

SYNTHESES, ELECTROCHEMICAL AND SPECTROELECTROCHEMICAL  
CHARACTERIZATIONS OF BENZOTHIADIAZOLE AND  
BENZOSELENADIAZOLE CONTAINING RANDOM COPOLYMERS

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SPECTROELECTROCHEMICAL CHARACTERIZATIONS OF  
BENZOTHIADIAZOLE AND BENZOSELENADIAZOLE CONTAINING  
RANDOM COPOLYMERS**

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## ABSTRACT

# SYNTHESES, ELECTROCHEMICAL AND SPECTROELECTROCHEMICAL CHARACTERIZATIONS OF BENZOTHIADIAZOLE AND BENZOSELENADIAZOLE CONTAINING RANDOM COPOLYMERS

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Donor-acceptor-donor type conjugated polymers have drawn a tremendous attention in the synthetic modification of optical and electronic properties. Low redox potentials, low band gaps, broad absorption spectrum, processability and durability are some of the crucial parameters for conjugated polymers according to the application areas. Efficient combination of strong electron-accepting units with strong electron-donor species can produce polymers with low oxidation potentials and low band gaps. Besides, introducing alkyl chains onto these donor-acceptor units can solve the solubility problem and provide processability and stability. 2,1,3-Benzothiadiazole (BTh) and 2,1,3-benzoselenadiazole (BSe) are the most commonly preferred acceptor moieties in the donor-acceptor type polymer designs. When their literature examples are considered, it is seen that they are capable of producing low oxidation potential polymers with high efficiencies in optical applications like polymer solar cells when coupled with strong donor units. In this study, strong donor units like carbazole, fluorene and silafluorene were used to achieve an efficient donor-acceptor coupling and intramolecular charge transfer through the backbone. Three conjugated random copolymers were synthesized via Suzuki polycondensation reaction in the presence of Pd (0) catalyst. Characterizations of the synthesized monomers were

done by  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectroscopy. Electrochemical and spectroelectrochemical properties of the corresponding polymers were studied successfully. Cyclic Voltammetry (CV) was carried out in order to observe the redox behavior of polymers. Corresponding HOMO/LUMO energy levels and band gaps were calculated from the CV results. Absorption characteristics were observed via spectroelectrochemical studies and comparable maximum absorption wavelengths, polaron and bipolaron band formations and color changes upon oxidation were reported from the results of absorption spectra of the polymers. Percent transmittance changes and switching times were recorded via kinetic studies. Weight-average ( $M_w$ ) and number-average ( $M_n$ ) molecular weights were measured using Gel Permeation Chromatography (GPC) method. For further characterization, colorimetric studies were done and the scientific color values were reported according to the CIE coordinates. When the electronic and optical results of three copolymers were regarded, they showed enhanced properties such as low oxidation potentials, low band gaps, high solubility in common solvents and chemical stability compared to their counterparts in the literature. Hence they can be promising candidates for optoelectronic applications.

**Keywords:** Donor-Acceptor Type Conjugated Polymers, Benzothiadiazole, Benzoselenadiazole, Donor Effect on Electronic and Optical Properties

## ÖZ

# BENZOTİYADİYAZOL VE BENZOSELENADİYAZOL İÇEREN RASGELE DİZİLİMLİ KOPOLİMERLERİN SENTEZİ, ELEKTROKİMYASAL VE SPEKTROELEKTROKİMYASAL KARAKTERİZASYONU

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Elektronik ve optik özelliklerin sentetik modifikasyonlarında donör-akseptör-donör tipi rasgele dizilimli konjuge kopolimerler büyük ölçüde dikkat çekmektedirler. Uygulama alanları gözönüne alındığında düşük redoks potansiyelleri, dar bant aralıkları, geniş absorpsiyon spektrumları, işlenebilirlik ve dayanıklılık gibi özellikler konjuge kopolimerler için oldukça önemli parametrelerdir. Güçlü elektron-akseptör ünitelerinin elektron-donör üniteler ile verimli eşleşmesiyle düşük oksitlenme potansiyeli ve dar bant aralığı olan polimerler üretilebilir. Bunun yanı sıra elektron-akseptör ve donör ünitelerine alkil gruplarının bağlanması oluşabilecek çözünürlük problemlerinin çözülmesini sağlayıp üretilen polimerlerin işlenebilirliğini ve dayanıklılığını artırabilmektedir. 2,1,3-Benzotiyadiyazol ve 2,1,3-benzoselenadiyazol üniteleri donör-akseptör tipi konjuge polimer dizaynlarında en çok tercih edilen akseptör üniteleridir. Literatürdeki örnekleri göz önüne alındığında, kuvvetli elektron-donör üniteleri ile birlikte kullanılan benzotiyadiyazol ve benzoselenadiyazol moleküllerinin düşük redoks potansiyeline ve dar bant aralıklarına sahip polimer ürettiği ve üretilen bu polimerlerin de güneş pili gibi uygulama alanlarında yüksek verim gösterdiği görülmektedir. Bu çalışmada karbazol, fluoren ve silafluoren üniteleri verimli bir akseptör-donör eşleştirmesini ve bu sayede de polimer zinciri üzerinde

intramoleküler yük transferini sağlamak amacıyla kullanılmıştır. Üç yeni rasgele dizilimli kopolimerin sentezi Pd (0) katalizörü kullanılarak Suzuki polikondansiyon kenetlenme reaksiyonu ile gerçekleştirilmiştir. Sentezlenen monomerlerin karakterizasyonu  $^1\text{H}$  ve  $^{13}\text{C}$  Nükleer Manyetik Rezonans Spektroskopisi (NMR) ile yapılmıştır. Polimerlerin elektrokimyasal ve spektroeletrokimyasal özellikleri başarıyla çalışılmıştır. Redoks davranışlarını gözlemek ve de HOMO/LUMO enerji seviyeleri ve bant aralıklarını hesaplamak için Dönüşümlü Voltametre (CV) kullanılmıştır. Maksimum absorpsiyonun gerçekleştiği dalga boyu, polaron ve bipolaron bant oluşumları ve renk değişimleri gibi absorpsiyon özellikleri de UV-Vis spektrofotometre yardımıyla gözlemlenebilmiştir. Malzemelerin nötral ve yükseltgenmiş halleri arasındaki yüzde geçirimsizlik değişimi (T %) ve renk değişim süresi (s) kinetik çalışmalar ile hesaplanmıştır. Ağırlık ( $M_w$ ) ve sayısal ( $M_n$ ) ortalamalı moleküler ağırlıkları Pelte Geçirim Kromatografisi (GPC) ile ölçülmüştür. Kolorimetre metodu ile polimerlerin nötral ve oksitli hallerinin renkleri kaydedilmiş ve CIE koordinasyonları temel alınıp bilimsel olarak rapor edilmiştir. Tüm bu karakterizasyon çalışmalarının sonuçlarına bakılacak olunursa, sentezlenen üç kopolimer de literatürdeki benzer örneklerinden gelişmiş elektronik ve optik özelliklere sahiptir. Daha düşük potansiyelerde yükseltgenip-indirgenibilme, daha dar bant aralıklarına, daha geniş absorpsiyon spektrumlarına ve kimyasal kararlılığa sahip olma ve de yaygın çözücülerde çözünebilir olma özelliklerinden dolayı optoelektronik uygulama alanlarında yüksek potansiyele sahiptirler.

**Anahtar kelimeler:** Donör-Akseptör Tipi Konjuge Polimerler, Benzotiyadiyazol, Benzoselenadiyazol, Donör Ünitelerinin Elektronik ve Optik Özelliklerin Üzerindeki Etkisi

*To My Family*

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## TABLE OF CONTENTS

ABSTRACT .....	v
ÖZ.....	vii
ACKNOWLEDGMENTS .....	x
TABLE OF CONTENTS .....	xii
LIST OF TABLES .....	xv
LIST OF FIGURES .....	xvi
ABBREVIATIONS .....	xviii
CHAPTERS.....	1
1. INTRODUCTION .....	1
1.1. Chromism .....	1
1.2. Electrochromism.....	1
1.3. Electrochromic Material Types .....	2
1.3.1. Metal Oxides.....	2
1.3.2. Viologens .....	3
1.3.3. Prussian Blue .....	5
1.3.4. Conjugated Conducting Polymers .....	6
1.4. Toolbox for Electrochromism .....	7
1.4.1. Electrochromic Contrast .....	7
1.4.2. Coloration Efficiency.....	7
1.4.3. Colorimetric Analysis .....	8
1.4.4. Switching Time.....	9
1.4.5. Stability.....	9
1.4.6. Optical Memory .....	10
1.5. Electrochromic Devices: Types and Application Areas.....	10
1.5.1. Reflective Electrochromic Devices: Rear-view Mirrors.....	12
1.5.2. Transmissive Electrochromic Devices: Smart Windows.....	12
1.5.3. Electrochromic Displays .....	13
1.6. Conjugated Conducting Polymers .....	13
1.6.1. Conjugation in Conducting Polymers.....	15

1.6.2. Doping Process .....	17
1.6.3. Toolbox for Band Gap Engineering .....	20
1.6.4. Syntheses of Conducting Polymers .....	22
1.6.4.1. Electrochemical Polymerization .....	23
1.6.4.2. Oxidative Chemical Polymerization .....	24
1.6.4.3. Suzuki Coupling .....	26
1.6.4.4. Stille Coupling .....	26
1.6.4.5. Yamamoto Coupling.....	27
1.6.4.6. Heck Coupling .....	28
1.6.4.7. Tamao-Kumada-Corriu Coupling.....	28
1.6.4.8. Grignard Metathesis (GRIM).....	29
1.6.4.9. Rieke Method.....	30
1.6.4.10. Sonogashira Coupling.....	30
1.6.4.11. Knoevenagel Condensation .....	31
1.7. Strong Electron-Acceptor Units: Benzothiadiazole and Benzoselenadiazole	31
1.8. Strong Electron-Donor Units: Carbazole, Fluorene and Silafluorene .....	32
1.9. Aim of This Work .....	33
2. EXPERIMENTAL .....	35
2.1. Materials.....	35
2.2. Methods and Equipment .....	35
2.3. Syntheses of Monomers .....	37
2.3.1. Synthesis of 4,7-dibromobenzo[c][1,2,5]thiadiazole (1).....	37
2.3.2. Synthesis of 3,6-dibromobenzene-1,2-diamine (2) .....	38
2.3.3. Synthesis of 4,7-dibromo-benzo[c][1,2,5]selenadiazole (3) .....	38
2.4. Syntheses of Polymers .....	39
2.4.1. Synthesis of P1 .....	39
2.4.2. Synthesis of P2 .....	40
2.4.3. Synthesis of P3 .....	42
3. RESULTS and DISCUSSION .....	43
3.1. Electrochemical Characterizations of Polymers .....	43
3.1.1. Cyclic Voltammetry Studies .....	43
3.1.2. Scan Rate Dependence Studies .....	46

3.2. Spectroelectrochemical Characterizations of Polymers .....	48
3.2.1. Optical Studies .....	48
3.2.2. Kinetic Studies .....	50
3.2.3. Colorimetric Studies .....	52
CONCLUSION .....	55
REFERENCES .....	57
APPENDIX .....	63
NMR Spectra of Synthesized Monomer and Polymers.....	63

## LIST OF TABLES

### TABLES

Table1.1. Color control of the radical cation via suitable substituent on nitrogen atom .....	4
Table3.1: Electrochemical results of the polymers .....	45
Table3.2: Results of the optical studies of the polymers .....	49
Table3.3: Optical contrast and switching time results of the polymers .....	52
Table3.4: Results of the colorimetric studies of the polymers .....	53

## LIST OF FIGURES

### FIGURES

Figure1.1: A general representation of the electrochemical reduction of $\text{WO}_3$ .....	3
Figure1.2: Electrochemical reduction representation of viologens .....	5
Figure1.3: A general diagram for an electrochromic device .....	11
Figure1.4: An application of smart windows in buildings .....	13
Figure1.5: Structures of most commonly used conjugated polymers .....	14
Figure1.6: Energy level diagram showing the relation between electron affinity (EA), ionization potential (IP) and band gap ( $E_g$ ) .....	15
Figure1.7: Molecular orbital diagram and band gap depression in conjugated polymers .....	17
Figure1.8: Charge carriers in chemical terms .....	18
Figure1.9: A schematic description of the formation of polaron, bipolaron and soliton pair for PA doping .....	19
Figure1.10: In polythiophenes two mesomeric forms are not energetically equal unlike in polyenes .....	20
Figure1.11: Structural factors affecting the band gap of materials .....	22
Figure1.12: A representation of catalytic cycle of transition-metal catalyzed reactions .....	23
Figure1.13: Electrochemical polymerization (ECE mechanism) of heterocycles (X=S, O, NH) .....	25
Figure1.14: Oxidative chemical polymerization of thiophene .....	24
Figure1.15: A representation of Suzuki polycondensation .....	26
Figure1.16: Stille polycondensation reaction .....	27
Figure1.17: Synthesis of polycarbazole by Yamamoto reaction .....	28
Figure1.18: Heck reaction of a vinylthiophene .....	28
Figure1.19: General representation of Kumada cross-coupling reaction .....	29
Figure1.20: Synthesis of poly(3-hexylthiophene) by Kumada reaction .....	29
Figure1.21: Synthesis of regioregular poly(3-hexyl thiophene) by GRIM method .....	30
Figure1.22: Synthesis of poly(3-alkylthiophene) by Rieke reaction .....	30

Figure1.23: A general representation of Sonogashira coupling reaction .....	31
Figure1.24: A general representation of Knoevenagel coupling reaction .....	31
Figure2.1: A simple representation of the cyclic voltammetry set up .....	36
Figure2.2: Synthetic route of 4,7-dibromobenzo[c][1,2,5]thiadiazole.....	37
Figure2.3: Synthetic route of 3,6-dibromobenzene-1,2-diamine .....	38
Figure2.4: Synthetic route of 4,7-dibromo-benzo[c][1,2,5]selenadiazole .....	39
Figure2.5: Synthesis of P1 via Suzuki polycondensation .....	40
Figure2.6: Synthesis of P2 via Suzuki polycondensation .....	41
Figure2.7: Synthesis of P3 via Suzuki polycondensation .....	42
Figure3.1: Single scan cyclic voltammetry results of a) P1, b) P2 and c) P3 in 0.1 M TBAPF <sub>6</sub> /ACN solution at 100mV/s scan rate .....	44
Figure3.2: Scan rates studies of a) P1 and b) P2 in 0.1 M TBAPF <sub>6</sub> /ACN solution at different scan rates .....	47
Figure3.3: Electronic absorption spectrum of a) P1, b) P2 and c) P3 in 0.1 M TBAPF <sub>6</sub> /ACN solution upon oxidative doping potentials .....	50
Figure3.4: Percent transmittance changes and switching times of a) P2 and b) P3 when switched between neutral and oxidized states in 0.1 M TBAPF <sub>6</sub> /ACN solution .....	51
Figure3.5: Colors of a) P1, b) P2 and c) P3 in their neutral and oxidized states .....	53
FigureA1: <sup>1</sup> H-NMR spectrum of 4,7-dibromobenzo[c][1,2,5]thiadiazole .....	63
FigureA2: <sup>13</sup> C-NMR spectrum of 4,7-dibromobenzo[c][1,2,5]thiadiazole .....	64
FigureA3: <sup>1</sup> H-NMR spectrum of 3,6-dibromobenzene-1,2-diamine .....	65
FigureA4: <sup>13</sup> C-NMR spectrum of 3,6-dibromobenzene-1,2-diamine .....	66
FigureA5: <sup>1</sup> H-NMR spectrum of 4,7-dibromo-benzo[c][1,2,5]selenadiazole ....	67
FigureA6: <sup>13</sup> C-NMR spectrum of 4,7-dibromo-benzo[c][1,2,5]selenadiazole ....	68
FigureA7: <sup>1</sup> H-NMR spectrum of P1 .....	69
FigureA8: <sup>1</sup> H-NMR spectrum of P2 .....	70
FigureA9: <sup>1</sup> H-NMR spectrum of P3 .....	71

## ABBREVIATIONS

<b>ACN</b>	Acetonitrile
<b>BLA</b>	Bond Length Alternation
<b>BSe</b>	2,1,3-Benzoselenadiazole
<b>BTh</b>	2,1,3-Benzothiadiazole
<b>CB</b>	Conduction Band
<b>CE</b>	Coloration Efficiency
<b>CIE</b>	La Commission Internationale de l'Eclairage
<b>CP</b>	Conducting Polymer
<b>CV</b>	Cyclic Voltammetry
<b>DCM</b>	Dichloromethane
<b>EA</b>	Electron Affinity
<b>EC</b>	Electrochromic
<b>ECD</b>	Electrochromic Device
<b>E<sub>g</sub></b>	Band Gap Energy
<b>GPC</b>	Gel Permeation Chromatography
<b>HOMO</b>	Highest Occupied Orbital Level
<b>ICT</b>	Intramolecular Charge Transfer
<b>IP</b>	Ionization Potential
<b>ITO</b>	Indium Tin Oxide
<b>IVCT</b>	Intervalence Charge Transfer
<b>L, a, b</b>	Luminance, hue, saturation
<b>LUMO</b>	Lowest Unoccupied Orbital Level
<b>NHE</b>	Normal Hydrogen Electrode (Standard Hydrogen Electrode)
<b>NMR</b>	Nuclear Magnetic Resonance
<b>PA</b>	Polyacetylene
<b>PB</b>	Prussian Blue
<b>PEDOT</b>	Poly(3,4-ethylenedioxythiophene)
<b>PPV</b>	Poly(para phenylene vinylene)
<b>PPy</b>	Polypyrrole
<b>PT</b>	Polythiophene

<b>TBAPF<sub>6</sub></b>	Tetrabutylammonium hexafluorophosphate
<b>TMS</b>	Tetramethyl silane
<b>VB</b>	Valence Band



# CHAPTER 1

## INTRODUCTION

### 1.1. Chromism

Chromism is a reversible change in color of a material because of an external stimulus. There are several types of chromism such as thermochromism due to temperature change, photochromism as a result of electromagnetic radiation, halochromism based on a pH change of a solution, solvatochromism induced by solvents or electrochromism based on an applied potential or electrochemical redox reaction.

### 1.2. Electrochromism

Electrochromism can be defined as the visible and reversible change in optical properties of a material via external potential. The phenomenon of electrochromism first started with the studies of Deb with vanadium trioxide ( $\text{WO}_3$ ) thin film in 1969 [1]. Neutral thin film of  $\text{WO}_3$  ( $\text{W}^{\text{VI}}$ ) has a very pale yellow color; however, when it is reduced to  $\text{W}^{\text{V}}$  state it turns into an intense blue color. Since then electrochromic materials have gained increasing popularity due to their special spectroelectrochemical properties and potentials to be used in optical devices [2]. The color change can be between a colored and bleached state, between two colored states or electroactive materials can switch between multi colors and are referred as polyelectrochromic (multicolored) materials. Electrochromic (EC) materials can be classified into two main parts as inorganic



Thin films of  $\text{WO}_3$ , with all tungsten sites with oxidation state  $\text{W}^{\text{VI}}$ , are transparent. Upon electrochemical reduction,  $\text{W}^{\text{V}}$  sites are produced to yield an intense blue color [6]. Although the exact mechanism is unknown, electrons/protons/metal cations are responsible for the coloration mechanism. The generalized representation is shown in Figure 1.1.

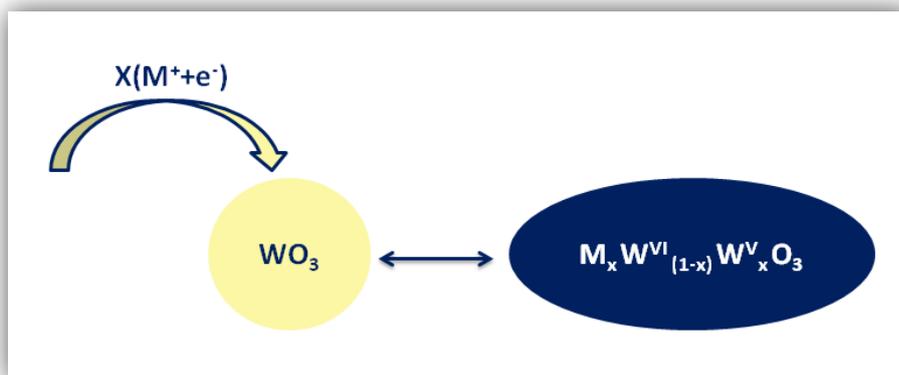


Figure 1.1. A general representation of the electrochemical reduction of  $\text{WO}_3$

Oxides of molybdenum, niobium, titanium, tungsten and vanadium are cathodically coloring materials. In contrast, some metal oxides such as cobalt, iridium and nickel become colored upon electrochemical oxidation (anodically coloring materials).

### 1.3.2. Viologens

Viologens or with another name 1,1'-disubstituted 4,4'-bipyridinium ions, are salts of quarternized 4,4'-bipyridine molecules. They have been known since Michaelis et al. reported electrochromic properties of those molecules and named as "viologens" in 1933 [7]. Viologens have been used as indicators, herbicides, electron-transfer mediators due to their unique electrochemical properties like having the lowest redox potential (most cathodic) of organic systems showing reversibility [8]. More recently electrochromic display devices such as liquid crystal displays or light emitting diodes constructed from the viologens or

viologens with polymer blends have gained the interest in industry [9]. Viologens possess three redox states, namely  $V^{2+}$ ,  $V^{+}$  and  $V^0$ . The first reduction step is highly reversible and can be cycled for many times; however, the second reduction is not as reversible as the first one since the uncharged form is an insoluble species. Of the three oxidation states dication form is the most stable and colorless state. When it is reduced to the radical cation form it shows an intense color. Charge transfer between +1-valent and 0-valent nitrogen atoms provides efficient coloration and high absorption coefficients. According to the substituent on nitrogen atoms radical cation reveals different colors. For example alkyl groups reveal blue-violet color whereas aryl groups like cyanophenyl show green color upon reduction.

Table1.1. Color control of the radical cation via suitable substituent on nitrogen atom

<b>R</b>	<b>Color (thin film)</b>
<b>Methyl</b>	Blue
<b>Ethyl</b>	Blue
<b>Phenyl</b>	Purple
<b>Heptyl</b>	Mauve
<b>Octyl</b>	Crimson
<b>Benzyl</b>	Mauve
<b>4-CN-Ph</b>	Green/Black

The most extensively studied material of the viologen family is methyl viologen. While dication form is colorless, its reduced state, radical cation, possesses deep blue color as shown in the Figure 1.2.

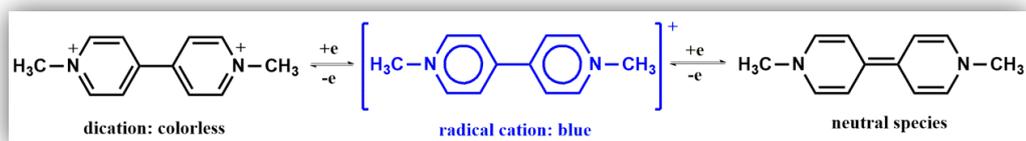
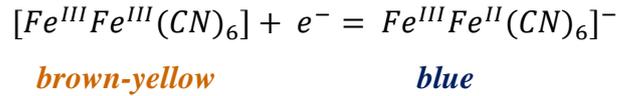


Figure 1.2. Electrochemical reduction representation of viologens

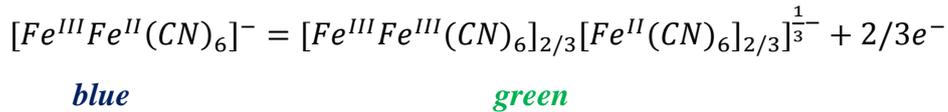
### 1.3.3. Prussian Blue

Prussian blue (PB) is the first modern synthetic pigment that dates back to 1700s [10]. Johann Jacob Diesbach, a color manufacturer in Berlin, discovered the intense blue color accidentally in 1706 [11]. He was producing the red color by extracting the cochineal with alum and vitriol (ferrous substrate) that he borrowed from Johann Konrad Dippel, a well-known alchemist. After four years of the discovery, first publication of this new pigment was published in *Miscellanea Berolinensia* by Johann Leonhard Frisch in 1710 [12]. Following this report, PB and its analogues have gained attention especially in electrochromic device applications [13]. Prussian blue is a precedent of polynuclear transition-metal hexacyano metallates that are insoluble mixed-valence compounds. These materials are represented with a general formula  $M'_x [M''(\text{CN})_6]_y \cdot z\text{H}_2\text{O}$  ( $x, y, z$  integrals) where  $M'$  and  $M''$  are transition metals with different oxidation states. Intense blue color of the iron (III) hexacyanoferrate (III) originates from the intervalence charge transfer (IVCT) between those different mixed-valence iron states. It does not pertain to ferric or ferrocyanide ion used in the preparation of PB and this unexpected color was attributed to the “oscillation of valence” [14].

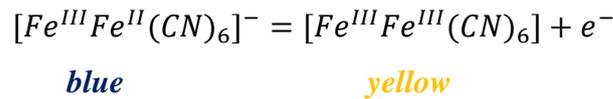
Electrochemical reduction of solutions containing iron (III) and hexacyanoferrate (III) ions is one of the PB thin film synthesis methods, in which the iron (III) hexacyanoferrate (III) ions are at equilibrium with iron (III) hexacyanoferrate (III) complex. Reduction of this brown-yellow complex is the principal charge transfer in PB electrodeposition process:



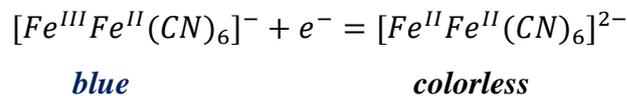
Prussian blue has several colors such as green, yellow or colorless according to the oxidation/reduction process:



While oxidation of the PB produces a green color state, further oxidation yields the yellow state as shown:



Reduction of the PB forms the colorless state:



### 1.3.4. Conjugated Conducting Polymers

Conjugated conducting polymers are a novel class of semiconductors that combine the optical and electronic properties of semiconductors with the processing advantages and mechanical properties of the polymers. While they are insulator in their neutral states, they become electro active upon chemical or electrochemical oxidation of aromatics such as thiophene, pyrrole, furan, carbazole and derivatives [15]. Colors of conjugated polymers (CP) can switch between a colored and bleached state or material can show multichromism (polyelectrochromism) upon applied potential. The color change between the neutral and oxidized states depends on the band gap between valence and

conduction band. Polymers with band gaps higher than 3 eV (which means maximum absorption wavelengths smaller than 400 nm) are transparent in their neutral states. Thus, polymers with arbitrate band gaps possess clear/visible optical changes and can show different colors.

## **1.4. Toolbox for Electrochromism**

### **1.4.1. Electrochromic Contrast**

Electrochromic contrast is generally reported as the percent transmittance change ( $\Delta T$  %) at a given wavelength. Although this wavelength is chosen from the spectroelectrochemical studies at which the electrochromic compound shows the maximum optical contrast, the electrochromic contrast can be observed and reported at any absorption wavelength when desired. Transmittance change is recorded upon applied square-wave potential to the electrochromic compound placed in a spectrophotometer.

### **1.4.2. Coloration Efficiency**

Coloration efficiency (CE) can be defined as the proportionality factor that shows the relationship between the optical absorption change of an electrochromic compound ( $\Delta A$ ) and the density of injected/ejected charges ( $Q_d$ ) to provide a full switch at a given wavelength [16]. An ideal electrochrome should demonstrate a large transmittance change with a small amount of charge to provide high coloration efficiency. The quantitative calculation of the coloration efficiency is made according to the Beer-Lambert equation:

$$CE = \frac{\Delta A}{Q_d} = \frac{\log \frac{T_{ox}}{T_{neut}}}{Q_d}$$

where  $T_{\text{neut}}$  and  $T_{\text{ox}}$  are the transmittance values at neutral (dedoped) and oxidized (doped) states of the electrochrome.  $Q_d$  is in  $\text{C}\cdot\text{cm}^{-2}$  and CE is in  $\text{cm}^2\cdot\text{C}^{-1}$ . As seen from the equation, transmittance values are very crucial in coloration efficiency of electrochromes. Hence, especially working with compounds having a bleached state in their oxidized form, coloration efficiency becomes a very useful method for the color characterization. As the material gets oxidized and becomes colorless, the lower charge carrier bands tend to overlap in visible region and decrease the CE of the whole material since a fully bleached state is never accomplished.

### 1.4.3. Colorimetric Analysis

Description of a color or comparison of two colors is a subjective phenomenon because of personal errors. In order to avoid those errors and report a color with objective and scientific results there have been many studies in the literature [17]. Basically there are three main characters assigning a color. First one describes a color by its spectral location which means the wavelength of light is related with the color. This character is known as the “hue” which is the wavelength character of the color. Second one is known as the saturation, intensity, purity or tone of a color. It is related with the level of black/white intensity. Third attribution is the luminescence or brightness of color.

The most commonly used color system is the one reported by The Commission Internationale de l’Eclairage (International Commission on Illumination) which is known as the CIE color coordination [18]. CIE colorimetric system defines the color coordinates with tristimulus ( $x, y, z$ ) in order to give all color spaces. Three most commonly used CIE color spaces are 1931 Yxy, 1976  $L^*u^*v^*$  and 1976  $L^*a^*b^*$  systems. Among them  $L^*a^*b^*$  system is the mostly preferred one in the industry. It is also calculated from the Yxy tristimulus values determined from a colorimeter, where Y represents the luminescence and xy two-dimensional coordination values define the hue and saturation of a color. Brightness of a color,

Y, is defined as the percentage of the light transmitted relative to the light incoming:

$$Y\% = \frac{Y}{Y_0} * 100$$

#### **1.4.4. Switching Time**

Switching time can be defined as the time required for an electrochrome switching from one redox state to another. There are several parameters affecting it such as the chemical stability of the electrochrome, conductivity of the electrolyte, ease of diffusion of counter balancing ions across the electrochromic layer, thickness and morphology of the film or electrochromic device (ECD) construction (architecture). Small switching times (rapid switching) is required especially in electrochromic display applications.

#### **1.4.5. Stability**

An electrochromic material can possess stable redox processes in order to show reproducible repeated switching. For an electrochromic device, degradation of one of the redox state will decrease the overall performance of the redox couples. Generally degradation can occur via irreversible redox behavior, redox interferences of water and oxygen, degradation of electrode materials or evaporation of electrolyte upon heating. Long-term stability experiments are generally performed in a three-electrode system for electrochromes or a two-electrode system for electrochromic devices via repeated potential cycles. Electrochromic devices can be sealed or encapsulated in order to prevent solvent evaporation and decrease the air related oxidations of the electroactive materials.

#### **1.4.6. Optical Memory**

The optical or electrochromic memory (also called as the open-circuit memory) can be defined as the tendency of an electrochrome to retain neutral/doped state color upon removal of the potential. A memory loss occurs when the inserted charge is removed via an electrical escape or ion diffusion. It can be performed applying potential pulses to the EC material and the self-erasing behavior of the material can be observed. For an efficient system EC material should quickly come back to its original state when the pulse is removed.

#### **1.5. Electrochromic Devices: Types and Application Areas**

Electrochromic materials and devices have gathered a huge attention due to their unique properties since they are discovered. An electrochromic device (ECD) which is a rechargeable battery consists of an electrochromic electrode separated from a charge balancing counter electrode by a suitable electrolyte. Color change occurs by charging and discharging the electrochemical cell with applied potentials, which means that electrochromic operation of an ECD is affected via an external power supply.

All electrochromic devices are electrochemical cells. Hence, as shown in Figure 1.3 each ECD contains a minimum of two electrodes separated by an ion-containing electrolyte, which is ionically conductor but electronically insulator [19]. One of the electrodes is an optical electrode consisting of a glass slide coated with a transparent conducting oxide such as indium tin oxide (ITO), fluorinated tin oxide (FTO), aluminum doped zinc oxide (AZO). The second electrochromic electrode (counter electrode) can be another inward-facing optically transparent electrode if the device is operating in transmittance mode. Alternatively, devices operating in a reflectance mode generally require the second electrode to be made of polished metal, the metal being chosen both for its electronic conductivity and ability to act as a reflector [20].

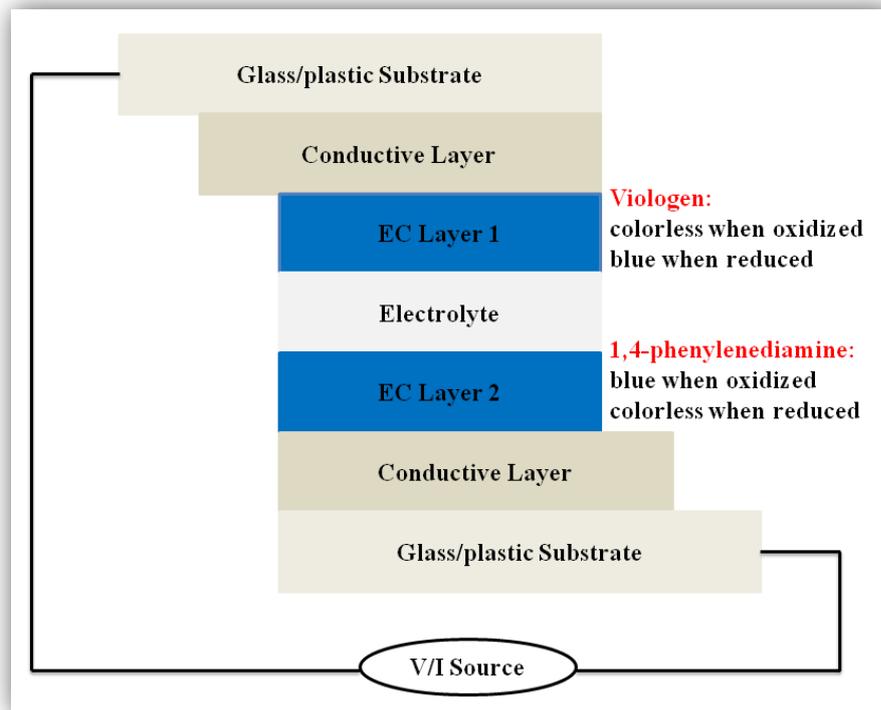


Figure1.3. A general diagram for an electrochromic device

Electrochromic devices can be classified according to two arguments; electrolyte type or working mode of the ECD.

According to the electrolyte used in the construction there are two types of ECDs:

a) Solid state devices: If solid organic or inorganic electrolytes are used it is called as solid state electrochromic device.

b) Laminated devices: If liquid electrolytes are used it is called laminated electrochromic device.

In addition to solid and liquid ones gel electrolytes can be used according to the application area of the device.

If the working principle is considered, there are two types of ECDs:

a) Transmissive mode devices: Transparent electrodes are used in order to control the light intensity like in smart windows.

b) Reflective mode devices: Transparent or reflective electrodes (Al, Ag, and Au) are used like in displays or rear-view mirrors of cars.

Generally all electrochromic devices utilizing color modulation fall into two main categories: electrochromic devices operating in transmission mode or in reflectance mode. They are used in displays, rear-view mirrors and sunroofs in cars, transmissive/absorptive windows, shutters, so on.

### **1.5.1. Reflective Electrochromic Devices: Rear-view Mirrors**

In rear-view mirrors of cars, each mirror has electrochromic gel between two pieces of glass and is equipped with sensors that detect the intensity of glare from the vehicles travelling behind. Then it sends voltage to the mirror's EC gel in proportion to the amount of glare detected, causing the gel to darken and the glass to be effectively tinted. The darkening of the gel is proportional with the intensity of glare detected, thus allowing the driver to see well through the rear-view mirror.

### **1.5.2. Transmissive Electrochromic Devices: Smart Windows**

Since Swensson and Granqvist coined the term “smart window” in 1985 to describe windows that electrochemically change in transmittance, they have been in trend where electrochemically driven modulations of light transmittance and reflectance have important roles like in the improvements in energy efficiency in buildings, aircrafts, and etc [21]. Electrochromic windows control the light transmittance and solar energy passing through the windows. As seen from the Figure 1.4 before direct sun enters the window, electrochromic glazings are fully bleached at their neutral states. After direct sun enters the window, these electrochromic glazings switch to fully colored, darkest transparent state and fluorescent light dims accordingly.

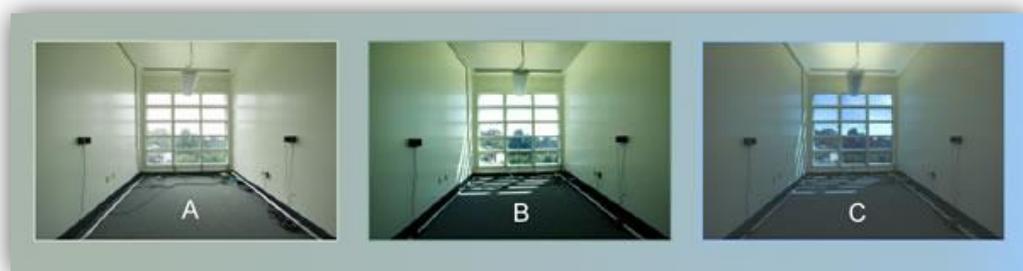


Figure 1.4. An application of smart windows in buildings

### 1.5.3. Electrochromic Displays

Electrochromic devices operating as displays can act in either reflective or transmissive modes; however, the majority belongs to the reflectance mode. Electrochromic devices have been used for flat-panel displays applications such as television screens, data boards at transport stations, advertising boards, and even as electrochromic indicators (based on  $\text{WO}_3$ ) on a cash card. Flat-panel display application areas increase very rapidly, and are combined with a wide array of electronic devices from calculators and watches to mobile phones and computer screens.

### 1.6. Conjugated Conducting Polymers

A polymer (a material containing a long chain of molecular structures) was the first and foremost an insulator. The idea that polymers or plastics could conduct electricity was considered as ridiculous. This idea was changed nearly a century ago, with the discovery of conductivity in polyacetylene upon doping with the pioneering study by Alan J. Heeger, Alan MacDiarmid, and Hideki Shirakawa [22]. Polyacetylene (PA) was known as a black powder until Shirakawa and et al. produced bright silvery polyacetylene film from acetylene using Ziegler-Natta catalyst in 1974. However, this shiny polyacetylene films were not conductive yet. Then in 1977, these three scientists discovered that when the polyacetylene

films were exposed to iodine vapor and oxidized at room temperature, its conductivity increased  $10^{12}$  times higher than the undoped polymer films'. This result not only was the highest value yet obtained, but also was the first capable of conducting electricity for an organic polymer. These three brilliant scientists were awarded with the Nobel Prize in 2000 in honor of founders of conjugated polymer science. Since that discovery, recent trends have arisen in order to understand the electronic and optical properties of conjugated polymers either in neutral or doped states.

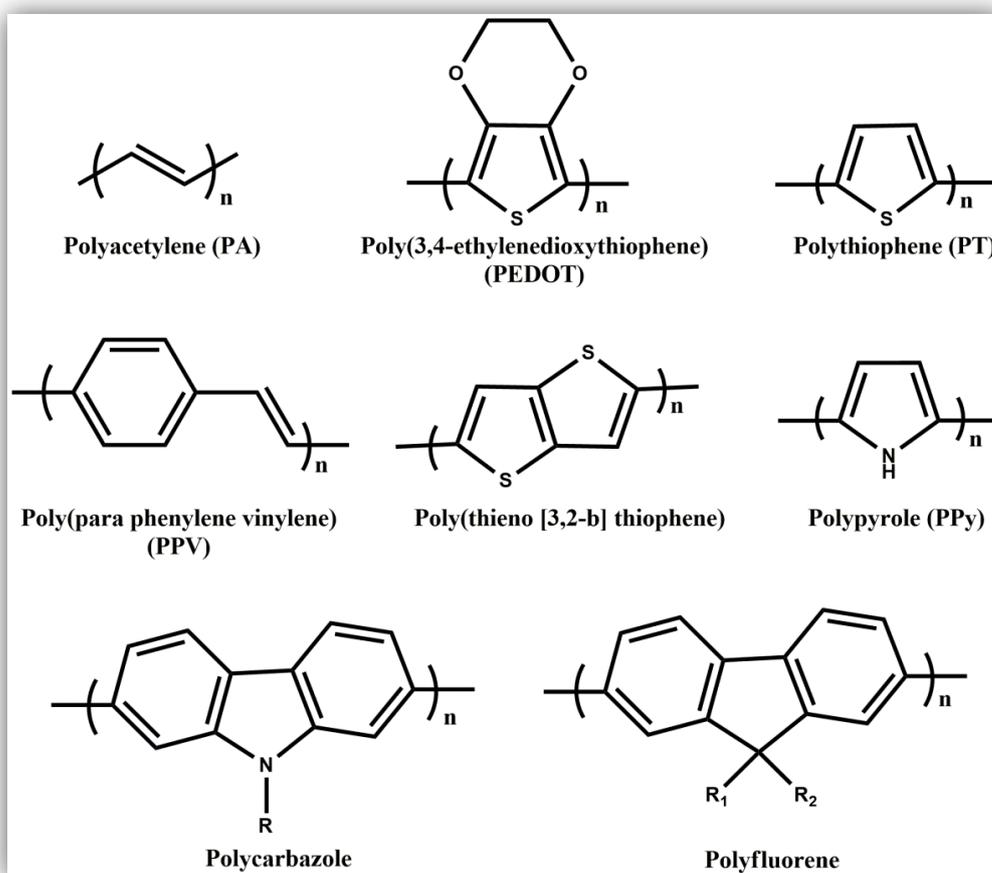


Figure1.5. Structures of most commonly used conjugated polymers

### 1.6.1. Conjugation in Conducting Polymers

All materials can be categorized into three parts as conductors, semiconductors, and insulators according to their ability to conduct the flow of current. Generally conjugated polymers are in the class of semiconductors which have narrow band gap ( $E_g$ ) between conduction and valence band.

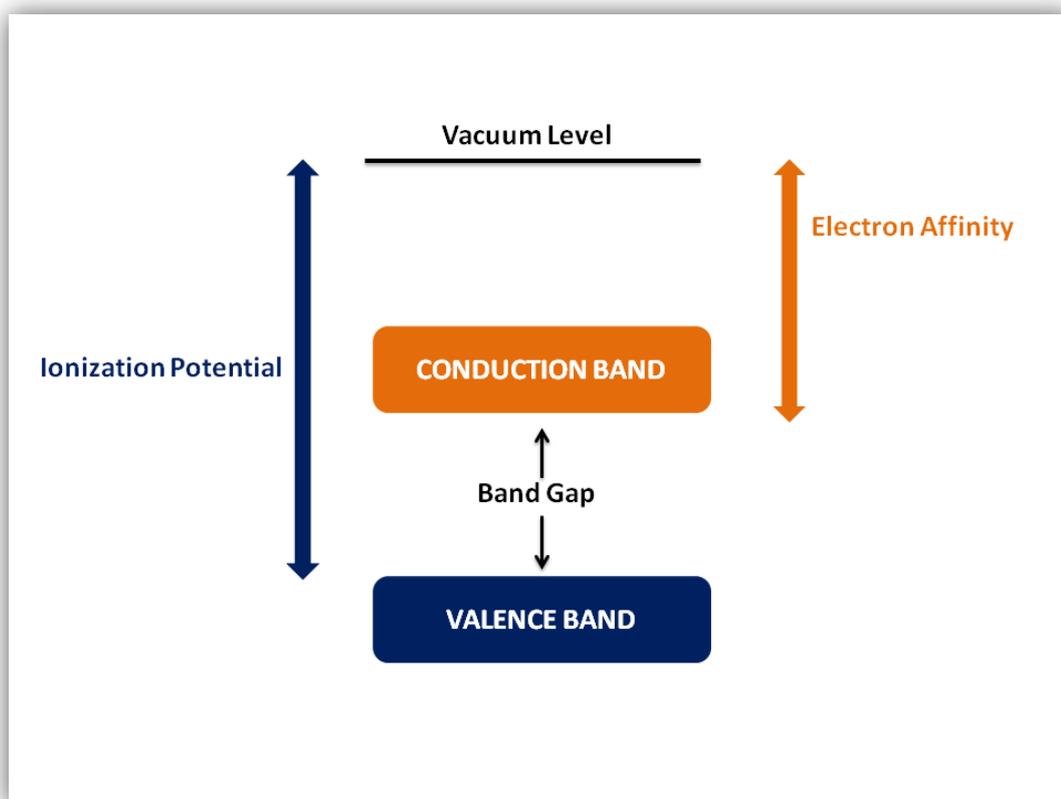


Figure 1.6. Energy level diagram showing the relation between electron affinity (EA), ionization potential (IP) and band gap ( $E_g$ )

Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels correspond to the valence and conduction bands in conjugated polymers. These energy levels consist of  $\pi$ - $\pi^*$  levels so close in energy that they are indistinguishable. The small energy gap is capable of the excitation of electrons from HOMO to LUMO energy level. When a free particle

with  $N$  atoms in a 1-D box is considered, the energy of the HOMO level of the molecule can be written as:

$$E_n = n^2 h^2 / 8ml^2$$

where  $n$  is the HOMO energy level (quantum number),  $m$  is the mass of the electron and  $h$  is the Planck's constant. According to the Pauli principle, maximum two electrons can occupy a molecular orbital so the equation can be corrected as:

$$E(HOMO) = \left(\frac{N}{2}\right)^2 h^2 / 8ml^2$$

And LUMO energy level can be written as:

$$E(LUMO) = \left(\frac{N}{2} + 1\right)^2 h^2 / 8ml^2$$

The required energy needed to excite an electron from HOMO ( $\pi$ ) to LUMO ( $\pi^*$ ) is equal to

$$\Delta E = \frac{(N + 1)^2 h^2}{8ml^2} = h\nu = \frac{hc}{\lambda}$$

Hence, as the conjugation length of the polymer increases, energy difference (band gap) of the polymer decreases. Besides conjugation length affects the absorption wavelength of the polymer in spectroelectrochemical studies.

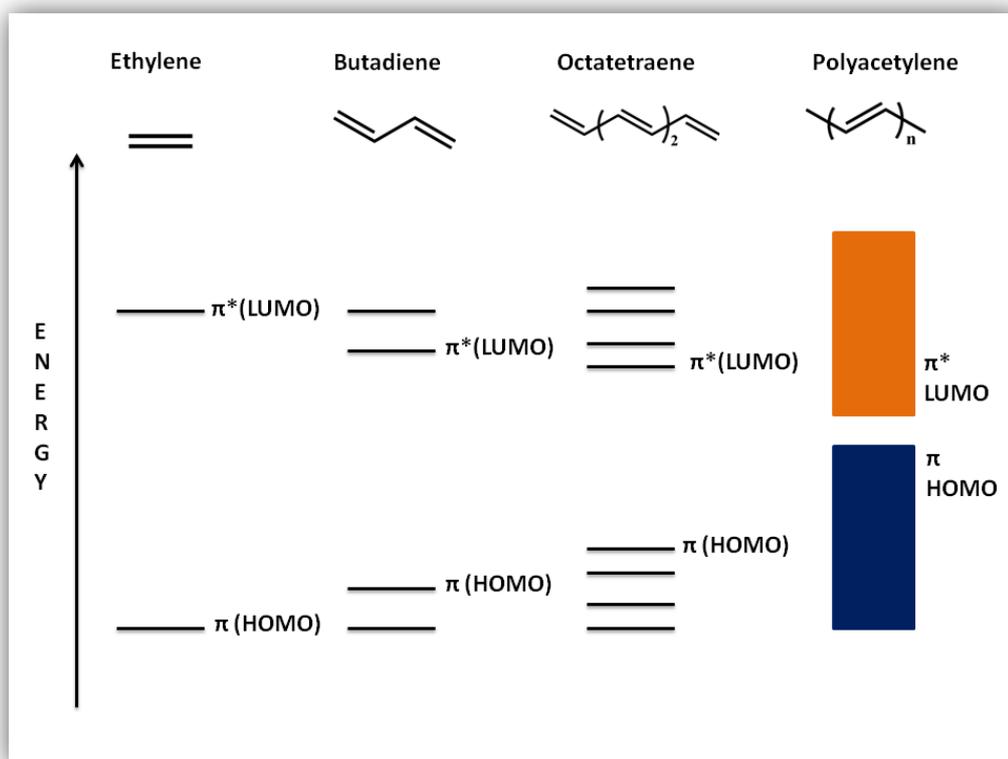


Figure 1.7. Molecular orbital diagram and band gap depression in conjugated polymers

### 1.6.2. Doping Process

Most organic polymers do not have inherent charge carriers so they need to be partially oxidized/reduced (p-doping/n-doping). Doping can be defined as ejection (injection) of charge from (to) the polymer chain and it should be reversible. The partially filled  $\pi$ -system of the conjugated polymers allows electron removal from (injection into) the polymer.

When an electron is removed (added) from the top of the valence band (to the bottom of the conduction band) of a conjugated polymer, the valence band (conduction band) is partially filled and a radical cation (anion) named as polaron is formed. The formation of polarons induces the formation of states from top of

the valence band and bottom of the conduction band. Further removal (addition) of the unpaired electron yields the formation of dication (dianion) named as bipolaron, lowering the total energy. High doping process can create a bipolaron-rich material and bipolaron bands are formed.

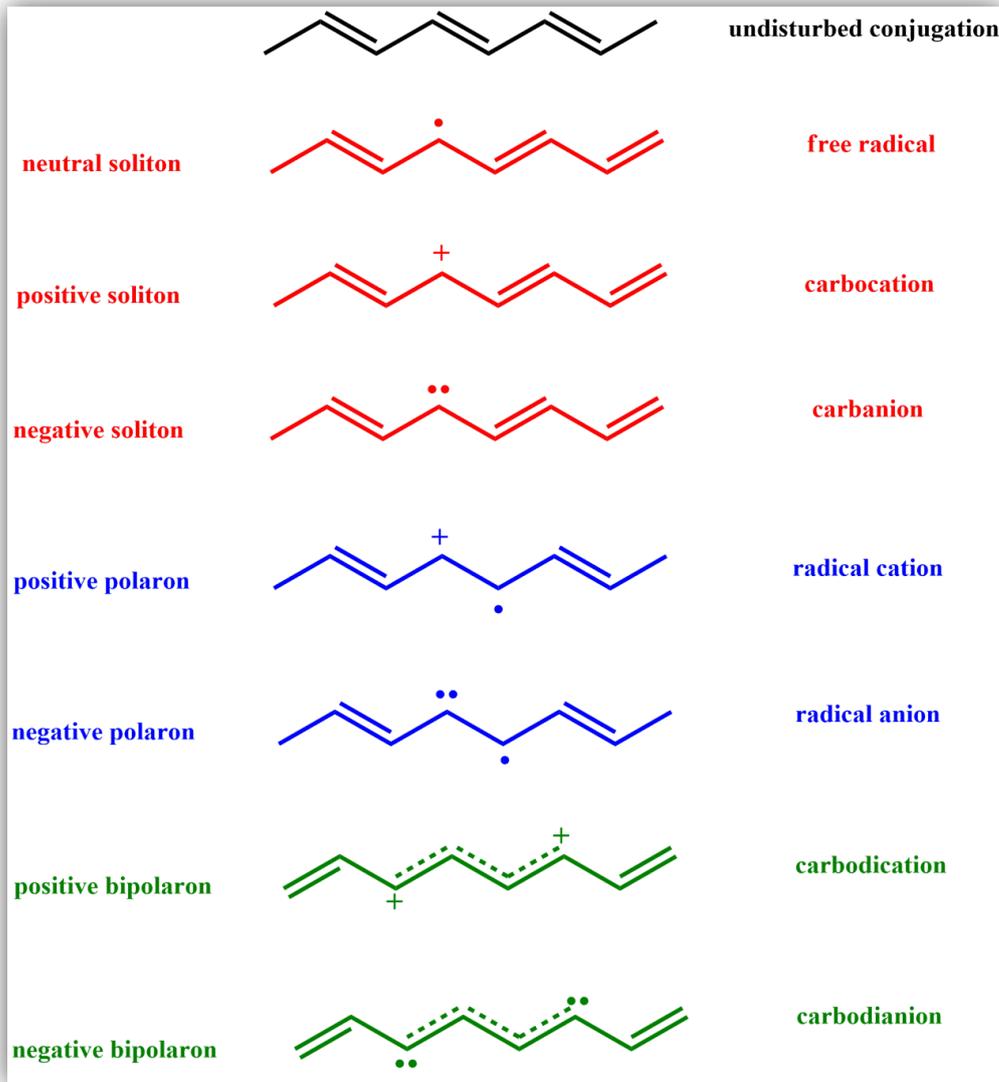


Figure1.8. Charge carriers in chemical terms

The mostly studied polymer polyacetylene showed  $10^{12}$  times higher conductivity when doped with iodine vapor. However, its doping process is a special case when its neutral and oxidized states are considered. Neutral forms of PA are

structurally identical so it has degenerate ground states (energetically equal). The bipolarons can lower the total energy by forming spinless solitons, which then combined to form soliton bands.

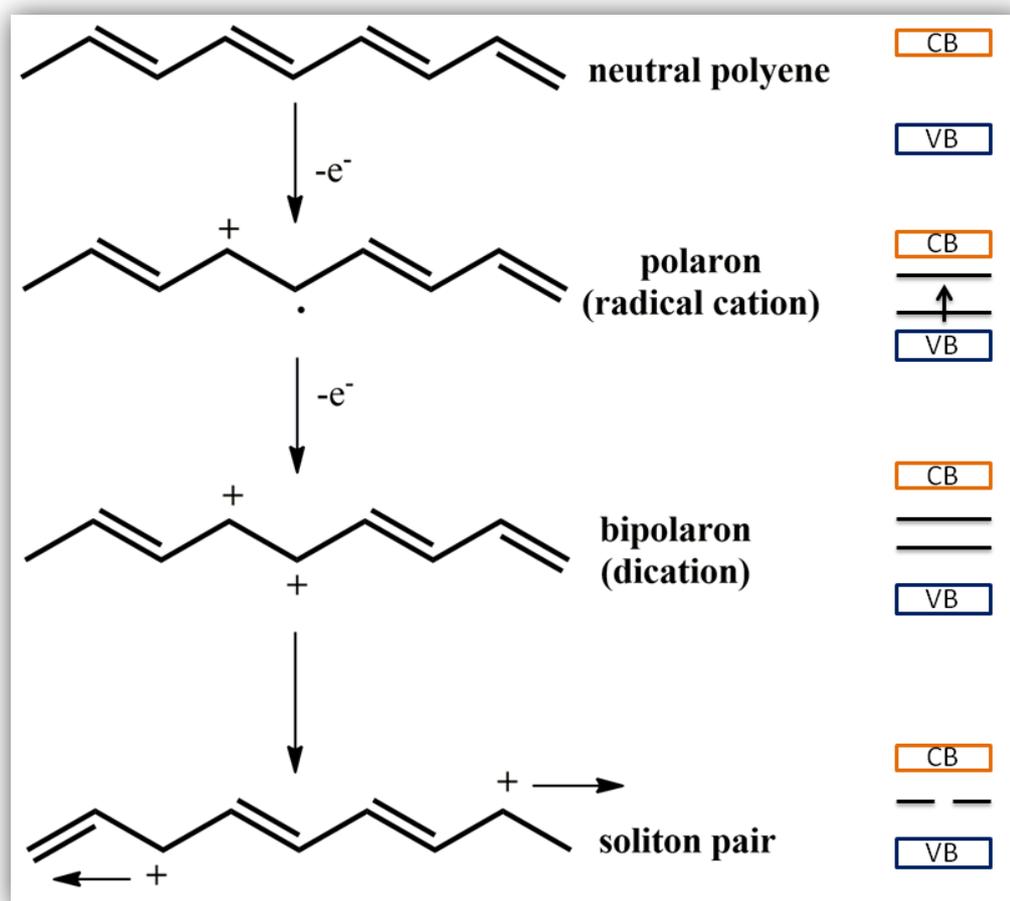


Figure 1.9. A schematic description of the formation of polaron, bipolaron and soliton pair for PA doping

Doping process can be carried out via several methods such as chemical, electrochemical, irradiation or charge-injection. Conjugated polymers can be easily doped and turn into a conductor electrochemically. When a suitable potential is applied to the polymer film, an electron is removed from (added to) the polymer and due to change in the electronic structure charge carriers (polaron, bipolaron or soliton) are formed and possess the conductivity.

### 1.6.3. Toolbox for Band Gap Engineering

Electronic and optical properties of conjugated polymers are the key properties when the application areas are concerned. Since those characteristics are related with the electronic states of the polymers, HOMO/LUMO energy levels and band gap become determinant parameters. In order to fulfill the required prerequisites for the applications, fine tuning of the band gap should be followed. There have been several studies in the literature regarding the band gap adjustment. When mainly categorized, there are five type parameters affecting the band gap, which are bond length alternation, aromaticity, planarity, donor-acceptor units and intermolecular interactions.

Aromatic systems like polythiophene (PT) have non-degenerate ground states; hence, two resonance forms are obtained by flipping the double bonds. Polymers preserve their aromaticity with definite  $\pi$ -electrons and restrict the delocalization on whole chain in their aromatic form. Quinoid form of polymers is less stable since the quinoid form destroys the aromaticity and causes a loss in energy. Hence, quinoid form has lower band gap than the aromatic form. The ratio of aromatic to quinoid form can be represented by bond length alternation (BLA). In theory, complete electron delocalization on polymer chain should be completed and all carbon-carbon bonds should have the equal length. However, polyaromatics do not comply this hypothesis as shown in Figure 1.10.

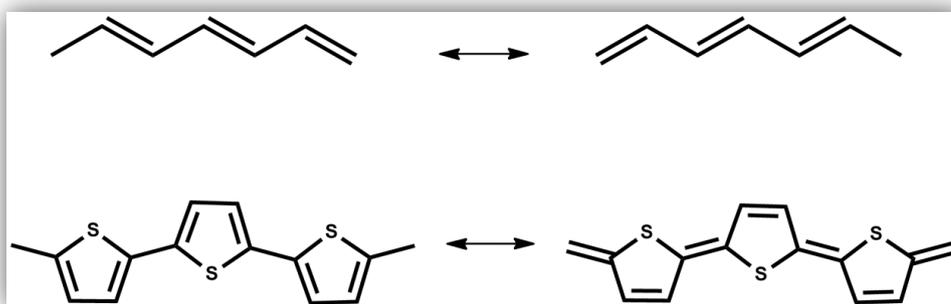


Figure1.10. In polythiophenes two mesomeric forms are not energetically equal unlike in polyenes

As the polymer adopts the quinoid form, C-C single bonds between two adjacent rings tend to follow double bonds and smaller BLA value is obtained. As Roncali showed that decreasing the aromaticity of polyaromatics reduces the band gap by inserting the ethylene linkages (double bonds) into the polymer chain [23]. Besides, introducing the ethylene linkages eliminate the torsion angle and allow the polymer adopting a planar structure. Rigidification (planarization) between adjacent aromatic units decreases the rotational disorder and band gap. Another structural modification method is the substituent effect on the band gap. Generally, electron-releasing units increase HOMO energy level whereas electron-accepting units decrease LUMO energy level, resulting in a reduced energy gap. To illustrate, poly(3,4-ethylenedioxythiophene) has a band gap around 2.0 eV but when electron-donating alkoxy groups are introduced to the polymer backbone, lower band gap decreases to 0.5 eV [24]. Alternating electron-donor and acceptor units in a polymer chain was proposed by Having et al. in 1992 [25]. Since then, it has shown that with efficient combination of donor-acceptor units low band gap polymers have been synthesized [26]. Although these four parameters are the main synthetic methods for lowering the band gap, intermolecular interactions can affect the band gap. When different molecules are assembled into a polymer chain a fifth contribution can exist. According to these contributions, band gap can be represented with the following equation:

$$E_g = E_{BLA} + E_{res} + E_{\theta} + E_{subs} + E_{int}$$

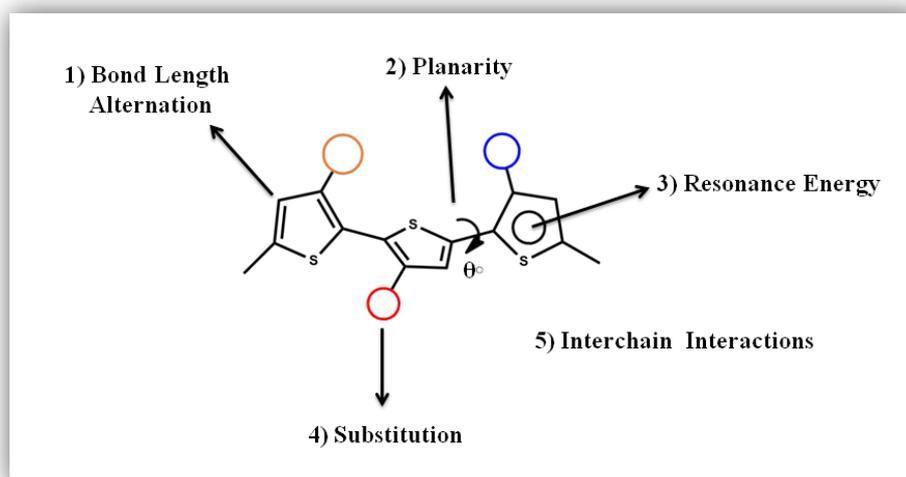


Figure 1.11. Structural factors affecting the band gap of materials

#### 1.6.4. Syntheses of Conducting Polymers

There are several synthetic routes for the synthesis of conjugated polymers. Chemical and electrochemical oxidative polymerizations or transition-metal catalyzed cross-coupling reactions can be performed [27]. The cross-coupling reactions start with a transition-metal catalyzed oxidative addition reaction followed by a transmetalation to form the organometallic nucleophile and conclude with a reductive elimination reaction leading to new C-C bond formation as shown in Figure 1.12. Nickel and palladium based complexes are the mostly preferred transition-metal catalysts. The organometallic nucleophiles can be stannylated molecules (Stille), boron reagents (Suzuki-Miyaura), Grignard reagents (Kumada-Corriu) or copper (Sonogashira).

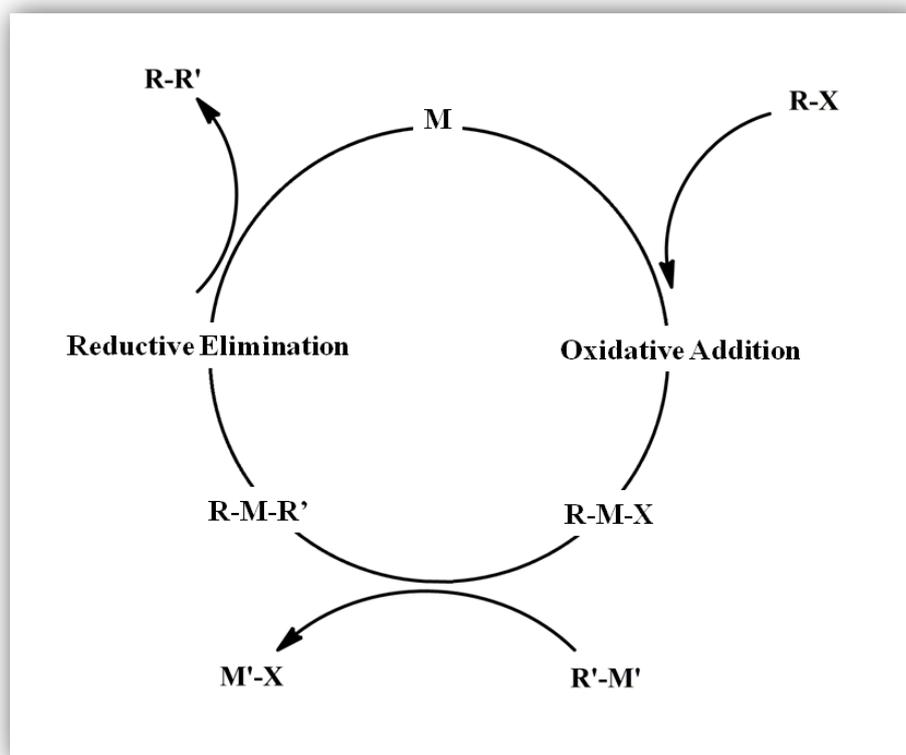


Figure 1.12. A representation of catalytic cycle of transition-metal catalyzed reactions

#### 1.6.4.1. Electrochemical Polymerization

In electrochemical polymerization, the system consists of a cell and three electrodes which are reference, working and counter electrodes. Monomer and supporting electrolyte are dissolved in a solvent. By applying a suitable potential, polymer is coated onto the working electrode. General mechanism of electropolymerization process (ECE-mechanism) is given in Figure 1.13 [28].

Electropolymerization starts with the oxidation of the monomer resulting in the formation of radical cation. Since electron transfer is faster than the monomer diffusion from bulk area through the electrode surface, radicals are formed fast with high concentrations. Then radical-monomer or radical-radical couplings occur (chemical process). In both coupling mechanisms, a neutral dimer is

produced via two protons loss. Then dimer couples with another monomer radical to form a trimer dication and it goes so on. Based on ECE mechanism, electrochemical and chemical steps continue till the insoluble polymer precipitates onto the working electrode. In electrochemical polymerization, very little amount of monomer can be sufficient and no purification is needed which makes it very advantageous and useful.

#### 1.6.4.2. Oxidative Chemical Polymerization

As in the electrochemical polymerization process, monomers are oxidized by an external potential. However, in this method electron transfer occurs from monomer or growing chain to the oxidant molecule. There are several examples used as chemical oxidants such as iron (III) trichloride, copper (II) perchlorate, ferric tetrafluoroborate or ferric sulfate. Unlike to electrochemical polymerization, polymers produced via this method need to be further reduction and purification using reducing agents such as  $\text{NH}_3$  and  $\text{N}_2\text{H}_2$  [29].

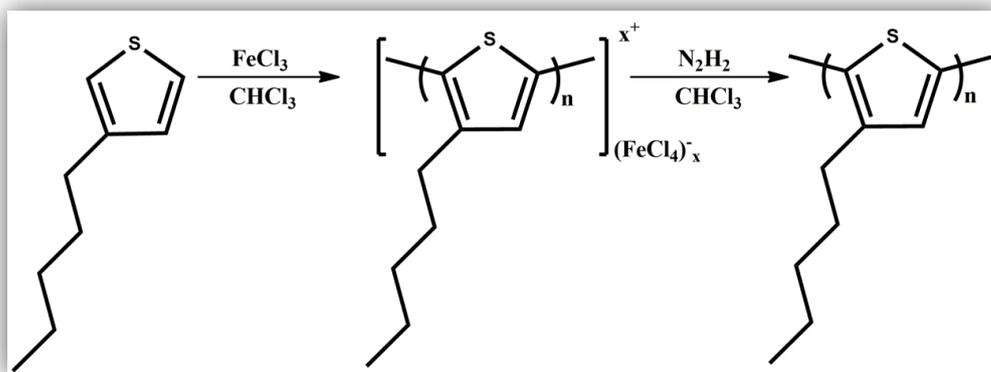


Figure 1.14. Oxidative chemical polymerization of thiophene

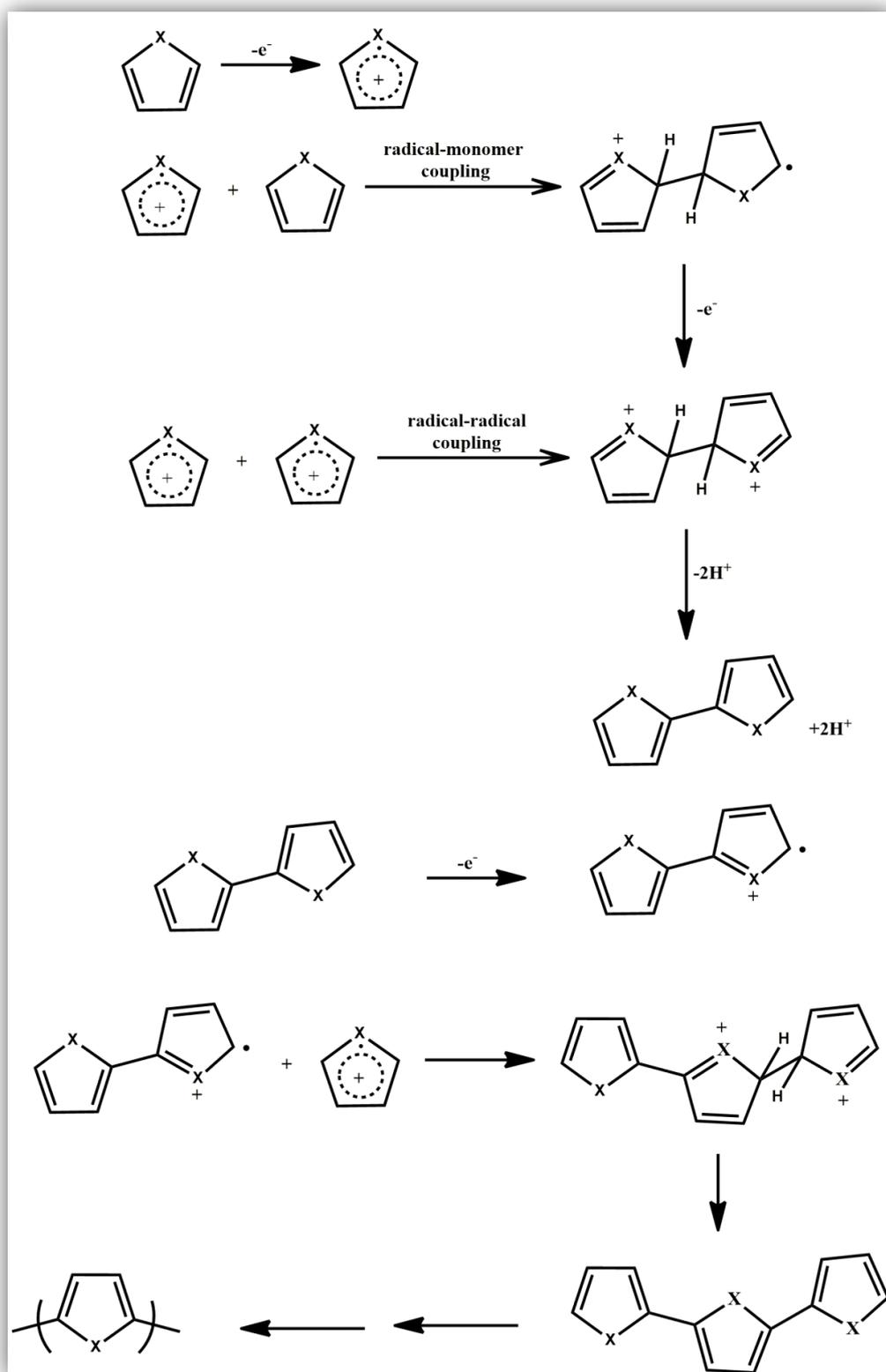


Figure 1.13. Electrochemical polymerization (ECE mechanism) of heterocyclics (X=S, O, NH)

### 1.6.4.3. Suzuki Coupling

The Suzuki reaction is the organic reaction of an aryl- or vinyl-boronic acid with an aryl- or vinyl-halide via a palladium (0) complex catalyst. The organo boron compounds that undergo coupling reactions include boronic acids, boronate esters and boranes. Suzuki coupling reaction was first published in 1979 by Akira Suzuki where boronic acids were coupled with halides [30]. Three scientists, Richard F. Heck, Ei-ichi Negishi and Akira Suzuki, were awarded with Nobel Prize in 2010 for “palladium catalyzed cross couplings in organic synthesis”. The commercial availability of boronic acids and mild reaction conditions make this reaction very feasible and advantageous. Suzuki polycondensation can proceed in two ways as shown in Figure 1.15. In AB type polycondensation reaction, a bifunctional monomer performs the polycondensation whereas in AA/BB type reaction two monomers with different functionalities are needed.

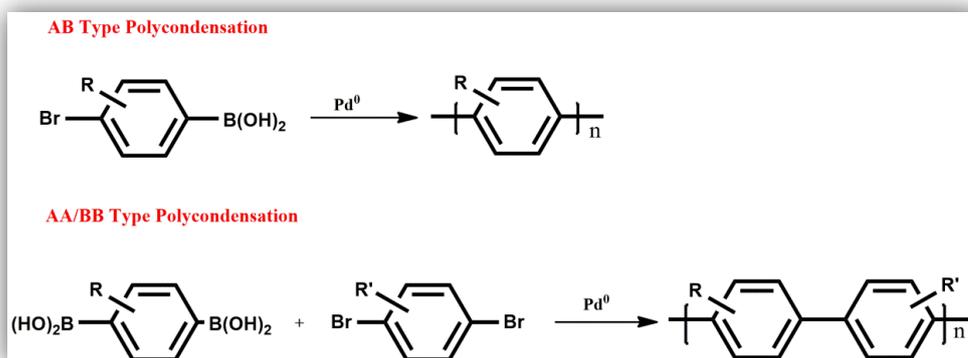


Figure 1.15. A representation of Suzuki polycondensation

### 1.6.4.4. Stille Coupling

The Stille reaction was discovered in 1978 by John Kenneth Stille and David Milstein [31]. It is C-C bond forming reaction between stannanes and halides, with very few limitations on R groups. Using two different monomers is the most common and efficient way for alternating copolymer synthesis via Stille coupling

reaction. Stannyl groups substituted on the benzene ring of the monomer always give poor reactivity with aryl halides under reaction medium. Hence, synthesis of thiophene-containing polymers with monomers with stannyl groups on the thiophene substrate is more feasible and suitable via Stille coupling.

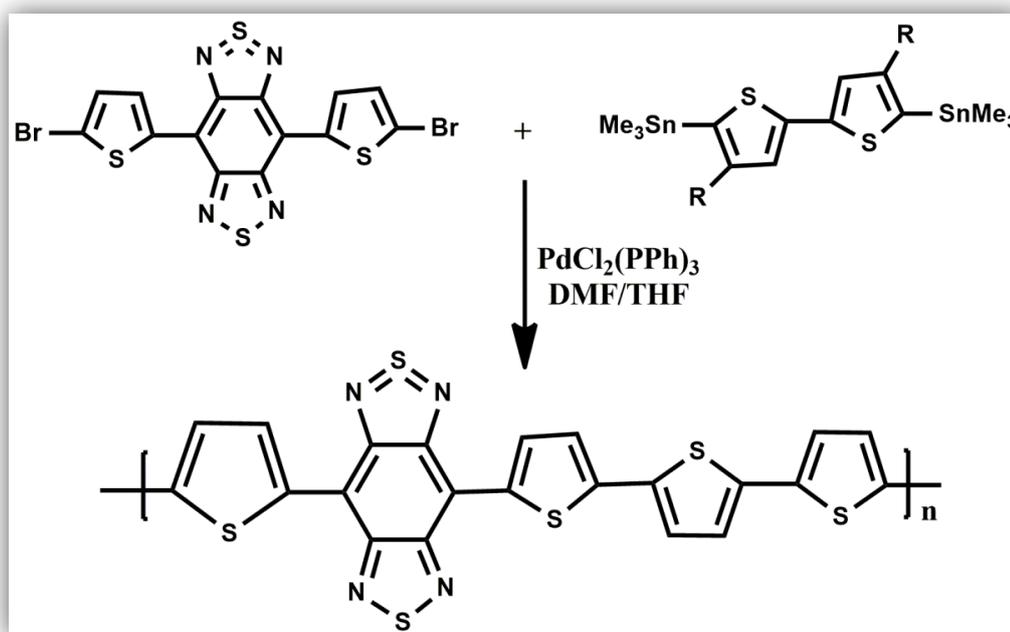


Figure 1.16. Stille polycondensation reaction [32]

#### 1.6.4.5. Yamamoto Coupling

Yamamoto coupling is a nickel mediated dehalogenation reaction of dihaloaromatic compounds. This reaction provides random copolymerization or self-polymerization of single monomers. The most commonly used reagents are  $\text{NiBr}_2$  and  $\text{NiCl}_2$  in the presence of  $\text{Zn}$ ,  $\text{PPh}_3$  and bipyridine or  $\text{Ni}(\text{COD})_2$  with co-reagents (2,2'-bipyridine and COD in dimethylacetamide and dimethylformamide as the solvent) [33].

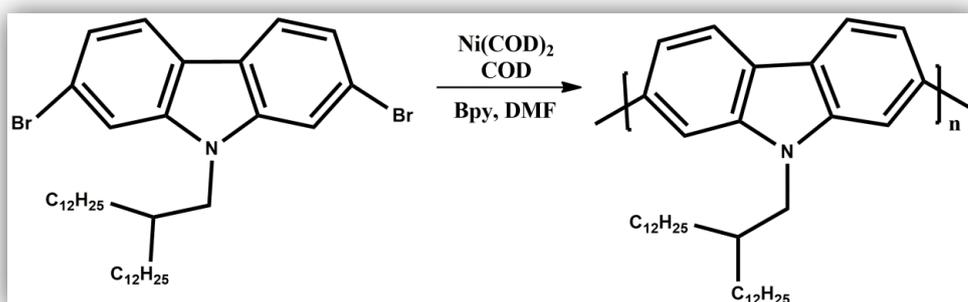


Figure1.17. Synthesis of polycarbazole by Yamamoto reaction

#### 1.6.4.6. Heck Coupling

The palladium-catalyzed C-C bond formation between aryl or vinyl halides and activated alkenes in the presence of a base is referred as the Heck reaction. The reaction starts with the oxidative addition of the aryl halide to the palladium catalyst, which is followed by the coordination of the olefin to the palladium. Relative to steric strain and  $\beta$ -hydride elimination trans product is formed. Regeneration of the palladium catalyst is supplied by the base.

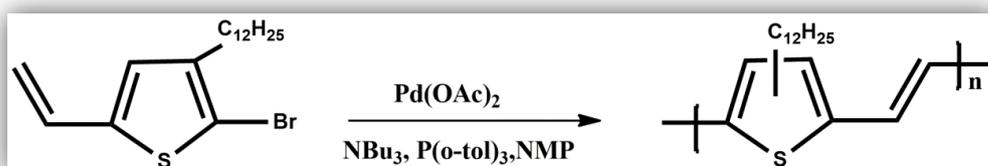


Figure1.18. Heck reaction of a vinylthiophene

#### 1.6.4.7. Tamao-Kumada-Corriu Coupling

Cross-coupling reaction of an alkyl or aryl Grignard reagent with an alkyl, aryl or vinyl halide is named as Tamao-Kumada-Corriu cross-coupling reaction [34].

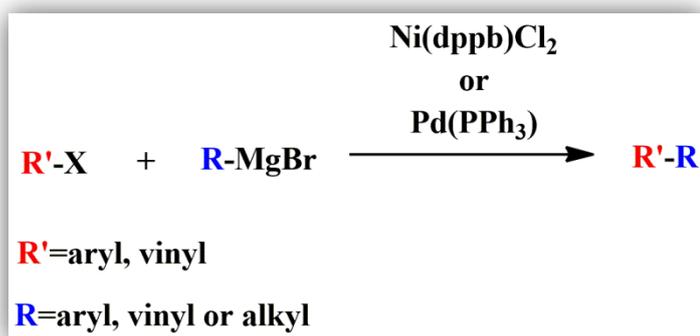


Figure 1.19. General representation of Kumada cross-coupling reaction

McCullough developed the Kumada cross-coupling reaction in 1993 in order to synthesize head-tail regioregular poly(3-hexyl thiophene) as shown in Figure 1.20 [35].

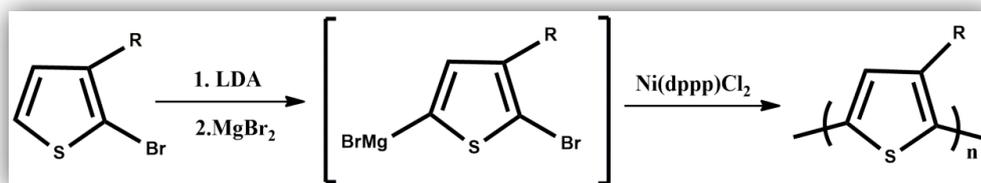


Figure 1.20. Synthesis of poly(3-hexylthiophene) by Kumada reaction

#### 1.6.4.8. Grignard Metathesis (GRIM)

McCullough developed another method to synthesize regioregular poly(3-hexyl thiophene) which is named as the Grignard metathesis (GRIM) in 1995. Reaction of 2,5-dibromo-3-hexylthiophene with alkyl Grignard reagents resulted in two regioisomers. Addition of catalytic amount of Ni(dppp)Cl<sub>2</sub> to the isomeric mixture formed 95% regioregular poly(3-hexylthiophene) [36].

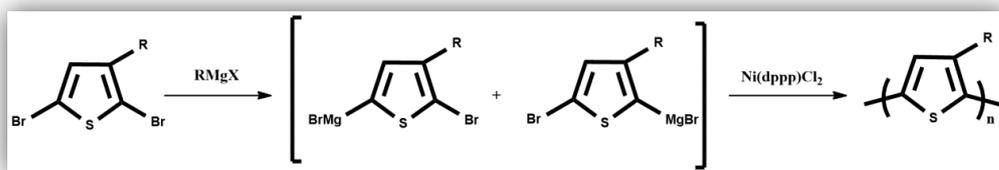


Figure 1.21. Synthesis of regioregular poly(3-hexyl thiophene) by GRIM method

#### 1.6.4.9. Rieke Method

Rieke method was developed as the second synthetic approach for the head-tail regioregular poly(alkylthiophene) in 1992. Rieke used rieke zinc for the synthesis of regiocontrolled poly(3-alkylthiophene) [37].

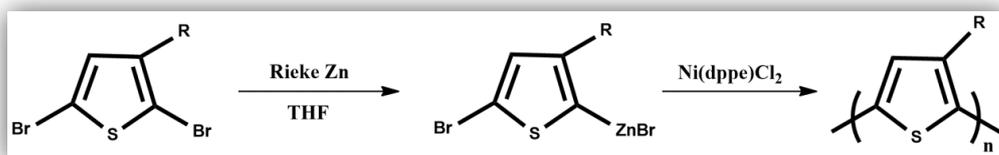


Figure 1.22. Synthesis of poly(3-alkylthiophene) by Rieke reaction

#### 1.6.4.10. Sonogashira Coupling

Coupling reaction of terminal alkynes with aryl or vinyl halides is named as Sonogashira coupling reaction. It was first reported by Kenkichi Sonogashira and Nobue Hagihara in 1975 [38]. Sonogashira coupling is performed in the presence of Pd (0) catalyst with a halide salt of copper [Cu (I)] as the co-catalyst under a basic medium. The reaction requires anhydrous and anaerobic conditions.

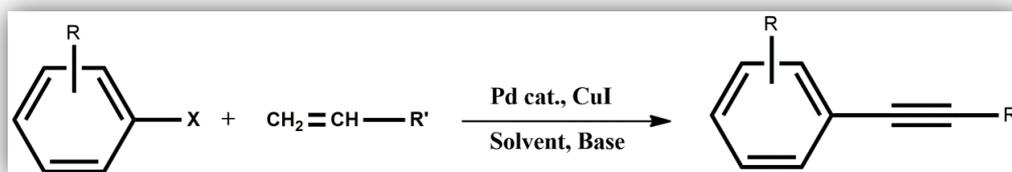


Figure1.23. A general representation of Sonogashira coupling reaction

#### 1.6.4.11. Knoevenagel Condensation

Knoevenagel reaction is the C-C double bond formation between carbonyl compounds and active methylene components. This reaction is useful for the synthesis of vinylenes containing conjugated polymers. It was one of the first methods used for the synthesis of PPV derivatives. It requires strong electron acceptor units (like cyano) in the methylene species. The method delivers the PPV containing cyano substituents on vinylenes units.

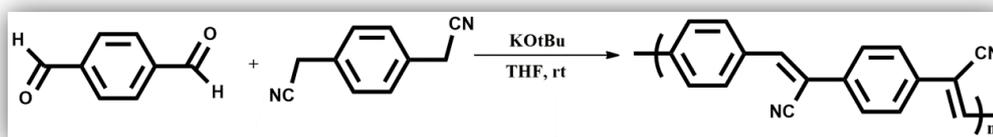


Figure1.24. A general representation of Knoevenagel coupling reaction

### 1.7. Strong Electron-Acceptor Units: Benzothiadiazole and Benzoselenadiazole

Using electron-donor and acceptor units in the polymer synthesis increases the intramolecular charge transfer (ICT) from electron rich part to the electron deficient part of the polymer resulting in enhanced electronic and optical properties. Hence, donor-acceptor type conjugated polymers have low band gaps and wide absorption band regions due to efficient intramolecular charge transfer. There have been several donor-acceptor type polymers that have been synthesized

in recent years. 1,2,3-Benzotriazole [39], diketopyrrolopyrrole [40], 2,1,3-benzooxadiazole [41], 2,1,3-benzothiadiazole (BTh) [42] and its analogue 2,1,3-benzoselenadiazole (BSe) [43] are commonly preferred electron acceptor units in the donor-acceptor polymer synthesis. Electron deficient atoms like nitrogen or oxygen make those acceptor species more willing candidates for electron accepting ability. Benzothiadiazoles and its derivatives are well-known heteroaromatics with a strong electron withdrawing character. Two imine groups (-C=N-) in the molecule increase the electron affinity and hence electron transfer between donor-acceptor units, resulting in low band gap polymers [44]. Its counterparts, benzoselenadiazoles are another example of mostly used acceptor units. They are synthesized by replacing the sulfur atom with selenium atom. These species are more forceful in extending the absorption region toward the IR region owing to larger size, less electronegativity and higher electron affinity of selenium atom than sulfur atom [45]. In addition, strong Se-Se interactions enhance the charge mobility of the polymers [46].

### **1.8. Strong Electron-Donor Units: Carbazole, Fluorene and Silafluorene**

In order to achieve a low band gap, wide absorption spectrum, low redox potential requires strong electron-donor units as much as acceptor units. Among the donor-acceptor type conjugated polymers heteroaromatics such as benzodithiophene, thiophene, carbazole, fluorene and silole containing molecules are the most famous ones [47]. Carbazoles are popular electron donor units due to their efficient hole transporting ability, thermal and morphological stability. The ability of nitrogen atom to donate its free electrons through the molecule increases the electron donating ability and hole-injection properties of carbazoles. They have many examples in the literature that are coupled from different positions like 2,7-, 1,8- or 3,6- carbazoles [48]. However, it was proved that 2,7- carbazoles are the most suitable ones for electron attacks [49]. Carbazoles are the nitrogen-bridged isoelectronic of fluorenes and they are compared with each other all the time. Fluorenes have promising properties such as high photoluminescence (PL) and

electroluminescence (EL), thermal and chemical stabilities, and good solubility in common solvents [50]. Polyfluorenes have broad absorption spectrum but large band gaps. However, incorporation of strong electron-acceptors into the polymer chain eliminates this drawback. Fluorene based polymers showed power conversion efficiencies up to 5.5% in photovoltaic applications when used as the active layer [51]. As an alternative electron donating unit, silole containing molecules have emerged in the recent years in addition to carbazoles and fluorenes [52]. Since the first synthesized silole containing polymer [53], silole based copolymers especially silafluorenes have attracted much attention. It was proved that silafluorene based polymers have good stabilities and high efficiencies in polymer solar cells [54]. In light of this information, these three similar electron releasing units were coupled with two acceptor units expecting efficient intramolecular interactions and efficient electron transfer.

### **1.9. Aim of This Work**

In this work, synthesizing copolymers with low band gap, low oxidation potentials and broad absorption spectrum for organic optoelectronic applications were aimed. In addition to these properties, chemical and thermal stability, solubility and feasibility of the polymers are also very important for the applications. There are several ways to achieve polymers with desired properties as mentioned above (section 1.6.3) and using electron rich and poor units in polymerization synthesis is a very feasible and efficient method. Hence on the basis of literature examples, choosing strong electron donating moieties such as carbazole, fluorene and silafluorene can produce promising polymers. Copolymers based on carbazole and fluorene coupled with either BTh or BSe showed low oxidations, chemical stabilities and high efficiencies in both solar cell and light emitting diode applications. In the light of these examples, three novel random copolymers based on three donor units (carbazole, fluorene and silafluorene) coupled with both BTh and BSe were designed in order to get lower oxidation potentials, lower band gaps and higher efficiencies in optoelectronic applications.

2,1,3-Benzothiadiazole (BTh) and its analogue 2,1,3-benzoselenadiazole (BSe) were used as the electron accepting species. These three copolymers were synthesized successfully via Suzuki polycondensation reaction. After the synthetic part of the monomers and corresponding polymers, electrochemical and spectroelectrochemical characterizations of polymers were performed. Effect of different donor units on the electronic and optical properties of P1, P2 and P3 were observed and compared with each other. All polymers were soluble in common solvents and had enhanced redox behaviors like lower oxidation potentials, lower band gaps and broad absorption spectrum compared their counterparts in the literature. Colorimetric studies were also carried out in order to report the colors of the polymers more precisely and scientifically.

## CHAPTER 2

### EXPERIMENTAL

#### 2.1. Materials

2,1,3-Benzothiadiazole, bromine, hydrobromic acid, selenium dioxide and sodium borohydride were purchased from Aldrich. 4,7-Dibromobenzo[c][1,2,5]thiadiazole, 3,6-dibromobenzene-1,2-diamine and 4,7-dibromobenzo[c][1,2,5]selenadiazole were synthesized according to the literature [55]. Toluene was freshly distilled over Na/benzophenone ketyl before use.

#### 2.2. Methods and Equipment

In order to investigate the redox and transport behaviors of polymers, cyclic voltammetry (CV) studies were performed. The system consists of a three electrode cell containing an ITO coated glass as the working electrode, a platinum wire as the counter electrode, and a silver wire as the pseudo-reference electrode. In cyclic voltammetry, a triangle waveform potential is applied to the working electrode on which the oxidation or reduction processes occur. The working electrode behaves as the anode or the cathode depending on the potential applied. Then, the auxiliary electrode will act as the cathode or the anode according to what working electrode is acting as. While the potential is scanned at the working electrode relative to the reference electrode, the resulting current flowing through the counter electrode is measured. So the current flow is a measure between the working and counter electrode. The constant known potential of the reference electrode is used to measure the redox potential; hence, the potential is a measure between the working and reference electrode. In order to perform the cyclic

voltammetry studies GAMRY Reference 600 potentiostat was used (Figure 2.1). All reactions were carried out at room temperature and solutions were purged with nitrogen for 5–10 min prior to each experiment to remove the dissolved oxygen. A Varian Cary 5000 UV–Vis spectrophotometer was used to determine spectroelectrochemical properties of the polymers. Maximum absorption wavelength,  $\pi$ - $\pi^*$  transition, optical band gap and polaron and bipolaron region formation are observed via spectroelectrochemical studies. Absorption behaviors were scanned through visible-NIR region from neutral to oxidized states of the polymers. In addition to absorption, percent transmittance changes were measured at constant wavelengths at which maximum absorptions occur in neutral and oxidized states. Besides to these characterizations, Bruker Spectrospin Avance DPX-400 Spectrometer was used to run  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the synthesized monomers. The chemical shifts were reported as  $\delta$  values (ppm) relative to an internal tetramethylsilane (TMS) standard. Number-average ( $M_n$ ) and weight-average ( $M_w$ ) molecular weights were determined by Gel Permeation Chromatography (GPC) using polystyrene as the standard.

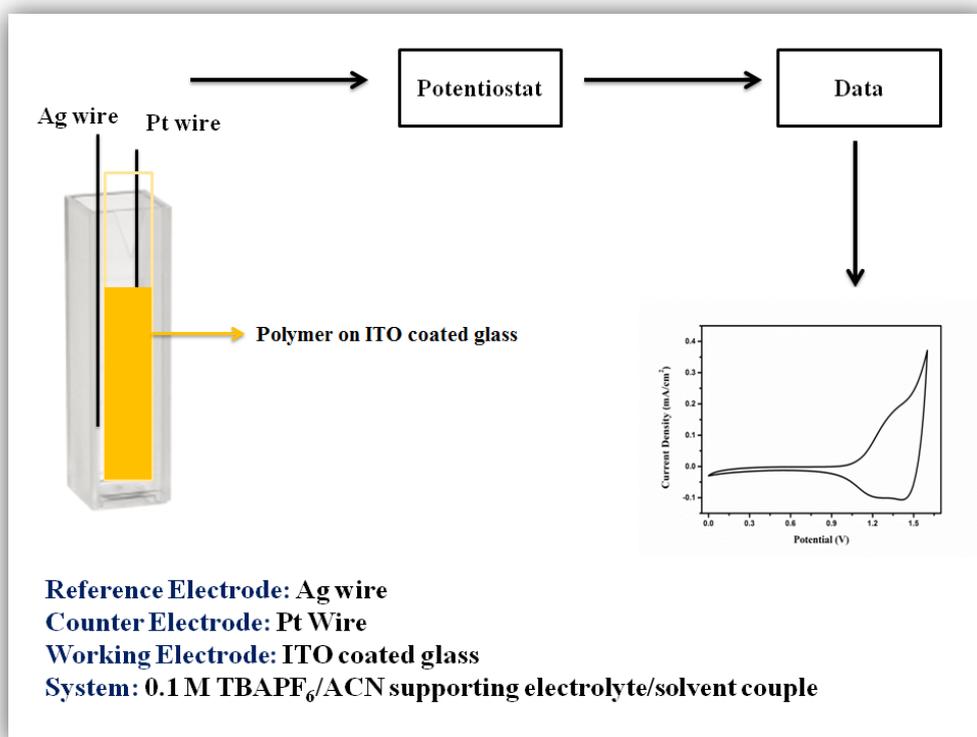


Figure 2.1. A simple representation of the cyclic voltammetry set up

## 2.3. Syntheses of Monomers

### 2.3.1. Synthesis of 4,7-dibromobenzo[c][1,2,5]thiadiazole (1)

2,1,3-Benzothiadiazole (5.00 g, 36.7 mmol) and HBr (47%, 75 mL) were added to a 250 mL two-necked round bottom flask and mixed at 100°C. A solution containing Br<sub>2</sub> (17.6 g, 0.110 mol) in 50 mL of HBr was added dropwise to the solution. After the addition of bromine solution was completed, the mixture was refluxed for 12 h at 135°C to obtain an orange precipitate. The mixture was allowed to cool to room temperature and the excess bromine was quenched by aqueous NaHSO<sub>3</sub> solution. The mixture was filtered and the crude product was washed with water and brine. The residue was dissolved in dichloromethane (DCM) and dried over anhydrous MgSO<sub>4</sub>. The evaporation of solvent under reduced pressure afforded a yellow solid. The solid was then washed once with cold Et<sub>2</sub>O to remove mono-brominated product. After filtration, 5.40 g light yellow solid was obtained. Yield: 50%.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 7.66 (s, 1H).

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ 115.92, 134.35, 155.95.

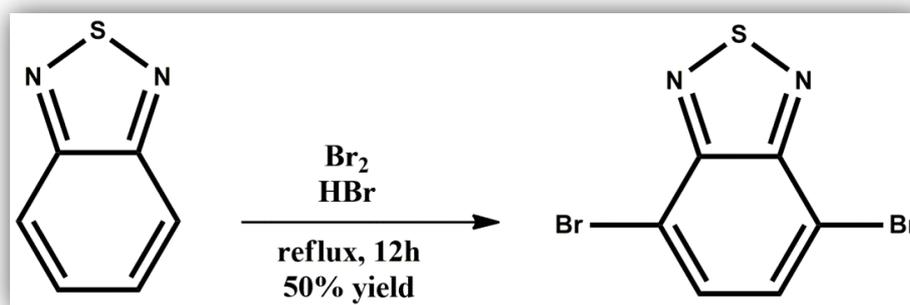


Figure 2.2. Synthetic route of 4,7-dibromobenzo[c][1,2,5]thiadiazole

### 2.3.2. Synthesis of 3,6-dibromobenzene-1,2-diamine (2)

4,7-Dibromo-benzo[c][1,2,5]thiadiazole (2.00 g, 6.80 mmol) was dissolved in ethanol (50 mL) at 0°C. NaBH<sub>4</sub> (10.0 g, 0.264 mol) was added slowly to the reaction medium. After addition of sodium borohydride was completed, then mixture was stirred overnight at room temperature. The evaporation of solvent under reduced pressure afforded an orange solid. The crude product was dissolved in diethyl ether and the mixture was washed with water and brine three times. The organic layer was collected and dried over anhydrous MgSO<sub>4</sub>. After removal of solvent under reduced pressure, 1.70 g beige solid was obtained. Yield: 95%.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 6.78 (s, 1H), 3.65 (s, 1H)

<sup>13</sup>C-NMR (100MHz, CDCl<sub>3</sub>): δ 107.65, 121.22, 131.69.

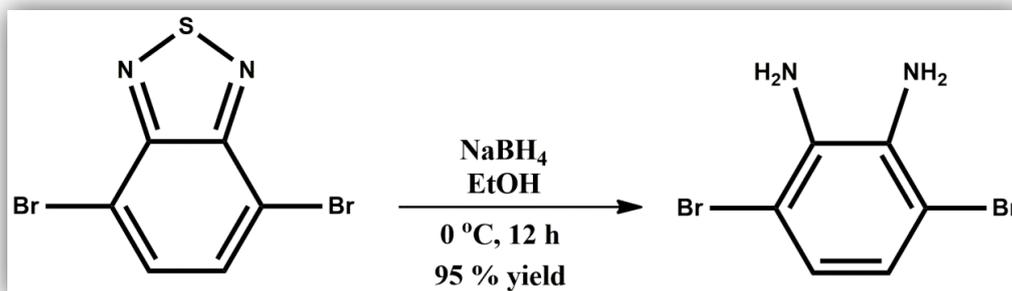


Figure2.3. Synthetic route of 3,6-dibromobenzene-1,2-diamine

### 2.3.3. Synthesis of 4,7-dibromo-benzo[c][1,2,5]selenadiazole (3)

3,6-Dibromobenzene-1,2-diamine (1.00 g, 3.78 mmol) was dissolved in ethanol (21.0 mL) in a two neck round bottom flask. SeO<sub>2</sub> (0.500 g, 4.50 mmol) was dissolved in hot distilled water (8.50 mL) and added slowly to the mixture. The mixture was refluxed for 12 h at 100°C to obtain a yellow precipitate. The mixture was filtered and the crude product was washed with water and ethanol. 1.00 g light yellow solid was obtained. Yield: 78%.

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.58 (s, 1H).

$^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  132.16.

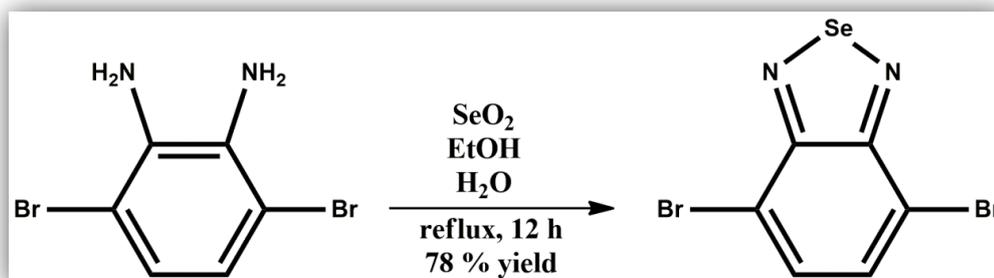


Figure 2.4. Synthetic route of 4,7-dibromo-benzo[*c*][1,2,5]selenadiazole

## 2.4. Syntheses of Polymers

### 2.4.1. Synthesis of P1

4,7-Dibromo-benzo[*c*][1,2,5]thiadiazole (45.0 mg, 152  $\mu\text{mol}$ ), 4,7-dibromo benzo[*c*][1,2,5]selenadiazole (52.0 mg, 152  $\mu\text{mol}$ ), 9-(9-heptadecanyl)-9H-carbazole-2,7-boronic acid bis(pinacol)ester (200 mg, 304  $\mu\text{mol}$ ), potassium carbonate ( $\text{K}_2\text{CO}_3$ , 2 M in  $\text{H}_2\text{O}$ ),  $\text{Pd}(\text{PPh}_3)_4$  (5 mol%) and aliquot 336 (1 mol%) were dissolved in anhydrous toluene (30 mL) and refluxed at  $120^\circ\text{C}$  under an argon atmosphere for 48 h. The reaction was controlled by TLC. After solvent removal under reduced pressure, chloroform was added to crude product and the mixture was washed with distilled water to remove alkali solution and residual catalyst. The organic layer was dried over  $\text{MgSO}_4$ . The solvent was removed under reduced pressure. To remove oligomers, the crude product was washed with methanol, acetone, and hexane using Soxhlet extractor. To extract the polymer,

chloroform was used and a dark orange solid was obtained after precipitation from cold methanol. Yield: 80%.

Mw: 59200 Da, Mn: 42700 Da, PDI: 1.38.

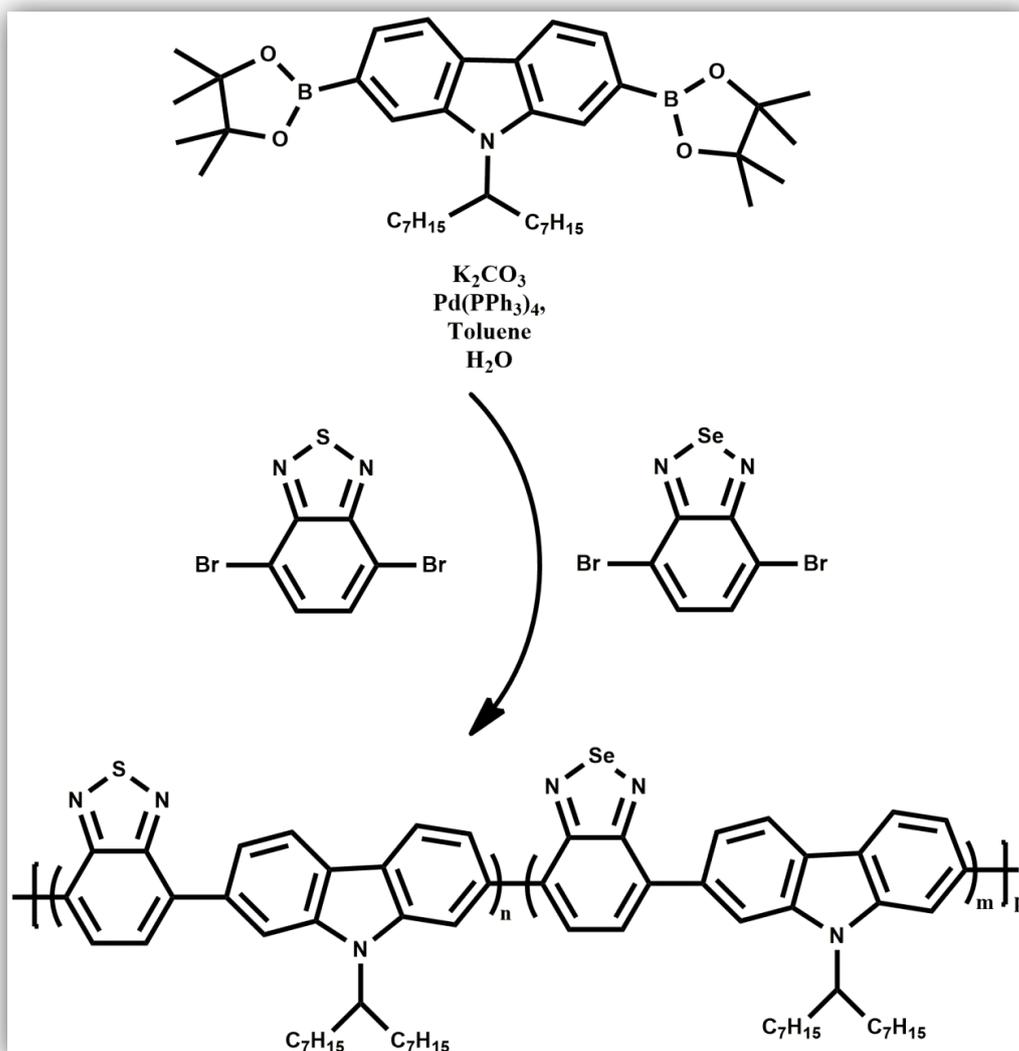


Figure 2.5. Synthesis of P1 via Suzuki polycondensation

#### 2.4.2. Synthesis of P2

4,7-Dibromo-benzo[c][1,2,5]thiadiazole (53.0 mg, 0.180 mmol), 4,7-dibromo-benzo[c][1,2,5]selenadiazole (61.0 mg, 0.180 mmol), 9,9-dioctylfluorene-2,7-

diboronic acid bis(1,3-propanediol) ester (200 mg, 0.358 mmol), potassium carbonate ( $K_2CO_3$ , 2 M in  $H_2O$ ),  $Pd(PPh_3)_4$  (5 mol%) and aliquot 336 (1 mol%) were dissolved in anhydrous toluene (30 mL) and refluxed at  $120^\circ C$  under an argon atmosphere for 48 h using a similar polymerization procedure to give P2. Yield: 85%.

Mw: 20400 Da, Mn: 14660 Da, PDI: 1.39.

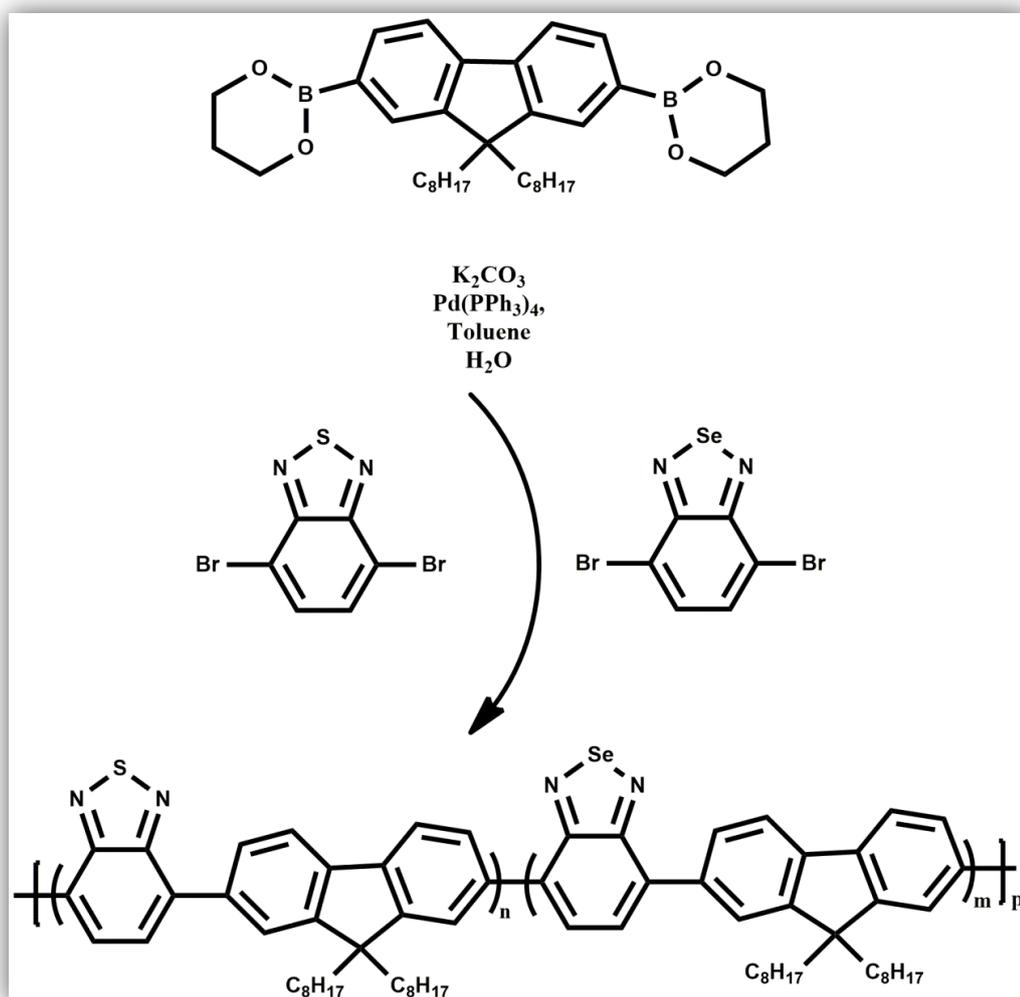


Figure 2.6. Synthesis of P2 via Suzuki polycondensation

### 2.4.3. Synthesis of P3

4,7-Dibromo-benzo[c][1,2,5]thiadiazole (45.0 mg, 0.152 mmol), 4,7-dibromo-benzo[c][1,2,5]selenadiazole (52.0 mg, 0.152 mmol), 9,9-dioctyl-9H-9-silafluorene-2,7-bis(boronic acid pinacol ester) (200 mg, 0.304mmol), potassium carbonate ( $K_2CO_3$ , 2 M in  $H_2O$ ),  $Pd(PPh_3)_4$  (5 mol%) and aliquot 336 (1 mol%) were dissolved in anhydrous toluene (30 mL) and refluxed at  $120^\circ C$  under an argon atmosphere for 60 h using a similar polymerization procedure to give P3. Yield: 24%.

Mw: 35300 Da, Mn:27800 Da, PDI: 1.27.

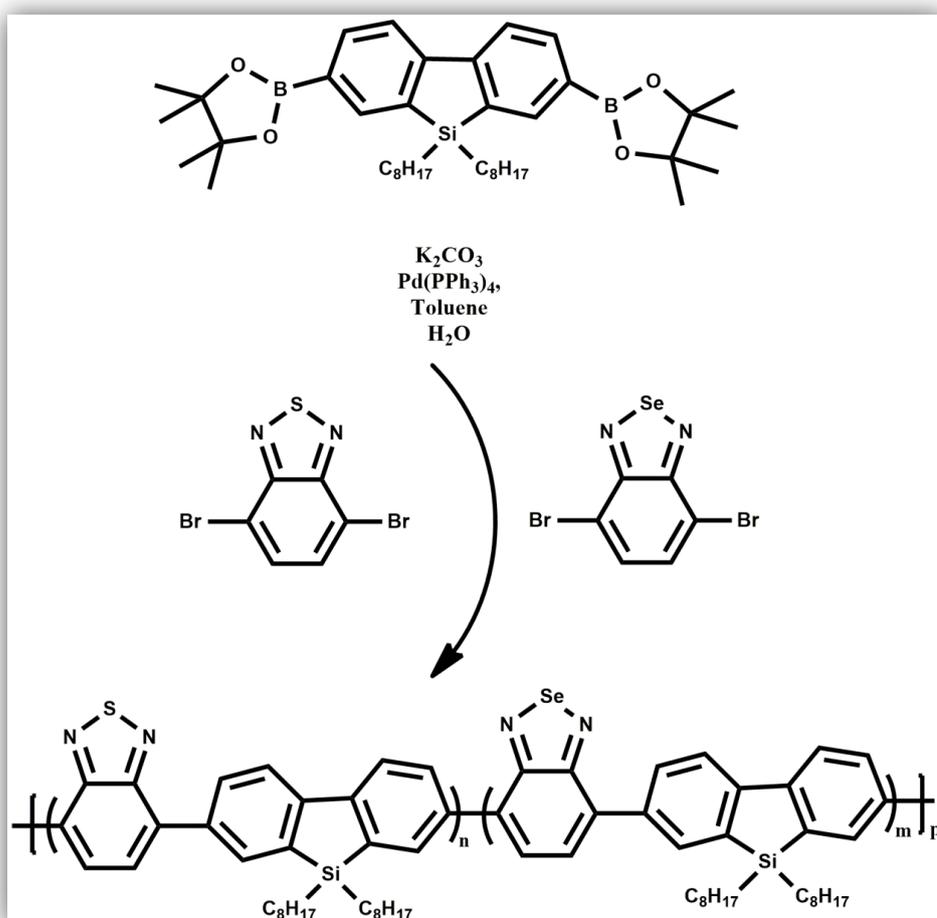


Figure 2.7. Synthesis of P3 via Suzuki polycondensation

## CHAPTER 3

### RESULTS and DISCUSSION

#### 3.1. Electrochemical Characterizations of Polymers

##### 3.1.1. Cyclic Voltammetry Studies

The oxidation/reduction behaviors of polymers P1, P2 and P3 were investigated by cyclic voltammetry (CV) method. The system consists of a potentiostat and an electrochemical cell bearing a silver wire as pseudo-reference electrode, a platinum wire as counter electrode and indium tin oxide (ITO) coated glass as the working electrode. Polymer solutions were prepared in chloroform with a  $5 \text{ mg.ml}^{-1}$  concentration and spray coated onto the ITO coated glass electrode using a spray gun. Cyclic voltammetry measurements were carried out in 0.1 M tetrabutylammonium hexafluorophosphate/acetonitrile (TBAPF<sub>6</sub>/ACN) supporting electrolyte/solvent solution at room temperature at a scan rate of 100mV/s. As shown in Figure 3.1, P1, P2 and P3 had only p-dopable character, which means they were only doped and showed electrochromism upon applied positive potential. Single scan cyclic voltammograms were recorded in 0.0-1.6 V for P1, 0.0-1.8 V for P2, and 0.0-2.0 V for P3, respectively. Polymer oxidation/reduction potentials were observed as 1.40/1.27 V for P1, 1.53/1.20 V for P2 and 1.80/1.30 V for P3 (Table 3.1).

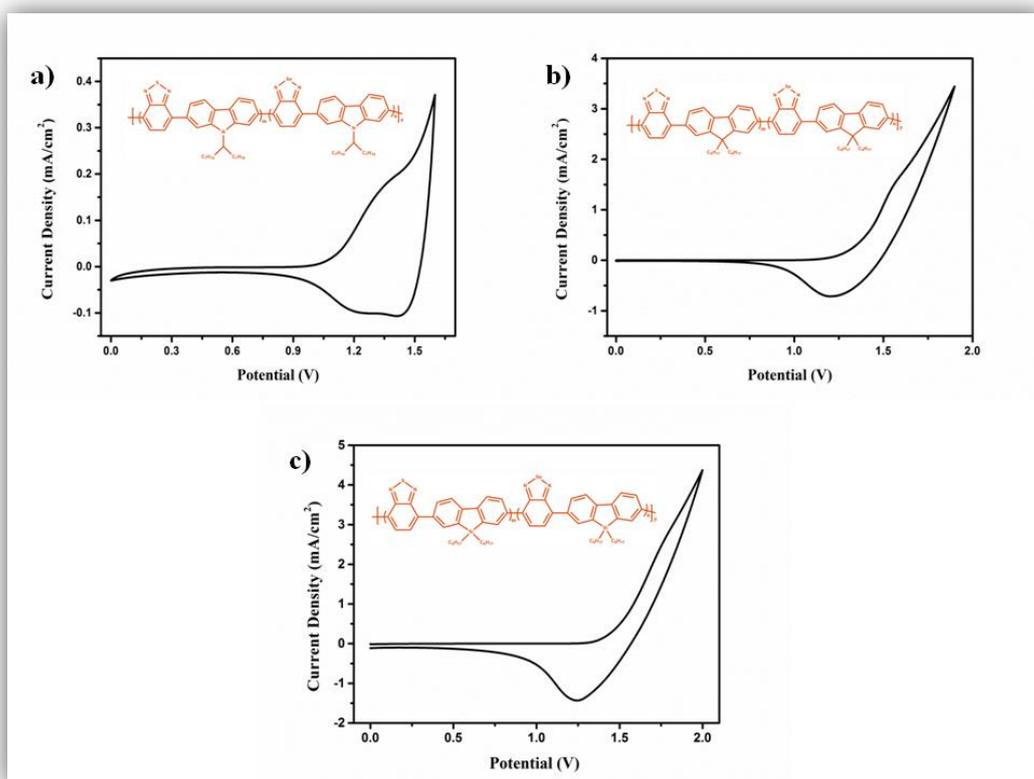


Figure 3.1. Single scan cyclic voltammetry results of a) P1, b) P2 and c) P3 in 0.1 M TBAPF<sub>6</sub>/ACN solution at 100mV/s scan rate

P1 and P3 had broad oxidation potentials range whilst P2 had a sharp oxidation peak potential. In addition, P1 had a lower oxidation potential than P2 and P3 had. This result showed that nitrogen atom in the carbazole molecule increases the electron density on polymer chain and doping/dedoping process could be achieved easily, which is consistent with the literature [56]. Kuznetsal et al. stated that carbazole based copolymers have lower oxidation potential due to their strong electron donating ability through the polymer backbone. Increasing the carbazole content in the polymer chain decreases the oxidation potential of the polymer [57].

HOMO/LUMO energy levels of the polymers were determined from the onset values of the corresponding oxidation and reduction potentials determined from

the cyclic voltammetry studies. NHE was taken as -4.75eV vs. vacuum while calculating the HOMO/LUMO energy levels. Accordingly, HOMO/LUMO energy values ( $E_{\text{HOMO}}/E_{\text{LUMO}}$ ) were calculated using equations 1 and 2, respectively:

$$\text{HOMO} = -(4.75 + E_{\text{ox}}^{\text{onset}}) \quad (1)$$

$$\text{LUMO} = -(4.75 + E_{\text{red}}^{\text{onset}}) \quad (2)$$

Since all polymers were only p-dopable polymers, their LUMO energy levels were calculated from HOMO and optical band gap obtained from the spectroelectrochemical studies of the polymers. According to these calculation methods, HOMO energy levels were found as -5.85 eV, -6.05 eV and -6.15 eV while LUMO energy levels were computed as -3.67 eV, -3.84 eV and -3.77 eV for P1, P2 and 3, respectively. As seen from the results, P1 had a higher HOMO energy level than other two polymers had due to its electron donating nitrogen atom in consistent with the literature reports. Previous studies proved that carbazole containing polymers have higher HOMO energy levels and lower band gaps especially than the fluorene derivatives [58]. Besides, introducing both BTh and BSe acceptor units into the polymer chain decreased LUMO energy level compared to those used either BTh or BSe species. Electrochemical results of the polymers were summarized in Table 3.1.

Table3.1. Electrochemical results of the polymers

	$E_{\text{p-doping}}$ (V)	$E_{\text{p-dedoping}}$ (V)	$E_{\text{ox}}^{\text{onset}}$ (V)	HOMO (eV)	LUMO (eV)
<b>P1</b>	1.40	1.27	1.10	-5.85	-3.67
<b>P2</b>	1.53	1.20	1.30	-6.05	-3.84
<b>P3</b>	1.80	1.30	1.40	-6.15	-3.77

### 3.1.2. Scan Rate Dependence Studies

One of the important characteristics of a cyclic voltammetry is the relation between the peak current ( $i_p$ ) and scan rate of the measurement. Cyclic voltammetry studies of the polymer thin films in monomer free solutions showed well-defined redox processes (Figure 3.1). The obtained current response was directly proportional to the scan rate. As the scan rate of the measurement increased, current response also increased with proportional to the square root of the scan rate as Randles-Sevcik equation states:

$$i_p = 0.4463 * n * F * A * C \sqrt{\frac{n * F * v * D}{R * T}}$$

When the solution is at 25°C, the equation turns into:

$$i_p = 2.72 * 10^5 * n^{\frac{3}{2}} * A * D^{\frac{1}{2}} * C * v^{\frac{1}{2}}$$

where,

$i_p$  = current maximum in amps

$n$  = number of electrons transferred in the redox process

$A$  = electrode area in  $\text{cm}^2$

$F$  = Faraday constant in  $\text{C.mol}^{-1}$

$D$  = diffusion coefficient in  $\text{cm}^2.\text{s}^{-1}$

$C$  = concentration in  $\text{mol.cm}^{-3}$

$v$  = scan rate in  $\text{V.s}^{-1}$

$R$  = Gas constant in  $\text{J.mol}^{-1}.\text{K}^{-1}$

T = temperature in K.

Hence, the scan rate for the anodic and cathodic peak currents gave a linear dependence as a function of the scan rate as illustrated in Figure 3.2. Scan rate studies revealed that polymer films were electroactive and adhered well to the electrode surface. Besides, it was understood that non-diffusion controlled mass transfer occurred in the redox process. Counter ions in the electrolyte solution ( $\text{PF}_6^-$  in our system) diffuse in and out of the polymer film surface and they cannot catch the speed of charges (positive charges) moving through the polymer chain. Thus, if a diffusion-controlled mass transfer occurs during the redox process a linear relation between the current and scan rate could not be established.

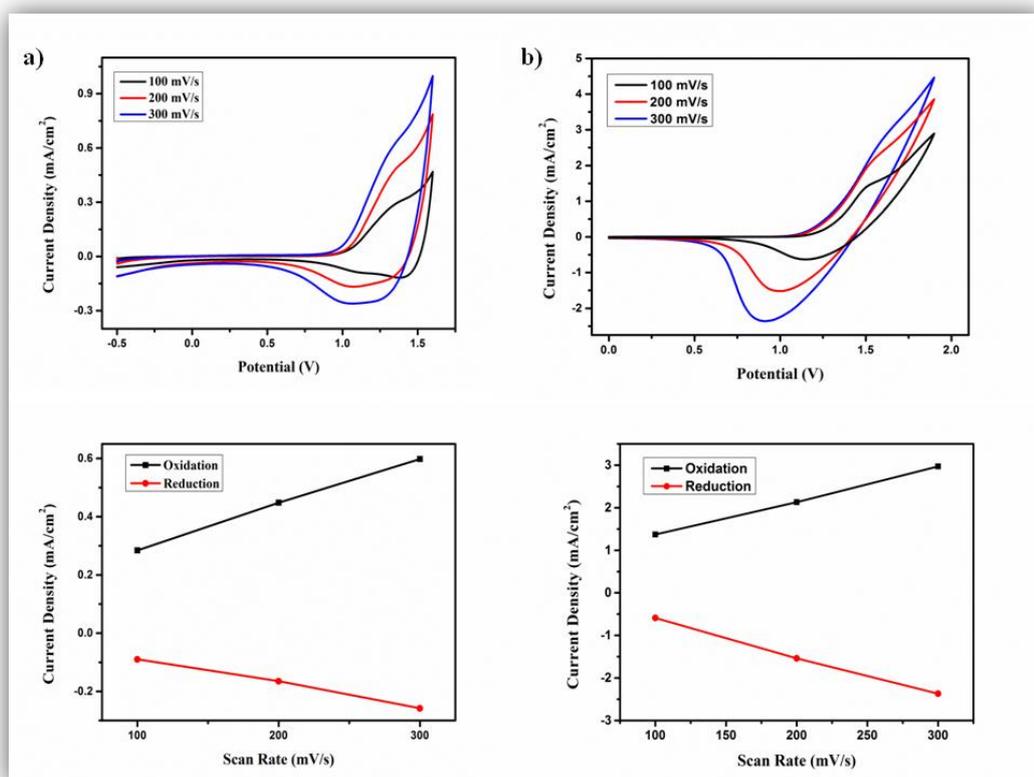


Figure 3.2. Scan rates studies of a) P1 and b) P2 in 0.1 M TBAPF<sub>6</sub>/ACN solution at different scan rates

## 3.2. Spectroelectrochemical Characterizations of Polymers

### 3.2.1. Optical Studies

Spectroelectrochemical studies were performed to observe the absorption behavior of the polymer from Visible to NIR range, starting from the neutral to oxidized states of polymers. Maximum absorption wavelength ( $\lambda_{\max}$ ), polaron and bipolaron bands which are regarded as the charge carriers in polymer backbone or optical band gaps were estimated from the spectroelectrochemical studies. Maximum absorption wavelength of the polymer is related with the neutral color of polymer ( $\lambda_{\max}$ ) and the polymer shows the compensate color of the absorbed wavelength. System consists of a spectrophotometer and a potentiostat with three electrodes. 5 mg.mL<sup>-1</sup> solutions of polymers were prepared in chloroform and spray coated onto the ITO working electrode. Starting from the neutral state of the polymers, their absorption behaviors were scanned between Vis-NIR ranges via external potential application step wise step. As a result of these experiments, P1 had a maximum absorption wavelength around 485 nm, P2 had a maximum around 475 nm and P3 had a maximum around 420 nm. To calculate the band gaps, onset values of maximum wavelengths were found as 569 nm for P1, 561 nm for P2 and 520 nm for P3. For the calculation of the optical band gaps of polymers general equation for a photon was used:

$$E = h\nu = \frac{h * c}{\lambda}$$

where

h is Planck's constant (  $h = 6.626 \times 10^{-34}$  J·s)

c is the speed of light (  $c = 2.998 \times 10^8$  m.s<sup>-1</sup>).

When these two parameters are used and conversion of Joules to electron volt (eV) is made equation turns into the following:

$$E = \frac{1241}{\lambda_{max}^{onset}} (eV)$$

Hence, corresponding optical band gap values of the polymers were calculated as 2.18 eV, 2.21 eV and 2.38 eV for P1, P2 and P3, respectively. Upon applied potential to the polymers neutral absorption band started to decrease since the polymer films turned into a different color and polaron and bipolaron bands started to form. P2 had more definite polaron and bipolaron bands than P1 and P3. Since the oxidation potential of P2 was well defined compared to other two polymers', P2 was rapidly oxidized and showed clear polaron and bipolaron band formations. However, a decrease in the neutral absorption band of P2 could not be achieved. It can be explained by the dark gray color of the polymer in its oxidized state, hence very broad absorption in the visible region was observed. Results of spectroelectrochemical studies were summarized in Table 3.2.

Table3.2. Results of the optical studies of the polymers

	$\lambda_{max}$ (nm)	$\lambda_{max}^{onset}$ (nm)	$E_g^{op}$ (eV)
<b>P1</b>	485	569	2.18
<b>P2</b>	475	561	2.21
<b>P3</b>	420	520	2.38

There are several examples of carbazole and fluorene based polymers coupled with benzothiadiazoles or benzoselenadiazoles [59]. Introduction of two strong electron accepting units into the polymer backbone decreased LUMO energy levels and thus the optical band gaps. Efficient combination of strong electron donor units with acceptor species resulted in the synthesis of three copolymers with high HOMO and low LUMO levels and low band gaps as expected.

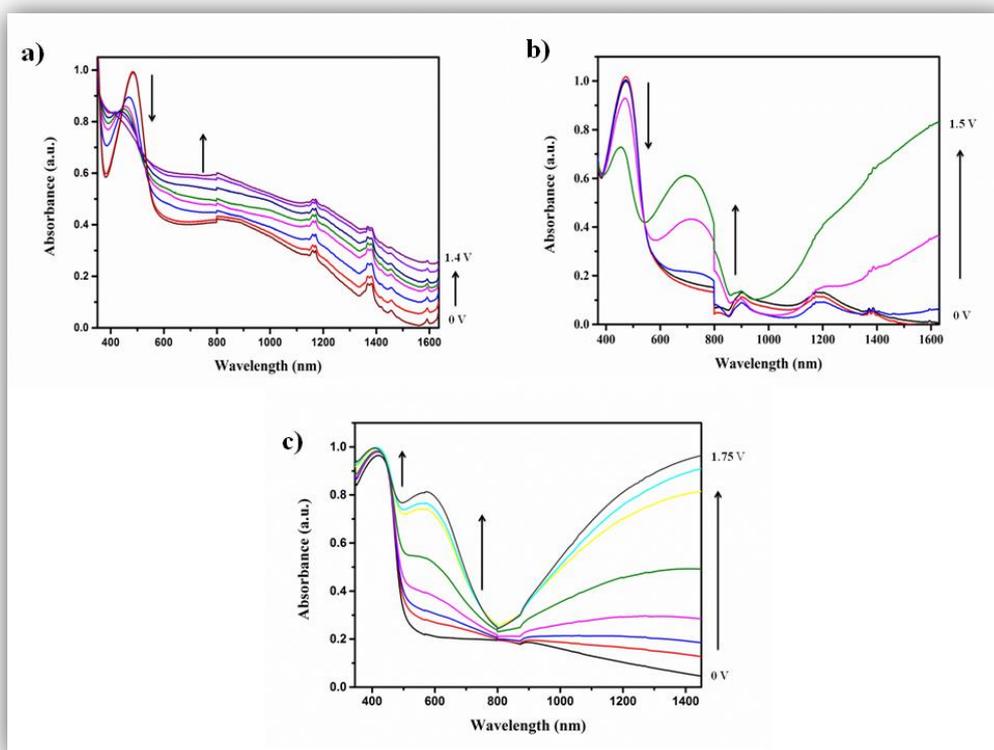


Figure 3.3. Electronic absorption spectrum of a) P1, b) P2 and c) P3 in 0.1 M TBAPF<sub>6</sub>/ACN solution upon oxidative doping potentials

### 3.2.2. Kinetic Studies

Kinetic studies were performed to investigate the percent transmittance change ( $\Delta T$  %) and switching time of the polymers. Percent transmittance change or optical contrast is the change in transmittance value of the polymer between the extreme states at a constant value. Switching time is the time for a polymer required to switch between its extreme states (neutral and oxidized/reduced states) at a 95% contrast value since the human eye is sensitive up to 95% full of contrast. Kinetic studies show the electrochromic stability of the polymer, how well and fast the polymer switches between two states. Kinetic studies were performed in visible and NIR regions via square-wave potential application to the polymer film for 5 s time intervals. Hence, polymer shows the transmittance value at the corresponding state for 5 s. Wavelengths for neutral, polaron and bipolaron

regions were chosen from the spectrum of the polymers at which maximum absorption values were obtained.

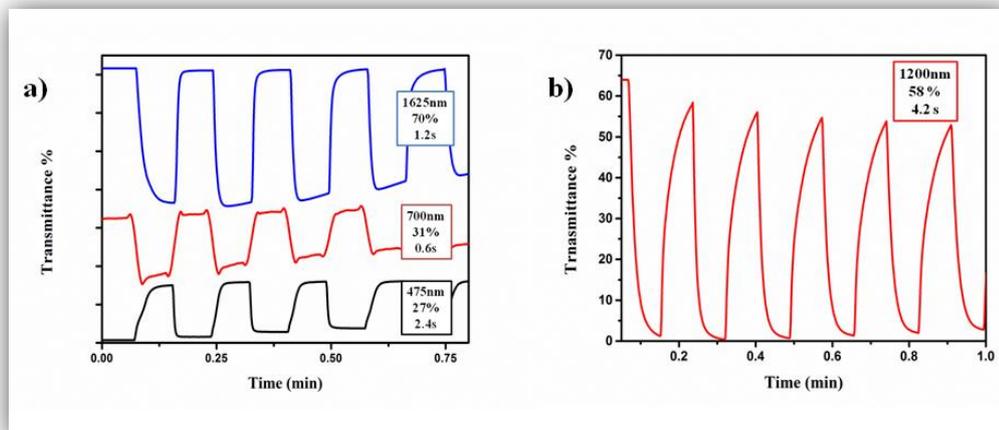


Figure 3.4. Percent transmittance changes and switching times of a) P2 and b) P3 when switched between neutral and oxidized states in 0.1 M TBAPF<sub>6</sub>/ACN solution

The optical contrasts were calculated as 27% at 475 nm, 31% at 700 nm and 70% at 1625 nm for P2 whilst P3 showed an optical contrast of 58% at 1200 nm as shown in Figure 3.4. Corresponding switching time and optical contrast values were summarized in Table 3.3. Since the stability of P1 was not as good as P2 and P3 its kinetic studies could not be performed successfully.

Table 3.3. Optical contrast and switching time results of the polymers

	<b>Wavelength (nm)</b>	<b>Transmittance (%)</b>	<b>Switching Time (s)</b>
<b>P1</b>	485	4	1.4
	1200	30	2.4
<b>P2</b>	475	27	2.4
	700	31	0.6
	1625	70	1.2
<b>P3</b>	485	4	1.4
	1200	58	4.2

### 3.2.3. Colorimetric Studies

Statement of a color is a relative concept that can create personal errors in scientific aspect. In order to eliminate the subjective view, a standard color reporting method based on CIE coordinates (International Commission on Illumination) has been used most commonly. According to this standard, colors are described with three values which are luminance (L), hue (a) and saturation (b). a represents the color between red/magenta and green and b represents between yellow and blue colors. Since all polymers have similar structures, they had similar color in their neutral states. All of them were yellowish-orange in their neutral states and upon applied potential P1 and P2 had greenish-gray color and P3 had dark gray color (Figure 3.5). L, a, b values of the polymers were summarized in Table 3.4.

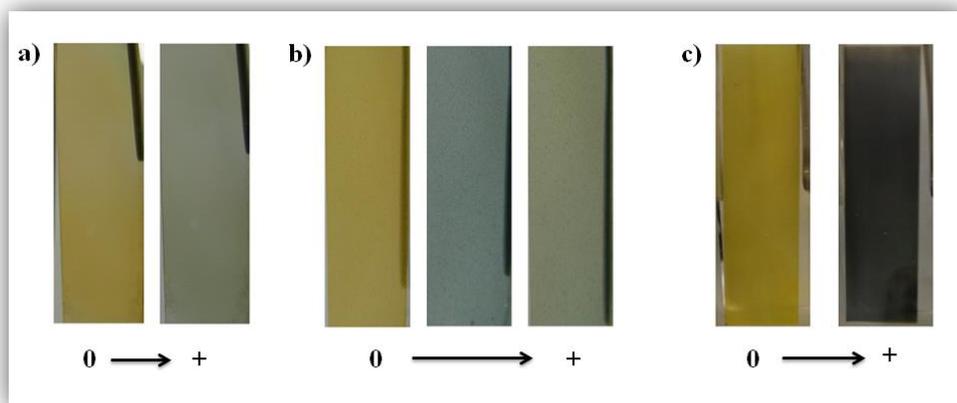


Figure 3.5. Colors of a) P1, b) P2 and c) P3 in their neutral and oxidized states

Table 3.4. Results of the colorimetric studies of the polymers

	Applied Potential (V)	L	a	b
<b>P1</b>	0.0	65	4.2	51
	1.3	65	-4.6	15
<b>P2</b>	0.0	75	-8.8	54
	1.4	57	-7.4	2.2
	1.7	66	-9.9	13
<b>P3</b>	0.0	84	-15	76
	1.7	32	-2.0	6.0



## CHAPTER 4

### CONCLUSION

Three novel donor-acceptor-donor type conjugated random copolymers were designed and synthesized via Suzuki polycondensation reaction under inert atmosphere. 2,1,3-Benzothiadiazole (BTh) and 2,1,3-benzoselenadiazole (BSe) were chosen as the acceptor units. In order to combine these strong acceptor units with strong electron releasing molecules and get efficient intramolecular charge transfers, three donor units which are carbazole, fluorene and silafluorene were coupled with both BTh and BSe. There are several examples of carbazoles and fluorenes coupled with either BTh or BSe unit; however, using both acceptor units in a polymer chain was for the first time. Synthesized monomers were characterized using  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectroscopy method. After the characterization of the monomers, they were coupled with donor units via Suzuki coupling reactions in the presence of Pd (0) catalyst yielding P1 (carbazole based copolymer), P2 (fluorene based copolymer) and P3 (silafluorene based copolymer), respectively. Number-average ( $M_n$ ) and weight-average ( $M_w$ ) molecular weights of the polymers were measured via GPC method. All polymers were characterized electrochemically and spectroelectrochemically. Electrochemical studies were performed via cyclic voltammetry method with a three electrode system. Polymer solution with  $5 \text{ mg.mL}^{-1}$  concentration were prepared in chloroform ( $\text{CHCl}_3$ ) solution and spray coated with a spray gun onto the ITO working electrode. Single scan cyclic voltammograms showed that oxidation potentials were recorded as 1.4 V, 1.53 V and 1.80 V for P1, P2 and P3, respectively. Due to the efficient electron donating ability of nitrogen atom on P1 increased the electron density and intramolecular charge transfer; hence, doping/dedoping process could be performed easily. Since all polymers had only

p-dopable character, only HOMO energy levels were calculated from the onset values of the oxidation potentials. LUMO energy levels were calculated from HOMO and optical band gap values measured from the spectroelectrochemistry studies. Corresponding HOMO energy levels were calculated as -5.85eV, -6.05eV and -6.15 eV whereas LUMO energy levels were calculated as -3.67 eV, -3.84 eV and -3.77 eV for P1, P2 and P3, respectively. Comparing HOMO/LUMO energy levels with each other, it was proved that carbazole based copolymer had higher HOMO energy level in accordance with the literature, which means that its electron releasing ability is higher than P2 and P3. In order to measure the percent transmittance change (optical contrast) and calculate the switching times of the polymers kinetic studies were performed. Square-wave form potentials were applied to the polymer film with 5 s time intervals in Visible and NIR regions. The wavelengths were chosen from the spectroelectrochemical studies at which polymers exhibited maximum absorption values in neutral and doped states. Corresponding optical contrasts were measured as 27 % at 475 nm, 31 % at 700 nm and 70 % at 1625 nm for P2 while P3 revealed 58 % percent transmittance at 1200 nm. For a further characterization, colorimetric studies were carried out. All polymers had yellowish-orange color in their neutral states due to their similar structures. As the polymers were doped, P1 and P2 turned into a greenish-gray color whereas P3 showed dark gray color in its oxidized form. Colors of polymers were reported with L, a, b values in accordance with CIE coordination.

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## REFERENCES

- [1] S. K. Deb, *Appl. Opt.*, 1969, 8, 192
- [2] P. R. Somani and S. Radhakrishnan, *Mater. Chem. Phys.*, 2002, 77, 117
- [3] P. M. S. Monk, R. J. Mortimer and D. R. Rosseinsky (2007) *Electrochromism and Electrochromic Devices*. Cambridge, UK: Cambridge Univ. Press
- [4] J. J. Berzelius, *Afh. Fys. Kemi Miner.*, 1815, 4, 293
- [5] F. Wöhler, *Ann. Phys.*, 1824, 2, 350
- [6] N. Kobosew and N. I. Nekrassow, *Z. Electrochem.*, 1930, 36, 529
- [7] L. Michaelis and E. S. Hill, *J. Gen. Physiol.*, 1933, 859
- [8] P. M. S. Monk (1998) *The Viologens: Physicochemical Properties, Synthesis and Applications of the Salts of 4,4'-Bipyridine*. Chichester: J Wiley & Sons
- [9] a) C. J. Schoot, J. J. Ponjee, H. T. van Dam, R. A. van Doom and P. J. Bolwijn, *Appl. Phys. Lett.*, 1973, 23, 64  
b) R. J. Jasinski, *J. Electrochem. Soc.*, 1978, 125, 619
- [10] a) L. J. M. Coleby, *Annals of Sci.*, 2006, 4, 206  
b) A. Kraft and G. GmbH, *Bull. Hist. Chem.*, 2008, 33, 61
- [11] A. Kraft and G. GmbH, *Bull. Hist. Chem.*, 2011, 36, 3
- [12] J. L. Frisch, *Miscellanea Berolinensia and Incrementum Scientiarum*, 1710, 1, 377
- [13] a) K. C. Ho, T. G. Rukavina and C. B. Greenberg, *J. Electrochem. Soc.*, 1994, 141, 2061  
b) L. M. N. Assis, J. R. Andrade, L. H. E. Santos, A. J. Motheo, B. Hajduk, M. Łapkowski and A. Pawlicka, *Electrochim. Acta*, 2015, 175, 176
- [14] K. Itaya and I. Uchida, *Acc. Chem. Res.*, 1986, 19, 162
- [15] a) L. Groenendaal, G. Zotti, P. H. Aubert, S. M. Waybright and J. R. Reynolds, *Adv. Mater.*, 2003, 15, 855  
b) R. M. Walczak and J. R. Reynolds, *Adv. Mater.*, 2006, 18, 1121  
c) J. Li and A.C. Grimsdale, *Chem. Soc. Rev.*, 2010, 39, 2399
- [16] P. M. Beaujuge and J. R. Reynolds, *Chem. Rev.*, 2010, 110, 268

- [17] a) B. C. Thomposon, P. Schottland, K. Zong and J. R. Reynolds, *Chem. Mater.*, 2000, 12, 1563  
 b) B. C. Thompson, P. Schottland, G. Sonmez and J. R. Reynolds, *Synth. Met.*, 2001, 119, 333
- [18] R. D. Overheim, and D. L. Wagner (1982) *Light and Color*, New York: Wiley
- [19] M. Mastragostino (1993) *Electrochromic Devices*. In B. Scrosati (Ed.), *Applications of Electroactive Polymers* (pp. 223-249) Dordrecht: Springer Science + Business Media
- [20] a) I. Schwendeman, J. Hwang, D. M. Welsh, D. B. Tanner and J. R. Reynolds, *Adv. Mater.*, 2001, 13, 634  
 b) P. Chandrasekhar (1999) *Conducting Polymers, Fundamentals and Applications*. Dordrecht: Kluwer Academic Publishers
- [21] J. S. E. M. Svensson, and C. G. Granqvist, *Sol. Energy Mater.*, 1985, 12, 391
- [22] H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang and A. J. Heeger, *J.C.S. Chem. Comm.*, 1977, 578
- [23] J. Roncali, *Macromol. Rapid. Commun.*, 2007, 28, 1761
- [24] W. C. Chen, C. L. Liu, C. T. Yen, F. C. Tsai, C. J. Tonzola, N. Olson and S. A. Jenekhe, *Macromolecules*, 2004, 37, 5959
- [25] E. E. Having, W. ten Hoeve and H. Wynberg, *Polym. Bull.*, 1992, 29
- [26] J. Roncali, *Chem. Rev.*, 1997, 97, 173
- [27] a) A. Malinauskas, *Polymer*, 2001, 42, 3957  
 b) S. Xu, E. H. Kim, A. Wei and E. Negishi, *Sci. Technol. Adv. Mater.*, 2014, 15, 23
- [28] J. F. Robinson and H. B. Mark (1999) *Conducting Polymer Films as Electrodes*. In .a. Wieckowski (Ed.), *Interfacial Electrochemistry: Theory, Experiment and Application* (pp. 689) New York: Marcel Dekker Inc.
- [29] a) R. D. McCullough, *Adv. Mater.*, 1998, 10, 93  
 b) C. Jianga, G. Chenb, and X. Wang, *Synth. Met.*, 2012, 162, 1968
- [30] N. Miyaura, K. Yamada and S. Akira, *Tetrahedron Lett.*, 1979, 20, 3437
- [31] D. Milstein and J. K. Stille, *J. Of Am. Chem. Soc.*, 1979, 101, 4992

- [32] E. Bundgaard and F. C. Krebs, *Macromolecules*, 2006, 39, 2823
- [33] C. Brabec, U. Scherf and V. Dyakonov (Eds.) (2011) *Organic Photovoltaics: Materials, Device Physics, and Manufacturing Technologies*. Weinheim: Wiley
- [34] a) K. Tamao, K. Sumitani and M. Kumada, *J. Am. Chem. Soc.*, 1972, 94, 4374
- b) R. J. P. Corriu and J. P. Massae, *Chem. Soc., Chem. Commun.*, 1972, 144a
- c) M. Yamamura, I. Moritani and S. Murahashi, *J. Organomet. Chem.*, 1975, 91, C39
- d) K. Tamao and M. Kumada et al., *Bull. Chem. Soc.*, 1976, 49, 1958
- [35] R. D. McCullough, S. P. Williams, S. Tristram-Nagle, M. Jayaraman, P. C. Ewbank, and L. Miller, *Synth. Met.*, 1995, 69, 279
- [36] R. S. Loewe, S. M. Khersonsky and R. D. McCullough, *Adv. Mater.*, 1999, 11, 250
- [37] a) T-An Chen and R. D. Rieke, *J. Am. Chem. Soc.*, 1992, 114, 10087
- b) T-An Chen, X. Wu, and R. D. Rieke, *J. Am. Chem. Soc.*, 1995, 117, 233
- [38] K. Sonogashira, Y. Tohda, and N. Hagihara, *Tetrahedron Lett.*, 1975, 16, 4467
- [39] S. Baysec, N. A. Unlu, S. O. Hacıoglu, Y. A. Udum, A. Cirpan and L. Toppare, *J. of Macromol. Sci. Part A: Pure and Appl. Chem.*, 2014, 52, 1
- [40] P. Xiao, W. Hong, Y. Li, Y. Dumur, B. Graff and J. P. Fouassier, D. Gigmes and J. Lalevee. *Polymer*, 2014, 55, 746
- [41] S. Goker, G. Hizalan, Y. A. Udum and L. Toppare, *Synth. Met.*, 2014, 191, 19
- [42] a) B. Yao, X. Zhou, X. Ye, J. Zhang, D. Yang, d. Ma and X. Wan, *Org. Electron.*, 2015, 26, 305
- b) P. Deng, Y. Lei, X. Zheng, S. Li, J. Wu, F. Zhu, B. S. Ong and Q. Zhang, *Dyes and Pigments*, 2016, 125, 407
- [43] a) Y. Lei, H. Li, X. Huang, J. Chen, M. Liu, W. Gao, J. Ding, D. Lin and H. Wu, *Tetrahedron*, 2015, 71, 3453

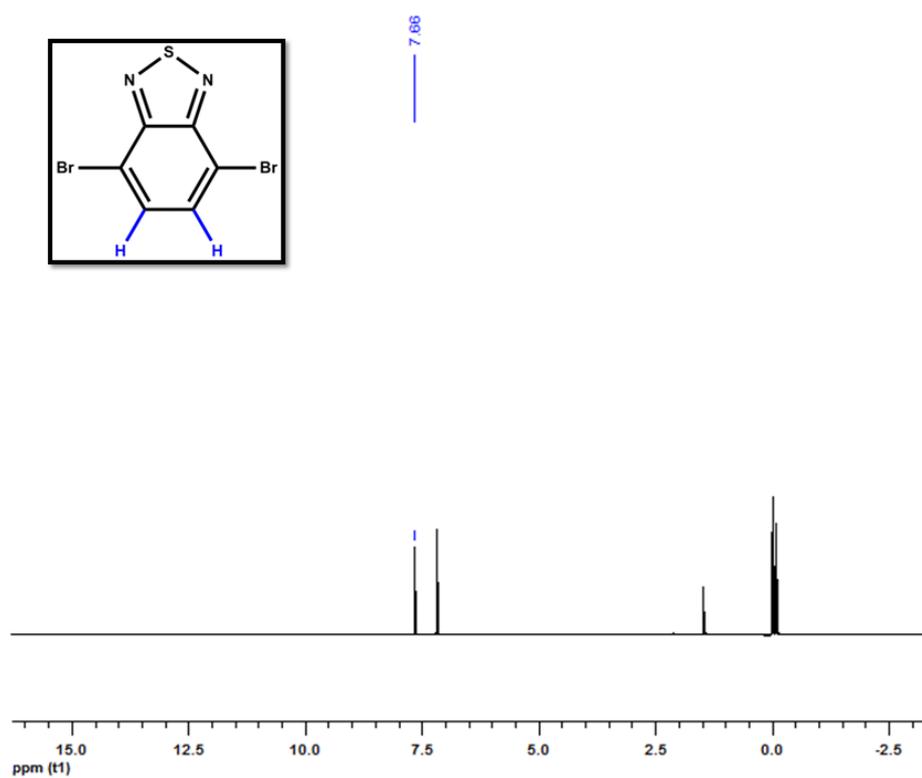
- b) S. A. Shin, J. B. Park, J. H. Kim and D. H. Hwang, *Synth. Met.*, 2013, 172, 54
- c) F. B. Emre, F. E. Kiz, A. Balan, S. Emre, S. Timur and L. Toppare, *Sensors and Actuators B: Chem.*, 2011, 158, 117
- [44] Y. Li and J. B. Lagowski, *Comp. Theo. Chem.*, 2011, 977, 157
- [45] J. Hou, M. H. Park, S. Zhang, Y. Yao, L. M. Chen, J. H. Li and Y. Yang, *Macromolecules*, 2008, 41, 6012
- [46] a) A. Patra, Y. H. Wijsboom, S. S. Zade, M. Li, Y. Sheymin, G. Leitun and M. Bendikov, *J. Am. Chem. Soc.*, 2008, 130, 6734
- b) E. Zhou, J. Cong, K. Hashimoto and K. Tajima, *Macromolecules*, 2013, 46, 763
- [47] a) V. Tamilavan, J. B. Park, I. N. Kang, D. H. Hwang, and M. H. Hyun, *Synth. Met.*, 2014, 198, 230
- b) R. Qin, J. Yang, P. Li, Q. Wu, Y. Zhou, H. Luo and F. Chang, *Sol. En. Mat. Sol. C.*, 2016, 145, 412
- c) F. Wu, S. Chen, L. Chen, and Y. Chen, *Polymer*, 2015, 78, 154
- d) Y. Zhang, Y. Li, F. Wang, Y. Zhao, C. Zhang, X. Wang and J. X. Jiang, *Polymer*, 2014, 55, 5746
- [48] a) T. Michinobu, H. Osako and K. Shigehara, *Polymers*, 2010, 2, 159
- b) H. Xie, K. Zhang, C. Duan, S. Liu, F. Huang and Y. Cao, *Polymer*, 2012, 25, 5675
- [49] J. Li and A. C. Grimsdale, *Chem. Soc. Rev.*, 2010, 39, 2399
- [50] a) A. Babel and S. A. Jenekle, *Macromolecules*, 2003, 36, 7759
- b) X. Gong, M. R. Robinson, J. C. Ostrowski, D. Moses, G. C. Bazan and A. J. Heeger, *Adv. Mater.*, 2003, 14, 581
- c) D. Neher, *Macromol. Rapid Comm.*, 2001, 22, 1365
- [51] J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger and G. Bazan, *Nature Mater.*, 2007, 6, 497
- [52] a) J. H. Huang, A. T. Huang, C. Y. Hsu, J. T. Lin and C. W. Chu, *Sol. En. Mat. Sol. C.*, 2012, 98, 300
- b) R. F. Chan, Q. L. Fan, S. J. Liu, R. Zhu, K. Y. Pu and W. Huang, *Synth. Met.* 2006, 156, 1161

- c) J. Chen and Y. Cao, *Macromol. Rapid. Comm.*, 2007, 28, 1714
- [53] K. Tamao, S. Yamaguchi, M. Shiozaki, Y. Nakagawa and Y. Ito, *J. Am. Chem. Soc.*, 1992, 114, 5867
- [54] a) M. Yuan, P. Yang, M. M. Durban and C. K. Luscombe, *Macromolecules*, 2012, 45, 5934
- b) O. Erlik, N. A. Unlu, G. Hizalan, S. O. Hacıoglu, S. Comez, E. D. Yildiz, L. Toppare and A. Cirpan, *J. Polym. Sci. Part A: Polym. Chem.*, 2015, 53, 1451
- [55] a) K. Pilgram, M. Zupan and S. Skiles, *J. Heterocycl. Chem.*, 1970, 7, 629
- b) Y. Tsubata, T. Suzuki, T. Miyashi and Y. Yamashita, *J. Org. Chem.*, 1992, 57, 6749
- [56] a) N. Blouin, A. Michaud and M. Leclerc, *Adv. Mater.*, 2007, 19, 2295
- b) J. H. Kim, J. B. Park, S. A. Shin, M. H. Hyun and D. H. Hwang, *Polymer*, 2014, 55, 3605
- [57] I. E. Kuznetsov, D. K. Susarova, L. N. Inasaridze, M. V. Klyuev and P. A. Troshin, *Mendeleev. Commun.*, 2015, 25, 277
- [58] L. Yang, J. K. Feng and A. M. Ren, *J. Mol. Str.: Theochem.*, 2007, 816, 161
- [59] a) W. Zhao, W. Cai, R. Xu, W. Yang, X. Gong, H. Wu and Y. Cao, *Polymer*, 2010, 51, 3196
- b) N. Blouin, A. Michaud, D. Gendron, S. Wakim, E. Blair, R. Neagu-Plesu, M. Belletete, G. Durocher, Y. Tao and M. Leclerc, *J. Am. Chem. Soc.*, 2008, 130, 732
- c) R. Yang, R. Tian, Q. Hou, W. Yang and Y. Cao, *Macromolecules*, 2003, 36, 7453
- d) J. Iou, Q. Hou, J. Chen and Y. Cao, *Synth. Met.*, 2006, 156, 470
- e) B. Qu, L. Feng, H. Yang, Z. Gao, C. Gao, Z. Chen, L. Xiao and Q. Gong, *Synth. Met.*, 2012, 162, 1587
- f) Z. Chen, J. Fang, F. Gao, T. J. K. Brenner, K. K. Banger, X. Wang, W. T. S. Huck and H. Siringhaus, *Org. Electron.*, 2011, 12, 461
- g) P. Herguth, X. Jiang, M. S. Liu and A. K. Y. Jen, *Macromolecules*, 2002, 35, 6094

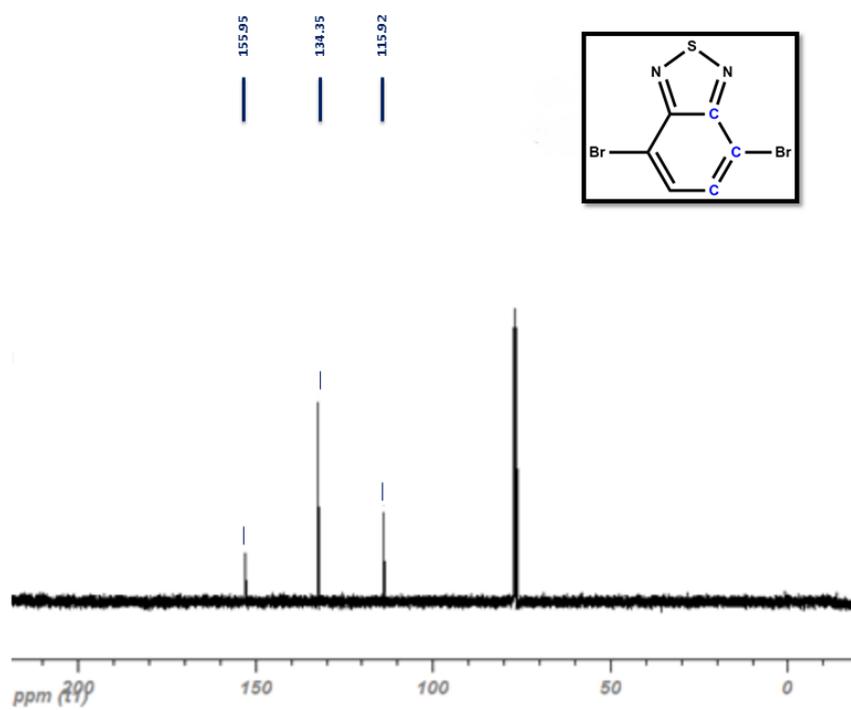
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## APPENDIX

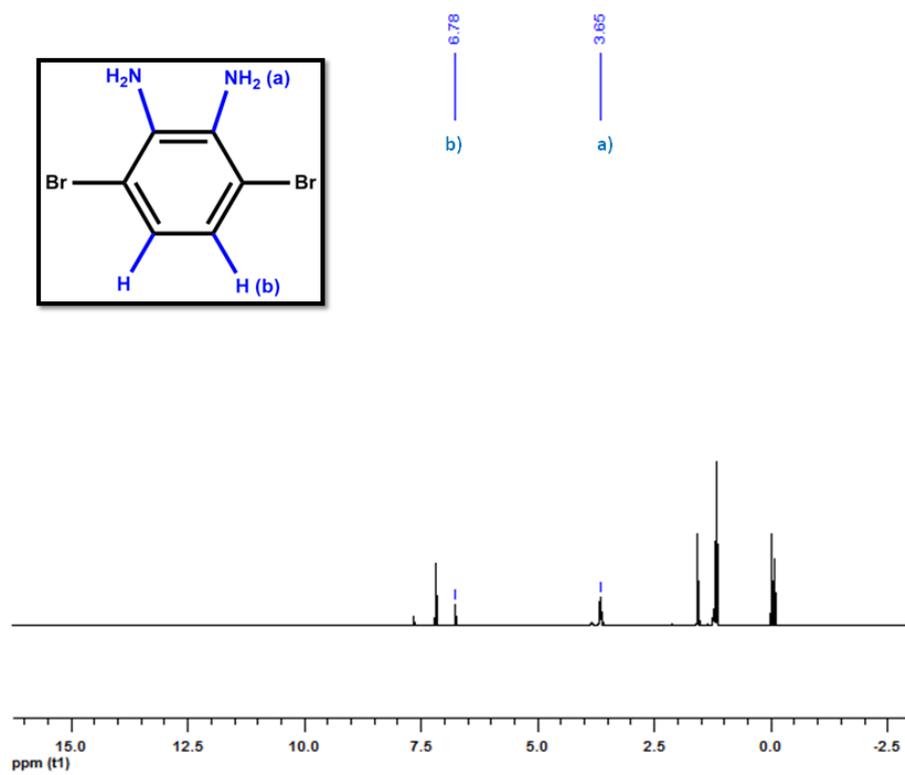
### NMR Spectra of Synthesized Monomers and Polymers



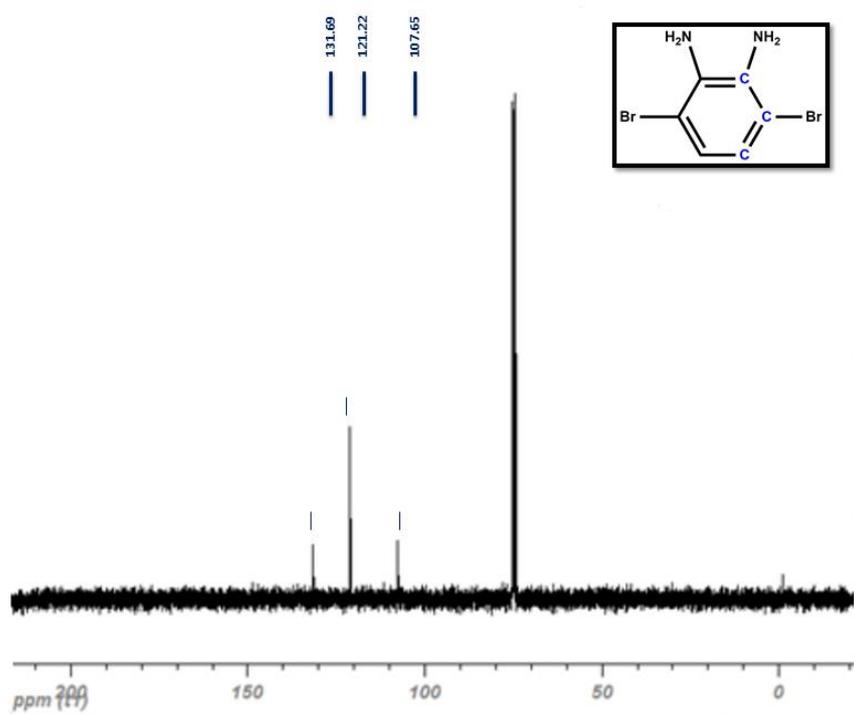
**Figure A1.** <sup>1</sup>H-NMR spectrum of 4,7-dibromobenzo[c][1,2,5]thiadiazole



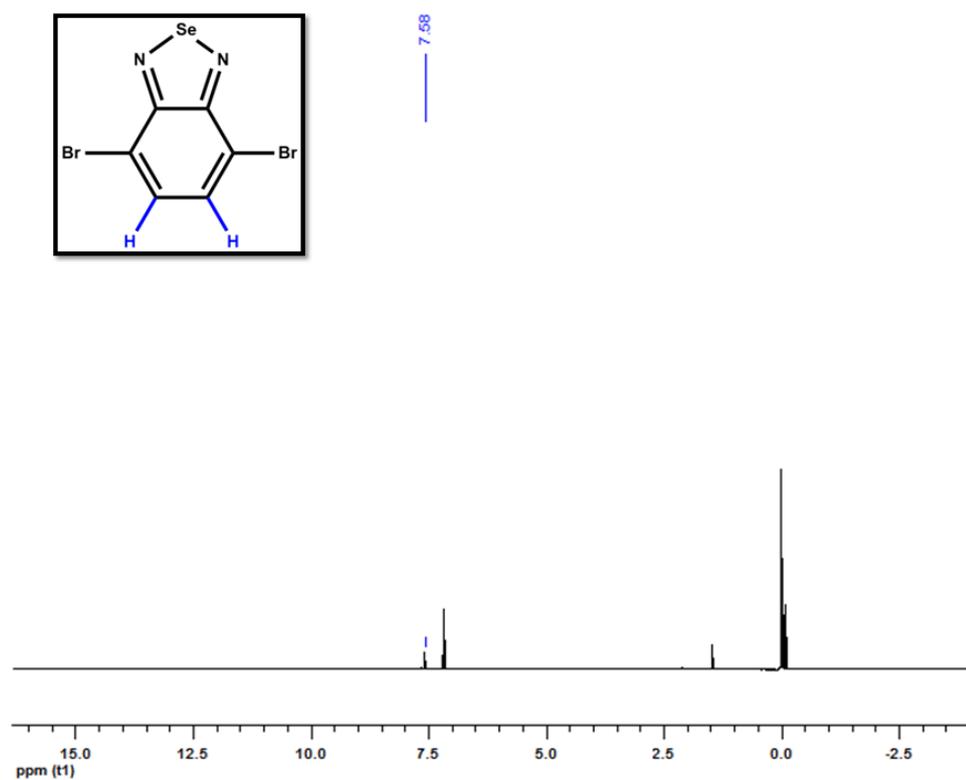
**Figure A2.**  $^{13}\text{C}$ -NMR spectrum of 4,7-dibromobenzo[c][1,2,5]thiadiazole



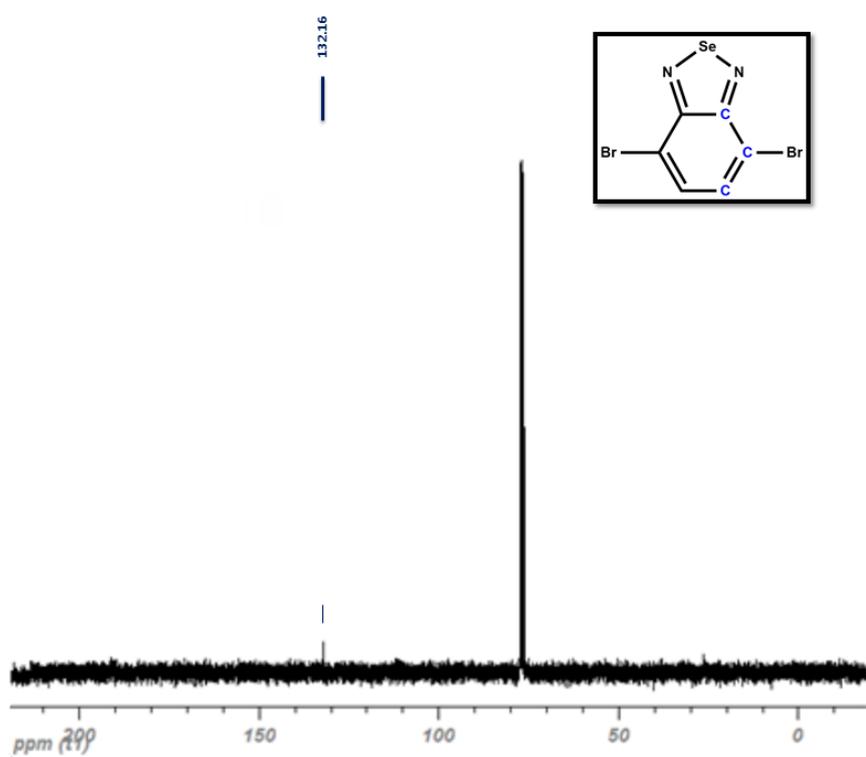
**Figure A3.**  $^1\text{H-NMR}$  spectrum of 3,6-dibromobenzene-1,2-diamine



**Figure A4.**  $^{13}\text{C}$ -NMR spectrum of 3,6-dibromobenzene-1,2-diamine



**Figure A5.** <sup>1</sup>H-NMR spectrum of 4,7-dibromo-benzo[*c*][1,2,5]selenadiazole



**Figure A6.**  $^{13}\text{C}$ -NMR spectrum of 4,7-dibromo-benzo[*c*][1,2,5]selenadiazole

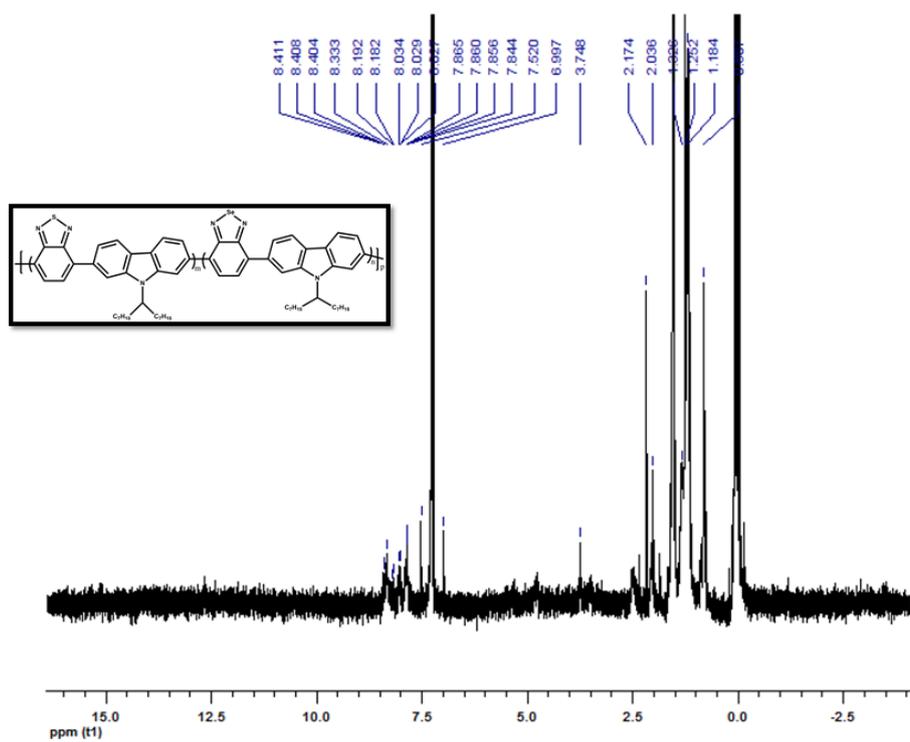
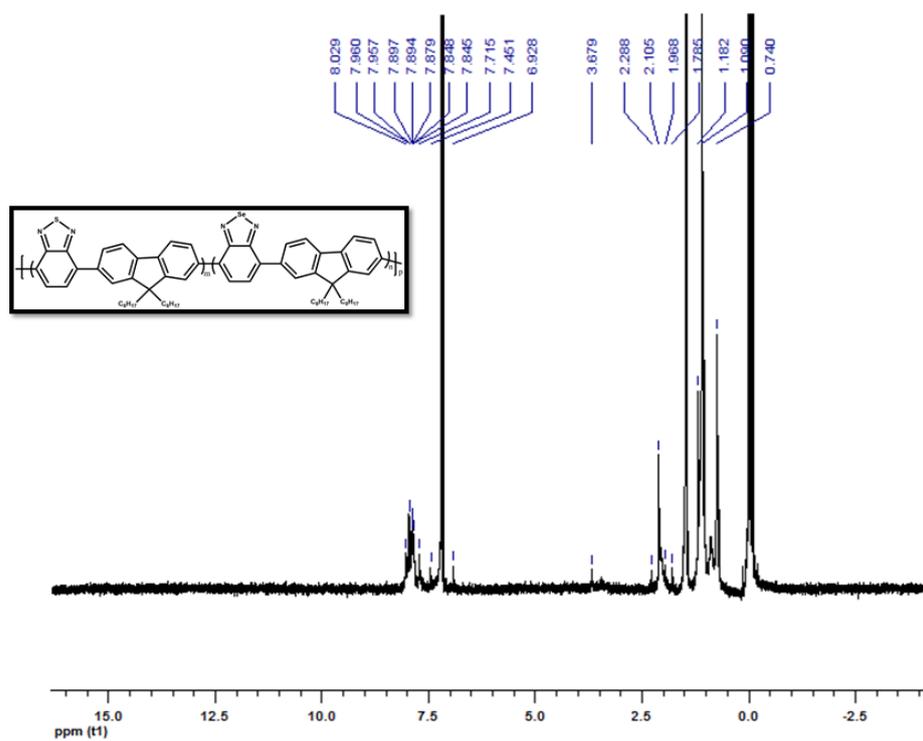


Figure A7. <sup>1</sup>H-NMR spectrum of P1



**Figure A8.** <sup>1</sup>H-NMR spectrum of P2

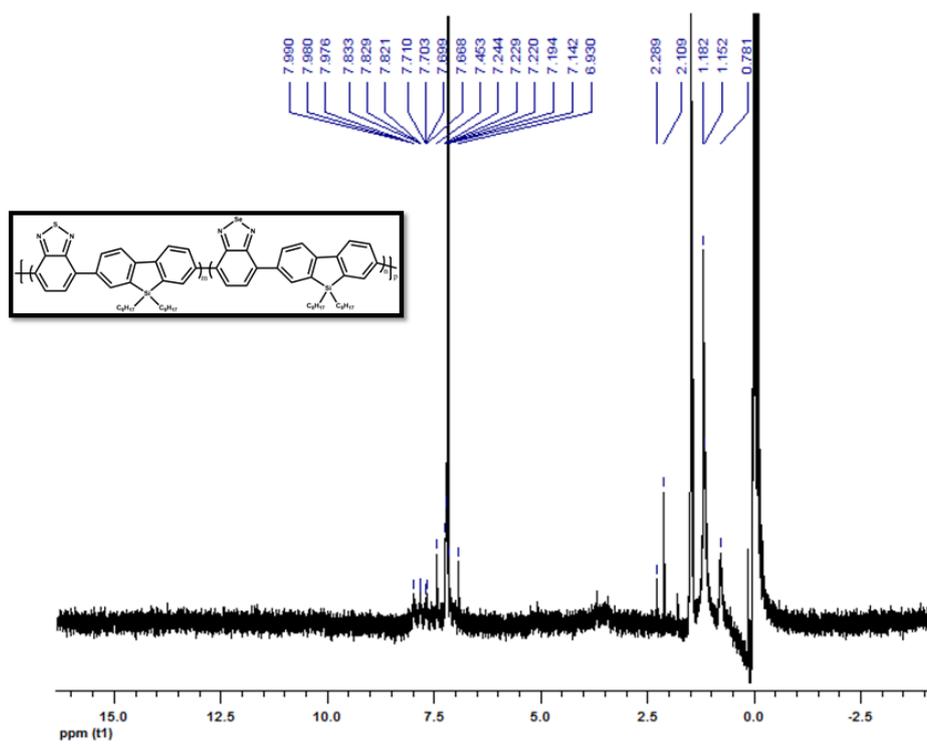


Figure A9. <sup>1</sup>H-NMR spectrum of P3