REALIZATION OF NEUTRAL STATE GREEN POLYMERIC MATERIALS

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
CHEMISTRY

JULY 2009

REALIZATION OF NEUTRAL STATE GREEN POLYMERIC MATERIALS

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ABSTRACT

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July 2009, 75 pages

Polymeric electrochromic materials that has as one of the three complementary colors (red, green, and blue) in the neutral form and become transparent via oxidation (or reduction), has a crucial importance towards use of these materials in electrochromic devices and displays. To reflect red or blue color in neutral state, the materials have to absorb at only one dominant wavelength. On the contrary, to have a green color, there should exist at least two simultaneous absorption bands in the red and blue regions of the visible spectrum where these bands should be controlled with the same applied potential. The transmissivity in the oxidized state is significantly important in addition to the neutral state color of the polymer. The optical contrast between the states is the decisive point for use of these materials for many electrochromic applications, especially as smart windows and displays. Hence, the material should possess two absorption bands with definite maximum points, and upon oxidation these bands should simultaneously vanish to have a transmissive state. A donor–acceptor approach can be utilized to solve this puzzle. It has been shown that insertion of alternating donor–acceptor units on the polymer backbone leads to a significant decrease in band gap due to the increased double bond character in the structure. In this study novel donor-acceptor type polymers were synthesized, and electrochromic properties were investigated in detail. PBDT is the first green electrochromic material which has a highly transmissive sky blue oxidized state. PDETQ was shown to be one of the few examples of neutral state green polymeric materials in literature. PDEQ has a bluish green color in the neutral state and a highly transmissive light blue oxidized state.

Keywords: Electrochromism, Donor-Acceptor Polymers, Green Polymers, High Optical Contrast

ÖZ

İNDİRGENMİŞ HALİNDE YEŞİL POLİMERİK MALZEMELERİN GERÇEKLEŞTİRİLMESİ

Asuman Durmuş

Yüksek Lisans, Kimya Bölümü
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Temmuz 2009, 75 sayfa

Yüksüz halinde üç tamamlayıcı renkten (kırmızı, yesil ve mavi) birini gösteren yükseltgendiğinde (veya indirgendiğinde) yüksek geçirgenliğe sahip elektrokromik polimerler , elektrokromik ve görüntü cihazları uygulamaları alanında cok önemli bir yere sahiptir. Mavi ve kırmızı rengi yansıtması için malzemenin bir tane soğurma bandı olmalıdır. Fakat yeşil renk elde etmek için en az iki soğurma bandına ihtiyaç vardır ve bu bantlar aynı uygulama gerilimi ile kontrol edilmelidir. Akıllı camlarda ve görüntü cihazlarında kullanılabilmesi için iki hal arasındaki optik kontrastın iyi olması gerekmektedir. Bu nedenle malzemenin iki soğurma bandına sahip olması ve yükseltgendikçe renksiz hal alması gerekmektedir. Donör-akseptör moleküller bu problemi çözmek için anahtar malzemelerdir. Aynı zamanda donör-akseptör moleküller, bu birimler arasında yüksek çift bağ karakterinin yarattığı rezonanstan dolayı bant aralığını düşürürler. Bu tip malzemelerin üretiminin karmaşık doğasında donör akseptör yaklaşım kilit nokta olduğu için, özgün donör akseptör tipi malzemeler sentezlenmiş ve elektrokromik özellikleri detaylıca incelenmiştir. PBDT, yüksek geçirgenliğe sahip ilk yeşil elektrokromik malzemedir. PDETQ, literatürdeki sınırlı sayıda olan indirgenmiş halinde yeşil elektrkromik malzemelerden birtanesidir. PDEQ ise indirgenmiş halinde yeşil yükseltgenmiş halinde yüksek geçirgenliğe sahiptir.

Anahtar Sözcükler: Elektrokromizm, Donör-Akseptör Polimerler, Yeşil Polimerler, Yüksek Optik Kontrast

To my Family

ACKNOWLEDGMENTS

I would like to present my feelings of gratitude to my supervisor Prof. Dr. Levent Toppare for his invaluable guidance, support, suggestions and stimulating advice for the completion of my thesis.

It is a great pleasure to thank Gorkem Gunbas for giving me huge love and support without expecting anything in return. I wish I would have said YES to his proposal at the first time. Thanks are extended for the organic synthesis work which makes this thesis got completed.

I would like to thank Dr. Pınar Çamurlu, Metin Ak, Dr. Senem Kıralp and Ozlem Turkarslan for their endless helps, stimulating conversations besides their kind friendships.

Many thanks to Abidin Balan for always being there for me, for his true friendship and for his extraordinary help towards the completion of this thesis.

Thanks should also be extended to my second family; Funda Ozyurt, Erman Ucal, Asli Taskin, Reha Torun, Yasemin Udum, Aysegul Yildirim, Serhat Varis, Simge Tarkuc, Ersin Yildiz, Basak Yigitsoy, Bugra Epik for their kind friendship, useful conversations and cooperation about everything.

I would like to present my appreciation to Tugba Ozdemir for having good humor everytime. It would not be possible to overcome difficulties throughout my university life without her close friendship and love.

I would like to express my special thanks to my friends Tamer Tezel, Berk Mujde and Bahadir Dogan for their support and kind friendship throughout my university life.

I would like to extend my deepest gratitude to Kazim Durmuş for everything that he has done for me.

Finally, I would like to express my special thanks to my family for believing in me and giving me endless support.

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ABBREVIATIONS

BDT 4,7-Di(2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)benzo[1,2,5]thiadiazole

DETQ 5,8-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-di(thiophen2-yl) quinoxaline

DEQ 5,8-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)

PBDT Poly4,7-di(2,3-dihydro-thieno[3,4-b][1,4]dioxin-5- yl)benzo[1,2,5] thiadiazole

PDETQ Poly5,8-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl)quinoxaline

PDEQ Poly5,8-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)

EDOT 3,4-Ethylenedioxythiophene

Th Thiophene

MeTh 3-Methylthiophene

Py Pyrrole

PEDOT Poly(3,4-ethylenedioxythiophene)

PXDOT Poly(3,4-alkylenedioxythiophene)s

PXDOP Poly(3,4-alkylenedioxypyrrole)s

TBAFB Tetrabutylammonium tetrafluoroborate

$TBAPF_6$ Tetrabutylammonium hexafluorophosphate

ACN Acetonitrile

PC Propylene carbonate

NMR Nuclear Magnetic Resonance

FTIR Fourier Transform Infrared Spectrometer

CV Cyclic Voltammetry

SEM Scanning Electron Microscopy

ECD	Electrochromic Device
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
CB	Conduction Band
VB	Valence Band
E_g	Band Gap Energy
CIE	La Commission Internationale de l'Eclairage
L a b	Luminance, hue, saturation
ITO	Indium Tin Oxide
CP	Conducting Polymer
LED	Light Emitting Diode
OFET	Organic Field Effect Transistor
PTh	Polythiophene
PPy	Polypyrrole
SCE	Standard Calomel Electrode

CHAPTER 1

INTRODUCTION

1.1 Conducting Polymers

Conducting polymers (CPs) are organic materials possessing electrical, electronic, magnetic and optical properties of a metal while retaining the mechanical properties and processability to a certain extent. The unique intrinsic property of these organic materials, which are generally comprised simply of C, H and simple heteroatom such as N and S, and the myriad of properties emanating from it, arise uniquely from π-conjugation, which is the basic prerequisite for conduction in polymers.

Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa won the Nobel Prize in Chemistry in year 2000 "for the discovery and development of electrically conductive polymers." Before this breakthrough discovery, polyacetylene (PAc) was known as a black powder in 1974. Later, it was prepared as a film by Shirakawa and co-workers; although it was not a conductor. In 1977, these three scientists discovered that PAc films can be made conductive when treated with iodine, chlorine or bromine vapor, and “doped” form of PAc was found to possess a conductivity of 103 S/cm [1].

Normally the electrons in the bonds remain localized and cannot carry electric current, but when the polymer was doped with strong electron acceptors such as iodine, it began to conduct nearly as a metal, with conductivity 10^{11} times

higher than pure polyacetylene (PA) [1,2]. Further research in the field has led to other conjugated polymers like polythiophenes, polypyrroles and many others (Figure 1.1.) [3-9].

Although the initial interest in conducting polymers was entirely due to their ability to conduct electricity, the current technology around these materials is more than that. Some of these materials have practical and potential applications including light emitting diodes [7], microwave absorbing materials [10], smart windows [11], solar cells [12], and field effect transistors [13].

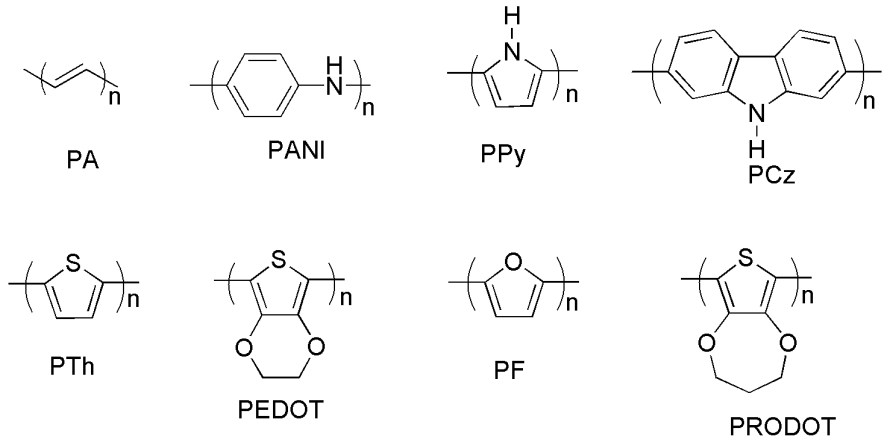


Figure1. 1 Structures of some common conducting polymers

1.2 Band Theory

It is believed that electronically conducting polymers have a spatially delocalized band-like electronic structure and they are extensively conjugated

molecules. The electronic structure and conduction mechanism is explained using band theory. According to this theory, materials are defined as insulators, semiconductors, or metals depending on the relative separation of occupied and unoccupied energy states. (Figure 1.2)

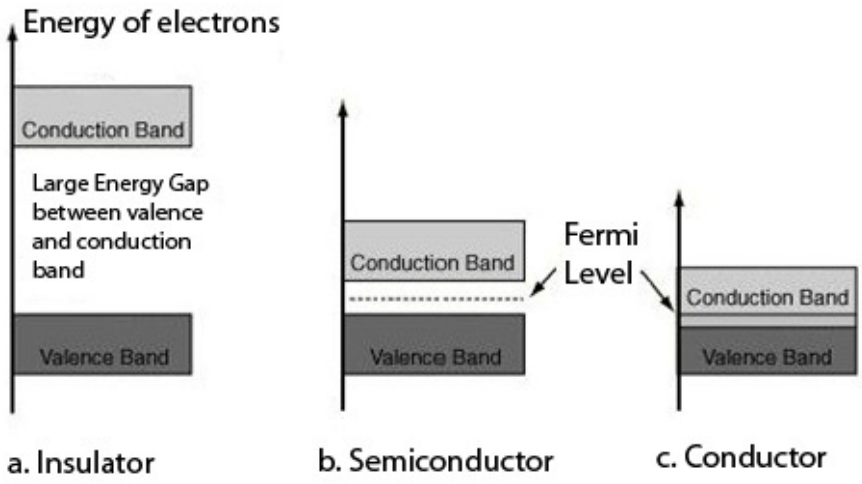


Figure1. 2 Band structures of insulator, semiconductor, and conductor

The electrical properties of conventional materials depend on the electronic band structure and on the distribution of available electrons in the bands. In the solid state, the atomic orbitals of each atom overlap with the same orbitals of the neighboring atoms in all directions to produce molecular orbitals similar to those in small molecules. In a polymer, the interaction of a polymer unit cell with all its neighbors leads to the formation of electronic bands. The highest occupied electronic levels constitute the valence band (VB), and the lowest unoccupied levels, the conduction band (CB). (Figure 1.3) The energy spacing between the highest occupied and lowest unoccupied band is called the

band gap. The width of the band gap determines the intrinsic electrical properties of the material (whether a material is an insulator, semiconductor or a conductor).

In metals, there is no energy gap between the valence and conduction bands; therefore electrons can easily flow through the material. On the other hand, insulators have large energy gap between two bands, which is the result of their low conductivities. In the case of semiconductors, there is a filled valence band and an empty conduction band separated by a band gap (Eg) where no energy levels are present. The conduction band can be populated by electrons across the band gap either thermally or photochemically. Semiconductors can be doped to increase the conductivity of the material. Charge carriers can be holes (p-type) or electrons (n-type) [14]. In semiconductors the conduction band is separated from the valence band by an energy gap ranging from 1-4 eV. This range of energies correlates to the visible spectrum and is associated with electronic transitions [15], hence these materials often display intense color.

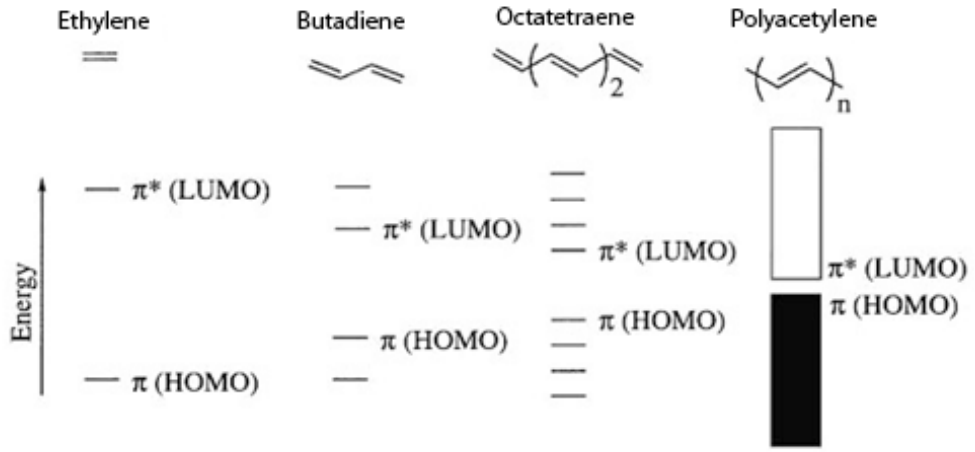


Figure1. 3 Generation of bands in conjugated polymer systems

The band gap of a conducting polymer can be calculated using the absorption band edge in the UV-vis spectrum of the polymer. The absorption band edge is the minimum energy needed to excite an electron to the conduction band from the valence band, which represents the real energy gap between these two bands. However, sometimes the absorption maximum is used and referred as the band gap. Another method to calculate the band gap is to measure the oxidation and reduction potentials of the polymer. The energy difference between oxidation and reduction potentials gives the band gap [16].

1.3 Conduction in Conducting Polymer

In conjugated polymers, conductivity is achievable upon doping. This term can explain the behavior of semiconductors but the physics of conjugated polymers differs remarkably from that of inorganic semiconductors such as Si or GaAs. They are generally in rigid structure, and this rigidity of their lattice ensures that charge carriers added to the system are accommodated in the conduction and valence bands with negligible rearrangement of the bonding. Furthermore the amount of dopant added is in the order of thousandth of a percent for inorganic semiconductors and doping process does not change the structure of material. Therefore, charge transport can be allowed by formation of a partially filled valence band.

On the other hand, conjugated polymers are generally more susceptible to structural distortions since they have two-fold coordination. As a result, the dominant electronic excitations are inherently coupled to chain distortions. During the doping process the specific types of charged defects formed on the polymer backbone which depends on the structure of the polymer chain: Those

with degenerate ground state structures such as polyacetylene and those with nondegenerate ground states structures such as polypyrrole. The amount of dopant inserted to conducting polymers is generally around 10-33 % [17] and the doped structures are different from that of the undoped species. The doped structures of conducting polymers can produce *solitons, polarons* and *bipolarons* on the chains with higher energies than the neutral polymer.

1.3.1 Solitons, Polarons, Bipolarons

The concept of solitons, polarons and bipolarons brings better understanding in the conduction mechanism of CPs since the Band Theory is not sufficient to explain the conduction behavior of CPs [18].

Conjugational defects (solitons, polarons and bipolarons) are formed when polymers are doped in the polymer chain. Oxidation of the polymer breaks one double bond leaving a radical and a positive charge on the polymer chain, which is referred as polaron. Soliton is another charge defect which is classified into three categories: Neutral soliton, positive soliton and negative soliton. In neutral soliton, energy level is singly occupied and therefore, the spin has the value of ½. Neutral solitons have spin but no charge. The positively soliton is obtained by the insertion of acceptor band (p-type doping) or electrochemical oxidation, where an electron is removed. By the insertion of donor band, an electron is added, which results in the generation of negatively charged soliton (Figure 1.4).

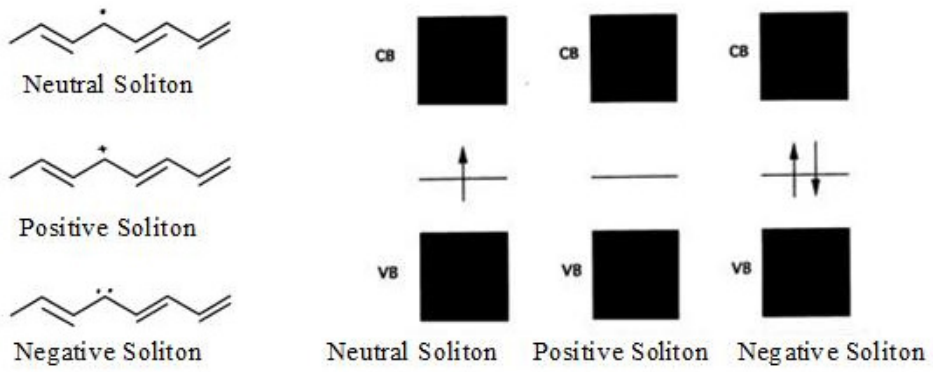


Figure1. 4 Soliton structures of polyacetylene

In the case of polypyrrole (Figure 1.5), chemical oxidation removes an electron from the π-system of its backbone creating an unpaired electron with spin ½ (a free radical) and a spinless positive charge (cation). The radical and the cation are coupled to each other via a local bond rearrangement, creating a polaron which appears in the band structure as a single unpaired electron possessing charge and spin. The formation of two new electronic states, which appear within the valence and conduction band of the polymer, takes place as a result of this deformation.

Further oxidation of the polymer creates dications in the polymer. An electron can be removed either from the polaron or from the remaining neutral portion of the chain. Formation of bipolaron is thermodynamically favorable since the formation of a bipolaron produces a larger decrease in ionization energy compared to the formation of two polarons [19]. These new empty bipolaron states are also located symmetrically within the band gap. Further doping creates additional localized bipolaron states, which eventually overlap to form continuous bipolaron bands at high enough doping levels.

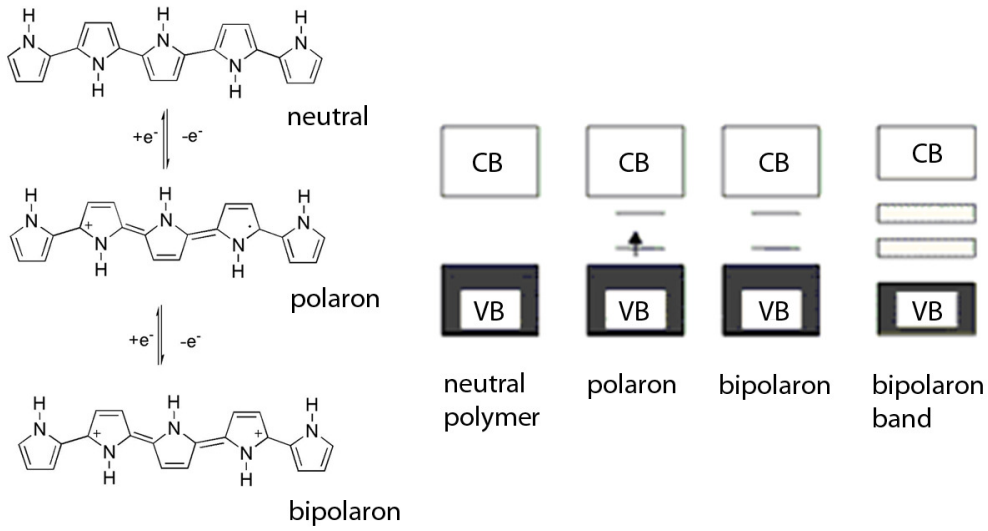


Figure1. 5 Charge carries in PPy and its corresponding energy bands in the mid gap

1.3.2 Doping Types in Conducting Polymers

Doping is defined as the process which enhances the conductivity of a polymer by incorporating a certain "impurity". Doping of conducting polymers has been accomplished by redox processes. This involves the partial addition (reduction) or removal (oxidation) of electrons to or from the π system of the polymer backbone [18, 20]. Moreover, doping and dedoping are generally reversible which do not change the chemical nature of the original backbone (Figure 1.6).

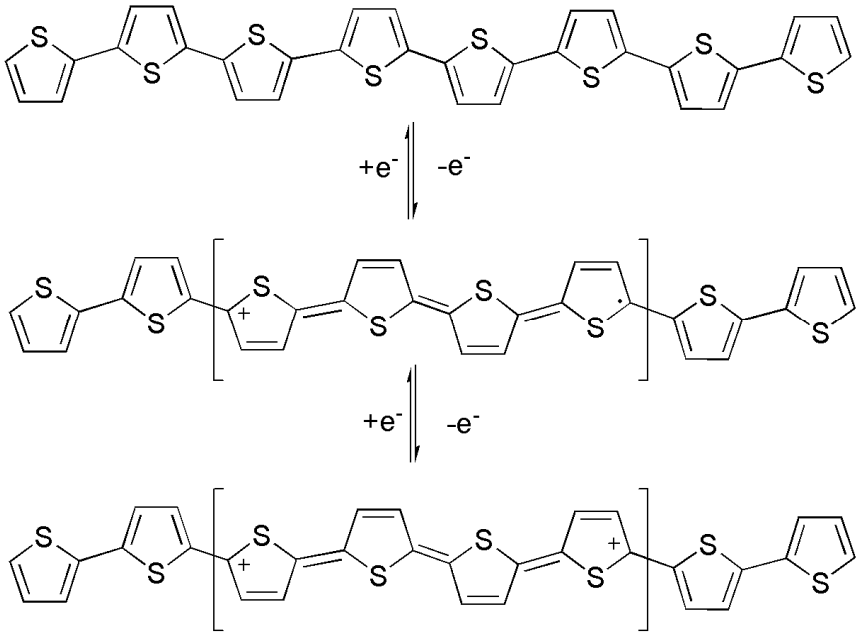


Figure1. 6 Reversible doping-dedoping process of polythiophene

Conducting polymers can be doped by chemical, photochemical, interfacial or electrochemical means. In the chemical pathway, reaction of the polymer with suitable oxidizing or reducing agents causes doping [14]. Chemical doping can be performed either by reaction with gaseous species, such as AsF_3, PF_3, I_2, or in solution by reaction with aqueous $FeCl_3$. Generally, sodium naphthalide (Na^+Npt^-) is used to perform n-type doping of a polymer in tetrahydrofuran solution.

A conductivity anywhere between that of the un-doped (insulation or semiconducting) and that of the fully doped (highly conducting) form of the polymer can be easily obtained by adjusting the doping level (Figure 1.7) [21].

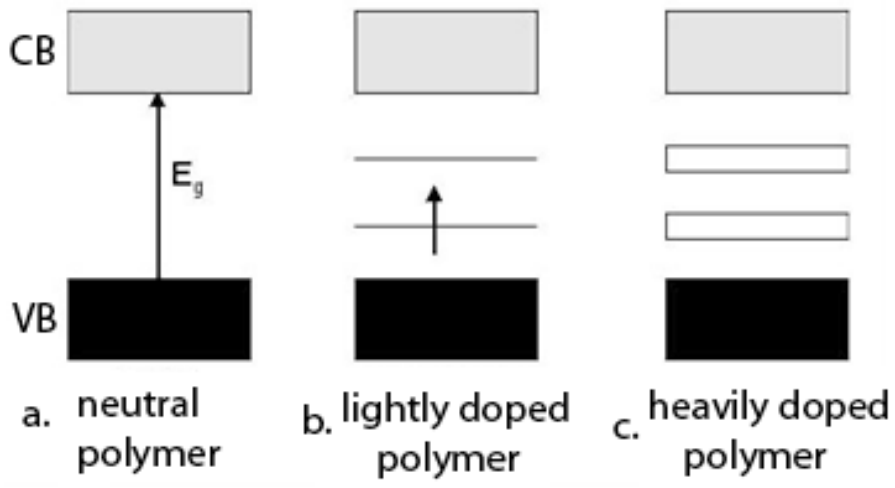


Figure1. 7 Band model of (a) non-doped, (b) slightly doped, and (c) heavily doped conducting polymers

Electrochemical doping is most useful and easy way to control doping process. It is performed by biasing the polymer film in a suitable solution to an appropriate potential [22]. In electrochemical doping, the electrode gives electrons to the conjugated polymer in reduction process. For oxidation process, the electrode accepts electrons from the conjugated polymer. At the same time counterions in the electrolyte diffuse into (or out) the polymer chains for charge compensation. Figure 1.8 represents a schematic illustration of the band diagrams for the p-doping (a) and n-doping (b) of a conducting polymer [23].

The relative positions of the Fermi level of the substrate ($E_{F,m}$) with respect to either the valence band ($E_{VB,p}$) or the conduction band ($E_{CB,p}$) of the polymer determine whether electrons are extracted (p-doping) or inserted (n-doping). If the Fermi level of the substrate is below the valence band of the polymer, a flow of electrons form the polymer to the substrate will occur (Figure 1.8 (a)). This is termed as p-doping. Likewise, if the Fermi level of the substrate is above the conduction band of the conducting polymer, then electrons flow into the film (Figure 1.8 (b)). This is termed as n-doping.

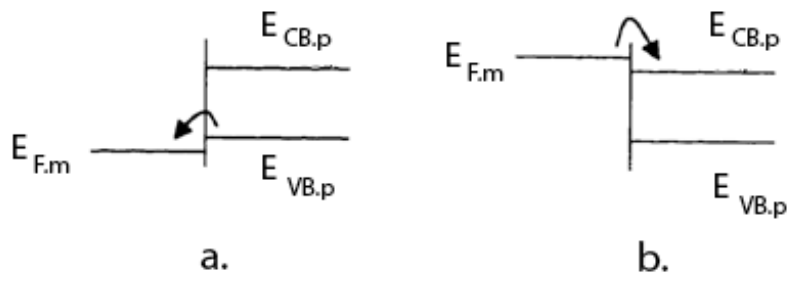


Figure1. 8 a) p-doping and b) n-doping of conducting polymer

Electrochemical doping is illustrated by the following examples:

For p-type:

$$(poly)_n + ny\,[Li^+(BF_4^-)(sol'n)] \underset{Reduction}{\overset{Oxidation}{\rightleftharpoons}} [(poly)^{+y}\,(BF_4^-)_y]_n + nyLi(elec'd)$$

For n-type:

$$(poly)_n + ny\,Li(elec'd) \underset{Oxidation}{\overset{Reduction}{\rightleftharpoons}} [(Li^+)_y(poly)^{-y}]_n + n\,y\,[Li^+(BF_4^-)]\,(sol'n)$$

where sol'n is solution and elec'd is electrode.

1.4 Polymerization Methods

Chemical and electrochemical polymerizations are widely employed techniques in the synthesis of conductive polymers. Other techniques used to synthesize conducting polymers include photochemical polymerization,

metathesis polymerization, plasma, pyrolysis, solid state polymerizations, Grignard reaction, ring-opening metathesis and transition metal-catalyzed polymerization [24]. Polymers are obtained in their insulating form by a chemical procedure and then they can be doped to their conducting form by chemically or electrochemically. On the other hand, polymers generated electrochemically are in their oxidized, conducting state. It is possible to control the thickness and morphology of the polymer film during the electrolysis process [25].

1.4.1 Electrochemical Polymerization

Electrochemical synthesis is a simple, selective and a reproducible method. It has the advantage of producing the material on an electrode. Furthermore; the method allows easy control of the film thickness by the deposition charge. During electrochemical polymerization, doping of the polymer and processing take place simultaneously while in conventional method, first polymer synthesis is carried on which is subsequently followed by doping and processing. It can be concluded that electrochemical polymerization is the most important technique for fundamental studies regarding synthesis and properties of the corresponding polymers [26]. The major drawback of this technique is that rather small amounts of polymer are produced which are generally insoluble. Therefore, characterization of these products with conventional methods like NMR and GPC are very difficult.

1.4.1.1 Mechanism of Electropolymerization

Electrochemical oxidation of various resonance stabilized aromatic molecules, such as pyrrole, thiophene, aniline, furan etc., generate electronically conductive polymers. It has been proposed that the polymerization involves either radical-cation/radical cation coupling or reaction of a radical cation with a neutral monomer (Figure 1.9) [27, 28].

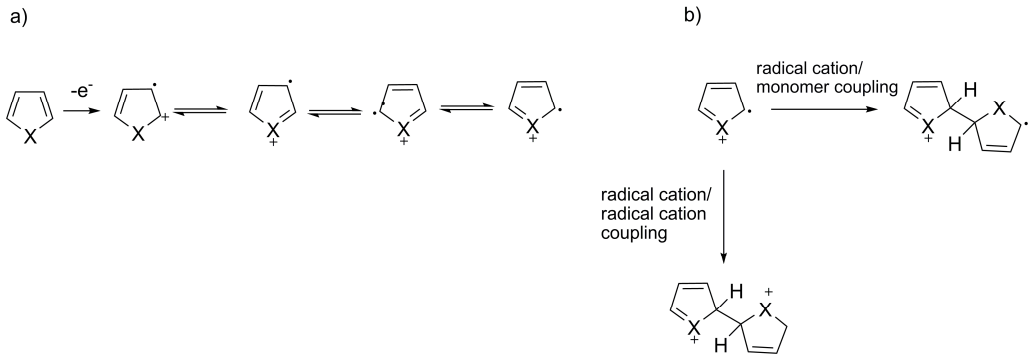


Figure1. 9 a) Resonance stabilization of a five membered heterocyclic compound upon formation of radical-cation b) Radical-cation/monomer and radical cation/ radical cation coupling where X = N-H, S, O

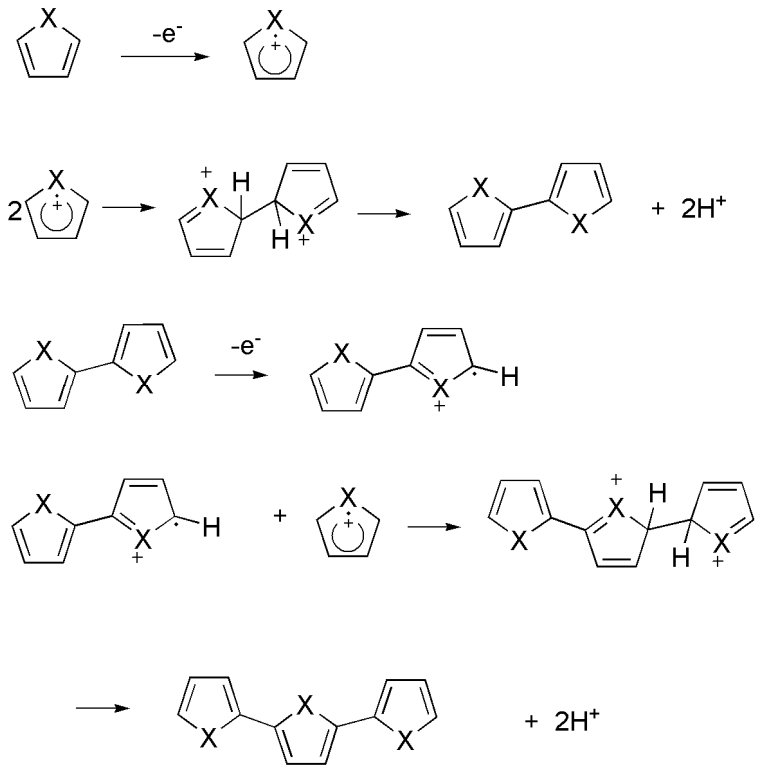


Figure1. 10 Electropolymerization mechanisms of heterocycles (X = S, O, NH)

Figure 1.10 shows the mechanism proposed for the electropolymerization of heterocycles by anodic coupling. The first electrochemical step (E) starts with the oxidation of the monomer to its radical cation. The electron-transfer reaction is much faster than the diffusion of the monomer from the bulk solution which provides that the solution in the vicinity of the electrode surface has a high concentration of radicals continuously. Coupling follows the first step. This step is controversy step because coupling may proceed via two different routes which are the combination of two radical cations or addition of radical cation to heterocyclic monomer. In the case of radical-radical coupling, dihydro dimer dication is formed which leads to a dimer upon release of two protons and re-aromatization. This rearomatization constitutes the driving force of the chemical step (C). Due to the applied potential, the dimer occurs in its radical form and

undergoes a further coupling with a monomeric radical. In a radical–monomer coupling mechanism, the radical cation reacts with the monomer to yield a neutral dimer by the loss of another electron and two protons. The dimer and succeeding oligomers are more easily oxidized than the monomer and the resulting dimer radical cation undergoes further coupling reactions, proton loss and re-aromatization. Electropolymerization advances through successive electrochemical and chemical steps according to a general ECE (E for electrochemical, C for chemical), until the oligomers become insoluble in the electrolyte solution and precipitate onto the electrode surface.

1.4.1.2 Factors Affecting Electropolymerization

It is known that experimental parameters like solvent, temperature and pH effect the mechanical, morphological and electrical properties of conducting polymer films after many years of research about electropolymerization conditions have been established.

There are two major methods to achieve electropolymerization which are potentiostatic (constant potential) and galvanostatic (constant current). Electrochemical methods have an influence on the morphology, appearance and adhesion of the polymer. It was shown that proper choice of supporting electrolyte was very effective for using potentiodynamic method.

The solvent to be used in the electrochemical polymerization should have sufficiently high dielectric constant so that ionic conductivity of the medium is fulfilled. The solvent should dissolve and dissociate the supporting electrolyte and should have potential range to oxidize or reduce polymer and it also should have high resistance against decomposition upon applied potential. Acetonitrile, benzonitrile, propylene carbonate, nitrobenzene are aprotic solvents which posses

high dielectric constant and low nucleophilicity. Especially nitriles are favored due to their wide range in both oxidation and reduction with a high dielectric constant (ε= 37 for ACN).

The electrode used during the synthesis has an effect on both the polymerization process and the properties of the resultant polymer. The polymers are generally deposited on inert substrate such as platinum, gold or optically transparent electrodes such as indium-tin-oxide (ITO) coated glass. The highly conducting polymers have been obtained on bulk platinum, presumably because thiophene adsorbs more efficiently on platinum and also presents a larger number of potentially active sites leading to a high density of nucleation sites and to more compact materials.

The most important criteria of the choice of electrolyte are the solubility and degree of dissociation and its nucleophilicity. The nature of electrolyte used significantly affects the morphology of the resulting film [29]. Supporting electrolyte used in electrochemical polymerization serves for two purposes [30]. First of all, it makes electrolytic bath solution conducting and it dopes the polymer by allowing one of its ions to couple with the monomer unit. The nature of the anion used during the synthesis step plays a determining role on the structure of the polymer. The nature of the cation, on the other hand, affects essentially the behavior of the polymer films during the charge-discharge processes. Conducting polymers are generally electrogenerated in the presence of lithium or tetraalkylammonium salts of either perchlorate, tetrafluoroborate and hexafluorophosphate anions [29].

1.5 Electrochromism

Electrochromism, is broadly defined as the reversible change in optical properties when a material is electrochemically oxidized or reduced and has been

an important branch of conducting polymer research both in academia and industry. A material can be defined as electrochromic when it reveals drastic color changes. However, the definition of electrochromic materials has been extended by recent interest in electrochromic devices for multispectral energy modulation by reflectance and absorbance. Electrochromic devices are now being studied for modulation of radiation in the near infrared, thermal infrared [31] and microwave [10] regions.

The first examples of electrochromic materials and devices were demonstrated by Deb et al. [32]. After this discovery, many scientists have investigated different kinds of electrochromic materials. Having many potential applications had increased the commercial interest in electrochromic materials. Displays, mirrors, windows and computer data storage are the most known applications of electrochromic materials. Optical contrast, electrochromic memory, coloration efficiency, switching speed, and stability are commonly used characteristics to define the fundamental properties of EC materials. The contrast ratio is defined as the difference in transmittance in the visible spectrum between the two different colored states. The electrochromic memory is the ability of the material to sustain its color without applied current. The long term stability is the ability of the material to retain its electrochromic properties over a large number of switching cycles.

There are basically three categories of electrochromic materials; metal oxide films, molecular dyes and conducting polymers. Among electrochromic materials, transition-metal oxides, especially the high band-gap semiconductor tungsten oxide, WO_3, have been widely studied over the past 30 years [33]. It is convenient to explain electrochromism in tungsten oxide by referencng to the simple reaction

$$\underset{\text{(transparent)}}{WO_3} + xM^+ + xe^- \rightarrow \underset{\text{(blue)}}{M_xWO_3}$$

with $M^+ = H^+$, Li^+, Na^+, or K^+ [34].

Tungsten oxide has a nearly cubic structure which may be simply described as an "empty-perovskite" type formed by WO_6 octahedral that share corners. Tungsten trioxide, with all tungsten sites have the oxidation state of six, is a transparent thin film. On electrochemical reduction, W_V sites are generated to give the electrochromic (blue coloration) effect. WO_3 is a cathodically ion insertion material. The blue coloration in the thin film of WO_3 can be reversed by the electrochemical oxidation. Many other inorganic materials have received attention for their electrochromic properties such as Prussian Blue, oxides of V, Mo, Nb, and Ti (cathodically coloring), and oxides of Ni, Co, and Ir (anodically coloring) [35].

Other EC materials include organic small molecules, such as the bipyridiliums. They are known as viologens and are a class of materials that are transparent in the stable dicationic state [36]. Reductive electron transfer to viologen dications forms radical cations. Generally the viologen radical cations are intensely colored, with high molar absorption coefficients, owing to optical charge transfer between the (formally) +1 and zero valent nitrogens. N-substituted viologens such as heptyl viologen and polyviologens show thin film electrochromism [37]. Composite systems, where organic molecules are adsorbed on mesoporous nanoparticles of doped metal oxides have been reported because of their improved electrochromic properties [38].

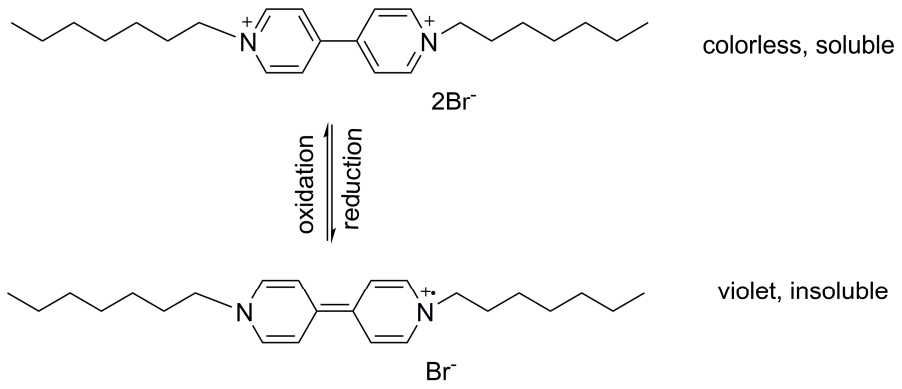


Figure1. 11 Redox process of Diheptyl viologen

1.5.1 Electrochromism in Conducting Polymer

Conjugated polymers as a class of EC materials have received attention due to their ease of processability, (they can be easily prepared by simple chemical, electrochemical polymerization and the films can be obtained by simple techniques such as dip coating, spin coating, etc), rapid response times (less than 1 second), and high optical contrasts and the ability to modify their structure. Moreover, by adjusting the electronic character of the π system along the neutral polymer backbone, the π - π * transition can be adjusted across the electromagnetic spectrum from the UV, through the visible and into the near-infrared [39]. In the light of these advantages, conjugated polymers have gained popularity in common applications of EC materials include a variety of displays, smart windows, optical shutters, and mirror devices.

Derivatives of PPy, PTh, PEDOT, and PANI which have been studied most recently display electrochromism in thin film form. The working principle of electrochromism in conjugated polymers is that reversible insertion and extraction of ions through the polymer film upon electrochemical oxidation and

reduction change the conjugated polymer's π-electronic character. These polymers show semiconducting behavior with an energy gap (Eg) in their neutral states. The band structure of the neutral polymer is modified upon electrochemical or chemical doping ("p-doping" for oxidation and "n-doping" for reduction) that results lower energy intraband transitions and creation of charged carriers (polarons and bipolarons). These charge carriers have the responsibility for increased conductivity and optical modulation. Generally spectroelectrochemical experiments are most vividly used to illustrate the doping process and the resultant optical changes in conjugated polymers. According to literature, the expected transitions in a conjugated polymer can be explained by following explanations [40]. In the neutral state the polymer exhibits single broad transition from the valence band to the conduction band (π to π *). The energy difference between these two levels is the band gap (Eg), and it is measured as the onset of the π to π * absorption in the neutral state of the polymer. A new absorption band in the near-IR region forming at the expense of the π-π* transition upon oxidation (p-doping), which is related to polarons (radical cations) generated along the polymer chain. Upon further electrochemical oxidation, the intensity of both of the π - π * transition and the polaron absorption decrease, while a new absorption band peaked in the near-IR beyond the range of the spectrophotometer, arises. This absorption is assigned to the bipolaronic (dication) state of the conjugated polymer. Such optical and structural changes make polymers change color and that makes EC polymers potentially useful in applications for modulating transmissivity and color.

Among the conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) (Figure 1.12) which is known as one of the most successful conducting polymers as an electrochromic material, has been studied in electrochromic devices. Scientists at the Bayer AG research laboratories in Germany developed this polythiophene derivative, poly(3,4-ethylenedioxythiophene) during the second half of the 1980s [41]. Doped (oxidized) PEDOT film is light blue. Electrochemical reduction yields the blue (λ_{max} = 580-600 nm) "undoped" form. Removal of all dopant anions from PEDOT yields a blue film. This polymer

provides high conductivity and especially stable doped states, and enhanced redox properties, making it useful for numerous electrochemical devices.

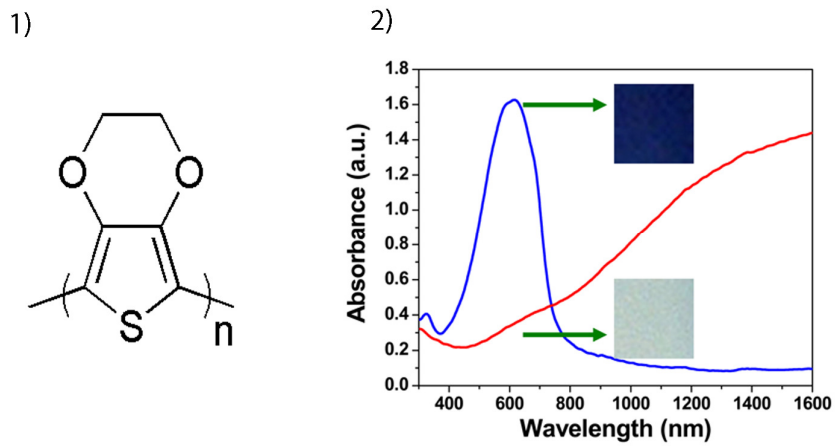


Figure1. 12 1) Structure of PEDOT 2) Colors of PEDOT in its reduced and oxidized state

1.5.2 Factors Affecting the Band Gap and Coloring of Conducting Polymer

Applications of conjugated systems in electronic and photonic devices such as light-emitting diodes (LEDs) [7], solar cells [12] and field-effect transistors (FETs) [13] have been investigated by many researchers. It becomes important to control the electronic properties especially band gap of the materials derived from π-conjugated systems since these applications mentioned above , based on the electronic properties of the neutral semiconducting form of conjugated systems.

It is known that the band gap is influenced by energy related to the bond length alternation (E_{BLA}), the mean deviation from planarity (E_{θ}), the aromatic resonance energy (E_{Res}), the inductive and mesomeric electronic effects of substituents (E_{Sub}) and interchain interactions (E_{Int}) As a result of that the band gap of a material derived from a linear π-conjugated system can be expressed by the sum of these five affects: [42].

$$Eg = E_{BLA} + E_{Res} + E_{Sub} + E_{\theta} + E_{Int}$$

The band gap of conjugated polymer generally decreases with decrease in the resonance energy per electron and it was shown that aromaticity in poly(aromatics) is then related to a competition between π -electron confinement within the rings and delocalization along the chain. Moreover, one of the most efficient approaches for gap reduction is the conversion of a polyaromatic chain into a conjugated system with an enhanced quinoid character. As stated before, polymers of aromatic compounds such as polythiophene have non-degenerate ground state in other words; the aromatic and quinoid structures are not energetically equivalent. The band gap of a polymer can be drastically decreased as the quinoid geometry of the polymer increased. One of the most important examples of this effect has been observed throughout the investigation of the properties of polyisothianaphthene. [43]. PITN prefers to have the quinodial form since benzene, with energy of aromatization of 1.56 eV, is more aromatic than thiophene (1.26 eV). This forces PITN to be more energetically stable in the quinoidal state, which provides the lowered band gap, 1.1 eV, compared to polythiophene with a band gap of 2.0 eV. Poly(dihexylthieno[3,4b]pyrazine) is another example of this approach [44]. Poly(dihexylthieno[3,4b]pyrazine) was initially prepared by oxidative polymerization using iron trichloride and was reported to have a band gap of 0.95 eV. While not directly resorting to the fusion of cycles with different E_{Res}, poly(thieno[3,4-b]thiophene) is also a typical low-band-gap polymer (Eg¼0.80–0.90 eV) based on fused ring systems [45]. A major drawback of some of these fused systems lies in their limited stability.

The bond alternation was defined by Bredas et al [42b], as the maximum difference between the length of a C-C bond that has been inclined relative to the chain axis and a C-C bond that is parallel to the axis. It has been shown by theoretical and experimental work that one-dimensional conjugated systems are unstable due to the effects of electron-phonon coupling and electron-electron correlation. These effects lead to the localization of π-electrons with the aperture of a gap of a least ~1.50 eV in the case of a simple polyenic system. Therefore, bond length alternation (BLA) shows the major contribution E_{BLA} to the magnitude of the energy gap. As a result of that, researchers expect that structural modifications resulting in a reduced BLA can produce a decrease in the band gap [42a].

The single bonds between the aromatic units in the polymer backbone generate sites for interannular rotation, which causes deviation from co-planarity. This has been shown to cause drastic increases in the band gap of the polymer. Polythiophene backbone with flexible side chains have shown to have considerably higher band gaps compared to regioregular poly(3-alkylthiophene)s. As the torsinal angle between the neighboring rings increases, the band gap of the system tends to decrease due to the decreased overlap in the conjugated system. This knowledge led researchers to design and synthesize highly planar systems. One of the successful approach was the synthesis of ladder-type polymers, for example polyacene family. The high planarity in these systems achieved by excluding all the single bonds in the polymer backbone resulting in all π conjugated polymeric systems [46].

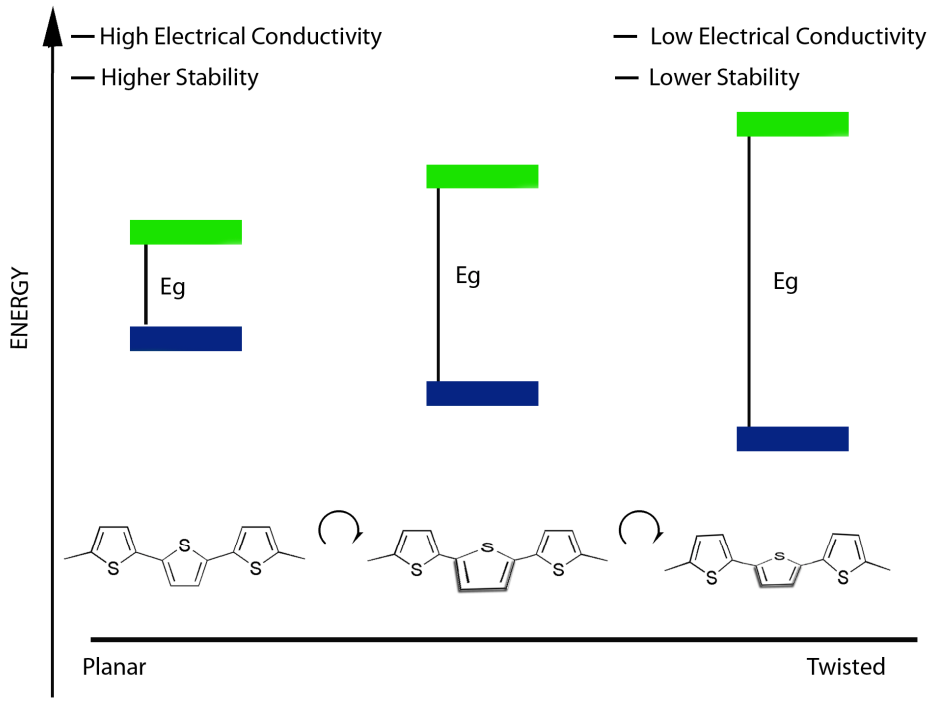


Figure1. 13 Planarity effects on band gap and the electrical and optical properties of conjugated polymers [46]

One of the most commonly used methods to decrease the oxidation potential of polymers is the introduction of powerful electron-donating groups on the polymer backbone hence, raising the valence band energy and reducing the band gap. It is also known that electron-withdrawing groups lower the valence band energy. The incorporation of electron donating alkoxy chains on the polythiophene backbone resulted in polymers with low oxidation potentials and good stabilities in the oxidized form since this allows electrochemical synthesis to be performed in much milder conditions. Additionally, the steric hindrance in the surroundings of the main chain has been reduced with the presence of alkoxy-chains since oxygen has a smaller Van der Waals radius compared to the methylene counterpart. Eventually, this helps the polymer to be more planar and results in polymers with lower band gaps. The cross-linking during the polymer

synthesis found to result in non-processable and hard to characterize materials. Di-substitution at the 3,4 positions of the thiophene ring stands as a sensible idea to prevent this problem. However, this approach was proven to be unsuccessful since the poly(3,4-dialkylthiophenes) are turned out to have higher oxidation potentials, higher optical band gaps and lower conductivities due to the steric interactions between the substituents [42a]. Another approach involves fusing a heterocyclic ring on the 3,4 positions of the thiophene unit. This approach was successful to reduce the steric hinderence and still have the alkoxy groups to reduce the band gap. One of the most important examples is poly(3,4-ethylenedioxythiophene).

The family of poly(3,4-alkylenedioxythiophenes) were proven to be one of the most successful electrochromic materials, due their low oxidation potentials and band gap with high long-term stabilities [26]. Electron donating ability of the oxygen atoms in a fixed geometry lowers the oxidation potential. Since α-β and β-β coupling routes are eliminated, resulting polymer turns out to have a more ordered structure and longer conjugations lengths. The first anodic polymerization of EDOT was performed by Jonas et al. and the results showed that compared to many other substituted polythiophenes, this materials revealed tremendous stability in the doped state due to high conductivity achieved by the material. Electrochromic properties of the material were also proven to be superior compared the other thiophene anologs. PEDOT is highly transmissive in the oxidized state and dark blue in its reduced state. This is a revolutionary step towards high optical contrast materials which are highly important for commercial applications like smart windows. A great number of analogs were synthesized up to date to investigate the structure-property relationship. A number of solution processable derivatives have been realized which makes it possible to coat bigger surfaces with simple techniques like spin coating or spray coating. The processibility was achieved by introduction of alkyl substituent on the parent polymers backbone. These alkyl chains not only increase the solubility of the polymer but also proven to contribute to a higher degree of optical contrasts [47] and faster switching times [48].

After poly(3,4-alkylenedioxythiophenes)s were proven to be superior poly(3,4-alkylenedioxypyrrole)s were extensively studied. PEDOP has a higher HOMO than PEDOT and also higher LUMO. Since the differences between the HOMO levels are larger than the difference between the LUMO levels, PEDOP has a higher band (up to 2.0V). This difference resulted in red color in the reduced and sky-blue transparent in the oxidized state. As the number of methylene groups increased in the bridge, steric interactions started to decrease the overlap along the π bonds and resulted in slight increase in the band gap without any significant changes in the redox properties [49].

Number of studies has been performed where heterocycles, phenylenes and/ or vinylenes are combined in extended conjugation monomers. Many polymers containing both EDOT and arylene moieties have been successfully synthesized. A group of monomers have been realized with two EDOT units combined with different arylenes such as carbazole [50] Also use of vinylene group in a similar approach resulted polymers with even lower band gaps [51]. These types of polymers are called donor-acceptor polymers. These polymers are generally synthesized with electron donating and withdrawing groups in 1:1 ratio through the polymer backbone. The resulting materials have the valence bond of the donor and conduction band of the acceptor.

1.6 Donor-Acceptor Theory and Low Band Gap Systems

Recently, π-Conjugated polymers with donor-acceptor moieties have gained attention because the built-in intramolecular charge transfer can facilitate ready manipulation of the HOMO/LUMO levels (electronic structure), which lead to small band gap semiconducting polymers. It is important to get small

band gap polymers since the neutral conductivity of CPs increases while band gap decreases. Moreover, donor-acceptor approach also enhances third-order nonlinear optical properties of the materials [52, 53]. Donor-acceptor conjugated polymers' uses have been extended to systems with efficient photoinduced charge transfer and separation for photovoltaic devices and to bipolar charge transport materials for light-emitting diodes, lasers and other applications.

Most of CPs reported up to date have band gaps greater than 2 eV and they are called mid- to high band gap polymers. Polymers are considered relatively low band gap materials if their band gaps are lower than 1.5 eV. There are few examples available in the literature with band gaps below 0.8 eV [43]. Band gap is used to determine the conductivity and color of the neutral polymer; moreover the band edges determine ease of doping a polymer and the stability in the doped states compared to the neutral forms. Figure 1.14 describes the four ways that most CPs can be classified.

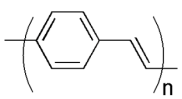
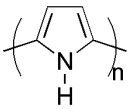
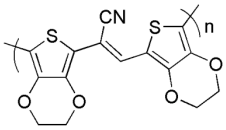
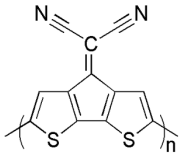
	High Eg Polymers with Low VB(HOMO)	High Eg Polymers with High VB(HOMO)	Low Eg Polymers with High CB(LUMO)	Low Eg Polymers with Low CB(LUMO)
easily p-type doped		X	X	X
easily n-type doped	X		X	X
examples	 PPV	 PPy	 PBEDOT-CNV	 PCDM

Figure1. 14 Possibilities for positioning of band edges in both high and low band gap polymers [54].

Generally, there are mostly high band gap polymers with a high VB in the literature. PPy, PTh, PEDOT and poly(3,4-alkylenedioxypyrroles) (PXDOPs) are some of the examples of polymers having this characteristic. These polymers are all prepared by oxidative polymerization routes and are easily p-type doped [55] by virtue of their high lying VB. On the other hand the CB is generally out of reach for stable electrochemical n-type doping due to their high band gap. However, PTh does exhibit n-type doping at very negative potentials and PEDOT is even more difficult to n-dope compared to PTh. Another category is the high gap/low VB polymer such as PPV and its analogues. PPV is not easily doped

electrochemically, [56] but its bands are positioned so that charge carriers of either sign can be injected making this class of polymer useful in light emitting devices where the emission energy is tuned by modifying the band gap. The other situation, which is the low band gap polymers with a low CB, is desirable for many applications and few examples are available.

As it is mentioned before low band gap polymers are relatively recent topic of research interest and these types of polymers have many interesting applications. The low band gap often causes these polymers to be transparent in the doped state (p- or n-type) regardless of how the band energies line up. This property makes these polymers useful in a variety of devices such as electrodes and smart windows where the transparency can be exploited. According to definition of low gap systems the distance between the edge of the VB and CB is smaller; hence the CB is generally more accessible to n-type doping even for low gap polymers with relatively high VBs. These classes of materials become important since they not only offer the transparency but also give the ability to be both n-type and p-type doped for the same polymer. The magnitude of the band gap dictate the color of low band gap polymers same as with the high band gap polymers.

As discussed in detail in section 1.5.2 there have been many methodologies developed in the design and synthesis of low band gap systems. The five main approaches are;

Controlling bond-length alternation (Peierls Distortion),

Creating highly planar systems,

Inducing order by interchain effects,

Resonance effects along the polymer backbone,

Donor-Acceptor Approach.

Although there are many promising polymers which were synthesized by the approaches discussed above, during recent years synthesis of donor-acceptor type polymers proven to be superior compared to the other methods. The main reason for that is the diversity in synthetic possibility and ease of finding solutions to the

solubility problems that has been a problem for especially ladder-type polymers. Donor-Acceptor approach generally divided into two different groups;

The first one is the polymers with acceptor group directly have resonance interaction on the polymer backbone and the second one is the polymers with acceptor group inductively modify the polymer backbone. (Figure 1.15)

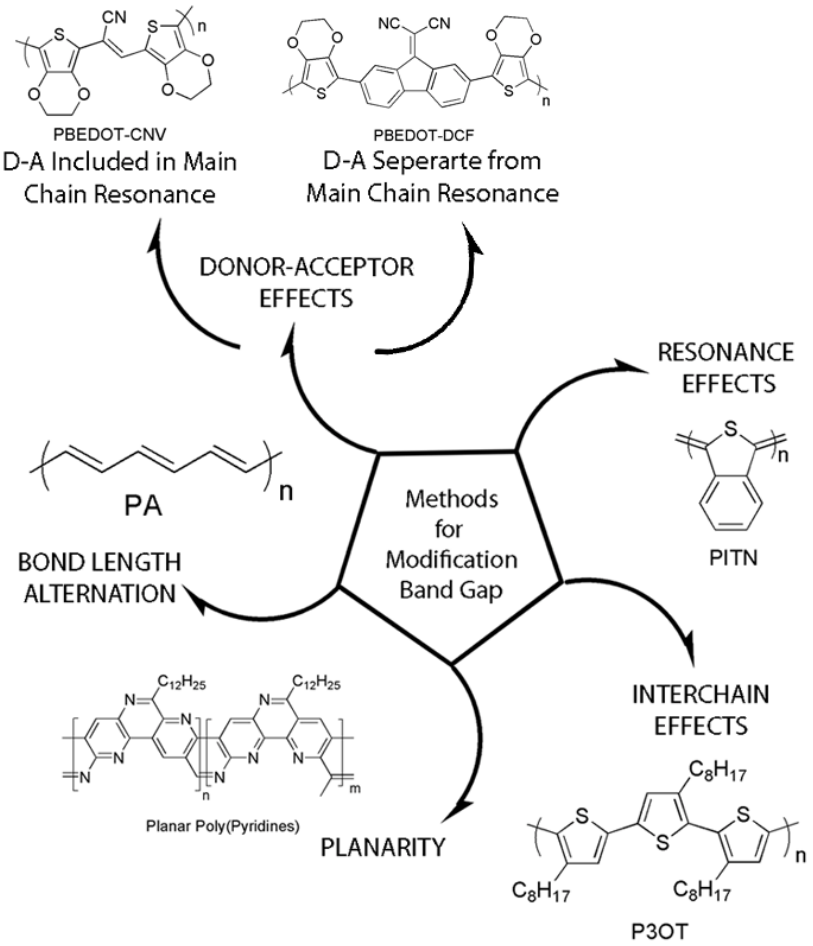


Figure1. 15 Methods for the modification of band gap [54]

Donor–acceptor systems lead to a narrower bandgap due to resonances that enable a stronger double bond character between the donor and acceptor units. This results in a decreased bond length alternation. This is attributed to hybridization between the energy levels, especially the HOMO of the donor and the LUMO of the acceptor [57]. The idea is to combine the high lying HOMO level of the donor and low lying level of LUMO of the acceptor in the same polymer to induce a lower band gap. Figure 1.16 illustrates this concept for PEDOT [58], poly(cyanoacetylene) (PCA) [59] and PBEDOT-CNV. All the HOMO and LUMO levels were anticipated from the spectroelectrochemical series, potentials for the electrochemical doping /undoping processes or from the known band gaps of the materials. This figure clearly illustrates that the resulting donor-acceptor type polymers has very similar valence band energy of the donor moiety and has a very close conduction band energy value of the acceptor moiety. This resulted in a tremendously decreased band gap compared to both PEDOT and PCA.

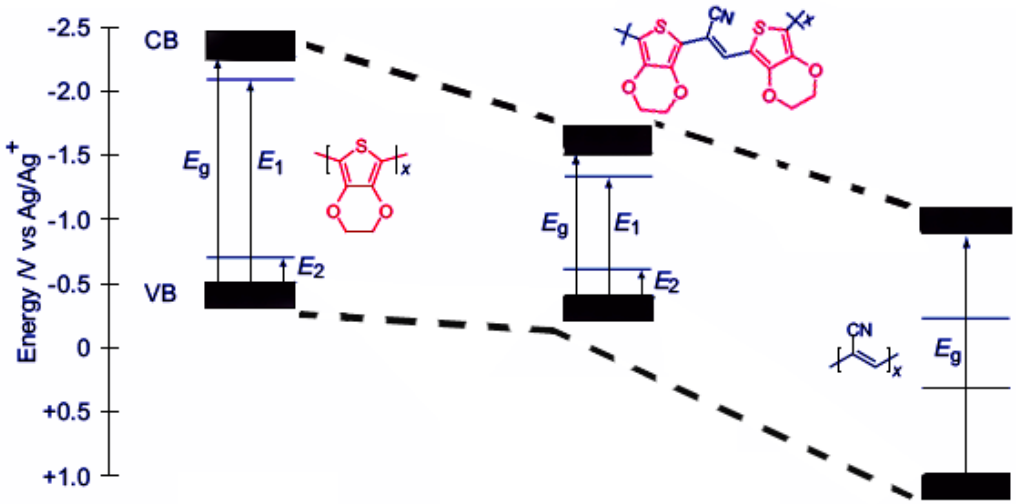
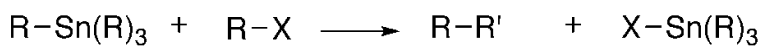


Figure1. 16 The Donor-Acceptor approach, alternating donor and acceptor moieties results in a polymer that has the combined optical properties of the parent donor or acceptor monomers [54].

1.6.1 Synthetic Methodologies for donor acceptor type materials

There are three types of reactions used mostly to synthesize D-A-D type monomers, which are Stille Coupling, Negishi Coupling, and Suzuki Coupling. The Stille reaction takes place between an organotin compound with sp^2-hybridized organic halide catalyzed by palladium [60,61].



where X is typically a halide, such as Cl, Br, I.

Figure 1.17 shows the mechanism of Stille Coupling. The reduction of the palladium catalyst (1) to the active Pd(0) species (2) is the first step of this catalytical cycle. The oxidative addition of the organohalide (3) gives a cis intermediate, which rapidly isomerizes to the trans intermediate (4) [60]. Transmetalation with the organostannane (5) forms intermediate (7), which produces the desired product (8) and the active Pd(0) species (2) after reductive elimination. In Stille coupling stannyl intermediate can easily be isolable which allows effective monomer purification. *Trans*-dichloro-*bis*-triphenylphosphin epalladium (II) and *bis*-(tri-*t*-butylphosphine) palladium (0) which are less expensive and less oxygen reactive can be used for Stille coupling reactions [62].

In the case of the Negishi coupling, an organozinc compound, an organic halide and a nickel or palladium catalyst are used to create a new carbon-carbon covalent bond [63]. In Negishi coupling it is easy to prepare organic-zincate complex by *in-situ* preparation while avoiding highly toxic tin reagents. In general Negishi couplings use *tetrakis*-triphenylphosphine palladium (0), which is a highly oxyphilic catalyst.

The Suzuki coupling is a reaction of an aryl- or vinyl-boronic acid with an aryl- or vinyl-halide catalyzed by a palladium (0) complex. Typically tetrakis(triphenylphosphine) palladium(0) is used as the catalyst.

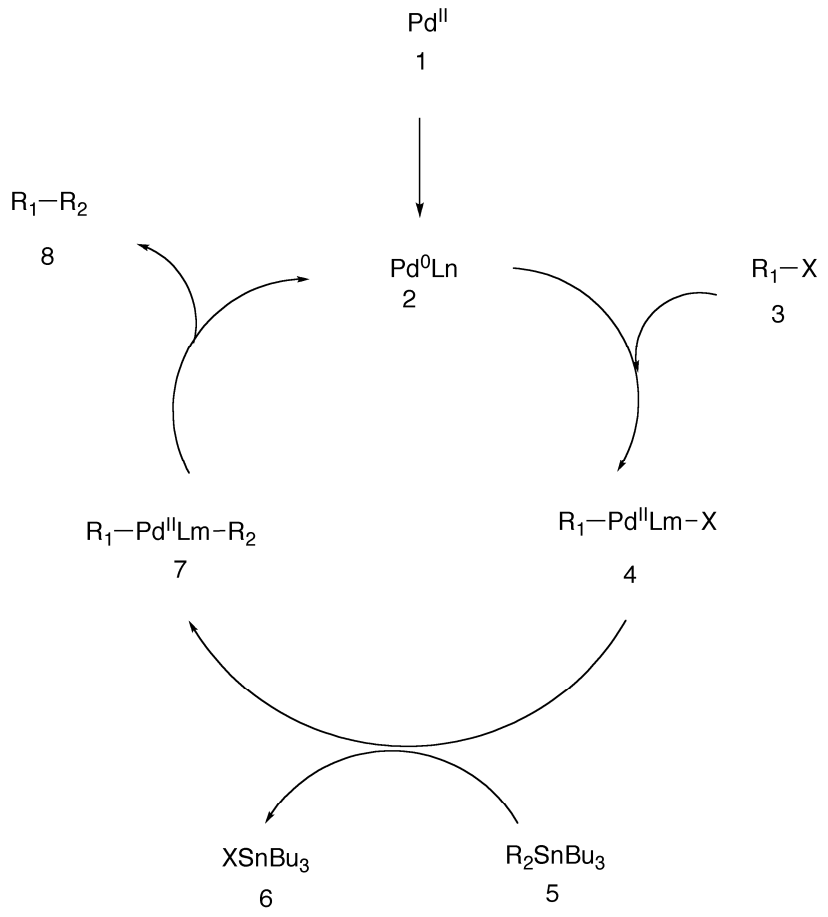


Figure1. 17 Catalytical cycle in Stille Coupling reaction

1.6.2 Importance of donor acceptor approach for Synthesis of n- Dopable Conjugated Systems

The availability of stable n-type doped semiconducting polymers is important to expand the scope of polymeric electronics since it would allow for the construction of stable light-emitting p(i)n diodes and bipolar transistors. However, due to the lack of environmentally stable n-type doped conducting

polymers, these devices have not been reported yet. In general conjugated polymers can be doped to both p and n-type semiconductors. It is known that there are conjugated materials that are stable as an undoped or very slightly p-type doped such as polythiophene and there are also some heavily p-type doped polymers which are very stable under ambient conditions such as polypyrrole and polyaniline. Up to date no n-type doped conjugated polymers having similar stabilities have been reported. The reason for that is the well-known instability of organic anions (especially of carbanions) where they are easily oxidized in contact with air or water.

Recently, some researchers have proved that introduction of nitrogen within the polymer repeat unit stabilizes the n-type doped state by lowering the LUMO and it is suggested that the polymers can have accessible oxidation and reduction potentials and lowered band gaps by controlling both the electron donating and electron accepting abilities of the monomer [64].

Figure 1.18 shows some reduction potentials of common nitrogen containing heterocyclics. As seen from Figure 1.18, when we compare pyridine with biphenyl, it is expected that biphenyl should have a lower reduction potential due to more extended aromatic system however, the reduction potentials are almost the same due to incorporation of single nitrogen (pyridine: 2.15 V vs SCE). In the case of heterocyclics with multiple nitrogens; they have potentials even more positive than pyridine. The other important factor is the relative placement of the nitrogen atoms. Incorporation of second nitrogen shifts the reduction potential 300 mV more positive value for pyrimidine and this is 500 mV for pyrazine. The lower molecular orbital energy of nitrogen in comparison to carbon for these systems explains this “nitrogen-effect” [65]. Such examples are; Quinoxaline has a reduction potential of -1.09 V, while pyrido[3,4-*b*]pyrazine gets reduced at -0.85 V.

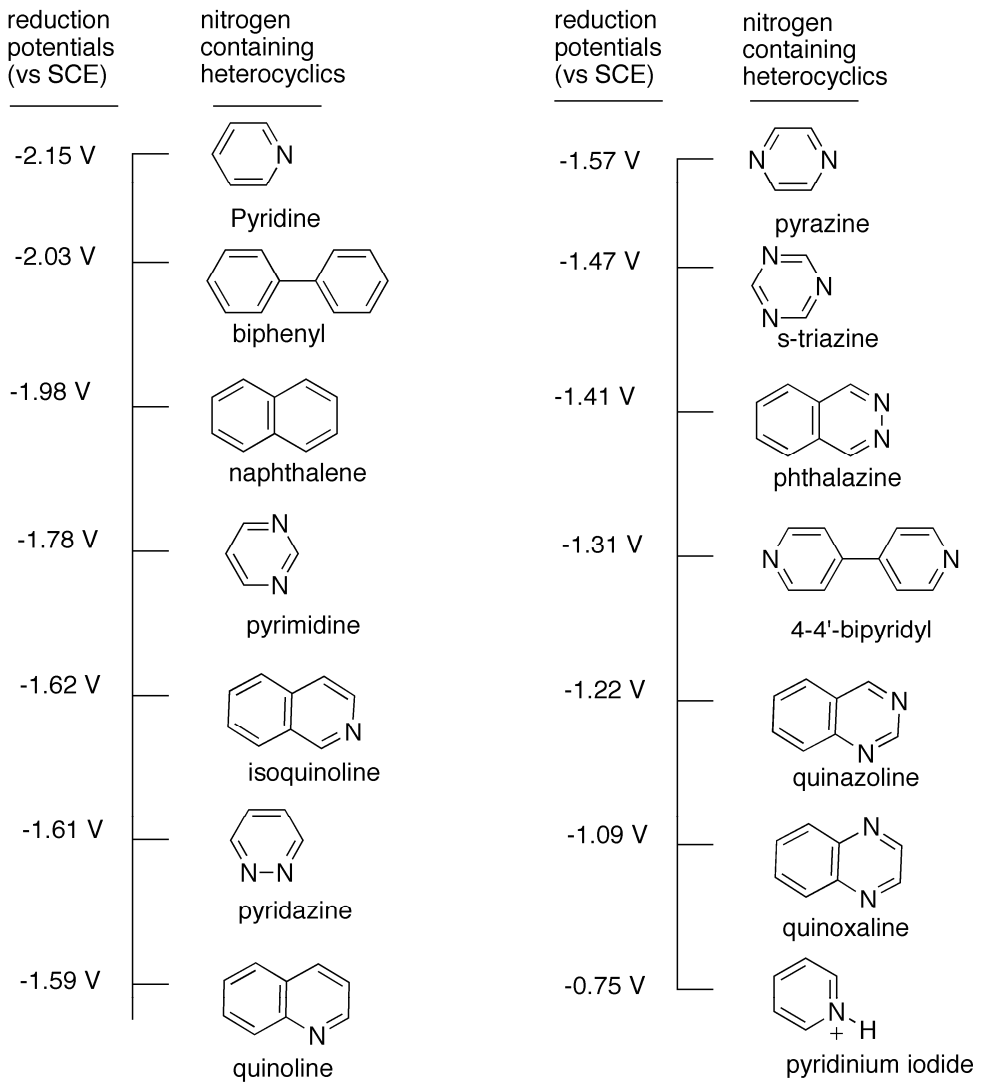


Figure1. 18 Reduction potentials of some nitrogen containing heterocyclics [42,66]

Several groups have used nitrogen containing heterocycles due to their ability to get easily protonated in order to reversibly lower the conduction band level, where it significantly alters the electrochemical and optical properties of these systems as a second method [66]. This factor affects the reduction potential

of both pyridinium and pyrazinium as 1.4 V more positive than pyridine and pyrazine, respectively.

PEDOT has been known as one of the highest change in transmittance upon doping among the electrochromic polymers [48]. To probe the electron acceptor strength effects in the conduction band energy levels, thieno[3,4-b]pyrazine and quinoxaline derivatives were incorporated within the EDOT donor structures to yield donor-acceptor systems with compressed band gaps. This allows both oxidation and reduction to be readily accessible within the desired electrochemical window. Donor-acceptor systems yield lower band gaps therefore, it is expected that these polymers can be transmissive in the oxidized state [67].

1.7 Neutral State Green Polymeric Materials

The discovery of a neutral state green polymer was definitely one of the most important breakthroughs for the commercialization of these materials in the history of polymeric electrochromic materials. Research on electrochromic polymers in the past 30 years has resulted in materials reflecting mainly blue and red colors in their neutral states. The main reason for these results is the one dominant wavelength revealed by these materials. To obtain a green color there should be at least two simultaneous absorption bands in the red and blue regions of the visible spectrum. Furthermore, the difficulty in controlling both absorption bands with the same applied potential must be overcome.

Many differently colored polymers can be synthesized by structural modification on a conjugated polymer. Different polymers in their different doped states, namely, neutral, intermediate, p-doped or n-doped, can result in completely different colors. However, from the practical point of view, if three

primary colored polymers in their neutral sate can be synthesized it would be possible to create all the colors in the visible spectrum. In theory, when two colors are mixed, the new one formed has to be on the line that connects the two colors on the chromaticity diagram. For a commercial display device to be realized one should have three polymers that have one of the primary colors in their reduced states and they have to be completely transparent in their oxidized state.

As stated before, most of the polymers synthesized so far generally have blue or red colors in their neutral states. The realization of green color can be only possible by having simultaneous absorption bands in the red and blue regions of the spectrum. In addition to that these absorption bands should be manipulated with the same applied potential. These phenomena have been fulfilled with ground-breaking work of Sonmez et al in 2004 and the first neutral state green polymer was characterized [68]. Although this material has green color in its neutral state and revealed an extreme stability (stable even after 10000 double potential steps), the residual brown color of the polymer in the oxidized state obstruct the potential use of this material as the missing third leg of additive primary color space.

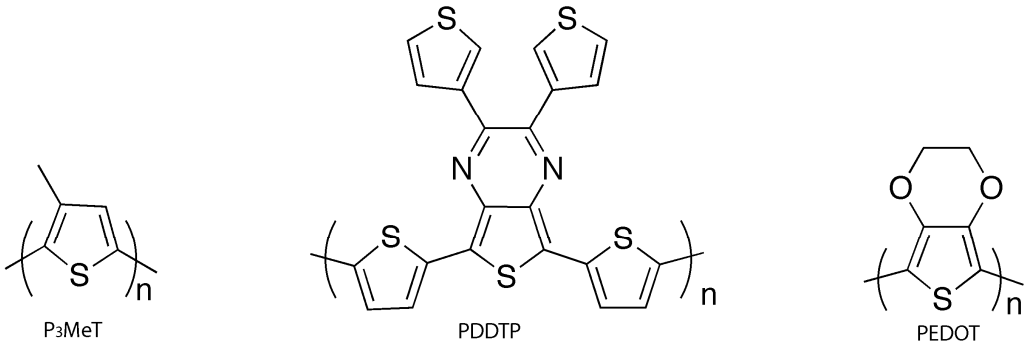


Figure1. 19 Poly(3-methylthiophene) (P3MT), poly(2,3-di(thien-2-yl)thieno[3,4-b]pyrazine) (PDDTP) and poly(3,4-ethylenedioxythiophene) (PEDOT) were the red,green and blue colored polymers respectively [68].

The transmissivity in the oxidized state is significantly important in addition to the neutral state color of the polymer. The materials having one of the three primary colors should also possess highly transmissive oxidized states in order to be used in commercial electrochromic device applications. Hence, the major prerequisite in the field for producing green polymeric materials with transmissive oxidized states is to have two absorption maxima and disappearance of these absorption bands in the visible region upon successive oxidation.

The polymers P3HT, PDDTP and PEDOT have proven to have highly saturated RGB colors in their neutral state respectively (Fig. 1.19). Although P3HT and PEDOT have acceptable transmissive oxidized states, the residual brown color of PDDTP in the oxidized state is a major drawback for use of this material as the green leg for RGB based display devices. The P3HT and PEDOT has a very similar spectrum at their oxidized state, if a neutral state green polymer with a similar spectrum relative to P3HT and PEDOT can be realized, a color filter simply bring the faint oxidized state colors to the white point in the CIE (Commission Internationale de l'Eclairge International Commission on Illumination) color space.

The optical contrasts (%ΔT) of the red (P3HT) and blue (PEDOT) colored polymers, were calculated to be 53 % and 55 % at their absorption maximums in the visible region. The green polymeric electrochromic (PDDTP) revealed relatively low optical contrasts at its absorption maxima. The calculated values are 23 % and 12 % transmittance changes (%ΔT) 370 and 725 nm, respectively. This is the main reason of the residual brown color in the oxidized state.

1.7.1 Donor-Acceptor Methods towards Green Polymeric Materials

It is reported that generally, donor-acceptor type polymers have two π-π^* transitions. In literature there are examples [69] where the resultant polymer

revealed two distinct π-π^* transitions due to the transitions from the thiophene based valence band 1) to its antibonding counterpart and 2) to the substituent localized and narrow conduction band [70]. Therefore donor-acceptor approach can not only narrow down the band gap but also can provide a green color to the polymer since to have a green color, there should exist at least two simultaneous absorption bands in the red and blue regions of the visible spectrum where these bands should be controlled with the same applied potential.

The transmissivity in the oxidized state is significantly important in addition to the neutral state color of the polymer. The materials having one of the three primary colors should also possess highly transmissive oxidized states in order to be used in commercial electrochromic device applications. Hence, the major prerequisite in the field for producing green polymeric materials with transmissive oxidized states is to have two absorption maxima and disappearance of these absorption bands in the visible region upon successive oxidation. This can be only achieved by means of donor-acceptor approach [71]. Donor-acceptor systems lead to narrower band gap due to resonances that enable a stronger double bond character between the donor and acceptor units [72]. The low band gaps as low as 0.45 eV [73] have been reported. This is attributed to the hybridization between the energy levels, especially the HOMO of the donor and the LUMO of the acceptor [57].

The donor acceptor approach leads to broadening of valence and conduction bands to induce a small band gap due to the regular alternation of conjugated donor and acceptor moieties in a conjugated chain [74]. In addition to the necessity of two absorption bands, the maximum absorption wavelengths are the decisive values to possess neutral state green polymers. Hence, the match between donor and acceptor moities is crucial.

1.8 Characterization methods of Eletrochromic Polymers

Conventional techniques for polymer characterization cannot be applied to all conductive polymers, since the highly conjugated backbone causes insolubility in common solvents. Therefore, the following are mostly used to characterize conductive polymers. Cyclic voltammetry is the key technique in order to get qualitative information about electrochemical reactions. CV is generally the first experiment for an electroanalytical study due to its capability of offering a rapid location of redox potentials of the active species [75]. Spectroelectrochemistry is another technique that examines electronic and optical changes of conducting polymers that occur upon doping. It provides information about electronic band gap intraband states formed upon doping (polaron and bipolaron). FTIR spectroscopy has always found wide applications in the characterization of polymeric materials. The utility of FTIR spectroscopy arises from its ability: i) to differentiate between functional groups, ii) to identify specific polymer systems, iii) its quantitative character with calibration, and iv) its speed and low cost [76]. One of the most important methods is electrochromic switching studies which are known to be the easiest and most efficient way to observe the ability of a polymer to switch rapidly and exhibit a striking color change. A square wave potential step method coupled with optical spectroscopy was used to probe switching times and optical contrasts for these polymers. In this double potential step experiment the potential was set at an initial value for a set period of time and was then stepped to a second potential for a set period of time before being switched back to the initial potential. In-situ colorimetry analysis is used as a means of precisely defining color and contrast ratio in electrochromic polymers. Colorimetry method allows for accurately reporting a quantitative measure of the color and graphically representing the track of doping-induced color changes of an electrochromic material or device. It provides a more precise way to define color than spectrophotometry. Rather than

measuring absorption bands, colorimetry measures the human eye's sensitivity to light across the visible region and gives a set of color coordinates to describe color such as the CIE 1931 Lab color space (Figure 1.20).

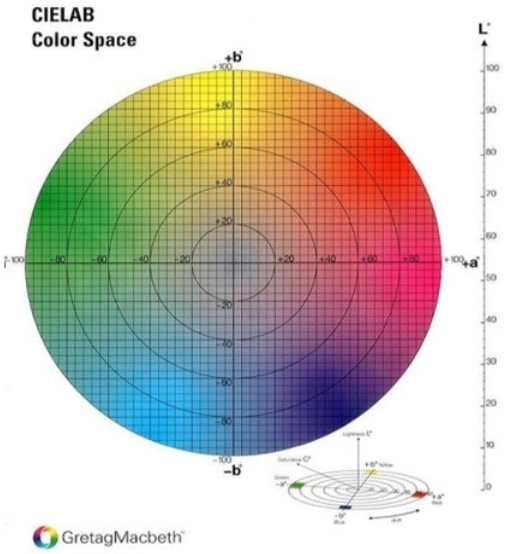


Figure1. 20 CIE LAB color space

This color coordinate has three values in relation to color; 'a' defines its hue (dominant wavelength), which is the wavelength where maximum contrast occurs, 'b' coordinate of color is its saturation (purity), which is the color's intensity, and 'L' corresponds to brightness (luminance) [68, 77].

1.9 Aim of this Work

The D-A-D type monomers were synthesized via Stille coupling cross coupling reactions. Poly4,7-di(2,3-dihydro-thieno[3,4-b][1,4]dioxin-5yl)benzo[1, 2,5]thiadiazole, PBDT, is the first green electrochromic material which has a highly transmissive sky blue oxidized state. Furthermore, two novel EDOT-bis-substituted quinoxaline monomers were synthesized via Stille coupling reaction. Benzo[1,2,5] thiadiazole, quinoxaline, 2,3- di(thiopene-2yl)quinoxaline were used as acceptor groups for neutral state green polymeric materials and EDOT was chosen as the donor group. The existence of the n-type doping process was proved by both electrochemical and spectral analyses for PDETQ films.

CHAPTER 2

EXPERIMENTAL

2.1. Materials

All chemicals were purchased from Aldrich. 4,7-Dibromo-2,1,3-benzothiadiazole [78], 3,6-dibromo-1,2-phenylenediamine [79], 5,8-dibromoquinoxaline [80], 5,8-dibromo-2,3-di(thiophen-2-yl)quinoxaline [81], and tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane [82] were synthesized according to the previously reported methods. Acetonitrile (ACN) was dried and distilled over calcium hydride under nitrogen. Tetrahydrofuran (THF) was distilled over Na/benzophenone prior to use.

2.2. Equipments

Electrochemical studies were accomplished with a Voltalab 50 potentiostat. Electropolymerizations were performed in a three-electrode cell consisting of platinum button or indium tin oxide (ITO) coated glass as the working electrode, platinum wire as the counter electrode, and Ag wire as the pseudo reference electrode. Measurements were carried out at room temperature

under nitrogen atmosphere. UV–vis-NIR spectra were recorded on a Varian Cary 5000 spectrophotometer at a scan rate of 2000 nm/min. A three-electrode cell was utilized consisting of a silver wire pseudo reference electrode, a Pt wire counter electrode, and an ITO coated glass working electrode. The potentials were controlled using a Solartron1285 potentiostat/galvanostat. Colorimetric measurements were achieved by a Minolta CS-100A Chroma Meter with a 0/0 (normal/normal) viewing geometry as recommended by CIE. NMR spectra of the monomers were recorded on a Bruker-Instrument-NMR Spectrometer (DPX-400) with $CDCl_3$ as the solvent and chemical shifts (δ/ ppm) were given relative to tetramethylsilane as the internal standard. The IR spectrum was recorded on a VARIAN 1000 FTIR spectrometer. Mass analysis was performed on TOF Bruker Mass Spectrometer with an electron impact ionization source.

2.3. Monomer Syntheses:

2.3.1 4,7-Di(2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)benzo [1,2,5]thiadiazole (BDT) (1)

A donor–acceptor type material 4,7-di(2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)benzo[1,2,5]thiadiazole (1) was synthesized according to a previously reported method [83]. 4,7-dibromobenzo[1,2,5]thiadiazole (400 mg, 1.36 mmol) and tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (3500 mg, 8.16 mmol) were dissolved in dry THF (90 ml), the solution was purged with argon for 30 min. and $PdCl_2(PPh_3)_2$ (212 mg, 0.302 mmol) was added at room temperature under argon atmosphere. The mixture was stirred at 100 ^{0}C under argon atmosphere for 15 hours, cooled, and concentrated on the rotary evaporator. The rediue dissolved in dichloromethane and extracted repeatedly

with brine and water. The organic phase dried over $MgSO_4$ and filtered. The solvent was evaporated and hexane added to the residue. The precipitate was filtered and subjected to column chromatography (DCM-Hexane 3:1) to afford a dark red solid. (Yield: 58%)

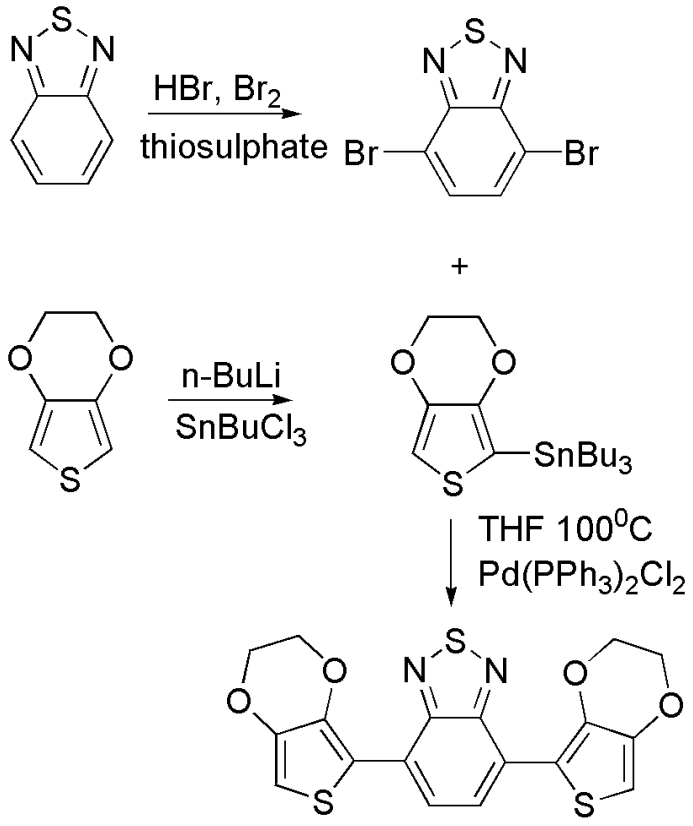


Figure 2. 1 Synthetic Route to Monomer BDT (1).

2.3.2 5,8-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl)quinoxaline (DETQ) (2)

2.3.2.1 5,8-Dibromo-2,3-di(thiophen-2-yl)quinoxaline

A solution of 3,6-dibromo-1,2-phenylenediamine (1.0 g, 3.8 mmol) and 1,2-di(thiophen-2-yl)ethane-1,2-dione (0.843 g, 3.8 mmol) in EtOH (40 ml) was refluxed overnight with a catalytic amount of PTSA. The mixture was cooled to 0 ^{0}C. The precipitate was isolated by filtration and washed with EtOH several times to afford the desired compound. (1.5 g, 72 %).

2.3.2.2 5,8-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl)quinoxaline (DETQ) (2).

5,8-Dibromo-2,3-di(thiophen-2-yl)quinoxaline (200 mg, 0.440 mmol) and tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (948 mg, 2.2 mmol) were dissolved in dry tetrahydrofuran (THF, 80 mL), the solution was purged with argon for 30 min, and $PdCl_2(PPh_3)_2$ (60 mg, 0.85 mmol) was added at room temperature under argon atmosphere. The mixture was stirred at 100 °C under argon atmosphere for 15 h, cooled, and concentrated on the rotary evaporator. The residue was subjected to column chromatography (DCM-hexane, 3:1) to afford an orange solid (148 mg, yield 58 %).

2.3.3 5,8-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl) quinoxaline (DEQ) (3).

5,8-Dibromoquinoxaline (200 mg, 0.70 mmol) and tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (1502 mg, 3.50 mmol) were

dissolved in dry THF (80 mL), the solution was purged with argon for 30 min, and $PdCl_2(PPh_3)_2$ (70 mg, 0.1 mmol) was added at room temperature under argon atmosphere. The mixture was stirred at 100 °C under argon atmosphere for 15 h, cooled, and concentrated on the rotary evaporator. The residue was subjected to column chromatography (DCM-hexane, 3:1) to afford an orange solid (172 mg, yield 60 %).

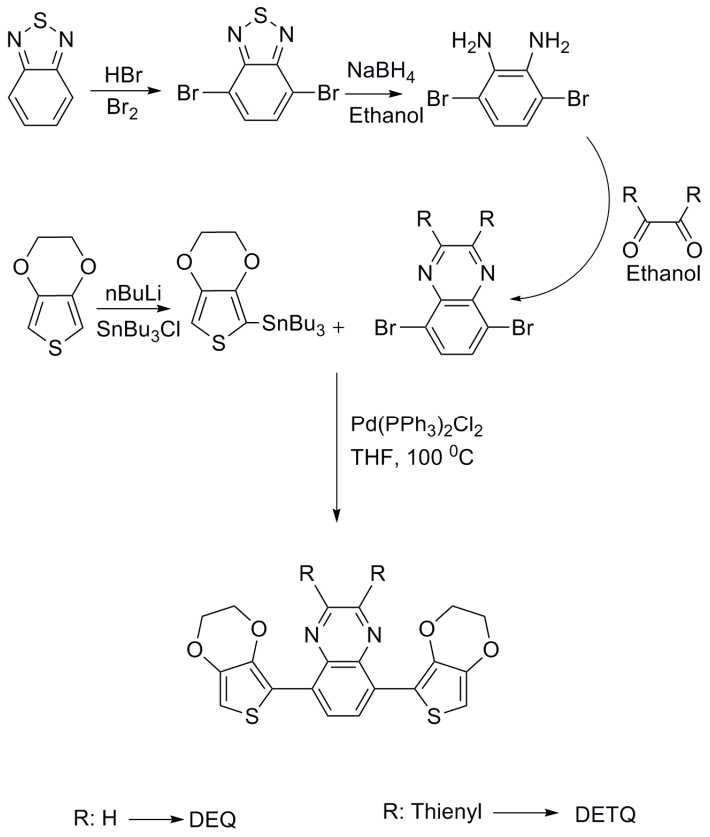


Figure 2. 2 Synthetic route to monomers DETQ (2) and DEQ (3).

2.4. Polymer Syntheses

2.4.1 Homopolymerization of BDT

The homopolymer of BDT, PBDT, was synthesized on platinum or indium tin oxide (ITO) coated glass slides by oxidative electropolymerization from a dichloromethane (DCM) solution containing 10^{-2} M BDT and 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$). The free standing homopolymers were washed with ACN in order to remove the excess $TBAPF_6$ and unreacted monomer after the electrolysis.

2.4.2 Homopolymerization of DETQ and DEQ

The potentiodynamic electropolymerizations of monomers (10 mM solutions) were carried out in 0.1 M $TBAPF_6$/DCM supporting electrolyte-solvent couple. The oxidation of DETQ on a bare electrode starts at 0.7 V and reveals a peak at 0.85 V versus Ag wire pseudo reference electrode in $TBAPF_6$/DCM. DEQ gets oxidized at a lower potential, 0.6 V. The free standing homopolymers were washed with ACN in order to remove excess $TBAPF_6$ and unreacted monomer after the electrolysis.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Characterization of the D-A-D Molecules.

^{1}H-NMR, ^{13}C-NMR spectra of monomers were investigated in $CDCl_3$ and d_6-DMSO and chemical shifts (δ) were given relative to tetramethylsilane as the internal standard. Mass analyses were also performed for the characterization of monomers.

3.1.1 4,7-Di(2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl) benzo[1,2,5]thiadiazole

^{1}H NMR ($CDCl_3$, δ): 4.19-4.49 (m, 8H); 6.56 (s, 2H), 8.39 (s, 2H,). ^{13}C NMR ($CDCl_3$, δ): 64.35 CH2; 64.99 CH2; 101.95 CH; 113.69C; 123.65 C; 126.61 CH; 140.24 C; 140.63 C; 152.32

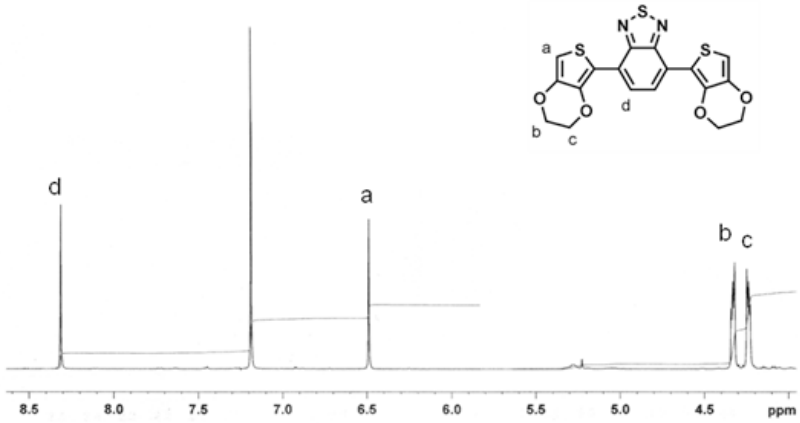


Figure 3. 1 ^{1}H-NMR spectrum of the BDT

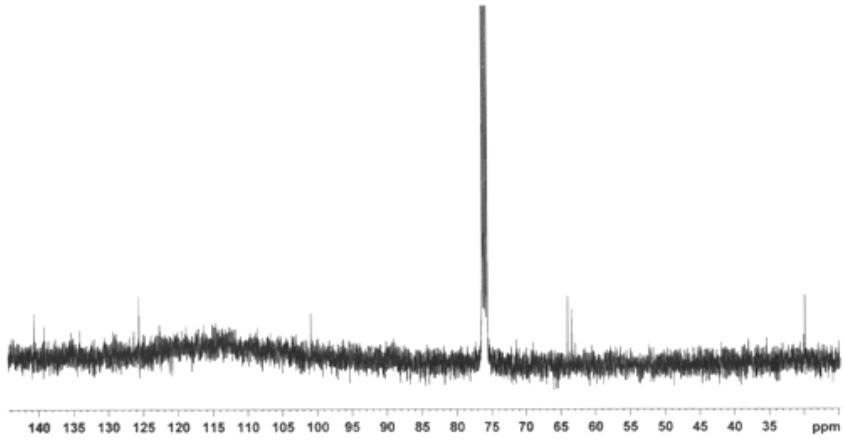


Figure 3. 2 ^{13}C-NMR spectrum of the BDT.

3.1.2 5,8-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl)quinoxaline (DETQ)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (m, 4 H), 4.28 (m, 4H), 6.5(s, 2 H), 6.95 (t, *J*) 3.97 Hz 2 H), 7.40 (d, *J*) 3.57 Hz, 2 H) 7.44(d, *J*) 4.8, 2 H), 8.46 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ63.35, 63.94, 102.05, 112.04, 126.34, 127.34, 127.48, 128.21,128.80, 135.56, 139.27, 140.38, 140.68, 142.89. MS: *m/e* 574 (M+).

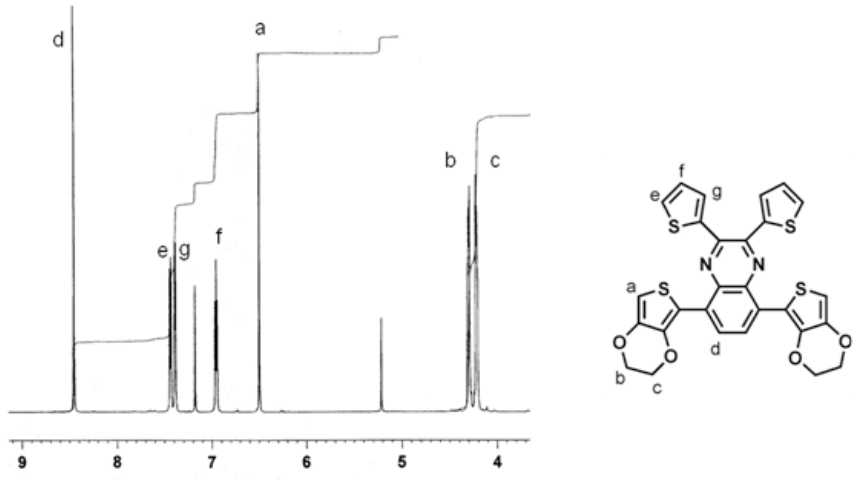


Figure 3. 3 ^{1}H-NMR spectrum of DETQ

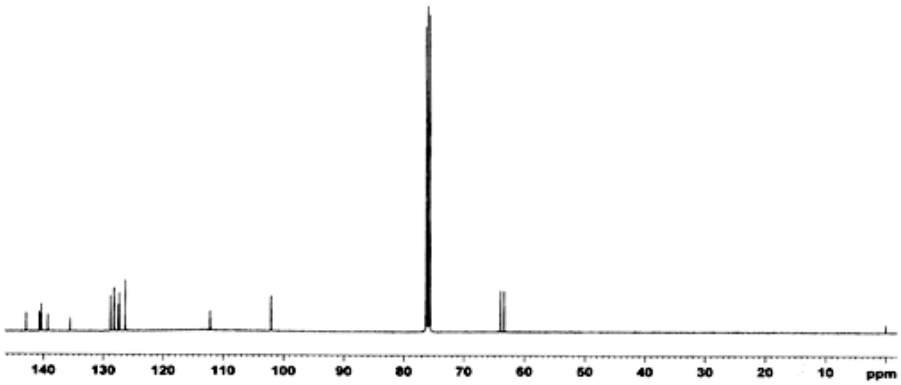


Figure 3. 4 ^{13}C-NMR spectrum of DETQ

3.1.3 5,8-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline (DEQ).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 (m, 4 H), 4.30 (m, 4H),6.48 (s, 2 H), 8.50 (s, 2 H), 8.85 (s, 2 H); ^{13}C NMR (100 MHz,$CDCl_3$) δ 63.33, 63.93, 101.91, 111.86, 127.71, 128.46, 138.78,139.30, 140.35, 141.38. MS: *m/e* 410 (M+).

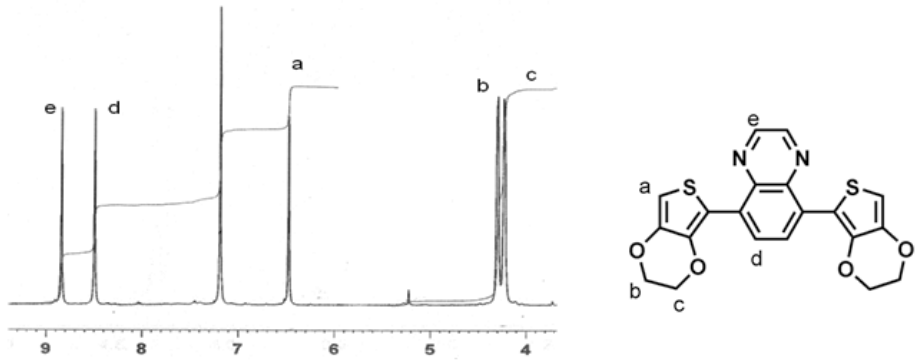


Figure 3. 5 ^{1}H-NMR spectrum of DEQ.

3.2 Electrochemical and Electrochromic Properties of Donor-Acceptor-Donor Type Polymers

3.2.1 Electrochemical and Electrochromic Properties of Poly(4,7-di(2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)benzo[1,2,5]thiadiazole) (PBDT)

3.2.1.1 Electrochemistry of 4,7-Di(2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)benzo[1,2,5]thiadiazole (BDT)

The homopolymer of BDT, PBDT, was synthesized on platinum or indium tin oxide (ITO) coated glass slides by oxidative electropolymerization from a dichloromethane (DCM) solution containing 10^{-2} M BDT and 0.1 M tetrabutyl- ammonium hexafluorophosphate ($TBAPF_6$). Some other electrolytes such as tetrabutylammonium tetrafluoroborate and tetrabutylammonium perchlorate were not as good as this one in terms of polymer film formation on electrodes. The monomer oxidation occurs at 0.95 V vs. Ag wire pseudo reference electrode. (0.01 M $AgPF_6$ in ACN) which is consistent with the previously reported data [84]. A reversible redox process evolved at significantly lower potentials as electroactive PBDT was deposited on ITO (Fig. 3.6).

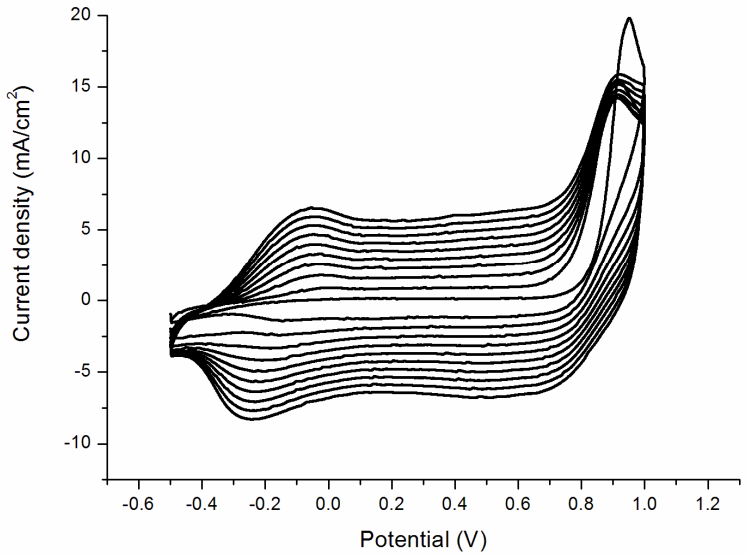


Figure 3. 6 Repeated potential scan electropolymerization of BDT at 100 mV/s in 0.1 M $TBAPF_6$/Dichloromethane (DCM).

The resultant polymer revealed both p and n doping properties where the p doping was indicated by the peak at -0.06 V and -0.26 V due to doping and dedoping. The rare property, n-doping, for conjugated polymer systems was clearly observed by CV studies for PBDT with a definite reversible redox couple with an Epa of -1.13 V and Epc of -1.4 V vs. the same reference electrode. This definite reversible redox couples are important indications for the n-dopable character of the film [85]. Further supporting data on n-doping properties of the polymer is provided in the spectroelectrochemistry section.

As seen in Fig. 3.7 the scan rate dependence of the polymer film was investigated by CV and a true linear relation was observed between the peak current and the scan rate, which indicates the presence of a well adhered electroactive film with a non-diffusion limited redox process [48].

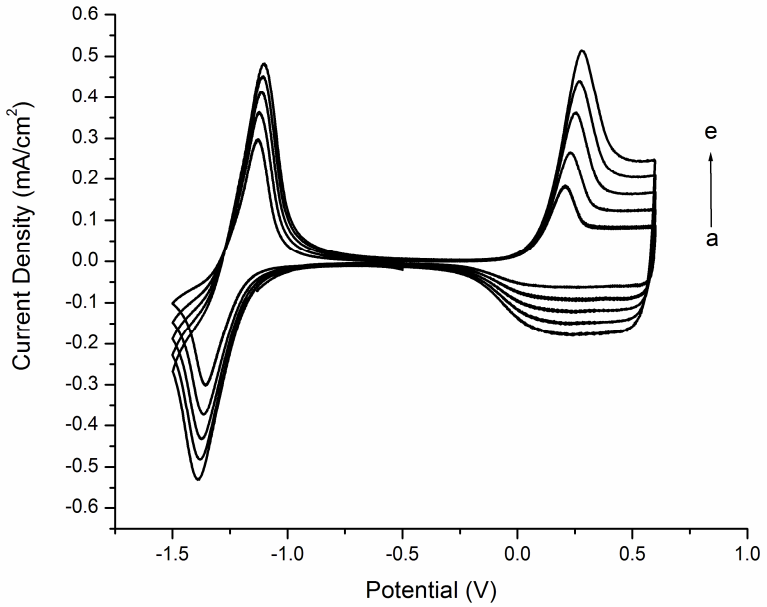


Figure 3. 7 Scan rate dependence of PBDT film in $TBAPF_6$/ACN (a) 100, (b) 150, (c) 200, (d) 250, (e) 300 mV s^{-1}.

3.2.1.2 Optoelectrochemistry and electrochromic switching of 4,7-di(2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)benzo[1,2,5] thiadiazole (BDT)

Spectroelectrochemistry experiments are performed to investigate the optical changes upon doping process.

The spectral behavior of the PBDT was investigated by UV-Vis-NIR spectrophotometer in a monomer free electrolyte system while incrementally increasing the applied potential from -0.8V to +1.1V. Fig. 3.8 illustrates the optoelectrochemistry of the PBDT films. In neutral state the polymer revealed two well separated absorption maxima at 428 nm and 755 nm which are essential

for a true green color to be observed. The band gap of the polymer was calculated as 1.19 eV taking the onset of the second $\pi - \pi^*$ transitions. Polymers with donor–acceptor units exhibit band gaps between 0.9 eV to 1.3 eV in general [68,69].

Upon oxidation of the PBDT film, the intensity of both of the absorption bands in the visible region decreases and a new absorption band in the NIR region arises due to the formation of charge carriers. This decrease in absorption in the visible region makes the polymer film nearly transparent with a residual tail starting from 600 nm. The human eye is not that sensitive. The higher absorption region of the tail begins at 750 nm where human eye is completely insensitive. As Sonmez et al. indicated, the residual pale brown color in the oxidized form of PDDTP (2,3-di(thien-3-yl)-5,7-di(thien-2-yl)thieno[3,4-b]pyrazine), the only example of a true green polymeric material in the literature, was the major problem that hindered possible applications and had to be improved [86].

This enhancement was achieved in our group with PBDT where the polymer not only displays a green color (Y: 376 x: 0.277 y: 0.415) in the neutral state but also a transmissive light blue (Y: 439 x: 0.268 y: 0.323) in the oxidized state. Hence, as previously predicted, this superior polymer can be utilized as the green polymer for RGB applications since poly(3-methylthiophene) (red in the neutral state) and poly(3,4-ethylenedioxythiophene) (blue in the neutral state) already reveal a light blue color in their oxidized state. The spectra of the blue and red polymers in their oxidized states are almost identical. Since the oxidized state of the green polymer also has a similar spectrum, a suitable color filter could be used to bring all the RGB colors to the ‘‘white point’’.

Electrochromic switching studies were performed to monitor the transmittance changes with time during repeated potential stepping between the neutral and oxidized states to differentiate the change in optical contrast. As illustrated in Fig. 3.9, PBDT was switched by stepping the potential between -1.0 and +1.0 V with a switching interval of 5 s in a 0.1 M $TBAPF_6$/ACN electrolyte/solvent system while measuring the transmittance at 428 nm, 755 nm and 1500 nm.

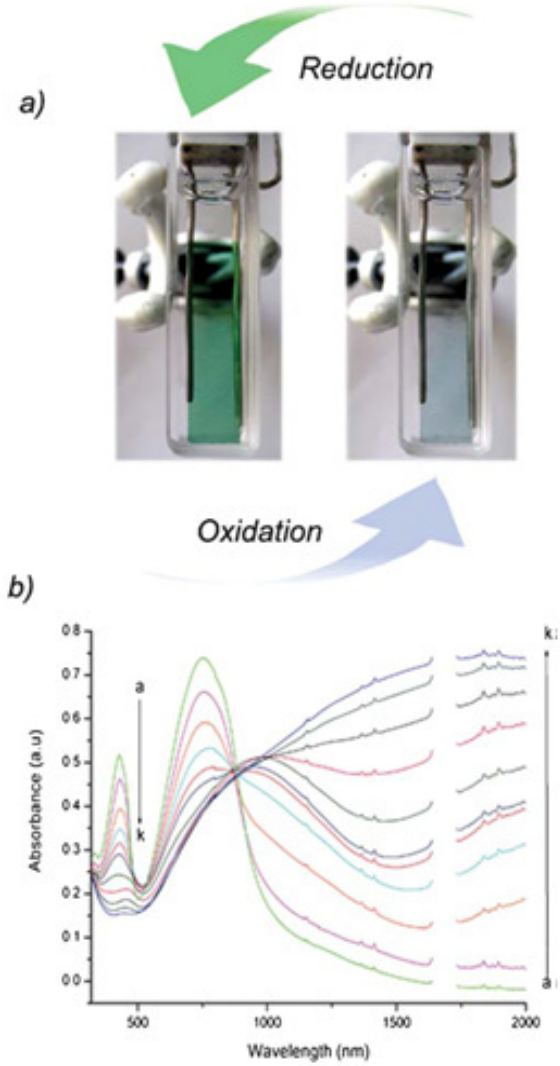


Figure 3. 8 a. Colors of PBDT film on an ITO coated glass slide in theneutral and oxidized states. b. Spectroelectrochemistry of PBDT film on an ITO coated glass slide in monomer-free, 0.1 M $TBAPF_6$–ACN electrolyte–solvent couple at applied potentials; (a) -0.8, (b) -0.5, (c) -0.2, (d) -0.15, (e) 0.0, (f) 0.1 (g) 0.3, (h) 0.5, (i) 0.7, (j) 0.9, (k) 1.1 V.

The PBDT films showed 80 % transmittance at the oxidized and a 43 % transmittance at the neutral state with a remarkable optical contrast of 37 % in the

visible region which is 14 % percent higher than the first green polymer PDDTP [68]. The polymer switches very rapidly and achieves 95 % of its optical contrast in less than 1 s at 428 nm. At 755 nm, which corresponds to the second π– π *transition, the optical contrast was calculated as 23 % with a very fast switching time of 0.4 s. At 1500 nm PBDT films show an outstanding optical contrast of 72 % with a fast switching time of approximately 1 s.

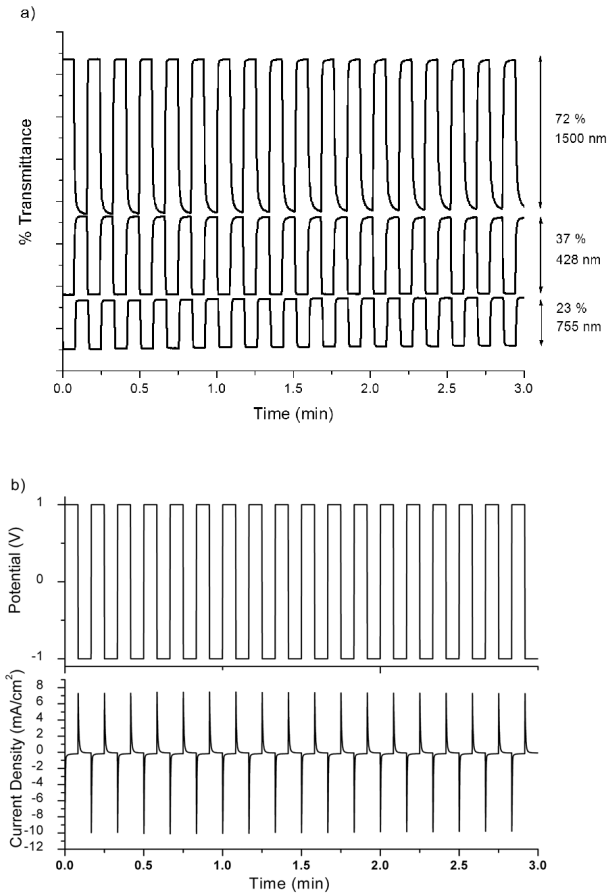


Figure 3. 9 Electrochromic switching; optical absorbance change monitored at 428 and 755 nm and 1500 nm for PBDT in 0.1 M $TBAPF_6$/ACN.

3.2.2 Electrochemical and Electrochromic Properties of 5,8-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl) quinoxaline (DETQ) and 5,8-Bis(2,3-dihydrothieno[3,4-b][1,4] dioxin-5-yl)quinoxaline (DEQ).

3.2.2.1 Electrochemistry of 5,8-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl)quinoxaline (DETQ) and 5,8-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline (DEQ).

The potentiodynamic electropolymerizations of monomers (10 mM) were carried out in 0.1 M $TBAPF_6$/DCM supporting electrolyte-solvent couple. The representative electrochemical growth revealing electroactivities of monomers DETQ and DEQ and formation of corresponding polymers are given in Figures 3.10 and 3.11 respectively. The oxidation of DETQ on a bare electrode starts at 0.7 V and reveals a peak at 0.85 V versus Ag wire pseudo reference electrode in $TBAPF_6$/DCM. The lower oxidation potential of DEQ (+0.6 V) can be attributed to the quinoxaline unit with a low acceptor capacity compared to 2,3-di(thiophen-2-yl)quinoxaline. Redox couples for both monomers rapidly grow at relatively low potentials (-0.3 V, -0.01V for DETQ, and -0.5 V, 0.02 V for DEQ vs. same reference electrode) which signify the formation of highly electroactive polymers.

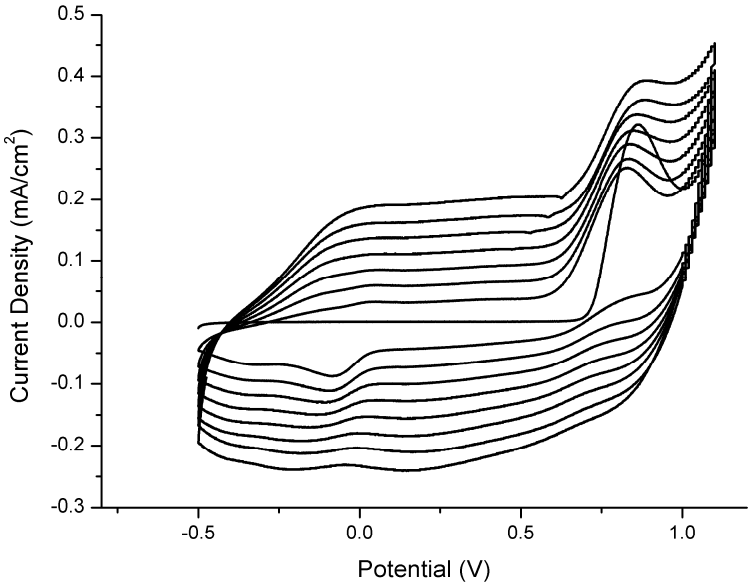


Figure 3. 10 Repeated potential scan electropolymerization of DETQ at 100 mV/s in 0.1 M $TBAPF_6$/DCM on the ITO electrode.

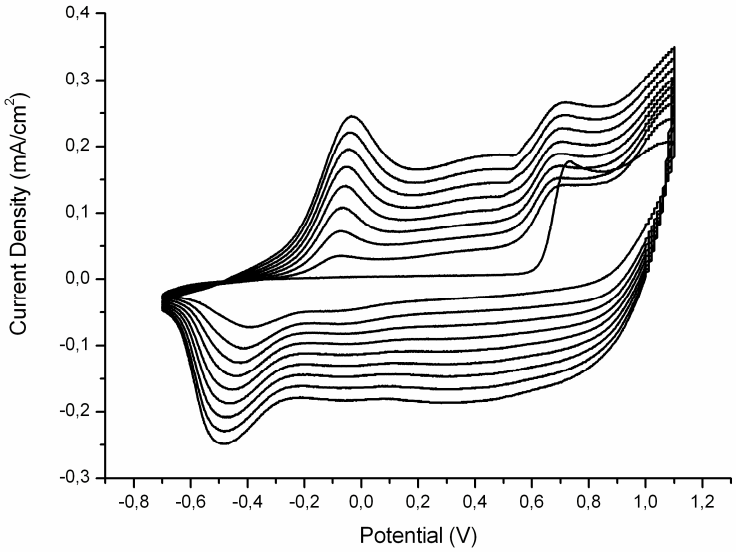


Figure 3. 11 Repeated potential scan electropolymerization of DEQ at 100 mV/s in 0.1 M $TBAPF_6$/DCM on the ITO electrode.

The scan rate dependence of the anodic and cathodic peak currents is illustrated in Figures 3.12 and 3.13 for the polymers. A linear dependence demonstrates that the films were well adhered and the electrochemical processes are reversible and non-diffusion-controlled [39].

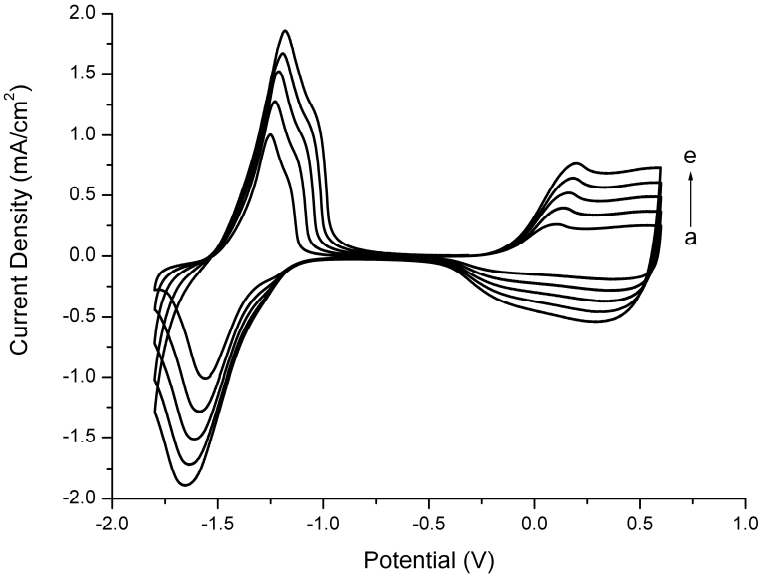


Figure 3. 12 Scan rate dependence of PDETQ film in $TBAPF_6$/ACN at (a) 100, (b) 150, (c) 200, (d) 250, and (e) 300 mV/s.

Using cyclic voltammograms of DETQ and DEQ, anodic to cathodic peak ratios were calculated. The values are very close to 1.0, which is a significant indication for superior reversibility of the redox processes.

The long-term switching stability between doped and neutral states is a crucial property for electrochromic polymers, since these materials have the potential to be used for commercially important device applications. To investigate this characteristic, PDETQ and PDEQ films were deposited on Pt

electrode with repeated scanning in $TBAPF_6$/DCM. The polymer films were washed with monomer-free solution and cycled 5000 times with a scan rate of 200 mV/s in 0.1 M $LiClO_4$/PC (propylene carbonate). The overall charge involved in the electrochemical process was calculated for each voltammogram. Once the polymer electrochemical equilibrations have been reached after 400 cycles, both polymers showed less than 5% decrease upon cycling for 5000 times. Since the charge under the curves remains intact after 5000 cycles, we did not proceed with further cycling. These results indicate that both polymers are extremely stable toward redox cycling, which makes them outstanding candidates for commercial device applications.

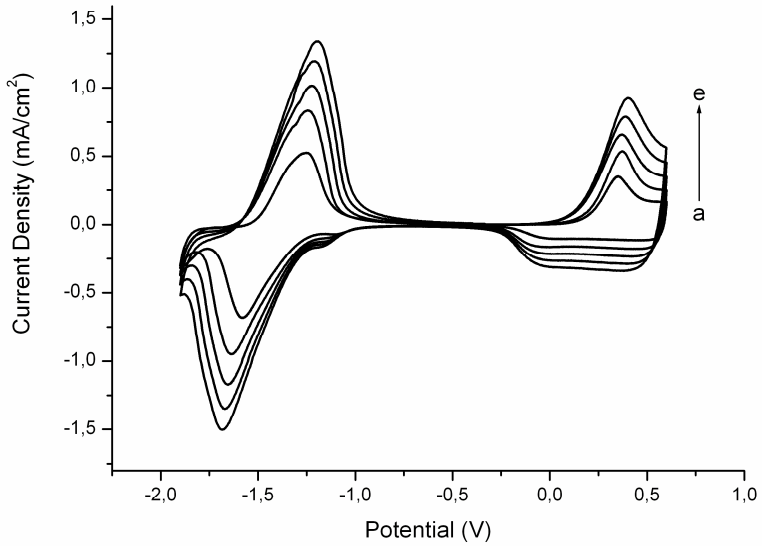


Figure 3. 13 Scan rate dependence of PDEQ film in $TBAPF_6$/ACN at (a) 100, (b) 150, (c) 200, (d) 250, and (e) 300 mV/s.

3.2.2.2 Optoelectrochemistry and electrochromic switching of poly5,8-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl) quinoxaline (PDETQ) and poly5,8-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline (PDEQ).

Polymer films were synthesized on ITO coated glass slides by oxidative electropolymerization in DCM containing 10^{-2} M monomer and 0.1 M $TBAPF_6$. UV–vis-NIR spectra were obtained as a function of applied potential and proved the typical bipolaronic nature of the charge carriers. Both polymers revealed two well-separated absorption maxima, which is a necessity for obtaining a green reduced state [68]. As seen from Figures 3.14 and 3.15, for PDETQ they were at 405 and 780 nm, whereas for PDEQ the absorption maxima were centered at 410 and 660 nm. This observation is attributed to the donor–acceptor match capacity of the polymer backbones. The higher acceptor capacity of 2,3-di(thiophen-2-yl)quinoxaline over quinoxaline, (which is a result of extended conjugation) leads to a better donor–acceptor match since EDOT is known to have a high donor capacity. As observed from the spectra, PDEQ absorption maxima (both higher and lower energy transitions) shifted toward 600 nm which is the absorption maximum of EDOT itself. Hence, the polymer is blue-green (*Y*, 433; *x*, 0.254; *y*, 0.321) in the neutral state. These results imply that as the donor–acceptor match decreases, the resultant polymer is more like the one with the higher capacity. Hence, after examining the spectroelectrochemistry of DEQ we decided to insert a higher acceptor capacity unit in the polymer backbone to synthesize a green polymeric material. This approach worked quite nicely and DETQ exhibited a saturated green color (*Y*, 236; *x*, 0.319; *y*, 0.481) in the neutral state. The band gaps of the polymers were calculated as 1.4 and 1.2 eV respectively for DEQ and DETQ according to the onset of the lower energy π-π^* transitions. The intensities of both absorption bands decreases for both polymers by stepwise oxidation, and a new absorption band in the NIR region appears due to the formation of charge carriers. The PDETQ becomes pale brown (*Y*, 361; *x*, 0.330; *y*, 0.380) in the

oxidized state whereas DEQ has a transmissive blue color (*Y*, 683; *x*, 0.283; *y*, 0.326).

Although the conjugated polymers have significant potential to be n-doped, only a little fraction can exhibit this unique property. The n-type polymers are expected to have a major contribution to organic electronics because it will be possible for the fabrication of light emitting p(*i*)n diodes, bipolar transistors, and the polymeric analogue of the silicon npn, pnp field-effective transistors [56].

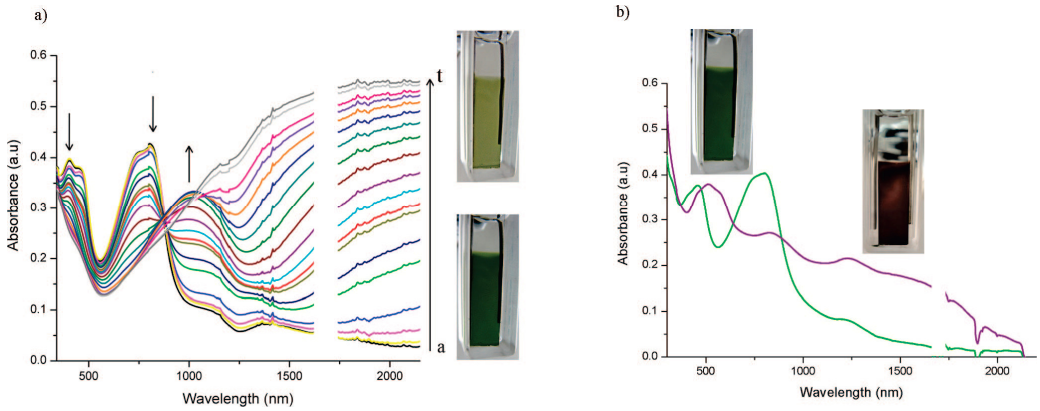


Figure 3. 14 a. p-Doping. Spectroelectrochemistry of PDETQ film on an ITO coated glass slide in monomer-free, 0.1 M $TBAPF_6$/ACN electrolyte-solvent couple at applied potentials (V): (a) -1.0, (b) -0.8, (c) -0.5, (d) -0.4, (e) -0.3, (f) -0.25, (g) -0.2, (h) -0.15, (i) -0.1, (j) -0.05, (k) 0, (l) 0.1, (m) 0.2,(n) 0.3, (o) 0.4, (p) 0.5, (q) 0.6, (r) 0.7, (s) 0.9, and (t) 1.0. b. n-Doping. Spectroelectrochemistry of PDETQ at -1.0 and -1.7 V.

An important aspect is to realize n-doping of a conjugated polymer system is not only the formation of a redox couple at a negative potential. There should be considerable structural and especially optical differences after the introduction of charge carries to the conjugated system. Spectroelectrochemistry studies were performed to probe the optical changes that occur during the n-doping of the

polymer. However, this property was hardly ever investigated in literature with an exception of a few studies [87]. The n-type doping process could not be observed for PDEQ films because EDOT moieties in the structure lead to an electron rich system. For PDETQ the absorption spectrum was recorded at -1.7 V, which is the cathodic potential of the redox couple observed in the reduced state. The optical spectrum was drastically changed to produce a purple color (*Y*, 423; *x*, 0.319; *y*, 0.325). It can be concluded that charge carriers are forming and a true n-type doping process occurs. The reason that PDETQ has an n-type character is most likely the higher capacity of stabilizing negative charge carriers by means of extended conjugation and a better donor–acceptor match. As more negative potentials were applied, the polymer film degrades because of over-reduction.

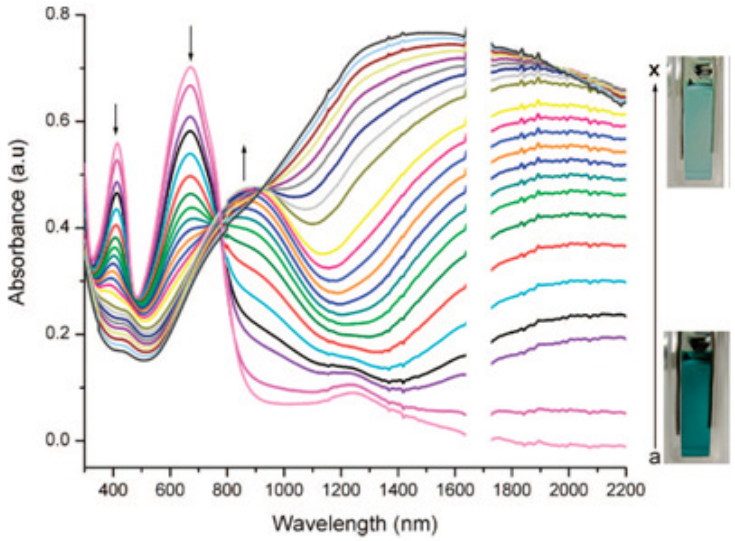


Figure 3. 15 Spectroelectrochemistry of PDEQ film on an ITO coated glassslide in monomer-free, 0.1 M $TBAPF_6$/ACN electrolyte-solvent couple atapplied potentials (V): (a) -1.0, (b) -0.6, (c) -0.5, (d) 0.0, (e) 0.05, (f)0.1, (g) 0.15, (h) 0.2, (i) 0.25, (j) 0.3, (k) 0.35, (l) 0.4, (m) 0.45, (n) 0.5, (o)0.55, (p) 0.6, (q) 0.65, (r) 0.7, (s) 0.75, (t) 0.8, (u) 0.85, (v) 0.9, (w) 0.95,and (x) 1.0.

Optical switching studies were examined for probing changes in transmittance while repeatedly stepping the potential between fully neutral and oxidized states. The polymer films were deposited on ITO glass slides by repeated scanning (40 cycles) in $TBAPF_6$/DCM. Throughout the experiment, the percent transmittance (*T*%) values at different wavelengths including both of the absorption maxima of both polymers were measured using a UV–vis-NIR spectrophotometer as the polymer films were switched between -1.0 V and +1.0 V with a residence time of 5 s. The results are shown in Figures 16 and 17. The optical contrasts for PDETQ were calculated as 20 % at 405 nm, 30 % at 780 nm, and 84 % at 1800 nm. The optical contrast for the second transition at around 780 nm is excellent while the other two are almost the same compared to that of the first example of green polymeric material [68] (12 % at 725 nm, 23 % at 370 nm, and 85 % at 1600 nm).

The optical contrast values for PDEQ are even better than those of PDETQ in the visible region in with 36 % transmittance change at 410 nm and 30 % at 660 nm. The PDEQ film revealed a 74 % optical contrast in the NIR region. The polymers switch very rapidly between their neutral and oxidized states and achieve 95% of their optical contrasts in the visible region in less than 1 s. PDETQ revealed impressing switching times of 0.72 s at 405 nm and 0.9 s at 780 nm. The polymer achieves an outstanding optical contrast of 84 % in the NIR region in only 1.5 s. PDEQ has exceptional switching times of 1 s at 410 nm and 0.72 s at 660 nm as well. No more than 1 s is required for PDEQ films to accomplish an excellent optical contrast of 74 % at 1450 nm.

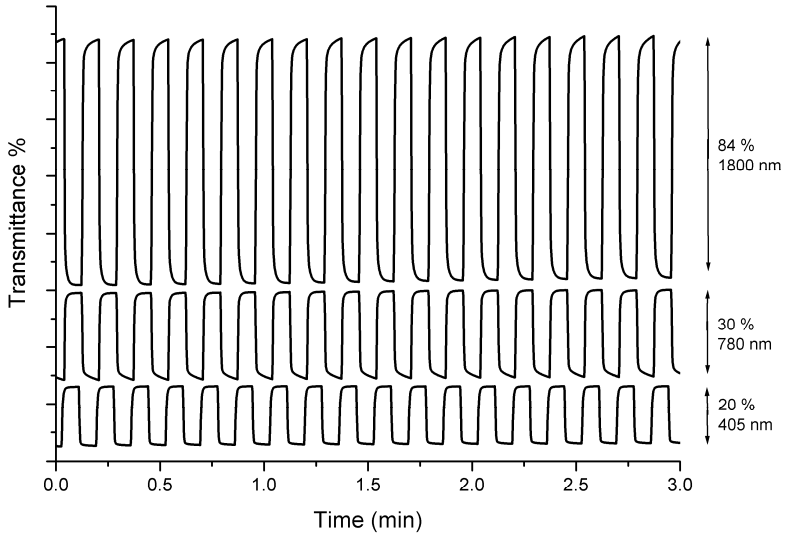


Figure 3. 16 Electrochromic switching and optical absorbance change monitored at 405, 780, and 1800 nm for PDETQ in 0.1 M $TBAPF_6$/ACN.

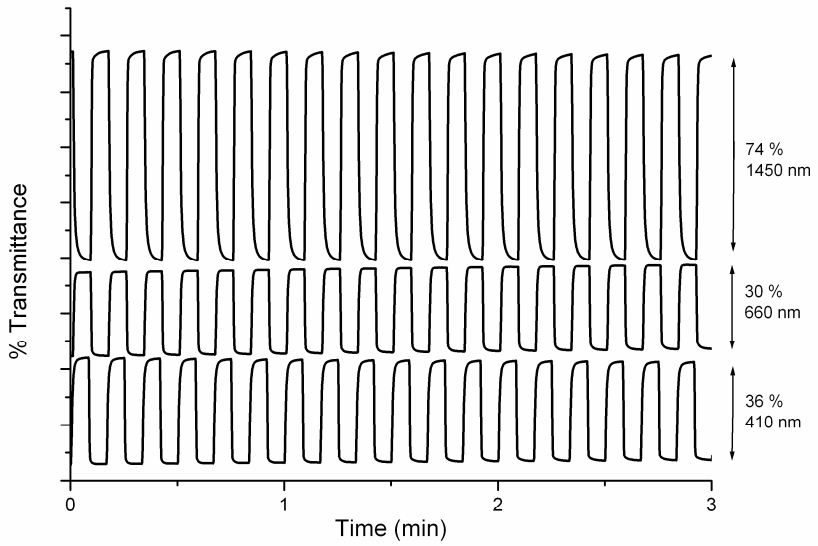


Figure 3. 17 Electrochromic switching and optical absorbance change monitored at 410, 660, and 1450 nm for PDEQ in 0.1 M $TBAPF_6$/ACN.

CHAPTER 4

CONCLUSION

The D-A-D type monomers were synthesized via Stille coupling reactions and full characterization of the materials were performed by NMR and mass analyses. The polymers of the corresponding monomers were synthesized by electrochemical methods. Cyclic voltammetry experiments, spectroelectrochemistry, kinetic studies and long-term switching experiments for all the polymers were performed in order to determine the electrochemical and electrochromic properties.

PBDT is the first green electrochromic material which has a highly transmissive sky blue oxidized state. It reveals nearly 40 % optical contrast in the visible and 70 % in the NIR region with exceptional switching properties and remarkable stability. PBDT showed superior properties compared to the first example of the neutral state green polymeric material, PDDTP. PBDT is tremendously stable. No considerable charge loss is observed after 5000 cycles. P BDT revealed a coloration efficiency of 130 cm^2 C^{-1}, which is almost identical with that of PEDOT. Hence, PBDT is the paramount choice for the ECD applications.

Furthermore, two novel EDOT-bis-substituted quinoxaline monomers were synthesized via Stille coupling reaction. They were electrochemically polymerized to investigate their potential use as neutral state green electrochromic material. PDEQ has a bluish green color in the neutral state and a highly transmissive light blue oxidized state. The polymer revealed high optical contrasts in both visible and NIR regions with excellent switching properties and stability. PDETQ was shown to be one of the few examples of neutral state green polymeric materials in literature. The polymer revealed relatively high optical

contrasts in the visible region and an excellent optical contrast of 84 % in the NIR. Exceptional stability and very fast switching times make this neutral state green polymer a robust candidate for completion of RGB color space. Moreover, the existence of the n-type doping process was proven by both electrochemical and spectral analyses for PDETQ films. Considering these advanced properties, many quinoxaline derivatives can be utilized in the polymer backbone for synthesis of new superior polymers for electrochromic device applications. Specifically, the introduction of substituents having long alkyl chains can drastically improve solubility and might be of high interest for the production of processable green electrochromics for many display applications.

REFERENCES

1. C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, A. J. Heeger, and H.Shirakawa, E. J. Louis ,S. C. Gau, Alan G. MacDiarmid, Phys. Rev.Letters, 39 (1977) 17
2. H. Shirakawa, E.J. Louis, A.G. MacDiarmid, C.K. Chiang, A.J. Heeger, J. Chem. Soc. Chem. Commun. (1977) 578
3. A.F. Diaz, Chem. Scr. 17 (1981) 142
4. G. Tourillon, F.J. Garnier, J. Electroanal. Chem. 135 (1982) 173
5. A.F. Diaz, K.K. Kanazawa, G.P. Gardini, J. Chem. Soc., Chem. Commun. (1979) 635
6. G. Grem, G. Leditzky, B. Ullrich, G. Leising, Adv. Mater. 4 (1992) 36
7. J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. MacKay, R.H. Friend, P.L. Burn, A.B. Holmes, Nature 347 (1990) 539
8. J. Rault-Berthelot, J. Simonet, J. Electrochem. Soc. 182 (1985) 187
9. A.G. MacDiarmid, A.J. Epstein, Faraday Discuss. Chem. Soc. 88 (1989) 317
10. T.L. Rose, S. D'Antonio, M.H. Jillson, A.B. Kon, R.Suresh, F. Wang, Synth. Methals 85 (1997) 1439
11. M.A. DePaoli, W.A. Gazotti, J. Braz. Chem. Soc., 13 (2002) 410
12. G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, Science 270 (1995) 1789
13. H. Koezuka, A. Tsumura, T. Ando, Synth. Met. 18 (1987) 699
14. J. l. Reddinger, J. R. Reynolds, Adv. Polym. Sci. 45 (1999) 59
15. G. Blasse, B.C. Grabmaier, Luminescent Materials, Springer-Verlag (1994)
16. a)M. Pomerantz, In Handbook of Conducting Polymers; 2nd ed.: b) T. A. Skotheim, R. L. Elesenbaumer, J. R. Reynolds, Ed: Marcel Dekker: New York, (1998) 227

17. M. Salmon, A.F. Diaz, A.J. Logan, M. Krounbi, J. Bargon, J Mol Cryst Liq Cryst 83 (1983) 1297
18. M. G. Kanatzidis, Chem. Eng. News, 68 (1990) 36
19. P. Chandrasekhar, Conducting Polymers Fundamentals and Applications, Boston, Kluwer Academic Publishers, (1999) Ch. 2
20. A. G. MacDiarmid, A. J. Heeger, Synthetic Metals, 1 (1979) 101
21. A. D. Child, J. R. Reynolds, J. Chem. Soc., Chem. Commun. (1991) 1779
22. A. G. MacDiarmid, Angew. Chem. Int. Ed., 40 (2001) 2581
23. S. Alkan, L. Toppare, Y. Hepuszer, Y. Yağcı, J. Polym. Sci. Part A: Polym. Chem. 37 (4218) 1999
24. D. Kumar, R. C. Sharma, Eur. Poly. J., 34 (1998) 1053
25. G. Schopf, G. Kossmehl, Adv. Polym. Sci., 129 (1997) 166
26. L. B. Groenendaal, G. Zotti,P. H. Aubert, S. M. Waybright, J. R. Reynolds Adv. Mater. 15 (2003) 855
27. R. J. Mortimer, A. L. Dyer, J. R. Reynolds, Displays 27 (2006) 2
28. A. F. Diaz, A. Martinez, K. K. Kanazawa, M. M. Salmon, J. Electroanal. Chem. 130 (1981) 181
29. J. R.Reynolds, S. G. Hsu, H. J. Arnott, J. Polym. Sci. Pol. Part B. Polym. Physic. 27 (1989) 2081.
30. K. Gurunathan, A.V. Murugan, R. Marimuthu, U.P. Mulik, D.P. Amalnerkar, Mater. Chem. Phys. 61 (1999) 173
31. S.F. Cogan, R.D. Rauh, J.D. Westwood, D.I. Plotkin,R.B. Jones, Proc. SPIE 1149 (1989) 2
32. (a) S. K. Deb, Appl. Opt., Suppl. 1969, No. 3, 192-195. (b) S. K. Deb, Philos. Mag. 27 (1973) 801
33. (a) C. G. Granqvist, Sol. Energy Mater. Sol. Cells 60 (2000) 201 (b) C. G. Granqvist, E. Avendano, A. Azens, Thin Solid Films 442 (2003) 201. (c) B. W. Faughnan, R. S. Crandall, P. M. Heyman, RCA Rev. 36 (1975) 177
34. D. R. Rosseinsky, R .J. Mortimer, Adv. Mater. 13 (2001) 783

35. M. A. Habib, Electrochem. Transition (1992) 51
36. R.J. Mortimer, Electrochimica Acta 44 (1999) 2971
37. P. R. Somani, S. Radhakrishnan, Mater. Chem. Phys. 77 (2003) 117
38. (a) U. Bach, D. Corr, D. Lupo, F. Pichot, Ryan, M. Adv. Mater. 14 (2002) 845. (b) D. Corr, U. Bach, D. Fay, M. Kinsella, C. McAtamney, F. O'Reilly, S. N. Rao, N. Stobie, Solid State Ionics, 165 (2003) 315
39. G. Sonmez, I. Schwendeman, P. Schottland, K. Zong, J. R. Reynolds Macromolecules 36 (2003) 639
40. K. Fesser, A. R. Bishop, D. K. Campbell, Phys. Rev. B 27 (1983) 4804
41. a) Bayer AG, Eur. Patent 339 340, 1988. b) F. Jonas, L. Schrader, Synth.Met. 41 (1991) 831. c) G. Heywang, F. Jonas, Adv. Mater. 4 (1992) 116 d) I. Winter, C. Reece, J. Hormes, G. Heywang, F. Jonas, Chem.Phys. 194 (1995) 207
42. a) J. Roncali, Chem. Rev. 97 (1997) 173 b) J. L.Bredas, J. Chem Phys. 82 (1985) 3808
43. F. Wudl, M. Kobayashi, A. J. Heeger, J. Org. Chem. 49 (1984) 3382
44. M. Pomerantz, B. Chalonner-Gill, M. O. Harding, J. J. Tseng,W. J. Pomerantz, J. Chem. Soc., Chem. Commun. (1992) 1672
45. a) S. Y. Hong, D. S. Marynick, Macromolecules 25 (1992) 4652 b) G. A. Sotzing, K. Lee, Macromolecules 35 (2002) 7281
46. C. J. Dubois, PhD Thesis, Uniersity of Florida, (2003)
47. S. A. Sapp, G.A. Sotzing, J. R. Reynolds, Chem. Mater. 10 (1998) 2101
48. A. Kumar , D. M. Welsh, M.C. Morvant, F. Piroux, K. A. Abbound, J. R. Reynolds, Chem. Mater. 10 (1998) 896
49. P. Schottland, K. Zong, C. L. Gaupp, B. C. Thompson, C. A. Thomas, I. Giurgiu, R. Hickman, K. A. Abound, J. R. Reynolds, Macromolecules 33 (2000) 7051
50. G. A. Sotzing, J. L. Reddinger, A. R. Katritzy, J. Soloducho, R. Musgarave, J. R. Reynolds, Chem. Mater 9 (1997) 1578.
51. G. A. Soltzing ,J. R. Reynolds, J Chem. Soc. Chem. Commun (1995) 703

52. T. Yamamoto, Z. H. Zhou, T. Kanbara, M. Shimura, K. Kizu, T. Maruyama, Y. Nakamura, T. Fukuda, B. L. Lee, N. Ooba, S. Tomaru, T. Kurihara, T. Kaino, K. Kubota, S. Sasaki, J. Am. Chem. Soc. 118 (1996) 10389
53. A. K. Agrawal, S. A. Jenekhe, H. Vanherzeele, J.S. Meth, J. Phys. Chem. 96 (1992) 2837
54. C. A. Thomas, PhD Thesis, University of Florida, (2002)
55. S. Tanaka, J. R. Reynolds, J. Macro. Sci., Pure Appl. Chem. A32 (1995) 1049
56. D. M.de Leeuw, M. M. J.Simenon, A. R.Brown, R. E. F.Einerhand, Synth. Met. 87 (1997) 53
57. G. Brocks, A. Tol, J. Phys. Chem., 100 (1996) 1838
58. H.J. Ahonen, J. Lukkari, J. Kankare, Macromolecules 33 (2000) 6787
59. C. B. Gorman, R. C.West, T. U.Palovich, S.Serron, Macromolecules 32 (1999) 4157
60. M.Kosugi, K. Sasazawa, Y. Shimizu, T. Migita Chem. Letters (1977) 301
61. D. Milstein, J. K. Stille, J. Am. Chem. Soc. 100 (1978) 3636
62. A. F. Littke, L. Schwarz, G. C. Fu, J. Amer. Chem. Soc., 124 (2002) 6343
63. O. A. King, N. Okukado, E. Negishi J. Chem. Soc. Chem.Commun (1977) 683
64. I. H. Jenkins, N. G. Rees, P. G. Pickup, Chem. Mater. 9 (1997) 1213
65. (a) I. H. Jenkins, U. Salzner, P. G. Pickup, Chem. Mater. 8 (1996) 2444 (b) T. Kanbara, Y. Miyazaki, T. J. Yamamoto, Polym. Sci.. Part A: Polym. Chem. 33 (1995) 999 (c) B.-L. Lee, T. Yamamoto, Macromolecules 32 (1999) 1375 (d) M. Onoda, J. Appl. Phys. 78 (1995) 1327 (e) N. Saito, T. Kanbara, T. Kushida, K. Kubota, T.Yamamoto, Chem. Lett. (1993) 1775 (f) T. Yamamoto, J. Polym. Sci., Part A: Polym. Chem. 34 (1996) 997 (g) K. B.Wiberg, T. P.Lewis, J. Amer. Chem. Soc. 92 (1970) 7154

66. (a) R. E. Martin, J. A. Wytko, F. Diederich, C. Boudon, J.-P. Gisselbrecht, M. Gross, Helv. Chim. Acta, 82 (1999) 1470 (b) H. Wang, R. Helgeson, B. Ma, F. Wudl, J. Org. Chem. 65 (2000) 5862
67. G. A. Sotzing, J. R.Reynolds, P. J.Steel, Adv. Mater. 9 (1997) 795
68. G. Sonmez, C. K. F. Shen, Y. Rubin and F. Wudl, Angew. Chem., Int. Ed. 43 (2004) 1498
69. A. Berlin, G. Zotti, S. Zecchin, G. Schiavon, B. Vercelli, A. Zanelli Chem.Mater. 16 (2004) 3667
70. U. Salzner, M.E. Kose, J. Phys. Chem. B. 106 (2002) 9221
71. E. E. Havinga, W. Ten Hoeve, H. Wynberg, Polym. Bull. 29 (1992) 119
72. P. Nils-Krister, S. Mengtao, K. Par, P. Tonu, I. Olle, J. Chem. Phys. 123 (2005) 204718
73. H. A. M. van Mullekom, J. A. J. M. Vekemans, E. E. Havinga, and E. W.Meijer, Mater. Sci. Eng., R., 32 (2001) 1
74. U. Salzner, J. Phys. Chem. B. 106 (2002) 9214
75. K. Kaneto, Y. Kohno, K. Yoshino, Y. Inushi, J. Chem. Soc. Chem.Commun. 382 (1983)
76. Q. T. Zhang, J. M. Tour, J. Am Chem. Soc., 119 (1997) 5065
77. B. C. Thompson, P. Schottland, K. Zong, J. R. Reynolds Chem. Mater. 12 (2000) 1563
78. B. A. Da Silveira Neto, A. Sant'Ana Lopes, G. Ebeling, R. S. Goncalves, V. E. U. Costa, F. H. Quina, J. Dupont, Tetrahedron 61 (2005) 10975
79. Y. Tsubata, T. Suzuki, T. Miyashi, Y. J. Yamashita, J.Org. Chem. 57 (1992) 6749
80. M. J. Edelmann, J.-M. Raimundo, N. F. Utesch, F. Diederich, HelV.Chim. Acta, 85 (2002) 2195
81. H. Becker, K. Treacher, H. Spreitzer, A. Falcou, P. Stoessel, A. Buesing, A. Parham, PCT International Patent WO 2003020790, (2003)
82. S. S. Zhu, T. M. Swager, J. Am. Chem. Soc. 119 (1997) 12568

83. D. Aldakov, M. A. Palacios and P. Anzenbacher, Jr., Chem. Mater. 17 (2005) 5238
84. P. Blanchard, J. M. Raimundo and J. Roncali, Synth. Met. 119 (2001) 527
85. J. Lee, B. Jung, S. Lee, J. Lee, H. Cho, H. Shim J. Polym. Sci. Part. A:Polym. Chem. 43 (2005) 1845
86. G. Sonmez, Chem. Commun. 42 (2005) 5251
87. C. J. DuBois, K. A. Abboud, J. R. Reynolds, J. Phys. Chem. B 108 (2004) 8550