# ADDIS ABABA UNIVERSITY
# SCHOOL OF GRADUATE STUDIES

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# ELECTROCHEMICAL POLYMERIZATION OF METAL CHELATES DERIVED FROM MULTIDENTATE THIOPHENES

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# ELECTROCHEMICAL POLYMERIZATION OF METAL CHELATES DERIVED FROM MULTIDENTATE THIOPHENES

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Sincerely Yours,

Prof. V.J.T. Raju Dr. Shimelis Admassie

______________ __________________

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# List of Abbreviations and Symbols

| | |
|---|---|
| Å | Angstrom |
| $^0$c | Degree centigrade |
| α | Alpha |
| β | Beta |
| I | Inductive effect |
| M | Mesomeric effect |
| $E^+$ | Electrophilic |
| DFT | Density Functional Theory |
| GPC | Gel permeation chromatography |
| $\overline{M_w}/\overline{M_n}$ | Average value of relative molecular masses |
| $M_n$ | Total relative mass |
| D-A-D | Donor-Acceptor-Donor |
| σ | Conductivity |
| e- | Electron |
| SEC | Standard calomel electrode |
| DDQ | 2,5-dichloro-3,6-dicyano-1,4-benzoqunione |
| ICP | Intrinsically conducting polymers |
| % | Percentage |
| m.pt | Melting point |
| gm | Gram |
| ml | Mililiter |
| mmole | Milimole |
| str | Stretching |
| vib | Vibration |
| C1 | [NiCl($H_2O$)$_3${3',4'-diamino-2,2':5',2"-terthiopene }] chloridehexahydrate |
| C2 | [Zn$Cl_2$($H_2O$)$_2${3',4'-diamino-2,2':5',2"-terthiopene }] dihydrate |
| C3 | [2Ni$Cl_2H_2O${3',4'-bis(2-iminomethylphenol)- 2,2':5',2"-terthiopene}] tetrahydrate |
| C4 | [Zn($NH_3$)$_2${3',4'-bis(2-iminomethylphenol)- 2,2':5',2"-terthiopene}] |

| | |
|---|---|
| L1 | 3',4'-Diamino-2,2':5',2"-terthiopene |
| L2 | 3',4'-bis(2-iminomethylphenol)- 2,2':5',2"-terthiopene |
| $Et_4NBF_4$ | Tetraethylammonium tetrafluoroborate |
| GCE | Glassy Carbon Electrode |
| IR | Infrared |
| UV-Vis | Ultraviolet-visible region |
| $^1$H NMR | Proton nuclear magnetic resonance |
| $^{13}$C {H}NMR | Cabon-13 nuclear magnetic resonance |
| S | Siemens |
| s | Singlet |
| d | Doublet |
| dd | Doublet of doublets |
| ppm | Parts per million |
| $\chi_g$ | Gram suceptibility |
| $\mu_{eff}$ | Effective magnetic moment |
| $\Lambda_m$ | Molar conductance |
| V | Voltage |
| CV | Cyclic voltammogram |
| mM | Milimolar |
| μ | Micro |
| M | Molar |
| mV/s | Milivoltpersecond |
| A | Amper |
| O | Oxidation |
| R | Reduction |
| Epa | Potential oxidation at anode |
| Epc | Potential reduction at cathode |
| Redox | Reduction Oxidation Reaction |
| HOMO | Highest occupied molecular orbital |
| LUMO | Lowest unoccupied molecular orbital |
| R | Regression constant |

# Abstract

The electrochemical polymerization and characterization studies were made for monomers: 3',4'-Diamino-2,2':5',2''-terthiopene (L1), 3',4'-bis(2-iminomethylphenol)-2,2':5',2''-terthiopene (L2), [NiCl($H_2O$)$_3${3',4'-diamino-2,2':5',2''-terthiopene }] chloride hexahydrate (C1), [Zn$Cl_2$($H_2O$)$_2${3',4'-diamino-2,2':5',2''-terthiopene }] dehydrate (C2), [2Ni$Cl_2H_2O$ {3',4'-bis(2-iminomethylphenol)-2,2':5',2''-terthiopene}]tetrahydrate (C3) and [Zn($NH_3$)$_2${3',4'-bis(2-iminomethylphenol)- 2,2':5',2''-terthiopene}] (C4) in $Et_4NBF_4/CH_3CN$ solution using glassy carbon and platinum as working electrodes, Ag/AgCl as reference electrode and platinum as counter electrode. When the potential was scanned between 0.0 and1.6 V for L1 and L2 as well as -0.3 to 1.1V for C1 and C2, they polymerize in $\alpha,\alpha''$-linked polyterthiophene systems except L2 which displays both phenylene and thienylene linkages. However, C3 and C4 do not polymerize between 0.0 and 1.6V. The polyterthiophene films prepared have further been cycled in $Et_4NBF_4/CH_3CN$ solution to check their electrochemical stability. Metal containing polymer films (C1 and C2) exhibit better cycling behavior than polymers of L1, and L2. Reduction of nickel from $Ni^{+2}$ to $Ni^{+1}$ was proposed during the first five cycles.

**Key words**: $Et_4NBF_4/CH_3CN$, $\alpha,\alpha''$-linked polyterthiophene, 3',4'-Diamino-2,2':5',2''-terthiopene(L1), 3',4'-bis(2-iminomethylphenol)- 2,2':5',2''-terthiopene(L2), [NiCl($H_2O$)$_3$ {3',4'-diamino-2,2':5',2''-terthiopene}] chloridehexahydrate(C1), [Zn$Cl_2$($H_2O$)$_2${3',4'diamino-2,2':5',2''-terthiopene }] dihydrate(C2), [2Ni$Cl_2H_2O${3',4'-bis(2-iminomethylphenol)-2,2':5',2''-terthiopene}] tetrahydrate(C3) and [Zn($NH_3$)$_2${3',4'-bis(2-iminomethylphenol)-2,2':5',2''-terthiopene}] (C4

## 1. Introduction

Polymers are as old as man himself - indeed very much older- since in one form or another they are a basic constituent of every kind of living matter, whether plant or animal. It is only in the present century, however, that as a result of a wide range of scientific studies their existence as a coherent group has come to be recognized and understood. Following the recognition and this understanding, the possibility has arisen of actually producing polymers by means of suitable chemical reactions[1].

Polymer was used first as a scientific term by J.J.Berzelius, the emillent Swedish chemist, in 1827[2]. The word polymers meaning literally many parts ( from the Greeck polus, many, and meros, parts, segments )[1], which are macromolecules built up by the linking together of large number of much smaller molecules. The small molecules that combine with each other to form polymers are termed monomers, and the reactions by which they combine are termed polymerizations[3].

### 1.1. Classification of Polymers

Polymers can be classified according to different criteria one is whether the material is natural, modified natural or synthetic in origin. Another is based on the chemical composition i.e organic, hybridic or organometallic and inorganic. Also they might be classified according to chains i.e. linear, branched, comblike, starlike, dendritic, cross-linked, and hyperbranched. Moreover, polymers are quite often classified based on different types of monomers they are prepared from i.e. homopolymer, alternating, statistic, block and graft-copolymers. For practical reasons it is useful to classify polymeric materials according to where and how they are employed. A common subdivision is that into structural polymers and functional polymers.

### 1.2. Properties of some Polymer types

Structural polymers are characterized by their good mechanical, thermal, and chemical properties. Hence they are primarily used as construction materials in addition to or in place of metals, ceramics, or wood in applications like plastics, fibers, films, elastomers, foams, paints and adhesives. Functional polymers, in contrast, have completely different property profiles, for example special electrical, optical, or biological properties. They can assume specific chemical or physical functions in devices for microelectronic, biomedical applications, analytics, synthesis, cosmetics, or hygiene[4].

Synthetic polymers are usually considered to be good insulators and the insulating properties of polymers are used in many applications of plastics, such as encapsulating of electrical materials and cases for batteries. On the other hand, natural polymers have existed in natural form since life began and those such as DNA, RNA, proteins and polysaccharides play crucial roles in plant and animal life[5-6].

Originally these synthetic products tended to be regarded as substitutes for existing natural polymers, such as rubber or silk, which were in short supply, but the more recent development of the polymer industry, dating roughly from the 1939-45 war, has led to the introduction of a vast range of entirely new compounds in the fields of plastics, rubbers and fibers, many of which have properties different from those of any existing natural materials[1].

## 1.3. Uses of Polymer

Polymers serve as the basis of life in the form of nucleic acids, proteins and polysaccharides. They permit replication, energy transformation, transmission of foods within plants and animals, acts as essential natural building materials… Polymers have served as the very building blocks of society-clays for jars, wood for fuel, hides for clothing, vegetation for food and shelter,…They are present in a variety of forms as fibers and cloths, paper, lumber, elastomers, plastics, coatings, adhesives, ceramics, enzymes, DNA, concretes, and are major ingredients in soils and plant life.

The basic concepts of polymer science apply equally to natural and synthetic polymers and to inorganic and organic polymers and as such are important in medicine, nutrition, engineering, biology, physics, mathematics, computers, environment, space, ecology, health, …[7].

### 1.4. Heterocyclic compounds

Heterocyclic compounds are organic compounds that contain a ring structure and atoms in addition to carbon, such as sulfur, oxygen or nitrogen, as part of the ring. They may be either simple aromatic rings or non-aromatic. Heterocyclic aromatics are not actually pure hydrocarbon but ring systems that have at least one atom in the ring that is other than carbon. Not all heterocyclic compounds are aromatic only those that follow the Hueckel conditions are aromatic[8].

### Five membered heterocyclic compounds

Five membered heteroaromatic are heterocyclic analogs of the cyclopentadienyl anions which is planar symmetrical pentagon with five $SP^2$ hybridized carbon atoms containing 6π electrons to form an aromatic sextet. Similarly, in the five membered heteroaromatics with one heteroatom, five $SP^2$ atoms sustain 6π electrons system. Each carbon atom contributes one electron, while heteroatom provides two electrons to the aromatic sextet[9].

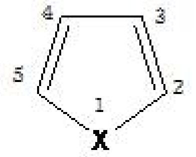


Figure-1: Structure of Five membered Heterocyclic compounds

X can be O, S, Se, Te and NH naming furan, thiophene, sclenophenes, tetrahydrotellurophene and pyrrole respectively. Molecular dimensions of these π-excessive heteroaromatic compounds are given in Table-1 and 2.

Table-1 Bond length data of some five membered heteroaromatics

| Bond length (Å) | | | | | | |
|---|---|---|---|---|---|---|
| X | $X\text{-}C_2$ | $C_2\text{-}C_3$ | $C_3\text{-}C_4$ | $C_2\text{-}H_2$ | $C_3\text{-}H_3$ | N-H |
| O | 1.362 | 1.361 | 1.431 | 1.075 | 1.077 | - |
| S | 1.714 | 1.370 | 1.423 | 1.080 | 1.080 | - |
| Se | 1.855 | 1.370 | 1.433 | 1.070 | 1.079 | - |
| Te | 2.055 | 1.375 | 1.423 | 1.078 | 1.081 | - |
| NH | 1.370 | 1.382 | 1.417 | 1.070 | 1.077 | 0.996 |

Table-2: Bond angles data of some five membered heteroaromatics [10].

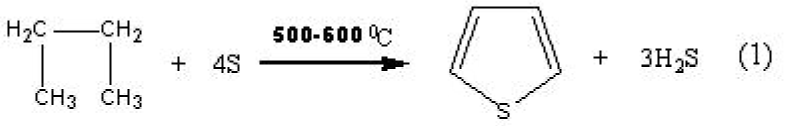
| Bond angles | | | | | |
|---|---|---|---|---|---|
| X | X-$C_2$-$C_3$ | $C_2$-$C_3$-$C_4$ | $C_5$-$X_1$-$C_2$ | $X_1$-$C_2$-H | $C_4$-$C_3$-H |
| O | 114$^{0}$41' | 106$^{0}$31' | 106$^{0}$33' | 115$^{0}$55' | 127$^{0}$57' |
| S | 111$^{0}$28' | 112$^{0}$27' | 92$^{0}$10' | 119$^{0}$51' | 124$^{0}$00' |
| Se | 111$^{0}$34' | 114 $^{0}$33' | 87$^{0}$46' | 121$^{0}$44' | 122$^{0}$52' |
| Te | 110$^{0}$81' | 117$^{0}$93' | 82$^{0}$53' | 124$^{0}$59' | 121$^{0}$04' |
| NH | 107$^{0}$42' | 107$^{0}$24' | 109$^{0}$48' | 121$^{0}$30' | 127$^{0}$06' |

### 1.5. Thiophene

Thiophene made its debut in the chemical literature with its discovery by Victor Meyer in 1882[11] as contaminant of coaltar benzene (commercial benzene). Thiophene is a π-excessive aromatic heterocycle and is uniquely aromatic among the five membered heterocycles. The presence of sulfur atom in thiophene has consequence particularly on the aromaticity which in turn considerably influences the properties and reaction of thiophene. The aromatic character of thiophene is retained even when it is substituted and fused with another aromatic ring.

#### 1.5.1. Synthesis from hydrocarbon

The cyclization of butane with sulfur at high temperature (500-600 $^{0}$C) provides thiophene (Scheme-1).



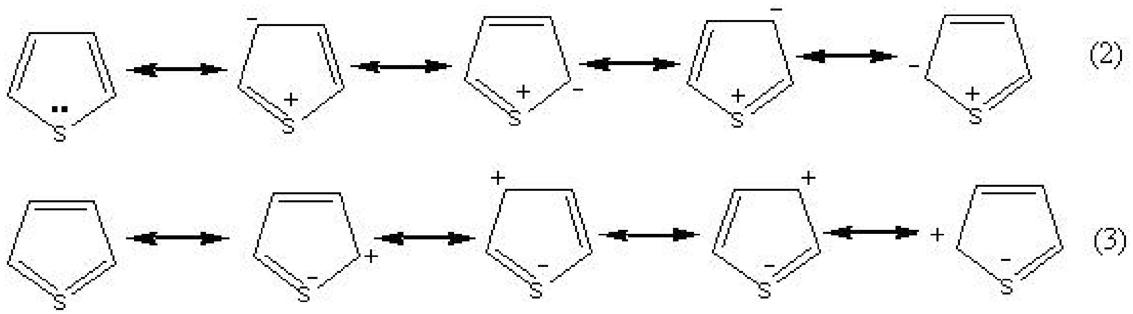
Scheme-1: Reaction of butane with sulfur to give thiophene

#### 1.5.2. Structure

Thiophene is a planar molecule with $sp^2$-hybridized ring atoms. Six π-electrons of the thiophene ring involved in an aromatic sextet are contributed by 4π-electrons from the 4 carbon atoms (one electron from each carbon atom) and two electrons by the sulfur atom.

The second lone pair on the sulfur atom occupies sp$^2$-hybridized orbital in the plane of σ-bond[11-12].

Thiophene is uniquely π-excessive aromatic heterocycle and has the highest resonance stabilization energy among the five membered heterocycles. The resonance stabilization of thiophene is attributed to the expansion of valence shell by using d-orbitals in hybridization. In the resonating structures (2), the sulfur atom uses p-orbitals and acts as an electron donor, while the resonating structures (3) involve d-orbital participation and in these structures sulfur acts as an electron acceptor[13].



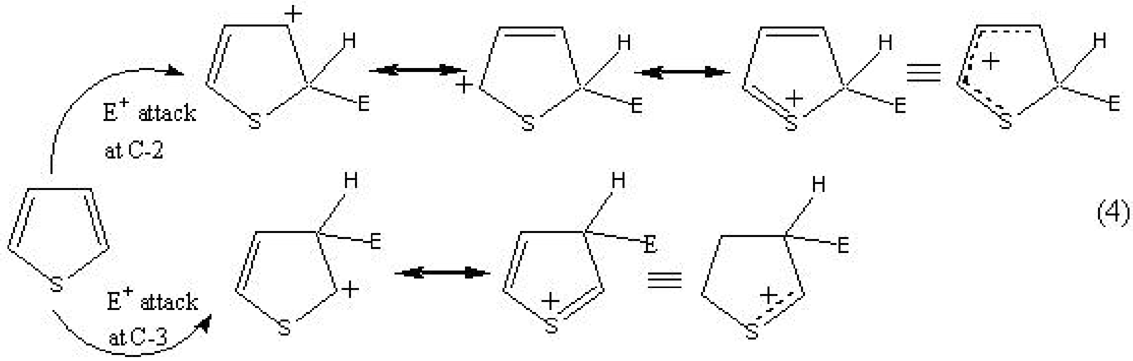
Scheme-2: Resonance structures of thiophene using 2) p-orbitals 3) d-orbitals

### 1.5.3. Reactions with Electrophiles

Thiophene is the least reactive towards electrophiles among the five membered aromatic heterocycles with the reactivity order: pyrrole > furan > thiophene. But it is more reactive than benzene by $10^3$-$10^5$ factors.

### 1.5.4. Orientation

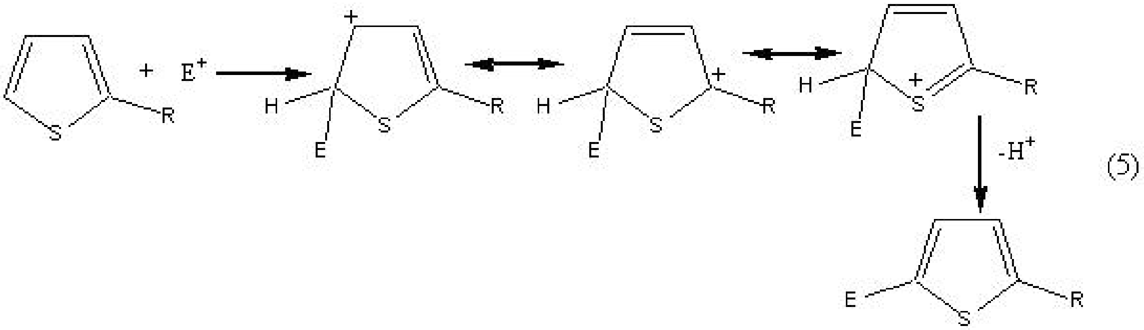
Thiophene undergoes electrophilic substitution reactions slowly and selectively at an α-position to sulfur rather than at the β-position. This is based on stability of transition state i.e the transition state resulting from the electrophilic attack at an α-position is stabilized over the transition state of β-electrophilic attack (three canonical structures for α-attack and two canonical structures for β-attack). The stability of transition state of α-electrophilic attack is attributed to an allylic stabilization and the electron donation from the sulfur atom, while in the transition state of β-electrophilic attack is due to electron releasing effect of sulfur only (Scheme-3)[14].



Scheme-3: Electrophilic substitution reactions of thiophene

### 1.5.5. Substituents at carbon-2

1. The presence of substituents (-R, -X, -OR, -NH$_2$, -NHR) with +I effect or –I (+M) effect at carbon-2 directs the electrophilic attack to the unsubstituted α-position (C-5) rather than to the β-position because these substituents are capable of stabilizing the adjacent positive charge by resonance or inductive effect (Scheme-4).

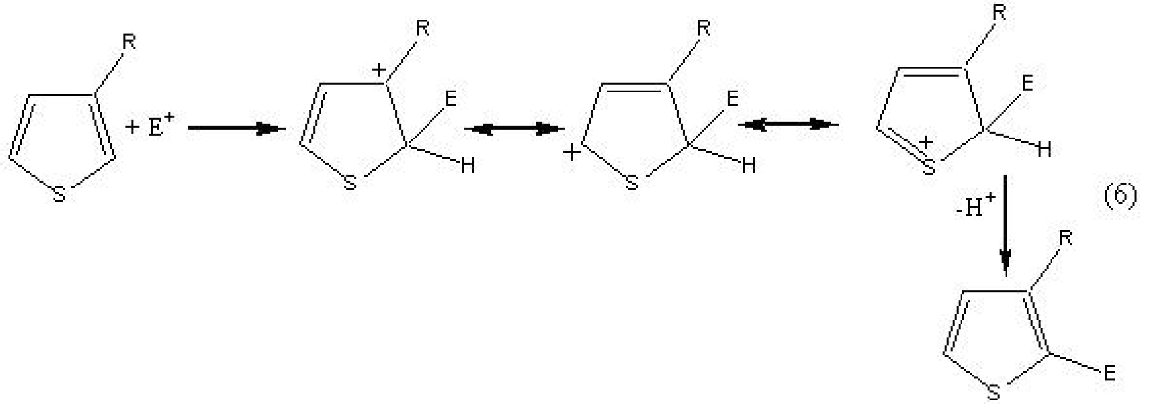


Scheme-4: Electrophilic attack at unsubstituted α-position of thiophene

2. However, the substituents with –I and –M effects (NO$_2$, -CN, -COR) destabilize the adjacent positive charge and cause the electrophilic substitution at the α-position ( C-5), but very slowly due to the balancing effect of α-directing or activating effect of the sulfur atom and the electron withdrawing effect of the substituent.

### 1.5.6. Substituents at carbon-3

1. The substituents with +I effect and –I (+M) effect (-R, -X, -OR, $-NH_2$, -NHR), which are capable of stabilizing the adjacent positive charge involving allylic carbonium ion, direct the electrophile to the adjacent position (C-2) (Scheme-5). But the substituents with considerable steric effect direct substitution to C-5.

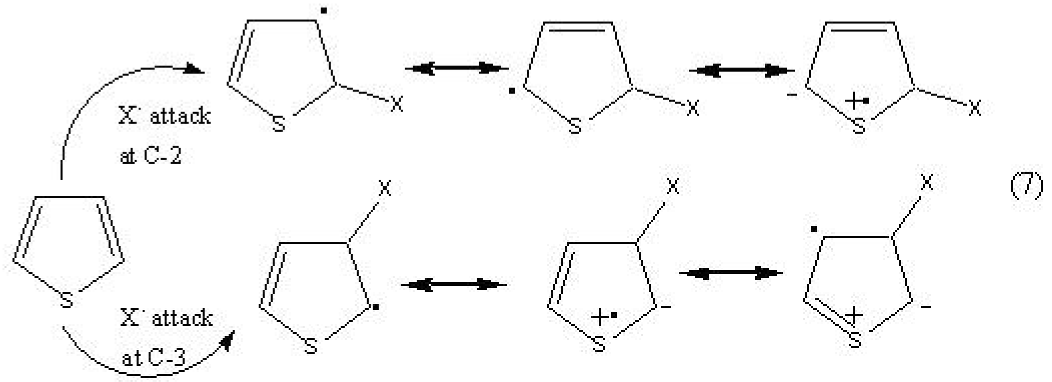


Scheme-5: Direct Electrophilic to the adjacent position of substituent at C-2

2. However, the electron withdrawing substituents with –I and –M effects ($-NO_2$, -CN, -COR, -COOR) at C-3 cause electrophilic substitution at C-5 because both the sffects are operating in the same direction.

### 1.5.7. Reactions with Free Radicals

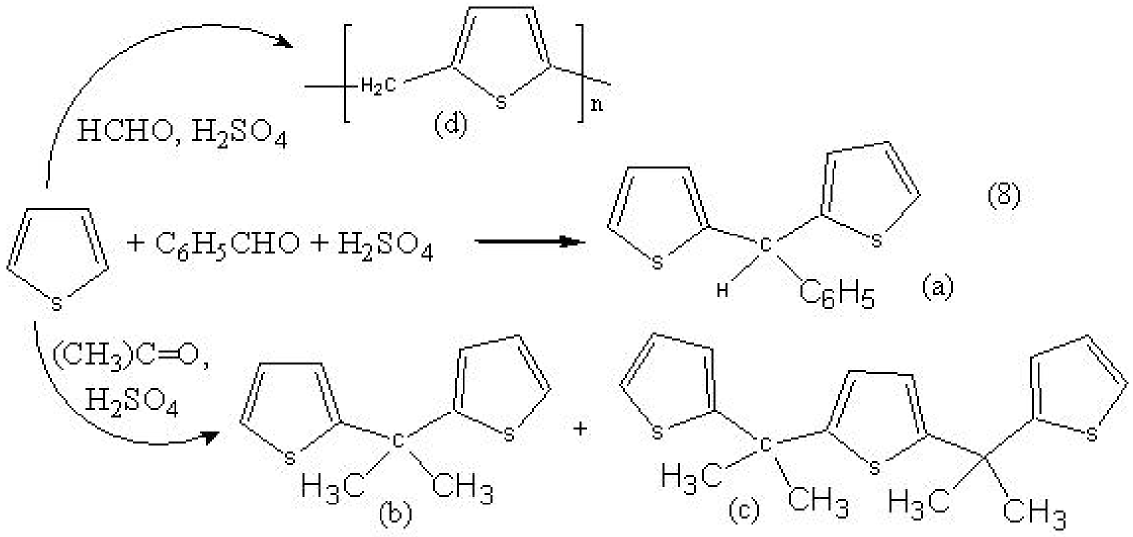
Thiophene undergoes free radical substitutions preferably at the position-2 because the transition state ( allylic free radical ) resulting from free radical attack at the position-2 is more stabilized than the transition state resulting from the attack at the position-3 (Scheme-6).



Scheme-6: Free radical substitutions of thiophene

### 1.5.8. Reaction with Aldehydes and Ketones

Acid catalyzed condensation of thiophene with benzaldehyde results in the formation of binuclear products (a) but with acetone in the ratio 2:1 and 3:1 gives the products (b) and (c) respectively. However, with formaldehyde polymeric product (d) is obtained. (reaction-8)[15].



Scheme-7: Reaction of thiophene with aldehydes and ketone.

### 1.6. Terthiophene

Based on Density Functional Theory (DFT) the bond length of neutral terthiophene molecule is given in Table-3.

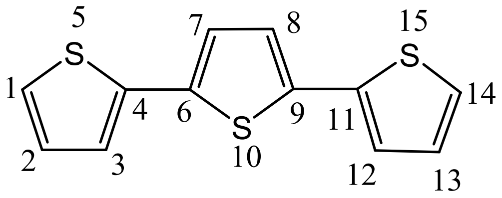


Figure-2: Structure of terthiophene

Table-3: Bond lengths of neutral terthiophene molecule[16].

| Bond length | DFT / 3-21G* | DFT / 6-31G* |
|---|---|---|
| C1C2 | 1.37010 | 1.3675 |
| C2C3 | 1.42723 | 1.4231 |
| C3C4 | 1.38147 | 1.3796 |
| C4S5 | 1.75635 | 1.7355 |
| S5C1 | 1.73423 | 1.7582 |
| C4C6 | 1.44400 | 1.44678 |
| C6C7 | 1.38171 | 1.37936 |
| C7C8 | 1.41877 | 1.41583 |
| C8C9 | 1.38171 | 1.37936 |
| C9S10 | 1.75531 | 1.75748 |

## 1.7. Literature Survey of polythiophene derivatives

Polythiophene derivatives have been synthesized by:

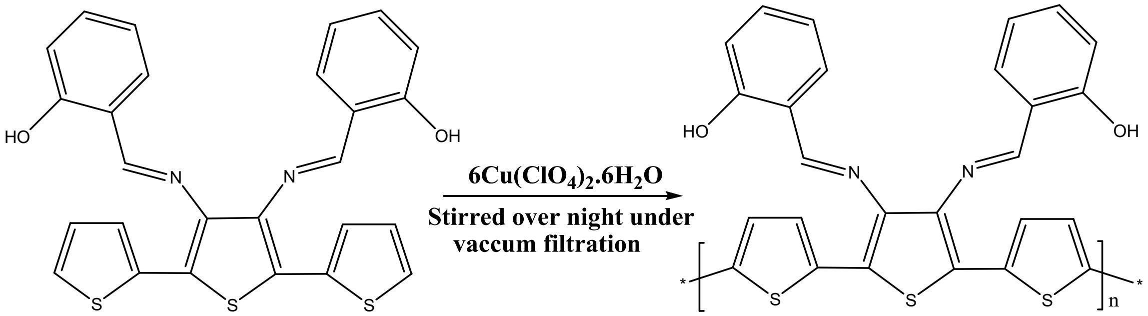
1. Chemical polymerization
2. Electrochemical polymerization as well as by,
3. Chemical coupling reactions (Copolymerization)[17-18].

### 1.7.1. Chemical synthesis

The chemical synthesis of polythiophene using a sulfuric acid catalyst has been known for more than 100 years. Polymerization can also be carried out using hydrogen fluoride, iron(III)chloride, aluminiumchloride, trifluoroacetic acid or Ziegler-type catalysts. However, these methods often lead to tetrahydrothiophene units being interspersed in the polythiophene chains. Grignard reactions, such as the coupling of 2, 5-dibromothiophene using a nickel catalyst, have provided an alternative chemical route to polythiophene[19].

### 1.7.1.1. Synthesis of poly-(3',4'-bis(2-iminomethylphenol)- 2,2':5',2''-terthiopene)

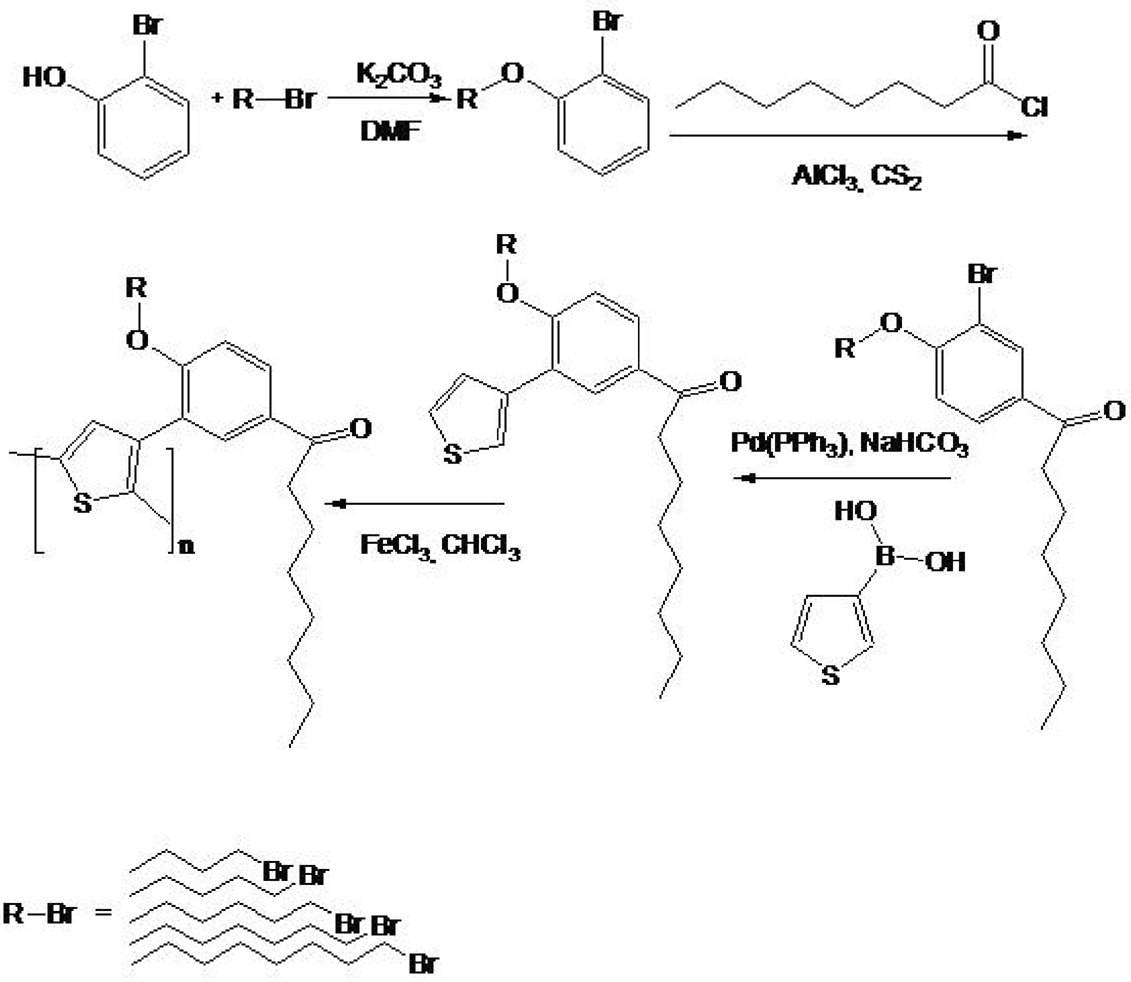
Synthesis of poly-(3',4'-bis(2-iminomethylphenol)- 2,2':5',2''-terthiopene) using chemical method was investigated in our laboratory (Scheme-8)[20].



Scheme-8: Synthesis of poly-(3',4'-bis(2-iminomethylphenol)- 2,2':5',2''-terthiopene)

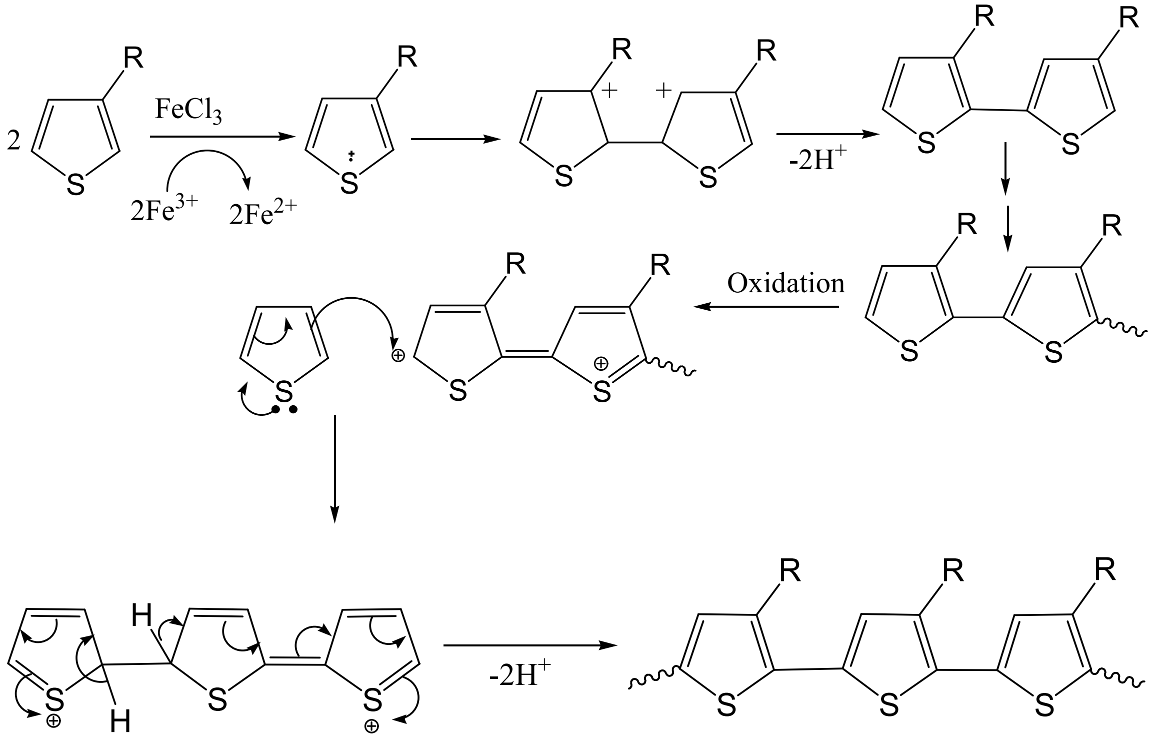
### 1.7.1.2. Synthesis of phenyl-substituted polythiophene containing both alkothy and octanoyl groups on the aromatic ring

Typical reaction sequences leading to the various groups of polythiophenes for example substituted polythiophene containing both alkothy and octanoyl groups on the aromatic ring is illustrated in Scheme-9. The solvatochromic and thermochromic behaviours were studied which exhibited blue-shifted absorption up on dissolution in chloroform. The solid films of the polymers showed significant blue-shifted as well as red shifted absorptions when heated. The addition of methanol to the chloroform solutions of the polymers caused dramatic chromic changes and developments of red shifted spectra for many of the polymer.



Scheme-9: Synthesis of phenyl-substituted polythiophene containing both alkothy and octanoyl groups on the aromatic ring[21].

The mechanism of propagation for regioselective polymerization by the ferric chloride method is believed to proceed as shown in Scheme-3. The propagation is believed to be initiated by a thiophene radical cation. But because polymer chain cannot be neutral under the strong oxidizing conditions, as soon as oligomers are formed, the propagation is formed by carbocation as in Scheme-10.



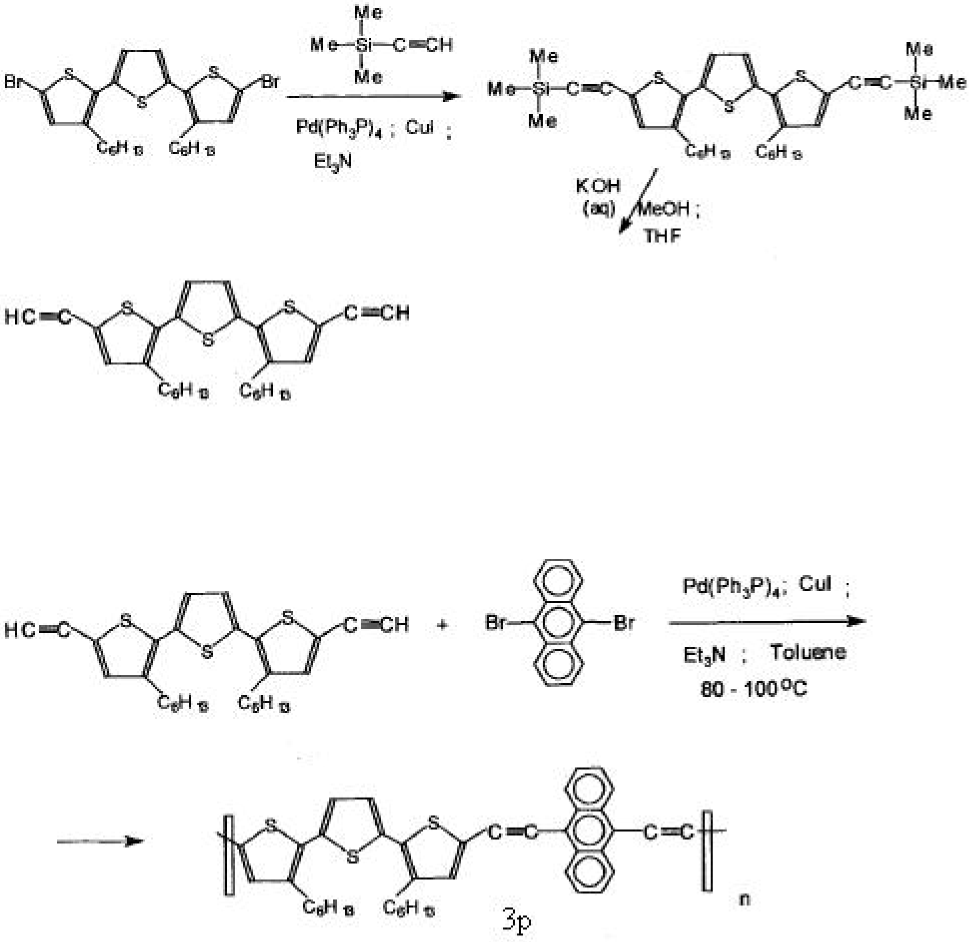
Schem-10: Polymerization mechanism of 3-substituted thiophene with $FeCl_3$ as oxidant[22].

### 1.7.2. Synthesis of some copolymers of thiophene derivatives

The preparation of the polymers was performed by a Heck coupling reaction, using a palladium complex as catalyst. The polymers synthesized by coupling of α , ω - dibromooligothiophenes with diethynyl derivatives of benzene, anthracene and dihexylsubstituted terthiophene, and of 9,10-dibromoanthracene with diethynyldihexylterthiophene. Inorder to synthesize regularly alternating sequences of acetylene, phenylacetylene, anthracene units and hexylsubstituted oligothiophenes with three and six thiophene rings. This is useful for investigation on the effect of the insertion of an anthracene moiety into thiophene-based polymers because of its luminescence properties. This are listed in Table-4.

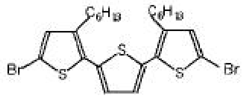
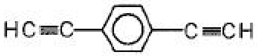
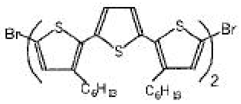
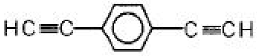
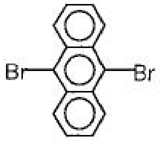
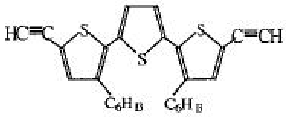
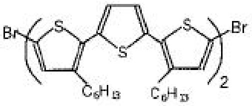
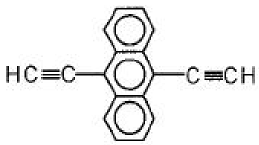
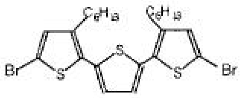
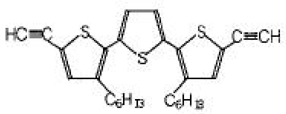
#### 1.7.2.1. Synthesis of Covalently-linked Linear Donor-Acceptor Copolymers Containing Porphyrins and Oligothiophenes

Typical polymerization conditions are presented in scheme 11 for polymer formation of 3p.



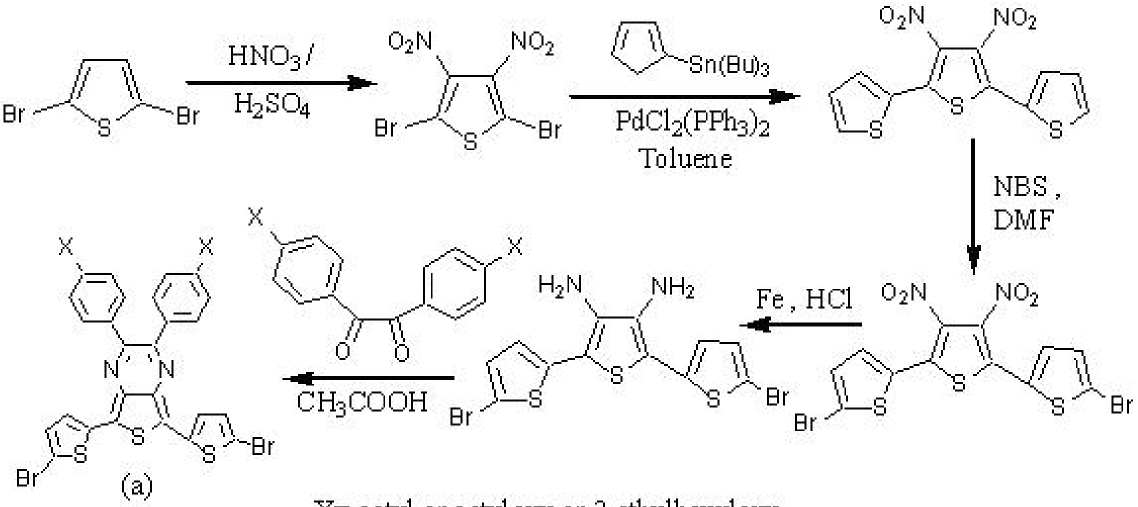
Scheme-11: Synthesis Covalently-linked Linear Donor-Acceptor Copolymers Containing Porphyrins and Oligothiophenes

Table-4 Copolymers obtained and GPC[23].

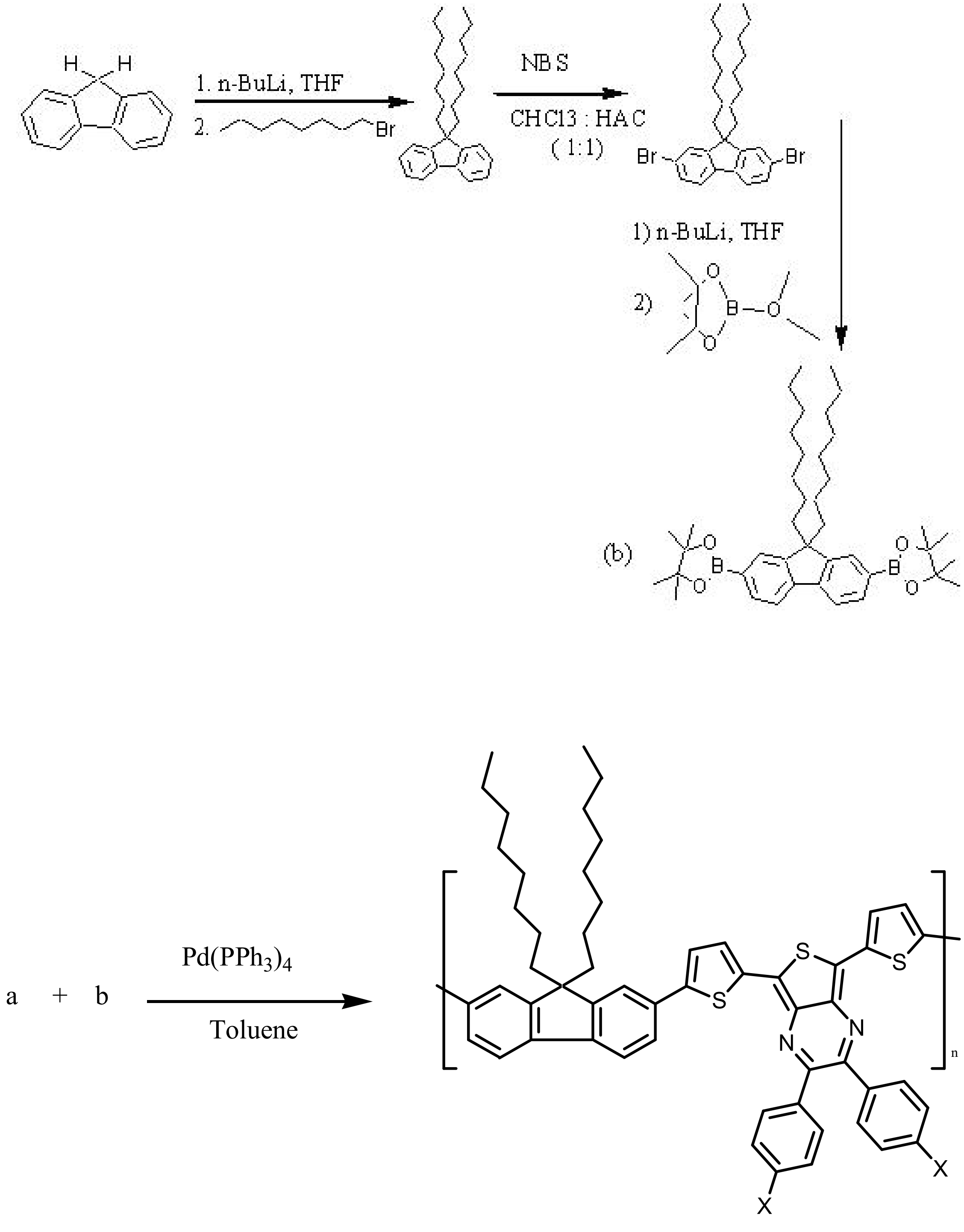
| No | Dibromide | Diethynyl compound | $\bar{M}_w/\bar{M}_n$ | $\frac{M_n}{\mathrm{g\cdot mol^{-1}}}$ |
|---|---|---|---|---|
| 1 |  |  | 2.8<br>5.6 | **a)** 7070<br>**b)** 5700 |
| 2 |  |  | 2.1 | 10400 |
| 3 |  |  | 4.5 | 3500 |
| 4 |  |  | 1.6<br>1.9 | 2000<br>**bis)** 2500 |
| 5 |  |  | 1.2 | 6040 |

### 1.7.2.2. Synthesis of alternating poly fluorine copolymers containing thienopyrazine units in the D-A-D segment

Synthesis of alternating poly fluorine copolymers containing thienopyrazine units in the D-A-D segment are summarized as (Scheme12).



X= octyl or octyloxy or 2-ethylhexyloxy



Scheme-12: Synthesis of alternating poly fluorine copolymers containing thienopyrazine units in the D-A-D segment[24].

## 1.8. Electrochemical Polymerization

Passage of current through a solution results in the loss of electrons, and compounds are oxidized at the anode. Electrons are gained and compounds reduced at the cathode. This process is referred to as electrochemical polymerization when polymer is formed[25]. Some of the most used techniques in electrochemical method are: Voltammetry, Amperometry, Potentiometry, Impedometry and Conductometry.

Voltammetry: refers to the measurement of current resulting from the application of potential. It utilizes three or two electrode electrochemical cell systems. The use of the three electrode (working, auxiliary, and reference) along with the potentiostat allows accurate application of potential functions and the measurement of the resultant current[26].

### 1.8.1. Preparation and Properties of Electrochemically Synthesized Polymers

Electrochemical synthesis is rapidly becoming the preferred general method for preparing electrically conducting polymers. The simplicity and reproducibility of this technique explain its growing popularity. The preparation of conducting polymers by electrochemical methods dates back at least 143 years to an experiment by Letheby which produced a form of polyaniline.

Two notable experiments in modern times have fueled the investigations of electrochemically synthesized conducting polymers by the scientific community. First, Dall'Olio et al. in 1968 produced conducting 'pyrrole black' ( $\sigma$ = 8Scm$^{-1}$ or $\Omega^{-1}$cm$^{-1}$) by the electrochemical oxidation of pyrrole in aqueous sulfuric acid. Secondly, Diaz et al. in 1979 ignited this field by synthesizing coherent, free-standing films of polypyrole with a high conductivity ($\sigma$ = 100 Scm$^{-1}$).

### 1.8.2. Polymerization Reaction

The reactions which produce conducting polymer films are electrochemically stoichiometric, since the polymerization and the subsequent oxidation of the polymer account for all the electrons transferred in the reaction. The electrochemical reactions which produce conducting polymers may be illustrated in hypothetical steps, given by equations 1-4:

$HMH \rightarrow HM^{+\cdot}H + e-$ …………………………………. (1)

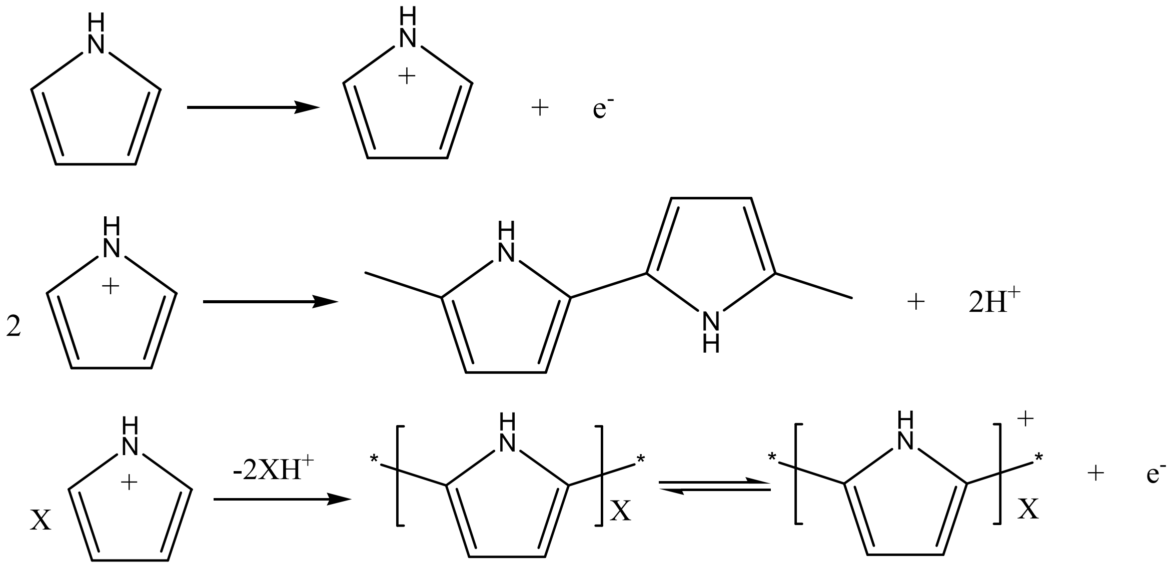
$2HM^{+\cdot}H \rightarrow HM^{+}HHM^{+}H \rightarrow HMMH + 2H^{+}$ …………. (2)

$xHMH \rightarrow HMxH + (2x-2)H^{+} + (2x-2)e-$ ……………. (3)

$HMxH \rightarrow H(Mx)^{+y}H + ye-$ ……………………………….. (4)

In the first step (eqn (1)), a monomer, M, is oxidized at the electrode surface, giving up an electron to form a radical cation, $M^{+\cdot}$. The second step (eqn (2)) involves the coupling of two radical cation to produce a dimmer, which then immediately splits off two protons. Step 1 and 2 repeat, continually increasing the length of the growing oligomer chain. The net reaction can be represented by eqn (3), in which x monomeric units, with x representing a large number, interact to form a polymer, HMxH, is oxidized, with the release of y electrons, to form the oxidized polymer $H(Mx)^{+y}H$. The degree of polymerization, x, is not known precisely.

The mechanism of electrochemically induced oxidative polythiophene polymerization appears to follow the general pathway outlined for polypyrole formation as (Scheme-13).



Scheme-13: An electrochemical polymerization for the formation of polypyrrole.

### 1.8.3. Electrodes

Standard electrochemical techniques which employ a divided cell containing a working electrode, a counter electrode and a reference electrode generally produce the best film. Electrodes should be chosen carefully so that they are not oxidized during the electrochemical oxidation process. For example, metals such as aluminum, indium, iron and silver are unsuitable anode materials for the polymerization of polypyrole (and polythiophene) since they will be oxidized (and dissolve) before polymerization occurs.

Metals which have been used successfully as anodes include chromium, gold, nickel, palladium, platinum and titanium. Platinum plate and glass coated with a conductive indium-tin oxide layer are the two most popular electrodes. The electrochemical reaction is limited basically only by the nature of the working electrode and by the nucleophilic character of the electrolyte.

### 1.8.4. Electrolytes

The choice of electrolyte is an important consideration for optimal film formation. It should be kept in mind that the electrochemical polymerization proceeds via radical cation intermediates which are generally very sensitive species, especially toward nucleophiles. Because of this, aprotic solvents, such as acetonitrile, which are poor nucleophiles, are often employed. Nucleophilic aprotic solvents, such as dimethylformamide, can only be used if protic acids are needed to decrease the nucleophilicity of the resulting electrolyte.

### 1.8.5. Physical properties

Since polythiophene and many of its substituted derivatives are insoluble in organic solvents, relative molar mass determinations are difficult. When the alkyl substituent was larger than or equal to a butyl group the polymers were soluble in common organic solvents such as tetrahydrofuran, toluene, methylene chloride, etc. Thiophene based polymers are generally stable in air up to 350$^{o}$c and up to higher temperatures in an inert atmosphere or under vacuum. They are very stable in concentrated acids, but undergo attack slowly in concentrated basic solutions[20].

## 1.9. Polymerization of transition-metal complexes

The largest classes of electropolymerizable monomers are those based on heterocyclic aromatic compounds, such as pyrrole and thiophene. Many transition-metal complexes of Conjugated organic polymers, such as polyacetylene, polythiophene, and polypyrrole, as well as oligomers and derivatives of these materials, have been extensively explored[27].

### Classification of metal complex polymer by kind

Metal-containing conducting polymers can be divided into four types, known as types I, II, III and IV.

### Macromolecular Metal Complexes

Type I: A metal ion, metal complex or metal is bound to a chain of a linear or cross-linked organic or inorganic macromolecules via a covalent (at the metal), a coordinative (at the metal), a complex (at the ligand of a complex), an ionic or a л-bond (so-called ‘‘Macromolecular Metal Complexes’’).

### Ligand Macromolecular Complexes

Type II: The ligand of a metal complex is part of a macromolecule chain or network (so called ‘‘Ligand Macromolecular Complexes’’).

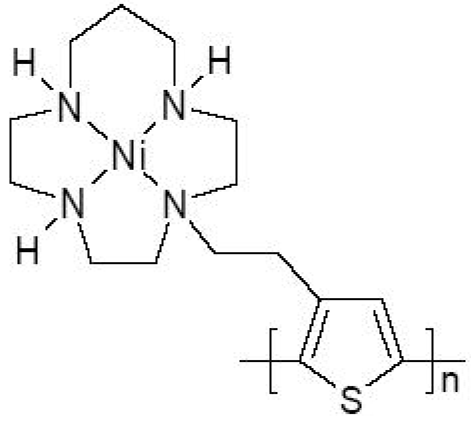
### Metal Macromolecular Complexes

Type III: Several examples of compounds exist in which the metal of a metal complex or another metal derivative is directly part of a macromolecular chain or network (so called ‘‘Metal Macromolecular Complexes’’). This type consist only metal atoms. But in most cases the metal is connected with another element such as C, N, O, S via a covalent, a coordinative, an ionic or a л-bond.

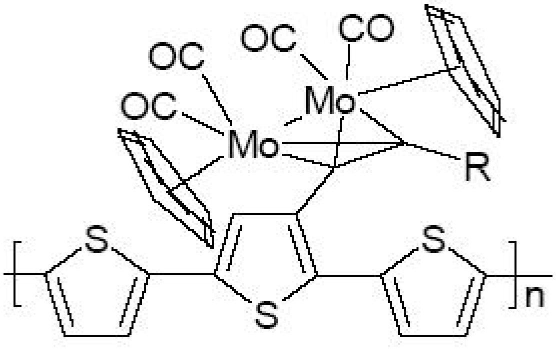
**Macromolecule Incorporated Metal Complexes and Metals**

Type IV: The physical incorporation of metal (and also semiconductor) clusters or metal complexes in macromolecules has become an important field (so called ‘‘Macromolecule Incorporated Metal Complexes and Metals’’).

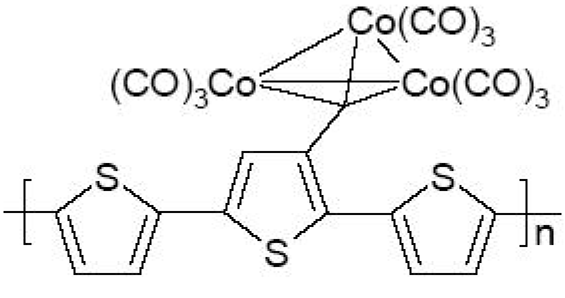
Some examples of Type-I are:



1



2 R=H or Ph



3

Figure-3: Structure of Macromolecule Incorporated Metal Complexes and Metals

Multicoloured electrochromism has been demonstrated with a copolymer of a thiophene bearing a tethered $Ni^{2+}$ cyclam and 3-methylthiophene synthesised electrochemically in acetonitrile. Polymers 2 and 3 were prepared electrochemically by[28-29].

Type II examples are listed in Table-5. A unique feature of this monomer architecture is that it possesses multiple polymerization sites that can be functionalized to selectively afford polymers comprised of phenylene or thienylene linkages or mixtures of the two.

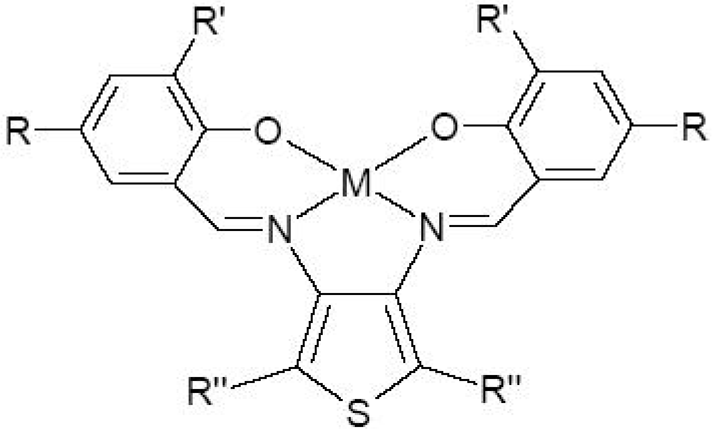
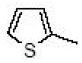
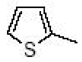
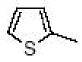
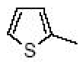
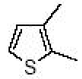
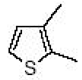


Figure-4: Structure of bis(salicylidene) – thiophene derivatives of metal complexes

Table-5: Electropolymerisation behavior of some Type II monomers

| M | R | R' | R'' | Polymerise | Linkage |
|---|---|---|---|---|---|
| - | H | H | H | No | - |
| Ni | H | H | H | Yes | Phenylene |
| Cu | H | H | H | Yes | Phenylene |
| Cu | $CH_3$ | H | H | No | - |
| Cu | H | H |  | Yes | Mixture |
| Cu | $CH_3$ | H |  | Yes | Thienylene |
| Co | $CH_3$ | H |  | Yes | Thienylene |
| Zn | $CH_3$ | H |  | Yes | Thienylene |
| Cu | $CH_3$ | $CH_3$ |  | Yes | Thienylene |
| Cu | H | H |  | Yes | Phenylene |
| Cu | $CH_3$ | H |  | No | - |

Type III: Another example of a chemically prepared conducting metallopolymer was the result of the reaction of tetrasodium tetrathiafulvalene tetrathiolate with metal halide to give the insoluble, amorphous polymer as shown in figure-5.

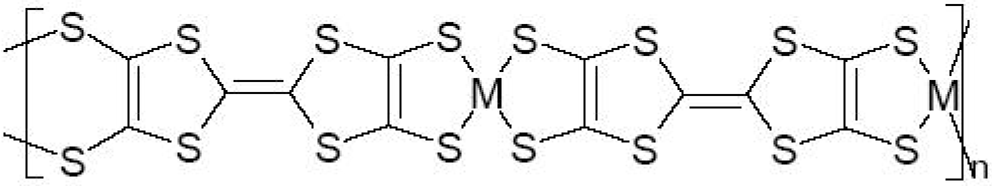


Figure-5: Tetrathiafulvalene tetrathiolate polymer of Cu(II), Fe(III), Pd(II)[32-33].

The incorporation of transition metal complexes into conjugated organic polymers offers a new dimension for the development of advanced electronic, catalytic, and sensing materials[34].

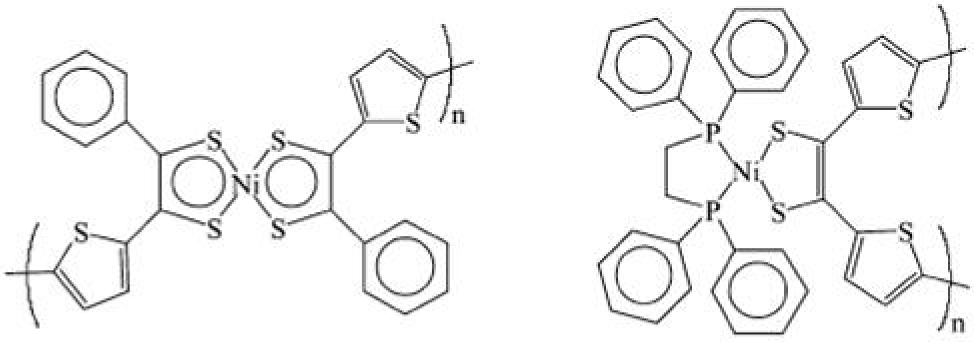
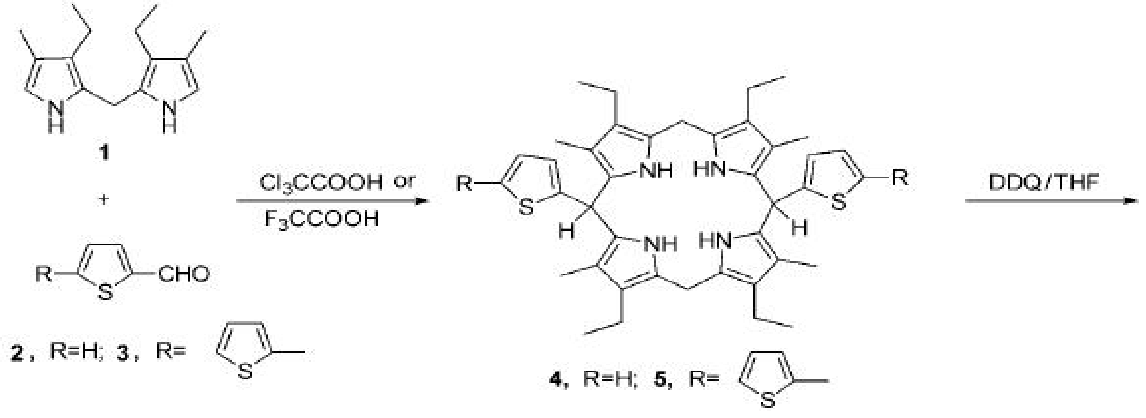


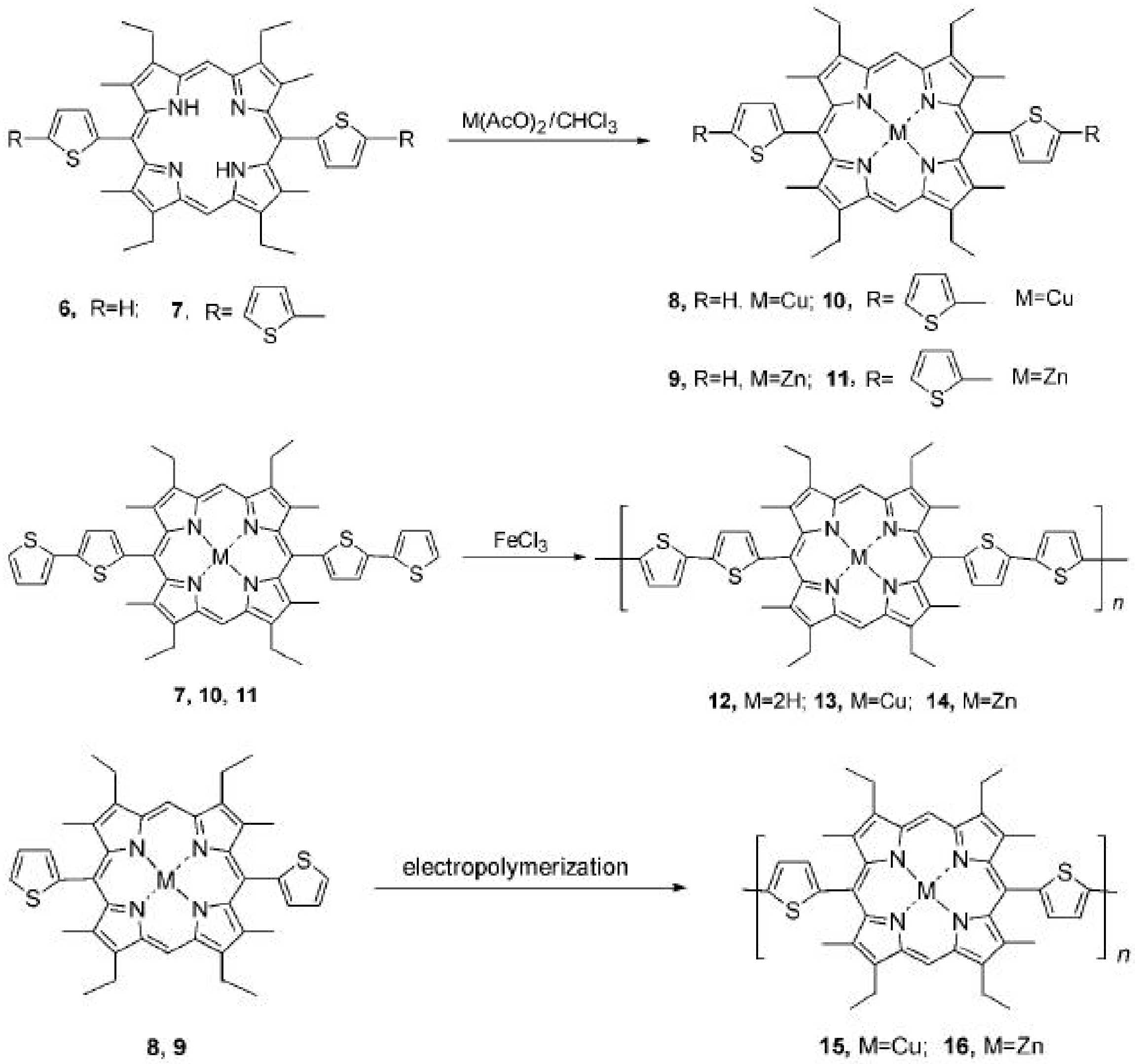
Figure-6: Structure of Ni-dithiolene complexes

### 1.10. Comparison of electrochemical and chemical methods of polymerization

The chemical method offers two advantages compared with electrochemical synthesis of polythiophenes; a greater selection of monomers, and using the proper catalyst the ability to synthesize perfectly regioregular substituted polythiophene.[23] The electrochemical polymerization of thiophene leads to an oxidized conducting form of polythiophene which is generally of higher quality and greater purity than that prepared chemically[26].

The thienylporphyrins (6, 8 and 9) could not be polymerized by chemical oxidation due to the effect of the steric hindrance. Compounds 8 and 9 were polymerized by the electrochemical oxidation (working electrode: gold-plate electrode; counter electrode: platinum; reference: standard calomel electrode (SEC); solvent: 0.1 mol•dm$^{-3}$ *n*-$Bu_4NClO_4$ in dry MeCN), whereas 6 could not be polymerized for its very low solubility in common organic solvents[34]. The copolymers of 12, 13 and 14 were synthesized by chemical polymerization using $FeCl_3$ as oxidant from corresponding monomers 7, 10 and 11 in high yields (90%)[34]. Their polymerization is shown in Scheme14.





Scheme-14: Poly(arylene ethynylene)s based on 3-Hexyl multisubstituted oligothiophene blocks

## 1.11. Application of polymers

In recent years, intrinsically conducting polymers (ICP) have become an important class of materials, mainly due to their electric properties and potential technological applications. Polythiophenes and their derivatives are among the most important and most studied ICP. The considerable attention directed toward polythiophenes is due to the combination of their electrical properties, environmental stability and, mainly, structural versatility. Another important feature is their low band gap, which makes them good materials for electrochromic devices. These characteristics and the outstanding chemical stability of the polythiophenes were key properties that lead to considerable research development regarding their uses in electrooptic, electroluminescent and electrochromic devices, photoswitches, light emitting devices, lasers, macromolecular electronic systems (diodes, transistors, etc.), and gas sensors.

In addition to their low cost and easy preparation, polythiophene and its derivatives have been used to develop new electrochromic devices. These devices are now applied in calculators, computers, car mirrors, clocks, intelligent and electrochromic windows and other equipment, which previously used liquid crystal displays. Electrochromism is a property of materials or systems that reversibly change color (optical absorption or reflection) in response to an applied external potential bias[32,35-37].

## 2. Objectives of the present investigation

Electrogenerated metallopolymers have received particular attention over recent years, with pyrrole, anilines, phenols, and thiophene derivatives as frequent monomers of choice. The oxidative electropolymerization of these to highly conducting polymers is well established. In order to achieve rapid electron transfer in a conducting polymer matrix to active sites at the electrode surface, suitable substituted metal complexes and their ligands, such as porphyrins, phthalocyanines, schiff-base complexes, etc., were employed as monomers for electropolymerization.

The field of conducting and electroactive polymers continues to expand with the initiation of new systems suitable for an ever-growing numerous of applications that include fuel cells, biosensors, electroanalysis, electrocatalysis, electrochromic displays, and others.

In view of the wide range of potential applications of terthiophene derivative documented in literature, the present investigation is aimed at electropolymerization and characterization of multidentate metal binding system-containing derivatives of terthiophene and their complexes such as:

- 3',4'-Diamino-2,2':5',2"-terthiopene,
- 3',4'-bis(2-iminomethylphenol)- 2,2':5',2"-terthiopene,
- [NiCl($H_2O$)$_3${3',4'-diamino-2,2':5',2"-terthiopene }] chloridehexahydrate,
- [$ZnCl_2$($H_2O$)$_2${3',4'-diamino-2,2':5',2"-terthiopene }] dihydrate,
- [2$NiCl_2H_2O${3',4'-bis(2-iminomethylphenol)- 2,2':5',2"-terthiopene}] tetrahydrate and
- [Zn($NH_3$)$_2${3',4'-bis(2-iminomethylphenol)- 2,2':5',2"-terthiopene}]

using cyclic voltammetry.

## 3. Experimental Part

### 3.1. Materials and Methods

#### 3.1.1. Chemicals

5mM of L1, L2, C1, C2, C3 and 2mM of C4 solution were prepared in 0.1M of $Et_4NBF_4$/ $CH_3CN$ solution. All solutions were prepared with once distilled analytical-reagent grade of acetonitiril. Sulphuric acid solution is used for examination the electrodes.

#### 3.1.2. Instruments

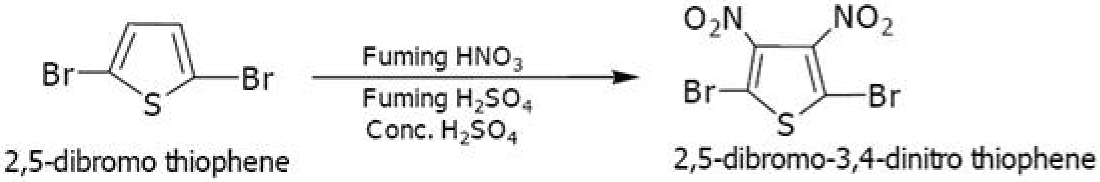
Voltammetric measurements were performed with a Bas CV-50W Voltammetric. The three electrode system consisted of glassy carbon electrode (GCE) and platinium electrode as working electrode, a platinium wire as counter electrode and a Ag/AgCl (in saturated KCl) electrode as reference electrode. The IR spectra of the ligands and complexes were obtained using KBr pellets (4000-400cm$^{-1}$) on Perkin-Elmer BTX FT-IR spectrophotometer.

### 3.2. Synthesis and Spectral Characteristics of monomers

Before recording the cyclic voltammogram of each ligand and complex the IR spectra were run. The run spectra (Appendix1-4) show superimposes with the previous IR spectra recorded. Moreover, the UV, $^1$H NMR, $^{13}$C NMR and other qualitative and quantitative recorded data clearly indicates the proposed structures were truthful. The data and procedures are reproduced and presented in this document as follow.

**3.2.1. Synthesis of 2, 5-dibromo-3, 4-dinitro thiophene** (Scheme15)

Concentrated $H_2SO_4$ (74.3 ml), fuming $H_2SO_4$ (114 ml) and fuming $HNO_3$ (63 ml) were combined in one liter round flask and cooled in an ice bath. 2, 5 dibromo thiophene (22.94 gm, 95 mmole) was added drop wise maintaining at temperature of 20-30 0C, the mixture was allowed to react for a total of 8 hrs and then poured over 515 gm of ice. Up on the melting of the ice, the solid residue was recovered by vaccum filtration, washed with distilled water and recrystalized via hot isopropyl alcohol to obtain a pure product (2). Yield 92.15%, m.pt 135.3 -136 (literature m.pt 135 -137 $^0$C)[20].

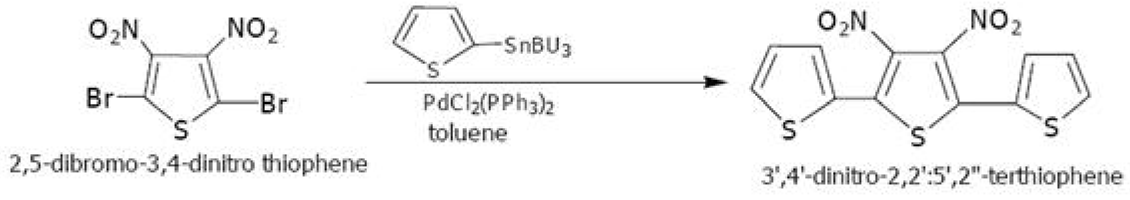


Scheme-15**:** Synthesis of 2, 5-dibromo-3, 4-dinitro thiophene

**3.2.2. Synthesis of 3', 4'-dinitro-2, 2':5', 2''-terthiophene Compound** (Scheme16)

To a solution of 2,5-dibromo-3,4-dinitro thiophene (20 gm, 60 mmole) and tributyl (thiophen -2-y1) stannane (38.2 ml) in toluene (200 ml) and $PdCl_2$ $(PPh_3)_2$ (0.844 gm, 1.2

mmole) was added. The mixture was refluxed for 12 hrs under nitrogen atmosphere and the solvent was removed over a rotavapour. The residue was separated using suction filtration to offer 17.48 gm of compound 3 and recrystalized using toluene-methanol solvent. Yield 85.85%, m.pt 143-143.6 $^{0}$C (literature m.pt 149 -151 $^{0}$C) [20].



Scheme-16**:** Synthesis of 3', 4'-dinitro-2, 2':5', 2"-terthiophene

### 3.2.3. Synthesis of 3',4'-Diamino-2,2':5',2''-terthiopene (L1)

Nitro compound (3) (3 gm, 8.9 mmole) was suspended in ethanol (31.26 ml) and concentrated HCl (62.49 ml). To the mixture a solution of anhydrous $SnCl_2$ (163 mmole, 31 gm) in ethanol (62.49 ml) was added. The mixture was stirred at 300C for 24 hr and poured in to a cold 25% NaOH (250 ml). Toluene (200 ml) was added to the above mixture, and then the reaction mixture was shaken vigorously and filtered through celite. The phases were separated and the aqueous layer was extracted with toluene. The combined organic layer was washed with brine and dried over $Na_2SO_4$. The solvent was removed under reduced pressure to offer compound (4) as yellowish brown solid. Yield 90.8%, m.pt 98.4 - 99.7 $^{0}$C (literature m.pt 96 – 96.5 $^{0}$C) [20].

### 3.2.4. Synthesis of the metal complexes (C1 and C2)

Ni (II) (1.71g, 7.2 mmol), Zn (II) (0.98 g, 7.2 mmol) were separately dissolved in 30 ml methanol. (1g, 3.6 mmol) of the ligand was also dissolved in 30 ml dichloromethane and this was added drop wise in to each of the metal salt solutions with continuous stirring at room temperature and refluxed for 16 and 30 hours for Ni (II) and Zn (II), respectively. Finally the mixture was cooled, the solid filtered, washed with methanol followed by dichloromethane and dried to afford (1.3 g, 2.28 mmol) of Ni-L (63 %) and (1.17 g, 2.4 mmol) of Zn-L (67 %).

### 3.2.5. Synthesis of 3',4'-bis(2-iminomethylphenol)- 2,2':5',2''-terthiopene(L2)

An attempt to prepare the ligand was done with the procedure as follows. Compound 4 (3 gm, 11 mmole) and salicylaldehyde (2.633 gm, 23.9 mmole) dissolved in acetic acid (155ml) were heated at $60^0$C for 8hr. The mixture was then cooled to room temperature and the precipitate was collected by filtration, washed with water and methanol and dried to yield a brownish yellow solid which is further purified by silica gel column chromatography using petroleum sprite: ethylacetate (9:1) as eluent to form the ligand. This compound will be referred to as ligand (L) throughout this paper. Yield **61.8**%. M.pt.,198-199 $^0$C.

### 3.2.6. Synthesis of the metal complex (C3)

(0.2 gm, 0.84 mmole) nickel chloride hexahydrate ($NiCl_2.6H_2O$) was dissolved in methanol (20 ml). To the mixture a solution of the ligand (0.2 gm, 412 mmole) in dichloromethane (20 ml) was added. The mixture was refluxed for 2 hr. Then aqueous ammonia diluted with methanol (1:19) was added to the mixture until the pH is 6 and then the mixture was refluxed for 14 hr. The precipitate was filtered, washed with methanol and finally dichloromethane and dried in vacuum Yield, 68%. M.pt., Stable up to 350 $^0$C.

### 3.2.7. Synthesis of the metal complex (C4)

Anhydrous zinc chloride ($ZnCl_2$) (.112 gm, .82 mmole) was dissolved in methanol (10ml). To the mixture a solution of the ligand (0.2 gm, .412 mmole) in dichloromethane (20ml) was added. The mixture was refluxed for 2 hr. Then aqueous ammonia diluted with methanol (1:19) was added to the mixture until the pH is 7-7.5 and then the mixture was refluxed for 6 hr. The precipitate was filtered, washed with methanol and dichloro methane and finally dried in vacuum. Yield, 70%. Decomposes at 254 $^0$C.

### 3.2.8. IR Specta of L1, C1, C2, C3 and C4 (data in $cm^{-1}$)

### 3.2.8.1. IR Spectrum of L1

In general, mono, di, tri and tetra substituted thiophenes all have bands in the region 530-450 due to the out-of-plane ring deformation. So the variable weak bands observed in this spectrum are because of this. Thiophenes have a band near 675 due to the C-S streaching vibrations. This band is usually of medium intensity in the infrared so the peak observed at 689 is due to this nature. The broad symmetrical doublet of weak intensity at 3297 ( one of the doublet) is due to it exist in condensed phase, for example, as liquid, $\alpha$-saturated primary amines always occur from 3200-3160 w-m intensities.

For aromatic and unsaturated amines = C-N, two bands are observed at 1360-1250 and 1280-1180 due to conjugation of the electron pair of the nitrogen with the ring imparting double bond character to the C-N bond, primary and secondary aromatic amines absorbing strongly in the first region. This band is observed at 1354 and 1214 respectively. Weak bands at ~1220, 1074 and 1039 are assigned due to the stretching mode of the C-C interring bond. Generally selected peaks of L1 are given in Table-6.

Table-6: IR Spectral data of L1

| Functional group | Stretching , cm$^{-1}$ | Found | Comment |
|---|---|---|---|
| Thiophene | 3120-3000m | 3095 | =C-H str. |
| | 1585-1480v | **4-peaks** | C=C in-plane vib. |
| | 530-450v | **w-peaks** | Ring def. |
| 2-monosubstituted thiophenes | 1540—1490v | **3-peaks** | C=C in-plane vib. |
| | 1455-1430m-s | 1445 | C=C in-plane vib. |
| 2-monosubstituted thiophenes | 1540—1490v | **3-peaks** | C=C in-plane vib. |
| | 935-880w | **unsigned** | C-S asym str. |

| | | | |
|---|---|---|---|
| | 850-825w | **unsigned** | C-S sym str. |
| 3,4-disubstituted thiophene | 860-835m | 842 | Out-of-plne C-H def. vib. |
| | 780-775m | 790 | Out-of-plne C-H def. vib. |
| Tetrahydrothiophenes | ~685m | 689 | C-S str |
| 1°-aromatic amines | 3520-3420m | 3441 | asym $NH_2$ str. |
| | 3420-3340m | 3374 | sym $NH_2$ str. |
| | 1360-1250s-m | 1354 | Car-N |
| | 1280-1180m | 1214 | $C_R$-N |

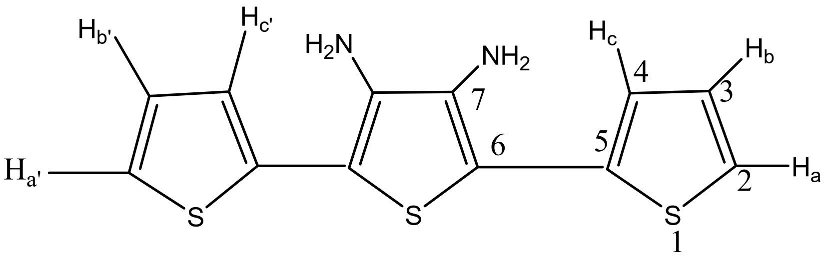


Figure-7: structure of 3',4'-Diamino-2,2':5',2''-terthiopene

### 3.2.8.2. IR Spectra of C1 and C2

It was found that the characteristic band both the symmetric and asymmetric of the primary aromatic amines group in the free ligand ( at 3441 and 3374 ) was shifted to lower frequency to 3284 and 3215 respectively in the C1 complex and this is also true for the C2 complex as the shift goes to ~3300 and 3213. This shift indicates the coordination of the amine nitrogen to the metals in the complex. This is further confirmed by an increase in the IR rocking frequency of $-NH_2$ from 973 to 992 and 1031 for C1 and C2 complexes respectively. Peaks at 546 and 545 of C1 and C2 complexes respectively is due to $M^{2+}OH_2$ stretch which is normally observed in a range of 580-530[20]. The comparison of major IR spectra peaks of L1, C1 and C2 is given in Table-7.

Table-7: Comparative IR spectral data of L1, C1 and C2

| Type of | νN-H | ν =C-H | νC-N | νC-S | $\rho_r$ $NH_2$ | νM-N | ν O-H | $\rho_r$ $H_2O$ |
|---|---|---|---|---|---|---|---|---|

| Abs. | (cm $^{-1}$) | (cm $^{-1}$) | (cm $^{-1}$) | (cm $^{-1}$) | (cm $^{-1}$) | (cm $^{-1}$) | (cm $^{-1}$) | (cm $^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| L1 | 3296-3440 | 3060-3095 | 1354 | 842 | 973 | - | - | - |
| C1 | 3215-3284 | 3059-3094 | 1226 | 847 | 992 | 585 | 3567 | 500-1000 |
| C2 | 3212-3284 | 3103 | 1227 | 848 | 1031 | 587 | 3500 | 500-1000 |

### 3.2.8.3. IR Spectra of L2, C3 and C4

The IR spectra of the complexes were compared with those of the free ligands inorder to determine the coordination sites that may be involved in chelation. Upon comparison, it was observed that the ν(C=N) stretching vibration found in the free ligand at 1611, was shifted to lower wave numbers (1604 & 1606) in the complexes, indicating the participation of imine nitrogen (M-N) in coordination. The medium intensity band at 845 observed in the free ligand assigned to ν(C-S-C) ring stretching vibration was shifted to lower values by 6 for Ni(II) complex but not in Zn(II) complex(1), which indicates the involvement of the thiophene sulfur atom in the bonding with the nickel ion.

The changes regarding νOH of the ligand could not be pinpointed due to the presence of $H_2O$ molecules in Ni(II) complex and $NH_3$ molecules in Zn(II) complex as revealed by the analytical data. However, their presence in complexes is confirmed by characteristic bands in the lower frequency regions and based on analytical and conductance data, it is already concluded that the ligand deprotonates its phenolic groups while complexing with Zn(II) and does not do so towards Ni(II). However, the involvement of phenolic oxygen in metal binding in both the complexes is simply evidenced by the changes in $\nu_{C-O}$ bands. The Phenolic C-O streching vibrations appeared at 1275 in the free ligand, which undergo a shift towards lower frequencies (1147 & 1243) in both complexes. This shift confirms the participation of oxygen in the formation of C-O-M bond.

The presence of coordinated water in Ni-L complex was suggested by very broad absorption centered around 3430 in the infrared spectrum. Bands at 755 and 645 may be attributed to rocking and wagging modes of the coordinated water. Based on geometrical consideration two water molecules are assumed to be in coordination sphere while the remaining is in lattice sites. In the spectrum of Zn-L complex, the sharp band at 3330, together with new bands at 3220, 1145 and 645 (due to symmetric stretching, deformation and rocking of $NH_3$ respectively) indicates the presence of coordinated ammonia. Appearance of new or non-ligand bands in the spectra of complexes in the region 420- 500 was attributed to ν(M-O) and the peaks in the region 500-669 was attributed to ν(MN). Therefore from the IR data, it can be concluded that the ligand **(L2)** behaves as a neutral bis-ONS donor towards Ni(II) and dibasic ONNO donor towards Zn(II). The comparison of major IR spectra peaks of L2, C3 and C4 is given in Table-8.

Table-8: Comparative IR spectral data of L2, C3 and C4

| Compound | ν(O-H) | νa ($NH_3$) | ν(C=N) | ν(C-O) | ν(C-S-C) | New bands |
|---|---|---|---|---|---|---|
| L2 | 3448b | - | 1611s | 1275m | 845w | - |
| C3 | 3430b | - | 1604s | 1266s | 852w | 668-535<br>467-450 |
| C4 | - | 3330s | 1606s | 1243s | 846w | 666-500<br>500-420 |

### 3.2.9. NMR Spectra of L1, L2 and C2

### 3.2.9.1. $^1$H NMR, $^{13}$C {H}NMR and DEPT of L1

Table-9: $^1$H NMR, $^{13}$C NMR and DEPT data of L1

| $^1$H NMR | | $^{13}$C {H}NMR (δ in ppm) ($CDCl_3$) | DEPT (δ in ppm) ($CDCl_3$) |
|---|---|---|---|
| Types of proton | (δ in ppm) ($CDCl_3$) | | |
| $NH_2$ | 3.80 (S,4H ) | 110.14 (C-5) | 123.93 ( C-3) |

| | | | |
|---|---|---|---|
| $H_b$ and $H_c$ | 7.0-7.1(complex spectra ,4 H ) | 123.93 (C-3)<br>124.01 (C-4)<br>127.78 (C-2)<br>133.61 (C-7)<br>135.96 (C-6) | 124.01 (C-4 )<br>127.78 ( C- 2) |
| $H_a$ | 7.29 (dd, 2H ) | | |

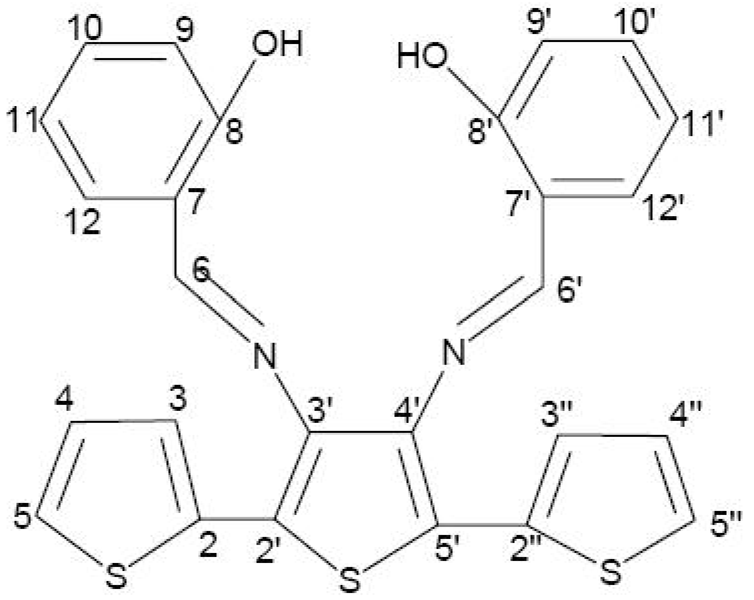


Figure-8: Structure of 3’,4’-bis(2-iminomethylphenol)- 2,2':5',2''-terthiopene

### 3.2.9.2. $^1$H NMR spectral data of L2

Table-10: $^1$H NMR spectral data of L2

| Type of proton | No. of protons | δ (ppm) | Appearance |
|---|---|---|---|
| $H_{8,8'}$ | 2 | 12.5 | broad singlet |
| $H_{6,6'}$ | 2 | 8.5 | Singlet |
| $H_{4,4''}$ | 2 | 7.3 | doubled of doublet |
| $H_{5,5''}$ | 2 | 7.27 | Doublet |

| | | | |
|---|---|---|---|
| $H_{9,9'}$ | 2 | 7.23 | Doublet |
| $H_{3'',3}$ | 2 | 7.16 | Doublet |
| $H_{10,10'}$ | 2 | 7.02 | doublet of doublet |
| $H_{12,12'}$ | 2 | 6.98 | Doublet |
| $H_{11,11'}$ | 2 | 6.85 | doublet of doublet |

### 3.2.9.3. $^{13}$C NMR and DEPT spectral data of L2 (δ in ppm)

Table-11: $^{13}$C {H}NMR and DEPT spectral data of L2

| Type of carbon | No. of carbon | $^{13}$C data | DEPT data | Remarks |
|---|---|---|---|---|
| $H_{6,6'}$ | 2 | 169.12 | 169.11 | C-H |
| $H_{8,8'}$ | 2 | 160.92 | - | Quaternary |
| $H_{3',4'}$ | 2 | 137.44 | - | Quaternary |
| $C_{2',5'}$ | 2 | 134.18 | - | Quaternary |
| $C_{5',5''}$ | 2 | 133.9 | 133.9 | C-H |
| $C_{9,9'}$ | 2 | 132.9 | 132.9 | C-H |
| $C_{4,4''}$ | 2 | 127.45 | 127.45 | C-H |
| $C_{3,3''}$ | 2 | 126.51 | 126.51 | C-H |
| $C_{10,10'}$ | 2 | 125.57 | 125.57 | C-H |
| $C_{2,2''}$ | 2 | 122.75 | - | Quaternary |
| $C_{12,12'}$ | 2 | 119.4 | 119.4 | C-H |
| $C_{7,7'}$ | 2 | 118.75 | - | Quaternary |
| $C_{11,11'}$ | 2 | 117.34 | 117.34 | C-H |

### 3.2.9.4. $^{1}$H NMR, $^{13}$C {H}NMR and DEPT of C2

The presence of –$NH_2$ group was confirmed by the addition of $D_2O$ to the solution. The $D_2O$ exchanges with the labile protons like –$NH_2$ to convert in to $ND_2$. Table-12 clearly indicates the $^{1}$H NMR, $^{13}$C NMR and DEPT characteristics of C2.

Table-12: $^{1}$H NMR, $^{13}$C NMR and DEPT data of C2

| $^{1}$H NMR | | $^{13}$C {H}NMR (δ in ppm) ($CDCl_3$) | DEPT (δ in ppm) ($CDCl_3$) |
|---|---|---|---|
| $NH_2$ | 5.0 (d, 4 H ) | 104.40 (C-5) | 122.74 (C-3) |

| | | | |
|---|---|---|---|
| $H_b$ | 7.10 (dd, 2H ) | 122.74 (C-3) | 123.43 (C-4) |
| $H_c$ | 7.17 (dd,2H ) | 123.43 (C-4) | 128.46 (C-2) |
| $H_a$ | 7.40 (dd,2H ) | 128.45 (C-2)<br>135.18 (C-7)<br>137.29 (C-6) | |

### 3.2.10. Uv-vis of L1, L2, C1, C2, C3 and C4

Table-13: Uv-vis of L1, L2, C1, C2, C3 and C4

| Compound | Band position, $\lambda_{max}$ (cm$^{-1}$) | Assignment of Transition |
|---|---|---|
| L2 | 42,373 & 35,971 | $\pi\rightarrow\pi^*$ |
| | 28,818 | $n\rightarrow\pi^*$ |
| C3 | 43,103, 37,313 & 27,933 | Intraligand |
| | 16,234 | $^3A_{2g}\rightarrow {}^3T_{2g}$ |
| | 19,455 | $^3A_2g \rightarrow {}^3T_1g$ (P) |
| | 22,936 | $^3A_2g \rightarrow {}^3T_2g$ (F) |
| C4 | 38,911& 33,113 | Intraligand |
| | 24,390 | LMCT |
| L1 | 40,000 & 28,689 | $\pi\rightarrow\pi^*$ & $n\rightarrow\pi^*$ respectively |
| C1 | 38,510 & 26,737 | $\pi\rightarrow\pi^*$ & $n\rightarrow\pi^*$ respectively |
| C2 | 39,370 & 26,737 | $\pi\rightarrow\pi^*$ & $n\rightarrow\pi^*$ respectively |

The electronic spectra of L1, C1, and C2 were recorded in dichloromethane at room temperature. These spectra clearly show bathochromic shift in $n\rightarrow\pi^*$ transition of $NH_2$ chromophore, imply evidencing the participation of this group in coordination. d-d transition of C1 is not observed due to poor solubility

### 3.2.11. Magnetic Susceptibility of C1, C3 and C4

Table-14**:** Magnetic susceptibility data of C1at 26 °C and C3 at 22 °C

| Complex | $\chi_g$ | $\mu_{eff}$ spin only | $\mu_{eff}$ experimental |
|---|---|---|---|
| C1 | 5.943 X 10$^{-6}$ | 2.83 | 2.84 |

| | | | |
|---|---|---|---|
| C3 | $2.07 \times 10^{-6}$ | 2.83 | 2.04 |

The data in Table-14 shows the geometries are octahedral. As C3 is binuclear then the $\mu_{eff}$ experimental is 2.04/2=1.02BM.

### 3.2.12. Atomic Absorption Spectral (AAS) data of C1, C2, C3 and C4

Table-15: Metal estimation of C1 and C2

| Metal complex | Percentage of metal mass | | Metal to ligand ratio |
|---|---|---|---|
| | Found | Calculated | |
| C1 | 9.54 % | 9.90 % | 1: 1 |
| C2 | 13.21 % | 13.44 % | 1:1 |
| C3 | 12.89 % | 13.76 % | 2:1 |
| C4 | 10.64 % | 11.21 % | 1:1 |

### 3.2.13. Chloride estimation of C1, C2, C3 and C4

Table-16: Chloride estimation of C1 and C2

| Complex | C1 | C2 | C3 | C4 |
|---|---|---|---|---|
| % of chloride in the complex (experimental) | 11.78 | 14.32 | 16.00 | No |
| % of chloride in the complex ( calculated ) | 12.40 | 14.59 | 16.64 | No |

### 3.2.14. Conductivity data of C1, C2, C3 and C4

As such the C1 complex has one outer sphere chloride and one inner sphere chloride, while the C2 complex has both chlorides in the inner sphere corresponding with the formula $[NiLCl(H_2O)_3]Cl.6H_2O$ and $[ZnLCl_2(H_2O)_2].2H_2O$ for octahedral geometry which is confirmed by other data.

Table-17: Conductivity of C1, C2, C3 and C4

| Complex | Solvent | Molar conductance $\Lambda_m$ (S cm$^2$ mol$^{-1}$) | Conductivity |
|---|---|---|---|
| C1 | DMSO | 88.23 | Electrolyte |

| | | | |
|---|---|---|---|
| C2 | DMSO | 6.08 | Non-electrolyte |
| C3 | Nitro benzene | 1.5 | Electrolyte |
| C4 | Nitro benzene | 4.376 | Non-electrolyte |

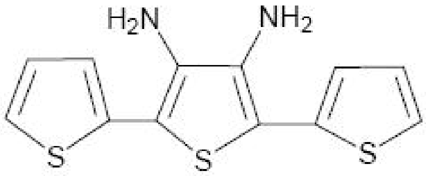
### 3.2.15. Mass spectrum of (L1)

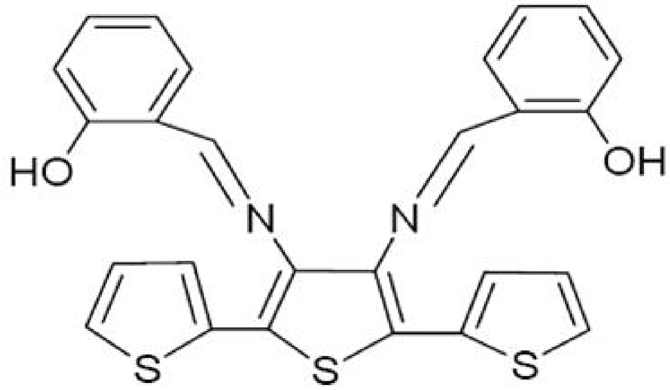
The molecular ion peak (m/z = 278) is an even number indicating the presence of two nitrogen atoms in the compound. The presence of the less abundant (M+2) ion will show the presence of sulfur. The molecular ion peaks (m/z =279 and 280) are due to the isotopic effect of $^{33}S$ and $^{34}S$. Cleavage of the bond β to the ring, as in the alkyl benzene is the general rule. Localizing the charge of the molecular ion on the heteroatom, rather than in the ring π structure, provides a satisfactory rationale for the observed modes of cleavage. The mass spectral fragmentation is consistent with the molecular formula $C_{12}H_{10}N_2S_3$.

### 3.2.16. Mass spectrum of (L2)

The mass spectrum of the ligand recorded under variable temperature ramped from RT to 300 $^{0}$C, resolves a molecular ion peak, m/z = 486 which precisely matches with the molecular weight of the ligand with molecular formula $C_{26}H_{18}S_3N_2O_2$. Another prominent ion peak (base peak) in one of the spectra is assignable to the molecular ion thiophene. Twenty eight fragment ions with m/z 485, 469, 393, 380, 366, 226, 227, 127, 120, 86, 51 and 49 are also recorded. The peak at M+1 (m/z = 487) is due to the presence of isotopic:-$^{13}C$ (1.1%), $^{33}S$ (0.76%) and $^{15}N$ (0.038%). The peak at M+2 (m/z = 488) is due to the presence of isotopic:- $^{34}S$ (4.29% ), $^{18}O$ (0.205%). The peak at M+3 (m/z=489) is due to the presence of 3(M+1) or (M+1) + (M+2) effect.

Based on the above spectral characteristics and qualitative and quantitative analysis the structure of the ligands and complexes were proposed as follow:

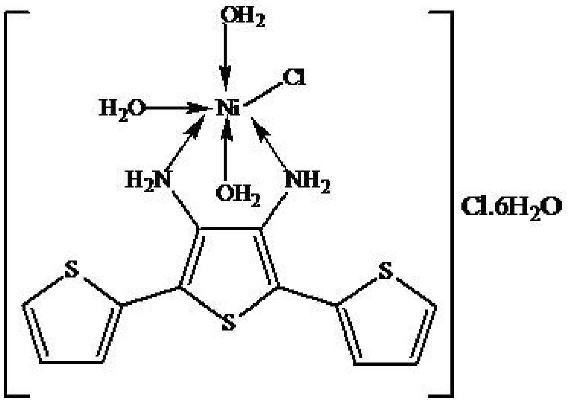


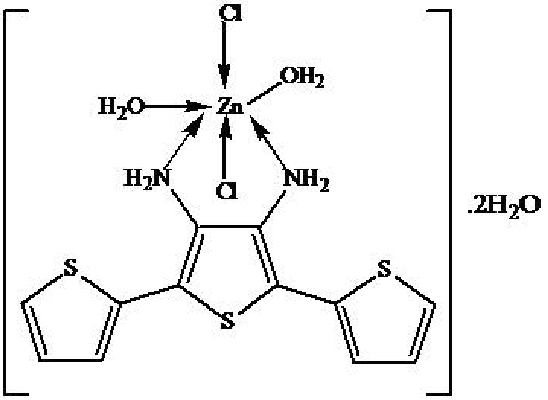


L1 L2

L1: 3',4'-Diamino-2,2':5',2''-terthiopene

L2: 3',4'-bis(2-iminomethylphenol)- 2,2':5',2''-terthiopene

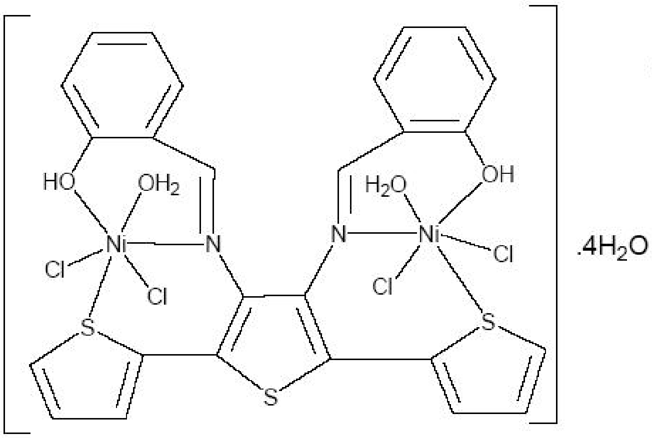




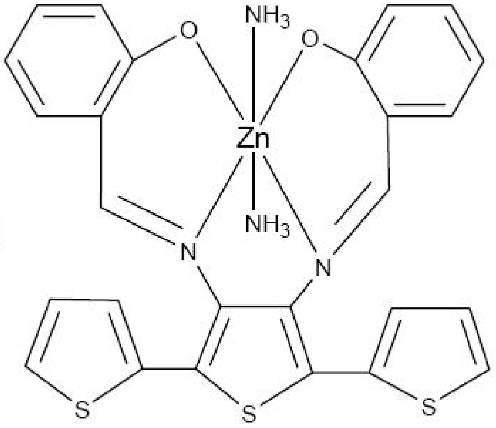
C1 C2

C1: [NiCl($H_2O$)$_3$ {3',4'-diamino-2,2':5',2''-terthiopene }] chloridehexahydrate

C2: [ZnCl$_2$($H_2O$)$_2${3',4'-diamino-2,2':5',2''-terthiopene }] dihydrate



C3



C4

C3: [2NiCl$_2$H$_2$O{3',4'-bis(2-iminomethylphenol)-2,2':5',2"-terthiopene}] tetrahydrate

C4: [Zn(NH$_3$)$_2${3',4'-bis(2-iminomethylphenol)- 2,2':5',2"-terthiopene}][19,38].

Figure-9: Structure of L1, L2, C1, C2, C3 and C4

### 3.3. Voltammetric Procedures

Prior to electropolymerization the glassy carbon electrode and a platinium electrode were prepared by polishing with alumina-water slurry on polishing cloth pads to a mirror like finish and rinsed with deionized water. After pretreating, the electrodes were cycled in $H_2SO_4$ with a potential range from -0.5 to +1.4V at a scan rate of 100 mv/s until the reproducible background was obtained.

The cyclic voltammogram of a 0.1M of blank solution (TEAF$_4$/ CH$_3$CN solution) was recorded between 0.0 and +1.6V (Vs Ag/AgCl) at a scan rate of 100mv/s for both electrodes. Repeated potential cycling of tentimes of a 5 mM of L1 and L2 were recorded in the potential range 0.0 to 1.6V (Vs Ag/AgCl) at a scan rate of 100 mv/s for both electrodes. With the same electrode, repeating potential cycling and scan rate, but with cycling in a potential between -0.3 and +1.1 V were recorded to C1, C2, C3 and C4. For each ligand and complex the scan rate at different potential in monomerfree solution was also recorded. After each run the film was rinsed with the electrolyte to remove excess monomers from the electrode surface.

## 4. Results and Discussion

### 4.1. L1: 3',4'-Diamino-2,2':5',2"-terthiopene

Figure-10 below shows a series of cyclic voltammograms (CVs) recorded for a 5 mM L1 monomer in a 0.1 M $Et_4NBF_4/CH_3CN$ solution, while the potential was cycled between 0.0 and +1.6 V versus Ag/AgCl. The CV exhibited three oxidation peaks at +0.48, +0.90 and +1.39 V (vs. Ag/AgCl) during the first anodic scan, which is due to the oxidation of amine group to imine group, followed by formation of radical species and then oxidation of monomer to form the polymer respectively. The currents of these peaks decreased as the cycle numbers increased. This clearly demonstrates that the polymer film immediately forms after the oxidation of the L1 monomer at +1.39 V. The small and broad reduction peak of the polymer was observed at +0.69 V (vs. Ag/AgCl) at the cathodic scan. This clearly observed in the inset Figure-10.

It is believed that the thickness of the polymer film increased as the cycle number increased[39]. This experiment also has similar character.

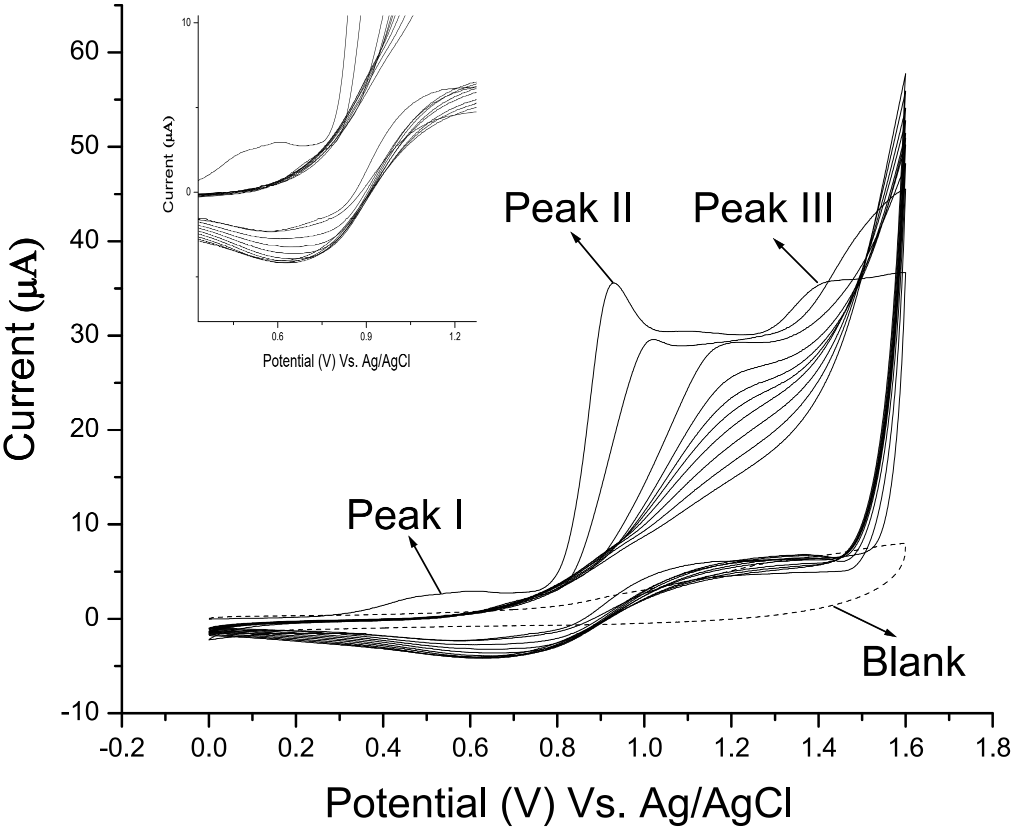


Figure-10: Repeated cyclic voltammograms recorded during the first 10 cycles of electropolymerization of 5 mM 3',4'-Diamino-2,2':5',2"-terthiopene in 0.1 M $Et_4NBF_4/CH_3CN$ solutions, scanning anodically from 0.0 to +1.6 V at a scan rate of 100 mV/s; working electrode, platinum electrode. The inset figure shows reduction peak of the polymer.

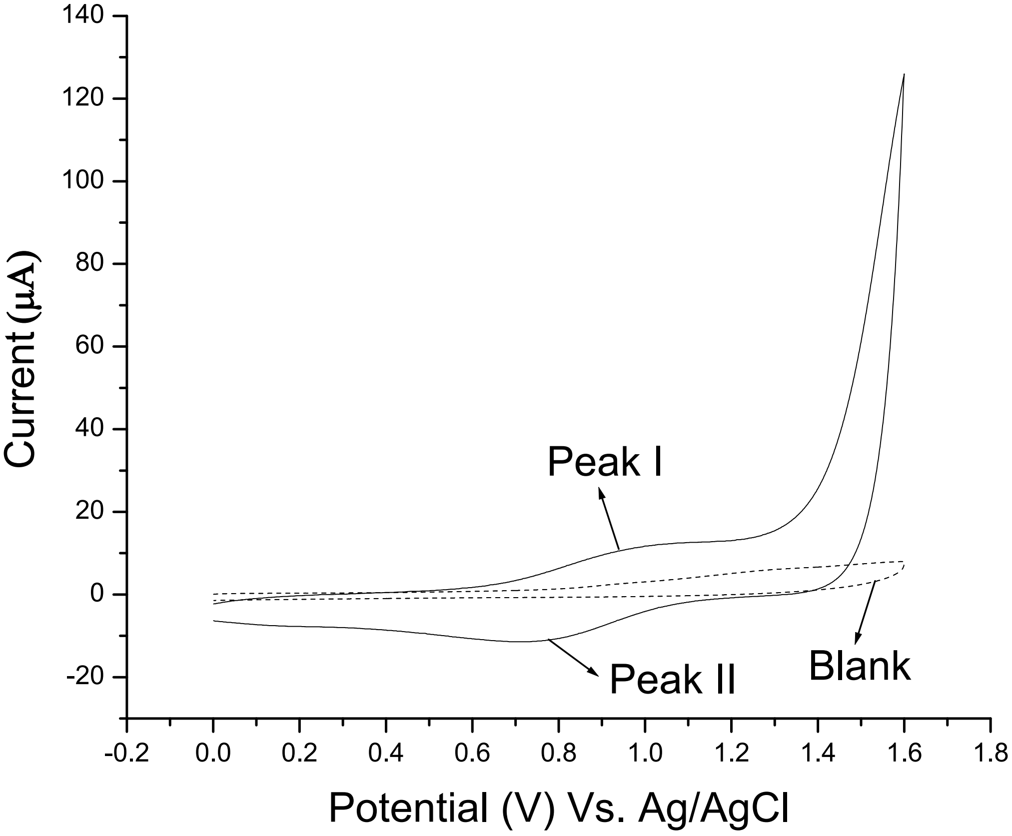
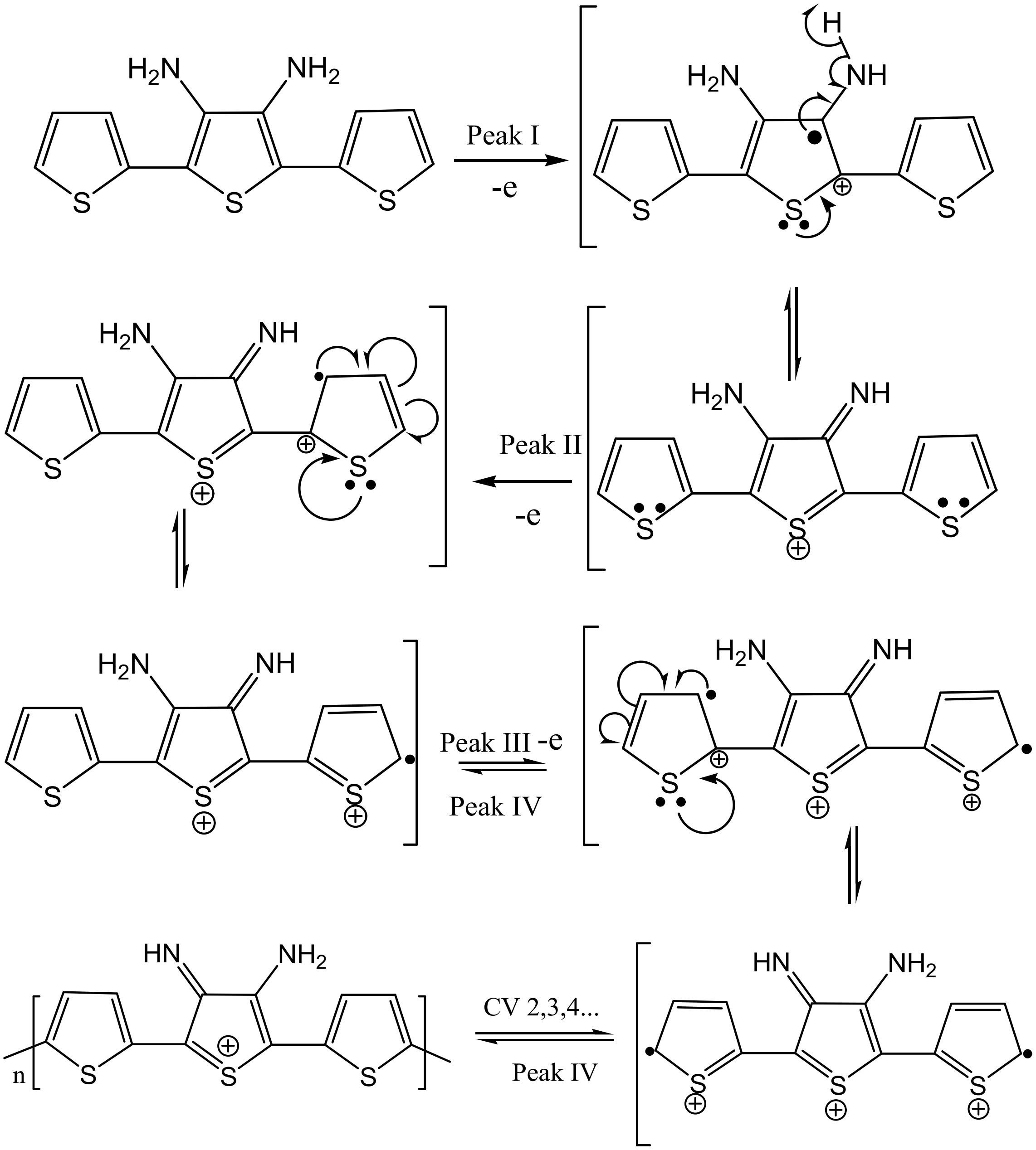


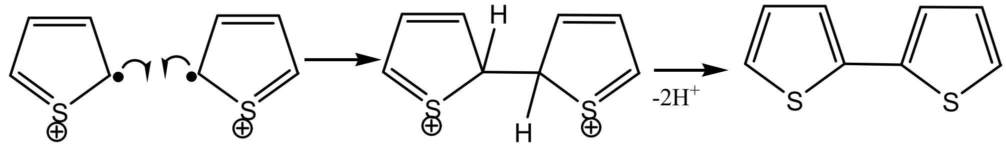
Figure-11: Polymer cyclic voltammogram for a film of Poly[3',4'-Diamino-2,2':5',2''-terthiopene] on a platinum electrode under anodic scanning from 0.0 to +0.6 V at a scan rate of 100 mV/s in 0.1 M $Et_4NBF_4/CH_3CN$ solutions.

The redox peak of the polymer film in monomerfree system was observed at 0.93/0.79 V (vs. Ag/AgCl) as shown in Figure-11, indicating that the polymer film is electrochemically active. The peak current of this redox peak was proportional to the scan rate, indicating that the current flow is due to the redox behavior of the adsorbed polymer film.

## 4.2. Proposed Mechanism



Mechanism steps after peak three formation follows the same procedure as shown below:



This mechanism above shows formation of Poly[3',4'-Diamino-2,2':5',2"-terthiopene]

### 4.3. C1: [NiCl($H_2O$)$_3$ {3',4'-diamino-2,2':5',2"-terthiopene }] chloridehexahydrate

Figure-12 below shows a series of cyclic voltammograms (CVs) recorded for a 5 mM C2 monomer in a 0.1 M $Et_4NBF_4/CH_3CN$ solution, while the potential was cycled between -0.3 and +1.1 V versus Ag/AgCl. The CV exhibited one oxidation peaks at +0.89V vs. Ag/AgCl during the first anodic scan, which is due to the formation of radical (i.e. due to oxidation of the metal thienylene unit ($C1 \rightarrow C1^{+\cdot}$).

Repeated cycling between 0 and 1.4 V vs. SCE produced highly reversible oxidation of the thiophene and the nickel redox centres and the $Ni^{2+/3+}$ wave. For the process in solution and that in the polymer, this was very important as, upon oxidation, the reaction:

$$[Ni(L)]^{2+} - e^{-} + 2CH_3CN \rightarrow [Ni(L)(CH_3CN)_2]^{3+}$$

occurred. In order for this to happen there must be enough solvent in the polymer, which must have been incorporated into the polymer matrix when the polymer film was being grown as the nickel would be in its oxidised state and able to complex with the solvent[40]. So this tells as that the reduction occurred during polymer formation is not due to $Ni^{3+/2+}$.

The reduction peaks (peak II) observed for about four cycles of the polymer at ~+0.4 V (vs. Ag/AgCl) at the cathodic scan, which is shown visibly in the inset Figure-3, is due to electrolytic reduction of $Ni^{+2}$ in $CH_3CN$ in the presence of terhiophene unit and can stabilize $Ni^{+}$ ion[41]. This reduction peak disappears after four cycles because of the insufficient solvent complexation in the growing backbone of the structure. This is well supported by the cyclic voltammogram of the polymer in monomerfree solution as shown in Figure-13.

Multiple cycles of the monomer solution showed both monomer oxidation and electropolymerization, yielding an electroactive film i.e. the increased in anodic potential shows the polymer formation. Most likely the most marked feature of a cyclic voltammogram of a totally irreversible system, for example $O + ne^{-} \rightarrow R$, is the total absence of a reversible peak. However, such a feature itself does not necessarily imply an irreversible electron transfer process but could also be due to a fast following chemical reaction.[42,43] These principles holds also to this case because Ni and $OH_2$ are electron sufficient where by they might facilitate fast chemical reactions.

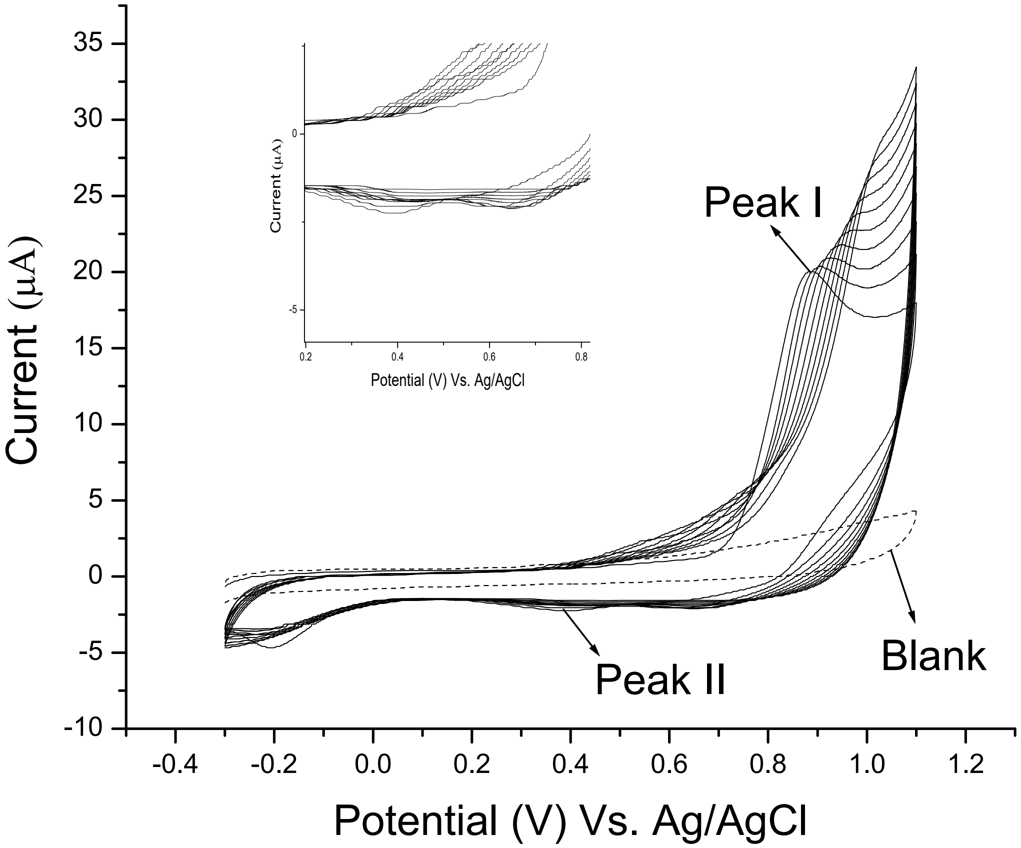


Figure-12: Repeated cyclic voltammograms recorded during the first 10 cycles of electropolymerization of 5mM [NiCl$(H_2O)_3$ {3',4'-diamino-2,2':5',2"-terthiopene }] chloridehexahydrate in 0.1 M $Et_4NBF_4/CH_3CN$ solutions, scanning anodically from -0.3 to +1.1 V at a scan rate of 100 mV/s; working electrode, glassy carbon electrode. The inset Figure shows reduction peak of the polymer.

The irreversible oxidation peak of the polymer film in monomerfree was observed at 0.975 and irreversible reduction peak at -0.29V (vs. Ag/AgCl) as shown in Figure-13, indicating that the polymer film is electrochemically active. The peak current was proportional to the scan rate, indicating that the current flows due to the redox behavior of the adsorbed polymer film.

As one can see from the cyclic voltammogram (Figure-4), electropolymerized polyC1 exhibited two set of peaks. The oxidized peak at more positive potential seemed to be a monomer type oxidative activity. This indicates that PolyC1 consist of terthiophene units covalently linked to each other. The absence of the reduction peak which was observed during polymer formation indicates that there is no enough solvent that has been incorporated in the polymer matrix.

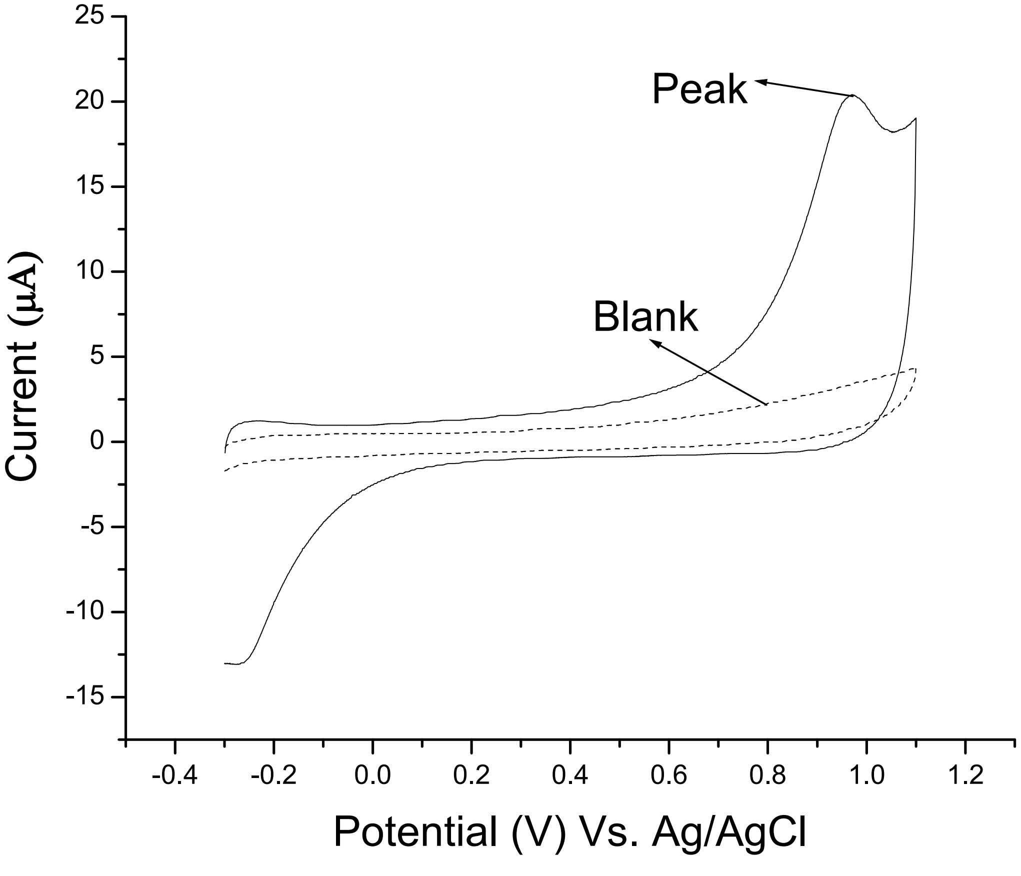


Figure-13: Polymer cyclic voltammogram for a film of Poly[[NiX($H_2O$)$_3$ {3',4'-diamino-2,2':5',2''-terthiopene }] chloridehexahydrate] on a glassy carbon electrode under anodic scanning from -0.3 to +1.1 V at a scan rate of 100 mV/s in 0.1 M $Et_4NBF_4/CH_3CN$ solutions.

**The cycling behavior of Poly[[NiX($H_2O$)$_3$ {3',4'-diamino-2,2':5',2''-terthiopene }] chloridehexahydrate]**

The polyC1 film obtained at +0.89V is further cycled between -0.3 and 1.1 V in 0.1 M $Et_4NBF_4/CH_3CN$ solutions. As shown in Figure-14, the cyclic voltammograms of the film display one anodic peak and one cathodic peak. Upon being continuously cycled, both the anodic and the cathodic current vary with the cycle number. In these cycles, the anodic current is obviously larger than the corresponding cathodic one; this behavior was explained by the oligomers in the pore of the thin film[37].

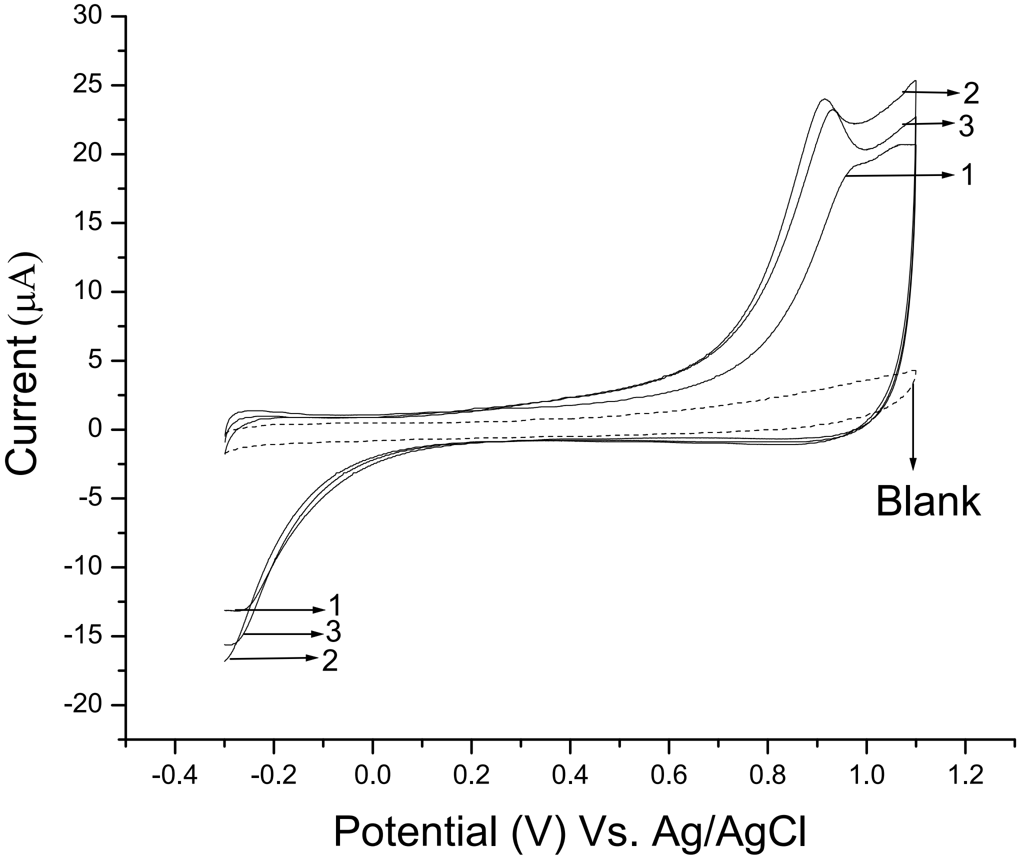
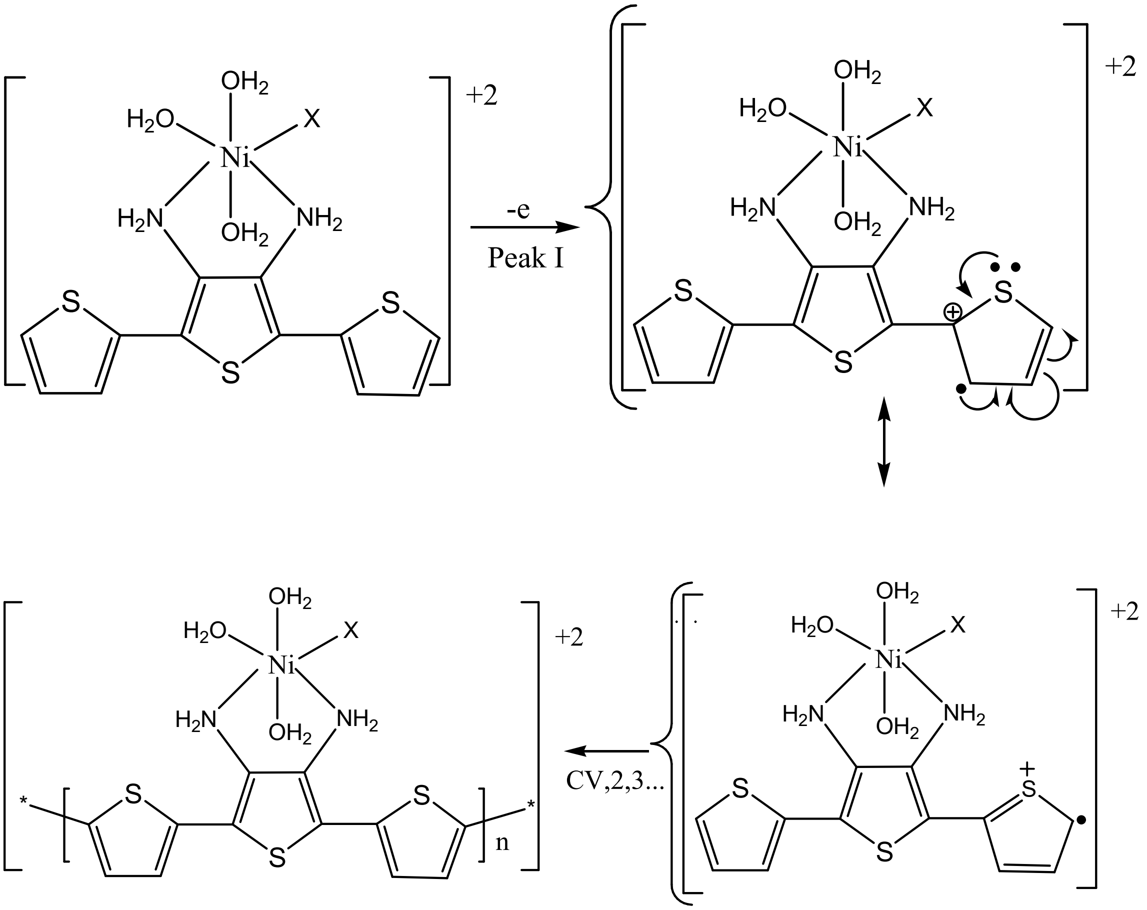


Figure-14: The cyclic voltammograms of Poly[[NiX($H_2O$)$_3$ {3',4'-diamino-2,2':5',2''-terthiopene }] chloridehexahydrate] on a glassy carbon electrode under anodic scanning from -0.3 to +1.1 V at a scan rate of 100 mV/s in 0.1 M $Et_4NBF_4/CH_3CN$ solutions, of the first three cycles.

## 4.4. Proposed Mechanism



Where X is a solvent, can be $CH_3CN$ or $H_2O$

This mechanism above shows formation of:
Poly[[NiX($H_2O$)$_3$ {3',4'-diamino-2,2':5',2''-terthiopene }] chloridehexahydrate]

## 4.5. C2: [ZnCl$_2$(H$_2$O)$_2${3',4'-diamino-2,2':5',2''-terthiopene }] dihydrate

Figure-15 below shows a series of cyclic voltammograms (CVs) recorded for a 5mM C2 monomer in a 0.1 M $Et_4NBF_4/CH_3CN$ solution, while the potential was cycled between -0.3 and +1.1 V versus Ag/AgCl. The CV exhibited two oxidation peaks at +0.75, and +0.99V (vs. Ag/AgCl) during the first anodic scan, which is due to the formation of radical (i.e. due to formation of imine moiety) and the other is due to formation of radical on thiophene moiety (i.e. due to oxidation of the metal thienylene unit ( $C2 \rightarrow C2^{+\cdot}$)) respectively. Subsequent oxidation is due to the linkage formation of thienylene groups (i.e. due to growing of the polymer film). The reduction peak of the polymer was observed at +0.65 V (vs Ag/AgCl) at the cathodic scan which is shown visibly in the inset Figure-15.

During the earlier cycles, however, two anodic peaks appear (Figure-15), and the peak at a more positive potential is eventually overlapped by the growth of the anodic peak due to electropolymerization. After six cycles the individuality of the peak is lost. This peak is assumed to be due to the extracting of an electron from the $NH_2$ group and was shown to be absent if the electropolymerization was attempted in acidic medium when protonation of the $NH_2$ groups is expected. The potential at which this peak appears is +0.700 V to +0.800 V[44], which is close to the +0.75 V quoted for the same process using 3',4'-diamino-2,2':5',2''-terthiophene metal complex. So, the protonation yields imine formation.

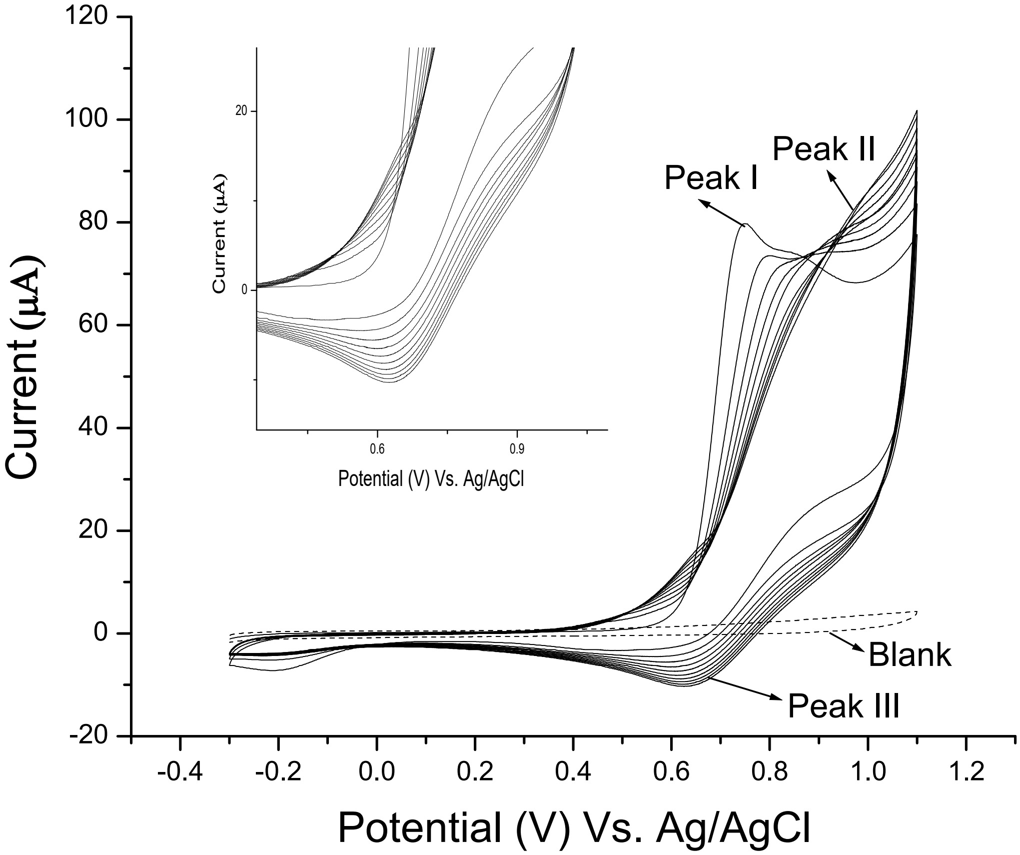


Figure-15: Repeated cyclic voltammograms recorded during the first 10 cycles of electropolymerization of 5 mM [$ZnCl_2(H_2O)_2${3',4'-diamino-2,2':5',2''-terthiopene }] dihydrate in 0.1 M $Et_4NBF_4/CH_3CN$ solutions, scanning anodically from -0.3 to +1.1 V at a scan rate of 100 mV/s; working electrode, glassy carbon electrode. The inset Figure shows reduction peak of the polymer.

The redox peak of the polymer film in monomerfree was observed at 0.88/0.64 V and one irreversible peak at 0.54 V (vs. Ag/AgCl) as shown in Figure-16, indicating that the polymer film is electrochemically active. The peak current of this redox peak was proportional to the scan rate, indicating that the current flows due to the redox behavior of the adsorbed polymer film.

As one can see from the cyclic voltammogram (Figure-16), electropolymerized polyC2 exhibited two set of peaks. Both the redox couple and the irreversible oxidation peak at more positive potential seemed to be a monomer type oxidative activity. This indicates that PolyC2 consist of terthiophene units covalently linked to each other. The absence of any other reduction as well as oxidation peaks assures zinc (II) can not increase or decrease its oxidation state by one i.e., zinc(I) or zinc(III) does not exist here.

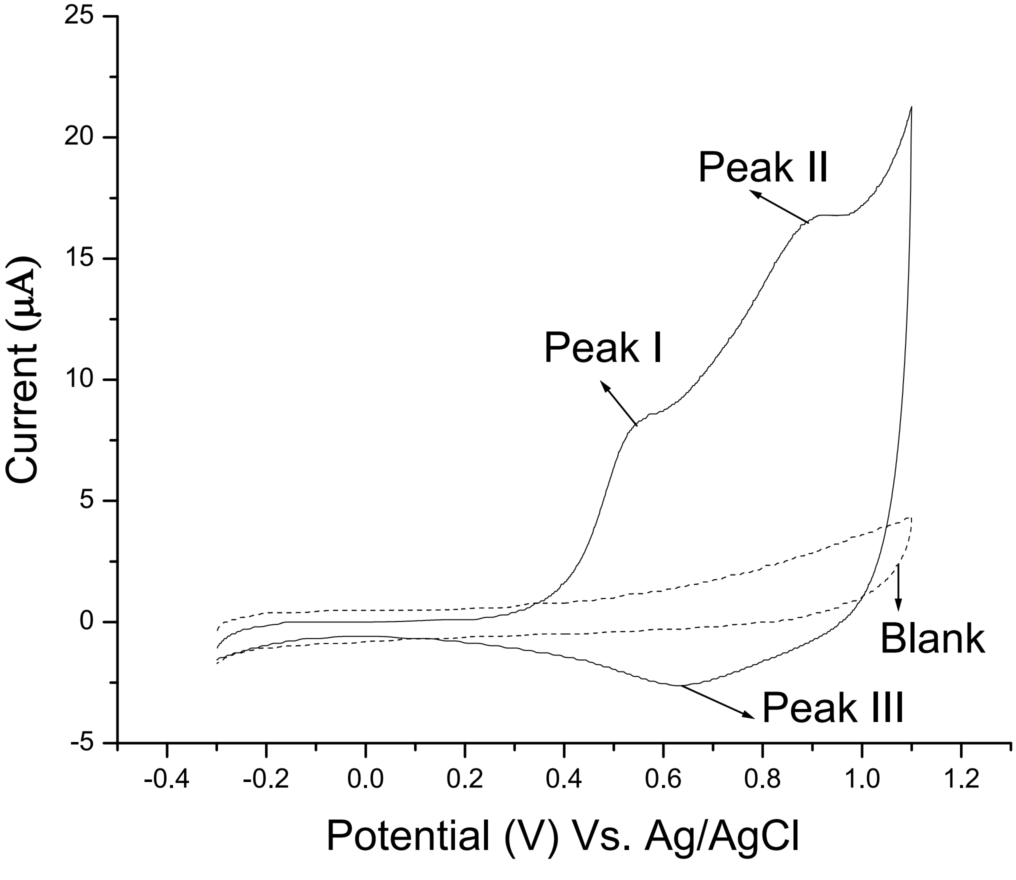


Figure-16: Polymer cyclic voltammogram for a film of poly[$ZnCl_2(H_2O)_2${3',4'-diamino-2,2':5',2''-terthiopene }] dihydrate on a glassy carbon electrode under anodic scanning from -0.3 to +1.1 V at a scan rate of 25 mV/s in 0.1 M $Et_4NBF_4/CH_3CN$ solutions.

Figure-17 clearly shows the extracting of an electron from the amine group and this is confirmed due to the absent of the electropolymerization on the first peak. Thus at this condition the medium is acidic because of the protonation of the amine group.

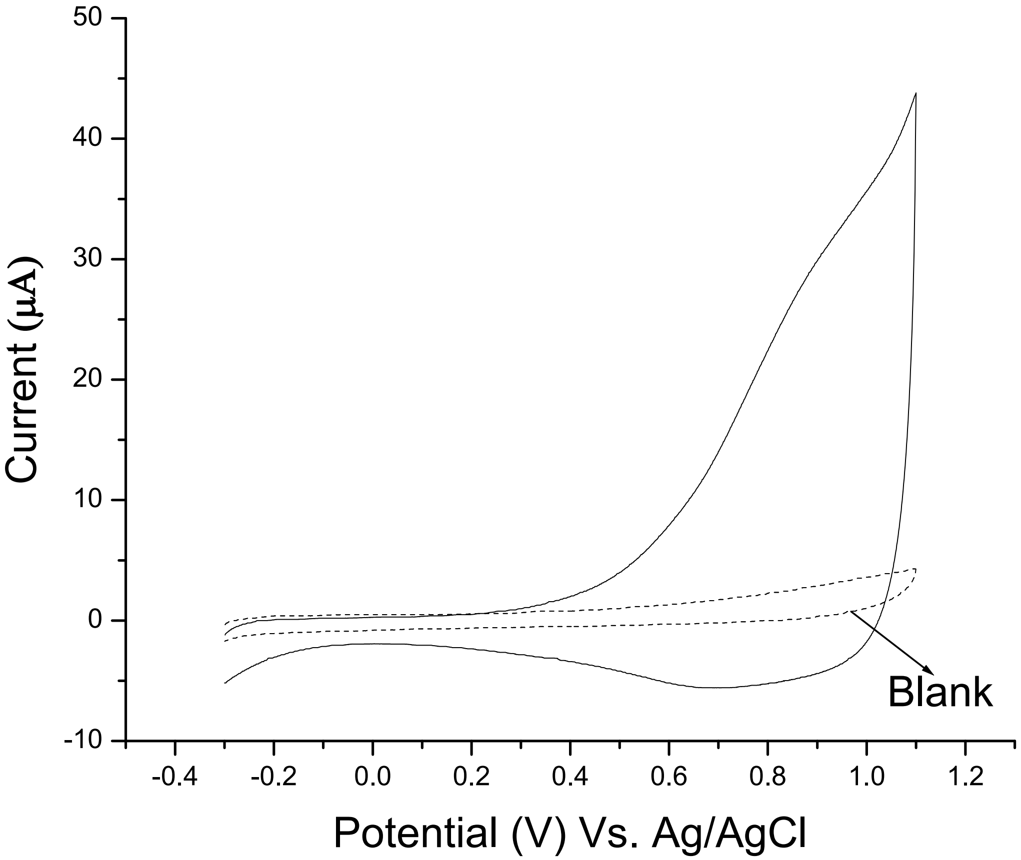


Figure-17: Polymer cyclic voltammogram for a film of poly[$ZnCl_2(H_2O)_2${3',4'-diamino-2,2':5',2''-terthiopene }] dihydrate on a glassy carbon electrode under anodic scanning from -0.3 to +1.1 V at a scan rate of 100 mV/s in 0.1 M $Et_4NBF_4/CH_3CN$ solutions.

### The cycling behavior of poly[$ZnCl_2(H_2O)_2${3',4'-diamino-2,2':5',2''-terthiopene }] dihydrate

The polyC2 film obtained at +0.75, and +0.99/+0.65V V is further cycled between -0.3 and 1.1 V in 0.1 M $Et_4NBF_4/CH_3CN$ solutions. As shown in Figure-18, the cyclic voltammograms of the film display two anodic peaks and one cathodic peak. Upon being continuously cycled, both the anodic and the cathodic current vary with the cycle number.

In the first few cycles, the anodic current is obviously larger than the corresponding cathodic one; this behaviour was explained by the oligomers in the pore of the thin film. The cathodic current, on the contrary, decreases with the increase of the cycle number. Therefore, it is concluded that overoxidation occurs during the oxido-reduction cycles[37].

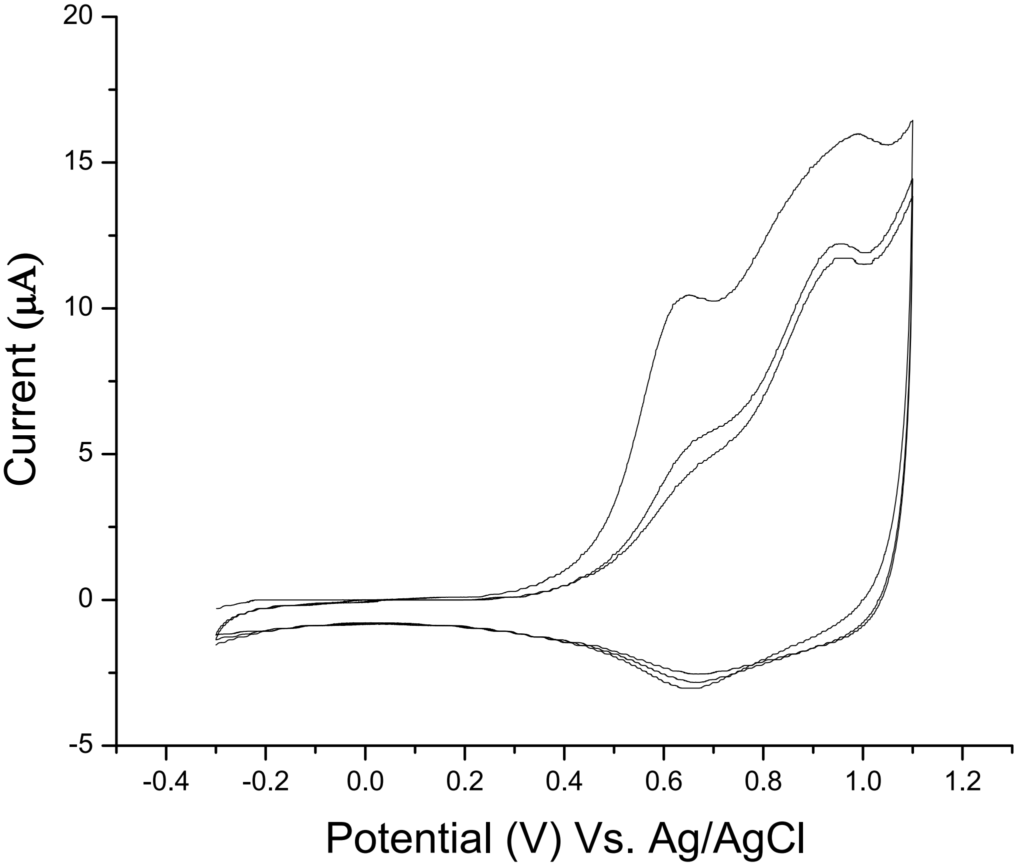
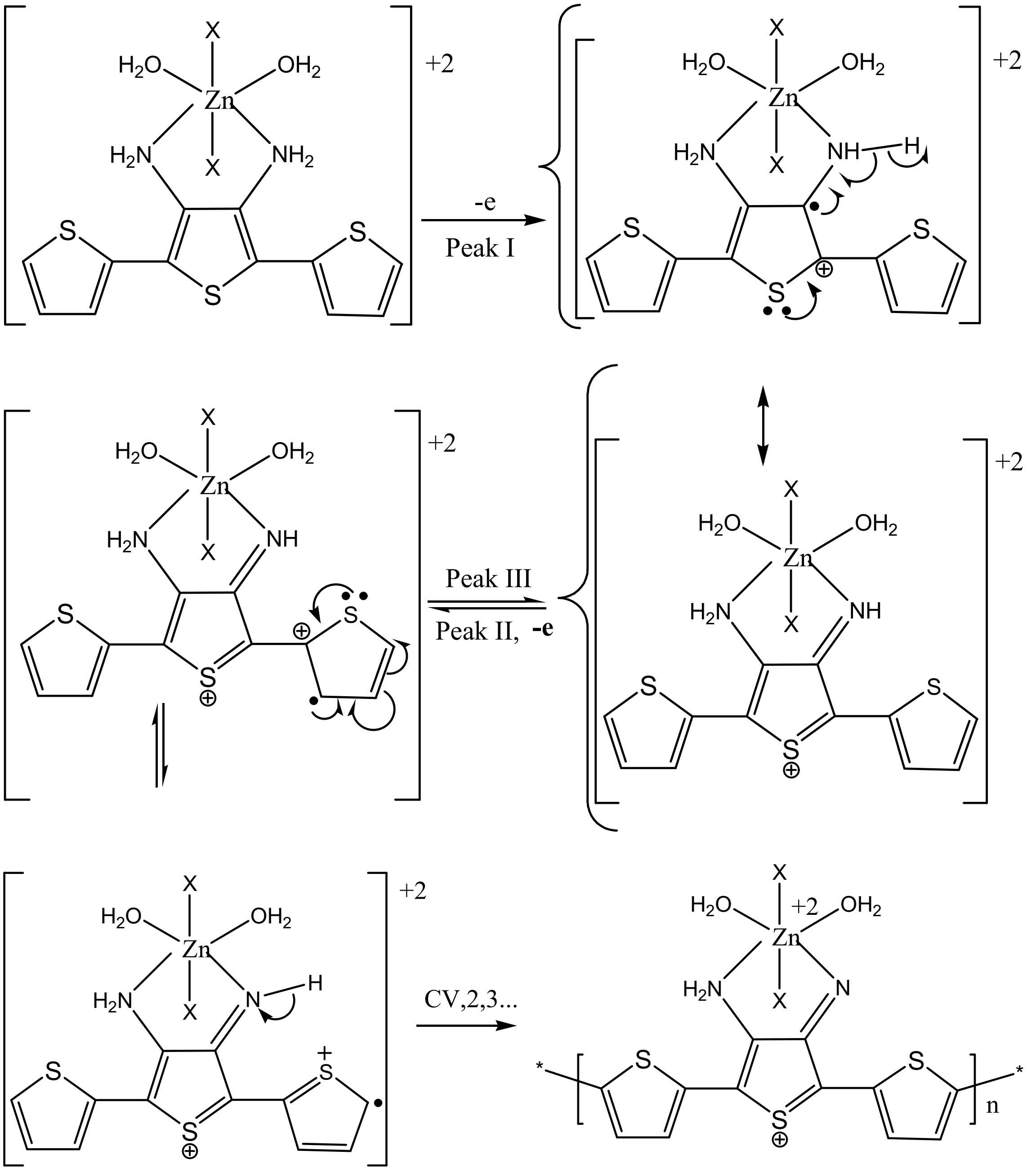


Figure-18: Polymer cyclic voltammogram for a film of poly[$ZnCl_2(H_2O)_2$\{3',4'-diamino-2,2':5',2''-terthiopene \}] dihydrate on a platinum electrode under anodic scanning from -0.3 to +1.1 V at a scan rate of 25 mV/s in 0.1 M $Et_4NBF_4/CH_3CN$ solutions, of first three cycles.

**4.6. Proposed Mechanism**



Where X is a solvent, can be $CH_3CN$ or $H_2O$

The last mechanism is because of the extracting electrons from amine group which is clearly visible in diminishing the peak oxidation of the amine moiety.

This mechanism above shows formation of:

Poly[[ZnX$(H_2O)_2${3',4'-diamino-2,2':5',2"-terthiopene }] dihydrate]

### 4.7. L2: 3',4'-bis(2-iminomethylphenol)- 2,2':5',2"-terthiopene

In general, phenol and its derivatives can be oxidatively electropolymerized by scanning in the potential range between 0 and +1.2 V. When the scan was limited to +1.0 V, a visibly rough and mechanically fragile film was deposited[45].

Figure-19 below shows a series of cyclic voltammograms (CVs) recorded for a 5 mM L2 monomer in a 0.1 M $Et_4NBF_4/CH_3CN$ solution, while the potential was cycled between 0.0 and +1.6 V versus Ag/AgCl. The CV exhibited three oxidation peaks at +0.63, +1.12 and +1.34V (vs. Ag/AgCl) during the first anodic scan, which is due to the oxidation of alcohol group to ketone group, formation of radical species on phenolic group and thiophene groups respectively. The subsequent increase in oxidation and reduction tells the formation of the polymer. The reduction peak of the polymer was observed at +1.18 V (vs. Ag/AgCl) at the cathodic scan.

The peak currents assigned to the oxidation of the monomer (peaks II and III) formed by losing electrons from the salicyledene and terthiophene ring were increased, which meant that the rings were unstable when either groups were oxidized to link each other. Consequently, it was concluded that the polymers obtained on the electrode were two-dimensional (mixture of linkage) polymers[27].

As one can see from the cyclic voltammogram (Figure-20), electropolymerized polyL2 exhibited two set of peaks. Both the redox couple and the irreversible oxidation peak at more positive potential seemed to be a monomer type oxidative activity. This indicates that PolyC2 consist of terthiophene and salicyledene units covalently linked to each other.

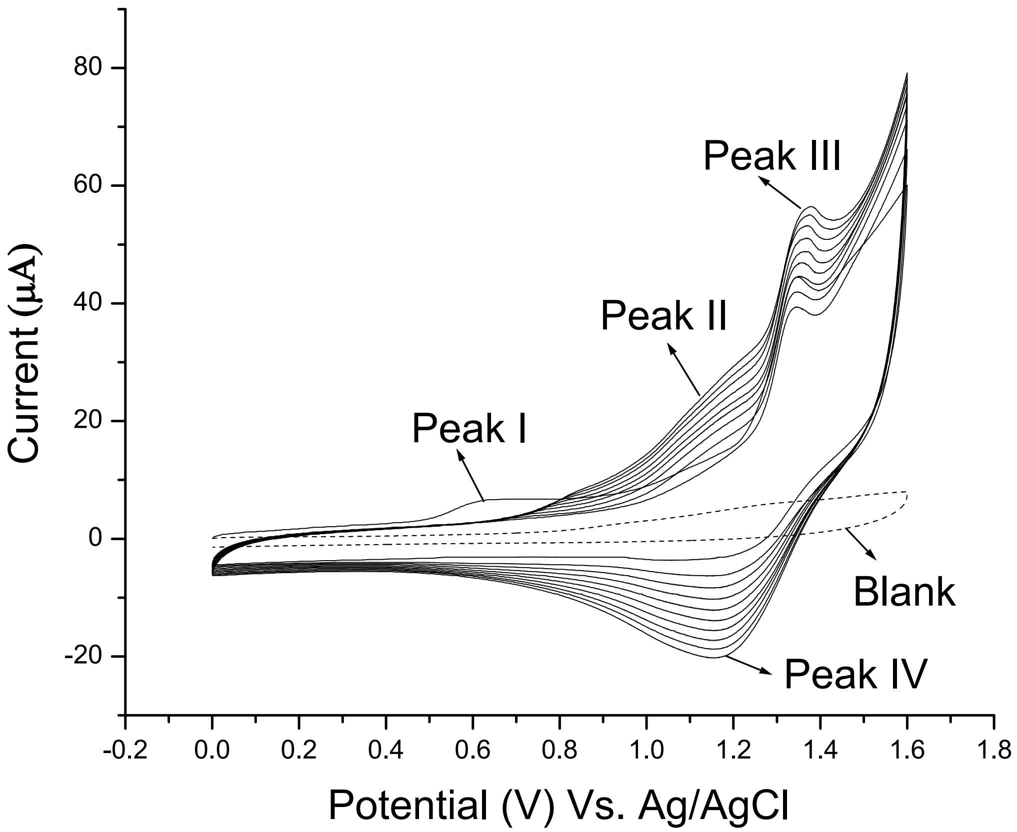


Figure-19: Repeated cyclic voltammograms recorded during the first 10 cycles of electropolymerization of 5 mM 3',4'-bis(2-iminomethylphenol)- 2,2':5',2"-terthiopene in 0.1 M $Et_4NBF_4/CH_3CN$ solutions, scanning anodically from 0.0 to +1.6 V at a scan rate of 100 mV/s; working electrode, glassy carbon electrode.

The redox peak of the polymer film in monomerfree was observed at 1.32/1.2V and one irreversible peak at 0.97 V (vs. Ag/AgCl) as shown in Figure-20, indicating that the polymer film is electrochemically active. The peak currents of this redox peaks were proportional to the scan rate, indicating that the current flows due to the redox behavior of the adsorbed polymer film.

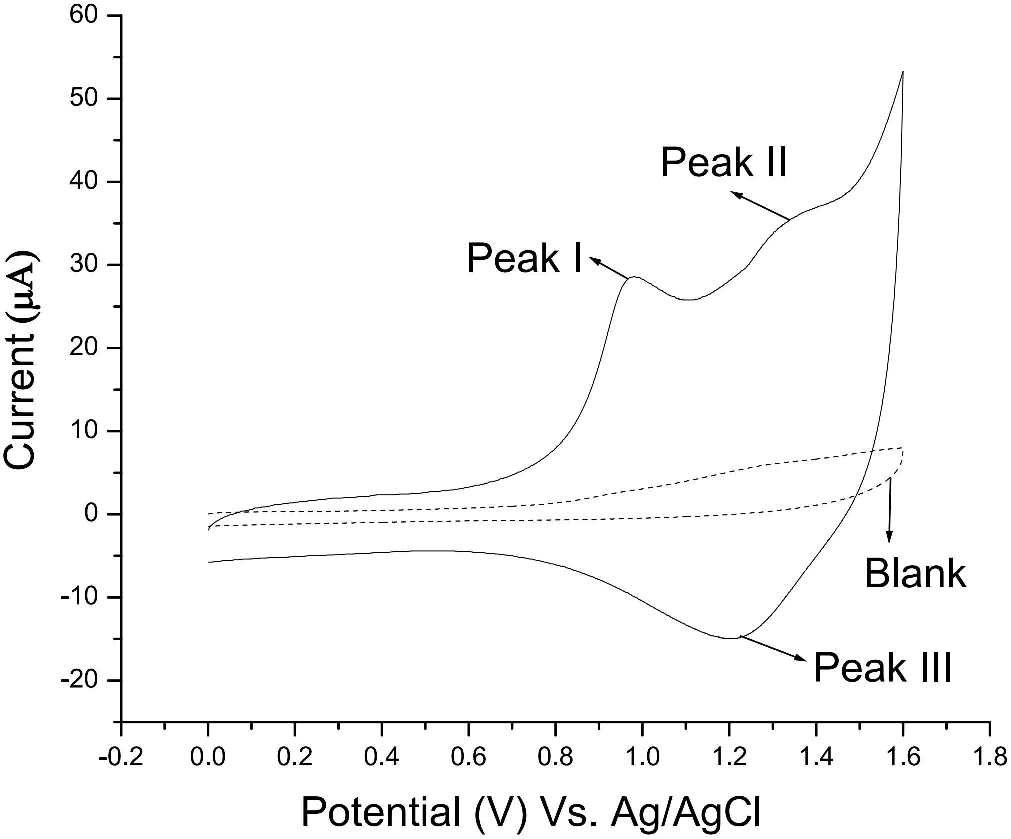


Figure-20: Polymer cyclic voltammogram for a film of poly[3',4'-bis(2-iminomethylphenol)- 2,2':5',2"-terthiopene] on a glassy carbon electrode under anodic scanning from 0.0 to +1.6 V at a scan rate of 100 mV/s in 0.1 M $Et_4NBF_4/CH_3CN$ solutions.

**The cycling behavior of poly[3',4'-bis(2-iminomethylphenol)- 2,2':5',2"-terthiopene]**

The first four cyclic voltammogram shown in Figure-21 of the polymer film in monomerfree solution is stable for the first peaks but unstable for the second peaks as the peak disappears after second cycle. A unique feature of the polymer film is the presence of clear anodic oxidation due to oxidation of phenolic moiety, which is not as such clear while the polymer is formed.

The polyL2 film obtained at +1.12 and +1.34 V /+1.18 V is further cycled between 0.0 and 1.6 V in 0.1 M $Et_4NBF_4/CH_3CN$ solutions. As shown in Figure-21, the cyclic voltammograms of the film display two anodic peaks and one cathodic peak. Upon being continuously cycled, both the anodic and the cathodic current vary with the cycle number. In the first few cycles, the anodic current is obviously larger than the corresponding cathodic one; this behavior was explained by the oligomers in the pore of the thin film. The cathodic current, on the contrary, decreases with the increase of the cycle number. Therefore, it is concluded that overoxidation occurs during the oxido-reduction cycle[37].

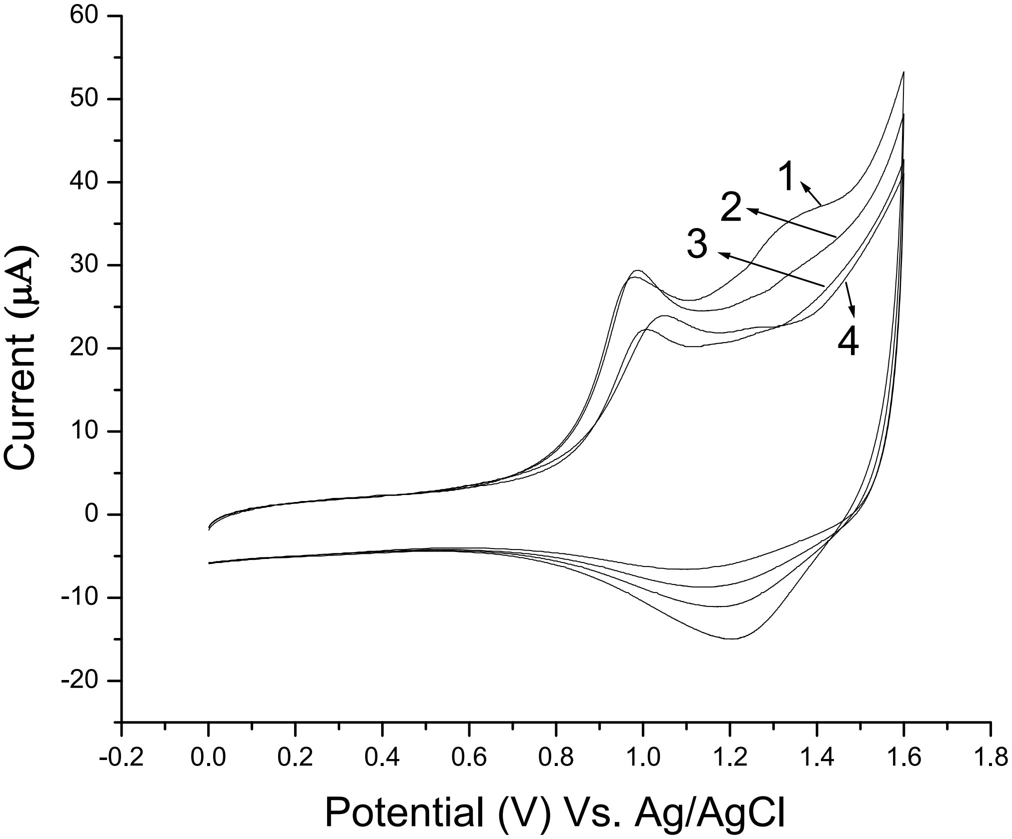
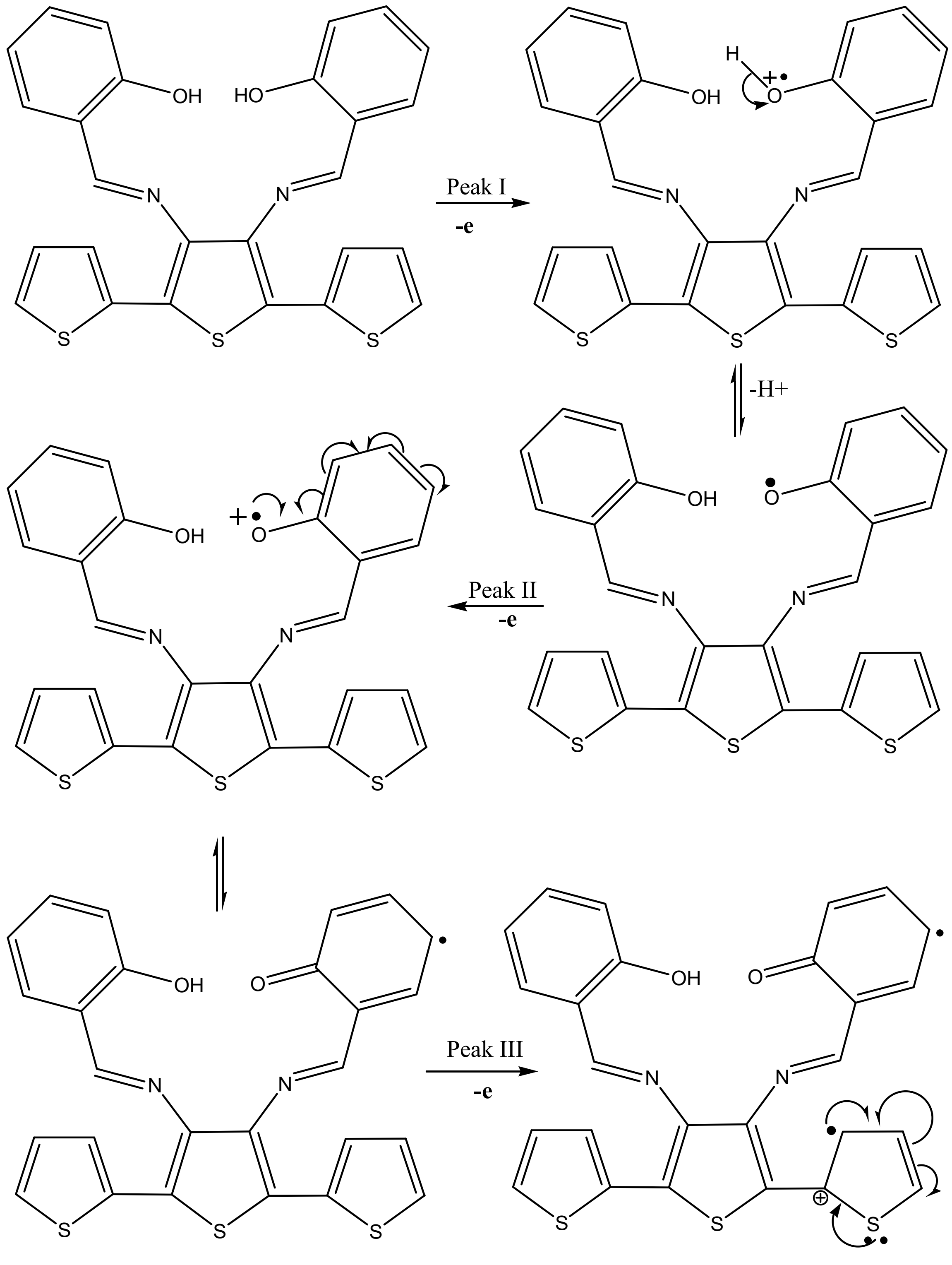
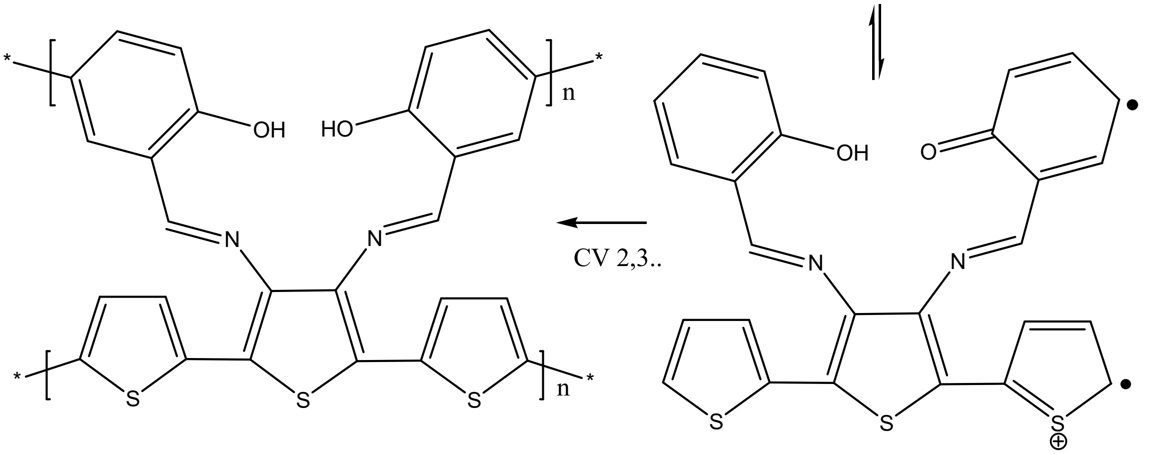


Figure-21: Polymer cyclic voltammogram for a film of poly[3',4'-bis(2-iminomethylphenol)- 2,2':5',2''-terthiopene] on a glassy carbon electrode under anodic scanning from 0.0 to +1.6 V at a scan rate of 100 mV/s in 0.1 M $Et_4NBF_4/CH_3CN$ solutions.

### 4.8. Proposed Mechanism


OH
HO
N
S
Peak I
-e
H
+•
O
-H+
Peak II
-e
+•
O
Peak III
-e
⊕



The product formed in the mechanism above during first and second peak is also approved by mass spectrum data.

This mechanism above shows formation of :

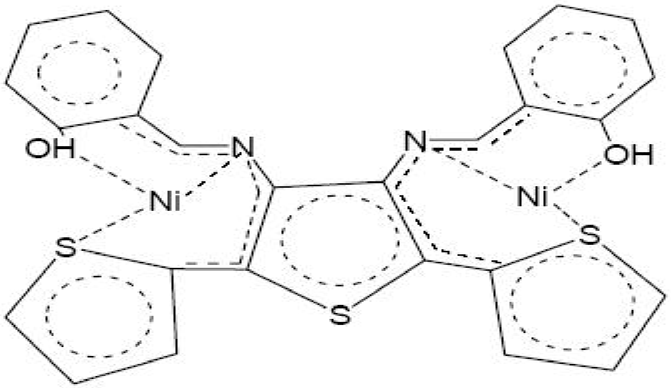
Poly[3',4'-bis(2-iminomethylphenol)- 2,2':5',2''-terthiopene]

### 4.9. C3:[$2NiCl_2H_2O${3',4'-bis(2-iminomethylphenol)-2,2':5',2''-terthiopene}] tetrahydrate

Figure-22: below shows a series of cyclic voltammograms (CVs) recorded for a 5 mM C3 monomer in a 0.1 M $Et_4NBF_4/CH_3CN$ solution, while the potential was cycled between 0.0 and +1.6 V versus Ag/AgCl. The CV exhibited no oxidation peaks vs. Ag/AgCl. This implies it can't polymerize. Some reasons for difficulty of polymerization are:

1. Globally, the decrease in electron density on the organic molecule upon complexation is consistent with the fact that oxidation becomes difficult[46].
2. If the active group is sterically hindered, then oxidation becomes difficult[27].
3. If the active group is linked to some functional group polymerization would be stopped.
4. Metal type can facilitate polymerization from blocked extended conjugation
5. Solubility is important as more concentrated solutions tend to more readily undergo electropolymerization[33].

The reason for this is similar to number one that is the electrons responsible for the radical formation occurring in the back bone is in delocalization (resonating within the molecule) as shown in the structure below, So that formation of a radical during oxidation is highly forbidden. That is why there is no any anodic oxidation in the repetitive CV. Delocalization of C3 is given below:



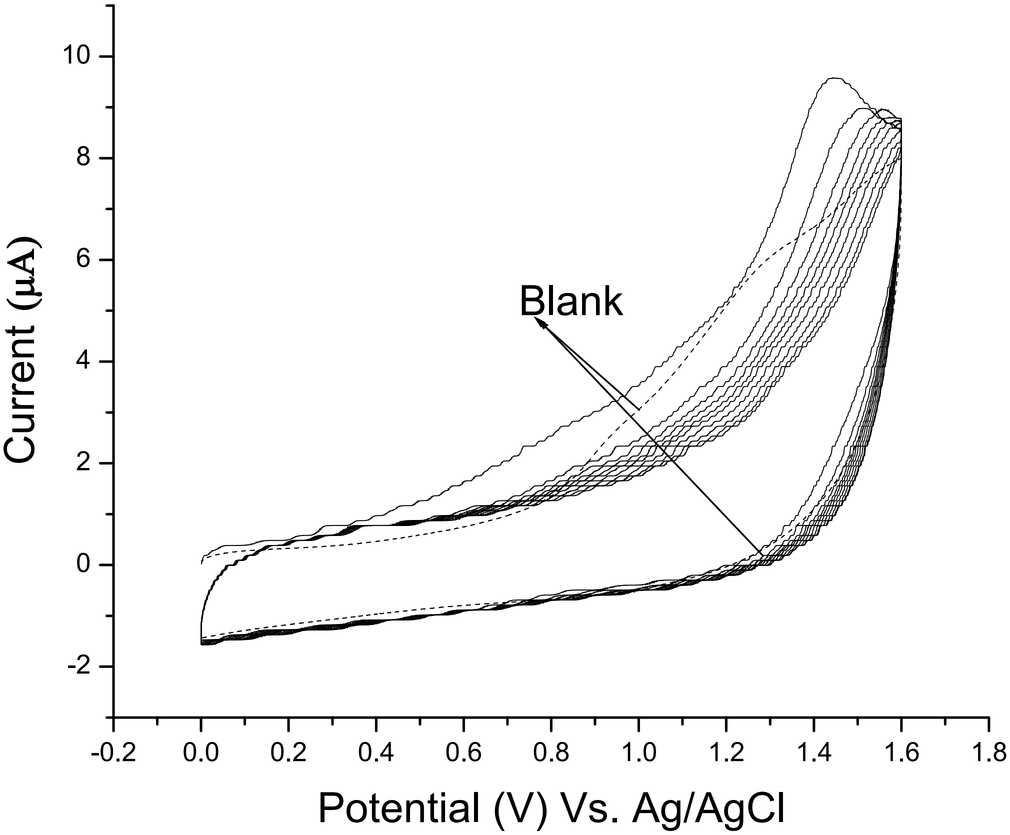


Figure-22: Repeated cyclic voltammograms recorded during the first 10 cycles of 5mM [$2NiCl_2H_2O${3',4'-bis(2-iminomethylphenol)-2,2':5',2''-terthiopene}] tetrahydrate in 0.1 M $Et_4NBF_4/CH_3CN$ solutions, scanning anodically from 0.0 to +1.6 V at a scan rate of 100mV/s; working electrode, glassy carbon electrode.

### 4.10. C4: $[Zn(NH_3)_2\{3',4'\text{-bis(2-iminomethylphenol)- }2,2':5',2''\text{-terthiopene}\}]$

Figure-23: below shows a series of cyclic voltammograms (CVs) recorded for a 5 mM C3 monomer in a 0.1 M $Et_4NBF_4/CH_3CN$ solution, while the potential was cycled between 0.0 and +1.6 V versus Ag/AgCl. The CV does not exhibit any increase in oxidation peaks vs. Ag/AgCl. This implies it can’t polymerize. The reasons might be the zinc metal present in the blocked extended conjugation lacks any donor groups on the para position relative to phenoxy group so that polymerizations will facilitate[33].

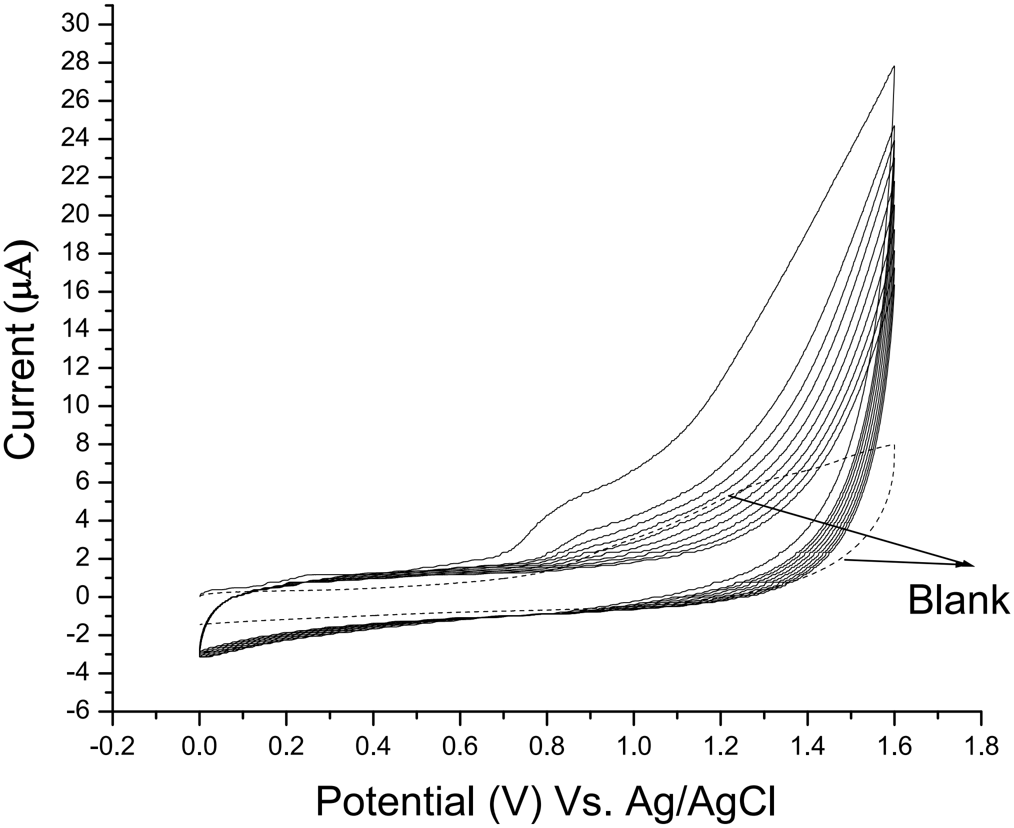


Figure-23: Repeated cyclic voltammograms recorded during the first 10 cycles of 5mM $[Zn(NH_3)_2\{3',4'\text{-bis(2-iminomethylphenol)-}2,2':5',2''\text{-terthiopene}\}]$ in 0.1 M $Et_4NBF_4$ $/CH_3CN$ solutions, scanning anodically from 0.0 to +1.6 V at a scan rate of 100 mV/s; working electrode, glassy carbon electrode.

### 4.11. Scan rate effect of L1, C1, C2 and L2

The electrochemical activities of PolyL1 and PolyC2 films on the GCE were investigated as shown in Figure 24-26. The redox waves appeared at potentials did not alter with increased scan rates while both of the peak currents enhanced proportionally with scan rates. The independence of peak potentials on scan rates demonstrates that the redox reaction is a reversal process controlled by adsorption. This also indicates that the deposition of the thiophene polymer on the electrode. From the linear regression data of L1, C1, and C2 the value of R is 0.995, 0.99, and 0.929 respectively. Due to the instability (degradation) of the polymer L2, it is difficult to observe the scan rate dependence.

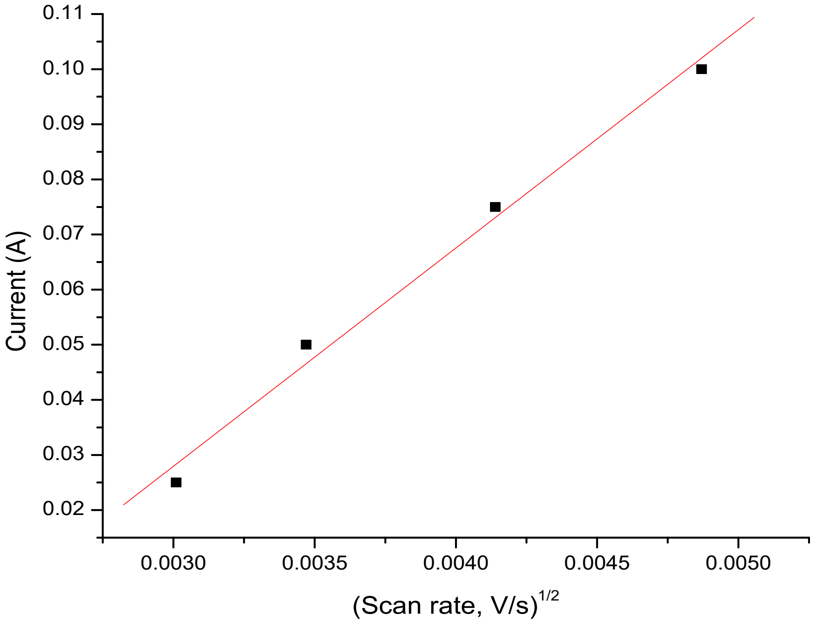


Figure-24: Scan rate dependence of a film of polymer L1 in monomerfree at 25, 50, 75, and 100 mv/s

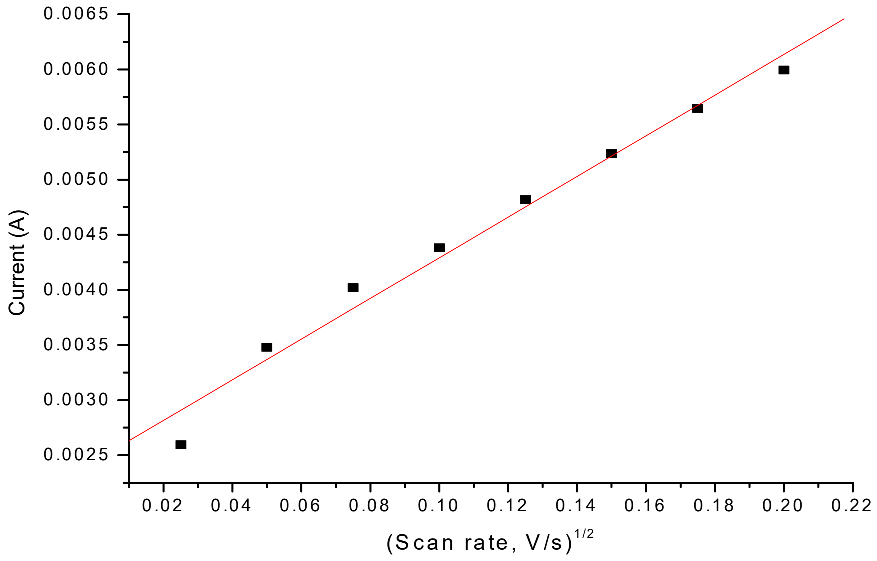


Figure-25: Scan rate dependence of a film of polymer C1 in monomerfree at 25, 50, 75, 100, 125, 150, 175 and 200 mv/s

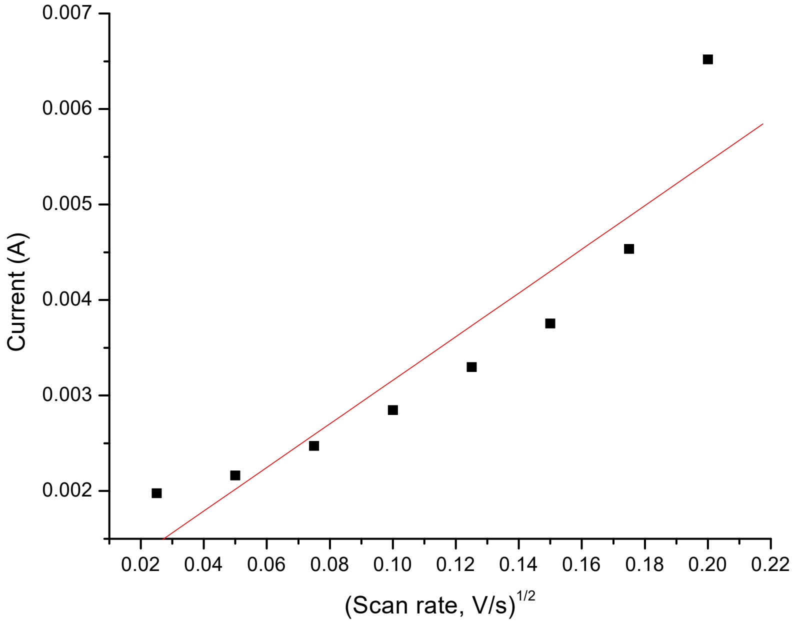


Figure-26: Scan rate dependence of a film of polymer C2 in monomerfree at 25, 50, 75, 100, 125, 150, 175 and 200 mv/s.

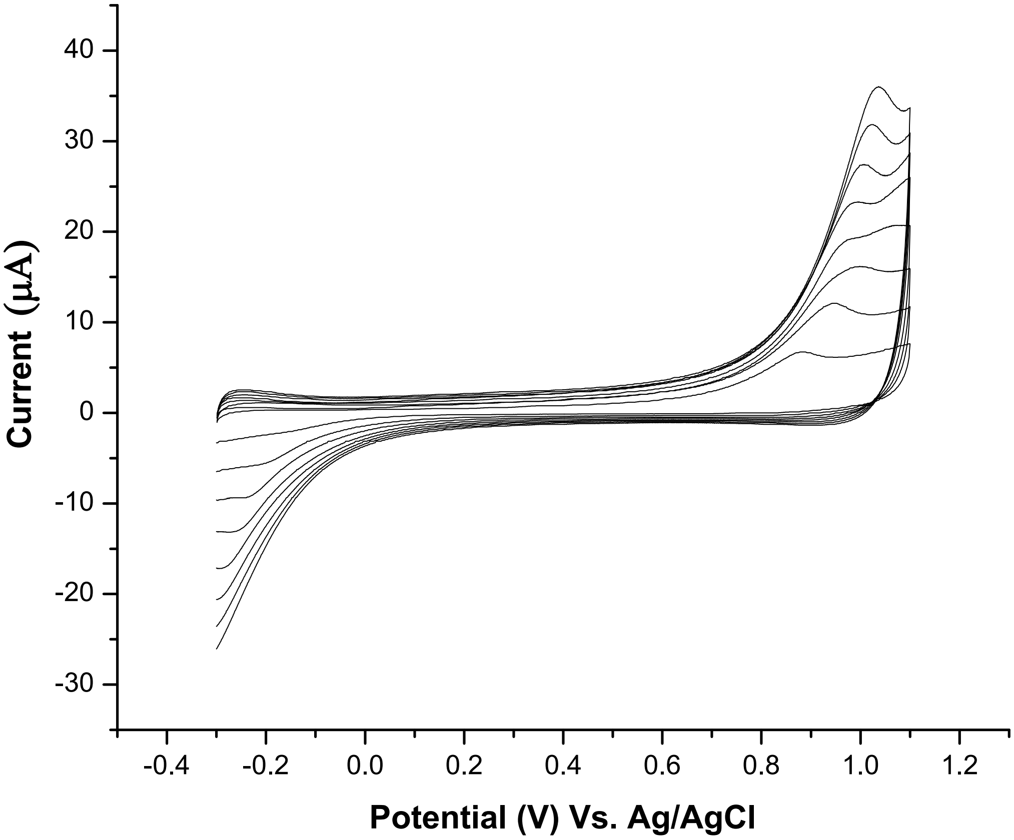


Figure-27: Scan rate dependence of a film of polymerC1 on a glassy carbon electrode. Scan rates were 25 (innermost), 50, 75, 100, 125, 150, 175 and 200 mV/s (outer most).

The voltammogram shape of the polymer film of polyC1 is affected by the scan rate as shown in Figure-27. The peak intensities of the anodic processes depend linearly on the scan rate. The anodic peak potentials move to more positive potentials as sweep rate is increased, and thus this behavior is characteristic of multi-layer modified electrodes, where mass transfer is done through the film, and also of the process with slow electron transfer.

Generally the cyclic voltammogram process values for all monomers and polymers studied are listed in Table-18. This shows the anodic potential of the polymers shifts to lower potential compared with their monomers due to extended conjugation.

The oxidation peak potentials Epa of the series of monomers vary from 0.75 to 1.39 V Vs. Ag/AgCl. The lower oxidation peak potential of C1 indicates higher electron donating ability than other monomers. Generally the oxidation peak potentials increase C1 > C2 > L2 > L1. Observing the cyclic voltammogram of the polyC1 film it has an irreversible reduction wave potential at -0.29V reflects the LUMO level of the terthiophene acceptor heterocycles. The difference in redox potential (Epa-Epc) approximately to the HOMO-LUMO separation determined by the absorption maxima. polyC1 has small values of redox potential which reflects introduction of complexing with nickel terthiophene is favorable for reducing HOMO-LUMO separation[47].

Table-18: Electrochemical results for the cyclic voltammogram processes of the oxidation peak potentials exhibited by the terthiophene based monomers and their corresponding polymers.

| monomer | Eonset | Epa | Epc | Polymer | Epa | Epc |
|---|---|---|---|---|---|---|
| L1 | 0.20 | 0.90, 1.39 | 0.69 | PolyL1 | 0.93 | 0.79 |
| L2 | 0.45 | 1.12, 1.34 | 1.18 | PolyL2 | 0.79, 1.32 | 1.20 |
| C1 | 0.71 | 0.89 | 0.40 | PolyC1 | 0.80 | - |
| C2 | 0.61 | 0.75, 0.99 | 0.65 | PolyC2 | 0.54, 0.88 | 0.64 |

## 5. Conclusions

The electrochemical polymerization and characterization studies of L1, L2, C1 and C2 were made successfully both on glassy carbon and platinum as working electrodes, platinum as counter electrode and silver wire as reference electrode. The result using this two working electrodes is reproducible.

It has developed a series of novel, metal-containing monomers when electropolymerized yield electroactive polymers containing transition metal centers directly attached to the conjugated backbone with $\alpha,\alpha''$-linked polyterthiophene systems. L1 has also the same linkage.

A unique feature of L2 is that it possesses multiple polymerization sites that can be functionalized to selectively afford polymers comprised of both phenylene and thienylene linkages.

Another distinctive feature of the nickel-containing monomer while electropolymerized it shows a reduction in oxidation state of the metal from $Ni^{+2}$ to $Ni^{+1}$. Zinc does not show such property.

It has noticed a distinct difference in the shape during scan of voltammograms for the different polymer types. The thienylene systems exhibit a smooth base current with a very sharp onset, as opposed to the presence broad, sloping onset found in the phenylene -linked systems.

The anodic potential of the polymers shifts to lower potential compared with their monomers due to extended conjugation.

Comparing the cyclic voltammogram of the thienylene unit oxido-reduction process of both metal containing polymer films (the polyC1 and polyC2 film) and ligand polymer films (polyL1 and PolyL2) in monomerfree solution the metal containing polymer films exhibits a better cycling behavior. PolyL1 is relatively stable than PolyL2.

The possible mechanisms for each polymer were suggested based on electrochemical property. Further confirmation of these mechanisms using EPR, UV-Vis, FTIR, $^{1}$H NMR, $^{13}$C {H}NMR, magnetic susceptibility and other advanced spectroscopic instruments are recommended.

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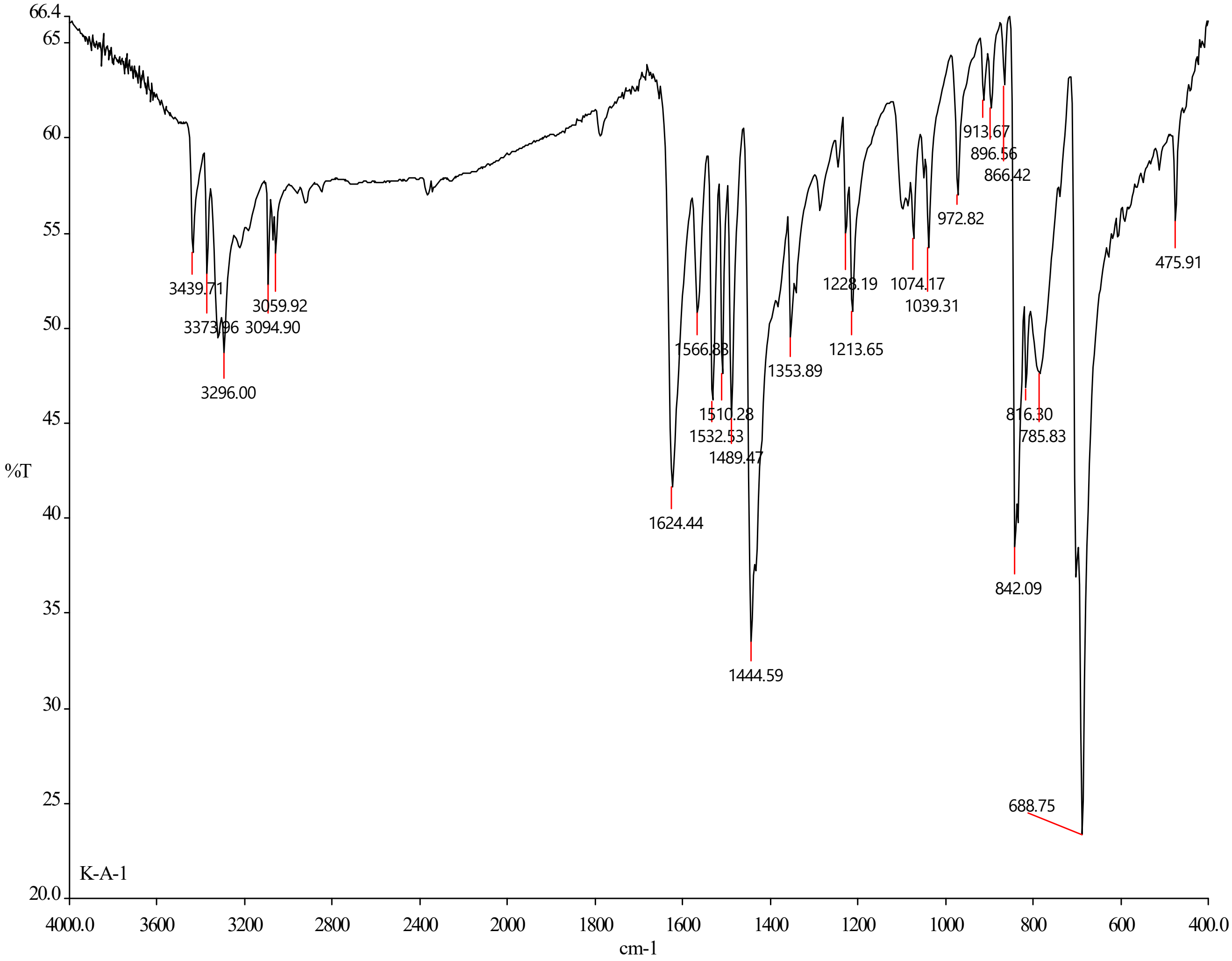
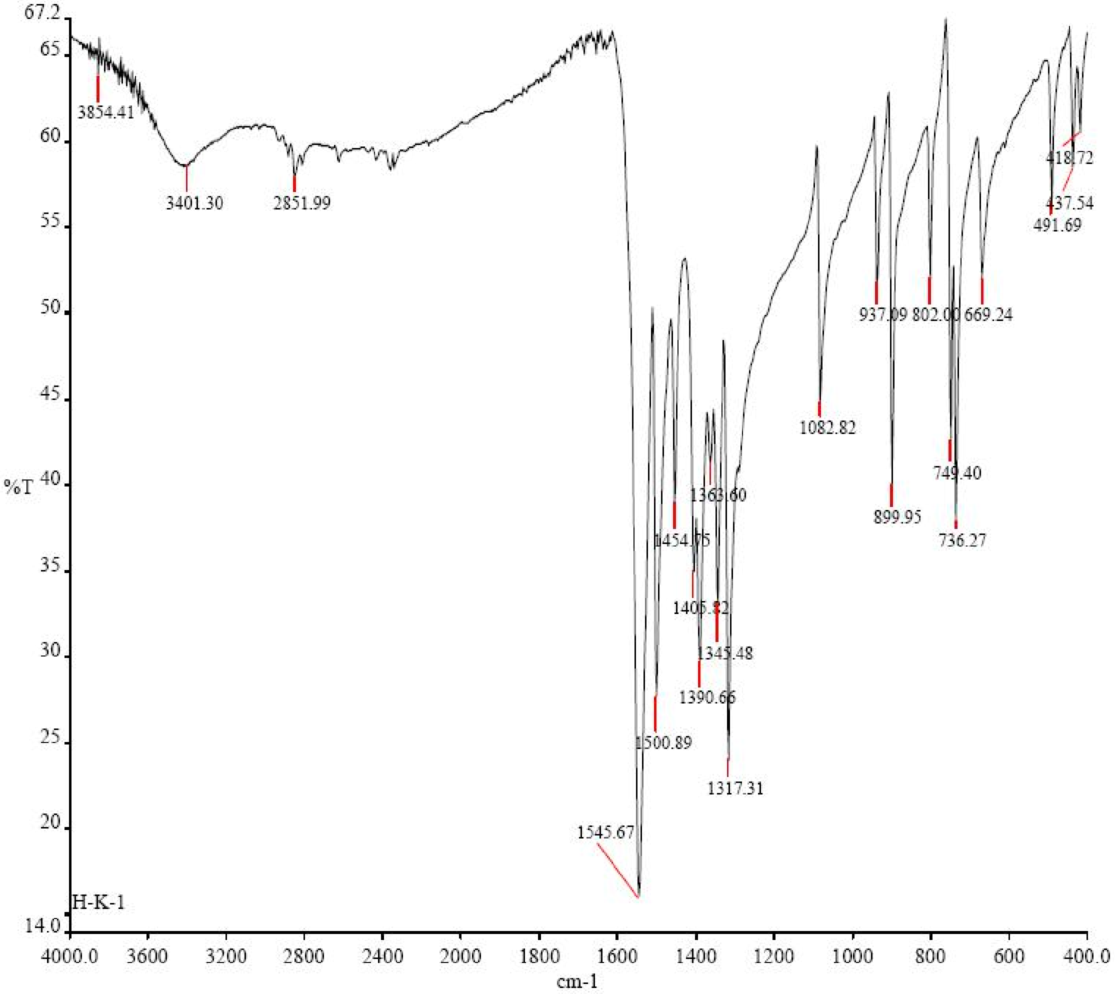
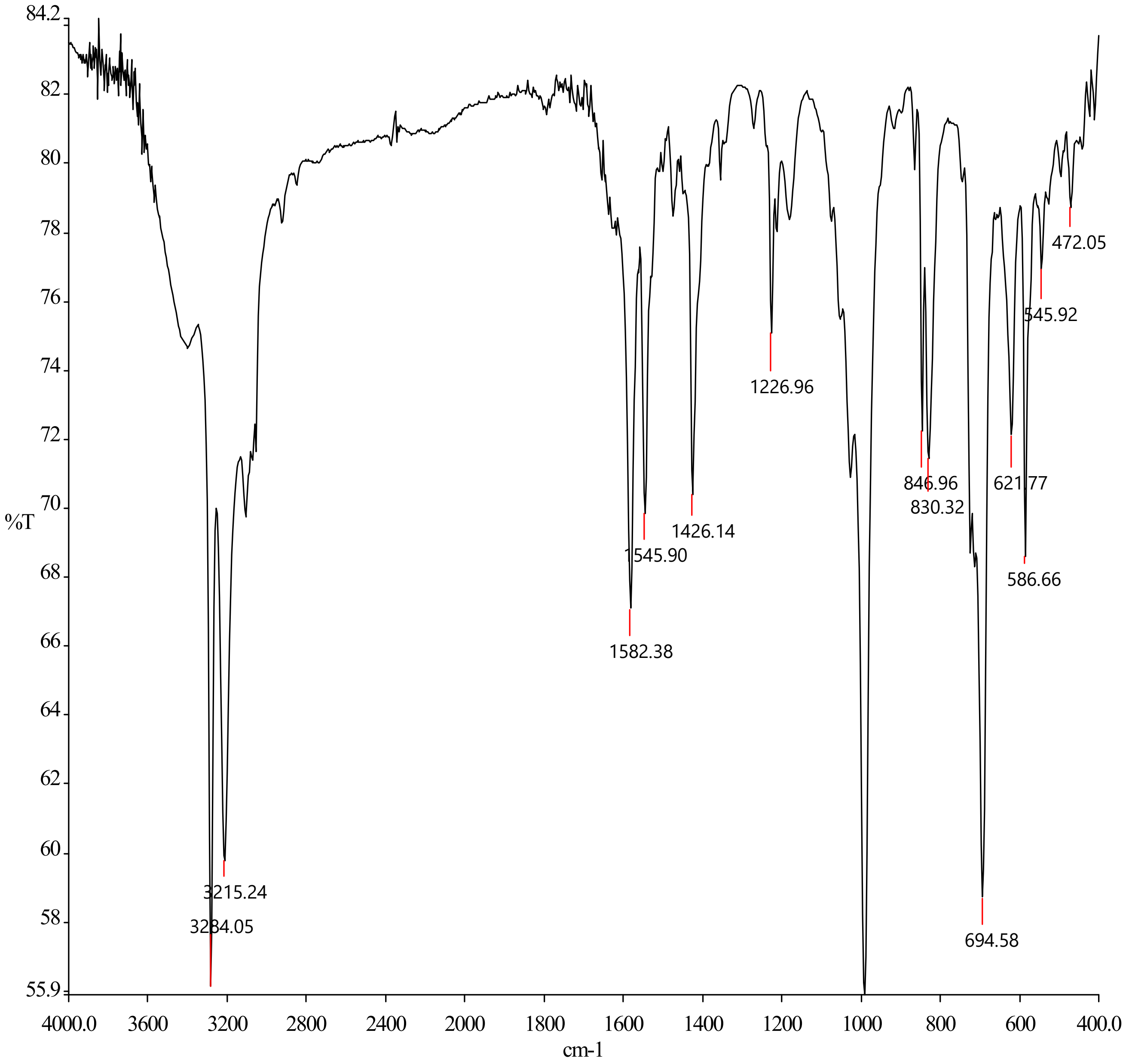
## Appendix 1 IR spectrum of L1



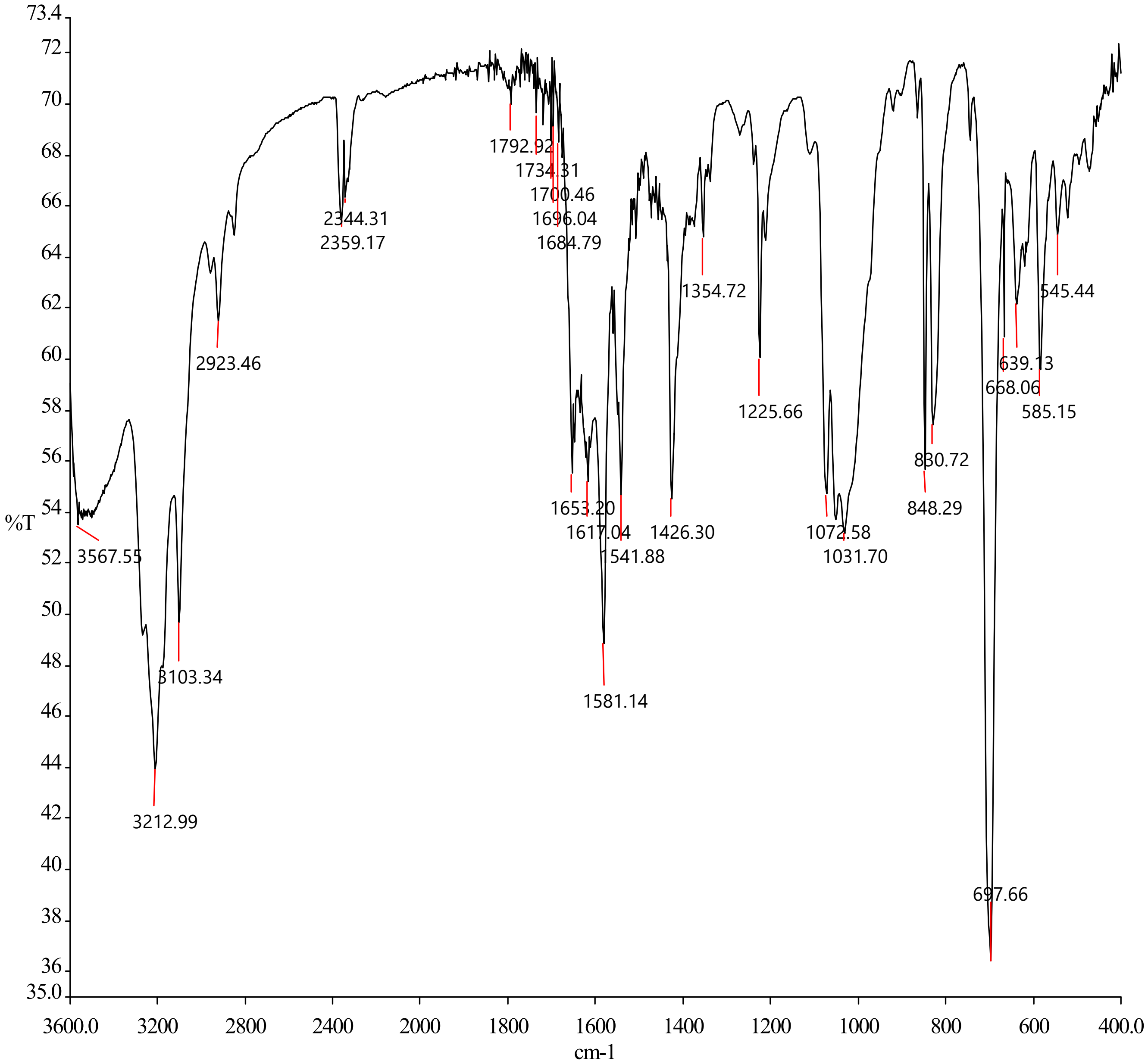
# Appendix 2  IR spectrum of L2



## Appendix 3 IR spectrum of C1



## Appendix 4 IR spectrum of C2



# Declaration

I the undersigned confirm that the results reported in this work were obtained by research carried out by me under the supervision of my advisors in the Faculty of Science, Department of Chemistry, Addis Ababa University in the academic year 2007-2008. No part of this work shall be published in scientific journals or reported in the media or presented at a conference without the knowledge and consent of my advisors, who are the principal scientists responsible for any publication. Furthermore if the work is published the institutional address given should be that of the Chemistry Department, AAU.

Name: ____________________ Signature: __________________

This project work has been submitted for examination with my approval as University advisors.

Advisor: ___________________ Advisor: ___________________

Signature: _________________ Signature: _________________

Place and date of submission: School of Graduate Studies
Addis Ababa University