THE COMBINATION OF BENZOTRIAZOLE AND N-FUNCTIONALIZED 2,5-DI(2-THIENYL)-1H-PYRROLE UNITS TO INVESTIGATE THE ELECTROCHROMIC PROPERTIES OF CONJUGATED POLYMERS

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THE COMBINATION OF BENZOTRIAZOLE AND N-FUNCTIONALIZED 2,5-DI(2-THIENYL)-1H-PYRROLE UNITS TO INVESTIGATE THE ELECTROCHROMIC PROPERTIES OF CONJUGATED POLYMERS

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ABSTRACT

THE COMBINATION OF BENZOTRIAZOLE AND N-FUNCTIONALIZED 2,5-DI(2-THIENYL)-1H-PYRROLE UNITS TO INVESTIGATE THE ELECTROCHROMIC PROPERTIES OF CONJUGATED POLYMERS

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Synthesis of new conducting polymers is desired since their electrochemical and optical properties enable them to be used as active layers in many device applications. Benzotriazole and n-functionalized 2,5-di(2-thienyl)-1h-pyrrole (SNS Series) containing polymers showed very promising results as electrochromic materials. In order to observe the effect of the combination of these two units three new monomers 2-(6-(2,5-bis(5-methylthiophen-2-yl)-1H-pyrrol-1-yl)hexyl)-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (M1), 2-(6-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)hexyl)-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (M2) and 2-(6-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)hexyl)-4,7-bis(5-methylthiophen-2-yl)-2H-benzo[d][1,2,3]triazole (M3) were synthesized and electrochemically polymerized. The resultant polymers were characterized with cyclic voltammetry and UV-Vis-NIR Spectroscopy techniques. An electrochromic device was constructed with electrochemical polymer of M2.The device switched between red and blue colors and showed exceptional optical memory.

Keywords: Benzotriazole, SNS Series, electrochromism, electrochromic device.

ÖZ

KONJUGE POLİMERLERİN ELEKTROKROMİK ÖZELLİKLERİNİN ARAŞTIRILMASI İÇİN BENZOTRİAZOL VE N-FONKSİYONLANMIŞ 2,5-Dİ(2-TİYENİL)-1H-PİROL ÜNİTELERİNİN KOMBİNASYONU

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Temmuz 2013, 49 sayfa

Elektrokimyasal ve optik özellikleri ile aktif katman olarak cihaz uygulamalarında kullanılabildiği için yeni konjige polimer sentezleri istenmektedir. Benzotriazol ve n-fonksiyonlandırılmış 2,5-di(2-tiyenil)-1h-pirol (SNS Serisi) yapıları içeren polimerler elektrokromik olarak umut verici sonuçlar vermektedirler. Bu iki ünitenin kombine edilmesinin etkilerini ve özelliklerini incelemek amacı ile üç yeni monomer olan; 2-(6-(2,5-bis(5-metilthyofen-2-il)-1H-pirol-1-yl)hegzil)-4,7-di(tiyofen-2-il)-2H-benzo[d][1,2,3]triazol (M1), 2-(6-(2,5-di(tiyofen-2-il)-1H-pirol-1-il)hegzil)-4,7-di(tiyofen-2-il)-2H-benzo[d][1,2,3]triazol (M2) ve 2-(6-(2,5-di(tiyofen-2-il)-1H-pirol-1-il)hegzil)-4,7-bis(5-metiltiyofen-2-il)-2H-benzo[d][1,2,3]triazol (M3) sentezlendi ve elektrokimyasal olarak olarak polimerleştirildi. Elde edilen polimerler dönüşümlü voltametre ve UV-Vis-NIR teknikleri ile karakterize edildi. M2 monomerinden elde edilen polimer ile elektrokimyasal cihaz uygulaması gerçekleştirildi. Cihaz kırmızı ve mavi renk değişimleri gösterdi ve cihazın renkleri uzun süre hatırladığı gözlendi.

Anahtar Kelimeler: Benzotriazol, SNS Serisi, Elektrokromizm, Elektrokromik Cihaz.

To My Beloved Family
and The One That I Love

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ABBREVATIONS

ACN	Acetonitrile
BT	Benzotriazole
CB	Conduction Band
CV	Cyclic Voltammetry
DCM	Dichloromethane
ECD	Electrochromic Device
E_g	Band Gap Energy
HOMO	Highest Occupied Molecular Orbital
ITO	Indium Tin Oxide
$LiCClO_4$	Lithium perchlorate
LUMO	Lowest Unoccupied Molecular Orbital
$NaClO_4$	Sodium perchlorate
NMR	Nuclear Magnetic Resonance
M1	2-(6-(2,5-bis(5-methylthiophen-2-yl)-1H-pyrrol-1-yl)hexyl)-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole
M2	2-(6-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)hexyl)-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole
M3	2-(6-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)hexyl)-4,7-bis(5-methylthiophen-2-yl)-2H-benzo[d][1,2,3]triazole
PEDOT	Poly(3,4-ethylenedioxythiophene)
PMMA	Poly(methyl methacrylate)
SNS	N-functionalized 2,5-di(2-thienyl)-1h-pyrrole
VB	Valence Band

CHAPTER 1

INTRODUCTION

1.1 Conducting Polymers

Materials which exhibit electrical and optical characteristics of metals or semiconductors while retaining mechanical properties and processing advantages of polymers are called conducting polymers. [1] Although all carbon based polymers were regarded as insulators about 30 years ago, the accidental discovery of conjugated polymers conducting electricity upon doping changed this bias. In 1977, Shrikawa group discovered that exposure of polyacetylene to halogen vapors such as bromine, chlorine or iodine increased its conductivity a billion fold. [2,3] With this discovery, three scientists; Hideki Shrikawa, Alan J. Heeger and Alan MacDiarmid were awarded with a Chemistry Nobel Prize in 2000. This progrees led to a great attention on conducting polymers from different scientific disiplines like chemistry, physics and materials science.

In spite of having high conductivity, polyacetylene is inflexible and unstable toward oxygen and hence it can not be commercialized. Therefore, the need for synthesizing soluble, stable and processable polymers led scientists to design new conducting polymers. These new classes of conducting polmers such as polypyrrole, polythiophene, poly(3,4-ethylenedioxythiophene) and many others showed better properties than polyacetylene. (Figure 1.1)

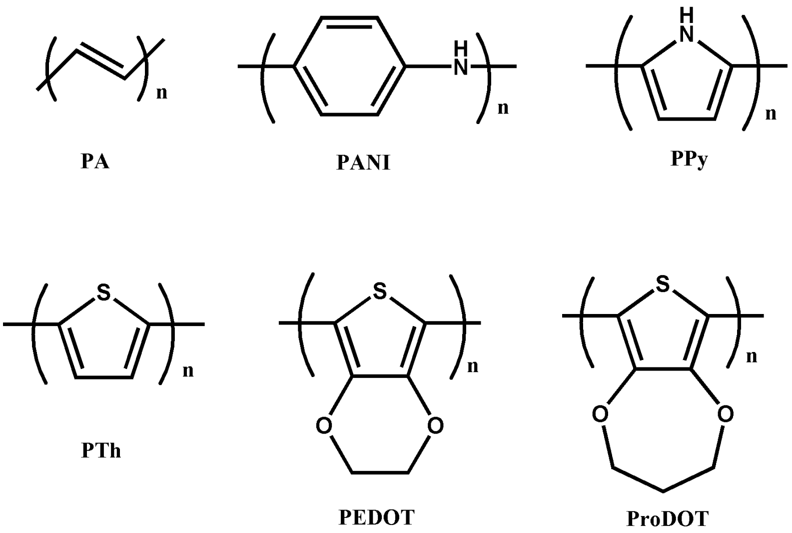


Figure 1.1 Some common conjugated polymers

Nowadays, not only their ability to conduct electricity but also their great optoelectronic properties of conducting polymers draw attention. They have wide application areas including smart windows [4], electrochromic devices [5-7], organic light emitting diodes [8], organic solar cells [9-10] and organic field effect transistors [11].

1.2 Band Theory

Electronic structure of a material determines its electrical properties. Conducting polymers, highly conjugated molecules, have delocalized band-like electronic structure and they are classified as semiconductors. This electronic structure and conduction mechanism can be explained by the band theory. With the help of this theory, materials are classified as insulators, semiconductors or metals depending on their relative separation of occupied and unoccupied energy states. (Figure 1.2) The energy spacing between the highest occupied molecular orbital (HOMO), constitutes the valance band (VB), and the lowest unoccupied molecular orbital (LUMO), constitutes the conduction band (CB), is entitled as tha band gap (E_g) [12]. For a conducting polymer, E_g can be calculated from either the onset of the π-π^* transition in the UV-Vis spectrum or the oxidation and reduction onset values.

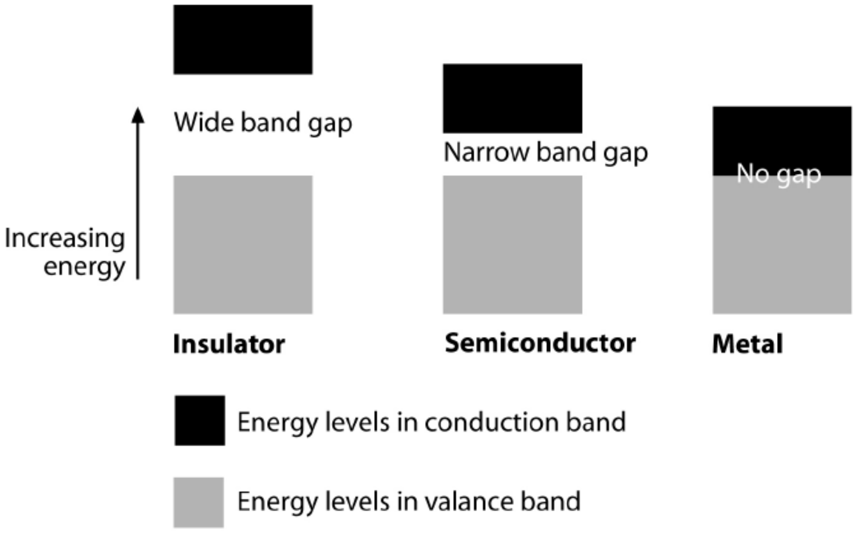


Figure 1.2 Band structures of insulator, semiconductor and metal

Metals possess no energy gap because their conduction and valence bands overlap. For this reason, electrons can flow through the material. On the other hand, insulators possess large energy gap between their conduction and valence bands, so the electron mobility does not occur. According to their band gaps conducting polymers are semiconductors in their neutral form. However, upon doping process interband transitions form between valence and conduction bands, thus band gap of the polymer becomes smaller and the charge carries along the polymer backbone form. Figure 1.3 demonstrates the formation of interbands as conjugation increases in a molecule. “As the conjugation increases, repeating units’ π orbitals are overlapping so that there is no more discrete energy levels, continium band structures are formed.” [12]

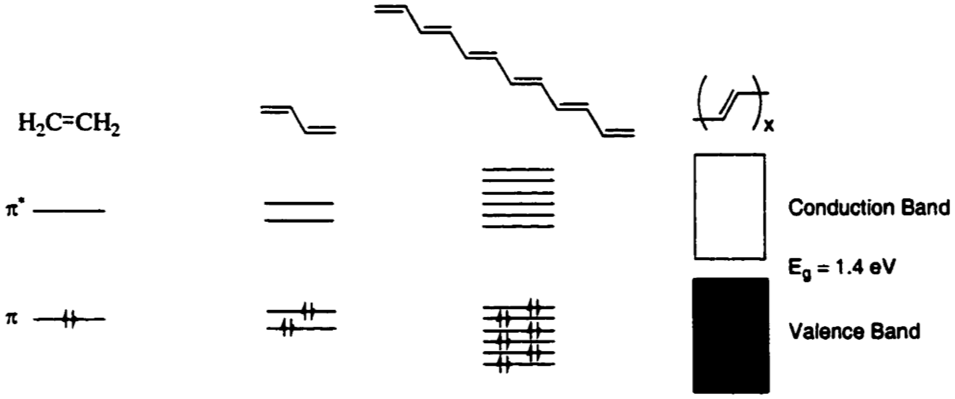


Figure 1.3 The formation of bands as conjugation increases

1.3 Conduction in Conjugated Polymers

In conjugated polymers, doping process causes the conductivity. The mechanism of conductivity in conjugated polymers stands for the movement of positive or negative charge carriers along the π-backbone of the polymer. These charge carriers are created via either oxidation, causing the formation of positively charged carriers (p-type), or reduction, causing the formation of negatively charged carriers (n-type) on the polymer backbone.

When a polymer is doped, its structure becomes different than its undoped one. The doped structure of conjugated polymer generates solitons, polarons and bipolarons, as conjugational defets on the polymer chain.

1.3.1 Charge Carriers

To have a better understanding of conductivity in conjugated polymer; the concept of solitons, polarons and bipolarons are defined as well as band theory.

Soliton is a conjugational defect which can be classified as neutral, positive and negative solitons. In neutral soliton, energy level is singly occupied and therefore, the spin has the value of ½. During the electrochemical oxidation and reduction, positively and negatively solitons are obtained by the insertion of acceptor band (an electron is removed) and donor band (an electron is added) respectively. (Figure 1.4)

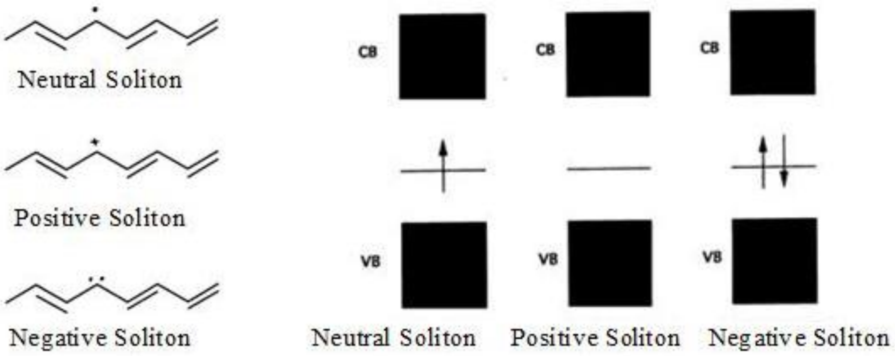


Figure 1.4 Neutral, positive and neative soliton structures of polyacetylene

A partially delocalized radical cation on the conjugated polymer backbone, which is generated during the oxidation process, is called polaron. If oxidation proceeds further, the unpaired electron of the polaron removes or two polarons combine to form bipolaron. (Figure 1.5) Due to the mobility of both polarons and bipolarons, they can move along the polymer backbone and conduct electricity.

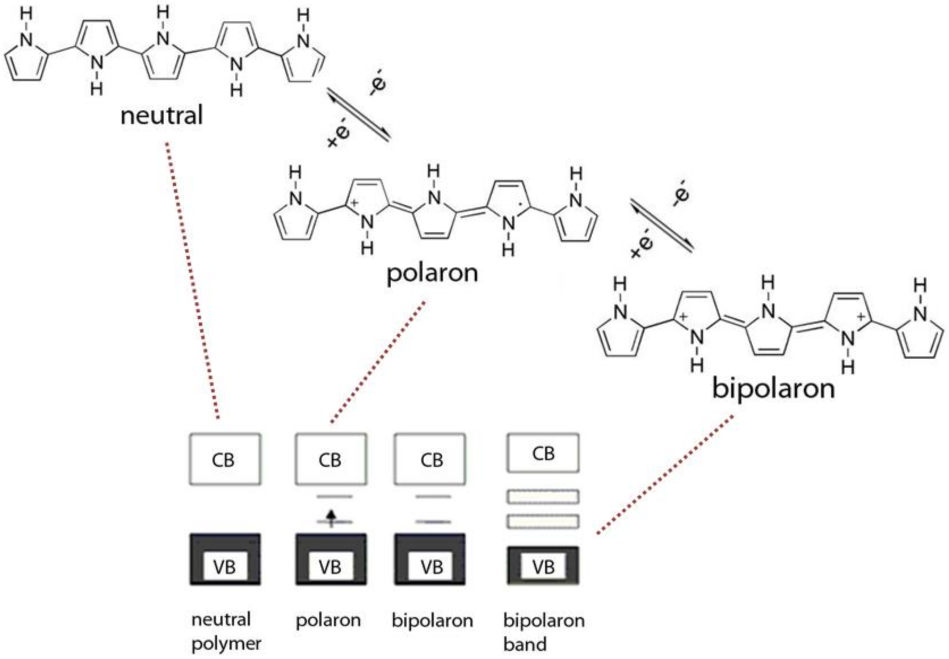


Figure 1.5 Charge carries in polypyrrole and its corresponding energy bands

During all conjugational defects, the diffusion of counter ions provides the charge neutrality. By doping process, these charge carriers are formed and at high levels of doping they interact with each other to form a band which can combine to create true metallic conductivity.

1.3.2 Doping Process

Doping process is defined as the enhancement of conductivity by charge injection into a conjugated polymer chain. Most conjugated polymers are semiconductors or insulators in their un-doped (neutral) form, with doping process they become higly conductive materials. This process involves the partial addition (reduction, n-type doping) or removal (oxidation, p-type doping) of electrons to (from) the polymer chain and it should be reversible. Doping can be done by different ways such as chemical, photochemical, interfacial or electrochemical and all of them consist of reversible oxidation and reduction in order to proceed doping-dedoping. (Figure 1.6)

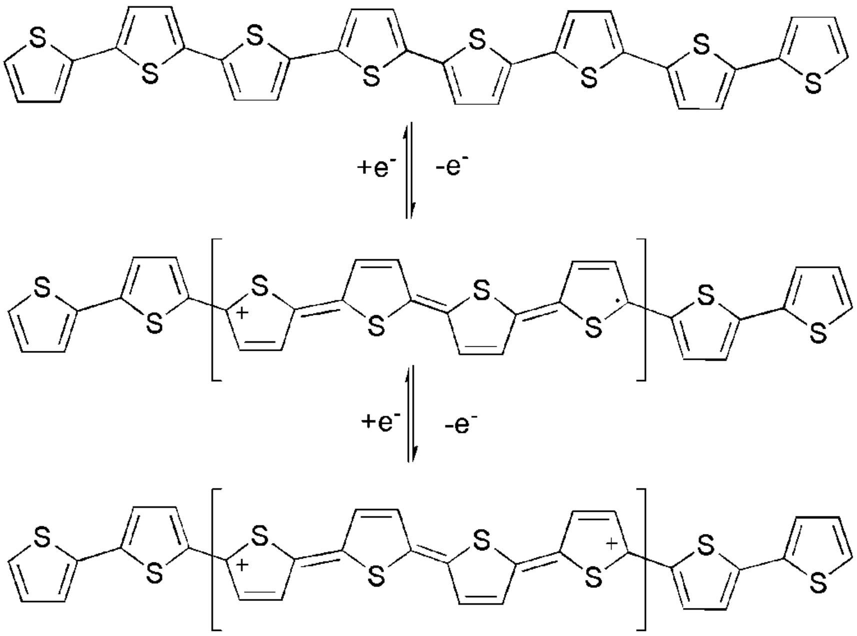


Figure 1.6 Reversible doping-dedoping process of polythiophene

Electrochemical doping is the most useful and easy way and performed by applying suitable potentials to the polymer in a suitable medium [13]. During p-doping process, electrons are removed from the polymer chain hence positive charges are produced. On the other hand, during n-doping process, electrons are introduced to the polymer chain thus negative charges are produced. At the same time, for the charge compensation the counterions diffuse into (or out) the polymer backbone.

1.4 Synthesis of Conducting Polymers

In literature, there are a number of techniques used to synthesize conducting polymers such as photochemical polymerization, metathesis polymerization, plasma, solid state polymerization, chemical polymerization and electrochemical polymerization. Among the other techniques, chemical and electrochemical polymerizations are the most preferred ones.

Chemical polymerization can be done either by metal catalyzed coupling reactions or the $FeCl_3$ mediated oxidative polymerization (Figure 1.7). Stille, Suzuki, Yamamoto coupling reactions are the most used metal catalyzed coupling polymerizations. In these types of reactions transition metal halides such as palladium, nickel and iron are used to monomer oxidation. $FeCl_3$ mediated oxidative polymerization, Sugimoto method, is an efficient route for obtaining high molecular weight polymers. Although chemical polymerization is a convenient technique, this type of polymerization needs more time and the resultant polymer's purification is troublesome.

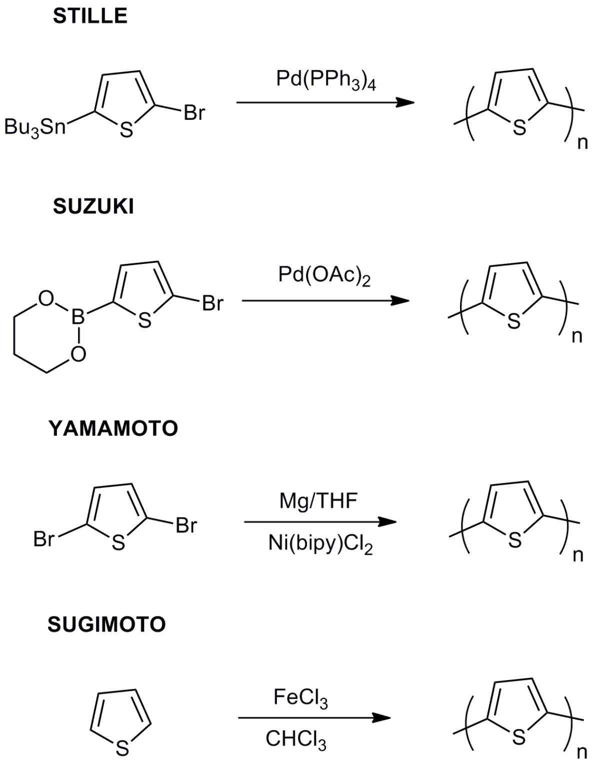


Figure 1.7 Some polymerization methods

In electrochemical polymerization, the synthesis of desired polymer is very quick and purification and characterization is simplier. This technique is discussed in detail in the following section.

1.4.1 Electrochemical Polymerization

Electrochemical polymerization is a simple, fast and reproducible technique also provides the rapid characterization of the resultant conjugated polymer. In this technique the electrodes (reference, working and counter electrodes) are placed in a monomer/electrolyte solution. By appliying appropriate potentials polymer is coated on working electrode.

Electropolymerization has several advantages over the other polymerization techniques such as absence of catalyst, easy control of the film thickness by the deposition charge, direct synthesis of the doped polymer on electrode surface and possibility to perform in situ characterization of the resultant polymer by both electrochemical and spectroelectrochemical techniques.

The mechanism of electrochemical polymerization is represented by $E(CE)_n$ mechanism [14] shown in Figure 1.8. Firstly, upon applied potential the monomer is converted to its radical cation by removal of an electron. Then two reactions can occur, one of them is the attack of the radical cation on a neutral monomer unit and the other one is the coupling of two radical cations. Both routes yield an intermediate that is rearomatized upon loss of two protons to give a dimer unit. As a result of repeated couplings, the resultant conjugated polymer is formed on the electrode surface.

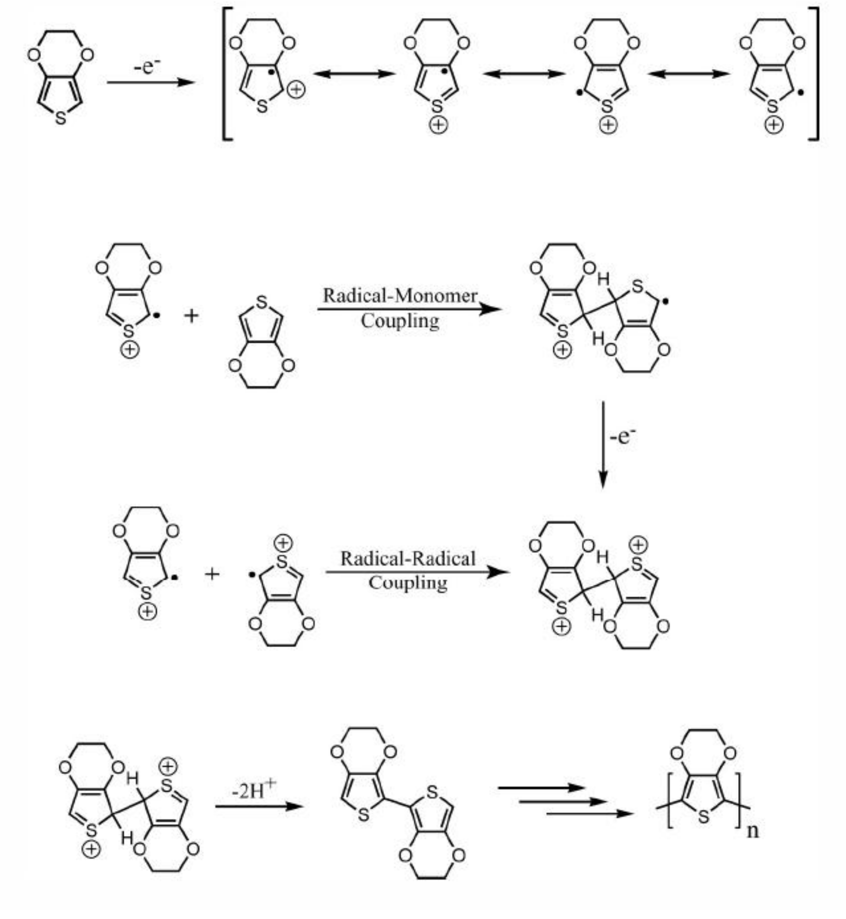


Figure 1.8 Electrochemical polymerization mechanism of EDOT

1.5 Characterization of Conducting Polymers

1.5.1 Cyclic Voltammetry

Cyclic voltammetry is the most common and very useful tool to analyze the electroactivity of the monomers, to convert monomers into polymers and to obtain the oxidation potentials of both monomer and polymer and the reduction potential of the polymer. (Figure 1.9)

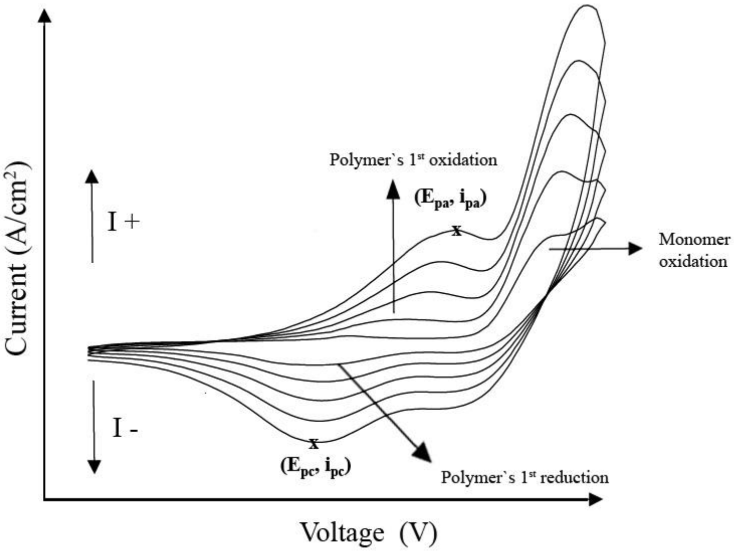


Figure 1.9 A schematic cyclic voltammogram

The characteristic peaks in the cyclic voltammetry (CV) are formed due to the diffusion layer near the electrode surface and using CV peak current (ip), peak current density (jp) and peak potential (Ep) can be measured. By Randles-Sevcik equation the peak current for a reversible couple is calculated;

$$i_p = (2.69\times10^5)\, n^{3/2}\, A\, D^{1/2}\; C\; \nu^{1/2}$$

In this equation, “n” is the number of electrons, “A” is the electrode area (cm^2), “D” is the diffusion coefficient of the analyte (cm^2/s), “C” is the concentration and “ν” is the scan rate (V/s). This equation says that the current is directly proportional to the concentration and increases with the square root of the sweep rate.

1.5.2 Spectroelectrochemistry

Spectroelectrochemistry is the combination of electrochemical and spectroscopic methods that can be operated in situ. It is very useful technique to monitor the absorbance changes, resulted by changes in electronic transitions, during the redox switching of conjugated polymers. These absorbance changes make conjugated polymers useful in electrochromic applications. While the electronic transitions are investigated by UV-Vis spectroscopy, spectra are recorded while the polymer is oxidized by increasing the potential stepwise. This combined experiment is called as spectroelectrochemistry.

The important properties of conjugated polymers such as band gap E_g, λ_{max}, the intergap states that appear upon doping and the evolution of polaron and bipolaron bands are obtained from the spectroelectrochemistry experiments. (Figure 1.10)

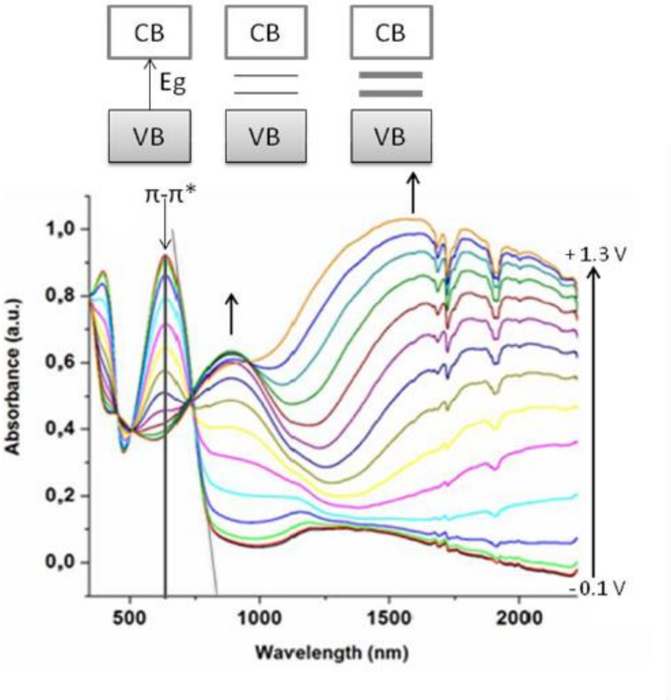


Figure 1.10 Spectra of a representative conjugated polymer

1.5.3 Switching Studies

Electrochromic switching studies are performed to monitor the optical contrast (the percent transmittance difference between oxidized and reduced state) as a function of time and to calculate the switching time (the time required to oxidize the polymer from its reduced state) of the conducting polymer at its λ_{max} by stepping potential repeatedly between the neutral and oxidized states.

1.6 Applications of Conducting Polymers

Conducting polymers are very promising materials for many applications due to their conductivity, good processibility, high stability and low cost manufacturing. The recent developments towards the synthesis of new and processable conducting polymers bring about the commercialization of them in many technological applications.

Conducting polymer are used especially in electronic/optoelectronic devices like electrochromic devices (ECDs) [15], organic solar cells [9], light emitting diodes [16], field effective transistors [17] and also in surface practices like antistatic protection, electromagnetic interference shielding [18] and corrosion protection. Moreover, due to their ability changing color, volume and conductivity these polymers have also some commercial applications such as batteries, supercapacitors [19], fuel cells [20], biosensors [21], chemical sensors [22], gas separation membranes, conductive textiles, drug delivery [23] and non-linear optics [24].

1.7 Chromism

For a material, chromism is defined as the reversible change in material's color, absorbance or reflection resulting from an external stimulus. This stimulus can be temperature change (thermochromism), light (photochromism), pH change (halochromism), mechanical (piezochromism) or electrochemical (electrochromism) effects that cause conformational modification and the energy change in π-π^* transition band gap lead to chromic behavior [25].

Among all types of chromism, electrochromism is the most commercially utilized one which has various potential applications such as displays, rear-view mirrors and smart windows.

1.7.1 Electrochromism

Electrochromism is the reversible and visible change in optical properties of a material that is associated with electrochemical oxidation and reduction. Switching between oxidized and reduced states causes the generation of different electronic bands in visible region. As a result of this, color of material changes between a transparent state and a colored state or between two colored states. In some cases, the material may show several colors and termed as multichromic and the process is called as multicolor electrochromism [26].

Electrochromic materials have some important characteristics such as switching times, coloration efficiency, long term stability, contrast ratio and electrochromic memory.

1.8 Electrochromic Devices

An electrochromic display consists of combining an electrode covered with a thin layer of electrochromic materials, transparent polymer electrolytes and a complimentary electrochromic material as a counter electrode. In terms of the working principles, it can be said that the electrochromic devices resemble to batteries.

In electrochromic devices, charging-discharging the electrochemical cell with applied potential of a few volts causes the color change. Electrochromic devices consist of at least one transparent electrode in electromagnetic spectrum with electrochemically reversible cathodic material (colors upon being oxidized) and anodic material (colors upon being reduced) and ion-conducting electrolyte. During the redox process upon applied potential, one of the materials is oxidized and the other one is reduced so that the electrochromic device switches between neutral and oxidized colors of the films and vice versa [27].

A dual-type electrochromic device is constructed by sandwiching the gel electrolyte between anodically and cathodically coloring polymers that are electrochemically deposited onto transparent indium tin oxide (ITO) coated glass electrodes (Figure 1.11). The gel electrolyte (ion conducting electrolyte) is a source of cations and anions to balance redox reactions is used in order to provide physical separation between cathode and anode. Moreover, it should be transparent in the given region of the spectrum.

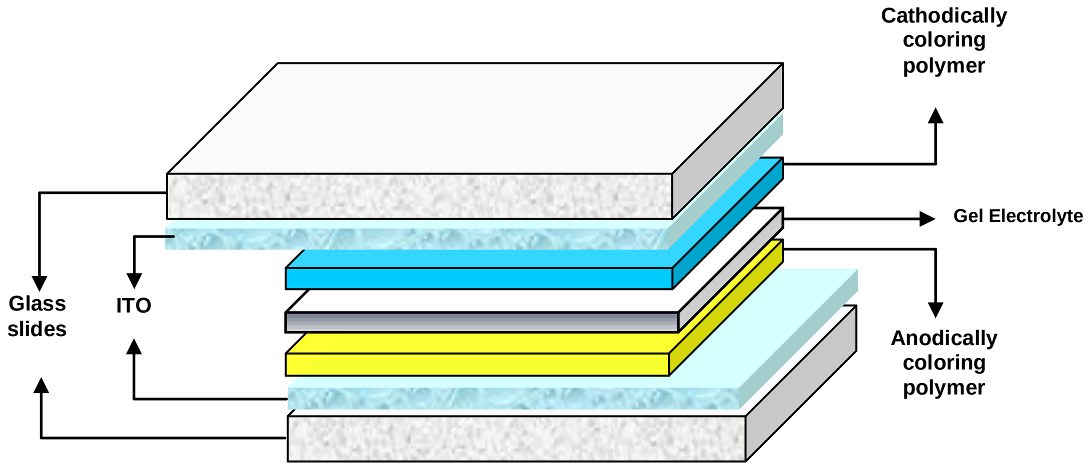


Figure 1.11 Schematic representation of an electrochromic device

1.9 Characteristics of Electrochromic Device

1.9.1 Electrochromic Contrast and Switching Speed

Electrochromic contrast is one of the important characteristic of evaluating an electrochromic device. In these experiments main aim is to monitor absorbance changes with time during repeated potential stepping between oxidized and reduced states.

Optical contrast is often reported as percent transmittance change (Δ%T) between the two colored redox states at a specific wavelength where the optical contrast has the highest value. Switching time is the time required to switch between oxidized and reduced states. The switching speed of an electrochromic material is closely related with ionic conductivity of the electrolyte, ion diffusion in thin films, magnitude of the applied potential, film thickness and morphology of the film [28].

1.9.2 Open Circuit Memory and Stability

The time during the material retains its color after the removal of applied potential is termed as the open circuit memory. For practical applications, the stability of the polymer for long term switching between bleached and colored states is a very important parameter. The performance of the electrochromic material is directly relevant to the stability of the active redox couple because any degradation of the active redox couple results in the loss of electrochromic contrast. Therefore, electrochromic stability is interrelated with electrochemical stability [29].

1.9.3 Colorimety

In situ colorimetry studies are performed to define color and contrast ratio of electrochromic polymers scientifically. Colorimetry measures colors and this allows colored objects to be described, ordered and compared. The International Commission on Illumination (Commission Internationale de l'Eclairage, CIE) developed a model defining colors as a quantitative scale. In this system, the color is represented by *L*, *a* and *b* coordinates where *L* corresponds to brightness or luminance (has values from 0 (dark) to 100 (light)), *a* refers to hue, dominant wavelength or chromatic color (ranges from –128 (green) to 127 (red)) and *b* known as the saturation, chroma, tone, or purity (ranges from –128 (blue) to 127 (yellow)) [30-31]. (Figure 1.12)

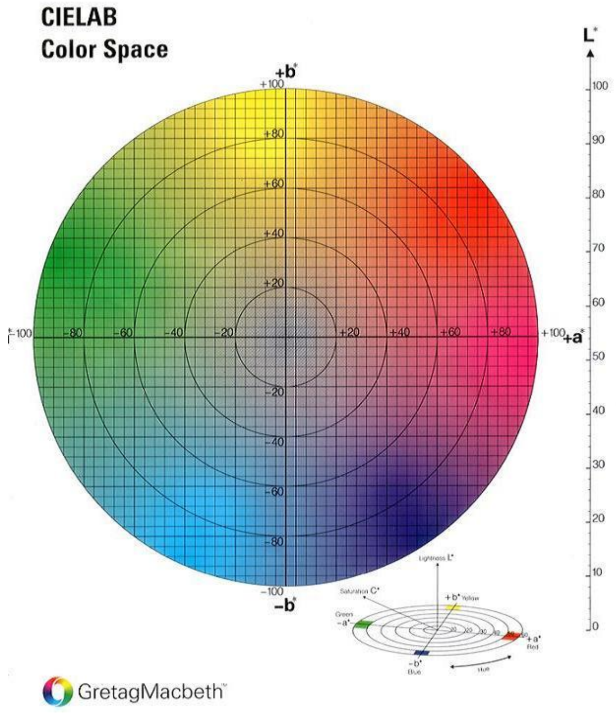


Figure 1.12 CIE *Lab* color space

1.10 Benzotriazole Based Conjugated Polymers

Benzotriazole (BT) is a heteroaromatic compound composed of two fused rings having three nitrogen atoms and having strong electron transporting ability arising from electron withdrawing nature of imine bonds (C=N). (Figure 1.13)

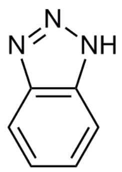


Figure 1.13 Structure of benzotriazole

In literature, there are a number of conjugated polymers containing BT and its derivatives and most of them showed amazing properties in terms of electrochromism. “The first electrochemically polymerized BT bearing conjugated polymer BEBT was designed by Toppare *et al.* in 2008.” [32] After that, several conjugated polymers containing BT on the polymer backbone were synthesized with different donor grups such as thiophene [33], 3-hexylthiophene [34], selenophene [35], pyrrole [36], furan [37], thienothiophene [37] and

3,3-didecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine [38] (Figure 1.13). “The polymer, PTBT, revealed the most promising characteristics among other polymers containing BT unit. PTBT is a major breakthrough due to its electrochromic properties including processability and red to transmissive switching with showing all RGB colors in addition to black color.” [33]

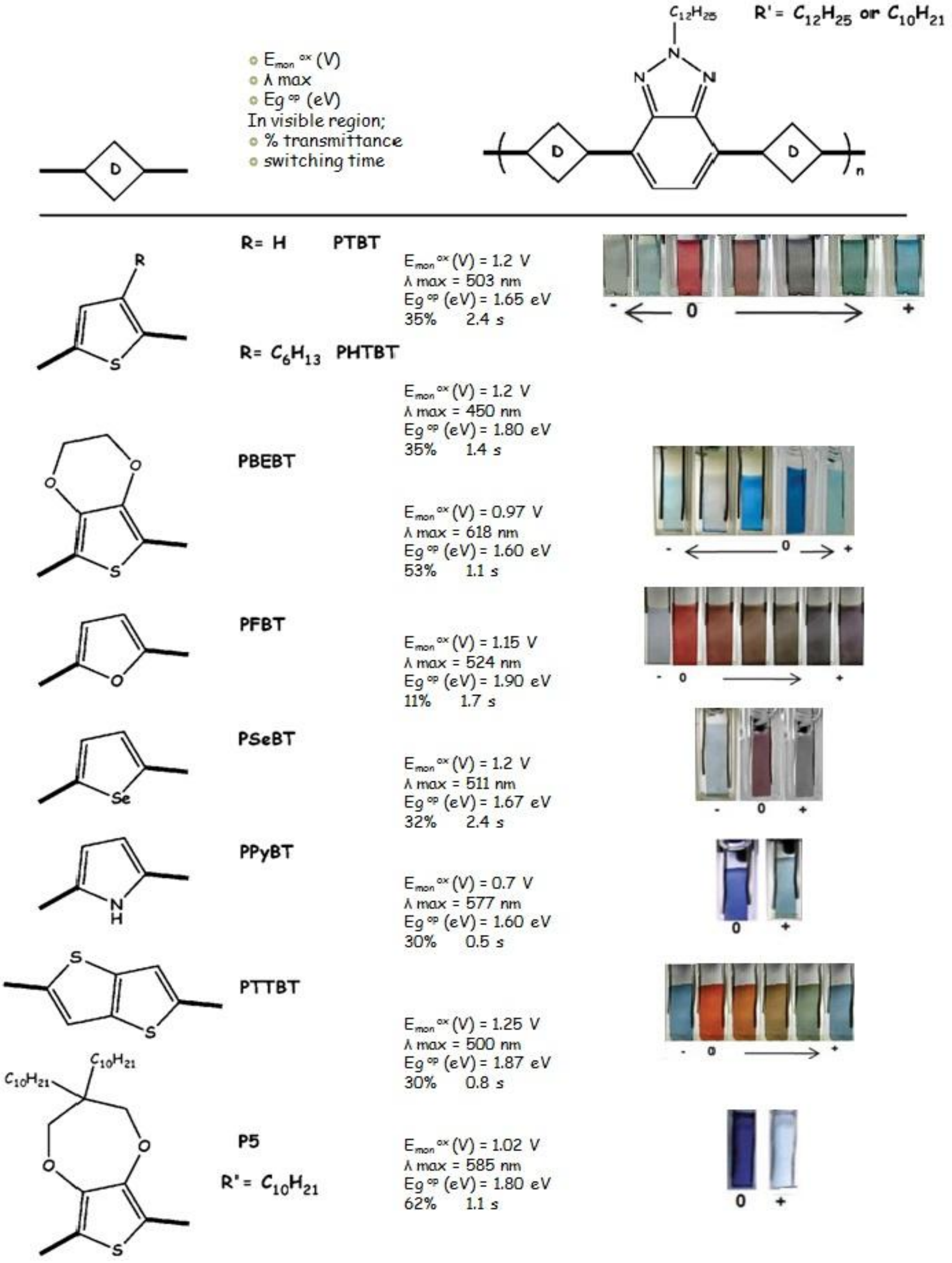


Figure 1.14 Benzotriazole bearing some conjugated polymers

1.11 N-functionalized 2,5-di(2-thienyl)-1H-pyrrole Based Conjugated Polymers

In order to use conducting polymers in electrochromic applications, they should be soluble and processable, should have fast switching with high optical contrasts and various colors. To synthesize the conducting polymer with desired properties, Toppare et al. proved that pyrrole and thiophene can be coupled appropriately in order to obtain these properties in several electrochromic polymers by sythesizing N-functionalized 2,5-di(2-thienyl)-1H-pyrrole (SNS derivatives). (Figure 1.14)

Low oxidation potentials of monomers caused easy electrochemical polymerization and polymers showed band gaps between 1.94 and 2.2 eV with relatively low switching times; 1.3–2s. Furthermore, a wide range of colors for neutral and oxidized states were observed with little changes in conjugated polymer structures [39-54].

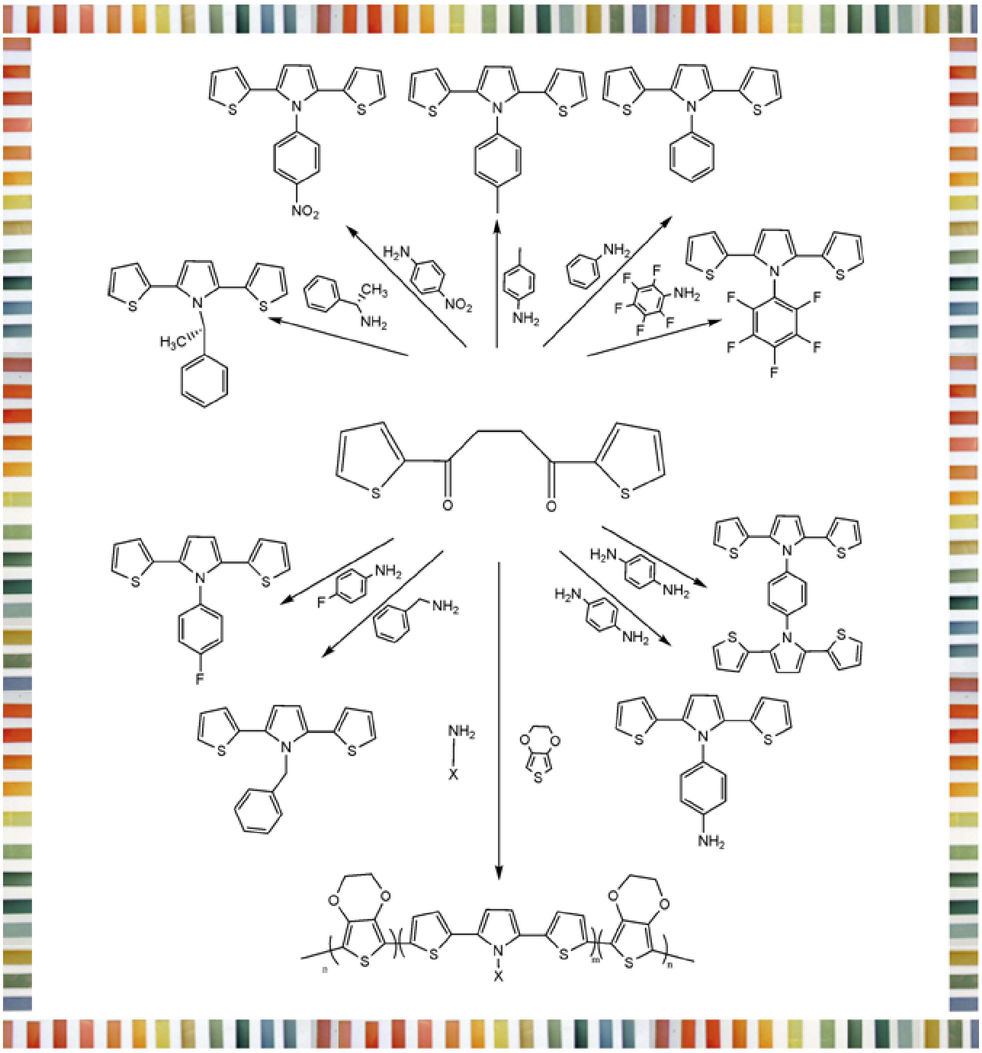


Figure 1.15 Chemical structures for the members of SNS series

1.12 Aim of This Work

The aim of this study is to synthesize and characterize three new conjugated polymers which are the combination of benzotriazole and n-functionalized 2,5-di(2-thienyl)-1H-pyrrole (SNS) units in order to observe the power of the combination on electrochromic properties of resultant conjugated polymers and to construct an electrochromic device.

For this purpose, three monomers 2-(6-(2,5-bis(5-methylthiophen-2-yl)-1H-pyrrol-1-yl)hexyl)-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (M1), 2-(6-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)hexyl)-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (M2) and 2-(6-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)hexyl)-4,7-bis(5-methylthiophen-2-yl)-2H-benzo[d][1,2,3]triazole (M3) were synthesized, electrochemically polymerized, characterized. Using M2 an electrochromic device is constructed.

CHAPTER 2

EXPERIMENTAL

2.1 Materials

For the synthesis of the monomers; benzotriazole (Fluka), 1,6-dibromohexane (Aldrich), potassium tert-butoxide ($(CH_3)_3COK$) (Aldrich), bromine (Br_2) (Merck), hydrobromic acid (HBr, 47%) (Merck), thiophene (Aldrich), 2-methylthiophene (Aldrich), n-butyllithium (n-BuLi, 2.5M in hexane) (Acros Organics), tributyltin chloride ($Sn(Bu)_3Cl$) (Aldrich), bis(triphenylphosphine)palladium(II) dichloride (Aldrich), potassium phthalimide (Aldrich), $AlCl_3$ (Aldrich), succinylchloride (Aldrich), propionic acid (Aldrich), $NaClO_4$ (Aldrich), $LiCClO_4$ (Aldrich), methanol (MeOH) (Aldrich), ethanol (EtOH) (Aldrich), hexane (C_6H_{14}) (Aldrich), chloroform ($CHCl_3$) (Aldrich), dichloromethane (DCM) (Aldrich), ethyl acetate (EtOAc) (Aldrich), dimethylformamide (DMF) (Acros Organics), toluene (Aldrich), acetonitrile (ACN) (Aldrich) and tetrahydrofuran (THF) (Acros Organics) were used as received.

2.2 Equipment

^{1}H-NMR and ^{13}C-NMR spectra of the molecules referenced to tetramethylsilane were recorded in $CDCl_3$ on Bruker Spectrospin Avance DPX-400 Spectrometer and chemical shifts were given in ppm. Products were purified by column chromatography using Merck Silica Gel 60 (particle size: 0.040–0.063 mm, 230–400 mesh ASTM). “Electrochemical studies were conducted in a three electrode cell system consisting of an Indium Tin Oxide doped glass slide (ITO) as the working electrode, platinum wire as the counter electrode and Ag wire as the reference electrode under ambient conditions using a Voltalab PST050 and Solartron 1285 potentiostats.” [33] Spectroelectrochemical studies for resultant polymers were conducted by using Varian Cary 5000 UV–Vis spectrophotometer. Colorimetry measurements were conducted by using a Conica Minolta CS-100 spectrophotometer. Solvents used for spectroscopy experiments were spectrophotometric grade.

2.3 Procedure

2.3.1 Synthesis of Monomers

2.3.1.1 Synthesis of 2-(6-bromohexyl)-2H-benzo[d][1,2,3]triazole

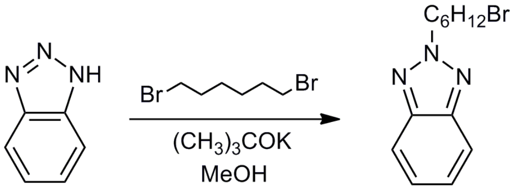


Figure 2.1 Synthetic route for 2-(6-bromohexyl)-2H-benzo[d][1,2,3]triazole

1H-benzo[d][1,2,3]triazole (10.0 g, 84 mmol) and potassium tert-butoxide (10.0 g, 89 mmol) were dissolved in methanol (100 mL) and 1,6-dibromohexane (24 g, 98 mmol) was added to the mixture. The reaction mixture was refluxed for 16 h. After evaporation of the solvent, the residue was dissolved in $CHCl_3$ and extracted with water. The combined organic extracts were dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. Column chromatography on silica gel was performed to obtain 2-(6-bromohexyl)-2H-benzo[d][1,2,3]triazole as a colorless oil (5.96 g, 25%).

2.3.1.2 Synthesis of 4,7-dibromo-2-(6-bromohexyl)-2H-benzo[d][1,2,3]triazole

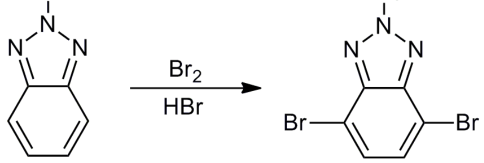


Figure 2.2 Synthetic route for 4,7-dibromo-2-(6-bromohexyl)-2H-benzo[d][1,2,3]triazole

2-(6-Bromohexyl)-2H-benzo[d][1,2,3]triazole (5.96 g, 13.5 mmol) and an aqueous HBr solution (5.8 M, 20 ml) were stirred for 1 h at 100^{o}C and then bromine (8.4 g, 52 mmol) was added to the mixture slowly. The resultant reaction mixture was stirred for 12 h at 135°C. After cooling the mixture to room temperature, an aqueous solution of $NaHCO_3$ was added and the product was extracted with $CHCl_3$. The combined organic extracts were dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. With column chromatography, 4,7-dibromo-2-(6-bromohexyl)-2H-benzo[d][1,2,3]triazole was obtained as light yellow solid (5.76 g, 96%).

2.3.1.3 Syntheses of tributyl(thiophen-2-yl)stannane

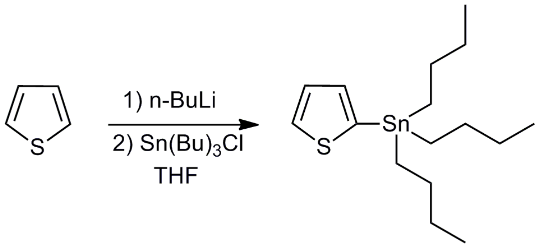


Figure 2.3 Synthetic route for tributyl(thiophen-2-yl)stannane

"Under argon atmosphere, thiophene (4.0 g, 47.1 mmol) was dissolved in dry THF (20 ml). After decreasing the temperature below -70 ^{0}C, n-BuLi (29.5 mL, 47.1 mmol, 2.5 M in hexane) was added dropwise to the solution. After addition was completed, the resulting yellow mixture was stirred for 1 h at room temperature. Then the yellow mixture was cooled to -70 ^{0}C and $Sn(Bu)_3Cl$ (15.4 g, 47.1 mmol) was added dropwise to the solution. After stirring overnight, the solvent was evaporated and the product was extracted with $CHCl_3$ and water. The combined organic extracts were dried over $MgSO_4$ and the solvent was evaporated under vacuum. The obtained crude product was purified by flash column chromatography over neutral alumina with hexane to obtain tributyl(thiophen-2-yl)stannane as brownish oil." [33]

2.3.1.4 Synthesis of tributyl(5-methylthiophen-2-yl)stannane

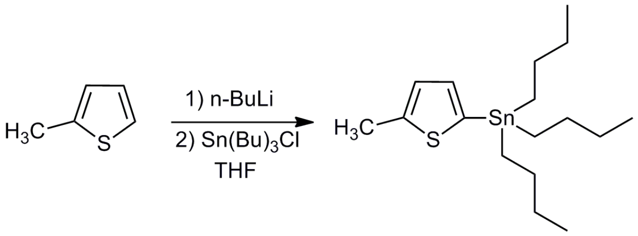


Figure 2.4 Synthetic route for tributyl(5-methylthiophen-2-yl)stannane

Under argon atmosphere, 2-methylthiophene (4.6 g, 47.1 mmol) was dissolved in dry THF (20 ml). After decreasing the temperature below -70 ^{0}C, n-BuLi (29.5 mL, 47.1 mmol, 2.5 M in hexane) was added dropwise to the solution. After addition was completed, the resulting yellow mixture was stirred for 1 h at room temperature. Then the yellow mixture was cooled to -70 ^{0}C and $Sn(Bu)_3Cl$ (15.4 g, 47.1 mmol) was added dropwise to the solution. After stirring overnight, the solvent was evaporated and the product was extracted with $CHCl_3$ and water. The combined organic extracts were dried over $MgSO_4$ and the solvent was evaporated under vacuum. The obtained crude product was purified by flash column chromatography over neutral alumina with hexane to obtain tributyl(thiophen-2-yl)stannane as light brown oil.

2.3.1.5 Synthesis of 2-(6-bromohexyl)-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole

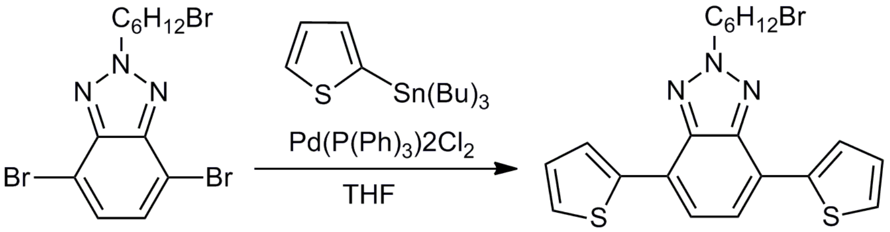


Figure 2.5 Synthetic route for 2-(6-bromohexyl)-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole

4,7-Dibromo-2-(6-bromohexyl)-2H-benzo[d][1,2,3]triazole (0.90 g, 2.0 mmol) and tributyl(thiophen-2-yl)stannane (3.82 g, 10 mmol) were dissolved in anhydrous THF (50 ml). After the mixture was heated, dichlorobis(triphenylphosphine)-palladium(II) (50 mg, 0.045 mmol) was added and reaction mixture was refluxed for 15 h under argon atmosphere. The reaction solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica gel to obtain 2-(6-bromohexyl)-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole as a yellow oil (0.39 g, 44%).

2.3.1.6 Synthesis of 2-(6-bromohexyl)-4,7-bis(5-methylthiophen-2-yl)-2H-benzo[d][1,2,3]triazole

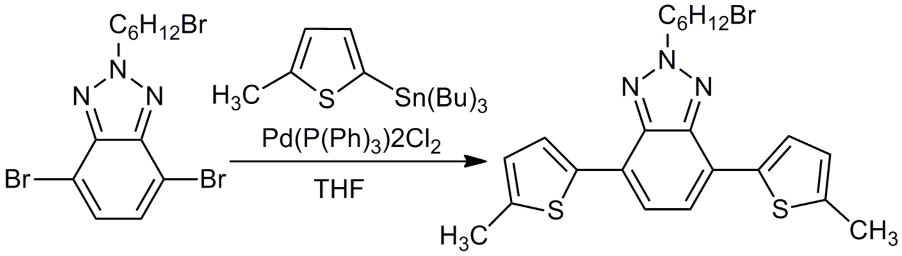


Figure 2.6 Synthetic route for 2-(6-bromohexyl)-4,7-bis(5-methylthiophen-2-yl)-2H-benzo[d][1,2,3]triazole

4,7-Dibromo-2-(6-bromohexyl)-2H-benzo[d][1,2,3]triazole (0.90 g, 2.0 mmol) and tributyl(5-methylthiophen-2-yl)stannane (3.87 g, 10 mmol) were dissolved in anhydrous THF (50 ml). After the mixture was heated, dichlorobis(triphenylphosphine)-palladium(II) (50 mg, 0.045 mmol) was added and reaction mixture was refluxed for 18 h under argon atmosphere. The reaction solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica gel to obtain 2-(6-bromohexyl)-4,7-bis(5-methylthiophen-2-yl)-2H-benzo[d][1,2,3]triazole as a yellow oil (0.37 g, 40%).

2.3.1.7 Synthesis of 2-(6-(4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazol-2-yl)hexyl)isoindoline-1,3-dione

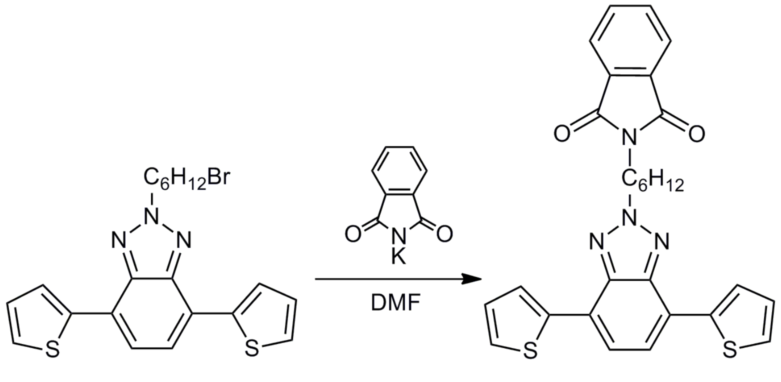


Figure 2.7 Synthetic route for 2-(6-(4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazol-2-yl)hexyl)isoindoline-1,3-dione

A mixture of 2-(6-bromohexyl)-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (0.39 g, 0.87 mmol) and potassium phthalimide (0.24 g, 1.3 mmol) in DMF (20 mL) was stirred for 12 h. After cooling to room temperature the mixture poured into saturated aqueous NH_4Cl and extracted with ethyl acetate. The organic layer washed with water and brine and then dried over $MgSO_4$. After the removal of solvent, the residue was purified with column chromatography to afford 2-(6-(4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazol-2-yl)hexyl)isoindoline-1,3-dione as a yellow solid (0.44 g, 99%).

2.3.1.8 Synthesis of 2-(6-(4,7-bis(5-methylthiophen-2-yl)-2H-benzo[d][1,2,3]triazol-2-yl)hexyl)isoindoline-1,3-dione

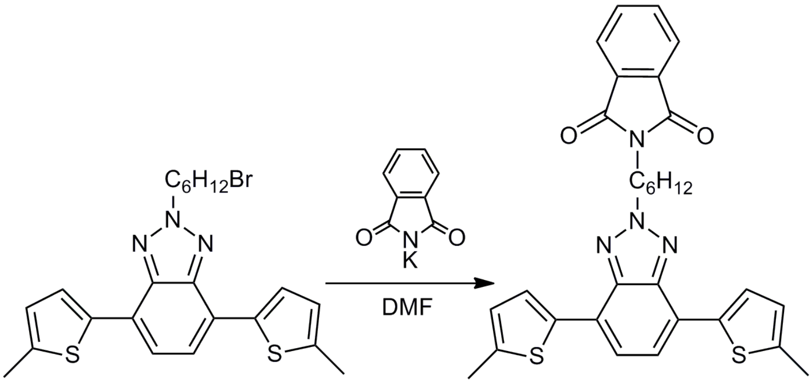


Figure 2.8 Synthetic route for 2-(6-(4,7-bis(5-methylthiophen-2-yl)-2H-benzo[d][1,2,3]triazol-2-yl)hexyl)isoindoline-1,3-dione

A mixture of 2-(6-bromohexyl)-4,7-bis(5-methylthiophen-2-yl)-2H-benzo[d][1,2,3]triazole (0.41 g, 0.87 mmol) and potassium phthalimide (0.24 g, 1.3 mmol) in DMF (20 mL) was stirred for 12 h. After cooling to room temperature the mixture poured into saturated aqueous NH_4Cl and extracted with ethyl acetate. The organic layer washed with water and brine and then dried over $MgSO_4$. After the removal of solvent, the residue was purified with column chromatography to afford 2-(6-(4,7-bis(5-methylthiophen-2-yl)-2H-benzo[d][1,2,3]triazol-2-yl)hexyl)isoindoline-1,3-dione as a yellow solid (0.45 g, 99%).

2.3.1.9 Synthesis of 6-(4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazol-2-yl)hexan-1-amine

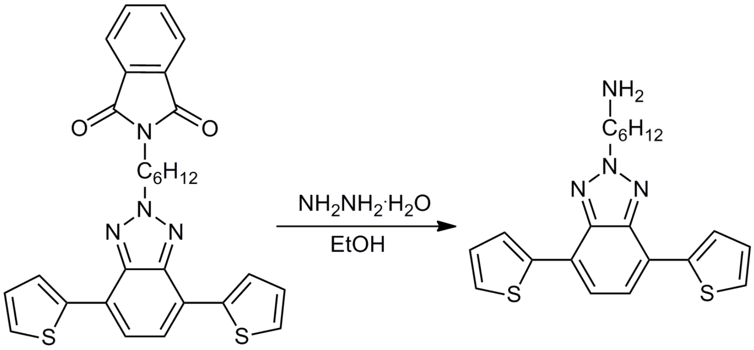


Figure 2.9 Synthetic route for 6-(4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazol-2-yl)hexan-1-amine

2-(6-(4,7-Di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazol-2-yl)hexyl)isoindoline-1,3-dione (0.44 g, 0.86 mmol) in ethanol/hydrazine monohydrate (1:1, 30 mL) solution was stirred for 12 hours under reflux. After removal of solvent, 10 % aqueous KOH solution was added to the residue and extracted with $CHCl_3$. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure to afford 6-(4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazol-2-yl)hexan-1-amine as a yellow oil (0.317 g, 96%).

2.3.1.10 Synthesis of 6-(4,7-bis(5-methylthiophen-2-yl)-2H-benzo[d][1,2,3]triazol-2-yl)hexan-1-amine

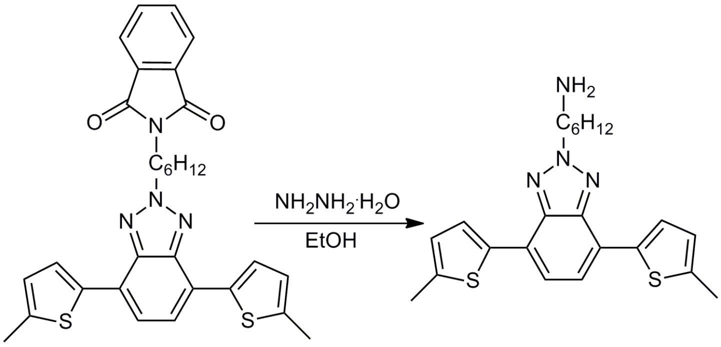


Figure 2.10 Synthetic route for 6-(4,7-bis(5-methylthiophen-2-yl)-2H-benzo[d][1,2,3]triazol-2-yl)hexan-1-amine

2-(6-(4,7-Bis(5-methylthiophen-2-yl)-2H-benzo[d][1,2,3]triazol-2-yl)hexyl)isoindoline-1,3-dione (0.46 g, 0.86 mmol) in ethanol/hydrazine monohydrate (1:1, 30 mL) solution was stirred for 12 hours under reflux. After removal of solvent, 10 % aqueous KOH solution was added to the residue and extracted with $CHCl_3$. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure to afford 6-(4,7-bis(5-methylthiophen-2-yl)-2H-benzo[d][1,2,3]triazol-2-yl)hexan-1-amine (0.32 g, 96%).

2.3.1.11 Synthesis of 1,4-di(thiophen-2-yl)butane-1,4-dione

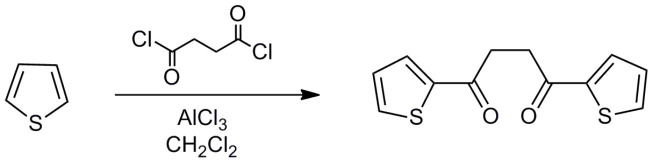


Figure 2.11 Synthetic route for 1,4-di(thiophen-2-yl)butane-1,4-dione

“A mixture of thiophene (4.8 mL, 60 mmol) and succinylchloride (2.75 mL, 25 mmol) in 30mL of DCM was added dropwise to a suspension containing 8.1 g (60 mmol) of $AlCl_3$ in 30mL of DCM, and the mixture was stirred for 4 h. The reaction mixture was poured into a mixture of 50 g ice and 5mL hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic extracts were dried over $MgSO_4$. After the removal of solvent, the residue was purified with column chromatography to afford 1,4-di(thiophen-2-yl)butane-1,4-dione.” [39]

2.3.1.12 Synthesis of 1,4-bis(5-methylthiophen-2-yl)butane-1,4-dione

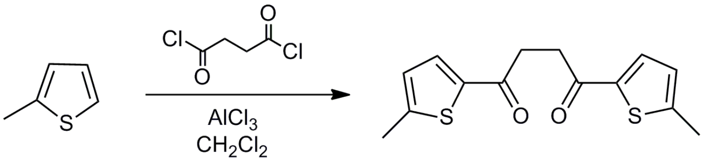


Figure 2.12 Synthetic route for 1,4-bis(5-methylthiophen-2-yl)butane-1,4-dione

“A mixture of 2-methylthiophene (5.8 mL, 60 mmol) and succinylchloride (2.75 mL, 25 mmol) in 30mL of DCM was added dropwise to a suspension containing 8.1 g (60 mmol) of $AlCl_3$ in 30mL of DCM, and the mixture was stirred for 4 h. The reaction mixture was poured into a mixture of 50 g ice and 5mL hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic extracts were dried over $MgSO_4$. After the removal of solvent, the residue was purified with column chromatography to afford 1,4-bis(5-methylthiophen-2-yl)butane-1,4-dione.” [39]

2.3.1.13 Synthesis of M1

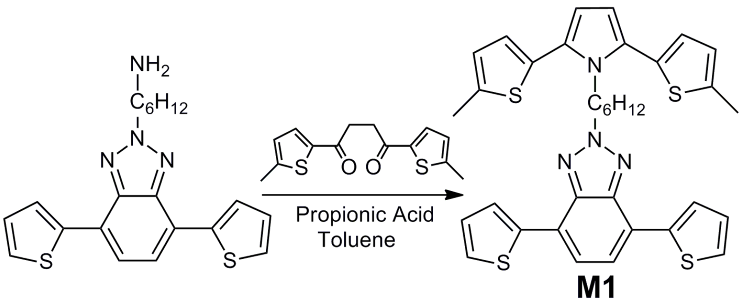


Figure 2.13 Synthetic route for M1

6-(4,7-Di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazol-2-yl)hexan-1-amine (1.91 g, 5 mmol) , 1,4-bis(5-methylthiophen-2-yl)butane-1,4-dione (1.94 g, 7 mmol) and propionic acid (0.53 mL, 7.2 mmol) were dissolved in 40 mL of toluene. The mixture was refluxed for 24 h under argon atmosphere. After cooling to room temperature, toluene was evaporated and the residue was separated by column chromatography to afford M1.

2.3.1.14 Synthesis of M2

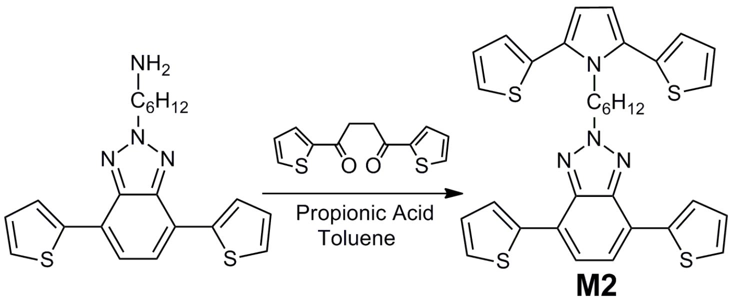


Figure 2.14 Synthetic route for M2

6-(4,7-Di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazol-2-yl)hexan-1-amine (1.91 g, 5 mmol) , 1,4-di(thiophen-2-yl)butane-1,4-dione (1.75 g, 7 mmol) and propionic acid (0.53

mL, 7.2 mmol) were dissolved in 40 mL of toluene. The mixture was refluxed for 24 h under argon atmosphere. After cooling to room temperature, toluene was evaporated and the residue was separated by column chromatography to afford M2.

2.3.1.15 Synthesis of M3

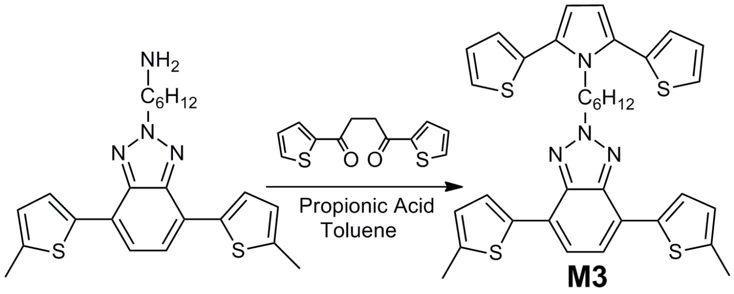


Figure 2.15 Synthetic route for M3

6-(4,7-Bis(5-methylthiophen-2-yl)-2H-benzo[d][1,2,3]triazol-2-yl)hexan-1-amine (2.05 g, 5 mmol) , 1,4-bis(5-methylthiophen-2-yl)butane-1,4-dione (1.94 g, 7 mmol) and propionic acid (0.53 mL, 7.2 mmol) were dissolved in 40 mL of toluene. The mixture was refluxed for 24 h under argon atmosphere. After cooling to room temperature, toluene was evaporated and the residue was separated by column chromatography to afford M3.

2.3.2 Synthesis of Conducting Polymers

1.3.2.1 Electrochemical Polymerization

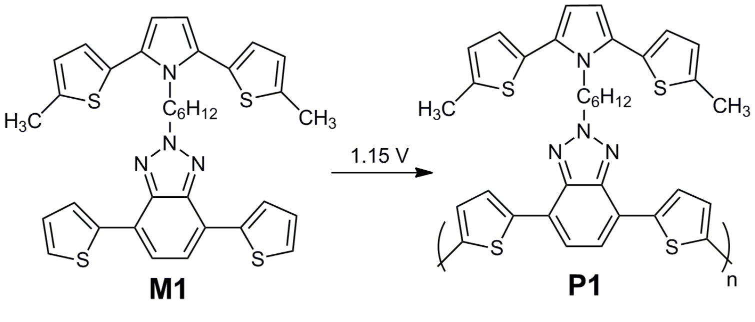


Figure 2.16 Electrochemical polymerization of M1

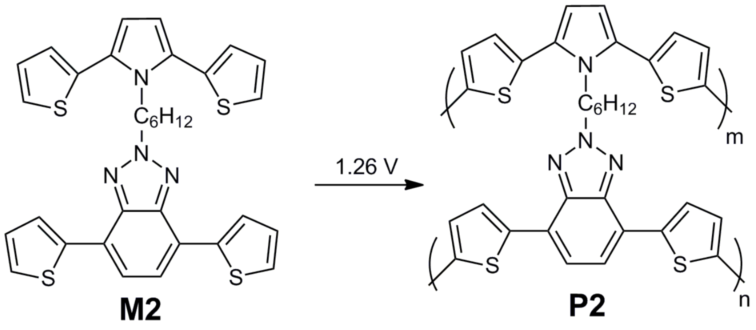


Figure 2.17 Electrochemical polymerization of M2

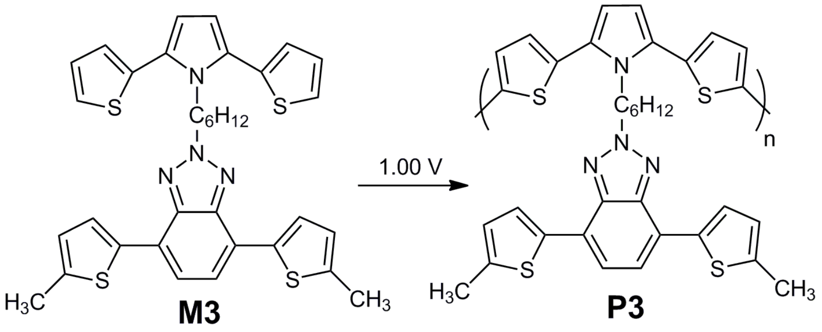


Figure 2.18 Electrochemical polymerization of M3

During the experiments, “Indium Tin Oxide doped glass slide (ITO) was used as the working electrode, platinum wire was used as the counter electrode and Ag wire was used as the reference electrode under ambient conditions.” [33] The in-situ potentiodynamic electropolymerization of both M1 and M2 were carried out by applying potentials between 0.0 V and +1.3 V, similarly M3 was carried out between 0.0 V and +1.1 V at a scan rate of 100 mV/s in $NaClO_4$-$LiClO_4$ / ACN solvent-electrolyte mixture. The resulting polymer films were washed with ACN to remove unreacted monomer and excess electrolyte after electrolysis.

2.4 Electrochromic Device Construction

2.4.1 P2/PEDOT Electrochromic Device

The electrochromic device was constructed using two complementary polymers (P2 as the anodically and PEDOT as the cathodically coloring polymers) which were electrochemically deposited onto ITO coated glass substrates. These two polymer films were arranged as to face each other and separated by a gel electrolyte. (Figure 2.19)

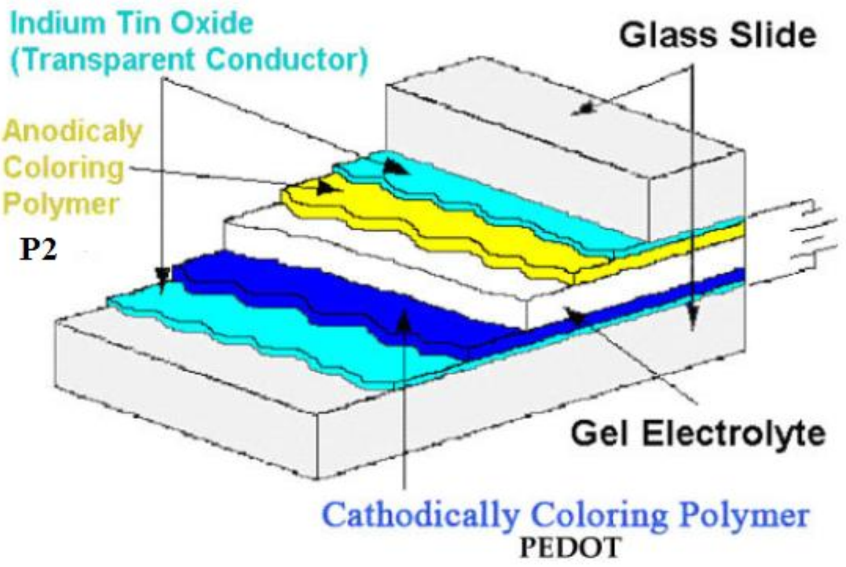


Figure 2.19 Schematic illustration of P2/Pedot electrochromic device

2.4.2 Preparation of Gel Electrolyte

$NaClO_4$/$LiClO_4$/ACN/PMMA/PC (1.5:1.5:70:7:20 percent respectively by weight) mixture was used to prepare the gel electrolyte. $NaClO_4$/$LiClO_4$ were dissolved in ACN and poly(methyl methacrylate) (PMMA) was added into the solution. This solution was stirred and heated until all the PMMA dissolved then propylene carbonate (PC), used as plasticizer, was added. The resultant mixture was stirred and heated at 70^0C to obtain highly conducting transparent gel.

CHAPTER 3

RESULTS & DISCUSSION

3.1 Synthesis and Characterization of Monomers

For synthesis of the monomers, firstly BT was alkylated in order to improve the solubility and provide the functional unit. Then alkylated BT was brominated and this brominated compound was coupled with stannylated donor unit via stille coupling. Then Gabriel synthesis was performed to transform primary alkyl halide into primary amine using potassium pthalimide. Thiophene diketone unit was prepared by Friedel-Crafts acylation. Finally Knorr-Paal reaction was performed to get the desired monomers. (Figure 3.1)

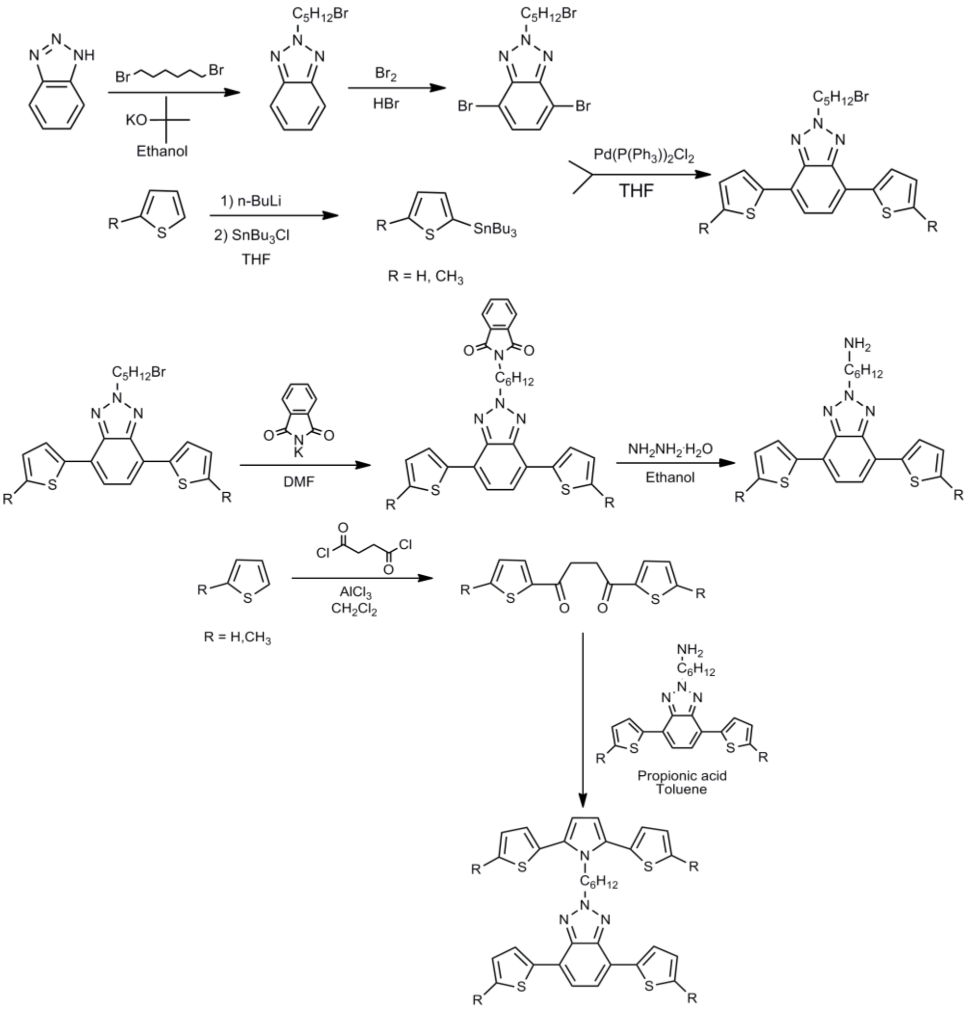


Figure 3.1 Synthetic pathways of monomers

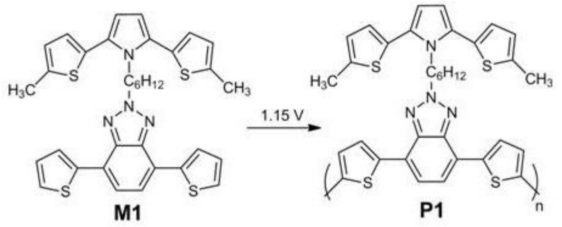
3.2 Electrochemical and Electrochromic Properties of Polymers

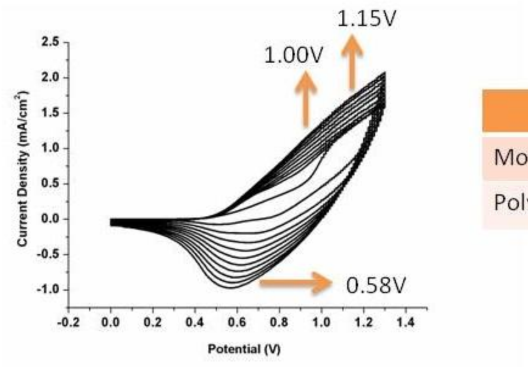
3.2.1 Cyclic Voltammetry of Polymers

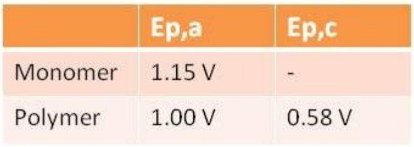
After the characterization of monomers to investigate the electrochromic properties of the resultant polymers M1, M2 and M3 were potentiodynamically polymerized. All electrochemical studies were performed on ITO glass substrates (as the working electrode) in three electrode system. Pt and Ag wires were used as the counter and pseudo reference electrodes respectively.

To polymerize monomers, multiple scan voltammetry was performed in sodium perchlorate/lithium perchlorate/acetonitrile ($NaClO_4$/$LiClO_4$/ACN) solution. The potentials were swept for M1 and M2 between 0.0 V and +1.3 V, for M3 between 0.0 V and +1.1 V at a scan rate of 100 mV/s.

As seen in the Figure 3.2, Figure 3.3 and Figure 3.4, all monomers revealed an irreversible oxidation peaks and all resultant polymers showed reversible oxidation and reduction peaks. For M1 an irreversible monomer oxidation peak revealed at 1.15 V and a reversible redox peak was centered at 1.00 V and 0.58 V. For M2 an irreversible monomer oxidation peak revealed at 1.26 V and a reversible redox peak was centered at 1.00 V and 0.92 V. For M3 an irreversible monomer oxidation peak revealed at 1.00 V and a reversible redox peak was centered at 0.70 V and 0.57 V. Moreover, their current densities increased with repeated cycling which indicates the deposition of polymer films on ITO surfaces. This can be concluded as both monomers and polymers are electroactive.

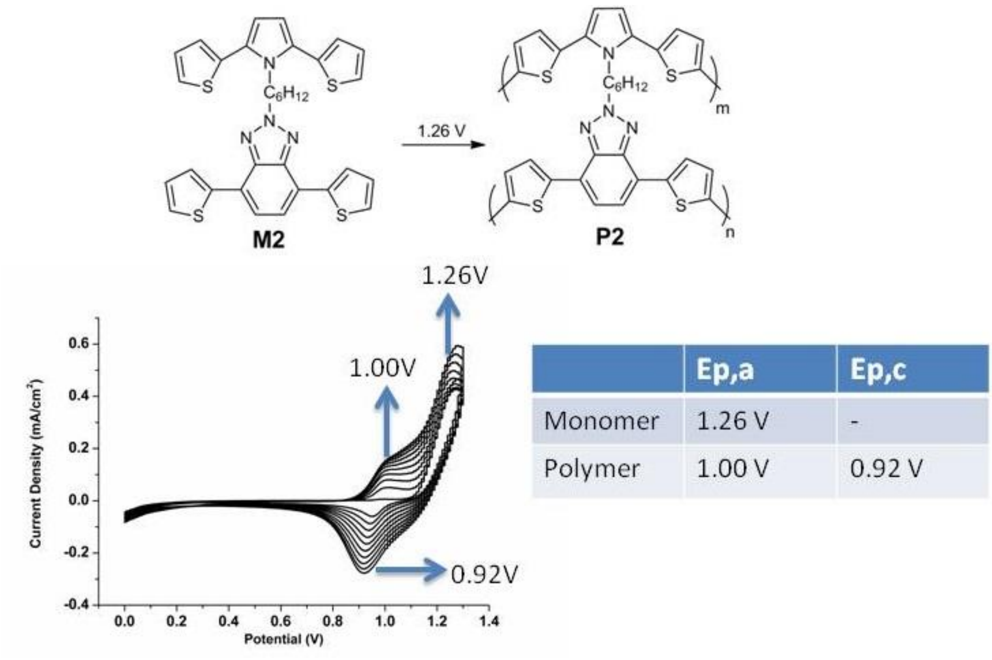






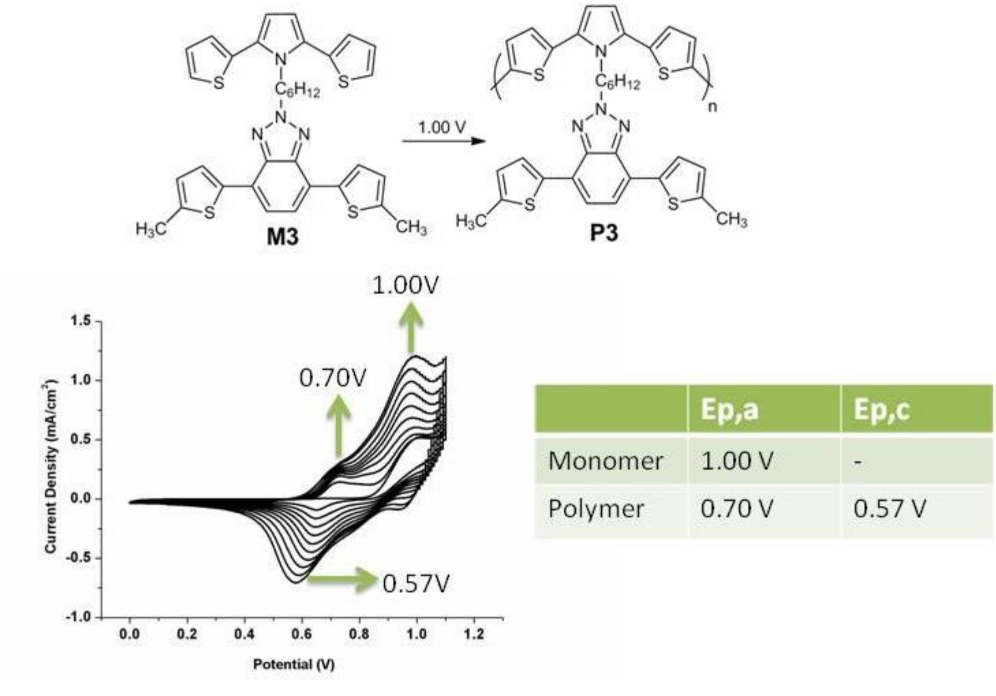
	Ep,a	Ep,c
Monomer	1.15 V	-
Polymer	1.00 V	0.58 V

Figure 3.2 CV and onset potentials of M1



	Ep,a	Ep,c
Monomer	1.26 V	-
Polymer	1.00 V	0.92 V

Figure 3.3 CV and onset potentials of M2



	Ep,a	Ep,c
Monomer	1.00 V	-
Polymer	0.70 V	0.57 V

Figure 3.4 CV and onset potentials of M3

3.2.2 Spectroelectrochemistry and Colorimetry Studies of Polymers

Spectroelectrochemistry studies, which are the in situ performance of electrochemical and spectroscopic techniques, were done to probe the optical changes arising from the electronic transitions of material throughout the oxidation reduction process in a monomer free 0.1 M $NaClO_4$/$LiClO_4$/ACN solution.

As seen in Figure 3.5, P1 revealed red color (*L*: 52.063, *a*: 50.360, *b*: 49.446) in its neutral state at absorption maximum 475 nm which corresponds to the π-π^* transition. The band gap of the polymer was calculated as 1.87 eV from the onset of this maximum absorption. Upon oxidation, the absoption at 475 nm decreased and due to the formation of polaron and bipolaron bands new absoption bands formed at 690 and 1200 nm. The red color of polymer turned into dark brown as the potential was increased. P1 revealed similar properties in terms of band gap and color to those bezotriazole containing polymers.

In its neutral state, P2 revealed nearly the same red color (*L*: 50.097, *a*: 43.237, *b*: 57.590) as P1 at its absorption maximum 400 nm. The band gap of the polymer was calculated as 1.95 eV from the onset of this maximum absorption. Upon oxidation, the red color firstly turned into brown, then into dark grey. As the potential further increased, the color turned into blue. The polymer showed several colors and termed as multichromic which is a desired property for electrochromic device applications. (Figure 3.6)

P3 revealed yellowish-green color (*L*: 68.533, *a*: 33.141, *b*: 49.414) in its neutral state at absorption maximum 400 nm (Figure 3.7). The band gap of the polymer was calculated as 2.40 eV from the onset of this maximum absorption. Upon oxidation, the color of the polymer turned into green which is a very remarkable property since the generation of a green color requires two simultaneous absorption bands at around 400 and 700 nm.

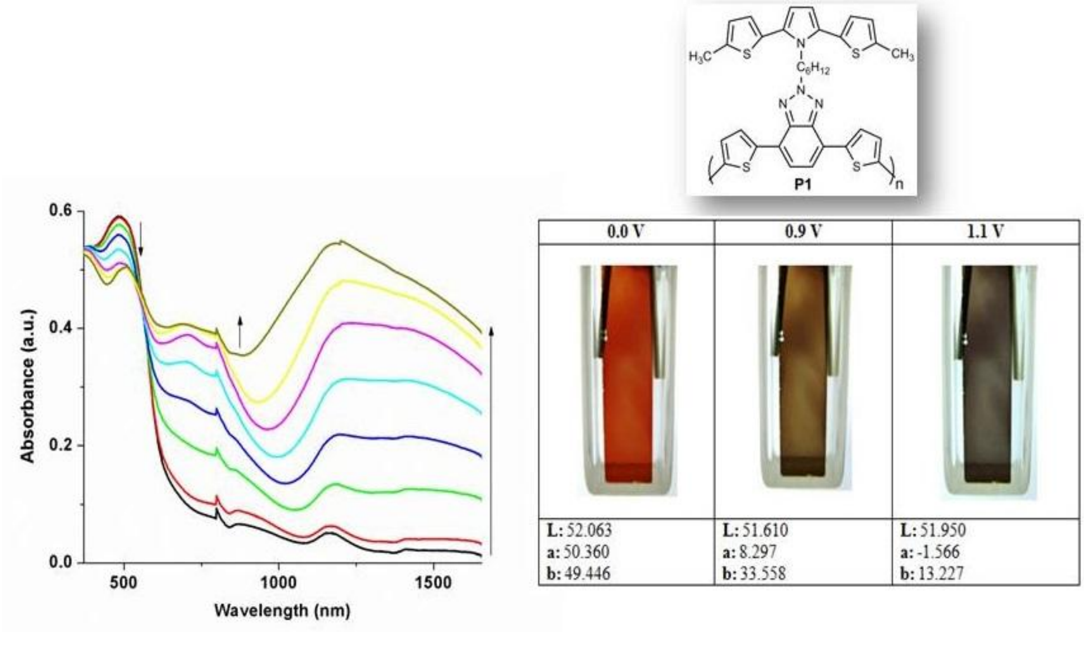


Figure 3.5 Spectroelectrochemistry and colors of P1

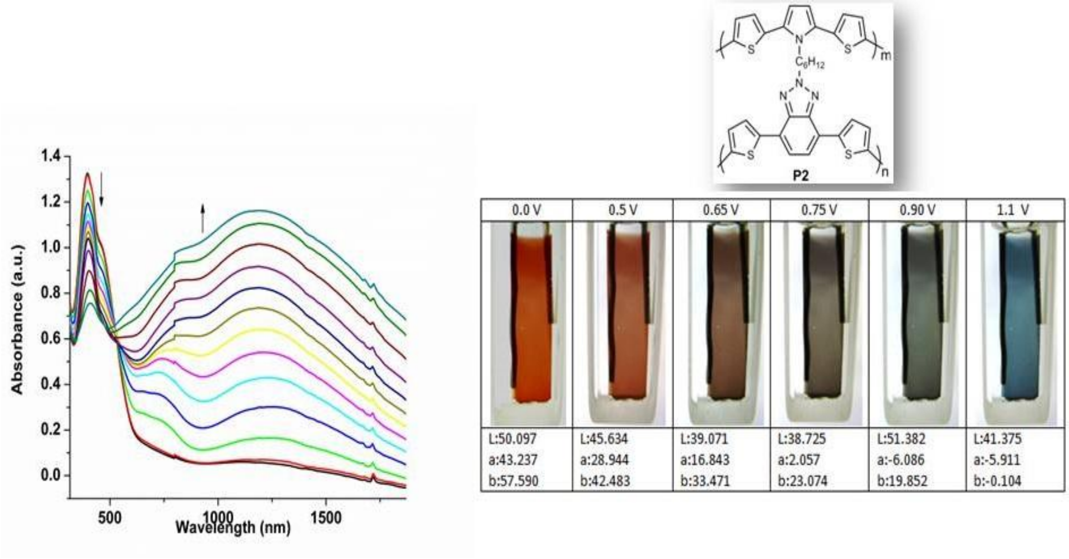


Figure 3.6 Spectroelectrochemistry and colors of P2

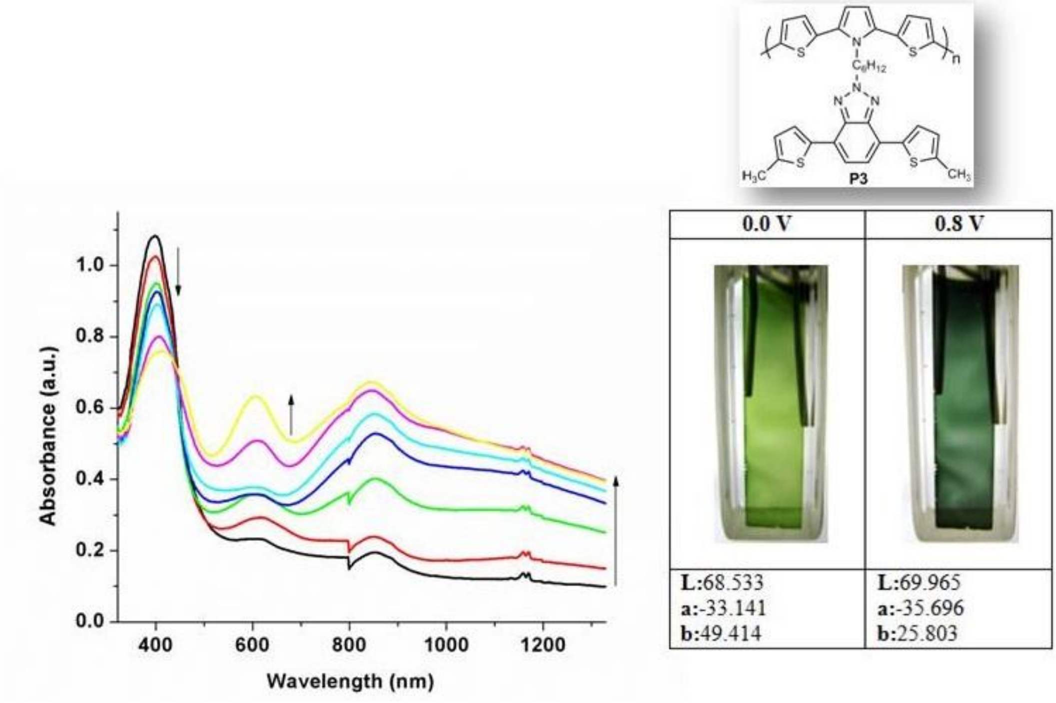


Figure 3.7 Spectroelectrochemistry and colors of P3

3.2.3 Switching Studies of Polymers

Switching studies were performed to monitor the optical contrast as a function of time and to calculate the switching of the conducting polymer at its λ_{max} by stepping potential repeatedly between the neutral and oxidized states.

P1 showed 32 % transmittance change at 690 nm with a short switching time 0.5 s. This switching time is shorter than the other benzotriazole containing polymers especially thiophene bearing analogue (PTBT) [33]. The transmittance change of the polymer in NIR region was 64% with a switching time 0.6s. (Figure 3.8)

Switching abilities of P2 were measured at its highest absorption values in visible and NIR regions (Figure 3.9). It showed 22 % and 60 % optical contrast at 400 and 1200 nm with switching times 1.5 and 0.9 s respectively. Both P1 and P2 revealed hig optical contrast in NIR region which makes them good candidates for NIR electrochromic application such as optical data transmission and the NIR dyes [55-56].

P3 showed 30 % optical contrast at 850 nm with 0.5 s switching time (Figure 3.10). These values are consistent with the values of the polymers in SNS series.

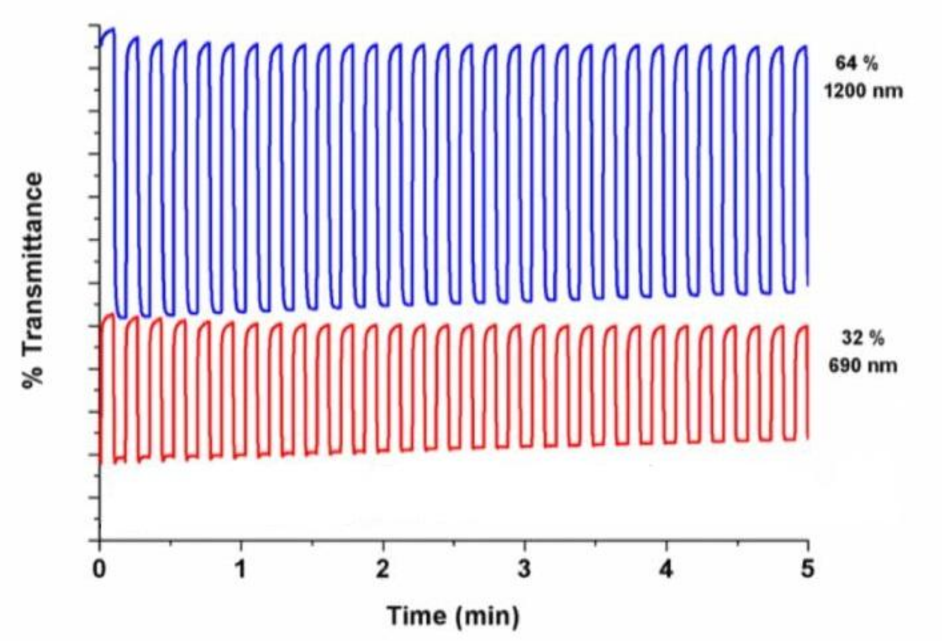


Figure 3.8 Optical contrast changes of P1

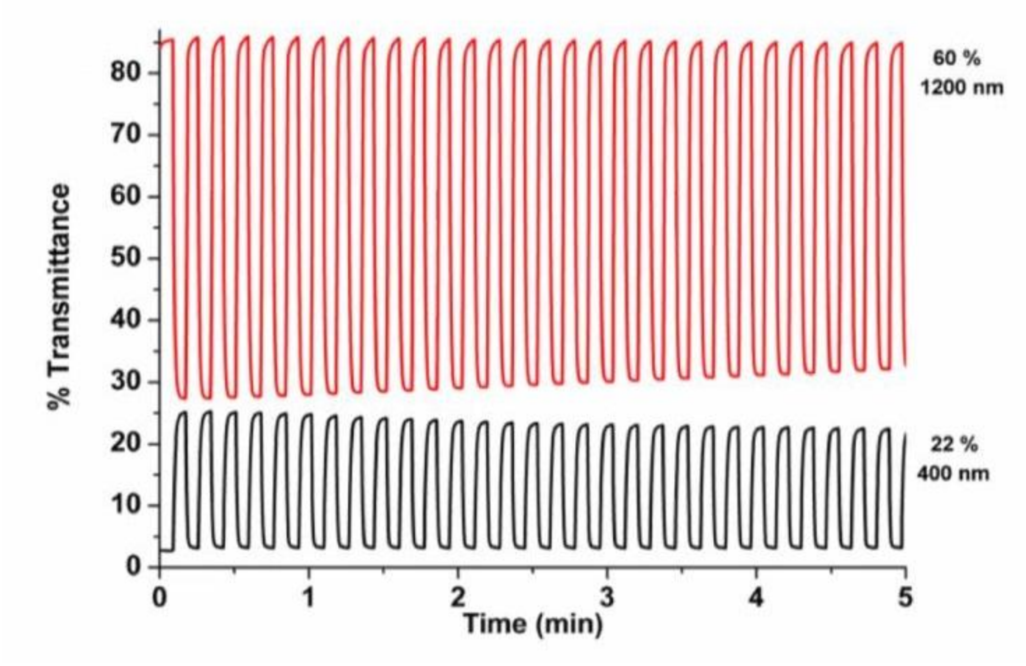


Figure 3.9 Optical contrast changes of P2

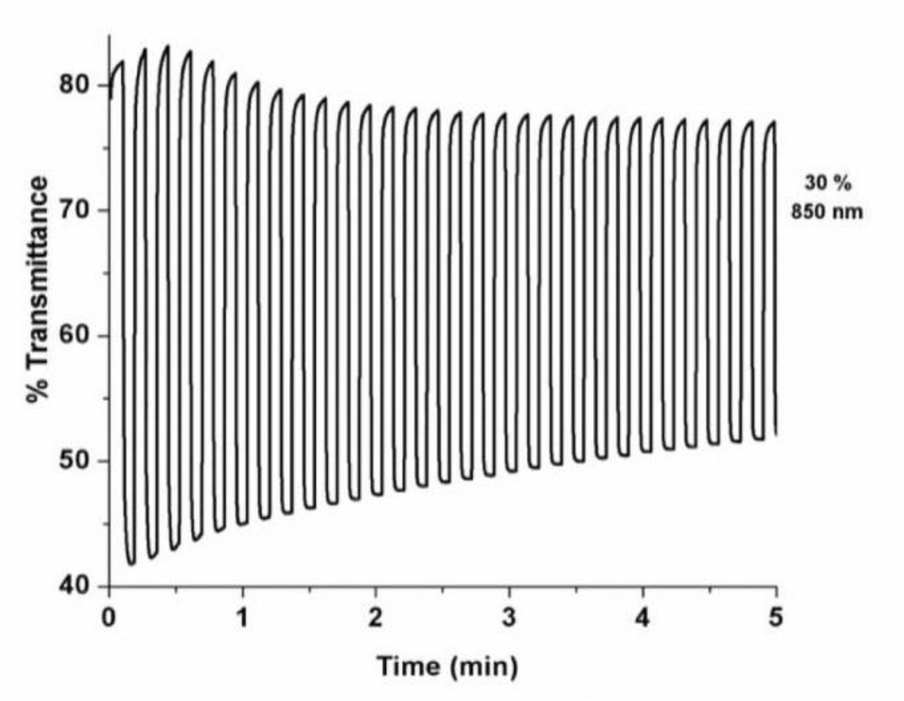


Figure 3.10 Optical contrast changes of P3

3.3 Characterization of Electrochromic Device

3.3.1 Spectroelectrochemistry Studies of Electrochromic Device

Spectroelectrochemistry experiments were performed to monitor the optical properties, resulted by changes in electronic transitions, during the redox switching of polymers. As seen Figure 3.11, the red color of the device turned into blue upon stepwise increasing the potential from -1.8 V to +1.8V. At -1.8 V, cathodically coloring polymer PEDOT layer was transparent sky blue color since it was in its oxidized state and anodically coloring polymer P2 has dominant red color which was in its reduced state and had a maximum absorption at 480 nm. Application of positive potentials caused the oxidation of P2 layer whereas complete reduction of PEDOT layer. Therefore, at +1.8 V PEDOT layer was dominant with blue color and the maximum absorbtion was at around 600nm due to the π-π* transition of PEDOT.

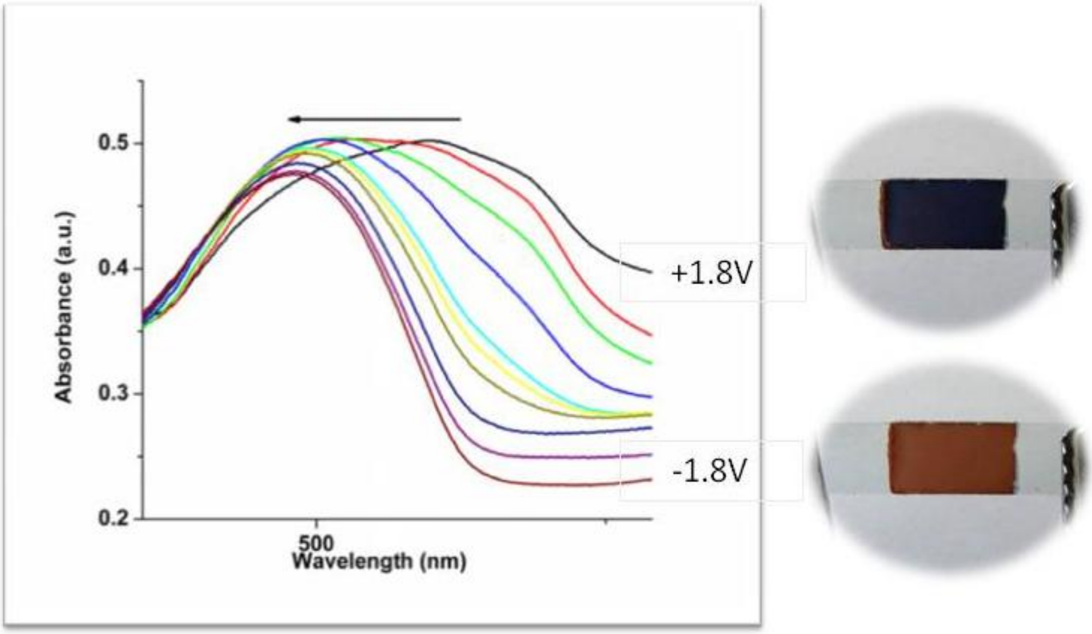


Figure 3.11 Spectroelectrochemical spectrum of P2/PEDOT device

3.3.2 Switching Studies of Electrochromic Device

In order to investigate the electrochromic switching properties of P2/PEDOT device, the device switched between the reduced and oxidized states. It showed 14 % optical contrast with 1.2 s switching time. (Figure 3.12)

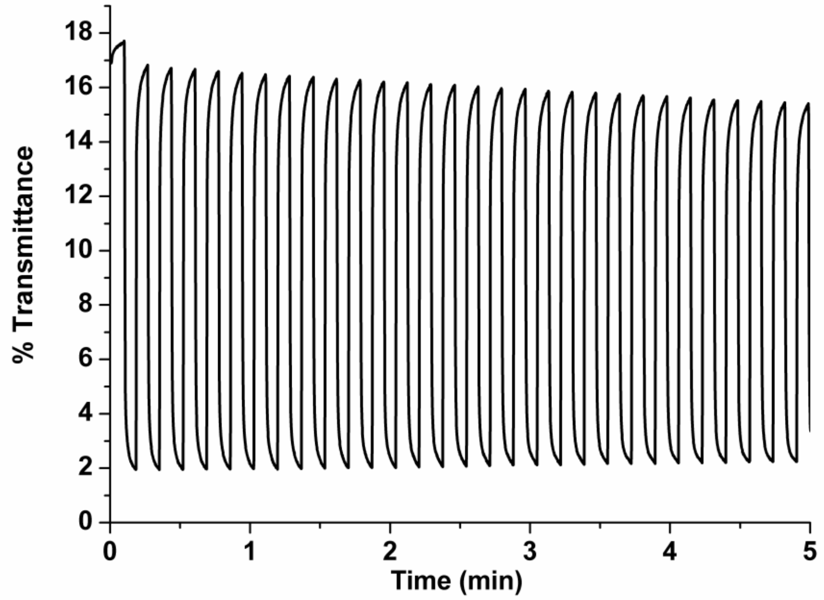


Figure 3.12 Optical contrast changes of electrochromic device

3.3.3 Open Circuit Memory of Electrochromic Device

In oreder to investigate open circuit memory of P2/PEDOT device, a pulse was applied for 1s and the device was kept under open circuit conditions for 200 seconds. In the blue colored state, after 200 seconds the absorbance was reduced by nearly 10 %. This is a reasonable optical memory under open circuit conditions. On the other hand, in the red colored state, there was no absorbance loss indicating that the device is stable in red colored state. (Figure 3.13)

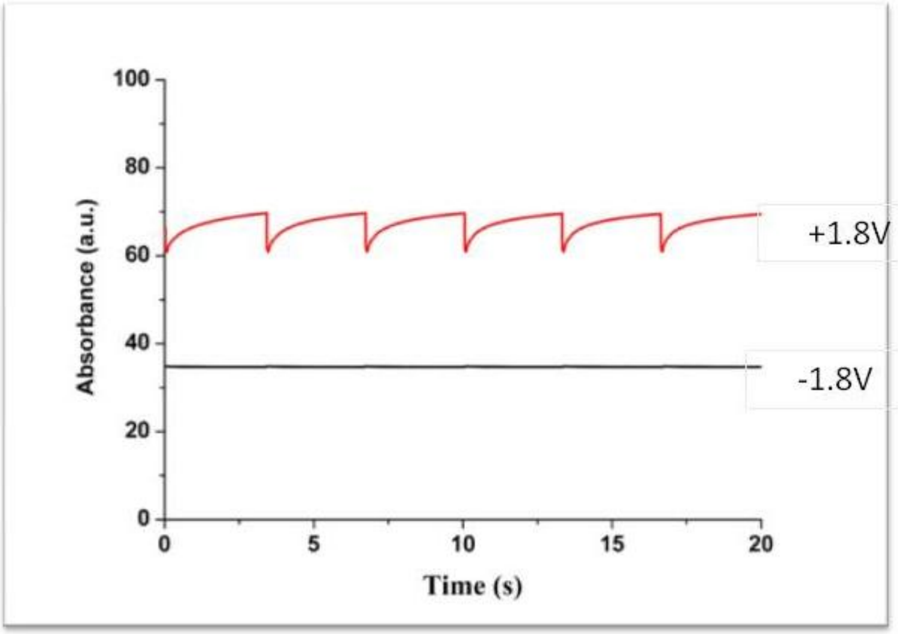


Figure 3.13 Open circuit memory of P2/PEDOT device

CHAPTER 4

CONCLUSION

Three new monomers; 2-(6-(2,5-bis(5-methylthiophen-2-yl)-1H-pyrrol-1-yl)hexyl)-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (M1), 2-(6-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)hexyl)-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (M2) and 2-(6-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)hexyl)-4,7-bis(5-methylthiophen-2-yl)-2H-benzo[d][1,2,3]triazole (M3) were successfully synthesized. Electropolymerization of monomers were achieved in the presence of ACN/NaClO4/LiClO4 solvent-electrolyte system. The electrochemical and optical properties of polymers were characterized by cyclic voltammetry and spectroelectrochemistry. P1 and P2 have small band gap values of 1.87 and 1.95 eV. All polymers showed low switching times and high optical contrasts in NIR region that makes them good candidate for NIR applications. An electrochromic device was constructed using the electrochemical polymer of M2 against PEDOT. The device switched between red and blue colors exhibiting 14 % optical contrast with 1.2 s switching time. Additionally, the device showed exceptional optical memory.

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APPENDIX A

NMR DATA

NMR spectra were recorded on a Bruker Spectrospin Avance DPX-400 Spectrometer. Chemical shifts δ are reported in ppm relative to $CHCl_3$ (^{1}H: δ=7.27), $CDCl_3$ (^{13}C: δ=77.0) and CCl_4 (13C: δ=96.4) as internal standards.

M1: ^{1}H NMR (400MHz, $CDCl_3$, δ): 7.98 (d, *J*=3.5 Hz, 2H), 7.52 (s, 2H), 7.27 (d, *J*=5.0 Hz, 2H), 7.09-7.06 (m, 2H), 6.71 (d, *J*=3.3 Hz, 2H), 6.57 (d, *J*=2.5 Hz, 2H), 6.14 (s, 2H), 4.61 (t, *J*=7.0 Hz, 2H), 4.02 (t, *J*=7.5 Hz, 2H), 2.35 (s, 6H), 1.98-1.87 (m, 2H), 1.50-1.46 (m, 2H), 1.19-1.12 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 141.0, 138.8, 138.6, 131.6, 127.3, 127.0, 125.9, 124.8, 124.5, 124.3, 122.5, 121.7, 109.2, 55.5, 43.7, 29.6, 28.7, 24.8, 24.7, 14.2.

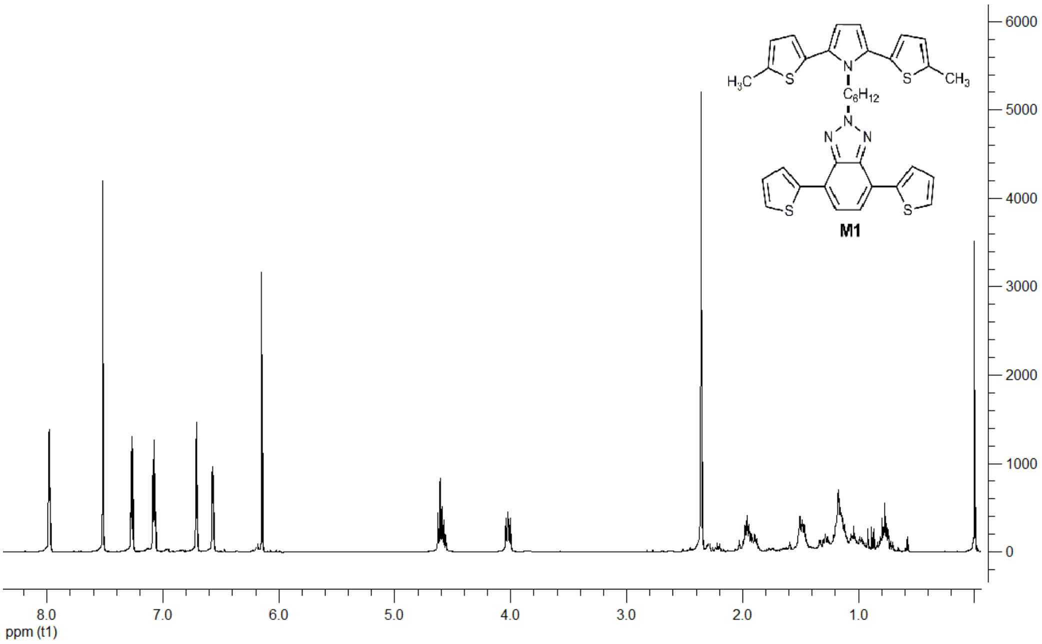

Figure A.1 ^{1}H-NMR spectrum of M1

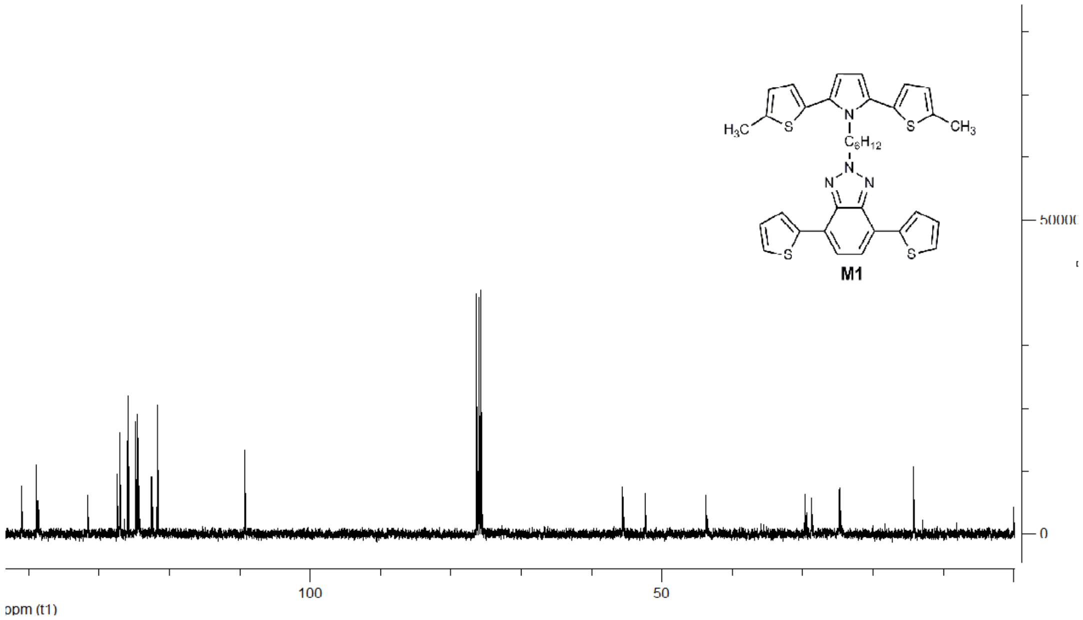

Figure A.2 ^{13}C-NMR spectrum of M1

M2: ^{1}H NMR (400MHz, CDCl$_3$, δ): 7.99 (d, *J*=2.9 Hz, 2H), 7.54 (s, 2H), 7.29 (d, *J*=5.0 Hz, 2H), 7.18-7.16 (m, 2H), 7.09 (dd, *J*=3.7 Hz, *J* = 5.0, 2H), 6.94-6.92 (m, 4H), 6.22 (s, 2H), 4.62 (t, *J*=7.1 Hz, 2H), 4.02 (t, *J*=7.6 Hz, 2H), 1.98-1.91 (m, 2H), 1.51-1.43 (m, 2H), 1.17-1.11 (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$, δ): 142.1, 139.9, 134.9, 128.3, 128.1, 127.2, 126.9, 126.0, 125.6, 125.3, 123.6, 122.8, 110.8, 56.6, 44.8, 30.7, 29.7, 25.8, 25.7.

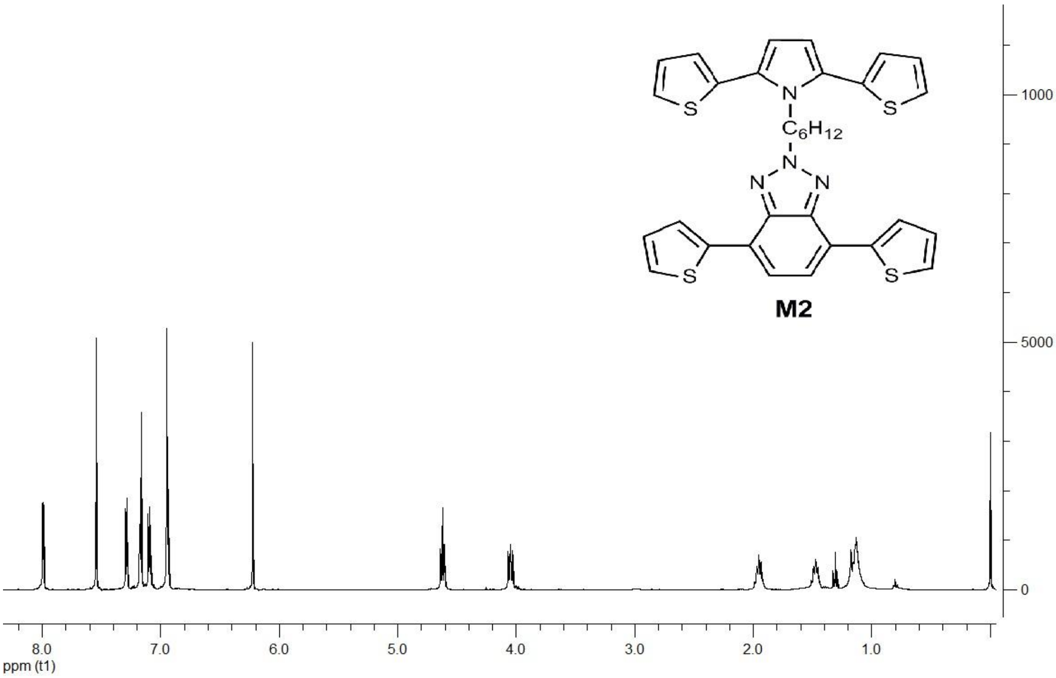

Figure A.3 ^{1}H-NMR spectrum of M2

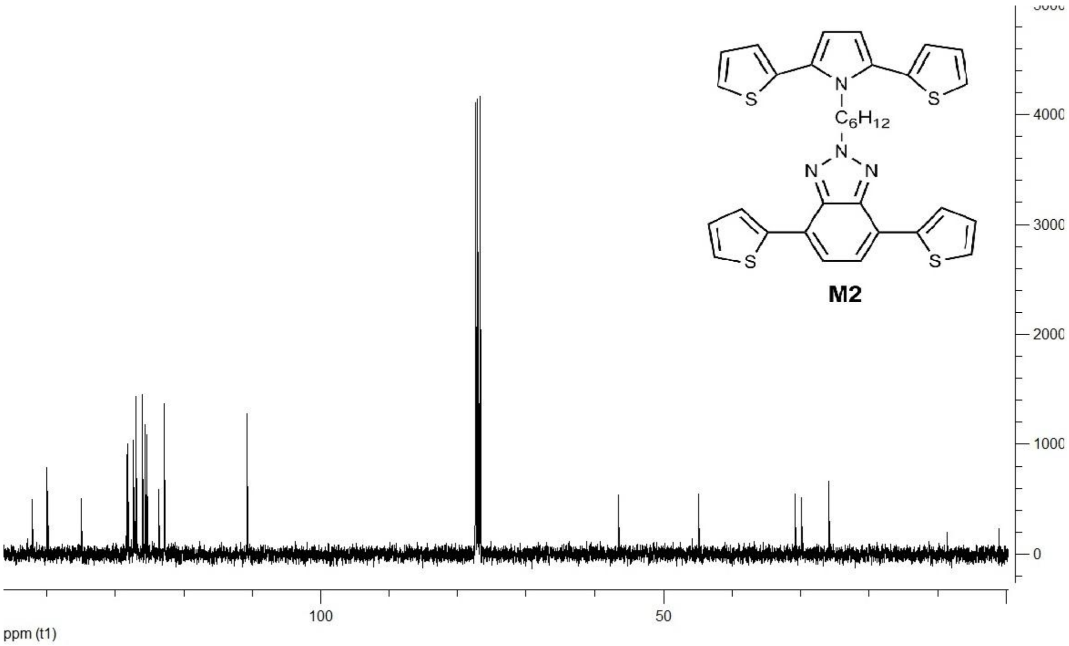

Figure A.4 ^{13}C-NMR spectrum of M2

M3: ^{1}H NMR (400MHz, $CDCl_3$, δ): 7.77 (d, *J*=3.5 Hz, 2H), 7.43 (s, 2H), 7.19-7.18 (m, 2H), 6.96-6.95 (m, 2H), 6.74 (dd, *J*=1.0 Hz, *J* = 3.5, 2H), 6.23 (s, 2H), 4.61 (t, *J*=7.1 Hz, 2H), 4.05 (t, *J*=7.6 Hz, 2H), 2.47 (s, 6H), 1.98-1.91 (m, 2H), 1.51-1.44 (m, 2H), 1.18-1.10 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 141.0, 139.2, 136.7, 133.8, 127.2, 126.2, 125.9, 125.3, 124.9, 124.2, 122.3, 121.1, 109.8, 55.4, 43.8, 29.6, 28.7, 24.7, 24.6, 14.4.

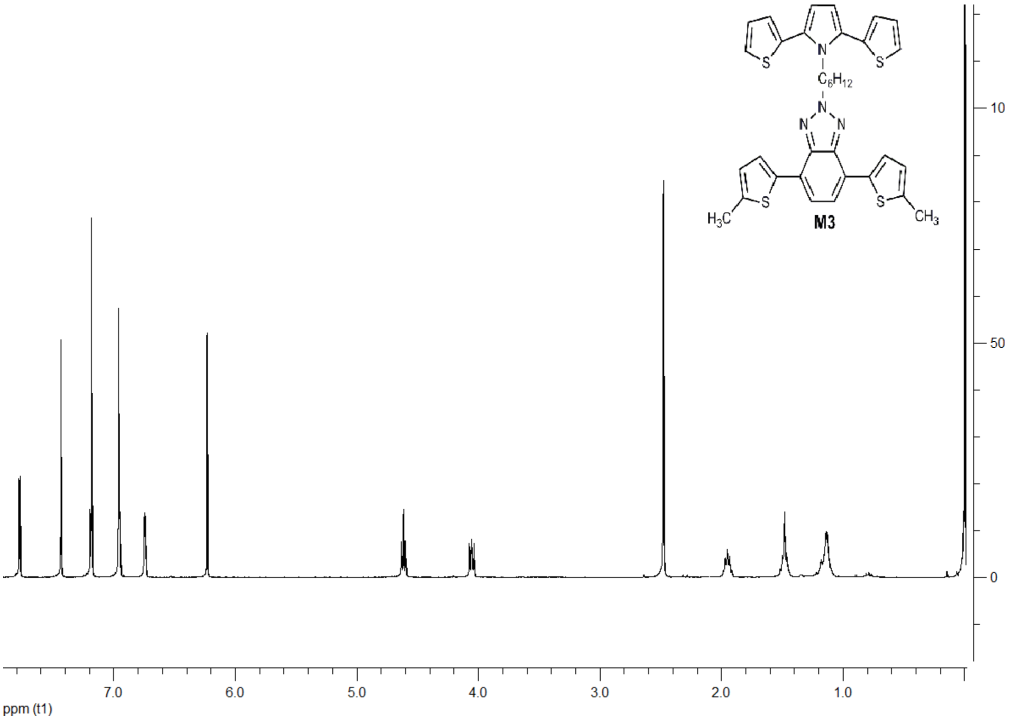

Figure A.5 ^{1}H-NMR spectrum of M3

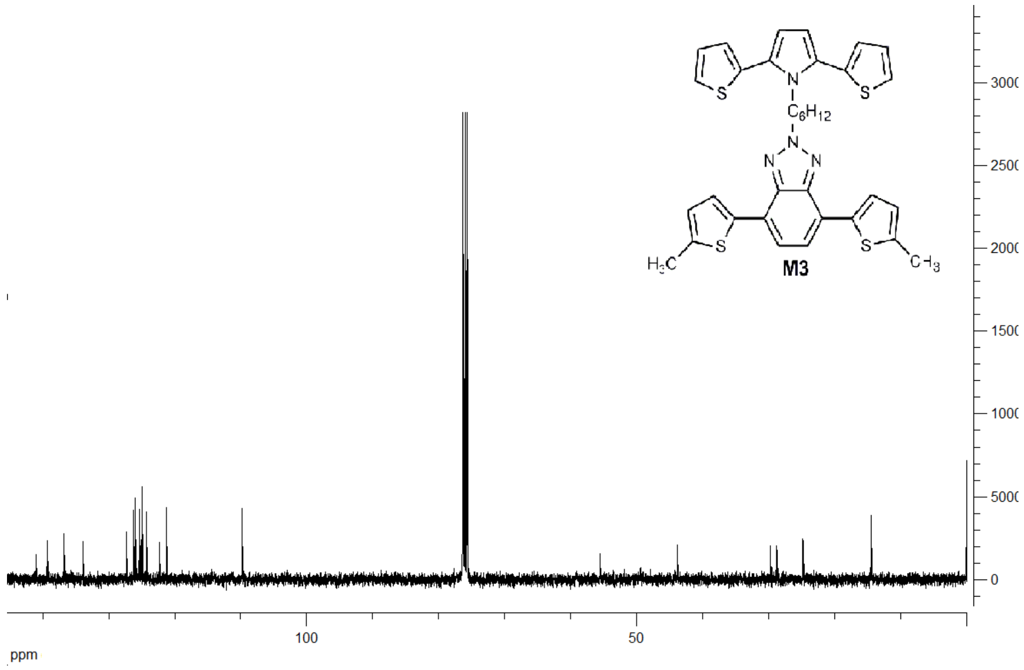

Figure A.6 ^{13}C-NMR spectrum of M3