SYNTHESIS AND CHARACTERIZATION OF A LOW BAND GAP POLYMER BASED ON SELENOPHENE AND BENZOBIS(THIADIAZOLE)

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AT

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Approval of the Graduate School of Natural and Applied Sciences, Atılım University

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Prof. Dr. Ali Kara
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I certify that this thesis satisfies all the requirements as a thesis for the degree of the Master of Sciences.

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This is to certify that we have read the thesis "SYNTHESIS AND CHARACTERIZATION OF A LOW BAND GAP POLYMER BASED ON SELENOPHENE AND BENZOBIS(THIADIAZOLE)" submitted by "Mohammed Abdulrazzaq" and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF A LOW BAND GAP POLYMER BASED ON SELENOPHENE AND BENZOBIS(THIADIAZOLE)

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M.S., Chemical Engineering and Applied Chemistry Department

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A new derivative of benzobis(thiadiazole) based electron donor–acceptor–donor type monomers, namely 4,7-di(selenophen-2-yl)benzo[1,2-c;4,5-c']bis[1,2,5]thiadiazole (SeBTSe), was synthesized and its polymerization was carried out successfully via electrochemical polymerization in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate dissolved in dichloromethane. The monomer SeBTSe is a deep red chromophore and it has four redox states: one oxidation, one neutral and two reduction states. The electrochemical behaviour of the corresponding polymer called PSeBTSe was studied by cyclic and differential pulse voltammetry. There is a good agreement between electrochemical (0.62-0.66 eV) and optical (0.63 eV) bandgaps of the polymer. Like the monomer, the ambipolar polymer has four redox states and electrochromic properties: gray beige at neutral state, smoky azurite at oxidized state, beige at first reduced state and dark beige at second reduced state.

Keywords: Electropolymerization, Electrochromism, Ambipolar, Donor-Acceptor-Donor, Selenophene, Benzobis(thiadiazole)

ÖZ

SELENOFEN VE BENZOBIS(TİYADİAZOL) ESASLI DÜŞÜK BANT ARALIKLI BİR POLİMERİN SENTEZİ VE KARAKTERİZASYONU

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Tez Yöneticisi: Prof. Dr. Atilla Cihaner

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4,7-di(selenofen-2-il)benzo[1,2-c;4,5-c']bis[1,2,5]tiyadiazol (SeBTSe) olarak isimlendirilen benzo(bistiyadiazol) esaslı elektron verici-alıcı-verici tipi monomerlerin yeni bir türevi sentezlendi ve polimerizasyonu diklorometan içinde çözülmüş 0,1 M tetrabütilamonyum heksaflorofosfatın elektrolit çözeltisinde elektrokimyasal polimerizasyon yoluyla başarıyla gerçekleştirildi. Monomer SeBTSe koyu kırmızı bir kromofordur ve dört redoks haline sahiptir: bir yükseltgenme, bir nötr ve iki indirgenme hali. PSeBTSe adı verilen ilgili polimerin elektrokimyasal davranışı, döngüsel ve diferansiyel puls voltametrisi ile incelenmiştir. Polimerin elektrokimyasal (0.62-0.66 eV) ve optik (0.63 eV) bant aralıkları arasında iyi bir uyum vardır. Monomer gibi, ambipolar polimer de dört redoks haline ve elektrokromik özelliklere sahiptir: nötr halinde gri bej, yükseltgenmiş halde dumanlı azürit, ilk indirgenmiş halinde bej ve ikinci indirgenmiş halinde koyu bej.

Anahtar Kelimeler: Elektropolimerizasyon, Elektrokromizm, Verici-Alıcı-Verici, Selenofen, Benzobis(tiyadiazol)

DEDICATION

To the first Chemist i have even known. To the person who used to show us some fireworks at our house's yard by igniting megesium strips. To the hero who loved,protected,provided and took care of us all these years patiently. Thank you for your guidance, and thank you for the mental, emotional, achademic and finincial support that you provided for us. Thank you for every single second from the first moment you held me between your hands till today, to the day i die! i am forever in your debt. I hope i made you proude **DAD.**

To my guardian angel, to the sweetest, kindest, most generous and the most warm hearted woman in this world, to first hands which helped me to walk. To the first woman who stole my heart. To the teacher that used to walk me to school and back home. Life would have not been easier without your angelic wings, your prayers, gentle love, kind voice and your warm heart. To my queen **MOM.**

To my spiritual twin, to my second father. To the person who tremendously contributed of molding the person i am today. To the far by distance but present in the heart. To my mentor, my big brother **IBRAHEEM.**

To my travel partner, my team mate and my friend. To the person who I shared this tremendous journey with. To the wild adventurer, the stubborn entrepreneur who does not take NO for an answer, to man of the steel will and to the dreamer. Thank you for being here with me **ANAS**

To our house's gentle spirit, our family's heart. You are our most precious treasure. I cannot imagine a life without your sense of humor, kindness, passion, strength and your joyful soul. No parents could ever ask for a better daughter and no brothers could ever ask for a better sister. Thank my sweet sister **SUMEYA**

To my soulmate. To the person whom I share my life's most precious memories with, growing up together is what I cherish the most. I am eternally grateful that you are a part of my life. Thank you for my little brother **AMMAR.**

To my friend, flat mate and my brother. By looking at this day I cannot but remember the day when we were just undergraduates, and we are here again doing our masters together. Since the day I met you, i have seen nothing but honesty, trust, loyalty, respect, support and the most profound friends quality. Thank you for pushing me harder to become a better version of myself, thank you for all the support that you provided which helped me reach this point. From the deepest part of my heart thank you **JUNAID.**

To all my friends, family and relatives, uncles and aunts I dedicate this work to you all.

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LIST OF ABBREVIATIONS

CP	-	Conductive Polymers
D-A-D	-	Donor – Acceptor – donor
EDOT	-	3,4-Ethylene dioxythiophene
E_g	-	Band Gap Energy
Fc	-	Ferrocene
Fc^+	-	Ferrocenium
HOMO	-	Highest Occupied Molecular Orbital
ITO	-	Indium Tin Oxide
LUMO	-	Lowest Unoccupied molecular Orbital
NMR	-	Nuclear Magnetic Resonance
PEDOT	-	Poly(3,4-Ethylene dioxythiophene)
PSeBTSe	-	Poly(4,7-di(selenophen-2-yl)benzo[1,2-c;4,5-c']bis[1,2,5]thiadiazole)
Pt	-	Platinum
SeBTSe	-	4,7-di(selenophen-2-yl)benzo[1,2-c;4,5-c']bis[1,2,5]thiadiazole
TBAH	-	Tetrabutylammonium hexafluorophosphate
UV-VIS	-	Ultraviolet-Visible

CHAPTER 1

INTRODUCTION

1.1 Historical Background of Conjugate and Conductive Polymers

In the early 1930's after the discovery of how macromolecules can be formed, polymers, colloquially was known as plastics, became one of the widely studied and researched material. The vast possibility of how polymeric macromolecules are formed from subunit building blocks, i.e. monomers, inherently gave polymers a set of unique characteristics, such as thermal insulation, light weight, and low manufacturing cost. Beyond those superior properties, in 1977 by Shirakawa, Heeger and McDiarmid managed to add conductivity to these exclusive polymeric properties, they were able to make polyacetylene conductive upon a process called "Doping", for which they were awarded the 2000 Nobel Prize in Chemistry.[1]

Polyacetylene, the *cis*- and *trans*- forms of which are known as first generation semiconducting polymers which demonstrated a conductivity of $1.0x10^{3}$-1.7×10^{5} S/cm and a band gap of 1.5 eV. Polyacetylene opened a new era of organic conductive materials. The unique characteristic of conducting polymers is the conjugated molecular structure of the polymer's main chain, the alternative single-double bonds creates a system where p-orbitals overlap each other and make the π-electrons able to delocalize over the whole polymer chain thus many atoms may share these electrons; therefore, conjugation is an essential property to make the polymer able to conduct.

The intrinsic drawbacks of polyacetylene, such as air sensitivity and missing processability of doped polymer, rendered it hard and difficult to be useful for industries. However, among many approaches in order to overcome these drawbacks, stabilizing the sensitive π-electron system was the most promising one. Which was through by the

substitution of heteroatoms within the polymer chain or as in electron-donating substituents. The first has been realized only in polyaniline, where the last offered more different options - N and S are considered the most interesting heteroatoms substituents, incorporated in a heterocyclic conjugated structure and that led to introducing a wide variety of what it is called "Second Generation Conductive Polymers", such as polypyrrole (a conductivity (σ) of $1.0x10^2$-7.5×10^3 S/cm and a band gap (E_g) of 3.1 eV, polyaniline (σ = 20-300 S/cm and E_g = 3.2 eV), polythiophene (σ = 10-10^3 S/cm and E_g= 2.0 eV), and poly(phenylene vinylene) (σ = 3-5×10^3 S/cm and E_g = 2.5 eV) as well as alternating copolymers.[2]

Although, and even with the progress made, polyacetylene, polypyrrole, polythiophene, and polyaniline demonstrated insufficient conductivity half-life values, limited solubility and air instability which reduced the scope of their practical applications. However, a new conductive polymer was discovered in which it demonstrates the opposite, from being stable in air up to a very high temperatures, resistance to humidity and moist air, low oxidation potential and high transparency in conductive form known as PEDOT (poly(3,4-ethylenedioxythiophene)).[3] 3,4-ethylenedioxythiophene (EDOT) monomer is a five-membered thiophene ring with a dioxy-ethyl substituent group replaced with the 3 and 4 positions hydrogens . Note that EDOT monomer eliminated the possibility of having chemical defects in it's structure due to the existence of only two (2 and 5 positions) reactive hydrogens. The regularity of the PEDOT's molecular structure has been associated with its outstanding chemical stability, additionally, the existence of electron donating groups decreased the band gap to 1.6 eV which made PEDOT capable of a higher conductivity. PEDOT was the start of the third generation of conductive polymers.

1.2 PEDOT

The birth of PEDOT originated by the trails to increase the solubility and altering the electronic properties of polythiophenes (PTs). However, it was found that the addition

of alkyl and alkoxy side chains increased the solubility of PTs. Also, it was noticed that with the addition of electron donating or withdrawing groups that in direct electronic communication with the polymer's backbone maximizes the electronic properties.

A great deal of work has been done on the 3-alkyl derivatives to enhance the solubility and electronic properties of PT, resulted in lowering the monomer oxidation potential, and decreasing the bandgap from 2.20 to 1.90 eV.[3]

In the search for a method to increase solubility and lower monomer oxidation potential, thiophene monomers with alkoxy substituents in the 3 or 3,4- positions have been explored.[3] The incorporation of an electron donating group increases the electron density, such as the alkoxy group on the thiophene, and increases the energy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The LUMO is increased to a lesser extent compared to that of the HOMO, and as a result, the band gap is decreased. If an additional alkoxy group is placed on thiophene, the steric interaction between adjacent rings forces them out of plane and decreases conjugation. To overcome this problem, EDOT was synthesized with the purpose of "pinning back" the alkoxy groups to limit the steric interactions. As a result of the above benefits, PEDOT is highly conductive and has a comparatively low band gap of 1.6 eV.[3]

1.3 Concept of Band Gap

Electrical conductivity is the material's ability of the to conduct electrical current via electron flow. This property mainly depends on the energy difference between the the main two energy bands (valance band (HOMO) and conduction band (LUMO)). The difference between these two bands is known as the band gap, in other words, it is the minimum energy required to excite an electron to participate in conduction process. Band gap energy was measured by electron per-volt (eV) for conductors (E_g= zero eV), semiconductors (E_g = 1.0 - 3.0 eV), and insulators (E_g = >3.0 eV) **(Figure 1.1)**

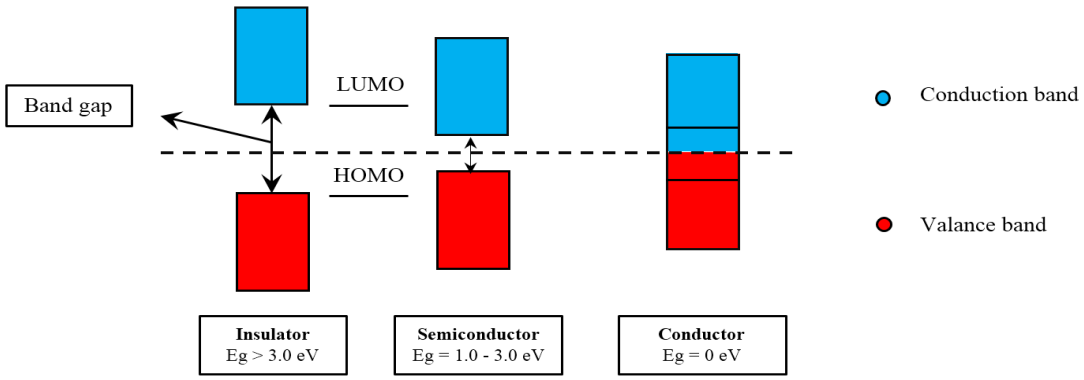


Figure 1.1: A band gap diagram showing the different band gaps for insulators, semiconductors and conductors.

However, the chemical structure of conductive polymers differs from their ordinary plastic counterparts. They have p_z-orbitals overlapping which leads to conjugation (alternating single-double bonds) in the one-dimensional chain. This π-conjugation imparts intrinsic conductivity to the polymer. This phenomena made conjugated polymers have low conductivity similar to semi-conductors. However, this low conductivity can be increased by a process called doping, which is mainly about creating defects (holes or extra electrons) on the polymer chain which. These impurities act as charge carriers, jumping from one molecule to the next in the effect of an electrical field. The polymers doping process was firstly introduced by Shirakawa et al. work by producing a conductive polyacetylene.[1]

Doping procedure can be two types: n-doping is when an extra electron induced to the system (reduction) which negatively charge the polymer's chain (anion) while p-doping, on the other hand, is when an electron is taken from system (oxidation) and positively charging the polymer's chain by leaving a hole. These radical ions called polarons, see **Figure 1.2(b)**. At low level of doping, polarons are the charge carriers across the polymer's chain. However, and when doping level is increased, the concentration of polarons increases as well, such that a probabilistic state of either attraction or repulsion

occur between polarons. The result of if two polarons may get coupled is called bipolaron (see **Figure 1.2(c)**).

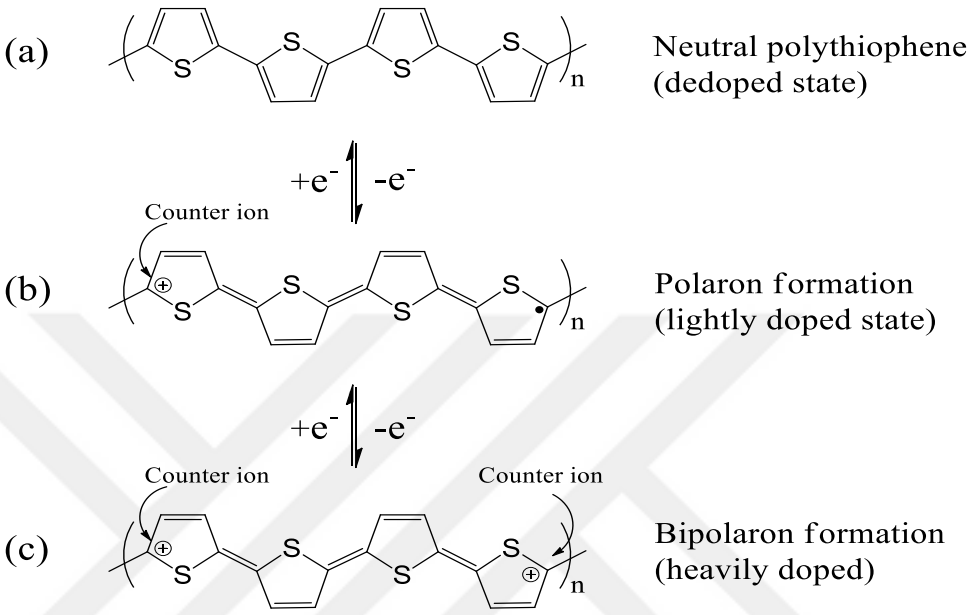


Figure 1.2 : Illustration of polaron and bipolaron formation on polythiophene structure upon doping.

1.4 Donor-Acceptor-Donor Approach in Conjugated Polymers

After the conductive polyacetylene discovery, an intense research on the molecular level rose up led to obtaining a stable and a processable polymer. However, the need for further modifications appeared in the horizon such as getting more chemically, optically or thermally stable materials for multiple applications, obtaining variable colors and most importantly decreasing the band gap (which is our main aim in this thesis).

Many conjugated systems have been designed and synthesized in favor of reaching these aims. During these developments, it was realized that the combination of an acceptor molecule with a donor one resulted in a reduced band gap conjugated system, this approach is called the "Donor-Accepter-Donor System" (D-A-D).[4] The underlying concept is that the D units determine the oxidation potential (HOMO energy level), and the A units determine the reduction potential (LUMO energy level).

Combining the A and D units in one polymer will form a valence band energetically near the HOMO of the donor and also a formation of a conduction band in the region of the LUMO of the acceptor (**Figure 1.3**).

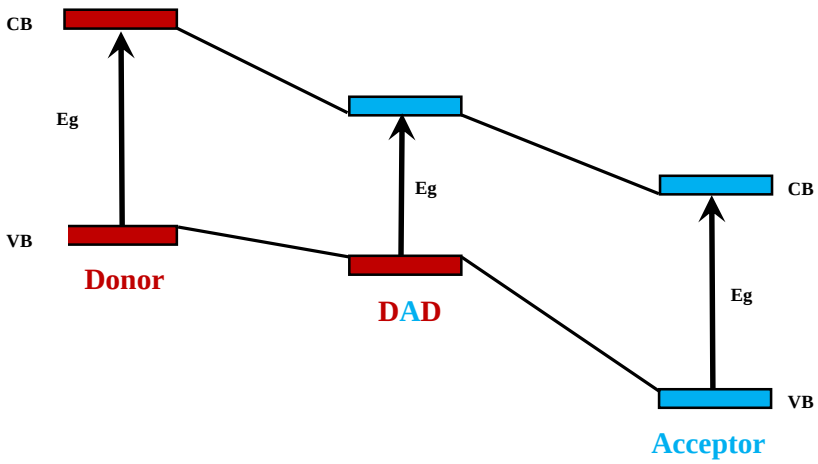


Figure 1.3 : A general representation of D-A-D system.

In general the magnitude of the band gap is determined by the difference between electron richness of the donor molecule and electron deficiency in the acceptor molecule. Thus, conjugated polymers with the highest electronegativity difference between donor and acceptor groups were claimed to have the lowest band gap.

Furthermore, it appeared that the molecular level modifications of such systems offered further wanted properties regarding the band gap, such as stability and enhanced electrochromic properties. Also, it allows low potentials multiple redox states; which provide the multicolor property with the p- and n-type doping ability. Furthermore, adding alkyl substituents showed that it can increase the solubility solubility.[5] Thus, according to the desired application area the D-A-D systems can be arranged. D-A-D type conjugated systems are desirable in electronic device applications such as electrochromic devices (ECDs), LEDs, SCs, and FETs.[6]

1.5 Polymerization Techniques

Generally, conjugated polymers can be synthesized by both chemical and electrochemical methods. However, there are many other methods such as emulsion copolymerization,[7] photochemical polymerization, metathesis polymerization, plasma polymerization, inclusion polymerization and solid state polymerization.

1.5.1 Chemical Polymerization

In the synthesis of conjugated polymers, the Chemical polymerization is considered the most widely used synthesis method, due to its simplicity and also being the least expensive technique. It provides the ability to synthesize a large scale of conjugated polymers with high yields in fairly inexpensive fashions. The polymerization process occurs spontaneously by constantly stirring conjugated monomers with a suitable

oxidizing agent such as ammonium peroxydisulfate ($(NH_4)_2S_2O_8$), ferric chloride ($FeCl_3$), potassium permanganate ($KMnO_4$) and hydrogen peroxide (H_2O_2).[8]

However, it is important to notify that the formed polymer chains are in the oxidized state (doped) which is rather less stable than the neutral state, a strong reducing agent must be used such as ammonium hydroxide or hydrazine in order to dedope the polymer to reach its neutral state.

Additionally, since the polymer is growing while being in the oxidized state, it becomes more rigid comparing to its neutral state. Also, residual oxidant may get trapped in the polymer, which can lead to poor device performance. The oxidative polymerization technique is preferable in the chemical polymerization of the substituted monomers.

However, the substitution in monomers must be considered in this technique because of the possibility of producing a regioirregular polymer, for example substitutions like alkyl chains as in the case of 3-hexylthiophene, would eventually effect the polymer's planarity. On the other hand, using metal catalysts provided a solution to have a regioregular and planer polymer chains.[9]

In the D-A-D type polymers or copolymers synthesis, the type of functionalized group on the monomer is considered an important factor for choosing the suitable polymerization technique among a variety of organometallic cross-coupling reactions. The most widely used chemical polymerization technique is the Stille coupling reaction:[10] Which is about attaching two both sides substituted monomers units, the first is halogenated (usually brominated) and the second is stannylated. These units attached together in an alternative pattern with the use of the proper catalyst (usually palladium compounds).

There are other famous coupling reactions such as Sonogashira Coupling, Suzuki Miyaura coupling, Kharash coupling, Negishi coupling, Himaya coupling and Kumuda coupling reactions.[11,12]

1.5.2 Electrochemical Polymerization

The electrochemical polymerization is a favorable method in the CPs synthesis due to the ability to control the film thickness easily by the deposition charge. The heterocycles electrochemical polymerization mechanism begins with the oxidation of the monomer leading to create its own radical cation which acts as a reaction intermediate. To form a polymer the radical cation will follow one of two different coupling paths/routes. The first one is a combination of two radical cations and forming a neutral dimer by losing two protons.[13] On the other hand, the other possibility is the addition of radical cation to another neutral monomer and forming a dimer also after losing two protons.[14] A general poly(heterocycles)'s electro-oxidative polymerization mechanism is given in **Figure 1.4**.

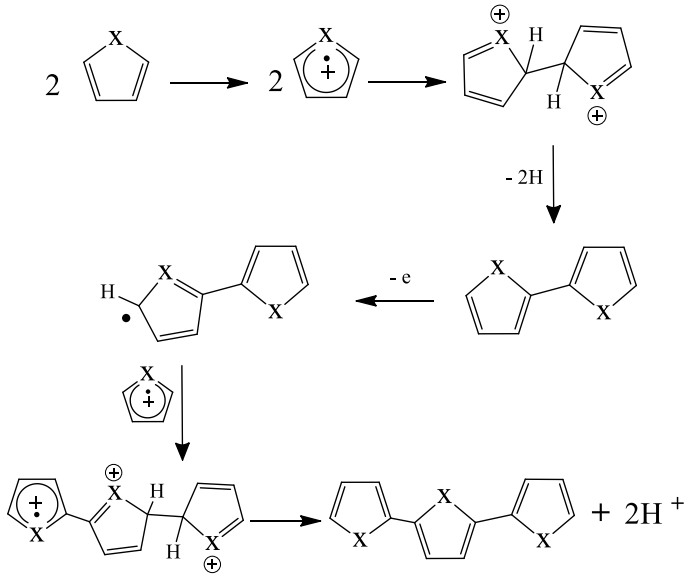


Figure 1.4 : Polymerization mechanism of a heterocyclic monomer via electrochemical techniques (X= S, O, NH)

Additionally there are two geometrically based coupling paths during the electrochemical polymerization of poly(heterocycles), α-α' which leads to a regular/linear polymer while α-β coupling results in chain branching (see **Figure 1.5**).

However, by replacing β and β' hydrogen atoms with suitable substituents chain branching can be avoided.

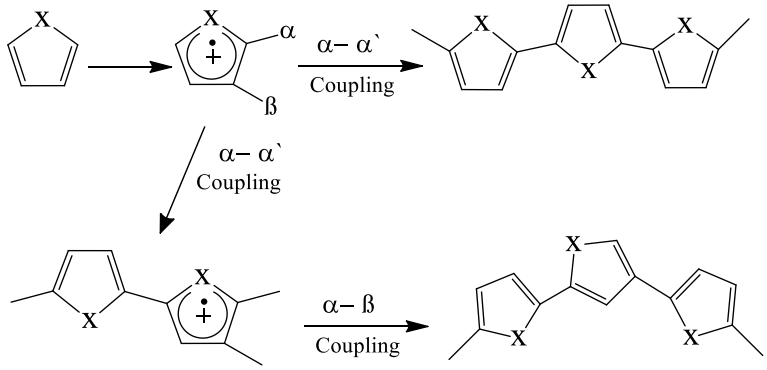


Figure 1.5 : Possible α-α' and α-β couplings of unsubstituted heterocyclic monomer (X = S, O, NH).

The electrochemical polymerization offers many advantages over other methods:

- Simple, short polymerization time duration
- To obtain a polymer film a small amount of monomer is enough
- By adjusting the applied voltage, scan rate and polymerization time, the film thickness, morphology and conductivity can be controlled
- It provides in situ analysis of CP's properties by methods such as spectroscopic and electroanalytical methods.

However, this method also has a main drawback which is the incapability of producing a mass production, even more importantly to mention the unwanted 3- and 4-positons along with the 2- and 5-positions coupling which leads to a decrease in the conjugation, cross-linking and poor electronic properties.[15]

1.6 Electrochemical Techniques

1.6.1 Cyclic Voltammetry

Cyclic voltammetry is the most widely used technique to obtain qualitative information in electrochemical polymerization. It monitors the redox behavior, and gives information about the oxidation-reduction potential values of the electroactive compounds (**Figure 1.6**).

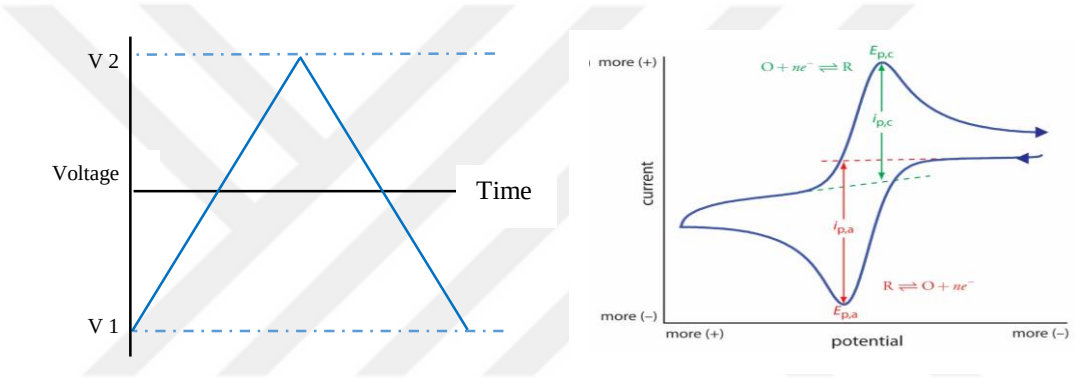


Figure 1.6 : Cyclic voltammetry waveform and cyclic voltammogram for a reversible redox reaction.

In this technique a potentiostat is connected to a three-electrode system (working electrode (WE), counter electrode (CE) and reference electrode (RE)) which immersed in a suitable electrolyte (see **Figure 1.7**).

Pt disc, glassy carbon disc and ITO coated glass electrodes are used as WE commonly in this method, while Ag wire or Ag/AgCl saturated calomel electrode is used as RE and for the CE is generally a Pt wire or a Pt plate.

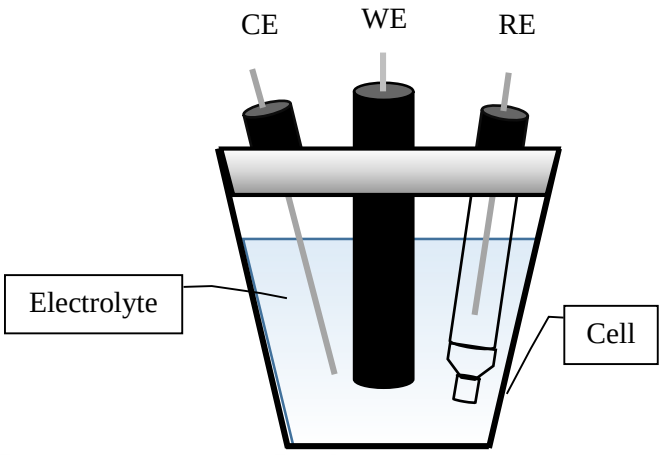


Figure 1.7 : A Schematic diagram of an electrochemical cell.

We can measure the potential between the WE and the RE, while the current is measured between the WE and the CE. The current can be calculated using Randles & Sevcik equation (**Equation 1.1**).[16]

$$i_p = (2.69\times10^5)n^{3/2}AD^{½}Cv^{½} \quad \text{.....} \quad \textbf{\textit{Equation 1.1}}$$

i_p = current maximum in amps

n = number of electrons transferred in the redox process

A = electrode area in cm^2

D = diffusion coefficient in cm^2/s

C = concentration in mol/cm^3

v = scan rate in V/s

In the equation the peak current is directly proportional to the square root of scan rate and the concentration of analyte.

1.6.2 Differential Pulse Voltammetry (DPV)

Differential pulse voltammetry (DPV) is an electrochemical technique used for both quantitative chemical analysis and to study the mechanism, kinetics, and thermodynamics of chemical reactions, it is often used with a Dropping Mercury Electrode (DME) or with a Static Mercury Drop Electrode (SMDE), where the cell current can measured as a function of the potential between the indicator and reference electrodes and also as a function of time. This technique scans with a series of fixed potential small amplitude pulses, superimposed on a slowly changing base potential.

Usually the interval between pulses varies between 0.5 - 5 s and the pulse length takes values between 40 - 60 ms, and. The current is measured at two points of each pulse, the first point is just before the pulse application and the second is at the end of the pulse. The current measurements difference between these two points of each pulse is determined and plotted against the base potential. This technique shows current peaks presented as voltammogram, where the height of the peaks is directly proportional to the analyte's concentration.[17]

DPV has several advantages over cyclic voltammetry while allowing the determination of the same basic values for polymer films

- It is several times faster than cyclic voltammetry over the same potential range.
- Very sensitive due to the relatively short pulse time which increases the measured currents
- Its superior elimination of the capacitive/background current

1.6.3 Square Wave Voltammetry

In the modern computer-controlled electroanalytical instruments, square-wave voltammetry (SWV) is considered as one of the four major voltammetric techniques. SWV is a differential technique with a large-amplitude, in which a wave is formed composed of a superimposed symmetrical square wave on a base staircase potential, the potential is applied to the WE, during each square-wave cycle the current is sampled twice, first at the end of the forward pulse and second at the end of the reverse pulse.[18]

SWV technique is a much faster technique than differential pulse techniques, which typically run at scan rates of 1 - 10 mV/sec. it employs up to 1 V/sec scan rates, or even faster, and buy which it allows much faster determinations. A typical experiment requiring takes matter of seconds by using SWV while takes about three minutes if the same experiment was done by differential pulse techniques.

1.7 Types of Electrodes [19]

1.7.1 Working Electrodes

- Pt, Hg, Au, graphite and glassy carbon etc.

1.7.2 Reference Electrodes

- Calomel (Hg/Hg_2Cl_2) Electrode
- Hydrogen ($H_2/H+$) Electrode
- Silver/Silver Chloride (Ag/AgCl) Electrode
- Silver/Silver Sulfate ($Ag/AgSO_4$) Electrode
- Mercury/Mercurous Sulfate (Hg/Hg_2SO_4) Electrode
- Mercury/Mercury Oxide (Hg/HgO) Electrode
- Ferrocinium/Ferrocene

1.7.3 Supporting Electrolytes [19]

- Tetrabutylammonium hexafluorophosphate (NBu_4PF_6)
- Tetrabutylammonium tetrafluoroborate (NBu_4BF_4)
- Lithium perchlorate ($LiClO_4$)
- Tetrabutylammonium perchlorate (NBu_4ClO_4)

1.8 Solvents [19]

Generally, high dielectric constant solvents such as

- Acetonitrile (ACN)
- Propylene carbonate (PC)
- Dichloromethane (DCM)
- Dimethylformamide (DMF)

1.9 Spectroelectrochemistry

As the name implies, spectroelectrochemistry is the combination of both spectroscopic and electroanalytic techniques, which provides an informative representation about the electronic transitions changes of conjugated polymers during the redox switching. Using spectroelectrochemistry during the doping process helps to monitor and prove the color and color changes in a scientific manner. Information such as λ_{max}, bang gap, colors of the polymer and intergap states (polarons and bipolarons) can all be obtained by utilizing this technique.

During this method, the ITO is coated with a thin layer of polymer and placed into a UV-VIS cuvette that contains the electrolyte/solvent couple (**Figure 1.8**). By increasing the applied potential, the polymer gradually stats to oxidize, the alternation of absorption spectrum is monitored by UV-VIS-NIR spectroscopy.

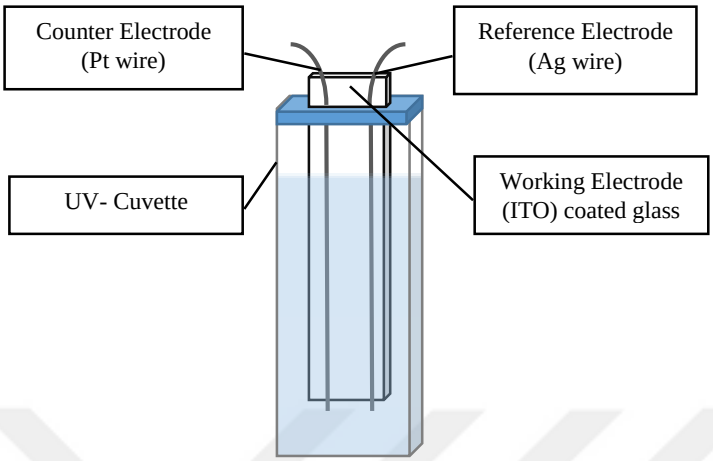


Figure 1.8 : General set up for potentiostatic methods in optical studies.

1.8 Literature Review

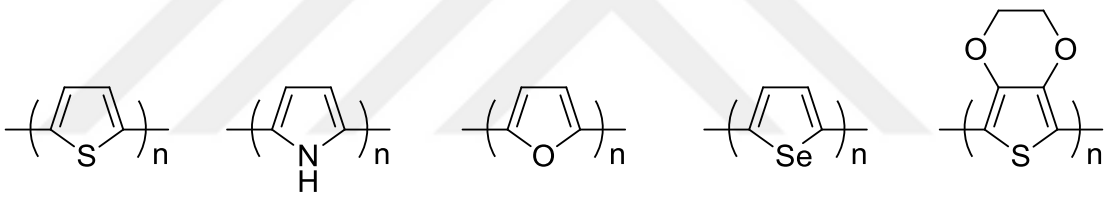
After the discovery of the Donor-Acceptor- Donor (D-A-D) approach by Havinga et al.[4] , a great amount of work was done in order to synthesize new conjugated polymers with low bandgaps. This method offered an efficient way to achieve tunable band gap polymers by alternation of D and A units in the polymer backbone. Utilization of proper choice of the D and A moieties allows selection of the approximate HOMO and LUMO energies of the resulting polymers, leading to fine control of band gap and optical characters.

Since the band gap is the difference between the two energy levels (HOMO/ LUMO), choosing the appropriate D and A units is crucial to obtain narrow or desired low band gap polymers. Also, keeping in mind that band gap tuning depends directly on the degree of the interaction of the D and A units energy levels. If there is no effective interaction between the Donor and Acceptor units, the band gap will be different than the expected value.

1.8.1 Donor and Acceptor Units

The donor unit is an electron rich group and they determines the polymer's oxidation potential also determines the HOMO level's energy. Therefore, D unit plays a crucial role for the D-A-D type conjugated polymers, which determines the structure of the polymer, optical character, fundamental colors and other electrochemical properties.

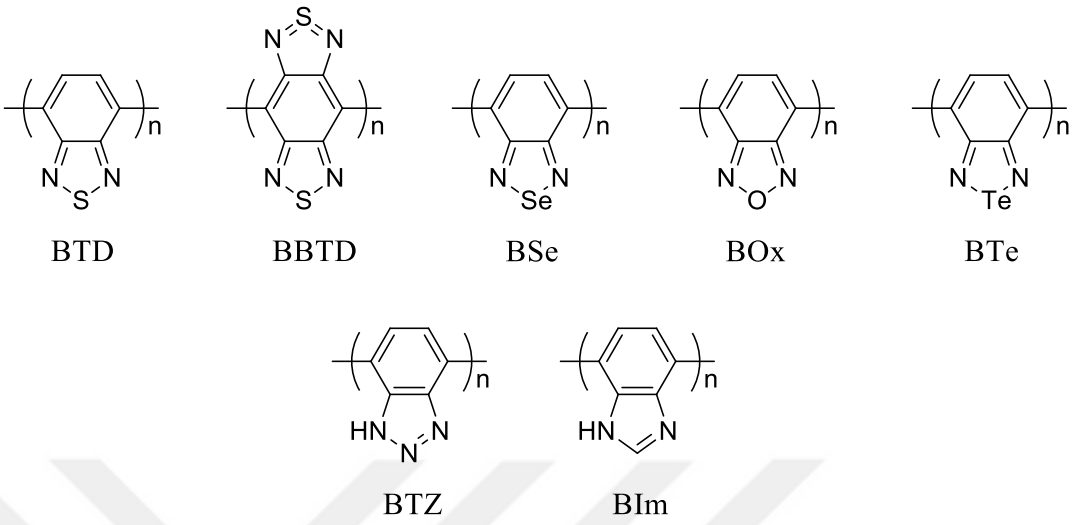
However, among many different donor types organic five membered heteroles such as polythiophene (PTh), poly(3,4-ethylenedioxythiophene) (PEDOT), polypyrrole (PPy), polyfuran (PFu) and recently polyselenophene (PSe) and their derivatives **(Scheme 1.1)** which are considered as very efficient donor units to design effective low band gap polymers.



PTh PPy t-Bu PSe PEDOT

Scheme 1.1 : Different types of polyheterocycles.

For the acceptor units on the other hand it has an electron deficiency in their structures and determines the polymer's reduction potential and the LUMO level's energy. Whereas mostly explored acceptor moieties are the benzazole derivatives due to its two electron withdrawing imine (C=N) nitrogens such as benzothiadiazole (**BTD**), benzobisthiadiazole (**BBTD**), benzoselenadiazole (**BSe**), benzoxadiazole (**BOx**), benzotelluradiazole (**BTe**), benzotriazole (**BTZ**) and benzimidazole (**BIm**) (see **Scheme 1.2**).



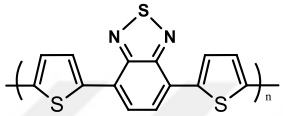
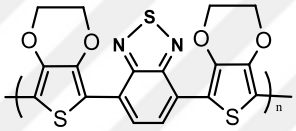
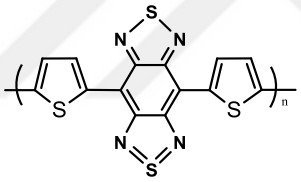
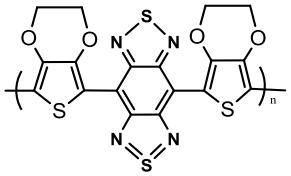
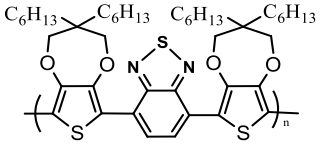
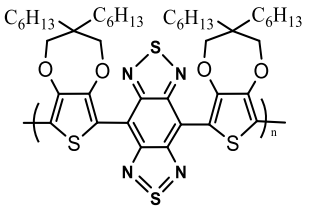
Scheme 1.2 : Different types of acceptor groups

Under the shade of D-A-D systems by combining the two units together and decreasing the band gap scientists aimed to produce metal like conductive polymers by hoping reaching the zero band gap. Polythiophenes are considered as one of the promising candidates due to their excellent stability, easy tailoring and tunable colors with the introduction of different electron-acceptor units. It has a band gap of 1.94 eV, which made thiophenes and its derivatives to be considered as a good D units.[20]

For example A. Erden et al. reported a D-A polymer PSTS containing benzothiadiazole (T) as the A unit, and thiophene (S) as a D unit with a band gap of 1.5 eV, it exhibited an absorption at about 560 nm with purple-red color in the neutral form and it switched to a blue color. Upon doping due to two new peaks at about 760 nm and 1100 nm for polarons and bipolarons, respectively (**Table 1.1**).[21] A. Durmus et.al. introduced 3,4-ethylenedioxythiophene (EDOT) (**E**) as a D unit with benzothiadiazole (T) as an A unit. EDOT is considered a stronger donor than its thiophene parent. That is mainly due to the existence of electron donating group (alkoxy group) which lowers the oxidation potential. PEDOT has a band gap of 1.6 eV. Therefore, the introduction of an

appropriate A units can control the band gap of the EDOT containing D-A-D polymers to less than 1.6 eV.[22]

Table 1.1: Structures and bandgap values of different D-A-D type polymers.[23]

Polymer's name	Polymer's structure	E_g (eV)	REF
PSTS		1.5	24
PETE		1.19	25
PSBTS		0.5	24
PSeBTSe		0.5-0.8	23
PPTP		1.5	26
PPBTP		0.63-0.99	27

A. Durmus et al. managed to decrease the band gap to 1.19 eV. The polymer (PETE) presented two absorption bands at 428 nm and 755 nm, a green color in the neutral state and a highly transmissive light blue color in the oxidized state.[28] Adding electron donating groups to the donor units to increase its strength showed a tremendous results regarding band gap tuning, lower oxidation potential and multiple colors.

Furthermore, other different approaches were conducted to enhance the electron donation ability of the donor, such as changing the donor's heteroatom by a heavier atoms. For example, changing the sulfur with selenium in the donor unit led to lowering the bandgap values; that was due to selenium's low electronegativity and selenophene's lower oxidation potential and higher HOMO energy level resulting in lower band gap values when compared to its thiophene analogues.[29,30]

G. Gokce et al. reported replacing thiophene unit by the selenophene unit resulted in a decrease in the bandgap. The D-A-D based polymer contained thiadiazoloquinoxaline as the acceptor unit. The selenophene based derivative PSeTQSe resulted in a lower band gap ranging from 0.21 eV to 0.60 eV while its thiophene analogue PSTQS has 0.77 eV (**Figure 1.9**).[31]

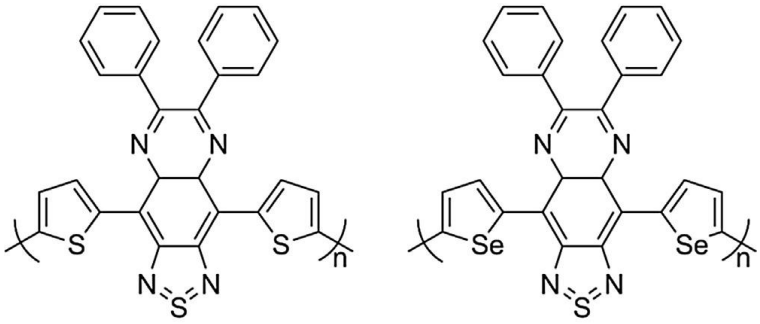


Figure 1.9 : Chemical structures and band gap values of two thiadiazoloquinoxaline derivatives.

On the other hand, in terms of changing the acceptor units, benzo[c][1,2,5]thiadiazole (BT) used enormously and considered as a strong acceptor as shown in the previous examples, whereas benzoselenadiazole and benzotriazole are also used often to tune the bandgap of conjugated polymers.

However, a study published by Tanaka et al. showed that BT is to be a stronger acceptor unit than BT.[24] Tanaka used BT as an acceptor unit with the thiophene as the donor. The polymer (PSBTS) showed band gap about 0.5 eV which is much lower than its BT analogue (**Table 1.1**). This small band gap can be attributed to its considerable quinoidal character leading to greater electron delocalization and the high electron affinity.[24] By looking at this trend, the stronger the donor/acceptor the lower the bandgap!

So, Timothy T. Steckler et al.[23] tried to combine the BT as an A unit and EDOT (E) as the D unit aiming to have even lower bandgaps. Unfortunately, that wasn't reached, the polymer PEBTE gave a bandgap of 0.5 eV which is the same as benzobis(thiadiazole)'s thiophene analogue (PSBTS), that was mainly due to the dihedral angle between the donor and the acceptor units, the larger the angle's degree the poorer the overlap between the two units which leads to less electron intramolecular movement that mainly effects the HOMO - LUMO levels. The dihedral angle between BT and S in PSBTS was 0^{o} while between the EDOT and BT in PEBTE is 53^{o}, which mainly resulted in decreasing the effect of the EDOT unit in lowering the bandgap.

1.9 The aim of this study

According to the literature review mentioned above and under the roof of D-A-D approach a new low bandgap conductive polymer will be synthesized and characterized. In this study, selenophene and BT were combined as donor and acceptor units, respectively, by using Stille Coupling reaction to get namely 4,7-di(selenophen-2-yl)-[1,2-c: 4,5-cI] bis([1,2,5]thiadiazole) (SeBTSe). The monomer was characterized via ^{1}H NMR, ^{13}C NMR and HRMS.

The corresponding polymer PSeBTSe was polymerized electrochemically and its electrochemical and optical properties were studied via electrochemical and spectroscopic techniques.

CHAPTER 2

MATERIALS AND METHODS

2.1 General Methods and Instrumantation

All chemicals were obtained from Sigma Aldrich and used as received. Tetrahydrofuran (THF) and dichloromethane were freshly distilled before being in any chemical or electrochemical experiments.

^{1}H and ^{13}C NMR spectra of the prepared materials were obtained by using Agilent NMR Spectrometer. The samples were prepared in $CDCl_3$ with tetramethylsilane as the internal standard which led to a chemical shifts. The monomer's molecular weight was obtained using Waters SYNAPT G1 MS instrument on positive mode. By using Specord S600 (standard illuminator D65, field of width 10^{o} observer) Colorimetric measurements were recorded and the color space was given by the International Commission of Illumination with luminance (L), hue (a), and intensity (b). Platinum cobalt DIN ISO 621, iodine DIN EN 1557, and Gardner DIN ISO 6430 are the references of colorimetric measurements. Fluorescence measurements were recorded on a Thermo Lumina Fluorescence Spectrometer.

2.2 Electroanalytical studies

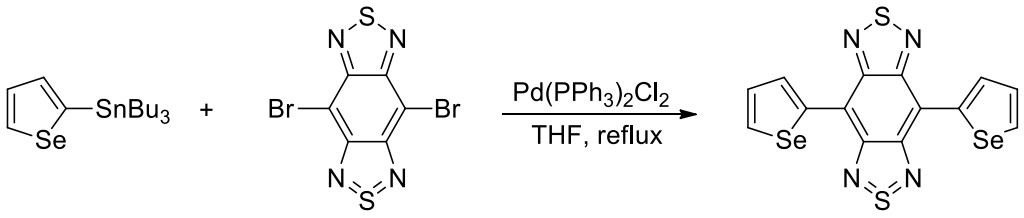
At room temperature all the electrochemistry studies were recorded by using a Gamry PCI4/300 and Gamry Reference 600 potentiostat–galvanostat. For Spectroelectrochemistry studies, Specord S600 Spectrometer and Shimadzu UV-3600 Plus UV-VIS-*NIR* Spectrophotometer were used. The optoelectrochemical spectra of the film were recorded in-situ under applied different potentials. The square wave potential method and cyclic voltammetry were used to determine the switching behavior and the

electrochemical stability of the polymer film at various redox states. Three-electrode system was used during the electrochemical studies, it consisted of a platinum disc (0.0314 cm^2) and a platinum wire as the working and counter electrodes, respectively, and Ag/AgCl electrode was used as the reference electrode calibrated externally with 2.56 mM solution of ferrocene/ferrocenium couple in CH_2Cl_2. The Fc^+/Fc has a reversible redox couple at a half wave of 0.475 mV (E_{ox}= 0.55 V and E_{red}= 0.40 V) with an onset oxidation value at 0.40 V vs Ag/AgCl.

During the electrochemical studies tetrabutylammonium hexafluorophosphate (TBAH) was dissolved in dichloromethane and used as the electrolyte solution. The obtained polymers were polymerized electrochemically by applying constant potential electrolysis on both platinum disc electrode and indium-tin oxide (ITO, Delta. Tech. 8–12 Ω, 0.7x5.0 cm^2). Switching time and percent transmittance studies were recorded in situ by using three-electrode system (ITO as a working electrode, a platinum wire and a silver wire as a counter electrode and as a reference electrode respectively) in a UV cuvette.

2.3 Chemical synthesis

2.3.1 Synthesis of 4,7-di(selenophen-2-yl)benzo[1,2-c;4,5-c']bis[1,2,5]thiadiazole (SeBTSe)



Scheme 2.1: Synthesis of SeBTSe.

In 50 mL of freshly distilled THF, 200 mg (0.568 mmol) of 4,7-dibromobenzo[1,2-c;4,5-c']bis[1,2,5]thiadiazole, 596 mg (1.42 mmol) of tributyl(selenophen-2-yl) stannane and 80 mg (0.1136 mmol) of $Pd(PPh_3)_2Cl_2$ were mixed and purged with Ar gas (**Scheme 2.1**). Then, under inert atmosphere the mixture was refluxed for 6 h. The solvent was evaporated under reduced pressure by using a rotary evaporator and the residue was extracted by using dichloromethane and water. Organic phase was dried over anhydrous magnesium sulfate $MgSO_4$ and the solvent was removed under reduced pressure. Residue was poured into methanol and the precipitate was filtered obtaining a solid crude product. The product SeBTSe was purified using column chromatography with hexane: dichloromethane (1:1, v:v) mixture as eluents.

SeBTSe: 25 % yield, blue solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ(ppm)): 9.34 (dd, *J*= 4.2 Hz, 0.9 Hz, 2H), 8.51 (dd, *J*= 5.7 Hz, 0.9 Hz, 2H), 7.58 (dd, *J*= 5.7 Hz, 4.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ(ppm)) 153.66, 149.92, 140.97, 139.18, 136.23, 131.01. HRMS (ESI, m/z): [M+K] calculated for $C_{14}H_6N_4S_2K\ Se_2$, 492.8016; found, 492.8001 (see **Figures 2.1**).

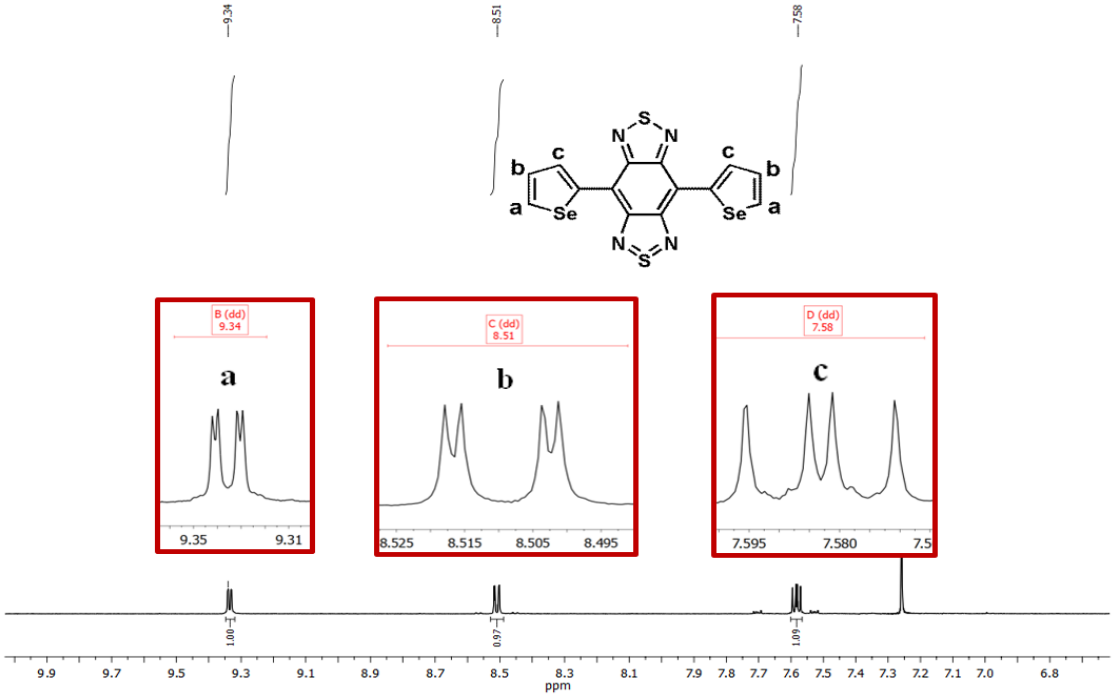


Figure 2.1: ^{1}H NMR spectrum of SeBTSe in d-$CHCl_3$.

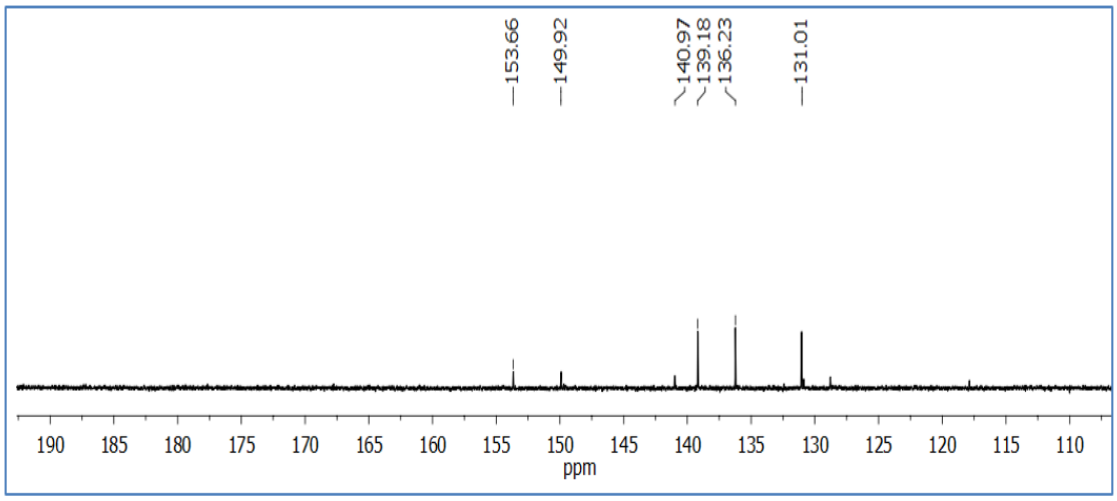


Figure 2.2 : ^{13}C NMR spectrum of SeBTSe in d-$CHCl_3$.

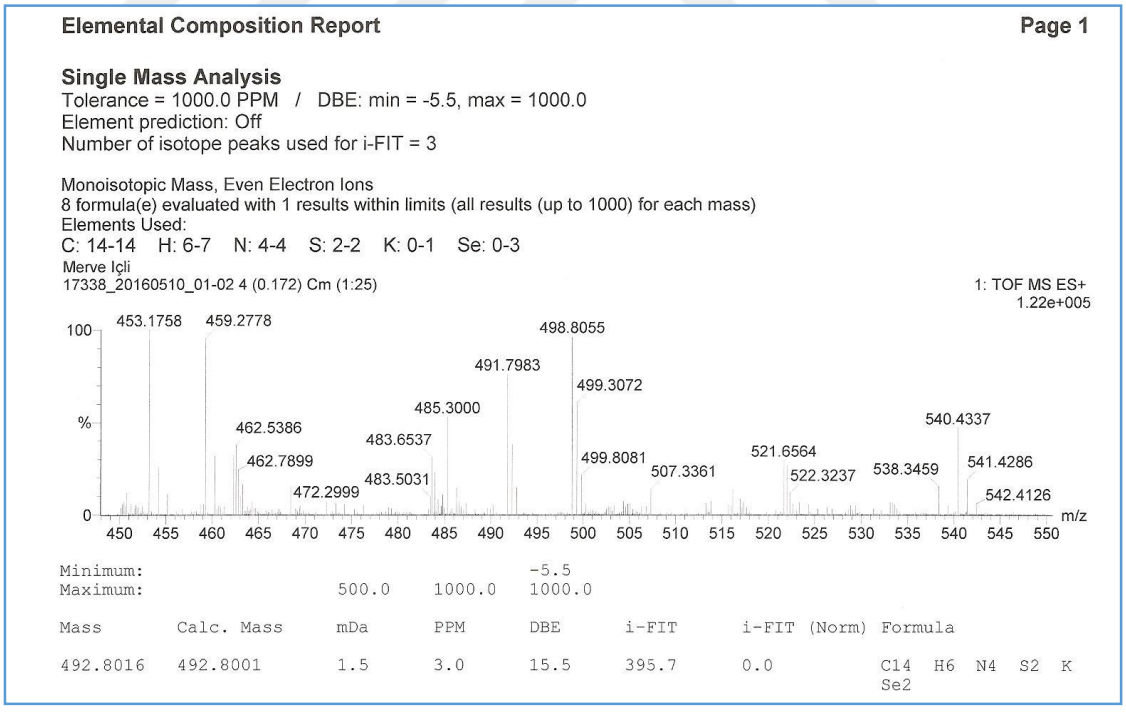


Figure 2.3 : HRMS spectrum of SeBTSe.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Optical Properties of SeBTSe

In order to understand the effect/role of benzobis(1,2,5-thiadiazole) acceptor unit and selenophene donor unit, we must keep in mind that the optical properties of the D-A-D type monomers are directly affected by the type of the chosen acceptor/ donor units. Such effects can be seen by the shift in the monomer's absorbance and emission spectra compared to its analogues. The monomer SeBTSe exhibited at least two absorption bands,[32] as expected from a D-A-D type monomer.[33]

As it can be seen in **Figure 3.1**, the monomer SeBTSe showed two absoption bands with higher energy at 254 nm and 357 nm related to the conjugation and π-π* energetic transitions, and one lower energy absorption band at 649 nm due to the intramolecular charge transfer from selenophene (electron donating unit) to benzobis(1,2,5-thiadiazole) (electron withdrawing unit).[34]

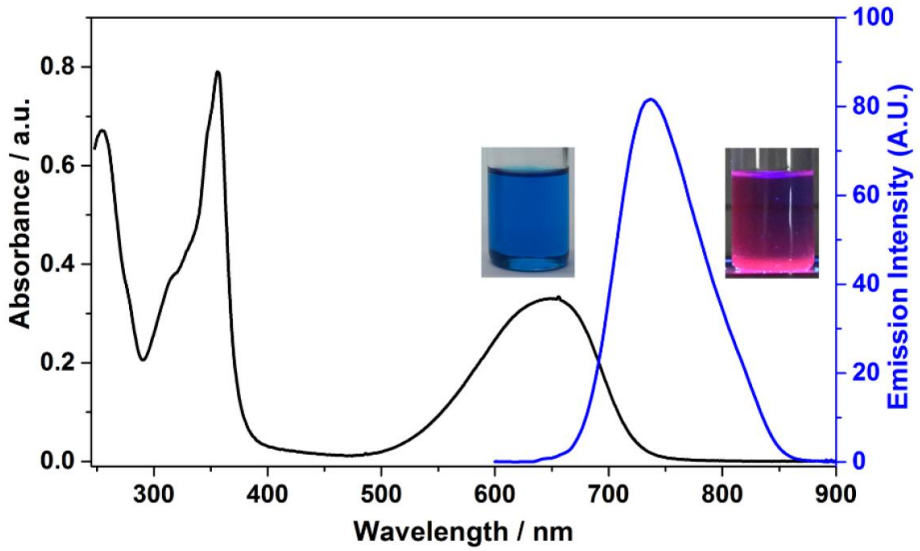


Figure 3.1: Absorbance and emission spectra of the monomer SeBTSe in $CHCl_3$. Inset: Colors of the monomer SeBTSe in $CHCl_3$ under ambient light (left) and handheld UV lamp (right) at 365 nm.

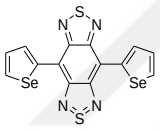
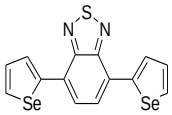
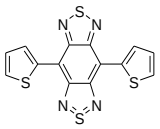
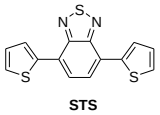
Comparing to thiadiazole (SeTSe) analogue,[24] The absorption peaks of the benzobis(thiadiazole) acceptor unit are red shifted, due to the high electron affinity and large quinoid contribution of the this acceptor unit and proves it to be a stronger acceptor unit than the benzothiadiazole.

Additionally, replacing the donor group in D-A-D type systems also showed its effectiveness on the monomer's absorption bands, it can be seen when the thiophene ring in thiophene based monomer STS was replaced with selenophene donor unit SeTSe. The later illustrated a red shift in the absorption bands comparing to its STS analogue as shown in **Table 3.1**. The red region shift is due to the stronger electron donating ability of the selenophene compared to the thiophene ring.[24]

By following similar pattern (changing the weak unit with a stronger one) similar results were expected regarding the acceptor unit. When SeBTSe monomer was compared to its thiophene analogue SBTS, it showed the opposite. A significant blue shift was

observed at 649 nm at the lower energy band of SeBTSe monomer while the thiophene analogue's (SBTS) band was at 702 nm. In literature, EDOT as a stronger donor unit than thiophene also expressed such behavior.[23] This behaviour was explained by the dihedral angle between donor and acceptor units. The dihedral angle of the SBTS monomer is found to be 0º while its EDOT analogue's is 53º. The presence of a dihedral angle results in a poor overlap in the p-orbital which leads to a limited donor - acceptor intramolecular charge transfer.

Table 3.1: Optical properties of some benzo[c][1,2,5]thiadiazole and benzobis(1,2,5-thiadiazole) based D-A-D type monomers.

Compounds	λ_{max} (nm) $CHCl_3$	E_{ox} (onset) (V vs AgCl)	E_{red} (onset) (V vs AgCl)	E_g^{op} (eV)	HOMO (eV)	LUMO (eV)	Ref
 SeBTSe	254, 357, 649	1.43 (1.28) 1.03 vs Fc^+/Fc	-0.39 (-0.31) -1.08 (-0.99)	1.71^{OPT} 1.59^{CV} 1.53^{DPV}	-5.68	-4.09^{CV}	This work
					-5.68	-3.97^{OPT}	
 SeTSe	317, 461	1.13 0.78 vs Fc^+/Fc	-	2.33^{OPT}	-5.51	-3.18	35
 SBTS	702	0.95*	-0.53*	-	-	-	24
	699, 350, 333	-	-	1.49^{OPT} 1.47^{CV}	-5.42	-3.95	36
 STS	309, 445	1.23 0.88 vs Fc^+/Fc	-	2.43^{OPT}	-5.57	-3.14	35
	445	1.23*	-1.22*	-	-	-	24

* vs SCE: Saturated Calomel Electrode. Fc^+/Fc demonstrates the onset oxidation potential of ferrocene.

Therefore, due to the same circumstances the SeBTSe monomer's low energy band is blue shifted compared to the SBTS analogue. Additionally, the poor interaction between the HOMO energy levels of the acceptor (benzobis(1,2,5-thiadiazole)) and donor units (selenophene) can lead to such shift. As it can be seen in **Figure 3.2**, the HOMO energy level of the SeBTSe monomer is lower than that of the SBTS, while the LUMO energy levels are nearly the same.

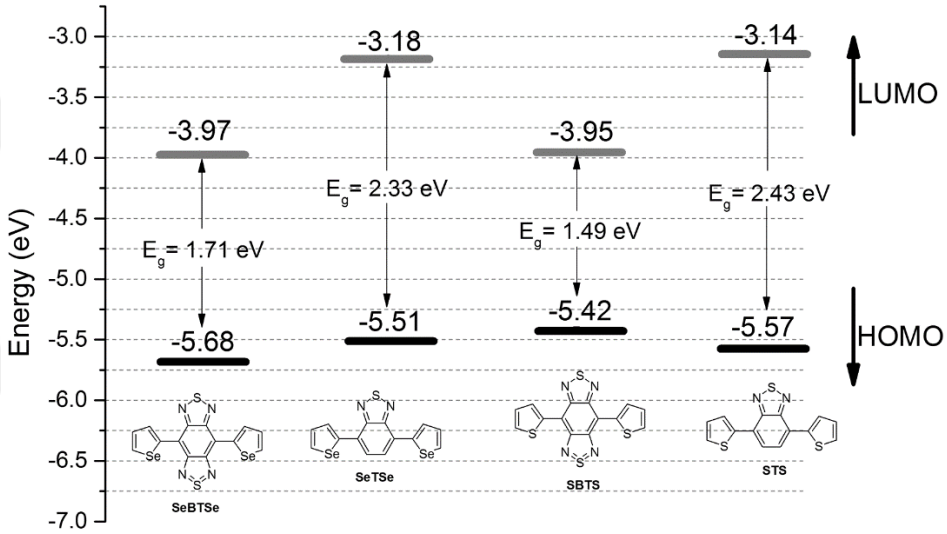


Figure 3.2: HOMO and LUMO energy levels (unit: eV) calculated from the electrochemical and optical experimental results of the monomers.

The HOMO/LUMO levels values of SeBTSe were calculated from the cyclic voltammetry using the following equations.[37]

$$E_{HOMO} = -(E_{[onset,ox\ vs\ Fc+/Fc]} + 4.80)\ (eV) \qquad \textbf{Equation 3.1}$$

$$E_{LUMO} = -(E_{[onset,red\ vs\ Fc+/Fc]} + 4.80)\ (eV) \qquad \textbf{Equation 3.2}$$

The monomer's bandgap value (E_g) was found by calculating the difference between the onsets of first oxidation and reduction peaks. (**Table 3.1**).

On the other hand, the SeBTSe monomer demonstrated a Strokes shift about 88 nm and exhibited a maximum wavelength at 737 nm in the emission spectrum. This shift can be attributed to the charge transfer degree commonly observed in D-A-D type monomers. However, the monomer can be used as a promising NIR fluorescent tag for bioimaging or an emitter candidate in NIR light-emitting diodes for having a deep-red emitter chromophore (**Figure 3.1**).[38]

In order to confirm the accuracy of the intramolecular charge transfer between the D and A units, the monomer's solvatochromic behaviour was investigated in various polar solvents. As shown in **Figure 3.3(a)**, the monomer SeBTSe represented a solvatochromic property. Due to interaction of the monomer and solvent bearing various polarities a shift from 633 to 655 nm was observed in the maximum wavelenght of the lower energy band which is responsible from charge transfer. Also, similar behavior can be observed in the emission spectrum of SeBTSe.

It is well known that the monomer's exited state can be stabilized by polar solvents if there is enough charge transfer between the D and A units[39] and therefore, upon increasing the polarity of the solvents a red shift is observed in the emission spectrum. As expected, the emission spectrum of the SeBTSe monomer shifted to a longer wavelenght (red shift) upon increasing the solvent's polarity from hexane (713 nm) to toluene (732 nm), and to CH_2Cl_2 (737 nm nm) and finally to DMF (745 nm) as shown in **Figure 3.3(b)**. Thus, form the red shift in the emission spectrum it can be concluded that the presence of intramolecular charge transfer led to the appearance of the low-energy band in the absorption spectrum. Also as the polarity of the solvents increases the maximum emission value decreased,[39] which indicates a limited intramolecular charge transfer from the D units to the A unit.

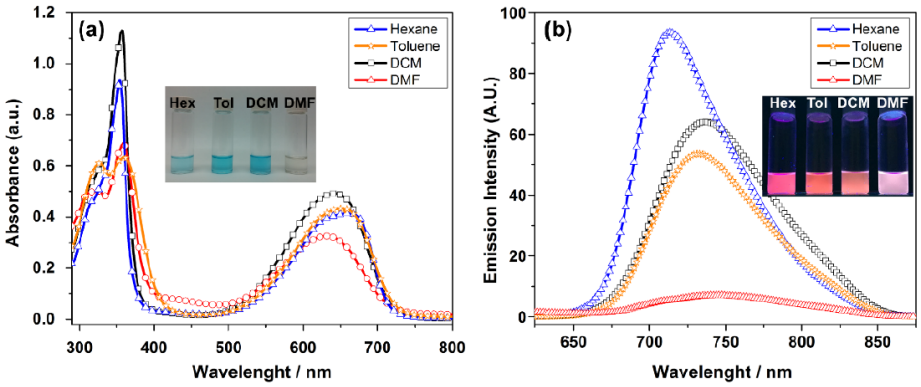


Figure 3.3 : (a) Absorption and (b) emission spectra of SeBTSe in hexane (Hex), toluene (Tol), dichloromethane (DCM) and N,N-dimethylformamide (DMF). The monomer was excited at 350 nm

3.2 Electrochemical Properties of the Monomer SeBTSe

The electrochemical studies were performed using cyclic voltammetry with an electrolyte solution of 0.1 M TBAH dissolved in dichloromethane. As shown in **Figure 3.4(a)**, the monomer SeBTSe showed one irreversible oxidation peak at 1.43 V (1.03 V vs Fc/Fc^{+}), which is unexpectedly higher when compared to its thiophene analogue (0.88 V vs Fc/Fc^{+} for STS and 0.95 V vs SCE for SBTS) and benzothiadiazole (0.78 V vs Fc/Fc^{+} for SeTSe) analogues (**Table 3.1**). It can be explained by a poor overlap of the HOMO and LUMO energy levels matching of the D and A units.

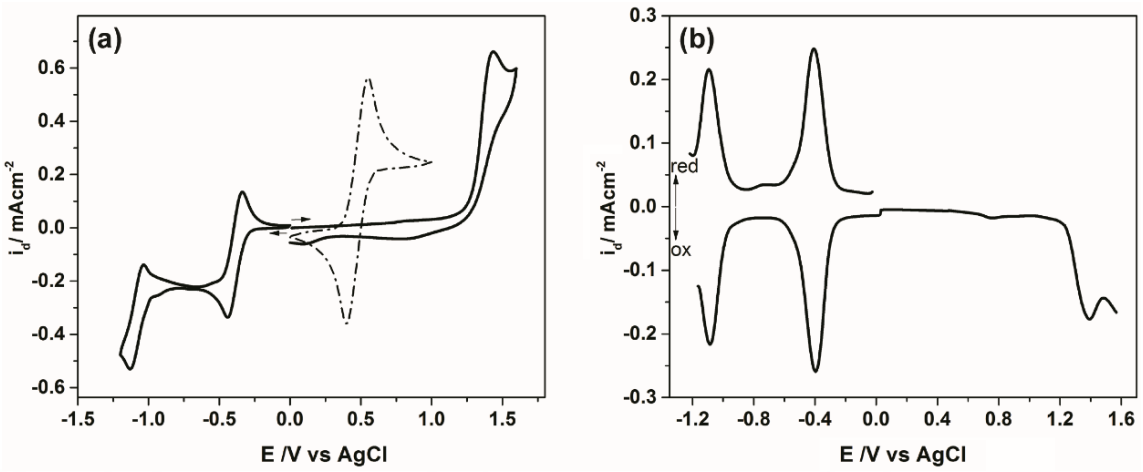


Figure 3.4: (a) Cyclic and (b) differential pulse voltammograms of the SeBTSe monomer ($2.50x10^{-3}$ M) (straight line) and ferrocene ($2.56x10^{-3}$ M) (dash line) in an electrolyte solution of 0.1 M TBAH dissolved in dichloromethane at a scan rate of 100 mV/s on Pt electrode. Step size= 3mV, pulse size= 50 mV and pulse time= 0.05 s.

Under N_2(g) inert atmosphere the reduction behavior of the monomer SeBTSe was studied. During a cathodic scan by moving from 0.0 V to -1.20 V at a scan rate of 100 V/s SeBTSe exhibited two nearly reversible reduction redox couples at half wave potentials ($E_{1/2}$) of -0.39 and -1.08 V vs Ag/AgCl as seen in **Figure 3.3**. These two reduction redox couples can be attributed to the two electron withdrawing groups present in the acceptor unit. These values are lower than its thiophene analogues bearing benzothiadiazole and benzobis(1,2,5-thiadiazole) units (**Table 3.1**). This behaviour can be explained by the strength of the electron withdrawing power of the acceptor unit in SeBTSe monomer.[23,24,27,40] In conclusion, within a potential window of -1.2 V to 1.6 V the monomer SeBTSe has four redox states.

From the onsets of oxidation and the first reduction peaks (1.28 V) and (-0.31 V) respectively, the band gap (E_g) of SeBTSe was calculated as 1.59 eV, which is compatible with the optical E_g (1.71 eV) from the onset of the low energy end of longer absorption band at 649 nm. Unexpectedly, the optical E_g is higher than its thiophene analogue (1.49

eV for SBTS) and lower than its benzothiadiazole (2.33 eV for SeTSe and 2.43 eV for STS) analogues (**Table 3.1**).

In order to support the electrochemically and optically obtained E_g values, differential pulse voltammetry was used to determine the E_g value of SeBTSe, and by following the same way from the onsets of oxidation (1.24 V) and the first reduction (-0.29 V) peaks, the E_g was calculated as 1.53 eV which is in good agreement with the E_g obtained from cyclic voltammetry (1.59 eV) and somewhat lower than optical band gap (1.71 eV). As shown in **Figure 3.4(b)**, the redox processes appear sharper with differential pulse voltammetry due to the high sensitivity of the method.

3.3 Electropolymerization

Electropolymerization of the monomer SeBTSe was successfully carried out within the range of 0.0 V and 1.55 V using potentiodynamic electrolysis (**Figure 3.5**). During repetitive cycles, the occured change to the cyclic voltammogram is concidered as the fingerprint of the conjugated polymer formation on the electrode surface (**Scheme 3.1**). As seen in **Figure 3.5**, a new redox couple apeared after the first cycle and its current intensity increased after each successive scan due to the increasment of the polymer thickness.

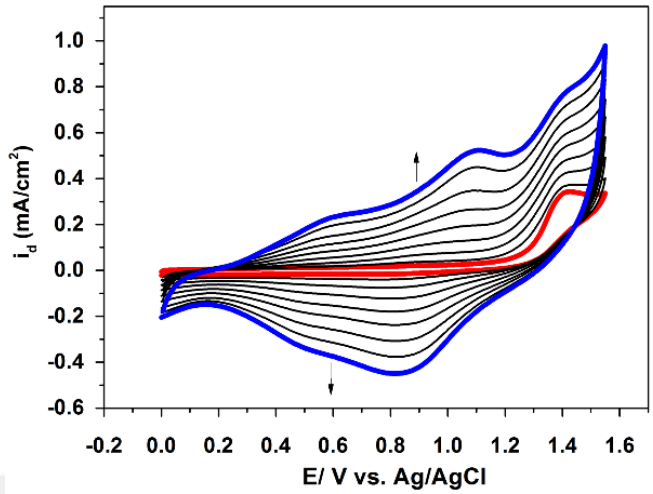
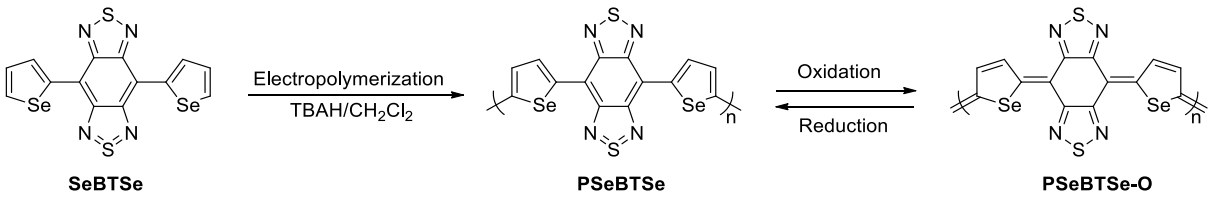


Figure 3.5 : Potentiodynamic polymerization of SeBTSe (1.0x10-3 M) to get the polymer PSeBTSe in an electrolyte solution of 0.1 M TBAH dissolved in dichloromethane between 0.0 V and 1.55 V at a scan rate of 100 mV/s on a Pt electrode. In cyclic voltammogram 1st cycle is red line and 40th cycle is blue line and the voltammogram was taken with 5 cycle increments



Scheme 3.1 : Chemical structures of the monomer SeBTSe and its corresponding polymer PSeBTSe at different redox states.

When the corresponging polymer PSeBTSe is studied in a monomer free electrolyte solution, its redox behaviour represented two reversible cathodic and one reversible anodic redox couples (see **Figure 3.6**). Half waves of reversible reduction redox couple of PSeBTSe film were calculated as -0.78 V and -1.28 V vs Ag/AgCl, which are

higher than the cathodic redox couples of its monomer SeBTSe. It can be explained by the acceptor unit's strenght decrease due to the increase in conjugation and electron density during polymerization. Unfortunately, a lose in the polymer film's electroactivity was noticed when the polymer film was reduced further up to second reduction state (**Figure 3.6**). However, the polymer film reversibly repeated its redox behaviour when switched after first reduction scan (see **Figure 3.7 (a)**).

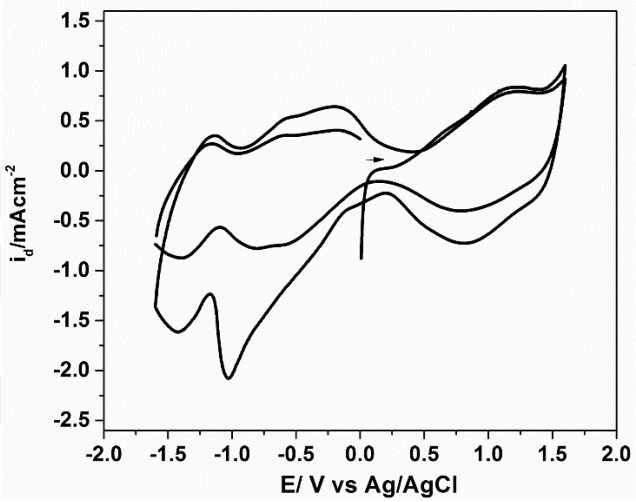


Figure 3.6 : Cyclic voltammograms of the PSeBTSe coated on Pt electrode in a monomer free electrolyte solution of 0.1 M TBAH dissolved in dichloromethane under N_2 atmosphere.

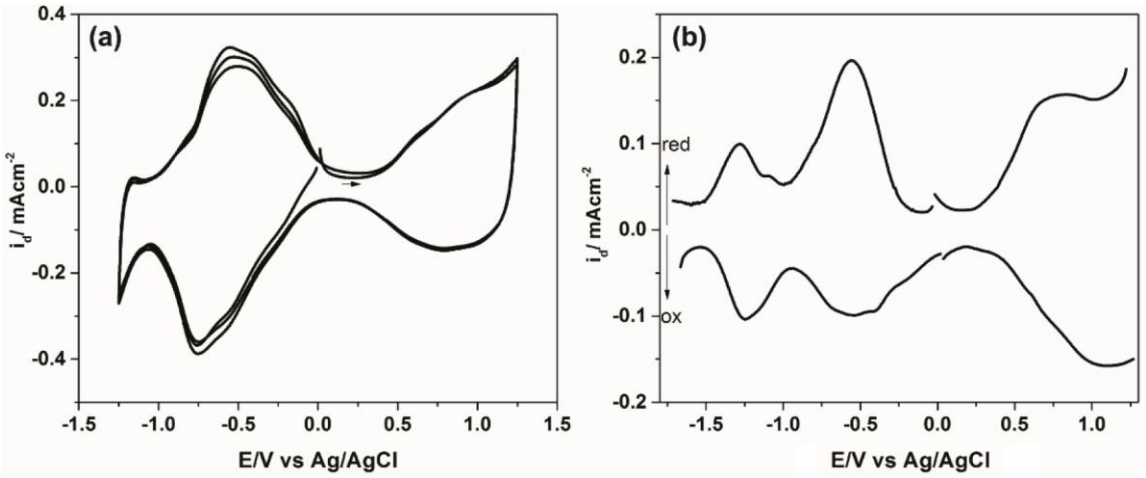


Figure 3.7 : (a) Cyclic and (b) differential pulse voltammograms of the PSeBTSe coated on Pt electrode in a monomer free electrolyte solution of 0.1 M TBAH dissolved in dichloromethane under N_2 atmosphere. Scan rate= 100 mV/s, step size= 3 mV, pulse size= 50 mV and pulse time= 0.05 s.

The polymer film represented one reversible redox couple at a half wave of 0.90 V during the anodic scan. The current intensity of the polymer redox couple changed as a function of scan rate and the reversibility of the redox behaviour was preserved even studied at higher scan rates like 200 mV/s (**Figure 3.8(a)**). Also, a linear increase in the redox couple's peak currents as a function of scan rate was observed, which indicates a non-diffusional redox process of a well-adhered polymer film on the electrode surface (**Figure 3.8(b)**).

With the polymer's two cathodic (n-doping) and one anodic (p-doping) redox couples we can conclude that the polymer has an ambipolar property, which can make it a promising candidate for ambipolar charge transfer materials.[41,42]

The polymer film has a narrow band gap of 0.62 eV calculated from the onsets of oxidation (0.42 V) and the first reduction (-0.20) peaks (see **Figure 3.7(a)**). Fortunately, the redox behaviour of the monomer between the cyclic voltammetry and differencial

pulse voltammetry was consistent. Therefore, similar behaviour could also be obtained in the polymer. As shown in **Figure 3.7(b)**, similar to cyclic voltammetry, the polymer obtained four redox states in differential pulse voltammetry: one neutral, one oxidation and two reduction states, and the E_g of the polymer was calculated as 0.66 eV, which is well agree with cyclic voltammetry result.

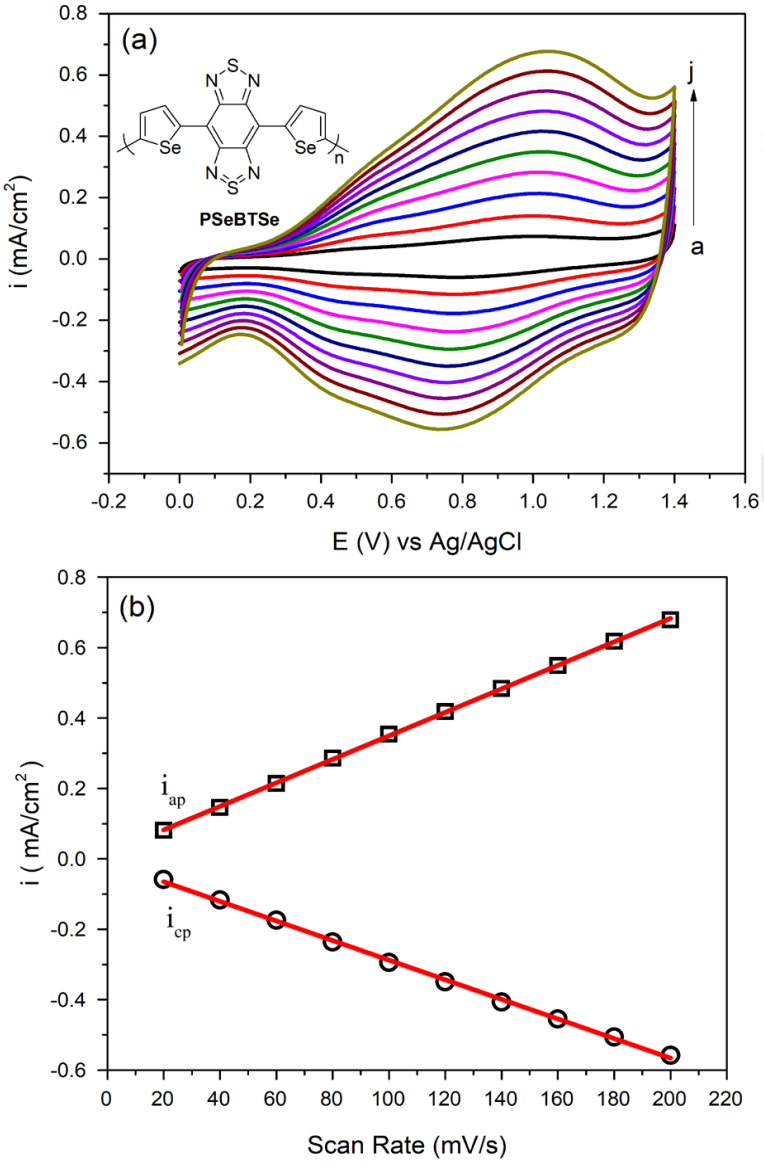


Figure 3.8 : (a) Cyclic voltammogram of the polymer PSeBTSe film on Pt electrode in 0.1 M TBAH/dichloromethane solution at scan rates: a: 20, b: 40, c: 60, d: 80, e: 100, f: 120, g: 140, h: 160, i:180 and j: 200 mV/s. (b) Relationships of anodic (i_{ap}) and cathodic cathodic peak currents (i_{cp}) as a function of the scan rate for PSeBTSe film.

In addition, in order to have a better understanding of the stability and reversibility of the polymer film, a number of repeated cycles were applied between its redox states under inert atmosphere. As seen in **Figure 3.9**, the test showed that the PSeBTSe film on Pt electrode did not show any appreciable change in the redox behaviour even after thousands of cycles, which confirmed its robust and stable nature.

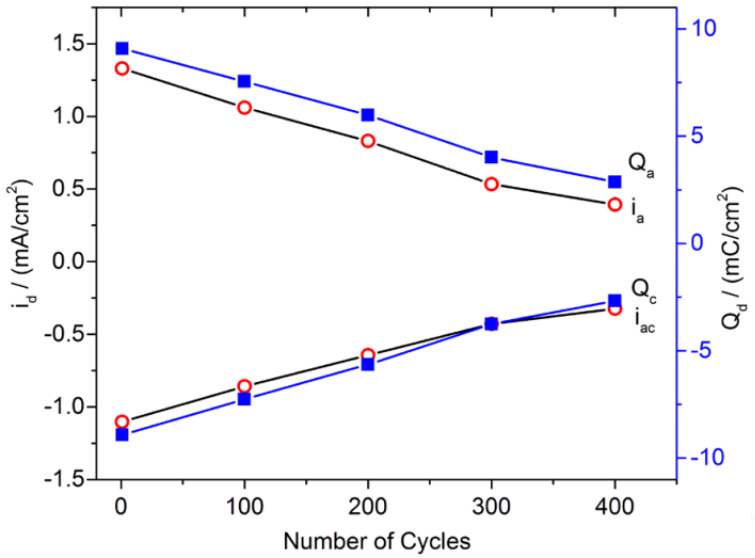


Figure 3.9 : Stability test for PSeBTSe film in 0.1 M TBAH/CH_2Cl_2 at a scan rate of 75 mV/s under Ar atmosphere by cyclic voltammetry between 0.0 V and 1.35 V; Q_a (anodic charge stored), Q_c (cathodic discharge), (b) i_a (anodic peak current), (c) i_c (cathodic peak current).

3.4 Optical Properties of the Polymer PSeBTSe

In order to be more accurate and support the electrochemically measured bandgap, the ITO coated polymer's optical spectrum was measured and as shown in **Figure 3.10(a)**. The neutral state polymer film has a broad absorption band centered at 975 nm, attributed to the π-π* transition, and the onset of its low energy end yields an optical band gap of 0.63 eV, which is agreeable with Tauc plot used to find optical band gap (0.62 eV) [43] (**Figure 3.10 b**). Also, by using cyclic voltammetry and differential pulse voltammetry the electrochemical band gap was calculated as 0.62-0.66 eV. Additionally, from cyclic voltammetry the polymer's HOMO and LUMO energy levels were calculated as -4.90 eV and -3.76 eV, respectively.

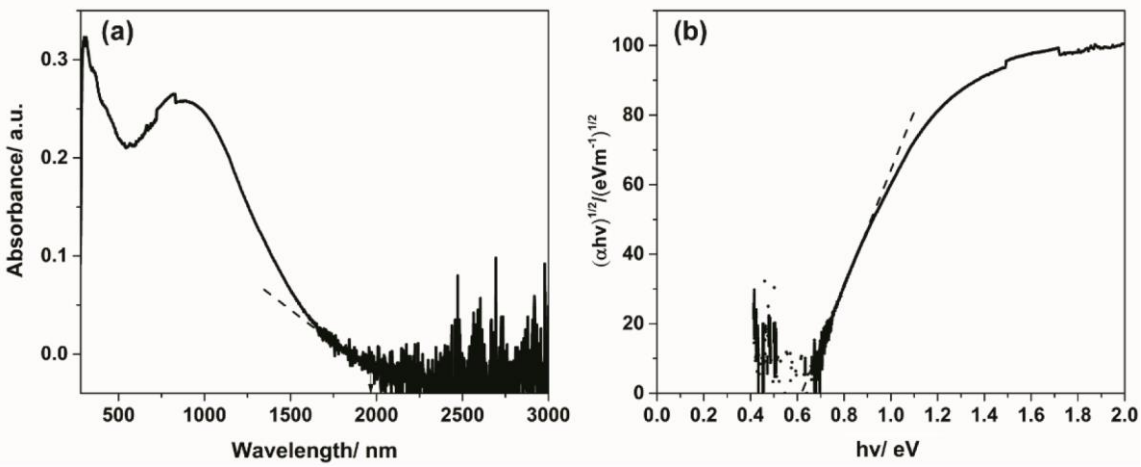
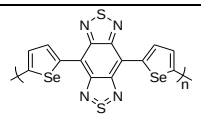
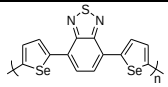
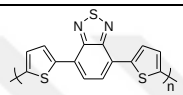
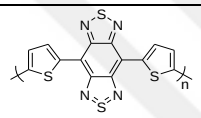
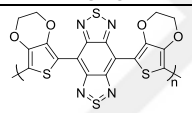
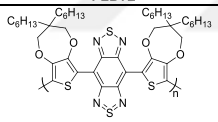
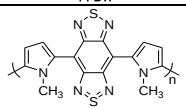


Figure 3.10 : (a) Absorption spectrum and (b) Tauc plot of the neutral state PSeBTSe polymer film on ITO electrode.

The neutral state polymer PSeBTSe has nearly the similar band gap of 0.63 eV with a maximum wavelength of 975 nm when compared to its pyrrole (0.6 eV for PNBTN) and thiophene (0.5-0.88 eV for PSBTS, PEBTE and PPBTP) analogues, which is expected from a D-A-D system containing stronger acceptor units (see **Table 3.2**).

Table 3.2: Optical properties of some benzo[c][1,2,5]thiadiazole and benzo-bis(1,2,5-thiadiazole) based D-A-D type polymers.

Polymers	$E_{ox,1/2}$ (V vs Ag/AgCl)	$E_{red,1/2}$ (V vs Ag/AgCl	λ_{max} (nm)	E_g[a] (eV)	Color at Neut. state	Color at Ox. state	Ref
 PSeBTSe	0.99	-0.77 -1.26	360, 975	0.62^{CV} 0.66^{DPV}	Gray beige	Smoky azurite	This work
 PSeTSe	-	-	-	-	-	-	-
 PSTS				1.1^{OPT}			24
 PSBTS				$< 0.5^{OPT}$			24
		-0.68 *		0.5^{OPT}			40
 PEBTE	0.38 *	-0.55 * -1.33 *	~ 450 974	~ 0.5^{DPV} ~ 0.53-88^{OPT}	Olive Green	Dark Blue	23
 PPBTP	0.42 0.73	-0.42 -0.63	358 900	0.63^{CV} 0.59^{OPT}	Gray	Blue	27
 PNBTN		-0.73*		0.6^{OPT}			40

* vs SCE. E_{pc}, cathodic peak potential, CV: cyclic voltammetry, DPV: differential pulse voltammetry, OPT: optical.

Also, under external potential the PSeBTSe film has an electrochromic behaviour: gray beige (L= 70.5, a= -1.24, b= 11.6) when neutralized, smoky azurite (L= 69.7, a= -6.76, b= 2.97) when oxidized, beige (L= 70.3, a= 0.33, b= 11.9) dark beige (L= 63.6, a= 6.00, b= 10.6) at first and second reduced states (see **Figure 3.11**).

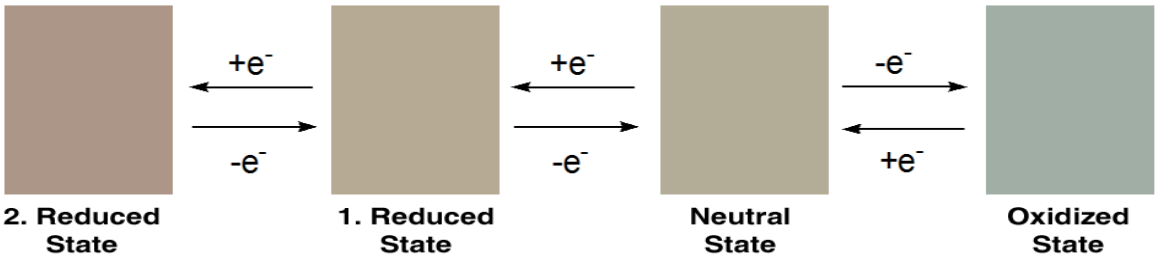


Figure 3.11 : Colors of PSeBTSe film on ITO at different redox states.

Under applied external potentials the PSeBTSe film's color changes (the electrooptical properties) can be followed by monitoring the changes in electronic absorption spectra. For example, as shown in **Figure 3.12(a)**, during cathodic scan the absorption band at 975 nm attributed to the π-π* transition band started to decrease and new absorption bands started to intensify between 360 and 700 nm. Upon further oxidation, the π-π* transition band at 975 nm diminished completely. On the other hand, the absorption band at 360 nm went under a decrease in its intensity upon moving from 0.0 V to 1.4 V, whereas the band at 975 nm intensified as a function of applied external potential in **Figure 3.12(b)**. Additionally, during the p-doping process a new absorption band centered at 650 nm started to appear attributed to the formation of the charge carriers and then intensified upon further doping.

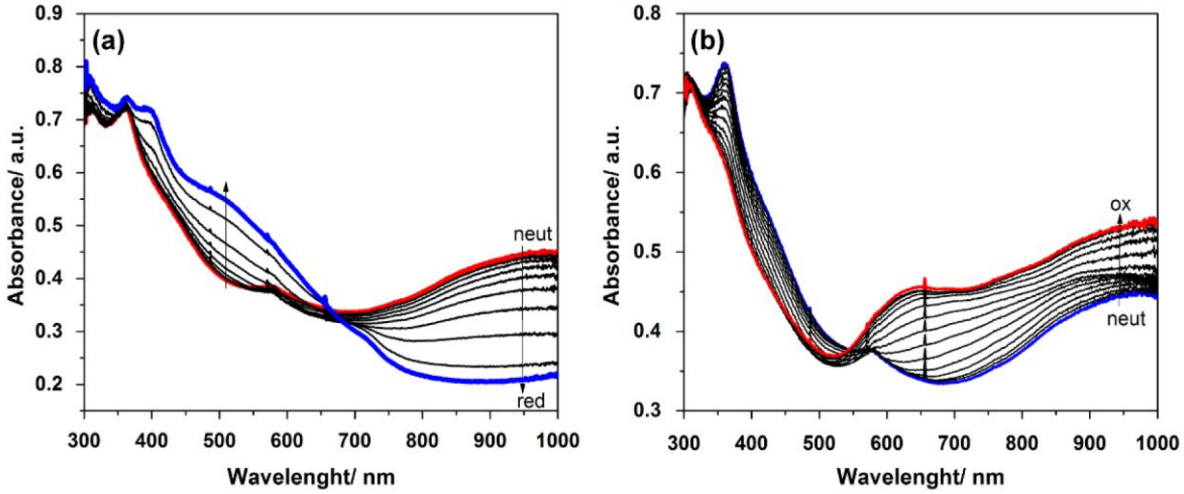


Figure 3.12: Electronic absorption spectra of the neutral state PSeBTSe film on ITO in 0.1 M TBAH/CH_2Cl_2 at various applied potentials upon moving (a) from 0.0 V to -1.6 V under N_2 atmosphere and (b) from 0.0 V to 1.4 V.

CHAPTER 4

CONCLUSION

In summary, a new derivative of benzobis(1,2,5-thiadiazole) based D-A-D type monomer was synthesized and polymerized electrochemically. According to the literature, both the monomers based on selenophene and their corresponding polymers exhibited better electrochemical and optical properties so better optical properties like smaller E_g value were expected since. Unfortunately, that expectation was not reached, the SeBTSe monomer and its polymer represented various behaviors than expected. This can be due to either the poor overlapping of HOMO and LUMO energy levels of the donor and acceptor units or to the presence of dihedral angle greater than 0^o. Work in this line is in progress.

On the other hand, the monomer can be a promising candidate as a deep-red emitter chromophore for bioimaging or an emitter candidate in NIR light-emitting. Also, the polymer with its four redox states can be amenable to use in various devices. For example, the ambipolar (n- and p-dopings) polymer can be used in ambipolar charge transfer materials or its electrochromic behaviour can make it a promising material in optical and electrocromic devices.

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