SYNTHESIS OF NEW CONJUGATED DONOR-ACCEPTOR TYPE POLYMERS FOR PHOTOVOLTAIC DEVICE APPLICATIONS

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

BY

HAVA ZEKİYE AKPINAR

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY
IN
POLYMER SCIENCE AND TECHNOLOGY

MAY 2015

Approval of the thesis:

SYNTHESIS OF NEW CONJUGATED DONOR-ACCEPTOR TYPE POLYMERS FOR PHOTOVOLTAIC DEVICE APPLICATIONS

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ABSTRACT

SYNTHESIS OF NEW CONJUGATED DONOR-ACCEPTOR TYPE POLYMERS FOR PHOTOVOLTAIC DEVICE APPLICATIONS

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May 2015, 104 pages

Electrochromism and photoelectric effect are the mostly investigated areas of conducting polymers. In electrochromism, electrochemical parameters of the polymers are firstly examined. Spectroelectrochemical studies are performed with specified wavelengths. Parameters, such as optical contrast and switching times of the polymer films are explored. In bulk heterojunction polymer solar cells, semiconducting polymer materials in combination with fullerene are used as the active layer. Photons are absorbed by conjugated polymer and strongly bounded excitons are formed. In order to efficiently separate the bounded electron hole pairs, HOMO and LUMO levels of the polymer and fullerene should be compatible with each other. The performance of the devices is also highly dependent on the molecular structure of the polymer side chains. In this thesis study, five novel conjugated polymers containing donor-acceptor units such as thiazolothiazole, thiophene, furan, benzotriazole and fluorene were synthesized via Suzuki and Stille coupling polymerizations. Electrochemical and optical properties of the polymers were examined and bulk heterojunction organic photovoltaic devices were fabricated using (C 61) fullerene. Solar cell parameters such as open circuit voltage, short circuit current density, fill factor and power conversion efficiency were measured.

Keywords: Conducting Polymers, electrochromism, polymer solar cells, thiazolothiazole.

ÖZ

YENİ DONÖR-AKSEPTÖR TİPİ POLİMERLERİN SENTEZİ VE FOTOVOLTAİK UYGULAMALARI

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Mayıs 2015, 104 sayfa

İletken polimerlerde elektrokromism ve fotoelektrik etki en çok araştırılan alanlardır. Elektrokromik çalışmalarda ilk olarak polimerlerin elektrokimyasal özellikleri incelenir. Belirlenen dalga boylarında spektroelektrokimyasal çalışmalar gerçekleştirilir. Polimer filmlerin optik kontrast ve dönüşüm zamanı gibi parametreleri incelenir. Bulk heterojunction güneş pillerinin aktif katmanında, yarı iletken polimerler fullerene ile karışım halde kullanılır. Fotonlar kullanılan konjuge polimer tarafından absorplanır ve eksitonlar oluşur. Oluşturulan elektron-boşluk çiftlerinin verimli bir şekilde ayrılabilmesi için polimerin ve fullerenin HOMO ve LUMO seviyelerinin uyum içerisinde olması gerekir. Pil performansı ayrıca, polimere bağlı yan gruplar ile de ilgilidir. Bu tez çalışmasında, Suzuki ve Stille birleşme reaksiyonları kullanılarak tiyazolotiyazol, tiyofen, furan, benzotriazol ve fluoren gibi donor-akseptör gruplar içeren 5 yeni polimer sentezlenmiştir. Polimerlerin elektrokimyasal ve optic özellikleri incelenmiştir. (C 61) PCBM kullanılarak bulk heterojunction güneş pilleri yapılmış ve açık devre potansiyeli, kısa devre akım yoğunluğu, dolum faktörü, güç çevrim verimi ve fotonun akıma dönüşüm verimi gibi parametreler hesaplanmıştır.

Anahtar Kelimeler: İletken polimerler, elektrokromism, polimer güneş pilleri, tiyazolotiyazol.

To My Twin Brother, Süleyman

ACKNOWLEDGMENTS

I would like to express my sincere appreciations to my supervisor Prof. Dr. Levent Toppare for his diligent guidance, advice, endless patience and enthusiasm for science. I am grateful to him not only scientific instructions but also his valuable contributions all steps of real life.

I would like to express my deepest gratitude to my co-advisor Prof. Dr. Necati Özkan for his support and consideration.

I would like to give my special thanks to Assoc. Prof. Dr. Yasemin Arslan Udum, Fulya Ekiz Kanık, Ayda Göyçek Nurioğlu, and Melike Karakuş for sharing their knowledge on electrochromism, guidance and motivation during my studies and real friendship.

I want to give many thanks to Seval Ataman, Tuğba Kaya Deniz and Saniye Söylemez for the great friendship, endless laughs, help and discussions.

I would like to thank all Toppare Research Group members for their collaborations and kind friendships.

Thanks to Dr. Eric Glowacki and Dr. Matthew White for helpful discussion and training during the visit to LIOS where a part of this work was performed.

Words fail to express my eternal gratitude to my parents and my brother Süleyman Akpınar for their insistently support, endless love, always believing in me and motivation during all my life. I am grateful to them for their financial support during my entire career and every single thing makes me stronger.

I want to express my sincere thanks to my husband, Yakup Kaya, for his patience, great love, always encouraging me and never let me alone. I also would like to express my great attitude to him for being my best friend besides his everlasting love and always supporting me whoever I am.

Finally, I would like to thank METU Chemistry Department for supporting research.

TABLE OF CONTENTS

CHAPTERS

APPENDICES

LIST OF FIGURES

FIGURES

LIST OF TABLES

TABLES

ABBREVIATIONS

ACN	Acetonitrile
BIM	Benzimidazole
BTD	Benzothiadiazole
BTZ	Benzotriazole
CB	Conducting band
$CDCl_3$	Chloroform-d
CP	Conducting Polymer
DA	Donor – acceptor
DAD	Donor-acceptor-donor
DCM	Dichloromethane
DFT	Density functional theory
DMF	Dimethylformamide
DOTs	Dioxythiophenes
ECDs	Electrochromic devices
EDOT	3,4-Ethylenedioxythiophene
Eg	Band gap
ETL	Electron transport layer
HOMO	Highest Occupied Molecular Orbital
HTL	Hole transport layer
GPC	Gel permeation chromatography

ITO	Indium tin oxide
LED	Light emitting diodes
LiF	Lithium Fluoride
LUMO	Lowest Unoccupied Molecular Orbital
NIR	Near-infrared
NBS	N-Bromosuccinimide
OFET	Organic Field Effect Transistors
OLED	Organic Light Emitting Diodes
OPVs	Organic photovoltaics
PAc	Polyacetylene
PEDOT	Poly(2,3-dihydrothieno[3,4-b][1,4]dioxine)
PEDOT:PSS	Poly(2,3-dihydrothieno[3,4-b][1,4]dioxine):Polystyrene sulfonate
PF	Polyfuran
PFO	Polyfluorene
PP	Polyphenylene
PproDOT	Poly(3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine
PPV	Polyphenylenevinylene
PPy	Polypyrrole
PTh	Polythiophene
RGB	Red-green-blue
VB	Valence band

TGA	Thermal Gravimetric Analysis
THF	Tetrahydrofuran
TMS	Tetramethylsilane
TTz	Thiazolo[5,4-d]thiazole

CHAPTER 1

INTRODUCTION

1. Conducting Polymers

Invention of conducting polymers opened a new era in the construction of organic electronics. [1] Consequently, it is a special topic having special interest from quite a number of researchers all over the world and published several works on their properties and application areas since their discovery. [2-9] Conducting polymers basically defined as long conjugated chains, which have ability to conduct electricity. Conducting capability of a material depends on its energy gap between its conducting band (LUMO; lowest unoccupied molecular orbital) and its valence band (HOMO; highest occupied molecular orbital). (Figure 1.1.)

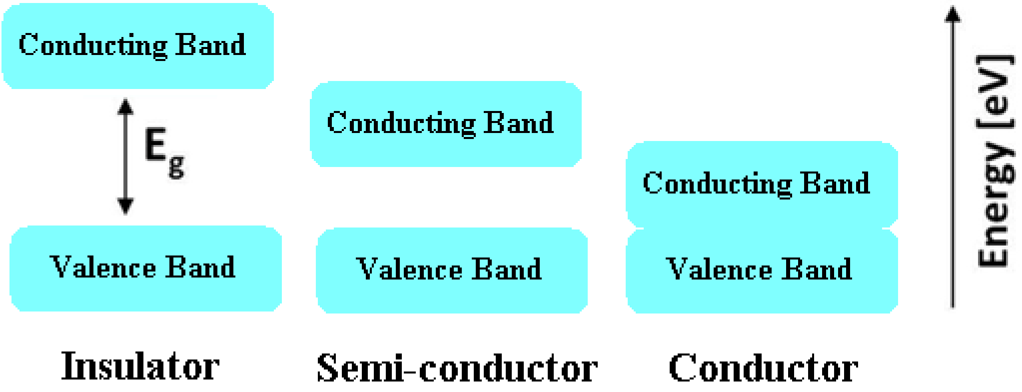


Figure 1. 1 Band structures of conductor, semi-conductor and insulator.

As it is seen in the figure, there is no gap in conductors, on the contrary, the gap between valence band and conducting bands are very high in insulators. As for the semiconductors, the gap between the energy levels is somewhere between the insulators and the metal-like materials. Semiconducting polymers need energy for excitation of an electron from its valence band to its conducting band. This energy should be equal or higher than their band gaps.

Conjugated materials simply are chains having alternating single and double bonds. Delocalization of the electrons through the backbone resulted in conductivity. (Figure 1.2.)

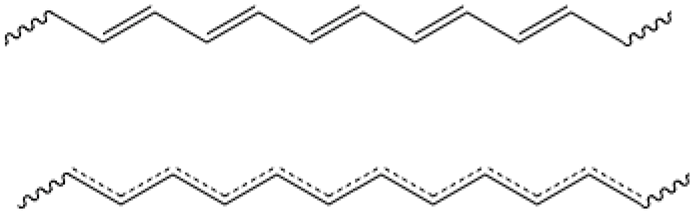


Figure 1. 2 Delocalization of double bonds in polyacetylene.

After well understanding of polymer engineering in structure modification, alternating donor and acceptor group containing conjugated polymers attracted great attention. One of the most desirable properties of these types of polymers is their low band gap, which is necessary for applications especially in photovoltaics. Narrow band bap is also important for electrochromism since it makes easier to switch between the two extreme states of the polymers using small potential differences. That is why; recent efforts on conjugated polymers are focused on arranging energy levels of the resulting polymer which is the characteristic that should be determined before further investigation.

2. Application of Conducting Polymers

The usefulness of conducting polymers originates from the point where they can be tailored for use in different plenty of applications. Electrochromism [10], polymer solar cells [11], organic light emitting diodes [12], biosensors [13], and organic field effect transistors [14] are common ones.

Modification capability of conducting polymers makes them more useful in the intended area of use. As an example, introducing alkyl chains to the polymer's backbone satisfies solubility, which is indispensable for developing low cost and large area optoelectronic devices. [15]

In this thesis, electrochromism and solar cell behaviour of the conducting polymers are the major topics among all these application areas. That is why, there will be given basic definitions and related information about the electrochromism and the polymer solar cells in the following sections.

3. Electrochromism

As it is mentioned before, conducting polymers have various types of applications. Electrochromism is one of these application areas due to its exciting potential application fields such as flexible displays [16] and military camouflage [17].

Colors of the electrochromic polymers can be changed in between their excited states upon applied external potentials. In principle, when an electrochromic material is excited to an upper state, the region it absorbs in the spectrum changes and this is resulted in a change of color it emits. (Figure 1.3.)

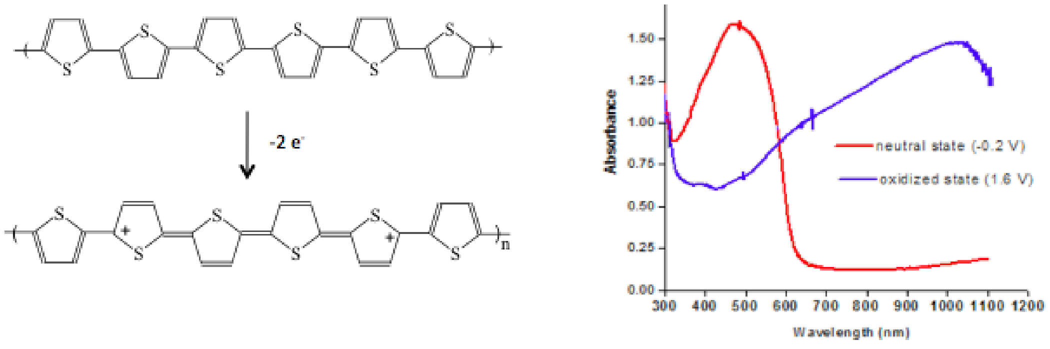


Figure 1. 3 Absorption bands of neutral and doped polythiophene.

Electrochromic effect of the materials is known for a long time and there exist quite a number of researches on them. Transition metal oxides (e.g. WO_3, V_2O_5), purissian blue systems (e.g. $[Fe^{III}Fe^{II}(CN)_6]^-$), viologens (e.g. 1,1`Disubstituted-4,4`-bipyridinum salts) and conducting polymers are the well known ones. Polymers have superior advantageous over their counterparts. Some of them are easy processing, low cost, large number of colors and very high contrast ratio. [18] Electrochromic parameters such as redox potentials, switching ability and optical contrast of an electrochromic polymer vary their conjugation length, packing ability and band gap. In the following section, these parameters will be explained.

4. Parameters of Electrochromism

Redox potentials of electrochromic polymers are usually characterized by cyclic voltammetry, which is a useful electrochemical technique. Polymer films are cycled between two potentials in a three-electrode system. (Figure 1.4.)

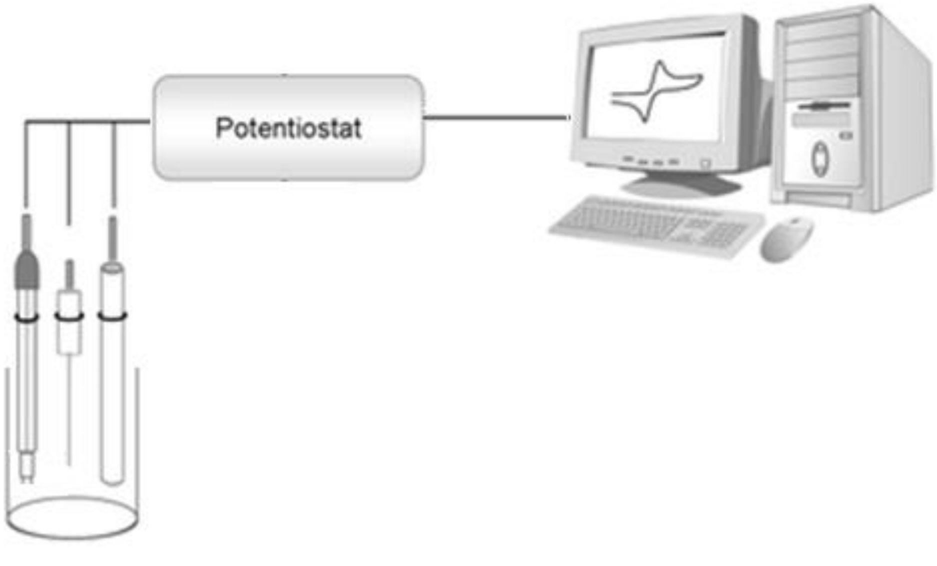


Figure 1. 4 Schematic representation of three electrode cell system.

In the characterization of the conducting polymers, ITO (indium tin oxide) coated glass or platinum disc electrode are used as the working electrode; silver wire or $Ag^+/AgCl$ are used for the reference electrode and platinum wire is used as the auxiliary (counter) electrode, usually. Cyclic voltammetry technique can be used not only for defining redox couple of an electrochemically active material but also used for polymerization.

Determining the oxidized states of a p-type electrochromic polymer is important since each state result in a different color if it is in visible region (multichromism). Optical contrast of an electrochromic polymer is usually reported as difference in percent transmittance (Δ%T) between two distinct states at a specified wavelength. Spectroelectrochemistry is used in order to define the optical behaviour of an electrochromic polymer. Spectroelectrochemistry is a technique which consists of a spectrometer and a potentiostat. During the measurement, the film coated electrode is placed in the spectrometer and connected to a potentiostat with a three-electrode cell system and the transmittance change of the film under stepwise oxidation is observed. (Figure 1.5.)

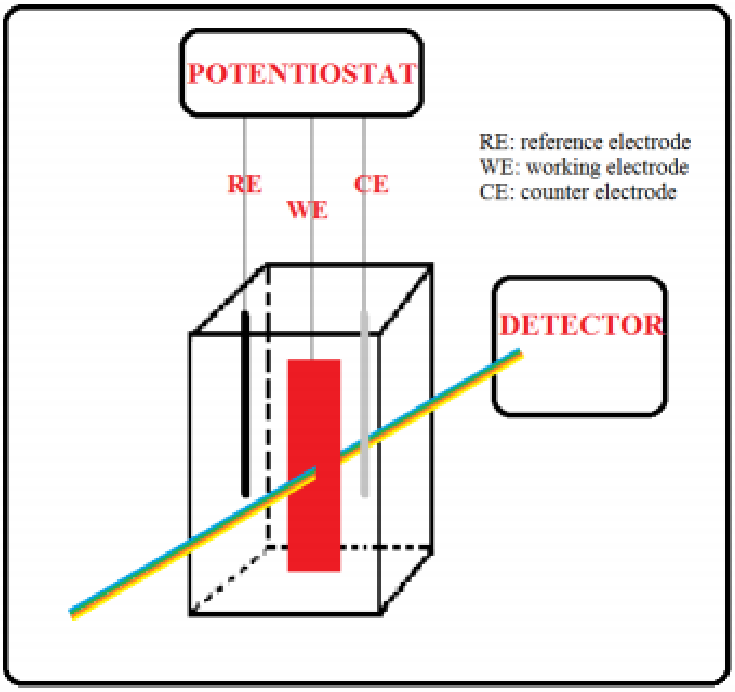


Figure 1. 5 Schematic representation of spectroelectrochemistry study.

Additionally, optical band gap, polaron and bi-polaron bands are determined using this setup.

Switching time is an important parameter, which is calculated from polymer's recorded percent transmittance change. Polymer film is switched between its fully oxidized and fully reduced states at a specified wavelength via spectroelectrochemistry.

5. Low band gap polymers

Low band gap polymers are exclusive materials since they used to modify all organic electronics to design novel organic conductors. [19]

Low band gap polymers, which have broad long wavelength absorbance, where the photon flux is maximum, are crucial for organic photovoltaics. Using both donor and acceptor units in the same chain alternatively also may result in ambipolarity which is essential for organic semiconductors for the development of integrated microelectronic organic circuits. Additionally, they have several accessible energy states between HOMO-LUMO levels, which make the charge transport easy such energy levels. Small applied potential differences enable the control of the hue and shade of the polymer color. Moreover, tuneable energy levels make possible to control the absorption and emission wavelengths of the polymers for use in organic light emitting diodes.

The possibility of structural modification is the most important property of these type of materials which was realized after it has been shown that band gap of the polythiophene can be lowered about 1eV via incorporating a benzene ring (poly(isothianaphthene)), which pushes thiophene to stay in its quinoid form in ground state. [20]

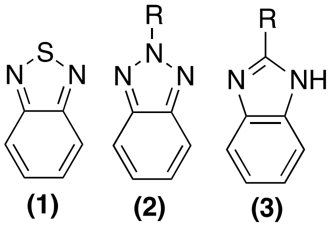
After the proposal to use the alternating donor and acceptor moieties in the polymeric backbone to reduce the band gap by Havinga et al. [21, 22] it became a mostly used concept for band gap engineering by the groups studying conjugated polymers.

Alternation of the electron donor and acceptor moieties is the mostly used system for recently designed conducting polymers for organic electronics due to its effect on the realization of planarity of the organic molecules. Using alternating electron donating and accepting groups on the same chain of the polymer basically relaxes the electron transfer resulting in the low band gap due to the interchain charge transfer between the HOMO and the LUMO energy levels of the incorporated segments. In the light of this information, polymer scientists discovered numerous systems showing fabulous properties with the reason they have been designed for.

Since the band gap is one of the most important properties to control both optical and physical properties of a polymer, DA theory is the mostly used method in the preparation of low band gap polymer in the field of material science. Benzazole derivatives, which are the commonly used as electron deficient heterocycles, gain great attention to be used in donor- acceptor systems in order to modify the energy gap of the polymers.

6. Benzazole Derivatives in Electrochromism

Following section is devoted to summarize benzazoles including 2,1,3-benzothiadiazole (BTD) **(1)**, benzotriazole (BTZ) **(2)** and benzimidazole (BIM) **(3)** as the low band gap containing systems and their electrochromic properties.

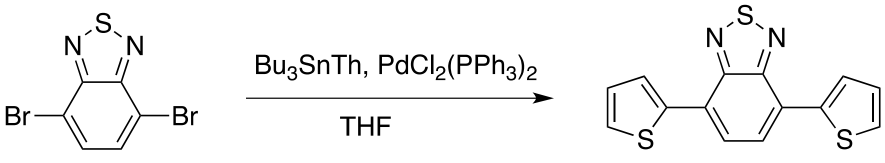


6.1 Benzothiadiazole

Benzothiadiazole is the most investigated acceptor unit among the benzazole derivatives. It has been coupled with several types of donor and acceptor units for different applications. At this stage it is tried to tell its story over the investigation of neutral green polymer since it took an important role in electrochromics.

Until early of this century missing color green was the most challenging one to discover in order to satisfy RGB colors. There are a number of examples of red [23, 24] and blue colors [25, 26], which were easily obtained with the polymers of a variety of donor units.

2,1,3-Benzothiadiazole was firstly designed and synthesized in a donor-acceptor-donor system by Yamashita et. al. with the purpose of creating narrow band gap polymers. [27] Thiophene substituted BTD derivative **(4)** is a widely used molecule in many copolymers due to the ease of its synthesis and ease of copolymerization with other systems. The synthesis of the monomer was achieved using palladium catalyzed Stille coupling reaction.



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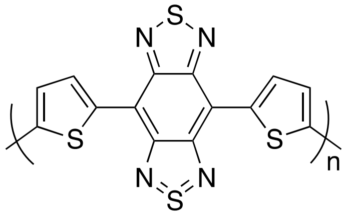
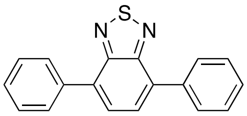


(5)

Yamashita designed bisbenzothiadiazole unit to improve the planarity and strong ability to demand the quinoid geometry on the ground state of the final monomer. The polymer **(5)** was reported as the one having the smallest band gap value up to that date. [28]

In the guidance of these investments, Roncali designed several DAD type monomers **(6-9).** [29]



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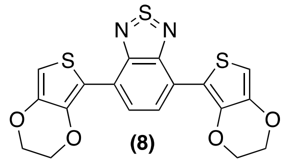

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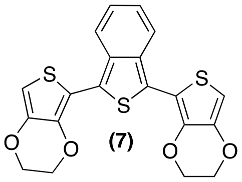

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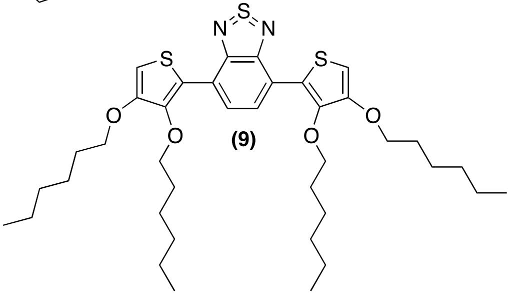


(9)

The monomer **8** was prepared via Stille coupling using tributyl stannylated 3,4-ethylenedioxythiopene and di-brominated benzothiadiazole. In that work the monomer was only investigated in terms of its electrochemical and fluorescence properties.

After seven years of its synthesis, di-EDOT substituted BTD derivative **(8)** was reported as the second green electrochromic material in the literature. However the most amazing part of that work, it was the first electrochromic which has a highly sky blue oxidized state (Figure 1.6.). Polymer has 40% and 70% optical contrast values in the visible and in NIR regions respectively with admirable switching properties. [30]

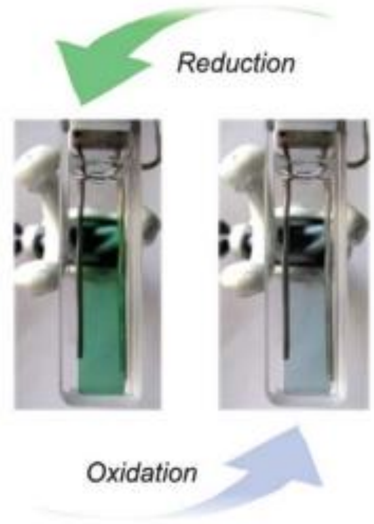
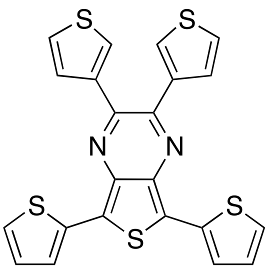


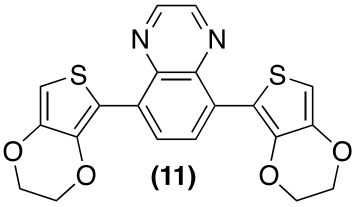
Figure 1. 6 Neutral and oxidized state colors of 8 which was polymerized on ITO coated glass slide.

The first neutral green electrohromic in the literature was the work of Sonmez et. al. which was published as a communication in 2004. [31] The polymer was obtained from the monomer DDTP **(10)** via electrochemically on ITO coated glass slides which switches between neutral green and transmissive yellowish brown. Polymer has 23%, 12% and 85% optical contrast values in the 370nm, 725nm and 1600nm, respectively with 0.5s switching time.



(10)

After this quinoxaline derivative, Toppare group concentrated on this acceptor unit, which is easily synthesized from 2,7-dibrominated benzothiadiazole in two steps as reduction and condensation reactions. The resulting di-functionalized acceptor unit was ready to get polymerized with di-stannylated donor groups for cross coupling reations such as Stille and Suzuki. It is worth to mention that one of the derivatives of quinoxaline unit, which was coupled with EDOT **(11)**, resulted in a neutral green electrochromic material with highly transmissive light blue oxidized state. [32]



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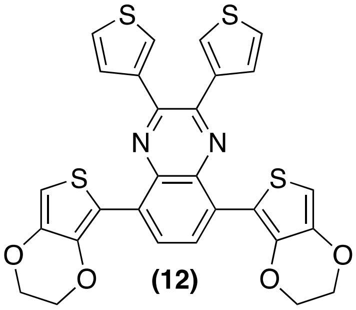
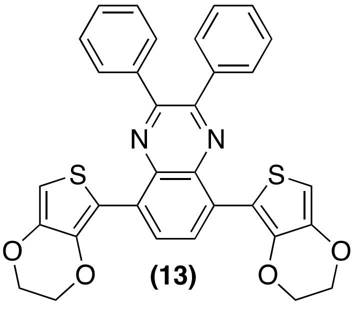


(12)

A year later, two novel monomers **(13, 14)** were designed and revealed to be a true neutral state green polymeric material with fully transmissive oxidized state. This study was published with the title “could green be greener” which emphasizes the ongoing effort on advancing the properties of the neutral state green polymer. Besides, n-dopable property makes these monomers more valuable than the former derivatives. [33]



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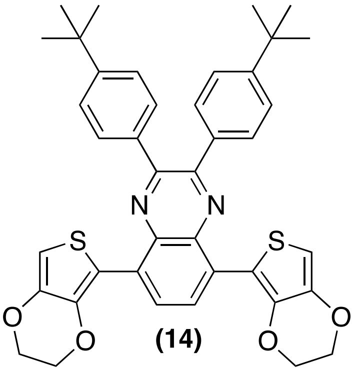
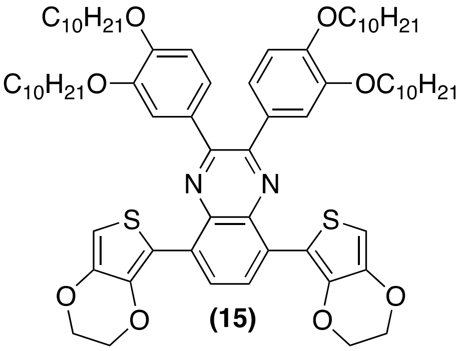


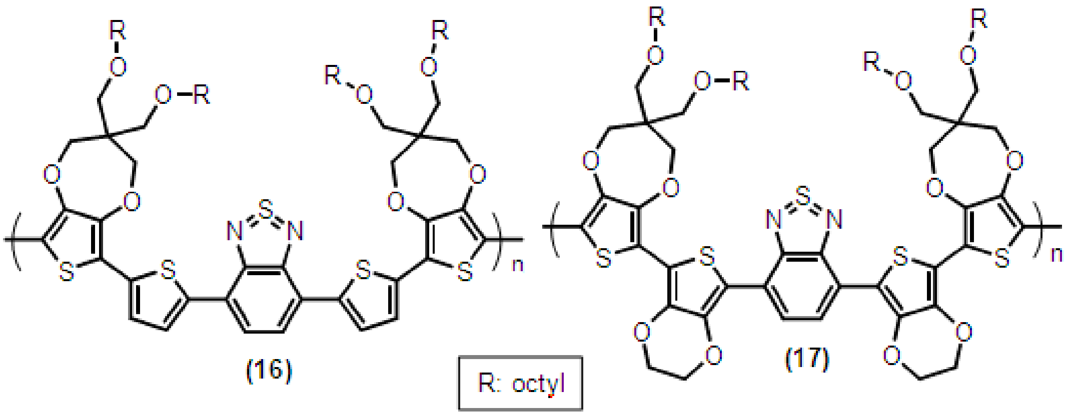
(14)

A new, solution processable derivative was designed and published in 2008. The acceptor quinoxlaine unit was synthesized via a simple condensation of 3,6-dibromobenzene-1,2-diamine and 1,2-bis(3,4-bis(decyloxy)phenyl)ethane-1,2-dione **(15)**. The resulting polymer, obtained electrochemically, revealed a saturated green in its neutral and a high transmittance in the oxidized state with 90 % optical contrast in 1800 nm a switching time of less than a second in the visible region. [34]



(15)

In the same year Reynold’s group synthesized two new solution processable polymers using 2,1,3-benzothiadiazole, EDOT, thiophene and 3,4-propylenedioxythiophene (proDOT) molecules and investigated their electrochromic properties. [35] Each molecule was carefully selected and designed to catch the missing color green in neutral state. They firstly coupled BTD with thiophene and EDOT to obtain the molecules **4** and **8**. Then, they are recoupled with proDOT, which enrichs the electrochromic properties in terms of high optical contrast and to tune the band gap of the resulting polymers **(16-17)**. Oligomers were chemically polymerized in chloroform using $FeCl_3$.



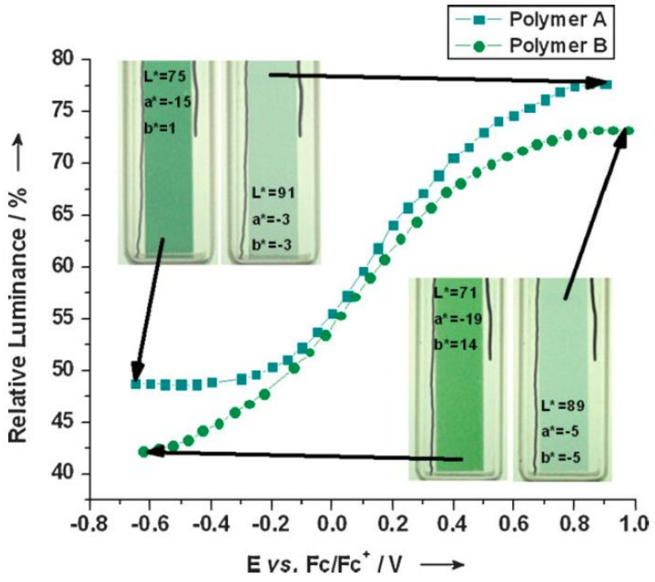
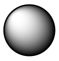
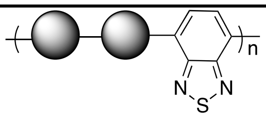
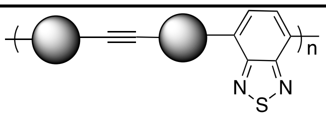
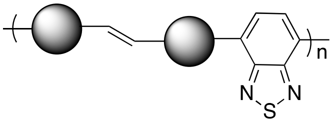
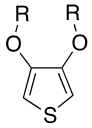
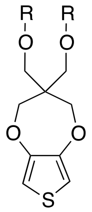


Figure 1. 7 Colors of the neutral and fully oxidized states of the polymers 16 (polymer A) and 17 (polymer B).

Both polymers revealed green color in their neutral states and transmissive oxidized states with a high optical contrast and a short switching time (Figure 1.7.).

After realizing that two-band absorption is required for green color, it was possible to achieve it with the donor-acceptor theory. Researchers concentrated on the new way of modification the polymeric backbone for envision of the band gap engineering. Unsaturated linkages are also worth to mention in band gap modification. In the work of Reynold's in 2009 a series of polymers **(18-23)** was prepared to understand the effect of the unsaturated linkages on electrochromism as well as the to understand the requirements of high optical contrasts and optical tunability.

Table 1. 1 Structures of polymers 18-23.

			
	**(18)** R = 2-ethylhexyl	**(19)** R = 2-ethylhexyl	**(20)** R = 2-ethylhexyl
	**(21a)** R = 2-ethylhexyl	**(22)** R = 2-ethylhexyl	**(23)** R = 2-ethylhexyl
	(21b) R = octyl		

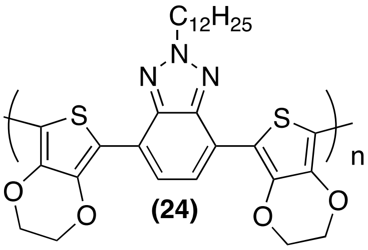
The polymers containing dioxythiophenes as the donor group were coupled with BTD as the acceptor group with ethynylene and trans ethylene linkages between the donor groups. Results of spectroelectrochemistry study showed that while ethynylene linkers hamper the evolution of the bipolaronic transition in the NIR region, the incorporation of trans ethylene linkers between the dioxythiophenes

(DOTs) resulted in smaller band gap. Ethylene spacers also caused less stable electroactivity since they tend to get overoxidized easily compared to control parents in the Table 1, with only loss of 10 % of their peak currents after 100 switches. [36]

Benzothiadiazole unit also took an important role for investigation of black to transmissive polymer for the first time in the literature. In order to synthesize such a kind of polymer the neutral and oxidized absorbance region of the polymer in the spectrum should be carefully determined. With changing the strengths of the donor and acceptor unit it is possible to obtain all colors in the spectrum. [37] This strategy resulted in the invention of the polymer switching black to transmissive regime by only changing the feed ratios of the donor unit. [19, 38, 39]

6.2 Benzotriazole

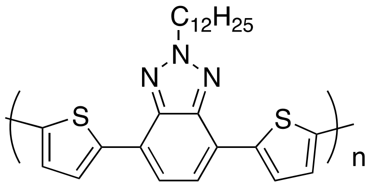
In 2008 a new donor-acceptor-donor (DAD) type polymer **(24)** containing EDOT as the donor unit and the benzotriazole as the acceptor unit was designed and synthesized and its electrochromic properties were investigated. [40]



(24)

Resulting polymer showed superior electrochromic properties than that of PEDOT. PBEBT has 53% and 71% optical contrast values in the visible and NIR regions, respectively. This polymer can be counted as one of the most valuable examples of the donor acceptor match since it a) healed the electrochromic properties of PEDOT, b) has n-dopable character, c) is solution processable. All these characteristics make this polymer as a good alternative to PEDOT in the electrochromic displays.

Ability of the alkylation of the acceptor or donor group in a polymer chain makes the resulting polymer soluble in several solvents. Solubility opens the gate for several applications for this kind of conducting polymers in organic electronics. That is why, benzotriazole is a valuable unit since it can be incorporated using cross coupling reactions into polymers containing non-alkylated donor units for desired applications such as organic photovoltaics [41] and as long wavelength synthesizers [42].



(25)

A year later benzotriazole was incorporated again in a DAD type monomer, where thiophene was used instead of EDOT as the donor unit and this work was published with the title “one polymer for all” **(25)**. This polymer switches between all RGB colors, additionally having black and transmissive states in a small potential range. In other words, it reveals multichromism with six distinct colors with high stability [43] (Figure 1.8.).

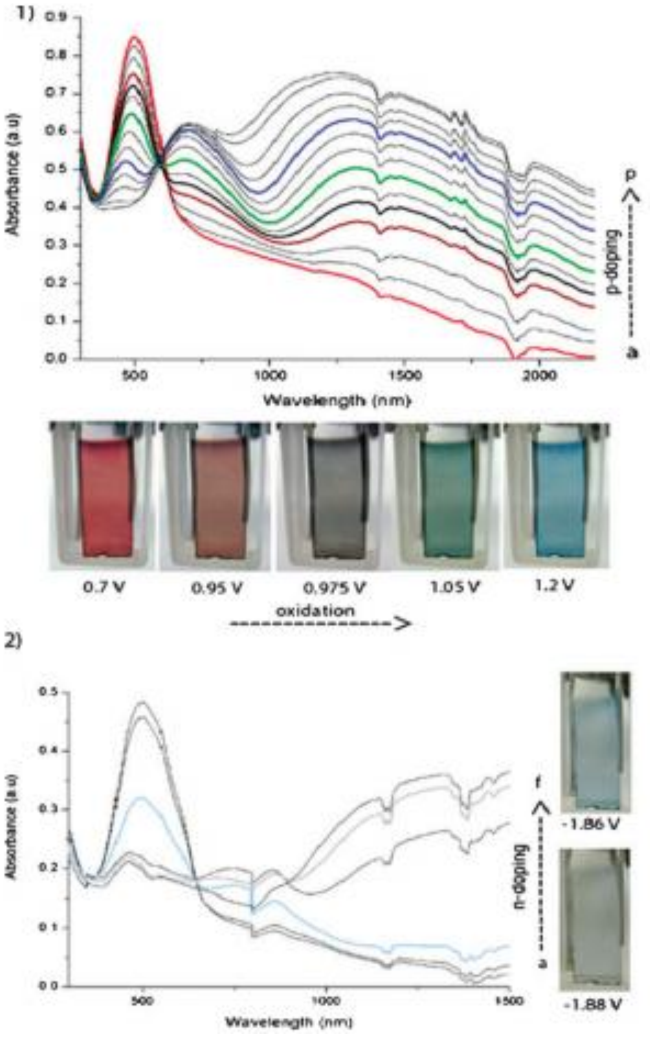


Figure 1. 8 1) p-doping and 2) n-doping spectrum of **(25)**

Moreover, it is also solution processable and n-dopable which are quite important properties in device construction.

After these two articles, a number of studies were published using benzotriazole unit to investigate its contribution on electrochromism. Several copolymers of benzotriazole showed different shades of nearly all major colors. Using the benzotriazole acceptor unit M. İçli et al. simply copolymerized two donor-acceptor-donor type monomers to obtain a full cover of spectrum together with a transmissive state [44] (Figure 1.9).

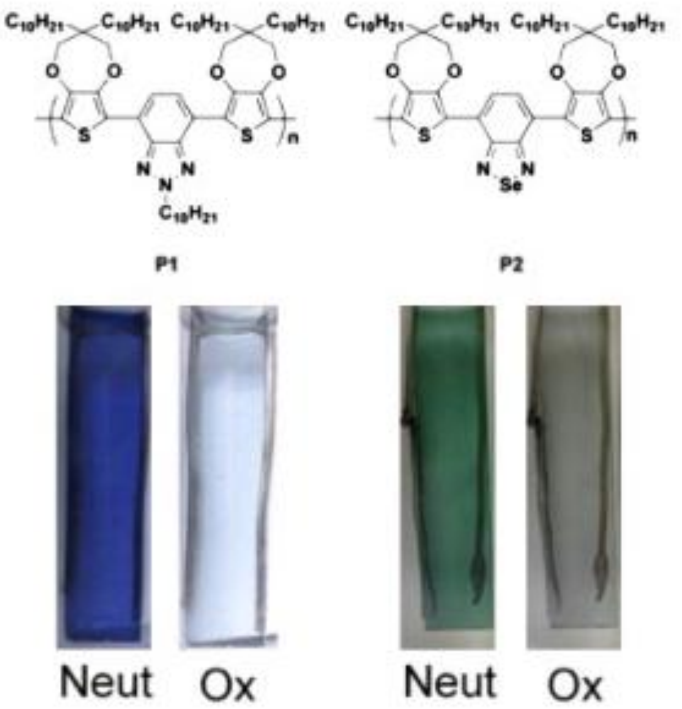
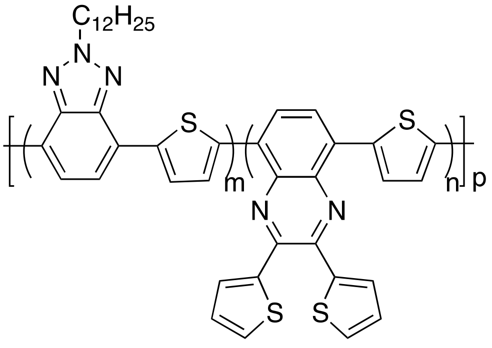


Figure 1. 9 Colors of neutral and oxidized state of polymers containing benzatriazole and benzoselenadiazole units as acceptor.

The polymer was obtained via electrochemical method on ITO glass slide from a known feed ratio of monomers in DCM:ACN mixture. Polymer with the feed ratio of 1:4 (monomer of P1 : monomer of P2) resulted in neutral state black color. It is also soluble in several organic solvents due to having alkylated DOT units in its structure. ALthough it has a low optical contrast value it only decreases from 15.3% to 14.2% after 2000 cycles, which shows the stability of the polymer film.

Another example of copolymerization to obtain full visible absorption is the coupling of benzatriazole unit with quinoxaline derivative [45] (Figure 1.10).



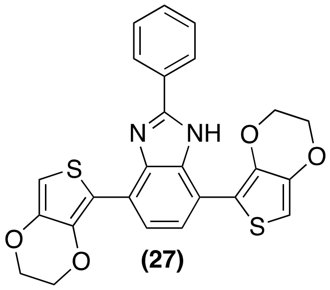
(26)

Figure 1. 10 Colors of **(26)** on ITO; neutral (0.0 V, left) , oxidized (1.2 V, right).

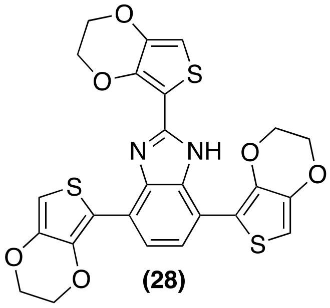
Copolymer **(26)** in this work was obtained via random copolymerization of the thiophene coupled quinoxaline and thiophene coupled benzotriazole units. Resulted polymer is not only solution processable, which is required for low cost flexible organic electronics, but also has 23% optical contrast value within only 0.7 seconds.

6.3 Benzimidazole

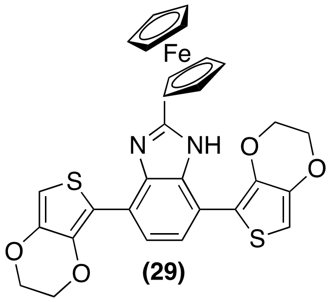
Benzimidazole derivatives were firstly investigated as electrochromic materials in 2010. Three DAD type monomers **(27-29)** were synthesized using EDOT as the donor and the BIM as the acceptor units. 2-C position of the imidazole ring was functionalized with three different units to observe substitution effect of the side group on electrochromic properties of the resulting polymers.



(27)



(28)

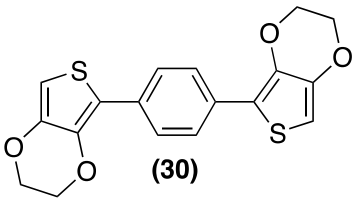


(29)

The polymers of **(27)** and **(28)** revealed high stability and showed excellent switching times even when the switching time intervals decreased to 1s from 5s. Optical contrast values of these monomers are also worth mentioning (nearly 45 % in the visible and 70% in the NIR region). Due to high film quality, all experiments were completed with only one single film coated on ITO surface. Polymer of **(28)** has the ability to change its two intrinsic states in only 0.3s at 1800 nm. Switching times ranges from 0.3s to 0.6s for these two polymers. The third polymer with bulky ferrocene pendant group, also showed multichromic property as the other two [46].

In 2012, alkyl chain incorporated derivates were investigated with respect to substitution effect of two different donor units; thiophene and EDOT [47].

The higher oxidation potential value of EDOT coupled monomer than the thiophene bearing one directed us to investigate deeply on the idea of controlling the amount of the possible H-bondings between the oxygen atom of the EDOT group and the free hydrogen of the secondary amine group of the imidazole ring **(27)**. By this way, the presence of C7 intramolecular H-bonding in the polymer chain was proven which hinders the rotation of the donor units of the DAD polymers enhancing nonplanar conformation [48].



(30)

In order to prove the C7 intramolecular H-bonding a control monomer was synthesized which does not include an imidazole ring **(30)**. According to the IR results the peak at 3384 cm^{-1} was found to be due to C7 intramolecular hydrogen bonded amine stretching besides intermolecular hydrogen bonding [49, 50] (Figure 1.11).

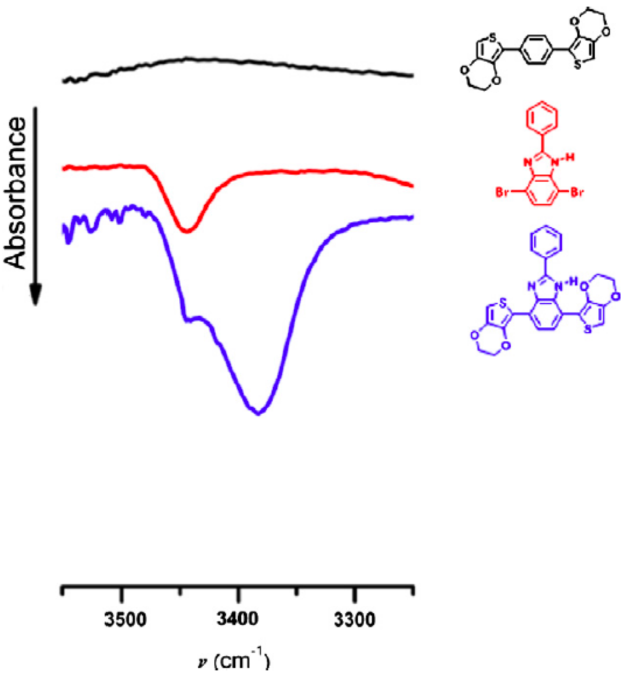


Figure 1. 11 FT-IR spectra of (30), acceptor unit (middle) and **(27)** scanned in the amine stretching region in $CHCl_3$ solution.

With this study, a new way of tuning the optical and electrochemical properties of electrochromic polymers has been found.

During electropolymerization of the monomers changes in the pH of the medium has no effect on the color of the control unit. However, **(27)** revealed different colors at different pH media (Figure 1.12).

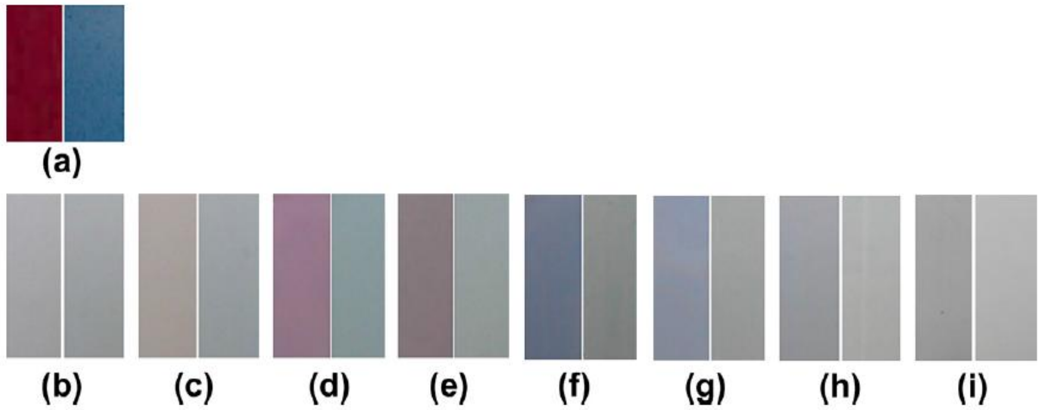


Figure 1. 12 Colors of the polymer films polymerized with related acid and base concentrations; (a) **(30)** (stands for both the neutral and the acid added states), (b) +0.4 mL base, (c) +0.3 mL base, (d) +0.2 mL base, (e) +0.1 mL base, (f) +0.1 mL acid, (g) +0.2 mL acid, (h) +0.3 mL acid and (i) +0.4 mL acid added in the during polymerization of **(27)**.

As a continuation of these studies, a further investigation was performed to support the possibility of the modification of the electrochromic properties of an insoluble polymer during electropolymerization. A communication was reported showing the XPS and the DFT results of the related monomeric structures. [51] Four different possible conformations of the **(27)** monomer were calculated theoretically. According to the DFT results, the most probable conformation is the number 1 in Figure 1.13 which shows the H-bonding between the acceptor and the donor unit. Additionally, XPS results proved the possibility of this H-bonding concentration in the polymeric backbone during electropolymerization via adding acid or base directly into the electrolyte medium.

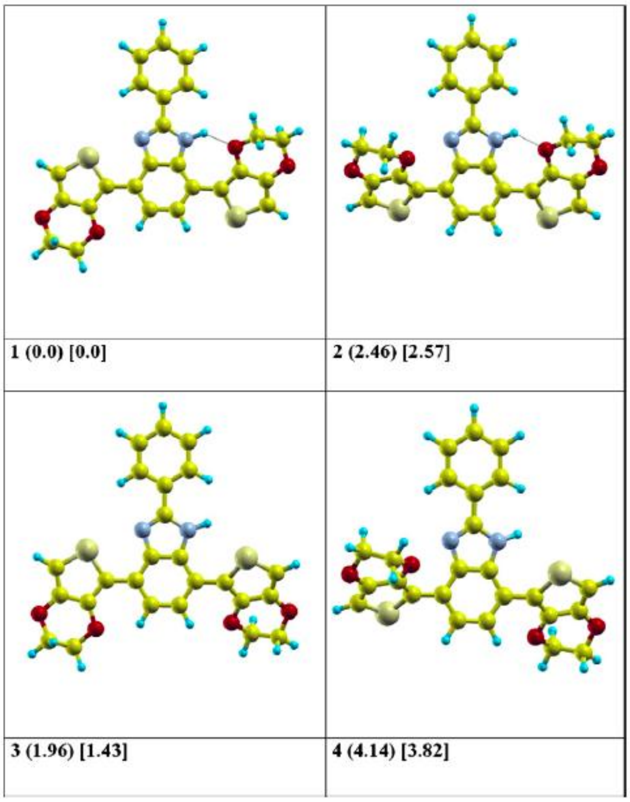


Figure 1. 13 Gas-phase B3LYP/6-311++G(d,p) optimized structures of the four conformers of **(27).** The total energies, (DE, kcal/mol), and Gibbs free energies (DG, kcal/mol) relative to the most stable conformer are also given in parenthesis and square brackets respectively.

With all these inventions, with the contribution of several researchers over the years, investigation of all colors could be done. Studies to synthesize processable RGB (red, green, blue) polymers, which are obligatory for electronic displays, and subtractive colors CMYK (cyan, magenta, yellow, black) for printing technologies are the proof of great efforts spent on DA theory. Use of acceptor units with carefully designed donor groups over two decades opened the way of development of organic based technology.

7. Thiazolothiazole

Thiazolo[5,4-d]thiazole (TTz) molecule has a rigid and coplanar fused ring which ensures highly extended π-electron system. Thanks to its quite straightforward preparation starting from the corresponding aldehyde and dithiooxamide, TTz is used to modify the target molecule to design and obtained novel structures for different purposes such as liquid crystalline [52] binucleating heterocyclic ligands [53] biological activity [54] electroluminescent properties [55] and fluorescent chemosensor. [56] Due to high on/off ratio and stability to oxygen as well as taking a π-stacked structure, which leads to strong intermolecular interactions in solid state, TTz derivatives emerged recently as promising semiconductors. [57-67] Additionally, TTz derivatives appear to be very useful as active materials in bulk heterojunction solar cells for effective charge transport. Therefore, TTz containing small molecules and conjugated copolymers were designed and synthesized for organic photovoltaics (OPVs). [68-75]

In obtaining a low band gap a conjugated polymer DA system and planarity are the two important parameters that should be considered. Absence of the H-atoms in the core of TTz molecule should enhance both stability and the planarity of the polymer when this molecule is introduced into the main chain. In the literature, there is a review on thiazole-based organic semiconductors for organic electronics published in 2012, which summarizes all small molecules and polymers containing TTz molecule used in OFETs and OPVs. [76] To the best of our knowledge, electrochromic properties of TTz based polymers were never explored so far.

8. Solar Cells

It is quite necessary to understand the importance of the question “Why renewable energy?” Marion King Hubbert (1903-1989) who was a geoscientist worked at Shell Research Lab in USA and also was also professor of geology and geophysics at Stanford University from 1963 to 1968 and at UC Berkeley in between 1973 and 1976, suggested a bell-shaped petroleum production curve considering the future discoveries (Figure 1.14).

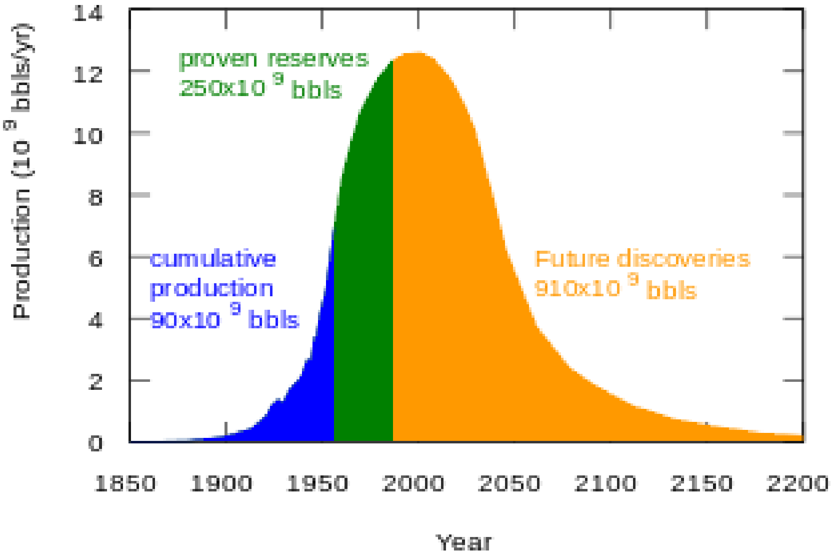


Figure 1. 14 Petroleum production curve. [Presented before the Spring Meeting of the Southern District, American Petroleum Institute, Plaza Hotel, San Antonio, Texas, March 7–8-9, 1956]

Even though his prediction was criticized at first, it is proved as correct in 1970. He explained the significance of the situation with the sentences;

"You can only use oil once. You can only use metals once. Soon all the oil is going to be burned and all the metals mined and scattered."

According to his statement we have already passed the peak of the curve and oil will be consumed totally in near future. Hubbert believed that solar energy would be an efficient renewable energy source.

Today we use several renewable energy sources such as wind power, biomass, hydroelectricity, geothermal power, wave power and tidal power besides solar energy. Richard Perez, research professor and senior research associate at SUNY Atmospheric Sciences Research Center in Albany, New York, USA, clearly demonstrated the world energy consumption and global energy potential annually as well as total reserves in his publications. [77, 78]

As shown in figure 1.15, world energy consumption in 2009 was 16 TW. When it is compared with other renewable energies, coal and uranium are large energy sources but they are both limited. World energy consumption is expected to increase and will reach to 50TW in 2100. That is why; we need a clean and unlimited energy.

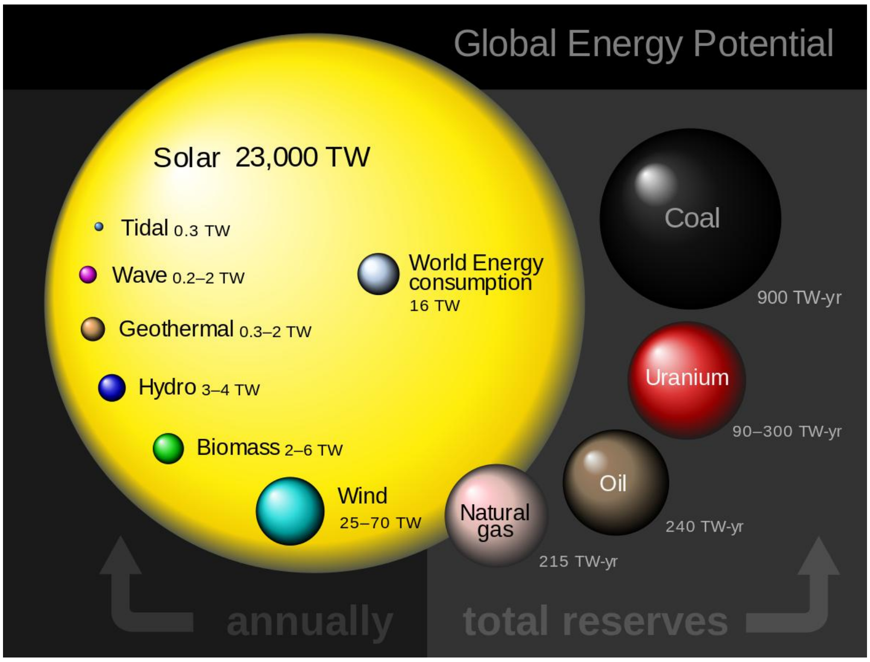


Figure 1. 15 http://en.wikipedia.org/wiki/Renewable_energy Global energy potential.

There are several ways to use sun power to generate energy, which are solar fuel, solar thermal and solar electricity. Solar thermal is the most efficient one in this category. Sun light is used to generate heat to be used in industrial heating, process heating and domestic heating. 85% efficiency is quite remarkable however heat is not the only need for humanity. In solar electricity, sunlight is directly converted into electricity. It is achieved 10 to 20% efficiency values according the type of the material and way of used in the device construction. Photovoltaics cannot be ignored in assessing the energy sources with this high percentage.

9. Photovoltaic Effect

Photovoltaic effect is defined as the formation of electric current in a material via light illumination. It was firstly demonstrated by A. E. Becquerel in 1839. He achieved to generate electricity via hitting the platinum or gold electrodes in neutral, acidic and basic medium with different source of light including sunlight. [79-80] In 1087 H. R. Hertz also observed the photoelectric effect in his article, published in “Annalen der Physik” explained that a charged particle losses its energy under UV light. Although he was not realized the importance of his work, the studies helped to explain the photoelectric effect. A. Einstein was awarded with Nobel Prize in physic in 1921 for the discovery of the law of photovoltaic effect.

In order to build an efficient photovoltaic device, there are some requirements must be followed; low cost, efficiency, high photon absorption capacity and stability.

The first photovoltaic device was constructed in 1950s in Bell’s laboratory having 6% efficiency.

10. Types of Solar Cells

All types of solar cells can be classified in three categories as 1st generation, 2nd generation and 3rd generation. 1st generation solar cells are made of crystalline silicone. Examples of this category can be easily seen on the roofs. The most important advantage of these solar cells is their stability beside their high efficiency reaching 20%. However, they are not easy and too expensive to produce. Although their construction is simple, they are inflexible and not scalable. 2nd generation solar cells are also known as thin film solar cells. Construction materials are amorphous silicon, cadmium-telluride [81], Galium-Arsenide (GaAs) [82] and copper indium gallium selenide (CIGS) [83]. Their biggest advantage over 1st generation is low manufacturing temperature, hence lower use of energy. However, they are unstable against ambient conditions. The last category is the 3rd generation solar cells, also known as organic solar cells. Dye-synthesized solar cells, quantum-dot solar cells and polymer solar cells are belong to this category. When they are compared to the 1st and 2nd generation solar cells, their construction cost and temperature is lower and manufacturing speed is faster. [84] They utilize thin film technology. Although, they are not stable as the other two types, they are not toxic and have low environmental impact.

In this thesis, it is focused on the polymer solar cells. The most important advantage of polymer solar cells is having unlimited types of construction materials. This advantage results in tuning the energy levels more easily.

11. Polymer Solar Cells

11.1 Polymerization Methods

There are various types of polymerization methods. In conducting polymers two of them are common; Stille coupling and Suzuki coupling polymerizations. In the Stille coupling polymerization a halogen activated monomer (usually bromine) reacts with an organo-tin compound activated monomer (Figure 1.16).

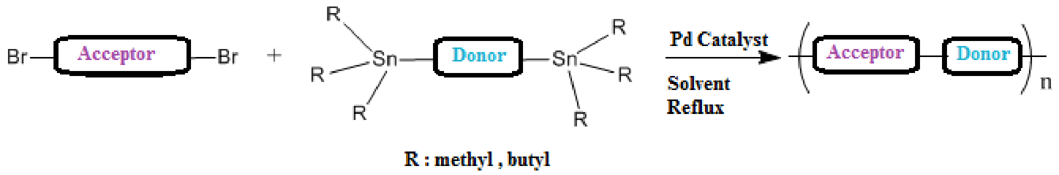


Figure 1. 16 Stille coupling polymerization

In the Suzuki coupling polymerization, a halogen activated monomer same as in the Stille coupling reacts with a boronic ester/acid activated monomer (Figure 1.17).

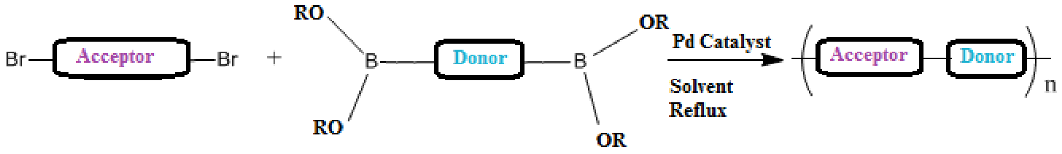


Figure 1. 17 Suzuki coupling polymerization.

Both of them are palladium-catalyzed polymerizations which occur in an inert environment.

11.2 Characterization of Polymers for Solar Cell Application

Determining the HOMO-LUMO level of the polymers and measuring the molecular weight of the polymers are essential for organic electronics. Electrochemical techniques are used to define the oxidation and reduction potentials of the conducting polymers. Cyclic voltammetry is one of the mostly used ones. During linear sweep of the potential, current density and the potentials of the peaks are observed. Onset potentials of the peaks are determined taking the intersection of the tangent lines between the signal and the baseline (Figure 1.18). Energy levels of the polymers are calculated using these onset potentials while taking into account the vacuum level and the correction for a reference electrode. Electrochemical band gap (Eg) is calculated by taking the difference of the two energy levels.

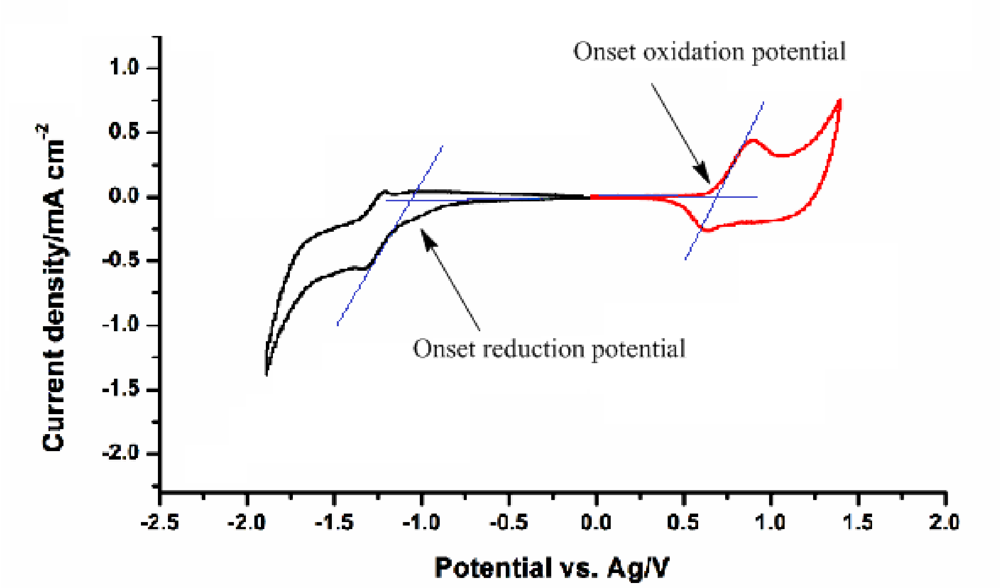


Figure 1. 18 Calculation of HOMO-LUMO energy levels by cyclic voltammogram.

Optical band gap is calculated from the thin film UV-Vis spectrum of the neutral polymer. Each molecule is specific to the different wavelengths of the light. According to their chemical structure, they absorb light at different wavelength region. Incident light causes vibration of the molecules and helps to the electrons to transfer to the nearest excited state. The optical band gap is calculated using the Planck’s equation in electron volts.

$$E_{opt} = h\nu = h\frac{c}{\lambda}$$

Where h is planks constant, c is the speed of light in vacuum and the lambda is the wave frequency. While determining the optical band gap, the onset wavelength of the absorption spectrum is stated using tangent line through the maximum wavelength (Figure 1.19).

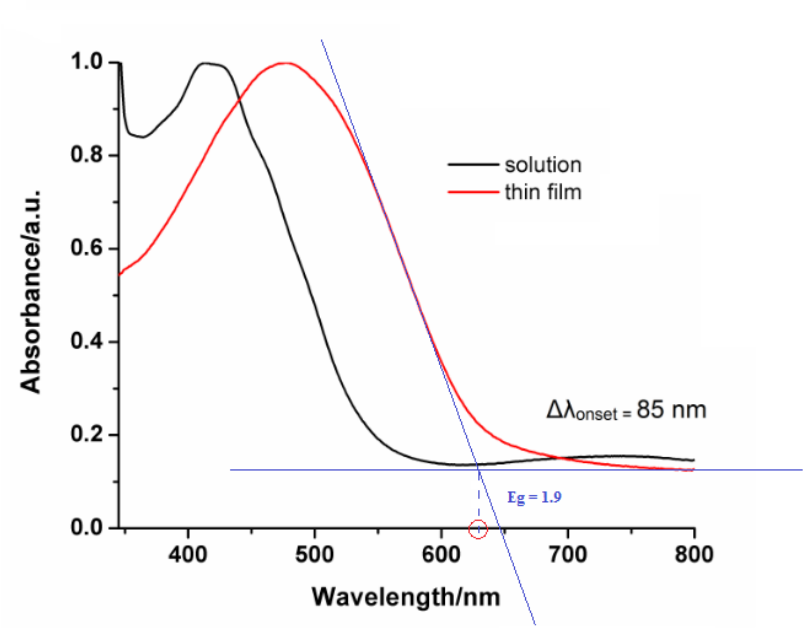


Figure 1. 19 Calculation of bandgap by UV-vis spectrum.

11.3. Construction of a Polymer Photovoltaic

Polymer photovoltaics consist of 5 layers namely; an anode (ITO coated substrate), a cathode (aluminum), an electrontransport layer (lithium fluoride, LiF), a hole transport layer (PEDOT:PSS) and an active layer. Active layer is usually a mixture of a donor (polymer) and an acceptor molecule (fullerene) (Figure 1.20).

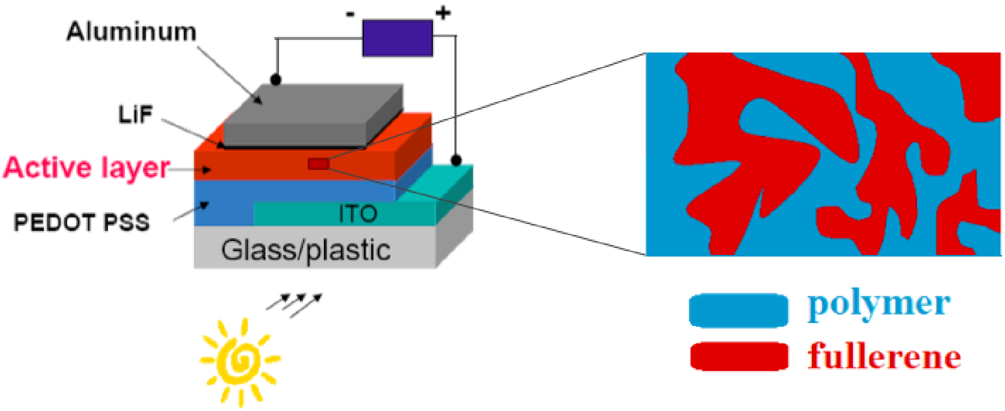


Figure 1. 20 Schematic structure of a polymer photovoltaic.

Electrodes of the solar cells must be highly conductive thus; separated charges can be easily collected both by anode and cathode. In order to accomplish the absorption of sunlight by active layer, one of the electrodes must be transparent to sunlight. ITO, FTO and the metal grids are potential transparent electrodes. Transport layers make easier to collect separated charges through the electrodes via modifying the energy level for hole and electron transfer. PEDOT:PSS (Poly(3,4-ethylenedioxythiophene) Polystyrene sulfonate) is used as the hole transport layer whereas LiF is used as the electron transport layer. There are several fabrication types with different geometries. Two types (normal and inverted) are common (Figure 1.21).

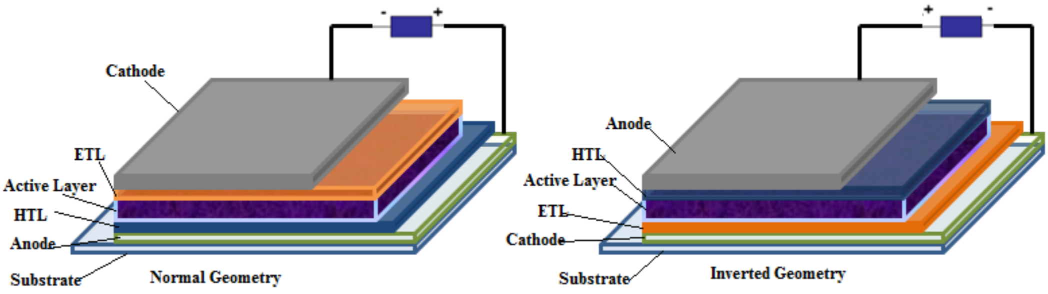


Figure 1. 21 Normal and inverted geometry of polymer photovoltaics.

In the fabrication of normal geometry, substrate should be prepared for HTL and active layer coating. Annealing is performed to the polymer-coated substrates at required temperatures if necessary. To finalize the construction substrates are transferred into an evaporator and ETL and cathode layers are coated under vacuum.

11.4 Working Principle of the Polymer Photovoltaics

Solar cells are devices converts sunlight into current and voltage. Whole process starts with the absorption of photons by the active layer and electron-hole pairs (excitons) are created. Created excitons are drifted to the interface of the donor and the acceptor material in the active layer and they are separated from each other. After charge separation charge transfer are occur with the help of transport layer (Figure 1.22).

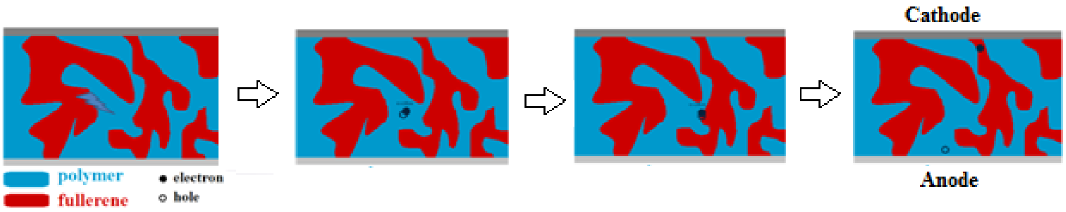


Figure 1. 22 Schematic representation of the working principle of photovoltaics.

CHAPTER 2

ELECTROCHROMIC PROPERTIES OF THIAZOLOTHIAZOLE CONTAINING POLYMERS

1. Aim of the Study

In this study, we aimed to design and preparation of two new polymers named poly[2-(5-(2-decyl-2H-benzo[d][1,2,3]triazol-4-yl)thiophen-2-yl)-5-(thiophen-2-yl)thiazolo[5,4-d]thiazole] (BTzTh) and poly[2-(5-(2-decyl-2H-benzo[d][1,2,3]triazol-4-yl)furan-2-yl)-5-(furan-2-yl)thiazolo[5,4-d]thiazole] (BTzFr) to explore their electrochromic properties using electron rich and electron deficient moieties. Thiophene and furan were selected as the donor and BTZ and TTZ were selected as the acceptor units to get a donor-acceptor structure configuration. Chemically synthesized polymers appeared fast switching times, multichromic properties and low band gap values. These properties make them promising candidates for electrochromic device applications.

2. Experimental

2.1 Instrumentation and Materials

Electrochemical studies were performed in a three-electrode cell system containing an ITO coated glass slide (12 ohm-cm), a platinum wire, and a silver wire as the working, counter and pseudo-reference electrodes respectively, with a Voltalab PST 050 potentiostat. Spectroelectrochemical and kinetic studies were conducted by Varian Cary 5000 UV–vis–NIR spectrophotometer together with Solartron 1285 Potentiostat. Minolta CS-100 spectrophotometer was used for quantitative determination of the colors of the films coated on ITO slides. For structural characterization ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker Spectrospin Avance DPX-400 Spectrometer. Chemical shifts are given in ppm downfield from tetramethylsilane (TMS). Average molecular weight was determined by gel permeation chromatography (GPC) using a Polymer Laboratories GPC 220 in tetrahydrofuran (THF) and polystyrene as the standard.

All chemicals were purchased from Aldrich and Acros and used as they received without further purification. THF was dried in benzophenone/Na prior to use. Polymerization reactions were carried out under argon atmosphere. 4,7-dibromo-2-decyl-2H-benzo[d][1,2,3]triazole [85], 2,5-di(thiophen-2-yl)thiazolo[5,4-d]thiazole, 2,5-bis(5-bromothiophen-2-yl)thiazolo[5,4-d]thiazole, 2,5-di(furan-2-yl)thiazolo[5,4-d]thiazole, 2,5-bis(5-bromofuran-2-yl)thiazolo[5,4-d]thiazole [58, 73] were synthesized according to the literature.

2.2 Synthesis of 2,5-bis(5-(tributylstannyl)thiophen-2-yl)thiazolo[5,4-d]thiazole:

This monomer was synthesized using a modified procedure from the literature. [62] 2,5-Bis(5-bromothiophen-2-yl)thiazolo[5,4-d]thiazole (500 mg, 1.08 mmol) were dissolved in dry THF (50 ml) under argon atmosphere. After adjusting the temperature to -78 ^{o}C, 2.5 M solution of n-BuLi in hexane (1.07 ml, 2.68 mmol) were added drop wise and stirred for 2h. $SnBu_3Cl$ (3.21 ml, 2.62 mmol) were added in one portion to the mixture under same condition and the mixture was warmed up to room temperature. 50 ml of ethyl acetate and 50 ml of water were added. Organic layer was separated and washed with water several times and dried with $MgSO_4$. After removing the solvent, the residue was purified via column chromatography over Al_2O_3 (eluent: DCM:hexane (1:1)) to obtain the product (yield: 65%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.59 (d, ^{3}J: 3.6, 2H), 7.08 (d, ^{3}J: 3.6, 2H), 1.51 (m, 12H), 1.28 (m, 12H), 1.08 (t, ^{3}J: 8, 12H), 0.83 (t, ^{3}J: 7.6/7.2, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 162.3, 142.7, 142.6, 142.6, 136.1, 127.7, 28.9, 27.2, 13.6, 11.0.

2.3 Synthesis of 2,5-bis(5-(tributylstannyl)furan-2-yl)thiazolo[5,4-d]thiazole:

This monomer was synthesized using the same procedure described above with 2,5-bis(5-bromofuran-2-yl)thiazolo[5,4-d]thiazole (1.33 g, 3.0 mmol), n-BuLi (3.0 ml, 4.73 mmol), and $SnBu_3Cl$ (9.0 ml, 7.35 mmol) to obtain the monomer as a dark orange oil. (yield: 60%) ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.02 (d, ^{3}J: 3.6, 2H), 6.62 (d, ^{3}J: 3.6, 2H), 1.54 (m, 12H), 1.28 (m, 12H), 1.08 (t, ^{3}J: 8, 12H), 0.84 (t, ^{3}J: 7.6/7.2, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 165.5, 158.9, 153.3, 150.6, 124.1, 109.8, 28.9, 27.2, 13.7, 10.4.

2.4 General Procedure for the Synthesis of the Copolymers (BTzTh and BTzFr):

Polymers were synthesized according to the similar procedure in the literature [74] starting from respective monomers. Equal equivalents of distannylated and dibrominated compounds were dissolved in dry toluene. The mixture was purged with argon for 15 min and $Pd(PPh_3)_4$ was added. Under argon flow, the reactants were refluxed for 36 h. After removing the 90 % of the solvent of the mixture was poured into the cold MeOH and filtered through a Soxhlet thimble. The polymers were washed with MeOH and hexane via Soxhlett and recovered with DCM. The ^{1}H NMR and gel permeation chromatography (GPC) data of the polymers are listed below.

BTzTh: Mw: 17900 g mol^{-1}; Mn: 8300 g mol^{-1}; Mw/Mn: 2.2. ^{1}H NMR (400 MHz, $CDCl_3$, δ: 7.91 (benzotriazole), 7.77-7.32 (thiophene), 4.70 (N-CH_2), 2.11 (CH_2), 1.50-1.22 (alkyl chain), 0.80 (CH_3).

BTzFr: Mw: 6000 g mol^{-1}; Mn: 1500 g mol^{-1}; Mw/Mn: 4.0. ^{1}H NMR (400 MHz, $CDCl_3$, δ: 7.79 (benzotriazole), 7.30-6.84 (furan), 4.71 (N-CH_2), 2.10 (CH_2), 1.30-1.12 (alkyl chain), 0.79 (CH_3).

3. Results and Discussion

3.1 Monomer and Copolymer Synthesis

In order to synthesize the thiophene and furan containing thiazolothiazole building block, corresponding aldehyde was condensed with dithiooxamide in DMF. After bromination with NBS stannylation reactions were performed using a strong base (n-BuLi) in an inert atmosphere. In order to obtain solution processable copolymers alkylated dibromobenzotriazole derivative was coupled with distannylated TTz derivatives in dry toluene. Reaction times were kept as 36 h for both copolymers. After precipitated in methanol, copolymers were purified by Soxhlett extraction. Both copolymers exhibited good solubility in common organic solvents, such as chloroform, dichloromethane and toluene. (Figure 2.1)

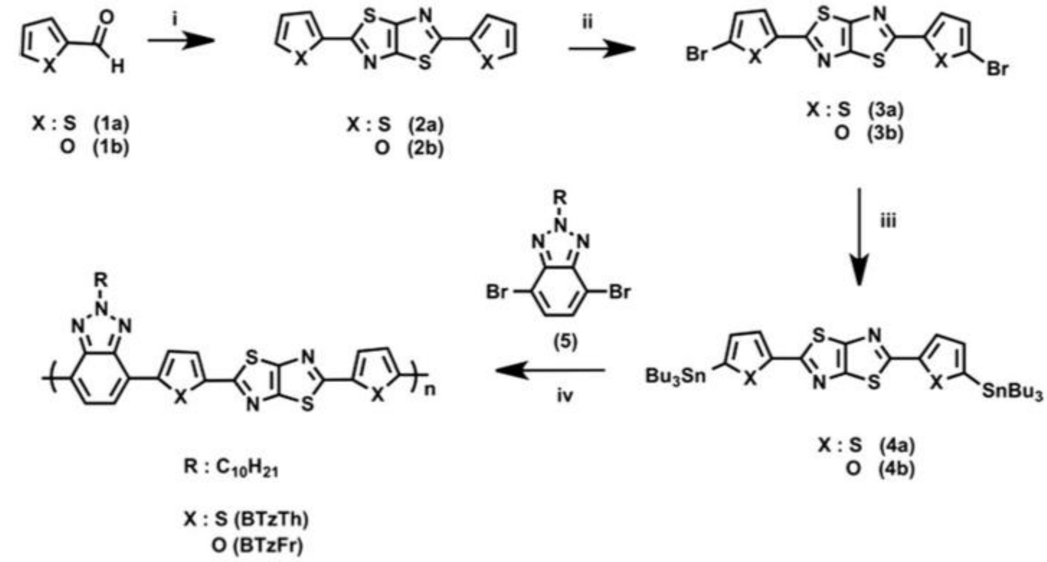


Figure 2. 1 Synthetic route of the copolymers BTzTh and BTzFr [(i) dithiooxamide, DMF, reflux, 5 h; (ii) NBS, DMF, reflux, 1 h; (iii) n-BuLi, tributyltin chloride, THF; (iv) $Pd(PPh_3)_4$, toluene, reflux, 36 h.

3.2 Polymer Electrochemistry

To investigate how the redox potentials of the copolymers differ by changing the structure of the repeating unit, cyclic voltammetry (CV) was performed. The spray-cast thin films on ITO slides were prepared from the DCM solutions (5 mg ml^{-1}) to use as the working electrode in combination with a platinum wire as the counter and an Ag wire as the pseudo reference electrodes. Figure 2.2 shows a set of cyclic voltammograms performed in the potential range 0.0/1.6 V for BTzTh and BTzFr at a scan rate of 100 mV s^{-1}. In Table 1., obtained electrochemical results and HOMO/LUMO energy levels of the copolymers are listed. HOMO levels are given relative to the vacuum level, considering that the SCE is 4.7 eV vs vacuum [86] and Fc/Fc+ is 0.38 eV vs SCE [87].

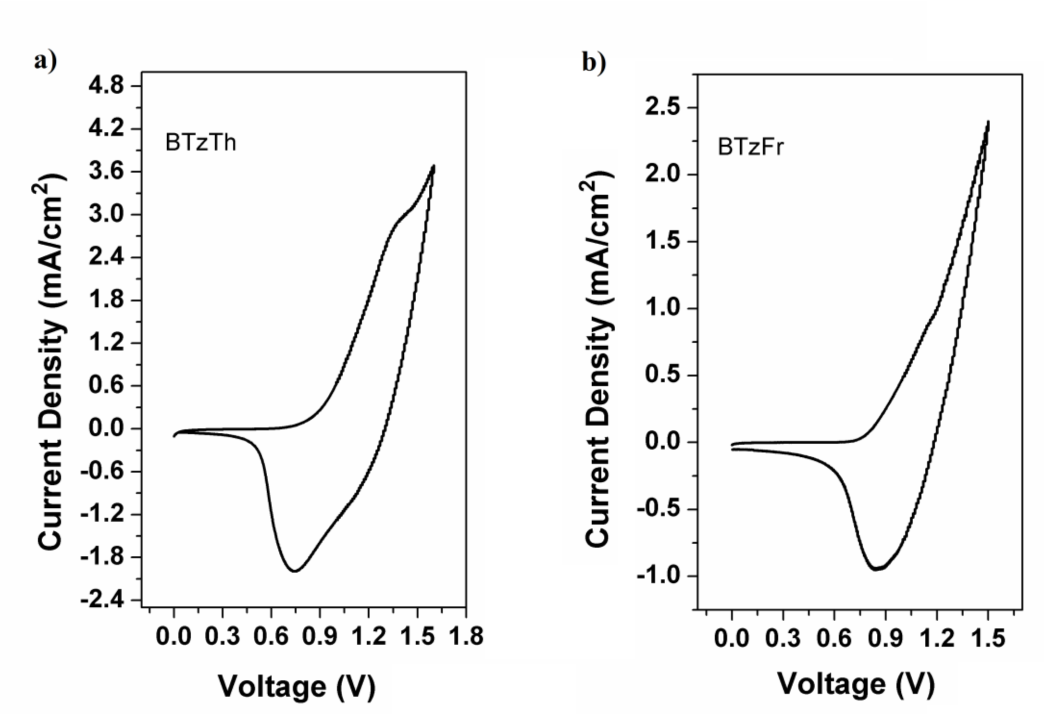


Figure 2. 2 Cyclic voltammograms of the copolymers a) BTzTh and b) BTzFr

All electrochemical experiments were performed in same electrolyte solution (0.1 M TBAPF$_6$/ACN). A reversible redox couple observed for copolymer BTzTh positioned at 1.55 and 1.00 V. Instead of thiophene, furan incorporated copolymer showed a lower redox couple versus same reference electrode located at 1.30 and 1.10 V in anodic region. As in the literature, furan substitution into a polymer backbone rather than thiophene, reduces the oxidation potential since oxygen-containing furan is more electron rich than thiophene. In other words, when oxygen-containing heterocycles used as the donor group in a polymer chain they reduce the HOMO energy level. [88]

HOMO levels of the BTzTh and BTzFr were calculated from the onset oxidation potentials; 1.00 V and 0.95 V, respectively. Upon replacing thiophene with furan moiety, a smaller E^{ox} onset value and a more destabilized HOMO level was detected. LUMO levels were also calculated subtracting the optical band gap values from the HOMO energy levels of the copolymers (Table 2.1).

Table 2. 1 Electrochemical and electrochromic properties of thiophene and furan bridged thiazolothiazole containing copolymers

	BTzTh	**BTzFr**
$E^{doped, ox}$ (V)	1.55	1.30
$E^{dedoped, ox}$ (V)	1.00	1.10
$E^{doped, ox}$ (onset) (V)	1.00	0.95
HOMO (eV)	-5.32	-5.27
LUMO* (eV)	-3.62	-3.37
Eg^{op}	1.7	1.9
λ^{max} (nm)	460/630/1230	440/700/1280
Optical contrasts (%)	10/40/65	-/35/25
Switching times (s)	2.5/0.5/0.5	-/0.6/1.8

*** LUMO energy levels calculated from subtracted optical band-gap values from HOMO levels.**

3.3 Spectroelectrochemistry and Colorimetry

In order to figure out the relation between the redox processes and UV-vis-NIR absorptions, spectroelectrochemistry experiments were performed in the same electrolytic medium ($TBAPF_6$/ACN) with the same electrodes (ITO: working, platinum: counter and Ag wire: pseudo-reference), for both copolymers. Thin films (160 nm) of the copolymers were prepared with the same procedure used for electrochemistry (5 mg ml^{-1} in $CHCl_3$). All copolymers showed multi electrochromic nature since the absorption bands of oxidized states generated mostly in visible region at higher applied external bias across the films with a very small potential differences.

In Figure 2.3, a full characterization of all bands was shown for related states via oxidation for both copolymers. UV-vis-NIR spectra for polymer films were obtained first in their fully reduced states at 0.0 V, which show different hues of orange. Color discrepancies of the copolymers were clearly characterized during sequentially stepping to higher oxidizing potentials with 0.1 V increments, which lead to the generation of polaronic and bipolaronic bands at longer wavelengths. Due to intramolecular donor-acceptor electronic interaction of the neutral polymers, they have a single broad absorption bands with maximum peak values of 460 and 440 nm for BTzTh and BTzFr, respectively. BTzTh has a 20 nm red-shifted broader absorption band than BTzFr. This may be attributed to both thiophene which has a wider absorption band compared to furan [88] and also to the longer chain length of BTzTh than BTzFr. Since the polaron bands of both copolymers are in the visible region (630 nm (BTzTh) and 700 nm (BTzFr)), these have an important effect on the polymer colors at oxidized states. In both cases, the distinct increase in the intensities of the absorptions was observed when applied bigger potentials than their E^{ox} onset values which were determined from the cyclic voltammetry.

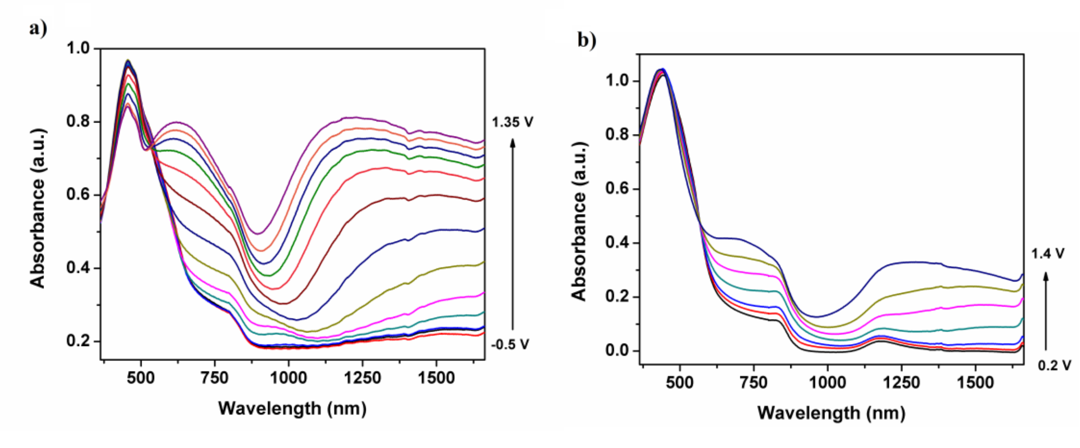


Figure 2. 3 Electronic absorption spectra of the copolymers in $TBAPF_6$/ACN solutions with 0.1 V potential steps a) BTzTh and b) BTzFr

As shown in Figure 2.3.a, intensities of the newly generated bands increased as the π-π* band of BTzTh depleted. While oxidizing the polymer BTzTh, three additional intermediate film colors were observed at potentials 0.9 V, 1.2 V, 1.3 V. Upon fully oxidation a dark blue color was observed at 1.5 V. However, for complete oxidation of BTzFr (Figure 2.3.b) a green color observed at 1.2 V. As known, to observe the green color the presence of two bands is a must in the regions around 400 and 700 nm. During stepwise oxidation, the polaron band revealed at 700 nm of the BTzFr and the intensity of the neutral absorption band did not lose its intensity. At potentials 1.0 V and 1.1 V two additional colors, which are different shades of neutral and fully oxidized color tones were determined. The variety of the polymer film colors for BTzTh than BTzFr may be explained as the polaron band of the thiophene-containing polymer has a wider absorption range in the visible region than that of furan containing polymer. Bipolaron band of the both copolymers were generated in the low energy region with maximum peak values of 1230 and 1280 nm for BTzTh and BTzFr, respectively.

The optical band gaps of the copolymers were calculated from their onset absorption wavelengths of the π-π* transitions. A smaller band gap value for thiophene containing polymer (1.7 eV) was calculated than that of BTzFr (1.9 eV), which are compatible with the electrochemical results. According to the both optical and electrochemical results both copolymers are promising candidates for the optoelectronic device applications as organic solar cells. With the help of optical band gap values of the copolymers LUMO energy levels were calculated and reported in table 2.1.

To report the polymer film colors (Figure 2.4) quantitatively in a scientific manner, colorimetry studies were performed to define three attributes “L” (brightness), and two color components “a” (the axis extends from -a: green to +a: red) and “b” (the axis extends from -b: blue to +b: yellow) in color space defined by Commission Internationale de l’e´clairage (CIE). Neutral polymer film colors defined as L: 50.334, a: 40.684 and b: 61.332 for BTzTh and L: 60.516, a: 41.501

and b: 101.426 for BTzFr. Upon oxidation of the BTzTh film, color turns into blue and showing b: -30.056 value. During oxidation of the BTzFr, a component had a more negative value, which specifies the green region. “L”, “a” and “b” components of all states of the films of both copolymers were listed in table 2.2.

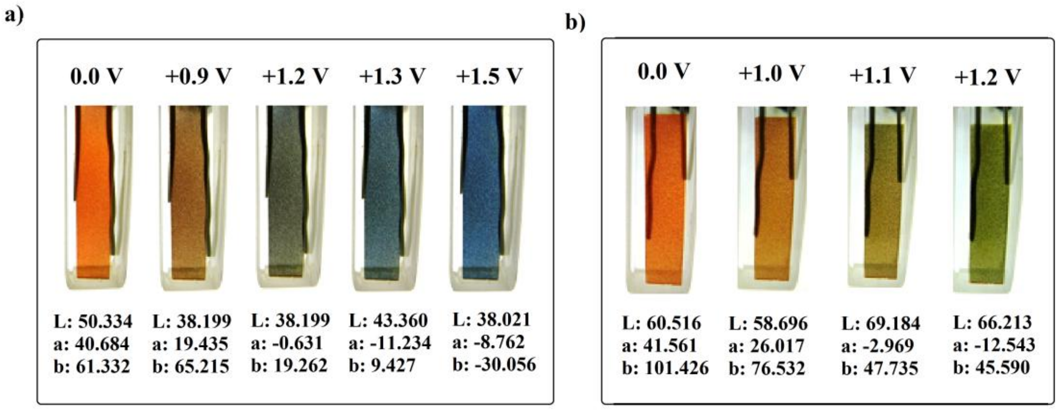


Figure 2. 4 L, a, b values of the polymer films at different applied voltages a) BTzTh and b) BTzFr

Table 2. 2 List of L, a, and b, values for polymer films obtained from BTzTh and BTzFr

	L	**a**	**b**
BTzTh (0.0 V)	50.334	40.684	61.332
BTzTh (0.9 V)	38.199	19.435	65.215
BTzTh (1.2 V)	38.199	-0.631	19.262
BTzTh (1.3 V)	43.360	-11.234	9.427
BTzTh (1.5 V)	38.021	-8.762	-30.056
BTzFr (0.0 V)	60.516	41.561	101.426
BTzFr (1.0 V)	58.696	26.017	76.532
BTzFr (1.1 V)	69.184	-2.969	47.735
BTzFr (1.2 V)	66.213	-12.543	45.590

3.4 Switching Studies

As explained in the spectroelectrochemistry section, both copolymers showed multichromism with prominent color changes at different applied potentials. In order to define the switching speeds of the polymer films double potential step chronoamperometry studies were performed between their neutral and fully oxidized states using a UV-vis-NIR spectrophotometer at their local maximum absorption wavelengths. (Figure 2.5) Experiments were carried out for BTzTh at its all absorption regions whereas for the BTzFr only in its polaronic and bipolaronic regions since there is nearly no change in the π-π* absorption intensity. Switching times, listed in Table 2.1., were calculated by taking 95% of a full transition from neutral fully doped states.

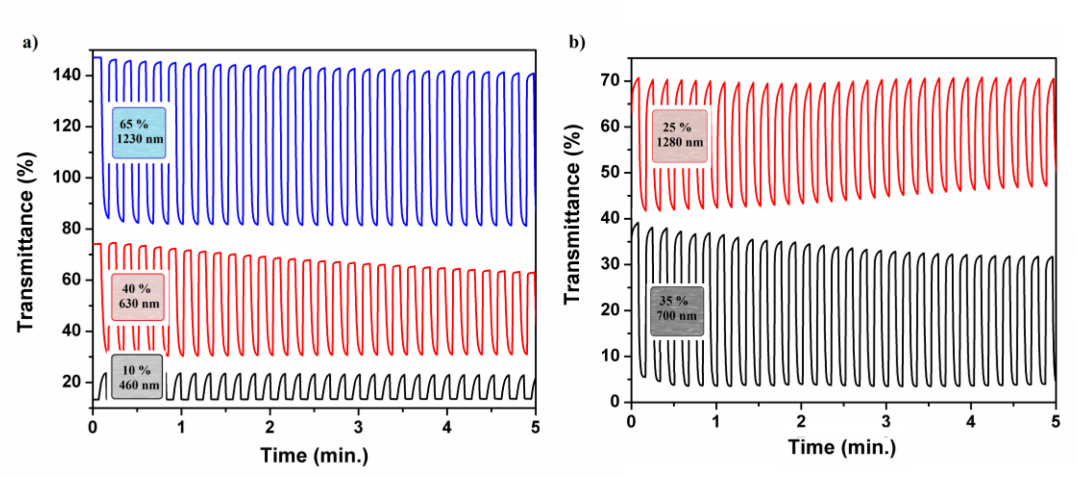


Figure 2. 5 Double potential step chronoamperometry studies with 5 s time intervals at local absorption maximums a) BTzTh (0.0 and 1.5 V) and b) BTzFr (0.0 V and 1.2 V)

To evaluate the kinetic properties of the BTzTh and BTzFr, new polymer films were firstly spray-casted on ITO coated glass slides. Thiophene containing polymer films were consecutively stepped between neutral (0.0 V) and oxidized (1.5 V) (vs. Ag wire) using platinum as the counter in 5 s time intervals. At 460 nm only 10 % optical contrast value was determined with a switching speed of 2.5 s. In longer wavelengths a faster switching time (0.5 s) was observed at both 630 and 1230 nm with increased optical contrast values 40% and 65%, respectively. This result shows charge transport is easier in its lower energy bands. For the furan containing polymer smaller optical contrast values (35% at 700 nm, 25 % at 1280 nm) were observed than the thiophene containing one. These results are also consistent with their electrochemical studies. The charge loaded (area under the curve of oxidative doping) on the furan-containing polymer is lower with respect to the thiophene containing copolymer [89].

All switching times and percent optical transmittance differences (Δ%T) at specific wavelengths are listed in Table 2.1.

4. Conclusions

In conclusion, a new series of alternating DA conjugated copolymers were synthesized containing benzotriazole and thiazolothiazole unit in the main chain via Stille coupling polymerization by altering the thiophene and furan moieties. Electrochemical and electrochromic properties of the copolymers were reported. They showed low oxidation potentials and low optical band gap values. With the help of the spectroelectrochemistry technique, we defined the redox affected color change of the polymer films. Copolymers showed multichromic properties in a small potential range. It is known that consequential variation in electrochromic performance can be rationalized with small structural modifications in polymer chain. Since having suitable energy levels and multichromic properties, electrochromic and solar cell application of a branched chain introduced BTzTh derivative is an issue in our ongoing research.

CHAPTER 3

ALKYL CHAIN EFFECT IN ELECTROCHROMIC PROPERTIES OF THIAZOLOTHIAZOLE CONTAINING POLYMERS

1. Aim of the Study

In the class of organic semiconductors designed and synthesized so far, fluorene and thiozolothiazole containing copolymers come forth as essential materials due to their high chemical stability, exclusive electronic and optical properties, and the possibility of introducing appropriate side-groups on the backbone. One of the biggest advantages of the polyfluorenes (PFs) is their tunability of C-9 position. Alkyl chain substitution to the fluorene molecule enabled to obtain a large number of soluble conducting polymers with various physical and chemical properties [90-92]. Additionally, fluorene containing polymers show good film forming and hole transporting properties [93].

In chapter 2, we examined the effect of thiazolothiazole containing polymer on electrochromism with altered electron donor spacers; thiophene and furan [94]. In this chapter, the effect of fluorene and benzatriazole on electrochromic behavior of thiazolothiazole containing polymers was firstly discussed in terms of their electrochromic and optical properties. Additionally, the results of the poly[2-(5-(2-decyl-2Hbenzo[d][1,2,3]triazol-4-yl)thiophen-2-yl)-5-(thiophen-2-yl)thiazolo[5,4-d]thiazole] (BTzTh) were also compared with that of PBTTz to have a better understanding of branched chain effect on optoelectronic properties.

2. Experimentation

2.1 Instrumentation and Materials

All commercially available chemicals and substances used for synthesis and cleaning of the polymers used without purification. THF was dried over benzophenone/sodium system before used. Stannylation and polimerizations were performed under argon atmosphere. 2,5-di(thiophen-2-yl)thiazolo [5,4-d]thiazole, 2,5-bis(5-bromothiophen-2-yl)thiazolo[5,4-d]thiazole [24,25] 2,5-Bis(5-(tributylstannyl)thiophen-2- yl)thiazolo[5,4-d]thiazole [94], 4,7-Dibromo-2-(2-octyldodecyl)-2H-benzo[d][1,2,3] triazole [95] were synthesized according to the previously published procedures. For structural characterization of the polymers, ^1H NMR spectra were recorded in $CDCl_3$ on Bruker Spectrospin Avance DPX-400 Spectrometer. Chemical shifts are given in ppm downfield from tetramethylsilane. Molecular weights of the polymers were measured by GPC on Polymer Laboratories GPC 220 with polypropylene glycol universal calibration method and THF as the solvent. Thermal properties of the polymer were conducted by Perkin Elmer Pyris 1 TGA under nitrogen atmosphere at a heating rate of 10 °C/min in the temperature range of 25-950 °C.

Polymers were spray cast on ITO coated glass slides and measurements were performed in 0.1 M $TBAPF_6$/acetonitrile (ACN) solution for cyclic voltammetry measurements by Voltalab PST 050 potentiostat. Both spectroelectrochemical and kinetic studies were performed by Varian Cary 5000 UV–vis– NIR spectrophotometer coupled with a Solartron 1285 Potentiostat. Minolta CS-100 spectrophotometer was used for quantitative determination of the polymer film colors. The color changes were investigated by colorimetry using the CIE 1931 Yxy color space.

2.2 General procedure of the synthesis of polymers PBTTz and PFTTz

PBTTz was synthesized according to the published procedure [75] using distanylated thiazolothiazole (a4) and dibrominated benzotriazole derivative (a7) as monomers. Equivalents of monomers were dissolved in dry toluene and purged with argon for 15 min. After addition of $Pd(PPh_3)_4$, solution was refluxed for 48 hours under argon flow. On the other hand, in the synthesis of PFTTz Suzuki coupling was performed according to the procedure [96] 0.5 mmoles of monomers (dibrominated thiazolothiazole derivative (a3) and 2,2'-(9,9-dioc-tyl-9H-fluorene-2,7-diyl)bis(1,3,2-dioxaborinane) (c) were coupled in a mixture of potassium carbonate (K_2CO_3, 2M in H_2O) and toluene (3:2 toluene:water) in presence of $Pd(PPh_3)_4$ (5 mol%), and tetrabutylammonium iodide ($N(Bu)_4I$, 1 mol%). Solution was refluxed for 40 hours under argon flow. After polymerization of both PBTTz and PFTTz, solutions were concentrated and poured into cold ethanol. Precipitates were purified by Soxhlett extraction. ^1H NMR of PBTTz (400 MHz, $CDCl_3$), d: 7.98 (benzotriazole), 7.53–7.36 (thiophene), 4.59 ($N\text{-}CH_2$), 2.22 (CH_2), 1.50–1.16 (alkyl chain), 0.80 (CH_3). ^1H NMR of PFTTz (400 MHz, $CDCl_3$), d: 7.61-7.0 (fluorene and thiophene), 2.01–0.74 (pendant alkyl chain).

3. Results and discussion

3.1 Synthesis and thermal properties

PBTTz was prepared using Stille coupling while PFTTz was prepared via Suzuki coupling reactions as shown in Figure 3.1. All monomers were synthesized except for dioctyl-substituted fluorene, which was purchased from commercial sources. Previously published procedures were used for the preparation of alkylated benzotriazole unit as well as brominated (for PFTTz) and stannylated (for PBTTz) thiazolothiazole derivatives. After preparation of polymers they were firstly precipitated in cold ethanol and purified using Soxhlett extraction with ethanol, hexane and acetone respectively and polymers were collected using dichloromethane. For further purification both polymers were recrystallized. They were firstly dissolved in minimum amount of dichloromethane and poured into cold ethanol. The molecular weights and the polydispersity indices of the polymers were characterized with gel-permeation chromatography (GPC) with polypropylene glycol universal calibration method. Number average molecular weights of the polymers were found as 12300 and 21900 g mol^{-1} for PFTTz and PBTTz with associated Mw values of 18000 and 22000 g mol^{-1}, respectively.

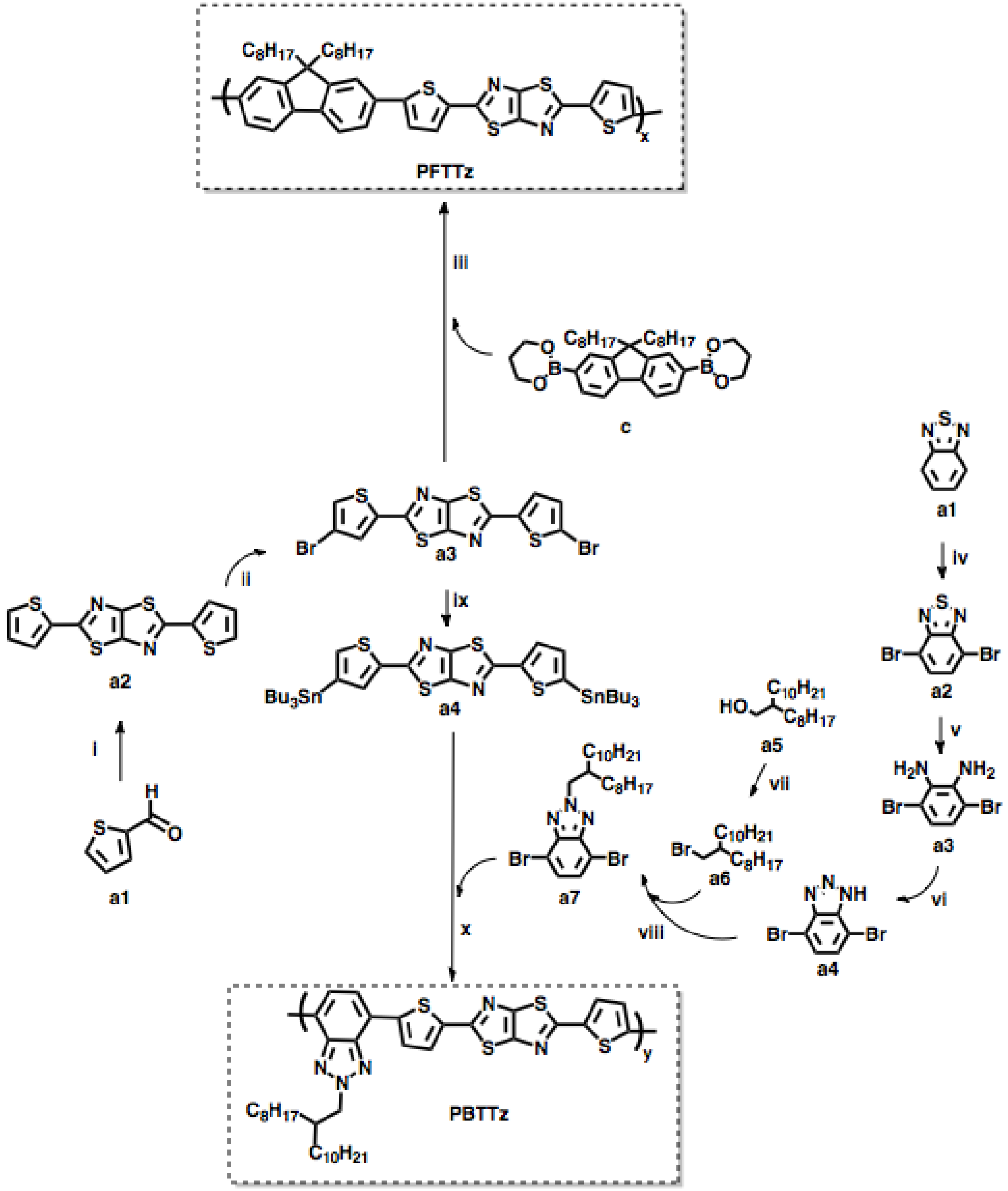


Figure 3. 1 Synthetic route of the polymers i) dithiooxamide, DMF; ii) NBS, DMF; iii) Pd$(PPh_3)_4$, toluene, K_2CO_3, TBAI iv) HBr, Br_2; v)EtOH, $NaBH_4$; vi) $NaNO_2$, H_2O, AcOH; vii) PPh_3, Br_2, CH_2Cl_2; viii) NaH, DMF; ix) n-BuLi, tributyltin chloride, THF; x) Pd$(PPh_3)_4$, toluene

Substituted alkyl chains are significant units to obtain a soluble polymer. However, alkyl chain grafted polymers usually have low decomposition temperatures. The thermal properties of the polymers were investigated to explore their decomposition temperatures and figure out if they can resist during optoelectronic device construction. Thermal gravimetry analysis (TGA) (Figure 3.2) results revealed that both polymers are thermally stable with decomposition temperatures of (5% weight loss) 274°C and 291°C for PFTTz and PBTTz, respectively. Branched chain substituted benzatriazole containing polymer showed higher thermal resistivity since it lost 10% by weight at 360°C whereas PFTTz revealed the same at 290 °C. Additionally, 50% residual weights for polymers recorded at 430°C for PFTTz and at 720°C for PBTTz. It can be concluded that, both PFTTz and PBTTz are suitable polymers for organic electronic device constructions. GPC and TGA results of the polymers are listed in Table 3.1.

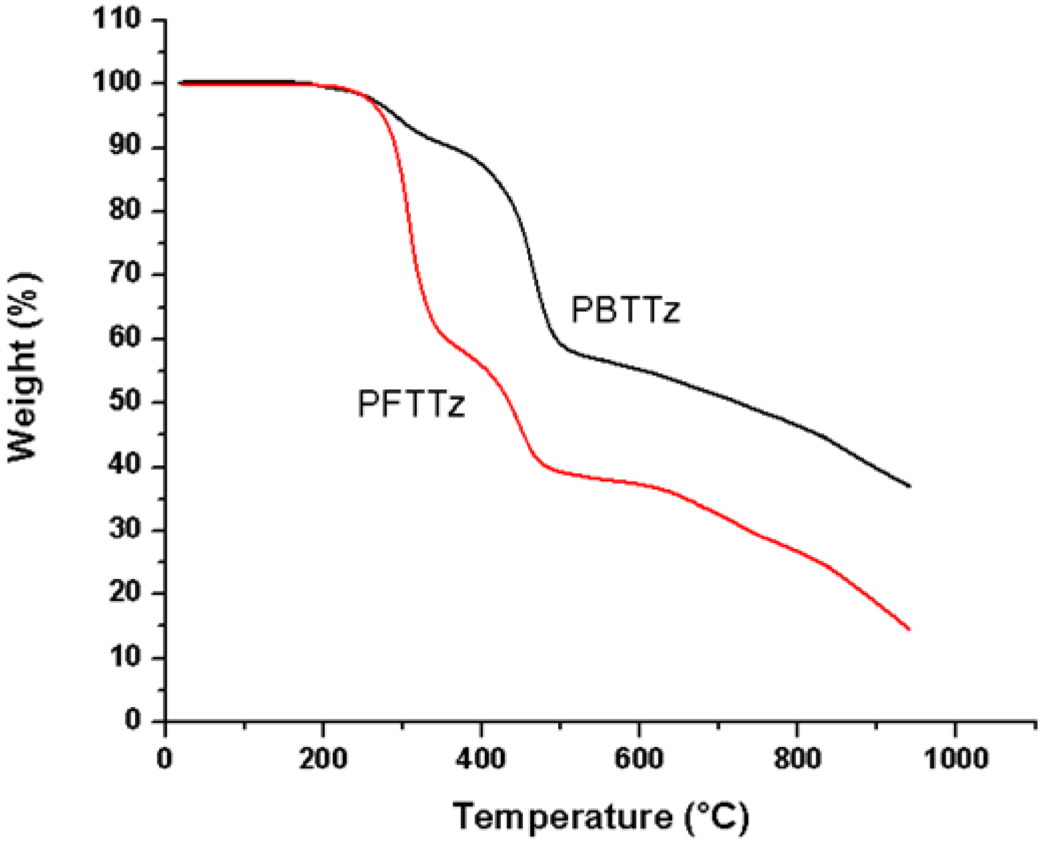


Figure 3. 2 TGA thermograms of the polymers PFTTz and PBTTz.

Table 3. 1 GPC and TGA results of the polymers

Polymers	M_w (g mol^{-1})	M_n (g mol^{-1})	M_w/ M_n	T_d (°C)[a]
PBTTz	21932	21885	1.0	291
PFTTz	18025	12370	1.5	274
BTzTh[b]	17889	8288	2.2	-

[a] The temperature at 5% weight loss measured by TGA under nitrogen atmosphere at a heating rate of °C/min.

[b] Ref. 94

3.2 Polymer Electrochemistry

In order to investigate the electron transfer of the polymer films, the redox potentials were measured by cyclic voltammetry. Polymers, PFTTz and PBTTz, were dissolved in DCM (10 mg/mL) and spray cast on ITO coated glass slides, which were used as the working electrodes in characterization. The CV curves of the two polymers are shown in figure 3.3 in the potential range of 0–1.7 V for PFTTz and 0-1.5 V for PBTTz versus pseudo reference silver wire. All CV measurements of the polymers were determined using platinum wire as the counter electrode in 0.1 M $TBAPF_6$/acetonitrile (ACN). Anodic scan doping/dedoping potential couple was detected for PFTTz as 1.38 V and 0.95 V at a scan rate of 100 mV/s. Similar redox potentials were recorded for PBTTz as 1.35 V/ 1.10 V. Same anodic doping potentials reveal that oxidation of the polymers are highly dependent on the electron rich thiophene unit [97].

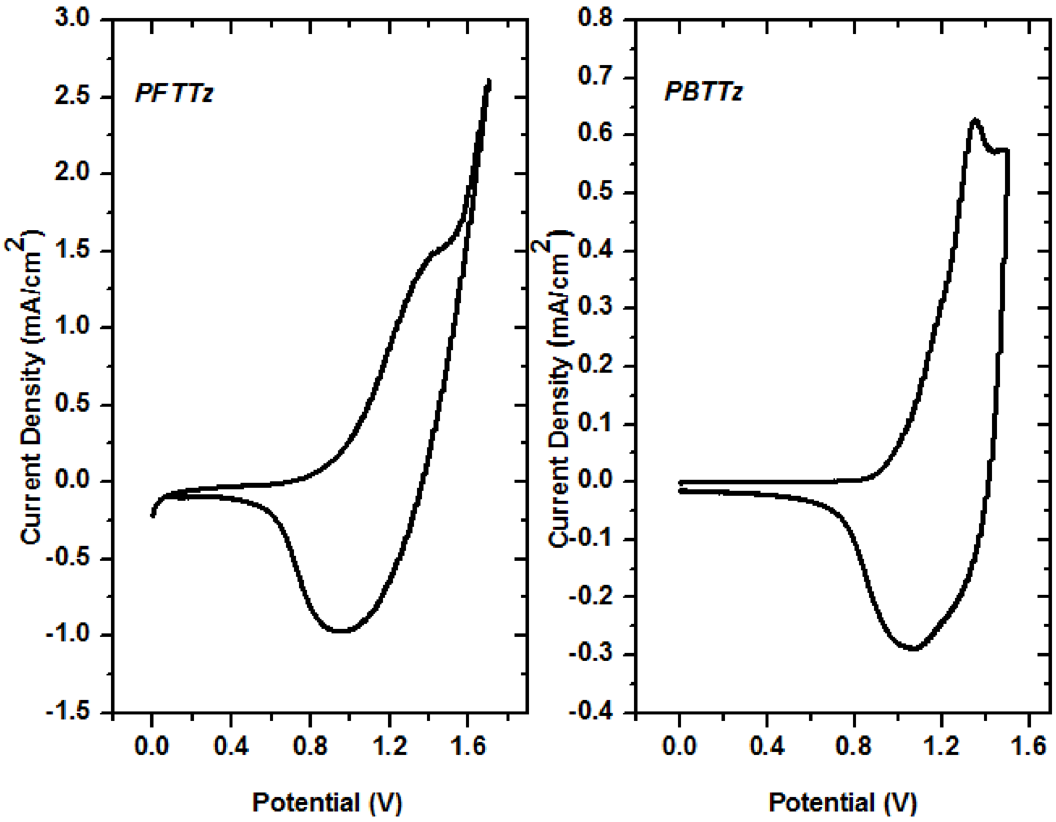


Figure 3. 3 Cyclic voltammograms of the polymers PFTTz and PBTTz.

Energy levels of the conducting polymers play a crucial role in their applications. To calculate the HOMO levels of the polymers, the onset doping potentials of the polymers were determined from the anodic region of the cyclic voltammogram. Onset oxidation potentials of the polymers were determined as 0.99 V for both polymers as their Eox potentials. Eventually, they have same HOMO level as -5.34 eV which was calculated using the empirical formula $E_{HOMO} = -(Eox_{ONSET} - 0.35)-4.7$ eV taking SCE as 4.7 eV versus vacuum [86] and Fc/Fc$^+$ as 0.35 V versus SCE [87].

LUMO levels of the polymers were calculated subtracting the optical band-gap values from the HOMO energy levels of the polymers, which are listed in table 3.2. LUMO levels are found as -3.19 eV for PFTTz and -3.55 eV for PBTTz. From these results it can be concluded that presence of the benzotriazole unit, which is more electron deficient than fluorine, lowers the LUMO energy level and hence the band gap as expected [98].

Table 3. 2 Electrochemical and optical properties of the polymers.

	PBTTz	**PFTTz**	**BTzTh**[a]
$E_{doped,ox}$ (V)	1.35	1.38	1.55
$E_{dedoped,ox}$ (V)	1.10	0.95	1.00
$E_{doped,ox\ (onset)}$ (V)	0.99	0.99	1.00
HOMO (eV)	-5.34	-5.34	-5.32
LUMO[b] (eV)	-3.55	-3.19	-3.62
Eg^{op}	1.8	2.1	1.7
λ^{max} (nm)	520/720/1430	465/670/1560	460/630/1230
Optical contrasts (%)	21/28/50	22/23/52	10/40/65
Switching times (s)	1.5/1.9/0.7	2.5/0.7/0.8	2.5/0.5/0.5

a Ref 94

b LUMO energy levels calculated by subtracting the optical band-gap values from HOMO levels.

In table 3.2 the electrochemical results of the previously published polymer (BTzTh), were also inserted to discuss the effect of the linear and the branched alkyl chain. The similarity of the HOMO energy levels is in consistence with the similarity of the oxidation potentials. It is concluded that the substitution of linear or branched alkyl chain into the polymer backbone has almost no effect on the electrochemical behavior of the polymers [99].

3.3 Spectroelectrochemistry

Spectroelectrochemistry studies were performed to explore the electronic structures of the polymers upon applied external bias. Measurements were conducted in 0.1 M TBAPF$_6$/acetonitrile (ACN) solvent medium with same electrodes used in electrochemical studies. The UV-vis-NIR absorption spectra of the polymers are shown in figure 3.4.

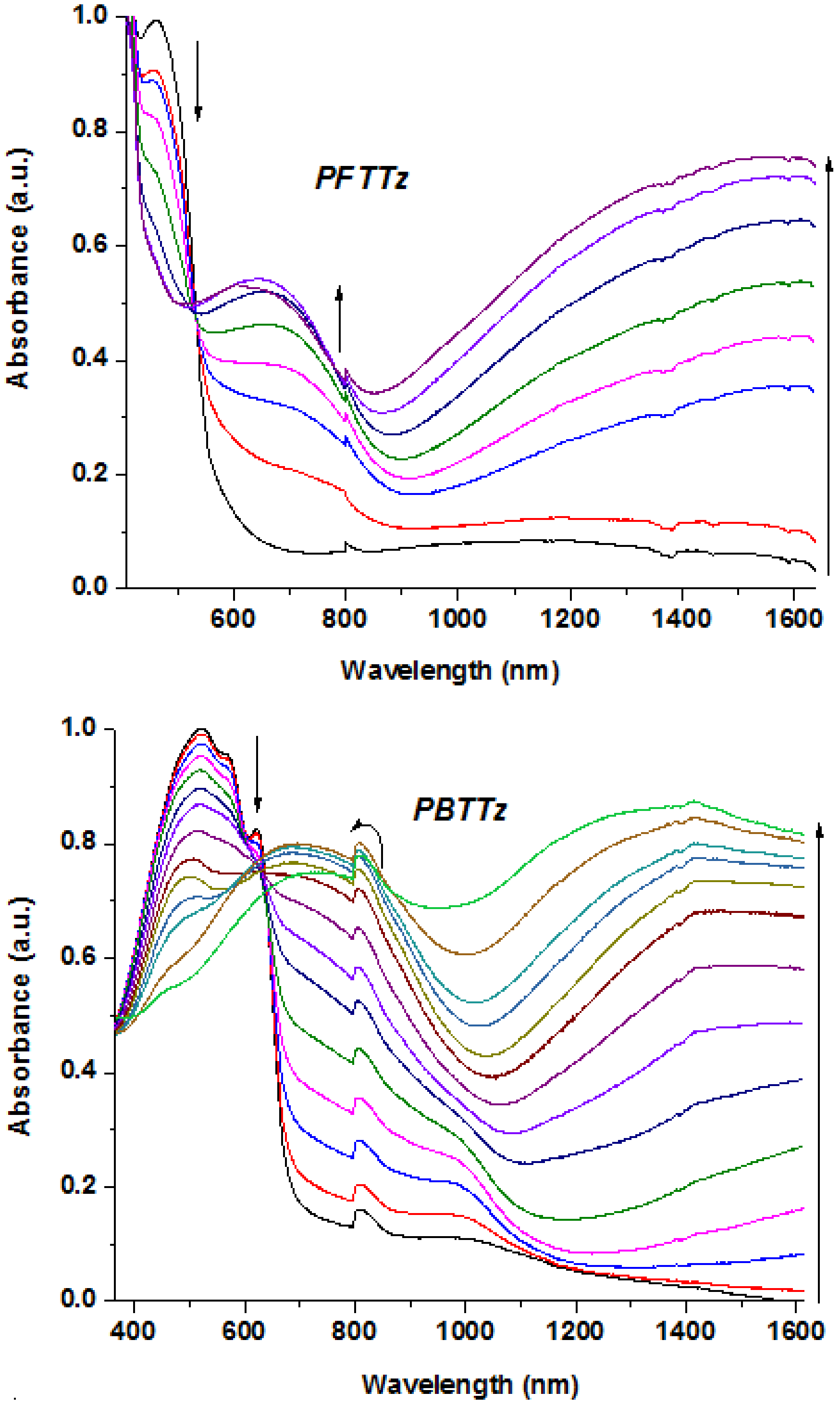


Figure 3. 4 Electronic spectra of polymers PFTTz and PBTTz in their neutral and oxidized states.

Color change of the polymer films were observed during stepwise oxidation with applied potentials higher than their onset potentials. Absorption spectra of the polymer films recorded at each oxidized state were achieved via applying 0.1 V step intervals. Characterization of fully doped and fully dedoped states of conjugated polymers means a lot in terms of their electrochromic properties. It requires sensitive measurements since colors (thereby the energy levels of the polymer films) change with very small potential differences. Five colors were observed for PBTTz. Purple in neutral state, different shades of grey at potentials 1.025 V, 1.075 V and 1.15V and dark blue in fully doped state at 1.5 V. Fluorene addition into the polymer backbone instead of branched chain substituted benzotriazole resulted an orange film in its neutral state, light brown at the potential 1.2 V and blue at the potential 1.4 V. L, a, b values of the polymer films are listed in table 3.3.

Table 3. 3 L*a*b* color coordinates of the polymer films at their various states

	PFTTz			**PBTTz**				
	0.0 V	1.2 V	1.4 V	0.0 V	1.02 V	1.07 V	1.15 V	1.5 V
								
L*	75.202	72.760	73.675	36.176	35.518	38.234	42.399	44.347
a*	2.868	-6.018	-16.444	17.498	0.279	-1.413	-10.486	-15.080
b*	64.091	56.614	8.012	4.752	10.426	3.682	5.035	-4.215

In the neutral states of the polymers main absorption bands were located at 465 nm for PFTTz and 520 nm for PBTTz. The extension of the absorption bands of the polymer films are directly related to their film conductivity hence to their band gap energies. Optical band gap energies of the polymers were calculated as 2.1 eV (PFTTz) and 1.8 eV (PBTTz) from their lower π-π^* transitions in other words from their onset absorption edge of the neutral state spectrum. While increasing the applied potential new absorption bands emerged for PFTTz in both visible and NIR region with absorption maxima at 670 nm and 1560 nm. Similar phenomena were observed for the polymer PBTTz with absorption maxima at 720 and 1430 nm. These newly emerged bands resulted from radical cations and dications. At their fully oxidized states, polaronic and bipolaronic bands of the polymers reached their maximum points at longer wavelengths. Since the tails of the newly emerged bands were more likely placed in the visible region different colors of the oxidized states were specified for both polymers.

To investigate the effect of branched and linear alkyl chain effect we compared the thin film absorptions of the polymer PBTTz with that of the polymer prepared in our previous work (BThTz) (Figure 3.5). Branched alkyl chain containing polymer showed more distinct shoulders in its neutral state. The reason is that it has a higher molecular weight than the linear chain grafted one [100]. Additionally branched chain substitution resulted with broader absorption with a red shift, which is highly beneficial for the polymers considering their use as active materials in organic photovoltaics. This surprising result showed that although the branched alky chain-containing polymer is sterically more crowded, it has stronger π-π interactions in solid state as shown by Kim et al., [101] which is an important parameter for high hole mobility for donor materials.

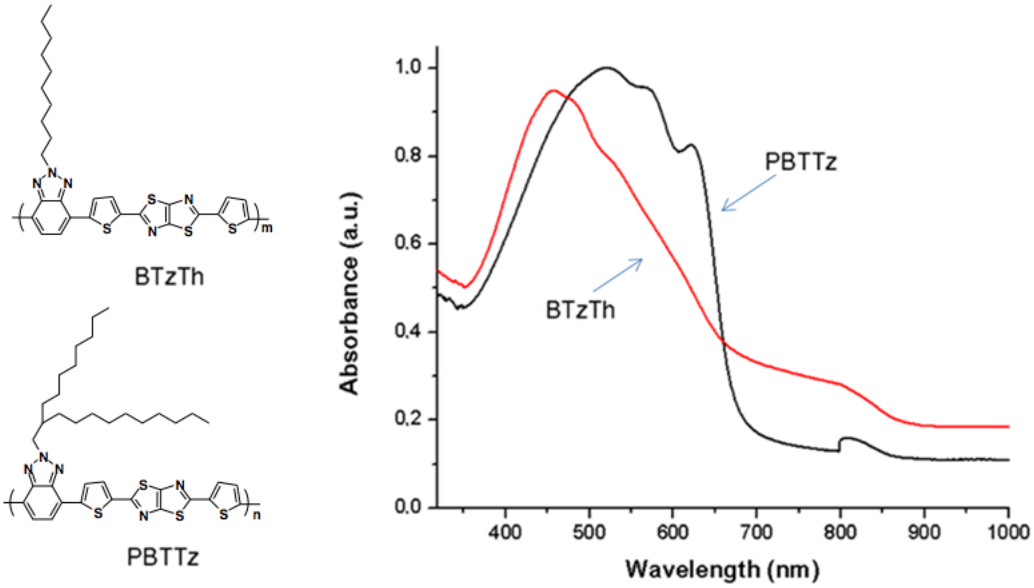
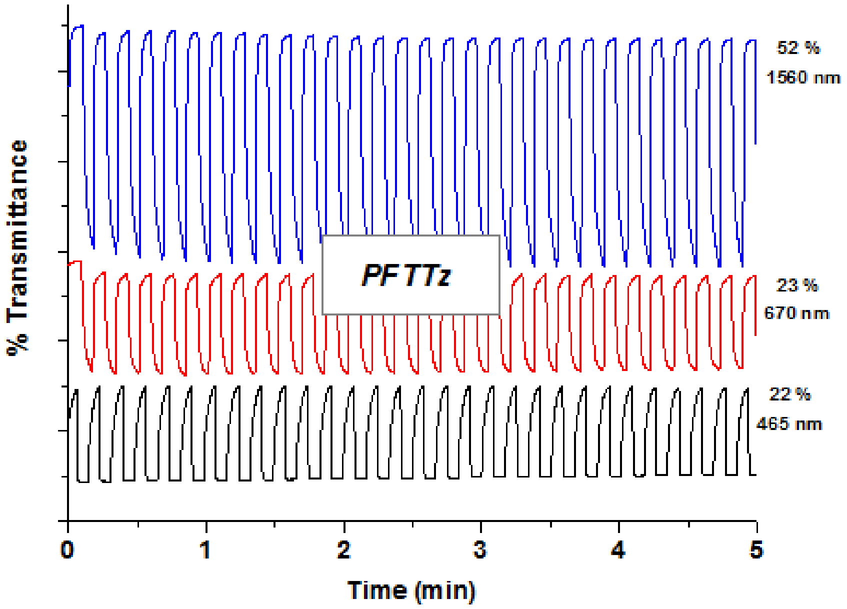


Figure 3. 5 Neutral film absorption spectra of polymers PBTTz and BTzTh.

3.4 Switching Studies

Fast switching time and high optical contrast values of an electrochromic material are critical parameters. Chronoabsorptometry studies were performed in order to define the switching properties. Polymers were spray cast onto ITO coated glass slides and studied between their neutral and fully doped potentials. Percent transmittance as a function of time were found as 22% at 465nm, 23% at 670 nm and 52% at 1560 nm (Figure 3.6) for the PFTTz. Quite similar percent transmittance values for the polymer PBTTz were observed as 21% at 520 nm, 28% at 720 nm and 50% at 1430 nm. The optical contrasts of the polymers, especially in the NIR region, are quite satisfactory. Such high optical contrasts make the polymers good candidates for the NIR region electrochromic device applications.



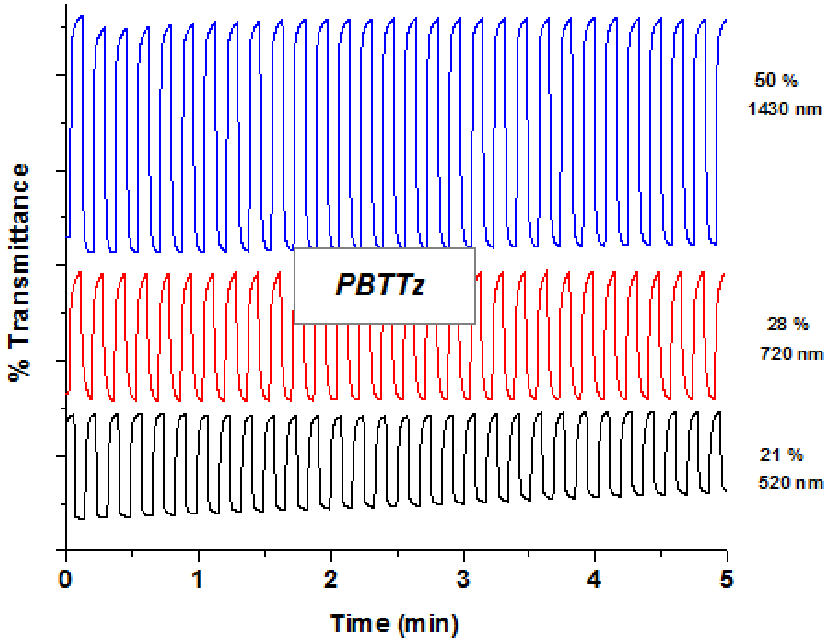


Figure 3. 6 % Transmittance vs time charts of the polymers PFTTz and PBTTz.

Switching times of the polymers were calculated by taking 95% of a full transition of neutral- fully doped states from their % transmittance versus time graphs. They are recorded for both polymers in their each local maximum absorption. Short switching times as 0.7 s (670 nm) and 0.8 s (1560 nm) (table 3.2) show that charge transport is easier in its polaronic and bipolaronic states for the polymer PFTTz. On the contrary, for the polymer PBTTz, 1.9 s switching time was observed in its polaronic absorption region, which is longer than the value recorded in its lower energy band (1.5 s). The fastest switching time for PBTTz is observed in its NIR region as 0.7 s, which also backs up its NIR applications.

4. Conclusions

Two multichromic donor–acceptor type conjugated polymers PBTTz and PFTTz were synthesized containing benzotriazole, fluorene and thiazolothiazole units in the main chain via Stille and Suzuki coupling polymerizations to explore their electrochromic properties. Ability to change their colors in a very small potential range makes them suitable candidates in different applications in due course. Low band gap and strong absorption ability in visible region of PBTTz suggest that it could be used in the construction of organic photovoltaics. Reported properties showed that PBTTz is more multicolored with wider absorption, smaller band gap and faster switching time than the fluorene containing one.

CHAPTER 4

SOLAR CELL PARAMETERS OF A THIAZOLOTHIAZOLE CONTAINING POLYMER

1. Aim of the Study

As it is discussed earlier, organic solar cells have remarkable advantages over their inorganic counterparts. Manufacturing organic solar cells notably costs very low and has much less environmental impact. Additionally, it is worth to note that, solution processable polymer solar cells are one of the most important classes among other organic photovoltaics. Soluble polymers can be easily coated on the substrates via simple techniques such as spin coating or drop casting whereas insoluble organic small molecules need to be evaporated on the surface during construction via organic molecule evaporator. Building the active layer with vapor deposition technique causes longer operation times and requires higher energy consumption compared to simple spin coating. The other advantage of the solution processable polymer is that it is possible to built bulk heterojunction solar cells. In bulk heterojunction solar cells, a donor material (polymer) and an acceptor material (fullerene) are simply mixed in an appropriate solvent.

Generation of the bounded electron-hole pairs (excitons) and their separation ability in the active layer are the key parameters for an organic photovoltaic since they are directly related to the efficiency. In the working principle of an organic solar cell excitons are created by photon absorption. Created excitons need a driving force for separation. The difference between the energy levels of the polymer and the fullerene derivative in the mixed active layer results in an efficient charge separation [102]. Excitons have very short diffusion length (~10 nm) with very short lifetime (<1 ns) [103]. Therefore, for an efficient solar cell, the surface area of the interface between the donor and acceptor material need to be large. In the bilayer structure the interface is just in the middle, however in the bulk heterojunction it lies between two electrodes with increased surface area (Figure 4.1). Bulk heterojunction is firstly applied by Yu et al. using the polmer (poly(2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene vinylene)) with fullerene C60 in 1995. Results showed that the incident photon to electron conversion efficiency increased 10 fold compared to bilayer devices. [104]

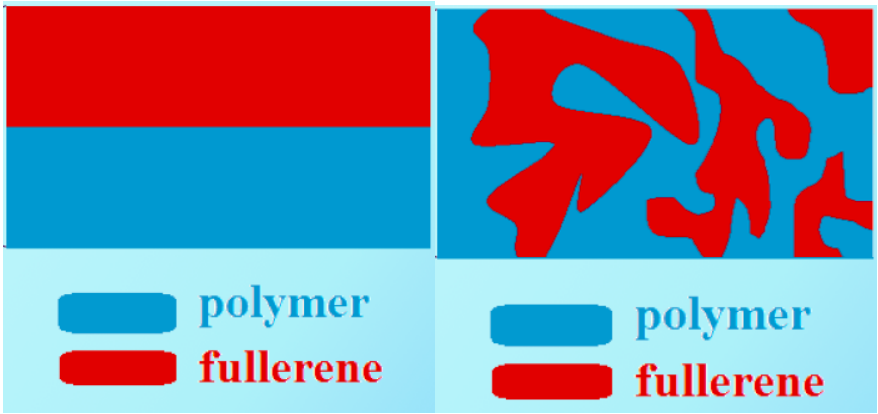


Figure 4. 1 Schematic representation of bilayer (left) and bulk heterojunction (right) solar cell structures.

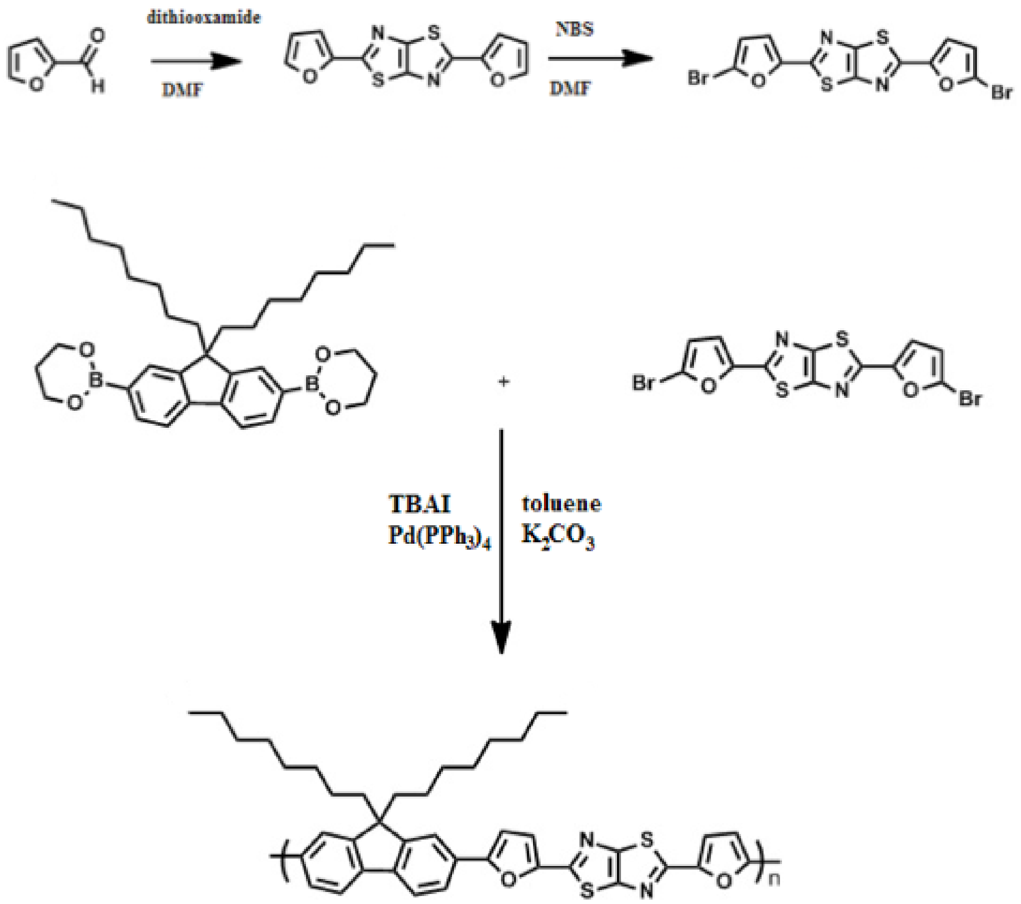
Morphology of the mixed polymer-fullerene film is also an important issue to deal with. Optimization should be made before the construction of the device. Transfer of the separated charges to the electrons is as important as the charge separation for high efficiency. There are several methods for morphology optimization in the literature. The mostly used one is the thermal annealing of the active layer [105]. In some cases, thermal treatment to the coated active layer at a specified temperature for a specified time is beneficial to increase the efficiency. Adding some solvents into the active layer solution mixture can also help to the arrangement of the polymer-fullerene distribution. It is reported in the literature that adding some alkenedithiols into the polymer-fullerene mixture is resulted an increase in the power conversion efficiency of the solar cell from 2.8% to 5.5% [106].

In this chapter, thiazolothiazole, fluorene and furan containing polymer (PFFTTz) was successfully synthesized using Suzuki coupling polymerization technique. HOMO and LUMO energy levels were calculated from the cyclic voltammogram, which is obtained in an inert environment. The absorption band of the polymer was detected in the UV –vis region. Band gap was determined both from cyclic voltammetry and the thin film absorption spectrum. After characterization of the polymer, bulk heterojunction solar cell was constructed and characterized successfully.

2. Result and Discussion

2.1 Synthesis and characterization of the polymer

In the synthesis of the polymer, firstly dibromo derivative was prepared. Furan-2-carbaldehyde was condensed with dithiooxamide in DMF to obtain 2,5-di(furan-2-yl)thiazolo[5,4-d]thiazole. Bromination was performed with NBS, which was added slowly into the reaction flask covered with aluminum foil to prevent sunlight. Polymerization was achieved in the presence of palladium and TBAI catalysts. Purification of the polymer was performed by Soxhlett extraction using ethanol, hexane and acetone solvents to get rid of the impurities and short polymeric chains. For further purification, precipitation of the polymer was performed in cold ethanol (Figure 4.2).



PFTTz

Figure 4. 2 Synthetic route for polymer PFFTTz.

The molecular weights and the polydispersity index (PDI) of the polymer were characterized with gel-permeation chromatography (GPC) with polypropylene glycol universal calibration method. Number average molecular weight of the polymer was found as 14400 with associated M_W value of 42200. PDI of the polymer were calculated as 2.9.

The thermal property of the polymers was investigated to explore its decomposition temperature and figure out if it can resist conditions applied during solar cell device construction. Thermal gravimetry analysis (TGA) result showed that polymer is thermally stable with decomposition temperature of (5% weight loss) 400 °C, which is a remarkable value for an alkyl chain containing polymer.

The polymer lost its 45% by weight at a temperature higher than 500 °C. (Figure 4.3)

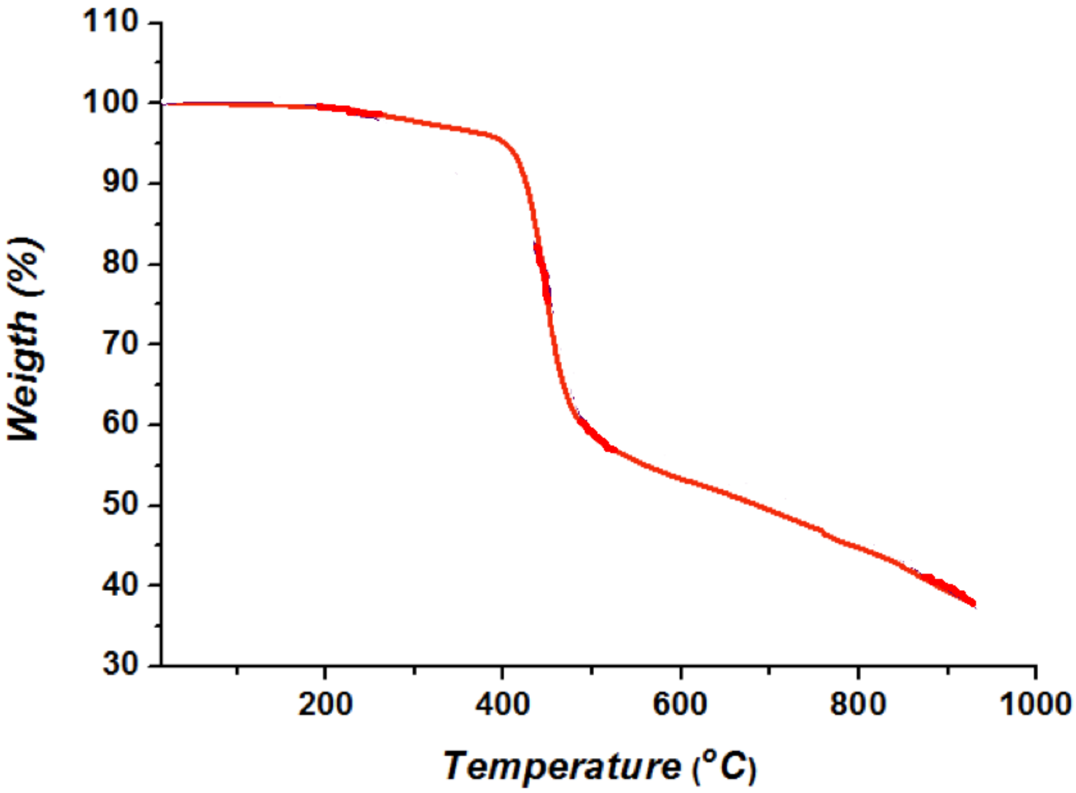


Figure 4. 3 Thermal gravimetric analysis of the polymer PFFTTz.

According to this results polymer can be annealed for morphology optimization during the solar cell device construction, safely. GPC results of the polymer are shown in the table 4.1.

Table 4. 1 Results of the gravimetric analysis of the polymer PFFTTz.

	Mn (g/mol)	Mw (g/mol)	PDI
PFFTTz	14398	42199	2.9

2.2 Polymer Electrochemistry

Electrochemical characterization of the polymer was performed under nitrogen atmosphere in a glove box using a three-electrode system. ITO coated substrates were cleaned before polymer coating. Substrates were sonicated in a cleaning solution “hellmanex” for 15 minutes and washed with purified water. Substrates were heated at 120 °C to get rid of the water residue after dried with a nitrogen gun. Polymer was dissolved in chloroform (10mg/mL) and spin coated at 1500 rpm. Polymer coated substrates were used as the working electrode. Ag/AgCl electrode was used as the reference electrode. It is prepared via immersing an Ag wire into 2mL of 1M HCl solution under applied voltage (5V) for 3 minutes. A platinum foil was used as the counter electrode.

The CV curve of the polymer is shown in figure 4.4 in the potential range of 0–1.25 V for anodic scan and 0-(-2.2) V for cathodic scan in 0.1 M $TBAPF_6$/acetonitrile (ACN) solution. Anodic scan doping/dedoping dpotential couple was detected for PFFTTz as 0.86 V/0.78 V whereas cathodic scan doping/dedoping potential couple was detected as -2.14/-2.01 at a scan rate of 20 mV/s versus Fc/Fc^+. Onset potentials were determined to calculate the HOMO/LUMO energy levels. Onset potential in anodic doping was found as 0.63 V and the onset potential in the cathodic doping was found as -1.87 V. According to the determined onset potentials the HOMO and LUMO energy levels were calculated as -5.38 eV and -2.33 eV, respectively. Additionally, electrochemical band gap of the polymer is calculated as 2.5 eV. Electrochemical results are listed in table 4.2, which showed that polymer is suitable for building a bulk heterojunction solar cell mixing with $PC_{61}BM$.

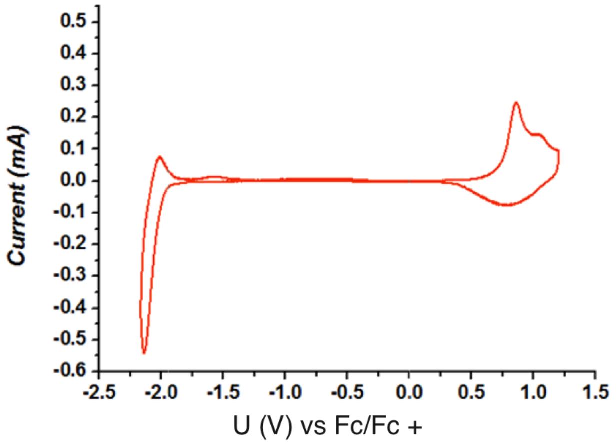


Figure 4. 4 Cyclic voltammogram of the polymer PFFTTz.

Table 4. 2 Electrochemical properties of the polymer PFFTTz.

	PFFTTz
$\mathbf{E_{doped,ox}}$ **(V)**	0.86
$\mathbf{E_{dedoped,ox}}$ **(V)**	0.78
$\mathbf{E_{doped,ox\ (onset)}}$ **(V)**	0.63
$\mathbf{E_{doped,red}}$ **(V)**	-2.14
$\mathbf{E_{dedoped,red}}$ **(V)**	-2.01
$\mathbf{E_{doped,red\ (onset)}}$ **(V)**	-1.87
HOMO (eV)	-5.38
$\mathbf{LUMO^{b}}$ **(eV)**	-2.33
$\mathbf{Eg^{ec}}$ **(eV)**	2.5
$\mathbf{Eg^{op}}$ **(eV)**	2.3

2.3 Optical Properties

Thin film absorption range of a polymer is very important property since it is directly related to the ability of photon absorption. In order to determine the absorption range and the optical band gap or the polymer Uv-vis spectrum was recorded. (Figure 4.5) Thin film of the polymer was prepared as in the electrochemistry study from 10mg/mL polymer solution in $CHCl_3$.

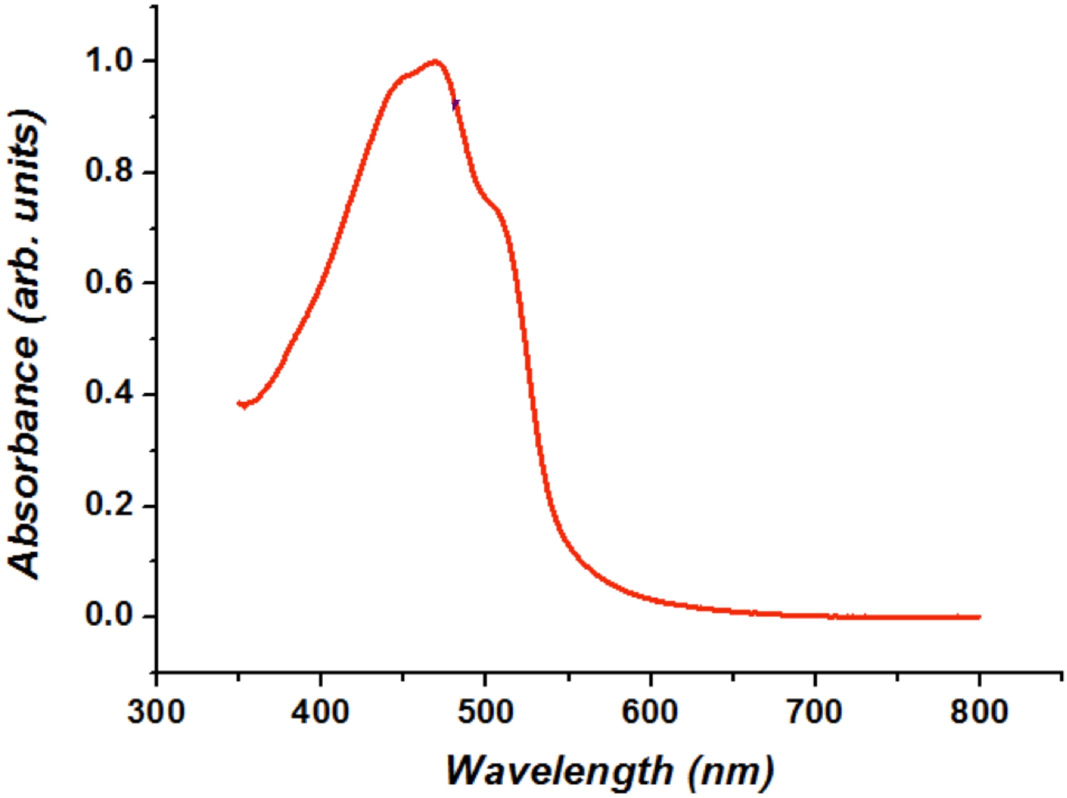


Figure 4. 5 Thin film absorption spectrum of the polymer PFFTTz.

The absorption band covers the region between 350nm and 550 nm with a λ^{max} 475nm. The optical band gap of the polymer was calculated as 2.3 eV which is slightly smaller value from its electrochemical band gap. This difference is common for these two techniques. The reason of obtaining a higher value from the cyclic voltammetry is explained as the presence of a barrier for electron transfer from the ITO coated glass slide to the polymer film.

2.4 Photovoltaic Properties

Photovoltaic properties of the polymer were examined building the device structure of ITO/PEDOT:PSS/active layer/LiF/Al. Active layer of the devices were prepared mixing the polymer solution with PC61BM in chlorobenzene.

The effect of the annealing temperature was firstly studied for the morphology optimization. In the figure 4.6, the I-V curves are given for the devices of PFFTTz:PC61BM mixture with ratio 1:1 20mg/mL in CB. After coating the active layers the substrates were heated on a hot plate at 140 oC and 200 oC for 10 minutes.

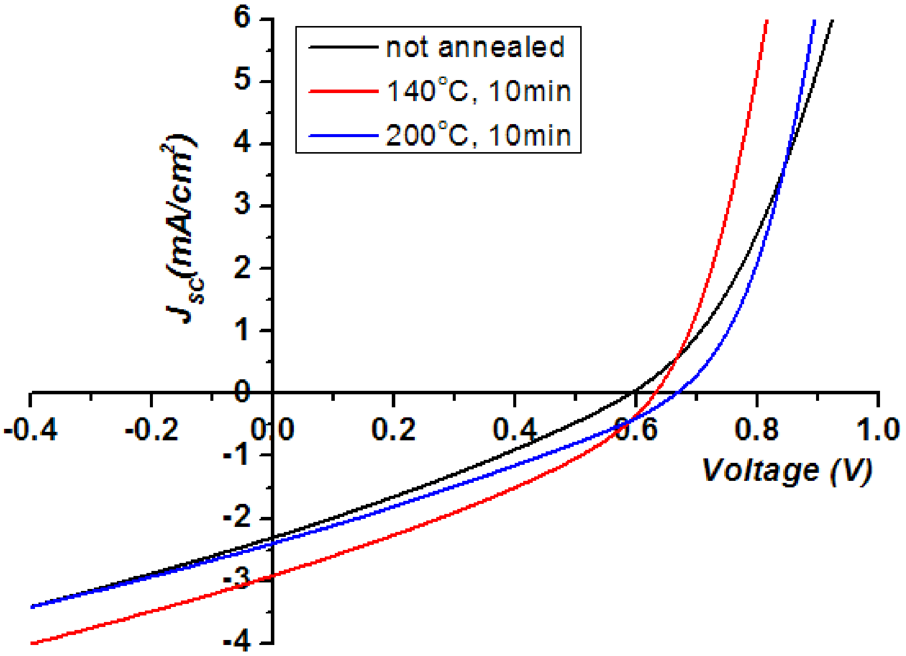


Figure 4. 6 I-V curves of the not annealed and annealed films.

The highest PCE of the solar cell is obtained from the device annealed at 140 °C for 10 minutes as 0.74 %. The open circuit voltage, fill factor and the short circuit current parameters of the devices were summarized in table 4.3. Annealing of the polymer mixture is both increased the Voc and the Jsc values.

Table 4. 3 Solar cell parameters of the not annealed and annealed films.

	J_{SC} (mA/cm^2)	**V_{OC} (V)**	**FF**	**PCE (%)**
Not annealed	2.3	0.58	0.29	0.48
140°C, 10min	2.9	0.62	0.33	0.74
200°C, 10min	2.4	0.66	0.30	0.60

After deciding the annealing temperature, the effect of the polymer:PCBM mixture ratio and active layer thickness were determined. I-V curve results of the devices were given in figure 4.7.

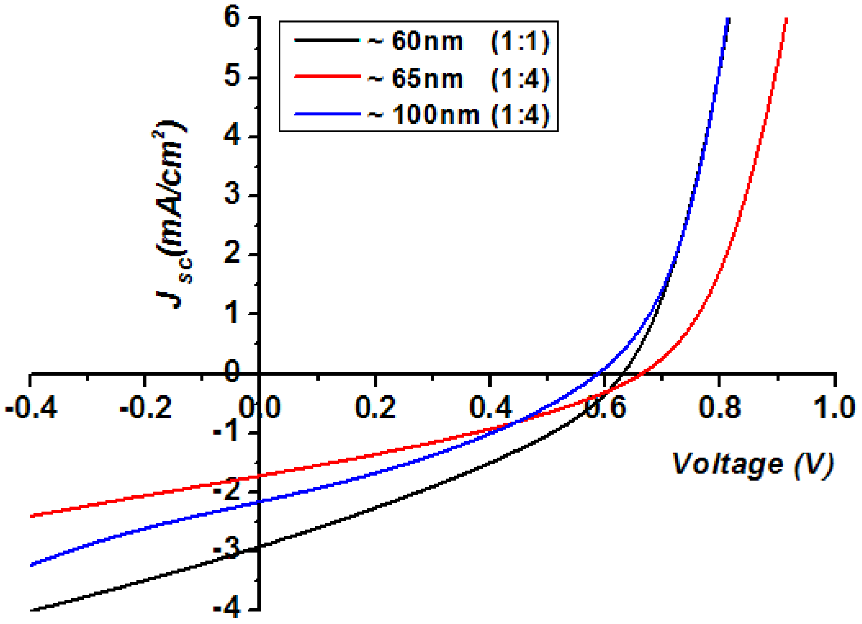


Figure 4. 7 I-V curves of the polymer solar cells with different film thickness.

The highest efficiency for the photovoltaic device was recorded for the solution with 1:1 ratio. (Table 4.4)

Table 4. 4 Solar cell parameters of different film thicknesses.

	J_{SC} (mA/cm^2)	**V_{OC} (V)**	**FF**	**PCE (%)**
60nm (1:1)	2.9	0.62	0.33	0.74
65nm (1:4)	1.7	0.66	0.33	0.47
100nm (1:4)	2.1	0.58	0.33	0.55

Increasing the PCBM ratio in the mixture resulted in a lower value of short circuit current although the Voc value increased. When the thickness of the active layer increased to 100nm from 65nm, the current increased, however a lower value was obtained for the Voc as 0.58 V.

3. Experimental

3.1 Materials and Instrumentation

All chemicals used in the synthesis of the polymer were purchased from Sigma Aldrich and Acros with no further purification. Toluene was allowed to dry for several days keeping a Na wire inside the bottle before use. Polymerization was performed under an inert atmosphere (argon). 2,5-Di(furan-2-yl)thiazolo[5,4-d]thiazole, and 2,5-bis(5- bromofuran-2-yl)thiazolo[5,4-d]thiazole [58, 73] were synthesized according to the literature procedures.

For structural characterization of the polymer, ^{1}H NMR spectra was recorded in $CDCl_3$ on Bruker Spectrospin Avance DPX-400 Spectrometer. Chemical shifts are given in ppm downfield from tetramethylsilane. Molecular weights of the polymer were measured by GPC on Polymer Laboratories GPC 220 with polypropylene glycol universal calibration method and THF as the solvent. Thermal properties of the polymer were conducted by Perkin Elmer Pyris 1 TGA under nitrogen atmosphere at a heating rate of 10 °C/min in the temperature range of 25–950 °C.

Characterization of the solar cells were performed under illumination of a solar simulator (AM 1.5 Global spectrum with 100mW/cm^2 intensity). Keithley 2400 source meter was used while recording I-V curves which were performed in a glove box filled with nitrogen. The active layer thicknesses of the devices were measured with a Bruker Dektak stylus profilometer. While measuring the absorption range of the polymer film Perkin-Elmer Lambda 1050 spectrometer was used.

3.2 Construction of the Solar Cells

In the construction of the solar cells, firstly the substrates are prepared. The ITO coated glass slides were cut into small pieces and some ITO was removed from the surface in order to prevent short circuits. ITO film was etched via immersing the substrates in concentrated HCl solution. After etching the acid residue was cleaned with deionized water. The substrates were cleaned with acetone (at room temperature, 10min), isopropanol (at 50 C, 15 min), hellmanex solution (at 50 C , 15 min) and deionized water (at room temperature, 2 min), successively. Finally, the substrates were washed with deionized water and dried with nitrogen gun. Cleaned substrates were subjected to oxygen plasma for further purification.

Hole transport layer (PEDOT:PSS) were coated onto the substrates at 4000 rpm via spin coater and heated 5 minutes at 150 C. The active layer of the polymer was coated using the polymer:PCBM mixture at 1500 rpm. Mixture was prepared a night before the construction and let to stir overnight. After annealing procedure the substrates were transferred to the evaporator and the electron transport layer (LiF) and the aluminum (cathode) were deposited in the glove box.

3.3 Procedure of the synthesis of PFFTTz

PFFTTz was synthesized according to the published procedure [96] using equivalents of monomers. Both brominated thiazolothiazole derivative and the fluorene derivative were dissolved in dry toluene and purged with argon for 15 min. Solution was refluxed for 72 h under argon flow in a mixture of potassium carbonate (K_2CO_3, 2 M in H_2O) and toluene (3:2 toluene:water) in presence of $Pd(PPh_3)_4$ (5 mol%), and tetrabutylammonium iodide ($N(Bu)_4I$, 1 mol%). After polymerization, the solution was concentrated and poured into cold ethanol. Precipitates purified by Soxhlett extraction.

^{1}H NMR of PFFTTz (400 MHz, $CDCl_3$), d: 7.61– 6.84 (fluorene and furan), 2.01–

0.74 (pendant alkyl chain).

4. Conclusion

Fluorene and thiazolothiazole containing polymer was synthesized via Suzuki-coupling polymerization, successfully. Thermal, electrochemical and optical characterization of the polymer showed that it is a suitable candidate for a solar cell application. Solar cell parameters of the devices were measured. The PSC device based on PFFTTz:$PC_{61}BM$ (1:1 wt ratio, annealed at 140 C for 10 min) exhibited the best PCE of 0.74% with a Voc of 0.62 V, a Jsc of 2.9 mA/cm^2, and a FF of 33% under the illumination of AM 1.5, 100 mW/cm^2.

CHAPTER 5

CONCLUSION

In this thesis, thiazolothiazole derivatives were the main concern. Five novel copolymers containing TTZ unit were synthesized using Stille and Suzuki coupling polymerization methods. Alkyl chain substituted BTZ and fluorene groups were selected as the side monomers in order to obtain soluble copolymers. The ease of synthesis of the benzotriazole group with different types of alky chains led us to explore the effect of branched and linear types of alkyl chains on electrochromic properties of the resulted polymers. Deep HOMO level of the copolymer PFFTTz was the main reason of deciding to exploit the monomer in concern for the polymerization. That property resulted in both good stability of the film and the wide range of absorption in the spectrum.

As shown in the results all thiazolothazole containing polymers have multichromic property. Their ability of changing their colors in a very small potential range and also having small switching times means that these polymers are good candidates for electrochromic device applications. Additionally, their high optical contrast values in the NIR region make them suitable for aerospace applications.

When they all discussed in detail and compared with each other, it is found that BTZ containing copolymers have smaller band gap, faster switching times and wider absorption when it is replaced with fluorene. This result makes benzotriazole a more convenient sub-monomer to couple with thiazolothiazole unit than fluorene. Furthermore, type of the alkyl chain attached to benzotriazole unit has almost no effect on electrochemical properties of the polymers but the colors of the polymer films.

Two articles were published from this thesis. First one, discussed in chapter 2, “Spray-Processable Thiazolothiazole-Based Copolymers with Altered Donor Groups and Their Electrochromic Properties” which was published in Journal of Polymer Science Part A Polymer Chemistry in 2013. [94] Second one, as discussed in chapter 3, “Multichromic and Soluble Conjugated Polymers Containing Thiazolothiazole Unit for Electrochromic Applications”, which was published in European Polymer Journal in 2015. [107] This thesis was prepared with the permission of other authors; Prof. Dr. Levent Toppare and Assoc. Prof. Dr. Yasemin Arslan Udum.

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APPENDIX A

NMR DATA

NMR spectra were recorded on a Bruker DPX 400.

Chemical shifts δ were reported in ppm relative to $CHCl_3$ (^1H: δ=7.2), $CHCl_3$ (^{13}C: δ=77.0), $DMSO_4$-d6 (^1H: δ=2.5) and $DMSO_4$-d6 (^{13}C: δ=39.5) as internal standards.

^1H and ^{13}C NMR spectra of products are given below.

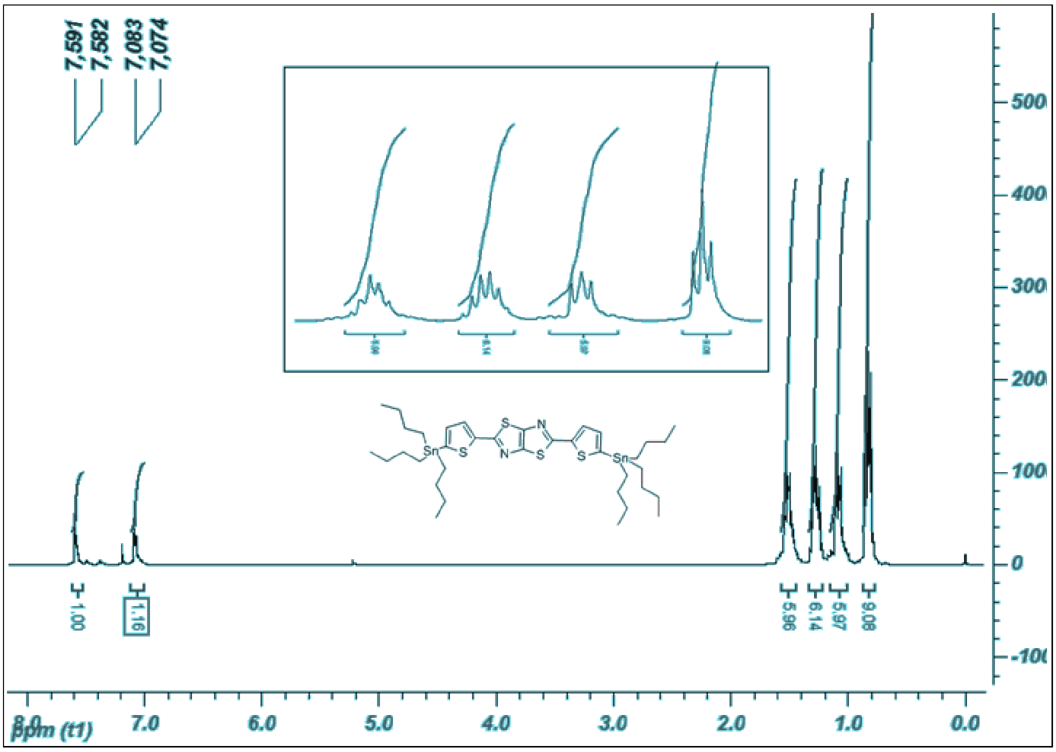

Figure A.1 ^1H-NMR spectrum of 2,5-bis(5-(tributylstannyl)thiophen-2-yl)thiazolo[5,4-d]thiazole

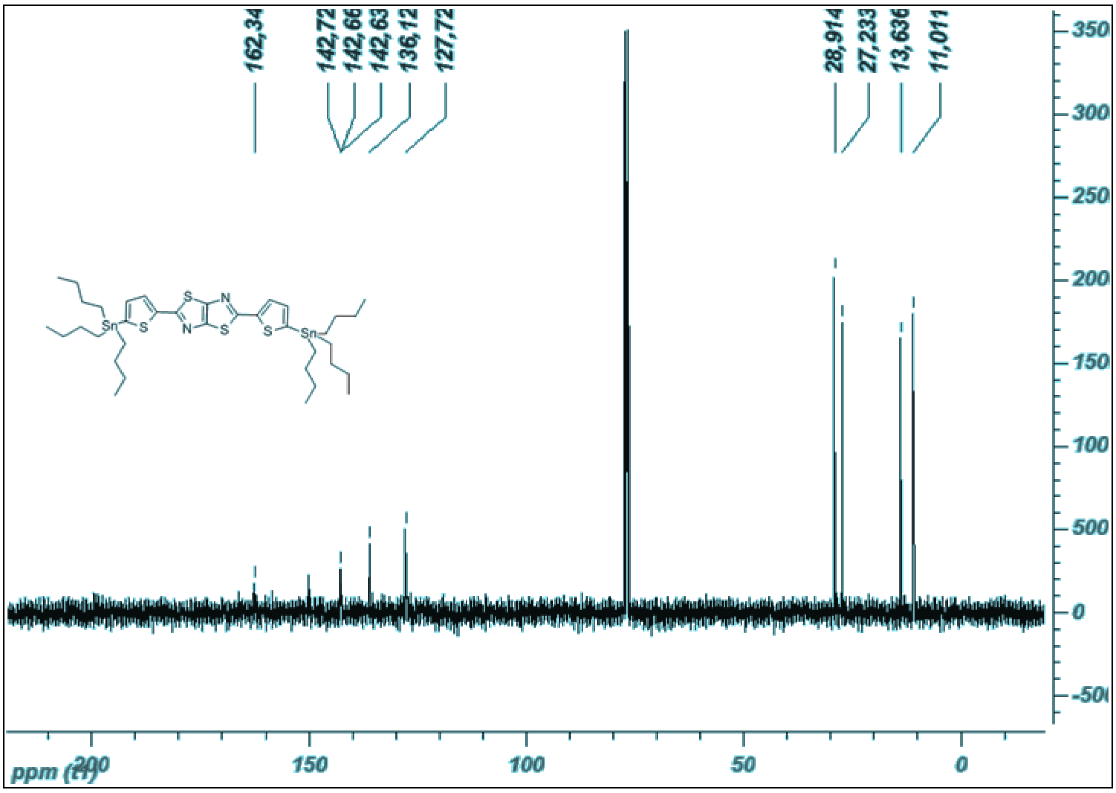

Figure A.2 ^{13}C-NMR spectrum of 2,5-bis(5-(tributylstannyl)thiophen-2-yl)thiazolo[5,4-d]thiazole

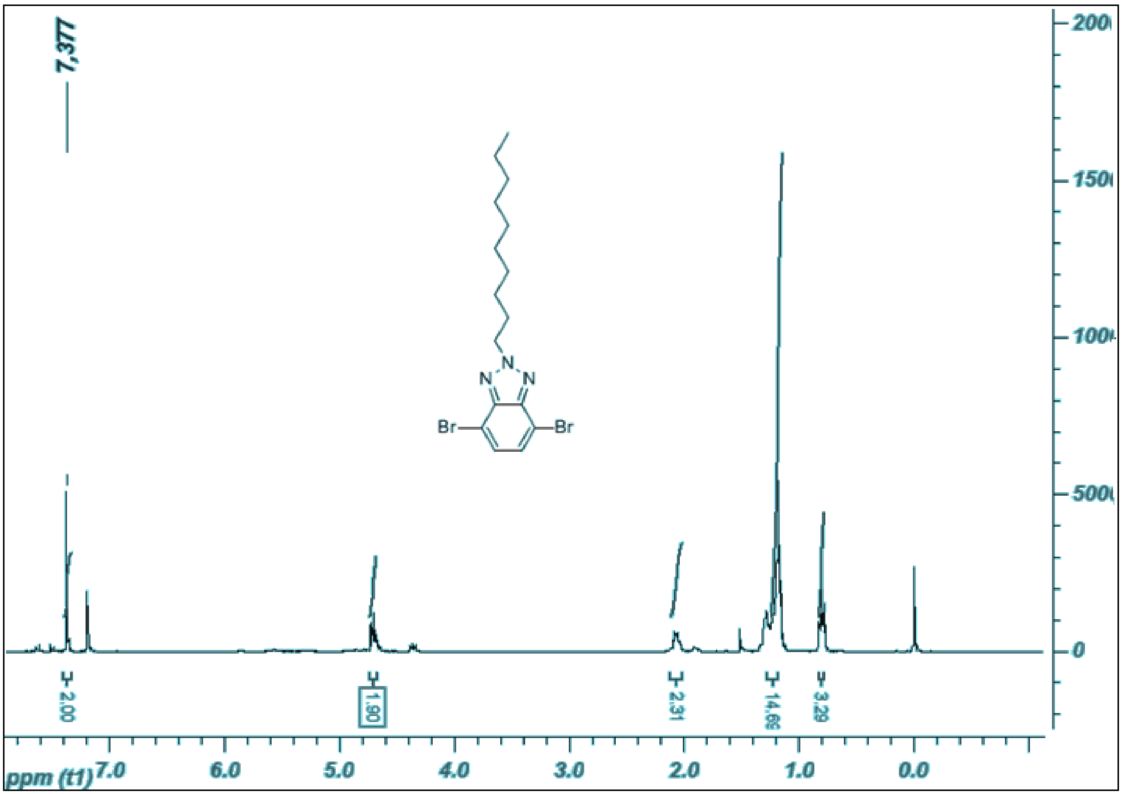

Figure A.3 ^{1}H-NMR spectrum of 4,7-dibromo-2-decyl-2H-benzo[d][1,2,3]triazole

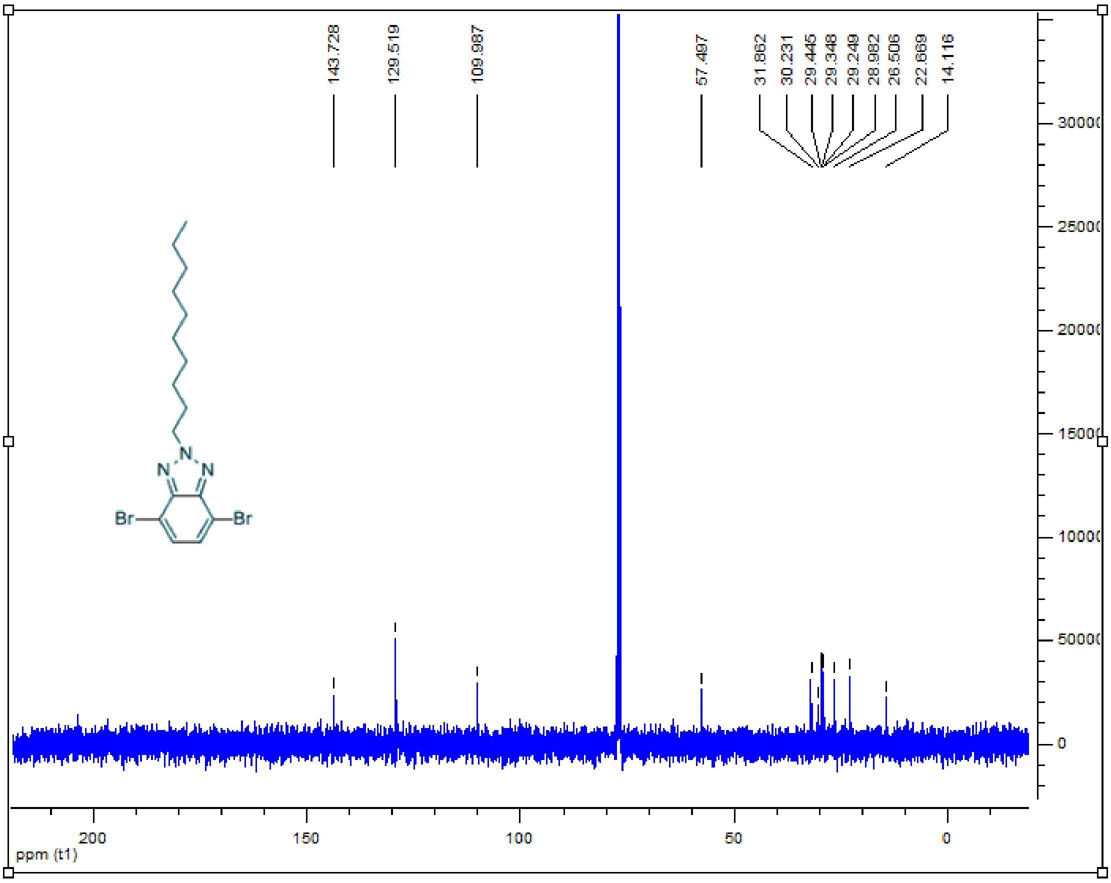

Figure A.4 ^{13}C-NMR spectrum of 4,7-dibromo-2-decyl-2H-benzo[d][1,2,3]triazole

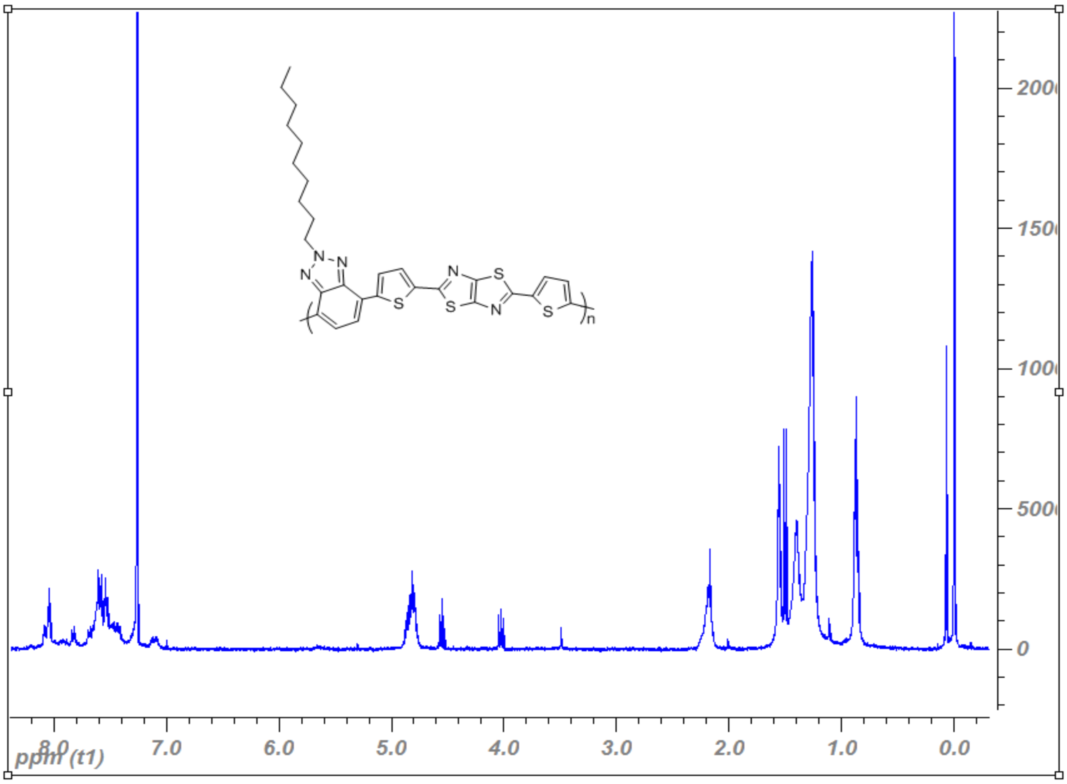

Figure A.5 ^{1}H-NMR spectrum of poly[2-(5-(2-decyl-2H-benzo[d][1,2,3]triazol-4-yl)thiophen-2-yl)-5-(thiophen-2-yl)thiazolo[5,4-d]thiazole]

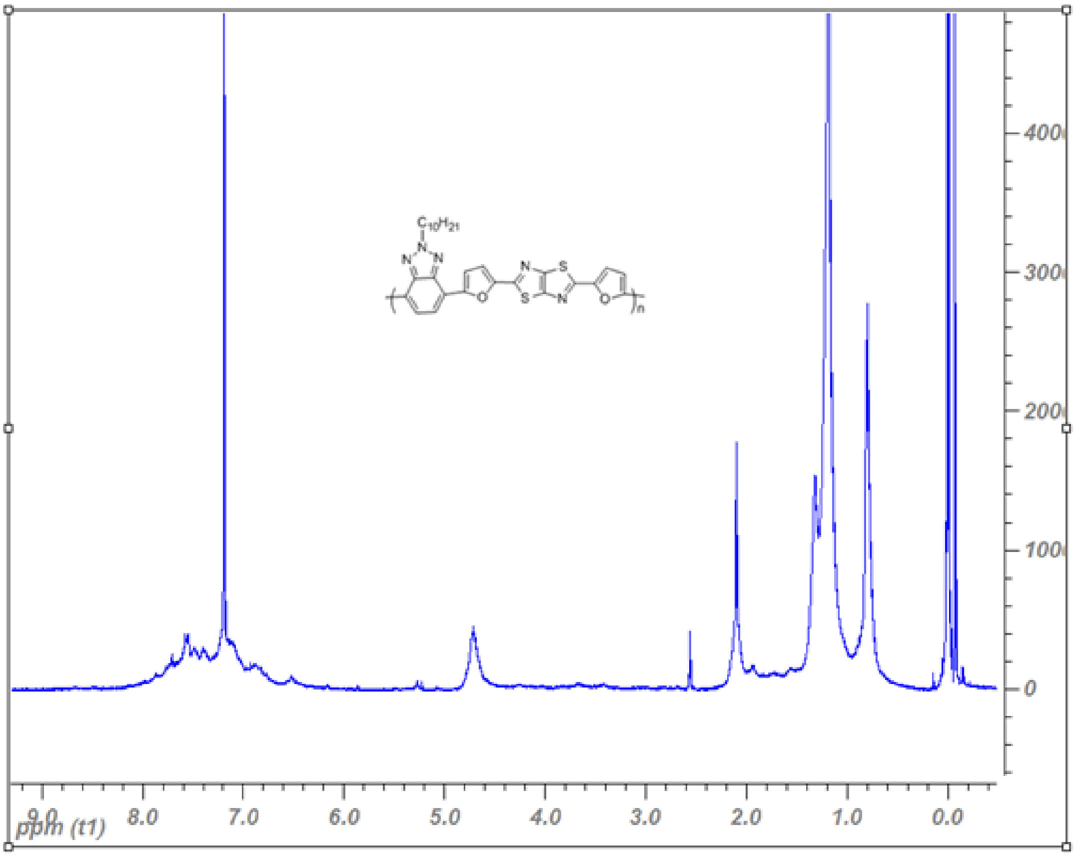

Figure A.6 ^{1}H-NMR spectrum of poly[2-(5-(2-decyl-2H-benzo[d][1,2,3]triazol-4-yl)furan-2-yl)-5-(furan-2-yl)thiazolo[5,4-d]thiazole]

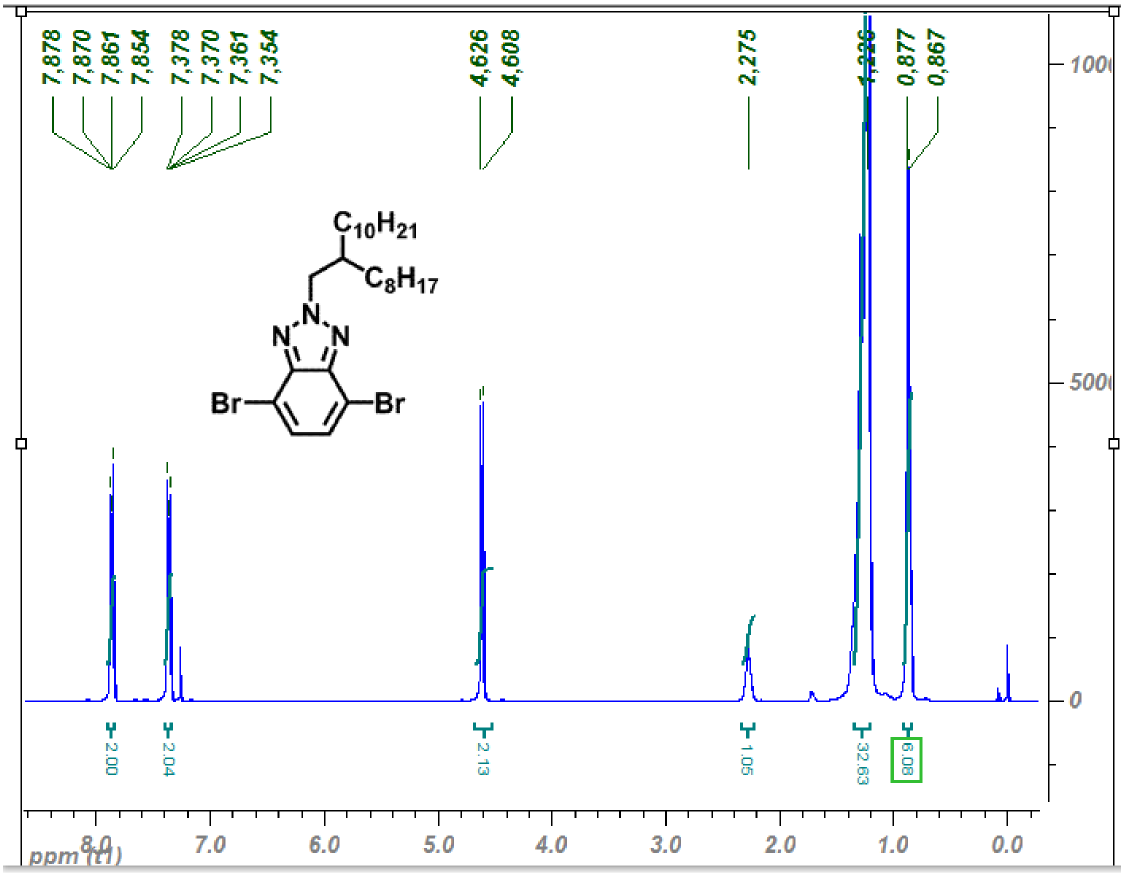

Figure A.7 ^{1}H-NMR spectrum of 4,7-Dibromo-2-(2-octyldodecyl)-2H-benzo[d][1,2,3] triazole

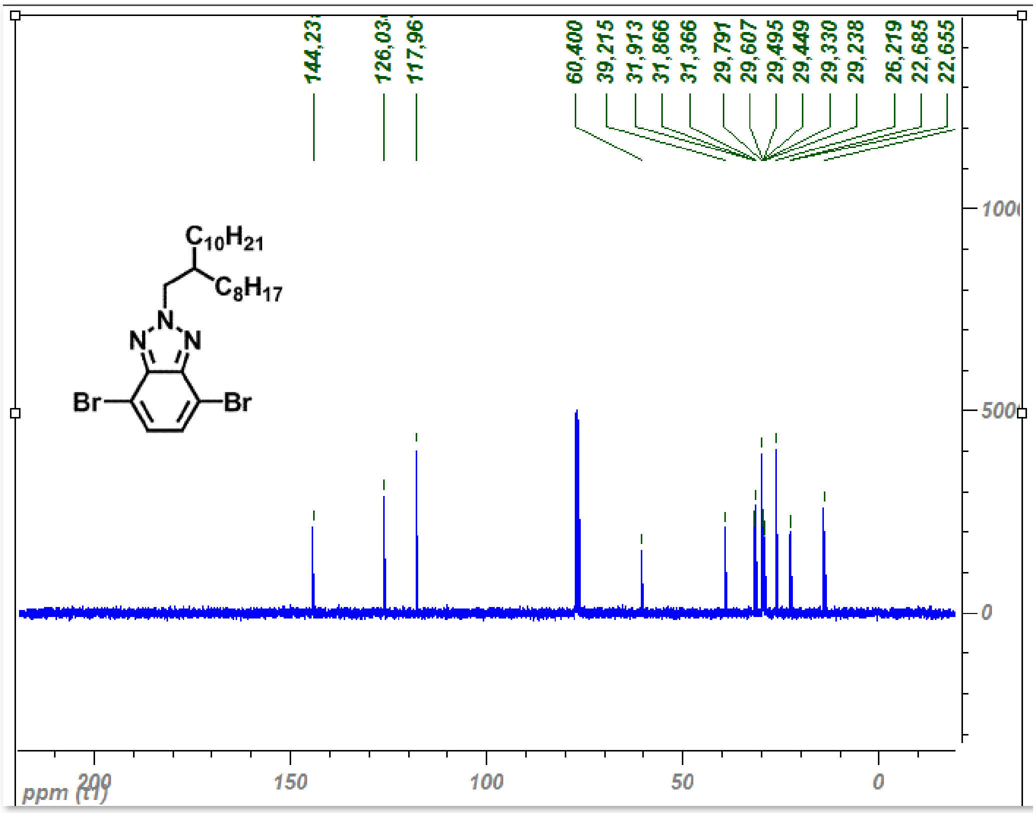

Figure A.8 ^{13}C-NMR spectrum of 4,7-Dibromo-2-(2-octyldodecyl)-2H-benzo[d][1,2,3] triazole

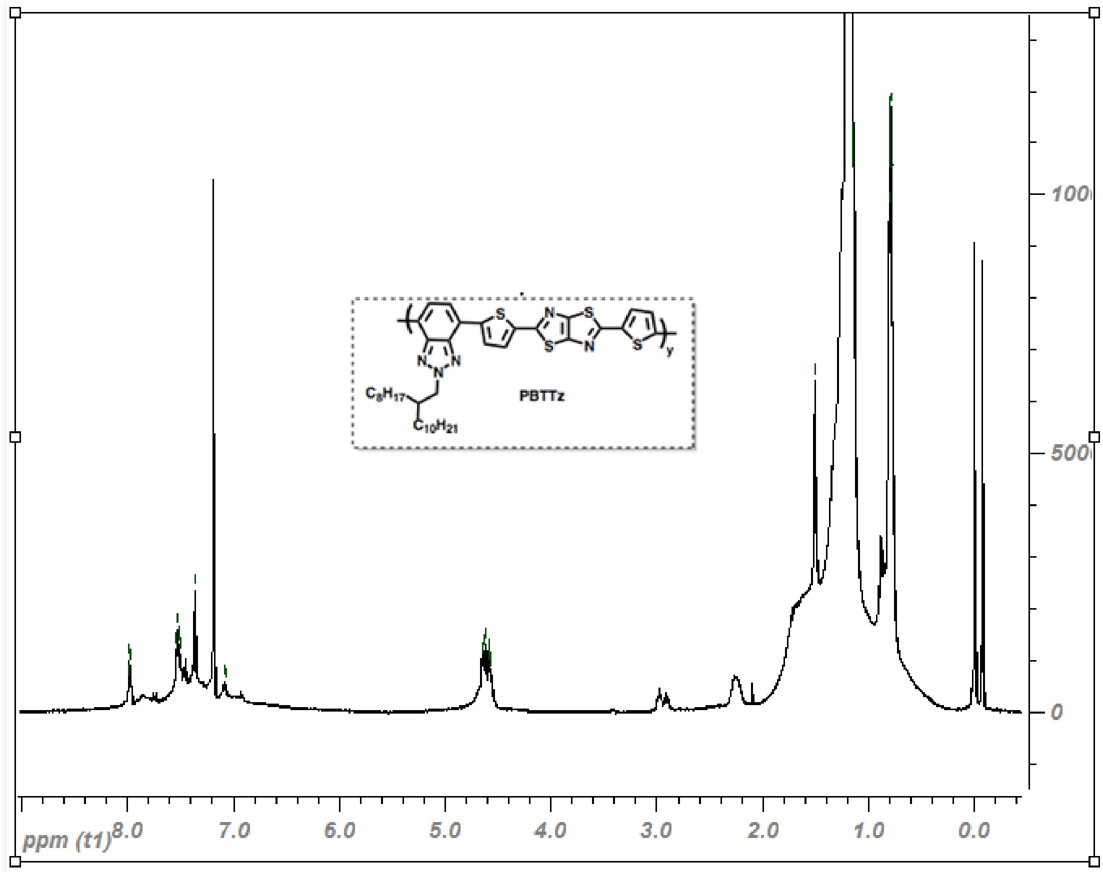

Figure A.9 ^{1}H-NMR spectrum of poly[2-(5-(2-(2-octyldodecyl)-2H-benzo[d][1,2,3]triazol-4-yl)thiophen-2-yl)-5-(thiophen-2-yl)thiazolo[5,4-d]thiazole]

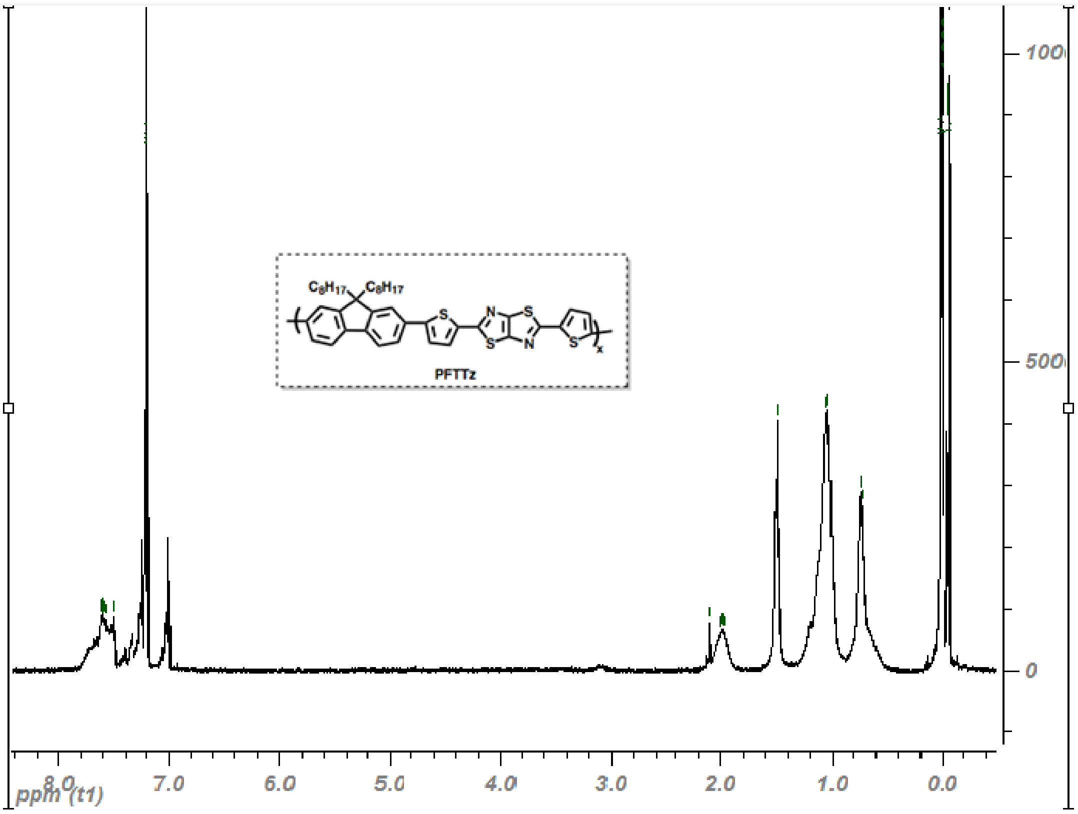

Figure A.10 1H-NMR spectrum of poly[2-(5-(9,9-dioctyl-9H-fluoren-2-yl)thiophen-2-yl)-5-(thiophen-2-yl)thiazolo[5,4-d]thiazole]

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PERSONAL DATA

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EDUCATION

- 2011 February – 2015 May - Middle East Technical University- METU Ankara, Turkey
  PhD in Polymer Science and Technology Advisor: Prof. Dr. Levent Toppare
- 2009 February – 2011 February - Middle East Technical University- METU Ankara, Turkey
  MSc in Chemistry Advisor: Prof. Dr. Levent Toppare
- 2002 September – 2008 June - Middle East Technical University- METU Ankara, Turkey
  BSc degree in Chemistry

PROJECTS

- 2012 October - 2013 January - Oganic Field Effect Transistors by Indigo Derivatives.

Johannes Kepler University (Linz, Austria) Institude for Organic Solar Cells Project
Supervisor: Prof. Dr. N. Serdar Sarıçiftçi

- 2012 February - 2012 August - Flexible Organic Light Emitting Diode (OLED) Display Devices.
  Middle East Technical University (Ankara, TURKEY) Chemistry Department / Aselsan A.Ş.
  Supervisor: Prof. Dr. Levent Toppare
- 2011 February – 2013 January - Synthesis of new conjugated donor-acceptor type polymers for photovoltaic device applications.
  Middle East Technical University (Ankara, TURKEY) Polymer Science and Technology Department
  Supervisor; Prof. Dr. Levent Toppare
- 2009 February – 2011 February - Synthesis of benzimidazole containing donor acceptor type conjugated polymers and their electrochromic applications.
  Middle East Technical University (Ankara, TURKEY) Chemistry Department
  Supervisor; Prof. Dr. Levent Toppare

INSTRUMENTAL KNOWLEDGE

- Liquid Chromatography – Mass Spectrometry (LC-MS)
- High Performance Liquid Chromatography (HPLC)
- Gas Chromatography – Mass Spectrometry (GC-MS)
- Gas Chromatography (GC)
- Inductively Coupled Plasma Emission Spectrometer (ICPE-AES)
- Atomic Absorption Spectroscopy (AAS)
- Instruments (glove-box system, spin coater, metal evaporator, hot-wall evaporator, etc.) used in building organic electronics such as organic light emitting diodes (OLEDs) and organic photovoltaics (OPVs)

PUBLICATIONS

- Multichromic and soluble conjugated polymers containing thiazolothiazole unit for electrochromic applications
  HZ Akpinar, YA Udum, L Toppare (European Polymer Journal, 63 (2015) 255-261)
- A Novel DAD Type and Folic acid Conjugated Fluorescent Monomer as a Targeting Probe for Imaging of Folate Receptor Overexpressed Cells
  FE Kanık, D Ag, M Seleci, FB Barlas, M Kesik, G Hızalan, H Akpınar, S Timur, L Toppare (Biotechnology Progress, 30 (2014) 952-959)
- Spray-Processable Thiazolothiazole-Based Copolymers with Altered Donor Groups and Their Electrochromic Properties
  HZ Akpinar, YA Udum, L Toppare (Journal of Polymer Science Part A: Polymer Chemistry, 51 (2013) 3901-3906)
- Synthesis and Electrochromic Properties of trans-stilbene Bearing Copolymers Obtained with Different Repeat Unit and Chain Length
  M Karakus, AG Nurioglu, H Akpınar, L Toppare, A Çırpan (Electrochimica Acta, 100 (2013) 110-117)
- Natural Resin Shellac as Substrate and Dielectric Layer for Organic Electronics Applications
  M Irimia-Vladu, ED Głowacki, G Schwabegger, L Leonat, HZ Akpinar, H Sitter, S Bauerb, NS Sariciftci (Green Chemistry, 15 (2013) 1473-1476)
- Further Investigation of Intramolecular H-Bonding in Benzimidazole and EDOT containing Monomer
  AG Nurioglu, H Akpinar, FE Kanik, D Toffoli, L Toppare (Journal of Electroanalytical Chemistry, 693 (2013) 23-27)
- A Novel Conducting Copolymer: Investigation of Its Matrix Properties for Cholesterol Biosensor Applications
  S Soylemez, FE Kanik, AG Nurioglu, H Akpinar, L Toppare (Sensors and Actuators B: Chemical, 182 (2013) 322-329)
- Influence of Hydrogen Bonding on Electrochromic Properties of Conducting Polymers

H Akpinar, AG Nurioglu, L Toppare (Journal of Electroanalytical Chemistry, 683 (2012) 62-69)

- Multichromic benzimidazole-containing polymers: Comparison of donor and acceptor unit effects
  AG Nurioglu, H Akpınar, M Sendur, L Toppare (Journal of Polymer Science Part A: Polymer Chemistry, 50 (2012) 3499-3506)
- Electrochromism in Multichromic Conjugated Polymers: Thiophene and Azobenzene Derivatives on the Main Chain
  DH Apaydin, H Akpinar, M Sendur, L Toppare (Journal of Electroanalytical Chemistry, 665 (2012) 52-57)
- Donor-Acceptor-Donor Type Conjugated Polymers for Electrochromic Applications; Benzimidazole as the acceptor unit
  H Akpinar, A Balan, D Baran, EK Unver, L Toppare (Polymer, 51 (2010) 6123-6131)
- Organik Güneş Gözeleri (Tübitak Bilim ve Teknik, 523 (2011) 56-57)

CONFERENCES

- Synthesis and Electrochromic Applications of Thiophene and Furan Containing Polymers, (oral presentation) 26th National Chemistry Congress (with international participation), Mugla, 2012
- Donor-acceptor-donor type conjugated polymers for electrochromic applications: benzimidazole as the acceptor unit, (poster presentation) 9th International Electrochemistry Meeting, İzmir, 2011