

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**SYNTHESES AND EXAMINING THE ELECTROCHEMICAL AND
SPECTROSCOPIC PROPERTIES OF FUSED-THIOPHENE BASED
MATERIALS WITH BENZONITRILE FUNCTIONAL GROUP**



Ph.D. THESIS

İlknur DEMİRTAŞ

Department of Chemistry

Chemistry Programme

JULY 2017

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JULY 2017

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To my family,



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ABBREVIATIONS

A	: Acceptor
ACN	: Acetonitrile
BLA	: Bond Length Alternation
BTFE	: Borontrifluoride/Ethylene Ether
CDCl₃	: Deuterated Chloroform
CHCl₃	: Chloroform
D	: Donor
DCB	: 1,2-Dichlorobenzene
DCM	: Dichloromethane
DMF	: <i>N,N</i> -Dimethylformamide
DTT	: Dithienothiophene
EDOT	: 3,4-Ethylenedioxythiophene
E_g	: Band Gap
EL	: Electroluminescence
Et₂O	: Diethyl Ether
F	: 9,9-Dioctyl-9 <i>H</i> -fluorene
FeCl₃	: Iron(III) chloride
FTIR	: Fourier Transform Infrared Spectroscopy
HOMO	: Highest Occupied Molecular Orbital
ITO	: Indium Tin Oksit
LDA	: Lithium Diisopropylamide
LUMO	: Lowest Unoccupied Molecular Orbital
MeOH	: Methyl Alcohol
mp	: Melting Point
MS	: Mass Spectrometry
NBS	: <i>n</i> -Bromo Succinimide
<i>n</i>-BuLi	: <i>n</i> -Butyllithium
NMR	: Nuclear Magnetic Resonance
OFET	: Organic Field Effect Transistors
OLED	: Organic Light Emitting Device
PAC	: Polyacetylene
PEDOT	: Poly(3,4-ethylenedioxythiophene)
PITN	: Polyisothianaphthene
PL	: Photoluminescence
PPA	: Polyphosphoric Acid
PPP	: Poly(<i>p</i> -phenylene)
PPy	: Polypyrrole
PT	: Polythiophene
<i>t</i>-BuLi	: <i>t</i> -Butyllithium
THF	: Tetrahydrofuran
TT	: Thienothiophene



SYMBOLS

A	: Current
c	: Speed of light
h	: Planck's constant
V	: Potential
λ	: Wavelength





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SYNTHESES AND EXAMINING THE ELECTROCHEMICAL AND SPECTROSCOPIC PROPERTIES OF FUSED-THIOPHENE BASED MATERIALS WITH BENZONITRILE FUNCTIONAL GROUP

SUMMARY

Conjugated polymers with low band gaps have been taking growing attention due to their intrinsic electrical conductivities. These polymers are lightweight, flexible and have interesting electronic and optoelectronic properties which make them use in organic light-emitting diodes (OLEDs), field-effect transistors (FETs), plastic lasers, photovoltaic cells, chemical sensors and indicators.

Fused thiophenes, generated by the annulation of thiophene rings, have rigid structures with an extended π -conjugation compared to thiophene. While the simplest fused thiophene called thienothiophene (TT) is formed by annulation of two thiophene rings, fusing another thiophene ring into TT gives dithienothiophene (DTT). TTs and DTTs are electron rich compounds with flat and rigid delocalized systems, which make them appropriate candidates to be used in conjugated and low band gap semiconductors.

Since the electronic characteristics of conjugated polymers are strongly depend on the electronic energy levels of the polymer, it is very important to tune the position of the energy levels and the extent of the band gap in the design and the synthesis of conjugated polymers. Use of strong donor (D) and acceptor (A) units is one of the most effective ways in low band gap materials architecture. In D–A systems, both electron-withdrawing and donating groups diminish E_g . While electron withdrawing unit lowers LUMO (Lowest Unoccupied Molecular Orbital) energy, electron donating group increases HOMO (Highest Unoccupied Molecular Orbital) level. Fused thiophenes are commonly used as electron-donating groups, and cyano substituted units are the most widely employed as electron withdrawing units in design of low band gap conjugated polymers.

In this study, novel π -conjugated monomers 4-(2,5-di(thiophen-2-yl)thieno[3,2-*b*]thiophen-6-yl)benzonitrile, 4-(2,5-bis(4-hexylthiophen-2-yl)thieno[3,2-*b*] thiophen-3-yl)benzonitrile, 4,4'-(2,6-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile, 4,4'-(dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile, 4,4'-(2,6-di(thiophen-2-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile, 4,4'-(2,6-bis(4-hexylthiophen-2-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile, 4'-(2,6-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl) dibenzonitrile with electron-donating TT and DTT units and electron-withdrawing cyano group were designed to investigate the electronic and steric effects of substiutents on electrochemical and optoelectronic features of the final polymers. Syntheses of the TTs and DTTs were achieved through the ring closure reactions of mono and diketones using polyphosphoric acid (PPA) in refluxing chlorobenzene. Thiophene, 3-hexylthiophene and EDOT were linked to the TT and DTT units to rationalize the influence of electron density enhancement along monomer backbone. Monomers were synthesized via Suzuki or Stille cross-coupling

methods. Polymers were prepared by electrochemical potentiodynamic method in acetonitrile/dichloromethane NaClO₄/LiClO₄ (0.1:0.1 M) solvent-electrolyte mixture. Chemical polymers were synthesized via Suzuki and Stille cross-coupling reactions or oxidative chemical polymerization through FeCl₃. The electrochemical and spectroscopic properties of polymers were investigated *via* cyclic voltammetry (CV), and UV-Vis spectroscopy, respectively. The color changes emerging from the redox switching of polymers synthesized through electrochemical method were examined by CIE 1931 Yxy color space. Fine tuning of the band gaps was achieved by making structural variations to adjust optical band gap values between 1.79 and 2.18 eV for TT polymers, 1.71 and 2.34 eV for DTT polymers synthesized through electrochemical method, 1.69 and 2.51 eV for TT polymers, and 1.60 and 2.46 eV for DTT polymers synthesized through chemical method. In addition, the copolymer of 4-(thieno[3,2-*b*]thiophen-3-yl)benzonitrile and 4,4'-(dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile with 9,9-dioctyl-9*H*-fluorene were synthesized to produce poly(9,9-dioctylfluorene-2,7-diyl-*alt*-3-(4'-cyanophenyl) thieno[3,2-*b*]thiophene-2,5-diyl) and poly(9,9-dioctylfluorene-2,7-diyl-*alt*-3,5-bis(4'-cyanophenyl)dithieno[3,2-*b*:2':3'-*d*]thiophene-2,5-diyl), respectively. Their photophysical, electrochemical and electroluminescent (EL) properties were examined. Synthesis and investigation of properties of the polymers were performed by Polymer Photonics group in Institute of Macromolecular Chemistry, The Czech Academy of Sciences.

BİRLEŞİK-TİYOFEN TEMELLİ BENZONİTRİL FONKSİYONEL GRUP İÇEREN MALZEMELERİN SENTEZLERİ VE ELEKTROKİMYASAL VE SPEKTROSKOPİK ÖZELLİKLERİNİN İNCELENMESİ

ÖZET

Polimerler 50 yıl öncesine kadar yalıtkan maddeler olarak bilinmekteyken Hideki Shirakawa, Alan Heeger ve Alan MacDiarmid tarafından asetilen monomerinin Ziegler Natta katalizörü ile brom, klor ya da iyot buharıyla etkileşimi sonucunda hemen hemen bir metal gibi elektriği iletebilen poliasetilenin (PAC) elde edilmesi ile polimerlerin de iletken olduğu gösterilmiştir. İletken poliasetilenin bulunuşu bu üç bilim adamına 2000 yılında Nobel Kimya Ödülü'nü kazandırmıştır. İletken polimerler elektriği metaller kadar iyi iletebilir, korozyona karşı dayanıklıdır ve kolay metotlar kullanarak elde edilebilirler. Polimerlerin bu önemli özelliklerinin bulunması, akademi ve teknoloji dünyasında büyük yankı uyandırmıştır ve çok çeşitli yapıda polimerler sentezlenmiştir. Çünkü iletken polimerler yarı iletken inorganik malzemelerle neredeyse aynı iletkenliğe sahip, daha çevreci ve üretim maliyetleri daha düşüktür. İletken polimerler elektronik dünyasında, yarı iletkenler ve organik iletkenler olarak geniş uygulama alanlarına sahiptir. İnorganik malzemelerin yerine kullanılan polimerik, organik veya biyolojik malzemeler moleküler elektronikler olarak adlandırılır. İletken polimerler, kapasitörlerden biosensörlere, güneş pillerinden ışık yayan diyotlara (LED) birçok alanda kullanılmaktadır.

İletken polimerler sp^2 hibrit yapıdaki iskelet sistemleri sayesinde yoğun π -konjugasyonu içerirler, diğer polimerler ile arasındaki en önemli özellik HOMO (Valens bant) ve LUMO (İletkenlik bandı) enerji seviyelerinin arasının kısa olması dolayısıyla düşük bant aralığına sahip olmalarıdır.

İletken polimerler yapısal özelliklerine bağlı olarak farklı uygulama alanlarında kullanılabilirler. Floresans özellik gösteren iletken polimerler, organik ışık yayan diyotlarda (Organic Light Emitting Diodes, OLED) kullanılırken güneş ışığının geniş bandını soğuran kromofor gruplar taşıyan polimerler ise fotovoltaiik hücrelerde kullanılmaktadır. Bu yüzden, iletken polimerlerin keşfinden beri yeni uygulama alanları oluşmuşsa da, bu uygulama alanları için gerekli özellikleri tam olarak barındıran malzemelerin dizaynı ve sentezi hala devam etmektedir.

İletken polimerlerin elde edilmesinde genellikle elektrokimyasal ve kimyasal polimerizasyon teknikleri kullanılır. Elektrokimyasal polimerizasyon, çalışma elektroduna uygun potansiyel uygulanıp elektrolit içerisinde bulunan monomerin oksitlenmesi sonucu oluşan radikal katyonlar üzerinden gerçekleşir. Elektrokimyasal polimerleştirme potansiyostatik bir sistemde belirli voltaj aralığında (döngülü voltametri) ya da sabit potansiyelde (kronoamperometri) yapılır. Kimyasal yöntemde, uygun bir çözücü kullanarak çözünen monomer bir yükseltgenme ya da indirgenme kimyasalı ile etkileşime girerek polimerleştirilir. Kimyasal polimerizasyon yöntemi ile

istenilen miktarda ve makul maliyetle ürün elde edilebilmektedir. Konjüge polimerlerin tümü kimyasal yöntemle sentezlenmektedir.

Konjüge polimerlerin en önemli özellikleri bant aralığı, optiksel özellikler (kuantum verimi, maksimum dalga boyu ($\lambda_{\max}$), elektrokimyasal özellikler, tersinir uyarılara cevap verebilme ve iletkenliktir.

Konjüge polimerlerin elektronik özellikleri büyük ölçüde polimerin elektronik enerji seviyelerine bağlı olduğundan bu polimerlerin dizaynı ve sentezinde enerji seviyelerinin ve bant aralığının ayarlanması çok önemlidir. Konjüge polimerlerin optik ve elektronik özellikleri malzemenin kimyasal yapısını modifiye ederek optimize edilebilir. Düşük bant aralıklı konjüge polimerlerin elde edilmesi için çeşitli çalışmalar yapılmıştır, konjüge polimerlerin ana iskeletinde halka-birleşik tiyofen birimlerinin kullanılması etkili yöntemlerden bir tanesidir. Halka birleşik ya da annule tiyofenler daha uzun π -konjugasyonuna sahiptir. Birleşik tiyofenler olarak bilinen iki tiyofen halkası içeren tiyenyotiyofenler (TT), üç tiyofen halkası içeren ditiyenyotiyofenler (DTT), elektronca zengin, düzlemsel ve π -konjugasyonuna sahip bileşikler oldukları için elektrik akımını daha iyi iletirler ve katı moleküller arası etkileşimleri daha fazladır. Bu özellikleri onları konjüge ve düşük bant aralıklı yarı iletkenlerin elde edilmesinde uygun adaylar yapmaktadır. TT ve DTT ile bunlardan elde edilen iletken polimerler lineer olmayan optik malzemelerin sentezinde, manyetik ve fotosensitiv reseptör yapımında, bazı sensörlerde, elektrokromik cihazlarda (ECD), elektronik devrelerin temel parçaları olan transistörlerde (Field Effect Transistors, FETs), ışığı doğrudan elektrik akımına dönüştüren (fotovoltaik) bir araç olan güneş pillerinde kullanılmaktadır.

Kuvvetli elektron verici (donör, D) ve çekici (akseptör, A) gruplarının kullanılması düşük bant aralıklı maddelerin tasarlanması için diğer etkili yöntemlerden biridir. D–A sistemlerinde, her iki grup da bant aralığını daraltır. Elektron çekici gruplar daha çok LUMO enerji seviyesini düşürürken, elektron verici gruplar ise HOMO enerji seviyesini artırırlar. Tiyofen türevleri genel olarak kullanılan elektron verici gruplardandır, elektron çekici grup olarak ise cyano içeren bileşikler geniş ölçüde kullanılmaktadır.

Bu çalışmada yeni, π -konjugasyonuna sahip, D ve A heterosiklik halkalar içeren TT monomerleri; 4-(2,5-di(thiophen-2-yl)thieno[3,2-*b*]thiophen-6-yl)benzonitrile, 4-(2,5-bis(4-hexylthiophen-2-yl)thieno[3,2-*b*]thiophen-3-yl)benzonitrile, 4,4'-(2,6-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl) dibenzonitrile , 4,4'-(dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl) dibenzonitrile, 4,4'-(2,6-di(thiophen-2-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile, 4,4'-(2,6-bis(4-hexylthiophen-2-yl)dithieno[3,2-*b*:2',3'-*d*] thiophene-3,5-diyl) dibenzonitrile, 4'-(2,6-bis(2,3-dihydrothieno[3,4-*b*][1,4] dioxin-5-yl)dithieno [3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile sentezlenmiştir. TT ve DTT'ler mono- ve di-ketonların reflaks olan klorobenzen içerisinde polifosforik asit ile halka kapama reaksiyonu ile kısa reaksiyon sürelerinde (1.5–4 saat) elde edilmiştir. Suzuki ve Stille kenetleme reaksiyonları ile tiyofen, 3-hekzil tiyofen ve EDOT elektron verici grupları yapıları bağlanmıştır. Monomerlerin elektropolimerizasyonu potansiyodinamik metotla asetonitril/diklorometan $\text{NaClO}_4/\text{LiClO}_4$ (0.1:0.1 M) çözücü-elektrolit karışımı kullanarak Pt elektrot yüzey ve ITO (İndium Tin Oksit) kaplı cam elektrot üzerine kaplanarak yapılmıştır. Ayrıca, kimyasal yöntemlerle de bu monomerlerin

polimerleri sentezlenmiştir. TT'nin tiyofen ile kopolimeri Suzuki kenetleme reaksiyonu, DTT'nin tiyofen ile kopolimeri Stille kenetleme reaksiyonu ile elde edilmiştir. Diğer geri kalan monomerler ise FeCl_3 ile oksidatif kimyasal polimerizasyonu ile polimerleştirilmiştir. Polimerlerin elektrokimyasal ve spektroskopik özellikleri sırasıyla döngülü voltametre (CV) ve UV-Vis spektroskopisi ile incelenmiştir. Elektropolimerizasyon ile elde edilen TT ve DTT polimerlerinin redox değişimleri sonucu oluşan renk farkları CIE 1931 Yxy color space ile tespit edilmiştir. Tüm polimerlerin optik ve elektronik bant aralıkları ile HOMO ve LUMO enerji seviyeleri hesaplanmıştır. Kimyasal yöntemler ile elde edilen polimerlerin optik bant aralıkları uygun çözücü içerisinde ve ITO üzerine spin kaplama tekniği ya da damlama tekniği kullanarak katı fazda hesaplanmıştır. Kimyasal polimerlerin elektronik bant aralıkları, HOMO ve LUMO enerji düzeyleri camsı karbon elektrot yüzeyine kaplanarak tespit edilmiştir. Yapısal değişiklikler yaparak düşük bant aralıklı TT ve DTT polimerleri elde edilmiştir. Elektropolimerizasyon ile elde edilen polimerlerin optik bant aralıkları 1.71–2.34 eV, elektronik bant aralıkları ise 1.44–2.34 eV arasında değişmektedir. Kimyasal yöntemlerle elde edilen polimerlerin çözelti içerisindeki optik bant aralıkları 1.60–2.51, katı film fazında optik bant aralıkları 1.64–2.33 eV, elektronik bant aralıkları ise 1.56–2.63 eV olarak hesaplanmıştır.

Ayrıca, 4-(thieno[3,2-*b*]thiophen-3-yl)benzonitrile ile 9,9-dioctyl-9H-fluorene kopolimeri poly(9,9-dioctylfluorene-2,7-diyl-*alt*-3-(4'-cyanophenyl)thieno[3,2-*b*]thiophene-2,5-diyl) ve 4,4'-(dithieno[3,2-*b*;2',3'-*d*]thiophene-3,5-diyl) dibenzonitrile ile 9,9-dioctyl-9H-fluorene kopolimeri poly(9,9-dioctylfluorene-2,7-diyl-*alt*-3,5-bis(4'-cyanophenyl)dithieno[3,2-*b*:2',3'-*d*]thiophen-2,6-diyl) Suzuki kenetleme reaksiyonu ile sentezlenip, fotofiziksel, elektrokimyasal ve elektroluminesans (EL) özellikleri Polymer Photonics grubu (Institute of Macromolecular Chemistry, The Czech Academy of Sciences) tarafından incelenmiştir.



1. INTRODUCTION

1.1 History of Conducting Polymers

Polymers have long been used for the purpose of insulation [1]. In general, any electrical conduction due to loosely bound ions in polymers was not desired. However, scientists have developed semiconducting polymers, namely, conjugated conducting polymers, charge transfer polymers, ionically conducting polymers and conductively filled polymers owing to the intrinsic characteristic of covalent bonding [2,3].

Conductively filled polymers were produced by the charging of loading conductive fillers, like carbon black, graphite, or metal oxide particles into an insulating polymer [2]. Although their easy processabilities, high stabilities and extensive range of electrical properties led to an increase in their use, their inhomogeneities and low reproducibilities hampered the further utilization of these polymers.

Ionic polymers having the easy processability took attention in 1975 owing to the efficient electrical conductivity. Then, their different types were synthesized for many uses, such as in rechargeable batteries, smart windows and supercapacitors. However, polymer electrolytes have low conductivity and high sensitivity to moisture [4].

Upon finding electrical conductivity in molecular charge transfer (CT) complexes in 1950s, conducting CT polymers were developed [5]. Superconductivity was discovered with molecular CT complexes in 1980 [6] and with fullerene in 1986 [7]. The conductivity in CT complexes is formed by the generation of properly segregated stacks of electron donor and acceptor molecules and significant charge transfer between stacks. The crystal structure needed for high conductivity endows them with inflexibility and unsuitability for processing.

In 1862, Letheby, a chemistry professor in College of London Hospital, obtained the first synthesized polyaniline known as “aniline black” by electrolytic oxidation of aniline under acidic conditions on platinum electrode [8]. In 1955, Natta and coworkers synthesized the polyacetylene (PAC) using a coordination catalyst system. However, PAC did not draw much attention as a result of its insoluble and infusible

property [9]. In 1960s, treatment of PAc with different catalyst systems revealed impressive results in electrical conductivity [10,11]. In 1977, the real story began with the discovery of 12 orders of magnitude increase in conductivity of doped trans-polyacetylene. A new kind of polymers having high electronic conductivity in oxidized state endured three scientists; Hideki Shirakawa, Alan J. Heeger and Alan G. MacDiarmid with awarding Nobel Prize for Chemistry in 2000 [12,13]. The field of conjugated polymers has become popular after the finding of organic conjugated polymers which can have metallic-like conductivity upon doping.

PAc is the simplest model of conjugated conducting polymer that shows characteristic structure of π -conjugated system over the polymer chain [14]. In spite of high conductivity of doped polyacetylene film, it is unstable against oxygen. PAc is still the archetype of conducting polymer and keeps theoretical and experimental attention due to being the simplest conjugated polymer [15].

Most studies on conjugated conducting polymers have been performed with the materials possessing heteroaromatic compounds such as thiophene, furan, pyrrole, 3,4-ethylenedioxythiophene (EDOT), aniline, furan, indole and carbazole (Figure 1.1) [16-23].

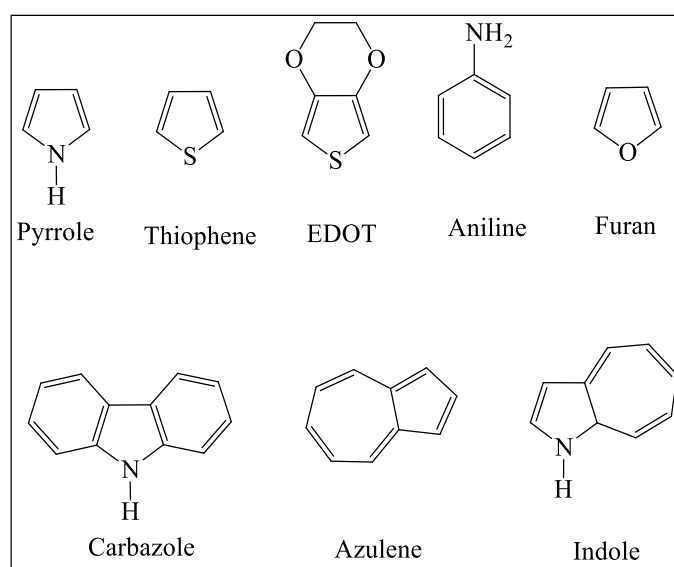


Figure 1.1 : Structures of common types of π -conjugated monomers.

In the early 1980s, electrochemical polymerization of pyrrole by Diaz et al. provided freestanding, stable polymer film with conductivity of 100 S.cm^{-1} [24]. They used modified method that was primarily reported by Dall'Olio in 1968; however, they

obtained fully adhered strong film that could be removed from the platinum electrode contrary to insoluble, soft solid [25]. This discovery of polypyrrole (PPy) made researchers concentrate on the development of conjugated polyheterocyclic systems. Although having lower conductivities than doped PAc, most common conjugated polymers (PPy, polythiophene (PT) and poly(3,4-ethylenedioxythiophene (PEDOT)) are not only environmentally stable in their *p*-doped form, and also have stunning characteristics like electrochromism, volume change during doping and photoluminescence, etc. [26].

PT has rapidly become the most interesting conducting polymer owing to the structural flexibility and improved stability in neutral and *p*-doped states. However, PTs are degraded under the potential needed for their production. So, controlling the properties of PT requires the modification of the monomer structure to get readily polymerized and soluble polymers resulting the synthesis of a large extend of PT variables with various properties [21,27].

PEDOT, polymer of thiophene derivative EDOT, is an appropriate material to be used in a wide range of applications such as electrochromic devices, LEDs, capacitors and sensors. Besides its high conductivity (300–400 S.cm⁻¹), it has superior electrochromic contrast owing to the transparency of thin and doped films [28,29]. Due to the industrial application of the PEDOT in photographic films as an antistatic layer, it has been the most commonly used conducting polymers [30].

Inflexibility and insolubility of conducting polymers especially in doped form hampered their applications. 3-substituted thiophenes [31,32] and aniline derivatives [33,34] were developed providing processable polymers to avoid this obstacle.

Different approaches have been used to design and produce new kinds of monomers to get together electrical, optical and mechanical features with processability and environmental stability. The relation between structural adjustment and compound's properties should be taken in consideration in order to improve an individual property.

Conjugated conducting polymers have been used as many purposes such as thin film transistors [35-37], sensors [38,39], polymer light emitting diodes [40,41], photovoltaics [42,43] and electrochromic devices [15,44] up-to-date.

1.2 Band Theory

Electronic features of the conducting polymers are explained by the band theory. The bonding and antibonding π - π orbitals of the sp^2 hybridized molecule produce two discrete energy bands; one of them is occupied (π - π) and the other one is unoccupied (π - π^*), the highest occupied band is named *valence band*, and the lowest unoccupied band is called as *conduction band* [2]. Molecular electronic states are overlapped to create electronic bands; valence electrons overlap to produce a valence band, electronic levels above valence band fuse to form a conduction band [45] and the electrons move within these energy states.

The energy difference between the top of the valence band and the bottom of the conduction band of the material is called the *band gap*, E_g . In other words it is equal to the energy difference between the ionization potential and electron affinity of the polymer [46]. To promote an electron from valence band to conduction band, the energy equals to band gap is needed.

The band gap of semiconductors is between those of metals and insulators (Figure 1.2). In metals, the valence and conduction bands are overlapped, this permits electrons flow easily. In general, the conductivity of conjugated polymer is less than that of metal, however there are some isolated conjugated polymers have a metal like copper conductivity [47].

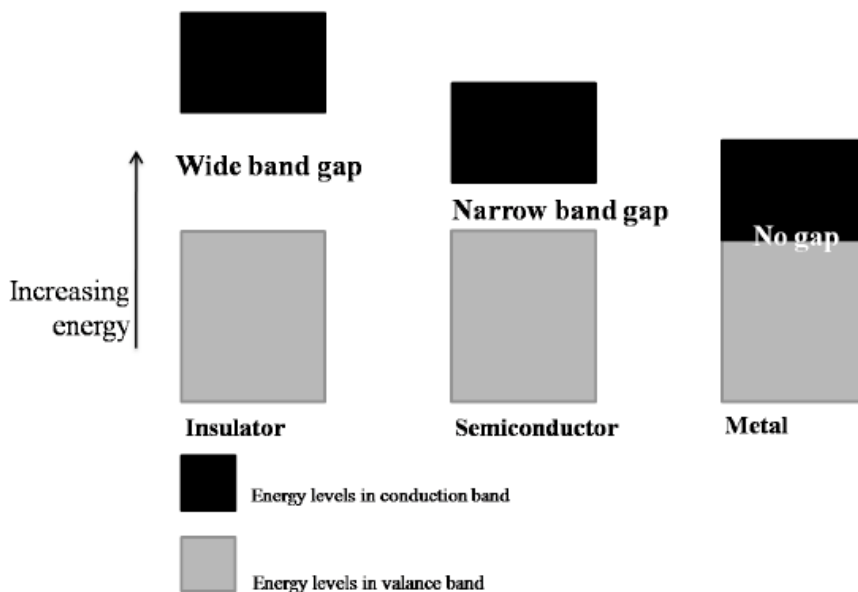


Figure 1.2 : A schematic representation of energy gaps in metal, semiconductor and insulator [15].

The band gap decreases with an extension in conjugation, union of repeating units into the polymer backbone, π and π^* orbitals start to aggregate on each other to form energy bands; valence and conduction bands. While the width of the conduction and valence bands increases with additional repeating units, band gap of the polymer decreases. Another effect which diminishes the band gap is the extending of π electron delocalization. As a result, a low band gap polymer can be obtained by considerable number of repeat units with free π orbital overlap (Figure 1.3).

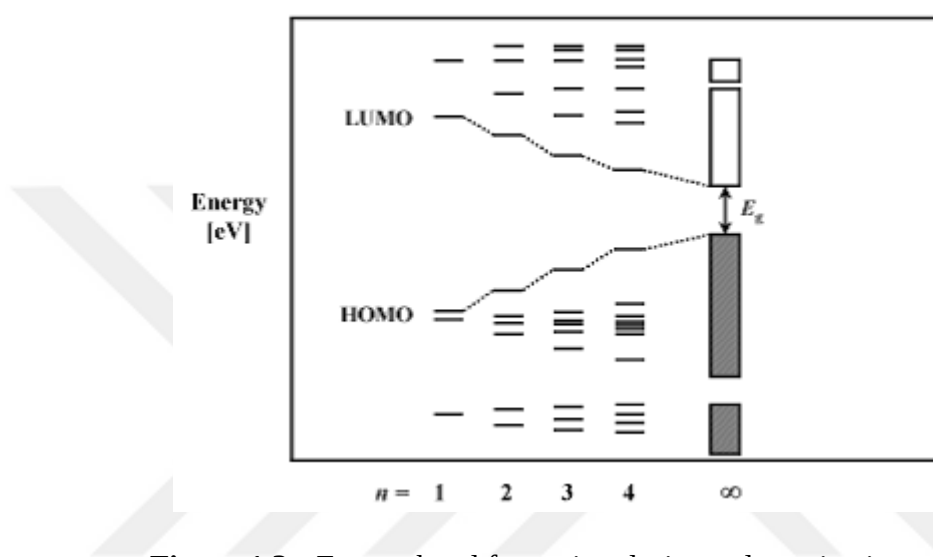


Figure 1.3 : Energy band formation during polymerization of conjugated monomers [48].

Band gap is a crucial factor to figure out the electronic, optical, redox and electrical attributes of conducting polymers [46]. Band gap of a linear π -conjugated polymer can be affected by several structural aspects like chain length, bond length variation, planarity and also by presence of electron-acceptor or electron-donor groups and resonance stabilization of aromatic cycles [49].

1.3 Conduction Mechanism in π -Conjugated Systems

Conjugated polymers are composed of linear chains formed by single (sigma-bonds) and double bonds (π -bonds) $[(-C=C-C=C-C=C-)_n]$. The carbon atoms in single and double bonds are sp^3 and sp^2 hybridized, respectively. The high delocalization and easy polarization of π -electrons existing in p_z orbitals of sp^2 carbons give different electrical and optical properties to polyconjugated systems [50].

In order to obtain conductivity in conjugated polymer, positive (*p*-type) or negative (*n*-type) charge carriers are created on the polymer backbone by oxidation or reduction process, respectively. Once the charge carriers are formed, their movement through the π -backbone of the polymer chain brings about the conduction [51].

The mechanism of conduction in PEDOT was illustrated in Figure 1.4. Once electrons are taken out from the valence band of the conjugated polymer, radical cations (holes) are created. Polaron is formed by the partially delocalization of radical cations over some structural units. Meanwhile, charge neutrality is kept by the diffusion of counter ions into the polymer structure. Any other oxidation can either transform the polaron into bipolaron (C), or creates double polaron (D) [52]. Polarons and bipolarons conduct electrical current by moving through the polymer chain in an electric field. There is a reversible transformation between neutral, polaronic and bipolaronic species by application of chemical or electrochemical processes to oxidize or reduce the polymer.

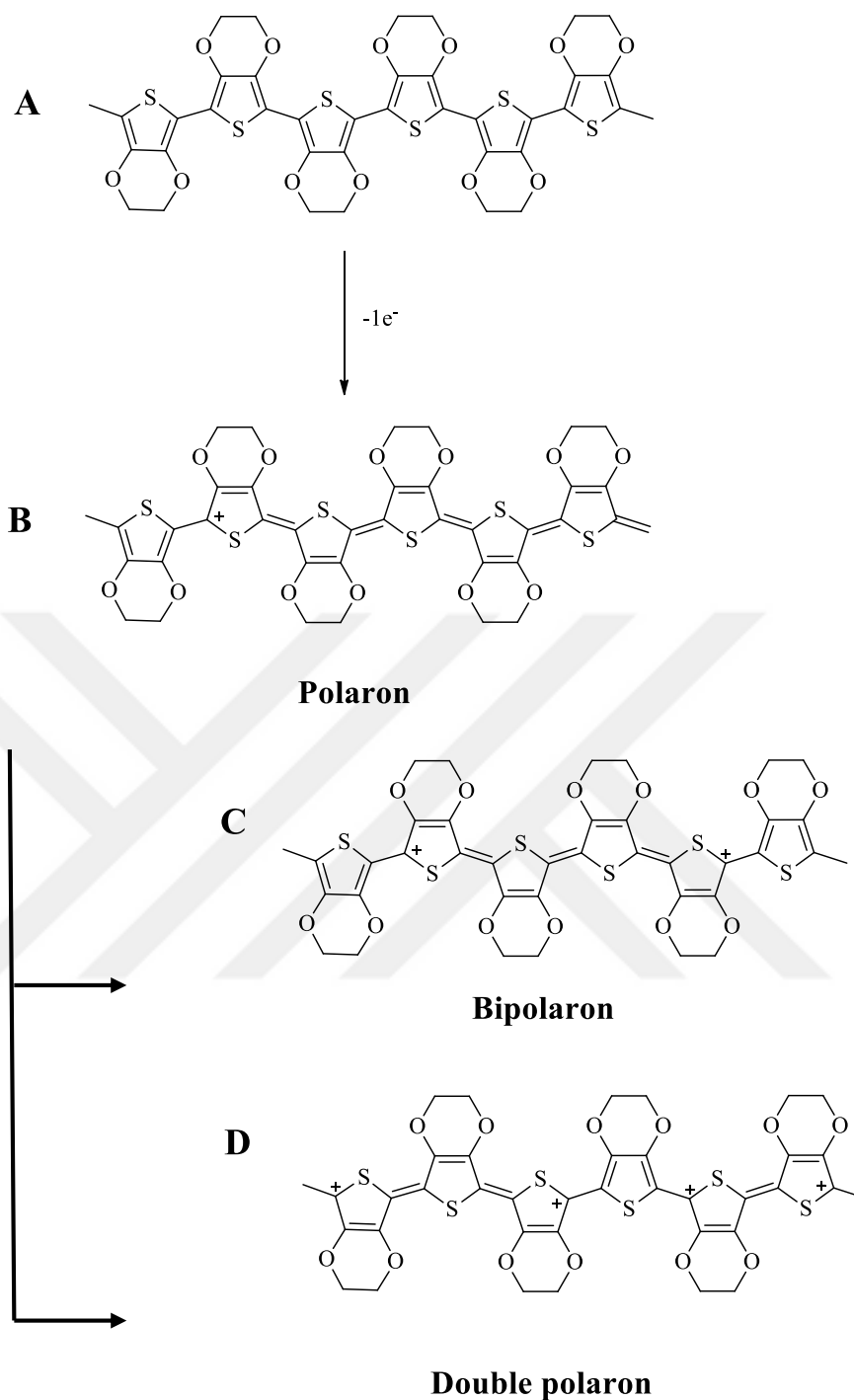


Figure 1.4 : Formation of charge carriers in PEDOT by oxidation process [51].

1.3.1 Doping types in conjugated conducting polymers

Doping is the process to convert insulating neutral polymer into an ionic complex including a polymer cation (or anion) and a counter ion (reduced or oxidized form of the oxidizing or reducing agent) by a number of anionic or cationic species called “dopants”. In other words, oxidation and reduction of the polymeric backbone to introduce charge centers is needed to create a conducting polymer. Oxidation of

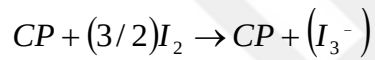
conjugated polymer is *p*-type doping and reduction of conjugated polymer is called *n*-type doping [53].

There are two main types of doping process; one is chemical doping by charge transfer of donors or acceptors and other one is electrochemical doping by electrochemical oxidation or reduction.

Chemical doping occurs when electrons are removed from the valence band to form positive charges on the polymer backbone. Conducting polymer can be doped by exposing to a solution or vapor of the dopant.

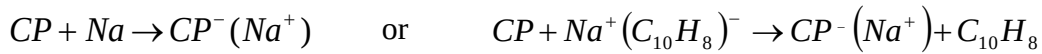
i) *p*-type doping

In *p*-type doping, the oxidant such as I₂, Br₂ or AsF₅ is used as a dopant. In this process, main chains of conjugated polymer were oxidized; dopant thereby obtains the released electrons and becomes counter anions.



ii) *n*-type doping

In *n*-type doping, the reductant such as Na vapor and Na⁺(C₁₀H₈)⁻ is used as a dopant. The main chains of the conjugated polymer were reduced to get electrons from dopant. Expression of the reaction equation is:

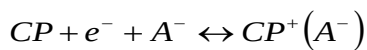


Chemical doping is an effective method to create charge holes in the polymer chain; however, it is difficult to operate. Electrochemical doping was applied since the efforts made to obtain optimum doping levels causes inhomogeneous doping [54].

Electrochemical doping is the process to oxidize or reduce the polymer by applying suitable potential in an electrochemical cell. The charge formed on the polymer chain is neutralized by the help of counter ions in electrolyte solution [53].

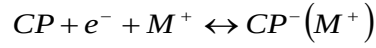
i) *p*-type electrochemical doping

For electrochemical *p*-doping, the conjugated main chains are oxidized and the solution anions will dope into the polymers as counter anions:



ii) *n*-type electrochemical doping

For electrochemical *n*-doping, the conjugated main chains are reduced and the solution cations will dope into the polymer as counter cations:



Although the conductivity of undoped polyconjugated polymers is of the order of 10^{-6} – 10^{-12} S.cm⁻¹ [50], this level can be increased over eight or more orders of magnitude by doping process. Figure 1.5 indicates the conductivity of ranges for insulators, some metals and semiconductors and three most common conjugated polymers; PAc, PT and PPy.

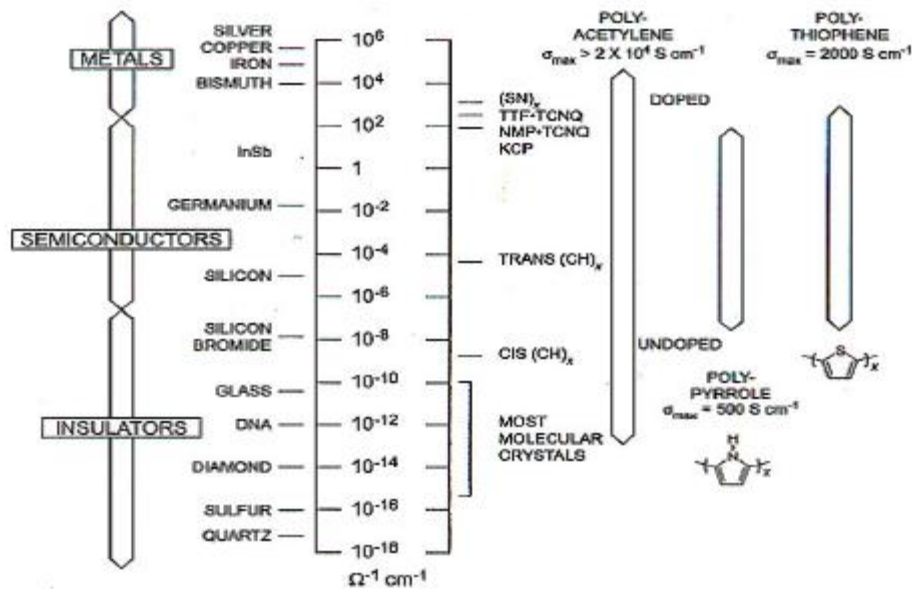


Figure 1.5 : Conductivity range for PAc, PTh and PPy [23].

1.4 Synthesis of Conjugated Conducting Polymers

Chemical and electrochemical polymerizations are the most widely used techniques to synthesize conjugated conducting polymers. Other techniques are photochemical, metathesis, plasma, pyrolysis and solid state polymerizations [55]. Electrochemical polymerization is a common method to produce polymer films in a few seconds and it is a facile and effective route to study optical and electronic properties of polymers [22]. On the other hand, in chemical polymerization, long time and laborious work-up

are required, and the polymer is obtained in its neutral state, so it can be chemically or electrochemically doped to form conductive.

1.4.1 Chemical polymerization

There are two basic methods applied for the polymerization of thiophene based monomers; first one is the oxidation of monomers in the presence of excess FeCl_3 or other transition metals, second one is the metal-catalyzed coupling reactions [54].

Ni-catalyzed polymerization of 2,5-dibromothiophene (**1**) was reported by Yamamoto et al. in 1980 [56]. Figure 1.6 shows the reaction of **1** with 2-thienyl Grignard reagent in presence of $\text{Ni}(\text{bipy})\text{Cl}_2$ (bipy:2,2'-bipyridyl) affording PT (**3**). Also, another way using the metal-catalysis to produce unsubstituted PTs from thiophene was described by Lin and Dudek, employing acetylacetonates of Ni, Pd, Co, or Fe as catalysts [57].

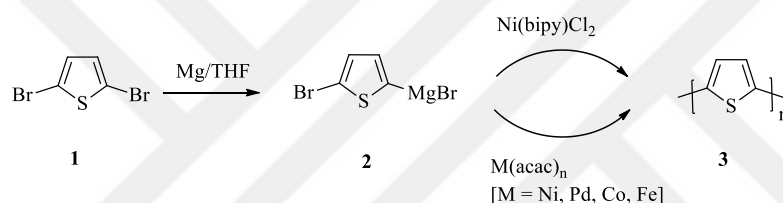


Figure 1.6 : Synthesis of PT (**3**) via metal-catalyzed coupling reaction.

Yamamoto et al. depicted another polycondensation method by heating of 2,5-dibromothiophene with $\text{Ni}(\text{1,5-cyclooctadiene})_2$ and triphenylphosphine in *N,N*-dimethylformamide (DMF) at 60–80 °C. The yield of reaction is so high that the procedure has been used in synthesis of many conjugated polymers [58].

Using FeCl_3 as oxidant for the polymerization of thiophene in chloroform was reported in 1984 [59], and it is the most general way for polymerization of 3- or 3,4- substituted PTs. High molecular weight polymers ranging from 20 to 400 kg.mol^{-1} with polydispersities indexes between 1.3 and 5 were produced via this method [34].

Although the introduction of side chains increases the solubility, polymerization via FeCl_3 produces polymers having 25 % regiochemical irregularity [60]. Irregular polymer chain results in loss in conjugation due to steric repulsion between the side groups and consequent twisting of thiophene units. As a result, band gap of polymer increases and conductivity decreases [61]. In order to eliminate this situation, McCullough reported regiospecific chemical synthesis based on the specific formation

of an organometallic group at a selected α -position of the thiophene ring. Figure 1.7 illustrates the McCullough's method for the selective metalation at 5-position of 3-alkylthiophene derivatives [62], this was the first synthesis of regioregular polyalkylthiophenes (PATs) yielding nearly 100 % head-to-tail coupling.

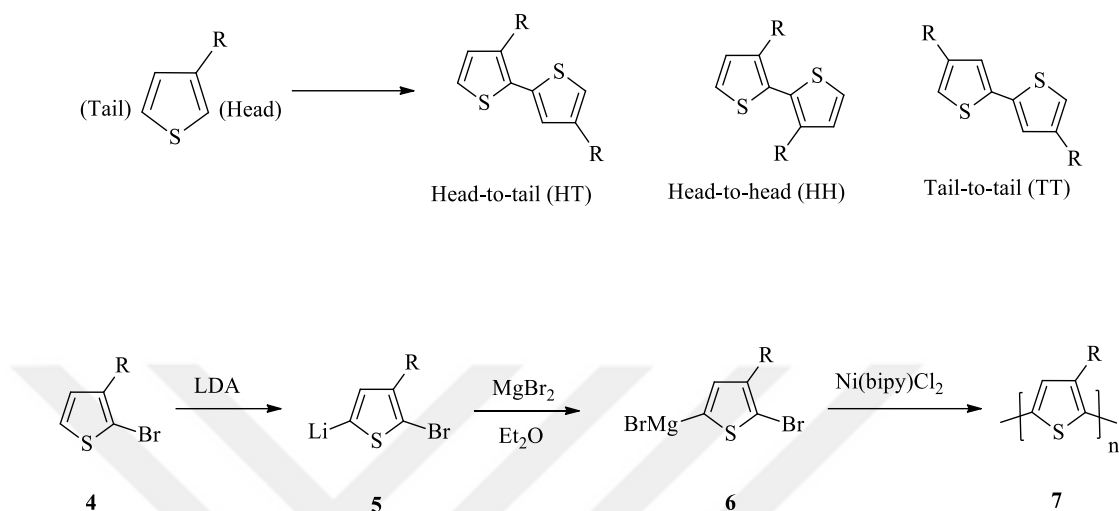


Figure 1.7 : McCullough's method for the synthesis of regioregular HT-PATs [62].

Stille [63] and Suzuki [64] cross-coupling reactions are other methods applied for regioregular PT synthesis. Rieke reported a route using “Rieke zinc” (Zn^*) that reacts with 2,5-dibromo-3-R-thiophenes (**8**) at low temperature, producing 5-metallated compound as major product to be polymerized with the Kumada catalyst ($\text{Ni}(\text{dppe})\text{Cl}_2$) affording head-to-tail regioregular PATs. On the other hand, using $\text{Pd}(\text{PPh}_3)_4$ as catalyst gave regiorandom PATs (Figure 1.8) [65].

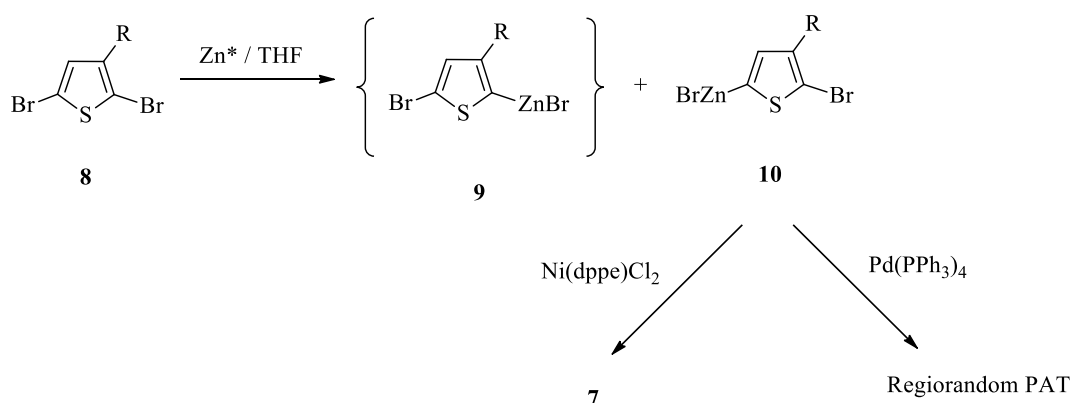


Figure 1.8 : Rieke's method for the synthesis of regioregular HT-PATs.

1.4.2 Electrochemical polymerization

Electrochemical polymerization depends on the formation of anions, cations or radicals on the electrode surface, such as platinum, gold or ITO in an electrolytic solution containing the monomer. Oxidation of monomers to polymers was initiated by the potential applied. Small amount of monomer is needed for the formation of electrode-supported and free standing films in a fast and easy way by this method.

While the electropolymerization of conducting polymers is still subject to discussion, the mechanism that Diaz suggested is widely accepted in the literature (Figure 1.9) [66-68]. The mechanism is similar to the radicalic or ionic polymerization processes. The polymerization of heterocycle starts with the dimerization of monomers at the α -position after oxidation at the electrode. Then proton was eliminated from the doubly charged dimer to form an aromatic neutral dimer. This dimer is immediately oxidized to its cation to produce subsequent coupling step with a monomeric radical cation to form charged trimer, and then the protons are eliminated from the resultant trimer. Polymer formation continues through electrochemical and chemical reactions according to general E(CCE)_n mechanism. Electropolymerization process terminates until the oligomer becomes insoluble and precipitates onto the surface of the electrode [21].

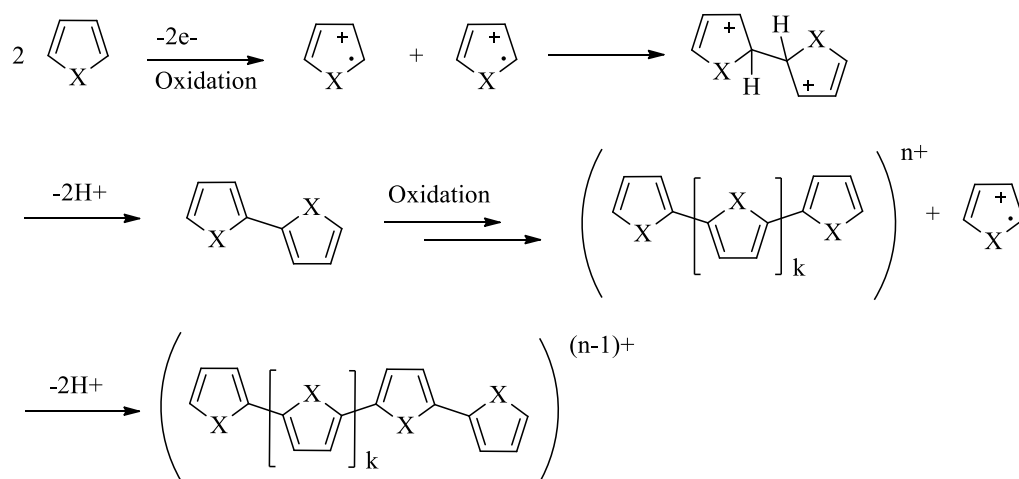


Figure 1.9 : Proposed mechanism of the electropolymerization of conducting polymers.

Although this mechanism is still accepted, many experimental findings show that the chain propagation step is not complicated. The strategy “oligomer approach” provides characterization of the properties and processes of conjugated oligomers during the

chain formation [69]. Results of oligomeric pyrroles and thiophenes studies suggested that there is a drastical decrease in the reactivities of monomeric compounds during the oligomerization process. Therefore, the coupling intensity of charged oligomers and a monomer radical cation decreased as the oligomer chain length increased. There are two reasons responsible for this result, first one is the high rate constants of dimerization of radical cations, which is responsible for the dimerization of the monomeric cations at low concentrations. Second, recent investigations indicated that the rate determining step is the proton elimination from intermediate σ -dimer not the rate of coupling. Heinze reported that sequential oligomerization of conducting polymers initiates in solution and dimerization steps take place from dimer to a tetramer and then to an octameric coupling compounds (Figure 1.10) [70].

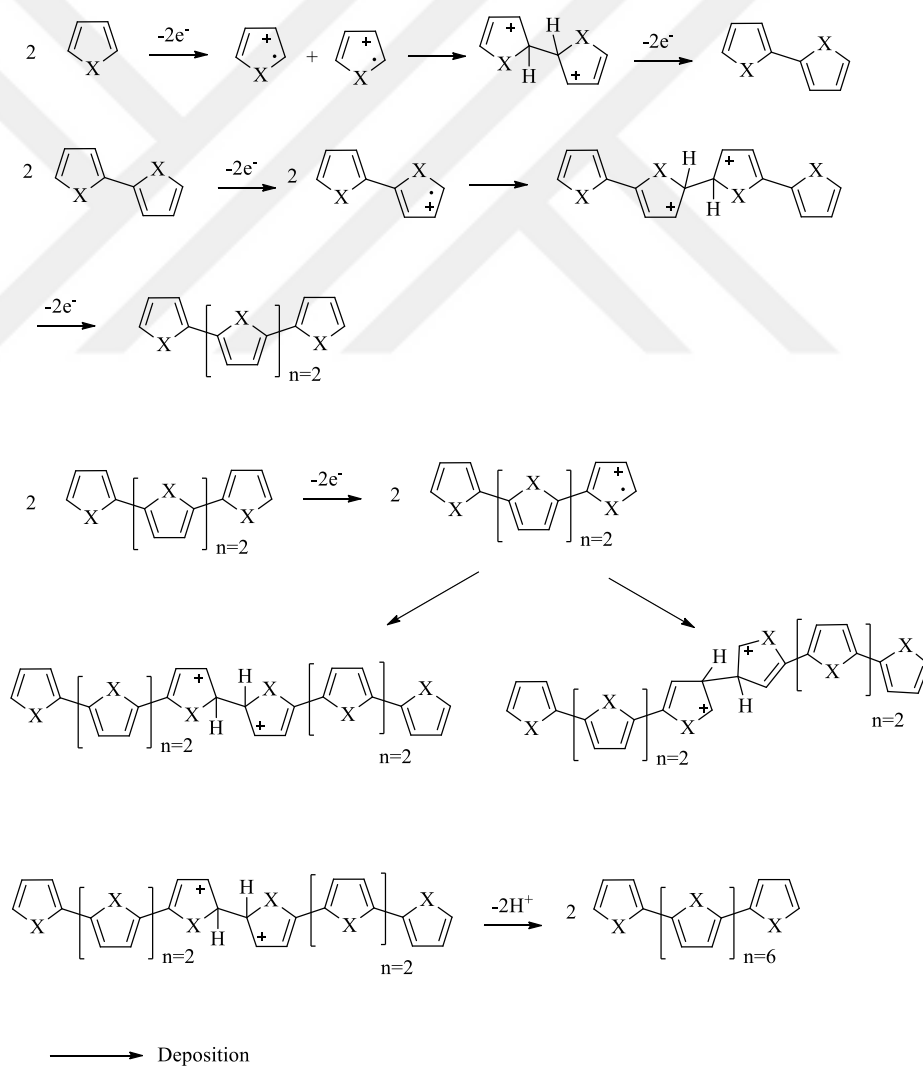


Figure 1.10 : Oligomerization steps of electropolymerization through σ -bonded intermediates [68].

Experimental advances such as absence of catalyst, readily formation of the doped polymer on electrode surface, and easy adjustment of the film thickness make the electrochemical polymerization one of the common ways in the production of conducting polymers.

1.5 Band Gap in Conjugated Polymers

The degree of the E_g and the locations of the HOMO and LUMO energy levels are the most crucial features to decide the optical and electrical properties of the conjugated polymers. The most simple approach to decrease the band gap is either increasing the HOMO or reducing the LUMO level of the polymer or bringing together the two levels at the same time [71]. Therefore, many methods have been improved to adjust the degree of band gap.

Band gap in conducting polymers are affected by several factors, namely bond length alternation (BLA) ($E^{\Delta r}$), the mean deviation from planarity (E^{θ}), the aromatic resonance energy (E^{res}), the inductive and mesomeric electronic effects of substituents (E^{sub}) and the interchain interactions (E^{int}) (Figure 1.11) [21,27]. The factors that affect the band gap in conducting polymers are indicated in Equation 1.1.

$$E_g = E^{\Delta r} + E^{\theta} + E^{\text{res}} + E^{\text{sub}} + E^{\text{int}} \quad (1.1)$$

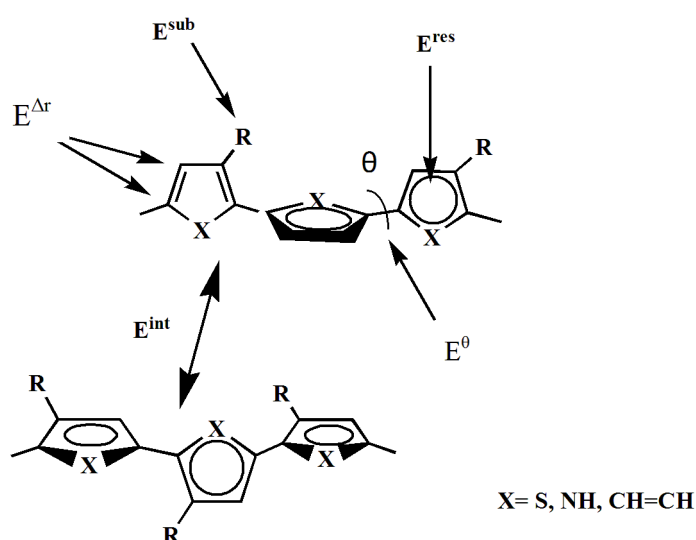


Figure 1.11 : Factors affecting the band gap in conducting polymers.

Polyheterocyclic polymers have two nondegenerate forms, aromatic and quinoid. $E^{\Delta r}$ is dependent on the alteration in single and double bond length. (Figure 1.12). In other

words, it is the amount of the relative degree of aromatic and quinoid structure in conjugated polymers [72].



Figure 1.12 : Aromatic (left) and quinoid (right) structures of conjugated polymers.

E^θ is the energy corresponding to the structure deviation from coplanarity, and results from the interannular rotations formed by the single bonds linking the aromatic cycles in conjugated polymers. Conductivity is related to the delocalization of π electrons, so any variation in planarity limits the conjugation length, and consequently makes E_g higher [73].

Mesomerism brings about a competition between π -electron restriction in the rings and delocalization through the chain. Therefore, enhanced resonance stabilization energy of aromatic monomers results in the delocalization of π electrons through the chain, causing a higher E_g . Therefore, E^{res} accounts for the resonance energy of the monomer [74].

E^{sub} is the effect of electron donating or electron withdrawing groups on the extent of band gap. While electron donating substituents increase the HOMO level, electron withdrawing groups lower the LUMO level. As a result, both substituents diminish E_g (Figure 1.13) [75].

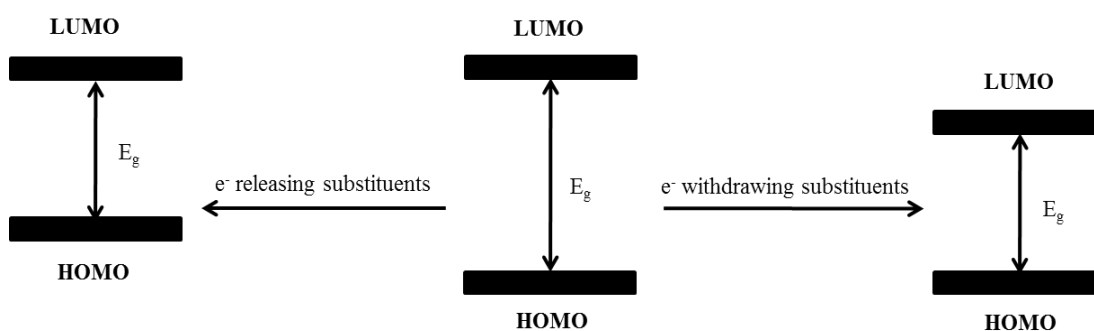


Figure 1.13 : Inductive and mesomeric effects of the substituents on E_g of conjugated polymers.

E^{int} is the energy result from intermolecular interchain couplings due to the orientation and organization of individual molecules in solid state [27].

1.6 Different Kinds of Conjugated Polymers

Conjugated polymers are classified according to the method applied for adjustment of band gap.

1.6.1 Fused aromatics

The backbone of the heterocyclic conjugated polymer such as poly(*p*-phenylene) (PPP), polyphenylene vinylene (PPV) and PT comprised of carbon-carbon double bonds attached by carbon-carbon single bonds. So, there are two resonance structures for these kinds of compounds for the ground state with nondegenerate energy; aromatic and quinoid forms. Quinoid form is energetically less stable and has a lower band gap due to the loss in the stabilization energy needed to disturb the aromaticity. The ratio of the aromatic to quinoid intensity in a heterocyclic conjugated compound is described as the BLA. Increasing quinoid structure with decreasing BLA simultaneously results in a lower band gap of a given conjugated polymer [76-78].

Figure 1.14 shows the aromatic and quinoid resonance forms of PPP, PPV and PT; PPP has a high band gap of 3.2 eV owing to the high degree of aromaticity of benzene rings. However, PPV has lower band gap of 2.5 eV emerging from the introduction of double bonds between benzene rings which results in the reduction of aromaticity. Also, PT has a lower bad gap of 2.0 eV since the aromaticity of thiophene is smaller than benzene. Fusing of benzene ring to thiophene to produce polyisothianaphthene (PITN) is an innovative strategy to increase the quinoid character of PT. Since benzene has a higher aromatic character than thiophene, PITN prefers the quinoid structure to keep the benzene aromaticity [79-81].

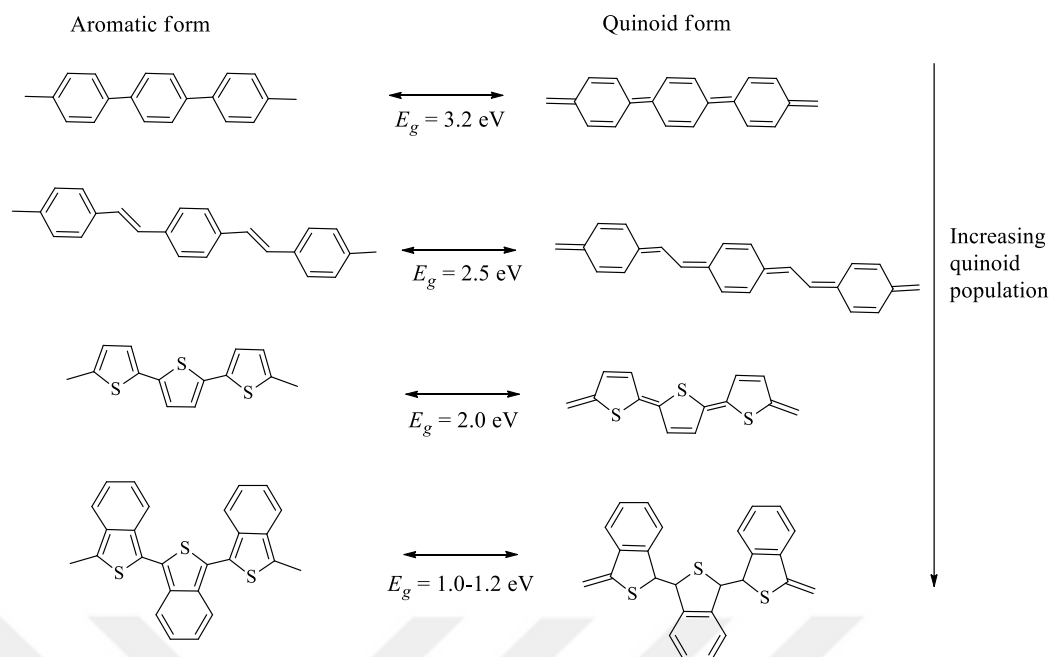
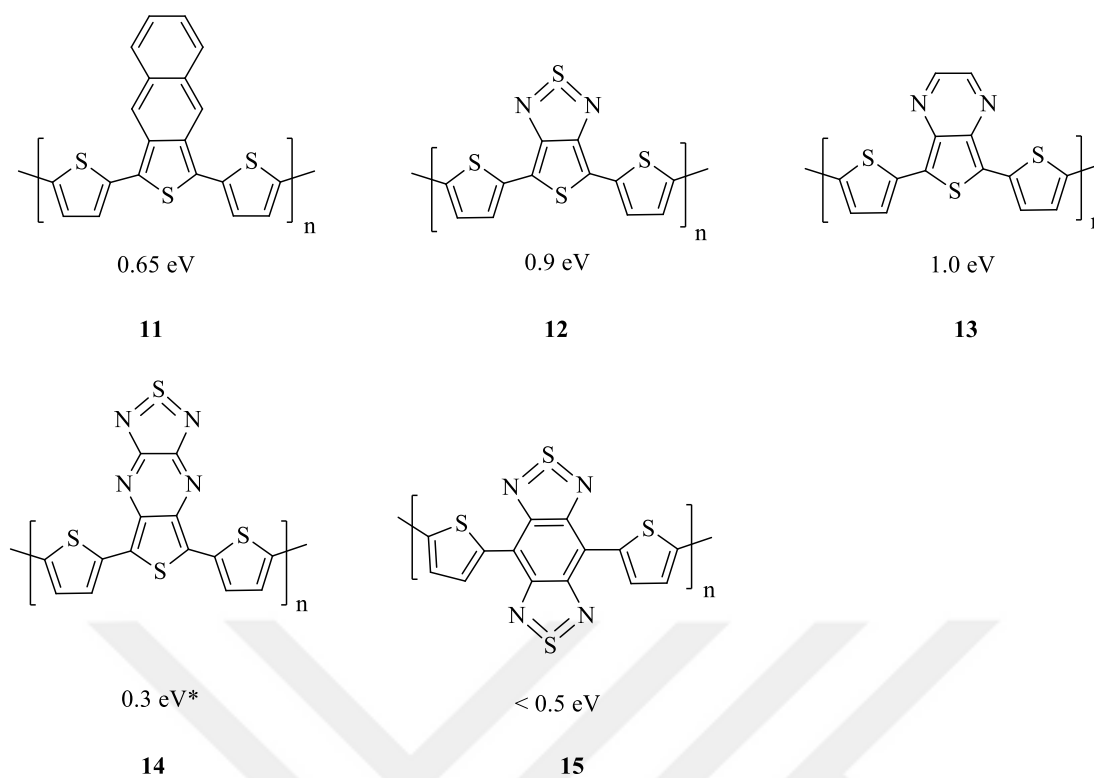


Figure 1.14 : Aromatic and quinoid structures of PPP, PPV, PT, and PITN [77].

PITN is noted as the first prominent conjugated polymer which has a narrow band gap of 1.0–1.2 eV. The small E_g of PITN comes from the stabilization of its quinoid form by the aromatic benzene ring. It is assumed that there is a competition between two aromatic cycles to keep their aromaticity, since benzene has a higher aromatic resonance energy (1.56 eV) than the thiophene (1.26 eV), of which quinonoidal form is more favorable over aromatic form [75,79]. The conductivity of *p*-doped PITN was found as 50 S.cm⁻¹ [82].

Some common examples of polymers having fused aromatics are depicted in Figure 1.15. Polymers **11** [83,84] and **12** [85] have band gaps lower than 1.0 eV, polymer **13** [86] have E_g of 1.0 eV. Polymers **14** [87] and **15** [88] have the lowest band gap materials reported so far.



* Electrochemical band gap

Figure 1.15 : Low E_g polymers obtained from aromatic-quinoidal system.

1.6.2 Electron-donating substituents

Introduction of electron-donating groups is a very effective way to obtain low band gap polymers; also energy gap can be tuned by alternating electron donation capabilities of the substitutes. The most common groups using for this purpose are alkoxy and amino groups.

Although, 3,4-disubstituted thiophenes were synthesized in order to make monomers selective and reactive, occupation of 3- and 4- positions decrease the conjugation length because of the steric hindrance between groups on neighboring monomer.

Electron-donating alkoxy groups at 3- and 4- positions of 3,4-alkylenedioxythiophene reduces the band gap (1.5–1.7 eV) of the polymer by increasing the HOMO energy level. Since the both β positions to sulfur are occupied, polymerization continues via the α positions to give linear and regular polymers [75].

Hergué and Frère reported the synthesis of 3,4-ethylenedioxythieno[2,3-*b*]thiophene and EDOT-based co-oligomer (Figure 1.16) [89]. Electronic properties of the oligomer by X-ray diffraction, optical and electrochemical techniques, and theoretical

calculations indicates that the S $\cdots$ O intramolecular interactions through polymer backbone contributes compound a self-rigidified structure. These interactions stabilize a planar *anti* conformation of the thiophene rings with a coherence length for varying EDOT-thiophene systems [89,90].

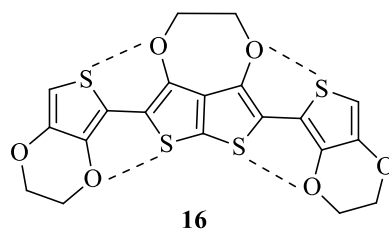


Figure 1.16 : Block copolymer incorporating EDOT with 3,4-ethylenedioxythieno[2,3-*b*]thiophene.

1.6.3 Electron-withdrawing substituents

Lowering the LUMO energy level by substitution of electron-withdrawing groups is another method for tailoring the band gap of the conjugated polymer. Cyano, nitro and carbonyl groups are the most generally used electron-withdrawing substituents.

Examples of cylopenta[2,1-*b*:3',4'-*b'*]dithiophene systems consisting of electron-withdrawing substituents is given in Figure 1.17. In addition to the electron-withdrawing effect, resonance form of the monomer unit lowers the E_g by decreasing aromaticity (**17a** and **17b**) [91].

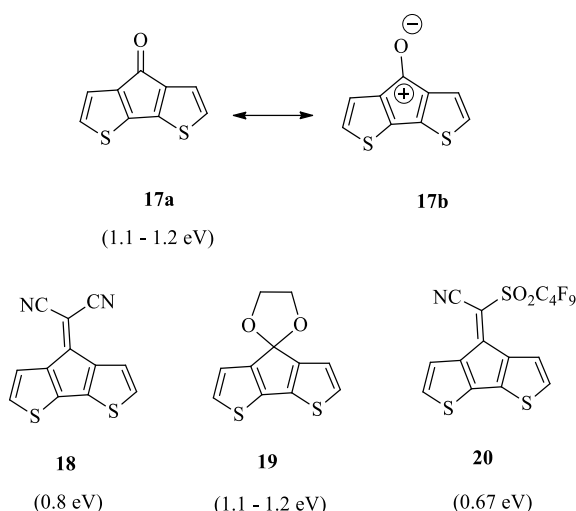


Figure 1.17 : Examples of cylopenta [2,1-*b*:3',4'-*b'*]dithiophene systems containing electron-withdrawing substituents.

The strong electron withdrawing effect of dicyanomethylene group makes polymer **18** [92] has lower band gap as compared to polymer **17** which has carbonyl group. The lower band gaps of polymer **18** and polymer **20** [93] than polymer **17** indicates that the attachment position (bridged sp^2 carbons) of electron withdrawing substituents has a significant importance on the band gap lowering. The E_g of polymer **19** was reported as 1.1–1.2 eV while poly bithiophene without any electron-withdrawing group has a band gap of ~ 2.1 eV. Besides the electron-withdrawing effect resonance form of the monomer causes the lowering of E_g by decreasing the aromaticity of the monomer. In addition, dioxy ethylene bridges increases the rigidity and planarity of the compound [75].

1.6.4 Push-pull donor/acceptors

Push-pull systems are the polymers which contain both donors and acceptors (DA) in direct conjugation with each other. These systems use the advantages of electron acceptors and electron donor groups to decrease the band gap by reducing LUMO energy state and increasing HOMO energy state [75]. An interaction of donor–acceptor groups improves the double bond character between the repeating units; hence quinoid form of the polymer backbone is stabilized. As a result, introduction of suitable electron-donating or electron-withdrawing moieties onto the main chain leads a decrease in a band gap [48].

To create a polymer with optimum push-pull system the energies of HOMO level of the donor group and LUMO level of the acceptor group should be close to each other (Figure 1.18).

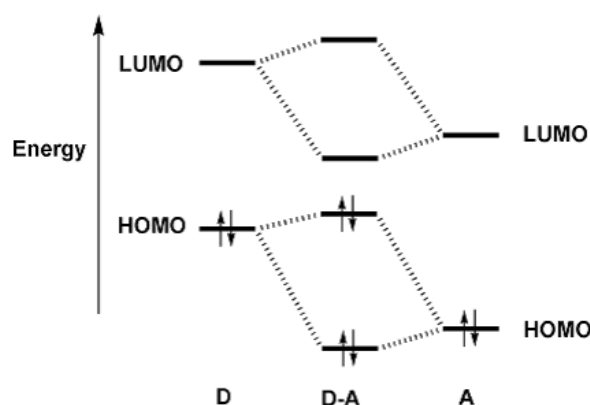


Figure 1.18 : Molecular orbital interaction of donor (D) and acceptor (A) groups to create DA monomer [48].

Energy level of the polymer was decreased as a result of the transforming of HOMO and LUMO levels of the monomer unit into valence and conduction bands, respectively. However, subsequent aromatic groups on polymer backbone may create a steric interaction. D–A system decreases the twisted arrangements between neighboring repeating units in conjugated polymers [48].

In general, while nitro, cyano, pyrazine and their derivatives are used as electron-acceptors, amino, selenophene, EDOT, aromatic rings such as thiophene, furan, pyrrole, and their derivatives are chosen as electron-donors [75]. Common examples of D–A systems (**21–25**) are depicted in Figure 1.19. Polymer **22** has a band gap of 0.36 eV and maximum absorption appearing at 1430 nm [94], whereas polymer **21** has a band gap of 1.1 eV in solid state [95].

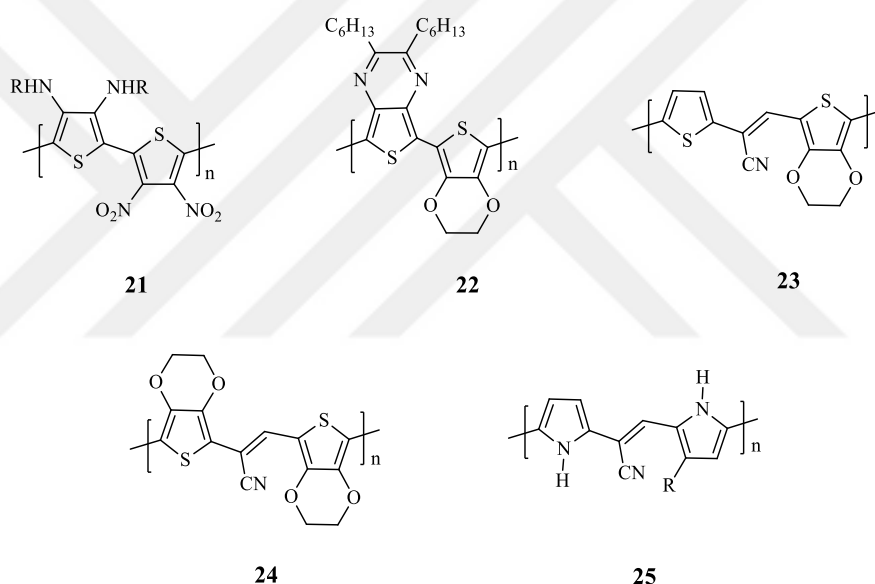


Figure 1.19 : Examples of low band gap polymers having push-pull system.

1.7 Thiophene and Polythiophene

Thiophene is a 5 membered aromatic compound with 6 π -electron cyclic system. One of two lone pairs on S is located in sp^3 orbital and contributes to aromatic sextet. Aromatic stabilization of 5-membered heterocyclic systems are in the relative order (kJ mol^{-1}): thiophene (122), pyrrole (90) and furan (68) [96]. This order is directly related to the electronegativity values for the sulfur (2.58), oxygen (3.44) and nitrogen (3.04) [97]. Due to the high electronegativity of sulfur, thiophene prefers electrophilic substitution at α -position [98].

Thiophene systems are used in many technologies such as sensors, organic solar cells, light-emitting diodes and organic field effect transistors as a result of their easy functionalization and versatility in reactions [99].

PTs are the most studied and crucial groups of linear conjugated polymers [21]. Available synthetic approaches to PTs, chemical [100] and electrochemical [22] polymerization techniques, structural versatility, and singular tunable electronic properties make them interesting class of materials for electronic and optoelectronic applications. The electron-rich character of thiophene ring makes PTs readily and reversibly oxidized by chemical and electrochemical methods to give *p*-doped materials with high conductivity [61]. The band gap of electrochemically synthesized PTs varies in between 2.0–2.2 eV depending on molecular weights of the polymer [101]. PTs emit red to blue and red to black-green switches on *p*- and *n*-dopings, respectively [102,103]. The first electronic transition of undoped PT is observed between 300–500 nm [100], doping causes PT to give noticeable bathochromic shift turning into the conduction band which lies from the visible to the deep-IR region [99].

Many studies have been performed to adjust thiophene to get electrochemically qualified materials, namely, PEDOT [101], polybenzothiophene [104,105] and polythienothiophene (PTT) [105,106], affording low energy gaps of 1.6–1.7, 0.92 and 0.85 eV, respectively. Poly(3-hexyl)thiophene and PEDOT are primarily applied in optoelectronic device manufacturing, particularly in photovoltaic (PV) cells and organic light-emitting diodes (OLEDs) [61,107].

1.7.1 Fused thiophenes

Fusing of aromatic rings is one of the effective ways to create low band gap conjugated polymers, Wudl et al. synthesized isothianaphthene by fusing benzene to thiophene and obtained the first conjugated polymer with a small band gap as low as 1.0–1.2 eV [79]. The low band gap emerges from quinoidal structure of PITN, which was stabilized by fusing of benzene ring possessing a larger aromatic resonance energy with respect to that of thiophene [80]. Then, many fused conjugated polymers have been produced and studied.

Fused thiophenes are formed by the annulation of thiophene rings and they have rigid structures with an extended π -conjugation compared to thiophene. While annulation of two thiophene rings forms the simplest fused thiophene called thienothiophenes

(TTs), fusing another thiophene ring into TTs provides dithienothiophenes (DTTs). TTs and DTTs are electron rich compounds with flat and rigid delocalized systems, which make them appropriate candidates to be used in conjugated and low band gap semiconductors [21,108,109].

1.7.1.1 Thienothiophenes

Two fused thiophene rings restrict the intramolecular rotation and give molecule a better π -conjugation. TTs have four structural isomers; namely thieno[3,4-*c*]thiophene **26**, thieno[3,4-*b*]thiophene **27**, thieno[2,3-*b*]thiophene **28**, and thieno[3,2-*b*]thiophene **29** were shown in Figure 1.20 [99].

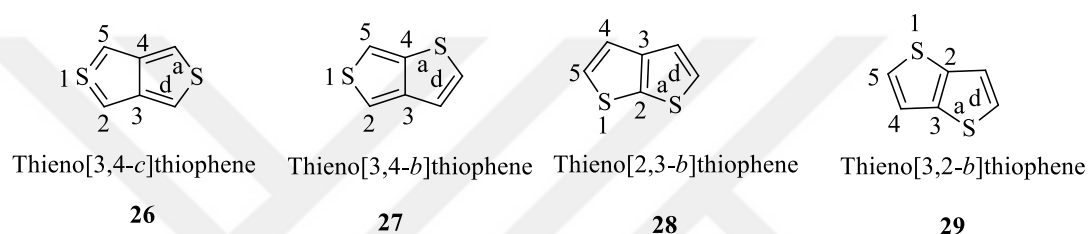


Figure 1.20 : Structural isomers of TTs.

Due to the planar structure of fused TTs the probability of π - π stacking is high, which results in an effective charge transportation in the bulk solid. Therefore, materials containing TTs are appropriate candidates for Organic Field Effect Transistors (OFETs) [99]. **27**, **28** and **29** are important building blocks for the construction of organic semiconductors having various conjugation lengths owing to stable and electron-rich natures [110]. **27** and **29** contribute low band gap conjugated systems, on the other hand, **28** provides cross-conjugated system, ceases the conjugation and increases the band gap. **27** has nearly as the same conjugation length as thiophene, but in conjugated system its oxidized quinoid structure is stabilized by the addition of second fused aromatic thiophene [111].

26 is the least stable isomer formed by two chemically equivalent thiophene rings sharing a mutual 3,4-bond, the molecule is highly aromatic possessing 10- π -electron system with a small band gap; however, HOMO is non-bonding orbital and the molecule is kinetically unstable [112]. The unsubstituted molecule has not been isolated; however, cycloadduct of *N*-phenylmaleimide **32** was obtained when 1H,3H-thieno[3,4-*c*]thiophene-2-oxide, **30** reacts with acetic anhydride under reflux condition

and on addition of the *N*-phenylmaleimide (Figure 1.21) [113]. According to reaction, **31** can only be obtained as a short-lived intermediate. The pure isomer is not stable, but many derivatives including bulky aryl groups [114,115], alkylthio chains [116,117], and electron withdrawing groups [118,119] have been isolated.

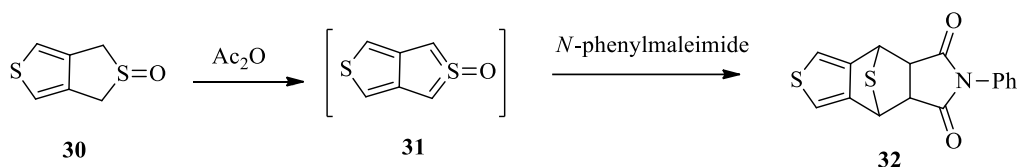


Figure 1.21 : Synthesis of cycloadduct of *N*-phenylmaleimide, **32**.

27 was first synthesized in 1967 by Wynberg and Zwanenburg [120], but the favorable route for the synthesis was described by Brandsma and Verkruijsse [121]. In this strategy **27** was obtained in two steps from 3,4-dibromothiophene, **33**. First, **34** was synthesized by the Sonogashira cross-coupling reaction with trimethylsilylacetylene. In the second step thermal ring closure in aqueous medium gave the corresponding product, **27** (Figure 1.22).

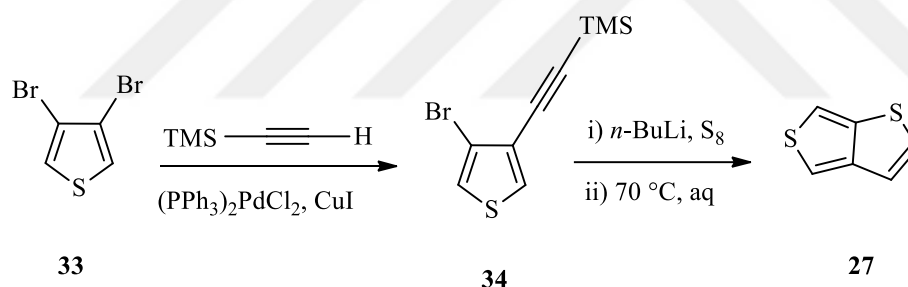


Figure 1.22 : Synthesis of thieno[3,4-*b*]thiophene, **27** starting from 3,4-dibromothiophene, **33**.

Unsubstituted **27** was polymerized and characterized. The band gap of the polymer was investigated as 0.85 eV. The polymer has high optical transparency in the neutral and oxidized states [105].

Many synthetic routes have been reported to obtain **29** and its derivatives. Fuller et al. synthesized **29** from 3-bromothiophene (**35**) in four steps [122]. **35** was treated with lithium diisopropylamide (LDA) leading to abstracting proton from the 2-position followed by addition of *N*-formylpiperidine giving rise to thieno[3,2-*b*]thiophene-2-carbaldehyde, **36**. Esterification of **36** with ethyl 2-sulfanylacetate afforded **37** and

subsequent hydrolysis and decarboxylation steps furnished the target compound **29** in an overall yield of 60 % (Figure 1.23).

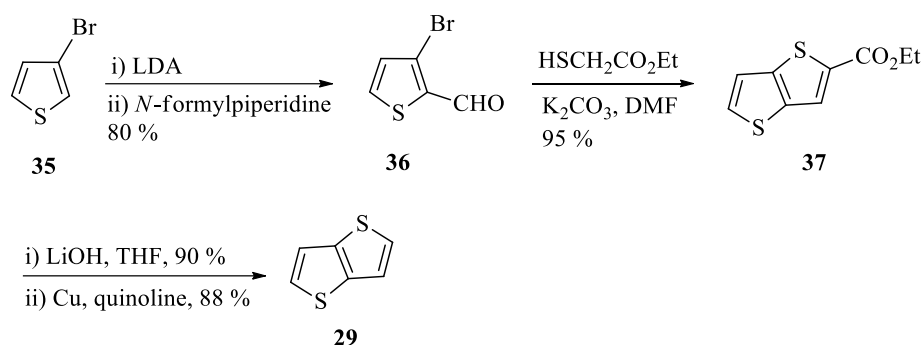


Figure 1.23 : Synthesis of **29** from 3-bromothiophene, **35**.

Kobayashi et al. reported the synthesis of the 3-bromothieno[3,2-*b*]thiophene (**38**) starting from **33** (Figure 1.24) [123].

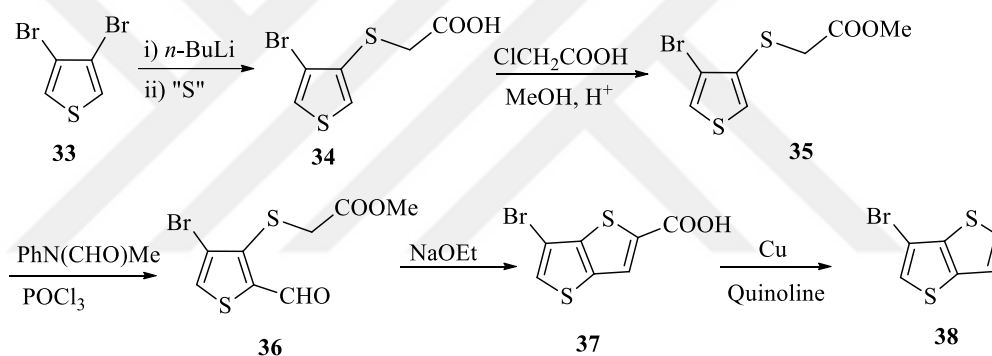


Figure 1.24 : Synthesis of **38** starting from 3,4-dibromothiophene, **33**.

Ozturk et al. reported the synthesis of TTs possessing *para*-substituted aryl groups at C-3 position (**40 a–f**) by using P₄S₁₀ in the ring closure reaction of monoketones (**39 a–f**) (Figure 1.25) [124].

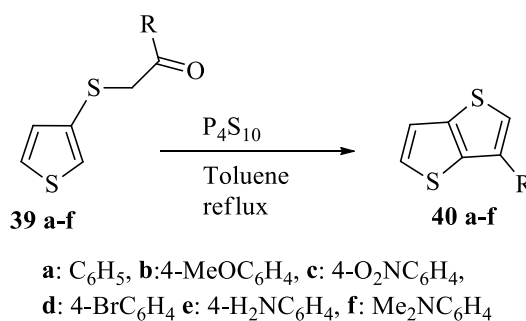


Figure 1.25 : Synthesis of TTs (**40 a–f**) using P₄S₁₀.

In another method, commercially available 2,5-dimethylhex-3-yne-2,5-diol (**41**) was treated with elemental sulfur in benzene to form 3,6-dimethylthieno[3,2-*b*]thiophene (**42**) in 26 % yield (Figure 1.26) [125].

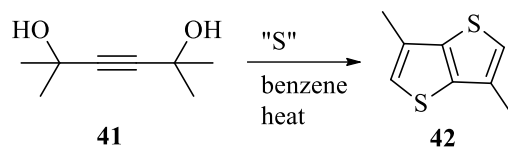


Figure 1.26 : Formation of 3,6-dimethylthieno[3,2-*b*]thiophene, **42**.

TT-based semiconductors were synthesized for OFETs from co-oligomers, **43** and **44** (Figure 1.27). According to the X-ray crystal structure analysis, **44** had almost coplanarity between biphenylene and TT groups, however **43** was partially disturbed by fluorene units. **44** has slightly better charge transport mobilities of $0.08\text{--}0.09\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ than that of **43** ($0.05\text{--}0.06\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$). On the other hand, the rigid TT units provided **45** with high charge carrier mobility ($1.1 \times 10^{-3}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$) and a narrow fluorescence band with a green emission in OLED devices [126].

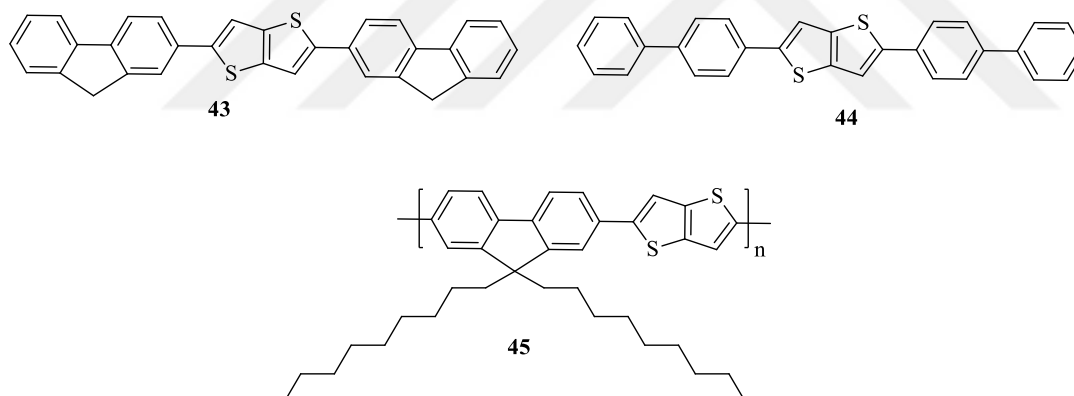
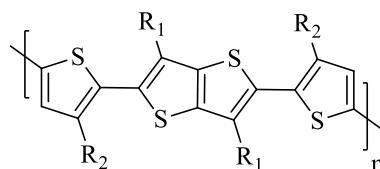


Figure 1.27 : TT-based materials **43–45** for OFETs.

Soluble and less sterically hindered copolymers (**46 a, b**) (Figure 1.28) were synthesized from TTs and thiophenes. Polymers had liquid crystalline features and in thin solid films they afforded large crystalline domains resulting possible candidates for fabrication of “quasi-single-crystal” transistors. In addition, both polymers have high charge carrier mobilities of $0.2\text{--}0.6\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ [127].



46a: $R_1 = H$, $R_2 = C_{10}H_{21}$

b: $R_1 = C_{12}H_{25}$; $R_2 = H$

Figure 1.28 : Soluble and less sterically hindered TT copolymers **46 a, b**.

Different kinds of methods have been described to synthesize **28** and its derivatives. Otsuba et. al. [128] described the synthesis of **28**, in this route, trimethylsilyl-1,3-pentadiene (**47**) obtained from 6-methoxyhex-4-en-1-yne was treated with potassium *t*-Butoxide, *n*-Butyllithium and carbondisulfide, followed by *t*-butanol in hexamethylphosphoramide (HMPA) to give the corresponding compound (Figure 1.29).

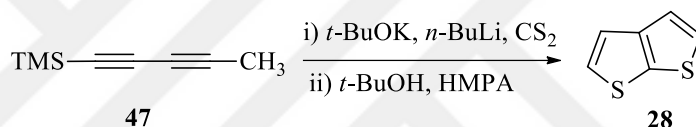


Figure 1.29 : Synthesis of **28**.

Few publications reported the incorporation of **28** into conjugated polymers, which pointed out the drawback of its incomplete conjugation between 2,5-positions of the fused thiophene rings [99]. Therefore, it is called cross-conjugated system.

1.7.1.2 Dithienothiophenes

Dithienothiophenes are formed by fusing three thiophene rings; there are six types of isomers: dithieno[3,2-*b*:2',3'-*d*]thiophene **48**, dithieno[2,3-*b*:2',3'-*d*]thiophene **49**, dithieno[3,4-*b*:3',4'-*d*]thiophene **50**, dithieno[2,3-*b*:3',2'-*d*]thiophene **51**, dithieno[3,4-*b*:3',2'-*d*]thiophene **52** and dithieno[3,4-*b*:2',3'-*d*]thiophene **53** (Figure 1.30) [109].

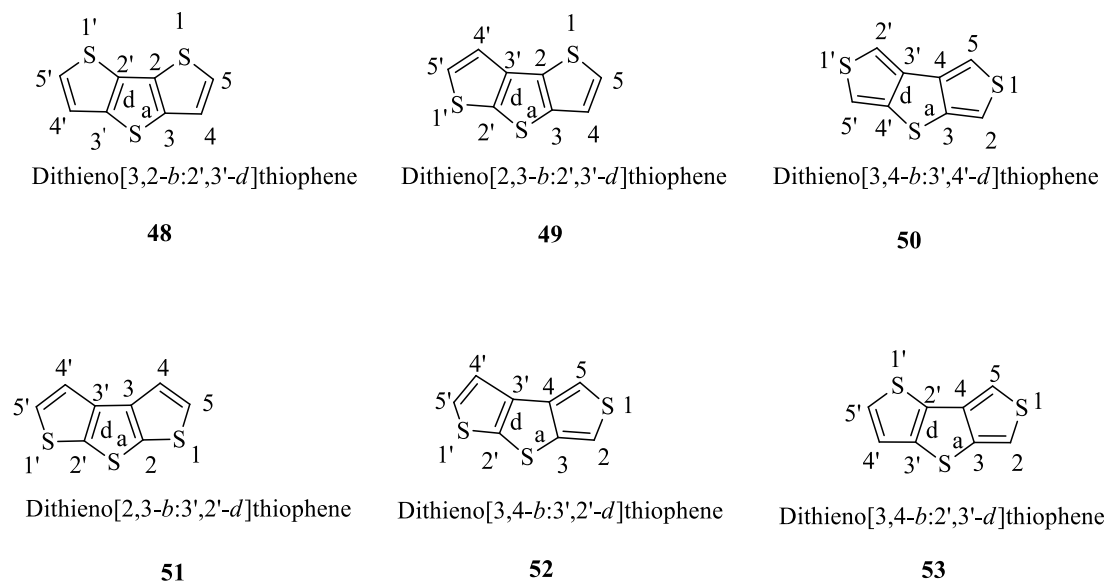


Figure 1.30 : Structural isomers of DTT.

Like TTs, DTTs are electron rich, planar, and rigid π -conjugated materials which have been crucial building blocks of many materials for electronic and optical applications like electroluminescence, two-photon absorption, excited fluorescence, photochromism, nonlinear optical chromophores, transistors with high mobilities of on/off ratios, conducting polymers and charge transfer complexes. Also, DTTs are fluorescence molecules due to the easily oxidized thiophene sulfur of the middle ring and this feature allows them to be used in labelling especially for biological systems [109]. The planar and rigid structure of DTT makes them use as *p*-type semiconductors for OFETs.

Design and synthesis of organic semiconductors for thin film transistor (TFT) application, using **48** as a building block was reported [129] (Figure 1.31). The dimer of the fused thiophene was synthesized through a coupling reaction of the lithiated monomer (**48**) by an oxidative coupling reagent, $\text{Fe}(\text{acac})_3$. The X-ray study of **54** showed a fully planar structure, strong intermolecular $\text{S} \cdots \text{S}$ interactions in the solid state, face-to-face π - π stacking, and effective molecular orbital overlap of the DTT units. High charge carrier mobility of $0.002\text{--}0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was observed for **54** in OFET devices.

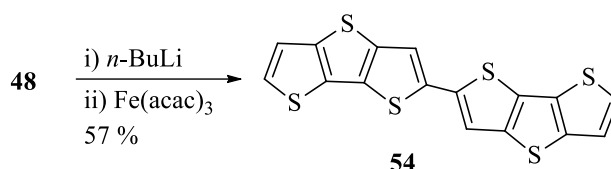


Figure 1.31 : Dimerization of **48**.

DTT derivative having two bithiophenyl substituents at 2- and 6- positions (**57**) was synthesized by microwave-assisted Suzuki coupling of 3,5-dimethyl-2,6-diiodo-DTT (**55**) with bithiophenylboronic acid ester (**56**) (Figure 1.32). They built OFET successfully by both vacuum sublimation and drop casting [130].

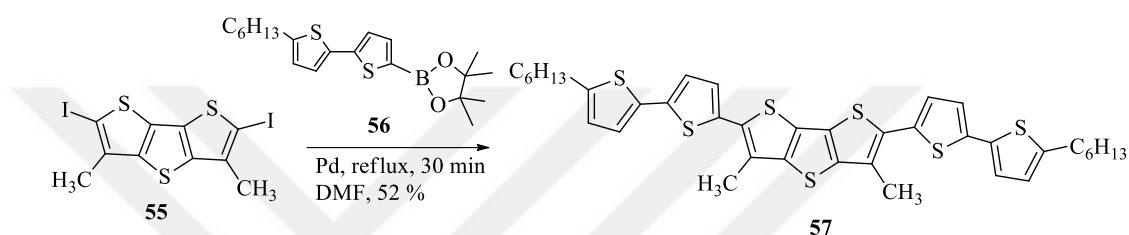


Figure 1.32 : Synthesis of **57**.

Bithiophenyl groups of **57** were replaced with dimesitylborane units to produce **58** which showed broad blue-green and weak red emissions (Figure 1.33). OLEDs constructed from ITO/PEDOT:PSS/**58**/LiF/Al displayed both broad blue-green emission and red emission at 680 nm emerging from the isolated molecules. The superposition of emissions generated white light up to 3800 cd m⁻² with external quantum efficiency of 0.35 % [131] .

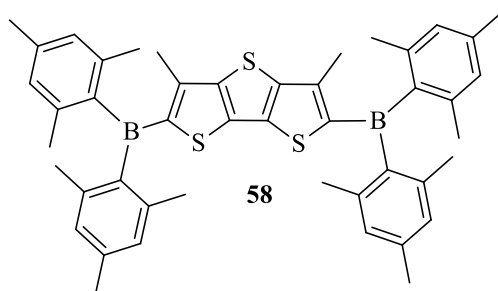


Figure 1.33 : DTT-based compound **58** used for OLEDs.

DTTs were also used as conjugated spacer to obtain D- π -D and D- π -A systems (**59 a-c**) for nonlinear optical materials (Figure 1.34) [132,133].

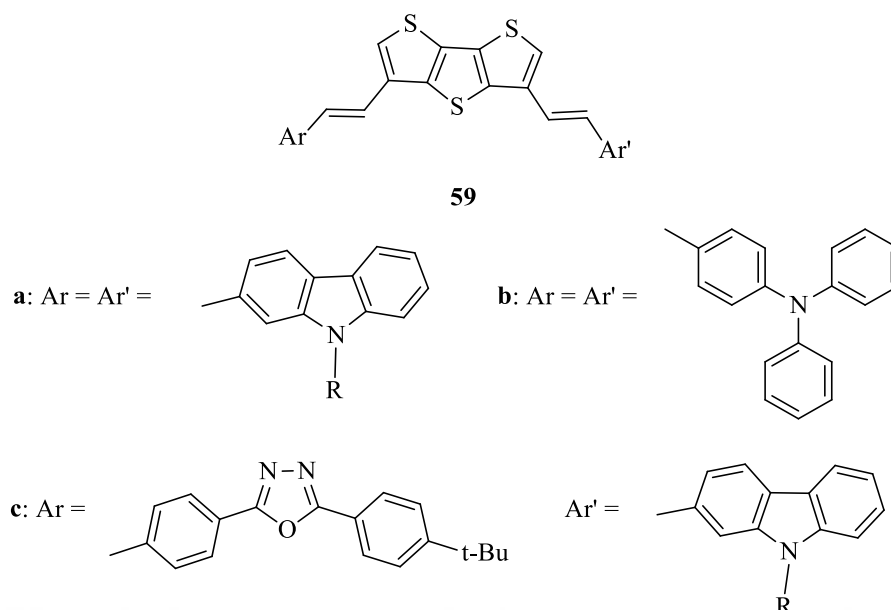
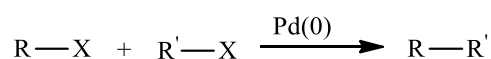


Figure 1.34 : D- π -D and D- π -A systems based on DTTs.

1.8 Coupling in Heterocyclic Chemistry

Where standard methods are not suitable for transformations in organic syntheses, palladium catalyzed coupling reactions has found widespread use for the functionalization of aromatics and heterocyclic compounds due to the moderate reaction conditions and application in a broad range of functional groups. Pd-catalyzed cross-coupling reactions are one of the most applied methods for the creation of Csp^2-Csp^2 bonds from aryl or vinyl halides [134].



R = usually sp^2 hybridized carbon

X = usually I, Br, Cl or OTf

In 2010 Richard F. Heck, Ei-ichi Negishi and Akira Suzuki were awarded with the Nobel Prize for their contributions to palladium-catalyzed coupling reactions [135].

Cross-coupling reactions are categorized into subgroups depending on the use of main-group metal (Figure 1.35). Organostannanes (Stille coupling) [63], organoboranes (Suzuki coupling) [64], organosilanes (Hiyama coupling) [136], and organozinc (Negishi coupling) [137] are the most frequently exploited main-group organometallics.

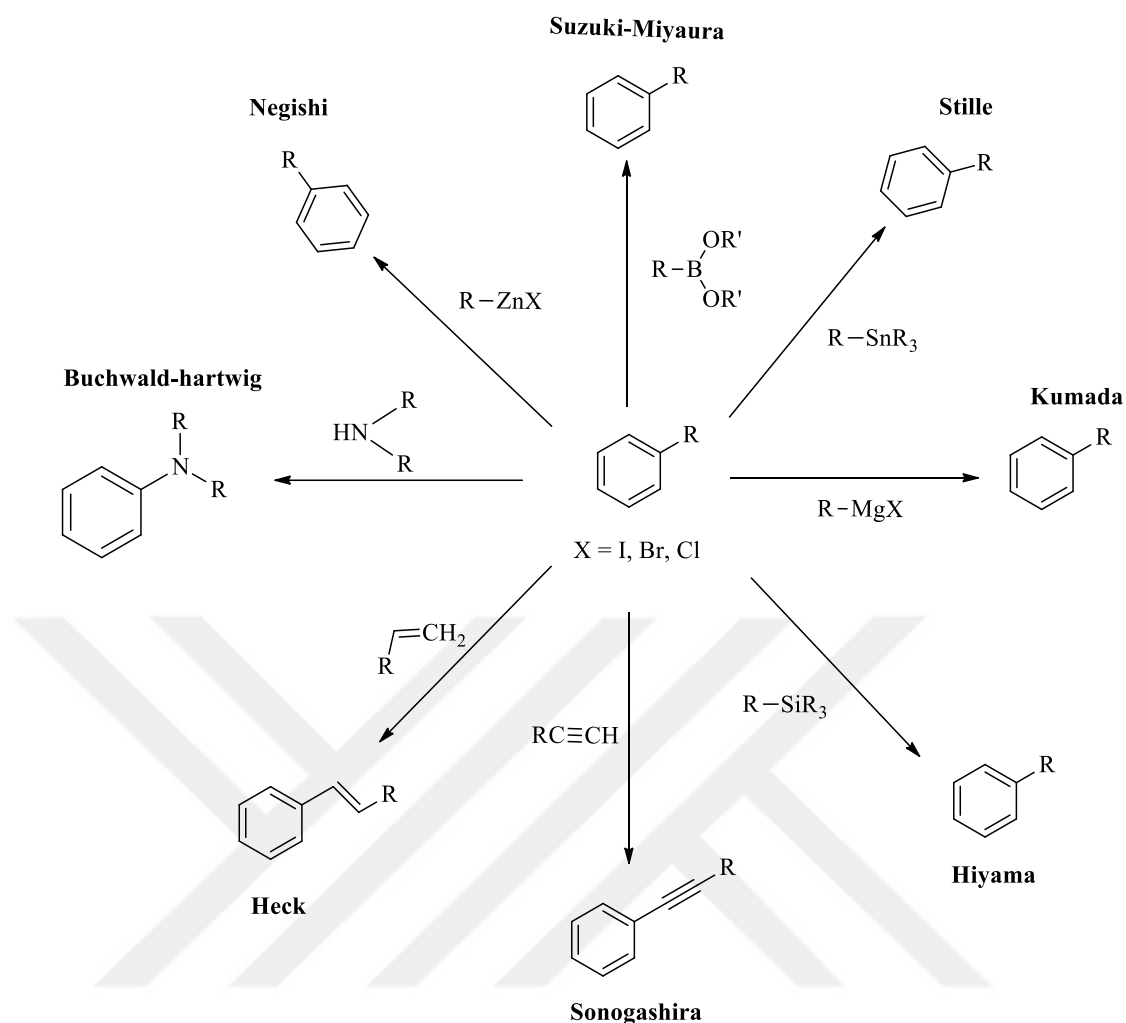


Figure 1.35 : Cross-coupling reactions [134].

There are three main stages of cross-coupling reaction. First one is the oxidative addition of aryl/vinyl halide to a Pd complex, in this step Pd catalyst with a strong σ -donating ligand acts as a nucleophile and attacks the most electron poor center of aromatic, decreases the bond dissociation energy for R-X and gives organopalladium halide complex. The second stage is the transmetalation with the main-group coupling reactant to form diorganopalladium compound. The last one is the reductive elimination step in which coupling partners with contrary electronic characteristics afford the target product by carbon-carbon bond formation (Figure 1.36) [96].

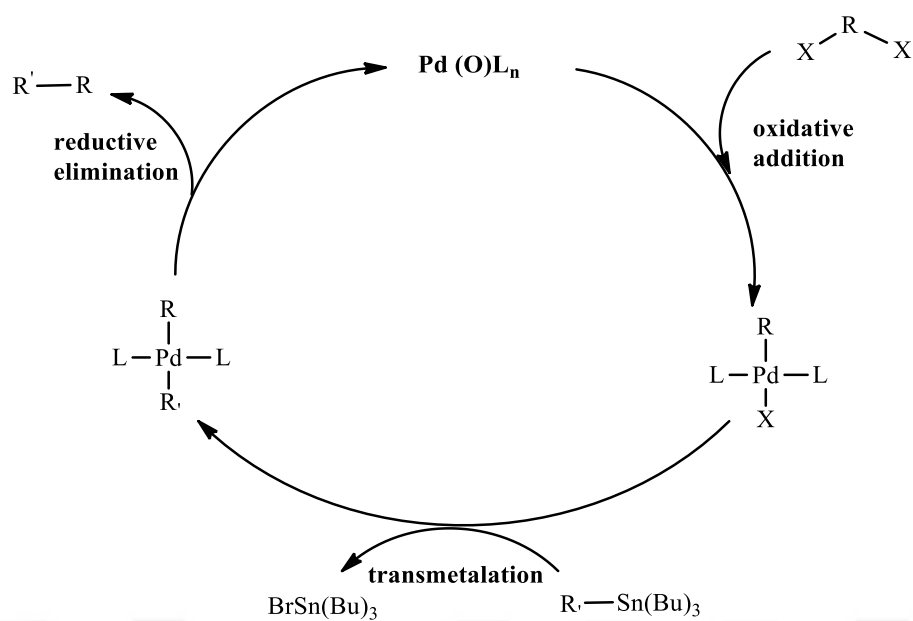


Figure 1.36 : Catalytic cycle of cross coupling reaction.

2. EXPERIMENTAL

2.1 Materials

Thiophene, 2,5-dibromothiophene and bromine were purchased from Acros Organics. 3-Bromothiophene and 4-(2-bromoacetyl)benzonitrile were obtained from ABCR. *n*-Butyllithium (*n*-BuLi), tertiary-butyllithium (*t*-BuLi), 2,5-dibromothiophene, polyphosphoric acid (PPA), ammonium chloride (NH₄Cl), *N*-bromosuccinimide (NBS), zinc, glacial acetic acid, trimethyltin chloride, tributylstannyl chloride, chlorobenzene, 3-hexylthiophene, 3-bromothiophene, 2,3-dihydrothieno[3,4-*b*][1,4]dioxane, potassium carbonate (K₂CO₃), potassium hydroxide (KOH), tetra-*n*-butyl ammonium bromide, tetramethylethylenediamine (TMEDA), dichloromethane (DCM), *n*-hexane, dimethylformamide (DMF), ethyl acetate (EtOAc), methyl alcohol (MeOH), tetrakis(triphenylphosphine)palladium(0) (Pd[(C₆H₅)₃P]₄), dichlorobis(triphenylphosphine)palladium(II) (PdCl₂(PPh₃)₂), iron(III) chloride (FeCl₃) and hydrochloric acid (HCl) were supplied from Sigma Aldrich. 2,3-Dihydrothieno[3,4-*b*][1,4]dioxane, diethyl ether (Et₂O), 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, sulfur (S₈), sodium bicarbonate (NaHCO₃), sodium sulfate (Na₂SO₄) and sodium thiosulfate (Na₂S₂O₃) were obtained from Merck.

2.2 Equipments

¹H and ¹³C NMR spectra were recorded on a Varian model NMR (500 and 126 or 600 and 150 MHz). Chemical shifts were reported in ppm relative to tetramethylsilane. Mass spectra were recorded on Bruker MICROTOFQ and Thermo LCQ-Deca ion trap mass instruments. FTIR measurements were performed on a Thermo Nicolet 6700 FT-IR spectrometer. Melting points of compounds were determined by Buchi Melting Point Analyzer (B-540).

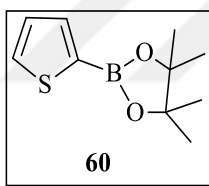
Synthesized compounds were purified by column chromatography. Merck Silica Gel (0.015-0.040 mesh) was used as the solid adsorbent packed in a glass column.

Commercial TLC (Merck TLC Silica Gel 60 F₂₅₄) was used to control the reaction and decide the eluent for the column chromatography.

Electrochemical and redox behaviors of the π -conjugated monomers and polymers were checked potentiodynamically using Versa Stat 3. Electropolymerization of the monomers was realized in a three-electrode cell containing ITO-coated glass slide as the working electrode, platinum wire as the counter electrode, and Ag wire as the pseudo-reference electrode. Electrochromic measurements and spectroelectrochemistry of the polymer films deposited on ITO-coated glass slide were performed in a suitable solvent/supporting electrolyte system using HITACHI U-0080D spectrophotometer. Colorimetry measurements were done by Conica Minolta CS-100 spectrophotometer. Polymer thin films were prepared by SCS Spincoat G3-B from THF or chlorobenzene solutions.

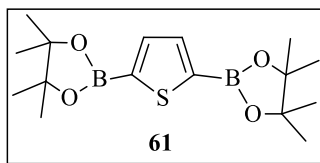
2.3 Syntheses of Monomers

2.3.1 4,4,5,5-Tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (**60**)



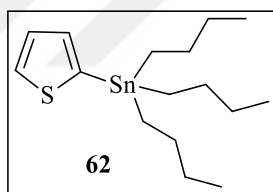
To a solution of thiophene (1.5 mL, 18.7 mmol) in THF (50 mL) *n*-Butyllithium (8.24 mL, 2.5 M in *n*-hexane, 20.6 mmol) by syringe under N₂ atmosphere was added at -78 °C. The mixture was stirred for 20 min at the same temperature. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.29 mL, 20.6 mmol) was added rapidly to the solution, and the resulting mixture was stirred for 24 h at room temperature (RT). The solvent was removed under reduced pressure. The crude product was dissolved in DCM and washed with 5 M HCl_(aq) solution (100 mL). The organic phase was dried over Na₂SO₄ and filtered, and the solvent was evaporated. The title product (**60**) was obtained by recrystallization from *n*-hexane/DCM as a white solid in 81 % yield with a melting point of 64–67 °C [106].

2.3.2 2,5-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene (**61**)



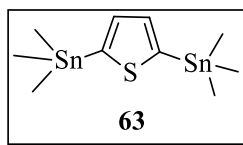
2,5-Dibromothiophene (1.10 mL, 9.80 mmol) was dissolved in 50 mL of dry THF. At -78 °C, under N₂ atmosphere 2.5 M *n*-BuLi (8.24 mL, 20.6 mmol) was added to the solution. After stirring for 1 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10.0 mL, 49.0 mmol) was added by syringe, and the stirring was continued for further 1 h at -78 °C, then the mixture was left stirring at RT for 24 h. It was poured into water and extracted with ethyl acetate (100 mL) and washed with brine (100 mL). The extracted solution was dried over anhydrous Na₂SO₄. The crude product was purified by recrystallization from *n*-hexane/DCM to give the title compound (**61**) in 93 % yield as a white solid, mp. 210–212 °C [106].

2.3.3 Tributyl(thiophen-2-yl)stannane (**62**)



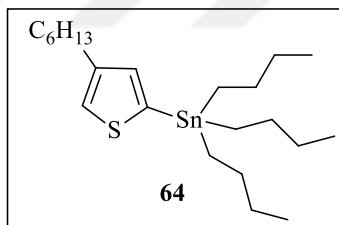
A solution of thiophene (1.00 mL, 12.5 mmol) in 30 mL anhydrous THF under N₂ was cooled to -30 °C. 2.5 M *n*-BuLi (5.99 mL, 15.0 mmol) was added dropwise to the stirred precooled solution and the mixture was stirred at the same temperature for 2 h. Then, tributylstannyl chloride (4.88 mL, 15.0 mmol) was added and the mixture continued to stir at -30 °C for 1.5 h. After stirring overnight at RT, the mixture was poured into 200 mL saturated aqueous solution of NaHCO₃ and extracted with DCM (2 x 100 mL). The organic phase was washed with brine solution and dried over anhydrous Na₂SO₄. The organic phase was evaporated under reduced pressure. The compound **62** was obtained as oil and used without further purification [138].

2.3.4 2,5-Bis(tributylstannyl)thiophene (**63**)



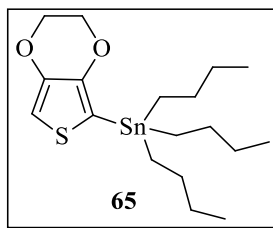
To a solution of thiophene (1.00 mL, 12.5 mmol) and TMEDA (3.19 g, 27.5 mmol) in 40 mL anhydrous *n*-hexane, *n*-BuLi (11.0 mL, 27.5 mmol) was added within 10 min at 0 °C under N₂. The reaction mixture was refluxed for 45 min, and cooled to 0 °C. Then, trimethyltin chloride (27.0 mL, 27.5 mmol) was added within 10 min, cooling bath was removed and the reaction mixture was stirred at RT for 15 h. Reaction was quenched with a saturated aqueous solution of NH₄Cl (50 mL). The aqueous part was extracted with Et₂O (2 x 100 mL) and organic layer was washed with brine (2 x 100 mL). The organic layer was dried over Na₂SO₄ and the solvent was removed under reduced pressure to give the product **63** in 93 % yield as a pale yellow solid, mp. 93–102 °C [139].

2.3.5 Tributyl(4-hexylthiophen-2-yl)stannane (**64**)



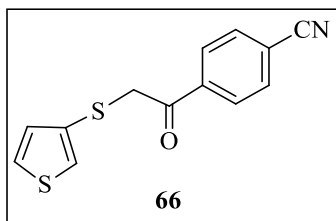
3-Hexylthiophene (2.50 mL, 13.9 mmol) dissolved in anhydrous THF under N₂ was cooled to -78 °C and 6.12 mL *n*-BuLi (2.5 M, 15.3 mmol) was added to the solution. It was stirred for 1.5 h at -78 °C, tributylstannyl chloride (4.15 mL, 15.3 mmol) was added slowly and the reaction mixture was stirred for 4 h. Then, the solution was warmed to RT and stirred overnight at the same temperature. The solvent was evaporated at a reduced pressure. The remaining part was dissolved in DCM (150 mL) and washed with saturated aqueous NaHCO₃ solution (100 mL) and saturated aqueous brine (100 mL). Organic layers were combined and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure to give the title product **64** as colorless oil [138].

2.3.6 Tributyl(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)stannane (65)



To a solution of 3,4-ethylenedioxythiophene (1.50 mL, 14.0 mmol) in 100 mL of anhydrous THF under N₂ at -78 °C was added 5.70 mL *n*-BuLi (2.5 M, 14.3 mmol). The solution was stirred for 1.5 h at -78 °C and tributylstannyl chloride (3.97 mL, 14.6 mmol) was added to the solution. After stirring for 4 h at the same temperature, solution was warmed to RT and stirred overnight. The solvent was removed; the residue was poured into saturated aqueous NH₄Cl solution (100 mL) and extracted with DCM (2 x 100 mL). The organic phase was separated and washed with brine (100 mL) and dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure to give target compound **65** as a yellow liquid. The compound was used without purification [140].

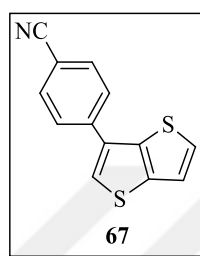
2.3.7 4-(2-(Thiophen-3-ylthio)acetyl)benzonitrile (66)



3-Bromothiophene (2.0 mL, 21.0 mmol) was dissolved in dry Et₂O (40 mL), under N₂ at -78 °C *n*-BuLi (9.39 mL, 23.5 mmol, 2.5 M solution in *n*-hexane) was added to the solution. After the mixture was stirred for 1 h, S₈ (67 mg, 21.0 mmol) was added portion wise and the mixture was further stirred for 1 h. Then, 4-(2-bromoacetyl) benzonitrile (4.71 g, 21.0 mmol) was added portion wise and the stirring was continued for overnight at RT. The solution was extracted with water (3 x 200 mL), washed with NaHCO₃ (10 %) solution (2 x 200 mL). Organic layer was dried over Na₂SO₄, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by recrystallization from Et₂O/MeOH mixture to give the title compound **66** (4.10 g, 74 %) as an orange solid, mp 80 °C. FT IR (ATR): ν = 3110, 2898, 2223,

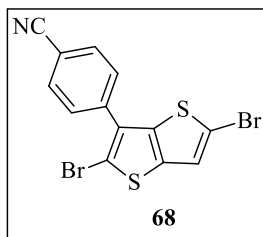
1682, 1503, 1394, 1286, 1194, 996, 826, 757, 599, 573 cm^{-1} (Figure A.1). ^1H -NMR (500 MHz, CDCl_3): δ 7.95 (d, J = 8.8 Hz, 2H), 7.72 (d, J = 8.8 Hz, 2H), 7.29 (dd, J = 5.0, 3.0 Hz, 1H), 7.21 (dd, J = 3.0, 1.5 Hz, 1H), 6.98 (d, J = 5.0, 1.5 Hz, 1H), 4.08 (s, 2H) (Figure A.2). ^{13}C -NMR (126 MHz, CDCl_3 , δ): 192.8, 138.4, 132.7, 130.4, 129.1, 128.7, 127.6, 126.9, 117.9, 116.7, 42.0 (Figure A.3). MS m/z = 259.8 (M^+) (Figure A.4).

2.3.8 4-(Thieno[3,2-*b*]thiophen-3-yl)benzonitrile (**67**)



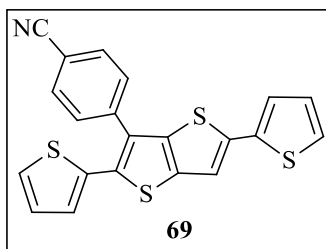
Polyphosphoric acid, PPA (5.21 g) was weighed into two-necked round bottom flask, dissolved in chlorobenzene (4 mL) and heated to 100 $^{\circ}\text{C}$. Then **66** (200 mg, 770 μmol) dissolved in a minimum amount of chlorobenzene was added to the flask. The reaction mixture was refluxed for 4 h at 130 $^{\circ}\text{C}$ and the liquid part was decanted. The remaining viscous part was washed with chlorobenzene couple of times, organic parts were combined and chlorobenzene was evaporated under reduced pressure. The remaining pale green solid was dissolved in DCM (100 mL), washed with aqueous NaHCO_3 (10 %) (100 mL) and water (100 mL). Organic layer was dried over Na_2SO_4 , filtered and solvent was evaporated under reduced pressure. The crude product was purified by recrystallization from DCM/MeOH to give the title compound **67** (150 mg, 81 %) as a yellow-green solid, mp 150 $^{\circ}\text{C}$. FT IR (ATR): ν = 3098, 2228, 1594, 1344, 1089, 936, 833, 731, 704, 660, 535 cm^{-1} (Figure A.5). ^1H -NMR (500 MHz, CDCl_3): δ 7.79 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 1.5 Hz, 1H), 7.44 (dd, J = 5.4, 1.5 Hz, 1H), 7.30 (d, J = 5.4 Hz, 1H) (Figure A.6). ^{13}C -NMR (126 MHz, CDCl_3): δ 140.1, 138.9, 137.3, 132.8, 132.5, 127.7, 126.7, 125.1, 119.9, 118.8, 110.9 (ppm) (Figure A.7). MS m/z 241.9 (M^+) (Figure A.8).

2.3.9 4-(2,5-Dibromothieno[3,2-*b*]thiophen-6-yl)benzonitrile (**68**)



To a solution of **67** (200 mg, 83 μ mol) in DMF (10 mL) in dark at -10 °C, NBS (310 mg, 1.74 mmol) dissolved in DMF (4 mL) was added dropwise. The mixture was stirred for 4 h at -10 °C. The reaction mixture was poured into water (30 mL). The solid was filtered and purified by column chromatography over silica gel using *n*-hexane/DCM (1:1) as eluent to give the title compound **68** (290 mg, 90 %) as a white solid, mp 190 °C. FT IR (ATR): ν = 2224, 1603, 1462, 1303, 1153, 1019, 836, 798, 465 cm^{-1} (Figure A.9). ^1H -NMR (500 MHz, CDCl_3): δ 7.79–7.75 (m, 4H), 7.25 (s, 1H) (Figure A.10). ^{13}C (126 MHz, CDCl_3): δ 138.3, 137.9, 136.8, 132.7, 131.5, 129.1, 122.3, 118.4, 114.2, 112.3, 111.5 (Figure A.11). MS m/z 399.0 (M^+) (Figure A.12).

2.3.10 4-(2,5-Di(thiophen-2-yl)thieno[3,2-*b*]thiophen-6-yl)benzonitrile (**69**)



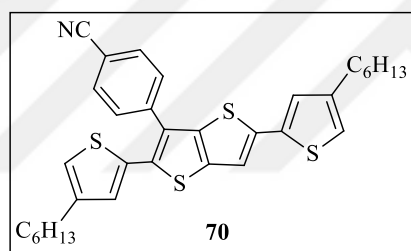
4-(2,5-Di(thiophen-2-yl)thieno[3,2-*b*]thiophen-6-yl)benzonitrile, **69** was synthesized through Suzuki cross-coupling reaction. **68** (250 mg, 630 μ mol), **60** (290 mg, 1.38 mmol) were weighed into a schlenk tube and dissolved in 50 mL anhydrous THF. K_2CO_3 (2.00 mL, 2 M) was added to the mixture and degassed with N_2 for 30 min. Then, $\text{Pd}[(\text{C}_6\text{H}_5)_3\text{P}]_4$ (72.8 mg, 63.0 μ mol) was added at RT and the mixture was stirred at the same temperature for 72 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography over silica gel eluting with *n*-hexane/DCM (1:3) 110 mg of the target compound (**69**) (55 %) was obtained as a yellow solid, mp > 200 °C. FT IR (ATR): ν = 3085, 2226, 1601, 1218, 815, 693, 556, 463 cm^{-1} (Figure A.13). ^1H -NMR (500 MHz, CDCl_3): δ 7.67 (d, J = 8.3 Hz, 2H),

7.59 (d, $J = 8.3$ Hz, 2H), 7.31 (s, 1H), 7.25–7.23 (m, 2H), 7.17 (d, $J = 3.0$ Hz, 1H), 7.01 (dd $J = 7.0, 4.0$ Hz, 1H), 6.98 (dd $J = 3.8, 1.5$ Hz, 1H), 6.96–6.95 (m, 1H) (Figure A.14). ^{13}C (126 MHz CDCl_3): δ 139.6, 139.5, 139.4, 139.0, 137.4, 137.2, 135.2, 134.2, 132.3, 129.9, 129.0, 128.0, 127.6, 127.4, 127.0, 125.2, 124.3, 118.7, 115.9, 111.8, 111.7 (Figure A.15). MS m/z 405.20 (M^+) (Figure A.16).

General procedure for the syntheses of **70**, **71** via Stille cross-coupling reaction

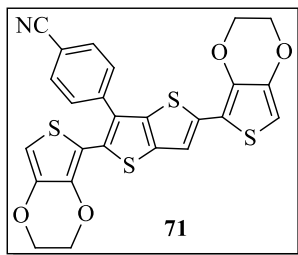
To a solution of **68** (250 mg, 630 μmol) in 50 mL anhydrous THF, tributyl stannane derivatives, (2.52 mmol) were added. The solution was purged with N_2 for 30 min and $\text{PdCl}_2(\text{PPh}_3)_2$ (91.0 mg, 130 μmol) was added at RT. The mixture was refluxed for 72 h under N_2 atmosphere. Solvent was evaporated under reduced pressure and the crude product was purified by column chromatography over silica gel.

2.3.11 4-(2,5-Bis(4-hexylthiophen-2-yl)thieno[3,2-*b*]thiophen-3-yl)benzonitrile (**70**)



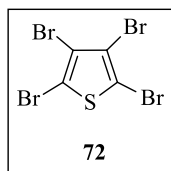
The residue was purified by column chromatography over silica gel, with *n*-hexane/DCM (1:3) giving a target compound (**70**) as a yellow solid (360 mg, 40 %), mp 98 °C. FT IR (ATR): $\nu = 2923, 2851, 2234, 1601, 1457, 1185, 960, 858, 820, 803, 720, 544$ cm^{-1} (Figure A.17). ^1H -NMR (500 MHz, CDCl_3): δ 7.67 (d, $J = 8.5$ Hz, 2H), 7.60 (d, $J = 8.5$ Hz, 2H), 7.28 (s, 1H), 7.01 (d, 1.0 Hz, 1H), 6.82 (d, $J = 2.0$ Hz, 2H), 6.79 (d, $J = 1.0$ Hz, 1H), 2.55 (t, 2 H), 2.50 (t, 2H), 1.62–1.52 (m, 4H), 1.34–1.27 (m, 12H), 0.86 (m, 6H) (Figure A.18). ^{13}C (126 MHz, CDCl_3 , δ): 144.3, 143.9, 139.7, 139.3, 139.2, 137.2, 136.8, 134.8, 134.6, 132.6, 129.9, 128.6, 125.6, 121.6, 119.8, 118.7, 115.5, 111.6, 31.6, 30.5, 30.3, 29.0, 28.9, 22.6, 14.0 (Figure A.19). MS m/z 573.8 (M^+) (Figure A.20).

2.3.12 4,4'-(2,6-Bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (71)



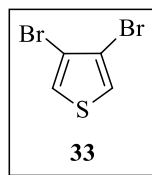
The residue was purified by column chromatography over silica gel, with *n*-hexane/DCM (1:3) providing the title compound (**71**) as an orange solid (180 mg, 53 %), mp > 200 °C. FT IR (ATR): ν = 2918, 2850, 2222, 1605, 1515, 1441, 1363, 1158, 1065, 908, 666, 578 cm^{-1} (Figure A.21). ^1H -NMR (500 MHz, CDCl_3): δ 7.68 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 8.3 Hz, 2H), 7.36 (s, 1H), 6.30 (s, 1H), 6.24 (s, 1H), 4.33–4.22 (m, 4H), 4.09–3.96 (m, 4H) (Figure A.22). ^{13}C (126 MHz, CDCl_3): δ 141.9, 141.6, 140.5, 138.7, 138.5, 138.2, 138.1, 136.6, 132.3, 130.9, 129.5, 129.3, 118.9, 114.9, 112.1, 111.1, 109.9, 100.5, 97.8, 65.1, 64.6, 64.5, 64.4 (Figure A.23). MS m/z 622.2 ($\text{M}^+ + 1$) (Figure A.24).

2.3.13 2,3,4,5-Tetrabromothiophene (72)



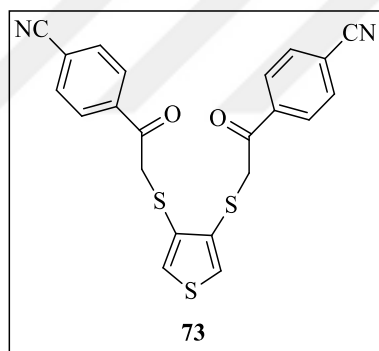
Thiophene (8.40 g, 100 mmol) was dissolved in 4.00 mL chloroform and Br_2 (23.0 mL, 1.40 mol) was added dropwise into the vigorously stirred solution. The mixture was stirred at RT for 17 h and then refluxed for 2 h. After cooling to RT, KOH (11.0 g) in EtOH (60 mL) was added. The mixture was refluxed for 4 h, and poured into an ice/water mixture (130 mL), extracted with CHCl_3 and recrystallized in $\text{CHCl}_3/\text{EtOH}$ to give **72** [141].

2.3.14 3,4-Dibromothiophene (33)



An acetic acid/water mixture (1:2, 60 mL) was poured to a round-bottom flask and zinc powder (21.3 g, 326 mmol) and **72** (37.7 g, 94.3 mmol) was added in small portions while stirring. The mixture was stirred at RT for 1 h, and refluxed for 3 h. After the reaction was over, the mixture was filtered through a celite bed and the product was extracted with Et₂O. Organic layer was dried over Na₂SO₄, filtered and the solvent was removed. The resultant liquid was purified by column chromatography eluting with *n*-hexane to give **33** [141].

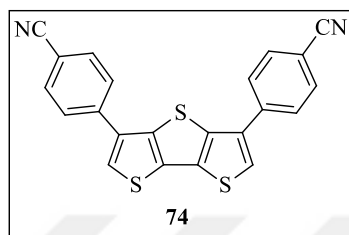
2.3.15 4,4'-(2,2'-(Thiophene-3,4-diylbis(sulfaneyl))bis(acetyl))dibenzonitrile (73)



33 (1.50 ml, 14.0 mmol) was dissolved in dry Et₂O under N₂ atmosphere and the solution was cooled to -78 °C. *t*-BuLi (8.65 mL, 14.7 mmol, 1.7 M in *n*-pentane) was added dropwise and left stirring for 45 min, after which elemental sulfur (470 mg, 14.7 mmol) was added portion wise and reaction was stirred for 45 min. Addition of *t*-BuLi and elemental sulfur was repeated and the reaction was stirred for another 45 min at -78 °C. Finally, 4-(2-bromoacetyl)benzonitrile (5.83 g, 26.0 mmol) was introduced to the mixture portion wise. Stirring was continued over night at room temperature. The solution was extracted with water (3 x 200 mL), washed with NaHCO₃ (10 %) solution (2 x 200 mL). Organic layer was dried over Na₂SO₄, filtered and the solvent was evaporated under reduced pressure. The product was recrystallized from DCM/MeOH to obtain the target compound **73** as a white solid (3.70 g, 68 %), mp 175 °C. FT IR

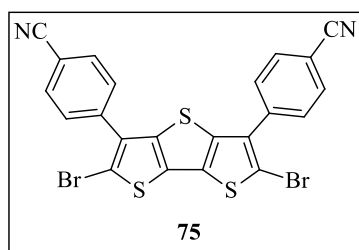
(ATR): $\nu = 2360, 2229, 1695, 1401, 1198, 991, 817, 565 \text{ cm}^{-1}$ (Figure A.25). $^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$): δ 8.11 (d, $J = 8.5 \text{ Hz}$, 4H) 8.05 (d, $J = 8.5 \text{ Hz}$, 4H), 7.48 (s, 2H), 4.55 (s, 4H) (Figure A.26). $^{13}\text{C-NMR}$ (126 MHz, $\text{DMSO-}d_6$): δ 193.9, 138.9, 133.2, 131.1, 129.6, 126.1, 118.6, 115.8, 41.4 (Figure A.27). MS m/z 434.8 (M^+) (Figure A.28).

2.3.16 4,4'-(Dithieno[3,2-b:2',3'-d]thiophene-3,5-diyl)dibenzonitrile (74)



PPA (6.22 g) was weighed into two necked round bottom flask 4.00 mL chlorobenzene was added and the mixture was stirred under reflux condition at 100°C for 10 minutes. **73** (200 mg, 460 μmol) was dissolved in minimum amount of chlorobenzene and introduced into the mixture and refluxed for 1.5 h at 130°C . After 1.5 h the liquid part was decanted. The remaining viscose part was washed with chlorobenzene couple of times, organic parts were combined and chlorobenzene was evaporated under reduced pressure giving rise to a yellow solid which was dissolved in DCM and washed with NaHCO_3 (10 %) (100 mL) and water (100 mL). Organic layer was dried over Na_2SO_4 , filtered and solvent was evaporated under reduced pressure. The crude product was purified by recrystallization from DCM/MeOH to give the title compound **74** (130 mg, 65 %) as a white solid, $\text{mp} > 250^\circ\text{C}$. FT IR (ATR): $\nu = 3085, 2223, 1600, 1523, 1349, 1309, 1178, 941, 834, 764, 550 \text{ cm}^{-1}$ (Figure A.29). $^1\text{H-NMR}$ (600 MHz, CDCl_3): δ 7.84 (d, $J = 7.8 \text{ Hz}$, 4H), 7.77 (d, $J = 8.4 \text{ Hz}$, 4H), 7.60 (s, 2H) (ppm) (Figure A.30). $^{13}\text{C-NMR}$ (150 MHz, CDCl_3): δ 139.3, 138.5, 133.9, 132.9, 131.9, 130.8, 127.0, 124.0, 118.6, 111.5 (Figure A.31). MS m/z 399.7 ($\text{M}^+ + 1$) (Figure A.32).

2.3.17 2,5-Dibromo4,4'-(dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (75)

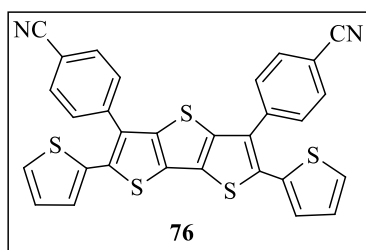


To a stirred solution of **74** (200 mg, 500 μmol) in CHCl_3 (35 mL) at 50 $^\circ\text{C}$ was added excess Br_2 (77 μL , 1.51 mmol) in dark and the reaction mixture was stirred at 50 $^\circ\text{C}$ for 3 h. The reaction mixture was poured into a saturated solution of $\text{Na}_2\text{S}_2\text{O}_3$ (150 mL) to remove all residual bromine. The mixture was filtered giving the crude product **75** (250 mg, 89 %) was obtained as a cream colored powder, mp > 250 $^\circ\text{C}$. FT IR (ATR): $\nu = 2227, 1604, 1527, 1334, 1112, 1014, 843, 753, 597, 549 \text{ cm}^{-1}$ (Figure A.33). $^1\text{H-NMR}$ (600 MHz, $\text{DMSO-}d_6$): δ 8.04 (d, $J = 6.6 \text{ Hz}$, 4H), 7.86 (d, $J = 6.6 \text{ Hz}$, 4H) (ppm) (Figure A.34). MS m/z 556.4 (M^+) (Figure A.35).

General procedure for the synthesis of **76**, **77**, **78** via Stille coupling

To a solution of **75** (200 mg, 360 μmol) in 50 mL anhydrous THF, tributylstannane derivative (1.44 mmol) and tetra-*n*-butyl ammonium bromide (460 mg, 1.44 mmol) were added. After purging the solution with N_2 for 30 min, $\text{PdCl}_2(\text{PPh}_3)_2$ (51.0 mg, 72 μmol) was added at RT. The mixture was refluxed for 72 h. Solvent was evaporated under vacuum. The residue was purified by column chromatography.

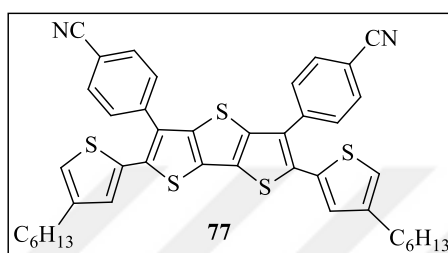
2.3.18 4,4'-(2,6-Di(thiophen-2-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (76)



The crude product was purified by column chromatography over silica gel eluting with *n*-hexane/DCM (1:3) which gave a yellow solid (**76**) (152 mg, 76 %), mp > 200 $^\circ\text{C}$. FT IR (ATR): $\nu = 2223, 1600, 1523, 1403, 1209, 1047, 834, 764, 556 \text{ cm}^{-1}$ (Figure

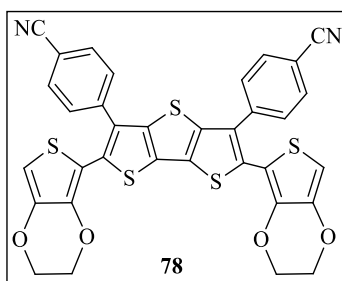
A.36). ^1H -NMR (500 MHz, CDCl_3): δ 7.67 (d, J = 8.3 Hz, 4H), 7.57 (d, J = 8.3 Hz, 4H), 7.27 (d, J = 5.0 Hz, 2H), 7.02 (d, J = 3.0 Hz, 2H), 6.98–6.97 (m, 2H) (Figure A.37). ^{13}C (126 MHz, CDCl_3): δ 142.0, 139.0, 134.9, 134.0, 132.7, 130.0, 129.9, 129.0, 127.7, 127.6, 127.2, 118.5, 112.0 (Figure A.38). MS m/z 561.3 (M^+) (Figure A.39).

2.3.19 4,4'-(2,6-Bis(4-hexylthiophen-2-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (77)



The crude product was purified by column chromatography over silica gel, eluting with *n*-hexane/DCM (1:3) which provided a yellow solid (**77**) (150 mg, 52 %), mp 136 °C. FT IR (ATR): ν = 2924, 2854, 2229, 1605, 1358, 1177, 1026, 836, 744, 536 cm^{-1} (Figure A.40). ^1H -NMR (500 MHz, CDCl_3): δ 7.66 (d, J = 8.5 Hz, 4H), 7.58 (d, J = 8.5 Hz, 4H), 6.84 (d, J = 1.0 Hz, 2H), 6.83 (d, J = 1.5 Hz, 2H), 2.51 (t, 4H), 1.53 (p, 4H), 1.29–1.27 (m, 12H), 0.87 (t, 6H) (Figure A.41); ^{13}C (600 MHz, CDCl_3): δ 144.0, 141.9, 139.1, 134.5, 134.4, 132.7, 129.9, 129.7, 128.8, 121.9, 118.5, 112.0, 111.9, 31.6, 30.2, 28.9, 22.6, 14.1 (Figure A.42). MS m/z 730.5 (M^+) (Figure A.43).

2.3.20 4,4'-(2,6-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (78)

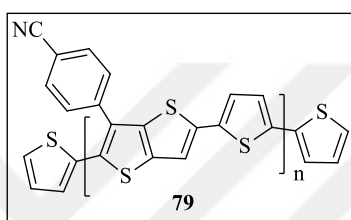


The crude product was purified by column chromatography over silica gel, eluting with *n*-hexane/DCM (1:3) which furnished an orange solid (**78**) (150 mg, 51 %), mp > 200 °C. FT IR (ATR): ν = 2290, 2220, 1589, 1478, 1430, 1358, 1158, 1069, 884,

834, 666, 549 cm^{-1} (Figure A.44). $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.66 (d, J = 8.5 Hz, 4H), 7.58 (d, J = 8.5 Hz, 4H), 6.33 (s, 2H), 4.12–4.02 (m, 8H) (Figure A.45). ^{13}C (600 MHz, CDCl_3): δ 144.1, 141.6, 141.2, 139.8, 139.1, 132.7, 132.5, 131.2, 130.3, 129.9, 129.5, 129.3, 118.7, 111.6, 100.8, 64.8, 64.4 (Figure A.46). MS m/z 678.9 (M^+) (Figure A.47).

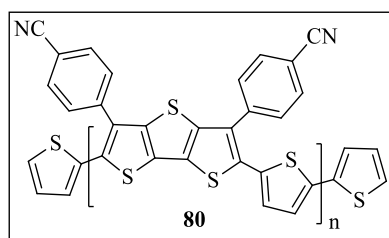
2.4 Syntheses of Chemical Polymers

2.4.1 Poly(4-(5-methyl-2-(5-methylthiophen-2-yl)thieno[3,2-*b*]thiophen-3-yl)benzonitrile) (79)



68 (150 mg, 380 μmol), **61** (511 mg, 1.52 mmol) and K_2CO_3 (4.00 mL, 2 M) were dissolved in 50 mL anhydrous THF in a schlenk tube and degassed under N_2 for 30 min. Then, $\text{Pd}[(\text{C}_6\text{H}_5)_3\text{P}]_4$ (88.0 mg, 76.0 μmol) was added at RT and the mixture was stirred at 72 $^\circ\text{C}$ for 72 h. A solution of 2-bromothiophene (248 mg, 1.52 mmol) in 1.00 mL THF was added to the reaction and degassed with N_2 , and mixture was left to reflux for 24 h. Finally, a solution of **60** (319 mg, 1.52 mmol) in 1.00 mL THF was added, degassed with N_2 , and refluxed for 24 h. Reaction was concentrated under reduced pressure and the polymer was precipitated out from cold MeOH and subjected to Soxhlet extraction for 48 h, using MeOH and *n*-hexane as solvents.

2.4.2 Poly(4,4'-(2-methyl-6-(5-methylthiophen-2-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile) (80)



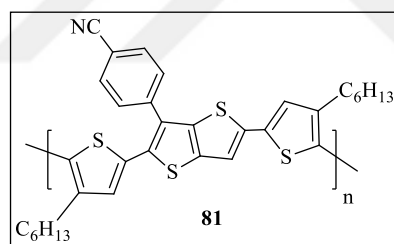
75 (150 mg, 260 μmol), **63** (430 mg, 1.04 mmol) and tetra-*n*-butylammonium bromide (335 mg, 1.04 mmol) were dissolved in 50 mL anhydrous THF in a schlenk tube and

degassed under N₂ for 30 min. After addition of PdCl₂(PPh₃)₂ (60.0 mg, 52.0 μmol), reaction mixture was refluxed for 72 h. Then, a solution of 2-bromothiophene (170 mg, 1.04 mmol) in 1.00 ml THF was added to the reaction and degassed with N₂, and mixture was left to reflux for 24 h. Finally, a solution of **62** (390 mg, 1.04 mmol) in 1.00 mL THF was added, degassed with N₂, and refluxed for 24 h. Reaction was concentrated under reduced pressure and the polymer was precipitated out from cold MeOH and subjected to Soxhlet extraction for 48 h, using MeOH and *n*-hexane as solvents.

General Procedure for Oxidative Chemical polymerization

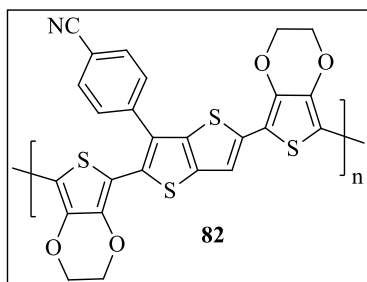
FeCl₃ (120 mg, 710 μmol) was dissolved in 20 mL anhydrous CHCl₃ and stirred for 30 min under N₂ atmosphere. Then a solution of monomer (**70**, **71**, **74**, **76**, **77**) (100 mg, 250 μmol) in anhydrous CHCl₃ (10–15 mL) was added to the suspension drop by drop and the mixture was refluxed for 48 h.

2.4.3 Poly(4-(2,5-bis(4-hexylthiophen-2-yl)thieno[3,2-*b*]thiophen-3-yl) benzonitrile) (**81**)



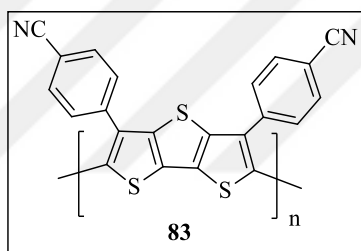
The precipitate was filtered and stirred with a solution of MeOH and HCl (1 N) for 1 h. After removal of the solvent, the residue was Soxhlet-extracted with MeOH (24 h), and *n*-hexane (24 h). The remaining black solid was dried overnight under vacuum to yield the target compound (**81**), (90 mg).

2.4.4 Poly(4-(2,5-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)thieno[3,2-*b*]thiophen-3-yl)benzonitrile) (82)



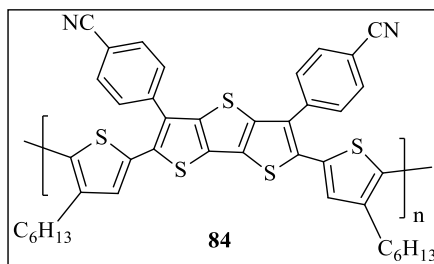
The precipitate was filtered and stirred with a solution of MeOH and HCl (1 N) for 1 h. After removal of the solvent, the residue was Soxhlet-extracted with MeOH (24 h), and *n*-hexane (24 h). The remaining black solid was dried overnight under vacuum to yield the target compound (**82**), (98 mg).

2.4.5 Poly(4,4'-(dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile) (83)



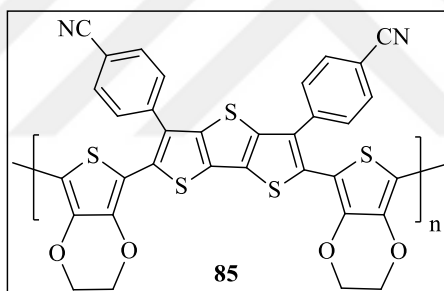
The precipitate was filtered and stirred with a solution of MeOH and HCl (1 N) for 1 h. After removal of the solvent, the residue was Soxhlet-extracted with MeOH (24 h), and *n*-hexane (24 h). The remaining black solid was dried overnight under vacuum to yield the target compound (**83**), (94 mg).

2.4.6 Poly(4,4'-(2,6-bis(4-hexylthiophen-2-yl)dithieno[3,2-b:2',3'-d]thiophene-3,5-diyl)dibenzonitrile) (84)



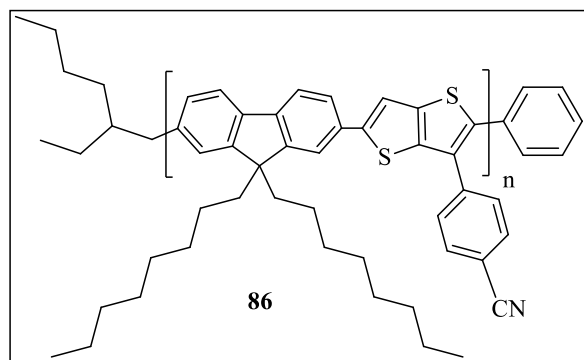
The precipitate was filtered and stirred with a solution of MeOH and HCl (1 N) for 1 h. After removal of the solvent, the residue was Soxhlet-extracted with MeOH (24 h), and *n*-hexane (24 h). The remaining red solid was dried overnight under vacuum to yield the target compound (**84**), (91 mg).

2.4.7 Poly(4,4'-(2,6-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)dithieno[3,2-b:2':3'-d]thiophene-3,5-diyl)dibenzonitrile) (85)



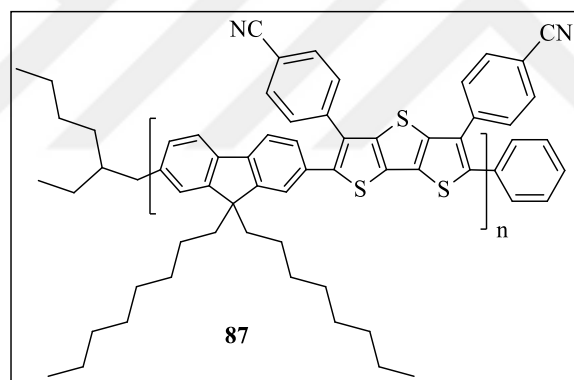
The precipitate was filtered and stirred with a solution of MeOH and HCl (1 N) for 1 h. After removal of the solvent, the residue was Soxhlet-extracted with MeOH (24 h), and *n*-hexane (24 h). The remaining black solid was dried overnight under vacuum to yield the target compound (**85**), (98 mg).

2.4.8 Poly(9,9-dioctylfluorene-2,7-*alt*-3-(4'-cyanophenyl)thieno[3,2-*b*]thiophene-2,5-diyl) (86)



86 was synthesized by Polymer Photonics group in Institute of Macromolecular Chemistry, The Czech Academy of Sciences, and stated in [142].

2.4.9 Poly(9,9-dioctylfluorene-2,7-diyl-*alt*-3,5-bis(4'-cyanophenyl)dithieno[3,2-*b*:2':3'-*d*]thiophene-2,5-diyl) (87)



87 was synthesized by Polymer Photonics group in Institute of Macromolecular Chemistry, The Czech Academy of Sciences, and stated in [142].

2.5 Electrochemistry

There are two methods for calculation of E_g . First method is the electrochemistry, in this method the potentials for electron removal from the HOMO and electron injection into the LUMO are calculated as indicated in Equation 2.1. The energy difference between two electron transfer gives the energy gap. The electrochemical method neglects intermolecular interactions [143,144].

$$E_g \sim (E_{ox} - E_{red}) + (S^{++} S^-) \left\{ 1 - \frac{[1 - (1/\epsilon_2)]}{[1 - (1/\epsilon_1)]} \right\} \quad (2.1)$$

Where,

E_{ox} and E_{red} are the onsets of the polymer oxidation and reduction, respectively.

S^+ is the difference in solvation energy of positive ion and neutral molecule, S^- is the difference in solvation energy of negative ion and neutral molecule.

ϵ_1 is the dielectric constant of the solution and ϵ_2 is the dielectric constant of the solid.

The HOMO and LUMO energy levels of the polymers were calculated from their onset oxidation (*p*-doping) potential and onset reduction (*n*-doping) potential, respectively.

If θ_{ox} and θ_{red} shows the onset oxidation and reduction potentials, respectively, the HOMO and LUMO energy levels of the polymers are calculated from Equation 2.2.

$$\text{HOMO} = -(\theta_{ox} + C)(\text{eV}); \quad \text{LUMO} = -(\theta_{red} + C)(\text{eV}) \quad (2.2)$$

Where,

The unit of the potential is V versus reference electrode (RE).

C is the constant related to the reference electrode used.

If the RE is SCE, ferrocene/ferrocium (Fc/Fc^+), Ag/Ag^+ , then C is 4.4, 4.8, 4.71, respectively. If silver wire is applied as the reference electrode, the calibration of electrode potential should be performed with Fc/Fc^+ reference electrode [75].

Second method needs the electromagnetic spectrum of the neutral conjugated polymer. In this method, E_g is calculated from the long wavelength absorption edge of their absorption spectra. If the absorption edge is λ_{edge} (nm), then $E_g = 1240 / \lambda_{\text{edge}}$ (eV). The E_g calculated from the onset absorption edge is called the optical E_g^{opt} , for differentiating from the E_g value estimated from electrochemical measurement.

The oxidation and reduction potentials of the polymers were estimated using CV measurements of the polymer films produced by spin coating or drop-casting on ITO in anhydrous, degassed solutions of ACN with NaClO_4 / LiClO_4 (0.1 M) electrolyte. Monomer-free ACN solution was bubbled for 30 min prior to use.

2.5.1 Syntheses and characterization of polymer films

Electrochemical polymerization is an essential method for the production of conjugated polymer films. The electrochemical preparation of the conjugated polymers is performed by the oxidative polymerization of their corresponding monomers in an electrolyte solution.

Figure 2.1 shows a three electrode electrochemical cell set up for electrochemical polymerization. The cell is composed of an indium-tin oxide (ITO) coated glass slide working electrode, a platinum wire as a counter electrode, and a silver wire as pseudo-reference electrode in a suitable supporting electrolyte/solvent media.

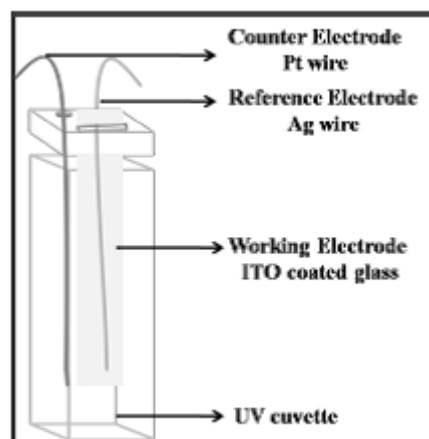


Figure 2.1 : Electrochemical cell set up [51].

All electrodes were connected to Versa Stat 3 potentiostat which applied the required potential between a working and reference electrodes. The solvent should be electrically inert and non-nucleophilic in order not to decompose at the applied potential and have high dielectric constant to let the motion of doping ions into or out of the conducting polymer. Acetonitrile, benzonitrile, tetrahydrofuran, propylene carbonate, and DCM are convenient solvents in electrochemical studies. Among them, acetonitrile is the most favored one because solvent retention within the polymer matrix is less due to its higher volatility and inertness.

Electropolymerization of monomers and cyclic voltammetry experiments of polymers were studied in a standard three-electrode cell using a silver wire as the pseudo-reference electrode, a platinum wire as the counter electrode and ITO-coated glass slide, Pt or carbon glassy electrode as the working electrode. Ferrocene was used to as an internal reference for all measurements as ferrocene/ferrocenium redox couple [143]. Electropolymerization of monomers (1×10^{-3} M) was performed in anhydrous solvents (ACN/DCM, 90/10 v/v for **67**, **69**, **70**, **76**, and **78**, 80/10 v/v for **71**, 70/10 v/v for **74**, and **77**) with NaClO_4 (0.1 M) / LiClO_4 (0.1 M) as the supporting electrolyte at a scan rate of 100 mV s^{-1} under ambient conditions. The colored polymer films were

electrodeposited on the Pt disk electrode or ITO coated glass slide under the repetitive CV between the potentials of the neutral and oxidized states of the monomers.

The films of polymers synthesized through chemical methods were prepared by spin-coating or drop-casting from THF, chlorobenzene or 1-methyl-2-pyrrolidinone solutions for investigation of optical properties. Polymer concentration in the solvent was approximately 1.1 wt %. Thin films were coated on carbon glassy electrode for electrochemical measurements.

2.5.2 Spectroelectrochemistry

Spectroelectrochemistry is a crucial and regular method used to characterize electrochromic polymers by providing information about the material's band gap and interband states (polaron and bipolaron bands) which are formed upon doping process. The films were produced potentiodynamically on ITO coated glass slides. Variations in optical properties by applied potential were examined via UV-Vis spectroscopy.

In the neutral state, conjugated polymer has $\pi-\pi^*$ transition (valence band to conduction band) and the energy difference of these two levels gives E_g^{opt} . E_g^{opt} is calculated using the onset of the $\pi-\pi^*$ absorption of the polymer at the neutral state. With the applying potential, reduction in the intensity of the $\pi-\pi^*$ transitions is accompanied with formation of new absorption bands. These transitions are attributed to polaron and bipolaron charge carrier bands. Spectroelectrochemical properties of the polymer films coated on ITO-coated glass electrode were examined by a series of spectra collected while the polymer film was switched from neutral state to oxidized state by increasing the potential stepwise.

2.5.3 Colorimetry

Colorimetry is applied to describe the color of electrochromic polymers exactly because for electrochromic material to be commercialized specific and reproducible color states are required. Colorimetry measures the human eye's sensitivity to light across the visible region and gives a mathematical function to define the color.

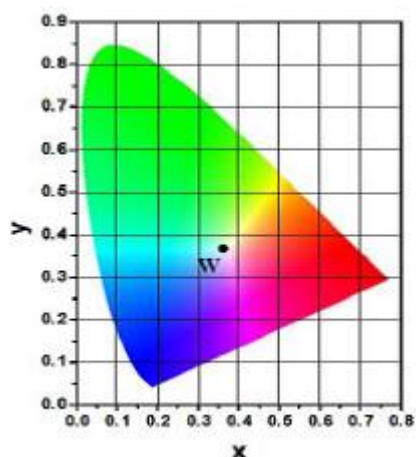


Figure 2.2 : CIE 1931 Yxy color space [145].

Three values are recorded; the hue (dominant wavelength) is the wavelength where maximum contrast occurs and depends on the illumination and surroundings, saturation (purity) is the intensity of color, and brightness (luminance) is the relative lightness of the color. Commission Internationale de l'Eclairage (CIE 1931) Yxy color space is a quantitative scale to find out colors (Figure 2.2). Colors of the polymer films on ITO surface were measured by Conica Minolta CS-100 spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Donor–Acceptor–Donor Type π -Conjugated Monomers

Donor-acceptor-donor type (D–A–D) π -conjugated monomers were synthesized in order to investigate the effects of the donor and acceptor units on the electrochemical and optoelectrochemical features of the ultimate monomers and their copolymers. Effects of electron donor strength were studied by varying donor units. D–A–D type TT and DTT monomers; Th-TT-Th (**69**), HexylTh-TT-hexylTh (**70**), E-TT-E (**71**), DTT (**74**), Th-DTT-Th (**76**), hexylTh-DTT-hexylTh (**77**), and E-DTT-E (**78**) were synthesized (Figure 3.1). Influence of the change in the electron density through monomer backbone was investigated.

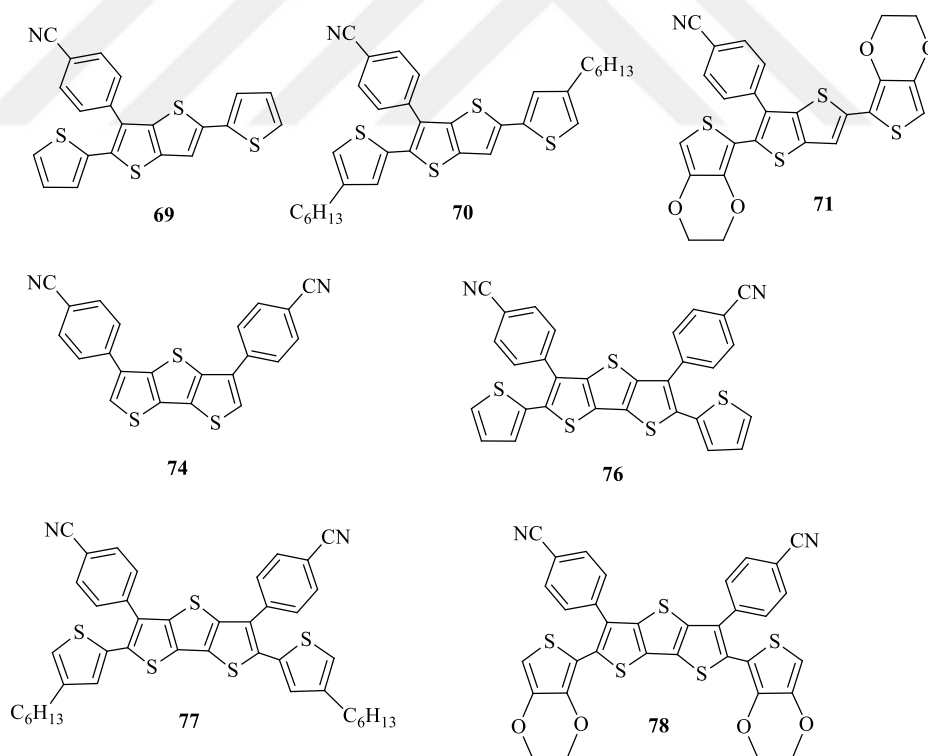


Figure 3.1 : D–A–D type TT and DTT monomers.

3.1.1 Syntheses of monomers

Application of thiophene and its derivatives as the donor units is one of the most effective ways for the improvement of π -conjugated materials with low band gaps. Electron-rich character of the donor unit increases the energy level of the HOMO causing the lower band gap value. D–A–D monomers were produced by palladium catalyzed Suzuki and Stille coupling reactions.

3.1.1.1 Syntheses of isopropoxy borolane derivatives of thiophene

Isopropoxy borolane derivatives of thiophene were synthesized by lithiation of thiophene (**88**) and 2,5-dibromothiophene (**1**) and consequent addition of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**89**) to produce 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (**60**) and 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene (**61**), respectively (Figure 3.2) [106].

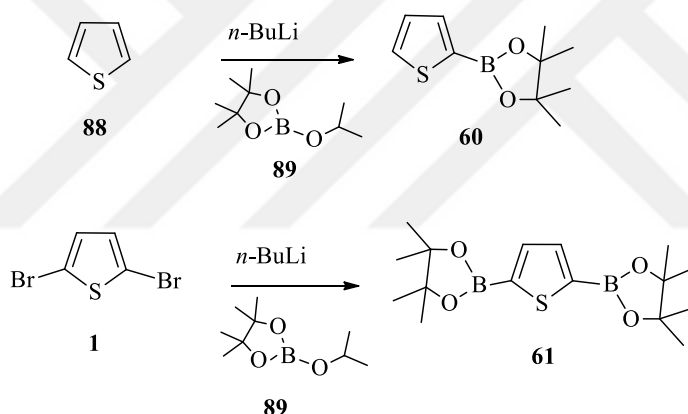


Figure 3.2 : Syntheses of isopropoxy borolane derivatives of thiophene, **60** and **61**.

3.1.1.2 Syntheses of organotin compounds

Tributyltin substituted thiophene [138], 3-hexylthiophene [138] and EDOT [140] were synthesized in high yield by lithiation of thiophene (**88**), 3-hexylthiophene (**90**) and 2,3-dihydrothieno[3,4-*b*][1,4]dioxane (**91**) with *n*-BuLi and subsequent addition of tributyltin chloride, respectively. Trimethyltin substituted thiophene was synthesized by lithiation of thiophene (**88**) with *n*-BuLi in *n*-hexane followed by the addition of trimethyltin chloride [139] (Figure 3.3).

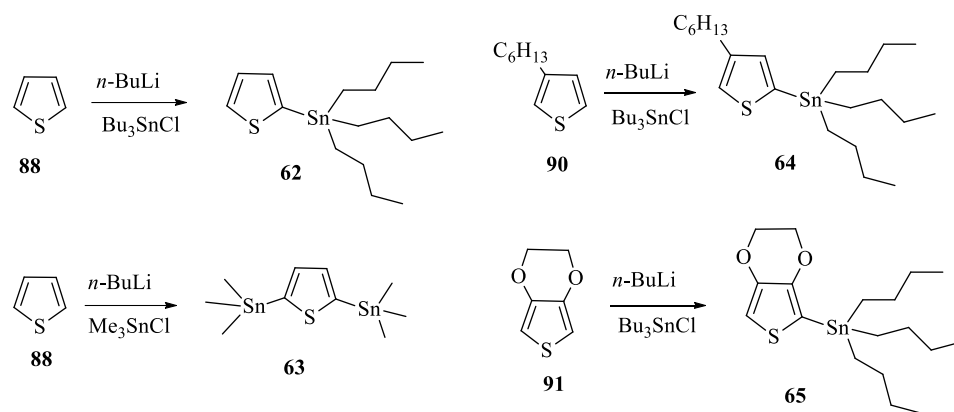


Figure 3.3 : Syntheses of organotin compounds **62–65**.

3.1.1.3 Synthesis of 4-(2,5-dibromothieno[3,2-*b*]thiophen-6-yl)benzonitrile (**68**)

Dibromo-TT (**68**) having benzonitrile functional group at C-3 was synthesized in three steps. First, 3-bromothiophene (**35**) was lithiated using *n*-BuLi at $-78\text{ }^{\circ}\text{C}$, followed by successive addition of elemental sulfur and 4-(2-bromoacetyl) benzonitrile (**92**) producing α -thioketone (**66**). Second step involved the ring closure reaction of the ketone in refluxing chlorobenzene in the presence of PPA giving rise to the corresponding TT (**67**). Last, bromination of **67** with NBS at $-10\text{ }^{\circ}\text{C}$ furnished the dibromo-TT (**68**) (Figure 3.4) [124].

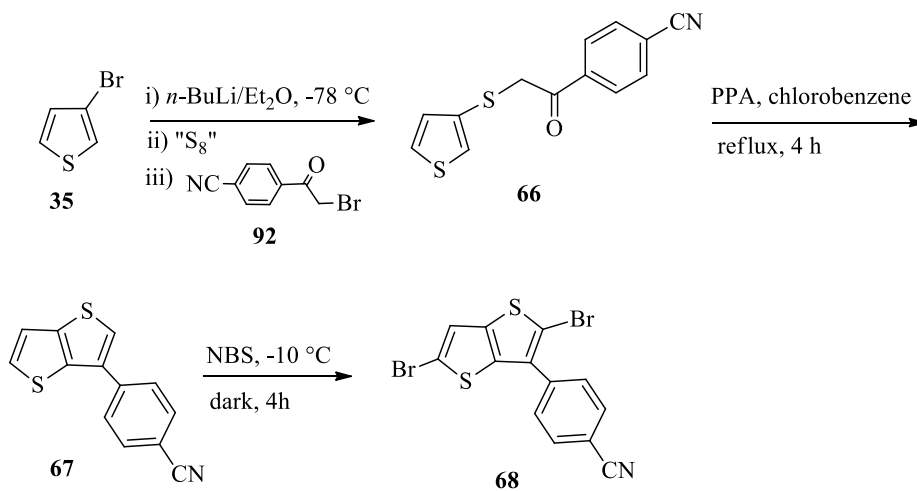


Figure 3.4 : Synthetic route to dibromo-TT (**68**).

PPA was used for cyclization reactions in this study. Cyclization mechanism of α -thioketone via PPA was illustrated in Figure 3.5. PPA yields intramolecular cyclization at different temperatures also it is a good solvent and a proton donor to facilitate

condensation reactions. Less amount of side reactions, straightforward and high yield reactions are the advantages of PPA over P_4S_{10} [146].

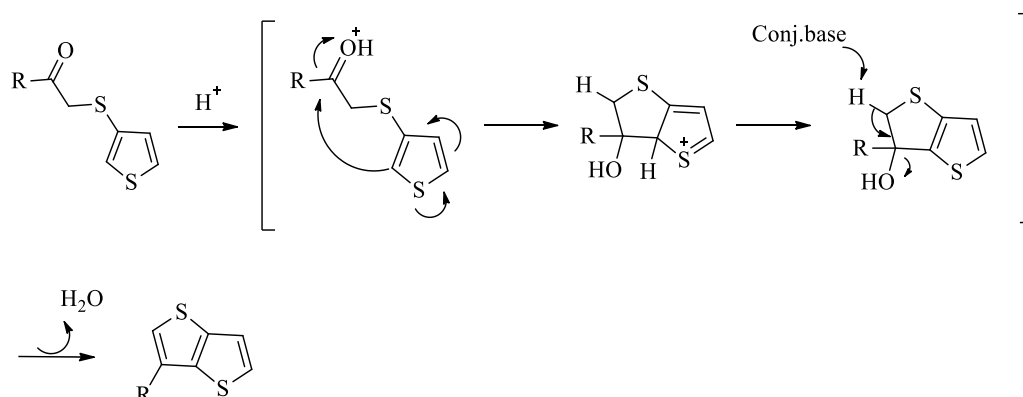


Figure 3.5 : Ring closure mechanism of α -thioketone via PPA.

3.1.1.4 4,4'-(2,6-dibromodithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (75)

Dibromo-DTT (75) having benzonitrile functional groups at C-3 and C-5 was achieved in three steps. Treatment of 3,4-dibromothiophene (33) with *t*-BuLi was followed by addition of elemental sulfur and then 4-(2-bromoacetyl)benzonitrile (92) to obtain 1,8-diketone (73) [147]. Ring closure reaction of the diketone in refluxing chlorobenzene in the presence of PPA produced the DTT (74). Electron-withdrawing substituents decrease the reactivity of the DTT moiety and bromination proceeds at 50 °C with excess bromine to afford dibromo-DTT (75) in 89 % yield (Figure 3.6) [148].

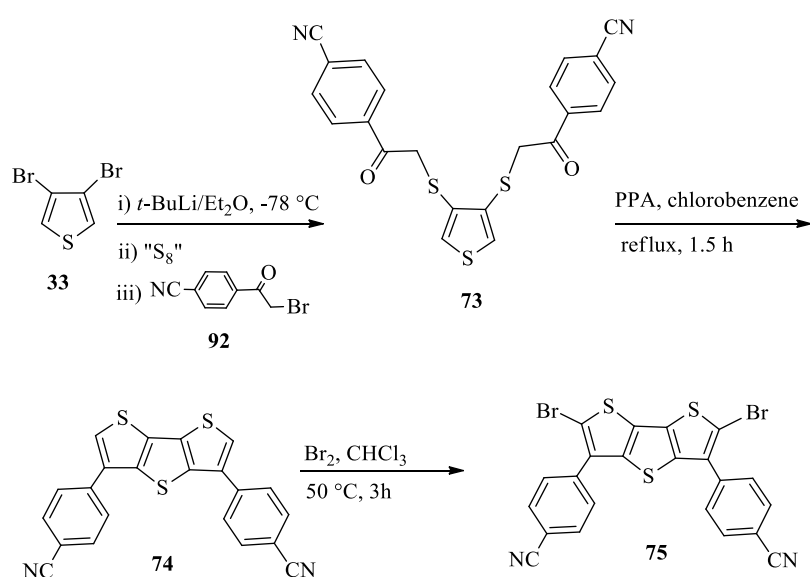


Figure 3.6 : Synthetic route to dibromo-DTT (75).

3.1.1.5 Syntheses of donor-acceptor-donor type TT and DTT derivatives

Palladium catalyzed Suzuki [64] and Stille [63] cross coupling reactions were used to connect the donor groups to the TT and DTT units. Th-TT-Th (**69**) was afforded by Suzuki cross coupling reaction of the dibromo-TT (**68**) with 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (**60**) using $\text{Pd}[(\text{C}_6\text{H}_5)_3\text{P}]_4$ as a catalyst under THF / aq K_2CO_3 reflux condition for 48 h. HexylTh-TT-hexylTh (**70**) and E-TT-E (**71**) were synthesized by Stille cross coupling reaction of the dibromo-TT (**68**) with tributyl(4-hexylthiophen-2-yl)stannane (**64**) and tributyl(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)stannane (**65**), respectively using $\text{PdCl}_2(\text{PPh}_3)_2$ as a catalyst THF under reflux condition for 72 h (Figure 3.7).

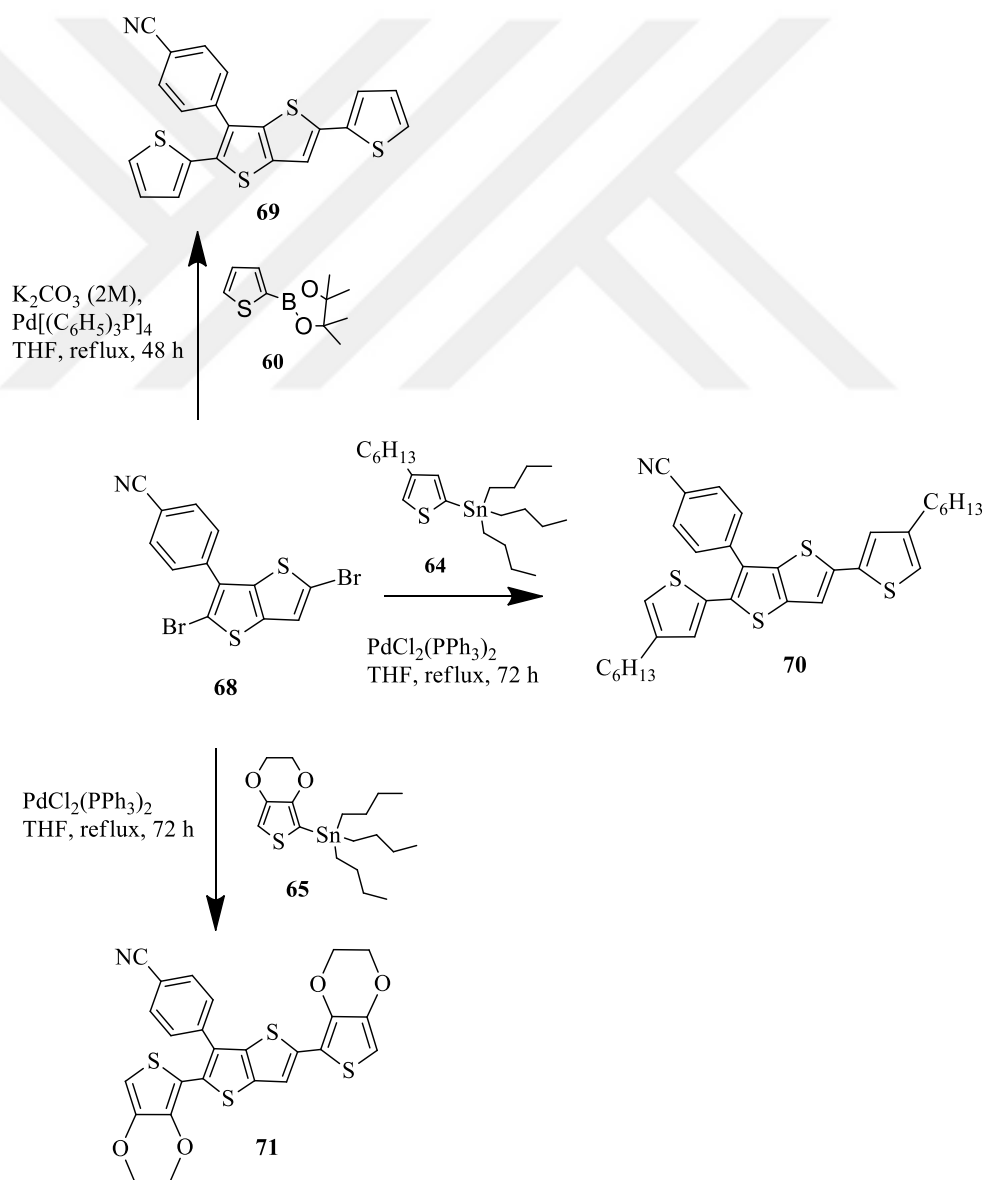


Figure 3.7 : Syntheses of TT monomers.

Th-DTT-Th (**76**), hexylTh-DTT-hexylTh (**77**), and E-DTT-E (**78**) were synthesized by Stille cross coupling reaction of the dibromo-DTT (**75**) with tributyl(thiophen-2-yl)stannane (**62**), tributyl(4-hexylthiophen-2-yl)stannane (**64**) and tributyl(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)stannane (**65**), respectively, using $\text{PdCl}_2(\text{PPh}_3)_2$ as a catalyst and tetra-*n*-butylammonium bromide as a phase transfer catalyst in a refluxing THF under nitrogen for 72 h (Figure 3.8).

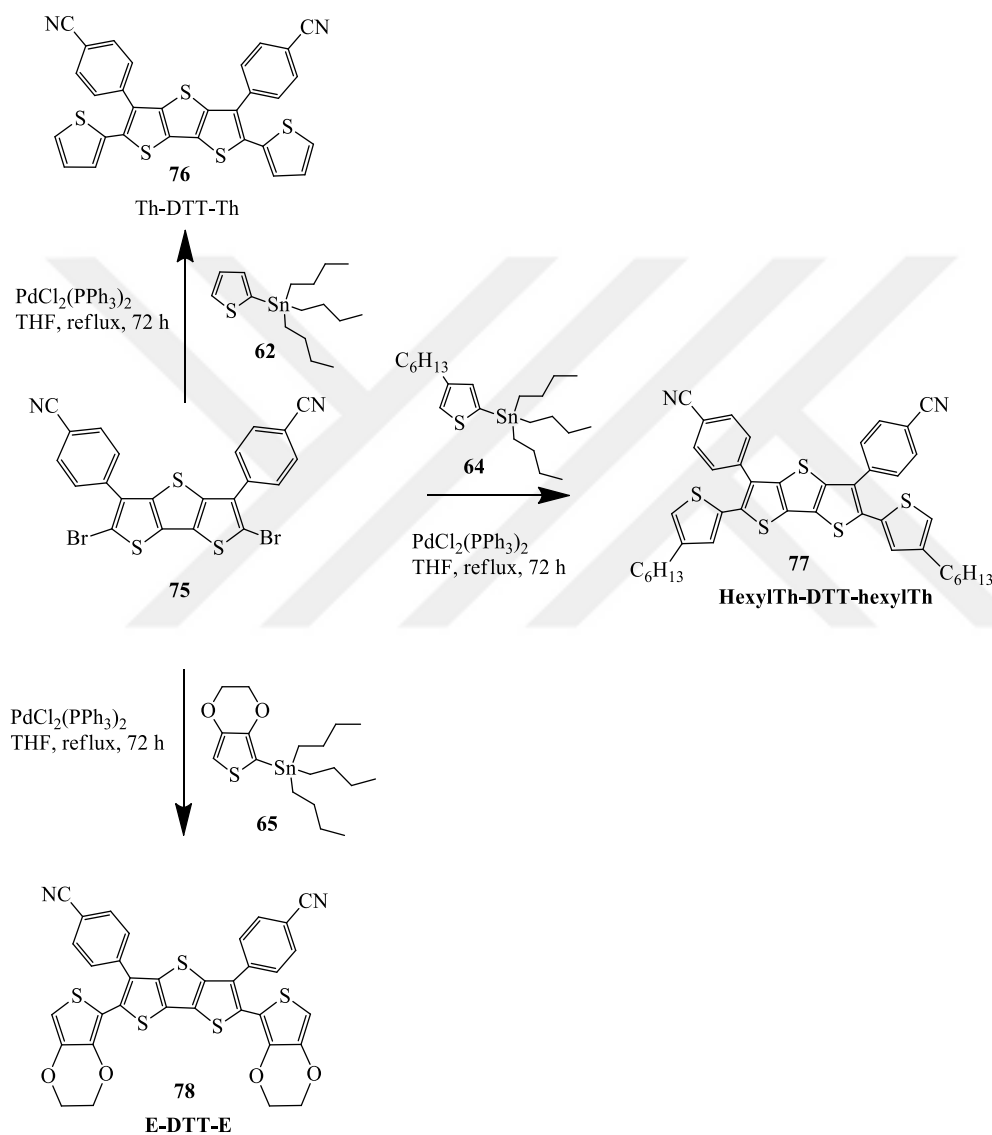


Figure 3.8 : Syntheses of DTT monomers.

3.2 Chemical Polymers

The copolymers P(Th-TT) (**79**), P(Th-DTT) (**80**), P(F-TT) (**86**) and P(F-DTT) (**87**) which were synthesized by Stille or Suzuki cross-coupling methods were illustrated in Figure 3.9.

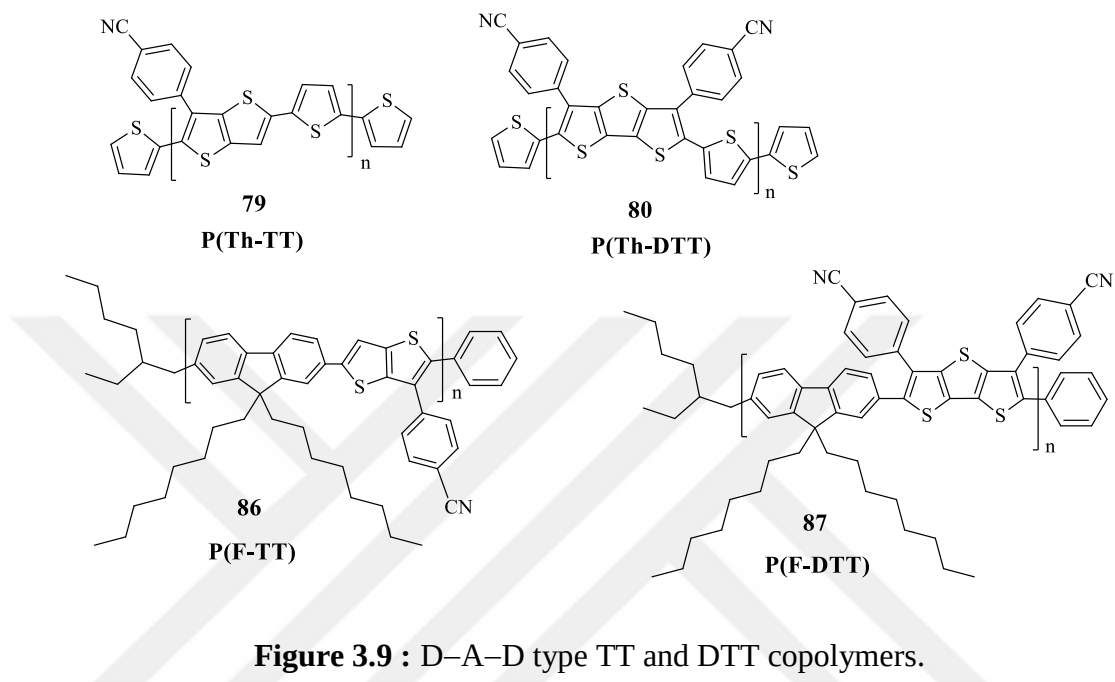


Figure 3.9 : D–A–D type TT and DTT copolymers.

The polymers P(HexylTh-TT-hexylTh) (**81**), P(E-TT-E) (**82**), P(DTT) (**83**), P(HexylTh-DTT-hexylTh) (**84**) and P(E-DTT-E) (**85**) were synthesized by oxidative chemical polymerization method by using FeCl₃ as oxidant (Figure 3.10).

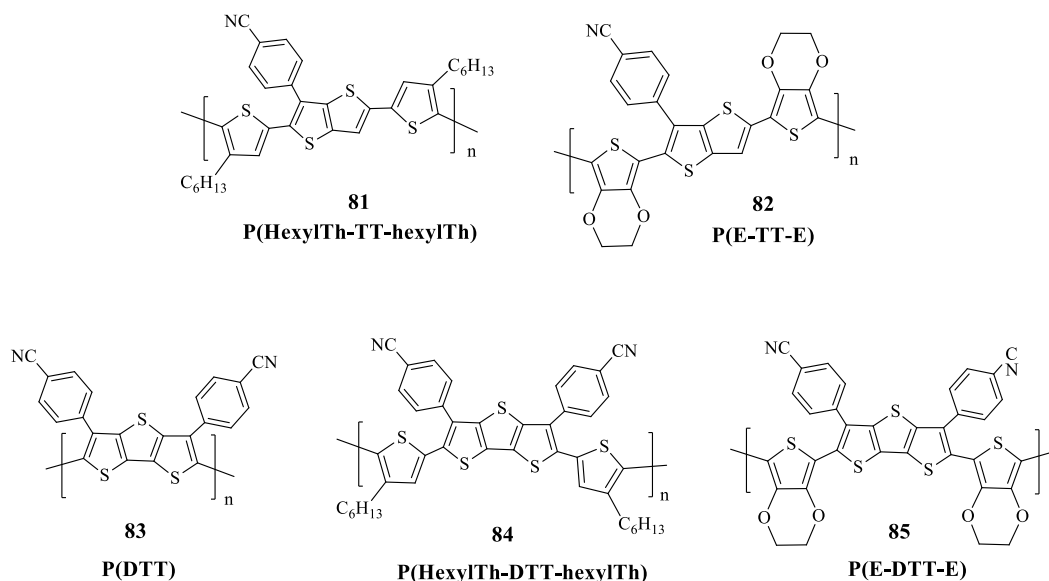


Figure 3.10 : D–A–D type TT and DTT polymers synthesized through oxidative chemical polymerization.

3.2.1 Syntheses of copolymers

Poly(4-(5-methyl-2-(5-methylthiophen-2-yl)thieno[3,2-*b*]thiophen-3-yl)benzonitrile) (**79**) was synthesized via Suzuki cross-coupling reaction. Dibromo-TT (**68**) reacted with 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene (**61**), then the reaction was terminated by addition of 2-bromothiophene (**93**) and 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (**60**) to produce the polymer **79** in a refluxing THF / K_2CO_3 (aq) system under N_2 using $\text{Pd}[(\text{C}_6\text{H}_5)_3\text{P}]_4$ as a catalyst (Figure 3.11).

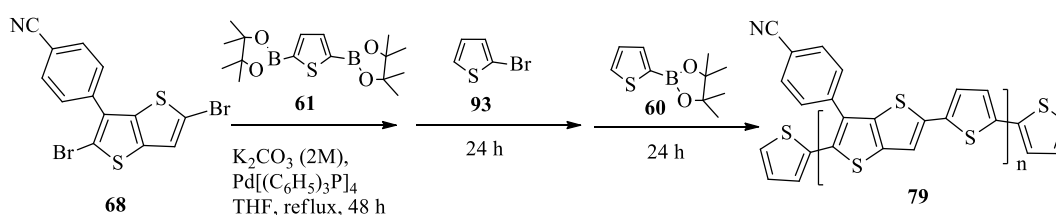


Figure 3.11 : Synthesis of **79**.

Poly(4,4'-(2-methyl-6-(5-methylthiophen-2-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile) (**80**) was synthesized via Stille cross-coupling reaction. Dibromo-DTT (**75**) reacted with 2,5-bis(tributylstannyl)thiophene (**63**) then the reaction was terminated by addition of 2-bromothiophene (**93**) and tributyl(thiophen-2-yl)stannane (**62**) to produce the polymer (**80**) in a refluxing THF under N_2 using $\text{PdCl}_2(\text{PPh}_3)_2$ as a

catalyst and tetra-*n*-butyl ammonium bromide as a phase transfer catalyst (Figure 3.12).

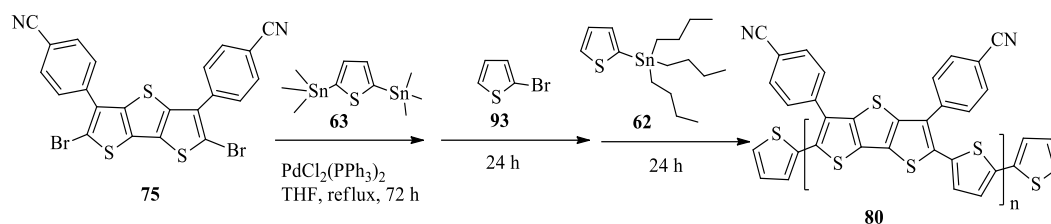


Figure 3.12 : Synthesis of 80.

Poly(9,9-dioctylfluorene-2,7-diyl-*alt*-3-(4'-cyanophenyl)thieno[3,2-*b*]thiophene-2,5-diyl) (**86**) was synthesized via Suzuki cross-coupling reaction. Dibromo-TT (**68**) reacted with 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (**94**) in high-boiling xylene / NaHCO₃ (aq) solvent system under argon atmosphere using Pd(PPh₃)₄ as a catalyst and Aliquat[®] 336 as a phase transfer catalyst for 90 min. The reaction was terminated by addition of phenylboronic acid pinacol ester (**95**) and 2-ethylhexyl bromide (**96**) to produce the polymer (**86**) (Figure 3.13). (The synthesis of **86** was performed by Polymer Photonics group in Institute of Macromolecular Chemistry, The Czech Academy of Sciences).

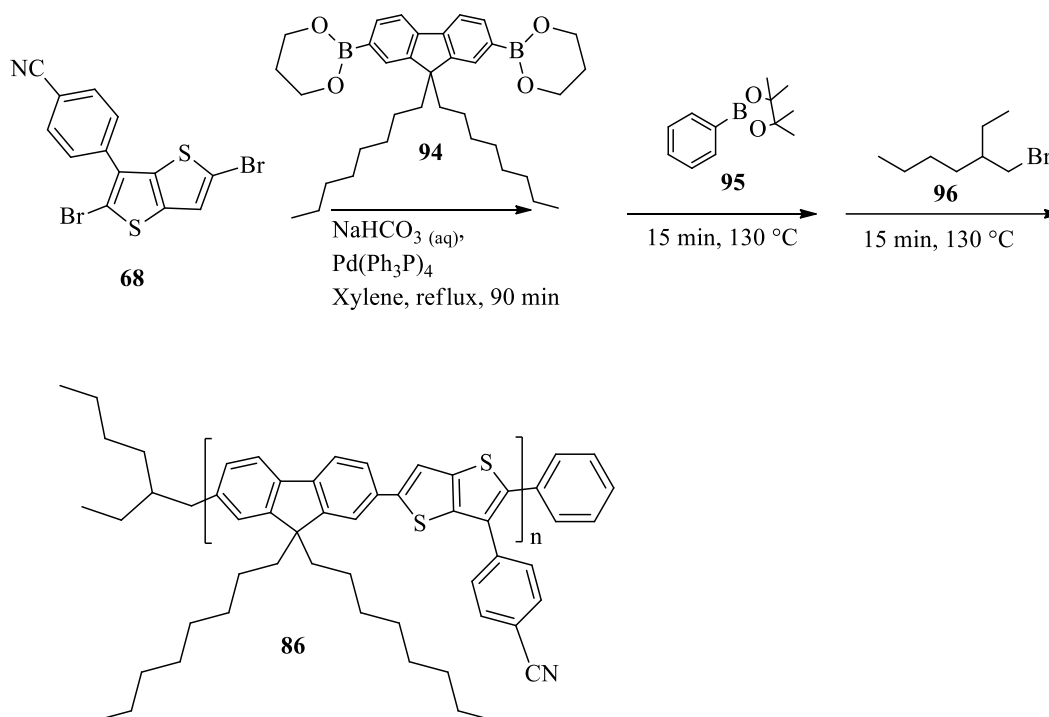


Figure 3.13 : Synthesis of 86.

Poly(9,9-dioctylfluorene-2,7-diyl-*alt*-3-(4'-cyanophenyl)thieno[3,2-*b*]thiophene-2,5-diyl) (**87**) was synthesized by Suzuki cross-coupling reaction. Dibromo-DTT (**75**) reacted with **94** in refluxing THF / Na₂CO₃ (aq) solvent system under argon atmosphere using Pd(PPh₃)₄ as a catalyst and Aliquat[®] 336 as a phase transfer catalyst for 67 h. The reaction was terminated by addition of phenylboronic acid pinacol ester (**95**) and 2-ethylhexyl bromide (**96**) to produce the polymer (**87**). (Figure 3.14). (The synthesis of **87** was performed by Polymer Photonics group in Institute of Macromolecular Chemistry, The Czech Academy of Sciences).

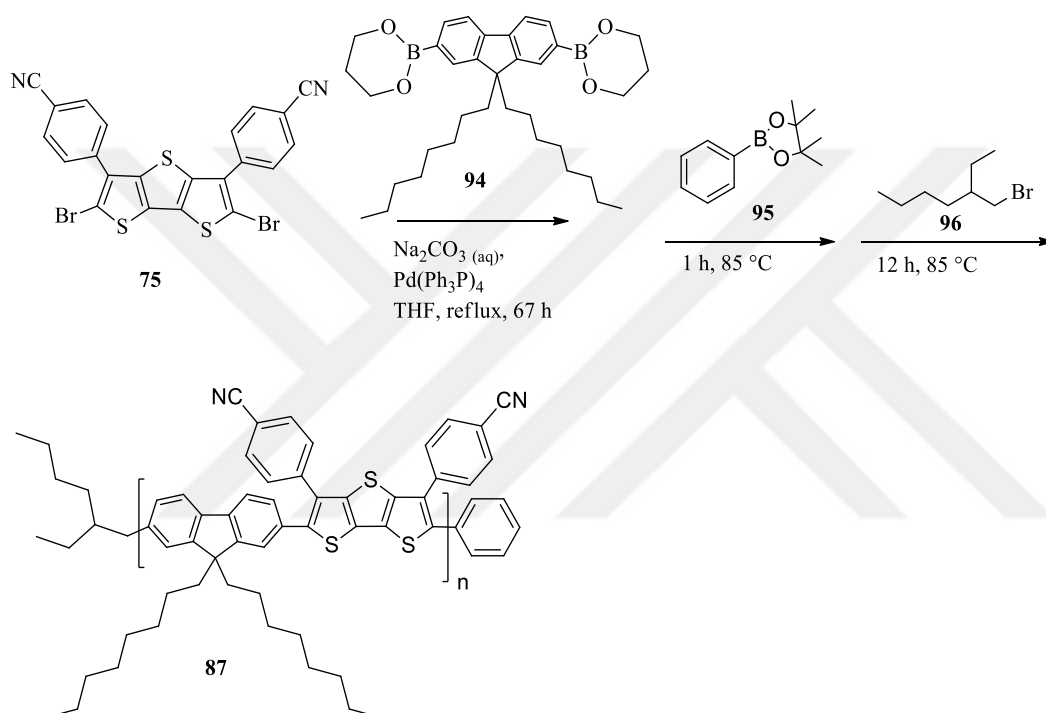


Figure 3.14 : Synthesis of 87.

3.2.2 Oxidative Chemical Polymerization of TT and DTT Monomers

Conducting polythienothiophenes (PTT) and polydithienoyhiophenes (PDTT) can also be prepared by oxidative polymerization with oxidant. Poly(4-(2,5-bis(4-hexylthiophen-2-yl)thieno[3,2-*b*]thiophen-3-yl)benzonitrile) (**81**), poly(4-(2,5-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)thieno[3,2-*b*]thiophen-3-yl)benzonitrile) (**82**) (Figures 3.15), poly(4,4'-(dithieno[3,2-*b*;2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile) (**83**), poly(4,4'-(2,6-bis(4-hexylthiophen-2-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile) (**84**), poly(4,4'-(2,6-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile) (**85**)

(Figures 3.16), were synthesized through oxidative polymerization by FeCl_3 in refluxing anhydrous CHCl_3 under nitrogen atmosphere [149].

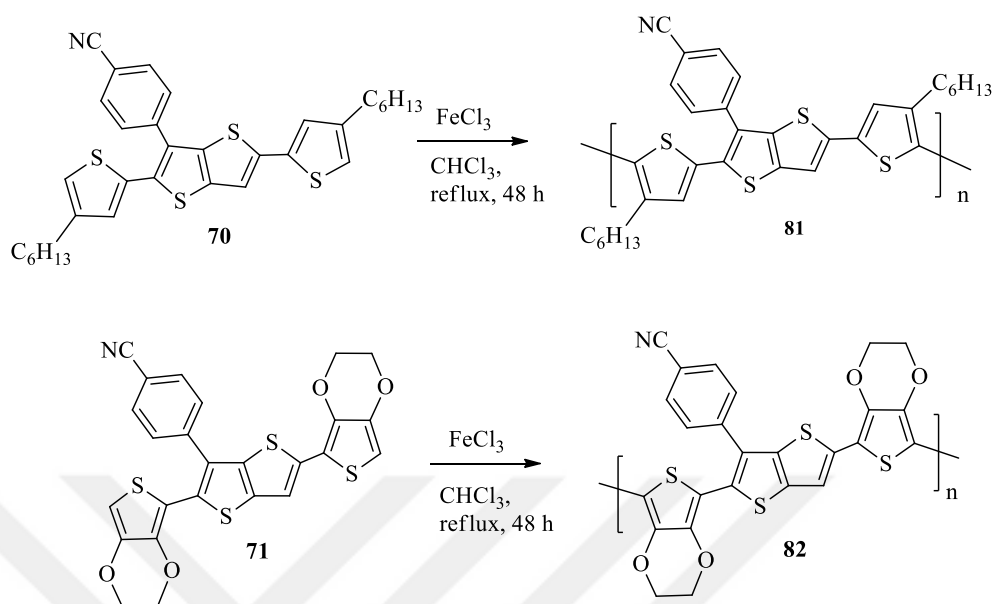


Figure 3.15 : Oxidative chemical polymerization of TTs (**70** and **71**).

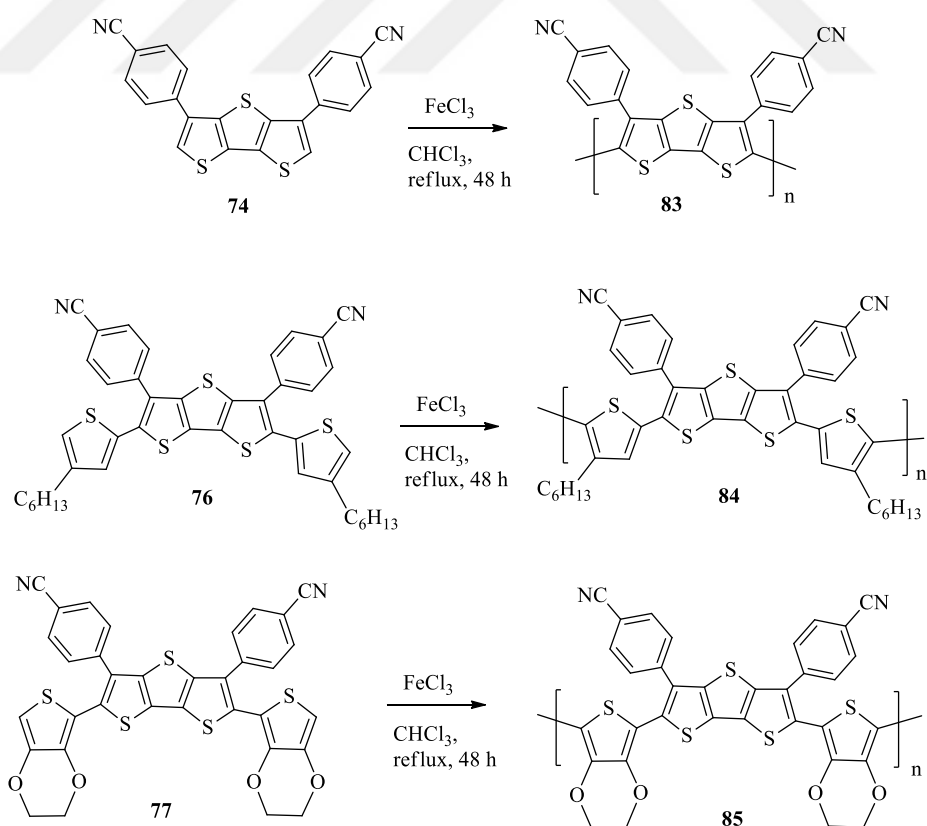


Figure 3.16 : Oxidative chemical polymerization of DTTs (**74**, **76** and **77**).

3.3 Optical Properties of TT and DTT Monomers

Absorption spectra of TT monomers were measured in DCM. Introduction of thiophene, 3-hexyl thiophene and EDOT to **67** redshifted the absorption by 59, 63 and 70 nm, respectively (Figure 3.17 a). While **67** does not have fluorescence property, **69–71** have emission maxima appearing at 499, 510 and 515 nm, respectively (Figure 3.17 b).

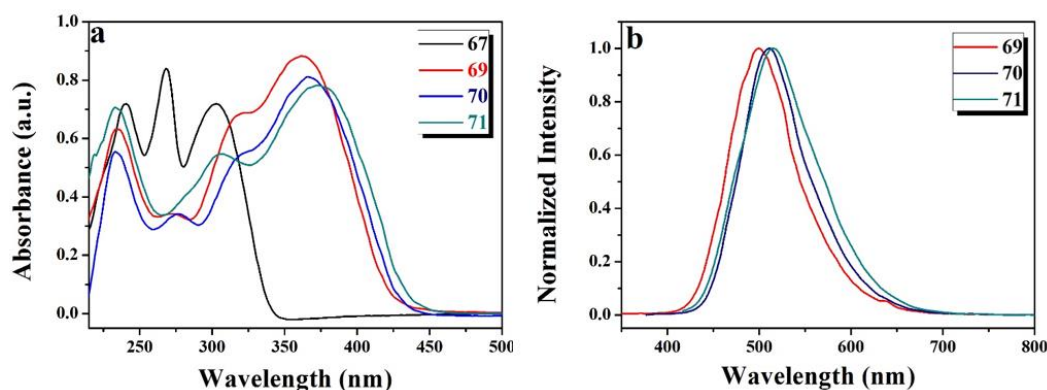


Figure 3.17 : Absorption (a) and fluorescence (b) spectra of TT monomers (**67**, **69–71**) in DCM.

Optical band gaps of the monomers were calculated from the onset of absorption bands. The optical band gap of **67** is found as 3.64 eV, introduction of thiophene (**69**), 3-hexyl thiophene (**70**) and EDOT (**71**) units diminished the band gap to 2.93, 2.88 and 2.84 eV, respectively (Table 3.1).

Table 3.1 : Optical Properties of TT monomers.

TT Monomer	$\lambda_{\max}^{\text{abs}}$ (nm)	$\lambda_{\max}^{\text{em } c}$ (nm)	$E_g^{\text{opt}d}$ (eV)
67	303 ^a / 339 ^b	-	3.64
69	362 ^a / 421 ^b	500	2.93
70	366 ^a / 429 ^b	511	2.88
71	373 ^a / 435 ^b	515	2.84

^a Absorption maxima in DCM. ^b Onset of the absorption in DCM. ^c Emission maxima in DCM.

$$^d E_g^{\text{opt}} = \frac{hc}{\lambda_{\text{onset}}}$$

Absorption spectra of DTT monomers were measured in DCM. The absorption of **74** (300 nm) was redshifted to 378, 382 and 390 nm with the introduction of thiophene, 3-hexyl thiophene and EDOT, respectively (Figure 3.18 a). The obvious change in the emission maxima was observed as well (Figure 3.18 b).

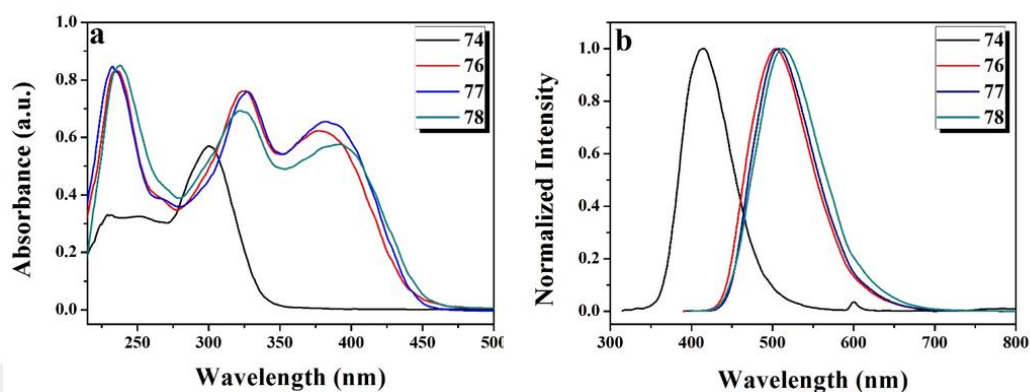


Figure 3.18 : Absorption (a) and fluorescence (b) spectra of DTT monomers (**74**, **76–78**) in DCM.

The calculated optical band gap of **74** is 3.67 eV, assembling of thiophene (**76**), 3-hexylthiophene (**77**) and EDOT (**78**) units lowered the band gap to 2.81, 2.77 and 2.75 eV, respectively (Table 3.2).

Table 3.2 : Optical Properties of DTT monomers.

DTT Monomer	$\lambda_{\max}^{\text{abs}}(\text{nm})$	$\lambda_{\max}^{\text{em } c}(\text{nm})$	$E_g^{\text{opt}d}(\text{eV})$
74	300 ^a / 337 ^b	414	3.67
76	378 ^a / 440 ^b	504	2.81
77	382 ^a / 446 ^b	506	2.77
78	390 ^a / 449 ^b	512	2.75

^a Absorption maxima in DCM. ^b Onset of the absorption in DCM. ^c Emission maxima in DCM.

$$^d E_g^{\text{opt}} = \frac{hc}{\lambda_{\text{onset}}}$$

3.4 Characterization of Conducting Polymers Synthesized Through Electrochemical Polymerization

Electrochemical properties are among the most important features of the conjugated polymers since they are related to the many applications such as batteries, electrochromic displays and modified electrodes [75]. Electrochemical polymerization

is an essential method for the production of conjugated polymer films. The electrochemical preparation of the conjugated polymers is performed by the oxidative polymerization of their corresponding monomers in an electrolyte solution.

3.4.1 TT based polymers synthesized through electrochemical polymerization

3.4.1.1 Electrochemistry

Oxidative polymerization of **69–71** (0.1 M) was realized under potentiodynamic conditions in a mixed solvent (ACN/DCM, 90/10 v/v for **69** and **71**, 80/20 v/v for **70**) using NaClO₄ (0.1 M) / LiClO₄ (0.1 M) as a supporting electrolyte, Pt as working and counter electrodes and Ag wire as a pseudo-reference electrode. The electron-withdrawing effect of benzonitrile group increased the oxidation potential of **67** (+ 1.50 V) (Figure 3.19 a). The high oxidative polymerization potential caused over oxidation resulting in the degradation of the prepared polymer film. Therefore, electropolymerization of **69** was performed in borontrifluoride/ethylene ether (BTFE) solution. In the BTFE solution, the electropolymerization potential of **69** was decreased to + 1.14 V (Figure 3.19 b) [150].

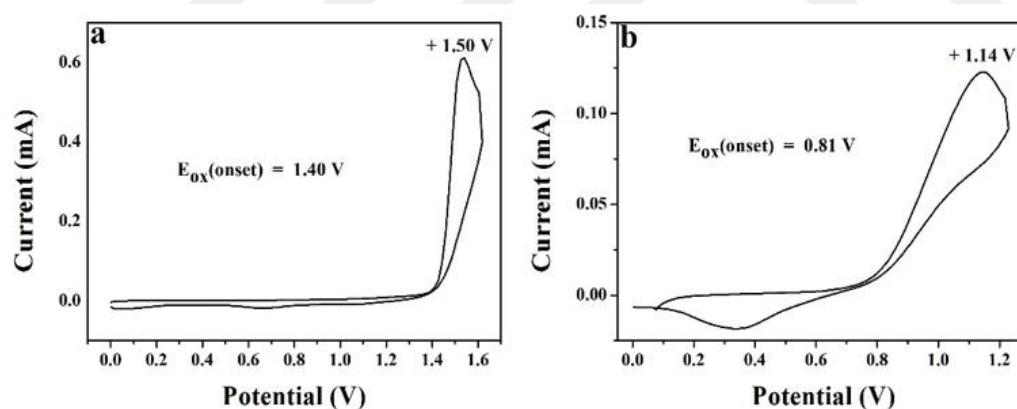


Figure 3.19 : Oxidation and reduction potentials of **69** in (a) ACN/DCM, (b) BTFE solutions.

Multiple cyclic voltammograms for the repeated scanning electropolymerization of **67**, **69–71** were shown in Figure 3.20. The onset of oxidation was detected to be at + 1.40 V in ACN/DCM solvent mixture using NaClO₄ (0.1 M) / LiClO₄ (0.1 M) as a supporting electrolyte for **67**. On the other hand, the onset of oxidation appeared at + 0.81 V in BTFE solution. However; the tough handling conditions makes BTFE difficult to work with it. Coupling of thiophene and 3-hexylthiophene units to the TT backbone made oxidation wave shift to + 1.04 V and + 0.94 V, respectively, under the

described conditions. The onset of oxidation of **71** (+ 0.89 V) is the lowest among the others because the strong electron donating EDOT group increased the HOMO level. Electron-rich character of the donor groups decreased the oxidation potential of TT monomer. Three heterocyclic groups follow the trend EDOT>3-hexylthiophene>thiophene as evidenced by their oxidation potentials.

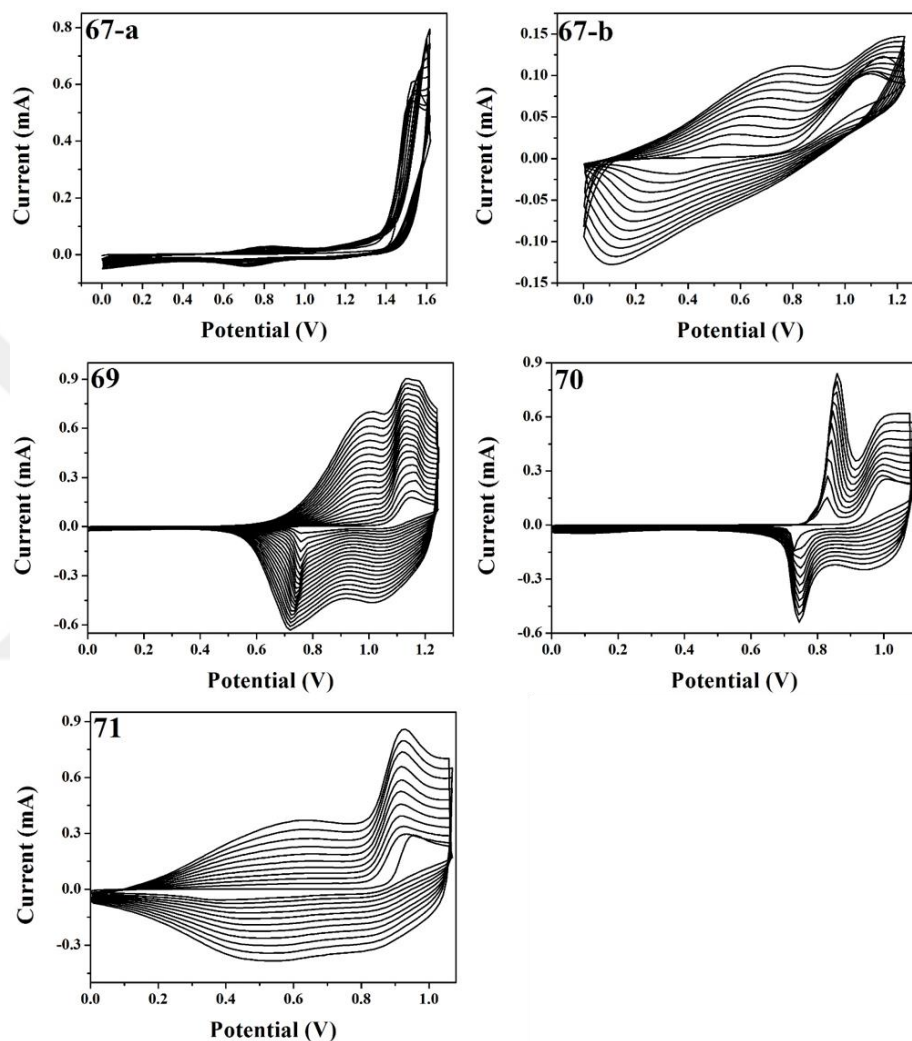


Figure 3.20 : Electropolymerization of 0.1 M TT monomers: **67-a** (ACN/DCM, 90/10, v/v), **67-b** (BTFE) **69**, **70** (ACN/DCM, 90/10, v/v) and **71** (ACN/DCM, 80/10, v/v) with NaClO₄ (0.1 M) / LiClO₄ (0.1 M) on the Pt disk electrode at 100 mV s⁻¹.

The polymer films were rinsed with ACN to get rid of the monomers and the electrolyte before their electrochemical response was tested by CV in ACN / NaClO₄ (0.1 M) / LiClO₄ (0.1 M) for both *p*- and *n*-doping processes.

Polymer films **P69–P71** showed irreversible *n*-doping in cathodic scans with onset reduction potentials of - 1.18 V, - 1.43 V and - 1.33 V, respectively (Figure 3.21). The

gradual decreasing of irreversible reduction peaks on cycle exhibits the instability of the polymers to *n*-doping process emerging from the high reactivity of the reduced types of the polymers [151].

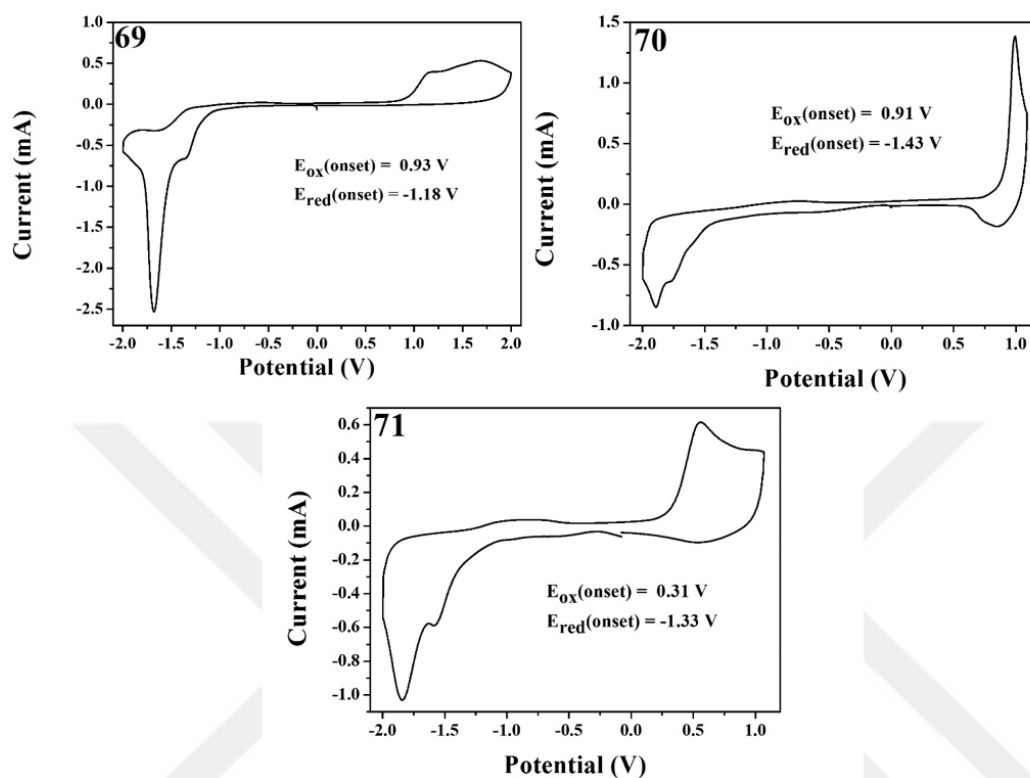


Figure 3.21 : Cyclic voltammograms of polymer films of **69–71** on the Pt disk electrode in a monomer-free ACN / LiClO₄ (0.1 M) / NaClO₄ (0.1 M) solution at 100 mV s⁻¹.

On the cathodic scans, polymer oxidations were observed at about + 0.99 V for **P69**, + 0.85 V for **P70** and + 0.62 V for **P71**. Reduction of the polymers formed a peak at + 0.72 V for **P69**, + 0.75 V for **P70** and + 0.54 V for **P71** (Figure 3.22).

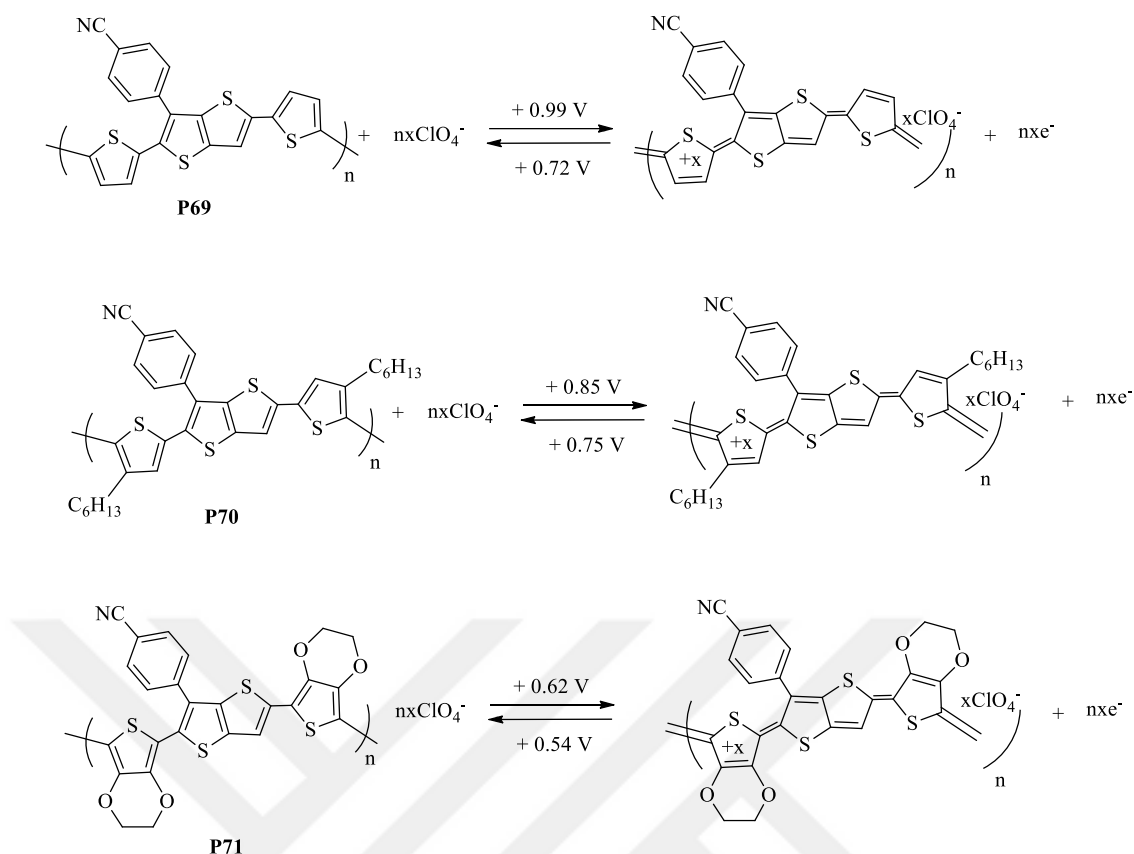


Figure 3.22 : p-Doping of P69–P71.

Cyclic voltammograms and scan rate dependences of current densities of polymer films, **P69** (Figure 3.23), **P70** (Figure 3.24) and **P71** (Figure 3.25) at different scan rates (25–500 mVs⁻¹) were investigated. A linear correlation between the peak current and scan rate indicates that the films were well adhered to the Pt electrode surface and the electrochemical processes were diffusion-controlled and reversible.

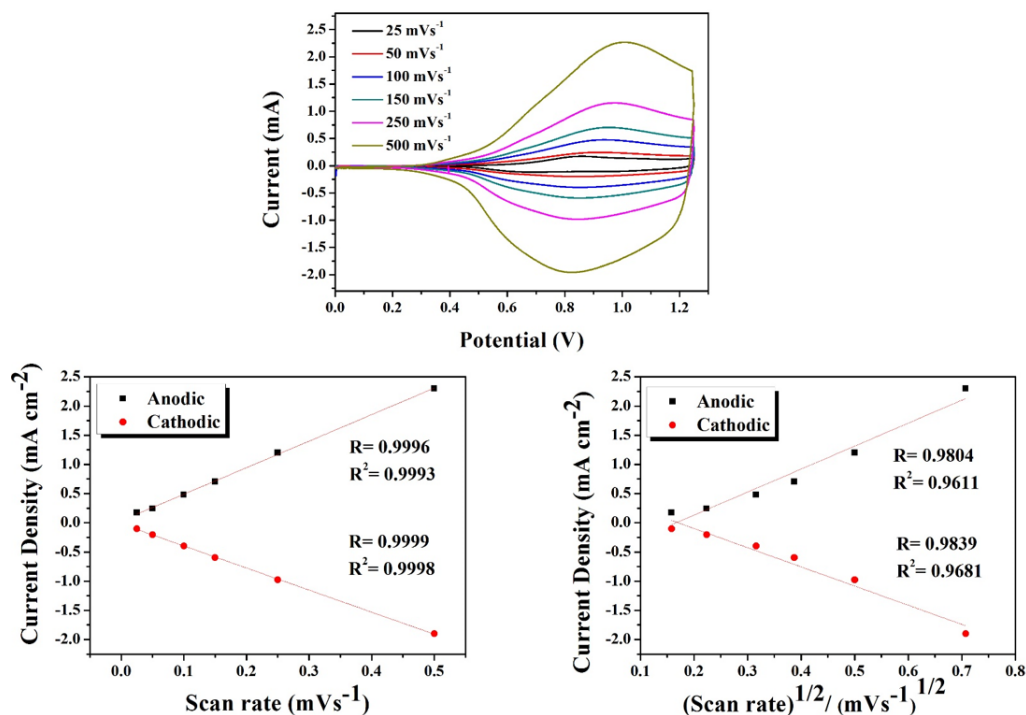


Figure 3.23 : Cyclic voltammograms of and scan rate dependences of current densities of **P69** on Pt disk electrode in a monomer-free ACN / LiClO₄ (0.1 M) / NaClO₄ (0.1 M) solution at different scan rates from 25 to 50, 100, 150, 250 and 500 mV s⁻¹.

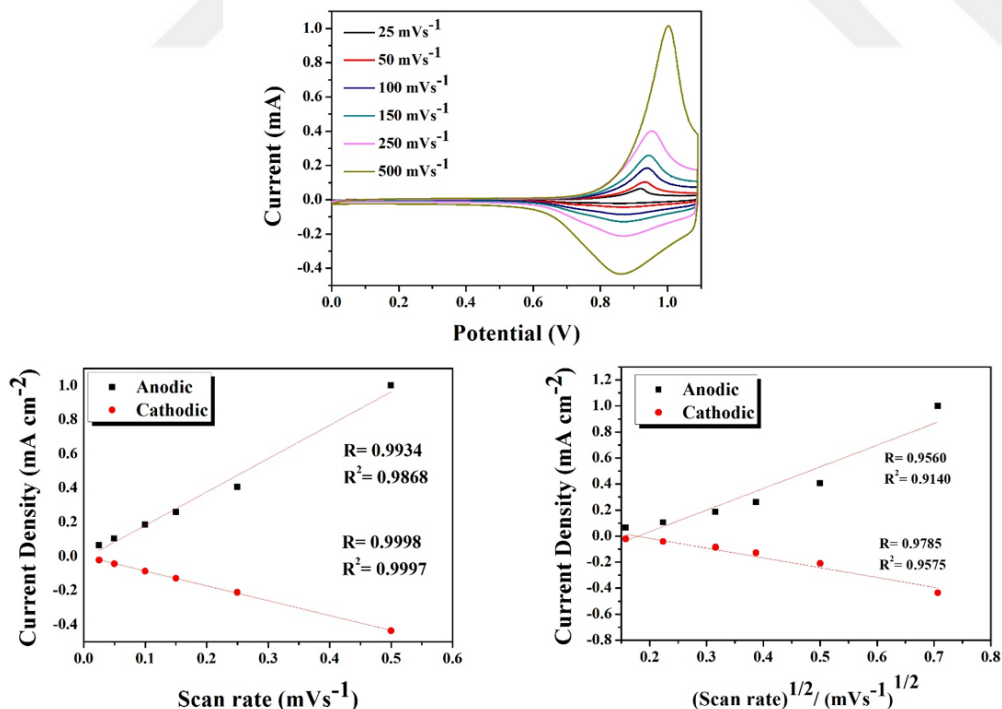


Figure 3.24 : Cyclic voltammograms of scan rate dependences of current densities of **P70** on Pt disk electrode in a monomer-free ACN / LiClO₄ (0.1 M) / NaClO₄ (0.1 M) solution at different scan rates from 25 to 50, 100, 150, 250 and 500 mV s⁻¹.

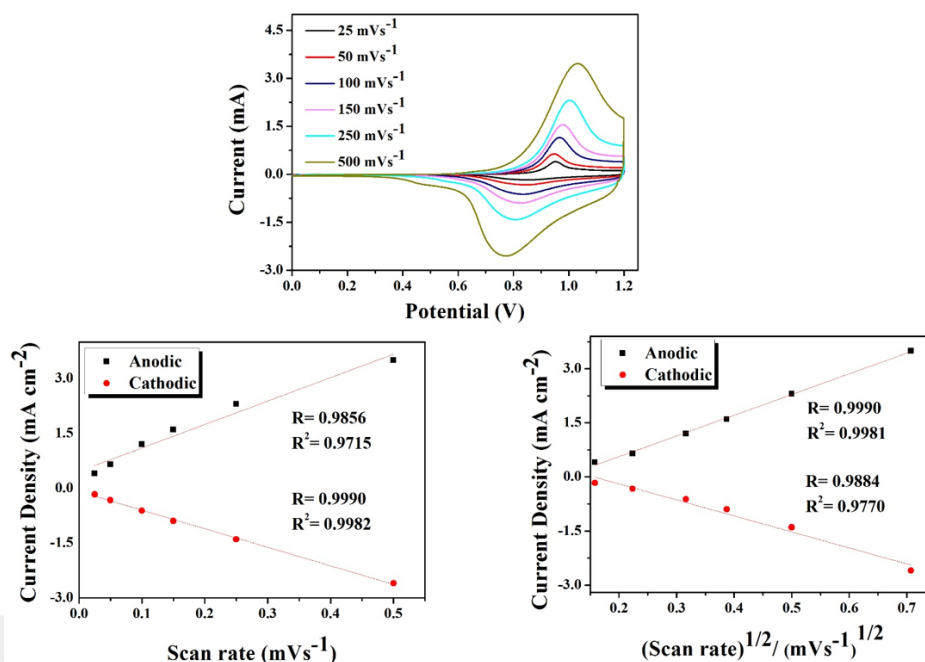


Figure 3.25 : Cyclic voltammograms and scan rate dependences of current densities of **P71** on Pt disk electrode in a monomer-free ACN / LiClO₄ (0.1 M) / NaClO₄ (0.1 M) solution at different scan rates from 25 to 50, 100, 150, 250 and 500 mV s⁻¹.

3.4.1.2 Spectroelectrochemistry

The spectroelectrochemical studies were conducted in order to investigate the optical variations of the polymer films on *p*-doping process. The films of **P69–P71** were produced potentiodynamically on ITO coated glass slides. Variations in optical properties by applied potential were examined via UV-Vis spectroscopy. Figure 3.26 shows the spectroelectrochemical features of the **P69** polymer film and the related colors of the film. The absorption peak of the neutral **P69** is located at 507 nm exhibiting red, which is related to the π - π^* absorption of the conjugated main chains. After increasing the potential from 0 V to + 1.3 V, a strong absorption peak at a wavelength longer than 1000 nm appeared with blue color, and the visible absorption peak redshifted and weakened. A peak appearing at 753 nm showed the formation of charge carriers. The optical band gap of polymer estimated from the onset of π - π^* absorption was recorded as 1.89 eV.

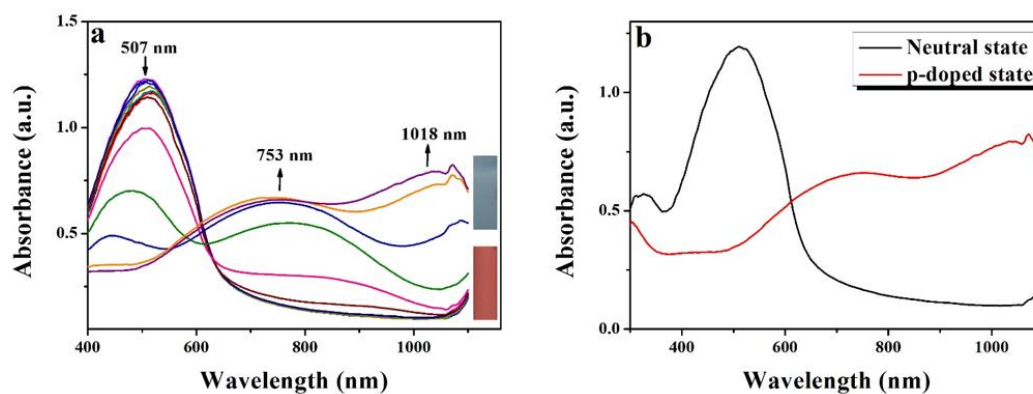


Figure 3.26 : (a) *p*-Doping spectroelectrochemistry of **P69** film on ITO coated glass slide, (b) absorption spectra of **P69** at neutral and *p*-doped state in monomer free ACN/DCM, NaClO₄/LiClO₄ (0.1 M, 0.1 M) solvent-electrolyte couple at applied potentials, Pt wires as counter, and Ag wire as pseudo reference electrode.

Spectroelectrochemistry of **P70** shows λ_{max} of 443 nm for the neutral polymers, which is orange-yellow in color (Figure 3.27). Upon oxidation (0 V to +1.2 V) there was a decrease in the π - π^* transition and the new transition bands evolved at lower energy (at 744 and 1064 nm) emitting pale blue color, accompanying to the polaronic and bipolaronic charge carriers. The alkyl groups on 3-hexylthiophene caused the steric hindrance on polymer chain resulting in less order and less conjugation. Therefore the band gap of polymer increased to 2.18 eV.

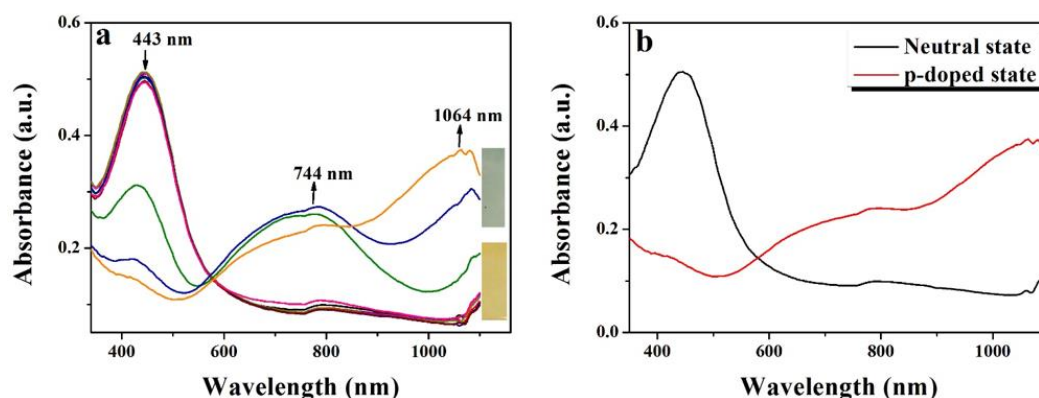


Figure 3.27 : (a) *p*-Doping spectroelectrochemistry of **P70** film on ITO coated glass slide, (b) absorption spectra of **P70** at neutral and *p*-doped state in monomer free ACN/DCM, NaClO₄/LiClO₄ (0.1 M, 0.1 M) solvent-electrolyte couple at applied potentials, Pt wires as counter, and Ag wire as pseudo reference electrode.

In neutral state **P71** absorbs at 579 nm, displaying purple color with an optical band gap of 1.79 eV. Upon incremental application of potential from 0 V to + 1.1 V, absorption of neutral polymer decreased in intensity. The intermediate potentials produced a peak at 823 nm attributed to the charge carriers (Figure 3.28). **P71** has the

lowest band gap of all the polymers due to the higher HOMO level of the EDOT unit compared to thiophene and 3-hexylthiophene. This can be explained by better intermolecular π - π^* interactions with increasing planarity. The fused thiophene ring stabilizes the quinoidal form of **P69** as does the EDOT (**P71**). The higher band gap of **P70** with respect to **P69** can be associated with the difference in stability of the quinoidal state by 3-hexylthiophene and thiophene ring.

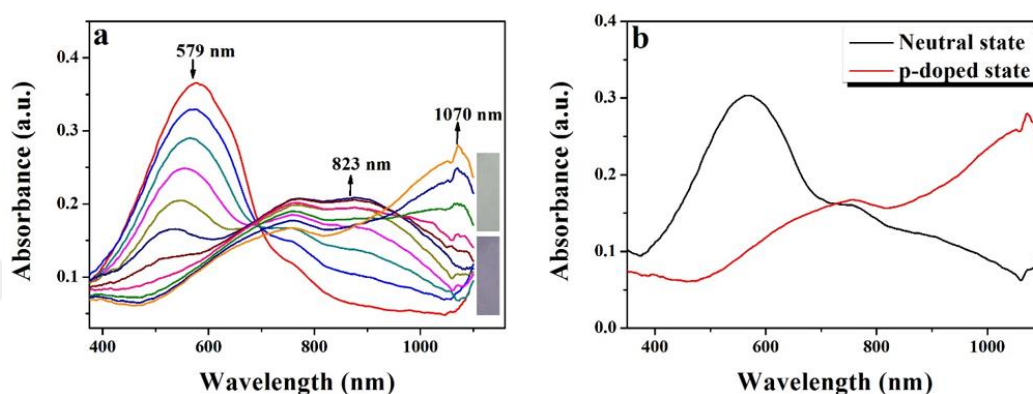


Figure 3.28 : *p*-Doping spectroelectrochemistry of **P71** film on ITO coated glass slide, (b) absorption spectra of **P71** at neutral and *p*-doped state in monomer free ACN/DCM, NaClO₄/LiClO₄ (0.1 M, 0.1 M) solvent-electrolyte couple at applied potentials, Pt wires as counter, and Ag wire as pseudo reference electrode.

3.4.1.3 Evaluation of electrochemical, optical and electronic properties of the TT polymers synthesized through electrochemical polymerization

Absorption spectra is of primary importance for the neutral conjugated polymers. Figure 3.29 shows the variations in absorption spectra of TT polymers produced through electrochemical method on ITO surface. It can be seen that the absorption spectra of conjugated polymer with EDOT side group (**P71**) is redshifted in comparison with that composed of thiophene (**P69**) and 3-hexylthiophene (**P70**).

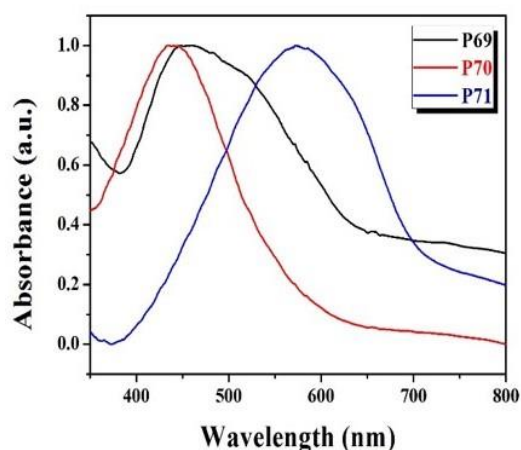


Figure 3.29 : Absorption spectra of TT polymers synthesized through electrochemical method.

The electrochemical, optical and electronic properties of TT polymers were summarized in Table 3.3. Optical band gaps of conjugated polymers were estimated from the long wavelength absorption edge of their absorption spectra. The HOMO and LUMO energy levels of the polymers were found from their onset oxidation (*p*-doping) potential and onset reduction (*n*-doping) potential, respectively. Electronic band gap was calculated from the difference of LUMO and HOMO energy levels.

Table 3.3 : Electrochemical, optical and electronic properties of **P69–P71**.

Polymer	E_{ox} (eV)	E_{red} (eV)	HOMO ^c (eV)	LUMO ^c (eV)	E_g^d (eV)	UV _{max} λ (nm)	E_g^{opt} ^g (eV)
P69	1.16 ^a / 0.93 ^b	-1.68 ^a / -1.18 ^b	- 5.64	- 3.53	2.11	507 ^e / 653 ^f	1.89
P70	0.99 ^a / 0.91 ^b	-1.89 ^a / -1.43 ^b	- 5.62	- 3.28	2.34	443 ^e / 566 ^f	2.18
P71	0.56 ^a / 0.31 ^b	-1.84 ^a / -1.33 ^b	- 5.02	- 3.38	1.64	579 ^e / 691 ^f	1.79

^a Oxidation and reduction maxima. ^b Onsets of oxidation and reduction. ^c Calculated using the empirical equation: $HOMO$ (or $LUMO$)(eV) = $-(E_{onset} + 4.71)$. ^d Difference of LUMO and HOMO. ^e Absorption maxima of the polymer film coated on ITO. ^f Onset of the absorption of the polymer film coated on ITO. ^g $E_g^{opt} = \frac{hc}{\lambda_{onset}}$.

Electron-rich character of the donor groups decreased the oxidation potential of TT monomer. The alkyl groups on 3-hexylthiophene caused the steric hindrance on polymer chain resulting in less order and less conjugation. Therefore the band gap of polymer increased to 2.18 eV. The lowest band gap (1.79 eV) was estimated for **P71**, this is mainly due to the substitution of 2- and 4- positions of thiophene rings with

electron-donating alkoxy groups, which reduced the E_g of polymer by increasing the HOMO energy level. In addition, both the β positions to sulfur are substituted and as a result polymerization continues mainly through α positions to form linear, perfect polymers [75]. Also, the S $\cdots$ O intramolecular interactions through polymer backbone made the structure of compound rigid and planar. Anti conformation of the thiophene rings were stabilized by these interactions [90,152]. The optical band gap of thieno[3,2-*b*]thiophene based polymer poly(2,5-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)thieno[3,2-*b*]thiophene) was reported as 1.82 eV [153], in this study the optical band gap of **P71** was found as 1.79 eV. The difference between these two results gives the e-withdrawing effect of benzonitrile unit on band gap of the polymer.

3.4.1.4 Colorimetry studies of TT polymers synthesized through electrochemical polymerization

The color changes were determined by measuring CIE 1931 color coordinates Yxy in spectroelectrochemical studies. The color coordinates, Y, x, y values were listed in Table 3.4. **P69** became red (Y, 74.4; x, 0.428; y, 0.360) in the neutral state, upon incremental doping by application of oxidative potentials, **P69** changed to a blue color (Y, 79.6; x, 0.295; y, 0.333). The neutral form of **P70** was orange (Y, 76.6; x, 0.365; y, 0.406) in color, upon oxidation color changed to pale blue (Y, 54.9; x, 0.280; y, 0.307). **P71** film showed a purple color at its neutral state (Y, 37.8; x, 0.280; y, 0.280) and turned to blue at its oxidized form (Y, 63.8; x, 0.287; y, 0.307).

Table 3.4 : Electrochromic properties of **P69–P71**.

Polymer	Neutral State	Oxidized State
	Y / x / y	Y / x / y
P69	74.4 / 0.428 / 0.360	79.6 / 0.295 / 0.333
P70	76.6 / 0.365 / 0.406	54.9 / 0.280 / 0.307
P71	37.8 / 0.280 / 0.280	63.8 / 0.287 / 0.307

3.4.2 DTT based polymers synthesized through electrochemical polymerization

3.4.2.1 Electrochemistry

Oxidative polymerization of **74**, **76–78** (0.1 M) was carried out under potentiodynamic conditions in a mixed solvent (ACN/DCM, 70/30 v/v for **74** and **76**, 90/10 v/v for **77** and **78**) using NaClO₄ (0.1 M) / LiClO₄ (0.1 M) as supporting electrolyte, Pt as working and counter electrodes and Ag wire as a reference electrode. Multiple cyclic voltammograms for the repeated scanning electropolymerization of **74**, **76–78** were shown in Figure 3.30. The onset of oxidation starts at + 1.39 V for **74**, + 1.16 V for **76**, + 0.96 V for **77** and + 0.78 V for **78** vs Ag wire a pseudo-reference electrode. The oxidation wave for **78** is shifted to + 0.87 V due to the presence of a strong electron donating group on donor moiety. The onset of the oxidation of **78** (+ 0.87 V) is the lowest among the others due to increased HOMO level by EDOT group. Electron-rich character of the donor groups decreased the oxidation potential of DTT monomer.

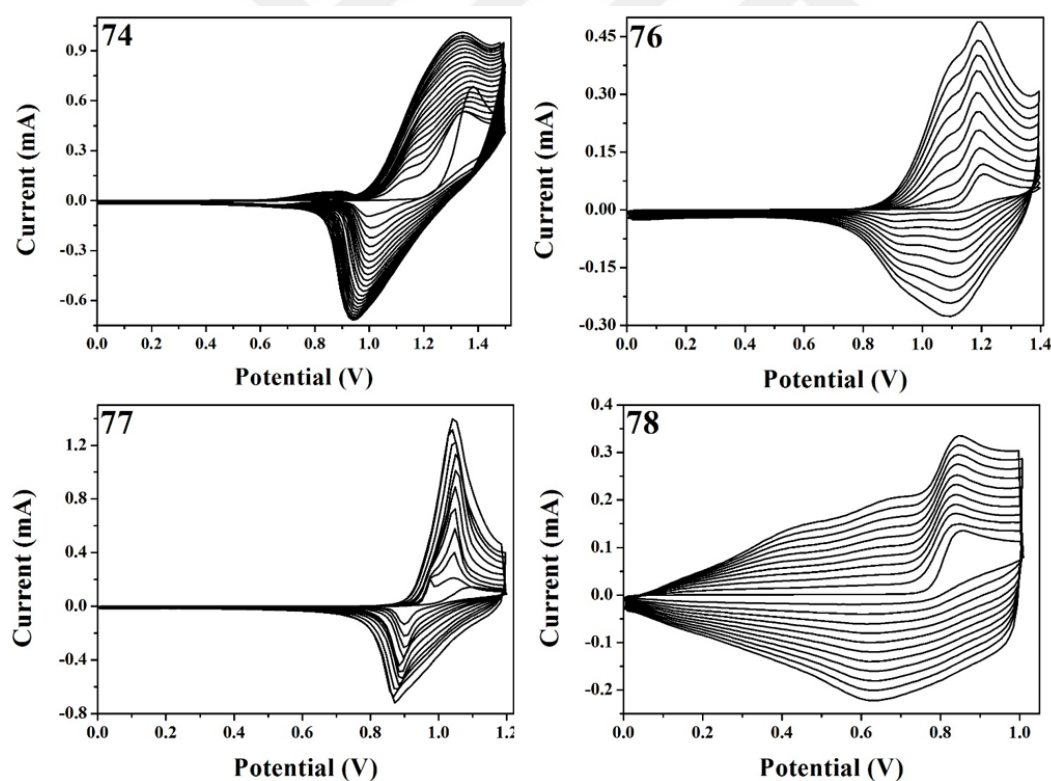


Figure 3.30 : Electropolymerization of 0.1 M DTT monomers: (ACN/DCM, 70/10, v/v), **76** (ACN/DCM, 90/10, v/v), **77** (ACN/DCM, 70/10, v/v) and **78** (ACN/DCM, 90/10, v/v), with NaClO₄ (0.1 M) / LiClO₄ (0.1 M) on the Pt disk electrode at 100 mV s⁻¹.

The polymer films were rinsed with ACN to get rid of the monomers and the electrolyte before their electrochemical responses were tested by CV for both *p*- and *n*-doping processes. The polymer films **P74**, **P76–P78** showed irreversible *n*-doping in cathodic scans with onset reduction potentials of - 1.04, - 1.11, - 1.22 and - 1.34 V, respectively (Figure 3.31).

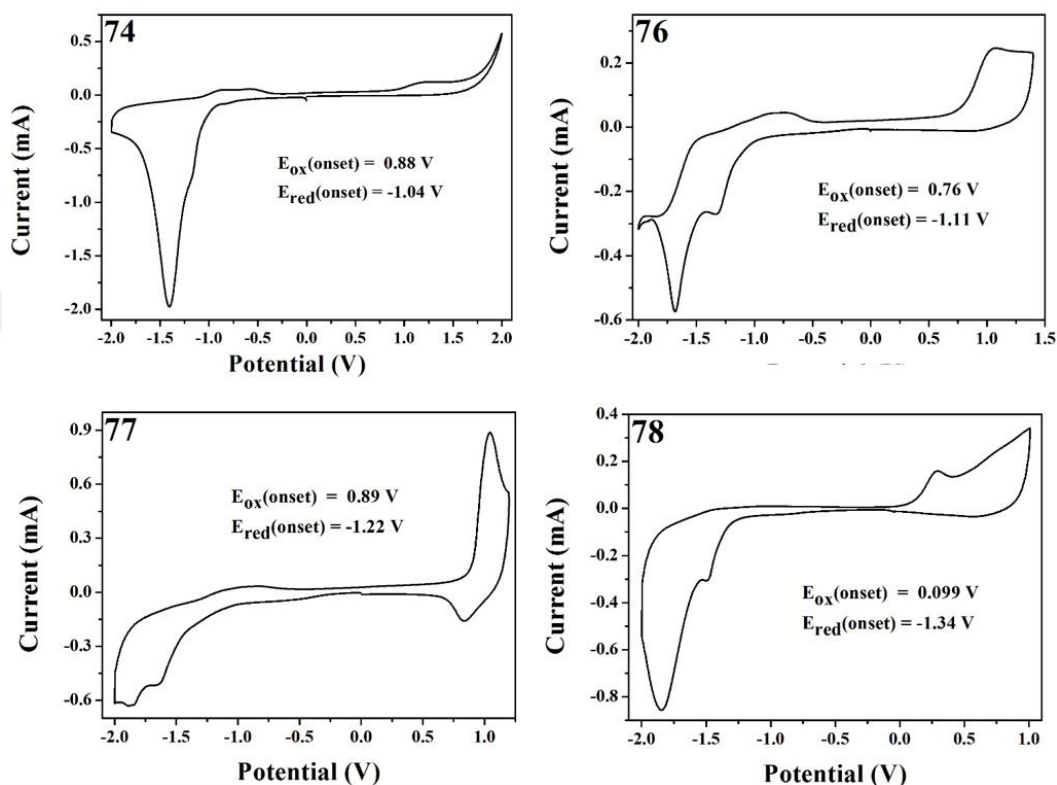


Figure 3.31 : Cyclic voltammograms of polymer films of **P74**, **P76–78** on the Pt disk electrode in a monomer-free ACN/ LiClO₄ (0.1 M) / NaClO₄ (0.1 M) solution at 100 mV s⁻¹.

On the cathodic scans, polymer oxidations were observed at about + 1.34 V for **P74**, + 1.19 V for **P76**, + 1.05 V for **P77** and + 0.84 V for **P78**. Reduction of the polymers formed a peak at + 0.95 V for **P74**, + 1.09 V for **P76**, + 0.88 V for **P77** and + 0.63 V for **P78** (Figure 3.32).

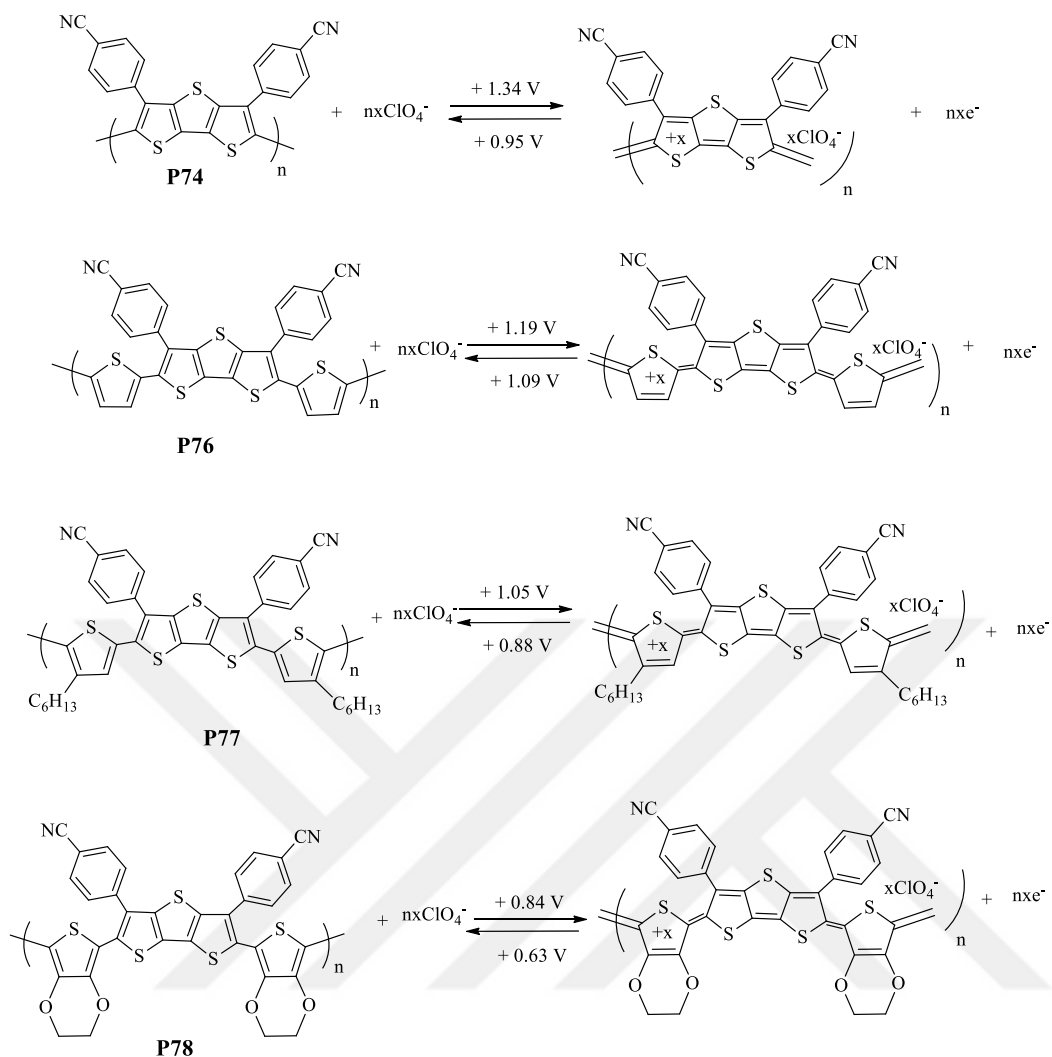


Figure 3.32 : *p*-Doping of **P74 and **P76–78**.**

Cyclic voltammograms and scan rate dependences of current densities of polymer films, **P74** (Figure 3.33), **P76** (Figure 3.34), **P77** (Figure 3.35), and **P78** (Figure 3.36) at different scan rates (25–500 mVs⁻¹) were investigated. A linear correlation between the peak current and scan rate indicates that the films were well adhered to the Pt electrode surface and the electrochemical processes were diffusion-controlled and reversible.

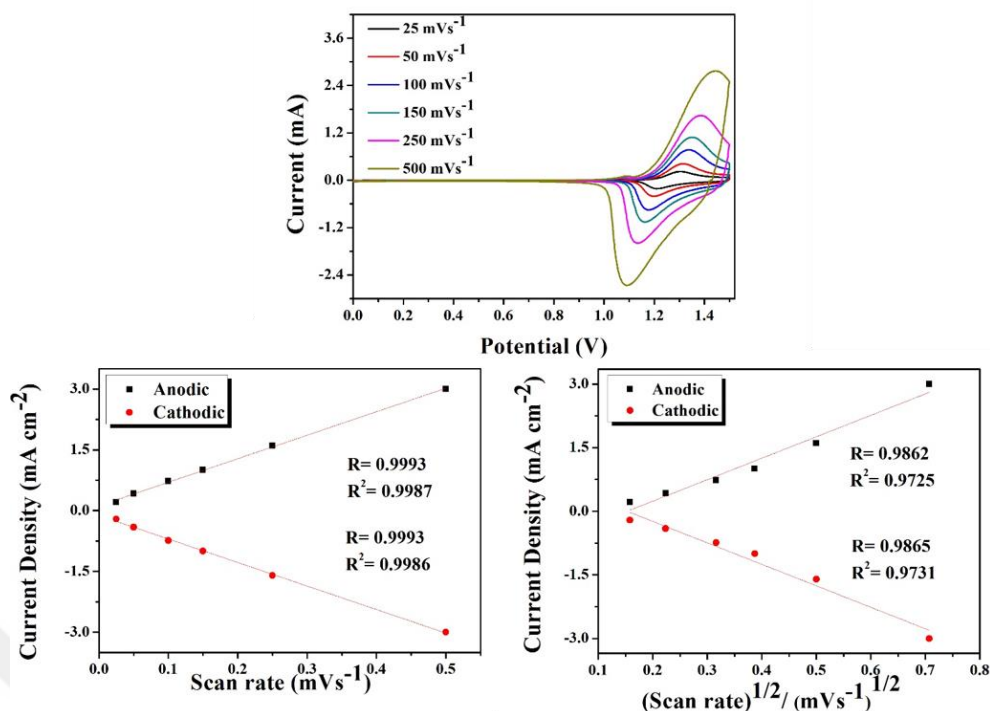


Figure 3.33 : Cyclic voltammograms and scan rate dependences of current densities of **P74** on Pt disk electrode in a monomer-free ACN/ LiClO_4 (0.1 M) / NaClO_4 (0.1 M) solution at different scan rates from 25 to 50, 100, 150, 250 and 500 mV s^{-1} .

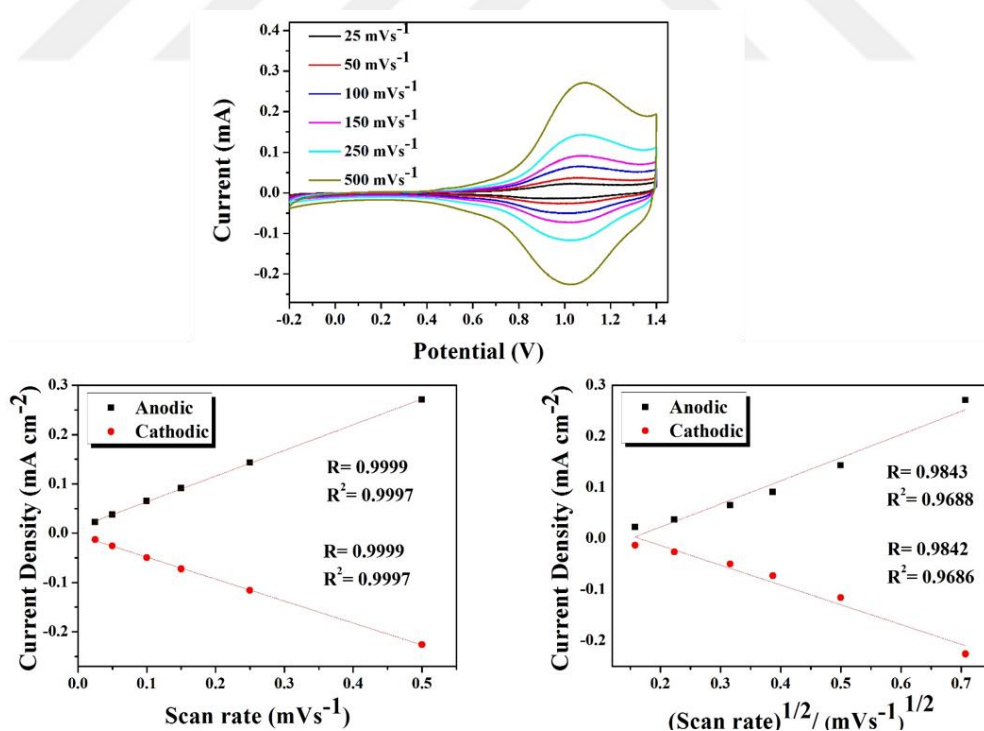


Figure 3.34 : Cyclic voltammograms and scan rate dependences of current densities of **P76** on Pt disk electrode in a monomer-free ACN/ LiClO_4 (0.1 M) / NaClO_4 (0.1 M) solution at different scan rates from 25 to 50, 100, 150, 250 and 500 mV s^{-1} .

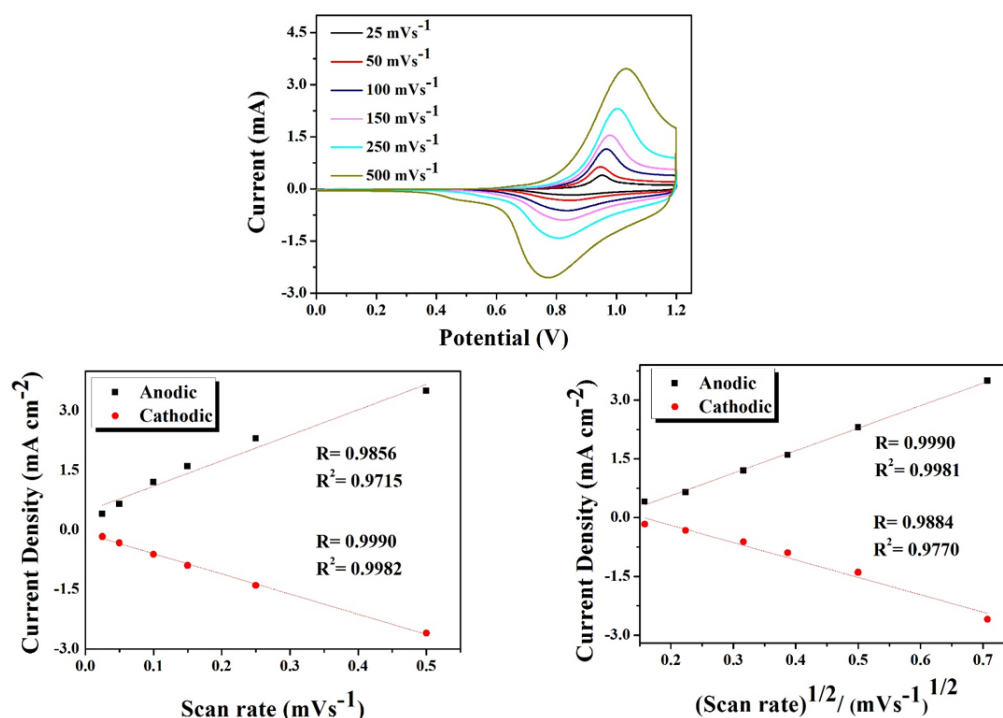


Figure 3.35 : Cyclic voltammograms and scan rate dependences of current densities of **P77** on Pt disk electrode in a monomer-free ACN/LiClO₄ (0.1 M) / NaClO₄ (0.1 M) solution at different scan rates from 25 to 50, 100, 150, 250 and 500 mV s^{-1} .

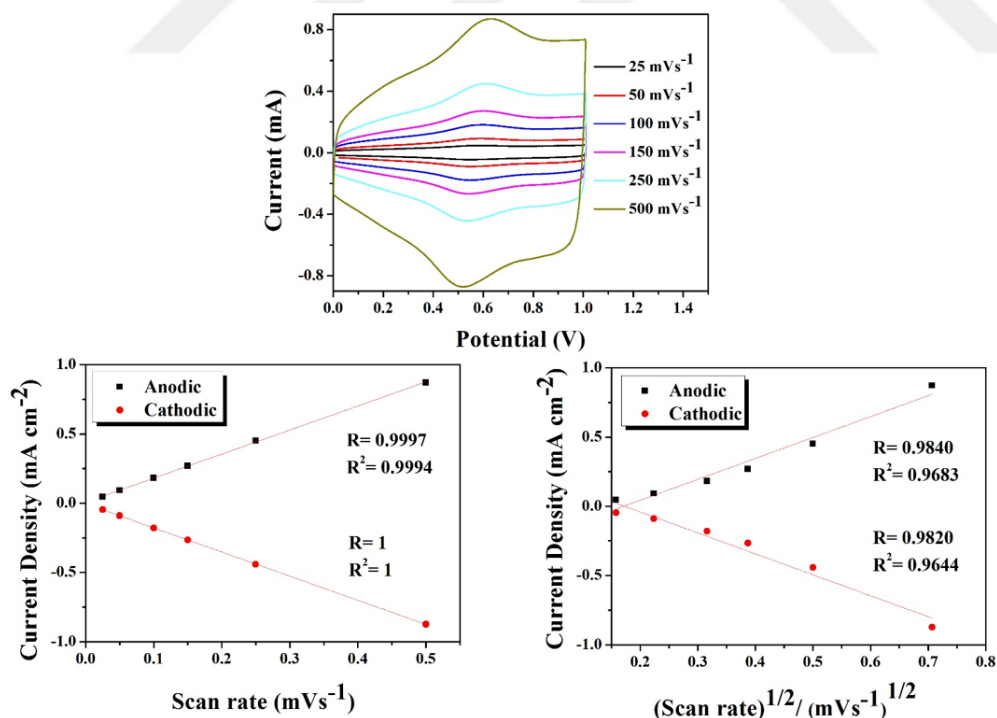


Figure 3.36 : Cyclic voltammograms and scan rate dependences of current densities of **P78** on Pt disk electrode in a monomer-free ACN/LiClO₄ (0.1 M) / NaClO₄ (0.1 M) solution at different scan rates from 25 to 50, 100, 150, 250 and 500 mV s^{-1} .

3.4.2.2 Spectroelectrochemistry

The spectroelectrochemical analyses were studied to investigate the electronic structures of the polymer films. The films of **P74** and **P76–78** were produced potentiodynamically on ITO coated glass slides. Variations in optical properties as a function of applied potentials were examined via UV-Vis spectroscopy. Neutral **P74** was yellow in color with a λ_{max} of 449 nm (Figure 3.37). Upon oxidation (0 V to + 1.3 V) π - π^* absorption decreases and new transition bands at lower energy (726 and 1027 nm) related to the polaronic and bipolaronic charge carriers form. The optical band gap of polymer was determined as 2.34 eV using the onset of the π - π^* transitions.

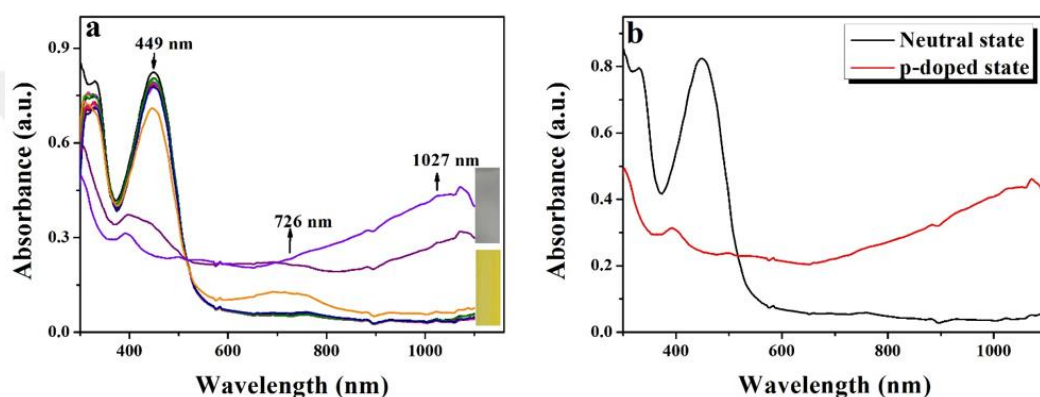


Figure 3.37 : (a) *p*-Doping spectroelectrochemistry of **P74** film on ITO coated glass slide, (b) absorption spectra of **P74** at neutral and *p*-doped state in monomer free ACN/DCM, NaClO₄/LiClO₄ (0.1 M, 0.1 M) solvent-electrolyte couple at applied potentials, Pt wires as counter electrode, and Ag wire as pseudo reference electrode.

Neutral form of **P76** gives rise to π - π^* absorption band at 452 nm. Band gap of the polymer was determined as 2.06 eV. As polymer film was oxidized (0 V to + 1.5 V), the moderate (711 nm) and strong absorption band (1011 nm) corresponding to the two low-energy charge carriers showed up at the expense of the π - π^* transition of absorption band. They were attributed to the polaronic and bipolaronic states, respectively (Figure 3.38).

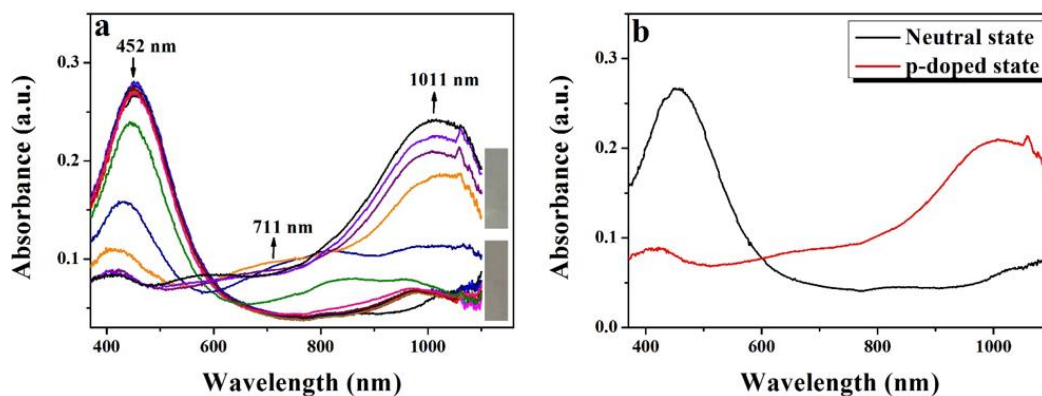


Figure 3.38 : (a) *p*-Doping spectroelectrochemistry of **P76** film on ITO coated glass slide, (b) absorption spectra of **P76** at neutral and *p*-doped state in monomer free ACN/DCM, NaClO₄/LiClO₄ (0.1 M, 0.1 M) solvent-electrolyte couple at applied potentials, Pt wires as counter electrode, and Ag wire as pseudo reference electrode.

Spectroelectrochemistry of **P77** showed λ_{max} of 454 nm for the neutral polymers, which was orange-yellow color (Figure 3.39). Upon oxidation (0 V to + 1.1 V) the π - π^* transition diminished and the new transition bands evolved at lower energy (at 707 and 1047 nm), emitting pale blue in color, accompanying to the polaronic and bipolaronic charge carriers. The alkyl groups on 3-hexylthiophene brought about the steric hindrance on polymer chain resulting in less order and less conjugation. Therefore the band gap of the polymer increased to 2.09 eV.

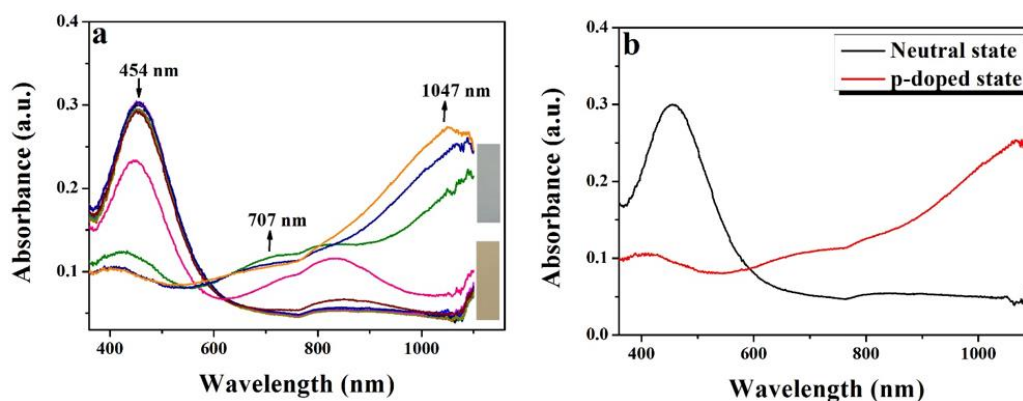


Figure 3.39 : (a) *p*-Doping spectroelectrochemistry of **P77** film on ITO coated glass slide, (b) Absorption spectra of **P77** at neutral and *p*-doped state in monomer free ACN/DCM, NaClO₄/LiClO₄ (0.1 M, 0.1 M) solvent-electrolyte couple at applied potentials, Pt wires as counter electrode, and Ag wire as pseudo reference electrode.

In neutral state **P78** absorbs at 578 nm, displaying purple color with an optical band gap of 1.71 eV. Upon incremental increase of potential from 0 V to + 1.1 V, absorption

of neutral polymer decreased in intensity. At intermediate potentials, new peaks evolved at 838 and 1081 nm attributed to the charge carriers (Figure 3.40). **P78** had the lowest band gap of all the polymers due to the higher HOMO level of the EDOT unit compared to thiophene and 3-hexylthiophene. This can be explained by better intermolecular π - π^* interactions with increasing planarity. The fused thiophene ring stabilizes the quinoidal form of **P76** as does the EDOT (**P78**).

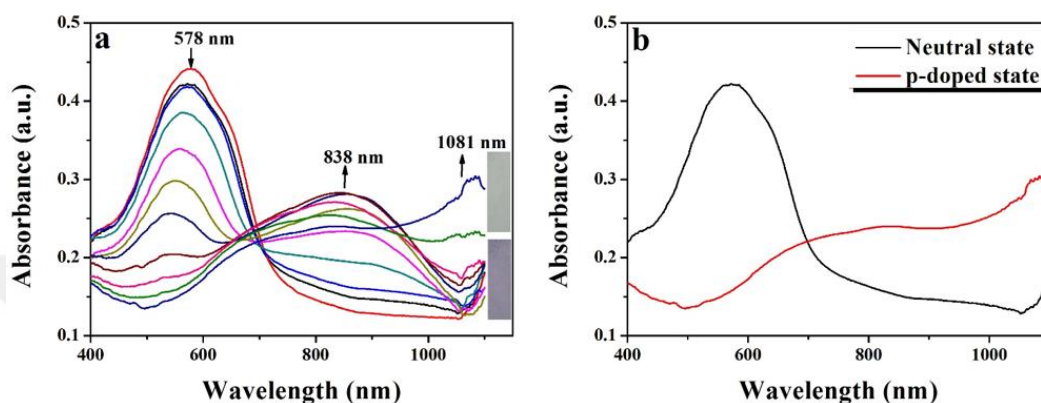


Figure 3.40 : (a) *p*-Doping spectroelectrochemistry of **P78** film on ITO coated glass slide, (b) Absorption spectra of **P78** at neutral and p-doped state in monomer free ACN/DCM, NaClO₄/LiClO₄ (0.1 M, 0.1 M) solvent-electrolyte couple at applied potentials, Pt wires as counter electrode, and Ag wire as pseudo reference electrode.

3.4.2.3 Evaluation of electrochemical, optical and electronic properties of the DTT polymers synthesized through electrochemical polymerization

The absorption spectra of DTT polymers produced through electrochemical method on ITO surface is depicted in Figure 3.41. The same result with TT polymers is observed in the case of DTT polymers, conjugated polymer with EDOT side (**P78**) group is redshifted in comparison with that composed of thiophene (**P76**) and 3-hexylthiophene (**P77**). While the maximum absorption of **P74** and **P76** are nearly same, the onset of absorption edges are different.

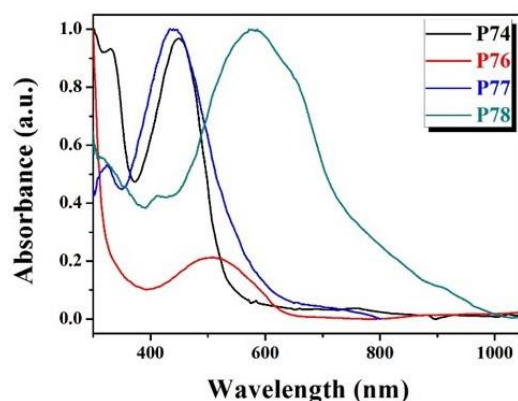


Figure 3.41 : Absorption spectra of DTT polymers synthesized through electrochemical method.

The electrochemical, optical and electronic properties of DTT polymers were summarized in Table 3.5. Optical band gaps of conjugated polymers were calculated from the edge of the long wavelength absorption. The HOMO and LUMO energy levels of the conjugated polymers were recorded from their onset oxidation (*p*-doping) potential and onset reduction (*n*-doping) potential, respectively. Electronic band gap was calculated from the difference of LUMO and HOMO energy levels.

Table 3.5 : Electrochemical, optical and electronic properties of **P74**, **P76**, **P77** and **P78**.

Polymer	E_{ox} (eV)	E_{red} (eV)	HOMO ^c (eV)	LUMO ^c (eV)	E_g^d (eV)	UV_{max} λ (nm)	$E_g^{opt g}$ (eV)
P74	1.19 ^a / 0.88 ^b	-1.41 ^a / -1.04 ^b	- 5.59	- 3.67	1.92	449 ^e / 528 ^f	2.34
P76	1.06 ^a / 0.76 ^b	-1.69 ^a / -1.11 ^b	- 5.47	- 3.60	1.87	452 ^e / 600 ^f	2.06
P77	1.05 ^a / 0.89 ^b	-1.67 ^a / -1.22 ^b	- 5.60	- 3.49	2.11	454 ^e / 592 ^f	2.09
P78	0.58 ^a / 0.099 ^b	-1.92 ^a / -1.34 ^b	- 4.81	- 3.37	1.44	578 ^e / 725 ^f	1.71

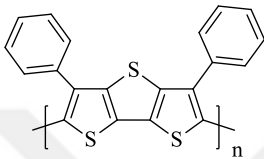
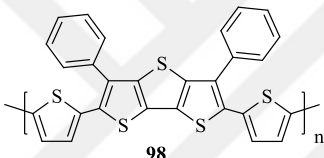
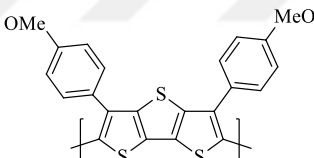
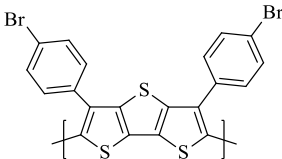
^a Oxidation and reduction maxima. ^b Onsets of oxidation and reduction. ^c Calculated using the empirical equation: $HOMO$ (or $LUMO$)(eV) = $-(E_{onset} + 4.71)$. ^d Difference of LUMO and HOMO. ^e Absorption maxima of the polymer film coated on ITO. ^f Onset of the absorption of the polymer film coated on ITO. ^g $E_g^{opt} = \frac{hc}{\lambda_{onset}}$.

Fusing another electron rich thiophene ring reduced the oxidative potential (+ 1.19 V) of **P74** although there is a second electron deficient benzonitrile group. Almost similar optical band gap values were obtained for **P76** and **P77**. The lowest band gap of 1.71

eV was recorded for **P78**, which emerged from the electronic effect of EDOT group as stated in 3.4.1.3.

The band gaps of different kinds of DTT polymers (**97**, **98**, **99**, **100**) were illustrated in Table 3.6. Low band gaps between 1.94–2.28 eV were obtained. In this study, introduction of EDOT group to DTT backbone decreased the energy level to 1.60 eV.

Table 3.6 : Optical properties of different kinds of DTT polymers.

DTT polymer	E_g^{opt} (eV)
 97	2.18 [154]
 98	1.94 [155]
 99	2.20 [156]
 100	2.28 [147]

3.4.2.4 Colorimetry studies of DTT polymers synthesized through electrochemical polymerization

The color changes that results from the redox switching of DTT polymers were examined by CIE 1931 Yxy color space. The color coordinates, Y, x, y values were depicted in Table 3.7. **P74** becomes yellow (Y, 75.8; x, 0.387; y, 0.423) in the neutral state, upon incremental doping by application of oxidative potentials, **P74** changed to

a grey color (Y, 67.3; x, 0.310; y, 0.337). The neutral form of **P76** is a pale red (Y, 128.0; x, 0.314; y, 0.321), upon oxidation color changed to a pale gray (Y, 145.0; x, 0.303; y, 0.321). **P77** is an orange color in its neutral form (Y, 100.0; x, 0.353; y, 0.357) and it turned into a pale blue upon oxidation (Y, 105.0; x, 0.303; y, 0.326). **P78** film shows a purple color at its neutral state (Y, 30.6; x, 0.284; y, 0.266) and turned to blue at its oxidized form (Y, 37.1; x, 0.284; y, 0.300).

Table 3.7 : Electrochromic properties of **P74**, **P76**, **P77** and **P78**.

Polymer	Neutral State	Oxidized State
	Y / x / y	Y / x / y
P74	75.8 / 0.387 / 0.423	67.3 / 0.310 / 0.337
P76	128.0 / 0.314 / 0.321	145.0 / 0.303 / 0.321
P77	100.0 / 0.353 / 0.357	105.0 / 0.303 / 0.326
P78	30.6 / 0.284 / 0.266	37.1 / 0.284 / 0.300

3.4.3 Conjugated polymers synthesized through chemical methods

3.4.3.1 Optical and electronic properties of copolymers

Absorption spectrum is the crucial parameter for the conjugated polymers. The solution and solid-state absorption spectra of copolymers were investigated; optical band gaps of both states and electronic band gaps were calculated. Figure 3.42 illustrates the absorption spectrum of P(TT-Th) (**79**) in solvent and as a film on ITO coated glass slide. The absorption onsets of **79** are 548 and 667 nm and the optical band gaps of 2.26 eV and 1.86 eV were calculated in THF and as solid-state, respectively. The low E_g calculated for the solid state indicates that the rigidity results from the contribution of the mesomeric structure in solid state is higher than in solution [48].

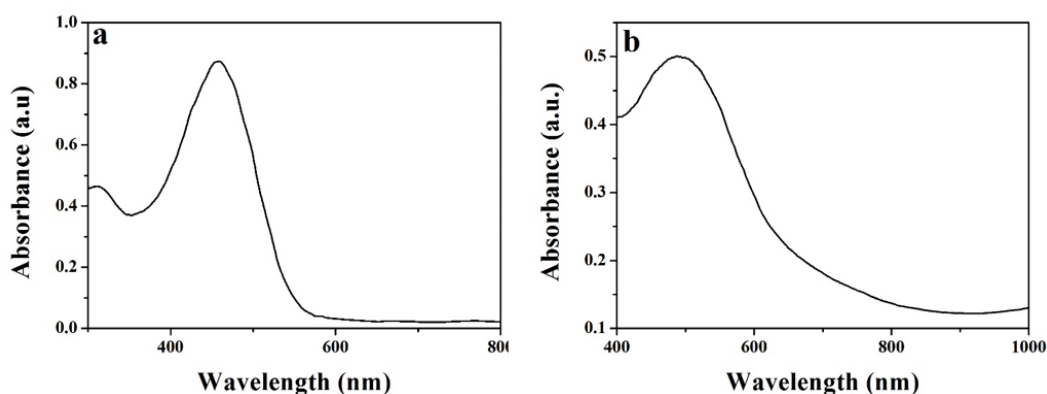


Figure 3.42 : UV spectrum of P(TT-Th) (**79**) (a) in THF, (b) film from THF on ITO.

Figure 3.43 shows the absorption spectrum of P(DTT-Th) (**80**) in solvent and as a film on ITO. The absorption onsets of **80** are 564 and 572 nm and the optical band gaps of 2.19 eV and 2.16 eV were calculated in THF and as solid-state, respectively.

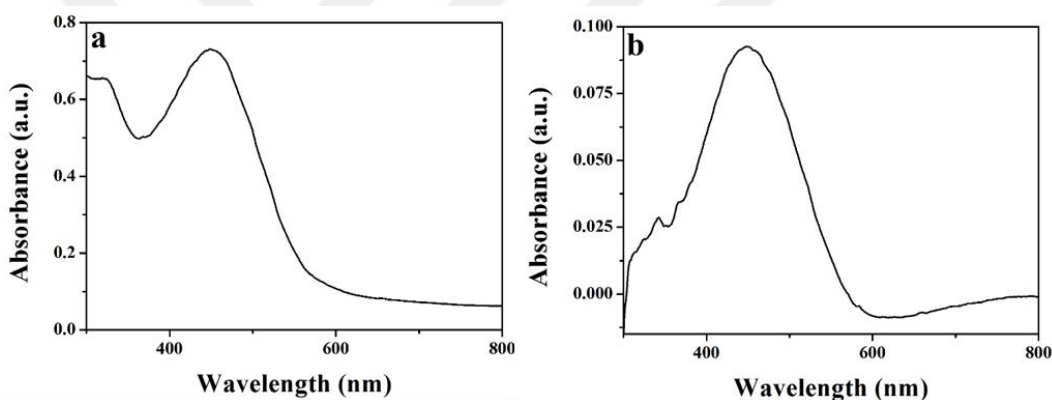


Figure 3.43 : UV spectrum of P(DTT-Th) (**80**) (a) in THF, (b) film from THF on ITO by spin coating.

CV of copolymers **79** and **80** were investigated in dry and degassed monomer-free ACN / LiClO₄ (0.1 M) / NaClO₄ (0.1 M) solution at 100 mV s⁻¹, by drop-coating onto glassy carbon disk electrode from their THF solutions (Figure 3.44). Pt and Ag wires were used as counter and pseudo-reference electrodes. The electronic band gaps were calculated as 1.97 and 1.91 eV from the differences between the onsets of oxidation and reduction peaks, respectively.

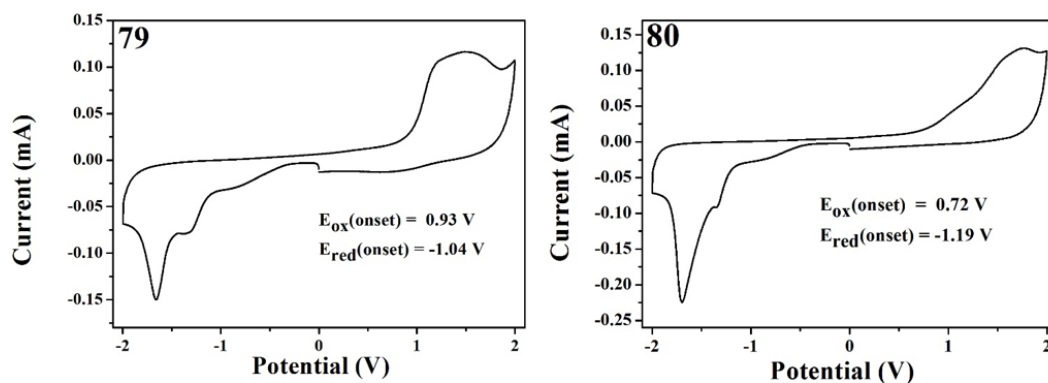
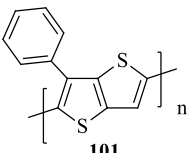
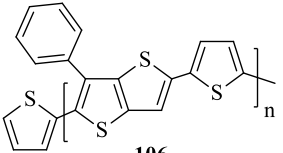
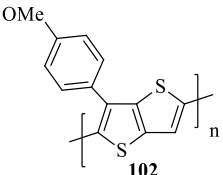
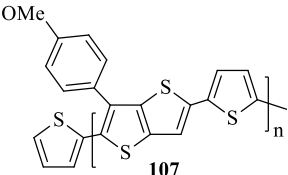
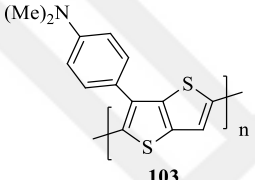
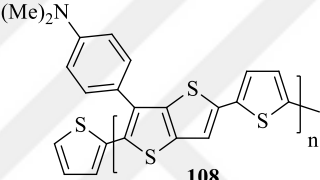
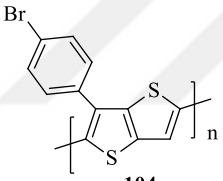
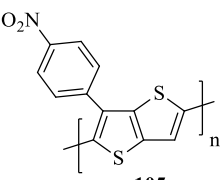
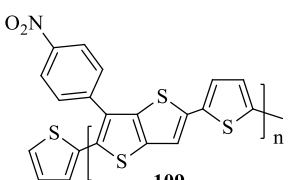
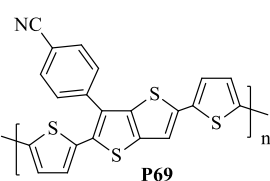
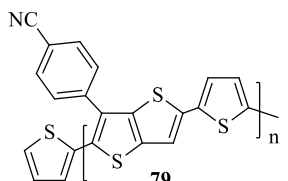


Figure 3.44 : Cyclic voltammograms of copolymers **79**, **80** on the glassy carbon disk electrode in a monomer-free ACN/ LiClO₄ (0.1 M) / NaClO₄ (0.1 M) solution at 100 mV s⁻¹.

Table 3.8 shows the optical band gaps of different kinds of TT polymers reported. TT polymers with functional groups such as phenyl (**101**), methoxyphenyl (**102**), dimethylamine (**103**), bromophenyl (**104**) and nitrophenyl (**105**) have small band gaps between 1.99–2.19 eV. Methoxy and dimethylamine units had nearly same e-donating effect on band gap of the polymer. On the other hand, e-withdrawing groups increased the band gap of the corresponding polymers compared with the polymer with phenyl side group. The copolymers (**106**, **107**, **108** and **109**) had higher band gaps. This could be the result of decreasing the planarity of the TT polymer with the introduction of thiophene. The same result was observed in the case of TT copolymer (**79**), E_g^{opt} in solution increased compared to TT polymer (**P69**) synthesized by electrochemical method.

Table 3.8 : Optical band gaps of different kinds of TT polymers.

TT polymer	E_g^{opt} (eV)	TT copolymer	E_g^{opt} (eV)
 101	2.05*	 106	2.28*
 102	1.99*	 107	2.42*
 103	2.01*	 108	2.29*
 104	2.19*	-	-
 105	2.16*	 109	2.57*
 P69	1.89	 79	2.26

*[124].

3.4.3.2 Optical and electronic properties of chemical polymers synthesized by oxidative chemical polymerization

The solution and solid-state absorption spectra of polymers produced via oxidative chemical polymerization were investigated. The absorption spectra of the polymers showed broad absorption peaks in both solution and as thin films. Optical band gaps for both states and electronic band gaps were calculated. Optical studies showed the absorption onsets and optical band gaps of TT based polymers **81–82** at 493 and 735 nm, and 2.51 and 1.69 eV, respectively in solution. In solid-state, absorption onsets and optical band gaps of **81–82** were recorded as 573 and 674 nm, and 2.16 and 1.84 eV, respectively (Figure 3.45 and 3.46).

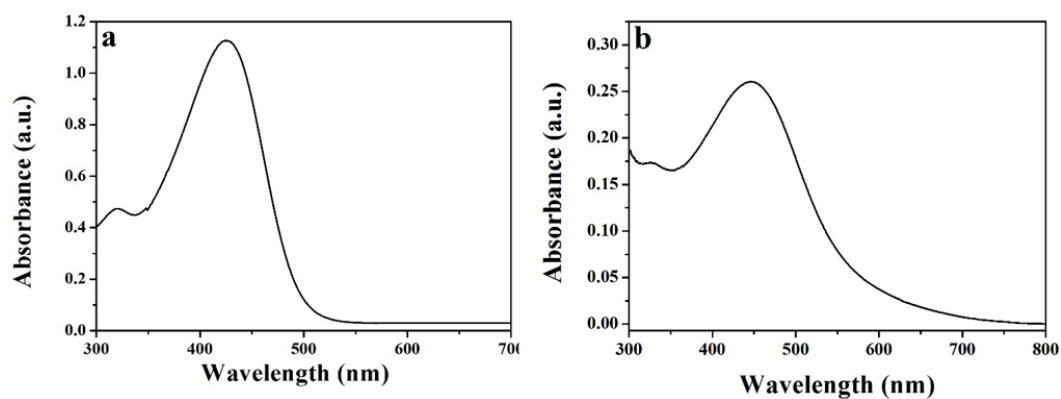


Figure 3.45 : UV spectrum of P(HexylTh-TT-HexylTh) (**81**) (a) in THF, (b) film from 1-methyl-2-pyrrolidinone on ITO.

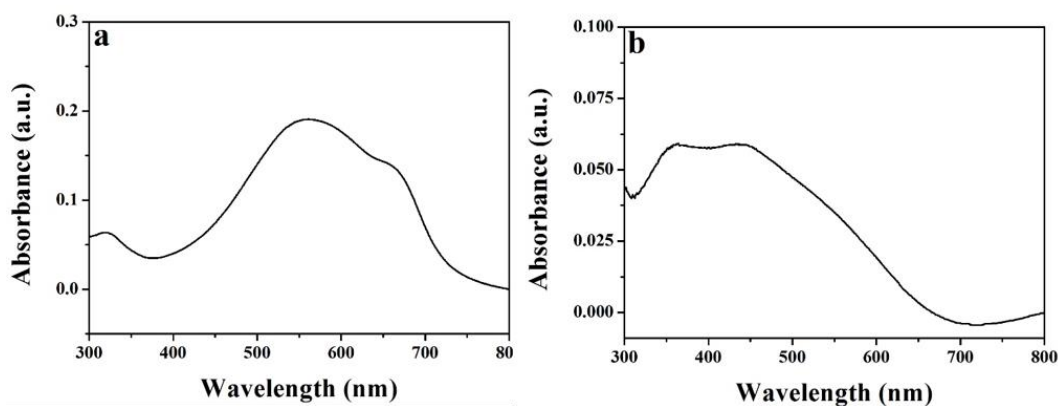


Figure 3.46 : UV spectrum of P(E-TT-E) (**82**) (a) in 1-methyl-2-pyrrolidinone, (b) film from 1-methyl-2-pyrrolidinone on ITO.

Optical studies showed the absorption onsets and optical band gaps of DTT based polymers **83–85** at 513, 503 and 779 nm, and 2.41, 2.46 and 1.60 eV, respectively in solution. In solid-state, absorption onsets and optical band gaps of **83–85** were

obtained to be 566, 533 and 757 nm, and 2.18, 2.33 and 1.64 eV, respectively (Figure 3.47, 3.48 and 3.49).

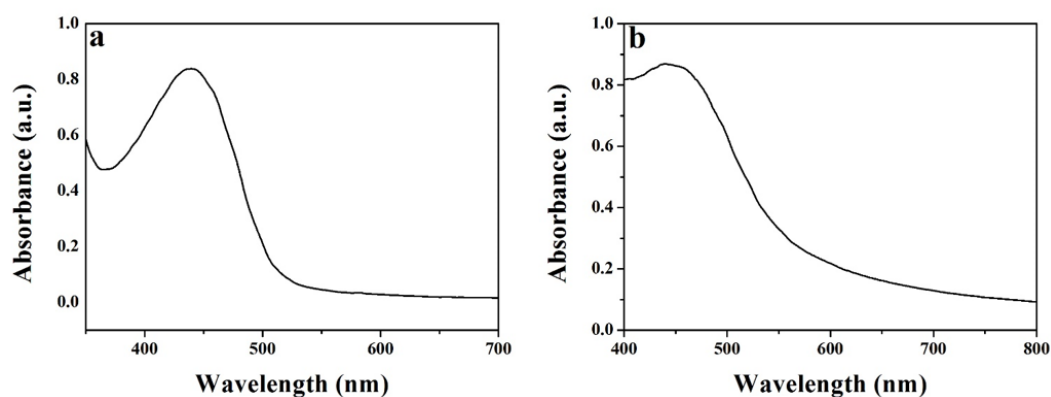


Figure 3.47 : UV spectrum of P(DTT) (**83**) (a) in THF, (b) film from THF on ITO.

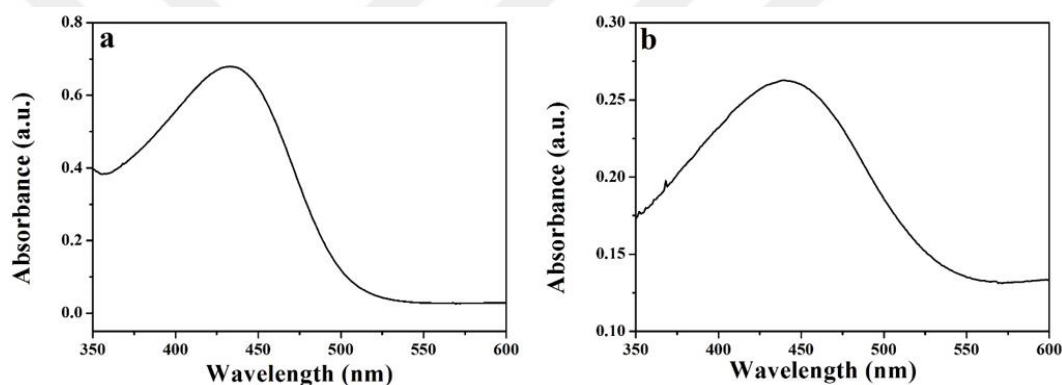


Figure 3.48 : UV spectrum of P(Hexyl-DTT-Hexyl) (**84**) (a) in THF, (b) film from THF on ITO.

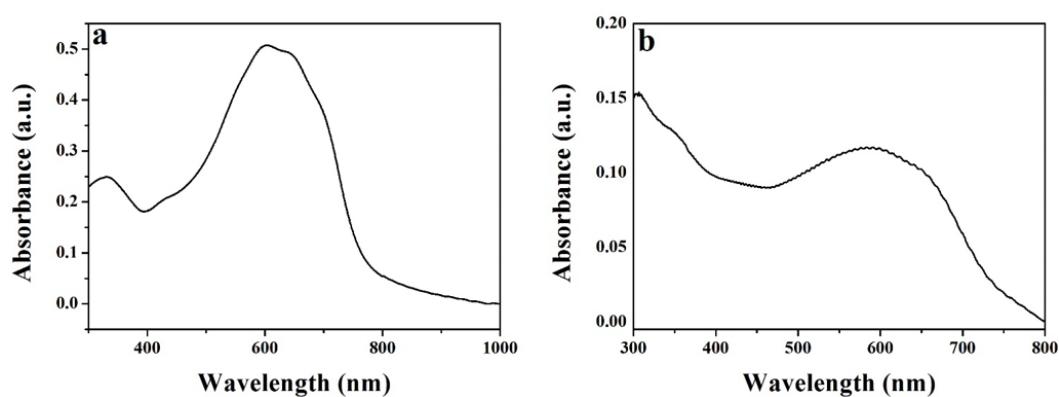


Figure 3.49 : UV spectrum of P(E-DTT-E) (**85**) (a) in 1-methyl-2-pyrrolidinone, (b) film from 1-methyl-2-pyrrolidinone on ITO.

3.4.3.3 Electronic properties of polymers synthesized through chemical methods

The electrochemical behavior of the polymers **81–85** was checked by CV in a solution of dry and degassed monomer-free ACN / LiClO₄ (0.1 M) / NaClO₄ (0.1 M) solution at a scan rate of 100 mV s⁻¹, by drop-coating onto the glassy carbon disk electrode from THF (**81**, **83**, **84**) and 1-methyl-2-pyrrolidinone (**82** and **85**) solutions. Pt and Ag wires were used as counter and pseudo-reference electrodes, respectively. Figure 3.50 shows the CV curves of polymers **81–85**. The polymers were scanned between - 2 and + 2 V and their electronic band gaps were estimated between 1.56 and 2.63 eV from the difference between the onsets of oxidation and reduction peaks.



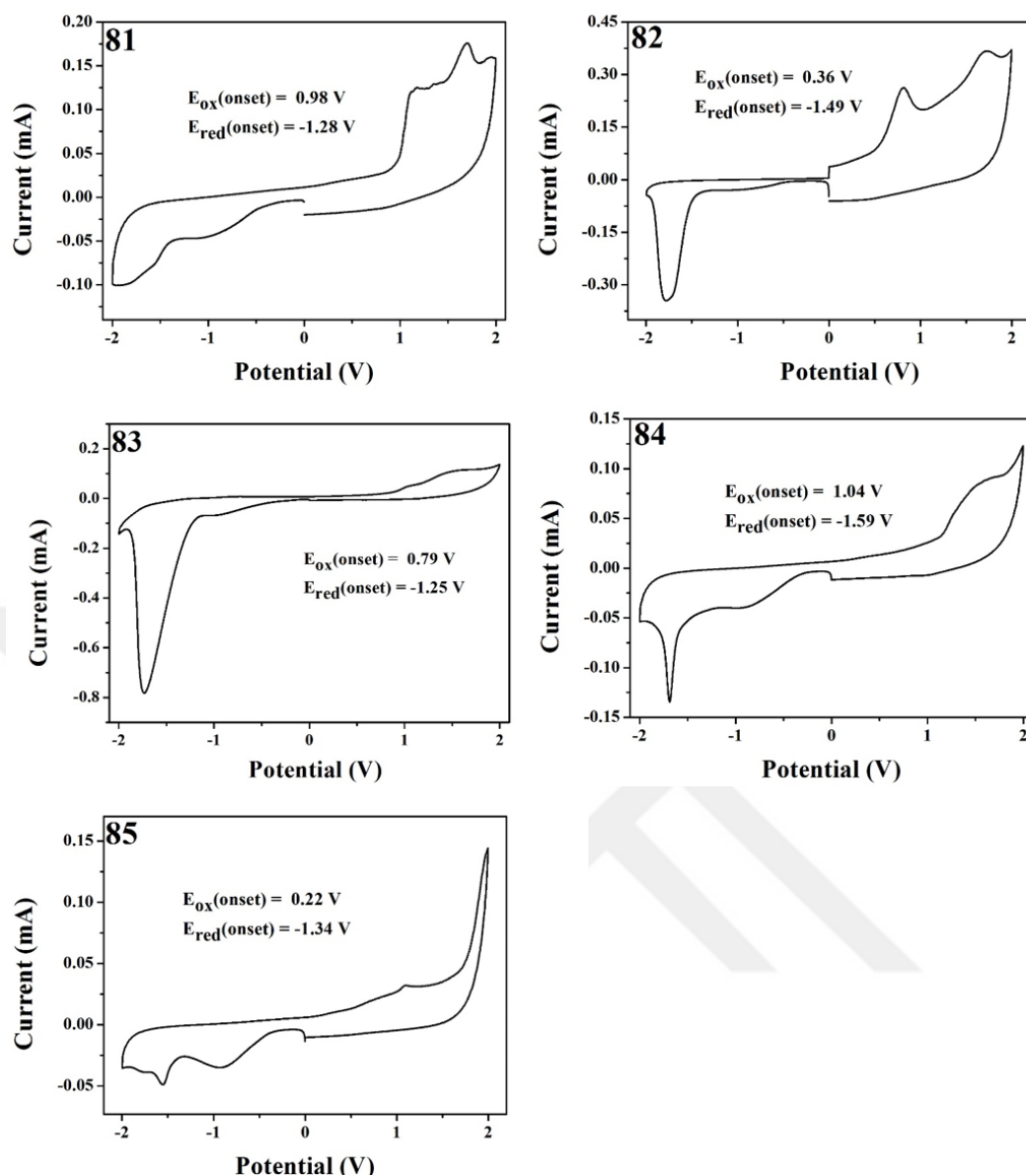


Figure 3.50 : Cyclic voltammograms of chemical conjugated polymers **81–85** on the glassy carbon disk electrode in a monomer-free ACN/ LiClO₄ (0.1 M) / NaClO₄ (0.1 M) solution at 100 mV s⁻¹.

3.4.3.4 Evaluation of electrochemical, optical and electronic properties of the polymers synthesized through chemical methods

The electrochemical, optical and electronic properties of the conjugated polymers were summarized in Table 3.9. The band gaps of TT and DTT polymers donated with 3-hexyl thiophene (**81** and **84**) are the highest; it is mainly due to the steric hindrance on polymer chain resulting in less order and less conjugation. The lowest energy gaps were estimated for the TT and DTT polymers with EDOT donor group (**82** and **85**). The substitution of 2- and 5- positions of TT rings with strong electron donating EDOT groups increase the HOMO energy level of the polymer inducing the reduction

of the E_g . Also, since the β positions to sulfur are substituted, polymerization proceeds through α positions to produce linear polymers. In addition, planar anti conformation of the thiophene rings are stabilized by $S \cdots O$ intramolecular interactions to give the polymer more rigid structure. The low E_g^{opt} calculated for the solid state polymers (**79**, **81**, **83** and **84**) results from the rigidity of the higher mesomeric structure in solid state. HOMO and LUMO energy levels were estimated from the onset potentials of the oxidation and reduction peaks. The electron-withdrawing benzonitrile substituents electronically influence the frontier molecular orbital energy levels, decreasing LUMO and HOMO orbital energies and causes band gap reduction due to the pronounced effect on the LUMO [157].

Table 3.9 : Electrochemical, optical and electronic properties of the polymers synthesized through chemical methods.

Polymer	E_{ox} (eV)	E_{red} (eV)	HOMO ^c (eV)	LUMO ^c (eV)	E_g^d (eV)	UV _{max} λ (nm)	E_g^{opt} (eV)
79	1.35 ^a / 0.93 ^b	-1.66 ^a / -1.04 ^b	- 5.64	- 3.67	1.97	458 ^e , 548 ^f / 490 ^g , 667 ^h	2.26 ^{i, j} / 1.86 ^{i, k}
80	1.74 ^a / 0.72 ^b	-1.70 ^a / -1.19 ^b	- 5.43	- 3.52	1.91	451 ^e , 564 ^f / 446 ^g , 572 ^h	2.19 ^{i, j} / 2.16 ^{i, k}
81	1.16 ^a / 0.98 ^b	-1.87 ^a / -1.28 ^b	-5.69	-3.43	2.26	425 ^e , 493 ^f / 447 ^g , 573 ^h	2.51 ^{i, j} / 2.16 ^{i, k}
82	0.81 ^a / 0.36 ^b	-1.79 ^a / -1.49 ^b	-5.07	-3.22	1.85	558 ^e , 735 ^f / 437 ^g , 674 ^h	1.69 ^{i, j} / 1.84 ^{i, k}
83	1.19 ^a / 0.88 ^b	-1.41 ^a / -1.04 ^b	-5.59	- 3.67	1.92	439 ^e , 513 ^f / 446 ^g , 566 ^h	2.41 ^{i, j} / 2.18 ^{i, k}
84	1.51 ^a / 1.04 ^b	-1.69 ^a / -1.59 ^b	-5.75	-3.12	2.63	433 ^e , 503 ^f / 440 ^g , 533 ^h	2.46 ^{i, j} / 2.33 ^{i, k}
85	1.10 ^a / 0.22 ^b	-1.56 ^a / -1.34 ^b	-4.93	-3.37	1.56	605 ^e , 779 ^f / 596 ^g , 757 ^h	1.60 ^{i, j} / 1.64 ^{i, k}

^a Oxidation and reduction maxima. ^b Onset of oxidation and reduction. ^c Calculated using the empirical equation: $HOMO (or LUMO)(eV) = -(E_{onset} + 4.71)$. ^d Difference of LUMO and HOMO. ^e Absorption maxima of the polymer in solvent. ^f Onset of the absorption of the polymer in solvent. ^g Absorption maxima of the polymer film coated on ITO. ^h Onset of the absorption of the polymer film coated on ITO. ⁱ $E_g^{opt} = \frac{hc}{\lambda_{onset}}$. ^j From the onset absorption of polymer in solvent. ^k From the onset absorption of polymer film coated on ITO.

3.4.3.5 Photophysical, electrochemical and electroluminescent properties of **86** and **87**

Photophysical, electrochemical and electroluminescent properties of **86** and **87** were conducted by Polymer Photonics group in Institute of Macromolecular Chemistry, The Czech Academy of Sciences. The results were summarized below.

The films were obtained by spin-coating from DCB solutions. The films were spin-coated onto fused silica substrates for optical studies or coated on a Pt electrode by dipping for electrochemical applications. Absorption spectra of polymers measured in DCB solution and for solid state were demonstrated in Figure 3.51. In DCB solution absorption maxima of long-wavelength band for **86** and **87** appeared at 423 and 430 nm, respectively. In solid state, the long-wavelength absorption maxima are located at 422 and 427 nm for **86** and **87**, respectively. They are bluish-shifted compared with the related maxima in the solution spectra.

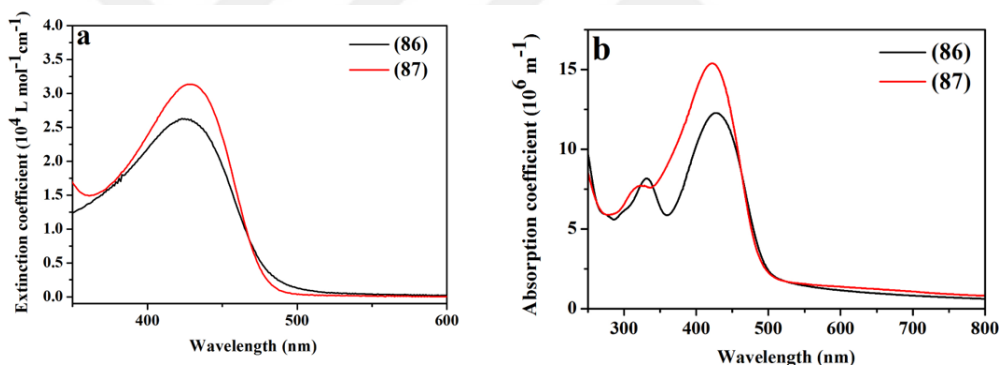


Figure 3.51 : UV-Vis absorption spectra of **86** and **87** (a) in dilute DCB solution, (b) as thin film.

In solution, the PL emission spectra demonstrated a band located at 494 nm for **86** and **87** (Figure 3.52), for thin films the red-shifts of the emission maxima compared to the solutions are noticed (Figure 3.53).

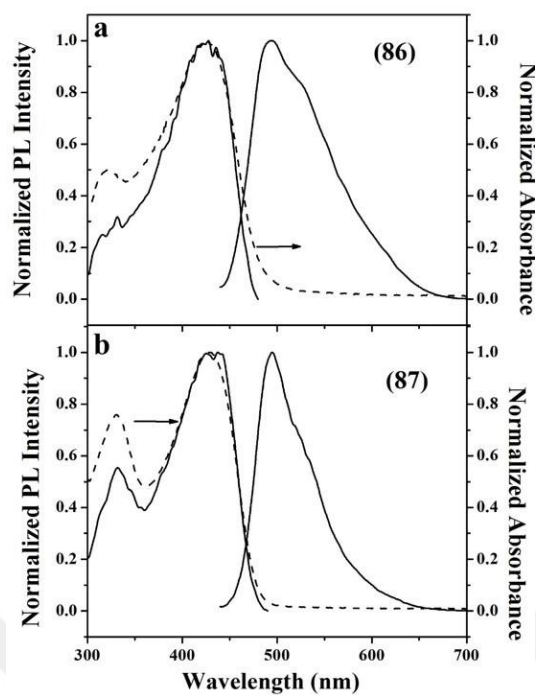


Figure 3.52 : PL excitation and emission spectra of **86** and **87** in DCB solution. Normalized absorption spectra are shown in dashed lines.

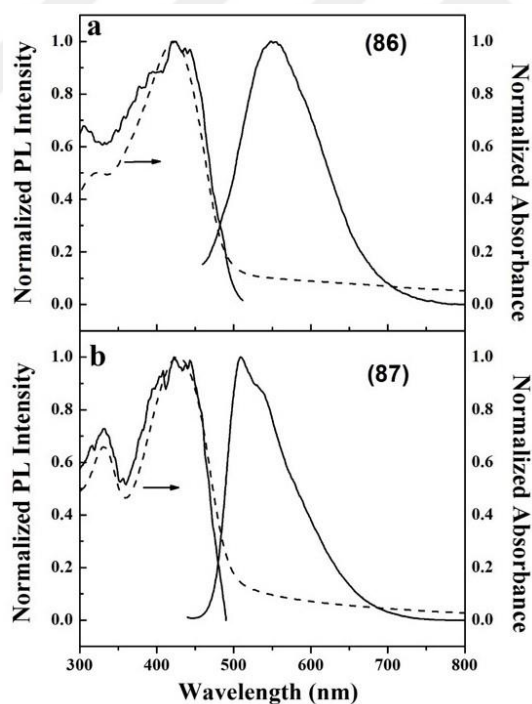


Figure 3.53 : PL excitation and emission spectra of **86** and **87** as thin film.

The photophysical properties of the polymers were summarized in Table 3.10. The polymers exhibited greenish photoluminescence in solution and as thin films.

Table 3.10 : Photophysical properties of **86** and **87**.

Copolymer	$\lambda_{\text{abs, max}}$ (nm)	$\lambda_{\text{PL, max}}^{\text{a}}$ (nm)	$\lambda_{\text{PL, exc, max}}^{\text{b}}$ (nm)
86 (Solution)	423	494	428
86 (Thin film)	422	550	423
87 (Solution)	430	494	437
87 (Thin film)	427	509	422

^a Excitation wavelength at λ_{absmax} , ^b emission wavelength at λ_{PLmax} .

CV measurements of thin films of **86** and **87** coated on Pt electrode were recorded in order to obtain information about the electronic nature of the copolymers (Figure 3.54). Quasi-reversible oxidation and reduction waves were detected. Electrochromic properties of copolymers were summarized in Table 3.11. HOMO and LUMO values of - 5.39 and - 2.81 eV, respectively, were calculated for **86**. Compound **87** had HOMO of - 5.47 and LUMO of - 2.92 eV. The electrochemical band gaps of 2.58 and 2.55 eV were estimated for **86** and **87**, respectively. Electrochemical and optical band gaps determined for thin films are in good agreement.

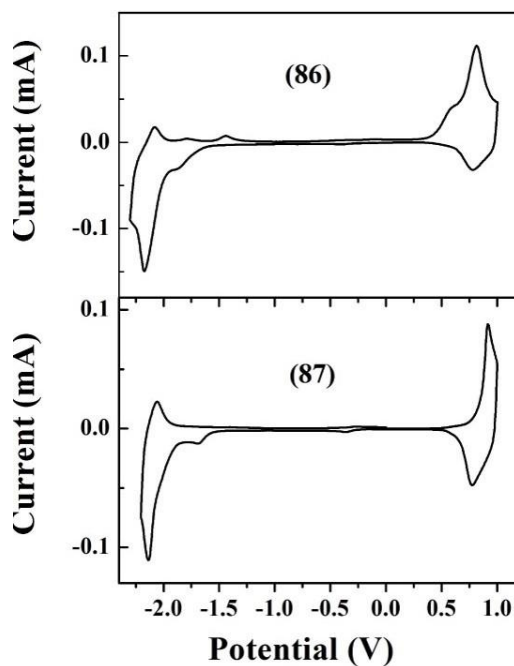
**Figure 3.54** : Cyclic voltammograms of **86** and **87**.

Table 3.11 : Electrochromic properties of **86** and **87**.

Copolymer	HOMO ^a (eV)	LUMO ^a (eV)	E_g^b (eV)	E_g^{opt} (eV)
86	-5.39	-2.81	2.58	2.58
87	-5.47	-2.92	2.55	2.55

^a Calculated using the empirical equation: $HOMO$ (or $LUMO$)(eV) = $-(E_{onset} + 4.8)$. ^b Difference of LUMO and HOMO.

Polymers were applied in organic light-emitting devices (OLEDs) as an active layer. OLEDs with a hole-injecting electrode were prepared by ITO covered with a PEDOT:PSS layer and an electron-injecting electrode of calcium covered with aluminum (Ca/Al). The EL of the OLEDs were depicted in Figure 3.55. The **87** OLEDs had a greenish EL emission with a maximum of 509 nm and the EL maximum of **86** OLEDs is redshifted to 630 nm.

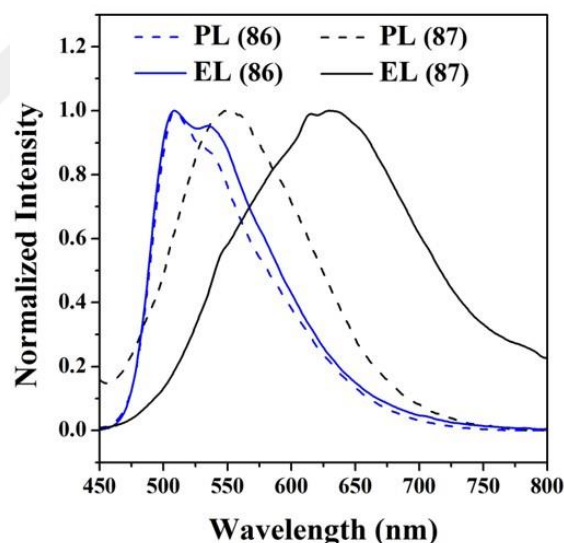


Figure 3.55 : Normalized EL spectra (solid) of the ITO/PEDOT:PSS/**86**/Ca/Al OLEDs (black) and ITO/PEDOT:PSS/**87**/Ca/Al (blue). PL emission spectra of the corresponding thin films (dashed) are displayed for comparison.

Figure 3.56 shows the dependences of current density and luminance on the applied potential measured in ITO/PEDOT:PSS/**86**/Ca/Al and ITO/PEDOT:PSS/**87**/Ca/Al OLEDs. **87** OLEDs shows higher luminance values up to 400 cd m⁻², where saturation occurred, and a lower EL onset voltage than **86** OLEDs.

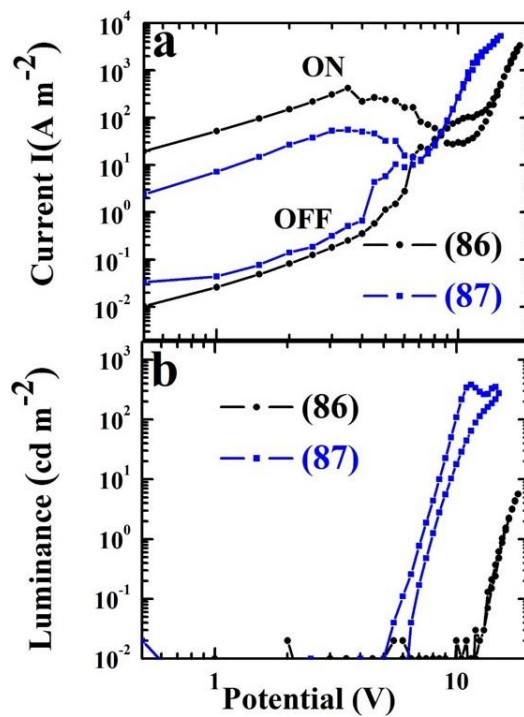


Figure 3.56 : Dependence of current density (a) and luminance (b) on the applied voltage measured on the ITO/PEDOT:PSS/**86**/Ca/Al (circles) and ITO/PEDOT:PSS/**87**/Ca/Al (squares) OLEDs.



4. CONCLUSIONS AND RECOMMENDATIONS

In this study, novel π -conjugated seven novel monomers 4-(2,5-di(thiophen-2-yl)thieno[3,2-*b*]thiophen-6-yl)benzonitrile (**69**), 4-(2,5-bis(4-hexylthiophen-2-yl)thieno[3,2-*b*]thiophen-3-yl)benzonitrile (**70**), 4,4'-(2,6-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (**71**), 4,4'-(dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (**74**), 4,4'-(2,6-di(thiophen-2-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (**76**), 4,4'-(2,6-bis(4-hexylthiophen-2-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (**77**), 4'-(2,6-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (**78**) based on TT and DTT rigid units functionalized with electron-deficient benzonitrile at β -positions and electron-rich thiophene, EDOT and 3-hexylthiophene peripheral groups have been successfully synthesized via Suzuki or Stille cross-coupling reactions. The polymers of the corresponding D–A–D type monomers were produced by electrochemical and oxidative chemical polymerization methods.

Cyclic voltammetry and spectroelectrochemical studies on the polymers were performed in order to investigate the electrochemical and electrochromic properties.

The electrochemical, optical and electronic properties of the polymers synthesized through electrochemical and chemical methods were illustrated in Table 4.1. It is concluded that structural differences of the molecules due to the variations in donor/acceptor moiety affected the monomer oxidation and the polymer redox couple potential and the maximum absorption wavelengths of the corresponding transition. Electron withdrawing and electron donating groups influenced the HOMO and LUMO energy states and thereby E_g of the conjugated polymers. The spectroelectrochemical analysis suggested that the introduction of fused aromatics as an acceptor unit resulted in a red-shift in the π - π^* transition. Intermolecular interactions between the conjugated main chains leads to the reduction of E_g of the solid state conjugated polymers. The conjugated polymers possess relatively small E_g^{opt} of around 1.60–2.46 eV in solution, and 1.64–2.33 eV in solid-state. The photon energies of the polymers should be in the

range of 3.1–1.8 eV in order to absorb solar light [75]. As a result, the polymers synthesized in this study could be suitable materials for solar cell applications.

Table 4.1 : Electrochemical, optical and electronic properties of the polymers.

Polymer	E_{ox} (eV)	E_{red} (eV)	HOMO ^c (eV)	LUMO ^c (eV)	E_g ^d (eV)	UV _{max} λ (nm)	E_g^{opt} (eV)
P69	1.16 ^a / 0.93 ^b	-1.68 ^a / -1.18 ^b	- 5.64	- 3.53	2.11	507 ^e / 653 ^f	1.89 ^{i, j}
P70	0.99 ^a / 0.91 ^b	-1.89 ^a / -1.43 ^b	- 5.62	- 3.28	2.34	443 ^e / 566 ^f	2.18 ^{i, j}
P71	0.56 ^a / 0.31 ^b	-1.84 ^a / -1.33 ^b	- 5.02	- 3.38	1.64	579 ^e / 691 ^f	1.79 ^{i, j}
P74	1.19 ^a / 0.88 ^b	-1.41 ^a / -1.04 ^b	- 5.59	- 3.67	1.92	449 ^e / 528 ^f	2.34 ^{i, j}
P76	1.06 ^a / 0.76 ^b	-1.69 ^a / -1.11 ^b	- 5.47	- 3.60	1.87	452 ^e / 600 ^f	2.06 ^{i, j}
P77	1.05 ^a / 0.89 ^b	-1.67 ^a / -1.22 ^b	- 5.60	- 3.49	2.11	454 ^e / 592 ^f	2.09 ^{i, j}
P78	0.58 ^a / 0.099 ^b	-1.92 ^a / -1.34 ^b	- 4.81	- 3.37	1.44	578 ^e / 725 ^f	1.71 ^{i, j}
79	1.35 ^a / 0.93 ^b	-1.66 ^a / -1.04 ^b	- 5.64	- 3.67	1.97	458 ^e , 548 ^f / 490 ^g , 667 ^h	2.26 ^{i, j} / 1.86 ^{i, k}
80	1.74 ^a / 0.72 ^b	-1.70 ^a / -1.19 ^b	- 5.43	- 3.52	1.91	451 ^e , 564 ^f / 446 ^g , 572 ^h	2.19 ^{i, j} / 2.16 ^{i, k}
81	1.16 ^a / 0.98 ^b	-1.87 ^a / -1.28 ^b	-5.69	-3.43	2.26	425 ^e , 493 ^f / 447 ^g , 573 ^h	2.51 ^{i, j} / 2.16 ^{i, k}
82	0.81 ^a / 0.36 ^b	-1.79 ^a / -1.49 ^b	-5.07	-3.22	1.85	558 ^e , 735 ^f / 437 ^g , 674 ^h	1.69 ^{i, j} / 1.84 ^{i, k}
83	1.19 ^a / 0.88 ^b	-1.41 ^a / -1.04 ^b	-5.59	- 3.67	1.92	439 ^e , 513 ^f / 446 ^g , 566 ^h	2.41 ^{i, j} / 2.18 ^{i, k}
84	1.51 ^a / 1.04 ^b	-1.69 ^a / -1.59 ^b	-5.75	-3.12	2.63	433 ^e , 503 ^f / 440 ^g , 533 ^h	2.46 ^{i, j} / 2.33 ^{i, k}
85	1.10 ^a / 0.22 ^b	-1.56 ^a / -1.34 ^b	-4.93	-3.37	1.56	605 ^e , 779 ^f / 596 ^g , 757 ^h	1.60 ^{i, j} / 1.64 ^{i, k}

^a Oxidation and reduction maxima. ^b Onset of oxidation and reduction. ^c Calculated using the empirical equation: $HOMO$ (or $LUMO$)(eV) = $-(E_{onset} + 4.71)$. ^d Difference of LUMO and HOMO. ^e Absorption maxima of the polymer in solvent. ^f Onset of the absorption of the polymer in solvent. ^g Absorption maxima of the polymer film coated on ITO. ^h Onset of the absorption of the polymer film coated on ITO. ⁱ $E_g^{opt} = \frac{hc}{\lambda_{onset}}$. ^j From the onset absorption of polymer in solvent. ^k From the onset absorption of polymer film coated on ITO.

The lowest band gaps were obtained for polymers decorated with EDOT (**P71**, **P78**, **82** and **85**). Planar anti conformation of the thiophene rings are stabilized by S $\cdots$ O intramolecular interactions to give the polymer more rigid structure [89,90,152] (Figure 4.1). In addition, both the β positions to sulfur are substituted, polymerization proceeds through α positions to produce linear polymers.

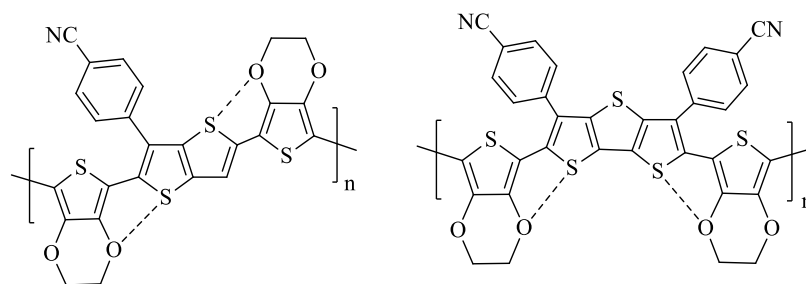


Figure 4.1 : Intramolecular interactions of S and O in TT and DTT polymers.

Figure 4.2 shows the correlation of band gaps with HOMO energy levels of chemical polymers. The polymers (**85** and **82**) with strong electron-donating group EDOT have the smallest E_g (1.56 and 1.85 eV) with highest HOMO levels (-4.93 and -5.07 eV). The polymers (**81** and **84**) possessing 3-hexylthiophene have the highest E_g (2.26 and 2.63 eV) and lowest HOMO levels (-5.69 and -5.75 eV), the alkyl groups on 3-hexylthiophene caused the steric hindrance on polymer chain resulting in deviation from planarity, less ordered and less conjugation and consequently the increase in the band gaps of polymers.

In D–A systems, use of electron-withdrawing and electron-donating groups reduces E_g by decreasing the LUMO level and increasing HOMO level, respectively. The final E_g is the summation or the combination of the influence of both effects. The intensive interaction between donor and acceptor units improves double bond character or the quinoidal structure of the conjugated polymer causing a small E_g .

P(F-TT) (**86**) and P(F-DTT) (**87**) were synthesized and their photophysical, electrochemical and electroluminescent (EL) properties were investigated by Polymer Photonics group in Institute of Macromolecular Chemistry, The Czech Academy of Sciences. HOMO and LUMO values of - 5.54 and - 2.58 eV were estimated for P(F-TT) (**86**) and -5.57 and -2.92 eV for P(F-DTT) (**87**) , respectively. **86** and **87** were applied as active layers in polymer OLEDs. OLEDs with **87** as an active layer had a better performance than OLEDs with **86**.

As a result, electrochemical and optoelectrochemical features of the π -conjugated polymers can be fine-tuned by altering the nature of acceptor and donor groups.



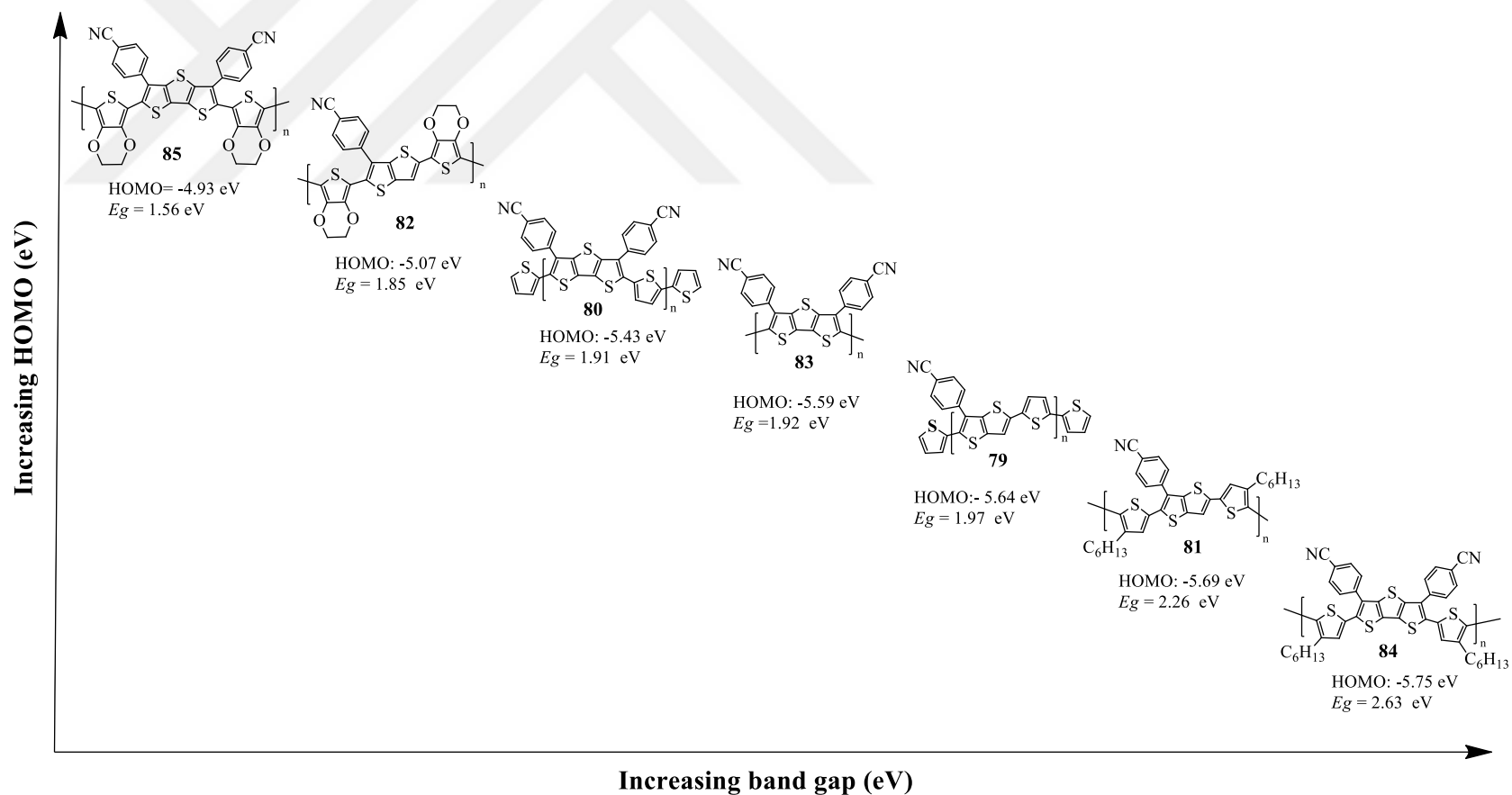


Figure 4.2 : Correlation of band gaps with HOMO energy levels of chemical polymers.



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APPENDICES

APPENDIX A: Selected FT IR, NMR and MS data



APPENDIX A

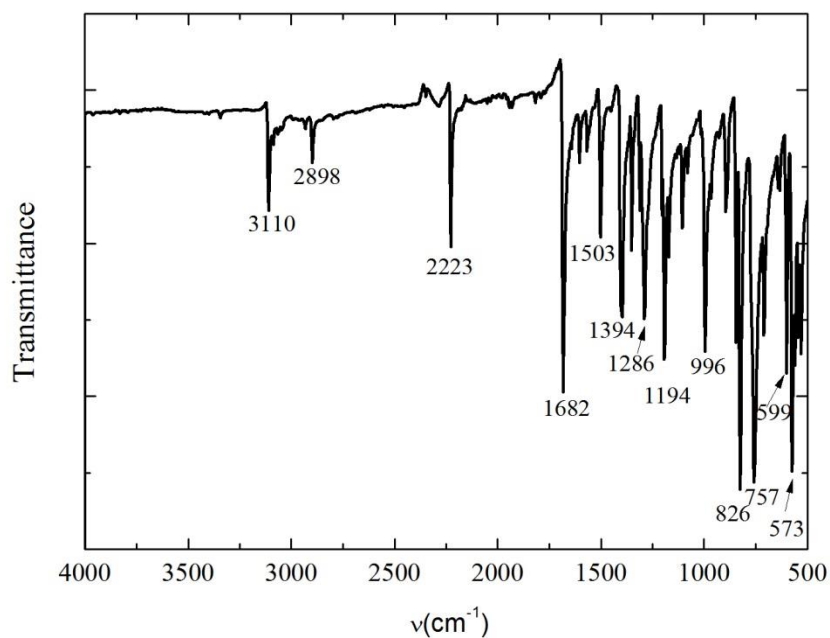


Figure A.1 : FT IR (ATR) of 4-(2-(thiophen-3-ylthio)acetyl)benzonitrile (**66**).

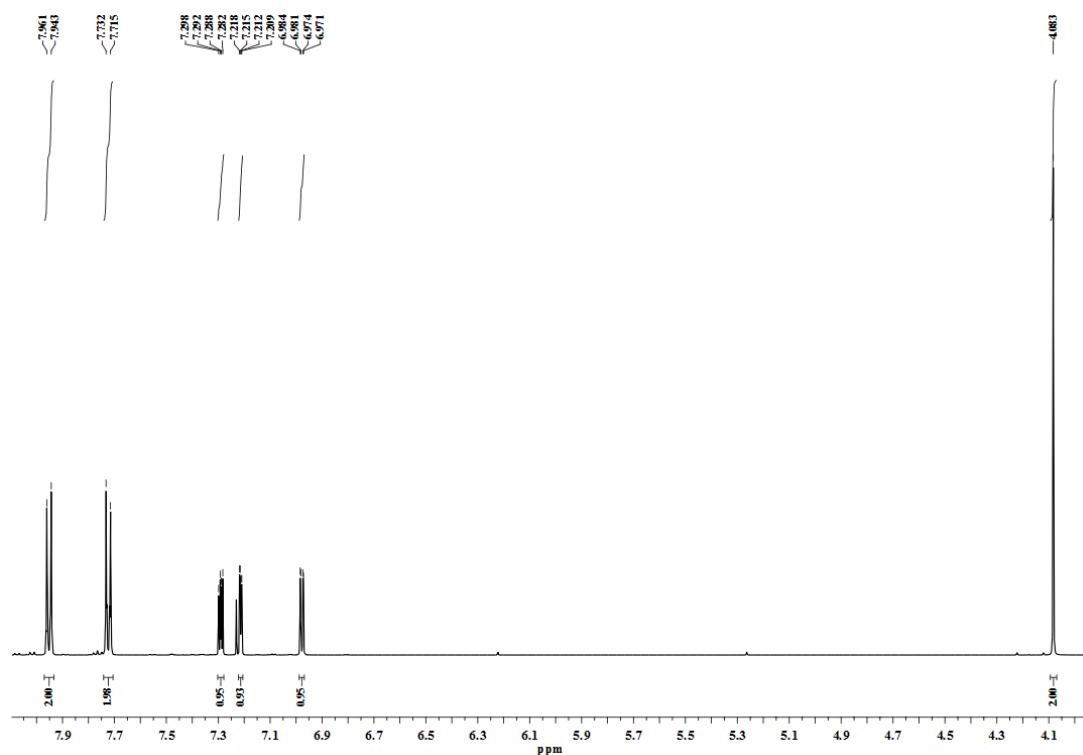


Figure A.2 : ^1H NMR (500 MHz) of 4-(2-(thiophen-3-ylthio)acetyl)benzonitrile (**66**) in CDCl_3 .

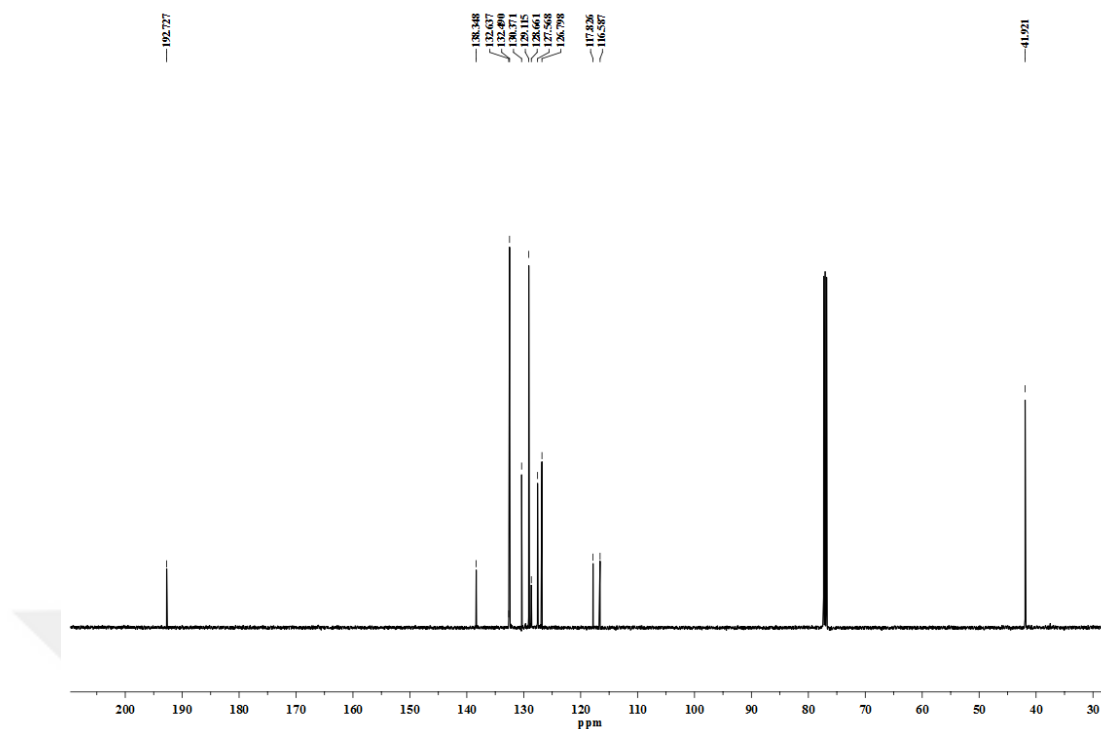


Figure A.3 : ^{13}C NMR (126 MHz) of 4-(2-(thiophen-3-ylthio)acetyl)benzonitrile (**66**) in CDCl_3 .

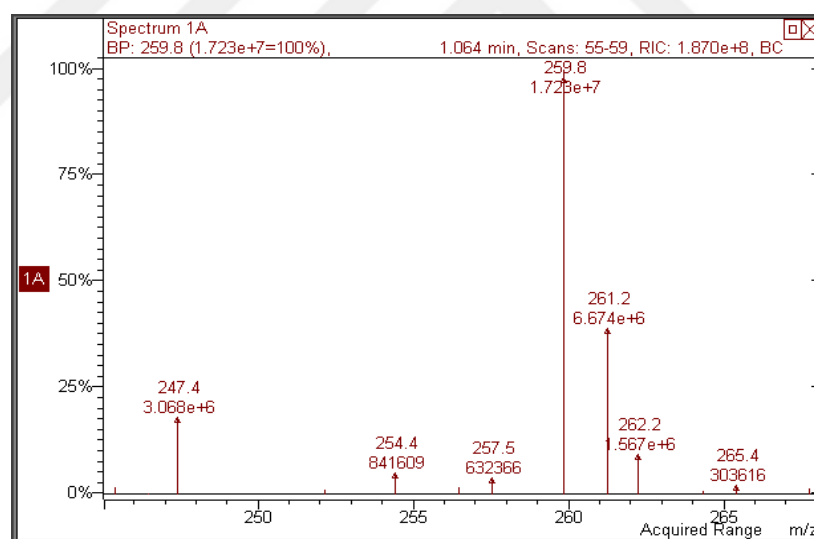


Figure A.4 : MS of 4-(2-(thiophen-3-ylthio)acetyl)benzonitrile (**66**).

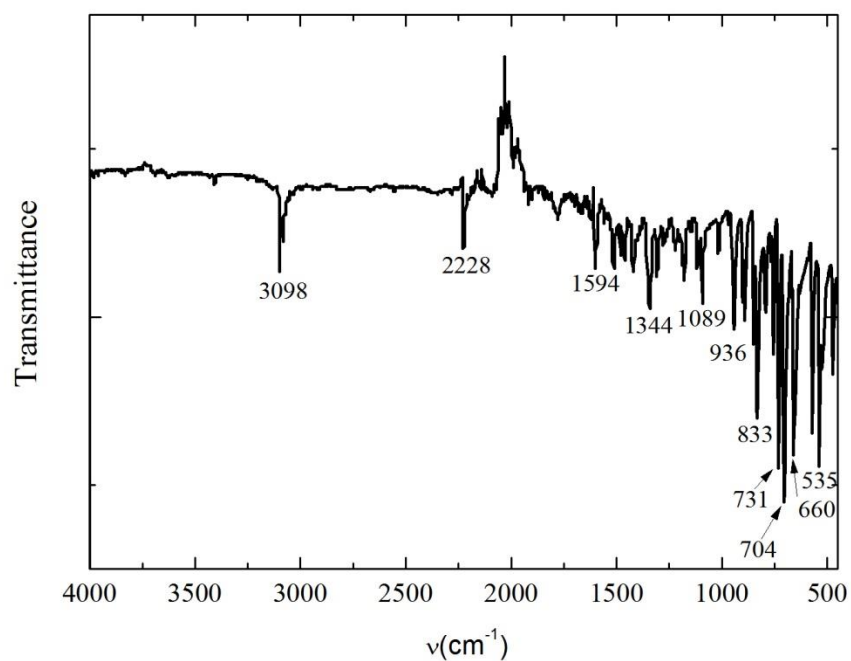


Figure A.5 : FT IR (ATR) of 4-(thieno[3,2-*b*]thiophen-3-yl)benzonitrile (**67**).

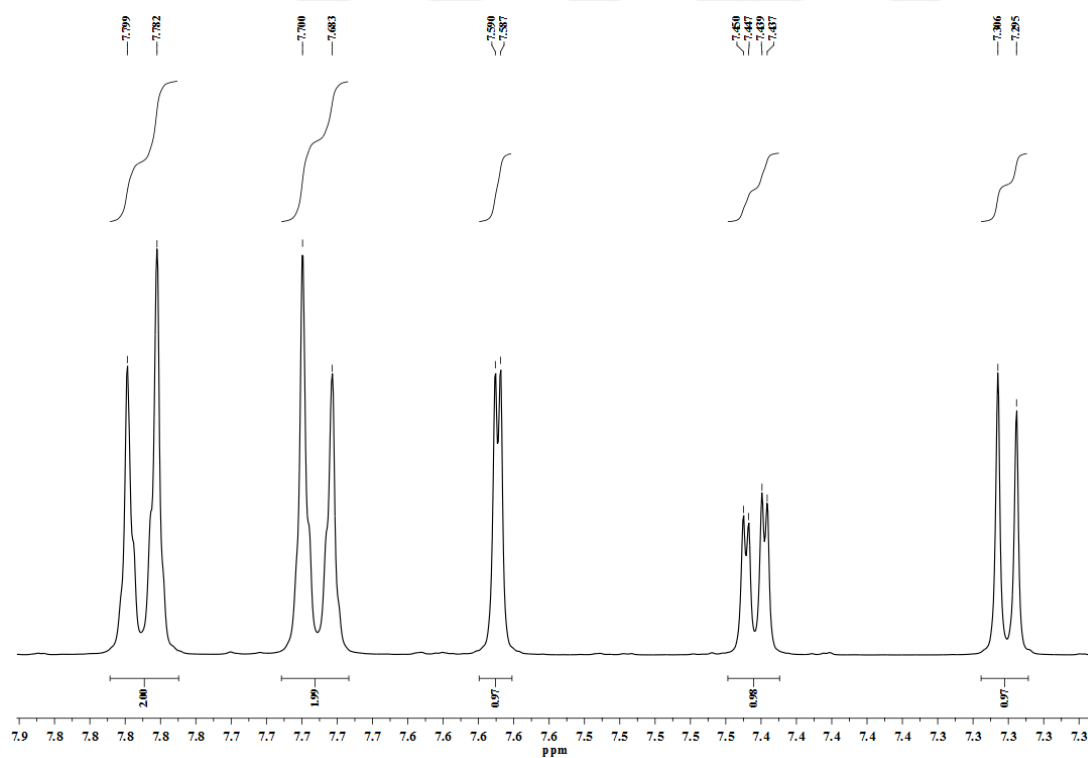


Figure A.6 : ^1H NMR (500 MHz) 4-(thieno[3,2-*b*]thiophen-3-yl)benzonitrile (**67**) in CDCl_3 .

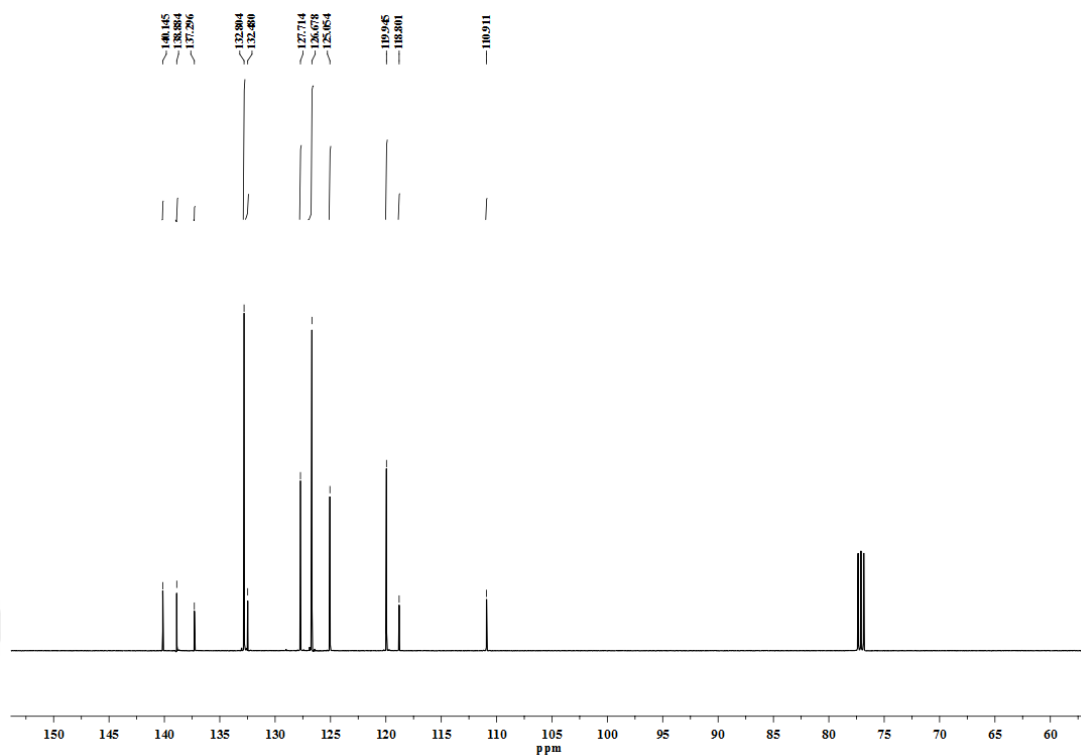


Figure A.7 : ^{13}C NMR (126 MHz) of 4-(thieno[3,2-*b*]thiophen-3-yl)benzonitrile (**67**) in CDCl_3 .

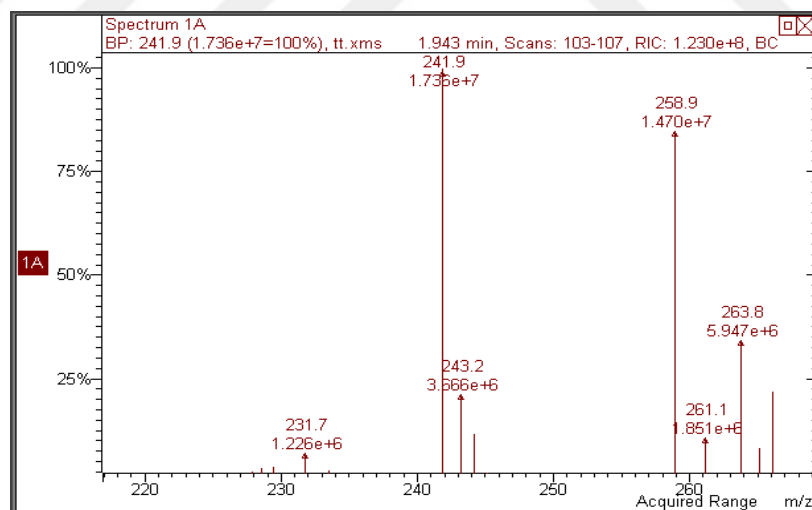


Figure A.8 : MS of 4-(thieno[3,2-*b*]thiophen-3-yl)benzonitrile (**67**).

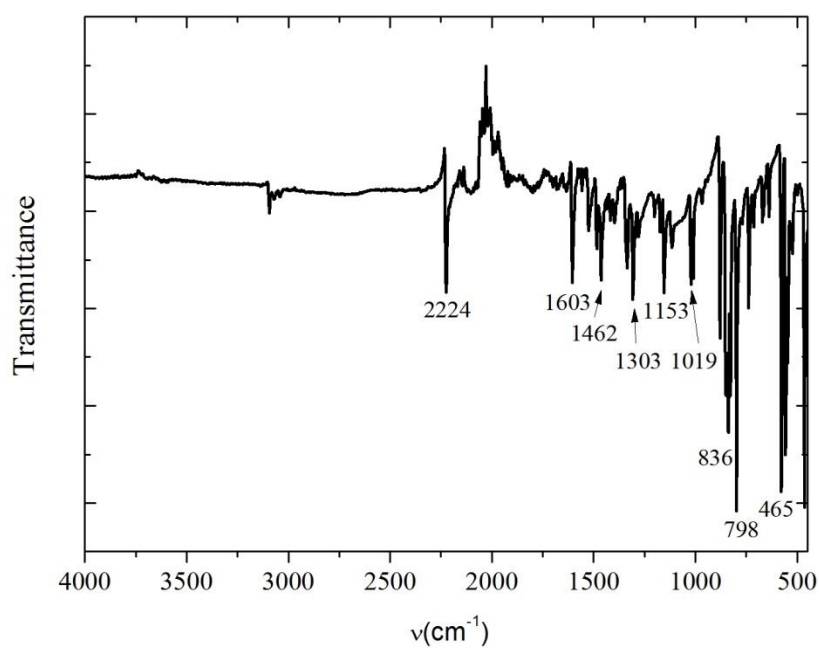


Figure A.9 : FT IR (ATR) of 4-(2,5-dibromothieno[3,2-*b*]thiophen-6-yl)benzonitrile (**68**).

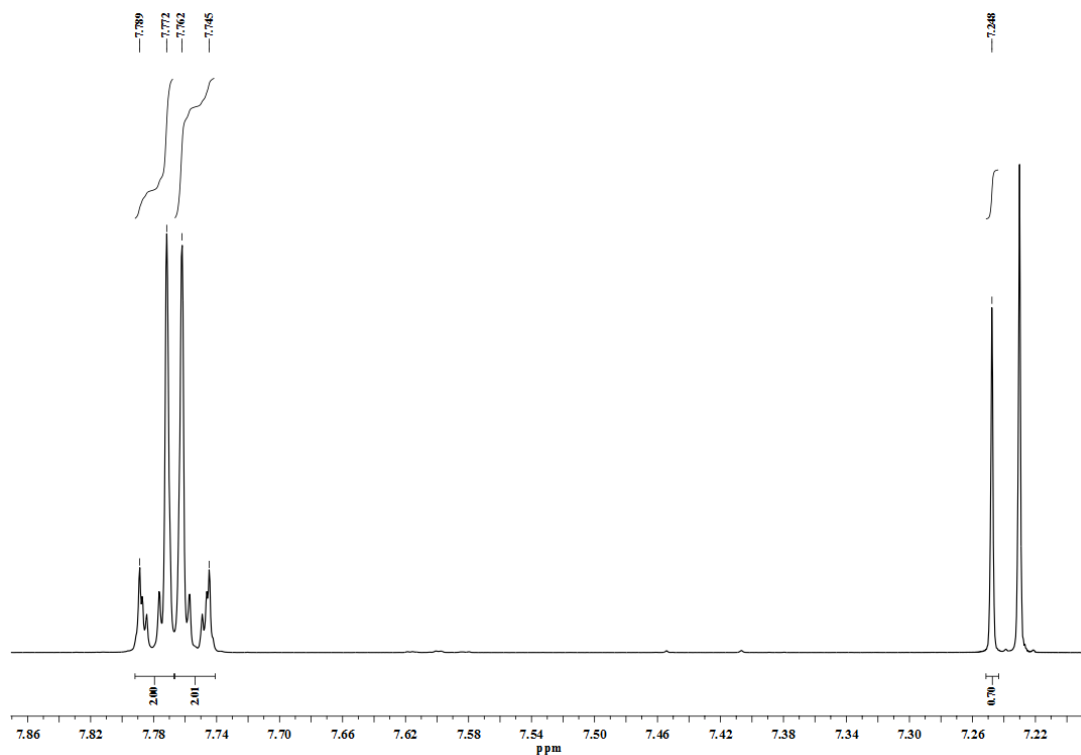


Figure A.10 : ^1H NMR (500 MHz) of 4-(2,5-dibromothieno[3,2-*b*]thiophen-6-yl)benzonitrile (**68**) in CDCl_3 .

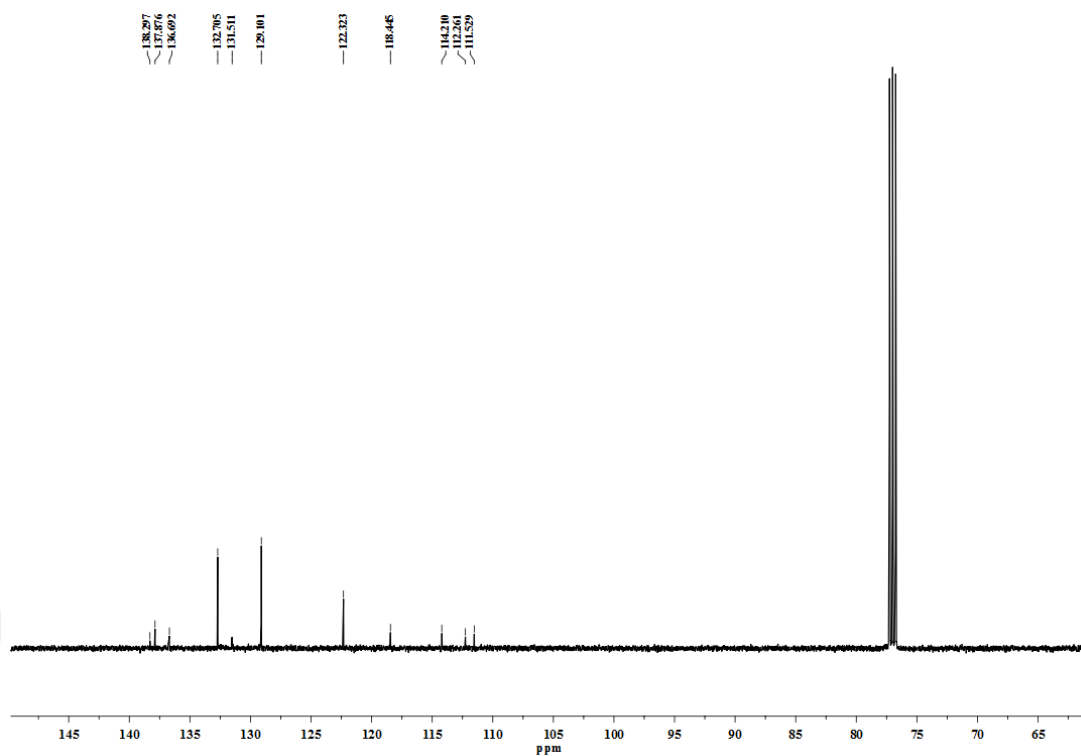


Figure A.11 : ^{13}C NMR (126 MHz) of 4-(2,5-dibromothieno[3,2-*b*]thiophen-6-yl)benzonitrile (**68**) in CDCl_3 .

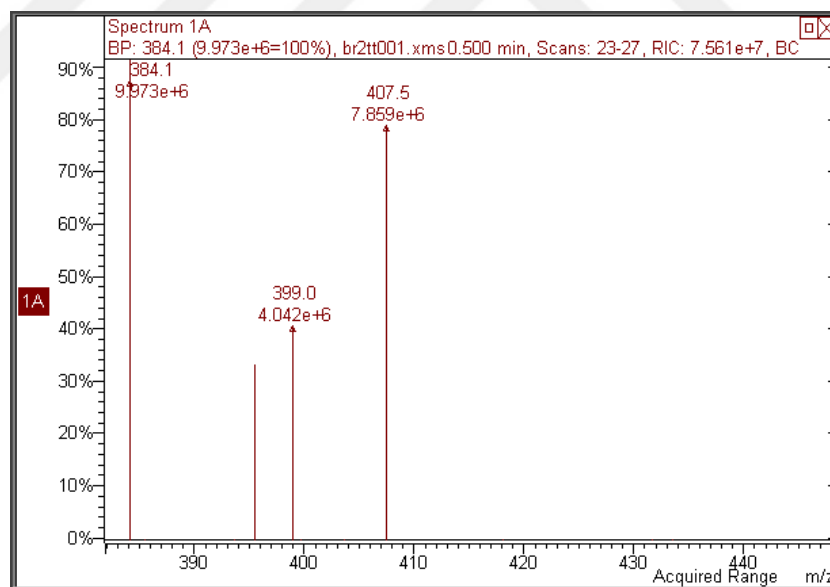


Figure A.12 : MS of 4-(2,5-dibromothieno[3,2-*b*]thiophen-6-yl)benzonitrile (**68**).

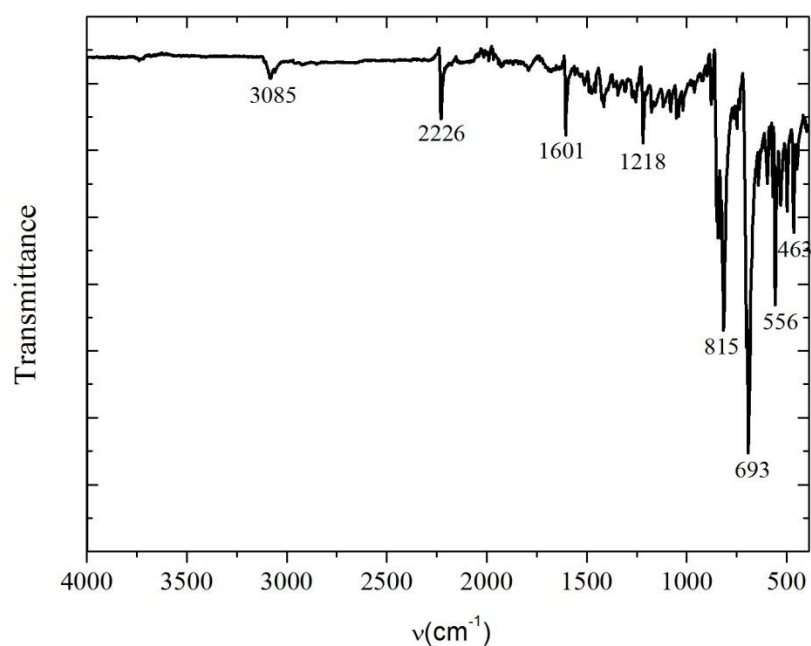


Figure A.13 : FT IR (ATR) of 4-(2,5-di(thiophen-2-yl)thieno[3,2-*b*]thiophen-6-yl)benzonitrile (**69**).

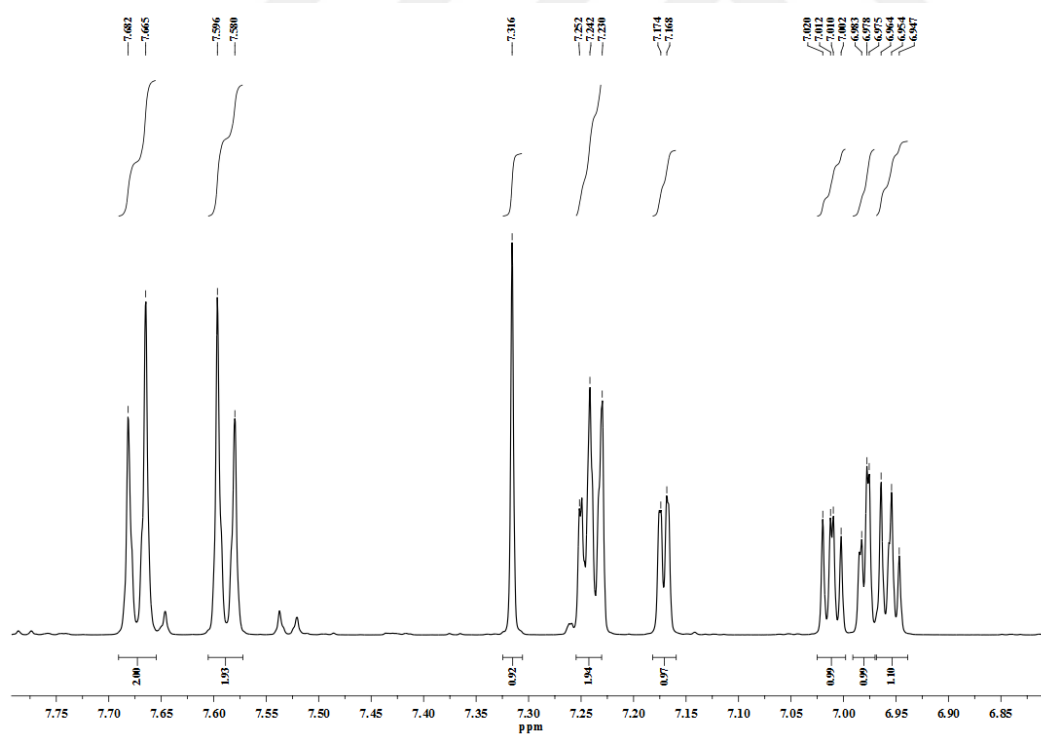


Figure A.14 : ^1H NMR (500 MHz) of 4-(2,5-di(thiophen-2-yl)thieno[3,2-*b*]thiophen-6-yl)benzonitrile (**69**) in CDCl_3 .

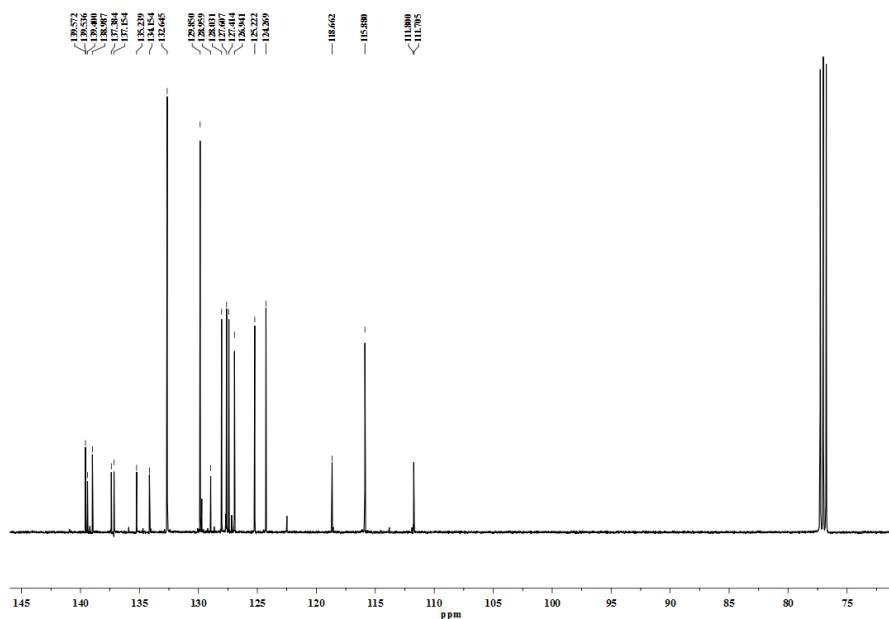


Figure A.15 : ^{13}C NMR (126 MHz) of 4-(2,5-di(thiophen-2-yl)thieno[3,2-*b*]thiophen-6-yl)benzonitrile (**69**) in CDCl_3 .

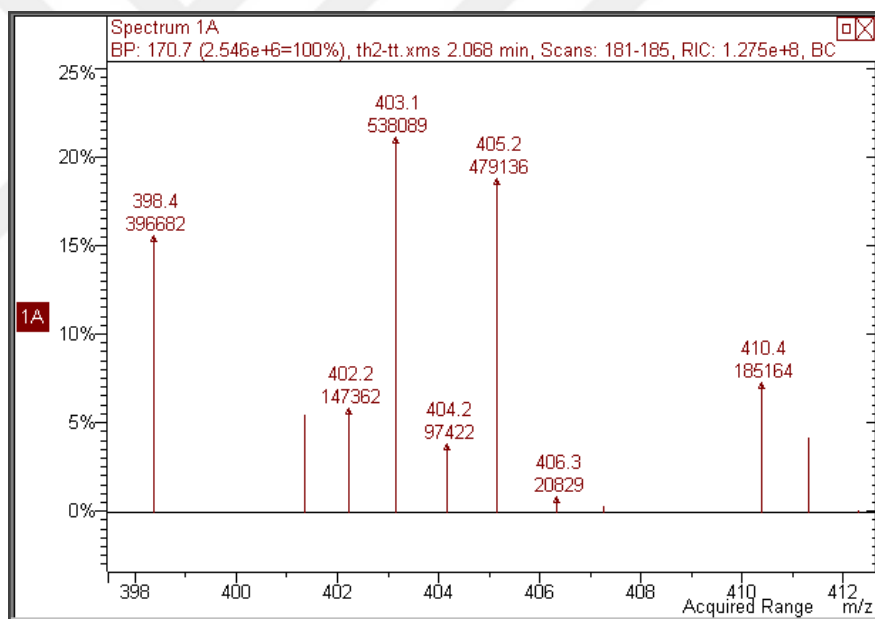


Figure A.16 : MS of 4-(2,5-di(thiophen-2-yl)thieno[3,2-*b*]thiophen-6-yl)benzonitrile (**69**).

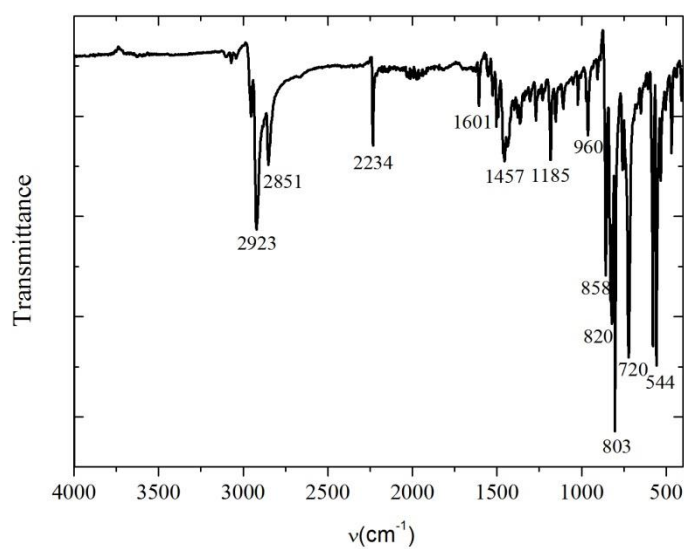


Figure A.17 : FT IR (ATR) of 4-(2,5-bis(4-hexylthiophen-2-yl)thieno[3,2-*b*]thiophen-3-yl)benzonitrile (**70**).

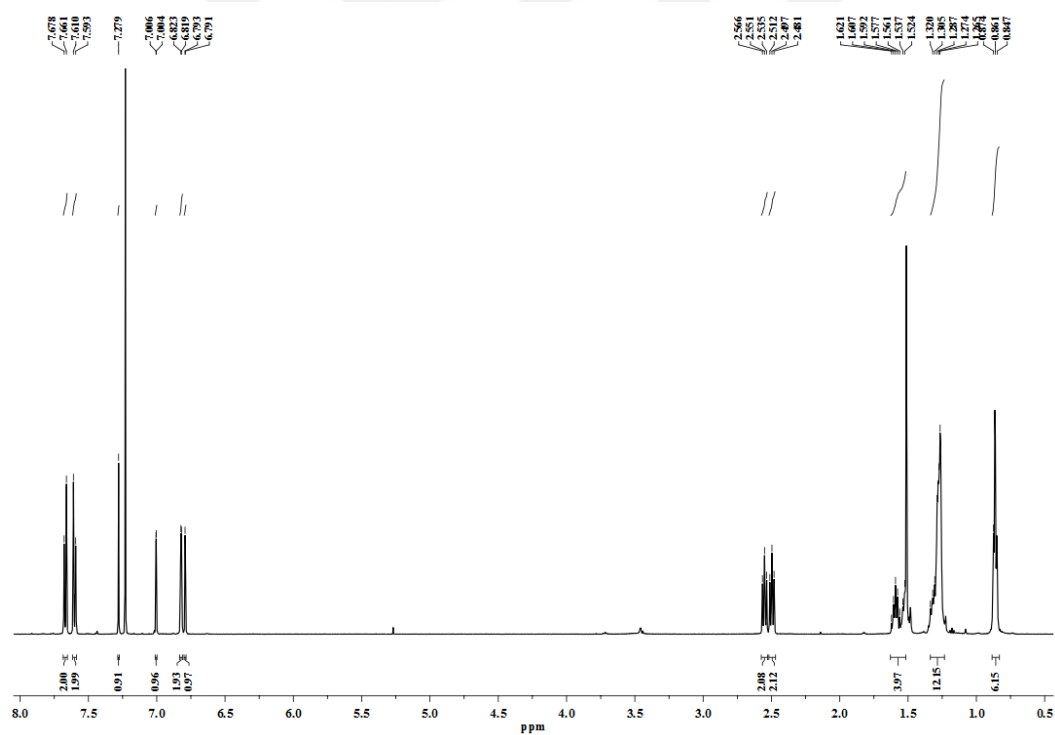


Figure A.18 : ^1H NMR (500 MHz) of 4-(2,5-bis(4-hexylthiophen-2-yl)thieno[3,2-*b*]thiophen-3-yl)benzonitrile (**70**) in CDCl_3 .

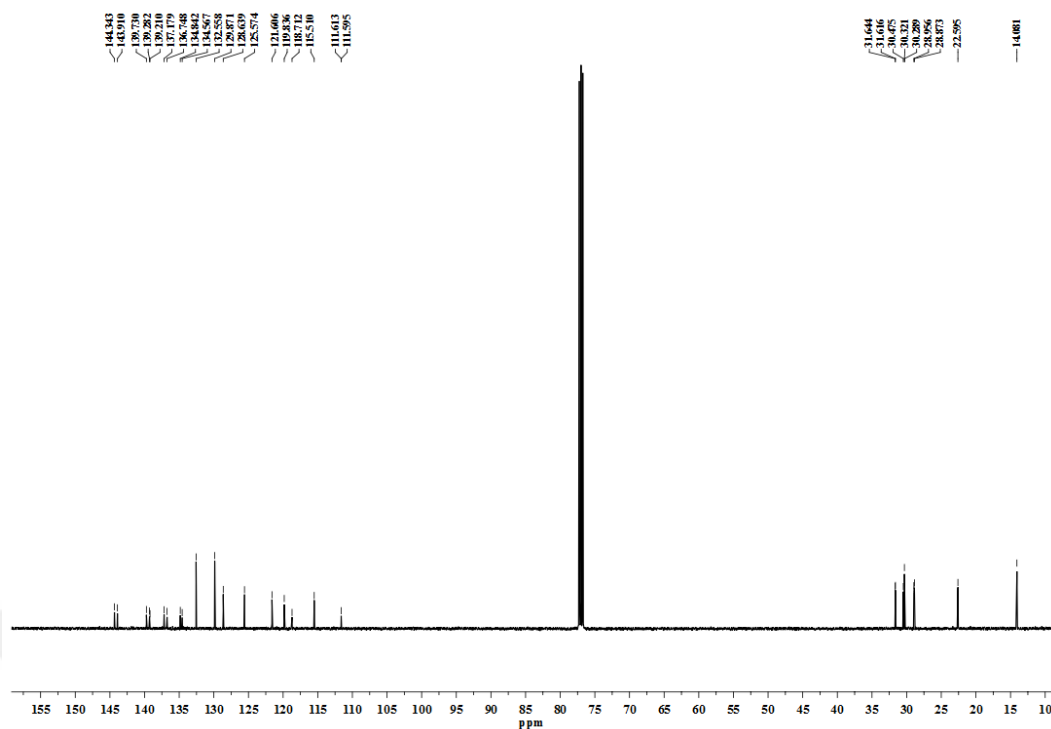


Figure A.19 : ^{13}C NMR (126 MHz) of 4-(2,5-bis(4-hexylthiophen-2-yl)thieno[3,2-*b*]thiophen-3-yl)benzonitrile (**70**) in CDCl_3 .

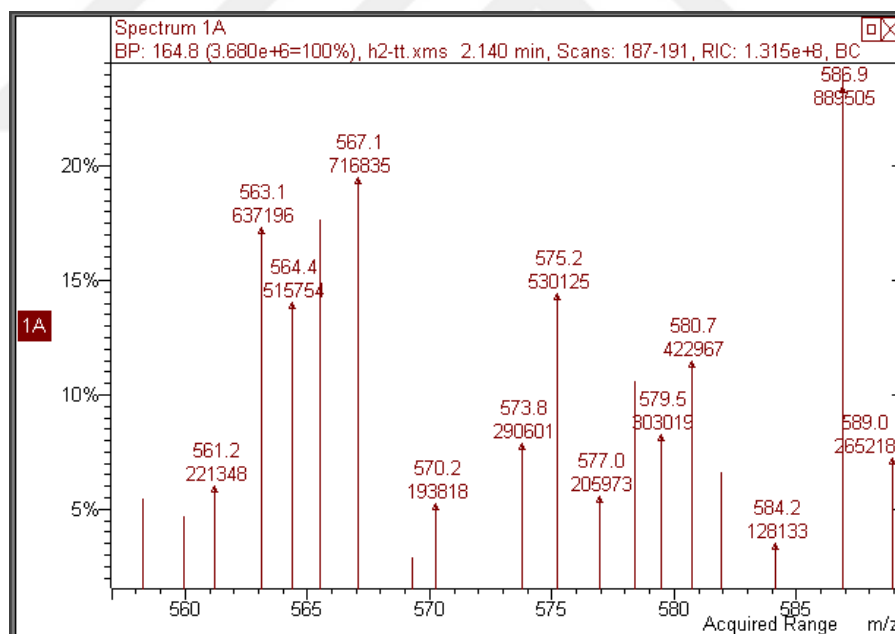


Figure A.20 : MS of 4-(2,5-bis(4-hexylthiophen-2-yl)thieno[3,2-*b*]thiophen-3-yl)benzonitrile (**70**).

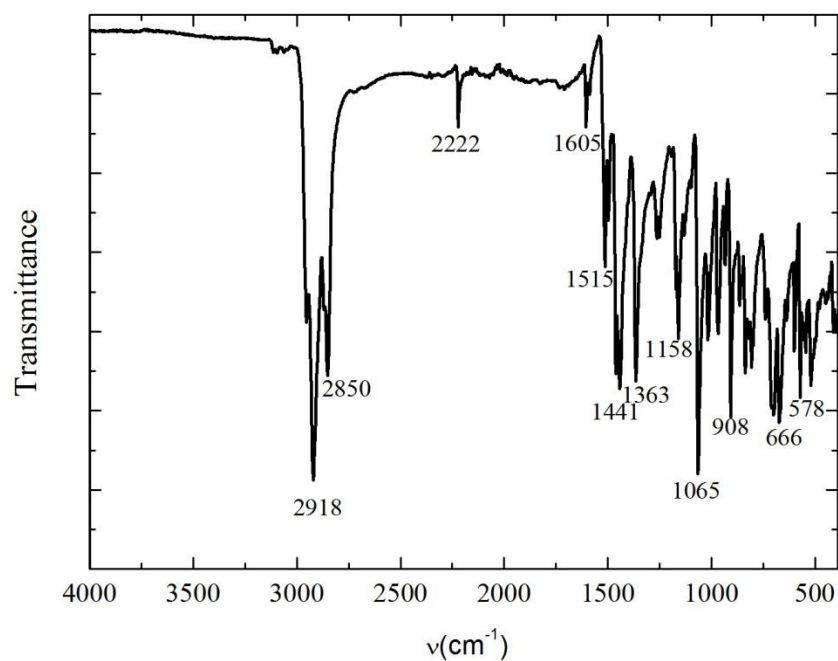


Figure A.21 : FT IR (ATR) of 4,4'-(2,6-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (**71**).

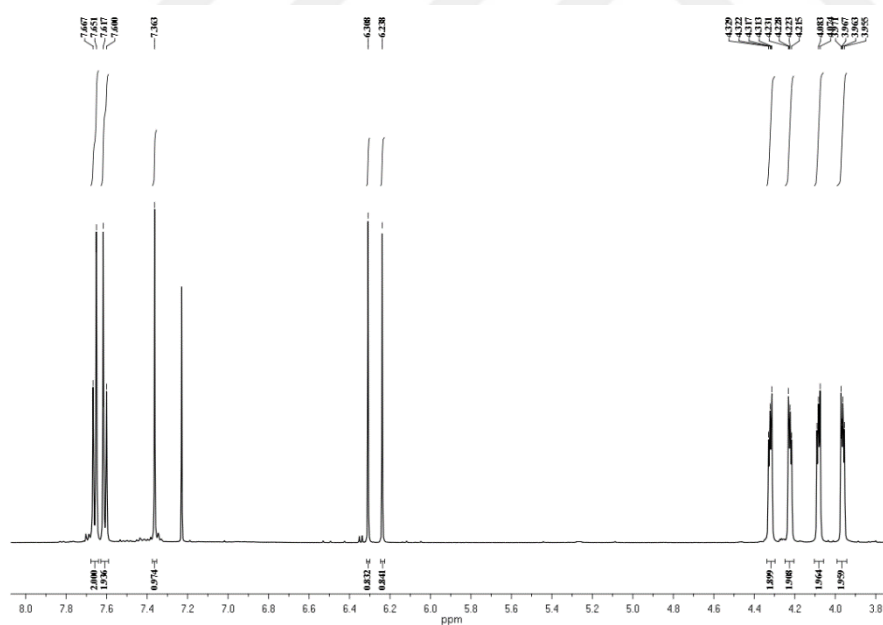


Figure A.22 : ^1H NMR (500 MHz) of 4,4'-(2,6-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (**71**) in CDCl_3 .

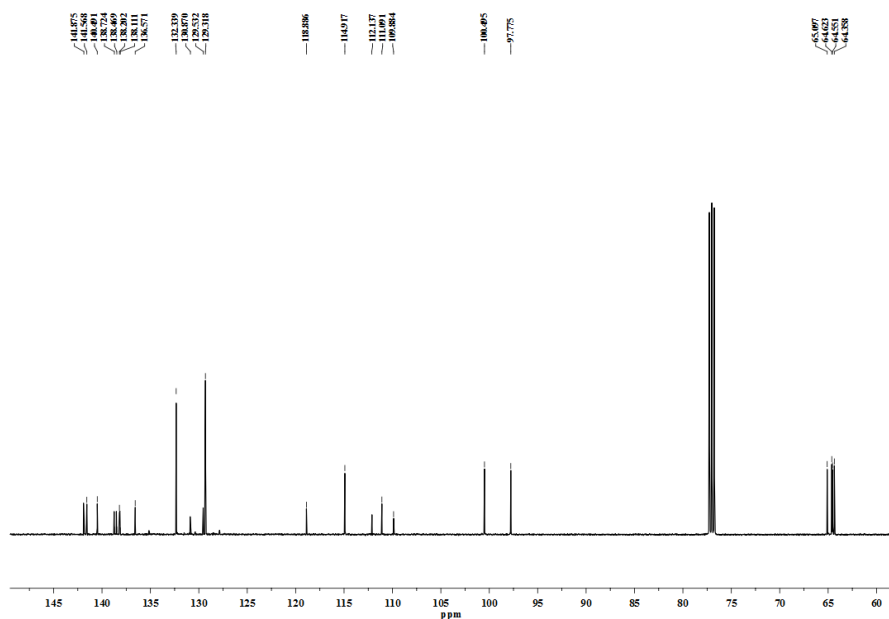


Figure A.23 : ^{13}C NMR (126 MHz) of 4,4'-(2,6-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (**71**) in CDCl_3 .

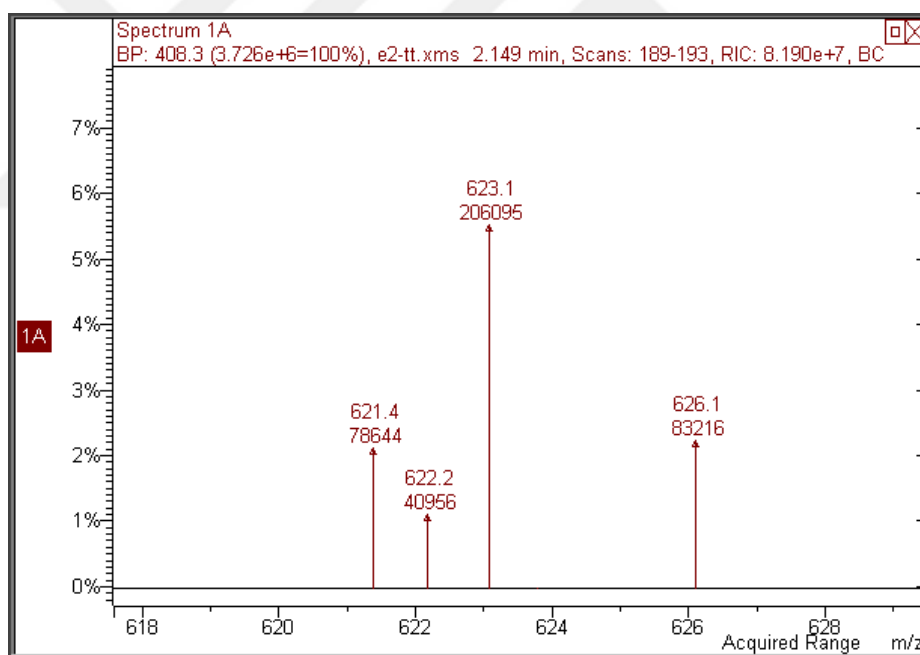


Figure A.24 : MS of 4,4'-(2,6-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (**71**).

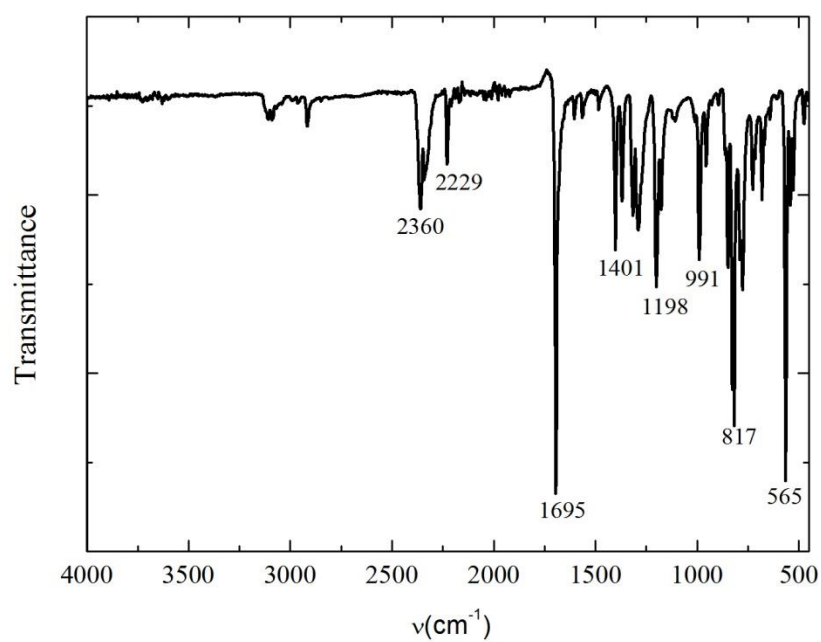


Figure A.25 : FT IR (ATR) of 4,4'-(2,2'-(thiophene-3,4-diylbis(sulfanediyl))bis(acetyl))dibenzonitrile (**73**).

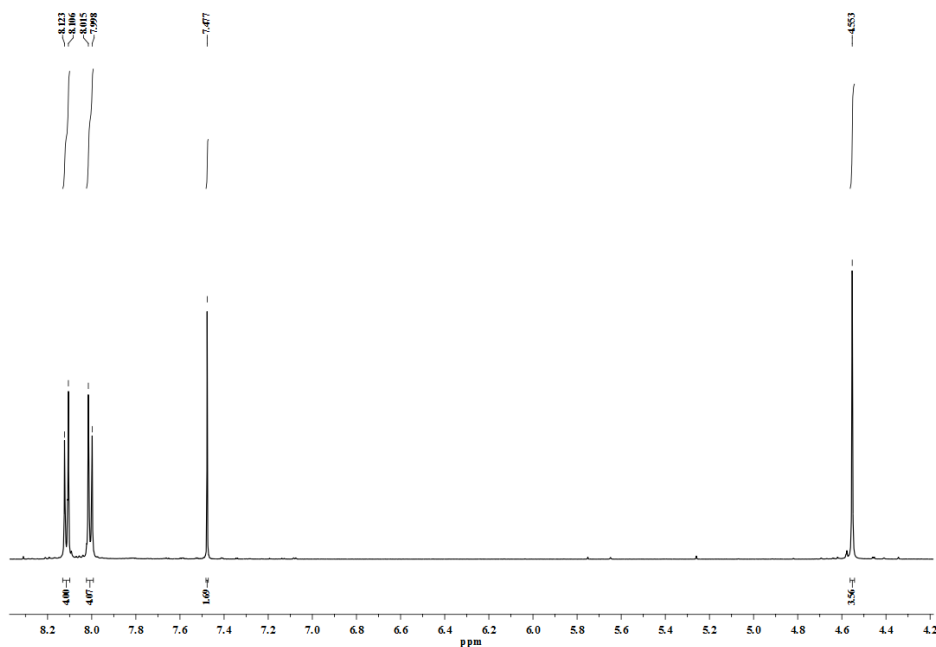


Figure A.26 : ^1H (500 MHz) NMR of 4,4'-(2,2'-(thiophene-3,4-diylbis(sulfanediyl))bis(acetyl))dibenzonitrile (**73**) in $\text{DMSO-}d_6$.

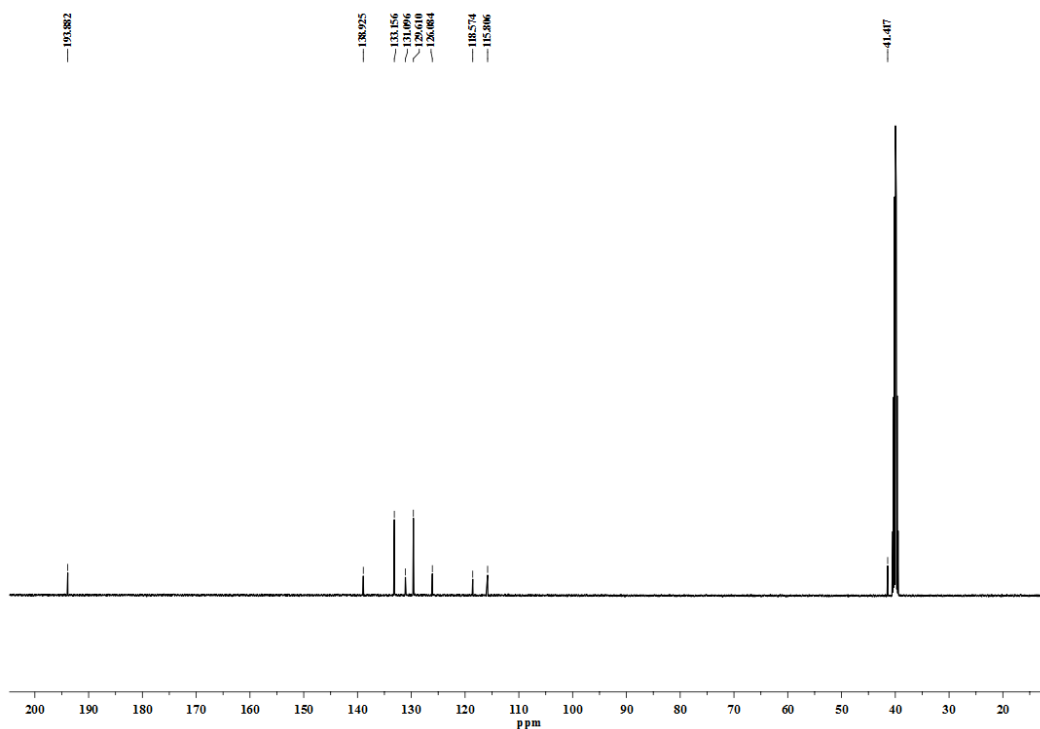


Figure A.27 : ^{13}C NMR of 4,4'-(2,2'-(thiophene-3,4-diylbis(sulfanediyl))bis(acetyl))dibenzonitrile (**73**) in $\text{DMSO-}d_6$.

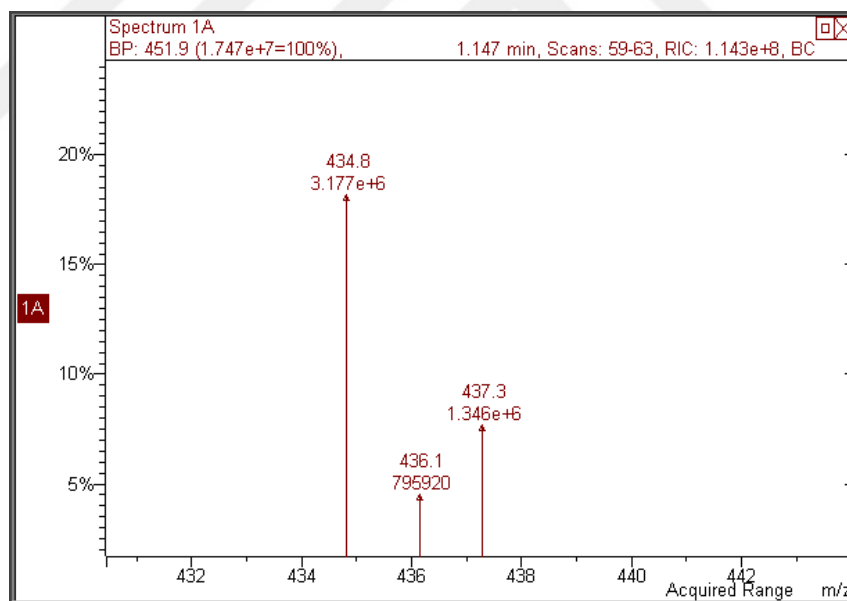


Figure A.28 : MS of 4,4'-(2,2'-(thiophene-3,4-diylbis(sulfanediyl))bis(acetyl))dibenzonitrile (**73**).

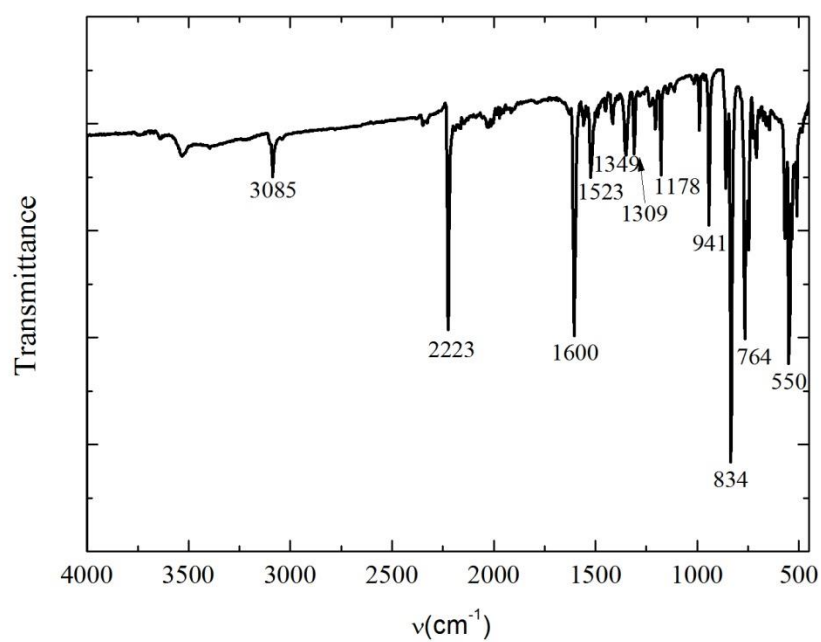


Figure A.29 : FT IR (ATR) of 4,4'-(dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (**74**).

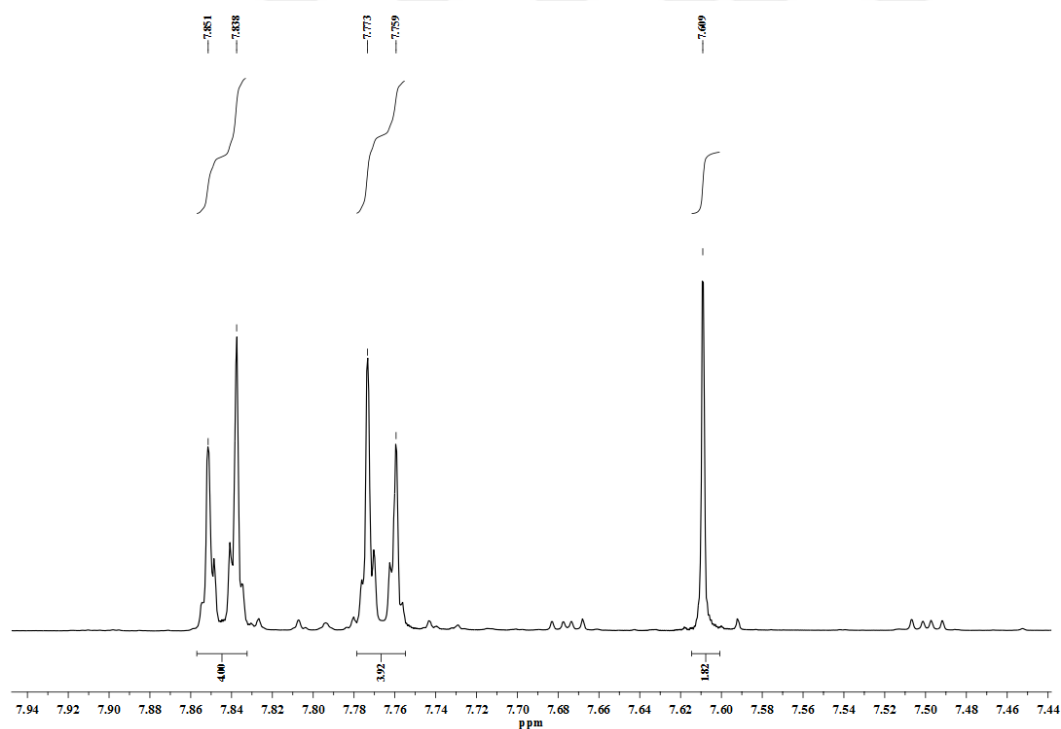


Figure A.30 : ^1H NMR (600 MHz) of 4,4'-(dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (**74**) in CDCl_3 .

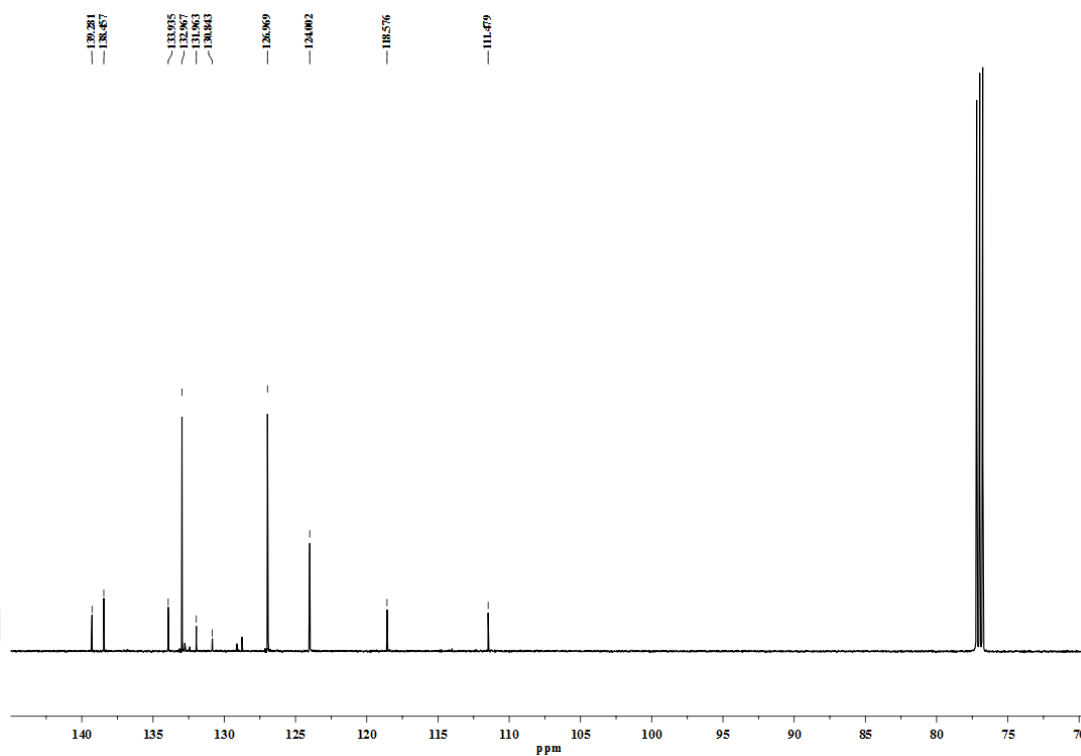


Figure A.31 : ^{13}C NMR (150 MHz) of 4,4'-(dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (**74**) in CDCl_3 .

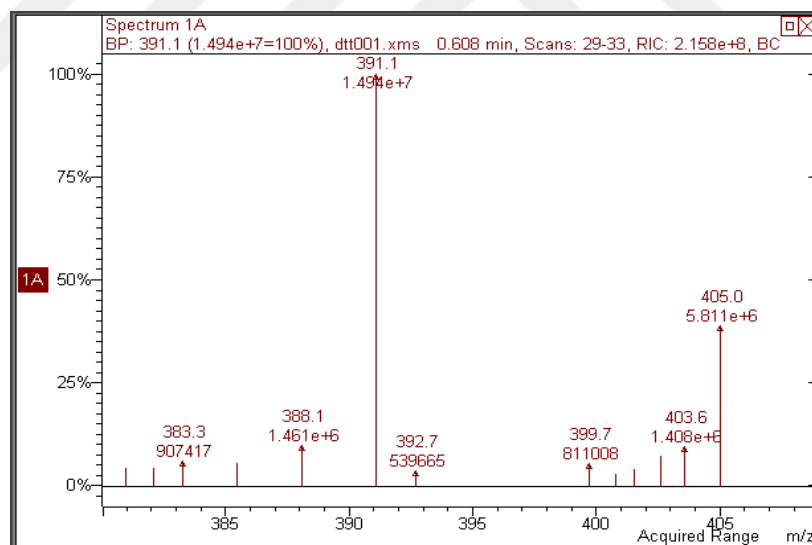


Figure A.32 : MS of 4,4'-(dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (**74**).

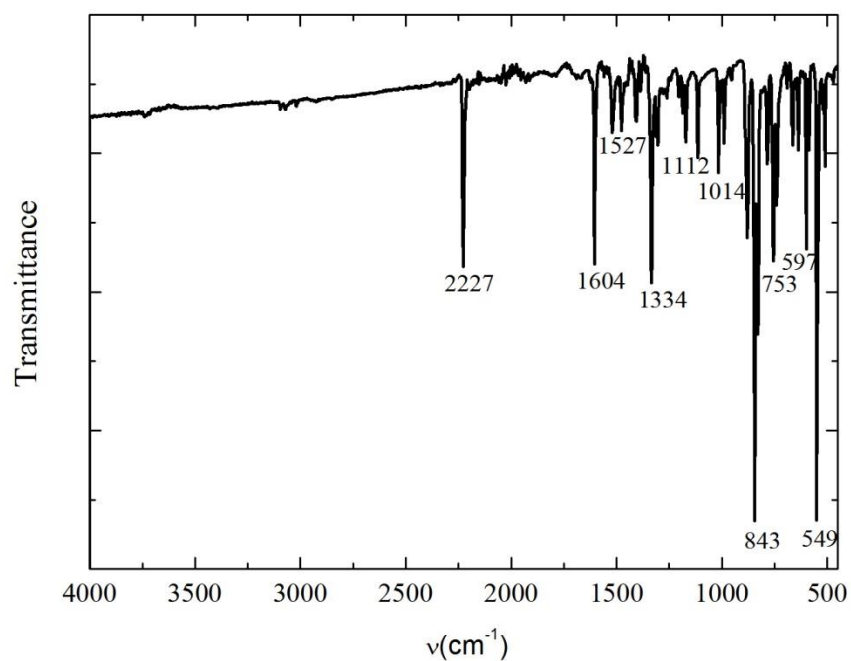


Figure A.33 : FT IR (ATR) of 2,5-dibromo4,4'-(dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (**75**).

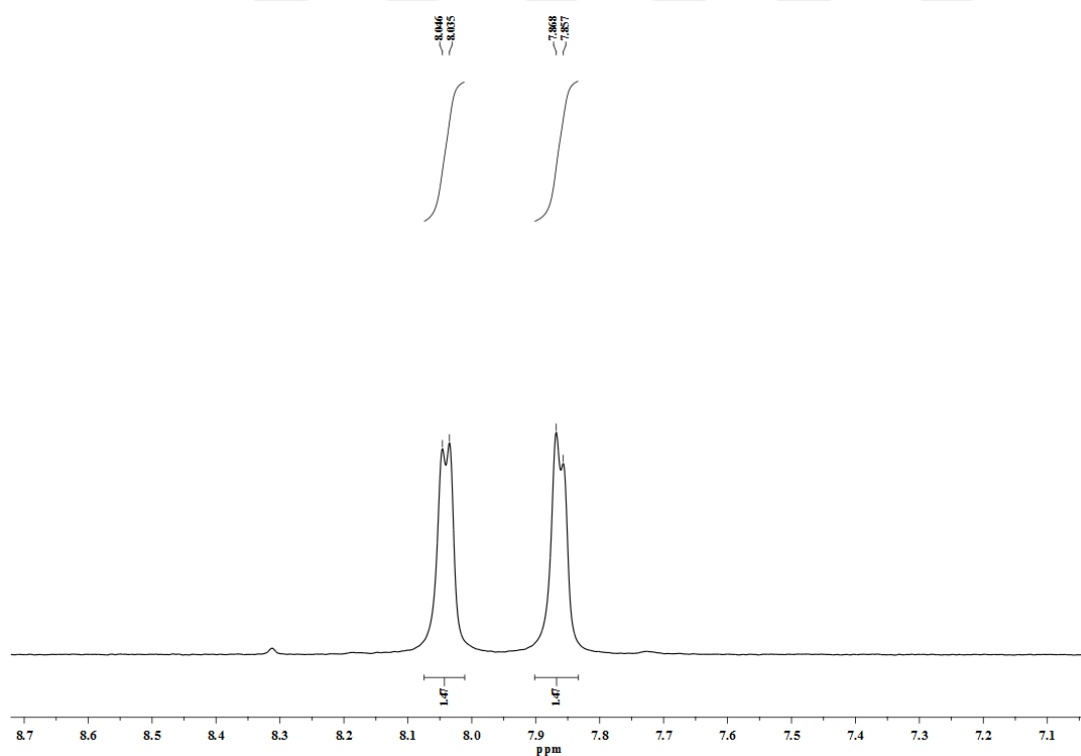


Figure A.34 : ^1H NMR (600 MHz) of 2,5-dibromo4,4'-(dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (**75**) in $\text{DMSO-}d_6$.

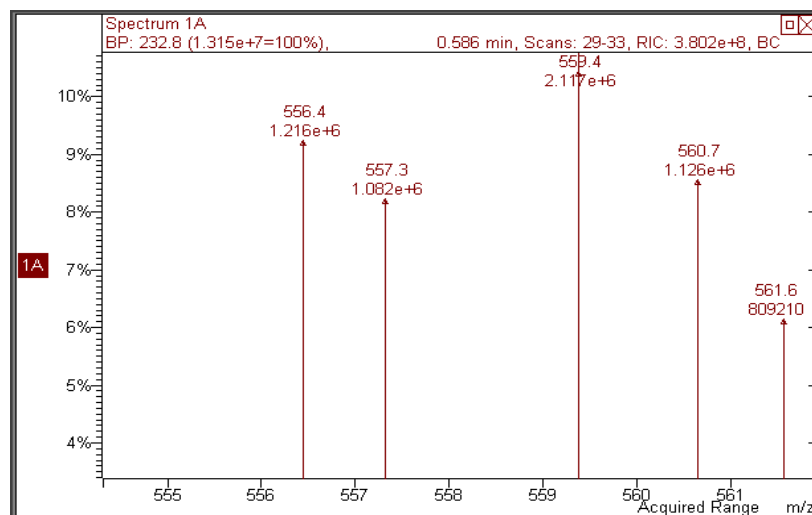


Figure A.35 : MS of 2,5-dibromo-4,4'-(dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (75).

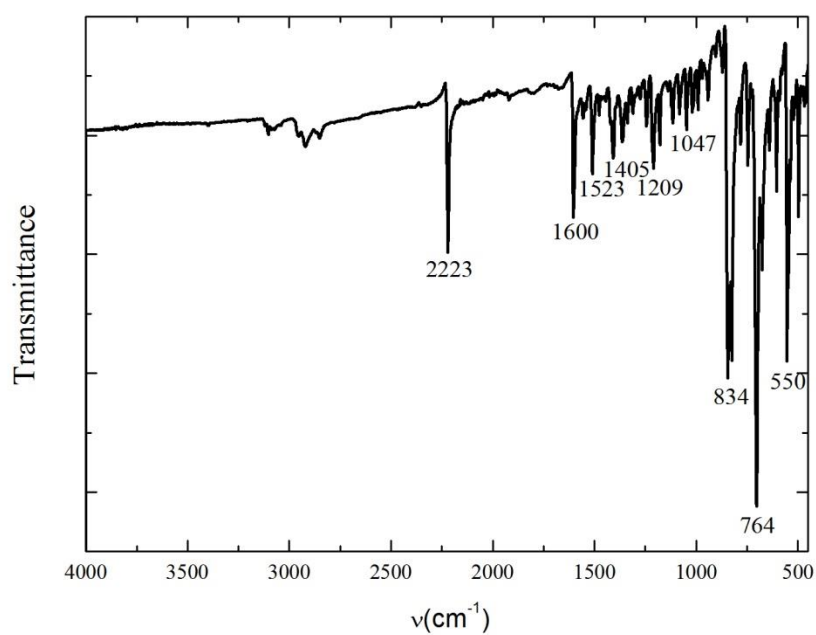


Figure A.36 : FT IR (ATR) of 4,4'-(2,6-di(thiophen-2-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (76).

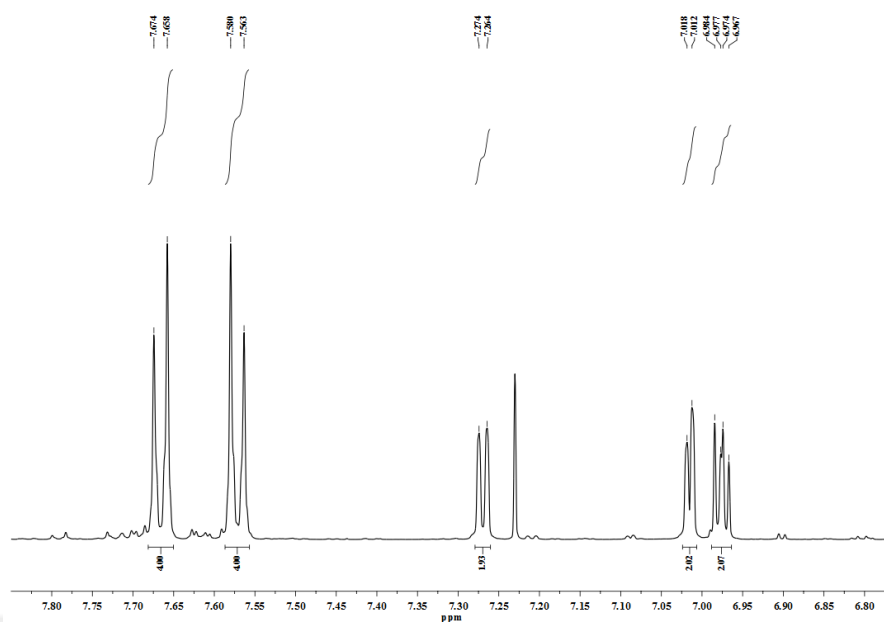


Figure A.37 : ^1H NMR (500 MHz) of 4,4'-(2,6-di(thiophen-2-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (**76**) in CDCl_3 .

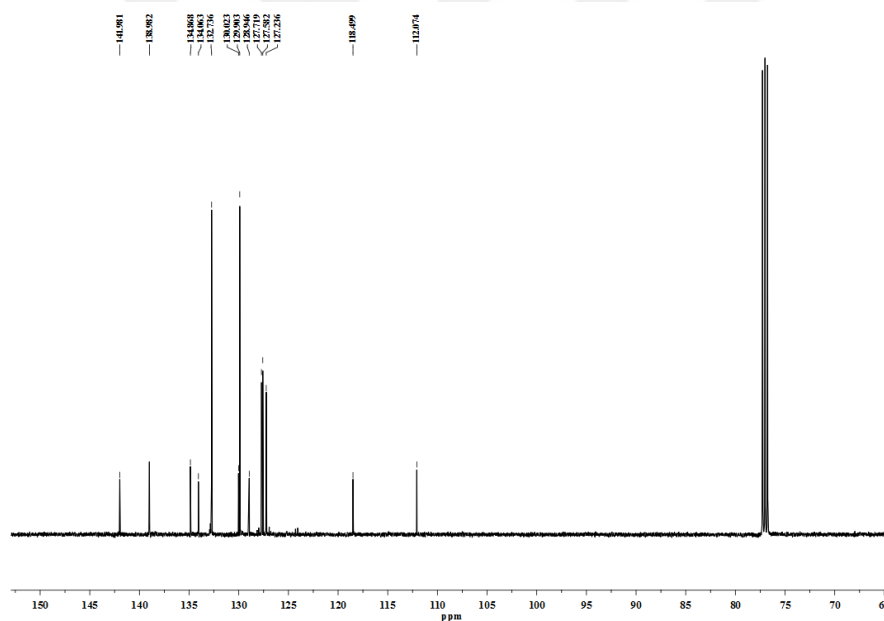


Figure A.38 : ^{13}C NMR (126 MHz) of 4,4'-(2,6-di(thiophen-2-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (**76**) in CDCl_3 .

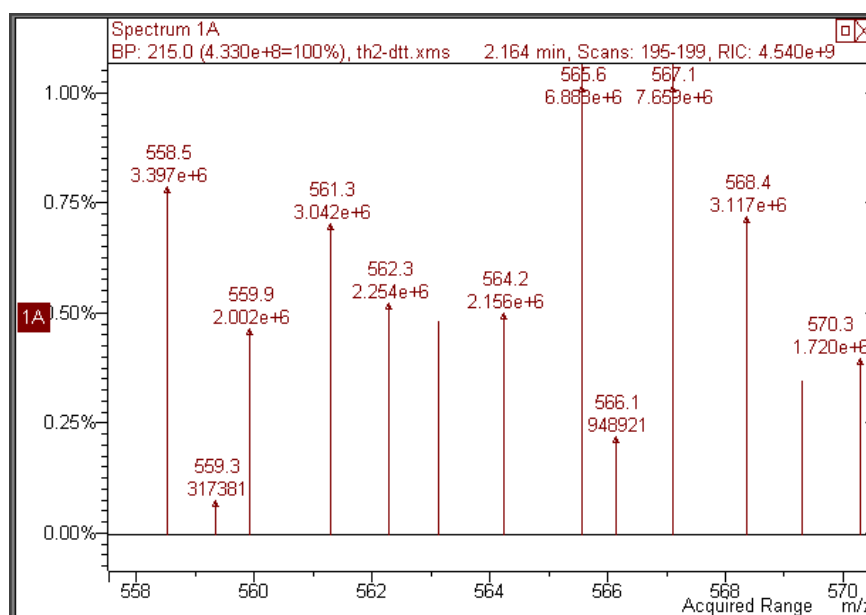


Figure A.39 : MS of 4,4'-(2,6-di(thiophen-2-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (76).

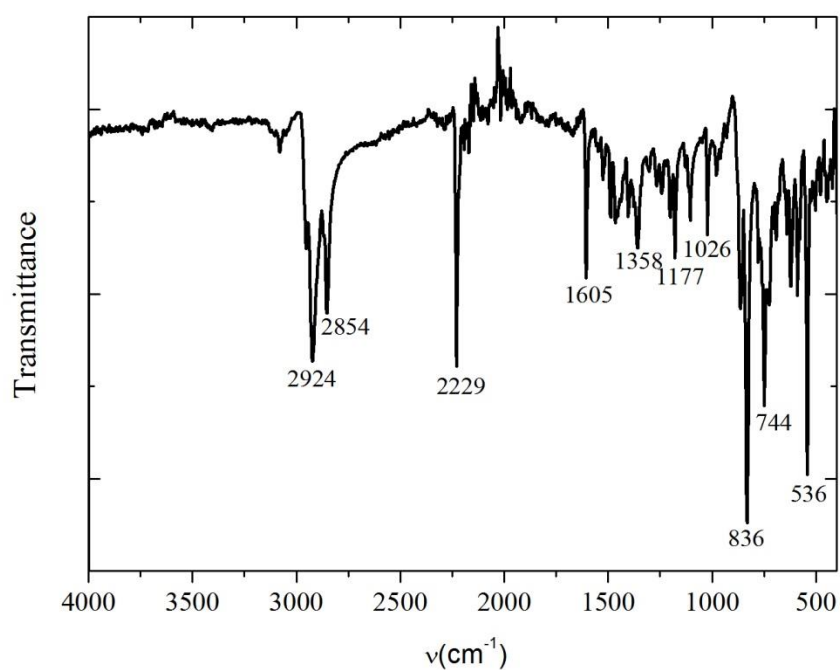


Figure A.40 : FT IR (ATR) of 4,4'-(2,6-bis(4-hexylthiophen-2-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (77).

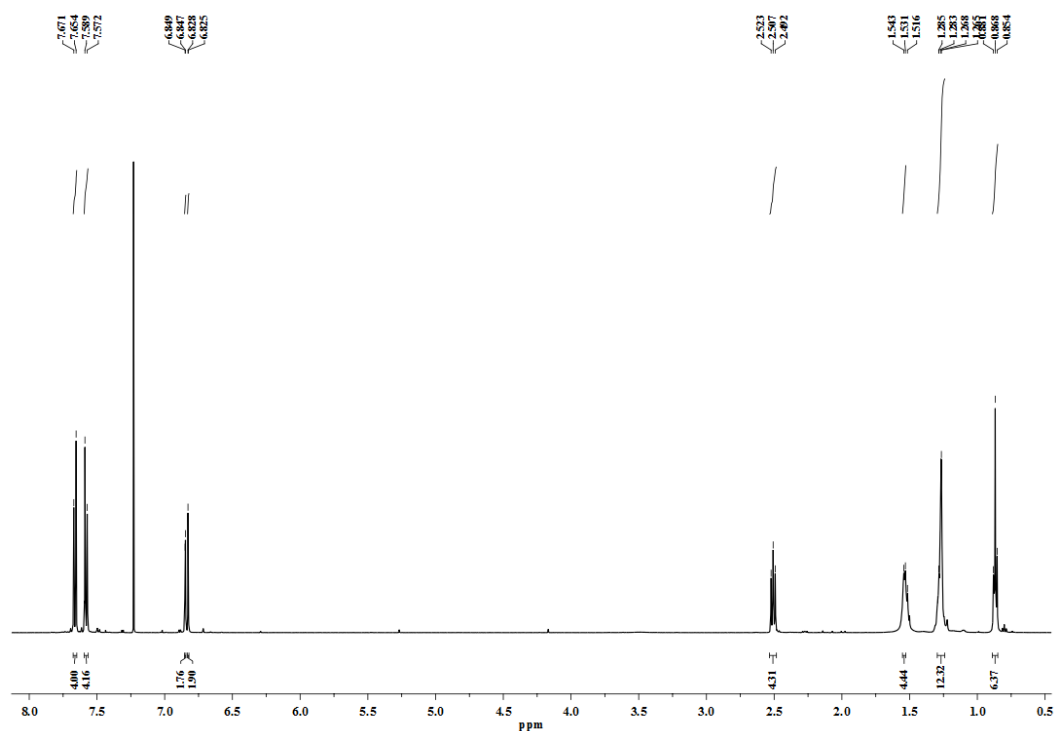


Figure A.41 : ¹H NMR (500 MHz) of 4,4'-(2,6-bis(4-hexylthiophen-2-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (**77**) in CDCl₃.

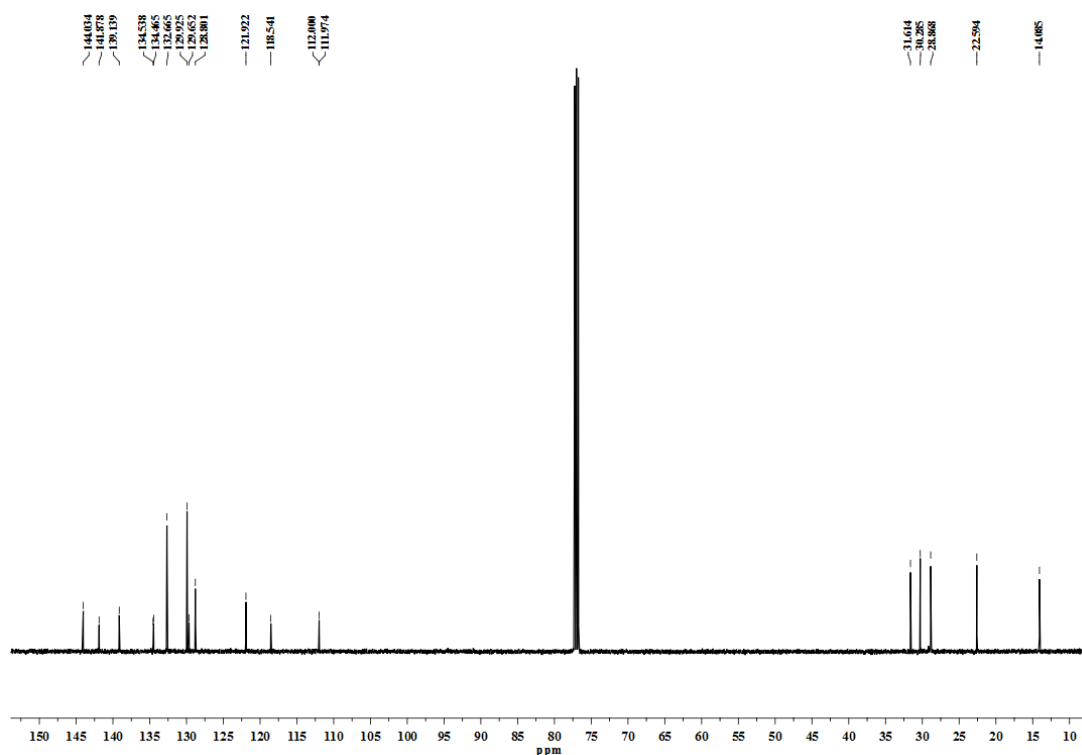


Figure A.42 : ¹³C NMR (126 MHz) of 4,4'-(2,6-bis(4-hexylthiophen-2-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (**77**) in CDCl₃.

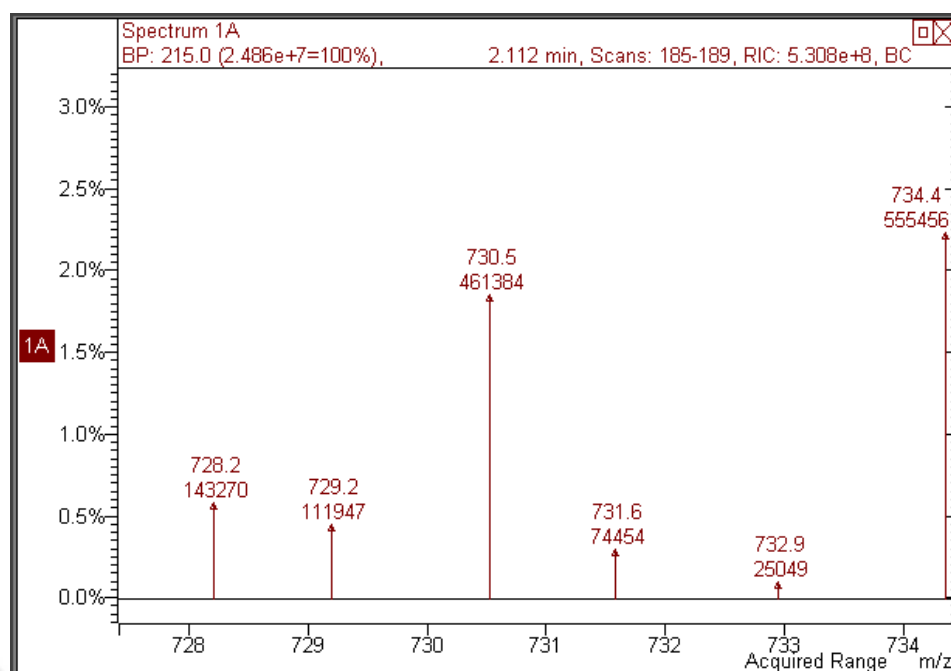


Figure A.43 : MS of 4,4'-(2,6-bis(4-hexylthiophen-2-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (**77**).

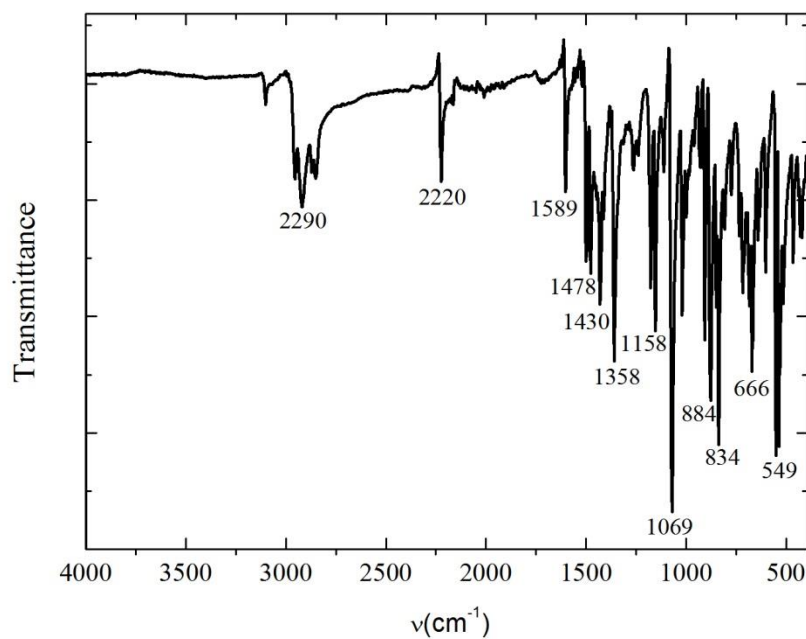


Figure A.44 : FT IR (ATR) of 4,4'-(2,6-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (**78**).

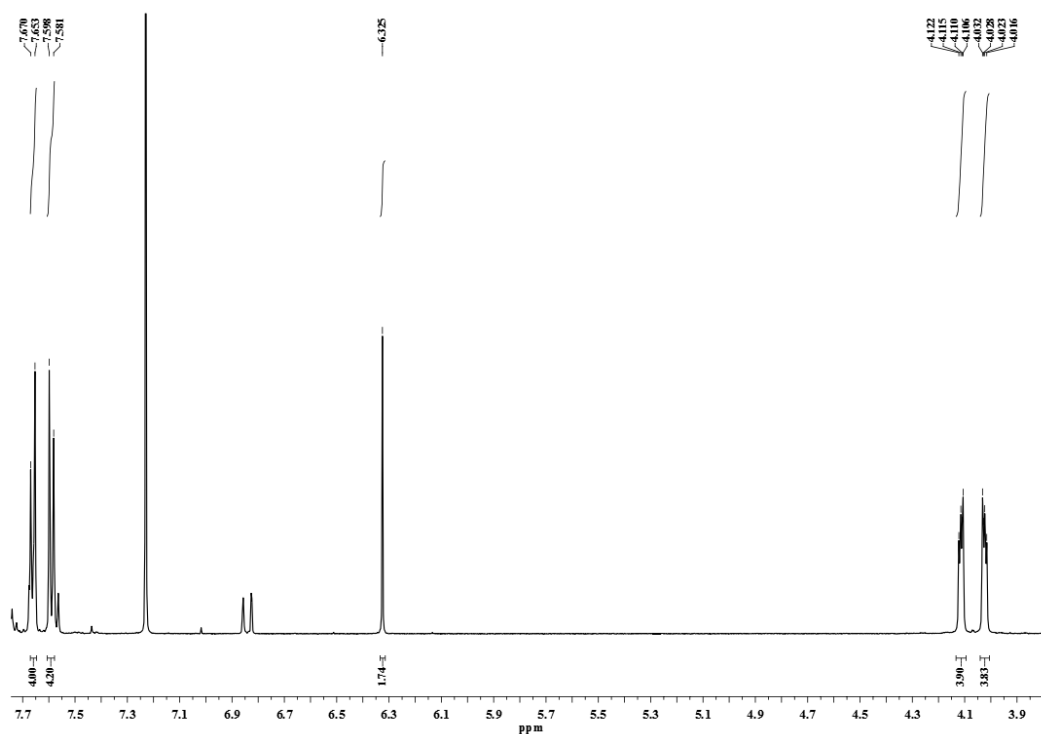


Figure A.45 : ¹H NMR (500 MHz) of 4,4'-(2,6-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (**78**) in CDCl₃.

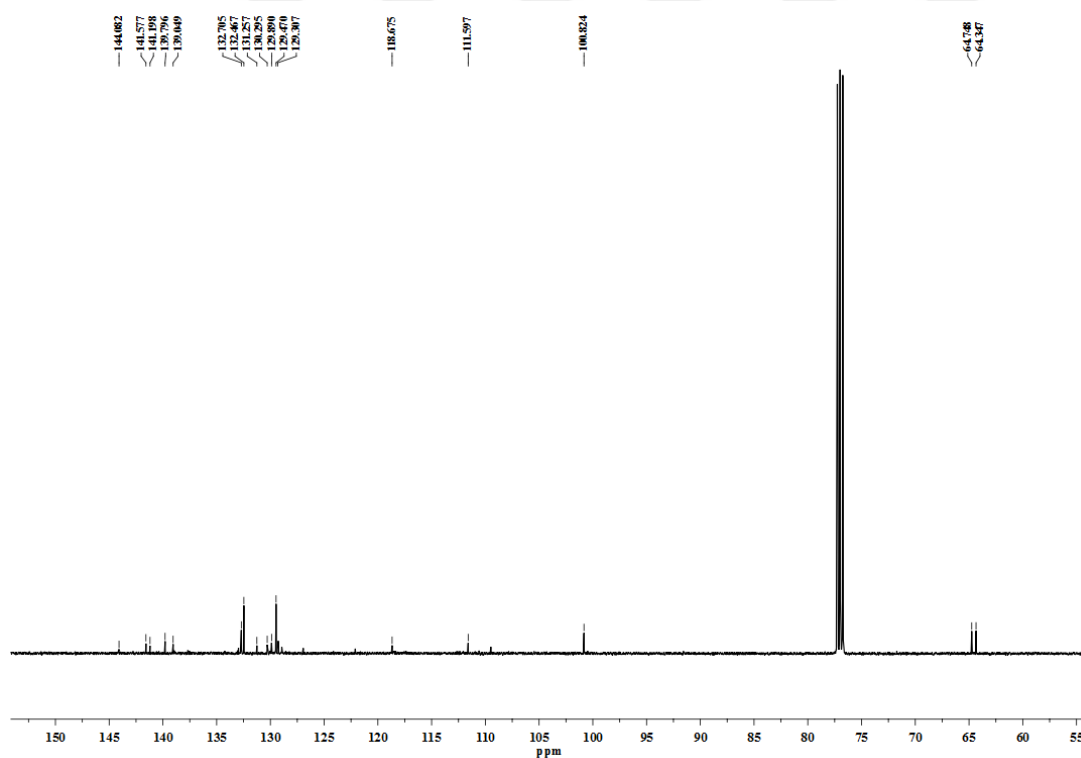


Figure A.46 : ¹³C NMR (126 MHz) of 4,4'-(2,6-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (**78**) in CDCl₃.

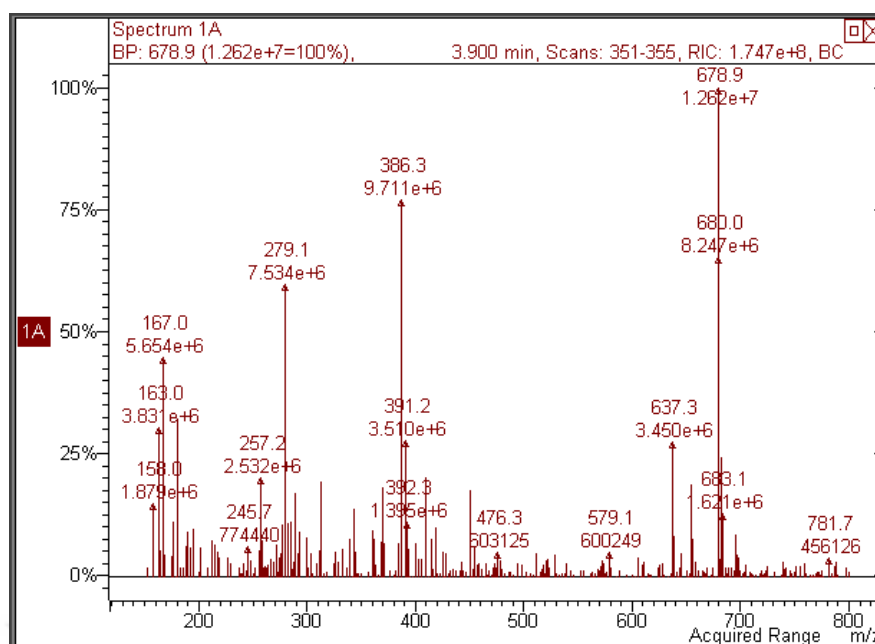


Figure A.47 : MS of 4,4'-(2,6-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-diyl)dibenzonitrile (**78**).



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