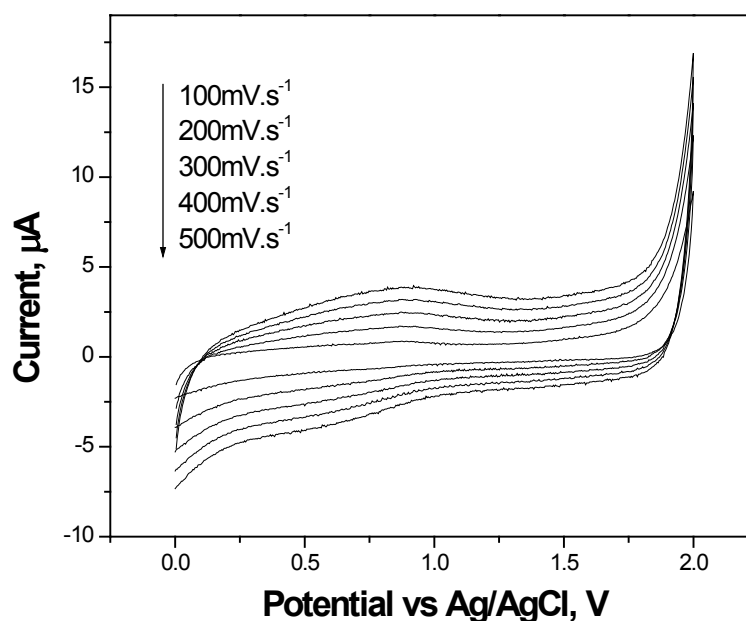


Figure 2.54 Cyclic voltamogram of the Fc-PTh (2.18) film in 0.05M TBAPF₆/DCM monomer free electrolyte solution, at scan rates of 100, 200, 300, 400 and 500 mVs⁻¹.

The scan rate dependencies of the Fc-PEDOT and Fc-PTh films between 100 and 500 mVs⁻¹ in 0.05M TBAPF₆/DCM were represented in Figure 2.51 and 2.54, respectively. The oxidation and reduction peaks for Fc-PEDOT film did not really appear in the voltamogram after 200 mVs⁻¹ applied potential. However, Fc-PTh film has a rectangular shaped cyclic voltamogram between 100 mVs⁻¹ and 500 mVs⁻¹, indicating supercapacitor behaviour.

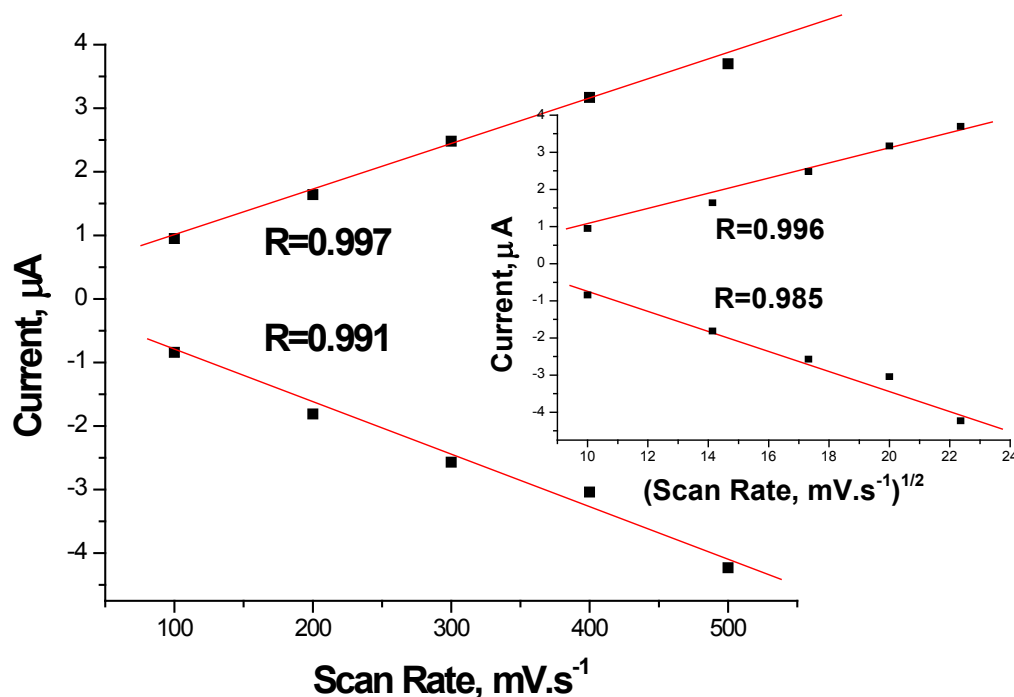


Figure 2.55 Anodic and cathodic peak current density vs. scan rate and dependence of Fc-PTh (2.18) thin film in 0.05M TBAPF₆/DCM monomer free electrolyte solution. Inset: Anodic and cathodic peak current density vs. square root of scan rate.

The peak current for a reversible process is described by the Randles-Sevcik [248] equation which assumes that mass transport occurs only by a diffusion process. The electropolymerization reaction of Fc-PTh was found to be a thin layer process due to the higher correlation coefficient values ($R_a=0.997$, $R_c=0.991$) in current vs scan rate plot (Figure 2.55). Correlation between ΔE values and the polymerization charges (ΔQ) revealed that Fc-PEDOT film ($\Delta Q=367.5\text{mC}$, $\Delta E=0.53$) was thicker than the Fc-PTh film ($\Delta Q=27.7\text{mC}$, $\Delta E=0.338$).

2.2.3.2 Electrochemical Impedance Spectroscopic Characterization

The electrochemical impedance spectroscopy (EIS) measurements were performed at room temperature (25°C) using three electrode cell configuration in 0.05M TBAPF₆/DCM monomer-free electrolyte solution with perturbation amplitude 10mV over a frequency range of 0.01Hz to 100 kHz with PARSTAT 2273.

The specific capacitance values were calculated from Nyquist plots (Figure 2.56) for Fc-PEDOT ($C_{sp}=28 \text{ mFcm}^{-2}$) and Fc-PTh ($C_{sp}=42.12 \text{ } \mu\text{Fcm}^{-2}$) thin films. The nyquist diagrams were not superimposed due to different scale ranges. At low frequency, there is a semicircle indicating the resistive behaviour of Fc-PEDOT film and the solvent resistance was found as 409.9 ohms whereas the charge transfer resistance was calculated as 116 ohms. After 525 ohms the modified electrode showed capacitive property. As seen from the capacitance values, thickness of the films affected the ion penetration through the film and lowered the charge-discharge capacity.

The phase angles of modified CFME were monitored from Bode magnitude plots. In the frequency region of 0.475Hz-24.6Hz the phase angle was found to be 75° for Fc-PTh film, whereas Fc-PEDOT film has a phase angle of 84° at 0.017Hz, which is a very small time interval. The transition region for Fc-PEDOT film from capacitive behaviour to resistor occurred in a very small frequency range (0.017Hz-11.16Hz. However, in this range Fc-PTh film reached a plateau indicating capacitive attitude (Figure 2.57).

Double layer capacitance values were calculated using the IZI values at 1Hz frequencies. Double layer capacitance values were determined to be 26.6 mFcm⁻² and 89.3 μFcm⁻² for Fc-PEDOT and Fc-PTh, respectively (Figure 2.58). The Cdl value proved that Fc-PEDOT film was thicker than Fc-PTh film.

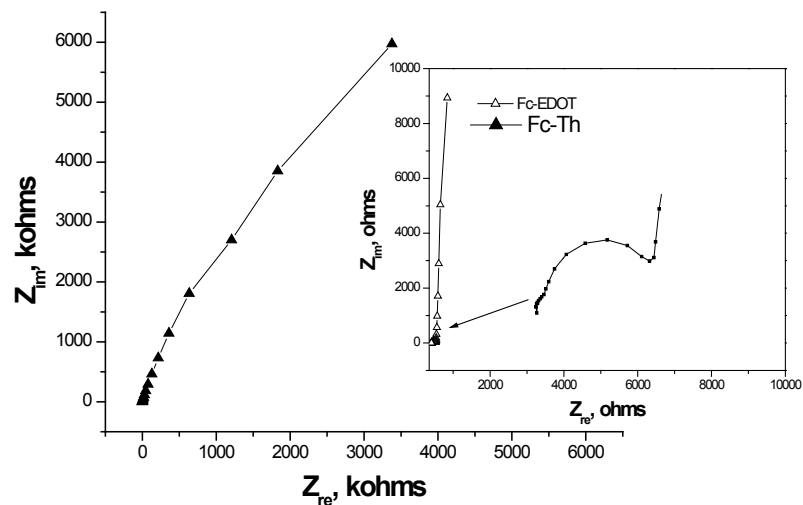


Figure 2.56 Nyquist plots for CFME/Fc-PTh (2.18) and inset: CFME/ Fc-PEDOT (2.17) in 0.05M TBAPF₆/DCM monomer free electrolyte solution, measured between 0.01Hz-100 kHz.

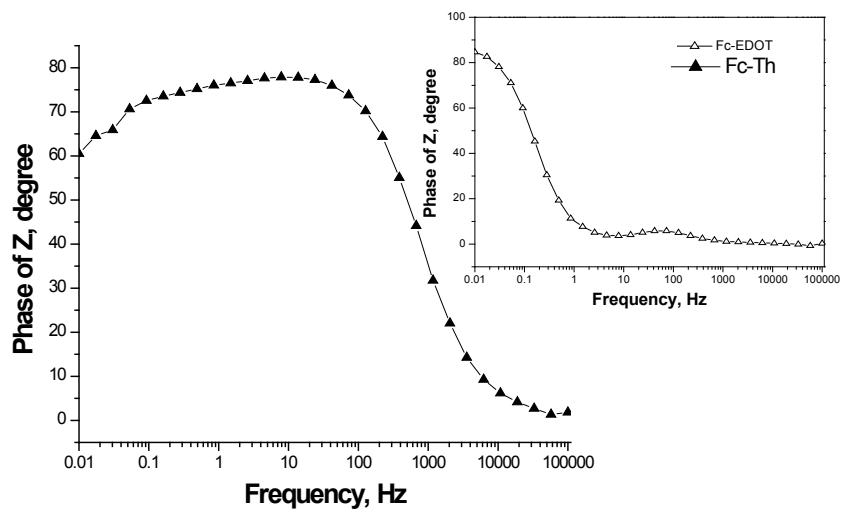


Figure 2.57 Bode Phase diagrams for CFME/Fc-PTh (2.18) and inset: CFME/ Fc-PEDOT (2.17) in 0.05M TBAPF₆/DCM monomer free electrolyte solution, measured between 0.01Hz-100 kHz.

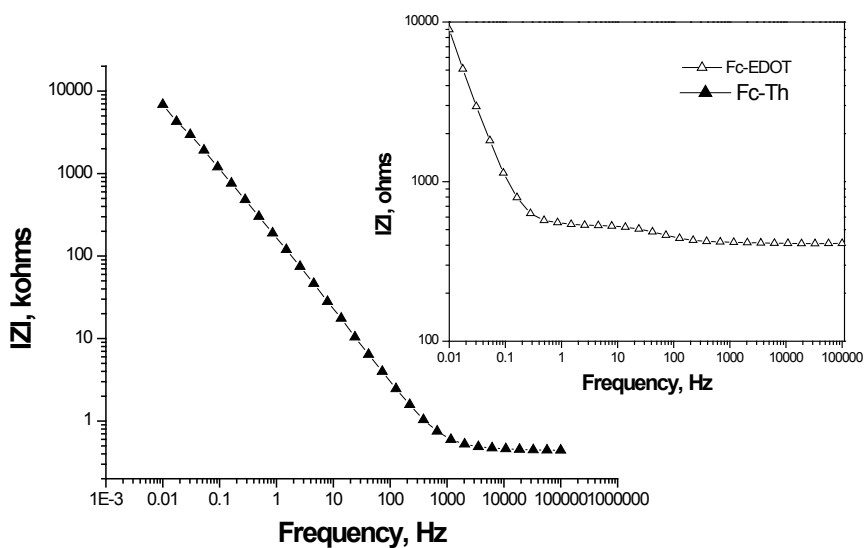


Figure 2.58 Bode magnitude plots for CFME/Fc-PTh (2.18) and inset: CFME/ Fc-PEDOT (2.17) in 0.05M TBAPF₆/DCM monomer free electrolyte solution, measured between 0.01Hz-100 kHz.

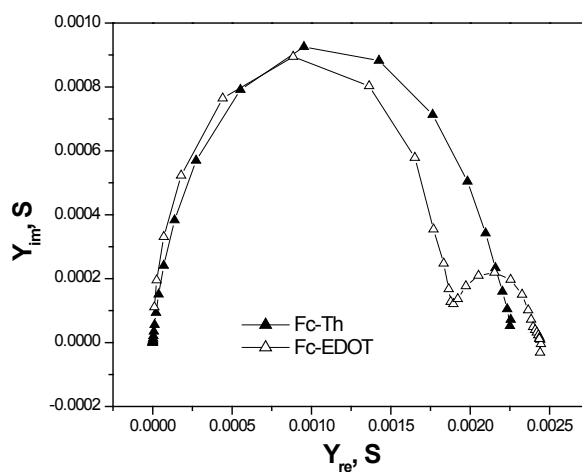


Figure 2.59 Admittance plots for CFME/Fc-PTh (2.18) and inset: CFME/Fc-PEDOT (2.17) in 0.05M TBAPF₆/DCM monomer free electrolyte solution, measured between 0.01Hz-100 kHz.

Electrochemical conductivities were determined to be 13.9 mScm^{-2} for Fc-PTh and 13.4 mScm^{-2} for the Fc-PEDOT film (Fig.2.59). The comparison of the capacitance plots (Fig.2.60) indicates that Fc-PTh film behaves like a resistor at very low frequencies for a short time interval whereas Fc-PEDOT film is quite resistive in a long frequency range.

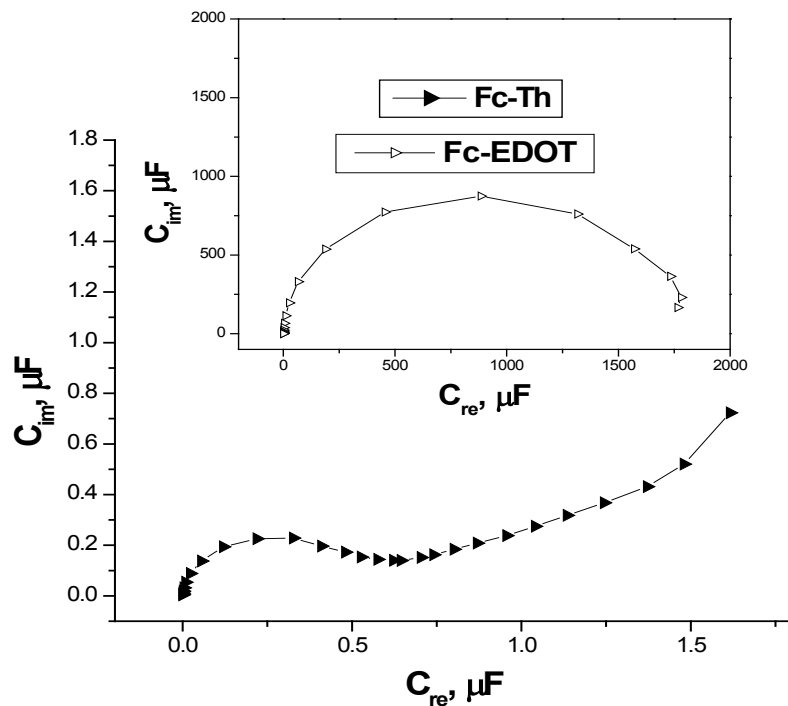


Figure 2.60 Capacitance plots for CFME/Fc-PTh (2.18) and inset: CFME/Fc-PEDOT (2.17) in 0.05M TBAPF₆/DCM monomer free electrolyte solution, measured between 0.01Hz-100 kHz.

2.2.3.3 Morphological Analysis

The morphology of the Fc-PEDOT and Fc-PTh films obtained by electropolymerization with 100 mVs^{-1} scan rate, was analyzed via SEM.

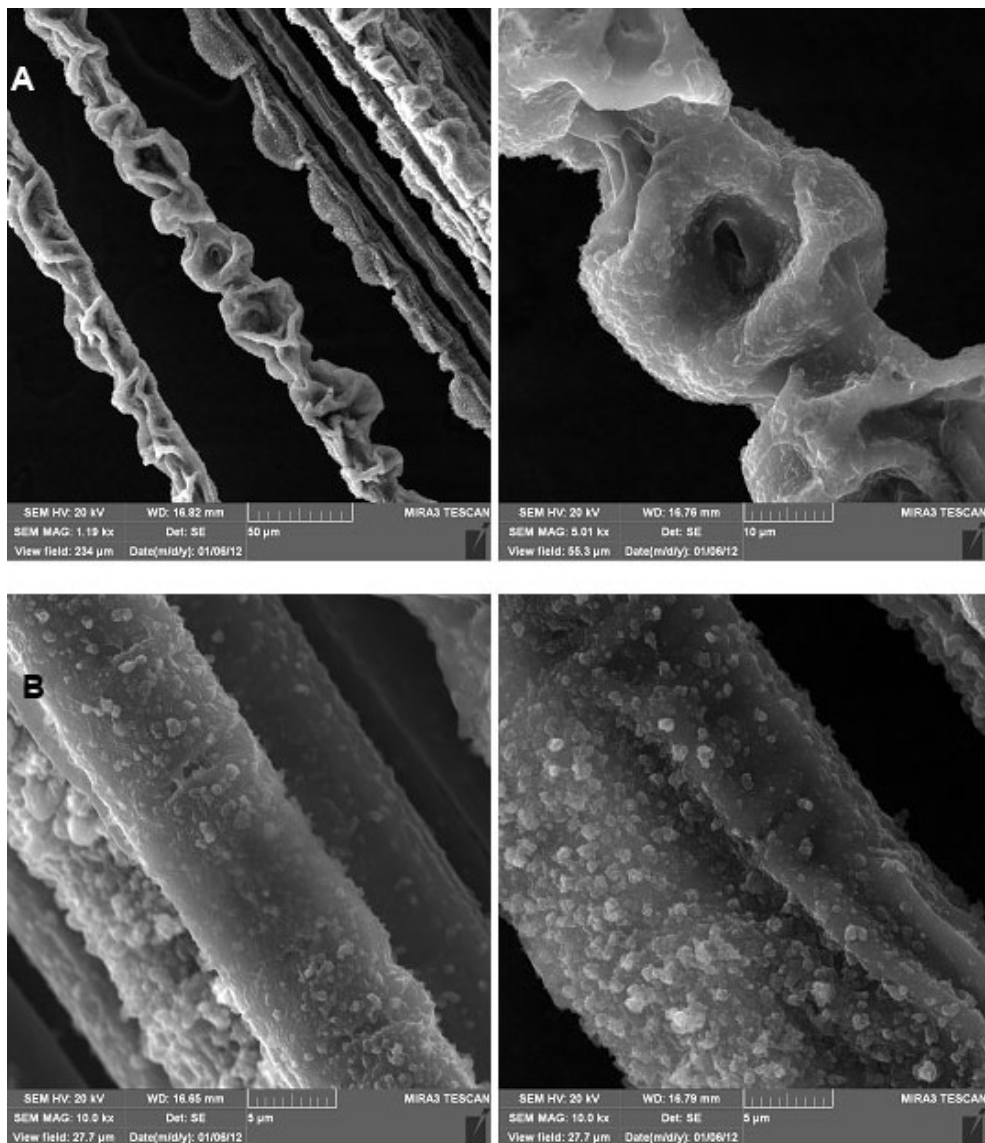


Figure 2.61 SEM images of electropolymerized a) Fc-PEDOT (2.18) and b) Fc-PTh (2.17) on CFME.

The Fc-PEDOT film on CFME surface displayed extremely different morphology than the other films. The film coated on the surface along the carbon fibre filament like a spherical, continuous, carnation-like structure. On the other hand, the Fc- PTh film coated on the surface more homogenously including nano-sized spherical particles on it which were caused by the oligomeric radical cations generated at the electrode surface. Additionally, the striation along the bare carbon fibre was not seen due to the successful deposition (Fig.2.61). The film thicknesses were found to be approximately 25 μ m and 14 μ m for Fc-PEDOT and Fc- PTh, respectively.

As a future direction, the chemically synthesized iron containing linear polymers could be demetallated to obtain more flexible polymers with lower Tg values which would be more convenient for film applications. Especially Fc-EDOT and Fc-Th monomers showed very high capacitive properties, so these monomers could be studied more detailed by different electrocoating techniques to achieve better modified electrode surface which could be used for capacitor device application. On the other hand, interesting morphology of the Fc-PEDOT polymer on carbon fibre surface needs to be identified. The cationic iron containing Th and EDOT polymers indicated porous films on the electrode; more study needs to be done to achieve well adhered films on the electrode surface by changing concentration or substrate.

2.3 Experimental

2.3.1 Materials

All reagents were purchased from Sigma-Aldrich and used without further purification. All solvents were high-performance-liquid-chromatography grade, purchased from Fisher Scientific, and used without further purification. Complexes **1.21**, **1.23** and **1.25** were prepared through an established procedure [212].

2.3.2 Characterizations

^1H and ^{13}C NMR spectra were recorded at 400 MHz and 101 MHz, respectively, on a Varian Mercury Plus spectrometer equipped with a gradient field probe, with chemical shifts referenced to residual solvent peaks and coupling constants reported in Hz. Infrared spectroscopy was performed on an IRPrestige-21FTIR by Shimadzu with a MIRacle ATR by PIKE Technologies. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on Mettler-Toledo TGA/SDTA851^e and DSC821^e instruments at heating rates of 20 °C/min under nitrogen atmospheres. Cyclic voltammetric studies were performed using a conventional three-electrode cell. In these studies, the working electrode was a glassy carbon disk electrode (~ 2 mm diameter), the auxiliary electrode was a Pt wire, and a Ag/AgCl reference electrode was utilized. Temperatures ranging from 293 to 243 K were obtained using an acetone/water/ $\text{N}_{2(l)}$ mixture. The concentration of the analyte was 2 mM, while that of the supporting electrolyte (TBAPF_6) was 0.1 M in DCM. The solutions were deaerated with nitrogen prior to use. A PARSTAT2273 model potentiostat with an attached power suite software program was used in all experiments. All reactions and complexes containing the η^6 -aryl- η^5 -cyclopentadienyliron hexafluorophosphate moiety were kept in the dark to prevent

decomposition. Scanning electron microscopy (SEM) with a secondary detector was performed for imaging of the powders.

2.3.3 Carbon Fibre Microelectrode Preparation

High strength (HS) and high modulus (HM) carbon fibres C320.000A (CA) (Sigri Carbon, Meitingen, Germany) containing 320.000 single filaments in a roving were used as working electrodes. All of the electrodes were prepared using a 3 cm long bundle of the CFME (with average diameter of around 7 μm) attached to a copper wire with Teflon tape. The numbers of carbon fibres in the bundle were about ~ 30 . One centimeter of the CFME was dipped into the solution to keep the electrode area constant ($\sim 0.066 \text{ cm}^2$) and the rest of the electrode was covered with Teflon tape. The CFME were first cleaned with acetone and then dried with an air-dryer before the experiments.

2.3.4 General Procedure for Esterification Reaction

The monomer synthesis is shown in Scheme 2.1. The compound containing the carboxylic acid functionality (1 mmol) was reacted with the terminal hydroxyl group of EDOT or Thiophene derivative (1 mmol) in the presence of N,N-dimethylaminopyridine (DMAP) (2 mmol) in $\text{CH}_2\text{Cl}_2/\text{DMF}$ (10 mL/2 mL), cooled to 0 $^\circ\text{C}$, and stirred under N_2 for 5 minutes. Dicyclohexylcarbodiimide (DCC) (2 mmol) was dissolved in 1-2 mL of CH_2Cl_2 and added to the stirring mixture at 0 $^\circ\text{C}$. The solution was stirred in the dark at room temperature under N_2 for 24 hours. The solvent was evaporated *in vacuo*, the resulting product was dissolved in a minimum amount of acetone, and the mixture was poured into 1.2 M HCl containing equi-metal molar amounts of ammonium hexafluorophosphate (NH_4PF_6). The resulting precipitate was collected in a sintered glass crucible, washed with water, and dried under reduced pressure. Dicyclohexyl

urea (DCU) was removed by dissolving the crude product in CH₂Cl₂, placing the solution in the freezer for 30 minutes, and filtering through a crucible. The neat product was collected in a crucible and dried under reduced pressure to afford expected compound.

2.3.4.1 Synthesis of VBM-EDOT Monomer (2.3)

¹H NMR (DMSO) δ 7.38 (d, *J* = 8.6 Hz, 4H), 7.27 (d, *J* = 8.6 Hz, 4H), 6.80 (d, *J* = 6.6 Hz, 4H), 6.60 (s, 2H), 6.42 (d, *J* = 6.5 Hz, 4H), 5.28 (s, 10H), 4.40 (m, 1H), 4.34 - 4.19 (m, 3H), 4.02 (dd, *J* = 11.8, 7.3 Hz, 1H), 2.47 (t, 2H), 2.22 (t, 2H), 1.68 (s, 3H). ¹³C NMR (101 MHz, dmso) δ 172.53, 151.11, 146.13, 141.02, 140.90, 131.86, 129.26, 120.07, 103.56, 99.96, 99.90, 86.74, 79.29, 76.34, 71.22, 64.91, 62.17, 45.01, 35.79, 29.51, 26.93.

IR: 1736 (C=O), Yield: 72%

2.3.4.2 Synthesis of VBM-Th Monomer(2.4)

¹H NMR (400 MHz, dmso) δ 7.47 (dd, *J* = 4.8, 2.9 Hz, 1H), 7.35 (d, *J* = 8.7 Hz, 4H), 7.26 (d, *J* = 8.8 Hz, 5H), 7.03 (d, *J* = 4.9 Hz, 1H), 6.80 (d, *J* = 6.7 Hz, 4H), 6.42 (d, *J* = 6.6 Hz, 4H), 5.27 (s, 10H), 4.20 (t, *J* = 6.8 Hz, 2H), 2.90 (t, *J* = 6.6 Hz, 2H), 2.44 – 2.37 (t, 2H), 2.18 – 2.11 (t, 2H), 1.65 (s, 3H). ¹³C NMR (101 MHz, dmso) δ 172.79, 151.19, 146.23, 138.21, 131.95, 129.34, 128.55, 126.05, 121.89, 120.33, 120.17, 103.67, 86.84, 79.39, 76.44, 63.95, 36.05, 29.84, 28.95, 26.95.

IR: 1715 (C=O), Yield: 65%

2.3.4.3 Synthesis of Acid complex-EDOT Monomer (2.10)

¹H NMR (400 MHz, dmso) δ 8.12 (d, *J* = 8.9 Hz, 2H), 7.44 (d, *J* = 8.9 Hz, 2H), 6.84 (d, *J* = 6.9 Hz, 2H), 6.63 (s, 2H), 6.55 (d, *J* = 6.9 Hz, 2H), 5.30 (s, 5H), 4.57 (dtd, *J* = 12.7, 6.1, 4.0

Hz, 3H), 4.40 (dd, $J = 11.7, 2.0$ Hz, 1H), 4.18 (dd, $J = 11.7, 6.8$ Hz, 1H). ^{13}C NMR (101 MHz, dmso) δ 164.55, 157.37, 156.58, 141.12, 141.09, 132.19, 130.61, 130.18, 120.42, 100.02, 99.98, 86.89, 79.55, 77.52, 71.31, 65.05, 63.15.

IR: 1748 (C=O), Yield: 74%

2.3.4.4 Synthesis of Acid complex-Th Monomer (2.11)

^1H NMR (400 MHz, dmso) δ 8.07 (d, $J = 8.7$ Hz, 2H), 7.49 (dd, $J = 4.8, 2.9$ Hz, 1H), 7.43 (d, $J = 8.7$ Hz, 2H), 7.33 (d, $J = 1.8$ Hz, 1H), 7.11 (d, $J = 4.0$ Hz, 1H), 6.84 (d, $J = 6.7$ Hz, 2H), 6.55 (d, $J = 6.8$ Hz, 2H), 5.30 (s, 5H), 4.51 (t, $J = 6.6$ Hz, 2H), 3.07 (t, $J = 6.6$ Hz, 2H). ^{13}C NMR (101 MHz, dmso) δ 164.68, 157.12, 138.08, 131.78, 131.45, 128.38, 125.94, 121.79, 121.62, 120.26, 103.92, 86.79, 79.44, 77.44, 64.75, 28.87

IR: 1745 (C=O), Yield: 63%

2.3.4.5 Synthesis of Fc-EDOT Monomer (2.15)

^1H NMR (400 MHz, dmso) δ 6.62 (q, $J = 3.6$ Hz, 2H), 4.79 – 4.75 (m, 2H), 4.52 – 4.49 (m, 2H), 4.45 (d, $J = 3.7$ Hz, 1H), 4.42 – 4.35 (dd, 2H), 4.24 (s, 5H), 4.15 (dd, $J = 11.4, 7.6$ Hz, 2H). ^{13}C NMR (101 MHz, dmso) δ 170.35, 141.15, 141.12, 99.95, 99.90, 71.57, 71.44, 70.01, 69.85, 69.84, 69.68, 65.09, 61.82.

IR: 1728 (C=O), Yield: 67%

2.3.4.6 Synthesis of Fc-Th Monomer (2.16)

^1H NMR (400 MHz, dmso) δ 7.51 (dd, $J = 4.9, 2.9$ Hz, 1H), 7.35 (d, $J = 1.8$ Hz, 1H), 7.14 (dd, $J = 4.9, 1.1$ Hz, 1H), 4.71 (t, $J = 1.9$ Hz, 2H), 4.47 (t, $J = 1.9$ Hz, 2H), 4.36 (t, $J = 6.5$

Hz, 2H), 4.12 (s, 5H), 3.01 (t, $J = 6.5$ Hz, 2H). ^{13}C NMR (101 MHz, dmso) δ 170.54, 138.53, 128.55, 125.89, 121.79, 71.30, 70.74, 69.66, 69.52, 63.72, 29.14.

IR: 1732 (C=O), Yield: 59%

2.3.5 General Procedure for Condensation Polymerization

Condensation polymerization is a powerful tool that can attach monomers together via a condensation reaction. The condensation polymerization was achieved by reacting VBM-EDOT or VBM-Th complexes (0.5 mmol) with bisphenol-A (0.5 mmol) in the presence of K_2CO_3 (5 mmol). The compounds were dissolved in 1 mL DMF and stirred under nitrogen at 55-60 °C until the solution became viscous. The reaction was then precipitated into 1.2 M HCl, followed by the addition of a concentrated aqueous solution of ammonium hexafluorophosphate. The precipitate was filtered, washed with water, and covered to give VBM-PEDOT or VBM-PTh polymers.

2.3.5.1 Synthesis of Poly (VBM-EDOT-Bisphenol-A) (2.6)

^1H NMR (DMSO) δ 7.33 (br d, 4H), 7.20 (br d, 4H), 6.71 (br d, 4H), 6.59 (br s, 2H), 6.47 (br d, 4H), 5.16 (br s, 10H), 4.37 (br s, 1H), 4.23 (br m, 3H), 4.00 (br m, 1H), 2.45 (br s, 2H), 2.33 (br s, 2H), 1.56 (br s, 3H).

IR: 1738 (C=O), Yield: 67%

2.3.5.2 Synthesis of Poly (VBM-Th-Bisphenol-A) (2.7)

^1H NMR (DMSO) δ 7.33 (br d, 4H), 7.20 (br d, 4H), 6.71 (br d, 4H), 6.59 (br s, 2H), 6.47 (br d, 4H), 5.16 (br s, 10H), 4.37 (br s, 1H), 4.23 (br m, 3H), 4.00 (br m, 1H), 2.45 (br s, 2H), 2.33 (br s, 2H), 1.56 (br s, 3H).

IR: 1733 (C=O), Yield: 62%

3 Synthesis, Electrochemistry and Fluorescence Behaviour of Thiophene Derivatives Decorated with Naphthol, Coumarin and Pyrene as well as Terpyridine

3.1 Overview

In the last few years there has been a great interest in newly functionalized electrically conducting organic polymers due to their scientific and technological properties, which could lead to a number of device applications based on these materials [213-216]. Among the numerous conducting polymers, polythiophenes are the most interesting polymers due to their favourable properties for their potential applications in organic electronics and sensors as well as having the high environmental stability of both its doped and undoped states [78,119]. The first compulsory step in their study is the characterization of the monomers by both photophysics and electrochemistry.

Coumarin and its derivatives occur widely in nature and many natural and synthetic derivatives of coumarin are used in different applications in chemistry, biology, medicine and physics, due to their luminescence properties [217]. Coumarin derivatives have a significant role in pharmacologically as antibacterial and anticancer activity [218-221], as well as use in laser dyes, nonlinear optical chromophores, fluorescent whiteners, fluorescent probes and solar energy collectors due to their outstanding optical properties [217,222-225]. Coumarins are relatively photo-stable and their excitation and emission maxima, in many cases, are long enough to

minimize the so-called “background” fluorescence of cellular components, tissues, and biological fluids. They exhibit Stokes shifts large enough to avoid significant overlap of the excitation and emission spectra, and the fluorescence quantum yields allow for ion detection at low indicator concentrations [226].

Pyrene is another chromophore that has attracted considerable attention for the past several years due to its ability to monitor various processes and functions on a microscopic level [227-231]. Its ability to form homo- and hetero-dimers in the excited state (excimers, exciplexes) and their long lifetimes in non-polar media (~ 400 ns) makes them important. The photophysical properties of pyrene excimers have been studied over quite a few years [232]. Excimer fluorescence appears if an excited-state molecule associates with a ground-state molecule after which the photon is delocalized over the conjugate to show a net change in fluorescence spectral profile [233]. The resulting photophysical properties can be used to derive structural information about the conjugate system and gives more information about stacking interactions.

It has been revealed that naphthol-containing monomers may trap ultraviolet radiation, partially or completely. They are mostly used in the synthesis of dyes and in organic synthesis. Naphthol and its derivatives stand out due to their extremely fast deprotonation rate resulting in low emission intensity of the neutral species [234-236]. The naphthol containing polymers may have intramolecular excimer fluorescence, providing information on polymer structure and mobility, both in solution and in the solid phase [237-242]. Furthermore, it has been well known that transition metal terpyridine complexes with functional groups [243-246] are excellent electroactive materials for preparing optical/electronic ultrathin films and synthetic receptors for detecting metal ions or chiral molecules as well. Due to these unique properties, a terpyridine moiety was attached to thiophene with different lengths of diols. Terpyridine functionalized

thiophene derivatives were electrochemically oxidized to obtain electro active thin films on electrode surfaces.

Fluorescence is a widely used technique to study chemical sensors, and its applications are rapidly expanding; fluorescence studies reveal various possibilities to study the behaviour of a sensor, based upon changes in the signal intensity, the formation of excimer/excimer compounds, energy or electron transfer processes. In this chapter, we have studied a novel series of functionalized thiophene derivatives incorporating naphthol, coumarin and pyrene pendants because of their excellent photophysical and the electrochemical behaviour. Additionally, terpyridine attached thiophenes with different spacer lengths were synthesized and electrochemically characterized.

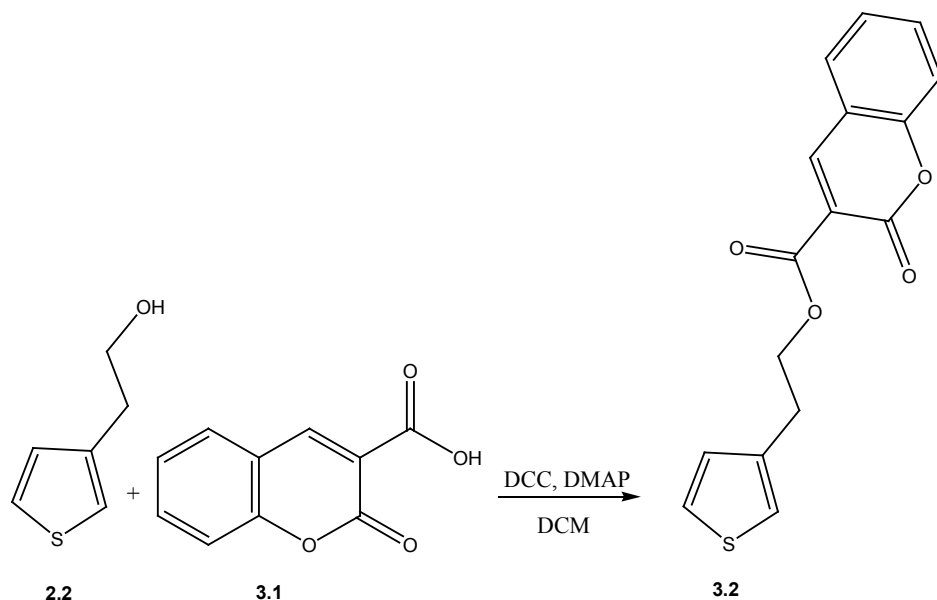
3.2 Results and Discussion

3.2.1 Synthesis of Thiophene Derivatives with Naphthol, Coumarin and Pyrene Pendants

This study presents the synthesis of thiophene derivatives having fluorescence properties, which are created by combining a well-known p-type electron donating thiophene with coumarin (Scheme 3.1), pyrene (Scheme 3.2) and naphthol (Scheme 3.3). The newly synthesized monomers were electrochemically deposited onto carbon fibre and glassy carbon electrode which allowed us to validate capacitive behaviours of polymer growth via electrochemical impedance spectroscopy. Also, the comparison of photophysical properties of monomers was studied with fluorescence spectrometer, revealing the quantum yields.

The FTIR spectrum of thiophene derivatives including coumarin, pyrene and naphthol were also characterized. It was obviously seen that the strong band ascribed to the C-S vibration was present at 759, 842 and 997 cm^{-1} for compounds ThC, ThP and ThN, respectively. Each

compound has representative bands between 1705cm^{-1} and 1724cm^{-1} , which corresponded to the ester carbonyl stretches of the synthesized monomers. Vibrations at 1500 , 1485 and 1456 cm^{-1} were attributed to the stretching modes of $\text{C}=\text{C}$ and $\text{C}-\text{C}$ in the thiophene ring. On the other hand, the aromatic $\text{C}-\text{H}$ stretch was observed at 2926cm^{-1} indicated the phenyl rings of functional groups.



Scheme 3.1 The esterification reaction of 2-(3-Thienyl) ethanol with Coumarin-3-carboxylic acid.

Identification of the synthesized thiophene monomer with a coumarin side group was achieved using NMR analysis. As a result of esterification reaction, the terminal hydroxyl proton resonance of 2-(3-Thienyl) ethanol at 4.67 ppm and the carboxylic acid proton resonance of coumarin-3-carboxylic acid at 13.18 ppm disappeared and a new set of peaks formed at 7.48 ppm , 7.36 ppm and 7.12 ppm belonging to the heterocyclic thiophene ring appeared (Fig.3.1). Additionally, aliphatic CH_2 protons shifted downfield and resonated at 3.05 ppm and 4.45 ppm . HSQC (Fig.3.3) and ^{13}C NMR (Fig.3.2.) further confirmed the structure formation. The ester

carbonyl peak was observed at 162.52 ppm indicating the successful formation, whereas the quaternary carbon of coumarin-3-carboxylic acid next to the ester carbonyl shifted to 117.77 ppm.

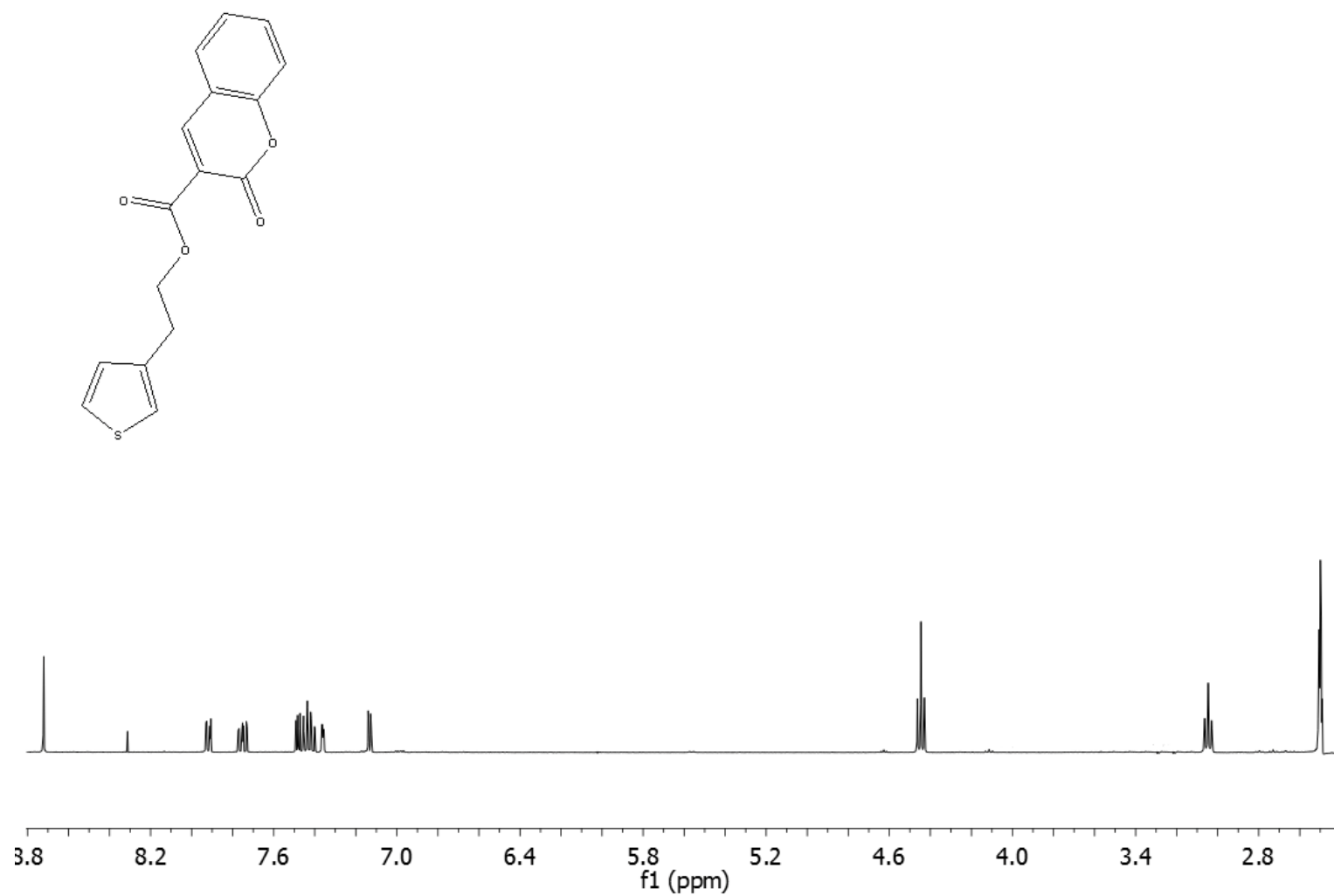


Figure 3.1 ¹H NMR spectrum of 2-(3-Thienyl)ethanol with Coumarin-3-carboxylic acid (3.2).

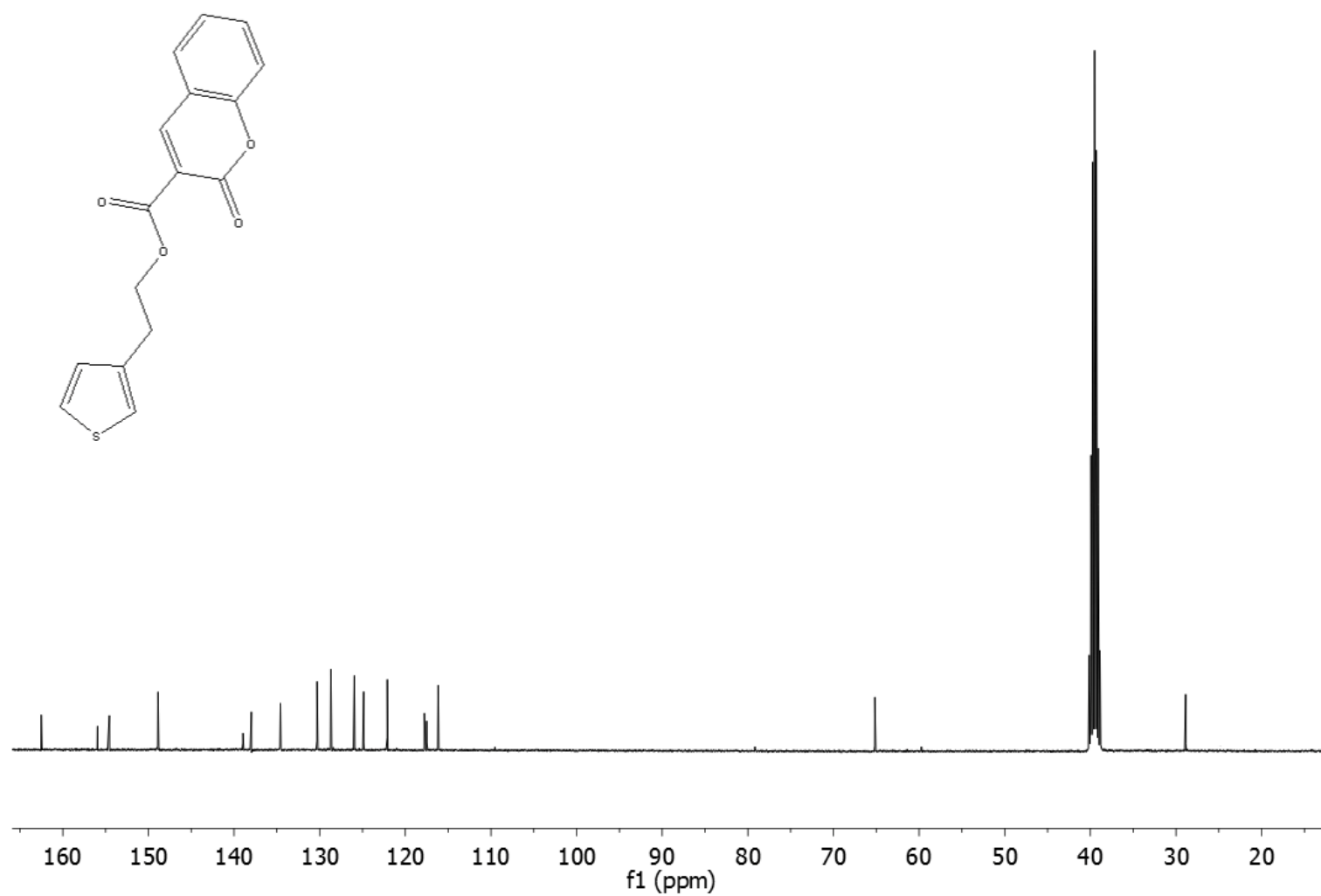


Figure 3.2 ^{13}C NMR spectrum of 2-(3-Thienyl)ethanol with Coumarin-3-carboxylic acid (3.2).

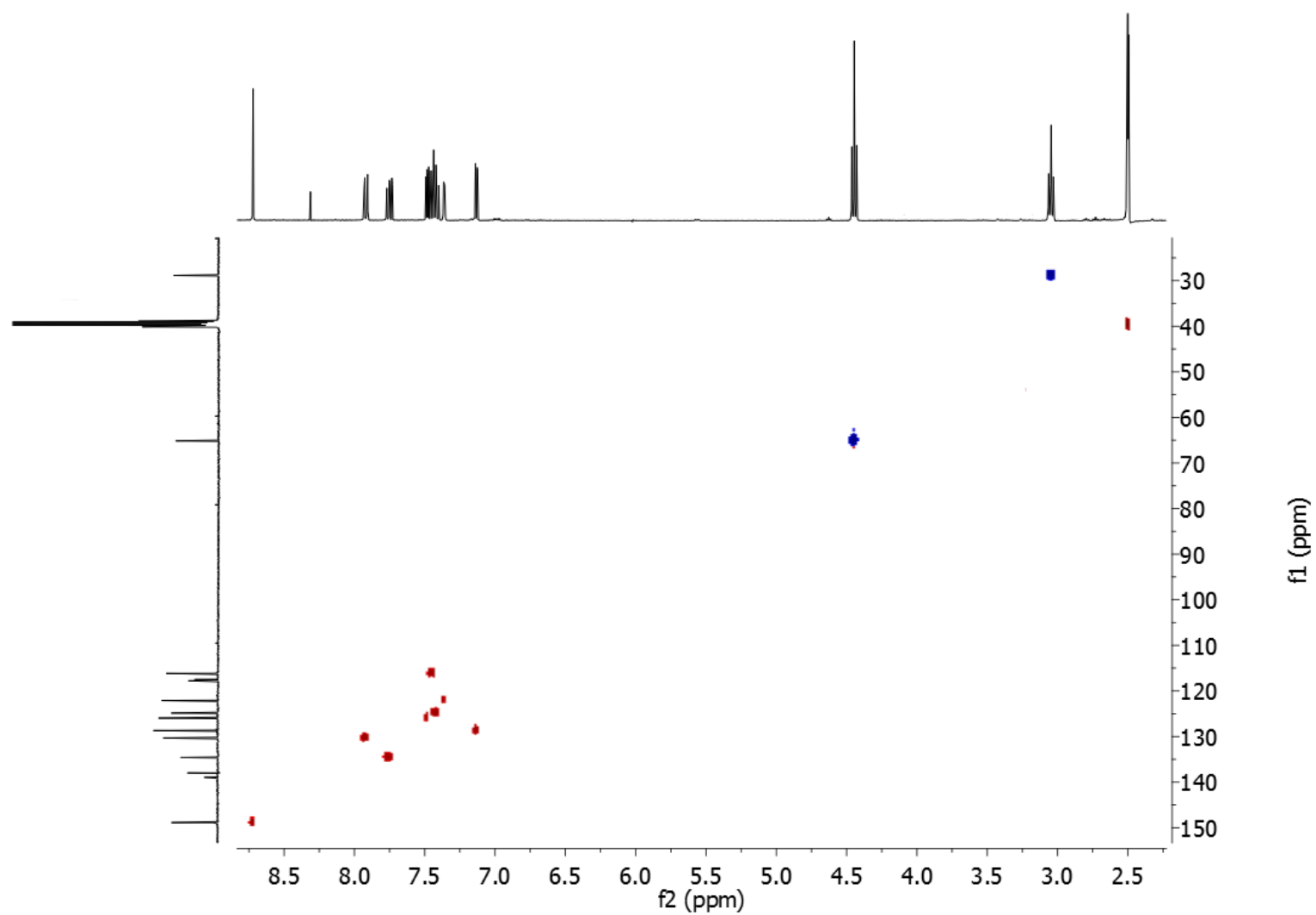
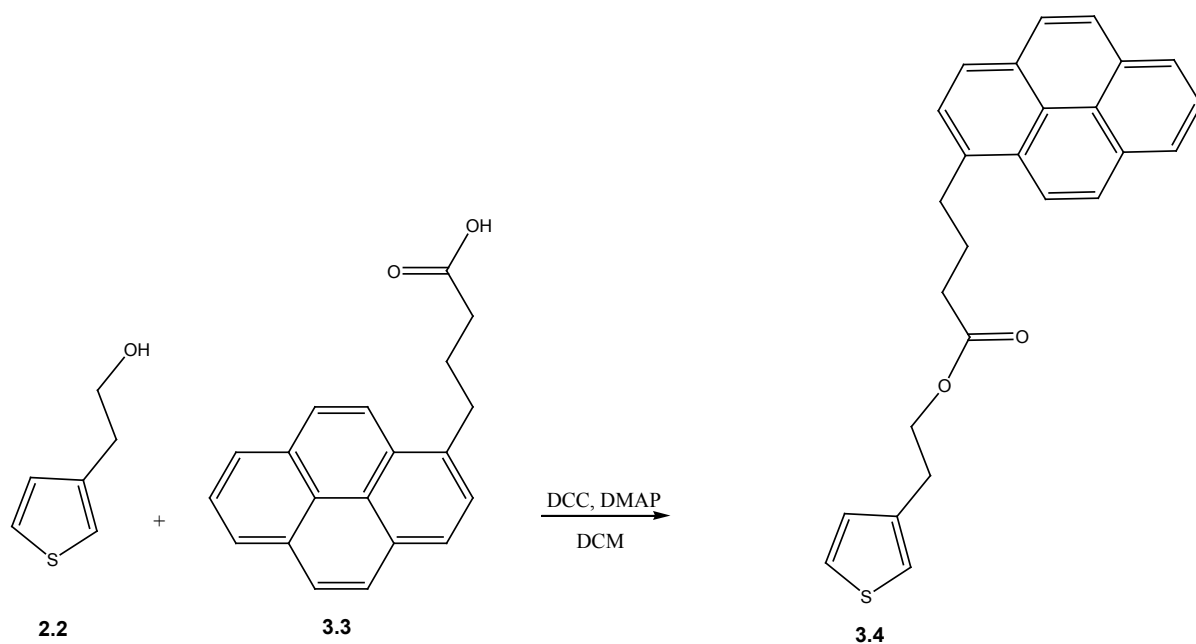


Figure 3.3 2D-HSQC NMR spectrum of 2-(3-Thienyl)ethanol with Coumarin-3-carboxylic acid(3.2).



Scheme 3.2 The esterification reaction of 2-(3-Thienyl) ethanol with 1-Pyrenebutyric acid (3.4).

The ^1H NMR spectrum (Fig.3.4) of the complex showed two distinct shifts at 3.67 ppm and 4.63 ppm which are representative of the aliphatic CH_2 protons next to the ester carbonyl and oxygen, respectively. The other identifying feature is the CH protons of the heterocyclic thiophene ring resonating at 7.28 ppm, 7.33 ppm and 7.55 ppm. The ^{13}C NMR (Fig.3.5) and HSQC (Fig.3.6) analysis has also confirmed the successful isolation of the desired complex. The terminal aliphatic methylene carbon of 2-(3-Thienyl) ethanol appeared further downfield at 64.37 ppm. The other identifying peak of the ester carbonyl resonated at 173.53 ppm.

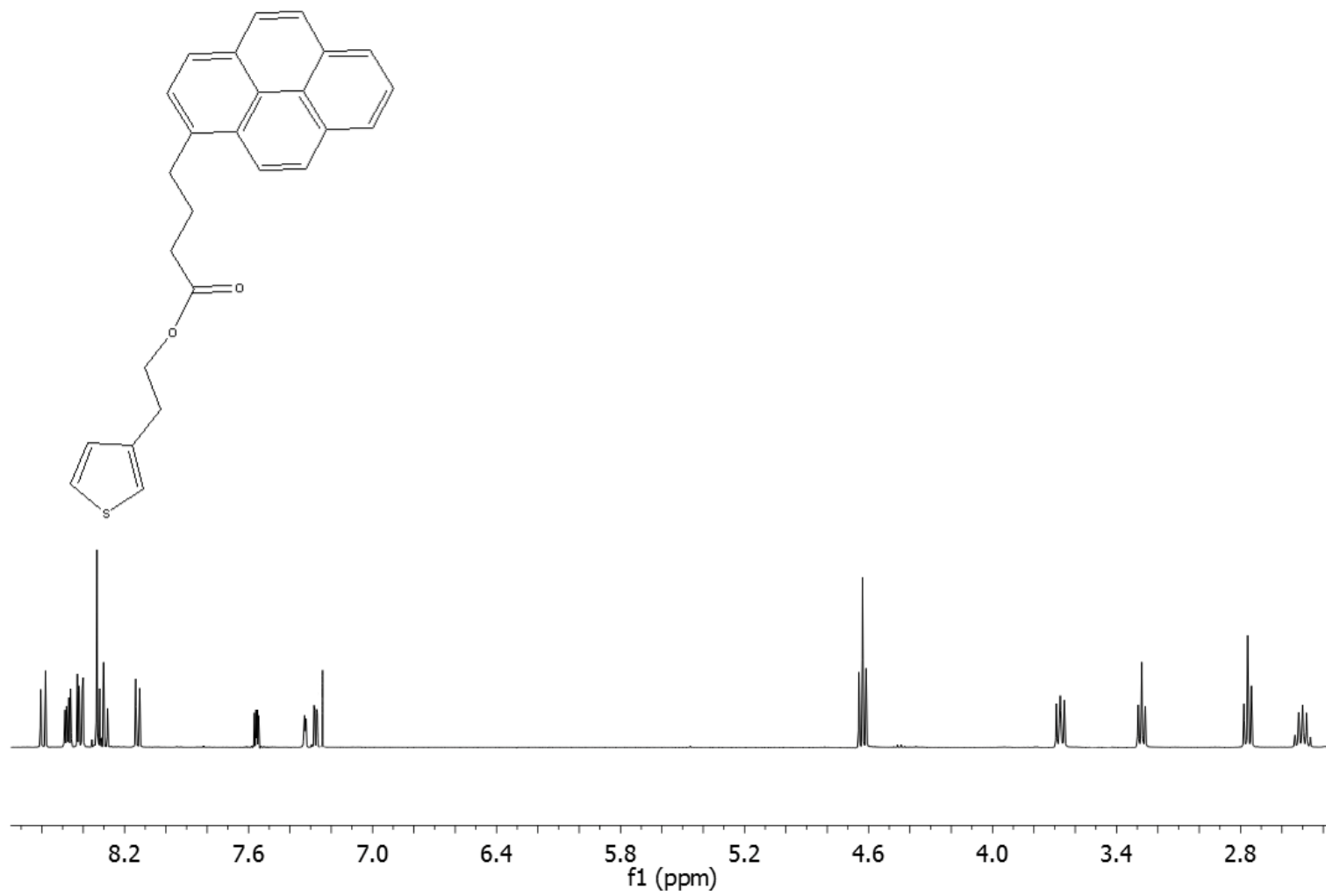


Figure 3.4 ¹H NMR spectrum of 2-(3-Thienyl)ethanol with 1-Pyrenebutyric acid (3.4).

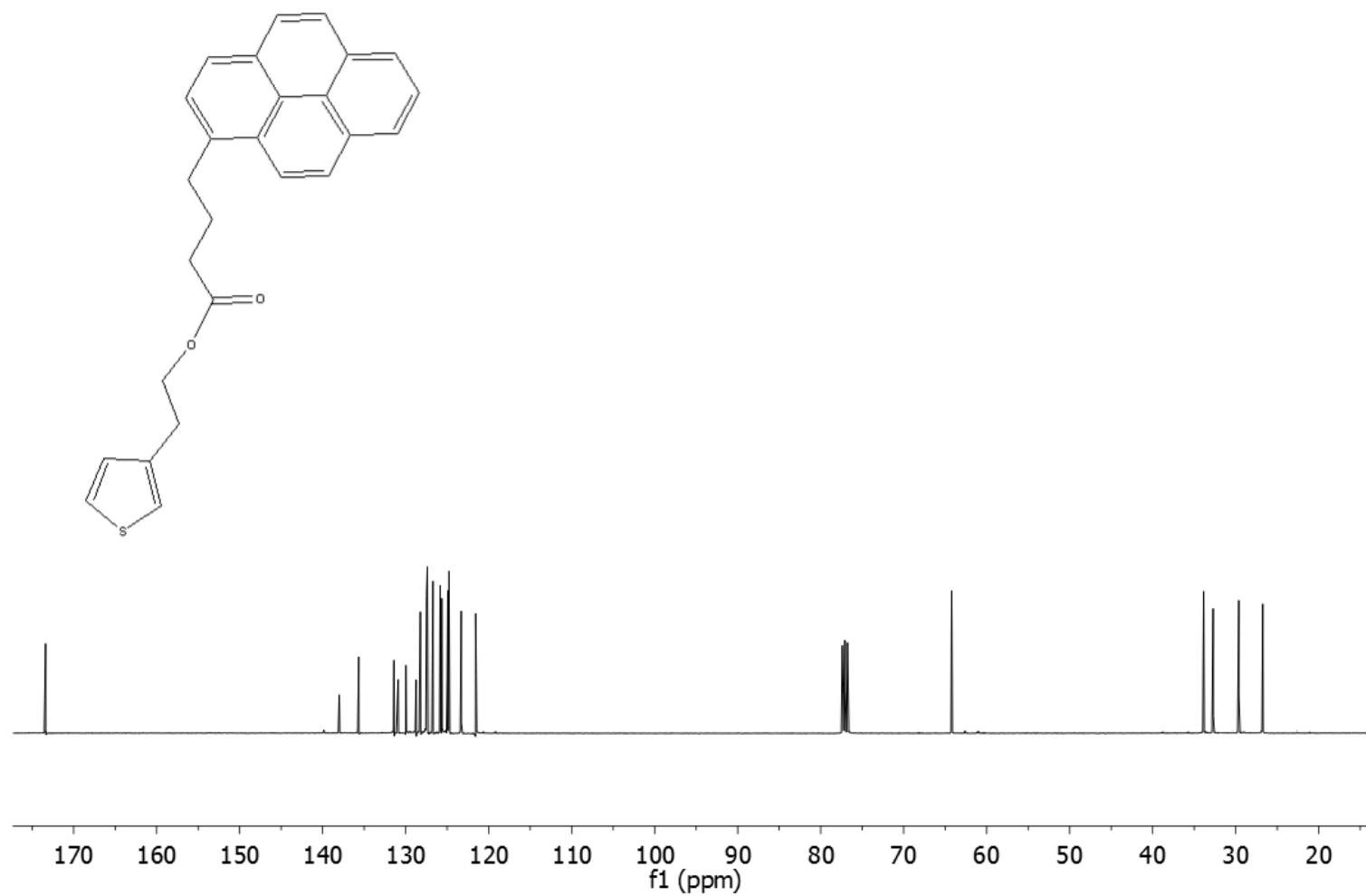


Figure 3.5 ^{13}C NMR spectrum of 2-(3-Thienyl)ethanol with 1-Pyrenebutyric acid (3.4).

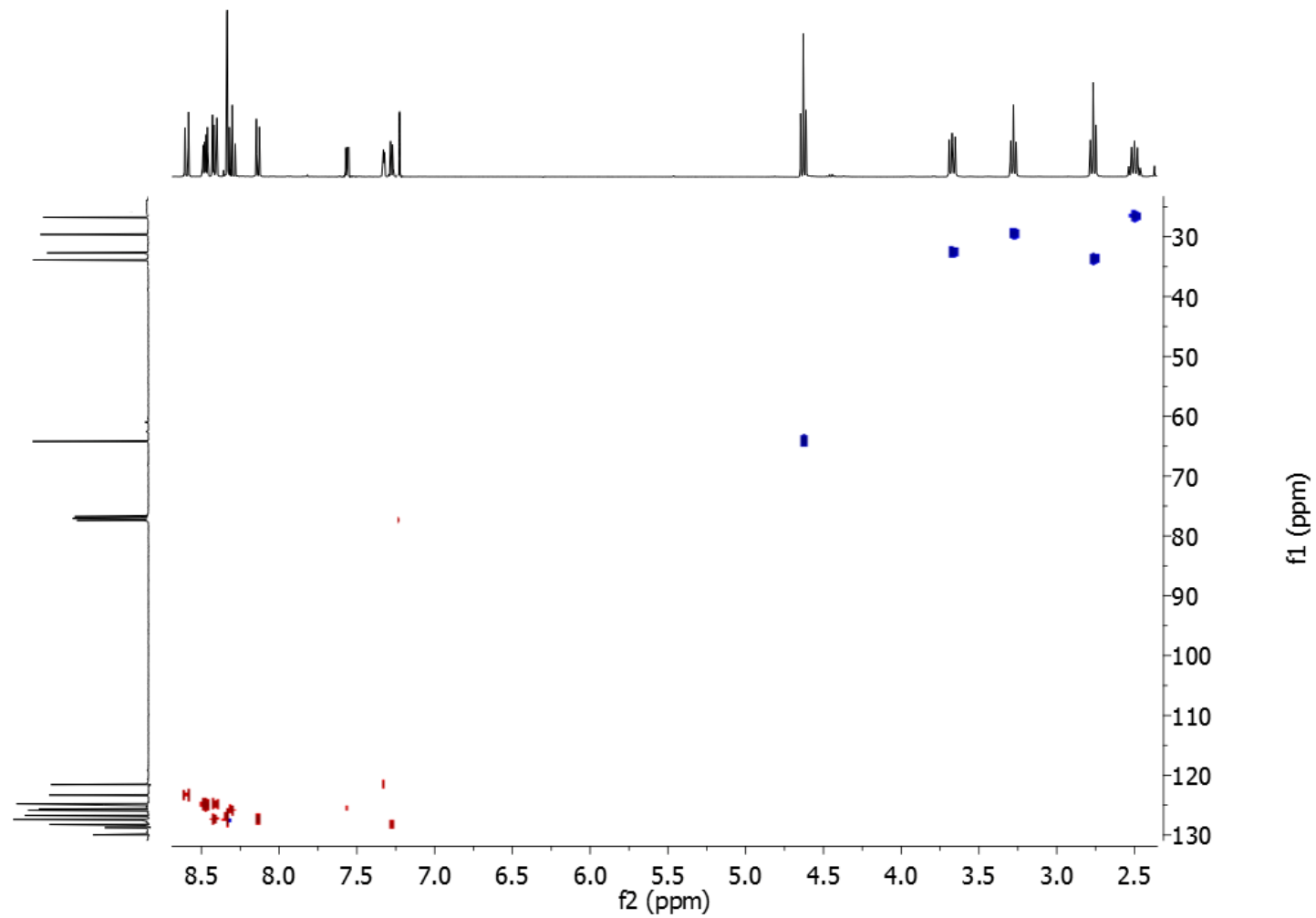
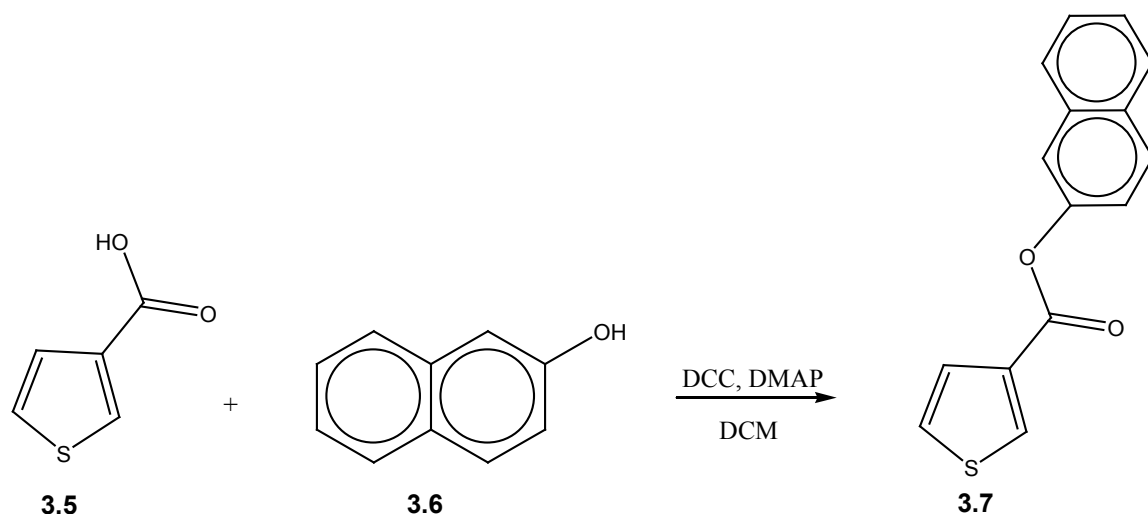


Figure 3.6 2D-HSQC NMR spectrum of 2-(3-Thienyl)ethanol with 1-Pyrenebutyric acid (3.4).



Scheme 3.3 The esterification reaction of 3-Thiophenecarboxylic acid with 2-Naphthol (3.7).

The ^1H NMR spectrum (Fig.3.7) of the naphthol substituted thiophene monomer indicated a successful reaction. The disappearance of the carboxylic OH of thiophene-3-carboxylic acid at 12.64 ppm and the terminal alcohol proton of naphthol at 9.74 ppm proved the new monomer formation. Further confirmation was made with the ^{13}C NMR spectrum (Fig.3.8). The main peak indicating the ester carbonyl resonated at 160.79 ppm whereas the aromatic methyl carbon peaks of the compound appeared in between 118 and 135 ppm. The HSQC NMR spectrum (Fig.3.9) confirmed the formation of the desired product, showing the correlation between protons and carbons.

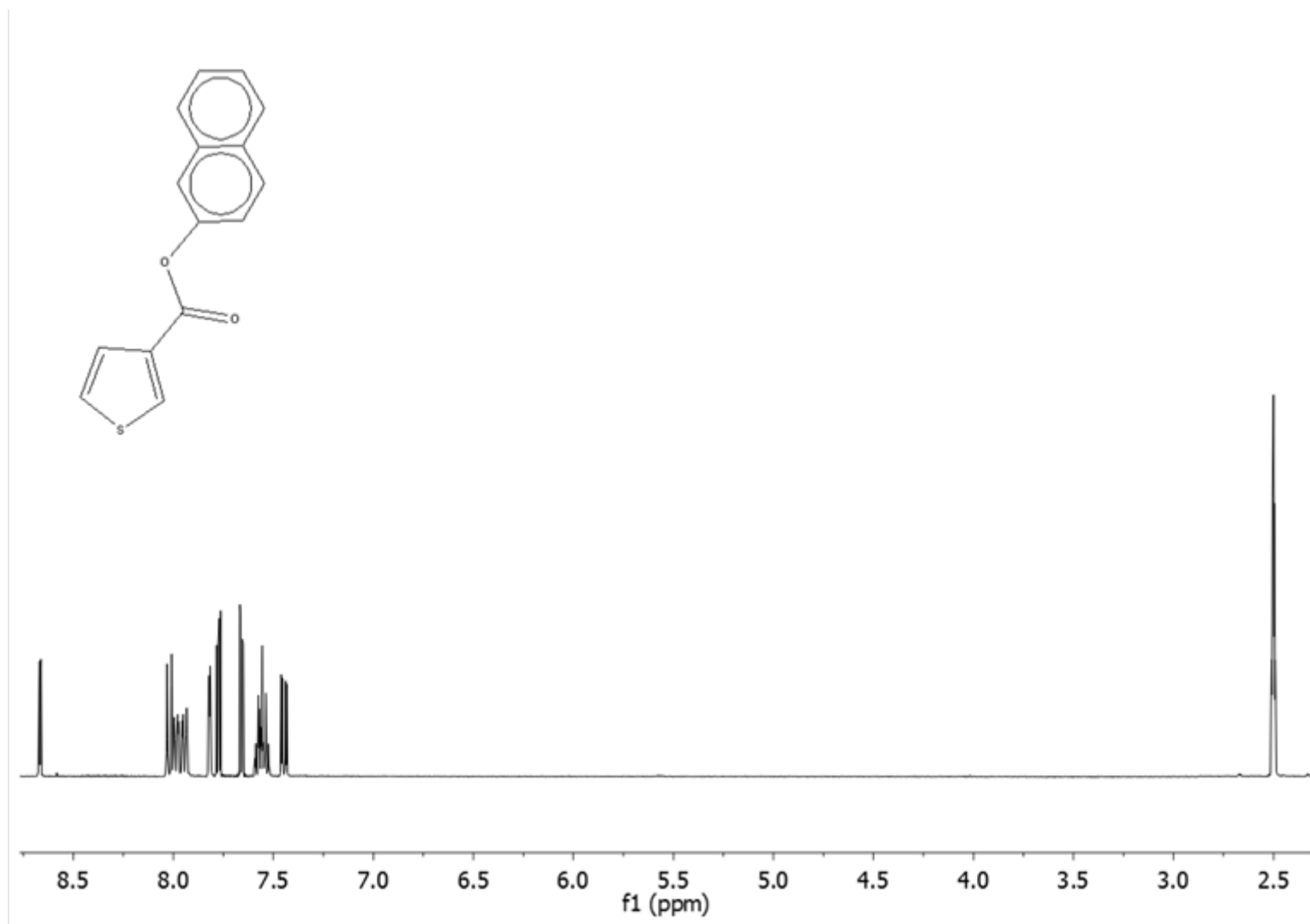


Figure 3.7 ^1H NMR spectrum of 3-Thiophenecarboxylic acid with 2-Naphthol (3.7).

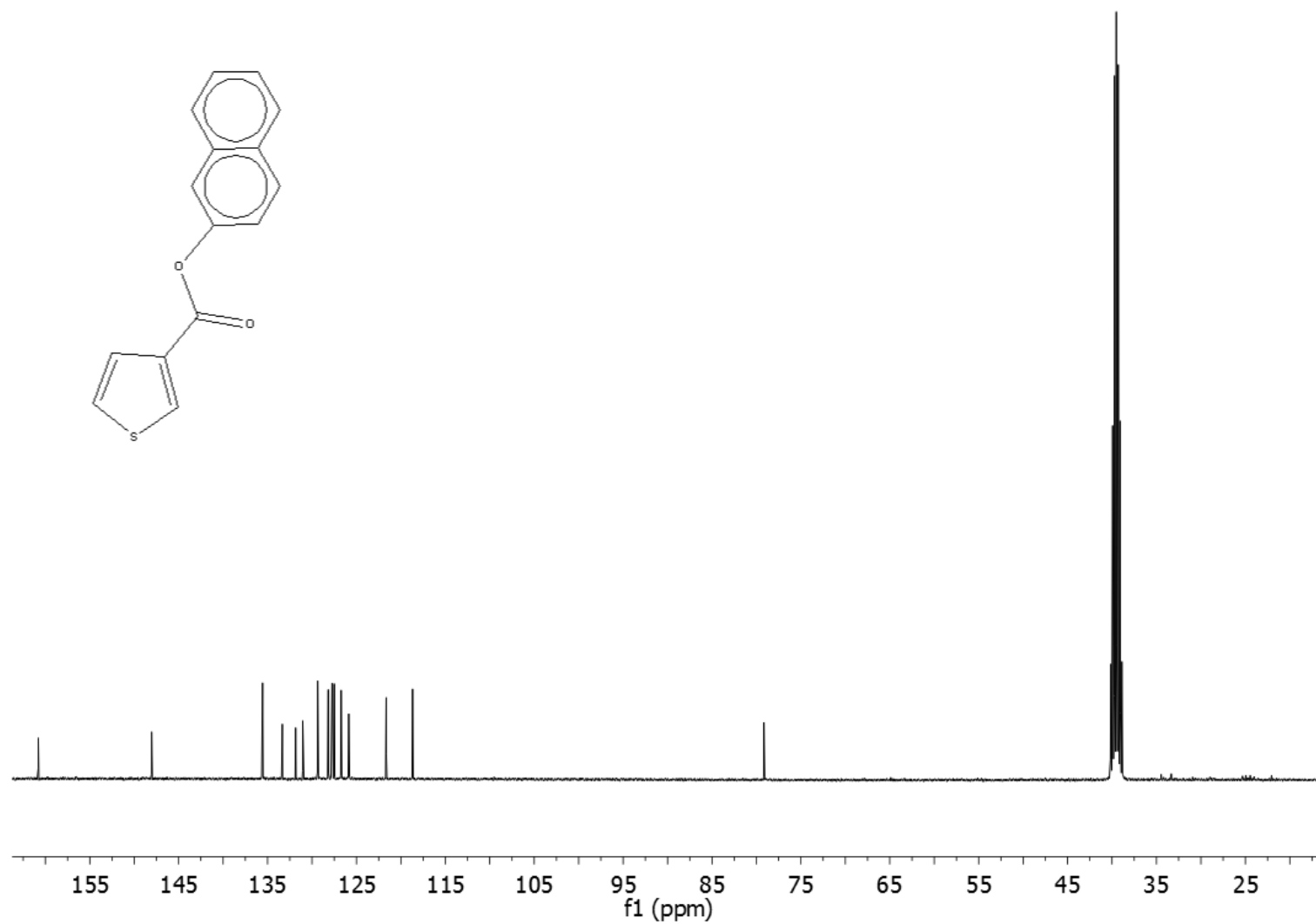


Figure 3.8 ^{13}C NMR spectrum of 3-Thiophenecarboxylic acid with 2-Naphthol (3.7).

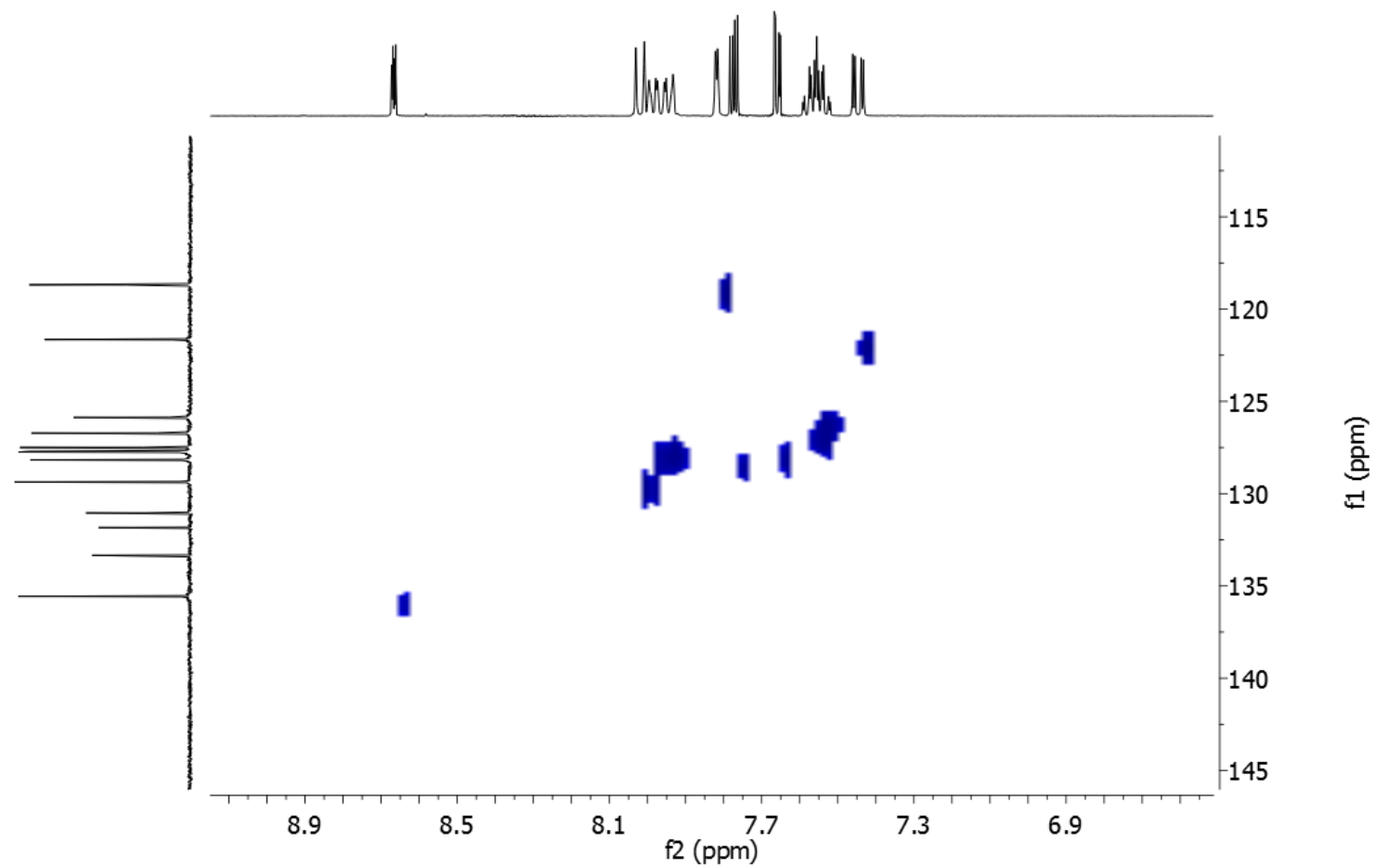


Figure 3.9 2D-HSQC NMR spectrum of 3-Thiophenecarboxylic acid with 2-Naphthol (3.7).

3.2.1.1 Electropolymerization of ThC (3.2), ThP (3.4) and ThN (3.7)

Oxidative electropolymerization of the synthesized monomers was carried out in DCM with 0.1M $\text{Bu}_4\text{NClO}_4^-$ as supporting electrolyte using the conventional three electrode system. Polymer growths were achieved at 100 mVs^{-1} of 2mM solutions of monomers onto carbon fibre micro electrodes (area $\sim 0.066 \text{ cm}^2$) and glassy carbon disk electrode (2 mm diameter).

In Figure 3.10, 3.11 and 3.12 the first 5 scans for the anodic electropolymerization of ThC, ThP and ThN on carbon fibre micro electrodes via cyclic voltammetry are illustrated, respectively. Multi-sweep cyclic voltamogram showed an increasing current with each cycle ($E_{\text{pa,ThC}}=1.18\text{V}$, $E_{\text{pa,ThP}}=1.10\text{V}$, $E_{\text{pa,ThN}}=1.24\text{V}$ at 5th cycle), resulting in the formation of a thin film of conducting polymer on GC and CFME. The irreversible oxidation of the monomers appears clearly on the first cycle at around 1V.

Functional polymers always have higher onset potentials compared to the thiophene itself. The lowest onset potential value was observed at 0.938 V corresponding to the oxidation of ThC monomer which indicates that it easily undergoes anodic oxidation and radical cation formation compared to ThP and ThN [247]. The anodic and cathodic peak potential difference is higher for the ThN which dominates for higher conjugation length and electro-activity as well as highest ion penetration resistance.

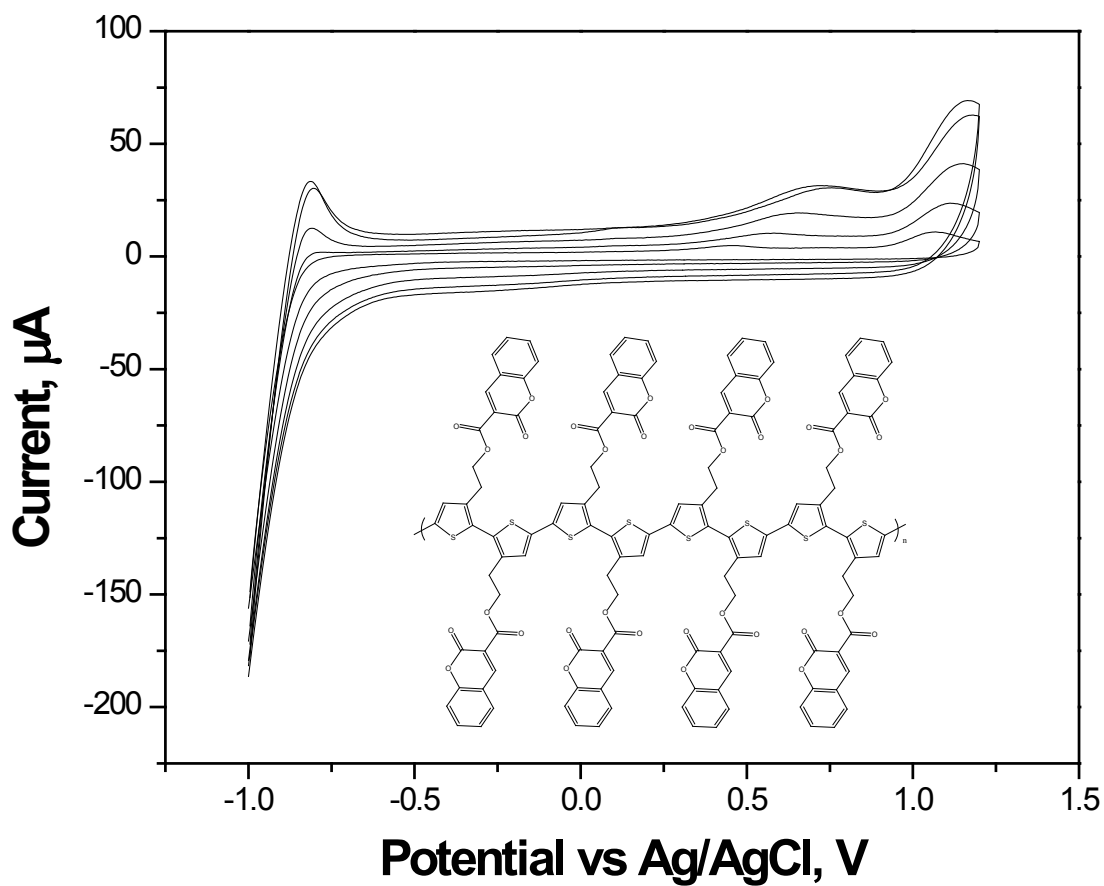


Figure 3.10 Electrodeposition of 2-(3-Thienyl)ethanol with Coumarin-3-carboxylic acid pendant, ThC (3.2) by potentiodynamic growth from a 2mM solution of monomer in 0.1M Bu₄NClO₄/DCM at 100 mVs⁻¹ onto CFME.

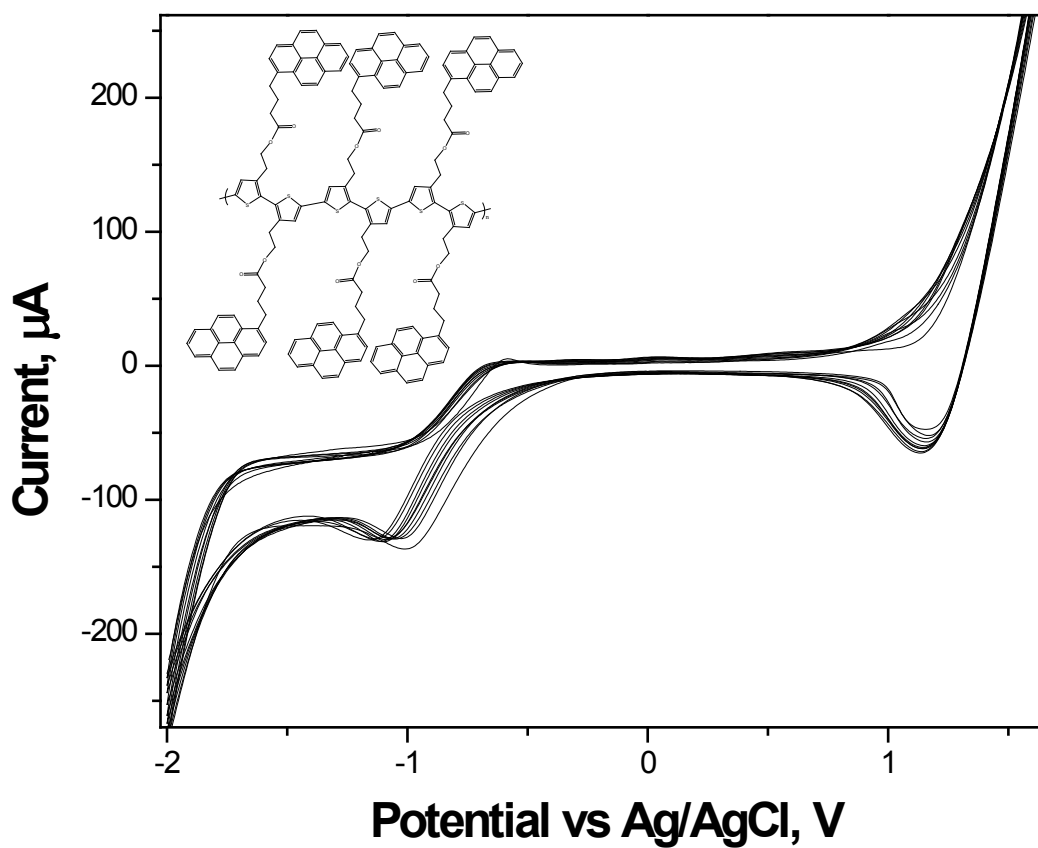


Figure 3.11 Electrodeposition of 2-(3-Thienyl)ethanol with 1-Pyrenebutyric acid pendant, ThP (3.4) by potentiodynamic growth from a 2mM solution of monomer in 0.1M Bu₄NClO₄/DCM at 100 mVs⁻¹ onto CFME.

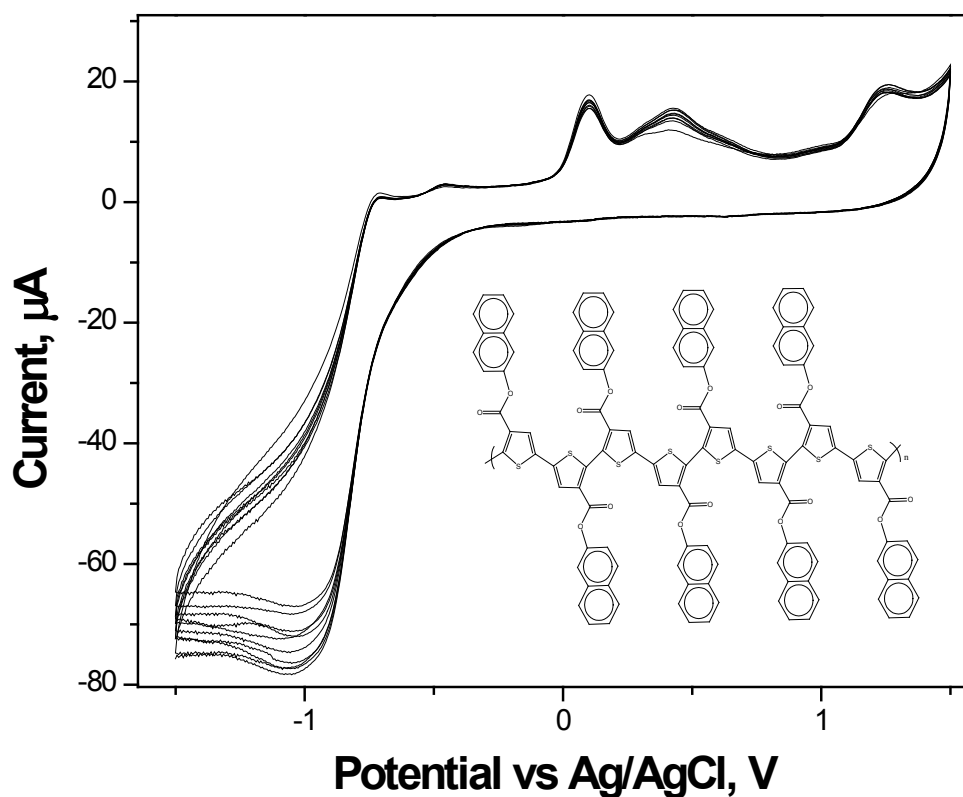


Figure 3.12 Electrodeposition of 3-Thiophenecarboxylic acid with 2-Naphthol pendant, ThN (3.7) by potentiodynamic growth from a 2mM solution of monomer in 0.1M Bu₄NClO₄/DCM at 100 mVs⁻¹ onto CFME.

Poly(ThC, ThP, ThN)/CFME thin films were immersed into a monomer free electrolyte solution and their redox behaviour was investigated at different scan rates. The scan rate dependencies were illustrated in Figure 3.13.

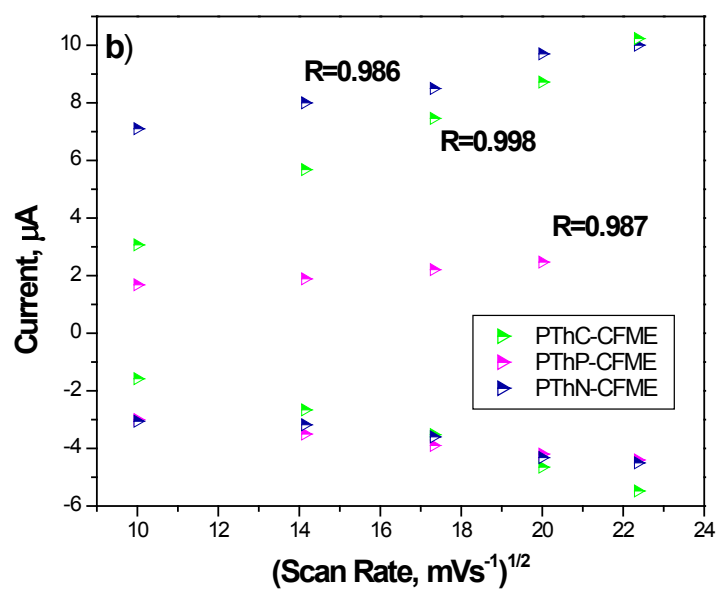
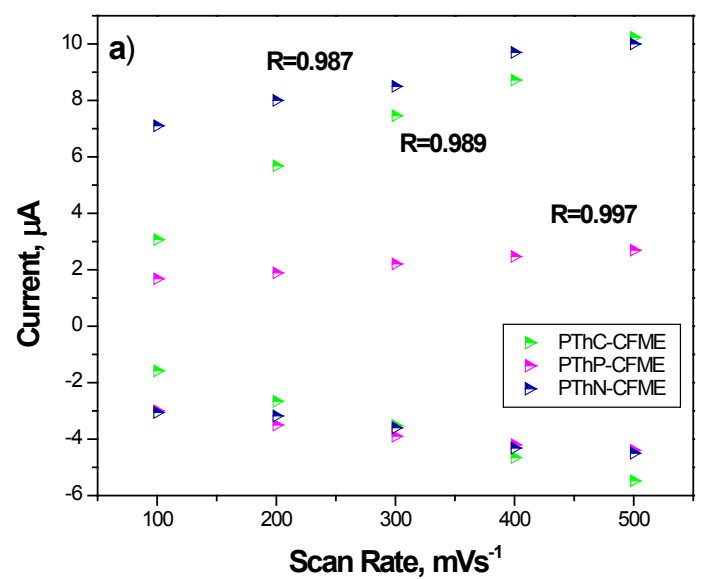


Figure 3.13 a) Scan rate dependencies b) square root of scan rate dependencies of polymer films in 0.1M $\text{Bu}_4\text{NClO}_4/\text{DCM}$ monomer free electrolyte solution.

The anodic and cathodic peaks were well defined at slow scan rates and an increase in the scan rate caused broadened and less well defined peaks indicating the process is not diffusion controlled. The peak correlation coefficients (R) were found to be 0.987 (PThC), 0.989 (PThP) and 0.997 (PThN) as a function of scan rate. The deviation from linearity at 400 mVs⁻¹ indicates that the films have thin layer behaviour but are not diffusion controlled.

3.2.1.2 Electrochemical Impedance Spectroscopic Characterization

The electrochemical impedance spectroscopy (EIS) measurements were taken at room temperature (25 °C) using a conventional three electrode cell configuration. EIS measurements were conducted in monomer-free electrolyte solution with a perturbation amplitude of 10 mV over a frequency range of 10mHz to 100 kHz with PARSTAT 2273 (software; powersuit).

The low frequency capacitance (Csp) values of electrochemically deposited thin films (at 0.01 Hz) were calculated by the following equation: $C_{sp} = (2\pi \cdot f \cdot Z'')^{-1}$, where Csp is the specific capacitance; Z'' is the slope of a plot of the imaginary component of impedance versus the inverse of the frequency (f) [249]. The calculated Cps and Cdl values for electrochemically polymerized thin films on different substrates are represented in Table 3.1.

The Nyquist diagram for PThP on GC electrode displays the highest capacitive behaviour ($C_{sp}=7083.3 \mu\text{F}/\text{cm}^2$) whereas the PThP film shows pure resistor behaviour at higher frequencies. At low frequency, the imaginary part of the impedance sharply increases and the plot tends to a vertical line characteristic of capacitive behaviour. On the other hand the PThC film on GC indicates the lowest specific capacitance value ($C_{sp}=30.8 \mu\text{F}/\text{cm}^2$) due to the slowest electron transfer, resulting in a lower charge storage ability and divergence from the capacitive line.

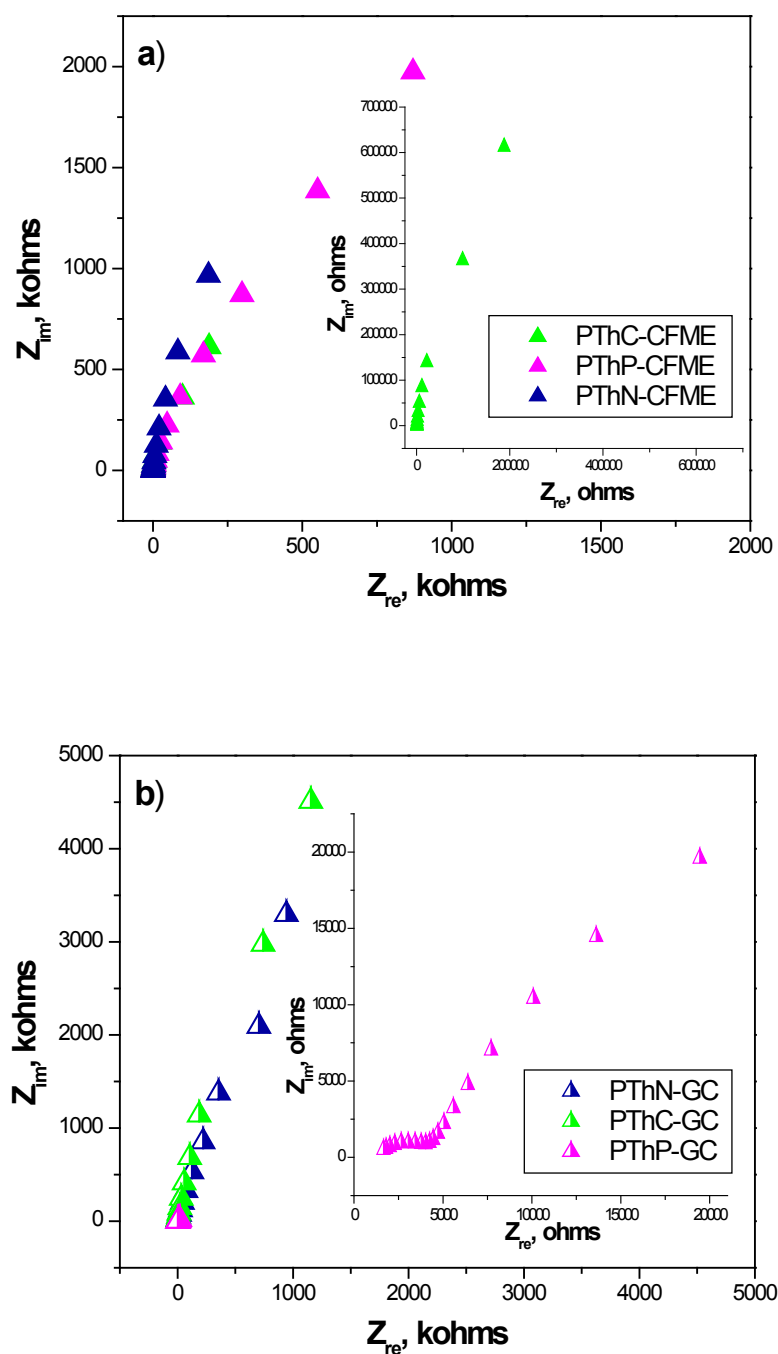


Figure 3.14 Nyquist plots for electrochemically polymerized ThC, ThP and ThN a) on CFME b) on GC electrode in 0.1M Bu_4NClO_4/DCM electrolyte solution, measured between 0.01Hz-100 kHz.

The Bode phase angle, which is very close to 90° as observed in highly capacitive behaviour, could be assigned as supercapacitor. In the Bode phase plot (Figure 3.15), the phase angle approaches a plateau at 85.4° and 84° (near ideal capacitor) in the frequency region ~ 1 Hz for PThN and PThC on CFMEs, respectively. The comparison of the maximum phase angles shows that the films deposited onto CFMEs have higher degrees than they have on GC electrodes.

Extrapolating line from the Bode magnitude plot to the $\log Z$ axis at $\omega = 1$ ($\log \omega = 0$) yields the value of C_{dl} from the equation $|Z| = 1/C_{dl}$ [42]. The highest C_{dl} value was obtained as $1515 \mu F cm^{-2}$ for PThC polymer film on CFME electrode surface (Figure 3.16). Therefore, PThC/CFME film was found to be thicker than the other thin films as well as possessing higher capacitive behaviour.

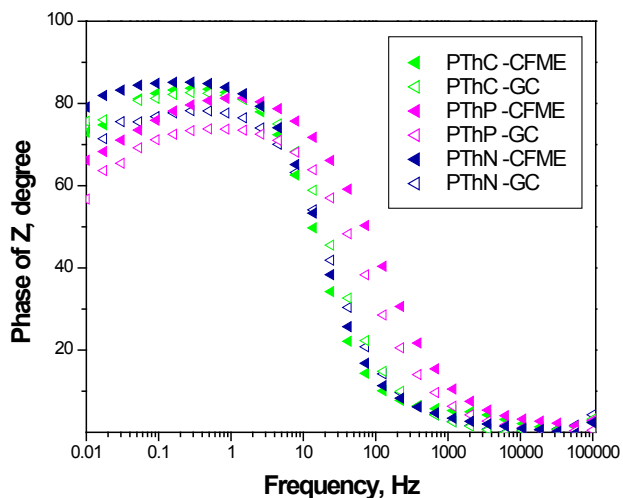


Figure 3.15 Bode Phase plots for electrochemically polymerized ThC, ThP and ThN in 0.1M Bu_4NClO_4 /DCM electrolyte solution, measured between 0.01Hz-100 kHz.

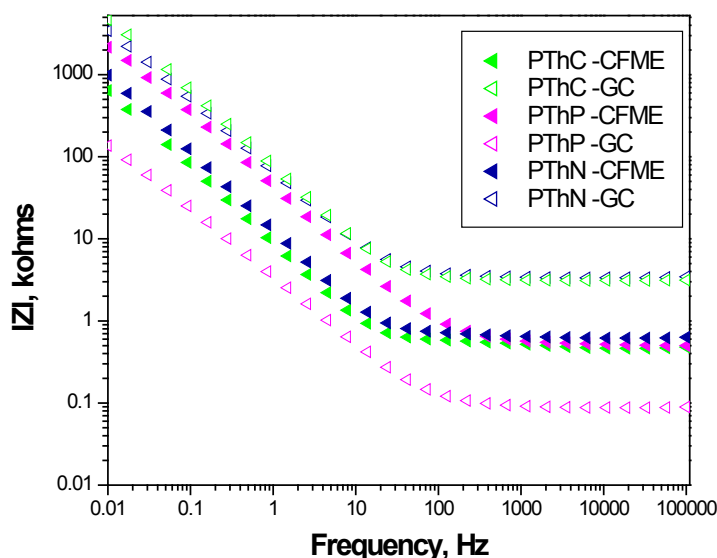


Figure 3.16 Bode Magnitude plots for electrochemically polymerized ThC, ThP and ThN in 0.1M Bu₄NClO₄/DCM electrolyte solution, measured between 0.01Hz-100 kHz.

The higher charge transfer resistance and low deposition charges (PThC_{ΔQ}= 37.23 mC, PThN_{ΔQ}= 15.07 mC, PThP_{ΔQ}= 9.35 mC) resulted in thinner PThC film on electrode surfaces which have low phase angles and low electrical conductivity (Figure 3.17). The complex plane impedance data for polymer films are indicated in Table 1.3.

The E_g values for the polymer films were verified by CV analysis. Potentiodynamically grown polymer films were washed with electrolyte solvent and measurement was taken in monomer-free electrolyte solution. CV shows onset potentials of n- and p- doping processes. The approximate E_g value of the polymer films were calculated from the difference of these onset potentials and found as E_g(PThN)~1.57 eV., E_g(PThP)~1.65 eV. and E_g(PThC)~1.61 eV.

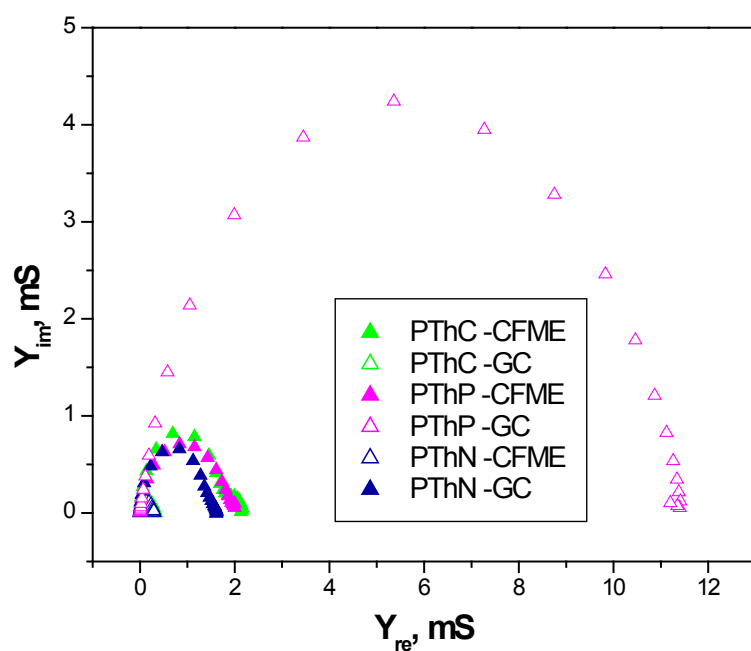


Figure 3.17 Admittance plots for electrochemically polymerized ThC, ThP and ThN in 0.1M Bu₄NClO₄/DCM electrolyte solution, measured between 0.01Hz-100 kHz.

Table 3.1 Complex plane impedance data of CFME, GC/PThC, PThP, PThN.

Polymer	Electrode	C _{sp} , μFcm ⁻²	C _{dl} , μFcm ⁻²	Phase angle, degree	Conductivity, mS
PThC	CFME	409	1515	84.0	0.795
PThC	GC	30.8	100	82.7	0.120
PThP	CFME	127.2	287.8	82.1	0.692
PThP	GC	7083.3	300	74.5	4.172
PThN	CFME	257.5	1090	85.4	0.589
PThN	GC	42.5	116.6	79.1	0.110

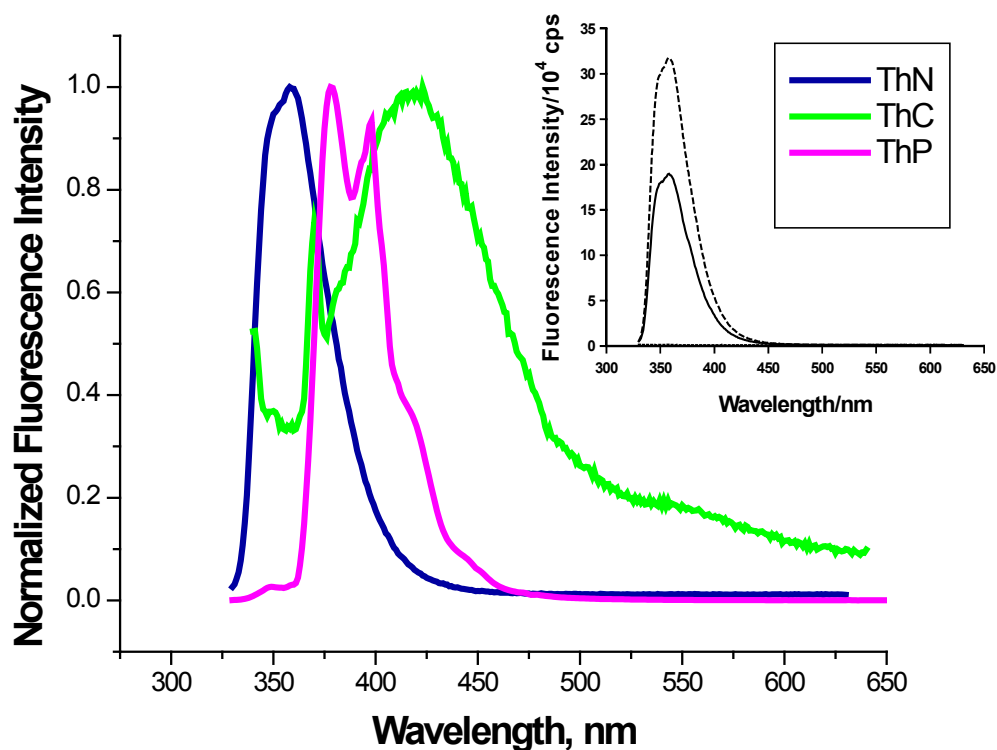


Figure 3.18 Fluorescence spectroscopy for chemically synthesized ThC (3.2), ThP (3.4) and ThN (3.7) monomer in DMSO. Inset: Fluorescence emission spectra of naphthol (—) and DMSO solvent blank (- - -), 330 nm excitation.

The fluorescence properties of ThC, ThP and ThN were characterized via fluorescence spectroscopy (Fig.3.18). In a single fluorescence spectrum, there is more than one peak that is visible for the ThP monomer (380nm and 400nm), which is typically because of vibrational resolution, so different specific S_1 ($v=0$) to S_0 ($v'=x$) of the same electronic fluorescence band are seen. Observation of vibronic resolution depends on a number of factors, and is usually seen for highly symmetrical molecules in nonpolar solvents. In this case, the pyrene fluorophore shows very detailed vibronic structure. However, both the coumarin (420nm) and the naphthol (360nm) show only a broad single peak, which is the envelope of all of the vibronic transitions.

In the case of the coumarin here, what looks like a second sharp band (370nm), is in fact a Raman scattering band from the solvent (DMF).

The effect of attachment of the thiophene moiety to the three fluorophores is markedly different in each case. This difference in the effect of attachment of the thiophene moiety on the fluorescence properties of these three compounds ThC, ThP and ThN relative to their fluorophore precursors can be partly related to the differences in sensitivity and the nature of the electronic states of these three very different fluorophores, but can also be at least partly related to a dependence on the length of the tether between the thiophene and fluorophore parts of the molecule.

The relative emission (relative quantum yields) of the three compounds excited at 330 nm is quite different, and is similar to that of the fluorophore precursors themselves, with ThP being by far the most highly emissive. Correcting for the absorbance of each solution at 330 nm and normalizing the peak emission intensity of ThP to 100, the relative emission of ThN is 27 and that of ThC is only 0.08. Thus, the ThP compound is over 1,000 times more fluorescent than is the ThC compound.

3.2.1.3 Morphological Characterization

The morphologies of electrochemically synthesized polymer films on CFME were investigated by SEM at low voltages to avoid electron charging during imaging. As illustrated in Figure 3.19, each polymer has different surface morphologies and film thicknesses. The comparison of film thicknesses revealed that PThN (2.2 μ m) was found quite thicker than PThP (0.77 μ m) and PThC (0.33 μ m) films and homogeneously distributed along the fibre. However, the PThC film has spherical particles forming a uniform film whereas the PThP indicated non-homogeneous and transparent thin film on CFME surface.

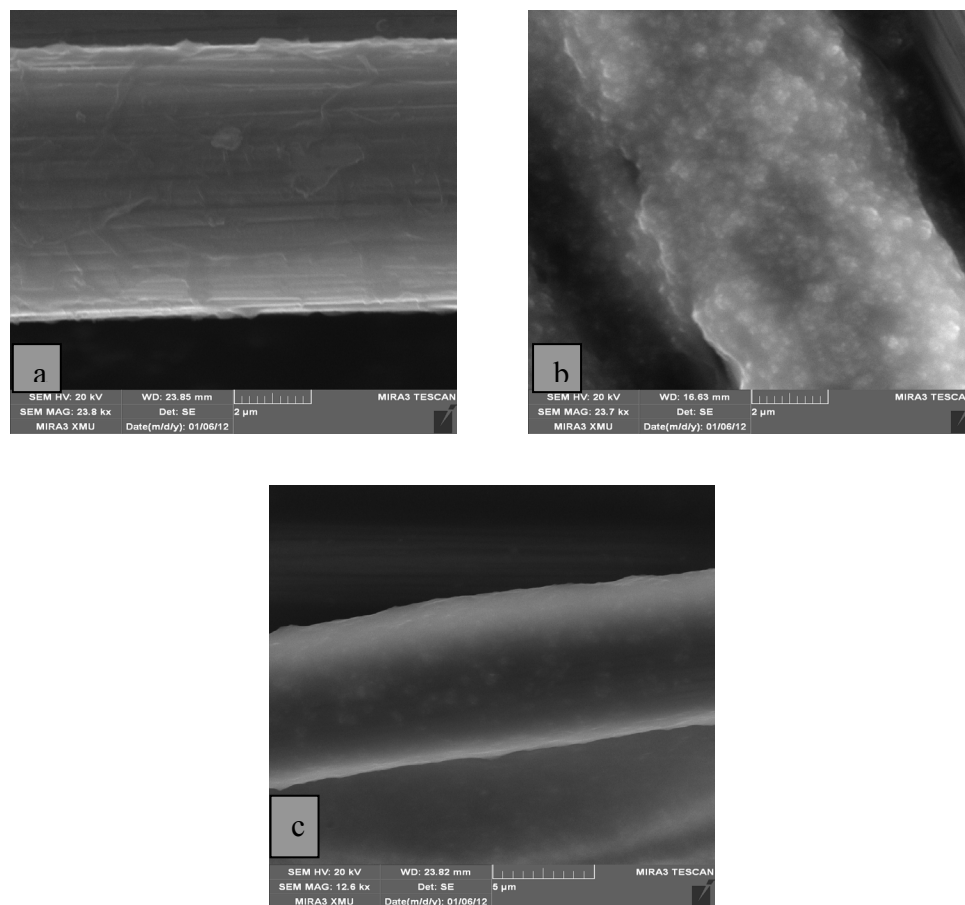
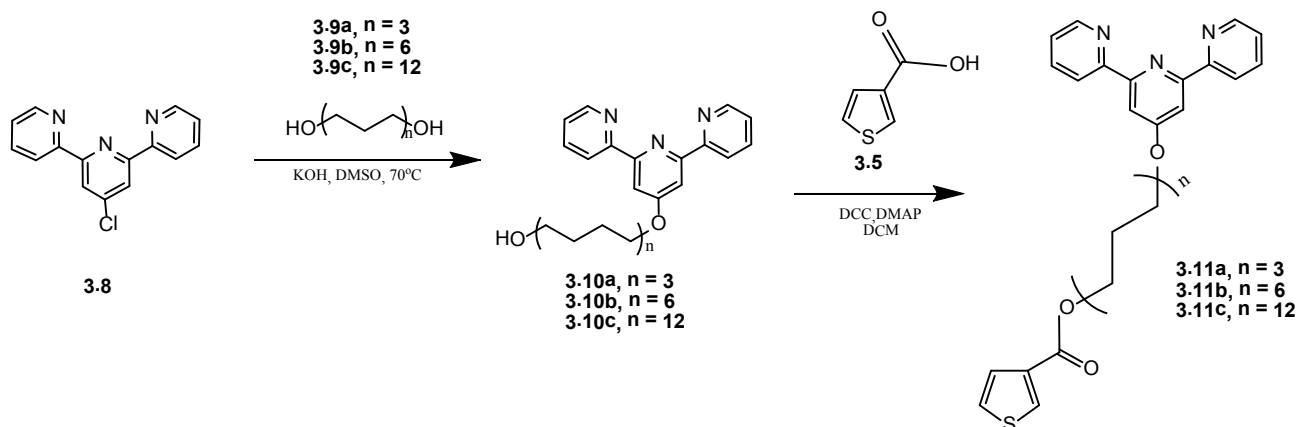


Figure 3.19 SEM images of electrodeposited a) PThP, b) PThC, c) PThN on CFME (20cycles).

3.2.2 Novel Synthesis of Thiophene Derivatives with Terpyridine Side Groups

A novel series of thiophenes with terpyridine pendant groups were synthesized by Steglich esterification in the presence of DCC/DMAP and the synthesized monomers were electrochemically polymerized onto glassy carbon and carbon fibre micro electrodes as an active electrode material. Each pendant group has aliphatic spacers with different chain lengths affecting the movement of the terpyridine groups. The synthesized thiophene derivatives were characterized by ^1H NMR, ^{13}C NMR, FTIR, cyclic voltammetry, electrochemical impedance spectroscopy and fluorescence spectroscopy. The electrochemical impedance spectroscopic measurements of terpyridine functionalized polythiophene derivatives were given comparatively.

The existence of a capacitance behavior is shown by Nyquist, Bode magnitude, Bode phase and admittance plots relationship. Variation of capacitance values was explained according to the spacer lengths between the thiophene and terpyridine as well as the different substrates. The fluorescence behaviours of the compounds in dimethylsulfoxide were observed. The morphological characterization was achieved via scanning electron microscopy.



Scheme 3.4 Synthesis steps for terpyridine attached thiophene derivatives.

The molecular identification of synthesized complexes was achieved via ^1H , ^{13}C and HSQC NMR spectra. The 4'-chloro-2,2':6',2''-terpyridine was reacted with different chain length diols. In Figure 3.20, the superimposed ^1H NMR spectrum was illustrated for three different diol substituted terpyridines. The heterocyclic terpyridine CH peaks shifted further downfield at 7 ppm due to the non-bonding electron pair of nitrogen. Additionally, nucleophilic substitution of diols were confirmed with the appearance of the aliphatic CH_2 peaks and the terminal CH_2 protons of diol at the bonded side were shifted to 4.20 ppm due to electron withdrawing effect of oxygen and nitrogen whereas the other terminal aliphatic methylene protons were assigned at 3.40 ppm. When comparing the ^1H NMR spectra, it is observed that the aliphatic CH_2 protons of propanediol, which was attached to terpyridine, was shifted more

downfield than the longer diols. The electron withdrawing effect of lone pairs of nitrogen and oxygen were observed in ^{13}C NMR as well (Fig. 3.21). The heterocyclic terpyridine carbons resonated further downfield than 110 ppm whereas the carbons in the aliphatic chain appeared in the range of 20 ppm and 70 ppm.

The esterification reaction of terpyridine-diols with thiophene-3-carboxylic acid was also confirmed with ^1H and ^{13}C NMR spectrum (Fig. 3.22 and Fig. 3.23). Disappearance of the carboxylic OH at 12.63 ppm and the shifts of heterocyclic thiophene methylenes downfield (7.49 ppm, 7.60 ppm and 8.30 ppm) as well as the disappearance of the terminal hydroxyl proton at 4.34 ppm proved the successful esterification reaction. In particular, the new ester carbonyl peaks appear at 166.57 ppm, 162.48 ppm and 166.71 ppm was further proof of the successful formation of the desired products. Further characterization was also achieved with 2D-HSQC NMR spectrum indicating successful esterification reactions (Fig.3.21, Fig.3.22, and Fig.3.26).

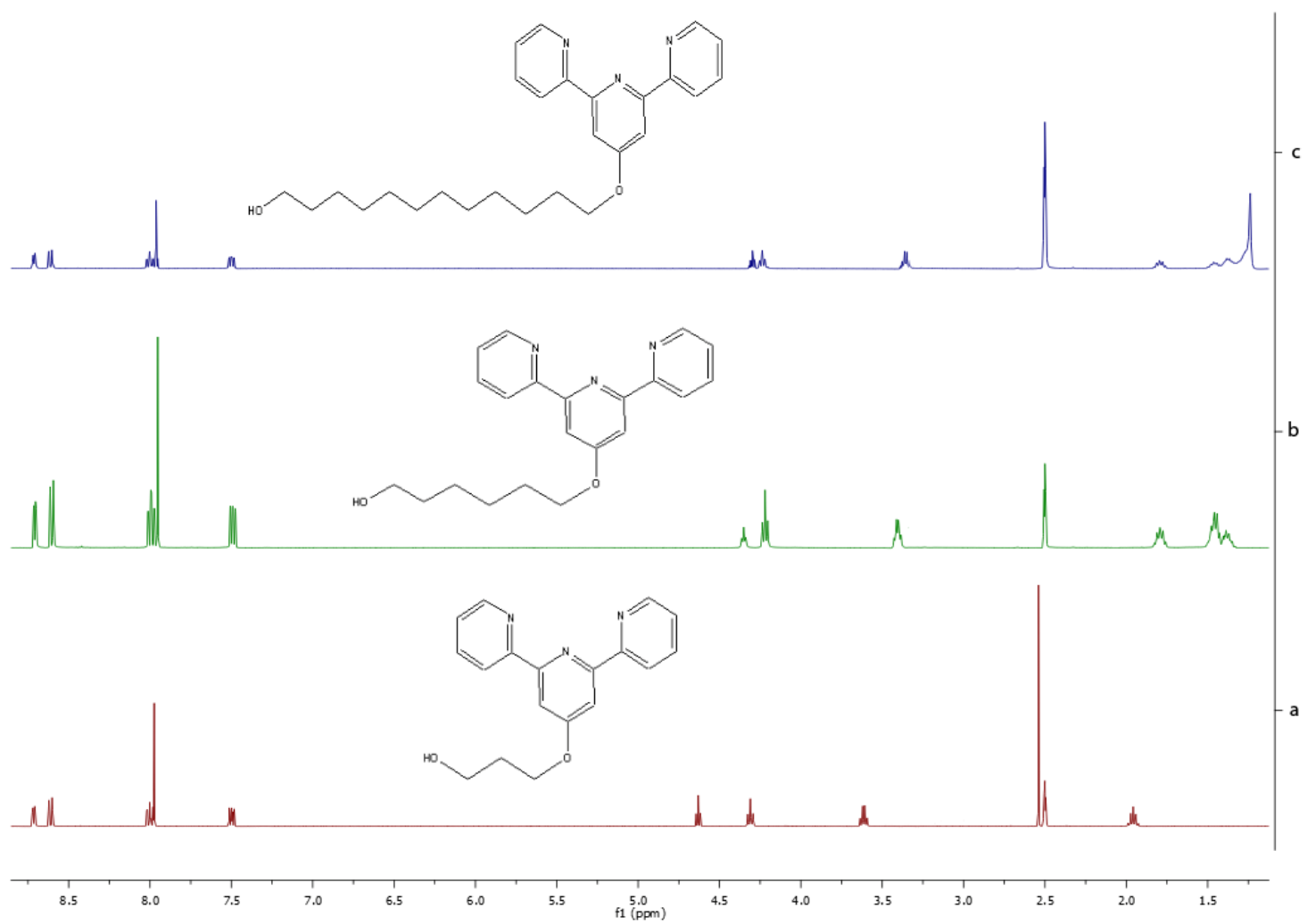


Figure 3.20 ^1H NMR spectrum of complex 3.10a, 3.10b and 3.10c.

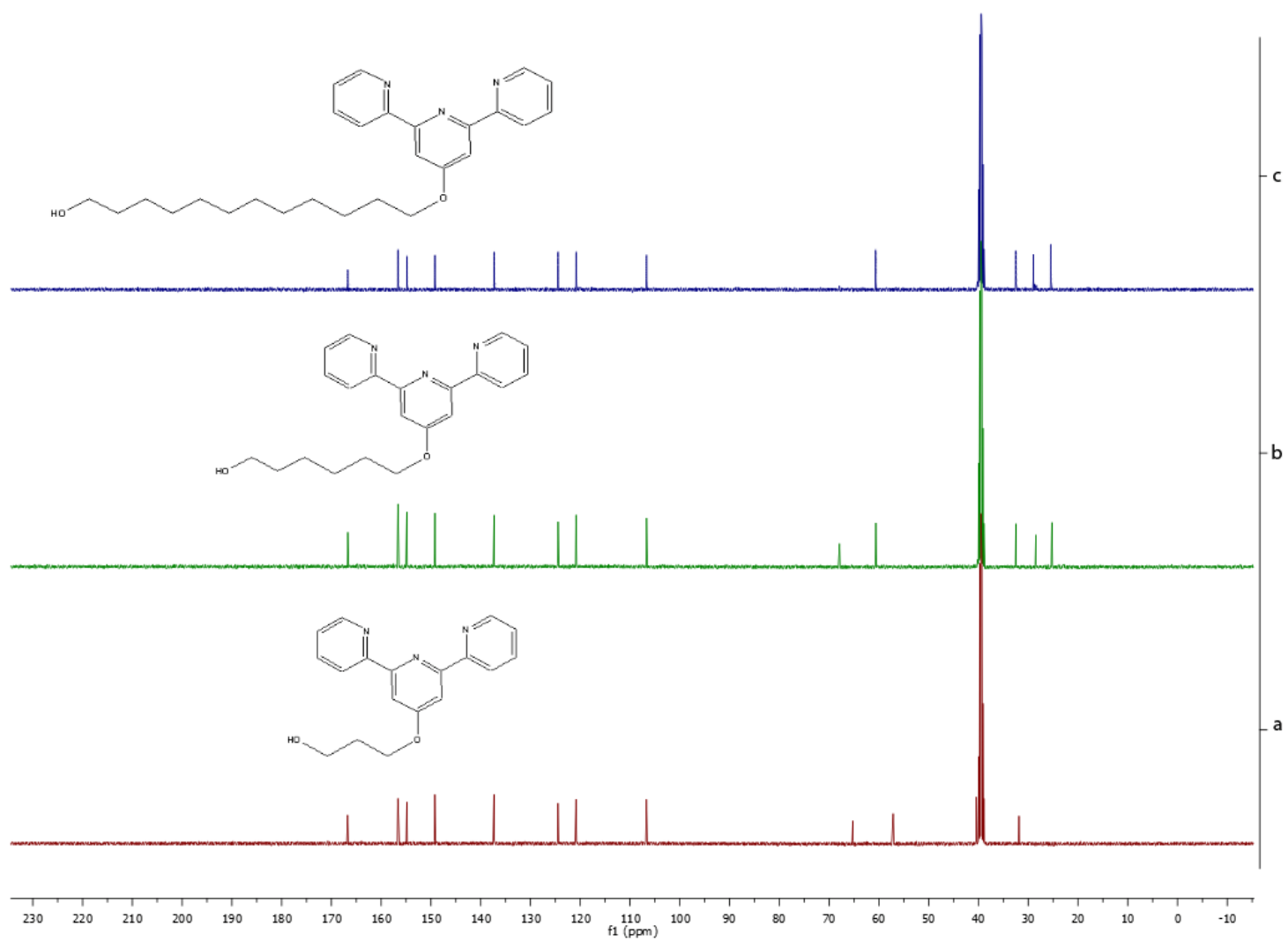


Figure 3.21 ^{13}C NMR spectrum of complex 3.10a, 3.10b and 3.10c.

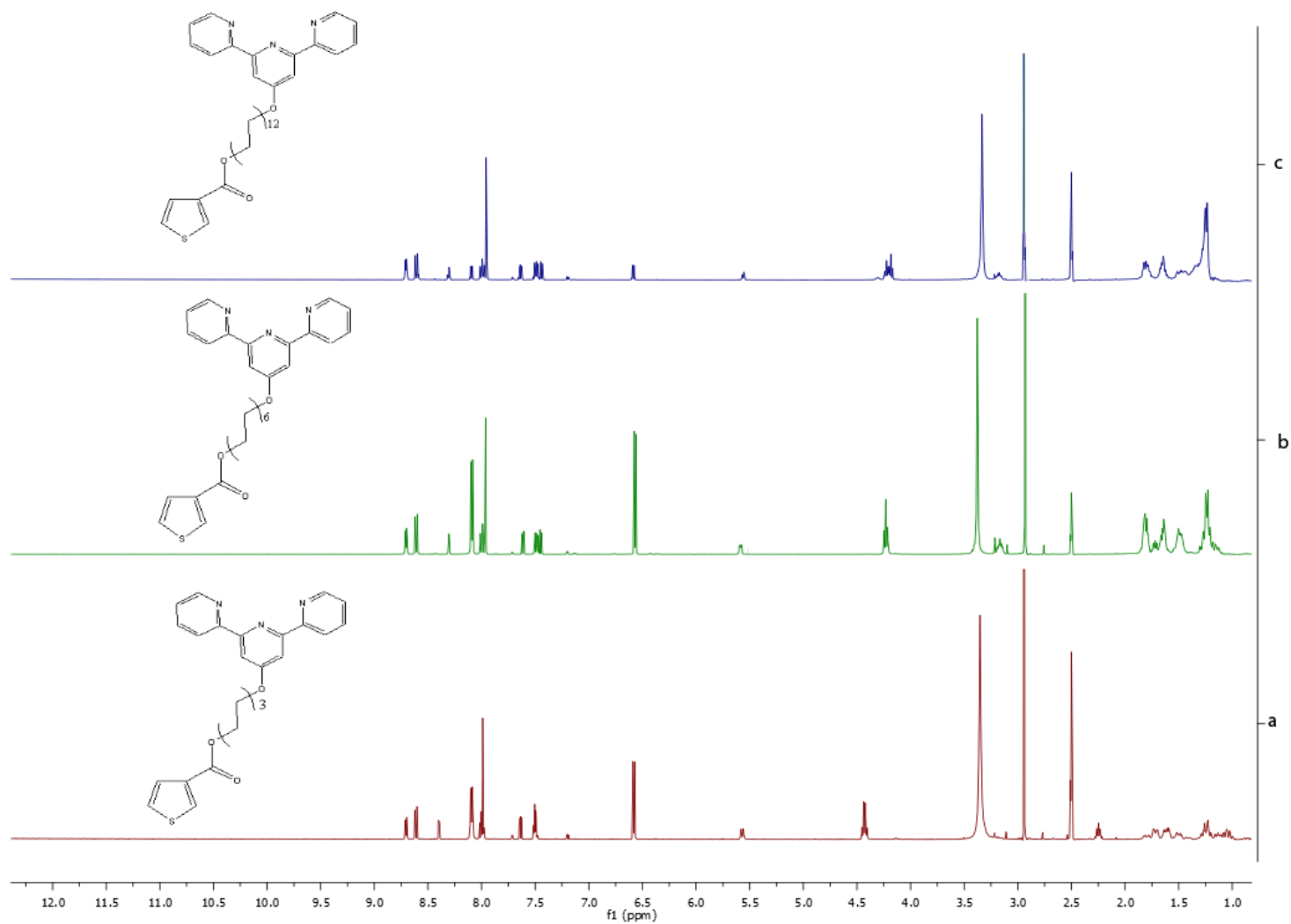


Figure 3.22 ^1H NMR spectrum of complex 3.11a, 3.11b and 3.11c.

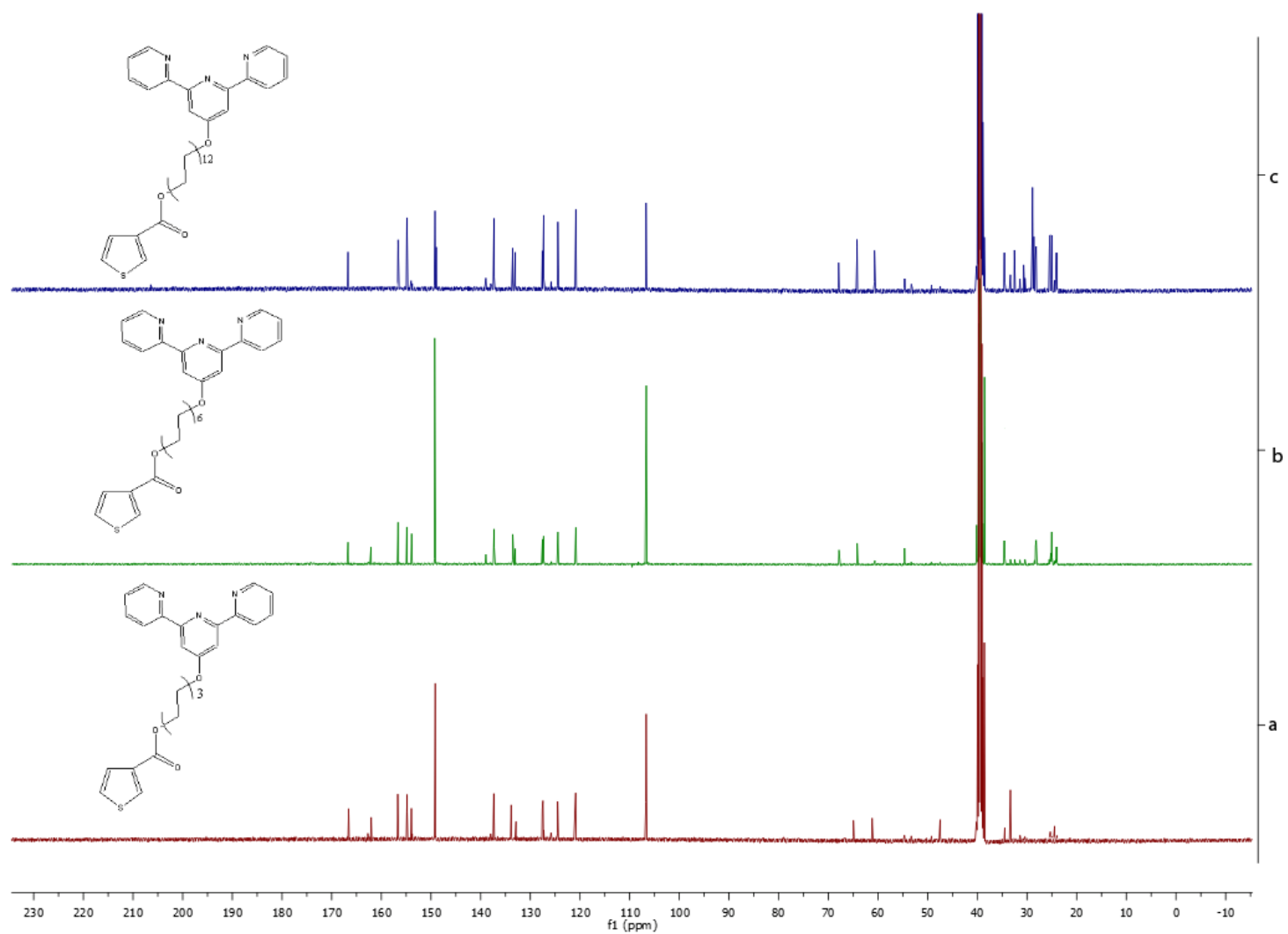


Figure 3.23 ^{13}C NMR spectrum of complex 3.11a, 3.11b and 3.11c.

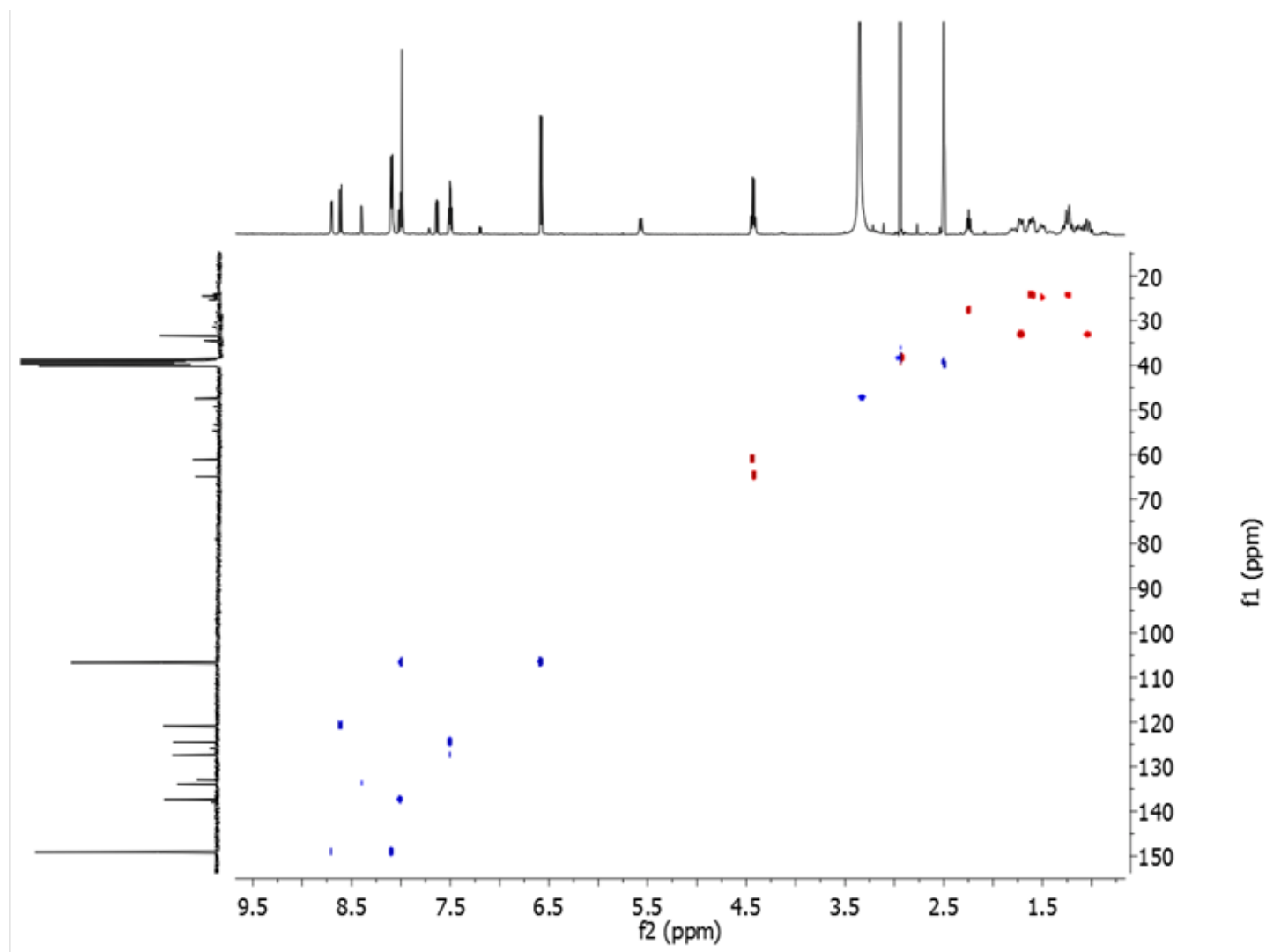


Figure 3.24 2D-HSQC NMR spectrum of complex 3.11a.

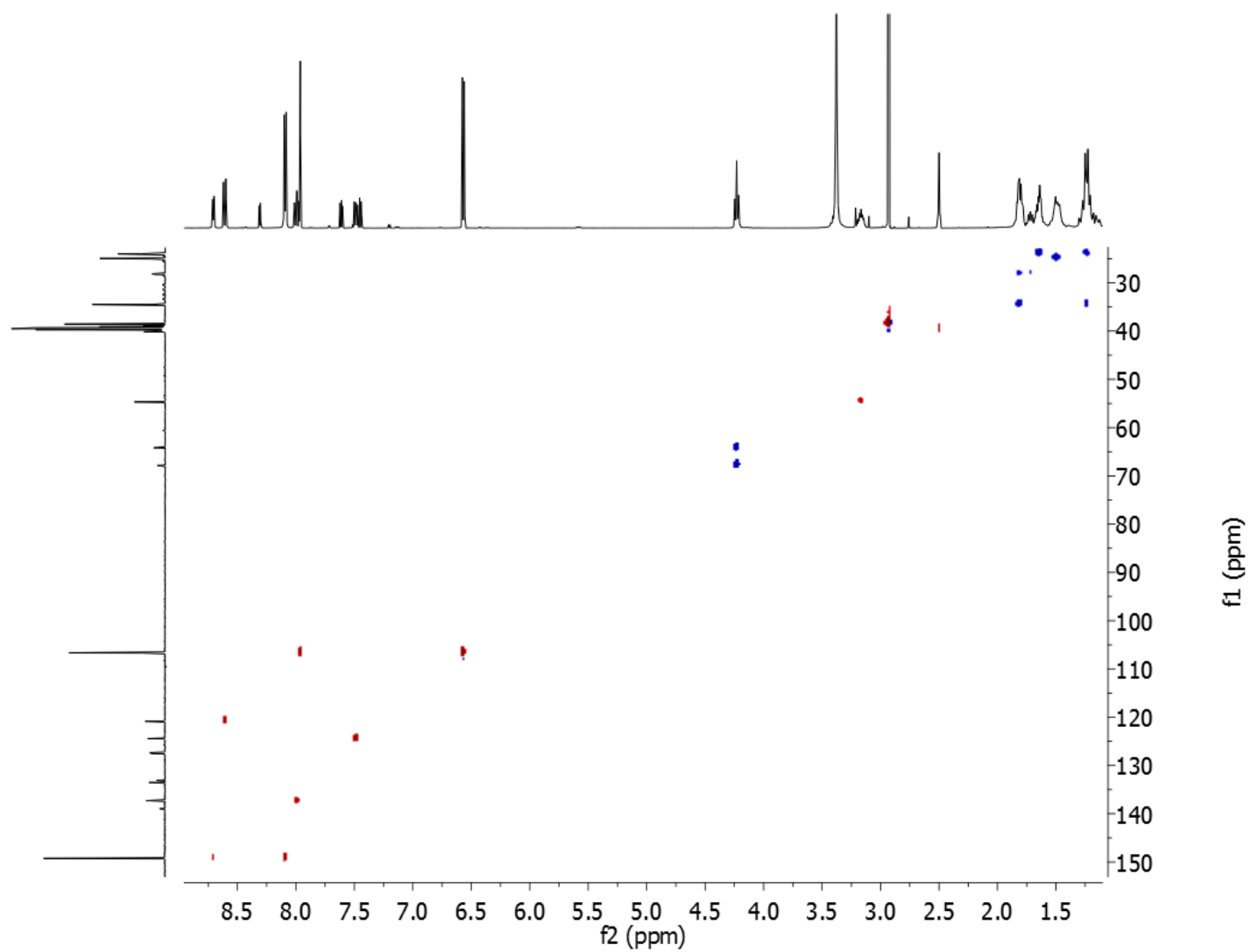


Figure 3.25 2D-HSQC NMR spectrum of complex 3.11b.

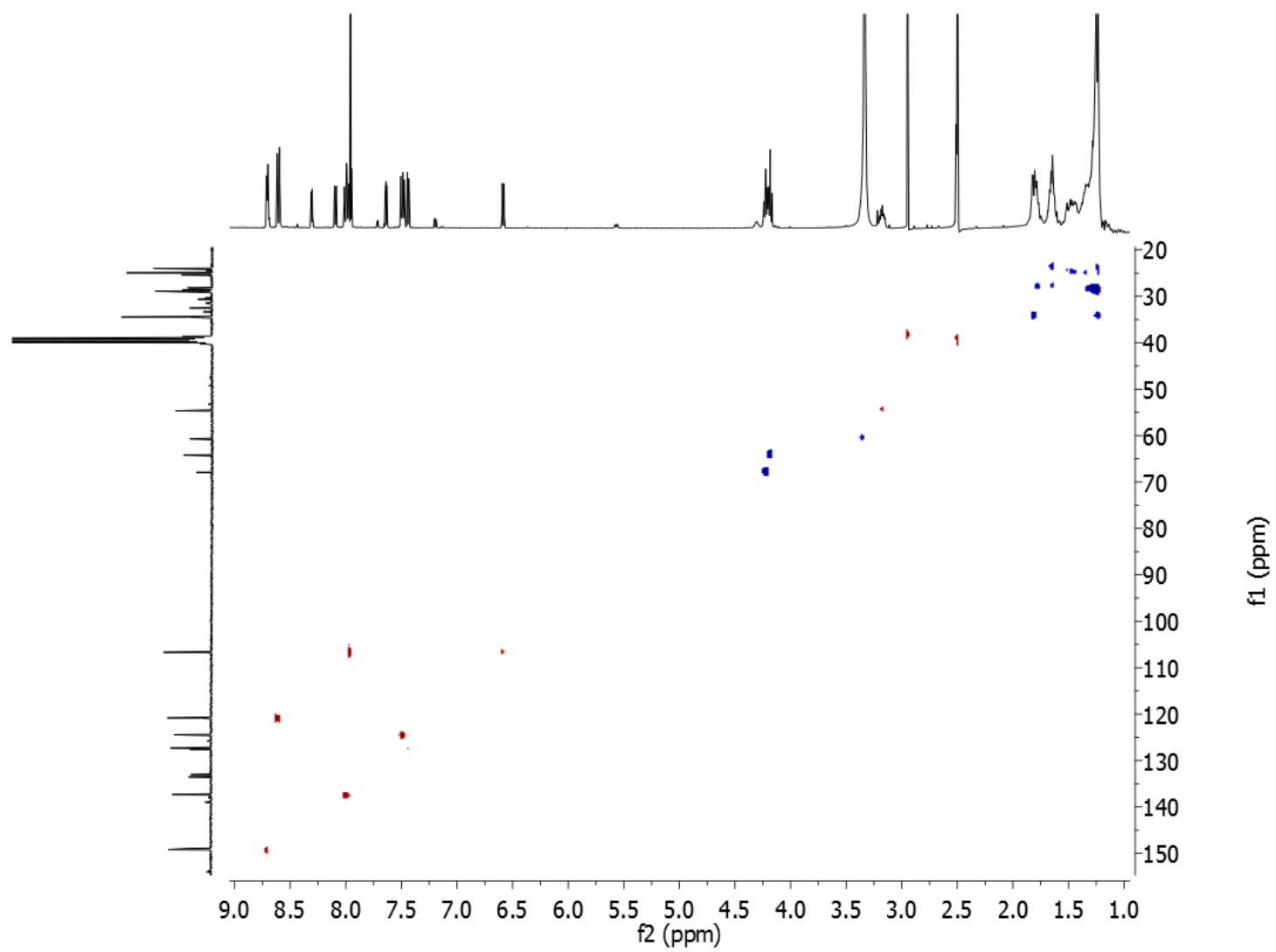


Figure 3.26 2D-HSQC NMR spectrum of complex 3.11c.

3.2.2.1 Electropolymerization of ThPTerpy (3.11a), ThHTerpy (3.11b) and ThDTerpy (3.11c)

Potentiodynamic electrogrowth processes of terpyridine functionalized thiophene derivatives were coated on carbon fibre micro electrodes and glassy carbon electrodes in 0.05M TBAPF₆/DCM solution using three electrode cell system at 25°C. The gradual increase in the intensity of anodic oxidation waves with repeated sweeps indicates that the polymer is gradually deposited on the surface of the electrodes. However, the cyclic voltamogram of ThPTerpy (Fig.3.27), ThHTerpy (Fig.3.28), and ThDTerpy (Fig.3.29), in DCM exhibited weak reduction peaks.

Decrease in the oxidation potential of the polymer provides a better stability in the oxidized state. Therefore, the onset potential value for ThDTerpy was found to be lower compared to the others ($E_{\text{onset}}=0.47\text{V}$) due to the ease of movement of bulky side group and flexibility of the longer spacer. The monomer oxidation potentials (ThPTerpy=0.66V, ThHTerpy=0.56V) increased while the spacer length decreased. Since ThDTerpy showed the highest peak current value ($I_a=75\mu\text{A}$) the ThDTerpy film was found to be thicker than the ThPTerpy and ThHTerpy thin films. The peak separations (ΔE) were calculated as 1.22V for ThDTerpy, which is higher than 0.059V, indicating an irreversible process.

The polymer films resulted in apparently poor electrochemical reversibility of redox couples involving electron-rich molecular species. The second oxidation reduction peaks located at negative potential values belonged to terpyridine side groups, which were also found to be irreversible due to the peak separation value and the peak current ratios.

It is also possible that electrochemical reaction of the solution species may occur at the electrode-polymer interface and this phenomenon is followed by the diffusion of these species through the polymer lattice. Electron transfer at the polymer-solution interface due to the intrinsic electronic conductivity of the polymer film has to be considered. In our reaction conditions, oxidation and reduction potentials could be affected due to the interaction between non-bonding electron pairs of terpyridine structure with dichloromethane solution.

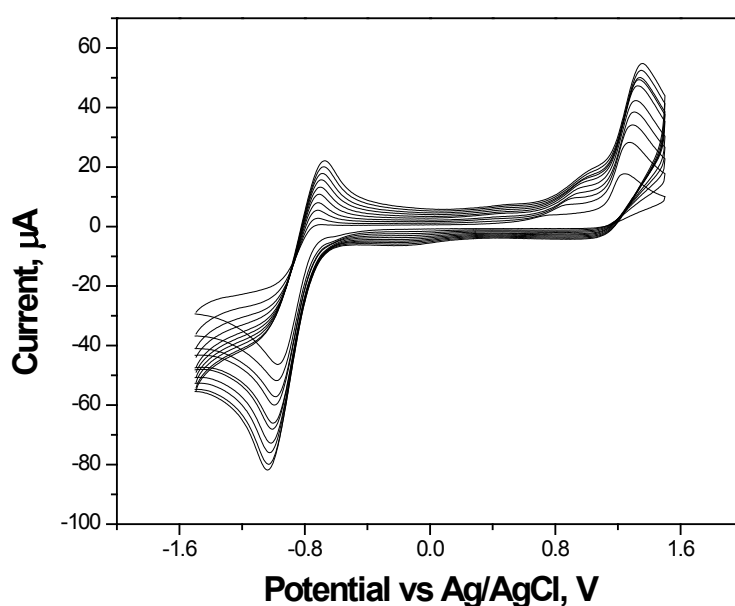


Figure 3.27 Potentiodynamic electrodeposition of the ThPTerpy complex (3.11a) at 100 mVs⁻¹ in 0.05 M in TBAPF₆/DCM electrolyte solution on CFME at 25°C.

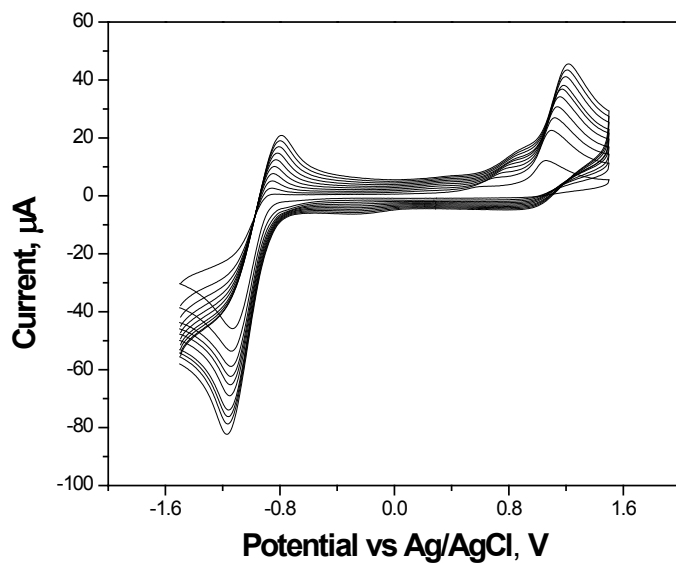


Figure 3.28 Potentiodynamic electrodeposition of the ThHTerpy complex (3.11b) at 100 mVs^{-1} in 0.05 M in $\text{TBAPF}_6/\text{DCM}$ electrolyte solution on CFME at 25°C.

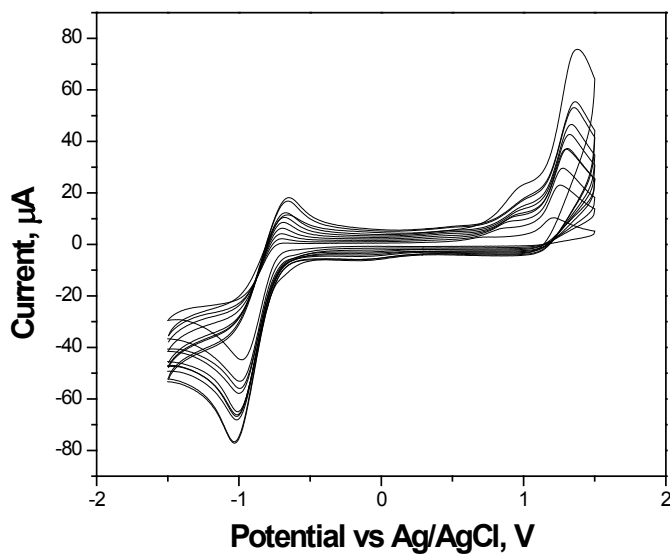


Figure 3.29 Potentiodynamic electrodeposition of the ThDTERpy complex (3.11c) at 100 mVs^{-1} in 0.05 M in $\text{TBAPF}_6/\text{DCM}$ electrolyte solution on CFME at 25°C.

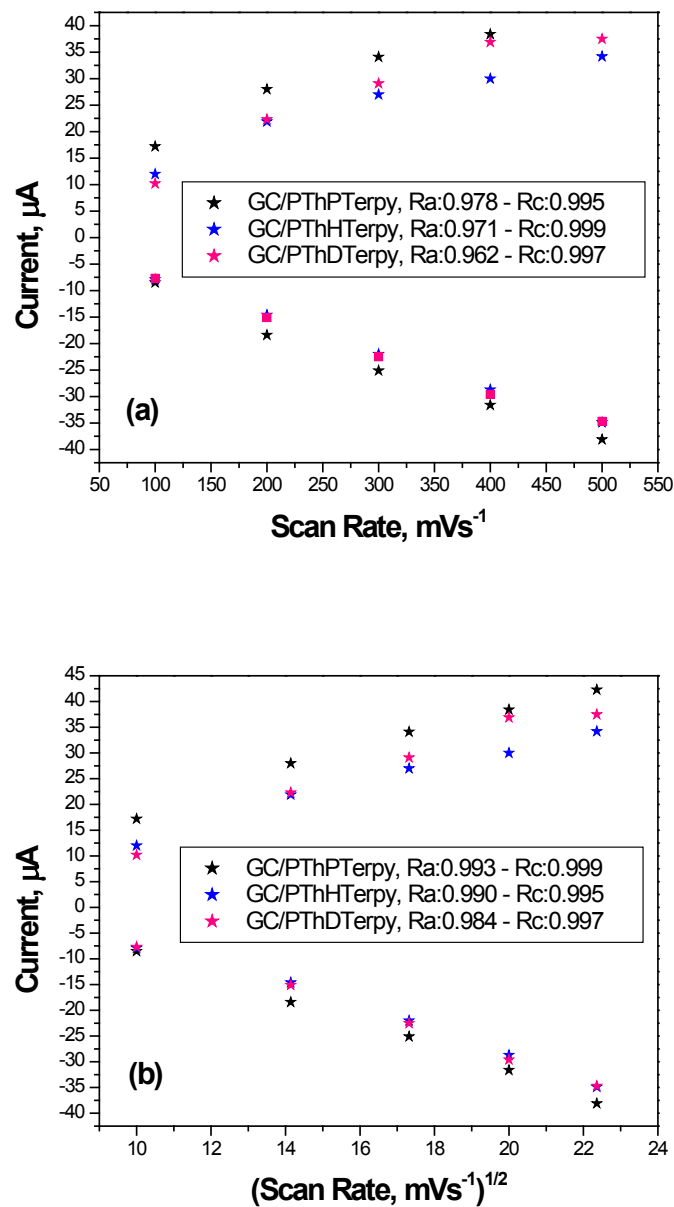


Figure 3.30 a) Scan rate dependencies b) square root of scan rate dependencies of PThPTerpy, PThHTerpy, PThDTerpy films on CFME electrode in 0.05 M TBAPF₆/DCM monomer free electrolyte solution.

The scan rate dependencies of the polymer electrodes were achieved in the monomer free electrolyte solution between 100 and 1000 mVs^{-1} sweep rate. Peak currents for both anodic and

cathodic peaks showed linear dependence and the film formations were found to be diffusion controlled processes according to the correlation coefficient values (Fig.3.30). The peak current values were found to be linearly proportional to $v^{1/2}$.

3.2.2.2 Electrochemical Impedance Spectroscopic Characterization

In terms of capacitive characterizations, electrochemical impedance spectroscopic measurements were achieved at 25°C in monomer-free electrolyte solution with a perturbation amplitude 10mV over a frequency range of 10mHz to 100 kHz with PARSTAT 2273 (software; powersuit).

The specific capacitance (C_{sp}) values of electrochemically prepared thin films (at 0.01 Hz) were calculated by the following equation: $C_{sp} = (2\pi.f.Z'')^{-1}$, where C_{sp} is the specific capacitance; Z'' is the slope of a plot of the imaginary component of impedance versus the inverse of the frequency (f). The C_{sp} and C_{dl} values were calculated for electrochemically prepared glassy carbon and carbon fibre micro electrodes with ThPTerpy, ThHTerpy, ThDTERpy.

Comparative Nyquist diagrams were illustrated in Figure 3.31a and 3.31b. The calculated capacitance values indicated that polymer coated CFMEs were found to be more capacitive than polymer coated GC electrodes. The highest C_{sp} value ($295 \mu Fcm^{-2}$) belongs to CFME/PThHTerpy whereas the GC/PThHTerpy showed the lowest specific capacitance ($48.5 \mu Fcm^{-2}$) value.

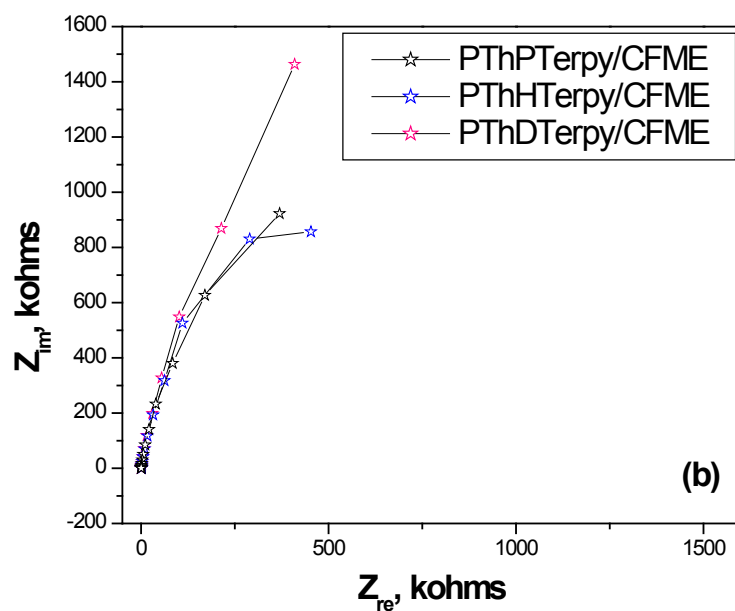
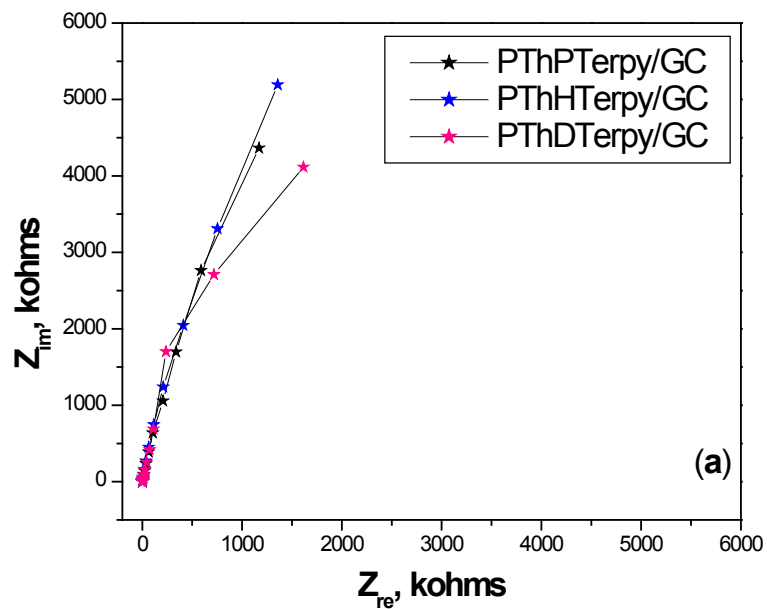


Figure 3.31 Nyquist plots of (a) GC/PThPTerpy, PThHTerpy, PThDTerpy and (b) CFME/PThPTerpy, PThHTerpy, PThDTerpy in 0.05M TBAPF₆/DCM monomer free electrolyte solution, measured between 0.01Hz-100 kHz.

On the other hand, the double layer capacitance is attributed to charge accumulation at the polymer-electrolyte interface that was highest ($1053 \mu\text{Fcm}^{-2}$) for CFME/PThPTerpy and followed by CFME/PThDTERpy with $812 \mu\text{Fcm}^{-2}$ (Fig.3.33a, b). The low frequency capacitance value is usually preferred to be low since it leads to faster electron transfer and faster charge-discharge capability. In this case, CFME/PThDTERpy indicated quite low C_{sp} value ($172.7 \mu\text{Fcm}^{-2}$) and higher C_{dl} value ($812 \mu\text{Fcm}^{-2}$) compared to the other polymer films.

There is no drastic change occurring in Bode phase angles of modified electrodes. However, CFME/PThDTERpy film has the highest phase angle (84.7°) value, indicating greater capacitive behaviour than the other polymer films (Fig.3.32a, b). The phase angles approached a plateau in the frequency range of 0.5Hz and 2.2Hz and at this time scale, the electric signal reached a maximum penetration in the pores of the PThDTERpy electrode. Additionally, phase transition between capacitive and resistive behaviour was observed in the range of 5Hz and 1055Hz. Pure resistor attitude was observed between 2800Hz and 100000Hz.

Admittance plot (Fig.3.34) gives information about the electrical conductivities of polymer coated electrodes. Therefore, fast electron transfer and higher double layer capacitive behaviour become important having high conductivity. As expressed previously, CFME/PThDTERpy thin film showed higher electrical conductivity (1.48mS) compared to other polymer films. The complex plane impedance data for each polymer film was indicated in Table3.2.

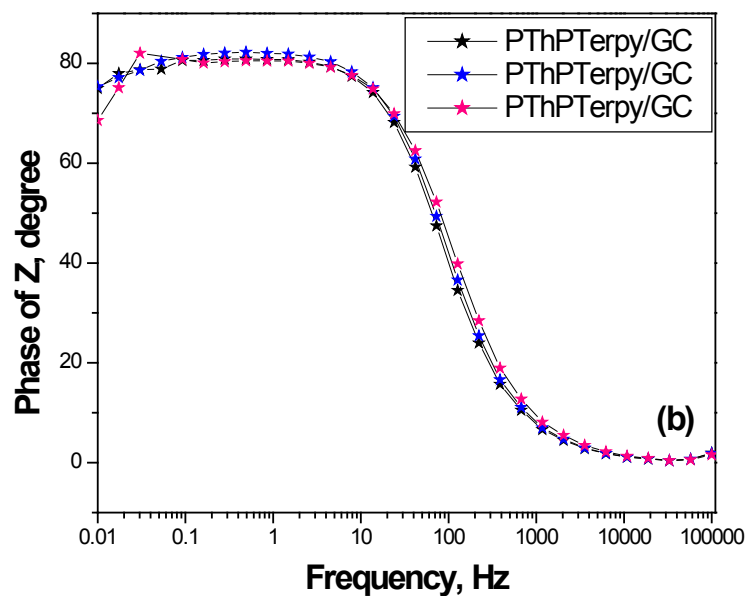
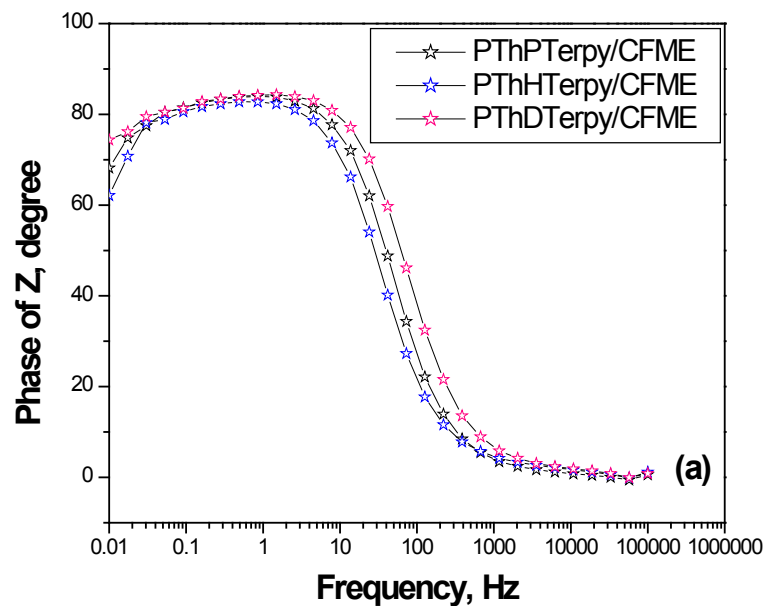


Figure 3.32 Bode Phase diagrams of (a) GC/PThPTerpy, PThHTerpy, PThDTerpy and (b) CFME/PThPTerpy, PThHTerpy, PThDTerpy in 0.05M TBAPF₆/DCM monomer free electrolyte solution, measured between 0.01Hz-100 kHz.

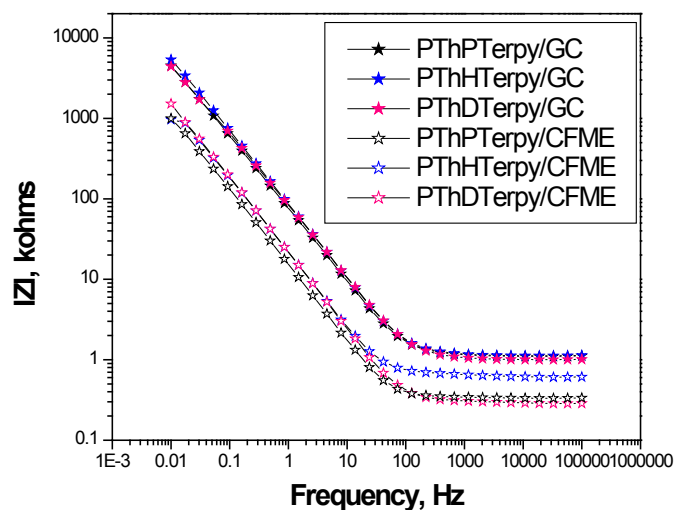


Figure 3.33 Bode Magnitude plots of GC/PThPTerpy, PThHTerpy, PThDTerpy and CFME/PThPTerpy, PThHTerpy, PThDTerpy in 0.05M TBAPF₆/DCM monomer free electrolyte solution, measured between 0.01Hz-100 kHz.

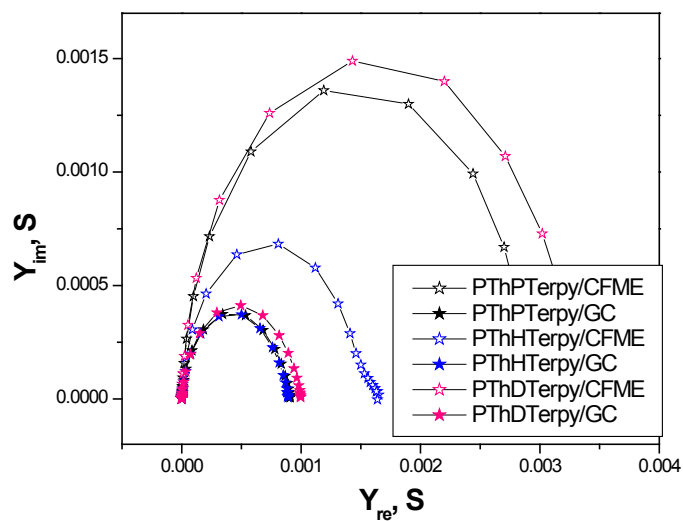


Figure 3.34 Admittance plots of GC/PThPTerpy, PThHTerpy, PThDTerpy and CFME/PThPTerpy, PThHTerpy, PThDTerpy in 0.05M TBAPF₆/DCM monomer free electrolyte solution, measured between 0.01Hz-100 kHz.

Table 3.2 Complex plane impedance data of GC/PThPTerpy, PThHTerpy, PThDTerpy and CFME/PThPTerpy, PThHTerpy, PThDTerpy.

Polymer	Electrode	$C_{sp}, \mu F cm^{-2}$	$C_{dl}, \mu F cm^{-2}$	Phase angle, degree	Conductivity, mS
PThPTerpy	CFME	272.7	1053	84.3	1.35
PThPTerpy	GC	212	221.2	81	0.37
PThHTerpy	CFME	295.4	553	82.7	0.689
PThHTerpy	GC	48.5	186.5	82	0.373
PThDTerpy	CFME	172.7	812	84.7	1.48
PThDTerpy	GC	60.6	171.2	80.3	0.41

The superimposed fluorescence absorption spectra of ThPTerpy (330nm and 450nm), ThHTerpy (330nm and 438nm), ThDTerpy (340nm) are illustrated in Figure 3.35. When comparing the spectra, only dodecanediol attached terpyridine has one absorbance peak whereas the propanediol and hexanediol attached terpyridines showed two absorbance peaks. It is likely that the observed difference would be a result of the much longer tether in the dodecane diol case, but this would have to be a result of electronic interaction between the terpyridine and thiophene in the ground state. Therefore, the long and flexible chain allows for close ground state interaction by direct interaction of the terpyridine and the thiophene ends, causing this change in the absorption spectrum.

In terms of fluorescence intensity and its relation to absorption wavelength, the major effect is the energy gap between S_1 and S_0 by the energy gap law [249], the rate of internal conversion from S_1 to S_0 decreases with increasing energy gap, so molecules which absorb further to the blue (shorter wavelengths) will have lower rates of internal conversion. Since internal conversion competes with fluorescence, molecules which absorb further to the blue will tend to have higher quantum yields.

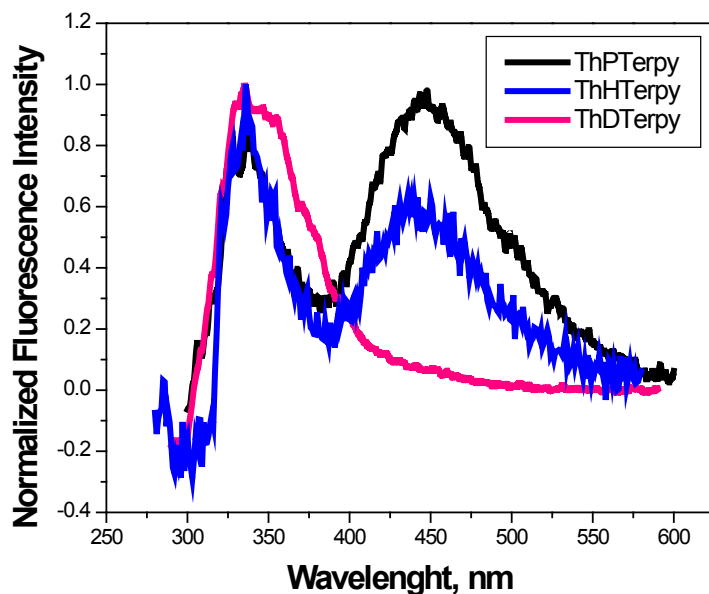


Figure 3.35 Fluorescence absorbance spectra of ThPTerpy, ThHTerpy, ThDTERpy in DMSO at 25°C.

3.2.2.3 Morphological Analysis

The morphology of electrochemically polymerized PThPTerpy, PThHTerpy and PThDTERpy film was examined with SEM images (Fig.3.36a-c). There is significant thickness difference between thin films according to the spacer length.

Since there are bulky terpyridine side groups, the possibility of polymerization increased with the increase in alkyl chain length. As a result of this, we observed increase in the film thicknesses and uniformity when the spacer length increased. The PThDTERpy has 1.4 μm film thickness followed by PThHTerpy and PThPTerpy with 1 μm and 0.9 μm film thicknesses, respectively.

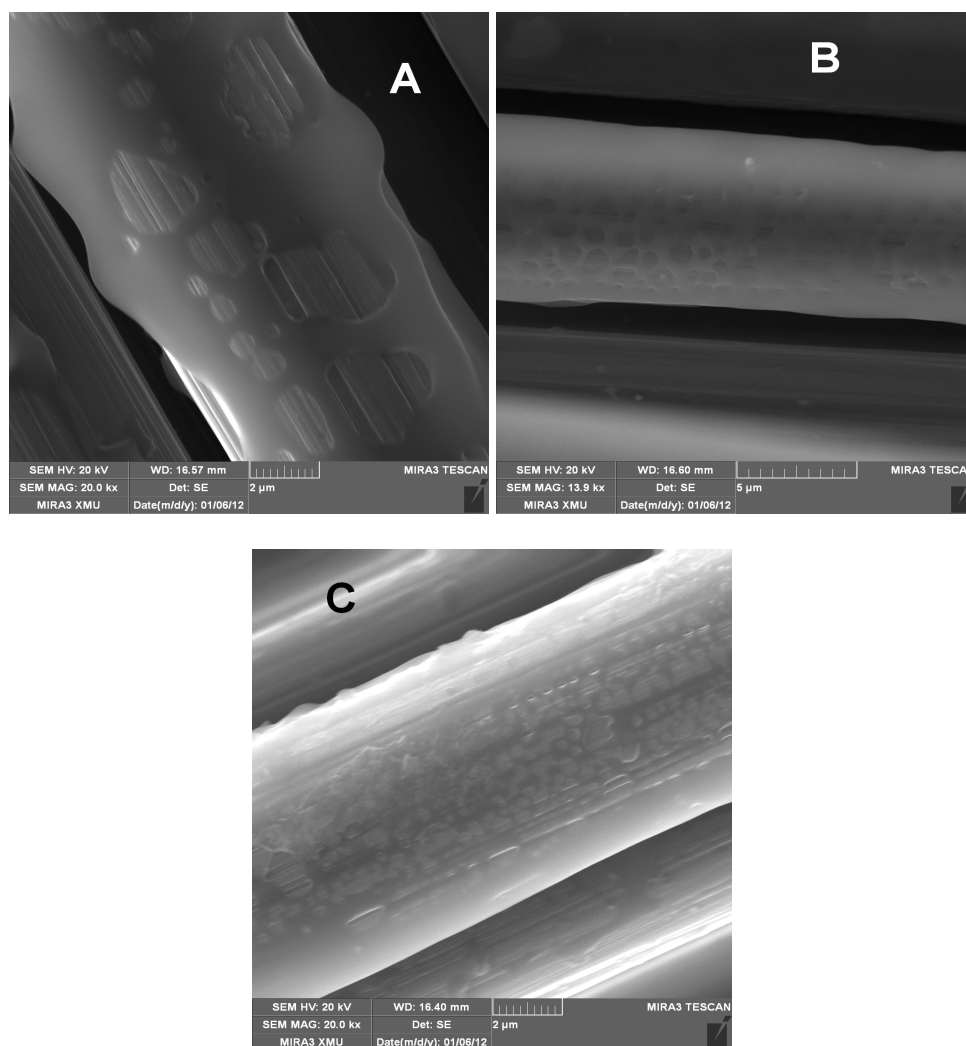


Figure 3.36 SEM images of electropolymerized a) PThPTerpy, b) PThHTerpy and c) PThDTerpy on CFME (20 cycles).

In this chapter, we obtained several modified electrodes indicating fluorescence and capacitive properties. However, having longer tether between pyrene and thiophene group increased the electropolymerization possibility and resulted in higher electrical conductivity and higher fluorescence property compared to the other films. For the future studies, ThP monomer could be synthesized with different length of spacer groups to be able to explain the changes in fluorescence spectroscopy and then these monomers could be electro coated on indium tin oxide surface. The fluorescence response of the modified electrode surface could be checked under

different conditions to use them as fluorescence sensors. On the other hand, terpyridine attached thiophene polymers could be used as syntetic metal receptors due to the coordinating ability of terpyridine groups.

3.3 Experimental

3.3.1 Materials

All reagents were purchased from Sigma-Aldrich and used without further purification. All solvents were high-performance-liquid-chromatography-grade and purchased from Fisher Scientific and used without further purification.

High strength (HS) carbon fibres C 320.000 (CA) (Sigri Carbon, Meitingen, Germany) containing 320.000 single filaments in roving and high modulus (HM) carbon fibres were used as working electrodes. All of the electrodes were prepared using a 3 cm long bundle of the CFME (with average diameter of around 7 μm) attached to a copper wire with a Teflon tape. The number of carbon fibres in the bundle was approximately 30. One centimetre of the CFME was dipped into the solution to keep the electrode area constant ($\sim 0.066 \text{ cm}^2$) and the rest of the electrode was covered with Teflon tape. The CFMEs were first cleaned with acetone and then dried with an air-dryer before the experiments.

3.3.2 Instrumentation

^1H and ^{13}C NMR spectra were recorded at 400 MHz and 101 MHz, respectively on a Varian Mercury Plus spectrometer equipped with a gradient field probe, with chemical shifts referenced to residual solvent peaks and coupling constants reported in Hz. Infrared spectroscopy was performed on an IRPrestige-21FTIR by Shimadzu with a MIRacle ATR by PIKE Technologies. Cyclic voltammetric studies were performed using a conventional three-electrode cell. In these studies, the working electrode was a glassy carbon disk electrode ($\sim 2 \text{ mm}$ diameter) and carbon fibre micro electrode, the auxiliary electrode was a Pt wire, and a Ag/AgCl reference electrode was utilized. Electrochemical measurements were performed at room temperature. The

concentration of the analyte was 2.0 mM, while that of the supporting electrolyte ($\text{Bu}_4\text{NClO}_4^-$) was 0.1 M in dichloromethane (DCM) for fluorophore attached thiophene derivatives whereas 0.05 M TBAPF_6^- supporting electrolyte used in DCM for terpyridine attached thiophene derivatives. The solutions were deaerated with nitrogen prior to use. A PARSTAT 2273 model potentiostat with an attached power suite software program was used in all experiments. Fluorescence spectra were measured on a Photon Technologies International PTI RF-M2004 spectrometer. SEM imaging was performed with MIRA3-XMU scanning electron microscopy.

3.3.3 Synthesis of Complex 3.2

The synthesis of the thienyl derivative with coumarine was illustrated in Scheme 3.1. The coumarin containing carboxylic acid functionality (1mmol) was reacted with 2-(3-Thienyl)ethanol (1mmol) in the presence of N,N-dimethylaminopyridine (DMAP) (2mmol) in $\text{CH}_2\text{Cl}_2/\text{DMF}$ (10ml/2ml), and cooled to 0 °C and stirred under N_2 for 30 minutes. Dicyclohexylcarbodiimide (DCC) (2mmol) was dissolved in 1- 2 mL of CH_2Cl_2 and added to the stirring mixture at 0 °C. The solution was stirred at room temperature under N_2 for 24 hours. The solvent was evaporated *in vacuo*. Dicyclohexyl urea (DCU) was removed by dissolving the crude product in CH_2Cl_2 and placed in the freezer for 30 min and filtered through a crucible. The crude product was purified with column chromatography ($\text{EtOAc}/\text{Hexane}=1.5/1$) to afford the pure thienyl-coumarin (ThC) compound as an off-white solid. The monomer was obtained in a 52% yield:

^1H NMR (400 MHz, dmso) δ 8.72 (s, 1H), 7.92 (dd, $J = 1.6, 7.7$, 1H), 7.75 (ddd, $J = 1.7, 7.3, 8.5$, 1H), 7.48 (dd, $J = 2.9, 4.9$, 1H), 7.43 (ddd, $J = 0.8, 7.2, 8.6$, 2H), 7.37 – 7.35 (m, 1H), 7.13 (dd, $J = 1.3, 4.9$, 1H), 4.45 (t, $J = 6.8$, 2H), 3.05 (t, $J = 6.7$, 2H) . ^{13}C NMR (101 MHz,

dmso) δ 162.97, 156.39, 155.01, 149.33, 139.41, 138.44, 135.03, 130.76, 129.14, 126.40, 125.31, 122.55, 118.23, 117.95, 116.61, 65.61, 29.32. IR 1705 cm^{-1} (C=O)

3.3.4 Synthesis of Complex 3.4

The esterification reaction of thienyl derivative with 1-Pyrenebutyric acid was shown in Scheme 3.2. The 1-Pyrenebutyric acid (1mmol) was reacted with 2-(3-Thienyl)ethanol (1mmol) in the presence of N,N-dimethylaminopyridine (DMAP) (2mmol) in $\text{CH}_2\text{Cl}_2/\text{DMF}$ (10ml/2ml), and cooled to 0 °C and stirred under N_2 for 30 minutes. Dicyclohexylcarbodiimide (DCC) (2mmol) was dissolved in 1- 2 mL of CH_2Cl_2 and added to the stirring mixture at 0 °C. The solution was stirred at room temperature under N_2 for 24 hours. The solvent was evaporated *in vacuo*. Dicyclohexyl urea (DCU) was removed by dissolving the crude product in CH_2Cl_2 and placed in the freezer for 30 min and filtered through a crucible. The crude product was purified with column chromatography (Chloroform) to afford the pure thienyl-pyrene (ThP) compound as a yellow solid. The monomer was obtained in a 68% yield:

^1H NMR (400 MHz, cdcl_3) δ 8.56 (d, J = 9.3, 1H), 8.47 (dt, J = 2.0, 7.7, 2H), 8.42 (dd, J = 2.5, 8.5, 2H), 8.34 (d, J = 0.6, 2H), 8.3 (t, J = 7.6, 1H), 8.14 (d, J = 7.8, 1H), 7.58 – 7.55 (m, 1H), 7.33 (ddd, J = 0.9, 2.0, 2.9, 1H), 7.28 (dd, J = 1.3, 4.9, 1H), 4.63 (t, J = 6.9, 2H), 3.71 – 3.64 (m, 2H), 3.28 (t, J = 6.9, 2H), 2.77 (t, J = 7.2, 2H), 2.5 (dt, J = 7.3, 9.2, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 173.53, 138.15, 135.81, 131.57, 131.05, 130.12, 128.89, 128.37, 127.64, 127.53, 127.49, 126.86, 125.99, 125.79, 125.24, 125.14, 125.07, 124.95, 124.93, 123.46, 121.71, 64.37, 34.00, 32.86, 29.77, 26.89. IR 1724 cm^{-1} (C=O)

3.3.5 Synthesis of Complex 3.7

The steglich esterification between 3-Thiophenecarboxylic acid and 2-Naphthol was performed in a one pot reaction as illustrated in Scheme 3.3. The 3-Thiophenecarboxylic acid (1mmol) was reacted with the terminal hydroxyl group of naphthol (1mmol) in the presence of N,N-dimethylaminopyridine (DMAP) (2mmol) in CH₂Cl₂/DMF (10ml/2ml) and the reaction mixture cooled to 0 °C and stirred vigorously under N₂ for 30 minutes. Dicyclohexylcarbodiimide (DCC) (2mmol) was dissolved in 1- 2 mL of CH₂Cl₂ and added to the stirring mixture at 0 °C. The solution was stirred at room temperature under N₂ for 24 hours. The solvent was evaporated *in vacuo*. Dicyclohexyl urea (DCU) was removed by dissolving the crude product in CH₂Cl₂ and placed in the freezer for 30 min and filtered through a crucible. The crude product was purified with column chromatography (Chloroform) to afford the pure thiophene-naphthol (ThN) compound as an off-white solid. The monomer was obtained in a 56% yield:

¹H NMR (400 MHz, dmso) δ 8.67 (dd, *J* = 1.3, 3.0, 1H), 8.02 (d, *J* = 9.0, 1H), 8.00 – 7.93 (m, 2H), 7.82 (d, *J* = 2.3, 1H), 7.77 (dd, *J* = 2.9, 5.1, 1H), 7.66 (dd, *J* = 1.3, 5.1, 1H), 7.60 – 7.52 (m, 2H), 7.45 (dd, *J* = 2.4, 8.8, 1H). ¹³C NMR (101 MHz, dmso) δ 160.79, 148.05, 135.57, 133.34, 131.85, 131.05, 129.37, 128.18, 127.75, 127.50, 126.73, 125.88, 121.66, 118.69, 79.16. IR 1714 cm⁻¹ (C=O)

3.3.6 Synthesis of Complex 3.10a

Potassium hydroxide (0.5945g, 10.6 mmol) was added to 8 ml dry DMSO and stirred under an inert atmosphere at 70 °C. To this mixture 1,3-propanediol (0.8 ml, 11.0 mmol) was added. After 30 minutes 4'-chloro-2,2':6',2''-terpyridine (0.5027 g, 1.9 mmol) was added and the reaction mixture was allowed to react for 5 hours. After 5 hours the reaction mixture was poured into 200 ml of water and extracted twice with 100 ml DCM, the combined organic

extracts were dried over magnesium sulphate, filtered, and the solvent was removed under vacuum to yield 0.3445 g, 1.1 mmol, 60% 4'-(3-hydroxypropyl)-2,2':6',2''-terpyridine.

^1H NMR (400 MHz, dmso) δ 8.72 (dd, $J = 1.8, 0.9$ Hz, 1H), 8.71 (dd, $J = 1.8, 0.9$ Hz, 1H), 8.62 (t, $J = 1.0$ Hz, 1H), 8.60 (t, $J = 1.0$ Hz, 1H), 8.02 (d, $J = 1.8$ Hz, 1H), 8.00 (d, $J = 1.8$ Hz, 1H), 7.99 – 7.97 (m, 3H), 7.50 (ddd, $J = 7.5, 4.8, 1.2$ Hz, 2H), 4.63 (t, $J = 5.2$ Hz, 1H), 4.31 (t, $J = 6.5$ Hz, 2H), 3.61 (q, $J = 6.1$ Hz, 2H), 3.33 (s, 3H), 2.54 (s, 4H), 1.96 (p, $J = 6.3$ Hz, 2H).

^{13}C NMR (101 MHz, dmso) δ 166.75, 156.64, 154.84, 149.21, 137.33, 124.47, 120.85, 106.71, 65.23, 57.12, 40.42, 31.84.

3.3.7 Synthesis of Complex 3.10b

Potassium hydroxide (0.5963g, 10.6 mmol) was added to 8 ml dry DMSO and stirred under an inert atmosphere at 70 °C. To this mixture 1,6-hexanediol (1.2365g, 10.5 mmol) was added. After 30 minutes 4'-chloro-2,2':6',2''-terpyridine (0.5086g, 1.9 mmol) was added and the reaction mixture was allowed to react for 5 hours. After 5 hours the reaction mixture was poured into 200 ml of water and extracted twice with 100 ml DCM, the combined organic extracts were dried over magnesium sulphate, filtered, and the solvent was removed under vacuum, the resulting solid was recrystallized using CH_3CN to yield 0.2173 g, 0.62 mmol, 33% 4'-(6-hydroxyhexyl)-2,2':6',2''-terpyridine.

^1H NMR (400 MHz, dmso) δ 8.71 (ddd, $J = 4.8, 1.8, 0.9$ Hz, 7H), 8.61 (t, $J = 1.0$ Hz, 3H), 8.59 (t, $J = 1.0$ Hz, 4H), 7.99 (td, $J = 7.7, 1.8$ Hz, 8H), 7.95 (s, 8H), 7.49 (ddd, $J = 7.5, 4.8, 1.2$ Hz, 8H), 4.35 (t, $J = 5.1$ Hz, 3H), 4.22 (t, $J = 6.5$ Hz, 8H), 3.41 (q, $J = 6.1$ Hz, 8H), 3.33 (s, 6H), 2.07 (s, 1H), 1.87 – 1.73 (m, 7H), 1.69 – 1.31 (m, 21H).

^{13}C NMR (101 MHz, dmso) δ 166.71, 156.62, 154.84, 149.19, 137.30, 124.44, 120.84, 106.68, 67.92, 60.61, 40.14, 39.93, 39.72, 39.51, 39.30, 39.09, 38.88, 32.45, 28.45, 25.26, 25.23.

3.3.8 Synthesis of Complex 3.10c

Potassium hydroxide (0.5344g, 9.5 mmol) was added to 8 ml dry DMSO and stirred under an inert atmosphere at 70 °C. To this mixture 1,12-dodecanediol (1.8967g, 9.4 mmol) was added. After 30 minutes 4'-chloro-2,2':6',2''-terpyridine (0.5800, 2.2 mmol) was added and the reaction mixture was allowed to react for 5 hours. After 5 hours the reaction mixture was poured into 200 ml of water and extracted three times with 100 ml DCM, the combined organic extracts were dried over magnesium sulphate, filtered, and the solvent was removed under vacuum. The resulting solid was triturated with methanol and filtered, the filtrate had the solvent removed under vacuum to yield 0.3357 g, 0.77 mmol, 36% 4'-(12-hydroxydodecyl)-2,2':6',2''-terpyridine.

^1H NMR (400 MHz, dmso) δ 8.75 – 8.67 (m, 1H), 8.61 (dd, J = 7.9, 3.4 Hz, 1H), 8.00 (tdd, J = 5.8, 4.1, 2.0 Hz, 1H), 7.96 (s, 1H), 7.54 – 7.46 (m, 1H), 4.30 (td, J = 5.2, 2.7 Hz, 1H), 4.24 (t, J = 6.5 Hz, 1H), 3.36 (qd, J = 6.5, 3.2 Hz, 1H), 3.32 (d, J = 0.5 Hz, 4H), 1.85 – 1.74 (m, 1H), 1.52 – 1.18 (m, 11H).

^{13}C NMR (101 MHz, dmso) δ 166.67, 156.64, 154.84, 149.20, 137.33, 124.46, 120.84, 106.70, 60.69, 32.53, 29.09, 29.00, 28.96, 28.35, 25.49, 25.32.

3.3.9 Synthesis of Complex 3.11a

The synthesis of the thiophene with terpyridine pendants was illustrated in Scheme 3.4. The thiophene-3-carboxylic acid (0.25mmol) was reacted with 4'-(3-hydroxypropyl)-2,2':6',2''-terpyridine (0.3mmol) in the presence of N,N-dimethylaminopyridine (DMAP) (0.6mmol) in

CH₂Cl₂/DMF (10ml/2ml) and cooled to 0 °C and stirred under N₂ for 30 minutes. Dicyclohexylcarbodiimide (DCC) (0.6mmol) was dissolved in 1- 2 mL of CH₂Cl₂ and added to the stirring mixture at 0 °C. The solution was stirred at room temperature under N₂ for 24 hours. The solvent was evaporated *in vacuo*. Dicyclohexyl urea (DCU) was removed by dissolving the crude product in CH₂Cl₂ and placed in the freezer for 30 min and filtered through a crucible. The monomer was obtained as off-white in a 62% yield:

¹H NMR (400 MHz, dmso) δ 8.70 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 4H), 8.61 (dt, *J* = 8.0, 1.0 Hz, 4H), 8.40 (dd, *J* = 3.0, 1.3 Hz, 1H), 8.09 (dd, *J* = 5.0, 1.4 Hz, 13H), 8.04 – 7.96 (m, 9H), 7.64 (dd, *J* = 5.1, 3.0 Hz, 1H), 7.54 – 7.46 (m, 6H), 6.58 (dd, *J* = 4.9, 1.6 Hz, 12H), 5.57 (d, *J* = 8.0 Hz, 2H), 4.43 (q, *J* = 6.2 Hz, 8H), 3.35 (s, 84H), 2.94 (s, 39H), 2.30 – 2.19 (m, 3H), 1.87 – 1.63 (m, 10H), 1.63 – 1.43 (m, 9H), 1.31 – 0.97 (m, 18H).

¹³C NMR (101 MHz, dmso) δ 166.57, 156.69, 154.81, 153.95, 149.14, 137.35, 133.82, 127.39, 124.43, 120.87, 106.68, 64.94, 61.17, 33.34, 25.31, 24.45.

3.3.10 Synthesis of Complex 3.11b

The thiophene-3-carboxylic acid (0.25mmol) was reacted with 4'-(3-hydroxyhexyl)-2,2':6',2''-terpyridine (0.3mmol) in the presence of N,N-dimethylaminopyridine (DMAP) (0.6mmol) in CH₂Cl₂/DMF (10ml/2ml) and cooled to 0 °C and stirred under N₂ for 30 minutes. Dicyclohexylcarbodiimide (DCC) (0.6mmol) was dissolved in 1- 2 mL of CH₂Cl₂ and added to the stirring mixture at 0 °C. The solution was stirred at room temperature under N₂ for 24 hours. The solvent was evaporated *in vacuo*. Dicyclohexyl urea (DCU) was removed by dissolving the crude product in CH₂Cl₂ and placed in the freezer for 30 min and filtered through a crucible. The monomer was obtained as white in a 53% yield:

^1H NMR (400 MHz, dmso) δ 8.70 (ddd, $J = 4.7, 1.7, 0.9$ Hz, 3H), 8.62 (t, $J = 1.0$ Hz, 1H), 8.60 (t, $J = 1.0$ Hz, 1H), 8.31 (dd, $J = 3.0, 1.2$ Hz, 1H), 8.09 (dd, $J = 4.9, 1.6$ Hz, 9H), 8.02 – 7.97 (m, 3H), 7.96 (s, 3H), 7.61 (dd, $J = 5.1, 3.0$ Hz, 1H), 7.53 – 7.41 (m, 4H), 6.60 – 6.53 (m, 8H), 4.23 (t, $J = 6.5$ Hz, 5H), 3.38 (s, 22H), 3.24 – 3.03 (m, 5H), 2.93 (s, 27H), 2.03 – 1.76 (m, 13H), 1.76 – 1.41 (m, 24H), 1.41 – 1.10 (m, 23H).

^{13}C NMR (101 MHz, dmso) δ 167.22, 162.48, 157.09, 155.32, 154.36, 149.73, 139.46, 137.75, 133.98, 133.50, 128.01, 127.78, 124.89, 121.33, 107.11, 68.30, 64.64, 55.13, 39.01, 34.93, 28.73, 28.59, 25.62, 25.39, 24.46.

3.3.11 Synthesis of Complex 3.11c

The thiophene-3-carboxylic acid (0.25mmol) was reacted with 4'-(3-hydroxydodecyl)-2,2':6',2''-terpyridine (0.3mmol) in the presence of N,N-dimethylaminopyridine (DMAP) (0.6mmol) in $\text{CH}_2\text{Cl}_2/\text{DMF}$ (10ml/2ml) and cooled to 0 °C and stirred under N_2 for 30 minutes. Dicyclohexylcarbodiimide (DCC) (0.6mmol) was dissolved in 1- 2 mL of CH_2Cl_2 and added to the stirring mixture at 0 °C. The solution was stirred at room temperature under N_2 for 24 hours. The solvent was evaporated *in vacuo*. Dicyclohexyl urea (DCU) was removed by dissolving the crude product in CH_2Cl_2 and placed in the freezer for 30 min and filtered through a crucible. The monomer was obtained as white in a 58% yield:

^1H NMR (400 MHz, dmso) δ 8.71 (ddt, $J = 4.8, 1.9, 1.0$ Hz, 4H), 8.64 – 8.56 (m, 4H), 8.31 (ddd, $J = 3.0, 2.3, 1.2$ Hz, 1H), 8.09 (dd, $J = 4.9, 1.6$ Hz, 1H), 8.04 – 7.92 (m, 9H), 7.64 (ddd, $J = 6.8, 3.2, 1.7$ Hz, 1H), 7.52 – 7.46 (m, 5H), 7.44 (ddd, $J = 5.1, 2.0, 0.9$ Hz, 2H), 6.58 (dd, $J = 4.9, 1.6$ Hz, 1H), 4.20 (ddd, $J = 10.7, 9.3, 5.4$ Hz, 8H), 3.33 (s, 41H), 2.94 (s, 5H), 2.01 – 1.78 (m, 11H), 1.78 – 1.54 (m, 16H), 1.54 – 1.18 (m, 69H).

^{13}C NMR (101 MHz, dmso) δ 166.71, 156.63, 154.85, 149.19, 148.94, 137.31, 133.54, 127.27, 124.45, 120.84, 106.70, 67.92, 64.21, 60.70, 54.67, 34.47, 32.53, 28.88, 28.65, 24.94, 24.00.

4 Micro and Nano-Sized Polysiloxanes Containing Organoiron Moieties

4.1 Overview

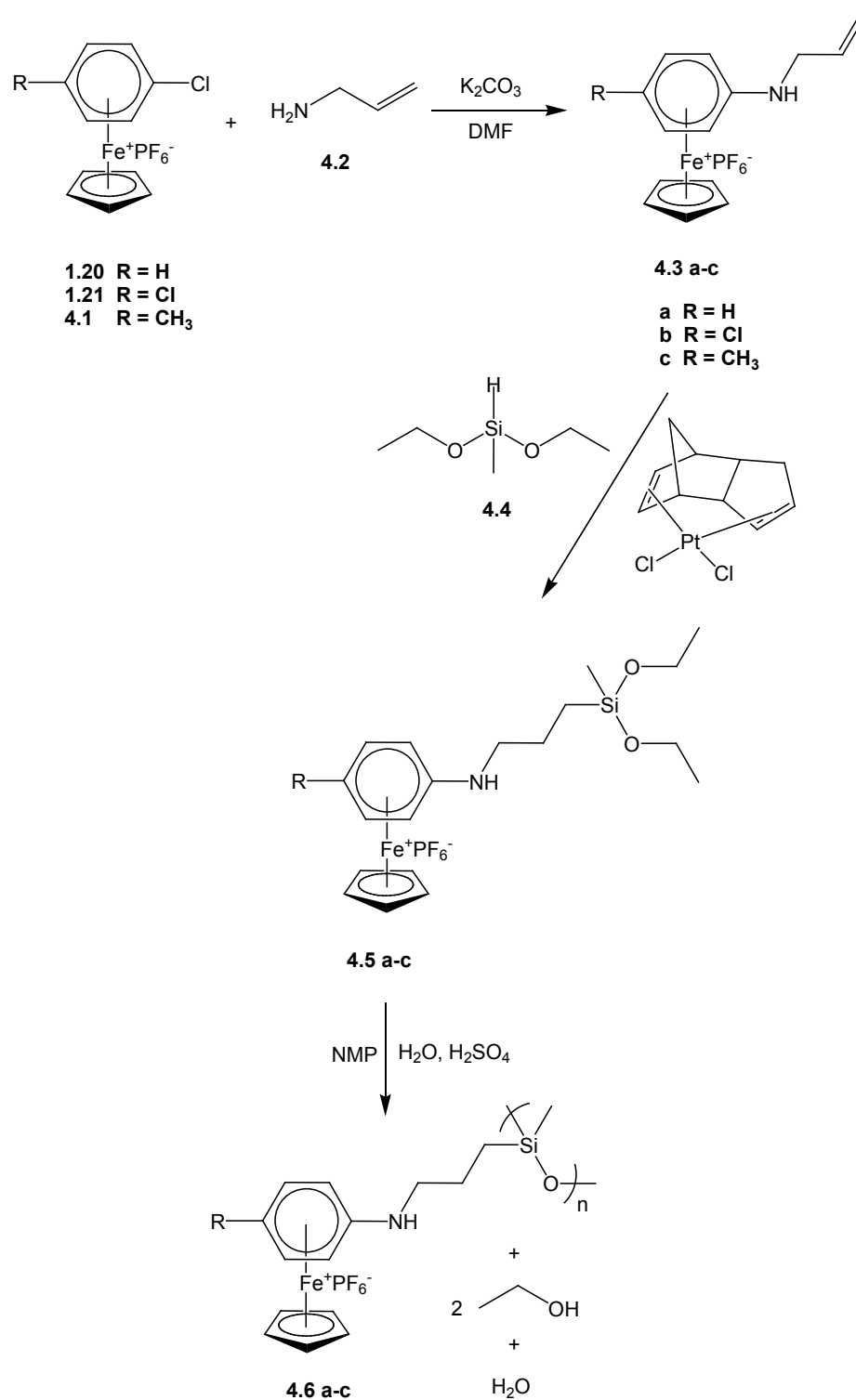
Siloxane containing polymers including metallic and semi-metallic subunits display thermal, electrochemical, catalytic, and photophysical properties [127,152,250-254]. Polysiloxanes are usually preferred due to their flexible backbone, thermal stability, durability, resistance to biological degradation, and insulation properties. The incorporation of transition metals into polymer chains offers potential for the preparation of new materials with unique properties.

Iron is one of the cheapest and most abundant transition metals both in the earth and in the human body. It is remarkable with its oxidation state, reduction potential, coordination number, and spin state. The organometallic chemistry of iron is dominated by complexes that contain cyclopentadienyl and ferrocene which is one of the most thermally stable organometallic compounds. The use of arene-coordinated cyclopentadienyliron moieties to enable nucleophilic aromatic substitution allows for the incorporation of cationic metal groups into new materials. [130,163,198-202] Therefore, it increases the solubility of the materials compared to their organic analogues and can give electrocatalytic properties [203-207]. On the other hand, synthesis and applications of ferrocene-based polysiloxane polymers have been well investigated [255-256]. However, the arene-coordinated cyclopentadienyliron moieties in the synthesis of this class of polymers have not been explored yet.

In this chapter, we aimed to prepare a series of organoiron containing polysiloxane and their composite thin film preparations based on PAN matrix. Firstly, allyl functionalized η^6 -arene- η^5 -cyclopentadienyliron(II) hexafluorophosphate complexes were synthesized via nucleophilic aromatic substitution reaction followed by hydrosilation and polymerization according to our previously published methods [257]. In addition to these syntheses, condensation reactions were used to functionalize ferrocene moieties with allyl amine using, 1,1-bis(carbonylchloride)-ferrocene. The acid catalyzed condensation polymerizations of the siloxane-based complexes were performed in one pot reactions to form various linear and cross-linked polymers. The obtained linear polymers were dissolved in DMF and then used as a precursor to make composite blends with polyacrylonitrile matrix. The morphological characterization of the films was also studied.

4.2 Results and Discussion

The polymers **4.6 (a-c)** and precursor complexes (Scheme 4.1) were prepared according to previously established methodology [257]. Hydrosilation was achieved using dichlorodicyclopentadiene platinum catalyst due to its ability to reduce the chance of crosslinking. The ethoxy groups of hydrosilated compounds are found to be unstable and react with atmospheric moisture to cleave the ethoxy groups from the silicon. Therefore, the siloxane compounds have to be kept under anhydrous condition both during the reaction and after. A significant colour change from brown to red-orange was observed during the hydrosilation reaction. As expressed in the literature, a colour change could be an indication for the formation of new organoiron complexes [258]. The acid catalyzed condensation polymerization was occasionally used to form polymers **4.6 (a-c)** in order to use them in composite film formation.



Scheme 4.1 Synthesis of polymers **4.6 (a-c)**.

Single crystals of **4.3a** were grown from 1:1 DCM: diethyl ether solvent mixture. The material crystallizes in orthorhombic space group *Pnma* (Figure 4.1). Atoms N1, H1n, and C4 are evenly distributed on each side of the plane, while atoms C5 and C6 reside directly on the mirror plane. The arene and Cp rings are almost parallel with a tilt angle of 0.44° and the allyl group N(1)-C(4)-C(5) is bent at 112.5°. The centrosymmetric *Pnma* was chosen according to the overall geometry and in *Pnma* the phenyl ring has more uniform bond lengths, all between 1.40 – 1.41 Å. (See Appendix A for detailed information)

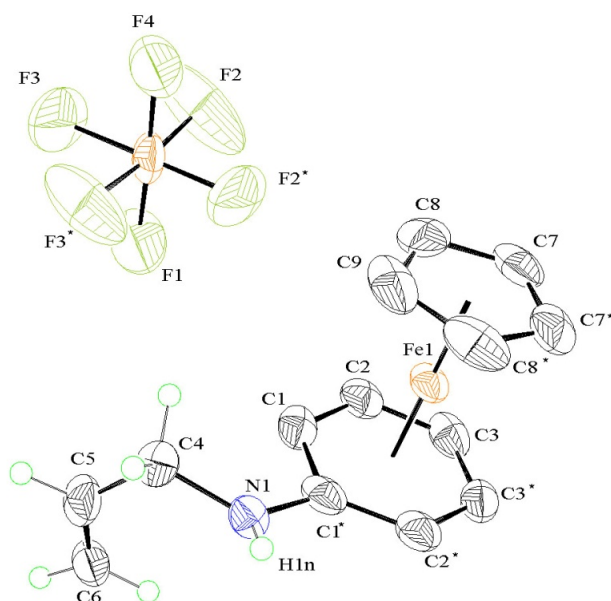


Figure 4.1 ORTEP representation of **4.3a**.

$^{29}\text{Si}\{^1\text{H}\}$ NMR spectra (Fig.4.2) of the monomer **4.5c** and the polymer **4.6b** were acquired, demonstrating a strong upfield shift in the $^{29}\text{Si}\{^1\text{H}\}$ NMR between monomeric species and polymeric species (-6.3 ppm to -22.6 ppm). This, along with signal broadening in the polymer, confirms that the silicon environment has changed from the diethoxy monomer to the siloxy polymer [259].

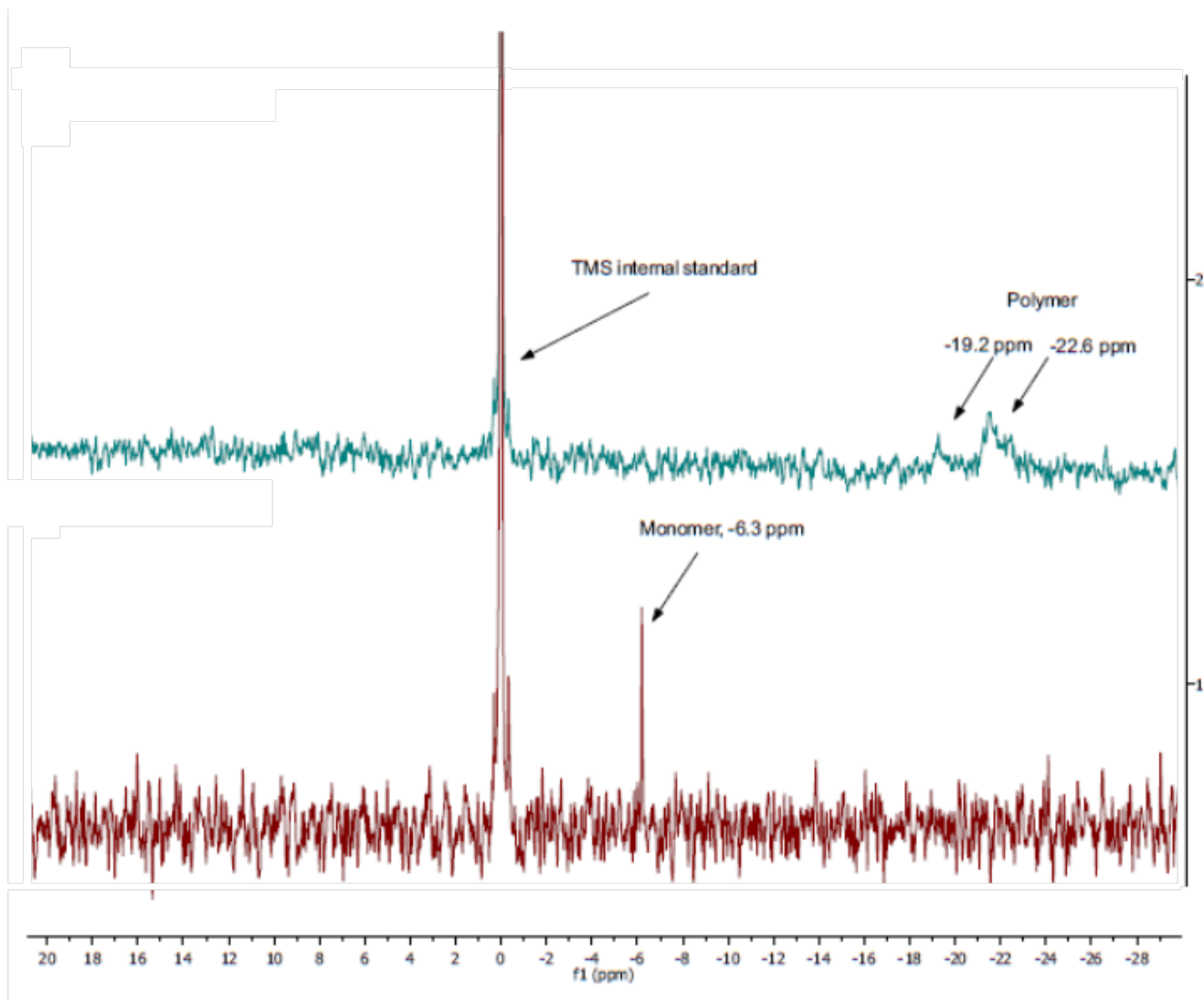
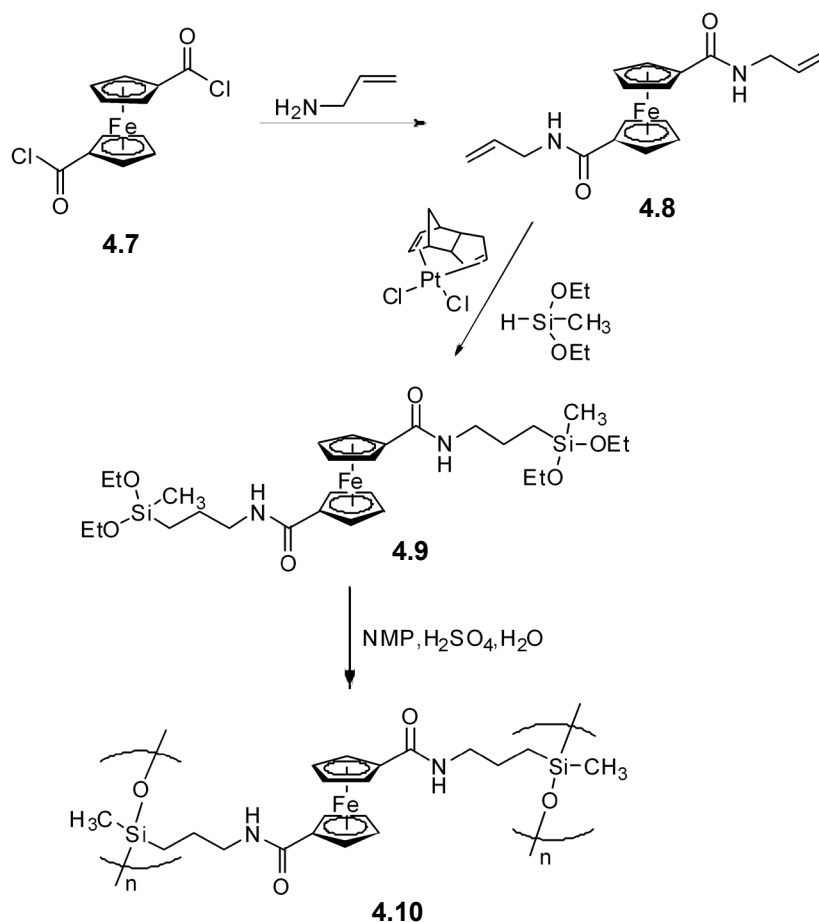


Figure 4.2 $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of 1) the monomer 4.5c and 2) the polymer 4.6b.

In addition, we attempted to prepare ferrocene-siloxane ladder polymers (Scheme 4.2). The reaction between 1,1'-ferrocene dicarbonyl chloride and allylamine resulted in the 1,1'-ferrocene diallylamide (**4.8**) (Fig.4.3) being subsequently hydrosilated, as described above, to afford 1,1'-ferrocene bisdiethoxymethylsilane (**4.9**) (Fig.4.4). Following similar methodology, as described for the cationic complexes, the reaction of **4.9** with H_2SO_4 resulted in the cleavage of the ethoxy groups, as well as induced polymerization to generate **4.10**. The polymerization of **4.9** resulted in highly insoluble materials, most likely due to a high level of cross-linking. As a result, characterization of these materials was limited to analysis in the solid state.



Scheme 4.2 Synthesis of ferrocene-siloxane polymer **4.10**.

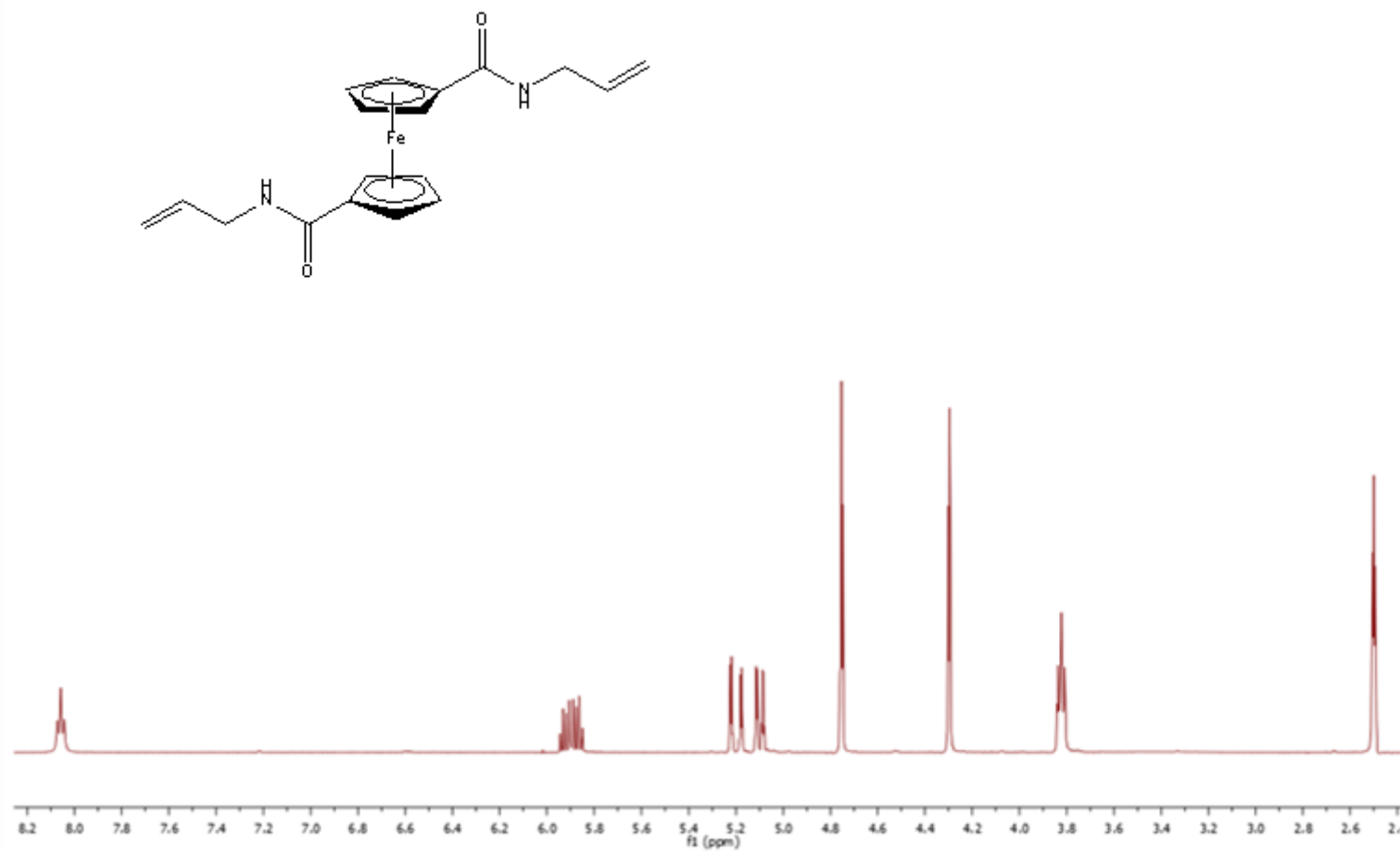


Figure 4.3 ¹H NMR Spectrum of 1,1'-ferrocene diallylamide 4.8.

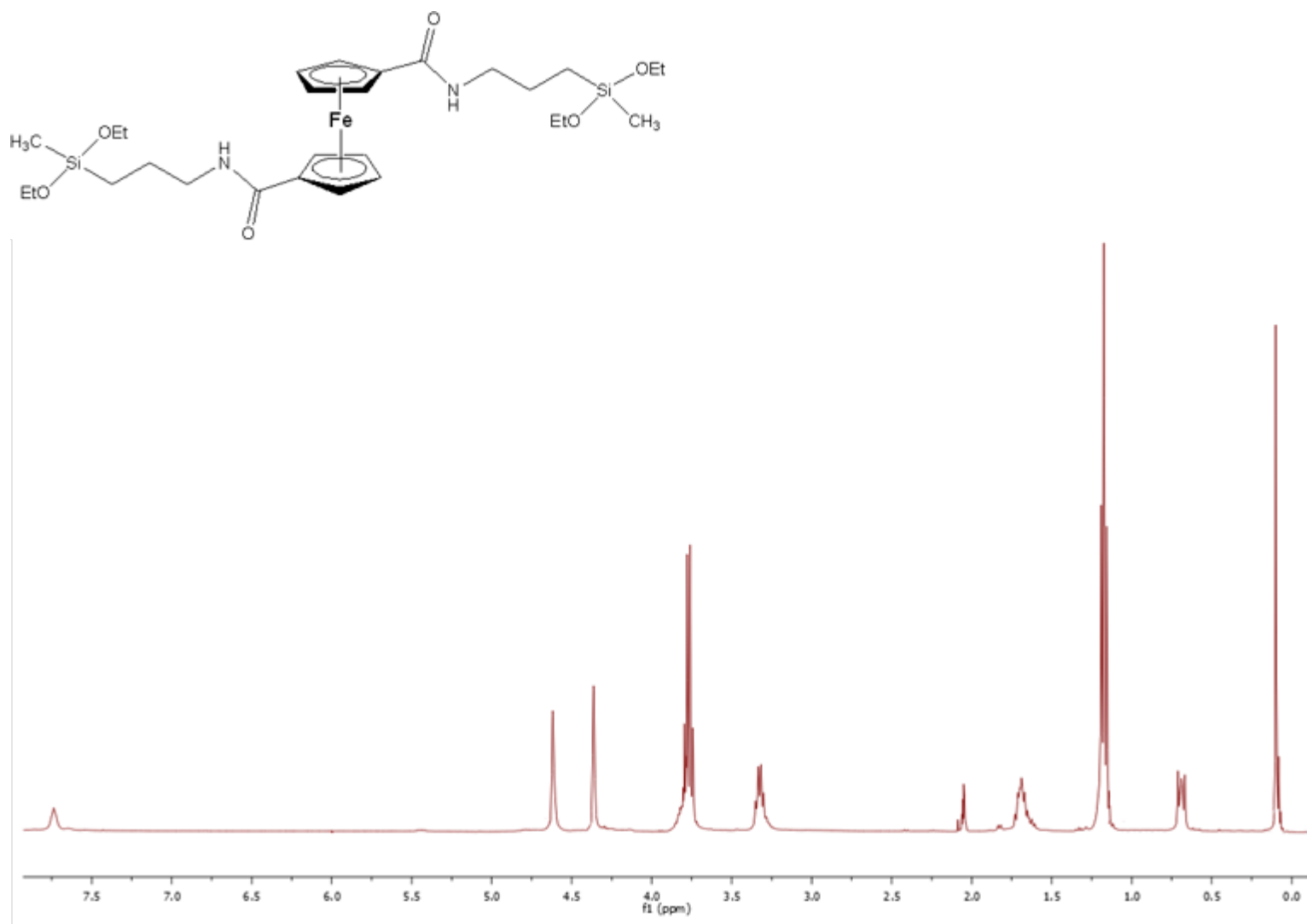


Figure 4.4 ^1H NMR Spectrum of 1,1'-ferrocene bisdiethoxymethylsilane 4.10.

4.2.1 Thermal Analysis of Polymers

Polymers **4.6a-c** and **4.10** were analyzed by both DSC and TGA to determine their thermal properties. The TGA data is illustrated in Figure 4.5, indicating that all of the polymers were stable up to approximately 130 °C, where the cationic cyclopentadienyliron complex decomposed. These decompositions belong to the cationic cyclopentadienyliron moieties which are pendent to the backbone of the polymer. The backbones of the polymers did not begin to degrade until approximately 350 °C. Polymer **4.10** was thermally stable up to 110 °C, where it began to decompose.

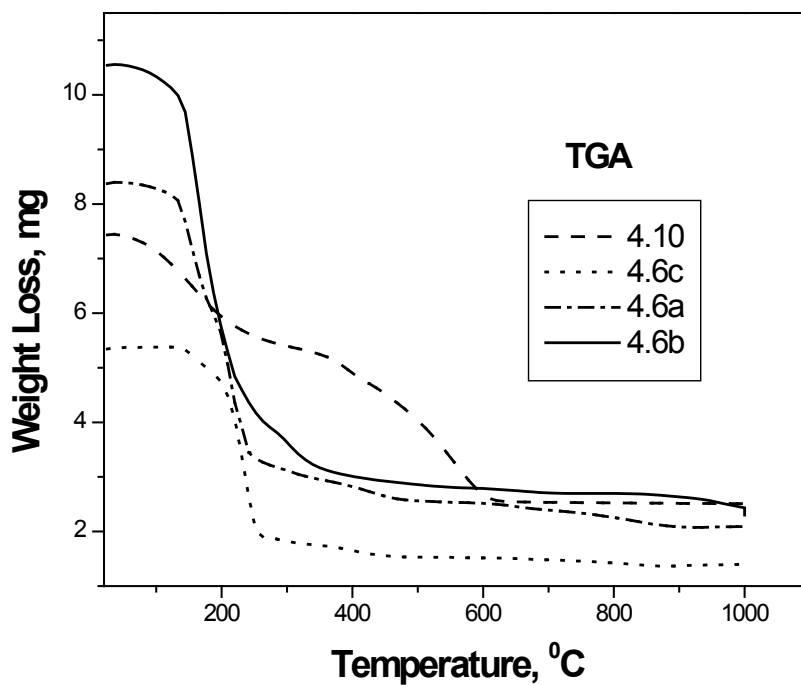


Figure 4.5 The superimposed TGA curves of the synthesized **4.6a-c** and **4.10** polymers.

Table 4.1 Thermal analysis of polymers 4.6a-c and 4.10.

Polymer	Step 1 ($^{\circ}\text{C}$), %	Step 2 ($^{\circ}\text{C}$), %	T_g ($^{\circ}\text{C}$)
4.6a	137 – 237, 36%	368 – 469, 16%	111
4.6b	142 – 222, 31%	364 – 487, 17%	95
4.6c	128 – 255, 47%	385 – 448, 8%	80
4.10	110 – 220, 17%	450 – 750, 39%	68

DSC analysis showed that polymers **4.6a-c** revealed glass transition temperatures between 80 $^{\circ}\text{C}$ and 111 $^{\circ}\text{C}$, whereas polymer **4.10** had a T_g value at 68 $^{\circ}\text{C}$ (Table 4.1). It is well-known that the common single-chain poly(dimethylsiloxane) is very flexible with a lower T_g value than 0 $^{\circ}\text{C}$. However, the cationic iron moiety highly increased the T_g value of synthesized polymers (68-111 $^{\circ}\text{C}$) due to having relatively stiff backbones. It could be also explained with strong H-bonding interactions, which remarkably restrict the internal rotation of the Si-O-Si bond and the segment mobility of the polymer.

4.2.2 Morphological Characterization of Organoiron Containing Polysiloxanes

Scanning electron microscopy (SEM) was performed on the polymer powders. Polymer **4.6a** showed highly irregular surface morphology (Figure 4.6). Close examination of fractured particles indicated the presence of nano-scale pores dispersed throughout each particle. The pores extended to the particle surface, increasing the reactivity of the polymers by increasing the surface area of the powders.

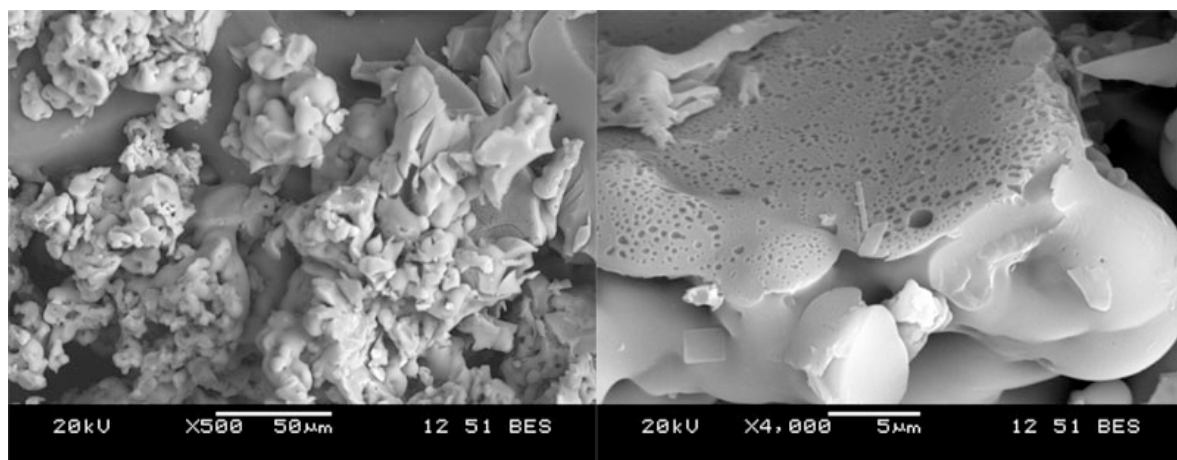


Figure 4.6 SEM images of 4.6a.

Polymer **4.6b** has fine and uniformly dispersed globular particles, with an average diameter of ~ 2 microns (Figure 4.7). These semi spherical particles did not indicate a growth direction and formed homogeneously.

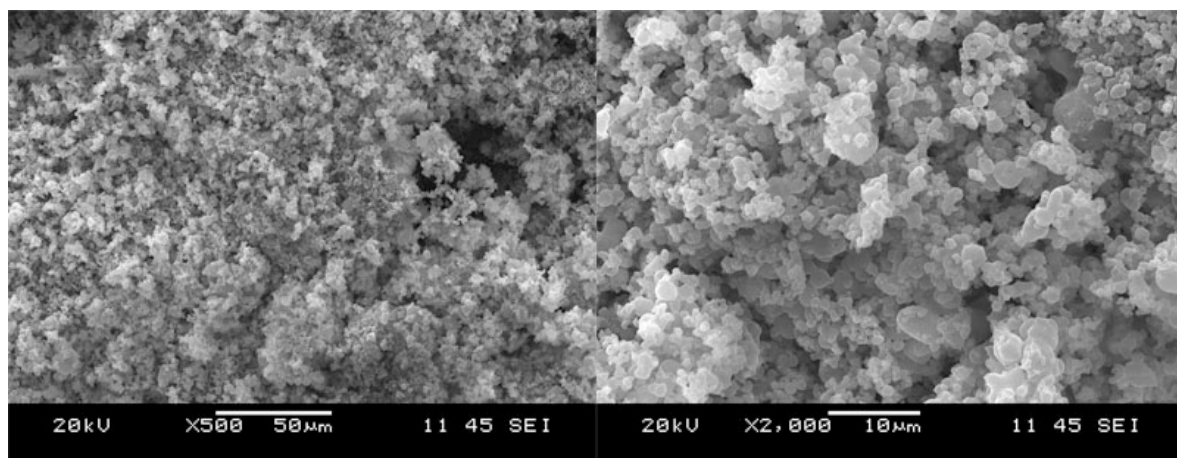


Figure 4.7 SEM images of 4.6b.

Polymer **4.6c** (Figure 4.8) had a crystalline-like chunky structure. The particles appeared to fracture/shear along specific cleavage planes, suggesting that the internal structure of the particles was periodically arranged, with stronger bonds along preferential directions. The SEM imaging indicated a homogeneous polymer without any secondary precipitates.

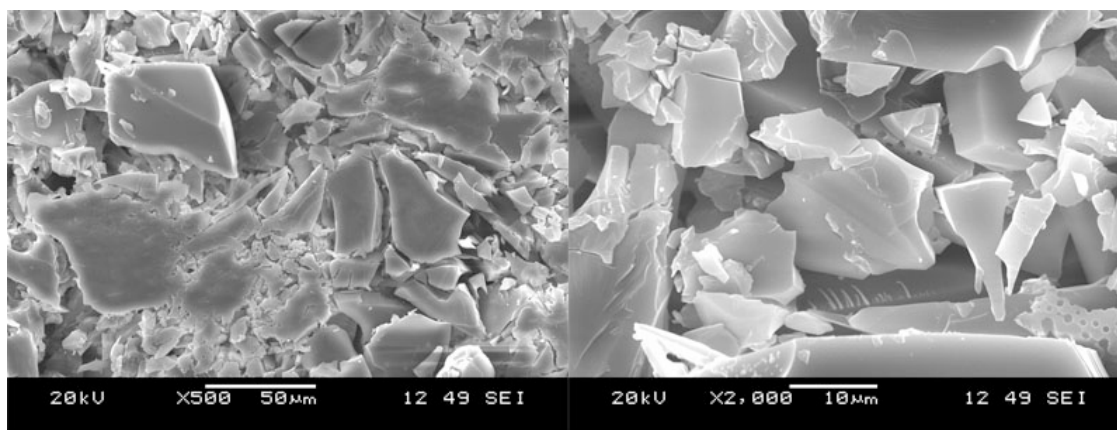


Figure 4.8 SEM images of polymer 4.6c.

The ferrocene polymer **4.10** has micron-sized particles as shown in Figure 4.9. The particles were approximately between 5 and 10µm in diameter, and we observed nano-sized particles (800 nm) present on the larger substrates.

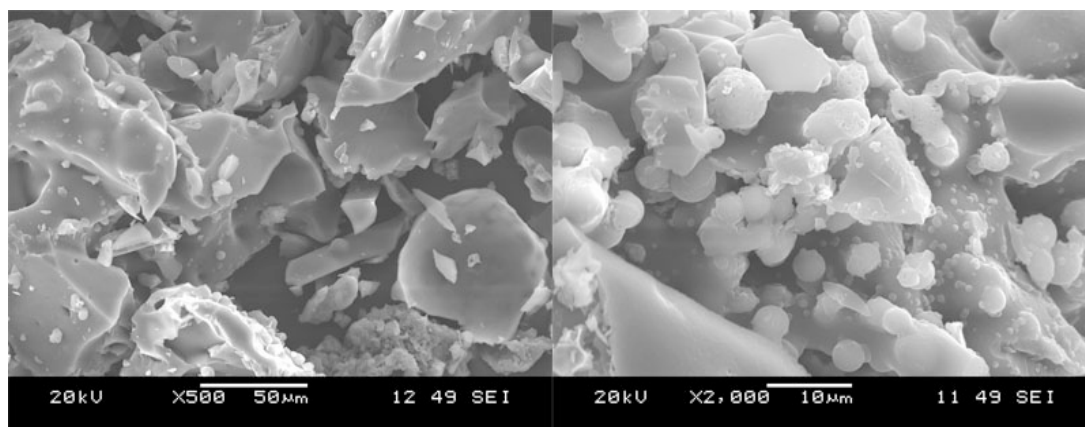


Figure 4.9 SEM images of polymer 4.10.

4.2.3 Preparation of PAN/Polysiloxane Composite Thin Films

Polyacrylonitrile (PAN) is an outstanding engineering material generally used in textile applications due to its good mechanical and thermal properties as well as its low cost [260]. Recently, PAN has been used in textiles to make them electrically conductive, such as

electromagnetic interference shielding, electrostatic dissipating, antistatic applications, gas sensors, biomechanical sensors, heating devices, flooring, and microwave reduction [261-264]. To achieve these unique properties PAN matrix is blended with another polymeric material to make new composite materials. Usually, dimethylformamide (DMF) is used as solvent for PAN since it provides increased mobility of individual segments of polymer molecules [265, 266].

In this study, we wanted to use previously synthesized organoiron containing polysiloxanes to make polyacrylonitrile composite thin films. First, polyacrylonitrile (0.5g) was dissolved in DMF (20ml) and stirred at room temperature for an hour. The organoiron containing polysiloxane (0.01g) was then added into PAN matrix and stirred at 70°C for 3 hours. The resulting viscous blend was cast on a piece of glass to form composite thin films as illustrated in Figure 4.10. Finally, the cast solutions were dried under vacuum for 24 h to evaporate the solvent.

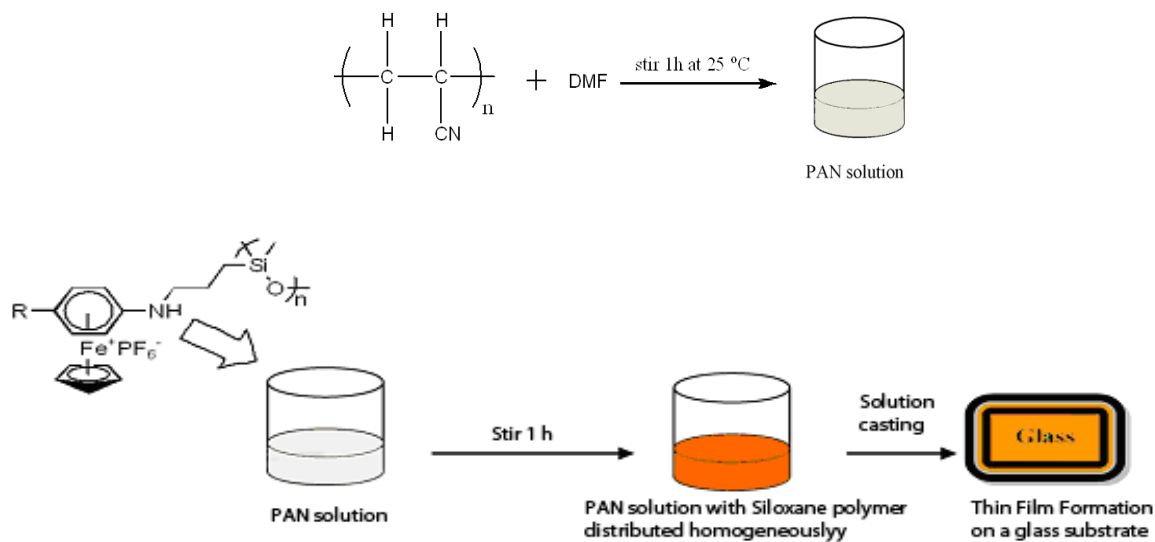


Figure 4.10 Schematic representation of preparation of PAN/Polysiloxane composite thin films.

4.2.4 Morphological Characterization of Composite Films

Scanning Electron Microscopy (SEM) imaging was performed with Hitachi Analytical table top microscope TM3000. In Figure 4.11 the composite film made of PAN and polymer **4.6b** was illustrated and the film thickness was calculated as 92 μm .

When zoomed in the cross-sectional area (Figure 4.12), it is obviously seen that the composite film has a quite porous formation indicating highly active surface area. The film surface was found to be smooth and uniform; however, micro porosity was not homogenously distributed along the film in terms of pore sizes which range from 4 μm and 6 μm . Due to its porosity, the film could find application where permeability is needed such as gas and biomechanical sensors.

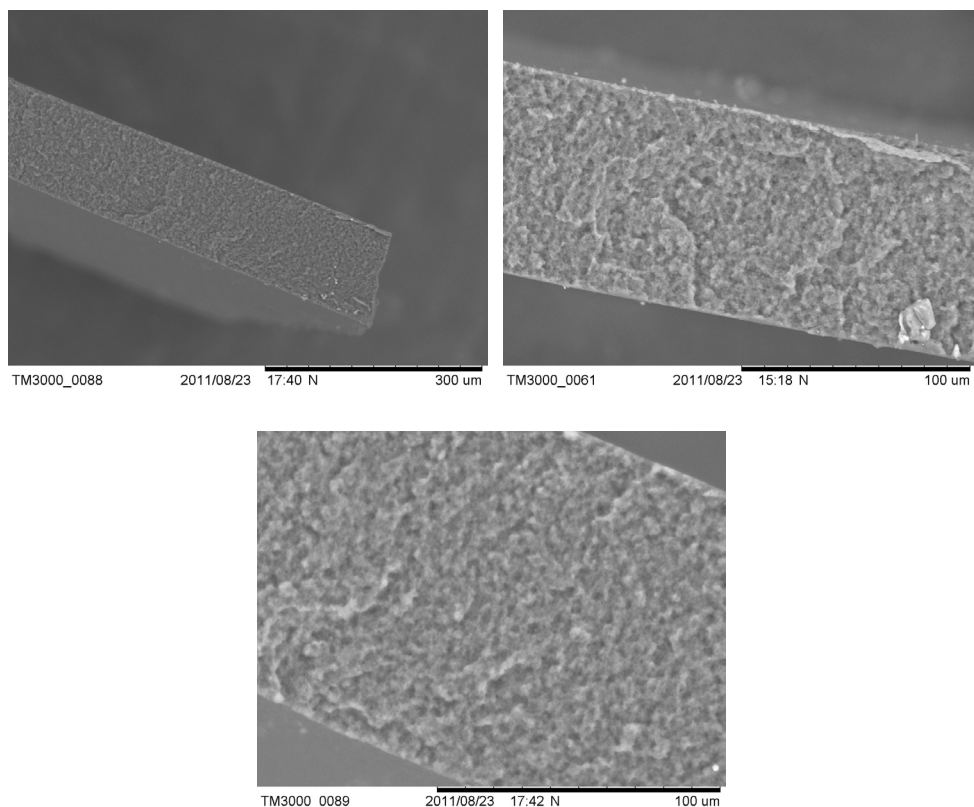


Figure 4.11 SEM images of cross-sectional area of PAN/Polysiloxane composite film prepared with polymer 4.6b with 3000X magnification.

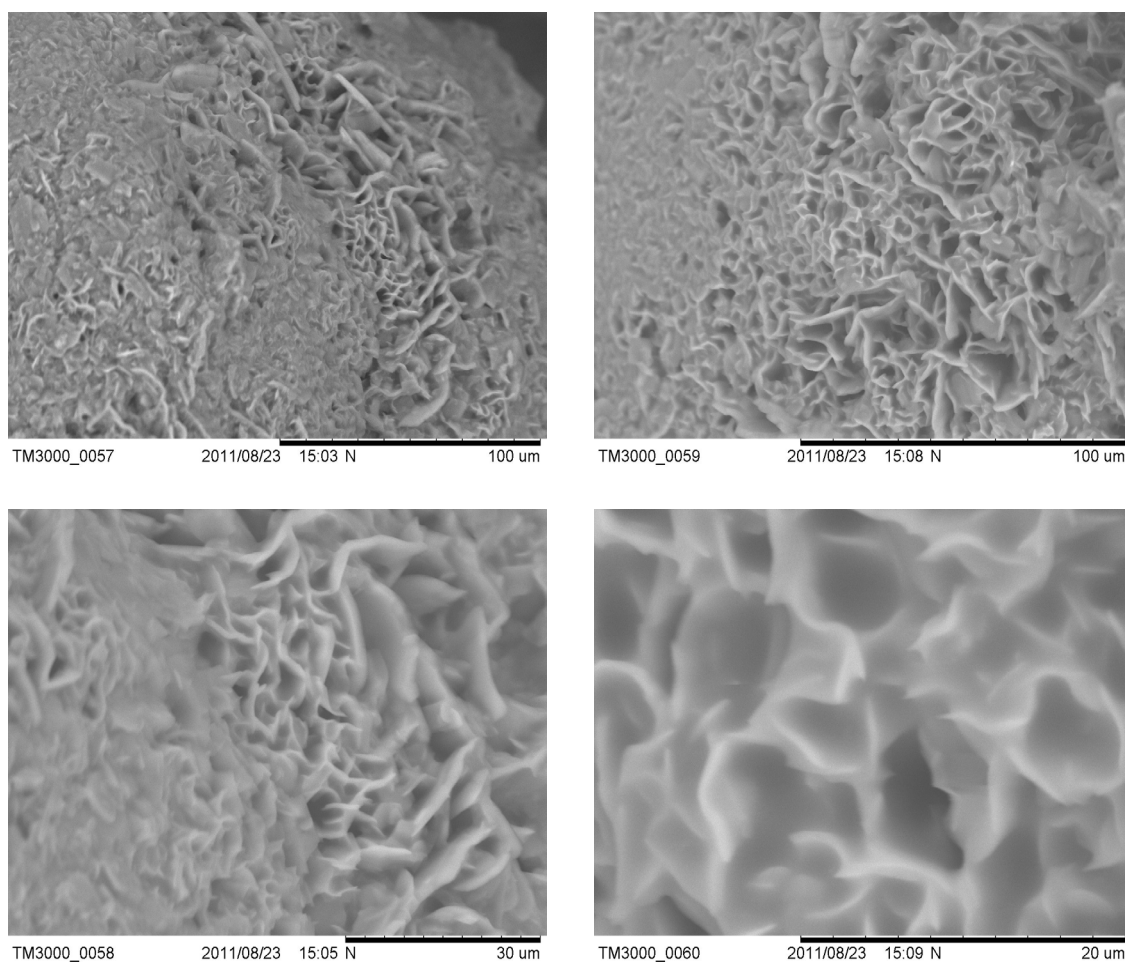


Figure 4.12 SEM images of cross-sectional area of PAN/Polysiloxane composite film prepared with polymer 4.6b with 3000X magnification (zoomed in).

The images of **4.6a-c** composite films are shown in Figure 4.13. The colours of films are slightly different from each other due to the different organoiron polysiloxane structure. Also, inhomogenous distribution of polymer **4.6a** is seen in the picture.



Figure 4.13 Images of 5x5cm sized PAN/Polysiloxane composite thin films with polymers 4.6a, 4.6b and 4.6c, respectively.

In this study we prepared non-linear polysiloxane derivatives which are sparingly soluble in organic solvents. For the future aspects, we could try to make them linear to increase the solubility and lower the T_g values by changing hydrosilation reagent and reaction conditions. Furthermore, we made composite thin films of siloxane polymer and PAN to get the advantages

of both compounds. Since we did not have a film applicator, we couldn't arrange the film thickness. For the future work, the film properties could be improved by changing the ratios of both compounds and more uniform films could be prepared with a film applicator for desired application. The morphology of the prepared composite films was found as micro porous which make them useful for sensor applications. Further studied should be done in biosensor application.

4.3 Experimental

4.3.1 Materials

All reagents were purchased from Sigma-Aldrich and used without further purification. All general solvents were HPLC grade and used without further purification. Complexes **1.20**, **1.21** and **4.1** were prepared through established procedures [152].

4.3.2 Characterizations

^1H and ^{13}C NMR spectra were recorded at 400 MHz and 101 MHz, respectively, on a Varian Mercury Plus spectrometer equipped with a gradient field probe, with chemical shifts referenced to residual solvent peaks and coupling constants reported in Hz. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra were recorded at 79.5 MHz using an inverse gated proton decoupled experiment with a five-second interpulse delay, in the region +50 ppm to -100 ppm from tetramethylsilane, the internal standard. Chemical shifts are reported in parts per million (δ) with reference to residual solvent resonances for ^1H and ^{13}C NMR. Infrared spectroscopy was performed on an IRPrestige-21FTIR by Shimadzu with a MIRacle ATR by PIKE Technologies. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on Mettler-Toledo TGA/SDTA851^e and DSC821^e instruments, respectively, at heating rates of 20 °C/min under nitrogen atmospheres. Scanning Electron Microscopy (SEM) imaging was performed with Hitachi Analytical table top microscope TM3000. Cyclic voltammetric studies were performed using a conventional three-electrode cell. In these studies, the working electrode was a glassy carbon disk electrode (~ 2 mm diameter), the auxiliary electrode was a Pt wire, and a Ag/AgCl reference electrode was utilized. Temperatures ranging from 293 to 243 K were obtained using an acetone/water/ $\text{N}_2(\text{l})$ mixture. The concentration of the analyte was 2.0 mM, while that of the

supporting electrolyte (TBAP) was 0.1 M. The solutions were deaerated with nitrogen prior to use. An EG&G Princeton Applied Research model 263A potentiostat was used in all experiments. All reactions and complexes containing η^6 -aryl- η^5 -cyclopentadienyliron hexafluorophosphate moiety were kept in the dark to prevent decomposition.

4.3.3 Synthesis of Complexes 4.3, 4.4 and 4.5 (a-c)

The synthesis of complex 4.3(a-c), 4.4 (a-c) and 4.5 (a-c) were prepared according to our previously published methods [257].

4.3.4 Synthesis of 1,1'-Ferrocene Diallylamide Complex 4.8

The precursor complex of the ferrocene-containing siloxane polymer was prepared by dissolving 1,1'-ferrocene dicarbonyl chloride (4.8 mmol), allylamine (28.8 mmol), and 10 drops of pyridine in 40 mL DCM. The solution was purged with nitrogen for 30 minutes and allowed to stir for 18 hours. 100 mL DCM was added to the reaction mixture and then washed with 100 mL 1.2 M HCl twice. The obtained DCM layer was dried over MgSO_4 , filtered, and the DCM was removed from the pure product *in vacuo*.

4.8: ^1H NMR (400 MHz, dmsO) δ 8.06 (t, J = 5.8 Hz, 2H), 5.90 (ddt, J = 17.2, 10.3, 5.2 Hz, 2H), 5.15 (ddq, J = 36.4, 10.3, 1.7 Hz, 4H), 4.76 – 4.74 (m, 4H), 4.31 – 4.29 (m, 4H), 3.82 (tt, J = 5.9, 1.7 Hz, 4H). ^{13}C NMR (101 MHz, DMSO- d_6) δ = 168.22, 135.88, 114.92, 77.81, 71.51, 69.50, 41.09 IR 3418 cm^{-1} (N-H), 1692 cm^{-1} (C=O). (62% yield).

4.3.5 Synthesis of 1,1'-Ferrocene Bisdiethyloxymethylsilane Complex 4.9

The hydrosilation of 1,1'-ferrocene diallylamide was achieved via Cp_2PtCl_2 catalyst. 1,1'-Ferrocene diallylamide (2.8 mmol) and Cp_2PtCl_2 (0.01 mmol) were purged with nitrogen for

15 minutes. Subsequently, 2.5 mL methyldiethoxysilane was added through the top of the condenser, followed by 50 mL dry THF. The reaction mixture was heated to 70 °C and allowed to stir for 24 hours. The pure product was obtained after evaporating the solvent *in vacuo*.

4.9: ^1H NMR (400 MHz, acetone- d_6) δ = 7.74 (s, 2H), 4.64 (d, J = 18.6 Hz, 4H), 4.38 (d, J = 15.6 Hz, 4H), 3.80–3.74 (m, 8H), 3.33 (dd, J =13.2, 6.7 Hz, 4H), 1.70 (dd, J =7.4, 16.1 Hz, 4H), 1.23–1.16 (m, 12H), 0.69 (dd, J = 10.0, 6.9 Hz, 4H), 0.10 (s, 6H). ^{13}C NMR (101 MHz, DMSO- d_6) δ = 168.40, 77.79, 71.49, 69.48, 56.00, 41.07, 22.56, 18.53, 11.43, -0.69. $\text{C}_{28}\text{H}_{48}\text{O}_6\text{N}_2\text{Si}_2\text{Fe}$: Calcd. C 52.99, H 7.57, N 4.41; found C 51.86, H 7.52, N 4.68. IR 3422 cm^{-1} (N-H), 1710 cm^{-1} (C=O), 1061 cm^{-1} (Si-O), 842 cm^{-1} (Si-CH₃). (78% yield).

4.3.6 Synthesis of Ferrocene Polymer 4.10

Monomer **4.9** (1 mmol) was dissolved in 15 mL NMP. The mixture of 0.15 mL water and 10 mL NMP was added dropwise into the monomer solution over 4 hours in an ice-water bath. The reaction mixture was stirred at 25 °C for several hours, then slowly warmed to 40 °C for 10 hours to complete hydrolysis. A drop of concentrated H_2SO_4 was added into the mixture to catalyze the condensation reaction. The reaction mixture was stirred at 40 °C for 72 hours under reduced pressure to remove the water released. A small amount of gel would appear during the condensation process, which was removed by filtering. For end-capping the terminal silanol of the polymer, a mixture of pyridine (0.1 mmol), trimethylchlorosilane (0.1 mmol), and 10 mL NMP was added dropwise into the reaction flask while stirring. The mixture was stirred for 24 hours at 25 °C, followed by the addition of 10 mL water as a precipitating agent. The precipitate was filtered and then dried in a vacuum oven at 50 °C for 24 hours to give polymer **4.10**.

4.10 IR 3429 cm^{-1} (N-H), 1680 cm^{-1} (C=O), 1047 cm^{-1} (Si-O), 833 cm^{-1} (Si-CH₃), 2765 cm^{-1} (sp^2 CH), 2980 cm^{-1} (sp^3 CH). There are no NMR results due to crosslinked polymer.

5 Conclusion

In this thesis, synthetic methodology of functionalizing thiophene derivatives and incorporation organoiron moieties into siloxane polymers were explored in detail.

The main goals of the first study was to synthesize novel metallo-conjugated monomers and polymers having mono and bimetallic cationic iron and ferrocene as pendant groups attached to conjugated monomers. A range of transition metal-containing polythiophene derivatives were prepared. Electropolymerization was demonstrated to be a powerful synthetic method for the preparation and detailed characterization of conjugated backbones with metal complexes as pendants. According to our hypothesis, we were expecting an increase in the capacitive properties with the increase of iron moiety in the polymer film. However, we observed decrease in the capacitance values with increasing the iron moiety since the pendant groups with bimetallic group was very bulky and decreased the electropolymerization possibility.

The electrochemical impedance spectroscopic measurements revealed that organoiron containing PEDOT films have higher capacitive properties and higher conductivities compared to PTh films. Especially Fc-PEDOT, **2.12** which have very high capacitive property with a 26.6 mFcm^{-2} double layer capacitance value indicating supercapacitor behavior, whereas the other polymers have capacitive properties in micro Farad scale.

On the other hand, synthesized VBM-EDOT (**2.3**) and VBM-Th (**2.4**) monomers were chemically polymerized through condensation polymerization with Bisphenol-A to have the metals in the polymer backbone and their thermal properties characterized. TGA results

indicated that the cationic polymers have thermal stability up to 150°C, when the cationic iron moiety decomposed followed by the polymer backbones degrading around 600°C. The presence of oxygen in the ethylenedioxy bridge in VBM-PEDOT (**2.8**) increasing the initial decomposition temperature around 40°C due to the stabilizing effect of oxygen may be explained by forming thermally stable radical species that suppress unzipping of the polymer.

According to the morphological analysis, the synthesized molecules with iron moieties had globular micro- and nano-sized thin film formations, suggestive of their use in thin film formation where the conductivity and metal moieties are desired. Applications in micro and nano electronics will need greater exploration as these newly synthesized materials may be suitable for a range of novel properties and the long term stability of these materials for various applications is important and still needs to be improved.

In the third chapter, thiophene monomers with different functional groups were synthesized from 3-Thiophene carboxylic and 2-(3-Thienyl) ethanol via Steglich esterifications which were conducted with Coumarin-3-carboxylic acid, 1-Pyrenebutyric acid, 2-Naphthol and terpyridine. The synthesized monomers were electrochemically polymerized onto CFME and GC electrodes to investigate the impedance properties and conductivities. As a research objective, we were expecting to see too much difference in the fluorescence intensity of the prepared monomers compared to the chromophores. However, the difference in fluorescence properties in between synthesized monomers and their precursors was observed due to the different lengths of tethers.

The electro activity and well-defined electrochemistry of functionalized thiophene derivatives on CFME makes them useful as electrochemical capacitor microelectrodes and electrochemical sensor electrodes. In terms of the capacitive properties and conductivity PThC

indicated better properties with a $1515 \mu\text{m.cm}^{-2}$ capacitance value and 0.795 mS conductivity value which is further supported with homogeneity of the film on the electrode surface. The fluorescence functional groups are important for chemical sensors through electrochemistry. The compared normalized absorbance spectra revealed that the ThN (**3.7**) monomer has a greater blue shifted than the others indicating the higher quantum yield.

On the other hand, terpyridine attached thiophenes with different spacer length were compared in terms of capacitive properties and fluorescence behavior. We were expecting to achieve better polymer with longer spacer groups. Therefore, ThDTerpy (**3.11c**) indicated a better chance for electropolymerization due to long and flexible side chain which was proved with the higher film thickness of PThDTerpy with $1.4\mu\text{m}$. It has also higher electrical conductivity (1.48mS) and quite good capacitance value. Additionally, the morphological characterizations of electro deposited CFME surfaces were achieved. The SEM images indicated well adhered micro structural and porous films on electrode surfaces.

In chapter four, a series of cationic organoiron complexes containing amines were synthesized which were followed by hydrosilation reactions to give precursor to cationic organoiron and ferrocene containing linear and crosslinked polymers. These polymers were successfully synthesized via acid catalyzed condensation polymerization. The cationic organoiron-containing polymers possessed glass transition temperatures ranging from 80-111 °C and were thermally stable up to 110-142°C, while the T_g value of the ferrocene-containing polymer was 68°C.

SEM images indicated that the polymers adopted very different solid-state morphologies ranging from fractured particles with nano-scale pores to crystalline-like structures. Additionally, composite thin film formation was achieved by blending the siloxane polymers with PAN

matrix. The monolayer films indicated uniformly distributed porous morphology increasing the activity. Therefore, the films could be used in the application of gas sensors and biomechanical sensors. However, the aim was to prepare flexible composite thin films due to the silicone content but the iron moieties increased the T_g values and made the films brittle.

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Appendices

Appendix A: X-Ray Crystallography of Complex 4.3a

Crystallographic data was measured, elucidated and reported by Brian Patrick at the University of British Columbia in Vancouver.

X-ray structure report for complex 4.3a

Data Collection

An orange needle crystal of $C_{14}H_{16}NFePF_6$ having approximate dimensions of 0.10 x 0.15 x 0.40 mm was mounted on a glass fibre. All measurements were made on a Bruker DUO APEX II diffractometer with graphite monochromated Mo-K α radiation..

The data were collected at a temperature of $-183.0 \pm 0.1^\circ\text{C}$ to a maximum 2θ value of 60.1° . Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 5.0-second exposures. The crystal-to-detector distance was 40.00 mm.

Data Reduction

Of the 25146 reflections that were collected, 2390 were unique ($R_{\text{int}} = 0.028$); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT¹ software package. The linear absorption coefficient, μ , for Mo-K α radiation is 11.43 cm^{-1} . Data were corrected for absorption effects using the multi-scan technique (SADABS²), with minimum and

maximum transmission coefficients of 0.808 and 0.892, respectively. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods³. The material crystallizes with one half-molecule residing on a mirror plane. Since the cation has no formal mirror symmetry, this manifests itself as disorder of the phenyl substituent across the mirror plane. Atoms N1, H1N, and C4 are evenly distributed on either side of the plane, while atoms C5 and C6 reside directly on the mirror plane. All non-hydrogen atoms were refined anisotropically. H1N was located in a difference map and refined isotropically, while all other hydrogen atoms were placed in calculated positions. The final cycle of full-matrix least-squares refinement⁴ on F^2 was based on 2390 reflections and 128 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.078$$

$$wR2 = [\Sigma (w (F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2} = 0.187$$

The standard deviation of an observation of unit weight⁵ was 1.05. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.06 and $-0.78 \text{ e}^-/\text{\AA}^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber⁶. Anomalous dispersion effects were included in F_{calc} ⁷; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley⁸. The values for the mass attenuation coefficients are those of Creagh and Hubbell⁹. All refinements were performed using the SHELXL-97¹⁰ via the WinGX¹¹ interface.

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(4) Least Squares function minimized:

$$\sum w(F_o^2 - F_c^2)^2$$

(5) Standard deviation of an observation of unit weight:

$$[\sum w(F_o^2 - F_c^2)^2 / (N_o - N_v)]^{1/2}$$

where: N_o = number of observations

N_v = number of variables

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EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$\text{C}_{14}\text{H}_{16}\text{NFePF}_6$
Formula Weight	399.10
Crystal Colour, Habit	orange, needle
Crystal Dimensions	0.10 X 0.15 X 0.40 mm
Crystal System	orthorhombic
Lattice Type	primitive
Lattice Parameters	$a = 12.5700(4) \text{ \AA}$ $b = 8.7661(3) \text{ \AA}$ $c = 13.9672(5) \text{ \AA}$ $\alpha = 90^\circ$ $\beta = 90^\circ$ $\gamma = 90^\circ$ $V = 1539.04(\text{p}) \text{ \AA}^3$
Space Group	$P nma$ (#62)
Z value	4
D_{calc}	1.722 g/cm^3
F_{000}	808.00
$\mu(\text{MoK}\alpha)$	11.43 cm^{-1}

B. Intensity Measurements

Diffractometer	Bruker DUO APEX II
Radiation	MoK α ($\lambda = 0.71073 \text{ \AA}$) graphite monochromated
Data Images	1616 exposures @ 5.0 seconds
Detector Position	40.00 mm
$2\theta_{\text{max}}$	60.1 $^{\circ}$
No. of Reflections Measured	Total: 25146
Corrections	Unique: 2390($R_{\text{int}} = 0.028$) Absorption ($T_{\text{min}} = 0.808$, $T_{\text{max}} = 0.892$) Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\sum w (F_o^2 - F_c^2)^2$
Least Squares Weights	$w=1/(\sigma^2(F_o^2)+(0.0908P)^2+ 3.8299P)$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I>0.00\sigma(I)$)	2390
No. Variables	128
Reflection/Parameter Ratio	18.67
Residuals (refined on F^2 , all data): R1; wR2	0.078; 0.187
Goodness of Fit Indicator	1.05
No. Observations ($I>2.00\sigma(I)$)	1906
Residuals (refined on F): R1; wR2	0.063; 0.173
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	1.06 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.78 e ⁻ /Å ³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for aa006. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U (eq)
C (1)	7398 (2)	1698 (4)	7617 (2)	38 (1)
C (2)	6942 (3)	908 (5)	6838 (2)	40 (1)
C (3)	6457 (3)	1695 (5)	6084 (2)	41 (1)
C (4)	8548 (5)	1924 (8)	9087 (5)	35 (1)
C (5)	7956 (4)	2500	9916 (4)	45 (1)
C (6)	6931 (4)	2500	10064 (3)	41 (1)
C (7)	8751 (3)	1707 (5)	5052 (3)	49 (1)
C (8)	9273 (3)	1193 (6)	5881 (3)	57 (1)
C (9)	9600 (4)	2500	6414 (4)	67 (2)
N (1)	7885 (5)	1146 (6)	8410 (4)	32 (1)
F (1)	8309 (4)	7500	8560 (4)	103 (2)
F (2)	9269 (4)	8786 (6)	7455 (3)	155 (2)
F (3)	9789 (4)	8702 (5)	8970 (3)	119 (2)
F (4)	10697 (4)	7500	7845 (3)	84 (1)
Fe (1)	7989 (1)	2500	6261 (1)	33 (1)
P (1)	9479 (1)	7500	8187 (1)	46 (1)
C (1B)	7398 (2)	1698 (4)	7617 (2)	38 (1)
C (5B)	7956 (4)	2500	9916 (4)	45 (1)
C (6B)	6931 (4)	2500	10064 (3)	41 (1)

Table 3. Bond lengths [Å] and angles [deg] for aa006.

C(1)-N(1)	1.355(6)
C(1)-C(1)#1	1.405(7)
C(1)-C(2)	1.412(5)
C(1)-Fe(1)	2.152(3)
C(2)-C(3)	1.400(5)
C(2)-Fe(1)	2.080(3)
C(2)-H(2)	0.9500
C(3)-C(3)#1	1.411(8)
C(3)-Fe(1)	2.067(3)
C(3)-H(3)	0.9500
C(4)-N(1)	1.433(8)
C(4)-C(5)	1.465(8)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.305(7)
C(5)-H(5)	0.9500
C(6)-H(6A)	0.9500
C(6)-H(6B)	0.9500
C(7)-C(7)#1	1.391(9)
C(7)-C(8)	1.406(6)
C(7)-Fe(1)	2.063(3)
C(7)-H(7)	0.9500
C(8)-C(9)	1.427(6)
C(8)-Fe(1)	2.049(4)
C(8)-H(8)	0.9500
C(9)-C(8)#1	1.427(6)
C(9)-Fe(1)	2.036(5)
C(9)-H(9)	0.9500
N(1)-H(1N)	0.747(19)
F(1)-P(1)	1.560(5)
F(2)-P(1)	1.544(4)
F(3)-P(1)	1.568(3)
F(4)-P(1)	1.603(5)
Fe(1)-C(8)#1	2.049(4)
Fe(1)-C(7)#1	2.063(3)
Fe(1)-C(3)#1	2.067(3)
Fe(1)-C(2)#1	2.080(3)
Fe(1)-C(1B)#1	2.152(3)
Fe(1)-C(1)#1	2.152(3)
P(1)-F(2)#2	1.544(4)
P(1)-F(3)#2	1.568(3)
N(1)-C(1)-C(1)#1	110.9(3)
N(1)-C(1)-C(2)	129.7(4)
C(1)#1-C(1)-C(2)	119.4(2)
N(1)-C(1)-Fe(1)	132.9(3)
C(1)#1-C(1)-Fe(1)	70.94(10)
C(2)-C(1)-Fe(1)	67.79(18)
C(3)-C(2)-C(1)	121.0(3)
C(3)-C(2)-Fe(1)	69.8(2)
C(1)-C(2)-Fe(1)	73.29(19)
C(3)-C(2)-H(2)	119.5
C(1)-C(2)-H(2)	119.5

Fe(1)-C(2)-H(2)	130.1
C(2)-C(3)-C(3)#1	119.5(2)
C(2)-C(3)-Fe(1)	70.80(19)
C(3)#1-C(3)-Fe(1)	70.05(11)
C(2)-C(3)-H(3)	120.2
C(3)#1-C(3)-H(3)	120.2
Fe(1)-C(3)-H(3)	131.7
N(1)-C(4)-C(5)	112.9(5)
N(1)-C(4)-H(4A)	109.0
C(5)-C(4)-H(4A)	109.0
N(1)-C(4)-H(4B)	109.0
C(5)-C(4)-H(4B)	109.0
H(4A)-C(4)-H(4B)	107.8
C(6)-C(5)-C(4)	128.8(4)
C(6)-C(5)-H(5)	115.6
C(4)-C(5)-H(5)	115.6
C(5)-C(6)-H(6A)	120.0
C(5)-C(6)-H(6B)	120.0
H(6A)-C(6)-H(6B)	120.0
C(7)#1-C(7)-C(8)	108.7(3)
C(7)#1-C(7)-Fe(1)	70.30(12)
C(8)-C(7)-Fe(1)	69.5(2)
C(7)#1-C(7)-H(7)	125.7
C(8)-C(7)-H(7)	125.7
Fe(1)-C(7)-H(7)	126.1
C(7)-C(8)-C(9)	107.9(4)
C(7)-C(8)-Fe(1)	70.5(2)
C(9)-C(8)-Fe(1)	69.0(3)
C(7)-C(8)-H(8)	126.1
C(9)-C(8)-H(8)	126.1
Fe(1)-C(8)-H(8)	126.0
C(8)-C(9)-C(8)#1	106.8(5)
C(8)-C(9)-Fe(1)	70.1(2)
C(8)#1-C(9)-Fe(1)	70.1(2)
C(8)-C(9)-H(9)	126.6
C(8)#1-C(9)-H(9)	126.6
Fe(1)-C(9)-H(9)	124.9
C(1)-N(1)-C(4)	129.2(5)
C(1)-N(1)-H(1N)	116.9(12)
C(4)-N(1)-H(1N)	109.4(11)
C(9)-Fe(1)-C(8)	40.88(16)
C(9)-Fe(1)-C(8)#1	40.88(16)
C(8)-Fe(1)-C(8)#1	68.0(3)
C(9)-Fe(1)-C(7)	67.94(18)
C(8)-Fe(1)-C(7)	39.98(17)
C(8)#1-Fe(1)-C(7)	67.09(17)
C(9)-Fe(1)-C(7)#1	67.94(18)
C(8)-Fe(1)-C(7)#1	67.09(17)
C(8)#1-Fe(1)-C(7)#1	39.98(17)
C(7)-Fe(1)-C(7)#1	39.4(2)
C(9)-Fe(1)-C(3)	160.00(11)
C(8)-Fe(1)-C(3)	120.81(19)
C(8)#1-Fe(1)-C(3)	153.36(18)
C(7)-Fe(1)-C(3)	102.66(15)
C(7)#1-Fe(1)-C(3)	116.69(15)
C(9)-Fe(1)-C(3)#1	160.00(11)
C(8)-Fe(1)-C(3)#1	153.36(18)

C (8) #1-Fe (1) -C (3) #1	120.81 (19)
C (7) -Fe (1) -C (3) #1	116.69 (15)
C (7) #1-Fe (1) -C (3) #1	102.66 (15)
C (3) -Fe (1) -C (3) #1	39.9 (2)
C (9) -Fe (1) -C (2)	126.06 (14)
C (8) -Fe (1) -C (2)	102.92 (17)
C (8) #1-Fe (1) -C (2)	166.80 (18)
C (7) -Fe (1) -C (2)	112.62 (16)
C (7) #1-Fe (1) -C (2)	146.80 (16)
C (3) -Fe (1) -C (2)	39.45 (14)
C (3) #1-Fe (1) -C (2)	71.67 (15)
C (9) -Fe (1) -C (2) #1	126.06 (14)
C (8) -Fe (1) -C (2) #1	166.80 (18)
C (8) #1-Fe (1) -C (2) #1	102.92 (17)
C (7) -Fe (1) -C (2) #1	146.80 (16)
C (7) #1-Fe (1) -C (2) #1	112.62 (16)
C (3) -Fe (1) -C (2) #1	71.67 (15)
C (3) #1-Fe (1) -C (2) #1	39.45 (14)
C (2) -Fe (1) -C (2) #1	84.2 (2)
C (9) -Fe (1) -C (1B) #1	104.54 (17)
C (8) -Fe (1) -C (1B) #1	133.04 (16)
C (8) #1-Fe (1) -C (1B) #1	108.50 (15)
C (7) -Fe (1) -C (1B) #1	172.32 (14)
C (7) #1-Fe (1) -C (1B) #1	140.44 (16)
C (3) -Fe (1) -C (1B) #1	83.99 (13)
C (3) #1-Fe (1) -C (1B) #1	70.88 (13)
C (2) -Fe (1) -C (1B) #1	70.12 (14)
C (2) #1-Fe (1) -C (1B) #1	38.92 (13)
C (9) -Fe (1) -C (1) #1	104.54 (17)
C (8) -Fe (1) -C (1) #1	133.04 (16)
C (8) #1-Fe (1) -C (1) #1	108.50 (15)
C (7) -Fe (1) -C (1) #1	172.32 (14)
C (7) #1-Fe (1) -C (1) #1	140.44 (16)
C (3) -Fe (1) -C (1) #1	83.99 (13)
C (3) #1-Fe (1) -C (1) #1	70.88 (13)
C (2) -Fe (1) -C (1) #1	70.12 (14)
C (2) #1-Fe (1) -C (1) #1	38.92 (13)
C (1B) #1-Fe (1) -C (1) #1	0.00 (17)
F (2) #2-P (1) -F (2)	93.8 (5)
F (2) #2-P (1) -F (1)	93.4 (2)
F (2) -P (1) -F (1)	93.4 (2)
F (2) #2-P (1) -F (3)	174.1 (3)
F (2) -P (1) -F (3)	90.8 (3)
F (1) -P (1) -F (3)	90.1 (2)
F (2) #2-P (1) -F (3) #2	90.8 (3)
F (2) -P (1) -F (3) #2	174.1 (3)
F (1) -P (1) -F (3) #2	90.1 (2)
F (3) -P (1) -F (3) #2	84.4 (4)
F (2) #2-P (1) -F (4)	88.1 (2)
F (2) -P (1) -F (4)	88.1 (2)
F (1) -P (1) -F (4)	177.8 (3)
F (3) -P (1) -F (4)	88.3 (2)
F (3) #2-P (1) -F (4)	88.3 (2)

Symmetry transformations used to generate equivalent atoms:
#1 x, -y+1/2, z #2 x, -y+3/2, z

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for aa006.
The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U11 + \dots + 2 h k a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
C (1)	26 (1)	55 (2)	32 (1)	10 (1)	6 (1)	-1 (1)
C (2)	36 (2)	47 (2)	37 (2)	2 (1)	13 (1)	-3 (1)
C (3)	29 (1)	64 (2)	31 (1)	-5 (2)	4 (1)	-8 (2)
C (4)	27 (2)	40 (3)	37 (3)	0 (2)	-7 (2)	6 (2)
C (5)	42 (3)	61 (3)	32 (2)	0	-15 (2)	0
C (6)	43 (3)	54 (3)	27 (2)	0	-1 (2)	0
C (7)	37 (2)	70 (2)	38 (2)	-9 (2)	16 (1)	2 (2)
C (8)	37 (2)	75 (3)	60 (2)	16 (2)	25 (2)	20 (2)
C (9)	19 (2)	148 (7)	35 (3)	0	7 (2)	0
N (1)	41 (3)	26 (2)	30 (2)	0 (2)	6 (2)	5 (2)
F (1)	44 (2)	190 (6)	75 (3)	0	-8 (2)	0
F (2)	175 (5)	184 (4)	105 (3)	94 (3)	49 (3)	110 (4)
F (3)	123 (3)	137 (4)	95 (2)	-73 (3)	27 (2)	-49 (3)
F (4)	77 (3)	121 (4)	54 (2)	0	4 (2)	0
Fe (1)	22 (1)	50 (1)	27 (1)	0	6 (1)	0
P (1)	61 (1)	48 (1)	29 (1)	0	-18 (1)	0
C (1B)	26 (1)	55 (2)	32 (1)	10 (1)	6 (1)	-1 (1)
C (5B)	42 (3)	61 (3)	32 (2)	0	-15 (2)	0
C (6B)	43 (3)	54 (3)	27 (2)	0	-1 (2)	0

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for aa006.

	x	y	z	U (eq)
H (2)	6966	-175	6825	48
H (3)	6129	1150	5575	49
H (4A)	8903	2790	8763	42
H (4B)	9108	1217	9313	42
H (5)	8375	2932	10412	54
H (6A)	6464	2085	9596	49
H (6B)	6651	2915	10640	49
H (7)	8448	1075	4571	58
H (8)	9389	159	6056	69
H (9)	9965	2500	7010	81
H (1B)	7702	1152	8137	45
H (5B)	8375	2932	10412	54
H (6B1)	6464	2085	9596	49
H (6B2)	6651	2915	10640	49
H (1N)	8020 (30)	310 (20)	8410 (20)	30 (20)

Table 6. Torsion angles [deg] for aa006.

N(1)-C(1)-C(2)-C(3)	179.0(4)
C(1)#1-C(1)-C(2)-C(3)	-2.4(3)
Fe(1)-C(1)-C(2)-C(3)	-53.0(3)
N(1)-C(1)-C(2)-Fe(1)	-128.0(4)
C(1)#1-C(1)-C(2)-Fe(1)	50.61(13)
C(1)-C(2)-C(3)-C(3)#1	2.4(3)
Fe(1)-C(2)-C(3)-C(3)#1	-52.22(12)
C(1)-C(2)-C(3)-Fe(1)	54.6(3)
N(1)-C(4)-C(5)-C(6)	-6.1(7)
C(7)#1-C(7)-C(8)-C(9)	0.4(3)
Fe(1)-C(7)-C(8)-C(9)	-59.2(3)
C(7)#1-C(7)-C(8)-Fe(1)	59.58(12)
C(7)-C(8)-C(9)-C(8)#1	-0.7(5)
Fe(1)-C(8)-C(9)-C(8)#1	-60.8(3)
C(7)-C(8)-C(9)-Fe(1)	60.1(2)
C(1)#1-C(1)-N(1)-C(4)	-14.2(7)
C(2)-C(1)-N(1)-C(4)	164.5(5)
Fe(1)-C(1)-N(1)-C(4)	68.8(7)
C(5)-C(4)-N(1)-C(1)	93.8(7)
C(8)#1-C(9)-Fe(1)-C(8)	117.3(5)
C(8)-C(9)-Fe(1)-C(8)#1	-117.3(5)
C(8)-C(9)-Fe(1)-C(7)	-37.3(3)
C(8)#1-C(9)-Fe(1)-C(7)	80.0(3)
C(8)-C(9)-Fe(1)-C(7)#1	-80.0(3)
C(8)#1-C(9)-Fe(1)-C(7)#1	37.3(3)
C(8)-C(9)-Fe(1)-C(3)	27.7(7)
C(8)#1-C(9)-Fe(1)-C(3)	145.0(4)
C(8)-C(9)-Fe(1)-C(3)#1	-145.0(4)
C(8)#1-C(9)-Fe(1)-C(3)#1	-27.7(7)
C(8)-C(9)-Fe(1)-C(2)	65.3(3)
C(8)#1-C(9)-Fe(1)-C(2)	-177.4(2)
C(8)-C(9)-Fe(1)-C(2)#1	177.4(2)
C(8)#1-C(9)-Fe(1)-C(2)#1	-65.3(3)
C(8)-C(9)-Fe(1)-C(1B)#1	141.0(3)
C(8)#1-C(9)-Fe(1)-C(1B)#1	-101.6(3)
C(8)-C(9)-Fe(1)-C(1)#1	141.0(3)
C(8)#1-C(9)-Fe(1)-C(1)#1	-101.6(3)
C(7)-C(8)-Fe(1)-C(9)	-119.0(4)
C(7)-C(8)-Fe(1)-C(8)#1	-80.1(3)
C(9)-C(8)-Fe(1)-C(8)#1	38.8(3)
C(9)-C(8)-Fe(1)-C(7)	119.0(4)
C(7)-C(8)-Fe(1)-C(7)#1	-36.7(3)
C(9)-C(8)-Fe(1)-C(7)#1	82.3(3)
C(7)-C(8)-Fe(1)-C(3)	71.7(3)
C(9)-C(8)-Fe(1)-C(3)	-169.3(2)
C(7)-C(8)-Fe(1)-C(3)#1	35.1(5)
C(9)-C(8)-Fe(1)-C(3)#1	154.1(3)
C(7)-C(8)-Fe(1)-C(2)	109.9(3)
C(9)-C(8)-Fe(1)-C(2)	-131.1(3)
C(7)-C(8)-Fe(1)-C(2)#1	-128.2(6)
C(9)-C(8)-Fe(1)-C(2)#1	-9.3(8)
C(7)-C(8)-Fe(1)-C(1B)#1	-175.3(2)
C(9)-C(8)-Fe(1)-C(1B)#1	-56.4(3)

C (7) -C (8) -Fe (1) -C (1) #1	-175.3 (2)
C (9) -C (8) -Fe (1) -C (1) #1	-56.4 (3)
C (7) #1-C (7) -Fe (1) -C (9)	-81.66 (9)
C (8) -C (7) -Fe (1) -C (9)	38.2 (3)
C (7) #1-C (7) -Fe (1) -C (8)	-119.8 (3)
C (7) #1-C (7) -Fe (1) -C (8) #1	-37.25 (18)
C (8) -C (7) -Fe (1) -C (8) #1	82.6 (4)
C (8) -C (7) -Fe (1) -C (7) #1	119.8 (3)
C (7) #1-C (7) -Fe (1) -C (3)	116.87 (13)
C (8) -C (7) -Fe (1) -C (3)	-123.3 (3)
C (7) #1-C (7) -Fe (1) -C (3) #1	76.96 (14)
C (8) -C (7) -Fe (1) -C (3) #1	-163.2 (3)
C (7) #1-C (7) -Fe (1) -C (2)	157.07 (14)
C (8) -C (7) -Fe (1) -C (2)	-83.1 (3)
C (7) #1-C (7) -Fe (1) -C (2) #1	41.1 (2)
C (8) -C (7) -Fe (1) -C (2) #1	160.9 (3)
C (7) #1-C (7) -Fe (1) -C (1B) #1	-93.5 (11)
C (8) -C (7) -Fe (1) -C (1B) #1	26.4 (13)
C (7) #1-C (7) -Fe (1) -C (1) #1	-93.5 (11)
C (8) -C (7) -Fe (1) -C (1) #1	26.4 (13)
C (2) -C (3) -Fe (1) -C (9)	50.9 (6)
C (3) #1-C (3) -Fe (1) -C (9)	-176.1 (5)
C (2) -C (3) -Fe (1) -C (8)	71.6 (3)
C (3) #1-C (3) -Fe (1) -C (8)	-155.39 (17)
C (2) -C (3) -Fe (1) -C (8) #1	174.1 (3)
C (3) #1-C (3) -Fe (1) -C (8) #1	-52.9 (3)
C (2) -C (3) -Fe (1) -C (7)	110.3 (2)
C (3) #1-C (3) -Fe (1) -C (7)	-116.69 (14)
C (2) -C (3) -Fe (1) -C (7) #1	149.7 (2)
C (3) #1-C (3) -Fe (1) -C (7) #1	-77.36 (15)
C (2) -C (3) -Fe (1) -C (3) #1	-132.98 (19)
C (3) #1-C (3) -Fe (1) -C (2)	132.98 (19)
C (2) -C (3) -Fe (1) -C (2) #1	-103.7 (3)
C (3) #1-C (3) -Fe (1) -C (2) #1	29.32 (12)
C (2) -C (3) -Fe (1) -C (1B) #1	-65.8 (2)
C (3) #1-C (3) -Fe (1) -C (1B) #1	67.20 (11)
C (2) -C (3) -Fe (1) -C (1) #1	-65.8 (2)
C (3) #1-C (3) -Fe (1) -C (1) #1	67.20 (11)
C (3) -C (2) -Fe (1) -C (9)	-160.8 (2)
C (1) -C (2) -Fe (1) -C (9)	66.0 (3)
C (3) -C (2) -Fe (1) -C (8)	-123.3 (2)
C (1) -C (2) -Fe (1) -C (8)	103.5 (2)
C (3) -C (2) -Fe (1) -C (8) #1	-168.3 (6)
C (1) -C (2) -Fe (1) -C (8) #1	58.5 (7)
C (3) -C (2) -Fe (1) -C (7)	-82.4 (2)
C (1) -C (2) -Fe (1) -C (7)	144.4 (2)
C (3) -C (2) -Fe (1) -C (7) #1	-55.5 (4)
C (1) -C (2) -Fe (1) -C (7) #1	171.3 (3)
C (1) -C (2) -Fe (1) -C (3)	-133.2 (3)
C (3) -C (2) -Fe (1) -C (3) #1	29.6 (2)
C (1) -C (2) -Fe (1) -C (3) #1	-103.6 (2)
C (3) -C (2) -Fe (1) -C (2) #1	68.0 (2)
C (1) -C (2) -Fe (1) -C (2) #1	-65.2 (2)
C (3) -C (2) -Fe (1) -C (1B) #1	105.3 (2)
C (1) -C (2) -Fe (1) -C (1B) #1	-27.88 (19)
C (3) -C (2) -Fe (1) -C (1) #1	105.3 (2)
C (1) -C (2) -Fe (1) -C (1) #1	-27.88 (19)

Symmetry transformations used to generate equivalent atoms:
#1 $x, -y+1/2, z$ #2 $x, -y+3/2, z$